Physics 3700

Entropy. Temperature. Chemical Potential. Thermodynamic Identities. Third Law. Relevant sections in text: §2.6, 3.1, 3.2, 3.4, 3.5

Entropy

We have seen that the equilibrium state for an isolated macroscopic thermal system is the one with the highest multiplicity. Obviously, the multiplicity of a macrostate is an important observable of the system. This is, of course, a huge number in general. To keep things manageable — and to give us other important properties, to be discussed later we define a corresponding observable using the natural logarithm of the multiplicity times Boltzmann's constant. This is the *entropy**

$$S = k \ln \Omega.$$

The SI units of entropy are J/K.

For the Einstein solid (with our macroscopic, high temperature approximation) the entropy is

$$S = k \ln \left(\frac{eq}{N}\right)^N = Nk(\ln \left(\frac{q}{N}\right) + 1).$$

With $N = 10^{22}$ and $q = 10^{24}$ we have S = 0.77J/K. This is a typical result. In SI units Boltzmann's constant is around 10^{-23} , and the logarithm of the multiplicity for a macroscopic system is typically around 10^{23} , so the entropy — which is on the order of Nk — is typically on the order of unity in SI units. Note that the more particles there are, the higher the entropy. The more energy there is, the higher the entropy. Both of these stem from the increased multiplicity that occurs when these observables are increased.

The entropy is an extensive observable. This is one of the key features of using the logarithm of the multiplicity to define entropy. We have seen that a system composed of two (weakly interacting) macroscopic subsystems, A and B, has its multiplicity coming as the product of the subsystem multiplicities:

$$\Omega = \Omega_A \Omega_B.$$

Thus

$$S = k \ln(\Omega_A \Omega_B) = S_A + S_B.$$

In terms of entropy we can restate the second law of thermodynamics as: An isolated macroscopic system in equilibrium will be found in the state with the largest entropy. Thus

^{*} The term was coined in 1865 (in analogy with German *Energie*) by physicist Rudolph Clausius from the Greek *entropia* "a turning toward."

you can interpret relaxation to equilibrium of an isolated system as corresponding to an increase of entropy until a maximum is reached.

Entropy of an ideal gas – Sackur-Tetrode formula.

Let us get a useful approximate formula for the entropy of an ideal gas in the macroscopic limit. We start with our (approximate) formula from the previous lecture:

$$S = k \ln \left\{ \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!} (2mU)^{3N/2} \right\}.$$

Using the product/ratio properties of the logarithm we have:

$$\frac{S}{k} = \ln(V^N) + \ln\left(\frac{2\pi mU}{h^2}\right)^{3N/2} - \ln N! - \ln\left(\frac{3N}{2}!\right).$$

Using Stirling's approximation in the form (for n >> 1)

$$\ln n! \approx n \ln(n) - n,$$

and with a tiny bit of algebra, we have

$$\frac{S}{k} \approx N \left[\ln V - \ln N + \ln \left(\frac{2\pi mU}{h^2} \right)^{3/2} - \frac{3}{2} \ln \left(\frac{3N}{2} \right) + \frac{5}{2} \right].$$

With a little more simplifying using standard logarithm properties we get

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

This result is known as the *Sackur-Tetrode formula* for the entropy of a monatomic ideal gas. Note that the entropy is here expressed as a function of the observables U, V and N:

$$S = S(U, V, N).$$

Note that the extensive variables U, V only appear in the intensive forms U/N and V/N, the energy per particle and volume per particle, respectively. The extensive nature of the entropy arises via the overall multiplicative factor of N. This factor illustrates the rule of thumb that (up to logarithmic corrections) the entropy of a system is on the order of Nk.

We can use the Sackur-Tetrode (ST) formula to investigate how the entropy of a monatomic ideal gas changes for various changes of the thermodynamic state. Here are a couple of examples.

Entropy of expansion

Expansion of a system can create entropy – something we saw via multiplicity for a free expansion. Let's check this out with the Sackur-Tetrode formula for an ideal gas. First of all, note that *if the energy and number of molecules remains fixed*, an increase in volume, $V_i \rightarrow V_f$, leads to an increase in entropy. Indeed, we have

$$\Delta S = Nk \ln \frac{V_f}{V_i}.$$

For example, suppose the ideal gas is in a piston/cylinder apparatus such as we discussed earlier. Let the gas expand, doing work on the piston while we add energy via heat so that it expands isothermally. Then we know that the energy remains constant. (How is the heat related to the work done?) We know that N remains constant. Thus the entropy increases if the volume increases, *e.g.*, if the volume doubles, then

$$\Delta S = Nk\ln 2.$$

As we shall see soon, we can interpret the entropy increase in this case (isothermal expansion) as being "caused" by the heat transfer. In some sense, the gas is trading energy which can do work for energy due to heat and this is what the change in entropy measures here.

