

## CHAPTER 6

### ENTROPY AND THE SECOND LAW

#### 6.1 Introduction

We have now developed the First Law of Thermodynamics for both closed and open systems, and shown how it may be used to solve practical problems. But the First Law is not the end of the story. There are many imaginable processes which satisfy the First Law, but are nevertheless don't seem to happen. We need another principle, or "law," to explain why not. In this chapter, we introduce this principle – the *second* law of thermodynamics and the new property associated with it, the entropy.

#### 6.2 Possible and Impossible Processes

Of all processes which satisfy the First Law, some actually happen and some never do. If a few ice cubes are added to a thermos bottle containing boiling water, the ice spontaneously melts and the initially-hot water cools. When equilibrium is reached, only warm water is left. The *reverse*, however, never happens: warm water has never been observed to spontaneously transform into hot water + ice cubes, even though it is possible to do so in a way which conserves energy.

If a rubber ball is held above a table and then dropped, it bounces a few times and comes to rest. The initial gravitational potential energy of the ball is converted to internal energy of the ball (and possibly of the table): the ball ends up slightly warmer than it began. The reverse process — a ball cooling off slightly and jumping off a table – has never been observed, although it could conserve energy.

In fact, for every process that really happens, the time-reversed version — in which the initial and final states of the system + environment are switched — never seems to. Eggs break when dropped on the floor; broken eggs have never been seen to "unbreak" and rise off the floor. Heat flows spontaneously from a high temperature body to a low temperature one it contacts; it has never been observed to flow spontaneously from low temperature to high. A helium balloon slowly deflates due to diffusion of helium atoms through the balloon

skin; a deflated balloon has never been observed to spontaneously inflate due to helium atoms diffusing from the surroundings to the interior.

Despite the observed one-way nature of real processes, the First Law makes no distinction between possible process and their impossible time-reversed versions. Consider, for example, a closed system which undergoes a process during which heat  $Q$  and work  $W$  are transferred to it from the environment. The First Law requires

$$E_{final} - E_{initial} = Q + W. \quad (6.1)$$

For the time-reversed version, the energy transfers occur in the other direction, so

$$E_{final}^{(rev)} - E_{initial}^{(rev)} = (-Q) + (-W). \quad (6.2)$$

But since  $E_{initial}^{(rev)} = E_{final}$  and  $E_{final}^{(rev)} = E_{initial}$ , this is equivalent to

$$-(E_{final} - E_{initial}) = (-Q) + (-W), \quad (6.3)$$

which is of course equivalent to Eq. (6.1). We see that the First Law is satisfied equally by the forward and reverse processes. This must be true, since the First Law takes the form of an *equality*: if  $A = B$ , then  $-A = -B$ . What we would need to distinguish forward from backward would be an *inequality*: if  $A$  and  $B$  satisfy  $A > B$ , then  $(-A)$  and  $(-B)$  do not. Evidently, the reason some energy-conserving processes occur spontaneously and others don't has nothing to do with the First Law.

### 6.3 The Microscopic View of Spontaneous Processes

When we consider what happens on an atomic level, it is clear why some processes happen spontaneously and others don't. We'll consider two specific examples — dropping a ball, and letting a gas expand into vacuum. The general principles apply to any spontaneous process.

#### 6.3.1 Dropping A Ball

Consider what happens on an atomic level when a rubber ball is dropped on a table (Fig. 6.1). To simplify matters, let's neglect the thermal energy the ball has before being dropped, ignore any energy transfer to the table, and assume the ball is dropped in vacuum, so there is no air resistance. Let's also imagine we have some way of taking an atomic-level “snapshot” of the positions and velocities of all atoms in the ball at any desired time — we can't do this in a real experiment, but it's quite easy in a thought experiment.

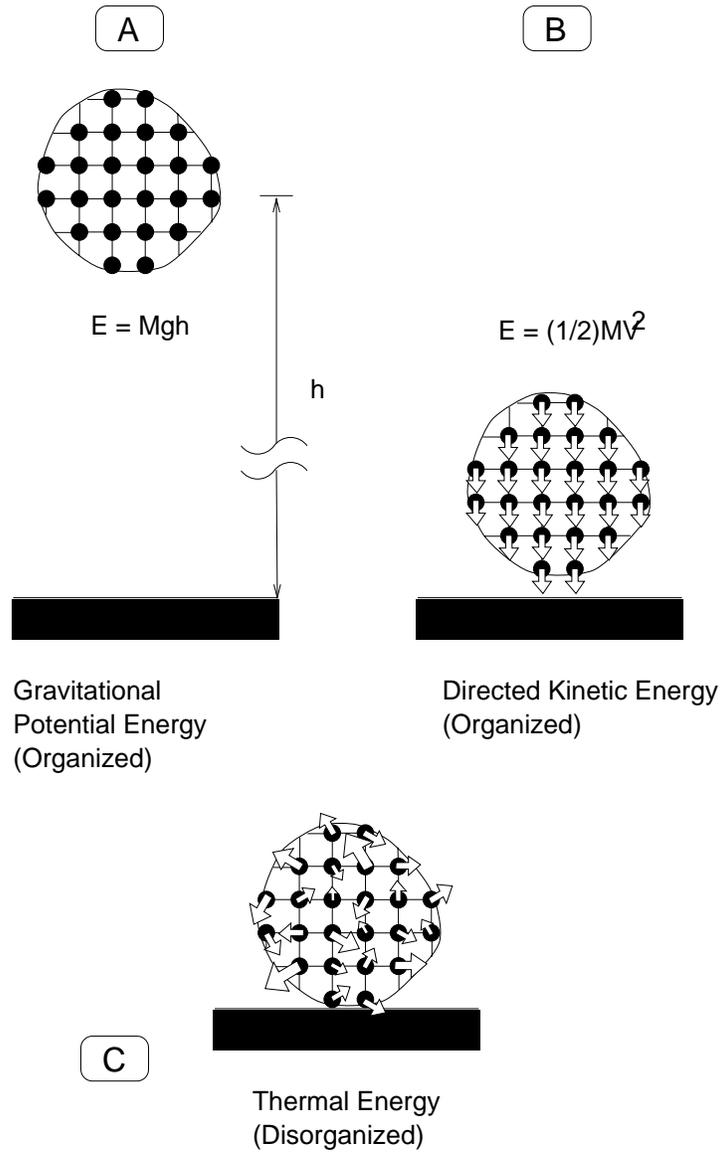


Figure 6.1: A rubber ball dropped on a table.

The ball has mass  $M$  and is dropped from a distance  $h$  above the table. Three different macroscopic states of the ball are shown in Fig. 6.1. In state A, the ball hasn't yet been dropped, so is stationary at a height  $h$  above the table. In state B, the ball is just about to strike the table the first time. In state C, the ball has stopped bouncing and reached the equilibrium state, resting on the table.

A set of atomic-level snapshots are taken in each state A, B, and C. In state A, all atoms are initially stationary (no thermal energy), so repeated snapshots always find the same atomic-level configuration. In state B, all atoms moving downward in unison at speed  $V = \sqrt{2gh}$ . Still, every snapshot is the same.

But in state C, every snapshot is different. The atoms are vibrating chaotically, and the velocity of each atom changes in an apparently random way from one snapshot to the next as the atom is pulled or pushed by the stretched or compressed bonds to neighboring atoms. Of course, energy is still conserved. If we computed for any snapshot the sum of the kinetic energies of all atoms plus the potential energies of all stretched or compressed bonds, the result would always be  $Mgh$ .

Each snapshot fully determines the instantaneous microscopic state of the ball, which we will call the *microstate*. In contrast, the *macroscopic* state of the ball is specified by only a few numbers, such as the height, center-of-mass velocity, temperature, etc. A macroscopic description of a ball (or any other system) is certainly simpler than a detailed, atomic-level specification of the microstate. But it is also much less precise, since a system in a given macroscopic state (sometimes called a *macrostate*) might be found in any one of a very large number of microstates.

