

PVT Relations and Equations of State

NOMENCLATURE

API	API Gravity defined in Eq. (2.4)	T_c	Critical temperature, K
A, B, C, \dots	Coefficients in various equations	T_{crit}	Cricondentherm temperature, K
a_c	Parameter defined in Eq. (5.41) and given in Table 5.1	T_r	Reduced temperature defined by Eq. (5.100) ($= T/T_c$), dimensionless
a, b, c, \dots	Constants in various equations	V	Molar volume, cm^3/gmol
B	Second virial coefficient	V^L	Saturated liquid molar volume, cm^3/gmol
C	Third virial coefficient	V^{sat}	Saturation molar volume, cm^3/gmol
c	Volume translation for use in Eq. (5.50), cm^3/mol	V^V	Saturated vapor molar volume, cm^3/gmol
d_{20}	Liquid density of liquid at 20°C and 1 atm, g/cm^3	V_c	Critical volume (molar), cm^3/mol (or critical specific volume, cm^3/g)
d_c	Critical density defined by Eq. (2.9), g/cm^3	V_r	Reduced volume ($= V/V_c$)
e	Correlation parameter, exponential function	x_i	Mole fraction of i in a mixture (usually used for liquids)
exp	Exponential function	y_i	Mole fraction of i in a mixture (usually used for gases)
F	Degrees of freedom in Eq. (5.4)	Z	Compressibility factor defined by Eq. (5.15)
f_ω	A function defined in terms of ω for parameter a in PR and SRK equations as given in Table 5.1 and Eq. (5.53)	Z_c	Critical compressibility factor defined by Eq. (2.8), dimensionless
h	Parameter defined in Eq. (5.99), dimensionless	Z_{RA}	Rackett parameter, dimensionless
k_B	Boltzman constant ($= R/N_A = 1.2 \times 10^{-20}$ J/K)	z_j	Mole fraction of i in a mixture
k_{ij}	Binary interaction parameter (BIP), dimensionless	$Z_1, Z_2, \text{ and } Z_3$	Roots of a cubic equation of state
I	Refractive index parameter defined in Eq. (2.36)		
M	Molecular weight, g/mol [kg/kmol]		
m	Mass of system, g		
N_A	Avogadro number = number of molecules in one mole ($6.022 \times 10^{23} \text{ mol}^{-1}$)		
N	Number of components in a mixture		
n	Number of moles		
n_{20}	Sodium D line refractive index of liquid at 20°C and 1 atm, dimensionless		
P	Pressure, bar		
P^{sat}	Saturation pressure, bar		
P_c	Critical pressure, bar		
P_r	Reduced pressure defined by Eq. (5.100) ($= P/P_c$), dimensionless		
R	Gas constant = $8.314 \text{ J}/\text{mol} \cdot \text{K}$ (values are given in Section 1.7.24)		
R_m	Molar refraction defined by Eq. (5.133), cm^3/mol		
r	Reduced molar refraction defined by Eq. (5.129), dimensionless		
r	Intermolecular distance in Eqs. (5.10)–(5.12), \AA (10^{-10} m)		
r	A parameter specific for each substance in Eq. (5.98), dimensionless		
u_1, u_2	Parameters in Eqs. (5.40) and (5.42)		
SG	Specific gravity of liquid substance at 15.5°C (60°F) defined by Eq. (2.2), dimensionless		
T	Absolute temperature, K		

Greek Letters

α	Parameter defined by Eq. (5.41), dimensionless
α	Polarizability factor defined by Eq. (5.134), cm^3
α, γ	Parameters in BWR EOS defined by Eq. (5.89)
β	A correction factor for b parameter in an EOS defined by Eq. (5.55), dimensionless
Δ	Difference between two values of a parameter
δ_{ij}	Parameter defined in Eq. (5.70), dimensionless
ε	Energy parameter in a potential energy function
Γ	Potential energy function defined by Eq. (5.10)
ϕ_i	Volume fraction of i in a liquid mixture defined by Eq. (5.125)
Π	Number of phases defined in Eq. (5.4)
μ	Dipole moment in Eq. (5.134)
θ	A property in Eq. (5.1), such as volume, enthalpy, etc.
θ	Degrees in Eq. (5.47)
ρ	Density at a given temperature and pressure, g/cm^3 (molar density unit: cm^3/mol)

ρ^o	Value of density at low pressure (atmospheric pressure), g/cm ³
σ	Size parameter in a potential energy function, Å (10 ⁻¹⁰ m)
ω	Acentric factor defined by Eq. (2.10)
ξ	Packing fraction defined by Eq. (5.91), dimensionless

Superscript

bp	Value of a property for a defined mixture at its bubble point
c	Value of a property at the critical point
cal	Calculated value
exp	Experimental value
g	Value of a property for gas phase
HS	Value of a property for hard sphere molecules
ig	Value of a property for an ideal gas
L	Saturated liquid
l	Value of a property for liquid phase
V	Saturated vapor
sat	Value of a property at saturation pressure
(0)	A dimensionless term in a generalized correlation for a property of simple fluids
(1)	A dimensionless term in a generalized correlation for a property of acentric fluids

Subscripts

c	Value of a property at the critical point
<i>i</i>	A component in a mixture
<i>j</i>	A component in a mixture
<i>i, j</i>	Effect of binary interaction on a property
m	Value of a property for a mixture
<i>P</i>	Value of a property at pressure <i>P</i>
p	Pseudoproperty for a mixture
P, N, A	Value of parameter <i>c</i> in Eq. (5.52) for paraffins, naphthenes, and aromatics
t	Value of a property for the whole (total) system

Acronyms

API-TDB	American Petroleum Institute—Technical Data Book
BIP	Binary interaction parameter
BWRS	Starling modification of Benedict–Webb–Rubin EOS (see Eq. 5.89)
COSTALD	corresponding state liquid density (given by Eq. 5.130)
CS	Carnahan–Starling EOS (see Eq. 5.93)
EOS	Equations of state
GC	Generalized correlation
HC	Hydrocarbon
HS	Hard sphere
HSP	Hard sphere potential given by Eq. (5.13)
KISR	Kuwait Institute for Scientific Research
IAPWS	International Association for the Properties of Water and Steam
LJ	Lennard–Jones potential given by Eq. (5.11)
LJ EOS	Lennard–Jones EOS given by Eq. (5.96)

LK GC	Lee–Kesler generalized correlation for <i>Z</i> (Eqs. 5.107–5.113)
LK EOS	Lee–Kesler EOS given by Eq. (5.109)
MRK	Modified Redlich–Kwong EOS given by Eqs. (5.38) and (5.137)–(5.140)
NIST	National Institute of Standards and Technology
OGJ	Oil and Gas Journal
PHCT	Perturbed Hard Chain Theory (see Eq. 5.97)
PR	Peng–Robinson EOS (see Eq. 5.39)
RHS	Right-hand side of an equation
RK	Redlich–Kwong EOS (see Eq. 5.38)
RS	<i>R</i> squared (<i>R</i> ²), defined in Eq. (2.136)
SRK	Soave–Redlich–Kwong EOS given by Eq. (5.38) and parameters in Table 5.1
SAFT	Statistical associating fluid theory (see Eq. 5.98)
SW	Square–Well potential given by Eq. (5.12).
vdW	van der Waals (see Eq. 5.21)
VLE	Vapor–liquid equilibrium
%AAD	Average absolute deviation percentage defined by Eq. (2.135)
%AD	Absolute deviation percentage defined by Eq. (2.134)
%MAD	Maximum absolute deviation percentage

AS DISCUSSED IN CHAPTER 1, the main application of characterization methods presented in Chapters 2–4 is to provide basic data for estimation of various thermophysical properties of petroleum fractions and crude oils. These properties are calculated through thermodynamic relations. Although some of these correlations are empirically developed, most of them are based on sound thermodynamic and physical principles. The most important thermodynamic relation is pressure–volume–temperature (PVT) relation. Mathematical PVT relations are known as *equations of state*. Once the PVT relation for a fluid is known various physical and thermodynamic properties can be obtained through appropriate relations that will be discussed in Chapter 6. In this chapter we review principles and theory of property estimation methods and equations of states that are needed to calculate various thermophysical properties.

5.1 BASIC DEFINITIONS AND THE PHASE RULE

The state of a system is fixed when it is in a thermodynamic or phase equilibrium. A system is in equilibrium when it has no tendency to change. For example, pure liquid water at 1 atm and 20°C is at stable equilibrium condition and its state is perfectly known and fixed. For a mixture of vapor and liquid water at 1 atm and 20°C the system is not stable and has a tendency to reach an equilibrium state at another temperature or pressure. For a system with two phases at equilibrium only temperature or pressure (but not both) is sufficient to determine its state. The state of a system can be determined by its properties. A property that is independent of size or mass of the system is called *intensive* property. For example, temperature, pressure, density, or molar volume are intensive properties, while total volume of a system is an extensive

property. All molar properties are intensive properties and are related to total property as

$$(5.1) \quad \theta = \frac{\theta^t}{n}$$

where n is the number of moles, θ^t is a total property such as volume, V^t , and θ is a molar property such as molar volume, V . The number of moles is related to the mass of the system, m , through molecular weight by Eq. (1.6) as

$$(5.2) \quad n = \frac{m}{M}$$

If total property is divided by mass of the system (m), instead of n , then θ is called *specific* property. Both molar and specific properties are intensive properties and they are related to each other through molecular weight.

$$(5.3) \quad \text{Molar Property} = \text{Specific Property} \times M$$

Generally thermodynamic relations are developed among molar properties or intensive properties. However, once a molar property is calculated, the total property can be calculated from Eq. (5.1).

The phase rule gives the minimum number of independent variables that must be specified in order to determine thermodynamic state of a system and various thermodynamic properties. This number is called *degrees of freedom* and is shown by F . The phase rule was stated and formulated by the American physicist J. Willard Gibbs in 1875 in the following form [1]:

$$(5.4) \quad F = 2 + N - \Pi$$

where Π is the number of phases and N is the number of components in the system. For example for a pure component ($N = 1$) and a single phase ($\Pi = 1$) system the degrees of freedom is calculated as 2. This means when two intensive properties are fixed, the state of the systems is fixed and its properties can be determined from the two known parameters. Equation (5.4) is valid for nonreactive systems. If there are some reactions among the components of the systems, degrees of freedom is reduced by the number of reactions within the system. If we consider a pure gas such as methane, at least two intensive properties are needed to determine its thermodynamic properties. The most easily measurable properties are temperature (T) and pressure (P). Now consider a mixture of two gases such as methane and ethane with mole fractions x_1 and x_2 ($x_2 = 1 - x_1$). According to the phase rule three properties must be known to fix the state of the system. In addition to T and P , the third variable could be mole fraction of one of the components (x_1 or x_2). Similarly, for a mixture with single phase and N components the number of properties that must be known is $N + 1$ (i.e., $T, P, x_1, x_2, \dots, x_{N-1}$). When the number of phases is increased the degrees of freedom is decreased. For example, for a mixture of certain amount of ice and liquid water ($\Pi = 2, N = 1$) from Eq. (5.4) we have $F = 1$. This means when only a single variable such as temperature is known the state of the system is fixed and its properties can be determined. Minimum value of F is zero. A system of pure component with three phases in equilibrium with each other, such as liquid water, solid ice, and vapor, has zero degrees of freedom. This means the temperature and pressure of the system are fixed and only under unique conditions of

T and P three phases of a pure component can coexist all the time. This temperature and pressure are known as *triple point temperature* and *triple point pressure* and are characteristics of any pure compound and their values are given for many compounds [2, 3]. For example, for water the triple point temperature and pressure are 0.01°C and 0.6117 kPa ($\sim 0.006\text{ bar}$), respectively [3]. The most recent tabulation and formulation of properties of water recommended by International Association for the Properties of Water and Steam (IAPWS) are given by Wagner and Pruss [4].

A thermodynamic property that is defined to formulate the first law of thermodynamics is called *internal energy* shown by U and has the unit of energy per mass or energy per mole (i.e., J/mol). Internal energy represents both kinetic and potential energies that are associated with the molecules and for any pure substance it depends on two properties such as T and V . When T increases the kinetic energy increases and when V increases the potential energy of molecules also increases and as a result U increases. Another useful thermodynamic property that includes PV energy in addition to the internal energy is *enthalpy* and is defined as

$$(5.5) \quad H = U + PV$$

where H is the molar enthalpy and has the same unit as U . Further definition of thermodynamic properties and basic relations are presented in Chapter 6.

5.2 PVT RELATIONS

For a pure component system after temperature and pressure, a property that can be easily determined is the volume or molar volume. According to the phase rule for single phase and pure component systems V can be determined from T and P :

$$(5.6) \quad V = f_1(T, P)$$

where V is the molar volume and f_1 represents functional relation between V, T , and P for a given system. This equation can be rearranged to find P as

$$(5.7) \quad P = f_2(T, V)$$

where the forms of functions f_1 and f_2 in the above two relations are different. Equation (5.6) for a mixture of N components with known composition is written as

$$(5.8) \quad P = f_3(T, V, x_1, x_2, \dots, x_{N-1})$$

where x_i is the mole fraction of component i . Any mathematical relation between P, V , and T is called an *equation of state* (EOS). As will be seen in the next chapter, once the PVT relation is known for a system all thermodynamic properties can be calculated. This indicates the importance of such relations. In general the PVT relations or any other thermodynamic relation may be expressed in three forms of (1) mathematical equations, (2) graphs, and (3) tables. The graphical approach is tedious and requires sufficient data on each substance to construct the graph. Mathematical or analytical forms are the most important and convenient relations as they can be

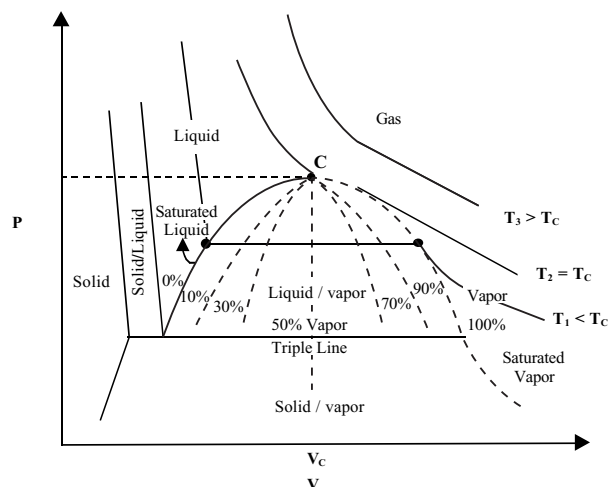


FIG. 5.1—Typical PV diagram for a pure substance.

used in computer programs for accurate estimation of various properties. Graphical and tabulated relations require interpolation with hand calculations, while graphical relations were quite popular in the 1950s and 1960s. With the growth of computers in recent decades mathematical equations are now the most popular relations.

A typical PVT relation in the form of PV and PT diagrams for a pure substance is shown in Figs. 5.1 and 5.2a, respectively. The solid, liquid, and vapor phases are clearly specified in the PT diagram. The two-phase region of vapor and liquid is best shown in the PV diagram. In Fig. 5.1, three isotherms of $T_1 < T_2 < T_3$ are shown where isotherm T_2 passes through the critical point, that is $T_c = T_2$. In the PV diagram lines of saturated liquid (solid line) and saturated vapor (dotted line) meet each other at the *critical point*. At this point properties of vapor phase and liquid phase become identical and two phases are indistinguishable. Since the critical isotherm exhibits a horizontal inflection at the critical point we may impose the following mathematical conditions at this point:

$$(5.9) \quad \left(\frac{\partial P}{\partial V} \right) \bigg|_{T_c, P_c} = \left(\frac{\partial^2 P}{\partial V^2} \right) \bigg|_{T_c, P_c} = 0$$

The first and second partial derivatives of P with respect to V (at constant T) may be applied to any EOS in the form of Eq. (5.7) and at the critical point they should be equal to zero. Simultaneous solution of resulting two equations will give relations for calculation of EOS parameters in terms of critical constants as will be seen later in Section 5.5.1.

The two-phase region in the PV diagram of Fig. 5.1 is under the envelope. As is seen from this figure the slope of an isotherm in the liquid region is much greater than its slope in the vapor phase. This is due to the greater change of volume of a gas with pressure in comparison with liquids that show less dependency of volume change with pressure under constant temperature condition. The dotted lines inside the envelope indicate percentage of vapor in a mixture of liquid and vapor, which is called *quality* of vapor. On the saturated vapor curve (right side) this percentage is 100% and on the saturated liquid curve (left side) this percentage is zero. Vapor region is part of a greater region called *gas phase*. Vapor is usually referred to a gas that can be liquefied under pressure. A vapor at a temperature above T_c cannot be liquefied no matter how

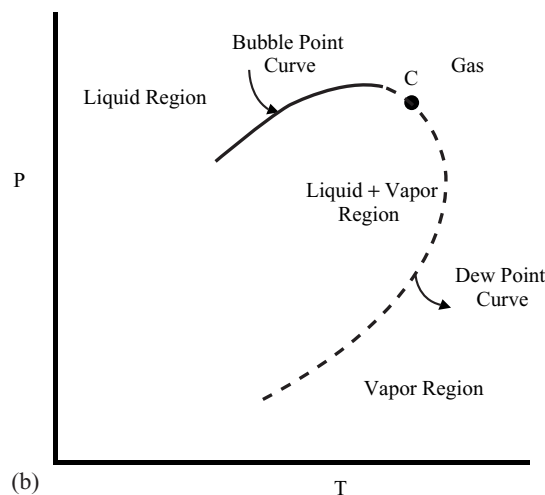
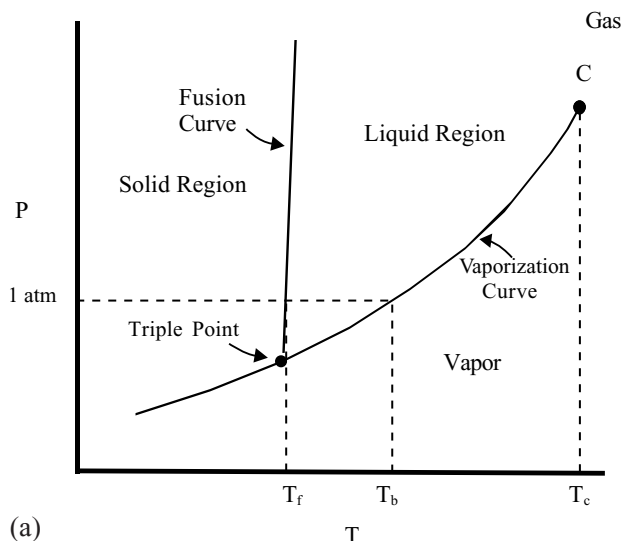


FIG. 5.2—Typical PT diagrams for a pure substances (a) and mixtures (b).

high the pressure is and it is usually referred as a gas. When T and P of a substance are greater than its T_c and P_c the substance is neither liquid nor vapor and it is called *supercritical fluid* or simply *fluid*. However, the word fluid is generally used for either a liquid or a vapor because of many similarities that exist between these two phases to distinguish them from solids.

As is seen in Fig. 5.1, lines of saturated liquid and vapor are identical in the PT diagram. This line is also called *vapor pressure* (or *vaporization*) curve where it begins from the triple point and ends at the critical point. The saturation line between solid and liquid phase is called *fusion* curve while between solid and vapor is called *sublimation* curve. In Fig. 5.2 typical PT diagrams for pure substances (a) and mixtures (b) are shown.

In Fig. 5.2a the freezing point temperature is almost the same as triple point temperature but they have different corresponding pressures. The normal boiling point and critical point both are on the vaporization line. A comparison between PV and PT diagrams for pure substances (Figs. 5.1 and 5.2a) shows that the two-phase region, which is an area in the PV diagram, becomes a line in the PT diagram. Similarly

triple point, which is a point on the PT diagram, becomes a line on the PV diagram. For a mixture, as shown in Fig. 5.2b, the two-phase region is under the envelope and bubble point and dew points curves meet each other at the critical point. The main application of PT diagram is to determine the phase of a system under certain conditions of temperature and pressure as will be discussed in Chapter 9 (Section 9.2.3). Figure 5.1 shows that as temperature of a pure substance increases, at constant pressure, the following phase changes occur:

Subcooled solid (1) → Saturated solid at sublimation temperature (2) → Saturated liquid at sublimation temperature (3) → Subcooled liquid (4) → Saturated liquid at vaporization temperature (5) → Saturated vapor at vaporization temperature (6) → Superheated vapor (7)

The process from (2) to (3) is called fusion or melting and the heat required is called *heat of fusion*. The process from (5) to (6) is called vaporization or boiling and the heat required is called *heat of vaporization*. Fusion and vaporization are two-phase change processes at which both temperature and pressure remain constant while volume, internal energy, and enthalpy would increase. A gas whose temperature is greater than T_c cannot be liquefied no matter how high the pressure is. The term *vapor* usually refers to a gas whose temperature is less than T_c and it can be converted to liquid as pressure exceeds the vapor pressure or saturation pressure at temperature T .

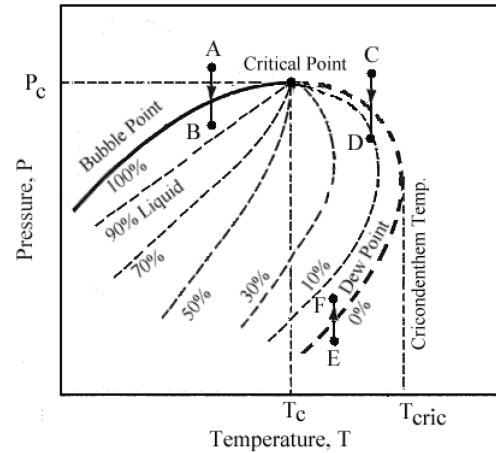


FIG. 5.3—Typical PT diagram for a reservoir fluid mixture.

An extended version of Fig. 5.2b is shown in Fig. 5.3 for a typical PT diagram of a reservoir fluid mixture. Lines of constant quality in the two-phase region converge at the critical point. The saturated vapor line is called *dewpoint* curve (dotted line) and the line of saturated liquid is usually called *bubblepoint* curve (solid line) as indicated in Figs. 5.2b and 5.3. In Fig. 5.3 when pressure of liquid is reduced at constant temperature (A to B), vaporization begins at the bubble point pressure. The bubblepoint curve is locus of all these bubble points. Similarly for temperatures above T_c when gas



FIG. 5.4—A DB Robinson computerized PVT cell (courtesy of KISR) [5].

pressure is reduced (C to D) or increased (E to F) at constant T , the first drop of liquid appears at the dew point pressure. The dewpoint curve is locus of all these dewpoints (dotted). The dotted lines under the envelope in this figure indicate constant percent vapor in a mixture of liquid and vapor. The 100% vapor line corresponds to saturated vapor (dewpoint) curve. The PT diagram for reservoir fluids has a temperature called *cricondetherm* temperature (T_{cric}) as shown in Fig. 5.3. When temperature of a mixture is greater than T_{cric} a gas cannot be liquefied when pressurized at constant temperature. However, as is seen in Fig. 5.3, at $T_c < T < T_{\text{cric}}$ a gas can be converted to liquid by either increase or decrease in pressure at constant temperature depending on its pressure. This phenomenon is called *retrograde condensation*. Every mixture has a unique *PT* or *PV* diagram and varies in shape from one mixture to another. Such diagrams can be developed from phase equilibrium calculations that require composition of the mixture and is discussed in Chapter 9.

Accurate measurement of fluid phase behavior and related physical properties can be obtained from a PVT apparatus. The central part of this equipment is a transparent cylindrical cell of about 2.0–2.5 cm diameter and 20 cm length sealed by a piston that can be moved to adjust desired volume. A typical modern and mercury-free PVT system made by D B Robinson, courtesy of KISR [5], is shown in Fig. 5.4. Variation of P and V can be determined at various isotherms for different systems of pure compounds and fluid mixtures. The PVT cell is particularly useful in the study of phase behavior of reservoir fluids and construction of *PT* diagrams as will be discussed in Chapter 9.

