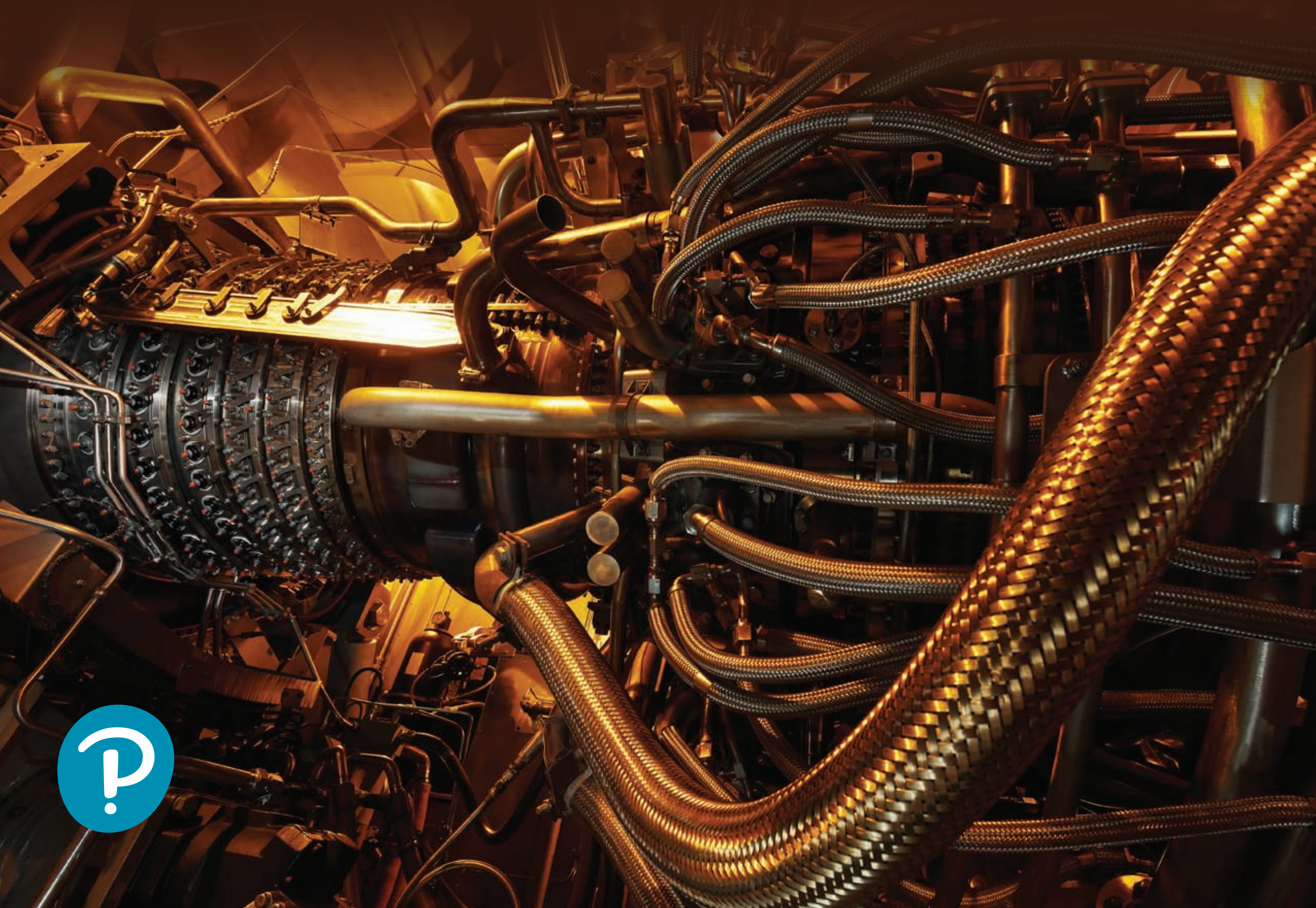
GLOBAL
EDITION

Thermodynamics, Statistical Thermodynamics, and Kinetics

FOURTH EDITION

Thomas Engel • Philip Reid



PHYSICAL CHEMISTRY

Thermodynamics, Statistical Thermodynamics, and Kinetics

FOURTH EDITION

GLOBAL EDITION

Thomas Engel
University of Washington

Philip Reid
University of Washington

Pearson

Section 6.10

P6.42 The shells of marine organisms are constructed of biologically secreted calcium carbonate $CaCO_3$, largely in a crystalline form known as calcite. There is a second crystalline form of calcium carbonate known as aragonite. Physical and thermodynamic properties of calcite and aragonite are given below.

