The maximum value of S is around $\alpha = 0.27$. The values of $S(\alpha)$ close to $\alpha = 0.271$ are given below.

α	0.2700	0.2705	0.2710	0.2715	0.2720
$S(\alpha)$	0.9784029	0.9784041	0.9784044	0.9784039	0.9784024

The Properties of Gases

PROBLEMS AND SOLUTIONS

16–1. In an issue of the journal *Science* a few years ago, a research group discussed experiments in which they determined the structure of cesium iodide crystals at a pressure of 302 gigapascals (GPa). How many atmospheres and bars is this pressure?

2.98×10^6 atm, 3.02×10^6 bar

16–2. In meteorology, pressures are expressed in units of millibars (mbar). Convert 985 mbar to torr and to atmospheres.

739 torr, 0.972 atm

16–3. Calculate the value of the pressure (in atm) exerted by a 33.9-foot column of water. Take the density of water to be 1.00 g·mL^{-1}.

We first convert the height of the column to metric units: 33.9 ft = 10.33 m. Now

$$P = \rho g h = (1.00 \text{ kg·dm}^{-3})(98.067 \text{ dm·s}^{-2})(103.3 \text{ dm})$$
$$= 1.013 \times 10^4 \text{ kg·dm}^{-1}\text{·s}^{-2}$$
$$= 1.013 \times 10^5 \text{ Pa} = 1.00 \text{ atm}$$

16–4. At which temperature are the Celsius and Farenheit temperature scales equal?

$-40°$

16–5. A travel guide says that to convert Celsius temperatures to Farenheit temperatures, double the Celsius temperature and add 30. Comment on this recipe.

This will provide a rough estimate of the temperature, decreasing in accuracy as temperature increases. (Of course, it is not valid for Celsius temperatures below zero degrees.) At room temperatures, it is accurate enough for ordinary purposes.

Actual T (°C)	Actual T (°F)	Travel T (°F)
0	32	30
10	50	50
20	68	70
30	86	90
40	104	110

16–6. Research in surface science is carried out using ultra-high vacuum chambers that can sustain pressures as low as 10^{-12} torr. How many molecules are there in a 1.00-cm^3 volume inside such an apparatus at 298 K? What is the corresponding molar volume $\overline{V}$ at this pressure and temperature?

We will assume ideal gas behavior, so

$$\frac{PV}{RT} = n \qquad (16.1a)$$

$$\frac{(10^{-12}\,\text{torr})(1.00\,\text{cm}^3)}{(82.058\,\text{cm}^3\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(760\,\text{torr}\cdot\text{atm}^{-1})(298\,\text{K})} = n$$

$$5.38 \times 10^{-20}\,\text{mol} = n$$

so there are 3.24×10^4 molecules in the apparatus. The molar volume is

$$\overline{V} = \frac{V}{n} = \frac{1.00\,\text{cm}^3}{5.38 \times 10^{-20}\,\text{mol}} = 1.86 \times 10^{19}\,\text{cm}^3\cdot\text{mol}^{-1}$$

16–7. Use the following data for an unknown gas at 300 K to determine the molecular mass of the gas.

P/bar	0.1000	0.5000	1.000	1.01325	2.000
ρ/g·L^{-1}	0.1771	0.8909	1.796	1.820	3.652

The line of best fit of a plot of P/ρ versus ρ will have an intercept of RT/M. Plotting, we find that the intercept of this plot is 0.56558 bar·g^{-1}·dm^3, and so $M = 44.10$ g·mol^{-1}.

16–8. Recall from general chemistry that Dalton's law of partial pressures says that each gas in a mixture of ideal gases acts as if the other gases were not present. Use this fact to show that the partial pressure exerted by each gas is given by

$$P_j = \left(\frac{n_j}{\sum n_j}\right) P_{\text{total}} = y_j P_{\text{total}}$$

where P_j is the partial pressure of the jth gas and y_j is its mole fraction.

The ideal gas law (Equation 16.1) gives

$$P_{\text{total}}V = n_{\text{total}}RT = \sum_j n_j RT$$

and

$$P_j V = n_j RT$$

for all component gases j. Solving each expression for RT/V and equating the results gives

$$\frac{P_{\text{total}}}{\sum_j n_j} = \frac{P_j}{n_j}$$

or

$$P_j = \frac{n_j}{\sum_j n_j} P_{\text{total}} = y_j P_{\text{total}}$$

16–9. A mixture of $H_2(g)$ and $N_2(g)$ has a density of 0.216 g·L^{-1} at 300 K and 500 torr. What is the mole fraction composition of the mixture?

The density of the mixture is 0.216 g·L^{-1}, so there are 216 g of gas present in one m^3 of gas. Take the total volume of the mixture to be 1 m^3. Then, using the ideal gas law (Equation 16.1), we find

$$P_{\text{tot}}V = n_{\text{tot}}RT$$

$$500\,\text{torr}\left(\frac{101\,325\,\text{Pa}}{760\,\text{torr}}\right)1\,\text{m}^3 = n_{\text{tot}}\left(8.3145\,\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\right)(300\,\text{K})$$

$$26.7\,\text{mol} = n_{\text{tot}}$$

There are 26.7 mol of gas per cubic meter. Let x be the number of moles of hydrogen gas. Then $n_{\text{tot}} - x$ is the number of moles of nitrogen gas. Since $M_{H_2} = 2.01588$ g·mol^{-1} and $M_{N_2} = 28.01348$ g·mol^{-1}, we can write

$$216\,\text{g} = \left(28.01348\,\text{g}\cdot\text{mol}^{-1}\right)(26.7\,\text{mol} - x\,\text{mol}) + \left(2.01588\,\text{g}\cdot\text{mol}^{-1}\right)(x\,\text{mol})$$

$$26x = 532.6\,\text{g}$$

$$x = 20.5\,\text{g}$$

The mole fractions of each component of the mixture are therefore

$$y_{H_2} = \frac{n_{H_2}}{n_{\text{tot}}} = \frac{20.5\,\text{mol}}{26.7\,\text{mol}} = 0.77$$

and

$$y_{N_2} = \frac{n_{N_2}}{n_{\text{tot}}} = \frac{6.2\,\text{mol}}{26.7\,\text{mol}} = 0.23$$

16–10. One liter of $N_2(g)$ at 2.1 bar and two liters of Ar(g) at 3.4 bar are mixed in a 4.0-L flask to form an ideal-gas mixture. Calculate the value of the final pressure of the mixture if the initial and final temperature of the gases are the same. Repeat this calculation if the initial temperatures of the $N_2(g)$ and Ar(g) are 304 K and 402 K, respectively, and the final temperature of the mixture is 377 K. (Assume ideal-gas behavior.)

a. Initially, we have one liter of N_2 at 2.1 bar and two liters of Ar at 3.4 bar. We can use the ideal gas law (Equation 16.1) to find the number of moles of each gas:

$$n_{N_2} = \frac{P_{N_2} V_{N_2}}{RT}$$

$$n_{Ar} = \frac{P_{Ar} V_{Ar}}{RT}$$

$$= \frac{(2.1 \times 10^5 \text{ Pa})(1 \times 10^{-3} \text{ m}^3)}{RT}$$

$$= \frac{(3.4 \times 10^5 \text{ Pa})(2 \times 10^{-3} \text{ m}^3)}{RT}$$

$$= \frac{210 \text{ Pa·m}^3}{RT}$$

$$= \frac{680 \text{ Pa·m}^3}{RT}$$

The total moles of gas in the final mixture is the sum of the moles of each gas in the mixture, which is $(890 \text{ Pa·m}^3)/RT$. So (Equation 16.1)

$$P = \frac{nRT}{V} = \frac{890 \text{ Pa·m}^3}{0.0040 \text{ m}^3} = 2.2 \times 10^5 \text{ Pa} = 2.2 \text{ bar}$$

b. Here, the initial temperatures of N_2 and Ar are different from each other and from the temperature of the final mixture. From above,

$$n_{\text{total}} = n_{N_2} + n_{Ar} = \frac{210 \text{ Pa·m}^3}{R(304 \text{ K})} + \frac{680 \text{ Pa·m}^3}{R(402 \text{ K})}$$

Substituting into the ideal gas law (Equation 16.1),

$$P = \left[\frac{210 \text{ Pa·m}^3}{R(304 \text{ K})} + \frac{680 \text{ Pa·m}^3}{R(402 \text{ K})} \right] \left[\frac{R(377 \text{ K})}{0.0040 \text{ m}^3} \right]$$

$$= 2.2 \times 10^5 \text{ Pa} = 2.2 \text{ bar}$$

16–11. It takes 0.3625 g of nitrogen to fill a glass container at 298.2 K and 0.0100 bar pressure. It takes 0.9175 g of an unknown homonuclear diatomic gas to fill the same bulb under the same conditions. What is this gas?

The number of moles of each gas must be the same, because P, V, and T are held constant. The number of moles of nitrogen is

$$n_{N_2} = \frac{0.3625 \text{ g}}{28.0135 \text{ g·mol}^{-1}} = 1.294 \times 10^{-2} \text{ mol}$$

The molar mass of the unknown compound must be

$$M = \frac{0.9175 \text{ g}}{1.294 \times 10^{-2} \text{ mol}} = 70.903 \text{ g·mol}^{-1}$$

The homonuclear diatomic gas must be chlorine (Cl_2).

16–12. Calculate the value of the molar gas constant in units of $dm^3 \cdot torr \cdot K^{-1} \cdot mol^{-1}$.

$$R = 8.31451 \text{ J·mol}^{-1} \cdot \text{K}^{-1}$$

$$= (8.31451 \text{ Pa·m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \left(\frac{10 \text{ dm}}{1 \text{ m}} \right)^3 \left(\frac{760 \text{ torr}}{1.01325 \times 10^5 \text{ Pa}} \right)$$

$$= 62.3639 \text{ dm}^3 \cdot \text{torr} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

16–13. Use the van der Waals equation to plot the compressibility factor, Z, against P for methane for $T = 180$ K, 189 K, 190 K, 200 K, and 250 K. *Hint*: Calculate Z as a function of $\overline{V}$ and P as a function of $\overline{V}$, and then plot Z versus P.

For methane, $a = 2.3026$ $dm^6 \cdot bar \cdot mol^{-2}$ and $b = 0.043067$ $dm^3 \cdot mol^{-1}$. By definition,

$$Z = \frac{P\overline{V}}{RT}$$

and the van der Waals equation of state is (Equation 16.5)

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

We can create a parametric plot of Z versus P for the suggested temperatures, shown below. Note that the effect of molecular attraction becomes less important at higher temperatures, as observed in the legend of Figure 16.4.
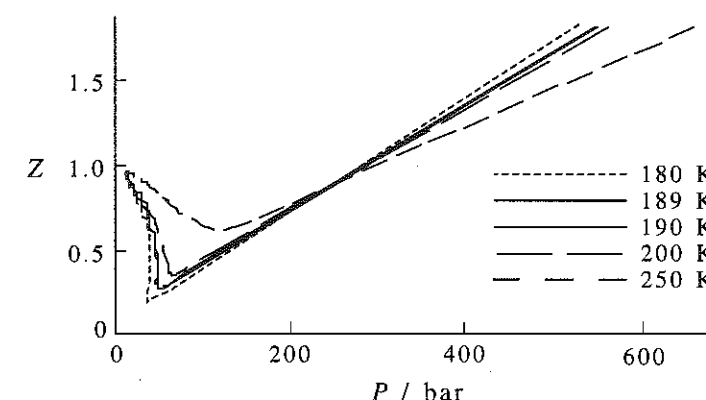
16–14. Use the Redlich-Kwong equation to plot the compressibility factor, Z, against P for methane for $T = 180$ K, 189 K, 190 K, 200 K, and 250 K. *Hint*: Calculate Z as a function of $\overline{V}$ and P as a function of $\overline{V}$, and then plot Z versus P.

For methane, $A = 32.205$ $dm^6 \cdot bar \cdot mol^{-2} \cdot K^{1/2}$ and $B = 0.029850$ $dm^3 \cdot mol^{-1}$. By definition,

$$Z = \frac{P\overline{V}}{RT}$$

and the Redlich-Kwong equation of state is (Equation 16.7)

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}(\overline{V} + B)}$$

We can create a parametric plot of Z versus P for the suggested temperatures, shown below. Note that the effect of molecular attraction becomes less important at higher temperatures, as observed in the legend of Figure 16.4.
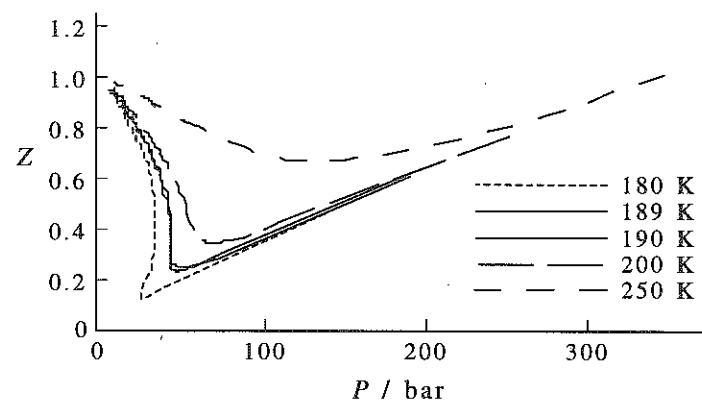
16–15. Use both the van der Waals and the Redlich-Kwong equations to calculate the molar volume of CO at 200 K and 1000 bar. Compare your result to the result you would get using the ideal-gas equation. The experimental value is 0.04009 L·mol^{-1}.

