

3.5 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 vapours at low to moderate pressures.

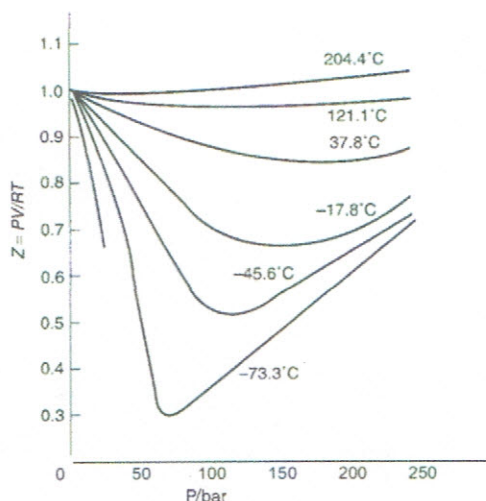


Figure 3.10 Compressibility-factor graph for methane

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

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

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. 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:

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

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), $B' = B/RT$:

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

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

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

However, Eq. (3.38) is more convenient in application and is at least as accurate as Eq. (3.39). Thus when the virial equation is truncated to two terms, Eq. (3.38) is preferred. This equation is satisfactory of pressure about up to 5 bar. The second virial coefficient B is substance dependent and a function of temperature.

For pressures above the range of applicability of Eq. (3.38) but below the critical pressure, the virial equation truncated to three terms often provides excellent results. In this case the appropriate form is:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \quad (3.40)$$

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.

Example 3.8

Reported values for the virial coefficients of isopropanol vapor at 200°C are:

$$B = -388 \text{ cm}^3 \text{ mol}^{-1} \quad C = -26,000 \text{ cm}^6 \text{ mol}^{-2}$$

Calculate V and Z for isopropanol vapor at 200°C and 10 bar by:

(a) The ideal-gas equation; (b) Equation (3.38); (c) Equation (3.40).

Solution 3.8

The absolute temperature is $T = 473.15$ K, and the appropriate value of the gas constant is $R = 83.14 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$.

(a) For an ideal gas, $Z = 1$, and

$$V = \frac{RT}{P} = \frac{(83.14)(473.15)}{10} = 3,934 \text{ cm}^3 \text{ mol}^{-1}$$

(b) Solving Eq. (3.38) for V gives:

$$V = \frac{RT}{P} + B = 3,934 - 388 = 3,546 \text{ cm}^3 \text{ mol}^{-1}$$

Whence,
$$Z = \frac{PV}{RT} = \frac{V}{RT/P} = \frac{3,546}{3,934} = 0.9014$$

(c) To facilitate iteration, write Eq. (3.40) 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 $V_0 = 3,934$, the ideal-gas value. Numerically,

$$V_1 = 3,934 \left[1 - \frac{388}{3,934} - \frac{26,000}{(3,934)^2} \right] = 3,539$$

The second iteration depends on this result:

$$V_2 = \frac{RT}{P} \left(1 + \frac{B}{V_1} + \frac{C}{V_1^2} \right) = 3,934 \left[1 + \frac{388}{3,539} - \frac{26,000}{(3,539)^2} \right] = 3,495$$

Iteration continues until the difference $V_{i+1} - V_i$ is insignificant, and leads after five iterations to the final value,⁷

$$V = 3,488 \text{ cm}^3 \text{ mol}^{-1}$$

from which $Z = 0.8866$. In comparison with this result, the ideal-gas value is 13% too high and Eq. (3.38) gives a value 1.7% too high.

3.5 CUBIC EQUATIONS OF STATE

If an equation of state is to represent the PVT behaviour of both liquids and vapours, 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 vapour behaviour.

The van der Waals Equation of State

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (3.41)$$

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 .

