Chapter Two

Theory

2.1 Equations of State

Equations of state take into account the repulsive and attractive interactions between molecules. The earliest empirical equation of state is that of van der Waals with two adjustable parameters which represent the repulsive and attractive interactions. The original equation is

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \, . \tag{2.1}$$

Its basic ideas concern with two important points which have remained major considerations in all subsequent equation of state development. First, the repulsion effects caused by molecular size should be separated from the cohesive effects caused by molecular attraction force. In addition, the equation should have the validity to connect both liquid and vapor phases continuously. This equation also provides the basis for the first theory of corresponding states and the first guidelines for a method of extending a pure component equation to mixtures. Due to

the fact that such a simple equation is able to give a remarkably qualitative description of the overall P-V-T behavior of vapors and liquids, an immediate effort to make it also quantitatively correct has been produced. Since then, modifications of the second or attractive term, such as changing its volume dependence and/or introducing a temperature dependence into it, have been made and many equations of state have been proposed. They range from simple expressions with one or two constants to complicated forms.

Although the equations with several parameters give precise representations of the PVT data and calculations of thermodynamic properties, they require tedious manipulations and excessive computer storage in lengthy iterative calculations. Thus, over the last decade, many authors have been interested in two or three-parameter cubic equations of state which are simple equations and can be transformed into cubic equations in compressibility factor, Z. The attractiveness of this type of equations lies in their simplicity and ease of manipulations. At the beginning, the two-parameters equations of state were developed, some of which introduced deviation function to fit pure substance PVT data and others improved their capability for VLE calculations. One of the most successful equations was that proposed by Redlich and Kwong (6), in 1949. In their equation, the VDW's attractive term that was changed from

"a/v^2" to "$a/T^{0.5}v(v+b)$" improved the volumetric representation of the VDW equation. The Redlich-Kwong (RK) equation can be used to calculate volumetric and thermal properties with a good degree of accuracy. However, the application of this equation to binary VLE calculations yields poor results. This is attributed to the lack of accuracy in expressing the influence of temperature. Therefore, different modifications of the temperature dependence function of the RK EOS parameters have been proposed by many authors. A successful modification was introduced by Soave (1) in 1972 who improved the temperature independent parameter "a" in the original RK EOS to a temperature dependent form. Further, he introduced the acentric factor and derived correlations for the modified parameter. This equation, the Soave-Redlich-Kwong equation (SRK) applies well to all nonpolar components and successfully to multicomponent VLE calculations for mixtures of nonpolar substances. However, it does not work that well for carbon dioxide and gives less accurate results for systems containing hydrogen. It also fails to generate satisfactory values for the liquid densities. It gives deviations that increase from about 7% at reduced temperature below 0.65 to about 27% at reduced temperature approaching 1.0. Using a similar approach, Peng and Robinson (2) presented in 1976 a two-parameter equation which performed equally well with the SRK EOS. In fact, it can predict the liquid phase densities better than SRK EOS

and give the accurate equilibrium ratio. Still, the prediction of liquid region is unsatisfactory compared to experimental values.

In recent years, however, there has been increased interest in developing three-parameter equations of state to yield better saturated liquid volume predictions. It is believed that the failure of SRK EOS to reproduce liquid state data is attributed to two reasons. One is that the critical compressibility factor, Z_C, is held constant at a value of 1/3 for any substance studied and the other reason is that the volume parameter b is independent of temperature while the arguments based on kinetic theory of gases indicate that the parameter b be a decreasing function of temperature. To predict good liquid state data, any cubic equation of state should predict accurately the critical compressibility factor, Z_C.

In 1976, Fuller (7) overcame this shortcoming by introducing a third parameter, c, and by modifying the SRK EOS to predict saturated liquid volumes and compressed liquid volumes of pure substances. He studied compressed liquid water in the temperature range of 32-700°F and pressure range of 500-5000 psi for 65 data points. The results showed an average absolute error of 3.8% compared to an average absolute error of 37.5% for the SRK equation. Harmens and Knapp (4) developed another three-parameter

equation of state in 1980 and their equation, the HK equation, was tested over an extensive range of pressure and temperature. Its overall performance was found to be superior to SRK and PR equations.

