

DETERMINING EQUATION OF STATE BINARY INTERACTION PARAMETERS USING K- AND L- POINTS

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ABSTRACT

The knowledge of the phase behaviour of heavy oils and bitumen is important in order to understand the phenomenon of coke formation. Computation of their phase behaviour, using an equation of state, faces problems due to their complex composition. Hence n-alkane binaries of polyaromatic hydrocarbons are used to approximate the phase behaviour of heavy oils and bitumen. Appropriate values of binary interaction parameters are required for an equation of state to predict the correct phase behaviour of these model binary fluids.

This thesis deals with fitting of the binary interaction parameter for the Peng-Robinson equation of state using landmarks in the binary phase space such as K- and L-points. A K- or an L-point is a point in the phase space where two phases become critical in the presence of another phase in equilibrium. An algorithm to calculate K- and L-points using an equation of state was developed. The variation of calculated K- and L-points with respect to the binary interaction parameter was studied and the results were compared with the experimental data in the literature. The interaction parameter was then fitted using the best match of experimental results with the computed ones. The binary interaction parameter fitted using a K- or an L-point was then used to predict the P - T projection of the binary system in phase space. Also, the qualitative effect of the binary interaction parameter on the P - T projection was studied.

A numerical and thermodynamic study of the algorithm was done. Numerical issues like the initial guesses, convergence criterion and numerical techniques were studied and the thermodynamic constraints in the generalization of the algorithm are discussed. It was observed that the binary interaction parameter not only affects the

location of K- and L-points in the phase space but also affects the calculation procedure of K- and L-points.

Along with the propane binaries of polyaromatic hydrocarbons, K- and L-points were also calculated for systems like methane binaries of higher n-alkanes and the ethane + ethanol binary. In the case of the ethane + ethanol system, K- and L-points, matching the experimental results were calculated with different values of the binary interaction parameter. But the Peng-Robinson equation of state was unable to predict the correct type of phase behaviour using any value of the binary interaction parameter.

The Peng-Robinson equation of state was able to predict the correct type of phase behaviour with the binary interaction parameter, fitted using K- and/or L-points for methane + n-alkane systems. The systems studied were the methane binaries of n-pentane, n-hexane and n-heptane.

For the propane binaries of polyaromatic hydrocarbons, no value of the binary interaction parameter was able to predict the K-point with a good accuracy. The binary interaction parameter which gave the best possible results for a K-point failed to predict the correct type of phase behaviour. The binary interaction parameter fitted using the P - T projection enabled the Peng-Robinson equation of state to give a qualitative match for the high pressure complex phase behaviour of these systems. Solid phase equilibria were not taken into consideration.

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DEDICATED TO,

My Family.

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NOMENCLATURE

a	Temperature dependant energy parameter of equation of state (Pa.m ⁶ /mol ²)
A	Helmholtz free energy (J/mol)
a'	Expansion coefficient for tangent plane distance
b	Co-volume parameter of equation of state (m ³ /mol)
\mathbf{B}	Hessian matrix in critical point calculations
B_{ij}	Element of \mathbf{B}
b'	Expansion coefficient for tangent plane distance
C	Cubic form of the Taylor series expansion of Helmholtz energy
c'	Expansion coefficient for tangent plane distance
C_1, C_2, C_3	Coefficients in Nishiumi's correlation
c_1^1, c_1^2, \dots	Constants in Nishiumi's correlation
CN	Carbon number
D	Vertical distance from the tangent to the Gibbs energy surface at the test phase composition to the Gibbs energy surface at a different composition
d'	Expansion coefficient for tangent plane distance
DF	Degree of freedom
e'	Expansion coefficient for tangent plane distance
F	Tangent plane distance
f_i	Fugacity of component i (Pa)

f'	Expansion coefficient for tangent plane distance
G	Gibbs free energy (J/mol)
\mathbf{g}	Function to be solved in equilibrium phase calculations
g_i	Element of \mathbf{g}
$\hat{\mathbf{g}}$	Gradient of F in \mathbf{X}
\hat{g}_i	Element of $\hat{\mathbf{g}}$
\mathbf{J}	Laplacian of G/RT
\mathbf{J}'	Matrix defined by equation (A.10), for three-phase line calculation
\mathbf{k}	Composition vector in the implementation of tangent plane criterion by Michelsen
k_i	Element of \mathbf{k}
\mathbf{k}_s	Composition vector at stationary point
K_i	Un-normalized mole fraction in the implementation of tangent plane criterion by Michelsen
L	A constant, representing the stationary value
\mathbf{m}	Composition vector of the test phase
m_i	Element of \mathbf{m}
M_i	Molecular weight of component i (gm/mol)
\mathbf{M}'	Matrix defined in equation
\mathbf{n}	Mole number vector
n_i	Number of moles of the i^{th} component

$\hat{\mathbf{n}}$	Vector representing trial phase mole numbers in critical point calculations
\hat{n}_i	Element of $\hat{\mathbf{n}}$
NC	Number of components
NP	Number of phases
P	Pressure (Pa)
Q	Four-phase point
\mathbf{Q}	Matrix in the quadratic form of expansion of A
Q	Determinant of \mathbf{Q}
\mathbf{q}	Coefficient in expansion of \mathbf{X}
q_1, q_2, \backslash	Parameters in the relation given by Kordas et al. for estimating binary interaction parameters
q_{ij}	Element of \mathbf{Q}
q_1^1, q_1^2, \backslash	Constants needed to evaluate q_1, q_2, \backslash
R	Gas constant (J/mol.K)
\mathbf{r}	Mole number vector
r_i	Element of \mathbf{r}
s	Distance parameter
T	Temperature (K)
\mathbf{u}	Coefficient in expansion of \mathbf{X}
U	Internal energy (J/mol)
v	Molar volume (m ³ /mol)
\mathbf{w}	Coefficient in expansion of \mathbf{X}

x_i	mole fraction of component i
\mathbf{X}	Translated mole number vector in critical point calculation
X_i	Element of \mathbf{X}
\mathbf{y}	Normalized mole fraction vector
y_1, y_2, \dots	Elements of \mathbf{y}
\mathbf{Y}	Un-normalized mole fraction vector
Y_1, Y_2, \dots	Elements of \mathbf{Y}
\mathbf{z}	Critical phase composition vector
z_i	Element of \mathbf{z}
Z_c	Compressibility at critical point

Greek Symbols

α	Dimensionless function of the reduced temperature and acentric factor
β_1, \dots, β_8	Equations to be solved for a three-phase point
γ	Lagrangian multiplier in critical point calculations
δ_{ij}	Binary interaction parameter for components i and j
ε	Number of moles
ϕ_i	Fugacity coefficient of component i
ϕ_{ij}	Binary interaction parameter for components i and j
κ	Characteristic constant of a substance
λ	Acceleration factor for successive substitution method
μ_i	Chemical potential of component i (J/mol)
π	Parameter in three-phase line calculation

θ	Dimensionless tangent plane distance
ρ_i	Parameter in Peterson's correlation
σ_{ij}	Kronecker delta
ς	Parameter in three-phase line calculation
ω	Acentric factor
ψ_i	Component deviation coefficient for component i

Subscripts and Superscripts

c	Critical
$crit$	Critical
i, j, k, \backslash	Component indices
F_{m+}	Heaviest fraction
m	Mixture property
O	Test phase
s	Stationary point
r	Reduced
ref	Reference phase
T	Total

1. INTRODUCTION

In a petroleum refinery, fractionation is the first step in the process of refining crude oil. Lighter fractions like gasoline, kerosene and diesel fuel are further processed to improve upon their quality and the heavier fractions are processed to get lubricants and waxes. Heavy oils and bitumen are the bottom products. Since the flexibility and the adaptability of catalytic cracking enables a refiner to maximize the yield of desired products like gasoline from diverse, low-value feedstocks, the heavy oils and bitumen undergo catalytic cracking. This cracking process helps the refinery, operate with higher profits and hence it is the heart of a modern petroleum refinery. But the catalytic cracking catalyst can deactivate very quickly due to coke formation. Although coke formation depends on the feedstock nature and catalyst properties, it has been found that at normal operating conditions (700-800 K and 1-3 MPa), primarily polyaromatic coke is produced (Guisnet et al., 2001).

1.1. Purpose

Regeneration or replacement of a catalyst in the catalytic process contributes to the capital and operating cost of the unit and also affects the efficiency of the process, and thus the quality of final product. In order to get a better insight into the phenomenon of coke formation, particularly the polyaromatic coke, understanding the physical and chemical changes at appropriate operating conditions is essential. From the

physical change point of view, knowledge of the phase behaviour of heavy oils and bitumen, under operation conditions will prove beneficial.

Experimental study of the phase behaviour of heavy oils and bitumen at elevated temperature and pressure conditions may face some hurdles on the technological and financial fronts. Mathematical modeling, if done successfully, will be very useful in this context. An equation of state can be used to model the phase behaviour of these heavy fractions, but their complex composition, which is mostly unknown, poses difficulty in modeling. A binary system of a polyaromatic hydrocarbon with an n-alkane, polyaromatic hydrocarbons being the precursor to coke, can be thought of as a model fluid to approximate the phase behaviour of heavy oils and bitumen. Hence successful modeling of the phase behaviour of these model fluids is a preliminary step towards successful modeling of heavy oils.

Use of a cubic equation of state requires appropriate values of empirical parameters, called *Binary Interaction Parameters*, in the equation of state. Different methods have been suggested in the literature to calculate binary interaction parameters, but the interaction parameters calculated using those methods may fail to predict the complex phase behaviour at high pressures (Shaw et al., 2002). The motivation behind this project was to estimate an interaction parameter using a fixed point in the phase space and evaluate its effect on the ability of the cubic equation of state to give correct predictions in the region of interest.

1.2. Two-Constant Cubic Equations of State

An equation of state which is cubic in volume and gives pressure in terms of volume and temperature of a substance is called a cubic equation of state. They are

more successful than any other type of equation of state with a simpler form (Walas, 1985). Several equations of this type have been proposed like the van der Waals equation, the Redlich-Kwong equation, the Soave-Redlich-Kwong equation and the Peng-Robinson equation, to name a few. The van der Waals equation of state is the foremost of all and provided basis for the rest of the equations of state. All these cubic equations of state have two constants, an attraction parameter a and a repulsion parameter b , hence they are called two-constant equations of state. The later parameter is also referred as the co-volume parameter and is sometimes called the effective molecular volume. The Peng-Robinson equation of state (Peng and Robinson, 1976) is used in this work and is given as,

$$P = \frac{RT}{(v-b)} - \frac{a(T)}{v(v+b) + b(v-b)} \quad (1.1)$$

The vapour and liquid phases become identical at the critical point. Applying the mathematical criterion of a critical point to equation (1.1) gives

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (1.2)$$

$$b(T_c) = 0.07780 \frac{R T_c}{P_c} \quad (1.3)$$

$$Z_c = 0.307. \quad (1.4)$$

Z_c is the compressibility at the critical point. At temperatures other than the critical temperature

$$a(T) = a(T_c) \cdot \alpha(T_r, \omega) \quad (1.5)$$

$$b(T) = b(T_c) \quad (1.6)$$

where $\alpha(T_r, \omega)$ is a dimensionless function of the reduced temperature and acentric factor and equals unity at the critical conditions. The relationship between α and T_r is given by the following equation:

$$\alpha^{1/2} = 1 + \kappa(1 - T_r^{1/2}) \quad (1.7)$$

where κ is the characteristic constant of a substance, given by the equation:

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (1.8)$$

1.3. *Binary Interaction Parameters*

Application of the equation of state to mixtures requires the evaluation of parameters a and b (in equation 1.1) using mixing rules. The mixing rules that are most commonly used are,

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (1.9)$$

$$b = \sum_i x_i b_i \quad (1.10)$$

where

$$a_{ij} = (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2}. \quad (1.11)$$

The parameter δ_{ij} is the binary interaction parameter characterizing the binary formed by components i and j . Binary interaction parameters takes into account the difference in the interaction of unlike molecules. These binary interaction parameters are empirical and their significance lies in their ability to make a particular model predict the correct phase behaviour (Prausnitz et al., 1986).

1.4. *K and L Points*

When a liquid phase and a vapour phase become critical in the presence of a heavier liquid phase in equilibrium, it is referred to as a K-point and when two liquid

phases become critical in the presence of a vapour phase in equilibrium, it is referred to as an L-point.

The purpose of facilitating the equation of state in predicting the high pressure complex phase behaviour stimulated the thought of adjusting the binary interaction parameter values using some landmark in this phase space. K- and L-points were considered because they lie in the high pressure region and have a zero degree of freedom for a binary mixture. Also they lie in the vicinity of multiphase complex phase behaviour in the P - T projection of phase space of a binary system. The heavy liquid phase present in the K- and L-point carry the precursors to polyaromatic coke.

1.5. Objectives and Scope

The objectives of the project are as follows:

- a) Development of an algorithm to calculate K- and L-points since fitting the binary interaction parameter requires a procedure to compute K- and L-points using an equation of state
- b) Numerical study of the algorithm to check if the algorithm is capable of calculating K- and L-points for any mixture, given the critical properties and acentric factor data
- c) Study the effect of changing binary interaction parameters on K- and L-points
- d) Fitting the binary interaction parameter
- e) Study the effect of the binary interaction parameter on the P - T phase diagram
- f) Evaluate the success of fitting the binary interaction parameter using K- and L-points

The project focuses on the determination of K- and L-points for systems of alkane + alkanol, methane + n-alkane, and propane + polyaromatic hydrocarbon type. The mixing rules given by equations (1.9) and (1.10) were used in this work and the interaction parameter for b was not taken into consideration. When the P - T projection of phase space was developed for the validation of fitted binary interaction parameter, the multiphase equilibrium phenomenon involving a solid phase was not taken into consideration. Only one cubic equation of state, i.e. the Peng-Robinson equation of state, was used throughout the work.

1.6. Thesis Outline

The literature review to explain the background of the project and to gain the required knowledge for the computations is in chapter two. The project can be divided into two parts. The first part being the algorithm development and numerical and thermodynamic analysis, which is covered in chapter three, and the second part, being the fitting of binary interaction parameter and their validation from the P - T projection of phase space point of view, is discussed in chapter four. The conclusions are summarized in chapter five.

Appendix A contains the equations and the calculation procedure for finding a three-phase line, which was computed as a part of the phase diagram. Appendix B lists the critical properties and acentric factors of the systems studied in this project.

2. *LITERATURE SURVEY*

2.1. *Introduction*

An extensive literature survey was done to find the experimental data of hydrocarbons, available in the literature and to acquire the adequate background knowledge for accomplishing the objectives. Fixing the binary interaction parameter for a cubic equation of state being the motivation behind the project, a survey was done to find out the existing methods available in the literature to calculate binary interaction parameters. A study of the classification of binary phase diagrams was done since the influence of binary interaction parameter on phase diagrams had to be analysed as a part of the project.

Mathematical computation of the K- and L-points entails a good understanding of the tangent plane criterion, phase equilibrium calculations and the critical point calculations. A brief review of these calculation methods is also included in this chapter.

2.2. *Estimating Binary Interaction Parameters: A Literature Review*

The purpose of the binary interaction parameter is to enhance the capability of an equation of state to predict the desired phase behaviour; hence most of the methods to fit the binary interaction parameter match laboratory-data with that calculated by the equation of state. Many attempts have been made to generalize the interaction

parameter value for binary systems with one common compound and the other belonging to the same family or type. Particularly, the binaries involving hydrocarbon compounds have received more focus from the researchers since modeling of their phase behaviour has significant contribution in designing petroleum processes. Every method of determining binary interaction parameters has its applicability to predict phase behaviour in a specified region of phase space. Existence of a “universal” method to determine binary interaction parameters is doubtful.

Peng and Robinson (1976) determined the binary interaction parameter using experimental binary vapour-liquid equilibrium data. The value of the binary interaction parameter for a particular binary system was the one that gave minimum deviation in the predicted bubble point pressure. Various binary and ternary paraffinic systems were studied and binary interaction parameters were determined for those systems by matching the bubble point pressures.

Nishiumi et al. (1988) correlated the binary interaction parameters of the Peng-Robinson equation of state in terms of the ratio of critical molar volumes and the absolute difference in the acentric factor of each component.

$$(1 - \delta_{ij}) = C_1 + C_2 (v_{ci}/v_{cj}) + C_3 (v_{ci}/v_{cj})^2 \quad (2.1)$$

where

$$C_1 = c_1^1 + c_1^2 |\omega_i - \omega_j| \quad (2.2)$$

$$C_2 = c_2^1 + c_2^2 |\omega_i - \omega_j| \quad (2.3)$$

c_1^1, c_1^2, c_2^1 and c_2^2 are the constants. This correlation covered systems including carbon dioxide, nitrogen, hydrogen sulphide and hydrocarbons like alkanes, alkenes and

aromatics. Vapour liquid equilibrium data was used to check the validity of the correlation.

Petersen (1989) suggested a technique to determine the interaction parameters for complex hydrocarbon mixtures. A power function was proposed, which related the binary interaction parameters with the molecular weights of the components. The binary interaction parameter for components i and j was given as

$$\delta_{ij} = \rho_i \{ (M_j)^n - (M_i)^n \} \quad (2.4)$$

where

$$\rho_i = \delta_{iF_{m+}} / \{ (M_{F_{m+}})^n - (M_i)^n \}. \quad (2.5)$$

M_i represents the molecular weight of component i and F_{m+} represents the heaviest fraction.

This method helped to evaluate the binary interaction parameters for an extensive number of components in a systematic and consistent way. The equation of state was tuned with the aim of matching the laboratory measured data of constant composition expansion curves for six different complex fluid compositions. The fitting of interaction parameter was not only restricted to match the saturation pressure but an agreement with a range of laboratory measured data was taken into consideration. The sensitivity of the binary interaction parameter to the mixture composition and to the temperature was also studied in their work. This method of determination of binary interaction parameter was well suited for the complex paraffinic mixtures where the equation of state was used to predict the *PVT* data with a desired accuracy.

Carroll and Mather (1995) provided a generalised correlation for binary interaction parameters of the Peng-Robinson equation of state for the H₂S + paraffin system:

$$\delta_{ij} = 0.098 - 0.0069 \times CN, \quad (2.6)$$

where CN represents the number of carbon atoms in the paraffin.

Vapour-liquid equilibrium data for the system was used to find the correlation and a trend of decrease in the binary interaction parameter value with increase in the carbon number of the paraffin was observed. Apart from carbon number, additional parameters like normal boiling point, acentric factor, critical temperature and critical pressure were taken into account to improve the correlation. Even after using so many factors, a perfect match was not obtained and this correlation was limited to the binary systems containing H₂S and branched and straight chain paraffins.

Kordas et al. (1994) proposed a correlation for the binary interaction parameters characterizing CO₂ + n-alkane systems with the CO₂ reduced temperature and the alkane acentric factor as independent variables:

$$\delta_{ij} = q_1(\omega_j) + q_2(\omega_j)T_{ri} + q_3(\omega_j)T_{ri}^3 \quad (2.7)$$

where i stands for CO₂ and j stands for n-alkane. The parameters q_1, q_2 and q_3 are given as

$$q_1(\omega_j) = q_1^1 + q_1^2 \omega_j + q_1^3 \omega_j^2 \quad (2.8)$$

$$q_2(\omega_j) = q_2^1 + q_2^2 \omega_j + q_2^3 \omega_j^2 \quad (2.9)$$

$$q_3(\omega_j) = q_3^1 + q_3^2 \omega_j + q_3^3 / \omega_j \quad (2.10)$$

where $q_1^1 \setminus q_3^3$ are constants.

The correlation was also extended to other non-alkane hydrocarbons like alkenes and aromatics. Though the equation of state used in the work was the translated modified Peng-Robinson equation of state, the author claimed that the correlation was also valid for the Peng-Robinson equation of state because both equations of state required practically the same values of interaction parameter. Experimental vapour-liquid equilibrium data was used to check the validity of the method. The correlation works well for different hydrocarbons but in the case of aromatics, its applicability is limited to the single carbon ring compounds.

Trassy et al. (1997) recommended a method to determine the interaction parameters of the Peng-Robinson equation of state for heavy hydrocarbons. The model was validated by predicting the Henry's constant data of light hydrocarbons in high molecular weight hydrocarbons. The binary interaction parameters were determined using a group contribution method. The applicability of the model was limited to the extent of binary interaction parameters between light components (up to C₈) and heavy n-paraffins. The model was not extended to systems including aromatic hydrocarbons.

The method suggested by Petersen (1989) is applicable to the calculation of binary interaction parameters for paraffinic systems and did not mention about its applicability to other type of hydrocarbons. The correlation provided by Carroll and Mather (1995) is restricted to the systems containing H₂S, and the correlation given by Kordas et al. (1994), to the systems containing CO₂. Trassy et al. (1997) gave the correlation for interaction parameters of heavy n- paraffinic hydrocarbons but could not extend it to other type of hydrocarbons. Nishiumi et al. (1988) also provided a correlation for interaction parameters which is applicable to variety of hydrocarbons

including the aromatics. None of the above mentioned correlations authenticated the capacity of the binary interaction parameters of the Peng-Robinson equation of state to predict the high pressure complex phase behaviour. Also, there was no mention about the applicability of these correlations to the systems containing polyaromatic hydrocarbons, which is one of the components of a model binary system for heavy oils. Shaw et al. (2002) showed that the binary interaction parameter fitted using a general correlation sometimes fails to predict correct phase behaviour in the high pressure region. Figure 2.1 shows that the interaction parameter that predicts high pressure phase behaviour correctly is greater than the one calculated by general correlation by an order of magnitude.

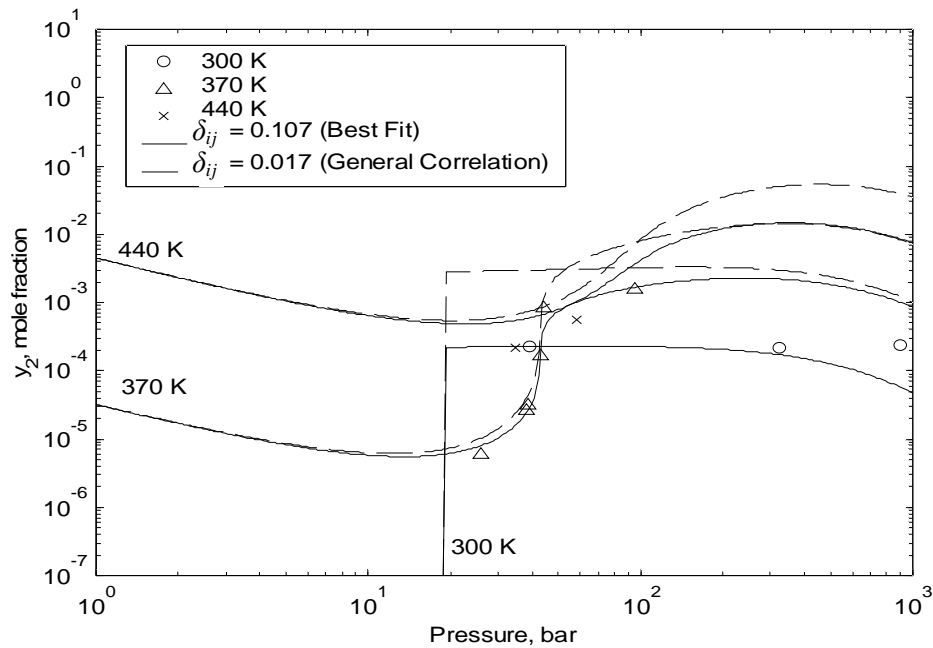


Figure 2.1: Interaction parameter values obtained from general correlation fail to predict correct phase behaviour at high pressures. δ_{ij} = Binary Interaction Parameter. (Shaw et al., 2002)

Though both the interaction parameters give good results in the low pressure region, a noticeable difference can be seen in prediction of high pressure phase equilibrium data.

2.3. *Alternate Mixing Rules*

Young (2000) suggested a new mixing rule to calculate the vapour-liquid equilibria of petroleum mixtures with the Peng-Robinson equation of state which is based on the concept of a component deviation factor. This new mixing rule eliminates the use of a binary interaction parameter. The mixing rule to calculate the parameter b was the same as in equation (1.10). Conventionally, the binary interaction parameters for a multi-component mixture are represented in a matrix form whereas the component deviation coefficients are represented in a vector form. Equation (1.9) was replaced by equation (2.11), given below:

$$a = \left[\sum_i x_i \psi_i a_i^{1/2} \right]^2 \quad (2.11)$$

where ψ_i is the component deviation coefficient. The component deviation coefficients were determined by matching the experimental vapour-liquid equilibrium data from specified reservoir fluids. This new mixing rule resulted in an improved accuracy and convergence behaviour in the calculation of the saturation temperature and pressure of certain petroleum mixtures. The mixing rule was suggested with the aim of modeling the reservoir fluid behaviour and no attempt was made to discover the improvement in prediction of complex high pressure phase behaviour of the fluids.

There also exists a different mixing rule for the parameter b of the Peng-Robinson equation of state, which incorporates a binary interaction parameter (ϕ_{ij}).

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (2.12)$$

where

$$b_{ij} = \frac{b_i + b_j}{2} (1 - \phi_{ij}) \quad (2.13)$$

Use of an interaction parameter to calculate the parameter b is beyond the scope of this project. Equation (2.12) reduces to equation (1.10) if $\phi_{ij} = 0$.