Properties **(T = 298 K, P = 1.00 bar)**	**Calcite**	**Aragonite**
$\Delta_f H^\ominus (\text{kJ mol}^{-1})$	−1206.9	−1207.0
$\Delta_f G^\ominus (\text{kJ mol}^{-1})$	−1128.8	−1127.7
$S^\ominus (\text{J K}^{-1}\text{ mol}^{-1})$	92.9	88.7
$C_{P,m} (\text{J K}^{-1}\text{ mol}^{-1})$	81.9	81.3
Density (g mL^{-1})	2.710	2.930

a. Based on the thermodynamic data given, would you expect an isolated sample of calcite at T = 298 K and P = 1.00 bar to convert to aragonite, given sufficient time? Explain.

b. Suppose the pressure applied to an isolated sample of calcite is increased. Can the pressure be increased to the point that isolated calcite will be converted to aragonite? Explain.

c. What pressure must be achieved to induce the conversion of calcite to aragonite at T = 298 K. Assume both calcite and aragonite are incompressible at T = 298 K.

d. Can calcite be converted to aragonite at P = 1.00 bar if the temperature is increased? Explain.

P6.43 The pressure dependence of G is quite different for gases and condensed phases. Calculate ΔG_m for the processes (C, solid, graphite, 1 bar, 298.15 K) → (C, solid, graphite, 200. bar, 298.15 K) and (He, g, 1 bar, 298.15 K) → (He, g, 200. bar, 298.15 K). By what factor is ΔG_m greater for He than for graphite?

P6.44 $Ca(HCO_3)_2(s)$ decomposes at elevated temperatures according to the stoichiometric equation $Ca(HCO_3)_2(s) \rightarrow CaCO_3(s) + H_2O(g) + CO_2(g)$.

a. If pure $Ca(HCO_3)_2(s)$ is put into a sealed vessel, the air is pumped out, and the vessel and its contents are heated, the total pressure is 0.150 bar. Determine K_P under these conditions.

b. If the vessel also contains 0.150 bar $H_2O(g)$ at the final temperature, what is the partial pressure of $CO_2(g)$ at equilibrium?

Section 6.12

P6.45 Use the equation $C_{P,m} - C_{V,m} = TV_m\beta^2/\kappa_T$ and the data tables to determine $C_{V,m}$ for $H_2O(l)$ at 310 K. Calculate $(C_{P,m} - C_{V,m})/C_{P,m}$.

FURTHER READING

Dahl. S., Logadottir, A., Egeberg, R. C., Larsen, J. H., Chorkendorff, I., Tornqvist, E., and Norskov, J. K. "Role of Steps in N_2 Activation on Ru(0001)." *Physical Review Letters* 83 (1999): 1814–1817.

Ertl, G. "Surface Science and Catalysis—Studies on the Mechanism of Ammonia Synthesis: The P.H. Emmett Award Address." *Catalysis Reviews—Science and Engineering* 21 (1980): 201–223.

Gislason, E. A., and Craig, N. C. "Criteria for Spontaneous Processes Derived from the Global Point of View." *Journal of Chemical Education* 90 (2013): 584–590.

Hwang, R. Q., Schroder, J., Gunther, C., and Behm, R. J. "Fractal Growth of Two-Dimensional Islands: Au on Ru(0001)." *Physical Review Letters* 67 (1991): 3279–3283.

Jacobsen, C. J. H., Dahl, S., Clausen, B. S., Bahn, S., Logadottir, A., and Norskov, J. K. "Catalyst Design by Interpolation in the Periodic Table: Bimetallic Ammonia Synthesis Catalysts." *Journal of the American Chemical Society* 123 (2001): 8404–8405.

Liphardt, J., Onoa, B., Smith, S., Tinoco, I., and Bustamante, C. "Reversible Unfolding of Single RNA Molecules by Mechanical Force." *Science*, 292 (2001): 733–737.

Raff, L. M. "Spontaneity and Equilibrium: Why '$\Delta G < 0$ Denotes a Spontaneous Process' and $\Delta G = 0$ Means the System Is at Equilibrium Are Incorrect." *Journal of Chemical Education* 91 (2014a): 386–395.

