PHY 410 Homework 10 solutions

1. K.+K. Ch 9, #1 Thermal expansion near absolute zero.

Independent variables are τ, p, N $\Rightarrow$ Use Gibbs free energy

$$G = U - \tau\sigma + pV \ , \quad dG = -\sigma\, d\tau + V dp + \mu\, dN$$

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

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

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

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

b) $$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial \tau}\right)_p = -\frac{1}{V}\left(\frac{\partial \sigma}{\partial p}\right)_\tau \quad \text{from part (a)}$$

3^{rd} Law says that $\sigma \to \sigma_0$ as $\tau \to 0$, independent of p.

Hence $$\lim_{\tau \to 0} \left(\frac{\partial \sigma}{\partial p}\right)_\tau = 0 \Rightarrow \lim_{\tau \to 0} \alpha = 0$$

2. K. + K. Ch. 9, # 2 Thermal ionization of H

a) $e^- + H^+ \rightleftarrows H$, or $e^- + H^+ - H = 0$

$A_1 = e \quad A_2 = H^+ \quad A_3 = H$

$\nu_1 = 1 \quad \nu_2 = 1 \quad \nu_3 = -1$

$$\prod_j n_j^{\nu_j} = K(\tau) = \prod_j n_{Qj}^{\nu_j} e^{-\nu_j F_{j\,int}/\tau}$$

The e^- and H^+ have no internal degrees of freedom, so they have no F_{int}. But H has a binding energy relative to the free e^-, H^+:

$$F_{3\,int} = U_0^H = -13.6\ \text{eV} \equiv -I \quad \text{(book's notation)}$$

$$\rightarrow \frac{n_e n_{H^+}}{n_H} = \frac{n_{Qe} n_{QH^+}}{n_{QH}} \cdot e^{+F_{3\,int}/\tau}$$

Recall $n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$ Since H^+ and H have almost the same mass, we'll say $n_{QH^+} \approx n_{QH}$

Use Chemistry notation $n_e = [e]$ etc.

$$\frac{[e][H^+]}{[H]} = n_{Qe}\, e^{-I/\tau}$$

If the system is neutral, then $[e] = [H^+]$, so

$$[e]^2 = [H]\, n_{Qe}\, e^{-I/\tau} \Rightarrow [e] = [H]^{\frac{1}{2}}\, n_{Qe}^{\frac{1}{2}}\, e^{-I/2\tau}$$

b) Each H atom is a quantum system in contact with a thermal reservoir at temperature τ. So use the Boltzmann factor to find the probabilities to be in excited state. H atom: $E_n = \frac{-1}{n^2} \cdot I$

$$\frac{[H_{exc}]}{[H]} = \frac{P(n=2)}{P(n=1)} = e^{-(E_n - E_1)/\tau} = e^{-\frac{3}{4} I/\tau}$$

Surface of the Sun: $T = 5000\,K$, $\tau = k_B T = 6.7 \cdot 10^{-20}\,J$

$$n_{Qe} = \left(\frac{9.1 \cdot 10^{-31}\,kg \cdot 6.7 \cdot 10^{-20}\,J}{2\pi \cdot (1.05 \cdot 10^{-34}\,J\text{-}s)^2} \right)^{3/2} = 8.5 \cdot 10^{26}\,m^{-3}$$

$I = 13.6\,eV = 2.18 \cdot 10^{-18}\,J \qquad [H] = 10^{23}\,cm^{-3} = 10^{29}\,m^{-3}$

$$[H_{exc}] = [H]\, e^{-\frac{3}{4} I/\tau} = 10^{29}\,m^{-3}\, e^{-23.7} = \underline{\underline{5 \cdot 10^{18}\,m^{-3}}}$$

$$[e]^2 = [H]\, n_{Qe}\, e^{-I/\tau} = 10^{29}\,m^{-3} \cdot 8.5 \cdot 10^{26}\,m^{-3} \cdot e^{-31.6} = 1.6 \cdot 10^{42}\,m^{-6}$$

$$[e] = \underline{\underline{1.3 \cdot 10^{21}\,m^{-3}}}$$

$$\frac{[H_{exc}]}{[e]} \approx 4 \cdot 10^{-3}$$

There are many more ionized atoms than excited atoms, even though it takes more energy to ionize. Free electrons have a lot of entropy!

