

0.1.2 The second law of thermodynamics

Now that we have seen the importance of probability in determining the equilibrium macrostates of macroscopic systems, we can give that the status of a law—the second law of thermodynamics. The usual statements of the law are expressed in terms of entropy, rather than multiplicity. Here is the way Gibbs stated it:

The general criterion for equilibrium can be stated simply and precisely: for the equilibrium of any isolated system, it is necessary and sufficient that, in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.

This is precisely the kind of situation we have encountered in considering the equilibrium state of a pair of any of our toy systems placed in thermal contact with each other, but isolated from everything else. The initial state of the combined system, prior to establishing the thermal contact, was constrained in such a way that one of the subsystems had more than its fair share of the energy. When the subsystems were placed in thermal contact, we found that the entropy (multiplicity) of the initial macrostate, characterized by the energy of one of the subsystems, was smaller than that of other macrostates having a more even distribution of energy. Thus, probability alone leads to the ultimate establishment of an equilibrium state with the entropy maximized over the set of all possible values of the energy characterizing the macrostates.

Gibbs's statement generalizes that to any kind of variation one might make between the subparts of a system, particle density, volume, electric charge, or whatever. That is, when entropy (or multiplicity) is expressed as a function of some parameter characterizing possible macrostates of an isolated system, the equilibrium state is the one that maximizes the entropy over the set of possible values of that parameter.

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0.1.3 The entropy of the ideal gas

HW Problem. Schroeder problem 2.34, p. 79.

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Recall that the multiplicity of the ideal gas is

$$\Omega = \frac{\epsilon_p}{(2mU)^{1/2}} \frac{V^N (2\pi mU)^{3N/2}}{N! h^{3N}} \frac{2}{\Gamma\left(\frac{3N}{2}\right)}. \quad (20)$$

Since $\Gamma(3N/2) = [(3N/2) - 1]!$, the third fraction can be written in the alternative form:

$$\frac{2}{\Gamma\left(\frac{3N}{2}\right)} = \frac{3N}{\left(\frac{3N}{2}\right)!}. \quad (21)$$

Also, we'll move the $N!$ from the second fraction to the third one, to keep the factorials together. Then it's a straightforward matter to calculate its entropy $S = k \ln \Omega$. We'll start by taking the logarithm:

$$\ln \Omega = \ln \left[\frac{\epsilon_p}{(2mU)^{1/2}} \right] + N \ln \left[\frac{V(2\pi mU)^{3/2}}{h^3} \right] + \ln \left[\frac{3N}{N! \left(\frac{3N}{2}\right)!} \right]. \quad (22)$$

The first term is just the logarithm of the ratio of the thickness of the thin shell in $3N$ -dimensional momentum space to its radius, a small number compared to the second term, which is proportional to N . So we'll drop the first term. We can use Stirling's approximation to approximate the logarithm in the third term:

$$\ln \left[\frac{3N}{N! \left(\frac{3N}{2}\right)!} \right] \approx \ln(3N) - N \ln N + N - \frac{3N}{2} \ln \left(\frac{3N}{2} \right) + \frac{3N}{2}. \quad (23)$$

All the terms are proportional to N except the first, so we'll drop the first term. Then we're left with

$$\begin{aligned} \ln \left[\frac{3N}{N! \left(\frac{3N}{2}\right)!} \right] &\approx N \left[-\ln N - \frac{3}{2} \ln \left(\frac{3N}{2} \right) + \frac{5}{2} \right] \\ &= N \left[\ln \left(\frac{1}{N} \right) + \ln \left(\frac{2}{3N} \right)^{3/2} + \frac{5}{2} \right]. \end{aligned} \quad (24)$$

Putting this back into the entropy, we have

$$\begin{aligned} S &= k \ln \Omega \\ &= Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\}. \end{aligned} \quad (25)$$

This is a famous equation, called the *Sackur-Tetrode equation*.

