

Chapter 3

Volumetric Properties of Pure Fluids

Thermodynamic properties, such as internal energy and enthalpy, from which one calculates the heat and work requirements of industrial processes, are often evaluated from volumetric data. Moreover, pressure/volume/temperature (PVT) relations are themselves important for such purposes as the metering of fluids and the sizing of vessels and pipelines. We therefore first describe the general nature of the PVT behavior of pure fluids. There follows a detailed treatment of the ideal gas, the simplest realistic model of fluid behavior. Equations of state are then considered, as they provide the foundation for quantitative description of real fluids. Finally, generalized correlations are presented that allow prediction of the PVT behavior of fluids for which experimental data are lacking.

3.1 PVT BEHAVIOR OF PURE SUBSTANCES

Measurements of the vapor pressure of a pure substance, both as a solid and as a liquid, lead to pressure-vs.-temperature curves such as shown by lines 1-2 and 2- C in Fig. 3.1. The third line (2-3) gives the solid/liquid equilibrium relationship. The three lines display conditions of P and T at which two phases may coexist, and are boundaries for the single-phase regions. Line 1-2, the sublimation curve, separates the solid and gas regions; line 2-3, the *fusion* curve, separates the solid and liquid regions; line 2- C , the vaporization curve, separates the liquid and gas regions. All three lines meet at the triple point, where the three phases coexist in equilibrium. According to the phase rule, Eq. (2.7), the triple point is invariant ($F = 0$). If the system exists along any of the two-phase lines of Fig. 3.1, it is univariant ($F = 1$), whereas in the single-phase regions it is divariant ($F = 2$).

The vaporization curve 2- C terminates at point C , the critical point. The coordinates of this point are the critical pressure P_c and the critical temperature T_c , the highest pressure and highest temperature at which a pure chemical species can exist in vapor/liquid equilibrium.

Homogeneous fluids are usually classified as liquids or gases. However, the distinction cannot always be sharply drawn, because the two phases become indistinguishable at the critical point. Paths such as the one shown in Fig. 3.1 from A to B lead from the liquid region to the gas region without crossing a phase boundary. The transition from liquid to gas is gradual. On the other hand, paths which cross phase boundary 2- C include a vaporization step, where an abrupt change from liquid to gas occurs.

The area existing at temperatures and pressures greater than T_c and P_c is marked off by dashed lines in Fig. 3.1, which do not represent phase boundaries, but rather are limits fixed by the meanings accorded the words liquid and gas. A phase is generally considered a liquid if vaporization results from pressure reduction at constant temperature. A phase is considered a gas if condensation results from temperature reduction at constant pressure. Since neither process occurs in the area beyond the dashed lines, it is called the *fluid region*.

The gas region is sometimes divided into two parts, as indicated by the dotted vertical line of Fig. 3.1. A gas to the left of this line, which can be condensed either by compression at constant temperature or by cooling at constant pressure, is called a vapor. The region everywhere to the right of this line, where $T > T_c$, including the fluid region, is termed *supercritical*.

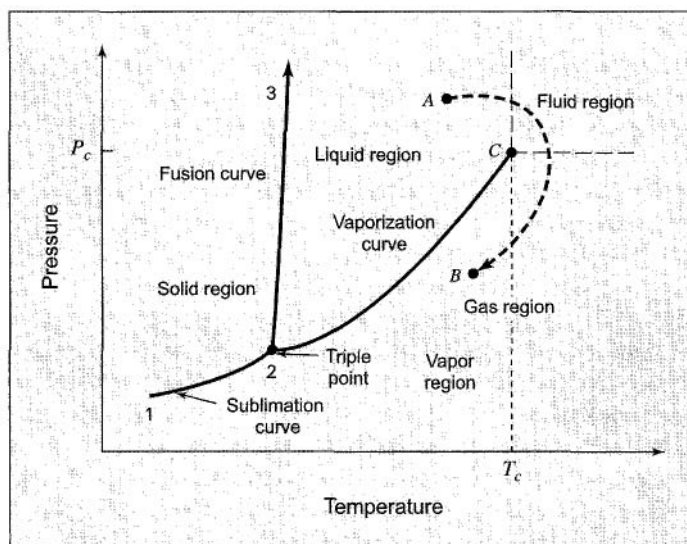


Figure 3.1 PT diagram for a pure substance

PV Diagram

Figure 3.1 does not provide any information about volume; it merely displays the phase boundaries on a PT diagram. On a PV diagram [Fig. 3.2(a)] these boundaries become areas, i.e., regions where two phases, solid/liquid, solid/vapor, and liquid/vapor, coexist in equilibrium. For a given T and P , the relative amounts of the phases determine the molar (or specific) volume. The triple point of Fig. 3.1 here becomes a horizontal line, where the three phases coexist at a single temperature and pressure.

Figure 3.2(b) shows the liquid, liquid/vapor, and vapor regions of the PV diagram, with four isotherms superimposed. Isotherms on Fig. 3.1 are vertical lines, and at temperatures greater than T_c do not cross a phase boundary. On Fig. 3.2(b) the isotherm labeled $T > T_c$ is therefore smooth.

The lines labeled T_1 and T_2 are for subcritical temperatures, and consist of three segments. The horizontal segment of each isotherm represents all possible mixtures of liquid and vapor in equilibrium, ranging from 100% liquid at the left end to 100% vapor at the right end. The locus of these end points is the dome-shaped curve labeled BCD, the left half of which (from B to C)

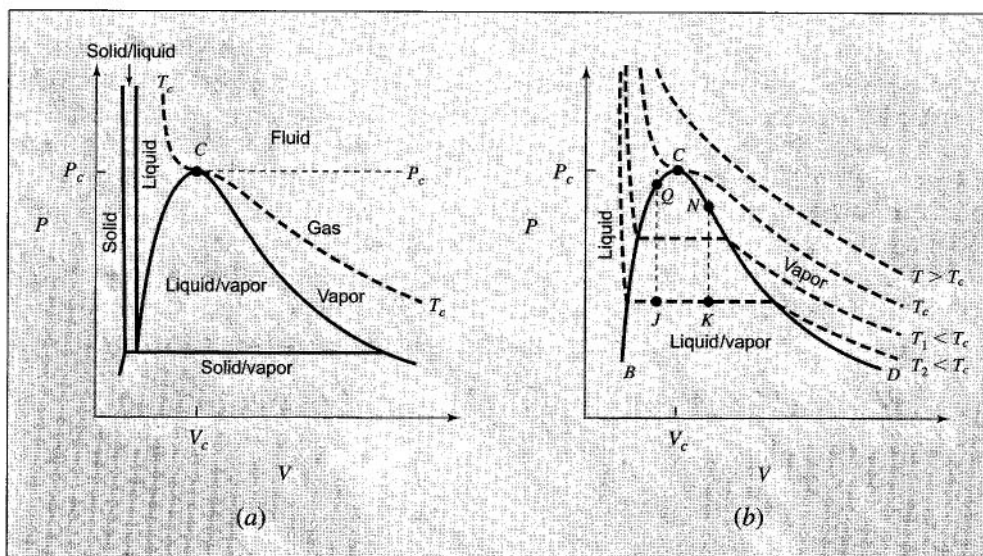


Figure 3.2 PV diagrams for a pure substance. (a) Showing solid, liquid, and gas regions. (b) Showing liquid, liquid/vapor, and vapor regions with isotherms

represents single-phase (saturated) liquids at their vaporization (boiling) temperatures, and the right half (from C to D), single-phase (saturated) vapors at their condensation temperatures. The horizontal portion of an isotherm lies at a particular saturation or vapor pressure, given by the point on Fig. 3.1 where the isotherm crosses the vaporization curve.

The two-phase liquid/vapor region lies under dome BCD, whereas the subcooled-liquid and superheated-vapor regions lie to the left and right, respectively. Subcooled liquid exists at temperatures below, and superheated vapor, at temperatures above the boiling point for the given pressure. Isotherms in the subcooled-liquid region are very steep, because liquid volumes change little with large changes in pressure.

The horizontal segments of the isotherms in the two-phase region become progressively shorter at higher temperatures, being ultimately reduced to a point at C. Thus, the critical isotherm, labeled T_c , exhibits a horizontal inflection at the critical point C at the top of the dome. Here the liquid and vapor phases cannot be distinguished from each other, because their properties are the same.

Critical Behavior

Insight into the nature of the critical point is gained from a description of the changes that occur when a pure substance is heated in a sealed upright tube of constant volume. The dotted vertical lines of Fig. 3.2(b) indicate such processes. They may also be traced on the P-T diagram of Fig. 3.3, where the solid line is the vaporization curve (Fig. 3.1), and the dashed lines are constant-volume paths in the single-phase regions. If the tube is filled with either liquid or gas, the heating process produces changes which lie along the dashed lines, e.g., by the change from E to F (subcooled-liquid) and by the change from G to H (superheated-vapor). The corresponding vertical lines on Fig. 3.2(b) lie to the left and to the right of BCD.

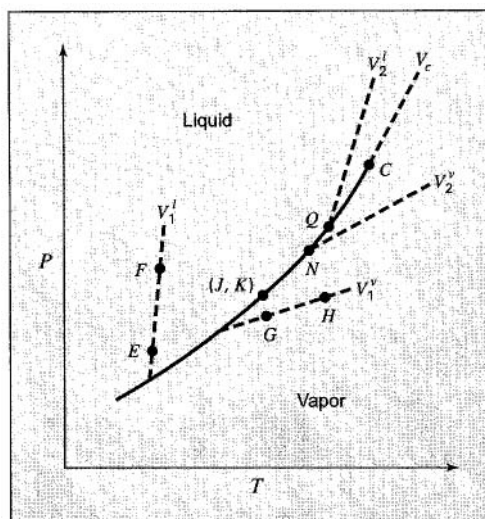


Figure 3.3 PT diagram for a pure fluid showing the vapor-pressure curve and constant-volume lines in the single-phase regions

If the tube is only partially filled with liquid (the remainder being vapor in equilibrium with the liquid), heating at first causes changes described by the vapor-pressure curve (solid line) of Fig. 3.3. For the process indicated by line J Q on Fig. 3.2(b), the meniscus is initially near the top of the tube (point J), and the liquid expands upon heating until it completely fills the tube (point Q). On Fig. 3.3 the process traces a path from (J, K) to Q, and with further heating departs from the vapor-pressure curve along the line of constant molar volume V_2^l .

The process indicated by line KN on Fig. 3.2(b) starts with a lower meniscus level in the tube (point K); heating causes liquid to vaporize, and the meniscus recedes to the bottom of the tube (point N). On Fig. 3.3 the process traces a path from (J, K) to N. With further heating the path continues along the line of constant molar volume V_2^v .

For a unique filling of the tube, with a particular intermediate meniscus level, the heating process follows a vertical line on Fig. 3.2(b) that passes through the critical point C. Physically, heating does not produce much change in the level of the meniscus. As the critical point is approached, the meniscus becomes indistinct, then hazy, and finally disappears. On Fig. 3.3 the path first follows the vapor-pressure curve, proceeding from point (J, K) to the critical point C, where it enters the single-phase fluid region, and follows V_c , the line of constant molar volume equal to the critical volume of the fluid.

Single-Phase Region

For the regions of the diagram where a single phase exists, Fig. 3.2(b) implies a relation connecting P, V, and T which may be expressed by the functional equation:

$$f(P, V, T) = 0$$

This means that an equation of state exists relating pressure, molar or specific volume, and temperature for any pure homogeneous fluid in equilibrium states. The simplest equation of state is for an ideal gas, $PV = RT$, a relation which has approximate validity for the low-pressure gas region of Fig. 3.2(b), and which is discussed in detail in Sec. 3.3.

An equation of state may be solved for any one of the three quantities P , V , or T as a function of the other two. For example, if V is considered a function of T and P , then $V = V(T, P)$, and

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \quad (3.1)$$

The partial derivatives in this equation have definite physical meanings, and are related to two properties, commonly tabulated for liquids, and defined as follows:

• **Volume expansivity:** $\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ (3.2)

■ **Isothermal compressibility:** $\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ (3.3)

Combination of Eqs. (3.1) through (3.3) provides the equation:

$$\frac{dV}{V} = \beta dT - \kappa dP \quad (3.4)$$

The isotherms for the liquid phase on the left side of Fig. 3.2(b) are very steep and closely spaced. Thus both $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ and hence both β and κ are small. This characteristic behavior of liquids (outside the critical region) suggests an idealization, commonly employed in fluid mechanics and known as the *incompressible fluid*, for which both β and κ are zero. No real fluid is truly incompressible, but the idealization is useful, because it often provides a sufficiently realistic model of liquid behavior for practical purposes. There is no PVT equation of state for an incompressible fluid, because V is independent of T and P .

For liquids β is almost always positive (liquid water between 273.15 K (0°C) and 277.15 K (4°C) is an exception), and κ is necessarily positive. At conditions not close to the critical point, β and κ are weak functions of temperature and pressure. Thus for small changes in T and P little error is introduced if they are assumed constant. Integration of Eq. (3.4) then yields:

$$\ln \frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1) \quad (3.5)$$

This is a less restrictive approximation than the assumption of an incompressible fluid.

Example 3.1

For acetone at 293.15 K (20°C) and 1 bar,

$$\begin{aligned} \beta &= 1.487 \times 10^{-3} \text{ K}^{-1} \\ \kappa &= 62 \times 10^{-6} \text{ bar}^{-1} \\ V &= 1.287 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \end{aligned}$$

Find:

- The value of $(\partial P/\partial T)_V$.
- The pressure generated when acetone is heated at constant volume from 293.15 K(20°C) and 1 bar to 303.15 K(30°C).
- The volume change when acetone is changed from 293.15 K(20°C) and 1 bar to 273.15 K(0°C) and 10 bar.

Solution 3.1

(a) The derivative $(\partial P/\partial T)_V$ is determined by application of Eq. (3.4) to the case for which V is constant and $dV = 0$:

$$\beta dT - \kappa dP = 0 \quad (\text{const. } V)$$

or

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa} = \frac{1.487 \times 10^{-3}}{62 \times 10^{-6}} = 24 \text{ bar K}^{-1}$$

(b) If β and κ are assumed constant in the 10 K temperature interval, then the equation derived in (a) may be written ($V = \text{const.}$)

$$\Delta P = \frac{\beta}{\kappa} \Delta T = (24)(10) = 240 \text{ bar}$$

and

$$P_2 = P_1 + \Delta P = 1 + 240 = 241 \text{ bar}$$

(c) Direct substitution into Eq. (3.5) gives

$$\ln \frac{V_2}{V_1} = (1.487 \times 10^{-3})(-20) - (62 \times 10^{-6})(9) = -0.0303$$

Whence

$$\frac{V_2}{V_1} = 0.9702$$

and

$$V_2 = (0.9702)(1.287)(10^{-3}) = 1.249 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$$

which gives

$$\Delta V = V_2 - V_1 = (1.249 - 1.287)(10^{-3}) = -(0.038)(10^{-3}) \text{ m}^3 \text{ kg}^{-1}$$

3.2 VIRIAL EQUATIONS OF STATE

Figure 3.2 indicates the complexity of the PVT behavior of a pure substance and suggests the difficulty of its description by an equation. However, for the gas region alone relatively simple equations often suffice. Along a vapor-phase isotherm such as T_1 in Fig. 3.2(b), V decreases as P increases. The PV product for a gas or vapor should therefore be much more nearly

constant than either of its members, and hence more easily represented. For example, PV along an isotherm may be expressed as a function of P by a power series:

$$PV = a + bP + cP^2 + \dots$$

If $b \equiv aB'$, $c \equiv aC'$, etc., then,

$$PV = a(1 + B'P + C'P^2 + D'P^3 + \dots) \quad (3.6)$$

where a , B' , C' , etc., are constants for a given temperature and a given chemical species.

In principle, the right side of Eq. (3.6) is an infinite series. However, in practice a finite number of terms is used. In fact, PVT data show that at low pressures truncation after two terms usually provides satisfactory results.

Ideal-Gas Temperatures; Universal Gas Constant

Parameters B' , C' , etc., in Eq. (3.6) are species dependent and functions of temperature, but parameter a is the same function of temperature for all species. This is shown experimentally by measurements of volumetric data as a function of P for various gases at constant temperature. Figure 3.4, for example, is a plot of PV vs. P for four gases at the triple-point temperature of water. The limiting value of PV as $P \rightarrow 0$ is the same for all of the gases. In this limit (denoted by the asterisk), Eq. (3.6) becomes:

$$(PV)^* = a = f(T)$$

It is this property of gases that makes them valuable in thermometry, because the limiting values are used to establish a temperature scale which is independent of the gas used as thermometric fluid. The functional relationship $f(T)$ and a quantitative scale must be established; both steps are completely arbitrary. The simplest procedure, and the one adopted internationally, is:

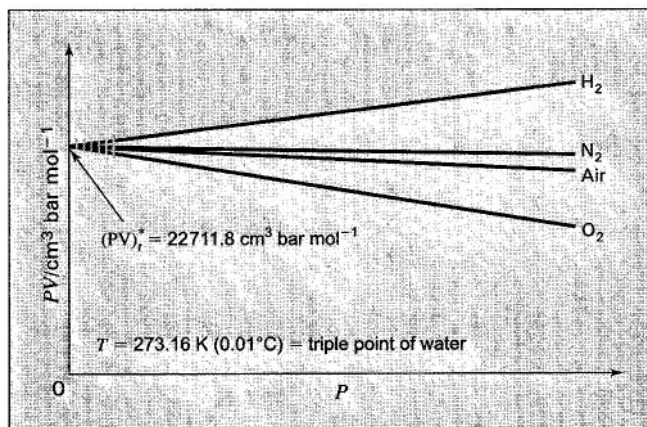


Figure 3.4 $(PV)^*$, the limiting value of PV as $P \rightarrow 0$, is independent of the gas

- Make $(PV)^*$ directly proportional to T , with R as the proportionality constant:

$$(PV)^* = a = RT \quad (3.7)$$

- Assign the value 273.16 K to the temperature of the triple point of water (denoted by subscript t):

$$(PV)_t^* = R \times 273.16 \text{ K} \quad (3.8)$$

Division of Eq. (3.7) by Eq. (3.8) gives:

$$\frac{(PV)^*}{(PV)_t^*} = \frac{T/\text{K}}{273.16 \text{ K}}$$

$$\boxed{T/\text{K} = 273.16 \frac{(PV)^*}{(PV)_t^*}} \quad (3.9)$$

Equation (3.9) establishes the Kelvin temperature scale throughout the temperature range for which values of $(PV)^*$ are experimentally accessible.