2.4. *K- and L-Points*

The K- and L-points, as defined in section 1.4, are also called upper critical end points (UCEP) and lower critical end points (LCEP). When the three-phase line (L_1L_2G) terminates in a critical endpoint upon increase in temperature, it is called an upper critical endpoint. The critical endpoint is called a lower critical endpoint when the three-phase line terminates in a critical endpoint upon lowering the temperature. A K-point is always a UCEP but an L-point can be a UCEP or an LCEP depending upon the type of phase behaviour. The degrees of freedom for the K- and L-points can be calculated using the phase rule given by Knobler and Scott (1984):

$$DF = NC - NP + 3 - n \quad (2.14)$$

where

DF = Degrees of freedom

NC = Number of components

NP = Number of phases

n = Order of critical point

A binary system has zero degrees of freedom for a K- or an L-point. The location of K- and L-points in the global binary phase diagram is discussed in the following section:

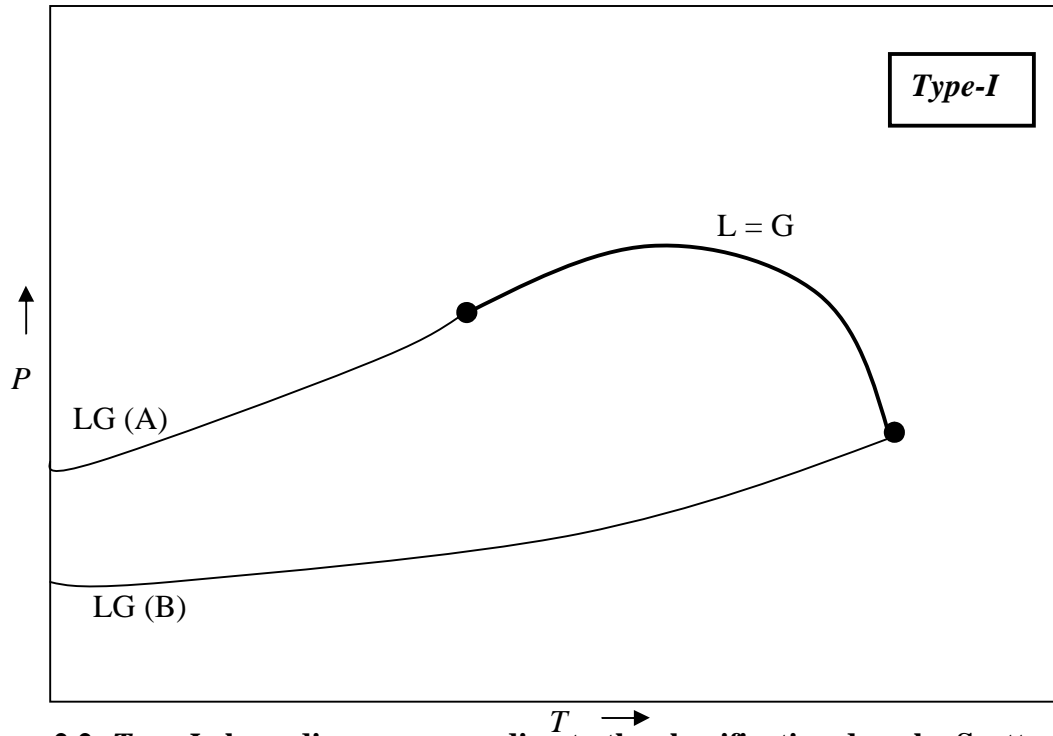


Figure 2.2: *Type-I* phase diagram, according to the classification done by Scott and Van Konynenburg (1980).

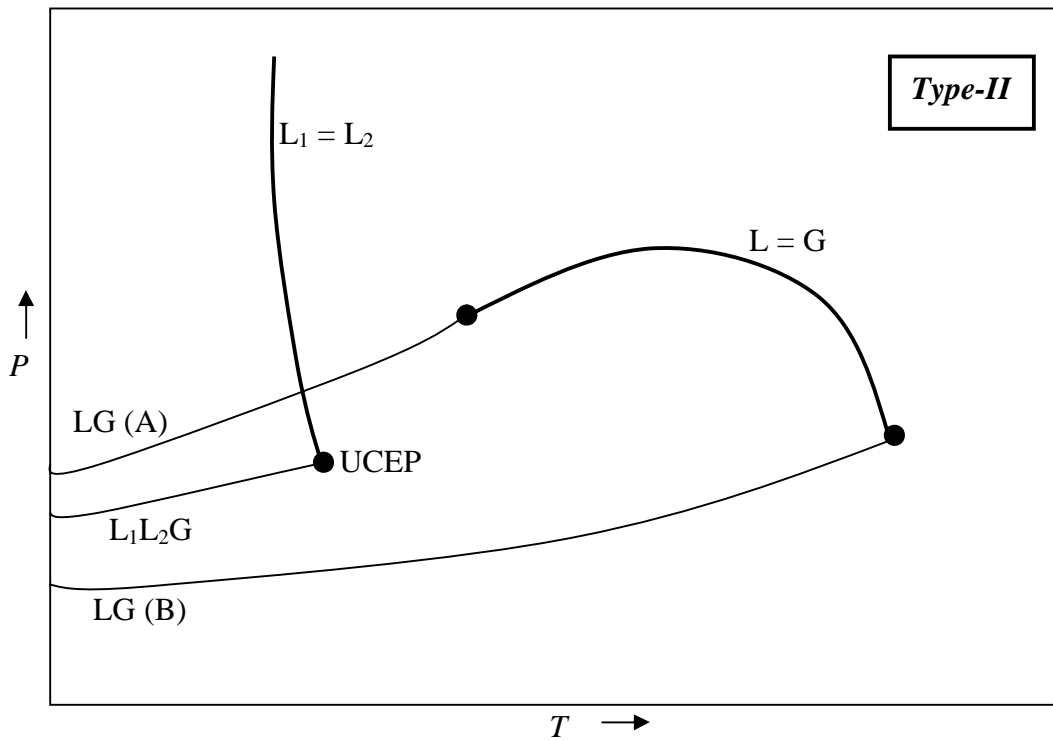


Figure 2.3: *Type-II* phase diagram, according to the classification done by Scott and Van Konynenburg (1980).

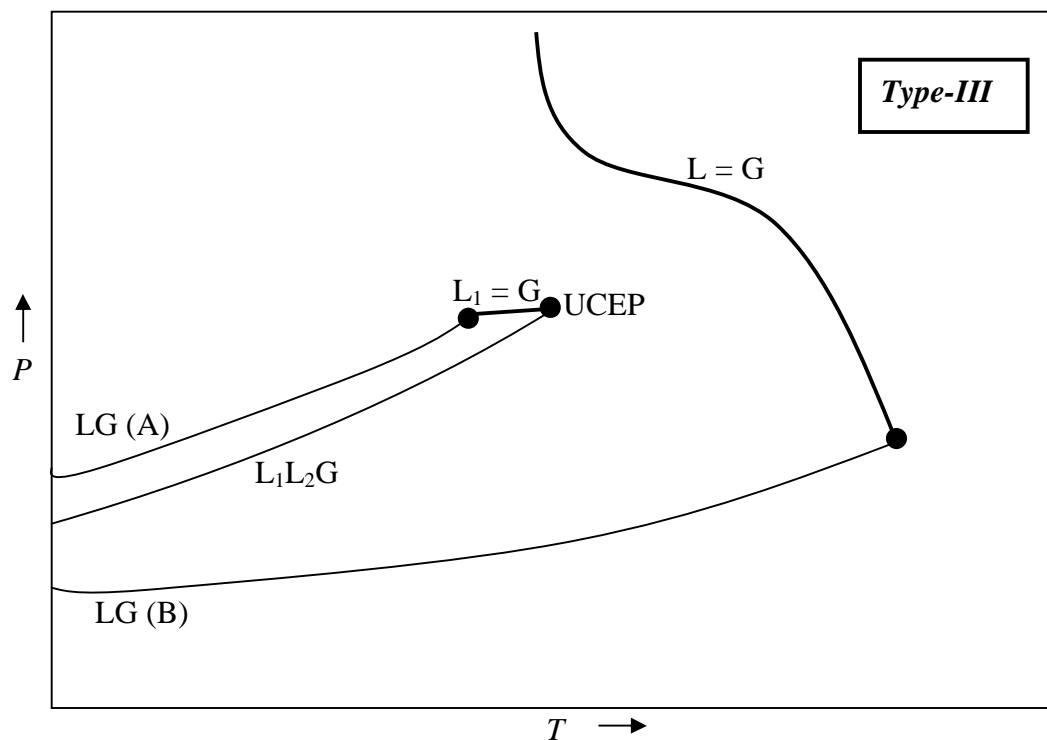


Figure 2.4: *Type-III* phase diagram, according to the classification done by Scott and Van Konynenburg (1980).

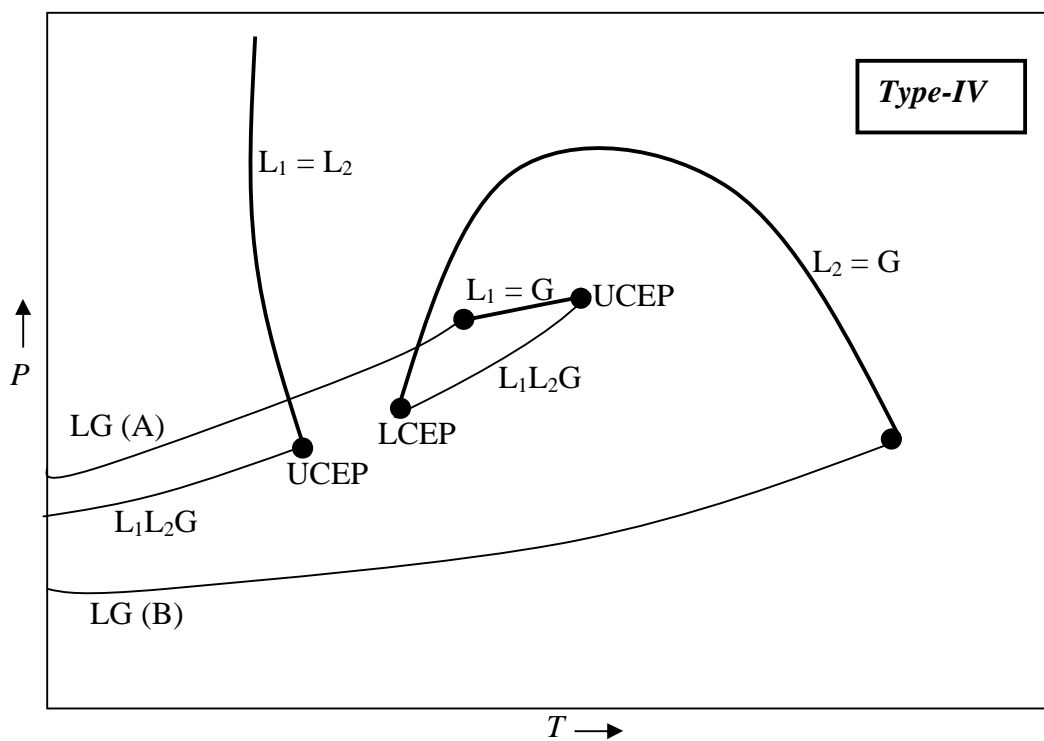


Figure 2.5: *Type-IV* phase diagram, according to the classification done by Scott and Van Konynenburg (1980).

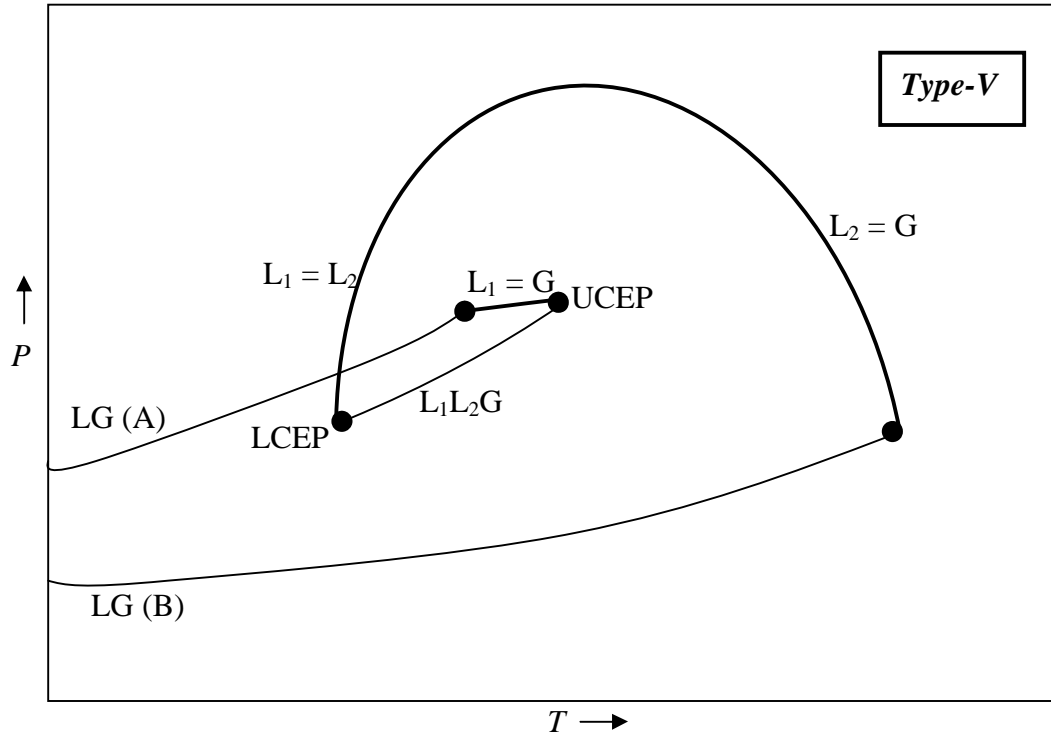


Figure 2.6: *Type-V* phase diagram, according to the classification done by Scott and Van Konynenburg (1980).

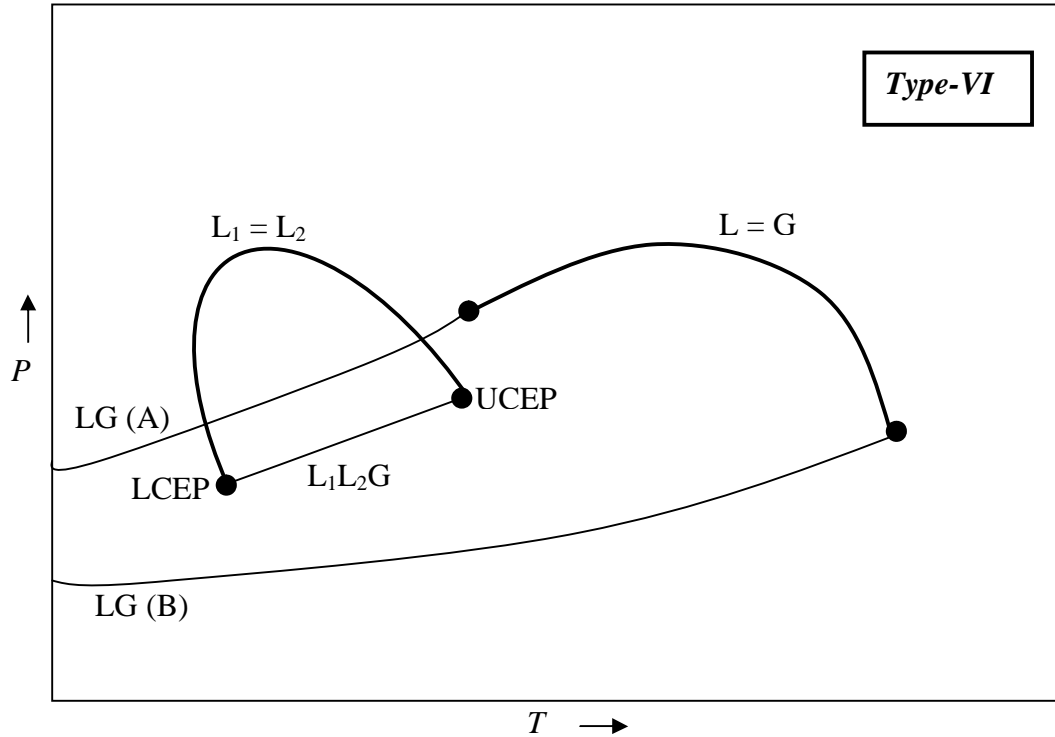


Figure 2.7: *Type-VI* phase diagram, according to the classification done by Scott and Van Konynenburg (1980).

2.4.1. Phase Diagrams and Location of K- and L-Points

Phase diagrams of the binary mixtures were classified by Van Konynenburg and Scott (1980) based on the nature of their P - T projections. The classification is based on the shape of critical lines, presence or absence of a three-phase line and critical endpoints and the way critical lines terminate. Figures 2.2-2.7 show different types of phase diagrams that a binary system of components A and B can exhibit, according to Van Konynenburg and Scott (1980). LG(A) and LG(B) represent the vapour pressure curve for pure components, A and B. L_1L_2G represents the three-phase line where two liquid phases, L_1 and L_2 are in equilibrium with the vapour phase. $L=G$ indicates the critical line, where a liquid phase and a vapour phase become identical.

Figure 2.2 shows a *Type-I* phase diagram in the binary classification scheme. A continuous critical line joining the critical points of pure components is observed in a *Type-I* phase diagram. Any other phenomenon like a critical endpoint or a three-phase line is not present in this type of phase behaviour. A *Type-II* phase diagram (see Figure 2.3) shows the presence of a three-phase line and a critical endpoint. Two critical lines are present in this type of phase diagram. One continuous critical line connects the critical points of pure components and the other one emerges from the upper critical endpoint. The UCEP lies at a temperature and pressure lower than the pure component critical point. A *Type-III* phase diagram (see Figure 2.4) shows two critical lines, each starting from the pure component critical point. The critical line starting from the critical point of the less volatile component goes to very high pressures and the other critical line starting from the critical point of more volatile component terminates in a UCEP, which is located at a higher temperature and pressure than the more volatile pure

component critical point. The three-phase line is also present in this type of phase diagram. A *Type-IV* phase diagram (see Figure 2.5) shows three critical lines. Those starting from the pure component critical points of the less volatile component and from the more volatile component terminate in an LCEP and in a UCEP respectively. The other critical line starts at a UCEP and goes to higher pressures. Also, this type of phase diagram shows two three-phase lines. A *Type-V* phase diagram (see Figure 2.6) has two critical lines, each terminating in a critical endpoint. The three-phase line is bounded between the critical endpoints. A *Type-VI* phase diagram (see Figure 2.7) shows both the critical lines bounded. It shows a critical line similar to a *Type-I* or a *Type-II* system that is restricted between the pure component critical points and the other restricted between the critical endpoints. The three-phase line is similar to the one in a *Type-V* phase diagram.

The critical endpoints that are the LCEPs and UCEPs are the K- and L-points. However there is a minor difference in the terminology. When a liquid and a vapour phase become critical, it is called a K-point and when the two liquid phases become critical, it is referred to as an L-point. The criterion for distinguishing LCEP and UCEP is not the type of critical point (LL or LG) but the location in P - T space. A UCEP is always located at a higher temperature and pressure than LCEP and when there is only one critical endpoint present, it is referred to as UCEP. Hence a K-point will be always a UCEP but an L-point can be a UCEP or an LCEP depending upon the type of phase diagram.

2.4.2. *Experimental Data*

A detailed survey was done to compile the experimental data available for K- and L-points in the literature. Validation of the algorithm to calculate K- and L-points and fitting the binary interaction parameter by matching the experimental data with computed K- and L-points required the knowledge of experimental data. The experimental K- and L-points data and binary phase diagram data for some of the systems studied in this project are tabulated in Table 2.1.

2.5. *Phase Equilibrium and Critical Point Calculations*

K- and L-points consist of a critical phase in equilibrium with a non-critical phase. Computation of K- and L-points using an equation of state was required in order to fit the binary interaction parameter. Computation of critical lines and three-phase line also formed a part of the project, since they are the elements of binary phase diagram. Development of procedures to calculate these multiphase complex phase behaviour demands a thorough understanding of the previous work done in this field so that based on this knowledge database a technique for the calculation of the desired type of phenomenon can be developed.

2.5.1. *Basic Phase Equilibrium Calculations*

Prediction of fluid phase equilibria using an equation of state forms an important part of simulations in the petroleum field. However, an equation of state can predict an incorrect number of phases or incorrect phase compositions even after satisfying the usual restriction of equality of chemical potentials and the material balances (Baker et al., 1982). The tangent plane criterion and its implementation were

studied in detail as a part of the literature review so that it could be implemented successfully to calculate a thermodynamically stable phase equilibrium phenomenon.

Table 2.1: Experimental K- and L-points data for the systems studied in the project.

Binary System	K-Point		L-Point		Phase Behaviour	Source of Experimental Data
	T (K)	P (MPa)	T (K)	P (MPa)		
Ethane + Ethanol	314.66	5.556	308.72	4.952	Type-V	Lam et al., 1977
Methane + n-Hexane	195.91	5.2055	182.46	3.4149	Type-V	Lin et al., 1977
Methane + n-Heptane	195.65	4.785	---	---	Type-III	Chang et al., 1966
Propane + Fluorene	385.5	5.11	---	---	Type-III	Peters et al., 1989
Propane + Phenanthrene	377.3	4.67	---	---	Type-III	Peters et al., 1989
Propane + Triphenylmethane	378.8	4.76	---	---	Type-III	Peters et al., 1989

2.5.1.1. *Gibbs Tangent Plane Criterion*

A phase equilibrium solution must satisfy three conditions; namely, preservation of the material balances, a zero chemical driving force, and the system must be at the lowest possible Gibbs free energy at a specified temperature and pressure. The condition of zero chemical driving force is satisfied by the equality of chemical potentials. Even if the system is satisfying the first two conditions, it is not stable unless it satisfies the minimum energy criterion. Baker et al. (1982) presented a method to determine the stability of the predicted equilibria using the Gibbs tangent plane criterion (1876). The Gibbs energy surface at the temperature and pressure of an equilibrium state and a tangent plane to the surface at the equilibrium solution are calculated using an equation of state. If the tangent plane lies below the Gibbs energy surface throughout the accessible composition range, the system is said to be stable. The slope of the tangent with respect to mole numbers corresponds to the chemical potential and thus satisfies the second condition for the equilibrium at points of tangency as well.

Figure 2.8 illustrates the tangent plane criterion. The Gibbs surface is generated using an equation of state for a hypothetical homogeneous phase and it does not represent an actual Gibbs energy. The feed composition is as shown in the figure. Since the Gibbs energy surface is not concave upwards at the feed composition, a phase split is required to give a stable solution. The possible phase splits are indicated by the tangents drawn to the Gibbs surface from points 2 and 3. Both the phase splits satisfy the equality of chemical potential criterion, but it can be seen from Figure 2.8 that the tangent passing through point 2 does not lie above the surface for the entire composition range and hence it does not represent a stable solution. The tangent passing through

point 3 lies below the surface and hence represents stable solution. Any feed having a composition between X_{L3} and X_{V3} will split into two phases to attain a state of lower Gibbs energy, which is more stable than the original feed mixture.

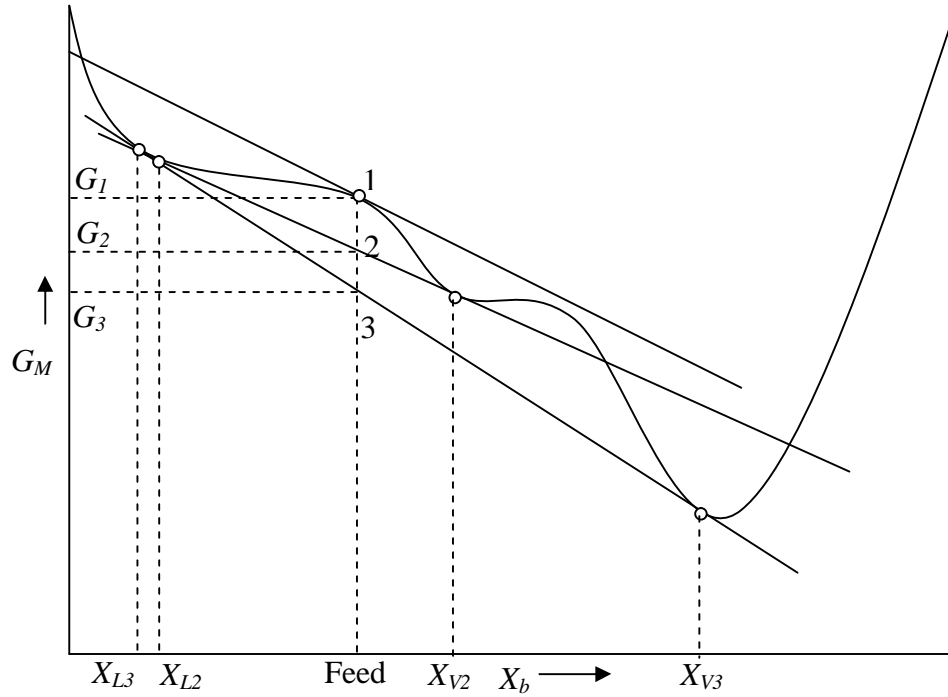


Figure 2.8: Gibbs energy diagram explaining the tangent plane criterion (Baker et al., 1982).

2.5.1.2. Numerical Implementation of Tangent Plane Criterion

Baker et al. (1982) presented a mathematical proof of the tangent plane criterion but did not suggest any method to implement it to find the stability of predicted phases. Michelsen (1982a) however suggested the following method to implement the tangent plane criterion in a phase stability check.

Consider a system of N components at temperature T_0 and pressure P_0 with component mole fractions (m_1, m_2, \dots, m_N) and R moles in total. The Gibbs energy of the mixture is given as,

$$G_0 = \sum_i \mu_i^0 r_i \quad (2.15)$$

where μ_i^0 is the chemical potential of component i in the mixture and r_i is the number of moles of component i . If the mixture is divided into two phases (*Phase-I* and *Phase-II*) with mole numbers $R - \varepsilon$ and ε respectively and amount ε of the second phase being infinitesimally small with mole fractions (k_1, k_2, \dots, k_N) , the change in the Gibbs energy is given as

$$\begin{aligned} \Delta G &= G_I + G_{II} - G_0 \\ &= G(R - \varepsilon) + G(\varepsilon) - G_0 \end{aligned} \quad (2.16)$$

A Taylor series expansion of $G(R - \varepsilon)$, neglecting second order terms gives

$$G(R - \varepsilon) = G(R) - \varepsilon \sum_i k_i \left(\frac{\partial G}{\partial r_i} \right)_R = G_0 - \varepsilon \sum_i k_i \mu_i^0. \quad (2.17)$$

From equations (2.16) and (2.17),

$$\begin{aligned} \Delta G &= G(\varepsilon) - \varepsilon \sum_i k_i \mu_i^0 = \varepsilon \sum_i k_i \mu_i(\mathbf{k}) - \varepsilon \sum_i k_i \mu_i^0 \\ &= \varepsilon \sum_i k_i (\mu_i(\mathbf{k}) - \mu_i^0) \end{aligned} \quad (2.18)$$

Stability of the original system with mole number R requires that the Gibbs energy should be at its global minimum and no phase split should cause a decrease in the Gibbs energy. This implies that the summation of the Gibbs energy of *Phase-I* and *Phase-II*

should be greater than G_0 , thus ΔG should be positive. Hence the necessary criterion for stability is that

$$D(\mathbf{k}) = \sum_i k_i (\mu_i(\mathbf{k}) - \mu_i^0) \geq 0 \quad (2.19)$$

for all trial compositions \mathbf{k} . Referring to the Gibbs energy plot, $D(\mathbf{k})$ is the vertical distance from the tangent to the Gibbs energy surface at composition \mathbf{m} to the Gibbs energy surface at composition \mathbf{k} . Stationary points are those points where the derivatives of $D(\mathbf{k})$ with respect to all the independent variables equal zero. Michelsen (1982a) showed that if $D(\mathbf{k})$ is non-negative at all stationary points then it will be non-negative at any other composition. Differentiation of equation (2.19) with respect to the $N - 1$ independent mole fractions yields the stationary condition

$$\mu_i(\mathbf{k}) - \mu_i^0 = L \quad (2.20)$$

where L is a constant independent of component index i . The graphical representation of the tangent plane criterion can be seen in Figure 2.9. It can be observed from the figure that $\mathbf{k} = \mathbf{m}$ is a stationary point with a stationary value equal to zero. At stationary point \mathbf{k}_s , the tangent plane to the Gibbs surface is parallel to the tangent plane at composition \mathbf{m} .

