

ME 3007
HW 3 Solutions

1.

$$a) \quad dS \stackrel{?}{=} \frac{C_v}{T} \left(\frac{\partial T}{\partial P} \right)_v dP + \frac{C_p}{T} \left(\frac{\partial T}{\partial V} \right)_p dV$$

From Maxwell $\left(\frac{\partial P}{\partial T} \right)_v = \left(\frac{\partial S}{\partial V} \right)_T$, $\left(\frac{\partial V}{\partial T} \right)_p = -\left(\frac{\partial S}{\partial P} \right)_T$

$$dS \stackrel{?}{=} \frac{C_v}{T} \left(\frac{\partial S}{\partial S} \right)_T dP - \frac{C_p}{T} \left(\frac{\partial S}{\partial S} \right)_T dV$$

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_v, \quad C_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

$$dS \stackrel{?}{=} \left(\frac{\partial S}{\partial T} \right)_v \left(\frac{\partial V}{\partial S} \right)_T dP - \left(\frac{\partial S}{\partial T} \right)_p \left(\frac{\partial P}{\partial S} \right)_T dV$$

$$dS \stackrel{?}{=} - \left(\frac{\partial V}{\partial T} \right)_S dP + \left(\frac{\partial P}{\partial T} \right)_S dV \quad \text{from Cyclic Rules}$$

$$\quad \quad \quad \parallel \quad \quad \quad \parallel$$

$$\quad \quad \quad + \left(\frac{\partial S}{\partial P} \right)_V \quad \quad \quad \left(\frac{\partial S}{\partial V} \right)_P$$

$$dS = \left(\frac{\partial S}{\partial P} \right)_V dP + \left(\frac{\partial S}{\partial V} \right)_P dV \quad \checkmark \quad \text{simple expansion}$$

b) Isentropic $\rightarrow dS = 0$

Ideal gas $PV = RT \rightarrow \left(\frac{\partial T}{\partial P} \right)_v = \frac{V}{R}, \quad \left(\frac{\partial T}{\partial V} \right)_p = \frac{P}{R}$

$$0 = C_v \frac{V}{RT} dP + C_p \frac{P}{RT} dV = C_v \frac{dP}{P} + C_p \frac{dV}{V}$$

so to solve this $PV^{C_p/C_v} = \text{const.}$

c) $TdS = C_v \left(\frac{\partial T}{\partial P} \right)_v dP + C_p \left(\frac{\partial T}{\partial V} \right)_p dV$

$$TdS = C_v \left(\frac{\partial T}{\partial P} \right)_v \left[dP + \underbrace{\frac{C_p}{C_v} \left(\frac{\partial P}{\partial T} \right)_v \left(\frac{\partial T}{\partial V} \right)_p}_{\gamma} dV \right]$$

$= -\left(\frac{\partial P}{\partial V} \right)_T$ Cyclic Rule

$$TdS = C_v \left(\frac{\partial T}{\partial P} \right)_v \left[dP - \gamma \left(\frac{\partial P}{\partial V} \right)_T dV \right]$$

2.

a) $V = \left(\frac{\partial H}{\partial P}\right)_S ? \rightarrow dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \checkmark$

b) $\left(\frac{\partial H}{\partial T}\right)_S \stackrel{?}{=} V \left(\frac{\partial P}{\partial T}\right)_S$ ~~isolate denominator~~
 from 4.34 $\Rightarrow = \frac{C_p}{\beta T}$ \hookrightarrow Divide by dT , hold @ const. S as in Ex. 3.10 (2nd half)

c) As in (b), divide by dV , hold @ const. S , as in Ex. 3.10 (2nd half)

d) From same expansion as part (a)

e) $\left(\frac{\partial H}{\partial S}\right)_T \stackrel{?}{=} T - V \left(\frac{\partial T}{\partial V}\right)_P$

As in b+c, divide by dS + hold T const, so that

$\left(\frac{\partial H}{\partial S}\right)_T = T + V \left(\frac{\partial P}{\partial S}\right)_T$. From Maxwell $\left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P \checkmark$

f) $\left(\frac{\partial H}{\partial S}\right)_V \stackrel{?}{=} T - V \left(\frac{\partial T}{\partial V}\right)_S$. $\left(\frac{\partial H}{\partial S}\right)_V = T + \frac{V dP}{dS} = T + V \left(\frac{\partial P}{\partial S}\right)_V$

From Maxwell, $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S \checkmark$

3.