Raff, L. M. "Spontaneity and Equilibrium III: A History of Misinformation." *Journal of Chemical Education* 91 (2014b): 2128–2136.

CHAPTER 7

The Properties of Real Gases

WHY is this material important?

The ideal gas law is only accurate for gases at low values of density. To design production plants that use real gases at high pressures, equations of state valid for gases at higher densities are needed. Such equations must take into account the finite volume of a molecule and the intermolecular potential.

WHAT are the most important concepts and results?

Equations of state for real gases accurately describe the P–V relationship of a given gas at a fixed value of T within their range of validity. These equations use parameters specific to a given gas. An important consequence of nonideality is that the chemical potential of a real gas must be expressed in terms of its fugacity rather than its partial pressure. Fugacities, rather than pressures, must also be used in calculating the thermodynamic equilibrium constant K_p for a real gas at elevated pressures.

WHAT would be helpful for you to review for this chapter?

It would be useful to review the material on ideal gases in Chapter 1.

7.1 REAL GASES AND IDEAL GASES

To this point, the ideal gas equation of state has been assumed to be sufficiently accurate to describe the P–V–T relationship for a real gas. This assumption has allowed calculations of expansion work and of the equilibrium constant K_P in terms of partial pressures using the ideal gas law. In fact, the ideal gas law provides an accurate description of the P–V–T relationship for many gases, such as He, for a wide range of P, V, and T values. However, it describes the P–V relationship for water for a wide range of P and V values within $\pm 10\%$ only for $T > 1300$ K, as shown in Section 7.4. What is the explanation for this different behavior of He and H_2O? Is it possible to derive a "universal" equation of state that can be used to describe the P–V relationship for gases as different as He and H_2O?

In Section 1.5, the two main deficiencies in the microscopic model on which the ideal gas law is based were discussed. The first assumption is that gas molecules are point masses. However, molecules occupy a finite volume; therefore, a real gas cannot be compressed to a volume that is less than the total molecular volume. The second assumption that was made is that the molecules in the gas do not interact; but molecules in a real gas do interact with one another through a potential as depicted in Figure 1.9. Because the potential has a short range, its effect is negligible at low densities, which correspond to large distances between molecules. Additionally, at low densities, the molecular volume is negligible compared with the volume that the gas occupies. Therefore, the P–V–T relationship of a real gas is the same as that for an ideal gas at sufficiently low densities and high temperatures. At higher densities and low temperatures, molecular interactions cannot be neglected. Because of these interactions, the pressure

Concept

Molecules of real gases have a finite molecular volume and interact with one another.

of a real gas can be higher or lower than that for an ideal gas at the same density and temperature. What determines which of these two cases applies? The questions raised in this section are the major themes of this chapter.

7.2 EQUATIONS OF STATE FOR REAL GASES AND THEIR RANGE OF APPLICABILITY

This section discusses several equations of state for real gases and the range of the variables P, V, and T over which they accurately describe a real gas. Such equations of state must exhibit a limiting P–V–T behavior identical to that for an ideal gas at low density. They must also correctly model the deviations for ideal gas behavior that real gases exhibit at moderate and high densities. The first two equations of state considered here include two parameters, a and b, that must be experimentally determined for a given gas. The parameter a is a measure of the strength of the attractive part of the intermolecular potential, and b is a measure of the minimum volume that a mole of molecules can occupy. Real gas equations of state are best viewed as empirical equations whose functional form has been chosen to fit experimentally determined P–V–T data.

The most widely used equation for real gases is the **van der Waals equation of state:**

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \tag{7.1}$$

A second useful equation of state is the **Redlich–Kwong equation of state:**

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}}\frac{1}{V_m(V_m + b)} = \frac{nRT}{V - nb} - \frac{n^2 a}{\sqrt{T}}\frac{1}{V(V + nb)} \tag{7.2}$$

Although the same symbols are used for parameters a and b in both equations of state, they have different values for a given gas.

