

Examples of Z_{int}

We have been discussing how to modify our treatment to allow for the internal states and energies of molecules in, for example, an ideal gas. To make further progress, we need to consider some specific examples of internal structure that can give rise to Z_{int} . Suppose the molecules are single atoms but these atoms have a spin quantum number S . Then there are $2S + 1$ internal states that correspond to the $2S + 1$ projections of the spin along an arbitrary axis. In the absence of a magnetic field, all these states have the same energy which we take as $\epsilon_{\text{int}} = 0$. Then $Z_{\text{int}} = 2S + 1$ and

$$F_{\text{int}} = -N\tau \log(2S + 1),$$

$$\sigma_{\text{int}} = N \log(2S + 1),$$

$$U_{\text{int}} = 0,$$

so the entropy is increased over that of a simple ideal gas, but the energy doesn't change. The increase in entropy is easy to understand. What's happening is that each atom has $2S + 1$ times as many states available as a simple atom with no internal structure. The entropy, the logarithm of the number of states, increases by $\log(2S + 1)$ per atom.

That was a fairly trivial example. Here's another one: Suppose that each molecule has one internal state with energy ϵ_1 . Then $Z_{\text{int}} = \exp(-\epsilon_1/\tau)$ and

$$F_{\text{int}} = -N\tau \log Z_{\text{int}} = +N\epsilon_1,$$

$$\sigma_{\text{int}} = 0,$$

$$U_{\text{int}} = N\epsilon_1,$$

and

$$\Delta\mu = -\tau \log Z_{\text{int}} = +\epsilon_1.$$

In this example, we didn't change the entropy (each molecule has just one state), but we added ϵ_1 to the energy of each molecule. This change in energy shows up in the chemical potential as a per molecule change and it shows up in the free energy and energy as N times the per molecule change. This example is basically a small test of the self-consistency of the formalism!

More realistic examples include the rotational and vibrational states of the molecules. Single atoms have neither rotational nor vibrational modes (they do have electronic excitations!). A linear molecule (any diatomic molecule and some symmetric molecules such as CO_2 , but not H_2O) has two rotational degrees of freedom. Non-linear molecules have three rotational degrees of freedom. Diatomic molecules have one degree of vibrational freedom. More complicated molecules have more degrees of vibrational freedom. If the molecule has M atoms, $3M$ coordinates are required to specify the locations of all the

atoms. The molecule thus has $3M$ degrees of freedom. Three of these are used in specifying the location of the center of mass. Two or three are used for the rotational degrees of freedom. The remainder are vibrational degrees of freedom.

You might be uncomfortable with 0 or two degrees of rotational freedom for point or linear molecules. To make this plausible, recall that an atom consists of a nucleus surrounded by an electron cloud. The electrons are in states with angular momentum, and to change the angular momentum one or more electrons must be placed in an excited electronic state. This is possible, but if there is an appreciable thermal excitation of such states, the atom has a fair chance of being ionized. If the atom is part of a molecule, that molecule has probably been dissociated as molecular binding energies are usually small compared to atomic binding energies. The upshot of all this is that such excitations are not important unless the temperature is high enough that molecules are dissociating and atoms are ionizing!

Rotational energy is the square of the angular momentum divided by twice the moment of inertia. (Ignoring things like the fact that inertia is a tensor!) Since angular momentum is quantized, so is rotational energy. This means that at high temperatures, we expect an average energy of $\tau/2$ per rotational degree of freedom, but at low temperatures we expect that the rotational modes are “exponentially frozen out.” In this case, they do not contribute to the partition function, the energy, or the entropy. The spacing between the rotational energy levels sets the scale for low and high temperatures.

Similarly, for each vibrational degree of freedom, we expect that the corresponding normal mode of oscillation can be treated as a harmonic oscillator and that at high temperatures there will be an average energy of τ per vibrational degree of freedom ($\tau/2$ in kinetic energy and $\tau/2$ in potential energy). At low temperatures the vibrational modes are exponentially frozen out and do not contribute to the internal partition function, the energy or the entropy. \hbar times the frequency of vibration sets the scale for low and high temperatures.