If we tried to compile a list of all observed microstates for the ball in macrostate C, it would be a *very* long list. In fact, if position and velocity are measured with arbitrary precision (and therefore specified by real numbers), we would never find *exactly* the same value for any atomic position or velocity; there would be an uncountably infinite number of microstates.

But usually there is some uncertainty in measurements. For example, if the measurements are acquired by a computer or stored in one, they need to be represented by a finite number of bits, leading to round-off error. In this case, positions which differ by less than the round-off error  $\Delta x$  would be recorded as the same position, and velocities which differ by less than the velocity round-off error  $\Delta v$  would be recorded as the same velocity. In this case, the number of microstates observed in state C would be finite, but extremely large.

If we were extraordinarily patient, we could take enough snapshots to build

up statistics on the number of times each microstate is found. If after taking  $N_s$  snapshots, the ball was found in the  $j^{\text{th}}$  microstate in  $N_{j,s}$  snapshots, then as  $N_s \rightarrow \infty$  the probability  $p_j$  of finding the ball in microstate  $j$  is

$$p_j = \lim_{N_s \rightarrow \infty} \frac{N_{j,s}}{N_s}. \quad (6.4)$$

There is no particular reason to think that any one microstate of the ball in macrostate C should be found more often than any other one. Remember, we said the ball is in equilibrium in state C, which means it has been sitting on the table a very long time (at least compared to atomic vibration time scales). After enough time has elapsed, the atoms of the ball have “forgotten” about any coordinated motion (bouncing) they were executing previously, and are all moving more or less randomly.

Of course, we’re only considering microstates which are “accessible,” given the initial conditions and the conserved quantities (total energy, number of atoms, etc.). There are microstates of the ball which have total energy different than  $Mgh$ , or with a few atoms missing or bonded differently, but with the given initial conditions the ball will never be found in one of these inaccessible states.

With the assumptions we’ve made, the ball does not interact in any way with the environment, which is why its total energy must be constant. This means we are treating the ball as an isolated system.

The assumption that all microstates of the ball are equally probable at equilibrium can be generalized to any isolated system. In fact, this is the basic *postulate* of statistical mechanics:

**Postulate:** At equilibrium, all accessible microstates of an isolated system are equally probable.

We can’t prove this postulate, but we can ask what consequences follow from it, and whether they agree with experiment.

Let’s now return to the question of why some processes occur, and some don’t. On a microscopic level, all accessible microstates are equally likely at equilibrium. A particular microstate of the ball with atoms moving in various directions such that there is no center of mass velocity is just as likely as another one which has all atoms moving upward with the same speed, or one with the ball hovering completely stationary a distance  $h$  above the table. At first glance, this might lead you to conclude that a ball should be just as likely to jump off a table as to remain sitting there.

But of course, once the atoms are moving randomly in state C, it is highly unlikely that they would just happen to all move in such a way to push off from the table and rise up in unison, although there is no physical law preventing it.

Another way of saying this is that the number of microstates in which the ball is sitting on the table with all atoms moving more or less randomly (and thus with negligible net center-of-mass velocity) is *huge* compared to those few special microstates with the atoms all moving in one direction, or all displaced above the table. All accessible microstates — even ones corresponding to bizarre macroscopic behavior — are equally probable, but there are *far, far more* microstates which correspond to the ball simply sitting on the table.

Therefore, we would expect to hardly ever observe one of the microstates corresponding to the ball doing anything but sitting on the table. If we worked out the numbers, we would find that we would have to wait *much* longer than the age of the universe to see the ball spontaneously move — during which time, of course, other processes would occur which would make the whole experiment moot (disintegration of the ball and table, the end of life on earth, etc.)

So the basic idea is as follows. Denote by  $\Omega$  the number of microstates which a system might be in when it is in some specified macroscopic state. Suppose an isolated system starts out in some equilibrium macrostate 1 which has a certain number of microstates  $\Omega_1$ . Now some process occurs within the system (e.g. the ball is dropped) which changes the number of available microstates to  $\Omega_2 \gg \Omega_1$ . Once enough time has elapsed, the system is again in equilibrium, so it could be in any one of its  $\Omega_2$  microstates with equal probability. It is still possible that it could be found in one of the original microstates, which would mean that macroscopically it would appear to be in macrostate 1. But the probability of this happening is  $\Omega_1/\Omega_2$ , which is very small if  $\Omega_2 \gg \Omega_1$ .

### 6.3.2 Irreversible Expansion of an Ideal Gas

To see how the numbers work out, we need a system so simple that we can actually compute the number of microstates. (This would be hard to do in practice for a rubber ball.) Consider a gas of  $N$  identical point atoms in a container of volume  $V$ .

For the purposes of this discussion, we'll only specify the microstate by the spatial location of the atoms, and not consider how many ways there are to assign velocities to the atoms consistent with a specified energy. We'll come back to the question of how to partition the energy in Section 6.7.

If we specify the microstate by the *exact* position of each atom ( $\{\mathbf{x}_1, \dots, \mathbf{x}_N\}$ ), then there are an uncountably infinite number of microstates, since each coordi-

nate position is specified by a real number. To make the number of microstates countable, let's assume each position measurement has some finite round-off error  $\Delta x$ . This is equivalent to dividing the volume into small cubes of volume  $(\Delta x)^3$ , and only recording *which* small cube an atom is in, rather than the exact co-ordinates within the cube. This makes the number of microstates finite and countable, although the answer will depend on  $\Delta x$ .

The number of small cubes  $n_c$  is

$$n_c = \frac{V}{(\Delta x)^3}. \quad (6.5)$$

We will assume that  $n_c \gg N$ , so that if we place the  $N$  atoms in cubes randomly, the odds of finding two or more in the same cube are very low. The vast majority of states do not have any cubes multiply-occupied. We'll allow multiple-occupancy in counting states, but it won't affect the result much one way or the other as long as  $n_c \gg N$ .

The number of spatial arrangements  $\Omega_x$  is the number of ways of placing  $N$  identical atoms in  $n_c$  cubes. Since the atoms are identical,<sup>1</sup> we won't count arrangements which differ only by a permutation of atom labels as being different. That is, for  $N = 2$ , the arrangement with atom 1 in cube 47 and atom 2 in cube 129 is no different than arrangement with atom 2 in cube 47 and atom 1 in cube 129. We should count this arrangement once, but not twice. Therefore, for  $N = 2$ ,  $\Omega_x(N = 2) = n_c^2/2$ . For  $N = 3$ , we have to divide the number of arrangements of 3 labeled atoms ( $n_c^3$ ) by the number of ways to permute labels among 3 atoms ( $3! = 6$ ). So  $\Omega_x(N = 3) = n_c^3/6$ . The general result is

$$\Omega_x(V, N) = \frac{1}{N!} n_c^N = \frac{1}{N!} \left[ \frac{V}{(\Delta x)^3} \right]^N. \quad (6.6)$$

Let's use this result to analyze the process shown in Fig. 6.2.

A container is divided into two compartments, of volume  $V_A$  and  $V_B$ , respectively. Initially, compartment A contains an equilibrium gas of  $N$  identical point atoms, and compartment B is empty. A shutter is now opened in the partition, allowing atoms to move freely between A and B. Enough time is allowed to elapse so that the gas comes to equilibrium in the new volume  $V_A + V_B$ .

Now a sensitive detector is turned on, which can detect the presence of even one atom in compartment B. The detector looks for atoms in B every  $\Delta t$

<sup>1</sup>Quantum mechanics requires that identical atoms (the same isotope of the same element) are indistinguishable *even in principle*. So just exchanging two identical atoms, keeping everything else the same, can't yield a new microstate.