To implement the criterion using an equation of state, a more suitable stationary criterion is suggested by Michelsen (1982a). The distance D is calculated in terms of fugacity coefficients as

$$D(\mathbf{k})/RT_0 = \sum_i k_i (\ln k_i + \ln \phi_i(\mathbf{k}) - \ln m_i - \ln \phi_i(\mathbf{m})) \geq 0 \quad (2.21)$$

Differentiating the above equation, the stationary criterion is obtained as

$$\theta = (\ln k_i + \ln \phi_i(\mathbf{k}) - \ln m_i - \ln \phi_i(\mathbf{m})) \quad (2.22)$$

Introducing a new variable,

$$K_i = \exp(-\theta)k_i, \quad (2.23)$$

$$\ln K_i + (\ln \phi_i(\mathbf{k}) - \ln m_i - \ln \phi_i(\mathbf{m})) = 0. \quad (2.24)$$

The new independent variables K_i are interpreted as unnormalized mole fractions or mole numbers, the corresponding mole fractions being $k_i = K_i / \sum_i K_i$. Solving equation

(2.24) will give the stationary point, and the stability of original system is confirmed if $\theta \geq 0$, or equivalently, if $\sum_i K_i \leq 1$. If $\theta = 0$, the trial phase is in equilibrium with the

original system.

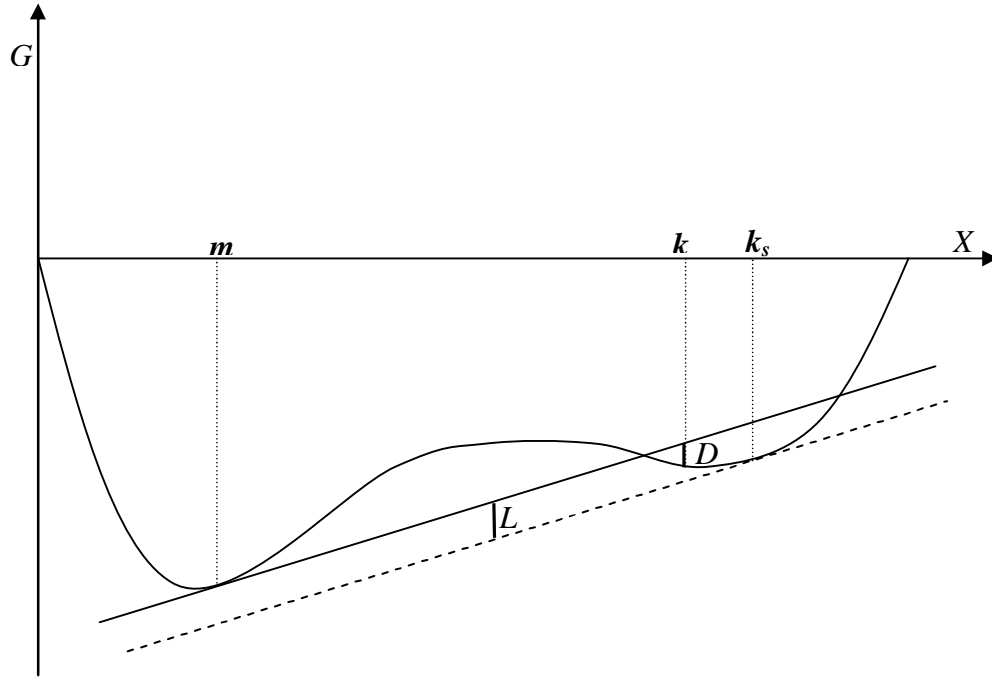


Figure 2.9: Gibbs energy diagram showing the tangent at mole fraction m and the tangent plane distance D at mole fraction k . The tangent at stationary point k_s and distance L can be seen. (Michelsen, 1982a)

2.5.2. Critical Point Calculations

One of the two equilibrium phases in a K- or L-point is the critical phase. Different methods available in the literature to calculate the critical point are summarized below.

2.5.2.1. Definition of Critical Point

The critical point of a pure component can be defined as the highest temperature and pressure at which liquid and vapour phases coexist (Walas, 1985). Mathematically the critical point of a pure substance is expressed as

$$\left(\frac{\partial P}{\partial V} \right)_T = \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad (2.25)$$

The critical state of mixtures can also be defined in a similar fashion, where the properties of two or more coexisting phases become identical. The mathematical definition of the critical point of an n-component mixture was given by Gibbs and it was in the form of the two equations given below (Peng and Robinson, 1977):

$$\begin{vmatrix} \frac{\partial^2 G}{\partial x_1^2} & \frac{\partial^2 G}{\partial x_1 x_2} & \frac{\partial^2 G}{\partial x_1 x_{n-1}} \\ \frac{\partial^2 G}{\partial x_2 x_1} & \frac{\partial^2 G}{\partial x_2^2} & \frac{\partial^2 G}{\partial x_2 x_{n-1}} \\ \frac{\partial^2 G}{\partial x_{n-1} x_1} & \frac{\partial^2 G}{\partial x_{n-1} x_2} & \frac{\partial^2 G}{\partial x_{n-1}^2} \end{vmatrix} = 0 \quad (2.26)$$

$$\begin{vmatrix} \frac{\partial U}{\partial x_1} & \frac{\partial U}{\partial x_2} & \frac{\partial U}{\partial x_{n-1}} \\ \frac{\partial^2 G}{\partial x_2 x_1} & \frac{\partial^2 G}{\partial x_2^2} & \frac{\partial^2 G}{\partial x_2 x_{n-1}} \\ \frac{\partial^2 G}{\partial x_{n-1} x_1} & \frac{\partial^2 G}{\partial x_{n-1} x_2} & \frac{\partial^2 G}{\partial x_{n-1}^2} \end{vmatrix} = 0 \quad (2.27)$$

where $G = G(T, P, x_1, x_2, \dots, x_{n-1})$ and the partial derivatives with respect to x_i are obtained at constant T, P and $x_{k, k \neq i, n}$.

2.5.2.2. *Methods to Calculate Critical Point*

Many researchers have attempted to develop methods for calculating the critical properties of mixtures. The application of the definition of a critical point given by Gibbs in combination with an equation of state to calculate the critical point was first made by Spear et al. (1971). The critical temperature and pressure of a ternary mixture was specified and the composition was searched. However, the procedure was limited to ternary systems.

Peng and Robinson (1977) presented a method to calculate the critical point of a multicomponent mixture using the Peng-Robinson equation of state and the critical state criterion, as given by Gibbs (1876). The authors claimed that the method was more reliable and more generally applicable than any of the previous methods. Large determinants had to be evaluated in order to calculate the functions associated with the calculation procedure.

Heidemann and Khalil (1980), in their attempt to calculate the critical point, took a different approach for the computation. The efforts of calculating the determinants were saved in this method, thereby significantly reducing the computational time when applied to large systems. The critical criteria were calculated by examining the stability of homogeneous phases. The formulation introduced for the critical criteria used an equation of state to calculate the quadratic and cubic forms of the Taylor series expansion of the Helmholtz free energy as a function of mole numbers. The method calculates a critical point for a multicomponent mixture with a

specified composition using a strategy of initial guess for critical temperature and critical volume, which is common to all the systems. A technique to look into the possibility of existence of more than one critical point was also suggested. The details of the equations associated with this method are given in section 3.2.1 of the thesis as they are a part of development of the algorithm to calculate K- and L-points.

Michelsen (1984) suggested a method to calculate the critical point of a multicomponent mixture at a specified composition. The criticality conditions were based on the Gibbs tangent plane stability criterion. For the calculation of critical points, a good initial estimate of the critical temperature and pressure are needed in this method. The procedure is very efficient from a computational point of view and uncomplicated in terms of calculating thermodynamic properties and their derivatives. The benefit of the method is that the quantities calculated during the critical point computation can be related to relative changes in temperature, pressure and the composition and distribution of equilibrium phases in the critical region.

Michelsen and Heidemann (1988) were the first to calculate the critical points of higher than first order. That is the second order critical point where three phases become identical, also called a tricritical point. An ordinary critical point criterion is explained using two equations in the thermodynamic variables and a tricritical point is described by four such equations. The procedure for calculating the tricritical point was an extension of the critical point calculation procedure and criterion given by Michelsen (1984). The computational procedure had the potential to calculate the critical points of even higher orders.

Kohse and Heidemann (1993) suggested a different approach to evaluate the intermediate functions involved in the tricritical point computation method given by Michelsen and Heidemann (1988). A different solution procedure was also suggested. A combination of the approach taken by Heidemann and Khalil (1980) and Michelsen and Heidemann (1988) was used in this work. From the available methods to calculate critical point, the Kohse and Heidemann approach, restricted to an ordinary critical point calculation, was used in the current project. The reasons for using this approach were the simplicity in computation, the good strategy for an initial guess and the documented better convergence.

3. *ALGORITHM TO CALCULATE K- AND L-POINTS*

3.1. *Introduction*

A critical phase and a non-critical phase in equilibrium constitute a K- or an L-point. Methodologies for the calculation of critical point and for the search of equilibrium phase were combined to locate the K- and L-points in phase space. Detailed explanation of these two procedures is given in the following sections along with the flowchart of the algorithm. The difference between the calculation method used in this work and the calculation method used by other researchers (Gauter et al., 1999) is identified. The numerical and thermodynamic issues in the generalization of the algorithm are discussed.

3.2. *Critical Point Calculations*

K- and L-points were calculated using the approach followed by Kohse and Heidemann (1993) for calculating tricritical points of ternary mixtures. This technique is a combination of two procedures (Heidemann and Khalil, 1980 and Michelsen and Heidemann, 1988) with some modifications in the evaluation method of the intermediate functions and the solution procedure. The equations associated with this approach are explained in the following sections with a detailed solution procedure and numerical methods.

3.2.1. Methods to Calculate Critical Point

Heidemann and Khalil (1980) implemented the following procedure to calculate critical points:

Consider a test phase of N components where the i^{th} component contributes n_i moles. At a constant volume and temperature, stability of the homogeneous test phase requires that the Helmholtz free energy, A , generated by a small change in the composition of the test phase, Δn_i , is bound by the constraint:

$$\left[A - A_0 - \sum_{i=1}^N \mu_{i0} \Delta n_i \right]_{T_0, V_0} > 0 \quad (3.1)$$

μ_i is the chemical potential of component i and the subscript '0' refers to the test phase.

Expanding the Helmholtz free energy function in Taylor series about the test phase results in the following stability requirement:

$$\begin{aligned} & \left[A - A_0 - \sum_{i=1}^N \mu_{i0} \Delta n_i \right]_{T_0, V_0} \\ &= \left[\frac{1}{2!} \sum_{i=1}^N \sum_{j=1}^N \left(\frac{\partial^2 A}{\partial n_i \partial n_j} \right)_{T_0, V_0} \Delta n_i \Delta n_j \right. \\ & \quad \left. + \frac{1}{3!} \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k} \right)_{T_0, V_0} \Delta n_i \Delta n_j \Delta n_k + O(\Delta n^4) \right] \\ & > 0 \end{aligned} \quad (3.2)$$

Reid and Beegle (1977) defined a critical point as a stable point which lies on the limit of stability. Using this definition, at a critical point, the quadratic form of equation (3.2) will be positive semi-definite. That is, the matrix \mathbf{Q} , defined with elements

$$q_{ij} = \left(\frac{\partial^2 A}{\partial n_i \partial n_j} \right) \quad (3.3)$$

will have a zero determinant,

$$Q = \det(\mathbf{Q}) = 0 \quad (3.4)$$

and the cubic term of equation (3.2) will also be zero:

$$C = \frac{1}{3!} \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k} \right) \Delta n_i \Delta n_j \Delta n_k = 0 \quad (3.5)$$

Furthermore, the stability of the critical point requires that the quadratic term in the expansion be positive. Δn_i in equation (3.5) and in the quadratic term are determined from one of the non-zero solutions of

$$\mathbf{Q}\Delta\mathbf{n} = 0 \quad (3.6)$$

where $\Delta\mathbf{n} = (\Delta n_1, \Delta n_2, \dots, \Delta n_N)^T$.

The derivatives within equations (3.3) and (3.5) may be replaced with

$$\left(\frac{\partial^2 A}{\partial n_i \partial n_j} \right) = RT n_T \left(\frac{\partial \ln f_i}{\partial n_j} \right) \quad (3.7)$$

$$\left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k} \right) = RT n_T^2 \left(\frac{\partial^2 \ln f_i}{\partial n_j \partial n_k} \right) \quad (3.8)$$

where n_T is the total number of moles in the system and f_i is the fugacity of i^{th} component. Equations (3.7) and (3.8) can be evaluated using any equation of state. Equations (3.4), (3.5) and (3.6) give the method to calculate the critical point. The two conditions for a critical point are equations (3.4) and (3.5) and Δn_i in equation (3.5) is calculated using equation (3.6).

Michelsen and Heidemann (1988), in their approach for calculating a tricritical point, used the criterion for critical points derived from the Gibbs tangent plane criterion for stability (Michelsen, 1982a). These criterion were developed as follows:

Let \mathbf{z} be the composition of the mixture for which the critical point is to be calculated. The condition for the stability of the mixture with respect to a trial phase at a specified temperature and pressure (T_0, P_0) is

$$F(\hat{\mathbf{n}}) = 1 + \sum_i \hat{n}_i (\ln \hat{n}_i + \ln \phi_i(\hat{\mathbf{n}}) - \ln z_i - \ln \phi_i(\mathbf{z}) - 1) \geq 0 \quad (3.9)$$

which is similar to equation (2.8). $\hat{\mathbf{n}}$ represents the mole numbers of any trial phase.

The first and second partial derivatives of F with respect to \hat{n}_i are,

$$\partial F / \partial \hat{n}_i = \ln \hat{n}_i + \ln \phi_i(\hat{\mathbf{n}}) - \ln z_i - \ln \phi_i(\mathbf{z}) \quad (3.10)$$

$$\partial^2 F / \partial \hat{n}_i \partial \hat{n}_j = (1/\hat{n}_i) \sigma_{ij} + \left(\partial \ln \phi_i / \partial \hat{n}_j \right)_{\hat{\mathbf{n}}} \quad (3.11)$$

where

$$\begin{aligned} \sigma_{ij} &= 1 \setminus \setminus (i = j) \\ &= 0 \setminus \setminus (i \neq j) \end{aligned} \quad (3.12)$$

If the modified tangent plane distance is considered as the function of translated mole numbers defined as,

$$X_i = (\hat{n}_i - z_i) / z_i^{1/2} \quad (3.13)$$

the partial derivatives of F with respect to these translated mole numbers become

$$\frac{\partial F}{\partial X_i} = z_i^{1/2} (\ln \hat{n}_i + \ln \phi_i(\hat{\mathbf{n}}) - \ln z_i - \ln \phi_i(\mathbf{z})) = \hat{g}_i \quad (3.14)$$

$$\partial^2 F / \partial X_i \partial X_j = \sigma_{ij} + (z_i z_j)^{1/2} \left(\partial \ln \phi_i / \partial \hat{n}_j \right) = B_{ij} \quad (3.15)$$

\hat{g}_i is an element of $\hat{\mathbf{g}}$ and B_{ij} is an element of \mathbf{B} .

A distance parameter s is introduced such that

$$\mathbf{u}^T \mathbf{X} = s \quad (3.16)$$

where \mathbf{u} is a vector with property $\mathbf{u}^T \mathbf{u} = 1$. Considering the dependence of F on s , the Taylor series expansion of F about the phase, with composition \mathbf{z} , can be written as

$$F = \sum_{p=0}^{\infty} (s^p / p!) \left(d^p F / ds^p \right)_{s=0} \quad (3.17)$$

$$= a's + b's^2 + c's^3 + d's^4 + e's^5 + f's^6 + \dots$$

At $s = 0$, $F = 0$ ($\hat{n}_i = z_i$) and also $a' = \sum_i \hat{n}_i \hat{g}_i(s=0) = 0$. To obtain the

coefficients, b', c', d', \dots , in equation (3.17), mole number \mathbf{X} is expanded as

$$\mathbf{X} = s\mathbf{u} + s^2\mathbf{w} + s^3\mathbf{q} + \dots \quad (3.18)$$

For the mole numbers to satisfy the constraint in equation (3.16), \mathbf{w} and \mathbf{q} must be orthogonal to \mathbf{u} . $b' = c' = 0$ satisfies the condition for an ordinary critical point (similar to conditions defined in equations (3.4) and (3.5)) (Michelsen, 1984) and $b' = c' = d' = e' = 0$ is the condition for a tricritical point. Stability of an ordinary critical point is assured if $d' \geq 0$ and $f' \geq 0$ is the condition for the stability of a tricritical point. The task of calculating an ordinary critical point involves the evaluation of coefficients b', c' and d' and solving the equations such that the coefficients b' and c' are equal to zero.

Michelsen (1984) and Michelsen and Heidemann (1988) calculated an ordinary critical point by finding the temperature and pressure (taking temperature and pressure as independent variables) using a two-dimensional Newton-Raphson search to make the coefficients equal to zero. But Kohse and Heidemann (1993) modified this technique and employed the solution procedure of Heidemann and Khalil (1980), thereby taking temperature and volume as independent variables. The coefficient b' is made zero by adjusting the temperature in the inner loop and coefficient c' is made

zero in the outer loop by adjusting the volume. A Newton-Raphson technique was used in both the loops. This improvement in the solution procedure helps in finding multiple critical points, if present.

3.2.2. Evaluation of b' , c' and d'

Michelsen and Heidemann (1988) chose \mathbf{u} to be an eigenvector corresponding to the minimum eigenvalue of the Hessian \mathbf{B} with the coefficient b' being half the minimum eigenvalue. With the coefficient b' being zero at the critical point, the minimum eigenvalue of \mathbf{B} has to be zero, since \mathbf{B} must be singular. In the inner loop of the critical point calculation, the temperature is adjusted to make the determinant of \mathbf{B} equal to zero. The vector \mathbf{u} is then calculated from

$$\mathbf{B}\mathbf{u} = 0 \quad (3.19)$$

Once the coefficient b' is made zero in the inner loop, the algorithm proceeds to calculate c' in the outer loop. The development of an equation to calculate the coefficient c' (Michelsen and Heidemann, 1988) is described below.

As the calculation of a critical point is based on the tangent plane criterion, stability of the critical phase is determined by the sign of F . \mathbf{X} is found by minimizing F subject to the constraint of equation (3.16) using the method of Lagrangian multipliers. The minimization criterion is equation (3.20) where γ , the Lagrangian multiplier, is given by equation (3.21).

$$\hat{\mathbf{g}}(\mathbf{X}(s)) = \gamma \mathbf{u} \quad (3.20)$$

$$\gamma = dF/ds = 2b's + 3c's^2 + 4d's^3 + 5e's^4 + \dots \quad (3.21)$$

The elements of $\hat{\mathbf{g}}$ are given by equation (3.14). Differentiating equation (3.20) twice gives,

$$\mathbf{r} + 2\mathbf{B}\mathbf{w} = 3!c'\mathbf{u} \quad (3.22)$$

where

$$\mathbf{r} = \left(\partial^2 \hat{\mathbf{g}} / \partial s^2 \right)_{s=0} \text{ with } \mathbf{X} = s\mathbf{u}. \quad (3.23)$$

\mathbf{r} is calculated by numerical differentiation of $\hat{\mathbf{g}}$ around $s = 0$. \hat{n}_i , required for the evaluation of \hat{g}_i , is calculated using equation (3.13) with $\mathbf{X} = s\mathbf{u}$. Pre-multiplying equation (3.22) by \mathbf{u}^T gives,

$$c' = (\mathbf{u}^T \mathbf{r}) / 3! \quad (3.24)$$

Equation (3.24) is used to calculate coefficient c' once the values of \mathbf{u} and \mathbf{r} are known.

Coefficient d' can be calculated from the numerical differentiation of F_s about $s = 0$:

$$d' = \frac{\left(\partial^3 F_s / \partial s^3 \right)_{s=0}}{4!}. \quad (3.25)$$

F_s is the gradient of function F along the distance parameter s , which can be analytically calculated as

$$F_s = \partial F / \partial s = \sum_i \hat{g}_i (\partial X_i / \partial s). \quad (3.26)$$

The value of coefficient c' depends only on \mathbf{u} but to calculate the coefficient d' , the translated mole number vector is expressed as a function of \mathbf{u} and \mathbf{w} :

$$\mathbf{X} = s\mathbf{u} + s^2\mathbf{w} \quad (3.27)$$

Equation (3.27) is used to calculate the term $(\partial X_i / \partial s)$ in equation (3.26) as

$$\partial X_i / \partial s = u_i + 2w_i s \quad (3.28)$$

\mathbf{w} is found by solving equations (3.22) and (3.29) simultaneously.

$$\mathbf{u}^T \mathbf{w} = 0 \quad (3.29)$$

3.2.3. *Numerical Methods Used*

At a fixed composition, the critical point temperature and volume were found using a nested one dimensional search. The inner loop updates the temperature at a fixed volume and the outer loop updates the volume. The temperature was altered using a Newton-Raphson method, to make the determinant of \mathbf{B} equal to zero. The determinant of \mathbf{B} was calculated by performing the Gaussian elimination to get an upper triangular matrix and then taking the product of the diagonal elements. The derivative of the determinant of \mathbf{B} with respect to temperature was calculated numerically, using the central difference formula. The convergence criterion employed for the inner loop was $|\Delta T|/T < 10^{-5}$. Equation (3.19) was then solved using the upper triangular form of \mathbf{B} , and \mathbf{u} was determined using back substitution by setting $u_N = 1$. \mathbf{u} was then normalized. After calculating the temperature on a stability limit, c' is calculated in the outer loop and the volume is altered to equate c' to zero, using a Newton-Raphson method. The derivative of c' with respect to the volume is calculated numerically using a central difference formula. The two nested loops repeat until the critical temperature and volume are found at the specified composition. The convergence criterion used for the outer loop was $|\Delta v|/v < 10^{-10}$. The flowchart of the critical point calculation method is shown in Figure 3.1 (b).

3.3. *Search for Equilibrium Phase*

Equilibrium phase calculations were done by implementing the tangent plane criterion (Michelsen, 1982a). The temperature and pressure were fixed as the critical temperature and pressure when the search of equilibrium phase began.

3.3.1. Equations

The critical phase is the reference phase for equilibrium phase computations and the reference composition is represented by $\mathbf{z} = (z_1, z_2, \dots, z_N)^T$. Let $\mathbf{y} = (y_1, y_2, \dots, y_N)^T$ represent the composition of the trial phase and $\mathbf{Y} = (Y_1, Y_2, \dots, Y_N)^T$ represent the unnormalized mole fractions of the trial phase (\mathbf{y} is analogous to \mathbf{k} and \mathbf{Y} is analogous to \mathbf{K} , in section 2.5.1.2). The equations associated with the tangent plane criterion, already discussed in section 2.5.1.2, are

$$\ln f_i(\mathbf{Y}) - \ln f_i^{crit}(\mathbf{z}) - \theta = 0 \quad (3.30)$$

and

$$\theta = -\ln \left(\sum_{i=1}^N Y_i \right) \quad (3.31)$$

which are analogous to equations (2.9) and (2.10). Combining these two equations we get our N working equations to solve for N unknowns, Y_i :

$$g_i = Y_i - \exp(\ln f_i^{crit} - \ln \phi_i(\mathbf{Y}) - \ln P). \quad (3.32)$$

3.3.2. Numerical Methods Used

The search for an equilibrium phase begins with an initial guess for the equilibrium phase composition. Equations (3.32) are solved iteratively using an accelerated successive substitution method (Mehra and Heidemann, 1983) or Newton-Raphson method. Upon convergence, θ is calculated using equation (3.31). If θ is not zero, the critical composition can be changed using a secant step and a new critical point can be found.

An accelerated successive substitution method was given by Mehra et al. (1983) with the introduction of an acceleration factor, λ . In the case of an ordinary

successive substitution method, to solve equation (3.32) the mole number \mathbf{Y} would be updated as,

$$\Delta\mathbf{Y} = -\mathbf{g} \quad (3.33)$$

But in the case of an accelerated successive substitution method, the mole numbers were updated as

$$\Delta\mathbf{Y} = -\lambda\mathbf{g} \quad (3.34)$$

The acceleration factor, λ , is chosen so as to minimize/maximize the distance from the tangent to the Gibbs surface at the reference phase composition to the Gibbs surface at the trial composition i.e. to find the stationary point. Expanding the distance D in a Taylor series, taking mole numbers as the independent variables, we get

$$\frac{\Delta D}{RT} = \mathbf{g}\Delta\mathbf{Y} + [\Delta\mathbf{Y}^T \mathbf{J}\Delta\mathbf{Y}] \quad (3.35)$$

where \mathbf{g} is the vector with elements g_i , \mathbf{J} is defined by equation (3.36) and the terms ΔD and $\Delta\mathbf{Y}$ hold the significance similar to that in equations (2.8) and (3.31) respectively.

$$\mathbf{J} = \frac{\nabla^2 D}{RT} \quad (3.36)$$

The acceleration factor can be chosen so as to minimize/maximize D after the iteration of successive substitution by taking

$$\partial(\Delta D/RT)/\partial\lambda = 0 \quad (3.37)$$

Putting the value of $\Delta\mathbf{Y}$ from equation (3.34) and applying the condition in equation (3.37),

$$\lambda = \frac{\mathbf{g}^T \mathbf{g}}{\mathbf{g}^T \mathbf{J}^{-1} \mathbf{g}} \quad (3.38)$$

To avoid the complication in accelerated successive substitution method an approximation of

$$\mathbf{J}\Delta\mathbf{Y} \cong \mathbf{g}_n - \mathbf{g}_{n-1} \quad (3.39)$$

can be used, where the subscript indicate the iteration count. From equations (3.32), (3.38) and (3.39)

$$\lambda_n = \left[\frac{(\mathbf{g}_{n-1}^T \mathbf{g}_{n-1})}{\mathbf{g}_{n-1}^T (\mathbf{g}_{n-1} - \mathbf{g}_n)} \right] \lambda_{n-1} \quad (3.40)$$

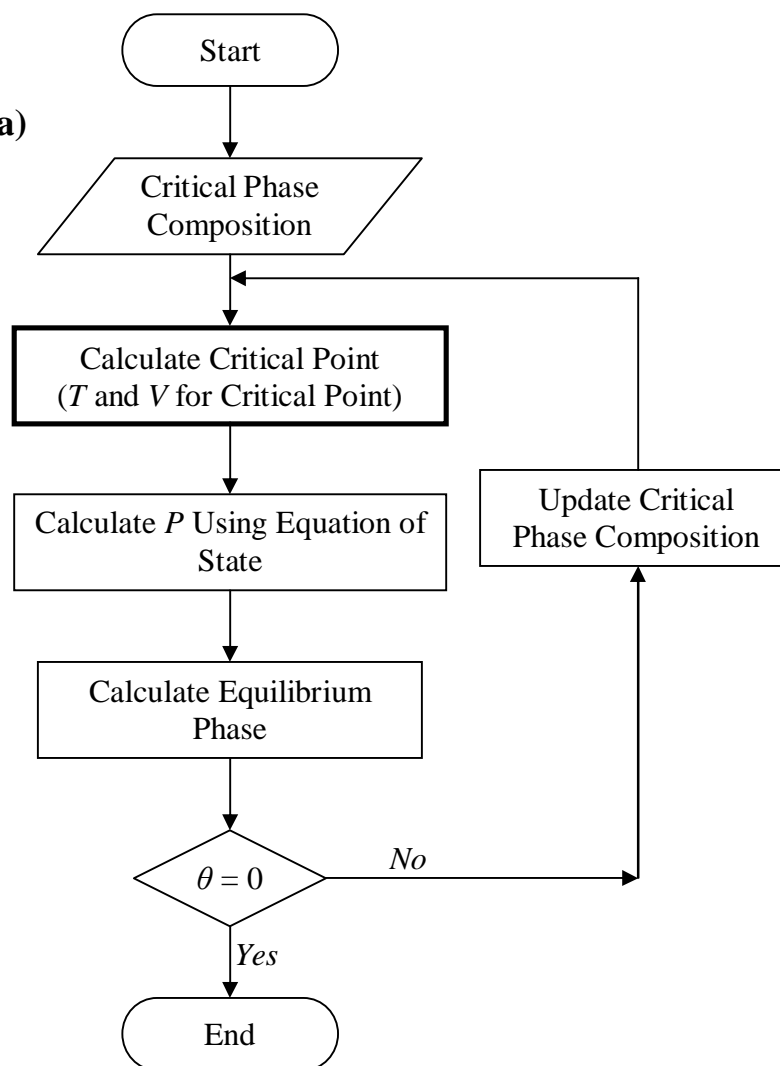
The algorithm was initiated using $\lambda = 1$.

