

# 7 The Properties of Real Gases

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual*.

## Conceptual Problems

- Q7.1** Using the concept of the intermolecular potential, explain why two gases in corresponding states can be expected to have the same value for  $z$ .
- Two different gases will have different values for the depth of the intermolecular potential and for the distance at which the potential becomes positive. By normalizing  $P$ ,  $T$ , and  $V$  to their critical values, the differences in the intermolecular potential are to a significant extent also normalized.
- Q7.2** Consider the comparison made between accurate results and those based on calculations using the van der Waals and Redlich–Kwong equations of state in Figures 7.1 and 7.5. Is it clear that one of these equations of state is better than the other under all conditions?
- The Redlich–Kwong gives more accurate results for almost all of the values of pressure shown in these figures. However, it is not better under all conditions.
- Q7.3** Why is the standard state of fugacity,  $f^\circ$ , equal to the standard state of pressure,  $P^\circ$ ?
- If this were not the case the fugacity would not become equal to the pressure in the limit of low pressures.
- Q7.4** Explain the significance of the Boyle temperature.
- The Boyle temperature provides a way to classify the way in which  $z$  varies with  $P$  at low values of  $P$  for different gases. If  $T > T_B$ ,  $z$  increases with increasing  $P$ ; if  $T < T_B$ ,  $z$  decreases with increasing  $P$ . At the Boyle temperature, the repulsive and attractive interactions cancel one another out so that the gas behaves ideally over a larger range of pressure than at other temperatures.
- Q7.5** A van der Waals gas undergoes an isothermal reversible expansion under conditions such that  $z > 1$ . Is the work done more or less than if the gas followed the ideal gas law?
- For a reversible expansion,  $P_{\text{external}} = P$ . Because  $V > V_{\text{ideal}}$ , for  $z > 1$ ,  $\Delta V > \Delta V_{\text{ideal}}$ . Therefore,
- $$|w| = \left| \int P dV \right| > \left| \int P dV_{\text{ideal}} \right|.$$
- Q7.6** For a given set of conditions, the fugacity of a gas is greater than the pressure. What does this tell you about the interaction between the molecules of the gas?
- If the fugacity is greater than the pressure, the repulsive part of the potential dominates the interaction between the molecules.
- Q7.7** What can you conclude about the ratio of fugacity to pressure for  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  at 500 bar using the data in Figure 7.10?
- $f > P$  for  $\text{N}_2$  and  $\text{H}_2$ , and  $f < P$  for  $\text{NH}_3$
- Q7.8** Is the ratio of fugacity to pressure greater to or less than one if the attractive part of the interaction potential between gas molecules dominates?
- If attractive interactions dominate,  $P < P_{\text{ideal}}$ , so  $f/P < 1$ .

- Q7.9** A gas is slightly above its Boyle temperature. Do you expect  $z$  to increase or decrease as  $P$  increases?  
Above the Boyle temperature,  $\left(\frac{\partial z}{\partial P}\right)_T > 0$ , so  $z$  increases as  $P$  increases.
- Q7.10** Explain why the oscillations in the two-phase coexistence region using the Redlich–Kwong and van der Waals equations of state (see Figure 7.4) do not correspond to reality.  
The oscillations predict that as  $V$  increases,  $P$  will increase. No real gas exhibits this behavior.
- Q7.11** A van der Waals gas undergoes an isothermal reversible expansion under conditions such that  $z < 1$ . Is the work done more or less than if the gas followed the ideal gas law?  
For a reversible expansion,  $P_{\text{external}} = P$ . Because  $V > V_{\text{ideal}}$ , for  $z < 1$ ,  $\Delta V < \Delta V_{\text{ideal}}$ . Therefore,  $|w| = \left| \int P dV \right| < \left| \int P dV_{\text{ideal}} \right|$ .
- Q7.12** The value of the Boyle temperature increases with the strength of the attractive interactions between molecules. Arrange the Boyle temperatures of the gases Ar, CH<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub> in increasing order.  
Because the strength of dispersive interactions increases with the number of electrons and atoms, Ar < CH<sub>4</sub> < C<sub>6</sub>H<sub>6</sub>.
- Q7.13** A system containing argon gas is at pressure  $P_1$  and temperature  $T_1$ . How would you go about estimating the fugacity coefficient of the gas?  
Use the critical constants of the gas to determine the reduced pressure and temperature. With these results, estimate the fugacity coefficient using Figure 7.11.
- Q7.14** By looking at the  $a$  and  $b$  values for the van der Waals equation of state, decide whether 1 mole of O<sub>2</sub> or H<sub>2</sub>O has the higher pressure at the same value of  $T$  and  $V$ .  
 $a$  is significantly larger for H<sub>2</sub>O. Therefore, the attractive forces between H<sub>2</sub>O molecules are greater than between O<sub>2</sub> molecules. Consequently, O<sub>2</sub> will have a higher pressure.
- Q7.15** Will the fugacity coefficient of a gas above the Boyle temperature be less than 1 at low pressures?  
No. The integral  $\int_0^P \frac{z-1}{P'} dP'$  is always greater than zero for this case. Therefore,  $\gamma > 1$  for all  $P$ .
- Q7.16** Show that the van der Waals and Redlich–Kwong equations of state reduce to the ideal gas law in the limit of low gas density.