We can use the Newton-Raphson method (MathChapter G) to solve these cubic equations of state. We can express $f(\overline{V})$ for the van der Waals equation as (Example 16–2)

$$f(\overline{V}) = \overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P}$$

and $f'(\overline{V})$ as

$$f'(\overline{V}) = 3\overline{V}^2 - 2\left(b + \frac{RT}{P}\right)\overline{V} + \frac{a}{P}$$

For CO, $a = 1.4734$ dm^6·bar·mol^{-2} and $b = 0.039523$ dm^3·mol^{-1} (Table 16.3). Then, using the Newton-Raphson method, we find that the van der Waals equation gives a result of $\overline{V} = 0.04998$ dm^3·mol^{-1}. Likewise, we can express $f(\overline{V})$ for the Redlich-Kwong equation as (Equation 16.9)

$$f(\overline{V}) = \overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)\overline{V} - \frac{AB}{T^{1/2}P}$$

and $f'(\overline{V})$ as

$$f'(\overline{V}) = 3\overline{V}^2 - \frac{2RT}{P}\overline{V} - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)$$

For CO, $A = 17.208$ dm^6·bar·mol^{-2}·K$^{1/2}$ and $B = 0.027394$ dm^3·mol^{-1} (Table 16.4). Applying the Newton-Raphson method, we find that the Redlich-Kwong equation gives a result of $\overline{V} = 0.03866$ dm^3·mol^{-1}. Finally, the ideal gas equation gives (Equation 16.1)

$$\overline{V} = \frac{RT}{P} = \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(200 \text{ K})}{1000 \text{ bar}} = 0.01663 \text{ dm}^3\cdot\text{mol}^{-1}$$

The experimental value of 0.04009 dm^3·mol^{-1} is closest to the result given by the Redlich-Kwong equation (the two values differ by about 3%).

16–16. Compare the pressures given by (a) the ideal-gas equation, (b) the van der Waals equation, (c) the Redlich-Kwong equation, and (d) the Peng-Robinson equation for propane at 400 K and $\rho = 10.62$ mol·dm^{-3}. The experimental value is 400 bar. Take $\alpha = 9.6938$ L^2·mol^{-2} and $\beta = 0.05632$ L·mol^{-1} for the Peng-Robinson equation.

The molar volume corresponding to a density of 10.62 mol·dm^{-3} is 0.09416 dm^3·mol^{-1}.

a. The ideal gas equation gives a pressure of (Equation 16.1)

$$P = \frac{RT}{\overline{V}} = \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(400 \text{ K})}{0.09416 \text{ dm}^3\cdot\text{mol}^{-1}} = 353.2 \text{ bar}$$

b. The van der Waals equation gives a pressure of (Equation 16.5)

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

For propane, $a = 9.3919$ dm^6·bar·mol^{-2} and $b = 0.090494$ dm^3·mol^{-1} (Table 16.3). Then

$$P = \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(400 \text{ K})}{0.09416 \text{ dm}^3\cdot\text{mol}^{-1} - 0.090494 \text{ dm}^3\cdot\text{mol}^{-1}} - \frac{9.3919 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}}{(0.09416 \text{ dm}^3\cdot\text{mol}^{-1})^2}$$
$$= 8008 \text{ bar}$$

c. The Redlich-Kwong equation gives a pressure of (Equation 16.7)

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}(\overline{V} + B)}$$

For propane, $A = 183.02$ dm^6·bar·mol^{-2}·K$^{1/2}$ and $B = 0.062723$ dm^3·mol^{-1} (Table 16.4). Then

$$P = \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot^{-1})(400 \text{ K})}{0.09416 \text{ dm}^3\cdot\text{mol}^{-1} - 0.062723 \text{ dm}^3\cdot\text{mol}^{-1}}$$
$$- \frac{183.02 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}\cdot\text{K}^{1/2}}{(400 \text{ K})^{1/2}(0.09416 \text{ dm}^3\cdot\text{mol}^{-1})(0.09416 \text{ dm}^3\cdot\text{mol}^{-1} + 0.062723 \text{ dm}^3\cdot\text{mol}^{-1})}$$
$$= 438.4 \text{ bar}$$

d. The Peng-Robinson equation gives a pressure of (Equation 16.8)

$$P = \frac{RT}{\overline{V} - \beta} - \frac{\alpha}{\overline{V}(\overline{V} + \beta) + \beta(\overline{V} - \beta)}$$

For propane, $\alpha = 9.6938$ dm^6·bar·mol^{-2} and $\beta = 0.05632$ dm^3·mol^{-1}. Then

$$P = \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot^{-1})(400 \text{ K})}{0.09416 \text{ dm}^3\cdot\text{mol}^{-1} - 0.05632 \text{ dm}^3\cdot\text{mol}^{-1}}$$
$$- \frac{9.6938 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}}{(0.09416)(0.09416 + 0.05632) \text{ dm}^6\cdot\text{mol}^{-2} + (0.05632)(0.09416 - 0.05632) \text{ dm}^6\cdot\text{mol}^{-2}}$$
$$= 284.2 \text{ bar}$$

The Redlich-Kwong equation of state gives a pressure closest to the experimentally observed pressure (the two values differ by about 10%).

16–17. Use the van der Waals equation and the Redlich-Kwong equation to calculate the value of the pressure of one mole of ethane at 400.0 K confined to a volume of 83.26 cm^3. The experimental value is 400 bar.

Here, the molar volume of ethane is 0.08326 dm^3·mol^{-1}.

a. The van der Waals equation gives a pressure of (Equation 16.5)

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

For ethane, $a = 5.5818 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2}$ and $b = 0.065144 \text{ dm}^3 \cdot \text{mol}^{-1}$ (Table 16.3). Then

$$P = \frac{(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(400 \text{ K})}{0.08326 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.065144 \text{ dm}^3 \cdot \text{mol}^{-1}} - \frac{5.5818 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2}}{(0.08326 \text{ dm}^3 \cdot \text{mol}^{-1})^2}$$
$$= 1031 \text{ bar}$$

b. The Redlich-Kwong equation gives a pressure of (Equation 16.7)

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}(\overline{V} + B)}$$

For ethane, $A = 98.831 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}$ and $B = 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}$ (Table 16.4). Then

$$P = \frac{(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(400 \text{ K})}{0.08326 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}}$$
$$- \frac{98.831 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}}{(400 \text{ K})^{1/2}(0.08326 \text{ dm}^3 \cdot \text{mol}^{-1})(0.08326 + 0.045153) \text{ dm}^3 \cdot \text{mol}^{-1}}$$
$$= 410.6 \text{ bar}$$

The value of P found using the Redlich-Kwong equation of state is the closest to the experimentally observed value (the two values differ by about 3%).

16–18. Use the van der Waals equation and the Redlich-Kwong equation to calculate the molar density of one mole of methane at 500 K and 500 bar. The experimental value is $10.06 \text{ mol} \cdot \text{L}^{-1}$.

We can use the Newton-Raphson method (MathChapter G) to solve the cubic equations of state for $\overline{V}$, and take the reciprocal to find the molar density. We use the experimentally observed molar volume of $0.09940 \text{ dm}^3 \cdot \text{mol}^{-1}$ as the starting point for the iteration. We can express $f(\overline{V})$ for the van der Waals equation as (Example 16–2)

$$f(\overline{V}) = \overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P}$$

and $f'(\overline{V})$ as

$$f'(\overline{V}) = 3\overline{V}^2 - 2\left(b + \frac{RT}{P}\right)\overline{V} + \frac{a}{P}$$

For methane, $a = 2.3026 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2}$ and $b = 0.043067 \text{ dm}^3 \cdot \text{mol}^{-1}$ (Table 16.3). Then (using the Newton-Raphson method) we find that the van der Waals equation gives a result of $\overline{V} = 0.09993 \text{ dm}^3 \cdot \text{mol}^{-1}$, which corresponds to a molar density of $10.01 \text{ mol} \cdot \text{dm}^{-3}$. Likewise, we can express $f(\overline{V})$ for the Redlich-Kwong equation as (Equation 16.9)

$$f(\overline{V}) = \overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)\overline{V} - \frac{AB}{T^{1/2}P}$$

and $f'(\overline{V})$ as

$$f'(\overline{V}) = 3\overline{V}^2 - \frac{2RT}{P}\overline{V} - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)$$

For methane, $A = 32.205 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}$ and $B = 0.029850 \text{ dm}^3 \cdot \text{mol}^{-1}$ (Table 16.4). Then (using the Newton-Raphson method) we find that the Redlich-Kwong equation gives a result of $\overline{V} = 0.09729 \text{ dm}^3 \cdot \text{mol}^{-1}$, which corresponds to a molar density of $10.28 \text{ mol} \cdot \text{dm}^{-3}$. The molar density of methane found using the van der Waals equation of state is within 0.5% of the experimentally observed value.

16–19. Use the Redlich-Kwong equation to calculate the pressure of methane at 200 K and a density of $27.41 \text{ mol} \cdot \text{L}^{-1}$. The experimental value is 1600 bar. What does the van der Waals equation give?

The molar volume of the methane is $0.03648 \text{ dm}^3 \cdot \text{mol}^{-1}$.

a. The van der Waals equation gives a pressure of (Equation 16.5)

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

For methane, $a = 2.3026 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2}$ and $b = 0.043067 \text{ dm}^3 \cdot \text{mol}^{-1}$ (Table 16.3). Then

$$P = \frac{(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(200 \text{ K})}{0.03648 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.043067 \text{ dm}^3 \cdot \text{mol}^{-1}} - \frac{2.3026 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2}}{(0.03648 \text{ dm}^3 \cdot \text{mol}^{-1})^2}$$
$$= -4256 \text{ bar}$$

b. The Redlich-Kwong equation gives a pressure of (Equation 16.7)

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}(\overline{V} + B)}$$

For ethane, $A = 32.205 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}$ and $B = 0.029850 \text{ dm}^3 \cdot \text{mol}^{-1}$ (Table 16.4). Then

$$P = \frac{(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot {}^{-1})(200 \text{ K})}{0.03648 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.029850 \text{ dm}^3 \cdot \text{mol}^{-1}}$$
$$- \frac{32.205 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}}{(200 \text{ K})^{1/2}(0.03648 \text{ dm}^3 \cdot \text{mol}^{-1})(0.03648 \text{ dm}^3 \cdot \text{mol}^{-1} + 0.029850 \text{ dm}^3 \cdot \text{mol}^{-1})}$$
$$= 1566 \text{ bar}$$

The value of P found using the Redlich-Kwong equation of state is within 2% of the experimentally observed value. The value of P found using the van der Waals equation is obviously incorrect (as it is negative). This is a good example of the problems associated with the van der Waals equation.

16–20. The pressure of propane versus density at 400 K can be fit by the expression

$$P/\text{bar} = 33.258(\rho/\text{mol} \cdot \text{L}^{-1}) - 7.5884(\rho/\text{mol} \cdot \text{L}^{-1})^2$$
$$+ 1.0306(\rho/\text{mol} \cdot \text{L}^{-1})^3 - 0.058757(\rho/\text{mol} \cdot \text{L}^{-1})^4$$
$$- 0.0033566(\rho/\text{mol} \cdot \text{L}^{-1})^5 + 0.00060696(\rho/\text{mol} \cdot \text{L}^{-1})^6$$

for $0 \le \rho/\text{mol} \cdot \text{L}^{-1} \le 12.3$. Use the van der Waals equation and the Redlich-Kwong equation to calculate the pressure for $\rho = 0 \text{ mol} \cdot \text{L}^{-1}$ up to $12.3 \text{ mol} \cdot \text{L}^{-1}$. Plot your results. How do they compare to the above expression?