As another example, suppose we let the gas expand into an evacuated, insulated, larger container by vaporizing the piston. This is the "free expansion" we talked about earlier. No work is done by the gas. No heat transfer takes place. Again the energy (and temperature) does not change; ΔS is the same as before. Obviously we cannot view the increase of entropy in this case as being "caused" by heat transfer – there is no heat transfer. One can only say it is "caused" by the increase in volume. Of course, from a microscopic point of view, the increase in entropy corresponds to the increase in microstates you get from increasing the volume and so is intimately associated with the *irreversibility* of the process. Contrast this with the isothermal expansion of a gas, which is quasi-static and *reversible*. In that case the increase in multiplicity "causes" the transfer of energy via heat.

Entropy of Mixing

Suppose you have an ideal gas filling both compartments (labeled A and B) of a partitioned container of volume $V = V_A + V_B$, with number of atoms $N = N_A + N_B$ and energy $U = U_A + U_B$. The gas in the two compartments is in equilibrium, so $T_A = T_B$ and $P_A = P_B$

What happens to the entropy when you remove the partition? Nothing! To see this, note that before the partition is removed the entropy is

$$S = S_A + S_B = kN_A \left\{ \ln \left[\frac{V_A}{N_A} \left(\frac{4\pi m U_A}{3N_A h^2} \right)^{3/2} \right] + 5/2 \right\} + kN_B \left\{ \ln \left[\frac{V_B}{N_B} \left(\frac{4\pi m U_B}{3N_B h^2} \right)^{3/2} \right] + 5/2 \right\}$$

I remind you that the energies and volumes in the logarithms only appear divided by the number of particles. Because the gases A and B are in equilibrium, these quantities are equal in each of the logs — the arguments of the logs are the same. Thus we can combine the two terms using $N = N_A + N_B$, $V/N = V_A/N_A = V_B/N_B$, $U/N = U_A/N_A = U_B/N_B$; we then get

$$S = kN \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + 5/2 \right\}.$$

This is just the entropy of the ideal gas in the state defined by N, U, V – exactly the entropy you would compute when the partition is removed.

Note that this result is really just what you should expect. Ignoring the thickness of the partition, there is no real difference between the state before the partition is removed and after. To be sure, the particles mix when the partition is removed. But since the particles are *indistinguishable* this mixing is unobservable from the point of view of counting microstates.*

From this last observation you might wonder what happens when the gases in the two compartments are *distinguishable*. To answer this question we proceed as before, but we introduce $m_A \neq m_B$. The initial entropy is now

$$S = S_A + S_B$$

= $kN_A \left\{ \ln \left[\frac{V_A}{N_A} \left(\frac{4\pi m_A U_A}{3N_A h^2} \right)^{3/2} \right] + 5/2 \right\} + kN_B \left\{ \ln \left[\frac{V_B}{N_B} \left(\frac{4\pi m_B U_B}{3N_B h^2} \right)^{3/2} \right] + 5/2 \right\},$

where thermal and mechanical equilibrium guarantee

$$\frac{U_A}{N_A} = \frac{U_B}{N_B}, \quad \frac{V_A}{N_A} = \frac{V_B}{N_B}.$$

The final entropy can be computed by noting that the final state is obtained by supposing each of the gases increase its volume by a free expansion, keeping everything else fixed. For simplicity, let us set $V_A = V_B = V/2$. As we have seen, this leads to

$$\Delta S_A = N_A k \ln 2, \quad \Delta S_B = N_B k \ln 2.$$

^{*} The formula for multiplicity of an ideal gas which we started from supposes that all the particles are indistinguishable. So, for instance, swapping the location of two molecules in the gas does not create a new microstate.

Thus

$$\Delta S = \Delta S_A + \Delta S_B = (N_A + N_B)k\ln 2.$$

This increase in entropy is called the *entropy of mixing*. It comes about from a combination of the entropy of expansion and the distinguishability of the particles. Note that the final state (unlike the initial state) is one of *diffusive* (or chemical) equilibrium. The increase in entropy in this case comes from the irreversibility of the process. This process is not quasi-static.

Reversible and irreversible processes

We have a version of the second law of thermodynamics telling us that, for an isolated system, at equilibrium the multiplicity – equivalently, the entropy – is maximized. This means that when a dynamical process occurs, *i.e.*, when the state changes, the equilibrium that occurs will be constrained by the requirement that the entropy of the isolated system will not decrease. This fact controls the way many processes operate in nature. Processes which actually increase the entropy of an isolated system — such as the free expansions studied in the last section — are called *irreversible*. These processes cannot run in the reverse direction since that would violate the second law. It is in principle possible, however, for the entropy to stay the same during a process. Such processes are called *isentropic*. A rather trivial example of an isentropic process is provided by the partitioned container business from the last section in the case of identical gases. It is possible that such processes are rather special (and in fact are an idealization), while irreversible processes are very common. We shall see some more examples in the near future.