$$P_{\text{vdW}} = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} = \frac{nRT}{V\left(1-\frac{n}{V}b\right)} - n\frac{a}{V^2}$$

As  $n/V$  decreases,  $1 - nb/V \rightarrow 1$  and the second term in the van der Waals equation becomes small relative to the first term, leading to the ideal gas law.

$$P_{\text{R-K}} = \frac{nRT}{V-nb} - \frac{n^2a}{\sqrt{T}V(V+nb)} = \frac{nRT}{V\left(1-\frac{n}{V}b\right)} - \left(\frac{n}{V}\right)^2 \frac{a}{\sqrt{T}\left(1+\frac{n}{V}b\right)}$$

As  $n/V$  decreases,  $1 \mp nb/V \rightarrow 1$  and the second term in the Redlich–Kwong equation becomes small relative to the first term, leading to the ideal gas law.

- Q7.17** Which of Ne or Ar has the larger van der Waals parameter  $a$ ? Explain your reasoning.  
The degree to which the electron charge cloud is polarizable determines  $a$ . Ar has the larger van der Waals parameter  $a$  because it has more electrons and is therefore more polarizable.

- Q7.18** Which of Ne or Ar has the larger van der Waals parameter  $b$ ? Explain your reasoning.  
Ar has the larger van der Waals parameter  $b$  because argon atoms are larger than Ne atoms.
- Q7.19** You have calculated the pressure exerted by ethane using the ideal gas law and the Redlich–Kwong equations of state. How do you decide if the repulsive or attractive part of the molecular potential dominates under the given conditions?  
If  $P_{R-K} > P_{ideal}$ , repulsion dominates. If  $P_{R-K} < P_{ideal}$ , attraction dominates.
- Q7.20** Equation (1.19) states that the total pressure in a mixture of gases is equal to the sum of the partial pressures. Is this equation valid for real gases? If so, under what conditions?  
This is only valid if the molecules do not interact with one another or if the pairwise interactions for all of the different gases are equal.

### Numerical Problems

- P7.1** A van der Waals gas has a value of  $z = 1.00061$  at 410. K and 1 bar and the Boyle temperature of the gas is 195 K. Because the density is low, you can calculate  $V_m$  from the ideal gas law. Use this information and the result of Problem 7.28,  $z = 1 + (b - a/RT)(1/V_m)$ , to estimate  $a$  and  $b$ .

$$z - 1 = \frac{1}{V_m} \left( b - \frac{a}{RT} \right); \quad T_B = \frac{a}{Rb}$$

$$z - 1 = \frac{b}{V_m} \left( 1 - \frac{T_B}{T} \right)$$

$$b = \frac{z - 1}{1 - \frac{T_B}{T}} \frac{RT}{P} = \frac{0.00061}{1 - \frac{195 \text{ K}}{410. \text{ K}}} \times \frac{8.314 \times 10^{-2} \text{ dm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} \times 410. \text{ K}}{1 \text{ bar}}$$

$$= 0.0397 \text{ dm}^3 \text{ mol}^{-1} = 3.97 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$a = RbT_B = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.97 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \times 195 \text{ K} = 6.43 \times 10^{-2} \text{ m}^6 \text{ Pa mol}^{-2}$$

- P7.2** a. Using the relationships derived in Example Problem 7.1 and the values of the critical constants for water from Table 7.2, calculate values for the van der Waals parameters  $a$ ,  $b$ , and  $R$  from  $z_c$ ,  $T_c$ ,  $P_c$ , and  $V_c$ . Do your results agree with those in Tables 1.2 and 7.4 in Appendix A?
- b. Calculate the van der Waals parameters  $a$  and  $b$  using the critical constants for water and the correct value for  $R$ . Do these results agree with those in Tables 1.2 and 7.4?

