

Thermodynamics and Statistical Mechanics Homework Assignment 4

Todd Hirtler

03May20

Problem 1

In class, using the exactness of Helmholtz free energy, we derived one of the Maxwell relations, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$. Now, let us derive another Maxwell relation: The Gibbs free energy is defined as, $G = F + pV$.

a) Show that $dG = -SdT + Vdp$.

b) Using the result from part a, prove that $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$.

Solution

a) We know that

$$dG = dF + Vdp + pdV$$

and

$$dF = -SdT - pdV$$

Plugging in the expression for dF into Gibbs equation gives

$$dG = Vdp + pdV - SdT - pdV = Vdp - SdT$$

Which is what we're after.

b) We can also express the Gibbs free energy in a different way using partial differentials.

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

Comparing it to what we found in part a, this gives us

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

A neat feature of partial differentiation is that the order doesn't matter so we can say

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}$$

Using what we know about the first order partial derivatives of G , we find that

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

which is exactly what we are looking for.

Problem 2

Over the past decade, there has been much discussion in the press of centrifuges, suspected parts for centrifuges, and their impact on nuclear non-proliferation. In this problem, we will examine the capabilities of centrifuges for Uranium isotope separation.

a) Consider a hollow cylinder of radius R and length L that rotates about its axis with an angular velocity ω . Assume that the cylinder is filled with an ideal gas of atoms of mass M at temperature T . Find an expression for the concentration of atoms $n(r)$ as a function of the radial distance r from the axis. Express your answer in terms of the concentration on the axis $n(0)$.

b) Use your result from part a to solve for the concentration on the axis of rotation $n(0)$ under the constraint that the average density is \bar{n} . Use this result to write an expression for the concentration as a function of radius. Centrifuges can be used to separate isotopes of Uranium. The natural abundances of U-238 and U-235 are roughly 99 percent and 1 percent respectively. The highly enriched uranium typically used in nuclear weapons contains about 90 percent of U-235.

c) Assume that the cylinder is filled with an ideal gas of UF_6 (Uranium Hexafluoride, $A = 19$ for fluorine) where the uranium has the natural isotopic abundance. Find an expression for the ratio of the isotopic concentrations in the gas at the axis of the centrifuge m_{238} and m_{235} and the concentrations before centrifuge is set to spinning \bar{n}_{235} and \bar{n}_{238} .

d) Find an approximate expression for the required speed of the centrifuge shell in order to achieve enrichment of the gas on the centrifuge axis by a factor of $\approx e$. How does this speed compare with the speed of sound in air? Note: The speed of sound in air is $v_s \approx \sqrt{\gamma kT/m}$ with $\gamma = 7/5$ and m the mass of a

N_2 molecule. In practice, several centrifuges will need to be cascaded to achieve sufficient enrichment for weapons production.

Solution

a) While in the non-inertial frame of the centrifuge, the only force acting on the gas is a centrifugal force

$$\mathbf{F} = M\omega^2 R\hat{r}$$

This gives us a potential energy of

$$V = - \int \mathbf{F} \cdot d\mathbf{r} = -\frac{M\omega^2 r^2}{2}$$

The probability distribution will then be

$$n(r) = Ce^{\beta E_r} = Ce^{\frac{\beta M\omega^2 r^2}{2}}$$

At the axis, the concentration will be

$$n(0) = C$$

So the concentration is

$$n(r) = n(0)e^{\frac{\beta M\omega^2 r^2}{2}}$$

b) The total amount of particles is

$$N = \int n(r)dV = 2\pi L \int n(r)rdr = \bar{n}\pi LR^2$$

We can plug in the result from part a and integrate

$$N = 2\pi L \int_0^R n(0)e^{\frac{\beta M\omega^2 r^2}{2}} rdr$$

$$\bar{n}R^2 = 2n(0) \int_0^R e^{\frac{\beta M\omega^2 r^2}{2}} rdr = 2n(0) \frac{k_B T}{M\omega^2} \left(1 - e^{-\frac{MR^2\omega^2}{2k_B T}}\right)$$

