

## CHAPTER II

### THEORY

In this chapter, the theory concerning equations of state, fugacity and fugacity coefficient, vapor-liquid equilibrium calculations, binary interaction parameters and mixing rules will be described.

#### 2.1 Equations of State

An equation of state is the relation of three properties of a substance -- pressure, temperature and volume in the form of equation,

$$f(P, V, T) = 0 \quad (2.1)$$

A suitable EOS can be used to evaluate many important properties of pure substances and mixtures, including the following :

1. Densities of liquid and vapor phases.
2. Vapor pressure.
3. Critical properties of mixtures.
4. Vapor-liquid equilibrium relations.
5. Deviation of enthalpy from ideality.
6. Deviation of entropy from ideality.

At present no one equation of state exists that is equally suitable for all these properties of any large variety of substances, but many useful results of limited scope have been achieved.

To start with, it was the Boyle's work in 1662, Charles and Gay-lussac's work in 1802 and Clapeyron's work in 1834 with the ideal gas law,

$$PV = RT \quad (2.2)$$

From the beginning, it was realized that the ideal gas law often is

only a rough approximation of true behavior. Deviations were ascribed to the finite volumes occupied by the molecules themselves and to forces of repulsion and attraction between the molecules. Both these factors were taken into account quantitatively by van der Waals (vdW) in 1873. He proposed an equation that is generally accepted as the first realistic equation of state,

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \quad (2.3)$$

where  $a$ ,  $b$  and  $R$  are constants. The repulsive term is the first term and the attractive term is the second.

Scores of modifications of the van der Waals equation have been made. Among these equations, cubic EOS, like van der Waals EOS, have received much attention due to their simplicity and practical success. They are explicit in pressure and of the third degree in volume or compressibility factor. When a cubic EOS in volume or compressibility factor has three positive real roots, the largest one is that of the vapor, the smallest one that of the liquid and the intermediate one without physical significance. Parameters of cubic equations are basically expressible in terms of critical properties but include modifications for temperature and another properties such as critical compressibility or acentric factor.

Following the studies of Martin in 1979, Abbott in 1979 and Vera et al. in 1984 [1], the most general form of a cubic EOS is

$$P = \frac{RT}{(V-b)} - \frac{a(T)(V-k_3b)}{(V-b)(V^2+k_1bV+k_2b^2)} \quad (2.4)$$

This equation may be modified by changing the value of  $a(T)$ ,  $k_1$ ,  $k_2$  and  $k_3$  in the attractive term, for example the van der Waals EOS uses  $a(T) = a$ ,  $k_1 = 0$ ,  $k_2 = 0$  and  $k_3 = 1$ . Table 2.1 shows the value of  $a(T)$ ,  $k_1$ ,  $k_2$  and  $k_3$  of some cubic EOS.

At the beginning of modifications of van der Waals EOS, the two-parameter equations of state were developed. And mostly the attractive term was modified. The attractive term (the second term) is caused by molecular

Table 2.1 the value of  $a(T)$ ,  $k_1$ ,  $k_2$  and  $k_3$  of some cubic equations of state in form:

$$P = \frac{RT}{[V-b]} - \frac{a(T)[V-k_3b]}{[V-b][V^2+k_1bV+k_2b^2]}$$

Investigator	$a(T)$	$k_1$	$k_2$	$k_3$
vdw (1873)	$a$	0	0	1
Clausius (1880)	$a/T$	$2c/b$	$(c/b)^2$	1
RK (1949)	$a/T^{0.5}$	1	0	1
Soave (1972)	$a\alpha$	1	0	1
PR (1976)	$a\alpha$	2	-1	1
SW (1980)	$a\alpha$	$1+3\omega$	$-3\omega$	1
PT (1982)	$a\alpha$	$1+(c/b)$	$-(c/b)$	1