In 1980, Schmidt and Wenzel (3) developed an equation of state that showed better prediction of liquid density values and vapor pressures particularly in the low pressure area. Their equation is still of the van der Waals's type where the parameter "a" is given by an expression similar to that of Soave. Vapor pressures of more than one hundred substances and liquid densities of 65 substances were tested and the results were compared with the SRK and PR equations. In 1982, Patel and Teja (5) proposed a new equation of state for fluids and fluid mixtures which predicted well volumetric properties in the liquid region while giving accurate VLE calculations. It retained many good features of the SRK and PR equations while overcoming some of their limitations for polar fluids. A general density cubic equation of state for nonpolar fluids was also presented in 1982 by Kumar and Starling (8). Their equation, the KS equation, can be extended to polar and associative fluids, mainly nonpolar hydrocarbons. Results showed their equation to be superior to the PR EOS and to perform as well as the three-parameter corresponding states modified BWR equation. It was also shown to perform as well as other noncubic equation of state. Finally, in 1985, Adachi et al. (9)

presented a three-parameter cubic equation of state for representing specifically saturated liquid volumes. This equation gave the lowest overall average percent deviation in the calculated values of saturated liquid volumes. In spite of these improvements, the two-parameter SRK and PR equations of state remain the most widely used equations in industry up to now.

2.2 The Soave-Redlich-Kwong Equation of State

The original Redlich-Kwong equation of state (6), developed in 1949, was a considerable improvement over current equations of relatively simple forms at the time of its introduction. Redlich and Kwong succeeded in demonstrating that a simple adjustment in the attractive terms of van der Waals equation could considerably improve the prediction of vapor-phase properties. Their equation has the following form :

$$P = \frac{RT}{V - b} - \frac{a}{T^{\frac{1}{2}}V(V+b)} \, , \qquad (2.2)$$

and by application of the criticality conditions, the parameters a and b are found in terms of the critical properties as

$$a = 0.427480 \ (RT_C)^2/P_C \ , \qquad (2.3)$$

$$b = 0.086640 \ RT_C/P_C \ , \qquad (2.4)$$

and

$$Z_C = 1/3 \ . \qquad (2.5)$$

To a large extent, it has retained its popularity over the past three decades, with various modifications. One of the most significant modification of this equation was made by Soave (1) in 1972. He replaced the temperature-dependent term "$a/T^{\frac{1}{2}}$" of the equation by a function "$a(T,w)$" involving the temperature and the acentric factor, so that the equation of state became

$$P = \frac{RT}{V - b} - \frac{a(T,w)}{V(V+b)} \ . \qquad (2.6)$$

The parameter a(T,w) was formulated primarily to make the equation fit the vapor pressure data of hydrocarbon, with the result

$$a(T,w) = a\alpha = 0.427480\alpha(RT_c)^2/P_c \qquad (2.7)$$

where

$$\alpha^{\frac{1}{2}} = 1 + m(1 - T_r^{\frac{1}{2}}) , \qquad (2.8)$$

$$m = 0.480 + 1.57w - 0.176w^2 . \qquad (2.9)$$

The coefficients "m" of this term were modified by Graboski and Daubert (10) in 1978 to

$$m = 0.48508 + 1.55171w - 0.15613w^2 . \qquad (2.10)$$

Eqn. 2.6 can be expressed in terms of the compressibility factor as

$$Z^3 - Z^2 + (A-B-B^2)Z - AB = 0 , \qquad (2.11)$$

where Z is the compressibility factor and A and B are defined by

$$A = a\alpha P/(RT)^2 \qquad (2.12)$$

and

$$B = bP/(RT) .$$ (2.13)

This polynomial form is solved for the largest root at a given vapor composition and for the smallest root at a given liquid composition.

2.3 The Peng-Robinson Equation of State

Several goals were set by Peng and Robinson in developing a new two-parameter equation of state cubic in volume (2) :

1. The parameter should be expressible in terms of P_c, T_c, and acentric factor (w).

2. The model should result in improved performance in the vicinity of the critical point, particularly for calculation of Z_c and liquid density.

3. The mixing rule should not employ more than one binary interaction coefficient, and that should be independent of temperature, pressure, and composition.