Solving for $n(0)$ gives us

$$n(0) = \frac{\bar{n}M\omega^2 R^2}{2k_B T \left(1 - e^{-\frac{MR^2\omega^2}{2k_B T}}\right)}$$

which gives us

$$n(r) = \frac{\bar{n}M\omega^2 R^2 e^{\frac{Mr^2\omega^2}{2k_B T}}}{k_B T \left(1 - e^{-\frac{MR^2\omega^2}{2k_B T}}\right)}$$

c) The ratio of concentrations along the axis is

$$\frac{n_{235}(0)}{n_{238}(0)} = \left(\frac{n_{235}^- M_{235}}{n_{238}^- M_{238}} \right) \left(\frac{e^{\frac{M_{238} \omega^2 R^2}{2k_B T}} - 1}{e^{\frac{M_{235} \omega^2 R^2}{2k_B T}} - 1} \right)$$

d) The exponents will need to be large, so we can simplify the concentration ratio as

$$\frac{n_{235}(0)}{n_{238}(0)} = \left(\frac{n_{235}^- M_{235}}{n_{238}^- M_{238}} \right) e^{\frac{(M_{238} - M_{235}) \omega^2 R^2}{2k_B T}}$$

We want this exponent to have a value of e , so

$$\frac{(M_{238} - M_{235}) \omega^2 R^2}{2k_B T} = 1$$

Solving for $v = R\omega$, we get

$$v = R\omega = \sqrt{\frac{2k_B T}{M_{238} - M_{235}}}$$

The speed of sound for the nitrogen is

$$v_s = \sqrt{\frac{\gamma k_B T}{m}} = \sqrt{\frac{k_B T}{20}}$$

compared to the velocity from before

$$v = \sqrt{\frac{2k_B T}{3}}$$

Shows us that the shell of the centrifuge is moving faster than the speed of sound.

Problem 3

This problem involves a simplified model for the hemoglobin molecule. Assume that there is a single site on the hemoglobin molecule consisting of an F^{+2} ion that can bind one oxygen molecule (In reality, the situation is somewhat more complex.) Take the energy of the free and bound states to be 0 and ϵ_{O_2} respectively. Assume that the hemoglobin molecule is much more massive than the O_2 molecule, and that the system is at a temperature of 300K.

a) Write down an expression for the Gibbs sum in this system.

b) Through the action of the lungs, the blood is an approximate diffusive equilibrium with the atmosphere. Assume that the atmosphere is an ideal gas

with a partial pressure for O_2 of about 0.2 atm. Calculate the chemical potential of oxygen molecules in the blood at room temperature. Express your answer in electron volts. (Hint: An atom of oxygen has an atomic weight of about 16 atomic mass units.)

c) Write an expression for the probability that any given hemoglobin molecule will have an O_2 molecule bound to it. Evaluate your answer using the result from part b and the approximate binding energy of the O_2 to the hemoglobin $\epsilon = -0.7eV$.

d) Now, assume that there is also some carbon monoxide present that can be bound to the site on the hemoglobin molecule instead of the oxygen. Write down the Gibbs sum of the new system. Express your result in terms of the energies for the bound states ($\epsilon_{O_2}, \epsilon_{CO}$) and the chemical potentials (μ_{O_2}, μ_{CO}) of the O_2 and CO molecules.

e) We somewhat arbitrarily define asphyxiation as occurring when only 50 percent of the available hemoglobin molecules have bound oxygen molecules. Find an expression for the ratio of the CO and O_2 concentrations when this condition occurs. The CO molecule is bound to the hemoglobin with an energy $\epsilon_{CO} = -0.85eV$. What partial pressure of CO molecules will result in asphyxiation? Express your answer in atmospheres.

Solution

a) The Gibbs sum is

$$\zeta = \sum_N \sum_{s(N)} e^{-\beta(\epsilon_s(N) - \mu N)} = 1 + e^{-\beta(\epsilon - \mu)}$$

we can define

$$\lambda = e^{\beta\mu}$$

so

$$\zeta = 1 + \lambda e^{-\beta\epsilon_{O_2}}$$

b) The chemical potential for an ideal gas is

$$\mu = kT \ln(\lambda) = kT \ln\left(\frac{n}{n_Q}\right) = kT \ln\left(\frac{p}{kT n_Q}\right) = kT \ln\left(\frac{p(2\pi\hbar^2)^{\frac{3}{2}}}{kT^{\frac{5}{2}} M^{\frac{3}{2}}}\right)$$