<u>Note</u>	vdw	-	van der Waals
	Claussius	-	Clausius
	RK	-	Redlich and Kwong [2]
	Soave	-	Soave [5]
	PR	-	Peng and Robinson [6]
	SW	-	Schmidt and Wenzel [10]
	PT	-	Patel and Teja [12]

attraction forces while the repulsive term (the first term) is caused by molecular size that should not be much modified. Therefore Eq. (2.4) has the same repulsive term as the van der Waals EOS. However, it is not sure. Some investigators [1] have modified the repulsive term as well such as Scott in 1971, Guggenheim in 1965 and Carnahan & Starling in 1972. In addition to using two parameters in EOS like the van der Waals EOS, many investigators proposed more parameters for flexible applications such as the three-parameter equation of Clausius in 1880.

In 1949, Redlich and Kwong [2] proposed an equation of state which adjusted the attractive term by the influence of temperature. This EOS could considerably improve the P-V-T prediction, especially, the critical isotherm. It could also improve the prediction of vapor-phase properties such as the vapor enthalpies, the vapor fugacity coefficients.

In 1964, Wilson [3] modified the original Redlich-Kwong EOS. The  $a$  parameter in Eq. (2.3) be made a function of temperature to improve the prediction of the pure-compound vapor pressure. The parameter  $\alpha$  was a linear function of reduced temperature. However, This recommendation was largely ignored, even though this EOS was applied successfully to many systems.

In 1970, Joffe and Zudkevitch [4] recommended that  $a$  and  $b$  in Eq. (2.3) be functions of temperature. The temperature dependence of  $a$  and  $b$  was determined by simultaneously matching liquid density and forcing the vapor and liquid fugacities to be equal to the pure component's vapor pressure. This modification proved to be a powerful VLE method, however, it cannot be used for enthalpy calculations.

In 1972, Soave [5] proposed an EOS in the same form as the Wilson EOS. Unlike the Wilson EOS, Soave's modification gained quick and wide acceptance and became the most popular method for high-pressure VLE calculations. This equation, called the Soave-Redlich-Kwong equation, applied well to all nonpolar components.

In 1976, Peng and Robinson [6] modified the attractive term by using only two parameters. This EOS is generally similar to Soave's for VLE, but

better than Soave's for liquid density by without making  $b$  a function of temperature. However, it was not able to simultaneously improve the vapor density.

In 1979, Martin [7] concluded that his equation was the best cubic EOS. The equation is a four-parameter form of the Clausius EOS. The parameters includes  $a$ ,  $b$ ,  $c$  and  $Z_C$ . The parameter  $Z_C$  is the experimental compressibility factor at the critical point. It gave added flexibility to the Martin EOS which enabled it to represent P-V-T properties for a variety of substances with greater accuracy than would be the case with the Soave or Peng-Robinson EOS.

In 1980, Heyen [8] used two temperature-dependent parameters in the modification of the Redlich-Kwong EOS, but his EOS had a total of three parameters. The  $a$  and  $b$  in Heyen's modification are well-behaved, continuous functions of the temperature. This EOS is developed for VLE calculations.

In 1980, Harmens and Knapp [9] proposed a cubic EOS which possessed three adjustable parameters and therefore was more flexible than the Redlich-Kwong and Peng-Robinson equations. The parameters were correlated in terms of  $T_C$ ,  $P_C$  and acentric factor  $\omega$ . The equation was found in good overall performance such as the volumes along the critical isotherm, boiling temperatures and saturated liquid volumes for pure and normal substances.

In 1980, Schmidt and Wenzel [10] proposed an equation of state of the van der Waals type which use the critical data  $T_C$  and  $P_C$  and the Pitzer's acentric factor  $\omega$  as input data and which yielded a substance-dependent critical compressibility factor. Parameters  $a$ ,  $b$  are given by an expression similar to that proposed by Soave. The suggested equation yields improved liquid densities and vapor pressures. However, the equation is restricted to non-associated compounds.