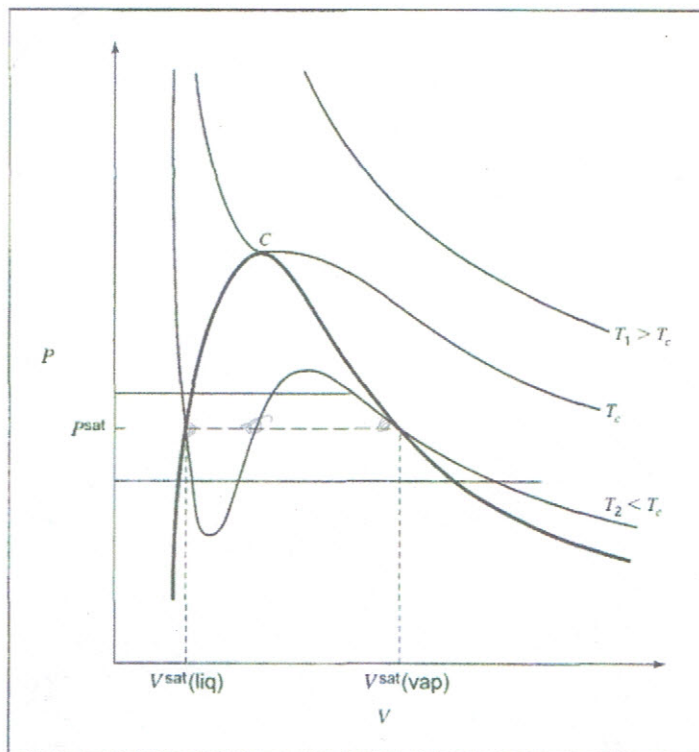


Figure 3.12 Isotherms as given by a cubic equation of state

Figure 3.12 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 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.

Saturated liquid and saturated vapor coexist in varying proportions at the saturation or vapor 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.

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 ($T = T_c$), this is also true, except at the critical pressure, where there are three roots, all equal to V_c .
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 $P = P^{\text{Sat}}$, namely $V^{\text{sat}}(\text{liq})$ and $V^{\text{sat}}(\text{vap})$, 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 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. It reduces to the van der Waals equation when $\theta = a$, and $\kappa = \lambda = 0$

An important class of cubic equations results from the preceding equation with the assignments: $\eta = b$ $\theta = a(T)$ $\kappa = (\epsilon + \sigma)b$ $\lambda = \epsilon\sigma b^2$

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:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)} \quad (3.42)$$

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 PVT 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:

$$\left(\frac{\partial P}{\partial V} \right)_{T,c} = 0 \quad (3.43) \quad \left(\frac{\partial^2 P}{\partial V^2} \right)_{T,c} = 0 \quad (3.44)$$

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 $V = V_c$.

These three equations contain five constants: P_c , V_c , T_c , $a(T_c)$, and b .

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,

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

or

$$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad (A)$$

Equation (3.41) 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:

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

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

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

Different values are found for different equations of state, as indicated in Table 3.1, p. 93.

Table B.1 of App. B for various substances is 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. (3.42), 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

$$a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c} \quad (3.45)$$

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

$$b = \Omega \frac{RT_c}{P_c} \quad (3.46)$$

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 **Redlic/Kwong (RK)** equation:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \quad (3.47)$$

where, in Eq. (3.45), $\alpha(T_r) = T_r^{-1/2}$.

Theorem of Corresponding States; Acentric Factor

Experimental observation shows that compressibility factors Z for different fluids exhibit similar behaviour when correlated as a function of reduced temperature T , and reduced pressure P ; 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.

Acentric factor ω : introduced by K. S. Pitzer and coworker.

The acentric factor for a pure chemical species is defined with reference to its vapour pressure.

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

$$\omega \equiv -1.0 - \log(P_r^{\text{sat}})_{T_r = 0.7} \quad (3.48)$$

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 behaviour 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. (3.42), is in practice far more commonly solved by iterative procedures>

For the largest root, i.e., a vapour or vapour-like volume, Eq. (3.42) is multiplied through by $(V - b)/RT$. It can then be written:

$$V = \frac{RT}{P} + b - \frac{a(T)}{P} \frac{V - b}{(V + \epsilon b)(V + \sigma b)} \quad (3.49)$$

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. (3.49). 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. (3.49) is obtained through the substitution $V = ZRT/P$. In addition, the definition of two dimensionless quantities leads to simplification.

Thus,

$\beta \equiv \frac{bP}{RT} \quad (3.50)$	$q \equiv \frac{a(T)}{bRT} \quad (3.51)$
---	--

With these substitutions Eq. (3.49) becomes:

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \quad (3.52)$$

Equations (3.50) and (3.51) in combination with Eqs. (3.45) and (3.46) yield:

$\beta = \Omega \frac{P_r}{T_r} \quad (3.53)$	$q = \frac{\Psi \alpha(T_r)}{\Omega T_r} \quad (3.54)$
---	--

Iterative solution of Eq. (3.52) 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 $V = ZRT/P$.