It is important to note that the second law of thermodynamics tells us the entropy of an *isolated system* does not decrease. This does *not* mean that the entropy of a system may not decrease! The key word here is "isolated". If the system is coupled to the outside world (it can exchange energy, volume, particles, *etc.* with its environment) it may very well happen that during relaxation to equilibrium the entropy of the system or the environment will decrease. All the second law guarantees is that the entropy of the system + environment (the closed/isolated system) is non-decreasing.

Equilibrium of a closed system maximizes the entropy

Our discussion of the second law shows that equilibrium states of a closed system are the ones with the biggest entropy. Thus entropy is a maximum at equilibrium.^{*} We normally consider (at least) 3 types of equilibrium: thermal, mechanical, and diffusive. If

^{*} I emphasize that one must have a closed system to use this idea. It is easy to forget this and make incorrect deductions.

we view the closed system as composed of coupled subsystems (all macroscopic), then by definition these equilibria are obtained via an exchange of energy (U), volume (V) and particles (N) among the subsystems. Equilibrium corresponds to the maximum value of the total entropy as a function of these observables for the subsystems. We can use this reasoning to obtain a fundamental relationship – indeed, a *definition* – of temperature, pressure, and chemical potential from the entropy.

Entropy and Temperature

Temperature has been defined (via the zeroth law) as the observable which is the same for two systems in thermal equilibrium. It has also been seen to represent (using a microscopic point of view) the energy per degree of freedom. We can now give a precise, purely macroscopic *definition* of temperature via the entropy.

Consider two systems in thermal contact, A and B, with some given total energy $U = U_A + U_B$ and otherwise isolated from the rest of the universe. As we have discussed, the two systems will exchange energy (with U not changing) until the entropy of the combined system is as big as possible, at which point we have equilibrium. This means that the derivative of the total entropy $S = S_A + S_B$ with respect to either U_A or U_B must vanish at equilibrium. We have

$$0 = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = \frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B}.$$

The last equality above uses the fact that the total energy is fixed so that

$$0 = dU = dU_A + dU_B \implies dU_A = -dU_B$$

So, we conclude that (holding fixed all other variables which the entropy may depend upon) the slope of the entropy vs. energy graph for each of systems A and B will become equal at equilibrium. This means that we can define temperature via the slope of these graphs.

The precise definition is

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

where the notation " N, V, \ldots " indicates that we hold fixed the volume and number of particles of the system. The idea here is that "equilibrium" means thermal, mechanical, and diffusive equilibrium. The latter two forms of equilibrium involve equality of pressure and chemical potential (as we shall discuss below), which we will analyze by varying the volume and number of particles of each subsystem. The entropy is to be maximized with respect to changes in each of U, V, N; we are currently considering the conditions coming from varying energy.

Notice that the temperature might have been defined as any function of the slope of S(U). The particular form of the definition – temperature is the reciprocal of the slope of entropy versus energy – is forced on us simply to get the units right. To check that this definition makes sense, let's look at a couple of examples.

Ideal Gas

The Sackur-Tetrode formula for the entropy of a monatomic ideal gas is

$$S = kN \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + 5/2 \right\}.$$

Notice that we have expressed S = S(U, V, N) so that varying S while holding V and N fixed corresponds to simply taking the partial derivative of the S-T formula with respect to U.

You can easily check that

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{3}{2}\frac{Nk}{U}.$$

So, according to our definition,

$$T = \frac{2}{3Nk}U,$$

which agrees with the temperature coming from the familiar equation of state for a monatomic ideal gas:

$$U = \frac{3}{2}NkT.$$

Note that if we had, say, expressed V in terms of P and N we could not simply take the derivative and get the temperature. This is because *that* derivative would not be taken keeping the volume fixed, but rather P and N.

Einstein Solid

For a large Einstein solid at high enough temperature we have

$$S = k \ln \left[\left(\frac{eq}{N}\right)^N \right],$$

where N >> 1 is the number of oscillators and q >> N is a dimensionless version of the energy. We have

$$U = q\epsilon,$$

where $\epsilon = \hbar \omega$.

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We then have

$$S = k \ln \left[\left(\frac{eU}{N\epsilon} \right)^N \right],$$
$$\frac{\partial S}{\partial U} = \frac{Nk}{U}.$$
$$T = \frac{1}{k} \frac{U}{N},$$

U = NkT.

and

This leads us to

$$T = \frac{1}{p}$$

i.e.,

which agrees with the equipartition result for energy versus temperature.*

Entropy, Equipartion, Energy and Temperature

You will recall we made an argument for the monatomic ideal gas which said that the multiplicity should be proportional to $U^{(3N-1)/2} \approx U^{3N/2}$, where N is the number of atoms. It is possible to generalize this result to say that the multiplicity will be proportional to $U^{fN/2}$, where f is the number of degrees of freedom a la equipartition.

