HW 4

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1.) Show $\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right]$

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

- $\left(\frac{\partial T}{\partial P}\right)_W = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$

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

- $\left(\frac{\partial E}{\partial V}\right)_S = -P \qquad dE = TdS - PdV$

$$dE = C_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

$$dS = \frac{C_v dT}{T} + \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV$$

$$\frac{dS}{dV} = \frac{C_v}{T}\frac{dT}{dV} + \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

$$\frac{C_v}{T} = \left(\frac{\partial E}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{C_v}{T}\frac{dT}{dV} + \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

$$\frac{dE}{dV} = C_v\frac{dT}{dV} + \left(\frac{\partial E}{\partial V}\right)_T$$

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right]$$

2.) $\beta_T \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \beta_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$$

$$P(V - Nb) = Nk_BT$$

$$V - Nb = \frac{Nk_BT}{P}$$

$$V = \frac{Nk_BT}{P} + Nb = N\left(\frac{k_BT}{P} + b\right)$$

$$\alpha = -1 \left(\partial V\right)$$

$$P_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$= -\frac{1}{V}\left\{\frac{\partial}{\partial P}\left[N\left(\frac{k_B T}{P} + b\right)\right]\right\}$$

$$= -\frac{1}{V} N k_B T\left(-\frac{1}{P^2}\right) = \frac{N k_B T}{V P^2}$$

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{N k_B}{P}$$

3.) $\alpha_P = \alpha_S$ if P and S are constants

4.) $\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = N k_B T$

$$P = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2}$$

$$\frac{\partial P}{\partial V} = Nk_BT\frac{\partial}{\partial V}\left(\frac{1}{V-Nb}\right) - N^2a\frac{\partial}{\partial V}\left(\frac{1}{V^2}\right)$$

$$= \frac{-Nk_BT}{(V-Nb)^2} + \frac{2N^2a}{V^3}$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{2Nk_BT}{(V-Nb)^3} - \frac{6N^2a}{V^4}$$

$$\left(\frac{\partial P}{\partial V}\right)\left(\frac{2}{V-Nb}\right) = \frac{-2Nk_BT}{(V-Nb)^3} + \frac{4N^2a}{V^3(V-Nb)}$$

$$\frac{-2Nk_BT}{(V-Nb)^3} + \frac{4N^2a}{V^3(V-Nb)} + \frac{2Nk_BT}{(V-Nb)^3} - \frac{6N^2a}{V^4} = 0$$

$4N^2a$ $\quad 6N^2a$ $\quad 0$

$$\frac{4N\ a}{V^3(V-Nb)} - \frac{6N\ a}{V^4} = 0$$

$$\boxed{V = 3Nb = V_c}$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{2Nk_BT}{(3Nb-Nb)^3} - \frac{6N^2a}{(3Nb)^2} = 0$$

$$\boxed{T = \frac{8a}{27bk_B} = T_c}$$

$$P_c = \frac{Nk_BT_c}{V_c-Nb} - \frac{N^2a}{V_c^2}$$

$$= \frac{\cancel{N}\cancel{k_B}\,8a}{27b\cancel{k_B}(3\cancel{N}b-\cancel{N}b)} - \frac{\cancel{N^2}a}{(3\cancel{N}b)^2}$$

$$= \frac{8a}{54b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$$

$$\frac{P_c V_c}{N k_B T_c} = \left(\frac{\cancel{a}}{\cancel{27b^2}}\right)\frac{3N\cancel{b}(\cancel{27bk_B})}{\cancel{Nk_B}\, 8\cancel{a}}$$

$$= \frac{3}{8}$$

$$P(V-Nb) = Nk_BTe^{-a/Nk_BTV}$$

$$P = \frac{Nk_BTe^{-a/Nk_BTV}}{V-Nb}$$

$$\frac{\partial P}{\partial V} = Nk_BT\left[e^{-a/Nk_BTV}\frac{\partial}{\partial V}\left(\frac{1}{V-Nb}\right) + \frac{1}{V-Nb}\frac{\partial}{\partial V}\left(e^{-\frac{a}{Nk_BTV}}\right)\right]$$

$$= Nk_BT\left[\frac{e^{-a/Nk_BTV}}{\ldots} + \frac{1}{\ldots}\left(\frac{a}{Nk_BTV^2}\right)e^{-a/Nk_BTV}\right]$$

$$\left[-(V-Nb)^2 \quad V-Nb\,(Nk_BTV) \right]$$

$$= \frac{Nk_BT e^{-a/Nk_BTV}}{V-Nb}\left[\frac{-1}{V-Nb} + \frac{a}{Nk_BTV^2}\right]$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{Nk_BT e^{-a/Nk_BTV}}{V-Nb}\left[\frac{a}{Nk_BTV^2} - \frac{1}{V-Nb}\right] \times$$

$$\left[\frac{a}{Nk_BTV^2} - \frac{a}{V-Nb}\right] +$$

$$\frac{Nk_BT e^{-a/Nk_BTV}}{V-Nb}\left[\frac{-2a}{Nk_BTV^3} + \frac{1}{(V-Nb)^2}\right]$$

$$\frac{\partial P}{\partial V} = 0 = \frac{\partial^2 P}{\partial V^2}$$

$$\partial V \qquad \partial V$$

$$\cancel{\frac{Nk_B T e^{-a/Nk_BTV}}{V-Nb}} \left\{ \left[\frac{a}{Nk_BTV^2} - \frac{1}{V-Nb} \right] \left[\frac{a}{Nk_BTV^2} - \frac{a}{V-Nb} \right] \right.$$

$$\left. + \left[\frac{1}{(V-Nb)^2} - \frac{2a}{Nk_BTV^3} \right] \right\} =$$

$$\cancel{\frac{Nk_B T e^{-a/Nk_BTV}}{V-Nb}} \left[\frac{a}{Nk_BTV^2} - \frac{1}{V-Nb} \right]$$

$$\Rightarrow V_c = 2b \qquad T_c = \frac{a}{4bk_B} \qquad P_c = \frac{a}{4e^2b^2}$$

$$\frac{P_cV_c}{Nk_BT_c} = \left(\frac{a}{4e^2b^2}\right)\left(\frac{2b}{Nk_B}\right)\left(\frac{4bk_B}{a}\right) = \frac{2}{Ne^2}$$

so the values are dimensionless

Born ...

$$P(V-Nb) = Nk_B T e^{-a/Nk_BTV}$$

$$P(V-Nb) = Nk_B T\left(1 - \frac{a}{Nk_BTV}\right)$$

$$P(V-Nb) = Nk_B T - \frac{a}{V}$$

$$T = \frac{P(V-Nb) + \frac{a}{V}}{Nk_B}$$

$$= \frac{P}{Nk_B}(V-Nb) + \frac{a}{Nk_BV}$$

$$= \frac{PV}{Nk_B} - \frac{P\cancel{N}b}{\cancel{N}k_B} + \frac{a}{Nk_BV}$$

$$= \frac{P}{k_B}\left(\frac{V}{N} - \frac{b}{k_B}\right) + \frac{a}{Nk_BV}$$

$$\frac{\partial T}{\partial P} = \frac{1}{k_B}\left(\frac{V}{N} - \frac{b}{k_B}\right)$$