(a)  $R = \frac{V_c P_c}{z_c T_c} = \frac{55.95 \times 10^{-3} \text{ L mol}^{-1} \times 220.64 \text{ bar}}{0.229 \times 647.14 \text{ K}} = 8.33 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1}$

$$b = \frac{RT_c}{8P_c} = \frac{8.33 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 647.14 \text{ K}}{8 \times 220.64 \text{ bar}} = 0.0305 \text{ L mol}^{-1}$$

$$a = \frac{27R^2 T_c^2}{64P_c} = \frac{27 \times (8.33 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1})^2 \times (647.14 \text{ K})^2}{64 \times 220.64 \text{ bar}} = 5.56 \text{ L}^2 \text{ bar mol}^{-2}$$

(b)  $b = \frac{RT_c}{8P_c} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 647.14 \text{ K}}{8 \times 220.64 \text{ bar}} = 0.0305 \text{ L mol}^{-1}$

$$a = \frac{27R^2 T_c^2}{64P_c} = \frac{27 \times (8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1})^2 \times (647.14 \text{ K})^2}{64 \times 220.64 \text{ bar}} = 5.53 \text{ L}^2 \text{ bar mol}^{-2}$$

- P7.3** Assume that the equation of state for a gas can be written in the form  $P(V_m - b(T)) = RT$ . Derive an expression for  $\beta = 1/V(\partial V/\partial T)_P$  and  $\kappa = -1/V(\partial V/\partial P)_T$  for such a gas in terms of  $b(T)$ ,  $db(T)/dT$ ,  $P$ , and  $V_m$ .

$$P\left(\frac{V}{n} - b(T)\right) = RT; \quad \frac{V}{n} = \frac{RT}{P} + b(T)$$

$$V = nb(T) + \frac{nRT}{P}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{ndb(T)}{dT} + \frac{nR}{P}\right) = \frac{1}{V_m}\left(\frac{db(T)}{dT} + \frac{R}{P}\right)$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{nRT}{P^2}\right) = \frac{RT}{V_m P^2}$$

- P7.4** One mole of Ar initially at 310. K undergoes an adiabatic expansion against a pressure  $P_{\text{external}} = 0$  from a volume of 8.5 L to a volume of 82.0 L. Calculate the final temperature using the ideal gas and van der Waals equations of state. Assume  $C_{V,m} = 3/2 R$ .

$w = q = 0$ .  $\Delta U = 0$  for an ideal gas and  $\Delta T = 0$  because  $U$  is a function of  $T$  only. There is no change in temperature for the ideal gas;  $T = 310$ . K. Using the results of Example Problem 3.5 for a van der Waals gas, because  $w = 0$  and  $q = 0$ ,  $\Delta U = 0$ . Therefore the change in  $U$  due to expansion,  $\Delta U_V$ , must be equal in magnitude to the change in  $U$  due to the change in temperature,  $\Delta U_T$ .

$$\Delta U_V = n^2 a \left( \frac{1}{V_{m,i}} - \frac{1}{V_{m,f}} \right)$$

$$= 1 \text{ mol}^2 \times 1.355 \text{ dm}^6 \text{ bar mol}^{-2} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times \frac{10^{-6} \text{ m}^6}{\text{dm}^6}$$

$$\times \left( \frac{1}{8.5 \times 10^{-3} \text{ m}^3} - \frac{1}{82.0 \times 10^{-3} \text{ m}^3} \right)$$

$$= 14.3 \text{ J}$$

$$\Delta U_T = -\Delta U_V$$

$$\Delta T = \frac{\Delta U_T}{nC_{V,m}} = \frac{-14.3 \text{ J}}{1 \text{ mol} \times 1.5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} = -1.15 \text{ K}$$

$$T_f = 309 \text{ K}$$

- P7.5** Calculate the  $P$  and  $T$  values for which  $\text{Br}_2(g)$  is in a corresponding state to  $\text{Xe}(g)$  at 330. K and 72.0 bar.

The gases are in corresponding states if the reduced pressures and temperatures have the same values. Using the data in Table 7.2,

$$T_R^{\text{Xe}} = \frac{T^{\text{Xe}}}{T_C^{\text{Xe}}} = \frac{330. \text{ K}}{289.74 \text{ K}} = 1.14; \quad T^{\text{Br}_2} = 1.14 T_C^{\text{Br}_2} = 1.14 \times 588 \text{ K} = 670. \text{ K}$$

$$P_R^{\text{Xe}} = \frac{P^{\text{Xe}}}{P_C^{\text{Xe}}} = \frac{72.0 \text{ bar}}{58.40 \text{ bar}} = 1.23; \quad P^{\text{Br}_2} = 1.23 P_C^{\text{Br}_2} = 1.23 \times 103.4 \text{ bar} = 127 \text{ bar}$$

- P7.6** For values of  $z$  near one, it is a good approximation to write  $z(P) = 1 + (\partial z/\partial P)_T P$ . If  $z = 1.00104$  at 298 K and 1 bar, and the Boyle temperature of the gas is 155 K, calculate the values of  $a$ ,  $b$ , and  $V_m$  for the van der Waals gas.

