

1. **The Helmholtz free energy and the canonical partition function.** In lecture I showed that in a macroscopic system ($N \gg 1$), the Helmholtz free energy A can be equated with the logarithm of the canonical partition function Q :

$$\beta A(N, V, T) = -\ln Q(N, V, T).$$

This problem develops a different (friendlier?) way to show that connection between macroscopic thermodynamics and statistical mechanics.

- (i) Start with the microscopic picture. Each microstate ν has energy $E(\nu)$, so the canonical partition function is

$$Q(N, V, T) = \sum_{\nu \text{ consistent with } N, V} e^{-E(\nu)/k_B T}.$$

Show that

$$\left(\frac{\partial \ln Q}{\partial \beta} \right)_{V, N} = -\langle E \rangle.$$

$$\begin{aligned} \left(\frac{\partial \ln Q}{\partial \beta} \right)_{V, N} &= \frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{V, N} \\ &= -\frac{1}{Q} \sum_{\nu \text{ consistent with } N, V} E(\nu) e^{-E(\nu)/k_B T} \\ &= - \sum_{\nu \text{ consistent with } N, V} E(\nu) P(\nu) \\ &= -\langle E \rangle. \end{aligned}$$

- (ii) Now let's think about the thermodynamic picture. Apply the chain rule to demonstrate that

$$\left(\frac{\partial(-\beta A)}{\partial \beta} \right)_{V, N} = -E.$$

$$\begin{aligned}
\left(\frac{\partial(-\beta A)}{\partial\beta}\right)_{V,N} &= -A - \beta \left(\frac{\partial A}{\partial\beta}\right)_{V,N} \\
&= -A - \beta \left(\frac{\partial T}{\partial\beta}\right)_{V,N} \left(\frac{\partial A}{\partial T}\right)_{V,N} \\
&= -A + \beta(k_B T^2) \left(\frac{\partial A}{\partial T}\right)_{V,N} \\
&= -A - TS \\
&= -E.
\end{aligned}$$

(iii) In the thermodynamic limit ($N \rightarrow \infty$), we replace $\langle E \rangle$ by E , which we now take to be a deterministic quantity. Hence in that limit, the derivative of $\ln Q$ with respect to β is exactly the same as the derivative of $-\beta A$ with respect to β . Conclude that it must be the case that in the large system size limit $-\beta A = \ln Q + C$, where C is some constant that does not depend on β . Why do you think we suppressed the constant in lecture?

We have equated the derivatives. If we integrate both sides with respect to β then we get

$$\beta A = -\ln Q + C$$

where C is a constant of integration. We consider the low-temperature limit of both sides

$$\lim_{T \rightarrow 0} \beta A = \lim_{T \rightarrow 0} \frac{E + TS}{k_B T} = \beta E_{\text{ground}}$$

since $\lim_{T \rightarrow 0} S = 0$. Similarly,

$$\lim_{T \rightarrow 0} \ln Q + C = -\ln e^{-\beta E_{\text{ground}}} + C = \beta E_{\text{ground}} + C.$$

For the left- and right-hand sides to be equal in the low temperature limit, we must set the integration constant C to zero.

2. **Practice with Legendre transforms and Maxwell relations.** In class we discussed how the Helmholtz free energy could be constructed as $A = E - TS$ to yield a “thermodynamic potential” which is a natural function of T , V , and N . This is to be contrasted with the first thermodynamic potential we introduced: S , a function of E , V , and N . Notice that the transformation passing from S to A is a lot like the transition from the microcanonical (constant E) to canonical (constant T) ensemble, a similarity which is very much not an accident. In that transformation from microcanonical to canonical we were motivated to study an open system which had a fluctuating energy since energy was exchanged with a very large bath. Suppose we have a system which, through interactions with the outside environment, has a fluctuating energy *and a fluctuating volume*.

(i) Show that the Gibbs free energy, $G = E - TS + pV$, is a thermodynamic potential which is naturally a function of T , p , and N by writing out an expression for dG in terms of dT , dp , and dN .

