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EVALUATION OF THE GENERALIZED PERTURBED HARD SPHERE EQUATION  
OF STATE USING THERMODYNAMIC DATA OF  
MULTICOMPONENT MIXTURES

by  
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1990

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Golden, Colorado

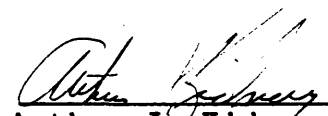
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## ABSTRACT

A previous study has developed a generalized perturbed hard sphere equation of state which is able to represent the vapor pressures for both non-polar and polar associating pure fluids accurately. The attractive term of the equation was determined so that it can reasonably predict the liquid volumes of hydrocarbons.

The reported equation of state was then evaluated in this study by comparing it with a modification of the Soave-Redlich-Kwong equation of state, using phase behaviour and enthalpy data for the binary and the ternary mixtures of m-cresol, quinoline, and tetralin, also for the binary and ternary mixtures of n-pentane, methanol, and acetone. The approach consisted of obtaining the binary interaction parameters by fitting the binary phase behaviour using a maximum likelihood method. The resulting binary interaction parameters were then applied to predict the ternary phase behaviour, the enthalpy of binary mixtures, and the enthalpy of the ternary mixtures. The generalized perturbed hard sphere equation gives comparable results for both binary and ternary fits with the modified SRK equation, yet the modified SRK equation is slightly better. In predicting enthalpy, the generalized perturbed hard sphere equation is more accurate than the modified SRK equation, particularly

for the  $k_{ij} = A+B/T$  mixing rule. The average absolute percent error in calculating enthalpy resulting from the generalized perturbed hard sphere equation ranges from 0.4 to 7.0, while the error from the modified SRK varies from 0.4 to 10.0.

It is recommended that a more reliable generalized perturbed hard sphere equation should be found so that it can predict better phase behaviour, as well as enthalpy, by developing or choosing a more accurate temperature dependency of the attractive term,  $a(T)$ .

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## INTRODUCTION

Reliable methods for predicting physical properties of pure components and their mixtures, such as phase equilibria and enthalpy are frequently required in process design and materials handling. In view of the wide variety of compounds and mixtures involved in the process industries, the frequent lack of experimental data, and also inaccuracy in predicting the physical properties for non-ideal systems, considerable efforts have been made for the development of these methods. Particularly, variations of the perturbed hard sphere equation of state have been proposed to meet this demand [1-3].

Mulia and Yesavage [2], developed a generalized perturbed hard sphere equation of state for both non-polar and polar associating fluids. The form of the equation is typical with that proposed by Carnahan and Starling [3], but the attractive term of the equation was enlarged to account for polar compounds by adding a third polar factor to the  $a(T)$  expression. The volume dependency of the attractive term was also determined so that it can reasonably describe the volumetric properties of hydrocarbons. The results of their study show a good representation of vapor pressure of both non-polar and polar pure fluids.

This study was done as a continuation of their work by extending the proposed equation of state to mixtures. First, binary interaction parameters corresponding to the selected mixing rules were determined for each mixture pair by fitting the binary phase behaviour data using the maximum likelihood method. The resulting binary interaction parameters were then used to correlate the phase behaviour and to predict the enthalpy of mixtures. Application of the three different mixing rules were overviewed in a fashion similar with that done by Yanaki and Yesavage [1].

Enthalpy and phase behaviour data at elevated temperatures and pressures for the binary and the ternary systems of m-cresol, quinoline, and tetralin [4-13] as well as for mixtures of methanol, acetone, and n-pentane [14-16] were used for evaluating the ability of the reported equation in predicting the thermodynamic properties. The results of calculations using the generalized perturbed hard sphere equation of state were then compared with the results from a modification of Soave-Redlich-Kwong (SRK) equation of state. This equation was proposed by Soave in 1979 [18]. Soave introduced the new  $\alpha(T)$  expression into the original SRK equation of state to replace the old  $\alpha(T)$ . The old  $\alpha(T)$  expression is dependent of the accentric factor, while the new  $\alpha(T)$  is a purely empirical expression developed by fitting vapor pressures.

It was previously shown that the Soave-Redlich-Kwong (SRK) equation of state [17], with conventional mixing rules could not be used to predict ternary behaviour using binary interaction parameters [13], nor could the equation be used to predict both enthalpy and phase behaviour simultaneously [9]. A potential source of error for any cubic equation of state is the inaccurate repulsive term where the equation incorrectly estimates volume that is occupied by molecules [19]. The modified SRK equation of state gave slightly better results than the generalized hard sphere equation of state in predicting the phase behaviour for both binary and ternary systems. On the other hand, the modified SRK equation of state resulted in poorer predictions of enthalpy than the generalized perturbed hard sphere equation of state. However, the generalized perturbed hard sphere equation evaluated in this report still gives poorer results if compared to the equation proposed by Yanaki and Yesavage. Therefore, development of the generalized perturbed hard sphere equation of state should be continued. Perhaps it should use a different approach in determining the volume dependency of the attractive term, rather than using compromise values as a generalization for all compounds.

## CORRELATION METHOD

Carnahan and Starling noticed that the development of improved analytical models of the equation of state proceeded along two routes, empirical and theoretical. The totally empirical models of the equation of state are generally employed to correlate experimental data. On the other hand, theoretical equations of state do not require vast amounts of experimental data for evaluation [3]. They developed an equation of state based upon the theoretical formulations utilizing the molecular model of rigid spheres with long range attractions. This then led to a rigid-sphere repulsion term, plus something else which accounted for the cohesion effects. Such a model corresponds to the general form of Van der Waals equation :

$$P = P_R + P_A \quad (1)$$

Subscript R denotes the rigid sphere repulsion effect, while subscript A denotes the effects of attractions.

Obviously, the perturbed hard sphere equation of state is theoretically superior to any cubic equation of state, since it includes the effect of the hard sphere repulsions which the cubic equation of state neglects.

Equations of State :

A former study evaluating the hard sphere equation of state was done by Yanaki and Yesavage [1], in which the general form of their equation follows Wong and Prausnitz's suggestion [20] :

$$Z = \frac{1+y+y^2-y^3}{(1-y)^3} - \frac{a_c \alpha(T)}{RT(v+nb)} \quad (2)$$

$$\alpha(T) = (c - d T_r^{0.5})^2 \quad (3)$$

where  $P$ ,  $Z$ ,  $R$ ,  $T$ ,  $v$  are pressure, compressibility factor, ideal gas constant, and molar volume.  $y$  is equal to  $b/4v$ , where  $b$  is the volume parameter and  $a_c$  is the energy parameter evaluated at the critical point. The  $\alpha(T)$  expression above is determined by fitting the vapor pressure data, then  $c$  and  $d$  in the equation (3) are determined by a regression of  $\alpha(T)$  versus  $T_r$  (ratio of temperature and critical temperature).  $n$  in the equation (2) is a constant allowing variation of the equation of state. In their study, three different values of  $n$  were employed:  $n=0$ , the Van der Waals form;  $n=0.2$ , as suggested by Wong and Prausnitz; and  $n=1$ , as used by Soave. The results of their study showed a remarkable improvement over the cubic equation of state in enthalpy predictions, and gave comparable accuracy in predicting the phase behaviour.

Recently, Mulia and Yesavage have developed a generalized type of perturbed hard sphere equation of state with the attractive term similar to that of Yu et al. [21] :

$$P = \frac{RT(1+y+y^2-y^3)}{v(1-y)^3} - \frac{a(T)}{v^2+ubv+wb^2} \quad (4)$$

$$a(T) = a_c \alpha(T) \quad (5)$$

where  $P$ ,  $R$ ,  $T$ , and  $v$  are the pressure, the ideal gas constant, the temperature, and the molar volume, respectively.  $y$  is equal to  $b/4v$ , and the volume dependency  $u$  is equal to 0.2, while  $w$  is equal to -0.1. The values of  $u = 0.2$ , and  $w = -0.1$  were selected as compromise values for fitting volumetric properties of selected hydrocarbons from C1 to C16. For this equation the energy and volume parameters are as follows :

$$a = 0.49897R^2T_c^2/P_c \quad (6)$$

$$b = 0.17091RT_c/P_c \quad (7)$$

The  $\alpha(T)$  expression for non-polar fluids is as follows :

$$\alpha(T) = \alpha_s(T) \alpha_n(T) \quad (8)$$

where,

$$\alpha_s(T) = 1 - 0.244797(1-T_r) + 0.16047(1-T_r)^{2.7} \quad (9)$$

$$\alpha_n(T) = 1 + C(1-T_r) + D(1-T_r)^2 \quad (10)$$

$$C = 0.00632 + 1.13094 \omega - 0.03118 \omega^2 \quad (11)$$

$$D = - 0.02312 + 0.26654 \omega - 0.28888 \omega^2 \quad (12)$$

$\alpha_s(T)$  is the function required for fitting the vapor pressures of spherically symmetric fluids argon and krypton, and  $\alpha_n(T)$  is a function that represents the shape effects for non-polar fluids.

For polar fluids the approach follows Yesavage suggestion [22]. The  $\alpha(T)$  expression therefore turns out to be the following :

$$\alpha(T) = \alpha_s(T) \alpha_n(T) \alpha_p(T) \quad (13)$$

$$\alpha_p(T) = 1 + \pi/C[\exp(-\pi)^e - \exp\{-\pi/T_r\}^e] \quad (14)$$

where  $\pi$  is the polar parameter,  $C$  and  $e$  are parameters that produce the best fit when  $C=1$ , and  $e=0.48$ . In their study, Mulia and Yesavage made the assumption that the term  $\alpha_n(T)$  for polar fluids represents the effect of shape in interaction with other molecules. A pseudo-acentric factor  $\omega_0$  was introduced as the fourth parameter in the non-polar term to represent this effect. The pseudo-acentric factor and the polar parameter were obtained by fitting the values of  $\alpha(T)$ .

The modified Soave equation of state was selected to provide a comparison for the results of the generalized perturbed hard sphere equation. The form of the modified SRK equation of state is as follows :

$$P = RT/(V-b) - a(T)/(V(V+b)) \quad (15)$$

$$\text{where, } b = 0.08664RT_c/P_c \quad (16)$$

$$a(T) = 0.42747R^2T_c^2/P_c \alpha(T) \quad (17)$$

$$\alpha(T) = 1 + (1-T_r)(m+n/T_r) \quad (18)$$

The  $\alpha(T)$  expression in the above equation is independent of the acentric factor, but dependent of the two additional parameters  $m$  and  $n$ . These parameters are obtained by fitting pure component vapor pressures. Therefore, the above  $\alpha(T)$  expression is a purely empirical expression. This equation was proposed by Soave in 1979 [18]. The equation was designed to predict both pure component and mixture phase equilibria for systems with one or more associating components.

In a companion paper [30], Soave described three methods for extracting values for the pure component parameters  $m$  and  $n$ . The first method is a rigorous optimization of  $m$  and  $n$  to fit pure component vapor pressures. The last two methods were used by Sandarusi in accomplishing his work [23]. The second method consists of doing least square fit on  $m$  and  $n$  for pure component vapor pressure data. Soave claimed that this method is as accurate as the more complex and rigorous first method. The final method is a simple corresponding state correlation for  $m$  and  $n$ . The required input parameters are the critical constants, the acentric factor, and the boiling

points at 760 and 10 mmHg. The values of  $m$  and  $n$  required for the calculations are referred to in the results on the best fit method used in Sandarusi's work [23]. In predicting the enthalpy, Sandarusi stated that the best fit  $m$  and  $n$ 's produce better results than the simple fit  $m$  and  $n$ 's; however, for predicting the phase behaviour, both the best fit and simple fit  $m$  and  $n$ 's practically produce the same results.

In general, Sandarusi's work reveals that the modified SRK equation of state works better than either the original SRK or Peng-Robinson equations of state, particularly for the polar fluids. Therefore, the modified SRK equation of state is selected for comparison study in this thesis.

#### Mixing rules :

Mixing rules are required for representation of the effect of interactions between molecules. In applying equation (4) to mixtures, simple arithmetic and quadratic means of parameters  $a$  and  $b$  proposed by van der Waals were used :

$$b = \sum x_i b_i \quad (19)$$

$$a = \sum \sum x_i x_j a_{ij} \quad (20)$$

Where  $x_i$  is the liquid or vapor mole fraction of component  $i$

in the mixture, and  $b_i$  is the volume parameter of the pure component  $i$ . The cross parameter  $a_{ij}$  is then determined by a combining rule, for instance :

$$a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij})$$

where  $k_{ij}$  is referred to as binary interaction parameter, which was originally introduced for systems containing other than the light hydrocarbons so that the equation of state can make better prediction of the phase behaviour.

Until recently, many mixing rules have been proposed and used for the purpose of obtaining more accurate results in describing mixture properties. Several of them are listed below :

1.  $a = \sum \sum x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})$
2.  $a = \sum \sum x_i x_j (a_i a_j)^{0.5} (1 - A - B/T)$
3.  $a = \sum \sum x_i x_j (a_i a_j)^{0.5} (1 - A + B/v)$
4.  $a = \sum \sum x_i x_j (a_i a_j)^{0.5} (1 - A + B/vRT)$
5.  $a = \sum \sum x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) +$   
 $1/(vRT) \sum \sum x_i x_j (x_i C_{ij} + x_j C_{ji} C_{ji})$
6.  $a = \sum \sum x_i x_j (a_i a_j)^{0.5} (1 - k_{ij} + (k_{ij} - k_{ji}) x_i + C_{ij}/T)$

Where  $k_{ij}$ ,  $k_{ji}$ ,  $A$ ,  $B$ , and  $C_{ij}$  are parameters obtained from fitting the binary vapor-liquid equilibrium data, while  $i$  and  $j$  refer to specific components in a mixture. Mixing rules 3, 4, and 5 are different density dependent interaction

parameters. A study done by Diagiacinto [13] concluded that mixing rules 3, 4, and 5 were not better than the other mixing rules; therefore, in this study only three mixing rules were applied to the generalized perturbed hard sphere equation. Those rules are as follows :

$$\text{Mixing rule I : } a = \sum \sum x_i x_j (a_i a_j)^{0.5(1-k_{ij})}$$

$$\text{Mixing rule II : } a = \sum \sum x_i x_j (a_i a_j)^{0.5(1-A-B/T)}$$

Mixing rule III:

$$a = \sum \sum x_i x_j (a_i a_j)^{0.5(1-k_{ij}+(k_{ij}-k_{ji})x_i+C_{ij}/T)}$$

The third mixing rule is similar to that proposed by Panagiotopoulos and Reid [25]. Later on, Yanaki and Yesavage added a third parameter,  $C_{ij}$ , as an adjustment for the effect of temperature. They explained that the intermolecular associations will begin to break and can effect the model when the temperature rises due to increasing the kinetic energy of molecules. Therefore, an adjustment to the temperature changes is needed.

#### Fugacity Coefficient :

The concept of fugacity arises from a consideration of the change in Gibbs energy that results from changes in pressure and temperature, namely :

$$dG = -SdT + VdP$$

where  $G$ ,  $S$ ,  $T$ ,  $V$ , and  $P$  are the Gibbs energy, the entropy, the temperature, the volume, and the system pressure, respectively. For an ideal gas at constant temperature,

$$dG = VdP = RTd\ln(P) .$$

The simplicity of this equation suggests writing another equation of exactly the same form for a real fluid that defines a new property  $f$ -which is called fugacity-that also has dimensions of pressure :

$$dG = RTd\ln(f) .$$

The dimensionless ratio  $f/P$  is the so-called fugacity coefficient and given the symbol  $\Phi$ .

The fugacity coefficient of a component in the mixture can be derived from the equation below :

$$RT\ln \Phi_i = \int_V^{\infty} \left[ \left( \frac{dP}{dn_i} \right)_{T,V} - \frac{RT}{V} \right] dV - RT\ln z . \quad (21)$$

Easier mathematical work can be done by splitting the  $\left( \frac{dP}{dn_i} \right)_{T,V}$  expression into two terms, i.e., the repulsion term and the attractive term, as follows :

$$\left[ \left( \frac{dP}{dn} \right) = \left( \frac{dP}{dn} \right)_R + \left( \frac{dP}{dn} \right)_A \right] \quad (22)$$

Variation of the mixing rule does not affect the fugacity coefficient resulting from the repulsion term, since the "a" only appears in the attractive term. The fugacity coefficient of pure component  $i$  in a mixture corresponding

to the repulsion term which refers to the generalized perturbed hard sphere equation of state (22) is :

$$\ln \Phi_{i,R} = - \ln V + \frac{18bv-3b^2}{16v^2-8bv+b^2} + \frac{b_i(258v^2-32bv)}{4(64v^3-48bv^2+12b^2v-b^3)} \quad (23)$$

Mathematical derivation of the above equation is given in Appendix A of this report.

The fugacity coefficient of pure component  $i$  in a mixture resulting from the attractive term is :

$$\ln \Phi_{i,A} = \frac{A \ln\left(\frac{2v+ub-b(u^2-4w)^{0.5}}{2v+ub+b(u^2-4w)^{0.5}}\right)}{RTb(u^2-4w)^{0.5}} - \frac{ab_i v}{RT(wb^3+bv^2+ub^2v)} - \frac{ab_i \ln\left(\frac{2v+ub-b(u^2-4w)^{0.5}}{2v+ub+b(u^2-4w)^{0.5}}\right)}{RTb_i(u^2-4w)^{0.5}} \quad (24)$$

$$\text{Where, } A = \sum x_k a_{ik} + \sum x_j a_{ji} + \sum \sum x_j x_k (da_{jk}/dn_i) \quad (25)$$

$$u = 0.2$$

$$w = -0.1$$

For mixing rule I and II,

$$A = \sum x_k (a_{ik} + a_{ki}) \quad (26)$$

For mixing rule III,

$$A = \sum x_k (a_{ik} + a_{ki}) + \sum \sum x_j x_k (a_{ja} a_k)^{0.5} (k_{jk} - k_{kj}) (d_{ij} - x_j) \quad (27)$$

where,  $d_{ij} = 0$  for  $i \neq j$   
 $d_{ij} = 1$  for  $i = j$

To obtain the fugacity coefficient of component  $i$  in the mixture, equation (23) is combined with equation (24), plus the remaining factors in the equation (21).

For the modified SRK equation of state the expression of fugacity coefficient of pure  $i$  in the mixture is given by the following :

$$\begin{aligned} \ln \Phi_i = & b_i(Z-1)/b_m - \ln(Z-B) - (A/B)* \\ & (2 \sum x_k a_{ki}/a_m - b_k/b_m) \ln((Z+B)/Z) \end{aligned} \quad (28)$$

where,  $A = a_m P / (RT)^2$

$$B = b_m P / RT$$

Subscripts  $i$ ,  $k$  refer to components  $i$  and  $k$ , respectively;  $m$  refers to a mixture property defined using some type of mixing rule (see mixing rules I, II, and III p.11).

#### Enthalpy Correlation :

Computer programs implementing the generalized perturbed hard sphere and the modified SRK equations of state were used to correlate the enthalpy data [9,12]. Such computer programs are presented in Appendix C of this report. For this purpose, fugacity coefficient and enthalpy

departure expressions are required. The fugacity coefficients are already discussed in the previous section.

At a specified temperature and composition, one can use one of Maxwell's relations to give the effect of pressure on enthalpy, as follows :

$$dH = \int_V^{\infty} [V - T(dV/dT)_{P,n}] dP . \quad (29)$$

Equation (29) forms the basis of derivation for the desired equation for enthalpy calculation. The further derivation is not presented here because it has been clearly given in several, readily available publications by Beattie [31]. The result is given in the following equation,

$$H = \int_V^{\infty} [P - T(dP/dT)_V] dV + PV + \sum n_i u_i^{\circ} . \quad (30)$$

This expression can be rearranged to represent the enthalpy departure :

$$H-H^{\circ} = \int_V^{\infty} [P - T(dP/dT)_V] dV + PV - RT . \quad (31)$$

The generalized perturbed hard sphere equation of state (4) yields the enthalpy departure as :

$$H-H^{\circ} = \frac{1.5076[a-T(da/dT)]}{b} \ln\left(\frac{10v-2.3166b}{10v+2.3166b}\right) + PV - RT. \quad (32)$$

The values of  $a$  and  $(da/dT)$  are dependent on mixing rule; therefore, the mixing rule affects the results of enthalpy

calculation. Mathematical derivations of the enthalpy expressions for each mixing rule are presented in Appendix A.

The enthalpy departure equation derived from the modified SRK equation of state is :

$$H-H^O = (T(da/dT) - a) \ln(Z/(Z+B)) / b + PV - RT \quad (33)$$

Where,  $B = bP/RT$

$$Z = PV/RT.$$

Again,  $a$  and  $da/dT$  correspond to the mixing rule used. The ideal gas enthalpy can be calculated using Self-Consistent Equations proposed by Rehman and Lee [26].

### Volume Calculation

Equation (4) forms a sixth order polynomial in terms of volume; that is why more than three roots can possibly exist. The volume calculation is then easier performed by iteration method. Newton-Raphson technique can be applied. A different approach should be used in calculating the liquid volume and the vapor volume. For vapor volume calculation, a polynomial in terms of compressibility factor,  $Z$ , should be used :

$$f(V) = Z^6 + c_5Z^5 + c_4Z^4 + c_3Z^3 + c_2Z^2 + c_1Z + c_0$$

$$\begin{aligned}
 \text{where, } c_5 &= - 0.55B - 1 \\
 c_4 &= - 0.0625B^2 - 0.45B + A \\
 c_3 &= 0.0969B^3 - 0.0125B^2 - 0.75AB \\
 c_2 &= - 0.0219B^4 + 0.0281B^3 + 0.1875AB^2 \\
 c_1 &= 0.0016B^5 + 0.0094B^4 - 0.0156AB^3 \\
 c_0 &= - 0.0016B^5 \\
 A &= a_c P_c / (R T_c)^2 \\
 B &= b P_c / (R T_c) .
 \end{aligned}$$

The above equation monotonically decreases from  $Z = 1$  (ideal-gas state); that is why  $Z = 1$  is used as the initial guess. Derivation of the above function is not given in this study, because this was already done by Mulia [32]. Liquid volume calculation can be done directly from the following equation :

$$f(V) = \frac{RT(1+y+y^2-y^3)}{v(1-y)^3} - \frac{a(T)}{v^2+0.2bv-0.1b} - P .$$

The initial guess for the liquid volume calculation  $v = b/4$  is chosen since it is small enough and the above function decreases monotonically from  $v = b/4$  until it converges to the liquid volume root within the specified accuracy.

The calculation of both liquid and vapor volumes using the modified SRK equation of state can be done by Newton-Raphson technique or by cubic solver technique. For this

purpose, equation (15) should be rearranged to give the following function :

$$f(V) = v^3 - RTv^2/P + v(a-bRT-b^2P)/P - ab/P .$$

When using the Newton-Raphson technique,  $v = RT/P$  should be chosen as the first guess for calculating the vapor volume. For the liquid volume calculation, one can use  $v = 0.1 b$  as the first guess.

#### Pure Component Parameters

Listed in Table 1 are the critical properties and acentric factors of the compounds from Reid et al. (1977) and Lin et al. (1980). The polar parameters ( $\pi$ ) and the pseudo-acentric factors ( $\omega_0$ ) of the compounds are taken from Mulia's study [32] and tabulated in Table 2. As explained in a previous section, the polar parameter is required to represent the effect of polarity. The pseudo-acentric factor  $\omega_0$  is used instead of the acentric factor as the fourth correlating parameter in the non-polar term to represent the shape effect for the polar compound.

Table 3 contains the modified SRK equation constants  $m$  and  $n$  of the compounds taken from the results of Sandarusi's study [23]. The listed  $m$  and  $n$  are the values derived by the least square method and referred to in Soave's paper as

Table 1

## Critical Properties and Acentric Factors

Compound	$T_c$ (K)	$P_c$ (kPa)	$\omega$
m-cresol	705.8	4560	0.454
quinoline	800.2	5775	0.316
tetralin	719.2	3515	0.327
n-pentane	469.7	3370	0.251
methanol	512.6	8090	0.556
acetone	508.1	4700	0.304

Table 2

## Polar Parameters and Pseudo-Acentric Factors

Compound	$T_r$ range	$\pi$	$\omega_o$
m-cresol	0.60-0.96	0.000	0.449
quinoline	0.65-0.81	63.060	0.220
tetralin	0.70-0.88	0.056	0.310
n-pentane	0.65-0.93	0.000	0.251
methanol	0.56-0.98	29.760	0.202
acetone	0.52-0.96	89.850	0.265

Table 3

## The Modified SRK Equation Constants

Compound	$T_r$ range	$n$	$n$
m-cresol	0.60-0.67	0.7265	0.4537
quinoline	0.58-0.71	0.8351	0.2060
tetralin	0.48-0.70	0.7565	0.2426
n-pentane	0.46-0.72	0.7094	0.2103
methanol	0.56-0.70	1.3013	0.2005
acetone	0.61-0.65	0.7951	0.2205

the best fit  $m$  and  $n$ . Other  $m$  and  $n$  values are also presented in Sandarusi's study; these are derived from the simple fit procedure. The best fit  $m$  and  $n$  are selected since Sandarusi explained that the best fit  $m$  and  $n$  outperformed the simple fit  $m$  and  $n$  in enthalpy predictions.

## DISCUSSION OF RESULTS

The correlational methods discussed in the previous section were applied to the phase behaviour data for both binary and ternary mixtures of m-cresol/quinoline/tetralin and n-pentane/methanol/acetone. Evaluation on the enthalpy calculation results was done only for the binary and the ternary mixtures of m-cresol/quinoline/tetralin, since experimental data of enthalpy were not available for the n-pentane/methanol/acetone system.

Results on the Binary Phase Behaviour

The equation of state evaluated in this study is the generalized perturbed hard sphere equation proposed by Mulia and Yesavage (see equation (4) of this report). The initial step of the analysis is obtaining the interaction parameters which correspond to the selected mixing rule. This was done by fitting the interaction parameters to the binary phase behaviour data using a maximum likelihood method reported by Niesen [27]. In applying this method, the following function was minimized :

$$S^2 = \sum [(P_{\text{calc}} - P_{\text{exp}})_i^2 / s_{p,i}^2 + (y_{\text{calc}} - y_{\text{exp}})_i^2 / s_{y,i}^2 + (T_{\text{calc}} - T_{\text{exp}})_i^2 / s_{T,i}^2 + (x_{\text{calc}} - x_{\text{exp}})_i^2 / s_{x,i}^2] / (N-L)$$

where the sum is over all N data points and L is the number

of parameters being fit. The  $s$ 's are the estimates of the variances for each experimental observation. The resulting binary interaction parameters and  $S^2$  obtained for each binary pair of m-cresol, quinoline, and tetralin, for each equation of state and mixing rule are presented in Table 4. Typical results for binary mixtures of n-pentane, methanol, and acetone are reported in Table 5. The value of  $S^2$  is then used for measuring how well the equation of state predicts the phase behaviour. The lower the  $S^2$  the better the correlation. Looking at the  $S^2$ 's, the generalized perturbed hard sphere equation of state using the third mixing rule gives comparable predictions with the modified SRK equation. The third mixing rule shows the best fit since the lower the  $S^2$  the better the fitting. In order to clearly illustrate the results on prediction of the binary phase behaviour, binary phase diagrams were made for each binary mixture. Figures 1 through 9 show binary phase diagrams of m-cresol, quinoline, tetralin system at 523 K, while figures 13 through 18 illustrate the binary phase diagrams of n-pentane, methanol, acetone system. The solid line represents the predictions work, and the symbols represent the experimental data.

Table 4

Binary Interaction Parameters of  
m-cresol/quinoline/tetralin

Generalized PHS EOS :

	<u>m-Cresol/ Tetralin</u>		<u>m-Cresol/ Quinoline</u>		<u>Tetralin/ Quinoline</u>	
Rule	S <sup>2</sup>	parameters	S <sup>2</sup>	parameters	S <sup>2</sup>	parameters
1	25.7	k <sub>ij</sub> = 0.0225	34.8	k <sub>ij</sub> = -0.0622	17.5	k <sub>ij</sub> = -0.0193
2	24.5	A = 0.0408 B = -8.9762	30.1	A = 0.0107 B = -33.1622	15.9	A = 0.0019 B = -8.2400
3	8.2	k <sub>ij</sub> = 0.0170 k <sub>ji</sub> = 0.0167 C <sub>ij</sub> = -0.0133	9.8	k <sub>ij</sub> = -0.0333 k <sub>ji</sub> = -0.0733 C <sub>ij</sub> = 0.0142	9.0	k <sub>ij</sub> = -0.0168 k <sub>ji</sub> = -0.0167 C <sub>ij</sub> = 0.0056

Modified SRK EOS :

Rule	S <sup>2</sup>	parameters	S <sup>2</sup>	parameters	S <sup>2</sup>	parameters
1	17.2	k <sub>ij</sub> = 0.0345	30.9	k <sub>ij</sub> = -0.0789	14.8	k <sub>ij</sub> = -0.0182
2	16.1	A = 0.0042 B = 14.7607	15.3	A = -0.0636 B = -7.3961	13.4	A = 0.0109 B = -12.539
3	7.3	k <sub>ij</sub> = 0.0470 k <sub>ji</sub> = 0.0320 C <sub>ij</sub> = 3.0037	5.3	k <sub>ij</sub> = -0.0847 k <sub>ji</sub> = -0.1024 C <sub>ij</sub> = -9.1822	6.4	k <sub>ij</sub> = -0.0088 k <sub>ji</sub> = -0.0010 C <sub>ij</sub> = 8.5168

- Rule : 1.  $a_{ij} = \text{SQRT}(a_i a_j)(1 - k_{ij})$   
 2.  $a_{ij} = \text{SQRT}(a_i a_j)(1 - A - B/T)$   
 3.  $a_{ij} = \text{SQRT}(a_i a_j)(1 - k_{ij} + (k_{ij} - k_{ji})x_i + C_{ij}/T)$

Table 5

Binary Interaction Parameters of  
n-pentane/methanol/acetone

Generalized PHS EOS :

	<u>n-Pentane/Methanol</u>		<u>n-Pentane/Acetone</u>		<u>Methanol/Acetone</u>	
Rule	S <sup>2</sup>	parameters	S <sup>2</sup>	parameters	S <sup>2</sup>	parameters
1	698.4	k <sub>ij</sub> = 0.0791	44.2	k <sub>ij</sub> = 0.0736	15.0	k <sub>ij</sub> = -0.0054
2	626.8	A = 0.0957 B = -6.2138	35.9	A = 0.0713 B = 0.8962	9.5	A = 0.0127 B = -5.7845
3	23.7	k <sub>ij</sub> = 0.0551 k <sub>ji</sub> = 0.1589 C <sub>ij</sub> = 0.2245	9.8	k <sub>ij</sub> = 0.0242 k <sub>ji</sub> = 0.0484 C <sub>ij</sub> = -15.038	5.4	k <sub>ij</sub> = 0.0272 k <sub>ji</sub> = 0.0210 C <sub>ij</sub> = 9.9415

Modified SRK EOS :

Rule	S <sup>2</sup>	parameters	S <sup>2</sup>	parameters	S <sup>2</sup>	parameters
1	879.3	k <sub>ij</sub> = 0.1368	19.3	k <sub>ij</sub> = 0.1043	38.7	k <sub>ij</sub> = 0.0097
2	428.2	A = 0.5360 B = -125.96	18.7	A = 0.0872 B = 6.1166	39.2	A = 0.0107 B = -0.3041
3	21.4	k <sub>ij</sub> = 0.1142 k <sub>ji</sub> = 0.1726 C <sub>ij</sub> = 1.1815	7.2	k <sub>ij</sub> = 0.0532 k <sub>ji</sub> = 0.0878 C <sub>ij</sub> = -12.902	3.6	k <sub>ij</sub> = 0.0276 k <sub>ji</sub> = 0.0087 C <sub>ij</sub> = 2.9026

- Rule : 1.  $a_{ij} = \text{SQRT}(a_i a_j)(1 - k_{ij})$   
 2.  $a_{ij} = \text{SQRT}(a_i a_j)(1 - A - B/T)$   
 3.  $a_{ij} = \text{SQRT}(a_i a_j)(1 - k_{ij} + (k_{ij} - k_{ji})x_i + C_{ij}/T)$

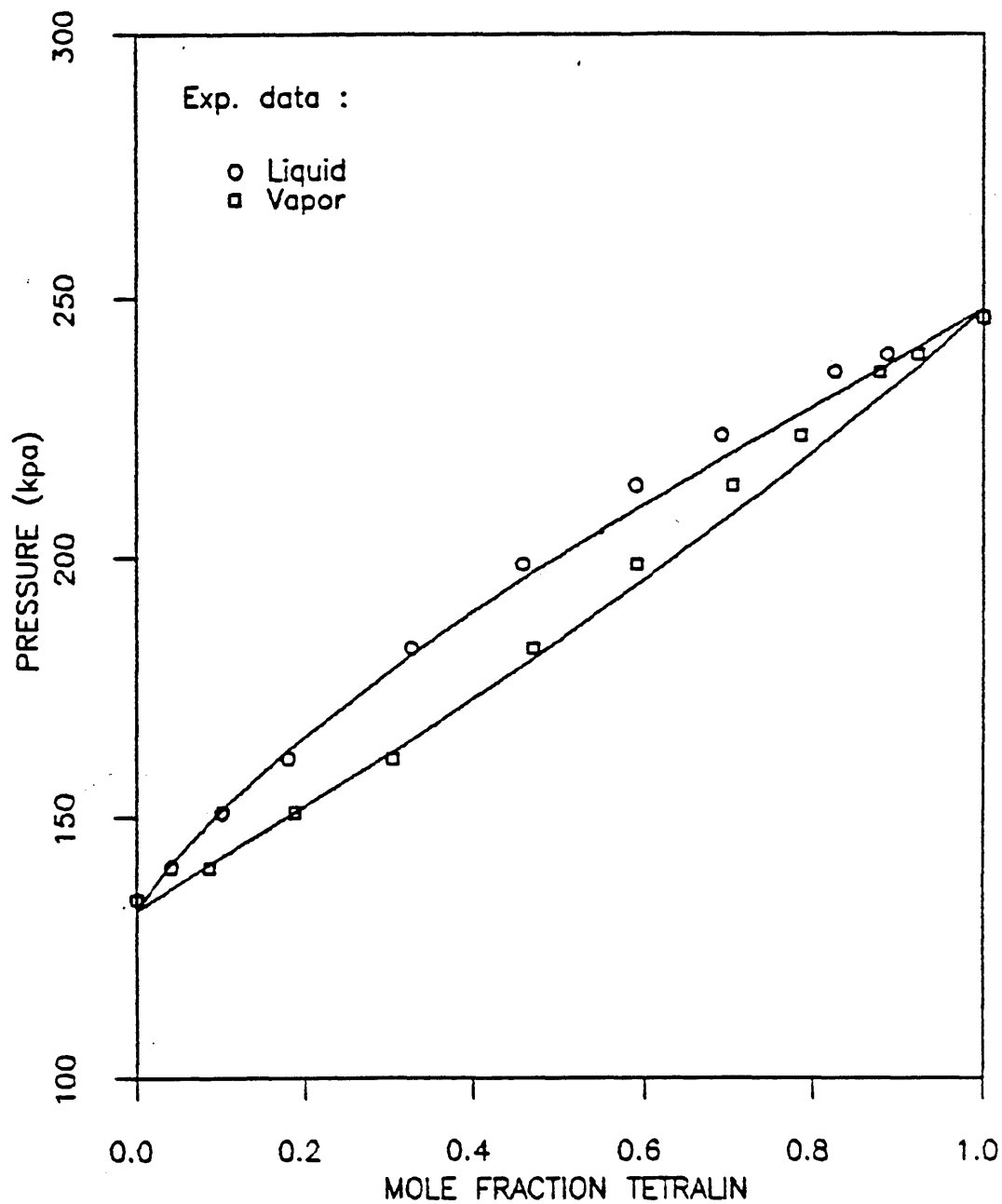


Figure 1. Binary Phase Diagram of Tetralin-Quinoline at 523 K, Equation = PHS, Mixing rule = III.

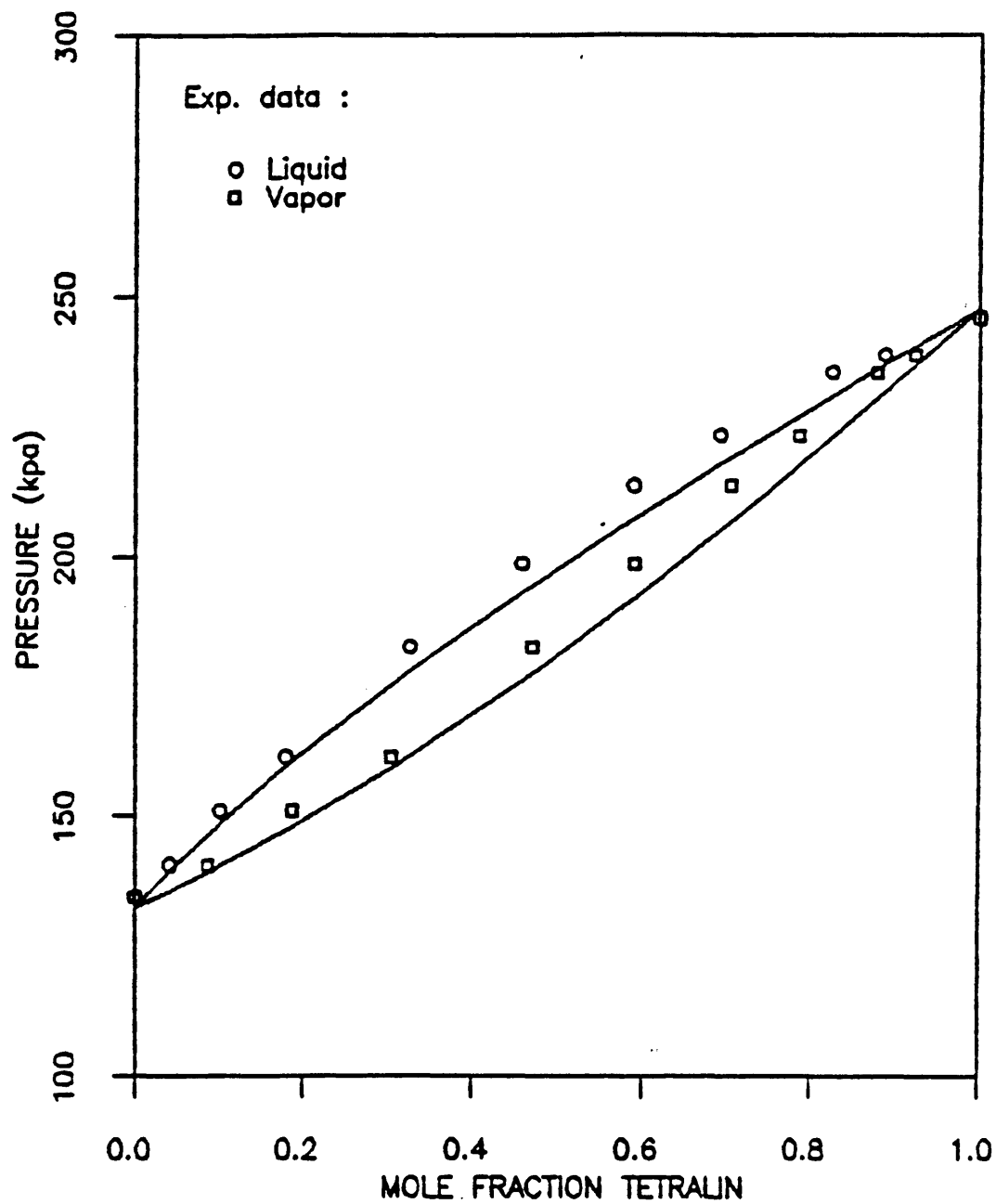


Figure 2. Binary Phase Diagram of Tetralin-Quinoline at 523 K, Equation = PHS, Mixing Rule = II

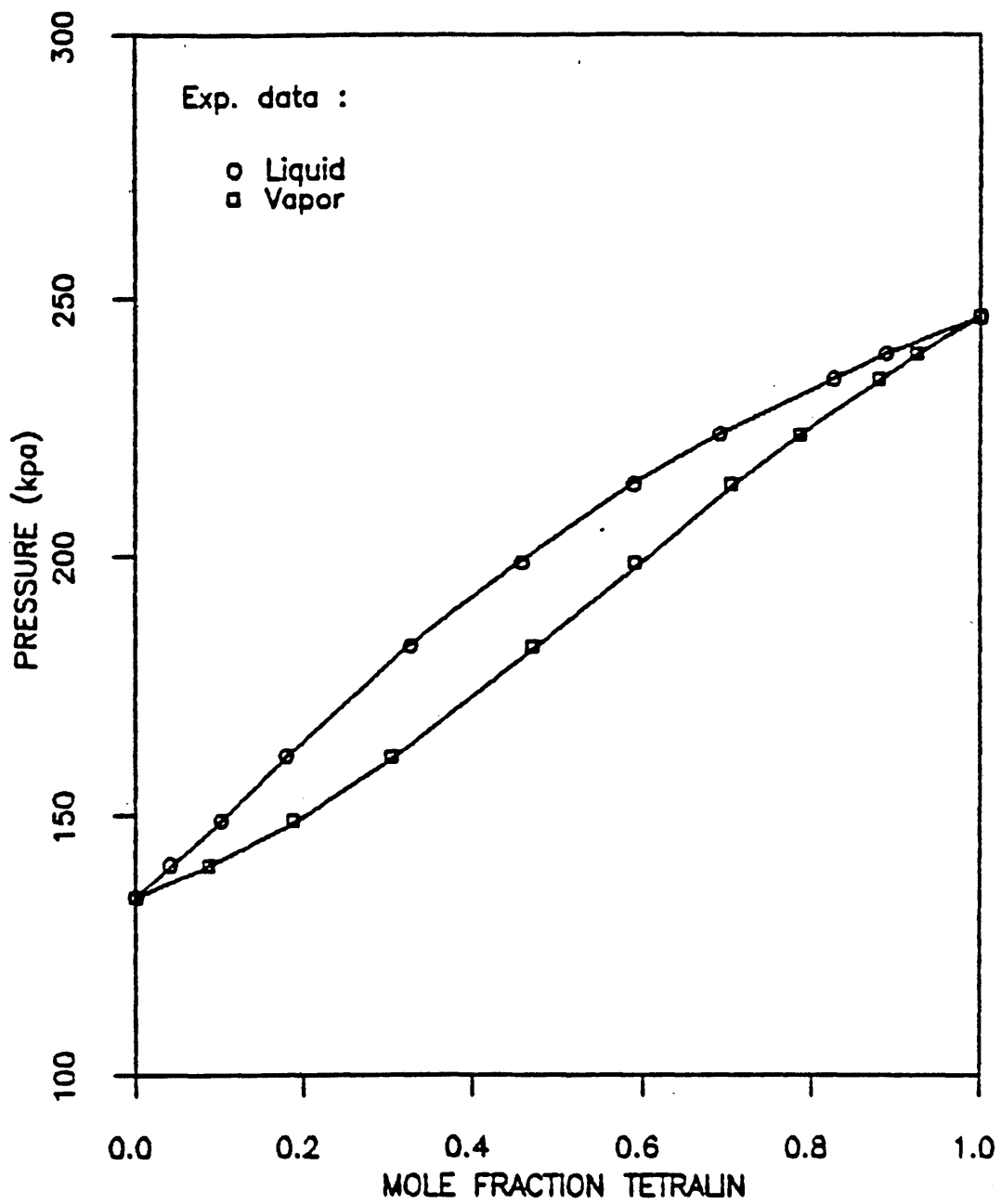


Figure 3. Binary Phase Diagram of Tetralin-Quinoline at 523 K, Equation = modified SRK, Mixing Rule = III.