The van der Waals constants for propane are (Table 16.3) $a = 9.3919$ $dm^6 \cdot bar \cdot mol^{-2}$ and $b = 0.090494$ $dm^3 \cdot mol^{-1}$. From Equation 16.5, we can write the pressure calculated using the van der Waals equation of state as

$$P = \frac{RT}{\rho^{-1} - b} - \frac{a}{\rho^{-2}}$$

$$= \frac{(0.083145 \ dm^3 \cdot bar \cdot mol^{-1} \cdot K^{-1})(400 \ K)}{\rho^{-1} - 0.090494 \ dm^3 \cdot mol^{-1}} - \frac{9.3919 \ dm^6 \cdot bar \cdot mol^{-2}}{\rho^{-2}}$$

Likewise, the Redlich-Kwong constants for propane are (Table 16.4) $A = 183.02$ $dm^6 \cdot bar \cdot mol^{-2} \cdot K^{1/2}$ and $B = 0.062723$ $dm^3 \cdot mol^{-1}$. From Equation 16.7, we can write the pressure calculated using the Redlich-Kwong equation of state as

$$P = \frac{RT}{\rho^{-1} - B} - \frac{A}{T^{1/2} \rho^{-1}(\rho^{-1} + B)}$$

$$= \frac{(0.083145 \ dm^3 \cdot bar \cdot mol^{-1} \cdot K^{-1})(400 \ K)}{\rho^{-1} - 0.062723 \ dm^3 \cdot mol^{-1}}$$
$$- \frac{183.02 \ dm^6 \cdot bar \cdot mol^{-2} \cdot K^{1/2}}{(400 \ K)^{1/2} \rho^{-1}(\rho^{-1} + 0.062723 \ dm^3 \cdot mol^{-1})}$$

We plot these equations expressing pressure as a function of ρ as shown below.
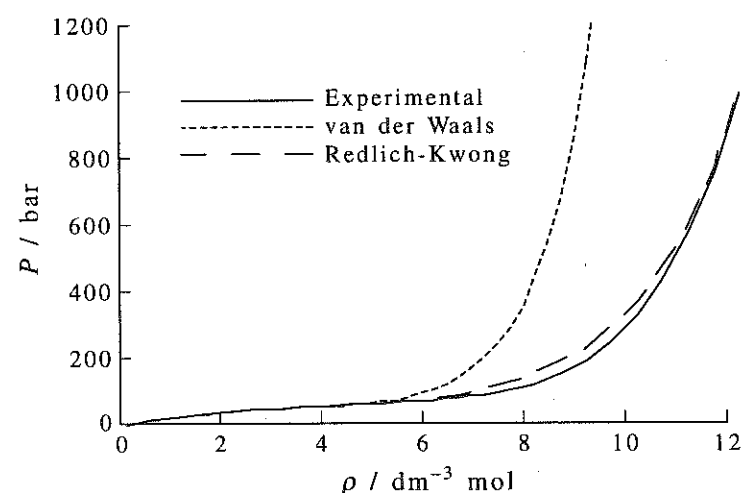
The Redlich-Kwong equation of state describes the data very well, while the van der Waals equation gives a markedly poorer approximation of the observed behavior, especially at high densities.

16–21. The Peng-Robinson equation is often superior to the Redlich-Kwong equation for temperatures near the critical temperature. Use these two equations to calculate the pressure of $CO_2(g)$ at a density of 22.0 $mol \cdot L^{-1}$ at 280 K [the critical temperature of $CO_2(g)$ is 304.2 K]. Use $\alpha = 4.192$ $bar \cdot L^2 \cdot mol^{-2}$ and $\beta = 0.02665$ $L \cdot mol^{-1}$ for the Peng-Robinson equation.

The molar volume of CO_2 is 0.04545 $dm^3 \cdot mol^{-1}$.

a. The Redlich-Kwong equation gives a pressure of (Equation 16.7)

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2} \overline{V}(\overline{V} + B)}$$

For CO_2, $A = 64.597$ $dm^6 \cdot bar \cdot mol^{-2} \cdot K^{1/2}$ and $B = 0.029677$ $dm^3 \cdot mol^{-1}$ (Table 16.4). Then

$$P = \frac{(0.083145 \ dm^3 \cdot bar \cdot mol^{-1} \cdot \, ^{-1})(280 \ K)}{0.04545 \ dm^3 \cdot mol^{-1} - 0.029677 \ dm^3 \cdot mol^{-1}}$$
$$- \frac{64.597 \ dm^6 \cdot bar \cdot mol^{-2} \cdot K^{1/2}}{(280 \ K)^{1/2}(0.04545 \ dm^3 \cdot mol^{-1})(0.04545 + 0.029677) \ dm^3 \cdot mol^{-1}}$$

$$= 345 \ bar$$

b. The Peng-Robinson equation gives a pressure of (Equation 16.8)

$$P = \frac{RT}{\overline{V} - \beta} - \frac{\alpha}{\overline{V}(\overline{V} + \beta) + \beta(\overline{V} - \beta)}$$

For CO_2, $\alpha = 4.192$ $dm^6 \cdot bar \cdot mol^{-2}$ and $\beta = 0.02665$ $dm^3 \cdot mol^{-1}$. Then

$$P = \frac{(0.083145 \ dm^3 \cdot bar \cdot mol^{-1} \cdot \, ^{-1})(280 \ K)}{0.04545 \ dm^3 \cdot mol^{-1} - 0.02665 \ dm^3 \cdot mol^{-1}}$$
$$- \frac{4.192 \ dm^6 \cdot bar \cdot mol^{-2}}{[(0.04545)(0.04545 + 0.02665) + (0.02665)(0.04545 - 0.02665)] \ dm^6 \cdot mol^{-2}}$$

$$= 129 \ bar$$

The Peng-Robinson result is much closer to the experimental value than the value predicted by the Redlich-Kwong equation.

16–22. Show that the van der Waals equation for argon at $T = 142.69$ K and $P = 35.00$ atm can be written as

$$\overline{V}^3 - 0.3664 \, \overline{V}^2 + 0.03802 \, \overline{V} - 0.001210 = 0$$

where, for convenience, we have supressed the units in the coefficients. Use the Newton-Raphson method (MathChapter G) to find the three roots to this equation, and calculate the values of the density of liquid and vapor in equilibrium with each other under these conditions.

For argon, $a = 1.3307$ $dm^6 \cdot atm \cdot mol^{-2}$ and $b = 0.031830$ $dm^3 \cdot mol^{-1}$ (Table 16.3). The van der Waals equation of state can be written as (Example 16–2)

$$\overline{V}^3 - \left(b + \frac{RT}{P}\right) \overline{V}^2 + \frac{a}{P} \overline{V} - \frac{ab}{P} = 0$$

$$\overline{V}^3 - \left[0.03183 + \frac{(0.082058)(142.69)}{35.00}\right] \overline{V}^2 + \frac{1.3307}{35.00} \overline{V} - \frac{(1.3307)(0.031830)}{35.00} = 0$$

$$\overline{V}^3 - 0.3664 \overline{V}^2 + 0.03802 \overline{V} - 0.001210 = 0$$

where we have suppressed the units of the coefficients for convenience. (The quantity $\overline{V}$ is expressed in $dm^3 \cdot mol^{-1}$.) We apply the Newton-Raphson method, using the function

$$f(\overline{V}) = \overline{V}^3 - 0.3664 \overline{V}^2 + 0.03802 \overline{V} - 0.001210$$

and its derivative

$$f'(\overline{V}) = 3\overline{V}^2 - 0.7328 \overline{V} + 0.03802$$

to find the three roots of this equation, 0.07893 $dm^3 \cdot mol^{-1}$, 0.07073 $dm^3 \cdot mol^{-1}$, and 0.21674 $dm^3 \cdot mol^{-1}$. The smallest root represents the molar volume of liquid argon, and the largest root represents the

molar volume of the vapor. The corresponding densities are 14.14 mol·dm^{-3} and 4.614 mol·dm^{-3}, respectively.

16–23. Use the Redlich-Kwong equation and the Peng-Robinson equation to calculate the densities of the coexisting argon liquid and vapor phases at 142.69 K and 35.00 atm. Use the Redlich-Kwong constants given in Table 16.4 and take $\alpha = 1.4915$ atm·L^2·mol^{-2} and $\beta = 0.01981$ L·mol^{-1} for the Peng-Robinson equation.

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a. For argon, $A = 16.566$ dm^6·atm·mol^{-2}·K$^{1/2}$ and $B = 0.022062$ dm^3·mol^{-1} (Table 16.4). The Redlich-Kwong equation of state can be written as (Equation 16.9)

$$0 = \overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)\overline{V} - \frac{AB}{T^{1/2}P}$$

$$0 = \overline{V}^3 - \frac{(0.082058)(142.69)}{35.00}\overline{V}^2 - \left[(0.022062)^2 + \frac{(0.022062)(0.082058)(142.69)}{35.00} - \frac{16.566}{(142.69)^{1/2}(35.00)}\right]\overline{V} - \frac{(16.566)(0.022062)}{(142.69)^{1/2}(35.00)}$$

$$0 = \overline{V}^3 - 0.3345\overline{V}^2 + 0.03176\overline{V} - 0.0008742$$

where we have suppressed the units of the coefficients for convenience. (The quantity $\overline{V}$ is expressed in dm^3·mol^{-1}.) We apply the Newton-Raphson method, using the function

$$f(\overline{V}) = \overline{V}^3 - 0.3345\overline{V}^2 + 0.03176\overline{V} - 0.0008742$$

and its derivative

$$f'(\overline{V}) = 3\overline{V}^2 - 0.6690\overline{V} + 0.03176$$

to find the three roots of this equation to be 0.04961 dm^3·mol^{-1}, 0.09074 dm^3·mol^{-1}, and 0.19419 dm^3·mol^{-1}. The smallest root represents the molar volume of liquid argon, and the largest root represents the molar volume of the vapor. The corresponding densities are 20.16 mol·dm^{-3} and 5.150 mol·dm^{-3}, respectively.

b. The Peng-Robinson equation is given as (Equation 16.8)

$$P = \frac{RT}{\overline{V} - \beta} - \frac{\alpha}{\overline{V}(\overline{V} + \beta) + \beta(\overline{V} - \beta)}$$

This can be expressed as the cubic equation in $\overline{V}$

$$0 = \overline{V}^3 + \left(\beta - \frac{RT}{P}\right)\overline{V}^2 + \left(\frac{\alpha - 3\beta^2 P - 2\beta RT}{P}\right)\overline{V} + \frac{\beta^3 P + \beta^2 RT - \alpha\beta}{P}$$

Substituting the values given in the text of the problem, we find that the Peng-Robinson equation for argon at 142.69 K and 35.00 atm becomes

$$0 = \overline{V}^3 + \left[(0.01981) - \frac{(0.082058)(142.69)}{35.00}\right]\overline{V}^2$$
$$+ \left[\frac{(1.4915) - 3(0.01981)^2(35.00) - 2(0.01981)(0.082058)(142.69)}{35.00}\right]\overline{V}$$
$$+ \frac{(0.01981)^3(35.00) + (0.01981)^2(0.082058)(142.69) - (1.4915)(0.01981)}{35.00}$$

$$= \overline{V}^3 - 0.3147\overline{V}^2 + 0.02818\overline{V} - 0.0007051$$

where we have suppressed the units of the coefficients for convenience. (The quantity $\overline{V}$ is expressed in dm^3·mol^{-1}.) We apply the Newton-Raphson method, using the function

$$f(\overline{V}) = \overline{V}^3 - 0.3147\overline{V}^2 + 0.02818\overline{V} - 0.0007051$$

and its derivative

$$f'(\overline{V}) = 3\overline{V}^2 - 0.6294\overline{V} + 0.02818$$

to find the three roots of this equation to be 0.04237 dm^3·mol^{-1}, 0.09257 dm^3·mol^{-1}, and 0.17979 dm^3·mol^{-1}. The smallest root represents the molar volume of liquid argon, and the largest root represents the molar volume of the vapor. The corresponding densities are 23.60 mol·dm^{-3} and 5.562 mol·dm^{-3}, respectively.

16–24. Butane liquid and vapor coexist at 370.0 K and 14.35 bar. The densities of the liquid and vapor phases are 8.128 mol·L^{-1} and 0.6313 mol·L^{-1}, respectively. Use the van der Waals equation, the Redlich-Kwong equation, and the Peng-Robinson equation to calculate these densities. Take $\alpha = 16.44$ bar·L^2·mol^{-2} and $\beta = 0.07245$ L·mol^{-1} for the Peng-Robinson equation.

