CHAPTER II

EQUATION OF STATE

2.1 Literature review

Vinod et al. (1994) have developed a generalized four - parameter quartic EOSs for nonpolar fluids. The objective of their research was to obtain a new set of regressed coefficients for polar and nonpolar fluids using the generalized EOSs.

The performance of the generalized quartic EOSs in evaluating various physical and thermodynamic properties of polar fluids was demonstrated. A comparison was made between the generalized quartic EOS and the Peng - Robinson EOS for prediction of various thermodynamic properties.

Cubic EOSs have received much attention in natural gas and chemical industries since the first practical equation of state was introduced by van der Waals (Rowlinson, 1988) in (1873). After the van der Waals equation was used for several decades, Redlich and Kwong (1949) modified the attractive pressure term of the van der Waals equation of state. The Redlich - Kwong EOS was widely popular and was used in the place of the van der Waals equation in industry. Soave (1972) and Peng and Robinson (1976) proposed EOSs that are able to more accurately predict the vapor pressure, liquid density, and equilibrium ratios than the Redlich - kwong equation. However, these cubic equations are not accurate at high densities, predict a fixed value of the critical compressibility factor for all compounds, and have limited applicability to polar compounds.

Perturbed hard - sphere EOSs are a comparatively recent and highly promising development. Several EOSs based on perturbed hard - sphere EOSs have been proposed.

One root of this equation has no physical significance, because it is always less than the close packed volume of the fluids. The behavior of the remaining three roots is equivalent to that of three roots of a cubic EOS. Thus, the resulting equation retains the advantages of the cubic EOS, existence of analytical solutions and accuracy, the resulting equation only requires three properties of nonpolar fluids; the critical temperature, the properties of nonpolar fluids; the critical temperature, the critical volume, and the acentric factor. Moreover, it marks a significant improvement over the Peng - Robinson EOS in the supercritical and condensed phase regions.

2.2 NEW QUARTIC EQUATION OF STATE

2.2.1 PURE NONPOLAR FLUIDS

A mathematically simple, hard-sphere equation was used to model the repulsive interaction between molecules. To keep the equation of state a quartic in volume.

$$Zhs = \frac{V}{(V-k_0\beta)} + \frac{\beta k_1 V}{(V-k_0\beta)^2} \tag{2.1}$$

where β is the molar hard-sphere volume. Regression of the MD results led to values of and of 1.2864 and 2.8225, respectively. Equation 2.1 was used to represent the repulsive pressure in the new equation of state. Because of its algebraic simplicity. Eq2.1 could be used to develop a quartic equation of state. The attractive forces were modeled using an empirical equation. The following approach was used to develop the attractive term: using real fluid data for argon and hard-sphere compressibility calculated from Eq2.1, plots of Zatt vs. Reduced density were prepared for various reduced temperatures:

$$Zatt = Zexp - Zhs \tag{2.2}$$

where   Zatt   is the attractive contribution to the compressibility,

Zexp   is the experimental comressibility value,

and Zhs   is the   hard-sphere contribution given by Eq 2.1

Plots of Zatt vs. Reduced density were constructed for different reduced temperatures and fit with an empirical equation for Zatt.

Zatt given by

$$\text{Zatt} = \frac{-a V^2 + k_0 \beta c V}{(V+e)(V - k_0 \beta)RT} \tag{2.3}$$

where e is constant, and a and c are temperature- dependent, gave the best results. Combining Eqs 2.1 and 2.3 ,the resulting equation of state can be written as :

$$P = \frac{RT}{(V - k_0 \beta)} + \frac{\beta k_1 RT}{(V - k_0 \beta)} - \frac{a V^2 + k_0 \beta c}{V(V+e)(V - k_0 \beta)} \tag{2.4}$$