5.3 INTERMOLECULAR FORCES

As discussed in Section 2.3.1, properties of a substance depend on the intermolecular forces that exist between its molecules. The type of PVT relation for a specific fluid also depends on the intermolecular forces. These forces are defined in terms of potential energy function (Γ) through Eq. (2.19). Potential energy at the intermolecular distance of r is defined as the work required to separate two molecules from distance r to distance ∞ where the intermolecular force is zero and mathematically Γ is defined in the following forms:

$$\begin{aligned} d\Gamma &= -F dr \\ \Gamma(r) &= \int_r^{\infty} F(r) dr \end{aligned} \quad (5.10)$$

where the first equation is the same as Eq. (2.19) and the second one is derived from integration of the first equation considering the fact that $\Gamma(\infty) = 0$. Γ is composed of repulsive and attractive terms where the latter is negative. For ideal gases where the distance between the molecules is large, it is assumed that $\Gamma = 0$ as shown in Fig. 5.5 [6]. For nonpolar compounds such as hydrocarbon systems for which the dominant force is London dispersion force, the potential energy may be expressed by Lennard-Jones (LJ) model given by Eq. (2.21) as

$$\Gamma = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (5.11)$$

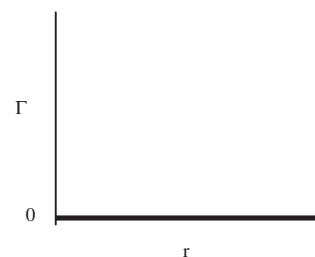


FIG. 5.5—Potential energy for ideal gases.

where ϵ and σ are energy and size parameters, which are characteristics of each substance. The significance of this function is that (a) at $r = \sigma$, $\Gamma = 0$ (i.e., at $r = \sigma$ repulsion and attraction forces are just balanced) and (b) $F = -d\Gamma/dr = 0$ at $\Gamma = -\epsilon$. In fact $\Gamma = -\epsilon$ is the minimum potential energy, which defines equilibrium separation where force of attraction is zero. The potential model is illustrated in Fig. 5.6.

Since the LJ potential is not mathematically convenient to use, the following potential model called *Square-Well potential* (SWP) is proposed to represent the LJ model for nonpolar systems:

$$\Gamma(r) = \begin{cases} \infty & r \leq \sigma \\ -\epsilon & \sigma \leq r \leq r^*\sigma \\ 0 & r \geq r^*\sigma \end{cases} \quad (5.12)$$

where in the region $1 < r/\sigma < r^*$ we have Square-Well (SW). This model is also shown in Fig. 5.6. The SW model has three parameters (σ , ϵ , r^*), which should be known for each substance from molecular properties. As will be seen later in this chapter, this model conveniently can be used to estimate the second virial coefficients for hydrocarbon systems.

Another potential model that has been useful in development of EOS is *hard-sphere potential* (HSP). This model assumes that there is no interaction until the molecules collide. At the time of collision there is an infinite interaction. In this model attractive forces are neglected and molecules are like rigid billiard balls. If the molecular diameter is σ , at the time of collision, the distance between centers of two molecules is $r = \sigma$ and it is shown in Fig. 5.7. As shown in this figure, the HSP can be expressed in the following form:

$$\Gamma = \begin{cases} \infty & \text{at } r \leq \sigma \\ 0 & \text{at } r > \sigma \end{cases} \quad (5.13)$$

It is assumed that as $T \rightarrow \infty$ all gases behave like hard sphere molecules. Application of this model will be discussed in Chapter 6 for the development of EOS based on velocity of sound. In all models according to definition of potential

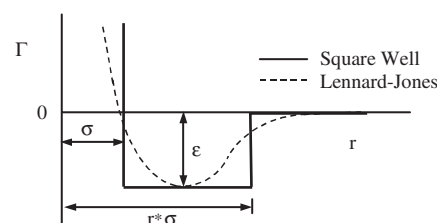


FIG. 5.6—Lennard-Jones and Square-Well potential models.

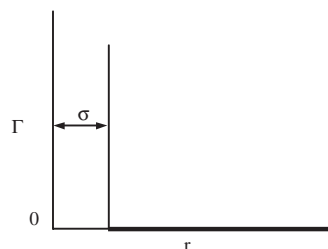


FIG. 5.7—Hard sphere potential model.

energy we have, as $r \rightarrow \infty$, $\Gamma \rightarrow 0$. For example, in the Sutherland model it is assumed that the repulsion force is ∞ but the attraction force is proportional with $1/r^n$, that is for $r > \sigma$, $\Gamma = -D/r^n$, where D is the model parameter [6]. Potential energy models presented in this section do not describe molecular forces for heavy hydrocarbons and polar compounds. For such molecules, additional parameters must be included in the model. For example, dipole moment is a parameter that characterizes degree of polarity of molecules and its knowledge for very heavy molecules is quite useful for better property prediction of such compounds. Further discussion and other potential energy functions and intermolecular forces are discussed in various sources [6, 7].

5.4 EQUATIONS OF STATE

An EOS is a mathematical equation that relates pressure, volume, and temperature. The simplest form of these equations is the ideal gas law that is only applicable to gases. In 1873, van der Waals proposed the first cubic EOS that was based on the theory of continuity of liquids and gases. Since then many modifications of cubic equations have been developed and have found great industrial application especially in the petroleum industry because of their mathematical simplicity. More sophisticated equations are also proposed in recent decades that are useful for certain systems [8]. Some of these equations particularly useful for petroleum fluids are reviewed and discussed in this chapter.

5.4.1 Ideal Gas Law

As discussed in the previous section the intermolecular forces depend on the distance between the molecules. With an increase in molar volume or a decrease in pressure the intermolecular distance increases and the intermolecular forces decrease. Under very low-pressure conditions, the intermolecular forces are so small that they can be neglected ($\Gamma = 0$). In addition since the empty space between the molecules is so large the volume of molecules may be neglected in comparison with the gas volume. Under these conditions any gas is considered as an *ideal gas*. Properties of ideal gases can be accurately estimated based on the kinetic theory of gases [9, 10]. The universal form of the EOS for ideal gases is

$$(5.14) \quad PV^{\text{ig}} = RT$$

where T is absolute temperature, P is the gas absolute pressure, V^{ig} is the molar volume of an ideal gas, and R is the

universal gas constant in which its values in different units are given in Section 1.7.24. The conditions that Eq. (5.14) can be used depend on the substance and its critical properties. But approximately this equation may be applied to any gas under atmospheric or subatmospheric pressures with an acceptable degree of accuracy. An EOS can be nondimensionalized through a parameter called *compressibility factor*, Z , defined as

$$(5.15) \quad Z \equiv \frac{V}{V^{\text{ig}}} = \frac{PV}{RT}$$

where for an ideal gas $Z = 1$ and for a real gas it can be greater or less than unity as will be discussed later in this chapter. Z in fact represents the ratio of volume of real gas to that of ideal gas under the same conditions of T and P . As the deviation of a gas from ideality increases, so does deviation of its Z factor from unity. The application of Z is in calculation of physical properties once it is known for a fluid. For example, if Z is known at T and P , volume of gas can be calculated from Eq. (5.15). Application of Eq. (5.15) at the critical point gives *critical compressibility factor*, Z_c , which was initially defined by Eq. (2.8).

In ideal gases, molecules have mass but no volume and they are independent from each other with no interaction. An ideal gas is mathematically defined by Eq. (5.14) with the following relation, which indicates that the internal energy is only a function of temperature.

$$(5.16) \quad U^{\text{ig}} = f_4(T)$$

Substitution of Eqs. (5.14) and (5.16) into Eq. (5.5) gives

$$(5.17) \quad H^{\text{ig}} = f_5(T)$$

where H^{ig} is the ideal gas enthalpy and it is only a function of temperature. Equations (5.14), (5.16), and (5.17) simply define ideal gases.

5.4.2 Real Gases—Liquids

Gases that do not follow ideal gas conditions are called *real gases*. At a temperature below critical temperature as pressure increases a gas can be converted to a liquid. In real gases, volume of molecules as well as the force between molecules are not zero. A comparison among an ideal gas, a real gas, and a liquid is demonstrated in Fig. 5.8. As pressure increases behavior of real gases approaches those of their liquids. The space between the molecules in liquids is less than real gases and in real gases is less than ideal gases. Therefore, the intermolecular forces in liquids are much stronger than those in real gases. Similarly the molecular forces in real gases are higher than those in ideal gases, which are nearly zero. It is for this reason that prediction of properties of liquids is more difficult than properties of gases.

Most gases are actually real and do not obey the ideal gas law as expressed by Eqs. (5.14) and (5.16). Under limiting conditions of $P \rightarrow 0$ ($T > 0$) or at T and $V \rightarrow \infty$ (finite P) we can obtain a set of constraints for any real gas EOS. When $T \rightarrow \infty$ translational energy becomes very large and other energies are negligible. Any valid EOS for a real gas should obey the following constraints:

$$(5.18) \quad \lim_{P \rightarrow 0} (PV) = RT$$

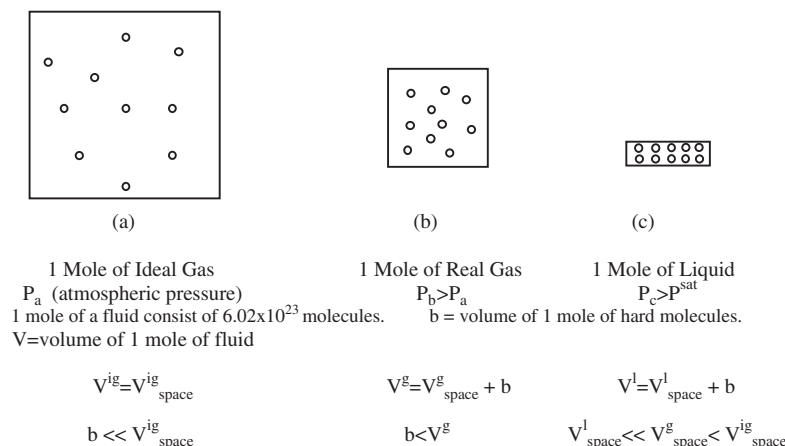


FIG. 5.8—Difference between an ideal gas, a real gas, and a liquid.

$$(5.19) \quad \lim_{T \rightarrow \infty} \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$(5.20) \quad \lim_{T \rightarrow \infty} \left(\frac{\partial^2 V}{\partial T^2} \right)_P = 0$$

In general for any gas as $P \rightarrow 0$ (or $V \rightarrow \infty$) it becomes an ideal gas; however, as $T \rightarrow \infty$ it is usually assumed that gas behavior approaches those of hard sphere gases. Constraints set by the above equations as well as Eq. (5.9) may be used to examine validity of an EOS for real fluids.

5.5 CUBIC EQUATIONS OF STATE

The ideal gas law expressed by Eq. (5.14) is neither applicable to real gases (high pressure) nor to liquids where the volume of molecules cannot be ignored in comparison with the volume of gas (see Fig. 5.8). Cubic EOS are designed to overcome these two shortcomings of ideal gas law with mathematical convenience. Several commonly used equations, their solution, and characteristics are discussed in this section.

5.5.1 Four Common Cubic Equations (vdW, RK, SRK, and PR)

The behavior of high-pressure gases approaches the behavior of liquids until the critical point where both gas and liquid behavior become identical. van der Waal (vdW) proposed the idea of continuity of gases and liquids and suggested that a single equation may represent the PVT behavior of both gases and liquids. He modified Eq. (5.14) by replacing P and V with appropriate modifications to consider real gas effects in the following form [1]:

$$(5.21) \quad \left(P + \frac{a}{V^2} \right) (V - b) = RT$$

where a and b are two constants specific for each substance but independent of T and P . The above equation is usually written as

$$(5.22) \quad P = \frac{RT}{V - b} - \frac{a}{V^2}$$

To find V from T and P , the above equation may be rearranged as

$$(5.23) \quad V^3 - \left(b + \frac{RT}{P} \right) V^2 + \left(\frac{a}{P} \right) V - \frac{ab}{P} = 0$$

where it is a cubic equation in terms of V . For this reason the vdW EOS, Eq. (5.22), is known as a cubic EOS. As a matter of fact any EOS that can be converted into a cubic form is called a *cubic* EOS. In Eq. (5.22), parameters a and b have physical meanings. Parameter b also called co-volume or repulsive parameter represents volume of 1 mol of hard cores of molecules and has the same unit as the molar volume (V). Parameter a is also referred to as attraction parameter and has the same unit as that of PV^2 (i.e., $\text{bar} \cdot \text{cm}^6/\text{mol}^2$). In Eq. (5.22), the term $RT/(V - b)$ represents the repulsive term of a molecule, while a/V^2 represents attractive term and accounts for nonideal behavior of gas. $V - b$ is in fact the space between molecules (Figs. 5.8b and 5.8c). When parameters a and b are zero Eq. (5.22) reduces to ideal gas law. Mathematically it can be shown from Eq. (5.22) that as $P \rightarrow \infty$, $V \rightarrow b$ and the free volume between molecules disappears.

Since Eq. (5.21) has only two parameters it is also known as a two-parameter EOS. Parameters a and b in the vdW EOS can be best determined from experimental data on PVT. However, mathematically these constants can be determined by imposing Eq. (5.9) as shown in the following example.

Example 5.1—Obtain vdW parameters in terms of T_c and P_c using Eq. (5.9) and (5.21). Also determine Z_c for fluids that obey vdW EOS.

Solution— $\partial P / \partial V$ and $\partial^2 P / \partial V^2$ are calculated from Eq. (5.22) by keeping T constant and set equal to zero at $T = T_c$, $P = P_c$, and $V = V_c$ as

$$(5.24) \quad \left. \frac{\partial P}{\partial V} \right|_{T_c} = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

$$(5.25) \quad \left. \frac{\partial^2 P}{\partial V^2} \right|_{T_c} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$

By taking the second terms to the right-hand side in each equation and dividing Eq. (5.24) by Eq. (5.25) we get

$$(5.26) \quad b = \frac{V_c}{3}$$

By substituting Eq. (5.26) into Eq. (5.24) we get

$$(5.27) \quad a = \frac{9}{8} T_c V_c$$

Since T_c and P_c are usually available, it is common to express parameters a and b in terms of T_c and P_c rather than T_c and V_c . For this reason V_c can be found from Eq. (5.21) in terms of T_c and P_c and replaced in the above equations. Similar results can be obtained by a more straightforward approach. At the critical point we have $V = V_c$ or $V - V_c = 0$, which can be written as follows:

$$(5.28) \quad (V - V_c)^3 = 0$$

Application of Eq. (5.23) at T_c and P_c gives

$$(5.29) \quad V^3 - \left(b + \frac{RT_c}{P_c}\right) V^2 + \left(\frac{a}{P_c}\right) V - \frac{ab}{P_c} = 0$$

Expansion of Eq. (5.28) gives

$$(5.30) \quad (V - V_c)^3 = V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0$$

Equations (5.29) and (5.30) are equivalent and the corresponding coefficients for V^3 , V^2 , V^1 , and V^0 must be equal in two equations. This gives the following set of equations for the coefficients:

$$(5.31) \quad -\left(b + \frac{RT_c}{P_c}\right) = -3V_c \quad \text{coefficients of } V^2$$

$$(5.32) \quad \frac{a}{P_c} = 3V_c^2 \quad \text{coefficients of } V$$

$$(5.33) \quad -\frac{ab}{P_c} = -V_c^3 \quad \text{coefficients of } V^0$$

By dividing Eq. (5.33) by (5.32), Eq. (5.26) can be obtained. By substituting $V_c = 3b$ (Eq. 5.26) to the right-hand side (RHS) of Eq. (5.31) the following relation for b is found:

$$(5.34) \quad b = \frac{RT_c}{8P_c}$$

Combining Eqs. (5.26) and (5.34) gives

$$(5.35) \quad V_c = \frac{3RT_c}{8P_c}$$

Substituting Eq. (5.35) into Eq. (5.27) gives

$$a = \frac{9}{8} RT_c \left(\frac{3RT_c}{8P_c}\right) = \frac{27R^2 T_c^2}{64P_c}$$

Therefore, the final relation for parameter a in terms of T_c and P_c is as follows:

$$(5.36) \quad a = \frac{27R^2 T_c^2}{64P_c}$$

In calculation of parameters a and b unit of R should be consistent with the units chosen for T_c and P_c . Another useful result from this analysis is estimation of critical compressibility factor through Eq. (5.35). Rearranging this equation and using definition of Z_c from Eq. (2.8) gives

$$(5.37) \quad Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8} = 0.375$$

Equation (5.37) indicates that value of Z_c is the same for all compounds. Values of Z_c given in Table 2.1 varies from 0.28 to 0.21 for most hydrocarbons. Therefore, vdW EOS significantly overpredicts values of Z_c (or V_c) and its performance in the critical region is quite weak. Similar approaches can be used to determine EOS parameters and Z_c for any other EOS. ♦

Since the introduction of the vdW EOS as the first cubic equation 130 years ago, dozens of cubic EOSs have been proposed, many of them developed in recent decades. The mathematical simplicity of a cubic EOS in calculation of thermodynamic properties has made it the most attractive type of EOS. When van der Waals introduced Eq. (5.21) he indicated that parameter a is temperature-dependent. It was in 1949 when Redlich and Kwong (RK) made the first modification to vdW EOS as [11]

$$(5.38) \quad P = \frac{RT}{V-b} - \frac{a}{V(V+b)}$$

where parameter a depends on temperature as $a_c/T^{0.5}$ in which a_c is related to T_c and P_c . Parameters a and b in Eq. (5.38) are different from those in Eq. (5.22) but they can be obtained in a similar fashion as in Example 5.1 (as shown later). The repulsive terms in Eqs. (5.38) and (5.22) are identical. Performance of RK EOS is much better than vdW EOS; however, it is mainly applicable to simple fluids and rare gases such as Kr, CH₄, or O₂, but for heavier and complex compounds it is not a suitable PVT relation.

The RK EOS is a source of many modifications that began in 1972 by Soave [12]. The Soave modification of Redlich-Kwong equation known as SRK EOS is actually a modification of parameter a in terms of temperature. Soave obtained parameter a in Eq. (5.38) for a number of pure compounds using saturated liquid density and vapor pressure data. Then he correlated parameter a to reduced temperature and acentric factor. Acentric factor, ω , defined by Eq. (2.10) is a parameter that characterizes complexity of a molecule. For more complex and heavy compounds value of ω is higher than simple molecules as given in Table 2.1. SRK EOS has been widely used in the petroleum industry especially by reservoir engineers for phase equilibria calculations and by process engineers for design calculations. While RK EOS requires T_c and P_c to estimate its parameters, SRK EOS requires an additional parameter, namely a third parameter, which in this case is ω . As it will be seen later that while SRK EOS is well capable of calculating vapor-liquid equilibrium properties, it seriously underestimates liquid densities.

Another popular EOS for estimation of phase behavior and properties of reservoir fluids and hydrocarbon systems is Peng-Robinson (PR) proposed in the following form [13]:

$$(5.39) \quad P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)}$$

where a and b are the two parameters for PR EOS and are calculated similar to SRK parameters. Parameter a was correlated in terms of temperature and acentric factor and later it was modified for properties of heavy hydrocarbons [14]. The original idea behind development of PR EOS was to improve liquid density predictions. The repulsive term in all four cubic equations introduced here is the same. In all these equations

TABLE 5.1—Constants in Eq. (5.40) for four common cubic EOS (with permission from Ref. [15]).

Equation	u_1	u_2	a_c	α	b	Z_c
vdW	0	0	$\frac{27}{64} \frac{R^2 T_c^2}{P_c}$	1	$\frac{RT_c}{8P_c}$	0.375
RK	1	0	$\frac{0.42748 R^2 T_c^2}{P_c}$	$T_r^{-1/2}$	$\frac{0.08664 RT_c}{P_c}$	0.333
SRK	1	0	$\frac{0.42748 R^2 T_c^2}{P_c}$	$\left[1 + f_\omega (1 - T_r^{1/2})\right]^2$ $f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$	$\frac{0.08664 RT_c}{P_c}$	0.333
PR	2	-1	$\frac{0.45724 R^2 T_c^2}{P_c}$	$\left[1 + f_\omega (1 - T_r^{1/2})\right]^2$ $f_\omega = 0.37464 + 1.54226\omega - 0.2699$	$\frac{0.07780 RT_c}{P_c}$	0.307

when $a = b = 0$, the equation reduces to ideal gas law, Eq. (5.14). In addition, all equations satisfy the criteria set by Eqs. (5.18)–(5.20) as well as Eq. (5.9). For example, consider the PR EOS expressed by Eq. (5.39). To show that criteria set by Eq. (5.18) are satisfied, the limits of all terms as $V \rightarrow \infty$ (equivalent to $P \rightarrow 0$) should be calculated. If both sides of Eq. (5.39) are multiplied by V/RT and taking the limits of all terms as $V \rightarrow \infty$ (or $P \rightarrow 0$), the first term in the RHS approaches unity while the second term approaches zero and we get $Z \rightarrow 1$, which is the EOS for the ideal gases.

Reid et al. [15] have put vdW, RK, SRK, and PR two-parameter cubic EOS into a practical and unified following form:

$$(5.40) \quad P = \frac{RT}{V-b} - \frac{a}{V^2 + u_1 bV + u_2 b^2}$$

where u_1 and u_2 are two integer values specific for each cubic equation and are given in Table 5.1. Parameter a is in general temperature-dependent and can be expressed as

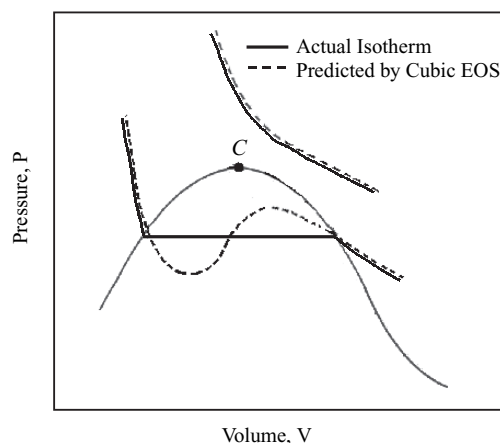
$$(5.41) \quad a = a_c \alpha$$

where α is a dimensionless temperature-dependent parameter and usually is expressed in terms of reduced temperature ($T_r = T/T_c$) and acentric factor as given in Table 5.1. For both vdW and RK equations this parameter is unity. Parameters u_1 and u_2 in Eq. (5.40) are the same for both RK and SRK equations, as can be seen in Table 5.1, but vdW and PR equations have different values for these parameters. Equation (5.40) can be converted into a cubic form equation similar to Eq. (5.23) but in term of Z rather than V :

$$(5.42) \quad \begin{aligned} & Z^3 - (1 + B - u_1 B)Z^2 + (A + u_2 B^2 - u_1 B - u_1 B^2)Z \\ & - AB - u_2 B^2 - u_2 B^3 = 0 \end{aligned}$$

where $A = \frac{aP}{R^2 T^2}$ and $B = \frac{bP}{RT}$

in which parameters A and B as well as all terms in Eq. (5.42) are dimensionless. Parameters a and b and Z_c have been determined in a way similar to the methods shown in Example 5.1. Z_c for both RK and SRK is the same as 1/3 or 0.333 while for the PR it is lower and equal to 0.307 for all compounds. As it will be shown later performance of all these equations near the critical region is weak and leads to large errors for calculation of Z_c . Prediction of an isotherm by a cubic EOS is shown in Fig. 5.9. As is seen in this figure, pressure prediction for an isotherm by a cubic EOS in the two-phase region is not reliable. However, isotherms outside the two-phase envelope may be predicted by a cubic EOS with a reasonable accuracy. In calculation of Z for saturated liquid and saturated vapor at the same T and P , Eq. (5.42) should be solved at once, which

**FIG. 5.9**—Prediction of isotherms by a cubic EOS.

gives three roots for Z . The lowest value of Z corresponds to saturated liquid, the highest root gives Z for the saturated vapor, and the middle root has no physical meaning.

5.5.2 Solution of Cubic Equations of State

Equation (5.42) can be solved through solution of the following general cubic equation [16, 17]:

$$(5.43) \quad Z^3 + a_1 Z^2 + a_2 Z + a_3 = 0$$

Let's define parameters Q , L , D , S_1 , and S_2 as

$$(5.44) \quad \begin{aligned} Q &= \frac{3a_2 - a_1^2}{9} \\ L &= \frac{9a_1 a_2 - 27a_3 - 2a_1^3}{54} \\ D &= Q^3 + L^2 \\ S_1 &= (L + \sqrt{D})^{1/3} \\ S_2 &= (L - \sqrt{D})^{1/3} \end{aligned}$$

The type and number of roots of Eq. (5.43) depends on the value of D . In calculation of $X^{1/3}$ if $X < 0$, one may use $X^{1/3} = -(-X)^{1/3}$.

