PHASE BEHAVIOR OF SYSTEMS CONTAINING NITROGEN, METHANE, ETHANE, AND PROPANE

BY

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ABSTRACT

The phase behavior for mixtures containing nitrogen, methane, ethane, and propane, essential for the design of equipment for the storage and processing of natural petroleum fluids and natural gas, has been studied in this investigation.

The vapor-liquid equilibria of binary and ternary mixtures at 114.05, 118.32 and 122.24 K, together with the conditions of partial miscibility in the liquid phase, have been experimentally determined. Liquid phase inversions have been experimentally investigated for the binary and ternary mixtures containing nitrogen, methane, and ethane; and the densities of these components have been found to be a main factor of the occurrence of the phenomenon.

In addition to the direct usefulness in the industry, these data also serve as a means to develope correlation and prediction methods, from which information can be obtained in areas where experimental data are not available.

It has been found, in this investigation, that the Redlich-Kwong equation of state, when its parameters Ω_a and Ω_b are considered as a function of temperature at both the subcritical and supercritical conditions, is capable of predicting vapor-liquid equilibrium within 2% for binary systems, within 4% for ternary systems, and within 1% for liquid-liquid equilibrium data.

Attempts have been made to predict critical temperatures, critical pressures and critical volumes of binary mixtures containing nitrogen, methane, ethane, and propane. Equations of state by Clausius, Wohl, and Redlich-Kwong have been used. It has been found that the modified Redlich-Kwong equation is capable of yielding improved results over those from existing methods. In the case of the system

methane-propane, for which a complete set of experimental data is available for comparison, the predicted results are within 0.5% for critical temperatures, within 0.7% for critical pressures, and within 2.3% for critical volumes.

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NOMENCLATURE

NOTATION

A, B, a, b	=	adjustable parameters or constants
C	=	number of components in phase rule
d	=	deviation
f	=	fugacity
F	=	degree of freedom
g, G	=	Gibbs' free energy
h, H	=	enthalpy
H	=	Henry's Constant
J	=	pure number
K	=	y/x, equilibrium constant, or degree Kelvin, for temperature
k	=	pure number, or interaction parameter
n	=	number of components
N	=	number of moles
p	=	number of phases
P	=	pressure
r	=	molecular size ratio
R	=	universal gas constant
S	=	entropy
T	=	temperature
v	=	molal volume

V	=	total volume or molal volume
w	=	weight
x	=	mole fraction in liquid phase
y	=	mole fraction in vapor phase
z	=	mole fraction either in vapor phase or in liquid phase
Z	=	compressbility factor

GREEK LETTERS

α	=	relative volatility
β	=	second virial coefficient
γ	=	activity coefficient
δ	=	solubility parameter
Δ	=	difference or property change on mixing
ε	=	electromotive force, e. m. f.
θ	=	volume fraction
μ	=	chemical potential
φ	=	fugacity coefficient
ω	=	acentric factor

SUPERSCRIPTS

ath	=	athermal
E	=	excess property
*	=	perfect gas state or asymmetric convention for activity coefficient

id	=	ideal behavior
M	=	mixing
°	=	reference state
s	=	saturated property
vap	=	vaporization
‾	=	partial molar quantities
∞	=	infinite dilution
^	=	property in a mixture
v	=	vapor phase

SUBSCRIPTS

a, b	=	experimental point identification
A, B	=	component identification
c	=	critical property
cal	=	calculated
cv	=	convergency
i, ii, ij or 1, 2	=	component identification
L	=	liquid phase
obs	=	observed
pc	=	pseudocritical property
r	=	reduced property
v	=	vapor phase

CHAPTER 1

INTRODUCTION

In the steadily growing petrochemical industry, efforts have been spent in collecting experimental data so that they can be used in the industry. Also, correlation and prediction methods have been developed so that necessary information can be obtained with the minimum amount of actual data. In this study, the mixtures of some of the major constituents of natural gas and natural petroleum fluid, namely, nitrogen, methane, ethane and propane were chosen as the systems for investigation. The molecular structures of these compounds are relatively simple so that predictive relationship may reveal its effects easier. They are major constituents of many kinds of fuel and chemicals and the properties of their mixture are useful in the design of equipment for storage and separation. In the literature, data are available for the systems nitrogen-methane [3],[4],[5], nitrogen-ethane [6], nitrogen-n-butane [7],[8], nitrogen-methane-ethane [9], nitrogen-methane-n-butane [10], and nitrogen-ethane-n-butane [8]. But the phase behavior concerning mixtures containing nitrogen and propane has been reported only partially for nitrogen-propane by Schindler, Swift and Kurata [13] in 1966; and no work has been done for the ternary system nitrogen-methane-propane. Therefore in this research attention has been directed to experimental investigation of these systems at cryogenic temperatures. To carry out the study, an experimental scheme was designed to investigate experimentally the three binary mixtures and the ternary mixtures containing nitrogen, methane and propane at three isothermal conditions. A complete set of experimental data of this kind enables one to test many correlation and prediction methods, and hopefully one method may be obtained so that minimum data are needed to establish the necessary information for the industry.

The phase behavior of these systems was found to be rather complicated. Liquid phase inversion and partial miscibility occur in addition to vapor-liquid equilibrium behavior. When two liquid phases were in equilibrium with the vapor phase, the equilibrium conditions were more sensitive to temperature control and to pressure differences, and the sampling procedure became more difficult. Experimental data were collected successfully even under those conditions. These data served as a test of the applicability of the Redlich-Kwong equation of state in a modified procedure, [77],[78] for predicting phase behavior.

The modified Redlich-Kwong equation of state was further applied in predicting critical loci of binary mixtures, which is important in the industry, and the experimental measurement of which has been difficult. It is hoped that by the application of an equation of state, such as the Redlich-Kwong equation, the Wohl equation, or the Clausius equation, the critical properties, Pc, Vc and Tc can be predicted.

CHAPTER 2

LITERATURE SURVEY

The study of phase behavior has been greatly advanced in recent years. Experimentally, equipment has been improved continuously, and high precision of measurements has been attained. Theoretically, due to the application of electronic computers,many of the complicated calculations can be accomplished.

Among many results of the research work, a short survey was made and discussions were made, only to those which are concerned with this work.

2.1 EXPERIMENTAL METHODS

STATIC AND TOTAL PRESSURE METHODS

In the static and total pressure methods, a liquid mixture is allowed to come to equilibrium with its vapor inside the equilibrium cell at isothermal conditions. The conditions of temperature and pressure are recorded. In a static method [14], samples of liquid and vapor at equilibrium are withdrawn and analyzed.
In the total pressure method, the vapor phase compositions are calculated directly from thermodynamic relationships based on the liquid composition and total pressure data [15], [16]. Agitation can be achieved by means by a magnetic stirrer or by the motion of rotating, rocking or shaking of the equilibrium cell.

In these two methods, it is possible to attain very close to true equilibrium. However, in the process of sampling in the case of static method, the equilibrium can be greatly disturbed due to the withdrawal of material which causes a pressure drop. Especially

at low pressures, the amount of vapor required for analysis becomes comparable to the total amount of vapor inside the equilibrium cell, and hence the removal of a sample will cause sharp disturbance.

DEW-POINT AND BUBBLE-POINT METHOD

In this method, a gas mixture of known composition is introduced into an equilibrium cell in measured increments, under isothermal conditions. The equilibrium cell may be transparent or opaque, and stirring device inside the cell is equipped to ensure well mixing. As more increments of mixture at constant composition are introduced, the mixture inside the cell comes to the dew point, and then goes through the two-phase region and reaches the bubble point. The conditions of dew-point and bubble-point are determined by direct observation or by some sensing device. This procedure is repeated at several temperatures for each constant composition mixture to determine the dew-point and bubble-point loop. The vapor-liquid equilibrium conditions are then determined through the intersection of the dew-point curve of one composition with the bubble-point curve of the other composition.

This method has been developed for many years and has been frequently employed. Sage and Lacey [17] improved this apparatus and used it for measuring equilibrium data of light hydrocarbons in the range of 20°C to 100°C. This apparatus was also adopted by the IGT* group for the study of vapor-liquid equilibrium [3],[6] at cryogenic conditions for the systems nitrogen-methane, nitrogen-ethane and methane-ethane.

The technique of sampling is avoided with this apparatus since the composition of the mixtures are pre-determined. However, the technique for the determinations of the dew-points and the bubble-points is difficult because to detect accurately the first minute drop

* Institute of Gas Technology

of liquid formed and the disappearance of the last small gas bubble is not easy at all. Moreover, this method cannot be used to study multicomponent systems.

DISTILLATION TOWER METHOD

In this method, the principle of a simple distillation is adopted. A distillating tower can be built for large scale operation, and modification of the tower or taking the tray efficiency into account can be used to improve quality of data. This method is poor in the sense of accuracy. Based on the acetone-water system by Chu et al. [28], and the study of argon-oxygen system by Wang [29], who construct a still with several sieve plates, the general reproducibility of data was $\pm$ 3%, prior to any correction. However, in the sense of practical application, this method provides an apparatus for quick investigations, and can be used to speed up the accumulation of data.

FLOW METHOD

In this method, a stream of gas mixture at constant flow rate is passed through a cooler, upon which partial liquefaction takes place. Continuous removal of the vapor phase in equilibrium with the liquid phase upon condensation is monitored. The removed vapor and liquid are stored and analyzed for composition.

Steckel [30] employed this method for the study of carbon monoxide-nitrogen system. Ruhemann and co-workers also adopted this method for the investigation of the systems methane-ethane [31], and methane-ethylene [32]. This method was also adopted by Stutzman and Brown [33] to study systems containing natural gas components.

The temperature and pressure inside the cell is difficult to control since rapid condensation takes place. Also, near the

critical region, the separation between the vapor phase and the liquid phase becomes very difficult. However, large vapor and liquid can be separated easily with only a small experimental assembly, and equilibrium can be approached rapidly due to the intimate contact between the liquid phase and vapor phase.

FORCED-RECIRCULATION METHOD

If the vapor phase is continuously brought back and bubbles through the liquid phase by recirculation, the vapor-liquid contact will be continuous and hence equilibrium could be achieved fast. On the other hand, the bubbling of the vapor phase supplies more than enough stirring and an additional agitator system could be omitted. This is the general idea of the force-recirculation method.

This method was first developed by Inglis [18] and was later modified and brought into practical application by Dodge and Dunber[19], who used a mercury pump to recirculate the vapor phase distilled from the liquid. Later. Torocheshuikov [20] adopted this apparatus to study the system carbon monoxide-nitrogen; and Arogan and Katz [21] for the system methane-hydrogen. Further application of this method was made by Dovis, Rodewald and Kurata [22], Harvey [23], Price and Kobayashi [24]. The use of a transparent equilibrium cell and the use of bath fluid in the cryostat were adopted by these researchers for the studies of systems containing methane, ethane and propane. This apparatus is probably the most accurate and reliable one among the existing methods, and it has been widely adopted [25] [26] [27].

In this investigation, this method was adopted, using a magnetic pump to recirculate the vapor phase. A detailed discussion will be given in the next chapter and also by Chang [11], who was the first person using the apparatus in this department.

2.2 METHODS OF CORRELATION

Researchers have developed many methods to correlate experimental data of mixtures related to phase equilibria. The idea of using correlation methods is to organize the available data and put them into some generalized analytical expressions or generalized charts so that one can put them into practical applications. Also methods of data reduction and consistency test are important for processing experimental data. Among the many, the following will list a few methods, which are of interest in this work.

2.2.1 CONVERGENCE PRESSURE METHOD

Katz [34] first observed that for mixtures of light hydrocarbons, isothermal component K-values appeared to converge to unity when plotted against pressure. This occurs in binary systems as well as in complex systems, as shown in Figure 2.2.1a. The pressure at which the K-values converge to unity is the convergence pressure for an isothermal plot of log K vs log P. It is found to be a function of composition. Therefore, the convergence pressure is considered as a parameter to represent the effect of composition at higher pressures when the ideal solution approximation is not valid. As shown in Figure (2.2.1a) the dotted lines represent the behavior according to Raoult's law. The solid lines represent the typical behavior of hydrocarbons at which the K-values approaches unity when the pressure approaches P_c.

The Natural Gas Producers'Supplier Association (NGPSA) of Tulsa, Oklahoma published a set of charts for twelve hydrocarbons plus nitrogen in its 1966 Engineering Data Book. The K-values are presented as a function of temperature, pressure and convergence pressure.

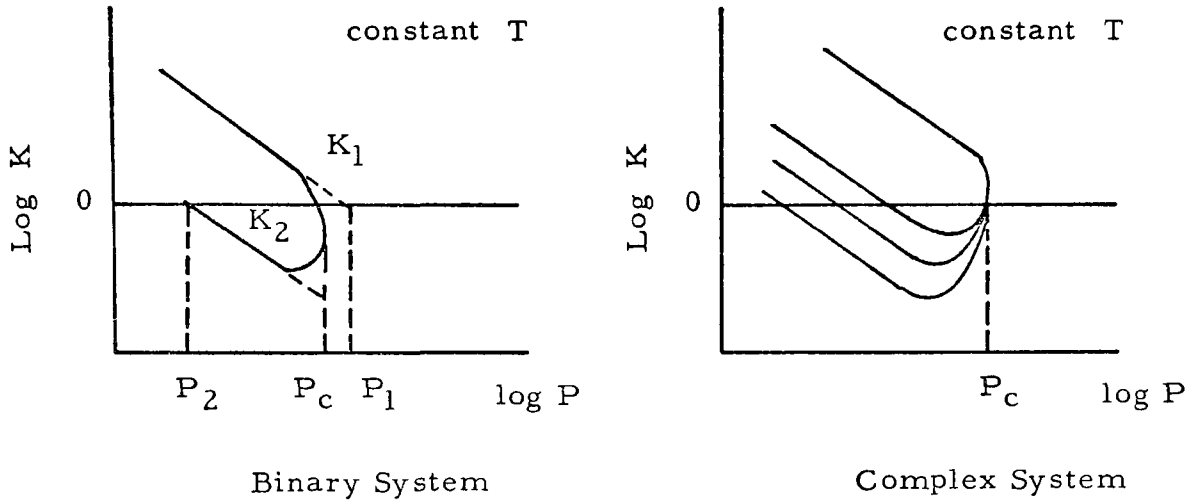


Figure 2.2.1 (a) A Log-Log Plot of Equilibrium Constant against Pressure.

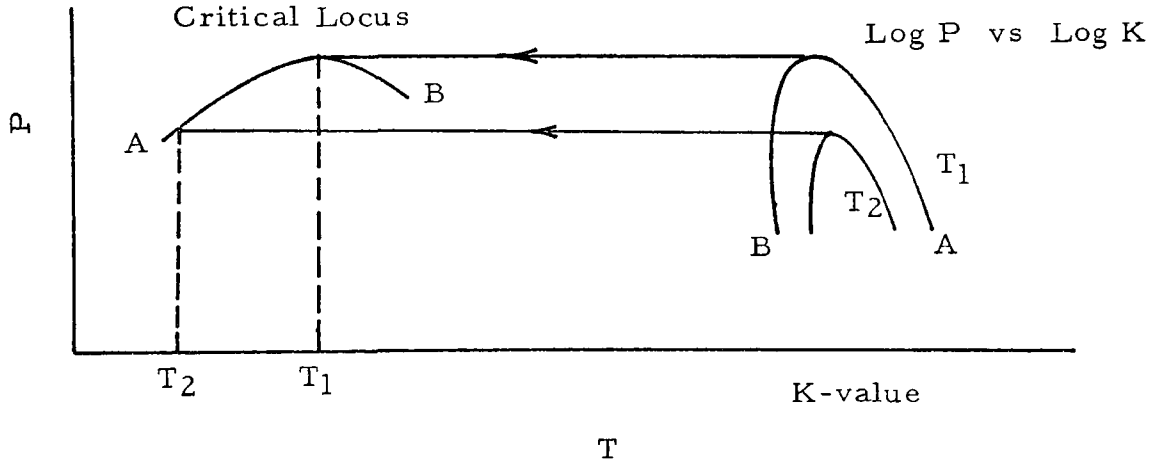


Figure 2.2.1 (b) Illustration of the Convergence Pressure Method to Evaluate Critical Temperature and Critical Pressure.

Hadden and Grayson gave a set of diagrams in 1964 [41] for more accurate determination of convergence pressure. Two nomographs for different temperature ranges are given. One of them goes down to -260°F. The convergence pressure can also be used to correlate binary and multicomponent data to evaluate the critical pressure and critical temperature of mixtures. This is illustrated in Figure 2.2.1b, for a binary mixture.

The convergence method is relatively convenient to use and yields generally acceptable results at pressures less than 80% of the convergence pressure. Its disadvantages are the difficulty of preparing the necessary charts and the uncertainties involved in estimating the convergence pressure. Considerable personal judgement is involved, with the result that different workers obtain different solutions to the same problem.

2.2.2 KELLOGG CHARTS [42]

The Kellogg Charts were published in 1950, by the M. W. Kellogg Company. 324 charts were included under the title "Liquid-Vapor Equilibria in Mixtures of Light Hydrocarbons, MWK Equilibrium Constants, Polyco Data". These charts were prepared in terms of composition and MABP in degrees Fahrenheit. MABP stands for the molar average boiling point. The construction of the charts is based on the Benedict-Webb-Rubin [43] equation of state. Twelve hydrocarbons are included, namely, methane, ethane, ethylene, propane, propylene, n-butane, i-butane, i-butylene, n-pentane, i-pentane, n-hexane and n-heptane. These charts cover the temperature range from -100°F to 400°F (MABP from -255°F to 180°F) and at 26 different pressures between atmospheric pressure up to 3600 psia. It should be mentioned that this chart does not include nitrogen.

2.2.3 LENOIR DIAGRAM

This also includes a set of diagrams and a nomograph, which were published by Canjander, Hipkin and Lenoir [44] in 1960. K-values as a function of temperature at 10 psia are given in the diagrams. Pressure correlation is given in terms of effective boiling point, which is a composition-dependent parameter. This is included in the nomograph. The method covers the temperature range 133 K to 466.5 K.

A similar set of diagrams was also prepared by Lenoir [37] in 1958, for carbon dioxide in hydrocarbon systems. The non-ideality caused by the presence of carbon dioxide in hydrocarbon systems are covered. The temperature range is between -60°F to 100°F.

2.2.4 HAND METHOD FOR LIQUID-LIQUID SOLUBILITY CURVE

For a ternary system with one consolute and two immiscible liquids, Hand [45] found that with a distribution equation, all the tie-lines can be converted to horizontal if the appropriate composition units were selected. He proposed Equation (2.2.4), in which a, b and c represent the mole or weight fractions of the diluent, the solute and the solvent, respectively; K is an empirical constant, and the subscripts denote liquid phases one and two respectively.

$$\frac{X_{a_1}}{X_{b_1} + K X_{c_1}} = \frac{X_{a_2}}{X_{b_2} + K X_{c_2}} \qquad (2.2.4)$$

The use of Equation (2.2.4) provides a method to predict the compositions of all pairs of conjugate phases of a system if the isotherm and one

tie-line are known. Good results were obtained for the system acetic acid (a) - benzene (b) - water(c), when the correlation established K = 9 for the system.

2.2.5 BLACK AND HARTWIG [46] METHOD FOR LIQUID-LIQUID EQUILIBRIUM

This method was primarily intended to use molecular structure to help correlate and predict distribution coefficients and solubilities as a function of the solvent distribution. It was designed to develop a model with the aid of a few equilibrium data for simple mixtures of selected compounds. This model includes the definition of the distribution coefficient K_j, the extraction factor E_j, the solubility function K_h, the solvent distribution K_s and the basic quantity K_r.

A simple ternary system contains 3 components r, i and s, in which r denotes the component which is more non-ideal with the solvent, i refers to the component which distributes between the two phase, and s denotes the solvent component. When the r-s binary is partially miscible, the liquid phase r rich in r component is in equilibrium with liquid phase s rich in s component. Then x will denote the composition in the s phase and y denotes composition in the r phase. The relationship with the parameters are given by

$$K_j = y_j/x_j \qquad (2.2.5a)$$

$$K_r = y_r/x_r \qquad (2.2.5b)$$

$$K_s = y_s/x_s \qquad (2.2.5c)$$

$$K_h = (1 - y_s)/(1 - x_s) \qquad (2.2.5d)$$

A log-log plot of K_r, K_h and K_j vs K_s is shown in Figure (2.5)

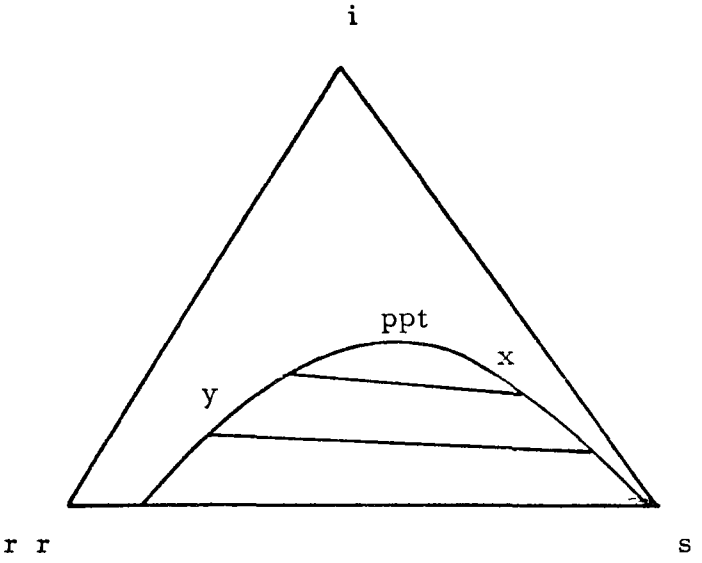


Figure 2.5 (a)

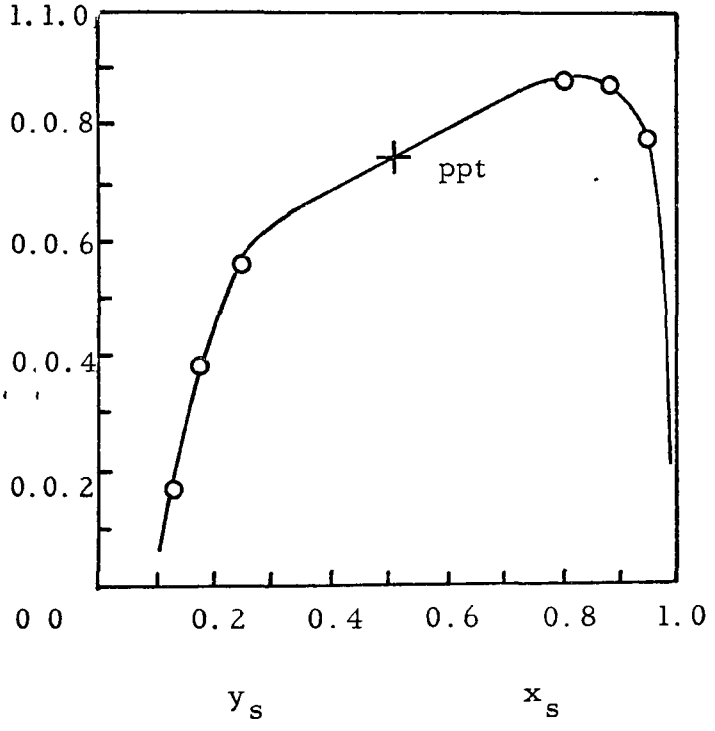


Figure 2.5 (c)

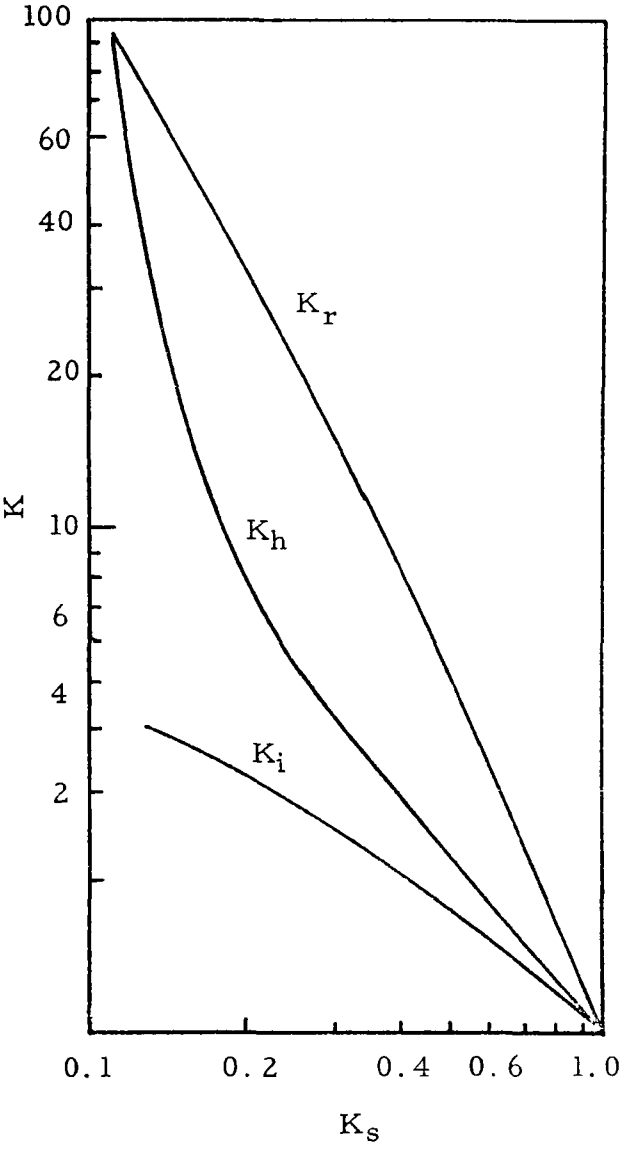


Figure 2.5 (b)

Figure 2.5 Illustration of the Method by Black and Hartwig.

(a) Ternary liquid-liquid phase equilibrium for the system (s)-(i)-(r).

(b) Log-log plot of K_r , K_h , and K_i vs K_s

(c) A plot of x_i and y_i vs x_s and y_s

In this plot, r-s binary is partially miscible, K_s as well as K_r, K_h and K_j approaches unity at the plait point. This condition is given by Equations (2.2.5b) and (2.2.5d) as $1 - y_s$ approaches y_r and $1 - x_s$ approaches x_r.

In Figure (2.5), the limiting slopes of the curves at the plait point are straight lines. Let a, b and c be the values of the slopes. Then the composition of the plait point is given by

$$(x_i)_{p.pt} = \frac{(a - c)}{(a - b)}$$

$$(x_q)_{p.pt} = \frac{c}{c - 1}$$

$$(x_r)_{p.pt} = 1 - (x_i)_{p.pt} - (x_s)_{p.pt}$$

At any fixed value of K_s, the quantities K_r, K_h and K_i provide the necessary and sufficient information for calculating complete ternary liquid-liquid equilibria. A detailed discussion of this method will be given in Chapter 4.

2.3 PREDICTION METHODS BASED ON SOLUTION THEORY

When two or more liquids mixed together to form a solution, the most natural way is to postulate a model for solutions so that the properties of the mixture can be established from the properties of the pure liquids. Present theoretical knowledge has not yet reached a stage of development where this can be done with any degree of generality, although the solution theory may be considered as the only rigorous way to solve the problem so far. Among the many models, either in macroscopic or microscopic approaches, it is only

intended to review a few in this work, namely, the regular solution theory, the athermal mixing theory, and the theory of group interactions.

2.3.1 SCATCHARD-HILDEBRAND'S EQUATION - REGULAR SOLUTION THEORY [47]

For some solutions [48], the excess entropy and the excess volume of mixing can be neglected. Hildebrand [48] found that several solutions of iodine behaved substantially in agreement with these simplified assumptions. And he defined a regular solution based on these two conditions, that is, when

$$\Delta S^E = 0 \qquad (2.3.1a)$$

$$\Delta V^E = 0 \qquad (2.3.1b)$$

the solution is called a regular solution.

Scatchard and Hildebrand [47] assumed that for molecules whose forces of attraction are due primarily to dispersion forces there is a simple relation between the cohesive-energy densities, C_{11}, C_{22} and C_{12} [49]. Introducing δ, the solubility parameter of a pure liquid as the positive square root of its cohesive-energy density, they arrived at the expressions for activity coefficients for a binary regular solution:

$$RT \ln \gamma_1 = V_1 \theta_2^2 [\delta_1 - \delta_2]^2 \qquad (2.3.1c)$$

$$RT \ln \gamma_2 = V_2 \theta_1^2 [\delta_1 - \delta_2]^2 \qquad (2.3.1d)$$

where θ_1 θ_2 are volume fractions and V_1, V_2 are liquid volumes for component 1 and 2, respectively. The regular-solution equations give a good semiquantitative representation of activity coefficients for many solutions containing non-polar components, and they are used as a basis for many prediction methods.

2.3.2 FLORY-HUGGIN'S EQUATION - ATHERMAL MIXING THEORY

The Gibbs energy of mixing consists of an enthalpy term and an entropy term. In the theory of regular solutions for molecules of similar size it is assumed that the entropy term corresponds to that for an ideal solution. However, when considering solutions of molecules of very different size, it has been found advantageous to assume zero enthalpy of mixing. These solutions are called athermal mixtures and this behavior is found in many polymer solutions.

Using the concept of a quasicrystalline lattice as a model for a liquid, an expression for the entropy of mixing in an athermal solution was derived independently by Flory [50] and by Huggins [51], based on statistical arguments, which is beyond the scope of this work and is not discussed here.

Flory and Huggins have shown that if the non-crystalline polymer and the solvent mix athermally, the change in Gibbs energy and in entropy are given by the remarkably simple expression

$$\frac{\Delta G^M}{RT} = \frac{\Delta S^M}{R} = \Sigma\, x_i \ln \theta_i \qquad (2.3.2a)$$

where θ_i is the volume fraction of component i.

2.3.3 THE THEORY OF GROUP INTERACTIONS

The early work on group contribution to solution properties is due to Pierotti [105], Deal [121] and Wilson [122]. The Analytical Solution of Groups developed by Derr and Deal [123] provides a flexible means for representing excess free energy data. Renon and Prausnitz [124], and Wiehe and Bagley [125] adopted a molecular association model in their studies of alkane-alcohol solutions. Lee, Greenkorn and Chao [126] developed a partition function for the description of the configurational

properties of non-polar and polar chain molecules by considering group interactions. This application has been successful in representing a variety of thermodynamic properties of pure liquids and solutions, including molar volume and heat of vaporization, excess enthalpies and free energies. Later, Coleman, Greenkorn and Chao [127] expressed the temperature dependence of the thermodynamic properties in terms of a Taylor series expansion about the base temperature at which the group property values are evaluated. However, the concept of additive group contribution is found inapplicable to structures that contain cross-linking or extensive branching.

APPLICATIONS OF REGULAR SOLUTION AND ATHERMAL MIXING THEORIES

With the solution models established, many researches have been carried out based on these models. Among the many important contributions, the following will be briefly reviewed:

(1) Method of Chao and Seader [52]

(2) Correlation of Chang, Chappelear and Kobayashi [53]

(3) Correlation of Orentilicher and Prausnitz [54]

(4) Correlation of van Horn and Kobayashi [55]

2.3.4 CHAO AND SEADER METHOD

According to Chao and Seader [52], the K-value is expressed in terms of three factors:

$$K_i = \frac{y_i}{x_i} = \left(\frac{f^\circ_{iL}}{P}\right)(\gamma_i)/\varphi_i \qquad (2.3.3a)$$

where (f°_{iL}/P) is the liquid fugacity coefficient of pure component i.

φ_i is the vapor phase fugacity coefficient of component i

γ_i is the liquid activity coefficient of component i

Following the three-parameter law of corresponding states of Pitzer [56], the (f°_{iL}/P) term is expressed as the following:

$$\log (f^{\circ}_i/P) = \log (f_i^{\circ}/P)^{(o)} + \omega \log (f^{\circ}_i/P)^{(1)} \quad (2.3.3\,b)$$

Both the quantities $(f^{\circ}_i/P)^{(o)}$ and $(f^{\circ}_i/P)^{(1)}$ can be expressed in terms of reduced temperature and reduced pressure:

$$\log (f^{\circ}_i/P)^{(o)} = (A_o + A_1/T_r + A_2 T_r + A_3 T_r^2 + A_4 T_r^3) + (A_5 + A_6 T_r + A_7 T_r^2) P_r + (A_8 + A_9 T_r) P_r^2 - \log P_r \quad (2.3.3\,c)$$

$$\log (f^{\circ}_i/P)^{(1)} = -4.23893 + 8.65806 T_r - 1.22060/T_r - 3.15224 T_r^3 - 0.025 (P_r - 0.06) \quad (2.3.3\,d)$$

The φ term can be calculated from the Redlich-Kwong [62] equation of state. For the evaluation of the γ_i term, the Scatchard-Hildebrand regular solution model is adopted. Heats of vaporization and liquid molar volume are not being used for the evaluation of the solubilities, instead experimental vapor-liquid equilibrium data are used. The correlation is applied to the systems containing paraffins, olefins, aromatics and naphthenes. At high temperature ranges, the correlation is successful but at lower temperature ranges, the correlation fails quite badly [52].

2.3.5 CORRELATION OF ORENTILICHER AND PRAUSNITZ [54]

Solubility data for hydrogen in liquids at low temperature and high pressure have been correlated by a relationship:

$$\ln (\hat{f}_2^V / x_2) = \ln \mathcal{H} + A/RT (x_1^2 - 1) + \bar{v}_2^{\infty} (P-P_1^s)/RT \qquad (2.3.4a)$$

where

$$\mathcal{H} = \lim_{x_2 \to 0} \frac{\hat{f}_2^L}{x_2} \qquad (2.3.4b)$$

$$\ln \gamma_1 = \frac{A}{RT} x_2^2 \qquad (2.3.4c)$$

$$\ln \gamma_2^* = \frac{A}{RT} (x_1^2 - 1) \qquad (2.3.4d)$$

$$\hat{f}_2^L = \gamma_2^* \mathcal{H} x_2 \qquad (2.3.4e)$$

Equations (2.3.4c) and (2.3.4d) involve a simple solution model for the evaluation of liquid activity coefficients. From Equation (2.3.4a), a semilogarithmic plot of the ratio $\hat{f}_2^V / x_2$ against total pressure at constant temperature should give a straight line for small values of x_2. Orentilicher and Prausnitz have evaluated the constant A and the Henry's law constant $\mathcal{H}$ for the following solvents: A, CO, CH_4, N_2, C_2H_6, C_3H_8, C_3H_6 and C_6H_{14}.

2.3.6 CORRELATION OF CHANG, CHAPPELEAR AND KOBAYASHI [53]

The correlation of K-values of methane in paraffinic and aromatic solvents at low temperatures and high pressures was suggested by Chang, Chappelear and Kobayashi. The correlation is based on an

equation similar to that of Chao and Seader. This equation is:

$$K_i = \frac{y_i}{x_i} = \left(\frac{f_i^{\circ L}}{P} \right) (\gamma_i)/\varphi_i \qquad (2.3.5a)$$

The vapor phase fugacity coefficient was evaluated from the Redlich-Kwong equation of state [58] [59].

The liquid phase activity coefficient is taken as the sum of the athermal effect and the thermal effect. The athermal effect is calculated by the Miller-Guggenheim [60] [61] relation, and an empirical expression is used for the thermal effect. The expression for the thermal effect is:

$$\ln \gamma_1^{th} = X \theta_2^n \qquad (2.3.5b)$$

where θ_2 is volume fraction of component 2;

n is taken as 2.6

X is determined through the expression:

$$X = [\ln (K_1 \varphi_1) - \ln (f_i^{\circ}/P) - \ln \gamma_1^{a_{th}}] \theta_2^{-n} \qquad (2.3.5c)$$

The correlated results are in good agreement with the K-values of methane, having a relative deviation of $\pm$ 5%, except in the vicinity of the critical point. However, the results are not so successful for heavier components.

2.3.7 METHOD FOR HYDROCARBONS BY VAN HORN AND KOBAYASHI [55]

In 1968, van Horn and Kobayashi [55] used an approach similar to that of Orentilicher and Prausnitz [54], to evaluate K-values for hydrocarbons in paraffinic and aromatic solvents. The Scatchard-Hildebrand equation is empirically modified for the calculation of liquid

fugacity and the B-W-R equation of state is used to calculate the vapor phase fugacities. The generalized form of the correlation is:

$$\ln \frac{\hat{f}_i^L}{x_i} = A + \frac{B}{T} + \frac{C}{T} x_1 + \frac{\bar{V}_1^{\infty} (P - P_o)}{RT} \qquad (2.3.6a)$$

where

$$A = A_1 + A_2 (\delta_1 - \delta_2)^2$$

$$B = B_1 + B_2 (\delta_1 - \delta_2)^2$$

$$C = C_1 + C_2 / V_2$$

$$\bar{V}_1^{\infty} = D_1 + D_2 (T/\delta_2^2)$$

The K-values are calculated by:

$$K_i = \left(\frac{\hat{f}_i^L}{x_i P} \right) / \left(\frac{\hat{f}_i^V}{y_i P} \right) \qquad (2.3.6b)$$

Excellent agreement of K-values was obtained by van Horn and Kobayashi. However, for heavier components, K-values at infinite dilution, required in the calculation, are not always available.

2.4 PREDICTION METHODS BASED ON AN EQUATION OF STATE

The prediction of phase equilibrium needs the information concerning the quantitative relationship between temperature, pressure and compositions. For the analysis of phase equilibrium, the equilibrium distribution of some component i between two phases α and β, we have

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad (2.4.0a)$$

where μ is the chemical potential.

In terms of fugacity, it will be:

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} \qquad (2.4.0b)$$

To calculate fugacity, volumetric data must be available, and preferably in the form of an equation of state. Some people consider that the more complicated an equation of state is, and the more constants it contains, the better representation it gives for volumetric properties. This is only true for a pure component if plenty of volumetric data are available to determine the constants with confidence and if the equation is used only under those conditions of temperature and pressure which were used to determine the constants. However, for predicting the properties of mixtures from pure component data alone, the more constants one has, the more mixing rules are required. Since these rules are subject to uncertainty, it frequently happens that a simple equation of state containing two or three constants is better for predicting mixture properties. The Benedict-Webb-Rubin [43] and the Redlich-Kwong [62] equations of state are typical of these kinds and a review will be made here.

2.4.1 BENEDICT-WEBB-RUBIN EQUATION OF STATE [43]

The following equation:

$$P = RT\rho + (B_o RT - A_o - \frac{C_o}{T^2})\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{1}{T^2}[C\rho^3(1+\gamma\rho^2)\exp(-\gamma\rho^2)] \quad (2.4.1a)$$

was proposed by Benedict and co-workers in 1940 [43], in which A_o, B_o, C_o, a, b, c, α and γ are constants; and ρ is the density.

The equation was used to represent volumetric properties of pure non-polar gases and liquids satisfactorily. In 1942 [63], this equation was used for hydrocarbon mixtures. In 1951 [64], this equation was used for the calculation of vapor-liquid equilibrium.

With eight constants, the B-W-R is a complex equation and therefore is usually reduced in the form of charts, for the purposes of practical application. The Kellogg chart discussed in Section (2.2.2) is one example. Another is the DePriester's Correlation.

DePriester [65] found that the fugacity functions $\hat{f}_i^L/P\,x_i$ and $P\,y_i/\hat{f}_i^V$ related to pressure in linear or nearly linear relations. Therefore the Kellogg charts are simplified. Two set of pressure-temperature-composition (P.T.C.) charts are prepared. In one set of charts, K-values are shown as functions of $(\hat{f}_i^L/P\,x_i)$ and $(P\,y_i/\hat{f}_i^V)$, for temperature from -100°F to +400°F, and pressures up to 1000 psia. K-values for twelve light hydrocarbons from methane to n-heptane are shown in 24 charts. In the other set of charts, a generalized correlation is also presented in the form of two nomographs; one for the temperature range of -100°F to 70°F, and the other 20°F to 400°F. The generalized correlation serves for preliminary calculations, with average absolute deviation from experimental data of 15.0%, while the P.T.C. charts give 6.4%.

The B-W-R equation has been applied to predict vapor-liquid equilibria for the system nitrogen-carbon monoxide satisfactorily by Schiller and Canjar [66]. However, for propane-carbon dioxide [67], nitrogen-methane [68] and the systems of light hydrocarbons containing hydrogen [69], the B-W-R prediction of K-values does not yield satisfactory results.

Some attempts have been made to modify the B-W-R equation in order to yield better results for the prediction of K-values. Lin and Naphtali [70] adopted the following form

$$P = RT\varphi + (B_o RT - A_o - C_o/T^{\beta})\,\rho^2 + (b\,RT - a)\,\rho^3 + a\,\alpha\,\rho^6 + [(C\rho^3/T^2)(1 + \gamma\varphi^2)\exp(-\gamma\varphi^2)] \qquad (2.4.1b)$$

for the systems nitrogen-methane, methane-carbon dioxide, propane-carbon dioxide and n-butane-carbon dioxide. Stotler and Benedict [68] made a change of the combining rule for A_o.

$$A_o = x_1^2 A_{o_1} + x_2^2 A_{o_2} + 2.874\, x_1 x_2 \qquad (2.4.1c)$$

and consider C_o as temperature dependent, for the system nitrogen-methane.

2.4.2 REDLICH-KWONG EQUATION OF STATE

In 1949, Redlich and Kwong [43] proposed the equation

$$P = \frac{RT}{(v - b)} - \frac{a}{T^{\frac{1}{2}} v\,(v + b)} \qquad (2.4.2a)$$

which can also be transformed into

$$Z = \frac{1}{1 - h} - \frac{A^2}{B}\left(\frac{h}{1 + h}\right) \qquad (2.4.2b)$$

where

$$h = BP/z \qquad (2.4.2c)$$

$$A^2 = \Omega_a T_c^{2.5}/(T^{2.5} P_c) = a/R^2 T^{2.5} \qquad (2.4.2d)$$

$$B = \Omega_b T_c/TP_c = b/RT \qquad (2.4.2e)$$

$$\Omega_a = 0.4278 \qquad (2.4.2f)$$

$$\Omega_b = 0.0867 \qquad (2.4.2g)$$

When applied to mixtures, the following combining rules were suggested:

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (2.2.4h)$$

$$b = \sum_i x_i b_i \qquad (2.4.2i)$$

$$a_{ij} = \sqrt{a_{ii}\ a_{jj}} \qquad (2.4.2j)$$

This equation of state has been chosen for correlation purposes and has been modified for prediction purposes by many researchers [50] [53], [71], [73], [74], [77], [78], [131]. The following will be a short review of some which are of interest concerning this work.

CORRELATION OF CHAO AND SEADER [52]

As discussed in Section (2.3.3), the vapor-phase fugacity coefficient of component i, $\hat{\varphi}_i^V$, is calculated from the Redlich-Kwong equation of state.

CORRELATION OF WILSON [71]

Wilson [71] proposed a modification of the Redlich-Kwong equation. In this modification while Ω_b is considered as 0.0867 in all conditions, Ω_a is considered as a temperature-dependent parameter, according to the relations:

$$a_{ii}/RT_{ci}^{1.5} = 4.934\left[1 + k\left(\frac{1}{T_{ri}} - 1\right)\right] T_{ri}^{1.5}\, b_i \qquad (2.4.2k)$$

$$a_{ij} = \theta_{ij}\, a_{ii} + (1 - \theta_{ij})\, a_{jj} \qquad (2.4.2l)$$

where k and θ_{ij} are temperature-independent parameters and T_{ri} is reduced temperature of component i. Two vapor pressure points were necessary to determine the temperature dependence of Ω_a at a certain temperature.

This was used to correlate vapor-liquid equilibrium data of the systems nitrogen-methane and helium-hydrogen. Later [72], Wilson

proposed another relation that combined Equations (2. 4. 2k), (2. 4. 21). Good results were obtained for the system hydrogen-nitrogen. However, for some other systems, especially those containing heavier hydrocarbons, good agreement with experimental data could not be attained.

CORRELATION OF CHANG, CHAPPELEAR AND KOBAYASHI [53]

As discussed in Section (2. 3. 5), the Redlich-Kwong equation of state was used to evaluate the vapor phase fugacity coefficient, $\hat{\varphi}^{V}_{i}$. Upon the application of the R-K equation, the modification of Wilson [72] was simplified to the relation:

$$a_{ii} = F\,(T_c/T\,,\,\omega)\, b_i\, RT^{1.5} \qquad (2.4.2m)$$

where

$$F\,(T_c/T,\omega) = a/(b\,RT^{1.5})$$

$$= 4.934\left[1 + (1.45 + 1.62\omega)\left(\frac{T_c}{T} - 1.0\right)\right]$$

$$(T_c/T)^{0.12} \qquad (2.4.2n)$$

or $$A_i^2 = a_{ii}/(R^2\,T^{2.5})$$

The constants for mixtures were given by:

$$A^2 = \sum_i y_i A_i \qquad (2.4.2o)$$

$$B = \sum_i y_i B_i \qquad (2.4.2p)$$

The description of the non-ideality of the heavier components in the vapor phase by using the Redlich-Kwong Equation in this way may be responsible for the failure of the method as discussed in Section (2. 3. 5).

METHOD OF CHUEH AND PRAUSNITZ [73]

In 1968, Chueh and Prausnitz proposed a data reduction method to obtain binary parameters from binary vapor-liquid equilibrium data; and from these binary parameters, the phase behavior of multicomponent system could be predicted. When two phases are in equilibrium, the following relation holds:

$$\hat{\varphi}_i^{V} \; y_i P = \gamma_i x_i f_i^{\circ} \qquad (2.4.2q)$$

The modified van Laar's model is used for the evaluation of the constant-pressure activity coefficient, γ_i.

$$\ln \gamma_i^{(P^r)} = A' \phi_2^2 + B' \phi_2^4 \qquad (2.4.219)$$

$$\ln \gamma_2^{*(P^r)} = A'\left(\frac{v_{c2}}{v_{c1}}\right)(\phi_2^2 - 2\phi_2) + B'\left(\frac{v_{c2}}{v_{c1}}\right)(\phi_2^4 - \frac{4}{3}\phi_2^3) \qquad (2.4.2r)$$

where

$$\phi_2 = \frac{x_2 v_{c2}}{x_1 v_{c1} + x_2 v_{c2}} \qquad (2.4.2s)$$

$$A' = a_{22(1)} v_{c1} \qquad (2.4.2t)$$

$$B' = 3\eta_{2(1)} a_{22(1)} v_{c1} \qquad (2.4.2u)$$

The asterisk in Equation (2.4.2r) indicates the adoption of the asymmetric convention for the normalization of activity coefficients. Subscript 1 refers to the condensable component, and subscript 2 to the non-condensable one. $a_{22(1)}$ is called the self-interaction constant and $\eta_{2(1)}$ the dilation constant.

For the evaluation of the vapor-phase fugacity coefficient, $\hat{\varphi}_i^{V}$, the Redlich-Kwong equation of state was used, with a modified procedure.

Instead of taking Ω_a and Ω_b as universal constants, as originally proposed by Redlich and Kwong, they evaluated the parameters for each pure substance by fitting the volumetric data of saturated vapor. The mixing rules used were:

$$b = \sum y_i b_i \qquad (2.4.2v)$$

$$b_i = \frac{\Omega_{bi} R T_{ci}}{P_{ci}} \qquad (2.4.2w)$$

$$a = \sum_i \sum_j y_i y_j a_{ij} \qquad (2.4.2x)$$

$$a_{ii} = \frac{\Omega_{ai} R^2 T_{ci}^{2.5}}{P_{ci}} \qquad (2.4.2y)$$

$$a_{ij} = \frac{(\Omega_{ai} + \Omega_{aj}) R^2 T_{cij}^{2.5}}{2 P_{cij}} \qquad (2.4.2z)$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}} \qquad (2.4.2aa)$$

$$v_{cij}^{1/3} = \tfrac{1}{2} (v_{ci}^{1/3} + v_{cj}^{1/3}) \qquad (2.4.2bb)$$

$$Z_{cij} = 0.291 - 0.08 \left(\frac{\omega_i + \omega_j}{2}\right) \qquad (2.4.2cc)$$

$$T_{cij} = (T_{cii} \; T_{cjj}) (1 - k_{ij}) \qquad (2.4.2dd)$$

The parameter k_{ij} represents the deviation from the geometric mean for T_{cij}. It is a constant characteristic of the i-j interaction. To a good approximation k_{ij} is independent of temperature, density or composition, and is estimated from experimental binary data.

The Redlich-Kwong equation was used again, for the evaluation of the partial molar volume, which was used for the calculation of pressure dependence of the activity coefficients. The mixing rule for V_{cij} was:

$$v_{cij} = \frac{1}{2}\left(v_{ci} + v_{cj}\right) \qquad (2.4.2\,ee)$$

For a solvent component, the standard-state fugacity was taken to be the pure liquid fugacity at zero pressure. For a solute component, the standard-state fugacity was Henry's constant in the mixed solvent, corrrected to zero pressure.