The state of a gas at the limiting condition where $P \rightarrow 0$ deserves some discussion. The molecules making up a gas become more and more widely separated as pressure is decreased, and the volume of the molecules themselves becomes a smaller and smaller fraction of the total volume occupied by the gas. Furthermore, the forces of attraction between molecules become ever smaller because of the increasing distances between them (Sec. 16.1). In the limit, as the pressure approaches zero, the molecules are separated by infinite distances. Their volumes become negligible compared with the total volume of the gas, and the intermolecular forces approach zero. At these conditions all gases are said to be *ideal*, and the temperature scale established by Eq. (3.9) is known as the *ideal-gas temperature scale*. The proportionality constant R in Eq. (3.7) is called the *universal gas constant*. Its numerical value is determined by means of Eq. (3.8) from experimental PVT data:

$$R = \frac{(PV)_t^*}{273.16 \text{ K}}$$

Since PVT data cannot in fact be taken at zero pressure, data taken at finite pressures are extrapolated to the zero-pressure state. Determined as indicated by Fig. 3.4, the accepted value of $(PV)_t^*$ is $22.7118 \text{ m}^3 \text{ bar kmol}^{-1}$, leading to the following value of R :

$$R = \frac{22.7118 \text{ m}^3 \text{ bar kmol}^{-1}}{273.16 \text{ K}} = 0.0831447 \text{ m}^3 \text{ bar kmol}^{-1} \text{ K}^{-1}$$

Through the use of conversion factors, R may be expressed in various units. Commonly used values are given by Table A.2 of App. A.

Two Forms of the Virial Equation

A useful auxiliary thermodynamic property is *defined* by the equation:

$$\boxed{Z \equiv \frac{PV}{RT}} \quad (3.10)$$

¹<http://physics.nist.gov/constants>.

This dimensionless ratio is called the *compressibility factor*. With this definition and with $a = RT$ [Eq. (3.7)], Eq. (3.6) becomes:

$$Z = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (3.11)$$

An alternative expression for Z is also in common use:²

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad (3.12)$$

Both of these equations are known as *virial expansions*, and the parameters B' , C' , D' , etc., and B , C , D , etc., are called *virial coefficients*. Parameters B' and B are *second* virial coefficients; C' and C are *third* virial coefficients; etc. For a given gas the virial coefficients are functions of temperature only.

The two sets of coefficients in Eqs. (3.11) and (3.12) are related as follows:

$$B' = \frac{B}{RT} \quad C' = \frac{C - B^2}{(RT)^2} \quad D' = \frac{D - 3BC + 2B^3}{(RT)^3} \quad \text{etc.}$$

The derivation of these relations requires first the elimination of P on the right of Eq. (3.11). An expression for P comes from Eq. (3.12) with Z replaced by PV/RT . The resulting equation is a power series in $1/V$ which is compared term by term with Eq. (3.12) to provide the equations relating the two sets of virial coefficients. They hold exactly only for the two virial expansions as infinite series, but are acceptable approximations for the truncated forms treated in Sec. 3.4.

Many other equations of state have been proposed for gases, but the virial equations are the only ones having a firm basis in theory. The methods of statistical mechanics allow derivation of the virial equations and provide physical significance to the virial coefficients. Thus, for the expansion in $1/V$, the term B/V arises on account of interactions between pairs of molecules (Sec. 16.2); the C/V^2 term, on account of three-body interactions; etc. Since two-body interactions are many times more common than three-body interactions, and three-body interactions are many times more numerous than four-body interactions, etc., the contributions to Z of the successively higher-ordered terms decrease rapidly.

3.3 THE IDEAL GAS

Since the terms B/V , C/V^2 , etc., of the virial expansion [Eq. (3.12)] arise on account of molecular interactions, the virial coefficients B , C , etc., would be zero if no such interactions existed. The virial expansion would then reduce to:

$$Z = 1 \quad \text{or} \quad PV = RT$$

For a real gas, molecular interactions do exist, and exert an influence on the observed behavior of the gas. As the pressure of a real gas is reduced at constant temperature, V increases and the contributions of the terms B/V , C/V^2 , etc., decrease. For a pressure approaching zero, Z approaches unity, not because of any change in the virial coefficients, but because V becomes

²Proposed by H. Kamerlingh Onnes, "Expression of the Equation of State of Gases and Liquids by Means of Series," *Communications from the Physical Laboratory of the University of Leiden*, no. 71, 1901.

infinite. Thus in the limit as the pressure approaches zero, the equation of state assumes the same simple form as for the hypothetical case of $B = C = \dots = 0$; i.e.,

$$Z = 1 \quad \text{or} \quad PV = RT$$

We know from the phase rule that the internal energy of a real gas is a function of pressure as well as of temperature. This pressure dependency is the result of forces between the molecules. If such forces did not exist, no energy would be required to alter the average intermolecular distance, and therefore no energy would be required to bring about volume and pressure changes in a gas at constant temperature. We conclude that in the absence of molecular interactions, the internal energy of a gas depends on temperature only. These considerations of the behavior of a hypothetical gas in which no intermolecular forces exist and of a real gas in the limit as pressure approaches zero lead to the definition of an ideal gas as one whose macroscopic behavior is characterized by:

- The equation of state:

$$\boxed{PV = RT} \quad (\text{ideal gas}) \quad (3.13)$$

- An internal energy that is a function of temperature only:

$$\boxed{U = U(T)} \quad (\text{ideal gas}) \quad (3.14)$$

Implied Property Relations for an Ideal Gas

The definition of heat capacity at constant volume, Eq. (2.16), leads for an ideal gas to the conclusion that C_V is a function of temperature only:

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT} = C_V(T) \quad (3.15)$$

The defining equation for enthalpy, Eq. (2.11), applied to an ideal gas, leads to the conclusion that H also is a function of temperature only:

$$H \equiv U + PV = U(T) + RT = H(T) \quad (3.16)$$

The heat capacity at constant pressure C_P , defined by Eq. (2.20), like C_V , is a function of temperature only:

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P = \frac{dH}{dT} = C_P(T) \quad (3.17)$$

A useful relation between C_P and C_V for an ideal gas comes from differentiation of Eq. (3.16):

$$C_P = \frac{dH}{dT} = \frac{dU}{dT} + R = C_V + R \quad (3.18)$$

This equation does not imply that C_P and C_V are themselves constant for an ideal gas, but only that they vary with temperature in such a way that their difference is equal to R .

For any change of state of an ideal gas Eq. (3.15) may be written:

$$dU = C_V dT \quad (3.19a)$$

Whence,

$$\Delta U = \int C_V dT \quad (3.19b)$$

By Eq. (3.17),

$$dH = C_P dT \quad (3.20a)$$

Whence,

$$\Delta H = \int C_P dT \quad (3.20b)$$

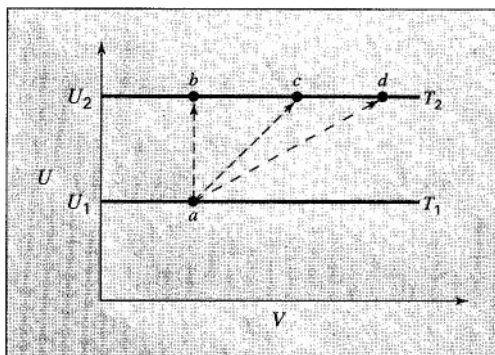


Figure 3.5 Internal energy changes for an ideal gas

Since both the internal energy and C_V of an ideal gas are functions of temperature only, ΔU for an ideal gas is *always* given by Eq. (3.19b), regardless of the kind of process causing the change. This is demonstrated in Fig. 3.5, which shows a graph of internal energy as a function of molar volume with temperature as parameter. Since U is independent of V , a plot of U vs. V at constant temperature is a horizontal line. For different temperatures, U has different values, with a separate line for each temperature. Two such lines are shown in Fig. 3.5, one for temperature T_1 and one for a higher temperature T_2 . The dashed line connecting points a and b represents a constant-volume process for which the temperature increases from T_1 to T_2 and the internal energy changes by $\Delta U = U_2 - U_1$. This change in internal energy is given by Eq. (3.19b) as $\Delta U = \int C_V dT$. The dashed lines connecting points a and c and points a and d represent other processes not occurring at constant volume but which also lead from an initial temperature T_1 to a final temperature T_2 . The graph shows that the change in U for these processes is the same as for the constant-volume process, and it is therefore given by the same equation, namely, $\Delta U = \int C_V dT$. However, ΔU is *not* equal to Q for these processes, because Q depends not only on T_1 and T_2 but also on the path of the process. An entirely analogous discussion applies to the enthalpy H of an ideal gas. (See Sec. 2.16.)

The ideal gas is a model fluid described by simple *property relations*, which are frequently good approximations when applied to actual gases. In *process calculations*, gases at pressures up to a few bars may often be considered ideal, and simple equations then apply.

Equations for Process Calculations: Ideal Gases

For an ideal gas in any mechanically reversible closed-system process, Eq. (2.6), written for a unit mass or a mole, may be combined with Eq. (3.19a):

$$dQ + dW = C_V dT$$

The work for a mechanically reversible closed-system process is given by Eq. (1.2), also written for one mole or a unit mass:

$$dW = -P dV$$

Whence,

$$dQ = C_V dT + P dV$$

The two preceding equations for an ideal gas undergoing a reversible process in a closed system take several forms through elimination of one of the variables P , V , or T by Eq. (3.13). Thus, with $P = RT/V$ they become:

$$dQ = C_V dT + RT \frac{dV}{V} \quad (3.21)$$

$$dW = -RT \frac{dV}{V} \quad (3.22)$$

Alternatively, let $V = RT/P$:

$$dQ = C_V dT + P \left(\frac{R}{P} dT - \frac{RT}{P^2} dP \right)$$

With Eq. (3.18) this reduces to:

$$dQ = C_P dT - RT \frac{dP}{P} \quad (3.23)$$

Also,

$$dW = -R dT + RT \frac{dP}{P} \quad (3.24)$$

Finally, let $T = PV/R$:

$$dQ = C_V \left(\frac{V}{R} dP + \frac{P}{R} dV \right) + P dV$$

Again with Eq. (3.18) this becomes:

$$dQ = \frac{C_V}{R} V dP + \frac{C_P}{R} P dV \quad (3.25)$$

The work is simply:

$$dW = -P dV$$

These equations may be applied to various processes, as described in what follows. The general restrictions implicit in their derivation are:

- The equations are valid for ideal gases.

- The process is mechanically reversible.
- The system is closed.

Isothermal Process

By Eqs. (3.19b) and (3.20b), $\Delta U = \Delta H = 0$

By Eqs. (3.21) and (3.23), $Q = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_2}{P_1}$

By Eqs. (3.22) and (3.24), $W = -RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_2}{P_1}$

Note that $Q = -W$, a result that also follows from Eq. (2.3). Therefore,

$$Q = -W = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_2}{P_1} \quad (\text{const } T) \quad (3.26)$$

Isobaric Process

By Eqs. (3.19b) and (3.20b),

$$\Delta U = \int C_V dT \quad \text{and} \quad \Delta H = \int C_P dT$$

and by Eqs. (3.23) and (3.24),

$$Q = \int C_P dT \quad \text{and} \quad W = -R(T_2 - T_1)$$

Note that $Q = \Delta H$, a result also given by Eq. (2.13). Therefore,

$$Q = \Delta H = \int C_P dT \quad (\text{const } P) \quad (3.27)$$

Isochoric (Constant-V) Process

Equations (3.19b) and (3.20b) again apply:

$$\Delta U = \int C_V dT \quad \text{and} \quad \Delta H = \int C_P dT$$

By Eqs. (3.21) and (1.3),

$$Q = \int C_V dT \quad \text{and} \quad W = 0$$

Note that $Q = \Delta U$, a result also given by Eq. (2.10). Therefore,

$$Q = \Delta U = \int C_V dT \quad (\text{const } V) \quad (3.28)$$

Adiabatic Process: Constant Heat Capacities

An adiabatic process is one for which there is no heat transfer between the system and its surroundings; that is, $dQ = 0$. Each of Eqs. (3.21), (3.23), and (3.25) may therefore be set equal to zero. Integration with C_V and C_P constant then yields simple relations among the variables T , P , and V . For example, Eq. (3.21) becomes:

$$\frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V}$$

Integration with C_V constant then gives:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V}$$

Similarly, Eqs. (3.23) and (3.25) lead to:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_P} \quad \text{and} \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{C_P/C_V}$$

These equations may also be expressed as:

$$TV^{\gamma-1} = \text{constant} \quad (3.29a)$$

$$TP^{(1-\gamma)/\gamma} = \text{constant} \quad (3.29b)$$

$$PV^\gamma = \text{constant} \quad (3.29c)$$

Where by *definition*,³

$$\gamma \equiv \frac{C_P}{C_V} \quad (3.30)$$

Equations (3.29) apply to an ideal gas with constant heat capacities undergoing a mechanically reversible adiabatic process.

The work of an adiabatic process may be obtained from the relation:

$$dW = dU = C_V dT$$

If C_V is constant, integration gives:

$$W = \Delta U = C_V \Delta T \quad (3.31)$$

Alternative forms of Eq. (3.31) are obtained when C_V is eliminated in favor of the heat-capacity ratio γ :

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$$

³If C_V and C_P are constant, γ is necessarily constant. For an ideal gas, the assumption of constant γ is equivalent to the assumption that the heat capacities themselves are constant. This is the only way that the ratio $C_P/C_V \equiv \gamma$ and the difference $C_P - C_V = R$ can *both* be constant. Except for the monotonic gases, both C_P and C_V actually increase with temperature, but the ratio γ is less sensitive to temperature than the heat capacities themselves.

Whence,

$$C_V = \frac{R}{\gamma - 1}$$

Therefore

$$W = C_V \Delta T = \frac{R \Delta T}{\gamma - 1}$$

Since $RT_1 = P_1 V_1$ and $RT_2 = P_2 V_2$, this expression may be written:

$$W = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \quad (3.32)$$

Equations (3.31) and (3.32) are general for an adiabatic process, whether reversible or not. However, V_2 is usually not known, and is eliminated from Eq. (3.32) by Eq. (3.29c), valid only for mechanically reversible processes. This leads to the expression:

$$W = \frac{P_1 V_1}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] = \frac{RT_1}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (3.33)$$

The same result is obtained when the relation between P and V given by Eq. (3.29c) is used for integration of the expression $W = - \int P dV$.

Equations (3.29), (3.31), (3.32), and (3.33) are for ideal gases with constant heat capacities. Equations (3.29) and (3.33) also require the process to be mechanically reversible; processes which are adiabatic but not mechanically reversible are *not* described by these equations.

When applied to real gases, Eqs. (3.29) through (3.33) often yield satisfactory approximations, provided the deviations from ideality are relatively small. For monatomic gases, $\gamma = 1.67$; approximate values of γ are 1.4 for diatomic gases and 1.3 for simple polyatomic gases such as CO_2 , SO_2 , NH_3 , and CH_4 .

Polytropic Process

Since *polytropic* means "turning many ways," *polytropic process* suggests a model of some versatility. With δ a constant, it is defined as a process for which

$$P V^\delta = \text{constant} \quad (3.34a)$$

For an ideal gas equations analogous to Eqs. (3.29a) and (3.29b) are readily derived:

$$T V^{\delta-1} = \text{constant} \quad (3.34b)$$

and

$$T P^{(1-\delta)/\delta} = \text{constant} \quad (3.34c)$$

When the relation between P and V is given by Eq. (3.34a), evaluation of $\int P dV$ yields Eq. (3.33) with γ replaced by δ :

$$W = \frac{RT_1}{\delta - 1} \left[\left(\frac{P_2}{P_1} \right)^{(\delta-1)/\delta} - 1 \right] \quad (3.35)$$

Moreover, for constant heat capacities, the first law solved for Q yields:

$$Q = \frac{(\delta - \gamma)RT_1}{(\delta - 1)(\gamma - 1)} \left[\left(\frac{P_2}{P_1} \right)^{(\delta-1)/\delta} - 1 \right] \quad (3.36)$$

The several processes already described correspond to the four paths shown on Fig. 3.6 for specific values of δ :

- Isobaric process: By Eq. (3.34a), $\delta = 0$.
- Isothermal process: By Eq. (3.34b), $\delta = 1$.
- Adiabatic process: $\delta = \gamma$.
- Isochoric process: By Eq. (3.34a), $dV/dP = V/P\delta$; for constant V , $\delta = \pm\infty$.

