2. At high pressure (ie, $p \rightarrow \infty$) the volume, V, becomes very small and approaches the value b, which is the actual molecular volume, as mathematically given by

$$\lim_{p \rightarrow \infty} V(p) = b$$

The van der Waals or any other equation of state can be expressed in a more generalized form as follows:

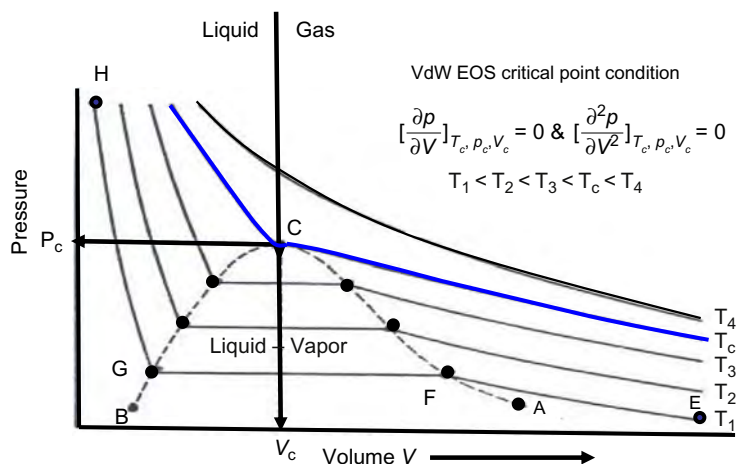$$p = p_{\text{repulsion}} - p_{\text{attraction}} \tag{5.47}$$

where the repulsion pressure term, $p_{\text{repulsion}}$, is represented by the term $RT/(V-b)$, and the attraction pressure term, $p_{\text{attraction}}$, is described by a/V^2.

In determining the values of the two constants, a and b, for any pure substance, van der Waals observed that the critical isotherm has a horizontal slope and an inflection point at the critical point, as shown in Fig. 5.7. This observation can be expressed mathematically as follows:

$$\begin{aligned} \left[\frac{\partial p}{\partial V}\right]_{T_c, p_c} &= 0 \\ \left[\frac{\partial^2 p}{\partial V^2}\right]_{T_c, p_c} &= 0 \end{aligned} \tag{5.48}$$

Differentiating Eq. (5.46) with respect to the volume at the critical point results in

$$\left[\frac{\partial p}{\partial V}\right]_{T_c, p_c} = \frac{-RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \tag{5.49}$$

■ **FIGURE 5.7** An idealized pressure-volume relationship for a pure component.

$$\left[\frac{\partial^2 p}{\partial V^2}\right]_{T_c, p_c} = \frac{2RT_c}{(V_c - b)^3} + \frac{6a}{V_c^4} = 0 \qquad (5.50)$$

Solving Eqs. (5.49), (5.50) simultaneously for the parameters a and b gives

$$b = \left(\frac{1}{3}\right)V_c \qquad (5.51)$$

$$a = \left(\frac{8}{9}\right)RT_c V_c \qquad (5.52)$$

Eq. (5.51) suggests that the covolume "b" is approximately 0.333 of the critical volume "V_c" of the substance. Numerous experimental studies revealed that the co-volume "b" is in the range 0.24–0.28 of the critical volume and pure component.

Applying Eq. (5.48) to the critical point (i.e., by setting $T = T_c$, $p = p_c$, and $V = V_c$) and combining with Eqs. (5.51), (5.52) yields

$$p_c V_c = (0.375)RT_c \qquad (5.53)$$

Eq. (5.53) indicates that regardless of the type of the substance, the Van der Waals EOS gives a universal *critical gas compressibility factor* "Z_c" of 0.375. Experimental studies show that Z_c values for substances are ranging between 0.23 and 0.31.

Eq. (5.53) can be combined with Eqs. (5.51), (5.52) to give more convenient and traditional expressions for calculating the parameters a and b, to yield

$$a = \Omega_a \frac{R^2 T_c^2}{p_c} \qquad (5.54)$$

$$b = \Omega_b \frac{RT_c}{p_c} \qquad (5.55)$$

where

$R = $ gas constant, 10.73 psia-ft^3/lb-mol-°R
$p_c = $ critical pressure, psia
$T_c = $ critical temperature, °R
$\Omega_a = 0.421875$
$\Omega_b = 0.125$

Eq. (5.46) can also be expressed in a cubic form in terms of the volume "V" as follows:

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