Figure 7.1 shows that the degree to which the ideal gas, van der Waals, and Redlich–Kwong equations of state correctly predict the P–V behavior of CO_2 depends on P, V, and T. At 426 K, all three equations of state reproduce the correct P–V behavior reasonably well over the range shown, with the ideal gas law having the largest error. By contrast, the three equations of state give significantly different results at 310. K. The ideal gas law gives unacceptably large errors, and the Redlich–Kwong equation of state is more accurate than is the van der Waals equation. We will have more to say about the range over which the ideal gas law is reasonably accurate when discussing the compression factor in Section 7.3.

Concept

All equations of state for real gases have a limited range of P, V, and T over which they are applicable.

A third widely used equation of state for real gases is the **Beattie–Bridgeman equation of state.** The form of the equation is

$$P = \frac{RT}{V_m^2}\left(1 - \frac{c}{V_m T^3}\right)(V_m + B) - \frac{A}{V_m^2} \quad \text{with}$$

$$\mathrm{A} = \mathrm{A}_0\left(1 - \frac{a}{V_m}\right) \quad \text{and} \quad B = B_0\left(1 - \frac{b}{V_m}\right) \tag{7.3}$$

This equation uses five experimentally determined parameters to fit P–V–T data. Because of its complexity, it will not be discussed further.

A further important equation of state for real gases has a different form than any of the previous equations. The **virial equation of state** is written in the form of a power series in $1/V_m$

$$P = RT\left[\frac{1}{V_m} + \frac{B(T)}{V_m^2} + \cdots\right] \tag{7.4}$$

The power series does not converge at high pressures where V_m becomes small. The $B(T)$, $C(T)$, and so on are called the second, third, and so on virial coefficients. This equation is more firmly grounded in theory than the previously discussed three equations because a series expansion is always valid in its convergence range. In practical