3.4. *Flowchart of algorithm calculating K- and L-points*

Figure 3.1 (a) shows the flowchart of the algorithm to calculate K- and L-points. The algorithm starts with the input of critical properties and acentric factor data for the components and an initial guess for the critical phase composition is made. With the specified critical composition, control enters the critical point calculation loop where the critical point for the specified composition is calculated. After calculating the critical temperature and volume, the critical pressure is calculated using the Peng-Robinson equation of state. The control then enters the loop to calculate the equilibrium phase. If θ meets the convergence criterion ($\theta < 10^{-5}$), a K- or L-point has been found. If it does not meet the convergence criterion then the critical phase composition is updated using a secant method.

Figure 3.1 (b) shows the flowchart of the calculation procedure for the critical point. A nested one dimensional search is used to calculate the critical point. The temperature is altered in the inner loop to make the determinant of \mathbf{B} equal to zero and the volume is updated in the outer loop to get $c' = 0$.

(3.1a)



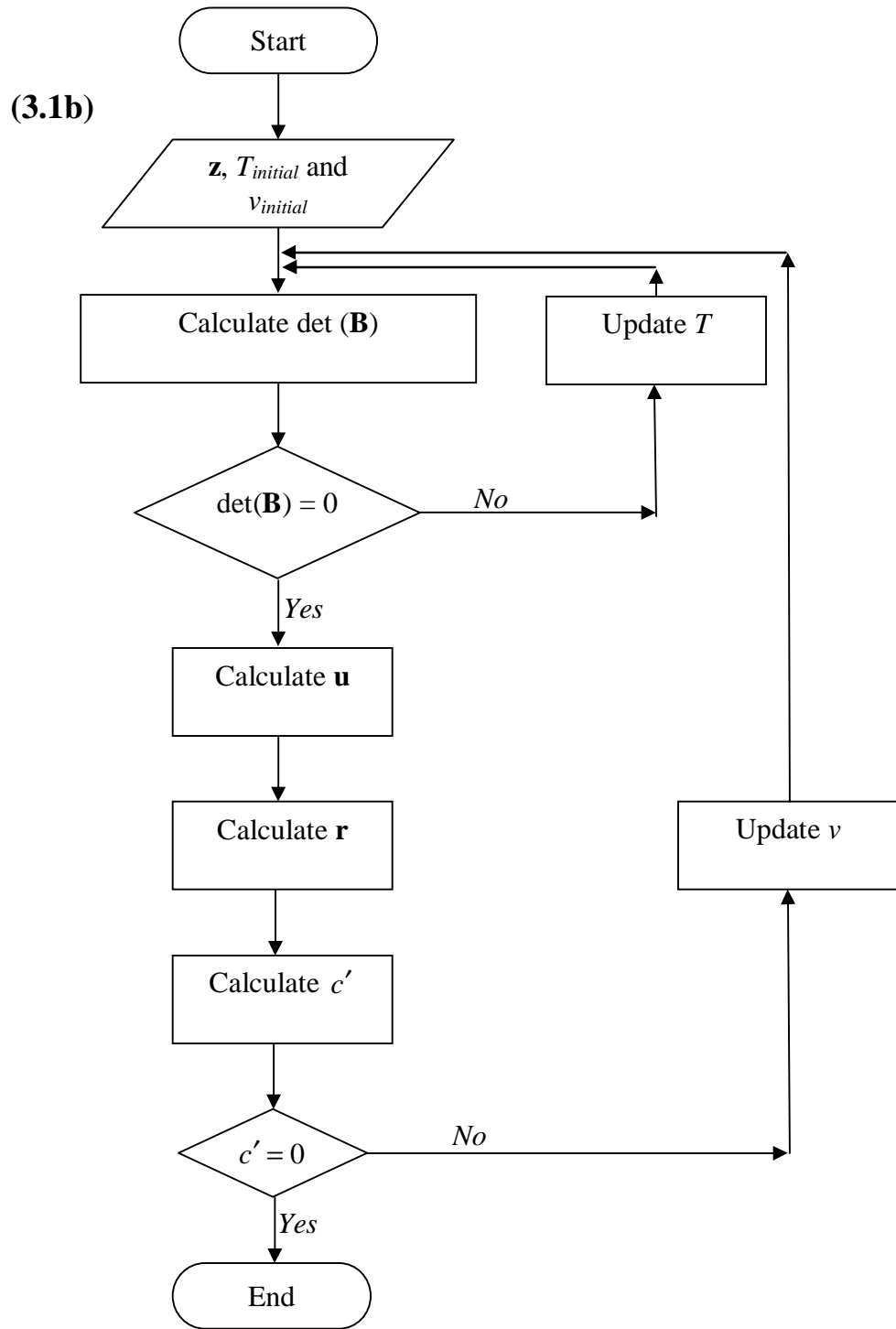


Figure 3.1: (a) Flow chart of the algorithm calculating K- and L-points. (b) Flowchart of the algorithm calculating a critical point.

3.5. *Mathematical and Thermodynamic Concerns*

The algorithm to calculate K- and L-points had to be generalized in order to be used with other simulations. By generalization, it is meant that with the input of critical properties of the components and the binary interaction parameter values, the algorithm should be able to calculate the K- and L-point without any modifications from the user. However there were some thermodynamic and numerical concerns in the generalization or automation of the algorithm which are addressed in the following sub-sections of the thesis. Also a comparison was done amongst different numerical methods and a study of their speed of convergence, robustness and accuracy is reported.

3.5.1. *Effect of Binary Interaction Parameter*

The binary interaction parameter not only affects the end results of the algorithm calculating K- and L-points, but also has an impact on the calculation procedure of K- and L-points. In the systems with identified K- and L-points, before searching for the mathematical K- or L-point with a specified binary interaction parameter, an analysis was done to confirm the existence of the point

The Gibbs free energy of mixing was plotted for different values of the binary interaction parameter at the temperature and pressure of the experimentally determined K- or L-point using the Peng-Robinson equation of state. An example of such a plot is shown in Figure 3.2 for an ethane + ethanol binary system. In Figure 3.2, for $\delta_{ij} = 0.04$, the Gibbs free energy surface is concave upwards throughout the composition range and there is no sign of any phase split. With $\delta_{ij} = 0.135$, the Gibbs energy plot is convex upwards between mole fractions 0.2 and 0.95 and a system with any composition between these points will split into two phases to attain a state that is

thermodynamically more stable. Therefore, it is imperative for the Gibbs energy plot at a K- or L-point to become convex upwards at least once in the composition range for two equilibrium phases to co-exist. If this property does not exist for a given interaction parameter, the equilibrium phase search converges to a trivial solution, i.e. the reference phase composition. The reason for converging to the trivial solution is that due to absence of another equilibrium phase, the only composition that satisfies equation (3.32) is the composition of the reference phase itself.

Figures 3.3 and 3.4 show the Gibbs free energy of mixing surface, drawn using the Peng-Robinson equation of state, for a ternary system of CO₂ + 1-Pentanol + Tri-decane at one of the experimental K-points of the system. Figure 3.3 shows the plot with the values of binary interaction parameters as zero. The Gibbs energy surface is concave upwards through out the composition plane and the tangent plane drawn at any point does not have two points of tangency, to indicate the presence of two equilibrium phases. Conversely the Gibbs surface in Figure 3.4, drawn with non-zero values of the binary interaction parameters ($\delta_{12} = 0.17, \delta_{13} = 0.15, \delta_{23} = 0.10$), clearly shows a possible phase split if the feed composition lies near $x_{CO_2} = 0.6$. This sort of preliminary analysis allowed initial binary interaction parameters to be chosen such that a K- or L-point did exist.

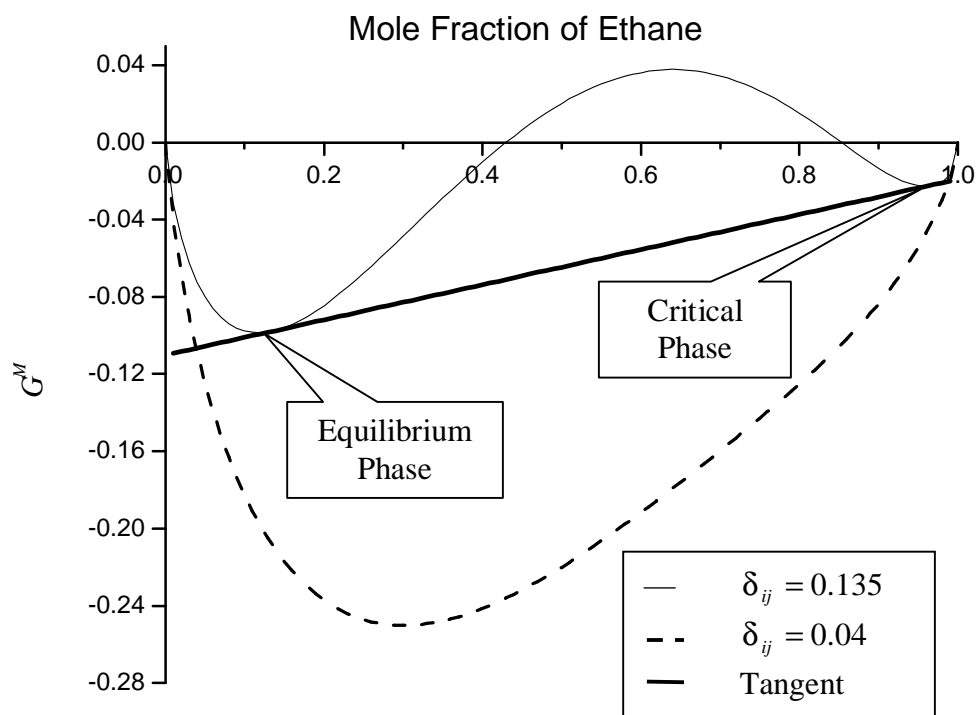


Figure 3.2: Gibbs energy plot for ethane + ethanol system at 315 K and 5.34 MPa.

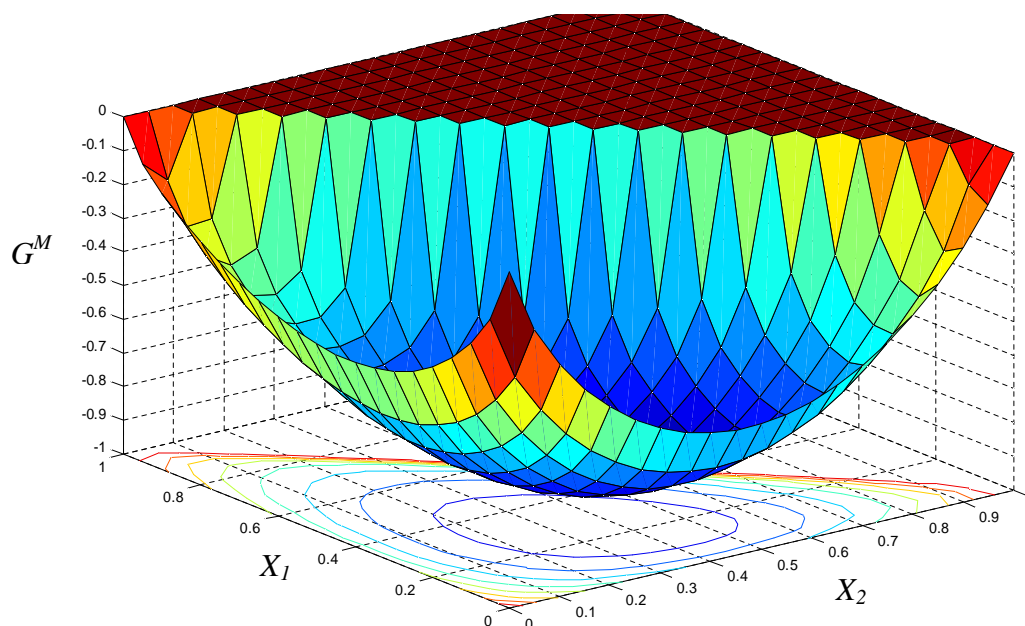


Figure 3.3: Gibbs energy plot for a ternary system of $\text{CO}_2(1)$ + 1-pentanol (2) + Tri-decane (3) at 317.43 K and 9.22 MPa, an experimental K-point for the system. $\delta_{ij} = 0.0$.

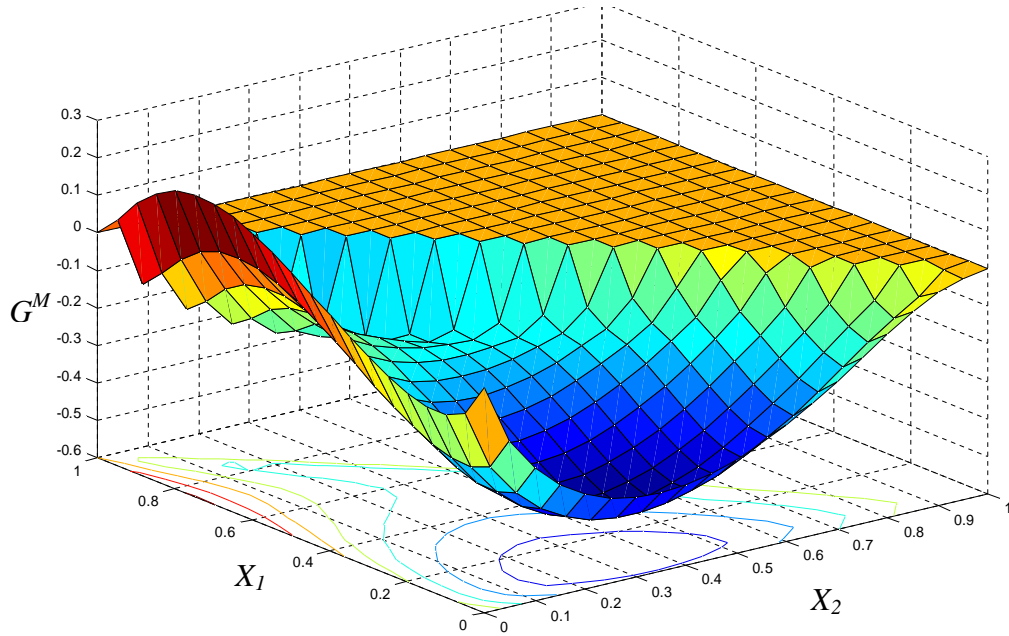


Figure 3.4: Gibbs energy plot for ternary system of CO₂ (1) + 1-pentanol (2) + Tri-decane (3) at 317.43 K and 9.22 MPa, an experimental K-point for the system. $\delta_{12} = 0.17, \delta_{13} = 0.15$ and $\delta_{23} = 0.10$.

3.5.2. Initial Guess for Critical Phase Composition

An initial guess for the critical phase composition is one of the parameters to be provided to initiate the algorithm to calculate a K- or L-point. The critical point calculation part of the algorithm calculates the critical temperature and volume for this specified composition. For any binary system, there exists a critical line comprising of critical points at different compositions. For a particular initial guess of the critical phase composition, the algorithm may fail to calculate the critical point (for example, in the case of a *Type-III* phase diagram where there is no continuous critical line joining the two pure component critical points) which leads to the failure of the algorithm in this initial stage. To avoid this situation, the range of initial guesses for the critical phase can be narrowed down significantly by taking into consideration the fact that a K- or an L-point exists much closer to the critical point of the lighter component than to the

critical point of the heavier component, in P - T space. This implies that the critical phase in a K- or an L-point is rich in the lighter component. A mole fraction of lighter component between 0.95 and 1.0 can be thought of as a good initial guess, but this initial guess also has an impact on the equilibrium phase calculation.

If a critical point calculated using an initial guess does not have an equilibrium phase, the search converges to a trivial solution, the critical composition. This is illustrated in Figure 3.5. With an initial critical composition guess of 0.99 for the critical phase, the critical point of anthracene + n-pentane system is calculated at 478.433 K and 3.6188 MPa. Figure 3.5 shows the Gibbs energy surface at this temperature and pressure and the tangent drawn to the surface at this critical composition. Equation (3.31) is solved to search for the equilibrium phase, which can be interpreted physically as the search for a solution in the composition space, such that the tangent drawn to the surface at that point is parallel to the tangent drawn to the surface at the critical or the reference phase composition. However Figure 3.5 shows that none of the lines parallel to the tangent at the critical composition are tangents to the surface. Conversely, a tangent to any point in the composition range is not parallel to the tangent at the critical composition except the tangent at the critical composition itself. Hence the algorithm converged to a trivial solution in this case.

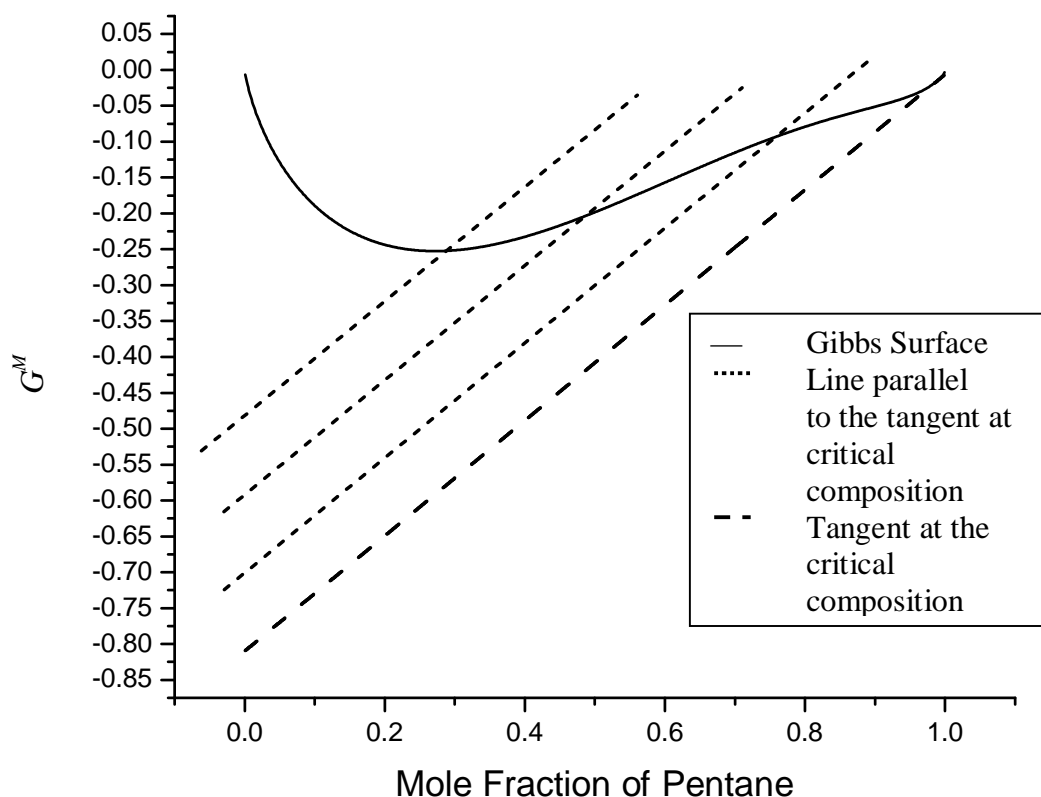


Figure 3.5: Gibbs energy surface and tangent to the surface at critical phase composition. $X_{pentane} = 0.99$, $T = 478.433$ K and $P = 3.6188$ MPa (Anthracene + n-Pentane).

With an initial composition guess of 0.975 for the critical phase, the critical point of the same system is calculated at 489.216 K and 3.9735 MPa. Figure 3.6 shows the Gibbs energy surface at this temperature and pressure and a tangent drawn to the surface at the critical composition. In this figure it can be seen that there exists a tangent which is parallel to the tangent drawn at the critical composition and hence the algorithm gives a non-trivial solution.

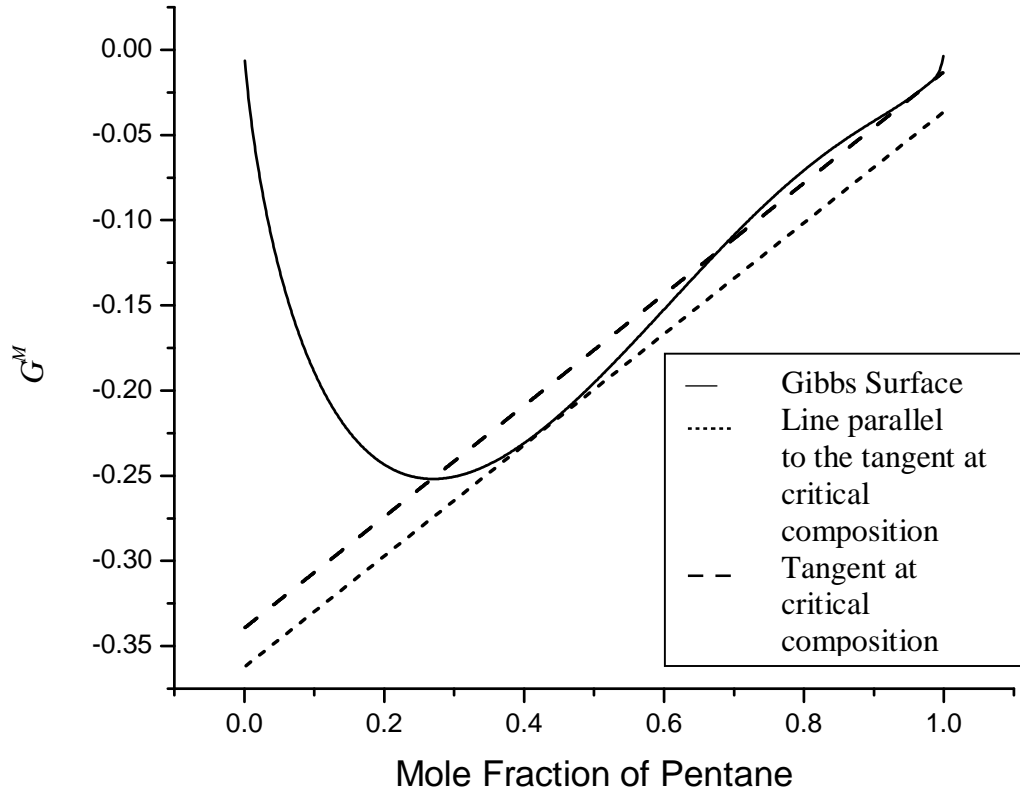


Figure 3.6: Gibbs energy surface and tangent to the surface at critical phase composition. $X_{pentane} = 0.975$, $T = 489.216$ K and $P = 3.9735$ MPa (Anthracene + n-Pentane).

3.5.3. Initial Guess for Critical Volume and Temperature

A strategy for the initial guess of critical temperature and volume was given by Heidemann and Khalil (1980). The same strategy was followed in this work with some modifications to calculate the higher density critical points. Calculating a point on the stability limit for a mixture of specified composition requires finding a temperature-volume pair, which makes the coefficient b' equal to zero, or equivalently, the determinant of \mathbf{B} equal to zero. To make the algorithm converge to a meaningful

temperature, it was suggested that the elements of \mathbf{B} be multiplied by the factor $(T/100)$ and an initial guess for the temperature to be taken as $1.5 \sum_i z_i T_{c_i}$.

For the critical point calculation to converge to a liquid-vapour critical point, the coefficient c' was multiplied by the factor $\{(v - b_m)/2b_m\}^2$ and the initial guess for the volume was taken as $3.85b_m$.

3.5.4. *Multiple Critical Points*

The strategies mentioned in section 3.5.3 give excellent results for calculating the vapour-liquid critical point which is needed in case of a K-point calculation. But in case of an L-point calculation, a liquid-liquid critical point is to be evaluated. There may be a situation where both liquid-liquid and vapour-liquid critical points exist and the one of interest is the liquid-liquid critical point. Once the temperature-volume pair which lies on the stability limit is found, a plot of the coefficient c' vs. volume can be plotted to see the presence of a higher density critical point (See Figure 3.7). It was observed that some changes in the initial guess of volume and the multiplication factor for the coefficient c' can also lead to the convergence of a liquid-liquid critical point. If there exists a liquid-liquid critical point then an initial guess for critical volume of $2b_m$ and the coefficient c' , without the multiplication factor, would result in the algorithm converging to the desired critical point.