4. The equation should be applicable to all calculations of all fluid properties in natural gas processes.

Their equation is given by

$$P = \frac{RT}{V - b} - \frac{a\alpha}{V(V+b) + b(V-b)} \;, \qquad (2.14)$$

with the parameters at the critical point,

$$a = 0.457235 \; (RT_C)^2/P_C \;, \qquad\qquad (2.15)$$

$$b = 0.077796 \; RT_C/P_C \;, \qquad\qquad (2.16)$$

and

$$Z_C = 0.307. \qquad\qquad (2.17)$$

The addition of the b(V-b) term in the denominator of the attractive term resulted in an improved prediction of the liquid density without making "b" a function of temperature, therefore, this equation is considered to be one of the most important modification of the attractive term that uses only two parameters (11).

Peng and Robinson adopted Soave's approach for calculating α as given by eqn. 2.8. They also used w as the

correlating parameter for the slope, m, in eqn. 2.8 as given by

$$m = 0.37464 + 1.54226w - 0.26992w^2. \tag{2.18}$$

This expression was later expanded by the investigators to give the relationship

$$m = 0.3796 + 1.485w - 0.1644w^2 + 0.01667w^3. \tag{2.19}$$

Introducing the Z factor into eqn. 2.14 yields

$$Z^3 + (B-1)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0 , \tag{2.20}$$

where parameters A and B are defined as in eqn. 2.12 and eqn. 2.13.

2.4 The Schmidt-Wenzel Equation of State

Schmidt and Wenzel (3) proposed a generalized form of the van der Waals type equation which used the acentric factor (w) as the third parameter in addition to the critical data, critical temperature (T_c) and critical pressure (P_c). Also, the denominator "V^2" in the attractive term of the original equation was replaced by an expression

quadratic in volume to obtain the equation of the following form :

$$P = \frac{RT}{V - b} - \frac{a\alpha}{V^2 + (1+3w)bV - 3wb^2} \quad , \quad (2.21)$$

where a and b are given in terms of the critical properties by

$$a = \Omega_a (RT_c)^2 / P_c \quad , \quad\quad\quad\quad (2.22)$$

$$b = \Omega_b RT_c / P_c \quad , \quad\quad\quad\quad (2.23)$$

with

$$\Omega_a = [1 - \xi_c(1-\beta_c)]^3 \quad\quad\quad\quad (2.24)$$

and

$$\Omega_b = \beta_c \xi_c \quad . \quad\quad\quad\quad (2.25)$$

The critical compressibility factor, ξ_c, is expressed as an empirical parameter instead of letting it have a fixed value as in the SRK or PR equations or have a value equal to the experimental value. Since it is proved that

the fixed values in two previous equations result in considerably deviations of predicted saturated liquid densities and predicted critical volumes from the experimental data.

The proposed expression for critical compressibility factor is

$$\zeta_c = 1/3[(1+\beta_c w)] \tag{2.26}$$

with the approximation value of β_c being given by

$$\beta_c = 0.25989 - 0.0217w + 0.00375w^2 .$$

The dimensionless factor α is also a function of temperature and is given by eqn. 2.8. However, they made the modification in the slope term and proposed the following expressions

for $w \leq 0.4$, $m = m_1$,
for $w \geq 0.55$, $m = m_2$,

and for the intermediate range, $0.4 < w < 0.55$,

$$m = [(w-0.4)/0.15]m_2 + [(0.55-w)/0.15]m_1 , \tag{2.28}$$

with

$$m_1 = m_0 + (1/70)(5T_r - 3m_0 - 1)^2 \; , \tag{2.29}$$

$$m_2 = m_0 + 0.71(T_r - 0.779)^2 \; , \tag{2.30}$$

$$m_0 = 0.465 + 1.347w - 0.528w^2 \; , \; \text{for } w \leq 0.3671; \tag{2.31}$$

and

$$m_0 = 0.5361 + 0.9593w \; , \; \text{for } w > 0.3671. \tag{2.32}$$

For supercritical compounds, the temperature dependence of the parameter a is also the acentric factor, w, dependence as

$$a = 1 - (0.4774 + 1.328w)\ln T_r \; , \; \text{for } T_r > 1. \tag{2.33}$$

Finally, the polynomial form of the eqn. 2.21 in terms of the compressibility factor is