To predict multicomponent vapor-liquid equilibria from the determined binary constants, the following relations were used.

$$\hat{f}_i^V = \hat{f}_i^L \qquad (2.4.2\,ff)$$

where

$$\hat{f}_i^V = \hat{\varphi}_i^V\, y_i\, P \qquad (2.4.2\,gg)$$

$$\hat{f}_i^L = \gamma_i^{(P_r)}\, x_i\, f_i^{\circ\,(P_r)} \exp\left[(P - P^r)\,\bar{v}_{iL}/(RT)\right] \qquad (2.4.2\,hh)$$

This method generally gives rather good results in systems containing non-polar components. But an empirical relation like the van Laar's model cannot represent the activity coefficient of the heavier component reliably even for non-polar substances because it is directly evaluated from the vapor-liquid equilibrium compositions. The equilibrium vapor composition of the heavier component is small at low temperatures, and therefore is subject to much greater experimental error. Therefore the activity coefficient evaluated based on this vapor composition is bound to be erroneous.

METHOD OF ZUDKEVITCH AND JOFFE [74]

The Redlich-Kwong equation of state was used to evaluate fugacity coefficients of a component, both in the liquid and the vapor phases. The approach of Wilson [71] [58] and Chueh and Prausnitz [73] were modified. The modified approach evaluated both Ω_a and Ω_b from experimental data. It was intended to evaluate Ω_a and Ω_b separately for the saturated liquid phase and the saturated vapor phase. But it was found that negative values would result for the vapor phase. Therefore the values of Ω_a and Ω_b were established from the saturated liquid properties. In the establishment of Ω_a, Ω_b values, the generalized correlation of Lyckman, Eckert and Prausnitz [75] for fugacity coefficients was employed:

$$\log \varphi = (\log \varphi)^{(0)} + \omega (\log \varphi)^{(1)} \qquad (2.4.2ii)$$

where, $(\log \varphi)^{(o)}$ and $(\log \varphi)^{(1)}$ are functions of the reduced temperature, tabulated by Lyckman, Eckert and Prausnitz. Most of the combining rules were retained, except that for the interaction constant, a_{ij}. From experimental vapor-liquid equilibrium data, the following relation was used:

$$a_{ij} = (1 - C_{ij}) (a_i a_j)^{0.5} \qquad (2.4.2jj)$$

The constant C_{ij} represents the deviation from the standard Redlich-Kwong combining rules for a_{ij}. It was assumed that C_{ij} was independent of the temperature, pressure, and composition of the system.

The drawback of this method is that the fundamental condition, $\hat{\varphi}_i^V = \hat{\varphi}_i^L$, would not be satisfied. To avoid this, a method was proposed by Joffe, Schroeder and Zudkevitch [76]. This method was similar to that proposed by Lu et al. [132], and Chang and Lu [77]

in the calculation of partial molar volumes of liquid mixtures. In this method, the condition of $\hat{\varphi}_i^V = \hat{\varphi}_i^L$ is imposed on the vapor-liquid equilibrium. With the derived working equation:

$$\Omega_a = \Omega_b \left[\frac{\ln \left[(V_v - b)/(V_L - b) \right] - P (V_v - V_L)/RT}{(T_c/T)^{3/2} \ln \left[V_L (V_L + b)/V_L (V_v + b) \right]} \right]$$

(2.4.2 kk)

a simultaneous solution with the Redlich-Kwong equation would yield the values of Ω_a and Ω_b at temperatures below the critical point. But Equation (2.4.2 kk) becomes indeterminate at the critical point, and therefore the previous [74] method has to be used at that condition. Of course, at conditions above the critical point, the temperature dependence of the Ω_a and Ω_b values were not taken care of.

METHODS OF LU ET AL., [132] CHANG AND LU [77], AND HSI AND LU [78]

The Redlich-Kwong equation of state with a modified procedure was used to predict liquid partial molar volumes. The parameters Ω_a and Ω_b were treated as temperature-dependent. Values of these parameters were evaluated as a function of temperature by using vapor pressures and saturated liquid densities of the pure components. It was shown that this modification did give a considerable improvement for the representation of the behavior of pure liquids at high pressures.

Partial molar volumes of six binary systems methane-ethane, methane-propane, ethane-propane, nitrogen-oxygen, nitrogen-argon and argon-oxygen were studied and satisfactory results were obtained. The differences between the calculated and experimental $\bar{V}_i$ values are generally less than 0.2%. The success in the volumetric properties

of normal fluid mixtures by employing the modified Redlich-Kwong equation of state initiates some further applications for the prediction of other thermodynamic properties such as vapor-liquid equilibrium or excess thermodynamic properties of mixing, etc.

Hsi and Lu [78] further modified this procedure, by evaluating the Ω_a, Ω_b parameters as a function of temperature in the supercritical state. The values of Ω_a and Ω_b for a supercritical component were evaluated by means of existing properties of binary mixtures. It was assumed that these values were unique for the component concerned. Therefore, the Ω_a and Ω_b values of a supercritical component A obtained from the properties of the A-B binary could be used for predicting properties for the A-C, A-D etc... pairs. The solubility of methane in n-hexane, cyclohexane, benzene and carbon tetrachloride were predicted and were found in satisfactory agreement with experimental data of Lannung and Gjaldback [79]. Total pressures and vapor compositions were also predicted for the systems methane-n-pentane, methane-n-hexane, methane-n-heptane, methane-ethane-propane and methane-propane-n-pentane, and were found in satisfactory agreement with available data in the literature.

MODIFICATION OF THE REDLICH-KWONG EQUATION OF STATE BY SOAVE

Soave [130] proposed a modification of the Redlich-Kwong equation of state by replacing the constant a by a more general temperature dependent term, a(T), such that

$$a_i(T) = a_{ii}\,\alpha_i(T) \qquad (2.4.211)$$

where $\alpha_i(T)$ is an adimensional factor which becomes unity at $T = T_{ci}$. It was found that in a plot of $\alpha_i^{0.5}$ vs $T_{ri}^{0.5}$, straight lines were obtained.

Hence the following relationship was proposed for the evaluation of a_i for pure substances:

$$a_i^{0.5} = 1 + m_i (1 + T_{ri}^{0.5}) \qquad (2.4.2mm)$$

$$m_i = 0.480 + 1.574 \omega_i - 0.176 \omega_i^2 \qquad (2.4.2nn)$$

where ω_i was the acentric factor of the substance. It was also claimed that this modification produced good results for the methane-n-butane mixture up to the critical region. However it was found that the computed vapor pressures showed slightly S-shape deviations and that greater deviations were found for mixtures containing hydrogen.

2.5 CALCULATION OF CRITICAL LOCUS

The theory of critical state of mixtures was well established by the work of Gibbs [12] in 1928. Since that time only limited attempts have been made to obtain quantitative predictions of the critical state from the rigorous thermodynamic relations that define the critical state of mixtures. Empirical correlations for either the critical temperature or the critical pressure of mixtures were applied to mixtures usually restricted to paraffins or light hydrocarbons. Recently, efforts have been made to use an equation of state for the prediction of critical locus. A few correlation and prediction methods will be discussed here.

2.5.1 THE METHOD OF CONVERGENCE PRESSURE

As discussed in Section (2.2.1), the method of convergence pressure serves as a correlation method of calculating critical properties for binary mixtures and multicomponent mixtures [128].

2.5.2 CORRELATION OF MAYFIELD [80]

The additive law was adopted by Mayfield to correlate critical temperature and pressure of a binary mixture. He found that the T_c of a binary mixture could be quite well predicted from the pure component properties if T_c was expressed in terms of volume fractions. The working equation was:

$$T_{CM} = T_{CL} \left(\frac{\%L}{100}\right) + T_{CH} \left(\frac{\%H}{100}\right) \qquad (2.5.2a)$$

For the correlation of P_C, he proposed a relation, which is :

$$P_{CD} = P_{CM} - P_{CH} - \frac{\%L}{100} (P_{CL} - P_{CH}) \qquad (2.5.2b)$$

where P_{CD} was the deviation of the critical pressure from the values of the additive law. It was found that all these deviations passed through a maximum value which fell near the point of 50% volume fraction. A common plot was established for $P_{CD}/P_{CD\ max.}$ based on the hydrocarbon data. The author was aware of some limitations of this correlation, that the method was applicable to binary paraffin hydrocarbon systems, and that the method for P_C was not recommended for branched paraffins, olefins or cyclic compounds.

2.5.3 CORRELATION OF GRIEVES AND THODOS [81] FOR P_C AND ρ_C OF MIXTURES

Grieves and Thodos found that the relationship of the critical pressure of the mixture to that of its pure components could be described by the relationship of the vapor pressure behavior of the mixture compared with that of its pure components. It was also found that the same could be applied to the critical density. Plots

of P_C/P'_C and ρ_C/ρ'_C against T'_b/T_b were constructed at constant compositions for binary systems. The two ratios P_C/P'_C and ρ_C/ρ_C' are ratios of actual critical pressure to pseudocritical pressure (molar average), and actual critical density to the reciprocal of the molar average of the critical molar volumes of the pure components. The dimensionless parameter T'_b/T_b was chosen to represent the differences in the properties of the components. T'_b was the molar average of the normal boiling points of the two components, and T_b was the boiling point of the mixture at atmospheric pressure calculated from the following equation by a trial-and-error procedure:

$$\pi = 14.7 = P_1 x_1 + P_2 x_2 \qquad (2.5.3\,a)$$

The correlation was mainly derived for hydrocarbon mixtures, and different charts were established for "non-methane systems" and for "methane systems". This method was also applicable to multicomponent systems. For example, for a quaternay system, the two heaviest component was first considered; then the property of the mixture was combinedwith a third component to form a binary mixture, and so on until the last component was considered. The expected error was claimed to be 2%.

2.5.4 METHOD OF HISSONG AND KAY [82]

In 1970, Hissong and Kay used the Redlich-Kwong equation of state for the prediction of T_C and P_C for binary mixtures, and used Dieterici equation for V_C. This method put its attention in the evaluation of the interaction parameters a_{12} and b_{12}. a_{12} and b_{12} were evaluated by an optimization technique from experimental critical property data. Comparing the results of using these a_{12} and b_{12} with the results from a_{12} and b_{12} calculated by combining rules from the values of a and b

for the pure components, this method yielded better results. Twenty-one binary systems composed of mixtures of paraffinic, naphthenic and aromatic hydrocarbons have been tested. A correlation curve for reduced interaction parameters a_{12}^* and one for b_{12}^* were presented. But in this method, experimental critical data are needed for the evaluation of the interaction parameters and hence it is considered as a method of correlation.

2.5.5 THE METHOD OF PAK AND KAY [83]

Pak and Kay calculated critical properties of binary hydrocarbon mixtures in two different ways. The Redlich-Kwong equation of state and the Redlich-Ngo equation of state were used separately, and results were compared. The approach of Hissong and Kay [82] was adopted. Interaction parameters a_{12} and b_{12} were evaluated by best fit from experimental data of critical properties. In this approach, the best fit for a_{12} and b_{12} is based on P_C and T_C values of the mixture. A weighing factor α was used when the minimizing factor F was calculated according to the equation

$$F = P_D + \alpha T_D \qquad (2.5.5a)$$

where P_D and T_D are the differences of the calculated and experimental P_C and T_C values.

If experimental data of T_C and P_C were not available. Pak and Kay presented a correlation method to evaluate the interaction parameters a_{12} and b_{12}. In that correlation, the size, structure and chemical nature of the components were also considered. The correlations are listed below:

With the Redlich-Kwong Equation, the correlations for 34 aliphatic systems are:

$$a^*_{12} = 1.024862 - 0.323559\ V_R + 0.019509\ M_R V_R + 0.314712\ Z_R \qquad (2.5.5b)$$

$$b^*_{12} = 0.650971 + 0.373944\ P_R \qquad (2.5.5c)$$

With the Redlich-Kwong Equation, the correlations for 30 cyclic systems are:

$$a^*_{12} = 1.270310 - 0.045239\ M_R V_R - 0.214428\ T_R \qquad (2.5.5d)$$

$$b^*_{12} = 0.981005 - 0.051121\ M_R V_R + 0.079274\ V_R - 0.0141091\ \omega_R \qquad (2.5.5e)$$

With the Redlich-Ngo Equation, the correlations for 24 aliphatic systems are:

$$a^*_{12} = 1.060929 - 0.405490\ M_R - 0.366815\ T_R \qquad (2.5.5f)$$

$$b^*_{12} = 0.092480 + 0.720709\ P_R + 0.762800\ Z_R - 0.045713\ V_R^2 \qquad (2.5.5g)$$

With the Redlich-Ngo Equation, the correlations for 20 cyclic systems are:

$$a^*_{12} = 0.27116 + 0.039951\ M_R^2 - 1.047819\ TB_R^2 + 0.002928\ \omega_R^2 \qquad (2.5.5h)$$

$$- 0.472000\ T_R + 2.432344\ TB - 0.170396\ V_R$$

$$b^*_{12} = 0.861850 - 0.106540\ M_R^2 - 0.033744\ M_R V_R + 0.2279552\ Z_R \qquad (2.5.5i)$$

M_R is the molecular weight ratio, m_1/m_2, $m_1 \neq m_2$,

T_R is the critical temperature ratio, T_{c1}/T_{c2},

V_R is the critical volume ratio, V_{c1}/V_{c2},

Z_R is the critical compressibility ratio, Z_{c1}/Z_{c2},

ω_R is the acentric factor ratio, ω_1/ω_2,

and TB_R is the normal boiling point ratio, TB_1/TB_2.

2.5.6 METHOD OF LIMITING SLOPES BY REDLICH AND KISTER [84]

In 1962, Redlich and Kister derived two expressions from the condition of a critical point for a binary mixture. The derivation was thermodynamically rigorous, and the equation were expressed in terms of volumetric data.

$$\int_{\infty}^{v} \left(\frac{\partial^2 P}{\partial y_1^2}\right)_{v,T} dv - \left(\frac{\partial P}{\partial y_1}\right)^2_{v,T} \left(\frac{\partial v}{\partial y_1}\right)_{y,T} = \frac{RT}{y_1 y_2} \qquad (2.5.6a)$$

$$\int_{\infty}^{v} \left(\frac{\partial^3 P}{\partial y_1^3}\right)_{v,T} dv + 2\left(\frac{\partial^2 P}{\partial y_1^2}\right)_{v,T} \left(\frac{\partial v}{\partial y_1}\right)_{P,T} + \left(\frac{\partial^2 P}{\partial y_1 \partial v}\right)_{T} \left(\frac{\partial v}{\partial y_1}\right)^2_{P,T} + \left(\frac{\partial P}{\partial y_1}\right)_{v,T} \left(\frac{\partial^2 v}{\partial y_1^2}\right)_{P,T} = \frac{RT(y_1 - y_2)}{(y_1 y_2)^2} \qquad (2.5.6b)$$

From these equations, it can be shown that the limiting slopes of the T_C and P_C curves are represented by

$$\left(\frac{dT}{dy_1}\right)_C = \frac{(y_1 - y_2)\left(\frac{\partial P}{\partial y_1}\right)^2_{v,T}/RT - \left(\frac{\partial^2 P}{\partial v\, \partial y_1}\right)_T}{(\partial^2 P/\partial T\, \partial v)_y} \qquad (2.5.6c)$$

$$\left(\frac{dP}{dy_1}\right)_C = \left(\frac{\partial P}{\partial y_1}\right)_{v,T} + \left(\frac{\partial P}{\partial T}\right)_{v,y}\left(\frac{dT}{dy}\right)_C \qquad (2.5.6d)$$

Hence interpolation of the critical temperature and pressure between the critical points of the pure components can be performed based on these two equations. The limiting slopes at the critical points of the pure components for critical temperature and pressure are given by:

$$p_1 = \lim_{y_1 = 1} \left(\frac{dP}{dy_1}\right)_C \qquad (2.5.6e)$$

$$p_2 = \lim_{y_1 = 0} \left(\frac{dP}{dy_1}\right)_C \qquad (2.5.6f)$$

$$t_1 = \lim_{y_1 = 1} \left(\frac{dT}{dy_1}\right)_C \qquad (2.5.6g)$$

$$t_2 = \lim_{y_1 = 0} \left(\frac{dT}{dy_1}\right)_C \qquad (2.5.6h)$$

And these values can be obtained from Equations (2.5.6c) and (2.5.6d).

An interpolation function for critical pressure was proposed as the following:

$$P_C = y_1 P_{C1} + y_2 P_{C2} = \frac{(P_{C1} - P_{C2} - p_2)(P_{C1} - P_{C2} - p_1)\, y_1 y_2}{(P_{C1} - P_{C2} - p_2)\, y_1 - (P_{C1} - P_{C2} - p_1)\, y_2} \qquad (2.5.6i)$$

The same function was applied for critical temperature interpolation, with the pressure terms replaced by temperature terms.

An equation of state was needed for the evaluation of the necessary terms, and the Redlich-Kwong equation of state was used. The combining rules used were:

$$a^{0.5} = 0.6541\, R\, (y_1\, T_{C1}^{1.25}/P_{C1}^{0.5} + y_2\, T_{C2}^{1.25}/P_{C2}^{0.5}) \qquad (2.5.6j)$$

$$b = 0.0867\, R\, (y_1\, T_{C1}/P_{C1} + y_2\, T_{C2}/P_{C2}) \qquad (2.5.6k)$$

The critical volumes of the pure components were given by:

$$V_{C1} = b_1/0.260 \qquad (2.5.6l)$$

$$V_{C2} = b_2/0.260 \qquad (2.5.6m)$$

The method was demonstrated for the systems containing paraffins.

2.5.7 THE METHOD OF SPEAR, ROBINSON AND CHAO [85]

The Redlich-Kwong equation of state was used to calculate critical properties. The following combining rules were used:

$$a = a_{11}\, x_1^2 + 2\, a_{12}\, x_1\, x_2 + b_{22}\, x_1^2 \qquad (2.5.7a)$$

$$b = b_{11}\, x_1^2 + 2\, b_{12}\, x_1\, x_2 + b_{22}\, x_2^2 \qquad (2.5.7b)$$

The interaction parameters a_{12} and b_{12} were related to the pure component properties by the relations:

$$a_{12} = \theta\sqrt{a_{11}\, a_{22}} \qquad (2.5.7c)$$

$$b_{12} = \phi\sqrt{b_{11}\, b_{22}} \qquad (2.5.7d)$$

where θ and ϕ were treated as empirical parameters. Empirical adjustment was made on θ with the intention to improve the calculation of critical pressure. It was found that with the adjustment, an average error for critical pressure was 5.3%, among the 38 binary systems investigated, in which the following mixtures were included: paraffin-paraffin, paraffin-non paraffin hydrocarbon, hydrocarbon-non hydrocarbon and nonhydrocarbon-non hydrocarbon mixtures.

Certainly improvement was obtained when compared with $\theta = 1$ and $\phi = \dfrac{(b_1 + b_2)}{2\sqrt{b_1\, b_2}}$, which was the case as Redlich-Kwong originally adopted when they treated a_{12} as a geometric average and b_{12} as an arithmetic average of the pure parameters.

2.5.8 METHOD OF CHUEH AND PRAUSNITZ [86]

A correlation was proposed to express critical temperature of a mixture as a quadratic function of the surface fraction θ defined by:

$$\theta_i = \frac{x_i\, V_{ci}^{\,2/3}}{\Sigma\, x_i\, V_{ci}^{\,2/3}} \qquad (2.5.8a)$$

For a binary mixture,

$$T_C = \theta_1\, T_{C1} + \theta_2\, T_{C2} + 2\,\theta_1\,\theta_2\,\tau_{12} \qquad (2.5.8b)$$

where τ_{12} was a parameter characteristic of the 1-2 interaction.

A similar expression was used for the correlation of critical volume.

$$V_C = \theta\, V_{C1} + \theta_2\, V_{C2} + 2\,\theta_1\,\theta_2\, V_{12} \qquad (2.5.8c)$$

As for the critical pressure, the correlations of critical temperature and critical volume were coupled with the Redlich-Kwong equation of state with modifications.

The combining rules (2.4.2v), (2.4.2w), (2.4.2x) (2.4.2y) and (2.4.2dd) were used. Also, the following combining rule was used:

$$a_{ij} = \frac{\frac{1}{4}\left(\Omega_{ai} + \Omega_{aj}\right) R\, T_{Cij}^{1.5} \left(V_{Ci} + V_{Cj}\right)}{0.291 - 0.04\left(\omega_i + \omega_j\right)} \qquad (2.5.8d)$$

In these expressions, the following relationships were used:

$$\Omega_{bi} = 0.0867 - 0.0125\,\omega_i + 0.011\,\omega_i^2 \qquad (2.5.8e)$$

$$\Omega_{ai} = \left(\frac{R\,T_{Ci}}{V_{Ci} - b_i} - P_{Ci}\right) \frac{P_{Ci}\,V_{Ci}\left(V_{Ci} + b_i\right)}{\left(RT_{Ci}\right)^2} \qquad (2.5.8f)$$

where ω_i is the acentric factor of the pure components.

2.5.9 METHOD OF JOFFE AND ZUDKEVITCH [87]

The rigorously derived expressions of Redlich and Kister [84] for the existence of the critical state of a binary mixture was adopted. Instead of using the limiting slopes calculation, Joffe and Zudkevitch proposed a prediction method by solving simultaneously those two expressions with an equation of state, yielding the values of T_C, V_C and P_C of a binary mixture. The Redlich-Kwong equation was used, and the combining rules (2.5.7a) and (2.5.7b) were used.

The interaction parameters a_{12} and b_{12} were evaluated from the following procedures:

(1) The pseudocritical temperature and pressure values of Pitzer and Hultgren [88] were used to evaluate T_{C12} and P_{C12} by:

$$T_{Cm}^{2.5}/P_{Cm} = \sum_i \sum_j y_i y_j T_{Cij}^{2.5}/P_{Cij} \qquad (2.5.9\,a)$$

$$T_{Cm}/P_{Cm} = \sum_i \sum_j y_i y_j Y_{Cij}/P_{Cij} \qquad (2.5.9\,b)$$

(2) The evaluated values of T_{C12} and P_{C12} were used to establish a_{12} and b_{12} by

$$a_{ij} = 0.4278\, R^2\, T_{Cij}^{2.5}/P_{Cij} \qquad (2.5.9\,c)$$

$$b_{ij} = 0.0867\, R\, T_{Cij}/P_{Cij} \qquad (2.4.9\,d)$$

The critical loci for the systems carbon dioxide - n-butane, and carbon dioxide-ethane were studied. Improvement was achieved comparing with the results obtained by the limiting slopes method of Redlich and Kister [84].

A short-cut method was also used to calculate critical loci of binary systems as well as multicomponent systems. This short-cut method was a modification of the limiting slopes method of Redlich and Kister. They adopted the relation of Sutton [89] for the correlation of P_C and T_C

$$P_C = P_{C1}\, y_1^2 + P_{C2}\, y_2^2 + y_1 y_2/[A + B(y_1 - y_2) + C(y_1 - y_2)^2] \qquad (2.5.9\,e)$$

$$T_C = T_{C1}\, y_1^2 + T_{C2}\, y_2^2 + y_1 y_2/[D + E(y_1 - y_2) + F(y_1 - y_2)^2] \qquad (2.5.9\,f)$$

From these expressions, it followed that,

$$\left(\frac{dP}{dy_1}\right)_{y_1 = 1} = 2 P_{C1} - 1/[A + B + C] \qquad (2.5.9\,g)$$

$$\left(\frac{dP}{d y_1}\right)_{y_1 = 0} = -2 P_{C2} + 1/[A - B + C] \qquad (2.5.9\,h)$$

Given one reliable value of the critical pressure at one composition and the values of the terminal slopes, the equations (2.5.9 e) (2.5.9 g) and (2.5.9 h) were solved simultaneously for the three constants A, B and C. Hence the critical pressures for the whole composition range could be evaluated from this set of constants A, B and C. The same could be done for critical temperatures by evaluating D, E and F.

In 1969, Zudkevitch et al [90] used another modification of Redlich-Kwong equation of state for the calculation of critical locus. In this procedure, the parameters Ω_a and Ω_b were considered as temperature-dependent parameters, and were evaluated with saturated liquid density data of pure components. The combining rules used were:

$$a = \Sigma \Sigma x_i x_j a_{ij} \qquad (2.4.2\,x)$$

$$b = \Sigma x_i b_i \qquad (2.4.2\,v)$$

where $$a_{ij} = (1 - C_{ij}) \sqrt{a_i a_j} \qquad (2.4.2\,jj)$$

The parameter C_{ij} was evaluated by best fitting of vapor-liquid equilibrium data.

This modification has achieved improvement on the calculation of critical loci of binary mixtures. However, at temperatures above the critical temperature of a pure component the critical values of Ω_a and Ω_b are used. In the calculation of critical locus of a binary mixture, most of the time it occurs that the locus goes in between the two critical temperatures of the pure components. Thus the critical temperature of a mixture is often higher than the critical temperature of one of the pure components. If the critical values of Ω_a and Ω_b are used all the time for this component, the idea of temperature-dependence of the Ω_a, Ω_b values is sacrificed partially. If the practice of considering Ω_a and Ω_b as temperature-dependent is successful, it would be logical to consider that better results could be obtained if Ω_a and Ω_b are also considered temperature-dependent at temperatures above the critical values. This modification has been adopted in this research and will be discussed later in Chapter Four.

CHAPTER 3

EXPERIMENTAL INVESTIGATION OF PHASE BEHAVIOR OF SYSTEMS CONTAINING NITROGEN, METHANE, ETHANE AND PROPANE

The phase behavior of mixtures containing nitrogen and propane has been reported only partially, and it is desirable to investigate experimentally, as has been discussed in Chapter 1. A preliminary study about the liquid phase inversion, the partial miscibility, the vapor-liquid equilibrium, and the critical region of these mixtures has been made, and a scheme has been designed to investigate experimentally the vapor-liquid equilibrium, and partial miscibility of the liquid phase for the binary and ternary systems containing nitrogen, methane and propane, at 114.05, 118.32 and 122.24 K. Liquid phase inversions of the systems nitrogen-ethane and nitrogen-methane-ethane occur at lower temperatures and has been experimentally investigated separately. According to the scheme, the critical loci of these mixtures are to be investigated through the study of prediction methods. The details of the experimental investigation will be discussed in the following sections.

3.1 APPARATUS

A forced-recirculation type apparatus was used in this investigation. The vapor phase was recirculated past a closed loop and through the liquid phase until the two phases reached equilibrium. The whole apparatus included the feeding system, the equilibrium cell, the recirculation loop, the sampling system, the analysis apparatus, the cryostat, the temperature and pressure measurement devices, and the temperature-controlling system. The experimental apparatus is shown in Figure (3.1a), and a schematic flow diagram is shown in Figure (3.1b).

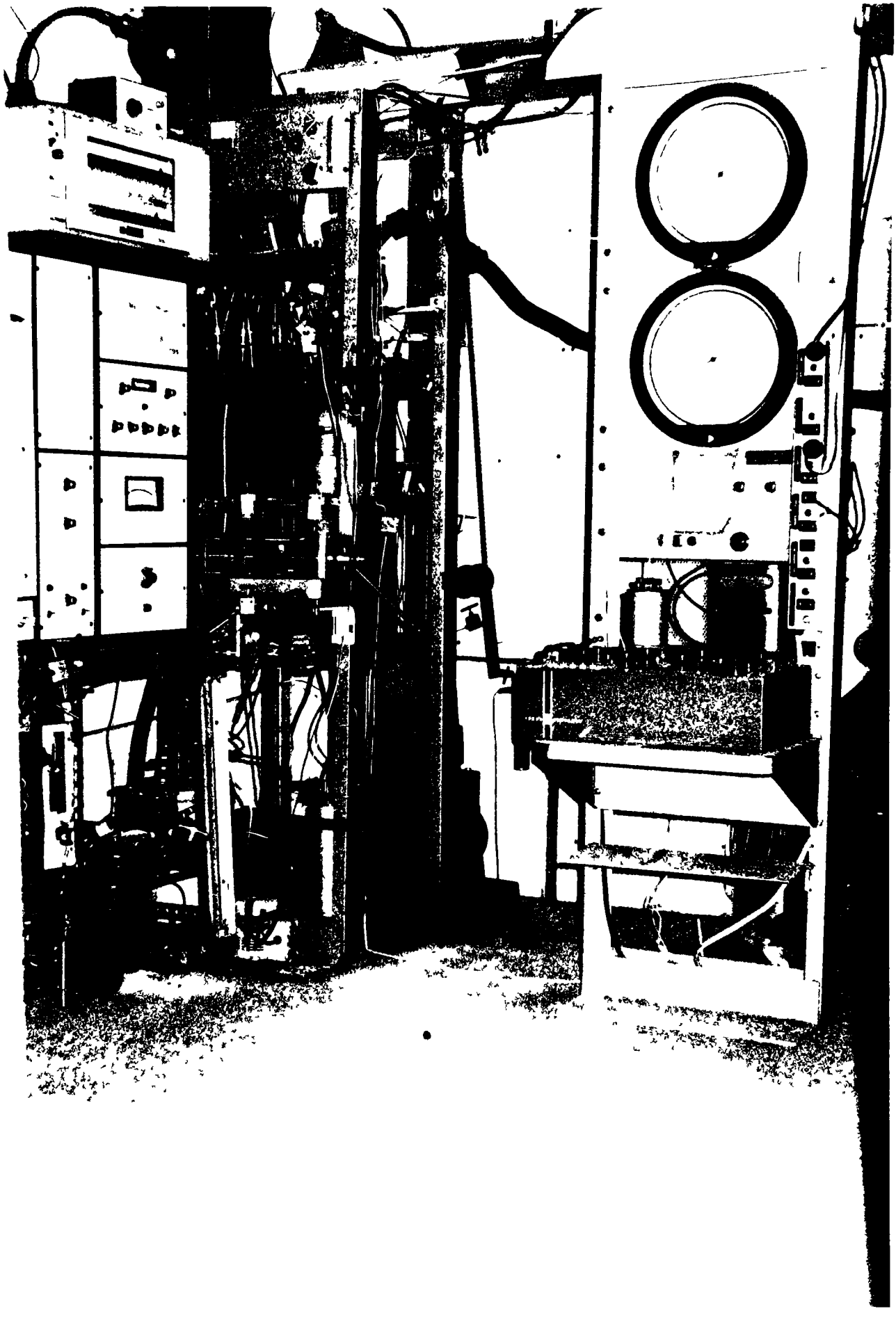
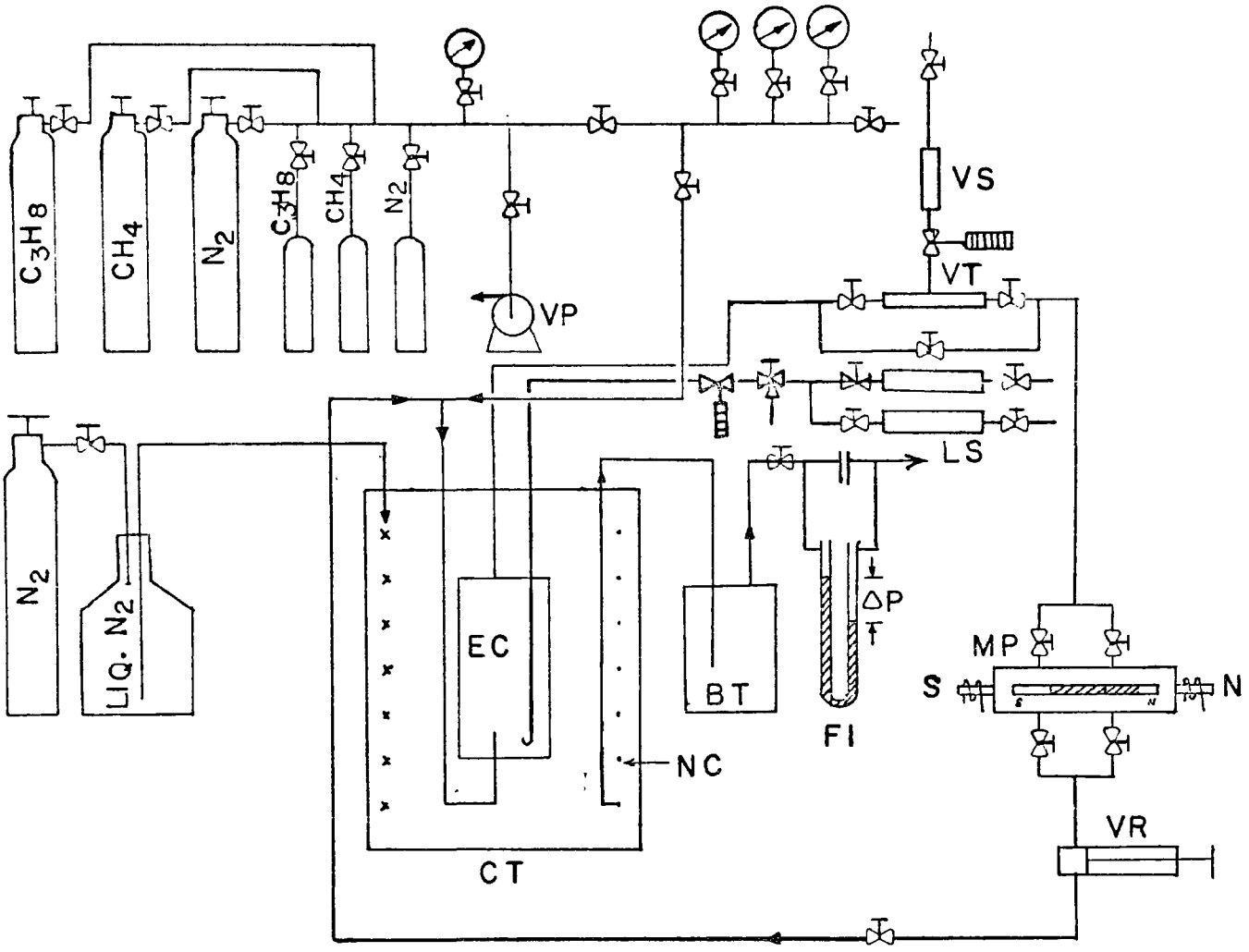


Figure 3.1a The Experimental Apparatus



BT	BUFFER TANK	MP	MAGNETIC PUMP
CT	CRYOSTAT	NC	NITROGEN VAPORIZATION COIL
EC	EQUILIBRIUM CELL	VP	VACUUM PUMP
FI	FLOW INDICATOR	VR	VOLUME REGULATOR
FR	FREON COMPRESSOR	VS	VAPOR SAMPLING BULB
LS	LIQUID SAMPLING BULB	VT	VAPOR SAMPLING TUBE

Figure 3.1b A Schematic Flow Diagram of the Apparatus

THE FEEDING DEVICE

Two vacuum pumps were connected to the main feeding line. A calibrated pressure gage, three tanks of pure gases, and three empty mixing-tanks were also parallelly connected. One of the vacuum pump was a Welch "dual-seal" vacuum pump for lower vacuum, and the other was another Welch "dual-seal" pump equipped with a diffusion pump, for high vacuum. The three tanks of pure gases were equipped with individual pressure regulators. The three mixing-tanks, one of 2-litre and two of 300-ml capacity, were used for the preparation of the feeding gas mixtures.

THE EQUILIBRIUM CELL

The equilibrium cell was made of a 100-ml Jerguson transparent gauge. The body was made of stainless steel, and was able to stand a pressure of 3000 psia at 100°F. It was tested that it could stand better than 1000 psia at cryogenic temperatures. Its visible glasses were both 6-$\frac{3}{4}$ inches long and $\frac{1}{2}$ inch wide. All fittings were made of stainless steel and were tested to be able to stand pressures greater than 1000 psia. The details of the equilibrium cell are shown in Figure (3.2), and a schematic diagram of the equilibrium cell and the cryostat is shown in Figure (3.3).

THE RECIRCULATION LOOP

The recirculation of the vapor phase was produced by the action of an electromagnetic pump. The circuit is shown in Appendix B. It contains three sections: the power supply section, the timing control section and the pumping section. The major part of the circuit is similar to that of a Flip-Flop circuit to produce a square wave-output. The action of the pump is within the range of

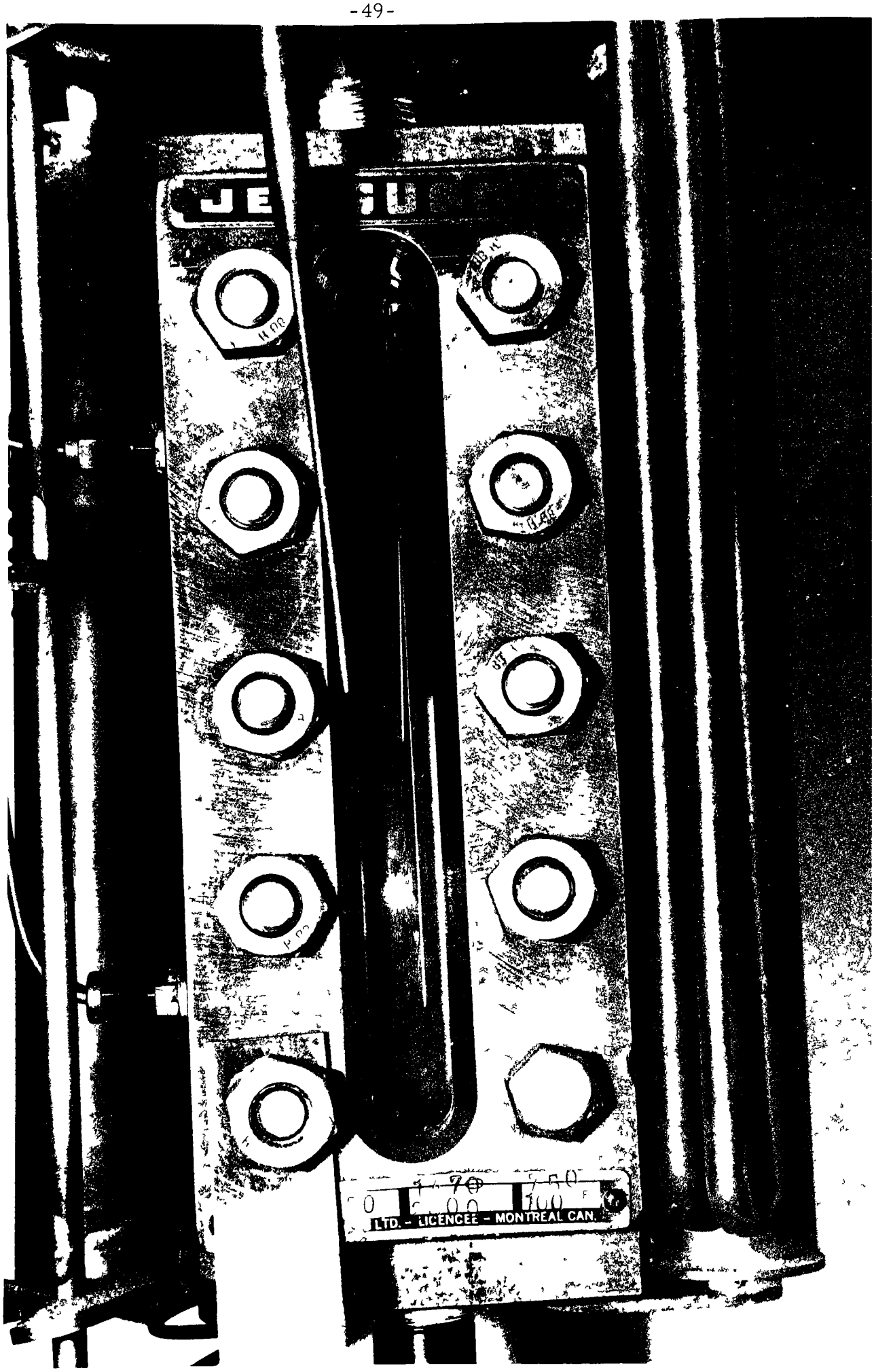


Figure 3.2 The Equilibrium Cell

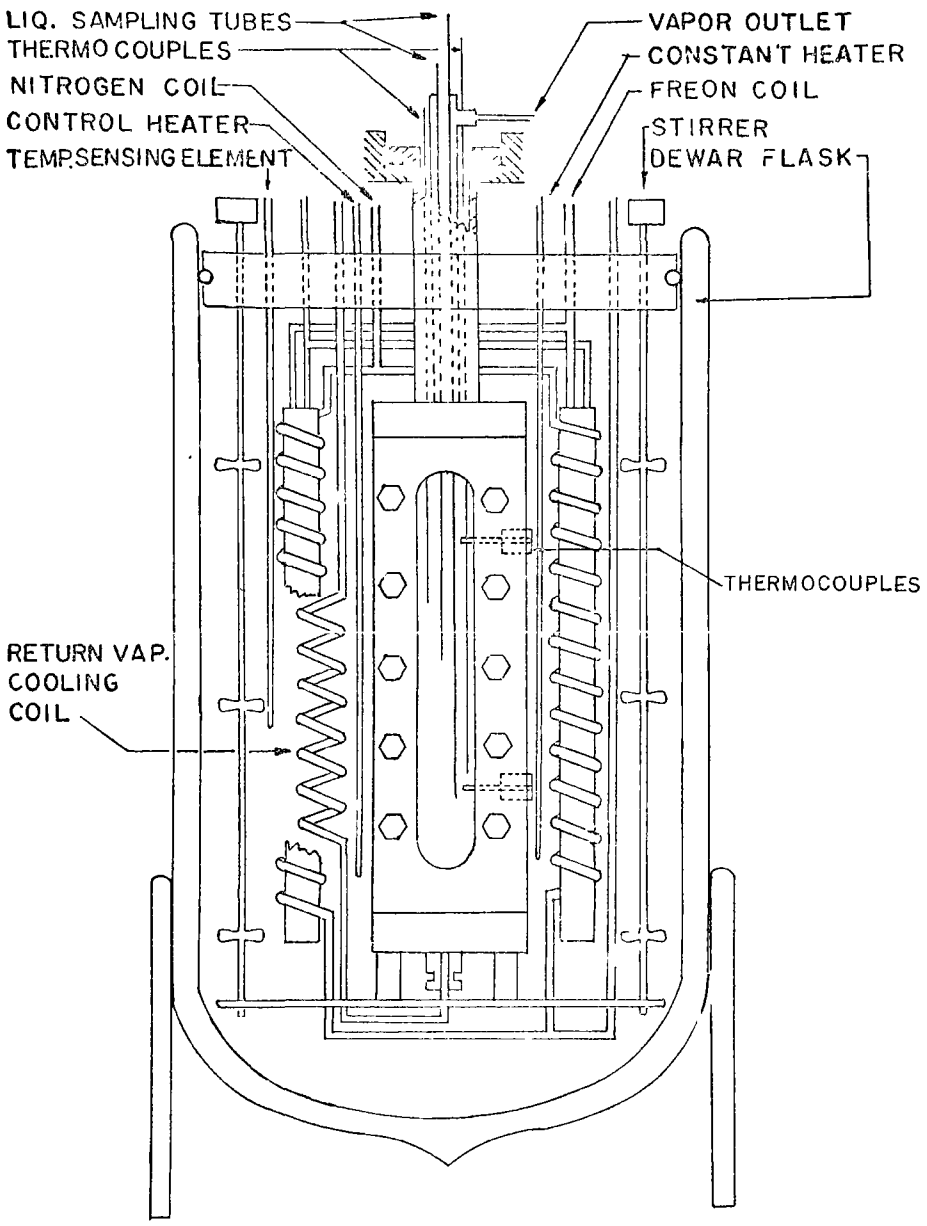


Figure 3 3 A Schematic Diagram of the Equilibrium Cell and the Cryostat

1.5 millisecond to 1 second per cycle, and can be adjusted through a variable resistance. A portion of the recirculation loop was in the form of a short coil. This portion was installed before the entrance into the equilibrium cell at its bottom. This part would bring the recirculating vapor phase to system temperature before it entered into the equilibrium cell.

THE SAMPLING SYSTEM

Vapor and liquid phases were sampled separately. In the case of two liquid phases in equilibrium with a vapor phase, all three phases were sampled separately. The vapor phase was entrapped in a sampling bulb of 2 cc capacity connected along the recirculating loop. Three more sampling bulbs were connected separately to three sampling tubes, which were made of 1/16" stainless steel tubing and installed in the equilibrium cell in such a way so that liquid samples at three different positions could be withdrawn. Evacuation facilities were connected to the sampling lines and a vacuum of 10^{-3} mm Hg could be ensured before a sample was taken. Between the equilibrium cell and the sampling bulbs, needle valves were installed so that only small samples were taken for analysis all the time.

THE CRYOSTAT

A Dewar flask of 18 - litre capacity was used as the cryostat. The Dewar flask was specially made such that there were two transparent strips on opposite sides to allow visibility within the equilibrium cell. Isopentane was used as the bath fluid, and at temperatures lower than 110 K, a mixture of isopentane and propane was used as the bath fluid. Two high power Hi Torque stirrers supplied by Cole-Palmer Company was used to ensure well mixing of the bath fluid. Two heating elements, one of 200 watts was used as a constant

heater: the other, of 100 watts, was connected to a temperature controller, to regulate the cryostat temperature to ± 0.03 K. The Thermotrol temperature controller, model 1053, was supplied by Hallikainen Instruments Company. The controller was capable of operating by anyone of the three modes: On-Off, Proportional or Proportional with Reset. The controller was set in the "Proportion with Reset" mode, in connection with a resistance type sensing element. The cryostat was equipped with two refrigeration coils. Liquid nitrogen was fed into the refrigeration coils, passed into a buffer tank and was vented into atmosphere under controlled rates to give desired degree of refrigeration.

THE ANALYSIS FACILITIES

The samples were analyzed with a gas chromatograph model GC 200/DIT supplied by the Micro-Tek Instruments Inc., in conjunction with a Laboratory Recorder, also supplied by the Micro-Tek Instruments Corporation. The details of sample analysis will be discussed later in this chapter.

THE PRESSURE AND TEMPERATURE MEASURING DEVICES

Three calibrated pressure gages supplied by Heise Bourdon Tube Co. Inc., were used. They cover pressure ranges of 200, 500 and 1000 psia, with 0.2, 0.5 and 1 psia subdivisions, respectively. Each had been checked with a dead-weight gage. At lower pressure range a mercury manometer was used to measure the system pressure, to ± 0.5 mm Hg. The temperature of the system was measured by two protected-type copper-constantan thermocouples, installed in the equilibrium cell. One thermocouple was located at the upper part of the equilibrium cell, the other was located at the lower part,

meant to measure the temperature of the vapor and liquid phases respectively. Measurements were made with a Leeds and Northrup K-3 potentiometer and a Tinsley SRI galvanometer. The uncertainties involved in the pressure and temperature measurements are believed to be $\pm$ 1 psi and 0.05 K respectively. The details of error analysis will be discussed later in this Chapter.

3.2 EXPERIMENTAL PROCEDURES

The apparatus was evacuated to lower than 10^{-2} mm Hg for over 24 hours, at room temperature. The equilibrium cell was then immersed into the cryostat, which was filled with isopentane. The cryostat was well insulated, and the top of the Dewar flask was appropriately covered, for the purpose of insulation and for the purpose of preventing evaporation of isopentane at the beginning of an experiment when the cryostat was under room temperature. Nitrogen gas under a pressure of 10 psig was used to force liquid nitrogen into the cooling coils of the cryostat, and the temperature of the system was lowered graduately as the liquid nitrogen evaporated. The rate of evaporation of the liquid nitrogen was controlled in the buffer tank. The control was manipulated by a valve, and the rate was indicated by a mercury manometer installed with a venturi.

About 4 to 6 hours were needed to bring the temperature of the cryostat to the operation temperature of this work, approximately to 115 K. The system temperature was checked from time to time by taking readings on the potentiometer. When it was indicated that the temperature was within a few degrees of the desired temperature, the temperature controller was turned on. The pure gases were charged into the equilibrium cell one at a time, with the heavy component first and the light component last. As the saturation pressure was reached, liquified gas would be obtained in the equilibrium cell. It was always arranged that approximately 50% of

the equilibrium cell was filled with liquid. When the desired temperature was reached indicated by the controller and by the thermocouple measurements, the electromagnetic pump was activated and the vapor phase was withdrawn from the cell. The vapor phase was passed through the vapor sampling tube, the volume regulator, the electromagnetic pump, the coil passage and was returned to the equilibrium cell bubbling through the liquid phase. The temperature of the vapor phase was raised in the path outside of the cryostat, but it was brought back to the system temperature in the coiling passage before returning to the equilibrium cell. From repeated experimentation, it was established that 4 hours of continuous recirculation was long enough for the establishment of equilibrium. If two liquid phases were in equilibrium with the vapor phase, two extra hours were allowed for recirculation. One hour was allowed for the phases to settle after the recirculation had been stopped. The vapor sample was entrapped in the vapor-sampling tube and could be analyzed at the end of a run. Sampling of a liquid phase was carried out by manipulating the needle valve which allowed the sample to be sucked into the evacuated sampling tube. A smaller amount was first sampled and discarded and was used to purge the sampling tube and the connecting line. Then about 5 to 10 minutes were allowed to take another sample. The sampling tubes were warmed by hot air streams to ensure well mixing of the gases inside prior to analysis. If the system pressure dropped slightly due to sampling, the hand-operated volume regulator was used to maintain the system pressure.

The complete time required for one experimental point was approximately 7 hours, including the preparation of gas mixtures and the analysis of samples. In the case of vapor-liquid-liquid equilibrium, an extra 2-$\frac{1}{2}$ hours were required. To prepare the apparatus

for a new system, 2 days were required, including the procedure of establishing the desired temperature for operation.

The operations of temperature controlling and sample analysis were comparatively more complicated than the other operations and both will be discussed separately in the following sections.