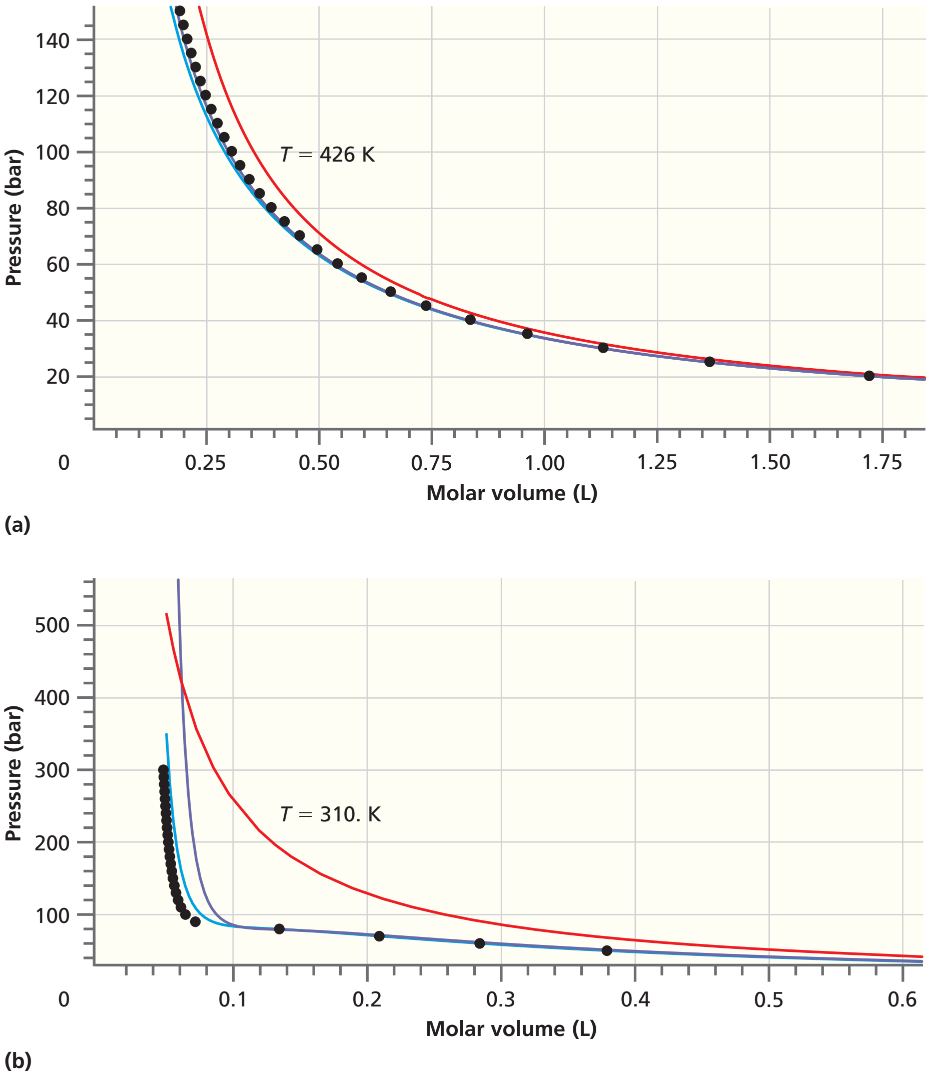


Figure 7.1

Comparison of real gas equations of state to ideal gas equation of state. Isotherms for $CO_2(g)$ are shown at (a) 426 K and (b) 310 K. The purple curve is calculated using the van der Waals equation of state, the blue curve is calculated using the Redlich–Kwong equation of state, and the red curve is calculated using the ideal gas equation of state. The black dots are accurate values taken from the *NIST Chemistry Webbook*, which are derived from experimental results. Note that in (a) the purple curve is mostly obscured by the blue curve.

use, the series is usually terminated after the second virial coefficient because values for the higher coefficients are not easily obtained from experiments. Table 7.1 (see Appendix A, Data Tables) lists values for the second virial coefficient for selected gases for different temperatures. If $B(T)$ is negative, the attractive part of the potential dominates at that value of T. In contrast, if $B(T)$ is positive, the repulsive part of the potential dominates at that value of T. Statistical thermodynamics can be used to relate the virial coefficients with the intermolecular potential function. As you will show in the end-of-chapter problems, $B(T)$ for a van der Waals gas is given by $B(T) = b - (a/RT)$.

The principal limitation of the ideal gas law is that it does not predict that a gas can be liquefied under appropriate conditions. Consider the approximate P–V diagram for CO_2 shown in Figure 7.2. (It is approximate because it is based on the van der Waals equation of state rather than experimental data.) Each of the curves is an isotherm (that is, each corresponds to a fixed temperature). The behavior predicted by the ideal gas law is shown for $T = 334$ K.

To understand the behavior indicated by diagram in Figure 7.2, consider the isotherm for $T = 258$ K. Starting at large values of V_m, at first as V_m decreases the pressure increases. Then, with a further decrease in V_m, P is constant over a range of values of V_m. The value of V_m at which P becomes constant depends on T. As V_m decreases further, the pressure suddenly increases rapidly.

The reason for this unusual dependence of P on V_m becomes clear when the CO_2 compression experiment is carried out in the piston and transparent cylinder assembly shown in Figure 7.3. The system consists of either a single phase or two phases separated by a sharp interface, depending on the values of T and V_m. For points a, b, c, and d on

