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AUTOMATED CONSTRUCTION OF QUATERNARY PHASE DIAGRAMS FOR HYDROCARBON SYSTEMS

by

Clive Robert Cartlidge

A thesis submitted in conformity with the requirements
for the degree of Master of Applied Science.
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Automated Construction of Quaternary Phase Diagrams for Hydrocarbon Systems

Master of Applied Science, 1995
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ABSTRACT

A computer modelling algorithm has been developed to represent ternary and quaternary phase diagrams using a combination of custom *Mathematica* and *CorelDRAW!* programs in combination with the commercial phase behaviour and properties package *CMGPROP* developed by the Computer Modelling Group (CMG). The three-dimensional phase diagrams (at fixed temperature and pressure) are displayed in true perspective and can be rotated continuously or "folded-out" to facilitate easy viewing of all faces of the diagrams. Sections of these phase diagrams at constant composition of one of the four components can by viewed using a sectioning algorithm which allows one to view two dimensional slices (standard ternary diagrams) of individual phase diagrams or to view the impact of temperature or pressure variations on the placement of various multiphase regions. The quaternary phase diagram construction and sectioning routines were applied to three systems at various temperatures and pressures: a simple ternary hydrocarbon system (methane + propane + *n*-decane), a model condensate rich reservoir fluid (ethane + *n*-butane + propane + phenanthrene), and a heavy oil mixture (athabasca bitumen vacuum bottoms (ABVB) + hydrogen). These routines were found to represent the experimental phase behaviour of each system accurately and to provide an efficient visual tool for generating and presenting quaternary and ternary phase diagrams. A combination of the routines is envisaged as a prototype for a phase diagram teaching aid and from a research point of view, the automated construction of phase diagrams allows for easy interpolation of experimental data especially in the case of heavy oil systems where the cost of experiments is high.

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NOMENCLATURE

a	equation of state parameter
b	equation of state parameter
C	number of components
f_i	fugacity of component i
F	degrees of freedom
F_i	mole fraction of phase i
G	Gibbs' free energy
H	Hydrogen
$H1$	Pseudo-component HEAVY1
$H2$	Pseudo-component HEAVY2
k_{ij}	binary interaction parameter
K_{ij}	Partition coefficient
L	Pseudo-component LIGHT
n_c	number of components
n_p	number of phases
P	pressure
R	universal gas constants
S	solid phase
T	temperature
u_i	stablility constant
v	partial molar volume
V	vapour phase
x_i, y_i	mole fractions of component i
z_i	global mole fraction of component I
Z	compressability factor

Subscripts

c	critical property
r	reduced property
l	liquid phase
s	solid phase
v	vapour phase

Greek Symbols

ϕ_{ij}	fugacity coefficient of component i in phase j
ω	Pitzer's acentric factor
κ	equation of state parameter
ζ	single degree of freedom parameter used to describe the feed composition

1.0 *INTRODUCTION*

1.1 General Introduction

The World Energy Council (*The Economist*, 1994) estimates that at the current rate of consumption there is enough light crude oil to last for approximately sixty years. However, there is believed to be another 170 years supply contained in more costly "unconventional" oil reserves as heavy oils and bitumen. Currently, only Canada and Venezuela are devoting a considerable amount of research money and effort into the processing of "unconventional" oil reserves.

Canadian interest in the efficient and profitable refining and upgrading of heavy oils and bitumen is understandable due to the large reserves located in Alberta (208.7 million cubic metres) and Saskatchewan (111.8 million cubic metres). Heavy oil and bitumen are an important source for conventional oil products in both Alberta and Saskatchewan especially in the latter where more than 30% of annual petroleum production over the past decade has been from "unconventional" oil reserves. Over that same period, the proportion of conventional crude production from these reserves has nearly tripled from 8% to 23% (*Oilweek*, 1993).

The term "heavy oil" is useful only in a qualitative sense since it does not have a universally accepted definition. The Alberta Energy Resources Conservation Board defines

heavy oil as conventional crudes with densities of 900 kilograms per cubic metre or greater but often includes much lighter crudes in its heavy oil category. Saskatchewan Energy and Mines does not have such a threshold, but from recent reports it appears to be closer to 950 kilograms per cubic metre.

Canadian heavy oil producers have overcome many obstacles in both bringing their products to market and making some money doing it. They have shown the ability to produce a high quality, light oil product, termed "synthetic crude oil" which is more valuable than diesel fuel and road asphalt. But despite these recent innovations, an optimal method of processing bitumen has yet to be developed. The phase behaviour of bitumen and the problems that arise during their processing such as asphaltene deposition and excessive coking must be fully understood before an optimal process can be developed.

Two steps must be taken to design refining and upgrading processes for heavy oil and bitumen mixtures: (1) the phase behaviour of typical heavy oil/bitumen mixtures must be fully understood at reservoir and processing conditions; (2) a thermodynamic model for these mixtures based on this phase behaviour must be developed such that phase diagrams can be constructed with a minimal amount of experimentation.

With regard to the first point, preliminary investigations have shown that model reservoir fluids and model heavy oil systems have surprisingly complex phase behaviour under typical operating temperatures and pressures. However, most of these findings have been predominantly qualitative and do not provide sufficient quantitative information. More specific studies have shown that asymmetric reservoir fluids (Shelton and Yarborough, 1976)

and heavy oil + gas mixtures (Turek *et al.*, 1988) exhibit solid-liquid-liquid-vapour and liquid-liquid-vapour, respectively, at elevated temperatures and pressures which verified the existence of such behaviour.

The most recent study to date into the phase behaviour of heavy oil/bitumen mixtures is that reported by Dukhedin-Lalla (Ph.D. thesis, 1995) who provides phase diagrams for athabasca bitumen vacuum bottoms + hydrogen and athabasca bitumen vacuum bottoms + hydrogen + *n*-dodecane mixtures over a wide range of temperatures and pressures. Through the use of an x-ray imaging system, complex phase transitions such as liquid-vapour to liquid-liquid-vapour to solid-liquid-liquid-vapour were noted.

1.2 Objectives

The objective of this thesis deals in part with the second point which is to develop a thermodynamic model for bitumen mixtures which will describe the complex phase behaviour of these mixtures over the temperature and pressure ranges of interest. Due to the very exact nature of data reported by Dukhedin-Lalla (1995), this study serves as the basis for the proposed models. From these proposed models, constant temperature and pressure phase diagrams are constructed using algorithms described in a subsequent section. Many commercially available computer packages (i.e. *CMGPROP* or *HYSIM*) allow for only rudimentary phase diagram construction (i.e. two or three phase envelope construction

routines) or ternary and quaternary phase diagram construction (i.e. *ChemSep*) using experimental data and therefore, the need for a detailed and general phase diagram construction routine is apparent. The modelling approach adopted in this thesis is a general one. The phase behaviour prediction package as well as the graphics routines can evolve independently. Thus, the phase diagram construction routines can be applied to any sort of mixture and become an important teaching and research tool.

2.0 *PHASE DIAGRAMS*

Phase diagrams have been described as graphical representations of the phase relationships in heterogeneous systems using the intensive independent variables (temperature, pressure, and composition) as coordinates. They provide insights into the phase relationships (i.e. how many phases are present for a given mixture at a specified temperature and pressure) and the possible changes in phase relationships with a change in temperature or pressure for systems that are at thermodynamic equilibrium (Ricci, 1951). They can also provide initial estimates of phase relationships for systems that are meta-stable.

Perhaps the easiest way to classify phase diagrams is by the number of phases present. The discussion in the following section begins with a brief explanation of the Phase Rule and then proceeds to one, two, three, and four component phase diagrams with an emphasis on the interpretation of the latter two.

2.1 The Phase Rule

The Phase Rule, first stated by Josiah Willard Gibbs in the 1870's, is a thermodynamic law which underlies the study of phase equilibria and is of utmost importance to the

representation of such equilibria in the form of equilibrium phase diagrams. It deals with heterogeneous systems (i.e. those possibly having more than one phase) at equilibrium involved in physical or chemical processes so long as they are dynamic and reversible in nature (Ricci, 1951).

The phase rule states that the relationship, at equilibrium, between the number of phases P, the number of components C, and the number of degrees of freedom F of a particular state of equilibrium can be expressed as follows:

$$P + F = C + 2 + j \qquad (2.1.1)$$

The *phases* are defined as the homogeneous portions of the heterogeneous system that are bounded by surfaces and can be mechanically separated from one another. The *number of components* is the smallest number of independently variable constituents necessary to describe the composition of all phases present in the system. The *number of degrees of freedom* is the number of independent intensive variables which have to be specified to determine the state of the system entirely. The Phase Rule assumes that the temperature, pressure, and compositions are the only externally controllable variables that influence the phase equilibria. If this is the case, the j term in Equation 2.1.1 is set equal to zero. Otherwise, each additional effect (i.e. magnetic, gravitational, etc.) must be taken into account in the Phase Rule by increasing the j term by one.

Thus, the Phase Rule is a convenient summary of the variability of a heterogeneous system at equilibrium, and its use in a one to four component system is illustrated in subsequent sections. However, it should be pointed out that the Phase Rule does not deal with the size of phases in the system, but merely their number. Thus, it deals only with intensive properties and not extensive properties (i.e. molar volume or amount of each phase) (Missen, 1992).

2.2 One Component Systems (Unitary Systems)

Since the composition of a one component system is fixed, the only variables remaining are temperature (T) and pressure (P). Thus, a plane with these coordinate axes is sufficient for the construction of a phase diagram. An example of a phase diagram for a single component system is shown in Figure 1.

Every phase in the system (S-solid, L-liquid, V-vapour) of Figure 1 is defined by an area with two degrees of freedom as shown by the Phase Rule:

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

Thus, each single phase regions constitutes a *bivariant* equilibrium state. That is, both T and P must be specified to completely define the system at any point within the single phase

regions. At any point along the phase boundary curves AO, OB, and OK (with the exception of point O) which have two phases coexisting in equilibrium (solid-vapour, solid-liquid, and liquid-vapour, respectively), the Phase Rule can be applied which results in:

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

Therefore, two phase equilibria points along the phase boundary curves are termed *univariable* as only one variable (T or P) needs to be fixed in order to define them completely.

However, at point O three phases coexist. Application of the Phase Rule at this point yields:

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Thus, the system has zero degrees of freedom at point O and is such termed the *invariant* or *triple point*.

At point K, in Figure 1, the liquid phase (L) becomes identical to the vapour phase (V) and this point is termed the *critical point*. Not only does each substance have specific critical values of T and P, but since the two phases at this point become identical, there is a critical value of any property of the system as a whole at the critical point (i.e. critical density, critical molar volume etc.).

A diagram for a one component system such as Figure 1 is often known as a P/T diagram which is then said to *define* the system by indicating the number and type of phases existing at equilibrium for various values of T and P. The diagram inherently assumes that the equilibrium relationships depend solely upon T and P and that all other effects (surface, magnetic field, gravity, etc.) are either absent, ignored, constant, or are completely determined by T and P.

2.3 Two Component Systems (Binary Systems)

When two components ($C = 2$) are mixed to form a binary mixture, a new degree of freedom - composition - is introduced. Thus, the phase behaviour of binary systems is completely represented by a three dimensional figure with the coordinates P, T, c, where c is the composition usually expressed as a mole fraction. This three dimensional figure is termed the "space model" for the binary system and an example is shown in Figure 2. The composition of the binary mixture is represented by a straight line, commonly the horizontal axis of the phase diagram as in Figure 2. The two ends of the horizontal axis represent the pure components A and B, respectively. The mole fraction of B in a given mixture X (Figure 2) is measured by the length AX where the length AB is defined as being 100%. The other variables T and P are marked on the other axes.

Often isobaric, isothermic, or constant composition sections of this three dimensional space model are taken to show the equilibrium relations either at constant P (in which case T varies), constant T (in which case P varies), or constant T and P, respectively. This results in two dimensional T/c, P/c, or P/T diagrams from which a considerably greater amount of information can be extracted. An example of a T/c diagram is shown on the front face of the space model shown in Figure 2. Like the one component systems, the bivariant, univariant, and invariant areas or points can also be found for binary mixtures.

From the Phase Rule, it can be shown that a maximum of four phases can be present for binary mixtures at equilibrium at a point with zero degrees of freedom. This invariant point is often referred to as the q-point and occurs at a specific pressure and temperature. For a more detailed analysis of the Phase Rule using binary systems, please refer to Ricci, 1951.

2.4 Three Component Systems (Ternary Systems)

To describe the composition of a three component system ($C = 3$) requires only the concentrations (mole fractions) of two of the three components. Therefore, there are four independent variables (T, P, and two composition terms) and four degrees of freedom in a ternary system. However, graphical representation of a system with four degrees of freedom is possible only if one of the four independent variables is held constant. A three dimensional figure is therefore used for ternary systems with P or T held constant. One of

the variables, P or T, is taken as an axis perpendicular to a two dimensional composition plane which is most commonly represented as an equilateral triangle. This three dimensional figure is termed the "space model" of the ternary system and an example at fixed P is shown in Figure 3. However, horizontal isobaric or isothermal sections are most often taken of the ternary space model by cutting through the space diagram at a specified temperature or pressure which results in conventional two dimensional equilateral triangle phase diagrams for the given mixture at fixed temperatures and pressures. An example is shown in Figure 4.

In the composition equilateral triangle (Figure 4) the three corners represent the three pure components, points on each side represent binary mixtures, and points within the equilateral triangle, ternary mixtures. The composition of a ternary mixture (e.g. mixture x in Figure 4) is obtained by the following: a line mn is drawn parallel to side BC and the percentage A is then given by the lengths mB or nC. The percentage of B is given by the lengths oA or pC, obtained by drawing line op parallel to side AC. Likewise, the percentage of C is obtained by drawing rs parallel to side AB and determining the lengths rA or sB. Please note that ternary phase diagrams at constant T and P such as in Figure 4 are not necessarily restricted to three components but can be applied to m component mixtures so long as the composition of (m - 3) components are held constant. The resulting ternary diagram for an m component mixture with the compositions of (m - 3) components held constant would have a maximum of m phases at equilibrium from the Phase Rule.

2.5 Four Component Systems (Quaternary Systems)

In a four component system with three independent composition variables, there are five degrees of freedom (T, P, and three composition terms) and graphical representation is limited to conditions of constant T and P since representation of composition for a quaternary system requires a three dimensional model in itself. The model for quaternary systems is therefore represented by a four sided, three dimensional figure with each face being one of the four ternary systems making up the quaternary system. The model is often termed an "isobaric isotherm" due to the conditions of fixed T and P.

The isobaric isotherm is most often represented by an equilateral tetrahedron so that each ternary face appears as an equilateral triangle (Figure 5). The corners represent the pure components, the sides the binary mixtures, the faces the ternary mixtures, and the interior quaternary compositions. The plotting of compositions within the tetrahedron is an extension of the principles used in ternary diagrams.

If we consider a point P within the tetrahedron ABCD, the mole fraction of each component for point P is taken as the distance from the point to the face opposite the component. Thus, the normal vectors Pa, Pb, Pc, Pd to the four faces BCD, ACD, ABD, ABC are used to measure the concentrations of components A, B, C, D, respectively. For example, since apex A represents a system consisting of 100% A, it follows that a point on the face BCD represents a system containing 0% A and that all points representing fixed intermediate mole fractions of A lie in planes parallel to the face BCD. These planes at fixed

fractions of A will appear as standard ternary diagrams for the system B + C + D at fixed T and P as described in the previous subsection.

3.0 *PHASE BEHAVIOUR MODELLING*

Computer packages are often used to model and predict experimental phase behaviour. The success of such predictions is based on the accurate prediction of the number, type, and properties of phases present for a given mixture at a specified temperature and pressure. Experimental data were modelled in this study with the Peng-Robinson equation of state as implemented in the commercial computer package *CMGPROP* (Computer Modelling Group, 1995). *CMGPROP v.95.01* is a multiphase equilibrium property package which employs the Peng-Robinson (1976) or Soave-Redlich-Kwong (Soave, 1972) equation of state and is specifically designed for field scale reservoir simulations. This program is capable of performing flash calculations which may involve a single component solid phase, using a cubic equation of state in combination with the tangent plane criterion (Michelson 1982a,b) and algorithms by Nghiem and Li (1984). These calculations determine phase behaviour by fitting tangent hyperplanes to Gibbs free energy hypersurfaces over an array of compositions at a given temperature and pressure for a given mixture (Baker *et al.*, 1982).

The algorithm and calculations employed by *CMGPROP v.95.01* to determine the phase properties of mixtures exhibiting multiple liquid and/or vapour phases at equilibrium are described below. The addition of pure solid formation to the algorithm is a separate issue and is treated in detail in a subsequent section.

3.1 Equations

3.1.1 Peng-Robinson Equation of State

The Peng-Robinson (1976) equation of state is of the form:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{3.1.1.1}$$

For pure components, the parameters a and b are expressed in terms of the critical properties and the acentric factor:

$$a = a(T_c)\cdot\alpha(T_r,\omega) \tag{3.1.1.2}$$

$$a(T_c) = 0.45724\frac{R^2T_c^2}{P_c} \tag{3.1.1.3}$$

$$\alpha(T_r,\omega) = \left[1+\kappa(1-T_r^{0.5})\right]^2 \tag{3.1.1.4}$$

$$b = 0.07780\frac{RT_c}{P_c} \tag{3.1.1.5}$$

The κ is a constant characteristic of each substance and is obtained from the following empirical correlations. Peng and Robinson (1976) correlated κ against the acentric factor with the resulting equation:

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (3.1.1.6)$$

and for hydrocarbons heavier than *n*-decane (Robinson and Peng, 1978):

$$\kappa = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3 \qquad (3.1.1.7)$$

The parameters a and b are often incorporated into dimensionless parameters A and B in order to minimize truncation errors and avoid floating point errors during calculations.

$$A = \frac{aP}{R^2T^2} \qquad (3.1.1.8)$$

$$B = \frac{bP}{RT} \qquad (3.1.1.9)$$

If these two dimensionless parameters and the compressibility factor Z

$$Z = \frac{Pv}{RT} \qquad (3.1.1.10)$$

are substituted into equation (3.1.1.1), equation (3.1.1.1) can be rewritten as:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \qquad (3.1.1.11)$$

For mixtures, the parameters a and b used in equation (3.1.1.1) are defined by Peng and Robinson (1976) using the following mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (3.1.1.12)$$

$$a_{ij} = (1 - k_{ij}) a_i^{0.5} a_j^{0.5} \qquad (3.1.1.13)$$

$$b = \sum_i x_i b_i \qquad (3.1.1.14)$$

where k_{ij} is an empirically determined binary interaction coefficient.

3.1.2 Fugacity Coefficient

The fugacity coefficient of component i in phase j (ϕ_{ij}) is needed in order to facilitate phase equilibrium calculations and can be derived from the Peng-Robinson equation of state by applying the thermodynamic relationship:

$$\phi_{ij} = \frac{f_{ij}}{y_{ij}P} \tag{3.1.2.1}$$

where

$$\ln\left(\frac{f}{P}\right) = \int_0^P \left(\frac{v}{RT} - \frac{1}{P}\right) dP \tag{3.1.2.2}$$

The fugacity of component i with a mole fraction of y_i in a mixture can be found by substituting equation (3.1.1.1) into equation (3.1.2.2):

$$\ln\left(\frac{f_i}{y_i P}\right) = \ln\phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\cdot\left(\frac{2\sum_k y_k a_{ki}}{a} - \frac{b_i}{b}\right)\ln\left(\frac{Z+2.414B}{Z-0.414B}\right) \tag{3.1.2.3}$$

3.1.3 Selection of Compressibility Root and Vapour/Liquid Identification

The compressibility factor (Z) used in equation (3.1.2.3) is determined by solving the cubic equation (3.1.1.11) for Z which may yield a single or two real roots depending upon the nature of the variables A and B. If two real unequal roots are found to exist, the smaller refers to a liquid phase, the larger to a gas phase. For example, let Z_A and Z_B be the two real compressibility factors found upon solving equation (3.1.1.11) which have corresponding values for Gibbs free energy G_A and G_B. Since Gibbs energy is defined as:

$$G = \sum_i y_i \ln f_i \tag{3.1.3.1}$$

it can be shown that:

$$G_A - G_B = \ln\left(\frac{Z_B - B}{Z_A - B}\right) + \frac{A}{2.8284B}\ln\left(\frac{Z_B + 2.4142B}{Z_A - 0.4142A}\cdot\frac{Z_A - 0.4142A}{Z_B - 0.4142A}\right) - (Z_B - Z_A) \tag{3.1.3.2}$$

If G_A-$G_B > 0$, the "B" phase is the more stable phase. For single phase systems, if the larger compressibility factor is chosen, the phase is said to be vapour, if the smaller one is chosen the phase is said to be liquid.

If upon solving equation (3.1.1.11) only a single real value for Z factor is found, the identification of a single phase system is made according to the classification scheme outlined by Gosset *et al.* (1986). For multiphase systems, the phases are classified with respect to their mass densities. The phase with the lowest mass density is denoted as vapour. Any additional phases are classified as liquids.

3.1.4 Phase Equilibrium Balances and Constraints

To predict a given number of phases to be at equilibrium, three restrictions must be satisfied (Baker *et al.*, 1982). First, the material balances must be preserved. Second, the fugacities of each component must be the same in all phases. Third, the system of predicted phases must have the lowest possible total Gibbs energy at the system temperature and pressure.

The molar Gibbs energy G of a closed system of n_p phases and n_c components is given by:

$$G = RT \sum_{j=1}^{n_p} \sum_{i=1}^{n_c} F_j y_{ij} \ln f_{ij} + \sum_{i=1}^{n_c} z_i G_i^o \qquad (3.1.4.1)$$

where F_j is the mole fraction of phase j, f_{ij} the fugacity of component i in phase j, y_{ij} the mole fraction of component i in phase j, z_i the global or feed fraction of component i, G_i^o the molar

Gibbs energy of component i in the standard state, R the universal gas constant, and T the absolute temperature.

If the multiphase equilibrium ratios (K values) are defined as by Nghiem and Heidemann (1982), i.e.,

$$K_{ij} = \frac{y_{ij}}{y_{ir}} \qquad i=1.....n_c; j=1.....n_p; j \neq r \tag{3.1.4.2}$$

following Nghiem and Li's development (1984), in an n_p phase system with n_c components with one of the phases, r, designated as a reference phase, the conditions for phase equilibrium can be represented as follows:

$$\ln K_{ij} + \ln \phi_{ij} - \ln \phi_{ir} = 0 \qquad i=1.....n_c; j=1.....n_p; j \neq r \tag{3.1.4.3}$$

$$\sum_{i=1}^{n_c} \left[\frac{(K_{ij} - 1) z_i}{\sum_{m=1}^{n_p} F_m K_{im}} \right] = 0 \qquad j=1,....n_p; j \neq r \tag{3.1.4.4}$$

where Equation (3.1.4.3) places the constraint that the fugacities of each component must be the same in all phases, and equation (3.1.4.4) is the material-balance constraint.

3.1.5 Stability Analysis

A stability analysis provides a means for determining whether the results of phase equilibrium calculations provide stable systems and thus, satisfy the third requirement for phase equilibrium. It is used in conjunction with flash calculations in order to introduce an additional phase into an unstable n_p-1 predicted phase system which will lower the Gibbs energy of the system.

A predicted n_p phase system defines a hyperplane tangent to the Gibbs energy hypersurface (Baker *et al.*, 1982), and if this number of phases represents the equilibrium state, the distance from the Gibbs energy surface to the tangent plane at all points in composition space must not be less than zero. It follows from this that all points where the derivative of this distance is zero (i.e. stationary points), the distance itself must not be less than zero. Michelson (1982a,b) summarized the conditions required for the n_p phases to be the equilibrium state as follows:

$$\ln u_i + \ln \phi_i - \ln y_{ir} - \ln \phi_{ir} = 0 \qquad i=1,\ldots,n_c \qquad (3.1.5.1)$$

$$\sum_{i=1}^{n_c} u_i \leq 1 \qquad (3.1.5.2)$$

where u_i is a stability analysis variable that combines a stationary point composition and the distance between the Gibbs energy surface and the tangent plane at that composition. The set

of u_i which satisfy equation (3.1.5.1) defines all the stationary points, and for these points, equation (3.1.5.2) must be valid for the predicted n_p phases to be the true equilibrium state.

3.2 Liquid/Vapour Flash Calculations and Algorithm

To determine the number of equilibrium phases and phase characteristics, flash calculations involve solving equations (3.1.4.3) and (3.1.4.4) and a stability analysis (equations (3.1.5.1) and (3.1.5.2)) at a given temperature (T), pressure (P), and feed composition (z_i). The primary variables of equations (3.1.4.3) and (3.1.4.4) are K_{ij}, T, P, F_j, and ζ (i=1,....n_c; j=1,....n_p; $j \neq r$). ζ is a parameter with a single degree of freedom used to describe the feed composition as follows:

$$z_i = (1-\zeta)z_{i,A} + \zeta z_{i,B} \qquad i=1,....n_c \tag{3.2.1}$$

where $z_{i,A}$ and $z_{i,B}$ are the compositions (mole fractions) of two given mixtures A and B, respectively. Since K_{ij} and F_j have $n_c(n_p\text{-}1)$ and n_p-1 unknowns, respectively, and equations (3.1.4.3) and (3.1.4.4) represent a system of $(n_c+1)(n_p-1)$ equations, it follows that it is sufficient to specify T, P, and ζ before the equations can be solved.