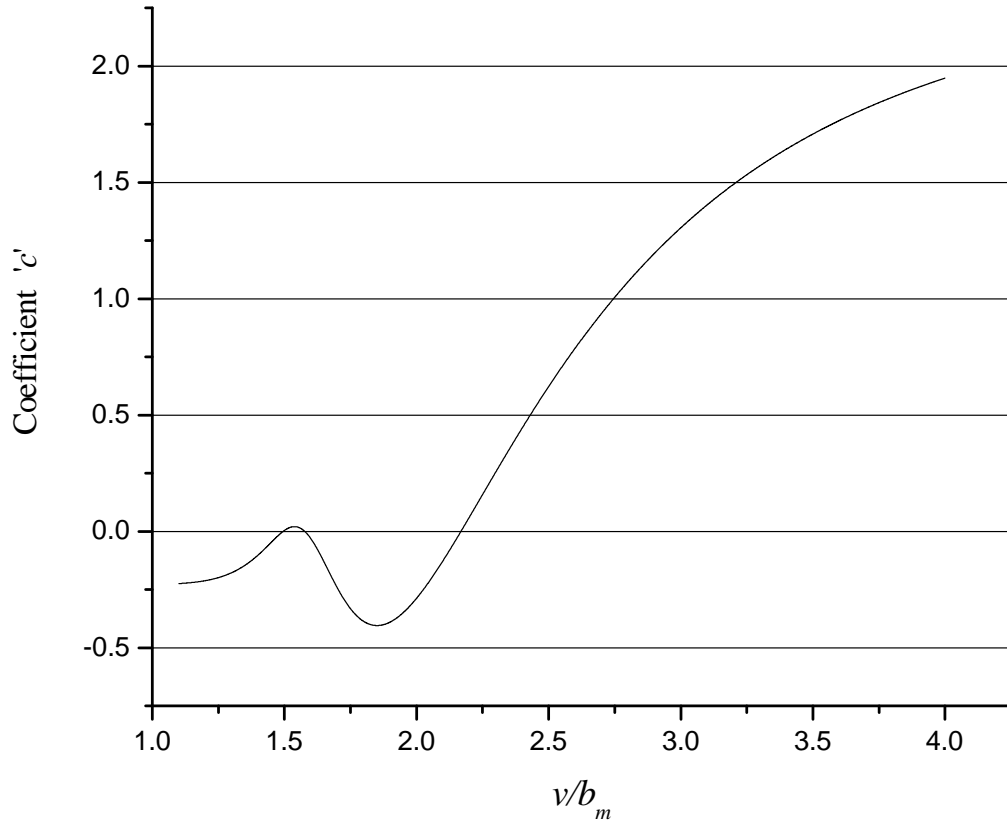


Figure 3.7: Multiple critical points for CO₂ + Tri-decane system at $z_{CO_2} = 0.915$.

3.5.5. Initial Guess for Equilibrium Phase

A good initial guess for the equilibrium phase composition is required for the subroutine to converge to a non-trivial solution, provided one exists. The numerical analysis of the equilibrium phase calculations was done using the anthracene + n-pentane system. Taking into consideration the location of K- and L-points in the composition space, as stated earlier, the critical phase is predominantly rich in the lighter component, n-pentane. Hence an initial guess for the equilibrium phase composition that is rich in the heavier component works for most of the cases. However, if the calculations are heading towards a trivial solution, they are terminated and new guess for the equilibrium phase is chosen. The matrix M' , defined as

$$M' = \begin{bmatrix} \frac{\partial g_1}{\partial Y_1} & \backslash & \backslash & \frac{\partial g_1}{\partial Y_n} \\ \wedge & & & \wedge \\ & \wedge & & \wedge \\ \frac{\partial g_n}{\partial Y_1} & \backslash & \backslash & \frac{\partial g_n}{\partial Y_n} \end{bmatrix} \quad (3.41)$$

becomes singular at the trivial solution. This phenomenon can be used to track the convergence and to avoid the algorithm from reaching a trivial solution. The spectral radius of M' reaches unity at the solution of the equilibrium phase calculations.

Figure 3.8 shows the convergence of the Newton-Raphson method for an equilibrium phase calculation, heading to the trivial solution. The system studied is anthracene + n-pentane and the temperature and pressure are that of the critical point calculated for the system at a mole fraction of n-pentane equal to 0.95. The initial guess for the equilibrium calculation is an n-pentane mole fraction of 0.6. Figure 3.9 shows the convergence of the equilibrium phase calculations to a non-trivial solution. The temperature and pressure are the same as those for Figure 3.8 but the initial guess is an n-pentane mole fraction of 0.2.

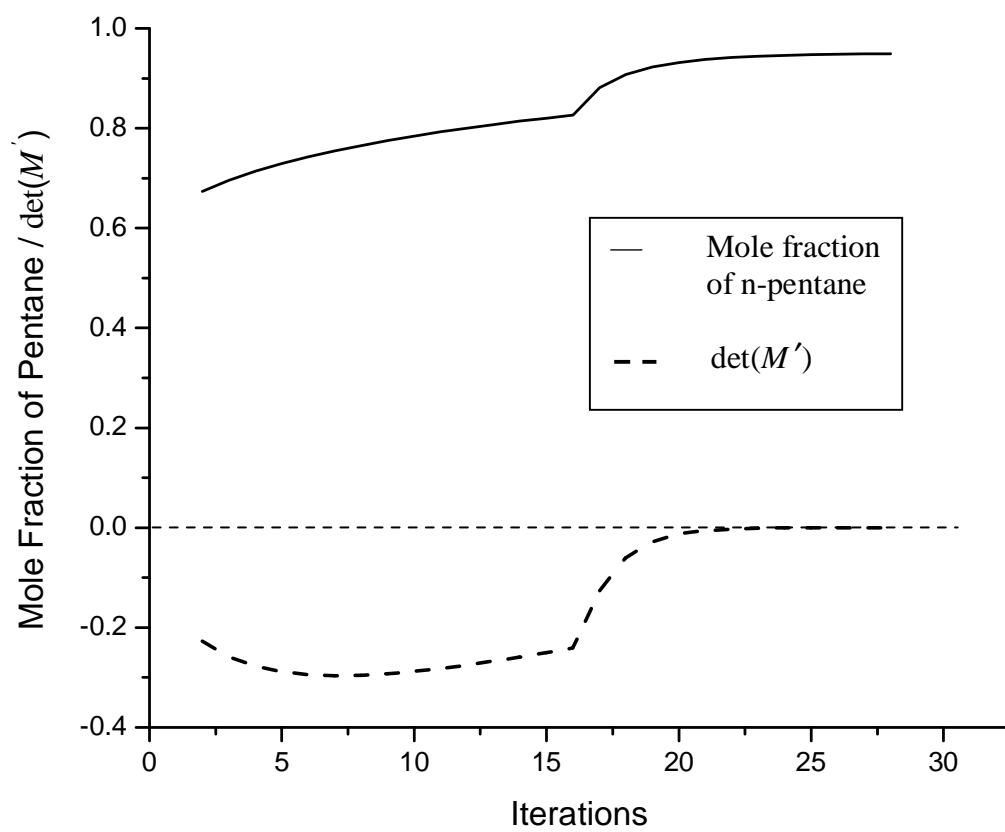


Figure 3.8: Equilibrium phase calculations converging to a trivial solution with an initial guess of 0.6 and Newton-Raphson method.

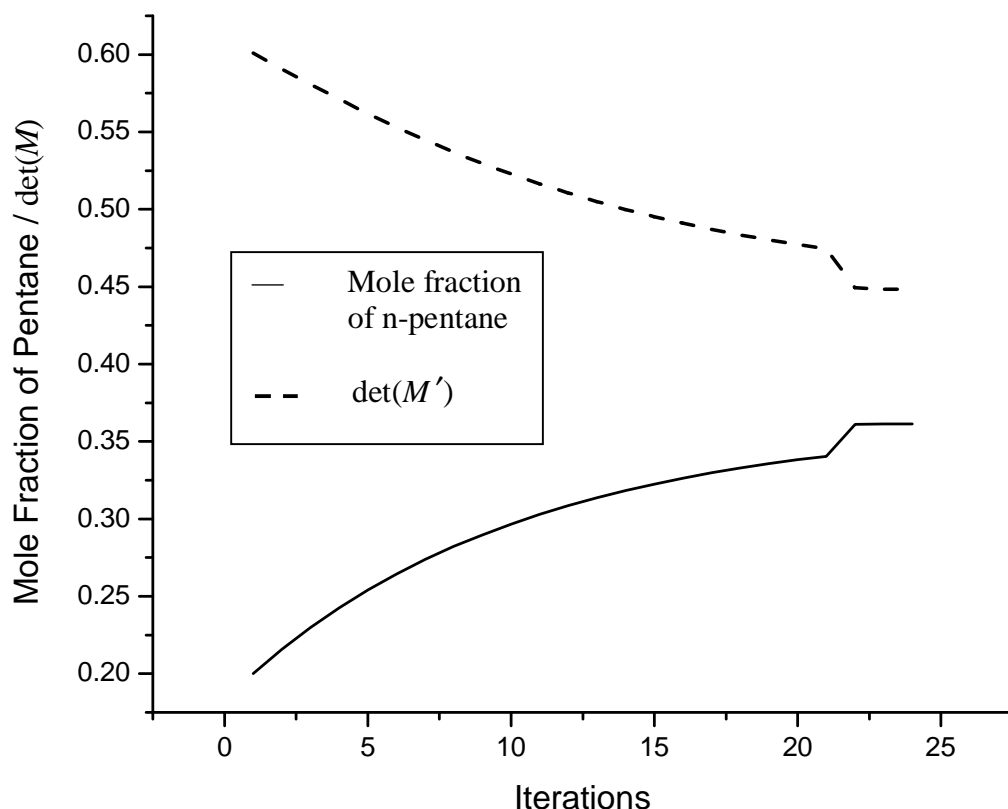


Figure 3.9: Equilibrium phase calculations converging to non-trivial solution with an initial guess of 0.2 with Newton-Raphson method.

3.5.6. Accelerated Successive Substitution vs. Newton-Raphson

A comparison of the accelerated successive substitution method and the Newton-Raphson method was done for the anthracene + n-pentane system at the temperature and pressure of the critical point calculated at an n-pentane mole fraction of 0.975. Figure 3.10 shows the convergence for both the methods. It can be observed from the figure that the accelerated successive substitution method approaches the solution faster than the Newton-Raphson method in the initial stage of the search but the Newton-Raphson method works better for fine-tuning the root near the solution. The actual solution lies at an n-pentane mole fraction of 0.3615. The chances of an

accelerated successive substitution method to diverging are less than that of the Newton-Raphson method with a poor initial guess (Peng, 1991).

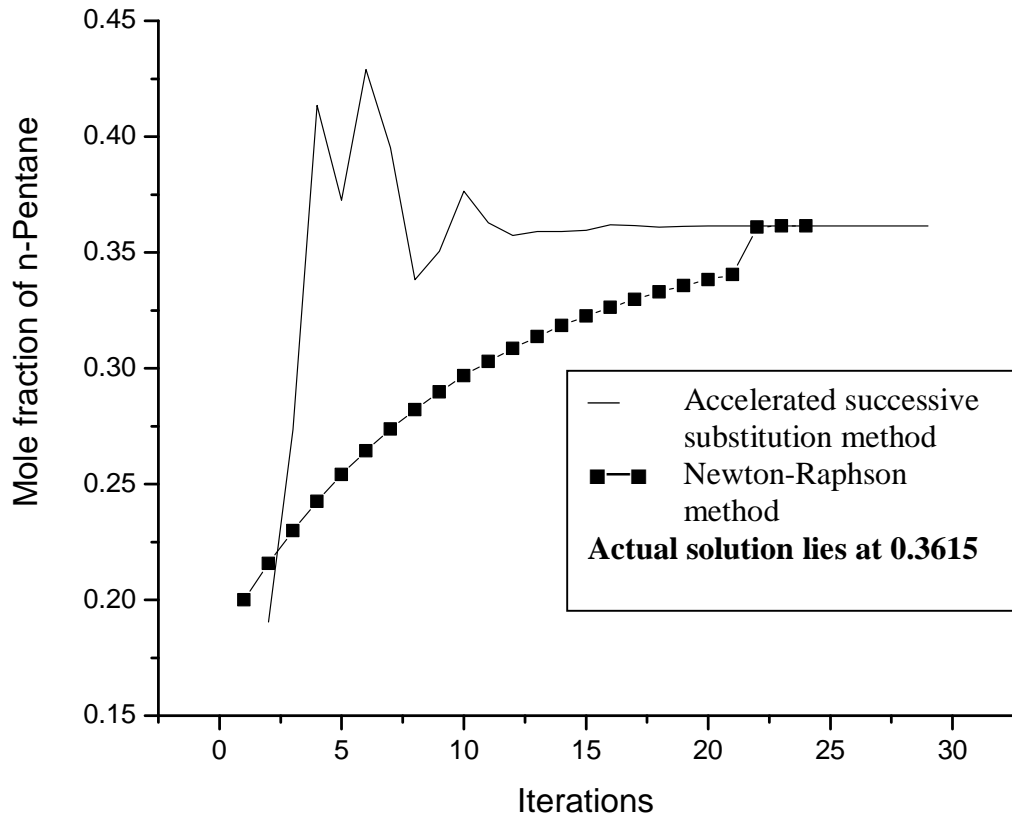


Figure 3.10: Comparison of the accelerated successive substitution method and the Newton-Raphson method. Anthracene + n-pentane system was used and an equilibrium phase was searched for the critical point of a mixture of 0.975 mole fraction of n-pentane.

Taking into consideration the ability of the accelerated successive substitution method to approach the solution faster from a general initial guess, and the ability of the Newton-Raphson method to work as a better fine-tuning technique, an attempt was made to combine both the methods. A switch from the accelerated successive substitution method to the Newton-Raphson method was made at

$\left(\left(\sum_i |g_i| / N C \right) \leq 10^{-4} \right)$. Table 3.1 shows the improvement in the speed of convergence

upon combining the two methods. The initial guess for the equilibrium phase was kept constant at an n-pentane mole fraction of 0.01. This comparison was done for the search of an equilibrium phase for critical points calculated at different compositions. The equilibrium phase search resulted in a finite value of θ everytime.

Table 3.1: Improvement in the convergence speed on combining the Newton-Raphson method and the accelerated successive substitution method. (Numbers in parenthesis are estimated CPU time)

Critical phase composition ($z_{pentane}$)	Iterations for N-R method	Iterations for Acc. S. S. method	Iterations for Acc. S. S. + N-R
0.96	34 (0.258)	34 (0.150)	17 + 7 = 24 (0.128)
0.965	38 (0.289)	45 (0.198)	15 + 15 = 30 (0.180)
0.97	35 (0.266)	103 (0.453)	17 + 13 = 30 (0.174)
0.975	36 (0.274)	84 (0.370)	13 + 5 = 18 (0.095)

The CPU time was also calculated for these two numerical methods and it was observed that a single iteration of the Newton-Raphson method takes 0.0076 units of CPU time whereas a single iteration of accelerated successive substitution method takes 0.0044 units of CPU time (measured for anthracene + n-pentane system at 496.84 K and 4.28 Mpa). In all cases tried, the hybrid method required less computing time than the Newton-Raphson or accelerated successive substitution method alone.

3.5.7. Convergence Criterion for Equilibrium Phase

The convergence criterion used for the equilibrium phase calculations in this work was $\left(\left(\sum_i |g_i| / N C \right) < 10^{-8} \right)$ and it was kept the same for all the systems studied.

A study was done to see the effect of the convergence criterion on the results of the equilibrium phase calculations. Table 3.2 shows the effect of changes in the convergence criterion on the calculated value of θ for the phase. The equilibrium phase calculations shown in Table 3.2 were done with the critical point calculated with the mole fraction of n-pentane equal to 0.975. With more stringent convergence criterion for the equilibrium phase, the θ value improves but, as can be seen from the table, when the convergence criterion was made as 10^{-10} , the algorithm converged to a trivial solution. Theoretically θ equals to zero at the equilibrium phase and critical phase but numerically it is much easier to get a zero value of θ at the critical phase. Hence tightening the convergence criterion results in the algorithm converging to a trivial solution (the critical phase composition).

Table 3.2: Sensitivity of results of the equilibrium phase calculations to the convergence criterion.

$\sum_i g_i / NC$	$\theta \times 10^6$
10^{-4}	11.545
10^{-6}	1.9124
10^{-8}	0.196
10^{-10}	Trivial Solution

3.5.8. *Upgrade of Critical Composition*

The critical phase composition is updated based on the value of θ calculated from equilibrium phase calculations using a secant method. In this process of upgrading the critical phase composition the composition may change to a value where there is no phase in equilibrium (see Figure 3.5). This situation may arise if θ calculated at a base and perturbed composition, which differ significantly. Hence, it is recommended that the composition of the critical phase be changed by a small margin to calculate θ at the perturbed composition. A perturbation of $x_{critical} \times 10^{-6}$ worked for most of the cases studied, where $x_{critical}$ is the mole fraction of the lighter component in the critical phase.

4. RESULTS AND DISCUSSION

4.1. Introduction

The algorithm described in chapter 3 was used to calculate K- and L-points for different systems. The K- and L-points were calculated using a range of binary interaction parameters for the Peng-Robinson equation of state. The effect of the binary interaction parameter on computed K- and L-points was studied and results were compared with the experimental data in literature to fit the binary interaction parameter. The qualitative effect of the binary interaction parameter on the P - T projection of the binary system in phase space was also studied. The P - T projection of a binary system, predicted with the binary interaction parameter fitted using a K- and/or an L-point, was then compared with the experimental phase behaviour data of the system.

The success of this method in fitting the binary interaction parameter and the capability of the Peng-Robinson equation of state to determine the high pressure complex phase behaviour are discussed.

4.2. Systems Studied

The propane + polyaromatic hydrocarbon binary system is a model heavy oil system and hence was chosen for this study. The experimental data of the phase behaviour of propane binaries with fluorene, with phenanthrene and with

triphenylmethane given by Peters et al. (1989) was used to compare with the computed results.

The phase behaviour of binary hydrocarbons has considerable theoretical importance because the multiphase equilibrium properties are required for the design of separating units in the production and refining of petroleum. The systems studied of this type were methane binaries with n-pentane, n-hexane and n-heptane.

Experimental phase behaviour of binary mixtures composed of a polar and a non-polar species was studied by Lam et al. (1990). The ethane + ethanol system, as a representative of this type, was studied in order to complement the experimental studies with the results computed using an equation of state. The pure component critical properties and acentric factors, used to calculate the equation of state parameters are listed in Appendix B, Table B.1.

4.2.1. *Alkane + Alkanol*

Multiphase equilibria of binary mixtures of ethane + n-alkanol were studied by Lam et al. (1977) and the experimental studies show that a three-phase line is present in all the cases. The phenomenon of a three-phase line extending from a lower critical end point to an upper critical end point was observed in ethane binaries of ethanol, n-propanol and n-butanol. The phase behaviour of this type of system was calculated in this work using the Peng-Robinson equation of state and the qualitative effect of the binary interaction parameter on the phase behaviour was studied.

4.2.1.1. *Ethane + Ethanol*

The ethane + ethanol system shows *Type-V* phase behaviour experimentally. Experimental studies of the phase behaviour of the system were done by Bruner

(1985b) and Lam et al. (1977), and both the researchers recorded similar observations regarding the phase behaviour of the system; however there was a slight variation in the experimental K- and L-points. Lam et al. (1977) observed the K-point of the system at 314.66 K and 5.556 MPa and the L-point at 309.04 K and 4.980 MPa. Bruner (1985b) observed the K-point at 314.36 K and 5.537 MPa and the L-point at 308.72 K and 4.952 MPa. The experimental data used in this work for comparison, was that taken from Lam et al. (1977).

K- and L-points for the ethane + ethanol system were calculated using different values for the binary interaction parameter. It was observed that the location of K- and L-points varied significantly in P - T space with change in the binary interaction parameter. The K-point calculated using a binary interaction parameter of 0.135 matched the experimental K-point temperature and the L-point calculated using a binary interaction parameter of 0.0362 matched the experimental L-point temperature. From this it is apparent that a single value of the binary interaction parameter was not able to predict both K- and L-points well. Additionally, it was noted that a single value of binary interaction parameter without a pressure and/or temperature dependence was unable to predict the presence of both the K- and L-points simultaneously.

A P - T phase diagram of the system was constructed with the two values of the binary interaction parameter which gave the best fit for the K- and L-points. The binary interaction parameter giving the best match for experimental L-point ($\delta_{ij} = 0.0362$) resulted in a *Type-II* phase behaviour for the system, and the binary interaction parameter giving the best match for experimental K-point ($\delta_{ij} = 0.135$) resulted in a

Type-III phase behaviour for the system. Figures 4.1 and 4.2 show the phase diagrams for the system with these two different values of binary interaction parameters.

A typical *Type-II* phase diagram can be seen in Figure 4.1 but the liquid-liquid critical line is seen extending past the upper critical end point. Though the critical points calculated in this case were stable by themselves, they were unstable when a three-phase solution was considered with the same overall composition. A similar phenomenon can be observed for the phase diagram shown in Figures 4.2a and 4.2b, where the critical liquid-vapour line extends past the upper critical end point. A magnified view of the part of the phase diagram in Figure 4.2a which is in the rectangle is shown in Figure 4.2b. The upper critical end point in this case is the K-point whereas it is an L-point in Figure 4.1. The calculations of the critical line were stopped in both the cases when the critical point calculated became unstable ($d < 0$).

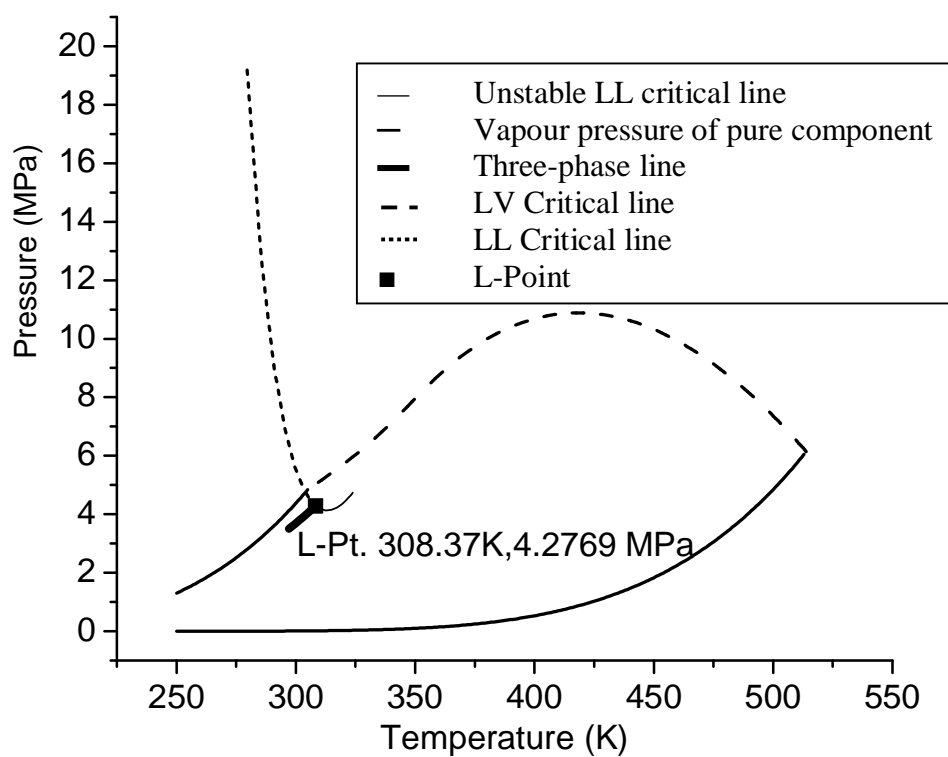
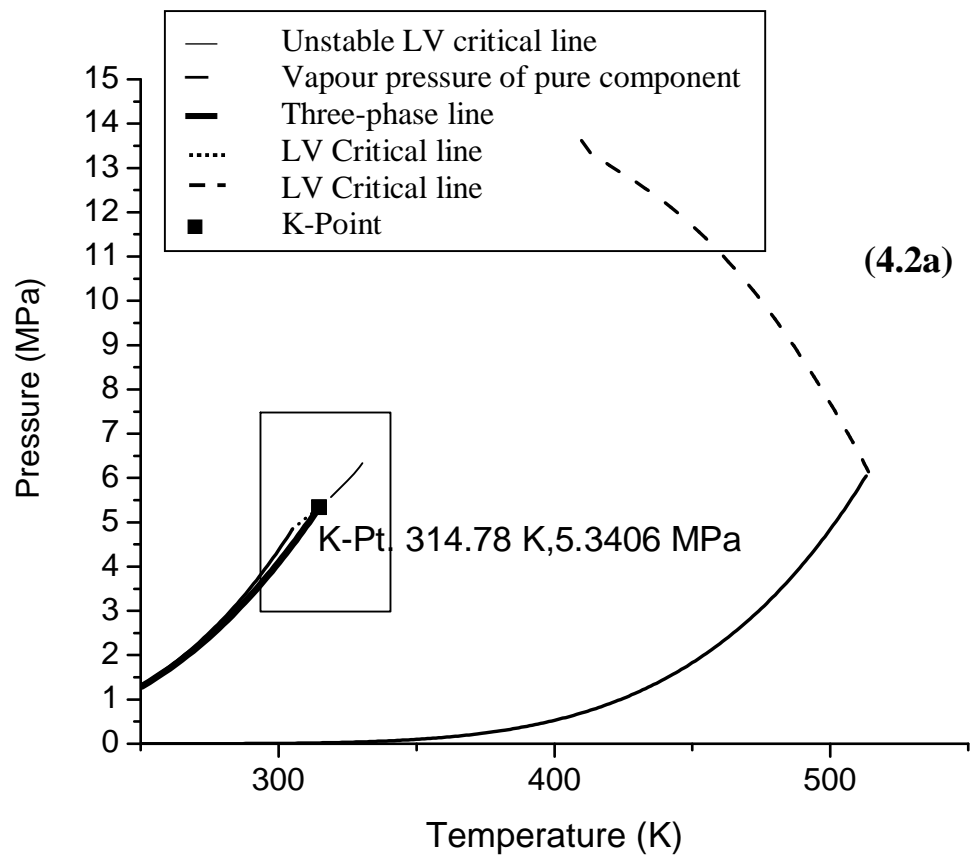


Figure 4.1: Phase diagram for the ethane + ethanol system using the Peng-Robinson equation of state with $\delta_{ij} = 0.0362$. *Type-II* phase behaviour.