$$\mu \approx -0.6eV$$

c) The probability of an occupied site is

$$P = \frac{\lambda e^{-\beta\epsilon_{O_2}}}{1 + \lambda e^{-\beta\epsilon_{O_2}}} = \frac{e^{0.1\beta}}{1 + e^{0.1\beta}} \approx \frac{47.86}{48.86} = 0.98$$

d) The new Gibbs sum will be

$$\zeta = 1 + e^{-\beta(\epsilon_{O_2} - \mu_{O_2})} + e^{-\beta(\epsilon_{CO} - \mu_{CO})}$$

e) We need to look at the chemical potentials for each gas. We can add in a term x that is the ratio of CO to O_2

$$\begin{aligned} \mu_{CO} &= kT \ln\left(\frac{n_{CO}}{n_Q}\right) = kT \ln\left(\frac{n_{O_2}x}{n_Q}\right) = kT \ln(x) + kT \ln\left(\frac{n_{O_2}}{n_Q}\right) \\ &= kT \ln(x) + \mu_{O_2} \end{aligned}$$

The probability of O_2 occupying the site can be set to 1/2 and we can use this chemical potential relation to solve for x .

$$\begin{aligned} P &= \frac{1}{2} = \frac{e^{-\beta(\epsilon_{O_2} - \mu_{O_2})}}{1 + e^{-\beta(\epsilon_{O_2} - \mu_{O_2})} + e^{-\beta(\epsilon_{CO} - \mu_{CO})}} \\ &= \frac{e^{-\beta(\epsilon_{O_2} - \mu_{O_2})}}{1 + e^{-\beta(\epsilon_{O_2} - \mu_{O_2})} + e^{-\beta(\epsilon_{CO} - \mu_{O_2} - kT \ln(x))}} \\ &= \frac{47.86}{48.86 + 15848.11x} \\ x &= 0.003 \end{aligned}$$

This is extremely small which shows that just a little bit of CO is enough to be killer. The O_2 has a partial pressure of 0.2 atm and we have the ratio of CO to O_2 so the partial pressure of CO to cause asphyxiation will be

$$p_{CO} = xp_{O_2} = 6.0 \times 10^{-4} \text{ atm}$$

Problem 4

A neutral gas consists of N_e electrons (e^-), N_p protons (p^+) and N_H hydrogen atoms (H). An electron and proton can combine to form hydrogen, $e^- + p^+ \rightarrow H$. At fixed temperature and volume, the free energy of the system is

$$F(T, V; N_e, N_p, N_H)$$

We can define a chemical potential for each of the three species $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$.

a) By minimizing the free energy, together with suitable constraints on the particle numbers, show that the condition for equilibrium is $\mu_e + \mu_p = \mu_H$. Such

reactions usually take place at constant pressure, rather than constant volume. What quantity should you consider instead of F in this case?

b) As you know, the Hydrogen atom (in its ground state) has binding energy $E = -\Delta = -13.6\text{eV}$. Let the number of Hydrogen atoms be $N_H = (1-x)N$ and the number of electrons and protons be $N_e = N_p = xN$. By treating the system as three ideal gases in the grand canonical ensemble, use the equilibrium condition found in part a to show that

$$\frac{x^2}{1-x} = \frac{V}{N} \left(\frac{m_e m_p}{2\pi\hbar^2 m_H} \right)^{\frac{3}{2}} (k_B T)^{\frac{3}{2}} e^{-\frac{\Delta}{k_B T}}$$

Solution

a) We have the three differentials for the chemical potential of each particle.

$$\mu_e = \frac{\partial F}{\partial N_e}, \quad \mu_p = \frac{\partial F}{\partial N_p}, \quad \mu_H = \frac{\partial F}{\partial N_H}$$

We also have the constraints

$$N = N_H + N_e, \quad N_e = N_p$$

Looking at the total differential of the Helmholtz free energy in respect to the quantity of electrons gives us

$$\begin{aligned} \frac{dF}{dN_e} &= \frac{\partial F}{\partial N_e} + \frac{\partial F}{\partial N_p} \frac{dN_p}{dN_e} + \frac{\partial F}{\partial N_H} \frac{dN_H}{dN_e} \\ &= \mu_e + \mu_p - \mu_H = 0 \end{aligned}$$

or

$$\mu_e + \mu_p = \mu_H$$

At constant pressure it is better to use the Gibbs free energy.