$$Z^3 + (UB - B - 1)Z^2 + (WB^2 - UB^2 - UB + A)Z - (WB^3 + WB^2 + AB) = 0 \; , \tag{2.34}$$

where parameters A and B are also defined as in eqn. 2.12 and eqn. 2.13 with

$$U = 1 + 3w \tag{2.35}$$

$$W = -3w. \tag{2.36}$$

A comparison of calculated and experimental vapor
pressure data for a wide range of pure substances (3) has
shown that the equation can reproduce the experimental data
at pressures above 1 bar with an accuracy similar to that of
the PR equation. However, in the lower pressure range, this
equation yields better agreement with the experiment data
than the SRK and PR equations as shown in Table 2.1. In
addition, in terms of liquid molar volume prediction, it is
shown that the SW equation give an accuracy equally well
with the SRK and PR equation. Figure 2.1, as an example,
shows the deviation of the calculated liquid volume for
methane as a function of temperature.

TABLE 2.1 Deviation between experimental and calculated vapor pressure.
Comparison between SW, PR, and SRK equations of state.

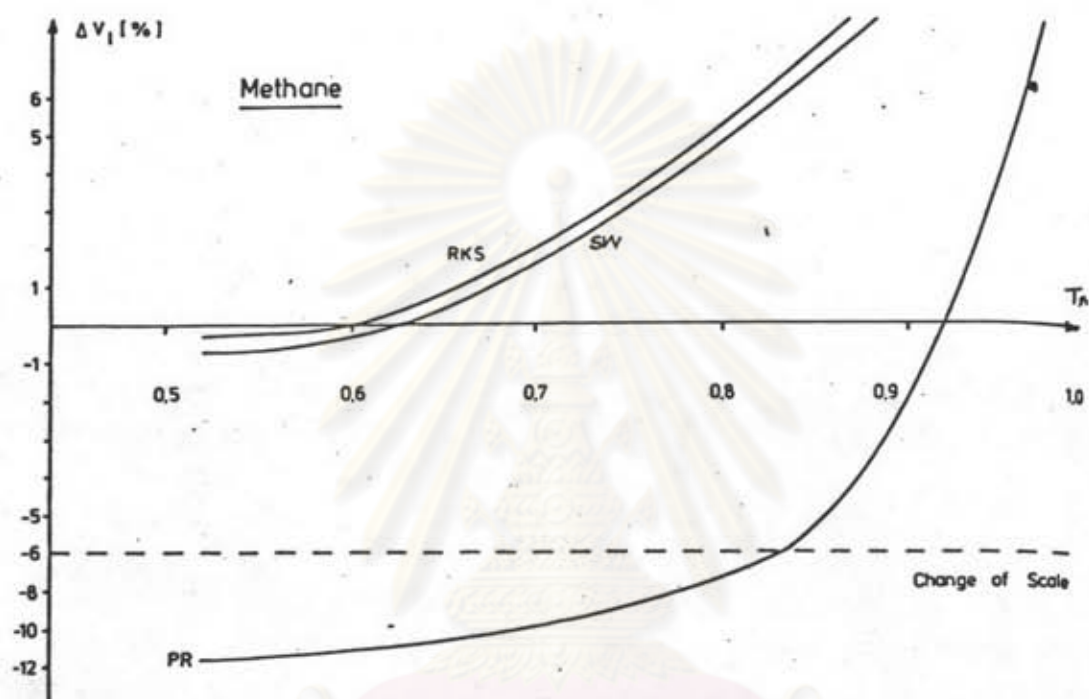| Substance group	No. of substance	No. of data points	Ps < 1 bar Av. Abs. Dev.			No. of data points	Ps > 1 bar Av. Abs. Dev.		
			SW	PR	SRK		SW	PR	SRK
Alkanes	40	978	1.07	4.16	1.96	1331	0.22	0.37	1.06
Alkenes	29	675	1.86	4.63	2.51	942	0.39	0.37	0.80
Alkylbenzenes	36	1118	1.93	2.51	3.85	1476	0.86	0.64	1.47

FIGURE 2.1 Deviation in liquid volume for methane as a
function of reduced temperature, T_r for the SRK,
PR, and SW equations of state (3)

2.5 The Patel-Teja Equation of State

The equation proposed by Patel and Teja (5) was an extension of those equations of Soave, Peng and Robinson, and Schmidt and Wenzel. Their equation used, in addition to the critical temperature (T_c) and critical pressure (P_c), two substance dependent parameters ζ_c and F as input parameters. The equation has the following form :

$$P = \frac{RT}{V - b} - \frac{a\alpha}{V(V+b) + c(V-b)} \quad . \qquad (2.37)$$

Obviously, the form of the cubic equation chosen was not new. A similar form had been chosen earlier by Harmens and Knapp (4) and Mollerup among others. By making certain assumptions, two previous equations can be obtained from this PT equation. When $c = b$, this equation reduces to the Peng-Robinson expression and when $c = 0$, it reduces to the Soave-Redlich-Kwong equation.