From Example Problem 7.2,

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

We can write three equations in three unknowns:

$$z - 1 = \left( b - \frac{a}{RT} \right) \frac{P}{RT}$$

$$1.04 \times 10^{-3} = \left( b - \frac{a}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} \right) \times \frac{1 \text{ bar}}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}$$

$$T_B = \frac{a}{Rb} = \frac{a}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times b} = 155 \text{ K}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{V_m - b} - \frac{a}{V_m} = 1 \text{ bar}$$

Using an equation solver, we obtain  $a$  and  $b$  by solving the first two equations simultaneously. We substitute these values into the third equation to obtain  $V_m$ .

The results are:

$$a = 0.692 \text{ L}^2 \text{ bar mol}^{-2}, \quad b = 0.0537 \text{ L mol}^{-1}, \quad V_m = 24.8 \text{ L mol}^{-1}$$

**P7.7** For a gas at a given temperature, the compression factor  $z$  is described by the empirical equation

$$z = 1 - 8.50 \times 10^{-3} \frac{P}{P^\circ} + 3.50 \times 10^{-5} \left( \frac{P}{P^\circ} \right)^2$$

where  $P^\circ = 1 \text{ bar}$ . Calculate the fugacity coefficient for  $P = 150., 250., 350., 450.,$  and  $550. \text{ bar}$ . For which of these values is the fugacity coefficient greater than 1?

$$\ln \gamma = \int_0^P \frac{z - 1}{P'} dP' = \int_0^P \frac{\left( 1 - 8.50 \times 10^{-3} \frac{P'}{P^\circ} + 3.50 \times 10^{-5} \left( \frac{P'}{P^\circ} \right)^2 \right) - 1}{P'} dP'$$

$$\ln \gamma = -8.50 \times 10^{-3} \frac{P}{P^\circ} + 1.75 \times 10^{-5} \left( \frac{P}{P^\circ} \right)^2$$

$\gamma = 0.414, 0.357, 0.436, 0.755,$  and  $1.86$  at  $150., 250., 350., 450.,$  and  $550. \text{ bar}$ , respectively.

**P7.8** The experimentally determined density of  $\text{O}_2$  at  $140. \text{ bar}$  and  $298 \text{ K}$  is  $192 \text{ g L}^{-1}$ . Calculate  $z$  and  $V_m$  from this information. Compare this result with what you would have estimated from Figure 7.8. What is the relative error in using Figure 7.8 for this case?

$$V_m = \frac{M}{\rho} = \frac{32.0 \text{ g mol}^{-1}}{192 \text{ g L}^{-1}} = 0.167 \text{ L mol}^{-1}$$

$$z = \frac{PV_m}{RT} = \frac{140. \text{ bar} \times 1.67 \times 10^{-1} \text{ L mol}^{-1}}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.942$$

Because  $P_r = \frac{140. \text{ bar}}{50.43 \text{ bar}} = 2.78$  and  $T_r = \frac{298 \text{ K}}{154.58 \text{ K}} = 1.93$ , Figure 7.8 predicts  $z = 0.88$ . The relative error in  $z$  is 6.6%.

**P7.9** At  $725 \text{ K}$  and  $280. \text{ bar}$ , the experimentally determined density of  $\text{N}_2$  is  $4.13 \text{ mol L}^{-1}$ . Compare this with values calculated from the ideal and Redlich-Kwong equations of state. Use a numerical equation solver to solve the Redlich-Kwong equation for  $V_m$  or use an iterative approach starting with  $V_m$  equal to the ideal gas result. Discuss your results.

