Solution Homework

1. The Gibbs free energy is given by $G = U - \tau\sigma + pV$. From this, we can identify:

$$\sigma = -\left(\frac{\partial G}{\partial \tau}\right)_{N,p} \quad V = \left(\frac{\partial G}{\partial p}\right)_{N,\tau} \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{\tau,p}$$

For all three pairs of these derivatives, take the second derivatives with respect to the pair's partner variable to identify a set of 3 "Maxwell relations" based on the fact that the order of partial derivatives doesn't matter. [See page 71 of the textbook.]

With p, N, τ we can only make 3 pair's partner $pN, N\tau, \tau p$. We have

$$\frac{\partial^2 G}{\partial \tau \partial N} = -\left(\frac{\partial \sigma}{\partial N}\right)_{\tau,p} = \left(\frac{\partial \mu}{\partial \tau}\right)_{N,p}$$

$$\frac{\partial^2 G}{\partial p \partial N} = \left(\frac{\partial V}{\partial N}\right)_{\tau,p} = \left(\frac{\partial \mu}{\partial p}\right)_{N,\tau}$$

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

2. At a fixed temperature of 1200 K, the gases

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

are in chemical equilibrium in a container of volume, V. If the volume of the container is increased at constant temperature does the relative concentration of CO_2 increase, decrease, or stay the same? Explain.

The law of mass action for ideal gases states that

$$\frac{[CO_2][H_2]}{[CO][H_2O]} = K(\tau)$$

where $K(\tau)$ is a function only of the temperature. If we change the volume such that we change the concentration of each constituent $[X]' = [X]\frac{V}{V+\Delta V}$ the relative concentration of CO_2 remains conserved.

3. At sufficiently high temperature, neutral hydrogen atoms ionize. At intermediate temperatures, equilibrium is established between the relative densities of neutral and ionized hydrogen. The equilibrium depends on the balance of the rate of ionization as a function of temperature, and the rate of dissociation as a function of temperature. The chemical reaction is: $e^- + H^+ \leftrightarrow H$ where an electron combines with a hydrogen ion to form neutral hydrogen and the reverse. Hydrogen is, by far, the most abundant element in the universe, so this process is the most common chemical reaction in the universe.

(a) Prove that

$$\frac{[e^-][H^+]}{[H]} \simeq n_Q e^{-I/\tau}$$

where I is the energy required to ionize hydrogen, and $n_Q = (m\tau/2\pi\hbar^2)^{3/2}$ is the quantum concentration of an electron. Ignore particle spins. This is called the "Saha equation".

The law of mass action:

$$\prod_j n_j^{\nu_j} = \prod_j n_{Qj}^{\nu_j} \exp[-\nu_j F_j(int)/\tau]$$

In our case

$$\frac{[e^-][H^+]}{[H]} = (\frac{m_{e^-} m_{H^+} \tau}{2\pi\hbar^2 m_H})^{3/2} \exp[F_H - (F_{e^-} + F_{H^+})/\tau]$$

We have $F_H - (F_{e^-} + F_{H^+}) = -I$ and $m_{H^+} \simeq m_H$ therefore

$$\frac{[e^-][H^+]}{[H]} \simeq (\frac{m_{e^-}\tau}{2\pi\hbar^2})^{3/2} e^{-I/\tau}$$

(b) Assume that all electrons and protons come only from the ionization of hydrogen atoms and solve for $[e^-]$ only in terms of $[H]$, I, n_Q ,and τ.

We can assume $[e^-] = [H^+]$ and we have

$$[e^-] = ([H]n_Q)^{1/2} e^{-I/2\tau}$$

4. Adapt to three dimensions the derivation of the gas-solid-equilibrium pressure curve done in one-dimension in class and in the text (pg 285).

In 3 dimension we have

$$Z_s = \sum_{n,m,l} \exp[-((n+m+l) - \epsilon_0)/\tau] = \frac{\exp(\epsilon_0/\tau)}{(1 - \exp(-\hbar\omega\tau))^3}$$

which leads to

$$p = (\frac{M}{2\pi\hbar^2})^{3/2} \tau^{5/2} \exp(-\epsilon_0\tau)[1 - \exp(-\hbar\omega\tau)]^3$$

5. The heat of vaporization of liquid water at 100°C is 2257 J/g. The heat of fusion of ice is 333 J/g (i.e., 333 J absorbed in ice melts 1 gram of the ice).

(a) Calculate the change in enthalpy, ΔH, for these two processes.

We have $L = \Delta H$ therefore $\Delta H = 2257$ J/g for the vaporization and $\Delta H = 333$ J/g for the fusion.

(b) How many grams of ice can be melted by 1.6 kJ of heat?

$$\frac{1600}{333} \simeq 4.8g$$

6. Heat is added to water to change its phase from liquid to vapor. How much of the heat (dQ) goes towards work ($dW = pdV$) versus increasing the internal energy (dU) of the water?

The vapor pressure of water is 0.1013×10^6 Pa at 100 C.

The specific enthalpy of water vapor is 2676 kJ/kg.

The specific enthalpy of liquid water is 419 kJ/kg.

The specific volume of water vapor is 1.67 m^3/kg.

The specific volume of water liquid is 0.001 m^3/kg.

We have $Q = L = \Delta H = 2676 - 419 = 2257 kJ/kg$. We have $W = P\Delta V = 0.1013 \times 10^6 (1.67 - 0.001) \simeq 169 kJ/kg$. Therefore $\Delta U = Q - W = 2257 - 169 = 2088 kJ/kg$. $W/Q = 169/2257 \simeq 7\%$ and $\Delta U/Q = 2088/2676 \simeq 93\%$.