Homework 3 solution

Short questions

1. Practice obtaining Maxwell's relations, show:

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

We first need to understand which auxiliary function we should use. By looking at the denominator and the constant, we understand that we need the Helmholtz free energy:

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$dA = -SdT - pdV$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad and \quad \left(\frac{\partial A}{\partial V}\right)_T = -p$$

$$\because \left[\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right]_V$$

$$\therefore \left[\frac{\partial}{\partial V}(-S)\right]_T = \left[\frac{\partial}{\partial T}(-p)\right]_V \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

2. An ideal gas system undergoes isothermal expansion from an initial volume V_i to a final volume V_f. What is the change in enthalpy of the system?

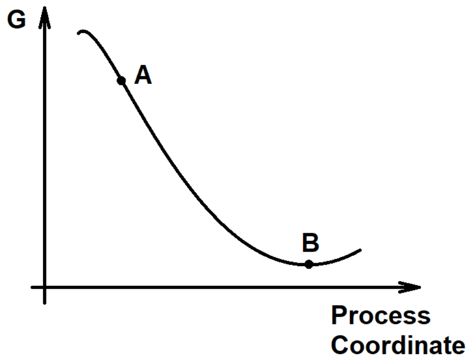
In a general case, enthalpy is defined as:

$$H = U + pV$$

For an ideal gas, the internal energy U and pV depend only on T ($pV = nRT$ and, for example, $U = \frac{3}{2}nRT$ for a monoatomic ideal gas). Therefore, the enthalpy of the idea gas also depends solely on T. Hence, the change of enthalpy ΔH of an isothermal expansion from V_i to V_f is zero.

$$H = U + pV = U + nRT \rightarrow \Delta H = 0$$

3. For an arbitrary process in a closed system, a plot of the Gibbs free energy looks like this:



If the process is at the state **A**, is it possible for the system to spontaneously go to state **B**? Why or why not?

A spontaneous reaction means $\Delta G<0$. Therefore, state **A** will spontaneously go to state **B**.

4. The heat capacity at constant volume C_V of many solids at low temperature has the proportionality: $C_V = \alpha T^3$. What function describes the internal energy of such a material?

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = \alpha T^3$$

Therefore the internal energy of this material at constant volume

$$U = \int C_V dT = \frac{1}{4}\alpha T^4 + c$$

5. In many thermodynamics' exercises a thermal bath is mentioned. Essentially, a thermal bath is an object or vessel, which can receive or give heat. We also consider it to be large enough so that it does not change its temperature. Usually water is used for such applications due to its large heat capacity. A copper piece (m = 10 g, C_{Cu} = 0.385 J/g·K) that has initial temperature T_{Cu} = 100 °C is dropped in a tank of water (C_{H2O} = 4.184 J/g·K) with temperature T_{H2O} = 25 °C. How much water is needed in the tank so the final equilibrium temperature of water and copper piece would be 25.1 °C? Note that in this exercise, we assume a constant heat capacity.

Heat is just the energy; therefore, it must be conserved:

$$m_{Cu}C_{Cu}\Delta T_{Cu} = m_{H2O}C_{H2O}\Delta T_{H2o}$$

$$m_{H2O} = \frac{m_{Cu}C_{Cu}\Delta T_{Cu}}{C_{H2O}\Delta T_{H2o}}$$

$$m_{H2O} = \frac{10\ \cdot 0.385\ \cdot (100 - 25.1)}{4.184\ \cdot\ 0.1}$$

$$m_{H2O} = 689\ g$$

The large heat capacity of water leads to a situation where water can give and take a lot of heat and not change its temperature a lot. In many cases, a change of temperature during an experiment by 0.1 °C can be easily neglected and the water bath can be considered as a thermal bath.

Exercise 1

The thermodynamics of a rubber band. Rubber bands are narrow bands of an elastic polymeric material used to hold things together. Suppose you apply a quasi-static stretching force that increases the length *L* of a rubber band. The force of retraction *f* exerted by the rubber band is equal and opposite to the applied stretching force.

a) Find the expressions of the differential of the internal and Gibbs free energy equations when elastic forces are involved. You have U= U (S, V, L) and n is fixed.

