

Homework 7 - Solutions

1st December 2004

Problem 1

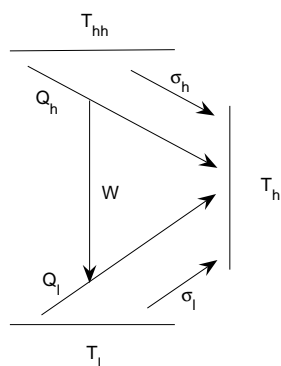


Figure 1: Energy-entropy flow diagram.

If the process is reversible the total change in entropy is zero

$$0 = \Delta S = -\frac{Q_{hh}}{\tau_{hh}} + \frac{Q_h}{\tau_h} - \frac{Q_l}{\tau_l}$$

The total energy is conserved and there is no work added to or extracted from the system

$$-Q_{hh} + Q_h - Q_l = 0$$

Eliminating Q_h we get

$$\frac{Q_l}{Q_{hh}} = \frac{\frac{1}{\tau_h} - \frac{1}{\tau_{hh}}}{\frac{1}{\tau_l} - \frac{1}{\tau_h}}$$

Problem 2

The bulb delivers $100W$ to the inside of the fridge, which is at a temperature τ_l . Thus we have to extract at least $100W$ from it, but since there can be some leaks through the walls say we need to extract $P_l = 100W + P_1$ (P is power - energy (heat, work...) per time). Now we do work $100W$ (from the outlet) and the resulting heat delivered to the reservoir (room) at the room temperature τ_h is $P_h = P_l + 100W = 200W + P_1$. The change in entropy is zero which gives us

$$\frac{P_l}{\tau_l} = \frac{P_h}{\tau_h}$$

This gives

$$\frac{\tau_l}{\tau_h} = \frac{100W + P_1}{200W + P_1} < 1$$

and thus we can keep it at lower temperature.

Problem 3

Let T be the temperature of the solid at some time. Let dQ_l be the heat taken from the solid and dQ_h heat delivered to the reservoir at some T when we change the T by dT .

Then from conservation of entropy we have

$$\frac{dQ_l}{T} = \frac{dQ_h}{T}$$

From the definition of the heat capacity

$$dQ_l = CdT_l$$

The work done when changing T by dT is

$$dW = dQ_h - dQ_l = dQ_l \left(\frac{T_h}{T} - 1 \right) = CdT \left(\frac{T_h}{T} - 1 \right) = aT^3 \left(\frac{T_h}{T} - 1 \right)$$

The total work is then

$$W = \int_0^\infty aT^3 \left(\frac{T_h}{T} - 1 \right) dT = \frac{1}{12} aT_h^4$$

Problem 4 The first law says

$$dU = \tau d\sigma - pdV + \mu dN$$

From this

$$dG = d(U - \tau\sigma + pV) = -\sigma d\tau + V dp + \mu dN$$

Thus

$$\begin{aligned}\sigma &= -\left(\frac{\partial G}{\partial \tau}\right)_{p,N} \\ V &= \left(\frac{\partial G}{\partial p}\right)_{\tau,N} \\ \left(\frac{\partial \sigma}{\partial p}\right)_{\tau,N} &= -\left(\frac{\partial^2 G}{\partial \tau \partial p}\right)_N = -\left(\frac{\partial V}{\partial \tau}\right)_{p,N}\end{aligned}$$

The other relations are obtained similarly:

$$\begin{aligned}\mu &= \left(\frac{\partial G}{\partial N}\right)_{p,\tau} \\ \left(\frac{\partial \mu}{\partial p}\right)_{\tau,N} &= \left(\frac{\partial^2 G}{\partial N \partial p}\right)_\tau = \left(\frac{\partial V}{\partial N}\right)_{p,\tau} \\ \left(\frac{\partial \mu}{\partial \tau}\right)_{p,N} &= \left(\frac{\partial^2 G}{\partial N \partial \tau}\right)_p = -\left(\frac{\partial \sigma}{\partial N}\right)_{p,\tau}\end{aligned}$$