The equation of state can be written as a quartic:

$$V^4 + q_3 V^3 + q_2 V^2 + q_1 V + q_0 = 0 \tag{2.5}$$

where

$$q_3 = (-2 k_0 \beta + e - \frac{RT}{P}) \tag{2.6}$$

$$q_2 = \frac{RT}{P} (\beta (k_0 - k_1)-e) + k_0 \beta (k_0 \beta - 2e)) + \frac{a}{P} \tag{2.7}$$

$$q_1 = e[k_0^2 \beta^2 + \frac{RT}{P} \beta (k_0 - k_1)] + [\frac{k_0 \beta(c-a)}{P}] \tag{2.8}$$

$$q_0 = \frac{-c k_0^2 \beta^2}{P} \tag{2.9}$$

Most equation of state determine the hard-sphere volume of a fluid by using the critical pressure . Such an approach requires that the critical compressibility of the fluid be know or specific by an empirical equation. If the critical volume is used, however , the critical compressibility does not have to be specific. The hard-sphere volumes of the fluids at the critical temperature were fixed to 0.165 times the critical volume of the fluid. A temperature dependence was incorporated into β according to

$$\beta \quad = \quad \beta c \, \{exp[-0.03125 \ln (Tr) - 0.0054[\ln (Tr)]^2]\}^3 \qquad (2.10)$$

where $\beta c = 0.165 \, Vc$. A temperature dependence was incorporated into a and c in the following manner:

$$a \quad = \quad a_c \alpha (Tr) \qquad (2.11)$$

where for $Tr \leq 1$

$$\alpha (Tr) \quad = \quad [1+X2(1- Tr^{1/2})+X3(1-Tr)^2+X4(1-Tr)^3]^2 \qquad (2.12)$$

and for $Tr > 1$

$$\alpha (Tr) \quad = \quad [1+X2(1- Tr^{1/2})+X5(1-Tr)^2+X6(1-Tr)^3]^2 \qquad (2.13)$$

Finally,

$$c \quad = \quad c_c \zeta (Tr) \qquad (2.14)$$

and

$$\zeta (Tr) \quad = \quad [1+X7(1- Tr^{1/2})]^2 \qquad (2.15)$$

where $X2, X3, X4, X5, X6$ and $X7$ are constants. The equation of state was extended to nonspherical fluids with the introduction of the acentric factor,ω ,as the third property to characterize the fluid. The parameters a, c and e, and the constants X1 throudh X7 were made functions of the acentric factor. The parameters a_c, c_c and e were defined and related to the acentric factor as shown in Eqs. 2.16-2.21.

$$a_c \quad = a_r RTc/\rho_c \qquad (2.16)$$

$$c_c \quad = c_r RTc/\rho_c \qquad (2.17)$$

$$e_c \quad = e_r/\rho_c \qquad (2.18)$$

$$a_r \quad = a_{r0}(1+a_{r1}\omega + a_{r2}\omega^2) \qquad (2.19)$$

$$c_r \quad = c_{r0}(1+c_{r1}\omega + c_{r2}\omega^2) \qquad (2.20)$$

$$e_r \quad = e_{r0}(1+e_{r1}\omega + e_{r2}\omega^2) \qquad (2.21)$$

where a_c and c_c are the values of a and c at the critical temperature. Equation 2.19-2.21 were required to keep the critical compressibility, calculated by the equation of state, dependent on the nature of the fluid. The constants to were made function of ω as:

$$Xi \quad =Xi1+Xi2\,\omega \qquad \text{for} \quad i = 2,3,4,5,6,7 \qquad (2.22)$$