We use the data in Table 7.4 for the Redlich-Kwong equation. For the ideal gas,

$$\frac{1}{V_m} = \frac{P}{RT} = \frac{280. \text{ bar}}{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 725 \text{ K}} = 4.65 \text{ mol L}^{-1}$$

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

$$280. \text{ bar} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 725 \text{ K}}{V_m - 0.02675 \text{ L mol}^{-1}} - \frac{15.55 \text{ L}^2 \text{ bar mol}^{-2} \text{ K}^{1/2}}{\sqrt{725 \text{ K}} V_m (V_m + 0.02675 \text{ L mol}^{-1})}$$

The three solutions to this equation are

$$V_m = (-0.00988 \pm 0.0117i) \text{ L mol}^{-1} \text{ and } V_m = 0.235 \text{ L mol}^{-1}$$

Only the real solution is of significance.

$$\frac{1}{V_m} = \frac{1}{0.235 \text{ L mol}^{-1}} = 4.25 \text{ mol L}^{-1}$$

The ideal gas density is greater than that calculated with the Redlich-Kwong equation of state, and the experimental result shows that the repulsive part of the potential dominates.

- P7.10** A 1.75 mole sample of Ar undergoes an isothermal reversible expansion from an initial volume of 2.00 L to a final volume of 85.00 L at 310. K. Calculate the work done in this process using the ideal gas and van der Waals equations of state. What percentage of the work done by the van der Waals gas arises from the attractive potential?

For the ideal gas,

$$w = -nRT \ln \frac{V_f}{V_i} = -1.75 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310. \text{ K} \times \ln \frac{85.0 \text{ L}}{2.00 \text{ L}}$$

$$= -16.9 \times 10^3 \text{ J}$$

For the van der Waals gas,

$$w = - \int_{V_i}^{V_f} \left( \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \right) dV = - \left[ nRT \ln(V - nb) + \frac{an^2}{V} \right]_{V_i}^{V_f}$$

$$= - \left[ 1.75 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310. \text{ K} \times \ln(V - 3.20 \times 10^{-5} \text{ m}^3) + \frac{(1.75 \text{ mol})^2 \times 0.1355 \text{ Pa m}^6}{V} \right]_{0.00200 \text{ m}^3}^{0.08500 \text{ m}^3}$$

$$= -17.0 \times 10^3 \text{ J} + 202.6 \text{ J} = -16.8 \times 10^3 \text{ J}$$

$$100 \times \frac{202.6 \text{ J}}{-16.8 \times 10^3 \text{ J}} = -1.2\%$$

- P7.11** Show that the second virial coefficient for a van der Waals gas is given by

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

Rather than differentiating with respect to  $\frac{1}{V_m}$ , we introduce the variable  $u = \frac{1}{V_m}$ .

Using this variable, 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  $B(T) = \frac{1}{2RT} \left[ \frac{d^2P(u)}{du^2} \right]_{u=0}$ .

We carry out this differentiation for the van der Waals equation written in terms of the variable  $u$ .

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

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

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

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

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

- P7.12** The volume of a spherical molecule can be estimated as  $V = b/(4N_A)$ , where  $b$  is the van der Waals parameter for the excluded molar volume and  $N_A$  is Avogadro's number. Justify this relationship by considering a spherical molecule of radius  $r$ , with volume  $V = 4/3\pi r^3$ . What is the volume centered at the molecule that is excluded for the center of mass of a second molecule in terms of  $V$ ? Multiply this volume by  $N_A$  and set it equal to  $b$ . Apportion this volume equally among the molecules to arrive at  $V = b/(4N_A)$ . Calculate the radius of a methane molecule from the value of its van der Waals parameter  $b$ .

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  $V_{\text{molecule}} = b/(4N_A)$ . We obtain the value for  $b$  from Table 7.4.

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

$$r = \left( \frac{3b}{16N_A\pi} \right)^{\frac{1}{3}} = \left( \frac{3 \times 0.431 \times 10^{-4} \text{ m}^3}{16\pi \times 6.022 \times 10^{23}} \right)^{\frac{1}{3}} = 1.62 \times 10^{-10} \text{ m}$$

- P7.13** Show that the van der Waals and Redlich-Kwong equations of state reduce to the ideal gas equation of state in the limit of low density.

$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$ : 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  $\frac{RT}{V_m - b} \rightarrow \frac{RT}{V_m}$ .

**P7.14** Use the law of corresponding states and Figure 7.8 to estimate the molar volume of propane at  $T = 500$  K and  $P = 75.0$  bar. The experimentally determined value is  $0.438 \text{ mol L}^{-1}$ . What is the relative error of your estimate?