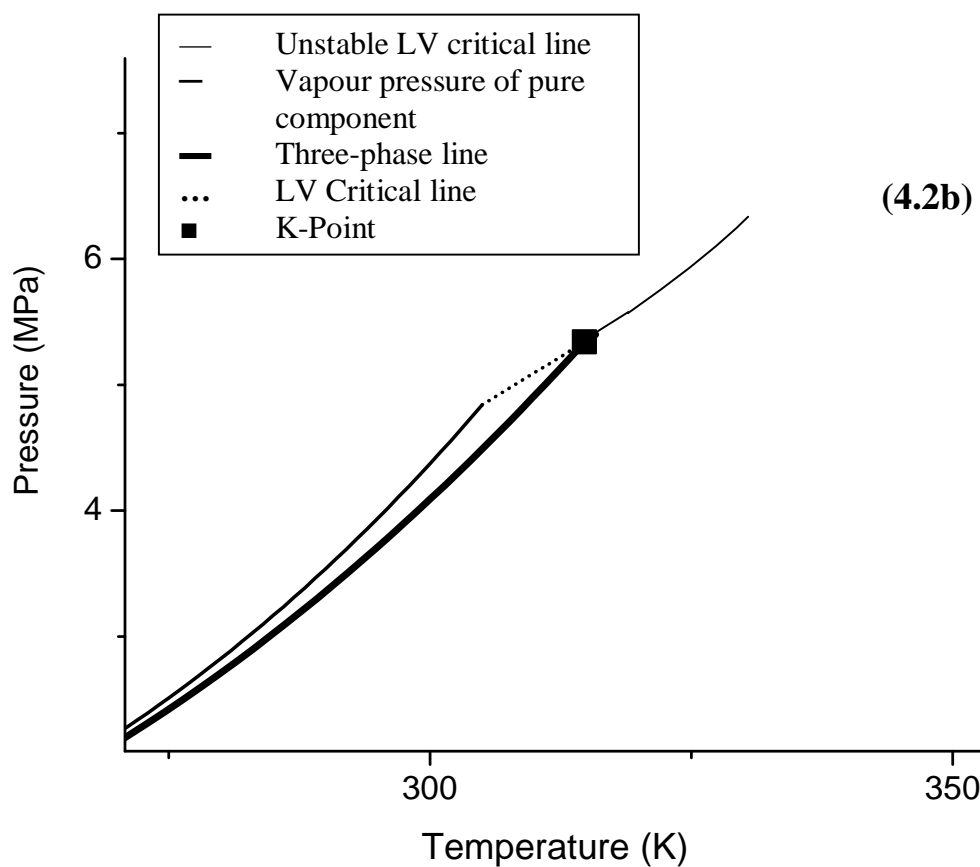


Figure 4.2: Phase diagram for the ethane + ethanol system using the Peng-Robinson equation of state with $\delta_{ij} = 0.135$. *Type-III* phase behaviour. A complete P - T projection can be seen in (4.2a) whereas (4.2b) shows the magnified view of the part of phase diagram in rectangle.

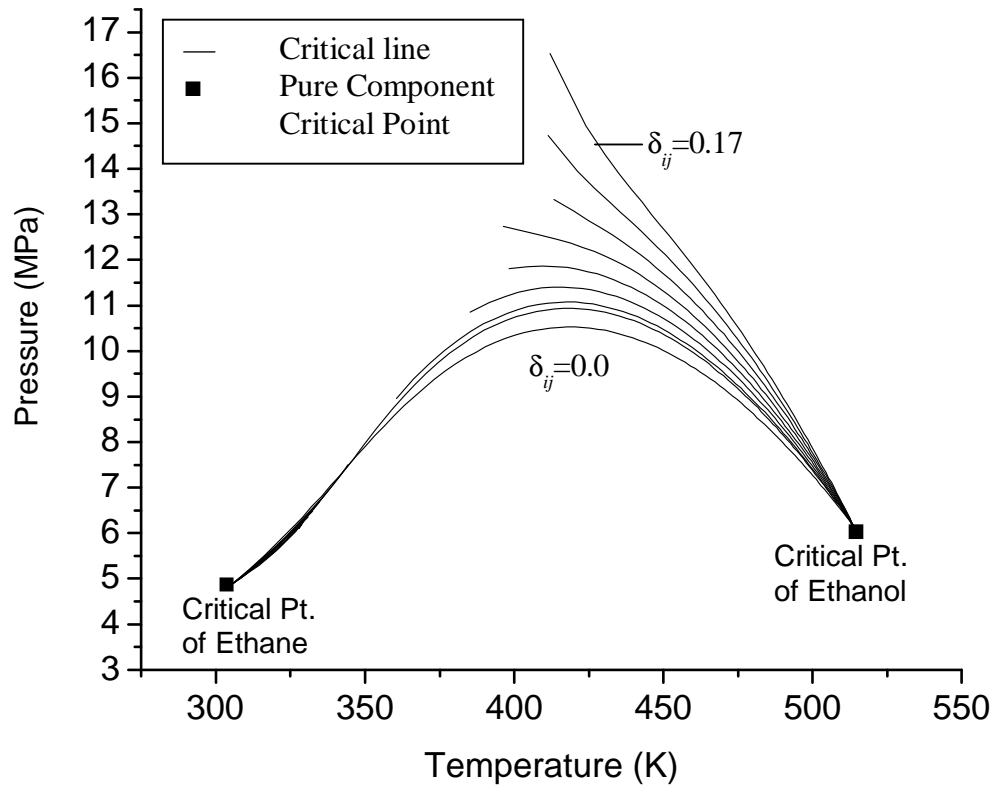


Figure 4.3: Variation of Critical Line with binary interaction parameter for ethane + ethanol system. Peng-Robinson equation of state was used.

A study was done to see if the experimentally observed *Type-V* phase behaviour can be reproduced in the ethane + ethanol system for any value of binary interaction parameter. Figure 4.3 shows a plot of the critical line for binary interaction parameters in the range of $0.0 \leq \delta_{ij} \leq 0.17$. A continuous critical line, starting and ending at the pure component critical points, can be observed for values of the binary interaction parameter between 0.0 and 0.03, inclusive. Three-phase lines calculated for different values of the binary interaction parameter revealed that for $\delta_{ij} \leq 0.05$, the three-phase line terminated in an L-point while for $\delta_{ij} \geq 0.07$; the three-phase line terminated in a K-point. For $\delta_{ij} \geq 0.05$ it was observed that the critical line was discontinuous. The critical lines for $\delta_{ij} > 0.13$, show a definitive *Type-III* behaviour. No value of δ_{ij} tried

resulted in a three-phase line terminating in both a K- and an L-point, a key characteristic of *Type-V* phase behaviour. For the binary interaction parameter values less than 0.0, a continuous critical line was observed. The effect of the binary interaction parameter value on the phase behaviour of ethane + ethanol system is summarized in Table 4.1.

Table 4.1: Binary Interaction parameter for the Peng-Robinson equation of state and phase behaviour of ethane + ethanol system.

Binary Interaction Parameter	Phase Behaviour
$\delta_{ij} \leq 0.03$	<i>Type-I</i>
$0.03 < \delta_{ij} \leq 0.05$	<i>Type-II</i>
$0.05 < \delta_{ij} \leq 0.13$	No definite type
$\delta_{ij} > 0.13$	<i>Type-III</i>

4.2.2. Methane + n-Alkane

Multiphase equilibria of binaries of methane and n-alkane were studied by Lin et al. (1977), Chang et al. (1966) and Shim et al. (1962) to name a few. The presence of a three-phase line and an upper and/or lower critical endpoint was observed in all the binaries of methane with n-butane and higher n-alkanes. The systems studied in this work are the binaries of methane with n-pentane, n-hexane and n-heptane. The binaries

of n-pentane and n-hexane show *Type-V* phase behaviour whereas *Type-III* phase behaviour was observed experimentally for the binary of n-heptane.

Multiphase equilibria of these systems were calculated using the Peng-Robinson equation of state with different values of the binary interaction parameter. The effect of the binary interaction parameter on the K- and L-points and on the overall phase behaviour of these systems is discussed in the following section.

4.2.2.1. Methane + n-Pentane

The methane + n-pentane system experimentally shows *Type-V* phase behaviour (Chu et al., 1976). The precise data for the critical endpoints of the methane + n-pentane system could not be found. However, the effect of the binary interaction parameter on the location of the K- and L-points in P - T space was studied. The K-points for the system were calculated for a range of interaction parameters between -0.1 to 0.1, inclusive. Figure 4.4 shows the variation of the K-points with respect to changes in the binary interaction parameter. The K-point moves to a higher temperature and pressure with an increase in the value of the binary interaction parameter but the trend reverses after the interaction parameter value of 0.0. The K-point calculated with the binary interaction parameter value of 0.0 is at the highest temperature and pressure. The variation of an L-point of the system with respect to the changes in the binary interaction parameter is shown in Figure 4.5. An L-point was not found for values of the binary interaction parameter greater than 0.03.

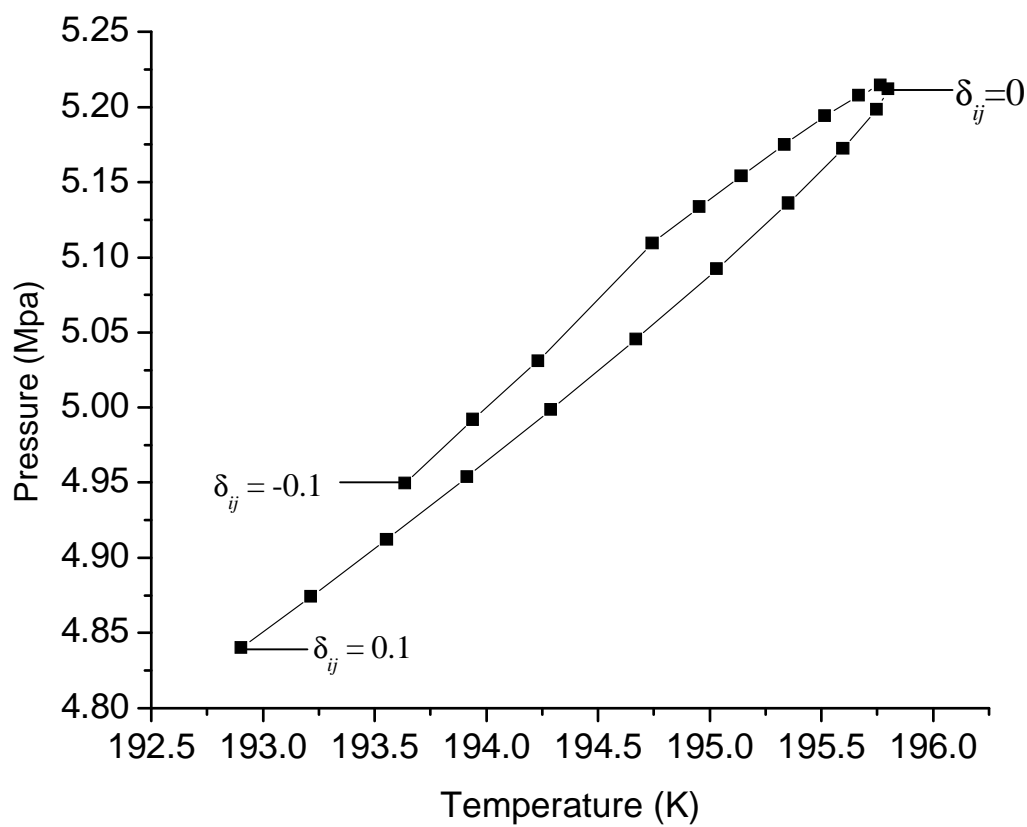


Figure 4.4: Variation of the K-point in the methane + n-pentane system with changes in the binary interaction parameter for the Peng-Robinson equation of state.

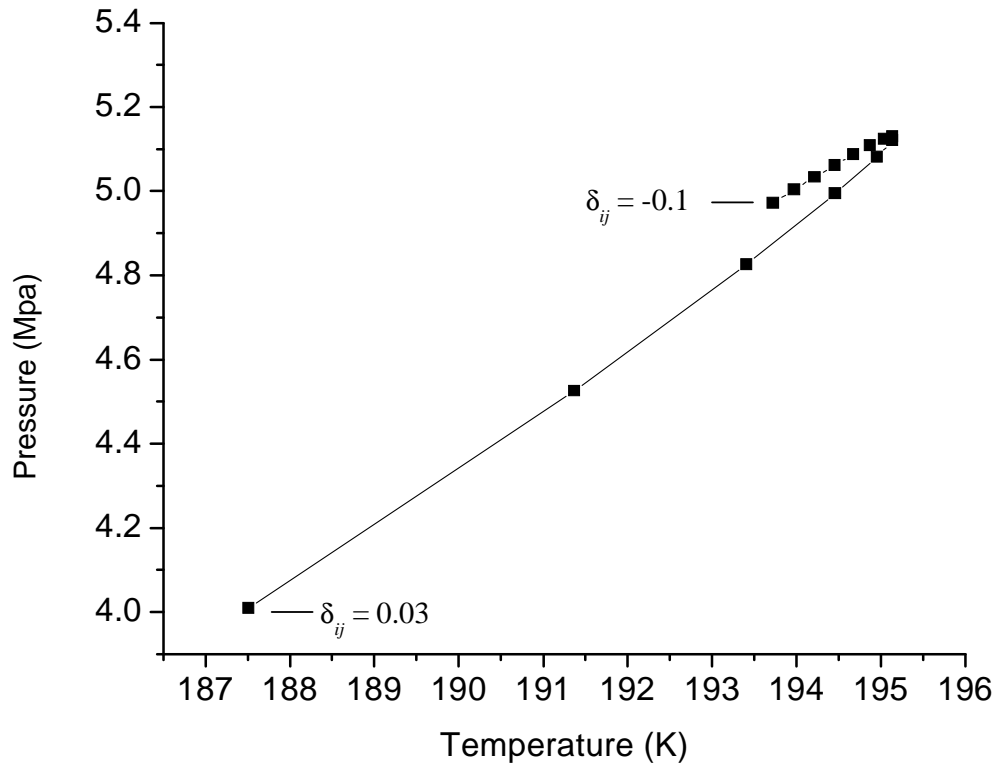


Figure 4.5: Variation of L-point in the methane + n-pentane system with changes in the binary interaction parameter for the Peng-Robinson equation of state.

The variation of the critical lines of the system with changes in the binary interaction parameter was also studied in order to understand the effect of the binary interaction parameter on the type of the P - T phase behaviour of the system. For interaction parameters in the range of $-0.1 \leq \delta_{ij} \leq 0.0$, a continuous critical line, starting and ending at the pure component critical points was observed, a characteristic of *Type-I* or *Type-II* phase behaviour. For the interaction parameter values between 0.01 and 0.03, it was observed that the critical lines showed *Type-V* phase behaviour. When the interaction parameter was increased further, the critical lines indicated *Type-III* phase behaviour. The variation of the phase behaviour of this system with change in the value of the binary interaction parameter is summarized in Table 4.2.

Table 4.2: Binary Interaction parameter for the Peng-Robinson equation of state and phase behaviour of methane + n-pentane system.

Binary Interaction Parameter	Phase Behaviour
$-0.1 \leq \delta_{ij} \leq 0.0$	<i>Type-I or Type-II</i>
$0.0 < \delta_{ij} \leq 0.03$	<i>Type-V</i>
$0.03 < \delta_{ij}$	<i>Type-III</i>

A binary interaction parameter of 0.02 proved to be successful in predicting the correct type of phase behaviour for the methane + n-pentane system. Figure 4.6 shows a part of that phase diagram which focuses on the location of the K- and L-points, the critical line and the three-phase line terminating in a K- and an L-point. The phase diagram is developed using an interaction parameter value of 0.02. Note that the critical line extends past the L-point (or lower critical endpoint). The critical points were stable by themselves but proved unstable when a three-phase solution at the same overall composition was considered. The calculations of the critical line were terminated when the calculated critical points became unstable ($d < 0$). A feature representing the typical *Type-V* phase behaviour, a three-phase line bounded between the upper and lower critical endpoint and the critical line terminating at one end in the lower critical endpoint, can be seen in Figure 4.6. The critical line seen in Figure 4.6 is the one that emerges from the pure component critical point of n-pentane. The critical point of n-pentane can not be seen as it is beyond the scale of the plot.

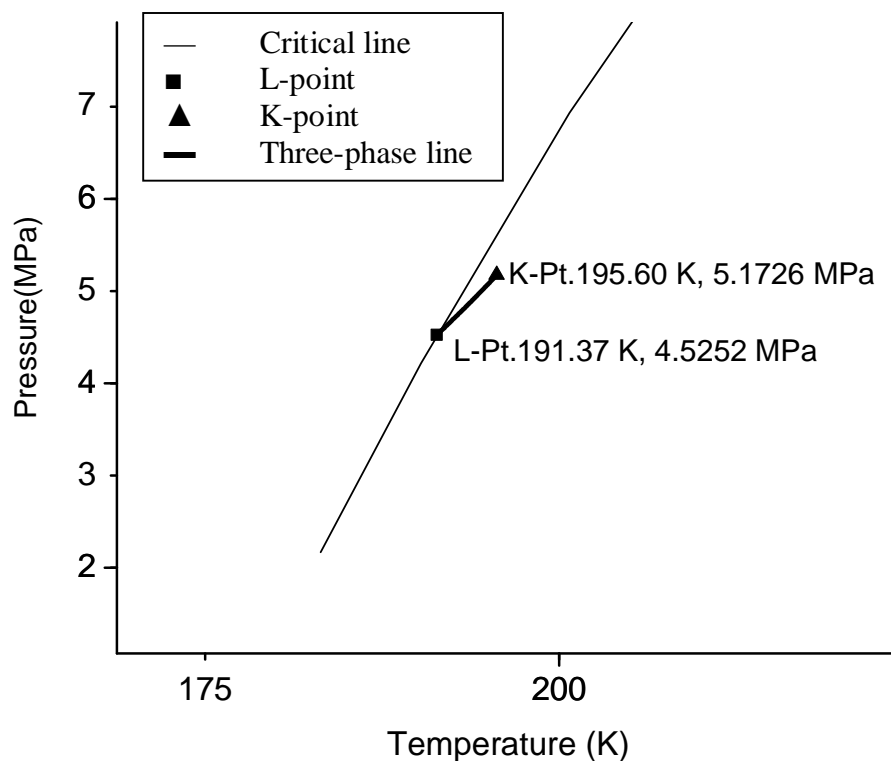


Figure 4.6: Phase diagram for the methane + n-pentane system using the Peng-Robinson equation of state with $\delta_{ij} = 0.02$. Type-V phase behaviour can be observed.

4.2.2.2. Methane + n-Hexane

An experimental K-point for the methane + n-hexane system occurs at 195.91 K and 5.2055 MPa while the experimental L-point is at 182.46 K and 3.4149 MPa (Lin et al., 1977). The effect of the binary interaction parameter on the location of computed K- and L-points of the system in P - T space was studied. Figure 4.7 shows the variation of K-points of the system with respect to changes in the binary interaction parameter and Figure 4.8 shows the variation of L-points of the system with respect to changes in the binary interaction parameter. An L-point was not found for a value of binary

interaction parameter greater than -0.02. The trend in the variation of the K- and L-points is similar to that observed for the methane + n-pentane system.

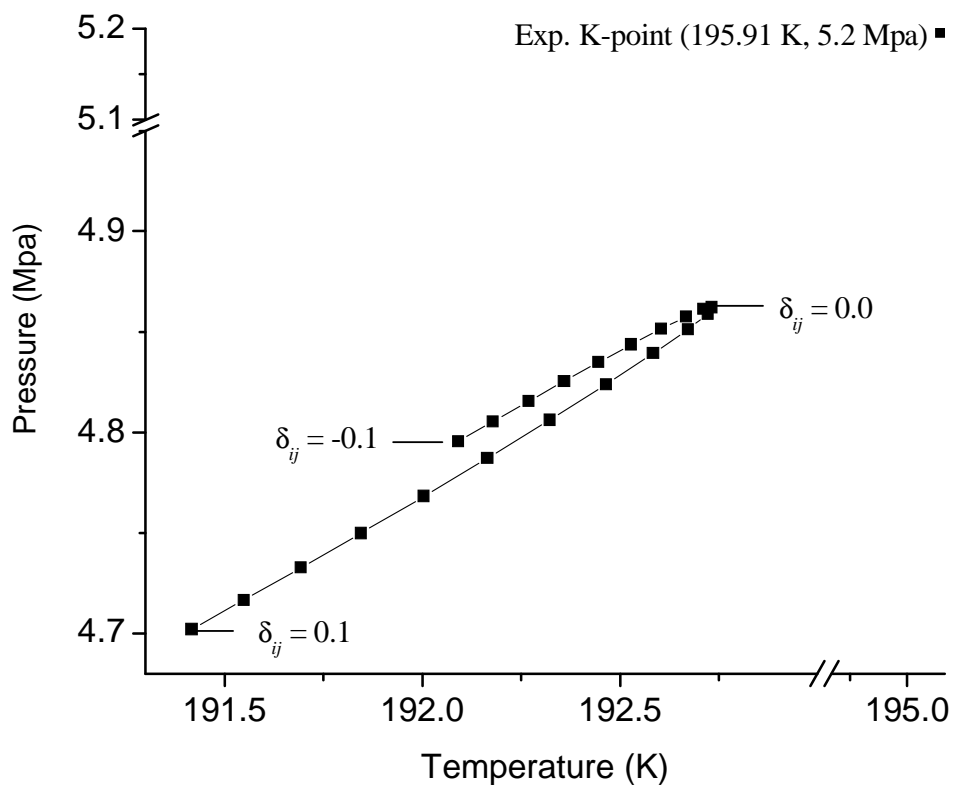


Figure 4.7: Variation of the K-point in the methane + n-hexane system with changes in the binary interaction parameter for the Peng-Robinson equation of state.

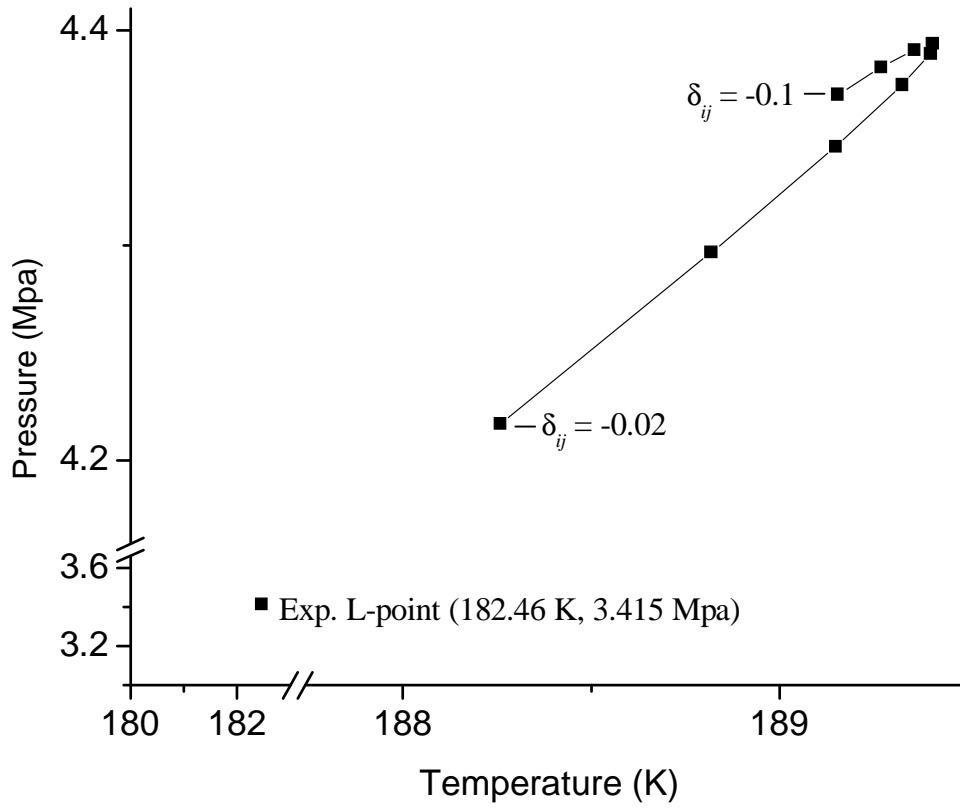


Figure 4.8: Variation of the L-point in the methane + n-hexane system with changes in the binary interaction parameter for the Peng-Robinson equation of state.

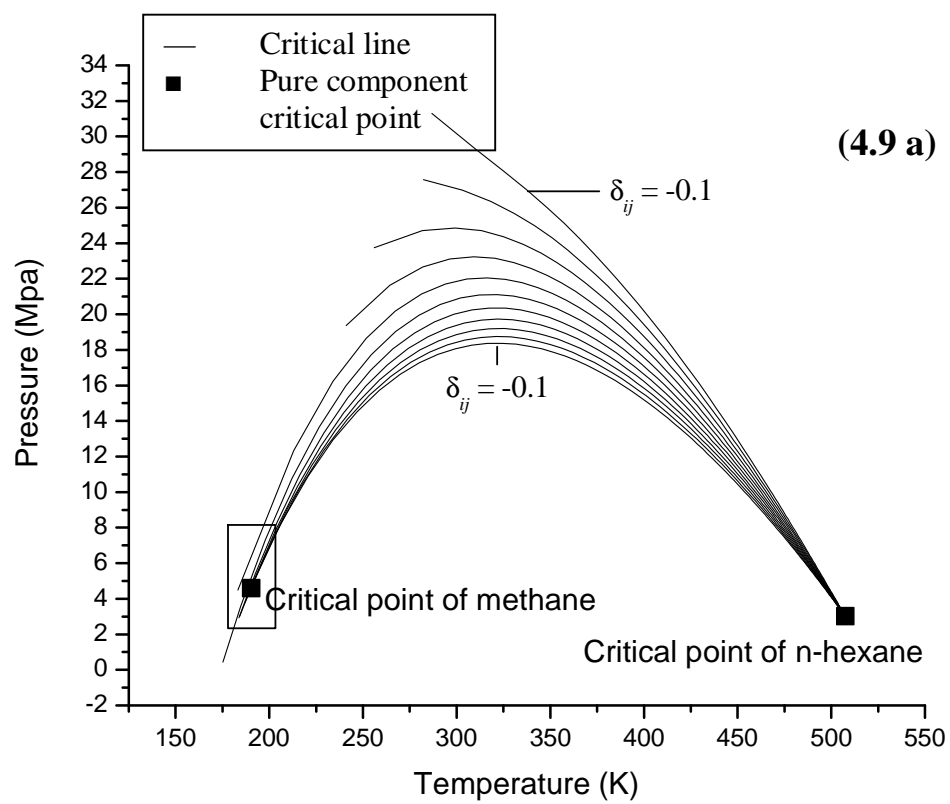
The variation of the critical lines of the system with respect to changes in the binary interaction parameter was also studied in order to understand the effect of the binary interaction parameter on the P - T phase behaviour of the system (see Figure 4.9). When the interaction parameter was increased from -0.1 to -0.08 , a continuous critical line was observed, similar to *Type-I* or *Type-II* phase behaviour. For the interaction parameter values between -0.08 and 0.03 , it was observed that the critical line showed *Type-V* phase behaviour. When the binary interaction parameter was increased further, the critical line became discontinuous and at the binary interaction parameter of 0.1 , a definitive of *Type-III* phase behaviour could be observed. Figure 4.9(a) shows the

variation of critical lines with respect to changes in the binary interaction parameter and Figure 4.9 (b) shows the change in the location of critical line with respect to changes in the binary interaction parameter near the critical point of pure methane. With decrease in the value of the binary interaction parameter the critical line shifts away from the critical point of methane, indicating a gradual shift from *Type-I* or *Type-II* phase behaviour towards *Type-V* phase behaviour. The effect of the changes in the binary interaction parameter on the phase behaviour of methane + n-hexane system is summarized in Table 4.3.

