CHAPTER

7

Equations of State

An equation of state (EOS) is an analytical expression relating the pressure p to the temperature T and the volume V. A proper description of this PVT relationship for real hydrocarbon fluids is essential in determining the volumetric and phase behavior of petroleum reservoir fluids and in predicting the performance of surface separation facilities.

The best known and the simplest example of an equation of state is the ideal gas equation, expressed mathematically by the expression

$$p = \frac{RT}{V} \tag{7-1}$$

where V = gas volume in cubic feet per 1 mol of gas. This PVT relationship is used to describe the volumetric behavior of real hydrocarbon gases only at pressures close to the atmospheric pressure for which it was experimentally derived.

The extreme limitations of the applicability of Equation 7-1 prompted numerous attempts to develop an equation of state suitable for describing the behavior of real fluids at extended ranges of pressures and temperatures.

The main objective of this chapter is to review developments and advances in the field of empirical cubic equations of state and demonstrate their applications in petroleum engineering.

7.1 THE VAN DER WAALS EQUATION OF STATE

In developing the ideal gas EOS (Equation 7-1), two assumptions were made:

- **First assumption**. The volume of the gas molecules is insignificant compared to the volume of the container and the distance between the molecules.

- **Second assumption**. There are no attractive or repulsive forces between the molecules or the walls of the container.

van der Waals (1873) [61] attempted to eliminate these two assumptions by developing an empirical equation of state for real gases. In his attempt to eliminate the first assumption, van der Waals pointed out that the gas molecules occupy a significant fraction of the volume at higher pressures and proposed that the volume of the molecules, as denoted by the parameter b, be subtracted from the actual molar volume V in Equation 7-1, to give

$$p = \frac{RT}{V - b}$$

where the parameter b is known as the covolume and is considered to reflect the volume of molecules. The variable V represents the actual volume in cubic feet per 1 mol of gas.

To eliminate the second assumption, van der Waals subtracted a corrective term, denoted by a/V^2, from the preceding equation to account for the attractive forces between molecules. In a mathematical form, van der Waals proposed the following expression:

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \tag{7-2}$$

where p = system pressure, psia
T = system temperature, °R
R = gas constant, 10.73 psi-ft^3/lb-mol = °R
V = volume, ft^3/mol

The two parameters a and b are constants characterizing the molecular properties of the individual components. The symbol a is considered a measure of the intermolecular attractive forces between the molecules. Equation 7-2 shows the following important characteristics:

1. At low pressures, the volume of the gas phase is large in comparison with the volume of the molecules. The parameter b becomes negligible in comparison with V and the attractive forces term a/V^2 becomes insignificant; therefore, the van der Waals equation reduces to the ideal gas equation (Equation 7-1).
2. At high pressure, i.e., $p \to \infty$, volume V becomes very small and approaches the value b, which is the actual molecular volume.

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

$$p = p_{\text{repulsive}} - p_{\text{attractive}}$$

where the repulsive pressure term $p_{repulsive}$ is represented by the term $RT/(V - b)$ and the attractive pressure term $p_{attractive}$ 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 Figure 7-1. This observation can be expressed mathematically as follows:

$$\left[\frac{\partial p}{\partial V}\right]_{T_C,p_C} = 0, \qquad \left[\frac{\partial^2 p}{\partial V^2}\right]_{T_C,p_C} = 0 \tag{7-3}$$

Differentiating Equation 7-2 with respect to the volume at the critical point results in

$$\left[\frac{\partial p}{\partial V}\right]_{T_C,p_C} = \frac{-RT_C}{(V_C - b)^3} + \frac{2a}{V_C^3} = 0 \tag{7-4}$$

$$\left[\frac{\partial^2 p}{\partial V^2}\right]_{T_C,p_C} = \frac{2RT_C}{(V_C - b)^3} + \frac{6a}{V_C^4} = 0 \tag{7-5}$$

Solving Equations 7-4 and 7-5 simultaneously for the parameters a and b gives

$$b = \left(\frac{1}{3}\right)V_C \tag{7-6}$$

$$a = \left(\frac{8}{9}\right)RT_C V_C \tag{7-7}$$

Equation 7-6 suggests that the volume of the molecules b is approximately 0.333 of the critical volume V_C of the substance. Experimental studies reveal that the covolume b is in the range of 0.24 to 0.28 of the critical volume and pure component.

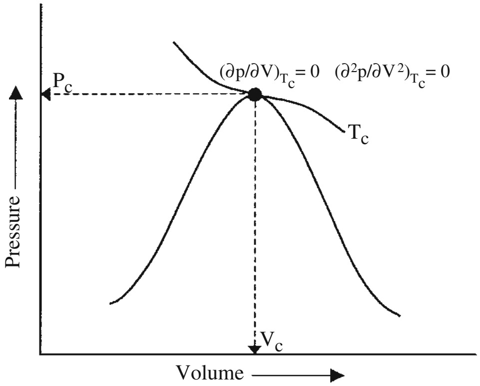

FIGURE 7-1 An idealized pressure–volume relationship for a pure compound.

By applying Equation 7-2 to the critical point (i.e., by setting $T = T_c$, $p = p_c$, and $V = V_c$) and combining with Equations 7-6 and 7-7, we get

$$p_C V_C = (0.375) R T_C \tag{7-8}$$

Equation 7-8 shows that regardless of the type of substance, the van der Waals EOS produces a universal critical gas compressibility factor Z_c of 0.375. Experimental studies show that Z_c values for substances range between 0.23 and 0.31.

Equation 7-8 can be combined with Equations 7-6 and 7-7 to give a more convenient and traditional expression for calculating the parameters a and b to yield

$$a = \Omega_a \frac{R^2 T_c^2}{p_c} \tag{7-9}$$

$$b = \Omega_b \frac{R T_c}{p_c} \tag{7-10}$$

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

Equation 7-2 can also be expressed in a cubic form in terms of the volume V as follows:

$$V^3 - \left(b + \frac{RT}{p}\right) V^2 + \left(\frac{a}{p}\right) V - \left(\frac{ab}{p}\right) = 0 \tag{7-11}$$

Equation 7-11 is usually referred to as the *van der Waals two-parameter cubic equation of state*. The term *two-parameter* refers to the parameters a and b. The term *cubic equation of state* implies an equation that, if expanded, would contain volume terms to the first, second, and third power.

Perhaps the most significant feature of Equation 7-11 is its ability to describe the liquid-condensation phenomenon and the passage from the gas to the liquid phase as the gas is compressed. This important feature of the van der Waals EOS is discussed in conjunction with Figure 7-2.

Consider a pure substance with a p-V behavior as shown in Figure 7-2. Assume that the substance is kept at a constant temperature T below its critical temperature. At this temperature, Equation 7-11 has three real roots (volumes) for each specified pressure p. A typical solution of Equation 7-11 at constant temperature T is shown graphically by the dashed

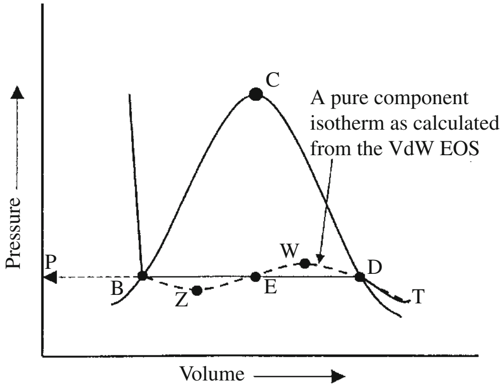

FIGURE 7-2 Pressure–volume diagram for a pure component.

isotherm: the constant temperature curve DWEZB in Figure 7-2. The three values of V are the intersections B, E, and D on the horizontal line, corresponding to a fixed value of the pressure. This dashed calculated line (DWEZB) then appears to give a continuous transition from the gaseous phase to the liquid phase, but in reality the transition is abrupt and discontinuous, with both liquid and vapor existing along the straight horizontal line DB. Examining the graphical solution of Equation 7-11 shows that the largest root (volume), as indicated by point D, corresponds to the volume of the saturated vapor, while the smallest positive volume, as indicated by point B, corresponds to the volume of the saturated liquid. The third root, point E, has no physical meaning. Note that these values become identical as the temperature approaches the critical temperature T_c of the substance.