The most common procedure used to determine the number of equilibrium phases is to start with a hypothetical one phase system composed of the feed composition. A stability

analysis is done on the one phase system using equations (3.1.5.1) and (3.1.5.2) with an equation of state to calculate the fugacity coefficients (equation 3.1.2.3) to determine if the one phase system is stable. If the one phase system is found to be unstable, two equilibrium phases are then assumed to exist and equations (3.1.4.3) and (3.1.4.4) are solved simultaneously for the amount and composition of both phases present. A further stability analysis determines whether the two phase system is stable or if a three phase flash should be done. This procedure is repeated until the stability analysis determines the current number of stable phases. Once a stable system of phases has been found, the phases are then classified by the criteria outlined in a previous subsection. Equation (3.1.4.3) is converged using the Quasi-Newton Successive Substitution (QNSS) technique (Nghiem and Li, 1984). After each QNSS iteration, Equation (3.1.4.4) is solved for F_j using Newton's method.

3.3 Flash Calculations Involving a Solid Phase

The prediction of multiphase behaviour involving solid formation such as solid-liquid (SL) and solid-vapour (SV) transitions have been of interest for some time (Lindemann, 1910; Lennard-Jones and Devonshire, 1939; Mansoori and Canfield, 1969) and attempts to model this phenomenon have varied widely. There has been a substantial effort made to incorporate a solid phase model into a standard cubic equation of state flash algorithm in order to predict solid-liquid-vapour (SLV) or solid-liquid-liquid-vapour (SLLV) phase

behaviour. Many researchers (Morimi & Nakanish. 1977; Gmehling *et al.*, 1978; Johnson *et al.*, 1982; Kwak & Mansoori. 1986; Pongsiri and Viswanath. 1989; Cygnarowicz *et al.*, 1990 and others) have successfully calculated solid phase fugacities at elevated pressures assuming a pure solid phase which enables the prediction of SL and SV transitions from the liquid or vapour phase fugacities calculated from an equation of state.

The *Single Component "Solid" Model* proposed by the Computer Modelling Group (CMG) was developed primarily for predicting solid asphaltene formation in reservoir fluids but can be used to predict solid formation in a wide variety of mixtures. The solid phase is modelled as a pure dense phase that can either be liquid or solid (Nghiem *et al.*, 1993). This characterization of the solid phase resolves many of the inadequacies of the solid models reported in the literature (Gupta, 1986; Thomas *et al.*, 1992). These models have often assumed that the solid phase is the heaviest component in the mixture but in the case of solid asphaltene formation in heavy oils, this assumption contradicts observations in the literature that many other heavy components of heavy oil (e.g. paraffins and resins) may not precipitate. The equations of this approach and their incorporation into the previously described liquid/vapour flash algorithm are described in the next section.

If impure solids are to be modelled, they are commonly treated as additional liquid phases since there is no universally accepted method for dealing with impurities.

3.3.1 Thermodynamic Model

The solid phase is represented as a pure dense phase. This fugacity of this dense phase can be calculated from:

$$\ln f_s = \ln f_s^* + \frac{v_s\left(P - P^*\right)}{RT} \qquad (3.3.1.1)$$

where f_s and f_s^* are the fugacities of pure solid at pressures P and P^*, respectively, v_s is the molar volume of pure solid, R is the gas constant and T the absolute temperature. From the nature of equation (3.3.1.1), the solid phase can be either a solid or a liquid. The use of equation (3.3.1.1) is dependent on prior knowledge of f_s^* and v_s at P^* and T which are both calculated from experimental solubility data (Nghiem *et al.*, 1993).

3.3.2 Flash Calculations

The solid characterization outlined above has been included in the Computer Modelling Group phase behaviour package *CMGPROP v. 95.01* where the original multiphase calculation algorithm of Nghiem and Li (1984) has been modified to include solids. The number of liquid and vapour phases present at equilibrium is computed from the phase

stability analysis based on a Gibbs energy hypersurface (Nghiem and Li, 1984) described previously. The testing of the existence of a solid phase requires only the following simple check:

If $\ln f_{n_c,l} \geq \ln f_s$ the solid phase exists

If $\ln f_{n_c,l} < \ln f_s$ the solid phase does not exist

where $f_{nc,l}$ is the fugacity of each component in the liquid phase.

This solid phase check is simply added to the end of the liquid/vapour flash algorithm described previously after the number of liquid and vapour phases (n_p) has already been determined. If an additional solid phase is found to be stable using the criterion above, equations (3.1.4.3) and (3.1.4.4) must be resolved for the new phase characteristics (K_{ij} and F_j) of the new n_p + *solid* system. Note that a further stability analysis (equations (3.1.5.1) and (3.1.5.2)) is not performed on the new n_p + *solid* system.

4.0 *QUATERNARY PHASE DIAGRAM CONSTRUCTION AND SECTIONING PROGRAM DESCRIPTIONS*

The flow charts depicted in Figures 6 and 7 are the core of this thesis. From these flowcharts, quaternary phase diagrams and sections of these phase diagrams were generated using a combination of custom *Mathematica* and *CorelDRAW!* programs along with the commercial package *CMGPROP v.95.01* developed by the Computer Modelling Group (CMG) in Calgary. A description of all programs listed in Figures 6 and 7 are provided in sequential order. Since the algorithms of both the phase diagram construction and sectioning routines involve some programs that are similar in nature, these are dealt with within the same section with any differences noted. All custom programs were written on a 486/66 MHz IBM compatible computer and the code for each is documented in Appendices F- M. Appendices A-E show sample input and output files generated by the various programs.

4.1 Data File Generation Programs: *dgendia.ma, dgensec.ma*

The initial step in both the phase diagram construction and sectioning routines is to create an input data file for the *CMGPROP* program which contains all the thermodynamic data, equation of state options, and the compositional points needed to fill the faces of the

quaternary phase diagram or the selected section. This is facilitated using the custom *Mathematica* programs titled *dgendia.ma* and *dgensec.ma*, respectively. These programs allow the user to specify the temperature and pressure at which the quaternary phase diagram or section is constructed and the equation of state (Peng-Robinson or Soave-Redlich-Kwong) to be used in the multiphase flash calculations. The user must also enter all the thermodynamic constants of the four components (critical temperature, critical pressure, critical molar volume, acentric factor, and molar mass) and the binary interaction parameters necessary for the multiphase flash routine. Additionally, parameters such as the component to section and the mole percentage at which the section occurs need to be specified in *dgensec.ma*. The programs then generate the composition grid located on each face of the quaternary phase diagram or on the specified section and compile this information into the data files "*datadia.in*" or "*datasec.in*" which are of the form necessary for input into the *CMGPROP* program. Note that only compositional points located on the faces of the equilateral tetrahedron are included in the input file of the phase diagram construction routine since those points located within the tetrahedron are not visible from the outside and are easily viewed using the sectioning routine of Figure 7. A sample input file for the *CMGPROP* program generated by *dgendia.ma* or *dgensec.ma* is provided in Appendix A.

4.2 *CMGPROP v.95.01*

The composition grid points (i.e. single, binary, and ternary) contained within "*datadia.in*" and "*datasec.in*" which define the faces of the three dimensional quaternary phase diagram and a section of this diagram, respectively, are classified with respect to their phase behaviour using the commercial computer package *CMGPROP* (CMG, 1995). *CMGPROP v.95.01* is a multiphase equilibrium property package which employs the Peng-Robinson (Peng and Robinson, 1976) or Soave-Redlich-Kwong (Soave, 1972) equation of state to carry out multiphase flash calculations for accurate phase behaviour prediction. This program uses the cubic equation of state in combination with the tangent plane criterion (Michelson, 1982a,b) and algorithms by Nghiem and Li (1984) at specific pressures, temperature, and compositions as discussed in section 3.2 to predict phase behaviour. The three main benefits of the package with respect to flash calculations are:

Efficient flash calculation technique

The numerical techniques used in *CMGPROP* include the quasi-Newton successive substitution method (QNSS, Nghiem and Heidemann, 1982) which allows for very fast computation of phase equilibria and detection of single phase regions. Options for Newton's method are also available.

Robust stability analysis

A robust stability analysis based on the Gibbs free energy surface enables efficient handling of phase appearance and disappearance in multiphase flash calculations.

Solid Phase Behaviour Prediction

The multiphase flash calculation plus a solid phase is a new option included in *CMGPROP v.95.01*. Due to considerations of computational efficiency and ease of use, the solid phase is described as a single (pure) component. The fugacity of the solid phase forming component is calculated based on a semi-empirical correlation.

Once the composition grid points contained within "*datadia.in*" or "*datasec.in*" are fed into *CMGPROP v.95.01* and classified with respect to their phase behaviour using the flash calculation algorithm outlined in section 3.2 at the specified temperature and pressure, the output from *CMGPROP* is stored in the output file "*datadia.out*" or "*datasec.out*", respectively. A sample output file from the *CMGPROP* program is provided in Appendix B.

4.3 String Extraction Programs: *extrdia.ma, extrsec.ma*

In addition to the phase behaviour associated with each composition grid point, the output data files generated by *CMGPROP* ("*datadia.out*" and "*datasec.out*") contain a vast amount of phase behaviour information (i.e. individual phase compositions and mole fractions) that is unnecessary for the construction of a phase diagram or section. Thus, only the strings which contain the composition points and their corresponding phase behavior identity (i.e. liquid liquid vapour) need to be extracted. The strings in the files "*datadia.out*" and "*datasec.out*" which contain each composition and corresponding phase behaviour are written to files titled "*ptsdia*" and "*ptssec*", using the programs *extrdia.ma and extrsec.ma*, respectively. A sample output file from the *extrdia.ma* or *extrsec.ma* program is shown in Appendix C.

4.4 Sorting of Composition Grid by Phase Behaviour: *sortdia.ma, sortsec.ma*

The next stage in both algorithms is to divide the composition grid points contained in the extraction files "*ptsdia*" and "*ptssec*" by phase behaviour, and write them to separate data files. This is accomplished using custom *Mathematica* programs titled *sortdia.ma* and *sortsec.ma*, respectively. Both programs are virtually identical except for certain portions of the code that allow for the larger size of the "*ptsdia*" file because of its greater number of grid points. Both programs begin by reading the lines of "*ptsdia*" or "*ptssec*" as strings and

assigning a line number to each. The program then searches for the string numbers that contain the phase behaviour identity (e.g. liquid liquid vapour) of each grid point. Once it has identified these string numbers, the program then searches for the string numbers that contain the corresponding compositions of each phase behaviour identity which are related to one another by a linear relationship. Once these have been found, the program then writes these strings (which contain the grid points) to different temporary data files based on which type of phase behaviour the grid point is predicted to have. For example, *sortdia.ma* scans the file "*ptsdia*" and finds the string "liquid liquid" on line 1329 (see Appendix C). Through a predetermined relationship *sortdia.ma* determines that the composition corresponding to this phase behaviour is contained on line 3 and reads "0 96. 4. 0". *Sortdia.ma* then opens a temporary data file titled "*lld.tmp*" and writes the string "0 96. 4. 0". This is continued until all types of phase behaviour have been identified and their compositions written to separate temporary data files. Thus, execution of *sortdia.ma* or *sortsec.ma* results in the generation of temporary data files each of which contain grid points of a specific type of phase behaviour. A sample data file is shown in Appendix D. These files are termed "temporary" since they are not of the form necessary for input into either *diagram.ma* or *section.ma* and must be adjusted further. Note that the temporary data files for the phase diagram and the sectioning program are labeled "**d.tmp*" and "**x.tmp*", respectively.

4.5 Adjusting Temporary (**.tmp*) Files: *cutdia.ma, cutsec.ma*

Since there are only three independent composition variables for each quaternary point, the programs *diagram.ma* and *section.ma* are based upon the input of only three mole fractions for each compositional point. Thus the fourth (i.e. dependent) compositional term of the data files "**.tmp*" must be eliminated. This is accomplished using the *Mathematica* programs *cutdia.ma* and *cutsec.ma* for the phase diagram construction and sectioning algorithms, respectively. These programs read in the "**.tmp*" data files generated by the sorting programs, eliminate the fourth composition term, and then rewrite the data files as "**.dat*" files. Once this has been accomplished, the data points are in the form necessary for input into either the phase diagram or section construction programs. Note that the adjusted data files for the phase diagram construction and sectioning programs are labeled "**d.dat*" and "**x.dat*", respectively.

4.6 Quaternary Phase Diagram Construction Program: *diagram.ma*

Once the extracted output file "*ptsdia*" has been sorted by *sortdia.ma* and the compositional data files have been adjusted using *cutdia.ma*, the next step in the quaternary phase diagram construction is to convert the triangular composition points into rectangular (x, y, z) coordinates such that they can be displayed in the three dimensional compositional

tetrahedron. This conversion and the displaying of the quaternary phase diagram is facilitated using the custom *Mathematica* program *diagram.ma*.

The quaternary phase diagrams are displayed using the standard isothermal isobaric tetrahedron method described in section 2.4, with each face being an equilateral triangle representing the ternary mixtures, the sides the binary mixtures, and the corners the pure components. Compositions within the tetrahedron (i.e. the quaternary points) are determined by specifying planes parallel to the four triangular faces which cut lines normal to these planes at a distance from the opposite apex of the tetrahedron. Only three composition inputs are required for each grid point since the fourth is dependent.

The phase diagram construction routine of the program *diagram.ma* begins by defining the four apexes of the equilateral tetrahedron in three dimensional space as (0, 0, 0) , (50, 86.60254, 0) , (100, 0, 0) , and (50, 28.867513, 86.60254), for the pure components A, B, C, and D, respectively, as shown in Figure 8. Thus, a grid point (such as those contained within the data files generated by *cutdia.ma* can be converted to rectangular coordinates (x, y, z) and placed within the three dimensional space bounded by these axes by defining three intersecting planes parallel to three of the axes. Figure 10 shows the steps for the determination of rectangular coordinates from the given composition data using analytical geometry..

First, the normal vectors to three arbitrarily chosen faces of the equilateral tetrahedron are assigned $\mathbf{n}_1$, $\mathbf{n}_2$, and $\mathbf{n}_3$. Since none of these vectors are parallel it follows that none of the faces (or of planes parallel to these faces) are parallel to each other. Thus, there exists a

singular point in three dimensional space when three planes that are drawn parallel to these three faces intersect. The intersection of these three planes, and therefore the conversion of composition data to rectangular coordinates, is determined by solving the following system of equations:

$$Plane1\ (\pi_1): a_1x + a_2y + a_3z + d = 0 \tag{4.6.1}$$

$$Plane2\ (\pi_2): b_1x + b_2y + b_3z + e = 0 \tag{4.6.2}$$

$$Plane3\ (\pi_3): c_1x + c_2y + c_3z + f = 0 \tag{4.6.3}$$

where the normal vectors to the planes π_1, π_2, and π_3 are $\mathbf{n_1} = (a_1,a_2,a_3)$, $\mathbf{n_2} = (b_1,b_2,b_3)$, and $\mathbf{n_3} = (c_1,c_2,c_3)$, respectively. Using the tetrahedron defined by the four apexes shown in Figure 9, three normal vectors $\mathbf{n_1}$, $\mathbf{n_2}$, and $\mathbf{n_3}$ were solved for by John Lo (1992) and equations (4.6.1) to (4.6.3) are solved simultaneously using *diagram.ma* to convert all grid points contained in the data files to points within or on the face of the phase diagram.

Once all grid points have been converted to rectangular coordinates in this manner, *diagram.ma* places the points within the phase diagram with a different colour representing each type of phase behaviour which is determined by the data file from which each point originates. Upon construction of the quaternary diagram, the tetrahedron can be rotated such that any side or corner can be viewed or can be "folded-out" to allow for simultaneous viewing of all faces of the tetrahedron. Since only phase behaviour on the faces of the tetrahedron can be viewed from an exterior viewpoint, points contained within the

tetrahedron can be viewed using a modified version of the phase diagram construction or the sectioning algorithm of Figure 7 which takes sections of the quaternary phase diagram at constant composition of one of the four components.

4.7 Sectioning Program: *section.ma*

Sections of the constructed quaternary phase diagrams may be taken at constant composition of one of the four components using the custom *Mathematica* program *section.ma*. Since many interesting phase phenomena occur in the quaternary space of the phase diagram, a sectioning program becomes necessary since only the phase behaviour located on the faces of the tetrahedron is visible from the outside.

Section.ma allows the user to section the quaternary diagram at any composition of either of the four components. It begins by converting the cc ɔositional coordinates contained within the sectioning data files ("*x.dat") to rectangular coordinates and then places and colours them within the quaternary phase diagram in the same procedure outlined in tne previous section. However, *section.ma* does not draw the tetrahedon but instead, only a ɹriangle around the data points and adjusts the view of the user perpendicular to the triangle which results in standard ternary diagrams as outlined in section 2.3. These diagrams were re-drawn using Corel*DRAW!* for presentation in this thesis.

5.0 *RESULTS AND DISCUSSION*

The quaternary phase diagram construction and sectioning routines depicted in Figures 6 and 7, respectively, were applied to three multicomponent systems: a simple ternary hydrocarbon system (methane + propane + *n*-decane) to test the sectioning routine and to demonstrate its use as a teaching tool; a model quaternary condensate rich reservoir fluid (ethane + propane + *n*-butane + phenanthrene) to test the quaternary phase diagram algorithm and the ability of the *CMGPROP* program to deal with complex phase behaviour involving pure solids (i.e. solid-liquid-liquid-vapour phase behaviour); and a real heavy oil mixture (athabasca bitumen vacuum bottoms (ABVB) + hydrogen) to see if these algorithms can be used as a predictive or correlative tool for "real" systems where experimental data are sparse.

5.1 Phase Diagram for the Methane + Propane + *n*-Decane System at P = 27.58 bar and T = 310.93 K

This simple ternary hydrocarbon mixture was chosen to demonstrate the proposed sectioning algorithm as a useful teaching tool for constructing and displaying ternary phase diagrams or sections of quaternary phase diagrams for several reasons. First, this mixture

demonstrates only liquid and vapour phase behaviour (i.e. liquid, vapour, and liquid + vapour) at the pressure and temperature tested (27.58 bar, 310.93 K) and the success of the Peng-Robinson EOS to predict such phase behaviour of alkane mixtures is well documented in the literature (e.g. Peng & Robinson, 1976). Second, the critical and thermodynamic constants of these compounds are well known and correlations that calculate binary interaction parameters between hydrocarbon components have been defined and found to be accurate (Hudson and McCoubrey, 1960). Thus, this mixture is well characterized and does not require fitted parameters. Third, there is a wide range of experimental data available for this mixture (Wiese *et al.*, 1970) at various temperatures and pressures which allow for extensive testing of the model.

The experimental data of this system at P = 27.58 bar and T = 310.93 K (Wiese *et al.*, 1989) was modelled with the Peng-Robinson equation of state as implemented in the *CMGPROP* program using the sectioning routine of Figure 7. Due to the fact that the sectioning routine is based on a four component system, an arbitrary fourth component was added to the model mixture at a mole fraction equal to zero. Thus, a ternary diagram of the given system may be seen as a section of the pseudo four component system taken at a mole fraction equal to zero of the arbitrary component. The experimental data and modelled phase diagram are shown in Figures 10 and 11, respectively.

Comparing these two diagrams, general agreement was found between the model and the experimental data. The tie lines joining the liquid and vapour phases are conserved as are the size, shape and proportion of all phase zones involved. This example provides a good

representation of the capabilities of the sectioning routine. The program was found to accurately predict and colourfully represent the phase behaviour of this hydrocarbon system and thereby demonstrate its usefulness as a teaching tool for phase equilibria and phase diagrams. However, due to the rather long run time (approximately twenty minutes on a 486/66 MHz computer), its use as an on-line phase diagram construction program is limited.

Approximately fifteen minutes (75%) of the total run time is devoted to the string extraction routine "*extrsec.ma*" which extracts the necessary strings from the output of the *CMGPROP* program. Thus, the program will work within a reasonable amount of time (less than five minutes) only if the user provides the data files necessary for the program and bypasses the string extraction subroutine altogether. Discussions are currently ongoing with Dr. Dennis Coombe of the CMG to optimize the sectioning routine and the quaternary phase diagram routine by modifying the source code of *CMGPROP* to output only those strings necessary for the algorithms of Figures 7 and 8. Currently, the output from the *CMGPROP* (see Appendix B) includes a large amount of information such as tie-line compositions, phase mole fractions etc. that are not used by either algorithm. This proposed adjustment would most probably result in reduction of the run time to an acceptable level (approximately five minutes).

5.2 Phase Diagram for the Ethane + Propane + *n*-Butane + Phenanthrene System at P = 5.0 MPa and T = 349.6 K

The effectiveness of the quaternary phase diagram construction routine (Figure 6) is illustrated through the phase diagram for ethane + propane + *n*-butane + phenanthrene, a model condensate-rich, reservoir fluid. This mixture was chosen for several reasons. First, there is a wide range of accurate quantitative experimental data available (Shaw *et al.*, 1994) including P/x, T/x, and P/T diagrams at various temperatures and pressures which allow for accurate extrapolation/interpolation of the experimental data. Second, the phase behaviour of this mixture involves pure solid phenanthrene formation in addition to liquid and vapour phases and thus provides a test for the single, pure solid prediction routines in *CMGPROP*; Third, due to this solid formation, this mixture provides the simplest analogue for modelling the phase behaviour of real oil systems which may exhibit asphaltene deposition in the same ranges of temperature and pressure.

An experimental P/x diagram for the system ethane + propane + *n*-butane + phenanthrene at 349.6 K (Shaw *et al.*, 1994) exhibiting solid-liquid-liquid-vapour phase behaviour, Figure 12, was modelled with the Peng-Robinson equation of state as implemented in the *CMGPROP* program. This mixture was selected since such phase behaviour is consistent with the expansion of a *q*-point (or quadruple point - a point where four organic phases are in equilibrium: solid (S), light liquid (L1), heavy liquid (L2), and vapour (V)) present in the propane + phenanthrene binary system to multicomponent systems. As more degrees of

freedom are added to the system through additional components, the four phase q-point expands to a curve for three component mixtures and becomes a region in P/T space for mixtures of four or more components. In addition, the mixture is well defined and the solid phase is crystalline phenanthrene. Thus, modelling this system with the four phase flash routine of the *CMGPROP* program provides a sound foundation for the modelling of the real heavy oil system ABVB + hydrogen with respect to whether this modelling method can be applied to more complex systems.

Although the *CMGPROP* program contains an extensive library of physical and thermodynamic constants, the physical constants of phenanthrene and its binary interaction parameters with the light components had to be input into the program. Known parameters of phenanthrene include its molar mass 178.234 g mol^{-1}, critical pressure 36.2 bar, critical molar volume 554 cm^3mol^{-1}, and critical temperature of 915.7 K. Other pertinent parameters such as acentric factor were approximated using estimation routines in the program.

The crucial step in the modelling of this system is the characterization of phenanthrene both in solution and as a pure solid phase. This is accomplished by splitting the phenanthrene into two components: a non-solid forming component (PHENANA) and a solid forming component (PHENANB). This is an extension of a model first developed at CMG for dealing with asphaltene formation in heavy oil mixtures. Both components have identical critical properties and acentric factors, but their binary interaction coefficients with the light components are different. The solid forming phenanthrene has larger binary interaction coefficients with the light components which corresponds to greater incompatibility between

components and favors the formation of a solid phase. This is said to model the experimental phenomena that not all phenanthrene in solution forms a solid phase. Using this characterization of phenanthrene, the binary interaction parameters needed for the *CMGPROP* program were obtained by fitting the experimental data of Shaw *et al.* (1994) at 349.6 K. A table of all the physical constants of phenanthrene and its binary interaction coefficients is shown in Table 1. The two phenanthrene components (PHENANA:PHENANB) were chosen in a mole fraction ratio of 2:98 as only a minute amount of the non-precipitating phenanthrene (PHENANA) was needed to model the experimental data. Predicted phase behaviour for the model system is shown in Figure 13. This result and much of the commentary which follows has been reported in the literature (Cartlidge *et al.*, 1996).

While there was general agreement between the model and experimental data, discrepancies are apparent. In particular, the solid-vapour zone present at low pressures in the experimental data is not predicted by the model. Consequently, the solid-liquid-vapour/liquid-vapour boundary is not predicted by the model and has been sketched in along with the solid-liquid-liquid-vapour/solid-liquid-vapour transition based on the location of predicted phase boundaries. In most other respects the match between predicted and modelled phase behaviour is quite good and given the similarities in phase behaviour of phenanthrene and bitumen containing mixtures, it may be possible to approximate the phase behaviour of bitumen/heavy oil systems using appropriate four component model fluids.