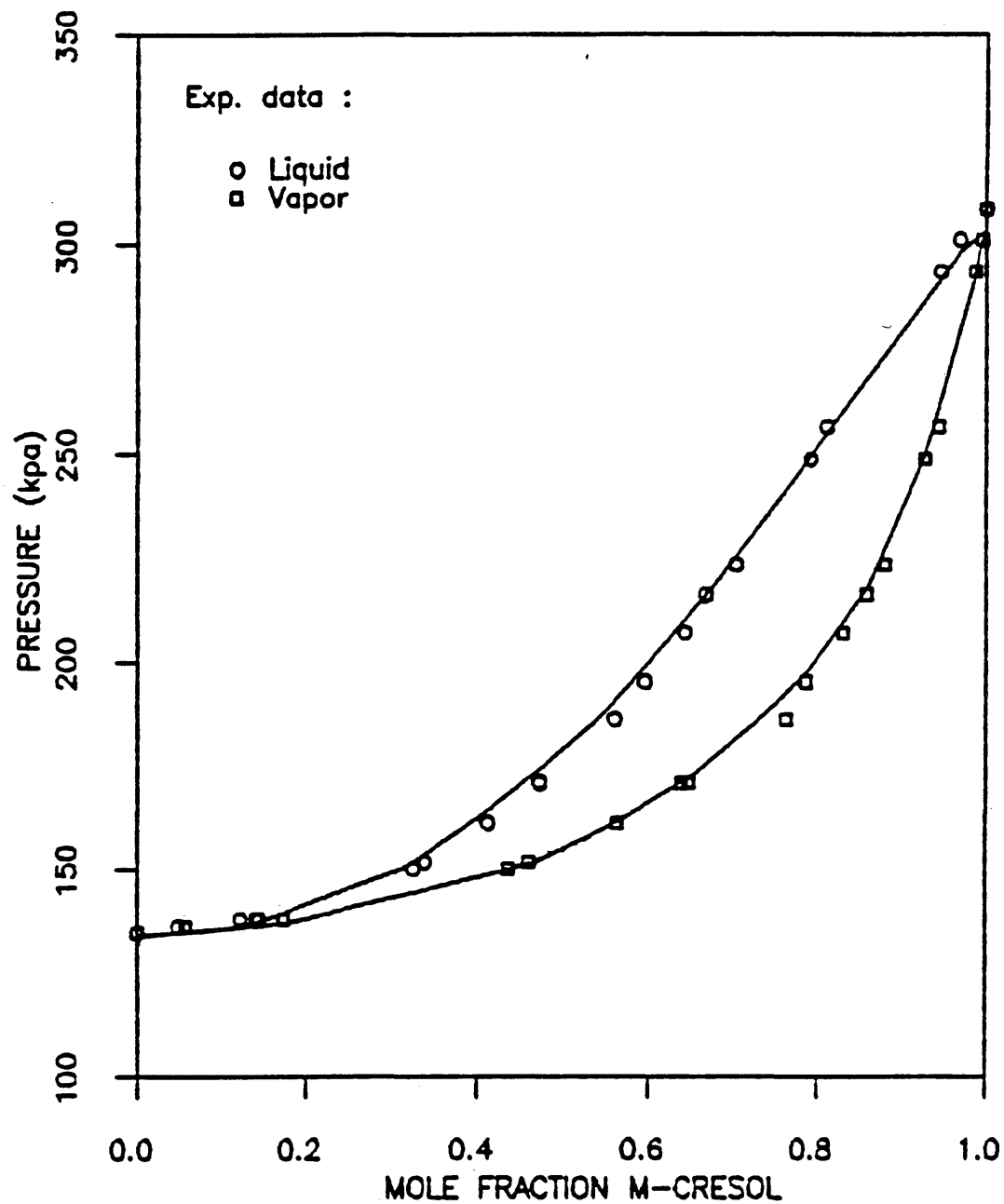


Figure 4. Binary Phase Diagram of m-Cresol/Quinoline at 523 K, Equation = PHS, Mixing Rule = III

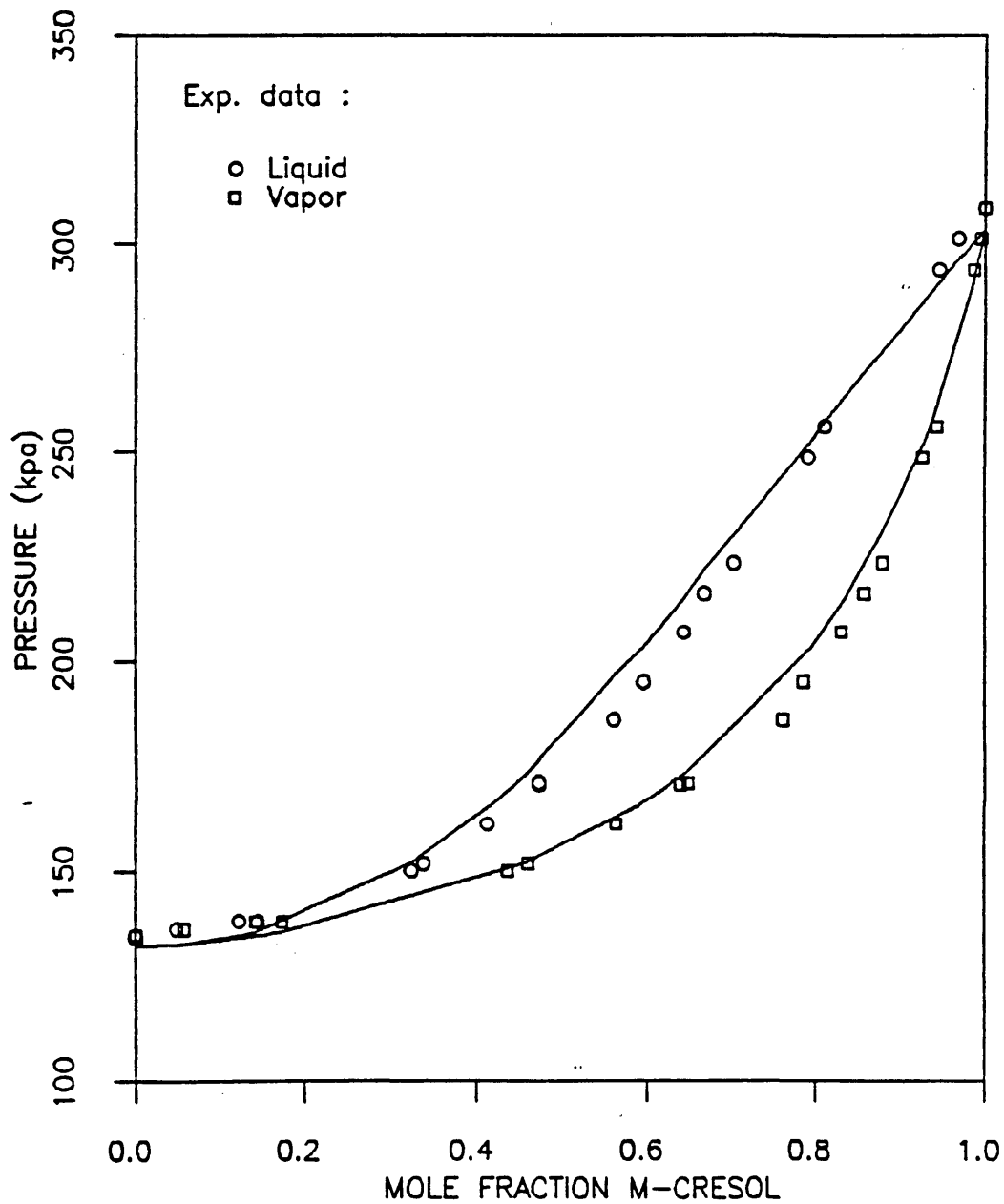


Figure 5. Binary Phase Diagram of m-Cresol/Quinoline at 523 K, Equation = PHS, Mixing Rule = II

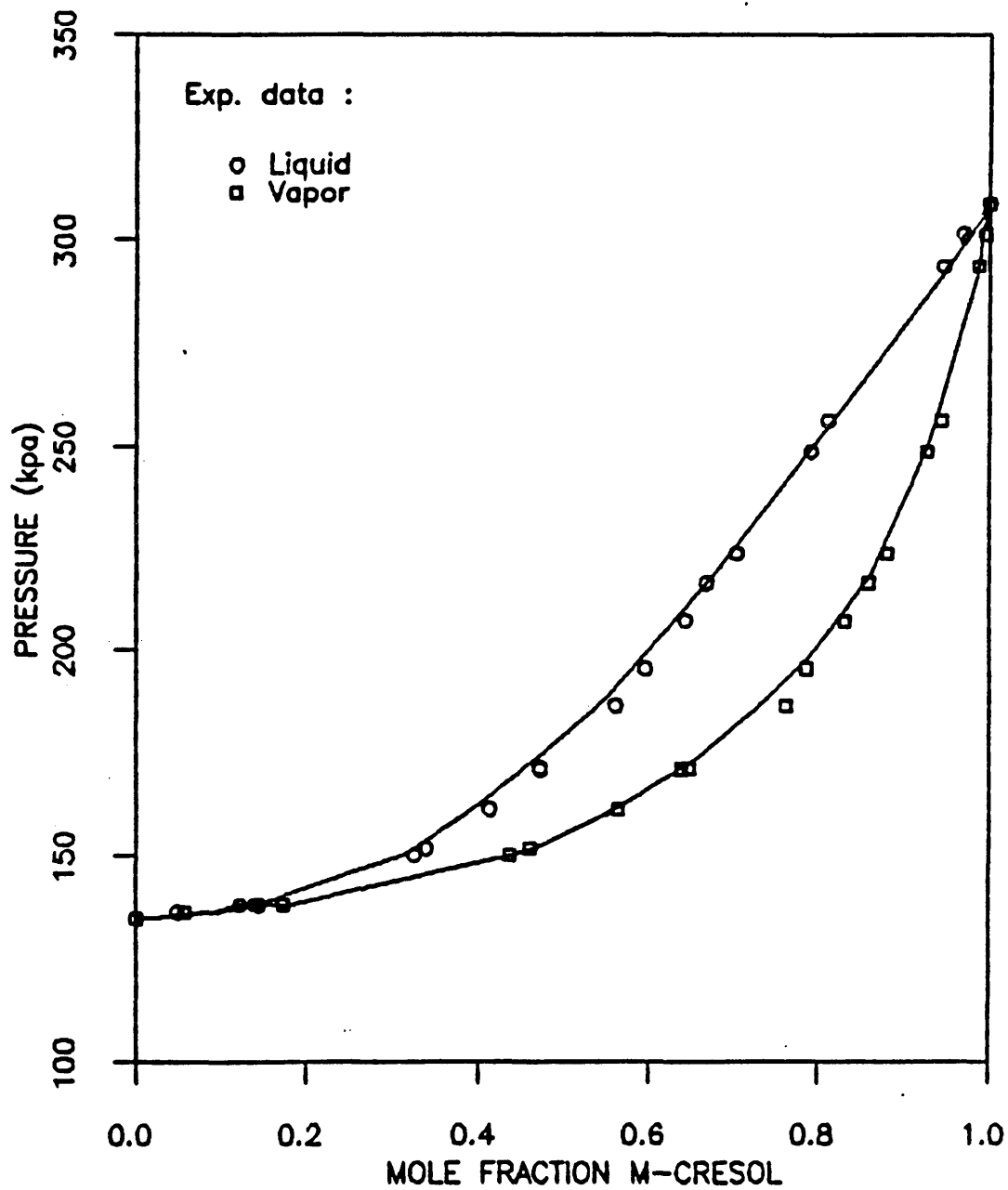


Figure 8. Binary Phase Diagram of m-Cresol/Quinoline at 523 K, Equation = modified SRK, Mixing Rule = III.

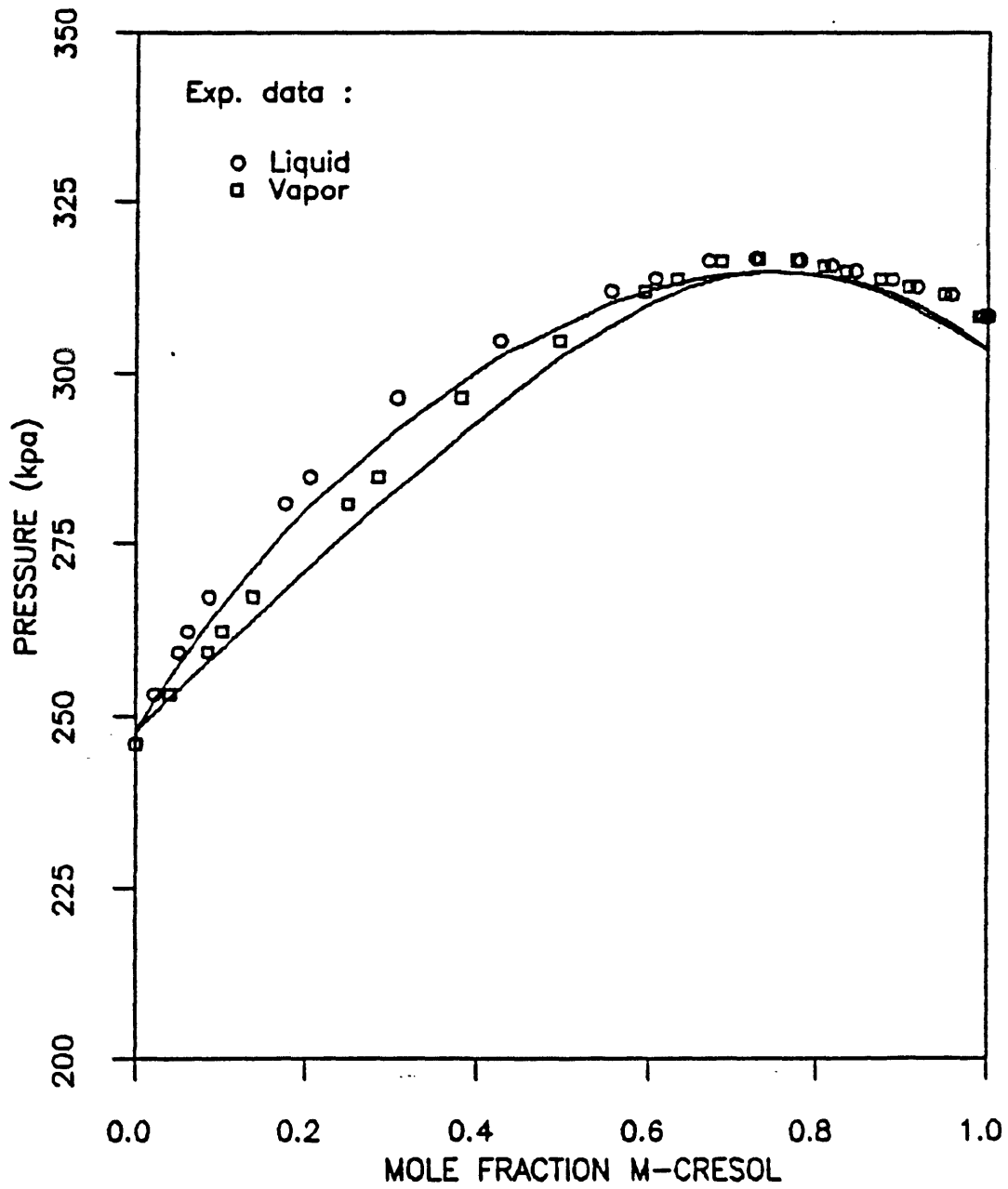


Figure 7. Binary Phase Diagram of m-Cresol/Tetralin at 523 K, Equation = PHS, Mixing Rule = III

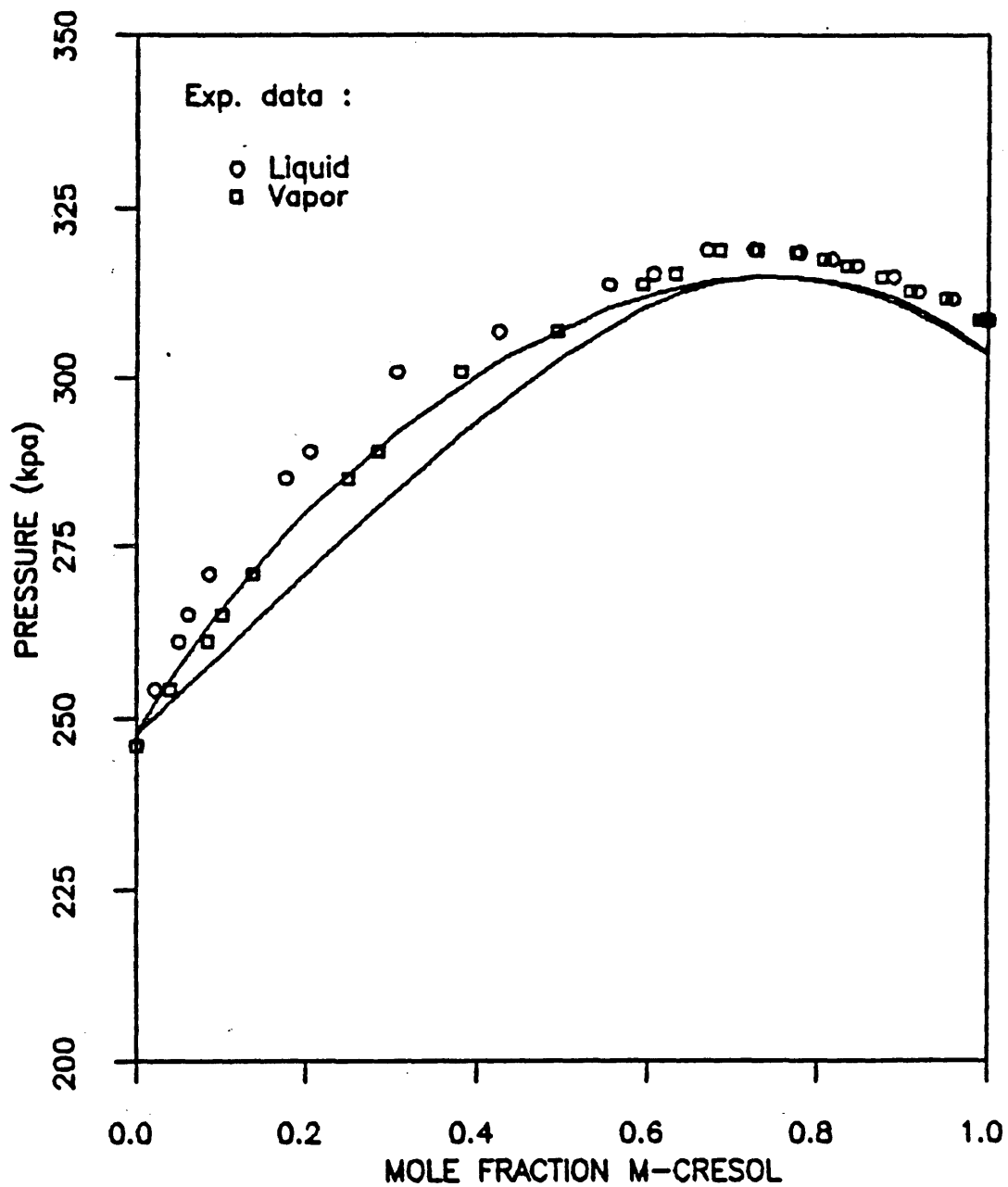


Figure 8. Binary Phase Diagram of m-Cresol/Tetralin at 523 K, Equation = PHS, Mixing Rule = II

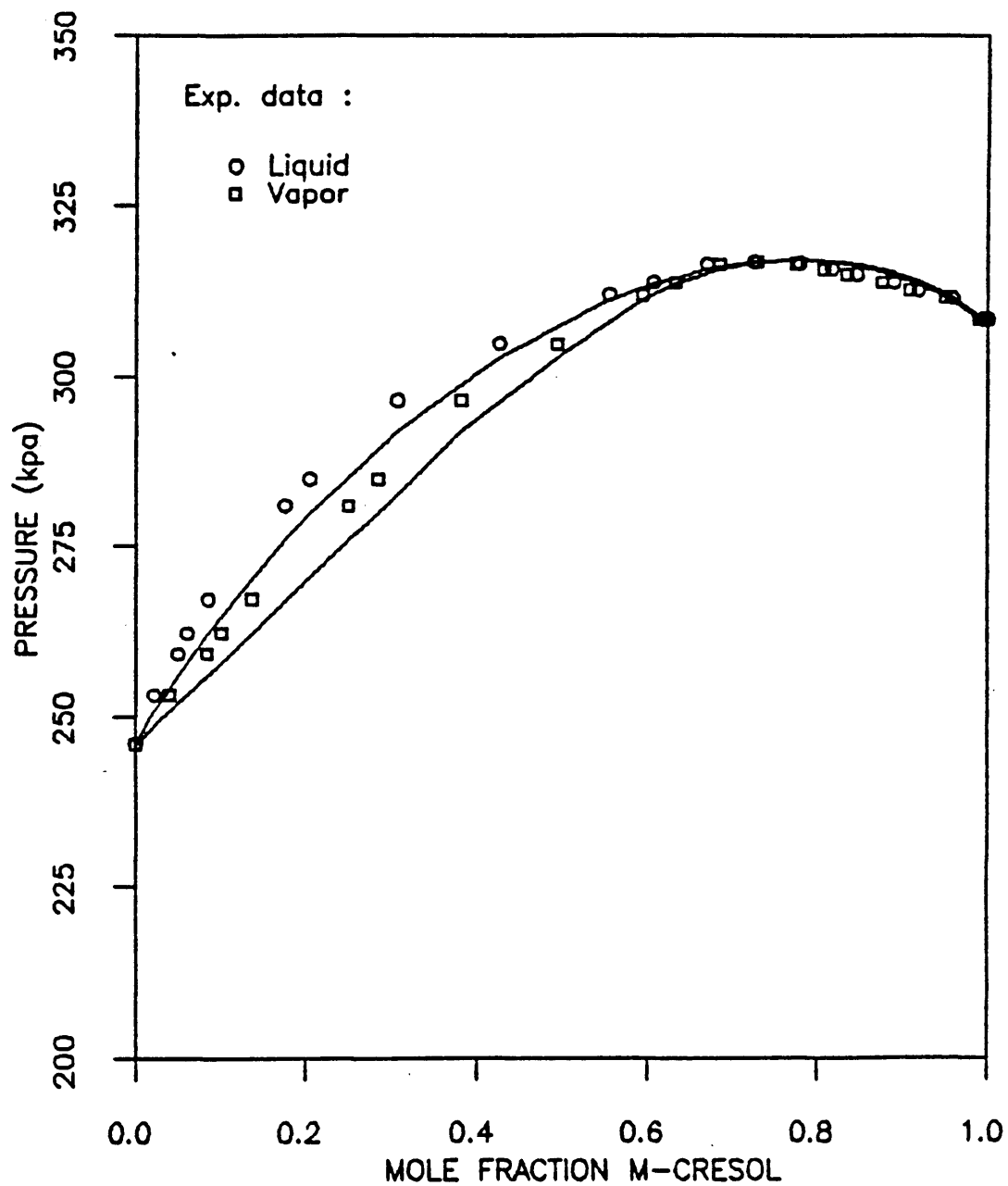


Figure 9. Binary Phase Diagram of *m*-Cresol/Tetralin at 523 K, Equation = modified SRK, Mixing Rule = III.

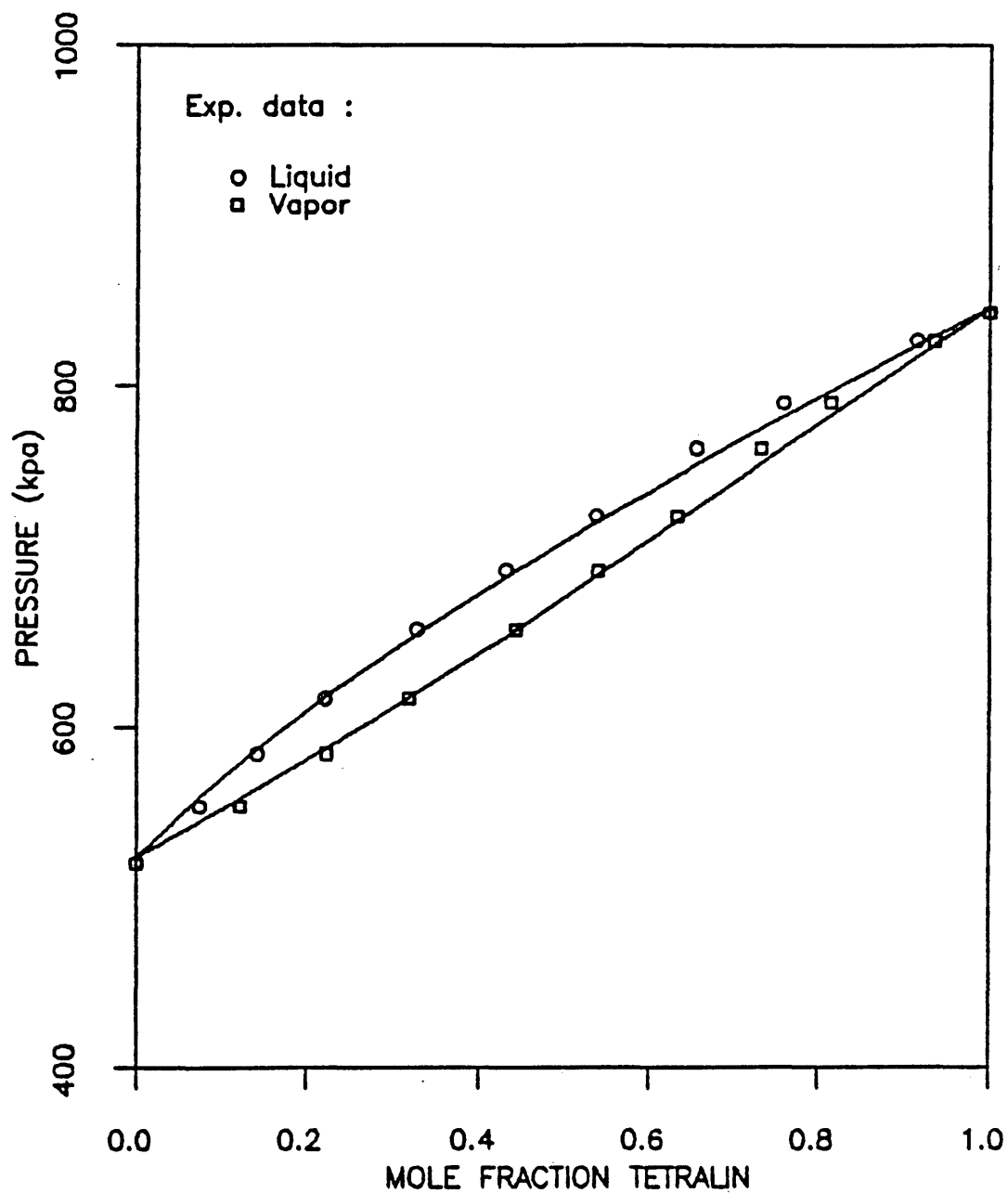


Figure 10. Binary Phase Diagram of Tetralin-Quinoline at 598 K, Equation = PHS, Mixing Rule = III.

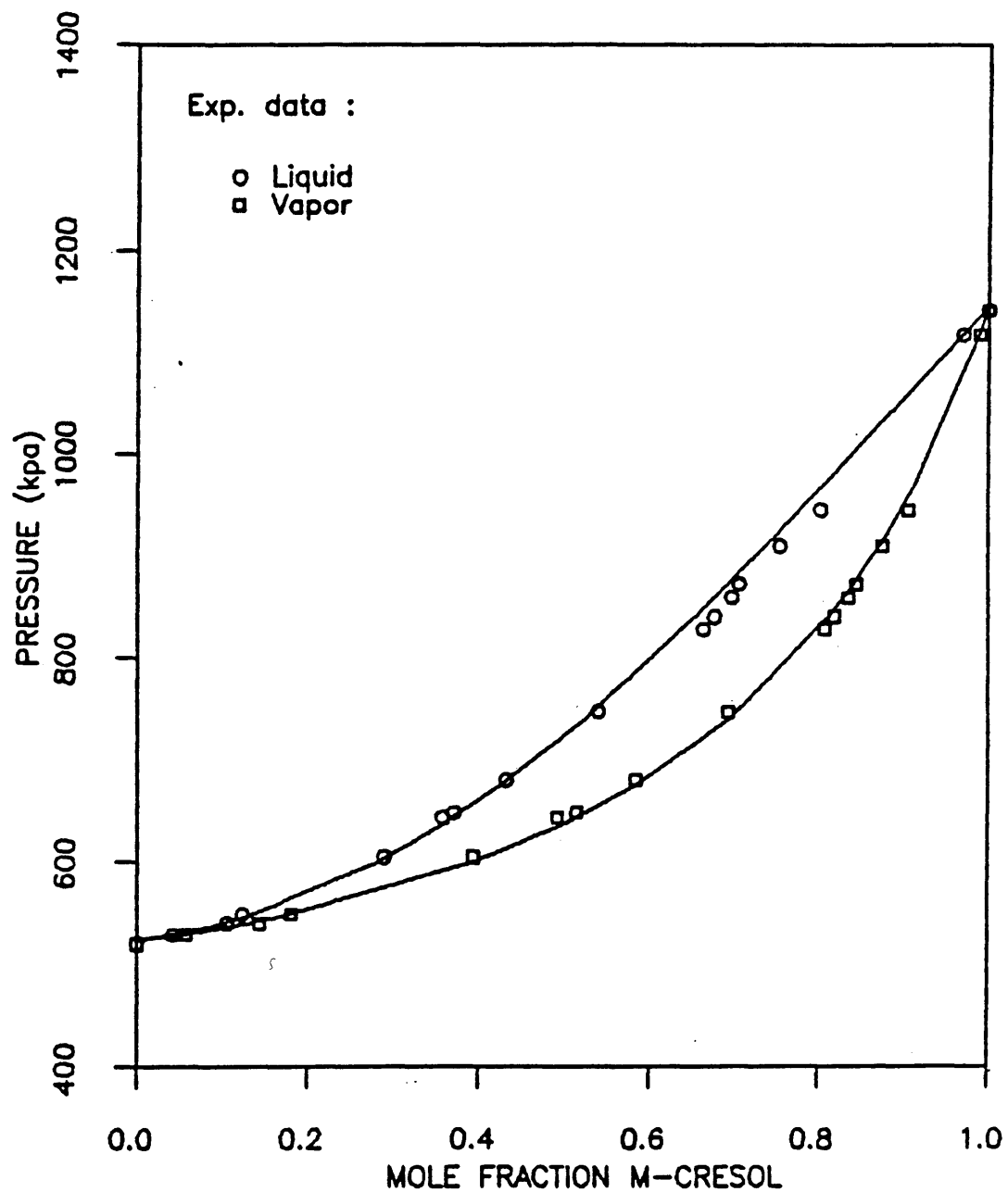


Figure 11. Binary Phase Diagram of m-Cresol/Quinoline at 598 K, Equation = PHS, Mixing Rule = III.

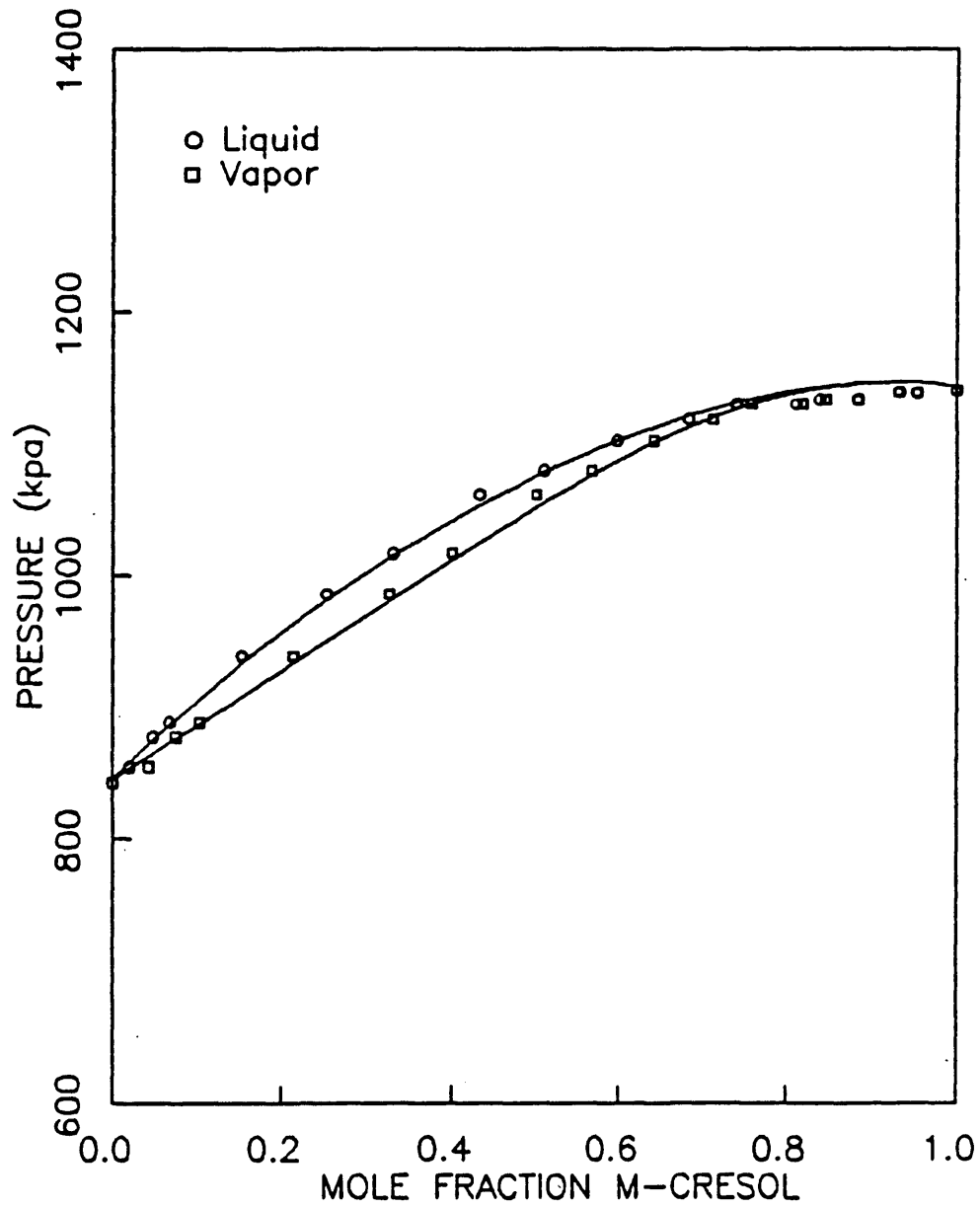


Figure 12. Binary Phase Diagram of *m*-Cresol/Tetralin at 598 K, Equation = PHS, Mixing Rule = III.

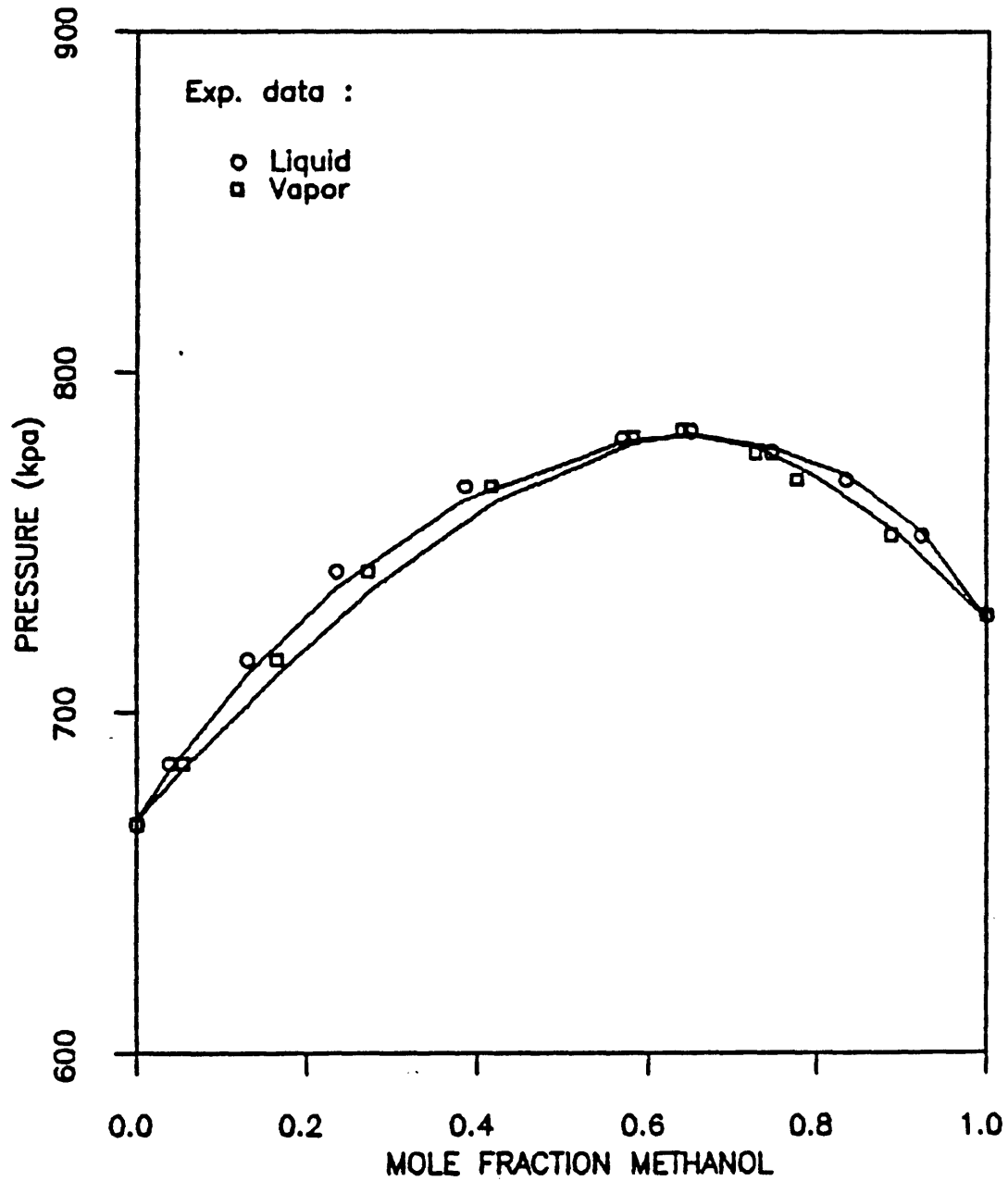


Figure 13. Binary Phase Diagram of Methanol-Acetone at 397 K, Equation = PHS, Mixing Rule = III

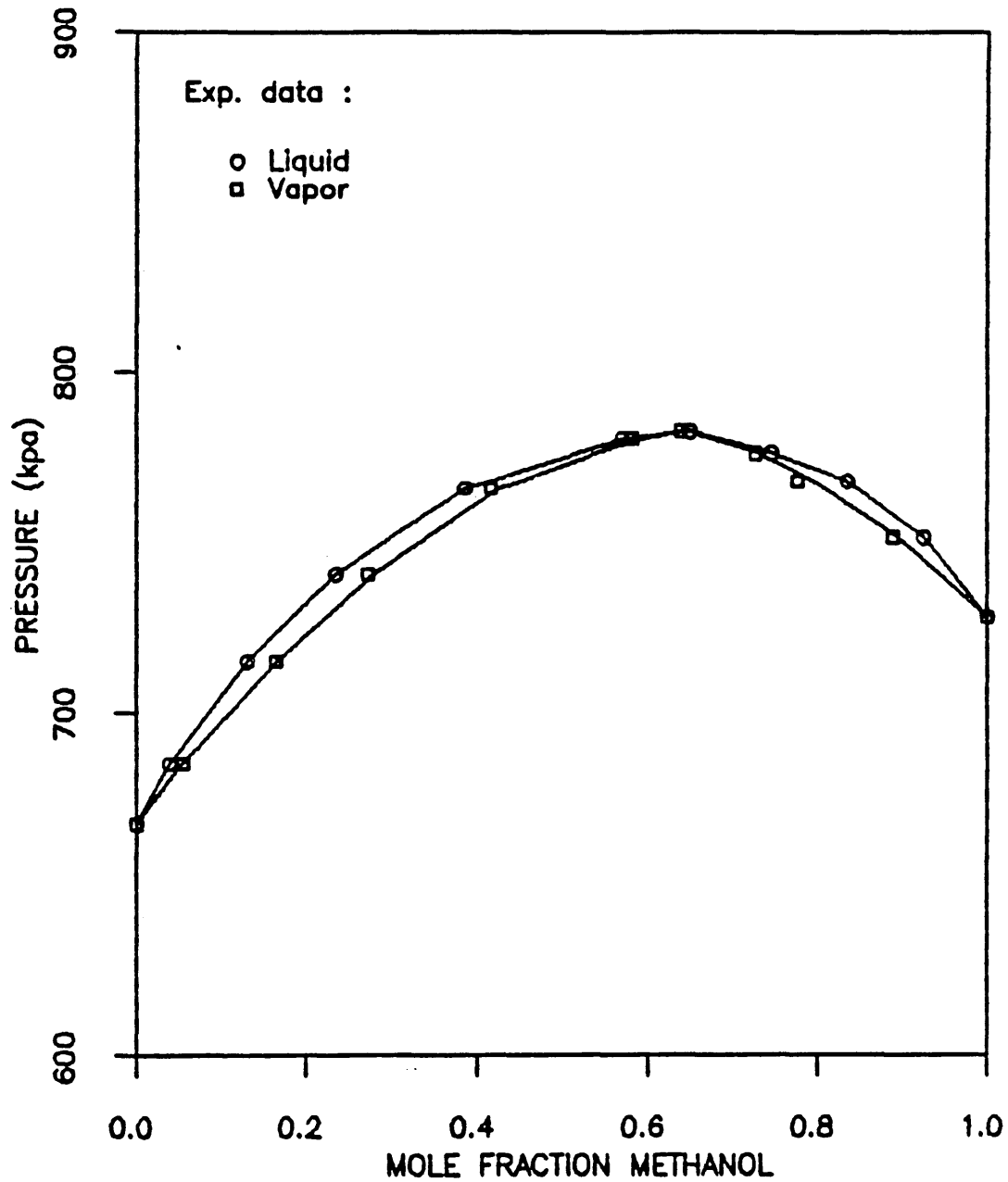


Figure 14. Binary Phase Diagram of Methanol-Acetone at 397 K, Equation = modified SRK, Mixing Rule = III.