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a. For butane, $a = 13.888$ dm^6·bar·mol^{-2} and $b = 0.11641$ dm^3·mol^{-1} (Table 16.3). The van der Waals equation of state can be written as (Example 16–2)

$$\overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P} = 0$$

$$\overline{V}^3 - \left[0.11641 + \frac{(0.083145)(370.0)}{14.35}\right]\overline{V}^2 + \frac{13.888}{14.35}\overline{V} - \frac{(13.888)(0.11641)}{14.35} = 0$$

$$\overline{V}^3 - 2.2602\overline{V}^2 + 0.9678\overline{V} - 0.1127 = 0$$

where we have suppressed the units of the coefficients for convenience. (The quantity $\overline{V}$ is expressed in dm^3·mol^{-1}.) We apply the Newton-Raphson method, using the function

$$f(\overline{V}) = \overline{V}^3 - 2.2602\overline{V}^2 + 0.9678\overline{V} - 0.1127$$

and its derivative

$$f'(\overline{V}) = 3\overline{V}^2 - 4.5204\overline{V} + 0.9678$$

to find the three roots of this equation to be 0.20894 dm^3·mol^{-1}, 0.30959 dm^3·mol^{-1}, and 1.7417 dm^3·mol^{-1}. The smallest root represents the molar volume of liquid butane, and the largest root represents the molar volume of the vapor. The corresponding densities are 4.786 mol·dm^{-3} and 0.5741 mol·dm^{-3}, respectively.

b. For butane, $A = 290.16$ dm^6·bar·mol^{-2}·K$^{1/2}$ and $B = 0.08068$ dm^3·mol^{-1} (Table 16.4). The Redlich-Kwong equation of state can be written as (Equation 16.9)

$$0 = \overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)\overline{V} - \frac{AB}{T^{1/2}P}$$

$$0 = \overline{V}^3 - \frac{(0.083145)(370.0)}{14.35}\overline{V}^2 - \left[(0.08068)^2 + \frac{(0.08068)(0.083145)(370.0)}{14.35} - \frac{290.16}{(370.0)^{1/2}(14.35)}\right]\overline{V} - \frac{(290.16)(0.08068)}{(370.0)^{1/2}(14.35)}$$

$$0 = \overline{V}^3 - 2.144\overline{V}^2 + 0.8717\overline{V} - 0.08481$$

where we have suppressed the units of the coefficients for convenience. (The quantity $\overline{V}$ is expressed in $dm^3 \cdot mol^{-1}$.) We apply the Newton-Raphson method, using the function

$$f(\overline{V}) = \overline{V}^3 - 2.144\overline{V}^2 + 0.8717\overline{V} - 0.08481$$

and its derivative

$$f'(\overline{V}) = 3\overline{V}^2 - 4.288\overline{V} + 0.8717$$

to to find the three roots of this equation to be $0.14640 \; dm^3 \cdot mol^{-1}$, $0.35209 \; dm^3 \cdot mol^{-1}$, and $1.6453 \; dm^3 \cdot mol^{-1}$. The smallest root represents the molar volume of liquid butane, and the largest root represents the molar volume of the vapor. The corresponding densities are $6.831 \; mol \cdot dm^{-3}$ and $0.6078 \; mol \cdot dm^{-3}$, respectively.

c.   The Peng-Robinson equation can be expressed as (Problem 16–23)

$$0 = \overline{V}^3 + \left(\beta - \frac{RT}{P}\right)\overline{V}^2 + \left(\frac{\alpha - 3\beta^2 P - 2\beta RT}{P}\right)\overline{V} + \frac{\beta^3 P + \beta^2 RT - \alpha\beta}{P}$$

Substituting the values given in the text of the problem, we find that the Peng-Robinson equation for butane at 370.0 K and 14.35 bar becomes

$$0 = \overline{V}^3 + \left[(0.07245) - \frac{(0.081345)(370.0)}{14.35}\right]\overline{V}^2$$
$$+ \left[\frac{(16.44) - 3(0.07245)^2(14.35) - 2(0.07245)(0.081345)(370.0)}{14.35}\right]\overline{V}$$
$$+ \frac{(0.07245)^3(14.35) + (0.07245)^2(0.081345)(370.0) - (16.44)(0.07245)}{14.35}$$

$$= \overline{V}^3 - 2.071\overline{V}^2 + 0.8193\overline{V} - 0.07137$$

where we have suppressed the units of the coefficients for convenience. (The quantity $\overline{V}$ is expressed in $dm^3 \cdot mol^{-1}$.) We apply the Newton-Raphson method, using the function

$$f(\overline{V}) = \overline{V}^3 - 2.071\overline{V}^2 + 0.8193\overline{V} - 0.07137$$

and its derivative

$$f'(\overline{V}) = 3\overline{V}^2 - 4.142\overline{V} + 0.8193$$

to find the three roots of this equation to be $0.12322 \; dm^3 \cdot mol^{-1}$, $0.36613 \; dm^3 \cdot mol^{-1}$, and $1.5820 \; dm^3 \cdot mol^{-1}$. The smallest root represents the molar volume of liquid butane, and the largest root represents the molar volume of the vapor. The corresponding densities are $8.116 \; mol \cdot dm^{-3}$ and $0.6321 \; mol \cdot dm^{-3}$, respectively.

Below is a table which summarizes the densities of liquid and vapor butane observed experimentally and calculated with the various equations of state above.

Equation used	Liquid $\rho/mol \cdot dm^{-3}$	Gas $\rho/mol \cdot dm^{-3}$
Experimental	8.128	0.6313
van der Waals	4.786	0.5741
Redlich-Kwong	6.831	0.6078
Peng-Robinson	8.116	0.6321

16–25. Another way to obtain expressions for the van der Waals constants in terms of critical parameters is to set $(\partial P/\partial \overline{V})_T$ and $(\partial^2 P/\partial \overline{V}^2)_T$ equal to zero at the critical point. Why are these quantities equal to zero at the critical point? Show that this procedure leads to Equations 16.12 and 16.13.

These values are equal to zero at the critical point because the critical point is an inflection point in a plot of P versus V at constant temperature.

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

So

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(\overline{V} - b)^2} + \frac{2a}{\overline{V}^3} \tag{1}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(\overline{V} - b)^3} - \frac{6a}{\overline{V}^4} \tag{2}$$

If $(\partial P/\partial V)_T$ and $(\partial^2 P/\partial V^2)_T$ are zero at the critical point, then Equations 1 and 2 give

$$RT_c\overline{V}_c^3 = 2a(\overline{V}_c - b)^2 \tag{3}$$

and

$$2RT_c\overline{V}_c^4 = 6a(\overline{V}_c - b)^3 \tag{4}$$

Multiplying Equation 3 by $2\overline{V}_c$ gives

$$2RT_c\overline{V}_c^4 = 4a\overline{V}_c(\overline{V}_c - b)^2$$

and then using Equation 4 yields

$$4a\overline{V}_c(\overline{V}_c - b)^2 = 6a(\overline{V}_c - b)^3$$
$$4\overline{V}_c = 6\overline{V}_c - 6b$$
$$3b = \overline{V}_c \tag{16.13a}$$

Substituting Equation 16.13a into Equation 3 gives

$$RT_c(3b)^3 = 2a(3b - b)^2$$
$$T_c = \frac{8ab^2}{27b^3R} = \frac{8a}{27bR} \tag{16.13c}$$

Now substitute Equations 16.13a and 16.13c into the van der Waals equation to find P_c:

$$P_c = \frac{RT_c}{\overline{V}_c - b} - \frac{a}{\overline{V}_c^2} = \frac{8aR}{27bR(3b - b)} - \frac{a}{(3b)^2} = \frac{a}{27b^2} \tag{16.13b}$$

Equation 16.12 follows naturally from these expressions for $\overline{V}_c$, P_c, and T_c.

16–26. Show that the Redlich-Kwong equation can be written in the form

$$\overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}}\right)\overline{V} - \frac{AB}{PT^{1/2}} = 0$$

Now compare this equation with $(\overline{V} - \overline{V}_c)^3 = 0$ to get

$$3\overline{V}_c = \frac{RT_c}{P_c} \tag{1}$$

$$3\overline{V}_c^2 = \frac{A}{P_c T_c^{1/2}} - \frac{BRT_c}{P_c} - B^2 \tag{2}$$

and

$$\overline{V}_c^3 = \frac{AB}{P_c T_c^{1/2}} \tag{3}$$

Note that Equation 1 gives

$$\frac{P_c \overline{V}_c}{RT_c} = \frac{1}{3} \tag{4}$$

Now solve Equation 3 for A and substitute the result and Equation 4 into Equation 2 to obtain

$$B^3 + 3\overline{V}_c B^2 + 3\overline{V}_c^2 B - \overline{V}_c^3 = 0 \tag{5}$$

Divide this equation by $\overline{V}_c^3$ and let $B/\overline{V}_c = x$ to get

$$x^3 + 3x^2 + 3x - 1 = 0$$

Solve this cubic equation by the Newton-Raphson method (MathChapter G) to obtain $x = 0.25992$, or

$$B = 0.25992\overline{V}_c \tag{6}$$

Now substitute this result and Equation 4 into Equation 3 to obtain

$$A = 0.42748\frac{R^2 T_c^{5/2}}{P_c}$$

We start with the Redlich-Kwong equation of state,

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}(\overline{V} + B)} \tag{16.7}$$

We can rewrite the above equation as

$$P\left(\overline{V} - B\right)\left(\overline{V} + B\right)T^{1/2}\overline{V} = RT^{3/2}\overline{V}\left(\overline{V} + B\right) - A\left(\overline{V} - B\right)$$

$$PT^{1/2}\overline{V}\left(\overline{V}^2 - B^2\right) = RT^{3/2}\overline{V}^2 + RT^{3/2}\overline{V}B - A\overline{V} + AB$$

We express this equation as a cubic equation in $\overline{V}$:

$$\overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}}\right)\overline{V} - \frac{AB}{PT^{1/2}} = 0 \tag{a}$$

Expanding the equation $(\overline{V} - \overline{V}_c^3) = 0$ gives

$$\left(\overline{V} - \overline{V}_c\right)^3 = \overline{V}^3 - \overline{V}_c^3 + 3\overline{V}_c^2\overline{V} - 3\overline{V}^2\overline{V}_c = 0 \tag{b}$$

Setting the coefficients of $\overline{V}^3$, $\overline{V}^2$, $\overline{V}$, and $\overline{V}^0$ in Equations a and b equal to one another at the critical point gives

$$3\overline{V}_c = \frac{RT_c}{P_c} \tag{1}$$

$$3\overline{V}_c^2 = -B^2 - \frac{BRT_c}{P_c} + \frac{A}{P_c T_c^{1/2}} \tag{2}$$

$$\overline{V}_c^3 = \frac{AB}{P_c T_c^{1/2}} \tag{3}$$

$$\frac{P_c \overline{V}_c}{RT_c} = \frac{1}{3} \tag{4}$$

We can solve Equation 3 for A to find

$$A = \frac{\overline{V}_c^3 P_c T_c^{1/2}}{B}$$

Substituting this result into Equation 2 gives

$$3\overline{V}_c^2 = -B^2 - \frac{BRT_c\overline{V}_c}{P_c\overline{V}_c} + \frac{\overline{V}_c^3 P_c T_c^{1/2}}{BP_c T_c^{1/2}}$$

$$3\overline{V}_c^2 = -B^2 - 3B\overline{V}_c + B^{-1}\overline{V}_c^3$$

$$0 = \frac{B^3}{\overline{V}_c^3} + \frac{3B^2}{\overline{V}_c^2} + \frac{3B}{\overline{V}_c} - 1$$

$$0 = x^3 + 3x^2 + 3x - 1$$

where we set $x = B/\overline{V}_c$. We solved this cubic equation using the Newton-Raphson method in Example G–1 and found that $x = 0.25992$. Then $B = 0.25992\overline{V}_c$, and substituting into Equation 3 gives

$$\left(\frac{P_c V_c}{RT_c}\right)T_c^{1/2}\overline{V}_c^2 = \frac{AB}{RT_c}$$

$$T_c^{1/2}\overline{V}_c^2 = \frac{3AB}{RT_c}$$

$$A = \frac{T_c^{3/2}\overline{V}_c^2 R}{3B} = \frac{T_c^{3/2}\overline{V}R}{3(0.25992)}$$

$$A = \frac{P_c\overline{V}_c}{RT_c}\left(\frac{RT_c}{P_c}\right)\frac{T_c^{3/2}R}{3(0.25992)}$$

$$A = 0.42748\frac{R^2 T_c^{5/2}}{P_c} \tag{7}$$

16–27. Use the results of the previous problem to derive Equations 16.14.

Equation 6 of Problem 16.26 gives $B = 0.25992\overline{V}_c$, and so

$$\overline{V}_c = 3.8473B \tag{16.14a}$$

Now we can use Equation 7 of Problem 16–26 to write

$$A = \frac{0.42748 R^2 T_c^{5/2}}{P_c} = 0.42748 R T_c^{3/2} \left(\frac{RT_c}{P_c \overline{V}_c}\right) \overline{V}_c$$

Substituting Equation 4 from Problem 16–26 and Equation 16.14a into the above expression gives

$$A = 3(0.42748) R T_c^{3/2} (3.8473 B)$$

$$T_c^{3/2} = \frac{A}{3(0.42748)(3.8473) R B}$$

$$T_c = 0.34504 \left(\frac{A}{BR}\right)^{2/3}$$

which is Equation 16.14c. Substitute this last result into the final equation of Problem 16–26 to find

$$P_c = \frac{0.42748 R^2 T_c^{5/2}}{A}$$

$$= \left(\frac{0.42748}{A}\right) R^2 \left[0.34504 \left(\frac{A}{BR}\right)^{2/3}\right]^{5/2}$$

$$= 0.029894 \frac{A^{2/3} R^{1/3}}{B^{5/3}}$$

which is Equation 16.14b.