THE CONTROL OF TEMPERATURE

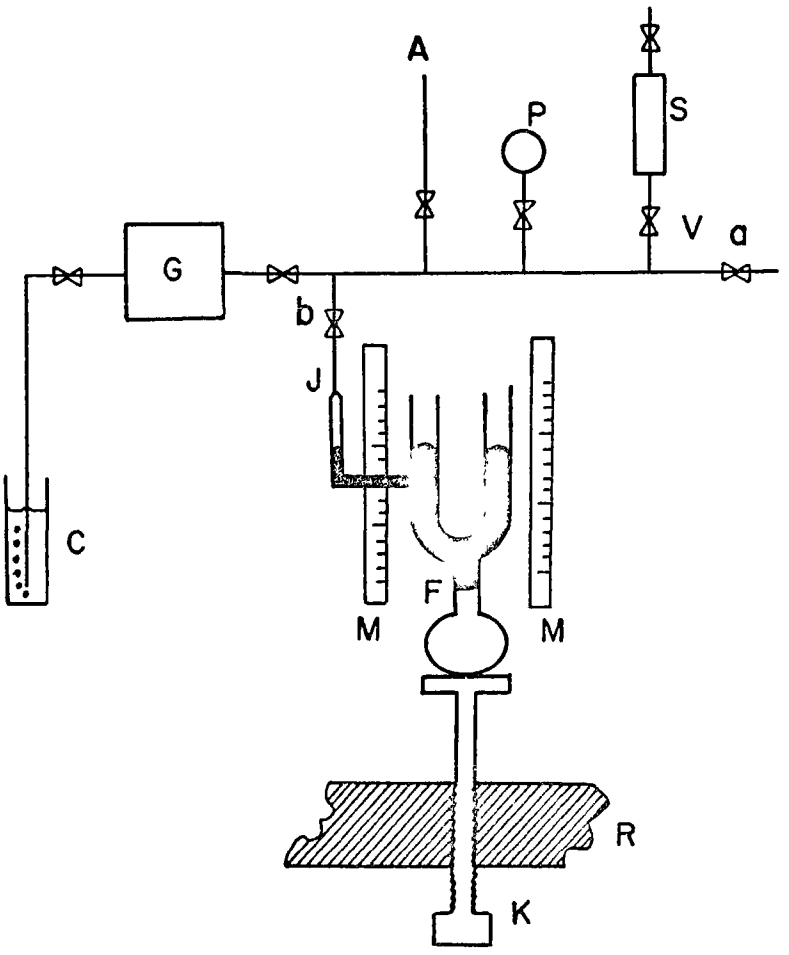
As described on page 52, the temperature of the cryostat was controlled by a Thermotrol temperature controller, model 1053, supplied by Hallikainen Instruments Company in conjunction with a sensing element which was a resistence thermometer type, model 1358-As3 and was also supplied by the same company. The Thermotrol was capable to working in either of the three modes: On-Off, Proportional, or Proportional with Reset. A complete description of the operation was given by the instrumental manual, which was closely followed to obtain maximum performance of the instrument. The On-Off mode was used to search the desired operation temperature. The Proportional mode was used to adjust the "gain" to maximum value possible without producing "hunting", which was indicated by the larger fluctuation of the time cycle modulation of heat output. The function of Reset was to reduce proportional offset to 1% of its value. When a desired temperature had been established, the Thermotrol was operated under the "Proportional with Reset" mode.

METHOD OF ANALYSIS

Analyses of samples were carried out by gas chromatography. A Micro-Tek gas chromatograph, model GC 200/DIT supplied by the Micro-Tek Instruments Inc., was used in conjunction with a

Micro-Tek Laboratory Recorder. The gas chromatograph was operated with a 4-filament hot wire thermal conductivity detector under the condition of 200°C and 200 ma of current. A 4-ft. long and ¼-in. diameter column packed with Porapak Q of 80-100 mesh in an oven of 65°C was used, together with helium as the carrier gas at a rate of 85 cc per minute at 60 psig pressure. A 7-port sampling valve with a 0.5 ml sampling loop supplied by Micro-Tek Instruments Inc., was operated in an oven controlled at 35°C. The gas chromatograph was operated in conjunction with a Westronic Recorder, of one millivolt span, supplied also by the Micro-Tek Instruments Inc.

As shown in the schematic diagram in Figure (3.4), the sampling manifold was built of $\frac{1}{8}$" O.D. stainless steel tubings and Autoclave high pressure valves. The unit consisted of the sampling tube S, a precision pressure gage P, the gas chromatograph G, a vacuum system A, a bubble counter C, and a mercury manometer F. A small sample was first taken to purge the evacuated manifold and the auxilliary parts. When a sample was collected in the sampling tube S, the valve was opened to the evacuated manifold. The pressure was shown on the pressure gage, usually about 35 psia. The sample was passed to the evacuated sampling loop in the gas chromatograph, and the excess was vented through the bubble counter C into the atmosphere. When the bubble counter gave 20 bubbles, valve "V" from the sampling tube was closed and valve "b" to the mercury manometer was opened. The excessive pressure in the unit was released through the mercury manometer until 765 mm Hg. This procedure was used to ensure all samples, including calibration runs, were of the same volume of 0.5 ml under the same pressure of 765 mm Hg. Of course, in some cases when the system pressures were lower than atmospheric, this method was not applied. In those



S	SAMPLING BULB	J	GLASS-METAL JOINT
V	VALVES	M	SCALES
P	PRESSURE GAGE	F	MERCURY MANOMETER
A	TO VACUUM	R	SUPPORT
C	BUBBLE COUNTER	G	GAS CHROMATOGRAPH
K	SCREW		

Figure 3.4 A Device to Maintain Constant Pressure in the Sampling Loop

cases, the system was purged with the gas mixture for three times before analysis was performed.

THE PHENOMENON OF LIQUID PHASE INVERSION

In the experimental investigation of liquid phase inversion, the cryostat was initially maintained at 113.7 K (-255°F). Ethane and methane gases were introduced into the system and a homogeneous liquid mixture was formed in the equilibrium cell. The nitrogen gas was gradually admitted and two liquid phases were formed. The temperature of the cryostat was lowered less than 0.2 K by controlling the evaporation rate of liquid nitrogen in the cooling coils. Then it was observed that the recirculated vapor, which was condensed before re-entering the cell, rose slowly in the form of large bubbles. The speed was so slow that bubbles accumulated. When the bubbles broke, the positions of the two liquid layers exchanged, as shown in Figure (3.13), in which the sequence of the exchange of positions was shown.

This liquid phase inversion was observed for the ternary system N_2 - C_1 – C_2, in the temperature range of 111.72 K (-258.8°F) to 113.67 K (-255.4 °F). The recorded values of temperature, pressure and compositions of both liquid phases are presented in Table (3.15). It should be mentioned that the analyses of the compositions were very difficult due to the fact that only small amount of samples were taken so that the total composition could be maintained fairly constant before and after the liquid phase conversion took place.

For the binary system nitrogen-ethane, the liquid phase inversion took place at 109.1 K (-263.6° F), and the numerical values are also recorded in Table (3.15). It should also be mentioned

here that the liquid phases did not always inverse thoroughly. In many times, there was a small portion of the original top layer left behind and stayed at the top while it should be at the bottom after the phase inversion. This is due to the fact that the densities of the two liquid phases are close to each other and hence a complete separation may not be obtained. A detailed discussion will be given in the "Discussion of Results".

3.3 MATERIALS

The pure gases of research grade used in this investigation were supplied by Matheson of Canada Limited, Whitby, Ontario. Their purities are listed below:

Gas	Minimum Purity (mole %)
Nitrogen	99.999
Methane	99.65
Ethane	99.9
Propane	99.99

These gases were used without further purification. No detectable impurities in these gases were shown from the results of the gas chromatograph.

3.4 ERROR ANALYSIS

In the experimental measurement of phase equilibria, the major part of error is contributed by the measurement of temperature, pressure, and composition.

ERROR IN TEMPERATURE MEASUREMENT

The accuracy of the temperature measurement is estimated to be ± 0.03 K. The estimation is based on the calibration of temperature against vapor pressure of methane. The experimental measurements of methane vapor pressure were compared with the smoothed data of Armstrong et al. [133]. The average absolute deviation was 0.02 K. The comparison is shown graphically in Figure (3.14). In this investigation, two thermocouples were employed in the measurement of system temperature, one for the vapor and one for the liquid. When the positions of these two thermocouples were exchanged, the calibration showed an additional average absolute deviation of 0.01 K. It is therefore estimated that the accuracy of the temperature measurement is ± 0.03 K. The calibration curve of thermocouple number 2 is shown in Appendix D.

ERROR IN PRESSURE MEASUREMENT

The accuracy of the Heise Gages is 0.1% of full scale. In this investigation, a 500 psia gage was used for the measurement between 150-450 psia; a 200-psia gage was used for the measurement between 30-150 psia; and a 1000-psia gage was used for the measurements of a few points between 450-490 psia. Hence the major portion of the data is within the precision of (0.1%) x 500 psia) 0.5 psia; a minor portion of the data is within (0.1% x 200 psia) 0.2 psia; and some points are within (0.1% x 1000 psia) 1 psia. Therefore the precision of the pressure measurement is estimated to be within 0.1% of the values. For a few points the pressures were below 30 psia, a mercury manometer was used, and the precision is estimated to be 1 % of the pressure value. Tests with a dead-weight gage were performed and the results confirmed that the accuracy given by the Heise Gage manufacturer were reliable.

ERROR IN CONCENTRATION MEASUREMENT

The concentration error is estimated by the reproducibility of the calibration curves. The responses of the gas chromatograph were calibrated against known synthetic samples. The peak area and peak height responses were compared and it was found that the peak height responses were simpler and they yielded better reproducibility. The calibration curves were plots of composition ratio against peak height ratio as well as reciprocal ratios and absolute quantities so that the whole concentration range could be covered.

The synthetic samples were blended in a blending unit. The mixture composition was determined volumetrically and gravimetrically.

In the gravimetrical determination, an aluminum bottle of 300 cc and 220 gm. was used to prepare samples under a total pressure of approximately 2 atmospheres. An analytical balance with accuracy better than 0.1 mg was used for weight measurements. The bottle was warmed and cooled a few times to ensure good mixing of the gases inside.

In the volumetric determination, gases were forced into the sampling bottle by a mercury manometer, the mercury level of which could be varied by raising or lowering the mercury reservoir and hence forced the gases into the bottle. The partial pressure of each component was recorded, and the composition of the mixture was calculated according to the recorded partial pressures.

It was found that both methods agreed with each other very well. Hence the latter method was usually employed, due to its simplicity. However, when the partial pressures of the components were close to each other and the effect of gas diffusion might be influential, the latter method was used for double checking.

The graph in Appendix B shows one of the calibration curves from which the reproducibility was estimated to be 1%.

However, these estimations of errors are meaningless when sampling problems are encountered. Experience from this experiment reveals that in this equipment the sampling of vapor has no problem at all, while the sampling of the liquid phase creates plenty of difficulties, especially in the vapor-liquid-liquid equilibrium experiments. In those cases, the withdrawal of the sample was made very slowly and the volume regulator was operated at the same time to maintain the system pressure constant so as to avoid the least possibility of disturbing the equilibrium.

3.5 EXPERIMENTAL RESULTS

Experiments were carried out according to the designed scheme and the measurements were made for the following systems.

System	Equilibrium	Isothermal condition (K)
Nitrogen-Propane	Vapor-Liquid	114.05, 118.32, 122.24
	Vapor-Liquid-Liquid	114.05, 118.32, 122.24
Methane-Propane	Vapor-Liquid	114.05, 118.32, 122.24
Nitrogen-Methane-Propane	Vapor-Liquid	114.05, 118.32, 122.24
	Vapor-Liquid-Liquid	114.05, 118.32, 122.24
Nitrogen-Methane-Ethane	Liquid phase Inversion	111.32 - 113.67

Numerical data are shown in Tables 3.1 - 3.6

BINARY SYSTEM NITROGEN-PROPANE

The P-T liquid-liquid locus is shown in Figure (3.5), together with the data by Schindler, Swift and Kurata [13]. This locus was measured in order to establish confidence of the apparatus for the measurement of pressure and temperature for the system containing nitrogen and propane. Also, these measurements served as a preliminary study, which helped in the selection of isothermal conditions for later experiments. It was found that the cryostat could only be operated conveniently at temperatures above 110 K when isopentane was used as bath fluid.

The vapor-liquid-liquid equilibrium compositions at saturation pressures are presented in Figure (3.6). Two data points are obtained from extrapolation of the data by Schindler, Swift and Kurata[13], and are compared with the experimental measurements of this work. As it is shown in Figure (3.6), some discrepancy is observed. Even though the discrepancy is not serious, it shows that extrapolation of data is not always reliable.

The vapor-pressure curves [133] for the liquid region which is rich in propane at the three isothermal conditions are shown in Figure (3.7). The curves are shown until the solubility line, at which two liquid phases separate from each other and are in equilibrium with the vapor phase. The vapor phase compositions are more than 99.94% in nitrogen and are not shown in Figure (3.7).

The numerical values of the data are presented in Tables (3.1), (3.2), (3.3), (3.4), and (3.5).

BINARY SYSTEM METHANE-PROPANE

Vapor-liquid equilibrium data for the binary system Methane-Propane are shown in Figure (3.8). Equilibrium data were determined

at the three isothermal conditions. The vapor phases are virtually all methane, and are included in Figure (3.8). The data of Wichterle and Kobayashi [100] at higher temperatures and the data of Wilson [121] at lower temperature are included for comparison in Figure (4.16). As will be shown later in Chapter 4, a consistent trend is indicated from these sets of data. The numerical values of the data are presented in Table (3.6), (3.7), and (3.8).

TERNARY SYSTEM NITROGEN-METHANE-PROPANE

The vapor-liquid equilibrium data and vapor-liquid-liquid equilibrium data are presented graphically in Figures (3.9), (3.10), and (3.11). Partial miscibility existed in the nitrogen-propane binary and the solubility curve for the nitrogen-methane-propane extended to the plait point, the composition of which will be estimated in Chapter 4. Experimental tie-lines were determined. The binodal curves obtained at the three temperatures indicate a gradual change in shape only in the vicinity of the plait points. The numerical values of the vapor-liquid equilibrium data and the vapor-liquid-liquid equilibrium data are presented in Tables (3.9) to (3.14). The amount of propane in all vapor phases is generally very small. Figure (3.12) depicts the vapor phase compositions of the vapor-liquid equilibrium data at three isothermal conditions.

TERNARY SYSTEM NITROGEN-METHANE-ETHANE

Liquid phase inversion for the systems nitrogen-ethane, and nitrogen-methane-ethane was investigated. The conditions of the occurrence of liquid phase inversion are presented in Table (3.15), which includes the conditions of temperatures, pressures, and compositions.

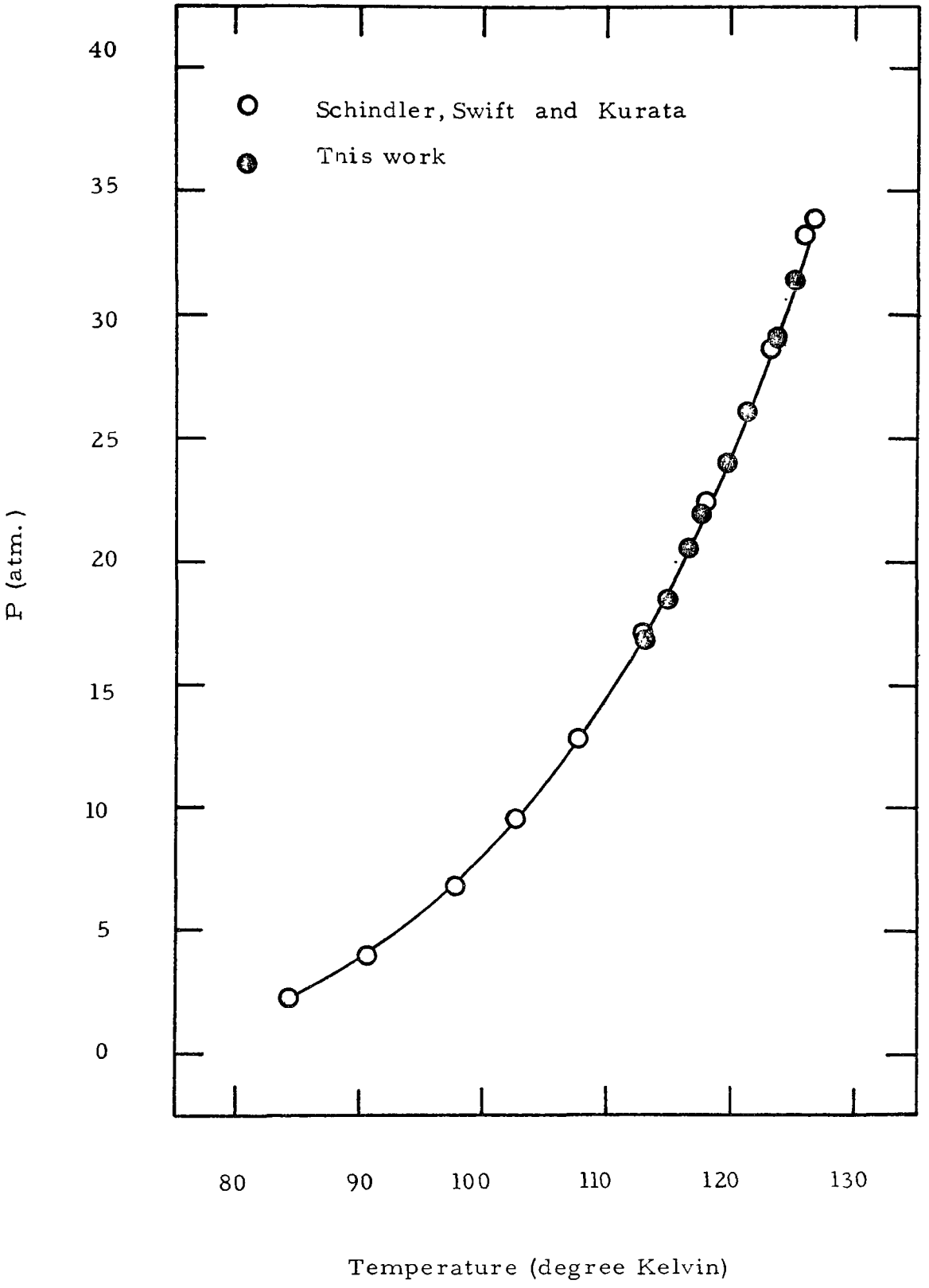


Figure 3.5 The P-T Curve of Vapor-Liquid-Liquid Equilibrium for the System Nitrogen(1)-Propane(2)

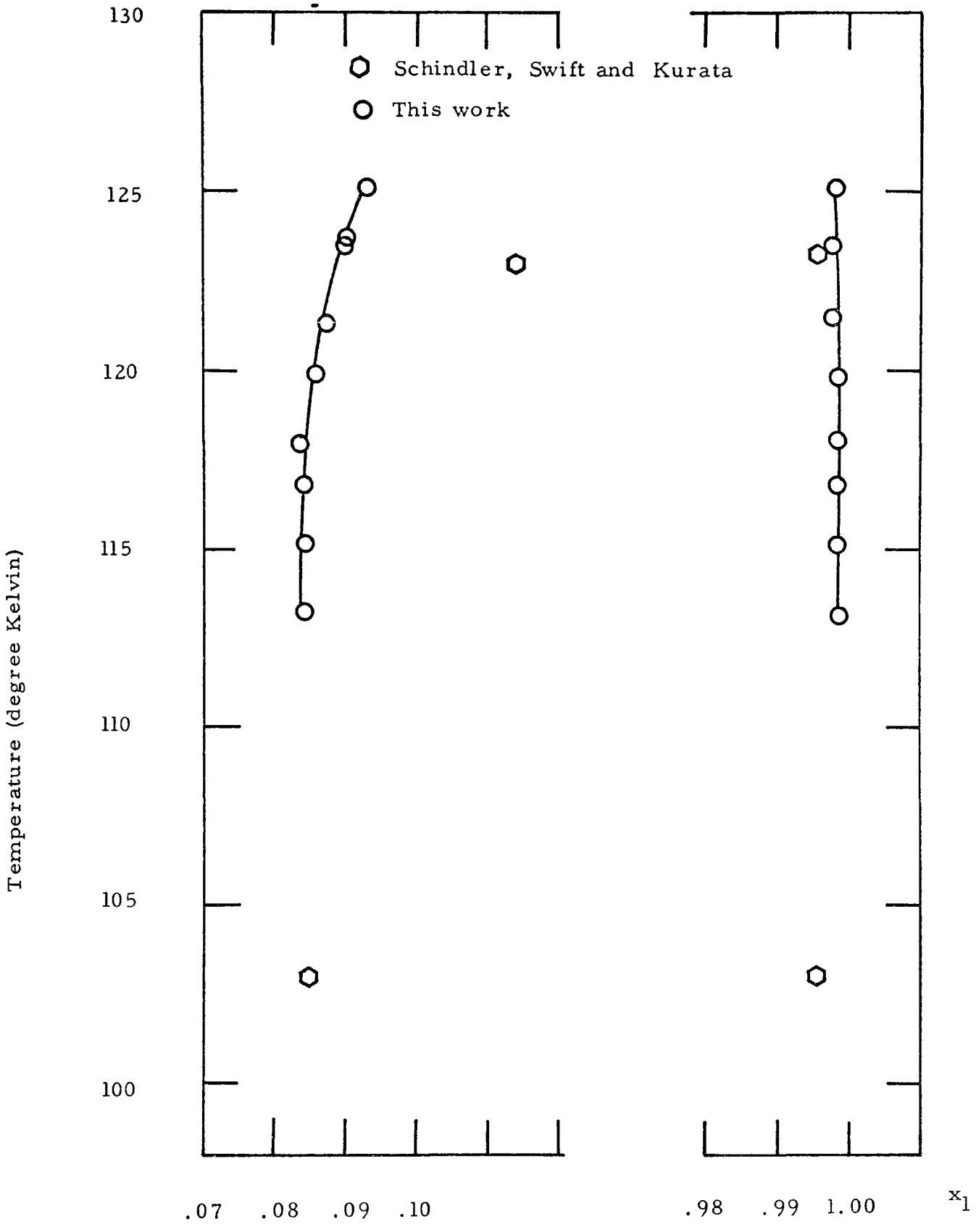


Figure 3 6 The T-x Curves for Vapor-Liquid-Liquid Equilibrium for the System Nitrogen(1)-Propane(2)

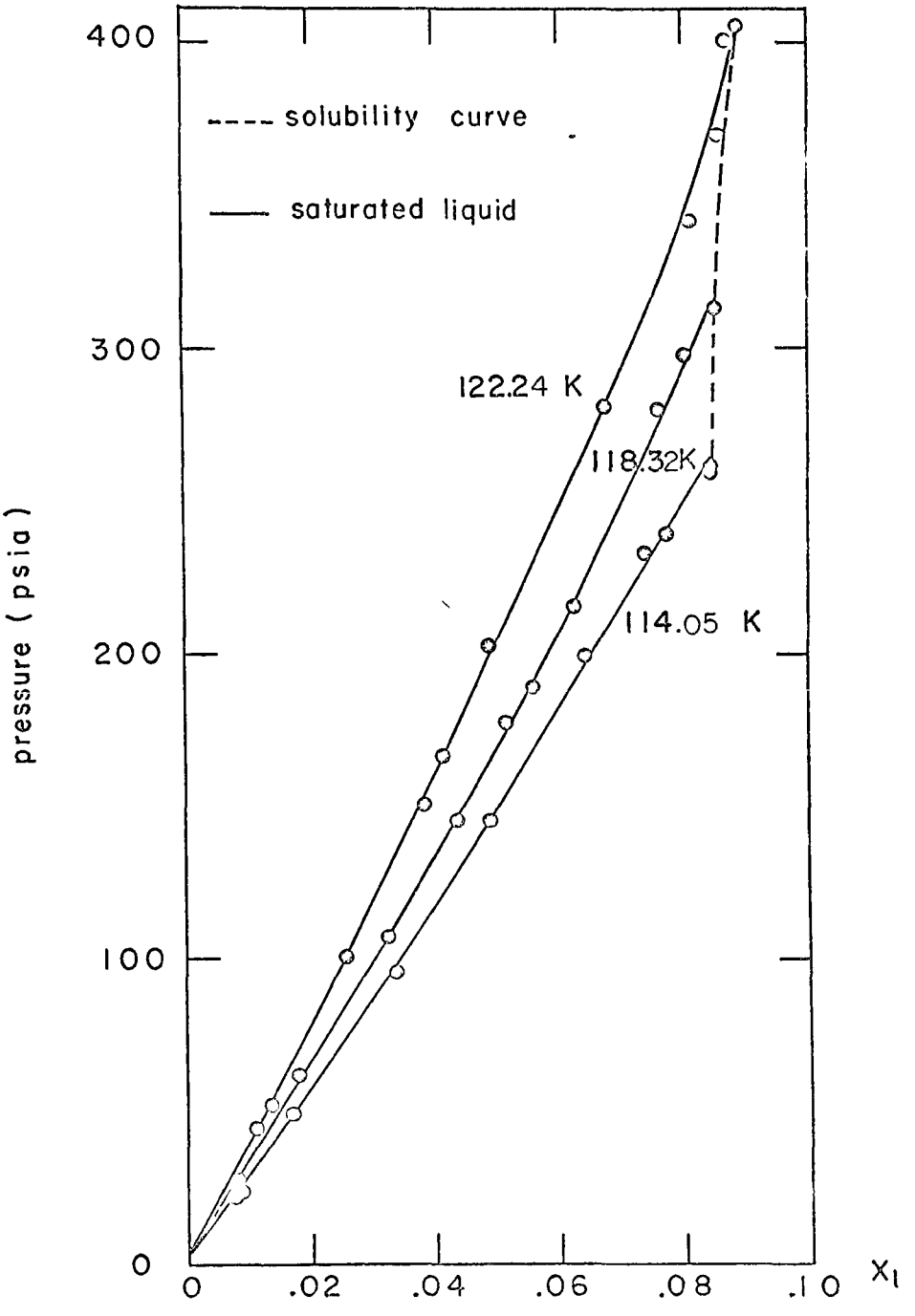


Figure 3 7 The Vapor-Pressure Curves for the Liquid Region which is Rich in Propane for the System Nitrogen(1)-Propane(2)

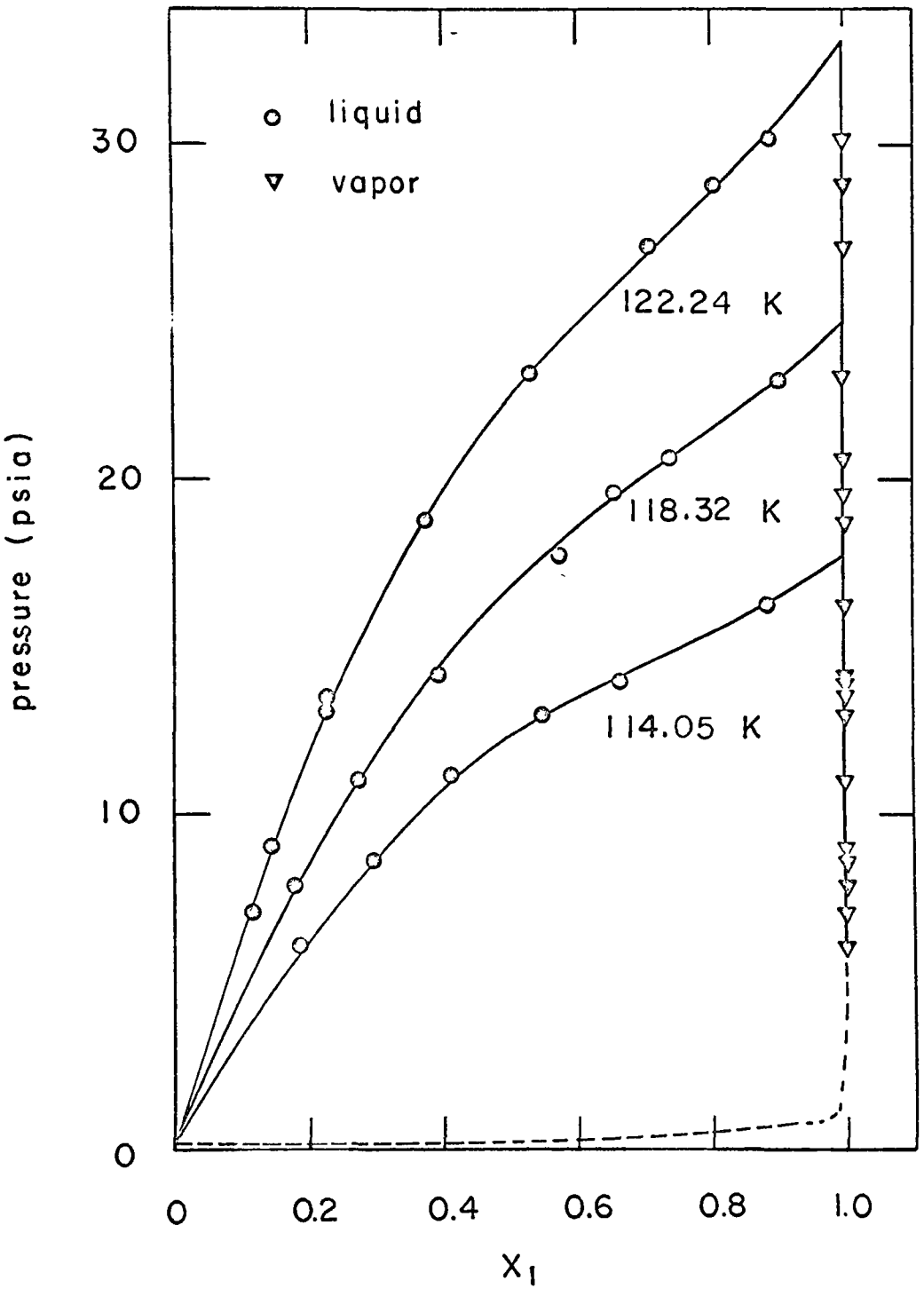


Figure 3.8 Vapor-Liquid Equilibriu n for the System Methane(1)-Propane(2)

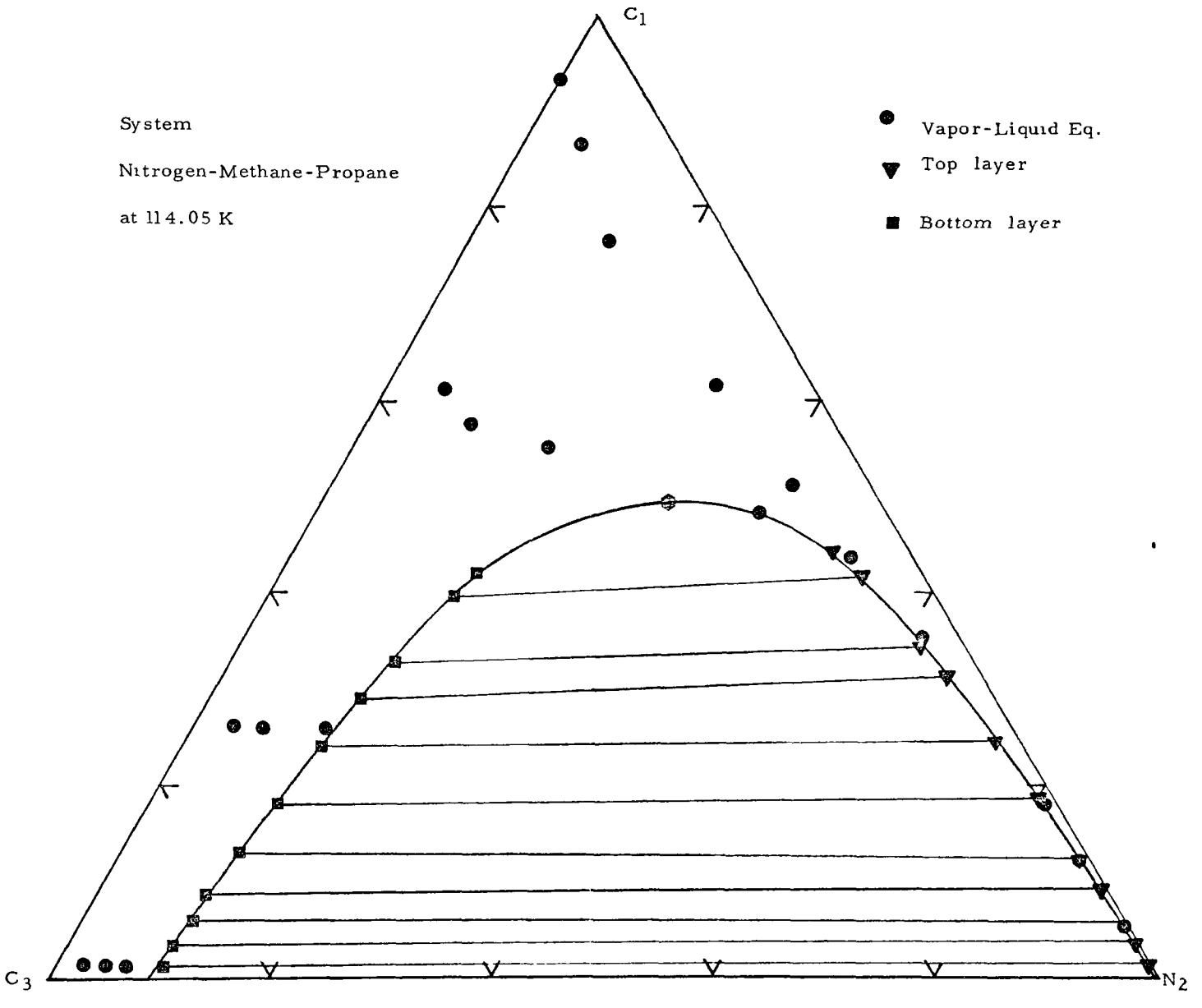


Figure 3.9 Liquid Compositions of Vapor-Liquid Equilibrium and Vapor-Liquid-Liquid Equilibrium for the System Nitrogen(1)-Methane(2)-Propane(3) at 114 05 K

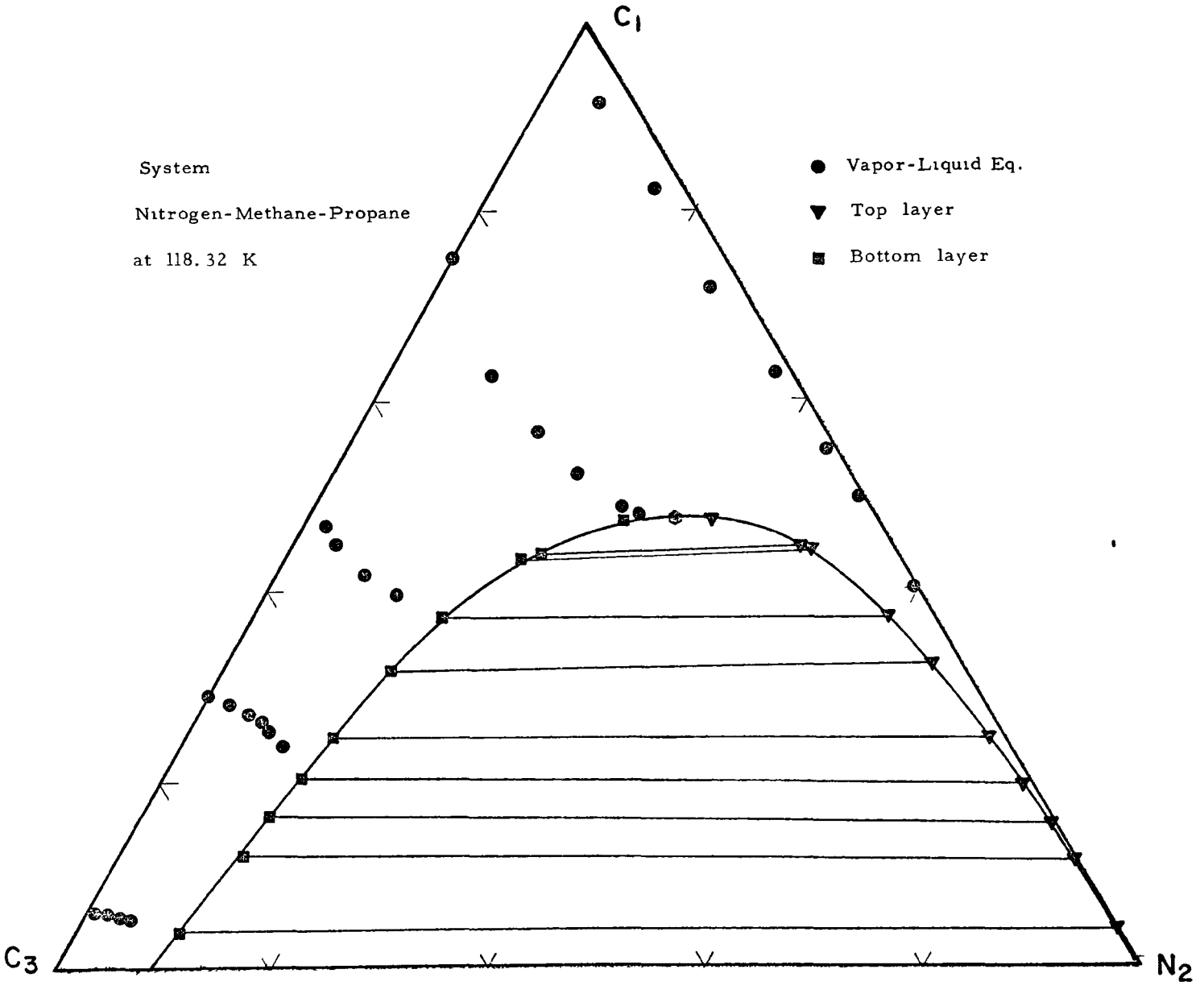


Figure 3 10 Liquid Compositions of Vapor-Liquid Equilibrium and Vapor-Liquid-Liquid Equilibrium for the System Nitrogen(1)-Methane(2)-Propane(3) at 118 32 K

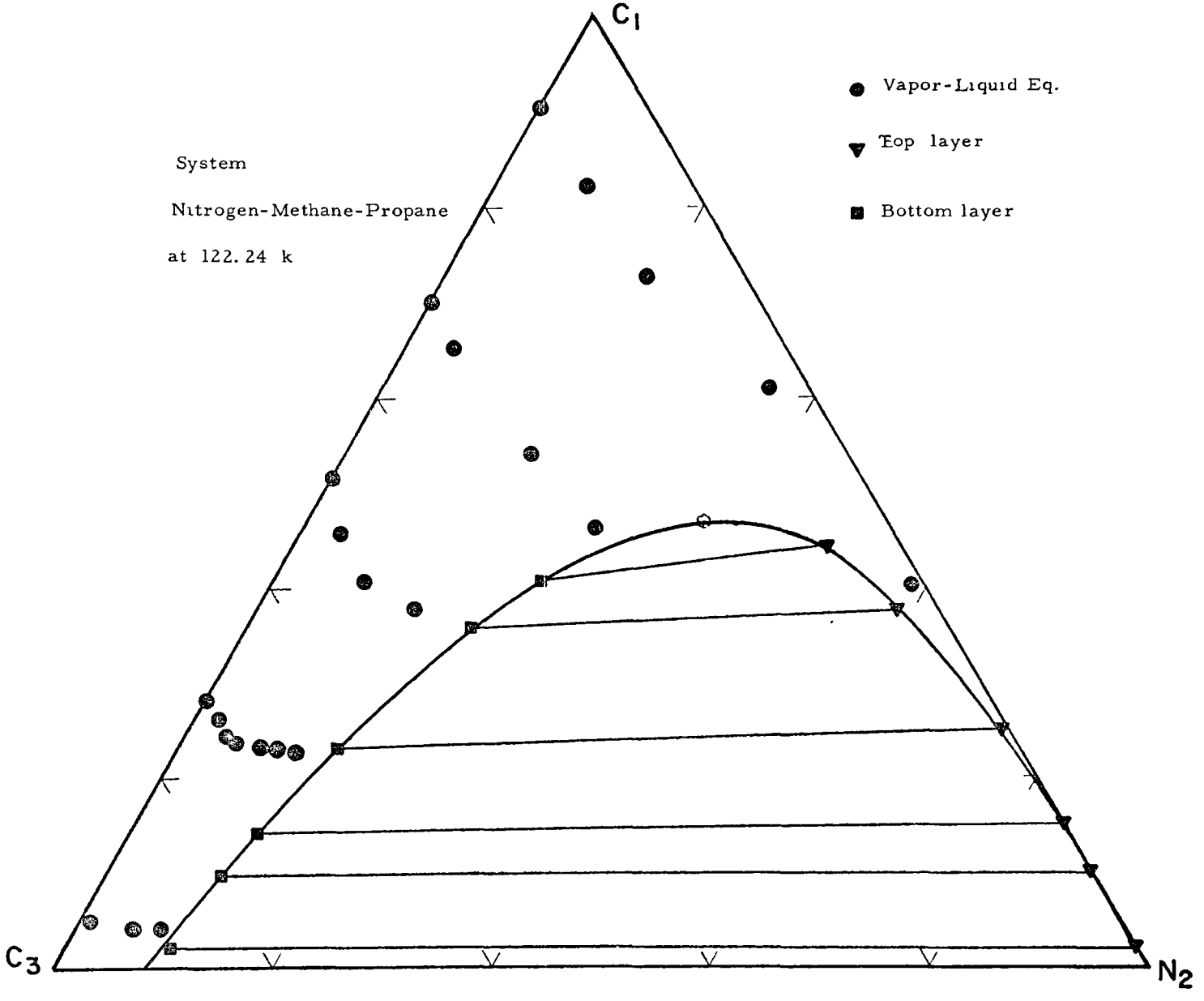


Figure 3.11 Liquid Compositions of Vapor-Liquid Equilibrium and Vapor-Liquid-Liquid Equilibrium for the System Nitrogen(1)-Methane(2)-Propane(3) at 122.24 K

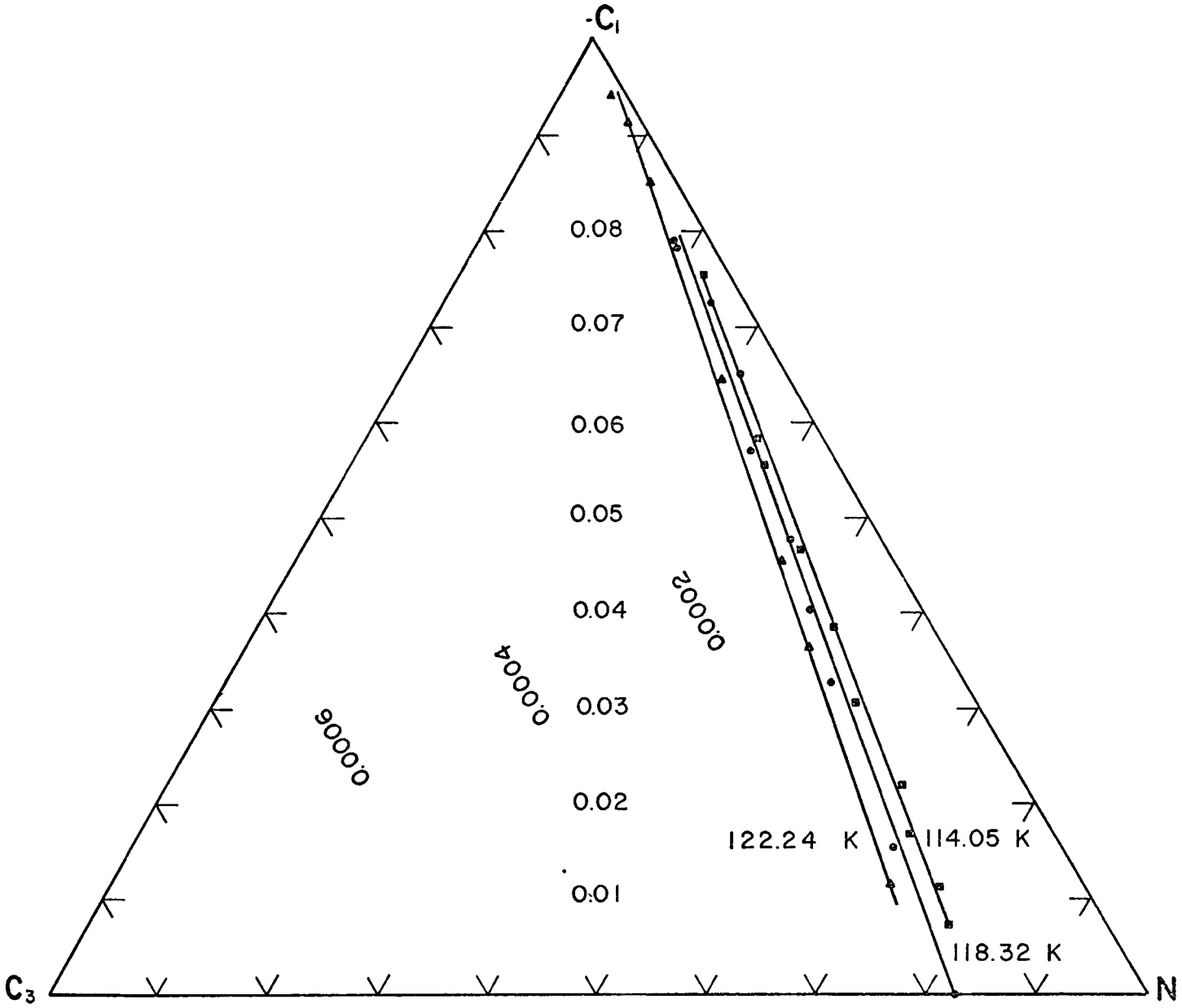


Figure 3.12 Vapor Phase Compositions of Vapor-Liquid Equilibrium for the System Nitrogen(1)-Methane(2)-Propane(3).