First, we write down the fundamental equation of internal energy in the differential form. n has a fixed value and, therefore, we consider the system closed. However, we have another form of work that we have to consider, the stretching force.

$$dU = TdS - pdV + fdL$$

You don't have to remember the expression for the differential of the Gibbs free energy. You can find it by recalling its definition, differentiate, and substitute for dU:

$$G = H - TS = U + pV - TS$$

$$dG = d(U + pV - TS) = dU + pdV + Vdp - TdS - SdT$$

$$dG = \cancel{TdS} - \cancel{pdV} + fdL + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

And we arrive at the Gibbs free energy equation for a rubber band:

$$dG = fdL + Vdp - SdT$$

b) The retractive force *f* of polymeric elastomers as a function of temperature *T* and expansion *L* is approximately given by $f(T,L) = aT(L-L_0)$ where a and L_0 are constants, and doesn't depend on the pressure p. Use Maxwell relations to determine the entropy $S(L)$ at constant *T* and p.

From the Gibbs free energy, we can see that

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

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

Now, we remember the equality of the second derivatives (i.e. deriving order does not matter for a second derivative). Here we are being very rigorous, but after understanding the basic principle of how the Maxwell's relations are built, you can do this step easily:

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial L}\right)_{p,T}\right]_{L,p} = \left(\frac{\partial f}{\partial T}\right)_{L,p}$$

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

And since the left hand side is equal to each other (Euler's reciprocal relation), the right hand side is also equal to each other:

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

Now we solve for S:

$$\left(\frac{\partial S}{\partial L}\right)_{T,p} = -\left(\frac{\partial f}{\partial T}\right)_{L,p} = -a(L - L_0)$$

$$S(L) = -a\left(\frac{L^2}{2} - L_0 L\right) + S_0$$

S_0 is an integration constant.

c) Based on the results for the entropy $S(L)$ you obtained in b), determine the enthalpy $H(L)$ at constant T and p.

Considering the enthalpy dependence on the length (T and p are constant), we recall the definition of the Gibbs free energy:

$$G = H - TS \quad \text{so} \quad H = G + TS$$

Now we write it in the differential form (no temperature derivative, because T=const):

$$\left(\frac{\partial H}{\partial L}\right)_{T,p} = \left(\frac{\partial G}{\partial L}\right)_{T,p} + T\left(\frac{\partial S}{\partial L}\right)_{T,p}$$

We add previously found values in the equation:

$$\left(\frac{\partial H}{\partial L}\right)_{T,p} = f - T\left(\frac{\partial f}{\partial T}\right)_{L,p} = aT(L - L_0) - T\big(a(L - L_0)\big) = 0$$

Therefore:

$$H(L) = const$$

d) If you adiabatically stretch a rubber band by a small amount its temperature increases, but its volume does not change. Derive an expression for its temperature T as a function of L, L_0, a and its heat capacity at constant volume. Assume that the heat capacity is constant.

$$dU = \delta q + \delta w_{Volume} + \delta w_{Elastic}$$

$$\delta q = 0$$

$$\delta w_{Volume} = 0$$

$$dU = \delta w_{Elastic} = f dL$$

As it is stated:

$$C = \frac{\partial U}{\partial T}$$

Therefore:

$$CdT = fdL = aT(L - L_0)dL$$

Now we just have to solve the differential equation. T_0 and L_0 are starting temperature of the band and starting length of the band, T and L are generalized ending temperature and ending length of the band:

$$\int_{T0}^{T} \frac{C}{T} dT = \int_{L0}^{L} a(L - L_0) dL$$

After integration and some simplification, we are left with:

$$C \ln\left(\frac{T}{T_0}\right) = \frac{a}{2}(L - L_0)^2$$

$$T = T_0 \exp\left(\frac{a}{2C}(L - L_0)^2\right)$$

e) Is the retraction of a rubber band driven by a change in enthalpy or in entropy? The answer to this question helps us to construct a model for the microscopic behaviour of polymeric materials. (Polymeric material refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties, e.g. plastics, etc.)

As we found out in the part (b), H(L)=const., but entropy has a dependence on the length:

$$S(L) = -a\left(\frac{L^2}{2} - L_0 L\right) + S_0$$

Entropy is maximized if $L=L_0$. Which indicates, that the rubber band naturally (i.e. driven by entropy) wants to be in the retracted state.

Usually materials increase in size, if the temperature is increased, but the rubber bands contract upon heating, which can be explained with the relation above. Microscopically it can be understood through the structural nature of fibres. The rubber band at microscopic scale contains many tiny fibres, which are tangled up, when the rubber band is stretched, the fibres become straight (associated with the decrease of entropy). On the other hand, if the rubber band is heated, entropy increases, the fibres tangle up more and macroscopically this can be observed as rubber band contraction.