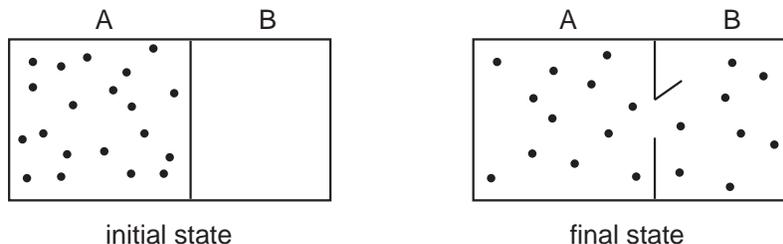


Figure 6.2: Irreversible expansion of a gas.

seconds. If the detector ever detects that B is empty, it sends a signal which closes the shutter, which returns the gas to its original state of being confined in compartment A. How much time elapses on average before B is found to be empty and the shutter closes?

Once the shutter has opened and the atoms have had ample time to move back and forth between A and B, the number of available microstates has increased by the factor

$$\frac{\Omega_{final}}{\Omega_{initial}} = \left( \frac{V_{A+B}}{V_A} \right)^N. \quad (6.7)$$

Since all microstates are equally probable at equilibrium, the probability  $p_{empty}$  that the detector will find none of the  $N$  atoms in B in any one measurement is simply the ratio of the number of microstates which have all of the atoms in A to the total number of microstates:

$$p_{empty} = \frac{\Omega_{initial}}{\Omega_{final}} = \left( \frac{V_A}{V_{A+B}} \right)^N. \quad (6.8)$$

If  $N$  is small, then  $p_{empty}$  is fairly large, and only a few measurements would be needed, on average, before the detector finds B empty. For example, if  $V_A = V_B$  and  $N = 2$ , then  $p_{empty} = 1/4$ , so the detector would be expected to find B empty after only about 4 measurements. If  $N = 20$ ,  $p_{empty} = 9.5 \times 10^{-7}$ . Now it is unlikely to find B empty on any given measurement, but statistically once every million or so times it should happen, and the shutter would then close, trapping the gas in A. If the detector took a measurement, say, every second, then it would take about 12 days (a million seconds) before we would expect the shutter to close and effectively “reverse” the effect of opening the shutter. We conclude that if  $N$  is small (say, 20 or so) then the process of opening the shutter can be reversed, if we are willing to wait a little while.

Suppose, however, that we have a macroscopic gas, with  $N \sim 10^{23}$ . Then

$$p_{empty} = \left( \frac{V_A}{V_{A+B}} \right)^{10^{23}}. \quad (6.9)$$

If  $V_A = V_B$ ,

$$\begin{aligned} p_{10^{23}} &= 2^{-10^{23}} \\ &= 10^{-10^{23} \log_{10} 2} \\ &\approx 10^{-3 \times 10^{22}}. \end{aligned} \quad (6.10)$$

Now *that* is a small probability — its reciprocal would be written as a “1” followed by about  $3 \times 10^{22}$  zeros.

The universe is of order  $10^{10}$  years old, which is  $3 \times 10^{17}$  seconds. Therefore, the chance of detecting no atoms in B during the age of the universe, checking every second, is

$$(3 \times 10^{17})(10^{-3 \times 10^{22}}) = 3 \times 10^{-(3 \times 10^{22} - 17)}.$$

Thus, it is *overwhelmingly* unlikely to occur in the age of the universe. Even if the detector looked every microsecond, this would only change the probability to  $3 \times 10^{-(3 \times 10^{22} - 23)}$  — still far too small. Even if we could wait  $10^{10}$  universe lifetimes it would still be overwhelmingly unlikely. We conclude therefore that if  $N \sim 10^{23}$ , the process of opening the shutter is truly *irreversible*: it won't spontaneously reverse, even over times much longer than the age of the universe. For this reason, the process of a macroscopic gas expanding into vacuum is called *irreversible expansion*. It is also called *unrestrained expansion*, since there is no piston restraining the gas expansion that the gas must do work against.

This example illustrates a common feature of macroscopic systems. Since the number of atoms is very large (say,  $> 10^{20}$ ), and the formula for  $\Omega$  typically has  $N$  in an exponent, making a minor change like opening a shutter to increase the volume expands the number of available microstates by an unimaginably huge degree. Once the system can be found in any of these with equal probability, the probability of finding it in one of its original allowed microstates is effectively zero, *even if we watch it for the age of the universe*. When this is the case, we say that the “minor change” which was made is *irreversible*.

Of course, it is possible to restore a system to its initial state, but only at the cost of altering the environment irreversibly. In the previous example, a piston could be used to compress the gas back into compartment A. However, this would require work input, which would increase the energy of the gas.

This extra energy would have to be removed to the environment as heat, which would irreversibly alter the microscopic state of the environment. In particular, the energy added to the environment would increase its number of possible microstates by a huge factor.

#### 6.4 The Second Law of Thermodynamics

The Second Law of Thermodynamics simply expresses as a general “law” the characteristics of spontaneous, irreversible processes discussed in the last section. Consider first an isolated system (constant energy), since in this case all accessible microstates have the same energy, and we don’t have to be concerned about what is happening in the environment. The Second Law states that

No process will occur within an isolated, macroscopic system that decreases the number of accessible microstates.

All this says is that isolated, macroscopic systems will proceed in the direction of increasing  $\Omega$  if allowed to (say, by letting go of a ball, or opening an internal shutter in a gas container, etc.), but will never proceed in the direction of decreasing  $\Omega$ . Of course, we mean “never” in the sense of the irreversible expansion example of the last section.

The second law says only that the number of possible microstates of an isolated system cannot decrease; it does not require the number to increase by any specific amount. In particular, processes which do not change the number of microstates are allowed. Such processes are called *reversible*, since they are the only ones which may be reversed without violating the Second Law.

For non-isolated systems which interact with the environment, the system + environment together constitute an isolated system, so the Second Law may be state more generally:

No process that decreases the number of accessible microstates of the system + environment will occur.

#### 6.5 The Entropy

The number of microstates  $\Omega$  associated with some macroscopic, equilibrium state of matter is a useful quantity to know. As we saw in the irreversible expansion example, knowing  $\Omega$  and its dependence on macroscopic parameters such as the volume allows us to determine what sort of processes can occur (expansion of gas through an opening in a partition), and what sort can’t (spontaneous collection of gas atoms in one part of a container).

However, there are two reasons why working with  $\Omega$  directly is inconvenient. First, it is difficult to work with numbers as large as, say,  $10^{10^{23}}$  – we don't have much intuitive feel for them.

The second problem becomes clear if we consider a system which is composed of two non-interacting parts,  $A$  and  $B$ . If  $A$  and  $B$  are independent, and  $A$  has  $\Omega_A$  microstates, and  $B$  has  $\Omega_B$  microstates, then

$$\Omega_{A+B} = \Omega_A \Omega_B. \quad (6.11)$$

Therefore, the property  $\Omega$  is multiplicative for systems composed of separate parts. Since other properties we've worked with like mass, volume, and energy are additive (extensive), it is inconvenient to have to work with a multiplicative property.

Both problems can be solved by working with  $\ln \Omega$ , rather than  $\Omega$ . The logarithm of  $\Omega$  typically is proportional to  $N$ , which is still a big number but is quite manageable compared to  $10^N$ . Also,  $\ln \Omega$  is additive:

$$\ln \Omega_{A+B} = \ln \Omega_A + \ln \Omega_B. \quad (6.12)$$

We will define the *entropy*  $S$  as

$$S = k_B \ln \Omega. \quad (6.13)$$

The constant  $k_B$  is “Boltzmann's constant,” named after Ludwig Boltzmann, who first proposed this equation. It is introduced only for convenience, and can be set to any desired value. Given  $S$ , it is always possible to recover  $\Omega = \exp(S/k_B)$ . Sometimes it is most convenient to use  $k_B = 1$ , in which case the entropy is dimensionless. But we'll soon see that the choice of  $k_B$  affects the units of other properties, in particular temperature. If we have already decided what units we want to use for temperature (e.g. Kelvin), then this will determine the value for  $k_B$ . We'll discuss this point more in Section 6.9.

It is important to remember that we have been considering equilibrium states of isolated systems (constant energy  $U$ , volume  $V$ , number of atoms  $N$ ). For isolated systems, the only accessible microstates are the ones with the right values of  $U$  and  $N$ , and for which all atoms are contained within  $V$ . The number of these will depend on  $U$ ,  $V$ , and  $N$ :  $\Omega(U, V, N)$ . Therefore, the entropy has the same functional dependence:  $S(U, V, N)$ .

