

Reading assignment. Schroeder, section 4.1.

0.1 Diffusive contact

The condition for equilibrium of two systems in thermal plus diffusive contact, that is, able to exchange both energy and particles, is obtained in much the same way as for thermal contact plus mechanical contact. There are two independent variables describing the macrostate of the combined system, as well as the individual subsystems. Those can be taken to be the energy, U_1 , and the number of particles, N_1 , of the first subsystem. In equilibrium, the total entropy, calculated as the sum of the entropies of the subsystems, is maximized with respect to both variables, so the partial derivatives of the total entropy with respect to both must vanish. In equilibrium, then, the temperatures of the two subsystems must be equal, and the particle-number derivatives must satisfy

$$\left(\frac{\partial S_1}{\partial N_1}\right)_{U_1, V_1} = \left(\frac{\partial S_2}{\partial N_2}\right)_{U_2, V_2}. \quad (1)$$

Prior to the establishment of equilibrium, the subsystem having the larger slope $(\partial S_i / \partial N_i)_{U_i, V_i}$ will gain particles at the expense of the other one, since that permits the total entropy to increase, whereas the reverse process would decrease the total entropy. Once the slopes have equalized, there is no entropic benefit to additional particle transfer, so particle transfer in one direction is balanced by particle transfer in the other direction.

If we permit the subsystems to exchange volume as well, then the pressures must also be equal in equilibrium. A nice example of such a system is a sealed, isolated container containing both liquid water and water vapor in equilibrium. There is a movable interface between the liquid and the gas, so they can exchange volume, as well as particles and energy.

It was easy for us to relate the partial derivatives of the entropy with respect to energy and volume to the familiar thermodynamic variables temperature and pressure, since they are so familiar and well understood. In the case of pressure, there is even a mechanical definition, which made the task even easier. The partial derivative of the entropy with respect to particle number, however, is not related to anything so simple. But it is related to the thermodynamic variable called *chemical potential*:

$$\left(\frac{\partial S}{\partial N}\right)_{U, V} = -\frac{\mu}{T}, \quad (2)$$

where μ denotes the chemical potential. Be careful not to confuse this with magnetic moment, for which we also used the symbol μ .

The chemical potential is familiar to chemists, who use it and quantities related to it routinely to analyze chemical reactions, where the numbers of particles of the reactant and product species necessarily change as a reaction

proceeds. But we'll try to develop a general feel for the meaning of both $\partial S/\partial N$ and μ without dealing with the complexities of chemical reactions.

First, let's think about the sign of $\partial S/\partial N$. We generally expect to have more microstates available when we add particles, since there are generally more ways to arrange more particles. Indeed, one of the homework problems was based on the idea that in many cases the entropy is just Nk times a number that is not large, so that the entropy could be estimated by Nk alone. This suggests that, to some rough approximation, $\partial S/\partial N$ has the constant, positive value k , and S is linear in the number of particles. That can't be quite the whole story, of course, or there would be no possibility of having two subsystems come to equilibrium through equalization of their partial derivatives, as in (2).

To get a more complete picture, let's return to the familiar example of the ideal gas, whose entropy is

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

Since we're interested in the partial derivative with respect to N with U and V held fixed, it will be useful to rewrite the expression to separate N from the other variables a little better:

$$S(U, V, N) = Nk \left[-\frac{5}{2} \ln N + \underbrace{\frac{3}{2} \ln \left(\frac{4\pi m V^{2/3} U}{3h^2} \right)}_{f(U, V)} + \frac{5}{2} \right]. \quad (4)$$

There are two important things to notice now. First, the negative sign on the first term implies that the behavior of S with N for fixed U and V is sublinear. That's a good thing, because it allows the slope of $S(N)$ to vary, permitting two subsystems in diffusive contact to have a well-defined equilibrium distribution of particles.