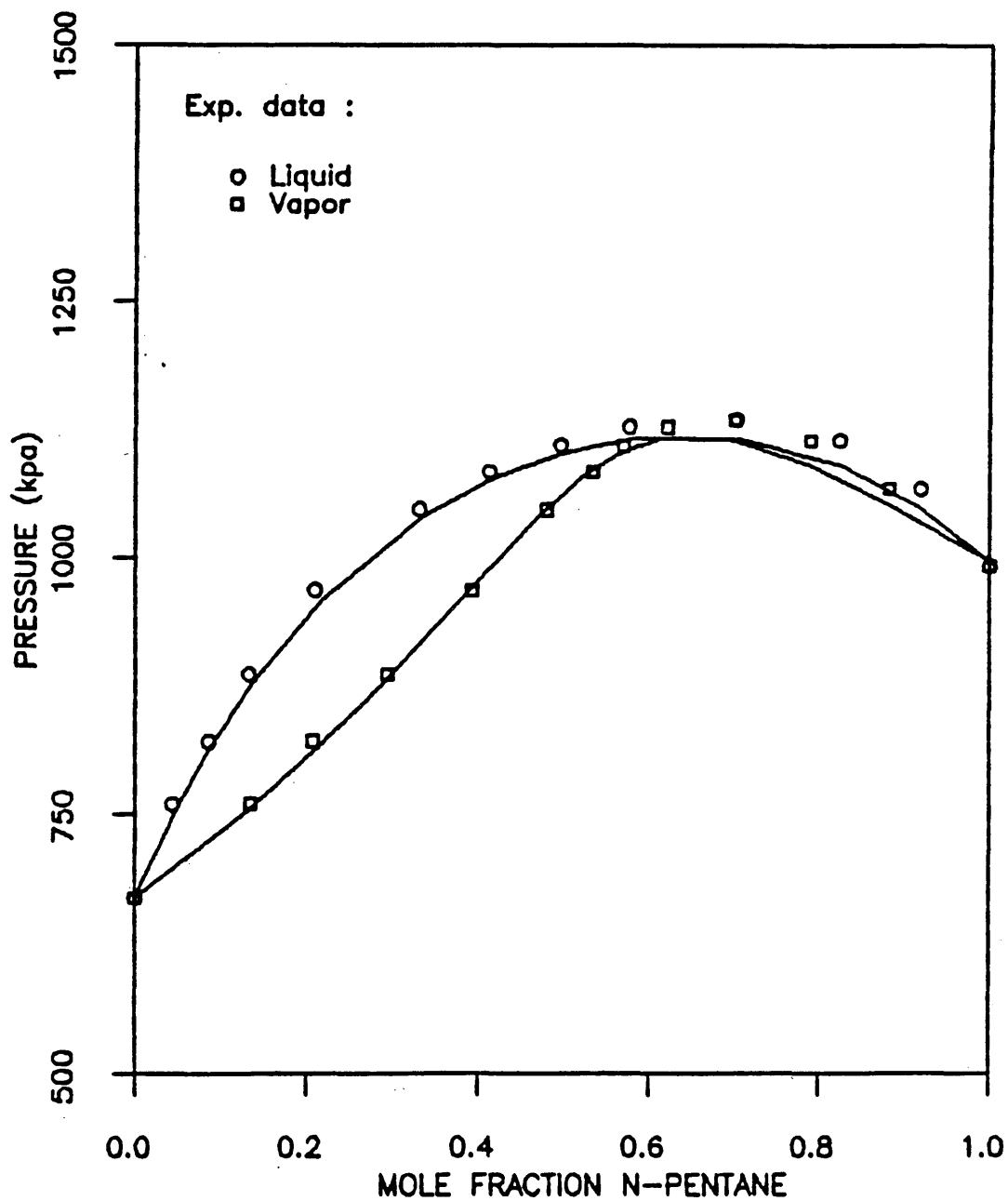


Figure 15. Binary Phase Diagram of n-Pentane/Acetone at 397 K, Equation = PHS, Mixing Rule = III

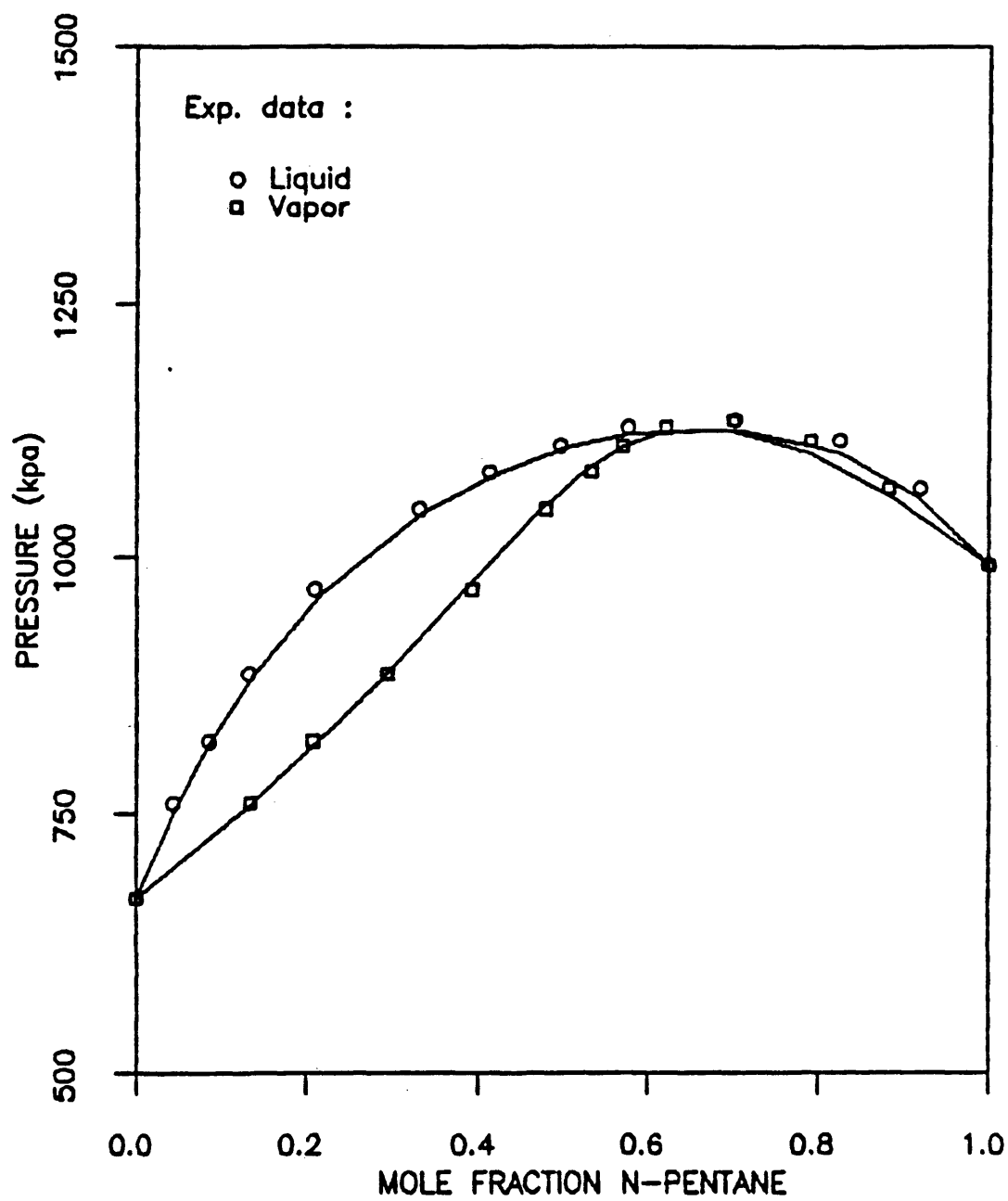


Figure 16. Binary Phase Diagram of n-Pentane/Acetone at 397 K, Equation = modified SRK, Mixing Rule = III.

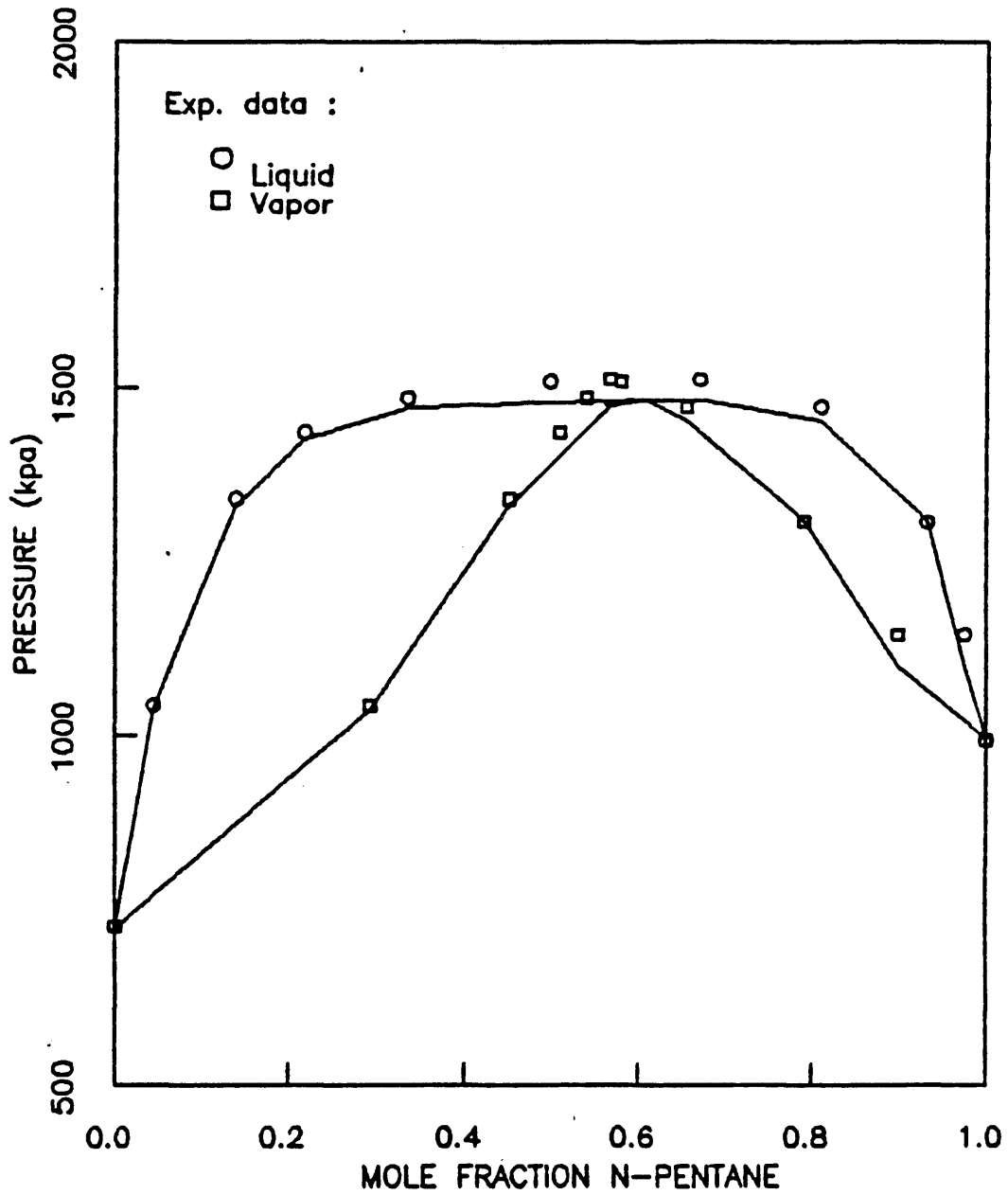


Figure 17. Binary Phase Diagram of n-Pentane/Methanol at 397 K, Equation = PHS, Mixing Rule = III

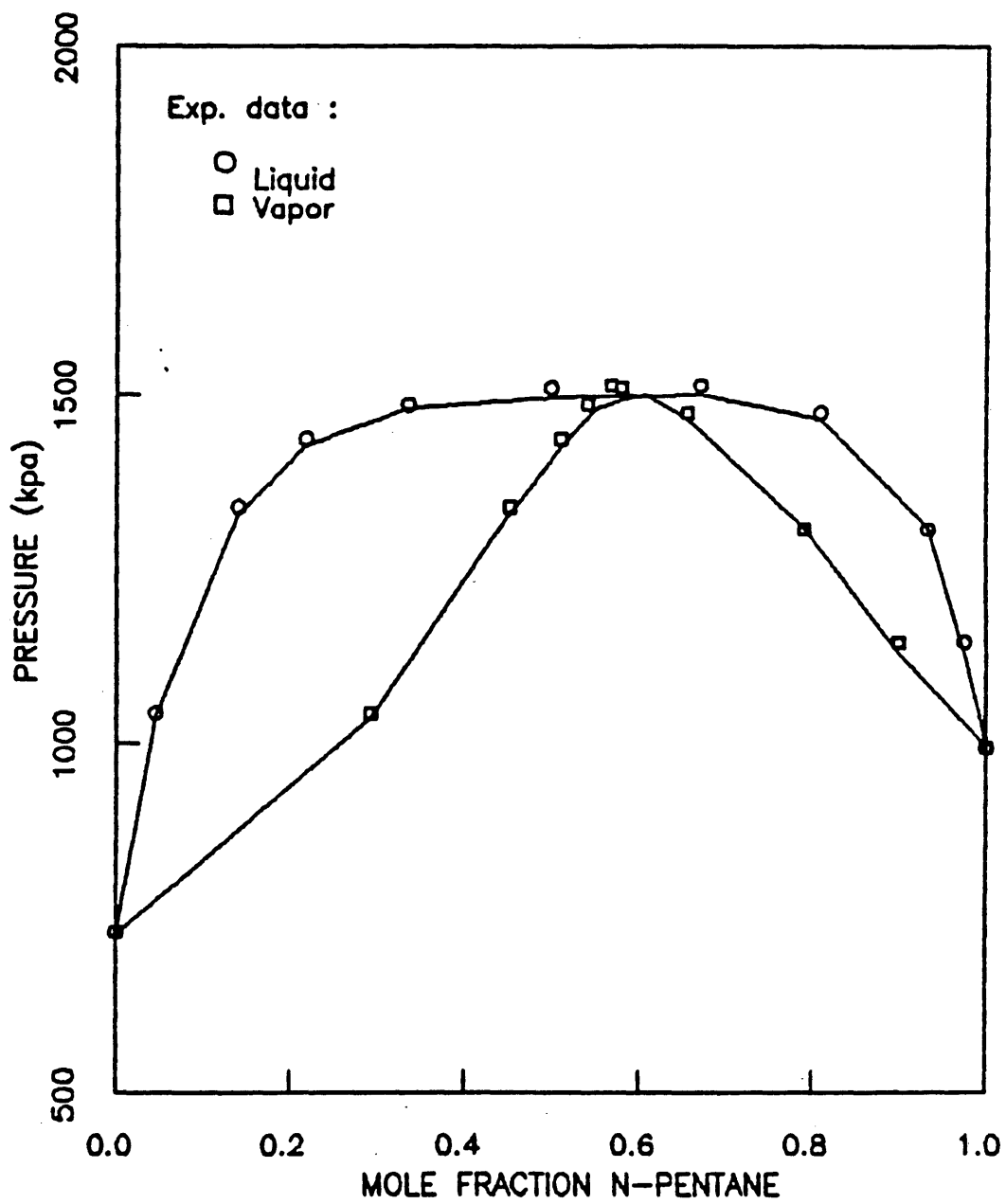


Figure 18. Binary Phase Diagram of n-Pentane/Methanol at 397 K, Equation = modified SRK, Mixing Rule = III.

Figures 2, 5, and 8 are binary phase diagrams of tetralin/quinoline, m-cresol/quinoline, m-cresol/tetralin, respectively, using the generalized perturbed hard sphere equation of state with mixing rule II. These figures are presented in order to clearly illustrate the different results on phase behaviour correlation between mixing rule II and mixing rule III. Figures 1, 4, and 7 are binary phase diagrams of the same systems resulted from the same equation of state with mixing rule III. Both sets of figures visualize the value of  $S^2$  obtained from the maximum likelihood method for both mixing rules II and III. From those figures one can easily acknowledge that smaller value of  $S^2$  depicted in Table 4 and 5 represents better phase behaviour correlation. Therefore, according to the above illustration, it can be concluded that mixing rule III is the best mixing rule for fitting the binary systems.

Using the same technique, the results on phase behaviour correlation from the generalized perturbed hard sphere equation of state are compared to the results from the modified SRK equation of state. Figures 3, 6, and 9 are binary phase diagrams of tetralin-quinoline, m cresol-quinoline, and m cresol-tetralin systems obtaining from the modified SRK using mixing rule III. These figures show better correlation than figures 1, 4, and 7 as results from the generalized perturbed hard sphere equation using the

same mixing rule. This is confirmed by the values of  $S^2$  in Table 4, where the modified SRK equation gives lower values than the generalized perturbed hard sphere equation. A typical analysis for the n-pentane/methanol/acetone system can be done also by looking at the Table 5 and figures 13 through 18. From this comparison study, it can be concluded that the modified SRK equation of state gives a better prediction of binary phase behaviour than the generalized perturbed hard sphere equation of state; however, the generalized perturbed hard sphere equation is still able to give reasonable results.

Figures 10, 11, and 12 are the binary phase diagrams of tetralin/quinoline, m-cresol/quinoline, and m-cresol/tetralin at 598 K resulting from the generalized perturbed hard sphere equation of state using mixing rule III.

### Results on the Ternary Phase Behaviour

The resulting binary interaction parameters were then used for prediction of ternary phase behaviour for both m-cresol, quinoline, tetralin and n-pentane, methanol, acetone mixtures. The m-cresol/quinoline/tetralin ternary system was evaluated at four isotherms, i.e. at 523, 548, 573, and 598 K within three different isobars [13], while the n-pentane/methanol/acetone system was evaluated at 373 K and various system pressures [16]. One of the computer programs developed for this calculation is presented in Appendix C. The results of calculation for the ternary mixture of m-cresol/quinoline/tetralin at 523 K, also those for the n-pentane/methanol/acetone system are listed in Appendix B of this report.

The average absolute difference in mole fraction between experimental data and calculated compositions for both the liquid and vapor phases are tabulated in Table 6 for the m-cresol/quinoline/tetralin system, and in Table 7 for the n-pentane/methanol/acetone system.

Looking into the results in both tables, it can be said that all models give comparable results in predicting the ternary composition to between 0.01 - 0.02 deviations in mole fraction. This is interesting since Yanaki [1] also reported the same results. This leads to the conclusion

Table 6

Average Absolute Differences in Mole Fraction for  
m-Cresol/Quinoline/Tetralin Ternary Mixture

	T=523 K		T=548 K		T=573 K		T=598 K	
	x	y	x	y	x	y	x	y
<u>Modified SRK EOS :</u>								
$k_{ij}$	0.0114	0.0127	0.0086	0.0095	0.0063	0.0084	0.0074	0.0088
$A+B/T$	0.0093	0.0139	0.0098	0.0104	0.0069	0.0095	0.0092	0.0097
$k_{ji} \neq k_{ij}$	0.0101	0.0129	0.0077	0.0091	0.0067	0.0067	0.0066	0.0082
<u>Generalized PHS EOS :</u>								
$k_{ij}$	0.0131	0.0178	0.0082	0.0121	0.0284	0.0085	0.0102	0.0169
$A+B/T$	0.0128	0.0144	0.0092	0.0107	0.0075	0.0081	0.0108	0.0158
$k_{ji} \neq k_{ij}$	0.0124	0.0137	0.0107	0.0113	0.0096	0.0101	0.0100	0.0142

Table 7

Average Absolute Differences in Mole Fraction for  
n-Pentane/Methanol/Acetone Ternary Mixture at 373 K

	x	y
<u>Modified SRK EOS :</u>		
$k_{ij}$	0.0125	0.0109
$A+B/T$	0.0117	0.0112
$k_{ji} \neq k_{ij}$	0.0108	0.0107
<u>Generalized PHS EOS :</u>		
$k_{ij}$	0.0121	0.0105
$A+B/T$	0.0102	0.0108
$k_{ji} \neq k_{ij}$	0.0113	0.0097

that perhaps in predicting the phase behaviour of mixtures with more than two components, the simplest mixing rule can give results as accurate as the more complex mixing rule. Figures 19 through 24 illustrate the ternary phase diagrams of the m-cresol/quinoline/tetralin system. No ternary phase diagrams can be drawn for the mixture system of n-pentane/methanol/acetone because the data available in the literature are given at random pressures and compositions (see Appendix B of this report).

Again, both the modified SRK equation of state and the generalized perturbed hard sphere equation of state using the three different mixing rules can predict the ternary phase behaviour very well. Both equations of state give comparable results, yet the modified SRK equation is slightly better than the generalized perturbed hard sphere equation for the m-cresol/quinoline/tetraline ternary mixtures (n-pentane/methanol/acetone systems results are the same).

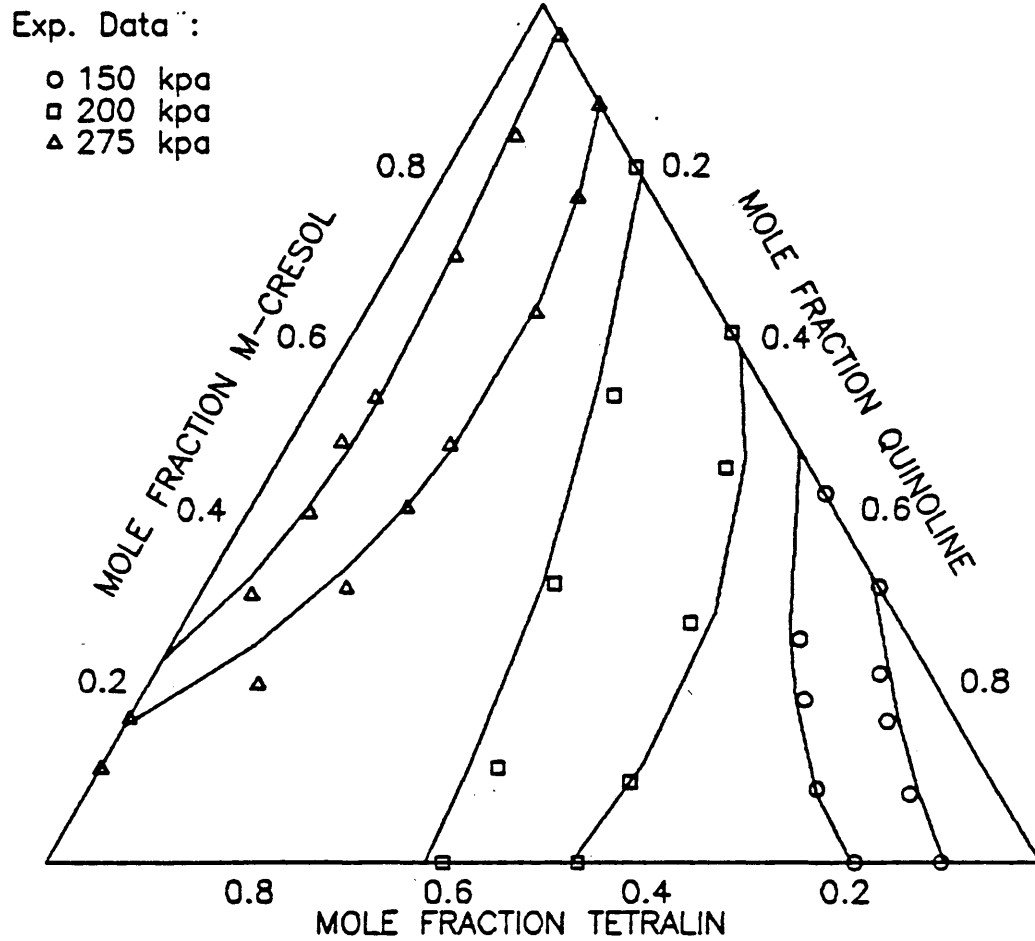


Figure 19. Ternary Phase Diagram of  
 n-Cresol/Quinoline/Tetralin  
 at 523 K, Equation = PHS,  
 Mixing rule = III.

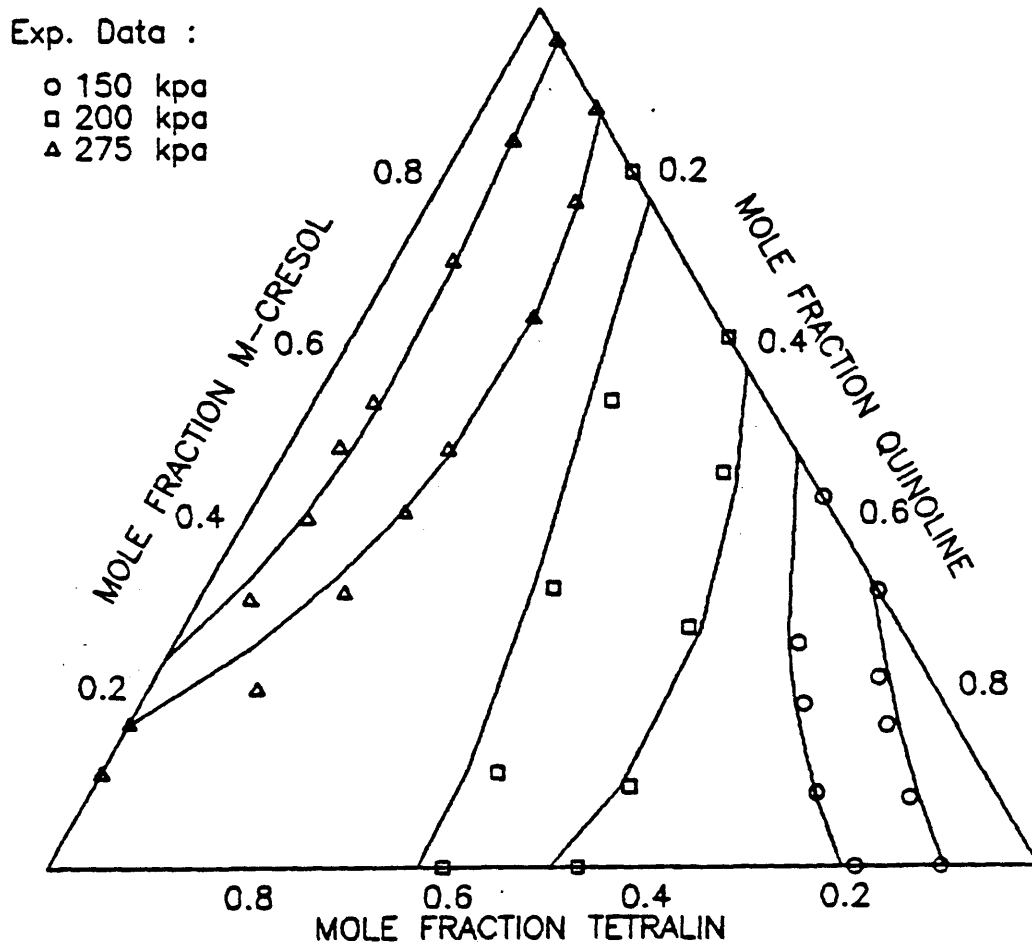


Figure 20. Ternary Phase Diagram of  
 m-Cresol/Quinoline/Tetralin  
 at 523 K, Equation = PHS,  
 Mixing rule = II.

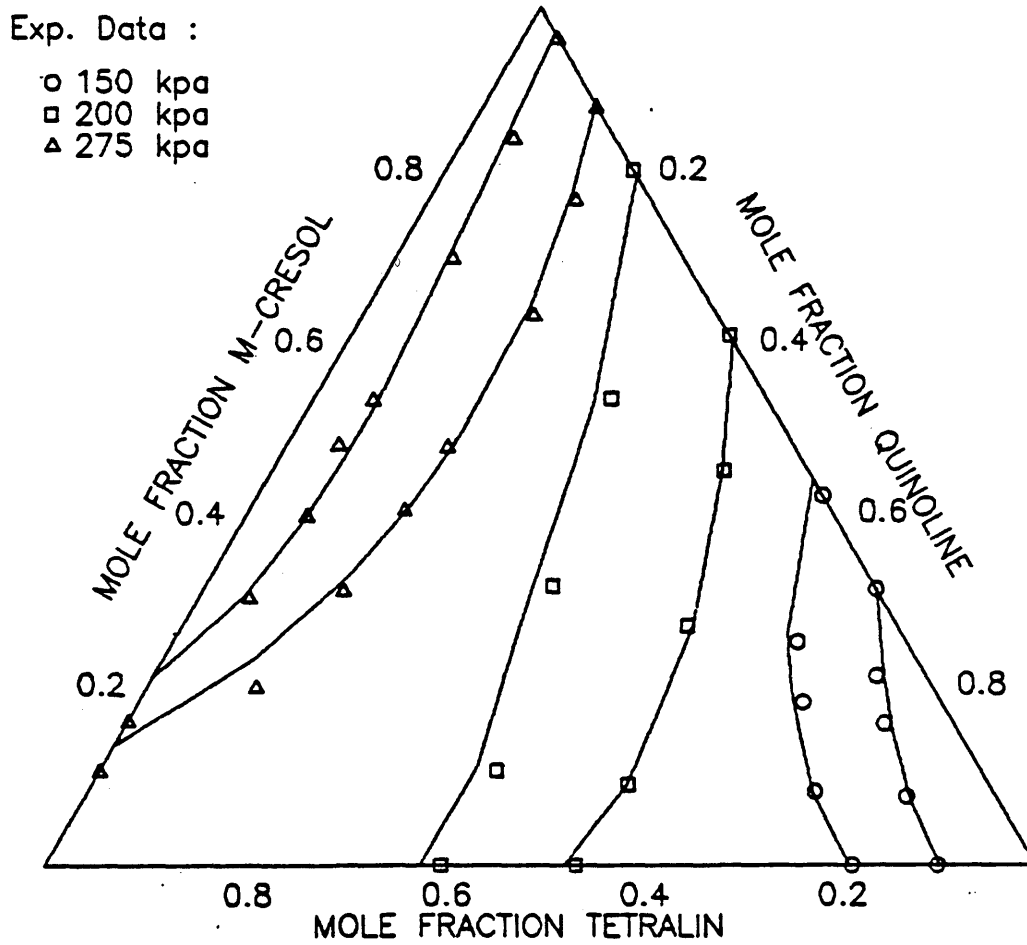


Figure 21. Ternary Phase Diagram of  
 m-Cresol/Quinoline/Tetralin  
 at 523 K, Equation = modified SRK,  
 Mixing Rule = III.

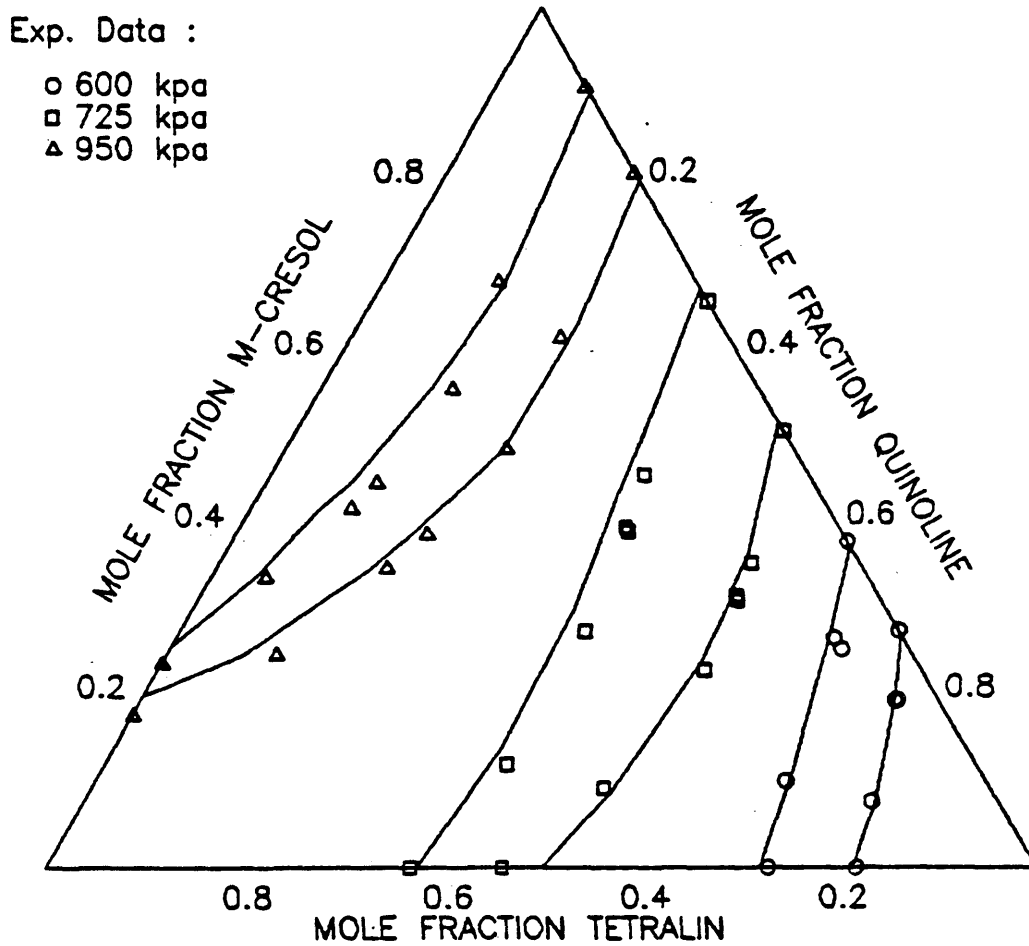


Figure 22. Ternary Phase Diagram of  
 m-Cresol/Quinoline/Tetralin  
 at 598 K, Equation = PHS,  
 Mixing rule = III.

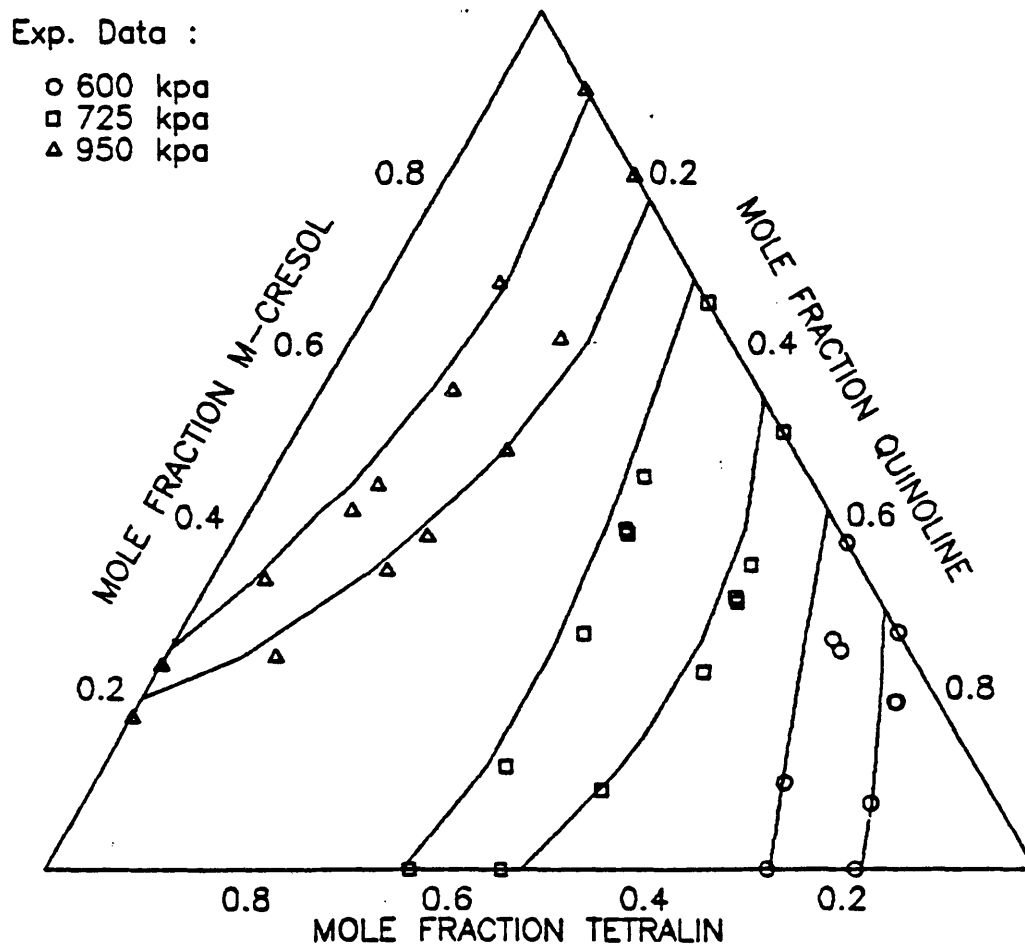


Figure 23. Ternary Phase Diagram of  
 m-Cresol/Quinoline/Tetralin  
 at 598 K, Equation = PHS,  
 Mixing rule = II.

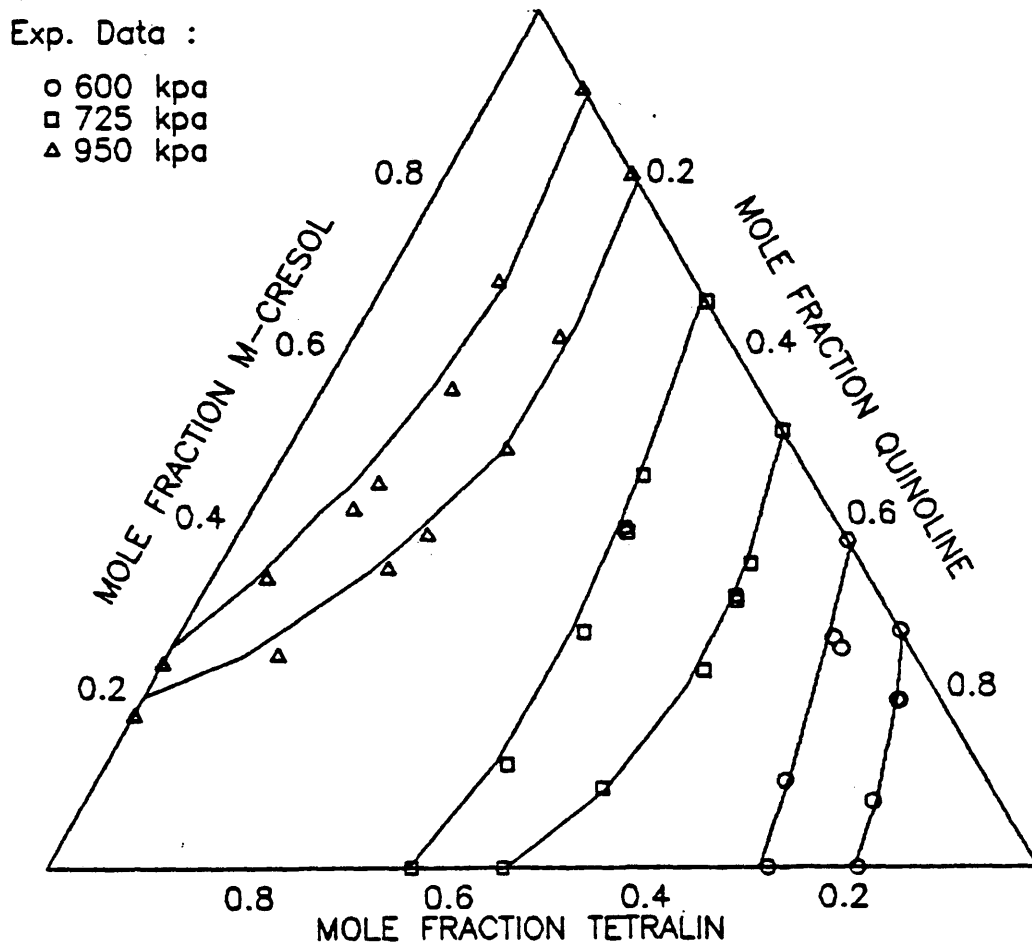


Figure 24. Ternary Phase Diagram of  
 m-Cresol/Quinoline/Tetralin  
 at 598 K, Equation = modified SRK,  
 Mixing Rule = III.