If $D > 0$ Eq. (5.43) has one real root and two complex conjugate roots. The real root is given by

$$(5.45) \quad Z_1 = S_1 + S_2 - a_1/3$$

If $D = 0$ all roots are real and at least two are equal. The unequal root is given by Eq. (5.45) with $S_1 = S_2 = L^{1/3}$. The

two equal roots are

$$(5.46) \quad Z_2 = Z_3 = -L^{1/3} - a_1/3$$

If $D < 0$ all roots are real and unequal. In this case S_1 and S_2 (Eq. 5.44) cannot be calculated and the computation is simplified by use of trigonometry as

$$(5.47) \quad \begin{aligned} Z_1 &= 2\sqrt{-Q} \cos\left(\frac{1}{3}\theta + 120^\circ\right) - \frac{a_1}{3} \\ Z_2 &= 2\sqrt{-Q} \cos\left(\frac{1}{3}\theta + 240^\circ\right) - \frac{a_1}{3} \\ Z_3 &= 2\sqrt{-Q} \cos\left(\frac{1}{3}\theta\right) - \frac{a_1}{3} \end{aligned}$$

where $\cos\theta = \frac{L}{\sqrt{-Q^3}}$

where θ is in degrees. To check validity of the solution, the three roots must satisfy the following relations

$$(5.48) \quad \begin{aligned} Z_1 + Z_2 + Z_3 &= -a_1 \\ Z_1 \times Z_2 + Z_2 \times Z_3 + Z_3 \times Z_1 &= a_2 \\ Z_1 \times Z_2 \times Z_3 &= -a_3 \end{aligned}$$

A comparison of Eq. (5.42) and (5.43) indicates that the following relations exist between coefficients $a_i(s)$ and EOS parameters

$$(5.49) \quad \begin{aligned} a_1 &= -(1 + B - u_1 B) \\ a_2 &= A + u_2 B^2 - u_1 B - u_1 B^2 \\ a_3 &= -AB - u_2 B^2 - u_2 B^3 \end{aligned}$$

For the case that there are three different real roots ($D < 0$), Z^{liq} is equal to the lowest root (Z_1) while Z^{vap} is equal to the highest root (Z_3). The middle root (Z_2) is disregarded as physically meaningless. Equation (5.42) may also be solved by successive substitution methods; however, appropriate forms of the equation and initial values are different for vapor and liquid cases. For example, for gases the best initial value for Z is 1 while for liquids a good initial guess is bP/RT [1]. Solution of cubic equations through Eq. (5.42) is shown in the following example.

Example 5.2—Estimate molar volume of saturated liquid and vapor for n -octane at 279.5°C and pressure of 19.9 bar from the RK, SRK, and PR cubic EOS. Values of V^{L} and V^{V} extracted from the experimental data are 304 and 1216 cm³/mol, respectively [18]. Also estimate the critical volume.

Solution—To use SRK and PR EOS pure component data for n -C₈ are taken from Table 2.1 as $T_c = 295.55^\circ\text{C}$ (568.7 K), $P_c = 24.9$ bar, $\omega = 0.3996$, and $V_c = 486.35$ cm³/mol. When T is in K, P is in bar, and V is in cm³/mol, value of R from Section 1.7.24 is 83.14 cm³ · bar/mol · K. Sample calculation is shown here for SRK EOS. $T_r = (279.5 + 273.15)/568.7 = 0.972$.

From Table 5.1, $u_1 = 1$, $u_2 = 0$ and a_{SRK} and b_{SRK} are calculated as

$$\begin{aligned} f_\omega &= 0.48 + 1.574 \times 0.3996 - 0.176 \times (0.3996)^2 = 1.08087 \\ a_{\text{SRK}} &= \frac{0.42748 \times (83.14)^2 \times (568.7)^2}{24.9} \\ &\quad \times [1 + 1.08087 \times (1 - 0.9717^{1/2})]^2 \\ &= 3.957 \times 10^7 \text{ cm}^6/\text{mol}^2. \\ b_{\text{SRK}} &= \frac{0.08664 \times 83.14 \times 568.7}{24.9} = 164.52 \text{ cm}^3/\text{mol}. \end{aligned}$$

Parameters A and B are calculated from Eq. (5.42):

$$A = \frac{3.957 \times 10^7 \times 19.9}{(83.14)^2 \times (552.65)^2} = 0.373$$

and

$$B = \frac{164.52 \times 19.9}{83.14 \times 552.65} = 0.07126$$

Coefficients a_1 , a_2 , and a_3 are calculated from Eq. (5.49) as

$$\begin{aligned} a_1 &= -(1 + 0.07126 - 1 \times 0.07126) = -1 \\ a_2 &= 0.373 + 0 \times 0.07126^2 - 1 \times 0.07126 - 1 \times 0.07126^2 \\ &= 0.29664 \\ a_3 &= -0.37305 \times 0.07126 - 0 \times 0.07126^2 - 0 \times 0.07126^3 \\ &= -0.026584 \end{aligned}$$

From Eq. (5.44), $Q = -0.01223$, $L = 8.84 \times 10^{-4}$, and $D = -1.048 \times 10^{-6}$. Since $D < 0$, the solution is given by Eq. (5.47). $\theta = \cos^{-1}(8.84 \times 10^{-4}/\sqrt{-(-0.01223)^3}) = 492^\circ$ and the roots are $Z_1 = 0.17314$, $Z_2 = 0.28128$, and $Z_3 = 0.54553$. Acceptable results are the lowest and highest roots while the intermediate root is not useful: $Z^{\text{L}} = Z_1 = 0.17314$ and $Z^{\text{V}} = Z_3 = 0.54553$. Molar volume, V , can be calculated from Eq. (5.15): $V = ZRT/P$ in which $T = 552.65$ K, $P = 19.9$ bar, and $R = 83.14$ cm³ · bar/mol · K; therefore, $V^{\text{L}} = 399.9$ cm³/mol and $V^{\text{V}} = 1259.6$ cm³/mol. From Table 5.1, $Z_c = 0.333$ and V_c is calculated from Eq. (2.8) as $V_c = (0.333 \times 83.14 \times 568.7)/24.9 = 632.3$ cm³/mol. Errors for V^{L} , V^{V} , and V_c are 31.5, 3.6, and 30%, respectively. It should be noted that Z_c can also be found from the solution of cubic equation with $T = T_c$ and $P = P_c$. However, for this case $D > 0$ and there is only one solution which is obtained by Eq. (5.45) with similar answer. As is seen in this example, liquid and critical volumes are greatly overestimated. A summary of results for RK, SRK, and PR EOSs are given in Table 5.2. ♦

5.5.3 Volume Translation

In practice the SRK and PR equations are widely used for VLE calculations in industrial applications [19–21]. However, their ability to predict volumetric data especially for liquid systems

TABLE 5.2—Prediction of saturated liquid, vapor and critical molar volumes for n -octane in Example 5.2.

Equation	V^{L} , cm ³ /mol	%D	V^{V} , cm ³ /mol	%D	V_c , cm ³ /mol	%D
Data*	304.0	...	1216.0	...	486.3	...
RK	465.9	53.2	1319.4	8.5	632.3	30
SRK	399.9	31.5	1259.6	3.6	632.3	30
PR	356.2	17.2	1196.2	−1.6	583.0	19.9

Source: V^{L} and V^{V} from Ref. [18]; V_c from Table 2.1.

is weak. Usually the SRK equation predicts densities more accurately for compounds with low acentric values, while the PR predicts better densities for compounds with acentric factors near 0.33 [21]. For this reason a correction term, known as volume translation, has been proposed for improving volumetric prediction of these equations [8, 15, 19, 22]:

$$(5.50) \quad V = V^{\text{EOS}} - c$$

where c is the volume translation parameter and has the same unit as the molar volume. Equation (5.50) can be applied to both vapor and liquid volumes. Parameter c mainly improves liquid volume predictions and it has no effect on vapor pressure and VLE calculations. Its effect on vapor volume is negligible since V^V is very large in comparison with c , but it greatly improves prediction of liquid phase molar volumes. Values of c have been determined for a number of pure components up to C_{10} for both SRK and PR equations and have been included in references in the petroleum industry [19]. Peneloux et al. [22] originally obtained values of c for some compounds for use with the SRK equation. They also suggested the following correlation for estimation of c for SRK equation:

$$(5.51) \quad c = 0.40768 (0.29441 - Z_{\text{RA}}) \frac{RT_c}{P_c}$$

where Z_{RA} is the Rackett parameter, which will be discussed in Section 5.8.1. Similarly Jhaveri and Yougren [23] obtained parameter c for a number of pure substances for use with PR EOS and for hydrocarbon systems have been correlated to molecular weight for different families as follows:

$$(5.52) \quad \begin{aligned} c_{\text{P}} &= b_{\text{PR}} (1 - 2.258 M_{\text{P}}^{-0.1823}) \\ c_{\text{N}} &= b_{\text{PR}} (1 - 3.004 M_{\text{N}}^{-0.2324}) \\ c_{\text{A}} &= b_{\text{PR}} (1 - 2.516 M_{\text{A}}^{-0.2008}) \end{aligned}$$

where b_{PR} refers to parameter b for the PR equation as given in Table 5.1. Subscripts P, N, and A refer to paraffinic, naphthenic, and aromatic hydrocarbon groups. The ratio of c/b is also called *shift parameter*. The following example shows application of this method.

Example 5.3—For the system of Example 5.2, estimate V^L and V^V for the PR EOS using the volume translation method.

Solution—For $n\text{-C}_8$, from Table 2.1, $M = 114$ and b_{PR} are calculated from Table 5.1 as $147.73 \text{ cm}^3/\text{mol}$. Since the hydrocarbon is paraffinic Eq. (5.51) for c_{P} should be used, $c = 7.1 \text{ cm}^3/\text{mol}$. From Table 5.2, $V^{\text{L(PR)}} = 356.2$ and $V^{\text{V(PR)}} = 1196.2 \text{ cm}^3/\text{mol}$. From Eq. (5.50) the corrected molar volumes are $V^L = 356.2 - 7.1 = 349.1$ and $V^V = 1196.2 - 7.1 = 1189.1 \text{ cm}^3/\text{mol}$. By the volume translation correction, error for V^L decreases from 17.2 to 14.8% while for V^V it has lesser effect and it increases error from -1.6% to -2.2% . ♦

As is seen in this example improvement of liquid volume by volume translation method is limited. Moreover, estimation of c by Eq. (5.51) is limited to those compounds whose Z_{RA} is known. With this modification at least four parameters namely T_c , P_c , ω , and c must be known for a compound to determine its volumetric properties.

5.5.4 Other Types of Cubic Equations of State

In 1972 Saove for the first time correlated parameter a in a cubic EOS to both T_r and ω as given in Table 5.1. Since then this approach has been used by many researchers who tried to improve performance of cubic equations. Many modifications have been made on the form of f_ω for either SRK or PR equations. Graboski and Daubert modified the constants in the f_ω relation for the SRK to improve prediction of vapor pressure of hydrocarbons [24]. Robinson and Peng [14] also proposed a modification to their f_ω equation given in Table 5.1 to improve performance of their equation for heavier compounds. They suggested that for the PR EOS and for compounds with $\omega > 0.49$ the following relation should be used to calculate f_ω :

$$(5.53) \quad f_\omega = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3$$

Some other modifications give different functions for parameter α in Eq. (5.41). For example, Twu et al. [25] developed the following relation for the PR equation.

$$(5.54) \quad \begin{aligned} \alpha &= T_r^{-0.171813} \exp[0.125283 (1 - T_r^{1.77634})] \\ &+ \omega \{ T_r^{-0.607352} \exp[0.511614 (1 - T_r^{2.20517})] \\ &- T_r^{-0.171813} \exp[0.125283 (1 - T_r^{1.77634})] \} \end{aligned}$$

Other modifications of cubic equations have been derived by suggesting different integer values for parameters u_1 and u_2 in Eq. (5.40). One can imagine that by changing values of u_1 and u_2 in Eq. (5.40) various forms of cubic equations can be obtained. For example, most recently a modified two-parameter cubic equation has been proposed by Moshfeghian that corresponds to $u_1 = 2$ and $u_2 = -2$ and considers both parameters a and b as temperature-dependent [26]. Poling et al. [8] have summarized more than two dozens types of cubic equations into a generalized equation similar to Eq. (5.42). Some of these modifications have been proposed for special systems. However, for hydrocarbon systems the original forms of SRK and PR are still being used in the petroleum industry. The most successful modification was proposed by Zudkevitch and Joffe [27] to improve volumetric prediction of RK EOS without sacrificing VLE capabilities. They suggested that parameter b in the RK EOS may be modified similar to Eq. (5.41) for parameter a as following:

$$(5.55) \quad b = b_{\text{RK}}\beta$$

where β is a dimensionless correction factor for parameter b and it is a function of temperature. Later Joffe et al. [28] determined parameter α in Eq. (5.41) and β in Eq. (5.55) by matching saturated liquid density and vapor pressure data over a range of temperature for various pure compounds. In this approach for every case parameters α and β should be determined and a single dataset is not suitable for use in all cases. SRK and ZJRK are perhaps the most widespread cubic equations being used in the petroleum industry, especially for phase behavior studies of reservoir fluids [19]. Other researchers have also tried to correlate parameters α and β in Eqs. (5.41) and (5.55) with temperature. Feyzi et al. [29] correlated $\alpha^{1/2}$ and $\beta^{1/2}$ for PR EOS in terms of T_r and ω for heavy reservoir fluids and near the critical region. Their correlations particularly improve liquid density prediction in comparison with SRK and PR equations while it has similar VLE

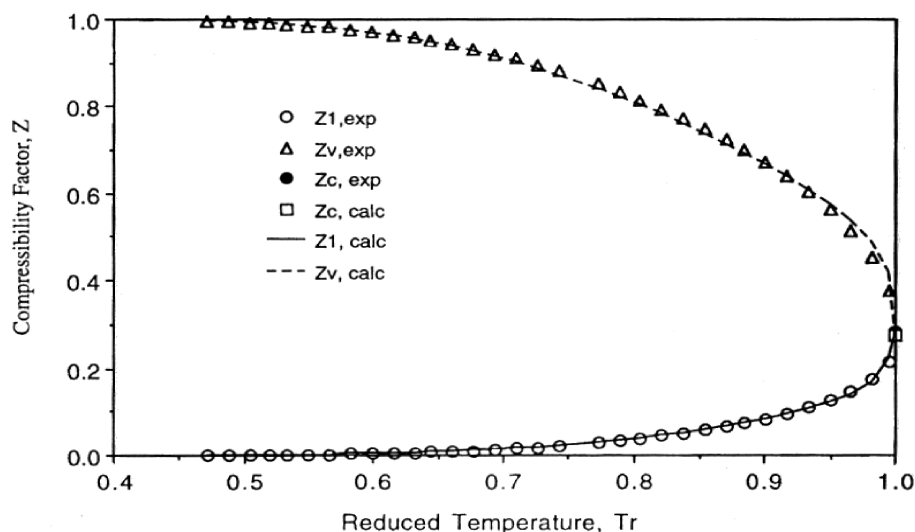


FIG. 5.10—Prediction of saturation curves for ethane using a modified PR EOS [29].

prediction capabilities. Another improvement in their correlation was prediction of saturation curves near the critical region. This is shown for prediction of compressibility factor of saturated liquid and vapor curves as well as the critical point for methane and ethane in Fig. 5.10.

Prediction of isotherms by a cubic EOS is shown on PV diagram in Fig. 5.9. As shown in this figure in the two-phase region the prediction of isotherm is not consistent with true behavior of the isotherm. In addition, performance of these cubic equations in calculation of liquid densities and derived thermodynamic properties such as heat capacity is weak. This indicates the need for development of other EOS. Further information on various types of cubic EOS and their characteristics are available in different sources [30–34].

5.5.5 Application to Mixtures

Generally when a PVT relation is available for a pure substance, the mixture property may be calculated in three ways when the mixture composition (mole fraction, x_i) is known. The first approach is to use the same equation developed for pure substances but the input parameters (T_c , P_c , and ω) are estimated for the mixture. Estimation of these pseudocritical properties for petroleum fractions and defined hydrocarbon mixtures were discussed in Chapter 3. The second approach is to estimate desired physical property (i.e., molar volume or density) for all pure compounds using the above equations and then to calculate the mixture property using the mixture composition through an appropriate mixing rule for the property (i.e., Eq. (3.44) for density). This approach in some cases gives good estimate of the property but requires large calculation time especially for mixtures containing many components. The third and most widely used approach is to calculate EOS parameters (parameters a and b) for the mixture using their values for pure components and mixture composition.

The simplest EOS for gases is the ideal gas law given by Eq. (5.14). When this is applied to component i with n_i moles in a mixture we have

$$(5.56) \quad PV_i^t = n_i RT$$

where V_i^t is the total volume occupied by i at T and P of the mixture. For the whole mixture this equation becomes

$$(5.57) \quad PV^t = n^t RT$$

where V^t is the total volume of mixture ($V^t = \sum V_i^t$) and n^t is the total number of moles ($n^t = \sum n_i$). By dividing Eq. (5.56) by Eq. (5.57) we get

$$(5.58) \quad y_i = \frac{n_i}{n} = \frac{V_i^t}{V^t}$$

where y_i is the mole fraction of i in the gas mixture. The above equation indicates that in an ideal gas mixture the mole fractions and volume fractions are the same (or mol% of i = vol% of i). This is an assumption that is usually used for gas mixtures even when they are not ideal.

For nonideal gas mixtures, various types of mixing rules for determining EOS parameters have been developed and presented in different sources [6, 8]. The mixing rule that is commonly used for hydrocarbon and petroleum mixtures is called *quadratic mixing rule*. For mixtures (vapor or liquid) with composition x_i and total of N components the following equations are used to calculate a and b for various types of cubic EOS:

$$(5.59) \quad a_{\text{mix}} = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij}$$

$$(5.60) \quad b_{\text{mix}} = \sum_{i=1}^N x_i b_i$$

where a_{ij} is given by the following equation:

$$(5.61) \quad a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij})$$

For the volume translation c , the mixing rule is the same as for parameter b :

$$(5.62) \quad c_{\text{mix}} = \sum_{i=1}^N x_i c_i$$

In Eq. (5.61), k_{ij} is a dimensionless parameter called *binary interaction parameter* (BIP), where $k_{ii} = 0$ and $k_{ij} = k_{ji}$. For most

TABLE 5.3—Recommended BIPs for SRK and PR EOS [19].

Comp.	PR EOS			SRK EOS		
	N ₂	CO ₂	H ₂ S	N ₂	CO ₂	H ₂ S
N ₂	0.000	0.000	0.130	0.000	0.000	0.120
CO ₂	0.000	0.000	0.135	0.000	0.000	0.135
H ₂ S	0.130	0.135	0.000	0.120	0.120	0.000
C ₁	0.025	0.105	0.070	0.020	0.120	0.080
C ₂	0.010	0.130	0.085	0.060	0.150	0.070
C ₃	0.090	0.125	0.080	0.080	0.150	0.070
<i>i</i> C ₄	0.095	0.120	0.075	0.080	0.150	0.060
<i>n</i> C ₄	0.090	0.115	0.075	0.800	0.150	0.060
<i>i</i> C ₅	0.100	0.115	0.070	0.800	0.150	0.060
<i>n</i> C ₅	0.110	0.115	0.070	0.800	0.150	0.060
C ₆	0.110	0.115	0.055	0.800	0.150	0.050
C ₇₊	0.110	0.115	0.050	0.800	0.150	0.030

Values recommended for PR EOS by Ref. [6] are as follows: N₂/CO₂: −0.013; N₂/C₁: 0.038; C₁/CO₂: 0.095; N₂/C₂: 0.08; C₁/C₂: 0.021.

hydrocarbon systems, $k_{ij} = 0$; however, for the key hydrocarbon compounds in a mixture where they differ in size value of k_{ij} is nonzero. For example, for a reservoir fluid that contains a considerable amount of methane and C₇₊ the BIP for C₁ and C₇ fractions cannot be ignored. For nonhydrocarbon–hydrocarbon pairs k_{ij} values are nonzero and have a significant impact on VLE calculations [20, 35]. Values of k_{ij} for a particular pair may be determined from matching experimental data with predicted data on a property such as vapor pressure. Values of k_{ij} are specific to the particular EOS being used. Some researchers have determined k_{ij} for SRK or PR equations. Values of BIP for N₂, CO₂, and methane with components in reservoir fluids from C₁ to C₆ and three subfractions of C₇₊ for PR and SRK are tabulated by Whitson [19]. Values that he has recommended for use with SRK and PR equations are given in Table 5.3. There are some general correlations to estimate BIPs for any equation [36, 37]. The most commonly used correlation for estimating BIPs of hydrocarbon–hydrocarbon (HC–HC) systems is given by Chueh and Prausnitz [37]:

$$(5.63) \quad k_{ij} = A \left\{ 1 - \left[\frac{2(V_{ci} V_{cj})^{1/6}}{(V_{ci})^{1/3} + (V_{cj})^{1/3}} \right]^B \right\}$$

where V_{ci} and V_{cj} are critical molar volume of components i and j in cm³/mol. Originally $A = 1$ and $B = 3$; however, in practical cases B is set equal to 6 and A is adjusted to match saturation pressure and other variable VLE data [20, 38]. For most reservoir fluids, A is within 0.2–0.25; however, as is seen in Chapter 9 for a Kuwaiti oil value of A was found as 0.18. As discussed by Poling et al. [8], Tsionopoulos recommends the original Chueh–Prausnitz relation ($A = 1$ and $B = 3$) for nonpolar compounds. Pedersen et al. [39] proposed another relation for calculation of BIPs for HC–HC systems. Their correlation is based on data obtained from North Sea reservoir fluids and it is related to molecular weights of components i and j as $k_{ij} \cong 0.001 M_i/M_j$ where $M_i > M_j$. Another correlation was proposed by Whitson [40] for estimation of BIPs of methane and C₇₊ fraction components based on the data presented by Katz and Firoozabadi [36] for use with PR EOS. His correlation is as: $k_{1j} = 0.14 \text{ SG}_j - 0.0688$, where 1 refers to methane and j refers to the C₇₊(j) fraction, respectively.

Equations (5.59)–(5.62) can be applied to either liquid or vapor mixtures. However, for the case of vapor mixtures with N components, mole fraction y_i should be used. Expansion

of Eq. (5.59) for a ternary gas mixture ($N = 3$) becomes

$$(5.64) \quad a_{\text{mix}} = y_1^2 a_{11} + y_2^2 a_{22} + y_3^2 a_{33} + 2y_1 y_2 a_{12} + 2y_1 y_3 a_{13} + 2y_2 y_3 a_{23}$$

where $a_{11} = a_1$, $a_{22} = a_2$, and $a_{33} = a_3$. Interaction coefficients such as a_{12} can be found from Eq. (5.61): $a_{12} = \sqrt{a_1 a_2} (1 - k_{12})$ where k_{12} may be taken from Table 5.3 or estimated from Eq. (5.63). a_{13} and a_{23} can be calculated in a similar way.

5.6 NONCUBIC EQUATIONS OF STATE

The main reason for wide range application of cubic EOS is their application to both phases of liquids and vapors, mathematical simplicity and convenience, as well as possibility of calculation of their parameters through critical constants and acentric factor. However, these equations are mainly useful for density and phase equilibrium calculations. For other thermodynamic properties such as heat capacity and enthalpy, noncubic equations such as those based on statistical associating fluid theory (SAFT) or perturbed hard chain theory (PHCT) may be used. Some of these equations have been particularly developed for special mixtures, polar molecules, hard sphere molecules, and near critical regions. Summary of these equations is given by Poling et al. [8]. In this section three important types of noncubic EOS are presented: (1) virial, (2) Carnahan–Starling, and (3) modified Benedict–Webb–Rubin.

5.6.1 Virial Equation of State

The most widely used noncubic EOS is the virial equation or its modifications. The original virial equation was proposed in 1901 by Kammerlingh–Onnes and it may be written either in the form of polynomial series in inverse volume (pressure explicit) or pressure expanded (volume explicit) as follows:

$$(5.65) \quad Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots$$

$$(5.66) \quad Z = 1 + \left(\frac{B}{RT} \right) P + \left(\frac{C - B^2}{R^2 T^2} \right) P^2 + \left(\frac{D - 3BC + 2B^3}{R^3 T^3} \right) P^3 + \dots$$

TABLE 5.4—Second virial coefficients for several gases [41].