However, although the classification of the phenanthrene is acceptable for this specific case, the pure solid model has some severe limitations with respect to the determination of the solid reference fugacity. Since the reference (solid) fugacity is set constant (i.e. temperature effects are not taken into consideration) by the program, this corresponds to a vertical solid transition line in P/T space which contradicts recent experiments in our group which show these lines may also be almost horizontal (see Figure 14). Related to this point, the program cannot deal with pure single component solids (i.e. a system of the pure "solid-forming" phenanthrene) and in fact predicts inverse stability with a trace amount of a second component. This is demonstrated by Figure 15 which shows the relationship between the liquid fugacity, constant solid fugacity, and the temperature dependent solid fugacity using the equation below:

$$f_s(T1) = f_s(T2) * \left(\frac{f_l(T1)}{f_l(T2)} \right) \exp\left(\frac{-\Delta H_{FUSION}}{R(T1 - T2)} \right) \qquad (5.2.1)$$

where the fugacities in the above expression indicate pure component fugacities.

For these reasons, the solid routines contained in the *CMGPROP* program were deemed marginally acceptable for this system and unacceptable for application to more complex solid forming systems such as the next example (ABVB + hydrogen). Thus, an alternative method was used to characterize solid formation of the more complex system.

To demonstrate the effectiveness and the three-dimensionality of the quaternary phase diagram routine, a four component phase diagram of this system was constructed at 349.6 K and 5.0 MPa lumping the two phenanthrene components together on one axis. This phase diagram contains a great deal of information, most of which is contained within the tetrahedron. To demonstrate the ability of the phase diagram construction routine to plot interior points, the programs outlined in Figure 6 were modified slightly to plot the solid-liquid-liquid zone of this system. The resulting phase diagram is shown in Figure 16 . This diagram shows that the majority of solid-liquid-liquid behaviour is encountered near the propane + phenanthrene binary system. This is expected as there is a *q*-point for this binary pair. This example provides a good representation of the capabilities of the quaternary phase diagram construction routine. The program was found to create an equilateral tetrahedron and to convert composition grid coordinates to the (x, y, z) coordinate system. It also shows the flexibility of the programs. With slight modifications any number or combination of phase behaviour types located on the interior of the tetrahedron may be shown. A demonstration of the output generated from unmodified versions of the sectioning and phase diagram construction routines are shown in the next example.

5.3 Phase Diagram for the Athabasca Bitumen Vacuum Bottoms + Hydrogen System at P = 3.5 MPa and T = 673.15 K

The most recent study to date into the phase behaviour of heavy oil/bitumen mixtures is that reported by Dukhedin-Lalla (Ph.D. thesis, 1995) who provides phase diagrams for athabasca bitumen vacuum bottoms (ABVB) + hydrogen and ABVB + hydrogen + *n*-dodecane mixtures over a wide range of temperatures and pressures. Data reported by Dukhedin-Lalla (1995) serve as the basis for the proposed models. Much of the commentary which follows has also been published (Cartlidge *et al.*, 1996).

The applicability of the quaternary phase diagram construction routine (Figure 6) and the sectioning routine (Figure 7) is illustrated through the phase diagram for ABVB (26.8 mole.%) + hydrogen (H) (73.2 mole.%). An experimental P/T diagram for this system (Dukhedin-Lalla, 1995) exhibiting "solid"-liquid-liquid-vapour phase behaviour, Figure 17, was modelled with the Peng-Robinson equation of state as implemented in the *CMGPROP* program. However, the nature of the "solid" is unclear. From the slope of the "solid"-liquid-vapour to liquid-vapour phase boundary, the enthalpy of fusion has been calculated (Dukhedin-Lalla, 1995) to be approximately 7 kJ/kg. This value is too low for crystalline solids and waxes where enthalpies of fusion are an order of magnitude higher. Thus it may be an amorphous solid, a viscous liquid, or micellular in nature.

Due to the "solids" of this mixture being non-crystalline and the inability of the *CMGPROP* program to predict phase behaviour of simple mixtures involving pure,

crystalline solid formation, the experimental "solid" phase was modelled as an additional liquid phase. The ABVB was modelled as three pseudo-components (LIGHT (L), HEAVY1 (H1), HEAVY2 (H2)). The critical and physical properties of these pseudo-components were estimated using the oil splitting subroutine of the *HYSIM* program so that the mean molar mass and density were matched. These properties as well as the binary interaction parameters used are shown in Table 2. The mole fraction ratio of L:H1:H2 was set at 25:52.5:22.5 which is in line with data published by Syncrude Ltd. Predicted phase behaviour for the model system and the experimental data are shown in Figure 18.

Although there is general agreement between the predicted and experimental phase boundaries, the match is purely qualitative. The general size and shape of the multiphase zones are conserved but the predicted phase behaviour is shifted to significantly lower temperatures and pressures. However, this model forms a basis for the construction of a phase diagram for the system ABVB + hydrogen since all model composition grid points can be transformed to their experimental values.

From this model, a constant temperature (673.15 K) and pressure (3.5 MPa) quaternary phase diagram was constructed using the algorithm of Figure 6 and is shown in Figure 19. This corresponds to an experimental pressure and temperature of approximately 8.0 MPa and 715 K, respectively. An application of such phase diagrams in the petrochemical industry could be to provide an important tool for determining optimal processing and refining conditions or aiding in the design of reactors without having to perform a large number of experiments.

To facilitate easy viewing of all faces, the phase diagram can either be rotated continuously (Figure 20) using *Mathematica* or can be "folded-out" as shown in Figure 21 using the sectioning routine of Figure 7 in combination with Corel*DRAW!*. The four ternary diagrams of the quaternary system in Figure 21 can be folded along the edges of the inner triangle and joined at the hydrogen (H) apex to reconstruct the tetrahedron. Discussions are ongoing with regard to automating the fold-out diagram and including it as an option in the phase diagram construction routine (June Ng, 1995 - in progress).

A section of Figure 19 was taken at 80 mole.% hydrogen using the algorithm of Figure 7 resulting in Figure 22. The sectioning routine allows one to view a two dimensional slice of the interior of the tetrahedron that is not visible from an exterior viewpoint. As shown in Figure 22, a large liquid-liquid-liquid-vapour zone exists at 80 mole.% hydrogen which is not visible from the exterior of the tetrahedron. A special note should be made about the lack of connection points (i.e. between the liquid-liquid-liquid-vapour region and two liquid-vapour regions) in Figure 22. Although these connection points exist, they are not shown due the grid size chosen. The only way to get around this problem is to increase the number of grid points, but because of poor performance times this is not a viable option. However, this example provides a good representation of the capabilities of the sectioning and phase diagram construction routines as extrapolation/interpolation tools. From a modelled P/T system (at a given composition), these programs were able to construct clear phase diagrams using an equation of state to extend predictions to other compositions.

Again, computation time is a problem as an average tetrahedron takes approximately one hour (on a 486/66 MHz computer) to construct. The sectioning routine takes approximately 20 minutes. The majority of run time in both programs is devoted to the string extraction routines "*extrdia.ma*" and "*extrsec.ma*" which extract the necessary strings from the output of the CMGPROP program. Previously discussed modifications to the *CMGPROP* program would most probably result in a 75% reduction in run time of both programs (to approximately fifteen and twenty minutes, respectively).

5.3.1 Liquid Phase Discrimination

It is important to note that neither the quaternary phase diagram construction or sectioning routine is able to distinguish between different liquid phases (i.e. liquid1, liquid2, etc.). This inadequacy is shown clearly in Figure 22 where the three liquid + vapour zones are shown as one type of phase behaviour although their liquid phases are dissimilar. To adjust the routines to account for different liquid phases is a significant task due to the format of both the output from the *CMGPROP* program (Appendix B) and the routines themselves. However, it is apparent from Figure 22 that the different liquid phases can be easily distinguished once the diagrams have been generated.

6.0 *CONCLUSIONS*

1. The phase diagram construction routine allows for:

a. Graphical representation of the phase relationships of up to four component systems.

b. Clear depiction of different phases in the phase diagram.

c. Visualization of the effect of temperature and/or pressure changes on the size and shape of different single or multiphase zones.

d. Viewing of all exterior faces simultaneously through rotation or "folding-out" of the diagram.

e. Extrapolation/interpolation of experimental data.

2. The sectioning routine allows for:

a. Sectioning of the quaternary phase diagram at constant composition of one of the four components resulting in a standard ternary phase diagram.

b. Ternary phase diagram construction.

c. Clear depiction of different phases in the phase diagram.

d. Visualization of the impact of temperature and/or pressure variations on the placement of various phase zones.

e. Extrapolation/interpolation of experimental data.

3.0 These computer programs offer benefits to both the student of phase diagrams as well as researchers, although the run times are long.

4.0 "Asphaltene" Deposition Model

The model presented offers a promising approach for predicting solid deposition in real heavy oil systems.

7.0 *RECOMMENDATIONS*

1. The *CMGPROP* program should be modified to output only those strings necessary for the sectioning and phase diagram routines.
2. A subroutine should be included in both routines that distinguishes between liquid phases (i.e. liquid1, liquid2, etc.) and plots them individually.
3. The "fold-out" diagram should be automated and included in the phase diagram construction routine.
4. General modifications should be made to both routines that reduce their run times.
5. Further work should be done to see if the proposed modelling approach for dealing with bitumen + hydrogen mixtures can be applied to ABVB + hydrogen + *n*-alkane systems.

8.0 *REFERENCES*

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Compound	Mole Fraction in Mix	Molar mass	P_c (atm)	T_c (K)	Acentric factor	k_{ij} for the PR-EOS		
						METHANE	PROPANE	BUTANE
PHENANA	0.02	178	36.68	915.7	0.98	0.1136	0.0564	0.004
PHENANB	0.98	178	36.68	915.7	0.98	0.1336	0.0664	0.006

Table 1. Physical and Thermodynamic Properties of Phenanthrene

Compound	Mole Fraction in Mix	Molar mass	P_c (MPa)	T_c (K)	Acentric factor	k_{ij} for the PR-EOS		
						LIGHT	HEAVY 1	HEAVY 2
LIGHT	0.25	292	1.39	798	0.844	0.0		
HEAVY1	0.525	862	1.75	921.9	0.813	0.2 > 633 K 0.15 < 633 K	0.0	
HEAVY2	0.225	1504	1.12	1073.9	1.153	0.4	0.3	0.0