Application of critical constraints to this equation yields

$$a = \Omega_a(RT_c)^2/P_c \quad , \qquad (2.38)$$

$$b = \Omega_b R T_c / P_c \ , \tag{2.39}$$

and

$$c = \Omega_c R T_c / P_c \ , \tag{2.40}$$

where

$$\Omega_c = 1 - 3\zeta_c \ , \tag{2.41}$$

$$\Omega_a = 3\zeta_c^2 + 3(1-2\zeta_c)\Omega_b + \Omega_b^2 + (1-3\zeta_c) \ , \tag{2.42}$$

and Ω_b is the smallest positive root of the cubic equation

$$\Omega_b^3 + (2-3\zeta_c)\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0 \ . \tag{2.43}$$

The authors gave an approximation value of Ω_b as

$$\Omega_b = 0.32429\zeta_c - 0.022005 \ . \tag{2.44}$$

For the dimensionless factor a, they chose the same function of reduced temperature as that used by previous equations in eqn. 2.8.

The equation, therefore, requires a knowledge of four characterization constants T_c, P_c, ζ_c, and slope m. The

authors pointed out that ς_c is not equal to the experimental critical compressibility factor, but is treated as an empirical parameter whose procedure is being identical to that of Schmidt and Wenzel (3). The ς_c, thus, is obtained from one or more liquid density data points and m is obtained from the vapor pressure of the pure fluids. As a result, they proposed the following generalized expressions for the parameters :

$$m = 0.452413 + 1.30982w - 0.295937w^2 \qquad (2.45)$$

and

$$\varsigma_c = 0.329032 - 0.076799w + 0.0211947w^2 \ . \qquad (2.46)$$

It should be noted that if $\varsigma_c = 0.3074$, this equation reduces to the PR equation. Similarly, if $\varsigma_c = 0.3333$, the equation reduces to the SRK equation. Thus, characteristics of both SRK and PR equations are implicit in this equation. However, the application of the equation extends to heavy hydrocarbons (up to n-eicosane) and polar substances.

If A, B, and C are defined as

$$A = a\alpha P/(RT)^2 \ , \qquad (2.47)$$

$$B = bP/(RT) \ , \qquad (2.48)$$

and

$$C = cP/(RT) ,$$ (2.49)

eqn. 2.37 can be rearranged in terms of Z to produce

$$Z^3 + (C-1)Z^2 + (A-2BC-B-C-B^2)Z + (BC+B^2C-AB) = 0 .$$ (2.50)

The tested results of this equation with pure substances (5) showed that the accuracy of the equation in the representation of saturated liquid and vapor densities were better than those obtained from other cubic equations of state as shown in Table 2.2 and 2.3. In conclusion, its overall average deviations was 2.4% compared with 3.3% for the PR equation for 3175 data points including available data for methane through n-eicosane. Figure 2.2 shows its superior performance over the PR equation in saturated liquid density calculations for n-eicosane. For the vapor pressures, this equation gave an overall average deviation between calculated and experimental values for the 38 substances at 0.86%.

Table 2.2 Comparison of the absolute average deviation in
saturated liquid densities for PT, PR, and SRK
EOS. (5)

Components	No. of points	T_r range	PT AAD(%)	PR AAD(%)	SRK AAD(%)
Methane	32	0.524-0.976	3.03	7.66	5.72
Ethane	28	0.563-0.982	3.63	7.12	13.32
Propane	33	0.570-0.984	2.86	5.93	14.51
n-Butane	28	0.627-0.980	3.39	5.61	19.36
i-Butane	29	0.578-0.980	2.61	3.40	15.64
n-Pentane	30	0.638-0.981	3.11	4.00	20.12
n-Hexane	32	0.613-0.974	2.24	3.22	24.02
n-Heptane	23	0.637-0.987	2.04	4.69	29.56
n-Decane	27	0.536-0.771	0.62	5.85	-
Carbon dioxide	44	0.712-0.987	1.78	5.22	23.00