Compound	Temperature, K			
	200	300	400	500
N ₂	−35.2	−4.2	9	16.9
CO ₂	...	−122.7	60.5	−29.8
CH ₄	−105	−42	−15	−0.5
C ₂ H ₆	−410	−182	−96	−52
C ₃ H ₈	...	−382	−208	−124

Note: Values of B are given in cm³/mol.

where B, C, D, \dots are called second, third, and fourth virial coefficients and they are all temperature-dependent. The above two forms of virial equation are the same and the second equation can be derived from the first equation (see Problem 5.7). The second form is more practical to use since usually T and P are available and V should be estimated. The number of terms in a virial EOS can be extended to infinite terms but contribution of higher terms reduces with increase in power of P . Virial equation is perhaps the most accurate PVT relation for gases. However, the difficulty with use of virial equation is availability of its coefficients especially for higher terms. A large number of data are available for the second virial coefficient B , but less data are available for coefficient C and very few data are reported for the fourth coefficient D . Data on values of virial coefficients for several compounds are given in Tables 5.4 and 5.5. The virial coefficient has firm basis in theory and the methods of statistical mechanics allow derivation of its coefficients.

B represents two-body interactions and C represented three-body interactions. Since the chance of three-body interaction is less than two-body interaction, therefore, the importance and contribution of B is much greater than C . From quantum mechanics it can be shown that the second virial coefficient can be calculated from the knowledge of potential function (Γ) for intermolecular forces [6]:

$$(5.67) \quad B = 2\pi N_A \int_0^{\infty} (1 - e^{-\Gamma(r)/kT}) r^2 dr$$

where N_A is the Avogadro's number (6.022×10^{23} mol^{−1}) and k is the Boltzman's constant ($k = R/N_A$). Once the relation for Γ is known, B can be estimated. For example, if the fluid follows hard sphere potential function, one by substituting Eq. (5.13) for Γ into the above equation gives $B = (2/3)\pi N_A \sigma^3$. Vice versa, constants in a potential relation (ε and σ) may be estimated from the knowledge of virial coefficients. For mixtures, B_{mix} can be calculated from Eq. (5.59) with a being replaced by B . For a ternary system, B can be calculated from Eq. (5.64). B_{ij} is calculated from Eq. (5.67) using Γ_{ij} with σ_{ij} and ε_{ij} given as [6]

$$(5.68) \quad \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$$

$$(5.69) \quad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$$

TABLE 5.5—Sample values of different virial coefficients for several compounds [1].

Compound	$T, ^\circ\text{C}$	$B, \text{cm}^3/\text{mol}$	$C, \text{cm}^6/\text{mol}^2$
Methane ^a	0	−53.4	2620
Ethane	50	−156.7	9650
Steam (H ₂ O)	250	−152.5	−5800
Sulfur dioxide (SO ₂)	157.5	−159	9000

^aFor methane at 0°C the fourth virial coefficient D is 5000 cm⁹/mol³.

Another form of Eq. (5.59) for calculation of B_{mix} can be written as following:

$$(5.70) \quad B_{\text{mix}} = \sum_{i=1}^N y_i B_{ii} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N y_i y_j \delta_{ij} \quad \text{where } \delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$$

There are several correlations developed based on the theory of corresponding state principles to estimate the second virial coefficients in terms of temperature. Some of these relations correlate B/V_c to T_r and ω . Prausnitz et al. [6] reviewed some of these relations for estimation of the second virial coefficients. The relation developed by Tsonopoulos [42] is useful to estimate B from T_c , P_c , and ω .

$$(5.71) \quad \begin{aligned} \frac{BP_c}{RT_c} &= B^{(0)} + \omega B^{(1)} \\ B^{(0)} &= 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \\ B^{(1)} &= 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8} \end{aligned}$$

where $T_r = T/T_c$. There are simpler relations that can be used for normal fluids [1].

$$(5.72) \quad \begin{aligned} \frac{BP_c}{RT_c} &= B^{(0)} + \omega B^{(1)} \\ B^{(0)} &= 0.083 - \frac{0.422}{T_r^{1.6}} \\ B^{(1)} &= 0.139 - \frac{0.172}{T_r^{4.2}} \end{aligned}$$

Another relation for prediction of second virial coefficients of simple fluids is given by McGlashan [43]:

$$(5.73) \quad \frac{BP_c}{RT_c} = 0.597 - 0.462e^{0.7002/T_r}$$

A graphical comparison of Eqs. (5.71)–(5.73) for prediction of second virial coefficient of ethane is shown in Fig. 5.11. Coefficient B at low and moderate temperatures is negative and increases with increase in temperature; however, as is seen from the above correlations as $T \rightarrow \infty$, B approaches a positive number.

To predict B_{mix} for a mixture of known composition, the interaction coefficient B_{ij} is needed. This coefficient can be calculated from B_{ii} and B_{jj} using the following relations [1, 15]:

$$(5.74) \quad \begin{aligned} B_{ij} &= \frac{RT_{cij}}{P_{cij}} (B^{(0)} + \omega_{ij} B^{(1)}) \\ B^{(0)} \text{ and } B^{(1)} &\text{ are calculated through } T_{rij} = T/T_{cij} \\ \omega_{ij} &= \frac{\omega_i + \omega_j}{2} \\ T_{cij} &= (T_{ci} T_{cj})^{1/2} (1 - k_{ij}) \\ P_{ij} &= \frac{Z_{ij} RT_{cij}}{V_{cij}} \\ Z_{cij} &= \frac{Z_{ci} + Z_{cj}}{2} \\ V_{cij} &= \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2} \right)^3 \end{aligned}$$

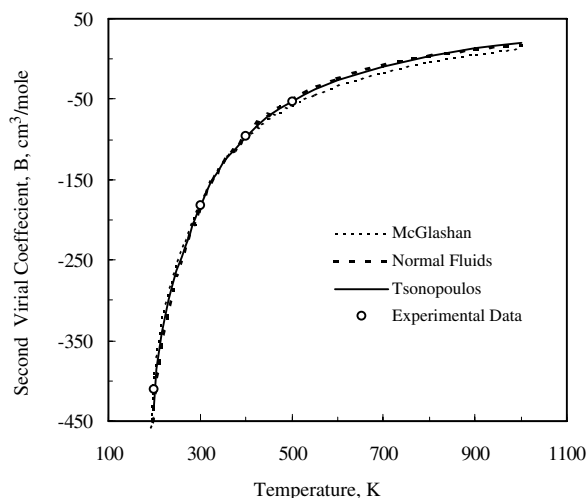


FIG. 5.11—Prediction of second virial coefficient for ethane from different methods. Experimental data from Table 5.4; McGlashan, Eq. (5.73); Normal fluids, Eq. (5.72); Tsopoulous, Eq. (5.71).

where k_{ij} is the interaction coefficient and for hydrocarbons of similar size it is zero. $B^{(0)}$ and $B^{(1)}$ must be calculated from the same relations used to calculate B_{ii} and B_{jj} . Another simpler method that is fairly accurate for light, nonpolar gases is the geometric mean:

$$B_{ij} = (B_i B_j)^{1/2}$$

$$B_{\text{mix}} = \left(\sum_{i=1}^N y_i B_i^{1/2} \right)^2$$

The importance of these relations is that at moderate pressures, Eq. (5.66) may be truncated after the second term as follows:

$$(5.75) \quad Z = 1 + \frac{BP}{RT}$$

This equation is usually referred to as the truncated virial equation and may be used with a reasonable degree of accuracy in certain ranges of reduced temperature and pressure: $V_r > 2.0$ [i.e., $(P_r < 0.5, T_r > 1)$, $(0.5 < P_r < 1, T_r > 1.2)$, $(1 < P_r < 1.7, T_r > 1.5)$]. At low-pressure range ($P_r < 0.3$), Eq. (5.72) provides good prediction for the second virial coefficients for use in Eq. (5.75) [1].

A more accurate form of virial equation for gases is obtained when Eq. (5.65) or (5.66) are truncated after the third term:

$$(5.76) \quad Z = 1 + \frac{B}{V} + \frac{C}{V^2}$$

An equivalent form of this equation in terms of P can be obtained by Eq. (5.66) with three terms excluding fourth virial coefficient and higher terms. Because of lack of sufficient data, a generalized correlation to predict the third virial coefficient, C , is less accurate and is based on fewer data. The generalized correlation has the following form [6]:

$$(5.77) \quad \frac{C}{V_c^3} = (0.232T_r^{-0.25} + 0.468T_r^{-5}) \times [1 - e^{-(1-1.89T_r^2)}] + de^{-(2.49-2.30T_r+2.70T_r^2)}$$

where V_c is the molar critical volume in cm^3/mol and d is a parameter that is determined for several compounds, i.e., $d = 0.6$ for methane, 1 for ethane, 1.8 for neopentane, 2.5 for benzene, and 4.25 for n -octane. In general when $T_r > 1.5$ the second term in the above equation is insignificant. A more practical and generalized correlation for third virial coefficient was proposed by Orbey and Vera [44] for nonpolar compounds in a form similar to Eq. (5.71), which was proposed for the second virial coefficients:

$$\frac{CP_c^2}{(RT_c)^2} = C^{(0)} + \omega C^{(1)}$$

$$(5.78) \quad C^{(0)} = 0.01407 + \frac{0.02432}{T_r^{2.8}} - \frac{0.00313}{T_r^{10.5}}$$

$$C^{(1)} = -0.02676 + \frac{0.0177}{T_r^{2.8}} + \frac{0.040}{T_r^3} - \frac{0.003}{T_r^6} - \frac{0.00228}{T_r^{10.5}}$$

where $C^{(0)}$ and $C^{(1)}$ are dimensionless parameters for simple and correction terms in the generalized correlation. Estimation of the third virial coefficients for mixtures is quite difficult as there are three-way interactions for C and it should be calculated from [6]:

$$(5.79) \quad C_{\text{mix}} = \sum_i \sum_j \sum_k y_i y_j y_k C_{ijk}$$

Methods of estimation of cross coefficients C_{ijk} are not reliable [6]. For simplicity, generally it is assumed that $C_{iij} = C_{iji} = C_{jii}$ but still for a binary system at least two cross coefficients of C_{112} and C_{122} must be estimated. In a binary system, C_{112} expresses interaction of two molecules of component 1 with one molecule of component 2. Orbey and Vera [44] suggest the following relation for calculation of C_{ijk} as

$$(5.80) \quad C_{ijk} = (C_{ij} C_{ik} C_{jk})^{1/3}$$

where C_{ij} is evaluated from Eq. (5.78) using T_{cij} , P_{cij} and ω_{ij} obtained from Eq. (5.74). This approach gives satisfactory estimates for binary systems.

There are certain specific correlations for the virial coefficients of some specific gases. For example, for hydrogen the following correlations for B and C are suggested [6]:

$$(5.81) \quad B = \sum_{i=1}^4 b_i x^{(2i-1)/4}$$

$$C = 1310.5x^{1/2} (1 + 2.1486x^3) \times [1 - \exp(1 - x^{-3})]$$

where $x = \frac{109.83}{T}$, $b_1 = 42.464$, $b_2 = -37.1172$,
 $b_3 = -2.2982$, and $b_4 = -3.0484$

where T is in K, B is in cm^3/mol , and C is in cm^6/mol^2 . The range of temperature is 15–423 K and the average deviations for B and C are $0.07 \text{ cm}^3/\text{mol}$ and $17.4 \text{ cm}^6/\text{mol}^2$, respectively [6].

As determination of higher virial coefficients is difficult, application of truncated virial EOS is mainly limited to gases and for this reason they have little application in reservoir fluid studies where a single equation is needed for both liquid and vapor phases. However, they have wide applications in estimation of properties of gases at low and moderate pressures. In addition, special modifications of virial equation has industrial applications, as discussed in the next section. From mathematical relations it can be shown that any EOS can be

converted into a virial form. This is shown by the following example.

Example 5.4—Convert RK EOS into the virial form and obtain coefficients B and C in terms of EOS parameters.

Solution—The RK EOS is given by Eq. (5.38). If both sides of this equation are multiplied by V/RT we get

$$(5.82) \quad Z = \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{RT(V+b)}$$

Assume $x = b/V$ and $A = a/RT$, then the above equation can be written as

$$(5.83) \quad Z = \frac{1}{1-x} - A \frac{1}{V} \times \frac{1}{1+x}$$

Since $b < V$, therefore, $x < 1$ and the terms in the RHS of the above equation can be expanded through Taylor series [16, 17]:

$$(5.84) \quad f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(x_0)}{n!} (x - x_0)^n$$

where $f^{(n)}(x_0)$ is the n th order derivative $d^n f(x)/dx^n$ evaluated at $x = x_0$. The zeroth derivative of f is defined to be f itself and both $0!$ and $1!$ are equal to 1. Applying this expansion rule at $x_0 = 0$ we get:

$$(5.85) \quad \begin{aligned} \frac{1}{1-x} &= 1 + x + x^2 + x^3 + x^4 + \dots \\ \frac{1}{1+x} &= 1 - x + x^2 - x^3 + x^4 - \dots \end{aligned}$$

It should be noted that the above relations are valid when $|x| < 1$. Substituting the above two relations in Eq. (5.83) we get

$$(5.86) \quad Z = (1 + x + x^2 + x^3 + \dots) - A \frac{1}{V} \times (1 - x + x^2 - x^3 + \dots)$$

If x is replaced by its definition b/V and A by a/RT we have

$$(5.87) \quad Z = 1 + \frac{b - a/RT}{V} + \frac{b^2 + ab/RT}{V^2} + \frac{+b^3 - ab^2/RT}{V^3} + \dots$$

A comparison with Eq. (5.65) we get the virial coefficients in terms of RK EOS parameters as follows:

$$(5.88) \quad B = b - \frac{a}{RT} \quad C = b^2 + \frac{ab}{RT} \quad D = b^3 - \frac{ab^2}{RT}$$

Considering the fact that a is a temperature-dependent parameter one can see that the virial coefficients are all temperature-dependent parameters. With use of SRK EOS, similar coefficients are obtained but parameter a also depends on the acentric factor as given in Table 5.1. This gives better estimation of the second and third virial coefficients (see Problem 5.10) ♦

The following example shows application of truncated virial equation for calculation of vapor molar volumes.

Example 5.5—Propane has vapor pressure of 9.974 bar at 300 K. Saturated vapor molar volume is $V^V = 2036.5 \text{ cm}^3/\text{mol}$ [Ref. 8, p. 4.24]. Calculate (a) second virial coefficient from Eqs. (5.71)–(5.73), (b) third virial coefficient from Eq. (5.78), (c) V^V from virial EOS truncated after second term using Eqs. (5.65) and (5.66), (d) V^V from virial EOS truncated after third term using Eqs. (5.65) and (5.66), and (e) V^V from ideal gas law.

Solution—(a) and (b): For propane from Table 2.1 we get $T_c = 96.7^\circ\text{C}$ (369.83 K), $P_c = 42.48 \text{ bar}$, and $\omega = 0.1523$. $T_r = 0.811$, $P_r = 0.23$, and $R = 83.14 \text{ cm}^3 \cdot \text{bar}/\text{mol} \cdot \text{K}$. Second virial coefficient, B , can be estimated from Eqs. (5.71) or (5.72) or (5.73) and the third virial coefficient from Eq. (5.78). Results are given in Table 5.6. (c) Truncated virial equation after second term from Eq. (5.65) is $Z = 1 + B/V$, which is referred to as V expansion form, and from Eq. (5.66) is $Z = 1 + BP/RT$, which is the same as Eq. (5.75) and it is referred to as P expansion form. For the V expansion (Eq. 5.65), V should be calculated through successive substitution method or from mathematical solution of the equation, while in P expansion form (Eq. 5.66) Z can be directly calculated from T and P . Once Z is determined, V is calculated from Eq. (5.15): $V = ZRT/P$. In part (d) virial equation is truncated after the third term. The V expansion form reduces to Eq. (5.76). Summary of calculations for molar volume is given in Table 5.6. The results from V expansion (Eq. 5.65) and P expansion (5.66) do not agree with each other; however, the difference between these two forms of virial equation reduces as the number of terms increases. When the number of terms becomes infinity (complete equation), then the two forms of virial equation give identical results for V . Obviously for truncated virial equation, the V expansion form, Eq. (5.65), gives more accurate result for V as the virial coefficients are originally determined from this equation. As can be seen from Table 5.6, when B is calculated from Eq. (5.71) better

TABLE 5.6—Prediction of molar volume of propane at 300 K and 9.974 bar from virial equation with different methods for second virial coefficient (Example 5.5).

Method of estimation of second virial coefficient (B)	B , cm^3/mol	Virial equation with two terms				Virial equation with three terms ^a			
		P expansion ^b		V expansion ^c		P expansion ^d		V expansion ^e	
		V , cm^3/mol	%D	V , cm^3/mol	%D	V , cm^3/mol	%D	V , cm^3/mol	%D
Tsonopoulos (Eq. 5.71)	−390.623	2110.1	3.6	2016.2	−1.0	2056.8	1.0	2031.6	−0.2
Normal fluids (Eq. 5.72)	−397.254	2103.5	3.3	2005.3	−1.5	2048.1	0.6	2021.0	−0.7
McGlashan (Eq. 5.73)	−360.705	2140.0	5.1	2077.8	2.0	2095.7	2.9	2063.6	1.3

The experimental value of vapor molar volume is: $V = 2036.5 \text{ cm}^3/\text{mol}$ (Ref. [8], p. 4.24).

^aIn all calculations with three terms, the third virial coefficient C is calculated from Eq. (5.78) as $C = 19406.21 \text{ cm}^6/\text{mol}^2$.

^bTruncated two terms (P expansion) refers to pressure expansion virial equation (Eq. 5.66) truncated after second term (Eq. 5.75): $Z = 1 + BP/RT$.

^cTruncated two terms (V expansion) refers to volume expansion virial equation (Eq. 5.65) truncated after second term: $Z = 1 + B/V$.

^dTruncated three terms (P expansion) refers to pressure expansion virial equation (Eq. 5.66) truncated after third term: $Z = 1 + BP/RT + (C - B^2)P^2/(RT)^2$.

^eTruncated three terms (V expansion) refers to volume expansion virial equation (Eq. 5.65) truncated after third term (Eq. 5.76): $Z = 1 + B/V + C/V^2$.

TABLE 5.7—Coefficients for the BWRS EOS—Eq. (5.89) [21].

$B_0/V_c = 0.44369 + 0.115449\omega$	$E_0/(RT_c^5 V_c) = 0.00645 - 0.022143\omega \times \exp(-3.8\omega)$	$d/(RT_c^2 V_c^2) = 0.0732828 + 0.463492\omega$
$A_0/(RT_c V_c) = 1.28438 - 0.920731\omega$		$\alpha/V_c^3 = 0.0705233 - 0.044448\omega$
$C_0/(RT_c^3 V_c) = 0.356306 + 1.7087\omega$	$b/(V_c^2) = 0.528629 + 0.349261\omega$	$c/(RT_c^3 V_c^2) = 0.504087 + 1.32245\omega$
$D_0/(RT_c^4 V_c) = 0.0307452 + 0.179433\omega$	$a/(RT_c V_c^2) = 0.484011 + 0.75413\omega$	$\gamma/V_c^2 = 0.544979 - 0.270896\omega$

predictions are obtained. Equation (5.72) also gives reasonable results but Eq. (5.73) gives a less accurate estimate of B . The best result is obtained from Eq. (5.76) with Eqs. (5.71) and (5.78), which give a deviation of 0.2%. (e) The ideal gas law ($Z = 1$) gives $V^V = 2500.7 \text{ cm}^3/\text{mol}$ with a deviation of +22.8%. ♦

5.6.2 Modified Benedict–Webb–Rubin Equation of State

Another important EOS that has industrial application is the Benedict–Webb–Rubin (BWR) EOS [45]. This equation is in fact an empirical expansion of virial equation. A modification of this equation by Starling [46] has found successful applications in petroleum and natural gas industries for properties of light hydrocarbons and it is given as

$$(5.89) \quad P = RT \frac{1}{V} + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right) \frac{1}{V^2} + \left(b RT - a - \frac{d}{T} \right) \frac{1}{V^3} + \alpha \left(a + \frac{d}{T} \right) \frac{1}{V^6} + \frac{c}{T^2 V^3} \left(1 + \frac{\gamma}{V^2} \right) \exp \left(\frac{-\gamma}{V^2} \right)$$

where the 11 constants $A_0, B_0, \dots, a, b, \dots, \alpha$ and γ are given in Table 5.7 in terms of V_c, T_c , and ω as reported in Ref. [21]. This equation is known as BWRS EOS and may be used for calculation of density of light hydrocarbons and reservoir fluids. In the original BWR EOS, constants D_0, E_0 , and d were all zero and the other constants were determined for each specific compound separately. Although better volumetric data can be obtained from BWRS than from cubic-type equations, but prediction of phase equilibrium from cubic equations are quite comparable in some cases (depending on the mixing rules used) or better than this equation in some other cases. Another problem with the BWRS equation is large computation time and mathematical inconvenience to predict various physical properties. To find molar volume V from Eq. (5.89), a successive substitutive method is required. However, as it will be discussed in the next section, this type of equations can be used to develop generalized correlations in the graphical or tabulated forms for prediction of various thermophysical properties.

5.6.3 Carnahan–Starling Equation of State and Its Modifications

Equations of state are mainly developed based on the understanding of intermolecular forces and potential energy functions that certain fluids follow. For example, for hard sphere fluids where the potential energy function is given by Eq. (5.13) it is assumed that there are no attractive forces. For such fluids, Carnahan and Starling proposed an EOS that has been used extensively by researchers for development of more accurate EOS [6]. For hard sphere fluids, the smallest possible

volume that be can occupied by N molecules of diameter σ is

$$(5.90) \quad V_{oN} = N \left(\frac{V_o}{N_A} \right) \\ V_o = \left(\frac{1}{\sqrt{2}} \sigma^3 \right) N_A$$

where N_A is the Avogadro's number and V_o is the volume of 1 mol (N_A molecules) of hard spheres as packed molecules without empty space between the molecules. V_{oN} is the total volume of packed N molecules. If the molar volume of fluid is V , then a dimensionless reduced density, ξ , is defined in the following form:

$$(5.91) \quad \xi = \left(\frac{\sqrt{2}}{6} \pi \right) \times \left(\frac{V_o}{V} \right)$$

Parameter ξ is also known as *packing fraction* and indicates fraction of total volume occupied by hard molecules. Substituting V_o from Eq. (5.90) into Eq. (5.91) gives the following relation for packing fraction:

$$(5.92) \quad \xi = \left(\frac{\pi}{6} \right) \times \left(\frac{N_A \sigma^3}{V} \right)$$

The Carnahan–Starling EOS is then given as [6]

$$(5.93) \quad Z^{\text{HS}} = \frac{PV}{RT} = \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3}$$

where Z^{HS} is the compressibility factor for hard sphere molecules. For this EOS there is no binary constant and the only parameter needed is molecular diameter σ for each molecule. It is clear that as $V \rightarrow \infty$ ($P \rightarrow 0$) from Eq. (5.93) $\xi \rightarrow 0$ and $Z^{\text{HS}} \rightarrow 1$, which is in fact identical to the ideal gas law. Carnahan and Starling extended the HS equation to fluids whose spherical molecules exert attractive forces and suggested two equations based on two different attractive terms [6]:

$$(5.94) \quad Z = Z^{\text{HS}} - \frac{a}{RTV}$$

and

$$(5.95) \quad Z = Z^{\text{HS}} - \frac{a}{RT} (V - b)^{-1} T^{-1/2}$$

where Z^{HS} is the hard sphere contribution given by Eq. (5.93). Obviously Eq. (5.94) is a two-parameter EOS (a, σ) and Eq. (5.95) is a three-parameter EOS (a, b, σ). Both Eqs. (5.94) and (5.95) reduce to ideal gas law ($Z \rightarrow Z^{\text{HS}} \rightarrow 1$) as $V \rightarrow \infty$ (or $P \rightarrow 0$), which satisfies Eq. (5.18). For mixtures, the quadratic mixing rule can be used for parameter a while a linear rule can be applied to parameter b . Application of these equations for mixtures has been discussed in recent references [8, 47]. Another modification of CS EOS is through LJ EOS in the following form [48, 49]:

$$(5.96) \quad Z = Z^{\text{HS}} - \frac{32\epsilon\xi}{3k_B T}$$

where ε is the molecular energy parameter and ζ (see Eq. 5.92) is related to σ the size parameter. ε and σ are two parameters in the LJ potential (Eq. 5.11) and k_B is the Boltzman constant. One advanced noncubic EOS, which has received significant attention for property calculations specially derived properties (i.e., heat capacity, sonic velocity, etc.), is that of SAFT originally proposed by Chapman et al. [50] and it is given in the following form [47]:

$$(5.97) \quad Z^{\text{SAFT}} = 1 + Z^{\text{HS}} + Z^{\text{CHAIN}} + Z^{\text{DISP}} + Z^{\text{ASSOC}}$$

where HS, CHAIN, DISP, and ASSOC refer to contributions from hard sphere, chain formation molecule, dispersion, and association terms. The relations for Z^{HS} and Z^{CHAIN} are simple and are given in the following form [47]:

$$(5.98) \quad Z^{\text{SAFT}} = 1 + r \left[\frac{4\xi - 2\xi^2}{(1 - \xi)^3} \right] + (1 - r) \left[\frac{5\xi - 2\xi^2}{(1 - \xi)(2 - \xi)} \right] + Z^{\text{DISP}} + Z^{\text{ASSOC}}$$

where r is a specific parameter characteristic of the substance of interest. ξ in the above relation is segment packing fraction and is equal to ζ from Eq. (5.92) multiplied by r . The relations for Z^{DISP} and Z^{ASSOC} are more complex and are in terms of summations with adjusting parameters for the effects of association. There are other forms of SAFT EOS. A more practical, but much more complex, form of SAFT equation is given by Li and Englezos [51]. They show application of SAFT EOS to calculate phase behavior of systems containing associating fluids such as alcohol and water. SAFT EOS does not require critical constants and is particularly useful for complex molecules such as very heavy hydrocarbons, complex petroleum fluids, water, alcohol, ionic, and polymeric systems. Parameters can be determined by use of vapor pressure and liquid density data. Further characteristics and application of these equations are given by Prausnitz et al. [8, 47]. In the next chapter, the CS EOS will be used to develop an EOS based on the velocity of sound.