Table 4.3: Binary Interaction parameter for the Peng-Robinson equation of state and phase behaviour of methane + n-hexane system.

Binary Interaction Parameter	Phase Behaviour
$-0.1 \leq \delta_{ij} \leq -0.08$	<i>Type-I</i> or <i>Type-II</i>
$-0.08 < \delta_{ij} \leq 0.03$	<i>Type-V</i>
$0.03 < \delta_{ij} \leq 0.09$	No definite type
$\delta_{ij} > 0.09$	<i>Type-III</i>

Though any value of interaction parameter between -0.08 and 0.03 predicts the correct shape of critical line for the system, $\delta_{ij} = -0.02$ is recommended, as it gives a better result for both the K- and L-points.



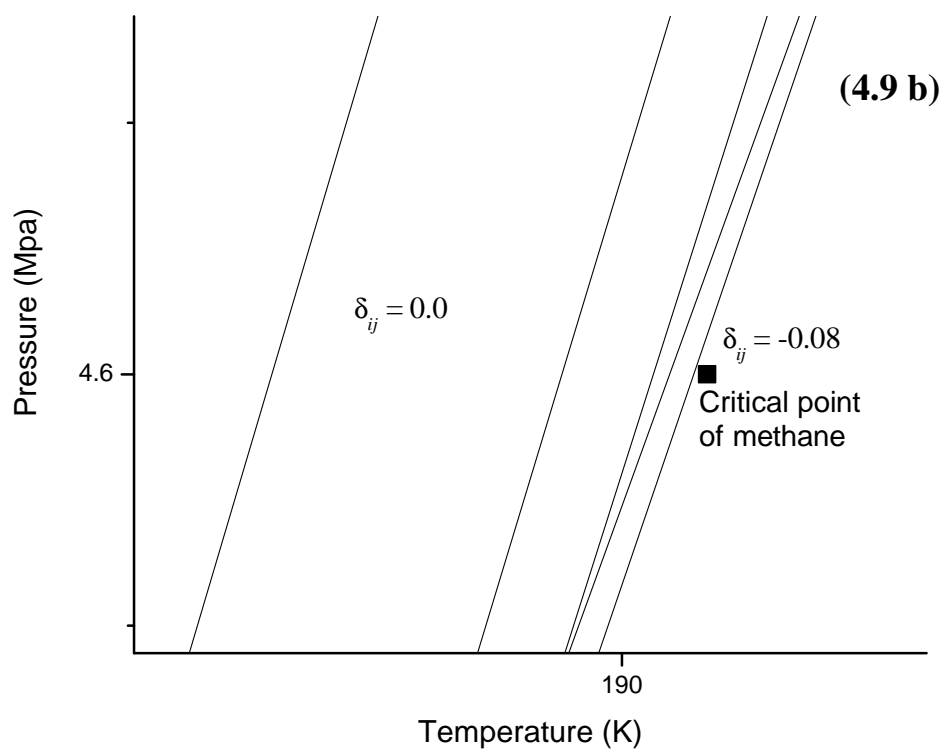


Figure 4.9 (a): Variation of the Critical Line of methane + n-hexane system with changes in the binary interaction parameter for Peng-Robinson equation of state. (b) Critical line moves away from the critical point of methane with increase in the value of binary interaction parameter. The interaction parameter is incremented using an interval of 0.02.

4.2.2.3. Methane + n-Heptane

Experimentally, the methane + n-heptane system shows *Type-III* phase behaviour and the K-point occurs at 191.65 K and 4.7850 MPa (Chang et al., 1966). The effect of the binary interaction parameter on the K-point in the methane + n-heptane system can be seen in Figure 4.10. The trend in the variation is similar to that observed in the previous cases of methane + n-alkane binaries. The critical lines for this system show typical *Type-V* phase behaviour in the range of interaction parameter between -0.1 and 0.0 , inclusive. *Type-I* or *Type-II* phase behaviour were not looked for at lower values of the binary interaction parameter. Further increasing the binary interaction parameter, results in a transition to *Type-III* phase behaviour. Experimental data for the methane + n-heptane system (Chang et al., 1966) shows the appearance of a solid phase in a phase diagram similar to *Type-III* behaviour where the three-phase line terminates in a four-phase point instead of an L-point. No solid models were used in this study to calculate multiphase equilibria involving a solid phase. The binary interaction parameter value of 0.0 is suggested for the system as it predicts the shape of critical lines similar to *Type-III* phase behaviour and calculates the K-point with the best possible accuracy. Table 4.4 shows the variation of phase behaviour of the methane + n-heptane system with changes in the binary interaction parameter value.

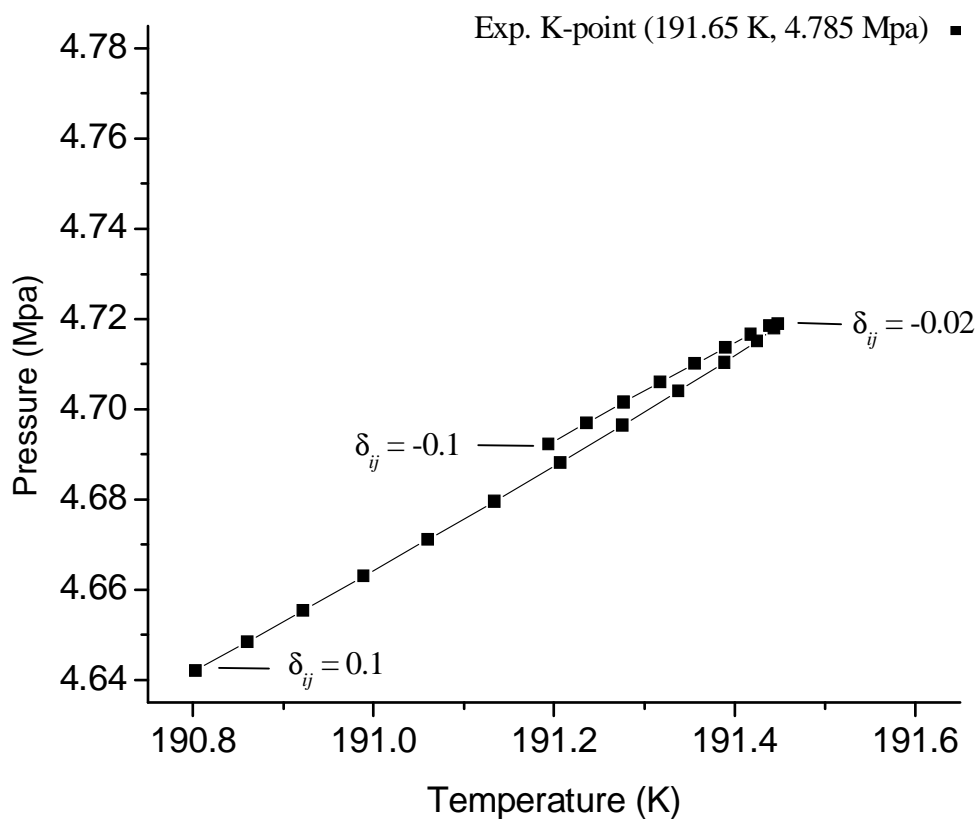


Figure 4.10: Variation of the K-point in the methane + n-heptane system with changes in the binary interaction parameter for the Peng-Robinson equation of state.

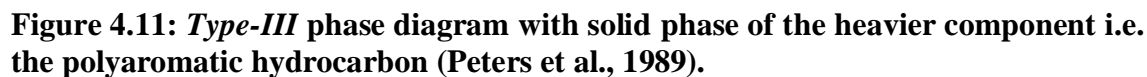
Table 4.4: Binary Interaction parameter for the Peng-Robinson equation of state and phase behaviour of methane + n-heptane system.

Binary Interaction Parameter	Phase Behaviour
$-0.1 \leq \delta_{ij} \leq 0.0$	<i>Type-V</i>
$\delta_{ij} \geq 0.0$	<i>Type-III</i>

4.2.3. Propane + Polyaromatic Hydrocarbons

Experimental studies of the binaries of propane and polyaromatic hydrocarbons were carried out by Peters et al. (1989). The phase diagrams of binaries of propane with polyaromatic hydrocarbons having a carbon number higher than 13 are marked with the presence of a four-phase point. The classification of binary phase diagrams done by Van Konynenburg and Scott (1980) does not take into account the occurrence of a solid phase.

Peters et al. (1989) observed the presence of a solid phase in the phase behaviour of propane binaries with polyaromatic hydrocarbons and extended the classification of phase diagrams to incorporate the solid phase. A *Type-III* phase diagram, incorporating the solid phase, is shown in Figure 4.11. This type of phase behaviour was observed experimentally by Peters et al. (1989) in the case of the propane binaries discussed in this work. The solid phase consists of the heavier component (i.e. the polyaromatic hydrocarbon). The intersection of the three-phase line (L_1L_2G) with another three phase line (S_BLG) results in a four-phase point. The three-phase line (S_BLG) has two branches with different liquid phases (L_1 or L_2). The three-phase line (L_1L_2G) is bounded between an upper critical endpoint (K-point, in this case) and a four-phase point (Q). The metastable parts of the critical line and three-phase line are indicated by dotted lines.



The experimental K-point for the fluorene + propane system lies at 385.5 K and 5.11 MPa (Peters et al., 1989). K-points were calculated for this system using different values of binary interaction parameters for the Peng-Robinson equation of state. The variation of the K-point in the P - T space with respect to the binary interaction parameter can be seen in Figure 4.12. The maximum temperature and pressure that can be attained are 375.642 K and 4.5829 MPa respectively using a binary interaction parameter value of -0.07. No value of the binary interaction parameter was able to reproduce the experimental K-point temperature or pressure. Experimentally, the system exhibits *Type-III* phase behaviour with the presence of a four-phase point instead of an L-point.

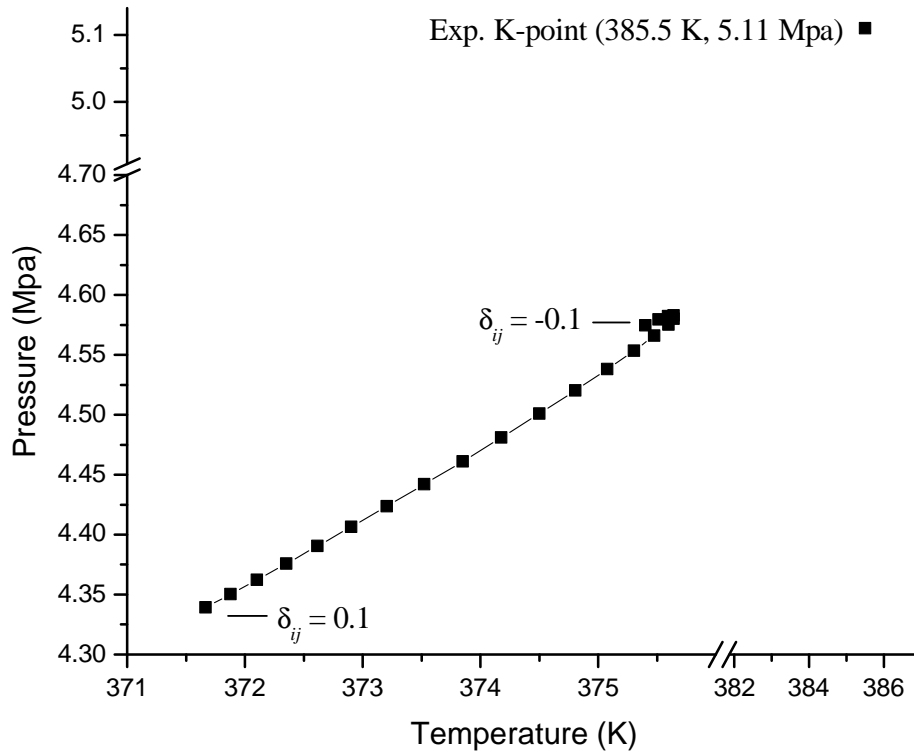


Figure 4.12: Variation of K-points of the propane + fluorene system with changes in the binary interaction parameter for the Peng-Robinson equation of state. Experimental K-point lies at 385.5 K and 5.11 MPa.

The effect of the binary interaction parameter on the shape of the critical line was studied. Computationally, it was noted that from $-0.1 \leq \delta_{ij} \leq 0.0$, a critical line representing *Type-V* phase behaviour was predicted. Lower values of binary interaction parameters were not tried. The critical line becomes discontinuous when the interaction parameter value is increased further and a definitive of *Type-III*, was observed for the interaction parameter value of 0.05 (see Figure 4.13).

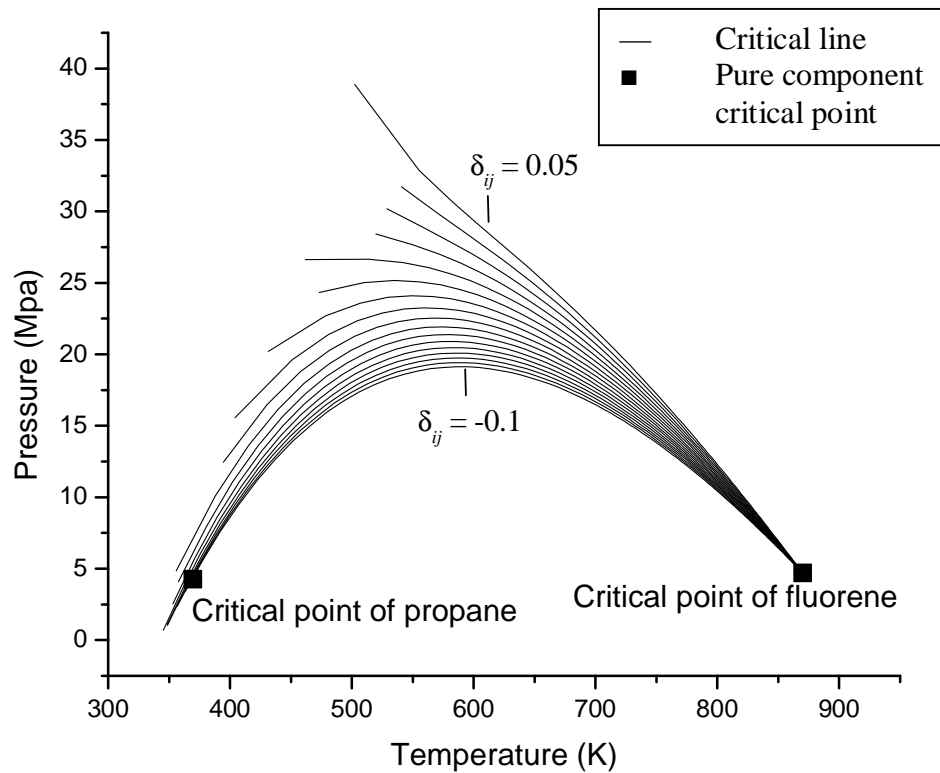


Figure 4.13: Variation of Critical Line of propane + fluorene system with changes in the binary interaction parameter for the Peng-Robinson equation of state.

Though the binary interaction parameter of -0.07 predicts the K-point with the best possible accuracy it is not the correct choice of interaction parameter for the system because it predicts the incorrect type of phase behaviour. A binary interaction parameter of 0.05 is the suggested value of binary interaction parameter for the system because it gives the closest K-point with the correct phase behaviour. Table 4.5 summarizes the effect of binary interaction parameter on the type of phase behaviour for the propane + fluorene system.

Table 4.5: Binary Interaction parameter for the Peng-Robinson equation of state and phase behaviour of propane + fluorene system.

Binary Interaction Parameter	Phase Behaviour
$-0.1 \leq \delta_{ij} \leq 0.0$	<i>Type-V</i>
$0.0 < \delta_{ij} < 0.05$	No definite type
$\delta_{ij} \geq 0.05$	<i>Type-III</i>

4.2.3.2. Propane + Phenanthrene

An experimental K-point for the phenanthrene + propane system was reported at 377.3 K and 4.67 MPa (Peters et al., 1980). The predicted K-points for this system using different binary interaction parameters can be seen in Figure 4.14. It can be observed from the figure that no value of the binary interaction parameter gives the same K-point temperature or pressure as the experimental results. A binary interaction parameter of -0.03 gives the best possible results for the K-point.

Experimentally, the phenanthrene + propane system shows *Type-III* phase behaviour with the existence of a solid phase. The LLG three-phase line ends in a four-phase point and two more three-phase lines (SLL and SLG) can be found. The critical locus becomes metastable at higher pressures (See Figure 4.11).

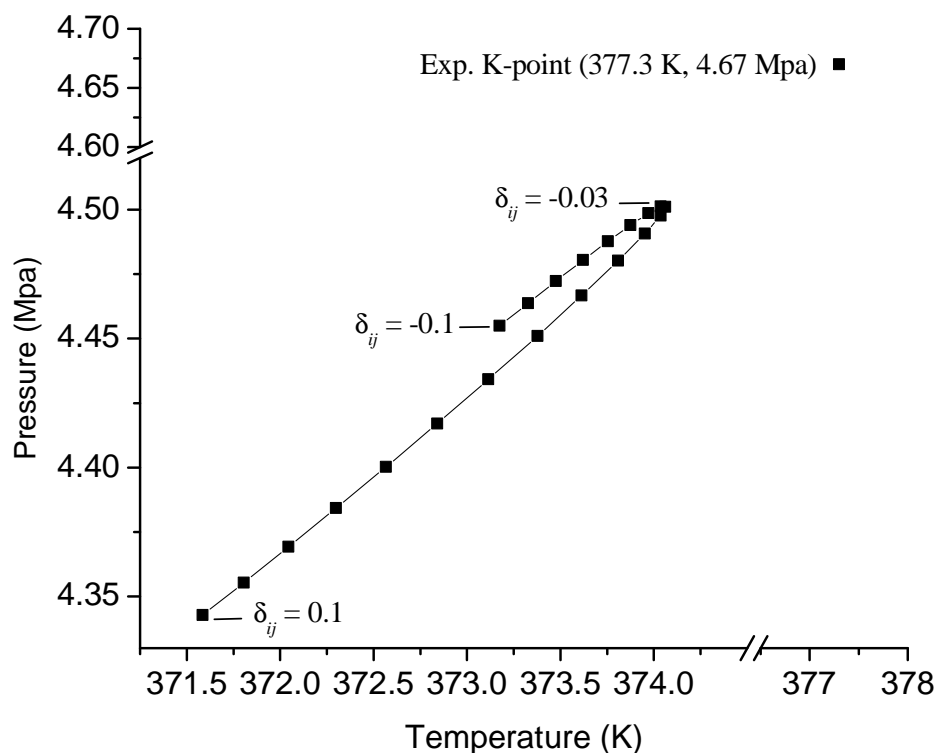


Figure 4.14: Variation of K-point of the propane + phenanthrene system with the changes in the binary interaction parameter for Peng-Robinson equation of state. Experimental K-point lies at 377.3 K and 4.67 MPa.

The variation of the critical line with the changes in the binary interaction parameter value was similar to that observed for the propane + fluorene system. The only difference was that for propane + phenanthrene system, *Type-III* phase behaviour was seen for $\delta_{ij} = 0.06$ and for propane + fluorene system it was observed at $\delta_{ij} = 0.05$. Though the interaction parameter of -0.03 gives the best results in calculating the K-point, it is not a good choice of interaction parameter for this system. At $\delta_{ij} = -0.03$, the shape of critical line does not match the experimental shape, and for $\delta_{ij} < 0.03$, the three-phase line terminates in an L-point, which does not exist experimentally.

A value of $\delta_{ij} = 0.06$ reproduces the appropriate type of phase behaviour keeping in mind that the four-phase point was not considered in the analysis. A portion

of the phase diagram near the critical point of the pure methane is shown in Figure 4.15, where one branch of the critical line goes towards the K-point and a three-phase line can also be seen. This is the typical characteristic of *Type-III* phase behaviour for a binary of propane and polyaromatic hydrocarbon, though the four-phase point is not shown as it is beyond the scope of this project.

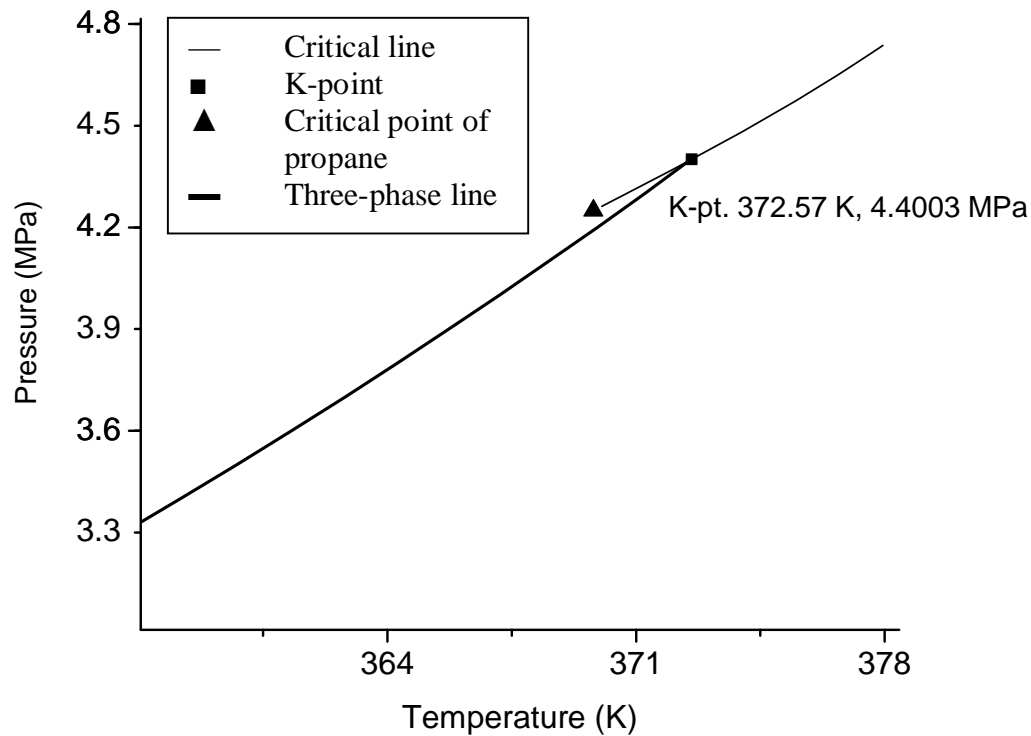


Figure 4.15: Phase diagram of propane + phenanthrene system near the critical point of methane with $\delta_{ij} = 0.06$, typical *Type-III* phase behaviour. Peng-Robinson equation of state was used.

4.2.3.3. Propane + Triphenylmethane

An experimental K-point for the propane + triphenylmethane system was reported at 378.8 K and 4.76 MPa (Peters et al., 1980). K-points were calculated for this system using different values of binary interaction parameters in the Peng-Robinson equation of state. The variation of the K-point in the P - T space with respect to the

binary interaction parameter can be seen in Figure 4.16. A binary interaction parameter of 0.0 gives a K-point at the maximum temperature of 374.257 K and a maximum pressure of 4.5198 MPa. No value of binary interaction parameter was able to compute a K-point matching the experimental result. Experimentally, the system exhibits *Type-III* phase behaviour with the presence of a four-phase point instead of an L-point.

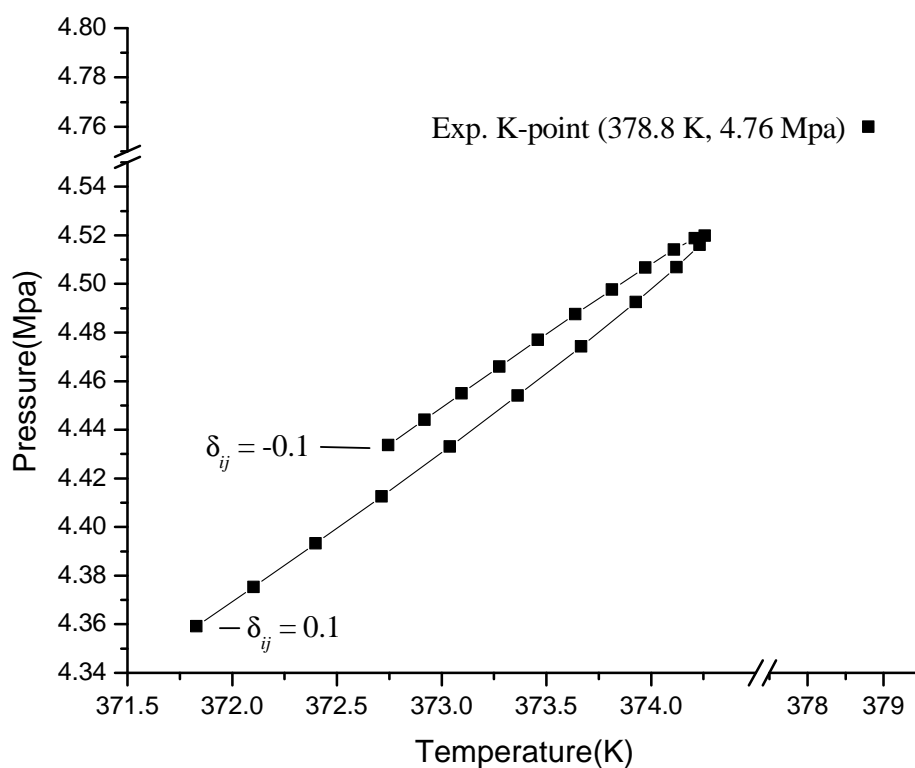


Figure 4.16: Variation of K-point of propane + triphenylmethane with changes in the binary interaction parameter for the Peng-Robinson equation of state.

The effect of binary interaction on the shape of the critical line was studied. Computationally, it was noted that for $-0.1 \leq \delta_{ij} \leq -0.08$, a continuous critical line representing *Type-I* or *Type-II* phase behaviour was predicted. Increasing the value of

the binary interaction parameter beyond -0.08 causes the critical line to show *Type-V* phase behaviour. When the binary interaction parameter was increased to 0.09 a critical locus definitive of *Type-III* phase behaviour was observed. Table 4.6 summarizes the effect of the binary interaction parameter of the Peng-Robinson equation of state on the type of phase behaviour of the system.