16–28. Write the Peng-Robinson equation as a cubic polynomial equation in $\overline{V}$ (with the coefficient of $\overline{V}^3$ equal to one), and compare it with $(\overline{V} - \overline{V}_c)^3 = 0$ at the critical point to obtain

$$\frac{RT_c}{P_c} - \beta = 3\overline{V}_c \tag{1}$$

$$\frac{\alpha_c}{P_c} - 3\beta^2 - 2\beta \frac{RT_c}{P_c} = 3\overline{V}_c^2 \tag{2}$$

and

$$\frac{\alpha_c \beta}{P_c} - \beta^2 \frac{RT_c}{P_c} - \beta^3 = \overline{V}_c^3 \tag{3}$$

(We write α_c because α depends upon the temperature.) Now eliminate α_c / P_c between Equations 2 and 3, and then use Equation 1 for $\overline{V}_c$ to obtain

$$64\beta^3 + 6\beta^2 \frac{RT_c}{P_c} + 12\beta \left(\frac{RT_c}{P_c}\right)^2 - \left(\frac{RT_c}{P_c}\right)^3 = 0$$

Let $\beta/(RT_c/P_c) = x$ and get

$$64x^3 + 6x^2 + 12x - 1 = 0$$

Solve this equation using the Newton-Raphson method to obtain

$$\beta = 0.077796 \frac{RT_c}{P_c}$$

Substitute this result and Equation 1 into Equation 2 to obtain

$$\alpha_c = 0.45724 \frac{(RT_c)^2}{P_c}$$

Last, use Equation 1 to show that

$$\frac{P_c \overline{V}_c}{RT_c} = 0.30740$$

First, we write the Peng-Robinson equation as a cubic polynomial in $\overline{V}$, as we did in Problem 16–23.

$$0 = \overline{V}^3 + \left(\beta - \frac{RT}{P}\right)\overline{V}^2 + \left(\frac{\alpha - 3\beta^2 P - 2\beta RT}{P}\right)\overline{V} + \frac{\beta^3 P + \beta^2 RT - \alpha\beta}{P} \tag{a}$$

Expanding the equation $(\overline{V} - \overline{V}_c^3) = 0$ gives

$$(\overline{V} - \overline{V}_c)^3 = \overline{V}^3 - \overline{V}_c^3 + 3\overline{V}_c^2 \overline{V} - 3\overline{V}^2 \overline{V}_c = 0 \tag{b}$$

Setting the coefficients of $\overline{V}^3, \overline{V}^2, \overline{V}$, and $\overline{V}^0$ in Equations a and b equal to one another at the critical point gives

$$\beta - \frac{RT_c}{P_c} = -3\overline{V}_c \tag{1}$$

$$\frac{\alpha_c}{P_c} - 3\beta^2 - 2\beta \frac{RT_c}{P_c} = 3\overline{V}_c^2 \tag{2}$$

$$\frac{\alpha_c \beta}{P_c} - \beta^3 - \frac{RT_c}{P_c}\beta^2 = \overline{V}_c^3 \tag{3}$$

Solving Equation 2 for α_c / P_c gives

$$\frac{\alpha_c}{P_c} = 3\overline{V}_c^2 + 3\beta^2 + 2\beta \frac{RT_c}{P_c}$$

We substitute this last result into Equation 3 to find

$$0 = \overline{V}_c^3 - \beta \left(3\overline{V}_c^2 + 3\beta^2 + 2\beta \frac{RT_c}{P_c}\right) + \beta^2 \frac{RT_c}{P_c} + \beta^3$$

$$= \overline{V}_c^3 - 2\beta^3 - \beta^2 \frac{RT_c}{P_c} - 3\beta\overline{V}_c^2$$

$$= \frac{1}{27}\left(\frac{RT_c}{P_c} - \beta\right)^3 - 2\beta^3 - \beta^2 \frac{RT_c}{P_c} - \frac{\beta}{3}\left(\frac{RT_c}{P_c} - \beta\right)^2$$

$$= \left(\frac{RT_c}{P_c}\right)^3 - 3\beta\left(\frac{RT_c}{P_c}\right)^2 + 3\beta^2 \frac{RT_c}{P_c} - \beta^3 - 54\beta^3 - 27\beta^2 \frac{RT_c}{P_c} - 9\left(\frac{RT_c}{P_c}\right)^2 \beta + 18\beta \frac{RT_c}{P_c} - 9\beta^3$$

$$= \left(\frac{RT_c}{P_c}\right)^3 - 12\beta\left(\frac{RT_c}{P_c}\right)^2 - 6\beta^2\left(\frac{RT_c}{P_c}\right) - 64\beta^3$$

Set $x = \beta/\left(RT_c/P_c\right)$ and the above equation becomes

$$64x^3 + 6x^2 + 12x - 1 = 0$$

Using the Newton-Raphson method (MathChapter G), we find $x = 0.077796$ and so

$$\beta = 0.077796 \frac{RT_c}{P_c}$$

We now substitute Equation 1 into Equation 2 and use the expression for β given above to write

$$
\begin{aligned}
\alpha_c &= P_c \left(3\overline{V}_c^2 + 3\beta^2 + 2\beta \frac{RT_c}{P_c} \right) \\
&= P_c \left[\frac{1}{3} \left(\frac{RT_c}{P_c} - \beta \right)^2 + 3\beta^2 + 2\beta \frac{RT_c}{P_c} \right] \\
&= P_c \left(\frac{RT_c}{P_c} \right)^2 \left[\frac{1}{3}(1 - 0.77796)^2 + 3(0.077796)^2 + 2(0.077796) \right] \\
&= 0.45724 \frac{(RT_c)^2}{P_c}
\end{aligned}
$$

Finally, substitute the expression of β given above into Equation 1 to write

$$(1 - 0.077796) \frac{RT_c}{P_c} = 3\overline{V}_c$$

$$0.92220 RT_c = 3 P_c \overline{V}_c$$

$$0.30740 = \frac{P_c \overline{V}_c}{RT_c}$$

16–29. Look up the boiling points of the gases listed in Table 16.5 and plot these values versus the critical temperatures T_c. Is there any correlation? Propose a reason to justify your conclusions from the plot.

A graph of boiling points versus critical temperatures of the gases listed in Table 16.5 is shown below. There appears to be a direct correlation between the boiling point of a gas and its critical temperature.
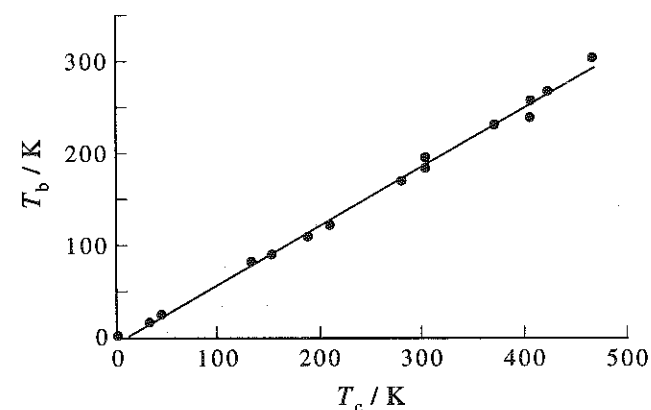
This is another illustration of the law of corresponding states: if we compare the boiling points of different gases relative to their critical temperatures, we find that all behaviors can be similarly explained (hence, the constant slope in the figure).

16–30. Show that the compressibility factor Z for the Redlich-Kwong equation can be written as in Equation 16.21.

The Redlich-Kwong equation of state is given by Equation 16.7. Thus

$$\left(\frac{\overline{V}}{RT} \right) P = \left(\frac{\overline{V}}{RT} \right) \frac{RT}{\overline{V} - B} - \frac{A}{RT^{3/2} \left(\overline{V} + B \right)}$$

or

$$Z = \frac{\overline{V}}{\overline{V} - B} - \frac{A}{RT^{3/2} \left(\overline{V} + B \right)}$$

We know from Equation 16.18 that

$$A = 0.42748 \frac{R^2 T_c^{5/2}}{P_c} \quad \text{and} \quad B = 0.086640 \frac{RT_c}{P_c}$$

We can then write Z as

$$Z = \overline{V} \left(\overline{V} - 0.086640 \frac{RT_c}{P_c} \right)^{-1} - \left(0.42748 \frac{R^2 T_c^{5/2}}{P_c} \right) \left[RT^{3/2} \left(\overline{V} + 0.086640 \frac{RT_c}{P_c} \right) \right]^{-1}$$

In the solution to Problem 16.26, we showed that $3\overline{V}_c P_c = RT_c$, so

$$
\begin{aligned}
Z &= \frac{\overline{V}}{\overline{V} - 0.086640 \left(3\overline{V}_c \right)} - \frac{0.42748 T_c^{3/2} \left(3\overline{V}_c \right)}{T^{3/2} \left[\overline{V} + 0.086640 \left(3\overline{V}_c \right) \right]} \\
&= \frac{\overline{V}_R}{\overline{V}_R - 0.25992} - \frac{1.28244}{T_R^{3/2} \left(\overline{V}_R + 0.25992 \right)}
\end{aligned}
$$

16–31. Use the following data for ethane and argon at $T_R = 1.64$ to illustrate the law of corresponding states by plotting Z against $\overline{V}_R$.

Ethane ($T = 500$ K)		Argon ($T = 247$ K)	
P/bar	$\overline{V}$/L·mol^{-1}	P/atm	$\overline{V}$/L·mol^{-1}
0.500	83.076	0.500	40.506
2.00	20.723	2.00	10.106
10.00	4.105	10.00	1.999
20.00	2.028	20.00	0.9857
40.00	0.9907	40.00	0.4795
60.00	0.6461	60.00	0.3114
80.00	0.4750	80.00	0.2279
100.0	0.3734	100.0	0.1785
120.0	0.3068	120.0	0.1462
160.0	0.2265	160.0	0.1076
200.0	0.1819	200.0	0.08630
240.0	0.1548	240.0	0.07348
300.0	0.1303	300.0	0.06208
350.0	0.1175	350.0	0.05626
400.0	0.1085	400.0	0.05219
450.0	0.1019	450.0	0.04919
500.0	0.09676	500.0	0.04687
600.0	0.08937	600.0	0.04348
700.0	0.08421	700.0	0.04108

We can use Table 16.5 to find the critical molar volumes of ethane and argon (0.1480 dm$^3 \cdot$mol^{-1} and 0.07530 dm$^3 \cdot$mol^{-1}, respectively) and use the data given in the problem text in the equations

$$Z = \frac{P\overline{V}}{RT} \qquad \text{and} \qquad \overline{V}_R = \frac{\overline{V}}{\overline{V}_c}$$

to plot Z versus $\overline{V}_R$. Note that the pressures for ethane are given in units of bar, while the pressures for argon are given in units of atm.
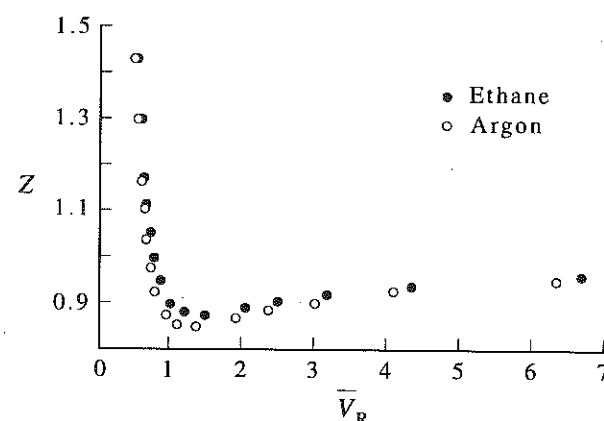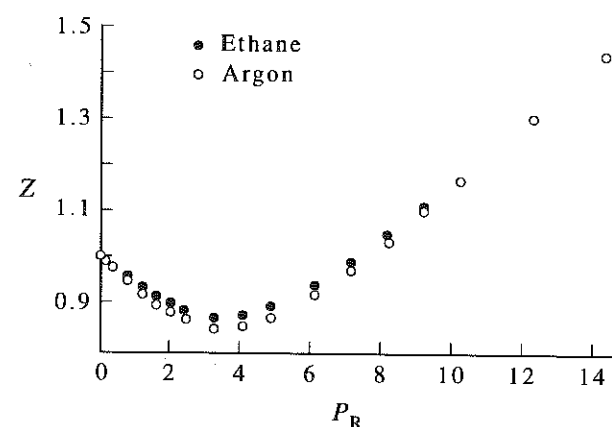

16–32. Use the data in Problem 16–31 to illustrate the law of corresponding states by plotting Z against P_R.