We use the values for the critical constants in Table 7.2.

$$T_r = \frac{500 \text{ K}}{369.83 \text{ K}} = 1.35 \quad P_r = \frac{75.0 \text{ bar}}{42.48 \text{ bar}} = 1.77$$

Therefore,  $z \approx 0.72$ .

$$\frac{PV_m}{RT} = 0.72; \quad V_m = 0.72 \frac{RT}{P} = 0.72 \times \frac{8.314 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}{75.0 \text{ bar}}$$

$$V_m = 0.399 \text{ L mol}^{-1}$$

$$\text{Relative error} = 100 \times \frac{V_m - V_m^{\text{exp}}}{V_m^{\text{exp}}} = \frac{0.399 \text{ L mol}^{-1} - 0.438 \text{ L mol}^{-1}}{0.438 \text{ L mol}^{-1}} = -8.9\%$$

**P7.15** Another equation of state is the Berthelot equation,  $V_m = (RT/P) + b - a/(RT^2)$ . Derive expressions for  $\beta = 1/V(\partial V/\partial T)_P$  and  $\kappa = -1/V(\partial V/\partial P)_T$  from the Berthelot equation in terms of  $V$ ,  $T$ , and  $P$ .

$$V = \frac{nRT}{P} + nb - \frac{na}{RT^2}$$

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left( \frac{nR}{P} + \frac{2na}{RT^3} \right) = \frac{1}{V_m} \left( \frac{R}{P} + \frac{2a}{RT^3} \right)$$

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( -\frac{nRT}{P^2} \right) = \frac{nRT}{P^2 V} = \frac{RT}{P^2 V_m}$$

**P7.16** Show that  $P\kappa = 1 - P \left( \frac{\partial \ln z}{\partial P} \right)_T$  for a real gas where  $\kappa$  is the isothermal compressibility.

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T; \quad P\kappa = -\frac{P}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$z = \frac{V}{V_{\text{ideal}}} = \frac{PV}{nRT}; \quad \ln z = \ln(PV) - \ln(nRT)$$

$$\left( \frac{\partial \ln z}{\partial P} \right)_T = \frac{1}{PV} \times \left[ V + P \left( \frac{\partial V}{\partial P} \right)_T \right] = \frac{1}{P} + \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \left( \frac{\partial \ln z}{\partial P} \right)_T - \frac{1}{P}$$

$$\text{Therefore } P\kappa = 1 - P \left( \frac{\partial \ln z}{\partial P} \right)_T.$$

**P7.17** Calculate the van der Waals parameters of carbon dioxide from the values of the critical constants and compare your results with the values for  $a$  and  $b$  in Table 7.4.

We use the values for the critical constants in Table 7.2.



$$b = \frac{RT_c}{8P_c} = \frac{8.314 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1} \times 304.13 \text{ K}}{8 \times 73.75 \text{ bar}} = 0.04286 \text{ dm}^3 \text{ mol}^{-1}$$

$$a = \frac{27R^2T_c^2}{64P_c} = \frac{27 \times (8.314 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1})^2 \times (304.13 \text{ K})^2}{64 \times 73.75 \text{ bar}}$$

$$= 3.657 \text{ dm}^6 \text{ bar mol}^{-2}$$

- P7.18** Calculate the Redlich-Kwong parameters of fluorine from the values of the critical constants and compare your results with the values for  $a$  and  $b$  in Table 7.4.

We use the values for the critical constants in Table 7.2.

$$a = \frac{R^2T_c^{5/2}}{9P_c(2^{1/3}-1)} = \frac{(8.314 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1})^2 \times (144.3 \text{ K})^{5/2}}{9 \times 51.72 \text{ bar} (2^{1/3}-1)}$$

$$= 14.29 \text{ dm}^6 \text{ bar K}^2 \text{ mol}^{-2}$$

$$b = \frac{(2^{1/3}-1)RT_c}{3P_c} = \frac{(2^{1/3}-1) \times 8.314 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1} \times 144.3 \text{ K}}{3 \times 51.72 \text{ bar}}$$

$$= 0.02010 \text{ dm}^3 \text{ mol}^{-1}$$

- P7.19** Calculate the critical volume for ethane using the data for  $T_c$  and  $P_c$  in Table 7.2 (see Appendix B, Data Tables) assuming (a) the ideal gas equation of state and (b) the van der Waals equation of state. Use an iterative approach to obtain  $V_c$  from the van der Waals equation, starting with the ideal gas result. How well do the calculations agree with the tabulated values for  $V_c$ ?

Using the ideal gas law,

$$V_c = \frac{RT_c}{P_c} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 305.32 \text{ K}}{48.72 \text{ bar}} = 0.5210 \text{ L}$$

Using the van der Waals equation of state,

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 305.32 \text{ K}}{V_c - 0.0651 \text{ L mol}^{-1}} - \frac{5.580 \text{ L}^2 \text{ bar mol}^{-2}}{V_c^2}$$

Setting  $V_c = 0.150, 0.200, 0.250, 0.300,$  and  $0.350$  gives  $P_c = 51.0, 48.7, 48.0, 46.0,$  and  $43.5$  bar, respectively. We repeat the calculation for  $0.160, 0.170, 0.180, 0.190, 0.120,$  and  $0.121$  L, and obtain the values  $49.52, 48.91, 48.70, 48.67, 48.67,$  and  $48.65$  bar, respectively. The best agreement is for  $0.180$  L. The tabulated value for  $V_c$  is  $0.1455$  L, which is reasonably close to the van der Waals value. The ideal gas value is far from correct.