3. K. + K. Ch 10, #2 Calculation of $\frac{dT}{dp}$ for water

This problem is all about units! Be careful.

$$\frac{dT}{dp} = \frac{1}{k_B}\frac{d\tau}{dp} = \frac{1}{k_B}\frac{\tau \Delta v}{L}$$

You can choose Δv, L to be per molecule or per mole, but it must be the <u>same</u> for both.

$p = 1$ atm, $T = 100^\circ C = 373$ K

$$L = 2260 \frac{J}{gm} \cdot 18 \frac{gm}{mole} = 4.07 \cdot 10^{4}\ J/mole = 6.76 \cdot 10^{-20}\ J/molecule$$

Neglect volume of liquid; use Ideal Gas Law

$$\Delta v = v_g - v_l \approx v_g = \frac{V}{N} = \frac{\tau}{p} = \frac{5.15 \cdot 10^{-21}\ J}{1\ atm}$$

$$= 5.15 \cdot 10^{-21}\ J/atm$$ this is per molecule

$$\frac{dT}{dp} = \frac{373\,K \cdot 5.15 \cdot 10^{-21}\ J/atm}{6.76 \cdot 10^{-20}\ J} = 28.4 \frac{K}{atm}$$

This is how a pressure cooker works: under pressure, water boils at a higher temperature, so the food cooks faster.

Similarly, water boils at a lower temperature at high altitudes where $p < 1$ atmosphere.

4. K. + K. Ch. 10, # 3   Heat of vaporization of ice

$$\frac{dp}{d\tau} = \frac{L}{\tau \Delta v} \Rightarrow L = \tau \Delta v \frac{dp}{d\tau} \approx \frac{\tau^2}{p}\frac{dp}{d\tau}$$

where I used $\Delta v = v_g - v_{solid} \approx v_g = \frac{V}{N} = \frac{\tau}{p}$

$$\frac{dp}{dT} \approx \frac{p_2 - p_1}{T_2 - T_1} = \frac{(4.58 - 3.88)\ \text{Torr}}{2\ \text{K}} = 0.35\ \frac{\text{Torr}}{\text{K}}$$

$$p_{ave} = \frac{1}{2}(p_1 + p_2) = 4.23\ \text{Torr} \qquad T_{ave} = 272\ \text{K}$$

$L = k_B \frac{T^2}{p}\frac{dp}{dT}$ ← per molecule. To get the answer per mole, multiply by Avogadro's number N_A, and use $N_A k_B = R$

$$L = R\,\frac{T^2}{p}\frac{dp}{dT} = 8.31\ \frac{\text{J}}{\text{mole-K}} \cdot \frac{(272\ \text{K})^2}{4.23\ \text{Torr}} \cdot 0.35\ \frac{\text{Torr}}{\text{K}}$$

$$L = \underline{\underline{5.1 \cdot 10^4\ \frac{\text{J}}{\text{mole}}}}$$

5. K + K. Ch 10, #5 gas-solid equilibrium

Ignore entropy of solid $\Rightarrow$ $F_{solid} = U_s = -N_s \varepsilon_0$

Independent variables are τ, V, N, so use $F = U - \tau\sigma$

a) $F = F_s + F_g = -N_s \varepsilon_0 + N_g \tau \left[\ln \frac{n_g}{n_Q} - 1 \right]$

$$= -N_s \varepsilon_0 + N_g \tau \left[\ln \frac{N_g}{n_Q V} - 1 \right]$$

b) $N = N_s + N_g = \text{constant} \Rightarrow N_s = N - N_g$

$$F = (N_g - N)\,\varepsilon_0 + N_g \tau \left[\ln \frac{N_g}{n_Q V} - 1 \right]$$

$$0 = \left(\frac{\partial F}{\partial N_g} \right)_{\tau, V} = \varepsilon_0 + \tau \left[\ln \frac{N_g}{n_Q V} - 1 \right] + N_g \tau \cdot \frac{1}{N_g}$$

$$0 = \varepsilon_0 + \tau \ln \frac{N_g}{n_Q V}$$

$$\ln \frac{N_g}{n_Q V} = -\frac{\varepsilon_0}{\tau} \Rightarrow \underline{\underline{N_g = n_Q V e^{-\varepsilon_0/\tau}}}$$

c) Use Ideal gas relation $pV = N_g \tau$

$$p = \frac{N_g \tau}{V} = \underline{\underline{n_Q \tau e^{-\varepsilon_0/\tau}}}$$