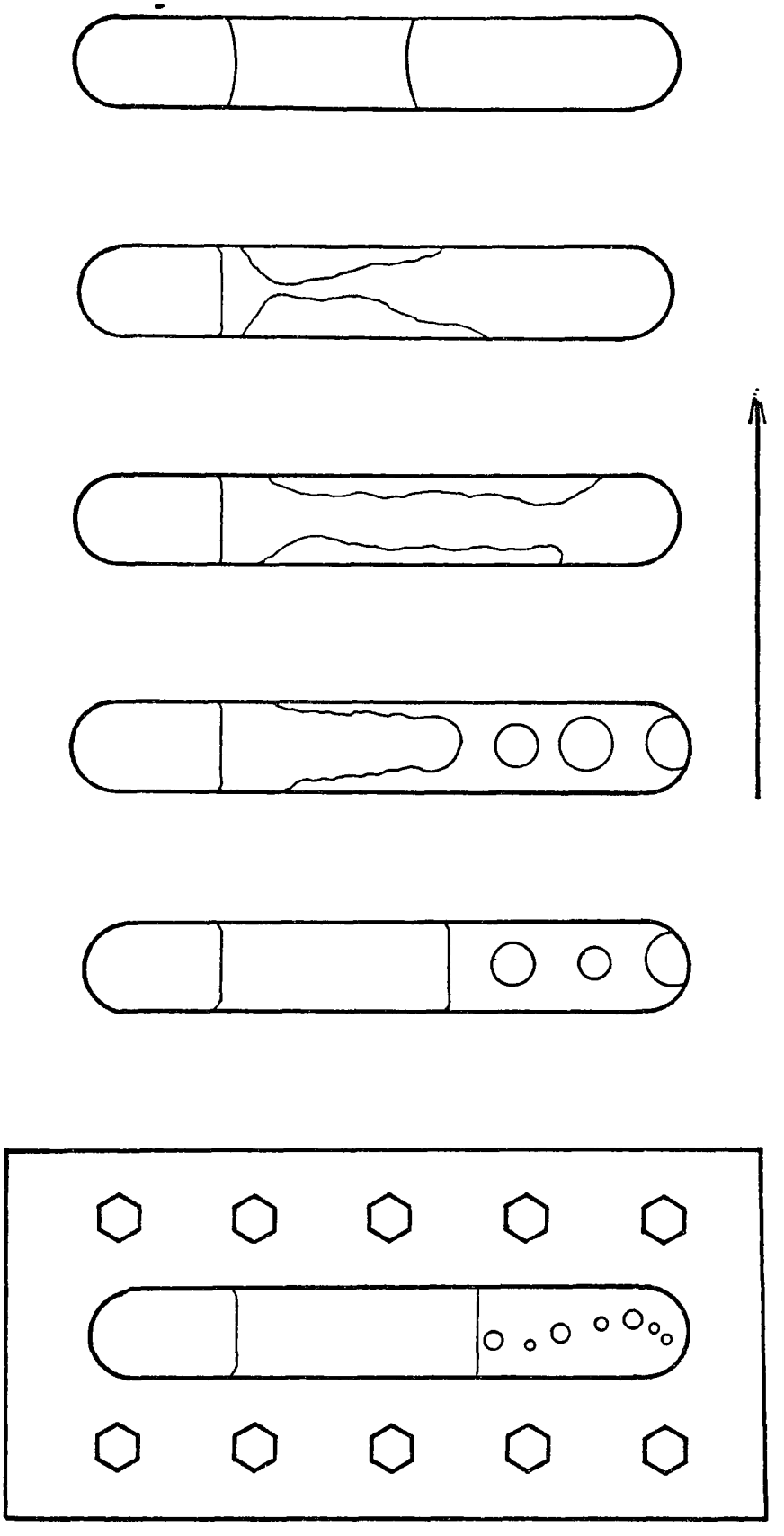


Figure 3.13 Liquid Phase Inversion of the System Nitrogen(1)-Methane(2)-Ethane(3)

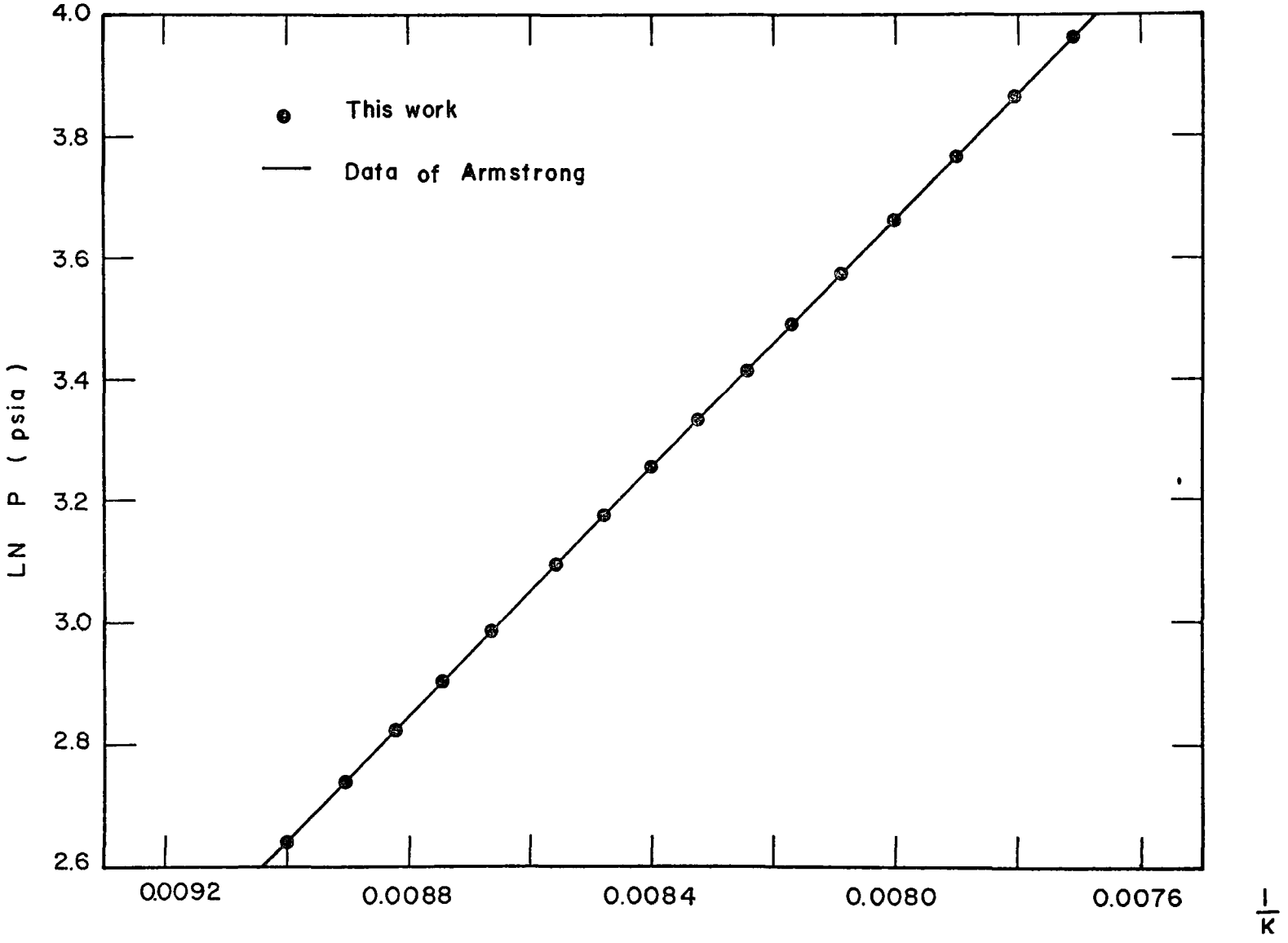


Figure 3.14 The pressure-Temperature Curves of Methane

CHAPTER 4

THERMODYNAMIC ANALYSIS AND PREDICTION OF DATA

The basic equation of equilibrium between two phases α and β, which are at the same temperature, is given by the equality of the fugacities for any component i in these phases:

$$f_i^{\alpha} = f_i^{\beta}$$

However it is necessary to relate the fugacity of a component to directly measurable properties. This can be done by studying the dependence of fugacity on temperature, pressure, and composition, which are most conveniently measurable parameters. For a component i in a system containing m components, the total differential of the logarithm of the fugacity $\hat{f}_i$ is given by:

$$d \ln \hat{f}_i = \left(\frac{\partial \ln \hat{f}_i}{\partial T} \right)_{P,x} dT + \left(\frac{\partial \ln \hat{f}_i}{\partial P} \right)_{T,x} dP + \sum_{j=1}^{m-1} \left(\frac{\partial \ln \hat{f}_i}{\partial x_j} \right)_{P,T,x_K} dx_j$$

$$K = 1 \ldots j-1, \; j+1 \ldots m-1 \qquad (4\text{-}1)$$

On the right hand side of Equation (4-1), the three terms denote the temperature, pressure and composition dependence on fugacity respectively. The first term can be expressed in terms of enthalpy by the thermodynamic relation:

$$\left(\frac{\partial \ln \hat{f}_i}{\partial T} \right)_{P,x} = \left(\frac{h^{\circ} - \bar{h}_i}{RT^2} \right) \qquad (4\text{-}2)$$

where $\bar{h}_i$ is the partial molar enthalpy of i, and h° is the molar enthalpy of i in the ideal gas state at the same temperature. At the present time, very little is known about enthalpies of fluid mixtures at high pressures, and usually experimental vapor-liquid equilibrium data are analyzed as a function of pressure and composition and empirical correlations are allowed to count for the temperature effect.

The second term in Equation (4.1) can be related to the partial molar volume $\bar{v}_i$ by

$$\left(\frac{\partial \ln \hat{f}_i}{\partial P}\right)_{T,x} = \left(\frac{\bar{v}_i}{RT}\right) \qquad (4.3)$$

This can be neglected at low pressures for liquid mixtures; but it must be taken into account at high pressure ranges.

A considerable body of knowledge has been accumulated for the third term. Many empirical and semi-empirical expressions have been proposed. The equation of van Laar, the Redlich-Kister equation, and the regular solution model of Scatchard and Hildebrand are some of the usually employed ones.

The following sections will give some discussions about these terms.

4.1 LIQUID PHASE ACTIVITY COEFFICIENTS

The fugacity of a compound i in a mixture is related to the activity coefficient by

$$\hat{f}_i = \gamma_i x_i f^\circ_i \qquad (4.4)$$

where f°_i is the fugacity of i in its standard state. The choice of a standard state is arbitrary; and to make a wise choice depends very much on experience. For a compound in the liquid phase, the usual practice is to have the temperature of the system, a fixed composition and a specified pressure as the independent variables which determine the standard state. For a mixture at the condition below the critical points of all its components, a convenient choice of the standard state is the pure liquid at the system temperature and a reference pressure P^r. If P^r is chosen to be higher than all saturation pressures encountered, then a hypothetical liquid state can be avoided.

In defining activity coefficients, there are two commonly used conventions:

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 \tag{4.5}$$

and

$$\begin{aligned} &\gamma_1 \rightarrow 1 \text{ as } x_1 \rightarrow 1 \quad \text{(solvent)} \\ &\gamma_2^* \rightarrow 1 \text{ as } x_2 \rightarrow 0 \quad \text{(solute)} \end{aligned} \tag{4.6}$$

The convention described by Equation (4.5) is symmetrical and is easily extended to solutions containing more than two components and will be adopted in this work.

The choice of P^r as the reference pressure gives the γ_i values as constant pressure activity coefficients. At isothermal conditions, this enables one to correlate the activity coefficients as a function of composition only so that the effect of temperature, pressure and composition on activity coefficient can be considered separately.

The pressure dependence of activity coefficient is given by the exact thermodynamic relation

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{v}_i}{RT} \tag{4.7}$$

The fugacity of component i in the liquid phase at pressure P, temperature T and mole fraction x_i, is given by

$$\hat{f}_i = \gamma_i^{(P^r)} x_i f_i^{\circ (P^r)} \exp \int_{P^r}^{P} \frac{\bar{v}_i}{RT} \, dP \tag{4.8}$$

where $f_i^{\circ (P^r)}$ is the standard-state fugacity of i at system temperature T, and reference pressure P^r.

The liquid phase activity coefficient can be evaluated by using the Redlich-Kwong equation of state to evaluate the fugacity and the partial molar volume.

Liquid phase activity coefficients can also be evaluated from gas phase fugacity coefficients.

At the condition of equilibrium, the following equation holds:

$$P y_i \hat{\varphi}_i^{v} = \gamma_i^{\circ} x_i f_i^{\circ \cdot L} \tag{4.9}$$

Also,
$$f_i^{\circ L} = f_i^{\circ v} = \varphi_i^{\circ v} P_i^{\circ} \tag{4.10}$$

and
$$\gamma_i^{P} = \gamma_i^{\circ} \exp\left[\frac{v_i^{L} (P_i^{\circ} - P)}{RT}\right] \tag{4.11}$$

Substituting (4.10) and (4.11) into (4.9), it is obtained that,

$$P y_i \hat{\varphi}_i^{v} = \gamma_i^{P} x_i \varphi_i^{\circ v} P_i^{\circ} \exp\left[\frac{v_i^{L} (P - P_i^{\circ})}{RT}\right] \tag{4.12}$$

or, after rearrangement,

$$\gamma_i^P = \frac{P\, y_i\, \hat{\varphi}_i^v}{x_i\, \varphi_i^{\circ v}\, P_i^{\circ} \exp\left[\frac{v_i^L (P - P_i^{\circ})}{RT}\right]} \qquad (4.13)$$

The gas phase fugacity coefficient can be evaluated from the second virial coefficients, by means of Equation (4.14)

$$\ln \hat{\varphi}_i^v = \frac{2}{v} (y_i B_{ii} + y_j B_{ij}) - \ln \left(\frac{Pv}{RT}\right) \qquad (4.14)$$

In this investigation, the following combining rules were used:

$$T_{ij} = (T_{ci}\, T_{cj})^{\frac{1}{2}} (1 - k_{ij}) \qquad (2.4.2\,dd)$$

$$v_{cij} = \tfrac{1}{8} (v_{ci}^{\frac{1}{3}} + v_{cj}^{\frac{1}{3}})^3 \qquad (2.4.2\,bb)$$

$$\omega_{ij} = \tfrac{1}{2} (\omega_i + \omega_j) \qquad (4.15)$$

Virial coefficients can be evaluated from the correlation of Pitzer and Curl [91].

4.2 PARTIAL MOLAR VOLUME

The evaluation of partial molar volume for the compounds in a mixture is necessary, to account for pressure effect on fugacity, which becomes significant at high pressure conditions.

From Equation (4.3) and (4.4),

$$\left(\frac{\partial \ln \hat{f}_i}{\partial P}\right)_{T,x} = \left[\frac{\partial (\ln \gamma_i\, x_i\, f_i^{\circ})}{\partial P}\right]_{T,x} = \frac{\bar{v}_i}{RT} \qquad (4.16)$$

which simplifies to

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} + \left(\frac{\partial \ln f^{\circ}_i}{\partial P}\right)_{T,x} = \frac{\bar{v}_i}{RT} \qquad (4.17)$$

If the standard-state fugacity, f°_i, is defined at a fixed reference pressure, P^r, then the second term in Equation (4.17) vanishes, and Equation (4.17) reduces to Equation (4.7). However, if f°_i is defined at the system pressure, then Equation (4.17) becomes

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{v}_i - v^{\circ}_i}{RT} \qquad (4.18)$$

where v°_i is the molar volume of i in the standard state.

Provided an equation of state is used, the partial molar volume of component i in a mixture can be expressed with the exact relation:

$$\bar{v}_i = \frac{-\left(\frac{\partial P}{\partial n_i}\right)_{T,v,n_j}}{\left(\frac{\partial P}{\partial v}\right)_{T,\text{ all } n}} \qquad (4.19)$$

where v is the total volume of the mixture containing n_i moles of component i, etc.

If the modified [77] Redlich-Kwong equation of state is used, Equation (4.19) becomes

$$\bar{v}_i = \frac{\frac{RT}{v-b}\left(1 + \frac{b_i}{v-b}\right) - \frac{2\left(\sum_j x_j a_{ij}\right) - ab_i/(v+b)}{v(v+b)T^{0.5}}}{\frac{RT}{(v-b)^2} - \frac{a}{T^{0.5}}\left[\frac{2v+b}{v^2(v+b)^2}\right]} \qquad (4.20)$$

where the parameters a, b, b_i and a_{ij} are defined as

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (2.4.2x)$$

$$b = \sum_i x_i b_i \qquad (2.4.2v)$$

$$b_i = \Omega_{bi} RT_{ci}/P_{ci} \qquad (2.4.2e)$$

$$a_{ij} = \Omega_{ai} R^2 T_{cij}^{2.5}/P_{cij} \qquad (4.21)$$

In these equations,

$$T_{cij} = (T_{ci} T_{cj})^{0.5} (1 - k_{ij}) \qquad (2.4.2dd)$$

$$\Omega_{aij} = (\Omega_{ai} + \Omega_{aj})/2 \qquad (4.22)$$

$$P_{cij} = Z_{cij} R T_{cij}/V_{cij} \qquad (2.4.2aa)$$

$$V_{cij} = \tfrac{1}{8}(V_{ci}^{\frac{1}{3}} + V_{cj}^{\frac{1}{3}})^3 \qquad (2.4.2bb)$$

$$Z_{cij} = 0.291 - 0.08 \omega_{ij} \qquad (4.23)$$

$$\omega_{ij} = (\omega_i + \omega_j)/2 \qquad (4.15)$$

These parameters reduce to those of pure components if i = j in Equations (2.4.2x) to (4.21). It should be mentioned that Equations (2.4.2x), (2.4.2v), (2.4.2e) and (4.21) follow the proposal of Redlich and Kwong [62], Equations (2.4.2dd), (4.22) and (2.4.2aa) those of Chueh and Prausnitz [94], and Equations (4.23) and (4.15), those of Pitzer and his co-workers [88] [92]. Equation (2.4.2bb) is the well-known Lorentz relationship.

4.3 EXCESS GIBBS FREE ENERGY

The Redlich-Kister [93] equation is a proper correlation in many cases for activity coefficients at conditions of constant temperature and pressure. The Excess Gibbs Free Energy for a binary system i-j can be expressed by a series function of composition:

$$Q_{ij} = \frac{G^E}{RT} = x_i x_j \left[B - C (x_i - x_j) + D (x_i - x_j)^2 + \ldots \right] \tag{4.24}$$

The term $x_i x_j$ provides for the zero value of G^E at compositions corresponding to the pure components.

Formulation of individual activity coefficients is obtained by differentiation of Equation (4.24), and the expressions are:

$$\ln \gamma_i = x_j^2 \left[B + C (3 x_i - x_j) + D (x_i - x_j) (5 x_i - x_j) \right] \tag{4.25}$$

$$\ln \gamma_i = x_i^2 \left[B + C (x_i - 3 x_j) + D (x_i - x_j) (x_i - 5 x_j) \right] \tag{4.26}$$

Wohl [57], in reviewing the various methods of representing activity coefficients, pointed out that the series should be developed in such a way that the higher terms are corrections of the terms of lower order. Thus the Redlich-Kister equation for a ternary system takes the form:

$$\ln \gamma_i = Q_{123} + \frac{\partial Q_{123}}{\partial x_i} - \sum_{i=1}^{3} x_i \left(\frac{\partial Q_{123}}{\partial x_i} \right) \tag{4.27}$$

where

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_i x_2 x_3 \left[c + D_1 (x_2 - x_3) + D_2 (x_3 - x_1) + D_3 (x_1 - x_2) + \ldots \right] \tag{4.28}$$

in which the terms Q_{12}, Q_{23} and Q_{31} are the binary excess-free-energy functions as expressed in Equation (4.24); and C, D_1, D_2 and D_3 are ternary constants. The terms containing C, D_1, D_2 and D_3 are used to take into account the interactions between the various binaries.

Combining Equations (4.27) and (4.28) [93], the activity coefficients are expressed in the following equations:

$$\begin{aligned}
\ln \gamma_1 = {} & B_{12} x_2 (1 - x_1) + C_{12} x_2 (2x_1 - x_2 - 2x_1^2 + 2x_1 x_2) \\
& + D_{12} x_2 (3x_1^2 - 3x_1^3 + 6x_1^2 x_2 - 4x_1 x_2 - 3x_1 x_2^2 + x_2^2) \\
& - B_{23} x_2 x_3 - 2C_{23} x_2 x_3 (x_2 - x_3) - 3D_{23} (x_2 - x_3)^2 \\
& + B_{31} x_3 (1 - x_1) + C_{31} x_3 (x_3 - 2x_1 x_3 + 2x_1^2 - 2x_1) \\
& + D_{31} x_3 (x_3^2 + 6x_1^2 x_3 - 4x_1 x_3 - 3x_2 x_3^2 + 3x_1^2 - 3x_1^3 \\
& + C x_2 x_3 (1 - 2x_1) + D_1 x_2 x_3 (x_2 - x_3 - 3x_1 x_2 + 3x_1 x_3) \\
& + D_2 x_2 x_3 (x_3 - 2x_1 - 3x_1 x_3 + 3x_1^2) \\
& + D_3 x_2 x_3 (2x_1 - x_2 - 3x_1^2 + 3x_1 x_2) \qquad (4.29)
\end{aligned}$$

$$\begin{aligned}
\ln \gamma_2 = {} & B_{12} x_1 (1 - x_2) + C_{12} x_1 (x_1 - 2x_2 - 2x_1 x_2 + 2x_2^2) \\
& + D_{12} x_1 (x_1^2 - 4x_1 x_2 + 3x_2^2 - 3x_1^2 x_2 + 6x_1 x_2^2 - 3x_2^3) \\
& + B_{23} x_3 (1 - x_2) + C_{23} x_3 (2x_2 - x_3 - 2x_2^2 + 2x_2 x_3) \\
& + D_{23} x_3 (x_3^2 + 3x_2^2 - 4x_2 x_3 - 3x_2^3 + 6x_2^2 x_3 - 3x_2 x_3) \\
& - B_{31} x_1 x_3 - 2C_{31} x_1 x_3 (x_3 - x_1) \\
& - 3D_{31} x_1 x_3 (x_3 - x_1)
\end{aligned}$$

$$+ C x_1 x_3 (1 - 2x_2)$$

$$+ D_1 x_1 x_3 (2x_2 - x_3 - 3x_2^2 + 3x_2 x_3)$$

$$+ D_2 x_1 x_3 (x_3 - x_1 + 3x_1 x_2 - 3x_2 x_3)$$

$$+ D_3 x_1 x_3 (x_1 - 2x_2 - 3x_1 x_2 + 3x_2^2) \qquad (4.30)$$

and

$$\ln \gamma_3 = -B_{12} x_1 x_2 - 2C_{12} x_1 x_2 (x_1 - x_2)$$

$$- 3D_{12} x_1 x_2 (x_1 - x_2)^2 + B_{23} x_2 (1 - x_3)$$

$$+ C_{23} x_2 (x_2 - 2x_3 - 2x_2 x_3 + 2x_3^2)$$

$$+ D_{23} x_2 (x_2^2 - 4x_2 x_3 + 3x_3^2 + 3x_2^2 x_3 + 6x_2 x_3^2 - 3x_3^2)$$

$$+ B_{31} x_1 (1 - x_3) + C_{31} x_1 (2x_3 - x_1 - 2x_3^2 + 2x_1 x_3)$$

$$+ D_{31} x_1 (x_1^2 + 3x_3^2 - 4x_1 x_3 - 3x_3^3 + 6x_1 x_3^2 - 3x_1^2 x_3)$$

$$+ C x_1 x_2 (1 - 2x_3)$$

$$+ D_1 x_1 x_2 (x_2 - 2x_3 - 3x_2 x_3 + 3x_3^2)$$

$$+ D_2 x_1 x_2 (-x_1 + 2x_3 - 3x_3^2 + 3x_1 x_3)$$

$$+ D_3 x_1 x_2 (x_1 - x_2 - 3x_1 x_3 + 3x_2 x_3) \qquad (4.31)$$

Some systems can be correlated adequately with only binary constants, meaning that all ternary constants can be considered zero.

4.4. THE MODIFIED REDLICH-KWONG [62] EQUATION OF STATE

The Redlich-Kwong equation of state has been discussed in Chapter 2. In this investigation, the procedure of modification by Lu

et al [132], Chang and Lu [79], and Hsi and Lu [78] was adopted. The evaluation of the parameters Ω_a and Ω_b as temperature-dependent at both subcritical and supercritical states will be discussed in the next section.

4.5 THE EVALUATION OF Ω_a and Ω_b

The Redlich-Kwong equation, as given by the original authors, is

$$Z = \frac{1}{1-h} - \frac{A^2}{B}\left(\frac{h}{1+h}\right) \qquad (2.4.2b)$$

where

$$h = BP/z \qquad (2.4.2c)$$

$$A^2 = \Omega_a T_c^{2.5}/T^{2.5} P_c = a/R^2 T^{2.5} \qquad (2.4.2d)$$

$$B = \Omega_b T_c/ T P_c = b/RT \qquad (2.4.2e)$$

Expressed in terms of fugacity coefficients, Equation (2.4.2b) becomes:

$$\ln \varphi^L = Z_L - 1 - \ln Z_L - \ln (1 - h_L) - (A^2/B) \ln (1 + h_L) \qquad (4.32)$$

or

$$\ln \varphi^v = Z_v - 1 - \ln Z_v - \ln (1 - h_v) - (A^2/B) \ln (1 + h_v) \qquad (4.33)$$

where φ^L and φ^v are fugacity coefficients of the liquid phase and vapor phase respectively.

At equilibrium, the fugacity of a component i in the liquid phase equals to the fugacity in the vapor phase, and so are the fugacity coefficients.

$$\hat{f}_i^v = \hat{f}_i^L \qquad (4.34)$$

$$\hat{\varphi}^{v}_{i} = \hat{\varphi}^{L}_{i} \qquad (4.35)$$

Combining Equations (4.32), (2.4.2b), (2.4.2c) and (4.35), the following relationship is obtained:

$$\ln Z_L \varphi^{v} + 1 - Z_L + \ln (1 - h_L) + \frac{[1 - Z_L (1 - h_L)](1 + h_L)}{h_L (1 - h_L)}$$

$$\ln (1 + h_L) = 0 \qquad (4.36)$$

An iteration loop [77] of computation is set up to evaluate Ω_a and Ω_b, employing Equation (4.36) as the working equation.

The first step of the iteration loop is the evaluation of h_L with a given value of Z_L while assuming $\varphi^{v} = 1$. The second step is to calculate A and B. The third step is to compute Z_v and h_v. The fourth step is to calculate φ^{v}. The fifth step is to calculate h_L. The iteration loop comes to an end when the change of h_L is less than a specified tolerance of 0.00005.

In this work, the Ω_a and Ω_b values for nitrogen, methane, ethane, propane and carbon dioxide were evaluated. Vapor pressure and saturated liquid density data of Din [95], Klosek and McKinley [96] were used. Vapor-liquid equilibrium data were also used for the systems nitrogen-methane [3] [4]

nitrogen-ethane [5] [6], nitrogen-n-butane [7] [8]
methane-ethane [97] [98], methane-propane [99] [100],
methane-n-butane [101] [102], ethane-propane [97], and
ethane-hexane [103].

The determined values of Ω_a and Ω_b are graphically presented in Figures (4.1) to (4.6).

4.6 PREDICTION OF VAPOR-LIQUID EQUILIBRIUM

The fugacity coefficients of component i in vapor and liquid phasescan be evaluated for vapor-liquid equilibrium data, by equations (4.32) and (4.33). For c components, the relationships are:

$$\hat{f}_i^L = \hat{f}_i^v \qquad i = 1, 2, \ldots\ldots c \tag{4.37}$$

in which $\hat{f}_i^L = \hat{\varphi}_i^L \, x_i \, P$

$\hat{f}_i^v = \hat{\varphi}_i^v \, y_i \, P$

If the temperature and (c-1) independent liquid-phase mole fractions are specified, it should be possible to calculate the total pressure and (c-1) independent vapor-phase mole fractions with the aid of Equation (4.37). The c simultaneous equations may be solved by a trial and error procedure. Arbitrary values of P and $\hat{\varphi}_i^v$ are assumed. $\hat{\varphi}_i^L$ is calculated with Equation (4.36), and the vapor phase compositions are calculated by:

$$y_i = (\hat{\varphi}_i^L / \hat{\varphi}_i^v) \, x_i \tag{4.38}$$

and the total pressure is calculated by

$$P = \sum_{i=1}^{c} \hat{f}_i^L / \hat{\varphi}_i^v \tag{4.39}$$

This value of P is compared with the value from the previous trial. Thus $\hat{\varphi}_i^v$ is recalculate again, until the difference of P is within a specified tolerance of 0.05 psia. Then the condition:

$$\sum_{i=1}^{c} y_i = 1 \tag{4.40}$$

is tested until a specified tolerance of 0.0001 is met.

A scheme[78] of this iteration is shown in Figure (4.7).

4.7 PREDICTION OF LIQUID-LIQUID EQUILIBRIUM WITH THE REDLICH-KWONG EQUATION OF STATE[62]

For a system with two liquid phases in equilibrium with the vapor phase, the following relationship holds:

$$\hat{f}_i^{L1} = \hat{f}_i^{L2} = \hat{f}_i^{V} \tag{4.41}$$

where the superscript L1 and L2 stand for liquid phase 1 and liquid phase 2, respectively.

Expressed in terms of fugacity coefficients, Equation (4.41) becomes:

$$\hat{\varphi}_i^{L1} x_i^{L1} = \hat{\varphi}_i^{L2} x_i^{L2} \tag{4.42}$$

and

$$\hat{\varphi}_i^{L1} x_i^{L1} = \hat{\varphi}_i^{V} y_i \tag{4.43}$$

also, it is necessary that

$$\sum_{i=1}^{c} x_i^{L1} = 1 \tag{4.44}$$

$$\sum_{i=1}^{c} x_i^{L2} = 1 \tag{4.45}$$

and

$$\sum_{i=1}^{c} y_i = 1 \tag{4.46}$$

For a system with c components, there are (3c + 2) variables, which is the sum of c (x_i^{L1}) + c (x_i^{L2}) + c (y_i) + T + P; and there are (2c + 3) equations, which is the sum of c times (4.42) + c times (4.43) + (4.44) + (4.45) + (4.46). If c = 2, that is, the system is a binary

mixture, then there are 8 variables and 7 equations; if c = 3, that is, the system in a ternary mixture, there are 11 variables and 9 equations.

For systems at isothermal conditions, if a liquid composition is specified, the other unknowns can be obtained from the simultaneous solution of the equations. An equation of state can be used to calculate the fugacity coefficients, and a modified Regula-Falsi method has been proposed by Yu [104] for the numerical solution.

4.8 CORRELATION OF LIQUID-LIQUID EQUILIBRIUM DATA: THE METHOD OF BLACK AND HARTWIG [46]

A simple ternary diagram for a system composed of components r, i and s is shown in Figure (2.5). The symbol s denotes a solvent, r denotes the component which is more nonideal with the solvent, and i refers to the component which distributes between the two phases. In this study, s represents nitrogen, r for propane and i for methane. Figure (2.5) shows the case in which only the r-s binary is partially miscible ; and the plait point, the binodal curve and the tie-lines are all shown. The symbol x refers to the composition in the solvent phase, and y refers to the r phase.

The distribution coefficient K_j is defined as y_j/x_j for any component j; the solubility function K_h is defined as the distribution coefficient for the total non-solvent material between phases r and s. These important quantities are given in accordance with the relationships:

$$K_r = y_r/x_r \qquad (2.2.5b)$$

$$K_h = (1 - y_s)/(1 - x_s) \qquad (2.2.5d)$$

$$K_i = y_i/x_i \qquad (2.2.5a)$$

$$K_s = y_s/x_s \qquad (2.2.5c)$$

Phase equilibria for ternary systems are developed in terms of the three basic quantities K_r, K_h and K_i. Each is correlated in terms of K_s, the "solvent distribution". Two basic plots serve to correlate and determine the consistency of ternary liquid-liquid equilibria. The first, Figure (2.5b), shows K_r, K_h and K_i plotted vs. K_s on log-log scales. In the second, Figure (2.5c), the composition of the solvent phase x'_i is plotted against the solvent concentration x_s. Similarly, y'_i is plotted against y_s. At the plait point $x'_i = y'_i$ and $x_s = y_s$. The solubilities x_s and y_s are

$$x_s = (K_h - 1)/(K_h - K_s) \tag{4.47}$$

and $y_s = x_s K_s$, which is defined in Equation (2.2.5c). The solvent-free compositions, the "aromaticity" when referred to an aromatic compound, are given by

$$x'_i = (K_r - K_h)/(K_r - K_i) \tag{4.49}$$

and

$$y'_i = x'_i K_i/K_h \tag{4.50}$$

The ternary compositions x_i and y_i are calculated by

$$x_i = x'_i (1 - x_s) \tag{4.51}$$

$$y_i = y'_i (1 - y_s) \tag{4.52}$$

As discussed in Chapter 2, the values of a, b and c were evaluated from plots of log K_r, log K_i and log K_h against log K_s.

$$(x'_i)_{ppt} = (a - c)/(a - b) \tag{4.53}$$

$$(x_s)_{ppt} = c/(c - 1) \tag{4.54}$$

Equations (4.53) and (4.54) were used to establish the plait points in this study.

4.9 LIQUID PHASE INVERSION

The phenomenon of liquid phase inversion has been observed by Schindler, Swift and Kurata [13] in 1967. But only the description of visual observations has been discussed that "the distribution of the two liquid phases changes" "at approximately -180°C", for the binary system nitrogen-propane. No details of temperature, pressure and composition were included, and no interpretation of the phenomenon was given. In this investigation, a detailed observation of the liquid phase inversion phenomenon was made, for the binary system nitrogen-ethane, and ternary system nitrogen-methane-ethane [1] [2]. With some research of the densities of the pure components, a suitable explanation of the phenomenon was also attained. This will be discussed in Section (4.11.c)

4.10 THE CRITICAL LOCI OF BINARY MIXTURES

The critical state has been defined by Gibbs [12] as that state of a system at which all distinctions between the two coexistent phases vanishes. A one-component system has only one critical state, whereas a multicomponent system has an infinite number of critical states. At a binary critical point, the conditions are:

$$\left(\frac{\partial^2 g}{\partial y_1^2}\right) = 0, \left(\frac{\partial^3 g}{\partial y_1^3}\right) = 0 \qquad (4.55)$$

where g is the molar free energy, and y_1 is the mole fraction of component 1 in the mixture.

Expressed in terms of fugacity coefficients $\hat{\varphi}_1$ and $\hat{\varphi}_2$ of the components 1 and 2 respectively, the conditions are

$$\left[\frac{\partial \ln\left(\frac{\hat{\varphi}_1}{\hat{\varphi}_2}\right)}{\partial y_1}\right]_{P,T} = \frac{-1}{y_1 y_2} \qquad (4.56)$$

$$\left[\frac{\partial^2 \ln \left(\frac{\hat{\varphi}_1}{\hat{\varphi}_2} \right)}{\partial y_1^2} \right]_{P,T} = \frac{(-y_1 + y_2)}{y_1^2 \, y_2^2} \qquad (4.57)$$

The fugacity coefficients can be expressed in terms of partial molal volumes $\bar{v}_1$ and $\bar{v}_2$ of components 1 and 2 respectively

$$\ln \hat{\varphi}_1 = \int_0^P \left(\bar{v}_1 / RT - \frac{1}{P} \right) dP \qquad (4.58)$$

$$\ln \hat{\varphi}_2 = \int_0^P \left(\bar{v}_2 / RT - \frac{1}{P} \right) dP \qquad (4.59)$$

Applying the Gibbs-Duhem equation to the molal volume v , of the mixture,

$$\left(\frac{\partial v}{\partial y_1} \right)_{P,T} = \bar{v}_1 - \bar{v}_2 \qquad (4.60)$$

the resulting expression is

$$\ln \left(\frac{\hat{\varphi}_1}{\hat{\varphi}_2} \right) = \int_0^P (\bar{v}_1 - \bar{v}_2) \frac{dP}{RT}$$

or

$$\ln \left(\frac{\hat{\varphi}_1}{\hat{\varphi}_2} \right) = \int_0^P \left(\frac{\partial v}{\partial y_1} \right)_{P,T} \frac{dP}{RT} \qquad (4.61)$$

Differentiate with respect to y_1 at constant P and T, and rearrange, two expressions are obtained:

$$\int_\infty^v \left(\frac{\partial^2 P}{\partial y_1^2} \right)_{v,T} dv - \left(\frac{\partial P}{\partial y_1} \right)_{v,T}^2 \left(\frac{\partial v}{\partial P} \right)_{y,T} = \frac{RT}{y_1 y_2}$$

(2.5.6a)

$$\int_{\infty}^{v} \left(\frac{\partial^3 P}{\partial y_1^3}\right)_{v,T} dv + 2\left(\frac{\partial^2 P}{\partial y_1^2}\right)_{v,T}\left(\frac{\partial v}{\partial y_1}\right)_{P,T}$$

$$+\left(\frac{\partial^2 P}{\partial y_1 \partial v}\right)_{T}\left(\frac{\partial v}{\partial y_1}\right)^2_{P,T} + \left(\frac{\partial P}{\partial y_1}\right)_{v,T}\left(\frac{\partial^2 v}{\partial y_1^2}\right)_{P,T}$$

$$= \frac{RT\,(y_1 - y_2)}{(y_1\, y_2)^2} \qquad (2.5.6b)$$

These are the two conditions for the existence of the critical state of a binary mixture, expressed in terms of volumetric data.

APPLICATION OF THE THERMODYNAMIC RELATIONS

The relations (2.5.6a) and (2.5.6b) can be solved together with an equation of state to yield the values of V_c, T_c and P_c. An equation of state gives the relationship of temperature, pressure and volume of a mixture. For a mixture of fixed composition, the derivative terms in Equations (2.5.6a) and (2.5.6b) can be obtained from the equation of state. With the convenience of electronic computer calculations, the values of temperature and volume for a mixture can be searched to satisfy the equations (2.5.6a) and (2.5.6b) simultaneously. And those values are the temperature and volume at the critical point of the mixture with the fixed composition. With the substitution of the calculated T_c and V_c into the equation of state, then P_c will be calculated. This procedure was discussed in details by Joffe and Zudkevitch [87].

APPLICATION OF THE MODIFIED REDLICH-KWONG EQUATION OF STATE

In this study, the modified Redlich-Kwong equation of state was used. The modification by Lu et al. [134], Chang and Lu [77]

and Hsi and Lu [78] which was discussed in Chapter 2, was adopted. The values of Ω_a and Ω_b presented in Figures (4.1) to (4.6) were used. In order to used Equation (2.5.6a) and (2.5.6b) together with the equation of state, the necessary terms were derived and will be shown in the following,

$$P = \frac{RT}{v - b} - \frac{a}{T^{\frac{1}{2}} v\ (v + b)}$$

$$a = a_1 y_1^2 + a_2 y_2^2 + 2 a_{12} y_1 y_2$$

$$b = b_1 y_1^2 + b_2 y_2^2 + 2 b_{12} y_1 y_2$$

$$(\partial a/\partial y_1)_{P,T,v} = 2 a_1 y_1 - 2 a_2 y_2 + 2 a_{12} (y_2 - y_1)$$

$$(\partial b/\partial y_1)_{P,T,v} = 2 b_1 y_1 - 2 b_2 y_2 + 2 b_{12} (y_2 - y_1)$$

$$(\partial^2 a/\partial y_1^2)_{P,T,v} = 2 a_1 + 2 a_2 - 4 a_{12}$$

$$(\partial^2 b/\partial y_1^2)_{P,T,v} = 2 b_1 + 2 b_2 - 4 b_{12}$$

$$(\partial^3 a/\partial y_1^3)_{P,T,v} = 0 \quad , \quad (\partial^3 b/\partial y_1^3)_{P,T,v} = 0$$

$$\int_{\infty}^{v} (\partial^2 P/\partial y_1^2)_{v,T}\, dv = - RT/(v - b)\ (\partial^2 b/\partial y_1^2) - RT/(v - b)^2$$

$$(\partial b/\partial y_1)^2 + 2 a/T^{\frac{1}{2}} b\ (\partial b/\partial y_1)^2\ \ln((v + b)/v)$$

$$+ 1/T^{\frac{1}{2}} [2\, \partial a/\partial y_1\ \partial b/\partial y_1 + a\ \partial^2 b/\partial y_1^2]$$

$$[1/b(v + b) - 1/b^2 \ln((v + b)/v)]$$

$$- 2 a/T^{\frac{1}{2}} (\partial b/\partial y_1)^2 [1/b^2/(v + b) - 1/b^3 \ln((v + b)/v)$$

$$+ 1/2\ b/(v + b)^2]$$

$$(\partial P/\partial y_1)_{V,T} = RT/(v-b)^2 \quad (\partial^2 b/\partial y_1^2) - 2RT/(v-b)^3$$

$$(\partial b/\partial y_1)(\partial v/\partial y_1 - \partial b/\partial y_1) - 1/[T^{\frac{1}{2}} v (v+b)](\partial^2 a/\partial y_1^2)$$

$$+ 1/[T^{\frac{1}{2}} v (v+b)^2][a(\partial^2 b/\partial y_1^2) + (\partial a/\partial y_1)(\partial v/\partial y_1)$$

$$+ 2(\partial a/\partial y_1)(\partial b/\partial y_1)] - 2a/[T^{\frac{1}{2}} v (v+b)^3](\partial b/\partial y_1)$$

$$(\partial v/\partial y_1 + \partial b/\partial y_1) + 1/T^{\frac{1}{2}} v^2 (v+b)(\partial a/\partial y_1)(\partial v/\partial y_1)$$

$$- a/[T^{\frac{1}{2}} v^2 (v+b)^2](\partial a/\partial y_1)(\partial v/\partial y_1)$$

$$(\partial P/\partial v)_{y,T} = -RT/(v-b)^2 + a(2v+b)/[T^{\frac{1}{2}} v^2 (v+b)^2]$$

$$\int_{\infty}^{V} (\partial^3 P/\partial y_1^3)_{v,T}\, dv = -RT/(v-b)(\partial^3 b/\partial y_1^3) - 3RT/(v-b)^2$$

$$(\partial b/\partial y_1)(\partial^2 b/\partial y_2) - 2RT/(v-b)^3 (\partial b/\partial y_1)^3 + 1/T^{\frac{1}{2}}$$

$$(\partial^3 a/\partial y_1^3)[1/b \ln((v+b)/v)] + 1/T^{\frac{1}{2}}[3(\partial a/\partial y_1)$$

$$(\partial^2 b/\partial y_1^2) + 3(\partial^2 a/\partial y_1^2)(\partial b/\partial y_1) + a(\partial^3 b/\partial y_1^3)]$$

$$[1/b(v+b) - 1/b^2 \ln((v+b)/v)] - 6/T^{\frac{1}{2}}$$

$$[(\partial a/\partial y_1)(\partial b/\partial y_1)^2 + a(\partial b/\partial y_1)(\partial^2 b/\partial y_1^2)]$$

$$[1/b^2/(v+b) - 1/b^3 \ln((v+b)/v) + 1/2\, b/(v+b)^2]$$

$$+ 6a/T^{\frac{1}{2}}(\partial b/\partial y_1)^3 [1/b^3/(v+b) - 1/b^4 \ln((v+b)/v)$$

$$+ 1/2\, b^2/(v+b)^2 + 1/3\, b/(v+b)^3]$$

$$(\partial^2 P/\partial y_1^2)_{v,T} = RT/(v-b)^2 (\partial^2 b/\partial y_1^2) + 2RT/(v-b)^3 (\partial b/\partial y_1)^2$$

$$- 1/[T^{\frac{1}{2}} v (v+b)](\partial^2 a/\partial y_1^2) + 1/[T^{0.5} v (v+b)^2]$$

$$[2(\partial a/\partial y_1)(\partial b/\partial y_1) + a(\partial^2 b/\partial y_1^2)] - 2a/[T^{\frac{1}{2}} v (v+b)^3]$$

$$(\partial b/\partial y_1)^2$$

$$(\partial^2 P/\partial y_1 \partial v)_T = -2RT/(v-b)^3 (\partial b/\partial y_1) + [(2v+b)/(T^{\frac{1}{3}} v^2 (v+b)^2)]$$

$$(\partial a/\partial y_1) - 2a/[T^{\frac{1}{2}} v (v+b)^3](\partial b/\partial y_1) - a/[T^{\frac{1}{2}} v^2 (v+b)^2]$$

$$(\partial b/\partial y_1)$$

$$(\partial v/\partial y_1)_{P,T} = -(\partial P/\partial y_1)_{v,T} / (\partial P/\partial v)_{y_1,T}$$

$$(\partial^2 v/\partial y_1^2)_{P,T} = -[\partial/\partial y_1 (\partial P/\partial y_1)_{v,T}]_{P,T} / (\partial P/\partial v)_{y_1,T}$$

$$+ [\partial/\partial y_1 (\partial P/\partial v)_{y_1,T}]_{P,T} (\partial P/\partial y_1)_{v,T} / (\partial P/\partial v)^2_{y_1,T}$$

$$[\partial/\partial y_1 (\partial P/\partial y_1)_{v,T}]_{P,T} = RT/(v-b)^2 (\partial^2 b/\partial y_1^2) - 2RT/(v-b)^3$$

$$(\partial b/\partial y_1)(\partial v/\partial y_1 - \partial b/\partial y_1)$$

$$- 1/[T^{\frac{1}{2}} v (v+b)](\partial^2 a/\partial y_1^2) + 1/[T^{\frac{1}{2}} v (v+b)^2]$$

$$[a\,\partial^2 b/\partial y_1^2 + \partial a/\partial y_1 \partial v/\partial y_1 + 2\,\partial a/\partial y_1 \partial b/\partial y_1]$$

$$- 2a/[T^{\frac{1}{2}} v (v+b)^3](\partial b/\partial y_1)(\partial v/\partial y_1 + \partial b/\partial y_1)$$

$$+ 1/[T^{\frac{1}{2}} v^2 (v+b)](\partial a/\partial y_1)(\partial v/\partial y_1) - a/[T^{\frac{1}{2}} v^2 (v+b)^2]$$

$$(\partial a/\partial y_1)(\partial v/\partial y_1)$$

$$[\partial/\partial y_1 (\partial P/\partial)_{y_1,T}]_{P,T} = 2RT/(v-b)^3 (\partial v/\partial y_1 - \partial b/\partial y_1)$$

$$+ 1/[T^{\frac{1}{2}} v^2 (v+b)^2][a(2\,\partial v/\partial y_1 + \partial b/\partial y_1) + (2v+b)(\partial a/\partial y_1)]$$

$$- 2/[T^{\frac{1}{2}} v^2 (v+b)^3][a(2v+b)(\partial v/\partial y_1 + \partial b/\partial y_1)] - 2/[T^{\frac{1}{2}} v^3 (v+b)^2]$$

$$[a(2v+b)\,\partial v/\partial y_1]$$

APPLICATION OF THE CLAUSIUS EQUATION OF STATE

In 1880 Clausius [111] supplemented the van der Waals equation by introducing a third constant. This supplementation makes a linear transformation in the volume coordinate for a pressure-volume plot so that the equation will fit experimental data in a better curve near the critical point. A comparison of various equations of state with experimental data by Shah and Thodos [112] showed that the Clausius equation of state was capable of predicting reasonably well the critical isotherm up to the critical point. It is hoped that with three constants, this equation will improve the prediction of critical properties of a binary mixture.

The Clausius equation of state is:

$$P = \frac{RT}{v - b} - \frac{a}{T (v + c)^2} \tag{4.62}$$

where

$$a = \frac{27 R^2 T_c^2}{64 P_c} \tag{4.63}$$

$$b = v_c - \frac{R T_c}{4 P_c} \tag{4.64}$$

$$c = \frac{3 R T_c}{8 P_c} - v_c \tag{4.65}$$

The Clausius equation of state was solved simultaneously together with Equations (2.5.6a) and (2.5.6b) following the same procedure as described in last section. The necessary terms are derived and are shown in the following :

$$P = \frac{RT}{v - b} - \frac{a}{T (v + c)^2}$$

$$a = \frac{27 R^2 T_c^3}{64 P_c}$$

$$b = v_c - \frac{R T_c}{4 P_c}$$

$$c = \frac{3 R T_c}{8 P_c} - v_c$$

the mixing rules

$$a = a_1 y_1^2 + a_2 y_2^2 + 2 a_{12} y_1 y_2$$

$$b = b_1 y_1 + b_2 y_2$$

$$c = c_1 y_1 + c_2 y_2$$

$$T_{cij} = (T_{ci} T_{cj})^{0.5} (1 - k_{ij})$$

$$P_{cij} = Z_{cij} \frac{R T_{cij}}{v_{cij}}$$

$$\omega_{ij} = (\omega_i + \omega_j) \frac{1}{2}$$

$$Z_{ij} = 0.291 - 0.08 \omega_{ij}$$

$$v_{cij} = \frac{1}{8} (v_{ci}^{\frac{1}{3}} + v_{cj}^{\frac{1}{3}})^3$$

$$a_{ii} = \Omega_{ai} R^2 \frac{T_{ci}^3}{P_{ci}}$$

$$b_{ii} = v_{ci} - \frac{R T_{ci}}{P_{ci}} \Omega_{bi}$$

$$c_{ii} = \Omega_{ci} \frac{R T_{ci}}{P_{ci}} - v_{ci}$$

$$a_{ij} = (\Omega_{ai} + \Omega_{aj}) \frac{1}{2} \frac{R^2 T_{cij}^3}{P_{cij}}$$

$$b_{ij} = v_{cij} - \frac{R\,T_{cij}}{P_{cij}} \left(\Omega_{bi} + \Omega_{bj} \right) \frac{1}{2}$$

$$c_{ij} = \left(\Omega_{ci} + \Omega_{cj} \right) \frac{1}{2} \frac{R\,T_{cij}}{P_{cij}} - v_{cij}$$

$$\left(\partial a / \partial y_1 \right)_{P,T,v} = 2\,a_1\,y_1 - 2\,a_2\,y_2 + 2\,a_{12}\,(y_2 - y_1)$$

$$\left(\partial^2 a / \partial y_1^2 \right)_{P,T,v} = 2\,a_1 + 2\,a_2 - 4\,a_{12}$$

$$\left(\partial^3 a / \partial y_1^3 \right)_{P,T,v} = 0$$

$$\left(\partial b / \partial y_1 \right)_{P,T,v} = b_1 - b_2$$

$$\left(\partial^2 b / \partial y_1^2 \right)_{P,T,v} = 0$$

$$\left(\partial c / \partial y_1 \right)_{P,T,v} = c_1 - c_2$$

$$\left(\partial^2 c / \partial y_1^2 \right)_{P,T,v} = 0$$

$$\int_{\infty}^{v} \left(\partial^2 P / \partial y_1^2 \right)_{v,T} dv = -RT/(v-b)\left(\partial^2 b / \partial y_1^2 \right) - RT/(v-b)^2 \left(\partial b / \partial y_1 \right)^2 + 1/T/(v+c)\left(\partial^2 a / \partial y_1^2 \right) - 1/T/(v+c)^2 \left[a\,\partial^2 c / \partial y_1^2 + 2\,\partial a / \partial y_1\,\partial c / \partial y_1 \right] + 2\,a/T/(v+c)^2 \left(\partial c / \partial y_1 \right)^2$$

$$\left(\partial P / \partial y_1 \right)_{v,T} = RT/(v-b)^2 \left(\partial b / \partial y_1 \right) - \left(\partial a / \partial y_1 / T / (v+c)^2 \right) + 2\,a / T(v+c)^3 \left(\partial c / \partial y_1 \right)$$

$$\left(\partial v / \partial P \right)_{y_1,T} = 1 / \left(\partial P / \partial v \right)_{y_1,T}$$

$$(\partial P/\partial v)_{y_1, T} = -RT/(v - b)^2 + 2a/T/(v + c)^3$$

$$\int_{\infty}^{v} (\partial^3 P/\partial y_1^3)_{v,T}\, dv = -RT/(v - b)(\partial^3 b/\partial y_1^3) - 3RT/(v - b)^2$$

$$(\partial b/\partial y)(\partial^2 b/\partial y_1^2) - 2RT/(v - b)^3 (\partial b/\partial y_1)^3$$

$$+ 1/T/(v + c)(\partial^3 a/\partial y_1^3) - a/T/(v + c)^2 (\partial^3 c/\partial y_1^3)$$

$$- 3/T/(v + c)^2 (\partial a/\partial y_1)(\partial^2 c/\partial y_1^2) - 3/T/(v + c)^2$$

$$(\partial^2 a/\partial y_1^2)(\partial c/\partial y_1) + 6a/T/(v + c)^3 (\partial c/\partial y_1)(\partial^2 c/\partial y_1^2)$$

$$+ 6/T/(v + c)^3 (\partial a/\partial y_1)(\partial c/\partial y_1)^2 - 6a/T/(v + c)^4$$

$$(\partial c/\partial y_1)^3$$

$$(\partial^2 P/\partial y_1^2)_{v,T} = RT/(v - b)^2 (\partial^2 b/\partial y_1^2) + 2RT/(v - b)^3$$

$$(\partial b/\partial y_1)^2 - 1/T/(v+c)^2 (\partial^2 a/\partial y_1^2) + 2/T/(v + c)^2$$

$$[a\ \partial^2 c/\partial y_1^2 + 2\ \partial a/\partial y_1\ \partial c/\partial y_1] - 6a/T/(v + c)^4$$

$$(\partial c/\partial y_1)^2$$

$$(\partial v/\partial y_1)_{P,T} = -(\partial P/\partial y_1)_{v,T}/(\partial P/\partial v)_{y_1, T}$$

$$(\partial^2 P/\partial y_1\, \partial v)_T = 2RT/(v - b)^3 (\partial v/\partial y_1 - \partial b/\partial y_1)$$

$$+ 2/T/(v + c)^3 (\partial a/\partial y_1) - 6a/T/(v + c)^4 (\partial V/\partial y_1 + \partial c/\partial y_1)$$

$$(\partial^2 v/\partial y_1^2)_{P,T} = -[\partial/\partial y_1 (\partial P/\partial y_1)_{v,T}]_{P,T}/(\partial P/\partial v)_{y_1, T}$$

$$+ [\partial/\partial y_1 (\partial P/\partial v)_{y_1,T}]_{P,T} (\partial P/\partial y_1)_{v,T}/(\partial p/\partial v)^2_{y_1, T}$$

$$\left[\partial/\partial y_1 \left(\partial P/\partial y_1\right)_{v,T}\right]_{P,T} = RT/(v-b)^2 \left(\partial^2 b/\partial y_1^2\right)$$

$$- 2\,RT/(v-b)^3 \left(\partial b/\partial y_1\right)\left(\partial v/\partial y_1 - \partial b/\partial y_1\right)$$

$$- 1/T\,(v+c)^2 \left(\partial^2 a/\partial y_1^2\right) + 2/\left[T(v+c)^3\right]$$

$$\left[a\,\partial^2 c/\partial y_1^2 + \partial a/\partial y_1\,\partial v/\partial y_1 + 2\,\partial c/\partial y_1\,\partial a/\partial y_1\right]$$

$$- 6\,a/T/(v+c)^4 \left(\partial c/\partial y_1\right)\left(\partial v/\partial y_1 + \partial c/\partial y_1\right)$$

$$\left[\partial/\partial y_1 \left(\partial P/\partial v\right)_{y_1,T}\right]_{P,T} = 2RT/(v-b)^3 \left(\partial v/\partial y_1 - \partial b/\partial y_1\right)$$

$$+ 2/T/(v+c)^2 \left(\partial a/\partial y_1\right) - 6a/T/(v+c)^4 \left(\partial v/\partial y_1 + \partial c/\partial y_1\right)$$

APPLICATION OF THE WOHL EQUATION OF STATE [113]

The Wohl equation is:

$$P = \frac{RT}{v-b} - \frac{a}{v(v-b)} + \frac{c}{v^3} \qquad (4.66)$$

where

$$a = 6\,v_c^2\,P_c \qquad (4.67)$$

$$b = \tfrac{1}{4}\,v_c \qquad (4.68)$$

$$c = 4\,v_c^3\,P_c \qquad (4.69)$$

This equation was proposed in 1914 and was a modification of the van der Waals equation. In this equation, the v_c was not an experimental value, but was recommended to be $v_c = RT_c/3.75\,P_c$. It was found [112] that for pure substances, along the critical isotherm, the values predicted by this equation agreed closely with the experimental values for the gaseous region up to $P_r = 1.0$. It also predicted well the PVT behavior at higher temperatures and did not indicate significant deviations for the gaseous state for pressures above $P_r = 1.0$.