This result should hold for any system (not just an ideal gas) if the temperature is high enough (so all the degrees of freedom are excited). Note, for example, that the Einstein solid obeys this rule (it has a translational and a oscillatory degree of freedom, so f = 2).

Thus, for any system obeying the equipartition result we will have (for some quantity α which is independent of U):

$$S = k \ln(\alpha U^{Nf/2}).$$

We then have

$$\frac{\partial S}{\partial U} = k \frac{f}{2} \frac{N}{U},$$
$$T = \frac{2}{kf} \frac{U}{N},$$

or

so that

 $U = \frac{f}{2}NkT.$

Entropy, Mechanical Equilibrium and Pressure

When two macroscopic systems are put into thermal and mechanical contact (e.q.,an ideal gas in a box with a movable partition), we have discussed how the subsystems

^{*} Recall that the Einstein solid obeys equipartition of energy with f = 2.

exchange volume until equilibrium is obtained – this is thermal *and mechanical* equilibrium. From Newton's laws you know that mechanical equilibrium occurs when all forces are balanced – typically this means the pressures become equal at (mechanical) equilibrium. This is entirely analogous to having the temperatures equal at thermal equilibrium by exchange of energy. We can use the same type of argument – multiplicity and hence entropy is maximized at equilibrium – to give an analogous definition of thermodynamic pressure in terms of entropy.

For fixed total volume $V = V_A + V_B$ of the combined system we have at equilibrium

$$0 = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}.$$

The last equality above uses the fact that the total volume is fixed so that

$$0 = dV = dV_A + dV_B \implies dV_A = -dV_B.$$

Therefore, at mechanical equilibrium,

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}.$$

It is thus reasonable to view $\frac{\partial S}{\partial V}$ to be a function of the pressure. Given that the two systems are also in thermal equilibrium, it makes dimensional sense to *define*

$$P = \left(T\frac{\partial S}{\partial V}\right)_{U,N,\dots}.$$

Let's check that this definition is consistent with the ideal gas use of pressure. Write the entropy as

$$S = k \ln \left[f(N) V^N U^{3N/2} \right] = k \left\{ \ln f(N) + N \ln V + \frac{3N}{2} \ln U \right\}.$$

We then get

$$T\frac{\partial S}{\partial V} = \frac{NkT}{V},$$

which agrees with the expression of pressure in terms of N, T, V coming from the ideal gas law.

A nice analogy

From the preceding discussion we can obtain an important analogy between the observable pairs (U, T) and (V, P): one might say, "temperature is to energy as pressure is to volume". So, if you want an intuitive interpretation of temperature, you can view it as akin to a sort of "pressure" for energy transfer.

The Thermodynamic Identity

So far we have considered thermal and mechanical equilibrium. We will soon consider diffusive equilibrium, but let us take stock of where we are thus far. We can summarize our previous discussion with a very important equation: the *thermodynamic identity*. First let me remind you of a basic math fact.

Given a function of n variables,

$$f = f(x^1, x^2, \dots, x^n),$$

the differential of f is given by

$$df = \frac{\partial f}{\partial x^1} dx^1 + \frac{\partial f}{\partial x^2} dx^2 + \ldots + \frac{\partial f}{\partial x^n} dx^n.$$

This gives the (infinitesimal) change in the value of a function at location $(x^1, \ldots x^n)$ due to a displacement along a vector with components $(dx^1, dx^2, \ldots dx^n)$.

Here is the setting for the thermodynamic identity. Let us have a thermodynamic system whose observables are functions of energy, pressure, volume, and temperature only. (There may be relations among these, *e.g.*, the ideal gas law.) Other observables may be present (e.g. the number of atoms), but we assume they are always held fixed and thus are just entering the observables as fixed numbers. For simplicity, we suppose that we can express the entropy as a function of the observables S = S(U, V).

We then have the following mathematical relationship between the variables (S, T, U, P, V):

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

Do you see why this works? It's because we have

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}.$$

The infinitesimal relation involving differentials is called the *thermodynamic identity* (really, it's specialization to the case where N is held fixed). Even if we haven't chosen to express S = S(U, V,) these relationships are still valid — but when varying the entropy one must do it in such a way as to keep fixed the indicated quantities.

We can massage the thermodynamic identity to get an equivalent, useful form of the thermodynamic identity:

$$dU = TdS - PdV.$$

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This means:

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -P.$$

The easiest way to implement these relations is to express U as a function of S and V and just take the indicated partial derivatives.