As an example, consider a diatomic gas. At low temperatures, the energy will be $3N\tau/2$, the entropy will be given by the Sackur-Tetrode expression and the molar heat capacities will be $C_V = 3R/2$ and $C_p = 5R/2$ with $\gamma = 5/3$. As the temperature is raised the rotational modes are excited and the energy becomes $5N\tau/2$ with molar specific heats of $C_V = 5R/2$ and $C_p = 7R/2$ and $\gamma = 7/5$. If the temperature is raised still higher the vibrational modes can be excited and $U = 7N\tau/2$, $C_V = 7R/2$, $C_p = 9R/2$, and $\gamma = 9/7$.

Ideal Gas Processes

We will consider various processes involving a fixed amount of an ideal gas. We will assume that the heat capacities are independent of temperature for these processes. (In other words, the temperature changes will not be large enough to thaw or freeze the rotational or vibrational modes.) We will want to know the work done, heat added, the change in energy and the change in entropy of the system.

Note that work and heat depend on the process, while energy and entropy changes depend only on the initial and final states. For the most part we will consider reversible processes.

Consider a constant volume process. About the only thing one can do is add heat! In this case, $p_f/p_i = T_f/T_i$.

$$\begin{aligned} Q &= nC_V(T_f - T_i), \\ W &= 0, \\ \Delta U &= nC_V(T_f - T_i), \\ \Delta S &= \int nC_V \frac{dT}{T} = nC_V \log \frac{T_f}{T_i}, \end{aligned}$$

where Q is the heat added to the gas, W is the work done on the gas, n is the number of moles, C_V and C_p are the molar heat capacities in conventional units and T and S are the temperature and entropy in conventional units.

Consider a constant pressure (isobaric) process. In this case, if heat is added, the gas will expand and $V_f/V_i = T_f/T_i$

$$\begin{aligned} Q &= nC_p(T_f - T_i), \\ W &= - \int_{V_i}^{V_f} p dV = -nR(T_f - T_i), \\ \Delta U &= nC_V(T_f - T_i), \\ \Delta S &= nC_p \int_{T_i}^{T_f} \frac{dT}{T} = nC_p \log \frac{T_f}{T_i} = nC_V \log \frac{T_f}{T_i} + nR \log \frac{V_f}{V_i}. \end{aligned}$$

Consider a constant temperature (isothermal) process. Heat is added and the gas expands to maintain a constant temperature. The pressure and volume satisfy $p_f/p_i =$

$(V_f/V_i)^{-1}$.

$$W = - \int_{V_i}^{V_f} p dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \log \frac{V_f}{V_i},$$

$$\Delta U = 0,$$

$$Q = -W = nRT \log \frac{V_f}{V_i},$$

$$\Delta S = nR \int_{V_i}^{V_f} \frac{dV}{V} = nR \log \frac{V_f}{V_i}.$$

Consider a constant entropy process. This is often called an adiabatic process. However, adiabatic is also taken to mean that no heat is transferred. Since it is possible to change the entropy without heat transfer, the term *isentropic* can be used to explicitly mean that the entropy is constant. It is left as an exercise to show that in an isentropic process with an ideal gas, $pV^\gamma = \text{constant}$. Then

$$W = - \int_{V_i}^{V_f} p dV = -p_i V_i^\gamma \int_{V_i}^{V_f} \frac{dV}{V^\gamma} = \frac{p_i V_i^\gamma}{\gamma - 1} \left(\frac{1}{V_f^{\gamma-1}} - \frac{1}{V_i^{\gamma-1}} \right)$$

$$= -\frac{nRT_i}{\gamma - 1} \left(1 - \left(\frac{V_i}{V_f} \right)^{\gamma-1} \right),$$

$$Q = 0,$$

$$\Delta U = W = -\frac{nRT_i}{\gamma - 1} \left(1 - \left(\frac{V_i}{V_f} \right)^{\gamma-1} \right),$$

$$\Delta S = 0.$$

Finally, let's consider an irreversible process. Suppose a gas is allowed to expand from a volume V_i into a vacuum until its volume is V_f . This is called a free expansion. No work is done to the gas and no heat is added, so the energy and temperature don't change. The initial and final states are the same as in the reversible isothermal expansion, so the entropy change is the same as for that case,

$$Q = 0,$$

$$W = 0,$$

$$\Delta U = 0,$$

$$\Delta S = nR \log \frac{V_f}{V_i}.$$

This is an adiabatic, but not isentropic, process. Note that if a gas is not ideal, then it may be that the energy depends on volume (or rather, concentration) as well as temperature.