To use this equation for predicting critical loci of binary mixtures by the method described, the necessary terms are derived and are shown in the following:

$$P = \frac{RT}{v - b} - \frac{a}{v(v - b)} + \frac{c}{v^3}$$

$$(\partial P/\partial y_1)_{v,T} = (\partial b/\partial y_1) PT/(v - b)^2 - (\partial a/\partial y_1)/v/(v - b)$$

$$- (\partial b/\partial y_1)\, a/v/(v - b)^2 + (\partial c/\partial y_1)/v^2$$

$$[\partial (\partial P/\partial y_1)_{v,T}/\partial y_1]_{P,T} = (\partial^2 b/\partial y_1^2)\, RT/(v - b)^2$$

$$- (\partial v/\partial y_1 - \partial b/\partial y_1)(\partial b/\partial y_1)\, 2RT/(v - b)^3$$

$$- (\partial^2 a/\partial y_1^2)/v/(v - b) - [a(\partial^2 b/\partial y_1^2) - (\partial a/\partial y_1)(\partial v/\partial y_1)$$

$$+ 2(\partial a/\partial y_1)(\partial b/\partial y_1)]/v/(v - b)^2 + 2(\partial b/\partial y_1)$$

$$a(\partial v/\partial y_1 - \partial b/\partial y_1)/v/(v - b)^3 - (\partial a/\partial y_1)(\partial v/\partial y_1)/v^2/(v-b)$$

$$+ a(\partial b/\partial y_1)(\partial v/\partial y_1)/v^2/(v - b)^2$$

$$+ (\partial^2 c/\partial y_1^2)/v^3 - 3(\partial c/\partial y_1)(\partial v/\partial y_1)/v^4$$

$$(\partial^2 P/\partial y^2)_{v,T} = RT(\partial^2 b/\partial y_1^2)/(v - b)^2 + 2RT(\partial b/\partial y_1)^2/(v - b)^3$$

$$- (\partial^2 a/\partial y_1^2)/v/(v - b) - [a(\partial^2 b/\partial y_1^2) + 2(\partial a/\partial y_1)$$

$$(\partial b/\partial y_1)]/v/(v - b)^2 - 2a(\partial b/\partial y_1)^2/v/(v - b)^3$$

$$+ (\partial^2 c/\partial y_1^2)/v^3$$

$$(\partial P/\partial v)_{y_1,T} = -RT/(v - b)^2 + a(2v - b)/v^2/(v - b)^2 - 3c/v^4$$

$$(\partial^2 P/\partial y_1\, \partial v)_T = -2RT(\partial b/\partial y_1)/(v - b)^3 + (2v - b)(\partial a/\partial y_1)/v^2/(v-b)^2$$

$$+a(3v - b)(\partial b/\partial y_1)/v^2/(v - b)^3 - 3(\partial c/\partial y_1)/v^4$$

$$\left[\partial\left(\partial P/\partial v\right)_{y,T}/\partial y_i\right]_{P,T} - 2RT\left(\partial v/\partial y_i - \partial b/\partial y_i\right)/(v-b)^3$$

$$+ \left[a\left(2\,\partial v/\partial y_i - \partial b/\partial y_i\right) + \left(\partial a/\partial y_i\right)(2v-b)\right]/v^2/(v-b)^2$$

$$- 2a(2v-b)\left(\partial v/\partial y_i - \partial b/\partial y_i\right)/v^2/(v-b)^3$$

$$- 2a(2v-b)\left(\partial v/\partial y_i\right)/v^3/(v-b)^2 - 3\left(\partial c/\partial y_i\right)/v^4$$

$$+ 12c\left(\partial v/\partial y_i\right)/v^5$$

$$\int_{\infty}^{v}\left(\partial^2 P/\partial y_i^2\right)_{v,T}\,dv = -RT\left(\partial^2 b/\partial y_i^2\right)/(v-b)$$

$$- RT\left(\partial b/\partial y_i\right)^2/(v-b)^2 - \left(\partial^2 a/\partial y_i^2\right)\left[\ln(v-b) - \ln v\right]/bT$$

$$- \left[a\left(\partial^2 b/\partial y_i^2\right) + 2\left(\partial a/\partial y_i\right)\left(\partial b/\partial y_i\right)\right]$$

$$\left\{-1/b/(v-b) - \ln\left[(v-b)/v\right]/b^2\right\}/T$$

$$- 2a\left(\partial b/\partial y_i\right)^2\left\{1/b^2/(v-b) - 0.5/b/(v-b)^2\right.$$

$$\left. + \ln\left[(v-b)/v\right]/b^3\right\}/T - \left(\partial^2 c/\partial y_i^2\right)/2/T^2/v^2$$

$$\int_{\infty}^{v}\left(\partial^3 P/\partial y_i^3\right)_{v,T}\,dv - RT\left(\partial^3 b/\partial y_i^3\right)/(v-b)$$

$$- 3RT\left(\partial b/\partial y_i\right)\left(\partial^2 b/\partial y_i^2\right)/(v-b)^2$$

$$- 2RT\left(\partial b/\partial y_i\right)^3/(v-b)^3 - \left(\partial^3 a/\partial y_i^3\right)\left\{\ln\left[(v-b)/v\right]\right\}/bT$$

$$- \left\{a\left(\partial^3 b/\partial y_i^3\right) + 3\left(\partial a/\partial y_i\right)\left(\partial^2 b/\partial y_i^2\right) + 3\left(\partial^2 a/\partial y_i^2\right)\right.$$

$$\left.\left(\partial b/\partial y_i\right)\right\}\left\{-1/b/(v-b) - \ln\left[(v-b)/v\right]/b^2\right\}/T$$

$$- \left\{a\left(\partial b/\partial y_i\right)\left(\partial^2 b/\partial y_i^2\right) + \left(\partial a/\partial y_i\right)\left(\partial b/\partial y_i\right)^2\right\}$$

$$\left\{1/b^2/(v-b) - 0.5/b/(v-b)^2 + \ln\left[(v-b)/v\right]/b^3\right\}/T$$

$$+ 6a\left(\partial b/\partial y_i\right)^3\left\{1/b^3/(v-b) - 0.5/b^2/(v-b)^2\right.$$

$$\left. + \ln\left[(v-b)/v\right]/b^4 + 1/3/b/(v-b)^3\right\}/T$$

4.11 RESULTS AND DISCUSSIONS

A) BINARY SYSTEMS

Experimental vapor-liquid equilibrium data were determined for binary systems containing nitrogen, methane, and propane.

For the system nitrogen-methane, data were available in the literature [3] [4]. The experimental dew - and bubble - point data of Bloomer and Parent [3] and the isothermal vapor-liquid equilibrium data of Cines et al. [4] were adopted. Isothermal P-x-y values at the conditions of 114.05, 118.32 and 122.24 K were obtained from graphically cross-plotting, and were shown in Figure (4.9). Also shown were three experimental points measured in this laboratory, and were found in good agreement with those interpolated values.

Data reduction was carried out for these three binary systems, each of which included three isotherms. These binary vapor-liquid equilibrium data were also used to test the applicability of the Redlich-Kwong equation of state for prediction purposes. Detailed discussions will be depicted in the following sections.

Liquid activity coefficients. Liquid phase activity coefficients were calculated for the binary systems nitrogen-propane, and methane-propane, and also for the smoothed values interpolated from the data of Cines et al. [4], and Bloomer and Parent [3] for the system nitrogen-methane, at 114.05, 118.32 and 122.24 K. The evaluations were based on Equation (4.8), coupled with the Redlich-Kwong equation of state, which was used for the evaluation of the component fugacities in the mixture and also the partial molar volumes. The reference pressure P^r in Equation (4.8) was arbitrarily chosen to be 500 psia, which was higher than any saturation pressure encountered in this study. In

doing so the hypothetical liquid state could be avoided. The numerical values are shown in Table (4.1) in Appendix A, and graphically in Figures (4.10) - (4.14). The conditions under which the Redlich-Kwong equation of state was applied were discussed in section (4.4).

The evaluated activity coefficients were correlated with the Redlich-Kister equation, Equations (4.25) and (4.26). The results are shown in Table (4.2) in Appendix A, in which the correlation constants as well as average absolute deviation and average absolute % deviation in γ_1 and γ_2 are reported. The data are well represented by the Redlich-Kister equation. With three binary constants, the data are represented better than 0.3% in average; with two binary constants, the data are represented with 1.0% in average. The values for the nitrogen-methane [3] [4] system exhibit least deviation of all due to the fact that the values were smoothed. The correlated values are shown in Figures (4.10) to (4.14) as lines, compared to the individual γ values shown as points.

A consistency test was performed by plotting $\ln\left(\frac{\gamma_1}{\gamma_2}\right)$ vs x_1 for the system methane (1) - propane (2) as shown in Figure (4.15). The area test shows that the data are consistent for this system. However it should be noticed that for the three isotherms 114.05, 118.32 and 122.24 K, this plot is almost identical , and this is probably due to the small temperature interval such that the temperature effect is small. This area test could not be performed for the system nitrogen-propane since the vapor-liquid equilibrium data were determined only in the region in which the liquid was not saturated but was rich in propane; and this region was less than 0.1 mole fraction of nitrogen. Beyond this region, two liquid phases appeared and vapor-liquid-liquid equilibrium took place.

A consistent trend is indicated when the data of methane-propane system was compared to those reported by Wichterle and Kobayashi [100], as shown in Figures (4.16) and (4.17). It should be pointed out that in Figure (4.17), as the activity coefficients at infinite dilution are compared, the values for the isotherm 130.37 K of Wichterle and Kobayashi show a greater discrepancy from the trend. This may be due to the fact that only three experimental vapor-liquid equilibrium points were reported besides the vapor pressures of pure substances.

Liquid activity coefficients were also calculated from gas phase fugacity coefficients, by using Equation (4.13). The results are shown in Table (4.3). Equation (4.13) involves directly the value of vapor composition, and the activity coefficients thus evaluated are sensitive to the accuracy of vapor composition of the data. The conditions of this investigation were at low temperatures such that the vapor compositions of propane in both nitrogen-propane and methane-propane systems were always lower than 0.003 mole fraction, which was lower than the experimental error, the value of which was 0.005 mole fraction. The results in Table (4.4) reveal very well this factor, as one can find that the activity coefficients for nitrogen and methane are of reasonable magnitude and agree well with those evaluated from Equation (4.8); while those for propane are low and scattering.

Prediction of vapor-liquid equilibrium. As discussed in Section (4.6), the modified Redlich-Kwong equation of state was used to predict equilibrium pressure and vapor composition from experimental data of temperature and liquid composition. The necessary pure component properties and their resources are listed in Table (4.5); and the Redlich-Kwong equation parameters Ω_a and Ω_b are shown in Figures (4.1) to (4.6), the details of which were discussed in Section 4.5. The numerical results are shown in Tables (4.6) and (4.7), ir

which the predicted values are compared with the experimental data. The deviation of the predicted pressure is less than 2% as an average and the average absolute deviation of vapor composition is less than 0.005 mole fraction. It should be mentioned that at the temperatures of 114.05, 118.32 and 122.24 K, the vapor pressure of propane at those temperatures were estimated by the Frost-Kalkwarf-Thodos [134] vapor-pressure correlation, and the estimated value was 0.002 psia at 122.24 K. The values of Ω_a, Ω_b and k_{ij} used in this calculation are listed in Table (4.9).

Prediction of liquid-liquid equilibrium. The vapor-liquid-liquid equilibrium data for the system nitrogen-propane were used to test the applicability of the modified Redlich-Kwong equation of state for prediction purposes. As discussed in Section (4.7), a procedure of using a modified Rugula-Falsi method [104] was used to predict the propane-rich liquid phase (bottom liquid phase) compositions from the experimental nitrogen-rich phase (top liquid phase) compositions. The results are shown in Table (4.8). Compared with experimentally measured compositions, the predicted values have an average absolute percentage deviation of 0.8%. The pure component properties used are shown in Table (4.5). However, it is observed, that the interaction constant k_{ij} of Eq. (2.4.-2dd) for this calculation exhibits a dependence on temperature, as shown in Figure (4.18). This interaction constant k_{ij} has been considered as independent of temperature, pressure or composition [94], and is the characteristic constant of an i - j pair. However, the temperature-dependence was observed here for a binary mixture, and composition dependence was also observed for the three ternary isotherms. This will be discussed in more details in next section.

B) TERNARY SYSTEMS

The ternary system nitrogen-methane-propane was investigated at three isothermal conditions, for vapor-liquid equilibrium and vapor-liquid-liquid equilibrium. The equilibrium data were thermodynamically analyzed and correlated. The Redlich-Kwong equation of state was tested for predicting the vapor-liquid equilibrium and liquid-liquid equilibrium data. The detailed discussion will be given in the following sections.

Liquid activity coefficients. Liquid phase activity coefficients were evaluated according to Section (4.1). The reference pressure was arbitrarily taken as 500 psia. The values of the activity coefficients were listed in Table (4.10) to (4.12). For each isothermal condition, the activity coefficients were evaluated for vapor-liquid equilibrium data, and also for the two liquid phases each of which was considered in equilibrium with the vapor phase in the case of vapor-liquid-liquid equilibrium. The excess-free-energy function Q_{123} was calculated from the experimental γ values according to

$$Q_{123} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3 \qquad (4.91)$$

The ternary Redlich-Kister equation was used to correlate the γ values and the results are shown in Tables (4.13). In Table (4.13), the values of Q_{123}, the excess-free-energy function, evaluated from correlation constants are compared with the experimental Q_{123} evaluated from Equation (4.91). It is indicated from the results that ternary effect appears to exist in this system. The values of Q_{123} evaluated with binary and ternary constants together give an average absolute deviation of 2.5% from the experimental Q_{123} values. But evaluated from the binary constants alone, a deviation of 12% was resulted.

However, attentions should be drawn to the fact that the nitrogen-propane binary system exhibited partial miscibility in the liquid phase at these temperatures. The vapor-liquid equilibrium data measured for this system covered a composition range of 0.088 mole fraction of nitrogen before the liquid phase reached the liquid-liquid boundary. Naturally the binary Redlich-Kister equation represents the activity coefficients of this system up to the same composition range of 0.088 mole fraction of nitrogen. If these constants were used to calculate Q_{123} for the ternary system over a complete range of composition, the long-range extrapolation would certainly introduce considerable error.

Also, an attempt was made to evaluate activity coefficients from gas fugacity coefficients with Equation (4.13). The numerical values are reported in Table (4.14) in Appendix A. Also included in these Tables are the comparison with the results from Equation (4.8). The results show a similar situation as for the binary systems discussed in the previous section.

Correlation of liquid-liquid equilibrium data. The empirical correlation of Black and Hartwig [46] was used to correlate the liquid-liquid equilibrium data. As discussed in Section (4.8), the values of K_r, K_H, K_i and K_s were evaluated and are shown in Table (4.15) in Appendix A. Plots of log K_r, log K_H and log K_i against log K_s are constructed as shown in Figures (4.19), (4.20) and (4.21), from which the slopes of the curves at the limiting condition as the plait points are approached are evaluated. The values of the slopes, a, b and c are shown in Table (4.15). From these values, the plait points were estimated for each isotherm, by Equations (4.53) and (4.54); and the compositions of the plait points are shown in Table (4.15). Also, the values of x_I' and y_I' were calculated by

Equations (4.51) and (4.52), and are shown in Table (4.15). The values of x'_i and y'_i are plotted against x_s and y_s, respectively, as shown in Figures (4.22), (4.23) and (4.24). From these plots, consistency of the data is indicated by the curves.

Prediction of vapor-liquid equilibrium. Vapor compositions and system pressures for the ternary system were predicted by using the modified Redlich-Kwong equation of state as discussed in Section (4.6). The average absolute deviation between the calculated and experimental values of vapor composition, Δy, is 0.003 mole fraction; while the average absolute deviation between the calculated and experimental total pressure values, ΔP, is 4%. If these results were compared to those of binary systems, the deviation of ΔP is higher for a ternary system. The results are shown in Tables (4.16) to (4.21). A main contribution of the deviation came from those points in the vicinity of the binodal curve near the section where the liquid was rich in propane. The Redlich-Kwong equation of state could not predict accurately the phase behavior when the vapor phase was considered in equilibrium with the bottom liquid phase at the vapor-liquid-liquid boundary. But the results were very good when the vapor was considered in equilibrium with the top liquid phase.

The predicted values, together with experimental data, are shown in Tables (4.17) and (4.20), for which the top liquid phase (the nitrogen-rich portion of the binodal curve) is considered in equilibrium with the vapor phase. The agreement is as good as that for vapor-liquid equilibrium data. However, when the bottom liquid phase is considered as in equilibrium with the vapor, as mentioned above, convergency problem was encountered, and it is not possible to yield reasonable results. Numerical values were shown in Tables (4.18) and (4.21).

The prediction of liquid-liquid equilibrium. The liquid-liquid equilibrium data was used to test the applicability of the Redlich-Kwong equation of state with a modified Regula-Falsi method [104], as discussed in Section (4.7). The calculated values, together with experimental measurements and the differences between the two are reported in Table (4.22) in Appendix A. The results show good agreement between the calculated and experimental values. The average absolute deviations in composition and pressure were below 1%, as observed from the calculations reported in Table (4.22). However, looking at the method with scrutiny, two points should be mentioned here.

First, this method is limited in predicting the section of binodal curve in which the liquid is rich in the heavier component. In this case, the bottom liquid phase rich in propane was predicted from the top liquid phase rich in nitrogen. Unfortunately, the system nitrogen-methane-propane at the temperatures of 114.05, 118.32 and 122.24 K contains rather minute amount of propane in the top liquid phase (rich in nitrogen). The experimental error on measurements may have a profound effect on the outcome of the results.

Secondly, it was observed that the interaction constant k_{ij} for the binary pairs containing propane and nitrogen exhibited dependence on temperature and composition. This has been mentioned in the previous section in the discussion of results about the prediction of liquid-liquid equilibrium for the system nitrogen-propane. For the system nitrogen-propane, the values of k_{ij} varied from 0.075 to 0.1 over the temperature range of 113.22 to 125.15 K, as shown in Figure (4.18). For the system nitrogen (1) - methane (2)- propane (3), the values of k_{12} was quite a constant with respect to temperature (0.032 for 114.05 K, 0.031 for 118.32 K and 0.0304 for 122.24 K)

and did not vary with composition at isothermal conditions. But the values of k_{23} and k_{13} showed dependence on temperature as well as on composition, as shown in Figures (4.25), (4.26) and (4.27). However, a theoretically sound explanation or interpretation cannot be given at the present stage, but nevertheless this is a point worthy to notice.

The plait points established from the method of Black and Hartwig [46] were processed with the calculations using Redlich-Kwong equation of state. The k_{23} and k_{13} values used were selected from the trend established as shown in Figures (4.18), (4.25) to (4.27). The results are shown in Table (4.23). The maximum deviation in the predicted pressure is lower than 3%.

Constant pressure diagrams. The modified Redlich-Kwong equation of state was used to construct constant pressure curves for the system nitrogen-methane-propane at the three isothermal conditions. At each isothermal condition, liquid compositions were selected systematically so that the whole ternary composition range was covered. Vapor compositions and system pressures were predicted from the values of temperature and liquid composition. The predicted values of pressure were plotted against liquid composition. From graphical interpolation, liquid compositions were established at constant pressure conditions. The results are shown in Figures (4.28), (4.29) and (4.30). It was established earlier in this discussion that the modified Redlich-Kwong equation of state predicted system pressures from liquid compositions and temperatures with an average absolute deviation of 4%. It is therefore assumed that these constant pressure curves are approximately 4% away from experimental data.

It should be mentioned here that the discrepancy between the predicted and experimental values of pressure is high in the vicinity

of the bottom liquid phase, the propane-rich portion of the binodal curve, as have been mentioned earlier in this discussion. This fact still stands when the constant pressure curves are constructed. Therefore the constant pressure curves cannot always connect with the experimental tie-lines, due to this discrepancy. Hence these connections could only be shown at the vicinity of the plait point, where the agreement between the predicted and experimental values is good.

C) LIQUID DENSITY AND LIQUID PHASE INVERSION

The experimental data of Klosek and McKinley [96], and those of Din [95] for densities at saturation pressure of pure nitrogen, methane, ethane and propane were plotted in Figure (4.8), as functions of temperature. For the light hydrocarbons containing 1, 2, and 3 carbons, at low temperature ranges, as shown in Figure (4.8), the dependence of density on temperature is small. However, the density of nitrogen does not behave in the same manner. The density change is much larger due to change of temperature. As a result, the density curve of nitrogen intersects the density curve of ethane at 109.1 K. At this temperature, the densities of nitrogen and ethane are identical. For a mixture of nitrogen-ethane at this temperature, partial miscibility occurs. At this temperature, liquid phase inversion also occurs, for a binary mixture with 0.2014 mole fraction of nitrogen at the bottom liquid phase and 0.9453 mole fraction of nitrogen at the top liquid phase.

Also from Figure (4.8), it is found that 94.2 K is the intersection of the density curves of nitrogen and propane. This agrees very well with the temperature of -180°C (93.2 K) which is the liquid phase inversion temperature for system nitrogen-propane, reported by Schindler, Swift and Kurata [13].

D) CRITICAL LOCI OF BINARY MIXTURES

Mixtures containing nitrogen, methane, and propane have been investigated experimentally at cryogenic temperature, and the experimental data thermodynamically analyzed as shown in the preceedings sections. As a part of the research scheme, the behavior of these mixtures at the critical region was also studied. The rigorously derived expressions of Redlich and Kister [84], Equations (2.5.6a), (2.5.6b) were adopted. These two expressions were combined with various equations of state, yielding different sets of critical loci for these mixtures. Comparisons were made among the different sets of results, and with available experimental data. From these results, it was found that the modified Redlich-Kwong equation of state, that with Ω_a and Ω_b considered as functions of temperature at subcritical state and at supercritical state, was capable of predicting the critical loci closest to experimental data, for binary mixtures.

THE CRITICAL LOCUS OF THE BINARY SYSTEM METHANE-PROPANE

The system methane-propane is one of those investigated in this study. It has been experimentally studied more thoroughly as far as the critical locus is concerned. The results reported by Reamer, Sage, and Lacey [99] included PVT values at critical conditions. The values of critical temperature, critical pressure, and critical volume were reported for six compositions for this system. In this study, the Clausius equation, the Redlich-Kwong equation and the modified Redlich-Kwong equation with Ω_a and Ω_b considered temperature-dependent at both subcritical and supercritical states, were all used, together with Equations (2.5.6a) and (2.5.6b) to predict P_c, T_c and V_c for the mixture over complete composition ranges. The results are shown in Figures (4.31), (4.32) and (4.33).

In Figure (4.31), the calculated T_c is shown as a function of composition, together with the results reported by Reamer, Sage and Lacey [99]. Only one curve is shown due to the fact that close results were obtained from the three different equations of state. For the sake of clarity, the presentation of this graph does not follow the conventional way in which calculated results are presented as a curve and only experimental values are presented as points. However, numerically compared with the values reported by Reamer, Sage and Lacey, the results from the modified Redlich-Kwong equation of state gave an average absolute deviation of 0.5%.

The results of the calculated P_c are compared with the results of Reamer, Sage, and Lacey [99] in Figure (4.32). It is obvious that the results from the modified Redlich-Kwong equation of state are closest to the experimental data. Numerical comparison shows an average absolute deviation of 0.7%. This result shows that improvement has been achieved over the 1.9% of that obtained by Spear, Robinson, and Chao [85], who were using the given T_c to calculate P_c and were comparing to the experimental data of the same authors.

The critical volumes are shown as a function of composition in Figure (4.33). It is also obvious that those results from the modified Redlich-Kwong equation of state agree better with the data of Reamer, Sage, and Lacey [99]. Numerical comparison shows an average absolute deviation of 6.0%. The point at 0.6772 mole fraction of methane from Reamer, Sage, and Lacey is far off the trend of the other points. If this point is screened, the deviation is reduced to 2.3%. The results from the Redlich-Kwong equation without modification are also shown in Figure (4.33). A discrepancy is shown from these results. It is that the predicted values do not show a consistent trend with the critical volumes of the pure components.

THE BINARY SYSTEMS NITROGEN-METHANE, NITROGEN-ETHANE, AND NITROGEN-PROPANE

Figures (4.34), (4.35) and (4.36) show the results of calculated T_c, P_c and V_c respectively, for the systems nitrogen-methane, and nitrogen-propane (results of system methane-propane are also shown in these graphs). The results of the system nitrogen-ethane are shown in Figures (4.37), (4.38) and (4.39). It is specially interesting to note that the calculated critical pressures of nitrogen-ethane and nitrogen-propane mixtures are extraordinarily high as compared to the critical pressures of the pure components. The highest P_c of the nitrogen-propane mixtures reaches a value 10-fold of those of the pure components. The extrapolated values from the data of Schindler, Swift, and Kurata [13] for nitrogen-propane; and those of Stryjek, Chappelear, and Kobayashi [114] for nitrogen-ethane are included in Figures (4.35) and (4.38). Although these two points for each system can not confirm the reliability of the predicted results, they do indicate that the predicted P_c values are at the right order of magnitude.

The experimental value of T_c and P_c for the system nitrogen-methane from Bloomer and Parent [3] are also shown in Figures (4.34) and (4.35). Good agreement is indicated between these data and the results predicted by the modified Redlich-Kwong equation of state, as shown in Figures (4.34) and (4.35).

The predicted critical volumes for the systems nitrogen-methane and nitrogen-propane are shown in Figure (4.36); and those for system nitrogen-ethane are shown in Figure (4.39).

A detailed comparison of the results obtained from different equations of state, for the systems nitrogen-methane, and nitrogen-propane are presented in Figures (4.46) to (4.51).

THE BINARY SYSTEMS METHANE-ETHANE AND ETHANE-PROPANE

The calculated curves of T_c, P_c and V_c, respectively, for the binary systems methane-ethane, and ethane-propane, together with those of nitrogen-ethane are shown in Figures (4.37), (4.38) and (4.39). The critical temperatures for the methane-ethane, and ethane-propane mixtures are shown in Figure (4.37). The results were calculated from the modified Redlich-Kwong equation. The results from the Redlich-Kwong equation without modification agree very well and hence are not shown in Figure (4.37). Also, the T_c data of Matschke and Thodos [115] for the system ethane-propane, and the data of Ruhemann [98] for the system methane-ethane are included in Figure (4.37). Good agreement is indicated for both systems. The calculated results of P_c from both the Redlich-Kwong equation and the modified Redlich-Kwong equation for the systems methane-ethane and ethane-propane are shown in Figure (4.38). The data of Matschke and Thodos [115] and of Ruhemann [98] are also included. It appears that the results from the modified Redlich-Kwong equation of state agree better with the data in the literature.

The calculated V_c for the systems methane-ethane, and ethane-propane from both Redlich-Kwong equation and the modified Redlich-Kwong equation are shown in Figure (4.39). The results from the latter show better agreement with the properties of the pure components.

THE SYSTEMS CARBON DIOXIDE -N BUTANE AND CARBON DIOXIDE - ETHANE

In order to compare the results obtained from different equations of state, the critical loci of these two systems were calculated

and are shown in Figures (4.40) to (4.46). For the system carbon dioxide-n-butane, the Clausius equation, the Redlich-Kwong equation, the modified Redlich-Kwong equation, and the Wohl equation were used. Critical temperatures are plotted against compositions in Figure (4.40). Good agreement is indicated between the experimental data of Poettmann and Katz [116] and the calculated results, except those from the Wohl equation of state. The critical pressures are shown as functions of compositions in Figure (4.41). Comparing to the data of Poettamann and Katz [116], the results from the Clausuis equation and the modified Redlich-Kwong equation show better agreement. The curves of critical volume are shown in Figure (4.42). The results from the Clausuis equation agree better with the data of Olds, Reamer, Sage, and Lacey [117].

The critical temperatures and critical pressures, respectively for the system carbon dioxide - ethane are shown in Figures (4.43) and (4.44). The data of Kuenen [118] are used for comparison. The results obtained from the Clausius equation, Redlich-Kwong equation and the modified Redlich-Kwong equation are quite close to each other It appears that those results from the modified Redlich-Kwong equation of state are slightly better. The critical volumes of the carbon dioxide - ethane system are shown in Figure (4.45). The data of Khazanova and Lesnevskaya [119] are also presented. None of the results obtained from the Clausius equation, the Redlich-Kwong equation, and the modified Redlich-Kwong equation seem to agree well with this set of data. Attempts have been made to compare these results with those reported by Joffe and Zudkevitch [87]. Although these authors used a slightly different combining rules, namely, $a_{12} = (a_1 a_2)^{0.5}$ and $b_{12} = \frac{1}{2}(b_1 + b_2)$ instead of Equations (4.24) to (4.26), the calculating procedures were identical to those used here. It is found that the results obtained from the Redlich-Kwong equation in this study agreed

well with those reported by Joffe and Zudkevitch. Since these authors only reported their results in graphical form, the comparison was difficult. However, the modified Redlich-Kwong equation of state was found to be able to improve the results over the Redlich-Kwong equation without the modification.

In this study of critical loci for binary mixtures, the Wohl equation, the Clausius equation, the Redlich-Kwong equation, and the modified Redlich-Kwong equation have been brought into application. Results were obtained for the binary systems nitrogen-methane, nitrogen-ethane, nitrogen-propane, methane-ethane, methane-propane, ethane-propane, carbon dioxide-ethane, and carbon dioxide-n-butane. These results were compared with the results of Reamer, Sage and Lacey [99], Spear , Robinson and Chao [85], Schindler, Swift, and Kurata [13], Stryjek, Chappelear, and Kobayashi [114], Bloomer and Parent [3], Matschke and Thodos [115], Ruhemann [98], Poettmann and Katz [116] Olds, Reamer, Sage, and Lacey [117], Kuenen [118], Khazanova and Lesnevskaya [119], and Joffe and Zudkevitch [87].

It was found that using an equation of state, together with the Equations (2. 5. 6a), (2. 5. 6b)derived by Redlich and Kister [84], the critical properties T_c, P_c and V_c of a binary mixture could be predicted with satisfactory accuracy, as was claimed by many researchers [82] [83] [85] [87]. It was found in this study, that with the modified Redlich-Kwong equation of state considering Ω_a and Ω_b as a function of temperature at both subcritical state and supercritical state, the results could be further improved. The system methane-propane is a typical example. For this system, a complete set of T_c, P_c and V_c data is available and more complete comparison can be performed. In general, the modified Redlich-Kwong equation of state appeared to be able to yield better values of critical pressures and more reasonable loci for critical volume of a binary mixture, while retaining the accuracy of the prediction of critical temperature.