Equation 7-11 can be expressed in a more practical form in terms of the compressibility factor Z. Replacing the molar volume V in Equation 7-11 with ZRT/p gives

$$Z^3 - (1 + B)Z^2 + AZ - AB = 0 \tag{7-12}$$

where

$$A = \frac{ap}{R^2T^2} \tag{7-13}$$

$$B = \frac{bp}{RT} \tag{7-14}$$

Z = compressibility factor
p = system pressure, psia
T = system temperature, °R

Equation 7-12 yields one real root[1] in the one-phase region and three real roots in the two-phase region (where the system pressure equals the vapor pressure of the substance). In the latter case, the largest root corresponds to the compressibility factor of the vapor phase Z^V, while the smallest positive root corresponds to that of the liquid Z^L.

An important practical application of Equation 7-12 is calculating density, as illustrated in the following example.

Example 7-1

A pure propane is held in a closed container at 100°F. Both gas and liquid are present. Calculate, using the van der Waals EOS, the density of the gas and liquid phases.

Solution

Step 1. Determine the vapor pressure p_v of the propane from the Cox chart (Figure 1-1). This is the only pressure at which two phases can exist at the specified temperature:

$$p_v = 185 \text{ psi}$$

Step 2. Calculate parameters a and b from Equations 7-9 and 7-10, respectively:

$$a = \Omega_a \frac{R^2 T_c^2}{p_c}$$

$$a = 0.421875 \frac{(10.73)^2 (666)^2}{616.3} = 34{,}957.4$$

and

$$b = \Omega_b \frac{R T_c}{p_c}$$

$$b = 0.125 \frac{10.73(666)}{616.3} = 1.4494$$

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[1] In some supercritical regions, Equation 7-12 can yield three real roots for Z. From the three real roots, the largest root is the value of the compressibility with physical meaning.

Step 3. Compute coefficients A and B by applying Equations 7-13 and 7-14, respectively.

$$A = \frac{ap}{R^2T^2}$$

$$A = \frac{(34,957.4)(185)}{(10.73)^2(560)^2} = 0.179122$$

$$B = \frac{bp}{RT}$$

$$B = \frac{(1.4494)(185)}{(10.73)(560)} = 0.044625$$

Step 4. Substitute the values of A and B into Equation 7-12 to give

$$Z^3 - (1 + B)Z^2 + AZ - AB = 0$$

$$Z^3 - 1.044625Z^2 + 0.179122Z - 0.007993 = 0$$

Step 5. Solve the preceding third-degree polynomial by extracting the largest and smallest roots of the polynomial using the appropriate direct or iterative method to give

$$Z^v = 0.72365$$

$$Z^L = 0.07534$$

Step 6. Solve for the density of the gas and liquid phases:

$$\rho_g = \frac{pM}{Z^vRT}$$

$$\rho_g = \frac{(185)(44.0)}{(0.72365)(10.73)(560)} = 1.87\ \text{lb/ft}^3$$

and

$$\rho_L = \frac{pM}{Z^LRT}$$

$$\rho_L = \frac{(185)(44)}{(0.7534)(10.73)(560)} = 17.98\ \text{lb/ft}^3$$

The van der Waals equation of state, despite its simplicity, provides a correct description, at least qualitatively, of the PVT behavior of substances in the liquid and gaseous states. Yet it is not accurate enough to be suitable for design purposes.

With the rapid development of computers, the EOS approach for the calculation of physical properties and phase equilibria proved to be a powerful tool, and much energy was devoted to the development of new and accurate equations of state. These equations, many of them a modification of the van der Waals equation of state, range in complexity from simple expressions containing 2 or 3 parameters to complicated forms containing more than 50 parameters. Although the complexity of any equation of state presents no computational problem, most authors prefer to retain the simplicity found in the van der Waals cubic equation while improving its accuracy through modifications.

All equations of state are generally developed for pure fluids first, then extended to mixtures through the use of mixing rules. These mixing rules are simply means of calculating mixture parameters equivalent to those of pure substances.

7.2 REDLICH-KWONG EQUATION OF STATE

Redlich and Kwong (1949) [45] demonstrated that, by a simple adjustment, the van der Waals attractive pressure term a/V^2 could considerably improve the prediction of the volumetric and physical properties of the vapor phase. The authors replaced the attractive pressure term with a generalized temperature dependence term. Their equation has the following form:

$$p = \frac{RT}{V-b} - \frac{a}{V(V+b)\sqrt{T}} \tag{7-15}$$

where T is the system temperature in °R.

Redlich and Kwong, in their development of the equation, noted that, as the system pressure becomes very large, i.e., $p \to \infty$, the molar volume V of the substance shrinks to about 26% of its critical volume regardless of the system temperature. Accordingly, they constructed Equation 7-15 to satisfy the following condition:

$$b = 0.26\,V_c \tag{7-16}$$

Imposing the critical point conditions (as expressed by Equation 7-3) on Equation 7-15 and solving the resulting equations simultaneously gives

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{p_c} \tag{7-17}$$

$$b = \Omega_b \frac{RT_c}{p_c} \tag{7-18}$$

where $\Omega_a = 0.42747$ and $\Omega_b = 0.08664$. Equating Equation 7-18 with 7-16 gives

$$p_c V_c = 0.333 R T_c \tag{7-19}$$

Equation 7-19 shows that the Redlich-Kwong EOS produces a universal critical compressibility factor (Z_c) of 0.333 for all substances. As indicated earlier, the critical gas compressibility ranges from 0.23 to 0.31 for most of the substances.

Replacing the molar volume V in Equation 7-15 with ZRT/p gives

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{7-20}$$

where

$$A = \frac{ap}{R^2 T^{2.5}} \tag{7-21}$$

$$B = \frac{bp}{RT} \tag{7-22}$$

As in the van der Waals EOS, Equation 7-20 yields one real root in the one-phase region (gas-phase region or liquid-phase region) and three real roots in the two-phase region. In the latter case, the *largest root* corresponds to the compressibility factor of the gas phase Z^v while the *smallest positive root* corresponds to that of the liquid Z^L.

Example 7-2

Rework Example 7-1 by using the Redlich-Kwong equation of state.

Solution

Step 1. Calculate the parameters a, b, A, and B:

$$a = 0.42747 \frac{(10.73)^2 (666)^{2.5}}{616.3} = 914{,}110.1$$

$$b = 0.08664 \frac{(10.73)(666)}{616.3} = 1.0046$$

$$A = \frac{(914,110.1)(185)}{(10.73)^2 (560)^{2.5}} = 0.197925$$

$$B = \frac{(1.0046)(185)}{(10.73)(560)} = 0.03093$$

Step 2. Substitute parameters A and B into Equation 7-20, and extract the largest and smallest root, to give

$$Z^3 - Z^2 + 0.1660384Z - 0.0061218 = 0$$
Largest root $Z^v = 0.802641$
Smallest root $Z^L = 0.0527377$

Step 3. Solve for the density of the liquid phase and the gas phase:

$$\rho = \frac{pM}{ZRT}$$

$$\rho^L = \frac{(185)(44)}{(0.0527377)(10.73)(560)} = 25.7\ \text{lb/ft}^3$$

$$\rho^v = \frac{(185)(44)}{(0.802641)(10.73)(560)} = 1.688\ \text{lb/ft}^3$$

Redlich and Kwong extended the application of their equation to hydrocarbon liquid or gas mixtures by employing the following mixing rules:

$$a_m = \left[\sum_{i=1}^{n} x_i \sqrt{a_i}\right]^2 \tag{7-23}$$

$$b_m = \sum_{i=1}^{n} [x_i b_i] \tag{7-24}$$

where n = number of components in mixture
a_i = Redlich-Kwong a parameter for the ith component as given by Equation 7-17
b_i = Redlich-Kwong b parameter for the ith component as given by Equation 7-18
a_m = parameter a for mixture
b_m = parameter b for mixture
x_i = mole fraction of component i in the liquid phase

To calculate a_m and b_m for a hydrocarbon gas mixture with a composition of y_i, use Equations 7-23 and 7-24 and replace x_i with y_i:

$$a_m = \left[\sum_{i=1}^{n} y_i \sqrt{a_i}\right]^2$$

$$b_m = \sum_{i=1}^{n} [y_i b_i]$$

Equation 7-20 gives the compressibility factor of the gas phase or the liquid phase with the coefficients A and B as defined by Equations 7-21 and 7-22. The application of the Redlich-Kwong equation of state for hydrocarbon mixtures can be best illustrated through the following two examples.

Example 7-3

Calculate the density of a crude oil with the following composition at 4000 psia and 160°F. Use the Redlich-Kwong EOS.

