Homework 8

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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:

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

Now we differentiate once again:

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

Setting these together:

$$\boxed{\left(\frac{\partial V}{\partial N}\right)_{P} = \left(\frac{\partial \mu}{\partial P}\right)_{N}}$$

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 $\tau \to 0$, $\sigma \to 0$. Thus, we know that:

$$\boxed{\alpha = -\frac{1}{V}\underbrace{\left(\frac{\partial\sigma}{\partial P}\right)_\tau}_{0}}$$

$$\alpha = 0 \ \text{ as } \tau \to 0$$

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)

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