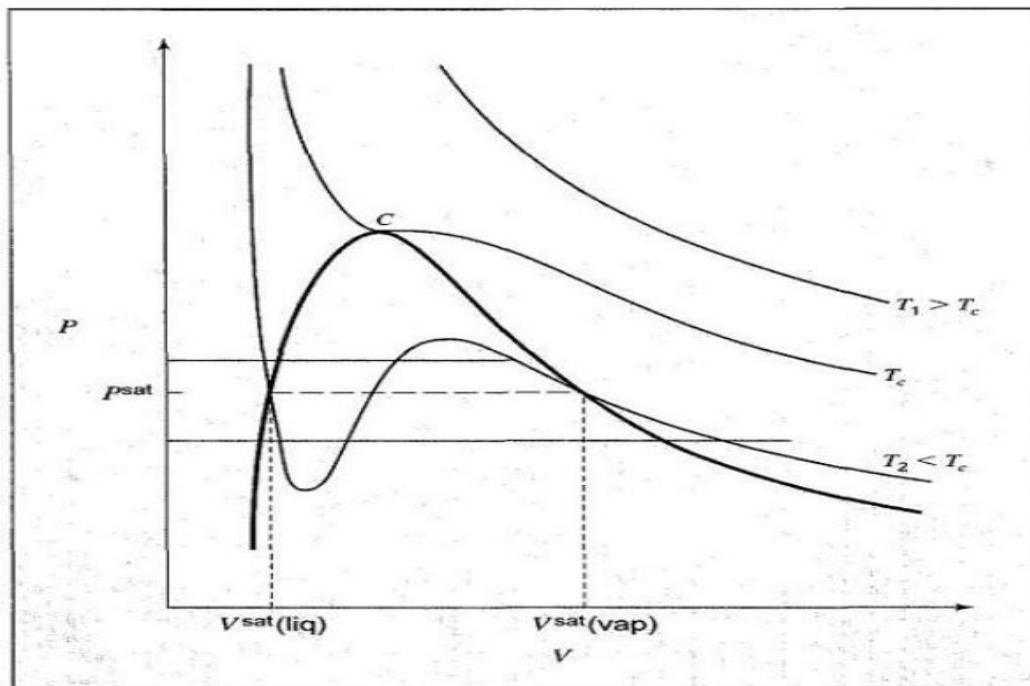# Cubic Equations of State

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 Waals in 1873:

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$ (1)

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**.

Fig.(1): Isotherms as given by a cubic equation of state

Figure (1) is a schematic P V 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 Tc) 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.

Saturated liquid and saturated vapor coexist in varying proportions at the saturation or vapor pressure. This behavior, shown by the dashed line in Fig.(1), is nonanalytic, and we accept as inevitable the unrealistic behavior of equations of state in the two-phase region.

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.

1. For an isotherm at $T > T_c$ at any positive value of P yields only one such root.
2. For the critical isotherm (T = Tc), this is also true, except at the critical pressure, where there are three roots, all equal to Vc.
3. 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$_{Sat}$, namely V$_{sat}$(liq) and V$_{sat}$(vap), are stable states.

For other pressures 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.

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

Soave-Redlick-Kwong (SRK) Equation

The Soave-Redlick-Kwong (SRK) equation belongs to a class of cubic equations of state because, when expanded, they yield third-degree equations for the specific volume. The SRK equation of state is:

In physics and thermodynamics, the Redlich–Kwong equation of state is an equation that is derived from the van der Waals equation. It is generally more accurate than the van der Waals equation and the ideal gas equation, but not used as frequently because the increased difficulty in its derivatives and overall use.

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

Where:

■P is the gas pressure

■R is the gas constant,

■T is temperature,

■$V_m$is the molar volume (V/n),

■a is a constant that corrects for attractive potential of molecules, and

■b is a constant that corrects for volume.