Recall from lecture that $dE = TdS + \mu dN - pdV$. Substituting this in for dE in the following equation, observe that

$$\begin{aligned} dG &= dE - d(TS) + d(pV) = TdS - pdV + \mu dN - TdS - SdT + pdV + Vdp \\ &= -SdT + Vdp + \mu dN \end{aligned}$$

gives a differential in terms of dT , dp and dN , so G is a natural function of T , p , and N .

(ii) You have no doubt come across the Gibbs free energy in a chemistry class when discussing whether or not a chemical reaction would occur spontaneously. Why did you focus on the Gibbs free energy and not the Helmholtz free energy?

Free energies help us predict what will occur spontaneously. Namely, systems tend to evolve in a manner that minimizes the free energy. The applicable free energy, however, depends on the macroscopic constraints that we impose (the choice of ensemble). For example, when we have fixed N , V , and E , we saw that the expected behavior was that which increased entropy S (entropy maximization could equivalently be thought of as minimizing $-S$). That simple principle of entropy maximization lets us predict the most likely macrostates if our system is truly unable to exchange particles, energy, or volume with an outside environment, but if the system can interact with an outside environment we must also weigh the impact on the environment's entropy. That's what we did when we studied the canonical ensemble and constructed the associated Helmholtz free energy. We saw that the system didn't want to merely minimize $-S$, it now wanted to minimize the function $E - TS$. The first term came from the bath penalizing situations when the system had high entropy. The second term was like the original microcanonical minimization of $-S$ (T is a fixed constant in the microcanonical ensemble). If, however, the system can also exchange volume with the environment, then we should work in an ensemble that holds N , T , and p fixed. In that case the free energy whose minimization predicts the equilibrated behavior is the one which is a natural function of N , T , and p : the Gibbs free energy. In chemistry, lots of experiments happen in a vessel that is not enclosed, so the volume of the solution can swell or contract. These constant-pressure, constant-temperature, fixed particle concentration experiments are therefore described by the Gibbs, not the Helmholtz, free energy.

(iii) From multivariable calculus you should have seen that the "mixed partial derivatives" of a multi-variable function are equal. For example, let $f(x, y)$ be a function of x and y such that

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy.$$

The order of differentiation with respect to both x and y does not matter:

$$\left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y \right)_x = \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x \right)_y = \frac{\partial^2 f}{\partial x \partial y}.$$

Use this fact and your expression for dG in (i) to relate $(\partial S / \partial p)_{T, N}$ to a partial derivative involving volume and temperature. Such an equality is called a Maxwell relation. There are lots of problems in thermodynamics which require you to pull out the right Maxwell relation at the right time. I'm going to try to avoid asking you to guess when you should try to use them. Rather, I want you to focus on

two main points: (1) they can always be derived from mixed partial derivatives of a thermodynamics potential and (2) they relate two different types of experiments. It is often the case that one experiment is easier to measure than the other. For example, $(\partial S/\partial p)_{T,N}$ requires a measurement of how entropy grows with pressure at fixed T and N , but you may only have a way of measuring how volume changes with temperature. In that case, the Maxwell relation saves the day.

Let's start with $dG = -SdT + Vdp + \mu dN$. The first step here is recognizing that $dG = \left(\frac{dG}{dT}\right)_{N,p} dT + \left(\frac{dG}{dp}\right)_{N,T} dp + \left(\frac{dG}{dN}\right)_{T,p} dN$, meaning that $-S = \left(\frac{dG}{dT}\right)_{N,p}$, $V = \left(\frac{dG}{dp}\right)_{N,T}$, and $\mu = \left(\frac{dG}{dN}\right)_{T,p}$. We then can make the following connection:

$$\left(\frac{\partial^2 G}{\partial p \partial T}\right)_N = \left(\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial T}\right)_{p,N}\right)_{T,N} = \left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p}\right)_{T,N}\right)_{p,N}$$

where we can take $-S = \left(\frac{dG}{dT}\right)_{N,p}$ and $V = \left(\frac{dG}{dp}\right)_{N,T}$ to say:

$$\left(\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial T}\right)_{p,N}\right)_{T,N} = -\left(\frac{\partial S}{\partial p}\right)_{T,N}$$

and

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p}\right)_{T,N}\right)_{p,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N}$$