We can use Table 16.5 to find the critical pressures of ethane and argon (48.714 bar and 48.643 atm, respectively) and use the data given in Problem 16–31 in the equations

$$Z = \frac{P\overline{V}}{RT} \qquad \text{and} \qquad P_R = \frac{P}{P_c}$$
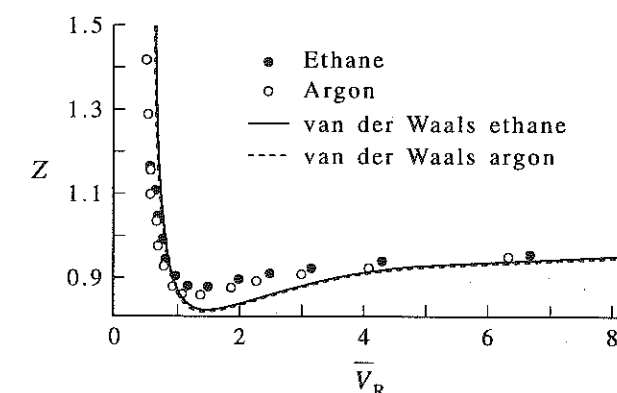
to plot Z versus P_R.

16–33. Use the data in Problem 16.31 to test the quantitative reliability of the van der Waals equation by comparing a plot of Z versus $\overline{V}_R$ from Equation 16.20 to a similar plot of the data.

We can use Equation 16.20 to express Z as a function of $\overline{V}_R$:

$$Z = \frac{\overline{V}_R}{\overline{V}_R - 1/3} - \frac{9}{8\overline{V}_R T_R}$$

We can substitute the appropriate values of $T_R = T/T_c$ (Problem 16–31) and plot Z versus $\overline{V}_R$ for both argon and ethane. The plot below shows the lines generated by applying the van der Waals equation and the actual data from Problem 16–31.


16–34. Use the data in Problem 16.31 to test the quantitative reliability of the Redlich-Kwong equation by comparing a plot of Z versus $\overline{V}_R$ from Equation 16.21 to a similar plot of the data.

We can use Equation 16.21 to express Z as a function of $\overline{V}_R$:

$$Z = \frac{\overline{V}_R}{\overline{V}_R - 0.25992} - \frac{1.2824}{T_R^{3/2}(\overline{V}_R + 0.25992)}$$

We can substitute the appropriate values of $T_R = T/T_c$ (Problem 16–31) and plot Z versus $\overline{V}_R$ for both argon and ethane. The plot below shows the lines generated by applying the Redlich-Kwong equation and the actual data from Problem 16–31.
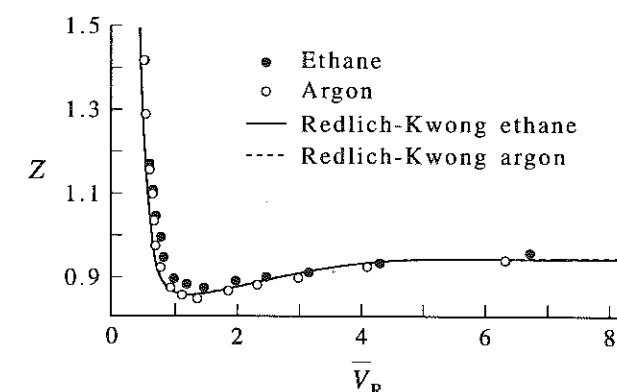
16–35. Use Figure 16.10 to estimate the molar volume of CO at 200 K and 180 bar. An accurate experimental value is 78.3 cm$^3 \cdot$mol^{-1}.

We use the critical values in Table 16.5 to write

$$T_R = \frac{T}{T_c} = \frac{200 \text{ K}}{132.85 \text{ K}} = 1.51$$

and

$$P_R = \frac{P}{P_c} = \frac{180 \text{ bar}}{34.935 \text{ bar}} = 5.15$$

From Figure 16.10,

$$Z = \frac{P\overline{V}}{RT} \approx 0.85$$

We can now find $\overline{V}$:

$$\overline{V} \approx \frac{0.85 \left(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\right) (200 \text{ K})}{180 \text{ bar}}$$

$$\overline{V} \approx 78.5 \text{ cm}^3 \cdot \text{mol}^{-1}$$

in excellent agreement with the experimental value.

16–36. Show that $B_{2V}(T) = RTB_{2P}(T)$ (see Equation 16.24).

We begin with Equations 16.22 and 16.23,

$$\frac{P\overline{V}}{RT} = 1 + \frac{B_{2V}(T)}{\overline{V}} + \frac{B_{3V}(T)}{\overline{V}^2} + O(\overline{V}^3)$$

and

$$\frac{P\overline{V}}{RT} = 1 + B_{2P}(T)\,P + O(P^2)$$

We now solve Equation 16.23 for P:

$$P = \frac{RT}{\overline{V}} + \frac{PRT}{\overline{V}}B_{2P}(T) + O(\overline{V}^2)$$

Substituting this expression for P into Equation 16.22 gives

$$1 + \frac{B_{2V}(T)}{\overline{V}} + O(\overline{V}^2) = 1 + B_{2P}(T)\frac{RT}{\overline{V}} + \frac{PRT}{\overline{V}}B_{2P}(T) + O(\overline{V}^2)$$

and equating the coefficients of $\overline{V}^{-1}$ on both sides of the equation gives
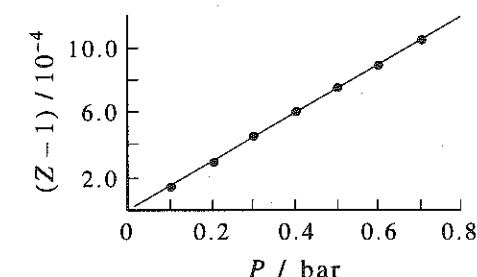
$$B_{2V}(T) = RTB_{2P}(T)$$

16–37. Use the following data for NH$_3$(g) at 273 K to determine $B_{2P}(T)$ at 273 K.

P/bar	0.10	0.20	0.30	0.40	0.50	0.60	0.70
$(Z-1)/10^{-4}$	1.519	3.038	4.557	6.071	7.583	9.002	10.551

Ignoring terms of $O(P^2)$, we can write Equation 16.23 as

$$Z - 1 = B_{2P}(T)P$$

A plot of $(Z-1)$ versus pressure for the data given for NH$_3$ at 273 K is shown below.

The slope of the best-fit line to the data is B_{2P} and is equal to 15.0×10^{-4} bar^{-1}.

16–38. The density of oxygen as a function of pressure at 273.15 K is listed below.

P/atm	0.2500	0.5000	0.7500	1.0000
$\rho/\text{g} \cdot \text{dm}^{-3}$	0.356985	0.714154	1.071485	1.428962

Use the data to determine $B_{2V}(T)$ of oxygen. Take the atomic mass of oxygen to be 15.9994 and the value of the molar gas constant to be 8.31451 J$\cdot$K$^{-1} \cdot$mol^{-1} = 0.0820578 dm$^3 \cdot$atm$\cdot$K$^{-1} \cdot$mol^{-1}.

We can express the molar volume of oxygen as

$$\overline{V} = \frac{(15.9994 \text{ g} \cdot \text{mol}^{-1})}{\rho}$$
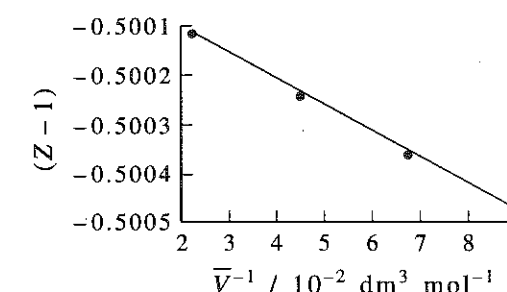
where ρ has units of g$\cdot$dm^{-3}. Using Equation 16.22 to express Z and neglecting terms of $O(\overline{V}^{-2})$, we find

$$Z - 1 = \overline{V}^{-1}B_{2V}(T)$$

or

$$\frac{P(15.994 \text{ g} \cdot \text{mol}^{-1})}{\rho RT} - 1 = \overline{V}^{-1}B_{2V}(T)$$

A plot of $(Z-1)$ versus $\overline{V}^{-1}$ for the data given for oxygen at 273.15 K is shown below.

The slope of the best-fit line to the data is B_{2V} and is equal to -5.33×10^{-3} dm$^3 \cdot$mol^{-1}.

16–39. Show that the Lennard-Jones potential can be written as

$$u(r) = \varepsilon \left(\frac{r^*}{r}\right)^{12} - 2\varepsilon \left(\frac{r^*}{r}\right)^6$$

where r^* is the value of r at which $u(r)$ is a minimum.

The Lennard-Jones potential is (Equation 16.29)

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

From Example 16.9, we know $\sigma = r^* 2^{-1/6}$, so

$$u(r) = 4\varepsilon \left[\left(\frac{r^*}{2^{1/6} r}\right)^{12} - \left(\frac{r^*}{2^{1/6} r}\right)^6\right]$$

$$= \frac{4\varepsilon (r^*)^{12}}{2^2 r^{12}} - \frac{4\varepsilon (r^*)^6}{2 r^6} = \varepsilon \left(\frac{r^*}{r}\right)^{12} - 2\varepsilon \left(\frac{r^*}{r}\right)^6$$

16–40. Using the Lennard-Jones parameters given in Table 16.7, compare the depth of a typical Lennard-Jones potential to the strength of a covalent bond.


The parameter ε is the depth of a Lennard-Jones potential. From Table 16.7, an average value of $\varepsilon/k_B \approx 139$ K for one molecule. So, for one mole,

$$\varepsilon \approx (139 \text{ K}) k_B N_A \approx \text{J} \approx 1 \text{ kJ}$$

In comparison, the strength of a covalent bond is on the order of 100 kJ per mole (Table 13.2).

16–41. Compare the Lennard-Jones potentials of $H_2(g)$ and $O_2(g)$ by plotting both on the same graph.

Shown below are plots of $u(r)$ versus r for both $H_2(g)$ and $O_2(g)$. Oxygen has a deeper potential well than hydrogen and the minimum of its potential curve occurs at a higher value of r than the minimum of the potential curve of hydrogen.
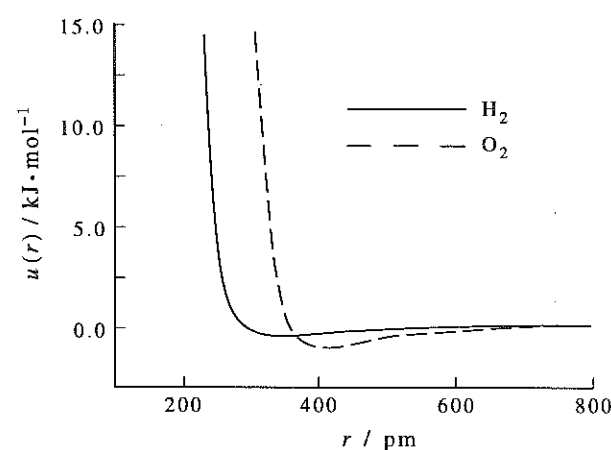
16–42. Use the data in Tables 16.5 and 16.7 to show that *roughly* $\varepsilon/k_B = 0.75 \ T_c$ and $b_0 = 0.7 \ \overline{V}_c$. Thus, critical constants can be used as rough, first estimates of ε and $b_0 \ (= 2\pi N_A \sigma^3/3)$.

Let us select argon as a representative molecule. For Ar, $\varepsilon/k_B = 120$ K, $b_0 = 50.0$ cm$^3 \cdot$mol^{-1}, $T_c = 150.95$ K, and $\overline{V}_c = 75.3$ cm$^3 \cdot$mol^{-1}.

$$0.75 \ T_c = 113 \text{ K} \qquad \text{compared to} \qquad \varepsilon/k_B = 120 \text{ K}$$

$$0.7 \ \overline{V}_c = 53 \text{ cm}^3 \cdot \text{mol}^{-1} \qquad \text{compared to} \qquad b_0 = 50.0 \text{ cm}^3 \cdot \text{mol}^{-1}$$

The equivalencies stated in the problem text hold for argon.

16–43. Prove that the second virial coefficient calculated from a general intermolecular potential of the form

$$u(r) = (\text{energy parameter}) \times f\left(\frac{r}{\text{distance parameter}}\right)$$

rigorously obeys the law of corresponding states. Does the Lennard-Jones potential satisfy this condition?