In 1982, Kubic [11] took a different approach. He made  $a$  and the third parameter  $c$  temperature-dependent. This EOS was modified from the Clausius EOS.

In 1982, Patel and Teja [12] proposed a new cubic EOS. The new equation required  $T_C$ ,  $P_C$  as well as two additional parameters, correlated with the acentric factor, to characterize each particular fluid. The new equation showed good predictions of volumetric properties in the liquid region and maintained accuracy in vapor-liquid equilibrium calculations.

## 2.2 The Soave-Redlich-Kwong Equation of State

From the beginning of the modification of vdW EOS, Redlich and Kwong [2] proposed an equation which showed a comparable improvement over the other equations in 1949. The equation was modeled on that of van der Waals but its parameter  $a$  is changed to a temperature dependence by inclusion of the term  $T^{0.5}$ . Since the arithmetic is simpler, the RK equation continues in limited use. It is satisfactory for gas-phase properties calculations, but not for liquid-phase calculations.

A number of adjustments of the parameters of the RK equation have been reported, one of the most significant modification of this equation was made by Soave [5] in 1972. In this equation, the temperature-dependent term  $a/T^{0.5}$  of the RK equation was replaced by a function  $a(T, \omega)$  involving the temperature and the acentric factor, so that the equation of state became

$$P = \frac{RT}{(V-b)} - \frac{a(T, \omega)}{V(V+b)} \quad (2.5)$$

The parameter  $a(T, \omega)$  was formulated primarily to make the equation fit the vapor pressure data of hydrocarbons. The acentric factor  $\omega$  is a measure of the acentricity which results in the deviation from simple-fluid behavior. Soave gave

$$a(T, \omega) = a \cdot \alpha \quad (2.6)$$

where

$$\alpha^{0.5} = 1 + m(1 - T_r^{0.5}) \quad (2.7)$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (2.8)$$

The coefficients  $m$  of this term were modified by Graboski & Daubert [13] in 1978 to

$$m = 0.48508 + 1.55171\omega - 0.15713\omega^2 \quad (2.9)$$

Soave suggested that the  $\alpha$  might be in a different form, such as in the case of strongly polar substances such as water, alcohols and others.

The parameters  $a$  and  $b$  are found in terms of the critical properties by comparing coefficients the polynomial forms of the equation at the critical point with the form of the equation derived on the observation that the three roots are equal at the critical point. Thus :

$$a = \Omega_a R^2 T_c^2 / P_c \quad (2.10)$$

$$b = \Omega_b RT_c / P_c \quad (2.11)$$

$$\Omega_a = 0.427480 \quad (2.12)$$

$$\Omega_b = 0.086640 \quad (2.13)$$

Although the coefficients  $\Omega_a$  and  $\Omega_b$  are constant, usually the fit of data to the equation of state is improved by allowing the coefficients to vary from substance to substance.

For convenience of calculations, Eq. (2.5) is expressed explicitly in the form of polynomials in terms of compressibility factor  $Z$ ,

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (2.14)$$

where

$$A = a \alpha P / (RT)^2 \quad (2.15)$$

$$B = b P / (RT) \quad (2.16)$$

The Soave equation is applicable to both physical states (liquid and gaseous), polar and apolar compounds and, by the use of proper mixing rules, can describe accurately the phase equilibria of binary and multicomponent systems, with a minimum of empirical parameters, whereas it retains the

simplicity.

### 2.3 The Peng-Robinson Equation of State

In 1976, Peng and Robinson [6] proposed that the attractive term in the vdW equation should be  $-a/g(v)$  where  $g(v)$  is a function of the molar volume  $V$  and the constant  $b$ . They also concluded that by choosing a suitable function for  $g(v)$ , the predicted critical compressibility factor can be made to approach a more realistic value. The applicability of the equation at very high pressures is affected by the magnitude of  $b/V_c$  where  $V_c$  is the predicted critical volume. And treating the dimensionless scaling factor for the temperature-dependence parameter as a function of acentric factor in addition to reduced temperature has significantly improved the prediction of vapor pressures for pure substances and consequently the equilibrium ratios for mixtures.