Since the system is in equilibrium, all accessible microstates are assumed to be equally likely, and therefore all that really matters is how many of them there are. If it were not in equilibrium, then some microstates would be more

probable than others. For example, in the irreversible expansion example, just after the shutter is opened microstates with most atoms in A are more probable than ones with most atoms in B. It can be shown that in this case the entropy should be defined as

$$S = k_B \sum_j p_j \ln p_j, \quad (6.14)$$

where the sum is over all accessible microstates. If all microstates are equally probable, ( $p_j = 1/\Omega$ ) Eq. (6.14) reduces to Eq. (6.13).

For our purposes, we won't need to evaluate  $S$  for non-equilibrium states, so we won't need Eq. (6.14). The only sort of non-equilibrium states we'll need to consider explicitly are ones composed of separate parts, each of which is in local thermodynamic equilibrium. Since  $S$  is extensive, in this case  $S$  can be written as

$$S = \sum_{k=1}^K S_k(U_k, V_k, N_k). \quad (6.15)$$

Here the system is divided into  $K$  parts, each of which is internally in equilibrium (all of its microstates are equally probable), but which may not be in equilibrium with one another. Each term  $S_k$  is evaluated as the entropy of the equilibrium state with energy  $U_k$ , volume  $V_k$ , and  $N_k$  atoms.

Once we have  $S(U, V, N)$ , we could change variables from number of atoms to the total mass, since  $M = mN$ , where  $m$  is the mass of one atom. This would produce the function  $S(U, V, M)$ , which depends only on macroscopically-measurable quantities.

Now we also know that  $S$  is extensive, like  $U$ ,  $V$ ,  $N$ , and  $M$ . The extensive properties have the characteristic that they all scale with the amount of the substance present. Therefore, if we scale up the size of the system by some factor  $\lambda$ , all extensive variables must be scaled by  $\lambda$ . The entropy function evaluated for the scaled-up system  $S(\lambda U, \lambda V, \lambda M)$  must be  $\lambda$  times larger than the entropy function evaluated for the original system  $S(U, V, M)$ :

$$\lambda S(U, V, M) = S(\lambda U, \lambda V, \lambda M). \quad (6.16)$$

Taking  $\lambda = 1/M$ ,

$$\frac{S}{M} = S\left(\frac{U}{M}, \frac{V}{M}, 1\right). \quad (6.17)$$

Therefore, as for the other extensive properties, we define the *specific entropy*  $s$  by

$$s = \frac{S}{M} = s(u, v), \quad (6.18)$$

which from Eq. (6.17) depends only on  $(u, v)$ .

Therefore, for a simple compressible substance in equilibrium, there exists some entropy equation of state  $s(u, v)$ . Of course, as we discussed in Chapter 3, any two independent properties can be used to specify the thermodynamic state. To construct, for example,  $s(h, P)$  we only need to know the equations of state  $u(h, P)$  and  $v(h, P)$ :  $s(h, P) = s(u(h, P), v(h, P))$ . The specific entropy can also be used as one of the properties to fix the state. For example,  $s(h, P)$  could be inverted to form  $h(s, P)$ .

For most substances, figuring out all of the microstates consistent with specified  $(U, V, N)$  is too difficult to do in practice, although in *principle* it can always be done. But the function  $s(u, v)$  still exists, even if we have difficulty calculating it directly from  $S = k_B \ln \Omega$ . Fortunately, as we'll discuss below, there are ways to determine  $s(u, v)$  purely from macroscopic measurements except for an arbitrary constant of integration.

## 6.6 Entropy Production

If some process occurs within an isolated system, the Second Law requires  $\Omega_{final} \geq \Omega_{initial}$ . Therefore,

$$\Delta S = S_{final} - S_{initial} = k_B \ln \left( \frac{\Omega_{final}}{\Omega_{initial}} \right) \geq 0. \quad (6.19)$$

Since this extra entropy wasn't transferred into the system from the environment (the system is isolated), *we must regard the extra entropy to have been produced inside the system during this process.*

Thus, irreversible processes produce entropy – unlike energy and mass, entropy is not conserved. We'll call the amount of entropy produced by a process the *entropy production*  $\mathcal{P}_s$ . Every irreversible process produces entropy ( $\mathcal{P}_s > 0$ ). Besides unrestrained expansion, some other processes which produce entropy include motion against frictional forces, combustion, electrical current flow through a resistor, heat transfer through a finite temperature difference, mixing of two different fluids, and even clearing data in the memory of a digital computer.

For a process occurring in a non-isolated system, the entropy produced by the process equals the increase in the entropy of the system + environment. A very compact, general way of writing the Second Law is

$$\boxed{\mathcal{P}_s \geq 0} \quad (6.20)$$

That is, entropy can be produced, but it can never be destroyed. Since this form of the Second Law applies to all types of systems, it is the form we will use most often.

The special class of processes for which  $\mathcal{P}_s = 0$  are reversible, since reversing them would not result in destruction of entropy, as it would for a process with  $\mathcal{P}_s > 0$ . Reversible processes can't be actually achieved in practice, since friction or other irreversibilities are always present, even if only in very small amounts. However, real processes can approach reversible ones as a limiting case, as we make irreversibilities (electrical resistance, friction, etc.) smaller and smaller.

## 6.7 The Entropy of a Monatomic Ideal Gas

One of the few systems which is simple enough to allow computing  $s(u, v)$  from first principles is the monatomic ideal gas. We've introduced the ideal gas previously as the low-density limit of a simple compressible substance, and stated that it satisfies  $Pv = RT$ . From a microscopic viewpoint, an ideal gas is a gas of particles of negligible size, which have kinetic energy but have negligible interaction potential energy. A real gas approximates this when the container volume per atom is much larger than the atomic size, and the average distance between atoms is much greater than the distance over which they exert appreciable attractive or repulsive forces on one another. A *monatomic* ideal gas (e.g. He, Ar, Ne) is particularly simple, since in this case the energy of each particle is simply  $(1/2)m|\mathbf{v}|^2$  – there is no rotational or vibrational energy, as there would be in a molecular ideal gas.

Consider an isolated system consisting of a monatomic ideal gas of  $N$  atoms contained in volume  $V$ . For simplicity, assume the volume is a cube with side length  $L$ . Since it is isolated, the total energy is fixed at some value; call it  $U$ . Then every possible microstate  $\{\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{v}_1, \dots, \mathbf{v}_N\}$  of the system must satisfy

$$\sum_{n=1}^N \frac{mv_n^2}{2} = U. \quad (6.21)$$

It will turn out to be more convenient to work with the momentum of an atom  $\mathbf{p}_n = m\mathbf{v}_n$ , rather than velocity. In terms of momentum, this equation becomes

$$\sum_{n=1}^N \frac{p_n^2}{2m} = U. \quad (6.22)$$

Also, all  $N$  atoms must be in the container, so the microstate must satisfy

$$0 \leq x_n \leq L, \quad n = 1, \dots, N$$

$$\begin{aligned} 0 \leq y_n \leq L, \quad n = 1, \dots, N \\ 0 \leq z_n \leq L, \quad n = 1, \dots, N. \end{aligned} \quad (6.23)$$

How many microstates are there which satisfy these constraints? Clearly, if we can really measure position and momentum with arbitrary accuracy, there is an uncountably-infinite number. So let's introduce some small round-off error to make the states countable. Say the position round-off error is  $\Delta x$ , and the momentum round-off error is  $\Delta p$ .