The constants are different depending on which gas is being analyzed. The constants can be calculated from the critical point data of the gas:

Let P be pressure in atm, Tbe temperature in K and V_m be molar volume in lit/gmol.The RedlichKwong equation is given by:

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

$$a = 0.42747\left(\frac{R^2 T_c^{\frac{5}{2}}}{P_c}\right)$$

$$b = 0.08664\left(\frac{RT_c}{P_c}\right)$$

1) Vapor Volume:

The equation above was multiplied through by (V-b) /P to give:

$$V - b = \frac{RT}{P} - \frac{a(V - b)}{T^{0.5}.P.V(V + b)}$$

For iteration, write:

$$V_i + 1 = \frac{RT}{P} + b - \frac{a(V_i - b)}{T^{0.5}.P.V_i(V_i + b)}$$

The initial value for V_i is obtained from ideal gas law:

$$\bar{V}_{\text{ideal}} = \frac{\bar{R}T}{p}$$

2) Liquid Volume:

$$V_i + 1 = \frac{1}{C}(V_i^3 - \frac{RT}{P}V_i^2 - \frac{a.b}{P.T^{0.5}})$$

For iteration, The initial value for V i take $V_0 = b$.

$$a = 0.42747\left(\frac{R^2 T_c^{\frac{5}{2}}}{P_c}\right)$$

$$b = 0.08664\left(\frac{RT_c}{P_c}\right)$$

$$C = b^2 + \frac{b.R.T}{P} - \frac{a}{P.T^{0.5}}$$

The values of **Tc** & **Pc** are available into appendix B, from book (Smith).

Generalized Correlations for Gases and for Liquid

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.

Pitzer Correlations for the Compressibility Factor :

The correlation for Z takes the form:

$$Z = Z^0 + \omega Z^1$$

Where

Z^o and Z' are functions of both T_r and P_r.

$$Z^o = F^o(T_r, P_r)$$

$$Z' = F'(T_r, P_r)$$

and ω :is the centric factor depend on of (T_c , P_c and V_c).

$$T_r = T / T_c$$

$$P_r = P / P_c$$

Equation of state that represents "Z" above is said to be generalized because of their general applicability to all gase.