Such a deviation from the ideal gas law can be uncovered by measuring the temperature of a gas before and after a free expansion.

The Gibbs Paradox Revisited

Last lecture's treatment of the N particle problem might have engendered some uneasiness; especially the example with two volumes of gas that were allowed to mix. Recall that we had two volumes, V , each containing N molecules of gas at temperature τ , and separated by a partition. We considered two cases: the same gas on both sides of the partition and different gases, A and B , on the two sides of the partition. When the partition is removed in the same gas case "nothing happens," the system is still in equilibrium and the entropy doesn't change—according to the correct expression which included the $N!$ over counting correction in the partition function. When the partition is removed in the different gas case, we must wait a while for equilibrium to be established and once this happens, we find that the entropy has gone up by $2N \log 2$. This is called the entropy of mixing. The incorrect expression for the entropy (omitting the $N!$ over counting correction in the partition function) gives the same entropy of mixing in both cases. This manifestation of the N particle problem is called the "Gibbs paradox."

The fact that we have to wait for equilibrium to be established means that the mixing of the two different gases is a non-reversible process. Entropy always increases in non-reversible processes! On the other hand, removing the partition between identical gases is a reversible process (in the limit of a negligible mass, frictionless partition...). In a reversible process, total entropy (system plus surroundings) does not increase, and there is obviously no entropy change in the surroundings when the partition is removed from the identical gases.

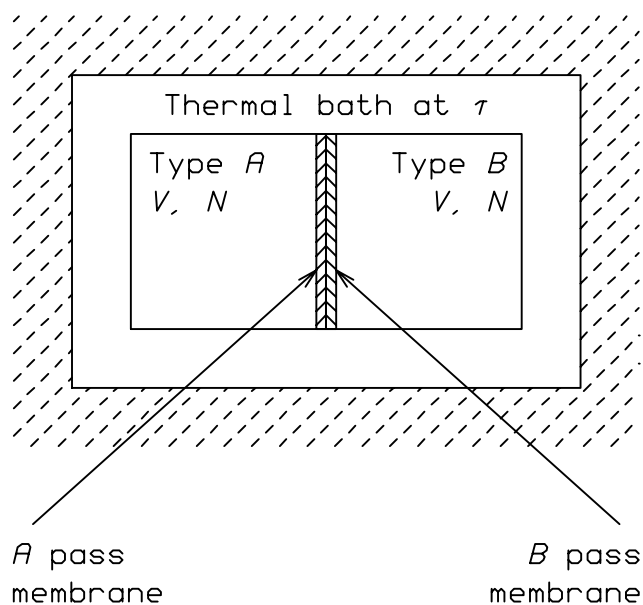
The question of measuring the entropy has come up several times. There is no such thing as an entropy meter that one can attach to a system and out pops a reading of the entropy! Changes of the entropy can be measured. Recall that $d\sigma = dQ/\tau$ for a reversible process. So if we can take a system from one state to another via a (close approximation of a) reversible process and measure the heat flow and temperature, we can deduce the entropy difference between the two states. To measure the absolute entropy of a state, we must start from a state whose absolute entropy we know. This is a state at $\tau = 0$! We will see how this goes in the comparison of the Sackur-Tetrode expression with experimental results.