The second thing to notice is that for a large enough value of N , the entropy can begin to decrease with increasing N , eventually even becoming negative. That's bad news, but we have already examined in a homework problem a similar difficulty, that the ideal-gas entropy can become negative at sufficiently low temperature. In fact, it's the same problem, since adding particles at fixed energy necessarily requires that those new particles have zero energy, which reduces the average energy per particle, making the temperature smaller. As you should recall, the problem is resolved by noting that the ideal gas becomes nonideal at low temperatures, where the assumptions made in deriving the Sackur-Tetrode expression for its entropy fail. Indeed, it is necessary to take into account the quantum-mechanical nature of the particles under those conditions, something we're not yet prepared to do. So, we'll just keep in mind that we don't want to add too many particles. To get a feel for how many that might be, let's consider a specific example, which will also provide us with some numbers to use in our examination of the chemical potential.

Example. Let's consider a system consisting of helium gas in a container of volume 1 m^3 with pressure 1 atm and temperature 300 K . We'll want to find explicit values for $f(U, V)$ and for the number of particles, so we can compare the positive and negative terms in the entropy. The number of particles under the stated conditions, which we'll denote by N_0 , is

$$N_0 = \frac{PV}{kT} \approx 2.445 \times 10^{25}, \quad (5)$$

so that

$$\frac{5}{2} \ln N_0 \approx 146.1. \quad (6)$$

The value of $f(U, V)$ is best calculated by first making use of the ideal-gas law $PV = NkT$ and the equipartition theorem $U = \frac{3}{2}kT$ to rewrite U as

$$U = \frac{3}{2}PV, \quad (7)$$

so that f becomes

$$f(P, V) = \frac{3}{2} \ln \left(\frac{2\pi m V^{5/3} P}{h^2} \right) + \frac{5}{2} \approx 161.3. \quad (8)$$

The entropy is then

$$S = N_0 k \left(f - \frac{5}{2} \ln N_0 \right) \approx N_0 k \times 15.18. \quad (9)$$

This shows that the multiplier of $N_0 k$ is, as claimed, not large and that we still can add quite a large number of particles before the entropy goes negative. Specifically, when $S = 0$, the ratio of the particle number to N_0 is

$$\frac{N}{N_0} \approx e^{\frac{2}{5} \times 15.18} \approx 433. \quad (10)$$

Now, at last, let's take a look at the derivative. With S expressed as in (4), we have

$$\begin{aligned} \left(\frac{\partial S}{\partial N} \right)_{U,V} &= \frac{S}{N} - \frac{5}{2}k \quad (\text{monatomic ideal gas}) \\ &= k \left[f(U, V) - \frac{5}{2} (1 + \ln N) \right]. \end{aligned} \quad (11)$$

Example. Using the numbers from the last example, we find

$$\begin{aligned} \frac{1}{k} \left(\frac{\partial S}{\partial N_0} \right)_{U,V} &= \underbrace{f(U, V)}_{\approx 161.3} - \frac{5}{2} \left(1 + \underbrace{\ln N_0}_{\approx 58.46} \right) \\ &\quad \approx 12.68. \end{aligned} \quad (12)$$

Notice first that this is a positive value, so the chemical potential

$$\mu = -T \left(\frac{\partial S}{\partial N_0} \right)_{U,V} \quad (13)$$

is negative.

In addition, it's clear that the derivative and the chemical potential can vanish, and it does so at the point where the Sackur-Tetrode entropy begins to decrease with increasing N . That happens when

$$f(U, V) = \frac{5}{2} (1 + \ln N), \quad (14)$$

which occurs when

$$\frac{N}{N_0} \approx e^{\frac{2}{5} \times 12.68} \approx 159. \quad (15)$$

So, there's still plenty of room to stuff more He atoms into the container before that happens.

Now we understand that μ is negative for “typical” systems under “typical” conditions, though there are significant exceptions in systems where the quantum nature of the particles is important. When two systems are placed in diffusive contact, the one with the higher (less negative) chemical potential, or smaller slope $(\partial S/\partial N)_{U,V}$, gives up particles to the other system.

Also, from (11) we see that the slope tends to decrease as N increases, which means the chemical potential increases as N increases.