Component	x_i	**M**	p_c	T_c
C_1	0.45	16.043	666.4	343.33
C_2	0.05	30.070	706.5	549.92
C_3	0.05	44.097	616.0	666.06
$n-C_4$	0.03	58.123	527.9	765.62
$n-C_5$	0.01	72.150	488.6	845.8
C_6	0.01	84.00	453	923
C_{7+}	0.40	215	285	1287

Solution

Step 1. Determine the parameters a_i and b_i for each component using Equations 7-17 and 7-18:

Component	a_i	b_i
C_1	161,044.3	0.4780514
C_2	493,582.7	0.7225732
C_3	914,314.8	1.004725
C_4	1,449,929	1.292629
C_5	2,095,431	1.609242
C_6	2,845,191	1.945712
C_{7+}	1.022348E7	4.191958

Step 2. Calculate the mixture parameters a_m and b_m from Equations 7-23 and 7-24 to give

$$a_m = \left[\sum_{i=1}^{n} x_i \sqrt{a_i}\right]^2 = 2{,}591{,}967$$

and

$$b_m = \sum_{i=1}^{n} [x_i b_i] = 2.0526$$

Step 3. Compute the coefficients A and B using Equations 7-21 and 7-22 to produce

$$A = \frac{a_m p}{R^2 T^{2.5}} = \frac{2{,}591{,}967(4000)}{10.73^2(620)^{2.5}} = 9.406539$$

$$B = \frac{b_m p}{RT} = \frac{2.0526(4000)}{10.73(620)} = 1.234049$$

Step 4. Solve Equation 7-20 for the largest positive root to yield

$$Z^3 - Z^2 + 6.93845Z - 11.60813 = 0$$
$$Z^L = 1.548126$$

Step 5. Calculate the apparent molecular weight of the crude oil:

$$M_a = \sum x_i M_i$$
$$M_a = 100.2547$$

Step 6. Solve for the density of the crude oil:

$$\rho^L = \frac{pM_a}{Z^L RT}$$

$$\rho^L = \frac{(4000)(100.2547)}{(10.73)(620)(1.548120)} = 38.93 \text{ lb/ft}^3$$

Notice that liquid density, as calculated by Standing's correlation, gives a value of 46.23 lb/ft^3.

Example 7-4

Calculate the density of a gas phase with the following composition at 4000 psia and 160°F. Use the Redlich-Kwong EOS.

Component	y_i	**M**	p_c	T_c
C_1	0.86	16.043	666.4	343.33
C_2	0.05	30.070	706.5	549.92
C_3	0.05	44.097	616.0	666.06
C_4	0.02	58.123	527.9	765.62
C_5	0.01	72.150	488.6	845.8
C_6	0.005	84.00	453	923
C_{7+}	0.005	215	285	1287

Solution

Step 1. Calculate a_m and b_m using Equations 7-23 and 7-24 to give

$$a_m = \left[\sum_{i=1}^{n} y_i \sqrt{a_i}\right]^2$$

$$a_m = 241{,}118$$

$$b_m = \sum b_i x_i$$

$$b_m = 0.5701225$$

Step 2. Calculate the coefficients A and B by applying Equations 7-21 and 7-22 to yield

$$A = \frac{a_m p}{R^2 T^{2.5}} = \frac{241{,}118(4000)}{10.73^2 (620)^{2.5}} = 0.8750$$

$$B = \frac{b_m p}{RT} = \frac{0.5701225(4000)}{10.73(620)} = 0.3428$$

Step 3. Solve Equation 7-20 for Z^V to give

$$Z^3 - Z^2 + 0.414688Z - 0.29995 = 0$$

$$Z^V = 0.907$$

Step 4. Calculate the apparent density of the gas mixture:

$$M_a = \sum y_i M_i = 20.89$$

$$\rho^v = \frac{pM_a}{Z^v RT}$$

$$\rho^v = \frac{(4000)(20.89)}{(10.73)(620)(0.907)} = 13.85 \text{ lb/ft}^3$$

7.3 SOAVE-REDLICH-KWONG EQUATION OF STATE AND ITS MODIFICATIONS

One of the most significant milestones in the development of cubic equations of state was the publication by Soave (1972) [54] of a modification to the evaluation of parameter a in the attractive pressure term of the Redlich-Kwong equation of state (Equation 7-15). Soave replaced the term $a/T^{0.5}$ in Equation 7-15 with a more generalized *temperature-dependent term*, as denoted by $(a\alpha)$, to give

$$p = \frac{RT}{V - b} - \frac{a\alpha}{V(V + b)} \tag{7-25}$$

where α is a dimensionless factor that becomes unity at $T = T_c$. At temperatures other than critical temperature, the parameter α is defined by the following expression:

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2 \tag{7-26}$$

The parameter m is correlated with the acentric factor to give

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{7-27}$$

where T_r = reduced temperature T/T_c
ω = acentric factor of the substance
T = system temperature, °R

For any pure component, the constants a and b in Equation 7-25 are found by imposing the classical van der Waals critical point constraints (Equation 7-3) on Equation 7-25 and solving the resulting equations to give

$$a = \Omega_a \frac{R^2 T_c^2}{p_c} \tag{7-28}$$

$$b = \Omega_b \frac{RT_c}{p_c} \tag{7-29}$$

where Ω_a and Ω_b are the Soave-Redlich-Kwong (SRK) dimensionless pure component parameters and have the following values:

$$\Omega_a = 0.42747 \quad \text{and} \quad \Omega_b = 0.08664$$

Edmister and Lee (1986) [13] showed that the two parameters a and b can be determined more conveniently by considering the critical isotherm:

$$(V - V_c)^3 = V^3 - [3V_c]V^2 + [3V_c^2]V - V_c^3 = 0 \tag{7-30}$$

Equation 4-11 can also be put into a cubic form to give

$$V^3 - \left[\frac{RT}{p}\right]V^2 + \left[\frac{a\alpha}{p} - \frac{bRT}{p} - b^2\right]V - \left[\frac{(a\alpha)b}{p}\right] = 0 \tag{7-31}$$

At the critical point, the coefficient α = 1 and the preceding two expressions are essentially identical. Equating the like terms gives

$$3V_c = \frac{RT_c}{p_c} \tag{7-32}$$

$$3V_c^2 = \frac{a}{p_c} - \frac{bRT_c}{p_c} - b^2 \tag{7-33}$$

and

$$V_c^3 = \frac{ab}{p_c} \tag{7-34}$$

Solving these equations for parameters a and b yields expressions for the parameters as given by Equations 7-28 and 7-29.

Equation 7-32 indicates that the SRK equation of state gives a universal critical gas compressibility factor of 0.333. Combining Equation 6-3 with 7-29 gives

$$b = 0.26V_c$$

Introducing the compressibility factor Z into Equation 6-2 by replacing the molar volume V in the equation with (ZRT/p) and rearranging gives

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{7-35}$$

with

$$A = \frac{(a\alpha)p}{(RT)^2} \tag{7-36}$$

$$B = \frac{bp}{RT} \tag{7-37}$$

where p = system pressure, psia
T = system temperature, °R
$R = 10.730$ psia ft^3/lb-mol-°R

Example 7-5

Rework Example 7-1 and solve for the density of the two phases by using the SRK EOS.

Solution

Step 1. Determine the critical pressure, critical temperature, and acentric factor to give

$$T_c = 666.01°R$$
$$p_c = 616.3 \text{ psia}$$
$$\omega = 0.1524$$

Step 2. Calculate the reduced temperature:

$$T_r = 560/666.01 = 0.8408$$

Step 3. Calculate the parameter m by applying Equation 7-27 to yield

$$m = 0.480 + 1.574\omega - 0.176\omega^2$$

$$m = 0.480 + 1.574(0.1524) - 0.176(1.524)^2 = 0.7051$$

Step 4. Solve for the parameter a by using Equation 7-26 to give

$$\alpha = \left[m + \left(1 - \sqrt{T_r}\right)\right]^2 = 1.120518$$

Step 5. Compute the coefficients a and b by applying Equations 7-28 and 7-29 to yield

$$a = 0.42747 \frac{10.73^2 (666.01)^2}{616.3} = 35{,}427.6$$

$$b = 0.08664 \frac{10.73(666.01)}{616.3} = 1.00471$$

Step 6. Calculate the coefficients A and B from Equations 7-36 and 7-37 to produce

$$A = \frac{(a\alpha)p}{R^2 T^2}$$

$$A = \frac{(35{,}427.6)(1.120518)185}{10.73^2 (560)^2} = 0.203365$$

$$B = \frac{bp}{RT}$$

$$B = \frac{(1.00471)(185)}{(10.73)(560)} = 0.034658$$

Step 7. Solve Equation 7-35 for Z^L and Z^v:

$$Z^3 - Z^2 + (A - B - B^2)Z + AB = 0$$
$$Z^3 - Z^2 + (0.203365 - 0.034658 - 0.034658^2)Z$$
$$+(0.203365)(0.034658) = 0$$