### Results on Enthalpy Calculation

Enthalpy can be found from the corresponding ideal-gas and residual property by simple addition. In this study the enthalpy of a fluid as an ideal gas is calculated using Self-Consistent Equations suggested by Rehman and Lee [26], and the residual enthalpy, or the so-called enthalpy departure, calculated using equation of state with selected mixing rule. Application of the three different mixing rules discussed in the previous section, and the  $k_{ij}=0$  mixing rule are evaluated. In order to accomplish this work, the binary interaction parameters obtaining from fitting the binary phase behaviour data were used. The results of enthalpy calculations were then compared with the experimental data reported by Joyce and Yesavage [28] for the ternary mixtures of m-cresol/quinoline/tetralin, and by Flanigan, Yesavage, Kidnay [6,11] for the binary mixtures of m-cresol/quinoline/tetralin. The reference temperature and pressure for this calculation is 291 K and 101 KPa, respectively. The differences between the calculated enthalpy and the experimental data are presented in Table 8 for the binary mixtures, and in Table 9 for the ternary mixtures. These results show that the generalized perturbed hard sphere equation gives significant improvements over the modified SRK equation of state in calculating enthalpy,

Table 8

Average Absolute Percent Differences Between  
Experimental and Calculated Enthalpy  
of Binary Mixtures

	<u>tetralin/ quinoline</u>		<u>m-cresol/ quinoline</u>		<u>m-cresol/ tetralin</u>	
	liquid	vapor	liquid	vapor	liquid	vapor
<u>Modified SRK EOS:</u>						
$k_{ij}=0$	5.62	0.64	7.34	3.26	5.72	2.02
$k_{ij}$	5.96	1.26	7.10	3.23	5.24	1.22
$A+B/T$	6.49	1.32	6.15	2.75	5.96	1.52
$k_{ij} \neq k_{ji}$	6.23	1.38	7.30	3.33	7.92	2.81
<u>Generalized PHS EOS :</u>						
$k_{ij}=0$	3.99	1.93	7.04	4.80	5.70	0.78
$k_{ij}$	3.90	1.43	6.59	3.19	5.48	0.48
$A+B/T$	2.84	0.48	3.67	1.21	5.57	1.17
$k_{ij} \neq k_{ji}$	3.95	1.47	6.80	3.29	5.85	1.28

Table 9  
Average Absolute Percent Differences Between  
Experimental and Calculated Enthalpy  
of Ternary Mixtures

	<u>equimolar mixture</u>		<u>tetralin fract.=2/3</u>		<u>quinoline fract.=2/3</u>		<u>m-cresol fract.=2/3</u>	
	liq.	vap.	liq.	vap.	liq.	vap.	liq.	vap.
<u>Modified SRK EOS:</u>								
$k_{ij}=0$	6.09	1.73	5.33	1.04	5.59	0.43	6.56	0.27
$k_{ij}$	6.49	0.76	5.62	1.61	6.15	0.70	6.99	0.72
$A+B/T$	6.39	0.74	6.53	1.85	5.68	0.71	8.17	1.23
$k_{ij} \neq k_{ji}$	9.01	0.27	7.42	1.88	7.83	1.21	9.81	1.67
<u>Generalized PHS EOS:</u>								
$k_{ij}=0$	5.82	3.13	5.55	2.37	5.73	2.68	6.32	3.39
$k_{ij}$	5.71	2.74	5.55	2.29	5.69	2.58	6.90	3.65
$A+B/T$	4.87	2.07	4.82	2.05	4.85	2.08	4.88	3.25
$k_{ij} \neq k_{ji}$	5.77	2.45	5.57	2.35	5.88	2.61	6.93	3.53

especially for the mixtures having high m-cresol content. The average absolute percent error of the calculated enthalpy using the generalized perturbed hard sphere equation of state varies from 0.4 to 7.0, while-using the modified SRK equation of state it ranges from 0.4 to 10.0.

However, if those results are compared with the results of the former study done by Yanaki and Yesavage [1], the deviations of enthalpy calculated using the evaluated equation of state are bigger. They reported that their average absolute percent error of the calculated enthalpy varies from 0.2 to 6.0. Regarding the above case, the development of the generalized perturbed hard sphere equation of state should be continued.

Looking into the results tabulated in Table 8 and Table 9, it can be concluded that the mixing rule II produces the best enthalpy estimation. Results of enthalpy calculation using the generalized perturbed hard sphere equation with the mixing rule III for the binary and the ternary mixtures of m-cresol/quinoline/tetralin are presented in Appendix B.

Figures 25 through 27 are plots of enthalpy versus temperature for the binary mixtures of tetralin/quinoline, m-cresol/quinoline, and m-cresol/tetralin, respectively. Figure 28 is a plot of enthalpy versus temperature for the ternary system of m-cresol 1/3, quinoline 1/3, and

tetralin  $1/3$ . The solid line of the plot represents experimental data, while the circle mark and the square mark represent enthalpy calculated from the modified SRK equation and from the generalized perturbed hard sphere equation, respectively.

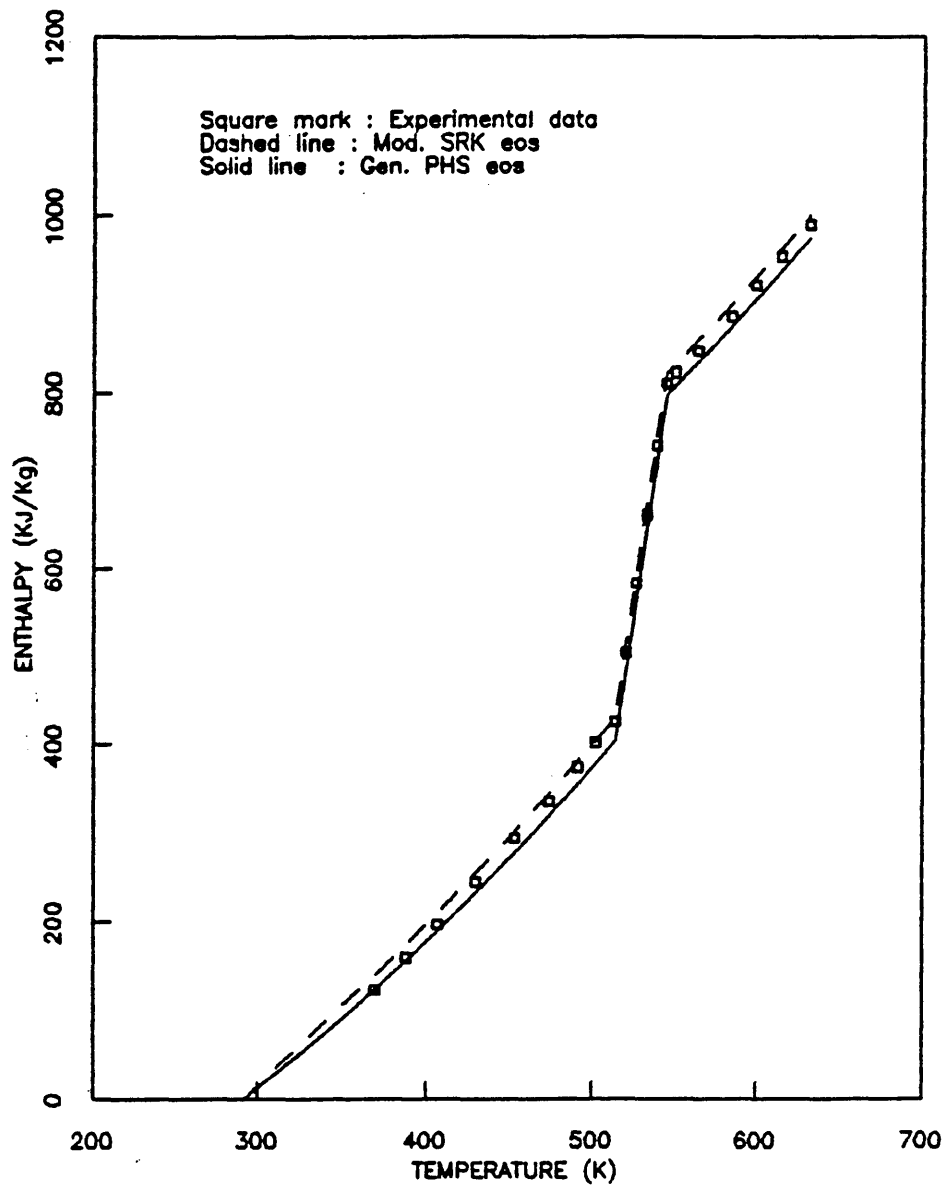


Figure 25. A Plot of Enthalpy vs Temperature for The Binary Mixture of Tetralin 1/2 - Quinoline 1/2 at 2.07 Bars, Using Mixing Rule III.

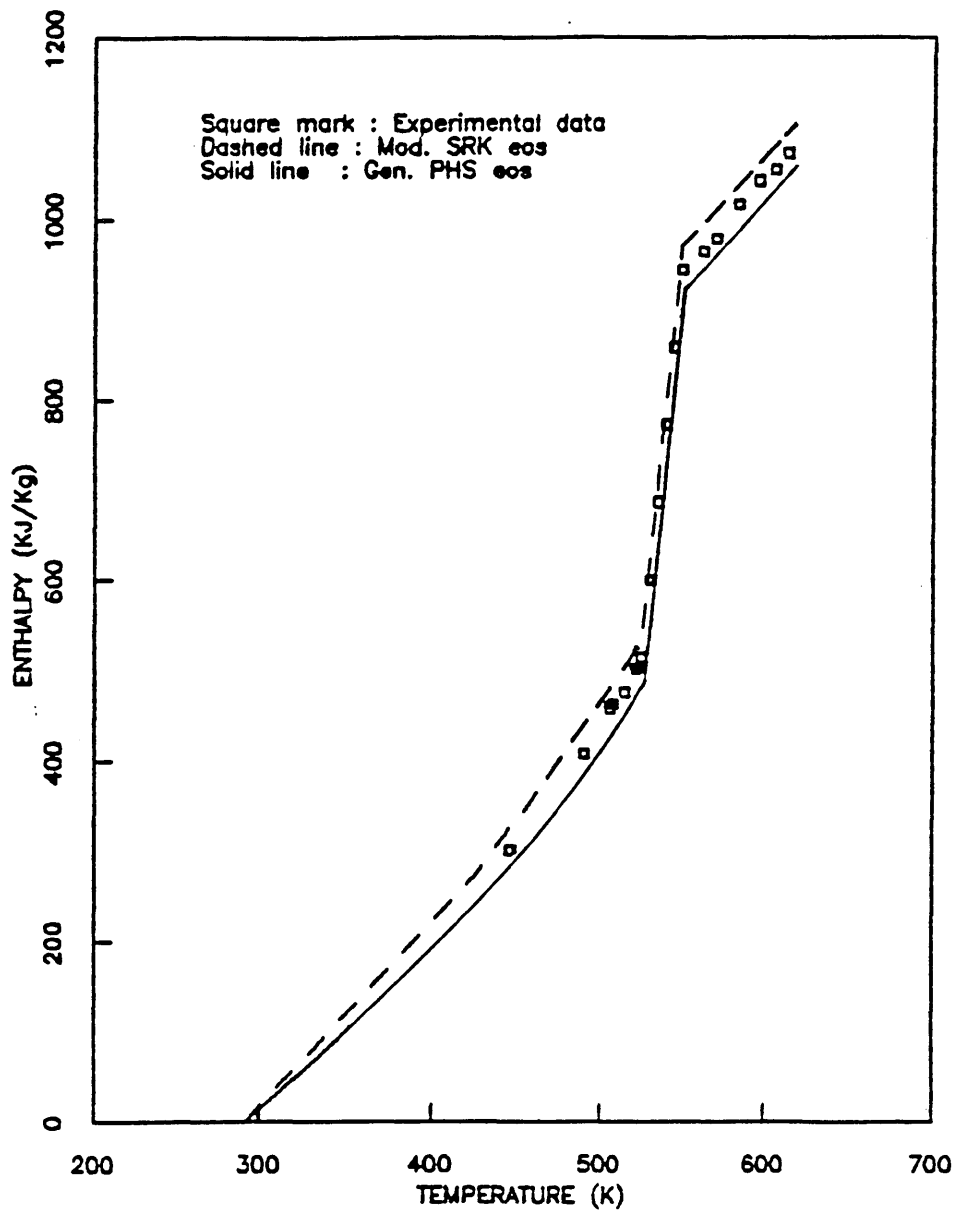


Figure 26. A Plot of Enthalpy vs Temperature for The Binary Mixture of *m*-Cresol 1/2 - Quinoline 1/2 at 2.07 Bars, Using Mixing Rule III.

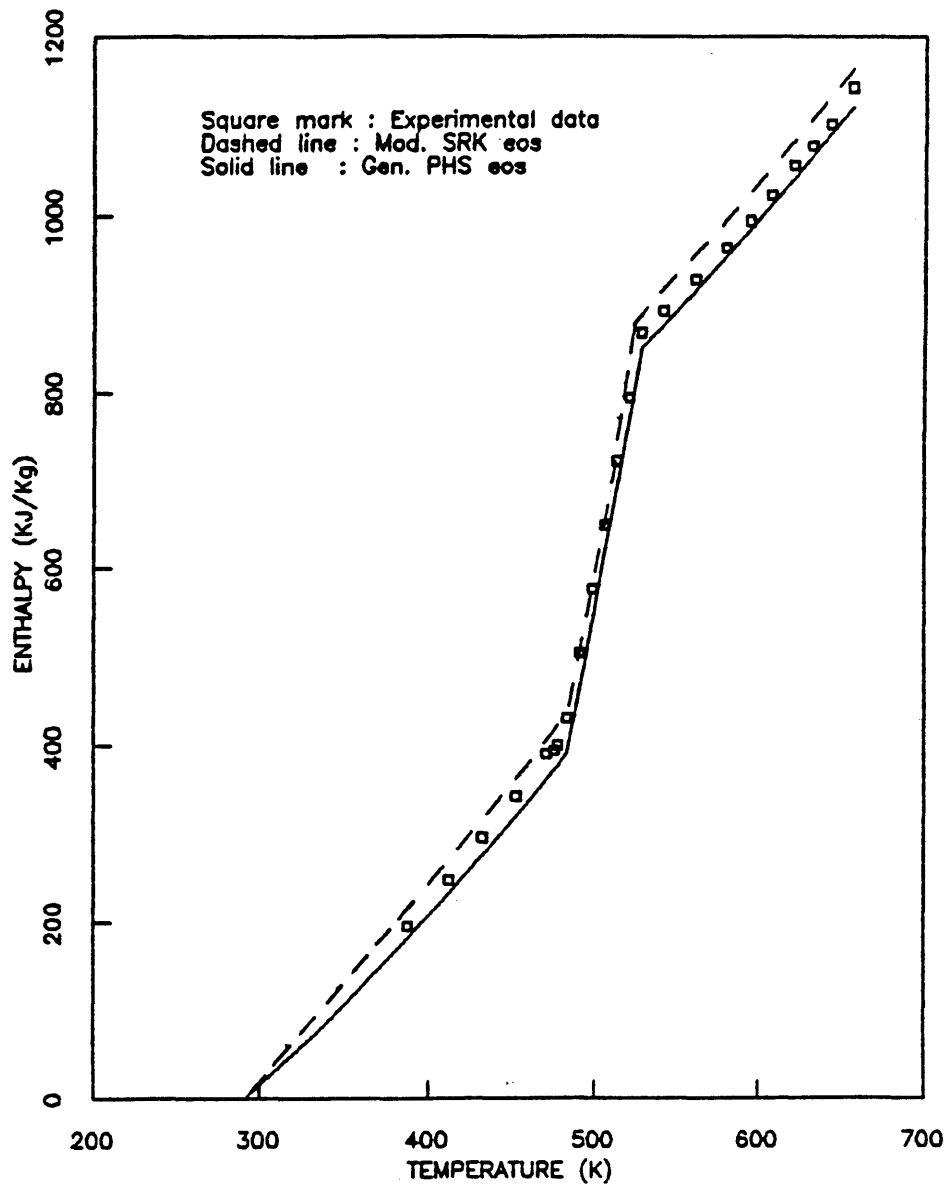


Figure 27. A Plot of Enthalpy vs Temperature for The Binary Mixture of m-Cresol 1/2 - Tetralin 1/2 at 2.07 Bars, Using Mixing Rule III

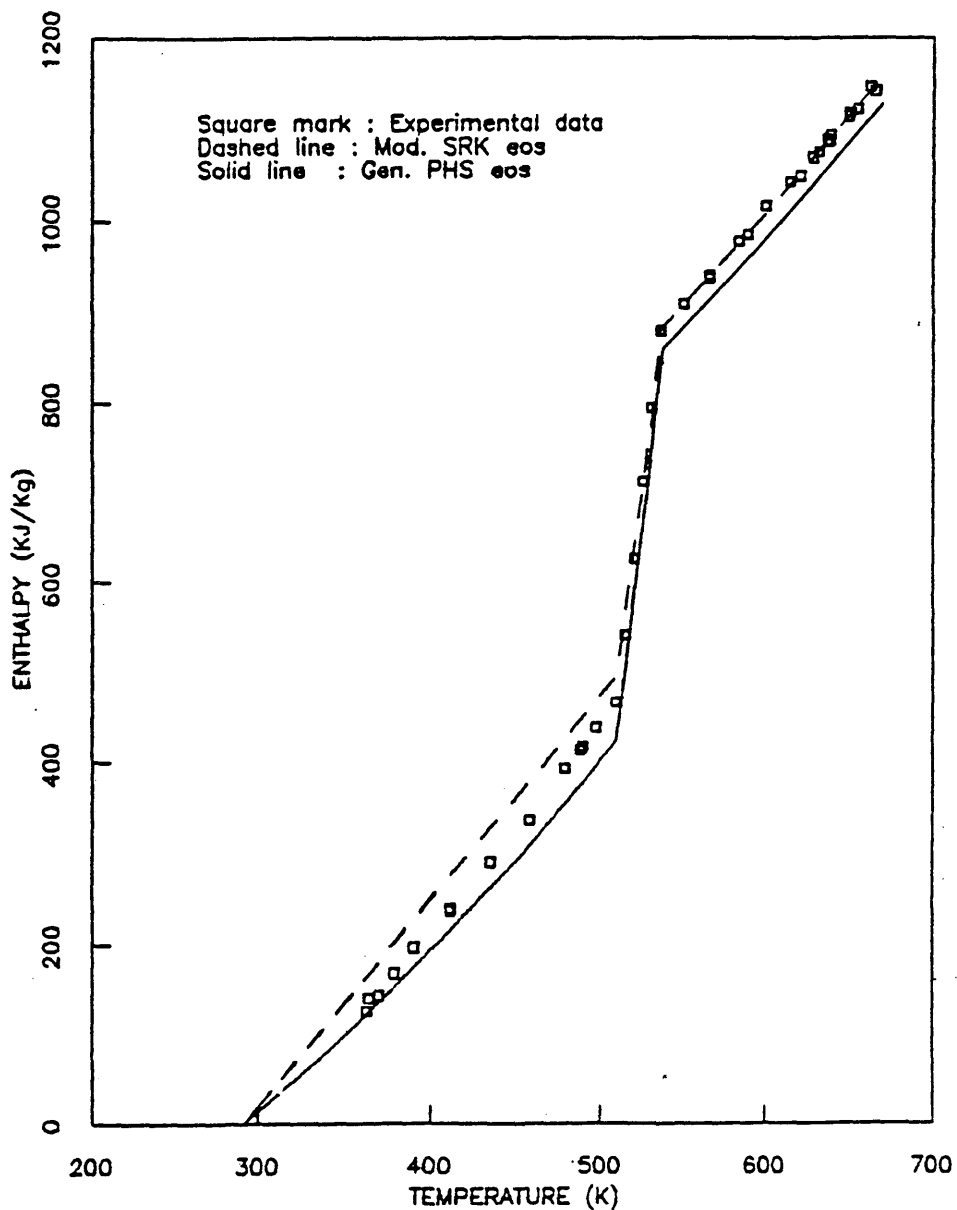


Figure 28. A Plot of Enthalpy vs Temperature for Ternary Mixture of m-Cresol 1/3, Quinoline 1/3, Tetralin 1/3, Using Mixing Rule III

## CONCLUSIONS

The purpose of this study is to evaluate the application of the generalized perturbed hard sphere equation proposed by Mulia and Yesavage to mixture systems. A comparison study with the modified Soave-Redlich-Kwong (SRK) equation of state was made to visualize how well the generalized perturbed hard sphere equation of state can predict the physical properties of mixtures. The application of the three different mixing rules were also investigated.

The results of the evaluation reveals that mixing rule III yields the best fit in predicting the binary phase behaviour compared to other mixing rules. In extending the binary results for predicting the ternary systems, all equations and all models of mixing rules give practically the same results. This is in contrast with the binary system. This leads to the conclusion that for predicting the mixture phase behaviour of more than two components, a more complex mixing rule is not needed, and perhaps the simplest mixing rule will suffice. If this is true it will be very beneficial since for a large number of components in the mixture the simpler equation can be used. Since this study evaluated only two different ternary mixtures, the above conclusion is still questionable and weak.

The generalized perturbed hard sphere equation shows comparable results with the SRK equation in predicting phase behaviour. Especially for the highly non-ideal binary mixture, the three parameter mixing rule for the hard sphere equation is superior. This is shown from the n-pentane/methanol binary mixture.

In predicting enthalpy, the generalized perturbed hard sphere equation of state produces significant improvement over the modified SRK equation. However, a perturbed hard sphere equation of state studied by Yanaki and Yesavage [1] demonstrates much better results. This is obvious since the present generalized perturbed hard sphere equation, generalizes the volume dependency by making a compromise value over various compounds. This of course allows inaccuracy in predicting the physical properties of pure components or mixtures where their optimum values of the volume dependency are away from the generalized value. Therefore, the best approach in generalizing the attractive term should be found so that the generalized perturbed hard sphere equation can consistently provide overall improvement in accuracy. It should be noted that the Soave equation does a poor job in predicting volumetric properties.

In conclusion, the perturbed hard sphere equation and its variations are able to describe accurately the phase behaviour and enthalpy of mixtures since their rigid sphere

molecular model is more effective to represent the repulsion and collision phenomena in real fluids than the kinetic theory applied by cubic equations.

## RECOMMENDATIONS

- 1). Application of the perturbed hard sphere equations of state for dealing with the phase behaviour and enthalpy predictions is recommended. A better result can be achieved by introducing mixing rule III for predicting the binary phase behaviour, and applying mixing rule II for calculating enthalpy.
- 2). More experimental data of phase behaviour for the other mixtures are needed so that the valid conclusion can be presented.
- 3). Results on evaluation of the generalized perturbed hard sphere equation are encouraging; however, referring to the previous evaluation done by Yanaki and Yesavage, the present generalized perturbed hard sphere equation does not show consistent improvement in accuracy. Therefore, a more accurate attractive term should be developed or selected.

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**APPENDIX A**  
**Mathematical Derivations**

Derivation of the fugacity coefficient for the generalized perturbed hard sphere equation of state

$$P = \frac{RT}{v} \left( \frac{1+y+y^2-y^3}{(1-y)^3} \right) - \frac{a(T)}{v^2+ubv+wb^2} \quad (1)$$

$$P = P_R + P_A \quad (2)$$

$$P_R = \frac{NRT}{V} \left( \frac{1+y+y^2-y^3}{(1-y)^3} \right) \quad (3)$$

$$P_A = - \frac{N a}{v^2+NubV+N^2wb^2} \quad (4)$$

Recall that for mixture,

$$\ln \Phi_i = \frac{1}{RT} \int_v^\infty \left[ \left( \frac{dP}{dn_i} \right)_{T,v} - \frac{RT}{v} \right] dv - \ln Z \quad (5)$$

The repulsion term,

$$\left( \frac{dP_R}{dn_i} \right)_{T,v} = \frac{NRT}{V} \frac{d}{dn_i} \left( N \cdot \frac{1+y+y^2-y^3}{(1-y)^3} \right) \quad (6)$$

applying the chain rule then,

$$\begin{aligned} \left( \frac{dP_R}{dn_i} \right)_{T,v} &= \frac{NRT}{V} \frac{d}{dn_i} \left( \frac{1+y+y^2-y^3}{(1-y)^3} \right) + \frac{RT}{V} \left( \frac{1+y+y^2-y^3}{(1-y)^3} \right) \frac{dN}{dn_i} \\ &= \frac{NRT}{V} \frac{d}{dy} \left( \frac{1+y+y^2-y^3}{(1-y)^3} \right) (dy/dn_i) \\ &\quad + \frac{RT}{V} \left( \frac{1+y+y^2-y^3}{(1-y)^3} \right) \end{aligned}$$

$$(dy/dn_i) = \frac{b}{4V}$$

$$(dP_R/dn_i) = \frac{Nb_i RT}{4V^2} \left[ \frac{1+3y}{(1-y)^2} + \frac{3(1+y+y^2-y^3)}{(1-y)^4} \right] + \frac{RT}{V} \left( \frac{1+y+y^2-y^3}{(1-y)^3} \right) \quad (7)$$

Integrate (7) with respect to V (refer to (5)) to give,

$$\begin{aligned} \ln \Phi_{i,R} = & - (\ln V - \frac{16NbV - 3N^2b^2}{16V^2 - 8NbV + N^2b^2}) \\ & + \frac{Nb_i(256V^2 - 32NbV)}{4(64V^3 - 48NbV^2 + 12N^2b^2V - N^3b^3)} \\ \ln \Phi_{i,R} = & - \ln V + \frac{16bv - 3b^2}{16v^2 - 8bv + b^2} + \frac{b_i(256v^2 - 32v)}{256v^3 - 192bv^2 + 48b^2v - b^3} \quad (8) \end{aligned}$$

The attractive term,

$$\begin{aligned} P_A = & - \frac{\sum \sum n_i n_j a_{ij}}{v^2 + uV \sum n_i b_i + (\sum n_i b_i)^2 w} \\ (dP_{i,A}/dn_i)_{T,V} = & - \frac{\sum n_k a_{ik} + \sum n_j a_{ji} + \sum \sum n_j n_k (da_{jk}/dn_i)}{v^2 + uNbV + N^2b^2 w} \\ & + \frac{\sum \sum n_i n_j a_{ij} (ub_i v + 2wb_i \sum n_j b_j)}{(v^2 + uNbV + N^2b^2 w)^2} \quad (9) \end{aligned}$$

$$a_{jk} = (a_j a_k)^{0.5} [1 - k_{jk} + (k_{jk} - k_{kj}) \frac{n_j}{N} + C/T]$$

$$(da_{jk}/dn_i) = (a_j a_k) (k_{jk} - k_{kj}) \frac{dn_j/N}{dn_i}$$

$$\frac{dn_j/N}{dn_i} = \frac{1}{N} \frac{dn_j}{dn_i} - \frac{n_j}{N^2} = (d_{ij} - x_j)/N$$

where,  $d_{ij} = 0$  for  $i \neq j$

$d_{ij} = 1$  for  $i = j$

$$\text{Let, } A = \frac{\sum n_k a_{ik} + \sum n_j a_{ji} + \sum \sum n_j n_k (da_{jk}/dn_i)}{V^2 + uNbV + N^2 b^2 w} \quad (10)$$

Integrate (9) with respect to  $V$  to give,

$$\begin{aligned} \text{Ln } \Phi_{i,A} = & \frac{A \text{Ln} \left( \frac{2v+ub-b(u^2-4w)^{0.5}}{2v+ub+b(u^2-4w)^{0.5}} \right)}{bRT(u^2-4w)^{0.5}} - \frac{ab_i v}{RT(b^3 w + bv^2 + b^2 uv)} \\ & - \frac{ab_i \text{Ln} \left( \frac{2v+ub-(u^2-4w)^{0.5}}{2v+ub+(u^2-4w)^{0.5}} \right)}{RTb^2(u^2-4w)^{0.5}} \quad (11) \end{aligned}$$

The expression of fugacity coefficient derived from the generalized perturbed hard sphere e.o.s. is,

$$\begin{aligned} \ln \Phi_i = & \frac{18bv-3b^2}{16v^2-8bv+b^2} + \frac{b_i(256v^2-32bv)}{256v^3-48bv^2+48b^2v-4b^3} \\ & + \frac{A \ln\left(\frac{2v+ub-b(u^2-4w)^{0.5}}{2v+ub+b(u^2-4w)^{0.5}}\right)}{bRT(u^2-4w)^{0.5}} - \frac{ab_i v}{RT(b^3w+bv^2+b^2uv)} \\ & - \frac{ab_i \ln\left(\frac{2v+ub-b(u^2-4w)^{0.5}}{2v+ub+b(u^2-4w)^{0.5}}\right)}{b^2RT(u^2-4w)^{0.5}} - \frac{\ln Z}{RT} \end{aligned} \quad (12)$$

For mixing rule I and II,

$$A = \sum x_k (a_{ik} + a_{ki})$$

For mixing rule III,

$$A = \sum x_k (a_{ik} + a_{ki}) + \sum \sum x_j x_k (a_j a_k)^{0.5} (k_{jk} - k_{kj}) (d_{ij} - x_j)$$

Derivation of enthalpy departure from the generalized  
perturbed hard sphere e.o.s.

Enthalpy expression,

$$H = \int_V^{\infty} [P - T(dP/dT)_V] dV + PV + \sum n_i u_i^{\circ} \quad (1)$$

where,  $u_i^{\circ} = h_i^{\circ} - RT =$  molar energy of pure  $i$   
as ideal gas at temperature  $T$ .

Rearranging (1) to give the enthalpy departure equation,

$$H - H^{\circ} = \int_V^{\infty} [P - T(dP/dT)_V] dV + PV - RT \quad (2)$$

Recall that,

$$P = \frac{RT(1+y+y^2-y^3)}{(1-y)^3} - \frac{a}{v^2+ubv+wb^2} \quad (3)$$

where,  $u = 0.2$  and  $w = -0.1$

Differentiate (3) with respect to  $T$  followed by integration with respect to  $V$ , and then substitute the result into (2) to give ;

$$H - H^{\circ} = \frac{1.5076(a-T(da/dT))}{b} \ln\left(\frac{10V-2.3168b}{10V+2.3168b}\right) + PV - RT \quad (3)$$

$a$  and  $da/dT$  are dependent of mixing rule being used.

For mixing rule I,

$$da_{ij}/dT = \frac{0.5(a_i da_j/dT + a_j da_i/dT)}{(a_i a_j)^{0.5}}$$

For mixing rule II,

$$da_{ij}/dT = \frac{0.5(a_i da_j/dT + a_j da_i/dT)}{(a_i a_j)^{0.5}} + (a_i a_j)^{0.5} B/T^2$$

For mixing rule III,

$$da_{ij}/dT = \frac{0.5(a_i da_j/dT + a_j da_i/dT)}{(a_i a_j)^{0.5}} - (a_i a_j)^{0.5} C/T^2$$

**APPENDIX B**  
**Tabulated Results**

Table B1

VLE Measurements for Tetralin/Quinoline at 523.15 K

P(KPa)	mole fraction of tetralin	
	x	y
134.60	0	0
140.60	0.041	0.087
151.00	0.102	0.188
161.30	0.180	0.304
182.60	0.326	0.469
198.60	0.457	0.590
213.80	0.589	0.785
223.50	0.691	0.879
235.60	0.826	0.879
238.80	0.888	0.924
248.00	1	1

Table B2

VLE Measurements for m-Cresol/Tetralin at 523.15 K

P(KPa)	mole fraction of m-xresol	
	x	y
246.00	0	0
254.10	0.022	0.040
261.90	0.050	0.085
265.10	0.061	0.102
270.80	0.087	0.138
285.00	0.178	0.250
289.00	0.205	0.285
300.80	0.307	0.381
306.80	0.425	0.493
313.70	0.554	0.593
315.30	0.606	0.632
318.80	0.670	0.685
318.80	0.725	0.729
318.40	0.779	0.775
317.40	0.817	0.807
316.40	0.845	0.834
314.70	0.889	0.875
312.60	0.918	0.908
311.40	0.958	0.950
308.30	0.994	0.990
308.30	1	1

Table B3

VLE Measurements for m-Cresol/Quinoline at 523.15 K

P(KPa)	mole fraction of m-cresol	
	x	y
134.60	0	0
136.20	0.049	0.058
137.90	0.123	0.143
137.80	0.145	0.174
150.00	0.325	0.435
151.60	0.339	0.459
161.10	0.412	0.563
170.70	0.471	0.639
171.00	0.471	0.648
186.10	0.560	0.762
195.10	0.595	0.786
207.00	0.643	0.831
216.19	0.668	0.858
223.30	0.703	0.880
248.39	0.791	0.927
256.10	0.811	0.943
293.29	0.946	0.987
301.10	0.969	0.995
308.29	1	1

Table B4

VLE Predictions for Tetralin/Quinoline at 523.15 K  
Using the Gen.PHS EOS with Mixing Rule III

P(KPa)	mole fraction of tetralin	
	x	y
132.36	0	0
139.17	0.041	0.088
147.99	0.102	0.191
158.99	0.180	0.307
177.08	0.326	0.475
191.95	0.457	0.598
208.41	0.589	0.709
217.12	0.691	0.788
230.58	0.826	0.883
238.81	0.888	0.926
247.78	1	1

Table B5

VLE Predictions for m-Cresol/Tetralin at 523.15 K  
Using the Gen.PHS EOS with Mixing Rule III

P(KPa)	mole fraction of m-cresol	
	x	y
247.78	0	0
252.18	0.022	0.039
257.28	0.050	0.084
259.22	0.081	0.101
263.45	0.087	0.137
276.65	0.176	0.250
280.81	0.205	0.284
291.89	0.307	0.384
302.64	0.425	0.493
310.28	0.554	0.595
312.34	0.606	0.635
314.15	0.670	0.685
314.83	0.725	0.729
314.73	0.779	0.774
314.14	0.817	0.806
313.39	0.845	0.832
311.66	0.889	0.874
309.94	0.918	0.906
307.17	0.958	0.949
303.98	0.994	0.991
303.27	1	1

Table B6

VLE Predictions for m-Cresol/Quinoline at 523.15 K  
Using the Gen.PHS EOS with Mixing Rule III

P(KPa)	mole fraction of m-cresol	
	x	y
132.36	0	0
132.87	0.049	0.057
134.86	0.123	0.146
135.86	0.145	0.177
150.87	0.325	0.443
152.83	0.339	0.466
163.51	0.412	0.571
173.76	0.471	0.648
174.58	0.471	0.654
194.35	0.560	0.761
201.20	0.595	0.790
212.97	0.643	0.832
219.95	0.668	0.854
228.34	0.703	0.877
250.32	0.791	0.926
258.06	0.811	0.937
289.95	0.946	0.986
295.77	0.969	0.992
303.25	1	1

Table B7

VLE Measurements for m-Cresol/Quinoline/Tetralin at 523 K

for P = 150 KPa

x(1)	x(2)	x(3)	y(1)	y(2)	y(3)
0	0.0987	0.9013	0	0.1850	0.8150
0.0770	0.0931	0.8299	0.0857	0.1796	0.7347
0.1650	0.0667	0.7663	0.1942	0.1372	0.6686
0.2196	0.0429	0.7375	0.2589	0.1093	0.6318
0.3210	0	0.6790	0.4305	0	0.5695

for P = 200 KPa

x(1)	x(2)	x(3)	y(1)	y(2)	y(3)
0	0.4638	0.5362	0	0.6000	0.4000
0.0940	0.3638	0.5422	0.1105	0.4888	0.4007
0.2788	0.2103	0.5109	0.3252	0.3248	0.3500
0.4596	0.0848	0.4556	0.5438	0.1552	0.3010
0.6170	0	0.3830	0.8100	0	0.1900

for P = 275 KPa

x(1)	x(2)	x(3)	y(1)	y(2)	y(3)
0.1117	0.8883	0	0.1701	0.8299	0
0.2091	0.6813	0.1096	0.3136	0.6357	0.0507
0.3216	0.5371	0.1413	0.4087	0.5303	0.0610
0.4153	0.4294	0.1553	0.4912	0.4574	0.0514
0.4888	0.3489	0.1623	0.5437	0.3973	0.0590
0.6425	0.1859	0.1716	0.7087	0.2335	0.0578
0.7765	0.0759	0.1476	0.8483	0.1028	0.0489
0.8849	0	0.1151	0.9650	0	0.0350

Table B8

VLE Predictions for m-Cresol/Quinoline/Tetralin at 523 K  
Using PHS EOS with Mixing Rule III

for P = 150 KPa

x(1)	x(2)	x(3)	y(1)	y(2)	y(3)
0	0.0817	0.9183	0	0.1676	0.8324
0.0782	0.0711	0.8507	0.0771	0.1636	0.7592
0.1635	0.0532	0.7833	0.1815	0.1375	0.6810
0.2176	0.0394	0.7430	0.2582	0.1091	0.6327
0.2921	0	0.7079	0.4034	0	0.5966

for P = 200 KPa

x(1)	x(2)	x(3)	y(1)	y(2)	y(3)
0	0.4835	0.5165	0	0.6176	0.3824
0.0969	0.3710	0.5321	0.1116	0.5231	0.3653
0.2838	0.2045	0.5117	0.3288	0.3608	0.3104
0.4616	0.0834	0.4550	0.5707	0.1829	0.2464
0.6103	0	0.3897	0.8101	0	0.1899

for P = 275 KPa

x(1)	x(2)	x(3)	y(1)	y(2)	y(3)
0.1581	0.8419	0	0.2360	0.7640	0
0.2534	0.6624	0.0841	0.3328	0.6269	0.0405
0.3395	0.5311	0.1294	0.4114	0.5319	0.0567
0.4191	0.4255	0.1553	0.4828	0.4547	0.0628
0.4844	0.3477	0.1679	0.5414	0.3948	0.0638
0.6540	0.1757	0.1702	0.7070	0.2374	0.0556
0.7838	0.0694	0.1468	0.8506	0.1067	0.0426
0.8828	0	0.1172	0.9690	0	0.0310

Table B9

Absolute Differences in Mole Fraction for Predictions  
Ternary Mixture of *m*-Cresol/Quinoline/Tetralin at 523 K  
Using PHS EOS with Mixing Rule III

for P = 150 KPa

dx(1)	dx(2)	dx(3)	dy(1)	dy(2)	dy(3)	AADX	AADY
0.0000	0.0170	0.0170	0.0000	0.0174	0.0174	0.0113	0.0116
0.0012	0.0220	0.0208	0.0086	0.0160	0.0246	0.0146	0.0164
0.0015	0.0135	0.0150	0.0127	0.0003	0.0124	0.0100	0.0085
0.0020	0.0035	0.0055	0.0007	0.0002	0.0009	0.0037	0.0006
0.0289	0.0000	0.0289	0.0271	0.0000	0.0271	0.0193	0.0181

for P = 200 KPa

0.0000	0.0197	0.0197	0.0000	0.0176	0.0176	0.0131	0.0117
0.0029	0.0072	0.0101	0.0011	0.0343	0.0350	0.0067	0.0230
0.0050	0.0056	0.0008	0.0036	0.0360	0.0396	0.0039	0.0262
0.0020	0.0014	0.0006	0.0269	0.0277	0.0546	0.0013	0.0363
0.0067	0.0000	0.0067	0.0001	0.0000	0.0001	0.0045	0.0001

for P = 275 KPa

0.0464	0.0464	0.0000	0.0659	0.0659	0.0000	0.0303	0.0439
0.0443	0.0189	0.0254	0.0190	0.0088	0.0102	0.0295	0.0127
0.0179	0.0060	0.0119	0.0027	0.0016	0.0043	0.0119	0.0029
0.0038	0.0039	0.0001	0.0088	0.0027	0.0115	0.0026	0.0077
0.0044	0.0012	0.0056	0.0023	0.0025	0.0048	0.0037	0.0032
0.0115	0.0102	0.0013	0.0017	0.0039	0.0022	0.0077	0.0026
0.0073	0.0065	0.0008	0.0023	0.0039	0.0062	0.0049	0.0041
0.0021	0.0000	0.0021	0.0040	0.0000	0.0040	0.0014	0.0027

Table B10

VLE Measurements of n-Pentane/Methanol/Acetone at 373 K  
 (1) n-Pentane, (2) Methanol, (3) Acetone.

