John Waczak
Ph 441
Homework 9

1. assume $\Delta V \simeq V_g$, assume that the gas is ideal.

a. Solve for $\frac{dp}{dT}$ in terms of the pressure of the vapor, the Latent heat (L), and the Temperature.

Recall $v = \frac{V}{N}$, $s = \frac{S}{N}$. then the Clausius-Clapeyron equation gives

$$\frac{dp}{dT} = \frac{L}{T(\Delta v)}$$ where $L = T(s_g - s_e)$ is the Latent heat

$$= \frac{L}{T v_g}$$

recall for ideal gas that $pV = NkT$

$$\Longrightarrow = \frac{L}{T \frac{kT}{p}} = \frac{Lp}{kT^2}$$

b. assume $L = L_0 \approx$ constant. Integrate to find $p = p(T)$.

$$\frac{dp}{dT} = \frac{L_0 p}{kT^2}$$

$$\int \frac{1}{p} dp = \int \frac{L_0}{kT^2} dT$$

$$\ln(p) = \frac{L_0}{k} \int \frac{1}{T^2} dT = -\frac{L_0}{k}\frac{1}{T} + \underset{P_0}{\underset{\|}{\text{const}}}$$

$$\Longrightarrow \boxed{p(T) = P_0 e^{-\frac{L_0}{kT}}}$$

2. a) Show that the entropy of the Van der Waals gas is:

$$S = Nk\left\{\ln\left(\frac{n_Q(V-Nb)}{N}\right) + \frac{5}{2}\right\}$$

Recall the Van der Waals free energy

$$F = -NkT\left\{\ln\left(\frac{n_Q(V-Nb)}{N}\right) + 1\right\} - \frac{N^2a}{V}$$

where b represents the volume per molecule and a represents the attraction

Then

$$= \ln(n_Q) + \ln(V-Nb) - \ln(N)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$= Nk\left\{\ln\left(\frac{n_Q(V-Nb)}{N}\right) + 1\right\} + \frac{NkT}{n_Q}\frac{dn_Q}{dT}$$

$$n_Q = \left(\frac{MkT}{2\pi\hbar^2}\right)^{3/2} \quad \text{and} \quad \frac{d}{dT}\left(T^{3/2}\right) = \frac{3}{2}T^{1/2}$$

$$\Rightarrow S = Nk\left\{\ln\left(\frac{n_Q(V-Nb)}{N}\right) + 1\right\} + NkT \cdot \frac{3}{2}T^{-1}$$

$$S = Nk\left\{\ln\left(\frac{n_Q(V-Nb)}{N}\right) + \frac{5}{2}\right\}$$

2. b) Show that the energy is $U = \frac{3}{2}NkT - \frac{N^2a}{V}$

$$F = U - TS$$

$$\rightarrow \quad U = F + TS$$

$$= -NkT\left\{ \ln\left(\frac{n_Q(V-Nb)}{N}\right) + 1 \right\} - \frac{N^2a}{V}$$

$$+ NkT\left\{ \ln\left(\frac{n_Q(V-Nb)}{N}\right) + 5/2 \right\}$$

$$= \frac{3}{2}NkT - \frac{N^2a}{V}$$

2. a) Show that the enthalpy $H \equiv U + pV$ is

$$H(T,V) = \frac{5}{2}NkT + \frac{N^2bkT}{V} - 2\frac{N^2a}{V}$$

$$H(T,p) = \frac{5}{2}NkT + Nbp - \frac{2Nap}{kT}$$

Recall that $p = -\left(\frac{\partial F}{\partial V}\right)_T$ which is derived in the text to be

$$p = \frac{NkT}{V-Nb} - \frac{N^2a}{V^2}$$

Then $\quad H = U + pV = \frac{3}{2}NkT - \frac{N^2a}{V} + \left[\frac{NkT}{V-Nb} - \frac{N^2a}{V^2}\right]V$

$$= \frac{3}{2}NkT - 2\frac{N^2a}{V} + \frac{NkTV}{V-Nb}$$

we can simplify right most term and power series expand.

$$= \frac{3}{2}NkT - 2\frac{N^2a}{V} + \frac{NkT}{\left(1-\frac{Nb}{V}\right)} \quad \approx \left(1 + \frac{Nb}{V}\right)$$

$$\approx \boxed{\frac{5}{2}NkT - \frac{2N^2a}{V} + \frac{N^2kTb}{V}}$$

Now we need to re-express this as a function for T, p.

$$p = \frac{NkT}{V-Nb} - \frac{N^2}{V^2}a$$

$$\left(p + \frac{N^2 a}{V^2}\right) = \frac{NkT}{V-Nb}$$

$$\left(p + \frac{N^2 a}{V^2}\right)(V-Nb) = NkT$$

$$pV - pNb + \frac{N^2 a}{V} - \frac{N^3 ab}{V^2} = NkT$$

$$pV^2 - pNbV - NkTV + N^2 a = 0$$

since $\frac{Nb}{V} << 1$ then $\frac{N^3 ab}{V^2} \approx 0$.