It may be useful to think about both of these observations in terms of analogies with charges and potentials in electrostatics. Consider only positively charged particles, for which the analogies are the most direct. Such particles, when placed in a region of high electrostatic potential, will flow toward regions of lower potential, just as uncharged particles in a region of high chemical potential flow toward regions of lower chemical potential. As well, an accumulation of many positively charged particles in a location causes that region to have high electrostatic potential in comparison to other regions having fewer positive particles. These analogies make it seem quite natural that μ has been given the name “chemical potential.”

Question. Suppose we evacuate a sealed container, then squirt some liquid water into the chamber, all placed in a gravitational field, so the liquid stays on the bottom. Describe what happens and why, using the concept of chemical potential.

Answer: Initially, consider two subsystems, the liquid water and the space above it. Since there are many water molecules in the liquid, and the space above initially has none, the chemical potential of water molecules in the water is much higher than that in the space above, so water molecules will “flow” from the liquid into the space above. That is, they evaporate. The

process continues until the chemical potentials, temperatures, and pressures in the two parts of the container are equal, at which point any further evaporation is balanced by an equivalent amount of condensation, and the system becomes macroscopically static.

HW Problem. Schroeder problem 3.36, p. 119.

[EOC, Mon. 2/20/2006, #18; HW06 closed, due Mon. 2/27/2006]

Now that we have examined all three of the variables upon which the entropy depends in simple systems, we can write down the full expression for the thermodynamic identity we presented last time. Since $S = S(U, V, N)$, its total differential is

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N}}_{\frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,N}}_{\frac{P}{T}} dV + \underbrace{\left(\frac{\partial S}{\partial N}\right)_{U,V}}_{-\frac{\mu}{T}} dN, \quad (16)$$

so that

$$\boxed{dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN.} \quad (17)$$

This can be rearranged to give:

$$\boxed{dU = T dS - P dV + \mu dN.} \quad (18)$$

The concept of chemical potential is easily generalized to systems with more than one type of particle. The entropy has a functional dependence upon the numbers of each species:

$$S = S(U, V, N_1, \dots, N_n), \quad (19)$$

so the equilibrium condition for systems placed in thermal, mechanical, and diffusive contact involves equalization of the partial derivatives of S with respect to all the variables, with each of the species having separately equal derivatives. The total differential of the entropy is then

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T} \sum_{i=1}^n \mu_i dN_i. \quad (20)$$

The corresponding total differential of the energy is

$$dU = T dS - P dV + \sum_{i=1}^n \mu_i dN_i. \quad (21)$$

Here's another interesting tidbit that follows from the ideal-gas entropy. From (11) and the definition of chemical potential, we have

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = \frac{S}{N} - \frac{5}{2}k = -\frac{\mu}{T}. \quad (22)$$

This means we can write the entropy in terms of the chemical potential as

$$\begin{aligned} S &= \frac{5}{2}Nk - \frac{\mu}{T}N \\ &= \frac{3}{2}Nk + Nk - \frac{\mu}{T}N. \end{aligned} \tag{23}$$

But the ideal-gas law, $PV = NkT$, and the equipartition theorem for the monatomic ideal gas, $U = \frac{3}{2}NkT$, permit rewriting the first two terms as U/T and PV/T , respectively, leading to

$$S = \frac{1}{T}U + \frac{P}{T}V = \frac{\mu}{T}N. \tag{24}$$

Notice the similarity with the thermodynamic identity (17), involving differentials of the variables S , U , V , and N .

Rearrangement of (24) leads to the expression

$$U = TS - PV + \mu N, \tag{25}$$

which should be compared to the differential form (18).

It turns out that (24) and (25) are generally valid, not just for the ideal gas, as our derivation would suggest. As such, they have some useful general implications. Consider, for example, the total differential of U as obtained from (25):

$$dU = T dS + S dT - P dV - V dP + \mu dN + N d\mu. \tag{26}$$

In view of (18), we must conclude that

$$S dT - V dP + N d\mu = 0, \tag{27}$$

a result known as the *Gibbs-Duhem* equation. This is often useful for finding the chemical potential in terms of the pressure and temperature.