Homework 9

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1. (a) We know the entropy may be written as:

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$$

The free energy of the Van der Waal's gas may be observed as:

$$F_{VdW} = -N\tau \left(\ln\left(\frac{n_Q(V - bN)}{N}\right) + 1\right) - \frac{N^2 a}{V}$$

$$F_{VdW} = -N\tau \ln\left(\frac{n_Q(V - bN)}{N}\right) - N\tau - \frac{N^2 a}{V}$$

We know that the concentration may be expressed as:

$$n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}}$$

For ease of calculation, let us redefine the quantum concentration as:

$$n_Q = \gamma\,(\tau)^{\frac{3}{2}}, \quad \text{where } \gamma = \left(\frac{M}{2\pi\hbar^2}\right)^{\frac{3}{2}}$$

Also, let us redefine:

$$(V - bN) \to V'$$

This gives us:

$$F_{VdW} = -N\tau \ln\left(\frac{\gamma\tau^{\frac{3}{2}} V'}{N}\right) - N\tau - \frac{N^2 a}{V}$$

Taking the partial with respect to τ, we find:

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$$\frac{\partial F}{\partial \tau} = -N \ln \left(\frac{\gamma \tau^{\frac{3}{2}} V'}{N} \right) - N - \frac{3}{2} N$$

We then take the negative of this to find:

$$\sigma = N \left(\ln \left(\frac{\gamma \tau^{\frac{3}{2}} V'}{N} \right) + \frac{5}{2} \right)$$

$$\boxed{\sigma = N \left(\ln \left(\frac{n_Q (V - bN)}{N} \right) + \frac{5}{2} \right)}$$

(b) The energy may be written as:

$$U = F + \tau \sigma$$

This gives us:

$$U = -N\tau \ln \left(\frac{n_Q (V - bN)}{N} \right) - N\tau - \frac{N^2 a}{V} + N\tau \left(\ln \left(\frac{n_Q (V - bN)}{N} \right) + \frac{5}{2} \right)$$

$$U = -N\tau \ln \left(\frac{n_Q (V - bN)}{N} \right) - N\tau - \frac{N^2 a}{V} + N\tau \ln \left(\frac{n_Q (V - bN)}{N} \right) + \frac{5}{2} N\tau$$

$$U = -N\tau - \frac{N^2 a}{V} + \frac{5}{2} N\tau$$

And finally:

$$\boxed{U = \frac{3}{2} N\tau - \frac{N^2 a}{V}}$$

(c) First and foremost, we may define the pressure as:

$$P = - \left(\frac{\partial F}{\partial V} \right)_{\tau, N}$$

This gives us:

$$- \left(\frac{\partial F}{\partial V} \right)_{\tau, N} = \frac{N\tau}{V - bN} - \frac{N^2 a}{V^2}$$

Plugging this into $H = U + PV$, we get:

$$H(\tau, P, V) = \frac{3}{2} N\tau - \frac{N^2 a}{V} + \frac{N\tau V}{V - bN} - \frac{N^2 a}{V}$$

$$H(\tau, P, V) = \frac{3}{2} N\tau - \frac{2N^2 a}{V} + \frac{N\tau V}{V - bN}$$

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We then take the appropriate partial differentials to find:

$$H(\tau, V) = \frac{5}{2}N\tau + \frac{N^2 b\tau}{V} - \frac{2N^2 a}{V}$$

$$H(\tau, P) = \frac{5}{2}N\tau + NbP - \frac{2NaP}{\tau}$$

2. We may use the vapor pressure equation, obtained from the Clausius-Clapeyron equation, is:

$$\frac{1}{P}\frac{\partial P}{\partial T} = \frac{L}{k_B T^2}$$

$$\frac{\partial P}{\partial T} = \frac{PL}{k_B T^2}$$

$$\frac{\partial T}{\partial P} = \frac{k_B T^2}{PL}$$

Substituting the values we know, we get:

$$\frac{\partial T}{\partial P} = \frac{(8.314)(100 + 273)^2}{(1)(2260)}$$

$$\frac{\partial T}{\partial P} = 511.82 \left[\frac{g\,K}{mol\,atm}\right]$$

For water, we know:

$$m_{H2O} = 18.015 \left[\frac{g}{mol}\right]$$

Thus, we get:

$$\frac{\partial T}{\partial P} = 511.82 \left[\frac{g\,K}{mol\,atm}\right] \cdot \frac{1}{18.015}\left[\frac{mol}{g}\right]$$

This gives us:

$$\frac{\partial T}{\partial P} = 28.411 \left[\frac{K}{atm}\right]$$

3. Using the same equation from (2), we get:

$$\frac{1}{P}\frac{\partial P}{\partial T} = \frac{L}{k_B T^2}$$

We rearrange to get:

$$L = \frac{k_B T^2}{P} \frac{\partial P}{\partial T}$$

$$L = k_B \frac{\partial P}{P} \frac{T^2}{\partial T}$$

$$L = k_B(\partial \ln(P)) \left(\frac{1}{\partial T^{-1}} \right)$$

We can approximate the differentials as:

$$\partial \ln(P) \approx \Delta \ln(P)$$

$$\partial \ln(P) \approx \ln \left(\frac{4.58}{3.88} \right)$$

$$\partial \ln(P) \approx .1659$$

We then approximate the temperature differential as:

$$\partial \frac{1}{T} \approx \frac{1}{271} - \frac{1}{273}$$

$$\partial \frac{1}{T} \approx 2.7 \cdot 10^{-5} \left[\frac{1}{K} \right]$$

Plugging this in, we get:

$$L = (8.314) \left(\frac{.1659}{2.7 \cdot 10^{-5}} \right)$$

$$\boxed{L = 5.1 \cdot 10^4 \left[\frac{J}{mol} \right]}$$