We already solved part of this problem when we calculated how many ways there are to arrange  $N$  atoms in volume  $V$  [Eq. (6.6)]. Since for an ideal gas the energy depends only on the atomic momenta, not on their positions, the calculation of the number of ways to arrange the atoms in space ( $\Omega_x$ ) and the number of ways to distribute the energy as kinetic energy among the atoms ( $\Omega_p$ ) can be done independently. The total number of microstates is simply the product:

$$\Omega = \Omega_x \Omega_p. \quad (6.24)$$

The details of the calculation of  $\Omega_p$  are relegated to Appendix A. The result is

$$\Omega_p = \frac{(2\pi mU)^{3N/2}}{(\Delta p)^{3N} \left(\frac{3N}{2}\right)!}. \quad (6.25)$$

Therefore, using Eq. (6.6), the total number of microstates is

$$\Omega = \Omega_x \Omega_p = \frac{1}{N!} \frac{V^N (2\pi mU)^{3N/2}}{(\Delta x \Delta p)^{3N} \left(\frac{3N}{2}\right)!}. \quad (6.26)$$

Classically, the choice of  $\Delta x \Delta p$  is arbitrary. Nevertheless, when  $S = k_B \ln \Omega$  is evaluated, the term involving  $\Delta x \Delta p$  just becomes an additive constant equal to  $-3Nk_B \ln(\Delta x \Delta p)$ , so this classical treatment determines the entropy of an ideal gas to within an arbitrary additive constant. Since we only need to know *differences* in entropy to determine if a process satisfies the Second Law, any additive constant will cancel when the difference is taken.

We can do a little better if we supplement this classical analysis with the uncertainty principle of quantum mechanics. The uncertainty principle states that a particle (which in quantum mechanics is a wave packet) cannot simultaneously have precise values of position and momentum —  $\mathbf{x}$  or  $\mathbf{p}$  or both must have some “fuzziness” or uncertainty. The momentum uncertainty in any direction  $\delta p$  and the position uncertainty in that direction  $\delta x$  are related by

$$(\delta x)(\delta p) \geq h, \quad (6.27)$$

where

$$h = 6.626 \times 10^{-34} \text{ J-s} \quad (6.28)$$

is *Planck's constant*.

It seems natural to choose  $\Delta x \Delta p = h$  in Eq. (6.26). In fact, it can be shown that this choice reduces Eq. (6.26) to what would result if we had done the analysis quantum-mechanically from the start. Making this substitution,

$$\Omega = \frac{1}{N!} \frac{V^N (2\pi m U)^{3N/2}}{h^{3N} \left(\frac{3N}{2}\right)!}. \quad (6.29)$$

The entropy is  $k_B \ln \Omega$ . If  $N$  is larger than about 100,  $\ln N!$  is well-approximated by  $\ln N! \approx N \ln N - N$ , which is known as *Stirling's approximation*. It is left as an exercise to show that in this case the entropy is

$$S = Nk_B \left[ \frac{3}{2} \ln \left( \frac{U}{N} \right) + \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{4\pi m}{3h^2} \right) + \frac{5}{2} \right]. \quad (6.30)$$

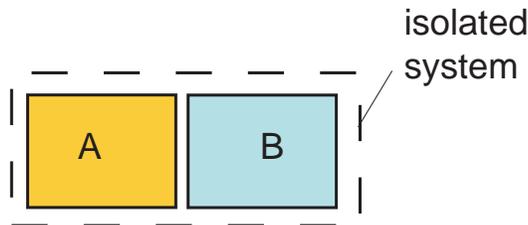
This expression for the absolute entropy of a monatomic ideal gas.

## 6.8 The Second Law and Equilibrium

The Second Law has significant implications regarding the nature of equilibrium. In this section, we'll take a look at equilibrium from the point of view of the Second Law. This will extend our analysis of Chapter 3, and result in relationships between the properties defined there (temperature, pressure, and chemical potential) and the entropy.

### 6.8.1 The Entropy Maximum Principle

Consider the process shown below. Two solid blocks, A and B, are brought into contact briefly and then separated. Heat may flow from one to the other during the contact time, but there is no energy or mass transfer to the environment. Therefore, the two blocks together constitute an isolated system.

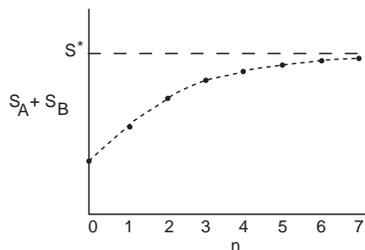


The Second Law ( $\mathcal{P}_s \geq 0$ ) prohibits any process occurring within an isolated system which would decrease its entropy. We will also exclude the possibility of

a reversible process occurring ( $\mathcal{P}_s = 0$ ), since every *real* process which occurs in finite time produces some entropy, although  $\mathcal{P}_s$  can be made arbitrarily small.

Therefore, if energy transfers as heat between the blocks, it must do so in a way which increases the entropy  $S = S_A(U_A) + S_B(U_B)$  of the whole system, measured after the blocks have been separated and each has again come into internal equilibrium (uniform temperature).

If this process is repeated many times, the entropy of the whole system must increase each time. But the entropy can't go on increasing *without bound*, since there is a finite number of ways to distribute the total energy  $U_A + U_B$  among all the atoms in block A and block B. Since  $\Omega$  is bounded, so is  $S$ . Therefore, the entropy must approach some limiting value as the number of contact periods goes to infinity.



In the limit of infinite contact periods (infinite contact time) the state is no longer changing, and by definition this is the condition of thermal equilibrium between blocks A and B. The same analysis would apply to any other process occurring in an isolated system, not only heat flow (chemical reaction, mixing of two different species, fluid motion, etc.). The process would occur for a while, continually increasing the entropy of the system, until it has maximized the entropy as much as it can, then no further change will be observed. The system will be in equilibrium.

So we have a general criterion for the attainment of equilibrium in an isolated system:

The equilibrium state of an isolated macroscopic system has the maximum entropy, compared to all other possible states of the system.

This is known as the *Entropy Maximum Principle*. By “state” we mean of course the macroscopic state, and by “possible” states, we mean ones with the same total energy, volume, mass, and elemental composition as the system began with, since these quantities are fixed for an isolated system.

A few examples will make clear how the Entropy Maximum Principle is used.

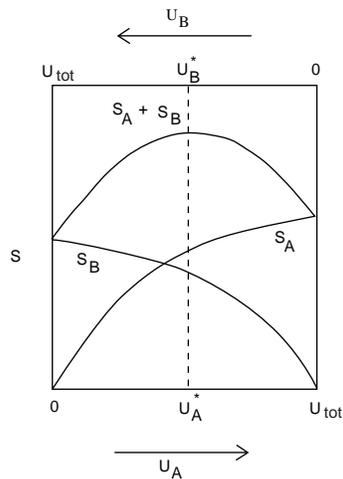


Figure 6.3: The equilibrium state of an isolated system maximizes the total entropy  $S_A + S_B$  with respect to the quantity being varied (here  $U_A$ ).

### 6.8.2 Thermal Equilibrium

Consider again the example of the last section. Suppose block A initially has internal energy  $U_{A,0}$ , and block B has  $U_{B,0}$ . After they have come to thermal equilibrium, energy may have transferred as heat from one to the other, changing  $U_A$  and  $U_B$ . What are the equilibrium values  $U_A^*$  and  $U_B^*$ ?

To answer this question, we can use the Entropy Maximum Principle. First note that the total energy  $U_{tot} = U_A + U_B$  is fixed, since the system is isolated. So at any time,  $U_B = U_{tot} - U_A$ .

The entropy of each block depends on its energy, volume, and number of atoms. So the total system entropy is

$$S = S_A(U_A, V_A, N_A) + S_B(U_B, V_B, N_B), \quad (6.31)$$

where

$$U_B = U_{tot} - U_A. \quad (6.32)$$

Note that in this problem the only independent variable we can change is  $U_A$ ; everything else is fixed.

The Entropy Maximum Principle says that at equilibrium,  $U_A$  will have the value which maximizes  $S$ . Therefore, by plotting  $S$  vs.  $U_A$ , it is possible to determine the equilibrium value  $U_A^*$  (Fig. 6.3).