A disadvantage of the generalized compressibility factor correlation is its graphical nature, thus figures may be used for quick estimates of Z^o and Z' verses P_r and T_r.
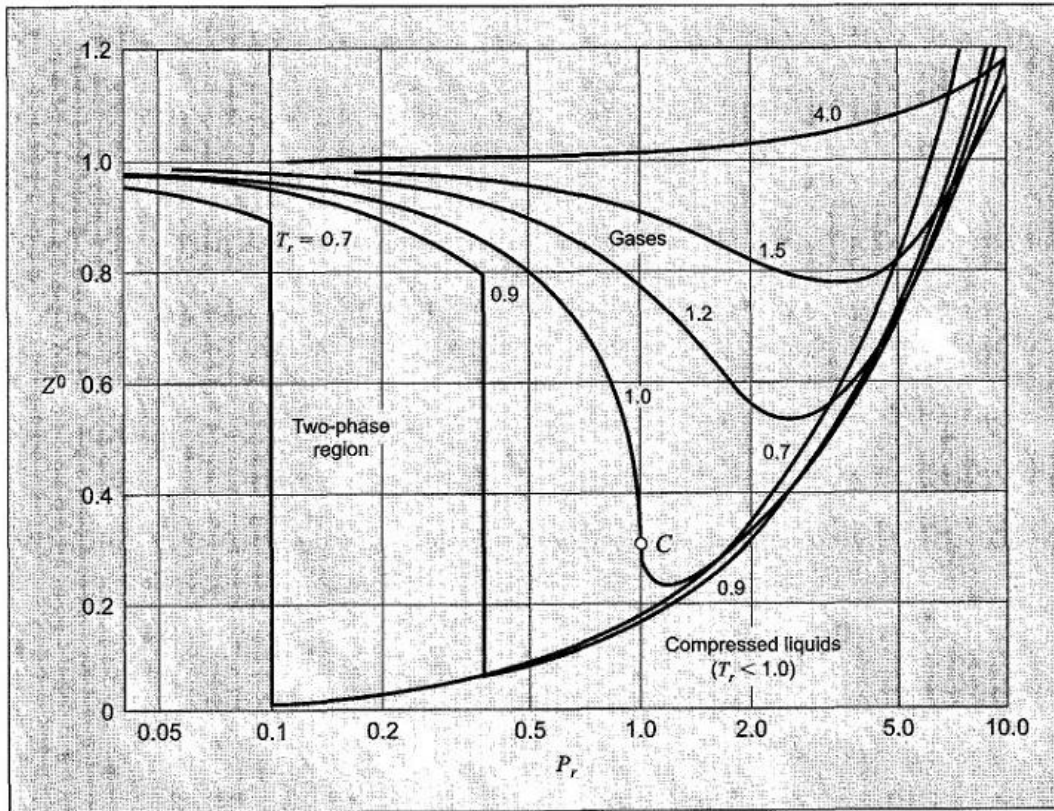
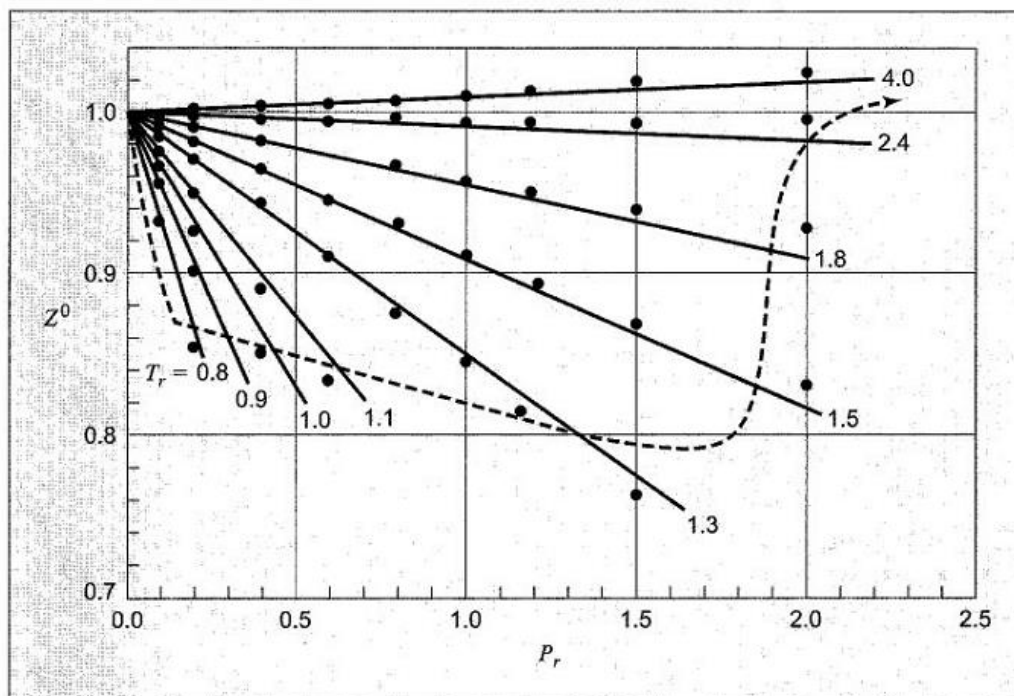**Figure 3.14** The Lee/Kesler correlation for $Z^0 = F^0(T_r, P_r)$
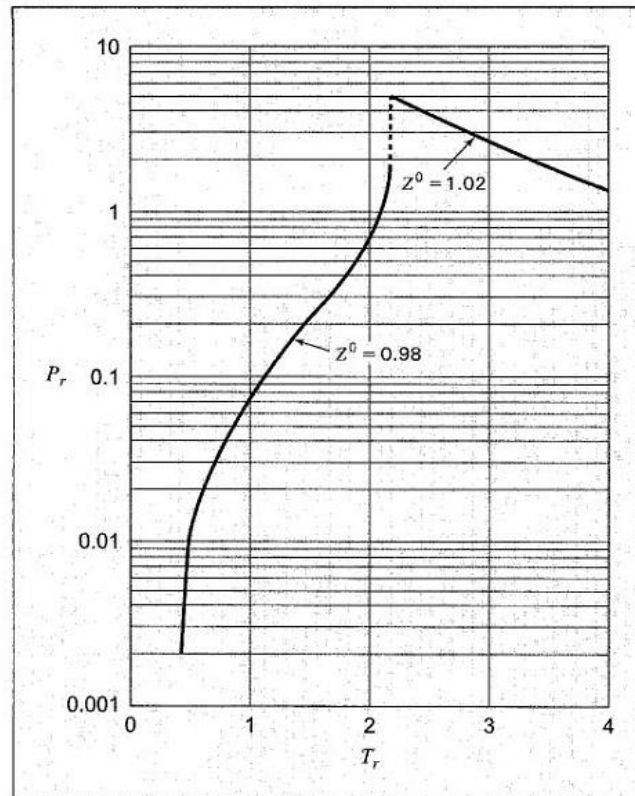