The thermodynamic identity is a set of mathematical relationships which must exist between the variables (S, T, U, P, V). It holds quite generally.

If other kinds of equilibrium are possible, associated with other intensive observables analogous to P and extensive variables analogous to V, then there would be additional work terms analogous to PdV in the thermodynamic identity. We will see an example of this later when we consider diffusive equilibrium, *i.e.*, we consider changes in N.

The thermodynamic identity is always true as a mathematical relation between observables, but the most common application of it is to quasi-static processes where we can view the differentials as changes in the observables as the state of the system changes during the quasi-static process. Suppose we have an infinitesimal quasi-static process which causes infinitesimal changes dV, dS and dU associated with work and heat δW and δQ . Sticking with compressional work for simplicity, we have $\delta W = -PdV$. In this quasi-static case we may use the infinitesimal form of the first law,

$$dU = \delta Q + \delta W = \delta Q - P dV,$$

in conjunction with the thermodynamic identity to identify

$$\delta Q = T dS,$$

or

$$dS = \frac{\delta Q}{T}.$$

This formula shows that for a quasi-static process the entropy changes purely via heat transfer; it is very convenient for computing the change in entropy, as we shall see. From the above equation we see that a process which is quasi-static and adiabatic is also *isentropic*.

It is important to emphasize that the formula $dS = \delta Q/T$, while extremely important, is not universally valid. For example, it does not apply to a free expansion of an ideal gas or the mixing of two gases. Indeed, we saw there that the entropy of the system increases in each of these cases, although there is no heat transfer. The reason is that the free expansion and mixing processes are not quasi-static.

Even though our relation between entropy and heat only applies to quasi-static processes, it has a wider validity in the following sense. Because the entropy is an observable, its value is determined solely by the state of the system. Consequently, the change in entropy of a system due to a process of any kind is completely determined by the initial and final states. Even if the process of interest is not quasi-static (or for some reason is just not convenient to calculate with) any quasi-static process connecting the same initial and final states can be used to compute the change in entropy via the above formula.

For example, consider the free expansion of an ideal gas to, say, double its volume. As we have discussed, there is no heat or work in a free expansion. The state changes according to

$$V \to 2V, \quad P \to \frac{1}{2}P.$$

And, as we have discussed, the change in entropy is $\Delta S = Nk \ln 2$. Consider an isothermal expansion connecting the same initial and final states. Now there is heat and work. We computed this already in the quasi-static case; we have:

$$Q = NkT \ln\left(\frac{V_{\text{final}}}{V_{\text{initial}}}\right) = NkT \ln 2, \quad \Longrightarrow \quad \Delta S = \frac{Q}{T} = Nk \ln 2.$$

Examples

Let's do a bunch of examples to understand all these relationships.

Example: Boiling water

You completely boil a liter of water – how much entropy did you create in the H_2O ? To answer this define the system to be the H_2O and suppose we boil it slowly enough for the quasi-static approximation to apply. We note that no work is done, but heat transfer occurs.* We have

$$dS = \frac{\delta Q}{T}.$$

Furthermore, the temperature never changes (T= 100C = 373K). The heat energy required is easy to compute using the latent heat and volume of the water, Q = 2260kJ. Because the temperature is constant, we have

$$\Delta S = \frac{Q}{T} = 6060 J/K.$$

^{*} Note that we are assuming that the energy transfer to the water is via heat. We can, of course, boil water in other ways. For example, consider a microwave oven where the boiling occurs via work. You might be tempted to conclude that the entropy change is zero in this case, but this is not so. Indeed, the initial and final states of the H_2O are as they were when we boiled the water via heat. Because the entropy is an observable its change is the same regardless of how the water got boiled. Evidently, boiling water with microwaves is not a quasi-static process.

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One way to see this is to write

$$\delta Q = \frac{Q}{\Delta t} dt,$$

where dt is an infinitesimal time interval during the time Δt it takes to boil the water. We can write

$$\Delta S = \frac{1}{T} \int_0^{\Delta t} dt \, \frac{dS}{dt} = \frac{1}{T} \int_0^{\Delta t} dt \, \frac{Q}{\Delta t} dt = \frac{Q}{T}$$

Example: Mixing hot and cold water

You add 50 L of hot water at 55 C with 25 L of cold water at 10 C. How much entropy is produced by the time equilibrium occurs?