The derivations are all very similar to what we did in #1 + #2, The more interesting question is why they $\rightarrow \infty$ for a phase transition.

a) $\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\frac{C_p}{T}$. $C_p \equiv \left(\frac{\partial H}{\partial T}\right)_P$. During a phase

transition, $\Delta T = 0 @ \text{const. } P$, so $C_p \rightarrow \infty$

b) $\left(\frac{\partial^2 G}{\partial P^2}\right)_T = -\kappa V$, $\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$, so $-\kappa V = \left(\frac{\partial V}{\partial P}\right)_T$

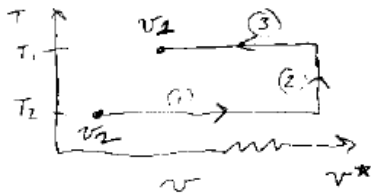
During a phase transition, $\Delta P = 0 @ \text{const. } T$, so $-\kappa V \rightarrow \infty$

c) $\frac{\partial^2 G}{\partial P \partial T} = \beta V$, $\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$, so $\beta V = \left(\frac{\partial V}{\partial T} \right)_P$, and, as in part (a), $\Delta T = 0 @ \text{const. } P$, so $\beta V \rightarrow \infty$

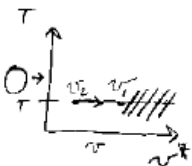
(For (a)-(c), it should be noted that all of the numerators in the differentials are nonzero for a phase change)

4.

i) $\Delta U = ?$ $\Delta S = ?$ vdW EOS, $v_1 > v_2$



$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$



$$\Delta U = \int_{v_2}^{v_1} \left(\frac{\partial u}{\partial v} \right)_{T_2} dv + \int_{T_2}^{T_1} C_{v,\infty} dT + \int_{v_1}^{v_2} \left(\frac{\partial u}{\partial v} \right)_{T_1} dv$$

$$\Delta S = \int_{v_2}^{v_1} \left(\frac{\partial s}{\partial v} \right)_{T_2} dv + \int_{T_2}^{T_1} \frac{C_{v,\infty}}{T} dT + \int_{v_1}^{v_2} \left(\frac{\partial s}{\partial v} \right)_{T_1} dv$$

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_v$$

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_v - P$$

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{R}{v-b}$$

$$\int_{u_2}^{u_1} du = \int_{v_2}^{v_1} \left(\frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} \right) dv = \int_{v_2}^{v_1} \frac{a}{v^2} dv = -\frac{a}{v} \Big|_{v_2}^{v_1} = -a \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$$

$$u_1 - u_2 = a \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$\int_{s_2}^{s_1} ds = \int_{v_2}^{v_1} \frac{R}{v-b} dv = R \ln(v-b) \Big|_{v_2}^{v_1} = R \left[\ln(v_1-b) - \ln(v_2-b) \right]$$

$$s_1 - s_2 = R \ln \left[\frac{v_1 - b}{v_2 - b} \right]$$

Interpretation: since $v_1 > v_2$ $u_1 - u_2 > 0$ } Does this make sense? yes.
 (M_r) $S_1 - S_2 > 0$ }
 Btw, $\frac{a}{v^2}$ represents an internal pressure. If it increases as $v \uparrow$, attractions are dominant. Otherwise repulsions are dominant.

5.

a) The reduced vdW EOS is:

$$Z = \frac{\bar{V}_r}{\bar{V}_r - \frac{1}{3}} - \frac{9}{8\bar{V}_r T_r}$$

Rewrite this equation in terms of reduced density $\rho_r = \rho / \rho_c = \bar{V}_r^{-1}$ rather than volume:

$$Z = (1 - \frac{1}{3}\rho_r)^{-1} - \frac{9}{8} \frac{\rho_r}{T_r}$$

Setting $Z = 1$ and rearranging:

$$\begin{aligned} 1 &= (1 - \frac{1}{3}\rho_r)^{-1} - \frac{9}{8} \frac{\rho_r}{T_r} \\ &= (1 - \frac{1}{3}\rho_r) \left(1 + \frac{9}{8} \frac{\rho_r}{T_r} \right) \\ &= 1 - \frac{1}{3}\rho_r + \frac{9}{8} \frac{\rho_r}{T_r} - \frac{3}{8} \frac{\rho_r^2}{T_r} \end{aligned}$$

which can be reduced to:

$$\boxed{T_r = \frac{27}{8} - \frac{9}{8}\rho_r}$$

Thus, the $Z=1$ locus of the van der Waal equation of state is indeed linear.

b)

The Boyle temperature is defined as that temperature at which $B_{2P}(T) = 0$, i.e. the temperature for which $Z = 0$ in the $\rho \rightarrow 0$. From the result of part (a) it is readily seen that $T_{r,Boyle} = 27/8$ or

$$\boxed{T_{Boyle} = (27/8)T_c}$$

c)

The critical parameters of methane are: $T_c = 190.53$ and $\rho_c = \bar{V}_c^{-1} = 10.10 \text{ mol dm}^{-3}$. Using the results of part (b) the intercept of the Zeno line should occur at **643 K**. Using the results of part (a) the slope of the Zeno line,

$$\frac{dT}{d\rho} = \frac{T_c}{\rho_c} \frac{dT_r}{d\rho_r}$$

is predicted by the van der Waals equation of state to be **-21.2 K dm³ mol⁻¹**. The predicted intercept and slope are in error by +27% and +12%, respectively.