Aside: the fact that we can only measure changes in entropy should not be that bothersome. At the macroscopic level, entropy is defined by an integral ($\int dQ/\tau$). There is always the question of the constant of integration. A similar problem occurs with potential energy. It is potential energy differences that are important to the dynamics and only differences can be measured. For example, consider a mass m on the surface of the Earth. If we take the zero of gravitational potential energy to be at infinite separation of

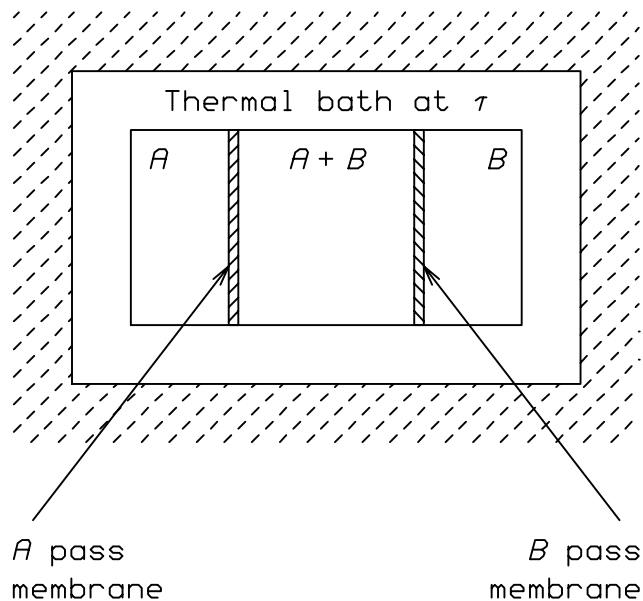
the mass and the Earth, then the potential energy of the mass-Earth system is $-GMm/R$ when the mass sits on the surface of the Earth at distance R from the center. I'm sure we're all happy with this, right? But, there is no potential energy meter that you can attach to the mass and out pops a potential energy value. Instead, $-GMm/R$ is a calculated value much like the entropy of mixing is a calculated value. What can we actually measure in the gravitational case? We can measure the force required to change the height (distance from the center of the Earth) of the mass and so measure $\int \mathbf{F} \cdot d\mathbf{r}$. That is, we can measure the change in gravitational potential energy between two states. Of course, we have to be careful that there is no friction, that $\mathbf{F} = -m\mathbf{g}$, that there is negligible acceleration of the mass, etc. In other words, we have to approximate a reversible process! Reversible processes aren't just for thermodynamics! I suspect they're easier to visualize in other branches of physics, so they don't cause as much comment and concern. What about measuring the "absolute" gravitational potential? This requires measuring the changes in potential energy between the state whose potential we know (infinite separation) and the state whose potential we want to know (mass on the surface of the Earth). I suppose if we had enough money, we might get NASA to help with this project! Of course, by calculation we can relate the "absolute" gravitational potential to other quantities, for example, the escape velocity, that can be more easily measured. This is one of the arts of theoretical physics.

Back to our mixing example: Can we think of a reversible process which would allow us to mix the gases? Then we could calculate the entropy change by keeping track of the heat added and the temperature at which it was added. Also, if we knew of such a process, we could use it—in reverse!—to separate the gases again. The process I have in mind uses semi-permeable membranes. We need two of them: one that passes molecules of type A freely but is impermeable to molecules of type B , and a second which does the opposite. It passes type B molecules and blocks type A molecules. We can call these "A-pass" and "B-pass" membranes for short. Do such membranes actually exist? Semi-permeable membranes certainly exist. The molecules that are passed may not pass through "freely," but if we move the membrane slowly enough, it should be possible to make the friction due to the molecules passing through the small holes in the membrane negligibly small. The possibility of finding the desired membranes depends on the molecules in question and almost certainly is not possible for most pairs of molecules. However, the fact that semi-permeable membranes do exist for some molecules would seem to make this a reasonable thought experiment (if not an actually realizable experiment).