Our strategy is to use the quasi-static assumption and find the entropy change in each of the hot and the cold water, then add these to get the total entropy change. The entropy changes can be computed by using

$$dS = \frac{\delta Q}{T},$$

with

$$\delta Q = C_P dT,$$

and then integrating to get ΔS

$$\Delta S = C_P \int_{T_i}^{T_f} \frac{dT}{T} = C_P \ln\left(\frac{T_f}{T_i}\right).$$

Evidently, we need to find the equilibrium temperature T_f . This is determined by the condition that the energy lost by the 50L is the energy gained by the 25 L. Let C_P be the heat capacity of the 25 L. Then the heat capacity of the 50 L is $2C_P$. We have

$$C_P(T_f - 10) = -2C_P(T_f - 55),$$

so that

$$T_f = 40C.$$

Now, we have

$$C_P = (25kg)(4186J/kg \cdot K) = 104,650J/K.$$

We compute

$$\Delta S_{cold} = C_P \int_{283K}^{313K} \frac{dT}{T} = C_P \ln \frac{313}{283} = 10,550 J/K,$$

and

$$\Delta S_{hot} = 2C_P \int_{328K}^{313K} \frac{dT}{T} = 2C_P \ln \frac{313}{328} = -9800J/K.$$

Notice that in this example one has to integrate the relation between heat, temperature and entropy. You will have to do this whenever the (quasi-static) process of interest is not isothermal. Note also that, because heat leaves the hotter water, its entropy actually *decreases* – see below for more on this. We have

$$\Delta S = \Delta S_{cold} + \Delta S_{hot} = 750 J/K.$$

Is ΔS big or small? Being a dimensionful quantity, it depends. But from the point of view of multiplicity, we see that

$$\ln \Omega_f - \ln \Omega_i \sim 10^{26}$$

so that

$$\frac{\Omega_f}{\Omega_i} \sim e^{10^{26}}.$$

That's pretty big!.

Decreasing entropy? We saw how the entropy of the hot water decreased. This might seem to violate the second law. It doesn't. The idea of maximizing the entropy is that this occurs for the whole (closed) system at equilibrium. If you only look at a piece of the whole system, its entropy may very well decrease during relaxation. Put differently, the idea of the second law is that the entropy of the universe – or just the system if it is sufficiently isolated from the rest of the universe – is always increasing.

Example: Entropy of Erasure

Here we consider some thermodynamics associated with computers (see problem 3.16). Suppose you erase a gigabyte of data on your hard disk. Ignoring the non-compressional work which may be done, how much heat must accompany this process? Huh? How can we possibly figure this out? As you will see, thermodynamic reasoning can be very powerful.

For computers, a byte is $8 = 2^3$ bits. A kilobyte is $1024 = 2^{10}$ bytes. A megabyte is 2^{10} kilobytes. A gigabyte is 2^{10} megabytes. So, a gigabyte is 2^{33} bits. Each bit has two states (0 and 1, conventionally). A gigabyte of data thus corresponds to a possible $2^{2^{33}}$ microstates. After erasure, there is only one microstate. So the reduction in entropy associated with the loss of information in the disk is essentially just*

$$\Delta S = k \ln 2^{2^{33}} = 8.2 \times 10^{-14} J/K.$$

⁶ The principle whereby the erasure of one bit of information corresponds to an entropy transfer to the environment of $k \ln 2$ (and corresponding heat) is due to Landauer and is one way to exorcise Maxwell's demon.

By the second law, at least this much entropy must appear in the environment. Assuming this transfer of entropy occurs quasi-statically at a constant temperature, say 300K, we have

$$Q = T\Delta S = 2.5 \times 10^{-11} J.$$

This is a very tiny amount of heat. Since this process is irreversible and may not be quasistatic, you actually expect more heat than this. In any case, it is impressive that purely thermodynamic considerations put a limit on how cool a computer can run!

Example: Entropy, Heat Capacity and the Third Law

As we have seen, for a quasi-static process

$$dS = \frac{\delta Q}{T}.$$

If we can quasi-statically connect the given initial and final states by a process involving heat and no work, we can compute the change in entropy using

$$\delta Q = C dT,$$

(where C is the heat capacity relevant to the process) so we have

$$\Delta S = \int_{T_i}^{T_f} dT \, \frac{C}{T}.$$

If the temperature interval is one for which C is (approximately) constant, then we have

$$\Delta S = C \ln \frac{T_f}{T_i}.$$

You can use this formula to compute entropy changes associated with heating and cooling. For example, if you heat 200g of water from 20C to 100C the change in entropy is 200J/K. (Try it!)

In general, the heat capacity changes with temperature. In particular, we have previously noted that it decreases if you lower the temperature enough. Indeed, we see that the integral defining the entropy difference from zero temperature will diverge unless $C \to 0$ as $T \to 0$. But the entropy difference should be finite, given its interpretation in terms of multiplicities. Moreover, viewing temperature as a measure of energy per degree of freedom, you can see that at zero temperature the microsystems making up the macrosystem must all be in their ground states. This means multiplicity should be unity and S = 0 at T = 0 (assuming, for simplicity, that all microsystems are identical and the ground state is unique). This yields a simplest version of the *third law of thermodynamics*, due orginially to Planck: as $T \to 0$ we have $S \to 0$ and $C \to 0$. You can think of this as a sort of "boundary condition" on thermodynamics — at this limiting temperature both S and its first derivative should vanish. A more general, if weaker, statement of the third law is due to Einstein: the entropy remains finite as $T \to 0$.