A multiproperty nonlinear regression analysis was employed using data from 16 nonpolar fluids to determine all of the constants necessary to specify the equation of

state. Second virial coefficient data, high- temperature residual enthalpy data , and density data were used for parameter evaluation. Accurate equation of state were used to generate the database whenever possible. Pure component physical properties , T_c ,P_c, and ω ,used in the regressions were obtained from Reid et. al .(1987). The vapor pressure for nonpolar fluids such as n-octane ,n-nonane , benzene and propane calculated from the quartic equation of state is excellent agreement with the experimental data that showed in figure 2.1 -2.4
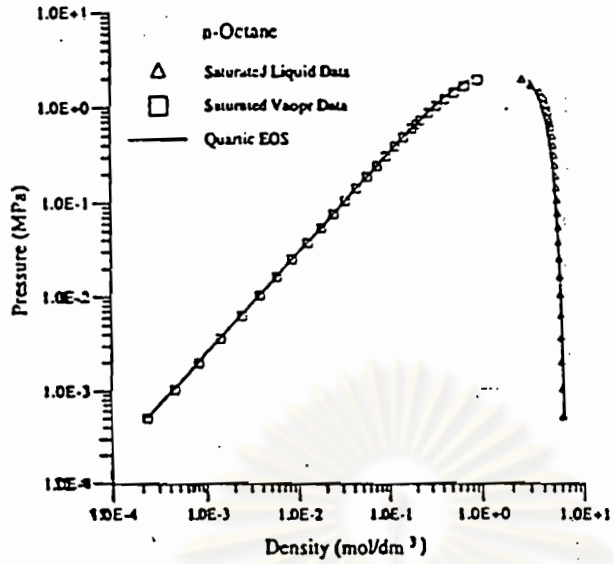
Figure 2.1 Saturated VLE calculations for n-octane
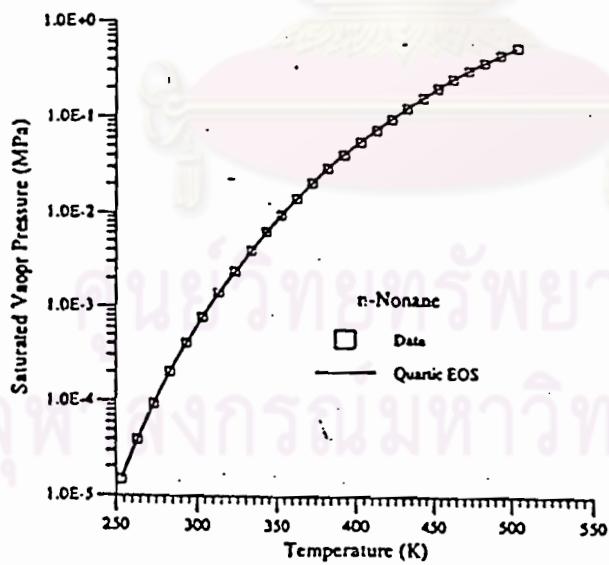Data of Starling (1973)

Figure 2.2 Vapor pressure calculations for n-nonane
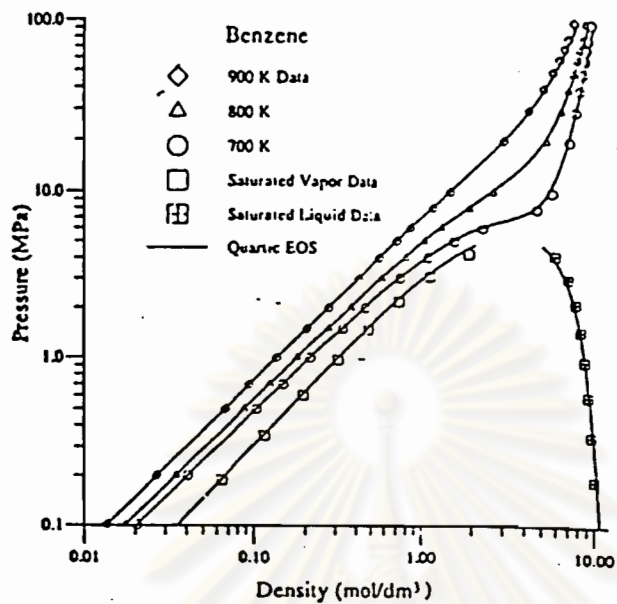Data of Vargaftik (1974)