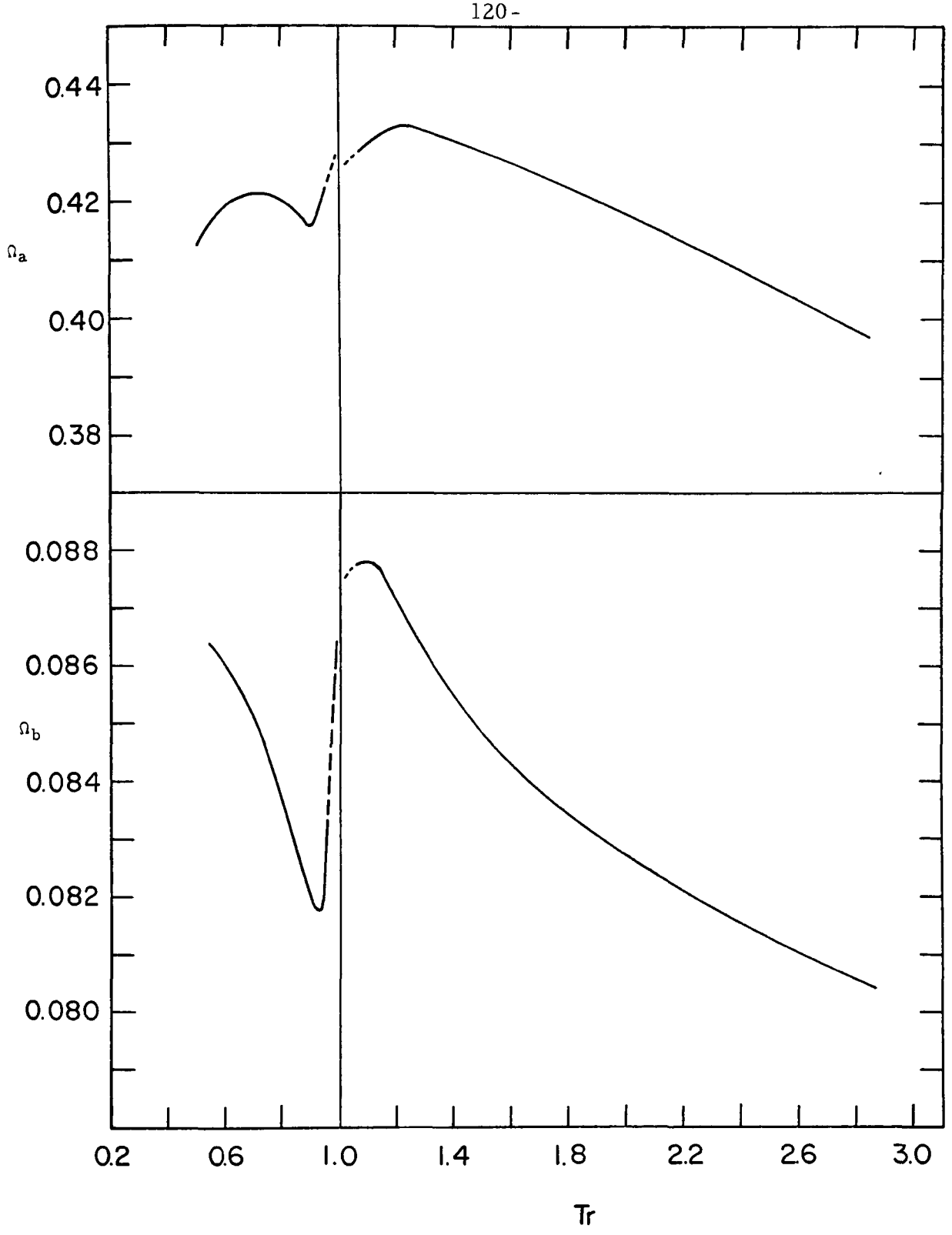


Figure 4.1 The Redlich-Kwong-Kwong Parameters Ωa and Ωb for Nitrogen

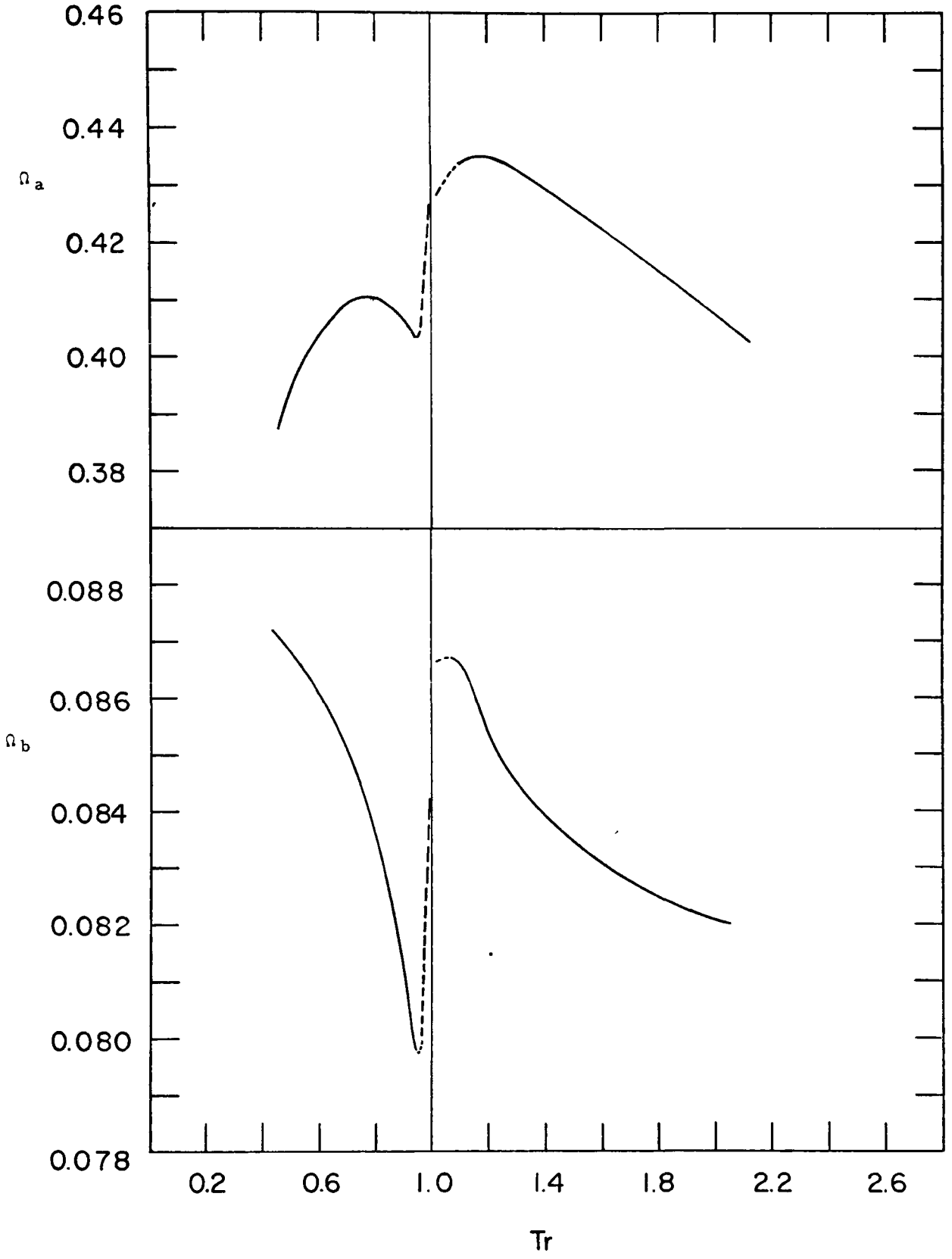


Figure 4.2 The Redlich-Kwong Parameters Ωa and Ωb for Methane

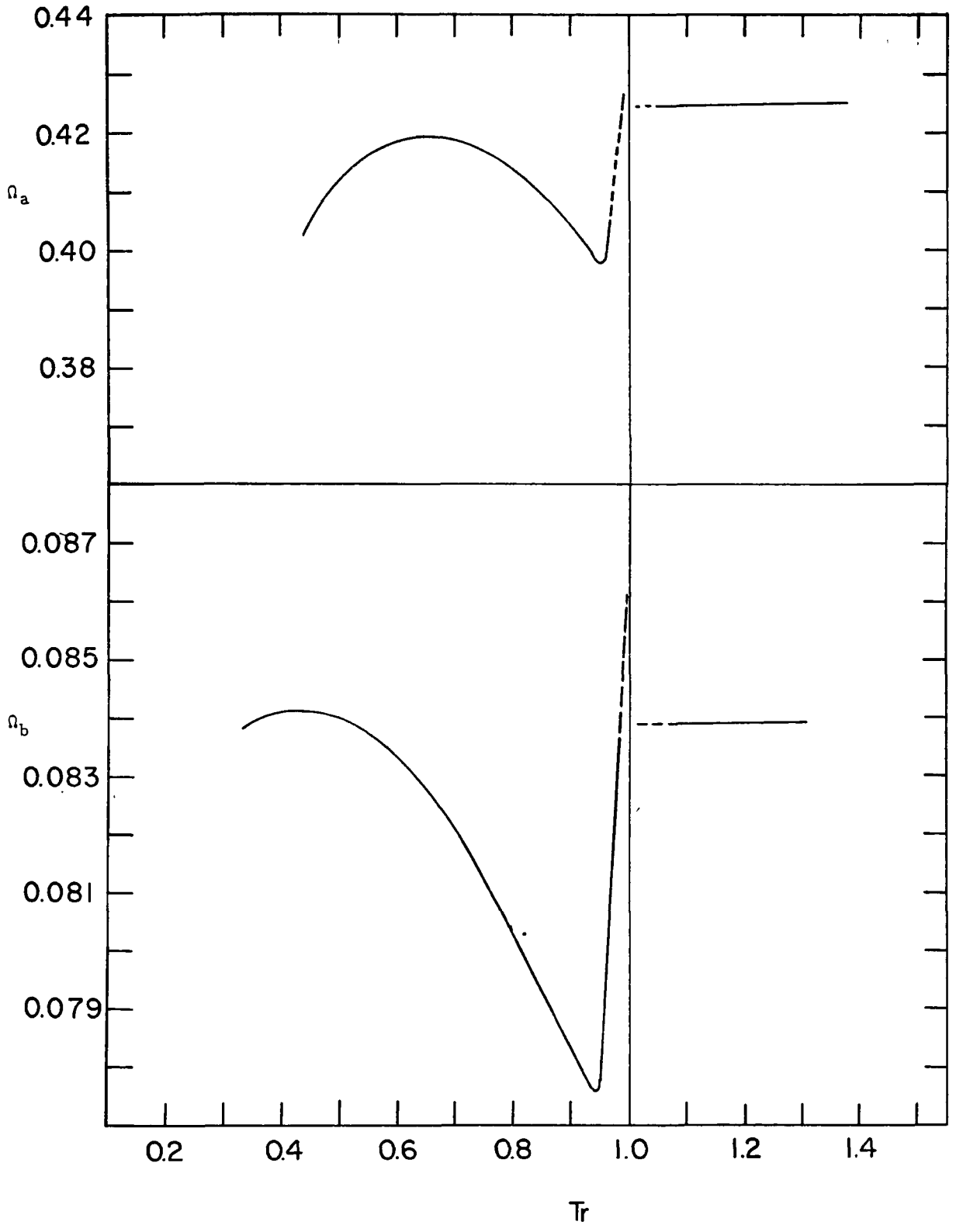


Figure 4.3 The Redlich-Kwong Parameters Ωa and Ωb for Ethane

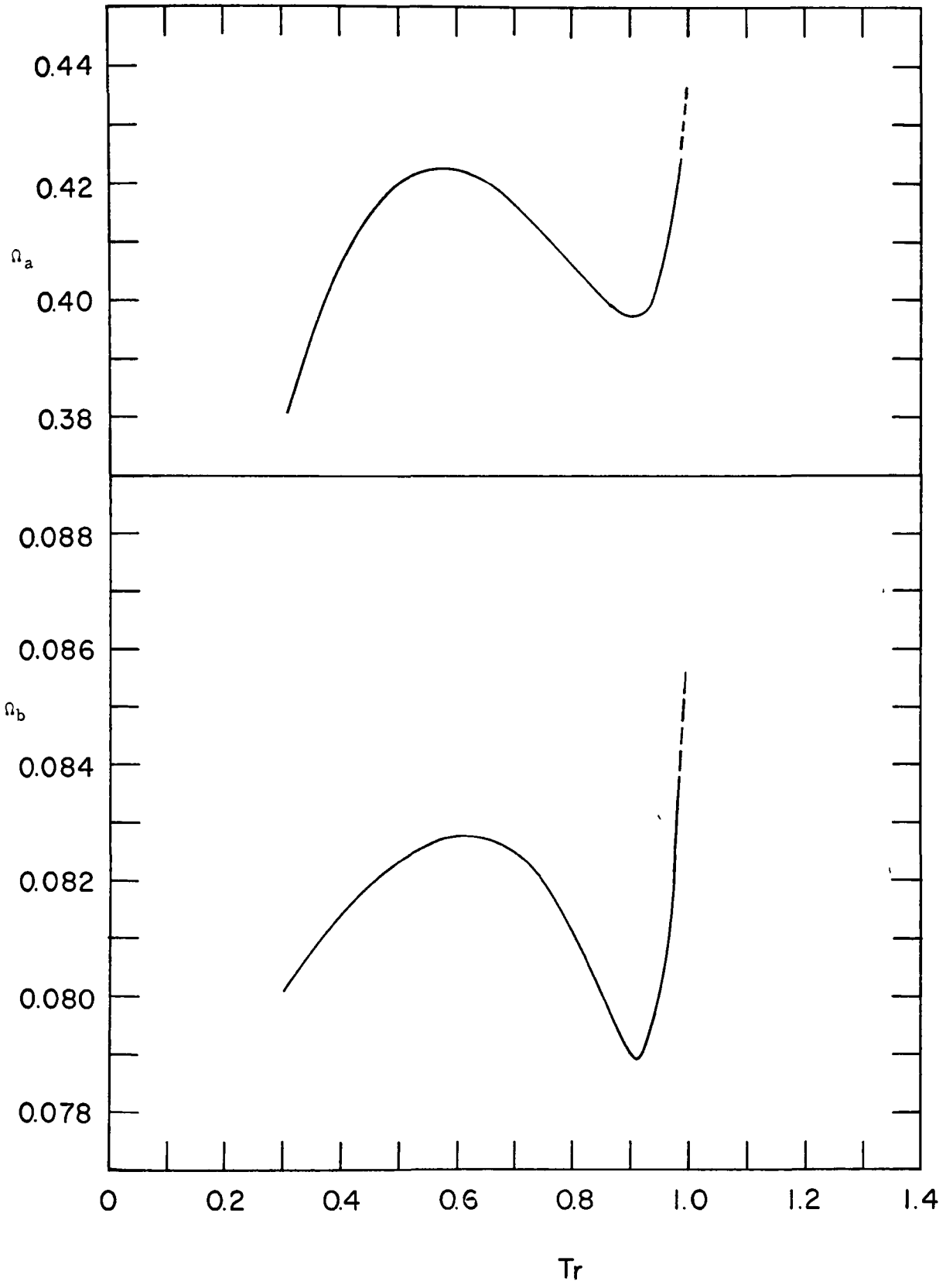


Figure 4.4 The Redlich-Kwong Parameters Ωa and Ωb for Propane

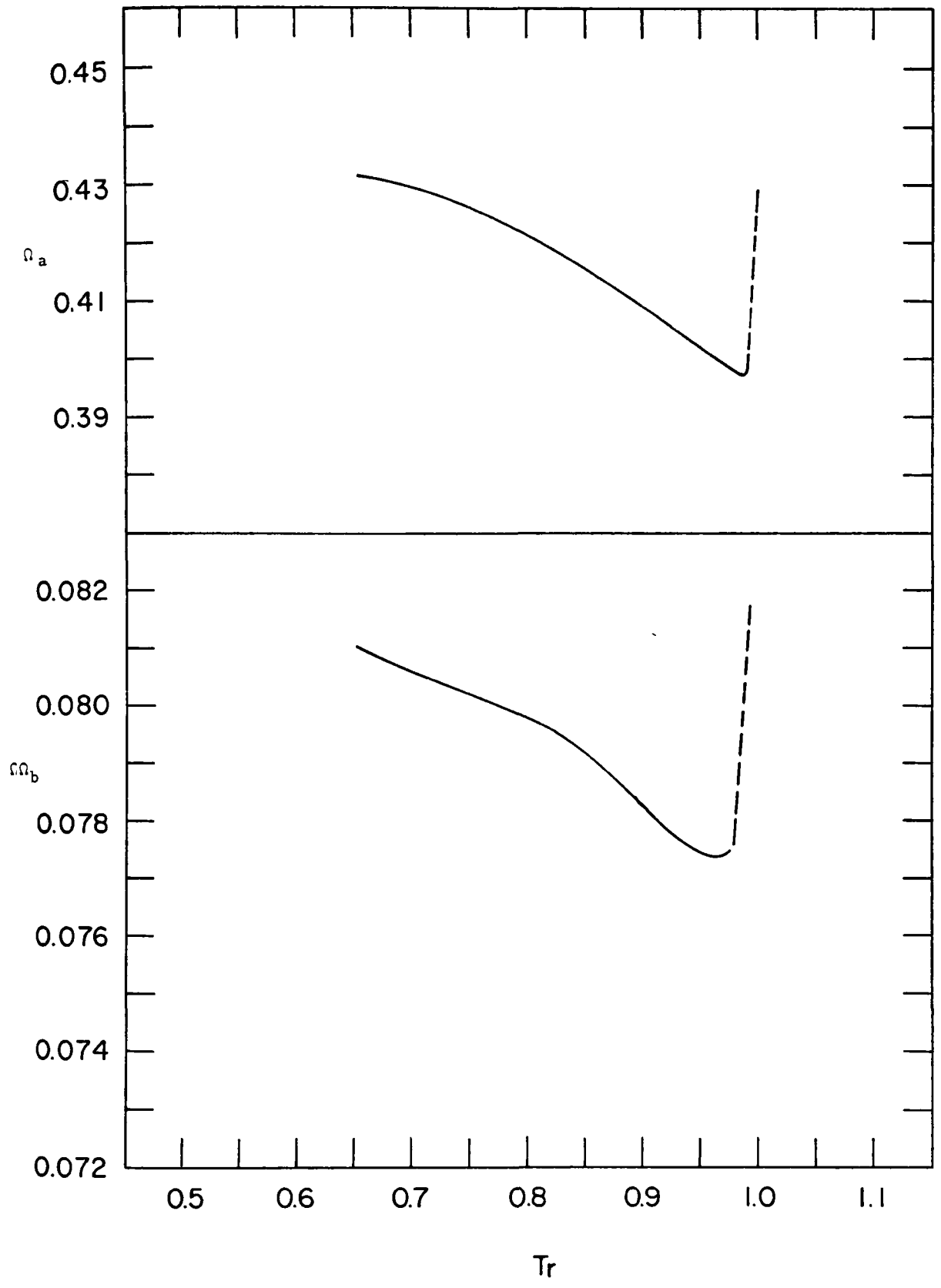


Figure 4.5 The Redlich-Kwong Parameters Ωa and Ωb for n-Butane

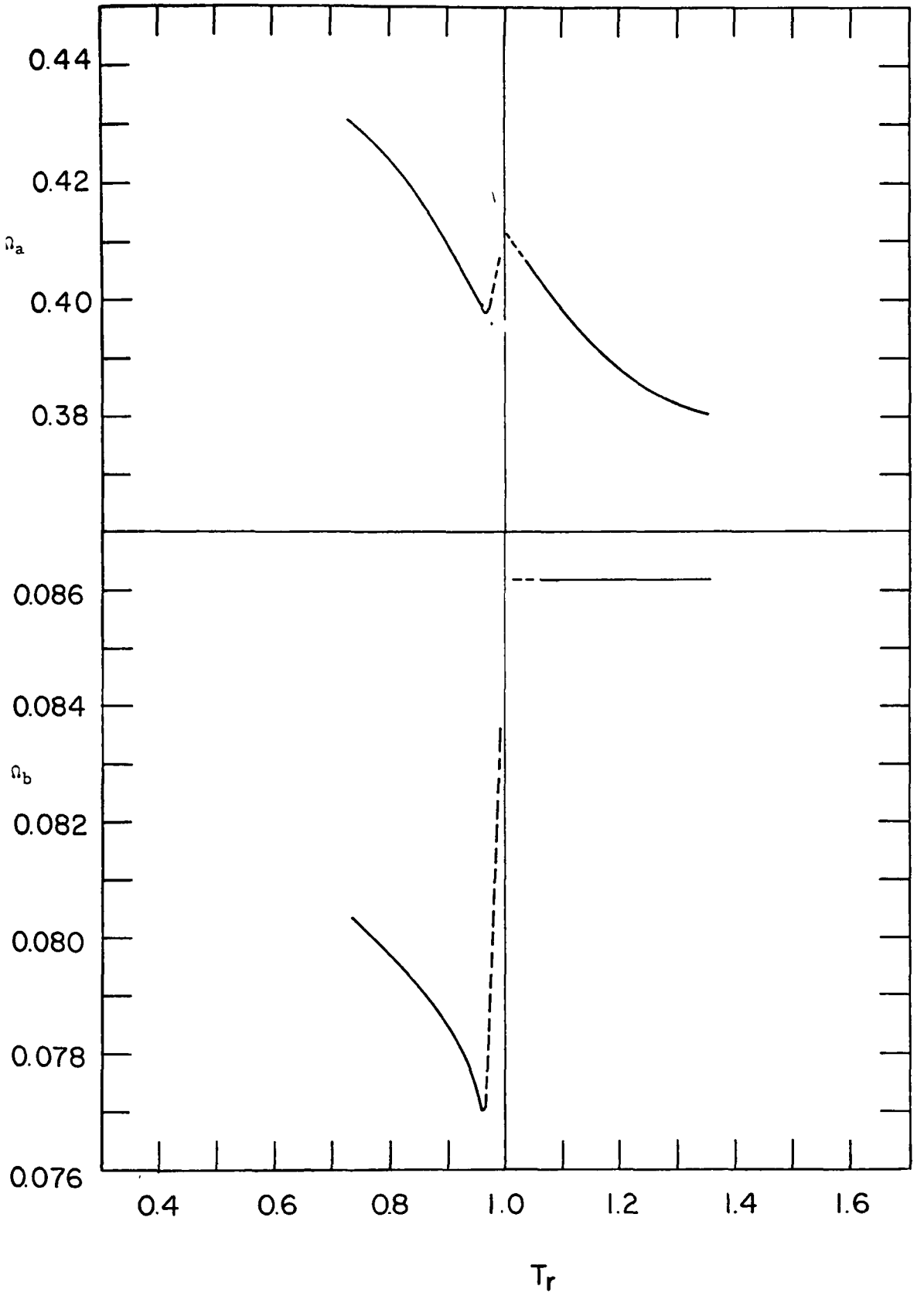


Figure 4.6 The Redlich-Kwong Parameters Ωa and Ωb for Carbon Dioxide

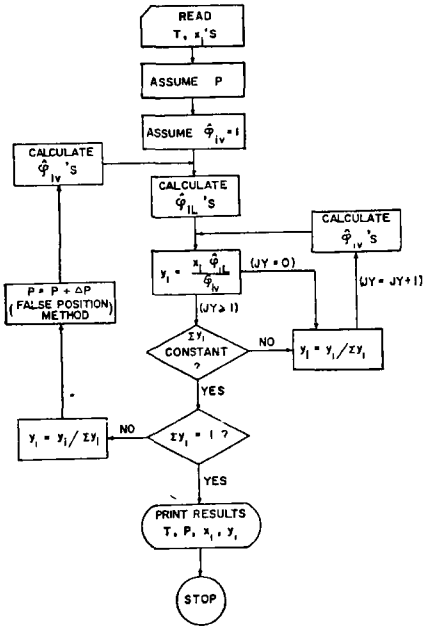


Figure 4.7 Block Diagram of the Iteration Scheme for the Calculation of Vapor-Liquid Equilibrium

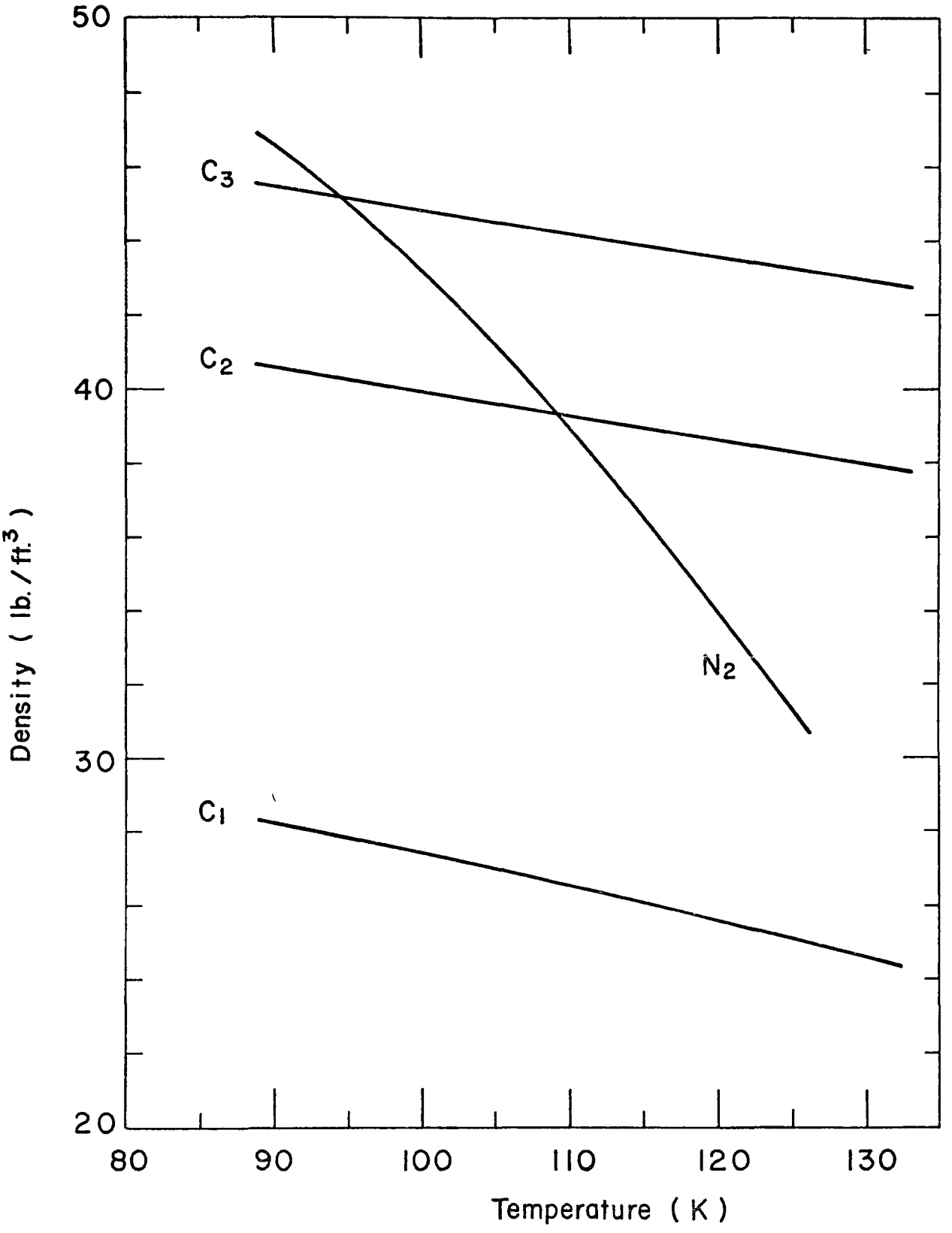


Figure 4.8 The Density Curves for Nitrogen, Methane, Ethane and Propane

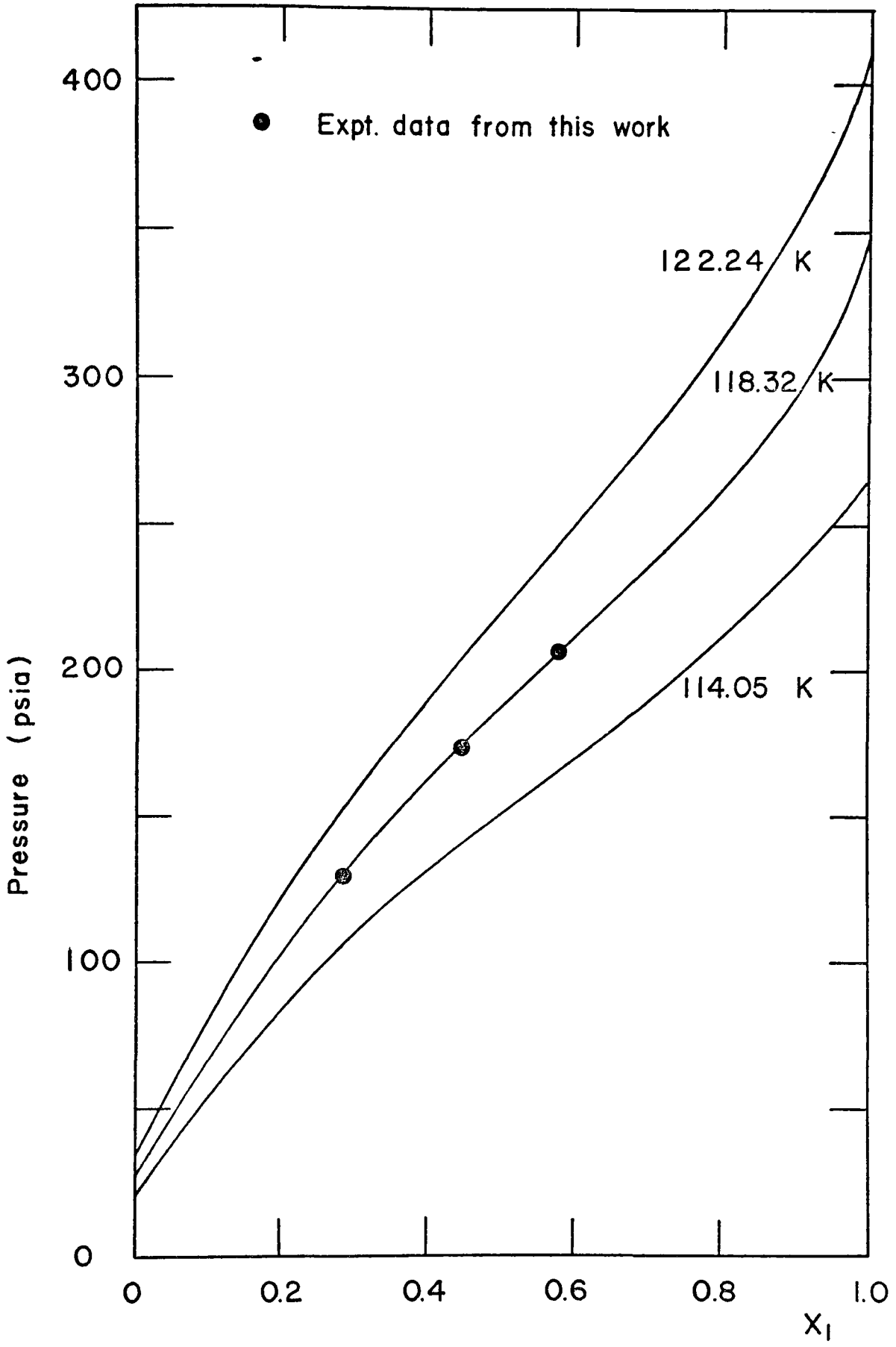


Figure 4.9 The Interpolated Values of Liquid Compositions for the System Nitrogen(1)-Methane(2). [4]

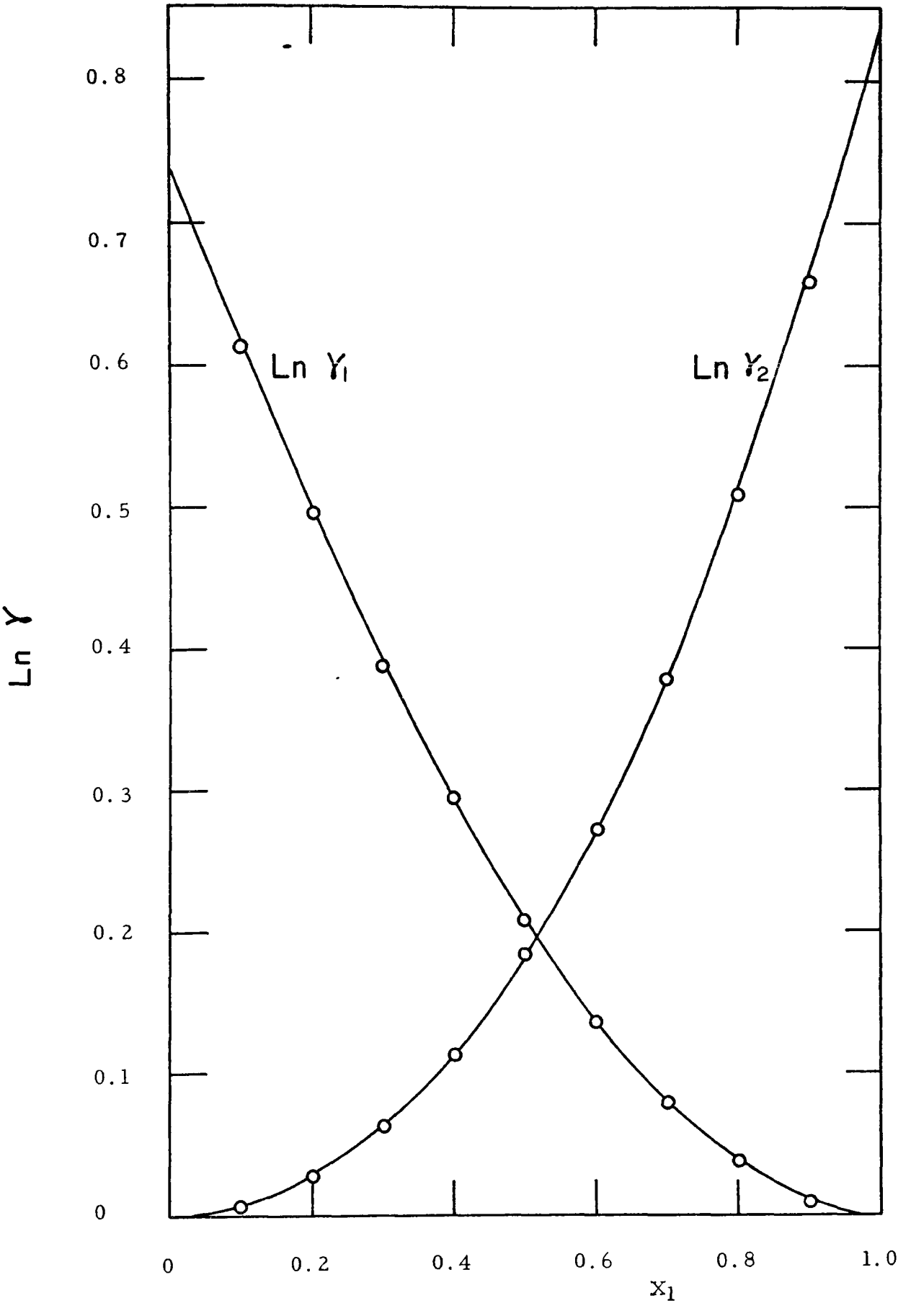


Figure 4.10 Liquid Activity Coefficients for the System Nitrogen(1)-Methane(2) at 114.05 K

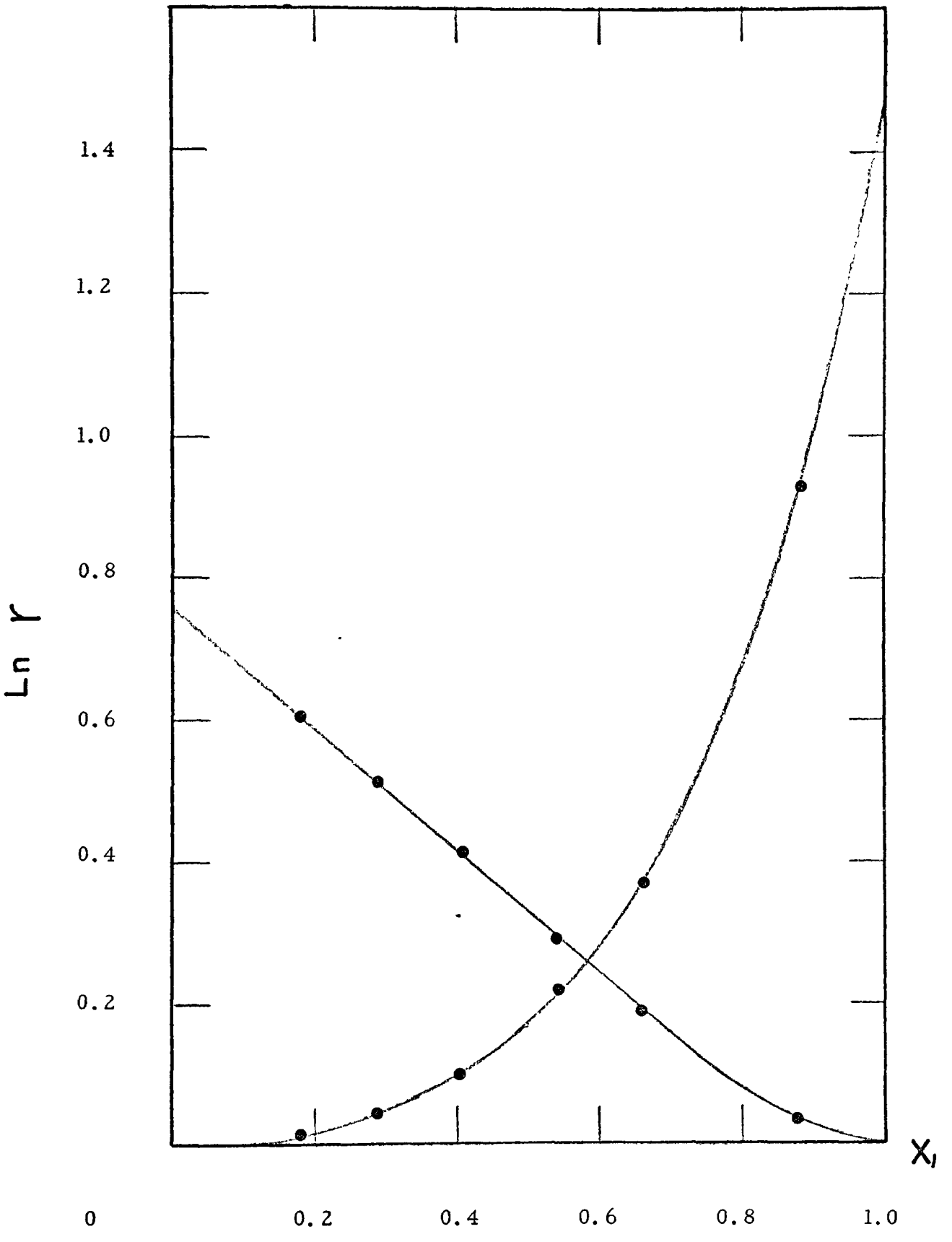


Figure 4.11 Liquid Activity Coefficients for the System Methane(1)-Propane(2) at 114.05 K

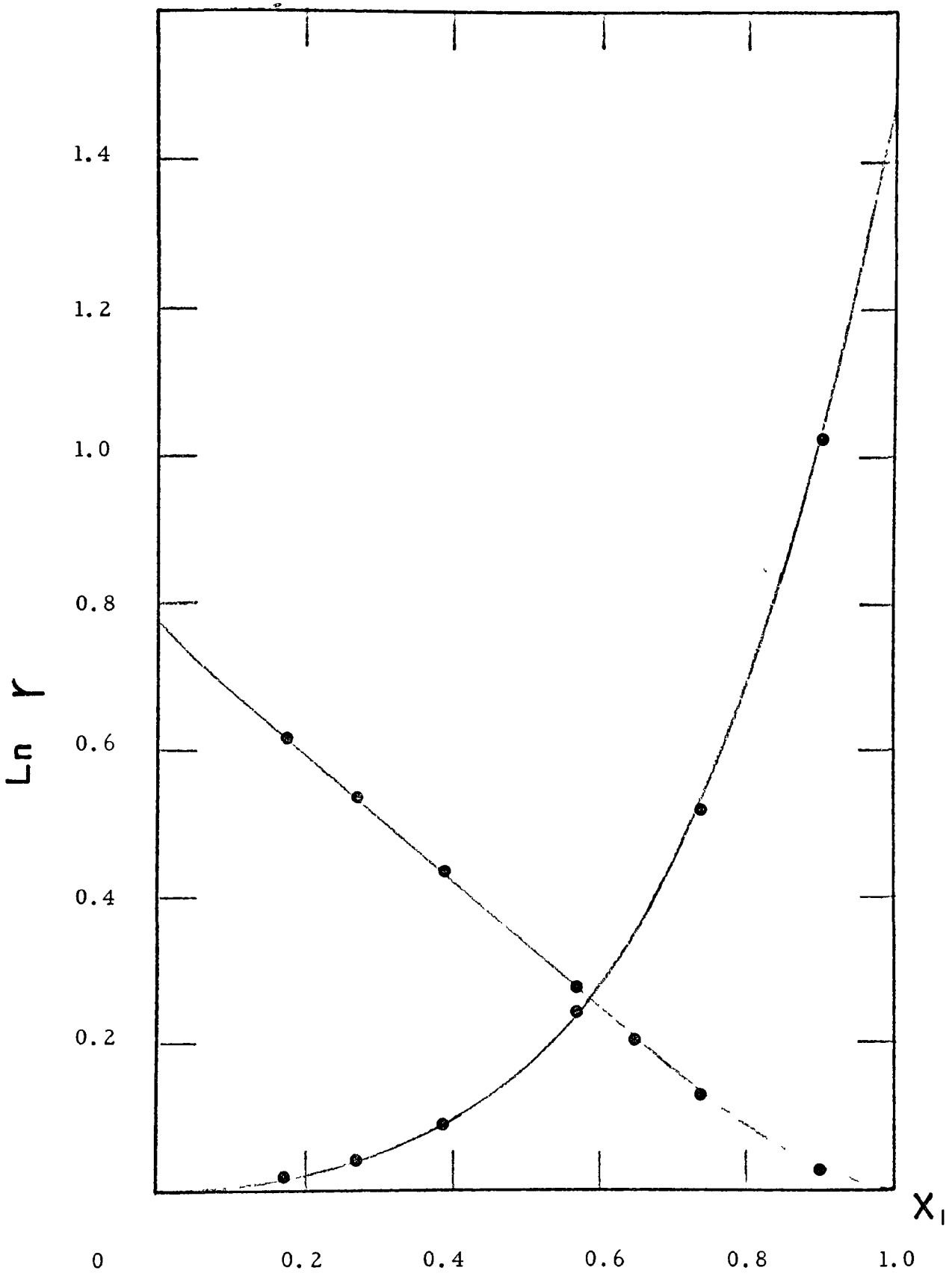


Figure 4.12 Liquid Activity Coefficients for the System Methane(1)-Propane(2) at 118.32 K

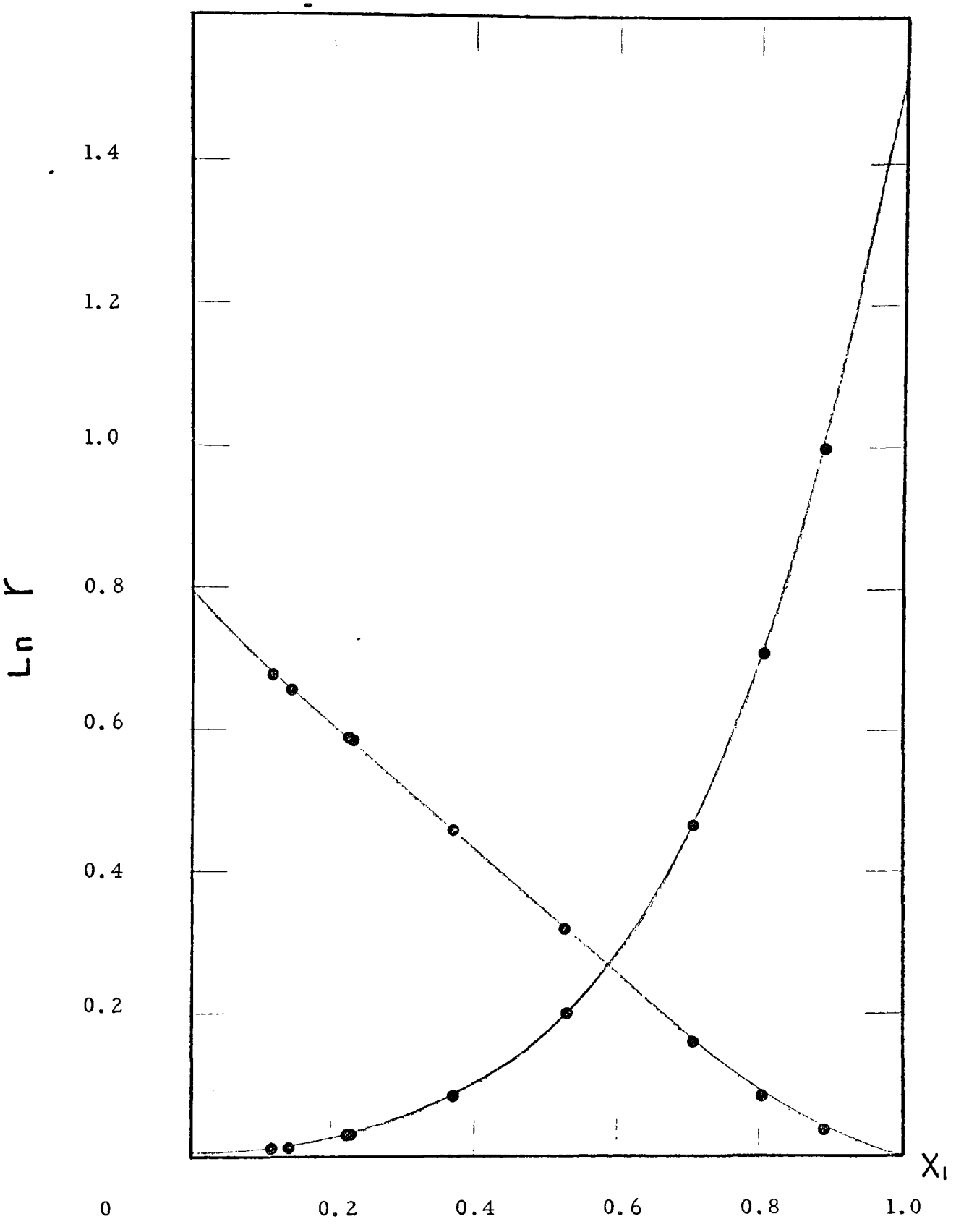


Figure 4.13 Liquid Activity Coefficient for the System Methane(1)-Propane(2) at 122.24 K

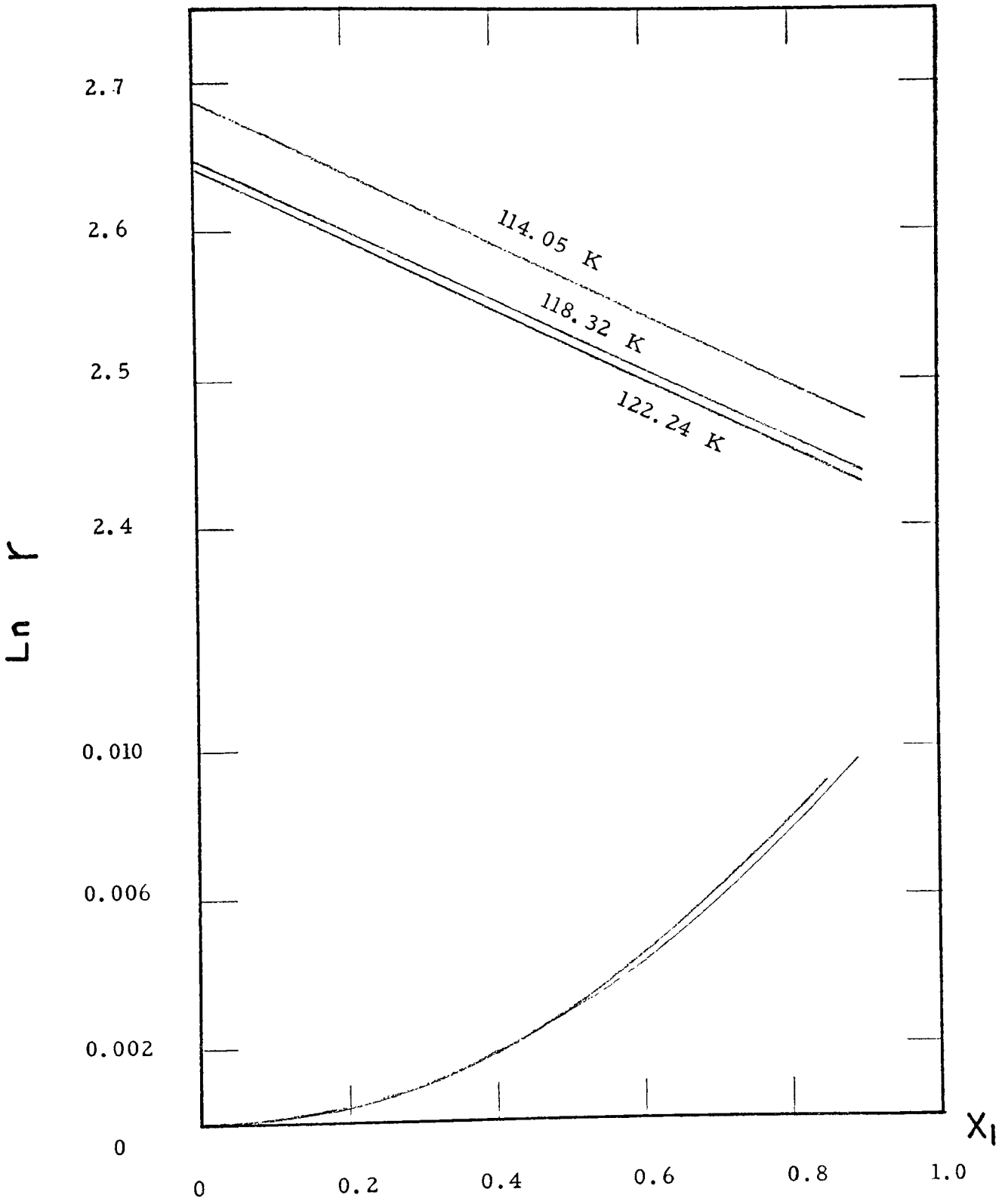


Figure 4.14 Liquid Coefficients for the System Nitrogen(1)-Propane(2) at 114.05 118.32 and 122.24 K

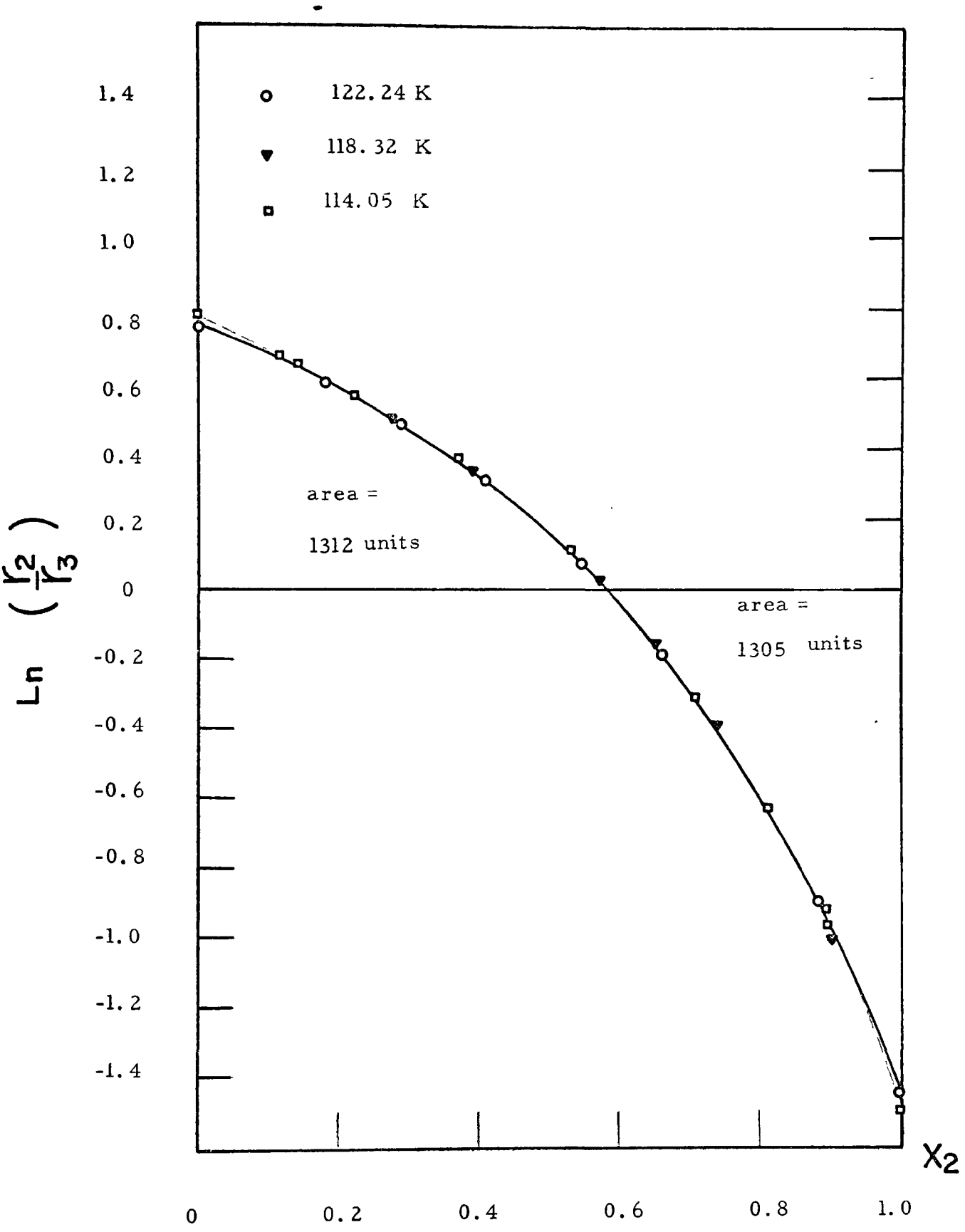


Figure 4.15 A Consistency Test for the System Methane(1)-Propane(2) at 114.05 118.32 and 122.24 K

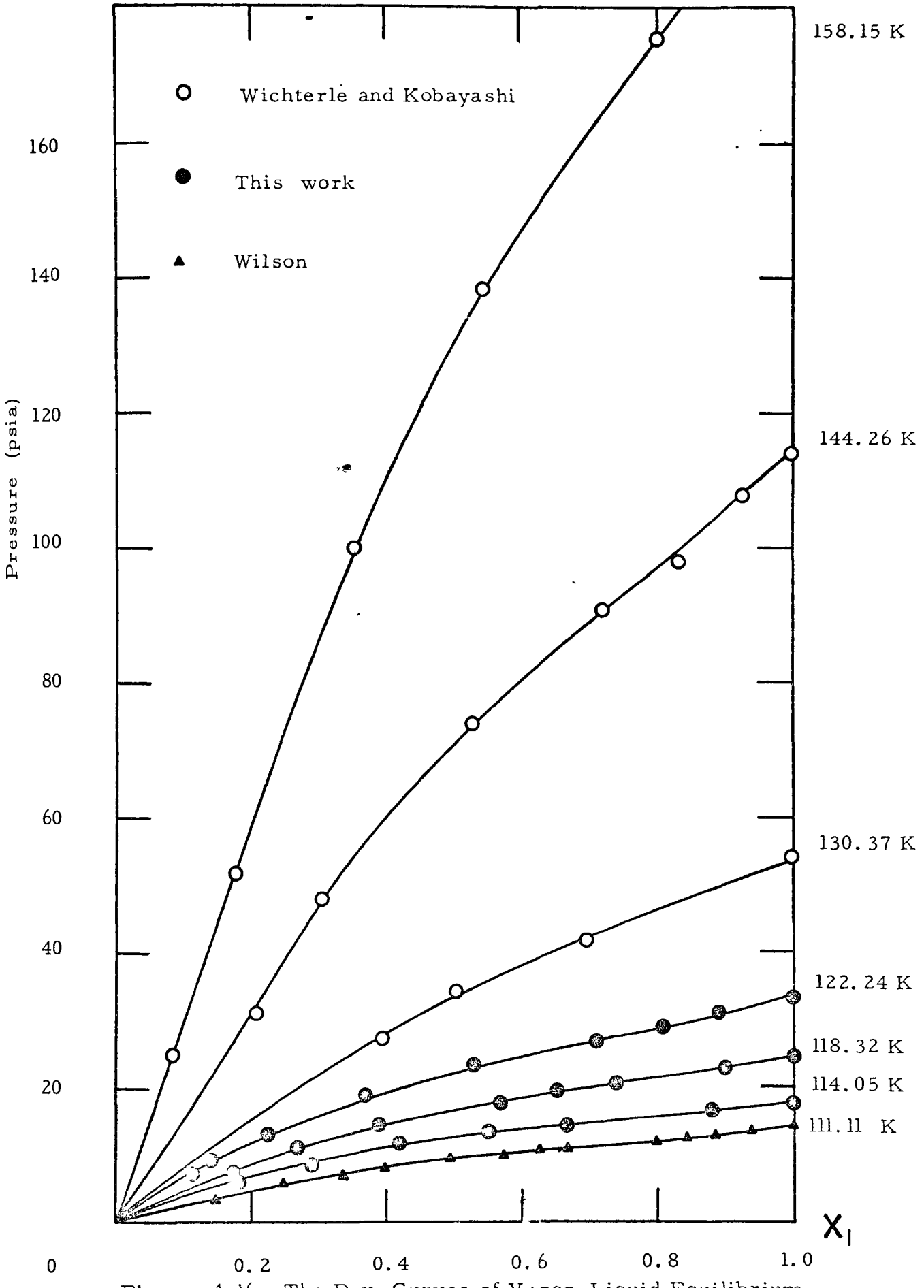


Figure 4.16 The P-x Curves of Vapor-Liquid Equilibrium for the System Methane(1)-Propane(2)

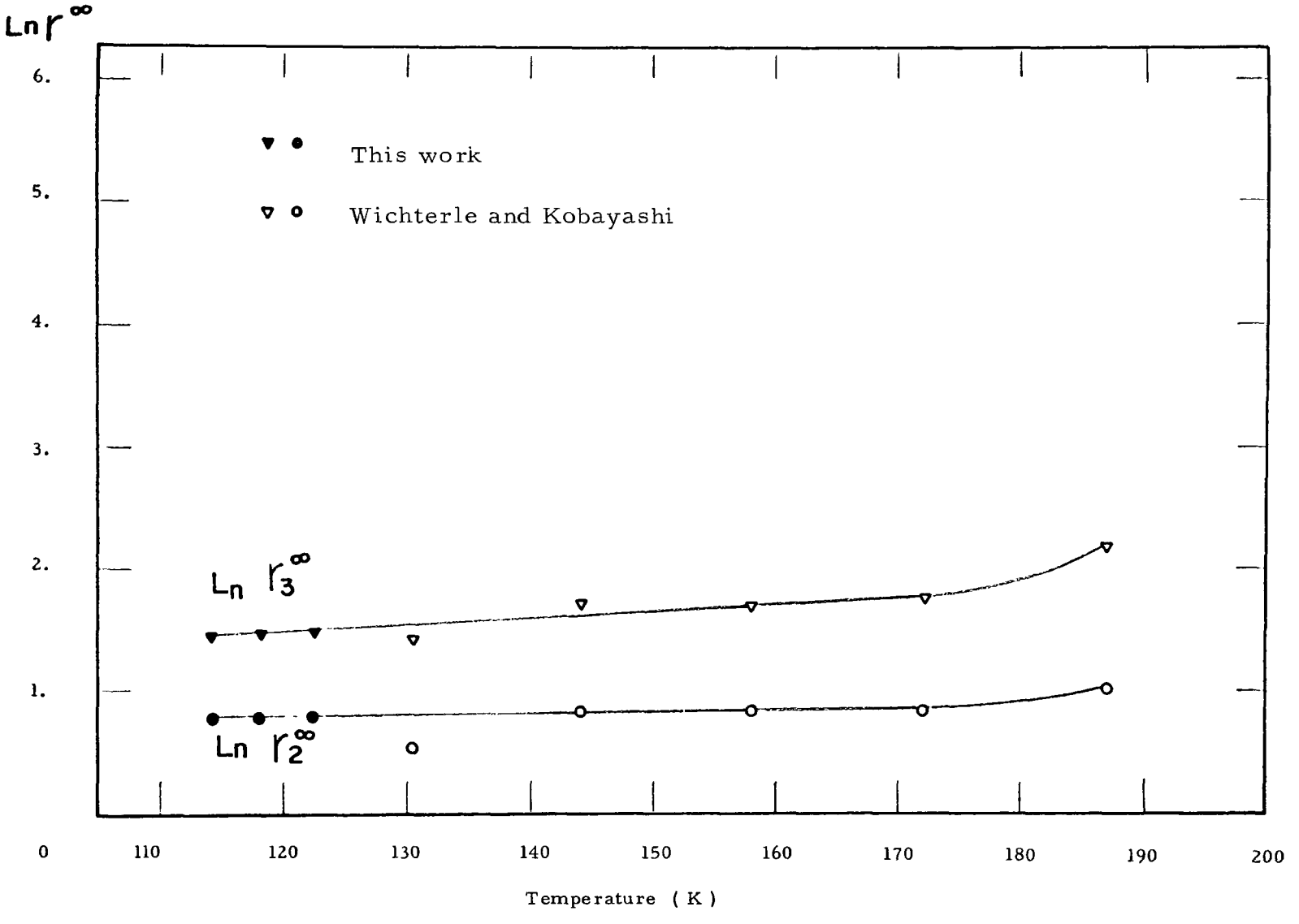


Figure 4.17 Liquid Activity Coefficients at the Conditions of Infinite Dilution for the System Methane(1)-Propane(2).

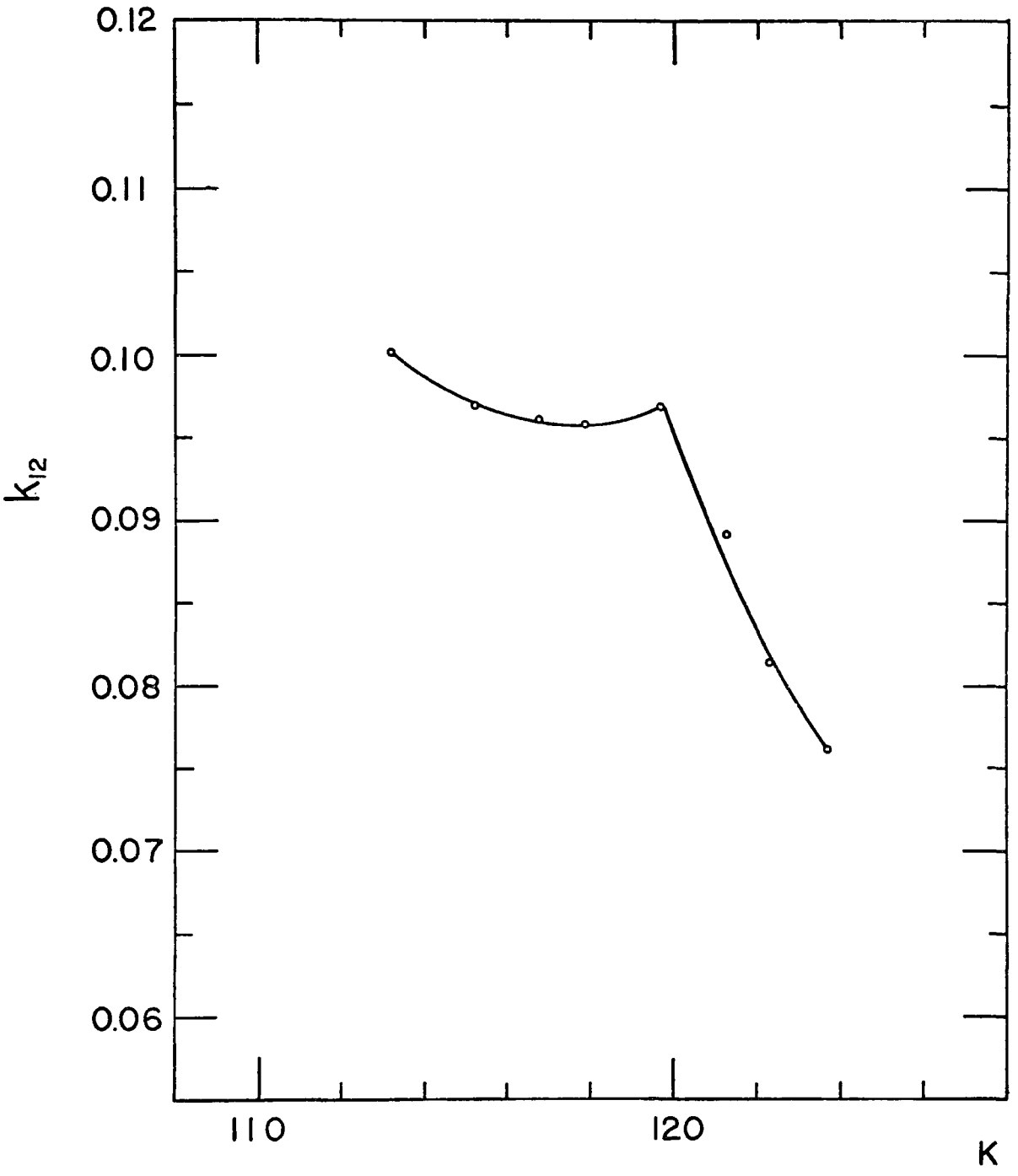


Figure 4.18 Dependence of k_{ij} on Temperature for the System Nitrogen(1)-Propane(2).