An alternate version of the third law says that the change in entropy due to any isothermal process should approach zero as $T \to 0$. This implies, mathematically, that the first derivatives of S with respect to other observables should vanish as $T \to 0$. This also implies it is impossible to construct a process which actually cools something down to absolute zero! Thus a slogan for the third law is sometimes: you can't reach absolute zero.*

In light of the third law, the entropy of a system at temperature T can be computed by

$$S = S_0 + \int_0^T dT \frac{C}{T},$$

where S_0 is a constant depending upon the system, but not its state. Of course, to compute the entropy via this formula you need to know how the heat capacity varies with temperature.

Entropy change: quasi-static versus non-quasi-static

The thermodynamic identity is

$$dU = TdS - PdV.$$

The first law says that

$$dU = \delta Q + \delta W.$$

We then get

$$TdS = \delta Q + \delta W + PdV.$$

As we have seen, for a quasi-static process, where $\delta W = -PdV$ we then get the very important result

$$dS = \delta Q/T.$$

Entropy change is controlled by heat transfer in the quasi-static case.

What happens in a non-quasi-static process? Well, in general the work done is greater than $-\int PdV$. Just consider what happens in the piston-cylinder example when you move the piston very rapidly. Or consider the work done in a free expansion. So, we see that in the general, non-quasi-static case where $\delta W \ge -PdV$,

$$dS \ge \frac{\delta Q}{T}.$$

^{* &}quot;You can't quit the game."

Chemical Potential

We have used maximization of the entropy with respect to variations in energy and volume to obtain thermodynamic definitions of temperature and pressure. The interpretation of temperature is that it is the same for two systems in thermal equilibrium. The pressure was the same for two systems in mechanical equilibrium.

As we have seen, the entropy is also a function of the number of particles (or oscillators, or magnetic moments...) making up the system. Two systems which can exchange particles are in *diffusive contact* and can come to *diffusive equilibrium*. We expect that two systems will adjust the concentration of particles until equilibrium is obtained — presumably the subsystem with the most particles will tend to give up particles to the other subsystem(s). What precisely happens? There is an observable, known as the *chemical potential*, which is analogous to the temperature and pressure in that it is the same for two systems in diffusive equilibrium. The chemical potential is the observable which controls the state of a system in diffusive equilibrium. Here we explore this idea a little bit.

Using the exact same arguments as before, we have that equilibrium between two systems A and B is obtained – the entropy is maximized – only if temperatures and pressures are the same and only if

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

It is convenient to define the chemical potential as

$$\mu = -T\frac{\partial S}{\partial N}$$

This derivative is taken with all other observables (U and V) held fixed. At equilibrium we have $\mu_A = \mu_B$. The factor of T gives μ the dimensions of energy. The minus sign makes the chemical potential act like temperature and volume during relaxation – see below.

To get a feel for what this quantity is all about, let us compute the chemical potential for a monatomic ideal gas via the Sackur-Tetrode equation. We have

$$S = kN \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + 5/2 \right\},\$$
$$\mu = -T \frac{\partial S}{\partial N} = -kT \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right].$$

Using $U = \frac{3}{2}NkT$, we have

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right].$$

Putting in the numbers for helium at STP we get $\mu = -0.3 \, eV$

Note that as N increases/decreases μ increases/decreases. More precisely, if the number density $\frac{N}{V}$ increases/decreases with T held fixed, the chemical potential increases/decreases. For two gases in diffusive contact we expect the gas with the higher concentration of particles to give up particles to the other gas during relaxation to equilibrium. Thus diffusive relaxation can be seen as an exchange of N with the system having more μ giving up particles to the system having less μ . This is why the minus sign is used in the definition of μ .

The thermodynamic identity again

Viewing S = S(U, V, N) we have defined the chemical potential as

$$\mu = -T\frac{\partial S}{\partial N}.$$

We can now generalize the thermodynamic identity to include changes in particle number:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN,$$

or

$$dU = TdS - PdV + \mu \, dN.$$

You can see from this last relation that if we view U = U(S, V, N) then

$$\mu = \frac{\partial U}{\partial N},$$

where it is understood that S and V are held fixed. We sometimes use the notation

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

to make it clear what U is a function of and what is being held fixed. In any case, we see from this formula that the chemical potential can be interpreted as the (infinitesimal) change in energy associated with adding a particle to the system (while holding entropy and volume fixed). This is a pretty nice and clear interpretation of μ . But for computational purposes it is usually more convenient to use

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

particularly when we have explicit formulas for S = S(U, V, N) (e.g., the Sackur-Tetrode equation).