Finally, they proposed an equation of the form

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (2.17)$$

Applying Eq. (2.17) at the critical point, parameters  $a(T_c)$ ,  $b(T_c)$  and  $Z_c$  are obtained as follows

$$a(T_c) = 0.45724 R^2 T_c^2 / P_c \quad (2.18)$$

$$b(T_c) = 0.07780 RT_c / P_c \quad (2.19)$$

$$Z_c = 0.307 \quad (2.20)$$

At any temperature the parameter  $a(T)$  and  $b(T)$  are corrected to

$$a(T) = a(T_c) \alpha(T_r, \omega) \quad (2.21)$$

$$b(T) = b(T_c) \quad (2.22)$$

where  $\alpha(T_r, \omega)$  is a dimensionless function of reduced temperature and acentric factor and equals unity at the critical temperature. Similarly to the Soave parameter, it is defined as in Eq. (2.7) but  $m$  is different.



$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (2.23)$$

Eq. (2.17) can be expressed in the form of polynomials in terms of compressibility factor,

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (2.24)$$

where A and B are defined as in Eq. (2.15) and (2.16).

According to the PR equation, the critical compressibility is  $Z_c = 0.307$ . This value is nearer the true values of many substances, particularly nonpolar ones, than are the  $Z_c$  of other two-parameter EOS's. This is a partial explanation for the fact that the PR equation is able to predict liquid densities more accurately than does the Soave equation, which is otherwise quite similar in performance. Although the PR equation has inherent limitations like the general two-constant equation, the justification for their equation is a compromise of simplicity and accuracy.

#### 2.4 The Patel-Teja Equation of State

In 1982, Patel and Teja [12] presented a new cubic EOS in their work. The EOS used, in addition to the critical temperature  $T_c$  and critical pressure  $P_c$ , two substance dependent parameters  $\xi_c$  and F as input parameters.

The EOS proposed in their work has the following form :

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)+c(V-b)} \quad (2.25)$$

where R is the universal gas constant,  $a$  is a function of temperature and  $b$  and  $c$  are constants. These parameters are obtained as follows:

$$a(T) = \Omega_a (R^2 T_c^2 / P_c) \alpha(T_r) \quad (2.26)$$

$$b = \Omega_b (RT_c / P_c) \quad (2.27)$$

$$c = \Omega_c (RT_c / P_c) \quad (2.28)$$

The values of  $\Omega_a$ ,  $\Omega_b$  and  $\Omega_c$  are obtained from the critical compressibility factor,  $\xi_c$ .

$$\Omega_c = 1 - 3 \xi_c \quad (2.29)$$

$$\Omega_a = 3\xi_c^2 + 3(1-2\xi_c)\Omega_b + \Omega_b^2 + 1 - 3\xi_c \quad (2.30)$$

and  $\Omega_b$  is the smallest positive root of the following cubic equation:

$$\Omega_b^3 + (2-3\xi_c)\Omega_b^2 + 3\xi_c^2\Omega_b - \xi_c^3 = 0 \quad (2.31)$$

For  $\alpha(T_r)$ , Patel and Teja chose the same function of reduced temperature as used by Soave, Peng and Robinson. It is given by:

$$\alpha(T_r) = [1 + F(1-T_r^{1/2})]^2 \quad (2.32)$$

The substance dependent parameters,  $\xi_c$  and  $F$  are evaluated by minimizing deviations in saturated liquid densities while simultaneously satisfying the equality of fugacities,  $f^L = f^V$  along the saturation curve. By this approach, in addition to nonpolar fluids, the new EOS can be applied to polar fluids such as water, ammonia and the alcohols, and extend to the mixtures.