- P7.20** Show that  $T\beta = 1 + T\left(\frac{\partial \ln z}{\partial T}\right)_P$  for a real gas where  $\beta$  is the volumetric thermal expansion coefficient.

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

$$z = \frac{V}{V_{\text{ideal}}} = \frac{PV}{nRT}; \quad \ln z = \ln \left( \frac{P}{nR} \right) + \ln \left( \frac{V}{T} \right)$$

$$\left( \frac{\partial \ln z}{\partial T} \right)_P = \frac{T}{V} \left( \frac{\partial [V/T]}{\partial T} \right)_P = \frac{T}{VT} \left( \frac{\partial V}{\partial T} \right)_P - \frac{T}{VT^2} = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P - \frac{1}{T}$$

$$\left( \frac{\partial \ln z}{\partial T} \right)_P = \beta - \frac{1}{T}$$

$$\text{Therefore } T\beta = 1 + T \left( \frac{\partial \ln z}{\partial T} \right)_P.$$

- P7.21** At what temperature does the slope of the  $z$  versus  $P$  curve as  $P \rightarrow 0$  have its maximum value for a van der Waals gas? What is the value of the maximum slope?

$$\left(\frac{\partial z}{\partial P}\right)_{T,P \rightarrow 0} = \frac{1}{RT} \left(b - \frac{a}{RT}\right)$$

For a van der Waals gas

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial z}{\partial P}\right)\right)_{T,P \rightarrow 0} = -\frac{1}{RT^2} \left(b - \frac{a}{RT}\right) + \frac{1}{RT^3} = -\frac{1}{RT^2} \left(b - \frac{2a}{RT}\right)$$

Setting this derivative equal to zero gives

$$b - \frac{2a}{RT_{\max}} = 0 \quad T_{\max} = \frac{2a}{Rb}$$

$$\text{The maximum slope is } \frac{1}{RT_{\max}} \left(b - \frac{a}{RT_{\max}}\right) = \frac{b}{2a} \left[b - a \left(\frac{b}{2a}\right)\right] = \frac{b^2}{4a}$$

- P7.22** Calculate the density of  $O_2(g)$  at 480. K and 280. bar using the ideal gas and the van der Waals equations of state. Use a numerical equation solver to solve the van der Waals equation for  $V_m$  or use an iterative approach starting with  $V_m$  equal to the ideal gas result. Based on your result, does the attractive or repulsive contribution to the interaction potential dominate under these conditions? The experimentally determined result is 208 g/L. What is the relative error of each of your two calculations?

$$V_m = \frac{RT}{P} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 480. \text{ K}}{280. \text{ bar}} = 0.1425 \text{ L}$$

$$P_{vdW} = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$= \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 480. \text{ K}}{V_m - 0.0319 \text{ L mol}^{-1}} - \frac{1.382 \text{ L}^2 \text{ bar mol}^{-2}}{(V_m)^2} = 280 \text{ bar}$$

The three solutions to this equation are

$$V_m = (0.01306 \pm 0.02985 i) \text{ L mol}^{-1} \text{ and } V_m = 0.1483 \text{ L mol}^{-1}$$

Only the real solution is of significance.

$$\rho_{\text{ideal gas}} = \frac{M}{V_m} = \frac{32.0 \text{ g mol}^{-1}}{0.1425 \text{ L mol}^{-1}} = 224 \text{ g L}^{-1}$$

$$\rho_{vdW} = \frac{M}{V_m} = \frac{32.0 \text{ g mol}^{-1}}{0.1483 \text{ L mol}^{-1}} = 216 \text{ g L}^{-1}$$

Because the van der Waals density is less than the ideal gas density, the repulsive part of the potential dominates. The relative error is 7.94% and 3.75% for the ideal gas and van der Waals equations of state, respectively.

- P7.23** Show that  $T\beta = 1 + T(\partial \ln z / \partial T)_P$  and that  $P\kappa = 1 - P(\partial \ln z / \partial P)_T$ .