Table 2. Physical and Thermodynamic Properties of ABVB Pseudo-Components

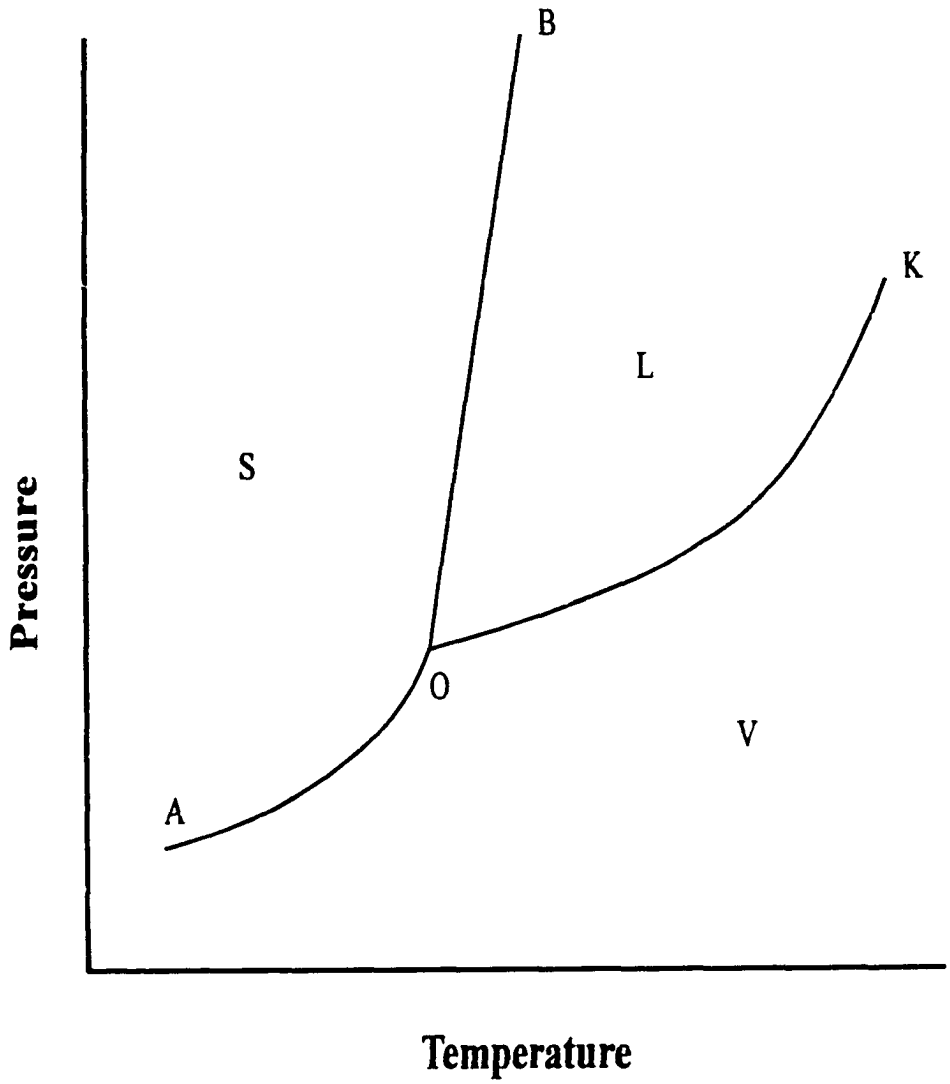

Figure 1. Single Component Phase Diagram

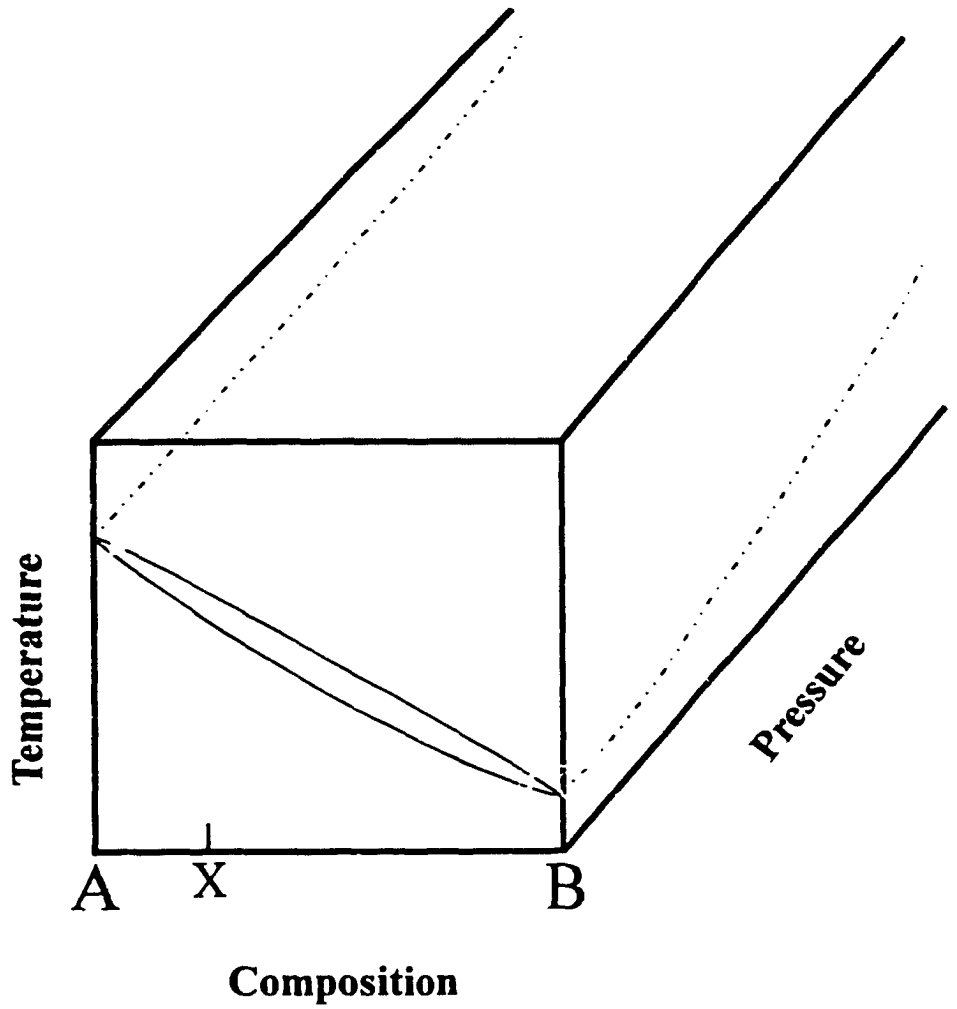

Figure 2. Two Component (Binary) Phase Diagram

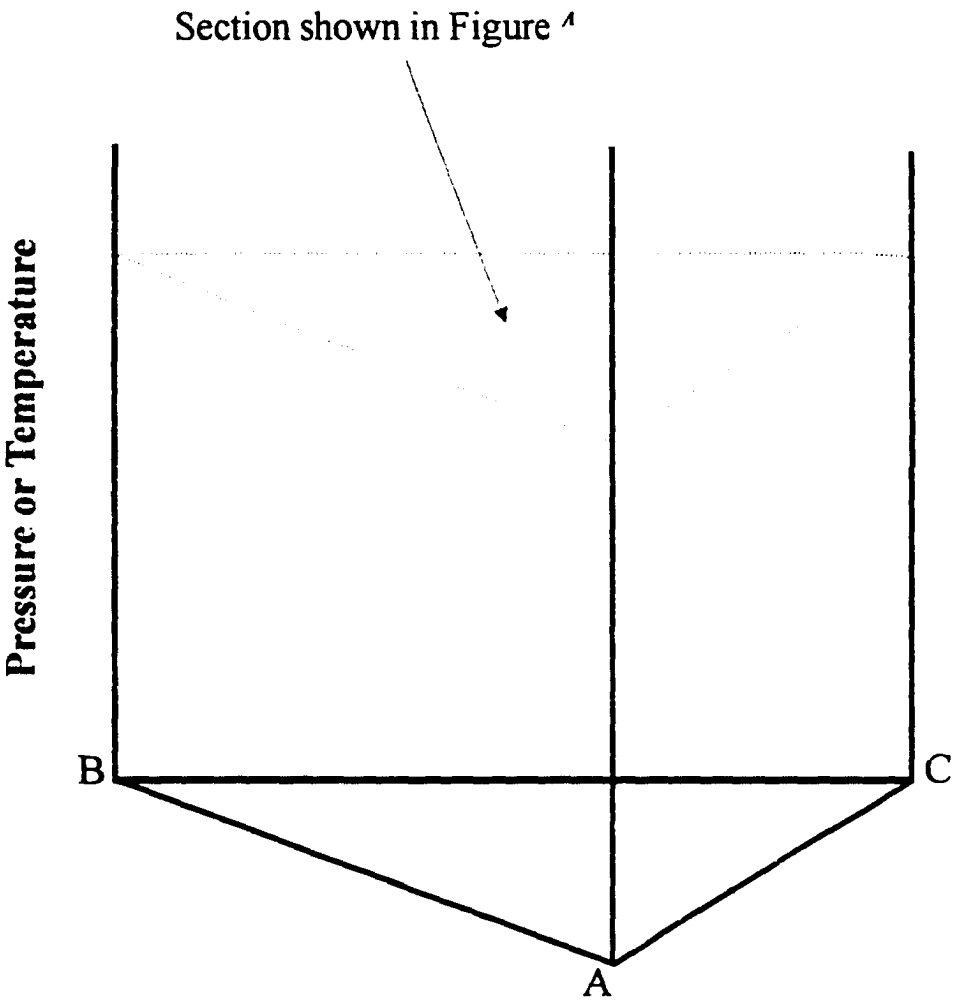

Figure 3. Three Component (Ternary) Phase Diagram

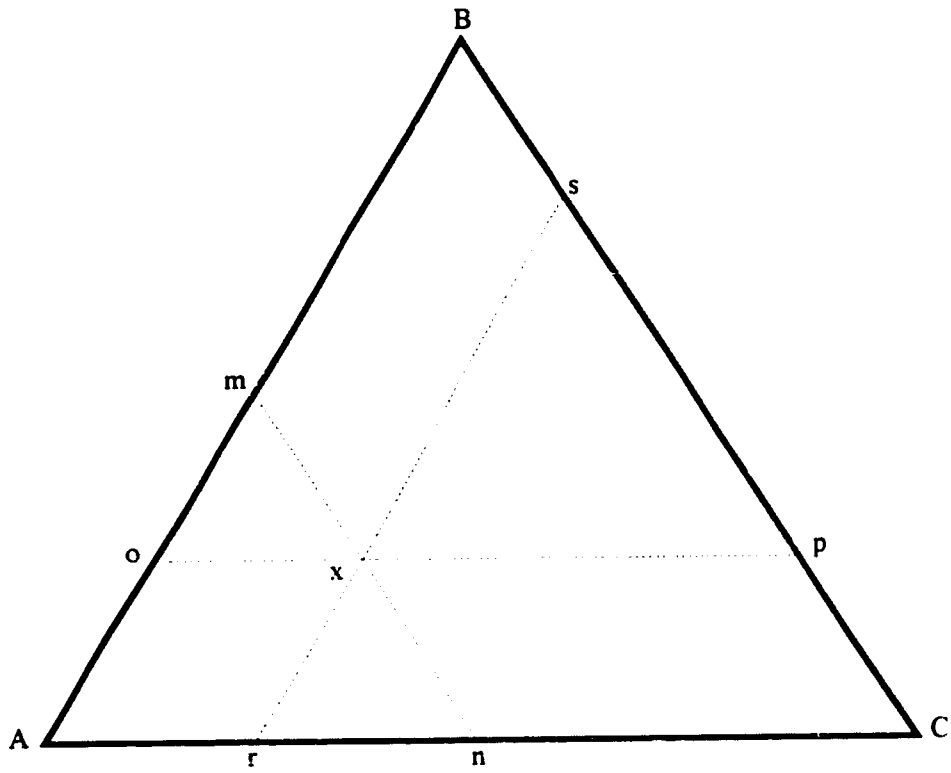

Figure 4. T/c or P/c Section of Figure 3

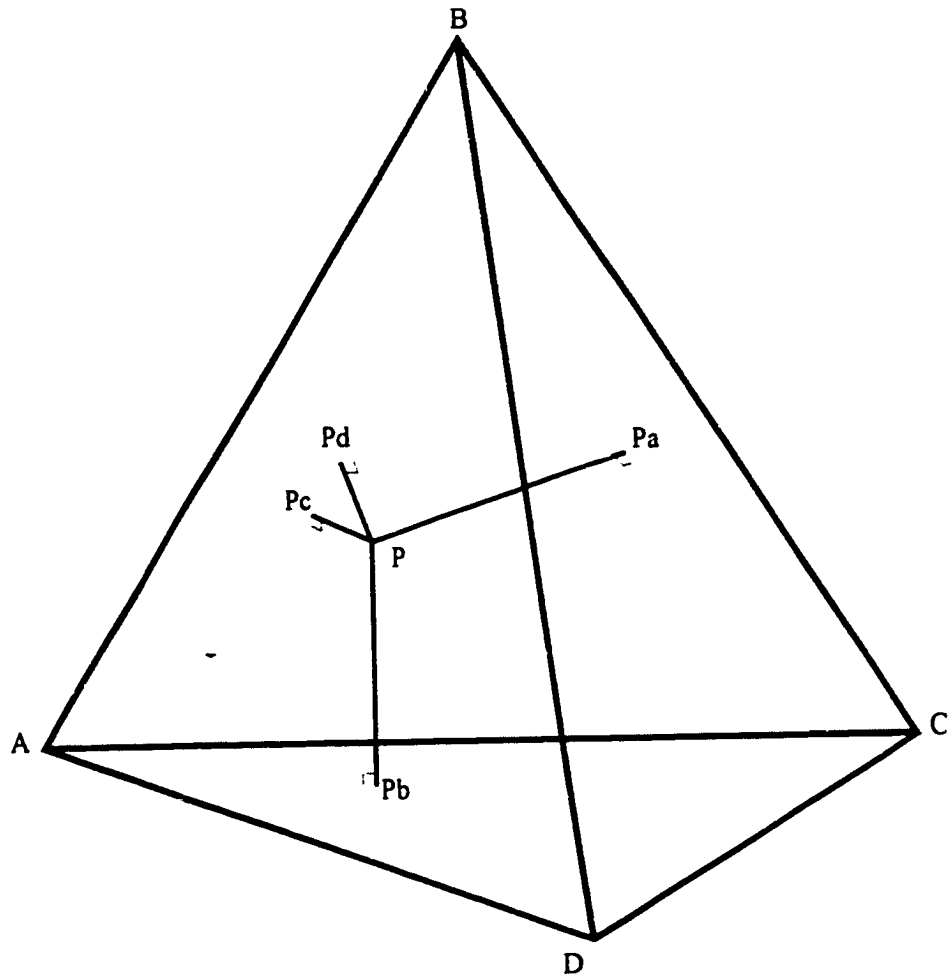

Figure 5. Four Component (Quaternary) Phase Diagram

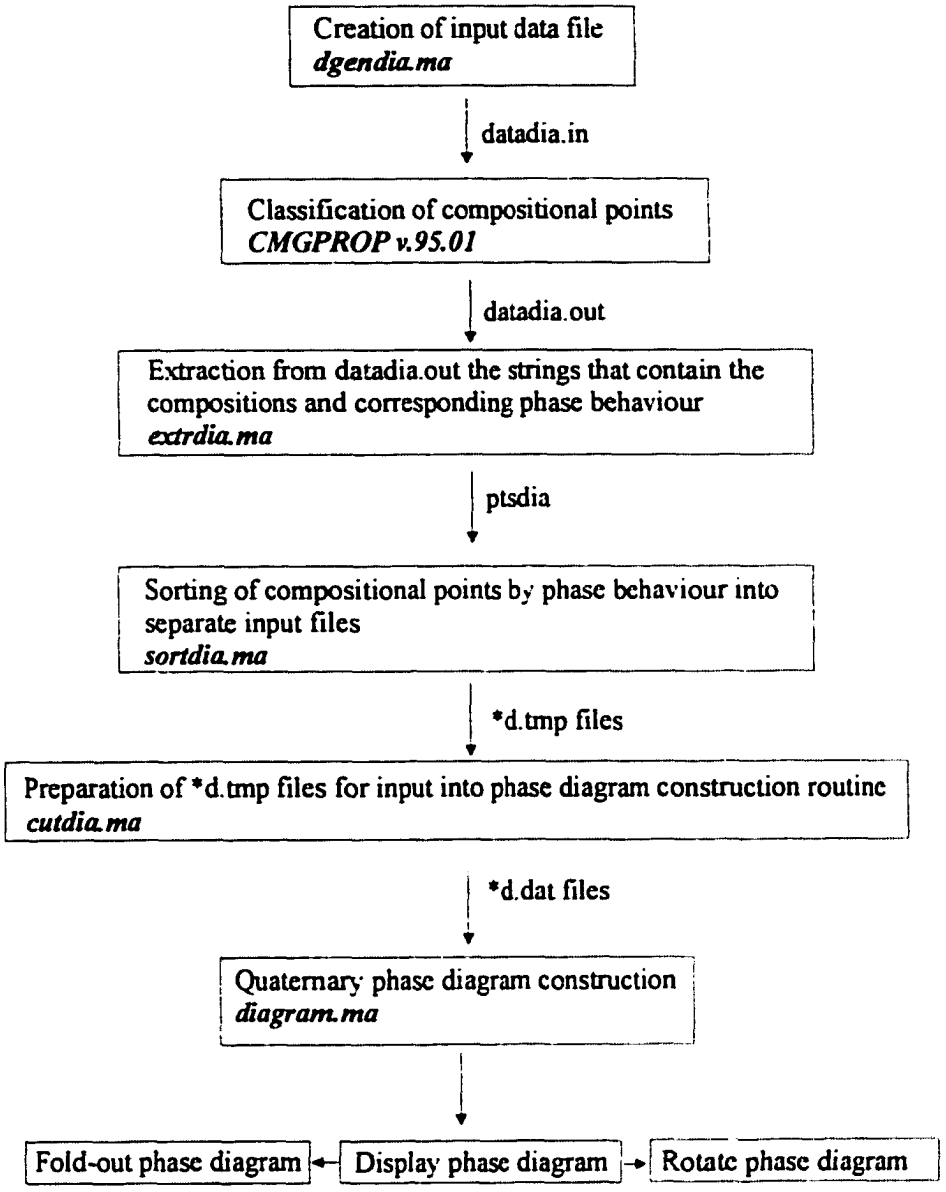

Figure 6. Quaternary Phase Diagram Construction Algorithm

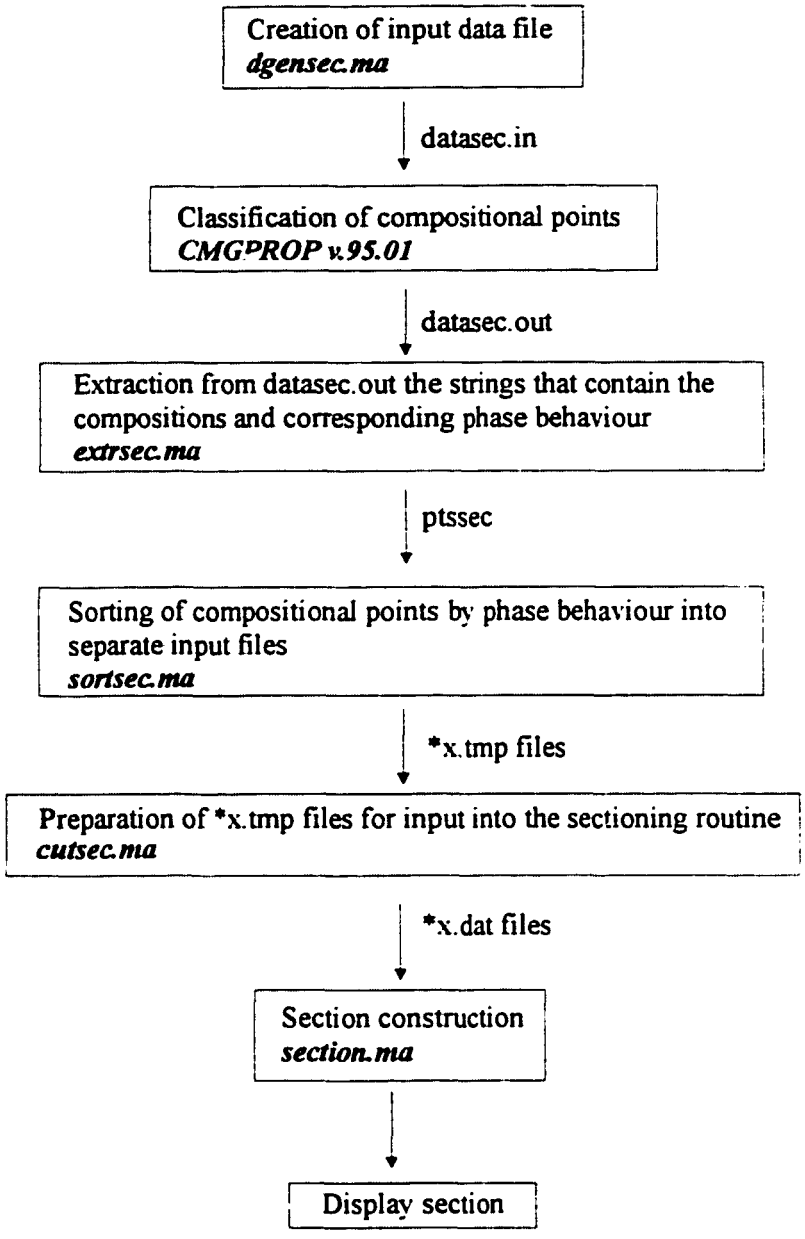

Figure 7. Section Construction Algorithm

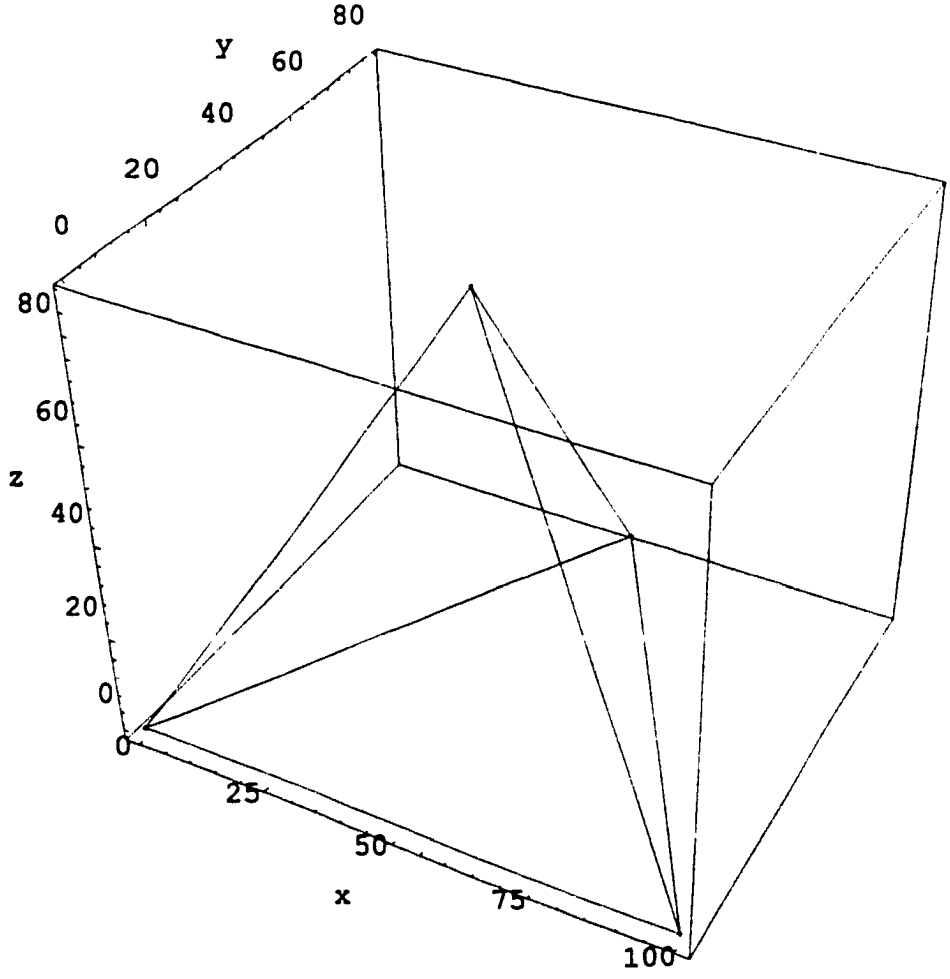

Figure 8. Presentation of the Quaternary Phase Diagram in the (x, y, z) Plane

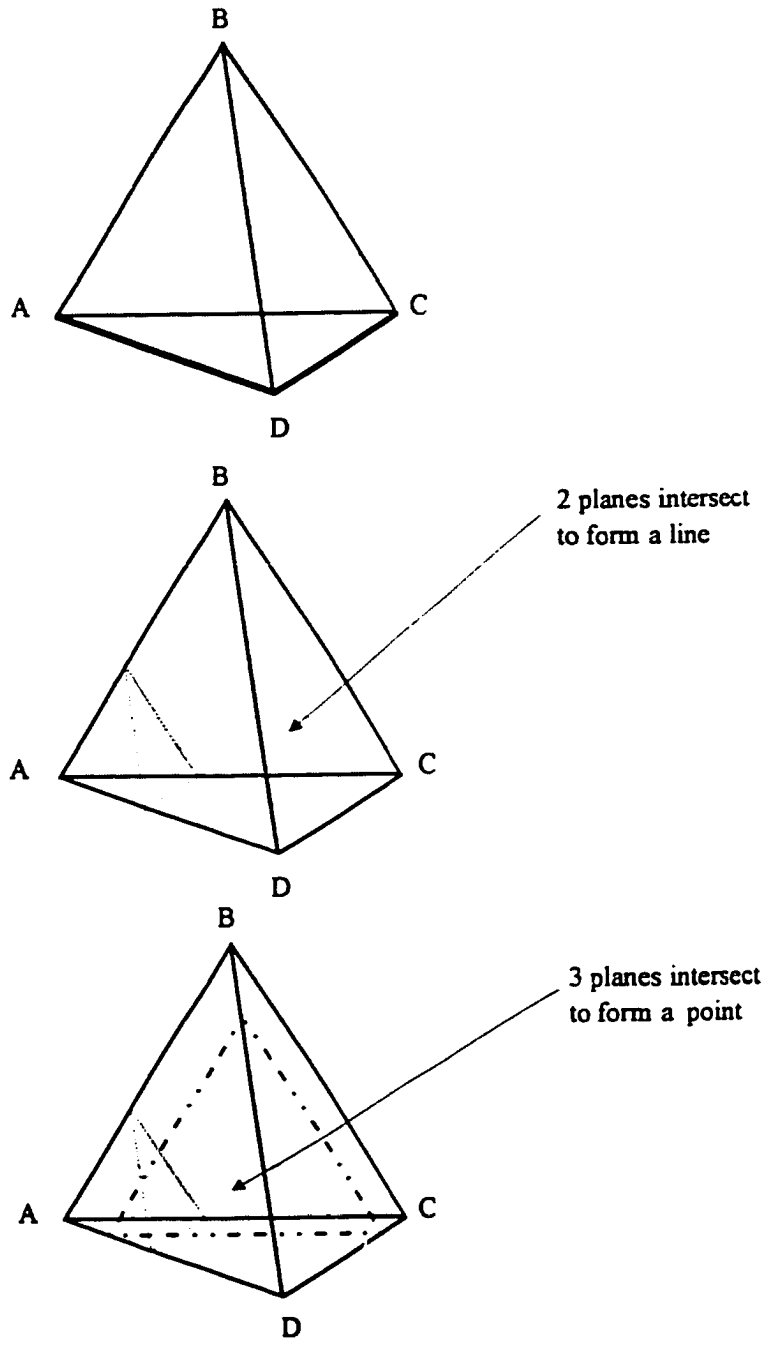

Figure 9. Graphical Presentation of the Triangulation Conversion Technique

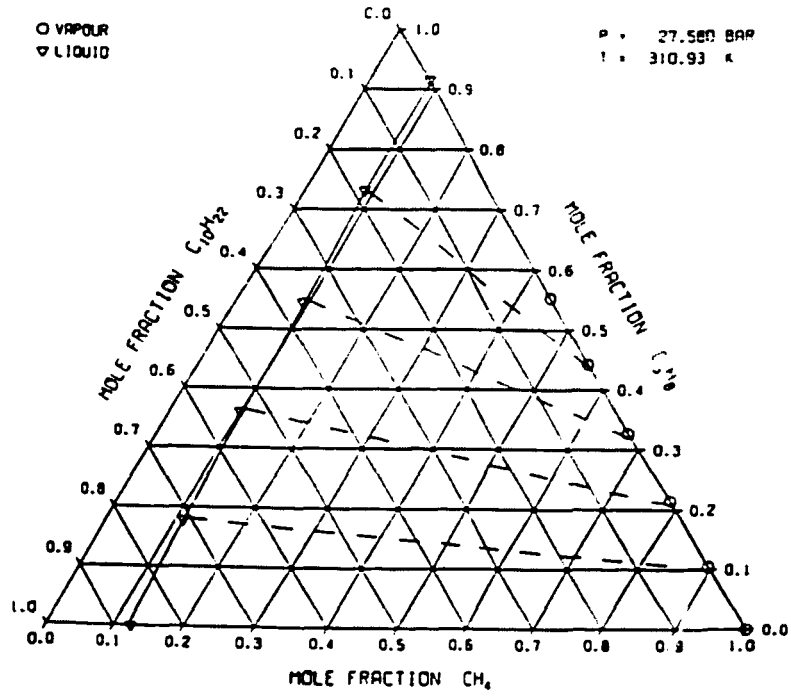

Figure 10. Experimental Phase Diagram for the Methane + Propane + *n*-Decane System at P = 27.58 bar and T = 310.93 K (Wiese, H.C. *et al.*, 1970)

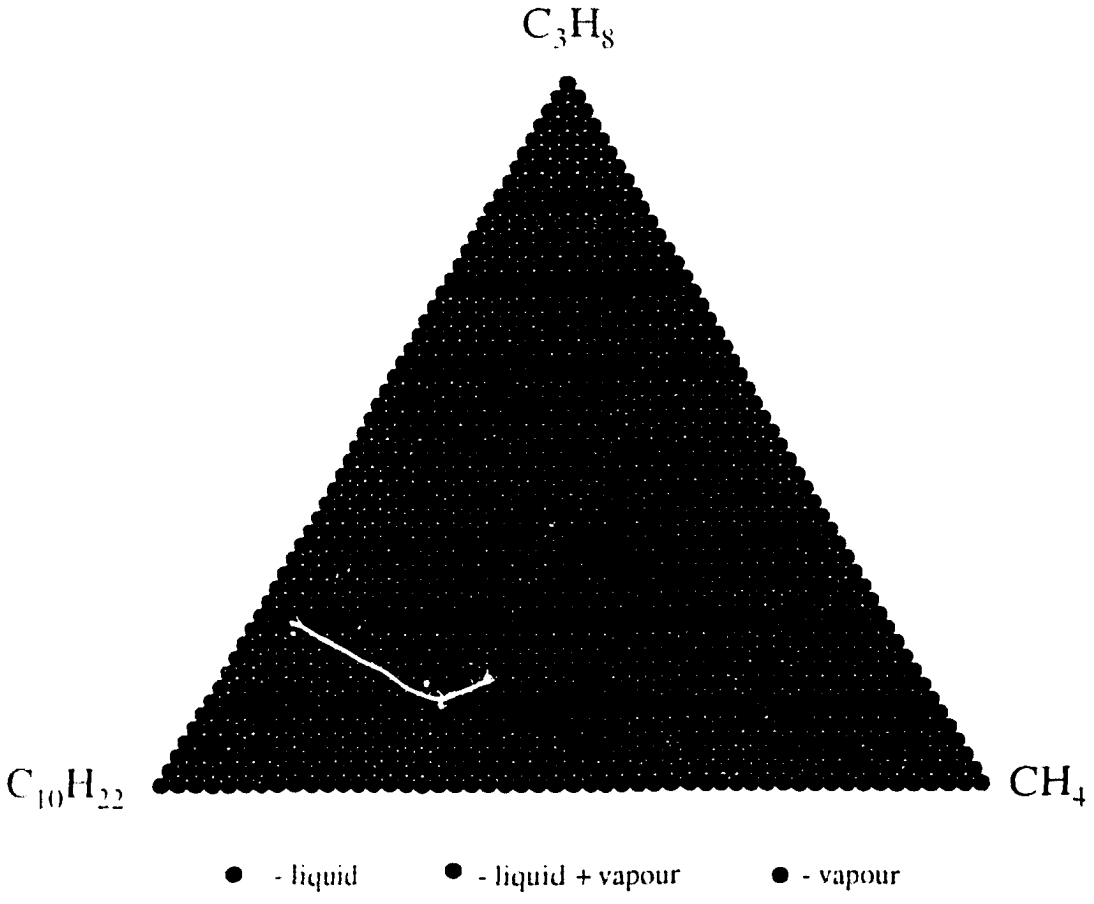

Figure 11. Modelled Phase Diagram for the Methane + Propane + n-Decane System at P = 27.58 bar and T = 310.93 K

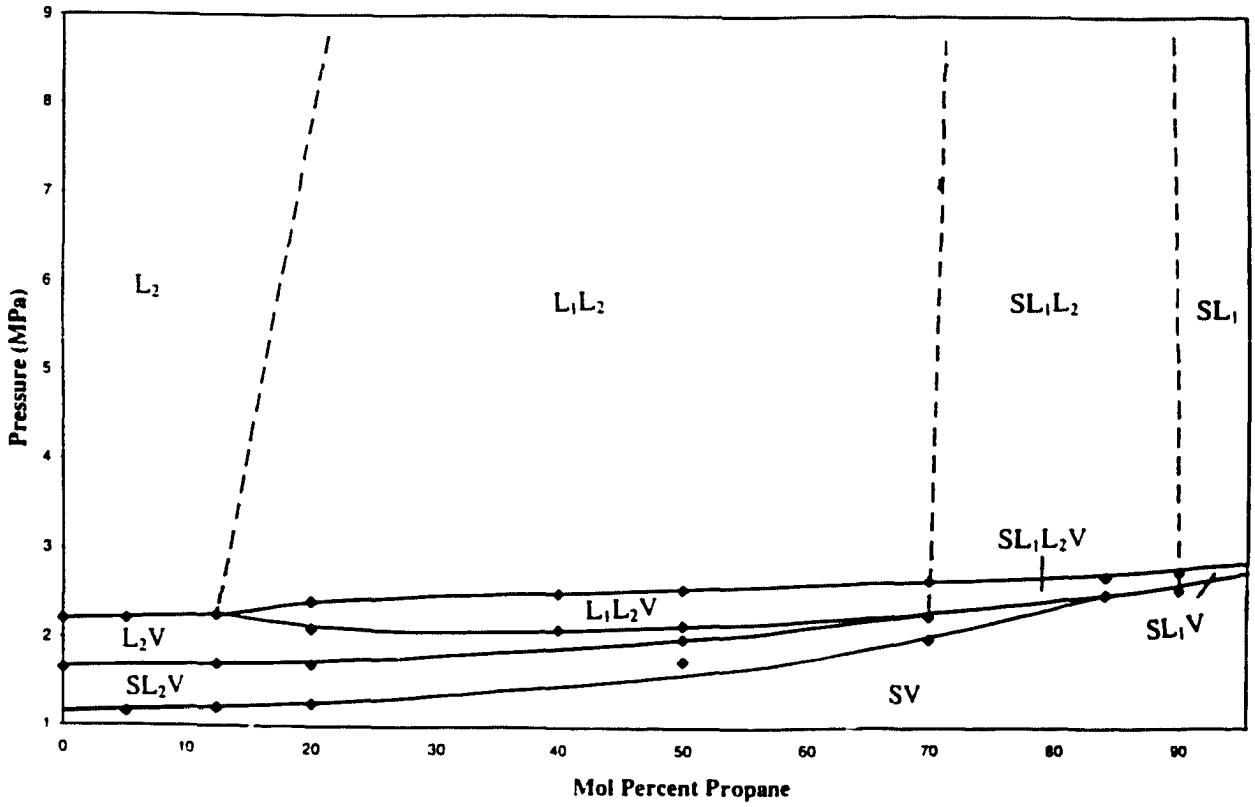

Figure 12. Experimental P/x Diagram for the Methane + Propane + *n*-Butane + Phenanthrene System at T = 349.6 K

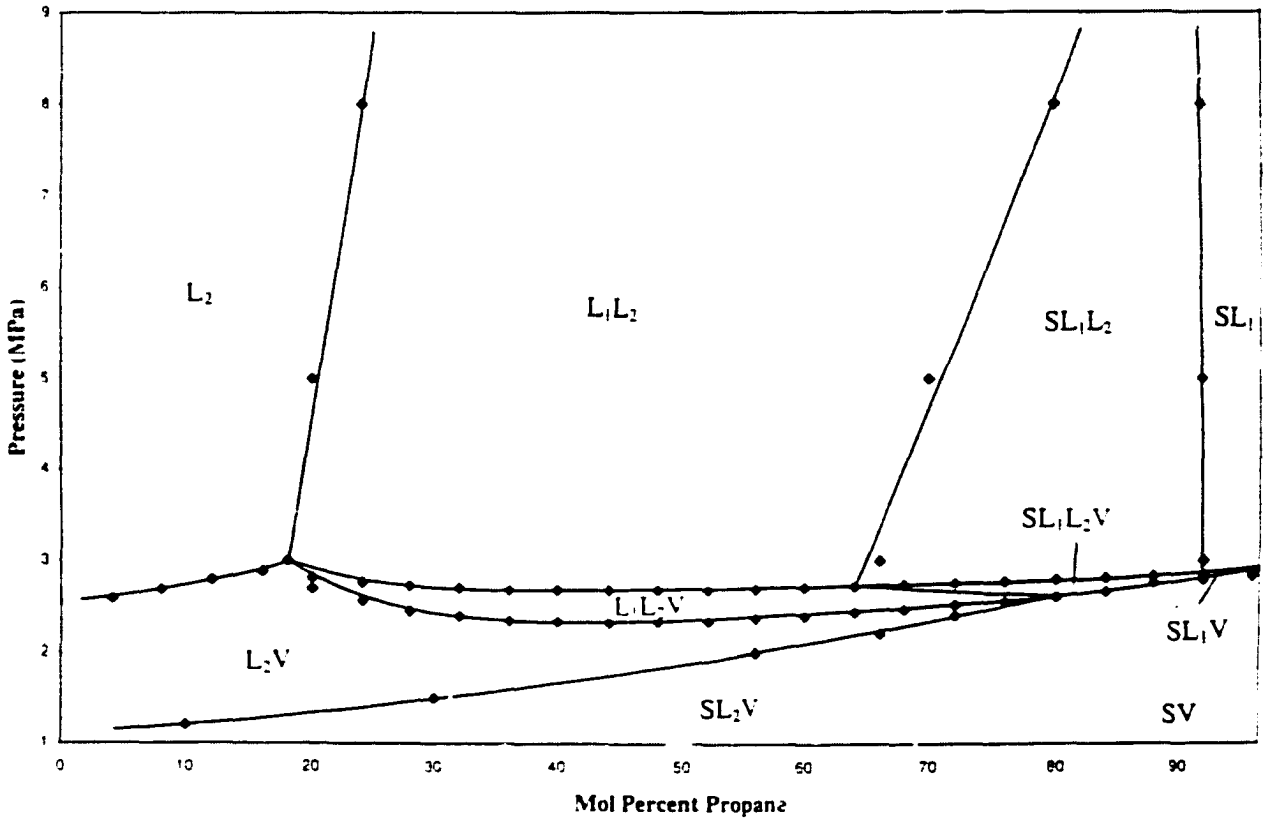

Figure 13. Modelled P/x Diagram for the Methane – Propane – *n*-Butane – Phenanthrene System at T = 349.6 K

