

E3E Homework #7

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① Temperature Change of an Ideal Gas

a) Derive change in pressure heat capacity ΔC_p .

Our equation of state is $P_0 V = N k_B T$. And we know an equation for $C_\alpha = T \left(\frac{\partial S}{\partial T} \right)_\alpha$. Allowing $\alpha = p$ we can say

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

If we zap our Enthalpy equation with d , we can write it as

$$H = U + PV \rightarrow dH = T \cdot dS + V \cdot dP$$

Since $P = P_0$, we know that $dP = 0$ and our equation becomes

$$dH = T \cdot dS + 0 \rightarrow T = \left(\frac{\partial H}{\partial S} \right)_p$$

Now, we can plug this into our C_p equation and cancel things.

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$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p \rightarrow C_p = \left(\frac{\partial H}{\partial S} \right)_p \left(\frac{\partial S}{\partial T} \right)_p \rightarrow C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

Now let's plug the other enthalpy equation into our derived specific heat capacity equation.

$$H = aT + bT^3 \rightarrow \text{Plug in} \rightarrow C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$C_p = \frac{d}{dT} (aT + bT^3) \rightarrow C_p = a + 3bT^2$$

So our change in heat capacity equation becomes

$$\Delta C_p = C_{p_f} - C_{p_i} \rightarrow \Delta C_p = (a + 3b(T_f)^2) - (a + 3b(T_i)^2)$$

$$\boxed{\Delta C_p = 3b(T_f^2 - T_i^2)}$$

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b) We need to do the same thing as part a but with ΔC_p . So we need to find

$$C_\alpha = T \left(\frac{\partial S}{\partial T} \right)_\alpha \rightarrow C_v = T \left(\frac{\partial S}{\partial T} \right)_v \text{ Allowing } \alpha = v$$

We can use $dU = T \cdot dS - P \cdot dV$ to solve for T.

$$dU = T \cdot dS - P \cdot dV \rightarrow dU = T \cdot dS \rightarrow T = \left(\frac{dU}{dS} \right)_v$$

We can plug this into C_v

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_v \rightarrow C_v = \left(\frac{\partial U}{\partial S} \right)_v \left(\frac{\partial S}{\partial T} \right)_v \rightarrow C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

We need U, so let's rearrange Gibbs

$$H = U + PV \rightarrow U = H - PV$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v \rightarrow C_v = \frac{d}{dT} (H - PV) \rightarrow C_v = \left(\frac{\partial H}{\partial T} - V \frac{\partial P}{\partial T} - P \frac{\partial V}{\partial T} \right)_v$$

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$$C_V = \left(\frac{\partial H}{\partial T} \right)_V - V \left(\frac{\partial P}{\partial T} \right)_V - P \left(\frac{\partial V}{\partial T} \right)_V$$

using the ideal gas law, $P = \frac{Nk_B T}{V}$. Then, plugging in H and P , we can say

$$C_V = \frac{d}{dT} (aT + bT^3) - V \cdot \frac{d}{dT} \left(\frac{Nk_B T}{V} \right)$$

$$C_V = a + 3bT^2 - Nk_B$$

So, our Change in C_V (ΔC_V), will be

$$\Delta C_V = (a + 3b(T_f)^2 - Nk_B) - (a + 3b(T_i)^2 - Nk_B)$$

$$\boxed{\Delta C_V = 3b(T_f^2 - T_i^2)}$$

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c) We need to find ΔU , and I think we have an equation for U .

$$U = H - PV \rightarrow U = H - Nk_B T \text{ where } H = aT + bT^3$$

$$\text{So, } U = (aT + bT^3) - Nk_B T \rightarrow U = T(a - Nk_B) + bT^3$$

Thus, our change in internal energy (ΔU) will be

$$\Delta U = U_f - U_i = ((T_f)(a - Nk_B) + b(T_f)^3) - ((T_i)(a - Nk_B) + b(T_i)^3)$$

$$\boxed{\Delta U = (a - Nk_B)(T_f - T_i) + b(T_f^3 - T_i^3)}$$

① Temperature Change of an Ideal Gas Cont.

d) Find ΔS . We know $\Delta S = \int \frac{dQ}{T}$. We need Q .

From chemistry and class we know $Q = mC\Delta T$

Heat capacity is Joules/Kelvin.