There is another way to find the maximum of  $S$ . Instead of plotting it, we

could calculate  $dS/dU_A$ , and set this derivative to zero to find  $U_A^*$ :

$$\frac{dS}{dU_A} = \left( \frac{\partial S_A}{\partial U_A} \right)_{V_A, N_A} + \left( \frac{dU_B}{dU_A} \right) \left( \frac{\partial S_B}{\partial U_B} \right)_{V_B, N_B} = 0 \quad (6.33)$$

at equilibrium. From Eq. (6.32),

$$\frac{dU_B}{dU_A} = -1. \quad (6.34)$$

Putting this into Eq. (6.33), we find

$$\frac{dS}{dU_A} = \left( \frac{\partial S_A}{\partial U_A} \right)_{V_A, N_A} - \left( \frac{\partial S_B}{\partial U_B} \right)_{V_B, N_B}. \quad (6.35)$$

At the maximum (thermal equilibrium),  $dS/dU_A = 0$ , so we conclude that at thermal equilibrium

$$\left( \frac{\partial S_A}{\partial U_A} \right)_{V_A, N_A} = \left( \frac{\partial S_B}{\partial U_B} \right)_{V_B, N_B} \quad (6.36)$$

or changing the notation slightly

$$\left[ \left( \frac{\partial S}{\partial U} \right)_{V, N} \right]_A = \left[ \left( \frac{\partial S}{\partial U} \right)_{V, N} \right]_B. \quad (6.37)$$

This equation states that at thermal equilibrium, A and B will have the same value of the property  $(\partial S/\partial U)_{V, N}$ . The functions  $S_A$  and  $S_B$  may differ, since A and B may be different substances. But when equilibrium is attained, the partial derivatives of these two different functions with respect to internal energy will be equal. Clearly, this is an important and useful partial derivative property.

Note that  $(\partial S/\partial U)_{V, N} = (\partial s/\partial u)_v$ , so we can state the thermal equilibrium condition more simply as

$$\left[ \left( \frac{\partial s}{\partial u} \right)_v \right]_A = \left[ \left( \frac{\partial s}{\partial u} \right)_v \right]_B. \quad (6.38)$$

In chapter 3, we already introduced the property *temperature* to tell us if two systems are in thermal equilibrium (they are if  $T_A = T_B$ ; otherwise they are not). Evidently, there must be a close relationship between temperature and  $(\partial s/\partial u)_v$ . We could in fact use any monotonic function of this derivative  $f((\partial s/\partial u)_v)$  to *define* a thermodynamic temperature scale.

What function should we pick? Let's first look at how heat flows, from Fig. 6.3. Suppose we start with  $U_A^{(0)} < U_A^*$  (to the left of the maximum in

Fig. 6.3. Then  $dS/U_A > 0$ , which from Eq. (6.35) means that  $[(\partial s/\partial u)_v]_A > [(\partial s/\partial u)_v]_B$ . As the system approaches equilibrium,  $U_A$  increases to  $U_A^*$ . Thus, heat must flow *into* A *from* B.

Now consider the other possibility: suppose we start with  $U_A^{(0)} > U_A^*$  (to the right of the maximum in Fig. 6.3). Then  $dS/U_A < 0$ , which from Eq. (6.35) means that  $[(\partial s/\partial u)_v]_A < [(\partial s/\partial u)_v]_B$ . As the system approaches equilibrium,  $U_A$  decreases to  $U_A^*$ . Thus, heat must flow *from* A *into* B.

So it seems that heat flows *from* the system with lower  $(\partial s/\partial u)_v$  to the system with higher  $(\partial s/\partial u)_v$ . By convention, we choose to define temperature so that heat flows from high to low temperature. So  $(\partial s/\partial u)_v$  is not a suitable definition of thermodynamic temperature, if we want heat to flow from high to low temperature. But we could fix this up by taking the reciprocal: if  $[(\partial s/\partial u)_v]_A > [(\partial s/\partial u)_v]_B$ , then  $[(\partial s/\partial u)_v]_A^{-1} < [(\partial s/\partial u)_v]_B^{-1}$ . Therefore, we define the *thermodynamic temperature* as

$$\boxed{\frac{1}{T} = \left( \frac{\partial s}{\partial u} \right)_v} \quad (6.39)$$

Of course, Eq. (6.39) is not the only possibility. We could have put  $1/T^2$  on the left instead of  $1/T$ , for example. What we need to show is that Eq. (6.39) is equivalent to temperature as measured on the ideal-gas temperature scale. It is, but we'll save the proof for the exercises.

### 6.8.3 Mechanical Equilibrium

Consider again the problem of mechanical equilibrium, first discussed in Chapter 3. Suppose a cylinder is divided into two parts A and B by a piston, which may freely move back and forth (Fig. 3.2). The cylinder is isolated from the environment, and has fixed total volume

$$V_{tot} = V_A + V_B \quad (6.40)$$

and total energy

$$U_{tot} = U_A + U_B. \quad (6.41)$$

The piston will be assumed to not only move, but also conduct heat. Therefore, at equilibrium, A and B will be in both thermal and mechanical equilibrium.

As before, according to the Entropy Maximum Principle, the equilibrium state will maximize  $S$ . But now we have two independent parameters to vary:

$U_A$  and  $V_A$ . We seek to maximize the function

$$S = S_A(U_A, V_A, N_A) + S_B(U_{tot} - U_A, V_{tot} - V_A, N_B), \quad (6.42)$$

$$0 \leq U_A \leq U_{tot}; 0 \leq V_A \leq V_{tot}. \quad (6.43)$$

At the maximum (the equilibrium state),

$$\left( \frac{\partial S}{\partial U_A} \right) = 0 \text{ and } \left( \frac{\partial S}{\partial V_A} \right) = 0. \quad (6.44)$$

The derivative with respect to  $U_A$  is the same condition as we discussed above; it leads to the conclusion that  $T_A = T_B$  at equilibrium.

But the derivative with respect to  $V_A$  gives us some new information:

$$\left( \frac{\partial S}{\partial V_A} \right) = \left( \frac{\partial S_A}{\partial V_A} \right)_{U_A, N_A} + \left( \frac{dV_B}{dV_A} \right) \left( \frac{\partial S_B}{\partial V_B} \right)_{U_B, N_B} \quad (6.45)$$

$$= \left( \frac{\partial S_A}{\partial V_A} \right)_{U_A, N_A} + (-1) \left( \frac{\partial S_B}{\partial V_B} \right)_{U_B, N_B}. \quad (6.46)$$

Here we used Eq. (6.40) to set  $dV_B/dV_A = -1$ .

Setting  $(\partial S/\partial V_A) = 0$  at equilibrium, we find

$$\left[ \left( \frac{\partial S}{\partial V} \right)_{U, N} \right]_A = \left[ \left( \frac{\partial S}{\partial V} \right)_{U, N} \right]_B. \quad (6.47)$$

or

$$\left[ \left( \frac{\partial s}{\partial v} \right)_u \right]_A = \left[ \left( \frac{\partial s}{\partial v} \right)_u \right]_B. \quad (6.48)$$

Thus, when the piston stops moving and A and B are in both thermal and mechanical equilibrium, A and B will have the same value for  $(\partial s/\partial v)_u$ .

We define the *thermodynamic pressure*  $P$  as follows:

$$\boxed{\frac{P}{T} = \left( \frac{\partial s}{\partial v} \right)_u} \quad (6.49)$$

Then at equilibrium,

$$\left( \frac{P}{T} \right)_A = \left( \frac{P}{T} \right)_B. \quad (6.50)$$

Since the wall is heat-conducting,  $T_A = T_B$ . Therefore, if the piston can move, then we must have  $P_A = P_B$  at equilibrium. The proof that the thermodynamic pressure equals the mechanical pressure is left as an exercise.

## 6.8.4 Diffusive Equilibrium

Finally, let's consider diffusive equilibrium. Imagine an isolated system divided into two parts A and B by a partition which is rigid but allows molecules to pass through it. It also conducts heat.

For now, we will say that substances A and B are the same chemically, but may be in different states (e.g. different pressures, temperatures, and/or phases). For example, we might place in A a cold, low-pressure mixture of liquid water and ice, and in B hot, high pressure water vapor.