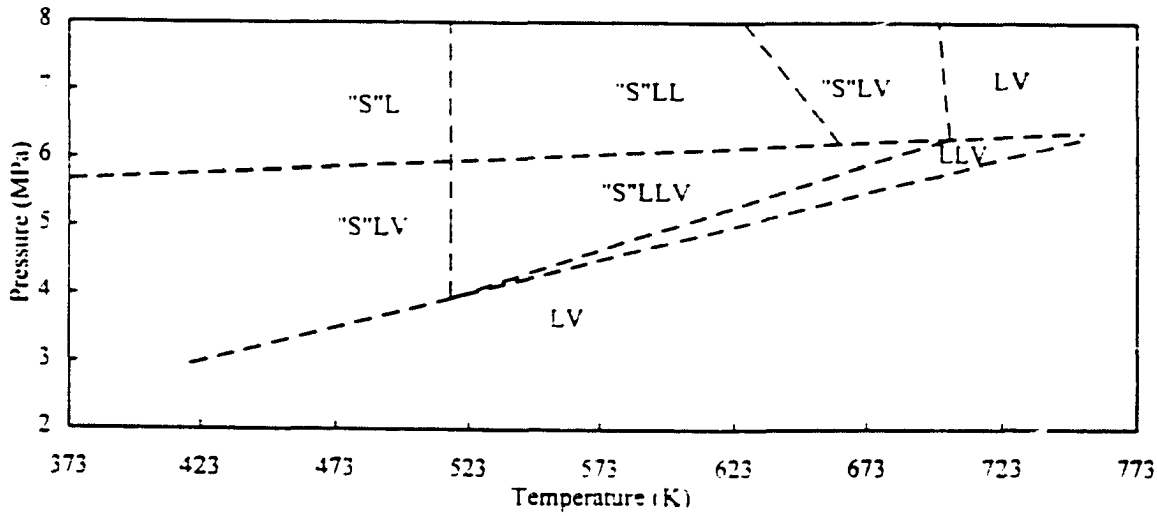

Figure 14. Preliminary Phase Diagram for 7.6 mole.% ABVB – 43.9 mole.% *n*-dodecane – 48.5 mole.% Hydrogen

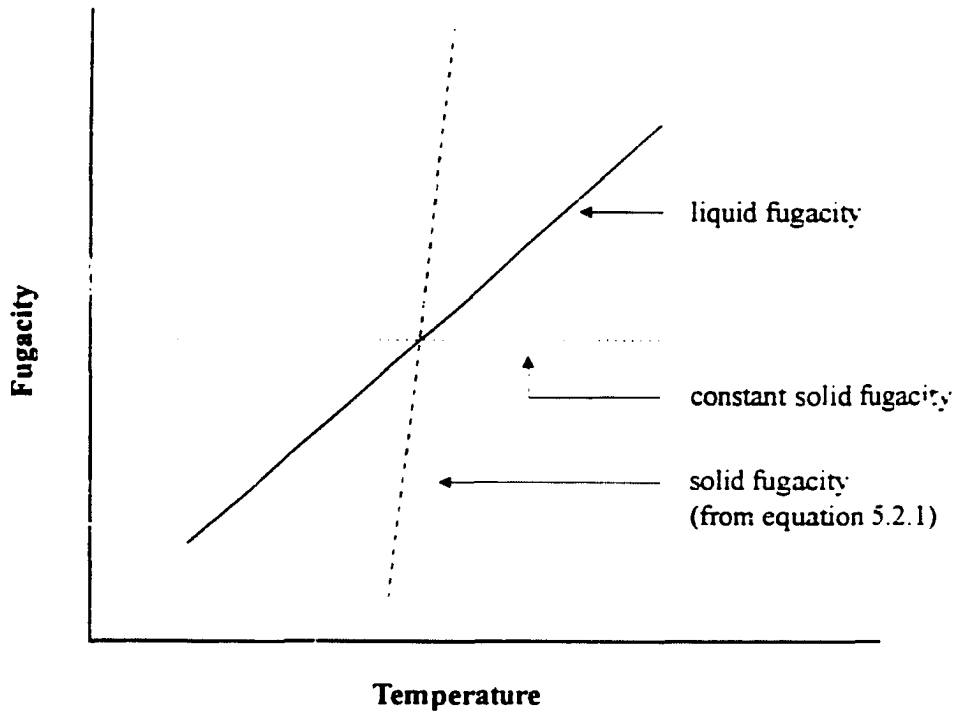

Figure 15. Fugacity as a Function of Temperature for a Pure Solid

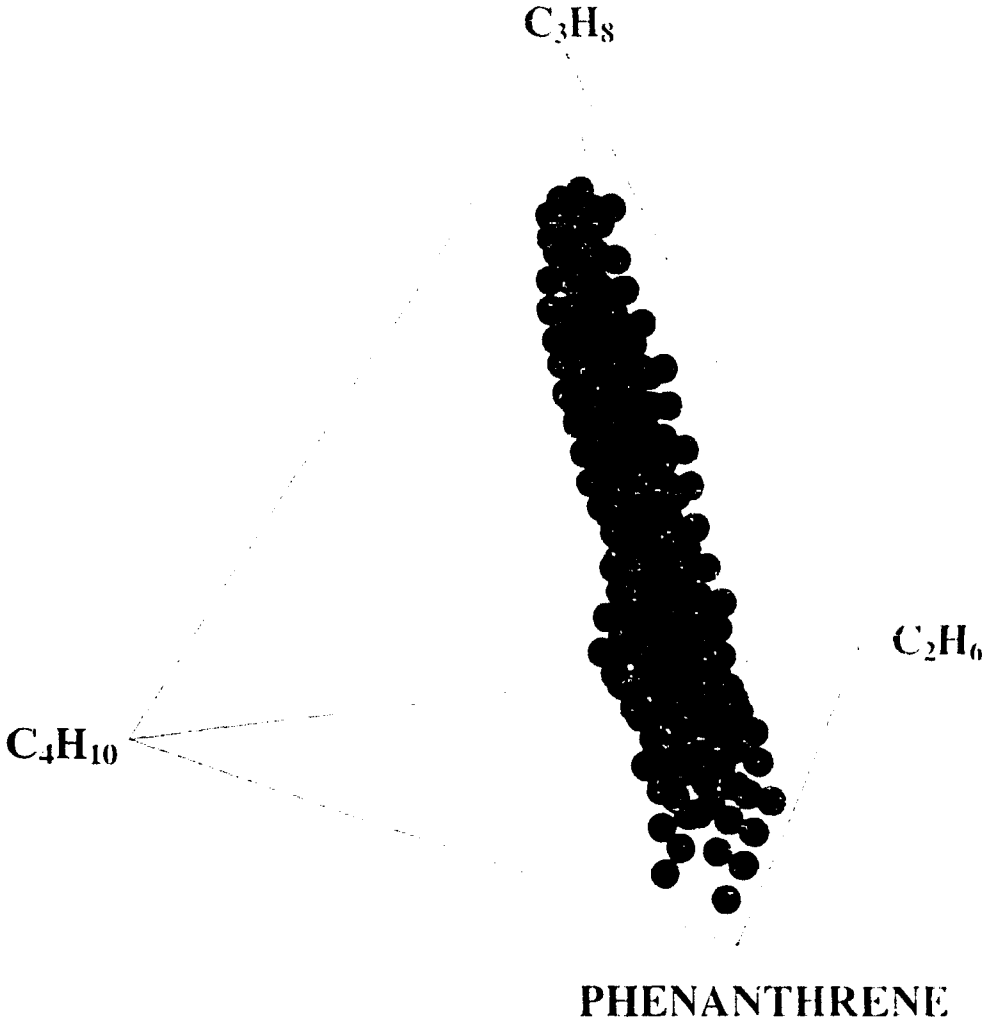

Figure 16. Phase Diagram for the Methane + Propane + n-Butane + Phenanthrene System at P = 5.0 MPa and T = 349.7 showing the solid-liquid-liquid zone

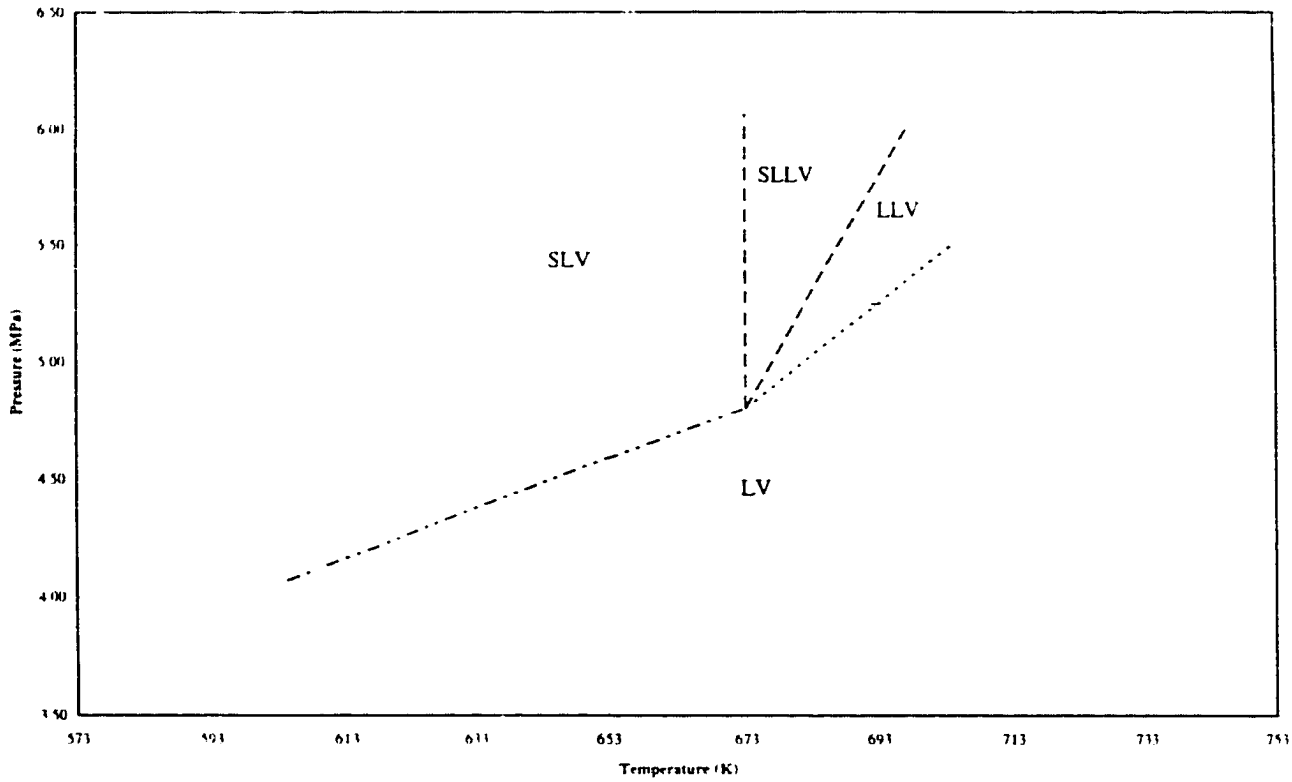

Figure 17. Preliminary Phase Diagram for 26.8 mole.% $AB^{V}B$ + 73.28 mole.% Hydrogen

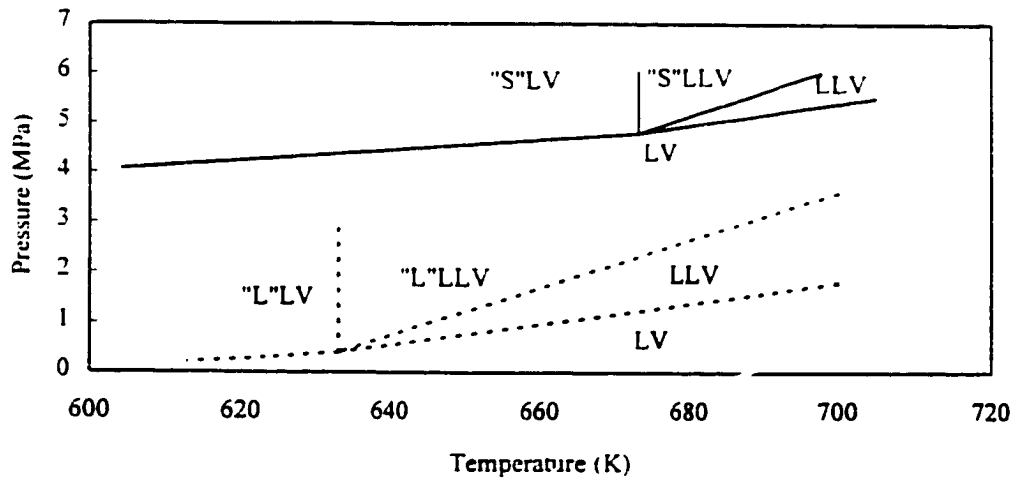

Figure 18. Preliminary (solid lines) and Modelled (dashed lines) Phase Diagram for 26.8 mole.% ABVB + 73.28 mole.% Hydrogen

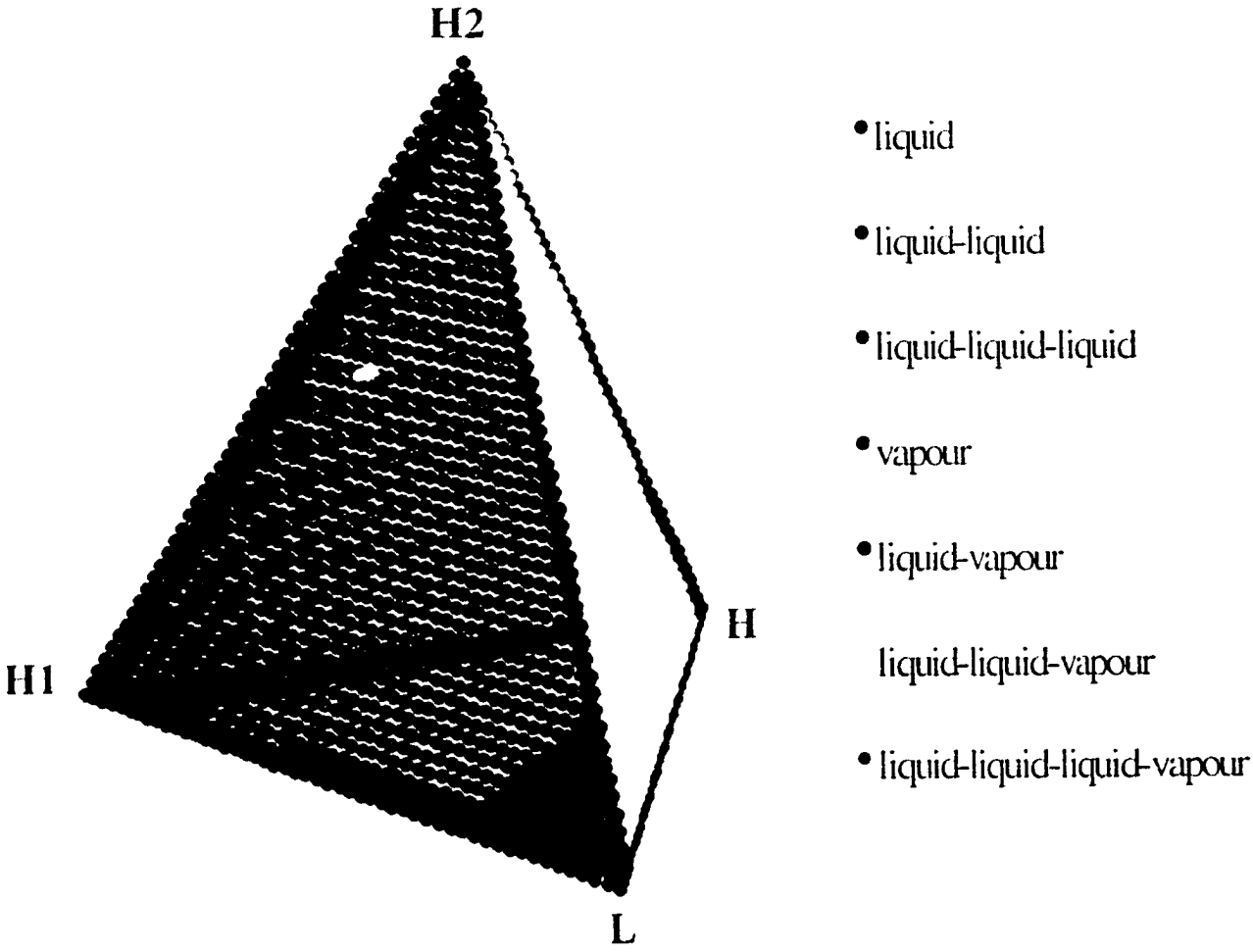

Figure 19. Modelled Phase Diagram for the ABVB + Hydrogen System at P = 3.5 MPa and T = 637.15 K

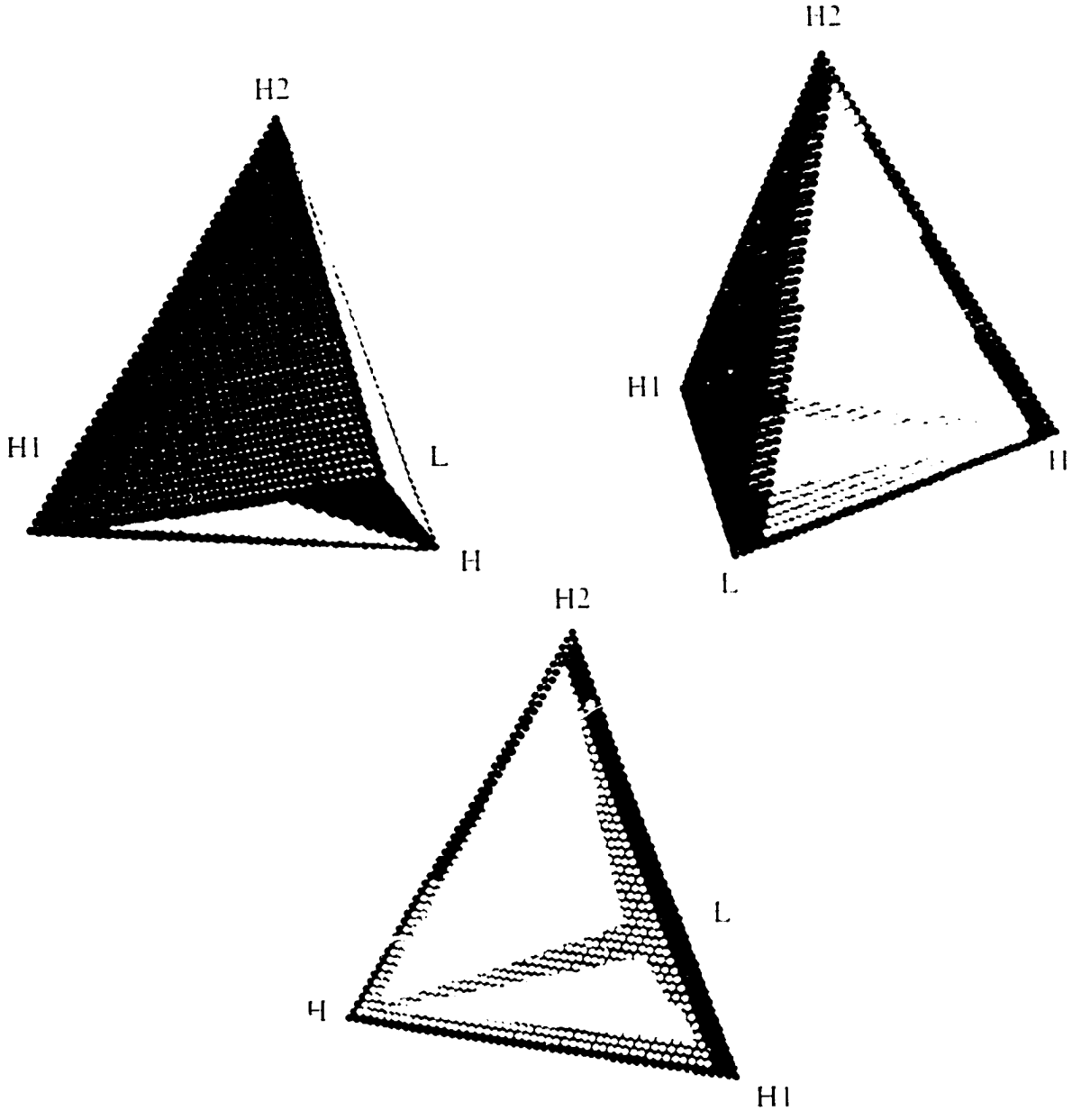

Figure 20. Rotations of the Modelled Phase Diagram for the ABVB + Hydrogen System at P = 3.5 MPa and T = 637.15 K

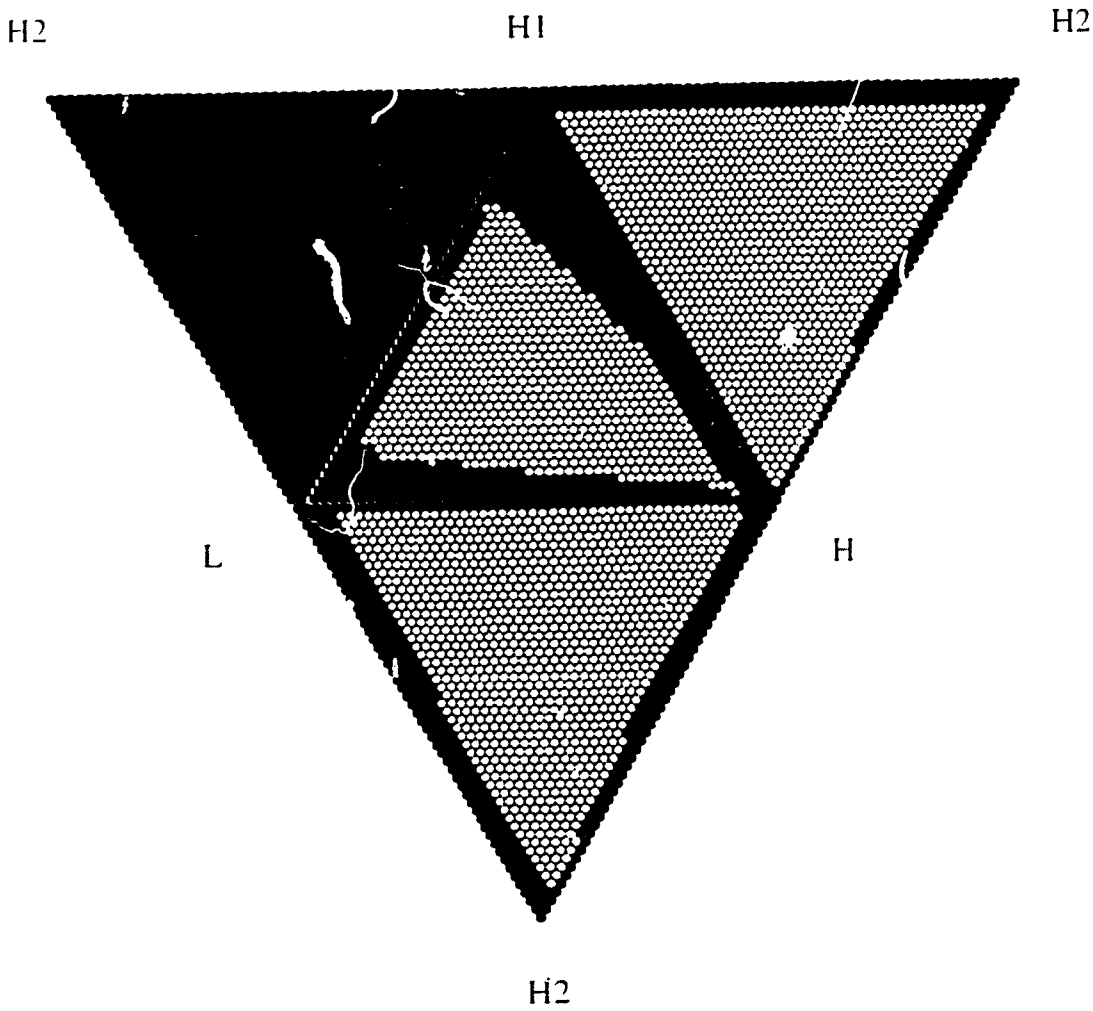

Figure 21. Modelled Fold-out Phase Diagram for the ABVB + Hydrogen System at P = 3.5 MPa and T = 367.15 K

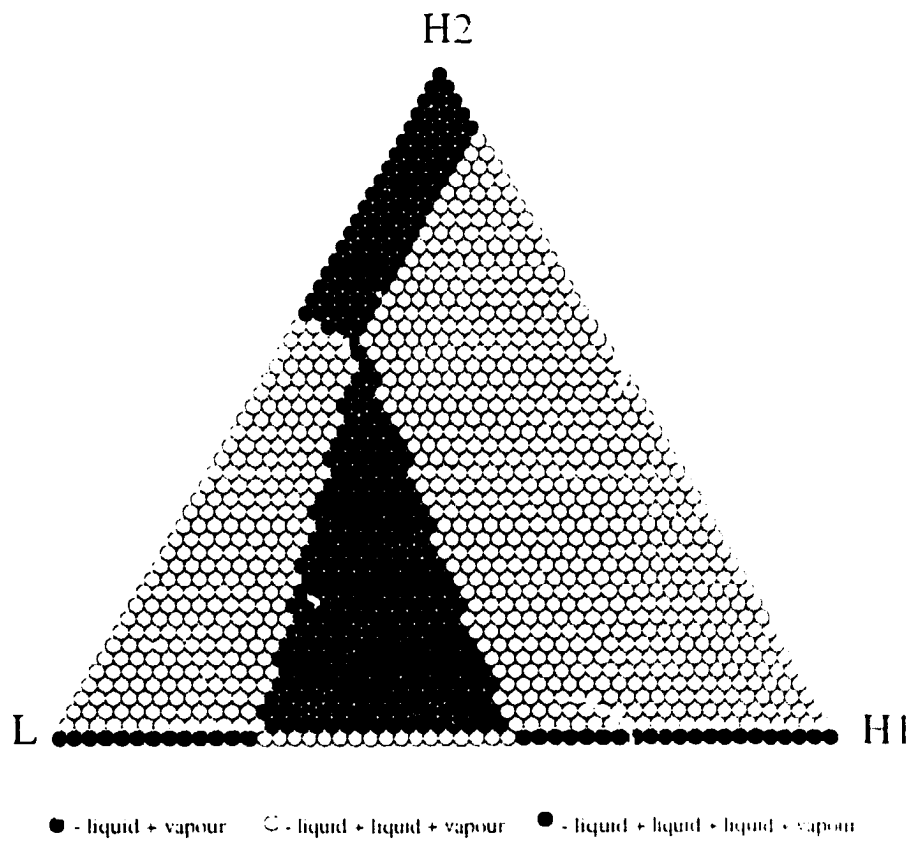

Figure 22. Section at 80 mole.% Hydrogen of the Modelled Phase Diagram for the ABVB + Hydrogen System at P = 3.5 MPa and T = 637.15 K

9.0 *APPENDICES*

Appendix A - Sample input file for the *CMGPROP* program generated by the "*dgendia.ma*" or "*dgensec.ma*" programs.