5.7 CORRESPONDING STATE CORRELATIONS

One of the simplest forms of an EOS is the two-parameter RK EOS expressed by Eq. (5.38). This equation can be used for fluids that obey a two-parameter potential energy relation. In fact this equation is quite accurate for simple fluids such as methane. Rearrangement of Eq. (5.38) through multiplying both sides of the equation by V/RT and substituting parameters a and b from Table 5.1 gives the following relation in terms of dimensionless variables [1]:

$$(5.99) \quad Z = \frac{1}{1 - h} - \frac{4.934}{T_r^{1.5}} \left(\frac{h}{1 + h} \right) \quad \text{where } h \equiv \frac{0.08664P_r}{ZT_r}$$

where T_r and P_r are called *reduced temperature* and *reduced pressure* and are defined as:

$$(5.100) \quad T_r \equiv \frac{T}{T_c} \quad P_r \equiv \frac{P}{P_c}$$

where T and T_c must be in absolute degrees (K), similarly P and P_c must be in absolute pressure (bar). Both T_r and P_r are dimensionless and can be used to express temperature and

pressure variations from the critical point. By substituting parameter h into the first equation in Eq. (5.99) one can see that

$$(5.101) \quad Z = f(T_r, P_r)$$

This equation indicates that for all fluids that obey a two-parameter EOS, such as RK, the compressibility factor, Z , is the only function of T_r and P_r . This means that at the critical point where $T_r = P_r = 1$, the critical compressibility factor, Z_c , is constant and same for all fluids (0.333 for RK EOS). As can be seen from Table 2.1, Z_c is constant only for simple fluids such as N_2 , CH_4 , O_2 , or Ar, which have Z_c of 0.29, 0.286, 0.288, and 0.289, respectively. For this reason RK EOS is relatively accurate for such fluids. Equation (5.101) is the fundamental of *corresponding states principle* (CSP) in classical thermodynamics. A correlation such as Eq. (5.101) is also called *generalized correlation*. In this equation only two parameters (T_c and P_c) for a substance are needed to determine its PVT relation. These types of relations are usually called two-parameter *corresponding states correlations* (CSC). The functionality of function f in Eq. (5.101) can be determined from experimental data on PVT and is usually expressed in graphical forms rather than mathematical equations. The most widely used two-parameter CSC in a graphical form is the Standing-Katz generalized chart that is developed for natural gases [52]. This chart is shown in Fig. 5.12 and is widely used in the petroleum industry [19, 21, 53, 54]. Obviously this chart is valid for light hydrocarbons whose acentric factor is very small such as methane and ethane, which are the main components of natural gases.

Hall and Yarborough [55] presented an EOS that was based on data obtained from the Standing and Katz Z -factor chart. The equation was based on the Carnahan-Starling equation (Eq. 5.93), and it is useful only for calculation of Z -factor of light hydrocarbons and natural gases. The equation is in the following form:

$$(5.102) \quad Z = 0.06125P_rT_r^{-1}y^{-1} \exp \left[-1.2(1 - T_r^{-1})^2 \right]$$

where T_r and P_r are reduced temperature and pressure and y is a dimensionless parameter similar to parameter ξ defined in Eq. (5.91). Parameter y should be obtained from solution of the following equation:

$$(5.103) \quad F(y) = -0.06125P_rT_r^{-1} \exp \left[-1.2(1 - T_r^{-1})^2 \right] + \frac{y + y^2 + y^3 - y^4}{(1 - y)^3} - (14.76T_r^{-1} - 9.76T_r^{-2} + 4.58T_r^{-3})y^2 + (90.7T_r^{-1} - 242.2T_r^{-2} + 42.4T_r^{-3})y^{(2.18+2.82T_r^{-1})} = 0$$

The above equation can be solved by the Newton-Raphson method. To find y an initial guess is required. An approximate relation to find the initial guess is obtained at $Z = 1$ in Eq. (5.102):

$$(5.104) \quad y^{(k)} = 0.06125P_rT_r^{-1} \exp \left[-1.2(1 - T_r^{-1})^2 \right]$$

Substituting $y^{(k)}$ in Eq. (5.103) gives $F^{(k)}$, which must be used in the following relation to obtain a new value of y :

$$(5.105) \quad y^{(k+1)} = y^{(k)} - \frac{F^{(k)}}{\frac{dF^{(k)}}{dy}}$$

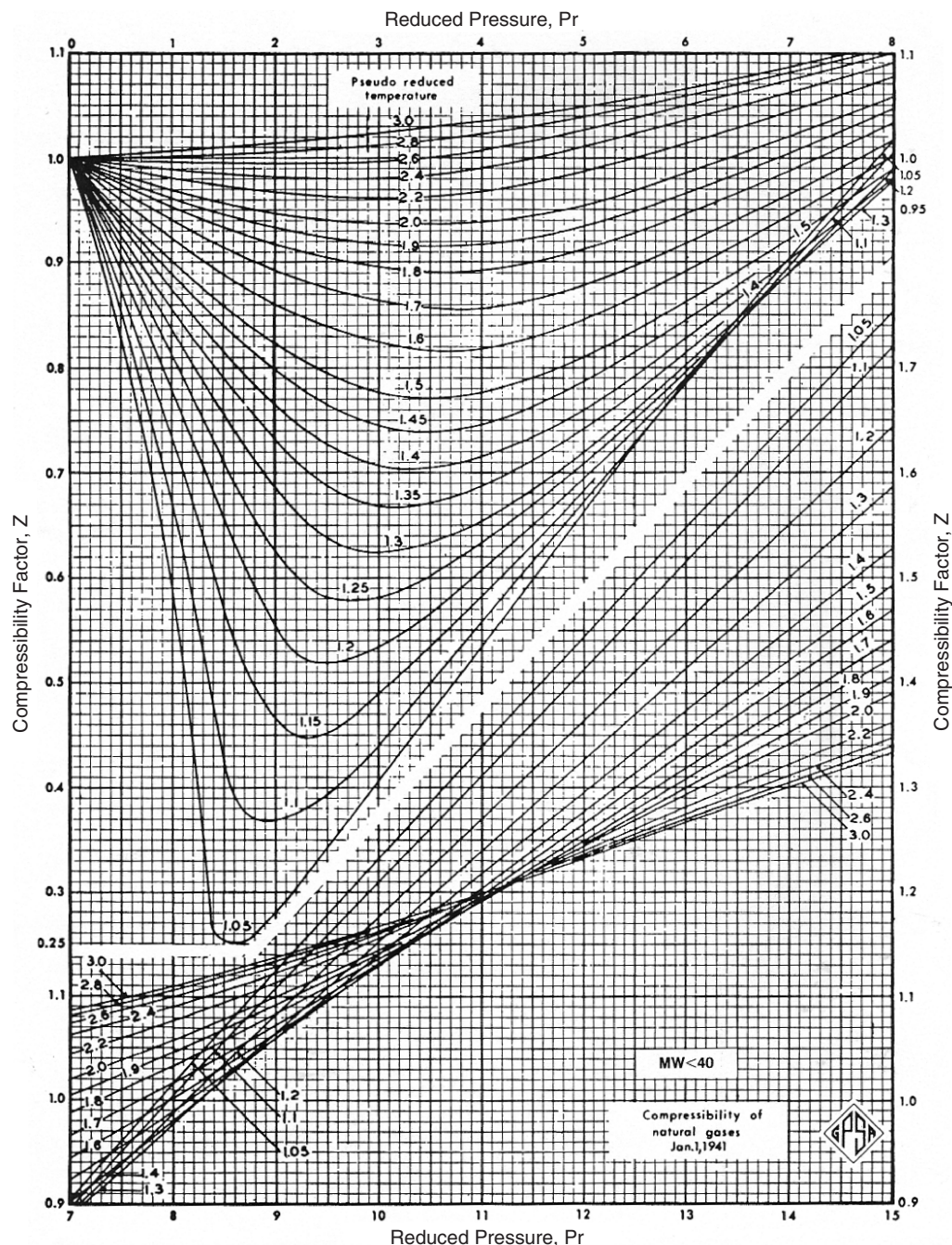


FIG. 5.12—Standing-Katz generalized chart for compressibility factor of natural gases (courtesy of GPSA and GPA [53]).

where $dF^{(k)}/dy$ is the derivative of F with respect to y at $y = y^{(k)}$ and it is given by the following relation:

$$\begin{aligned} \frac{dF}{dy} = & \frac{1 + 4y + 4y^2 - 4y^3 + y^4}{(1 - y)^4} \\ & - (29.52T_r^{-1} - 19.52T_r^{-2} + 9.16T_r^{-3})y \\ & + (2.18 + 2.82T_r^{-1}) \times (90.7T_r^{-1} - 242.2T_r^{-2} + 42.4T_r^{-3}) \\ & \times y^{(2.18+2.82T_r^{-1})} \end{aligned} \quad (5.106)$$

Calculations must be continued until the difference between $y^{(k+1)} - y^{(k)}$ becomes smaller than a tolerance (e.g., 10^{-10}).

As mentioned before, the Standing-Katz chart or its equivalent Hall-Yarborough correlation is applicable only to light hydrocarbons and they are not suitable to heavier fluids such as gas condensates, ω of which is not near zero. For this reason a modified version of two-parameter CSC is needed. As it can be seen from Table 2.1, for more complex compounds, value of Z_c decreases from those for simple fluids and Eq. (5.101) with constant Z_c is no longer valid. A parameter that indicates complexity of molecules is acentric factor that was defined by Eq. (2.10). Acentric factor, ω , is defined in a way

that for simple fluids it is zero or very small. For example, N_2 , CH_4 , O_2 , or Ar have acentric factors of 0.025, 0.011, 0.022, and 0.03, respectively. Values of ω increase with complexity of molecules. In fact as shown in Section 2.5.3, Z_c can be correlated to ω and both indicate deviation from simple fluids. Acentric factor was originally introduced by Pitzer [56, 57] to extend application of two-parameter CSC to more complex fluids. Pitzer and his coworkers realized the linear relation between Z_c and ω (i.e., see Eq. (2.103)) and assumed that such linearity exists between ω and Z at temperatures other than T_c . They introduced the concept of three-parameter corresponding states correlations in the following form:

$$(5.107) \quad Z = Z^{(0)} + \omega Z^{(1)}$$

where both $Z^{(0)}$ and $Z^{(1)}$ are functions of T_r and P_r . For simple fluids ($\omega \cong 0$), this equation reduces to Eq. (5.101). $Z^{(0)}$ is the contribution of simple fluids and $Z^{(1)}$ is the correction term for complex fluids. It can be shown that as $P \rightarrow 0$, $Z^{(0)} \rightarrow 1$ while $Z^{(1)} \rightarrow 0$, therefore, $Z \rightarrow 1$. The original three-parameter CSC developed by Pitzer was in the form of two graphs similar to Fig. (5.12): one for $Z^{(0)}$ and the other for $Z^{(1)}$, both in terms of T_r and P_r . Pitzer correlations found wide application and were extended to other thermodynamic properties. They were in use for more than two decades; however, they were found to be inaccurate in the critical region and for liquids at low temperatures [58].

The most advanced and accurate three-parameter corresponding states correlations were developed by Lee and Kesler [58] in 1975. They expressed Z in terms of values of Z for two fluids: simple and a reference fluid assuming linear relation between Z and ω as follows:

$$(5.108) \quad Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}} (Z^{(r)} - Z^{(0)})$$

where $Z^{(r)}$ and $\omega^{(r)}$ represent compressibility factor and acentric factor of the reference fluid. A comparison between Eqs. (5.107) and (5.108) indicates that $[Z^{(r)} - Z^{(0)}]/\omega^{(r)}$ is equivalent to $Z^{(1)}$. The simple fluid has acentric factor of zero, but the reference fluid should have the highest value of ω to cover a wider range for application of the correlation. However, the choice of reference fluid is also limited by availability of PVT and other thermodynamic data. Lee and Kesler chose *n*-octane with ω of 0.3978 (this number is slightly different from the most recent value of 0.3996 given in Table 2.1) as the reference fluid. The same EOS was used for both the simple and reference fluid, which is a modified version of BWR EOS as given in the following reduced form:

$$(5.109) \quad Z = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^3} + \frac{c_4}{T_r^3 V_r^2} \left(\beta + \frac{\gamma}{V_r^2} \right) \exp \left(\frac{-\gamma}{V_r^2} \right)$$

where V_r is the reduced volume defined as

$$(5.110) \quad V_r = \frac{V}{V_c}$$

Coefficients B , C , and D are temperature-dependent as

$$(5.111) \quad B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \quad C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \quad D = d_1 + \frac{d_2}{T_r}$$

TABLE 5.8—Constants for the Lee-Kesler modification of BWR EOS—Eq. (5.109) [58].

Constant	Simple fluid	Reference fluid
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0.0	0.016901
c_4	0.042724	0.041577
$d_1 \times 10^4$	0.155488	0.48736
$d_2 \times 10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754

In determining the constants in these equations the constraints by Eq. (5.9) and equality of chemical potentials or fugacity (Eq. 6.104) between vapor and liquid at saturated conditions were imposed. These coefficients for both simple and reference fluids are given in Table 5.8.

In using Eq. (5.108), both $Z^{(0)}$ and $Z^{(r)}$ should be calculated from Eq. (5.109). Lee and Kesler also tabulated values of $Z^{(0)}$ and $Z^{(1)}$ versus T_r and P_r for use in Eq. (5.107). The original Lee-Kesler (LK) tables cover reduced pressure from 0.01 to 10. These tables have been widely used in major texts and references [1, 8, 59]. However, the API-TDB [59] gives extended tables for $Z^{(0)}$ and $Z^{(1)}$ for the P_r range up to 14. Lee-Kesler tables and their extension by the API-TDB are perhaps the most accurate method of estimating PVT relation for gases and liquids. Values of $Z^{(0)}$ and $Z^{(1)}$ as given by LK and their extension by API-TDB are given in Tables 5.9–5.11. Table 5.11 give values of $Z^{(0)}$ and $Z^{(1)}$ for $P_r > 10$ as provided in the API-TDB [59]. In Tables 5.9 and 5.10 the dotted lines separate liquid and vapor phases from each other up to the critical point. Values above and to the right are for liquids and below and to the left are gases. The values for liquid phase are highlighted with bold numbers. Graphical representations of these tables are given in the API-TDB [59]. For computer applications, Eqs. (5.108)–(5.111) should be used with coefficients given in Table 5.8. Graphical presentation of $Z^{(0)}$ and $Z^{(1)}$ versus P_r and T_r with specified liquid and vapor regions is shown in Fig. 5.13. The two-phase region as well as saturated curves are also shown in this figure. For gases, as $P_r \rightarrow 0$, $Z^{(0)} \rightarrow 1$ and $Z^{(1)} \rightarrow 0$. It is interesting to note that at the critical point ($T_r = P_r = 1$), $Z^{(0)} = 0.2901$, and $Z^{(1)} = -0.0879$, which after substitution into Eq. (5.107) gives the following relation for Z_c :

$$(5.112) \quad Z_c = 0.2901 - 0.0879\omega$$

This equation is slightly different from Eq. (2.93) and gives different values of Z_c for different compounds. Therefore, in the critical region the LK correlations perform better than cubic equations, which give a constant value for Z_c of all compounds. Graphical presentations of both $Z^{(0)}$ and $Z^{(1)}$ for calculation of Z from Eq. (5.107) are given in other sources [60].

For the low-pressure region where the truncated virial equation can be used, Eq. (5.75) may be written in a generalized dimensionless form as

$$(5.113) \quad Z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_c}{RT_c} \right) \frac{P_r}{T_r}$$

TABLE 5.9—Values of $Z^{(0)}$ for use in Eq. (5.107) from the Lee-Kesler modification of BWR EOS (Eq. 5.109) [58].

$T_r \rightarrow$	0.01	0.05	0.1	0.2	0.4	0.6	0.8	1	1.2	1.5	2	3	5	7	10
0.30	0.0029	0.0145	0.0290	0.0579	0.1158	0.1737	0.2315	0.2892	0.3479	0.4335	0.5775	0.8648	1.4366	2.0048	2.8507
0.35	0.0026	0.0130	0.0261	0.0522	0.1043	0.1564	0.2084	0.2604	0.3123	0.3901	0.5195	0.7775	1.2902	1.7987	2.5539
0.40	0.0024	0.0119	0.0239	0.0477	0.0953	0.1429	0.1904	0.2379	0.2853	0.3563	0.4744	0.7095	1.1758	1.6373	2.3211
0.45	0.0022	0.0110	0.0221	0.0442	0.0882	0.1322	0.1762	0.2200	0.2638	0.3294	0.4384	0.6551	1.0841	1.5077	2.1338
0.50	0.0021	0.0103	0.0207	0.0413	0.0825	0.1236	0.1647	0.2056	0.2465	0.3077	0.4092	0.6110	1.0094	1.4017	1.9801
0.55	0.9804	0.0098	0.0195	0.0390	0.0778	0.1166	0.1553	0.1939	0.2323	0.2899	0.3853	0.5747	0.9475	1.3137	1.8520
0.60	0.9849	0.0093	0.0186	0.0371	0.0741	0.1109	0.1476	0.1842	0.2207	0.2753	0.3657	0.5446	0.8959	1.2398	1.7440
0.65	0.9881	0.9377	0.0178	0.0356	0.0710	0.1063	0.1415	0.1765	0.2113	0.2634	0.3495	0.5197	0.8526	1.1773	1.6519
0.70	0.9904	0.9504	0.8958	0.0344	0.0687	0.1027	0.1366	0.1703	0.2038	0.2538	0.3364	0.4991	0.8161	1.1341	1.5729
0.75	0.9922	0.9598	0.9165	0.0336	0.0670	0.1001	0.1330	0.1656	0.1981	0.2464	0.3260	0.4823	0.7854	1.0787	1.5047
0.80	0.9935	0.9669	0.9319	0.8539	0.0661	0.0985	0.1307	0.1626	0.1942	0.2411	0.3182	0.4690	0.7598	1.0400	1.4456
0.85	0.9946	0.9725	0.9436	0.8810	0.0661	0.0983	0.1301	0.1614	0.1924	0.2382	0.3132	0.4591	0.7388	1.0071	1.3943
0.90	0.9954	0.9768	0.9528	0.9015	0.7800	0.1006	0.1321	0.1630	0.1935	0.2383	0.3114	0.4527	0.7220	0.9793	1.3496
0.93	0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	0.1359	0.1664	0.1963	0.2405	0.3122	0.4507	0.7138	0.9648	1.3257
0.95	0.9961	0.9803	0.9600	0.9174	0.8206	0.6967	0.1410	0.1705	0.1998	0.2432	0.3138	0.4501	0.7092	0.9561	1.3108
0.97	0.9963	0.9815	0.9625	0.9227	0.8338	0.7240	0.5580	0.1779	0.2055	0.2474	0.3164	0.4504	0.7052	0.9480	1.2968
0.98	0.9965	0.9821	0.9637	0.9253	0.8398	0.7360	0.5887	0.1844	0.2097	0.2503	0.3182	0.4508	0.7035	0.9442	1.2901
0.99	0.9966	0.9826	0.9648	0.9277	0.8455	0.7471	0.6138	0.1959	0.2154	0.2538	0.3204	0.4514	0.7018	0.9406	1.2835
1.00	0.9967	0.9832	0.9659	0.9300	0.8509	0.7574	0.6355	0.2901	0.2237	0.2583	0.3229	0.4522	0.7004	0.9372	1.2772
1.01	0.9968	0.9837	0.9669	0.9322	0.8561	0.7671	0.6542	0.4648	0.2370	0.2640	0.3260	0.4533	0.6991	0.9339	1.2710
1.02	0.9969	0.9842	0.9679	0.9343	0.8610	0.7761	0.6710	0.5146	0.2629	0.2715	0.3297	0.4547	0.6980	0.9307	1.2650
1.05	0.9971	0.9855	0.9707	0.9401	0.8743	0.8002	0.7130	0.6026	0.4437	0.3131	0.3452	0.4604	0.6956	0.9222	1.2481
1.10	0.9975	0.9874	0.9747	0.9485	0.8930	0.8323	0.7649	0.6880	0.5984	0.4580	0.3953	0.4770	0.6950	0.9110	1.2232
1.15	0.9978	0.9891	0.9780	0.9554	0.9081	0.8576	0.8032	0.7443	0.6803	0.5798	0.4760	0.5042	0.6987	0.9033	1.2021
1.20	0.9981	0.9904	0.9808	0.9611	0.9205	0.8779	0.8330	0.7858	0.7363	0.6605	0.5605	0.5425	0.7069	0.8990	1.1844
1.30	0.9985	0.9926	0.9852	0.9702	0.9396	0.9083	0.8764	0.8438	0.8111	0.7624	0.6908	0.6344	0.7358	0.8998	1.1580
1.40	0.9988	0.9942	0.9884	0.9768	0.9534	0.9298	0.9062	0.8827	0.8595	0.8256	0.7753	0.7202	0.7761	0.9112	1.1419
1.50	0.9991	0.9954	0.9909	0.9818	0.9636	0.9456	0.9278	0.9103	0.8933	0.8689	0.8328	0.7887	0.8200	0.9297	1.1339
1.60	0.9993	0.9964	0.9928	0.9856	0.9714	0.9575	0.9439	0.9308	0.9180	0.9000	0.8738	0.8410	0.8617	0.9518	1.1320
1.70	0.9994	0.9971	0.9943	0.9886	0.9775	0.9667	0.9563	0.9463	0.9367	0.9234	0.9043	0.8809	0.8984	0.9745	1.1343
1.80	0.9995	0.9977	0.9955	0.9910	0.9823	0.9739	0.9659	0.9583	0.9511	0.9413	0.9275	0.9118	0.9297	0.9961	1.1391
1.90	0.9996	0.9982	0.9964	0.9929	0.9861	0.9796	0.9735	0.9678	0.9624	0.9552	0.9456	0.9359	0.9557	1.0157	1.1452
2.00	0.9997	0.9986	0.9972	0.9944	0.9892	0.9842	0.9796	0.9754	0.9715	0.9664	0.9599	0.9550	0.9772	1.0328	1.1516
2.20	0.9998	0.9992	0.9983	0.9967	0.9937	0.9910	0.9886	0.9865	0.9847	0.9826	0.9806	0.9827	1.0094	1.0600	1.1635
2.40	0.9999	0.9996	0.9991	0.9983	0.9969	0.9957	0.9948	0.9941	0.9936	0.9935	0.9945	1.0011	1.0313	1.0793	1.1728
2.60	1.0000	0.9998	0.9997	0.9994	0.9991	0.9990	0.9990	0.9993	0.9998	1.0010	1.0040	1.0137	1.0463	1.0926	1.1792
2.80	1.0000	1.0000	1.0001	1.0002	1.0007	1.0013	1.0021	1.0031	1.0042	1.0063	1.0106	1.0223	1.0565	1.1016	1.1830
3.00	1.0000	1.0002	1.0004	1.0008	1.0018	1.0030	1.0043	1.0057	1.0074	1.0101	1.0153	1.0284	1.0635	1.1075	1.1848
3.50	1.0001	1.0004	1.0008	1.0017	1.0035	1.0055	1.0075	1.0097	1.0120	1.0156	1.0221	1.0368	1.0723	1.1138	1.1834
4.00	1.0001	1.0005	1.0010	1.0021	1.0043	1.0066	1.0090	1.0115	1.0140	1.0179	1.0249	1.0401	1.0747	1.1136	1.1773

where BP_c/RT_c can be estimated from Eq. (5.71) or (5.72) through T_r and ω . Equation (5.114) may be used at low P_r and $V_r > 2$ or $T_r > 0.686 + 0.439P_r$ [60] instead of complex Eqs. (5.108)–(5.111). The API-TDB [59] also recommends the following relation, proposed by Pitzer et al. [56], for calculation of Z for gases at $P_r \leq 0.2$.

$$Z = 1 + \frac{P_r}{T_r} [(0.1445 + 0.073\omega) - (0.33 - 0.46\omega)T_r^{-1} - (0.1385 + 0.5\omega)T_r^{-2} - (0.0121 + 0.097\omega)T_r^{-3} - 0.0073\omega T_r^{-8}] \quad (5.114)$$

Obviously neither Eq. (5.113) nor (5.114) can be applied to liquids.