Figure 2.3 PVT calculations for benzene

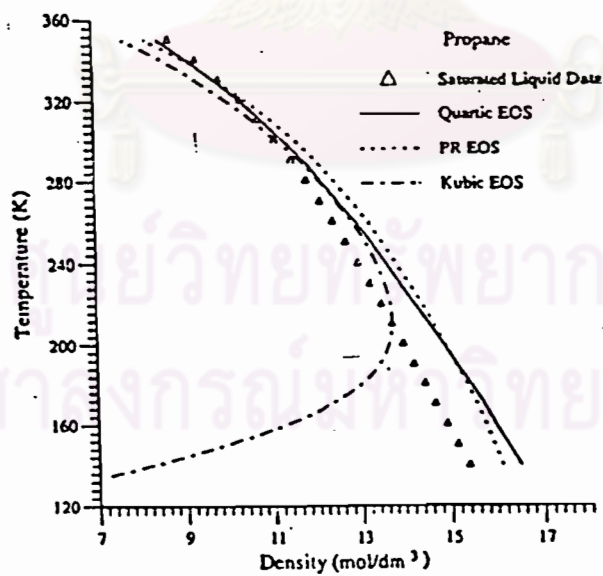Smoothed data of Goodwin (1988)

Figure 2.4 Comparison of saturated liquid calculations for propane

Smoothed data of Younglove and Ely (1987)

2.2.2 PURE POLAR FLUIDS

To apply the quartic equation of state to polar compounds, the parameters a and c are assumed to be functions of the acentric factor and the dipole moment of the fluid. Also, to express the parameters of the quartic equation in dimensionless form, the reduced dipole moment ($\mu*$) is used, as shown below:

$$\mu* = \frac{0.397 \mu}{(RTcVc)^{1/2}} \qquad (2.23)$$

where μ is the dipole moment of the polar fluid in debye units Thus, when investigating polar fluids, the regressed coefficients X2 through X7 were made linear functions of the acentric factor and quadratic functions of the reduced dipole moment. The regressed constants and were made quartic function of acentric factor and the reduced dipole moment. Equations 2.19, 2.21, and 2.22 were rewritten in the following forms:

$$X_i = X_{i1} + X_{i2} \omega + X_{i3} \mu* + X_{i4} \mu*^2 \qquad (2.24)$$

$$a_r = a_{r0}(1 + a_{r1} \omega + a_{r2} \omega^2 + a_{r3} \mu* + a_{r4} \mu*^2) \qquad (2.25)$$

$$c_r = c_{r0}(1 + c_{r1} \omega + c_{r2} \omega^2 + c_{r3} \mu* + c_{r4} \mu*^2) \qquad (2.26)$$

Replacing Eqs. 2.19, 2.21 and 2.22 by Eqs. 2.24, 2.25 and 2.26, the constants of the generalized quartic equation of polar fluids are expressed by Eqs. 2.1 through 2.22. Hence, only requiring four properties of the fluid (the critical temperature, the critical volume, the acentric factor, and the dipole moment) the generalized quartic EOS is extended to predict the behavior of polar fluids. If the dipole moment of the fluid is zero, then the entire system is reduced to the nonpolar fluid system. The new generalized quartic EOS has been applied to calculate thermodynamic properties of 30 polar compounds, such as refrigerants, esters, ethers, ketone, alcohols, and so on. The parameters in the generalized quartic EOS are expressed by the nondimensional forms. Thus, the reduced dipole moment, expressed in terms of the critical temperature, the critical volume, and the dipole moment, is used to represent the dipole moment of the fluid. The applicability and flexibility of most cubic EOSs are limited to certain regions when dealing with pure polar compounds. in order to overcome this advantage, the generalized quartic EOS has been extended to polar fluids over a wide range of states and for a wide varities of properties, such as