P(KPa)	x(1)	x(2)	y(1)	y(2)
537.8	0.096	0.160	0.296	0.142
609.1	0.188	0.146	0.431	0.124
662.6	0.305	0.126	0.506	0.118
691.2	0.390	0.109	0.552	0.105
709.5	0.497	0.083	0.591	0.106
720.5	0.585	0.070	0.626	0.102
724.3	0.726	0.049	0.685	0.093
707.4	0.822	0.029	0.744	0.078
660.2	0.930	0.010	0.846	0.047
570.9	0.089	0.373	0.332	0.273
663.6	0.194	0.330	0.452	0.240
705.3	0.280	0.283	0.508	0.220
729.8	0.360	0.254	0.540	0.216
752.2	0.480	0.199	0.583	0.200
785.0	0.592	0.154	0.620	0.193
767.4	0.683	0.115	0.658	0.177
755.7	0.805	0.065	0.702	0.164
713.3	0.899	0.031	0.785	0.124
601.6	0.088	0.556	0.375	0.363
702.9	0.197	0.489	0.489	0.312
748.8	0.284	0.436	0.531	0.299
775.7	0.405	0.347	0.562	0.291
790.8	0.503	0.301	0.605	0.258
798.1	0.595	0.236	0.618	0.262
799.1	0.703	0.171	0.649	0.251
790.5	0.803	0.111	0.690	0.226
729.1	0.922	0.040	0.786	0.160
626.4	0.093	0.727	0.427	0.435
737.4	0.211	0.624	0.530	0.367
786.0	0.299	0.564	0.579	0.334
806.7	0.400	0.484	0.597	0.328
816.7	0.488	0.410	0.618	0.317
823.2	0.603	0.322	0.633	0.310
823.6	0.710	0.227	0.662	0.288
800.1	0.858	0.108	0.710	0.254
728.1	0.951	0.035	0.807	0.173

Table B11

VLE Predictions of n-Pentane/Methanol/Acetone at 373 K  
 Using PHS EOS with Mixing Rule III  
 (1) n-Pentane, (2) Methanol, (3) Acetone.

Pmeas (Kpa)	X1	X2	X3	Y1	Y2	Y3
537.80	0.1091	0.1505	0.7404	0.3243	0.1502	0.5255
609.10	0.1977	0.1341	0.6682	0.4338	0.1328	0.4334
662.60	0.3078	0.1187	0.5735	0.5093	0.1251	0.3656
691.20	0.4150	0.0986	0.4864	0.5569	0.1177	0.3254
709.50	0.5233	0.0811	0.3956	0.5963	0.1148	0.2889
720.50	0.6049	0.0733	0.3218	0.6255	0.1183	0.2562
724.30	0.7163	0.0560	0.2277	0.6727	0.1153	0.2120
707.40	0.8078	0.0330	0.1592	0.7330	0.0914	0.1756
660.20	0.9205	0.0106	0.0689	0.8527	0.0485	0.0988
570.90	0.1000	0.3517	0.5483	0.3362	0.2849	0.3789
663.60	0.1986	0.3186	0.4828	0.4584	0.2455	0.2961
705.30	0.2857	0.2756	0.4387	0.5111	0.2256	0.2633
729.80	0.3635	0.2474	0.3891	0.5421	0.2207	0.2372
752.20	0.4992	0.1902	0.3106	0.5811	0.2103	0.2086
765.00	0.6099	0.1544	0.2357	0.6123	0.2105	0.1772
767.40	0.6868	0.1266	0.1866	0.6389	0.2059	0.1552
755.70	0.7808	0.0865	0.1327	0.6860	0.1842	0.1298
713.30	0.8855	0.0427	0.0718	0.7765	0.1338	0.0897
601.60	0.1003	0.5416	0.3581	0.3714	0.3738	0.2548
702.90	0.1951	0.4883	0.3166	0.4899	0.3155	0.1946
748.80	0.2798	0.4391	0.2811	0.5386	0.2952	0.1662
775.70	0.3963	0.3602	0.2435	0.5709	0.2832	0.1459
790.80	0.5276	0.2792	0.1932	0.5947	0.2782	0.1271
798.10	0.6119	0.2347	0.1534	0.6102	0.2781	0.1117
799.10	0.7015	0.1812	0.1173	0.6355	0.2700	0.0945
790.50	0.7793	0.1345	0.0862	0.6673	0.2539	0.0788
729.10	0.9022	0.0565	0.0413	0.7748	0.1742	0.0510
626.40	0.1026	0.7209	0.1765	0.4200	0.4461	0.1339
737.40	0.1918	0.6456	0.1626	0.5303	0.3637	0.1060
786.00	0.2706	0.5995	0.1299	0.5758	0.3384	0.0858
806.70	0.3481	0.5284	0.1235	0.5966	0.3290	0.0744
816.70	0.4798	0.4158	0.1044	0.6082	0.3261	0.0657
823.20	0.6197	0.3055	0.0748	0.6205	0.3278	0.0517
823.60	0.7115	0.2406	0.0479	0.6344	0.3216	0.0440
800.10	0.8293	0.1360	0.0347	0.6860	0.2815	0.0325
728.10	0.9274	0.0575	0.0151	0.7927	0.1896	0.0177

Table B12

Absolute Mole Fraction Differences for  
n-Pentane/Methanol/Acetone at 373 K

dx1	dx2	dx2	dy1	dy2	dy3	AADX	AADY
0.0131	0.0095	0.0036	0.0283	0.0082	0.0365	0.0087	0.0243
0.0097	0.0119	0.0022	0.0028	0.0088	0.0116	0.0079	0.0077
0.0028	0.0073	0.0045	0.0033	0.0071	0.0104	0.0049	0.0069
0.0250	0.0104	0.0146	0.0049	0.0127	0.0176	0.0167	0.0117
0.0263	0.0019	0.0244	0.0053	0.0088	0.0141	0.0175	0.0094
0.0199	0.0033	0.0232	0.0005	0.0163	0.0158	0.0155	0.0109
0.0097	0.0070	0.0027	0.0123	0.0223	0.0100	0.0065	0.0149
0.0142	0.0040	0.0102	0.0110	0.0134	0.0024	0.0095	0.0089
0.0095	0.0006	0.0089	0.0067	0.0015	0.0082	0.0063	0.0055
0.0110	0.0213	0.0103	0.0042	0.0119	0.0161	0.0142	0.0107
0.0046	0.0114	0.0068	0.0064	0.0055	0.0119	0.0076	0.0079
0.0057	0.0074	0.0017	0.0031	0.0056	0.0087	0.0049	0.0058
0.0035	0.0066	0.0031	0.0021	0.0047	0.0068	0.0044	0.0045
0.0192	0.0088	0.0104	0.0019	0.0103	0.0084	0.0128	0.0069
0.0179	0.0004	0.0183	0.0077	0.0175	0.0098	0.0122	0.0117
0.0038	0.0116	0.0154	0.0191	0.0289	0.0098	0.0103	0.0193
0.0242	0.0215	0.0027	0.0160	0.0202	0.0042	0.0161	0.0135
0.0135	0.0117	0.0018	0.0085	0.0098	0.0013	0.0090	0.0065
0.0123	0.0144	0.0021	0.0036	0.0108	0.0072	0.0096	0.0072
0.0019	0.0007	0.0026	0.0009	0.0035	0.0044	0.0017	0.0029
0.0042	0.0031	0.0011	0.0076	0.0038	0.0038	0.0028	0.0051
0.0087	0.0132	0.0045	0.0089	0.0078	0.0011	0.0088	0.0059
0.0246	0.0218	0.0028	0.0103	0.0202	0.0099	0.0164	0.0135
0.0169	0.0013	0.0156	0.0078	0.0161	0.0083	0.0113	0.0107
0.0015	0.0102	0.0087	0.0135	0.0190	0.0055	0.0068	0.0127
0.0237	0.0235	0.0002	0.0227	0.0279	0.0052	0.0158	0.0186
0.0198	0.0165	0.0033	0.0112	0.0142	0.0030	0.0132	0.0095
0.0096	0.0061	0.0035	0.0070	0.0111	0.0041	0.0064	0.0074
0.0192	0.0216	0.0024	0.0003	0.0033	0.0030	0.0144	0.0022
0.0284	0.0355	0.0071	0.0032	0.0044	0.0012	0.0237	0.0029
0.0519	0.0444	0.0075	0.0004	0.0010	0.0006	0.0346	0.0007
0.0082	0.0058	0.0024	0.0098	0.0091	0.0007	0.0055	0.0065
0.0167	0.0165	0.0002	0.0125	0.0178	0.0053	0.0111	0.0119
0.0015	0.0136	0.0151	0.0276	0.0336	0.0060	0.0101	0.0224
0.0287	0.0280	0.0007	0.0240	0.0275	0.0035	0.0191	0.0183
0.0236	0.0225	0.0011	0.0143	0.0166	0.0023	0.0157	0.0111

Table B13

Enthalpy Predictions for Binary Mixture of Tetralin/Quinoline  
 Composition : Tetralin = 1/2 and Quinoline = 1/2,  
 Using PHS EOS with Mixing Rule III.

T(K)	P(Bar)	Hcalc.(KJ/Kg)	Hexp.(KJ/Kg)	%Error
369.5	2.09	124.00	123.70	0.24
387.7	2.07	155.63	159.40	-2.37
407.0	2.07	190.34	197.30	-3.53
429.6	2.06	232.54	244.60	-4.93
453.0	2.05	277.98	294.50	-5.61
473.8	2.08	319.89	336.40	-4.91
491.0	2.07	355.64	375.30	-5.24
501.8	2.06	378.59	403.00	-6.06
513.9	2.01	404.78	427.40	-5.29
520.3	2.07	484.72	505.60	-4.13
528.7	2.07	564.67	583.80	-3.28
533.1	2.07	644.61	662.00	-2.63
539.5	2.06	724.56	740.20	-2.11
545.3	2.06	797.18	811.10	-1.72
550.8	2.10	807.74	823.10	-1.87
564.3	2.04	834.28	846.50	-1.44
584.3	2.08	874.81	885.10	-1.16
599.2	2.10	904.58	919.60	-1.63
614.9	2.07	937.24	952.40	-1.59
631.9	2.09	973.15	988.10	-1.51

Average error over the liquid phase = 4.24 %

Average error over the vapor phase = 1.56 %

Table B14

Enthalpy Predictions for Binary Mixture of Tetralin/Quinoline  
 Composition : Tetralin = 1/2 and Quinoline = 1/2,  
 Using Mod.SRK EOS with Mixing Rule III.

T(K)	P(Bar)	Hcalc.(KJ/Kg)	Hexp.(KJ/Kg)	%Error
369.5	2.09	142.48	123.70	15.18
387.7	2.07	176.83	159.40	10.93
407.0	2.07	213.99	197.30	8.46
429.6	2.08	258.56	244.60	5.71
453.0	2.05	306.02	294.50	3.91
473.8	2.08	349.38	338.40	3.86
491.0	2.07	386.10	375.30	2.88
501.8	2.08	409.58	403.00	1.63
513.9	2.01	436.27	427.40	2.08
520.3	2.07	515.63	505.60	1.98
526.7	2.07	594.99	583.80	1.92
533.1	2.06	674.36	662.00	1.87
539.5	2.07	753.72	740.20	1.83
545.3	2.06	825.64	811.10	1.79
550.8	2.10	836.22	823.10	1.59
564.3	2.04	862.86	846.50	1.93
584.3	2.08	903.47	885.10	2.08
599.2	2.10	933.31	919.60	1.49
614.9	2.07	966.05	952.40	1.43
631.9	2.09	1002.02	988.10	1.41

Average error over the liquid phase = 6.07 %

Average error over the vapor phase = 1.68 %

Table B15

Enthalpy Predictions for Binary Mixture of m-Cresol/Quinoline  
 Composition : m-Cresol = 1/2 and Quinoline = 1/2,  
 Using PHS EOS with Mixing Rule III

T(K)	P(Bar)	Hcalc.(KJ/Kg)	Hexp.(KJ/Kg)	%Error
445.5	2.07	288.76	302.10	-4.42
448.4	2.07	290.62	301.90	-3.73
490.2	2.03	384.01	409.00	-6.11
505.5	2.00	417.92	459.50	-9.05
507.4	2.16	422.18	463.70	-8.95
514.7	2.09	438.65	478.50	-7.94
521.8	2.14	454.83	501.80	-9.36
524.3	2.09	460.56	505.20	-8.84
525.4	2.07	463.09	515.40	-10.15
530.4	2.07	543.30	601.30	-9.65
535.4	2.07	632.21	687.20	-8.00
540.4	2.07	721.26	773.00	-6.69
545.4	2.07	811.17	858.90	-5.56
550.4	2.10	916.89	944.80	-2.95
562.7	2.14	939.69	965.70	-2.69
570.5	2.14	954.37	979.30	-2.55
584.0	2.14	980.09	1017.70	-3.70
596.4	2.21	1003.93	1043.20	-3.76
606.3	2.21	1023.28	1055.70	-3.07
614.0	2.10	1038.65	1073.30	-3.23

Average error over the liquid phase = 7.62 %

Average error over the vapor phase = 3.14 %

Table B16

Enthalpy Predictions for Binary Mixture of m-Cresol/Quinoline  
 Composition : m-Cresol = 1/2 and Quinoline = 1/2,  
 Using Mod.SRK EOS with Mixing Rule III

T(K)	P(Bar)	Hcalc.(KJ/Kg)	Hexp.(KJ/Kg)	%Error
445.5	2.07	328.90	302.10	8.21
448.4	2.07	325.42	301.90	7.79
490.2	2.03	439.51	409.00	7.46
505.5	2.00	493.12	459.50	7.31
507.4	2.18	494.11	463.70	6.58
514.7	2.09	497.75	478.50	4.46
521.8	2.14	524.59	501.80	4.54
524.3	2.09	522.09	505.20	3.34
525.4	2.07	533.44	515.40	3.50
530.4	2.07	621.48	601.30	3.36
535.4	2.07	709.70	687.20	3.27
540.4	2.07	798.00	773.00	3.23
545.4	2.07	886.46	858.90	3.21
550.4	2.10	978.93	944.80	3.61
562.7	2.14	999.69	965.70	3.52
570.5	2.14	1011.63	979.30	3.30
584.0	2.14	1057.59	1017.70	3.92
596.4	2.21	1075.96	1043.20	3.14
606.3	2.21	1087.36	1055.70	3.00
614.0	2.10	1106.57	1073.30	3.10

Average error over the liquid phase = 6.96 %

Average error over the vapor phase = 3.37 %

Table B17

Enthalpy Predictions for Binary Mixture of m-Cresol/Tetralin  
 Composition : m-Cresol = 1/2 and Tetralin = 1/2,  
 Using PHS EOS with Mixing Rule III

T(K)	P(Bar)	Hcalc.(KJ/Kg)	Hexp.(KJ/Kg)	%Error
387.8	2.07	181.97	195.20	-6.78
412.2	2.06	232.59	248.80	-6.51
432.5	2.09	276.22	296.70	-6.90
452.2	2.04	319.89	343.10	-6.77
470.6	2.10	361.90	390.60	-7.35
475.6	2.09	373.52	394.60	-5.34
477.7	2.07	378.43	400.30	-5.46
483.3	2.07	391.67	432.00	-9.35
491.0	2.07	467.41	504.50	-7.35
498.6	2.07	542.37	576.90	-5.99
506.3	2.07	618.35	649.40	-4.78
514.0	2.07	692.36	721.90	-4.09
521.6	2.07	767.28	794.30	-3.40
529.3	2.07	849.69	866.80	-1.97
542.3	2.07	875.52	890.70	-1.70
561.6	2.07	914.69	926.90	-1.32
580.0	2.07	952.91	963.20	-1.07
594.5	2.07	983.62	993.00	-0.94
607.4	2.06	1011.39	1022.40	-1.08
621.0	2.07	1041.05	1056.40	-1.45
632.1	2.06	1065.59	1077.60	-1.11
643.5	2.07	1091.04	1100.50	-0.86
658.6	2.07	1120.67	1142.40	-1.90

Average error over the liquid phase = 6.81 %

Average error over the vapor phase = 1.34 %

Table B18

Enthalpy Predictions for Binary Mixture of m-Cresol/Tetralin  
 Composition : m-Cresol = 1/2 and Tetralin = 1/2,  
 Using Mod.SRK EOS with Mixing Rule III

T(K)	P(Bar)	Hcalc.(KJ/Kg)	Hexp.(KJ/Kg)	%Error
387.8	2.07	216.04	195.20	10.68
412.2	2.06	270.96	248.80	8.91
432.5	2.09	317.32	296.70	6.95
452.2	2.04	363.03	343.10	5.81
470.6	2.10	406.46	390.60	4.06
475.6	2.09	418.40	394.60	6.03
477.7	2.07	423.43	400.30	5.78
483.3	2.07	436.91	432.00	1.14
491.0	2.07	508.00	504.50	0.69
498.6	2.07	581.03	576.90	0.72
506.3	2.07	655.67	649.40	0.97
514.0	2.07	730.58	721.90	1.20
521.6	2.07	806.69	794.30	1.56
529.3	2.07	890.91	866.80	2.78
542.3	2.07	916.83	890.70	2.93
561.6	2.07	956.12	926.90	3.15
580.0	2.07	994.46	963.20	3.25
594.5	2.07	1025.24	993.00	3.25
607.4	2.06	1053.07	1022.40	3.00
621.0	2.07	1082.79	1056.40	2.50
632.1	2.06	1107.38	1077.60	2.76
643.5	2.07	1132.87	1100.50	2.94
656.6	2.07	1162.55	1142.40	1.76

Average error over the liquid phase = 6.17 %

Average error over the vapor phase = 2.83 %

Table B19

Enthalpy Predictions for Ternary Mixture of  
 m-Cresol = 1/3, Quinoline = 1/3, and Tetralin = 1/3,  
 Using PHS EOS with Mixing Rule = III

T(K)	P(Bar)	Hcalc.(KJ/Kg)	Hexp.(KJ/Kg)	%Error
363.0	2.14	123.57	116.36	6.20
364.1	2.12	125.55	130.21	-3.58
369.9	2.06	136.30	134.40	1.41
378.9	2.12	152.97	157.98	-3.17
390.5	2.09	174.98	186.59	-6.22
411.4	2.07	215.56	227.30	-5.16
411.5	2.14	215.62	229.35	-5.99
434.5	2.07	261.77	280.20	-6.58
457.0	2.07	308.63	326.58	-5.50
478.2	2.06	354.24	383.08	-7.53
487.7	2.09	375.02	403.91	-7.15
489.2	2.10	378.33	407.91	-7.25
497.3	2.07	396.46	429.44	-7.68
509.3	2.08	423.77	457.16	-7.30
514.7	2.07	501.47	541.40	-7.38
520.1	2.07	583.86	625.60	-6.67
525.6	2.07	667.94	711.60	-6.14
530.8	2.07	748.65	794.13	-5.73
536.2	2.07	855.80	878.37	-2.57
550.6	2.08	883.37	908.38	-2.75
566.1	2.07	913.84	938.38	-2.41
566.3	2.09	914.04	938.41	-2.60
584.1	2.05	949.71	976.73	-2.77
589.5	2.06	960.67	984.26	-2.40
600.4	2.07	982.93	1015.28	-3.19
614.8	2.08	1012.82	1041.81	-2.78
621.0	2.08	1025.70	1047.34	-2.07
628.7	2.08	1041.84	1068.56	-2.50
632.6	2.08	1050.20	1074.11	-2.23
637.3	2.07	1060.27	1087.49	-2.50
639.1	2.07	1064.09	1085.68	-1.99
639.2	2.08	1064.36	1092.75	-2.60
650.5	2.08	1088.56	1113.59	-2.25
650.7	2.06	1089.11	1117.98	-2.58
655.5	2.06	1099.54	1121.48	-1.96
662.8	2.08	1115.28	1146.74	-2.74
665.8	2.05	1121.88	1141.63	-1.73

Average error over the liquid phase = 5.77 %

Average error over the vapor phase = 2.45 %

Table B20

Enthalpy Predictions for Ternary Mixture of  
 m-Cresol = 1/3, Quinoline = 1/3, and Tetralin = 1/3,  
 Using Mod.SRK EOS with Mixing Rule = III

T(K)	P(Bar)	Hcalc.(KJ/Kg)	Hexp.(KJ/Kg)	%Error
363.0	2.14	148.50	116.36	27.62
364.1	2.12	150.73	130.21	15.76
369.9	2.06	162.82	134.40	21.15
378.9	2.12	181.40	157.98	14.83
390.5	2.09	205.65	186.59	10.21
411.4	2.07	249.65	227.30	9.83
411.5	2.14	249.72	229.35	8.88
434.5	2.07	298.87	280.20	6.66
457.0	2.07	348.02	328.58	6.57
478.2	2.06	395.28	383.08	3.18
487.7	2.09	416.65	403.91	3.15
489.2	2.10	420.05	407.91	2.98
497.3	2.07	438.61	429.44	2.14
509.3	2.08	466.46	457.16	2.04
514.7	2.07	564.30	541.40	4.23
520.1	2.07	636.72	625.60	1.78
525.6	2.07	709.98	711.60	-0.23
530.8	2.07	777.44	794.10	-2.10
536.2	2.07	880.39	878.37	0.23
550.6	2.08	908.06	908.38	-0.04
566.1	2.07	938.62	936.38	0.24
566.3	2.09	938.81	938.41	0.04
584.1	2.05	974.60	976.73	-0.22
589.5	2.06	985.58	984.26	0.13
600.4	2.07	1007.89	1015.28	-0.73
614.8	2.08	1037.84	1041.81	-0.38
621.0	2.08	1050.75	1047.34	0.33
628.7	2.08	1066.92	1068.56	-0.15
632.6	2.08	1075.29	1074.11	0.11
637.3	2.07	1085.39	1087.49	-0.19
639.1	2.07	1089.21	1085.68	0.32
639.2	2.08	1089.48	1092.75	-0.30
650.5	2.08	1113.72	1113.59	0.01
650.7	2.06	1114.28	1117.98	-0.33
655.5	2.06	1124.72	1121.48	0.29
662.8	2.08	1140.48	1146.74	-0.55
665.8	2.05	1147.10	1141.63	0.48

Average error over the liquid phase = 9.01 %

Average error over the vapor phase = 0.27 %

**APPENDIX C**  
**Computer Programs**

This program calculates the binary interaction parameters for the perturbed hard sphere e.o.s. using the maximum likelihood method with the following mixing rule :

$$\begin{aligned} b &= \text{SUM}(xi \ bi) \\ a &= \text{SUM}(xi \ xj \ aij) \\ aij &= \text{SQRT}(ai \ aj)(1-kij+(kij-kji)xi+C/T) \end{aligned}$$

PARAMETER NN =72, KK = 2, LL = 3, NK =NN\*KK  
 IMPLICIT REAL\*8 (A-H,P-Z)  
 CHARACTER\*40 FILN1,FILN2,FILN3,FILN4,FILN5,FILN6,FILN7,  
 1FILN8,FILN9,FILN10,FILN11,COMPOUND

REAL\*8 YM(NN),XM(NK),PAR(LL),EVX(NK),EVY(NN),EVXSQ(NK),  
 1EVYSQ(NN),EVXD(NK,NK),EVYD(NN,NN),EVXDI(NK,NK),DFX(NN,  
 1NK),DFP(NN,LL),DFXT(NK,NN),DFPT(LL,NN),DELXM(NK),DELYM(  
 1NN),DUM(NK,NN),DUM1(NK,NK),DUM2(NK,NN),DUM3(NK,NK),AAPD  
 1(NN),DUM4(NK,NK),D(NK,NK),RDUM(NK,NN),RDUM1(NK,LL),RDUM2  
 1(NK,NN),RDUM3(NK,LL),R(NK,LL),RT(LL,NK),TDUM(LL,NN),TDUM1  
 1(LL,LL),TDUM2(LL,NN),TDUM3(LL,LL),T(LL,LL),UDUM(LL,1),  
 1UDUM1(LL,1),U(LL,1),QDUM(NK,1),QDUM1(NK,1),QDUM2(NK,1),  
 1Q(NK,1),D1UM(LL,NK),D2UM(LL,LL),D3UM(LL,LL),D4UM(LL,1),  
 1D5UM(LL,1),DELPN(LL),D6UM(NK,1),D7UM(NK,1),DELXN(NK),  
 1XR(NK),YR(NN),ZM(NN),EVZ(NN),EVZSQ(NN),EVZD(NN,NN),DGX(  
 1NN,NK),DGP(NN,LL),DGXT(NK,NN),DGPT(LL,NN),ZR(NN),  
 1DELZM(NN),CDFX(NN,NK),CDFP(NN,LL),CDGX(NN,NK),CDGP(NN,LL)  
 1,CDGZ(NN,NN),CDFY(NN,NN),CDGY(NN,NN),CDFZI(NN,NN),  
 1AAI(NN,NN),UUUI(NN,NN),DELZN(NN),DELYN(NN),DFR(NN),  
 1CDFYI(NN,NN),FR(NN),GR(NN),AA1(NN,NN),AA2(NN,NN),  
 1AA4(NN,NN),AA5(NN,NN),AA6(NN,1),AA7(NN,1),AA8(NN,1),  
 1AA9(NN,NN),AA10(NN,NK),AA11(NN,NK),AA12(NN,NN),  
 1AA14(NN,LL),AAO(NN,NN),AA15(NN,1),AA16(NN,1),AA17(NN,1)  
 1,AA18(NN,1),AA19(NN,NK),AA20(NN,NK),AA21(NN,NK),  
 1AA23(NN,LL),AA24(NN,LL),DELY1(NN,1),DELY2(NN,1),  
 1ZZZ1(NN,1),BBB1(NN,1),BBB2(NN,1),BBB(NN,1),YYY(NN,1),  
 1XXX(NN,1),ZZZ(NN,1),PART(LL),XRT(NK),ZRT(NN),YRT(NN),  
 1QDUM3(NK,1),CDFZ(NN,NN),AA(NN,NN),DGR(NN),AA3(NN,NN),  
 1AA13(NN,LL),AA22(NN,LL),DELY3(NN,1)

ITMX=5000

TYPE\*, ' '

TYPE\*, ' -----CAUTION----- '

TYPE\*, 'If the number of data points times the number of '  
 TYPE\*, 'the independent variables exceeds 150, change the '  
 TYPE\*, 'MATRIX DIMENSIONS in the subroutine SYMINV.'

TYPE\*, ' '

TYPE\*, 'Type the mixture name.'

READ(5,1)COMPOUND

TYPE\*, ' '

TYPE\*, 'Input the tolerance limit'

```

ACCEPT*,SSTL
TYPE*,
TYPE*, 'Input the filename containing the dep. variable Y'
TYPE*, '(pressure)'
READ(5,1)FILN1
TYPE*,
TYPE*, 'Input the filename containing the dep. variable Z'
TYPE*, '(mol.fractions of component 1 in the vapor phase).'
READ(5,1)FILN9
TYPE*,
TYPE*, 'Input the filename containing the indep. variables'
TYPE*, '(temperatures and mol.fractions of comp.1 in the'
TYPE*, 'liquid phase).'
READ(5,1)FILN2
TYPE*,
TYPE*, 'Input the filename containing parameter estimates'
READ(5,1)FILN3
TYPE*,
TYPE*, 'Input the filename containing the variances for the'
TYPE*, 'independent variables (T and X).'
READ(5,1)FILN4
TYPE*,
TYPE*, 'Input the filename containing the variances for the'
TYPE*, 'dependent variable Y (pressure).'
READ(5,1)FILN5
TYPE*,
TYPE*, 'Input the filename containing the variances for the'
TYPE*, 'dependent variable Z (mol.fraction of component 1'
TYPE*, 'in the vapor phase).'
READ(5,1)FILN10
TYPE*,
TYPE*, 'Input Tc1(K), Pc1(Bar), Omega1, Omega01, and Rp1'
ACCEPT*,TC1,PC1,ACCN1,W01,RP1
TYPE*,
TYPE*, 'Input Tc2(K), Pc2(Bar), Omega2, Omega02, and Rp2'
ACCEPT*,TC2,PC2,ACCN2,W02,RP2
21 TYPE*,
TYPE*, 'Input the limiting factor.'
ACCEPT*,V
IT=0

OPEN(UNIT=10,FILE=FILN1,STATUS='OLD')
OPEN(UNIT=20,FILE=FILN2,STATUS='OLD')
OPEN(UNIT=30,FILE=FILN3,STATUS='OLD')
OPEN(UNIT=40,FILE=FILN4,STATUS='OLD')
OPEN(UNIT=50,FILE=FILN5,STATUS='OLD')
OPEN(UNIT=90,FILE=FILN9,STATUS='OLD')
OPEN(UNIT=100,FILE=FILN10,STATUS='OLD')

```

C Read in dependent variables Y and Z

```
      READ(10,*,END=99) (YM(I),I=1,NN)
99  READ(90,*,END=101) (ZM(I),I=1,NN)
```

C Convert the unit of pressure from kpa to bar

```
101 DO I=1,NN
      YM(I)=YM(I)/100
      ENDDO
```

C Read in independent variables T and X

```
      READ(20,*,END=102) (XM(I),I=1,NK)
```

C Read in parameter estimates

```
102 READ(30,*,END=103) (PAR(I),I=1,LL)
```

C Read in variances for independent variables

```
103 READ(40,*,END=104) (EVX(I),I=1,NK)
```

C Read in variances for dependent variable Y and Z

```
104 READ(50,*,END=105) (EVY(I),I=1,NN)
105 READ(100,*,END=106) (EVZ(I),I=1,NN)
```

C Set initial true values to measured values

```
106 DO 10 I=1,NN
      YR(I)=YM(I)
      ZR(I)=ZM(I)
10  CONTINUE
      DO 20 I=1,NK
      XR(I)=XM(I)
20  CONTINUE
```

C Square and invert variances EVX and EVY, create diagonal C matrices

```
      DO 30 I=1,NK
      EVXSQ(I)=1./EVX(I)**2
30  CONTINUE
      DO 40 I=1,NN
      EVYSQ(I)=1./EVY(I)**2
      EVZSQ(I)=1./EVZ(I)**2
40  CONTINUE
      CALL DIAG(EVXSQ,NK,EVXD)
```

```
CALL DIAG(EVYSQ,NN,EVYD)
CALL DIAG(EVZSQ,NN,EVZD)
```

C Calculate the inverse of EVXD

```
CALL DIAGINV(NK,NK,EVXD,EVXDI)
```

C Calculate functions and derivatives

```
150 IT=IT+1
```

```
CALL FUNC(XR,PAR,YR,ZR,NN,LL,KK,NK,TC1,TC2,FR,GR,PC1,PC2,
1 ACCN1,ACCN2,RP1,RP2,CDFX,CDFP,CDGX,CDGP,CDFZ,CDGZ,
1 CDFY,CDGY,IT)
```

```
IF(IT.EQ.1)THEN
```

```
CALL SUM(SSQ,XR,YR,ZR,EVXSQ,EVYSQ,EVZSQ,YM,XM,ZM,NN,
1 NK,LL,KK)
```

```
ELSE
CONTINUE
ENDIF
```

C Calculate the groups of derivatives given in ANDERSON's  
C article as small f and small g

C For the derivatives of f the inverted term is AAI  
C (CDGY - CDGZ\*CDFZI\*CDFY)\*\*-1

```
151 CALL DIAGINV(NN,NN,CDFZ,CDFZI)
CALL MATMULT(CDGZ,CDFZI,AA,NN,NN,NN)
CALL MATMULT(AA,CDFY,AA3,NN,NN,NN)
CALL MATSUB(CDGY,AA3,AA4,NN,NN)
CALL DIAGINV(NN,NN,AA4,AAI)
```

C Calculate fr (DFR)

```
CALL MATMULT(CDGZ,CDFZI,AA5,NN,NN,NN)
CALL MATMULT(AA5,FR,AA6,NN,NN,1)
CALL MATSUB(GR,AA6,AA7,NN,1)
CALL MATMULT(AAI,AA7,AA8,NN,NN,1)
CALL MATSUB(YR,AA8,DFR,NN,1)
```

C Calculate fx (DFX)

```
CALL MATMULT(CDGZ,CDFZI,AA9,NN,NN,NN)
CALL MATMULT(AA9,CDFX,AA10,NN,NN,NK)
CALL MATSUB(CDGX,AA10,AA11,NN,NK)
CALL MATMULT(AAI,AA11,DFX,NN,NN,NK)
```

CALL NEG(DFX,DFX,NN,NK)

C Calculate f theta (DFP)

CALL MATMULT(CDGZ,CDFZI,AA12,NN,NN,NN)  
 CALL MATMULT(AA12,CDFP,AA13,NN,NN,LL)  
 CALL MATSUB(CDGP,AA13,AA14,NN,LL)  
 CALL MATMULT(AAI,AA14,DFP,NN,NN,LL)  
 CALL NEG(DFP,DFP,NN,LL)

C Calculate derivatives of function G.

C For the derivatives of G the inverted term is matrix UUII

C (CDGZ - CDGY\*CDFYI\*CDFZ)\*\*-1

CALL DIAGINV(NN,NN,CDFY,CDFYI)  
 CALL MATMULT(CDFYI,CDFZ,AAO,NN,NN,NN)  
 CALL MATMULT(CDGY,AAO,AA1,NN,NN,NN)  
 CALL MATSUB(CDGZ,AA1,AA2,NN,NN)  
 CALL DIAGINV(NN,NN,AA2,UUII)

C Calculate gr (DGR)

CALL MATMULT(CDFYI,FR,AA15,NN,NN,1)  
 CALL MATMULT(CDGY,AA15,AA16,NN,NN,1)  
 CALL MATSUB(GR,AA16,AA17,NN,1)  
 CALL MATMULT(UUII,AA17,AA18,NN,NN,1)  
 CALL MATSUB(ZR,AA18,DGR,NN,1)

C Calculate gx (DGX)

CALL MATMULT(CDFYI,CDFX,AA19,NN,NN,NK)  
 CALL MATMULT(CDGY,AA19,AA20,NN,NN,NK)  
 CALL MATSUB(CDGX,AA20,AA21,NN,NK)  
 CALL MATMULT(UUII,AA21,DGX,NN,NN,NK)  
 CALL NEG(DGX,DGX,NN,NK)

C Calculate gtheta (DGP)

CALL MATMULT(CDFYI,CDFP,AA22,NN,NN,LL)  
 CALL MATMULT(CDGY,AA22,AA23,NN,NN,LL)  
 CALL MATSUB(CDGP,AA23,AA24,NN,LL)  
 CALL MATMULT(UUII,AA24,DGP,NN,NN,LL)  
 CALL NEG(DGP,DGP,NN,LL)

C Calculate transpose of derivatives

CALL TRANS(DFX,DFXT,NN,NK)  
 CALL TRANS(DGX,DGXT,NN,NK)  
 CALL TRANS(DFP,DFPT,NN,LL)

```
CALL TRANS(DGP,DGPT,NN,LL)
```

```
C Calculate DELXM and DELYM
```

```
DO 90 I=1,NN
    DELYM(I)=(YR(I)-YM(I))
    DELZM(I)=(ZR(I)-ZM(I))
90 CONTINUE
DO 100 I=1,NK
    DELXM(I)=XR(I)-XM(I)
100 CONTINUE
```

```
C Calculate matrix D
```

```
CALL MATMULT(DFXT,EVYD,DUM,NK,NN,NN)
CALL MATMULT(DUM,DFX,DUM1,NK,NN,NK)
CALL MATMULT(DGXT,EVZD,DUM2,NK,NN,NN)
CALL MATMULT(DUM2,DGX,DUM3,NK,NN,NK)
CALL MATADD(EVXD,DUM1,DUM4,NK,NK)
CALL MATADD(DUM4,DUM3,D,NK,NK)
```

```
C Invert matrix D
```

```
CALL SYMINV (D,NK,IRR)
```

```
C Calculate matrix R
```

```
CALL MATMULT (DFXT,EVYD,RDUM,NK,NN,NN)
CALL MATMULT(RDUM,DFP,RDUM1,NK,NN,LL)
CALL MATMULT(DGXT,EVZD,RDUM2,NK,NN,NN)
CALL MATMULT(RDUM2,DGP,RDUM3,NK,NN,LL)
CALL MATADD(RDUM1,RDUM3,R,NK,LL)
CALL TRANS(R,RT,NK,LL)
```

```
C Calculate matrix T
```

```
CALL MATMULT(DFPT,EVYD,TDUM,LL,NN,NN)
CALL MATMULT(TDUM,DFP,TDUM1,LL,NN,LL)
CALL MATMULT(DGPT,EVZD,TDUM2,LL,NN,NN)
CALL MATMULT(TDUM2,DGP,TDUM3,LL,NN,LL)
CALL MATADD(TDUM1,TDUM3,T,LL,LL)
```

```
C Calculate matrix U
```

```
CALL MATMULT(TDUM,DELYM,UDUM,LL,NN,1)
CALL MATMULT(TDUM2,DELZM,UDUM1,LL,NN,1)
CALL MATADD(UDUM,UDUM1,U,LL,1)
```

```
C Calculate matrix Q
```

```

CALL MATMULT(EVXD,DELXM,QDUM,NK,NK,1)
CALL MATMULT(RDUM,DELYM,QDUM1,NK,NN,1)
CALL MATMULT(RDUM2,DELZM,QDUM2,NK,NN,1)
CALL MATADD(QDUM,QDUM1,QDUM3,NK,1)
CALL MATADD(QDUM3,QDUM2,Q,NK,1)

```

C Calculate DELPN

```

CALL MATMULT(RT,D,D1UM,LL,NK,NK)
CALL MATMULT(D1UM,R,D2UM,LL,NK,LL)
CALL MATSUB(T,D2UM,D3UM,LL,LL)
CALL SYMINV(D3UM,LL,IRR)
CALL MATMULT(D1UM,Q,D4UM,LL,NK,1)
CALL MATSUB(U,D4UM,D5UM,LL,1)
CALL MATMULT(D3UM,D5UM,DELPN,LL,LL,1)
CALL NEG(DELPN,DELPN,LL,1)

```

C Calculate DELXN

```

CALL MATMULT(R,DELPN,D6UM,NK,LL,1)
CALL MATADD(Q,D6UM,D7UM,NK,1)
CALL MATMULT(D,D7UM,DELXN,NK,NK,1)
CALL NEG(DELXN,DELXN,NK,1)

```

C Calculate new estimates of parameters, X, Y, and Z

```

DO 120 I=1,LL
    PAR(I)=V*DELPN(I) +PAR(I)
    TYPE*, 'PAR', PAR(I)
120 CONTINUE
DO 130 I=1,NK
    XR(I)=V*DELXN(I) + XR(I)
130 CONTINUE

```

C Calculate DELZN

```

CALL MATSUB(DGR,ZR,YYY,NN,1)
CALL MATMULT(DGP,DELPN,XXX,NN,LL,1)
CALL MATMULT(DGX,DELXN,ZZZ,NN,NK,1)
CALL MATADD(YYY,ZZZ,ZZZ1,NN,1)
CALL MATADD(ZZZ1,XXX,DELZN,NN,1)

```

C Calculate DELYN

```

CALL MATSUB(DFR,YR,BBB,NN,1)
CALL MATMULT(DFP,DELPN,BBB1,NN,LL,1)
CALL MATMULT(DFX,DELXN,BBB2,NN,NK,1)
CALL MATADD(BBB,BBB1,DELY1,NN,1)
CALL MATADD(DELY1,BBB2,DELYN,NN,1)

```

```

DO 140 I=1,NN

```

```

                ZR(I)=V*DELZN(I) + ZR(I)
                YR(I)=V*DELYN(I) + YR(I)
140  CONTINUE

        CALL SUM(SSQN,XR,YR,ZR,EVXSQ,EVYSQ,EVZSQ,YM,XM,ZM,NN,
        1NK,LL,KK)

        DIFF=(SSQ-SSQN)/SSQN
        TYPE*, 'DIFF',DIFF
        TYPE*, 'SSQ,SSQN',SSQ,SSQN
        IF(IT.EQ.5)THEN
                IF(DIFF.LT.0)THEN
                        TYPE*, ' '
                        TYPE*, 'REINPUT THE SMALLER VALUE.....!'
                        GOTO 21
                ENDIF
                TYPE*, ' '
                TYPE*, 'Reinput the limiting factor.'
                ACCEPT*,V
        ENDIF
        IF(ABS(DIFF).LT.SSTL)GO TO 200
        SSQ=SSQN
        IF(IT.LT.ITMX)GO TO 150
        TYPE*, 'NUMBER OF INTERATIONS GREATER THAN 5000'
        GO TO 200
200  S=SSQ/(NN-LL)
        TYPE*, ' '
        TYPE*, 'Type the name of file for the output.'
        READ(5,1)FILN6
        OPEN(UNIT=60,FILE=FILN6,STATUS='NEW')
        WRITE(60,3)COMPOUND
        WRITE(60,4)PAR(1)
        WRITE(60,5)PAR(2)
        WRITE(60,6)PAR(3)
        WRITE(60,7)S
        WRITE(60,8)
        WRITE(60,9)
        WRITE(60,11)
        DO I=1,NN
                AAPD(I)=ABS(100*((YR(I)-YM(I))/YM(I)))
                YM(I)=YM(I)*100
                YR(I)=YR(I)*100
        ENDDO
        WRITE(60,12)XM(2*I-1),XR(2*I-1),YM(I),YR(I),XM(2*I),
        1XR(2*I),ZM(I),ZR(I),AAPD(I)
        ENDDO
        WRITE(60,13)
1  FORMAT(A40)