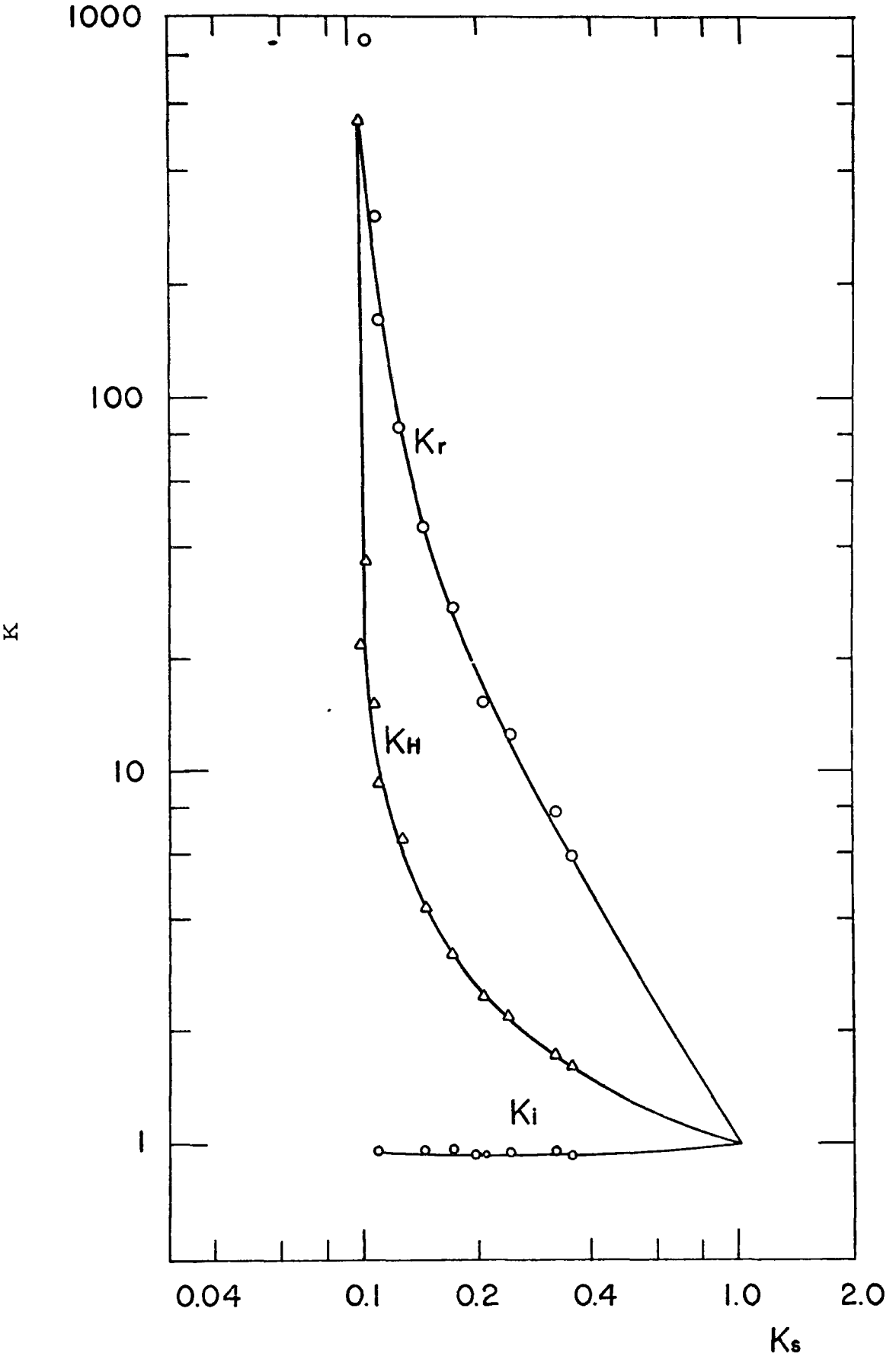


Figure 4.19 A Log-Log Plot of K_r, K_h, and K_i against K_s for the System Nitrogen(s)-Methane(i)-Propane(r) at 114.05 K, for the Method of Black and Hartwig.

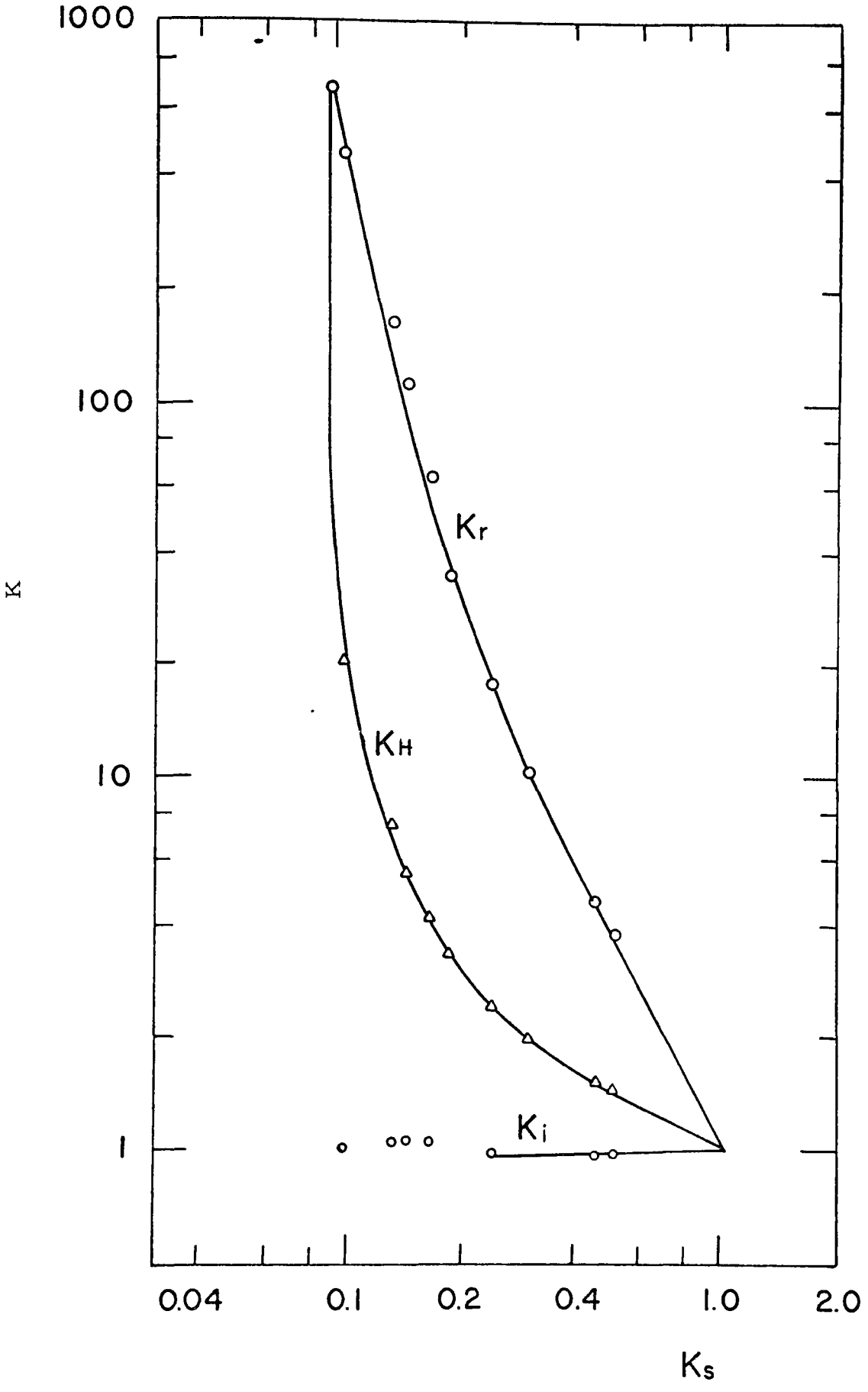


Figure 4.20 A Log-Log Plot of K_r, K_h, and K_i, against K_s for the System Nitrogen(s)-Methane(i)-Propane(r) at 118.32 K, for the Method of Black and Hartwig.

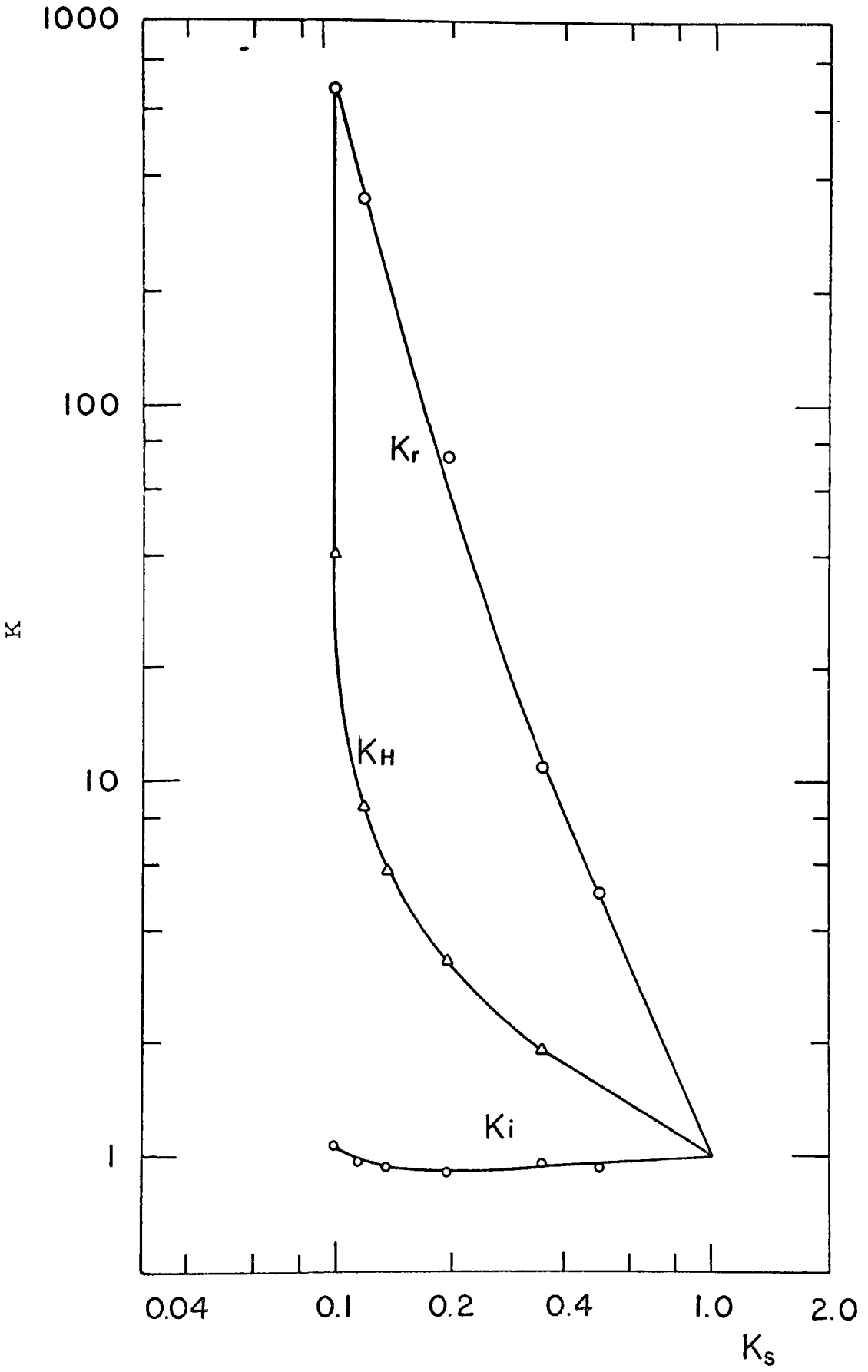


Figure 4.21 A Log-Log Plot of Kr, Kh, and Ki against ks for the System Nitrogen(s)-Methane(i)-Propane(r) at 122.24 K, for the Method of Black and Hartwig.

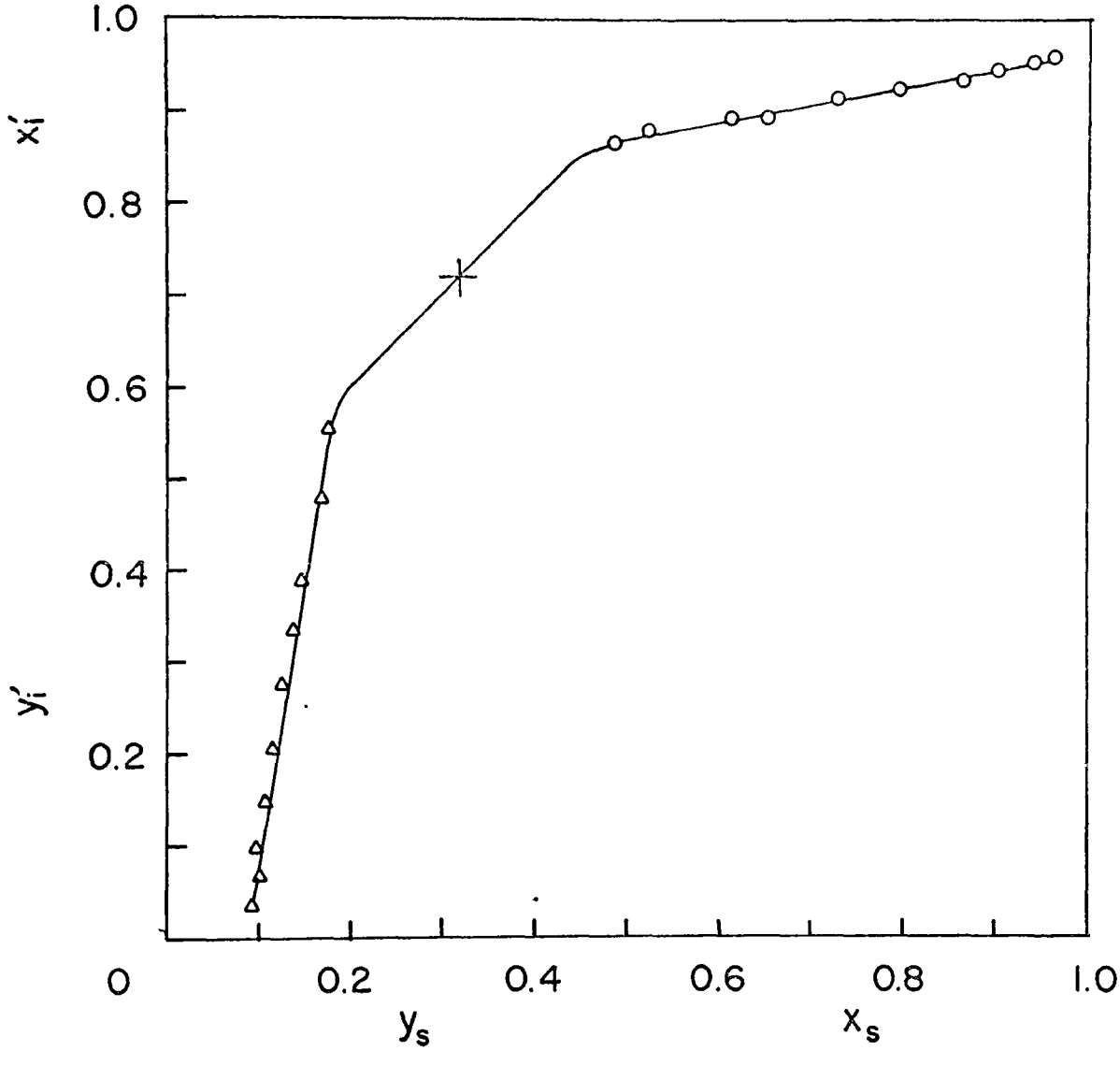


Figure 4.22 A Plot of x'_i and y'_i against x_s and y_s for the System Nitrogen(s)-Methane(i)-Propane(r) at 114.05 K, for the Method of Black and Hartwig.

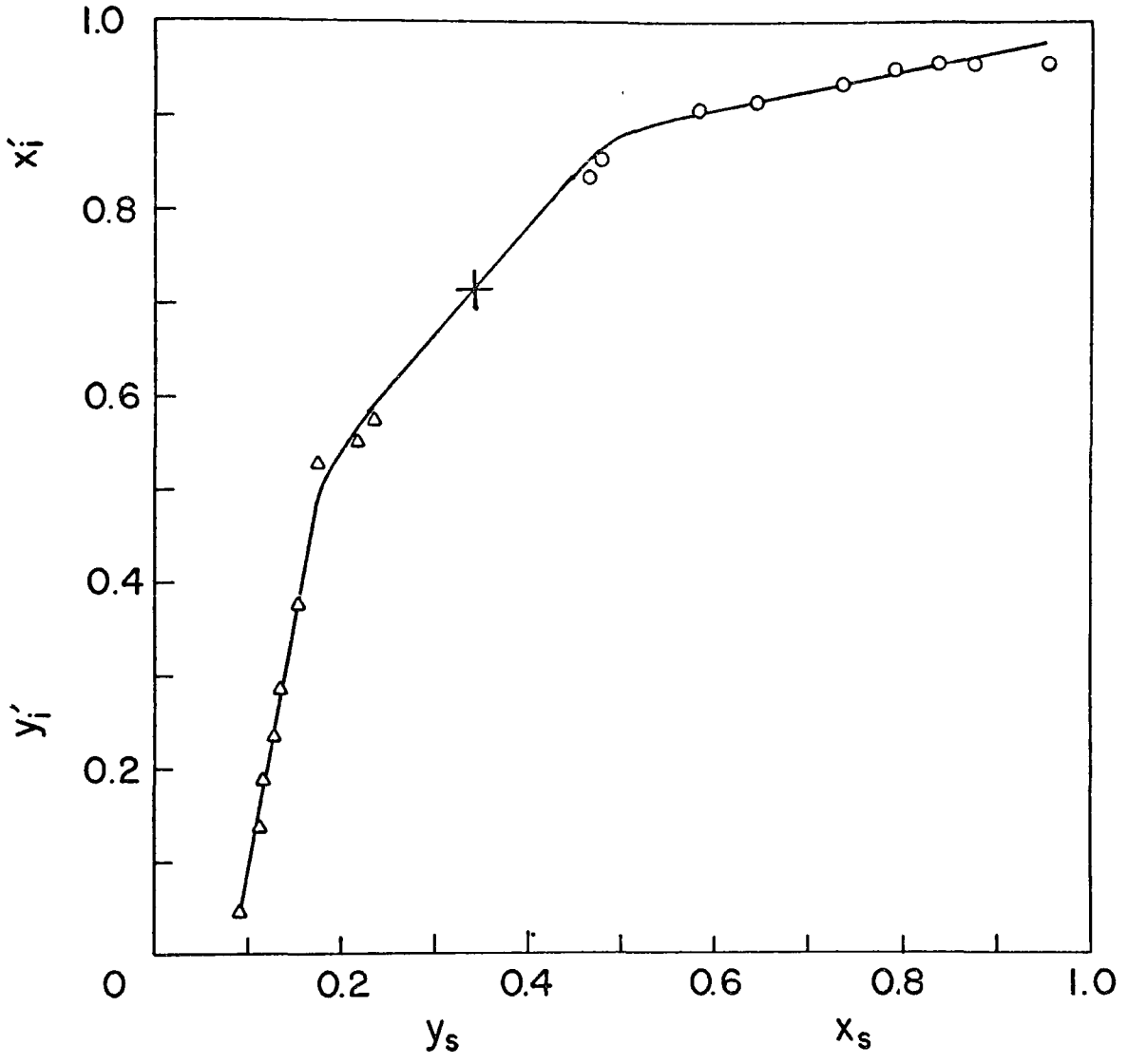


Figure 4.23 A Plot of x'_i and y'_i against x_s and y_s for the System Nitrogen(s)-Methane(i)-Propane(r) at 118.32 K, for the Method of Black and Hartwig.

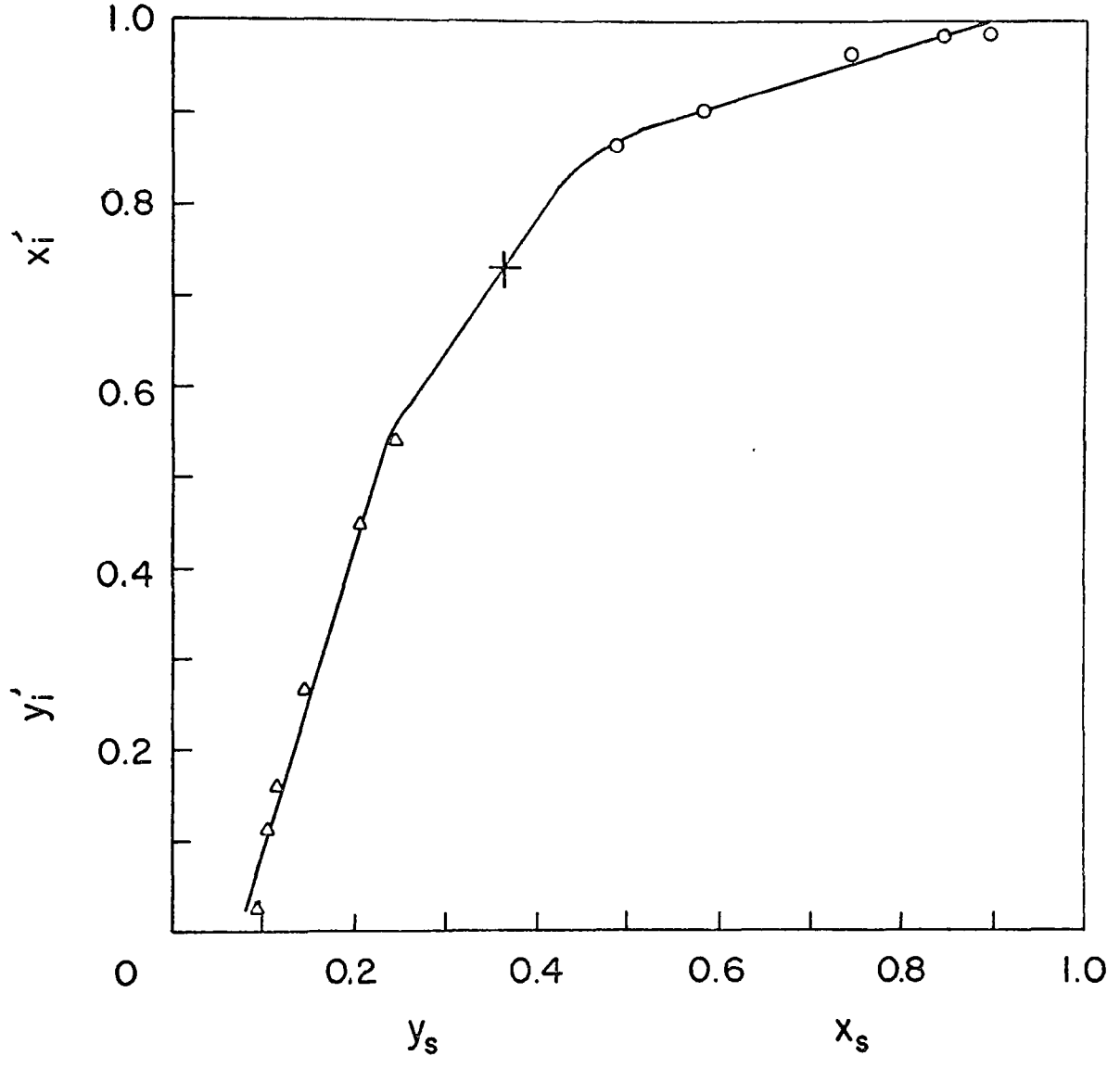


Figure 4.24 A Plot of x_i' and y_i' against x_s and y_s for the System Nitrogen(s)-Methane(i)-Propane(r) at 122.24 K, for the Method of Black and Hartwig.

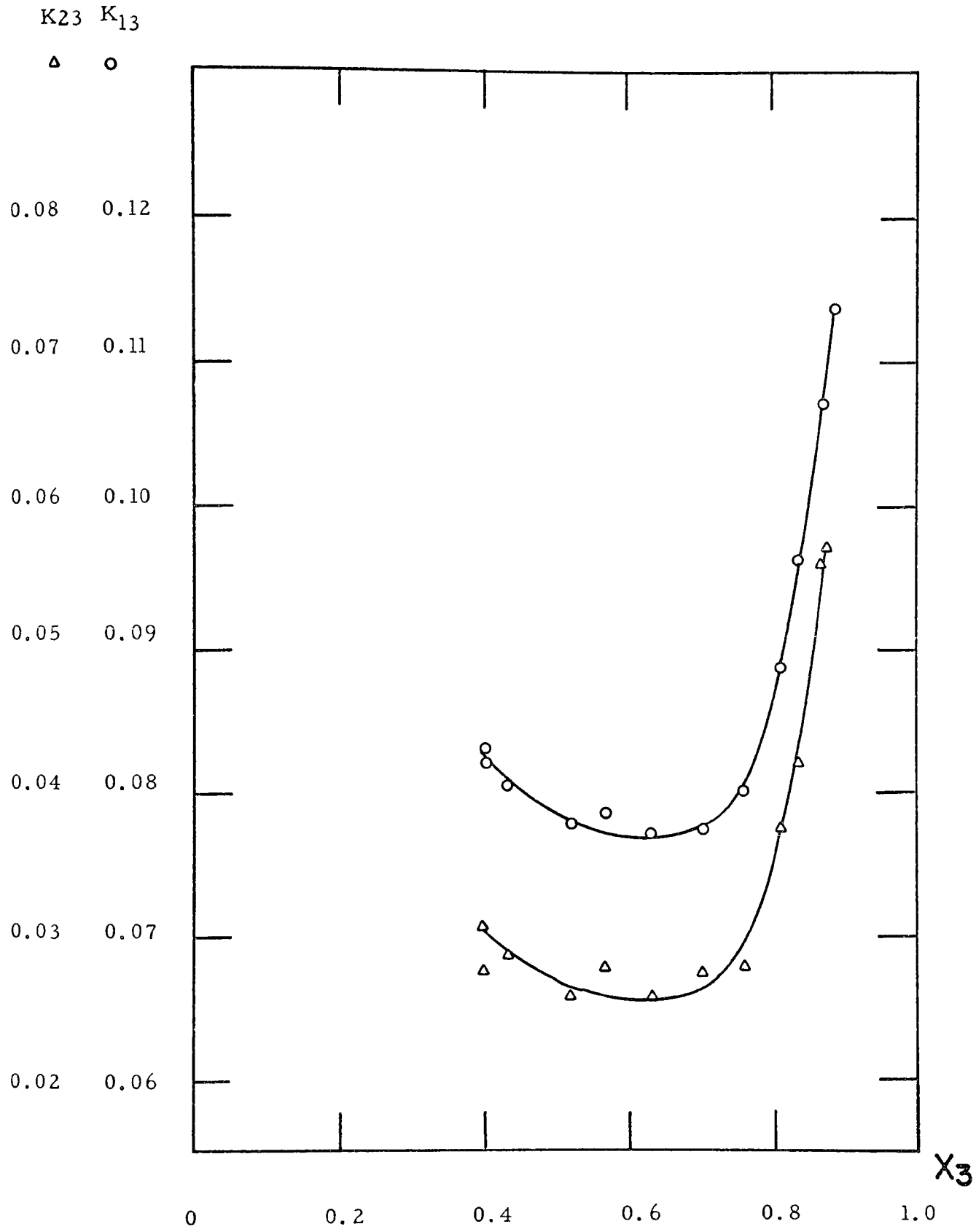


Figure 4.25 Dependence of k_{ij} on Composition for the Systems Nitrogen(1)-Propane(3) and Methane(2)-Propane(3) at 114.05 K.

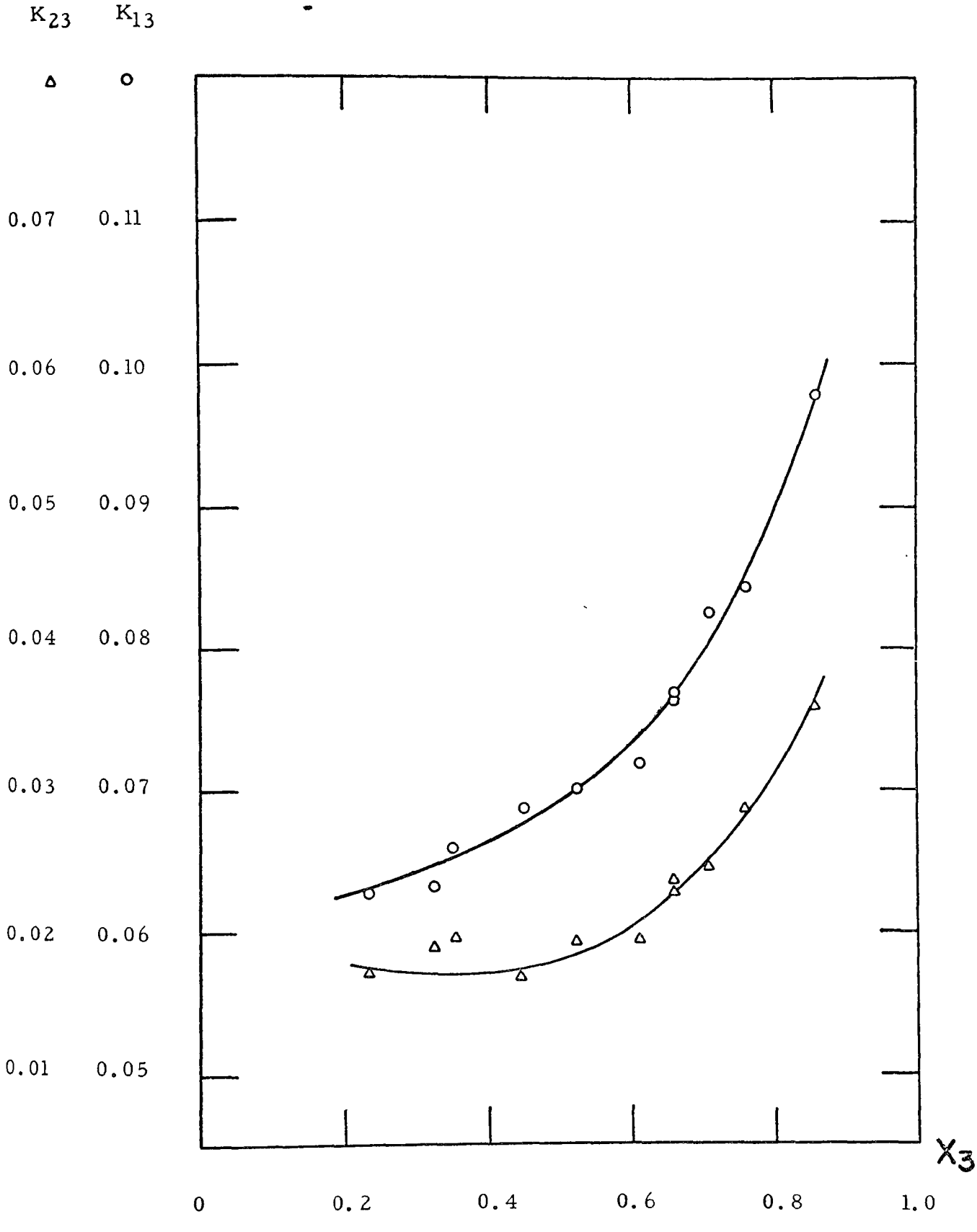


Figure 4.26 Dependence of k_{ij} on Composition for the Systems Nitrogen(1)-Propane(3), and Methane(2)-Propane(3) at 118.32 K.

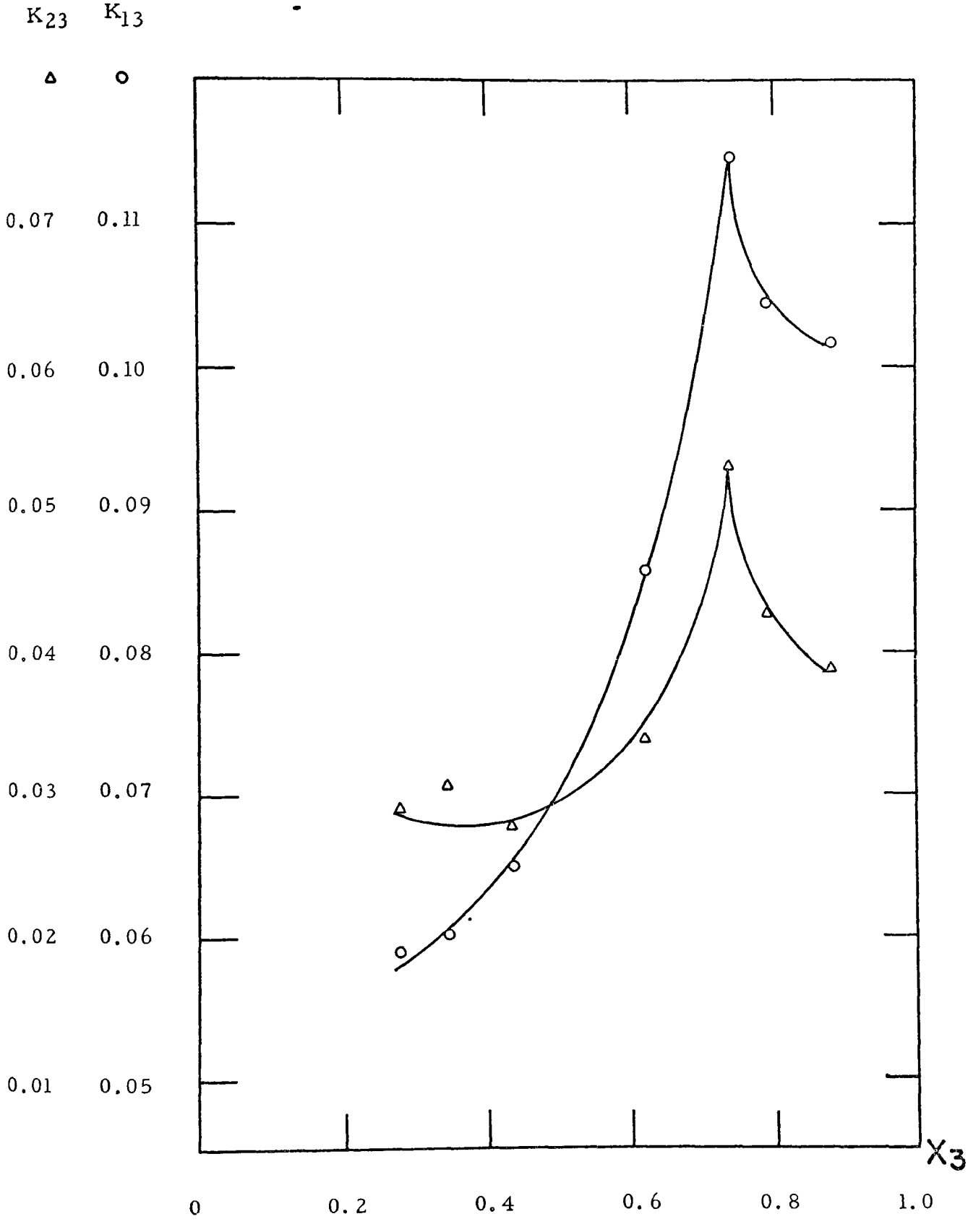


Figure 4.27 Dependence of k_{ij} on Composition for the Systems Nitrogen(1)-Propane(3) and Methane(2)-Propane(3) at 122.24 K.

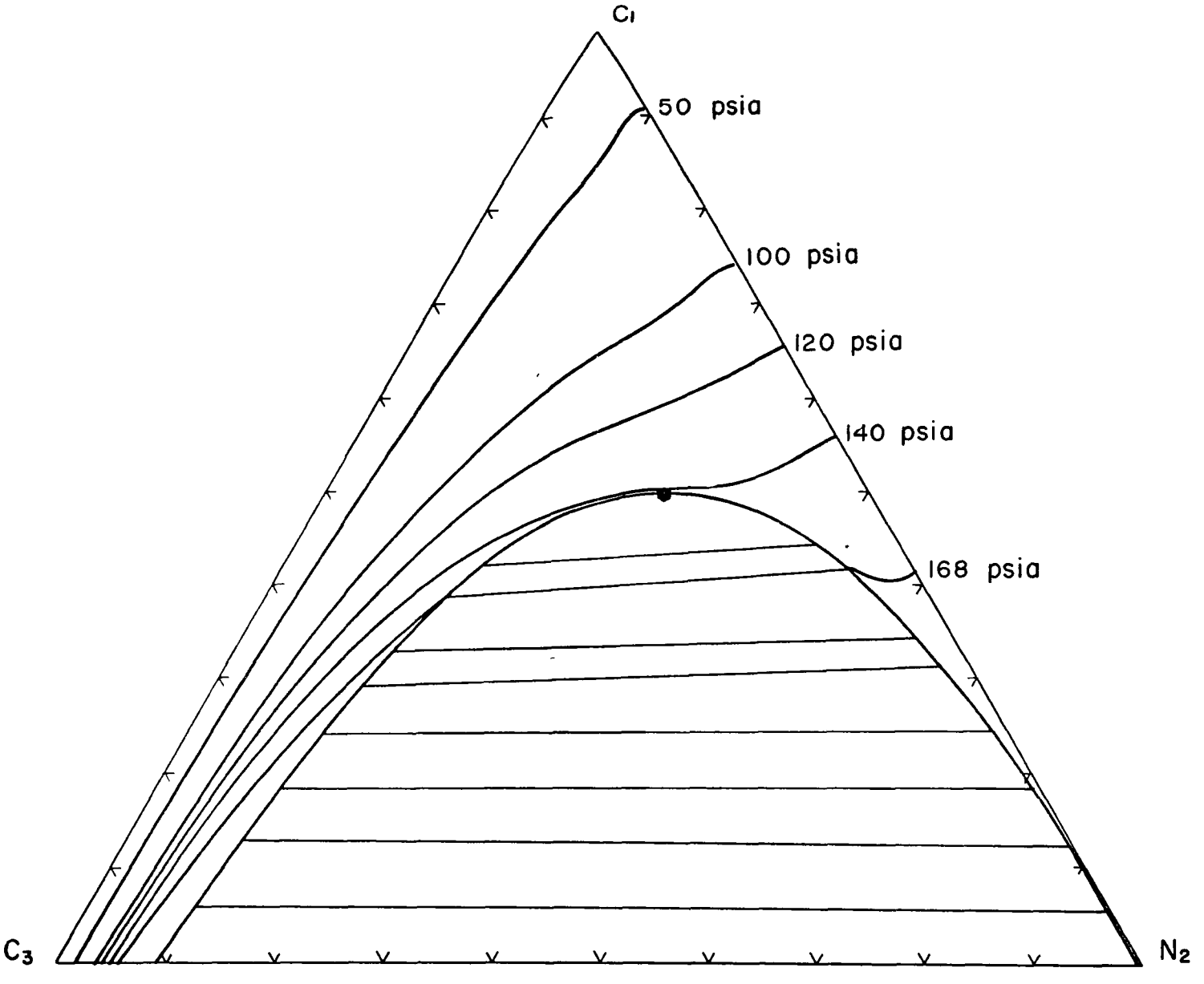


Figure 4.28 The Constant Pressure Curves for the System Nitrogen(1)-Methane(2)-Propane(3) at 114.05 K.

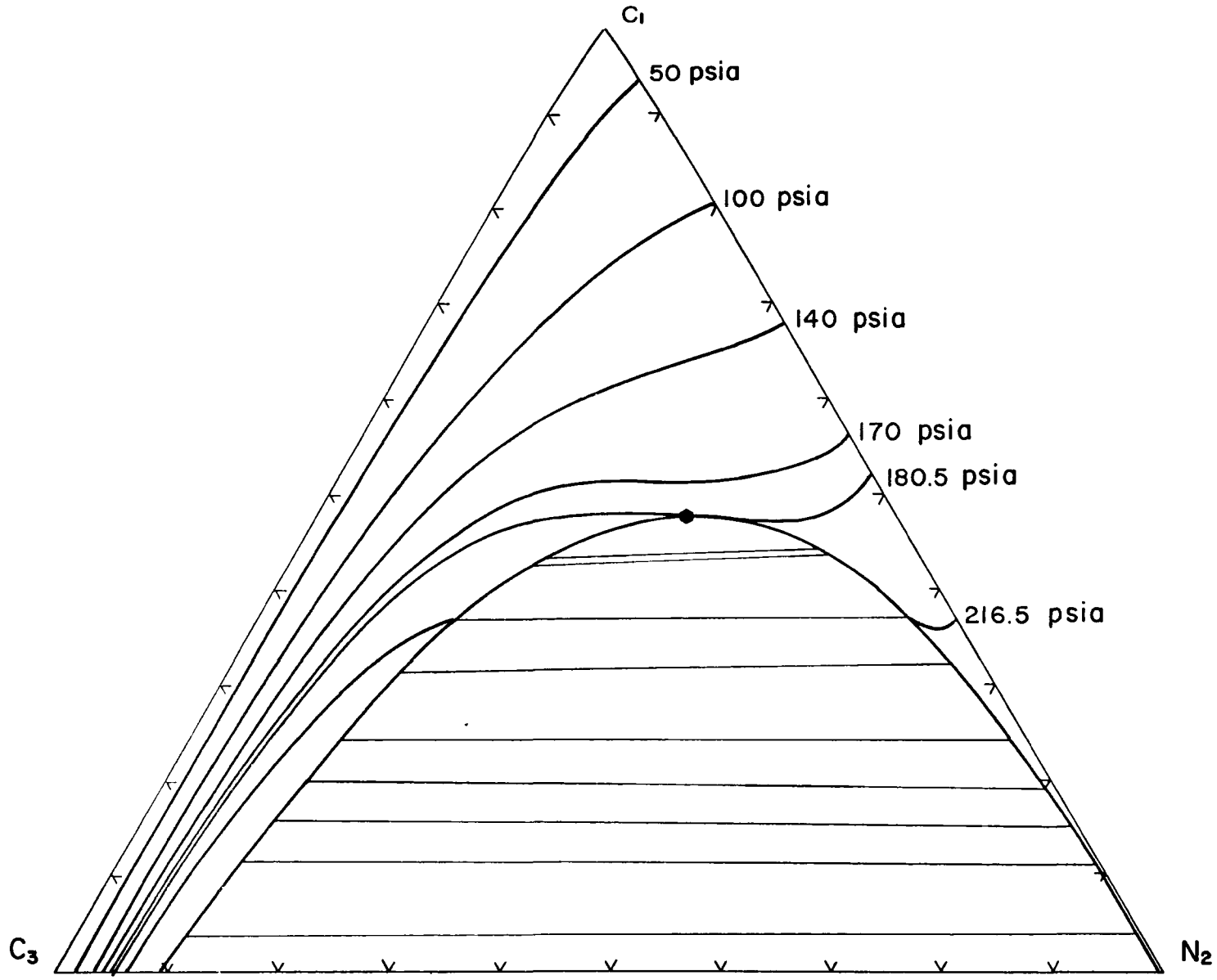


Figure 4.29 The Constant Pressure Curves for the System Nitrogen(1)-Methane(2)-Propane(3) at 118.32 K.

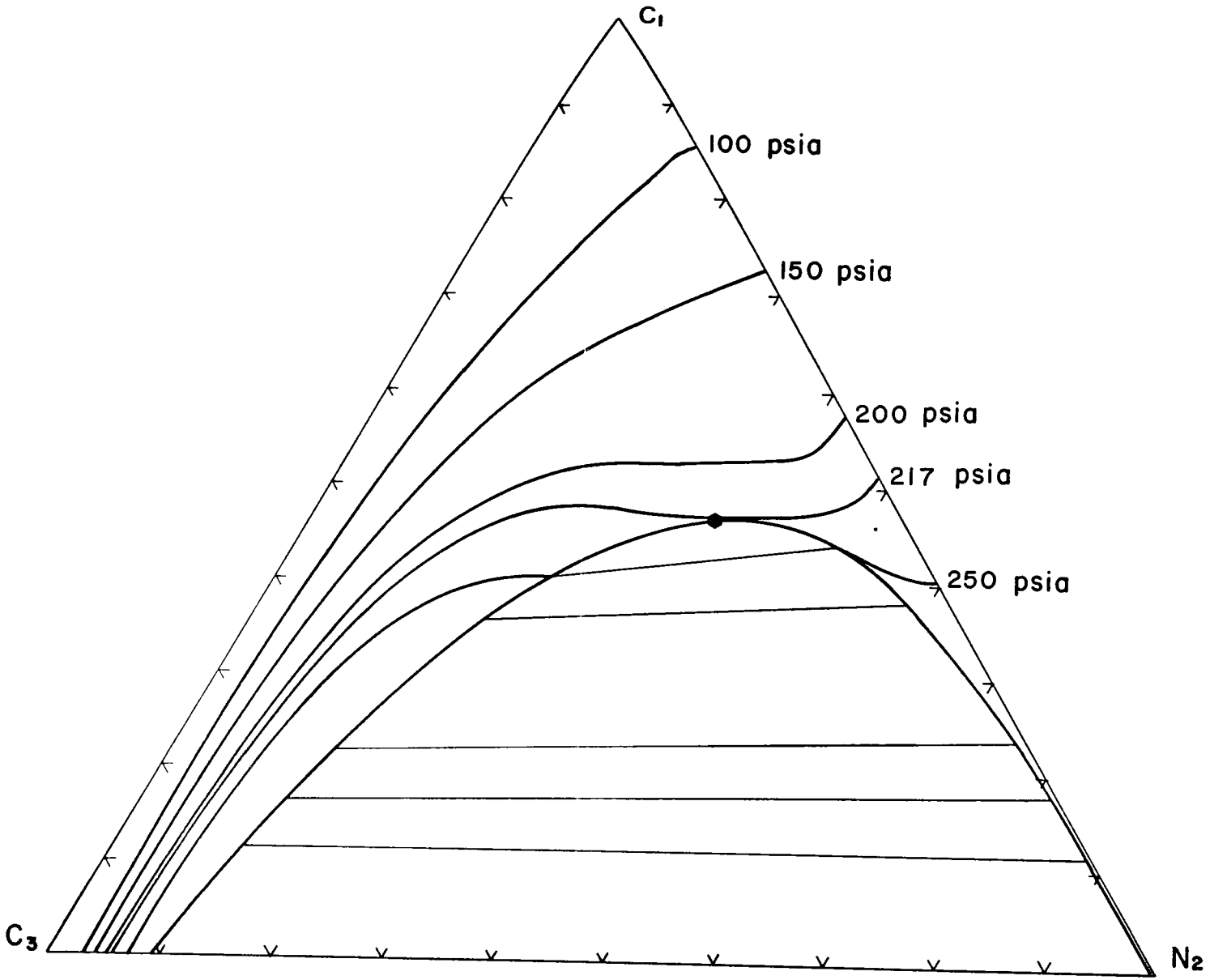


Figure 4.30 The Constant Pressure Curves for the System Nitrogen(1)-Methane(2)-Propane(3) at 122.24 K.