The analysis to find the equilibrium state is very similar to what we did in the previous section, except that the two variable quantities are  $U_A$  and  $N_A$ . The total energy and number of molecules are fixed, so

$$U_B = U_{tot} - U_A \quad (6.51)$$

and

$$N_B = N_{tot} - N_A. \quad (6.52)$$

Following the same procedures as above, we find that in the equilibrium state,

$$\left[ \left( \frac{\partial S}{\partial N} \right)_{U,V} \right]_A = \left[ \left( \frac{\partial S}{\partial N} \right)_{U,V} \right]_B \quad (6.53)$$

We define the *chemical potential*  $\mu$  by

$$\boxed{-\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right)_{U,V}} \quad (6.54)$$

and therefore at equilibrium

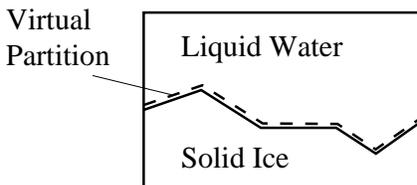
$$\left[ \frac{\mu}{T} \right]_A = \left[ \frac{\mu}{T} \right]_B. \quad (6.55)$$

Since the partition is heat-conducting,  $T_A = T_B$ , so the condition for equilibrium with respect to mass transfer is  $\mu_A = \mu_B$ . The negative sign is included in the definition so that mass will flow from the system with higher  $\mu$  to the one with lower  $\mu$ . The proof is left as an exercise.

Note that in this definition, the *total* values of  $U$  and  $V$  are being held constant (not  $\hat{u}$  and  $\hat{v}$ , or  $u$  and  $v$ ). So as more matter is added ( $N$  increases) at constant  $U$  and  $V$ ,  $\hat{u} = U/N$  and  $\hat{v} = V/N$  must decrease.

It is not necessarily the case that  $P_A = P_B$  for diffusive equilibrium, even though  $T_A = T_B$  and  $\mu_A = \mu_B$ . For example, if region A is a very small water

droplet and region B is the space around it containing water vapor, the liquid and vapor may be in equilibrium even though there is a pressure difference due to surface tension.



But in most cases other than small droplets or bubbles, the pressure is the same in all phases present in equilibrium. In this case, the phase-equilibrium conditions between, say, co-existing liquid and solid phases would be

$$T_\ell = T_s \quad (6.56)$$

$$P_\ell = P_s \quad (6.57)$$

$$\mu_\ell = \mu_s. \quad (6.58)$$

Clearly, these conditions would hold for any other type of phase equilibrium also (liquid/vapor, solid/vapor).

## 6.9 The Value of Boltzmann's Constant

We have not yet said what value should be assigned to  $k_B$  in  $S = k_B \ln \Omega$ . We have seen now that  $1/T = (\partial S / \partial U)_{V,N}$ , so the units of entropy must be [energy]/[temperature]. If we wish to use SI units, then, entropy must have units of J/K, and specific entropy J/kg-K. Since  $\ln \Omega$  is dimensionless, we must then give  $k_B$  the units of J/K.

Using the expression we have derived for the entropy of a monatomic, ideal gas along with the definitions of thermodynamic temperature and pressure, it is possible to prove that for an ideal gas

$$PV = Nk_B T. \quad (6.59)$$

Converting from units of molecules to units of moles,

$$PV = (N/N_A)(N_A k_B)T. \quad (6.60)$$

where  $N_A = 6.023 \times 10^{26} \text{ kmol}^{-1}$  is *Avagadro's Number*. This may be written in terms of molar volume as

$$\frac{P\hat{v}}{T} = N_A k_B \quad (6.61)$$

Experimentally, we know that this quantity equals 8314.4 J/kmol-K in the low-density, ideal gas limit (Chapter 4).

The experimental result uses temperature measured on the Kelvin scale (an ideal gas scale). If we wish the thermodynamic temperature to coincide with the Kelvin scale, then we must choose

$$k_B = (8314.3 \text{ J/kmol-K})(1 \text{ kmol}/6.023 \times 10^{26}). \quad (6.62)$$

Therefore,

$$k_B = 1.38 \times 10^{-23} \text{ J/K} \quad (6.63)$$

### 6.10 The Gibbs Equation

Often, we want to know how the entropy of a substance in equilibrium changes if its internal energy, volume, and number of molecules change by a small amount. Differentiating the function  $S(U, V, N)$  yields

$$dS = \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV + \left( \frac{\partial S}{\partial N} \right)_{U,V} dN. \quad (6.64)$$

Using the definitions for thermodynamic temperature, pressure, and chemical potential, this equation becomes

$$dS = \left( \frac{1}{T} \right) dU + \left( \frac{P}{T} \right) dV - \left( \frac{\mu}{T} \right) dN. \quad (6.65)$$

This equation is known as the *Gibbs equation*. It expresses a relationship among equilibrium *properties* of a substance, and doesn't depend on any particular type of process for its validity (e.g. reversible, etc.).

We can write the Gibbs equation on a per-mole or per-kg basis also. In this case,  $dN = 0$ , so

$$d\hat{s} = \frac{1}{T} d\hat{u} + \frac{P}{T} d\hat{v}, \quad (6.66)$$

and

$$ds = \frac{1}{T} du + \frac{P}{T} dv. \quad (6.67)$$

We can also solve Eq. (6.65) for  $dU$ :

$$\boxed{dU = TdS - PdV + \mu dN.} \quad (6.68)$$

This equation is completely equivalent to Eq. (6.65).

Now the property  $U$  exists, so it must be that Eq. (6.68) is what we would get if we differentiated the function  $U(S, V, N)$ . Therefore, we can identify

$$T = \left( \frac{\partial U}{\partial S} \right)_{V,N}; \quad P = - \left( \frac{\partial U}{\partial V} \right)_{S,N}; \quad \mu = \left( \frac{\partial U}{\partial N} \right)_{S,V}. \quad (6.69)$$

These equations are alternative ways to define the thermodynamic temperature, pressure, and chemical potential.

Applying Eq. (6.68) to a unit mass

$$du = Tds - Pdv, \quad (6.70)$$

and so

$$T = \left( \frac{\partial u}{\partial s} \right)_v; \quad P = - \left( \frac{\partial u}{\partial v} \right)_s. \quad (6.71)$$

Adding a “hat” would give the corresponding equations on a molar basis.

### 6.11 Macroscopic Determination of the Entropy

For most substances, it is virtually impossible to figure out  $\Omega(U, V, N)$ . Fortunately, the Gibbs equation gives us another way to determine  $S$ . If the equations of state  $T(u, v)$  and  $P(u, v)$  are known, then these may be inserted into Gibbs equation. For a unit mass,

$$ds = \frac{1}{T(u, v)} du + \frac{P(u, v)}{T(u, v)} dv. \quad (6.72)$$

This can be integrated along some path in the  $(u, v)$  plane, starting from some point  $(u_0, v_0)$ :

$$s(u, v) - s(u_0, v_0) = \int_{path} \left[ \frac{1}{T(u, v)} du + \frac{P(u, v)}{T(u, v)} dv \right]. \quad (6.73)$$

Since we know the function  $s(u, v)$  exists, the value of the integral won't depend on the particular path chosen. We can choose any convenient path.

This procedure, in slightly modified form, is how the entropy is usually determined for real substances. We will discuss this procedure more in Chapter 8.

We cannot determine the entropy of the initial state  $s_0 = s(u_0, v_0)$ . We have two choices. We can simply choose a convenient “reference” state  $(u_0, v_0)$  and assign the entropy in this state an arbitrary value (for example, zero). Then all entropies  $s(u, v)$  are really relative to  $s_0$ , the entropy in the reference state.

Or we can choose the reference state so that the ideal gas approximation holds for the reference state. In this case, we can use expressions from statistical mechanics for the absolute entropy of an ideal gas to get  $s_0$ . If the substance is monatomic, then Eq. (6.30) would be the right expression to evaluate  $s_0$ . If it is a molecular gas, the expression is slightly more complicated, but  $s_0$  still can be computed.