Filename: "*datadia.in*"

```
*filenames *output *srfout *none *reglumpsplit *none
*UNIT *SI
*NC 4 4
*PVC3 1.2
*COMPNAME  'H2' 'LIGHT' 'HEAVY1' 'HEAVY2'
*PCRIT 1.2830000E+01 1.3900000E+01 1.7288230E+01 1.1059260E+01
*VCRIT 6.4700000E-02 0.5540000E+00 0.9831000E+00 1.6307000E+00
*TCRIT 3.3100000E+01 7.9800000E+02 9.2188000E+02 1.0739300E+03
*AC     0.0000000E-01 0.8440000E+00 0.8130000E+00 1.1534000E+00
*MW     2.0160000E+00 2.9200000E+02 8.6196000E+02 1.5040000E+03
*HCFLAG 0 0 0 0
*KIN
0.07251
0.11253 0.2
0.15277 0.4 0.3

*COMPOSITION
0   100. 0   0

*FLASH
 *TYPE *GENERAL 4
 *PRES 3500
 *TEMP 400

*COMPOSITION
0  98. 2.  0

*FLASH
 *TYPE *GENERAL 4
 *PRES 3500
 *TEMP 400
```

Appendix B - Sample output file from the *CMGPROP* program.

Filename: "*datadia.out*"

```
*************************************************
*                                               *
*           CMGPROP  95.01                      *
*        EOS Phase Property Package             *
*         Keyword Input Version                 *
*            March, 1995                        *
*                                               *
*        (c) Copyright 1977 - 1995              *
*  Computer Modelling Group, Calgary, Canada.   *
*          All Rights Reserved.                 *
*                                               *
*************************************************

 Maximum Dimensions:
   Component            = 50
   SCN Group in + Fractions =  60;  Lab. Calculation points  =  40
   Streams in Process     =  40;      Units in Process       =  20
   Regression variables   =  25;      Regression data points  = 500

*filenames *output *srfout *none *reglumpsplit *none
*UNIT *SI
*NC 4 4
*PVC3 1.2
*COMPNAME  'H2' 'LIGHT' 'HEAVY1' 'HEAVY2'
*PCRIT 1.2830000E+01 1.3900000E+01 1.7288230E+01 1.1059260E+01
*VCRIT 6.4700000E-02 0.5540000E+00 0.9831000E+00 1.6307000E+00
*TCRIT 3.3100000E+01 7.9800000E+02 9.2188000E+02 1.0739300E+03
*AC      0.0000000E-01 0.8440000E+00 0.8130000E+00 1.1534000E+00
*MW      2.0160000E+00 2.9200000E+02 8.6196000E+02 1.5040000E+03
*HCFLAG 0 0 0 0
*BIN
0.07251
0.11253 0.2
0.15277 0.4 0.3
```

```
*COMPOSITION
0   100.0   0

*FLASH
 *TYPE *GENERAL 4
 *PRES 3500
 *TEMP 400

*COMPOSITION
0  98.2.  0

*FLASH
 *TYPE *GENERAL 4
 *PRES 3500
 *TEMP 400
```

.
.
.

```
1
 ***************************************************
 *                                                 *
 *            CMGPROP  95.01                        *
 *             March, 1995                         *
 *  Computer Modelling Group, Calgary, Canada.      *
 *                  1                              *
 ***************************************************
CMGPROP
Multiphase flash calculation
Multi-Phase (Maximum  4) General EOS Flash

Equilibrium Properties at   3500.000  kPa and  400.000 deg C
Peng-Robinson Equations of State

                 mole percent
               ---------------
      component      Feed    Phase01

      H2             0.00000   0.00000
```

LIGHT	100.00000	100.00000
HEAVY1	0.00000	0.00000
HEAVY2	0.00000	0.00000

component	ln (fug, atm)
H2	0.00000E+00
LIGHT	1.03760E+00
HEAVY1	0.00000E+00
HEAVY2	0.00000E+00

	liquid	
Z-factor	0.3162	
Molar vol, m3/kmol	0.50561	0.50561
MW, g/mol	292.000	292.00
Ideal H, cal/mol	74620.279	74620.28
Enthalpy, cal/mol	60896.408	60896.41
Ideal Cp,cal/mol-K	202.147	
Cp, cal/mol-K	228.543	
Density, Kg/m3	577.5171	
Viscosity, cp	0.0264	
Phase volume %	100.0000	
Phase mole %	100.0000	

Enthalpy is zero for ideal gas at absolute zero

Convergence status :

Total iterations in phase stability test	7
Residual sum of squares error	0.00000E+00

1

```
**************************************************
*                                                *
*            CMGPROP 95.01                       *
*             March, 1995                        *
*  Computer Modelling Group, Calgary, Canada.      *
*                2                               *
**************************************************
```

CMGPROP
Multiphase flash calculation
Multi-Phase (Maximum 4) General EOS Flash

Equilibrium Properties at 3500.000 kPa and 400.000 deg C

Peng-Robinson Equations of State

component	mole percent Feed	Phase01
H2	0.00000	0.00000
LIGHT	98.00000	98.00000
HEAVY1	2.00000	2.00000
HEAVY2	0.00000	0.00000

component	ln (fug. atm)
H2	0.00000E+00
LIGHT	1.01818E+00
HEAVY1	-2.32335E+00
HEAVY2	0.00000E+00

	liquid	
Z-factor	0.3161	
Molar vol, m3/kmol	0.50551	0.50551
MW, g/mol	303.399	303.40
Ideal H, cal/mol	76452.182	76452.18
Enthalpy, cal/mol	62793.698	62793.70
Ideal Cp,cal/mol-K	207.688	
Cp, cal/mol-K	233.969	
Density, Kg/m3	600.1814	
Viscosity, cp	0.0275	
Phase volume %	100.0000	
Phase mole %	100.0000	

Enthalpy is zero for ideal gas at absolute zero

Convergence status :

Total iterations in phase stability test	29
Residual sum of squares error	0.00000E+00

.
.
.

Appendix C - Sample output file from the "*extrdia.ma*" or "*extrsec.ma*" programs.

Filename: "*secpts*"

	Line #
0 98. 2. 0	1
0 98. 0 2.	2
0 96. 4. 0	3
0 96. 2. 2.	4
0 96. 0 4.	5
0 94. 6. 0	6
0 94. 4. 2.	7
0 94. 2. 4.	8
0 94. 0 6.	9

.
.
.

liquid		1327
liquid		1328
liquid	liquid	1329
liquid		1330
liquid	liquid	1331
liquid	liquid	1332
liquid		1333
liquid	liquid	1334
liquid	liquid	1335

.
.
.

Appendix D - Sample output files from the "*sortdia.ma*" or "*sortsec.ma*" programs.

Filename: "*lx.tmp*"

0 98. 2. 0
0 98. 0 2.
0 96. 2. 2.
0 94. 4. 2.

.
.
.

Filename: "*llx.tmp*"

0 96. 4. 0
0 96. 0 4.
0 94. 6. 0
0 94. 2. 4.
0 94. 0 6.

.
.
.

Appendix E - Sample output files from the "*cutdia.ma*" or "*cutsec.ma*" programs.

Filename: "*lx.dat*"

0 98. 2.
0 98. 0
0 96. 2.
0 94. 4.

.
.
.

Filename: "*llx.dat*"

0 96. 4.
0 96. 0
0 94. 6.
0 94. 2.
0 94. 0

.
.
.

Appendix F - *dgendia.ma*

```
Off[General::spell1]:
Off[DeleteFile::nffil]:

sec = 0:

a = {
{100,0,0},{98,2,0},{98,0,2},{96,4,0},{96,2,2},{96,0,4},{94,6,0},{94,4,2},{94,2,4},
{94,0,6},{92,8,0},{92,6,2},{92,4,4},{92,2,6},{92,0,8},{90,10,0},{90,8,2},{90,6,4},
{90,4,6},{90,2,8},{90,0,10},{88,12,0},{88,10,2},{88,8,4},{88,6,6},{88,4,8},{88,2,10},
{88,0,12},{86,14,0},{86,12,2},{86,10,4},{86,8,6},{86,6,8},{86,4,10},{86,2,12},{86,0,14},{
84,16,0},{84,14,2},{84,12,4},{84,10,6},{84,8,8},{84,6,10},{84,4,12},{84,2,14},
{84,0,16},{82,18,0},{82,16,2},{82,14,4},{82,12,6},{82,10,8},{82,8,10},{82,6,12},
{82,4,14},{82,2,16},{82,0,18},{80,20,0},{80,18,2},{80,16,4},{80,14,6},{80,12,8},
{80,10,10},{80,8,12},{80,6,14},{80,4,16},{80,2,18},{80,0,20},{78,22,0},{78,20,2},
{78,18,4},{78,16,6},{78,14,8},{78,12,10},{78,10,12},{78,8,14},{78,6,16},{78,4,18},
{78,2,20},{78,0,22},{76,24,0},{76,22,2},{76,20,4},{76,18,6},{76,16,8},{76,14,10},
{76,12,12},{76,10,14},{76,8,16},{76,6,18},{76,4,20},{76,2,22},{76,0,24},{74,26,0},
{74,24,2},{74,22,4},{74,20,6},{74,18,8},{74,16,10},{74,14,12},{74,12,14},{74,10,16},
{74,8,18},{74,6,20},{74,4,22},{74,2,24},{74,0,26},{72,28,0},{72,26,2},{72,24,4},
{72,22,6},{72,20,8},{72,18,10},{72,16,12},{72,14,14},{72,12,16},{72,10,18},{72,8,20},
{72,6,22},{72,4,24},{72,2,26},{72,0,28},{70,30,0},{70,28,2},{70,26,4},{70,24,6},
{70,22,8},{70,20,10},{70,18,12},{70,16,14},{70,14,16},{70,12,18},{70,10,20},{70,8,22},
{70,6,24},{70,4,26},{70,2,28},{70,0,30},{68,32,0},{68,30,2},{68,28,4},{68,26,6},
{68,24,8},{68,22,10},{68,20,12},{68,18,14},{68,16,16},{68,14,18},{68,12,20},{68,10,22},
{68,8,24},{68,6,26},{68,4,28},{68,2,30},{68,0,32},{66,34,0},{66,32,2},{66,30,4},
{66,28,6},{66,26,8},{66,24,10},{66,22,12},{66,20,14},{66,18,16},{66,16,18},{66,14,20},
{66,12,22},{66,10,24},{66,8,26},{66,6,28},{66,4,30},{66,2,32},{66,0,34},{64,36,0},
{64,34,2},{64,32,4},{64,30,6},{64,28,8},{64,26,10},{64,24,12},{64,22,14},{64,20,16},
{64,18,18},{64,16,20},{64,14,22},{64,12,24},{64,10,26},{64,8,28},{64,6,30},{64,4,32},
{64,2,34},{64,0,36},{62,38,0},{62,36,2},{62,34,4},{62,32,6},{62,30,8},{62,28,10},
{62,26,12},{62,24,14},{62,22,16},{62,20,18},{62,18,20},{62,16,22},{62,14,24},
{62,12,26},{62,10,28},{62,8,30},{62,6,32},{62,4,34},{62,2,36},{62,0,38},{60,40,0},
{60,38,2},{60,36,4},{60,34,6},{60,32,8},{60,30,10},{60,28,12},{60,26,14},{60,24,16},
{60,22,18},{60,20,20},{60,18,22},{60,16,24},{60,14,26},{60,12,28},{60,10,30},{60,8,32},
{60,6,34},{60,4,36},{60,2,38},{60,0,40},{58,42,0},{58,40,2},{58,38,4},{58,36,6},
{58,34,8},{58,32,10},{58,30,12},{58,28,14},{58,26,16},{58,24,18},{58,22,20},{58,20,22},
{58,18,24},{58,16,26},{58,14,28},{58,12,30},{58,10,32},{58,8,34},{58,6,36},{58,4,38},
{58,2,40},{58,0,42},{56,44,0},{56,42,2},{56,40,4},{56,38,6},{56,36,8},{56,34,10},
```

{56,32,12},{56,30,14},{56,28,16},{56,26,18},{56,24,20},{56,22,22},{56,20,24},
{56,18,26},{56,16,28},{56,14,30},{56,12,32},{56,10,34},{56,8,36},{56,6,38},{56,4,40},
{56,2,42},{56,0,44},{54,46,0},{54,44,2},{54,42,4},{54,40,6},{54,38,8},{54,36,10},
{54,34,12},{54,32,14},{54,30,16},{54,28,18},{54,26,20},{54,24,22},{54,22,24},
{54,20,26},{54,18,28},{54,16,30},{54,14,32},{54,12,34},{54,10,36},{54,8,38},{54,6,40},
{54,4,42},{54,2,44},{54,0,46},{52,48,0},{52,46,2},{52,44,4},{52,42,6},{52,40,8},
{52,38,10},{52,36,12},{52,34,14},{52,32,16},{52,30,18},{52,28,20},{52,26,22},
{52,24,24},{52,22,26},{52,20,28},{52,18,30},{52,16,32},{52,14,34},{52,12,36},
{52,10,38},{52,8,40},{52,6,42},{52,4,44},{52,2,46},{52,0,48},{50,50,0},{50,48,2},
{50,46,4},{50,44,6},{50,42,8},{50,40,10},{50,38,12},{50,36,14},{50,34,16},{50,32,18},
{50,30,20},{50,28,22},{50,26,24},{50,24,26},{50,22,28},{50,20,30},{50,18,32},
{50,16,34},{50,14,36},{50,12,38},{50,10,40},{50,8,42},{50,6,44},{50,4,46},{50,2,48},
{50,0,50},{48,52,0},{48,50,2},{48,48,4},{48,46,6},{48,44,8},{48,42,10},{48,40,12},
{48,38,14},{48,36,16},{48,34,18},{48,32,20},{48,30,22},{48,28,24},{48,26,26},
{48,24,28},{48,22,30},{48,20,32},{48,18,34},{48,16,36},{48,14,38},{48,12,40},
{48,10,42},{48,8,44},{48,6,46},{48,4,48},{48,2,50},{48,0,52},{46,54,0},{46,52,2},
{46,50,4},{46,48,6},{46,46,8},{46,44,10},{46,42,12},{46,40,14},{46,38,16},
{46,36,18},{46,34,20},{46,32,22},{46,30,24},{46,28,26},{46,26,28},
{46,24,30},{46,22,32},{46,20,34},{46,18,36},{46,16,38},{46,14,40},{46,12,42},
{46,10,44},{46,8,46},{46,6,48},{46,4,50},{46,2,52},{46,0,54},{44,56,0},{44,54,2},
{44,52,4},{44,50,6},{44,48,8},{44,46,10},{44,44,12},{44,42,14},{44,40,16},{44,38,18},
{44,36,20},{44,34,22},{44,32,24},{44,30,26},{44,28,28},{44,26,30},{44,24,32},
{44,22,34},{44,20,36},{44,18,38},{44,16,40},{44,14,42},{44,12,44},{44,10,46},{44,8,48},
{44,6,50},{44,4,52},{44,2,54},{44,0,56},{42,58,0},{42,56,2},{42,54,4},{42,52,6},
{42,50,8},{42,48,10},{42,46,12},{42,44,14},{42,42,16},{42,40,18},{42,38,20},{42,36,22},
{42,34,24},{42,32,26},{42,30,28},{42,28,30},{42,26,32},{42,24,34},{42,22,36},
{42,20,38},{42,18,40},{42,16,42},{42,14,44},{42,12,46},{42,10,48},{42,8,50},{42,6,52},
{42,4,54},{42,2,56},{42,0,58},{40,60,0},{40,58,2},{40,56,4},{40,54,6},{40,52,8},
{40,50,10},{40,48,12},{40,46,14},{40,44,16},{40,42,18},{40,40,20},{40,38,22},
{40,36,24},{40,34,26},{40,32,28},{40,30,30},{40,28,32},{40,26,34},{40,24,36},
{40,22,38},{40,20,40},{40,18,42},{40,16,44},{40,14,46},{40,12,48},{40,10,50},{40,8,52},
{40,6,54},{40,4,56},{40,2,58},{40,0,60},{38,62,0},{38,60,2},{38,58,4},{38,56,6},
{38,54,8},{38,52,10},{38,50,12},{38,48,14},{38,46,16},{38,44,18},{38,42,20},{38,40,22},
{38,38,24},{38,36,26},{38,34,28},{38,32,30},{38,30,32},{38,28,34},{38,26,36},
{38,24,38},{38,22,40},{38,20,42},{38,18,44},{38,16,46},{38,14,48},{38,12,50},
{38,10,52},{38,8,54},{38,6,56},{38,4,58},{38,2,60},{38,0,62},{36,64,0},{36,62,2},
{36,60,4},{36,58,6},{36,56,8},{36,54,10},{36,52,12},{36,50,14},{36,48,16},{36,46,18},
{36,44,20},{36,42,22},{36,40,24},{36,38,26},{36,36,28},{36,34,30},{36,32,32},
{36,30,34},{36,28,36},{36,26,38},{36,24,40},{36,22,42},{36,20,44},{36,18,46},
{36,16,48},{36,14,50},{36,12,52},{36,10,54},{36,8,56},{36,6,58},{36,4,60},{36,2,62},
{36,0,64},{34,66,0},{34,64,2},{34,62,4},{34,60,6},{34,58,8},{34,56,10},{34,54,12},
{34,52,14},{34,50,16},{34,48,18},{34,46,20},{34,44,22},{34,42,24},{34,40,26},

{34,38,28},{34,36,30},{34,34,32},{34,32,34},{34,30,36},{34,28,38},{34,26,40},
{34,24,42},{34,22,44},{34,20,46},{34,18,48},{34,16,50},{34,14,52},{34,12,54},
{34,10,56},{34,8,58},{34,6,60},{34,4,62},{34,2,64},{34,0,66},{32,68,0},{32,66,2},
{32,64,4},{32,62,6},{32,60,8},{32,58,10},{32,56,12},{32,54,14},{32,52,16},{32,50,18},
{32,48,20},{32,46,22},{32,44,24},{32,42,26},{32,40,28},{32,38,30},{32,36,32},
{32,34,34},{32,32,36},{32,30,38},{32,28,40},{32,26,42},{32,24,44},{32,22,46},
{32,20,48},{32,18,50},{32,16,52},{32,14,54},{32,12,56},{32,10,58},{32,8,60},{32,6,62},
{32,4,64},{32,2,66},{32,0,68},{30,70,0},{30,68,2},{30,66,4},{30,64,6},{30,62,8},
{30,60,10},{30,58,12},{30,56,14},{30,54,16},{30,52,18},{30,50,20},{30,48,22},
{30,46,24},{30,44,26},{30,42,28},{30,40,30},{30,38,32},{30,36,34},{30,34,36},
{30,32,38},{30,30,40},{30,28,42},{30,26,44},{30,24,46},{30,22,48},{30,20,50},
{30,18,52},{30,16,54},{30,14,56},{30,12,58},{30,10,60},{30,8,62},{30,6,64},
{30,4,66},{30,2,68},{30,0,70},{28,72,0},{28,70,2},{28,68,4},{28,66,6},{28,64,8},
{28,62,10},{28,60,12},{28,58,14},{28,56,16},{28,54,18},{28,52,20},{28,50,22},
{28,48,24},{28,46,26},{28,44,28},{28,42,30},{28,40,32},{28,38,34},{28,36,36},
{28,34,38},{28,32,40},{28,30,42},{28,28,44},{28,26,46},{28,24,48},{28,22,50},
{28,20,52},{28,18,54},{28,16,56},{28,14,58},{28,12,60},{28,10,62},{28,8,64},{28,6,66},
{28,4,68},{28,2,70},{28,0,72},{26,74,0},{26,72,2},{26,70,4},{26,68,6},{26,66,8},
{26,64,10},{26,62,12},{26,60,14},{26,58,16},{26,56,18},{26,54,20},{26,52,22},
{26,50,24},{26,48,26},{26,46,28},{26,44,30},{26,42,32},{26,40,34},{26,38,36},
{26,36,38},{26,34,40},{26,32,42},{26,30,44},{26,28,46},{26,26,48},{26,24,50},
{26,22,52},{26,20,54},{26,18,56},{26,16,58},{26,14,60},{26,12,62},{26,10,64},{26,8,66},
{26,6,68},{26,4,70},{26,2,72},{26,0,74},{24,76,0},{24,74,2},{24,72,4},{24,70,6},
{24,68,8},{24,66,10},{24,64,12},{24,62,14},{24,60,16},{24,58,18},{24,56,20},{24,54,22},
{24,52,24},{24,50,26},{24,48,28},{24,46,30},{24,44,32},{24,42,34},{24,40,36},
{24,38,38},{24,36,40},{24,34,42},{24,32,44},{24,30,46},{24,28,48},{24,26,50},
{24,24,52},{24,22,54},{24,20,56},{24,18,58},{24,16,60},{24,14,62},{24,12,64},
{24,10,66},{24,8,68},{24,6,70},{24,4,72},{24,2,74},{24,0,76},{22,78,0},{22,76,2},
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makepair2[x_] = {x, 2};
makepair3[x_] = {x, 3};
makepair4[x_] = {x, 4};
b = Insert[a, sec, Map[makepair1,vals]];
c = Insert[a, sec, Map[makepair2,vals]];
d = Insert[a, sec, Map[makepair3,vals]];
e = Insert[a, sec, Map[makepair4,vals]];
f = Join[b, c, d, e];
g = Union[f];

DeleteFile["c:\\datadia.in"];
file = OpenWrite["c:\\datadia.in"];
h = Count[g, {_,_,_,_}];
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                  "*NC 4 4 \n",
                  "*PVC3 1.2 \n",
                  "*COMPNAME \n"
                  " 'H2' 'LIGHT' 'HEAVY1' 'HEAVY2' \n",
              "*PCRIT 1.2830000E+01 1.3900000E+01 1.7288230E+01 1.1059260E+01\n",
              "*VCRIT 6.4700000E-02 0.5540000E+00 0.9831000E+00 1.6307000E+00\n",
              "*TCRIT 3.3100000E+01 7.9800000E+02 9.2188000E+02 1.0739300E+03\n",
              "*AC    0.0000000E-01 0.8440000E+00 0.8130000E+00 1.1534000E+00\n",
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Write[file, OutputForm[N[MatrixForm[g[[i]], TableDirections -> Row], 4]]];
WriteString[file, "\n",
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                    " *TYPE *GENERAL 4\n",
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Close[file];
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Appendix G - *dgensec.ma*