b) The chemical potential of hydrogen is

$$\mu_H = \mu_{intH} + \mu_{extH} = \mu_{intH} - \Delta$$

Treating the gases as ideal gases

$$\mu_{int} = k_B T \ln(n\lambda^3)$$

so

$$k_B T \ln(n_e \lambda_e^3) + k_B T \ln(n_p \lambda_p^3) = k_B T \ln(n_H \lambda_H^3) - \Delta$$

Combining the logarithm terms gives us

$$\ln\left(\frac{n_e n_p \lambda_e^3 \lambda_p^3}{n_H \lambda_H^3}\right) = -\frac{\Delta}{k_B T}$$

Now, we can simplify this using

$$n_e = n_p = \frac{xN}{V}, \quad n_H = \frac{(1-x)N}{V}, \quad n = \frac{N}{V}$$

so

$$\ln\left(\frac{x^2 N^2}{(1-x)NV} \sqrt{\frac{m_H^3 k_B^3 T^3 4\pi^2 \hbar^4}{m_e^3 m_p^3 k_B^6 T^6 2\pi \hbar^2}}\right) = -\frac{\Delta}{k_B T}$$

Solving for $x^2/(1-x)$ gives us

$$\frac{x^2}{1-x} = \frac{V}{N} \left(\frac{k_B T m_e m_p}{2\pi \hbar^2 m_H}\right)^{\frac{3}{2}} e^{-\frac{\Delta}{k_B T}}$$

which is what we are looking for.

Problem 5

Consider an absorbent surface having N sites each of which can absorb one gas molecule, and upon absorption the molecule's energy is $-\epsilon_0$. Suppose that these absorbing sites are in contact with the particle reservoir which is an ideal gas at pressure p . Assuming the number of particles in the ideal gas is much larger than N , so that even if all absorbing sites are full the change in the ideal gas particle number is negligible.

- Find the chemical potential of the ideal gas.
- Calculate the grand partition function of the absorbing surface.
- Show that the average fraction of occupied sites on the surface is

$$f = \frac{1}{1 + e^{-\beta(\epsilon_0 + \mu)}}$$

- Express the absorbed fraction as a function of p and T .

Solution

- We start off find the Helmholtz free energy

$$F = -k_B T N \ln\left(\frac{V}{\lambda^3}\right) + k_B T \ln(N!)$$

$$= -k_B T N \ln\left(\frac{V}{\lambda^3}\right) + N k_B T \ln(N) - N k_B T$$

To find the chemical potential, we just need to differentiate this with respect to the particle number

$$\mu = \frac{\partial F}{\partial N} = -k_B T \ln\left(\frac{V}{\lambda^3}\right) = k_B T \ln(n\lambda^3)$$

Using $PV = Nk_B T$ we can solve this in terms of the pressure

$$\mu = k_B T \ln\left(\frac{p\lambda^3}{k_B T}\right)$$

b) The grand partition function will be

$$\begin{aligned} Z_{GC} &= \sum_{n=0}^N \binom{N}{n} e^{-\beta n(-\epsilon_0 - \mu)} \\ &= (1 + e^{\beta(\epsilon_0 + \mu)})^N \end{aligned}$$

c) We can find the average occupied states by

$$\langle n \rangle = \frac{1}{Z_{GC}} \frac{\partial Z_{GC}}{\partial(\beta(\epsilon_0 + \mu))} = \frac{N}{1 + e^{-\beta(\epsilon_0 + \mu)}}$$

Dividing this by N gives us the average fraction of occupied states on the surface

$$f = \frac{\langle n \rangle}{N} = \frac{1}{1 + e^{-\beta(\epsilon_0 + \mu)}}$$

d) We need to rewrite the distribution function in a more useful way.

$$f = \frac{1}{1 + e^{-\beta(\epsilon_0 + \mu)}} = \frac{e^{\beta\mu}}{e^{-\beta\epsilon_0} + e^{\beta\mu}}$$

We can use what we found in part a to get this in terms of pressure to get

$$\begin{aligned} f &= \frac{\frac{p\lambda^3}{k_B T}}{e^{-\beta\epsilon_0} + \frac{p\lambda^3}{k_B T}} \\ &= \frac{p}{p + \frac{k_B T}{\lambda^3} e^{-\beta\epsilon_0}} \end{aligned}$$