

Problem Set 7 Solutions

1.-

$$V_m = \frac{0.165 \text{ L}}{35.0 \text{ g}} \times \frac{39.95 \text{ g}}{\text{mol}} = 0.1883 \text{ L mol}^{-1}$$

$$P_{\text{ideal gas}} = \frac{RT}{V_m} = \frac{8.314 \times 10^{-2} \text{ L} \times \text{bar K}^{-1} \text{ mol}^{-1} \times 390 \text{ K}}{0.1883 \text{ L mol}^{-1}} = 172 \text{ bar}$$

$$P_{\text{vdw}} = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 390 \text{ K}}{0.1883 \text{ L mol}^{-1} - 0.0320 \text{ L mol}^{-1}} - \frac{1.355 \text{ L}^2 \text{ bar mol}^{-2}}{(0.1883 \text{ L mol}^{-1})^2}$$

$$= 169 \text{ bar}$$

$$P_{\text{RK}} = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)}$$

$$= \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 390 \text{ K}}{0.1883 \text{ L mol}^{-1} - 0.02219 \text{ L mol}^{-1}}$$

$$- \frac{16.86 \text{ L}^2 \text{ bar mol}^{-2} \text{ K}^{\frac{1}{2}}}{\sqrt{390 \text{ K}}} \frac{1}{0.1883 \text{ L mol}^{-1} (0.1883 \text{ L mol}^{-1} + 0.02219 \text{ L mol}^{-1})}$$

$$P_{\text{RK}} = 174 \text{ bar}$$

3.-

For the ideal gas,

$$\frac{1}{V_m} = \frac{P}{RT} = \frac{400 \text{ bar}}{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}} = 9.62 \text{ mol L}^{-1}$$

$$P_{RK} = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)}$$

$$400 \text{ bar} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}{V_m - 0.02208 \text{ L mol}^{-1}} - \frac{17.40 \text{ L}^2 \text{ bar mol}^{-2} \text{ K}^{\frac{1}{2}}}{\sqrt{500 \text{ K}} V_m (V_m + 0.02208 \text{ L mol}^{-1})}$$

The three solutions to this equation are

$$V_m = (-0.00529 \pm 0.0186i) \text{ L mol}^{-1} \text{ and } V_m = 0.1145 \text{ L mol}^{-1}$$

Only the real solution is of significance.

$$\frac{1}{V_m} = \frac{1}{0.1145 \text{ L mol}^{-1}} = 8.73 \text{ mol L}^{-1}$$

The ideal gas density is greater than that calculated with the Redlich-Kwong equation of state and the experimental result showing that the repulsive part of the potential dominates. The Redlich-Kwong result is in error by +10%.

8.-

$$T_R^{Xe} = \frac{T^{Xe}}{T_C^{Xe}} = \frac{450 \text{ K}}{289.74 \text{ K}} = 1.55; \quad T^{H_2} = 1.55 T_C^{H_2} = 1.55 \times 32.98 \text{ K} = 51.2 \text{ K}$$

$$P_R^{Xe} = \frac{P^{Xe}}{P_C^{Xe}} = \frac{85.0 \text{ bar}}{58.40 \text{ bar}} = 1.46; \quad P^{H_2} = 1.46 P_C^{H_2} = 1.46 \times 12.93 \text{ bar} = 18.8 \text{ bar}$$

11.-

For the ideal gas,

$$w = -nRT \ln \frac{V_f}{V_i} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K} \times \ln \frac{65.0 \text{ L}}{1.00 \text{ L}} = -10.34 \times 10^3 \text{ J}$$

For the van der Waals gas,

$$\begin{aligned} w &= - \int_{V_i}^{V_f} \left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2} \right) dV = - \left[nRT \ln(V-nb) + \frac{an^2}{V} \right]_{V_i}^{V_f} \\ &= - \left[1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K} \times \ln(V - 3.20 \times 10^{-5} \text{ m}^3) + \frac{0.1355 \text{ Pa m}^6}{V} \right]_{0.001 \text{ m}^3}^{0.065 \text{ m}^3} \\ &= -10.42 \times 10^3 \text{ J} + 133 \text{ J} = -10.41 \times 10^3 \text{ J} \\ 100 \times \frac{133 \text{ J}}{10.41 \times 10^3 \text{ J}} &= 1.3\% \end{aligned}$$

15.-

Assuming an ideal gas,

$$V_c = \frac{RT_c}{P_c} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1}\text{K}^{-1} \times 647.14 \text{ K}}{220.64 \text{ bar}} = 0.2438 \text{ L}$$