Finally, we obtain the Maxwell relation:

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

3. **Ideal gas chemical potential.** We began our study by discussing the response to changes in three extensive macroscopic constraints, N , V , and E . We then swapped out two of those rigid constraints, V and E , for conjugate variables, p and T to allow volume and energy to fluctuate. I think you probably have a sense of how one could tune all of these five parameters: N , V , E , p and T in an experiment. The missing link is the chemical potential μ , the intensive quantity conjugate to N . I find it to be much more mysterious how one can make a giant bath with a tunable value of a chemical potential. In other words, suppose you have your system and want that system to exchange particles with a large particle reservoir with chemical potential μ . I know how to make a bath of a particular temperature with an ice bucket or a water bath. Similarly, I know how to make a bath with a particular pressure. In this problem, we show that you can make a bath with a particular μ out of an ideal gas by appropriately adjusting p and T . We assume that our bath consists of a dilute vapor, for which the ideal gas law, $pV = Nk_B T$, is a good approximation.

(i) Ideality implies that internal energy E depends only on T and N , and not on p . Show that this is true by evaluating the derivative $(\partial E/\partial p)_{T,N}$. Use as a starting point the fundamental relation

$$dE = TdS - pdV + \mu dN$$

and differentiate with respect to p at fixed T and N to get:

$$\left(\frac{\partial E}{\partial p}\right)_{T,N} = T \left(\frac{\partial S}{\partial p}\right)_{T,N} - p \left(\frac{\partial V}{\partial p}\right)_{T,N}.$$

From here, use your Maxwell relation from problem 2 and differentiate the ideal gas law.

As instructed, we start with

$$dE = TdS - pdV + \mu dN.$$

If we were to differentiate with respect to S , V , or N we'd get back the intensive quantities T , $-p$, and μ . But we can also differentiate with respect to one of these intensive quantities. The difference is that we will now have multiple terms because V and S are not held fixed:

$$\left(\frac{\partial E}{\partial p}\right)_{T,N} = T \left(\frac{\partial S}{\partial p}\right)_{T,N} - p \left(\frac{\partial V}{\partial p}\right)_{T,N}.$$

Inserting the Maxwell relation from problem 2, we have:

$$\left(\frac{\partial E}{\partial p}\right)_{T,N} = -T \left(\frac{\partial V}{\partial T}\right)_{p,N} - p \left(\frac{\partial V}{\partial p}\right)_{T,N}.$$

For an ideal gas, we can compute the derivatives of V with respect to both p and T after rearranging the ideal gas law to be $V = Nk_B T(p^{-1})$:

$$\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{k_B N}{p} \quad \text{and} \quad \left(\frac{\partial V}{\partial p}\right)_{T,N} = -\frac{k_B N T}{p^2},$$

which implies

$$\left(\frac{\partial E}{\partial p}\right)_{T,N} = -T \left(\frac{\partial V}{\partial T}\right)_{p,N} - p \left(\frac{\partial V}{\partial p}\right)_{T,N} = -\frac{k_B N T}{p} + \frac{k_B N T}{p} = 0.$$

(ii) Argue based on your result from part (i) and the property of extensivity that the energy of an ideal gas can be written in the form

$$E = N\epsilon(T).$$

From part (i), we know that the internal energy is only a function of T and N , but internal energy is also an extensive function. Consequently, E cannot be an arbitrary function of N , it must be linearly proportional to N . From this, we conclude that

$$E = N\epsilon(T),$$

where $\epsilon(T)$ is the temperature-dependent internal energy per particle.