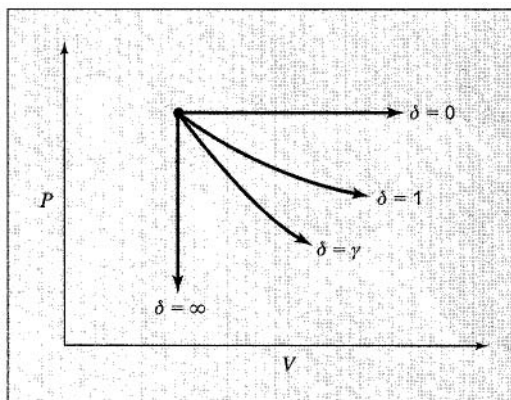


Figure 3.6 Paths of polytropic processes characterized by specific values of δ

Irreversible Process

The equations developed in this section have been derived for mechanically reversible, closed-system processes for ideal gases. However, those equations which relate changes in state functions only are valid for ideal gases regardless of the process. They apply equally to reversible and irreversible processes in both closed and open systems, because changes in state functions depend only on the initial and final states of the system. On the other hand, an equation for Q or W is specific to the process considered in its derivation.

The work of an irreversible process is calculated by a two-step procedure. First, W is determined for a mechanically reversible process that accomplishes the same change of state as the actual irreversible process. Second, this result is multiplied or divided by an efficiency to give the actual work. If the process produces work, the absolute value for the reversible process is too large and must be multiplied by an efficiency. If the process requires work, the value for the reversible process is too small and must be divided by an efficiency.

Applications of the concepts and equations developed in this section are illustrated in the examples that follow. In particular, the work of irreversible processes is treated in the last part of Ex. 3.3.

Example 3.2

Air is compressed from an initial condition of 1 bar and 298.15 K (25°C) to a final state of 5 bar and 298.15 K (25°C) by three different mechanically reversible processes in a closed system:

- (a) Heating at constant volume followed by cooling at constant pressure.
- (b) Isothermal compression.
- (c) Adiabatic compression followed by cooling at constant volume.

Assume air to be an ideal gas with the constant heat capacities, $C_V = (5/2)R$ and $C_P = (7/2)R$. Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air for each process.

Solution 3.2

Choose the system as 1 mol of air, contained in an imaginary frictionless piston/cylinder arrangement. For $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$C_V = 20.785$$

$$C_P = 29.099 \text{ J mol}^{-1} \text{ K}^{-1}$$

The initial and final conditions of the air are identical with those of Ex. 2.9, where the molar volumes are given as:

$$V_1 = 0.02479$$

$$V_2 = 0.004958 \text{ m}^3$$

Moreover, since the initial and final temperatures are the same, then for all parts of the problem:

$$\Delta U = \Delta H = 0$$

(a) The heat transferred, from Ex. 2.9(b), is $Q = -9915 \text{ J}$. Thus by the first law applied to the entire process:

$$W = \Delta U - Q = 0 + 9915 = 9915 \text{ J}$$

(b) Equation (3.26) for the isothermal compression of an ideal gas applies here:

$$Q = -W = RT \ln \frac{P_1}{P_2} = (8.314)(298.15) \ln \frac{1}{5} = -3990 \text{ J}$$

(c) The initial adiabatic compression of the air takes it to its final volume of 0.004958 m^3 . By Eqs. (3.29a) and (3.29c), the temperature and pressure at this point are:

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = (298.15) \left(\frac{0.02479}{0.004958} \right)^{0.4} = 567.57 \text{ K}$$

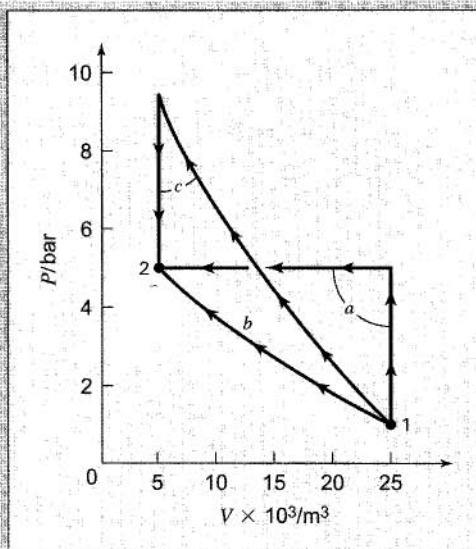


Figure 3.7 Diagram for Ex. 3.2

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^\gamma = (1) \left(\frac{0.02479}{0.004958} \right)^{1.4} = 9.52 \text{ bar}$$

For this step $Q = 0$, and by Eq. (3.31),

$$W = C_V \Delta T = (20.785)(567.57 - 298.15) = 5600 \text{ J}$$

For the second step at constant V , $W = 0$. For the overall process,

$$W = 5600 + 0 = 5600 \text{ J}$$

Moreover, $\Delta U = 0$; and by the first law,

$$Q = \Delta U - W = 0 - 5600 = -5600 \text{ J}$$

Although the property changes ΔU and ΔH are zero for each process, Q and W are path-dependent. Figure 3.7 shows each process on a PV diagram. Since the work for each of these mechanically reversible processes is given by $W = -\int P dV$, the work for each process is proportional to the total area below the paths on the PV diagram representing the process. The relative sizes of these areas correspond to the numerical values of W .

Example 3.3

An ideal gas undergoes the following sequence of mechanically reversible processes in a closed system:

- (a) From an initial state of 343.15 K (70°C) and 1 bar, it is compressed adiabatically to 423.15 K (150°C).

(b) It is then cooled from 423.15 to 343.15 K (150 to 70°C) at constant pressure.

(c) Finally, it is expanded isothermally to its original state.

Calculate W , Q , ΔU , and ΔH for each of the three processes and for the entire cycle. Take $C_V = (3/2)R$ and $C_P = (5/2)R$.

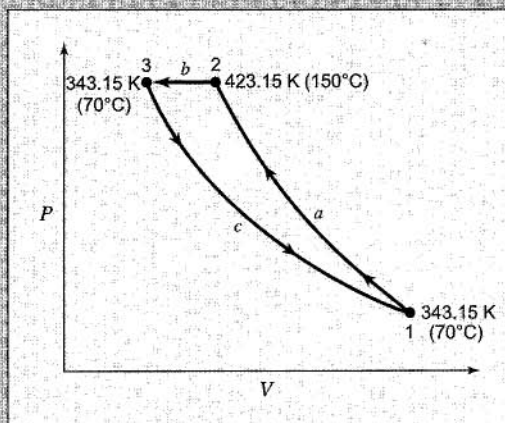


Figure 3.8 Diagram for Ex. 3.3

If these processes are carried out *irreversibly* but so as to accomplish exactly the same *changes of state* (i.e., the same changes in P , T , U , and H), then different values of Q and W result. Calculate Q and W if each step is carried out with an efficiency of 80%.

Solution 3.3

From the given information,

$$C_V = (3/2)(8.314) = 12.471 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_P = (5/2)(8.314) = 20.785 \text{ J mol}^{-1} \text{ K}^{-1}$$

The cycle is represented on a PV diagram in Fig. 3.8. Consider first the mechanically reversible operation of the cycle, and take as a basis 1 mol of gas.

(a) For an ideal gas undergoing adiabatic compression, $Q = 0$, and

$$\Delta U = W = C_V \Delta T = (12.471)(423.15 - 343.15) = 998 \text{ J}$$

$$\Delta H = C_P \Delta T = (20.785)(423.15 - 343.15) = 1663 \text{ J}$$

Pressure P_2 can be found from Eq. (3.29b):

$$P_2 = P_1 \left(\frac{T_2}{T_1} \right)^{\gamma/(\gamma-1)} = (1) \left(\frac{423.15}{343.15} \right)^{2.5} = 1.689 \text{ bar}$$

(b) Equation (3.27), applicable to the constant-pressure process, gives:

$$Q = \Delta H = C_P \Delta T = (20.785)(343.15 - 423.15) = -1663 \text{ J}$$

Also, for an ideal gas,

$$\Delta U = C_V \Delta T = (12.471)(343.15 - 423.15) = -998 \text{ J}$$

By the first law,

$$W = \Delta U - Q = -998 - (-1663) = 665 \text{ J}$$

(c) For ideal gases undergoing an isothermal process, ΔU and ΔH are zero; Eq. (3.26) yields:

$$Q = -W = RT \ln \frac{P_3}{P_1} = RT \ln \frac{P_2}{P_1} = (8.314)(343.15) \ln \frac{1.689}{1} = 1495 \text{ J}$$

For the entire process,

$$Q = 0 - 1663 + 1495 = -168 \text{ J}$$

$$W = 998 + 665 - 1495 = 168 \text{ J}$$

$$\Delta U = 998 - 998 + 0 = 0$$

$$\Delta H = 1663 - 1663 + 0 = 0$$

The property changes ΔU and ΔH both are zero for the entire cycle, because the initial and final states are identical. Note also that $Q = -W$ for the cycle. This follows from the first law with $\Delta U = 0$.

If the same changes of state are carried out by irreversible processes, the property changes for the steps are identical with those already calculated. However, the values of Q and W change.

(a) This step can no longer be adiabatic. For mechanically reversible, adiabatic compression, $W = 998 \text{ J}$. If the process is 80% efficient compared with this,

$$W = \frac{998}{0.80} = 1248 \text{ J}$$

Since ΔU is still 998 J, by the first law:

$$Q = \Delta U - W = 998 - 1248 = -250 \text{ J}$$

(b) The work for the mechanically reversible cooling process is 665 J. For the irreversible process,

$$W = \frac{665}{0.80} = 831 \text{ J}$$

and

$$Q = \Delta U - W = -998 - 831 = -1829 \text{ J}$$

(c) As work is done by the system in this step, the irreversible work in absolute value is less than the reversible work:

$$W = (0.80)(-1495) = -1196 \text{ J}$$

and $Q = \Delta U - W = 0 + 1196 = 1196 \text{ J}$

For the entire cycle, ΔU and ΔH are again zero, but

$$Q = -250 - 1829 + 1196 = -883 \text{ J}$$

and $W = 1248 + 831 - 1196 = 883 \text{ J}$

A summary of these results is given in the accompanying table. All values are in joules.

| | Mechanically reversible | | | | Irreversible | | | |
|-----|-------------------------|------------|-------|-------|--------------|------------|-------|-------|
| | ΔU | ΔH | Q | W | ΔU | ΔH | Q | W |
| (a) | 998 | 1663 | 0 | 998 | 998 | 1663 | -250 | 1248 |
| (b) | -998 | -1663 | -1663 | 665 | -998 | -1663 | -1829 | 831 |
| (c) | 0 | 0 | 1495 | -1495 | 0 | 0 | 1196 | -1196 |
| Sum | 0 | 0 | -168 | 168 | 0 | 0 | -883 | 883 |

The cycle is one which requires work and produces an equal amount of heat. The striking feature of the comparison shown in the table is that the total work required when the cycle consists of three irreversible steps is more than five times the total work required when the steps are mechanically reversible, even though each irreversible step is assumed 80% efficient.

Example 3.4

A 0.4 kg mass of nitrogen at 300.15 K (27°C) is held in a vertical cylinder by a frictionless piston. The weight of the piston makes the pressure of the nitrogen 0.35 bar higher than that of the surrounding atmosphere, which is at 1 bar and 300.15 K (27°C). Thus the nitrogen is initially at a pressure of 1.35 bar, and is in mechanical and thermal equilibrium with its surroundings. Consider the following sequence of processes:

- The apparatus is immersed in an ice/water bath and is allowed to come to equilibrium.
- A variable force is slowly applied to the piston so that the nitrogen is compressed reversibly at the constant temperature of 273.15 K (0°C) until the gas volume reaches one-half the value at the end of step (a). At this point the piston is held in place by latches.
- The apparatus is removed from the ice/water bath and comes to thermal equilibrium with the surrounding atmosphere at 300.15 K (27°C).
- The latches are removed, and the apparatus is allowed to return to complete equilibrium with its surroundings.

Sketch the entire cycle on a PV diagram, and calculate Q , W , ΔU , and ΔH for the

nitrogen for each step of the cycle. Nitrogen may be considered an ideal gas for which $C_V = (5/2)R$ and $C_P = (7/2)R$.

Solution 3.4

At the end of the cycle the nitrogen returns to its initial conditions of 300.15 K (27°C) and 1.35 bar. The steps making up the cycle are:

(a) 300.15 K (27°C), 1.35 bar $\xrightarrow{\text{const } P}$ 273.15 K (0°C), 1.35 bar

(b) 273.15 K (0°C), $V_2 \xrightarrow{\text{const } T}$ 273.15 K (0°C), $V_3 = \frac{1}{2}V_2$

(c) 273.15 K (0°C), $V_3 \xrightarrow{\text{const } V}$ 300.15 K (27°C), $V_4 = V_3$

(d) 300.15 K (27°C), $P_4 \xrightarrow{T_4=T_1}$ 300.15 K (27°C), 1.35 bar

Nitrogen has a molar mass $M = 28$; the number of moles comprising the system is therefore:

$$n = \frac{m}{M} = \frac{0.4 \times 1000}{28} = 14.286 \text{ mol}$$

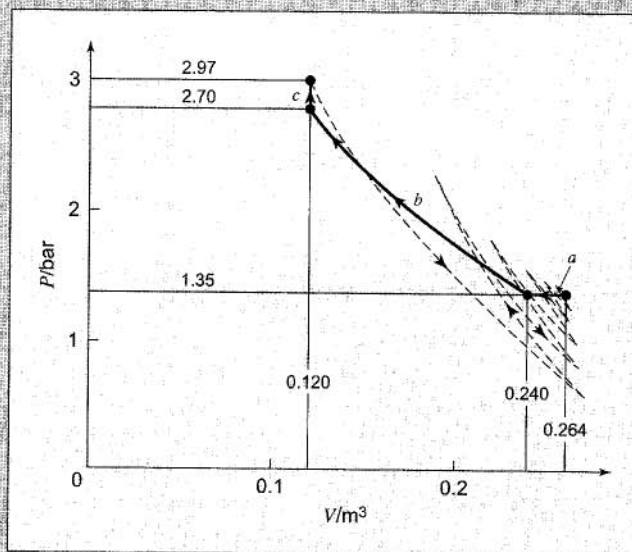


Figure 3.9 Diagram for Ex. 3.4

(a) In this step, represented by the horizontal line marked *a* in Fig. 3.9, the nitrogen is cooled at constant pressure. The process is mechanically reversible, even though the heat transfer occurs irreversibly as the result of a finite temperature difference. Thus, with $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$W_a = -n \int P dV = -nP \Delta V = -nR \Delta T$$

or $W_a = -(14.286)(8.314)(273.15 - 300.15 \text{ K}) = 3207 \text{ J}$

By Eq. (2.23),

$$Q_a = n \Delta H_a = n C_p \Delta T_a = (14.286)(7/2)(8.314)(273.15 - 300.15) = -11\,224 \text{ J}$$

From the first law,

$$n \Delta U_a = Q_a + W_a = -11\,224 + 3207 = -8017 \text{ J}$$

(b) The process carried out here is an isothermal compression shown by curve *b* in Fig. 3.9, and for which:

$$\Delta U_b = \Delta H_b = 0$$

Assume the compression to be mechanically reversible; then,

$$Q_b = -W_b = nRT \ln \frac{V_3}{V_2} = (14.286)(8.314)(273.15) \ln \frac{1}{2} = -22\,487 \text{ J}$$

(c) For this constant-volume process, $W_c = 0$ and, according to Eq. (2.19):

$$Q_c = n \Delta U_c = n C_v \Delta T_c = (14.286)(5/2)(8.314)(300.15 - 273.15) = 8017 \text{ J}$$

In addition,

$$n \Delta H_c = n C_p \Delta T_c = (14.286)(7/2)(8.314)(300.15 - 273.15) = 11\,224 \text{ J}$$

(d) The first three steps of the cycle can be sketched on a *PV* diagram without difficulty, because their paths are known. For the final step this is not possible, because the process is irreversible. When the latches holding the frictionless piston are removed, the piston moves rapidly upward, and owing to its inertia goes beyond its equilibrium position. This initial expansion approximates a reversible, adiabatic process, because little turbulence results from a single stroke of the piston and because heat transfer is relatively slow. The subsequent oscillations of the piston as it gradually reaches its final equilibrium position are the primary source of the irreversibility, because they cause turbulence and mixing in both the gas and the atmosphere. This process goes on for a considerable time during which heat transfer occurs in an amount sufficient to return the nitrogen to its initial temperature of 300.15 K (27°C) at a pressure of 1.35 bar. It is not possible to specify the exact path of an irreversible process and this makes impossible the calculation of either *Q* or *W*. However, the dashed lines in Fig. 3.9 suggest the form that it takes.

Unlike work and heat, the property changes of the system for step *d* can be computed, since they depend solely on the initial and final states, and these are known. Both ΔU_d and ΔH_d are zero, because the initial and final temperatures are 300.15 K (27°C). The first law applies to irreversible as well as to reversible processes, and for step *d* it becomes:

$$\Delta U_d = Q_d + W_d = 0$$

whence

$$Q_d = -W_d$$

Although neither Q_d nor W_d can be calculated, their absolute values are the same. Step d results in elevation of the piston and the atmosphere, and a compensating decrease in the internal energy of the surrounding atmosphere.

Example 3.5

Air flows at a steady rate through a horizontal insulated pipe which contains a partly closed valve. The conditions of the air upstream from the valve are 293.15 K (20°C) and 6 bar, and the downstream pressure is 3 bar. The line leaving the valve is enough larger than the entrance line so that the kinetic-energy change of the air as it flows through the valve is negligible. If air is regarded as an ideal gas, what is the temperature of the air some distance downstream from the valve?

Solution 3.5

Flow through a partly closed valve is known as a *throttling process*. The line is insulated, making Q small; moreover, the potential-energy and kinetic-energy changes are negligible. Since no shaft work is accomplished, $W_s = 0$. Hence, Eq. (2.32) reduces to: $\Delta H = 0$. Thus, for an ideal gas,

$$\Delta H = \int_{T_1}^{T_2} C_p dT = 0$$

Whence,

$$T_2 = T_1$$

The result that $\Delta H = 0$ is general for a throttling process, because the assumptions of negligible heat transfer and potential- and kinetic-energy changes are usually valid. If the fluid is an ideal gas, no temperature change occurs. The throttling process is inherently irreversible, but this is immaterial to the calculation, because Eq. (3.20b) is valid for an ideal gas whatever the process.