For nonpolar substances, the values of the parameters  $\xi_c$  and  $F$  can be correlated with an acentric factor. The resulting correlations are given by

$$F = 0.452413 + 1.30982\omega - 0.295937\omega^2 \quad (2.33)$$

$$\xi_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2 \quad (2.34)$$

The loss in accuracy in predicting compressibilities of nonpolar fluids using the generalized constants was less than 1% and, often, less than 0.1%. From Eq. (2.25), polynomial forms in the compressibility factor are more preferred in this work. It can be made by substitution  $V$  with  $ZRT/P$  in Eq. (2.25) then become

$$Z^3 + (C-1)Z^2 + (A-2BC-B-C-B^2)Z + (BC+B^2C-AB) = 0 \quad (2.35)$$

where

$$C = cP/(RT)^2 \quad (2.36)$$

and A and B are defined as in Eq. (2.15) and (2.16).

The new equation gives low average deviations between calculated values and experimental values for both liquid and vapor densities, for which it consistently gives better predictions than the P-R equation and the R-K equation. Even in the critical region ( $0.9 < T_r < 1.0$ ), the equation can correct deviations if  $\xi_c$  is differently modified. For vapor pressures of pure fluids, the overall average deviation between calculated and experimental values is mostly less than 1%, and less than 3% for enthalpy and entropy departures of saturated liquids. For VLE results, the new equation is as good as the Soave and Peng-Pobinson equations for mixtures of light hydrocarbons. For systems containing heavy hydrocarbons and polar substances, the new equation is superior to the Soave and Peng-Robinson equations.

### 2.5 The modified Soave-Redlich-Kwong Equation of State

In 1979, Soave [14] proposed a four-parameter extension of the original SRK equation (Soave, 1972) which was intended to improve vapor-liquid equilibria and vapor pressure calculations for compounds or systems which exhibit strong polar effects. The new equation of state, henceforth referred to as the modified SRK or MSRK, differs from the original only in the functional form of the temperature-dependent energy-attraction term. The expression for  $a(T)$  in Eq. (2.6) is recast to give a better representation of polar systems in terms of two parameters (in addition to  $T_c$  and  $P_c$ ). These two parameters ( $g$  and  $h$ ) are unique to the compound of interest and must be determined with an empirical data fit. This contrasts with the original SRK energy term which used only one fitted parameter, the acentric factor. The new expression which comprised the sole modification to the original SRK equation was

$$\alpha(T) = 1 + (1 - T_r)(g + h/T_r) \quad (2.37)$$

where  $g$  and  $h$  are the two adjustable MSRK parameters, replacing the acentric factor, which in general are fit to vapor pressure data for the compound of interest. The other concerned equations for calculations are defined like in the case of the SRK equations as in Eq. (2.5) and (2.10) - (2.16).

In spite of the enhancements, application of the equation has been hampered since it requires two adjustable parameters for which no known tabulation exists. In 1986, Sandaruci, Kidnay and Yesavage [15] undertook a program of fitting modified SRK parameters to Sondergard's extensive vapor pressure databank containing data for over 286 organic and inorganic compounds. Sandaruci and co-workers followed the Soave technique, which he discussed in a subsequent paper [16] in 1980, for acquiring the two parameter values, called the "simplified procedure". This method was found to be simple to program, robust, fast computationally and produced  $g$  and  $h$  values which could be used to reliably determine vapor pressures.

The MSRK equation can model VLE for polar systems well. The equation handles vapor pressures for both polar and nonpolar systems well with a little bias or deviation. In addition, it models enthalpy departures for polar organic (both pure and mixture) systems much better than the more common industrial equations of state : the original SRK and PR.

## 2.6 The modified Peng-Robinson Equation of State

Equation of states such as PR and SRK have been used widely in process design simulation. The accuracy of these equations in predicting the vapor-liquid equilibrium constants and enthalpies of light hydrocarbon systems is within the accuracy of experimental data. However, these equations give poor results when they are used to describe the liquid phase densities even for simple systems.

