(a) \[ R = \frac{V_p \rho}{e \rho} = \frac{55.95 \times 10^{-2} \text{ L mol}^{-1} \times 220.64 \text{ bar}}{0.229 \times 647.14 \text{ K}} = 8.33 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \]

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

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

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

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

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 \( C_{p,m} = 3/2 \ R \).

\( w = q = 0 \), \( \Delta U = 0 \) 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; \( T_f = 310 \text{ K} \). 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, \( \Delta U_r \), must be equal in magnitude to the change in \( U \) due to the change in temperature, \( \Delta U_T \).

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

\[ = 1 \text{ mol}^2 \times 1.355 \text{ dm}^6 \text{ bar mol}^{-2} \times \frac{10^5 \text{ Pa bar}}{\text{bar} \times 10^{-9} \text{ m}^6} \times \left( \frac{1}{8.5 \times 10^{-3} \text{ m}^3} - \frac{1}{82.0 \times 10^{-3} \text{ m}^3} \right) \]

\[ = 14.3 \text{ J} \]

\[ \Delta U_T = -\Delta U_r = -14.3 \text{ J} \]

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

\( T_f = 309 \text{ K} \)
For a gas at a given temperature, the compression factor \( z \) is described by the empirical equation

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

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

\[
\ln \gamma = \int_{0}^{1} \frac{1 - 8.50 \times 10^{-3} \frac{P'}{P^*} + 3.50 \times 10^{-5} \left( \frac{P'}{P^*} \right)^2}{P'} \, dP'
\]

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

\( z = 0.414, 0.357, 0.436, 0.755, \) and 1.86 at 150, 250, 350, 450, and 550 bar, respectively.

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

For the ideal gas,

\[
w = -nRT \ln \frac{V_f}{V_i} = -1.75 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310. \text{ K} \times \ln \frac{85.0 \text{ L}}{200 \text{ L}} = -16.9 \times 10^3 \text{ J}
\]

For the van der Waals gas,

\[
w = \left[ \frac{nRT}{V - nb - \frac{n^2 a}{V^2}} \right] V_i = \left[ \frac{nRT \ln(V - nb) + \frac{n^2 a^2}{V^2}}{V_i} \right] V_i
\]

\[
= -\left[ 1.75 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310. \text{ K} \times \ln\left( V - 3.20 \times 10^{-5} \text{ m}^3 \right) + \frac{(1.75 \text{ mol})^2 \times 0.1355 \text{ Pa m}^6}{V} \right] \frac{0.08590 \text{ m}^3}{\ln 0.00200 \text{ m}^3}
\]

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

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

(\text{Note: Work is shown by)}

\[\text{A van der Waals gas has a value of } z = 1.0061 \text{ at 410. K and 1 bar and the Boyle temperature of the gas is 195 K. Because the density is low, you can calculate } V_m \text{ from the ideal gas law. Use this information and the result of Problem 7.28, } z = 1 + \left( b - \frac{a}{RT} \right)(V/V_m), \text{ to estimate } a \text{ and } b.\]

\[
z = 1 = \frac{1}{V_m} \left( \frac{b - \frac{a}{RT}}{RT} \right)
\]

\[
z = 1 = \frac{b}{V_m} \left( \frac{T}{RT} \right)
\]

\[
b = \frac{z - 1}{1 - \frac{T}{T_B}} \frac{RT}{P} = \frac{0.0061}{1 - \frac{195 \text{ K}}{410 \text{ K}}} \times 8.314 \times 10^{-2} \text{ dm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} \times 410. \text{ K} = 0.0397 \text{ dm}^3 \text{ mol}^{-1} = 3.97 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}
\]

\[
a = Rbb = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.97 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \times 195 \text{ K} = 6.43 \times 10^{-2} \text{ m}^6 \text{ Pa mol}^{-2}
\]
P7.3 Assume that the equation of state for a gas can be written in the form \( P(V_n - b(T)) = RT \). Derive an expression for \( \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \) and \( \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \) for such a gas in terms of \( b(T) \), \( db(T)/dT \), \( P \), and \( V_n \).

\[
\begin{align*}
& P \left( \frac{V_n - b(T)}{n} \right) = RT; \quad \frac{V_n}{n} = \frac{RT}{P} + b(T) \\
& V = nb(T) + \frac{nRT}{P} \\
& \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left( \frac{n db(T)}{dT} + \frac{nR}{P} \right) = \frac{1}{V_n} \left( \frac{db(T)}{dT} + \frac{R}{P} \right) \\
& \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{nRT}{T^2} \right) = \frac{RT}{V_n P^2}
\end{align*}
\]

P7.8 The experimentally determined density of \( \text{O}_2 \) at 140 bar and 298 K is 192 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 6.2%.

P7.14 Use the law of corresponding states and Figure 7.8 to estimate the molar volume of propane at \( T = 500. \text{K} \) and \( P = 75.0 \text{ bar} \). The experimentally determined value is 0.438 L mol\(^{-1}\). 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, \( z = 0.72 \).

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

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

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