Table 2.3 Comparison of the absolute average deviation in saturated vapor densities for PT, PR, and SRK EOS. (5)

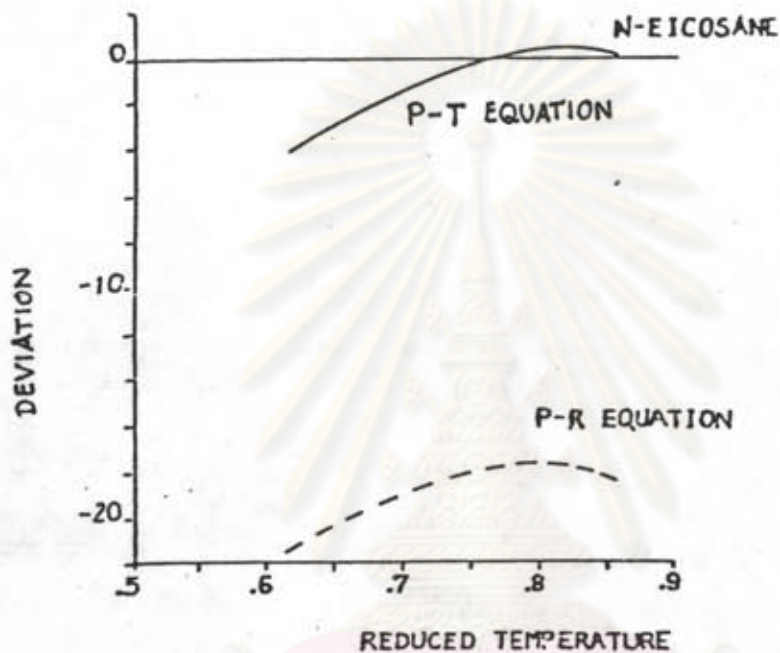| Components	PT AAD(%)	PR AAD(%)	SRK AAD(%)
Methane	1.50	1.66	0.51
Ethane	2.12	1.38	1.97
Propane	2.22	1.23	2.91
n-Butane	1.62	0.78	3.23
i-Butane	2.30	1.73	1.30
n-Pentane	1.78	0.62	3.30
n-Hexane	1.70	0.88	4.10
n-Heptane	1.32	0.63	3.54
Carbon dioxide	2.13	2.00	4.53

FIGURE 2.2 Comparison of calculated and experimental saturated liquid densities of n-eicosane for the PT and PR equations of state (5)

2.6 Vapor-Liquid Equilibrium Calculation

The calculations of VLE is concerned with finding the state of equilibrium between liquid and vapor phases when particular conditions or properties are specified. The properties in question may be the compositions and relative amounts of the phases, the temperature, pressure, enthalpy, entropy, or some other thermodynamic properties. Given some of these properties, the others can be calculated.

For every component i in the mixture, the condition of thermodynamic equilibrium between a vapor and a liquid is given by

$$f_i^V = f_i^L \qquad (2.51)$$

where

f_i = partial fugacity of component i

V = vapor phase

L = liquid phase .

The fundamental problem is to relate these fugacities to mixture compositions, since it is the latter which are of concern in process design. The fugacity of a component in a mixture depends on the temperature, pressure, and composition of that mixture. In principle, any measure of

composition can be used. For the vapor phase, as an example, the composition is nearly always expressed by the mole fraction y. To relate f_i^V to temperature, pressure, and mole fraction, it will be expressed in terms of fugacity coefficient as

$$\emptyset_i^V = f_i^V/y_i P \qquad (2.52)$$

where the partial fugacity coefficient may be derived from vapor-phase PVT data, usually given by an equation of state. The same expressions can be applied to the liquid phase by replacing mole fraction y by x.

The partial fugacity coefficient $\emptyset_i$ depends on temperature and pressure, and in a multicomponent mixture, on all mole fractions in that phase and not just on individual components. For the vapor phase, the partial fugacity coefficient is, by definition, normalized such that as P -- 0, $\emptyset_i^V$ -- 1 for all i. At low pressure, therefore, it is usually a good assumption to set $\emptyset_i^V = 1$.