In order to investigate the feasibility of improving the accuracy of liquid phase density, in 1986, Moshfeghian, Chariat and Maddox [17] expressed the  $b$  constant of the PR EOS as a function of temperature and added the new parameter  $\eta$  in it. This is different from the referred two-

parameter EOS that the parameter  $b$  depends on the critical temperature and pressure but is independent of the system temperature. They proposed the new  $b$  as :

$$b = b(T_c)\beta(T_r, \eta) \quad (2.38)$$

The value of  $\beta$  must become unity as the reduced temperature,  $T_r$ , approaches one. It was given in the following form.

$$\beta = 1 + \eta(1 - T_r) \quad (2.39)$$

The parameter  $\eta$  is a characteristic parameter. It can be determined for each pure component by the minimization of the objective function which is a function of calculated and experimental vapor pressure, calculated and experimental saturated vapor volume, calculated and experimental saturated liquid volume, as well as calculated and experimental heat of vaporization. In combination with the proposed modification, a new value of  $\eta$  for each pure component was also determined. In other words, the above procedure was followed to determine  $\eta$  and  $\omega$  simultaneously, the value of which had already been obtained for some substances. The  $b(T_c)$  in Eq. (2.38) and the other concerned equations for calculations are defined such as in the case of the PR equation as Eq. (2.17) - (2.21) and (2.23) - (2.24).

In this paper, it was indicated that the proposed modification not only improved the quality of saturated liquid volume (or density) but also improved the accuracy of vapor pressure and saturated vapor volume prediction capabilities. Finally, Moshfeghian, Shariat and Maddox concluded that more accurate performance could be obtained, while this modification did not present any complicated calculations.

## 2.7 Fugacity and Fugacity Coefficient

The concept of fugacity arises from a consideration of the change in Gibbs energy that results from changes in pressure and temperature. The fugacity and partial fugacity reduce to the pressure and partial pressure at low

values.

$$\lim_{p \rightarrow 0} \frac{f}{P} = \lim_{p \rightarrow 0} \phi = 1 \quad (2.40)$$

$$\lim_{p \rightarrow 0} \frac{\hat{f}_i}{x_i P} = \lim_{p \rightarrow 0} \hat{\phi}_i = 1 \quad (2.41)$$

The  $f$  and  $f_i$  are called fugacity and partial fugacity whereas the ratio  $\phi = f/P$  and  $\phi_i = f_i/(x_i P)$  are called fugacity and partial fugacity coefficients.

For pure substances and mixtures, the fugacity and partial fugacity coefficient coefficients can be evaluated for each equation of state by replacing  $P$  with its equivalent in the following equations:

For pure substances,

$$\ln \phi = Z - 1 - \ln Z - \frac{1}{RT} \int_{\infty}^V \left[ P - \frac{RT}{V} \right] dV \quad (2.42)$$

For mixtures,

$$RT \ln \hat{\phi}_i = \int_V^{\infty} \left[ \frac{\partial P}{\partial n_i} - \frac{RT}{V} \right] dV - RT \ln Z \quad (2.43)$$

when the infinite limit  $\infty$  implies the zero-pressure and the derivative  $\partial P / \partial n_i$  is taken at both constant temperature and total volume. The expression of the partial fugacity coefficients for some EOS are presented in Table 2.2.

In this work, the two-component mixtures are considered, so the partial fugacity coefficients are required. And it will be mentioned in the following section for vapor-liquid equilibrium calculation.

