

• Outline of the Solutions to Homework #3.

①

18.43

If you look at the $P(V)$ diagram (fig 18-4 p.482) the critical point is shown as C. There you have

$$\frac{\partial P}{\partial V} = 0, \text{ it is furthermore an inflexion point i.e. } \frac{\partial^2 P}{\partial V^2} = 0.$$

Since we have $P(n, V, T) = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$ ④

$$(1) \quad \frac{\partial P}{\partial V} = 0 = -\frac{nRT}{(V-nb)^2} + \frac{2an^2}{V^3}$$

$$(2) \quad \frac{\partial^2 P}{\partial V^2} = 0 = \frac{2nRT}{(V-nb)^3} - \frac{6an^2}{V^4}$$

Solving these two equations for T, V (for fixed n , take for example $n=1$, as really $\frac{V}{n}$ matters in eq. ④ we find the critical volume & temperature. (V_c, T_c)

Plugging (V_c, T_c) back in eq ④ gives us $P_c = P(1, V_c, T_c)$

(1) $\Rightarrow T = \frac{2a}{V^3} \frac{(V-b)^2}{R}$; substituting this T in (2)

we can get V : $0 = \frac{4a}{V^3(V-b)} - \frac{6a}{V^4} \Rightarrow 3(V-b) = 2V$

$\Rightarrow V_c = 3b$

$\Rightarrow T_c = \frac{2a}{27b^3} \frac{4b^2}{R} = \frac{8a}{27bR} \Rightarrow P_c = \frac{8a}{27b} / 2b - \frac{a}{9b^2}$

$\Rightarrow P_c = \frac{a}{27b^2}$

Knowing T_c & P_c one can then solve for a & b

$b = \frac{R T_c}{8 P_c}$; $a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}$

18.57

$$P = \frac{1}{\text{cm}^3} = 10^6 / \text{m}^3 ; T = 2.7 \text{ } ^\circ\text{K}$$

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} \quad (\text{does not involve the density})$$

$$P = \frac{nRT}{V} \quad \frac{n}{V} = \text{number of moles per unit volume (m}^3\text{)}$$

10^6 atoms per m^3 corresponds to $\frac{10^6}{N_A}$ moles per m^3

$$\Rightarrow P = \frac{10^6}{N_A} \cdot k_B N_A \cdot T = 10^6 k_B T$$

18.60

v_{avg} (not v_{rms}) is given by $\sqrt{\frac{8kT}{\pi m}}$

$$\Rightarrow T = \frac{\pi m v_{\text{avg}}^2}{8k_B}$$

$$m_{\text{O}_2} = 32 \text{ (amu)} = 32 \times 1.66 \cdot 10^{-27} \text{ kg}$$

$$m_{\text{He}} = 4 \text{ (amu)} = 4 \times 1.66 \cdot 10^{-27} \text{ kg}$$