Statistical and Thermal Physics: Homework 6

Due: 27 February 2018

1 Gibbs free energy

Consider a system that is in contact with a reservoir, which has temperature T and pressure P. MODERATE

a) Suppose that the system undergoes a process in which it is initially in equilibrium with the reservoir (i.e. has the same temperature and pressure as the reservoir) and is finally in equilibrium with the reservoir. Use the argument involving the first and second law to show that in this process

$$\Delta G - P\Delta V \leqslant W$$

where W is the work done on the system and the Gibbs free energy is

$$G = E - TS + PV.$$

b) Consider a quasistatic process in which the pressure of the system is constant and equal to that of the reservoir. Show that

$$\Delta G \leqslant 0.$$

c) Show that

$$G = H - TS$$

d) Liquid water and carbon dioxide react as:

$$\mathsf{H_2O}(\text{liquid}) + \mathsf{CO_2}(\text{gas}) \rightarrow \mathsf{H_2CO_3}(\text{liquid}).$$

For these the enthalpy (of formation from basic constituents) is

$$\begin{aligned} \Delta H(\mathsf{H_2O}(\text{liquid})) &= -285.83\,\text{kJmol}^{-1} \\ \Delta H(\mathsf{CO_2}(\text{gas})) &= -393.51\,\text{kJmol}^{-1} \\ \Delta H(\mathsf{H_2CO_3}(\text{liquid})) &= -699.65\,\text{kJmol}^{-1} \end{aligned}$$

and the entropies are

$$\begin{aligned} S(\mathsf{H_2O}(\text{liquid})) &= 69.91\,\text{JK}^{-1}\text{mol}^{-1} \\ S(\mathsf{CO_2}(\text{gas})) &= 213.74\,\text{JK}^{-1}\text{mol}^{-1} \\ S(\mathsf{H_2CO_3}(\text{liquid})) &= 187.4\,\text{JK}^{-1}\text{mol}^{-1} \end{aligned}$$

Determine ΔG for this reaction at $298\,\text{K}$. Will this occur spontaneously without any external non-mechanical work?

2 Work in a system for a "fixed" volume process

Consider a system that is in contact with a reservoir at temperature T_{res} and pressure P_{res}. Suppose that the system undergoes a process such that the initial and final states have the same temperature as the reservoir and the initial and final volumes are the same. It is possible that both mechanical and non-mechanical work is done on the system. Show that the non-mechanical work done on the system is bounded by

$$W_{\text{non-mech}} \geqslant \Delta F.$$

EASY

3 Helmholtz free energy and thermodynamic variables

a) Express $\mathrm{d}F$ in terms of $\mathrm{d}T, \mathrm{d}V$ and $\mathrm{d}N$ and use the result to express S, P, μ in terms of relevant derivatives of F (remember to indicate variables in the parenthesis subscript). MODERATE

b) Using the general rule of calculus that

$$\frac{\partial^2 f}{\partial x\, \partial y} = \frac{\partial^2 f}{\partial y\, \partial x}$$

and starting with the results from the previous part, show that

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

for any system.

c) For any ideal gas

$$S(T,V,N) = fNk\ln(T) + Nk\ln(V) + \text{constant}.$$

Use this to check the previous result.

4 Enthalpy and thermodynamic variables

a) Express $\mathrm{d}H$ in terms of $\mathrm{d}T, \mathrm{d}S$ and $\mathrm{d}N$ and use the result to express T, V, μ in terms of relevant derivatives of H (remember to indicate variables in the parenthesis subscript). EASY

b) Show that

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

for any system.

5 Gould and Tobochnik, *Statistical and Thermal Physics*, 2.28, page 88. assume dN=0, use the relationship $\frac{\partial S}{\partial P}_T = -\frac{\partial V}{\partial T}_P$EASY

6 Gould and Tobochnik, *Statistical and Thermal Physics*, 3.13, page 118. EASY

7 Gould and Tobochnik, *Statistical and Thermal Physics*, 3.14, page 118. EASY, counting

8 Gould and Tobochnik, *Statistical and Thermal Physics*, 3.15, page 118. EASY, counting

9 Gould and Tobochnik, *Statistical and Thermal Physics*, 3.54, page 168. EASY, counting

10 Gould and Tobochnik, *Statistical and Thermal Physics*, 3.55, page 168. EASY, counting