Example 3.6

If in Ex. 3.5 the flow rate of the air is 1 mol s^{-1} and if the pipe has an inner diameter of 5 cm, both upstream and downstream from the valve, what is the kinetic-energy change of the air and what is its temperature change? For air, $C_p = (7/2)R$ and the molar mass is $M = 29 \text{ g mol}^{-1}$.

Solution 3.6

Velocity is found from Eq. (2.24b):

$$u = \frac{\dot{n}}{A\rho} = \frac{\dot{n}V}{A}$$

where $A = \frac{\pi}{4}D^2 = \left(\frac{\pi}{4}\right)(5 \times 10^{-2})^2 = 1.964 \times 10^{-3} \text{ m}^2$

The upstream molar volume as given by the ideal-gas equation is:

$$V_1 = \frac{RT_1}{P_1} = \frac{(83.14)(293.15)}{6} \times 10^{-6} = 4.062 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$$

Then,
$$u_1 = \frac{(1)(4.062 \times 10^{-3})}{1.964 \times 10^{-3}} = 2.069 \text{ m s}^{-1}$$

If the downstream temperature is little changed from the upstream temperature, then to a good approximation:

$$V_2 = 2V_1 \quad \text{and} \quad u_2 = 2u_1 = 4.138 \text{ m s}^{-1}$$

The rate of change in kinetic energy is therefore:

$$\begin{aligned} \dot{m} \Delta\left(\frac{1}{2}u^2\right) &= \dot{m} \Delta\left(\frac{1}{2}u^2\right) \\ &= (1 \times 29 \times 10^{-3}) \frac{(4.138^2 - 2.069^2)}{2} = 0.186 \text{ J s}^{-1} \text{ or W} \end{aligned}$$

In the absence of heat transfer and work, the energy balance, Eq. (2.31), becomes:

$$\begin{aligned} \Delta\left(H + \frac{1}{2}u^2\right)\dot{m} &= \dot{m} \Delta H + \dot{m} \Delta\left(\frac{1}{2}u^2\right) = 0 \\ \dot{m} \frac{C_p}{M} \Delta T + \dot{m} \Delta\left(\frac{1}{2}u^2\right) &= \dot{m} C_p \Delta T + \dot{m} \Delta\left(\frac{1}{2}u^2\right) = 0 \end{aligned}$$

Whence
$$(1)(7/2)(8.314)\Delta T = -\dot{m} \Delta\left(\frac{1}{2}u^2\right) = -0.186$$

and
$$\Delta T = -0.0064 \text{ K}$$

Clearly, the initial assumption is justified: the temperature change across the valve is negligible. Even for an upstream pressure of 10 bar and a downstream pressure of 1 bar and for the same flow rate, the temperature change is only -0.076 K . We conclude that, except for very unusual conditions, $\Delta H = 0$ is a satisfactory energy balance for a throttling process.

3.4 APPLICATION OF THE VIRIAL EQUATIONS

The two forms of the virial expansion given by Eqs. (3.11) and (3.12) are infinite series. For engineering purposes their use is practical only where convergence is very rapid, that is, where two or three terms suffice for reasonably close approximations to the values of the series. This is realized for gases and vapors at low to moderate pressures.

Figure 3.10 shows a compressibility-factor graph for methane. Values of the compressibility factor Z (as calculated from PVT data for methane by the defining equation $Z = PV/RT$) are plotted vs. pressure for various constant temperatures. The resulting isotherms show graphically what the virial expansion in P is intended to represent analytically. All isotherms originate at the value $Z = 1$ for $P = 0$. In addition the isotherms are nearly straight lines at low pressures. Thus the tangent to an isotherm at $P = 0$ is a good approximation of the isotherm from $P \rightarrow 0$ to some finite pressure. Differentiation of Eq. (3.11) for a given temperature gives:

$$\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \dots$$

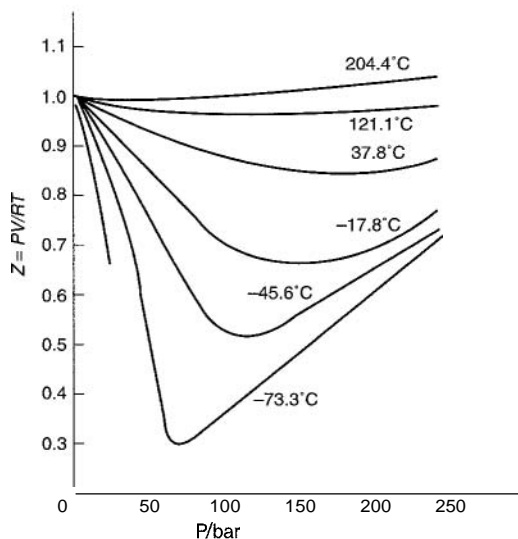


Figure 3.10 Compressibility-factor graph for methane

from which,

$$\left(\frac{\partial Z}{\partial P}\right)_{T;P=0} = B'$$

Thus the equation of the tangent line is:

$$Z = 1 + B'P$$

a result also given by truncating Eq. (3.11) to two terms. A more common form of this equation results from the substitution (Sec. 3.2), $B' = B/RT$:

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT} \quad (3.37)$$

Equation (3.12) may also be truncated to two terms for application at low pressures:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} \quad (3.38)$$

However, Eq. (3.37) is more convenient in application and is at least as accurate as Eq. (3.38). Thus when the virial equation is truncated to two terms, Eq. (3.37) is preferred. This equation satisfactorily represents the PVT behavior of many vapors at subcritical temperatures up to a pressure of about 5 bar. At higher temperatures it is appropriate for gases over an increasing pressure range as the temperature increases. The second virial coefficient B is substance dependent and a function of temperature. Experimental values are available for a number of gases.⁴ Moreover, estimation of second virial coefficients is possible where no data are available, as discussed in Sec. 3.6.

⁴J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures*, pp. 1–10, Clarendon Press, Oxford, 1980.

For pressures above the range of applicability of Eq. (3.37) but below the critical pressure, the virial equation truncated to three terms often provides excellent results. In this case Eq. (3.12), the expansion in $1/V$, is far superior to Eq. (3.11). Thus when the virial equation is truncated to three terms, the appropriate form is:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \quad (3.39)$$

This equation can be solved directly for pressure, but is cubic in volume. Solution for V is easily done by an iterative scheme with a calculator.

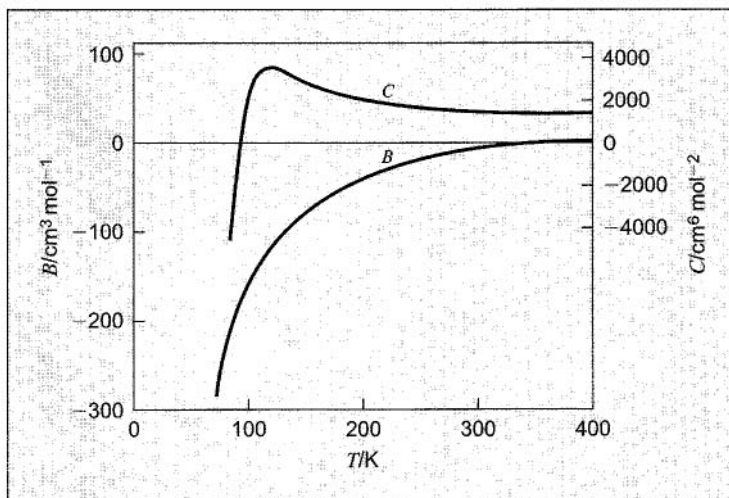


Figure 3.11 Density-series virial coefficients B and C for nitrogen

Values of C , like those of B , depend on the gas and on temperature. However, much less is known about third virial coefficients than about second virial coefficients, though data for a number of gases are found in the literature. Since virial coefficients beyond the third are rarely known and since the virial expansion with more than three terms becomes unwieldy, its use is uncommon.

Figure 3.11 illustrates the effect of temperature on the virial coefficients B and C for nitrogen; although numerical values are different for other gases, the trends are similar. The curve of Fig. 3.11 suggests that B increases monotonically with T ; however, at temperatures much higher than shown B reaches a maximum and then slowly decreases. The temperature dependence of C is more difficult to establish experimentally, but its main features are clear: C is negative at low temperatures, passes through a maximum at a temperature near the critical, and thereafter decreases slowly with increasing T .

A class of equations inspired by Eq. (3.12), known as *extended* virial equations, is illustrated by the Benedict/Webb/Rubin equation:⁵

⁵M. Benedict, G. B. Webb, L. C. Rubin, *J. Chem. Phys.*, vol. 8, pp. 334–345, 1940; vol. 10, pp. 747–758, 1942.

$$P = -\frac{RT}{V} + \frac{B_0 RT - A_0 - C_0/T^2}{V^2} - \frac{bRT - a}{V^3} + \frac{aa}{V^6} + \frac{c}{V^3 T^2} \left(1 + \frac{y}{V^2}\right) \exp \frac{-y}{V^2}$$

where A_0 , B_0 , C_0 , a , b , c , a , and y are all constant for a given fluid. This equation and its modifications, despite their complexity, are used in the petroleum and natural-gas industries for light hydrocarbons and a few other commonly encountered gases.

Example 3.7

Reported values for the virial coefficients of isopropanol vapor at 473.15 K (200°C) are:

$$B = -0.388 \text{ m}^3 \text{ kmol}^{-1}$$

$$C = -26 \times 10^{-3} \text{ m}^6 \text{ kmol}^{-2}$$

Calculate V and Z for isopropanol vapor at 473.15 K (200°C) and 10 bar by:

- The ideal-gas equation.
- Equation (3.37).
- Equation (3.39).

Solution 3.7

The absolute temperature is $T = 473.15 \text{ K}$ (200°C), and the appropriate value of the gas constant is $R = 83.14 \times 10^{-3} \text{ m}^3 \text{ bar kmol}^{-1} \text{ K}^{-1}$

(a) By the ideal-gas equation,

$$V = \frac{RT}{P} = \frac{(83.14 \times 10^{-3})(473.15)}{10} = 3.934 \text{ m}^3 \text{ kmol}^{-1}$$

and of course $Z = 1$.

(b) Solving Eq. (3.37) for V , we find

$$V = \frac{RT}{P} + B = 3.934 - 0.388 = 3.546 \text{ m}^3 \text{ kmol}^{-1}$$

Whence

$$Z = \frac{PV}{RT} = \frac{V}{RT/P} = \frac{3.546}{3.934} = 0.9014$$

(c) To facilitate iteration, we write Eq. (3.39) as

$$V_{i+1} = \frac{RT}{P} \left(1 + \frac{B}{V_i} + \frac{C}{V_i^2} \right)$$

where subscript i denotes the iteration number. For the first iteration, $i = 0$, and

$$V_1 = \frac{RT}{P} \left(1 + \frac{B}{V_0} + \frac{C}{V_0^2} \right)$$

where V_0 is an initial estimate of the molar volume. For this we use the ideal-gas value, which gives

$$V_1 = 3.933 \left(1 - \frac{0.388}{3.934} - \frac{(26)(10^{-3})}{(3.934)^2} \right) = 3.538 \text{ m}^3 \text{ kmol}^{-1}$$

The second iteration depends on this result:

$$V_2 = \frac{RT}{P} \left(1 + \frac{B}{V_1} + \frac{C}{V_1^2} \right)$$

whence

$$V_2 = 3.934 \left(1 - \frac{0.388}{3.538} - \frac{(26)(10^{-3})}{(3.538)^2} \right) = 3.493 \text{ m}^3 \text{ kmol}^{-1}$$

Iteration continues until the difference $V_{i+1} - V_i$ is insignificant, and leads after five iterations to the final value,

$$V = 3.488 \text{ m}^3 \text{ kmol}^{-1}$$

from which $Z = 0.8866$. In comparison with this result, the ideal-gas value is 13 percent too high and Eq. (3.37) gives a value 1.7 percent too high.

3.5 CUBIC EQUATIONS OF STATE

If an equation of state is to represent the PVT behavior of both liquids and vapors, it must encompass a wide range of temperatures and pressures. Yet it must not be so complex as to present excessive numerical or analytical difficulties in application. Polynomial equations that are cubic in molar volume offer a compromise between generality and simplicity that is suitable to many purposes. Cubic equations are in fact the simplest equations capable of representing both liquid and vapor behavior.

The van der Waals Equation of State

The first practical cubic equation of state was proposed by J. D. van der Waals⁶ in 1873:

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \quad (3.40)$$

Here, a and b are positive constants; when they are zero, the ideal-gas equation is recovered.

Given values of a and b for a particular fluid, one can calculate P as a function of V for various values of T . Figure 3.12 is a schematic PV diagram showing three such isotherms. Superimposed is the "dome" representing states of saturated liquid and saturated vapor. For the isotherm $T_1 > T_c$, pressure is a monotonically decreasing function with increasing molar volume. The critical isotherm (labeled T_c) contains the horizontal inflection at C characteristic of the critical point. For the isotherm $T_2 < T_c$, the pressure decreases rapidly in the subcooled-liquid region with increasing V ; after crossing the saturated-liquid line, it goes through a minimum, rises to a maximum, and then decreases, crossing the saturated-vapor line and continuing downward into the superheated-vapor region.

Experimental isotherms do not exhibit this smooth transition from saturated liquid to saturated vapor; rather, they contain a horizontal segment within the two-phase region where saturated liquid and saturated vapor coexist in varying proportions at the saturation or vapor

⁶Johannes Diderik van der Waals (1837–1923), Dutch physicist who won the 1910 Nobel Prize for physics.

pressure. This behavior, shown by the dashed line in Fig. 3.12, is nonanalytic, and we accept as inevitable the unrealistic behavior of equations of state in the two-phase region.

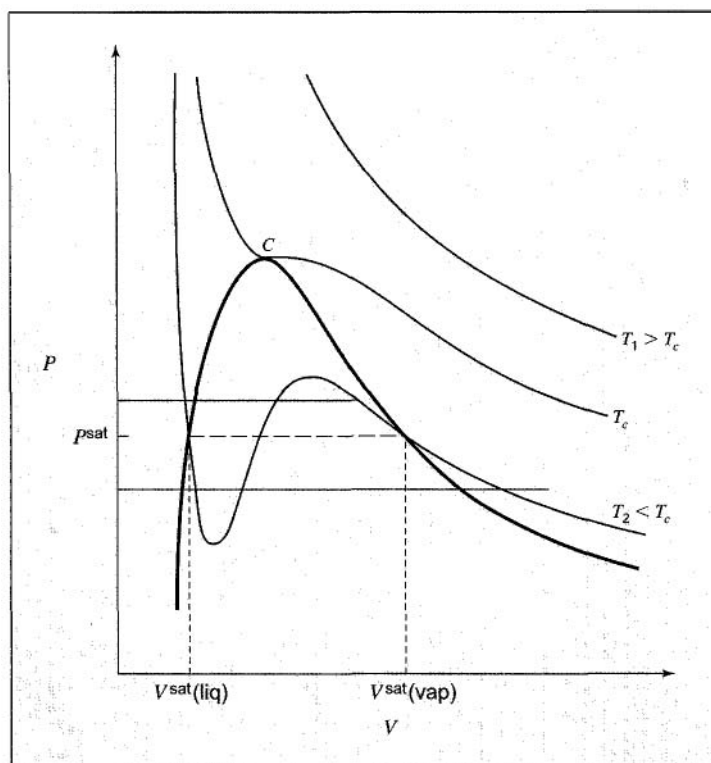


Figure 3.12 Isotherms as given by a cubic equation of state

Actually, the PV behavior predicted in this region by proper cubic equations of state is not wholly fictitious. When the pressure is decreased on a saturated liquid devoid of vapor-nucleation sites in a carefully controlled experiment, vaporization does not occur, and the liquid phase persists alone to pressures well below its vapor pressure. Similarly, raising the pressure on a saturated vapor in a suitable experiment does not cause condensation, and the vapor persists alone to pressures well above the vapor pressure. These nonequilibrium or metastable states of superheated liquid and subcooled vapor are approximated by those portions of the PV isotherm which lie in the two-phase region adjacent to the saturated-liquid and saturated-vapor states.

Cubic equations of state have three volume roots, of which two may be complex. Physically meaningful values of V are always real, positive, and greater than constant b . For an isotherm at $T > T_c$, reference to Fig. 3.12 shows that solution for V at any positive value of P yields only one such root. For the critical isotherm ($T = T_c$), this is also true, except at the critical pressure, where there are three roots, all equal to V_c . For isotherms at $T < T_c$, the equation may exhibit one or three real roots, depending on the pressure. Although these roots are real and positive, they are not physically stable states for the portion of an isotherm lying between saturated liquid and saturated vapor (under the "dome"). Only the roots for $P = P^{\text{sat}}$, namely $V^{\text{sat}}(\text{liq})$ and $V^{\text{sat}}(\text{vap})$, are stable states, connected by the horizontal portion of the true isotherm. For other pressures (as indicated by the horizontal lines shown on Fig. 3.12 above

and below P^{sat}), the smallest root is a liquid or "liquid-like" volume, and the largest is a vapor or "vapor-like" volume. The third root, lying between the other values, is of no significance.

A Generic Cubic Equation of State

Since the introduction of the van der Waals equation, scores of cubic equations of state have been proposed. All are special cases of the equation:

$$P = \frac{RT}{V - b} - \frac{\theta(V - \eta)}{(V - b)(V^2 + \kappa V + \lambda)}$$

Here, b , θ , κ , λ , and η are parameters which in general depend on temperature and (for mixtures) composition. Although this equation appears to possess great flexibility, it has inherent limitations because of its cubic form.⁷ It reduces to the van der Waals equation when $\eta = b$, $\theta = a$, and $\kappa = \lambda = 0$.