(b) With the help of above we get

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial \tau}\right)_p = -\frac{1}{V} \left(\frac{\partial \sigma}{\partial p}\right)_\tau$$

Now we have

$$\begin{aligned}\lim_{\tau \rightarrow 0} \frac{\partial \sigma(p, \tau)}{\partial p} &= \lim_{\tau \rightarrow 0} \lim_{\Delta p \rightarrow 0} \frac{\sigma(p + \Delta p, \tau) - \sigma(p, \tau)}{\Delta p} \\ &= \lim_{\Delta p \rightarrow 0} \lim_{\tau \rightarrow 0} \frac{\sigma(p + \Delta p, \tau) - \sigma(p, \tau)}{\Delta p} \\ &= \lim_{\Delta p \rightarrow 0} (0 + 0) = 0\end{aligned}$$

Note that we have switched the order of limits. This is possible if the partial derivatives of the function are continuous and have limits as $\tau \rightarrow 0$. Counterexample to this is for example

$$\sigma(p, \tau) = \tau(\tanh((p - p_0)/\tau) + 1)$$

which approaches to zero everywhere as $\tau \rightarrow 0$, but its derivative is 1 at p_0 , and 0 everywhere else.

In most physical situation we expect sufficiently regular behaviour so that the above assumptions are satisfied. The exception is possibly a quantum phase transition (e.i. a transition which happens at $T = 0$ when we change some internal parameter).

Problem 5 (a) The law of mass action for the reaction monomer + Nmer = (N+1)mer is

$$\frac{[I][N]}{[N+1]} = K_N$$

Multiplying together these equations for $1, 2, \dots, N$ we get

$$K_1 \cdots K_N = [I]^N \frac{[I]}{[N+1]}$$

which gives the desired equation.

(b) In the notes on page 20-6 we have that $K(\tau) = \prod_i c_i^{\nu_i}$ where $c_i = n_{i,Q} Z_{i,int}$. By the definition of free energy $Z_i = e^{-F_i/\tau}$. This then gives

$$K_N = \frac{c_N c_1}{c_{N+1}} = \frac{n_Q(N) n_Q(1)}{n_Q(N+1)} \exp((F_{N+1} - F_N - F_1)/\tau)$$

The $n_Q(N)$ is the quantum concentration as usual.

(c) We have

$$\frac{[N+1]}{[N]} = \frac{[I]}{K_N} = \frac{[I] n_Q(N+1)}{n_Q(N) n_Q(1)} e^{(F_1 + F_N - F_{N+1})/\tau} \approx \frac{[I]}{n_Q(1)}$$

$$\frac{[N+1]}{[N]} \approx [I] \left(\frac{2\pi\hbar^2}{M\tau} \right)^{3/2} \approx 10^{20} 10^6 \left(\frac{2 \times 3.1416 \times (1.05 \times 10^{-34})^2}{300 \times 200 \times 10^{-3} / (6 \times 10^{23})} \right)^{3/2} \approx 3.5 \times 10^{-8}$$

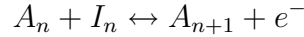
(d) To have more large molecules we need $\frac{[N+1]}{[N]} > 1$. The threshold for when this starts to happen is

$$\frac{[N+1]}{[N]} = 1 = \frac{[1]}{n_Q(1) \exp(\Delta F/\tau)}$$

$$\begin{aligned}
\Delta F &= \tau \log\left(\frac{[1]}{n_Q(1)}\right) \\
&= (1.38 \times 10^{-23}) 300 \log(3.54 \times 10^{-8}) \text{J} \\
&= -7.1 \times 10^{-20} \text{J} \\
&= -0.44 \text{eV}
\end{aligned}$$

Problem 6 Let's denote the n times ionized atom by A_n and its concentration by $[n]$, e.g. CaXIII is A_{12} and it's concentration is $[12]$.