There are a couple of important things to notice about this entropy. First, it expresses S as a function of three macroscopic variables characterizing the equilibrium state of the system, U , V , and N . Second, all three of these variables are proportional to the size of the system, and the overall factor of N makes it clear that S is as well. Such variables are called *extensive* variables, and they play an important role in all thermodynamic systems, not just the ideal gas. Finally, U and V appear only as ratios with N , so the dependence of S on U and V reduces to a dependence on the energy per particle U/N and the volume per particle V/N .

It's also important to notice that S , like U , V , and N is a state variable. Its value depends only on the state, not on the path taken from some other state. This is obvious from the statistical definition of the entropy, since the number of microstates corresponding to a given macrostate depends

only on the state, not on how it was produced. But it is also evident from the Sackur-Tetrode equation, which shows that the entropy of an ideal gas depends only on state variables, constants, and the particle mass.

Thus we see three obvious ways to increase the entropy of an ideal gas:

- Increase the number of particles. The N dependence isn't trivial, but the overall factor of N dominates the inverse dependences inside the logarithm. If the particles are added with fixed U/N and V/N , rather than with fixed U and V , then S changes in direct proportion to N . One expects, based on the behavior of multiplicities of combined systems, which are the products of the multiplicities of the individual systems, that S should be additive for the equilibrium state, and this demonstrates that for the ideal gas.
- Increase the energy per particle. For an ideal gas, recall that the total energy is

$$U = \frac{f}{2} NkT, \quad (26)$$

f being the number of degrees of freedom per particle, so the energy per particle is directly proportional to the temperature. Increasing the temperature increases U/N , hence it increases the entropy.

- Increase the volume per particle. Remember that when we quantized the ideal gas by putting it in a box of volume $V = L^3$, we found the possible single-particle states to lie on points in a cubic lattice in momentum space, with the momentum-space volume per point being h^3/V . Increasing the volume increases the density of the points representing possible states, so it increases the number of microstates having the fixed total energy of the system. Hence it increases the entropy.

Example. Now that we have an expression for the entropy of an ideal gas, let's try it out to find the equilibrium state of a pair of ideal gases in thermal contact. We'll suppose the systems have entropy functions

$$S_1(U_1, V_1, N_1) \quad \text{and} \quad S_2(U_2, V_2, N_2), \quad (27)$$

but we'll fix the volumes and particle numbers. We'll also fix the total energy of the combined system:

$$U = U_1 + U_2 = \text{constant}. \quad (28)$$

Then the total entropy of the combined system can be expressed as a function of U_1 alone (or U_2):

$$S(U_1) = S_1(U_1) + S_2(U_2) = S_1(U_1) + S_2(U - U_1). \quad (29)$$

In equilibrium the entropy is maximized with respect to changes in U_1 , so its derivative with respect to U_1 must vanish:

$$\frac{dS}{dU_1} = 0 \Rightarrow \left(\frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} + \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} \underbrace{\frac{dU_2}{dU_1}}_{-1} = 0. \quad (30)$$

The condition for equilibrium of the systems is then just

$$\left(\frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} = \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2}. \quad (31)$$

For the ideal gas, we can evaluate the derivative:

$$\begin{aligned} \left(\frac{\partial S}{\partial U} \right)_{V, N} &= Nk \left\{ \underbrace{\left[\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right]^{-1} \left[\frac{V}{N} \left(\frac{4\pi m}{3N h^2} \right)^{3/2} \right]}_{U^{-3/2}} \frac{3}{2} U^{1/2} \right\} \\ &= \frac{3}{2} \frac{Nk}{U}. \end{aligned} \quad (32)$$

But the equipartition theorem gives the energy in term of the temperature:

$$U = \frac{3}{2} NkT, \quad (33)$$

which means the derivative of S reduces to

$$\left(\frac{\partial S}{\partial U} \right)_{V, N} = \frac{1}{T}. \quad (34)$$

Thus, the condition for equilibrium of two ideal gases in thermal contact is simply:

$$\frac{1}{T_1} = \frac{1}{T_2} \quad \text{or} \quad T_1 = T_2, \quad (35)$$

which is a direct consequence of the maximization of the entropy. This agrees with a more general, but unsubstantiated, claim I made on the first day.