Solving the above third-degree polynomial gives

$$Z^L = 0.06729$$

$$Z^V = 0.80212$$

Step 8. Calculate the gas and liquid density to give

$$\rho = \frac{pM}{ZRT}$$

$$\rho^{v} = \frac{(185)(44.0)}{(0.802121)(10.73)(560)} = 1.6887\ \text{lb/ft}^3$$

$$\rho^{L} = \frac{(185)(44.0)}{(0.06729)(10.73)(560)} = 20.13\ \text{lb/ft}^3$$

To use Equation 7-35 with mixtures, mixing rules are required to determine the terms ($a\alpha$) and b for the mixtures. Soave adopted the following mixing rules:

$$(a\alpha)_m = \sum_i \sum_j \left[x_i x_j \sqrt{a_i a_j \alpha_i \alpha_j} (1 - k_{ij}) \right] \tag{7-38}$$

$$b_m = \sum_i [x_i b_i] \tag{7-39}$$

with

$$A = \frac{(a\alpha)_m p}{(RT)^2} \tag{7-40}$$

and

$$B = \frac{b_m p}{RT} \tag{7-41}$$

The parameter k_{ij} is an empirically determined correction factor (called the *binary interaction coefficient*) that is designed to characterize any binary system formed by component i and component j in the hydrocarbon mixture.

These binary interaction coefficients are used to model the intermolecular interaction through empirical adjustment of the $(a\alpha)_m$ term as represented mathematically by Equation 7-38. They are dependent on the difference in molecular size of components in a binary system, and they are characterized by the following properties:

- The interaction between hydrocarbon components increases as the relative difference between their molecular weights increases:

$$k_{i,j+1} > k_{i,j}$$

- Hydrocarbon components with the same molecular weight have a binary interaction coefficient of 0:

$$k_{i,i} = 0$$

- The binary interaction coefficient matrix is symmetric:

$$k_{j,i} = k_{i,j}$$

Slot-Peterson (1987) [53] and Vidal and Daubert (1978) [62] presented a theoretical background to the meaning of the interaction coefficient and techniques for determining their values. Grabowski and Daubert (1978) [17] and Soave (1972) [54] suggested that no binary interaction coefficients are required for hydrocarbon systems. However, with nonhydrocarbons present, binary interaction parameters can greatly improve the volumetric and phase behavior predictions of the mixture by the SRK EOS.

In solving Equation 7-30 for the compressibility factor of the liquid phase, the composition of the liquid x_i is used to calculate the coefficients A and B of Equations 7-40 and 7-41 through the use of the mixing rules as described by Equations 7-38 and 7-39. For determining the compressibility factor of the gas phase Z^v, the previously outlined procedure is used with composition of the gas phase y_i replacing x_i.

Example 7-6

A two-phase hydrocarbon system exists in equilibrium at 4000 psia and 160°F. The system has the following composition:

Component	x_i	y_i
C_1	0.45	0.86
C_2	0.05	0.05
C_3	0.05	0.05
C_4	0.03	0.02
C_5	0.01	0.01
C_6	0.01	0.005
C_{7+}	0.40	0.005

The heptanes-plus fraction has the following properties:

$$M = 215$$
$$p_c = 285 \text{ psia}$$
$$T_c = 700°F$$
$$\omega = 0.52$$

Assuming $k_{ij} = 0$, calculate the density of each phase using the SRK EOS.

Solution

Step 1. Calculate the parameters α, a, and b by applying Equations 7-21, 7-28, and 7-29:

Component	α_i	a_i	b_i
C_1	0.6869	8,689.3	0.4780
C_2	0.9248	21,040.8	0.7725
C_3	1.0502	35,422.1	1.0046
C_4	1.1616	52,390.3	1.2925
C_5	1.2639	72,041.7	1.6091
C_6	1.3547	94,108.4	1.9455
C_{7+}	1.7859	232,367.9	3.7838

Step 2. Calculate the mixture parameters $(a\alpha)_m$ and b_m for the gas phase and liquid phase by applying Equations 7-38 and 7-39 to give

- **For the gas phase using y_i.**

$$(a\alpha)_m = \sum_i \sum_j \left[y_i y_j \sqrt{a_i a_j \alpha_i \alpha_j} (1 - k_{ij}) \right] = 9219.3$$

$$b_m = \sum_i [y_i b_i] = 0.5680$$

- **For the liquid phase using x_i.**

$$(a\alpha)_m = \sum_i \sum_j \left[x_i x_j \sqrt{a_i a_j \alpha_i \alpha_j} (1 - k_{ij}) \right] = 104{,}362.9$$

$$b_m = \sum_i [x_i b_i] = 0.1.8893$$

Step 3. Calculate the coefficients A and B for each phase by applying Equations 7-40 and 7-41 to yield

- **For the gas phase.**

$$A = \frac{(a\alpha)_m p}{R^2 T^2} = \frac{(9219.3)(4000)}{(10.73)^2 (620)^2} = 0.8332$$

$$B = \frac{b_m p}{RT} = \frac{(0.5680)(4000)}{(10.73)(620)} = 0.3415$$

- **For the liquid phase.**

$$A = \frac{(a\alpha)_m p}{R^2 T^2} = \frac{(104{,}362.9)(4000)}{(10.73)^2 (620)^2} = 9.4324$$

$$B = \frac{b_m p}{RT} = \frac{(1.8893)(4000)}{(10.73)(620)} = 1.136$$

Step 4. Solve Equation 7-35 for the compressibility factor of the gas phase to produce

$$Z^3 - Z^2 + (A - B - B^2)Z + AB = 0$$
$$Z^3 - Z^2 + (0.8332 - 0.3415 - 0.3415^2)Z + (0.8332)(0.3415) = 0$$

Solving this polynomial for the largest root gives

$$Z^v = 0.9267$$

Step 5. Solve Equation 7-35 for the compressibility factor of the liquid phase to produce

$$Z^3 - Z^2 + (A - B - B^2)Z + AB = 0$$
$$Z^3 - Z^2 + (9.4324 - 1.136 - 1.136^2)Z + (9.4324)(1.136) = 0$$

Solving this polynomial for the smallest root gives

$$Z^L = 1.4121$$

Step 6. Calculate the apparent molecular weight of the gas phase and liquid phase from their composition to yield

- **For the gas phase**.

$$M_a = \sum y_i M_i = 20.89$$

- **For the liquid phase**.

$$M_a = \sum x_i M_i = 100.25$$

Step 7. Calculate the density of each phase:

$$\rho = \frac{pM_a}{RTZ}$$

- **For the gas phase**.

$$\rho^v = \frac{(4000)(20.89)}{(10.73)(620)(0.9267)} = 13.556 \text{ lb/ft}^3$$

- **For the liquid phase**.

$$\rho^L = \frac{(4000)(100.25)}{(10.73)(620)(1.4121)} = 42.68 \text{ lb/ft}^3$$

It is appropriate at this time to introduce and define the concept of the fugacity and the fugacity coefficient of the component. The *fugacity* f is a measure of the molar Gibbs energy of a real gas. It is evident from the definition that the fugacity has the units of pressure; in fact, the fugacity may be looked on as a vapor pressure modified to correctly represent the escaping tendency of the molecules from one phase into the other. In mathematical form, the fugacity of a pure component is defined by the following expression:

$$f = p \exp\left[\int_o^p \left(\frac{Z-1}{p}\right) dp\right] \tag{7-42}$$

where f = fugacity, psia
p = pressure, psia
Z = compressibility factor

The ratio of the fugacity to the pressure, i.e., f/p, is called the *fugacity coefficient* Φ and is calculated from Equation 7-42 as

$$\frac{f}{p} = \Phi = \exp\left[\int_o^p \left(\frac{Z-1}{p}\right) dp\right]$$

Soave applied this generalized thermodynamic relationship to Equation 7-25 to determine the fugacity coefficient of a pure component:

$$\ln\left(\frac{f}{p}\right) = \ln(\Phi) = Z - 1 - \ln(Z - B) - \frac{A}{B} \ln\left[\frac{Z+B}{Z}\right] \tag{7-43}$$

In practical petroleum engineering applications, we are concerned with the phase behavior of the hydrocarbon liquid mixture, which, at a specified pressure and temperature, is in equilibrium with a hydrocarbon gas mixture at the same pressure and temperature.