Finally, at the equilibrium

$$K_i = y_i/x_i = \emptyset_i^L/\emptyset_i^V \qquad (2.53)$$

where K_i is the Equilibrium ratio for component i in the mixture which is a key quantity in the analysis of

vapor-liquid equilibria. Its implementation will be made in calculations of dewpoints, bubble points, and flashes, normally by an equation of state.

In 1988, T.H. Ahmed (12) conducted a comparative study of several equations of state, including all these four equations, in the prediction of vapor-liquid equilibrium of multicomponent hydrocarbon systems. Comparison of the experimental and predicted K values from five equations for a selected system is shown in Figure 2.3. In his work, he concluded that, in terms of VLE prediction, the PR, PT and SW equations all perform equally well, whereas the PT and SW are found to give reliable gas compressibility factor predictions (12). It should be noted that, in this work, the interaction coefficient is added only between methane and the heaviest component by the adjustment with the experimental data.
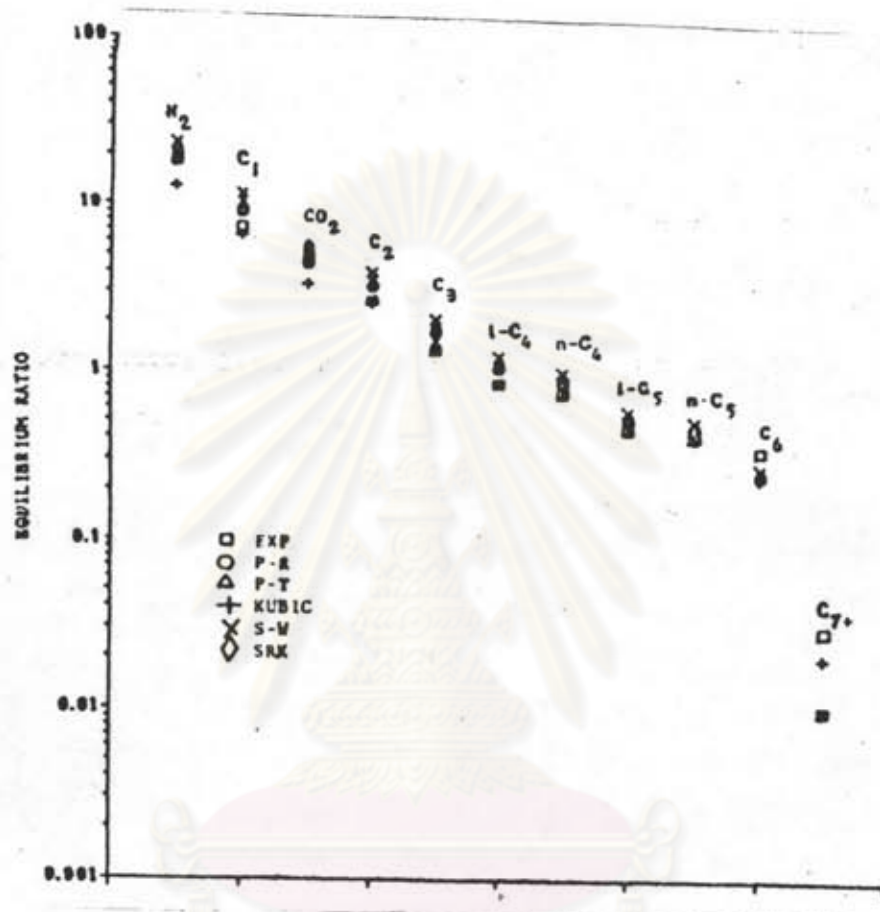
Figure 2.3 Comparison of the K values of the multicomponent

hydrocarbon system at 280 F and 714.7 psia

predicted by five equations of state (12)

2.7 Mixing Rules

The mixing rules have the purpose of responding to a property of a mixture in terms of the composition and the properties of the pure components. Depending on the property, the composition may be in mole or volume or weight fractions. Some of the mixing rules have a rational basis, but most are purely empirical. In many instances, the prediction of a property can be improved by incorporating a limited amount of experimental data on the mixture or on component pairs of the mixture, since binary interactions have a major impact on the mixture behavior.