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P; \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$z = \frac{PV}{RT}; \quad \left(\frac{\partial z}{\partial T}\right)_P = -\frac{VP}{RT^2} + \frac{P}{RT} \left(\frac{\partial V}{\partial T}\right)_P = -\frac{VP}{RT^2} + \frac{PV}{RT} \beta$$

$$\left(\frac{\partial \ln z}{\partial T}\right)_P = \frac{1}{z} \left(\frac{\partial z}{\partial T}\right)_P = \frac{RT}{VP} \left(-\frac{VP}{RT^2} + \frac{PV}{RT} \beta\right) = -\frac{1}{T} + \beta$$

$$\text{Therefore } 1 + T \left(\frac{\partial \ln z}{\partial T}\right)_P = 1 + T \left(-\frac{1}{T} + \beta\right) = \beta T.$$

$$\left(\frac{\partial z}{\partial P}\right)_T = \frac{V}{RT} + \frac{P}{RT} \left(\frac{\partial V}{\partial P}\right)_T = \frac{V}{RT} - \frac{PV}{RT^2} \kappa$$

$$\left(\frac{\partial \ln z}{\partial P}\right)_T = \frac{1}{z} \left(\frac{\partial z}{\partial P}\right)_T = \frac{RT}{PV} \left(\frac{V}{RT} - \frac{PV}{RT^2} \kappa\right) = \frac{1}{P} - \kappa$$

$$\text{Therefore } 1 - P \left(\frac{\partial \ln z}{\partial P}\right)_T = 1 - P \left(\frac{1}{P} - \kappa\right) = P\kappa$$

- P7.24** A sample containing 42.1 g of Ar is enclosed in a container of volume 0.0885 L at 375 K. Calculate  $P$  using the ideal gas, van der Waals, and Redlich–Kwong equations of state. Based on your results, does the attractive or repulsive contribution to the interaction potential dominate under these conditions?

$$V_m = \frac{0.0885 \text{ L}}{42.1 \text{ g}} \times \frac{39.95 \text{ g}}{\text{mol}} = 0.08398 \text{ L mol}^{-1}$$

$$P_{\text{ideal gas}} = \frac{RT}{V_m} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 375 \text{ K}}{0.08398 \text{ L mol}^{-1}} = 371 \text{ bar}$$

$$P_{\text{vdW}} = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 375 \text{ K}}{0.08398 \text{ L mol}^{-1} - 0.0320 \text{ L mol}^{-1}} - \frac{1.355 \text{ L}^2 \text{ bar mol}^{-2}}{(0.0885 \text{ L mol}^{-1})^2}$$

$$= 408 \text{ bar}$$

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

$$= \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 375 \text{ K}}{0.08398 \text{ L mol}^{-1} - 0.02219 \text{ L mol}^{-1}} - \frac{16.86 \text{ L}^2 \text{ bar mol}^{-2} \text{ K}^{1/2}}{\sqrt{375 \text{ K}} \cdot 0.08398 \text{ L mol}^{-1} (0.08398 \text{ L mol}^{-1} + 0.02219 \text{ L mol}^{-1})}$$

$$P_{\text{RK}} = 407 \text{ bar}$$

Because  $P_{\text{R-K}}$  and  $P_{\text{vdW}} > P_{\text{ideal gas}}$ , the repulsive part of the interaction dominates.

- P7.25** The experimental critical constants of  $\text{CH}_4$  are found in Table 7.2. Use the values of  $P_c$  and  $T_c$  to calculate  $V_c$ . Assume that  $\text{CH}_4$  behaves as (a) an ideal gas, (b) a van der Waals gas, and (c) a Redlich–Kwong gas at the critical point. For parts (b) and (c), use the formulas for the critical compression factor. Compare your answers with the experimental value. Are any of your calculated results close to the experimental value in Table 7.2?

Assuming an ideal gas,

$$V_c = \frac{RT_c}{P_c} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 190.56 \text{ K}}{45.99 \text{ bar}} = 0.344 \text{ L}$$

For a van der Waals gas,

$$z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8}; \quad V_c = \frac{3 RT_c}{8 P_c} = \frac{3}{8} \times \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 190.56 \text{ K}}{45.99 \text{ bar}} = 0.129 \text{ L}$$

For a Redlich–Kwong gas,

$$z_c = \frac{P_c V_c}{RT_c} = 0.333; \quad V_c = 0.333 \frac{RT_c}{P_c} = 0.333 \times \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 190.56 \text{ K}}{45.99 \text{ bar}}$$

$$= 0.115 \text{ L}$$

Although the agreement with experiment is significantly better for the van der Waals and Redlich–Kwong models than for the ideal gas model, all results differ from the true value of 0.0986 L.