The component fugacity in each phase is introduced to develop a criterion for thermodynamic equilibrium. Physically, the fugacity of a component i in one phase with respect to the fugacity of the component in a second phase is a measure of the potential for transfer of the component between phases. The phase with a lower component fugacity accepts the component from the phase with a higher component fugacity. Equal fugacities of a component in the two phases result in a zero net transfer. A zero transfer for all components implies a hydrocarbon system that is in thermodynamic equilibrium. Therefore, the condition of the thermodynamic equilibrium can be expressed mathematically by

$$f_i^v = f_i^L \quad 1 \le i \le n \tag{7-44}$$

where f_i^v = fugacity of component i in the gas phase, psi
f_i^L = fugacity of component i in the liquid phase, psi
n = number of components in the system

The fugacity coefficient of component i in a hydrocarbon liquid mixture or hydrocarbon gas mixture is a function of

- System pressure.
- Mole fraction of the component.
- Fugacity of the component.

For a component i in the gas phase, the fugacity coefficient is defined as

$$\Phi_i^v = \frac{f_i^v}{y_i p} \tag{7-45}$$

For a component i in the liquid phase, the fugacity coefficient is

$$\Phi_i^L = \frac{f_i^L}{x_i p} \tag{7-46}$$

where Φ_i^v = fugacity coefficient of component i in the vapor phase
Φ_i^L = fugacity coefficient of component i in the liquid phase

It is clear that, at equilibrium $f_i^L = f_i^v$, the equilibrium ratio K_i as previously defined by Equation 1-1, i.e., $K_i = y_i/x_i$, can be redefined in terms of the fugacity of components as

$$K_i = \frac{\left[f_i^L/(x_i p)\right]}{\left[f_i^v/(y_i p)\right]} = \frac{\Phi_i^L}{\Phi_i^v} \tag{7-47}$$

Reid et al. (1977) [46] defined the fugacity coefficient of component i in a hydrocarbon mixture by the following generalized thermodynamic relationship:

$$\ln(\Phi_i) = \left(\frac{1}{RT}\right)\left[\int_v^\infty \left(\frac{\partial p}{\partial n_i} - \frac{RT}{V}\right) dV\right] - \ln(Z) \tag{7-48}$$

where V = total volume of n models of the mixture
n_i = number of moles of component i
Z = compressibility factor of the hydrocarbon mixture

By combining this thermodynamic definition of the fugacity with the SRK EOS (Equation 7-25), Soave proposed the following expression for the fugacity coefficient of component i in the liquid phase:

$$\ln(\Phi_i^L) = \frac{b_i(Z^L - 1)}{b_m} - \ln(Z^L - B) - \left(\frac{A}{B}\right)\left[\frac{2\Psi_i}{(a\alpha)_m} - \frac{b_i}{b_m}\right] \ln\left[1 + \frac{B}{Z^L}\right] \tag{7-49}$$

where

$$\Psi_i = \sum_j \left[x_j \sqrt{a_i a_j \alpha_i \alpha_j}(1 - k_{ij})\right] \tag{7-50}$$

$$(a\alpha)_m = \sum_i \sum_j \left[x_i x_j \sqrt{a_i a_j \alpha_i \alpha_j}\,(1 - k_{ij})\right] \tag{7-51}$$

Equation 7-49 is also used to determine the fugacity coefficient of component i in the gas phase Φ_i^v by using the composition of the gas phase y_i in calculating A, B, Z^v, and other composition-dependent terms, or

$$\ln\left(\Phi_i^v\right) = \frac{b_i(Z^v - 1)}{b_m} - \ln(Z^v - B) - \left(\frac{A}{B}\right)\left[\frac{2\Psi_i}{(a\alpha)_m} - \frac{b_i}{b_m}\right]\ln\left[1 + \frac{B}{Z^v}\right]$$

where

$$\Psi_i = \textstyle\sum_j \left[y_j \sqrt{a_i a_j \alpha_i \alpha_j}\,(1 - k_{ij})\right]$$

$$(a\alpha)_m = \textstyle\sum_i \sum_j \left[y_i y_j \sqrt{a_i a_j \alpha_i \alpha_j}\,(1 - k_{ij})\right]$$

7.4 MODIFICATIONS OF THE SRK EQUATION OF STATE

To improve the pure component vapor pressure predictions by the SRK equation of state, Grabowski and Daubert (1978) [17] proposed a new expression for calculating parameter m of Equation 7-27. The proposed relationship originated from analyses of extensive experimental data for pure hydrocarbons. The relationship has the following form:

$$m = 0.48508 + 1.55171\omega - 0.15613\omega^2 \tag{7-52}$$

Sim and Daubert (1980) [52] pointed out that, because the coefficients of Equation 7-52 were determined by analyzing vapor pressure data of low-molecular-weight hydrocarbons, it is unlikely that Equation 7-52 will suffice for high-molecular-weight petroleum fractions. Realizing that the acentric factors for the heavy petroleum fractions are calculated from an equation such as the Edmister correlation or the Lee and Kessler (1975) correlation, the authors proposed the following expressions for determining the parameter m:

- If the acentric factor is determined using the Edmister correlation, then

$$m = 0.431 + 1.57\omega_i - 0.161\omega_i^2 \tag{7-53}$$

- If the acentric factor is determined using the Lee and Kessler correction, then

$$m = 0.315 + 1.60\omega_i - 0.166\omega_i^2 \tag{7-54}$$

Elliot and Daubert (1985) [14] stated that the optimal binary interaction coefficient k_{ij} would minimize the error in the representation of all thermodynamic properties of a mixture. Properties of particular interest in phase equilibrium calculations include bubble-point pressure, dew-point pressure, and equilibrium ratios. The authors proposed a set of relationships for determining interaction coefficients for asymmetric mixtures[2] that contain methane, N_2, CO_2, and H_2S. Referring to the principal component as i and the other fraction as j, Elliot and Daubert proposed the following expressions:

- **For N_2 systems**.

$$k_{ij} = 0.107089 + 2.9776 k_{ij}^{\infty} \tag{7-55}$$

- **For CO_2 systems**.

$$k_{ij} = 0.08058 - 0.77215 k_{ij}^{\infty} - 1.8404 \left(k_{ij}^{\infty}\right)^2 \tag{7-56}$$

- **For H_2S systems**.

$$k_{ij} = 0.07654 + 0.017921 k_{ij}^{\infty} \tag{7-57}$$

- **For methane systems with compounds of 10 carbons or more**.

$$k_{ij} = 0.17985 - 2.6958 k_{ij}^{\infty} - 10.853 (k_{ij}^{\infty})^2 \tag{7-58}$$

where

$$k_{ij}^{\infty} = \frac{-(\varepsilon_i - \varepsilon_j)^2}{2\varepsilon_i \varepsilon_j} \tag{7-59}$$

and

$$\varepsilon_i = \frac{0.480453\sqrt{a_i}}{b_i} \tag{7-60}$$

The two parameters a_i and b_i in Equation 7-60 were previously defined by Equations 7-28 and 7-29.

The major drawback in the SRK EOS is that the critical compressibility factor takes on the unrealistic universal critical compressibility of 0.333 for all substances. Consequently, the molar volumes are typically overestimated and, hence, densities are underestimated.

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[2] An asymmetric mixture is defined as one in which two of the components are considerably different in their chemical behavior. Mixtures of methane with hydrocarbons of 10 or more carbon atoms can be considered asymmetric. Mixtures containing gases such as nitrogen or hydrogen are asymmetric.

Peneloux et al. (1982) [40] developed a procedure for improving the volumetric predictions of the SRK EOS by introducing a volume correction parameter c_i into the equation. This third parameter does not change the vapor-liquid equilibrium conditions determined by the unmodified SRK equation, i.e., the equilibrium ratio K_i, but it modifies the liquid and gas volumes. The proposed methodology, known as the *volume translation method*, uses the following expressions:

$$V^L_{corr} = V^L - \sum_i (x_i c_i) \tag{7-61}$$

$$V^v_{corr} = V^v - \sum_i (y_i c_i) \tag{7-62}$$

where V^L = uncorrected liquid molar volume, i.e., $V^L = Z^L RT/p$, ft^3/mol
V^v = uncorrected gas molar volume $V^v = Z^v RT/p$, ft^3/mol
V^L_{corr} = corrected liquid molar volume, ft^3/mol
V^v_{corr} = corrected gas molar volume, ft^3/mol
x_i = mole fraction of component i in the liquid phase
y_i = mole fraction of component i in the gas phase

The authors proposed six schemes for calculating the correction factor c_i for each component. For petroleum fluids and heavy hydrocarbons, Peneloux and coworkers suggested that the best correlating parameter for the correction factor c_i is the Rackett compressibility factor Z_{RA}. The correction factor is then defined mathematically by the following relationship:

$$c_i = 4.43797878(0.29441 - Z_{RA})T_{ci}/p_{ci} \tag{7-63}$$

where c_i = correction factor for component i, ft^3/lb-mol
T_{ci} = critical temperature of component i, °R
p_{ci} = critical pressure of component i, psia

The parameter Z_{RA} is a unique constant for each compound. The values of Z_{RA} are in general not much different from those of the critical compressibility factors Z_c. If their values are not available, Peneloux et al. (1982) [40] proposed the following correlation for calculating c_i:

$$c_i = (0.0115831168 + 0.411844152\omega)\left(\frac{T_{ci}}{p_{ci}}\right) \tag{7-64}$$

where ω_i = acentric factor of component i.