When there is more than one species of particle in the system, then we have numbers N_i , i = 1, 2, ... labeling the number of each species. In this case there is a chemical potential $\mu_1, \mu_2, \mu_3, ...$ for each species of particle. The thermodynamic identity becomes

$$dU = TdS - PdV + \sum_{i} \mu_{i}dN_{i} = TdS - PdV + \mu_{1}dN_{1} + \mu_{2}dN_{2} + \dots$$

Example: Ideal Gas in a Gravitational Field

This example is stolen from problem 3.37 in the text — it is a simple model of the atmosphere. Let us compute the chemical potential $\mu(z)$ of a volume V of a monatomic ideal gas sitting at a height z in uniform gravitational field.[†] As you might imagine, this quantity will depend upon the number density of molecules at that height. Assuming the atmosphere is at (diffusive) equilibrium; the chemical potential cannot vary with altitude. This will lead to a nice prediction for the variation of number density with altitude (which jibes with a result we obtained using different methods in chapter 1).

Two strategies for computing the chemical potential are given by the two formulas:

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

or

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

To use the first strategy you will need to construct a formula for the entropy in terms of (N, U, V) — this is the Sackur-Tetrode equation. To use the second strategy you will need to construct a formula for the energy of the system in terms of (S, V, N). I'll show you both ways. The key observation for either method is that the *total* energy U is is the sum of the kinetic energy of the gas along with the potential energy of the gas. The potential energy of an atom at height z is mgz.

To use the first strategy, you need to realize that the U which appears in the S-T formula is in fact the *kinetic* energy of the ideal gas^{*} — let us denote it here as U_K . So, for this calculation, we start with the S-T formula written in the form:

$$S = kN \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m U_K}{3Nh^2} \right)^{3/2} \right] + 5/2 \right\},$$

Consider a thin slab of atmosphere at height z. The kinetic energy $U_K(z)$ is related to the total energy — here denoted $U_T(z)$ — of the gas by

$$U_T(z) = U_K(z) + Nmgz.$$

[†] Think of the volume as a very thin layer centered at a height z.

^{*} To see this, just review the derivation in Chapter 2 for the multiplicity.

So to express the entropy of the slab in the form S = S(U, V, N) needed for calculating the chemical potential — where U is the total energy of the gas — we need to use the S-T equation in the form

$$S = kN \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m(U - Nmgz)}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right\},$$

The derivative of S thus takes the form we found when we computed μ in the earlier section (which you can view as the z = 0 case) plus the terms coming from Nmgz. As a nice exercise, try the following. Take the derivative of S with respect to N. Then use

$$U_K(z) = U(z) - Nmgz = \frac{3}{2}kT.$$

Then simplify the result to get

$$\frac{\partial S}{\partial N} = k \ln \left[\frac{V}{N} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right] - \frac{m g z}{T},$$

and so the chemical potential is

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + mgz.$$

Note that this is just the formula we had before, but with mgz added on to it. You might have guessed this answer from the interpretation of the chemical potential in terms of the energy change upon adding a particle (at height z, in this case).

The second strategy,

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

is simpler computationally, but trickier because we need to somehow express the energy as a function of S and V. The trick comes from writing

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial U_K}{\partial N}\right)_{S,V} + \left(\frac{\partial (Nmgz)}{\partial N}\right)_{S,V} = \left(\frac{\partial U_K}{\partial N}\right)_{S,V} + mgz.$$

Then we use our previous result for an ideal gas when $U = U_K$:

$$\left(\frac{\partial U_K}{\partial N}\right)_{S,V} = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$

to recover

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + mgz$$

We can use this result to obtain a formula for the number of particles N(z) at height z in a given volume V relative to the number N(0) at z = 0 in the same volume. The key idea here is that the gas is at equilibrium, so that the chemical potentials for the quantity of gas at the two altitudes have to be the same,

$$\mu(z) = \mu(0).$$

This means

$$-kT\ln\left[\frac{V}{N(z)}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + mgz = -kT\ln\left[\frac{V}{N(0)}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right].$$

Canceling out the kT factors and exponentiating both sides gives (try it!)

$$N(z) = N(0)e^{-\frac{mg}{kT}z}.$$

You can see that the number of particles decays exponentially with altitude. The decay rate is determined by

$$\zeta = \frac{kT}{mg} \sim 10^4 \text{ meters},$$

where I have taken T = 300K. ζ is the amount you have to increase the altitude to get a reduction in N by a factor of 1/e. Assuming (as we did above) that the temperature is the same throughout the atmosphere under consideration, the ideal gas law then tells us (exercise)

$$P(z) = P(0)e^{-\frac{mg}{kT}z}$$

in agreement with problem 1.16 in the text.