Most equations of state accept the "classical" mixing rules, that is, the one-fluid van der Waals mixing rules :

$$(a\alpha)_m = \sum_i \sum_j z_i z_j a\alpha_{ij} , \qquad (2.54)$$

$$b_m = \sum_i z_i b_i , \qquad (2.55)$$

$$c_m = \sum_i z_i c_i , \qquad (2.56)$$

with the cross parameter taken to be

$$a\alpha_{ij} = (a\alpha_i a\alpha_j)^{\frac{1}{2}}(1-K_{ij}) . \qquad (2.57)$$

Once these expressions for the mixing rules are chosen, the fugacity coefficients of any component i in the vapor or liquid phase can be calculated. The equations of the fugacity coefficients for four equations of state are presented in Table 2.4.

2.8 Binary Interaction Coefficients

The behavior of mixtures naturally is affected by interactions of unlike molecules, particularly if some are polar. Interactions between tripods and higher combinations usually are less important than those between pairs of components. Higher-order interactions often are small and thus hidden by imperfections of practicable equations of state, so that incorporation of only binary data in addition to those of pure components generally leads to a major possible improvement in the accuracy of the equation of state. For an n-component mixture, there are $n(n-1)/2$ possible binary interaction coefficients.

TABLE 2.4 Fugacity coefficient expression for SRK, PR, SW, and PT equations of state.

Equation of state	Expression

SRK EOS

$$\ln(\phi_i) = b_i(Z-1)/b_m - \ln(Z-B)$$
$$- (A/B)\{2\sum_j y_j(a\alpha)_{ij}/(a\alpha)_m - b_i/b_m\}*$$
$$\ln(1+B/Z)$$

PR EOS

$$\ln(\phi_i) = b_i(Z-1)/b_m - \ln(Z-B) - (A/2.82843B)*$$
$$\{2\sum_j y_j(a\alpha)_{ij}/(a\alpha)_m - b_i/b_m\}*$$
$$\ln[(Z+2.414B)/(Z-0.414B)]$$

SW EOS

$$\ln(\phi_i) = b_i(Z-1)/b_m - \ln(Z-B) - (A/SB)*$$
$$\{2\sum_j y_j(a\alpha)_{ij}/(a\alpha)_m - b_i/b_m\}*$$
$$\ln[(Z+(U+S)B/2)/(Z-(U-S)B/2)]$$
$$\text{where } S = (U^2+4U-4)^{\frac{1}{2}}$$

PT EOS

$$RT\ln(\phi_i) = RTb_i/(V-b_m) - RT\ln(Z-B)$$
$$(\sum_j y_j(a\alpha)_{ij}/d)\ln[(Q+d)/(Q-d)]$$
$$+ (a\alpha)_m(b_i+c_i)/[2(Q^2-d^2)]$$
$$+[a_m/(8d^3)][c_i(3b_m+c_m)+b_i(3c_m+b_m)]$$
$$*\{\ln[(Q+d)/(Q-d)]-2Qd/(Q^2-d^2)\}$$
$$\text{where } V = ZRT/P$$
$$Q = V+(b_m+c_m)/2$$
$$d = [b_m c_m+(b_m+c_m)^2/4]^{\frac{1}{2}}$$

2.9 Evaluation Procedures of the Optimal Binary Interaction Coefficients (K_{ij})

In practice, the optimal values of K_{ij} should be determined from binary vapor-liquid equilibrium data by minimizing the difference between the calculated and experimental values of a selected equilibrium properties. A number of criteria have been used for the evaluation as follow :

1. minimization of deviation in predicted K values (13,14,15)

2. minimization of deviation in predicted bubble point pressures (16,17,18,19,20)

3. minimization of deviation in predicted bubble point vapor composition (17)

4. minimization of the flash volume variance (16)

5. minimization of the sum of variances of the flash vapor and liquid compositions (21)

6. minimization of the deviation between calculated component vapor and liquid fugacities. (22)

The binary interaction coefficients obtained by different models may not be identical, presenting a problem that which method will yield the most desirable results. Furthermore, all the listed methods above with the exception of the last one involve iterative calculations of either

bubble point or flash type for each datum (22). Thus, they may be rather time-consuming, especially in cases where there are more than one binary interaction coefficient in an equation of state, complicated state equation, and/or large data set.