Table 2.2 Partial fugacity coefficient expressions for the selected EOS

EOS	Expression
SRK,MSRK	$\ln(\hat{\phi}_i) = \frac{B_i}{B}(Z-1) - \ln(Z-B)$ $+ \frac{A}{B} \left[ \frac{B_i}{B} - \frac{2}{a\alpha_j} \sum y_j(a\alpha)_{ij} \right] \ln \left[ 1 + \frac{B}{Z} \right]$
PR, MPR	$\ln(\hat{\phi}_i) = \frac{B_i}{B}(Z-1) - \ln(Z-B)$ $+ \frac{A}{2.828B} \left[ \frac{B_i}{B} - \frac{2}{a\alpha_j} \sum y_j(a\alpha)_{ij} \right] \ln \left[ \frac{Z+2.414B}{Z-0.414B} \right]$
PT	$RT \ln(\hat{\phi}_i) = RT \left[ \frac{b_i}{V-b} \right] - RT \ln(Z-B) - \frac{1}{d} \left[ \frac{Q+d}{Q-d} \right] \sum y_i(a\alpha)_{ij}$ $+ \left[ \frac{2Qd}{Q^2-d^2} + \ln \left[ \frac{Q+d}{Q-d} \right] \right] \left[ \frac{a\alpha}{8d^3} \right] \left[ c_i(3b+c) + b_i(3c+b) \right]$ $+ \frac{a\alpha(b_i+c_i)}{2[Q^2+d^2]}$ <p>where</p> $V = \frac{ZRT}{P}$ $Q = \frac{b+c}{2} + V$ $d = \sqrt{bc + \frac{(b+c)^2}{4}}$

## 2.8 Vapor-liquid Equilibrium Calculation

The calculation of vapor-liquid equilibrium is concerned with description of the state of two or more phases which are free to interact and which have reached a state of equilibrium.

The starting point of all VLE calculations is the equilibrium condition :

$$f_i^V = f_i^L \quad (2.44)$$

That is, the partial fugacity of component  $i$  in the vapor should be equal to its partial fugacity in the liquid. If the partial fugacity is expressed in terms of the partial fugacity coefficient, referred to Section 2.7, Eq. (2.44) becomes

$$\phi_i^V y_i P = \phi_i^L x_i P \quad (2.45)$$

when the distribution coefficient,  $K_i = y_i / x_i$  is approached, the following expression is also obtained ,

$$K_i = y_i / x_i = \phi_i^L / \phi_i^V \quad (2.46)$$

The distribution coefficient  $K_i$  , also called the vaporization equilibrium ratio, is the key quantity in the analysis of vapor-liquid equilibria. Many relations are expressible compactly in terms of the  $K_i$ , but because they depend on  $T$ ,  $P$ , and the compositions of the two phases, solutions of typical problems in terms of  $K_i$  must be accomplished by successive approximation. Implementation of the  $K_i$  will be made in calculations of dewpoints, bubble points and flashes. That is, for the VLE calculation, Eq. (2.46) provides the simplest and most direct method by applying an equation of state to both phases.



## 2.9 Binary Interaction Parameters

The behavior of mixtures naturally is affected by interactions of unlike molecules, particularly if some are polar. Interactions between triplets and higher combinations are usually less important than those between pairs of components. Higher-order interactions often are small and thus hidden by imperfections of practicable equations of states, 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 parameters.

Such parameters are commonly applied in one of two ways:

1. As an adjustment of a pseudocritical property of a pair:

$K_{ij}$  usually is in the range from 0 to 0.2 or so.

2. As a direct adjustment of some of the parameters of an equation of state:

For hydrocarbon pairs, the interaction parameters are nearly zero, whereas for mixture of hydrocarbons with  $H_2S$ ,  $CO_2$  and  $N_2$ , they were correlated with solubility parameters for each of these gases, but no general correlation was achieved.

The various investigators who evaluated the  $K_{ij}$  for several systems found only a small effect of temperature over a  $100^\circ C$  range and found the definitely temperature dependent binary interaction parameters of water with  $CO_2$  and  $H_2S$ . Generally,  $K_{ij}$  is assumed to be independent of temperature, pressure, density and composition. In practice, however, this is not strictly true and  $K_{ij}$  should be determined at conditions of interest. It should be added that the temperature dependence may be used to predict VLE at other temperatures.