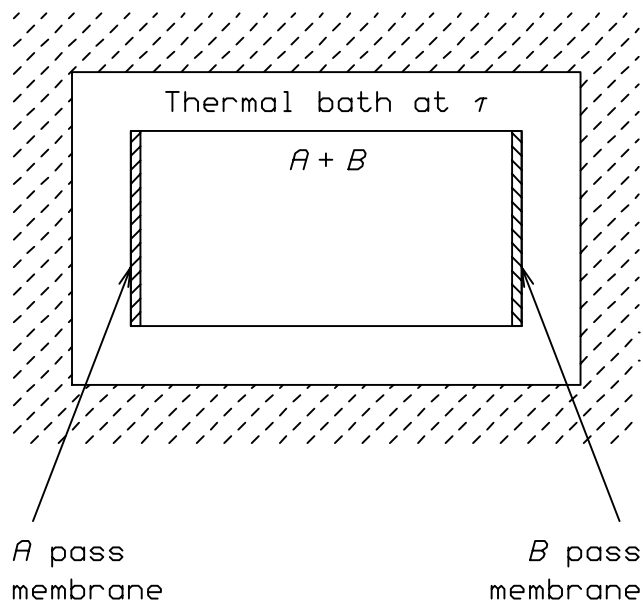
The figure is a schematic of our mixing apparatus. The volume $2V$ is in equilibrium with a thermal bath at temperature τ . At the center of the volume and dividing it into two sections of volume V are the two membranes. The A -pass membrane confines the N type B molecules to the right volume and the B -pass membrane confines the N type A molecules to the left volume. The next two figures show the situations when the gases are partially and fully mixed. The membranes are something like pistons and are moved by mechanical devices that aren't shown. These devices are actually quite important as each membrane receives a net force from the gases. The mechanical devices are used to counteract this force and do work on the gases as the membranes are moved slowly and reversibly through the volume.



What is the force on a membrane due to the gases? Consider the A -pass membrane. A molecules pass freely through this membrane so there is no interaction of this membrane with the A molecules. The B molecules are blocked by this membrane, so the B molecules are bouncing off the membrane as though it were a solid surface. Since there are B molecules on the right side of this membrane and not on the left, there is a pressure (only from the B molecules) which is just $N\tau/V_B$ where V_B is the volume occupied by B molecules to the right of the A -pass membrane. The net force from this pressure points to the left. So as we move the membrane to the left, the B molecules do work on it. This comes from the energy, U_B of the B molecules. The B molecule system would cool, except it is in contact with the heat bath, so heat flows from the bath to make up for the work done on the membrane and keep τ and hence U_B constant. The same thing happens with the B -pass membrane and the A gas. It is the heat transferred (reversibly) from the reservoir to each gas that increases the entropy of the gas.



By now, you're convinced that the A molecules can be treated as a gas occupying the volume to the left of the B -pass membrane without worrying what's going on with the B molecules and vice-versa. We've arranged this "by construction." Our model for an ideal gas is based on non-interacting molecules (well, weakly interacting, but only enough to maintain thermal equilibrium). We've also made the membranes so they interact only with A or B molecules but not both. So the A molecules interact strongly with the walls of the container and the B -pass membrane and interact weakly ($\rightarrow 0$) with everything else including other A molecules. So when the B pass membrane is moved all the way to the right, the A molecules undergo an isothermal expansion from V to $2V$. We apply our ideal gas results for an isothermal expansion and find



$$\Delta\sigma_A = \int_V^{2V} \frac{dQ}{\tau} = \int_V^{2V} \frac{p dV}{\tau} = \int_V^{2V} N \frac{dV}{V} = N \log \frac{2V}{V} = N \log 2.$$

Of course, a similar result applies to the B molecules when the A pass membrane is moved all the way to the left. The total change of entropy in this process is

$$\Delta\sigma = 2N \log 2,$$

which is what we had obtained before by applying the Sackur-Tetrode expression to the initial and final states of the irreversible process.

Aside: suppose we have several ideal gases occupying the same volume. $p_i = N_i\tau/V$ is called the partial pressure of gas i and is the pressure that the same N_i molecules of the gas would have if they occupied the volume by themselves (no other gases present). Then the total pressure is the sum of the partial pressures: $p = \sum_i p_i$. This is called Dalton's law. It falls out of our ideal gas treatment "by construction." Since the gases are non-interacting, the presence of other gases cannot affect the rate of momentum transfer by a given gas! So, Dalton's law seems trivial, but it probably helped point the way towards a non-interacting model as a good first approximation.