An important class of cubic equations results from the preceding equation with the assignments:

$$\eta = b \quad \theta = a(T) \quad \kappa = (\epsilon + \sigma)b \quad \lambda = \epsilon\sigma b^2$$

It is thus transformed into an expression general enough to serve as a generic cubic equation of state, which reduces to all others of interest here upon assignment of appropriate parameters:

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V + \epsilon b)(V + \sigma b)} \quad (3.41)$$

For a given equation, ϵ and σ are pure numbers, the same for all substances, whereas parameters $a(T)$ and b are substance dependent. The temperature dependence of $a(T)$ is specific to each equation of state. For the van der Waals equation, $a(T) = a$ is a substance-dependent constant, and $\epsilon = \sigma = 0$.

Determination of Equation-of-State Parameters

The constants in an equation of state for a particular substance may be evaluated by a fit to available P - V - T data. For cubic equations of state, however, suitable estimates are usually found from values for the critical constants T_c and P_c . Since the critical isotherm exhibits a horizontal inflection at the critical point, we may impose the mathematical conditions:

$$\left(\frac{\partial P}{\partial V}\right)_{T;\text{cr}} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T;\text{cr}} = 0$$

where the subscript "cr" denotes the critical point. Differentiation of Eq. (3.41) yields expressions for both derivatives, which may be equated to zero for $P = P_c$, $T = T_c$, and $V = V_c$. The equation of state may itself be written for the critical conditions. These three equations contain five constants: P_c , V_c , T_c , $a(T_c)$, and b . Of the several ways to treat these equations, the

⁷M. M. Abbott, *AIChE J.*, vol. 19, pp. 596601, 1973; Adv. in *Chem. Series 182*, K. C. Chao and R. L. Robinson, Jr., eds., pp. 47–70, Am. Chem. Soc., Washington, D.C., 1979.

most suitable is elimination of V_c to yield expressions relating $a(T_c)$ and b to P_c and T_c . The reason is that P_c and T_c are usually more accurately known than V_c .

An equivalent, but more straightforward, procedure is illustrated for the van der Waals equation. Since $V = V_c$ for each of the three roots at the critical point,

$$(V - V_c)^3 = 0$$

$$\text{or} \quad V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad (A)$$

Equation (3.40) expanded in polynomial form becomes:

$$V^3 - \left(b + \frac{RT_c}{P_c}\right) V^2 + \frac{a}{P_c} V - \frac{ab}{P_c} = 0 \quad (B)$$

Recall that for a particular substance parameter a in the van der Waals equation is a constant, independent of temperature.

Term-by-term comparison of Eqs. (A) and (B) provides three equations:

$$3V_c = b + \frac{RT_c}{P_c} \quad (C)$$

$$3V_c^2 = \frac{a}{P_c} \quad (D)$$

$$V_c^3 = \frac{ab}{P_c} \quad (E)$$

Solving Eq. (D) for a , combining the result with Eq. (E), and solving for b gives:

$$a = 3P_c V_c^2 \quad b = \frac{1}{3} V_c$$

Substitution for b in Eq. (C) allows solution for V_c , which can then be eliminated from the equations for a and b :

$$V_c = \frac{3}{8} \frac{RT_c}{P_c} \quad a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad b = \frac{1}{8} \frac{RT_c}{P_c}$$

Although these equations may not yield the best possible results, they provide reasonable values which can almost always be determined, because critical temperatures and pressures (in contrast to extensive PVT data) are often known, or can be reliably estimated.

Substitution for V_c in the equation for the critical compressibility factor reduces it immediately to:

$$Z_c \equiv \frac{P_c V_c}{RT_c} = \frac{3}{8}$$

A single value for Z_c , applicable alike to all substances, results whenever the parameters of a two-parameter equation of state are found by imposition of the critical constraints. Different values are found for different equations of state, as indicated in Table 3.1, p. 93. Unfortunately, the values so obtained do not in general agree with those calculated from experimental values of T_c , P_c , and V_c ; each chemical species in fact has its own value of Z_c . Moreover, the values

given in Table B.1 of App. B for various substances are almost all smaller than any of the equation values given in Table 3.1.

An analogous procedure may be applied to the generic cubic, Eq. (3.41), yielding expressions for parameters $a(T_c)$ and b . For the former,

$$a(T_c) = \Psi \frac{R^2 T_c^2}{P_c}$$

This result may be extended to temperatures other than the critical by introduction of a dimensionless function $\alpha(T_r)$ that becomes unity at the critical temperature. Thus

$$a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c} \quad (3.42)$$

Function $\alpha(T_r)$ is an empirical expression, specific to a particular equation of state. Parameter b is given by:

$$b = \Omega \frac{RT_c}{P_c} \quad (3.43)$$

In these equations Ω and Ψ are pure numbers, independent of substance and determined for a particular equation of state from the values assigned to ϵ and a .

The modern development of cubic equations of state was initiated in 1949 by publication of the Redlich/Kwong (RK) equation:⁸

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \quad (3.44)$$

where, in Eq. (3.42), $\alpha(T_r) = T_r^{-1/2}$.

Theorem of Corresponding States; Acentric Factor

Experimental observation shows that compressibility factors Z for different fluids exhibit similar behavior when correlated as a function of *reduced temperature* T_r and *reduced pressure* P_r ; by *definition*,

$$T_r \equiv \frac{T}{T_c} \quad \text{and} \quad P_r \equiv \frac{P}{P_c}$$

This is the basis for the *two-parameter theorem of corresponding states*:

All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree.

Although this theorem is very nearly exact for the *simple fluids* (argon, krypton, and xenon) systematic deviations are observed for more complex fluids. Appreciable improvement

⁸Otto Redlich and J. N. S. Kwong, *Chem. Rev.*, vol. 44, pp. 233–244, 1949.

results from introduction of a third corresponding-states parameter, characteristic of molecular structure; the most popular such parameter is the *acentric factor* ω , introduced by K. S. Pitzer and coworkers.⁹

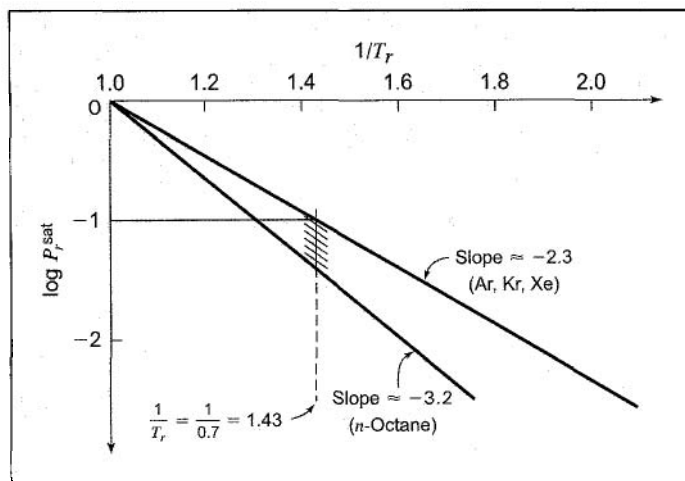


Figure 3.13 Approximate temperature dependence of the reduced vapor pressure

The acentric factor for a pure chemical species is defined with reference to its vapor pressure. Since the logarithm of the vapor pressure of a pure fluid is approximately linear in the reciprocal of absolute temperature,

$$\frac{d \log P_r^{\text{sat}}}{d(1/T_r)} = S$$

where P_r^{sat} is the reduced vapor pressure, T_r is the reduced temperature, and S is the slope of a plot of $\log P_r^{\text{sat}}$ vs. $1/T_r$. Note that "log" denotes a logarithm to the base 10.

If the two-parameter theorem of corresponding states were generally valid, the slope S would be the same for all pure fluids. This is observed not to be true; each fluid has its own characteristic value of S , which could in principle serve as a third corresponding-states parameter. However, Pitzer noted that all vapor-pressure data for the simple fluids (Ar, Kr, Xe) lie on the same line when plotted as $\log P_r^{\text{sat}}$ vs. $1/T_r$ and that the line passes through $\log P_r^{\text{sat}} = -1.0$ at $T_r = 0.7$. This is illustrated in Fig. 3.13. Data for other fluids define other lines whose locations can be fixed in relation to the line for the simple fluids (SF) by the difference:

$$\log P_r^{\text{sat}}(\text{SF}) - \log P_r^{\text{sat}}$$

The acentric factor is *defined* as this difference evaluated at $T_r = 0.7$:

$$\omega \equiv -1.0 - \log(P_r^{\text{sat}})_{T_r = 0.7} \quad (3.45)$$

⁹Fully described in K. S. Pitzer, *Thermodynamics*, 3d ed., App. 3, McGraw-Hill, New York, 1995

Therefore w can be determined for any fluid from T_c , P_c , and a single vapor-pressure measurement made at $T_r = 0.7$. Values of w and the critical constants T_c , P_c , and V_c for a number of fluids are listed in App. B.

The definition of w makes its value zero for argon, krypton, and xenon, and experimental data yield compressibility factors for all three fluids that are correlated by the same curves when Z is represented as a function of T_r and P_r . This is the basic premise of the following *three-parameter theorem of corresponding states*:

All fluids having the same value of ω , when compared at the same T_r and P_r , have about the same value of Z , and all deviate from ideal-gas behavior to about the same degree.

Vapor & Vapor-Like Roots of the Generic Cubic Equation of State

Although one may solve explicitly for its three roots, the generic cubic equation of state, Eq. (3.41), is in practice far more commonly solved by iterative procedures.¹⁰ Convergence problems are most likely avoided when the equation is rearranged to a form suited to the solution for a particular root. For the largest root, i.e., a vapor or vapor-like volume, Eq. (3.41) is multiplied through by $(V - b)/RT$. It can then be written:

$$V = \frac{RT}{P} + b - \frac{a(T)}{P} \frac{V - b}{(V + \epsilon b)(V + \sigma b)} \quad (3.46)$$

Solution for V may be by trial, iteration, or with the solve routine of a software package. An initial estimate for V is the ideal-gas value RT/P . For iteration, this value is substituted on the right side of Eq. (3.46). The resulting value of V on the left is then returned to the right side, and the process continues until the change in V is suitably small.

An equation for Z equivalent to Eq. (3.46) is obtained through the substitution $V = ZRT/P$. In addition, the definition of two dimensionless quantities leads to simplification. Thus,

$$\beta \equiv \frac{bP}{RT} \quad (3.47)$$

$$q \equiv \frac{a(T)}{bRT} \quad (3.48)$$

These substitutions into Eq. (3.46) yield:

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \quad (3.49)$$

Equations (3.47) and (3.48) in combination with Eqs. (3.42) and (3.43) yield:

$$\beta = \Omega \frac{P_r}{T_r} \quad (3.50)$$

¹⁰Such procedures are built into computer software packages for technical calculations. With these packages one can solve routinely for V in equations such as (3.41) with little thought as to how it is done.

$$q = \frac{\Psi \alpha(T_r)}{\Omega T_r} \quad (3.51)$$

Iterative solution of Eq. (3.49) starts with the value $Z = 1$ substituted on the right side. The calculated value of Z is returned to the right side and the process continues to convergence. The final value of Z yields the volume root through $V = ZRT/P$.

Liquid & Liquid-Like Roots of the Generic Cubic Equation of State

Equation (3.46) may be solved for the V in the numerator of the final fraction to give:

$$V = b + (V + \epsilon b)(V + \sigma b) \left[\frac{RT + bP - VP}{a(T)} \right] \quad (3.52)$$

This equation with a starting value of $V = b$ on the right side converges upon iteration to a liquid or liquid-like root.

An equation for Z equivalent to Eq. (3.52) is obtained when Eq. (3.49) is solved for the Z in the numerator of the final fraction:

$$Z = \beta + (Z + \epsilon\beta)(Z + \sigma\beta) \left(\frac{1 + \beta - Z}{q\beta} \right) \quad (3.53)$$

For iteration a starting value of $Z = \beta$ is substituted on the right side. Once Z is known, the volume root is $V = ZRT/P$.

Equations of state which express Z as a function of T_r and P_r are said to be *generalized*, because of their general applicability to all gases and liquids. Any equation of state can be put into this form to provide a generalized correlation for the properties of fluids. This allows the estimation of property values from very limited information. Equations of state, such as the van der Waals and Redlich/Kwong equations, which express Z as functions of T_r and P_r only, yield two-parameter corresponding states correlations. The Soave/Redlich/Kwong (SRK) equation¹¹ and the Peng/Robinson (PR) equation,¹² in which the acentric factor enters through function $\alpha(T_r; w)$ as an additional parameter, yield three-parameter corresponding-states correlations. The numerical assignments for parameters ϵ , a , Ω , and Ψ , both for these equations and for the van der Waals and Redlich/Kwong equations, are given in Table 3.1. Expressions are also given for $\alpha(T_r; w)$ for the SRK and PR equations.

Example 3.8

Given that the vapor pressure of *n*-butane at 350 K (76.85°C) is 9.4573 bar, find the molar volumes of (a) saturated-vapor and (b) saturated-liquid *n*-butane at these conditions as given by the Redlich/Kwong equation.

¹¹G. Soave, *Chem. Eng. Sci.*, vol. 27, pp. 1197–1203, 1972.

¹²D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, vol. 15, pp. 59–64, 1976.

Solution 3.8

Values of T_c and P_c for n -butane from App. B yield:

$$T_r = \frac{350}{425.1} = 0.8233 \quad \text{and} \quad P_r = \frac{9.4573}{37.96} = 0.2491$$

Parameter q is given by Eq. (3.51) with Ω , Ψ , and $\alpha(T_r)$ for the RK equation from Table 3.1:

$$q = \frac{\Psi T_r^{-1/2}}{\Omega T_r} = \frac{\Psi}{\Omega} T_r^{-3/2} = \frac{0.42748}{0.08664} (0.8233)^{-3/2} = 6.6048$$

Table 3.1 Parameter Assignments for Equations of State
For use with Eqs. (3.46) through (3.53)

| Eq. of State | $\alpha(T_r)$ | σ | ϵ | Ω | Ψ | Z_c |
|--------------|--|----------------|----------------|----------|---------|---------|
| vdW (1873) | 1 | 0 | 0 | 1/8 | 27/64 | 3/8 |
| RK (1949) | $T_r^{-1/2}$ | 1 | 0 | 0.08664 | 0.42748 | 1/3 |
| SRK (1972) | $\alpha_{\text{SRK}}(T_r; \omega)^{\dagger}$ | 1 | 0 | 0.08664 | 0.42748 | 1/3 |
| PR (1976) | $\alpha_{\text{PR}}(T_r; \omega)^{\ddagger}$ | $1 + \sqrt{2}$ | $1 - \sqrt{2}$ | 0.07779 | 0.45724 | 0.30740 |

$$^{\dagger}\alpha_{\text{SRK}}(T_r; \omega) = [1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_r^{1/2})]^2$$

$$^{\ddagger}\alpha_{\text{PR}}(T_r; \omega) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{1/2})]^2$$

Parameter β is found from Eq. (3.50):

$$\beta = \Omega \frac{P_r}{T_r} = \frac{(0.08664)(0.2491)}{0.8233} = 0.026214$$

(a) For the saturated vapor, write the RK form of Eq. (3.49) which results upon substitution of appropriate values for ϵ and σ from Table 3.1:

$$Z = 1 + \beta - q\beta \frac{(Z - \beta)}{Z(Z + \beta)}$$

Iteration with an initial value $Z = 1$ converges on $Z = 0.8305$. Thus,

$$V^v = \frac{ZRT}{P} = \frac{(0.8305)(83.14)(350)}{9.4573} = 2555 \text{ cm}^3 \text{ mol}^{-1}$$

An experimental value is $2482 \text{ cm}^3 \text{ mol}^{-1}$.

(b) For the saturated liquid, apply Eq. (3.53) in its RK form:

$$Z = \beta + Z(Z + \beta) \left(\frac{1 + \beta - Z}{q\beta} \right)$$

or
$$Z = 0.026\,214 + Z(Z + 0.026\,214) \frac{(1.026\,214 - Z)}{(6.6048)(0.026\,214)}$$

The initial step is substitution of $Z = \beta$ on the right side of this equation. Iteration leads to convergence on the value $Z = 0.043\,31$. Whence,

$$V^l = \frac{ZRT}{P} = \frac{(0.043\,31)(83.14)(350)}{9.4573} = 133.3 \text{ cm}^3 \text{ mol}^{-1}$$

An experimental value is $115.0 \text{ cm}^3 \text{ mol}^{-1}$.

For comparison, values of V^v and V^l calculated for the conditions of Ex. 3.8 by all four of the cubic equations of state considered here are summarized as follows:

| $V^v/\text{cm}^3 \text{ mol}^{-1}$ | | | | | $V^l/\text{cm}^3 \text{ mol}^{-1}$ | | | | |
|------------------------------------|------|------|------|------|------------------------------------|-------|-------|-------|-------|
| Exp. | vdW | RK | SRK | PR | Exp. | vdW | RK | SRK | PR |
| 2482 | 2667 | 2555 | 2520 | 2486 | 115.0 | 191.0 | 133.3 | 127.8 | 112.6 |

The Soave/Redlich/Kwong and the Peng/Robinson equations were developed specifically for vapor/liquid equilibrium calculations (Sec. 14.2).

Roots of equations of state are most easily found with a software package such as Mathcad® or Maple®, in which iteration is an integral part of the equation-solving routine. Starting values or bounds may be required, and must be appropriate to the particular root of interest. A Mathcad® program for solving Ex. 3.8 is given in App. D.2.