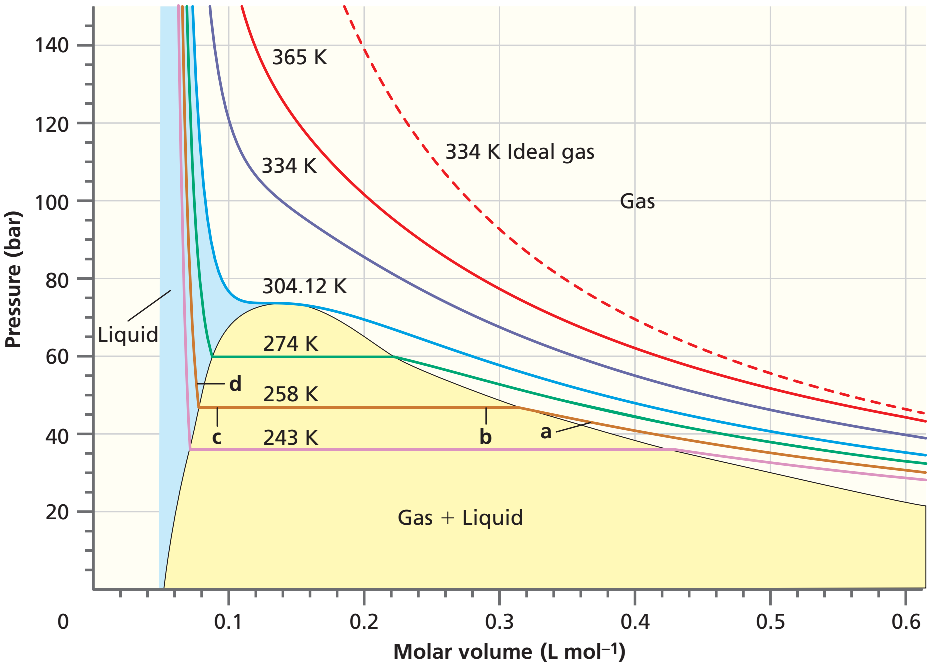


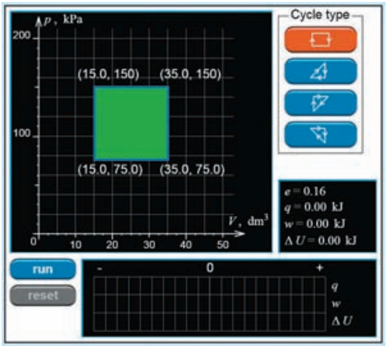
Figure 7.2
Calculated isotherms for CO_2 modeled as a van der Waals gas. The gas (green) and liquid (blue) regions and the gas–liquid (yellow) coexistence region are shown. The dashed curve was calculated using the ideal gas law. The isotherm at $T = 304.12$ K is at the critical temperature and is called the critical isotherm.

Concept

Ideal gases do not condense to form liquids or solids.

Concept

Real gases have two-phase coexistence regions.



$e = 0.16$
$q = 0.00$ kJ
$w = 0.00$ kJ
$\Delta U = 0.00$ kJ

W7.1 van der Waals equation of state isotherms

the 258 K isotherm of Figure 7.2, the system has the following composition: at point a: the system consists entirely of $CO_2(g)$. However, at points b and c, a sharp interface separates $CO_2(g)$ and $CO_2(l)$. Along the line linking points b and c, the system contains $CO_2(g)$ and $CO_2(l)$ in equilibrium with one another. The proportion of liquid to gas changes, but the pressure remains constant. The temperature-dependent equilibrium pressure is called the **vapor pressure** of the liquid. As the volume is decreased further, the system becomes a single-phase system again, consisting of $CO_2(l)$ only as at point d. The pressure changes slowly with increasing V if $V_m > 0.33$ L because $CO_2(g)$ is quite compressible. However, the pressure changes rapidly with decreasing V if $V_m < 0.06$ L because $CO_2(l)$ is nearly incompressible. The single-phase regions and the two-phase gas–liquid coexistence region are shown in Figure 7.2.

If the same experiment is carried out at successively higher temperatures, it is found that the range of V_m in which two phases are present becomes smaller, as seen in the 243, 258, and 274 K isotherms of Figure 7.2. The temperature at which the range of V_m has shrunk to a single value is called the **critical temperature,** T_c. For CO_2, $T_c = 304.12$ K. At $T = T_c$, the isotherm exhibits an inflection point so that

$$\left(\frac{\partial P}{\partial V_m}\right)_{T=T_c} = 0 \text{ and } \left(\frac{\partial^2 P}{\partial V_m^2}\right)_{T=T_c} = 0 \qquad \textbf{(7.5)}$$

What is the significance of the critical temperature? Although critical behavior will be discussed in Chapter 8, at this point it is sufficient to know that as the critical point is approached along the 304.12 K isotherm, the density of $CO_2(l)$ decreases and the density of $CO_2(g)$ increases, and at $T = T_c$ the densities are equal. At temperatures greater than T_c, no interface is observed in the experiment depicted in Figure 7.3, and liquid and gas phases can no longer be distinguished. Instead, the term **supercritical fluid** is used to describe the state of CO_2. As will be discussed in Chapter 8, T_c and the corresponding values P_c and V_c, which together are called the **critical constants,** take on particular significance in describing the phase diagram of a pure substance. The critical constants for a number of different substances are listed in Table 7.2 (see Appendix A, Data Tables).

The parameters a and b for the van der Waals and Redlich–Kwong equations of state are chosen so that the equation of state best represents real gas data. This can be done by using the values of P, V, and T at the critical point T_c, P_c, and V_c, as shown in Example Problem 7.1. Parameters a and b calculated from critical constants in this way are listed in Table 7.4 (see Appendix A, Data Tables).