(iii) The entropy of an ideal gas can be divided into two parts: that associated with intramolecular fluctuations $S_{\text{intra}} = Ns(T)$, and that associated with distributing molecules in space (i.e., center-of-mass translation), S_{trans} . In problem 1 of the last problem set, you calculated S_{trans} for a dilute

system to be

$$S_{\text{trans}} = -k_{\text{B}}V[\rho \ln(\rho v) - \rho],$$

where $\rho = N/V$ and v is the volume of a microscopic lattice cell introduced for the purpose of counting. Using that result, write the total entropy $S = S_{\text{intra}} + S_{\text{trans}}$ of our ideal gas as a function of p , N , and T . (Your answer may involve the unspecified function $s(T)$.)

$$\begin{aligned} S &= Ns(T) - k_{\text{B}}V[\rho \ln(\rho v) - \rho] \\ &= Ns(T) - k_{\text{B}}\frac{Nk_{\text{B}}T}{p} \left[\frac{p}{k_{\text{B}}T} \ln \left(\frac{pv}{k_{\text{B}}T} \right) - \frac{p}{k_{\text{B}}T} \right] \\ &= Ns(T) - Nk_{\text{B}} \ln \left(\frac{pv}{k_{\text{B}}T} \right) + Nk_{\text{B}}. \end{aligned}$$

(iv) Combining these results, compute the Gibbs free energy, $G = E - TS + pV$, of an ideal gas. Differentiate appropriately to determine the chemical potential $\mu(T, p)$.

We can now explicitly express the Gibbs free energy in terms of its natural variables T, p , and N :

$$\begin{aligned} G &= E - TS + pV \\ &= N\epsilon(T) - TNs(T) + Nk_{\text{B}}T \ln \left(\frac{pv}{k_{\text{B}}T} \right) - Nk_{\text{B}}T + Nk_{\text{B}}T \\ &= N\epsilon(T) - TNs(T) + Nk_{\text{B}}T \ln \left(\frac{pv}{k_{\text{B}}T} \right). \end{aligned}$$

Differentiating with respect to N at constant T and p gives the chemical potential

$$\mu(T, p) = \left(\frac{\partial G}{\partial N} \right)_{T, p} = \epsilon(T) - Ts(T) + k_{\text{B}}T \ln \left(\frac{pv}{k_{\text{B}}T} \right).$$

(v) Show that $\mu(T, p)$ can be written

$$\mu(T, p) = \mu^{(0)}(T) + k_{\text{B}}T \ln \left(\frac{p}{p_0} \right),$$

where p_0 is a reference value of pressure (e.g., 1 atm). Identify the quantity $\mu^{(0)}(T)$ in terms of T , v , and p_0 . (Your answer may involve the unspecified functions $\epsilon(T)$ and $s(T)$.) Just as the temperature T regulated how much our system wanted to donate or extract energy from a temperature bath, the chemical potential regulates how much the system wants to donate or extract particles from the surrounding environment. We have just derived how that propensity for adding/removing particles can be changed by tuning the temperature and pressure.

$$\begin{aligned}\mu(T, p) &= \epsilon(T) - Ts(T) + k_{\text{B}}T \ln \left(\frac{pv}{k_{\text{B}}T} \right) \\ &= \underbrace{\epsilon(T) - Ts(T) + k_{\text{B}}T \ln \left(\frac{p_0 v}{k_{\text{B}}T} \right)}_{\mu^{(0)}(T)} + k_{\text{B}}T \ln \left(\frac{p}{p_0} \right).\end{aligned}$$

A note about standard states:

It may seem silly that we just introduced the reference pressure p_0 out of nowhere. Why wouldn't we just write

$$\mu(T, p) = \underbrace{\epsilon(T) - Ts(T) + k_{\text{B}}T \ln \left(\frac{v}{k_{\text{B}}T} \right)}_{\mu^*(T)} + k_{\text{B}}T \ln p,$$

with $\mu^*(T)$ being our proposed standard state chemical potential? The problem with writing things this way is that I'm now computing the logarithm of a dimensionful quantity (p has dimensions of pressure and $v/k_{\text{B}}T$ has dimensions of one over pressure), yet logarithms only act on dimensionless numbers. Mathematically there's no problem with the expression since the two logarithm terms are going to combine together to give canceling units, but when we split out a term to define a standard state chemical potential, we would only be able to compute the $\mu^{(0)}$ if it is expressed in terms of logs of dimensionless quantities.