

# Homework 8

Michael Brodskiy

Professor: A. Stepanyants

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1. (a) We begin by implementing the definition of the Gibb's Free Energy:

$$G = U - \tau\sigma + PV$$

According to this, we know:

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

From here, we can obtain the first Maxwell relation since the order of partial differentiation should not matter. This gives us:

$$\left(\frac{\partial^2 G}{\partial P \partial \tau}\right)_{\tau} = -\left(\frac{\partial \sigma}{\partial P}\right)_{\tau} \quad \text{and} \quad \left(\frac{\partial^2 G}{\partial \tau \partial P}\right)_P = \left(\frac{\partial V}{\partial \tau}\right)_P$$

Setting the two together, we get:

$$\boxed{\left(\frac{\partial V}{\partial \tau}\right)_P = -\left(\frac{\partial \sigma}{\partial P}\right)_{\tau}}$$

We repeat similar steps for the other Maxwell relations:

$$\left(\frac{\partial G}{\partial N}\right)_P = \mu \quad \text{and} \quad \left(\frac{\partial G}{\partial V}\right)_{\tau} = P$$

Now we differentiate once again:

$$\left(\frac{\partial^2 G}{\partial P \partial N}\right)_N = \left(\frac{\partial \mu}{\partial P}\right)_N \quad \text{and} \quad \left(\frac{\partial^2 G}{\partial N \partial P}\right)_P = \left(\frac{\partial P}{\partial N}\right)_P$$

Setting these together:

$$\boxed{\left(\frac{\partial P}{\partial N}\right)_P = \left(\frac{\partial \mu}{\partial P}\right)_N}$$

Finally, we can write:

$$\left(\frac{\partial^2 G}{\partial \tau \partial N}\right)_N = \left(\frac{\partial \mu}{\partial \tau}\right)_N \quad \text{and} \quad \left(\frac{\partial^2 G}{\partial N \partial \tau}\right)_\tau = -\left(\frac{\partial \sigma}{\partial N}\right)_\tau$$

And then we obtain the final relation:

$$\boxed{\left(\frac{\partial \mu}{\partial \tau}\right)_N = -\left(\frac{\partial \sigma}{\partial N}\right)_\tau}$$

(b) First, we know:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial \tau}\right)_P$$

From above, we may write:

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

By the third law of thermodynamics, we know that, as  $\tau \rightarrow 0$ ,  $\sigma \rightarrow 0$ . Thus, we know that:

$$\boxed{\alpha = -\frac{1}{V} \underbrace{\left(\frac{\partial \sigma}{\partial P}\right)_\tau}_0}$$

$$\alpha = 0 \quad \text{as } \tau \rightarrow 0$$

2. (a) From the law of mass action, we may write:

$$\frac{[e^-][H^+]}{[H]} = \prod_j n_{Qj}^{v_j} e^{-\frac{v_j F_{j,int}}{\tau}}$$

From the product, we may write:

$$K(\tau) = (n_{e^-}) e^{-\frac{F_{e^-,int}}{\tau}} \cdot (n_{H^+}) e^{-\frac{F_{H^+,int}}{\tau}} \cdot (n_H)^{-1} e^{\frac{F_{H,int}}{\tau}}$$

We know that:

$$F_{e^-,int} + F_{H^+,int} - F_{H,int} = I$$

Summing the exponentials, we get:

$$K(\tau) = \frac{(n_{e^-})(n_{H^+})}{(n_H)} e^{-\frac{I}{\tau}}$$

Since  $n_{e^-} \approx n_Q$ , and  $n_{H^+} \approx n_H$ , we can finally obtain:

$$\boxed{\frac{[e^-][H^+]}{[H]} = n_Q e^{-\frac{I}{\tau}}}$$

(b) First and foremost, we are given:

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

Since  $H_{exc}$  is the first excited state, and  $H$  is the ground state, we may write:

$$\varepsilon_{H_{exc}} - \varepsilon_H = \frac{3}{4}I$$

This gives us:

$$\frac{[H_{exc}]}{[H]} = e^{-\frac{3I}{4\tau}}$$

This, however is not entirely correct. We must also account for the quadruple-degeneracy (one  $2s$  orbital and three  $2p$  orbitals) of the excited state:

$$\frac{[H_{exc}]}{[H]} = 4e^{-\frac{3I}{4\tau}}$$

This means:

$$[H_{exc}] = 4[H]e^{-\frac{3I}{4\tau}}$$

Now we can calculate and compare  $[e^-]$  and  $[H_{exc}]$  (note that, for working with eV,  $k_B = 8.617 \cdot 10^{-5}[\text{eV/K}]$ ):

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

$$[e^-] = \left(10^{23}n_Q e^{-\frac{13.6}{5000k_B}}\right)^{\frac{1}{2}}$$

$$[e^-] = 44221.8\sqrt{n_Q} \left[\frac{1}{\text{mL}}\right]$$

and

$$[H_{exc}] = 4[H]e^{-\frac{3I}{4\tau}}$$

$$[H_{exc}] = 4 \cdot 10^{23} e^{-\frac{3(13.6)}{4(5000)(8.617 \cdot 10^{-5})}}$$

$$[H_{exc}] = 2.092 \cdot 10^{13} \left[\frac{1}{\text{mL}}\right]$$

Comparing the two, we find that the concentration of electrons relative to excited hydrogen is:

$$\frac{[e^-]}{[H_{exc}]} = \frac{44221.8\sqrt{n_Q}}{2.092 \cdot 10^{13}}$$

$$\boxed{\frac{[e^-]}{[H_{exc}]} = 2.114 \cdot 10^{-9} \sqrt{n_Q}}$$

There are a factor of  $2.114 \cdot 10^{-9} \sqrt{n_Q}$  more electrons than excited hydrogen atoms.

3. Employing the law of mass action, we can write:

$$\frac{[e^-][d^+]}{[d]} = n_Q e^{-\frac{I^*}{\tau}}$$

To find  $I^*$ , we may write:

$$I^* = \frac{I \left( \frac{m^*}{m} \right)}{\varepsilon^2}$$

$$I^* = \frac{(13.6)(.3)}{\varepsilon^2}$$

$$I^* = .03[\text{eV}]$$

We can also redefine the concentration as:

$$n_Q = (2.415 \cdot 10^{15}) \left[ \frac{m^*}{m} \cdot T \right]^{1.5}$$

$$n_Q = (2.415 \cdot 10^{15}) [30]^{1.5}$$

$$n_Q = 3.97 \cdot 10^{17} \left[ \frac{1}{\text{mL}} \right]$$

Given this, we may find:

$$K = 1.22 \cdot 10^{16} \left[ \frac{1}{\text{mL}} \right]$$

Though we are given that there are  $10^{17}$  donors, we can find  $[d]$  by using:

$$[d] = 10^{17} - [d^+] = 10^{17} - [e^-]$$

Solving, we find:

$$[e^-] = \left[ \left( \frac{K}{2} \right)^2 + K(10^{17}) \right]^{\frac{1}{2}} - \left( \frac{K}{2} \right)$$

$$[e^-] = \left[ \left( \frac{1.22 \cdot 10^{16}}{2} \right)^2 + (1.22 \cdot 10^{16})(10^{17}) \right]^{\frac{1}{2}} - \left( \frac{1.22 \cdot 10^{16}}{2} \right)$$

$$[e^-] = 2.94 \cdot 10^{16} \left[ \frac{1}{\text{mL}} \right]$$

Thus, by the ratio of electrons to donors, we see that there is a 29.4% ionization.