Homework set 2

Huang 2.2

- $\Delta v = v^{(1)} - v^{(2)} = V^{(1)}/N^{(1)} - V^{(2)}/N^{(2)} = 0$
- $\Delta s = s^{(1)} - s^{(2)} = S^{(1)}/N^{(1)} - S^{(2)}/N^{(2)} = 0$
- $\Delta c_p = c_p^{(2)} - c_p^{(1)} \neq 0$ and $\Delta \alpha = \alpha^{(2)} - \alpha^{(1)} \neq 0$

If one takes $\frac{d}{dT}\left(s^{(1)} - s^{(2)}\right) = \frac{d}{dT}\Delta s = 0$ since $\Delta s = 0$

$$\Longrightarrow \quad ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP \quad \longrightarrow \quad \frac{ds}{dT} = \left(\frac{\partial s}{\partial T}\right)_P + \left(\frac{\partial s}{\partial P}\right)_T \frac{dP}{dT}$$

Thus:

$$\frac{d}{dT}(\Delta s) = \frac{d}{dT}\left(s^{(1)} - s^{(2)}\right) = \left(\frac{\partial s^{(1)}}{\partial T}\right)_P + \left(\frac{\partial s^{(1)}}{\partial P}\right)_T \frac{dP}{dT} - \left(\frac{\partial s^{(2)}}{\partial T}\right)_P - \left(\frac{\partial s^{(2)}}{\partial P}\right)_T \frac{dP}{dT} = 0$$

$$\Longrightarrow \quad \frac{dP}{dT} = \frac{\left(\frac{\partial s^{(2)}}{\partial T}\right)_P - \left(\frac{\partial s^{(1)}}{\partial T}\right)_P}{\left(\frac{\partial s^{(1)}}{\partial P}\right)_T - \left(\frac{\partial s^{(2)}}{\partial P}\right)_T}$$

However: $c_p = T\frac{\partial s}{\partial T}$ and $\alpha \equiv +\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = -\frac{1}{v}\left(\frac{\partial s}{\partial P}\right)_T$

From definition of g

$$\longrightarrow \quad \frac{dP}{dT} = \frac{\left(c_p^{(2)} - c_p^{(1)}\right)}{-Tv\left(\alpha^{(1)} - \alpha^{(2)}\right)} = \frac{\left(c_p^{(2)} - c_p^{(1)}\right)}{vT\left(\alpha^{(2)} - \alpha^{(1)}\right)} = \frac{\Delta c_p}{vT\Delta\alpha}$$

Also one can calculate $\frac{d}{dT}(\Delta v) = 0 = \frac{d}{dT}\left(v^{(1)} - v^{(2)}\right)$

$$\Rightarrow \frac{d}{dT}(\Delta v) = \left(\frac{\partial(\Delta v)}{\partial T}\right)_p + \left(\frac{\partial(\Delta v)}{\partial P}\right)_T \frac{dP}{dT} =$$

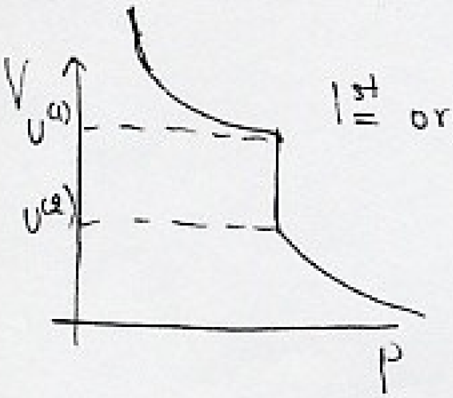
$$= \Delta\left(\frac{\partial v}{\partial T}\right)_p + \Delta\left(\frac{\partial v}{\partial P}\right)_T \frac{dP}{dT} =$$

$$= v\,\Delta\alpha - v\,\Delta k_T \frac{dP}{dT}$$

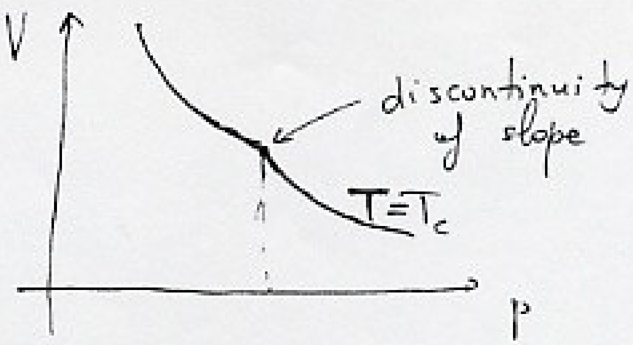
$$\Longrightarrow \boxed{\frac{dP}{dT} = \frac{\Delta\alpha}{\Delta k_T}}$$

There is discontinuity for Δk_T which is proport to the derivative $\left(\frac{\partial v}{\partial P}\right)_T$.