Example 7-7

Rework Example 7-6 by incorporating the Peneloux volume correction approach in the solution. Key information from Example 7-6 includes

- For gas: $Z^v = 0.9267$, $M_a = 20.89$.
- For liquid: $Z^L = 1.4121$, $M_a = 100.25$.
- $T = 160°F$, $p = 4000$ psi.

Solution

Step 1. Calculate the correction factor c_i using Equation 7-63:

Component	**c_i**	**x_i**	**c_ix_i**	**y_i**	**c_iy_i**
C_1	0.00839	0.45	0.003776	0.86	0.00722
C_2	0.03807	0.05	0.001903	0.05	0.00190
C_3	0.07729	0.05	0.003861	0.05	0.00386
C_4	0.1265	0.03	0.00379	0.02	0.00253
C_5	0.19897	0.01	0.001989	0.01	0.00198
C_6	0.2791	0.01	0.00279	0.005	0.00139
C_{7+}	0.91881	0.40	0.36752	0.005	0.00459
sum			0.38564		0.02349

Step 2. Calculate the uncorrected volume of the gas and liquid phase using the compressibility factors as calculated in Example 7-6:

$$V^v = \frac{(10.73)(620)(0.9267)}{4000} = 1.54119 \text{ ft}^3/\text{mol}$$

$$V^L = \frac{(10.73)(620)(1.4121)}{4000} = 2.3485 \text{ ft}^3/\text{mol}$$

Step 3. Calculate the corrected gas and liquid volumes by applying Equations 7-61 and 7-62:

$$V^L_{corr} = V^L - \sum_i (x_ic_i) = 2.3485 - 0.38564 = 1.962927 \text{ ft}^3/\text{mol}$$

$$V^v_{corr} = V^v - \sum_i (y_ic_i) = 1.54119 - 0.02349 = 1.5177 \text{ ft}^3/\text{mol}$$

Step 4. Calculate the corrected compressibility factors:

$$Z^v_{corr} = \frac{(4000)(1.5177)}{(10.73)(620)} = 0.91254$$

$$Z^L_{corr} = \frac{(4000)(1.962927)}{(10.73)(620)} = 1.18025$$

Step 5. Determine the corrected densities of both phases:

$$\rho = \frac{pM_a}{RTZ}$$

$$\rho^v = \frac{(4000)(20.89)}{(10.73)(620)(0.91254)} = 13.767\ \text{lb}/\text{ft}^3$$

$$\rho^L = \frac{(4000)(100.25)}{(10.73)(620)(1.18025)} = 51.07\ \text{lb}/\text{ft}^3$$

7.5 PENG-ROBINSON EQUATION OF STATE AND ITS MODIFICATIONS

Peng and Robinson (1976a) [41] conducted a comprehensive study to evaluate the use of the SRK equation of state for predicting the behavior of naturally occurring hydrocarbon systems. They illustrated the need for an improvement in the ability of the equation of state to predict liquid densities and other fluid properties, particularly in the vicinity of the critical region. As a basis for creating an improved model, Peng and Robinson proposed the following expression:

$$p = \frac{RT}{V-b} - \frac{a\alpha}{(V+b)^2 - cb^2}$$

where a, b, and α have the same significance as they have in the SRK model, and the parameter c is a whole number optimized by analyzing the values of the two terms Z_c and b/V_c as obtained from the equation. It is generally accepted that Z_c should be close to 0.28 and that b/V_c should be approximately 0.26. An optimized value of $c = 2$ gave $Z_c = 0.307$ and $(b/V_c) = 0.253$. Based on this value of c, Peng and Robinson proposed the following equation of state:

$$p = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b) + b(V-b)} \tag{7-65}$$

Imposing the classical critical point conditions (Equation 7-3) on Equation 7-65 and solving for parameters a and b yields

$$a = \Omega_a \frac{R^2T_c^2}{p_c} \tag{7-66}$$

$$b = \Omega_b \frac{RT_c}{p_c} \tag{7-67}$$

where $\Omega_a = 0.45724$ and $\Omega_b = 0.07780$. This equation predicts a universal critical gas compressibility factor Z_c of 0.307 compared to 0.333 for the

SRK model. Peng and Robinson also adopted Soave's approach for calculating the temperature-dependent parameter α:

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2 \tag{7-68}$$

where

$$m = 0.3796 + 1.54226\omega - 0.2699\omega^2$$

Peng and Robinson (1978) proposed the following modified expression for m that is recommended for heavier components with acentric values $\omega > 0.49$:

$$m = 0.379642 + 1.48503\omega - 0.1644\omega^2 + 0.016667\omega^3 \tag{7-69}$$

Rearranging Equation 7-65 into the compressibility factor form gives

$$Z^3 + (B - 1)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{7-70}$$

where A and B are given by Equations 7-36 and 7-37 for pure components and by Equations 7-40 and 7-41 for mixtures.

Example 7-8

Using the composition given in Example 7-6, calculate the density of the gas phase and liquid phase using the Peng-Robinson EOS. Assume $k_{ij} = 0$.

Solution

Step 1. Calculate the mixture parameters $(a\alpha)_m$ and b_m for the gas and liquid phase, to give

- **For the gas phase**.

$$(a\alpha)_m = \sum_i \sum_j \left[y_i y_j \sqrt{a_i a_j \alpha_i \alpha_j}\left(1 - k_{ij}\right)\right] = 10{,}423.54$$

$$b_m = \sum_i (y_i b_i) = 0.862528$$

- **For the liquid phase**.

$$(a\alpha)_m = \sum_i \sum_j \left[x_i x_j \sqrt{a_i a_j \alpha_i \alpha_j}\left(1 - k_{ij}\right)\right] = 107{,}325.4$$

$$b_m = \sum (y_i b_i) = 1.69543$$

Step 2. Calculate the coefficients A and B, to give

- **For the gas phase**.

$$A = \frac{(a\alpha)_m p}{R^2 T^2} = \frac{(10{,}423.54)(4000)}{(10.73)^2(620)^2} = 0.94209$$

$$B = \frac{b_m p}{RT} = \frac{(0.862528)(4000)}{(10.73)(620)} = 0.30669$$

- **For the liquid phase**.

$$A = \frac{(a\alpha)_m p}{R^2 T^2} = \frac{(107{,}325.4)(4000)}{(10.73)^2(620)^2} = 9.700183$$

$$B = \frac{b_m p}{RT} = \frac{(1.636543)(4000)}{(10.73)(620)} = 1.020078$$

Step 3. Solve Equation 7-70 for the compressibility factor of the gas phase and the liquid phase to give

$$Z^3 + (B - 1)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0$$

- **For the gas phase**. Substituting for $A = 0.94209$ and $B = 0.30669$ in the above equation gives

$$Z^v = 0.8625$$

- **For the liquid phase**. Substituting for $A = 9.700183$ and $B = 1.020078$ in the above equation gives

$$Z^L = 1.2645$$

Step 4. Calculate the density of both phases:

$$\rho^v = \frac{(4{,}000)(20.89)}{(10.73)(620)(0.8625)} = 14.566\ \text{lb/ft}^3$$

$$\rho^L = \frac{(4{,}000)(100.25)}{(10.73)(620)(1.2645)} = 47.67\ \text{lb/ft}^3$$

Applying the thermodynamic relationship, as given by Equation 7-43, to Equation 7-66 yields the following expression for the fugacity of a pure component:

$$\ln\left(\frac{f}{p}\right) = \ln(\Phi) = Z - 1 - \ln(Z - B) - \left[\frac{A}{2\sqrt{2}B}\right]\ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right] \tag{7-71}$$

The fugacity coefficient of component i in a hydrocarbon liquid mixture is calculated from the following expression:

$$\begin{aligned}\ln\left(\frac{f^L}{x_i p}\right) &= \ln\left(\Phi_i^L\right) = \frac{b_i(Z^L - 1)}{b_m} - \ln\left(Z^L - B\right) \\ &\quad - \left[\frac{A}{2\sqrt{2}B}\right]\left[\frac{2\Psi_i}{(a\alpha)_m} - \frac{b_i}{b_m}\right]\ln\left[\frac{Z^L + (1+\sqrt{2})B}{Z^L - (1-\sqrt{2})B}\right]\end{aligned} \tag{7-72}$$

where the mixture parameters b_m, B, A, Ψ_i, and $(a\alpha)_m$ are as defined previously.