Begin with Equation 16.25,

$$B_{2V}(T) = -2\pi N_A \int_0^\infty [e^{-u(r)/k_B T} - 1] r^2 dr$$

Let $u(r) = E f(r/r_0)$ and $T^* = k_B T$, so that we can write $B_{2V}(T)$ as

$$B_{2V}(T^*) = -2\pi N_A \int_0^\infty [e^{-Ef(r/r_0)/T^*} - 1] r^2 dr$$

Now let $r/r_0 = r_R$, where r_R is the reduced distance variable. Then $dr = r_0 dr_R$, so we can write

$$B_{2V}(T^*) = -2\pi r_0^3 N_A \int_0^\infty [e^{-Ef(r_R)/T^*} - 1] dr_R$$

We can divide both sides by $-2\pi r_0^3 N_A$ to obtain B_{2V}^* as a function of only reduced variables:

$$B_{2V}^*(T^*) = \int_0^\infty [e^{-Ef(r_R)/T^*} - 1] dr_R$$

Therefore, the functional form of $u(r)$ given in the problem text rigorously obeys the law of corresponding states. The Lennard-Jones potential can be written as (Equation 16.29)

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] = E[x^{12} - x^6]$$

where E is an energy parameter and x is a distance parameter $(x \sim r^{-1})$. So the Lennard-Jones potential can be written as $E f(r)$ and so satisfies the conditions of the above general intermolecular potential.

16-44. Use the following data for argon at 300.0 K to determine the value of B_{2V}. The accepted value is -15.05 cm$^3 \cdot$ mol^{-1}.

P/atm	ρ/mol$\cdot$L^{-1}	P/atm	ρ/mol$\cdot$L^{-1}
0.01000	0.000406200	0.4000	0.0162535
0.02000	0.000812500	0.6000	0.0243833
0.04000	0.00162500	0.8000	0.0325150
0.06000	0.00243750	1.000	0.0406487
0.08000	0.00325000	1.500	0.0609916
0.1000	0.00406260	2.000	0.0813469
0.2000	0.00812580	3.000	0.122094

We can use Equation 16.22 to express $Z - 1$ (neglecting terms of $O(\overline{V}^{-2})$) as

$$Z - 1 = \overline{V}^{-1} B_{2V}(T) = \rho B_{2V}(T)$$

A plot of $(Z - 1)$ versus $\overline{V}^{-1}$ for the data given for oxygen at 273.15 K is shown below.
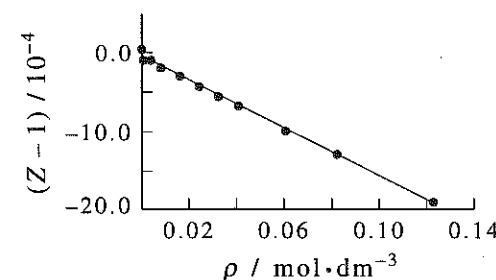
The slope of the best-fit line to the data is B_{2V} and is equal to -15.13 cm$^3 \cdot$ mol^{-1}.

16-45. Using Figure 16.15 and the Lennard-Jones parameters given in Table 16.7, estimate $B_{2V}(T)$ for CH$_4$(g) at 0°C.

For methane, $\epsilon/k_B = 149$ K and $2\pi\sigma^3 N_A/3 = 68.1$ cm$^3 \cdot$ mol^{-1} (Table 16.7). Then (by definition of T^*)

$$T^* = \frac{k_B T}{\epsilon} = \frac{273.15 \text{ K}}{149 \text{ K}} = 1.83$$

From Figure 16.15, we estimate $B_{2V}^*(T^*) \approx -0.9$. Then (also by definition)

$$B_{2V}(273.15 \text{ K}) = \frac{2\pi\sigma^3 N_A B_{2V}^*(T^*)}{3} \approx -60 \text{ cm}^3 \cdot \text{mol}^{-1}$$

16-46. Show that $B_{2V}(T)$ obeys the law of corresponding states for a square-well potential with a *fixed* value of λ (in other words, if all molecules had the same value of λ).

We use Equation 16.25 to express $B_{2V}(T)$:

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left[e^{-u(r)/k_B T} - 1 \right] r^2 dr$$

where, since we have a square-well potential of fixed value λ,

$$
\begin{aligned}
u(r) &= \infty & \text{if} \quad r < \sigma \\
&= -\epsilon & \text{if} \quad \sigma < r < \lambda\sigma \\
&= 0 & \text{if} \quad \lambda\sigma < r
\end{aligned}
$$

We can now integrate $B_{2V}(T)$ over the three intervals $0 < r < \sigma$, $\sigma < r < \lambda\sigma$, and $\lambda\sigma < r < \infty$:

$$
\begin{aligned}
B_{2V}(T) &= -2\pi N_A \int_0^\sigma (0 - 1) r^2 dr - 2\pi N_A \int_\sigma^{\lambda\sigma} \left[e^{\epsilon/k_B T} - 1 \right] r^2 dr + 0 \\
&= 2\pi N_A \left(\frac{\sigma^3}{3} \right) - 2\pi N_A \left(e^{\epsilon/k_B T} - 1 \right) \frac{\lambda^3 \sigma^3 - \sigma^3}{3} \\
&= \frac{2\pi N_A \sigma^3}{3} \left[1 - \left(\lambda^3 - 1 \right) \left(e^{\epsilon/k_B T} - 1 \right) \right]
\end{aligned}
$$

If we divide $B_{2V}(T)$ by σ^3 and let this quantity be a reduced value of $B_{2V}(T)$, this reduced second virial coefficient will be molecule-independent and therefore satisfy the law of corresponding states.

16-47. Using the Lennard-Jones parameters in Table 16.7, show that the following second virial cofficient data satisfy the law of corresponding states.

| Argon		Nitrogen		Ethane	
T/K	$B_{2V}(T)$ /10^{-3} dm$^3 \cdot$ mol^{-1}	T/K	$B_{2V}(T)$ /10^{-3} dm$^3 \cdot$ mol^{-1}	T/K	$B_{2V}(T)$ /10^{-3} dm$^3 \cdot$ mol^{-1}
173	-64.3	143	-79.8	311	-164.9
223	-37.8	173	-51.9	344	-132.5
273	-22.1	223	-26.4	378	-110.0
323	-11.0	273	-10.3	411	-90.4
423	$+1.2$	323	-0.3	444	-74.2
473	4.7	373	$+6.1$	478	-59.9
573	11.2	423	11.5	511	-47.4
673	15.3	473	15.3		
		573	20.6		
		673	23.5		

Find the reduced parameters of each gas by dividing T by ε/k_B and B_{2V} by $2\pi\sigma^3 N_A/3$ (Table 16.7). Below, we plot $B_{2V}^*(T)$ versus T^* for each gas.
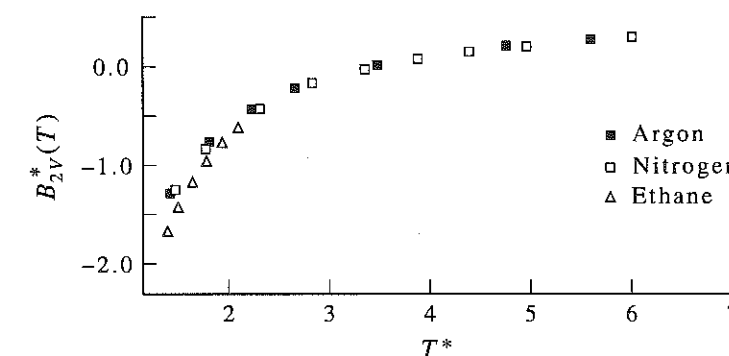
The data points for all three gases fall on the same curve, consistent with the law of corresponding states.

16–48. In Section 16–4, we expressed the van der Waals equation in reduced units by dividing P, $\overline{V}$, and T by their critical values. This suggests we can write the second virial coefficient in reduced form by dividing $B_{2V}(T)$ by $\overline{V}_c$ and T by T_c (instead of $2\pi N_A \sigma^3/3$ and ε/k as we did in Section 16–5). Reduce the second virial coefficient data given in the previous problem by using the values of $\overline{V}_c$ and T_c in Table 16.5 and show that the reduced data satisfy the law of corresponding states.

We find the reduced parameters of each gas by dividing T by T_c and B_{2V} by $\overline{V}_c$ (Table 16.5). Below, we plot $B_{2V}(T)/\overline{V}_c$ vs. T/T_c for each gas.
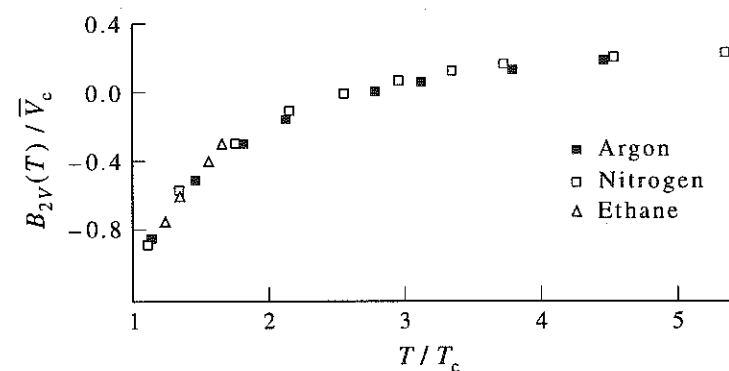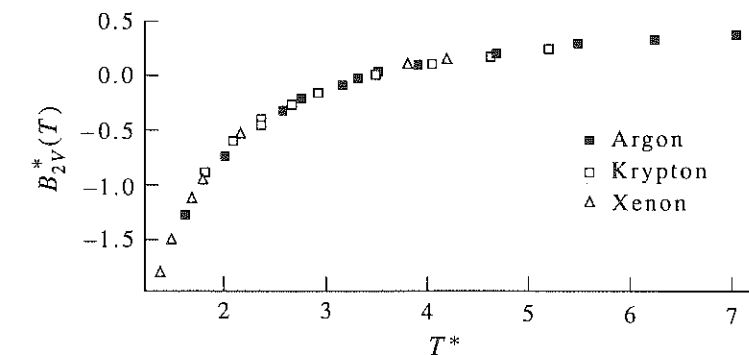

The data points for all three gases fall on the same curve, consistent with the law of corresponding states.

16–49. Listed below are experimental second virial coefficient data for argon, krypton, and xenon.

T/K	$B_{2V}(T)/10^{-3} dm^3 \cdot mol^{-1}$		
	Argon	Krypton	Xenon
173.16	−63.82		
223.16	−36.79		
273.16	−22.10	−62.70	−154.75
298.16	−16.06		−130.12
323.16	−11.17	−42.78	−110.62
348.16	−7.37		−95.04
373.16	−4.14	−29.28	−82.13
398.16	−0.96		
423.16	+1.46	−18.13	−62.10
473.16	4.99	−10.75	−46.74
573.16	10.77	+0.42	−25.06
673.16	15.72	7.42	−9.56
773.16	17.76	12.70	−0.13
873.16	19.48	17.19	+7.95
973.16			14.22

Use the Lennard-Jones parameters in Table 16.7 to plot $B_{2V}^*(T^*)$, the reduced second virial coefficient, versus T^*, the reduced temperature, to illustrate the law of corresponding states.


Find the reduced parameters of each gas by dividing T by ε/k_B and B_{2V} by $2\pi\sigma^3 N_A/3$ (Table 16.7). Below, we plot $B_{2V}^*(T)$ versus T^* for each gas.

The data points for all three gases fall on the same curve, consistent with the law of corresponding states.

16–50. Use the critical temperatures and the critical molar volumes of argon, krypton, and xenon to illustrate the law of corresponding states with the data given in Problem 16–49.

We find the reduced parameters of each gas by dividing T by T_c and B_{2V} by $\overline{V}_c$ (Table 16.5). Below, we plot $B_{2V}(T)/\overline{V}_c$ vs. T/T_c for each gas.
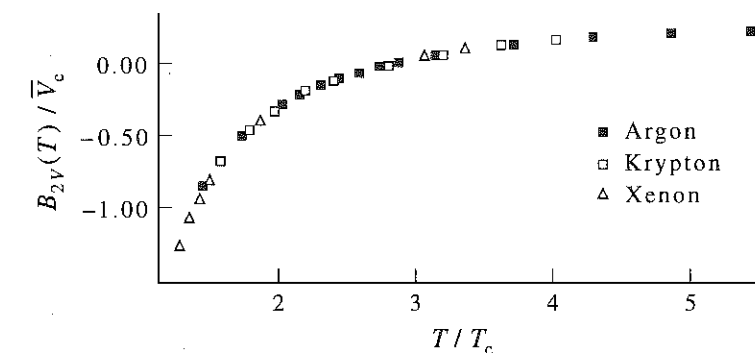
The data points for all three gases fall on the same curve, consistent with the law of corresponding states.

16–51. Evaluate $B_{2V}^*(T^*)$ in Equation 16.31 numerically from $T^* = 1.00$ to 10.0 using a packaged numerical integration program such as *MathCad* or *Mathematica*. Compare the reduced second virial coefficient data from Problem 16–49 and $B_{2V}^*(T^*)$ by plotting them all on the same graph.

Below is a table with some representative values of $B_{2V}^*(T^*)$ calculated using the numerical integration package in *Mathematica*.