Let's understand what is happening. We have a reactions



For this reaction we can write the Saha equation

$$\frac{[n]}{[n+1][e]} = \frac{n_{Q,n}}{n_{Q,n+1}n_{Q,e}} e^{I_n/\tau} c$$

Where c comes from spins and is some number of order one. The quantum concentrations of A_n and A_{n+1} are approximately the same because the mass of the electron is much smaller then the mass of the atom. We get

$$\frac{[n]}{[n+1]} = c \frac{[e]}{n_{Q,e}} e^{I_n/\tau}$$

Now what are I_n 's. They are the ionization energies. The I_0 is the energy needed to remove one electron from neutral atom. The I_1 is the energy needed to remove and electron from singly ionized ion. And so on. Now notice that more the atom is ionized, the stronger is its charge and more energy is needed to remove an electron. Thus I_n increase with n . Next the concentration of electrons is much smaller then their quantum concentration, e.i. $[e]/N_{Q,e} \ll 1$.

Now imagine the system is at some temperature τ which is closest to one of the I 's the I_n . Then if $m < n$ then $e^{I_m/\tau} \approx 1$ and so $[m] \ll [m+1]$. On the other hand, if $m > n$ then $e^{I_m/\tau}$ is very large and $[m] \gg [m+1]$. Thus the A_n is the most abundant and more we go away from it (more we ionized it, or more we deionize it) lower the concentration.

We are told that the lines from A_{12} and A_{14} are seen and the concentration of A_{14} is the much smaller the one of A_{12} . Thus we will assume that the A_{12} is the most concentrated. We have $I_{12} = 655 \text{eV}$ and $I_{14} = 814 \text{eV}$. If we

linearly extrapolate between them we find $I_{13} = 735eV$. We can for example consider

$$A_{12} + I_{12} + I_{13} \leftrightarrow A_{14} + 2e$$

For this

$$\frac{[12]}{[14]} = \left(\frac{[e]}{n_{Q,e}} \right)^2 e^{(I_{12}+I_{13})/\tau}$$

This gives

$$\tau = \frac{I_{12} + I_{13}}{2 \log \left(\frac{n_{Q,e}}{[e]} \right) + \log \left(\frac{[12]}{[14]} \right)}$$

We only know that the terms in the logarithms are large, but we don't know how much they are. However we are taking only the logarithms of them, and notice that $\log 10 \approx 2.3$ and $\log 10^{20} \approx 46$. With this we get the range of temperatures from about $2 \times 10^5 K$ to $3 \times 10^6 K$ which is much higher than the surface of the sun (which is $\approx 6000K$).

Problem 7 We start with

$$F = -N\tau(\log[n_Q(V - Nb)/N] + 1) - N^2a/V$$

$$n_Q = \left(\frac{M\tau}{2\pi\hbar^2} \right)^{3/2}$$

From $F = -\sigma d\tau - pdV + \mu dN$ we have

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_{V,N} = -N(\log[n_Q(V - Nb)/N] + 5/2)$$

(b)

$$U = F + \tau\sigma = \frac{3}{2}N\tau - N^2a/V$$

(c) From van der Waals equation

$$p = \frac{N\tau}{V - Nb} - \frac{N^2}{V^2}a \approx \frac{N}{V}\tau - \frac{N^2}{V^2}b\tau + \frac{N^2}{V^2}a$$

Then for H we get

$$H = U + pV = \frac{5}{2}N\tau - \frac{N^2}{V}b\tau - \frac{2N^2}{V}a$$

Expanding V from the van der Waals equation to the first order in a , b we get

$$V = \frac{N\tau}{p} + bN - a\frac{N^3\tau}{p^2V^2} = \frac{n\tau}{p} + bN - a\frac{N}{\tau}$$

Plugging this into H and keeping only terms first order in a , b we get

$$H = U + pV = \frac{5}{2}N\tau + Nbp - \frac{2Nap}{\tau}$$