The LK corresponding states correlations expressed by Eq. (5.107) and Tables 5.9–5.11 can also be applied to mixtures. Such correlations are sensitive to the input data for the pseudocritical properties. The mixing rules used to calculate mixture critical temperature and pressure may greatly affect calculated properties specially when the mixture contains dissimilar compounds. Lee and Kesler proposed special set of equations for mixtures for use with their correlations.

These equations are equivalent to the following equations as provided by the API-TDB [59].

$$\begin{aligned} V_{ci} &= Z_{ci} RT_{ci} / P_{ci} \\ Z_{ci} &= 0.2905 - 0.085\omega_i \\ V_{mc} &= \frac{1}{4} \left[\sum_{i=1}^N x_i V_{ci} + 3 \left(\sum_{i=1}^N x_i V_{ci}^{1/3} \right) \left(\sum_{i=1}^N x_i V_{ci}^{2/3} \right) \right] \\ T_{mc} &= \frac{1}{4V_{mc}} \left[\sum_{i=1}^N x_i V_{ci} T_{ci} + 3 \left(\sum_{i=1}^N x_i V_{ci}^{1/3} \sqrt{T_{ci}} \right) \left(\sum_{i=1}^N x_i V_{ci}^{2/3} \sqrt{T_{ci}} \right) \right] \\ \omega_m &= \sum_{i=1}^N x_i \omega_i \\ P_{mc} &= Z_{mc} RT_{mc} / V_{mc} = (0.2905 - 0.085\omega_m) RT_{mc} / V_{mc} \end{aligned} \quad (5.115)$$

where x_i is the mole fraction of component i , N is the number of compounds in the mixture, and T_{mc} , P_{mc} , and V_{mc} are the mixture pseudocritical temperature, pressure, and volume respectively. ω_m is the mixture acentric factor and it is calculated

TABLE 5.10—Values of $Z^{(1)}$ for use in Eq. (5.107) from the Lee-Kesler modification of BWR EOS—Eq. (5.109) [58].

$T_r \rightarrow$	0.01	0.05	0.1	0.2	0.4	0.6	0.8	1	1.2	1.5	2	3	5	7	10
0.30	-0.0008	-0.0040	-0.0081	-0.0161	-0.0323	-0.0484	-0.0645	-0.0806	-0.0966	-0.1207	-0.1608	-0.2407	-0.3996	-0.5572	-0.7915
0.35	-0.0009	-0.0046	-0.0093	-0.0185	-0.0370	-0.0554	-0.0738	-0.0921	-0.1105	-0.1379	-0.1834	-0.2738	-0.4523	-0.6279	-0.8863
0.40	-0.0010	-0.0048	-0.0095	-0.0190	-0.0380	-0.0570	-0.0758	-0.0946	-0.1134	-0.1414	-0.1840	-0.2799	-0.4603	-0.6365	-0.8936
0.45	-0.0009	-0.0047	-0.0094	-0.0187	-0.0374	-0.0560	-0.0745	-0.0929	-0.1113	-0.1387	-0.1840	-0.2734	-0.4475	-0.6162	-0.8606
0.50	-0.0009	-0.0045	-0.0090	-0.0181	-0.0360	-0.0539	-0.0716	-0.0893	-0.1069	-0.1330	-0.1762	-0.2611	-0.4253	-0.5831	-0.8099
0.55	-0.0314	-0.0043	-0.0086	-0.0172	-0.0343	-0.0513	-0.0682	-0.0849	-0.1015	-0.1263	-0.1669	-0.2465	-0.3991	-0.5446	-0.7521
0.60	-0.0205	-0.0041	-0.0082	-0.0164	-0.0326	-0.0487	-0.0646	-0.0803	-0.0960	-0.1192	-0.1572	-0.2312	-0.3718	-0.5047	-0.6928
0.65	-0.0137	-0.0072	-0.0078	-0.0156	-0.0309	-0.0461	-0.0611	-0.0759	-0.0906	-0.1122	-0.1476	-0.2160	-0.3447	-0.4653	-0.6346
0.70	-0.0093	-0.0507	-0.1161	-0.0148	-0.0294	-0.0438	-0.0579	-0.0718	-0.0855	-0.1057	-0.1385	-0.2013	-0.3184	-0.4270	-0.5785
0.75	-0.0064	-0.0339	-0.0744	-0.0143	-0.0282	-0.0417	-0.0550	-0.0681	-0.0808	-0.0996	-0.1298	-0.1872	-0.2929	-0.3901	-0.5250
0.80	-0.0044	-0.0228	-0.0487	-0.1160	-0.0272	-0.0401	-0.0526	-0.0648	-0.0767	-0.0940	-0.1217	-0.1736	-0.2682	-0.3545	-0.4740
0.85	-0.0029	-0.0152	-0.0319	-0.0715	-0.0268	-0.0391	-0.0509	-0.0622	-0.0731	-0.0888	-0.1138	-0.1602	-0.2439	-0.3201	-0.4254
0.90	-0.0019	-0.0099	-0.0205	-0.0442	-0.1118	-0.0396	-0.0503	-0.0604	-0.0701	-0.0840	-0.1059	-0.1463	-0.2195	-0.2862	-0.3788
0.93	-0.0015	-0.0075	-0.0154	-0.0326	-0.0763	-0.1662	-0.0514	-0.0602	-0.0687	-0.0810	-0.1007	-0.1374	-0.2045	-0.2661	-0.3516
0.95	-0.0012	-0.0062	-0.0126	-0.0262	-0.0589	-0.1110	-0.0540	-0.0607	-0.0678	-0.0788	-0.0967	-0.1310	-0.1943	-0.2526	-0.3339
0.97	-0.0010	-0.0050	-0.0101	-0.0208	-0.0450	-0.0770	-0.1647	-0.0623	-0.0669	-0.0759	-0.0921	-0.1240	-0.1837	-0.2391	-0.3163
0.98	-0.0009	-0.004	-0.0090	-0.0184	-0.0390	-0.0641	-0.1100	-0.0641	-0.0661	-0.0740	-0.0893	-0.1202	-0.1783	-0.2322	-0.3075
0.99	-0.0008	-0.0039	-0.0079	-0.0161	-0.0335	-0.0531	-0.0796	-0.0680	-0.0646	-0.0715	-0.0861	-0.1162	-0.1728	-0.2254	-0.2989
1.00	-0.0007	-0.0034	-0.0069	-0.0140	-0.0285	-0.0435	-0.0588	-0.0879	-0.0609	-0.0678	-0.0824	-0.1118	-0.1672	-0.2185	-0.290
1.01	-0.0006	-0.0030	-0.0060	-0.0120	-0.0240	-0.0351	-0.0429	-0.0223	-0.0473	-0.0621	-0.0778	-0.1072	-0.1615	-0.2116	-0.2816
1.02	-0.0005	-0.0026	-0.0051	-0.0102	-0.0198	-0.0277	-0.0303	-0.0062	-0.0227	-0.0324	-0.0432	-0.0524	-0.0722	-0.1021	-0.1556
1.05	-0.0003	-0.0015	-0.0029	-0.0054	-0.0092	-0.0097	-0.0032	0.0220	0.1059	0.0451	-0.0434	-0.0838	-0.1370	-0.1835	-0.2476
1.10	0.0000	0.0000	0.0001	0.0007	0.0038	0.0106	0.0236	0.0476	0.0897	0.1630	0.0698	-0.0373	-0.1021	-0.1469	-0.2056
1.15	0.0002	0.0011	0.0023	0.0052	0.0127	0.0237	0.0396	0.0625	0.0943	0.1548	0.1667	0.0332	-0.0611	-0.1084	-0.1642
1.20	0.0004	0.0019	0.0039	0.0084	0.0190	0.0326	0.0499	0.0719	0.0991	0.1477	0.1990	0.1095	-0.0141	-0.0678	-0.1231
1.30	0.0006	0.0030	0.0061	0.0125	0.0267	0.0429	0.0612	0.0819	0.1048	0.1420	0.1991	0.2079	0.0875	0.0176	-0.0423
1.40	0.0007	0.0036	0.0072	0.0147	0.0306	0.0477	0.0661	0.0857	0.1063	0.1383	0.1894	0.2397	0.1737	0.1008	0.0350
1.50	0.0008	0.0039	0.0078	0.0158	0.0323	0.0497	0.0677	0.0864	0.1055	0.1345	0.1806	0.2433	0.2309	0.1717	0.1058
1.60	0.0008	0.0040	0.0080	0.0162	0.0330	0.0501	0.0677	0.0855	0.1035	0.1303	0.1729	0.2381	0.2631	0.2255	0.1673
1.70	0.0008	0.0040	0.0081	0.0163	0.0329	0.0497	0.0667	0.0838	0.1008	0.1259	0.1658	0.2305	0.2788	0.2628	0.2179
1.80	0.0008	0.0040	0.0081	0.0162	0.0325	0.0488	0.0652	0.0814	0.0978	0.1216	0.1593	0.2224	0.2846	0.2871	0.2576
1.90	0.0008	0.0040	0.0079	0.0159	0.0318	0.0477	0.0635	0.0792	0.0947	0.1173	0.1532	0.2144	0.2848	0.3017	0.2876
2.00	0.0008	0.0039	0.0078	0.0155	0.0310	0.0464	0.0617	0.0767	0.0916	0.1133	0.1476	0.2069	0.2819	0.3097	0.3096
2.20	0.0007	0.0037	0.0074	0.0147	0.0293	0.0437	0.0579	0.0719	0.0857	0.1057	0.1374	0.1932	0.2720	0.3135	0.3355
2.40	0.0007	0.0035	0.0070	0.0139	0.0276	0.0411	0.0544	0.0675	0.0803	0.0989	0.1285	0.1812	0.2602	0.3089	0.3459
2.60	0.0007	0.0033	0.0066	0.0131	0.0260	0.0387	0.0512	0.0634	0.0754	0.0929	0.1207	0.1706	0.2484	0.3009	0.3475
2.80	0.0006	0.0031	0.0062	0.0124	0.0245	0.0365	0.0483	0.0598	0.0711	0.0876	0.1138	0.1613	0.2372	0.2915	0.3443
3.00	0.0006	0.0029	0.0059	0.0117	0.0232	0.0345	0.0456	0.0565	0.0672	0.0828	0.1076	0.1529	0.2268	0.2817	0.3385
3.50	0.0005	0.0026	0.0052	0.0103	0.0204	0.0303	0.0401	0.0497	0.0591	0.0728	0.0949	0.1356	0.2042	0.2584	0.3194
4.00	0.0005	0.0023	0.0046	0.0091	0.0182	0.0270	0.0357	0.0443	0.0527	0.0651	0.0849	0.1219	0.1857	0.2378	0.2994

TABLE 5.11—Values of $Z^{(0)}$ and $Z^{(1)}$ for use in Eq. (5.107) from the Lee–Kesler modification of BWR EOS—Eq. (5.109) [59].

$T_r \rightarrow P_r$	$Z^{(0)}$				$Z^{(1)}$			
↓	10	11	12	14	10	11	12	14
0.30	2.851	3.131	3.411	3.967	−0.792	−0.869	−0.946	−1.100
0.35	2.554	2.804	3.053	3.548	−0.886	−0.791	−1.056	−1.223
0.40	2.321	2.547	2.772	3.219	−0.894	−0.978	−1.061	−1.225
0.45	2.134	2.340	2.546	2.954	−0.861	−0.940	−1.019	−1.173
0.50	1.980	2.171	2.360	2.735	−0.810	−0.883	−0.955	−1.097
0.55	1.852	2.029	2.205	2.553	−0.752	−0.819	−0.885	−1.013
0.60	1.744	1.909	2.073	2.398	−0.693	−0.753	−0.812	−0.928
0.65	1.652	1.807	1.961	2.266	−0.635	−0.689	−0.742	−0.845
0.70	1.573	1.720	1.865	2.152	−0.579	−0.627	−0.674	−0.766
0.75	1.505	1.644	1.781	2.053	−0.525	−0.568	−0.610	−0.691
0.80	1.446	1.578	1.708	1.966	−0.474	−0.512	−0.549	−0.621
0.85	1.394	1.520	1.645	1.890	−0.425	−0.459	−0.491	−0.555
0.90	1.350	1.470	1.589	1.823	−0.379	−0.408	−0.437	−0.493
0.95	1.311	1.426	1.540	1.763	−0.334	−0.360	−0.385	−0.434
0.98	1.290	1.402	1.513	1.731	−0.308	−0.331	−0.355	−0.401
0.99	1.284	1.395	1.504	1.721	−0.299	−0.322	−0.345	−0.390
1.00	1.277	1.387	1.496	1.710	−0.290	−0.313	−0.335	−0.379
1.01	1.271	1.380	1.488	1.701	−0.282	−0.304	−0.326	−0.368
1.02	1.265	1.373	1.480	1.691	−0.273	−0.295	−0.316	−0.357
1.03	1.259	1.367	1.473	1.682	−0.265	−0.286	−0.307	−0.347
1.04	1.254	1.360	1.465	1.672	−0.256	−0.277	−0.297	−0.337
1.05	1.248	1.354	1.458	1.664	−0.248	−0.268	−0.288	−0.326
1.06	1.243	1.348	1.451	1.655	−0.239	−0.259	−0.278	−0.316
1.07	1.238	1.342	1.444	1.646	−0.231	−0.250	−0.269	−0.306
1.08	1.233	1.336	1.438	1.638	−0.222	−0.241	−0.260	−0.296
1.09	1.228	1.330	1.431	1.630	−0.214	−0.233	−0.251	−0.286
1.10	1.223	1.325	1.425	1.622	−0.206	−0.224	−0.242	−0.276
1.11	1.219	1.319	1.419	1.614	−0.197	−0.215	−0.233	−0.267
1.12	1.214	1.314	1.413	1.606	−0.189	−0.207	−0.224	−0.257
1.13	1.210	1.309	1.407	1.599	−0.181	−0.198	−0.215	−0.247
1.15	1.202	1.299	1.395	1.585	−0.164	−0.181	−0.197	−0.228
1.20	1.184	1.278	1.370	1.552	−0.123	−0.139	−0.154	−0.183
1.25	1.170	1.259	1.348	1.522	−0.082	−0.098	−0.112	−0.139
1.30	1.158	1.244	1.328	1.496	−0.042	−0.058	−0.072	−0.097
1.40	1.142	1.220	1.298	1.453	0.035	0.019	0.005	−0.019
1.50	1.134	1.205	1.276	1.419	0.106	0.090	0.076	0.052
1.60	1.132	1.197	1.262	1.394	0.167	0.152	0.138	0.116
1.70	1.134	1.193	1.253	1.374	0.218	0.204	0.192	0.171
1.80	1.139	1.192	1.247	1.359	0.258	0.247	0.237	0.218
2.00	1.152	1.196	1.243	1.339	0.310	0.305	0.300	0.290
2.50	1.176	1.210	1.244	1.316	0.348	0.356	0.362	0.371
3.00	1.185	1.213	1.241	1.300	0.338	0.353	0.365	0.385
3.50	1.183	1.208	1.233	1.284	0.319	0.336	0.350	0.376
4.00	1.177	1.200	1.222	1.268	0.299	0.316	0.332	0.360

High Pressure Range: Value of $Z^{(0)}$ and $Z^{(1)}$ for $10 \leq P_r \leq 14$.

similar to the Kay's mixing rule. Application of Kay's mixing rule, expressed by Eq. (3.45), gives the following relations for calculation of pseudocritical temperature and pressure:

$$(5.116) \quad T_{pc} = \sum_{i=1}^N x_i T_{ci} \quad P_{pc} = \sum_{i=1}^N x_i P_{ci}$$

where T_{pc} and P_{pc} are the pseudocritical temperature and pressure, respectively. Generally for simplicity pseudocritical properties are calculated from Eqs. (5.116); however, use of Eqs. (5.115) for the LK correlations gives better property predictions [59].

Example 5.6—Repeat Example 5.2 using LK generalized correlations to estimate V^V and V^L for n -octane at 279.5°C and 19.9 bar.

Solution—For n -octane, from Example 5.2, $T_c = 295.55^\circ\text{C}$ (568.7 K), $P_c = 24.9$ bar, $\omega = 0.3996$. $T_r = 0.972$, and $P_r = 0.8$. From Table 5.9 it can be seen that the point (0.972 and 0.8) is on the saturation line; therefore, there are both liquid and vapor phases at this condition and values of $Z^{(0)}$ and $Z^{(1)}$ are separated by dotted lines. For the liquid phase at $P_r = 0.8$, extrapolation of values of $Z^{(0)}$ at $T_r = 0.90$ and $T_r = 0.95$ to $T_r = 0.972$ gives $Z^{(0)} = 0.141 + [(0.972 - 0.93)/(0.95 - 0.93)] \times (0.141 - 0.1359) = 0.1466$, similarly we get $Z^{(1)} = -0.056$. Substituting $Z^{(0)}$ and $Z^{(1)}$ into Eq. (5.107) gives $Z^L = 0.1466 + 0.3996 \times (-0.056) = 0.1242$. Similarly for the vapor phase, values of $Z^{(0)}$ and $Z^{(1)}$ below the dotted line should be used. For this case linear interpolations between the values for $Z^{(0)}$ and $Z^{(1)}$ at $T_r = 0.97$ and $T_r = 0.98$ for the gas phase give $Z^{(0)} = 0.5642$, $Z^{(1)} = -0.1538$. From Eq. (5.107) we get $Z^V = 0.503$. From Eq. (5.15) corresponding volumes are $V^L = 286.8$ and

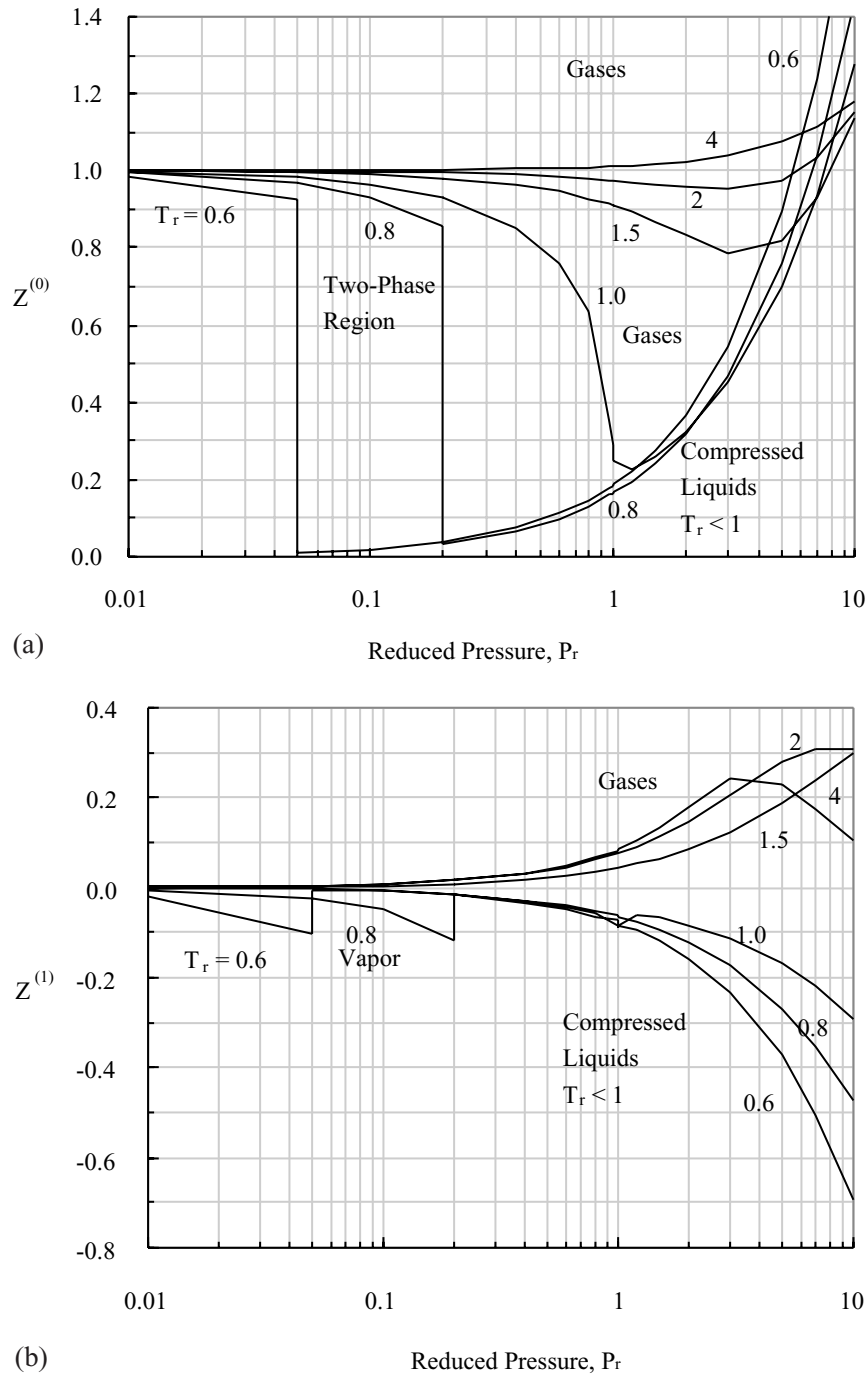


FIG. 5.13—Compressibility factor (a) $Z^{(0)}$ and (b) $Z^{(1)}$ from Tables 5.9 and 5.10.

$V^V = 1161.5 \text{ cm}^3/\text{mol}$, which give errors of -5.6 and -4.5% for the liquid and vapor volumes, respectively. ♦

The corresponding states correlation expressed by Eq. (5.107) is derived from principles of classical thermodynamics. However, the same theory can be derived from microscopic thermodynamics. Previously the relation between virial coefficients and intermolecular forces was shown through Eq. (5.67). From Eq. (5.11), Γ can be written in a

dimensionless form as

$$(5.117) \quad \frac{\Gamma}{\varepsilon} = f\left(\frac{\sigma}{r}\right)$$

which is the basis for the development of microscopic (molecular) theory of corresponding states. Substitution of Eq. (5.117) into Eq. (5.67) would result into a generalized correlation for the second virial coefficient [6].