```

```

3  FORMAT(1X,A40)
4  FORMAT(/,1X,'K12 = ',F12.6)
5  FORMAT(1X,'K21 = ',F12.6)
6  FORMAT(1X,'C   = ',F12.6)
7  FORMAT(1X,'S   = ',F12.6)
8  FORMAT(/,1X,'Tmeas',4X,'Tcalc',4X,'Pmeas',4X,'Pcalc',4X,
1  'Xmeas',3X,'Xcalc',3X,'Ymeas',3X,'Ycalc',3X,'APDP')
9  FORMAT(2X,'(K)',6X,'(K)',5X,'(Kpa)',4X,'(Kpa)',12X,
1  '(Component 1)')
11 FORMAT(1X,'-----',3X,'-----',3X,'-----',3X,'-----',3X,
1  '-----',3X,'-----',3X,'-----',3X,'-----')
12 FORMAT(F7.2,2X,F7.2,2X,F7.2,2X,F7.2,2X,F6.3,2X,F6.3,2X,
1  F6.3,2X,F6.3,2X,F6.3)
13 FORMAT(////,1X,
1  'APDP : Absolute percent deviation of pressure')
1000 STOP
1000 STOP

```

```

SUBROUTINE TRANS(W,WT,N,K)
REAL*8 W(N,K),WT(K,N)
DO 121 I=1,N
DO 122 J=1,K
WT(J,I)=W(I,J)
122 CONTINUE
121 CONTINUE
END

```

```

SUBROUTINE NEG(S,SN,N,K)
REAL*8 S(N,K),SN(N,K)
DO 10 I=1,N
DO 20 J=1,K
SN(I,J)=-S(I,J)
20 CONTINUE
10 CONTINUE
RETURN
END

```

```
SUBROUTINE MULT(S,N,K,C)
REAL*8 S(N,K)
DO 10 I=1,N
    DO 20 J=1,K
        S(I,J)=C*S(I,J)
20    CONTINUE
10 CONTINUE
RETURN
END
```

```
SUBROUTINE DIAG(S,N,W)
REAL*8 W(N,N),S(N)
DO 11 I=1,N
    DO 21 J=1,N
        IF (J.EQ.I) THEN
            W(I,J)=S(I)
        ELSE
            W(I,J)=0
        ENDIF
21    CONTINUE
11 CONTINUE
RETURN
END
```

```
SUBROUTINE DIAGINV(N,K,W,WI)
REAL*8 W(N,K),WI(N,K)
DO 31 I=1,N
    DO 41 J=1,K
        IF (J.EQ.I) THEN
            WI(I,J)=1./W(I,J)
        ELSE
            WI(I,J)=0
        ENDIF
41    CONTINUE
31 CONTINUE
RETURN
END
```

```
SUBROUTINE MATMULT(A,U,T,M,N,P)
INTEGER P
REAL*8 T(M,P),A(M,N),U(N,P)

DO 10 I=1,M
    DO 20 KKJ=1,P
        T(I,KKJ)=0
20    CONTINUE
10 CONTINUE
DO 30 I=1,M
    DO 40 KKJ=1,P
        DO 50 K=1,N
            T(I,KKJ)=A(I,K)*U(K,KKJ)+T(I,KKJ)
50        CONTINUE
40    CONTINUE
30 CONTINUE
RETURN
END
```

```
SUBROUTINE MATADD(A,B,C,M,N)
REAL*8 A(M,N),B(M,N),C(M,N)

DO 10 I=1,M
    DO 20 J=1,N
        C(I,J)=A(I,J)+B(I,J)
20    CONTINUE
10 CONTINUE
RETURN
END
```

END

```
SUBROUTINE MATSUB(A,B,C,M,N)
REAL*8 A(M,N),B(M,N),C(M,N)
```

```

      DO 10 I=1,M
          DO 20 J=1,N
              C(I,J)=A(I,J)-B(I,J)
20          CONTINUE
10 CONTINUE
   RETURN
   END

```

SUBROUTINE SYMINV(A,N,IRR)

```

IMPLICIT REAL*8 (A-H,P,Q,S-Z)
REAL*8 A(N,N),P(200),Q(200)
INTEGER R(200)

```

```

   IRR=0
   DO 10 I=1,N
10  R(I)=1
      DO 150 I=1,N
          BIG=0.
          DO 40 J=1,N
              TEST=ABS(A(J,J))
              IF (TEST-BIG) 40,40,20
20          IF (R(J)) 160,40,30
30          BIG=TEST
              K=J
40          CONTINUE
              IF(BIG.LT.1.E-19) GO TO 160
              R(K)=0
              Q(K)=1./A(K,K)
              P(K)=1.
              A(K,K)=0.0
              KP1=K+1
              KM1=K-1
              IF(KM1) 160,80,50
50          DO 70 J=1,KM1
              P(J)=A(J,K)
              Q(J)=A(J,K)*Q(K)
              IF(R(J)) 160,70,80
60          Q(J)=-Q(J)
70          A(J,K)=0.
80          IF(K=N)90,130,160
90          DO 120 J=KP1,N
              P(J)=A(K,J)

```

```

      IF (R(J)) 160,100,110
100 P(J)=-P(J)
110 Q(J)=-A(K,J)*Q(K)
120 A(K,J)=0.
130 DO 140 J=1,N
      DO 140 K=J,N
      A(J,K)=A(J,K)+P(J)*Q(K)
140 A(K,J)=A(J,K)
150 CONTINUE
      RETURN
160 IRR=1
      RETURN
      END

```

```

SUBROUTINE SUM(SSQ1,XR1,YR1,ZR1,EVXSQ1,EVYSQ1,EVZSQ1,
1YM1,XM1,ZM1,NN1,NK1,LL1,KK1)

```

```

      IMPLICIT REAL*8 (A-H,P-Z)
      REAL*8 XR1(NK1),YR1(NN1),EVXSQ1(NK1),EVYSQ1(NN1),YM1(NN1
1),XM1(NK1),ZR1(NN1),EVZSQ1(NN1),ZM1(NN1)

```

```

      SSQ1=0
      DO 10 I=1,NK1
      SSQ1=SSQ1+(XR1(I)-XM1(I))**2*EVXSQ1(I)
10 CONTINUE
      DO 20 I=1,NN1
      SSQ1=SSQ1+(YR1(I)-YM1(I))**2*EVYSQ1(I)
      SSQ1=SSQ1+(ZR1(I)-ZM1(I))**2*EVZSQ1(I)
20 CONTINUE
      RETURN
      END

```

```

SUBROUTINE FUNC(XR1,PAR1,YR1,ZR1,NN1,LL1,KK1,NK1,TC1,
1TC2,FR,GR,PC1,PC2,ACCN1,ACCN2,RP1,RP2,DFX,DFP,DGX,DGP,
1DFZ,DGZ,DFY,DGY,IT)

```

```

      PARAMETER C=.48,R=.0831434

```

```

      IMPLICIT REAL*8 (A-H,M,P-Z)
      REAL*8 XR1(NK1),PAR1(LL1),YR1(NN1),DFX(NN1,NK1),DFP(NN1,
1LL1),ZR1(NN1),DGX(NN1,NK1),DGP(NN1,LL1),DFY(NN1,NN1),DGY
1(NN1,NN1),DGZ(NN1,NN1),DFZ(NN1,NN1),FR(NN1),GR(NN1)

```

```

      DO 30 I=1,NN1

```

C Calculate the reduced temperatures

```

XRT=XR1(2*I-1)
XRX=XR1(2*I)
XR2=1-XRX
ZRZ=ZR1(I)
ZR2=1-ZRZ
TR1=XRT/TC1
TR2=XRT/TC2

```

```

IF(IT.EQ.1)THEN

```

```

CALL INITGUESS(XRT,XR2,XRX,ZRZ,ZR2,PAR1,YR1(I),TC1,TC2,PC1,
1PC2,ACCN1,ACCN2,RP1,RP2)

```

```

XR1(2*I)=XRX
ZR1(I)=ZRZ
ELSE
CONTINUE
ENDIF

```

C Calculate the functions F and G

```

CALL FUGC(XRT,XR2,XRX,ZRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,
1PC1,PC2,ACCN1,ACCN2,RP1,RP2,
1FUGV1I,FUGV2I,FUGL1I,FUGL2I,PAR1(2),PAR1(3))

```

```

FR(I)=XRX*FUGL1I-ZRZ*FUGV1I
GR(I)=XR2*FUGL2I-ZR2*FUGV2I

```

C Calculate the derivatives wrt parameters (currently set  
C for 1 parameter)

```

DO 44 J=1,LL1
IF(J.EQ.1)THEN
DPAR=PAR1(1)*.998
CALL FUGC(XRT,XR2,XRX,ZRZ,ZR2,DPAR,YR1(I),TC1,TC2,PC1,PC2,
1ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,PAR1(2),
1PAR1(3))

```

```

F2N=XRX*FUGL1-FUGV1*ZRZ
G2N=XR2*FUGL2-FUGV2*ZR2
DPAR=PAR1(1)*.999

```

```

CALL FUGC(XRT,XR2,XRX,ZRZ,ZR2,DPAR,YR1(I),TC1,TC2,PC1,PC2,
1ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,PAR1(2),
1PAR1(3))
F1N=XRX*FUGL1-FUGV1*ZRZ
G1N=XR2*FUGL2-FUGV2*ZR2

```

DPAR=PAR1(1)\*1.001

CALL FUGC(XRT, XR2, XRX, ZRZ, ZR2, DPAR, YR1(I), TC1, TC2, PC1, PC2,  
1ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2, PAR1(2),  
1PAR1(3))

F1=XR2\*FUGL1-FUGV1\*ZRZ  
G1=XR2\*FUGL2-FUGV2\*ZR2  
DPAR=PAR1(1)\*1.002

CALL FUGC(XRT, XR2, XRX, ZRZ, ZR2, DPAR, YR1(I), TC1, TC2, PC1, PC2,  
1ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2, PAR1(2),  
1PAR1(3))

F2=XR2\*FUGL1-FUGV1\*ZRZ  
G2=XR2\*FUGL2-FUGV2\*ZR2  
DFP(I, J)=(2\*F2N - 16\*F1N + 16\*F1 - 2\*F2)/(24\*PAR1(1)\*.001)  
DGP(I, J)=(2\*G2N - 16\*G1N + 16\*G1 - 2\*G2)/(24\*PAR1(1)\*.001)  
ELSE

C Derivative wrt second parameter

IF(J.EQ.2)THEN  
DPAR=PAR1(2)\*.998

CALL FUGC(XRT, XR2, XRX, ZRZ, ZR2, PAR1(1), YR1(I), TC1, TC2, PC1,  
1PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2, DPAR,  
1PAR1(3))

F2N=XR2\*FUGL1-FUGV1\*ZRZ  
G2N=XR2\*FUGL2-FUGV2\*ZR2  
DPAR=PAR1(2)\*.999  
CALL FUGC(XRT, XR2, XRX, ZRZ, ZR2, PAR1(1), YR1(I), TC1, TC2, PC1,  
1PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2, DPAR,  
1PAR1(3))

F1N=XR2\*FUGL1-FUGV1\*ZRZ  
G1N=XR2\*FUGL2-FUGV2\*ZR2  
DPAR=PAR1(2)\*1.001

CALL FUGC(XRT, XR2, XRX, ZRZ, ZR2, PAR1(1), YR1(I), TC1, TC2, PC1,  
1PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2, DPAR,  
1PAR1(3))

F1=XR2\*FUGL1-FUGV1\*ZRZ  
G1=XR2\*FUGL2-FUGV2\*ZR2  
DPAR=PAR1(2)\*1.002  
CALL FUGC(XRT, XR2, XRX, ZRZ, ZR2, PAR1(1), YR1(I), TC1, TC2, PC1,  
1PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2, DPAR,

1PAR1(3))

```

F2=XRX*FUGL1-FUGV1*ZRZ
G2=XR2*FUGL2-FUGV2*ZR2
DFP(I,J)=(2*F2N -16*F1N + 16*F1 - 2*F2)/(24*PAR1(2)*.001)
DGP(I,J)=(2*G2N -16*G1N + 16*G1 - 2*G2)/(24*PAR1(2)*.001)
ELSE

```

C Derivative wrt third parameter

```

DPAR=PAR1(3)*.998
CALL FUGC(XRT,XR2,XRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,PC1,
1PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,PAR1(2),
1DPAR)

```

```

F2N=XRX*FUGL1-FUGV1*ZRZ
G2N=XR2*FUGL2-FUGV2*ZR2
DPAR=PAR1(3)*.999

```

```

CALL FUGC(XRT,XR2,XRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,PC1,
1PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,PAR1(2),
1DPAR)

```

```

F1N=XRX*FUGL1-FUGV1*ZRZ
G1N=XR2*FUGL2-FUGV2*ZR2
DPAR=PAR1(3)*1.001

```

```

CALL FUGC(XRT,XR2,XRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,PC1,
1PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,PAR1(2),
1DPAR)

```

```

F1=XRX*FUGL1-FUGV1*ZRZ
G1=XR2*FUGL2-FUGV2*ZR2
DPAR=PAR1(3)*1.002

```

```

CALL FUGC(XRT,XR2,XRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,PC1,
1PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,PAR1(2),
1DPAR)

```

```

F2=XRX*FUGL1-FUGV1*ZRZ
G2=XR2*FUGL2-FUGV2*ZR2
DFP(I,J)=(2*F2N-16*F1N + 16*F1 - 2*F2)/(24*PAR1(3)*.001)
DGP(I,J)=(2*G2N-16*G1N + 16*G1 - 2*G2)/(24*PAR1(3)*.001)
ENDIF
ENDIF

```

44 CONTINUE

C Input the derivative of the func. wrt the ind.variables.  
C Put into an NN by NK matrix with the elements on the diag.

```

DO 38 J=1,NK1
      DFX(I,J)=0
      DGX(I,J)=0
38 CONTINUE
DO 40 J=1,NK1
  IF (J.EQ.(2*I-1)) THEN

```

C Calculate the derivative of the fugacity coef. wrt temp.

```
DXRT=XRT-.02
```

```
CALL FUGC(DXRT,XR2,XRX,ZRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,
1PC1,PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,
1PAR1(2),PAR1(3))
```

```
FT2N=XRX*FUGL1-FUGV1*ZRZ
GT2N=XR2*FUGL2-FUGV2*ZR2
DXRT=XRT-.01
```

```
CALL FUGC(DXRT,XR2,XRX,ZRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,
1PC1,PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,
1PAR1(2),PAR1(3))
```

```
FT1N=XRX*FUGL1-FUGV1*ZRZ
GT1N=XR2*FUGL2-FUGV2*ZR2
DXRT=XRT+.01
```

```
CALL FUGC(DXRT,XR2,XRX,ZRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,
1PC1,PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,
1PAR1(2),PAR1(3))
```

```
FT1=XRX*FUGL1-FUGV1*ZRZ
GT1=XR2*FUGL2-FUGV2*ZR2
DXRT=XRT+.02
```

```
CALL FUGC(DXRT,XR2,XRX,ZRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,
1PC1,PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,
1PAR1(2),PAR1(3))
```

```
FT2=XRX*FUGL1-FUGV1*ZRZ
GT2=XR2*FUGL2-FUGV2*ZR2
DFX(I,J)=(2*FT2N - 16*FT1N + 16*FT1 - 2*FT2)/(24*.01)
DGX(I,J)=(2*GT2N - 16*GT1N + 16*GT1 - 2*GT2)/(24*.01)
IF(XRX.LT..9998)THEN
DXRX=XRX*.998
DXR2=1-DXRX
```

```
CALL FUGC(XRT,DXR2,DXRX,ZRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,
```

1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2,  
1PAR1(2), PAR1(3))

FX2N=DXRX\*FUGL1-FUGV1\*ZRZ  
GX2N=DXR2\*FUGL2-FUGV2\*ZR2  
DXRX=XRX\*.999  
DXR2=1-DXR2

CALL FUGC(XRT, DXR2, DXRX, ZRZ, ZR2, PAR1(1), YR1(I), TC1, TC2,  
1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2,  
1PAR1(2), PAR1(3))

FX1N=DXRX\*FUGL1-FUGV1\*ZRZ  
GX1N=DXR2\*FUGL2-FUGV2\*ZR2  
DXRX=XRX\*1.001  
DXR2=1-DXR2

CALL FUGC(XRT, DXR2, DXRX, ZRZ, ZR2, PAR1(1), YR1(I), TC1, TC2,  
1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2,  
1PAR1(2), PAR1(3))

FX1=DXRX\*FUGL1-FUGV1\*ZRZ  
GX1=DXR2\*FUGL2-FUGV2\*ZR2  
DXRX=XRX\*1.002  
DXR2=1-DXR2

CALL FUGC(XRT, DXR2, DXRX, ZRZ, ZR2, PAR1(1), YR1(I), TC1, TC2,  
1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2,  
1PAR1(2), PAR1(3))

FX2=DXRX\*FUGL1-FUGV1\*ZRZ  
GX2=DXR2\*FUGL2-FUGV2\*ZR2  
DFX(I, J+1)=(2\*FX2N - 16\*FX1N + 16\*FX1 - 2\*FX2)/(24\*XRX\*  
1.001)  
DGX(I, J+1)=(2\*GX2N - 16\*GX1N + 16\*GX1 - 2\*GX2)/(24\*XRX\*  
1.001)

ELSE  
DXRX=XRX\*.9998  
DXR2=1-DXR2

CALL FUGC(XRT, DXR2, DXRX, ZRZ, ZR2, PAR1(1), YR1(I), TC1, TC2,  
1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2,  
1PAR1(2), PAR1(3))

FX2N=DXRX\*FUGL1-FUGV1\*ZRZ  
GX2N=DXR2\*FUGL2-FUGV2\*ZR2  
DXRX=XRX\*.9999  
DXR2=1-DXR2

CALL FUGC(XRT, DXR2, DXRX, ZRZ, ZR2, PAR1(1), YR1(I), TC1, TC2,

```
1PC1,PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,
1PAR1(2),PAR1(3))
```

```
FX1N=DXRX*FUGL1-FUGV1*ZRZ
GX1N=DXR2*FUGL2-FUGV2*ZR2
DXRX=XR2*1.0001
DXR2=1-DXRX
```

```
CALL FUGC(XRT,DXR2,DXRX,ZRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,
1PC1,PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,
1PAR1(2),PAR1(3))
```

```
FX1=DXRX*FUGL1-FUGV1*ZRZ
GX1=DXR2*FUGL2-FUGV2*ZR2
DXRX=XR2*1.0002
DXR2=1-DXRX
```

```
CALL FUGC(XRT,DXR2,DXRX,ZRZ,ZR2,PAR1(1),YR1(I),TC1,TC2,
1PC1,PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,
1PAR1(2),PAR1(3))
```

```
FX2=DXRX*FUGL1-FUGV1*ZRZ
GX2=DXR2*FUGL2-FUGV2*ZR2
DFX(I,J+1)=(2*FX2N - 16*FX1N + 16*FX1 - 2*FX2)/(24*XR2*
1.0001)
DGX(I,J+1)=(2*GX2N - 16*GX1N + 16*GX1 - 2*GX2)/(24*XR2*
1.0001)
ENDIF
ELSE
CONTINUE
ENDIF
```

```
40 CONTINUE
```

```
C Derivatives wrt pressure
```

```
DO 41 J=1,NN1
IF(J.EQ.I)THEN
P=YR1(I)*.998
```

```
CALL FUGC(XRT,XR2,XR2,ZRZ,ZR2,PAR1(1),P,TC1,TC2,PC1,PC2,
1ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,PAR1(2),PAR1
1(3))
```

```
FP2N=XR2*FUGL1-FUGV1*ZRZ
GP2N=XR2*FUGL2-FUGV2*ZR2
P=YR1(I)*.999
```

```
CALL FUGC(XRT,XR2,XR2,ZRZ,ZR2,PAR1(1),P,TC1,TC2,PC1,PC2,
1ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,PAR1(2),PAR1
1(3))
```

```

FP1N=XR1*FUGL1-FUGV1*ZRZ
GP1N=XR2*FUGL2-FUGV2*ZR2
P=YR1(I)*1.001

```

```

CALL FUGC(XRT, XR2, XR1, ZRZ, ZR2, PAR1(1), P, TC1, TC2, PC1, PC2,
1ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2, PAR1(2), PAR1
1(3))

```

```

FP1=XR1*FUGL1-FUGV1*ZRZ
GP1=XR2*FUGL2-FUGV2*ZR2
P=YR1(I)*1.002

```

```

CALL FUGC(XRT, XR2, XR1, ZRZ, ZR2, PAR1(1), P, TC1, TC2, PC1, PC2,
1ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2, PAR1(2), PAR1
1(3))

```

```

FP2=XR1*FUGL1-FUGV1*ZRZ
GP2=XR2*FUGL2-FUGV2*ZR2
DFY(I, J)=(2*FP2N - 16*FP1N + 16*FP1 - 2*FP2)/(24*YR1(I)*
1.0001)
DGY(I, J)=(2*GP2N - 16*GP1N + 16*GP1 - 2*GP2)/(24*YR1(I)*
1.0001)

```

#### C Derivative wrt vapor composition

```

IF(ZRZ.LT..9998)THEN
Z=ZRZ*.998
Z2=1-Z

```

```

CALL FUGC(XRT, XR2, XR1, Z, Z2, PAR1(1), YR1(I), TC1, TC2,
1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2,
1PAR1(2), PAR1(3))

```

```

FZ2N=XR1*FUGL1-FUGV1*Z
GZ2N=XR2*FUGL2-FUGV2*Z2
Z=ZRZ*.999
Z2=1-Z

```

```

CALL FUGC(XRT, XR2, XR1, Z, Z2, PAR1(1), YR1(I), TC1, TC2,
1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2
1, PAR1(2), PAR1(3))

```

```

FZ1N=XR1*FUGL1-FUGV1*Z
GZ1N=XR2*FUGL2-FUGV2*Z2
Z=ZRZ*1.001
Z2=1-Z

```

```

CALL FUGC(XRT, XR2, XR1, Z, Z2, PAR1(1), YR1(I), TC1, TC2,
1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2
1, PAR1(2), PAR1(3))

```

FZ1=XRX\*FUGL1-FUGV1\*Z  
 GZ1=XR2\*FUGL2-FUGV2\*Z2  
 Z=ZRZ\*1.002  
 Z2=1-Z

CALL FUGC(XRT, XR2, XRX, Z, Z2, PAR1(1), YR1(I), TC1, TC2,  
 1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2  
 1, PAR1(2), PAR1(3))

FZ2=XRX\*FUGL1-FUGV1\*Z  
 GZ2=XR2\*FUGL2-FUGV2\*Z2  
 DFZ(I, J)=(2\*FZ2N - 16\*FZ1N + 16\*FZ1 - 2\*FZ2)/(24\*ZRZ\*  
 1.0001)  
 DGZ(I, J)=(2\*GZ2N - 16\*GZ1N + 16\*GZ1 - 2\*GZ2)/(24\*ZRZ\*  
 1.0001)  
 ELSE  
 Z=ZRZ\*.9998  
 Z2=1-Z

CALL FUGC(XRT, XR2, XRX, Z, Z2, PAR1(1), YR1(I), TC1, TC2,  
 1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2  
 1, PAR1(2), PAR1(3))

FZ2N=XRX\*FUGL1-FUGV1\*Z  
 GZ2N=XR2\*FUGL2-FUGV2\*Z2  
 Z=ZRZ\*.9999  
 Z2=1-Z

CALL FUGC(XRT, XR2, XRX, Z, Z2, PAR1(1), YR1(I), TC1, TC2,  
 1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2  
 1, PAR1(2), PAR1(3))

FZ1N=XRX\*FUGL1-FUGV1\*Z  
 GZ1N=XR2\*FUGL2-FUGV2\*Z2  
 Z=ZRZ\*1.0001  
 Z2=1-Z

CALL FUGC(XRT, XR2, XRX, Z, Z2, PAR1(1), YR1(I), TC1, TC2,  
 1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2,  
 1PAR1(2), PAR1(3))

FZ1=XRX\*FUGL1-FUGV1\*Z  
 GZ1=XR2\*FUGL2-FUGV2\*Z2  
 Z=ZRZ\*1.0002  
 Z2=1-Z

CALL FUGC(XRT, XR2, XRX, Z, Z2, PAR1(1), YR1(I), TC1, TC2,  
 1PC1, PC2, ACCN1, ACCN2, RP1, RP2, FUGV1, FUGV2, FUGL1, FUGL2,

```

1PAR1(2),PAR1(3))

  FZ2=XR2*FUGL1-FUGV1*Z
  GZ2=XR2*FUGL2-FUGV2*Z2
  DFZ(I,J)=(2*FZ2N - 16*FZ1N + 16*FZ1 - 2*FZ2)/(24*ZRZ*
1.0001)
  DGZ(I,J)=(2*GZ2N - 16*GZ1N + 16*GZ1 - 2*GZ2)/(24*ZRZ*
1.0001)
  ENDIF
  ELSE
  DFZ(I,J)=0
  DGZ(I,J)=0
  DFY(I,J)=0
  DGY(I,J)=0
  ENDIF
41 CONTINUE
30 CONTINUE

  RETURN
  END

SUBROUTINE INITGUESS(XRT,XR2,XRX,ZRZ,ZR2,PAR,POLD,TC1,TC2,
1PC1,PC2,ACCN1,ACCN2,RP1,RP2)

  PARAMETER C=.48,R=.0831434
  IMPLICIT REAL*8 (A-H,M,P-Z)
  REAL*8 PAR(3)

  IT=0
29 IT=IT+1
  ZR2=1-ZRZ

  CALL FUGC(XRT,XR2,XRX,ZRZ,ZR2,PAR(1),POLD,TC1,TC2,
1PC1,PC2,ACCN1,ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,
1PAR(2),PAR(3))

  FR=XR2*FUGL1 - ZR2*FUGV1
  GR=XR2*FUGL2 - ZR2*FUGV2
  IF(ZR2.GT..75)THEN
  ZRZN=1-(FUGL2*XR2/FUGV2)
  PNEW=((POLD*FUGL1*XR2)/(FUGV1*ZRZN))*0.025 + .975*POLD
  ELSE
  ZRZN=FUGL1*XR2/FUGV1
  PNEW=(POLD*FUGL2*XR2/(FUGV2*(1-ZRZN)))*0.05 + .95*POLD
  ENDIF

```

```

      IF(ZRZN.GT.1)THEN
      ZRZN=1.0
      GO TO 1001
      ENDIF
      IF((ABS(FR).LT..00001.AND.ABS(GR).LT..00001).AND.(PNEW-POLD
1.001 POLD=PNEW
      ZRZ=ZRZN
      GO TO 1000
      ELSE
      POLD=PNEW
      ZRZ=ZRZN
      IF(IT.GE.500)THEN
      TYPE*, 'ITERATIONS GREATER THAN 500 FOR P,Y1',PNEW,ZRZ
      GO TO 1000
      ELSE
      GO TO 29
      ENDIF
      ENDIF
1000 RETURN
      END

```

```

SUBROUTINE FUGC(T,X2,X,Z,Z2,GAMMA,P,TC1,TC2,PC1,PC2,ACCN1,
1ACCN2,RP1,RP2,FUGV1,FUGV2,FUGL1,FUGL2,C12,C21)

```

```

C This subroutine calculates the fugacity coefficients of
C each components in the vapor phase and in the liquid
C phase.

```

```

PARAMETER CC=0.48,R=.0831434,UU=.2,WW=-.1,E=.6633
IMPLICIT DOUBLE PRECISION (A-H,P-Z)

```

```

C Calculate the reduced temperatures and pressures

```

```

TR1=T/TC1
TR2=T/TC2
PR1=P/PC1
PR2=P/PC2

```

```

C Calculate the critical parameters of the pure components
C and alpha parameters.

```

```

SMB1=(0.17091*R*TC1)/PC1
SMB2=(0.17091*R*TC2)/PC2

```

```

SMAC1=0.49897*R**2*TC1**2/PC1
SMAC2=0.49897*R**2*TC2**2/PC2

```

ALPHAS1=1.-0.244797\*(1.-TR1)+0.16047\*(1.-TR1\*\*2.7)  
 ALPHAS2=1.-0.244797\*(1.-TR2)+0.16047\*(1.-TR2\*\*2.7)

CCC1=0.00632+1.13094\*ACCN1-0.03116\*ACCN1\*\*2  
 CCC2=0.00632+1.13094\*ACCN2-0.03116\*ACCN2\*\*2

DDD1=-0.02312+0.26654\*ACCN1-0.28888\*ACCN1\*\*2  
 DDD2=-0.02312+0.26654\*ACCN2-0.28888\*ACCN2\*\*2

ALPHAN1=1.+CCC1\*(1.-TR1)+DDD1\*(1.-TR1)\*\*2  
 ALPHAN2=1.+CCC2\*(1.-TR2)+DDD2\*(1.-TR2)\*\*2

ALPHAP1=1.+RP1\*(DEXP(-RP1\*\*CC)-DEXP(-(RP1\*TC1/T)\*\*CC))  
 ALPHAP2=1.+RP2\*(DEXP(-RP2\*\*CC)-DEXP(-(RP2\*TC2/T)\*\*CC))

SMA1=SMAC1\*ALPHAS1\*ALPHAN1\*ALPHAP1  
 SMA2=SMAC2\*ALPHAS2\*ALPHAN2\*ALPHAP2

C Calculate the mixture parameter of the liquid phase

A12=((SMA1\*SMA2)\*\*0.5)\*(1.-GAMMA+(GAMMA-C12)\*X+C21/T)  
 A21=((SMA2\*SMA1)\*\*0.5)\*(1.-C12+(C12-GAMMA)\*X2+C21/T)  
 AMIX=X\*\*2\*SMA1+X2\*\*2\*SMA2+X\*X2\*A12+X2\*X\*A21  
 BMIX=X\*SMB1+X2\*SMB2

C Calculate the fugacity coefficients in the liquid phase

CALL LVOL(P,T,VL,AMIX,BMIX)

AIM1=2\*X\*SMA1+X2\*(A12+A21)+X\*X2\*(SMA1\*SMA2)\*\*.5\*(GAMMA  
 1-C12)\*(1-X)+X2\*X\*(SMA2\*SMA1)\*\*.5\*(C12-GAMMA)\*(-X2)  
 F=DLOG((2\*VL-E\*BMIX+UU\*BMIX)/(2\*VL+E\*BMIX+UU\*BMIX))

FUGL1=(16\*BMIX\*VL-3\*BMIX\*\*2)/(16\*VL\*\*2-8\*BMIX\*VL+BMIX\*\*2)+  
 1SMB1\*(256\*VL\*\*2-32\*BMIX\*VL)/(4\*(64\*VL\*\*3-48\*BMIX\*VL\*\*2+12\*  
 1BMIX\*\*2\*VL-BMIX\*\*3))+  
 1AIM1\*F/(BMIX\*R\*T\*E)-AMIX\*SMB1/(R\*T)\*(VL/(WW\*BMIX\*\*3+BMIX\*  
 1VL\*\*2+UU\*VL\*BMIX\*\*2)+F/(BMIX\*\*2\*E))  
 1-DLOG((P\*VL)/(R\*T))  
 FUGL1=DEXP(FUGL1)

AIM2=2\*X2\*SMA2+X\*(A12+A21)+X2\*X\*(SMA1\*SMA2)\*\*.5\*(C12  
 1-GAMMA)\*(-X2)+X\*X2\*(SMA2\*SMA1)\*\*.5\*(GAMMA-C12)\*(1-X2)

FUGL2=(16\*BMIX\*VL-3\*BMIX\*\*2)/(16\*VL\*\*2-8\*BMIX\*VL+BMIX\*\*2)  
 1+SMB2\*(256\*VL\*\*2-32\*BMIX\*VL)/(4\*(64\*VL\*\*3-48\*BMIX\*VL\*\*2+12\*  
 1BMIX\*\*2\*VL-BMIX\*\*3))+  
 1AIM2\*F/(BMIX\*R\*T\*E)-AMIX\*SMB2/(R\*T)\*(VL/(WW\*BMIX\*\*3+BMIX\*  
 1VL\*\*2+UU\*VL\*BMIX\*\*2)+F/(BMIX\*\*2\*E))

```
1-DLOG((P*VL)/(R*T))
FUGL2=DEXP(FUGL2)
```

C Calculate the mixture parameter of the vapour phase

```
AV12=((SMA1*SMA2)**0.5)*(1.-GAMMA+(GAMMA-C12)*Z+C21/T)
AV21=((SMA2*SMA1)**0.5)*(1.-C12+(C12-GAMMA)*Z2+C21/T)
AVIX=Z**2*SMA1+Z2**2*SMA2+Z*Z2*A12+Z2*Z*A21
BVIX=Z*SMB1+Z2*SMB2
```

C Calculate the fugacity coefficients in the vapour phase

```
CALL VVOL(P,T,VV,AVIX,BVIX)

AIV1=2*Z*SMA1+Z2*(AV12+AV21)+Z*Z2*(SMA1*SMA2)**.5*(GAMMA
1-C12)*(1-Z)+Z2*Z*(SMA2*SMA1)**.5*(C12-GAMMA)*(-Z2)
F=DLOG((2*VV-E*BVIX+UU*BVIX)/(2*VV+E*BVIX+UU*BVIX))

FUGV1=(16*BVIX*VV-3*BVIX**2)/(16*VV**2-8*BVIX*VV+BVIX**2)+
1SMB1/4*(256*VV**2-32*BVIX*VV)/(64*VV**3-48*BVIX*VV**2+12*
1BVIX**2*VV-BVIX**3)+
1AIV1*F/(BVIX*R*T*E)-AVIX*SMB1/(R*T)*(VV/(WW*BVIX**3+BVIX*
1VV**2+UU*VV*BVIX**2)+F/(BVIX**2*E))
1-DLOG((P*VV)/(R*T))
FUGV1=DEXP(FUGV1)

AIV2=2*Z2*SMA2+Z*(AV12+AV21)+Z2*Z*(SMA1*SMA2)**.5*(C12
1-GAMMA)*(-Z2)+Z*Z2*(SMA2*SMA1)**.5*(GAMMA-C12)*(1-Z2)

FUGV2=(16*BVIX*VV-3*BVIX**2)/(16*VV**2-8*BVIX*VV+BVIX**2)+
1SMB2/4*(256*VV**2-32*BVIX*VV)/(64*VV**3-48*BVIX*VV**2+12*
1BVIX**2*VV-BVIX**3)+
1AIV2*F/(BVIX*R*T*E)-AVIX*SMB2/(R*T)*(VV/(WW*BVIX**3+BVIX*
1VV**2+UU*VV*BVIX**2)+F/(BVIX**2*E))
1-DLOG((P*VV)/(R*T))
FUGV2=DEXP(FUGV2)
RETURN
END
```

```
SUBROUTINE LVOL(P,T,VL,AMIX,BMIX)
```

```
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
PARAMETER R=.0831434
```

```

      B=BMIX
      A=AMIX
      V=1.05*B/4
      ITER=0
10  IF (ITER.GT.500) THEN
          WRITE(*,100)
          STOP
      END IF
      FV = -(64*R*T*V**3+16*B*R*T*V**2+4*B**2*R*T*V-B**3*R*T)/
1/((64*V**4-48*B*V**3+12*B**2*V**2-B**3*V)+A/(V**2+0.2*B*V
1-0.1*B**2))+P
      DFDV=-((192*R*T*V**2+32*B*R*T*V+4*B**2*R*T)/(64*V**4-48*B
1*V**3+12*B**2*V**2-B**3*V)+(256*V**3-144*B*V**2+24*B**2*V
1-B**3)*(64*R*T*V**3+16*B*R*T*V**2+4*B**2*R*T*V-B**3*R*T)/
1((64*V**4-48*B*V**3+12*B**2*V**2-B**3*V)**2-A*(2*V+0.2*B)/
1(V**2+0.2*B*V-0.1*B**2)**2
      ITER=ITER+1
      VNEW=V-FV/DFDV
      DEV=(V-VNEW)/V
      IF (DABS(DEV).GT.0.0001) THEN
          V=VNEW
          GOTO 10
      END IF
      IF (DABS(FV).GT.0.0001) THEN
          V=VNEW
          GOTO 10
      END IF
      IF (VNEW.LE.0.0) THEN
          WRITE(*,220)
          STOP
      END IF
      VL=VNEW
      RETURN
100 FORMAT(5X,'ITERATION EXCEEDS 500')
220 FORMAT(5X,'Zero or negative liquid volume')
      END

```

```

SUBROUTINE VVOL (P,T,VV,AVIX,BVIX)

```

```

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
PARAMETER R=.0831434

```

```

A=AVIX

```

```

B=BVIX
AA=A*P/(R**2)/(T**2)
BB=B*P/R/T
ITERV=0
Z=1
10 IF (ITERV.GT.500) THEN
    WRITE(*,20)
    STOP
END IF
T5 = -(11*BB+20)/20.0
T4 = -(5*BB**2+36*BB-80*AA)/80.0
T3 = (31*BB**3-4*BB**2-240*AA*BB)/320.0
T2 = -(7*BB**4-9*BB**3-60*AA*BB**2)/320.0
T1 = (BB**5+6*BB**4-10*AA*BB**3)/640.0
T0 = -BB**5/640.0
FZ = Z**6+T5*Z**5+T4*Z**4+T3*Z**3+T2*Z**2+T1*Z+T0
DFDZ = 6*Z**5+5*T5*Z**4+4*T4*Z**3+3*T3*Z**2+2*T2*Z+T1
ITERV=ITERV+1
ZNEW=Z-FZ/DFDZ
DEL=Z-ZNEW
IF (DABS(DEL).GT.0.0001) THEN
    Z=ZNEW
    GO TO 10
END IF
IF (DABS(FZ).GT.0.0001) THEN
    Z=ZNEW
    GO TO 10
END IF
IF (ZNEW.LE.0.0) THEN
    WRITE(*,240)
    STOP
END IF
VV=ZNEW*R*T/P
RETURN
20 FORMAT (5X,'ITERATION EXCEEDS 500')
240 FORMAT(5X,'Zero or negative vapor volume')
END

```

C This program executes ternary flash calculation for  
C known T and P usis the perturbed hardsphere equation of  
C state (re.to K. Mulia's study)

IMPLICIT DOUBLE PRECISION (A-H,K,P-Z)  
CHARACTER\*40 NAMAMU,NAMAKU  
R=0.08314

C Component 1 : M-CRESOL  
C Component 2 : QUINOLINE  
C Component 3 : TETRALIN

TYPE\*, ' '  
TYPE\*, 'Type the filename the data'  
READ(5,1)NAMAMU  
TYPE\*, ' '  
TYPE\*, 'Type the filename the output'  
READ(5,1)NAMAKU  
TYPE\*, ' '  
TYPE\*, 'Input the number of data'  
ACCEPT\*,N

OPEN(1,FILE=NAMAMU,STATUS='OLD')  
OPEN(2,FILE=NAMAKU,STATUS='NEW')

WRITE(2,3)  
WRITE(2,8)  
WRITE(2,9)  
WRITE(2,11)

C Critial properties : Tc(K), Pc(Bar)

PC1 = 45.60  
PC2 = 57.75  
PC3 = 35.15  
TC1 = 705.80  
TC2 = 800.20  
TC3 = 719.20  
W1 = 0.454  
W2 = 0.318  
W3 = 0.327  
O1 = 0.449  
O2 = 0.22  
O3 = 0.31  
RP1 = 0  
RP2 = 63.08  
RP3 = 0.058

C Interaction parameters

51 TYPE\*, ' '

```

TYPE*, 'Select the following mixing rules :'
TYPE*, '
TYPE*, '      1.  $a_{ij} = \text{SQRT}(a_i a_j)(1-k_{ij})'$ 
TYPE*, '      2.  $a_{ij} = \text{SQRT}(a_i a_j)(1-A-B/T)'$ 
TYPE*, '      3.  $a_{ij} = \text{SQRT}(a_i a_j)(1-k_{ij}+(k_{ij}-k_{ji})x_i+C/T)'$ 
ACCEPT*, MIX

```

```

IF(MIX.EQ.1)THEN
  KP13 = .022501
  KP23 = -.019345
  KP12 = -.062213
ELSE IF(MIX.EQ.2)THEN
  KP32 = .001904
  KP23 = -8.24002
  KP13 = 0.04085
  KP31 = -8.97624
  KP12 = .01071
  KP21 = -33.1622
ELSE IF(MIX.EQ.3)THEN
  KP12 = -.033337
  KP21 = -.073304
  C12 = .014234
  KP32 = -.016808
  KP23 = -.016751
  C23 = -.005644
  KP13 = .017052
  KP31 = .016764
  C13 = -.013308
ELSE IF(MIX.LT.1.OR.MIX.GT.3)THEN
  GOTO 51
ENDIF

```

C Read in the experimental data

```

J=1
DO WHILE (J.LE.N)
  READ (1,*) T,P, XM1, XM3, YM1, YM3
  J=J+1
  XM2=1-XM1-XM3
  YM2=1-YM1-YM3
  IF(XM2.EQ.0)XM2=.000001
  IF(YM2.EQ.0)YM2=.000001

```

C Calculate the mole fractions of each component in  
C in the system from the experimental data.

```

VE=.0001
KK1=YM1/XM1
KK2=YM2/XM2
KK3=YM3/XM3