Figure 3.15 Comparison of correlations for Z^0. The virial-coefficient correlation is represented by the straight lines; the Lee/Kesler correlation, by the points. In the region above the dashed line the two correlations differ by less than 2%

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

Pitzer Correlations for the Second Virial Coefficient

Pitzer correlation provide reliable results for gases which are nonpolar or only slightly polar ; for these errors of no more than 2-3 % are indicated. A disadvantage of generalized compressibility factor correlation is its graphical nature. 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° and Z' are at least approximately linear functions of reduced pressure.The simplest form is:

$$Z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_C}{RT_C}\right)\frac{P_r}{T_r}$$

Pitzer proposed a second correlation , which expressed the quantity as
BP_C/RT_C

$$\left(\frac{BP_C}{RT_C}\right) = B^\circ + B\omega'$$

Together, these two equations become:

$$Z = 1 + B° \frac{P_r}{T_r} + \omega B' \frac{P_r}{T_r}$$

Comparison of this equation with generalized compressibility factor :

$$Z = Z^0 + \omega Z^1$$

Provides the following identifications:

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

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

Second Virial coefficients are functions of temperature only, and similarly B° and B' are functions of reduced temperature only. They are well represented by the following equations:

$$B° = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B' = 0.139 - \frac{0.172}{T_r^{4.2}}$$

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. In addition, generalized equations are available for the estimation of molar volumes of saturated liquids. The simplest equation, proposed by Rackett,

$$V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$$

The only data required are the critical constants, given in App. B. from Smith thermodynamics book.

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

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V}$$

Where
ρ_c : is the density at the critical point.

A better procedure is to make use of a single known liquid volume (state 1) by the identity,
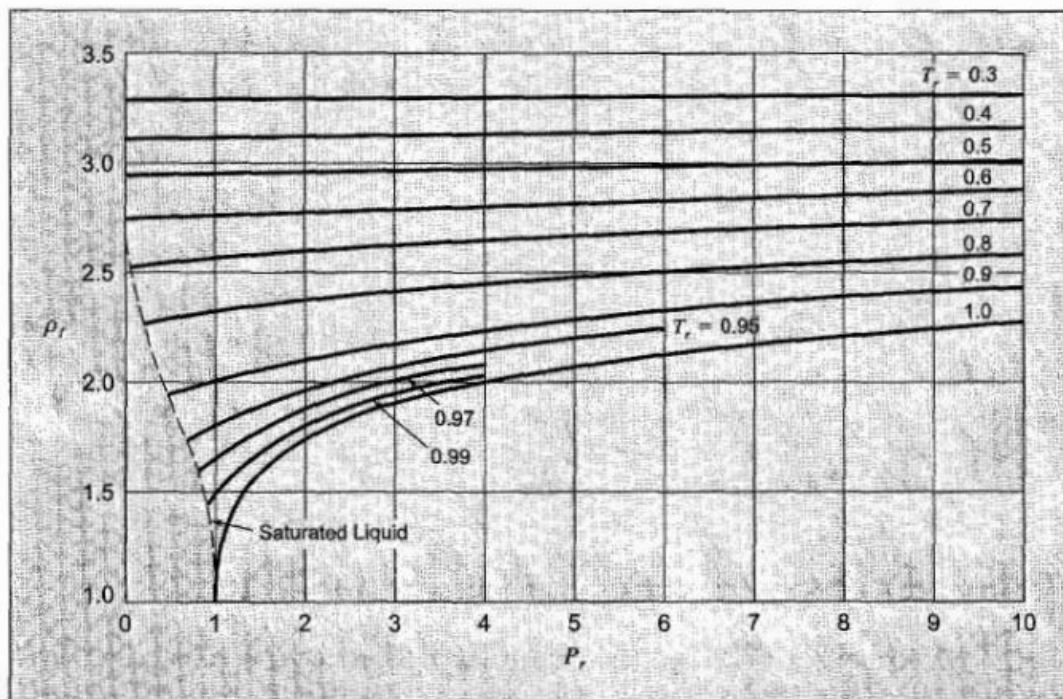
$$V_2 = V_1 \frac{\rho_{r_1}}{\rho_{r_2}}$$