Equation 7-72 is also used to determine the fugacity coefficient of any component in the gas phase by replacing the composition of the liquid phase x_i with the composition of the gas phase y_i in calculating the composition-dependent terms of the equation, or

$$\begin{aligned}\ln\left(\frac{f^v}{y_i p}\right) &= \ln\left(\Phi_i^v\right) = \frac{b_i(Z^v - 1)}{b_m} - \ln(Z^v - B) \\ &\quad - \left[\frac{A}{2\sqrt{2}B}\right]\left[\frac{2\Psi_i}{(a\alpha)_m} - \frac{b_i}{b_m}\right]\ln\left[\frac{Z^v + (1+\sqrt{2})B}{Z^v - (1-\sqrt{2})B}\right]\end{aligned}$$

The set of binary interaction coefficients k_{ij} in Table 7-1 is traditionally used when predicting the volumetric behavior of a hydrocarbon mixture with the Peng and Robinson (PR) equation of state.

To improve the predictive capability of the PR EOS when describing mixtures containing N_2, CO_2, and CH_4, Nikos et al. (1986) [37] proposed a generalized correlation for generating the binary interaction coefficient k_{ij}. The authors correlated these coefficients with system pressure, temperature, and the acentric factor. These generalized correlations were originated with all the binary experimental data available in the literature. The authors proposed the following generalized form for k_{ij}:

$$k_{ij} = \delta_2 T_{rj}^2 + \delta_1 T_{rj} + \delta_0 \tag{7-73}$$

where i refers to the principal components N_2, CO_2, or CH_4 and j refers to the other hydrocarbon components of the binary. The acentric factor-dependent coefficients δ_0, δ_1, and δ_2 are determined for each set of binaries by applying the following expressions:

TABLE 7-1 Binary Interaction Coefficients* k_{ij} for the peng and Robinson EOS

	CO_2	**N_2**	**H_2S**	**C_1**	**C_2**	**C_3**	**i-C_4**	**n-C_4**	**i-C_5**	**n-C_5**	**C_6**	**C_7**	**C_8**	**C_9**	**C_{10}**
CO_2	0	0	0.135	0.105	0.130	0.125	0.120	0.115	0.115	0.115	0.115	0.115	0.115	0.115	0.115
N_2		0	0.130	0.025	0.010	0.090	0.095	0.095	0.100	0.100	0.110	0.115	0.120	0.120	0.125
H_2S			0	0.070	0.085	0.080	0.075	0.075	0.070	0.070	0.070	0.060	0.060	0.060	0.055
C_1				0	0.005	0.010	0.035	0.025	0.050	0.030	0.030	0.035	0.040	0.040	0.045
C_2					0	0.005	0.005	0.010	0.020	0.020	0.020	0.020	0.020	0.020	0.020
C_3						0	0.000	0.000	0.015	0.015	0.010	0.005	0.005	0.005	0.005
i – C_4							0	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
n – C_4								0	0.005	0.005	0.005	0.005	0.005	0.005	0.005
i – C_5									0	0.000	0.000	0.000	0.000	0.000	0.000
n – C_5										0	0.000	0.000	0.000	0.000	0.000
C_6											0	0.000	0.000	0.000	0.000
C_7												0	0.000	0.000	0.000
C_8													0	0.000	0.000
C_9														0	0.000
C_{10}															0

*Notice that $k_{ij} = k_{ji}$.

- **For nitrogen-hydrocarbons.**

$$\delta_0 = 0.1751787 - 0.7043\log(\omega_j) - 0.862066\left[\log(\omega_i)\right]^2 \tag{7-74}$$

$$\delta_1 = -0.584474 + 1.328\log(\omega_j) + 2.035767\left[\log(\omega_i)\right]^2 \tag{7-75}$$

and

$$\delta_2 = 2.257079 + 7.869765\log(\omega_j) + 13.50466\left[\log(\omega_i)\right]^2 + 8.3864\left[\log(\omega)\right]^3 \tag{7-76}$$

They also suggested the following pressure correction:

$$k_{ij} = k_{ij}(1.04 - 4.2 \times 10^{-5}p) \tag{7-77}$$

where p is the pressure in pounds per square inch.

- **For methane-hydrocarbons.**

$$\delta_0 = -0.01664 - 0.37283\log(\omega_j) + 1.31757\left[\log(\omega_i)\right]^2 \tag{7-78}$$

$$\delta_1 = 0.48147 + 3.35342\log(\omega_j) - 1.0783\left[\log(\omega_i)\right]^2 \tag{7-79}$$

and

$$\delta_2 = -0.4114 - 3.5072\log(\omega_j) - 1.0783\left[\log(\omega_i)\right]^2 \tag{7-80}$$

- **For CO_2-hydrocarbons.**

$$\delta_0 = 0.4025636 + 0.1748927\log(\omega_j) \tag{7-81}$$

$$\delta_1 = -0.94812 - 0.6009864\log(\omega_j) \tag{7-82}$$

and

$$\delta_2 = 0.741843368 + 0.441775\log(\omega_j) \tag{7-83}$$

For the CO_2 interaction parameters, the following pressure correction is suggested:

$$k'_{ij} = k_{ij}(1.044269 - 4.375 \times 10^{-5}p) \tag{7-84}$$

Stryjek and Vera (1986) [59] proposed an improvement in the reproduction of vapor pressures of pure components by the PR EOS in the reduced temperature range from 0.7 to 1.0 by replacing the m term in Equation 7-72 with the following expression:

$$m_0 = 0.378893 + 1.4897153 - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{7-85}$$

To reproduce vapor pressures at reduced temperatures below 0.7, Stryjek and Vera further modified the m parameter in the PR equation by introducing an adjustable parameter m_1 characteristic of each compound to Equation 7-72. They proposed the following generalized relationship for the parameter m:

$$m = m_0 + \left[m_1\left(1+\sqrt{T_r}\right)(0.7 - T_r)\right] \tag{7-86}$$

where T_r = reduced temperature of the pure component

m_0 = defined by Equation 7-84

m_1 = adjustable parameter

For all components with a reduced temperature above 0.7, Stryjek and Vera recommended setting $m_1 = 0$. For components with a reduced temperature greater than 0.7, the optimum values of m_1 for compounds of industrial interest follow:

Parameter m_1 of Pure Compounds

Compound	m_1	Compound	m_1
Nitrogen	0.01996	Nonane	0.04104
Carbon dioxide	0.04285	Decane	0.04510
Water	−0.06635	Undecane	0.02919
Methane	−0.00159	Dodecane	0.05426
Ethane	0.02669	Tridecane	0.04157
Propane	0.03136	Tetradecane	0.02686
Butane	0.03443	Pentadecane	0.01892
Pentane	0.03946	Hexadecane	0.02665
Hexane	0.05104	Heptadecane	0.04048
Heptane	0.04648	Octadecane	0.08291
Octane	0.04464		

Due to the totally empirical nature of the parameter m_1, Stryjek and Vera could not find a generalized correlation for m_1 in terms of pure component parameters. They pointed out that the values of m_1 just given should be used without changes.