```

```

      FRAC=.1
41  ZZ1=YM1*VE+XM1*(1-VE)
      ZZ2=YM2*VE+XM2*(1-VE)
      ZZ3=YM3*VE+XM3*(1-VE)

42  FVE=ZZ1*(KK1-1)/(1+VE*(KK1-1))+ZZ2*(KK2-1)/(1+VE
      1*(KK2-1))+ZZ3*(KK3-1)/(1+VE*(KK3-1))
      FVEDV=ZZ1*((KK1-1)/(1+VE*(KK1-1)))**2+ZZ2*((KK2-1)/
      1/(1+VE*(KK2-1)))**2+ZZ3*((KK3-1)/(1+VE*(KK3-1)))**2
      VENEW=V+FVE/FVEDV
      IF(DABS(VE-VENEW).GT..001)THEN
          VE=(VENEW-VE)*FRAC+VE
          FRAC=FRAC+.3*(1-FRAC)
          GOTO 41
      ENDIF

      ZZ1=YM1*VE+XM1*(1-VE)
      ZZ2=YM2*VE+XM2*(1-VE)
      ZZ3=YM3*VE+XM3*(1-VE)

C   Using the E.O.S. then recalculate the fraction of
C   the vapor phase.

      X1=.97*XM1
      X2=.97*XM2
      X3=1-X1-X2
      Y1=.97*YM1
      Y2=.97*YM2
      Y3=1-Y1-Y2

      IF(MIX.EQ.1)THEN
          CALL FUGC1(TC1,TC2,TC3,PC1,PC2,PC3,O1,O2,O3,RP1,RP2,RP3,
          1T,P,X1,X2,X3,Y1,Y2,Y3,KP12,KP13,KP23,K1,K2,K3)
      ELSE IF(MIX.EQ.3)THEN
          CALL FUGC3(TC1,TC2,TC3,PC1,PC2,PC3,O1,O2,O3,RP1,RP2,RP3,
          1T,P,X1,X2,X3,Y1,Y2,Y3,KP12,KP21,KP13,KP31,KP23,KP32,C12,
          1C13,C23,K1,K2,K3)
      ELSE IF(MIX.EQ.2)THEN
          CALL FUGC2(TC1,TC2,TC3,PC1,PC2,PC3,O1,O2,O3,RP1,RP2,RP3
          1T,P,X1,X2,X3,Y1,Y2,Y3,KP12,KP21,KP13,KP31,KP23,KP32,
          1K1,K2,K3)
      ENDIF

      V=.0001
      FRAC=.1
80  FV=ZZ1*(K1-1)/(1+V*(K1-1))+ZZ2*(K2-1)/(1+V*(K2-1))+
      1ZZ3*(K3-1)/(1+V*(K3-1))
      FVDV=ZZ1*((K1-1)/(1+V*(K1-1)))**2+ZZ2*((K2-1)/(1+V*(K2-1)))

```

```

1**2+ZZ3*((K3-1)/(1+V*(K3-1)))**2
IF (FVDV.LT.1E-10)THEN
  V=VE
  GOTO 34
ENDIF
VNEW=V+FV/FVDV
IF(DABS(V-VNEW).GT..0001)THEN
  V=(VNEW-V)*FRAC+V
  FRAC=FRAC+.3*(1-FRAC)
  GOTO 80
ENDIF
34 VOLD=V
  V=VNEW

C Calculate the mole fraction of each component in the
C Vapor phase and in the liquid phase.

35 XN1=ZZ1/(1+V*(K1-1))
  XN2=ZZ2/(1+V*(K2-1))
  XN3=1-XN1-XN2
  YN1=XN1*K1
  YN2=XN2*K2
  YN3=1-YN1-YN2
  IF(DABS(XN1-X1).GT..0001.AND.DABS(XN2-X2).GT..0001.AND.
1DABS(VOLD-VNEW).GT..0001)THEN
    X1=XN1
    X2=XN2
    X3=XN3
    Y1=YN1
    Y2=YN2
    Y3=YN3
    IF(MIX.EQ.1)THEN
      CALL FUGC1(TC1,TC2,TC3,PC1,PC2,PC3,O1,O2,O3,RP1,RP2,RP3,
1T,P,X1,X2,X3,Y1,Y2,Y3,KP12,KP13,KP23,K1,K2,K3)
    ELSE IF(MIX.EQ.2)THEN
      CALL FUGC2(TC1,TC2,TC3,PC1,PC2,PC3,O1,O2,O3,RP1,RP2,RP3,
1T,P,X1,X2,X3,Y1,Y2,Y3,KP12,KP21,KP13,KP31,KP23,KP32,
1K1,K2,K3)
    ELSE IF(MIX.EQ.3)THEN
      CALL FUGC3(TC1,TC2,TC3,PC1,PC2,PC3,O1,O2,O3,RP1,RP2,RP3,
1T,P,X1,X2,X3,Y1,Y2,Y3,KP12,KP21,KP13,KP31,KP23,KP32,
1C12,C13,C23,K1,K2,K3)
    ENDIF
    FRAC=.3
    GOTO 80
  ENDIF
  IF(X3.LT.0)THEN
    X3=0
    X2=1-X1

```

```

ENDIF
IF(Y3.LT.0)THEN
  Y3=0
  Y2=1-Y1
ENDIF
TYPE*, ' '
TYPE*, 'X1,X2, ', X1,X2
TYPE*, ' '
TYPE*, 'Y1,Y2, ', Y1,Y2
PM=100*P
AAD=(DABS(X1-XM1)+DABS(X2-XM2)+DABS(X3-XM3)+DABS(Y1-YM1)+
1DABS(Y2-YM2)+DABS(Y3-YM3))/6

```

C Record the results

```

WRITE(2,12)T,PM,X1,X2,X3,Y1,Y2,Y3,AAD
ENDDO
REWIND(1)
WRITE(2,13)
1  FORMAT(A40)
3  FORMAT(7X,'Ternary VLE of m-cresol/quinoline/tetralin')
8  FORMAT(/,7X,'Tmeas ',2X,'Pmeas ',4X,'X1',6X,'X2',6X,
1  'X3',6X,'Y1',6X,'Y2',6X,'Y3',5X,'AAD')
9  FORMAT(8X,'(K)',5X,'(Kpa)')
11 FORMAT(7X,'-----',2X,'-----',2X,'-----',2X'-----',2X,
1  '-----',2X,'-----',2X,'-----',2X,'-----')
12 FORMAT(7X,F6.2,2X,F6.2,2X,F6.4,2X,F6.4,2X,F6.4,2X,F6.4,2X,
1  ,F6.4,2X,F6.4,2X,F6.4)
13 FORMAT(/,7X,'AAD : Absolute Average of Deviation')
100 STOP
END

```

```

SUBROUTINE FUGC1(TC1,TC2,TC3,PC1,PC2,PC3,O1,O2,O3,RP1,RP2,
1RP3,T,P,X1,X2,X3,Z1,Z2,Z3,KP12,KP13,KP23,K1,K2,K3)

```

```

PARAMETER CC=0.48,R=.08314,UU=.2,WW=-.1,E=.6633
IMPLICIT DOUBLE PRECISION (A-H,K,M,P-Z)

```

C Calculate the reduced temperatures and pressures

```

TR1=T/TC1
TR2=T/TC2
TR3=T/TC3
PR2=P/PC2
PR1=P/PC1

```

$$PR3=P/PC3$$

C Calculate the critical parameters of the pure components  
C and alpha parameters.

$$\begin{aligned}SMB1 &= 0.17091 * R * TC1 / PC1 \\SMB2 &= 0.17091 * R * TC2 / PC2 \\SMB3 &= 0.17091 * R * TC3 / PC3\end{aligned}$$

$$\begin{aligned}SMAC1 &= 0.49897 * R ** 2 * TC1 ** 2 / PC1 \\SMAC2 &= 0.49897 * R ** 2 * TC2 ** 2 / PC2 \\SMAC3 &= 0.49897 * R ** 2 * TC3 ** 2 / PC3\end{aligned}$$

$$\begin{aligned}ALPHAS1 &= 1. - 0.244797 * (1. - TR1) + 0.16047 * (1. - TR1 ** 2.7) \\ALPHAS2 &= 1. - 0.244797 * (1. - TR2) + 0.16047 * (1. - TR2 ** 2.7) \\ALPHAS3 &= 1. - 0.244797 * (1. - TR3) + 0.16047 * (1. - TR3 ** 2.7)\end{aligned}$$

$$\begin{aligned}CCC1 &= 0.00632 + 1.13094 * O1 - 0.03116 * O1 ** 2 \\CCC2 &= 0.00632 + 1.13094 * O2 - 0.03116 * O2 ** 2 \\CCC3 &= 0.00632 + 1.13094 * O3 - 0.03116 * O3 ** 2\end{aligned}$$

$$\begin{aligned}DDD1 &= -0.02312 + 0.28654 * O1 - 0.28888 * O1 ** 2 \\DDD2 &= -0.02312 + 0.28654 * O2 - 0.28888 * O2 ** 2 \\DDD3 &= -0.02312 + 0.28654 * O3 - 0.28888 * O3 ** 2\end{aligned}$$

$$\begin{aligned}ALPHAN1 &= 1. + CCC1 * (1. - TR1) + DDD1 * (1. - TR1) ** 2 \\ALPHAN2 &= 1. + CCC2 * (1. - TR2) + DDD2 * (1. - TR2) ** 2 \\ALPHAN3 &= 1. + CCC3 * (1. - TR3) + DDD3 * (1. - TR3) ** 2\end{aligned}$$

$$\begin{aligned}ALPHAP1 &= 1. + RP1 * (DEXP(-RP1 ** CC) - DEXP(-(RP1 * TC1 / T) ** CC)) \\ALPHAP2 &= 1. + RP2 * (DEXP(-RP2 ** CC) - DEXP(-(RP2 * TC2 / T) ** CC)) \\ALPHAP3 &= 1. + RP3 * (DEXP(-RP3 ** CC) - DEXP(-(RP3 * TC3 / T) ** CC))\end{aligned}$$

$$\begin{aligned}SMA1 &= SMAC1 * ALPHAS1 * ALPHAN1 * ALPHAP1 \\SMA2 &= SMAC2 * ALPHAS2 * ALPHAN2 * ALPHAP2 \\SMA3 &= SMAC3 * ALPHAS3 * ALPHAN3 * ALPHAP3\end{aligned}$$

C Calculate the mixture parameter of the liquid phase

$$\begin{aligned}BMIX &= X1 * SMB1 + X2 * SMB2 + X3 * SMB3 \\A12 &= DSQRT(SMA1 * SMA2) * (1 - KP12) \\A21 &= A12 \\A13 &= DSQRT(SMA1 * SMA3) * (1 - KP13) \\A31 &= A13 \\A23 &= DSQRT(SMA2 * SMA3) * (1 - KP23) \\A32 &= A23\end{aligned}$$

$$AMIX = X1 ** 2 * SMA1 + X2 ** 2 * SMA2 + X3 ** 2 * SMA3 + X1 * X2 * (A12 + A21) + X1 * X3 * (A13 + A31) + X2 * X3 * (A23 + A32)$$

C Calculate the fugacity coefficients in the liquid phase

CALL LVOL(P,T,VL,AMIX,BMIX)

F=DLOG((2\*VL-E\*BMIX+UU\*BMIX)/(2\*VL+E\*BMIX+UU\*BMIX))

AIM1=2\*X1\*SMA1+X2\*(A12+A21)+X3\*(A13+A31)

FUGL1=(16\*BMIX\*VL-3\*BMIX\*\*2)/(16\*VL\*\*2-8\*BMIX\*VL+BMIX\*\*2)+  
 1SMB1\*(256\*VL\*\*2-32\*BMIX\*VL)/(4\*(64\*VL\*\*3-48\*BMIX\*VL\*\*2+12\*  
 1BMIX\*\*2\*VL-BMIX\*\*3))+  
 1AIM1\*F/(BMIX\*R\*T\*E)-AMIX\*SMB1/(R\*T)\*(VL/(WW\*BMIX\*\*3+BMIX\*  
 1VL\*\*2+UU\*VL\*BMIX\*\*2)+F/(BMIX\*\*2\*E))  
 1-DLOG((P\*VL)/(R\*T))  
 FUGL1=DEXP(FUGL1)

AIM2=2\*X2\*SMA2+X1\*(A21+A12)+X3\*(A23+A32)

FUGL2=(16\*BMIX\*VL-3\*BMIX\*\*2)/(16\*VL\*\*2-8\*BMIX\*VL+BMIX\*\*2)+  
 1SMB2\*(256\*VL\*\*2-32\*BMIX\*VL)/(4\*(64\*VL\*\*3-48\*BMIX\*VL\*\*2+12\*  
 1BMIX\*\*2\*VL-BMIX\*\*3))+  
 1AIM2\*F/(BMIX\*R\*T\*E)-AMIX\*SMB2/(R\*T)\*(VL/(WW\*BMIX\*\*3+BMIX\*  
 1VL\*\*2+UU\*VL\*BMIX\*\*2)+F/(BMIX\*\*2\*E))  
 1-DLOG((P\*VL)/(R\*T))  
 FUGL2=DEXP(FUGL2)

AIM3=2\*X3\*SMA1+X2\*(A32+A23)+X1\*(A31+A13)

FUGL3=(16\*BMIX\*VL-3\*BMIX\*\*2)/(16\*VL\*\*2-8\*BMIX\*VL+BMIX\*\*2)+  
 1SMB3\*(256\*VL\*\*2-32\*BMIX\*VL)/(4\*(64\*VL\*\*3-48\*BMIX\*VL\*\*2+12\*  
 1BMIX\*\*2\*VL-BMIX\*\*3))+  
 1AIM3\*F/(BMIX\*R\*T\*E)-AMIX\*SMB3/(R\*T)\*(VL/(WW\*BMIX\*\*3+BMIX\*  
 1VL\*\*2+UU\*VL\*BMIX\*\*2)+F/(BMIX\*\*2\*E))  
 1-DLOG((P\*VL)/(R\*T))  
 FUGL3=DEXP(FUGL3)

C Calculate the mixture parameter of the vapour phase

BVIX=Z1\*SMB1+Z2\*SMB2+Z3\*SMB3

AV12=DSQRT(SMA1\*SMA2)\*(1-KP12)

AV21=AV12

AV13=DSQRT(SMA1\*SMA3)\*(1-KP13)

AV31=AV13

AV23=DSQRT(SMA2\*SMA3)\*(1-KP23)

AV32=AV23

AVIX=Z1\*\*2\*SMA1+Z2\*\*2\*SMA2+Z3\*\*2\*SMA3+Z1\*Z2\*(AV12+AV21)+  
 1Z1\*Z3\*(AV13+AV31)+Z2\*Z3\*(AV23+AV32)

C Calculate the fugacity coefficients in the vapour phase

CALL VVOL(P,T,VV,AVIX,BVIX)

F=DLOG((2\*VV-E\*BVIX+UU\*BVIX)/(2\*VV+E\*BVIX+UU\*BVIX))  
 AIV1=2\*Z1\*SMA1+Z2\*(AV12+AV21)+Z3\*(AV13+AV31)

FUGV1=(16\*BVIX\*VV-3\*BVIX\*\*2)/(16\*VV\*\*2-8\*BVIX\*VV+BVIX\*\*2)+  
 1SMB1\*(256\*VV\*\*2-32\*BVIX\*VV)/(4\*(64\*VV\*\*3-48\*BVIX\*VV\*\*2+12\*  
 1BVIX\*\*2\*VV-BVIX\*\*3))+  
 1AIV1\*F/(BVIX\*R\*T\*E)-AVIX\*SMB1/(R\*T)\*(VV/(WW\*BVIX\*\*3+BVIX\*  
 1VV\*\*2+UU\*VV\*BVIX\*\*2)+F/(BVIX\*\*2\*E))  
 1-DLOG((P\*VV)/(R\*T))  
 FUGV1=DEXP(FUGV1)

AIV2=2\*Z2\*SMA2+Z1\*(AV21+AV12)+Z3\*(AV23+AV32)

FUGV2=(16\*BVIX\*VV-3\*BVIX\*\*2)/(16\*VV\*\*2-8\*BVIX\*VV+BVIX\*\*2)+  
 1SMB2\*(256\*VV\*\*2-32\*BVIX\*VV)/(4\*(64\*VV\*\*3-48\*BVIX\*VV\*\*2+12\*  
 1BVIX\*\*2\*VV-BVIX\*\*3))+  
 1AIV2\*F/(BVIX\*R\*T\*E)-AVIX\*SMB2/(R\*T)\*(VV/(WW\*BVIX\*\*3+BVIX\*  
 1VV\*\*2+UU\*VV\*BVIX\*\*2)+F/(BVIX\*\*2\*E))  
 1-DLOG((P\*VV)/(R\*T))  
 FUGV2=DEXP(FUGV2)

AIV3=2\*Z3\*SMA1+Z2\*(AV32+AV23)+Z1\*(AV31+AV13)

FUGV3=(16\*BMIX\*VV-3\*BVIX\*\*2)/(16\*VV\*\*2-8\*BVIX\*VV+BVIX\*\*2)+  
 1SMB3\*(256\*VV\*\*2-32\*BVIX\*VV)/(4\*(64\*VV\*\*3-48\*BVIX\*VV\*\*2+12\*  
 1BVIX\*\*2\*VV-BVIX\*\*3))+  
 1AIV3\*F/(BVIX\*R\*T\*E)-AVIX\*SMB3/(R\*T)\*(VV/(WW\*BVIX\*\*3+BVIX\*  
 1VV\*\*2+UU\*VV\*BVIX\*\*2)+F/(BVIX\*\*2\*E))  
 1-DLOG((P\*VV)/(R\*T))  
 FUGV3=DEXP(FUGV3)

C Calculate the coefficient of separations

K1=FUGL1/FUGV1  
 K2=FUGL2/FUGV2  
 K3=FUGL3/FUGV3  
 RETURN  
 END

SUBROUTINE FUGC2(TC1,TC2,TC3,PC1,PC2,PC3,O1,O2,O3,RP1,RP2,  
 1RP3,T,P,X1,X2,X3,Z1,Z2,Z3,KP12,KP21,KP13,KP31,KP23,KP32,K1,

1K2, K3)

PARAMETER CC=0.48, R=.08314, UU=.2, WW=-.1, E=.6633  
 IMPLICIT DOUBLE PRECISION (A-H, K, M, P-Z)

C Calculate the reduced temperatures and pressures

TR1=T/TC1  
 TR2=T/TC2  
 TR3=T/TC3  
 PR2=P/PC2  
 PR1=P/PC1  
 PR3=P/PC3

C Calculate the critical parameters of the pure components  
 C and alpha parameters.

SMB1=0.17091\*R\*TC1/PC1  
 SMB2=0.17091\*R\*TC2/PC2  
 SMB3=0.17091\*R\*TC3/PC3

SMAC1=0.49897\*R\*\*2\*TC1\*\*2/PC1  
 SMAC2=0.49897\*R\*\*2\*TC2\*\*2/PC2  
 SMAC3=0.49897\*R\*\*2\*TC3\*\*2/PC3

ALPHAS1=1.-0.244797\*(1.-TR1)+0.16047\*(1.-TR1\*\*2.7)  
 ALPHAS2=1.-0.244797\*(1.-TR2)+0.16047\*(1.-TR2\*\*2.7)  
 ALPHAS3=1.-0.244797\*(1.-TR3)+0.16047\*(1.-TR3\*\*2.7)

CCC1 = 0.00632+1.13094\*O1-0.03116\*O1\*\*2  
 CCC2 = 0.00632+1.13094\*O2-0.03116\*O2\*\*2  
 CCC3 = 0.00632+1.13094\*O3-0.03116\*O3\*\*2

DDD1 = -0.02312+0.28854\*O1-0.28888\*O1\*\*2  
 DDD2 = -0.02312+0.28854\*O2-0.28888\*O2\*\*2  
 DDD3 = -0.02312+0.28854\*O3-0.28888\*O3\*\*2

ALPHAN1= 1.+CCC1\*(1.-TR1)+DDD1\*(1.-TR1)\*\*2  
 ALPHAN2= 1.+CCC2\*(1.-TR2)+DDD2\*(1.-TR2)\*\*2  
 ALPHAN3= 1.+CCC3\*(1.-TR3)+DDD3\*(1.-TR3)\*\*2

ALPHAP1=1.+RP1\*(DEXP(-RP1\*\*CC)-DEXP(-(RP1\*TC1/T)\*\*CC))  
 ALPHAP2=1.+RP2\*(DEXP(-RP2\*\*CC)-DEXP(-(RP2\*TC2/T)\*\*CC))  
 ALPHAP3=1.+RP3\*(DEXP(-RP3\*\*CC)-DEXP(-(RP3\*TC3/T)\*\*CC))

SMA1=SMAC1\*ALPHAS1\*ALPHAN1\*ALPHAP1  
 SMA2=SMAC2\*ALPHAS2\*ALPHAN2\*ALPHAP2  
 SMA3=SMAC3\*ALPHAS3\*ALPHAN3\*ALPHAP3

C Calculate the mixture parameter of the liquid phase

$$BMIX = X1 * SMB1 + X2 * SMB2 + X3 * SMB3$$

$$A12 = DSQRT(SMA1 * SMA2) * (1 - KP12 - KP21 / T)$$

$$A21 = A12$$

$$A13 = DSQRT(SMA1 * SMA3) * (1 - KP13 - KP31 / T)$$

$$A31 = A13$$

$$A23 = DSQRT(SMA2 * SMA3) * (1 - KP23 - KP32 / T)$$

$$A32 = A23$$

$$AMIX = X1 ** 2 * SMA1 + X2 ** 2 * SMA2 + X3 ** 2 * SMA3 + X1 * X2 * (A12 + A21) + X1 * X3 * (A13 + A31) + X2 * X3 * (A23 + A32)$$

C Calculate the fugacity coefficients in the liquid phase

CALL LVOL(P,T,VL,AMIX,BMIX)

$$F = DLOG((2 * VL - E * BMIX + UU * BMIX) / (2 * VL + E * BMIX + UU * BMIX))$$

$$AIM1 = 2 * X1 * SMA1 + X2 * (A12 + A21) + X3 * (A13 + A31)$$

$$FUGL1 = (16 * BMIX * VL - 3 * BMIX ** 2) / (16 * VL ** 2 - 8 * BMIX * VL + BMIX ** 2) + 1 * SMB1 * (256 * VL ** 2 - 32 * BMIX * VL) / (4 * (64 * VL ** 3 - 48 * BMIX * VL ** 2 + 12 * 1 * BMIX ** 2 * VL - BMIX ** 3)) + 1 * AIM1 * F / (BMIX * R * T * E) - AMIX * SMB1 / (R * T) * (VL / (WW * BMIX ** 3 + BMIX * 1 * VL ** 2 + UU * VL * BMIX ** 2) + F / (BMIX ** 2 * E))$$

$$1 - DLOG((P * VL) / (R * T))$$

$$FUGL1 = DEXP(FUGL1)$$

$$AIM2 = 2 * X2 * SMA2 + X1 * (A21 + A12) + X3 * (A23 + A32)$$

$$FUGL2 = (16 * BMIX * VL - 3 * BMIX ** 2) / (16 * VL ** 2 - 8 * BMIX * VL + BMIX ** 2) + 1 * SMB2 * (256 * VL ** 2 - 32 * BMIX * VL) / (4 * (64 * VL ** 3 - 48 * BMIX * VL ** 2 + 12 * 1 * BMIX ** 2 * VL - BMIX ** 3)) + 1 * AIM2 * F / (BMIX * R * T * E) - AMIX * SMB2 / (R * T) * (VL / (WW * BMIX ** 3 + BMIX * 1 * VL ** 2 + UU * VL * BMIX ** 2) + F / (BMIX ** 2 * E))$$

$$1 - DLOG((P * VL) / (R * T))$$

$$FUGL2 = DEXP(FUGL2)$$

$$AIM3 = 2 * X3 * SMA1 + X2 * (A32 + A23) + X1 * (A31 + A13)$$

$$FUGL3 = (16 * BMIX * VL - 3 * BMIX ** 2) / (16 * VL ** 2 - 8 * BMIX * VL + BMIX ** 2) + 1 * SMB3 * (256 * VL ** 2 - 32 * BMIX * VL) / (4 * (64 * VL ** 3 - 48 * BMIX * VL ** 2 + 12 * 1 * BMIX ** 2 * VL - BMIX ** 3)) + 1 * AIM3 * F / (BMIX * R * T * E) - AMIX * SMB3 / (R * T) * (VL / (WW * BMIX ** 3 + BMIX * 1 * VL ** 2 + UU * VL * BMIX ** 2) + F / (BMIX ** 2 * E))$$

$$1 - DLOG((P * VL) / (R * T))$$

$$FUGL3 = DEXP(FUGL3)$$

C Calculate the mixture parameter of the vapour phase

$$BVIX=Z1*SMB1+Z2*SMB2+Z3*SMB3$$

$$AV12=A12$$

$$AV21=A21$$

$$AV13=A13$$

$$AV31=A31$$

$$AV23=A23$$

$$AV32=A32$$

$$AVIX=Z1**2*SMA1+Z2**2*SMA2+Z3**2*SMA3+Z1*Z2*(AV12+AV21)+1Z1*Z3*(AV13+AV31)+Z2*Z3*(AV23+AV32)$$

C Calculate the fugacity coefficients in the vapour phase

CALL VVOL(P,T,VV,AVIX,BVIX)

$$F=DLOG((2*VV-E*BVIX+UU*BVIX)/(2*VV+E*BVIX+UU*BVIX))$$

$$AIV1=2*Z1*SMA1+Z2*(AV12+AV21)+Z3*(AV13+AV31)$$

$$FUGV1=(16*BVIX*VV-3*BVIX**2)/(16*VV**2-8*BVIX*VV+BVIX**2)+1SMB1*(256*VV**2-32*BVIX*VV)/(4*(64*VV**3-48*BVIX*VV**2+12*1BVIX**2*VV-BVIX**3))+1AIV1*F/(BVIX*R*T*E)-AVIX*SMB1/(R*T)*(VV/(WW*BVIX**3+BVIX*1VV**2+UU*VV*BVIX**2))+F/(BVIX**2*E))1-DLOG((P*VV)/(R*T))FUGV1=DEXP(FUGV1)$$

$$AIV2=2*Z2*SMA2+Z1*(AV21+AV12)+Z3*(AV23+AV32)$$

$$FUGV2=(16*BVIX*VV-3*BVIX**2)/(16*VV**2-8*BVIX*VV+BVIX**2)+1SMB2*(256*VV**2-32*BVIX*VV)/(4*(64*VV**3-48*BVIX*VV**2+12*1BVIX**2*VV-BVIX**3))+1AIV2*F/(BVIX*R*T*E)-AVIX*SMB2/(R*T)*(VV/(WW*BVIX**3+BVIX*1VV**2+UU*VV*BVIX**2))+F/(BVIX**2*E))1-DLOG((P*VV)/(R*T))FUGV2=DEXP(FUGV2)$$

$$AIV3=2*Z3*SMA1+Z2*(AV32+AV23)+Z1*(AV31+AV13)$$

$$FUGV3=(16*BMIX*VV-3*BVIX**2)/(16*VV**2-8*BVIX*VV+BVIX**2)+1SMB3*(256*VV**2-32*BVIX*VV)/(4*(64*VV**3-48*BVIX*VV**2+12*1BVIX**2*VV-BVIX**3))+1AIV3*F/(BVIX*R*T*E)-AVIX*SMB3/(R*T)*(VV/(WW*BVIX**3+BVIX*1VV**2+UU*VV*BVIX**2))+F/(BVIX**2*E))1-DLOG((P*VV)/(R*T))$$

FUGV3=DEXP(FUGV3)

C Calculate the coefficient of separations

K1=FUGL1/FUGV1  
K2=FUGL2/FUGV2  
K3=FUGL3/FUGV3

RETURN  
END

SUBROUTINE FUGC3(TC1,TC2,TC3,PC1,PC2,PC3,O1,O2,O3,RP1,RP2,  
1RP3,T,P,X1,X2,X3,Z1,Z2,Z3,KP12,KP21,KP13,KP31,KP23,KP32,  
1C12,C13,C23,K1,K2,K3)

PARAMETER CC=0.48,R=.08314,UU=.2,WW=-.1,E=.6633  
IMPLICIT DOUBLE PRECISION (A-H,K,M,P-Z)

C Calculate the reduced temperatures and pressures

TR1=T/TC1  
TR2=T/TC2  
TR3=T/TC3  
PR2=P/PC2  
PR1=P/PC1  
PR3=P/PC3

C Calculate the critical parameters of the pure components  
C and alpha parameters.

SMB1=0.17091\*R\*TC1/PC1  
SMB2=0.17091\*R\*TC2/PC2  
SMB3=0.17091\*R\*TC3/PC3

SMAC1=0.49897\*R\*\*2\*TC1\*\*2/PC1  
SMAC2=0.49897\*R\*\*2\*TC2\*\*2/PC2  
SMAC3=0.49897\*R\*\*2\*TC3\*\*2/PC3

ALPHAS1=1.-0.244797\*(1.-TR1)+0.16047\*(1.-TR1\*\*2.7)  
ALPHAS2=1.-0.244797\*(1.-TR2)+0.16047\*(1.-TR2\*\*2.7)  
ALPHAS3=1.-0.244797\*(1.-TR3)+0.16047\*(1.-TR3\*\*2.7)

CCC1 = 0.00632+1.13094\*O1-0.03116\*O1\*\*2

$$\begin{aligned} \text{CCC2} &= 0.00632+1.13094*02-0.03116*02**2 \\ \text{CCC3} &= 0.00632+1.13094*03-0.03116*03**2 \end{aligned}$$

$$\begin{aligned} \text{DDD1} &= -0.02312+0.26654*01-0.28888*01**2 \\ \text{DDD2} &= -0.02312+0.26654*02-0.28888*02**2 \\ \text{DDD3} &= -0.02312+0.26654*03-0.28888*03**2 \end{aligned}$$

$$\begin{aligned} \text{ALPHAN1} &= 1.+ \text{CCC1}*(1.-\text{TR1})+\text{DDD1}*(1.-\text{TR1})**2 \\ \text{ALPHAN2} &= 1.+ \text{CCC2}*(1.-\text{TR2})+\text{DDD2}*(1.-\text{TR2})**2 \\ \text{ALPHAN3} &= 1.+ \text{CCC3}*(1.-\text{TR3})+\text{DDD3}*(1.-\text{TR3})**2 \end{aligned}$$

$$\begin{aligned} \text{ALPHAP1} &= 1.+ \text{RP1}*(\text{DEXP}(-\text{RP1**CC})-\text{DEXP}(-(\text{RP1*TC1/T})**\text{CC})) \\ \text{ALPHAP2} &= 1.+ \text{RP2}*(\text{DEXP}(-\text{RP2**CC})-\text{DEXP}(-(\text{RP2*TC2/T})**\text{CC})) \\ \text{ALPHAP3} &= 1.+ \text{RP3}*(\text{DEXP}(-\text{RP3**CC})-\text{DEXP}(-(\text{RP3*TC3/T})**\text{CC})) \end{aligned}$$

$$\begin{aligned} \text{SMA1} &= \text{SMAC1}*\text{ALPHAS1}*\text{ALPHAN1}*\text{ALPHAP1} \\ \text{SMA2} &= \text{SMAC2}*\text{ALPHAS2}*\text{ALPHAN2}*\text{ALPHAP2} \\ \text{SMA3} &= \text{SMAC3}*\text{ALPHAS3}*\text{ALPHAN3}*\text{ALPHAP3} \end{aligned}$$

C Calculate the mixture parameter of the liquid phase

$$\text{BMIX} = \text{X1}*\text{SMB1} + \text{X2}*\text{SMB2} + \text{X3}*\text{SMB3}$$

$$\begin{aligned} \text{A12} &= \text{DSQRT}(\text{SMA1}*\text{SMA2})*(1-\text{KP12}+(\text{KP12}-\text{KP21})*\text{X1}+\text{C12/T}) \\ \text{A21} &= \text{DSQRT}(\text{SMA1}*\text{SMA2})*(1-\text{KP21}+(\text{KP21}-\text{KP12})*\text{X2}+\text{C12/T}) \\ \text{A13} &= \text{DSQRT}(\text{SMA1}*\text{SMA3})*(1-\text{KP13}+(\text{KP13}-\text{KP31})*\text{X1}+\text{C13/T}) \\ \text{A31} &= \text{DSQRT}(\text{SMA1}*\text{SMA3})*(1-\text{KP31}+(\text{KP31}-\text{KP13})*\text{X3}+\text{C13/T}) \\ \text{A23} &= \text{DSQRT}(\text{SMA2}*\text{SMA3})*(1-\text{KP23}+(\text{KP23}-\text{KP32})*\text{X2}+\text{C23/T}) \\ \text{A32} &= \text{DSQRT}(\text{SMA2}*\text{SMA3})*(1-\text{KP32}+(\text{KP32}-\text{KP23})*\text{X3}+\text{C23/T}) \end{aligned}$$

$$\begin{aligned} \text{AMIX} &= \text{X1**2}*\text{SMA1} + \text{X2**2}*\text{SMA2} + \text{X3**2}*\text{SMA3} + \text{X1*X2}*(\text{A12}+\text{A21}) + \\ &+ \text{X1*X3}*(\text{A13}+\text{A31}) + \text{X2*X3}*(\text{A23}+\text{A32}) \end{aligned}$$

C Calculate the fugacity coefficients in the liquid phase

$$\text{CALL LVOL}(P, T, \text{VL}, \text{AMIX}, \text{BMIX})$$

$$\text{F} = \text{DLOG}((2*\text{VL}-\text{E}*\text{BMIX}+\text{UU}*\text{BMIX})/(2*\text{VL}+\text{E}*\text{BMIX}+\text{UU}*\text{BMIX}))$$

$$\begin{aligned} \text{AIM1} &= 2*\text{X1}*\text{SMA1} + \text{X2}*(\text{A12}+\text{A21}) + \text{X3}*(\text{A13}+\text{A31}) \\ &+ \text{X1*X2}*(\text{SMA1}*\text{SMA2})** .5*(\text{KP12}-\text{KP21})*(1-\text{X1}) \\ &+ \text{X2*X1}*(\text{SMA2}*\text{SMA1})** .5*(\text{KP21}-\text{KP12})*(-\text{X2}) \\ &+ \text{X1*X3}*(\text{SMA1}*\text{SMA3})** .5*(\text{KP13}-\text{KP31})*(1-\text{X1}) \\ &+ \text{X3*X1}*(\text{SMA3}*\text{SMA1})** .5*(\text{KP31}-\text{KP13})*(-\text{X3}) \\ &+ \text{X2*X3}*(\text{SMA2}*\text{SMA3})** .5*(\text{KP23}-\text{KP32})*(-\text{X2}) \\ &+ \text{X3*X2}*(\text{SMA3}*\text{SMA2})** .5*(\text{KP32}-\text{KP23})*(-\text{X3}) \end{aligned}$$

$$\begin{aligned} \text{FUGL1} &= (16*\text{BMIX}*\text{VL}-3*\text{BMIX**2})/(16*\text{VL**2}-8*\text{BMIX}*\text{VL}+\text{BMIX**2}) + \\ &+ 1*\text{SMB1}*(256*\text{VL**2}-32*\text{BMIX}*\text{VL})/(4*(64*\text{VL**3}-48*\text{BMIX}*\text{VL**2}+12* \end{aligned}$$

```

1BMIX**2*VL-BMIX**3))+
1AIM1*F/(BMIX*R*T*E)-AMIX*SMB1/(R*T)*(VL/(WW*BMIX**3+BMIX*
1VL**2+UU*VL*BMIX**2)+F/(BMIX**2*E))
1-DLOG((P*VL)/(R*T))
FUGL1=DEXP(FUGL1)

```

```

AIM2=2*X2*SMA2+X1*(A21+A12)+X3*(A23+A32)
1+X2*X1*(SMA2*SMA1)**.5*(KP21-KP12)*(1-X2)
1+X1*X2*(SMA1*SMA2)**.5*(KP12-KP21)*(-X1)
1+X2*X3*(SMA2*SMA3)**.5*(KP23-KP32)*(1-X2)
1+X3*X2*(SMA3*SMA2)**.5*(KP32-KP23)*(-X3)
1+X1*X3*(SMA1*SMA3)**.5*(KP13-KP31)*(-X1)
1+X3*X1*(SMA3*SMA1)**.5*(KP31-KP13)*(-X3)
FUGL2=(16*BMIX*VL-3*BMIX**2)/(16*VL**2-8*BMIX*VL+BMIX**2)+
1SMB2*(256*VL**2-32*BMIX*VL)/(4*(64*VL**3-48*BMIX*VL**2+12*
1BMIX**2*VL-BMIX**3))+
1AIM2*F/(BMIX*R*T*E)-AMIX*SMB2/(R*T)*(VL/(WW*BMIX**3+BMIX*
1VL**2+UU*VL*BMIX**2)+F/(BMIX**2*E))
1-DLOG((P*VL)/(R*T))
FUGL2=DEXP(FUGL2)

```

```

AIM3=2*X3*SMA1+X2*(A32+A23)+X1*(A31+A13)
1+X3*X2*(SMA1*SMA2)**.5*(KP12-KP21)*(1-X3)
1X2*X3*(SMA2*SMA3)**.5*(KP23-KP32)*(-X2)
1+X1*X3*(SMA1*SMA3)**.5*(KP13-KP31)*(-X1)
1+X3*X1*(SMA3*SMA1)**.5*(KP31-KP13)*(1-X3)
1+X2*X1*(SMA2*SMA1)**.5*(KP21-KP12)*(-X2)
1+X1*X2*(SMA1*SMA2)**.5*(KP12-KP21)*(-X1)
FUGL3=(16*BMIX*VL-3*BMIX**2)/(16*VL**2-8*BMIX*VL+BMIX**2)+
1SMB3*(256*VL**2-32*BMIX*VL)/(4*(64*VL**3-48*BMIX*VL**2+12*
1BMIX**2*VL-BMIX**3))+
1AIM3*F/(BMIX*R*T*E)-AMIX*SMB3/(R*T)*(VL/(WW*BMIX**3+BMIX*
1VL**2+UU*VL*BMIX**2)+F/(BMIX**2*E))
1-DLOG((P*VL)/(R*T))
FUGL3=DEXP(FUGL3)

```

C Calculate the mixture parameter of the vapour phase

```
BVIX=Z1*SMB1+Z2*SMB2+Z3*SMB3
```

```

AV12=DSQRT(SMA1*SMA2)*(1-KP12+(KP12-KP21)*Z1+C12/T)
AV21=DSQRT(SMA1*SMA2)*(1-KP21+(KP21-KP12)*Z2+C12/T)
AV13=DSQRT(SMA1*SMA3)*(1-KP13+(KP13-KP31)*Z1+C13/T)
AV31=DSQRT(SMA1*SMA3)*(1-KP31+(KP31-KP13)*Z3+C13/T)
AV23=DSQRT(SMA2*SMA3)*(1-KP23+(KP23-KP32)*Z2+C23/T)
AV32=DSQRT(SMA2*SMA3)*(1-KP32+(KP32-KP23)*Z3+C23/T)

```

```

AVIX=Z1**2*SMA1+Z2**2*SMA2+Z3**2*SMA3+Z1*Z2*(AV12+AV21)+
1Z1*Z3*(AV13+AV31)+Z2*Z3*(AV23+AV32)

```

C Calculate the fugacity coefficients in the vapour phase

CALL VVOL(P,T,VV,AVIX,BVIX)

F=DLOG((2\*VV-E\*BVIX+UU\*BVIX)/(2\*VV+E\*BVIX+UU\*BVIX))

AIV1=2\*Z1\*SMA1+Z2\*(AV12+AV21)+Z3\*(AV13+AV31)  
 1+Z1\*Z2\*(SMA1\*SMA2)\*\*.5\*(KP12-KP21)\*(1-Z1)  
 1+Z2\*Z1\*(SMA2\*SMA1)\*\*.5\*(KP21-KP12)\*(-Z2)  
 1+Z1\*Z3\*(SMA1\*SMA3)\*\*.5\*(KP13-KP31)\*(1-Z1)  
 1+Z3\*Z1\*(SMA3\*SMA1)\*\*.5\*(KP31-KP13)\*(-Z3)  
 1+Z2\*Z3\*(SMA2\*SMA3)\*\*.5\*(KP23-KP32)\*(-Z2)  
 1+Z3\*Z2\*(SMA3\*SMA2)\*\*.5\*(KP32-KP23)\*(-Z3)

FUGV1=(16\*BVIX\*VV-3\*BVIX\*\*2)/(16\*VV\*\*2-8\*BVIX\*VV+BVIX\*\*2)+  
 1SMB1\*(256\*VV\*\*2-32\*BVIX\*VV)/(4\*(64\*VV\*\*3-48\*BVIX\*VV\*\*2+12\*  
 1BVIX\*\*2\*VV-BVIX\*\*3))+  
 1AIV1\*F/(BVIX\*R\*T\*E)-AVIX\*SMB1/(R\*T)\*(VV/(WW\*BVIX\*\*3+BVIX\*  
 1VV\*\*2+UU\*VV\*BVIX\*\*2)+F/(BVIX\*\*2\*E))  
 1-DLOG((P\*VV)/(R\*T))  
 FUGV1=DEXP(FUGV1)

AIV2=2\*Z2\*SMA2+Z1\*(AV21+AV12)+Z3\*(AV23+AV32)  
 1+Z2\*Z1\*(SMA2\*SMA1)\*\*.5\*(KP21-KP12)\*(1-Z2)  
 1+Z1\*Z2\*(SMA1\*SMA2)\*\*.5\*(KP12-KP21)\*(-Z1)  
 1+Z2\*Z3\*(SMA2\*SMA3)\*\*.5\*(KP23-KP32)\*(1-Z2)  
 1+Z3\*Z2\*(SMA3\*SMA2)\*\*.5\*(KP32-KP23)\*(-Z3)  
 1+Z1\*Z3\*(SMA1\*SMA3)\*\*.5\*(KP13-KP31)\*(-Z1)  
 1+Z3\*Z1\*(SMA3\*SMA1)\*\*.5\*(KP31-KP13)\*(-Z3)  
 FUGV2=(16\*BVIX\*VV-3\*BVIX\*\*2)/(16\*VV\*\*2-8\*BVIX\*VV+BVIX\*\*2)+  
 1SMB2\*(256\*VV\*\*2-32\*BVIX\*VV)/(4\*(64\*VV\*\*3-48\*BVIX\*VV\*\*2+12\*  
 1BVIX\*\*2\*VV-BVIX\*\*3))+  
 1AIV2\*F/(BVIX\*R\*T\*E)-AVIX\*SMB2/(R\*T)\*(VV/(WW\*BVIX\*\*3+BVIX\*  
 1VV\*\*2+UU\*VV\*BVIX\*\*2)+F/(BVIX\*\*2\*E))  
 1-DLOG((P\*VV)/(R\*T))  
 FUGV2=DEXP(FUGV2)

