Homework 5 : Solutions

1. Problem 2-6 of the text.

$$P = \frac{RT}{v-b} - \frac{a}{Tv^2}. \qquad (1)$$

At the "Critical Point";

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{Tv^3} = 0 \qquad (2)$$

&

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{Tv^4} = 0. \qquad (3)$$

$$(2) \Rightarrow RT^2 = \frac{2a(v-b)^2}{v^3} \quad \& \quad (3) \Rightarrow RT^2 = \frac{3a(v-b)^3}{v^4}.$$

Equating the two results, we get $v_c = 3b$.

It follows that $T_c = \sqrt{\frac{8a}{27bR}}$.

Eqn. (1) then gives:

$$P_c = \frac{\sqrt{8aR/27b}}{2b} - a\sqrt{\frac{27bR}{8a}} \cdot \frac{1}{9b^2}$$

$$= \sqrt{\frac{aR}{b^3}}\left[\sqrt{\frac{2}{27}} - \sqrt{\frac{1}{24}}\right]$$

$$= \sqrt{\frac{2aR}{3b^3}}\left[\frac{1}{3} - \frac{1}{4}\right] = \frac{1}{12b}\sqrt{\frac{2aR}{3b}}.$$

10

It readily follows that $RT_c / P_c v_c = \frac{8}{3} \simeq 2.67$ — rather low in comparison with the observed values!

Problem 2-7 of the text.

$$P = \frac{RT}{v-b}\, e^{-a/RTv} \qquad (1)$$

At the critical point,

$$\left(\frac{\partial P}{\partial v}\right)_T = \left[\frac{-RT}{(v-b)^2} + \frac{RT}{v-b}\cdot\frac{a}{RTv^2}\right] e^{-a/RTv}$$

$$= P\left[\frac{-1}{v-b} + \frac{a}{RTv^2}\right] = 0 \qquad (2)$$

&

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \underbrace{\left(\frac{\partial P}{\partial v}\right)_T}_{=\text{ zero!}} \left[\frac{-1}{v-b} + \frac{a}{RTv^2}\right] + P\left[\frac{1}{(v-b)^2} - \frac{2a}{RTv^3}\right] = 0. \qquad (3)$$

$$(2) \Rightarrow RT = \frac{a(v-b)}{v^2} \quad \& \quad (3) \Rightarrow RT = \frac{2a(v-b)^2}{v^3}.$$

Equating the two results, we get $\underline{v_c = 2b.}$ ✓

It follows that $T_c = \frac{a}{4bR}$. ✓

Eqn. (1) then gives $P_c = \frac{a}{4b^2}\, e^{-2}$. ✓

It readily follows that $RT_c/P_c v_c = \frac{e^2}{2} \simeq 3.69$ —

10 in fair agreement with the observed values!

X

$$\frac{\partial^3 P}{\partial v^3} = \frac{\partial^2 P}{\partial v^2}[\cdots] + \frac{\partial P}{\partial v}[\cdots]' + \frac{\partial P}{\partial v}[\cdots] + P_c\left[\frac{-2}{(v-b)^3} + \frac{6a}{RTv^4}\right]$$

$$\therefore \left(\frac{\partial^3 P}{\partial v^3}\right)_{C.P.} = 0 + 0 + 0 + P_c\left(\frac{-2}{b^3} + \frac{6a}{(a/4b)\cdot 16b^4}\right)$$

$$= P_c \cdot \frac{-1}{2b^3} \neq 0 \qquad \text{Hence } \delta = 3.$$

3. Given that $P = \dfrac{RT}{v-b} - \dfrac{a}{v^3}$.

The C.P. is determined by the conditions

$$\left(\frac{\partial P}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} + \frac{3a}{v^4} = 0, \text{ i.e. } RT = \frac{3a(v-b)^2}{v^4}$$

& $$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{12a}{v^5} = 0, \text{ i.e. } RT = \frac{6a(v-b)^3}{v^5}.$$

Equating the two, we get $2(v-b) = v$, i.e. $\underline{\underline{v = 2b}}$

Substituting this result into either of the two equations, we get

$$RT = \frac{3a}{16b^2}, \quad \text{so} \quad \underline{\underline{T = \frac{3a}{16b^2R}}}.$$

Clearly, these are the values of v_c and T_c.

Substituting these into the eqn. of state, we get

$$P_c = \frac{3a}{16b^3} - \frac{a}{8b^3} = \frac{a}{16b^3}.$$

10 It follows that the ratio $RT_c / P_c v_c = 3/2 = 1.5$ — pretty low!

4. Write $P = \frac{a}{16b^3} \cdot P_r$; $v = 2b \cdot v_r$ & $T = \frac{3a}{16b^2 R} \cdot T_r$.

The equation of state then assumes the "reduced" form:

3

$$\left(P_r + \frac{2}{v_r^3}\right)(2v_r - 1) = 3T_r, \text{ i.e.}$$

$$P_r = \frac{3T_r}{2v_r - 1} - \frac{2}{v_r^3}.$$

Now, write $P_r = 1 + P'$, $v_r = 1 + v'$ & $T_r = 1 + T'$, with $T' = 0$. We get:

3 why?

$$P' = \frac{3}{1 + 2v'} - \frac{2}{(1+v')^3} - 1.$$

Now, use the Binomial expansions

$$(1 + 2v')^{-1} = 1 - 2v' + 4v'^2 - 8v'^3 + \ldots$$

&

$$(1 + v')^{-3} = 1 - 3v' + 6v'^2 - 10v'^3 + \ldots,$$

with the result

$$P' = -4v'^3 + \ldots$$

$$\therefore |P'| \simeq 4|v'|^3.$$ note!

4 It follows that $\delta = 3$ — the <u>same</u> as for the normal van der Waals gas!

5. $$P = \frac{RT}{v} - \frac{1}{2}\frac{\beta_1 \lambda^3 RT}{v^2} - \frac{2}{3}\frac{\beta_2 \lambda^6 RT}{v^3}. \qquad (1)$$

At the critical point,

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{v^2} + \frac{\beta_1 \lambda^3 RT}{v^3} + \frac{2\beta_2 \lambda^6 RT}{v^4} = 0 \qquad (2)$$

&

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT}{v^3} - \frac{3\beta_1 \lambda^3 RT}{v^4} - \frac{8\beta_2 \lambda^6 RT}{v^5} = 0. \qquad (3)$$

Eqns. (2) & (3) give

$$\left.\begin{aligned} \frac{\beta_1 \lambda^3}{v} + \frac{2\beta_2 \lambda^6}{v^2} &= 1 \\ \& \quad \frac{3\beta_1 \lambda^3}{v} + \frac{8\beta_2 \lambda^6}{v^2} &= 2. \end{aligned}\right\}$$

8 It follows that $\left(\frac{\beta_1 \lambda^3}{v}\right)_c = 2$ & $\left(\frac{\beta_2 \lambda^6}{v^2}\right)_c = -\frac{1}{2}$.

Substituting these results into (1), we get

$$\left(\frac{Pv}{RT}\right)_c = 1 - \frac{1}{2}\times 2 - \frac{2}{3}\times\frac{-1}{2} = \frac{1}{3}.$$

2 $\therefore \ (RT_c / P_c v_c) = 3$ ✓