5.8 GENERALIZED CORRELATION FOR PVT PROPERTIES OF LIQUIDS—RACKETT EQUATION

Although cubic EOS and generalized correlations discussed above can be used for both liquid and vapor phases, it was mentioned that their performance for the liquid phase is weak especially when they are used for liquid density predictions. For this reason in many cases separate correlations have been developed for properties of liquids. As can be seen from Fig. 5.1, the variation of P with V for an isotherm in the liquid phase is very steep and a small change in volume of liquid, a big change in pressure is needed. In addition it is seen from this figure that when the pressure is near the saturation pressure, liquid volume is very close to saturation volume. In this section the Rackett equation, which is widely used for prediction of saturated liquid densities, is introduced for pure substances and defined mixtures. Then the method of prediction of liquid densities at high pressures is presented.

5.8.1 Rackett Equation for Pure Component Saturated Liquids

If Eq. (5.6) is applied at the saturation pressure, P_r^{sat} we have

$$(5.118) \quad V_r^{\text{sat}} = f_1(T, P^{\text{sat}})$$

Since for any substance, P^{sat} depends only on temperature thus the above equation can be rearranged in a reduced form as

$$(5.119) \quad V_r^{\text{sat}} = f_2(T_r)$$

where V_r^{sat} is the reduced saturation volume (V^{sat}/V_c) and T_r is the reduced temperature. To improve this generalized correlation a third parameter such as Z_c can be used and Rackett [61] suggested the following simple form for V_r^{sat} versus T_r :

$$(5.120) \quad V_r^{\text{sat}} = \frac{V^{\text{sat}}}{V_c} = Z_c^{(1-T_r)^{2/7}}$$

This equation is in fact a generalized correlation for saturated liquids and it is in dimensionless form. Later Spencer and Danner [62] modified this equation and replaced parameter Z_c with another parameter called Rackett parameter shown by Z_{RA} :

$$(5.121) \quad V_r^{\text{sat}} = \left(\frac{RT_c}{P_c} \right) Z_{\text{RA}}^n \quad n = 1.0 + (1.0 - T_r)^{2/7}$$

Values of Z_{RA} are close to the values of Z_c and they are reported by Spencer and Adler [63]. For some selected compounds, values of Z_{RA} are given in Table 5.12 as reported by the API-TDB [59]. A linear relation between Z_{RA} and ω similar to Eq. (5.112) was proposed based on the initial values of Rackett parameter [64].

$$(5.122) \quad Z_{\text{RA}} = 0.29056 - 0.08775\omega$$

It should be noted that the API-TDB [59] recommends values of Z_{RA} different from those obtained from the above equation. Usually when the value of Z_{RA} is not available, it may be replaced by Z_c . In this case Eq. (5.121) reduces to the original Rackett equation (Eq. 5.120). The most accurate way of predicting Z_{RA} is through a known value of density. If density of a liquid at temperature T is known and is shown by d_T , then

TABLE 5.12—Values of Rackett parameter for selected compounds [59].

No.		Z _{RA}	No.		Z _{RA}	
Paraffins			Olefins			
1	Methane	0.2880	32	Ethene (ethylene)	0.2813	
2	Ethane	0.2819	33	Propene (propylene)	0.2783	
3	Propane	0.2763	34	1-Butene	0.2735	
4	<i>n</i> -Butane	0.2730	35	1-Pentene	0.2692	
5	2-Methylpropane (isobutane)	0.2760	36	1-Hexene	0.2654	
6	<i>n</i> -Pentane	0.2685	37	1-Heptene	0.2614	
7	2-Methylbutane (isopentane)	0.2718	38	Di-olefin	0.2707	
8	2,2-Dimethylpropane (neopentane)	0.2763		Ethyne (acetylene)		
9	<i>n</i> -Hexane	0.2637		Aromatics		
10	2-Methylpentane	0.2673		Benzene		0.2696
11	<i>n</i> -Heptane	0.2610		39		Methylbenzene (toluene)
12	2-Methylhexane	0.2637	40	Ethylbenzene	0.2619	
13	<i>n</i> -Octane	0.2569	41	1,2-Dimethylbenzene (<i>o</i> -xylene)	0.2626	
14	2-Methylheptane	0.2581	42	1,3-Dimethylbenzene (<i>m</i> -xylene)	0.2594	
15	2,3,4-Trimethylpentane	0.2656	43	1,4-Dimethylbenzene (<i>p</i> -xylene)	0.2590	
16	<i>n</i> -Nonane	0.2555	44	<i>n</i> -Propylbenzene	0.2599	
17	<i>n</i> -Decane	0.2527	45	Isopropylbenzene (cumene)	0.2616	
18	<i>n</i> -Undecane	0.2500	46	<i>n</i> -Butylbenzene	0.2578	
19	<i>n</i> -Dodecane	0.2471	47	Naphthalene	0.2611	
20	<i>n</i> -Tridecane	0.2468	48	Aniline	0.2607	
21	<i>n</i> -Tetradecane	0.2270	49	Nonhydrocarbons		
22	<i>n</i> -Pentadecane	0.2420	50	Ammonia	0.2466	
23	<i>n</i> -Hexadecane	0.2386	51	Carbon dioxide	0.2729	
24	<i>n</i> -Heptadecane	0.2343	52	Hydrogen	0.3218	
25	<i>n</i> -Octadecane	0.2292	53	Hydrogen sulfide	0.2818	
26	<i>n</i> -Nonadecane	0.2173 ^a	54	Nitrogen	0.2893	
27	<i>n</i> -Eicosane	0.2281	55	Oxygen	0.2890	
Naphthenes			56	Water	0.2374	
28	Cyclopentane	0.2709	57	Methanol	0.2334	
29	Methylcyclopentane	0.2712	58	Ethanol	0.2502	
30	Cyclohexane	0.2729	59	Diethylamine (DEA)	0.2568	
31	Methylcyclohexane	0.2702				

^aCalculated from Eq. (5.123) using specific gravity.

Eq. (5.121) can be rearranged to get Z_{RA} :

$$(5.123) \quad Z_{RA} = \left(\frac{MP_c}{RT_c d_T} \right)^{1/n}$$

where n is calculated from Eq. (5.121) at temperature T at which density is known. For hydrocarbon systems and petroleum fractions usually specific gravity (SG) at 15.5°C is known and value of 288.7 K should be used for T . Then d_T (in g/cm³) is equal to 0.999SG according to the definition of SG by Eq. (2.2). In this way predicted values of density are quite accurate at temperatures near the reference temperature at which density data are used. The following example shows the procedure.

Example 5.7—For n -octane of Example 5.2, calculate saturated liquid molar volume at 279.5°C from Rackett equation using predicted Z_{RA} .

Solution—From Example 5.2, $M = 114.2$, $SG = 0.707$, $T_c = 295.55^\circ\text{C}$ (568.7 K), $P_c = 24.9$ bar, $R = 83.14$ cm³ · bar/mol · K, and $T_r = 0.972$. Equation (5.123) should be used to predict Z_{RA} from SG. The reference temperature is 288.7 K, which gives $T_r = 0.5076$. This gives $n = 1.8168$ and from Eq. (5.123) we calculate $Z_{RA} = 0.2577$. ($Z_{RA} = 0.2569$ from Table 5.12). From Eq. (5.121), V^{sat} is calculated: $n = 1 + (1 - 0.972)^{2/7} = 1.36$, $V^{\text{sat}} = (83.14 \times 568.7/24.9) \times 0.2577^{1.36} = 300$ cm³/mol. Comparing with actual value of 304 cm³/mol gives the error of -1.3%. Calculated density is $\rho = 114.2/300 = 0.381$ g/cm³. ♦

5.8.2 Defined Liquid Mixtures and Petroleum Fractions

Saturation pressure for a mixture is also called *bubble point* pressure and saturation molar volume is shown by V^{bp} . Liquid density at the bubble point is shown by ρ^{bp} , which is related to V^{bp} by the following relation:

$$(5.124) \quad \rho^{\text{bp}} = \frac{M}{V^{\text{bp}}}$$

where ρ^{bp} is absolute density in g/cm³ and M is the molecular weight. V^{bp} can be calculated from the following set of equations recommended by Spencer and Danner [65]:

$$(5.125) \quad \begin{aligned} V^{\text{bp}} &= R \left(\sum_{i=1}^N x_i \frac{T_{ci}}{P_{ci}} \right) Z_{RAm}^n \\ n &= 1 + (1 - T_r)^{2/7} \\ Z_{RAm} &= \sum_{i=1}^N x_i Z_{RAi} \\ T_r &= T/T_{cm} \\ T_{cm} &= \sum_{i=1}^N \sum_{j=1}^N \phi_i \phi_j T_{cij} \\ \phi_i &= \frac{x_i V_{ci}}{\sum_{i=1}^N x_i V_{ci}} \\ T_{cij} &= \sqrt{T_{ci} T_{cj}} (1 - k_{ij}) \\ k_{ij} &= 1.0 - \left[\frac{\sqrt{V_{ci}^{1/3} V_{cj}^{1/3}}}{(V_{ci}^{1/3} + V_{cj}^{1/3})/2} \right]^3 \end{aligned}$$

This method is also included in the API-TDB [59]. Another approach to estimate density of defined liquid mixtures at its bubble point pressure is through the following mixing rule:

$$(5.126) \quad \frac{1}{\rho^{\text{bp}}} = \sum_{i=1}^N \frac{x_{wi}}{\rho_i^{\text{sat}}}$$

where x_{wi} is weight fraction of i in the mixture. ρ_i^{sat} ($= M/V_i^{\text{sat}}$) is density of pure saturated liquid i and should be calculated from Eq. (5.121) using T_{ci} and Z_{RAi} .

For petroleum fractions in which detailed composition is not available Eq. (5.121) developed for pure liquids may be used. However, Z_{RA} should be calculated from specific gravity using Eq. (5.123) while T_c and P_c can be calculated from methods given in Chapter 2 through T_b and SG.

5.8.3 Effect of Pressure on Liquid Density

As shown in Fig. 5.1, effect of pressure on volume of liquids is quite small specially when change in pressure is small. When temperature is less than normal boiling point of a liquid, its saturation pressure is less than 1.0133 bar and density of liquid at atmospheric pressure can be assumed to be the same as its density at saturation pressure. For temperatures above boiling point where saturation pressure is not greatly more than 1 atm, calculated saturated liquid density may be considered as liquid density at atmospheric pressure. Another simple way of calculating liquid densities at atmospheric pressures is through Eq. (2.115) for the slope of density with temperature. If the only information available is specific gravity, SG, the reference temperature would be 15.5°C (288.7 K) and Eq. (2.115) gives the following relation:

$$(5.127) \quad \rho_T^o = 0.999SG - 10^{-3} \times (2.34 - 1.898SG) \times (T - 288.7)$$

where SG is the specific gravity at 15.5°C (60°F/60°F) and T is absolute temperature in K. ρ_T^o is liquid density in g/cm³ at temperature T and atmospheric pressure. If instead of SG at 15.5°C (288.7 K), density at another temperature is available a similar equation can be derived from Eq. (2.115). Equation (5.127) is not accurate if T is very far from the reference temperature of 288.7 K.

The effect of pressure on liquid density or volume becomes important when the pressure is significantly higher than 1 atm. For instance, volume of methanol at 1000 bar and 100°C is about 12% less than it is at atmospheric pressure. In general, when pressure exceeds 50 bar, the effect of pressure on liquid volume cannot be ignored. Knowledge of the effect of pressure on liquid volume is particularly important in the design of high-pressure pumps in the process industries. The following relation is recommended by the API-TDB [59] to calculate density of liquid petroleum fractions at high pressures:

$$(5.128) \quad \frac{\rho^o}{\rho} = 1.0 - \frac{P}{B_T}$$

where ρ^o is the liquid density at low pressures (atmospheric pressure) and ρ is density at high pressure P (in bar). B_T is called *isothermal secant bulk modulus* and is defined as $-(1/\rho^o)(\Delta P/\Delta V)_T$. Parameter B_T indicates the slope of change of pressure with unit volume and has the unit of pressure. Steps to calculate B_T are summarized in the following

set of equations:

$$\begin{aligned}
 B_T &= mX + B_I \\
 m &= 1492.1 + 0.0734P + 2.0983 \times 10^{-6}P^2 \\
 X &= (B_{20} - 10^5)/23170 \\
 \log B_{20} &= -1.098 \times 10^{-3}T + 5.2351 + 0.7133\rho^0 \\
 B_I &= 1.0478 \times 10^3 + 4.704P - 3.744 \times 10^{-4}P^2 \\
 &\quad + 2.2331 \times 10^{-8}P^3
 \end{aligned}
 \tag{5.129}$$

where B_T is in bar and ρ^0 is the liquid density at atmospheric pressure in g/cm^3 . In the above equation T is absolute temperature in kelvin and P is the pressure in bar. The average error from this method is about 1.7% except near the critical point where error increases to 5% [59]. This method is not recommended for liquids at $T_r > 0.95$. In cases that ρ^0 is not available it may be estimated from Eq. (5.121) or (5.127). Although this method is recommended for petroleum fractions but it gives reasonable results for pure hydrocarbons ($\geq C_5$) as well.

For light and medium hydrocarbons as well as light petroleum fractions the Tait-COSTALD (corresponding state liquid density) correlation originally proposed by Hankinson and Thomson may be used for the effect of pressure on liquid density [66]:

$$\rho_P = \rho_{P^0} \left[1 - C \ln \left(\frac{B + P}{B + P^0} \right) \right]^{-1}
 \tag{5.130}$$

where ρ_P is density at pressure P and ρ_{P^0} is liquid density at reference pressure of P^0 at which density is known. When ρ_{P^0} is calculated from the Rackett equation, $P^0 = P^{\text{sat}}$ where P^{sat} is the saturation (vapor) pressure, which may be estimated from methods of Chapter 7. Parameter C is a dimensionless constant and B is a parameter that has the same unit as pressure. These constants can be calculated from the following equations:

$$\begin{aligned}
 \frac{B}{P_c} &= -1 - 9.0702(1 - T_r)^{1/3} + 62.45326(1 - T_r)^{2/3} \\
 &\quad - 135.1102(1 - T_r) + e(1 - T_r)^{4/3} \\
 e &= \exp(4.79594 + 0.250047\omega + 1.14188\omega^2) \\
 C &= 0.0861488 + 0.0344483\omega
 \end{aligned}
 \tag{5.131}$$

where T_r is the reduced temperature and ω is the acentric factor. All the above relations are in dimensionless forms. Obviously Eq. (5.130) gives very accurate result when P is close to P^0 ; however, it should not be used at $T_r > 0.95$. The COSTALD correlation has been recommended for industrial applications [59, 67]. However, in the API-TDB [59] it is recommended that special values of acentric factor obtained from vapor pressure data should be used for ω . These values for some hydrocarbons are given by the API-TDB [59]. Application of these methods is demonstrated in Example 5.8. The most recent modification of the Thomson method for polar and associating fluids was proposed by Garvin in

the following form [68]:

$$\begin{aligned}
 V &= V^{\text{sat}} \left[1 - C \ln \left(\frac{B + P/P_{ce}}{B + P^{\text{sat}}/P_{ce}} \right) \right] \\
 \kappa &= -\frac{1}{V^{\text{sat}}} \left(\frac{\partial V}{\partial P} \right)_T = \frac{C}{(BP_{ce} + P)} \\
 B &= -1 - 9.070217\tau^{1/3} + 62.45326\tau^{2/3} \\
 &\quad - 135.1102\tau + e\tau^{4/3} \\
 C &= 0.0861488 + 0.0344483\omega \\
 e &= \exp(4.79594 + 0.250047\omega + 1.14188\omega^2) \\
 \tau &= 1 - T/T_c
 \end{aligned}
 \tag{5.132}$$

where V^{sat} is the saturation molar volume and P^{sat} is the saturation pressure at T . V is liquid molar volume at T and P and κ is the isothermal bulk compressibility defined in the above equation (also see Eq. 6.24). T_c is the critical temperature and ω is the acentric factor. P_{ce} is equivalent critical pressure, which for all alcohols was near the mean value of 27.0 bar. This value for diols is about 8.4 bar. For other series of compounds P_{ce} would be different. Garvin found that use of P_{ce} significantly improves prediction of V and κ for alcohols. For example, for estimation of κ of methanol at 1000 bar and 100°C, Eq. (5.132) predicts κ value of $7.1 \times 10^{-7} \text{ bar}^{-1}$, which gives an error of 4.7% versus experimental value of $6.8 \times 10^{-7} \text{ bar}^{-1}$, while using P_c the error increases to 36.6%. However, one should note that the numerical coefficients for B , C , and e in Eq. (5.132) may vary for other types of polar liquids such as coal liquids.

Another correlation for calculation of effect of pressure on liquid density was proposed by Chueh and Prausnitz [69] and is based on the estimation of isothermal compressibility:

$$\begin{aligned}
 \rho_P &= \rho_{P^0} [1 + 9\beta(P - P^0)]^{1/9} \\
 \beta &= \alpha (1 - 0.89\sqrt{\omega}) \exp(6.9547 - 76.2853T_r + 191.306T_r^2 \\
 &\quad - 203.5472T_r^3 + 82.7631T_r^4) \\
 \alpha &= \frac{V_c}{RT_c} = \frac{Z_c}{P_c}
 \end{aligned}
 \tag{5.133}$$

The parameters are defined the same as were defined in Eqs. (5.131) and (5.132). V_c is the molar critical volume and the units of P , V_c , R , and T_c must be consistent in a way that PV_c/RT_c becomes dimensionless. This equation is applicable for T_r ranging from 0.4 to 0.98 and accuracy of Eq. (5.134) is just marginally less accurate than the COSTALD correlation [67].

Example 5.8—Propane has vapor pressure of 9.974 bar at 300 K. Saturated liquid and vapor volumes are $V^L = 90.077$ and $V^V = 2036.5 \text{ cm}^3/\text{mol}$ [Ref. 8, p. 4.24]. Calculate saturated liquid molar volume using (a) Rackett equation, (b) Eqs. (5.127)–(5.129), (c) Eqs. (5.127) and (5.130), and (d) Eq. (5.133).

Solution—(a) Obviously the most accurate method to estimate V^L is through Eq. (5.121). From Table 2.1, $M = 44.1$, $SG = 0.507$, $T_c = 96.7^\circ\text{C}$ (369.83 K), $P_c = 42.48$ bar, and $\omega = 0.1523$. From Table 5.12, $Z_{RA} = 0.2763$, $T_r = 0.811$ so from Eq. (5.121), $V^{\text{sat}} = 89.961 \text{ cm}^3/\text{mol}$ (-0.1% error). (b) Use of Eqs. (5.127)–(5.129) is not suitable for this case that Rackett equation can be directly applied. However, to show the application of method V^{sat} is calculated to see their performance. From Eq. (5.127) and use of $SG = 0.507$ gives $\rho^o = 0.491 \text{ g/cm}^3$. From Eq. (5.129), $m = 1492.832$, $B_{20} = 180250.6$, $X = 3.46356$, $B_1 = 1094.68$, and $B_T = 6265.188$ bar. Using Eq. (5.128), $0.491/\rho = 1 - 9.974/6265.188$. This equation gives density at T (300 K) and P (9.974 bar) as $\rho = 0.492 \text{ g/cm}^3$. $V^{\text{sat}} = M/\rho = 44.1/0.492 = 89.69 \text{ cm}^3/\text{mol}$ (error of -0.4%). (c) Use of Eqs. (5.127) and (5.130) is not a suitable method for density of propane, but to show its performance, saturated liquid volume is calculated in a way similar to part (b): From Eq. (5.131), $B = 161.5154$ bar and $C = 0.091395$. For Eq. (5.130) we have $\rho_{po} = 0.491 \text{ g/cm}^3$, $P^o = 1.01325$ bar, $P = 9.974$ bar, and calculated density is $\rho_P = 0.4934 \text{ g/cm}^3$. Calculated V^{sat} is $89.4 \text{ cm}^3/\text{mol}$, which gives a deviation of -0.8% from experimental value of $90.077 \text{ cm}^3/\text{mol}$. (d) Using the Chueh–Prausnitz correlation (Eq. 5.133) we have $Z_c = 0.276$, $\alpha = 0.006497$, $\beta = 0.000381$, $\rho_P = 0.49266 \text{ g/cm}^3$, and $V_{\text{calc}}^{\text{sat}} = 89.5149 \text{ cm}^3/\text{mol}$, which gives an error of -0.62% from the actual value. ♦

5.9 REFRACTIVE INDEX BASED EQUATION OF STATE

From the various PVT relations and EOS discussed in this chapter, cubic equations are the most convenient equations that can be used for volumetric and phase equilibrium calculations. The main deficiency of cubic equations is their inability to predict liquid density accurately. Use of volume translation improves accuracy of SRK and PR equations for liquid density but a fourth parameter specific of each equation is required. The shift parameter is not known for heavy compounds and petroleum mixtures. For this reason some specific equations for liquid density calculations are used. As an example Alani–Kennedy EOS is specifically developed for calculation of liquid density of oils and reservoir fluids and is used by some reservoir engineers [19, 21]. The equation is in van der Waals cubic EOS form but it requires four numerical constants for each pure compound, which are given from C_1 to C_{10} . For the C_{7+} fractions the constants should be estimated from M_{7+} and SG_{7+} . The method performs well for light reservoir fluids and gas condensate samples. However, as discussed in Chapter 4, for oils with significant amount of heavy hydrocarbons, which requires splitting of C_{7+} fraction, the method cannot be applied to C_{7+} subfractions. In addition the method is not applicable to undefined petroleum fractions with a limited boiling range.

Generally constants of cubic equations are determined based on data for hydrocarbons up to C_8 or C_9 . As an example, the LK generalized correlations is based on the data for the reference fluid of $n\text{-C}_8$. The parameter that indicates complexity of a compound is acentric factor. In SRK and PR EOS parameter a is related to ω in a polynomial form of at least second order (see f_ω in Table 5.1). This indicates that extrapolation of such equations for compounds having acentric factors greater than those used in development of EOS parameters is not accurate. And it is for this reason that most cubic equations such as SRK and PR equations break down when they are applied for calculation of liquid densities for C_{10} and heavier hydrocarbons. For this reason Riazi and Mansoori [70] attempted to improve capability of cubic equations for liquid density prediction, especially for heavy hydrocarbons.

Most modifications on cubic equations is on parameter a and its functionality with temperature and ω . However, a parameter that is inherent to volume is the co-volume parameter b . RK EOS presented by Eq. (5.38) is the simplest and most widely used cubic equation that predicts reasonably well for prediction of density of gases. In fact as shown in Table 5.13 for simple fluids such as oxygen or methane (with small ω) RK EOS works better than both SRK and PR regarding liquid densities.

For liquid systems in which the free space between molecules reduces, the role of parameter b becomes more important than that of parameter a . For low-pressure gases, however, the role of parameter b becomes less important than a because the spacing between molecules increases and as a result the attraction energy prevails. Molar refraction was defined by Eq. (2.34) as

$$(5.134) \quad R_m = VI = \frac{M}{d_{20}} \left(\frac{n^2 - 1}{n^2 + 2} \right)$$

where R_m is the molar refraction and V is the molar volume both in cm^3/mol . R_m is nearly independent of temperature but is normally calculated from density and refractive index at 20°C (d_{20} and n_{20}). R_m represents the actual molar volume of molecules and since b is also proportional to molar volume of molecules (excluding the free space); therefore, one can conclude that parameter b must be proportional to R_m . In fact the polarizability is related to R_m in the following form:

$$(5.135) \quad \alpha = \frac{3}{4\pi N_A} R_m - \mu(T)$$

where N_A is the Avogadro's number and $\mu(T)$ is the dipole moment, which for light hydrocarbons is zero [7]. Values of R_m calculated from Eq. (5.134) are reported by Riazi et al. [70, 71] for a number of hydrocarbons and are given in Table 5.14. Since the original RK EOS is satisfactory for methane we choose this compound as the reference substance. Parameter

TABLE 5.13—Evaluation of RK, SRK, and PR EOS for prediction of density of simple fluids.

Compound	No. of data points	Temperature range, K	Pressure range, bar	%AAD			Data source
				RK	SRK	PR	
Methane	135	90–500	0.7–700	0.88	1.0	4.5	Goodwin [72]
Oxygen	120	80–1000	1–500	1.1	1.4	4.0	TRC [73]

TABLE 5.14—Data source for development of Eq. (5.139), values of parameter r and predicted Z_c from MRK EOS [70].