1+Z3\*Z2\*(SMA1\*SMA2)\*\*.5\*(KP12-KP21)\*(1-Z3)  
 1+Z2\*Z3\*(SMA2\*SMA3)\*\*.5\*(KP23-KP32)\*(-Z2)  
 1+Z1\*Z3\*(SMA1\*SMA3)\*\*.5\*(KP13-KP31)\*(-Z1)  
 1+Z3\*Z1\*(SMA3\*SMA1)\*\*.5\*(KP31-KP13)\*(1-Z3)  
 1+Z2\*Z1\*(SMA2\*SMA1)\*\*.5\*(KP21-KP12)\*(-Z2)  
 1+Z1\*Z2\*(SMA1\*SMA2)\*\*.5\*(KP12-KP21)\*(-Z1)

FUGV3=(16\*BMIX\*VV-3\*BVIX\*\*2)/(16\*VV\*\*2-8\*BVIX\*VV+BVIX\*\*2)+  
 1SMB3\*(256\*VV\*\*2-32\*BVIX\*VV)/(4\*(64\*VV\*\*3-48\*BVIX\*VV\*\*2+12\*  
 1BVIX\*\*2\*VV-BVIX\*\*3))+  
 1AIV3\*F/(BVIX\*R\*T\*E)-AVIX\*SMB3/(R\*T)\*(VV/(WW\*BVIX\*\*3+BVIX\*

```

1VV**2+UU*VV*BVIX**2)+F/(BVIX**2*E))
1-DLOG((P*VV)/(R*T))
FUGV3=DEXP(FUGV3)

```

C Calculate the coefficient of separations

```

K1=FUGL1/FUGV1
K2=FUGL2/FUGV2
K3=FUGL3/FUGV3

```

```

RETURN
END

```

```

SUBROUTINE LVOL(P,T,VL,AMIX,BMIX)

```

```

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
PARAMETER R=.08314

```

```

B=BMIX
A=AMIX
V=1.05*B/4
ITER=0
10 IF (ITER.GT.5000) THEN
WRITE(*,100)
STOP
END IF
FV = -(64*R*T*V**3+16*B*R*T*V**2+4*B**2*R*T*V-B**3*R*T)/
1(64*V**4-48*B*V**3+12*B**2*V**2-B**3*V)+A/(V**2+0.2*B*V-
10.1*B**2)+P
DFDV=- (192*R*T*V**2+32*B*R*T*V+4*B**2*R*T)/(64*V**4-48*B
1*V**3+12*B**2*V**2-B**3*V)+(256*V**3-144*B*V**2+24*B**2*V
1-B**3)*(64*R*T*V**3+16*B*R*T*V**2+4*B**2*R*T*V-B**3*R*T)/
1(64*V**4-48*B*V**3+12*B**2*V**2-B**3*V)**2-A*(2*V+0.2*B)/
1(V**2+0.2*B*V-0.1*B**2)**2
ITER=ITER+1
VNEW=V-FV/DFDV
DEV=(V-VNEW)/V
IF (DABS(DEV).GT.0.000001) THEN
V=VNEW
GOTO 10
END IF
IF (DABS(FV).GT.0.0001) THEN
V=VNEW
GOTO 10

```

```

END IF
IF (VNEW.LE.0.0) THEN
WRITE(*,220)
STOP
END IF
VL=VNEW
RETURN
100 FORMAT(5X,'ITERATION EXCEEDS 5000')
220 FORMAT(5x,'Zero or negative liquid volume')
END

```

```

SUBROUTINE VVOL (P,T,VV,AVIX,BVIX)

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
PARAMETER R=.08314

A=AVIX
B=BVIX
AA=A*P/(R**2)/(T**2)
BB=B*P/R/T
ITERV=0
Z=1
10 IF (ITERV.GT.5000) THEN
WRITE(*,20)
STOP
END IF
T5 = -(11*BB+20)/20.0
T4 = -(5*BB**2+36*BB-80*AA)/80.0
T3 = (31*BB**3-4*BB**2-240*AA*BB)/320.0
T2 = -(7*BB**4-9*BB**3-60*AA*BB**2)/320.0
T1 = (BB**5+6*BB**4-10*AA*BB**3)/640.0
T0 = -BB**5/640.0
FZ = Z**6+T5*Z**5+T4*Z**4+T3*Z**3+T2*Z**2+T1*Z+T0
DFDZ = 6*Z**5+5*T5*Z**4+4*T4*Z**3+3*T3*Z**2+2*T2*Z+T1
ITERV=ITERV+1
ZNEW=Z-FZ/DFDZ
DEL=Z-ZNEW
IF (DABS(DEL).GT.0.000001) THEN
Z=ZNEW
GO TO 10
END IF
IF (DABS(FZ).GT.0.0001) THEN
Z=ZNEW

```

```
GO TO 10
END IF
IF (ZNEW.LE.0.0) THEN
WRITE(*,240)
STOP
END IF
VV=ZNEW*R*T/P
RETURN
20 FORMAT (5X,'ITERATION EXCEEDS 5000')
240 FORMAT(5x,'Zero or negative vapor volume')
END
```

This program calculates the enthalpy of a binary mixture using generalized perturbed hardsphere e.o.s. with mixing rule II, where  $k_{ij} = A+B/T$ .

```
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION DELHID(3),Z(3),FM(3),RL(3,7)
CHARACTER*20 FILEIN,FILEOUT
COMMON/FRACT/Z
COMMON/IDEAL/RL
```

C (1) M-CRESOL, and (2) QUINOLINE

```
R=0.08314
TREF=291.48
PREF=1.013
FM(1)=108.14
FM(2)=129.16
```

```
RL(1,1)=19.5818
RL(1,2)=20.6896
RL(1,3)=1836.02
RL(1,4)=8927.76
RL(1,5)=-0.159817
RL(1,6)=47.5601
RL(1,7)=689.349
```

```
RL(2,1)=19.1643
RL(2,2)=19.9861
RL(2,3)=1839.59
RL(2,4)=9892.70
RL(2,5)=-0.157905
RL(2,6)=57.3143
RL(2,7)=701.587
```

C INPUT T, P, HEXP AND FLUID STATE DATA

14 FORMAT(A20)

```
WRITE(*,*)'INPUT DATA FILE NAME ?'
READ(*,14)FILEIN
WRITE(*,*)'OUTPUT DATA FILE NAME ?'
READ(*,14)FILEOUT
```

```
OPEN(1,FILE=FILEIN,STATUS='OLD')
OPEN(2,FILE=FILEOUT,STATUS='NEW')
```

```
WRITE(*,*)'ENTER COMPOSITION QN, TN'
READ(*,*)Z(1),Z(2)
WRITE(2,198)
WRITE(2,199)
```

```

WRITE(2,201)
WRITE(2,240)Z(1),Z(2)
WRITE(2,250)

```

C CALCULATE REFERENCE DEPARTURE

```

CALL MIX (TREF,AM,DAMDT,BM)
CALL VSATL (PREF,TREF,VREF,AM,BM)
EDREF = HDEP (PREF,VREF,TREF,AM,DAMDT,BM)

```

C CALCULATE ENTHALPY OF EXPERIMENTAL POINTS

```

ERRL=0.
ERRV=0.
NUML=0
NUMV=0

```

1 READ(1,\*,END=100)ISTATE,T,P,HEXP

C CALCULATE IDEAL GAS ENTHALPY CHANGE

```

HIDEAL=0.0
DO 80 I=1,2
DELHID(I)=(HID(I,T)-HID(I,TREF))/0.239
HIDEAL=HIDEAL+Z(I)*DELHID(I)

```

80 CONTINUE

C DETERMINE THE STATE OF THE FLUID, CALCULATE VOLUME &  
C ENTHALPY DEPARTURE

```

IF (ISTATE.EQ.0) THEN
NUML = NUML + 1
CALL MIX (T,AM,DAMDT,BM)
CALL VSATL (P,T,VLIQ,AM,BM)
ED = HDEP (P,VLIQ,T,AM,DAMDT,BM)
HDEPART = ED - EDREF
FLSTATE='liq'
END IF
IF (ISTATE.EQ.1) THEN
NUMV = NUMV + 1
CALL MIX (T,AM,DAMDT,BM)
CALL VSATV (P,T,VVAP,AM,BM)
ED = HDEP (P,VVAP,T,AM,DAMDT,BM)
HDEPART = ED - EDREF
FLSTATE='vap'
END IF

```

IF (ISTATE.EQ.2) GOTO 1

C PREDICT ENTHALPY OF MIXTURE  
HPRED=HIDEAL+HDEPART

```

C CALCULATE AVERAGE MOL.WEIGHT

  AMW=0.0
  DO 90 I=1,2
  AMW=AMW+FM(I)*Z(I)
90 CONTINUE

C CONVERT HPRED UNIT INTO kJ/kg

  HPRED=HPRED/AMW
  ERROR=100.*(HPRED-HEXP)/HEXP
  IF (FLSTATE.EQ.'liq') THEN
  ERRL = ERRL + DABS(ERROR)
  END IF
  IF (FLSTATE.EQ.'vap') THEN
  ERRV = ERRV + DABS(ERROR)
  END IF
  WRITE(2,260)T,P,HPRED,HEXP,ERROR,FLSTATE
  WRITE(*,260)T,P,HPRED,HEXP,ERROR,FLSTATE
  GO TO 1
100 AVERRL = ERRL/NUML
  AVERRV = ERRV/NUMV
  WRITE(2,270)AVERRL,AVERRV
  WRITE(*,*)'CALCULATION ENDS'
198 FORMAT(5X,'m-CRESOL/QUINOLINE')
199 FORMAT(5X,'PHS e.o.s')
201 FORMAT(5X,
  1'COMB.RULE : aij = SQRT(ai.aj)(1-A-B/T)')
240 FORMAT(5X,'COMPOSITION: MC=',F6.4,2X,' QN=',F6.4,/)
250 FORMAT(5X,'T/K',5X,'P/BAR',5X,'HPRED',5X,'HEXP',5X,
  1,'%-ERROR',2X,'STATE',/)
260 FORMAT(5X,F5.1,3X,F6.2,4X,F8.2,2X,F8.2,2X,F7.2,2X,A5)
270 FORMAT(5X,'Ave.liq.err=',F5.2,'% ',/5X,'Ave.vap.err='
  1,F5.2,'%')
  END

```

```

SUBROUTINE MIX (T,AM,DAMDT,BM)
  IMPLICIT DOUBLE PRECISION (A-H,K,O-Z)
  DIMENSION A(3,3),AC(3),ALSP(3),ALNS(3),ALPO(3),ALSP1(3),
  1ALNS1(3),ALPO1(3),B(3),C(3),D(3),DADT(3,3),DELHID(3),
  1PC(3),PI(3),TC(3),TR(3),FM(3),Z(3),RL(3,3),OM(3),OMP(3),
  1CC(3,3),K(3,3),HREF(1)
  CHARACTER*10 FLSTATE,FILEIN,FILEOUT

```

```
COMMON/FRACT/Z
R=0.08314
```

```
C Read the thermodynamic properties of components
```

```
C 1 = m-cresol
C 2 = quinoline
```

```
TC(1) = 705.8
TC(2) = 800.2
PC(1) = 45.6
PC(2) = 57.75
OM(1) = 0.454
OM(2) = 0.316
OMP(1)= 0.449
OMP(2)= 0.22
PI(1) = 0
PI(2) = 63.06
FM(1) = 108.14
FM(2) = 129.16
```

```
C Read the binary interaction parameters
```

```
Q1 = .010716
Q2 = -33.162239
```

```
C CALCULATE ac, b, alsp, alns, alpo & a FOR PURE FLUID
```

```
DO 10 I=1,2
AC(I)=0.49897*(R*TC(I))**2/PC(I)
B(I)=0.17091*R*TC(I)/PC(I)
TR(I)=T/TC(I)
C(I)=0.00632+1.13094*OM(I)-0.03116*OM(I)*OM(I)
D(I)=-0.02312+0.26654*OM(I)-0.28888*OM(I)*OM(I)
IF (OMP(I).NE.0) THEN
C(I)=0.00632+1.13094*OMP(I)-0.03116*OMP(I)*OMP(I)
D(I)=-0.02312+0.26654*OMP(I)-0.28888*OMP(I)*OMP(I)
END IF
ALSP(I)=1.-0.244797*(1-TR(I))+0.16047*(1-TR(I))**2.7)
ALNS(I)=1.+C(I)*(1.-TR(I))+D(I)*(1.-TR(I))**2
ALPO(I)=1+PI(I)*(DEXP(-PI(I)**.48)-DEXP(-(PI(I)/TR(I))
1**48))
ALSP1(I)=0.244797/TC(I)-.433269*T**1.7/TC(I)**2.7
ALNS1(I)=-C(I)/TC(I)-2*D(I)/TC(I)*(1-TR(I))
IF (PI(I).EQ.0) THEN
ALPO1(I)=0
GOTO 10
ENDIF
ALPO1(I)=-.48*PI(I)**2*TC(I)*DEXP(-(PI(I)/TR(I))**.48)/
```

```

      1(T**2*(PI(I)/TR(I))**.52)
10  CONTINUE

      C CALCULATE a AND dadT FOR PURE FLUID

      DO 30 I=1,2
      DO 20 J=1,2
      IF (I.EQ.J) THEN
      A(I,J)=AC(I)*ALSP(I)*ALNS(I)*ALPO(I)
      DADT(I,J)=AC(I)*(ALSP(I)*(ALNS(I)*ALPO1(I)+ALNS1(I)*
1ALPO(I))+ALSP1(I)*ALNS(I)*ALPO(I))
      END IF
20  CONTINUE
30  CONTINUE

      C CALCULATE a AND dadT FOR CROSS TERMS

      DO 50 I=1,2
      DO 40 J=1,2
      IF (I.NE.J) THEN
      A(I,J)=DSQRT(A(I,I)*A(J,J))*(1-Q1-Q2/T)
      DADT(I,J)=0.5*(DADT(I,I)*A(J,J)+DADT(J,J)*A(I,I))/
1DSQRT(A(I,I)*A(J,J))*(1-Q1-Q2/T)+DSQRT(A(I,I)*A(J,J))*
1Q2/T**2
      END IF
40  CONTINUE
50  CONTINUE

      C CALCULATE a and b FOR TERNARY MIXTURE

      AM=0.0
      DAMDT=0.0
      BM=0.0
      DO 70 I=1,3
      DO 60 J=1,3
      AM=AM+Z(I)*Z(J)*A(I,J)
      DAMDT=DAMDT+Z(I)*Z(J)*DADT(I,J)
60  CONTINUE
      BM=BM+Z(I)*B(I)
70  CONTINUE
      RETURN
      END

```

```

FUNCTION HDEP(P,V,T,AM,DAMDT,BM)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

```

```

R=0.08314

```

## C CALCULATE ENTHALPY DEPARTURE

```

HDEP=(1.50756*(AM-T*DAMDT)*DLOG((10.*V-2.3166*BM)/(10.*V+
14.3166*BM)))/BM+P*V-R*T)*100
RETURN
END

```

```

FUNCTION HID(ICOMP,T)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION CF(3,7)
COMMON/IDEAL/CF

```

```

I=ICOMP

```

## C CALCULATE IDEAL GAS ENTHALPY

```

HID=CF(I,1)*T+CF(I,2)*CF(I,3)/DTANH(CF(I,3)/T)-CF(I,4)
1*CF(I,5)*DTANH(CF(I,5)/T)+CF(I,6)*CF(I,7)/DTANH(CF(I,7)/T)
RETURN
END

```

```

SUBROUTINE VSATL (P,T,VF,A,B)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

```

```

R=0.08314
V=0.30*B
ITER=0

```

```

10 IF (ITER.GT.75) THEN
WRITE(*,100)
STOP
END IF

```

```

FV=- (64*R*T*V**3+16*B*R*T*V**2+4*B**2*R*T*V-B**3*R*T)/
1(64*V**4-48*B*V**3+12*B**2*V**2-B**3*V)+A/(V**2+0.2*B*
1V-0.1*B**2)+P
DFDV=- (192*R*T*V**2+32*B*R*T*V+4*B**2*R*T)/(64*V**4-48

```

```

1*B*V**3+12*B**2*V**2-B**3*V)+(256*V**3-144*B*V**2+24*B
1**2*V-B**3)*(64*R*T*V**3+16*B*R*T*V**2+4*B**2*R*T*V-B*
1*3*R*T)/(64*V**4-48*B*V**3+12*B**2*V**2-B**3*V)**2-A*(
12*V+0.2*B)/(V**2+0.2*B*V-0.1
1*B**2)**2

```

```

ITER=ITER+1
VNEW=V-FV/DFDV
DEV=(V-VNEW)/V

```

```

IF (DABS(DEV).GT.0.0001) THEN
V=VNEW
GOTO 10
END IF

```

```

IF (DABS(FV).GT.0.0001) THEN
V=VNEW
GOTO 10
END IF

```

```

IF (VNEW.LE.0.0) THEN
WRITE(*,220)
STOP
END IF
VF=VNEW

```

```

RETURN
100 FORMAT(5X,'ITERATION EXCEEDS 75')
220 FORMAT(5X,'Zero or negative liquid volume')
END

```

```

SUBROUTINE VSATV (P,T,VF,A,B)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

```

```

R=0.08314

```

```

AA=A*P/(R**2)/(T**2)
BB=B*P/R/T
ITERV=0
Z=1.

```

```

10 IF (ITERV.GT.75) THEN
WRITE(*,20)
STOP
END IF
T5 = -(11*BB+20)/20.0

```

```
T4 = -(5*BB**2+36*BB-80*AA)/80.0
T3 = (31*BB**3-4*BB**2-240*AA*BB)/320.0
T2 = -(7*BB**4-9*BB**3-60*AA*BB**2)/320.0
T1 = (BB**5+6*BB**4-10*AA*BB**3)/640.0
T0 = -BB**5/640.0
FZ = Z**6+T5*Z**5+T4*Z**4+T3*Z**3+T2*Z**2+T1*Z+T0
DFDZ = 6*Z**5+5*T5*Z**4+4*T4*Z**3+3*T3*Z**2+2*T2*Z+T1
ITERV=ITERV+1
ZNEW=Z-FZ/DFDZ
DEL=Z-ZNEW

IF (DABS(DEL).GT.0.0001) THEN
Z=ZNEW
GO TO 10
END IF

IF (DABS(FZ).GT.0.0001) THEN
Z=ZNEW
GO TO 10
END IF
IF (ZNEW.LE.0.0) THEN
WRITE(*,240)
STOP
END IF
VF=ZNEW*R*T/P
RETURN
20  FORMAT (5X,'ITERATION EXCEEDS 75')
240  FORMAT(5X,'Zero or negative vapor volume')
END
```

This program calculates the enthalpy of a ternary mixture of fluid using perturbed hardsphere e.o.s. with mixing rule as the following :

$$a_{ij} = \text{SQRT}(a_i a_j)(1 - k_{ij} + (k_{ij} - k_{ji})X_i + C/T)$$

```

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION DELHID(3),Z(3),FM(3),RL(3,7),TC(3),PC(3),OM(3),
1OMP(3),PI(3),KD(3),K(3,3),C(3,3),DT(3,3),X(3),XR(3),Y(3),
1YR(3)

```

```

CHARACTER*20 FILEIN,FILEOUT
COMMON/IDEAL/RL
COMMON/PAR/TC,PC,OM,OMP,PI,K,C,FM

```

```

R=0.08314

```

```

C Read the reference state

```

```

TREF=291.48
PREF=1.013

```

```

C Read the coefficients for ideal enthalpies calculation

```

```

C      1 = m-cresol
C      2 = quinoline
C      3 = tetralin

```

```

RL(1,1)=19.5818
RL(1,2)=20.6896
RL(1,3)=1838.02
RL(1,4)=8927.76
RL(1,5)=-0.159817
RL(1,6)=47.5601
RL(1,7)=689.349

```

```

RL(2,1)=19.1643
RL(2,2)=19.9861
RL(2,3)=1839.59
RL(2,4)=9892.70
RL(2,5)=-0.157905
RL(2,6)=57.3143
RL(2,7)=701.587

```

```

RL(3,1)=22.5788
RL(3,2)=31.9281
RL(3,3)=1838.38
RL(3,4)=10095.8
RL(3,5)=-0.179849
RL(3,6)=71.1577
RL(3,7)=714.318

```

C Read the thermodynamic properties of components

```
TC(1) = 705.8
TC(2) = 800.2
TC(3) = 719.2
PC(1) = 45.6
PC(2) = 57.75
PC(3) = 35.15
OM(1) = 0.454
OM(2) = 0.316
OM(3) = 0.327
OMP(1)= 0.449
OMP(2)= 0.22
OMP(3)= 0.31
PI(1) = 0
PI(2) = 63.06
PI(3) = 0.056
FM(1) = 108.14
FM(2) = 129.16
FM(3) = 132.21
```

C Read the binary interaction parameters

```
C(1,2)=0.01426
C(2,1)=C(1,2)
C(1,3)=-.01335
C(3,1)=C(1,3)
C(2,3)=0.00566
C(3,2)=C(2,3)
K(1,2)=-.033337
K(2,1)=-.073304
K(1,3)= .017015
K(3,1)= .016764
K(2,3)=-.016710
K(3,2)=-.016808
```

C Read the experimental data

14 FORMAT(A20)

```
WRITE(*,*)'INPUT DATA FILE NAME ?'
READ(*,14)FILEIN
WRITE(*,*)'OUTPUT DATA FILE NAME ?'
READ(*,14)FILEOUT
```

```
OPEN(1,FILE=FILEIN,STATUS='OLD')
OPEN(2,FILE=FILEOUT,STATUS='NEW')
WRITE(*,*)'ENTER COMPOSITION QN, TN'
READ(*,*)Z(1),Z(2),Z(3)
```

```

WRITE(2,198)
WRITE(2,199)
WRITE(2,201)
WRITE(2,240)Z(1),Z(2),Z(3)
WRITE(2,250)

```

C Calculate reference departure

```

CALL MIX (Z,TREF,AM,DAMDT,BM)
CALL VSATL (PREF,TREF,VREF,AM,BM)
EDREF = HDEP (PREF,VREF,TREF,AM,DAMDT,BM)

```

```

ERRL=0
ERRV=0
NUML=0
NUMV=0

```

```

1 READ(1,*,END=100)T,HEXP,P,ISTATE
P=P/100

```

C Calculate the delta enthalpy as ideal gas

```

HIDEAL=0.0
DO 80 I=1,2
DELHID(I)=(HID(I,T)-HID(I,TREF))/0.239
HIDEAL=HIDEAL+Z(I)*DELHID(I)
80 CONTINUE

```

C Determine the state of fluid and calculate the enthalpy  
C departure

```

IF (ISTATE.EQ.1) THEN
NUML = NUML + 1
CALL MIX (Z,T,AM,DAMDT,BM)
CALL VSATL (P,T,VLIQ,AM,BM)
ED = HDEP (P,VLIQ,T,AM,DAMDT,BM)
HDEPART = ED - EDREF
FLSTATE='liq'
GOTO 101
END IF

```

```

IF (ISTATE.EQ.2) THEN
NUMV = NUMV + 1
CALL MIX (Z,T,AM,DAMDT,BM)
CALL VSATV (P,T,VVAP,AM,BM)
ED = HDEP (P,VVAP,T,AM,DAMDT,BM)
HDEPART = ED - EDREF
FLSTATE='vap'
GOTO 101

```

```

ENDIF

IF (ISTATE.EQ.0) THEN

C Using Raoults Law estimate the coef. of separation

DO I=1,3
KD(I)=PC(I)*DEXP(-7*(1+OM(I))*(TC(I)/T-1)*DLOG(DFLOAT(10))
1/3)/P
ENDDO

C Calculate the fraction of the vapor phase (P,T FLASH)

500 VP=1
FV=0
SY=0
SYR=0
GV=0
IT=0
501 DO I=1,3
FV=FV+Z(I)/(1+VP*(KD(I)-1))
GV=GV+Z(I)*(KD(I)-1)/(1+VP*(KD(I)-1))**2
ENDDO
IT=IT+1
VPN=VP+(FV-1)/GV
IF (DABS(VPN-VP).GT..001) THEN
VP=VPN
GOTO 501
ENDIF
DO I=1,3
X(I)=Z(I)/(1+VP*(KD(I)-1))
Y(I)=KD(I)*X(I)
SY=SY+Y(I)
ENDDO
IF(IT.GT.1)THEN
IF(DABS(SY-SYR).LT..003)THEN
GOTO 502
ENDIF
ENDIF
DO I=1,3
XR(I)=X(I)
YR(I)=Y(I)
SYR=SYR+YR(I)
ENDDO
CALL FUGC(T,XR,YR,K,C,P,TC,PC,OMP,PI,KD)
GOTO 500

502 CALL MIX (Y,T,AM,DAMDT,BM)
CALL VSATV (P,T,VVAP,AM,BM)

```

```

EDV = HDEP (P,VVAP,T,AM,DAMDT,BM)
HDEPARTV = EDV - EDREF
CALL MIX (X,T,AM,DAMDT,BM)
CALL VSATL (P,T,VLIQ,AM,BM)
EDL = HDEP (P,VLIQ,T,AM,DAMDT,BM)
HDEPARTL = EDL - EDREF
HDEPART = VP*HDEPARTV + (1-VP)*HDEPARTL
ENDIF

101 HPRED=HIDEAL+HDEPART

  C Calculate the average molecular weight

  AMW=0.0
  FM(1)=108.14
  FM(2)=129.16
  FM(3)=132.21
  DO 90 I=1,2
  AMW=AMW+FM(I)*Z(I)
90 CONTINUE

  C Convert the unit of enthalpy to KJ/Kg

  HPRED=HPRED/AMW

  ERROR=100.*(HPRED-HEXP)/HEXP
  IF (FLSTATE.EQ.'liq') THEN
  ERRL = ERRL + DABS(ERROR)
  END IF
  IF (FLSTATE.EQ.'vap') THEN
  ERRV = ERRV + DABS(ERROR)
  END IF
  WRITE(2,260)T,P,HPRED,HEXP,ERROR,FLSTATE
  WRITE(*,260)T,P,HPRED,HEXP,ERROR,FLSTATE
  GO TO 1
100 AVERRL = ERRL/NUML
  AVERRV = ERRV/NUMV
  WRITE(2,270)AVERRL,AVERRV
  WRITE(*,*)'CALCULATION ENDS'

198 FORMAT(5X,'m-CRESOL/QUINOLINE/TETRALIN')
199 FORMAT(5X,'PHS e.o.s')
201 FORMAT(5X,
  1'COMB.RULE : aij = SQRT(ai.aj)(1-kij+(kij-kji)Xi+C/T)')
240 FORMAT(5X,'COMPOSITION: MC=',F6.4,2X,' QN=',F6.4,
  1 TN=',F6.4,
  1/)
250 FORMAT(5X,'T/K',5X,'P/BAR',5X,'HPRED',5X,'HEXP',5X,
  1'%-ERROR',2X,'STATE',/)

```

```

260 FORMAT(5X,F5.1,3X,F6.2,4X,F8.2,2X,F8.2,2X,F7.2,2X,A5)
270 FORMAT(5X,'Ave.liq.err=',F5.2,'% ',/5X,'Ave.vap.err=',F5.2,
1 '%')
END

```

```

SUBROUTINE MIX (Z,T,AM,DAMDT,BM)
IMPLICIT DOUBLE PRECISION (A-H,K,O-Z)
DIMENSION A(3,3),AC(3),ALSP(3),ALNS(3),ALPO(3),ALSP1(3),
1ALNS1(3),ALPO1(3),B(3),D(3),DADT(3,3),DELHID(3),HREF(1),
1PC(3),PI(3),TC(3),TR(3),FM(3),Z(3),RL(3,3),OM(3),OMP(3),
1CC(3,3),K(3,3),C(3,3),CP(3)
CHARACTER*10 FLSTATE,FILEIN,FILEOUT
COMMON/PAR/TC,PC,OM,OMP,PI,K,C,FM

```

```
R=0.08314
```

```
C CALCULATE ac, b, alsp, alns, alpo & a FOR PURE FLUID
```

```

DO 10 I=1,3
  AC(I)=0.49897*(R*TC(I))**2/PC(I)
  B(I)=0.17091*R*TC(I)/PC(I)
  TR(I)=T/TC(I)
  CP(I)=0.00632+1.13094*OM(I)-0.03116*OM(I)*OM(I)
  D(I)=-0.02312+0.26654*OM(I)-0.28888*OM(I)*OM(I)
  IF (OMP(I).NE.0) THEN
    CP(I)=0.00632+1.13094*OMP(I)-0.03116*OMP(I)*OMP(I)
    D(I)=-0.02312+0.26654*OMP(I)-0.28888*OMP(I)*OMP(I)
  END IF
  ALSP(I)=1.-0.244797*(1-TR(I))+0.16047*(1-TR(I)**2.7)
  ALNS(I)=1.+CP(I)*(1.-TR(I))+D(I)*(1.-TR(I))**2
  ALPO(I)=1+PI(I)*(DEXP(-PI(I)**.48)-DEXP(-(PI(I)/TR(I))
1 **.48))
  ALSP1(I)=0.244797/TC(I)-.433269*T**1.7/TC(I)**2.7
  ALNS1(I)=-CP(I)/TC(I)-2*D(I)/TC(I)*(1-TR(I))
  IF (PI(I).EQ.0) THEN
    ALPO1(I)=0
    GOTO 10
  ENDIF
  ALPO1(I)=-.48*PI(I)**2*TC(I)*DEXP(-(PI(I)/TR(I))**.48)/
1 (T**2*(PI(I)/TR(I))**.52)
10 CONTINUE

```

```
C Calculate a and dadT for the pure component
```

```

DO 30 I=1,3
DO 20 J=1,3
  IF (I.EQ.J) THEN
    A(I,J)=AC(I)*ALSP(I)*ALNS(I)*ALPO(I)
    DADT(I,J)=AC(I)*(ALSP(I)*(ALNS(I)*ALPO1(I)+ALNS1(I)*
1    ALPO(I))+ALSP1(I)*ALNS(I)*ALPO(I))
  END IF
20 CONTINUE
30 CONTINUE

```

C Calculate a and dadT for the cross terms

```

DO 50 I=1,3
DO 40 J=1,3
  IF (I.NE.J) THEN
    A(I,J)=DSQRT(A(I,I)*A(J,J))*(1-K(I,J)+(K(I,J)-K(J,I))
1    )*Z(I)+C(I,J)/T
    DADT(I,J)=0.5*(DADT(I,I)*A(J,J)+DADT(J,J)*A(I,I))/
1    DSQRT(A(I,I)*A(J,J))*(1-K(I,J)+(K(I,J)-K(J,I))*Z(I)+
1    C(I,J)/T)-DSQRT(A(I,I)*A(J,J))*C(I,J)/T**2
  END IF
40 CONTINUE
50 CONTINUE

```

C Calculate a and b for mixture

```

AM=0.0
DAMDT=0.0
BM=0.0
DO 70 I=1,3
DO 60 J=1,3
  AM=AM+Z(I)*Z(J)*A(I,J)
  DAMDT=DAMDT+Z(I)*Z(J)*DADT(I,J)
60 CONTINUE
BM=BM+Z(I)*B(I)
70 CONTINUE
RETURN
END

```

```

FUNCTION HDEP(P,V,T,AM,DAMDT,BM)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

```

```

R=0.08314

```

C Calculation for the enthalpy departure

```

HDEP=(1.50756*(AM-T*DAMDT)*DLOG((10.*V-2.3166*BM)/(10.*V+
14.3166*BM)))/BM+P*V-R*T)*100
RETURN
END

```

```

FUNCTION HID(ICOMP,T)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION CF(3,7)
COMMON/IDEAL/CF

```

```

I=ICOMP

```

C Calculation of the pure component enthalpy as ideal gas

```

HID=CF(I,1)*T+CF(I,2)*CF(I,3)/DTANH(CF(I,3)/T)-CF(I,4)
1*CF(I,5)*DTANH(CF(I,5)/T)+CF(I,6)*CF(I,7)/DTANH(CF(I,7)/T)
RETURN
END

```

```

SUBROUTINE FUGC(T,X,Z,K,C,P,TC,PC,ACCN,RP,KD)

```

C This subroutine calculates the fugacity coefficients of  
C each components in the vapor phase and in the liq.phase.

```

PARAMETER CC=0.48,R=.0831434,UU=.2,WW=-.1,E=.6633
IMPLICIT DOUBLE PRECISION (A-H,K,P-Z)
DIMENSION X(3),Z(3),K(3,3),C(3,3),TC(3),PC(3),ACCN(3),
1FUGV(3),FUGL(3),KD(3),TR(3),PR(3),SMA(3),SMB(3),SMAC(3),
1ALPHAS(3),ALPHAN(3),ALPHAP(3),CCC(3),DDD(3),A(3,3),AIM(3),
1DT(3,3),RP(3)

```

C Calculate the reduced temperatures and pressures

```

DO I=1,3
TR(I)=T/TC(I)
PR(I)=P/PC(I)

```

C Calculate the critical parameters of the pure components  
C and alpha parameters.

```

SMB(I)=(0.17091*R*TC(I))/PC(I)
SMAC(I)=0.49897*R**2*TC(I)**2/PC(I)
ALPHAS(I)=1.-0.244797*(1.-TR(I))+0.16047*(1.-TR(I)**2.7)
CCC(I)=0.00632+1.13094*ACCN(I)-0.03116*ACCN(I)**2
DDD(I)=-0.02312+0.26654*ACCN(I)-0.28888*ACCN(I)**2
ALPHAN(I)=1.+CCC(I)*(1.-TR(I))+DDD(I)*(1.-TR(I)**2)
ALPHAP(I)=1.+RP(I)*(DEXP(-RP(I)**CC)-DEXP(-(RP(I)*TC(I)/T)
1 **CC))
SMA(I)=SMAC(I)*ALPHAS(I)*ALPHAN(I)*ALPHAP(I)
ENDDO

```

C Calculate the mixture parameter of the liquid phase

```

AMIX=0
BMIX=0
DO 20 I=1,3
BMIX=BMIX+X(I)*SMB(I)
DO 10 J=1,3
A(I,J)=((SMA(I)*SMA(J))**0.5)*(1-K(I,J)+(K(I,J)-K(J,I))
1 *X(I)
1 +C(I,J)/T)
AMIX=AMIX+X(I)*X(J)*A(I,J)
10 CONTINUE
20 CONTINUE

```

C Calculate the fugacity coefficients in the liquid phase

```

CALL VSATL (P,T,VL,AMIX,BMIX)

DO 40 I=1,3
AIM(I)=0
DO 30 J=1,3
IF(I.EQ.J)THEN
DT(I,J)=1
ELSE
IF(I.NE.J)THEN
DT(I,J)=0
ENDIF
ENDIF
AIM(I)=AIM(I)+X(I)*(A(I,J)+A(J,I))+X(I)*X(J)*DSQRT(SMA(I)*
1SMA(J))*(K(I,J)-K(J,I))*(DT(I,J)-X(J))
F=DLOG((2*VL-E*BMIX+UU*BMIX)/(2*VL+E*BMIX+UU*BMIX))
30 CONTINUE
40 CONTINUE

DO I=1,3
FUGL(I)=(16*BMIX*VL-3*BMIX**2)/(16*VL**2-8*BMIX*VL+BMIX
1**2)+SMB(I)*(256*VL**2-32*BMIX*VL)/(4*(64*VL**3-48*BMIX

```

```

1*VL**2+12*BMIX**2*VL-BMIX**3))+
1AIM(I)*F/(BMIX*R*T*E)-AMIX*SMB(I)/(R*T)*(VL/(WW*BMIX**3
1+BMIX*VL**2+UU*VL*BMIX**2)+F/(BMIX**2*E))
1-DLOG((P*VL)/(R*T))
  FUGL(I)=DEXP(FUGL(I))
  ENDDO

```

C Calculate the mixture parameter of the vapour phase

```

  AVIX=0
  BVIX=0
  DO 60 I=1,3
  BVIX=BVIX+Z(I)*SMB(I)
  DO 50 J=1,3
  A(I,J)=((SMA(I)*SMA(J))**0.5)*(1-K(I,J)+(K(I,J)-K(J,I)))
1  *Z(I)
  1+C(I,J)/T)
  AVIX=AVIX+Z(I)*Z(J)*A(I,J)
50  CONTINUE
60  CONTINUE

```

C Calculate the fugacity coefficients in the vapour phase

```

  CALL VSATV (P,T,VV,AVIX,BVIX)

  DO 80 I=1,3
  AIM(I)=0
  DO 70 J=1,3
  IF(I.EQ.J)THEN
    DT(I,J)=1
  ELSE
    IF(I.NE.J)THEN
      DT(I,J)=0
    ENDIF
  ENDIF
  AIM(I)=AIM(I)+Z(I)*(A(I,J)+A(J,I))+Z(I)*Z(J)*DSQRT(SMA(I)*
1SMA(J))*(K(I,J)-K(J,I))*(DT(I,J)-Z(J))
  F=DLOG((2*VV-E*BVIX+UU*BVIX)/(2*VV+E*BVIX+UU*BVIX))
70  CONTINUE
80  CONTINUE

  DO I=1,3
  FUGV(I)=(16*BVIX*VV-3*BVIX**2)/(16*VV**2-8*BVIX*VV+BVIX
1**2)+SMB(I)*(256*VV**2-32*BVIX*VV)/(4*(64*VV**3-48*BVIX
1*VV**2+12*BVIX**2*VV-BVIX**3))+
1AIM(I)*F/(BVIX*R*T*E)-AVIX*SMB(I)/(R*T)*(VV/(WW*BVIX**3
1+BVIX*VV**2+UU*VV*BVIX**2)+F/(BVIX**2*E))
  1-DLOG((P*VV)/(R*T))
  FUGV(I)=DEXP(FUGV(I))

```

ENDDO

C Calculate the coef. of separations

```
DO I=1,3
KD(I)=FUGL(I)/FUGV(I)
ENDDO
```

```
RETURN
END
```

```
SUBROUTINE VSATL (P,T,VF,A,B)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
```

```
R=0.08314
V=0.30*B
ITER=0
10 IF (ITER.GT.75) THEN
WRITE(*,100)
STOP
END IF
FV=- (64*R*T*V**3+16*B*R*T*V**2+4*B**2*R*T*V-B**3*R*T)/
1/(64*V**4-48*B*V**3+12*B**2*V**2-B**3*V)+A/(V**2+0.2*B
1*V-0.1*B**2)+P
DFDV=- (192*R*T*V**2+32*B*R*T*V+4*B**2*R*T)/(64*V**4-48
1*B*V**3+12*B**2*V**2-B**3*V)+(256*V**3-144*B*V**2+24*B
1**2*V-B**3)*(64*R*T*V**3+16*B*R*T*V**2+4*B**2*R*T*V-B*
1*3*R*T)/(64*V**4-48*B*V**3+12*B**2*V**2
1-B**3*V)**2-A*(2*V+0.2*B)/(V**2+0.2*B*V-0.1
1*B**2)**2
ITER=ITER+1
VNEW=V-FV/DFDV
DEV=(V-VNEW)/V
IF (DABS(DEV).GT.0.0001) THEN
V=VNEW
GOTO 10
END IF
IF (DABS(FV).GT.0.0001) THEN
V=VNEW
GOTO 10
END IF
IF (VNEW.LE.0.0) THEN
```

```

        WRITE(*,220)
        STOP
    END IF
    VF=VNEW
    RETURN
100 FORMAT(5X,'ITERATION EXCEEDS 75')
220 FORMAT(5x,'Zero or negative liquid volume')
    END

```

```

SUBROUTINE VSATV (P,T,VF,A,B)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

R=0.08314

AA=A*P/(R**2)/(T**2)
BB=B*P/R/T
ITERV=0
Z=1.
10 IF (ITERV.GT.75) THEN
    WRITE(*,20)
    STOP
    END IF
    T5 = -(11*BB+20)/20.0
    T4 = -(5*BB**2+36*BB-80*AA)/80.0
    T3 = (31*BB**3-4*BB**2-240*AA*BB)/320.0
    T2 = -(7*BB**4-9*BB**3-60*AA*BB**2)/320.0
    T1 = (BB**5+6*BB**4-10*AA*BB**3)/640.0
    T0 = -BB**5/640.0
    FZ = Z**6+T5*Z**5+T4*Z**4+T3*Z**3+T2*Z**2+T1*Z+T0
    DFDZ = 6*Z**5+5*T5*Z**4+4*T4*Z**3+3*T3*Z**2+2*T2*Z+T1
    ITERV=ITERV+1
    ZNEW=Z-FZ/DFDZ
    DEL=Z-ZNEW
    IF (DABS(DEL).GT.0.0001) THEN
        Z=ZNEW
        GO TO 10
    END IF
    IF (DABS(FZ).GT.0.0001) THEN
        Z=ZNEW
        GO TO 10
    END IF
    IF (ZNEW.LE.0.0) THEN
        WRITE(*,240)

```

```
      STOP
    END IF
    VF=ZNEW*R*T/P
    RETURN
20  FORMAT (5X, 'ITERATION EXCEEDS 75')
240 FORMAT(5x, 'Zero or negative vapor volume')
    END
```