pressure - volume - temperature relations, vapor pressure, saturated vopour density , enthalpy of vaporization etc. Fiqure 2.5-2.10,the systems for water ,ammonia ,hydrogen sulfide , ethylbenzene, 1-1 difluoroethane ,toluene were demonstrated the ability of the generalized quartic EOS for polar fluids and compared with Peng- Robinson EOS .
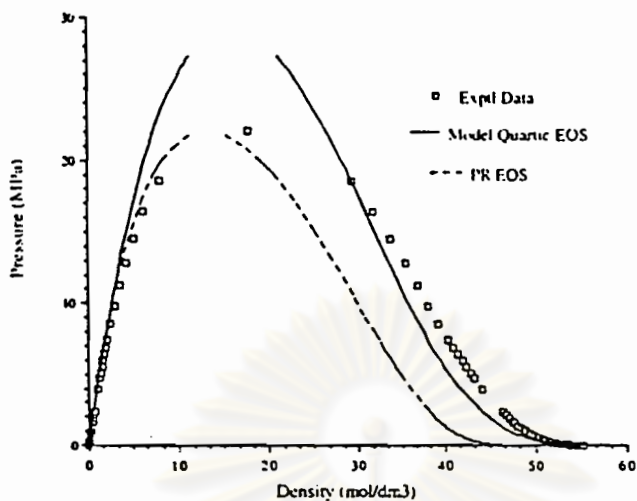
Figure 2.5 Comparison of saturated VLE calculation for water
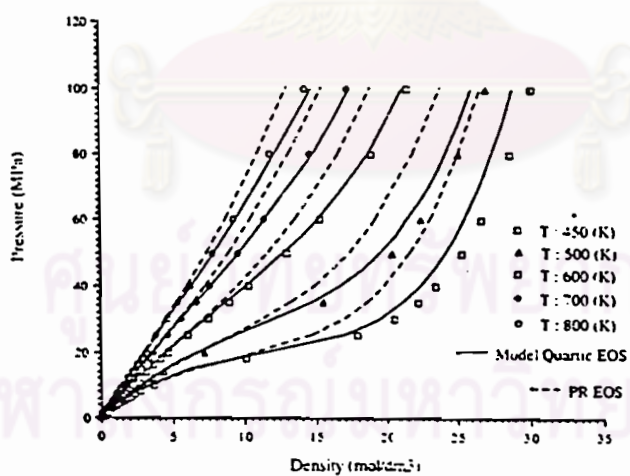
(Keenan et al., 1978)

Figure 2.6 Comparison of pressure-density calculation for ammonia
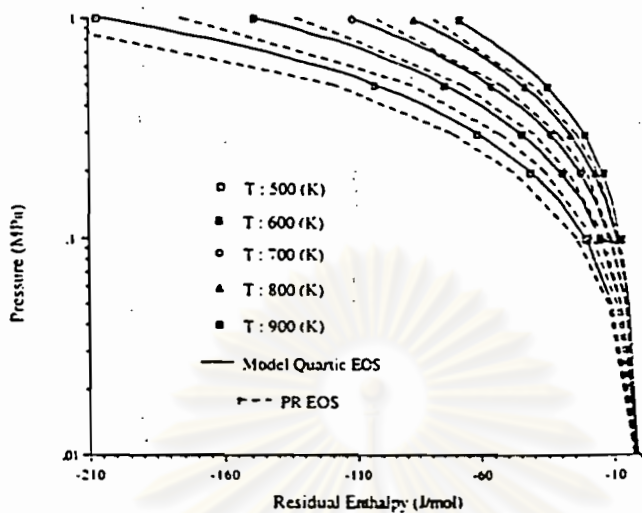
(Haar and Gallagher, 1978)