An outstanding success of the concept that binary interactions largely determine the deviations of multicomponent mixtures from ideality are related correlations for activity coefficients. Since activity coefficients often are adequately computed from molecular structural contributions. It may be possible that binary interaction parameters,  $K_{ij}$  also could be evaluated from pure component properties, but this has not yet been done in comprehensive

form. Compared with VLE predictions, the sensitivity of predicted bulk mixture properties such as density and enthalpy to the value of  $K_{ij}$  is small. Therefore, it is common practice to use binary VLE data for the determination of  $K_{ij}$  values.

## 2.10 Mixing Rules

The mixing rules are considered when the equations of state are applied to mixtures. The rules express the parameters of equations of state ( $a$ ,  $b$ ,  $c$  or more) in condition of mixtures ( $a_m$ ,  $b_m$ ,  $c_m$  or more). Most equations of state use the "classical" mixing rules, that is, the one-fluid van der Waals mixing rules:

$$a_m = \sum_i \sum_j z_i z_j a_{ij} \quad (2.47)$$

$$b_m = \sum_i z_i b_i \quad (2.48)$$

$$c_m = \sum_i z_i c_i \quad (2.49)$$

and popular term  $(a\alpha)_m$ ,

$$(a\alpha)_m = \sum_i \sum_j z_i z_j (a\alpha)_{ij} \quad (2.50)$$

with the cross parameter taken to be

$$a_{ij} = (1 - K_{ij})(a\alpha)_{ij}^{0.5} \quad (2.51)$$

$$a_{ij} = (1 - K_{ij})[(a\alpha)_i (a\alpha)_j]^{0.5} \quad (2.52)$$

the binary interaction parameters  $K_{ij}$  in Eq. (2.51) - (2.52), which will be discussed in the next section, are used to correct for deviation of  $a_{ij}$  and  $(a\alpha)_{ij}$  from the geometric mean.

The "classical" mixing rules are capable enough for general application, however, it is likely that an equation of state will have a significantly better vapor-liquid equilibrium performance if the improved

mixing rules are used.

The most obvious improvement of mixing rules [18] is the substitution of  $b_i$  with  $b_{ij}$  and proposing the new binary constant in Eq.(2.48). The  $b_{ij}$  is similar to the  $a_{ij}$  in Eq.(2.47) and the new binary constant corrects for the deviation of  $b_{ij}$  from the arithmetic mean. The equation has been shown to improve the temperature-dependence of vapor-liquid equilibrium predictions in very asymmetric  $H_2$  binaries. It has also been shown to improve the prediction of hydrocarbon/water vapor-liquid equilibrium.

Other mixing rules were proposed by Heyen [19] in 1981. The LMF (local mole fraction) model was used to account for non-random mixing. The  $b_m$  and  $c_m$  are the same "classical" mixing rules but, for  $a_m$ , the mixing rules with the new binary constant and the local mole fraction of a component in the vicinity of another component was recommended. These mixing rules improve the prediction of vapor-liquid equilibrium for highly non-ideal mixtures.

In 1979, Huron and Vidal [20] proposed the LMF mixing rules with three binary constants. The mixing rules were based on the excess Gibbs free energy and used in the complex systems.

For the difficult systems, the density-dependent mixing rules, proposed by Whiting and Prausnitz [21] in 1981; Mollerup [22] in 1981, may be accepted. These rules allow  $a_m$  to have quadratic mole fraction dependence at low density but the higher-order dependence of the LMF mixing rules at high density. However, they increase computation time and may be not compatible with cubic equations of state.

In this work, the "classical" mixing rules will be used. Perhaps,  $a_m$ ,  $b_m$  and  $c_m$  are used in form of  $A_m$ ,  $B_m$  and  $C_m$ . Equations for  $a_m$ ,  $b_m$  and  $c_m$  are similar to equations for  $A_m$ ,  $B_m$  and  $C_m$