Thus in a $V-p$ diagram



1st order



uang 2.4 $$\left(P+\frac{a}{V^2}\right)(V-b) = RT$$

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

Thus:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\frac{\partial^2 S}{\partial V\partial T} = T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = T\frac{\partial}{\partial T}\left(\left(\frac{\partial P}{\partial T}\right)_V\right)_V =$$

$$= T\left(\partial^2 P/\partial T^2\right)_V$$

For a van der Waal gas, $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

$$\Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = 0 \quad \text{and} \quad C_V(V,T) = C_V$$

Extra Problem 1.

"A hypothetical experimentalist measures - - - - "

- $A^{(\ell)}/V = \frac{1}{2}\frac{\alpha}{T}\rho^2$ where $\rho = \frac{n}{V}$ molar density
- $A^{(s)}/V = \frac{1}{3}\frac{b}{T}\rho^3$

We can write: $A^{(\ell)} = \frac{\alpha}{2T}\frac{n^2}{V}$ and $A^{(s)} = \frac{b}{3T}\frac{n^3}{V^2}$

which are functions of $\{n, V, T)$

(a) $\rho^{(\ell)}$ and $\rho^{(s)}$ are the densities near the coexistence curve. At coexistence,

$\mu^{(s)} = \mu^{(\ell)}$ and $\left.\begin{array}{l} P^{(s)} = P^{(\ell)} \\ T^{(s)} = T^{(\ell)} \end{array}\right\}$ $\begin{array}{l}\text{pressure}\\ \text{temp.}\end{array}$

Since $P = -\left(\frac{\partial A}{\partial V}\right)_{T,n}$ $\qquad dA = -PdV - SdT + \mu$

$\mu = \left(\frac{\partial A}{\partial n}\right)_{V,T}$

$$\Rightarrow \left(\frac{\partial A^{(s)}}{\partial n}\right)_{V,T} = \left(\frac{\partial A^{(\ell)}}{\partial n}\right)_{V,T} \quad \text{and} \quad -\left(\frac{\partial A^{(s)}}{\partial V}\right)_{T,n} = -\left(\frac{\partial A^{(\ell)}}{\partial V}\right.$$

$$\Rightarrow \frac{b}{T}\left[\left(\frac{n}{V}\right)^{(s)}\right]^2 = \frac{\alpha}{T}\left(\frac{n}{V}\right)^{(\ell)} \quad \text{and} \quad \frac{\alpha}{2T}\left[\left(\frac{n}{V}\right)^{(\ell)}\right]^2 = \frac{2b}{3T}\left[\left(\frac{n}{V}\right.\right.$$

$$\Rightarrow \quad \frac{b}{\alpha}\left[\rho^{(s)}\right]^2 = \rho^{(\ell)}$$ Substituting in the second equation

$$\Rightarrow \quad \frac{\alpha}{2T}\left[\rho^{(\ell)}\right]^2 = \frac{2b}{3T}\left[\rho^{(s)}\right]^3 \Rightarrow \frac{\alpha}{2T}\left\{\frac{b}{\alpha}\left[\rho^{(s)}\right]^2\right\}^2 = \frac{2b}{3T}\left[\rho^{(s)}\right]^3$$

$$\Rightarrow \quad \boxed{\rho^{(s)} = \frac{4\alpha}{3b}} \quad \text{and} \quad \boxed{\rho^{(\ell)} = \frac{16}{9}\frac{\alpha}{b}}$$

b) $$P_s = p^{(s)} = p^{(\ell)} = -\left(\frac{\partial A}{\partial V}\right)_{T,n} = \frac{\alpha}{2T}\left[\rho^{(\ell)}\right]^2 =$$

$$= \frac{\alpha}{2T}\left(\frac{16}{9}\frac{\alpha}{b}\right)^2 = \frac{128}{81}\frac{\alpha^3}{b^2}\frac{1}{T}$$