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Off[DeleteFile::nffil];
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{32,64,4},{32,62,6},{32,60,8},{32,58,10},{32,56,12},{32,54,14},{32,52,16},{32,50,18},
{32,48,20},{32,46,22},{32,44,24},{32,42,26},{32,40,28},{32,38,30},{32,36,32},
{32,34,34},{32,32,36},{32,30,38},{32,28,40},{32,26,42},{32,24,44},{32,22,46},
{32,20,48},{32,18,50},{32,16,52},{32,14,54},{32,12,56},{32,10,58},{32,8,60},{32,6,62},
{32,4,64},{32,2,66},{32,0,68},{30,70,0},{30,68,2},{30,66,4},{30,64,6},{30,62,8},
{30,60,10},{30,58,12},{30,56,14},{30,54,16},{30,52,18},{30,50,20},{30,48,22},
{30,46,24},{30,44,26},{30,42,28},{30,40,30},{30,38,32},{30,36,34},{30,34,36},
{30,32,38},{30,30,40},{30,28,42},{30,26,44},{30,24,46},{30,22,48},{30,20,50},
{30,18,52},{30,16,54},{30,14,56},{30,12,58},{30,10,60},{30,8,62},{30,6,64},
{30,4,66},{30,2,68},{30,0,70},{28,72,0},{28,70,2},{28,68,4},{28,66,6},{28,64,8},
{28,62,10},{28,60,12},{28,58,14},{28,56,16},{28,54,18},{28,52,20},{28,50,22},
{28,48,24},{28,46,26},{28,44,28},{28,42,30},{28,40,32},{28,38,34},{28,36,36},
{28,34,38},{28,32,40},{28,30,42},{28,28,44},{28,26,46},{28,24,48},{28,22,50},
{28,20,52},{28,18,54},{28,16,56},{28,14,58},{28,12,60},{28,10,62},{28,8,64},{28,6,66},
{28,4,68},{28,2,70},{28,0,72},{26,74,0},{26,72,2},{26,70,4},{26,68,6},{26,66,8},
{26,64,10},{26,62,12},{26,60,14},{26,58,16},{26,56,18},{26,54,20},{26,52,22},
{26,50,24},{26,48,26},{26,46,28},{26,44,30},{26,42,32},{26,40,34},{26,38,36},
{26,36,38},{26,34,40},{26,32,42},{26,30,44},{26,28,46},{26,26,48},{26,24,50},
{26,22,52},{26,20,54},{26,18,56},{26,16,58},{26,14,60},{26,12,62},{26,10,64},{26,8,66},
{26,6,68},{26,4,70},{26,2,72},{26,0,74},{24,76,0},{24,74,2},{24,72,4},{24,70,6},
{24,68,8},{24,66,10},{24,64,12},{24,62,14},{24,60,16},{24,58,18},{24,56,20},{24,54,22},
{24,52,24},{24,50,26},{24,48,28},{24,46,30},{24,44,32},{24,42,34},{24,40,36},
{24,38,38},{24,36,40},{24,34,42},{24,32,44},{24,30,46},{24,28,48},{24,26,50},
{24,24,52},{24,22,54},{24,20,56},{24,18,58},{24,16,60},{24,14,62},{24,12,64},
{24,10,66},{24,8,68},{24,6,70},{24,4,72},{24,2,74},{24,0,76},{22,78,0},{22,76,2},
{22,74,4},{22,72,6},{22,70,8},{22,68,10},{22,66,12},{22,64,14},{22,62,16},{22,60,18},
{22,58,20},{22,56,22},{22,54,24},{22,52,26},{22,50,28},{22,48,30},{22,46,32},
{22,44,34},{22,42,36},{22,40,38},{22,38,40},{22,36,42},{22,34,44},{22,32,46},
{22,30,48},{22,28,50},{22,26,52},{22,24,54},{22,22,56},{22,20,58},{22,18,60},
{22,16,62},{22,14,64},{22,12,66},{22,10,68},{22,8,70},{22,6,72},{22,4,74},{22,2,76},
{22,0,78},{20,80,0},{20,78,2},{20,76,4},{20,74,6},{20,72,8},{20,70,10},{20,68,12},
{20,66,14},{20,64,16},{20,62,18},{20,60,20},{20,58,22},{20,56,24},{20,54,26},
{20,52,28},{20,50,30},{20,48,32},{20,46,34},{20,44,36},{20,42,38},{20,40,40},
{20,38,42},{20,36,44},{20,34,46},{20,32,48},{20,30,50},{20,28,52},{20,26,54},
{20,24,56},{20,22,58},{20,20,60},{20,18,62},{20,16,64},{20,14,66},{20,12,68},
{20,10,70},{20,8,72},{20,6,74},{20,4,76},{20,2,78},{20,0,80},{18,82,0},{18,80,2},
{18,78,4},{18,76,6},{18,74,8},{18,72,10},{18,70,12},{18,68,14},{18,66,16},{18,64,18},
{18,62,20},{18,60,22},{18,58,24},{18,56,26},{18,54,28},{18,52,30},{18,50,32},
{18,48,34},{18,46,36},{18,44,38},{18,42,40},{18,40,42},{18,38,44},{18,36,46},

{18,34,48},{18,32,50},{18,30,52},{18,28,54},{18,26,56},{18,24,58},{18,22,60},
{18,20,62},{18,18,64},{18,16,66},{18,14,68},{18,12,70},{18,10,72},{18,8,74},{18,6,76},
{18,4,78},{18,2,80},{18,0,82},{16,84,0},{16,82,2},{16,80,4},{16,78,6},{16,76,8},
{16,74,10},{16,72,12},{16,70,14},{16,68,16},{16,66,18},{16,64,20},{16,62,22},
{16,60,24},{16,58,26},{16,56,28},{16,54,30},{16,52,32},{16,50,34},{16,48,36},
{16,46,38},{16,44,40},{16,42,42},{16,40,44},{16,38,46},{16,36,48},{16,34,50},
{16,32,52},{16,30,54},{16,28,56},{16,26,58},{16,24,60},{16,22,62},{16,20,64},
{16,18,66},{16,16,68},{16,14,70},{16,12,72},{16,10,74},{16,8,76},{16,6,78},{16,4,80},
{16,2,82},{16,0,84},{14,86,0},{14,84,2},{14,82,4},{14,80,6},{14,78,8},{14,76,10},
{14,74,12},{14,72,14},{14,70,16},{14,68,18},{14,66,20},{14,64,22},{14,62,24},
{14,60,26},{14,58,28},{14,56,30},{14,54,32},{14,52,34},{14,50,36},{14,48,38},
{14,46,40},{14,44,42},{14,42,44},{14,40,46},{14,38,48},{14,36,50},{14,34,52},
{14,32,54},{14,30,56},{14,28,58},{14,26,60},{14,24,62},{14,22,64},{14,20,66},
{14,18,68},{14,16,70},{14,14,72},{14,12,74},{14,10,76},{14,8,78},{14,6,80},{14,4,82},
{14,2,84},{14,0,86},{12,88,0},{12,86,2},{12,84,4},{12,82,6},{12,80,8},{12,78,10},
{12,76,12},{12,74,14},{12,72,16},{12,70,18},{12,68,20},{12,66,22},{12,64,24},
{12,62,26},{12,60,28},{12,58,30},{12,56,32},{12,54,34},{12,52,36},{12,50,38},
{12,48,40},{12,46,42},{12,44,44},{12,42,46},{12,40,48},{12,38,50},{12,36,52},
{12,34,54},{12,32,56},{12,30,58},{12,28,60},{12,26,62},{12,24,64},{12,22,66},
{12,20,68},{12,18,70},{12,16,72},{12,14,74},{12,12,76},{12,10,78},{12,8,80},{12,6,82},
{12,4,84},12,2,86},{12,0,88},{10,90,0},{10,88,2},{10,86,4},{10,84,6},{10,82,8},
{10,80,10},{10,78,12},{10,76,14},{10,74,16},{10,72,18},{10,70,20},{10,68,22},
{10,66,24},{10,64,26},{10,62,28},{10,60,30},{10,58,32},{10,56,34},{10,54,36},
{10,52,38},{10,50,40},{10,48,42},{10,46,44},{10,44,46},{10,42,48},{10,40,50},
{10,38,52},{10,36,54},{10,34,56},{10,32,58},{10,30,60},{10,28,62},{10,26,64},
{10,24,66},{10,22,68},{10,20,70},{10,18,72},{10,16,74},{10,14,76},{10,12,78},
{10,10,80},{10,8,82},{10,6,84},{10,4,86},{10,2,88},{10,0,90},{8,92,0},{8,90,2},{8,88,4},{
8,86,6},{8,84,8},{8,82,10},{8,80,12},{8,78,14},{8,76,16},{8,74,18},{8,72,20},{8,70,22},{8
,68,24},{8,66,26},{8,64,28},{8,62,30},{8,60,32},{8,58,34},{8,56,36},{8,54,38},
{8,52,40},{8,50,42},{8,48,44},{8,46,46},{8,44,48},{8,42,50},{8,40,52},{8,38,54},
{8,36,56},{8,34,58},{8,32,60},{8,30,62},{8,28,64},{8,26,66},{8,24,68},{8,22,70},
{8,20,72},{8,18,74},{8,16,76},{8,14,78},{8,12,80},{8,10,82},{8,8,84},{8,6,86},{8,4,88},
{8,2,90},{8,0,92},{6,94,0},{6,92,2},{6,90,4},{6,88,6},{6,86,8},{6,84,10},{6,82,12},
{6,80,14},{6,78,16},{6,76,16},{6,74,20},{6,72,22},{6,70,24},{6,68,26},{6,66,28},
{6,64,30},{6,62,32},{6,60,34},{6,58,36},6,56,38},{6,54,40},{6,52,42},{6,50,44},
{6,48,46},{6,46,48},{6,44,50},{6,42,52},{6,40,54},{6,38,56},{6,36,58},{6,34,60},
{6,32,62},{6,30,64},{6,28,66},{6,26,68},{6,24,70},{6,22,72},{6,20,74},{6,18,76},
{6,16,78},{6,14,80},{6,12,82},{6,10,84},{6,8,86},{6,6,88},{6,4,90},{6,2,92},{6,0,94},
{4,96,0},{4,94,2},{4,92,4},{4,90,6},{4,88,8},{4,86,10},{4,84,12},{4,82,14},{4,80,16},
{4,78,18},{4,76,20},{4,74,22},{4,72,24},{4,70,26},{4,68,28},{4,66,30},{4,64,32},
{4,62,34},{4,60,36},{4,58,38},{4,56,40},{4,54,42},{4,52,44},{4,50,46},{4,48,48},
{4,46,50},{4,44,52},{4,42,54},{4,40,56},{4,38,58},{4,36,60},{4,34,62},{4,32,64},

```
{4.30.66},{4.28.68},{4.26.70},{4.24.72},{4.22.74},{4.20.76},{4.18.78},{4.16.80},
{4.14.82},{4.12.84},{4.10.86},{4.8.88},{4.6.90},{4.4.92},{4.2.94},{4.0.96},{2.98.0},
{2.96.2},{2.94.4},{2.92.6},{2.90.8},{2.88.10},{2.86.12},{2.84.14},{2.82.16},{2.80.18},
{2.78.20},{2.76.22},{2.74.24},{2.72.26},{2.70.28},{2.68.30},{2.66.32},{2.64.34},
{2.62.36},{2.60.38},{2.58.40},{2.56.42},{2.54.44},{2.52.46},{2.50.48},{2.48.50},
{2.46.52},{2.44.54},{2.42.56},{2.40.58},{2.38.60},{2.36.62},{2.34.64},{2.32.66},
{2.30.68},{2.28.70},{2.26.72},{2.24.74},{2.22.76},{2.20.78},{2.18.80},{2.16.82},
{2.14.84},{2.12.86},{2.10.88},{2.8.90},{2.6.92},{2.4.94},{2.2.96},{2.0.98},{0.100.0},
{0.98.2},{0.96.4},{0.94.6},{0.92.8},{0.90.10},{0.88.12},{0.86.14},{0.84.16},{0.82.18},
{0.80.20},{0.78.22},{0.76.24},{0.74.26},{0.72.28},{0.70.30},{0.68.32},{0.66.34},
{0.64.36},{0.62.38},{0.60.40},{0.58.42},{0.56.44},{0.54.46},{0.52.48},{0.50.50},
{0.48.52},{0.46.54},{0.44.56},{0.42.58},{0.40.60},{0.38.62},{0.36.64},{0.34.64},
{0.32.68},{0.30.70},{0.28.72},{0.26.74},{0.24.76},{0.22.78},{0.20.80},{0.18.82},
{0.16.84},{0.14.86},{0.12.88},{0.10.90},{0.8.92},{0.6.94},{0.4.96},{0.2.98},{0.0.100}};


mult = ((100-sec)/100);
b = a*mult;
vals = Range[1,Length[b]];
makepair[x_] = {x, compsec};
Map[makepair,vals];
d = Insert[b, sec, Map[makepair,vals]];

DeleteFile["c:\\datasec.in"];
file = OpenWrite["c:\\datasec.in"];
c = Count[d, {_,_,_,_}];
WriteString[file, "*filenames *output *srfout *none *reglumpsplit *none \n",
                  "*UNIT *SI \n",
                  "*NC 4 4 \n",
                  "*PVC3 1.2 \n",
                  "*COMPNAME \n"
                  " 'H2' 'LIGHT' 'HEAVY1' 'HEAVY2' \n",
              "*PCRIT 1.2830000E+01 1.3900000E+01 1.7288230E+01 1.1059260E+01\n",
              "*VCRIT 6.4700000E-02 0.5540000E+00 0.9831000E+00 1.6307000E+00\n",
              "*TCRIT 3.3100000E+01 7.9800000E+02 9.2188000E+02 1.0739300E+03\n",
              "*AC    0.0000000E-01 0.8440000E+00 0.8130000E+00 1.1534000E+00\n",
              "*MW    2.0160000E+00 2.9200000E+02 8.6196000E+02 1.5040000E+03\n",
                  "*HCFLAG 0 0 0 0\n",
                  "*BIN\n",
                  "0.07251\n",
                  "0.11253 0.2\n",
                  "0.15277 0.4 0.3\n",
```

```
                "\n"];

For[f=1,f<=c,f++,
WriteString[file, "*COMPOSITION\n"];
Write[file, OutputForm[N[MatrixForm[d[[f]], TableDirections -> Row], 4]]];
WriteString[file, "\n",
                "*FLASH\n",
                " *TYPE *GENERAL 4\n",
                " *PRES 3500\n",
                " *TEMP 400\n",
                "\n"];
];
Close[file];
```

Appendix H - *extrdia.ma*

```
Off[DeleteFile::nffil];

DeleteFile["diapts"];
mylist = ReadList["c:\\datadia.out", String];

found = Select[mylist, StringMatchQ[#,"*COMPOSITION" <> "*"]& ];
positionsfound = Union[ Flatten[ Map[Position[mylist,#]& , found] ] ];
positionsnew = positionsfound + 1;
values = mylist[[positionsnew]];
found1 = Select[mylist, StringMatchQ[#, "*" <> "liquid" <> "*"] || StringMatchQ[#, "*" <>
                        "vapour" <>        "*"]& ];
positionsfound1 = Union[ Flatten[ Map[Position[mylist,#]& , found1] ] ];
values1 = mylist[[positionsfound1]];

stream = OpenWrite["c:\\diapts "];
OutputStream["c:\\diapts", 6];
Do[ WriteString[stream, values[[i]], "\n"], {i, 1, Length[values]} ];
Close[stream];
stream1 = OpenAppend["c:\\diapts"];
OutputStream["c:\\diapts", 6];
Do[ WriteString[stream1, values1[[i]], "\n"], {i,1,Length[values1]} ];
Close[stream1];
```

Appendix I - *extrsec.ma*

```
Off[DeleteFile::nffil];

DeleteFile["secpts"];
mylist = ReadList["c:\\datasec.out", String];

found = Select[mylist, StringMatchQ[#,"*COMPOSITION" <> "*"]& ];
positionsfound = Union[ Flatten[ Map[Position[mylist,#]& , found] ] ];
positionsnew = positionsfound + 1;
values = mylist[[positionsnew]];
found1 = Select[mylist, StringMatchQ[#, "*" <> "liquid" <> "*"] || StringMatchQ[#, "*" <>
                        "vapour" <>      "*"]& ];
positionsfound1 = Union[ Flatten[ Map[Position[mylist,#]& , found1] ] ];
values1 = mylist[[positionsfound1]];

stream = OpenWrite["c:\\secpts "];
OutputStream["c:\\secpts", 6];
Do[ WriteString[stream, values[[i]], "\n"], {i,1,Length[values]} ];
Close[stream];
stream1 = OpenAppend["c:\\secpts"];
OutputStream["c:\\secpts", 6];
Do[ WriteString[stream1, values1[[i]], "\n"], {i,1,Length[values1]} ];
Close[stream1];
```

Appendix J - *sortdia.ma*

```
Off[DeleteFile::nffil];
Off[General::stream];

l = "liquid";
v = "vapour";

data = ReadList["diapts", String];
found1 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> l <> "*" <> l <> "*" <> v <>
"*"]& ];
positionsfound1 = Union[ Flatten[ Map[Position[data,#]& , found1] ] ];
DeleteFile["c:\\lllvd.tmp"];
positionsnew1 = positionsfound1 - 1326;
values1 = data[[positionsnew1]];
stream1 = OpenWrite["c:\\lllvd.tmp"];
OutputStream["c:\\lllvd.tmp", 6];
Do[ WriteString[stream1, values1[[i]], "\n"], {i,1,Length[values1]} ];
Close[stream1];
found2 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> l <> "*" <> v <> "*"]& ];
positionsfoundtemp1 = Union[ Flatten[ Map[Position[data,#]& , found2] ] ];
positionsfound2 = Complement[positionsfoundtemp1, positionsfound1];
DeleteFile["c:\\llvd.tmp"];
positionsnew2 = positionsfound2 - 1326;
values2 = data[[positionsnew2]];
stream2 = OpenWrite["c:\\llvd.tmp"];
OutputStream["c:\\llvd.tmp", 6];
Do[ WriteString[stream2, values2[[i]], "\n"], {i,1,Length[values2]} ];
Close[stream2];
found3 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> l <> "*" <> l <> "*"]& ];
positionsfoundtemp2 = Union[ Flatten[ Map[Position[data,#]& , found3] ] ];
positionsfound3 = Complement[positionsfoundtemp2, positionsfound1];
DeleteFile["c:\\llld.tmp"];
positionsnew3 = positionsfound3 - 1326;
values3 = data[[positionsnew3]];
stream3 = OpenWrite["c:\\llld.tmp"];
OutputStream["c:\\llld.tmp", 6];
Do[ WriteString[stream3, values3[[i]], "\n"], {i,1,Length[values3]} ];
Close[stream3];
found4 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> v <> "*"]& ];
```

```
positionsfoundtemp3 = Union[ Flatten[ Map[Position[data,#]& , found4] ] ];
positionsfound4 = Complement[positionsfoundtemp3, positionsfoundtemp1];
DeleteFile["c:\\lvd.tmp"];
positionsnew4 = positionsfound4 - 1326;
values4 = data[[positionsnew4]];
stream4 = OpenWrite["c:\\lvd.tmp"];
OutputStream["c:\\lvd.tmp", 6];
Do[ WriteString[stream4, values4[[i]], "\n"], {i,1,Length[values4]} ];
Close[stream4];
found5 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> l <> "*"]& ];
positionsfoundtemp4 = Union[ Flatten[ Map[Position[data,#]&, found5] ] ];
positionsfound5 = Complement[positionsfoundtemp4, positionsfoundtemp1,
positionsfound3];
DeleteFile["c:\\lld.tmp"];
positionsnew5 = positionsfound5 - 1326;
values5 = data[[positionsnew5]];
stream5 = OpenWrite["c:\\lld.tmp"];
OutputStream["c:\\lld.tmp", 6];
Do[ WriteString[stream5, values5[[i]], "\n"], {i,1,Length[values5]} ];
Close[stream5];
found6 = Select[data, StringMatchQ[#, "*" <> v <> "*"]& ];
positionsfoundtemp5 = Union[ Flatten[ Map[Position[data,#]&, found6] ] ];
positionsfound6 = Complement[positionsfoundtemp5, positionsfoundtemp3,
positionsfoundtemp1];
DeleteFile["c:\\vd.tmp"];
positionsnew6 = positionsfound6 - 1326;
values6 = data[[positionsnew6]];
stream6 = OpenWrite["c:\\vd.tmp"];
OutputStream["c:\\vd.tmp", 6];
Do[ WriteString[stream6, values6[[i]], "\n"], {i,1,Length[values6]} ];
Close[stream6];
found7 = Select[data, StringMatchQ[#, "*" <> l <> "*"]& ];
positionsfoundtemp6 = Union[ Flatten[ Map[Position[data,#]&, found7] ] ];
positionsfound7 = Complement[positionsfoundtemp6, positionsfoundtemp4,
positionsfound4];
DeleteFile["c:\\ld.tmp"];
positionsnew7 = positionsfound7 - 1326;
values7 = data[[positionsnew7]];
stream7 = OpenWrite["c:\\ld.tmp"];
OutputStream["c:\\ld.tmp", 6];
Do[ WriteString[stream7, values7[[i]], "\n"], {i,1,Length[values7]} ];
Close[stream7];
```

Appendix K - *sortsec.ma*

```
Off[DeleteFile::nffil];
Off[General::stream];

l = "liquid";
v = "vapour";

data = ReadList["secpts", String];
found1 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> l <> "*" <> l <> "*" <> v <>
"*"]& ];
positionsfound1 = Union[ Flatten[ Map[Position[data,#]& , found1] ] ];
DeleteFile["c:\\lllvx.tmp"];
positionsnew1 = positionsfound1 - 1326;
values1 = data[[positionsnew1]];
stream1 = OpenWrite["c:\\lllvx.tmp"];
OutputStream["c:\\lllvx.tmp", 6];
Do[ WriteString[stream1, values1[[i]], "\n"], {i,1,Length[values1]} ];
Close[stream1];
found2 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> l <> "*" <> v <> "*"]& ];
positionsfoundtemp1 = Union[ Flatten[ Map[Position[data,#]& , found2] ] ];
positionsfound2 = Complement[positionsfoundtemp1, positionsfound1];
DeleteFile["c:\\llvx.tmp"];
positionsnew2 = positionsfound2 - 1326;
values2 = data[[positionsnew2]];
stream2 = OpenWrite["c:\\llvx.tmp"];
OutputStream["c:\\llvx.tmp", 6];
Do[ WriteString[stream2, values2[[i]], "\n"], {i,1,Length[values2]} ];
Close[stream2];
found3 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> l <> "*" <> l <> "*"]& ];
positionsfoundtemp2 = Union[ Flatten[ Map[Position[data,#]& , found3] ] ];
positionsfound3 = Complement[positionsfoundtemp2, positionsfound1];
DeleteFile["c:\\lllx.tmp"];
positionsnew3 = positionsfound3 - 1326;
values3 = data[[positionsnew3]];
stream3 = OpenWrite["c:\\lllx.tmp"];
OutputStream["c:\\lllx.tmp", 6];
Do[ WriteString[stream3, values3[[i]], "\n"], {i,1,Length[values3]} ];
Close[stream3];
found4 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> v <> "*"]& ];
```

```
positionsfoundtemp3 = Union[ Flatten[ Map[Position[data,#]& , found4] ] ];
positionsfound4 = Complement[positionsfoundtemp3, positionsfoundtemp1];
DeleteFile["c:\\lvx.tmp"];
positionsnew4 = positionsfound4 - 1326;
values4 = data[[positionsnew4]];
stream4 = OpenWrite["c:\\lvx.tmp"];
OutputStream["c:\\lvx.tmp", 6];
Do[ WriteString[stream4, values4[[i]], "\n"], {i,1,Length[values4]} ];
Close[stream4];
found5 = Select[data, StringMatchQ[#, "*" <> l <> "*" <> l <> "*"]& ];
positionsfoundtemp4 = Union[ Flatten[ Map[Position[data,#]&, found5] ] ];
positionsfound5 = Complement[positionsfoundtemp4, positionsfoundtemp1,
positionsfound3];
DeleteFile["c:\\llx.tmp"];
positionsnew5 = positionsfound5 - 1326;
values5 = data[[positionsnew5]];
stream5 = OpenWrite["c:\\llx.tmp"];
OutputStream["c:\\llx.tmp", 6];
Do[ WriteString[stream5, values5[[i]], "\n"], {i,1,Length[values5]} ];
Close[stream5];
found6 = Select[data, StringMatchQ[#, "*" <> v <> "*"]& ];
positionsfoundtemp5 = Union[ Flatten[ Map[Position[data,#]&, found6] ] ];
positionsfound6 = Complement[positionsfoundtemp5, positionsfoundtemp3,
positionsfoundtemp1];
DeleteFile["c:\\vx.tmp"];
positionsnew6 = positionsfound6 - 1326;
values6 = data[[positionsnew6]];
stream6 = OpenWrite["c:\\vx.tmp"];
OutputStream["c:\\vx.tmp", 6];
Do[ WriteString[stream6, values6[[i]], "\n"], {i,1,Length[values6]} ];
Close[stream6];
found7 = Select[data, StringMatchQ[#, "*" <> l <> "*"]& ];
positionsfoundtemp6 = Union[ Flatten[ Map[Position[data,#]&, found7] ] ];
positionsfound7 = Complement[positionsfoundtemp6, positionsfoundtemp4,
positionsfound4];
DeleteFile["c:\\lx.tmp"];
positionsnew7 = positionsfound7 - 1326;
values7 = data[[positionsnew7]];
stream7 = OpenWrite["c:\\lx.tmp"];
OutputStream["c:\\lx.tmp", 6];
Do[ WriteString[stream7, values7[[i]], "\n"], {i,1,Length[values7]} ];
Close[stream7];
```