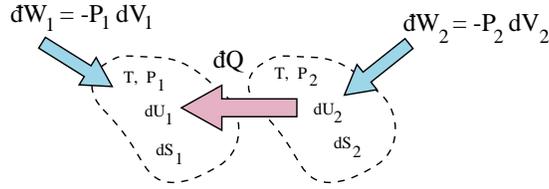
The choice of how to get  $s_0$  differs from one source of thermodynamic data to another. Care must be taken when comparing  $s$  (or  $h$  or  $u$ ) from different sources. In TPX, for most substances the reference state is taken to be saturated liquid at the lowest temperature for which the data are valid. Both the entropy and the enthalpy are assigned the value zero in the reference state. Of course, the value of  $s_0$  is irrelevant in computing entropy differences, as long as both entropy values are taken from the same source.

## 6.12 Entropy Flow with Heat

Consider two systems, each composed of some simple compressible substance which is internally in equilibrium. System 1 has temperature  $T_1$ , and system 2 has temperature  $T_2 = T_1 + \Delta T$ . We bring the into contact, and heat  $Q$  flows from 2 to 1.

Let’s take the limit  $\Delta T \rightarrow 0$ . In this limit, the temperature difference becomes infinitesimal ( $dT$ ) and the process approaches heat transfer at constant  $T$ . Of course, as  $\Delta T \rightarrow 0$ , the time  $t$  required to transfer a finite amount of heat  $Q$  increases proportional to  $Q/\Delta T$ . We’ll transfer only an infinitesimal amount of heat  $dQ$  (which only takes finite time).

The two systems start out internally in equilibrium. Since the heat transferred is infinitesimal, we can assume that the systems stay in internal equilibrium during this process, with the result that their intensive properties ( $T$  and  $P$ ) don’t change, and their extensive properties ( $U$ ,  $V$ , and  $S$ ) change only infinitesimally. This also means that there are no internal irreversibilities (viscous forces, electrical power dissipation, etc.) since these only exist when a system is not in internal equilibrium. Therefore, no entropy is being produced in either system, and this process is reversible.



Writing the first law for the process,

$$dU_1 = dQ - P_1 dV_1, \quad (6.74)$$

and

$$dU_2 = -dQ - P_2 dV_2. \quad (6.75)$$

Since 1 and 2 are not necessarily in mechanical equilibrium with one another, we allow  $P_1$  and  $P_2$  to differ. (For example, they may be sitting in environments at different pressures, and are connected by a copper wire allowing heat to flow.) Note that we have used the assumption of reversibility in writing the work terms as  $-PdV$ .

We can also write the Gibbs equation for each substance:

$$dS_1 = \frac{1}{T} dU_1 + \frac{P_1}{T} dV_1 \quad (6.76)$$

and

$$dS_2 = \frac{1}{T} dU_2 + \frac{P_2}{T} dV_2. \quad (6.77)$$

Since  $dN_1 = dN_2 = 0$ , we have left off the  $-(\mu/T)dN$  term. Substituting for  $dU$  from the first-law expressions, we find

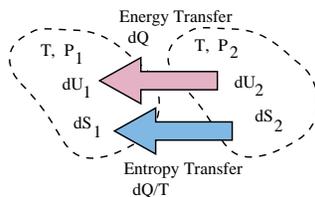
$$dS_1 = \frac{dQ}{T} \quad (6.78)$$

and

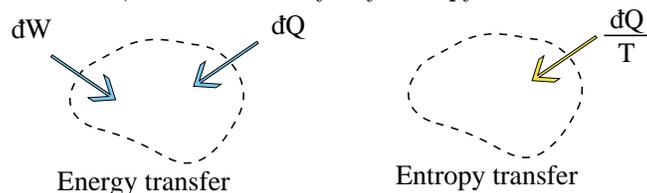
$$dS_2 = -\frac{dQ}{T}. \quad (6.79)$$

Although no entropy was produced by this process of heat transfer at constant  $T$ , the entropy of system 1 increased, and that of system 2 decreased by exactly the same amount. It must be, then, that entropy was *transferred* from 2 to 1 along with the energy transfer  $dQ$ . Therefore,

When heat  $dQ$  enters or leaves a system at temperature  $T$ , it carries with it entropy in the amount  $dQ/T$ .



Note that the work terms canceled out of the above equations. Evidently, entropy transfer is associated only with energy transfer as heat – when energy is transferred as work, it does not carry any entropy with it.



**Problems**

**6.1** A rectangular box contains  $N$  molecules. Suppose that each molecule can be on either side of the box with equal probability.

1. What is the probability that all  $N$  molecules are on one side? Compute this number for  $N = 1, 2, 20,$  and  $10^{20}$ .
2. Astronomers believe the universe is between 8 and 13 billion years old. Suppose you examine this system once every second, and the molecules are distributed completely randomly each time. Estimate the largest value  $N$  can have so that on average you will find all molecules on one side at least once in the age of the universe.

**6.2** Using Eq. (6.30) and the definitions of thermodynamic temperature and pressure, show that for a monatomic gas of  $N$  atoms

$$U = \frac{3}{2}Nk_B T$$

and

$$PV = Nk_B T.$$

**6.3** Prove that the thermodynamic pressure  $P$  equals the mechanical pressure  $P_{mech} = F/A$ . To do so, consider a quasi-static, reversible, adiabatic compression in which the volume changes by  $dV$ . The work done on the system is  $dW_{qs} = -P_{mech}dV$ . Use the first law, and the fact that  $dS = 0$  for this process. (Hint: write  $ds(u, v)$  in terms of  $du$  and  $dv$ .)

**6.4** Show that if  $\mu_A \neq \mu_B$ , mass flows from the one with higher  $\mu$  to the one with lower  $\mu$ .

**6.5** Using

$$S(U, V, N) = N\hat{s}(\hat{u}, \hat{v}) = N\hat{s}(U/N, V/N)$$

show that

$$\mu = \hat{u} + P\hat{v} - T\hat{s}.$$

The right-hand side of this equation is the definition of the molar Gibbs free energy, and thus  $\mu = \hat{g}$ .

( $N$  may be interpreted as either the number of molecules or the number of moles, and all “molar” quantities as per molecule or per mole, whichever is more convenient.)

**6.6** Consider a crystal composed of  $\mathcal{N}$  atoms, each of which can occupy one of *two* quantum states. The first state (the ground state) has energy zero, and the other one (the upper state) has energy  $\epsilon > 0$ .

1. Suppose the total internal energy of the crystal is  $U$ , where  $U$  is an integral multiple of  $\epsilon$ . Show that the number of different microscopic quantum states of the crystal which have this energy  $U$  is given by

$$\Omega = \frac{N!}{\left(\frac{U}{\epsilon}\right)! \left(N - \frac{U}{\epsilon}\right)!} \quad (6.80)$$

Neglect any other forms of energy, such as vibration.

2. In the limit  $N \rightarrow \infty$ , determine the entropy of the system at equilibrium. (Note that for large  $n$ ,  $\ln(n!) \approx n \ln n - n$ .)
3. From the entropy and the definition of thermodynamic temperature, determine the thermal equation of state  $U(T, N)$ .

**6.7** We showed that when two phases 1 and 2 of a substance are in equilibrium with one another,  $P_1 = P_2$ ,  $T_1 = T_2$ , and  $\mu_1 = \mu_2$ . Using TPX, verify that  $\mu_1 = \mu_2$  for saturated liquid water and water vapor at 300 K.

**6.8** A mixture of saturated liquid nitrogen and saturated vapor at 1 MPa is contained on one side of an insulated container which is divided in half by a partition. The initial vapor mass fraction is 0.7. The other side is evacuated. Now the partition is broken, and the nitrogen expands unrestrained to fill the container, doubling its volume. Using TPX:

1. Find the new pressure and temperature of the system once equilibrium has been re-established.
2. Determine how much entropy was produced by this process, per unit mass of nitrogen.