(c) $$S^{(\ell)} = -\left(\frac{\partial A^{(\ell)}}{\partial T}\right)_{n,V} = \frac{\alpha}{2T^2}\frac{n^2}{V}$$

$$S^{(s)} = -\left(\frac{\partial A^{(s)}}{\partial T}\right)_{n,V} = \frac{b}{3T^2}\frac{n^3}{V^2}$$

$$\Delta s_{\ell \to s} = \frac{S^{(s)} - S^{(\ell)}}{n} = \frac{1}{T^2}\left(\frac{b}{3}\left[\rho^{(s)}\right]^2 - \frac{\alpha}{2}\rho^{(\ell)}\right) =$$

$$= \frac{1}{T^2}\left(\frac{16}{27}\frac{\alpha^2}{b} - \frac{8}{9}\frac{\alpha^2}{b}\right) = -\frac{8}{27}\frac{1}{T^2}\frac{\alpha^2}{b}$$

d) Since $\Delta v = \left[\rho^{(s)}\right]^{-1} - \left[\rho^{(\ell)}\right]^{-1} = \frac{3b}{4\alpha} - \frac{9}{16}\frac{b}{\alpha} = \frac{3b}{16\alpha}$

and $\Delta s = -\frac{8}{27}\frac{1}{T^2}\frac{\alpha^2}{b}$ (question c)

$$\Rightarrow \quad \frac{\Delta s}{\Delta v} = -\frac{128}{81}\frac{\alpha^3}{b^2}\frac{1}{T^2}$$ Also $$\frac{dP_s}{dT} = -\frac{128}{81}\frac{\alpha^3}{b^2}\frac{1}{T^2}$$

$\Rightarrow \frac{\Delta s}{\Delta v} = \frac{dp}{dT}$ satisfies Clapeyron equat

Extra problems: (2) Determine the ratio $\frac{PV}{RT}$ at the critical point for a gas which obeys the equation of state (Dieterici's equation)

$$p(V-b) = RT\exp(-a/RTV) .$$

Give the numerical answer accurately to two significant figures.

- The critical point satisfies

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

From the equation of states, we get

$$\left(\frac{\partial p}{\partial V}\right)_T = RT\,\frac{\left[\frac{a(V-b)}{RTV^2} - 1\right] e^{-\frac{a}{RTV}}}{(V-b)^2} = 0$$

$$\Longrightarrow \quad \frac{a(V-b)}{RTV^2} - 1 = 0$$

Using this result, we get

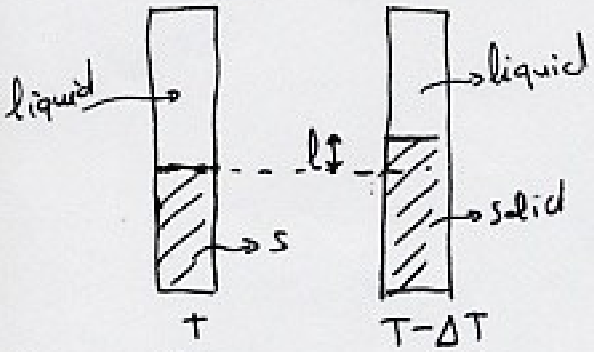
$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{a}{(V-b)V^3}\left(\frac{a}{RTV} - 2\right) e^{-\frac{a}{RTV}} = 0$$

Thus, $\frac{a}{RTV} = 2$. Then, $V = 2b$, $RT = \frac{a}{4b}$.

Substituting these back in the equation of state, we find $\frac{PV}{RT} = 0.2$

Extra Problem 3

"A long vertical cylindrical column ...."



The Clausius - Clapeyron equation gives:

$$\frac{dp}{dT} = \frac{L}{T(V_l - V_s)} = \frac{L}{T\left(\frac{1}{\rho_l} - \frac{1}{\rho_s}\right)} \leftarrow \text{latent heat}$$

However in the problem

$$dT = -\Delta T \quad \text{and} \quad dp = -g l \rho_s$$

$$\Rightarrow \quad \frac{g l \rho_s}{\Delta T} = \frac{L}{T(1/\rho_l - 1/\rho_s)} \quad \text{or}$$

$$\frac{1}{\rho_l} = \frac{1}{\rho_s} + \frac{L\,\Delta T/T}{g l \rho_s} = \frac{1}{\rho_s}\left(1 + \frac{L\,\Delta T/T}{g l}\right)$$

$$\Rightarrow \boxed{\rho_l = \rho_s\left[1 + \frac{\Delta T}{T}\frac{L}{lg}\right]^{-1}}$$