3.6 GENERALIZED CORRELATIONS FOR GASES

Generalized correlations find widespread use. Most popular are correlations of the kind developed by Pitzer and coworkers for the compressibility factor Z and for the second virial coefficient B .¹³

Pitzer Correlations for the Compressibility Factor

The correlation for Z takes the form:

$$Z = Z^0 + \omega Z^1 \quad (3.54)$$

where Z^0 and Z^1 are functions of both T_r and P_r . When $\omega = 0$, as is the case for the simple fluids, the second term disappears, and Z^0 becomes identical with Z . Thus a generalized correlation for Z as a function of T_r and P_r based on data for just argon, krypton, and xenon provides the relationship $Z^0 = F^0(T_r, P_r)$. By itself, this represents a two-parameter corresponding-states correlation for Z . Since the second term of Eq. (3.54) is a relatively small correction to this correlation, its omission does not introduce large errors, and a correlation for Z^0 may be

¹³See Pitzer, *op. cit.*

used alone for quick but less accurate estimates of Z than are obtained from a three-parameter correlation.

Equation (3.54) is a simple linear relation between Z and ω for given values of T_r and P_r . Experimental data for Z for nonsimple fluids plotted vs. ω at constant T_r and P_r do indeed yield approximately straight lines, and their slopes provide values for Z^1 from which the generalized function $Z^1 = F^1(T_r, P_r)$ can be constructed.

Of the Pitzer-type correlations available, the one developed by Lee and Kesler¹⁴ has found greatest favor. Although its development is based on a modified form of the Benedict/Webb/Rubin equation of state, it takes the form of tables which present values of Z^0 and Z^1 as functions of T_r and P_r . These are given in App. E as Tables E.1 through E.4. Use of these tables often requires interpolation, which is treated at the beginning of App. F. The nature of the correlation is indicated by Fig. 3.14, a plot of Z^0 vs. P_r for six isotherms.

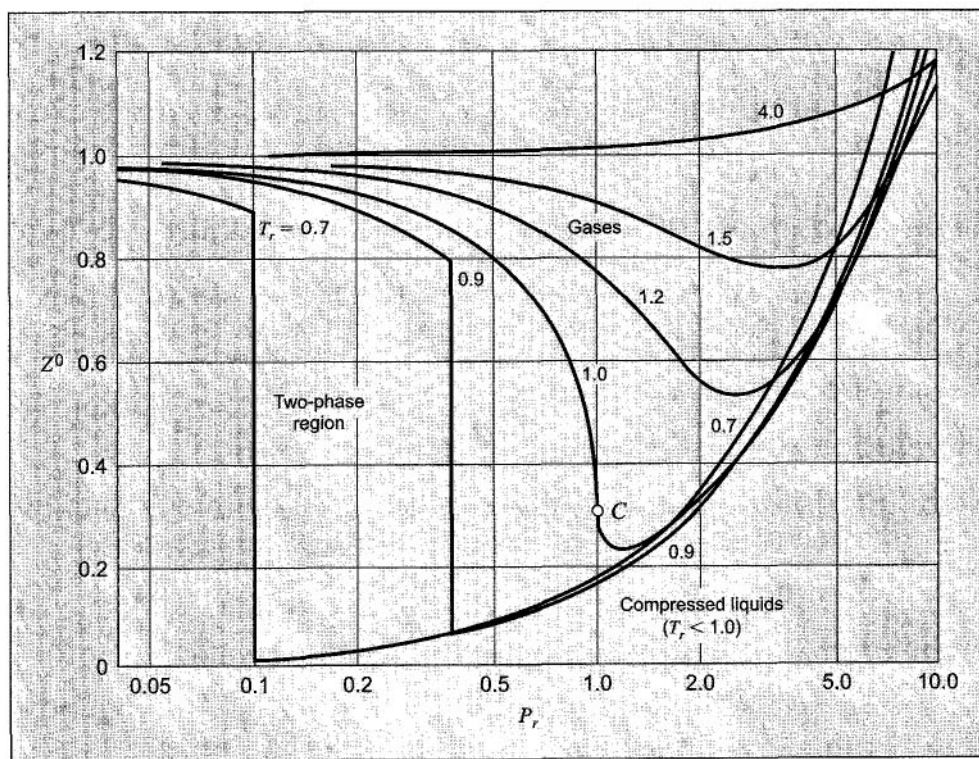


Figure 3.14 The Lee/Kesler correlation for $Z^0 = F^0(T_r, P_r)$

The Lee/Kesler correlation provides reliable results for gases which are nonpolar or only slightly polar; for these, errors of no more than 2 or 3 percent are indicated. When applied to highly polar gases or to gases that associate, larger errors can be expected.

The quantum gases (e.g., hydrogen, helium, and neon) do not conform to the same corresponding-states behavior as do normal fluids. Their treatment by the usual correlations is

¹⁴B. I. Lee and M. G. Kesler, *AIChE J.*, vol. 21, pp. 510–527, 1975

sometimes accommodated by use of temperature-dependent *effective* critical parameters.¹⁵ For hydrogen, the quantum gas most commonly found in chemical processing, the recommended equations are:

$$T_c/\text{K} = \frac{43.6}{1 + \frac{21.8}{2.016 T}} \quad (\text{for H}_2) \quad (3.55)$$

$$P_c/\text{bar} = \frac{20.5}{1 + \frac{44.2}{2.016 T}} \quad (\text{for H}_2) \quad (3.56)$$

$$V_c/\text{cm}^3 \text{ mol}^{-1} = \frac{51.5}{1 - \frac{9.91}{2.016 T}} \quad (\text{for H}_2) \quad (3.57)$$

where T is absolute temperature in kelvins. Use of these *effective* critical parameters for hydrogen requires the further specification that $\omega = 0$.

Pitzer Correlations for the Second Virial Coefficient

The tabular nature of the generalized compressibility-factor correlation is a disadvantage, but the complexity of the functions Z^0 and Z^1 precludes their accurate representation by simple equations. However, we can give approximate analytical expression to these functions for a limited range of pressures. The basis for this is Eq. (3.37), the simplest form of the virial equation:

$$Z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_c}{RT_c} \right) \frac{P_r}{T_r} \quad (3.58)$$

Thus, Pitzer and coworkers proposed a second correlation, which yields values for BP_c/RT_c :

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1 \quad (3.59)$$

Together, these two equations become:

$$Z = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r}$$

Comparison of this equation with Eq. (3.54) provides the following identifications:

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \quad (3.60)$$

and

$$Z^1 = B^1 \frac{P_r}{T_r}$$

¹⁵J. M. Prausnitz, R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3d ed., pp. 172–173, Prentice Hall PTR, Upper Saddle River, NJ, 1999.

Second virial coefficients are functions of temperature only, and similarly B^0 and B^1 are functions of reduced temperature only. They are well represented by the following equations:¹⁶

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (3.61)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad (3.62)$$

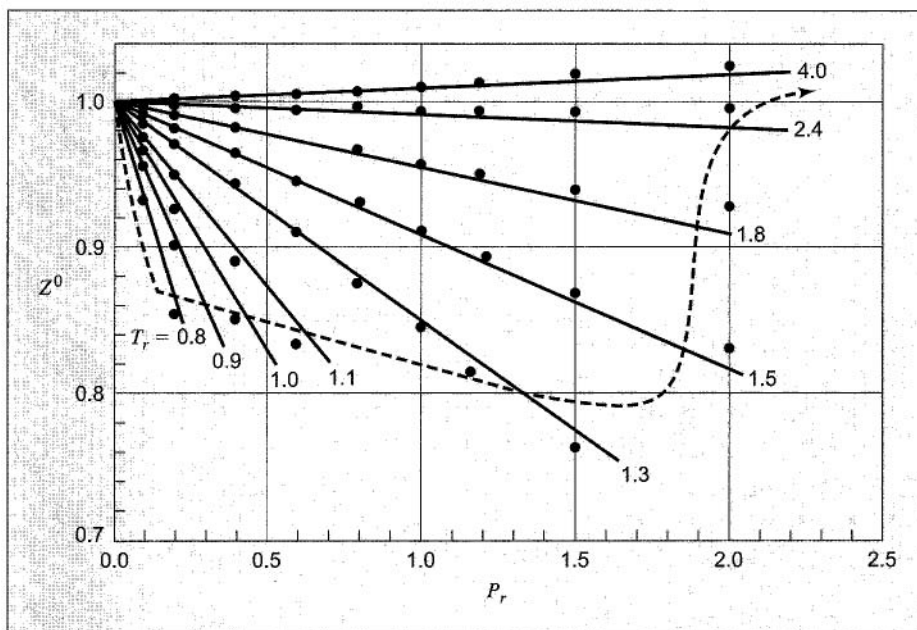


Figure 3.15 Comparison of correlations for Z^0 . The virial-coefficient correlation is represented by the straight lines; the Lee/Kesler correlation, by the points. In the region above the dashed line the two correlations differ by less than 2%

The simplest form of the virial equation has validity only at low to moderate pressures where Z is linear in pressure. The generalized virial-coefficient correlation is therefore useful only where Z^0 and Z^1 are at least approximately linear functions of reduced pressure. Figure 3.15 compares the linear relation of Z^0 to P_r as given by Eqs. (3.60) and (3.61) with values of Z^0 from the Lee/Kesler compressibility-factor correlation, Tables E.1 and E.3. The two correlations differ by less than 2% in the region above the dashed line of the figure. For reduced temperatures greater than $T_r \approx 3$, there appears to be no limitation on the pressure. For lower values of T_r the allowable pressure range decreases with decreasing temperature. A point is reached, however, at $T_r \approx 0.7$ where the pressure range is limited by the saturation pressure.¹⁷

¹⁶These correlations first appeared in 1975 in the third edition of this book, attributed as a personal communication to M. M. Abbott, who developed them.

¹⁷Although the Lee/Kesler tables, App. E, list values for superheated vapor and subcooled liquid, they do not provide values at saturation conditions.

This is indicated by the left-most segment of the dashed line. The minor contributions of Z^1 to the correlations are here neglected. In view of the uncertainty associated with any generalized correlation, deviations of no more than 2% in Z^0 are not significant.

The relative simplicity of the generalized virial-coefficient correlation does much to recommend it. Moreover, temperatures and pressures of many chemical-processing operations lie within the region where it does not deviate by a significant amount from the compressibility-factor correlation. Like the parent correlation, it is most accurate for nonpolar species and least accurate for highly polar and associating molecules.

The question often arises as to when the ideal-gas equation may be used as a reasonable approximation to reality. Figure 3.16 can serve as a guide.

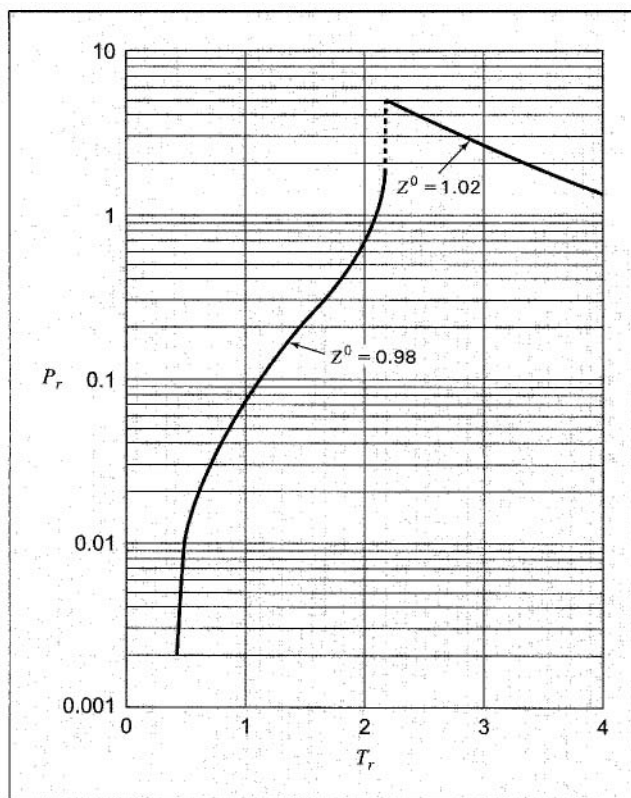


Figure 3.16 Region where Z^0 lies between 0.98 and 1.02, and the ideal-gas equation is a reasonable approximation

Example 3.9

Determine the molar volume of *n*-butane at 510K and 25 bar by each of the following:

- (a) The ideal-gas equation.

- (b) The generalized compressibility-factor correlation.
 (c) The generalized virial-coefficient correlation.

Solution 3.9

(a) By the ideal-gas equation,

$$V = \frac{RT}{P} = \frac{(0.08314)(510)}{25} = 1.691 \text{ m}^3 \text{ kmol}^{-1}$$

(b) Taking values of T_c and P_c from App. B, we find

$$T_r = \frac{510}{425.1} = 1.200 \quad P_r = \frac{25}{37.96} = 0.659$$

Interpolation in Tables E.1 and E.2 then provides

$$Z^0 = 0.865 \quad Z^1 = 0.038$$

Thus, by Eq. (3.54) with $\omega = 0.200$,

$$Z = Z^0 + \omega Z^1 = 0.865 + (0.200)(0.038) = 0.873$$

and

$$V = \frac{ZRT}{P} = \frac{(0.873)(0.08314)(510)}{25} = 1.4807 \text{ m}^3 \text{ kmol}^{-1}$$

If we take $Z = Z^0 = 0.865$, in accord with the two-parameter corresponding states correlation, then $V = 1.4671 \text{ m}^3 \text{ kmol}^{-1}$, which is less than 1 percent lower than the value given by the three-parameter correlation.

(c) Values of B^0 and B^1 are given by Eqs. (3.61) and (3.62):

$$B^0 = -0.232 \quad B^1 = 0.059$$

By Eq. (3.59),

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1 = -0.232 + (0.200)(0.059) = -0.220$$

Then by Eq. (3.58),

$$Z = 1 + (-0.220) \frac{0.659}{1.200} = 0.879$$

from which we find $V = 1.4891 \text{ m}^3 \text{ kmol}^{-1}$, a value less than 1 percent higher than that given by the compressibility-factor correlation. For comparison, the experimental value is 1.4807.

Example 3.10

What pressure is generated when 1 kmol of methane is stored in a volume of 0.125 m³ at 323.15 K (50°C)? Base calculations on each of the following:

- The ideal-gas equation.
- The Redlich/Kwong equation.
- A generalized correlation.

Solution 3.10

(a) By the ideal-gas equation,

$$P = \frac{RT}{V} = \frac{(0.08314)(323.15)}{0.125} = 214.9 \text{ bar}$$

(b) For the Redlich/Kwong equation, values of $a(T)$ and b come from Eqs. (3.42) and (3.43):

$$T_r = \frac{T}{T_c} = \frac{323.15}{190.6} = 1.695$$

$$a = \frac{(0.42748)(1.695)^{-0.5}(0.08314)^2(190.6)^2}{45.99} = 1.7922 \text{ bar m}^6$$

and

$$b = \frac{(0.08664)(0.08314)(190.6)}{45.99} = 0.02985 \text{ m}^3$$

where values of T_c and P_c from App. B. Substitution of known values into Eq. (3.41) now gives

$$P = \frac{(0.08314)(323.15)}{(0.125 - 0.02985)} - \frac{1.7922}{0.125(0.125 + 0.02985)} = 189.65 \text{ bar}$$

(c) Since the pressure here is high, the generalized compressibility-factor correlation is the proper choice. In the absence of a known value for P_r , an iterative procedure is based on the following equation:

$$P = \frac{ZRT}{V} = \frac{Z(0.08314)(323.15)}{0.125} = 214.9Z$$

Since $P = P_c P_r = 45.99 P_r$, this equation becomes

$$Z = \frac{45.99 P_r}{214.9} = 0.214 P_r$$

or

$$P_r = \frac{Z}{0.214}$$

One now assumes a starting value for Z , say $Z = 1$. This gives $P_r = 4.673$, and allows a new value of Z to be calculated by Eq. (3.54) from values interpolated in Tables E.3 and E.4 at the reduced temperature of $T_r = 323.15/190.6 = 1.695$. With this new value of Z , a new value of P_r is calculated, and the procedure continues until no significant change occurs from one step to the next. The final value of Z so found is 0.889 at $P_r = 4.14$. This may be confirmed by substitution into Eq. (3.54) of values for Z^0 and Z^1 from Tables E.3 and E.4 interpolated at $P_r = 4.14$ and $T_r = 1.695$. Since $\omega = 0.012$, we have

$$Z = Z^0 + \omega Z^1 = 0.887 + (0.012)(0.258) = 0.890$$

and

$$P = \frac{ZRT}{V} = \frac{(0.890)(0.08314)(323.15)}{0.125} = 191.3 \text{ bar}$$

Since the acentric factor is small, the two- and three-parameter compressibility-factor correlations are little different. Both the Redlich/Kwong equation and the generalized compressibility-factor correlation give answers very close to the experimental value of 187.5 bar. The ideal-gas equation yields a result that is high by 14.6 percent.

Example 3.11

A mass of 0.5 kg of gaseous ammonia is contained in a 0.03 m^3 vessel immersed in a constant-temperature bath at 338.15 K (65°C). Calculate the pressure of the gas by each of the following:

- The ideal-gas equation.
- A generalized correlation.