For a van der Waals gas,

$$z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8}; \quad V_c = \frac{3}{8} \frac{RT_c}{P_c} = \frac{3}{8} \times 0.2438 \text{ L} = 91.4 \times 10^{-3} \text{ L}$$

For a Redlich-Kwong gas,

$$z_c = \frac{P_c V_c}{RT_c} = 0.333; \quad V_c = 0.333 \frac{RT_c}{P_c} = 0.333 \times 0.2438 \text{ L} = 81.2 \times 10^{-3} \text{ L}$$

Although the agreement with experiment is better for the van der Waals and Redlich-Kwong models than for the ideal gas model, all results differ significantly from the true value.

17.-

Boyle temperature in terms of a , b , and R .

$$z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT} - \frac{Pa}{R^2T^3}$$

$$\left(\frac{\partial z}{\partial P}\right)_T = b - \frac{a}{R^2T^3} \text{ and at } T = T_B, \left(\frac{\partial z}{\partial P}\right)_T = 0$$

$$\text{Therefore } b - \frac{a}{R^2T_B^3} = 0$$

$$T_B = \sqrt{\frac{a}{Rb}}$$

19.-

The excluded volume is $\frac{4}{3}\pi(2r)^3 = 8V_{\text{molecule}}$, or $4V_{\text{molecule}}$ per molecule. Therefore, $b = 4N_A V_{\text{molecule}}$ and $V_{\text{molecule}} = b/4N_A$.

$$N_A \frac{16}{3}\pi r^3 = b$$

$$r = \left(\frac{3b}{16N_A\pi}\right)^{\frac{1}{3}} = \left(\frac{3 \times 4.31 \times 10^{-5} \text{ m}^3}{16\pi \times 6.022 \times 10^{23}}\right)^{\frac{1}{3}} = 1.63 \times 10^{-10} \text{ m}$$

21.-

$\frac{RT}{V_m - b} - \frac{a}{V_m^2}$: In the limit of low density, V_m is large and $V_m \gg b$. The second term in the van der Waals equation can be neglected because it goes as $\frac{1}{V_m^2}$, and in the first term,

$$\frac{RT}{V_m - b} \rightarrow \frac{RT}{V_m}$$

$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)}$: In the limit of low density, V_m is large and $V_m \gg b$. As for the van der Waals equation, the second term in the Redlich-Kwong equation can be neglected because it goes as $\frac{1}{V_m^2}$. In the limit, the first term becomes $\frac{RT}{V_m - b} \rightarrow \frac{RT}{V_m}$.

22.-

$$B(T) = \frac{1}{RT} \left(\frac{\partial z}{\partial \frac{1}{V_m}} \right)_T = b - \frac{a}{RT}$$

Let $u = \frac{1}{V_m}$. The virial expansion takes the form

$$P = RT \left([P(u)]_{u=0} + \left[\frac{dP(u)}{du} \right]_{u=0} u + \frac{1}{2} \left[\frac{d^2P(u)}{du^2} \right]_{u=0} u^2 + \dots \right)$$

Therefore, the second virial coefficient is $B(T) = \frac{1}{2RT} \left[\frac{d^2P(u)}{du^2} \right]_{u=0}$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{RT}{1/u - b} - au^2$$

$$\frac{dP}{du} = -\frac{RT}{(1/u - b)^2} \frac{d1/u}{du} - 2au = \frac{RT}{u^2 (1/u - b)^2} - 2au = \frac{RT}{(1 - ub)^2} - 2au$$

$$\frac{d^2P}{du^2} = \frac{2bRT}{(1 - ub)^3} - 2a$$

$$\lim_{u \rightarrow 0} \frac{2bRT}{(1 - ub)^3} - 2a = 2bRT - 2a \text{ and}$$

$$B(T) = \frac{1}{2RT} \left[\frac{d^2P(u)}{du^2} \right]_{u=0} = b - \frac{a}{RT}$$

23.-

$$\ln \gamma = \int_0^P \frac{z-1}{P'} dP' = \int_0^P \frac{(1 - 9.00 \times 10^{-3} P' + 4.00 \times 10^{-5} (P')^2) - 1}{P'} dP'$$

$$\ln \gamma = -9.00 \times 10^{-3} P + 2.00 \times 10^{-5} P^2$$

$\gamma = 0.497, 0.368, 0.406, 0.670,$ and 1.65 at $100, 200, 300, 400,$ and 500 bar, respectively.