T^*	$B_{2V}^*(T^*)$
1.00	−2.538081336
2.00	−0.6276252881
3.00	−0.1152339638
4.00	0.1154169217
5.00	0.2433435028
6.00	0.3229043727
7.00	0.3760884671
8.00	0.4134339539
9.00	0.4405978376
10.00	0.4608752841

The plot below shows both the curve obtained from numerically integrating $B_{2V}^*(T^*)$ and the reduced second virial coefficient data from Problem 16–49. The numerical integration is an excellent fit to the data.
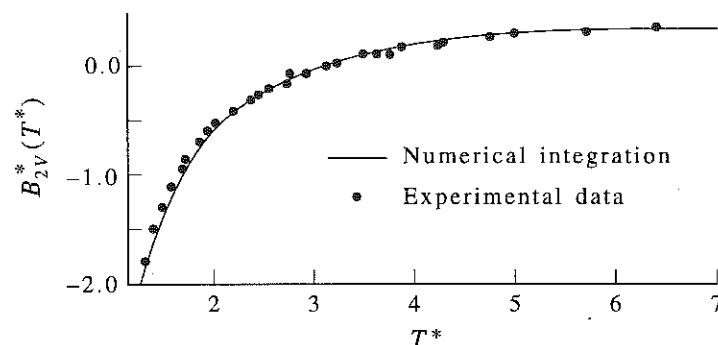
16–52. Show that the units of the right side of Equation 16.35 are energy.

$$u_{\text{induced}}(r) = -\frac{\mu_1^2\alpha_2}{(4\pi\varepsilon_0)^2 r^6} - \frac{\mu_2^2\alpha_1}{(4\pi\varepsilon_0)^2 r^6}$$

We know that $\alpha/4\pi\varepsilon_0$ has units of m^3, $4\pi\varepsilon_0$ has units of $C\cdot V^{-1}\cdot m^{-1}$, μ has units of $C\cdot m$, and r has units of m. Thus

$$\text{units}[u_{\text{induced}}(r)] = \frac{(C\cdot m)^2 m^3}{C\cdot V^{-1}\cdot m^{-1} m^6} = C\cdot V = J$$

16–53. Show that the sum of Equations 16.33, 16.35, and 16.36 gives Equation 16.37.

The sum of these three equations is

$$-\frac{\mu_1^2\alpha_2 + \mu_2^2\alpha_1}{(4\pi\varepsilon_0)^2 r^6} - \frac{2\mu_1^2\mu_2^2}{(4\pi\varepsilon_0)^2(3k_BT)}\frac{1}{r^6} - \frac{3}{2}\left(\frac{I_1 I_2}{I_1 + I_2}\right)\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2}\frac{1}{r^6}$$

For identical atoms or molecules, $I_1 = I_2 = I$, $\alpha_2 = \alpha_1 = \alpha$, and $\mu_1 = \mu_2 = \mu$, and so the sum becomes

$$\Sigma(u) = -\frac{1}{(4\pi\varepsilon_0)^2 r^6}\left(2\mu^2\alpha + \frac{2\mu^4}{3k_BT} + \frac{3I\alpha^2}{4}\right)$$

The coefficient of the r^6 term, C_6, is therefore

$$C_6 = \frac{2\mu^4}{3(4\pi\varepsilon_0)^2 k_B T} + \frac{2\alpha\mu^2}{(4\pi\varepsilon_0)^2} + \frac{3}{4}\frac{I\alpha^2}{(4\pi\varepsilon_0)^2}$$

as in Equation 16.37.

16–54. Compare the values of the coefficient of r^{-6} for $N_2(g)$ using Equation 16.37 and the Lennard-Jones parameters given in Table 16.7.

Using Equation 16.37, we find that

$$\begin{aligned}
C_6 &= \frac{2\mu^4}{3(4\pi\varepsilon_0)^2 k_B T} + \frac{2\alpha\mu^2}{(4\pi\varepsilon_0)^2} + \frac{3}{4}\frac{I\alpha^2}{(4\pi\varepsilon_0)^2} \\
&= 0 + 0 + 0.75\,(2.496\times10^{-18}\,\text{J})\,(1.77\times10^{-30}\,\text{m}^3)^2 \\
&= 5.86\times10^{-78}\,\text{J}\cdot\text{m}^6
\end{aligned}$$

Using the Lennard-Jones parameters,

$$\begin{aligned}
C_6 &= 4\varepsilon\sigma^6 = 4\frac{\varepsilon}{k_B}k_B\sigma^6 \\
&= 4\,(95.1\,\text{K})\,(1.381\times10^{-23}\,\text{J}\cdot\text{K}^{-1})\,(370\times10^{-12}\,\text{m})^6 \\
&= 1.35\times10^{-77}\,\text{J}\cdot\text{m}^6
\end{aligned}$$

The coefficient of r^{-6} obtained using the Lennard-Jones parameters is about twice that obtained using Equation 16.37.

16–55. Show that

$$B_{2V}(T) = B - \frac{A}{RT^{3/2}}$$

and

$$B_{3V}(T) = B^2 + \frac{AB}{RT^{3/2}}$$

for the Redlich-Kwong equation.

Begin with the Redlich-Kwong equation (Equation 16.7):

$$\begin{aligned}
P &= \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}(\overline{V} + B)} \\
&= \frac{RT}{\overline{V}\left(1 - \frac{B}{\overline{V}}\right)} - \frac{A}{T^{1/2}\overline{V}^2\left(1 + \frac{B}{\overline{V}}\right)}
\end{aligned}$$

Expanding the fractions $1/(1 - B/\overline{V})$ and $1/(1 + B/\overline{V})$ (Equation I.3) gives

$$P = \frac{RT}{\overline{V}}\left[1 + \frac{B}{\overline{V}} + \frac{B^2}{\overline{V}^2} + O(\overline{V}^{-3})\right] - \frac{A}{T^{1/2}\overline{V}^2}\left[1 - \frac{B}{\overline{V}} - \frac{B^2}{\overline{V}^2} - O(\overline{V}^{-3})\right]$$

$$= \frac{RT}{\overline{V}} - \frac{A}{T^{1/2}\overline{V}^2} + \left(\frac{RT}{\overline{V}} + \frac{A}{T^{1/2}\overline{V}^2}\right)\left[\frac{B}{\overline{V}} - \frac{B^2}{\overline{V}^2} - O(\overline{V}^{-3})\right]$$

We then use the definition of Z to find that

$$Z = \frac{P\overline{V}}{RT} = 1 - \frac{A}{RT^{3/2}\overline{V}} + \left(1 + \frac{A}{RT^{3/2}\overline{V}}\right)\left[\frac{B}{\overline{V}} - \frac{B^2}{\overline{V}^2} - O(\overline{V}^{-3})\right]$$

We compare this with Equation 16.22,

$$Z = 1 + \frac{B_{2V}(T)}{\overline{V}} + \frac{B_{3V}(T)}{\overline{V}^2} + O(\overline{V}^3)$$

Setting the coefficients of $1/\overline{V}$ and $1/\overline{V}^2$ equal to one another gives

$$B_{2V} = B - \frac{A}{RT^{3/2}}$$

and

$$B_{3V} = B^2 + \frac{AB}{RT^{3/2}}$$

16–56. Show that the second and third virial coefficients of the Peng-Robinson equation are

$$B_{2V}(T) = \beta - \frac{\alpha}{RT}$$

and

$$B_{3V}(T) = \beta^2 + \frac{2\alpha\beta}{RT}$$

Begin with the Peng-Robinson equation (Equation 16.8):

$$P = \frac{RT}{\overline{V} - \beta} - \frac{\alpha}{\overline{V}(\overline{V} + \beta) + \beta(\overline{V} - \beta)}$$

$$= \frac{RT}{\overline{V}\left(1 - \frac{\beta}{\overline{V}}\right)} - \frac{\alpha}{\overline{V}^2}\left[\frac{1}{1 - \left(\frac{\beta^2}{\overline{V}^2} - \frac{2\beta}{\overline{V}}\right)}\right]$$

Expanding the fractions $1/(1 - \beta/\overline{V})$ and $1/(1 - \beta^2/\overline{V}^2 - 2\beta/\overline{V})$ (Equation I.3) gives

$$P = \frac{RT}{\overline{V}}\left[1 + \frac{\beta}{\overline{V}} + \frac{\beta^2}{\overline{V}^2} + O(\overline{V}^{-3})\right] - \frac{\alpha}{\overline{V}^2}\left[1 + \left(\frac{\beta^2}{\overline{V}^2} - \frac{2\beta}{\overline{V}}\right) + \left(\frac{\beta^2}{\overline{V}^2} - \frac{2\beta}{\overline{V}}\right)^2 + O(\overline{V}^{-3})\right]$$

$$= \frac{RT}{\overline{V}}\left[1 + \frac{\beta}{\overline{V}} + \frac{\beta^2}{\overline{V}^2} + O(\overline{V}^{-3})\right] - \frac{\alpha}{\overline{V}^2}\left[1 + \frac{2\beta}{\overline{V}} + O(\overline{V}^{-2})\right]$$

We then use the definition of Z to find that

$$Z = \frac{P\overline{V}}{RT} = 1 + \frac{\beta}{\overline{V}} + \frac{\beta^2}{\overline{V}^2} - \frac{\alpha}{\overline{V}RT} - \frac{2\alpha\beta}{RT\overline{V}^2} + O(\overline{V}^{-3})$$

We compare this with Equation 16.22,

$$Z = 1 + \frac{B_{2V}(T)}{\overline{V}} + \frac{B_{3V}(T)}{\overline{V}^2} + O(\overline{V}^3)$$

Setting the coefficients of $1/\overline{V}$ and $1/\overline{V}^2$ equal to one another gives

$$B_{2V} = \beta - \frac{\alpha}{RT}$$

and

$$B_{3V} = \beta^2 + \frac{2\alpha\beta}{RT}$$

16–57. The square-well parameters for krypton are $\varepsilon/k_B = 136.5$ K, $\sigma = 327.8$ pm, and $\lambda = 1.68$. Plot $B_{2V}(T)$ against T and compare your results with the data given in Problem 16–49.

From Problem 16.46, we know that, for a square-well potential,

$$B_{2V}(T) = \frac{2\pi N_A \sigma^3}{3}\left[1 - (\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1)\right]$$

$$= \frac{2\pi(6.022 \times 10^{23}\ \text{mol}^{-1})(327.8\ \text{pm})^3}{3}$$

$$\times \left\{1 - [(1.68)^3 - 1](e^{(136.5\ \text{K})/T} - 1)\right\}$$

The plot below shows both the square-well potential curve and the experimental data from Problem 16–49 for krypton. The square-well potential is a very good fit to the data.
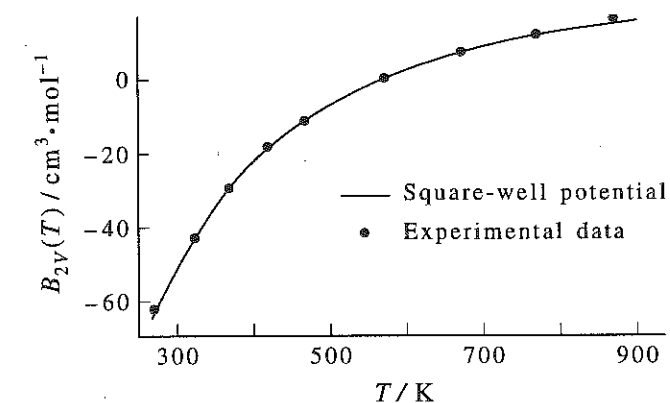
16–58. The coefficient of thermal expansion α is defined as

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

Show that

$$\alpha = \frac{1}{T}$$

for an ideal gas.

For an ideal gas, $P\overline{V} = RT$. Taking the partial derivative of both sides of this equation with respect to T gives

$$P\overline{V} = RT$$

$$\left(\frac{\partial \overline{V}}{\partial T}\right)_P = \frac{R}{P}$$

and so

$$\alpha = \frac{1}{\overline{V}}\left(\frac{\partial \overline{V}}{\partial T}\right)_P = \frac{R}{P\overline{V}} = \frac{1}{T}$$

16–59. The isothermal compressibility κ is defined as

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

Show that

$$\kappa = \frac{1}{P}$$

for an ideal gas.

For an ideal gas, $P = RT/\overline{V}$. Taking the partial derivative of both sides of this equation with respect to P gives

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

$$-\frac{\overline{V}^2}{RT} = \left(\frac{\partial \overline{V}}{\partial P}\right)_T$$

and so

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

Partial Derivatives

PROBLEMS AND SOLUTIONS

H–1. The isothermal compressibility, κ_T, of a substance is defined as

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

Obtain an expression for the isothermal compressibility of an ideal gas.

For an ideal gas, $PV = nRT$. Taking the partial derivative of both sides of this equation with respect to P gives

$$V\left(\frac{\partial P}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T = nR\left(\frac{\partial T}{\partial P}\right)_T$$

$$V + P\left(\frac{\partial V}{\partial P}\right)_T = 0$$

Then

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

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

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

H–2. The coefficient of thermal expansion, α, of a substance is defined as

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

Obtain an expression for the coefficient of thermal expansion of an ideal gas.