Table 4.6: Binary Interaction parameter for the Peng-Robinson equation of state and phase behaviour of propane + triphenylmethane system.

Binary Interaction Parameter	Phase Behaviour
$-0.1 \leq \delta_{ij} \leq -0.08$	<i>Type-I or Type-II</i>
$-0.08 < \delta_{ij} < 0.01$	<i>Type-V</i>
$0.01 \leq \delta_{ij} \leq 0.08$	No definite type
$\delta_{ij} \geq 0.09$	<i>Type-III</i>

Also it can be noted that the critical line for this value of interaction parameter passes through a minimum in the temperature and pressure before going to higher pressures. Peters et al. (1989) observed that the critical line, before going to higher pressures, goes through a minimum in pressure. This characteristic is present in some binaries of propane with the polyaromatic hydrocarbons. This feature was also observed for the propane + triphenylmethane system and can be seen in Figure 4.17. The critical line calculated using an interaction parameter value of 0.09 goes through a minimum in pressure.

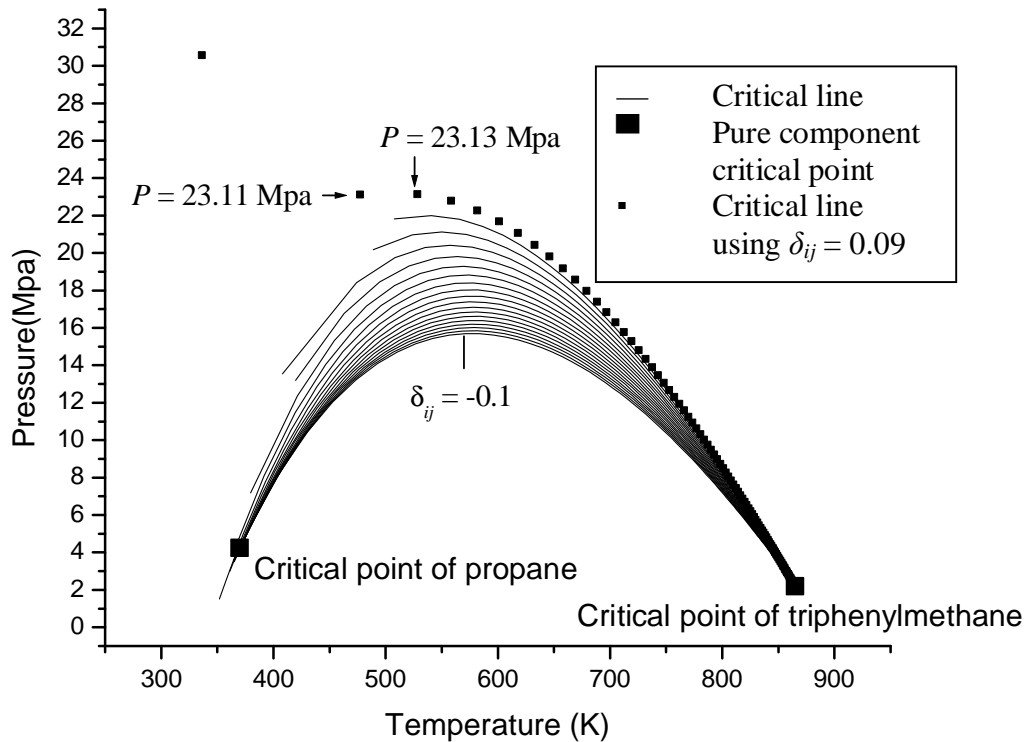


Figure 4.17: Variation of critical line of propane + triphenylmethane system with changes in the binary interaction parameter for Peng-Robinson equation of state.

Though the binary interaction parameter of 0.0 predicts the K-point with best possible accuracy, it is not the correct choice of interaction parameter for this system because it predicts the incorrect type of phase behaviour. A binary interaction parameter of 0.09 is the suggested value of binary interaction parameter for the system because it predicts the correct type of phase behaviour with the peculiar feature of the critical line going through a minimum in pressure.

It was observed for the propane + polyaromatic hydrocarbon systems that the binary interaction parameter fails to calculate the K-point with a good accuracy and the binary interaction parameter which gives the best possible result fails to predict the correct type of phase behaviour. Hence the binary interaction parameter values for the

system studied in this work were suggested using the criterion of the shape of critical line that represents the correct type of phase behaviour. If the interaction parameter were fitted taking into consideration the shape of critical lines and the interaction parameter was plotted against the carbon number of polyaromatic hydrocarbon, the variation would be as in Figure 4.18. The straight line fit for the data is shown in the figure. The equation of the straight line can be thought of as a correlation for the binary interaction parameter for the propane + polyaromatic hydrocarbon system and the carbon number of the heavier component.

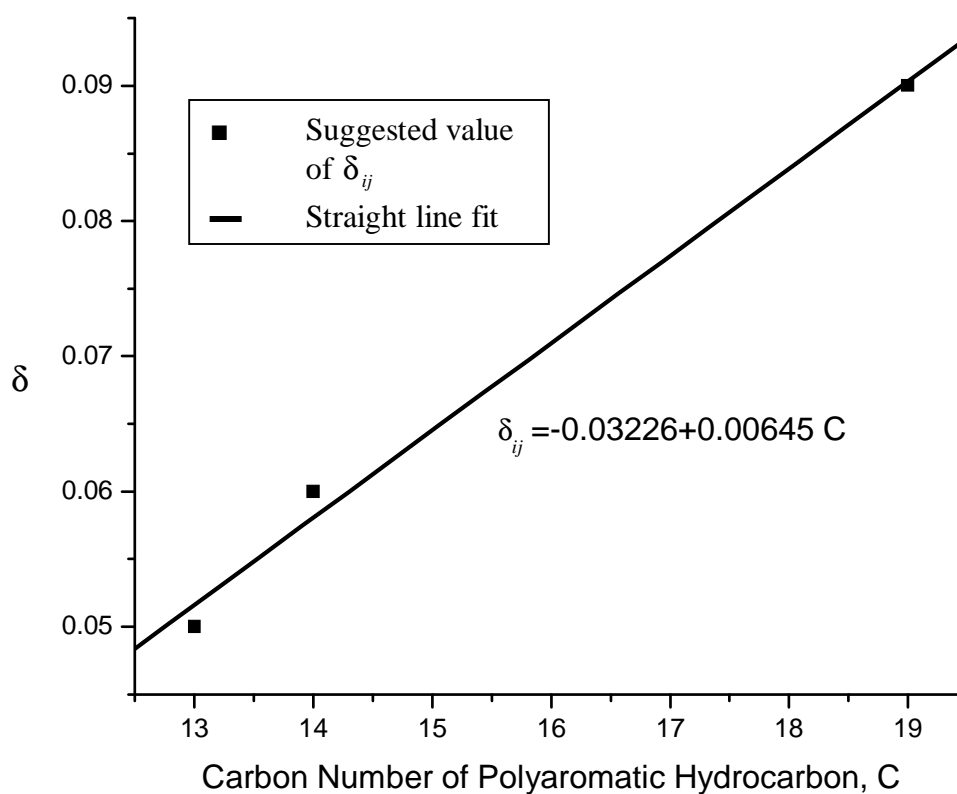


Figure 4.18: Variation of suggested value of the binary interaction parameter in the Peng-Robinson equation of state with carbon number of the polyaromatic hydrocarbon in propane + polyaromatic hydrocarbon system.

4.2.4. Ternary System

The algorithm developed for calculating K- and L-points is not only applicable to binary systems but can be applied to multicomponent systems as well. K- and L-points have one or more degrees of freedom in a system with three or more components respectively. In the case of a ternary system the K- or L-point has one degree of freedom. Instead of a single K- and/or L-point, a locus of K- and/or L-points can be observed in a ternary system. The effect of the binary interaction parameter on the calculation procedure of K- and L-points of a ternary system has been discussed in section 3.5.1. As an illustrative example, the algorithm was used to calculate the K- and L-points of a ternary system of CO₂ + 1-pentanol + tri-decane.

4.2.4.1. The CO₂ + 1-Pentanol + Tri-decane System

An experimental study of the multiphase equilibria of the ternary system of CO₂ + 1-pentanol + tri-decane was done by Gauter et al. (1998). Experimental data for the critical endpoints of this system was presented in their work. The purpose of calculating K-points for a ternary system in this work was to illustrate the ability of the algorithm to evaluate the critical endpoints of a ternary system. Fitting the interaction parameters of the binary subsystems by means of matching the calculated results with experimental critical endpoints of the ternary system was not done. However, Gauter et al. (1999) showed that the binary interaction parameters for the binary subsystems, fitted using the critical endpoint data of the subsystems, did not give a good match with the experimental critical end point locus of the ternary system. The variation of the binary interaction parameter of one subsystem caused change in the position of the critical locus of the ternary system. This can be seen in Figure 4.19. The binary

interaction parameters between CO₂ + tri-decane and 1-pentanol + tri-decane are kept constant as 0.079 and 0.015 respectively, whereas the binary interaction parameter between CO₂ + 1-pentanol is changed from 0.07 to 0.09. As the CO₂ + 1-pentanol binary interaction parameter was increased, the critical end point locus moved downwards in the P - T space.

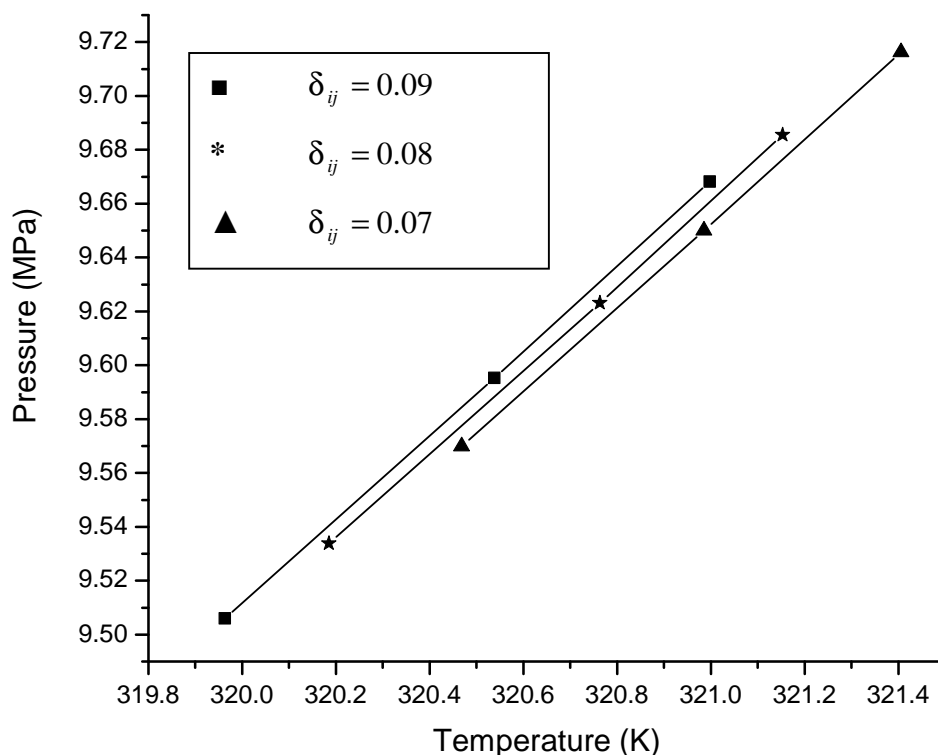


Figure 4.19: Variation of K-point lines for CO₂ + 1-pentanol + tri-decane system with respect to the binary interaction parameter in the Peng-Robinson equation of state.

4.3. Summary

The effect of the binary interaction parameter on K- and L-points and on the P - T projections in the binary space was discussed in this chapter. The effect of the binary interaction parameter on the K- and L-point of the ethane + ethanol system

showed that a single value of the binary interaction parameter could not reproduce both, K- and L-point simultaneously. It was also observed that no value of the binary interaction parameter could predict the correct shape of the critical line. From these observations it can be concluded that the Peng-Robinson equation of state was unsuccessful in predicting the correct high pressure complex phase behaviour of the ethane + ethanol system.

The results for methane + n-alkane system revealed that the binary interaction parameter fitted using the K- and/or L-point was successful in predicting the correct shape of the critical line and thus the correct type of phase behaviour. In the case of methane + n-heptane system no value of the binary interaction parameter could predict the K-point matching the experimental results but the one that computed the K-point with the best possible accuracy also predicted the correct type of phase behaviour. The phase equilibria involving a solid phase was not taken into consideration for this system.

Propane binaries of the polyaromatic hydrocarbons were studied as the model heavy oil systems. These systems are marked with the presence of a K-point and a four-phase point as the endpoints of the three-phase line. The computation of a four-phase point was beyond the scope of this project; however, when the effect of the binary interaction parameter on the K-points was studied, it was observed that no value of the binary interaction parameter in the Peng-Robinson equation of state could compute the K-point to match the experimental results. An interaction parameter which gave the best possible result for the K-point failed to predict the correct type of phase behaviour. Based on the analysis done for the K-points and critical lines, it can be said that the

Peng-Robinson equation of state with a single value of the binary interaction parameter is able to give a qualitative match to the experimentally observed complex phase behaviour of the system but fails to give a quantitative match for the landmarks in phase space like a K-point.

The algorithm to calculate the K- and L-points was also tested for a ternary system. The algorithm was able to calculate the K-points for the ternary system of CO₂ + 1-pentanol + tri-decane successfully. The effect of the binary interaction parameter on K- and L-points of the ternary system was not studied and the K-points were just calculated to illustrate the potential of the algorithm to calculate K- and L-points of multicomponent systems.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Introduction

In an attempt to better predict the high pressure, complex phase behaviour of model heavy oil binary systems, binary interaction parameters of the Peng-Robinson equation of state for numerous binary systems were fit to experimental K- and/or L-points with a priority to match P - T projected phase behaviour. In order to accomplish this goal an algorithm to calculate K- and L-points was developed, programmed and analysed. The conclusions of this project as discussed in the previous chapters are summarized in the following sections.

5.2. K- and L-Points

K- and L-points for propane binaries of polyaromatic hydrocarbons were calculated, these systems being representative of a model heavy oil system. Also, methane binaries of higher alkanes were studied due to the relevance of their phase behaviour in the design of petrochemical operations. The ethane + ethanol system was also studied; it being representative of a binary system consisting of a polar and a non-polar component.

It was observed that the location of K- and L-points vary significantly in phase space with changes in the binary interaction parameter. The trend observed in the variation of K- and L-points was similar for methane + n-alkane and propane +

polyaromatic hydrocarbon systems. The temperature and pressure of K- and L-points initially increase with the increase in the binary interaction parameter, but after a particular value of the binary interaction parameter the pattern reverses. The range of the binary interaction parameter used was $-0.1 \leq \delta_{ij} \leq 0.1$. The entire range of the binary interaction parameter could not be covered for all the systems due to the numerical constraints in calculating K- and L-points.

5.2.1. *Computational Concerns in Algorithm*

There were some thermodynamic and numerical concerns in the generalization of the algorithm to calculate K- and L-points. It was found that the binary interaction parameter plays a significant role in the computation of K- and L-points. If the Gibbs energy of mixing surface remains concave upwards throughout the composition range for a particular value of the binary interaction parameter, a mathematical K- or L-point does not exist and the equilibrium phase search converges to a trivial solution.

The initial guess for the critical phase composition also has a significant effect on the equilibrium phase computation. The Gibbs energy of mixing plot at a critical point may show signs of phase split but the algorithm may still converge to a trivial solution because any line parallel to the tangent drawn to the Gibbs energy surface at the critical point composition is not tangent to the Gibbs energy surface at any other composition. Hence the critical phase composition should be such that there exists a line parallel to the tangent at the critical phase composition, which is tangent to the Gibbs energy surface at any point in the composition range, other than the critical phase composition.

An accelerated successive substitution method and a Newton-Raphson method were used for the equilibrium phase computation. The accelerated successive substitution method approaches the solution faster in the initial stage of the search but the Newton-Raphson method is a better root polishing technique than the accelerated successive substitution method. A combination of the Newton-Raphson method and an accelerated successive substitution method works best, where the accelerated successive substitution method is used in the initial stage of the equilibrium phase search and the Newton-Raphson method is used for the fine tuning process.

The algorithm was also tested to calculate K-points of a ternary system and it could successfully calculate the K-points for a ternary system of CO₂ + 1-pentanol + tri-decane.

5.2.2. *Success in Evaluating Binary Interaction Parameter*

For the ethane + ethanol system, a single interaction parameter was unable to predict both K- and L-points successfully. The system exhibits *Type-V* phase behaviour experimentally. The binary interaction parameter fitted using an L-point predicts *Type-II* phase behaviour whereas the binary interaction parameter fitted using a K-point predicts *Type-III* phase behaviour for the system. Not only did the binary interaction parameter fitted using a K- or an L-point fail to predict the correct type of phase behaviour, but no other value of the binary interaction parameter could predict the correct type of phase behaviour for the system.

The results were better for methane + n-alkane systems. The binary interaction parameter fitted using the K- and/or L-point proved to be successful in predicting the experimental phase behaviour of the system. The methane + n-pentane system shows

Type-V phase behaviour experimentally and the binary interaction parameter value of 0.02 is recommended to predict the correct type of phase behaviour for the system.

The methane + n-hexane system also shows *Type-V* phase behaviour experimentally. The binary interaction parameter of -0.02, which gave the best possible results for K- and L-points, was able to provide a qualitative match with the experimental results of the phase behaviour of the system and is recommended for calculations near the pure component critical points.

The methane + n-heptane system shows *Type-III* phase behaviour experimentally with the presence of a four-phase point. No value of the binary interaction parameter was able to predict the experimental K-point temperature or pressure. However the binary interaction parameter of 0.0 was able to predict the correct type of phase behaviour for the system. The binary interaction parameter that predicted the best possible result for the K-point was -0.02. The four-phase point was not considered in the analysis because no solid model was incorporated in this work to compute the four-phase point. A binary interaction parameter of 0.0 is recommended for the system.

The propane binaries studied in this work (i.e. with fluorene, phenanthrene and triphenylmethane), exhibit *Type-III* phase behaviour with the existence of a solid phase. The three-phase line terminates in a four-phase point instead of an L-point and the solid phase consists of a pure polyaromatic hydrocarbon. The study of the variation of the K-points with respect to the binary interaction parameter revealed a similar trend as observed in methane binaries with higher alkanes, but no value of the binary interaction parameter was able to reproduce the experimental K-point for any of the model heavy

oil systems. The binary interaction parameter, if fitted using the P - T projection of the system showed a trend of increase in the binary interaction parameter value with increase in the carbon number of polyaromatic hydrocarbon. Binary interaction parameters of 0.05, 0.06 and 0.09 are recommended for fluorene, phenanthrene and triphenylmethane binaries respectively.

5.3. Two Parameter Cubic Equation of State and Complex Phase Behaviour

The predictions of complex phase behaviour for the ethane + ethanol system showed the inability of the Peng-Robinson equation of state to model phase behaviour of the alkane + alkanol type of system. For the systems of type methane + n-alkane, the Peng-Robinson equation of state was successful in predicting the complex phase behaviour. The Peng-Robinson equation of state was able to predict the correct shape of critical lines for propane binaries of polyaromatic hydrocarbons. However it was unable to predict the K-point with a good accuracy and the other phenomena in the complex phase behaviour such as the four-phase point and the three-phase lines incorporating a solid phase were not taken into account. Hence the capability of the equation of state to predict the complex phase behaviour of these model heavy oil systems is still doubtful.

5.4. Future Work

The future work in this research can be seen to take three different directions:

- The cubic Peng-Robinson equation of state was able to predict correct phase behaviour and was able to predict the K- and L-points with good accuracy for the binaries of methane with n-pentane and n-hexane. Though a qualitative match was obtained for the phase behaviour of these systems with a particular value of the binary interaction parameter, a quantitative comparison of each and every point on

the critical line and the three-phase line was not done in this work. This advancement can further fine tune the binary interaction parameters for these systems.

- For those systems where the solid phase appears in the P - T projection, algorithms to calculate the three-phase lines, involving a solid phase and the four-phase point can be developed to see if the cubic Peng-Robinson equation of state is able to predict those phenomena.
- The Peng-Robinson equation of state completely failed to predict the phase behaviour of ethane + ethanol system. The Peng-Robinson equation of state with a binary interaction parameter for the parameter b can be tested to see if there is some improvement in the results. Other complex equations of state can be tried, to check for a better outcome.

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APPENDICES

A: Three-Phase Line Calculation

An algorithm developed by Dr. Aaron V. Phoenix was used to calculate the three-phase line for a binary system. A three-phase point has one degree of freedom for a binary system and the equations for calculating a three-phase point in the phase space are as follows:

$$\beta_1 = \ln f_{11} - \ln f_{1ref} = 0 \quad (A.1)$$

$$\beta_2 = \ln f_{21} - \ln f_{1ref} = 0 \quad (A.2)$$

$$\beta_3 = \ln f_{12} - \ln f_{2ref} = 0 \quad (A.3)$$

$$\beta_4 = \ln f_{22} - \ln f_{2ref} = 0 \quad (A.4)$$

$$\beta_5 = x_{11} + x_{12} - 1 = 0 \quad (A.5)$$

$$\beta_6 = x_{21} + x_{22} - 1 = 0 \quad (A.6)$$

$$\beta_7 = x_{31} + x_{32} - 1 = 0 \quad (A.7)$$

$$\beta_8 = \zeta - \pi = 0 \quad (A.8)$$

β_1, \dots, β_8 are the functions to be solved. f_{ab} represents the fugacity of component a in the phase b . The subscript *ref* indicates the reference phase. The reference phase fugacity for a component is the arithmetic average of the fugacity of that component in all the three phases. x_{ab} represents the mole fraction of component b in phase a . ζ is either the temperature or pressure. π is a parameter and its significance lies in calculating a three-phase line once the first three-phase point is calculated. The role of this parameter in developing a three-phase line is explained in the later part of this section. To calculate a three-phase point, there are eight equations to be solved with

eight variables. The variables are temperature, pressure and mole fractions of both the components in all three phases.

The algorithm starts with an initial guess for the compositions and temperature of the three-phase point at a pressure ς . The initial guesses for the variables can be obtained from the compositions and temperature of the upper or lower critical endpoint. When the algorithm calculates the first point of the three-phase line, the parameter π has the same value as the pressure. The fugacity of each component is calculated using an equation of state and the functions $\beta_1, \backslash, \beta_8$ are calculated. Equations (A.1) to (A.8) are solved using a Newton-Raphson method. The derivatives of the functions with respect to the variables are calculated numerically. The variables are updated by solving

$$\mathbf{J}' \begin{bmatrix} \Delta P \\ \Delta T \\ \Delta x_{11} \\ \wedge \\ \Delta x_{32} \end{bmatrix} = - \begin{bmatrix} \beta_1 \\ \beta_2 \\ \beta_3 \\ \wedge \\ \beta_8 \end{bmatrix} \quad (\text{A.9})$$

where,

$$\mathbf{J}' = \begin{bmatrix} \frac{\partial \beta_1}{\partial P} &] &] & \frac{\partial \beta_1}{\partial x_{32}} \\ \wedge & \backslash & & \wedge \\ \wedge & & \backslash & \wedge \\ \frac{\partial \beta_8}{\partial P} &] &] & \frac{\partial \beta_8}{\partial x_{32}} \end{bmatrix} \quad (\text{A.10})$$

Once a three-phase point is calculated by solving equation (A.9) iteratively, the algorithm moves to calculate the next point on the three-phase line with a defined increment, either in temperature or in pressure. That is the parameter π is incremented

by a finite value, which becomes the desired pressure (or temperature) for the next three-phase point on line. The initial guesses for the rest of the variables required to calculate the three-phase point are obtained by solving

$$\frac{d\bar{\beta}}{d\pi} = 0 \quad (\text{A.11})$$

Equation (A.11) can be expanded as,

$$\left[\begin{array}{c} \frac{\partial \beta_1}{\partial P} \frac{\partial P}{\partial \pi} + \frac{\partial \beta_1}{\partial T} \frac{\partial T}{\partial \pi} + \frac{\partial \beta_1}{\partial x_{11}} \frac{\partial x_{11}}{\partial \pi} +] + \frac{\partial \beta_1}{\partial \pi} \\ \frac{\partial \beta_8}{\partial P} \frac{\partial P}{\partial \pi} + \frac{\partial \beta_8}{\partial T} \frac{\partial T}{\partial \pi} + \frac{\partial \beta_8}{\partial x_{11}} \frac{\partial x_{11}}{\partial \pi} +] + \frac{\partial \beta_8}{\partial \pi} \end{array} \right] = 0 \quad (\text{A.12})$$

Equation (A.11) can be rearranged as,

$$\mathbf{J}' \begin{bmatrix} \frac{\partial P}{\partial \pi} \\ \frac{\partial x_{32}}{\partial \pi} \end{bmatrix} = - \begin{bmatrix} \frac{\partial \beta_1}{\partial \pi} \\ \frac{\partial \beta_8}{\partial \pi} \end{bmatrix} \quad (\text{A.13})$$

Equation (A.13) is solved to get the vector $[\partial P / \partial \pi \quad \partial x_{32} / \partial \pi]^T$. Using this vector a new initial guess for the variables is obtained as

$$\begin{bmatrix} P \\ x_{32} \end{bmatrix}_{New} = \begin{bmatrix} P \\ x_{32} \end{bmatrix}_{Old} + \Delta \pi \begin{bmatrix} \frac{\partial P}{\partial \pi} \\ \frac{\partial x_{32}}{\partial \pi} \end{bmatrix} \quad (\text{A.14})$$

With the new initial guesses, the steps to calculate the three-phase point are repeated.

B: Critical Properties and Acentric Factor

The critical properties and acentric factors of the compounds studied in this work are listed in the following table:

Table B1: Critical properties and acentric factors (Yaws, 1999).

S.no.	Name	T_c (K)	P_c (bar)	ω
1	Ethane	305.4	48.8	0.0979
2	Ethanol	513.9	61.4	0.6430
3	Methane	190.4	46.0	0.0109
4	Propane	369.8	42.5	0.1518
5	n-Pentane	469.7	33.7	0.2522
6	n-Hexane	507.5	30.1	0.2990
7	n-Heptane	540.3	27.4	0.3494
8	Phenanthrene	869.3	29.0	0.4950
9	Anthracene	873.0	29.0	0.4890
10	Fluorene	870.0	47.0	0.3493
11	Triphenylmethane	865.0	22.0	0.5735
12	CO ₂	304.1	73.8	0.2390
13	Tri-decane	676.0	17.2	0.6203
14	1-Pentanol	588.2	39.1	0.5784