Figure 2.7 Comparison of residual enthalpy calculation for

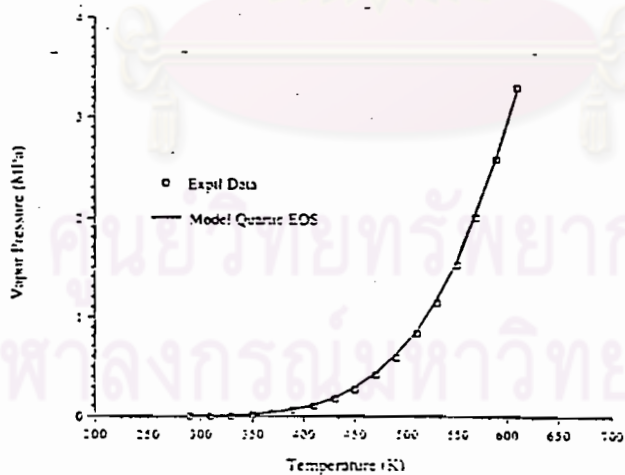hydrogen sulfide (Thermodynamics Rerearch center, 1993)

Figure 2.8 Vapor pressure calculation for ethylbenzene
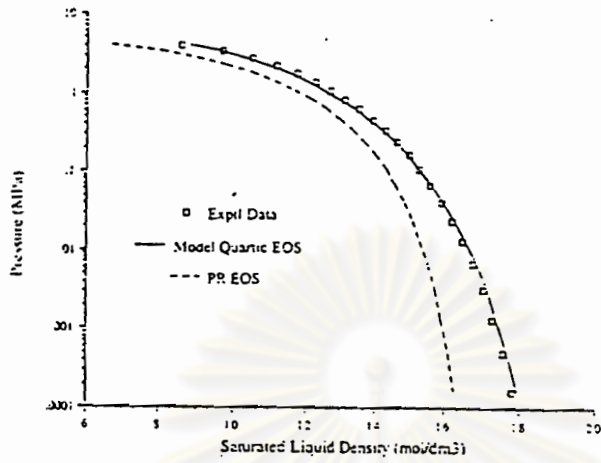
(Daubert and Danner, 1989)

Figure 2.9 Comparison of saturated liquid density calculation
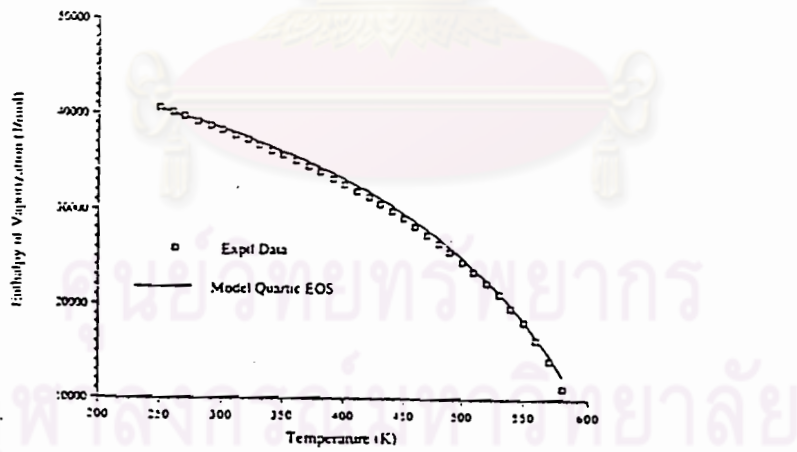
for 1,1 - difluoroethane (Daubert and Danner , 1988)

Figure 2.10 Enthapy of vaporization calculation for toluene

(Daubert and Danner , 1989)

TABLE 2.1 QUARTIC EQUATION OF STATE COEFFICIENTS OBTAINED BY NONLINEAR REGRESSIONS FOR 30 PURE POLAR COMPOUND DATA

(Vinod and Bienkowski, 1994)