Solution 3.11

The molar volume of ammonia in the vessel is given by

$$V = \frac{V'}{n} = \frac{V'}{m/M}$$

where n is the number of moles, m is the mass of ammonia in the vessel of total volume V' , and M is the molar mass of ammonia. Thus

$$V = \frac{0.03}{0.5/17.02} = 1.0212 \text{ m}^3 \text{ kmol}^{-1}$$

(a) By the ideal-gas equation,

$$P = \frac{RT}{V} = \frac{(0.08314)(338.15)}{1.0212} = 27.53 \text{ bar}$$

(b) Since the reduced pressure is low (≈ 0.244), we use the generalized virial-coefficient correlation. For a reduced temperature of $T_r = 338.15/405.7 = 0.834$, values of B^0 and B^1 as given by Eqs. (3.61) and (3.62) are

$$B^0 = -0.482 \quad B^1 = -0.232$$

Substitution into Eq. (3.59) with $\omega = 0.253$ yields

$$\frac{BP_c}{RT_c} = -0.482 + (0.253)(-0.232) = -0.541$$

and

$$B = \frac{-0.541 RT_c}{P_c} = \frac{-(0.541)(0.08314)(405.7)}{112.8} = -0.1618 \text{ m}^3 \text{ kmol}^{-1}$$

Solving Eq. (3.37) for P , we obtain

$$P = \frac{RT}{V - B} = \frac{(0.08314)(338.15)}{(1.0212 + 0.1618)} = 23.76 \text{ bar}$$

An iterative solution is not necessary, because B is independent of pressure. The calculated P corresponds to a reduced pressure of $P_r = 23.76/112.8 = 0.211$, and reference to Fig. 3.15 confirms the suitability of the generalized virial-coefficient correlation.

Experimental data indicate that the pressure is 23.82 bar at the given conditions. Thus the ideal-gas equation yields an answer that is high by about 15 percent, whereas the other two methods give answers in substantial agreement with experiment, even though ammonia is a polar molecule.

3.7 GENERALIZED CORRELATIONS FOR LIQUIDS

Although the molar volumes of liquids can be calculated by means of generalized cubic equations of state, the results are often not of high accuracy. However, the Lee/Kesler correlation includes data for subcooled liquids, and Fig. 3.14 illustrates curves for both liquids and gases. Values for both phases are provided in Tables E.1 through E.4. Recall, however, that this correlation is most suitable for nonpolar and slightly polar fluids.

In addition, generalized equations are available for the estimation of molar volumes of *saturated* liquids. The simplest equation, proposed by Rackett,¹⁸ is an example:

$$V^{\text{sat}} = V_c Z_c^{(1-T_r)^{0.2857}} \quad (3.63)$$

The only data required are the critical constants, given in App. B. Results are usually accurate to 1 or 2%.

Lydersen, Greenkorn, and Hougen¹⁹ developed a two-parameter corresponding-states correlation for estimation of liquid volumes. It provides a correlation of reduced density ρ_r as a function of reduced temperature and pressure. By definition,

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V} \quad (3.64)$$

¹⁸H. G. Rackett, *J. Chem. Eng. Data*, vol. 15, pp. 514–517, 1970; see also C. F. Spencer and S. B. Adler, *ibid.*, vol. 23, pp. 82–89, 1978, for a review of available equations.

¹⁹A. L. Lydersen, R. A. Greenkorn, and O. A. Hougen, "Generalized Thermodynamic Properties of Pure Fluids," *Univ. Wisconsin, Eng. Expt. Sta. Rept. 4*, 1955.

where ρ_c is the density at the critical point. The generalized correlation is shown by Fig. 3.17. This figure may be used directly with Eq. (3.64) for determination of liquid volumes if the value of the critical volume is known. A better procedure is to make use of a single known liquid volume (state 1) by the identity,

$$V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}} \quad (3.65)$$

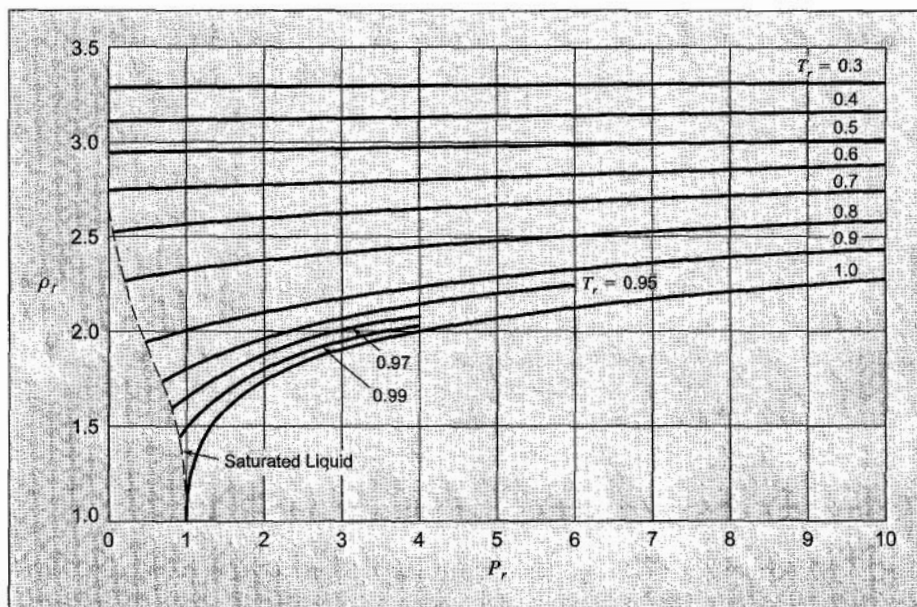


Figure 3.17 Generalized density correlation for liquids

where

V_2 = required volume

V_1 = known volume

ρ_{r1} , ρ_{r2} = reduced densities read from Fig. 3.17

This method gives good results and requires only experimental data that are usually available. Figure 3.17 makes clear the increasing effects of both temperature and pressure on liquid density as the critical point is approached.

Correlations for the molar densities as functions of temperature are given for many pure liquids by Daubert and coworkers.²⁰

Example 3.12

For ammonia at 310 K (36.85°C), estimate the density of:

²⁰T. E. Daubert, R. P. Danner, H. M. Sibul, and C. C. Stebbins, *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*, Taylor & Francis, Bristol, PA, extant 1995.

- (a) The saturated liquid;
 (b) The liquid at 100 bar.

Solution 3.12

(a) We apply the Rackett equation at the reduced temperature,

$$T_r = \frac{310}{405.7} = 0.7641$$

With $V_c = 0.07247 \text{ m}^3 \text{ kmol}^{-1}$ and $Z_c = 0.242$ (from App. B), we get

$$V^{\text{sat}} = V_c Z_c^{(1-T_r)^{0.2857}} = (0.07247)(0.242)^{(0.2359)^{0.2857}} = 0.02833 \text{ m}^3 \text{ kmol}^{-1}$$

This compares with the experimental value of $0.02914 \text{ m}^3 \text{ kmol}^{-1}$, and differs by 2.7 percent.

(b) The reduced conditions are

$$T_r = 0.7641 \quad P_r = \frac{100}{112.8} = 0.887$$

From Fig. 3.17, we have $\rho_r = 2.38$. Substituting this value along with V_c into Eq. (3.64) gives

$$V = \frac{V_c}{\rho_r} = \frac{0.07247}{2.38} = 0.03045 \text{ m}^3 \text{ kmol}^{-1}$$

In comparison with the experimental value of $0.0286 \text{ m}^3 \text{ kmol}^{-1}$, this result is in error by 6.5 percent.

If we start with the experimental value of $0.02914 \text{ m}^3 \text{ kmol}^{-1}$ for saturated liquid at 310 K, Eq. (3.65) may be used. For the saturated liquid at $T_r = 0.764$, we find from Fig. 3.17 that $\rho_{r1} = 2.34$. Substitution of known values into Eq. (3.65) gives

$$V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}} = (0.02914) \left(\frac{2.34}{2.38} \right) = 0.02865 \text{ m}^3 \text{ kmol}^{-1}$$

This result is in essential agreement with the experimental value.

Direct application of the Lee/Kesler correlation with values of Z^0 and Z^1 interpolated from Tables E.1 and E.2 leads to a value of $0.03387 \text{ m}^3 \text{ kmol}^{-1}$, which is significantly in error, no doubt owing to the highly polar nature of ammonia.

PROBLEMS

- 3.1. Express the volume expansivity and the isothermal compressibility as functions of density ρ and its partial derivatives. For water at 323.15 K (50°C) and 1 bar, $\kappa = 44.18 \times 10^{-6} \text{ bar}^{-1}$. To what pressure must water be compressed at 323.15 K (50°C) to change its density by 1%? Assume that κ is independent of P .

- 3.2.** Generally, volume expansivity β and isothermal compressibility κ depend on T and P . Prove that:

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

- 3.3.** The Tait equation for liquids is written for an isotherm as:

$$V = V_0 \left(1 - \frac{AP}{B + P}\right)$$

where V is molar or specific volume, V_0 is the hypothetical molar or specific volume at zero pressure, and A and B are positive constants. Find an expression for the isothermal compressibility consistent with this equation.

- 3.4.** For liquid water the isothermal compressibility is given by:

$$\kappa = \frac{c}{V(P + b)}$$

where c and b are functions of temperature only. If 1 kg of water is compressed isothermally and reversibly from 1 to 500 bar at 333.15 K (60°C), how much work is required? At 333.15 K (60°C), $b = 2700$ bar and $c = 0.125 \text{ cm}^3 \text{ g}^{-1}$.

- 3.5.** Calculate the reversible work done in compressing 0.0283 m^3 of mercury at a constant temperature of 273.15 K (0°C) from 1 atm to 3000 atm. The isothermal compressibility of mercury at 273.15 K (0°C) is

$$\kappa = 3.9 \times 10^{-6} - 0.1 \times 10^{-9} P$$

where P is in atm and κ is in atm^{-1} .

- 3.6.** Five kilograms of liquid carbon tetrachloride undergo a mechanically reversible, isobaric change of state at 1 bar during which the temperature changes from 273.15 K (0°C) to 293.15 K (20°C). Determine ΔV^t , W , Q , ΔH^t , and ΔU^t . The properties for liquid carbon tetrachloride at 1 bar and 273.15 K (0°C) may be assumed independent of temperature: $\beta = 1.2 \times 10^{-3} \text{ K}^{-1}$, $C_P = 0.84 \text{ kJ kg}^{-1} \text{ K}^{-1}$, and $\rho = 1590 \text{ kg m}^{-3}$.
- 3.7.** A substance for which κ is a constant undergoes an isothermal, mechanically reversible process from initial state (P_1, V_1) to final state (P_2, V_2), where V is molar volume.

(a) Starting with the definition of κ , show that the path of the process is described by:

$$V = A(T) \exp(-\kappa P)$$

(b) Determine an exact expression which gives the isothermal work done on 1 mol of this constant- κ substance.

- 3.8.** One mole of an ideal gas with $C_P = (7/2)R$ and $C_V = (5/2)R$ expands from $P_1 = 8$ bar and $T_1 = 600 \text{ K}$ to $P_2 = 1$ bar by each of the following paths:

(a) Constant volume; (b) Constant temperature; (c) Adiabatically.

Assuming mechanical reversibility, calculate W , Q , ΔU , and ΔH for each process. Sketch each path on a single P V diagram.

3.9. An ideal gas initially at 600 K and 10 bar undergoes a four-step mechanically reversible cycle in a closed system. In step 12, pressure decreases isothermally to 3 bar; in step 23, pressure decreases at constant volume to 2 bar; in step 34, volume decreases at constant pressure; and in step 41, the gas returns adiabatically to its initial state.

- (a) Sketch the cycle on a PV diagram.
- (b) Determine (where unknown) both T and P for states 1, 2, 3, and 4.
- (c) Calculate Q , W , ΔU , and ΔH for each step of the cycle.

Data: $C_P = (7/2)R$ and $C_V = (5/2)R$.

3.10. An ideal gas, $C_P = (5/2)R$ and $C_V = (3/2)R$, is changed from $P = 1$ bar and $V_1^t = 12 \text{ m}^3$ to $P_2 = 12$ bar and $V_2^t = 1 \text{ m}^3$ by the following mechanically reversible processes:

- (a) Isothermal compression.
- (b) Adiabatic compression followed by cooling at constant pressure.
- (c) Adiabatic compression followed by cooling at constant volume.
- (d) Heating at constant volume followed by cooling at constant pressure.
- (e) Cooling at constant pressure followed by heating at constant volume.

Calculate Q , W , ΔU^t , and ΔH^t for each of these processes, and sketch the paths of all processes on a single PV diagram.

3.11. The environmental lapse rate dT/dz characterizes the local variation of temperature with elevation in the earth's atmosphere. Atmospheric pressure varies with elevation according to the hydrostatic formula,

$$\frac{dP}{dz} = -M\rho g$$

where M is molar mass, ρ is molar density, and g is the local acceleration of gravity. Assume that the atmosphere is an ideal gas, with T related to P by the polytropic formula, Eq. (3.34c). Develop an expression for the environmental lapse rate in relation to M , g , R , and n .

3.12. An evacuated tank is filled with gas from a constant-pressure line. Develop an expression relating the temperature of the gas in the tank to the temperature T' of the gas in the line. Assume the gas is ideal with constant heat capacities, and ignore heat transfer between the gas and the tank. Mass and energy balances for this problem are treated in Ex. 2.12.

3.13. Show how Eqs. (3.35) and (3.36) reduce to the appropriate expressions for the four particular values of n listed following Eq. (3.36).

3.14. A tank of 0.1-m^3 volume contains air at 298.15 K (25°C) and 101.33 kPa. The tank is connected to a compressed-air line which supplies air at the constant conditions of 318.15 K (45°C) and 1500 kPa. A valve in the line is cracked so that air flows slowly into the tank until the pressure equals the line pressure. If the process occurs slowly enough that the temperature in the tank remains at 298.15 K (25°C), how much heat is lost from the tank? Assume air to be an ideal gas for which $C_P = (7/2)R$ and $C_V = (5/2)R$.

3.15. Gas at constant T and P is contained in a supply line connected through a valve to a closed tank containing the same gas at a lower pressure. The valve is opened to allow flow of gas into the tank, and then is shut again.

- (a) Develop a general equation relating n_1 and n_2 , the moles (or mass) of gas in the tank at the beginning and end of the process, to the properties U_1 and U_2 , the internal energy of the gas in the tank at the beginning and end of the process, and H' , the enthalpy of the gas in the supply line, and to Q , the heat transferred to the material in the tank during the process.
- (b) Reduce the general equation to its simplest form for the special case of an ideal gas with constant heat capacities.
- (c) Further reduce the equation of (b) for the case of $n_1 = 0$.
- (d) Further reduce the equation of (c) for the case in which, in addition, $Q = 0$.
- (e) Treating nitrogen as an ideal gas for which $C_P = (7/2)R$, apply the appropriate equation to the case in which a steady supply of nitrogen at 298.15 K (25°C) and 3 bar flows into an evacuated tank of 4-m³ volume, and calculate the moles of nitrogen that flow into the tank to equalize the pressures for two cases:
 1. Assume that no heat flows from the gas to the tank or through the tank walls.
 2. The tank weighs 400 kg, is perfectly insulated, has an initial temperature of 298.15 K (25°C), has a specific heat of 0.46 kJ kg⁻¹ K⁻¹, and is heated by the gas so as always to be at the temperature of the gas in the tank.

3.16. Develop equations which may be solved to give the final temperature of the gas remaining in a tank after the tank has been bled from an initial pressure P_1 to a final pressure P_2 . Known quantities are initial temperature, tank volume, heat capacity of the gas, total heat capacity of the containing tank, P_1 , and P_2 . Assume the tank to be always at the temperature of the gas remaining in the tank, and the tank to be perfectly insulated.

3.17. A rigid, nonconducting tank with a volume of 4 m³ is divided into two unequal parts by a thin membrane. One side of the membrane, representing 1/3 of the tank, contains nitrogen gas at 6 bar and 373.15 K (100°C), and the other side, representing 2/3 of the tank, is evacuated. The membrane ruptures and the gas fills the tank.

- (a) What is the final temperature of the gas? How much work is done? Is the process reversible?
- (b) Describe a reversible process by which the gas can be returned to its initial state. How much work is done?

Assume nitrogen is an ideal gas for which $C_P = (7/2)R$ and $C_V = (5/2)R$.

3.18. An ideal gas, initially at 303.15 K (30°C) and 100 kPa, undergoes the following cyclic processes in a closed system:

- (a) In mechanically reversible processes, it is first compressed adiabatically to 500 kPa, then cooled at a constant pressure of 500 kPa to 303.15 K (30°C), and finally expanded isothermally to its original state.
- (b) The cycle traverses exactly the same changes of state, but each step is irreversible with an efficiency of 80% compared with the corresponding mechanically reversible process.

Calculate Q , W , ΔU , and ΔH for each step of the process and for the cycle. Take $C_P = (7/2)R$ and $C_V = (5/2)R$.

3.19. One cubic meter of an ideal gas at 600 K and 1000 kPa expands to five times its initial volume as follows:

- (a) By a mechanically reversible, isothermal process.
- (b) By a mechanically reversible, adiabatic process.
- (c) By an adiabatic, irreversible process in which expansion is against a restraining pressure of 100 kPa.

For each case calculate the final temperature, pressure, and the work done by the gas. $C_P = 21 \text{ J mol}^{-1} \text{ K}^{-1}$.

3.20. One mole of air, initially at 423.15 K (150°C) and 8 bar, undergoes the following mechanically reversible changes. It expands isothermally to a pressure such that when it is cooled at constant volume to 323.15 K (50°C) its final pressure is 3 bar. Assuming air is an ideal gas for which $C_P = (7/2)R$ and $C_V = (5/2)R$, calculate W , Q , ΔU , and ΔH .

3.21. An ideal gas flows through a horizontal tube at steady state. No heat is added and no shaft work is done. The cross-sectional area of the tube changes with length, and this causes the velocity to change. Derive an equation relating the temperature to the velocity of the gas. If nitrogen at 423.15 K (150°C) flows past one section of the tube at a velocity of 2.5 m s^{-1} , what is its temperature at another section where its velocity is 50 m s^{-1} ? Let $C_P = (7/2)R$.