0.1.4 Entropy of mixing

We've seen that the entropy of an ideal gas can be increased by increasing the number of particles, the volume per particle, or the energy per particle, which is proportional to the temperature. But there's also a curious increase in entropy that arises from mixing of two different ideal gases. The same phenomenon occurs in liquids and solids, but our expression for the entropy of an ideal gas gives us a nice opportunity to see the effect in action in a specific system.

First, let's note that it's not surprising that mixing should increase the entropy, if we think of entropy as a measure of disorder—the mixed gases constitute a more disordered state than the separated gases. As well, we expect that there are many more mixed microstates of the gases than separated microstates, so the entropy must be greater in the mixed state. Still, there is a bit of a puzzle associated with the phenomenon, as we'll see shortly.

We can understand mixing of different ideal gases by considering the volume dependence of the entropy. Suppose a container is partitioned into two equal subvolumes, and the two sides are filled with equal numbers of neon and argon atoms, one type on each side. In thermal equilibrium, both gases have equal total energies, as well as volumes, and numbers of particles, so their entropies are equal. Removal of the partition permits both gases to occupy twice the volume they occupied originally, even though the volume per particle of any type remains the same.

The volume dependence of the entropy is expressed by the partial derivative of the Sackur-Tetrode entropy with respect to volume:

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{NK}{V}, \quad (36)$$

so the finite change in entropy accompanying a finite change in volume is

$$\begin{aligned} \Delta S &= \int_{V_i}^{V_f} \left(\frac{\partial S}{\partial V}\right)_{U,N} dV \\ &= Nk \int_{V_i}^{V_f} \frac{1}{V} dV \\ &= Nk \ln \frac{V_f}{V_i}. \end{aligned} \quad (37)$$

Each of the two gases experiences this change in entropy upon mixing, and with $V_f = 2V_i$, the total change in entropy is

$$\Delta S = 2Nk \ln 2. \quad (38)$$

Now, why should this bother us? It shouldn't really, but historically it was considered puzzling because if the gases are identical, there cannot be any change in entropy, since the entropy of the combined system before

and after the partition is removed is

$$\begin{aligned}
 S &= S_1 + S_2 \\
 &= N_1 k \left\{ \ln \left[\frac{V_1}{N_1} \left(\frac{4\pi m U_1}{3h^2 N_1} \right)^{3/2} \right] + \frac{5}{2} \right\} \\
 &\quad + N_2 k \left\{ \ln \left[\frac{V_2}{N_2} \left(\frac{4\pi m U_2}{3h^2 N_2} \right)^{3/2} \right] + \frac{5}{2} \right\} \\
 &= Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\},
 \end{aligned} \tag{39}$$

where $U_1 = U_2 = U/2$, $V_1 = V_2 = V/2$, and $N_1 = N_2 = N/2$ assures the final equality. One could imagine making the atoms of the gas more and more alike, say by using different isotopes of a single atomic type, with smaller and smaller differences in atomic mass, yet as long as the atoms were different in any way, no matter how small, the entropy change would be $2Nk \ln 2$. And if they were absolutely identical, the entropy change would suddenly and completely vanish.

The reason for the different behaviors is the $1/N!$ we had to introduce in the calculation of the multiplicity of the macrostate of energy U . That was required because of the indistinguishability of the particles, which forced identification of any of the $N!$ states with the particles permuted as the same microstate. Its consequences in the Sackur-Tetrode entropy are the N appearing in V/N and the constant term being $5/2$ rather than $3/2$. The first of those is required for the entropy sum for separated identical ideal gases to be the same as the entropy of the combined gas.

HW Problem. Schroeder problem 2.36, p. 79.

HW Problem. Schroeder problem 2.37, p. 81.

HW Problem. Schroeder problem 2.42, pp. 83–84.