thus we have the quadratic equation in V

$$pV^2 - (pNb + NkT)V + N^2 a = 0$$

which yields

$$V = \frac{pNb + NkT \pm \sqrt{(pNb+NkT)^2 - 4pN^2 a}}{2p}$$

$$= \frac{pNb + NkT \pm \sqrt{p^2N^2b^2 + N^2k^2T^2 + 2N^2kbTp - 4pN^2a}}{2p}$$

assuming b^2, a^2, ab are small, we have

got confused this point and connected the solutions

$$\approx \frac{pNb + NkT \pm \sqrt{(NkT)^2 + 2N^2kbTp - 4pN^2a}}{2p}$$

$$= \frac{pNb + NkT + NkT\underbrace{\sqrt{1 + \frac{2N^2kbTp - 4N^2ap}{N^2k^2T^2}}}_{\text{using power series}}}{2p}$$

$$= \frac{pNb + NkT + NkT + \frac{pNkbT - 2Nap}{kT}}{2p}$$

$$= \frac{pNbkT + 2Nk^2T^2 + pNkbT - 2pNa}{2pkT}$$

$$= \frac{2pNbkT + 2Nk^2T^2 - 2pNa}{2pkT}$$

$$\boxed{V = Nb + \frac{NkT}{p} - \frac{Na}{kT}}$$

Now we can plug this back into $H(T,V)$ to get $H(T,p)$.

$$H(T,V) = \frac{5}{2}NkT - \frac{2N^2a}{V} + \frac{N^2kTb}{V}$$

$$= \frac{5}{2}NkT - \frac{2N^2a}{Nb + \frac{NkT}{p} - \frac{Na}{kT}} + \frac{N^2kTb}{Nb + \frac{NkT}{p} - \frac{Na}{kT}}$$

$$= \frac{5}{2}NkT - \frac{2Na}{b + \frac{kT}{p} - \frac{a}{kT}} + \frac{NkTb}{b + \frac{kT}{p} - \frac{a}{kT}}$$

$$= \frac{5}{2}NkT + \frac{p}{kT}\frac{NkTb - 2Na}{\left(1 + \left(\frac{bp}{kT} - \frac{ap}{k^2T^2}\right)\right)}$$

$$\simeq \frac{5}{2}NkT + \frac{p}{kT}\left[(NkTb - 2Na)\left(1 - \left(\frac{bp}{kT} - \frac{ap}{k^2T^2}\right)\right)\right]$$

we do not care about any terms in second half of foil as we are keeping a, b linear

thus

$$= \frac{5}{2}NkT + \frac{p}{kT}NkTb - \frac{p}{kT}2Na$$

$$= \frac{5}{2}NkT + pNb - \frac{2Nap}{kT} \quad \checkmark$$

3. Calculation of $\frac{dT}{dp}$ for H_2O near $p = 1$ atm (6)

Heat of Vaporization at $100°c$ is 2260 J/g

Express result in Kelvin/atm.

$$\frac{dp}{dT} = \frac{L}{T(\Delta v)} \qquad \Delta v = \frac{V_g}{N_g} - \frac{V_l}{N_l}$$

assuming $\Delta V_e \approx 0$ gives

$$\frac{dp}{dT} = \frac{L}{T \frac{V_g}{N_g}}$$

Now assuming we can treat H_2O as ideal gas, then

$$\frac{V_g}{N_g} = \frac{kT}{p} \quad \text{thus,}$$

$$\frac{dp}{dT} = \frac{L}{T\,(kT/p)} = \frac{Lp}{kT^2}$$

also recall that $k_B = \frac{R}{N_A}$ $R \rightarrow$ gas const. $N_A \rightarrow$ avagadro's #.

$$\frac{dp}{dT} = \frac{L\,p\,N_A}{R\,T^2}$$ Now we need

To make the units work out (cancel grams)

choose $18 \frac{g}{mol}$ for N_a

so that

$$\frac{dp}{dT} = \frac{(2260\frac{J}{g})(1\,atm)(\frac{18g}{mol})}{(8.31\frac{J}{mol\,K})(373K)^2} = 0.035\,atm/K$$

$$\Longrightarrow \frac{dT}{dp} = 28.4 \text{ K/atm.}$$

4. Heat of vaporization of ICF

we had that $\frac{dp}{dT} = \frac{L}{T(\Delta v)}$ if we make the same assumption as the previous problem, then

$$= \frac{L}{T(v_g)} \qquad v_g = \frac{V_g}{N_g} = \frac{kT_g}{p_g}$$

thus $$= \frac{L}{T\left(\frac{kT}{p}\right)} = \frac{Lp}{kT^2}$$ and $R = N_A k$

so that $$\frac{dp}{dT} = \frac{Lp N_A}{RT^2}$$ solving for L gives

$$T_{vapor} = -2°c = 273 - 2 = 271 \text{ K}$$

$$T_{triple} = 0.01°c \simeq 273 \text{ K}.$$

$$N_A L = \frac{RT^2}{p}\frac{dp}{dT}$$ observe that $d\frac{1}{T} = -\frac{1}{T^2}dT$ and $d\log(p) = \frac{1}{p}dp$

thus $$= \frac{-R\, d\log p}{d\frac{1}{T}}$$

Now approximate as $\frac{\Delta \log p}{\Delta \frac{1}{T}}$ gives

$$= \frac{-R\log(518/611)}{\left(\frac{1}{271} - \frac{1}{273}\right)}$$

$$= \frac{-\left(8.314 \frac{J}{mol\,k}\right)\log(518/611)}{\left(\frac{1}{271} - \frac{1}{273}\right)k^{-1}}$$

$$= 50782 \text{ J/mol} = 5.1 \times 10^4 \text{ J/mol}$$