Jhaveri and Youngren (1984) [23] pointed out that, when applying the Peng-Robinson equation of state to reservoir fluids, the error associated with the equation in the prediction of gas-phase Z factors ranged from 3 to 5%, and the error in the liquid density predictions ranged from 6 to 12%. Following the procedure proposed by Peneloux and coworkers (see the SRK EOS), Jhaveri and Youngren introduced the volume correction parameter c_i to the PR EOS. This third parameter has the same units as the second parameter b_i of the unmodified PR equation and is defined by the following relationship:

$$c_i = S_i b_i \tag{7-87}$$

where S_i = dimensionless parameter, called the *shift parameter*

b_i = Peng-Robinson covolume as given by Equation 7-67

The volume correction parameter c_i does not change the vapor-liquid equilibrium conditions, i.e., equilibrium ratio K_i. The corrected hydrocarbon phase volumes are given by the following expressions:

$$V_{corr}^{L} = V^{L} - \sum_{i=1}(x_i\, c_i)$$

$$V_{corr}^{v} = V^{v} - \sum_{i=1}(y_i\, c_i)$$

where V^L, V^v = volumes of the liquid phase and gas phase as calculated by the unmodified PR EOS, ft^3/mol

$V^L{}_{corr}$, $V^v{}_{corr}$ = corrected volumes of the liquid and gas phase

Whitson and Brule (2000) [64] point out that the volume translation (correction) concept can be applied to any two-constant cubic equation, thereby eliminating the volumetric deficiency associated with application of EOS. Whitson and Brule extended the work of Jhaveri and Youngren (1984) and proposed the following shift parameters for selected pure components:

Shift Parameters for the PR EOS and SRK EOS

Compound	PR EOS	SRK EOS
N_2	−0.1927	−0.0079
CO_2	−0.0817	0.0833
H_2S	−0.1288	0.0466
C_1	−0.1595	0.0234
C_2	−0.1134	0.0605
C_3	−0.0863	0.0825
$i-C_4$	−0.0844	0.0830
$n-C_4$	−0.0675	0.0975
$i-C_5$	−0.0608	0.1022
$n-C_5$	−0.0390	0.1209
$n-C_6$	−0.0080	0.1467
$n-C_7$	0.0033	0.1554
$n-C_8$	0.0314	0.1794
$n-C_9$	0.0408	0.1868
$n-C_{10}$	0.0655	0.2080

Jhaveri and Youngren (1984) proposed the following expression for calculating the shift parameter for the C_{7+}:

$$S = 1 - \frac{d}{(M)^e}$$

where M = molecular weight of the heptanes-plus fraction

d, e = positive correlation coefficients

The authors proposed that, in the absence of the experimental information needed for calculating e and d, the power coefficient e can be set equal to 0.2051 and the coefficient d adjusted to match the C_{7+} density, with the values of d ranging from 2.2 to 3.2. In general, the following values may be used for C_{7+} fractions:

Hydrocarbon Family	**d**	**e**
Paraffins	2.258	0.1823
Naphthenes	3.044	0.2324
Aromatics	2.516	0.2008

To use the Peng-Robinson equation of state to predict the phase and volumetric behavior of mixtures, one must be able to provide the critical pressure, the critical temperature, and the acentric factor for each component in the mixture. For pure compounds, the required properties are well defined and known. Nearly all naturally occurring petroleum fluids contain a quantity of heavy fractions that are not well defined. These heavy fractions are often lumped together as the heptanes-plus fraction. The problem of how to adequately characterize the C_{7+} fractions in terms of their critical properties and acentric factors has been long recognized in the petroleum industry. Changing the characterization of C_{7+} fractions present in even small amounts can have a profound effect on the PVT properties and the phase equilibria of a hydrocarbon system as predicted by the Peng-Robinson equation of state.

The usual approach for such situations is to "tune" the parameters in the EOS in an attempt to improve the accuracy of prediction. During the tuning process, the critical properties of the heptanes-plus fraction and the binary interaction coefficients are adjusted to obtain a reasonable match with experimental data available on the hydrocarbon mixture.

Recognizing that the inadequacy of the predictive capability of the PR EOS lies with the improper procedure for calculating the parameters a, b, and α of the equation for the C_{7+} fraction, Ahmed (1991) [1] devised an approach for determining these parameters from the following two readily measured physical properties of C_{7+}: molecular weight, M_{7+}, and specific gravity, γ_{7+}.

The approach is based on generating 49 density values for the C_{7+} by applying the Riazi-Daubert correlation. These values were subsequently subjected to 10 temperature and 10 pressure values in the range of 60 to 300°F and 14.7 to 7000 psia, respectively. The Peng-Robinson EOS was then applied to match the 4900 generated density values by optimizing the parameters a, b, and α using a nonlinear regression model. The optimized parameters for the heptanes-plus fraction are given by the following expressions:

For the parameter a of C_{7+},

$$\alpha = \left[1 + m\left(1 - \sqrt{\frac{520}{T}}\right)\right]^2 \tag{7-88}$$

with m defined by

$$m = \frac{D}{A_0 + A_1 D} + A_2 M_{7+} + A_3 M_{7+}^2 + \frac{A_4}{M_{7+}} + A_5 \gamma_{7+} + A_6 \gamma_{7+}^2 + \frac{A_7}{\gamma_{7+}} \tag{7-89}$$

with the parameter D defined by the ratio of the molecular weight to the specific gravity of the heptanes-plus fraction, or

$$D = \frac{M_{7+}}{\gamma_{7+}}$$

where M_{7+} = molecular weight of C_{7+}
γ_{7+} = specific gravity of C_{7+}
$A_0 - A_7$ = coefficients as given in Table 7-2

For the parameters a and b of C_{7+}, the following generalized correlation is proposed:

$$a \text{ or } b = \left[\sum_{i=0}^{3}\left(A_i D^i\right)\right] + \frac{A_4}{D}\left[\sum_{i=5}^{6}\left(A_i \gamma_{7+}^{i-4}\right)\right] + \frac{A_7}{\gamma_{7+}} \tag{7-90}$$

The coefficients A_0 through A_7 are included in Table 7-2.

To further improve the predictive capability of the Peng-Robinson EOS, the author optimized coefficients a, b, and m for nitrogen, CO_2, and methane by matching 100 Z-factor values for each of these components. Using a nonlinear regression model, the optimized values given in Table 7.2 are recommended.

To provide the modified PR EOS with a consistent procedure for determining the binary interaction coefficient k_{ij}, the following computational steps are proposed.

Step 1. Calculate the binary interaction coefficient between methane and the heptanes-plus fraction from

$$k_{c_1-c_{7+}} = 0.00189T - 1.167059$$

where the temperature T is in °R.

TABLE 7-2 Coefficients for Equations 7-89 and 7-90

Coefficient	a	b	m
A_0	-2.433525×10^{7}	-6.8453198	-36.91776
A_1	8.3201587×10^{3}	1.730243×10^{-2}	$-5.2393763 \times 10^{-2}$
A_2	$-0.18444102 \times 10^{2}$	$-6.2055064 \times 10^{-6}$	1.7316235×10^{-2}
A_3	3.6003101×10^{-2}	9.0910383×10^{-9}	$-1.3743308 \times 10^{-5}$
A_4	3.4992796×10^{7}	13.378898	12.718844
A_5	2.838756×10^{7}	7.9492922	10.246122
A_6	-1.1325365×10^{7}	-3.1779077	-7.6697942
A_7	6.418828×10^{6}	1.7190311	-2.6078099

Component	a	b	m in Eq. 7-88
CO_2	1.499914×10^{4}	0.41503575	-0.73605717
N_2	4.5693589×10^{3}	0.4682582	-0.97962859
C_1	7.709708×10^{3}	0.46749727	-0.549765

Step 2. Set

$$\begin{aligned} k_{CO_2-N_2} &= 0.12 \\ k_{CO_2-\text{hydrocarbon}} &= 0.10 \\ k_{N_2-\text{hydrocarbon}} &= 0.10 \end{aligned}$$

Step 3. Adopting the procedure recommended by Petersen (1989), calculate the binary interaction coefficients between components heavier than methane (e.g., C_2, C_3) and the heptanes-plus fraction from

$$k_{C_n-C_{7+}} = 0.8 k_{C_{(n-1)}-C_{7+}}$$

where n is the number of carbon atoms of component C_n; e.g., the binary interaction coefficient between C_2 and C_{7+} is

$$k_{C_2-C_{7+}} = 0.8 k_{C_1-C_{7+}}$$

and the binary interaction coefficient between C_3 and C_{7+} is

$$k_{C_3-C_{7+}} = 0.8 k_{C_2-C_{7+}}$$

Step 4. Determine the remaining k_{ij} from

$$k_{ij} = k_{i-C_{7+}} \left[\frac{(M_j)^5 - (M_i)^5}{(M_{C_{7+}})^5 - (M_i)^5} \right]$$

where M is the molecular weight of any specified component. For example, the binary interaction coefficient between propane C_3 and butane C_4 is

$$k_{C_3-C_4} = k_{C_3-C_{7+}} \left[\frac{(M_{C_4})^5 - (M_{C_3})^5}{(M_{C_{7+}})^5 - (M_{C_3})^5} \right]$$