Regressed Coefficients		Regressed Coefficients	
a_{r0}	1.84713	x_{21}	0.14988
a_{r1}	-0.05218	x_{22}	0.97848
a_{r2}	1.06446	x_{31}	-0.32379
c_{r0}	1.78336	x_{32}	1.84591
c_{r1}	-1.29690	x_{41}	0.14833
c_{r2}	2.78945	x_{42}	-3.46693
e_{r0}	0.63189	x_{51}	0.11048
e_{r1}	-0.81660	x_{52}	0.57743
e_{r2}	3.25246	x_{61}	0.02581
k_0	1.28650	x_{62}	-0.02700
k_1	2.82250	x_{71}	-0.77357
a_{r3}	-0.02730	x_{72}	-1.45342
a_{r4}	0.02048	x_{43}	-0.39170
c_{r3}	0.07000	x_{44}	-0.01597
c_{r4}	0.01188	x_{53}	0.41218
x_{23}	-0.01390	x_{54}	-0.10676
x_{24}	0.02928	x_{63}	0.38327
x_{33}	0.39338	x_{64}	-0.09008
x_{34}	-0.25483	x_{73}	-0.04725
		x_{74}	-0.09669

2.3 Peng - Robinson Equation of state

The original Redlich-Kwong equation and modifications by Wilson and Soave have a common shortcoming ,i.e., they predict poor liquid densities and an unrealistic universal critical compressibility factor of 1/3 for all substances. To alleviate this shortcoming, Peng and Robinsion modified the following general form:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \tag{2.46}$$

as follows

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(v-b)} \tag{2.47}$$

or

$$P = \frac{RT}{V-b} - \frac{a}{[V(2^{0.5}+1)b]+[v-(2^{0.5}-1)b]} \tag{2.48}$$

Eq. 2.48 can be expressed in the form of polynomials in terms of compressibility factor,

$$Z^3 - (1-B)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0 \tag{2.49}$$

where

$$b = \sum_i^n x_i b_i \tag{2.50}$$

$$b_i = 0.077796 \frac{R \, T \, ci}{Pci} \tag{2.51}$$

$$amix = \sum_i^n \sum_j^n x_i x_j (a_i a_j)^{0.5} (1-Kij) \tag{2.52}$$

$$a_i = ac_i \, \alpha i \tag{2.53}$$

$$aci = 0.457235 \frac{R \, T \, ci}{Pci} \tag{2.54}$$

$$\alpha i^{0.5} = 1+m_i (1-Tr_i^{0.5}) \tag{2.55}$$

$$m_i = 0.37646 + 1.54226\,\omega i - 0.26992\omega i^2 \tag{2.56}$$

$$A = \frac{aP}{(RT)^2} \tag{2.57}$$

$$B = \frac{bP}{RT} \tag{2.58}$$

The Partial Fugacity $(\hat{\phi} i)$ for Peng - Robinson EOS

$$\ln \hat{\phi} i = \frac{Bi}{B}(Z-1) - \ln(Z-B) + \frac{A}{(4.828B)}\left[\frac{Bi}{B} - (2/a\alpha)\sum_j y_j(a\alpha)_{ij}\right]\ln\frac{[Z+2.414B]}{[Z+2.414B]} \tag{2.59}$$

where

$$A = \frac{amix\,P}{(RT)^2} \tag{2.60}$$

$$B = \frac{bmixP}{RT} \tag{2.61}$$

$$Bi = \frac{b_i\,P}{RT} \tag{2.62}$$

$$a\alpha = \sum_i^n \sum_j^n y_i\,y_j\,(a\alpha)_{ij} \tag{2.63}$$

$$(a\alpha)_{ij} = (1-Kij)\,[(a\alpha)_{ij}(a\alpha)_{ij}]^{0.5} \tag{2.64}$$

$$\sum_j^n y_j(a\alpha)_{ij} = y_2(1-K12)\,[(a\alpha1)(a\alpha2)]^{0.5} \quad : \text{for binary mixture} \tag{2.65}$$