Specific heat is Joules/(gram·kelvin)

Thus, we can say $mC = C_p$ and our equation becomes

$$Q = (C_p) \Delta T \rightarrow dQ = \cancel{d(C_p)} \int \cancel{dT} \xrightarrow{\text{const}} dQ = C_p dT$$

$$\Delta S = \int_{T_i}^{T_f} \frac{(C_p dT)}{T} \rightarrow \Delta S = \int_{T_i}^{T_f} \frac{(a + 3bT^2) dT}{T}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{a}{T} dT + \int_{T_i}^{T_f} 3bT dT \rightarrow \Delta S = a \ln(T) + \frac{3}{2} b T^2 \Big|_{T_i}^{T_f}$$

$$\boxed{\Delta S = a \ln\left(\frac{T_f}{T_i}\right) + \frac{3}{2} b (T_f^2 - T_i^2)}$$

② Isothermal/Adiabatic Compressibility

We need to show $\frac{k_T}{k_s} = \frac{C_p}{C_v}$. Let's just start subbing stuff in.

$$\frac{k_T}{k_s} \cdot \frac{C_p}{C_v} \rightarrow \frac{\left[-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \right]}{\left[-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_s \right]} = \frac{T \left(\frac{\partial S}{\partial T} \right)_P}{T \left(\frac{\partial S}{\partial T} \right)_V} \rightarrow \left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial P}{\partial V} \right)_s = \frac{\left(\frac{\partial S}{\partial T} \right)_P}{\left(\frac{\partial S}{\partial T} \right)_V}$$

Let's use the cyclic chain rule on the left hand side and simplify

$$\left(\frac{\partial S}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_S ; \left(\frac{\partial S}{\partial T} \right)_V = - \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_S$$

$$\frac{\left(\frac{\partial S}{\partial T} \right)_P}{\left(\frac{\partial S}{\partial T} \right)_V} = \frac{- \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_S}{- \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_S} \rightarrow \frac{\left(\frac{\partial S}{\partial T} \right)_P}{\left(\frac{\partial S}{\partial T} \right)_V} = \left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial P}{\partial V} \right)_S$$

Therefore, we can see that both sides are equal and we have shown what was desired.

③ Helmholtz Free energy of a Van Der Waals

Helmholtz of Van Der Waals :

$$F = -NK_B T \left\{ 1 + \ln \left[\frac{(V-Nb)T^{3/2}}{N} \right] \right\} - \frac{aN^2}{V}$$

We need to derive the equation of state for this.
Let's zap with \mathcal{D} because it's fun.

$$dF = -NK_B dT \left[1 + \ln \left[\frac{(V-Nb)T^{3/2}}{N} \right] + \left[\frac{N}{(V-Nb)T^{3/2}} \right] \left(\frac{3}{2} \frac{(V-Nb)}{N} T^{1/2} \right) \right]$$

$$+ \mathcal{D}V \left[-NK_B T \left(\frac{N}{(V-Nb)T^{3/2}} \right) \left(\frac{T^{1/2}}{N} \right) + \frac{aN^2}{V^2} \right]$$

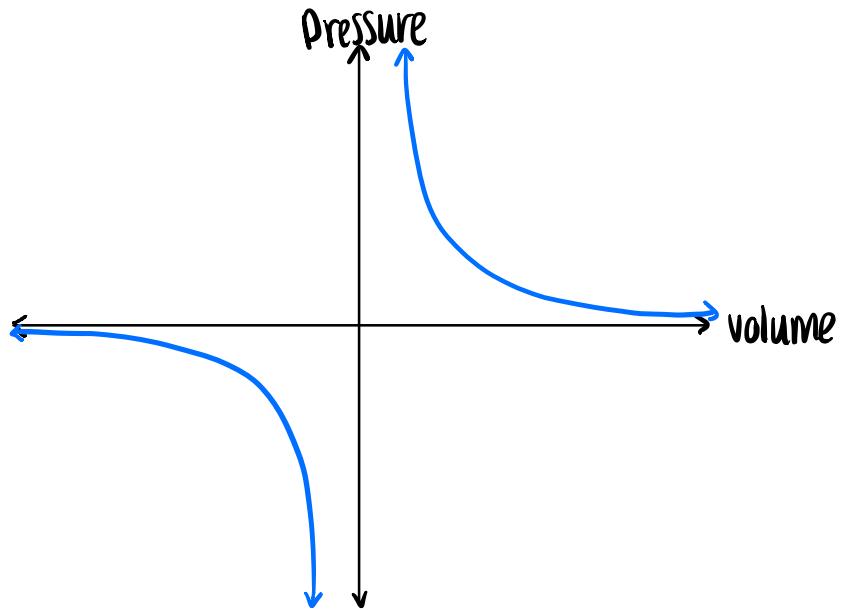
This looks a lot like $dF = -SdT - PdV$ which is a thing that we know. So,

$$S = NK_B + NK_B \ln \left[\frac{(V-Nb)T^{3/2}}{N} \right] + \left[\frac{3NK_B}{2T} \right]$$

$$P = \frac{NK_B T}{V-Nb} - \frac{aN^2}{V^2}$$

③ Helmholtz Free energy of a Van Deer Waals Cont.

We can graph our pressure expression



Since N and T are fixed, we would expect our plot to approach zero as we vary volume to infinity

As V approaches ∞ , $P = \frac{K_B T}{\infty} - \frac{aN^2}{\infty} \rightarrow P = 0 + 0$

As V approaches N , $P = \frac{K_B T}{(1-b)} - a$