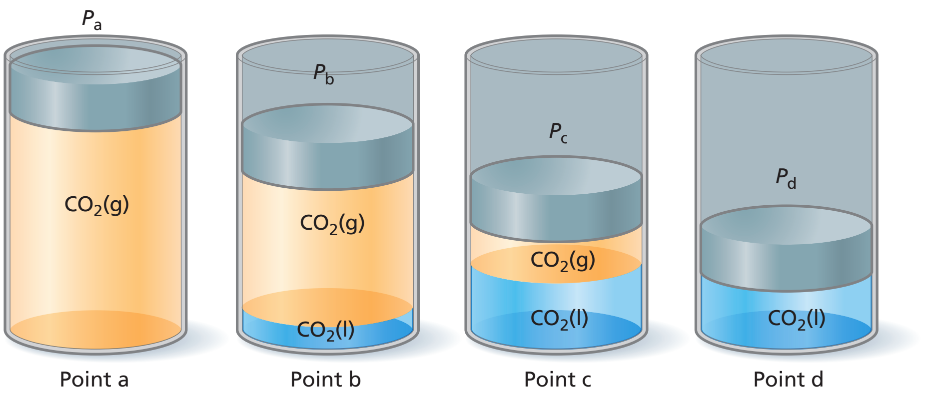


Figure 7.3
Schematic diagram of CO_2 volume and phases present in a transparent cylinder undergoing compression. The experiment is conducted at a constant temperature of 258 K, which corresponds to the brown isotherm in Figure 7.2. Also, cylinders with labeled points a, b, c, and d correspond to the same labeled points in Figure 7.2. The liquid and gas volumes are not shown to scale. Note that $P_b = P_c$.

EXAMPLE PROBLEM 7.1

At $T = T_c$, $(\partial P/\partial V_m)_{T=T_c} = 0$ and $(\partial^2 P/\partial V_m^2)_{T=T_c} = 0$. Use this information to determine a and b in the van der Waals equation of state in terms of the experimentally determined values T_c and P_c.

Solution

$$\left(\frac{\partial\left[\dfrac{RT}{V_m-b}-\dfrac{a}{V_m^2}\right]}{\partial V_m}\right)_{T=T_c} = -\frac{RT_c}{(V_{mc}-b)^2}+\frac{2a}{V_{mc}^3}=0$$

$$\left(\frac{\partial^2\left[\dfrac{RT}{V_m-b}-\dfrac{a}{V_m^2}\right]}{\partial V_m^2}\right)_{T=T_c} = \left(\frac{\partial\left[-\dfrac{RT_c}{(V_m-b)^2}+\dfrac{2a}{V_m^3}\right]}{\partial V_m}\right)_{T=T_c}$$

$$= \frac{2RT_c}{(V_{mc}-b)^3}+\frac{6a}{V_{mc}^4}=0$$

Equating RT_C from these two equations gives

$$RT_c = \frac{2a}{V_{mc}^3}(V_{mc}-b)^2 = \frac{3a}{V_{mc}^4}(V_{mc}-b)^3, \text{ which simplifies to } \frac{3}{2V_{mc}}(V_{mc}-b) = 1$$

The solution to this equation is $V_{mc} = 3b$. Substituting this result into $(\partial P/\partial V_m)_{T=T_c} = 0$ gives

$$-\frac{RT_c}{(V_{mc}-b)^2}+\frac{2a}{V_{mc}^3} = -\frac{RT_c}{(2b)^2}+\frac{2a}{(3b)^3} = 0 \quad \text{or} \quad T_c = \frac{2a}{(3b)^3}\frac{(2b)^2}{R} = \frac{8a}{27Rb}$$

Substituting these results for T_c and V_{mc} in terms of a and b into the van der Waals equation gives the result $P_c = a/27b^2$. We only need two of the critical constants T_c, P_c, and V_{mc} to determine a and b. Because the measurements for P_c and T_c are more accurate than those for V_{mc}, we use these constants to obtain expressions for a and b. These results for P_c and T_c can be used to express a and b in terms of P_c and T_c. The results are

$$b = \frac{RT_c}{8P_c} \quad \text{and} \quad a = \frac{27R^2T_c^2}{64P_c}$$

A similar analysis for the Redlich–Kwong equation gives

$$a = \frac{R^2T_c^{5/2}}{9P_c(2^{1/3}-1)} \quad \text{and} \quad b = \frac{(2^{1/3}-1)RT_c}{3P_c}$$