No.	Compound	R_m , at 20°C, cm ³ /mol	r	No. of data points	Temp. range, K	Pressure range, bar	Ref.	Critical compressibility, Z_c		
								Table 2.1	Pred. MRK	%AD
1	Methane (C ₁)	6.987	1.000	135	90–500	0.5–700	Goodwin [72]	0.288	0.333	15.6
2	Ethane (C ₂)	11.319	1.620	157	90–700	0.1–700	Goodwin et al. [74]	0.284	0.300	5.6
3	Ethylene	10.508	1.504	90	100–500	1–400	McCarty and Jacobsen [75]	0.276	0.295	6.9
5	Propane (C ₃)	15.784	2.259	130	85–700	0.1–700	Goodwin and Haynes [76]	0.280	0.282	0.7
6	Isobutane	20.647	2.955	115	110–700	0.1–700	Goodwin and Haynes [76]	0.282	0.280	0.7
7	<i>n</i> -Butane (C ₄)	20.465	2.929	183	130–700	0.1–700	Haynes and Goodwin [77]	0.274	0.278	1.5
8	<i>n</i> -Pentane (C ₅)	25.265	3.616	0.269	0.271	0.7
9	<i>n</i> -Hexane (C ₆)	29.911	4.281	100	298–1000	1–500	TRC Tables [73]	0.264	0.266	0.7
10	Cyclohexane	27.710	3.966	140	320–1000	1–500	TRC Tables [73]	0.273	0.269	1.5
11	Benzene	26.187	3.748	110	310–1000	1–500	TRC Tables [73]	0.271	0.270	0.4
12	Toluene	31.092	4.450	110	330–1000	1–500	TRC Tables [73]	0.264	0.265	0.4
13	<i>n</i> -Heptane (C ₇)	34.551	4.945	100	300–1000	1–500	TRC Tables [73]	0.263	0.262	0.4
14	<i>n</i> -Octane (C ₈)	39.183	5.608	80	320–1000	1–500	TRC Tables [73]	0.259	0.258	0.4
15	<i>i</i> -Octane	39.260	5.619	70	340–1000	1–500	TRC Tables [73]	0.266	0.256	3.8
16	<i>n</i> -Heptane (C ₇) ^a	34.551	4.945	35	303–373	50–500	Doolittle [78]
17	<i>n</i> -Nonane (C ₉) ^a	43.836	6.274	35	303–373	50–500	Doolittle [78]	0.255	0.254	0.4
18	<i>n</i> -Decane (C ₁₀) ^a	48.497	6.941	0.249	0.250	0.4
19	<i>n</i> -Undecane (C ₁₁) ^a	53.136	7.605	35	303–373	50–500	Doolittle [78]	0.243	0.247	1.6
20	<i>n</i> -Dodecane (C ₁₂) ^a	57.803	8.273	0.238	0.245	2.9
21	<i>n</i> -Tridecane (C ₁₃) ^a	62.478	8.942	30	303–373	50–500	Doolittle [78]	0.236	0.242	2.6
22	<i>n</i> -Tetradecane (C ₁₄) ^a	67.054	9.597	0.234	0.240	2.5
23	<i>n</i> -Pentadecane (C ₁₅) ^a	71.708	10.263	0.228	0.238	4.3
24	<i>n</i> -Hexadecane (C ₁₆) ^a	76.389	10.933	0.225	0.235	4.2
25	<i>n</i> -Heptadecane (C ₁₇) ^a	81.000	11.593	30	323–573	50–500	Doolittle [78]	0.217	0.233	7.4
26	<i>n</i> -Eicosane (C ₂₀) ^a	95.414	13.656	20	373–573	50–500	Doolittle [78]	0.213	0.227	6.6
27	<i>n</i> -Triacosane (C ₃₀) ^a	141.30	20.223	20	373–573	50–500	Doolittle [78]	...	0.213	...
28	<i>n</i> -Tetracontane (C ₄₀) ^a	187.69	26.862	20	423–573	50–500	Doolittle [78]
	Overall	1745	90–1000	0.1–700				3.0

Density data for compounds 16–28 are all only for liquids [78]. Compounds specified by bold are used in development of Eq. (5.139). Calculated values of Z_c from SRK and PR EOSs for all compounds are 0.333 and 0.307, respectively. These give average errors of 28.2 and 18.2%, respectively.

^aPVT data for the following compounds were not used in development of Eq. (5.139).

β is defined as

$$(5.136) \quad \beta = \frac{b_{\text{actual}}}{b_{\text{RK}}}$$

where b_{actual} is the optimum value of b and b_{RK} is the value of b obtained for RK EOS and is calculated through the relation given in Table 5.1. For the reference fluid, $\beta_{\text{ref}} = 1$. We now assume that

$$(5.137) \quad \frac{\beta}{\beta_{\text{ref}}} = \frac{\alpha}{\alpha_{\text{ref}}} = f\left(\frac{R_m}{R_{m,\text{ref}}}, T_r\right)$$

Parameter r is defined as

$$(5.138) \quad r = \frac{R_m}{R_{m,\text{ref}}} = \frac{R_m}{6.987}$$

r is a dimensionless parameter and represents reduced molecular size. Values of r calculated from Eq. (5.138) are also given in Table 5.14. By combining Eqs. (5.137) and (5.138) and based on data for densities of hydrocarbons from C₂ to C₈, the following relation was found for calculation of parameter b in the RK EOS:

$$(5.139) \quad \frac{1}{\beta} = 1 + \{0.02[1 - 0.92 \exp(-1000|T_r - 1|)] - 0.035(T_r - 1)\} \times (r - 1)$$

Once β is determined from the above relation, the co-volume parameter b for the RK can be calculated by substituting b_{RK}

from Table 5.1 into Eq. (5.136) as

$$(5.140) \quad b = \left(\frac{0.08664RT_c}{P_c}\right)\beta$$

Parameter a for the RK EOS is given in Table 5.1 as

$$(5.141) \quad a = \frac{0.42748R^2T_c^2}{P_c}$$

Therefore, the modified RK EOS is composed of Eq. (5.38) and Eqs. (5.138)–(5.141) for calculation of the parameters a and b . Equation (5.39) for the PVT relation and Eq. (5.141) for parameter a are the same as the original RK EOS. This modified version of RK EOS is referred as MRK. In fact when $\beta = 1$ the MRK EOS reduces to RK EOS. The exponential term in Eq. (5.139) is the correction for the critical region. At $T_r = 1$ this equation reduces to

$$(5.142) \quad b_{\text{at } T_c} = 1 + 0.0016(r - 1)$$

This equation indicates that the MRK EOS does not give a constant Z_c for all compounds but different values for different compounds. For this reason this EOS does not satisfy the constraints set by Eq. (5.9). But calculations show that $(\partial P/\partial V)_{T_c}$ and $(\partial^2 P/\partial V^2)_{T_c}$ are very small. For hydrocarbons from C₁ to C₂₀ the average values for these derivatives are 0.0189 and 0.001, respectively [70]. In summary 1383 data points on densities of liquids and gases for hydrocarbons from C₂ to C₈ with pressure range of 0.1–700 bar and temperature up to 1000 K were used in development of Eq. (5.139). The

TABLE 5.15—Evaluation of various EOS for prediction of liquid density of heavy hydrocarbons [70].

Compound	No. of data points	%AAD			
		MRK	RK	SRK	PR
<i>n</i> -Heptane (<i>n</i> -C ₇)	35	0.6	12.1	10.5	1.4
<i>n</i> -Nonane (<i>n</i> -C ₉)	35	0.6	15.5	13.4	3.4
<i>n</i> -Undecane (<i>n</i> -C ₁₁)	35	1.7	18.0	15.5	5.4
<i>n</i> -Tridecane (<i>n</i> -C ₁₃)	30	2.8	20.3	17.7	7.9
<i>n</i> -Heptadecane (<i>n</i> -C ₁₇)	30	1.2	27.3	24.8	16.0
<i>n</i> -Eicosane (<i>n</i> -C ₂₀)	20	2.8	29.5	26.7	18.2
<i>n</i> -Triacontane (<i>n</i> -C ₃₀)	20	0.6	41.4	39.4	32.5
<i>n</i> -Tetracontane (<i>n</i> -C ₄₀)	20	4.1	50.9	49.4	44.4
Total	225	1.6	24.3	22.1	13.3

MRK: Eqs. (5.38), (5.138), and (5.141). Note none of these data were used in development of Eq. (5.139).

interesting point about this equation is that it can be used up to C₄₀ for density estimations. Obviously this equation is not designed for VLE calculations as no VLE data were used to develop Eq. (5.139). Prediction of Z_c from MRK EOS is shown in Table 5.14. Evaluation of MRK with PR and SRK equations for prediction of liquid density of heavy hydrocarbons is given in Table 5.15. Data sources for these compounds are given in Table 5.14. Overall results for prediction of density for both liquid and gaseous hydrocarbon compounds from C₁ to C₄₀ is shown in Table 5.15. The overall error for the MRK EOS for more than 1700 data points is about 1.3% in comparison with 4.6 for PR and 7.3 for SRK equations.

To apply this EOS to defined mixtures a set of mixing rules are given in Table 5.17 [70]. For petroleum fractions parameters can be directly calculated for the mixture. For binary and ternary liquid mixtures containing compounds from C₁ to C₂₀ an average error of 1.8% was obtained for 200 data points [70]. For the same dataset RK, SRK, and PR equations gave errors of 15, 13, and 6%, respectively. Further characteristics and evaluations of this modified RK EOS are discussed by Riazi and Roomi [71]. Application of this method in calculation of density is shown in the following example.

Example 5.9—Repeat Example 5.2 for prediction of liquid and vapor density of *n*-octane using MRK EOS.

Solution—The MRK EOS is to use Eq. (5.38) with parameters obtained from Eqs. (5.139)–(5.141). The input data needed to use MRK EOS are *T_c*, *P_c*, and *r*. From Example 5.2, *T_c* = 568.7 K, *P_c* = 24.9 bar, and *T_r* = 0.9718 K. From Table 5.14 for *n*-C₈, *r* = 5.608. From Eq. (5.139), $\beta = 1.5001 \times 10^{-4}$. From Eq. (5.139), *b* = 150.01 cm³/mol and from Eq. (5.141), *a* = 3.837982 × 10⁷ cm⁶/mol². Solving Eq. (5.42) with *u*₁ = 1 and *u*₂ = 0 (Table 5.1) and in a way similar to that performed in Example 5.2 we get *V^L* = 295.8 and *V^V* = 1151.7 cm³/mol. Deviations of predicted values from experimental data are –2.7% and –5.3% for liquid and vapor molar volume, respectively.

TABLE 5.16—Comparison of various EOSs for prediction of density of liquid and gaseous hydrocarbons.

Compound	No. of data points	%AAD			
		MRK	RK	SRK	PR
C ₁ –C ₈ ^a	1520	1.3	4.9	5.1	3.3
C ₇ –C ₄₀ ^b	225	1.6	24.3	22.1	13.3
Total	1745	1.33	7.38	7.28	4.59

^aThese are the compounds that have been marked as bold in Table 5.14 and are used in development of Eq. (5.139).

^bThese are the same compounds as in Table 5.15.

TABLE 5.17—Mixing rules for MRK EOS parameters (Eqs. (5.38) and (5.137)–(5.140)).

$T_{cm} = \frac{\sum_i \sum_j x_i x_j T_{cij}^2 / P_{cij}}{\sum_i \sum_j x_i x_j T_{cij} / P_{cij}}$	$T_{cij} = (T_{ci} T_{cj})^{1/2} (1 - k_{ij})$
$P_{cm} = \frac{(\sum_i \sum_j x_i x_j T_{cij}^2 / P_{cij})}{(\sum_i \sum_j x_i x_j T_{cij} / P_{cij})^2}$	$P_{cij} = \frac{8 T_{cij}}{[(T_{cii} / P_{cii})^{1/3} + (T_{cjj} / P_{cjj})^{1/3}]^3}$
$r_m = \sum_i \sum_j x_i x_j r_{ij}$	$r_{ij} = \frac{(r_{ii}^{1/3} + r_{jj}^{1/3})^3}{8}$

Predicted liquid densities from SRK and PR equations (Example 5.2) deviate from experimental data by +31.5 and 17.2%, respectively. Advantage of MRK over other cubic equations for liquid density is greater for heavier compounds as shown in Table 5.15. ♦

This modified version of RK EOS is developed only for density calculation of hydrocarbon systems and their mixtures. It can be used directly to calculate density of petroleum fractions, once *M*, *d*₂₀, *n*₂₀, *T_c*, and *P_c* are calculated from methods discussed in Chapters 2 and 3. Moreover parameter *r* can be accurately estimated for heavy fractions, while prediction of acentric factor for heavy compounds is not reliable (see Figs. 2.20–2.22). The main characteristic of this equation is its application to heavy hydrocarbons and undefined petroleum fractions. The fact that Eq. (5.139) was developed based on data for hydrocarbons from C₂ to C₈ and it can well be used up to C₄₀ shows its extrapolation capability. The linear relation that exists between 1/β and parameter *r* makes its extrapolation to heavier hydrocarbons possible. In fact it was found that by changing the functionality of 1/β with *r*, better prediction of density is possible but the relation would no longer be linear and its extrapolation to heavier compounds would be less accurate. For example, for C₁₇ and C₁₈, if the constant 0.02 in Eq. (5.139) is replaced by 0.018, the %AAD for these compounds reduces from 2 to 0.5%.

Analysis of various EOS shows that use of refractive index in obtaining constants of an EOS is a promising approach. Further work in this area should involve use of saturation pressure in addition to liquid density data to obtain relations for EOS parameters that would be suitable for both liquid density and VLE calculations.

5.10 SUMMARY AND CONCLUSIONS

In this chapter the fundamental of PVT relations and mathematical EOS are presented. Once the PVT relation for a fluid is known various physical and thermodynamic properties can be determined as discussed in Chapters 6 and 7. Intermolecular forces and their importance in property predictions were discussed in this chapter. For light hydrocarbons two-parameter potential energy relations such as LJ describes the intermolecular forces and as a result two-parameter EOS are sufficient to describe the PVT relation for such fluids. It is shown that EOS parameters can be directly calculated from the potential energy relations. Criteria for correct EOS are given so that validity of any EOS can be analyzed. Three category of EOSs are presented in this chapter: (1) cubic type, (2) noncubic type, and (3) generalized correlations.

Four types of cubic equations vdW, RK, SRK, and PR and their modifications have been reviewed. The main advantage of cubic equations is simplicity, mathematical convenience, and their application for both vapor and liquid phases. The main application of cubic equations is in VLE calculations as will be discussed in Chapters 6 and 9. However, their ability to predict liquid phase density is limited and this is the main weakness of cubic equations. PR and SRK equations are widely used in the petroleum industry. PR equation gives better liquid density predictions, while SRK is used in VLE calculations. Use of volume translation improves capability of liquid density prediction for both PR and SRK equations; however, the method of calculation of this parameter for heavy petroleum fractions is not available and generally these equations break down at about C_{10} . Values of input parameters greatly affect EOS predictions. For heavy hydrocarbons, accurate prediction of acentric factor is difficult and for this reason an alternative EOS based on modified RK equation is presented in Section 5.9. The MRK equation uses refractive index parameter instead of acentric factor and it is recommended for density calculation of heavy hydrocarbons and undefined petroleum fraction. This equation is not suitable for VLE and vapor pressure calculations. In Chapter 6, use of velocity of sound data to obtain EOS parameters is discussed [79].

Among noncubic equations, virial equations provide more accurate PVT relations; however, prediction of fourth and higher virial coefficients is not possible. Any EOS can be converted into a virial form. For gases at moderate pressures, truncated virial equation after third term (Eq. 5.75) is recommended. Equation (5.71) is recommended for estimation of the second virial coefficient and Eq. (5.78) is recommended for prediction of the third virial coefficients. For specific compounds in which virial coefficients are available, these should be used for more accurate prediction of PVT data at certain moderate conditions such as those provided by Gupta and Eubank [80].

Several other noncubic EOS such as BWRS, CS, LJ, SPHC, and SAFT are presented in this chapter. As will be discussed in the next chapter, recent studies show that cubic equations are also weak in predicting derivative properties such as enthalpy, Joule Thomson coefficient, or heat capacity. For this reason, noncubic equations such as simplified perturbed hard chain (SPHC) or statistical associating fluid theory (SAFT) are being investigated for prediction of such derived properties [81]. For heavy hydrocarbons in which two-parameter potential energy functions are not sufficient to describe the intermolecular forces, three- and perhaps four-parameter EOS must be used. The most recent reference on the theory and application of EOSs for pure fluids and fluid mixtures is provided by Sengers et al. [82]. In addition, for a limited number of fluids there are highly accurate EOS that generally take on a modified MBWR form or a Helmholtz energy representation like the IAPWS water standard [4]. Some of these equations are even available free on the webs [83].

The theory of corresponding state provides a good PVT relation between Z -factor and reduced temperature and pressure. The LK correlation presented by Eqs. (5.107)–(5.111) is based on BWR EOS and gives the most accurate PVT relation if accurate input data on T_c , P_c , and ω are known. While the cubic equations are useful for phase behavior calculations, the LK corresponding states correlations are recommended for

calculation of density, enthalpy, entropy, and heat capacity of hydrocarbons and petroleum fractions. Analytical form of LK correlation is provided for computer applications, while the tabulated form is given for hand calculations. Simpler two-parameter empirical correlation for calculation of Z -factor of gases, especially for light hydrocarbons and natural gases, is given in a graphical form in Fig. 5.12 and Hall–Yarborough equation can be used for computer applications..

For calculation of liquid densities use of Rackett equation (Eq. 5.121) is recommended. For petroleum fractions in which Rackett parameter is not available it should be determined from specific gravity through Eq. (5.123). For the effect of pressure on liquid density of light pure hydrocarbons, defined hydrocarbon mixtures and light petroleum fractions, the COSTALD correlation (Eq. 5.130) may be used. For petroleum fractions effect of pressure on liquid density can be calculated through Eq. (5.128).

For defined mixtures the simplest approach is to use Kay's mixing rule (Eqs. 3.39 and 5.116) to calculate pseudocritical properties and acentric factor of the mixture. However, when molecules in a mixture are greatly different in size (i.e., C_5 and C_{20}), more accurate results can be obtained by using appropriate mixing rules given in this chapter for different EOS. For defined mixtures liquid density can be best calculated through Eq. (5.126) when pure component densities are known at a given temperature and pressure. For undefined narrow boiling range petroleum fractions T_c , P_c , and ω should be estimated according to the methods described in Chapters 2 and 3. Then the mixture may be treated as a single pseudo-component and pure component EOS can be directly applied to such systems. Some other graphical and empirical methods for the effect of temperature and pressure on density and specific gravity of hydrocarbons and petroleum fractions are given in Chapter 7. Further application of methods presented in this chapter for calculation of density of gases and liquids especially for wide boiling range fractions and reservoir fluids will be presented in Chapter 7. The theory of prediction of thermodynamic properties and their relation with PVT behavior of a fluid are discussed in the next chapter.

5.11 PROBLEMS

- 5.1. Consider three phases of water, oil, and gas are in equilibrium. Also assume the oil is expressed in terms of 10 components (excluding water) with known specifications. The gas contains the same compounds as the oil. Based on the phase rule determine what is the minimum information that must be known in order to determine oil and gas properties.
- 5.2. Obtain coefficients a and b for the PR EOS as given in Table 5.1. Also obtain $Z_c = 0.307$ for this EOS.
- 5.3. Show that the Dieterici EOS exhibits the correct limiting behavior at $P \rightarrow 0$ (finite T) and $T \rightarrow \infty$ (finite P)

$$P = \frac{RT}{V-b} e^{-a/RTV}$$

where a and b are constants.

- 5.4. The Lorentz EOS is given as

$$\left(P + \frac{a}{V^2}\right) \left(V - \frac{bV}{V+b}\right) = RT$$

where a and b are the EOS constants. Is this a valid EOS?

- 5.5. A graduate student has come up with a cubic EOS in the following form:

$$\left[P + \frac{aV^2}{(V+b)(V-b)} \right] (V-b) = RT$$

Is this equation a correct EOS?

- 5.6. Derive a relation for the second virial coefficient of a fluid that obeys the SWP relation. Use data on B for methane in Table 5.4 to obtain the potential energy parameters, σ and ϵ . Compare your calculated values with those obtained from LJ Potential as $\sigma = 4.01 \text{ \AA}$ and $\epsilon/k = 142.87 \text{ K}$ [6, 79].
- 5.7. Derive Eq. (5.66) from Eq. (5.65) and discuss about your derivation.
- 5.8. Show that for the second virial coefficient, Eq. (5.70) can be reduced to a form similar to Eq. (5.59). Also show that these two forms are identical for a binary system.
- 5.9. Derive the virial form of PR EOS and obtain the virial coefficients B , C , and D in terms of PR EOS parameters.
- 5.10. With results obtained in Example 5.4 and Problem 5.9 for the virial coefficients derived from RK, SRK, and PR equations estimate the following:
- The second virial coefficient for propane at temperatures 300, 400 and 500 K and compare the results with those given in Table 5.4. Also predict B from Eqs. (5.71)–(5.73).
 - The third virial coefficients for methane and ethane and compare with those given in Table 5.5.
 - Compare predicted third virial coefficients from (b) with those predicted from Eq. (5.78).
- 5.11. Specific volume of steam at 250°C and 3 bar is 796.44 cm³/g [1]. The virial coefficients (B and C) are given in Table 5.5. Estimate specific volume of this gas from the following methods:
- RK, SRK, and PR equations.
 - Both virial forms by Eqs. (5.65) and (5.66). Explain why the two results are not the same.
 - Virial equation with coefficients estimated from Eqs. (5.71), (5.72), and (5.78).
- 5.12. Estimate molar volume of n -decane at 373 K and 151.98 bar from LK generalized correlations. Also estimate the critical compressibility factor. The actual molar volume is 206.5 cm³/mol.
- 5.13. For several compounds liquid density at one temperature is given in the table below.

Component ^a	N ₂	H ₂ O	C ₁	C ₂	C ₃	n -C ₄
T , K	78	293	112	183	231	293
ρ , g/cm ³	0.804	0.998	0.425	0.548	0.582	0.579

^aSource: Reid et al. [15].

For each compound calculate the Rackett parameter from reference density and compare with those given in Table 5.12. Use estimated Rackett parameter to calculate specific gravity of C₃ and n -C₄ at 15.5°C and compare with values of SG given in Table 2.1.

- 5.14. For a petroleum fraction having API gravity of 31.4 and Watson characterization factor of 12.28 estimate liquid

density at 68°F and pressure of 5400 psig using the following methods. The experimental value is 0.8838 g/cm³ (Ref. [59] Ch 6)

- SRK EOS
 - SRK using volume translation
 - MRK EOS
 - Eq. (5.128)
 - COSTALD correlation (Eq. 5.130)
 - LK generalized correlation
 - Compare errors from different methods
- 5.15. Estimate liquid density of n -decane at 423 K and 506.6 bar from the following methods:
- PR EOS
 - PR EOS with volume translation
 - PR EOS with Twu correlation for parameter a (Eq. 5.54)
 - MRK EOS
 - Rackett equation with COSTALD correlation
 - Compare the values with the experimental value of 0.691 g/cm³
- 5.16. Estimate compressibility factor of saturated liquid and vapor (Z^L and Z^V) methane at 160 K (saturation pressure of 15.9 bar) from the following methods:
- Z^L from Rackett equation and Z^V from Standing–Katz chart
 - PR EOS
 - PR EOS with Twu correlation for parameter a (Eq. 5.54)
 - MRK EOS
 - LK generalized correlation
 - Compare estimated values with the values from Fig. 6.12 in Chapter 6.
- 5.17. Estimate Z^V of saturated methane in Problem 5.16 from virial EOS and evaluate the result.
- 5.18. A liquid mixture of C₁ and n -C₅ exists in a PVT cell at 311.1 K and 69.5 bar. The volume of liquid is 36.64 cm³. Mole fraction of C₁ is 0.33. Calculate mass of liquid in grams using the following methods:
- PR EOS with and without volume translation
 - Rackett equation and COSTALD correlation
 - MRK EOS
- 5.19. A natural gas has the following composition:

Component	CO ₂	H ₂ S	N ₂	C ₁	C ₂	C ₃
mol%	8	16	4	65	4	3

Determine the density of the gas at 70 bar and 40°C in g/cm³ using the following methods:

- Standing–Katz chart
 - Hall–Yarborough EOS
 - LK generalized correlation
- 5.20. Estimate Z^L and Z^V of saturated liquid and vapor ethane at $T_r = 0.8$ from MRK and virial EOSs. Compare calculated values with values obtained from Fig. 5.10.

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