Appendix L - *cutdia.ma*

```
Off[General::spell1];
Off[DeleteFile::nffil];

a1 = ReadList["c:\\vd.tmp", {Number, Number, Number, Number}];
b1 = a1[[ Range[1, Length[a1]], Range[1, 3] ]];
DeleteFile["c:\\vd.dat"];
file1 = OpenWrite["c:\\vd.dat"];
Write[file1, OutputForm[N[MatrixForm[b1], 4]]];
Close[file1];

a2 = ReadList["c:\\ld.tmp", {Number, Number, Number, Number}];
b2 = a2[[ Range[1, Length[a2]], Range[1, 3] ]];
DeleteFile["c:\\ld.dat"];
file2 = OpenWrite["c:\\ld.dat"];
Write[file2, OutputForm[N[MatrixForm[b2], 4]]];
Close[file2];

a3 = ReadList["c:\\lvd.tmp", {Number, Number, Number, Number}];
b3 = a3[[ Range[1, Length[a3]], Range[1, 3] ]];
DeleteFile["c:\\lvd.dat"];
file3 = OpenWrite["c:\\lvd.dat"];
Write[file3, OutputForm[N[MatrixForm[b3], 4]]];
Close[file3];

a4 = ReadList["c:\\lld.tmp", {Number, Number, Number, Number}];
b4 = a4[[ Range[1, Length[a4]], Range[1, 3] ]];
DeleteFile["c:\\lld.dat"];
file4 = OpenWrite["c:\\lld.dat"];
Write[file4, OutputForm[N[MatrixForm[b4], 4]]];
Close[file4];

a5 = ReadList["c:\\llvd.tmp", {Number, Number, Number, Number}];
b5 = a5[[ Range[1, Length[a5]], Range[1, 3] ]];
DeleteFile["c:\\llvd.dat"];
file5 = OpenWrite["c:\\llvd.dat"];
Write[file5, OutputForm[N[MatrixForm[b5], 4]]];
Close[file5];
```

```
a6 = ReadList["c:\\llld.tmp", {Number, Number, Number, Number}];
b6 = a6[[ Range[1, Length[a6]], Range[1, 3] ]];
DeleteFile["c:\\llld.dat"];
file6 = OpenWrite["c:\\llld.dat"];
Write[file6, OutputForm[N[MatrixForm[b6], 4]]];
Close[file6];

a7 = ReadList["c:\\lllvd.tmp", {Number, Number, Number, Number}];
b7 = a7[[ Range[1, Length[a7]], Range[1, 3] ]];
DeleteFile["c:\\lllvd.dat"];
file7 = OpenWrite["c:\\lllvd.dat"];
Write[file7, OutputForm[N[MatrixForm[b7], 4]]];
Close[file7];
```

Appendix M - *cutsec.ma*

```
Off[General::spell1];
Off[DeleteFile::nffil];

a1 = ReadList["c:\\vx.tmp", {Number, Number, Number, Number}];
b1 = a1[[ Range[1, Length[a1]], Range[1, 3] ]];
DeleteFile["c:\\vxdat"];
file1 = OpenWrite["c:\\vx.dat"];
Write[file1, OutputForm[N[MatrixForm[b1], 4]]];
Close[file1];

a2 = ReadList["c:\\lx.tmp", {Number, Number, Number, Number}];
b2 = a2[[ Range[1, Length[a2]], Range[1, 3] ]];
DeleteFile["c:\\lx.dat"];
file2 = OpenWrite["c:\\lx.dat"];
Write[file2, OutputForm[N[MatrixForm[b2], 4]]];
Close[file2];

a3 = ReadList["c:\\lvx.tmp", {Number, Number, Number, Number}];
b3 = a3[[ Range[1, Length[a3]], Range[1, 3] ]];
DeleteFile["c:\\lvx.dat"];
file3 = OpenWrite["c:\\lvx.dat"];
Write[file3, OutputForm[N[MatrixForm[b3], 4]]];
Close[file3];

a4 = ReadList["c:\\llx.tmp", {Number, Number, Number, Number}];
b4 = a4[[ Range[1, Length[a4]], Range[1, 3] ]];
DeleteFile["c:\\llx.dat"];
file4 = OpenWrite["c:\\llx.dat"];
Write[file4, OutputForm[N[MatrixForm[b4], 4]]];
Close[file4];

a5 = ReadList["c:\\llvx.tmp", {Number, Number, Number, Number}];
b5 = a5[[ Range[1, Length[a5]], Range[1, 3] ]];
DeleteFile["c:\\llvx.dat"];
file5 = OpenWrite["c:\\llvx.dat"];
Write[file5, OutputForm[N[MatrixForm[b5], 4]]];
Close[file5];
```

```
a6 = ReadList["c:\\lllx.tmp", {Number, Number, Number, Number}];
b6 = a6[[ Range[1, Length[a6]], Range[1, 3] ]];
DeleteFile["c:\\lllx.dat"];
file6 = OpenWrite["c:\\lllx.dat"];
Write[file6, OutputForm[N[MatrixForm[b6], 4]]];
Close[file6];

a7 = ReadList["c:\\lllvx.tmp", {Number, Number, Number, Number}];
b7 = a7[[ Range[1, Length[a7]], Range[1, 3] ]];
DeleteFile["c:\\lllvx.dat"];
file7 = OpenWrite["c:\\lllvx.dat"];
Write[file7, OutputForm[N[MatrixForm[b7], 4]]];
Close[file7];
```

Appendix N - *diagram.ma*

```
(* This program will produce a 4 Component Phase Diagram *)

Off[General::spell];
Off[General::spell1];
Off[Graphics3D::nlist3];

coora = {};
coorb = {};
coorc = {};
coord = {};
coore = {};
coorf = {};

coor3a = {};
coor3b = {};
coor3c = {};
coor3d = {};
coor3e = {};
coor3f = {};

c1 = 1;
c2 = 2;
c3 = 3;

axy = ReadList["c:\\ ld.dat" ,{Number,Number,Number}];

c = Count[axy,{_,_,_}];
For [f=1,f<=c,f++,

coora = {x,y,z} /. Solve[{
 1*(x-(100-axy[[f,c1]]))+0.5773502692*(y-0)+0.6666666664*(z-0)==0,
 0*(x-50)-1.154700538*(y-(86.60254*axy[[f,c2]]/100))+0.6666666664*(z-0)==0,
-1*(x-axy[[f,c3]])+0.5773502692*(y-0)+0.6666666664*(z-0)==0
 },{x,y,z}];

coor2a = coora[[1]];
coor2a = coor2a /. coor2a[[3]] -> (coor2a[[3]]/100*86.60254*2);
coor3a = Append[coor3a,coor2a];
```

```
];

pointsa = Table [ Point[coor3a[[i]]],{i,f-1}];
(* Print[pointsa]; *)


bxy = ReadList["c:\\lld.dat" ,{Number,Number,Number}];

cc = Count[bxy,{_,_,_}];
For [ff=1,ff<=cc,ff++,

coorb = {xx,yy,zz} /. Solve[{
 1*(xx-(100-bxy[[ff,c1]]))+0.5773502692*(yy-0)+0.6666666664*(zz-0)==0,
 0*(xx-50)-1.154700538*(yy-(86.60254*bxy[[ff,c2]]/100))+0.6666666664*(zz-0)==0,
-1*(xx-bxy[[ff,c3]])+0.5773502692*(yy-0)+0.6666666664*(zz-0)==0
 },{xx,yy,zz}];

coor2b = coorb[[1]];
coor2b = coor2b /. coor2b[[3]] -> (coor2b[[3]]/100*86.60254*2);
coor3b = Append[coor3b,coor2b];
];

pointsb = Table [ Point[coor3b[[i]]],{i,ff-1}];
(* Print[pointsb]; *)


cxy = ReadList["c:\\llld.dat" ,{Number,Number,Number}];

ccc = Count[cxy,{_,_,_}];
For [fff=1,fff<=ccc,fff++,

coorc = {xxx,yyy,zzz} /. Solve[{
 1*(xxx-(100-cxy[[fff,c1]]))+0.5773502692*(yyy-0)+0.6666666664*(zzz-0)==0,
 0*(xxx-50)-1.154700538*(yyy-(86.60254*cxy[[fff,c2]]/100))+0.6666666664*(zzz-0)==0,
-1*(xxx-cxy[[fff,c3]])+0.5773502692*(yyy-0)+0.6666666664*(zzz-0)==0
 },{xxx,yyy,zzz}];

coor2c = coorc[[1]];
coor2c = coor2c /. coor2c[[3]] -> (coor2c[[3]]/100*86.60254*2);
coor3c = Append[coor3c,coor2c];
];
```

```
pointsc = Table [ Point[coor3c[[i]]],{i,fff-1}];
(* Print[pointsc]; *)


dxy = ReadList["c:\\llvd.dat" ,{Number,Number,Number}];

cccc = Count[dxy,{_,_,_}];
For [ffff=1,ffff<=cccc,ffff++,

coord = {xxxx,yyyy,zzzz} /. Solve[{
 1*(xxxx-(100-dxy[[ffff,c1]]))+0.5773502692*(yyyy-0)+0.6666666664*(zzzz-0)==0,
 0*(xxxx-50)-1.154700538*(yyyy-(86.60254*dxy[[ffff,c2]]/100))+0.6666666664*(zzzz-
0)==0,
-1*(xxxx-dxy[[ffff,c3]])+0.5773502692*(yyyy-0)+0.6666666664*(zzzz-0)==0
 },{xxxx,yyyy,zzzz}];

coor2d = coord[[1]];
coor2d = coor2d /. coor2d[[3]] -> (coor2d[[3]]/100*86.60254*2);
coor3d = Append[coor3d,coor2d];
];

pointsd = Table [ Point[coor3d[[i]]],{i,ffff-1}];
(* Print[pointsd]; *)


exy = ReadList["c:\\lvd.dat" ,{Number,Number,Number}];

ccccc = Count[exy,{_,_,_}];
For [fffff=1,fffff<=ccccc,fffff++,

coore = {xxxxx,yyyyy,zzzzz} /. Solve[{
 1*(xxxxx-(100-exy[[fffff,c1]]))+0.5773502692*(yyyyy-0)+0.6666666664*(zzzzz-0)==0,
 0*(xxxxx-50)-1.154700538*(yyyyy-(86.60254*exy[[fffff,c2]]/100))+0.6666666664*(zzzzz-
0)==0,
-1*(xxxxx-exy[[fffff,c3]])+0.5773502692*(yyyyy-0)+0.6666666664*(zzzzz-0)==0
 },{xxxxx,yyyyy,zzzzz}];

coor2e = coore[[1]];
coor2e = coor2e /. coor2e[[3]] -> (coor2e[[3]]/100*86.60254*2);
coor3e = Append[coor3e,coor2e];
];
```

```
pointse = Table [ Point[coor3e[[i]]],{i,fffff-1}];
(* Print[pointse]; *)



fxy = ReadList["c:\\vd.dat" ,{Number,Number,Number}];

cccccc = Count[fxy,{_,_,_}];
For [ffffff=1,ffffff<=cccccc,ffffff++,

coorf = {xxxxxx,yyyyyy,zzzzzz} /. Solve[{
 1*(xxxxxx-(100-fxy[[ffffff,c1]]))+0.5773502692*(yyyyyy-0)+0.6666666664*(zzzzzz-
0)==0,
 0*(xxxxxx-50)-1.154700538*(yyyyyy-
(86.60254*fxy[[ffffff,c2]]/100))+0.6666666664*(zzzzzz-0)==0,
-1*(xxxxxx-fxy[[ffffff,c3]])+0.5773502692*(yyyyyy-0)+0.6666666664*(zzzzzz-0)==0
 },{xxxxxx,yyyyyy,zzzzzz}];

coor2f = coorf[[1]];
coor2f = coor2f /. coor2f[[3]] -> (coor2f[[3]]/100*86.60254*2);
coor3f = Append[coor3f,coor2f];
];

pointsf = Table [ Point[coor3f[[i]]],{i,ffffff-1}];
(* Print[pointsf]; *)

Show[Graphics3D[{RGBColor[0, 0, 0],Thickness[0.002],
                 Line[{{0,0,0},{100,0,0},{50,86.60254,0},
                      {0,0,0},{50,86.60254,0},{50,28.867513,86.60254},
                      {50,28.867513,86.60254},{50,86.60254,0},{100,0,0},
                      {100,0,0},{50,28.867513,86.60254},{0,0,0}}]}],
  Graphics3D[{PointSize[0.0085],Hue[0.35, 0.95, 0.75],pointsa}],
  Graphics3D[{PointSize[0.0085],Hue[0.75, 0.95, 0.75],pointsb}],
  Graphics3D[{PointSize[0.0085],RGBColor[0.05,0.85,1],pointsc}],
  Graphics3D[{PointSize[0.0085],RGBColor[0.99, 0.99, 0],pointsd}],
  Graphics3D[{PointSize[0.0085],Hue[0.65, 0.95, 1],pointse}],
  Graphics3D[{PointSize[0.0085],RGBColor[0,0,0],pointsf}],
  (* Graphics3D[Text["H", {-20, 0, 0}]], *)
  (* Graphics3D[Text["L", {50, 100, 0}]], *)
  (* Graphics3D[Text["H2", {60, 90,101}]], *)
  (* Graphics3D[Text["H1",{108,0,0}]], *)
  (* Graphics3D[{Polygon[coor3]}], *)
```

```
  Boxed->False,Shading->False,AspectRatio->1,PlotRange->All,ViewPoint->{1.107, 3.074,
0.880}
  ];
```

Appendix O - *section.ma*

```
Off[General::spell1];
Off[General::spell];
Off[Graphics3D::nlist3];
Off[Part::partw];
Off[Part::partd];

Compsec = 1;

sec  = 80.0;
sec1 = 100.0-sec;

c1 = 1;
c2 = 2;
c3 = 3;

seccoor  = {};
seccoora = {};
seccoorb = {};
seccoorc = {};
seccoord = {};

seccoor3  = {};
seccoor3a = {};
seccoor3b = {};
seccoor3c = {};
seccoor3d = {};

apts  = {};
bpts  = {};
cpts  = {};
dpts  = {};

If[Compsec == 1, axispts = {{sec,sec1,0.0},{sec,0.0,sec1},{sec,0.0,0.0}}, Continue[]];
If[Compsec == 2, axispts = {{sec1,sec,0.0},{0.0,sec,sec1},{0.0,sec,0.0}}, Continue[]];
If[Compsec == 3, axispts = {{sec1,0.0,sec},{0.0,sec1,sec},{0.0,0.0,sec}}, Continue[]];
If[Compsec == 4, axispts = {{sec1,0.0,0.0},{0.0,sec1,0.0},{0.0,0.0,sec1}}, Continue[]];

c = Count[axispts,{_,_,_}];
```

```
For [f=1,f<=c,f++,
seccoor = {spx,spy,spz} /. Solve[{

1.0*(spx-(100.0-axispts[[f,c1]]))+0.5773502692*(spy-0.0)+0.6666666664*(spz-0.0)==0.0,
0.0*(spx-50.0)-1.154700538*(spy-(86.60254*axispts[[f,c2]]/100.0))+0.6666666664*(spz-
0.0)==0.0,
-1.0*(spx-axispts[[f,c3]])+0.5773502692*(spy-0.0)+0.6666666664*(spz-
0.0)==0.0},{spx,spy,spz}];

seccoor2 = seccoor[[1]];
seccoor2 = seccoor2 /. seccoor2[[3]] -> (seccoor2[[3]]/100.0*86.60254*2.0);
seccoor3 = Append[seccoor3,seccoor2];

];

con1 = seccoor3[[1]];
con2 = seccoor3[[2]];
con3 = seccoor3[[3]];


a = ReadList["c:\\lllvx.dat",{Number,Number,Number}];

cc1 = Count[a,{_,_,_}];
For [ff=1,ff<=cc1,ff++,

seccoora = {spxa,spya,spza} /. Solve[{

1.0*(spxa-(100.0-a[[ff,c1]]))+0.5773502692*(spya-0.0)+0.6666666664*(spza-0.0)==0.0,
0.0*(spxa-50.0)-1.154700538*(spya-(86.60254*a[[ff,c2]]/100.0))+0.6666666664*(spza-
0.0)==0.0,
-1.0*(spxa-a[[ff,c3]])+0.5773502692*(spya-0.0)+0.6666666664*(spza-
0.0)==0.0},{spxa,spya,spza}];

seccoor2a = seccoora[[1]];
seccoor2a = seccoor2a /. seccoor2a[[3]] -> (seccoor2a[[3]]/100.0*86.60254*2.0);
seccoor3a = Append[seccoor3a,seccoor2a];

];


b = ReadList["c:\\lvx.dat",{Number,Number,Number}];
```

```
cc2 = Count[b,{_,_,_}];
For [fff=1,fff<=cc2,fff++,

seccoorb = {spxb,spyb,spzb} /. Solve[{

1.0*(spxb-(100.0-b[[fff,c1]]))+0.5773502692*(spyb-0.0)+0.6666666664*(spzb-0.0)==0.0,
0.0*(spxb-50.0)-1.154700538*(spyb-(86.60254*b[[fff,c2]]/100.0))+0.6666666664*(spzb-
0.0)==0.0,
-1.0*(spxb-b[[fff,c3]])+0.5773502692*(spyb-0.0)+0.6666666664*(spzb-
0.0)==0.0},{spxb,spyb,spzb}];

seccoor2b = seccoorb[[1]];
seccoor2b = seccoor2b /. seccoor2b[[3]] -> (seccoor2b[[3]]/100.0*86.60254*2.0);
seccoor3b = Append[seccoor3b,seccoor2b];

];

c = ReadList["c:\\vx.dat",{Number,Number,Number}];

cc3 = Count[c,{_,_,_}];
For [ffff=1,ffff<=cc3,ffff++,

seccoorc = {spxc,spyc,spzc} /. Solve[{

1.0*(spxc-(100.0-c[[ffff,c1]]))+0.5773502692*(spyc-0.0)+0.6666666664*(spzc-0.0)==0.0,
0.0*(spxc-50.0)-1.154700538*(spyc-(86.60254*c[[ffff,c2]]/100.0))+0.6666666664*(spzc-
0.0)==0.0,
-1.0*(spxc-c[[ffff,c3]])+0.5773502692*(spyc-0.0)+0.6666666664*(spzc-
0.0)==0.0},{spxc,spyc,spzc}];

seccoor2c = seccoorc[[1]];
seccoor2c = seccoor2c /. seccoor2c[[3]] -> (seccoor2c[[3]]/100.0*86.60254*2.0);
seccoor3c = Append[seccoor3c,seccoor2c];

];

d = ReadList["c:\\lx.dat",{Number,Number,Number}];

cc4 = Count[d,{_,_,_}];
For [fffff=1,fffff<=cc4,fffff++,

seccoord = {spxd,spyd,spzd} /. Solve[{
```

```
1.0*(spxd-(100.0-d[[fffff,c1]]))+0.5773502692*(spyd-0.0)+0.6666666664*(spzd-0.0)==0.0,
0.0*(spxd-50.0)-1.154700538*(spyd-(86.60254*d[[fffff,c2]]/100.0))+0.6666666664*(spzd-
0.0)==0.0,
-1.0*(spxd-d[[fffff,c3]])+0.5773502692*(spyd-0.0)+0.6666666664*(spzd-
0.0)==0.0},{spxd,spyd,spzd}];

seccoor2d = seccoord[[1]];
seccoor2d = seccoor2d /. seccoor2d[[3]] -> (seccoor2d[[3]]/100.0*86.60254*2.0);
seccoor3d = Append[seccoor3d,seccoor2d];

];


ccc = Count[seccoor3a,{_,_,_}];
For[fff=1,fff<=ccc,fff++,
apts = Table [ Point[seccoor3a[[i]]],{i,fff}];
];

cccc = Count[seccoor3b,{_,_,_}];
For[ffff=1,ffff<=cccc,ffff++,
bpts = Table [ Point[seccoor3b[[i]]],{i,ffff}];
];

ccccc = Count[seccoor3c,{_,_,_}];
For[fffff=1,fffff<=ccccc,fffff++,
cpts = Table [ Point[seccoor3c[[i]]],{i,fffff}];
];

cccccc = Count[seccoor3d,{_,_,_}];
For[ffffff=1,ffffff<=cccccc,ffffff++,
dpts = Table [ Point[seccoor3d[[i]]],{i,ffffff}];
];



If[Compsec == 1,

Show[Graphics3D[{RGBColor[0,0,0],Thickness[0.003],Line[{con1,con2,con3,con1}]}],
   Graphics3D[{PointSize[0.01],RGBColor[0.88,0.1,0.5],apts}],
   Graphics3D[{PointSize[0.01],RGBColor[0.16,0.56,1.0],bpts}],
   Graphics3D[{PointSize[0.01],RGBColor[0.1,0.6,0],cpts}],
```

```
   Graphics3D[{PointSize[0.01],RGBColor[0.8,0.2,0],dpts}],
   Graphics3D[Text["C1",{10,19,0.5},{1,0}]],
   Graphics3D[Text["C3",{24,0.5,1.0},{-1,0}]],
   Graphics3D[Text["C10",{10,5.75,19}]],
   PlotRange->All,AspectRatio->1, Boxed->False,Shading->False,ViewPoint->{-5.0,-3.0,-
1.5}];,

Continue[]];

If[Compsec == 2,

Show[Graphics3D[{RGBColor[0,0,0],Thickness[0.003],Line[{con1,con2,con3,con1}]}],
   Graphics3D[{PointSize[0.02],GrayLevel[0.3],apts}],
   Graphics3D[{PointSize[0.02],GrayLevel[0.5],bpts}],
   Graphics3D[{PointSize[0.02],RGBColor[0.1,0.6,0],cpts}],
   Graphics3D[{PointSize[0.02],RGBColor[0,0,0],dpts}],
   Graphics3D[Text["",{10,19,0.5},{1,0}]],
   Graphics3D[Text["",{24,0.5,1.0},{-1,0}]],
   Graphics3D[Text["",{10,5.75,19}]],

   PlotRange->All,AspectRatio->1,Boxed->False,Shading->False,ViewPoint->{0.0,-6.0,-
1.0}];,

Continue[]];

If[Compsec == 3,

Show[Graphics3D[{RGBColor[0,0,0],Thickness[0.003],Line[{con1,con2,con3,con1}]}],
   Graphics3D[{PointSize[0.02],RGBColor[0.88,0.1,0.5],apts}],
   Graphics3D[{PointSize[0.02],RGBColor[0.16,0.56,1.0],bpts}],
   Graphics3D[{PointSize[0.02],RGBColor[0.1,0.6,0],cpts}],
   Graphics3D[{PointSize[0.02],RGBColor[0,0,0],dpts}],
   Graphics3D[Text["Comp1",{10,19,0.5} ,{1,0}]],
   Graphics3D[Text["Comp2",{24,0.5,1.0} ,{-1,0}]],
   Graphics3D[Text["Comp4",{10,5.75,19}]],
   PlotRange->All,Boxed->False,Shading->False,AspectRatio->1,ViewPoint->{5.0,-3.0,-
1.5}];,

Continue[]];

Show[Graphics3D[{RGBColor[0,0,0],Thickness[0.003],Line[{con1,con2,con3,con1}]}],
   Graphics3D[{PointSize[0.02],RGBColor[0.88,0.1,0.5],apts}],
```

```
    Graphics3D[{PointSize[0.02],RGBColor[0.16,0.56,1],bpts}],
    Graphics3D[{PointSize[0.02],RGBColor[0.1,0.6,0],cpts}],
    Graphics3D[{PointSize[0.02],RGBColor[0,0,0],dpts}],
    Graphics3D[Text["Comp1", {10,19,0.5},{1,0}]],
    Graphics3D[Text["Comp2",{24,0.5,1.0}]],
    Graphics3D[Text["Comp3",{10,5.75,19} ,{-1,0}]],
    PlotRange->All,Boxed->False,Shading->False,AspectRatio->1,ViewPoint->{0.0,-
3.0,1.5}];,

Continue[]];
```

END

19-04-96

FIN