3.22. One mole of an ideal gas, initially at 303.15 K (30°C) and 1 bar, is changed to 403.15 K (130°C) and 10 bar by three different mechanically reversible processes:

- The gas is first heated at constant volume until its temperature is 403.15 K (130°C); then it is compressed isothermally until its pressure is 10 bar.
- The gas is first heated at constant pressure until its temperature is 403.15 K (130°C); then it is compressed isothermally to 10 bar.
- The gas is first compressed isothermally to 10 bar; then it is heated at constant pressure to 403.15 K (130°C).

Calculate Q , W , ΔU , and ΔH in each case. Take $C_P = (7/2)R$ and $C_V = (5/2)R$. Alternatively, take $C_P = (5/2)R$ and $C_V = (3/2)R$.

3.23. One kmol of an ideal gas, initially at 303.15 K (30°C) and 1 bar, undergoes the following mechanically reversible changes. It is compressed isothermally to a point such that when it is heated at constant volume to 393.15 K (120°C) its final pressure is 12 bar. Calculate Q , W , ΔU , and ΔH for the process. Take $C_P = (7/2)R$ and $C_V = (5/2)R$.

3.24. A process consists of two steps: (1) One kmol of air at $T = 800 \text{ K}$ and $P = 4 \text{ bar}$ is cooled at constant volume to $T = 350 \text{ K}$. (2) The air is then heated at constant pressure until its temperature reaches 800 K. If this two-step process is replaced by a single isothermal expansion of the air from 800 K and 4 bar to some final pressure P , what is the value of P that makes the work of the two processes the same? Assume mechanical reversibility and treat air as an ideal gas with $C_P = (7/2)R$ and $C_V = (5/2)R$.

3.25. A scheme for finding the internal volume V_B^I of a gas cylinder consists of the following steps. The cylinder is filled with a gas to a low pressure P_1 , and connected through a

small line and valve to an evacuated reference tank of known volume V_A' . The valve is opened, and gas flows through the line into the reference tank. After the system returns to its initial temperature, a sensitive pressure transducer provides a value for the pressure change ΔP in the cylinder. Determine the cylinder volume V_B' from the following data:

- $V_A' = 256 \text{ cm}^3$.
- $\Delta P/P_1 = -0.0639$.

- 3.26.** A closed, nonconducting, horizontal cylinder is fitted with a nonconducting, frictionless, floating piston which divides the cylinder into Sections A and B. The two sections contain equal masses of air, initially at the same conditions, $T_1 = 300 \text{ K}$ and $P_1 = 1 \text{ atm}$. An electrical heating element in Section A is activated, and the air temperatures slowly increase: T_A in Section A because of heat transfer, and T_B in Section B because of adiabatic compression by the slowly moving piston. Treat air as an ideal gas with $C_P = \frac{7}{2}R$, and let n_A be the number of moles of air in Section A. For the process as described, evaluate one of the following sets of quantities:

- (a) T_A , T_B , and Q/n_A , if $P(\text{final}) = 1.25 \text{ atm}$.
- (b) T_B , Q/n_A , and $P(\text{final})$, if $T_A = 425 \text{ K}$.
- (c) T_A , Q/n_A , and $P(\text{final})$, if $T_B = 325 \text{ K}$.
- (d) T_A , T_B , and $P(\text{final})$, if $Q/n_A = 3 \text{ kJ mol}^{-1}$.

- 3.27.** One mole of an ideal gas with constant heat capacities undergoes an arbitrary mechanically reversible process. Show that:

$$\Delta U = \frac{1}{\gamma - 1} \Delta(PV)$$

- 3.28.** Derive an equation for the work of mechanically reversible, isothermal compression of 1 mol of a gas from an initial pressure P_1 to a final pressure P_2 when the equation of state is the virial expansion [Eq. (3.11)] truncated to:

$$Z = 1 + B'P$$

How does the result compare with the corresponding equation for an ideal gas?

- 3.29.** A certain gas is described by the equation of state:

$$PV = RT + \left(b - \frac{\theta}{RT}\right)P$$

Here, b is a constant and θ is a function of T only. For this gas, determine expressions for the isothermal compressibility κ and the thermal pressure coefficient $(3P/\partial T)_V$. These expressions should contain only T , P , θ , $d\theta/dT$, and constants.

- 3.30.** For methyl chloride at 373.15 K (100°C) the second and third virial coefficients are:

$$B = -242.5 \text{ cm}^3 \text{ mol}^{-1} \quad C = 25\,200 \text{ cm}^6 \text{ mol}^{-2}$$

Calculate the work of mechanically reversible, isothermal compression of 1 mol of methyl chloride from 1 bar to 55 bar at 373.15 K (100°C). Base calculations on the following forms of the virial equation:

$$(a) \quad Z = 1 + \frac{B}{V} + \frac{C}{V^2}$$

$$(b) \quad Z = 1 + B'P + C'P^2$$

where

$$B' = \frac{B}{RT} \quad \text{and} \quad C' = \frac{C - B^2}{(RT)^2}$$

Why don't both equations give exactly the same result?

- 3.31.** Any equation of state valid for gases in the zero-pressure limit implies a full set of virial coefficients. Show that the second and third virial coefficients implied by the generic cubic equation of state, Eq. (3.41), are:

$$B = b - \frac{a(T)}{RT} \quad C = b^2 + \frac{(\epsilon + \sigma)ba(T)}{RT}$$

Specialize the result for B to the Redlich/Kwong equation of state, express it in reduced form, and compare it numerically with the generalized correlation for B for simple fluids, Eq. (3.61). Discuss what you find.

- 3.32.** Calculate Z and V for ethylene at 298.15 K (25°C) and 12 bar by the following equations:

- (a) The truncated virial equation [Eq. (3.39)] with the following experimental values of virial coefficients:

$$B = -140 \text{ cm}^3 \text{ mol}^{-1} \quad C = 7200 \text{ cm}^6 \text{ mol}^{-2}$$

- (b) The truncated virial equation [Eq. (3.37)], with a value of B from the generalized Pitzer correlation [Eq. (3.59)].
 (c) The Redlich/Kwong equation.
 (d) The Soave/Redlich/Kwong equation.
 (e) The Peng/Robinson equation.

- 3.33.** Calculate Z and V for ethane at 323.15 K (50°C) and 15 bar by the following equations:

- (a) The truncated virial equation [Eq. (3.39)] with the following experimental values of virial coefficients:

$$B = -156.7 \text{ cm}^3 \text{ mol}^{-1} \quad C = 9650 \text{ cm}^6 \text{ mol}^{-2}$$

- (b) The truncated virial equation [Eq. (3.37)], with a value of B from the generalized Pitzer correlation [Eq. (3.59)].
 (c) The Redlich/Kwong equation.
 (d) The Soave/Redlich/Kwong equation.
 (e) The Peng/Robinson equation.

- 3.34.** Calculate Z and V for sulfur hexafluoride at 348.15 K (75°C) and 15 bar by the following equations:

- (a) The truncated virial equation [Eq. (3.39)] with the following experimental values of virial coefficients:

$$B = -194 \text{ cm}^3 \text{ mol}^{-1} \quad C = 15\,300 \text{ cm}^6 \text{ mol}^{-2}$$

- (b) The truncated virial equation [Eq. (3.37)], with a value of B from the generalized Pitzer correlation [Eq. (3.59)].
- (c) The Redlich/Kwong equation.
- (d) The Soave/Redlich/Kwong equation.
- (e) The Peng/Robinson equation.

For sulfur hexafluoride, $T_c = 318.7$ K, $P_c = 37.6$ bar, $V_c = 198$ cm³ mol⁻¹, and $\omega = 0.286$.

3.35. Determine Z and V for steam at 523.15 K (250°C) and 1800 kPa by the following:

- (a) The truncated virial equation [Eq. (3.39)] with the following experimental values of virial coefficients:

$$B = -152.5 \text{ cm}^3 \text{ mol}^{-1} \quad C = -5800 \text{ cm}^6 \text{ mol}^{-2}$$

- (b) The truncated virial equation [Eq. (3.37)], with a value of B from the generalized Pitzer correlation [Eq. (3.59)].
- (c) The steam tables (App. F).

3.36. With respect to the virial expansions, Eqs. (3.11) and (3.12), show that:

$$B' = \left(\frac{\partial Z}{\partial P} \right)_{T, P=0} \quad \text{and} \quad B = \left(\frac{\partial Z}{\partial \rho} \right)_{T, \rho=0}$$

where $\rho \equiv 1/V$.

3.37. Equation (3.12) when truncated to four terms accurately represents the volumetric data for methane gas at 273.15 K (0°C) with:

$$B = -53.4 \text{ cm}^3 \text{ mol}^{-1} \quad C = 2620 \text{ cm}^6 \text{ mol}^{-2} \quad D = 5000 \text{ cm}^9 \text{ mol}^{-3}$$

- (a) Use these data to prepare a plot of Z vs. P for methane at 273.15 K (0°C) from 0 to 200 bar.
 - (b) To what pressures do Eqs. (3.37) and (3.38) provide good approximations?
- 3.38.** Calculate the molar volume of saturated liquid and the molar volume of saturated vapor by the Redlich/Kwong equation for one of the following and compare results with values found by suitable generalized correlations.

- (a) Propane at 313.15 K (40°C) where $P^{\text{sat}} = 13.71$ bar.
- (b) Propane at 323.15 K (50°C) where $P^{\text{sat}} = 17.16$ bar.
- (c) Propane at 333.15 K (60°C) where $P^{\text{sat}} = 21.22$ bar.
- (d) Propane at 343.15 K (70°C) where $P^{\text{sat}} = 25.94$ bar.
- (e) n-Butane at 373.15 K (100°C) where $P^{\text{sat}} = 15.41$ bar.
- (f) n-Butane at 383.15 K (110°C) where $P^{\text{sat}} = 18.66$ bar.
- (g) n-Butane at 393.15 K (120°C) where $P^{\text{sat}} = 22.38$ bar.
- (h) n-Butane at 403.15 K (130°C) where $P^{\text{sat}} = 26.59$ bar.
- (i) Isobutane at 363.15 K (90°C) where $P^{\text{sat}} = 16.54$ bar.
- (j) Isobutane at 373.15 K (100°C) where $P^{\text{sat}} = 20.03$ bar.

- (k) Isobutane at 383.15 K(110°C) where $P^{\text{sat}} = 24.01$ bar.
 - (l) Isobutane at 393.15 K(120°C) where $P^{\text{sat}} = 28.53$ bar.
 - (m) Chlorine at 333.15 K(60°C) where $P^{\text{sat}} = 18.21$ bar.
 - (n) Chlorine at 343.15 K(70°C) where $P^{\text{sat}} = 22.49$ bar.
 - (o) Chlorine at 353.15 K(80°C) where $P^{\text{sat}} = 27.43$ bar.
 - (p) Chlorine at 363.15 K(90°C) where $P^{\text{sat}} = 33.08$ bar.
 - (q) Sulfur dioxide at 353.15 K(80°C) where $P^{\text{sat}} = 18.66$ bar.
 - (r) Sulfur dioxide at 363.15 K(90°C) where $P^{\text{sat}} = 23.31$ bar.
 - (s) Sulfur dioxide at 373.15 K(100°C) where $P^{\text{sat}} = 28.74$ bar.
 - (t) Sulfur dioxide at 383.15 K(110°C) where $P^{\text{sat}} = 35.01$ bar.
- 3.39.** Use the Soave/Redlich/Kwong equation to calculate the molar volumes of saturated liquid and saturated vapor for the substance and conditions given by one of the parts of Pb. 3.38 and compare results with values found by suitable generalized correlations.
- 3.40.** Use the Peng/Robinson equation to calculate the molar volumes of saturated liquid and saturated vapor for the substance and conditions given by one of the parts of Pb. 3.38 and compare results with values found by suitable generalized correlations.
- 3.41.** Estimate the following:
- (a) The volume occupied by 18 kg of ethylene at 328.15 K (55°C) and 35 bar.
 - (b) The mass of ethylene contained in a 0.25-m³ cylinder at 323.15 K (50°C) and 115 bar.
- 3.42.** The vapor-phase molar volume of a particular compound is reported as 23 000 cm³ mol⁻¹ at 300 K and 1 bar. No other data are available. Without assuming ideal-gas behavior, determine a reasonable estimate of the molar volume of the vapor at 300 K and 5 bar.
- 3.43.** To a good approximation, what is the molar volume of ethanol vapor at 753.15 K (480°C) and 6000 kPa? How does this result compare with the ideal-gas value?
- 3.44.** A 0.35-m³ vessel is used to store liquid propane at its vapor pressure. Safety considerations dictate that at a temperature of 320 K the liquid must occupy no more than 80% of the total volume of the vessel. For these conditions, determine the mass of vapor and the mass of liquid in the vessel. At 320 K the vapor pressure of propane is 16.0 bar.
- 3.45.** A 30-m³ tank contains 14 m³ of liquid n-butane in equilibrium with its vapor at 298.15 K (25°C). Estimate the mass of n-butane vapor in the tank. The vapor pressure of n-butane at the given temperature is 2.43 bar.
- 3.46.** Estimate:
- (a) The mass of ethane contained in a 0.15-m³ vessel at 333.15 K (60°C) and 14 bar.
 - (b) The temperature at which 40 kg of ethane stored in a 0.15-m³ vessel exerts a pressure 20 bar.
- 3.47.** To what pressure does one fill a 0.15-m³ vessel at 298.15 K (25°C) in order to store 40 kg of ethylene in it?

- 3.48.** If 15 kg of H_2O in a 0.4-m^3 container is heated to 673.15 K (400°C), what pressure is developed?
- 3.49.** A 0.35-m^3 vessel holds ethane vapor at 298.15 K (25°C) and 2200 kPa . If it is heated to 493.15 K (220°C), what pressure is developed?
- 3.50.** What is the pressure in a 0.5-m^3 vessel when it is charged with 10 kg of carbon dioxide at 303.15 K (30°C)?
- 3.51.** A rigid vessel, filled to one-half its volume with liquid nitrogen at its normal boiling point, is allowed to warm to 298.15 K (25°C). What pressure is developed? The molar volume of liquid nitrogen at its normal boiling point is $34.7\text{ cm}^3\text{ mol}^{-1}$.
- 3.52.** The specific volume of isobutane liquid at 300 K and 4 bar is $1.824\text{ cm}^3\text{ g}^{-1}$. Estimate the specific volume at 415 K and 75 bar .
- 3.53.** The density of liquid *n*-pentane is 0.630 g cm^{-3} at 291.15 K (18°C) and 1 bar . Estimate its density at 413.15 K (140°C) and 120 bar .
- 3.54.** Estimate the density of liquid ethanol at 453.15 K (180°C) and 200 bar .
- 3.55.** Estimate the volume change of vaporization for ammonia at 293.15 K (20°C). At this temperature the vapor pressure of ammonia is 857 kPa .
- 3.56.** *PVT* data may be taken by the following procedure. A mass m of a substance of molar mass M is introduced into a thermostated vessel of known total volume V^t . The system is allowed to equilibrate, and the temperature T and pressure P are measured.
- Approximately what percentage errors are allowable in the measured variables (m , M , V^t , T and P) if the maximum allowable error in the calculated compressibility factor Z is $\pm 1\%$?
 - Approximately what percentage errors are allowable in the measured variables if the maximum allowable error in calculated values of the second virial coefficient B is $\pm 1\%$? Assume that $Z \simeq 0.9$ and that values of B are calculated by Eq. (3.32).
- 3.57.** For a gas described by the Redlich/Kwong equation and for a temperature greater than T_c , develop expressions for the two limiting slopes,

$$\lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P} \right)_T \quad \lim_{P \rightarrow \infty} \left(\frac{\partial Z}{\partial P} \right)_T$$

Note that in the limit as $P \rightarrow 0$, $V \rightarrow \infty$, and that in the limit as $P \rightarrow \infty$, $V \rightarrow b$.

- 3.58.** If 3.965 m^3 of methane gas at 288.75 K (15.6°C) and 1 atm is equivalent to $3.785 \times 10^{-3}\text{ m}^3$ of gasoline as fuel for an automobile engine, what would be volume of the tank required to hold methane at 207 bar and 288.75 K (15.6°C) in an amount equivalent to $3.785 \times 10^{-3}\text{ m}^3$ of gasoline?
- 3.59.** Determine a good estimate for the compressibility factor Z of saturated hydrogen vapor at 25 K and 3.213 bar . For comparison, an experimental value is $Z = 0.7757$.

3.60. The Boyle temperature is the temperature for which:

$$\lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P} \right)_T = 0$$

- (a) Show that the second virial coefficient B is zero at the Boyle temperature.
- (b) Use the generalized correlation for B , Eq. (3.59), to estimate the reduced Boyle temperature for simple fluids.

3.61. Natural gas (assume pure methane) is delivered to a city via pipeline at a volumetric rate of 4 normal Mm^3 per day. Average delivery conditions are 283.15 K (10°C) and 20.7 bar. Determine:

- (a) The volumetric delivery rate in actual m^3 per day.
- (b) The molar delivery rate in kmol per hour.
- (c) The gas velocity at delivery conditions in m s^{-1} .

The pipe is 600 mm heavy duty steel with an inside diameter of 575 mm. Normal conditions are 273.15 K (0°C) and 1 atm.

3.62. Some corresponding-states correlations use the critical compressibility factor Z_c , rather than the acentric factor ω , as a third parameter. The two types of correlation (one based on T_c , P_c , and Z_c , the other on T_c , P_c , and w) would be equivalent were there a one-to-one correspondence between Z_c and w . The data of App. B allow a test of this correspondence. Prepare a plot of Z_c vs. w to see how well Z_c correlates with w . Develop a linear correlation ($Z_c = a + bw$) for nonpolar substances.