Where

V_2 = required volume

V_1 = known volume

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

Figure 3.17 Generalized density correlation for liquids

Example 3.9

Determine the molar volume of n-butane at 510 K 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,

$$V = \frac{RT}{P} = \frac{(0.083\,14)(510)}{25} = 1.691\,\text{m}^3\,\text{kmol}^{-1}$$

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

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

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

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

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

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

and

$$V = \frac{ZRT}{P} = \frac{(0.873)(0.083\,14)(510)}{25} = 1.4807\,\text{m}^3\,\text{kmol}^{-1}$$

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):

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

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:
  (a) The ideal-gas equation.
  (b) The Redlich/Kwong equation.
  (c) A generalized correlation.

Solution 3.10

(a) By the ideal-gas equation,

$$P = \frac{RT}{V} = \frac{(0.083\,14)(323.15)}{0.125} = 214.9\,\text{bar}$$

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

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

$$a = \frac{(0.427\,48)(1.695)^{-0.5}(0.083\,14)^2(190.6)^2}{45.99} = 1.7922\,\text{bar m}^6$$

and

$$b = \frac{(0.086\,64)(0.083\,14)(190.6)}{45.99} = 0.029\,85\,\text{m}^3$$

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

$$P = \frac{(0.083\,14)(323.15)}{(0.125 - 0.029\,85)} - \frac{1.7922}{0.125(0.125 + 0.029\,85)} = 189.65\,\text{bar}$$

(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
$$P = \frac{ZRT}{V} = \frac{(0.890)(0.083\,14)(323.15)}{0.125} = 191.3 \text{ bar}$$

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 $338.15\,K(65^\circ\,C)$. Calculate the pressure of the gas by each of the following:
(a) The ideal-gas equation.
(b) A generalized correlation.

Solution 3.11

The molar volume of ammonia in the vessel is given by

$$V = \frac{V^t}{n} = \frac{V^t}{m/M}$$

where n is the number of moles, m is the mass of ammonia in the vessel of total volume V^t, 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,

$$P = \frac{RT}{V} = \frac{(0.083\,14)(338.15)}{1.0212} = 27.53 \text{ bar}$$

(b) Since the reduced pressure is low ($\simeq 0.244$), 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

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

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

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

and

$$B = \frac{-0.541 RT_c}{P_c} = \frac{-(0.541)(0.083\ 14)(405.7)}{112.8} = -0.1618\ \text{m}^3\ \text{kmol}^{-1}$$

Solving Eq. (3.37) for P, we obtain

$$P = \frac{RT}{V - B} = \frac{(0.083\ 14)(338.15)}{(1.0212 + 0.1618)} = 23.76\ \text{bar}$$

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.

Example 3.12

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

(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 $V_c = 0.072\,47\ \mathrm{m^3\,kmol^{-1}}$ and $Z_c = 0.242$ (from App. B), we get

$$V^{\mathrm{sat}} = V_c Z_c^{(1-T_r)^{0.2857}} = (0.072\,47)(0.242)^{(0.2359)^{0.2857}} = 0.028\,33\ \mathrm{m^3\,kmol^{-1}}$$

This compares with the experimental value of $0.029\,14\ \mathrm{m^3\,kmol^{-1}}$, and differs by 2.7 percent.

(b) The reduced conditions are

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

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

$$V = \frac{V_c}{\rho_r} = \frac{0.072\,47}{2.38} = 0.030\,45\ \mathrm{m^3\,kmol^{-1}}$$

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

If we start with the experimental value of $0.029\,14\ \mathrm{m^3\,kmol^{-1}}$ 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 $\rho_{r_1} = 2.34$. Substitution of known values into Eq. (3.65) gives

$$V_2 = V_1 \frac{\rho_{r_1}}{\rho_{r_2}} = (0.029\,14)\left(\frac{2.34}{2.38}\right) = 0.028\,65\ \mathrm{m^3\,kmol^{-1}}$$

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 $0.033\,87\ \mathrm{m^3\,kmol^{-1}}$, which is significantly in error, no doubt owing to the highly polar nature of ammonia.