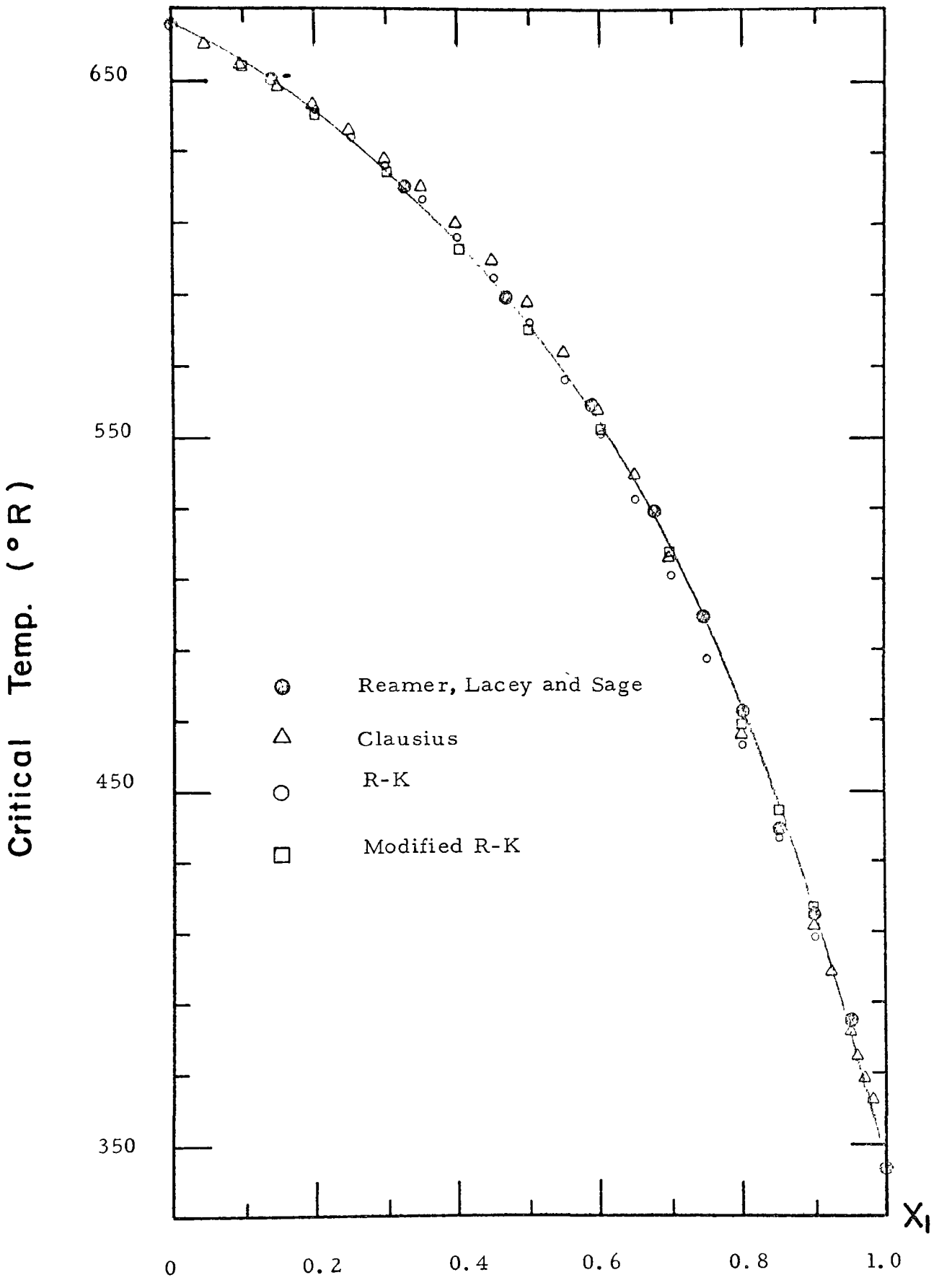


Figure 4.31 Critical Temperatures for the Methane(1)-Propane(2) Mixtures for Detailed Discussions for the System.

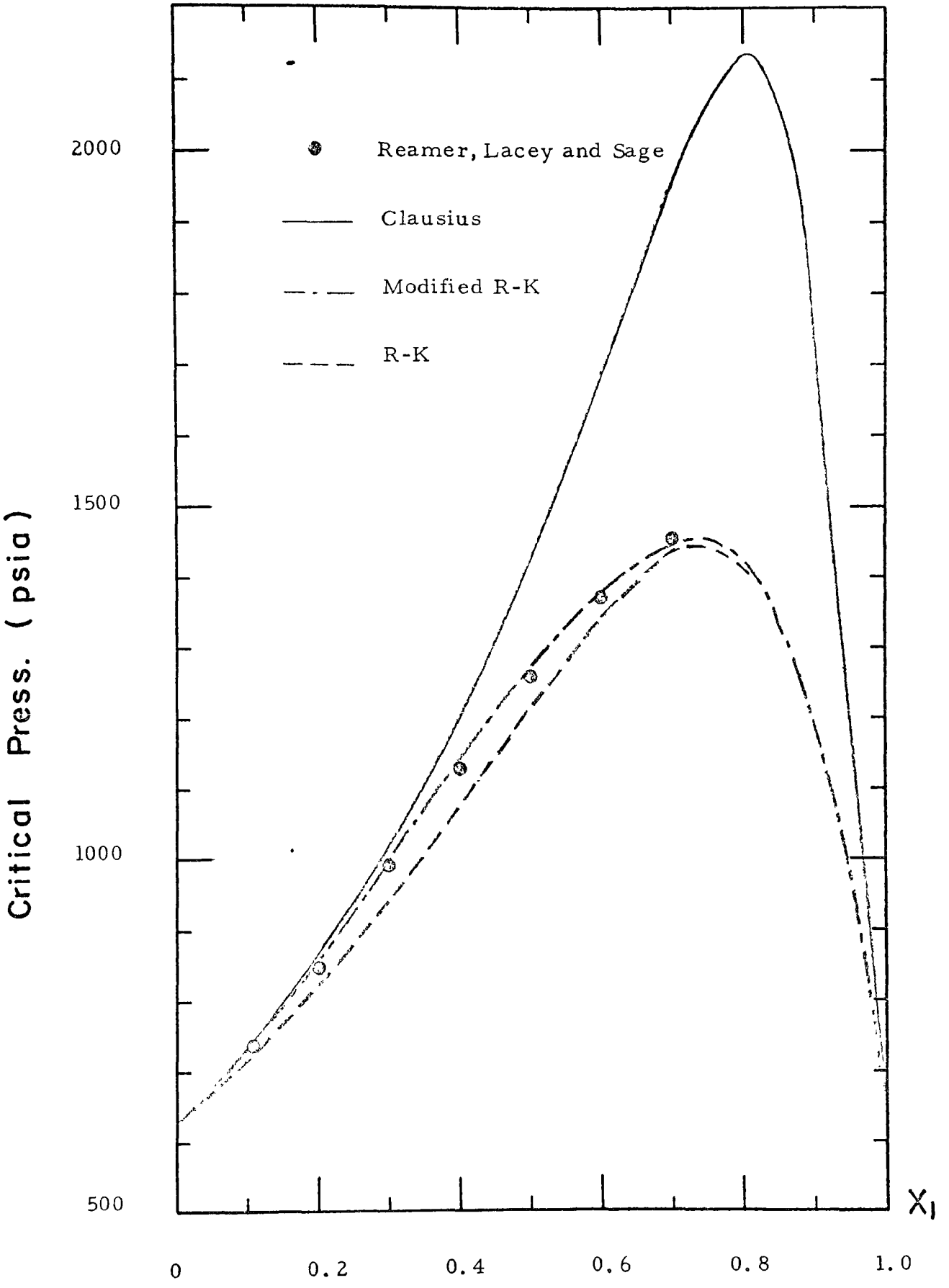


Figure 4.32 Critical Pressures for the Methane(1)-Propane(2) Mixtures for Detailed Discussions for the System.

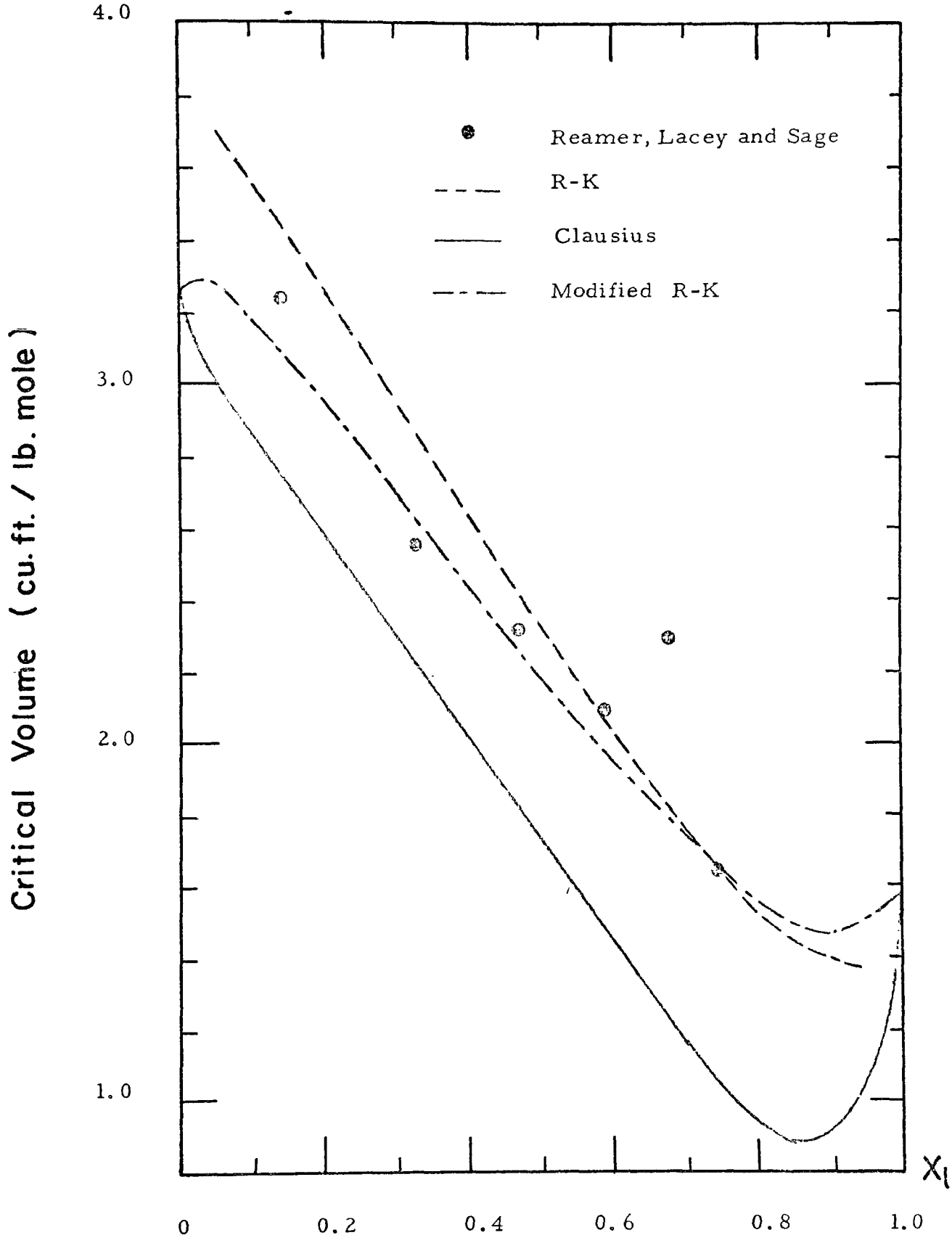


Figure 4.33 Critical Volumes for the Methane(1)-Propane(2) Mixtures for Detailed Discussions for the System.

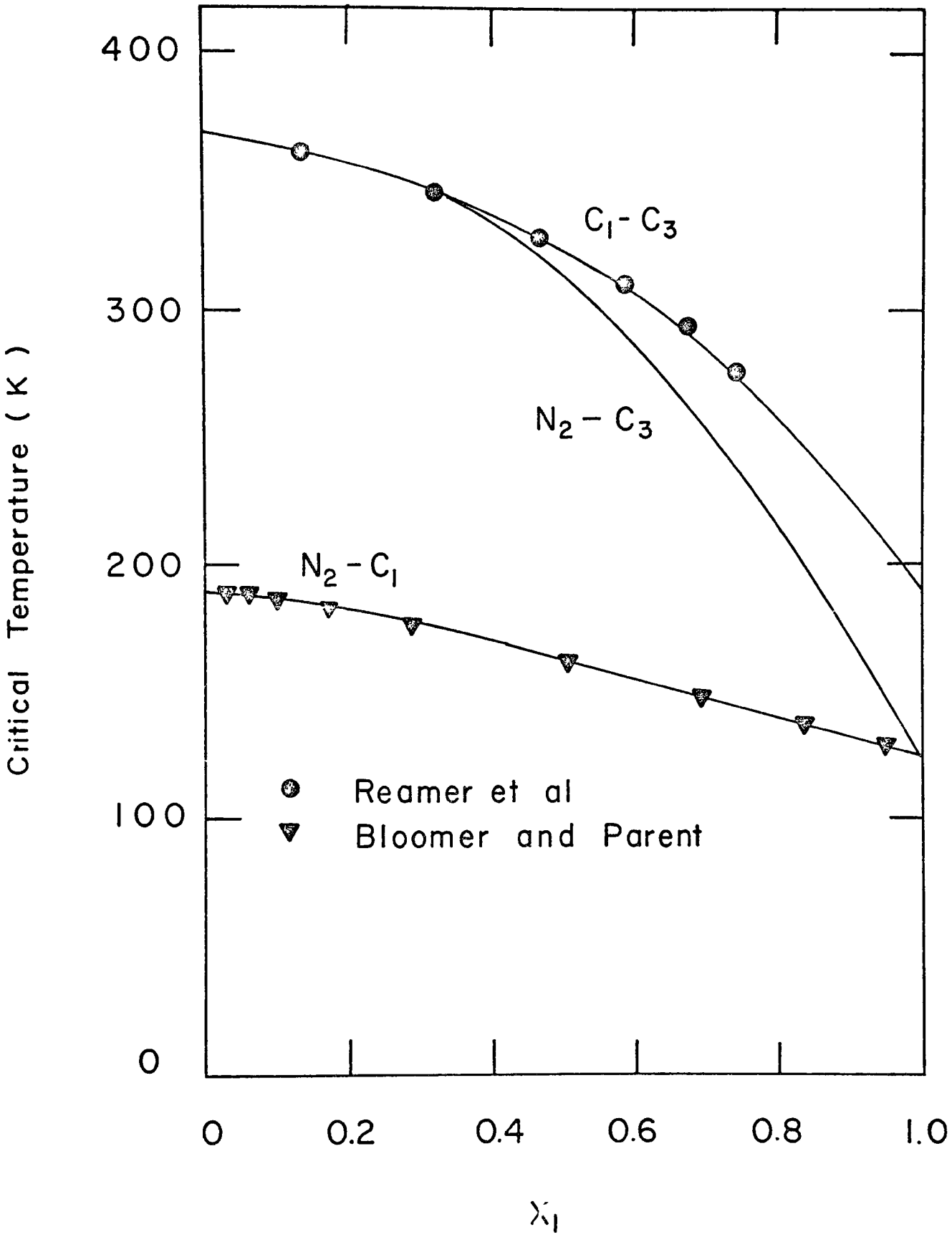


Figure 4.34 Critical Temperatures for the Methane(1)-Propane(2), Nitrogen(1)-Methane(2), and Nitrogen(1)-Propane(2) Mixtures.

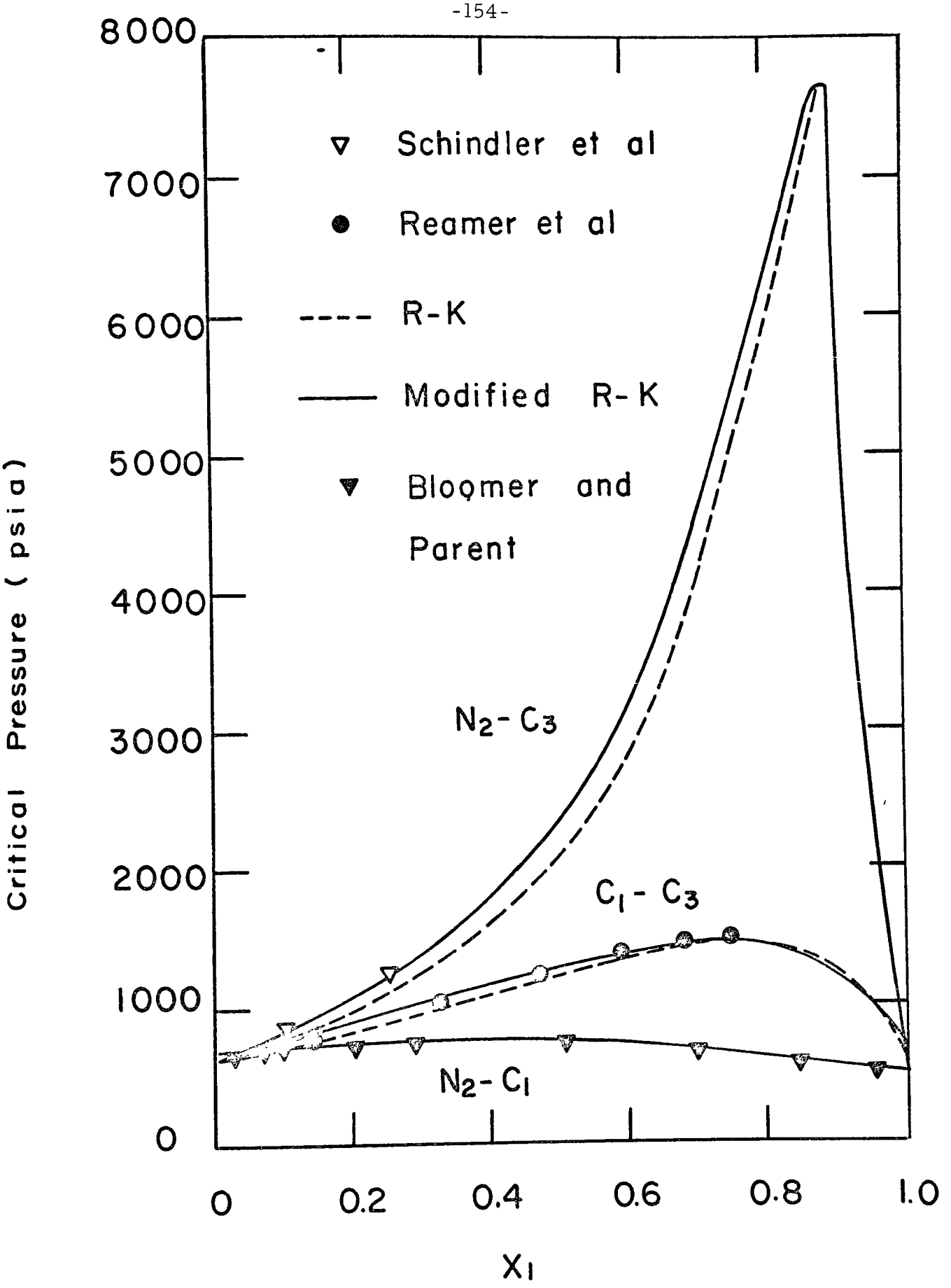


Figure 4.35 Critical Pressures for the Methane(1)-Propane(2), Nitrogen(1)-Methane(2), and Nitrogen(1)-Propane(2) Mixtures.

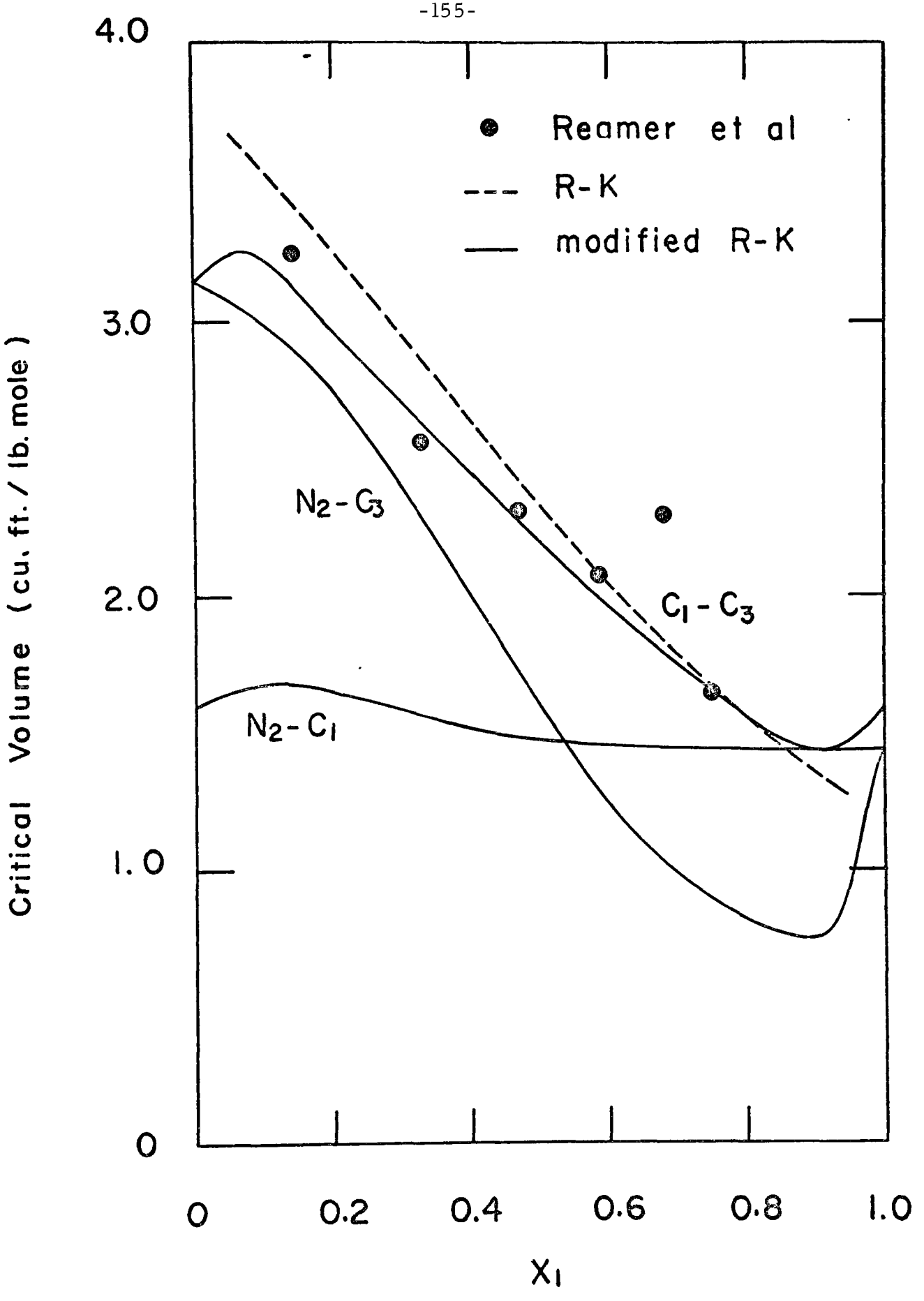


Figure 4.36 Critical Volumes for the Methane(1)-Propane(2) Nitrogen(1)-Methane(2), and Nitrogen(1)-Propane(2) Mixtures.

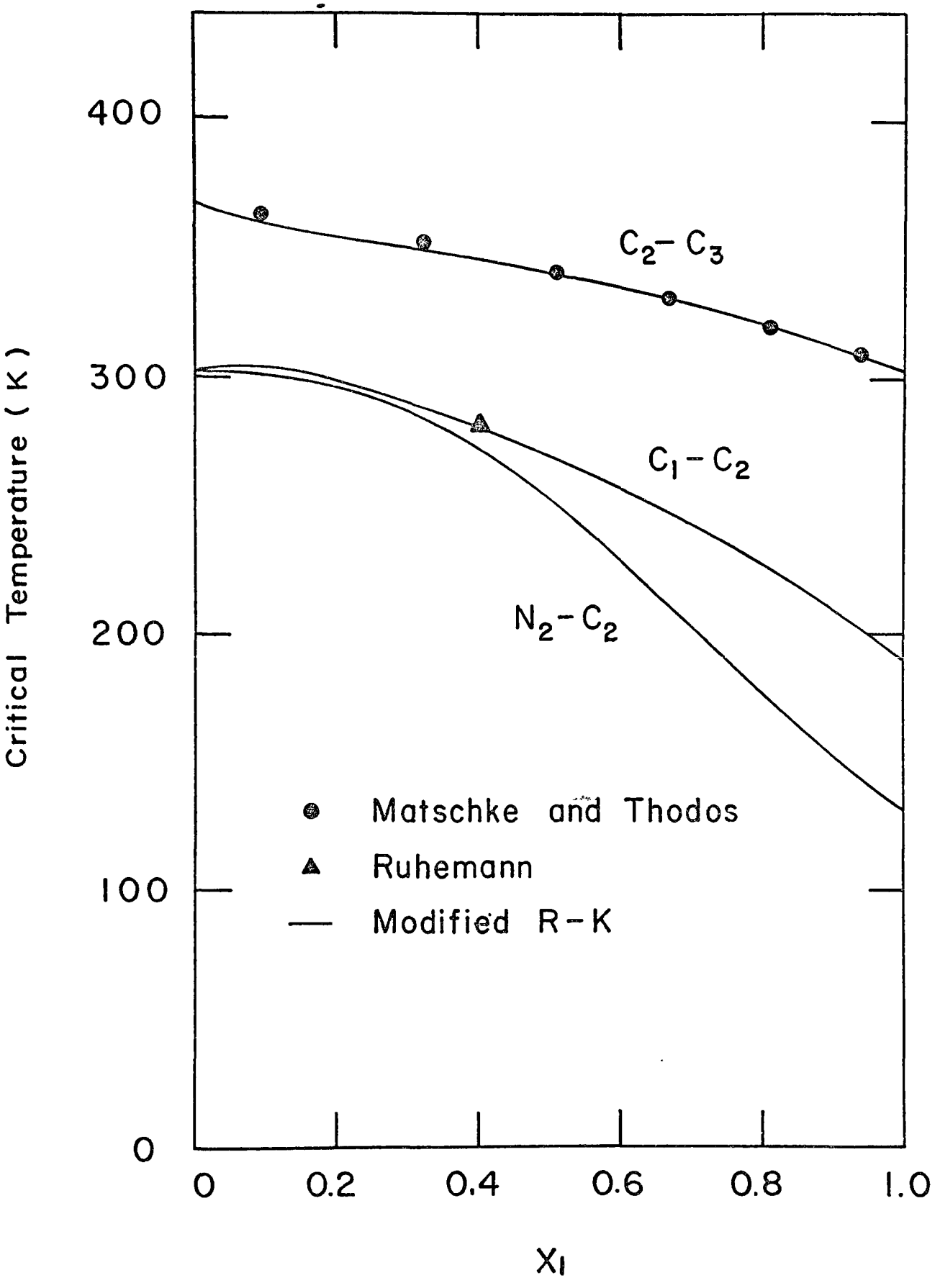


Figure 4.37 Criticl Temperatures for the Nitrogen(1)-Ethane(2), Ethane(1)-Propane(2), and Methane(1)-Ethane(2) Mixtures.

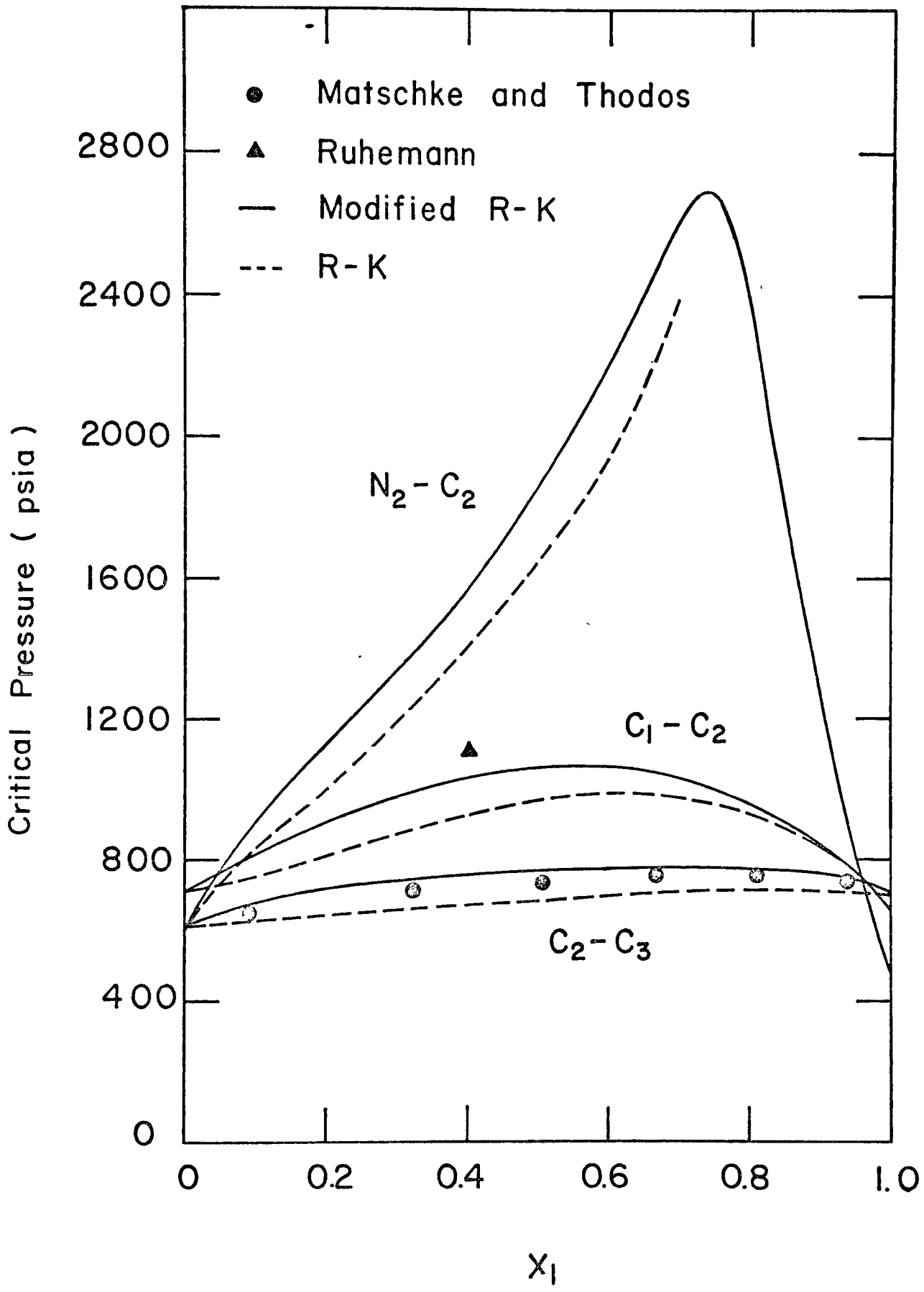


Figure 4.38 Critical Pressures for the Nitrogen(1)-Ethane(2), Ethane(1)-Propane(2), and Methane(1)-Ethane(2) Mixtures.

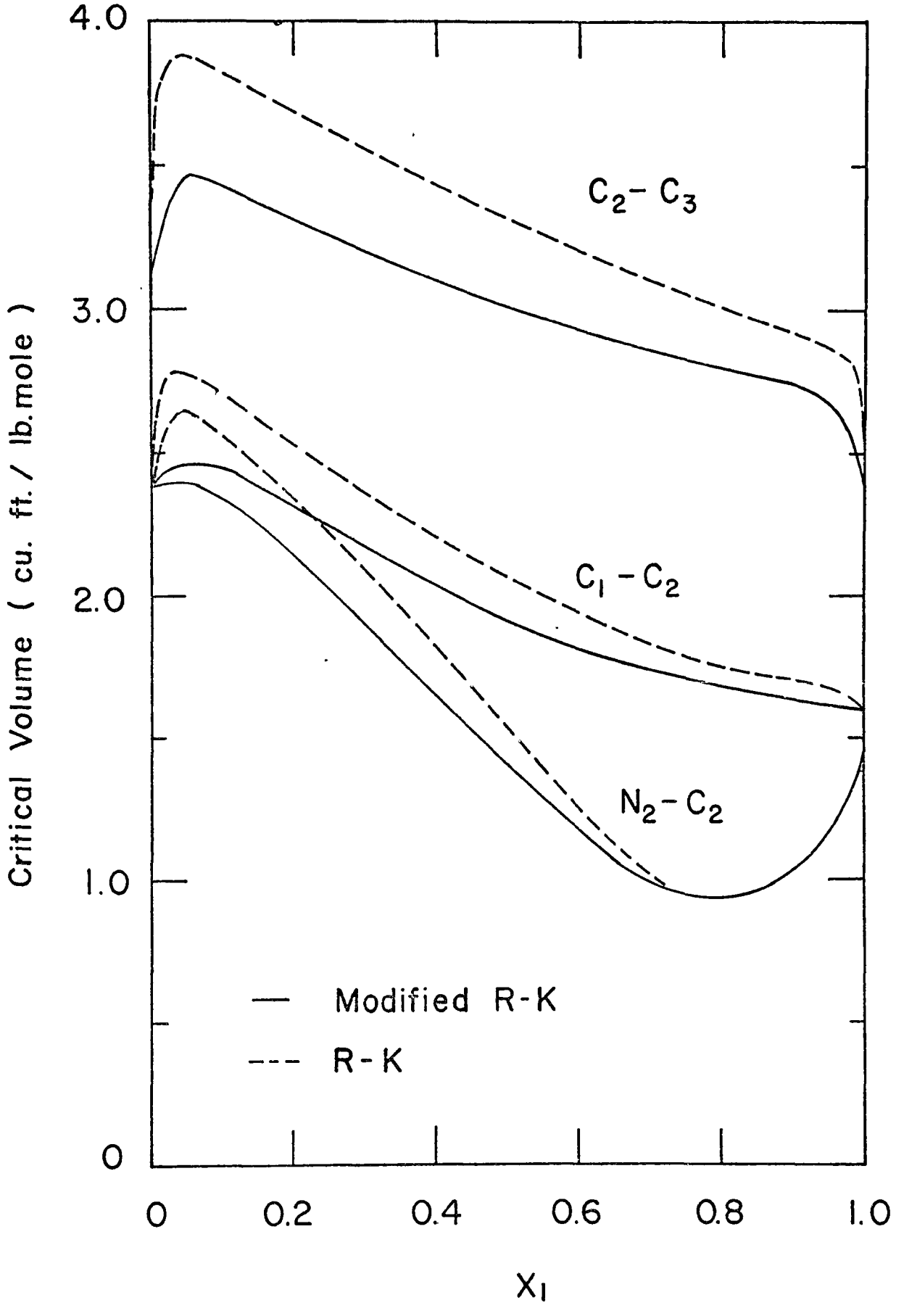


Figure 4.39 Critical Volumes for the Nitrogen(1)-Ethane(2), Ethane(1)-Propane(2), and Methane(1)-Ethane(2) Mixtures.

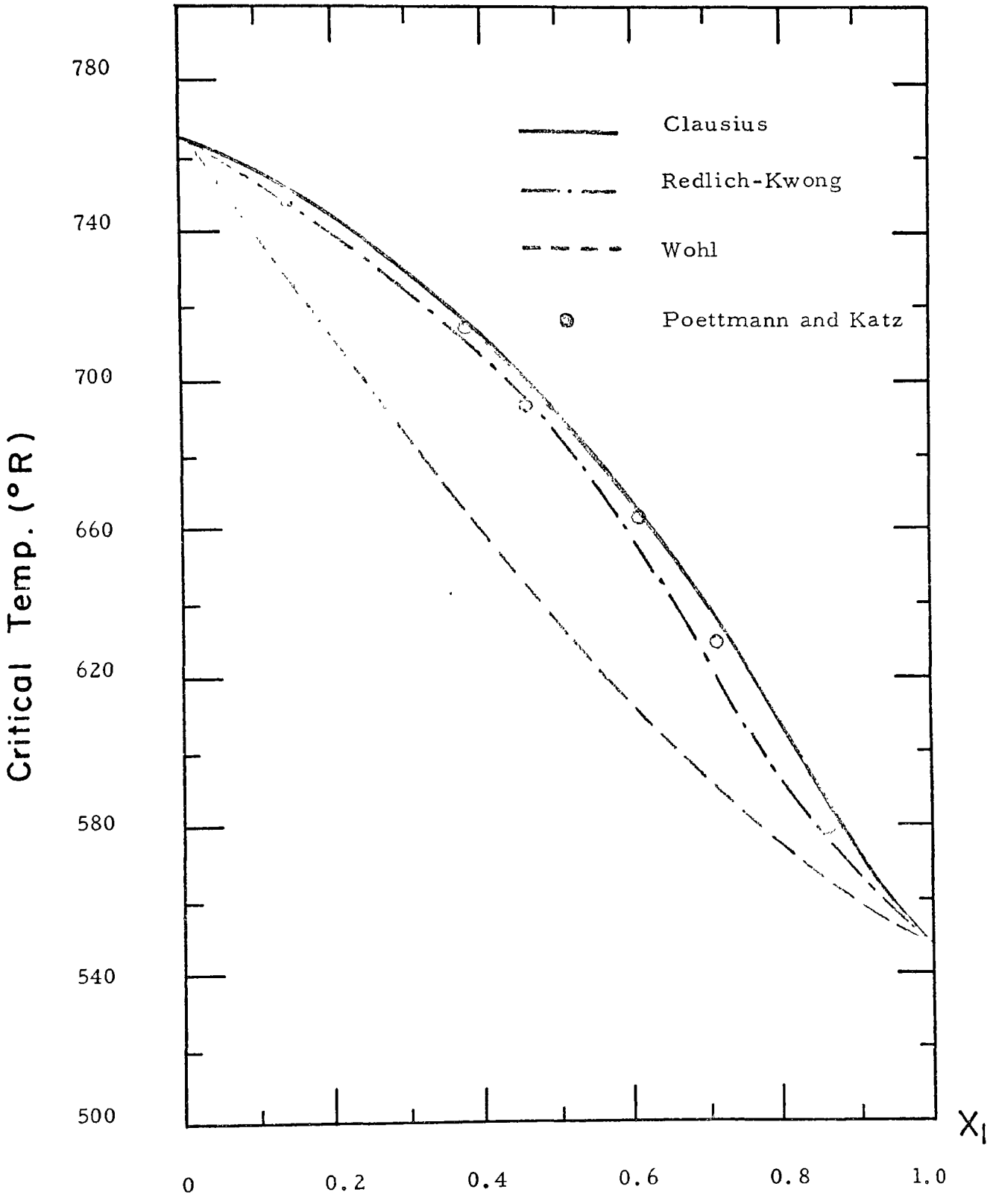


Figure 4.40 Critical Temperatures for the Carbon Dioxide(1)-n-Butane(2) Mixtures.

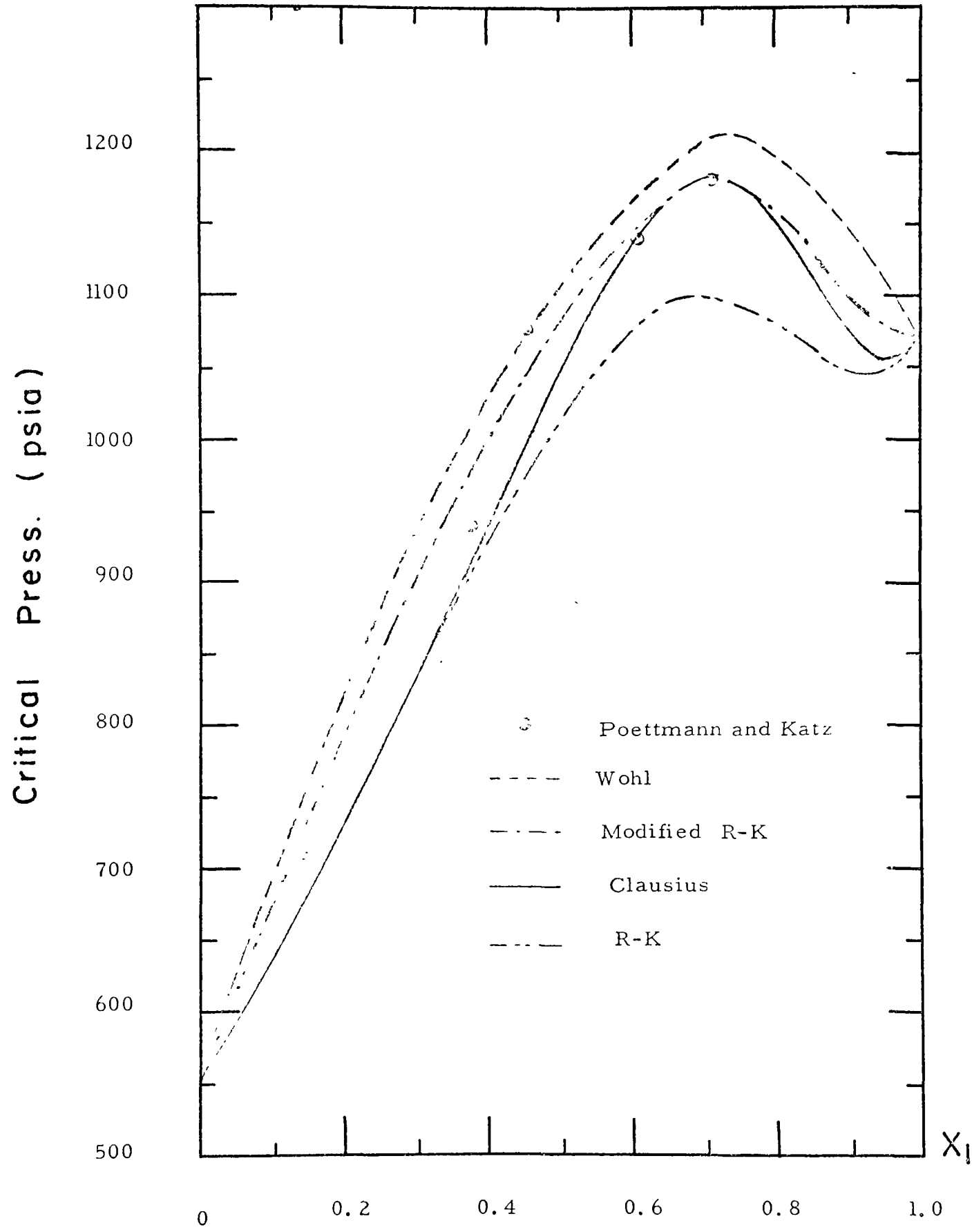


Figure 4.41 Critical Pressures for the Carbon Dioxide (1)-n-Butane(2) Mixtures.

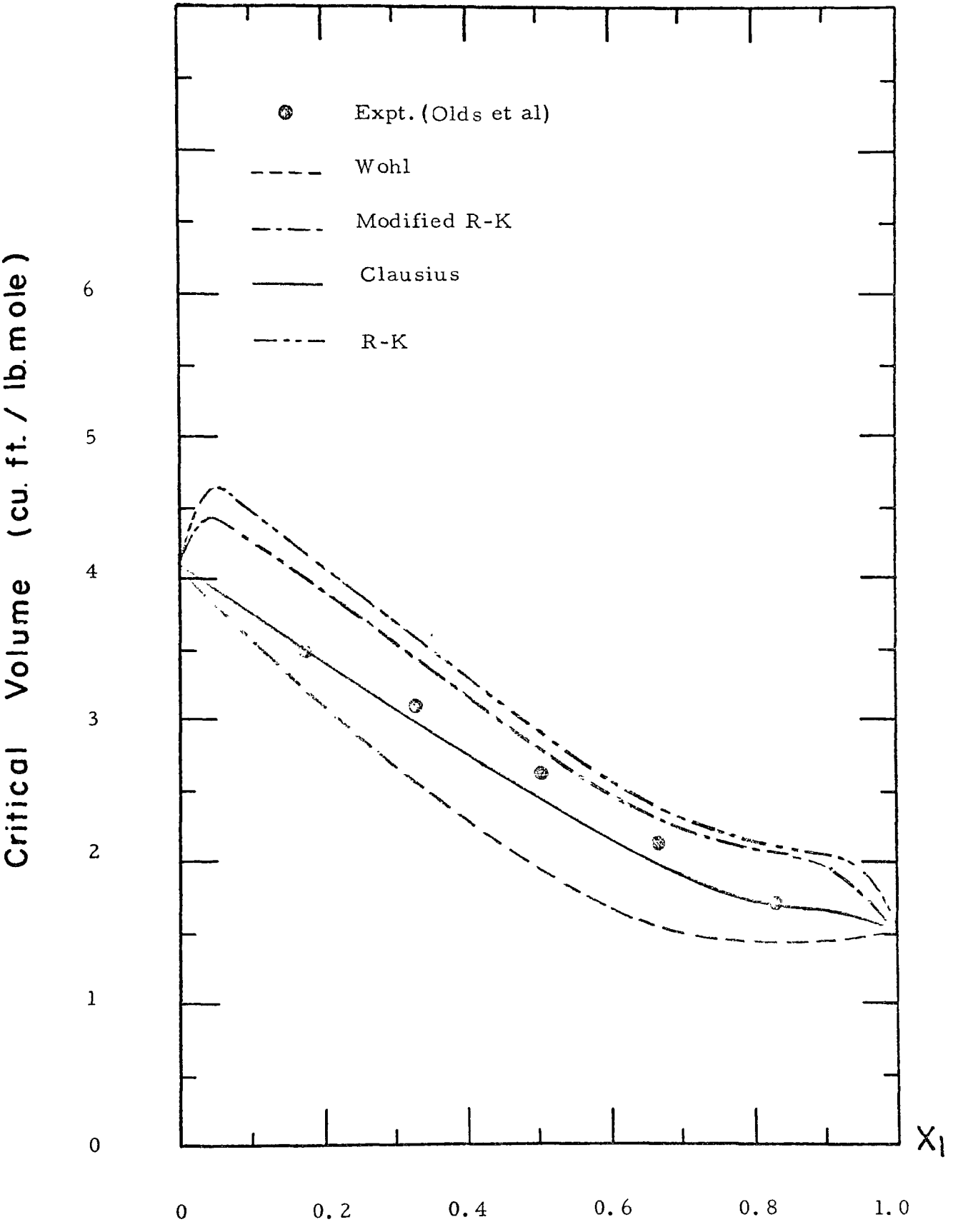


Figure 4.42 Critical Volumes for the Carbon Dioxide (1)-n-Butane(2) Mixtures.

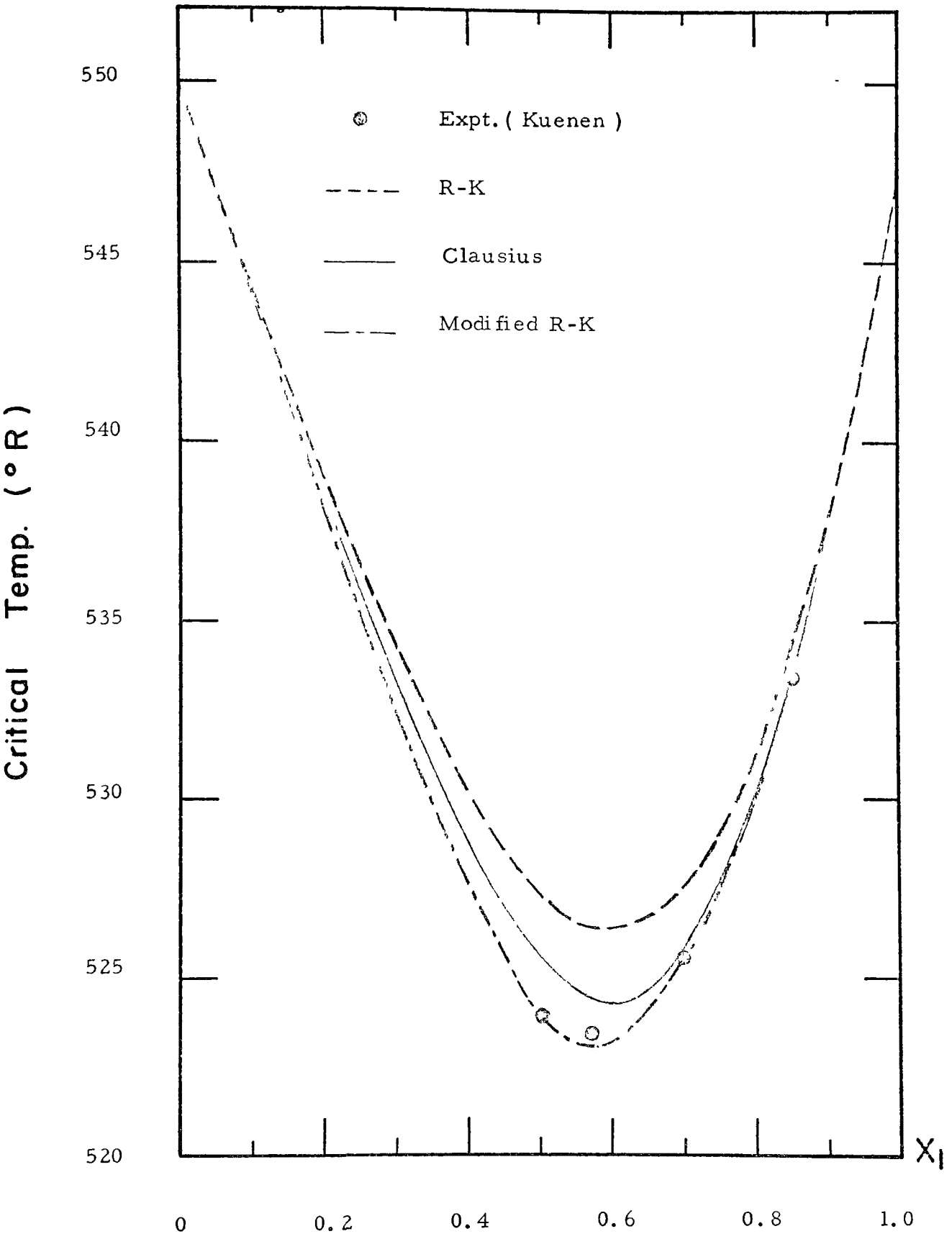


Figure 4.43 Critical Temperatures for the Carbon Dioxide (1)-Ethane(2) Mixtures.

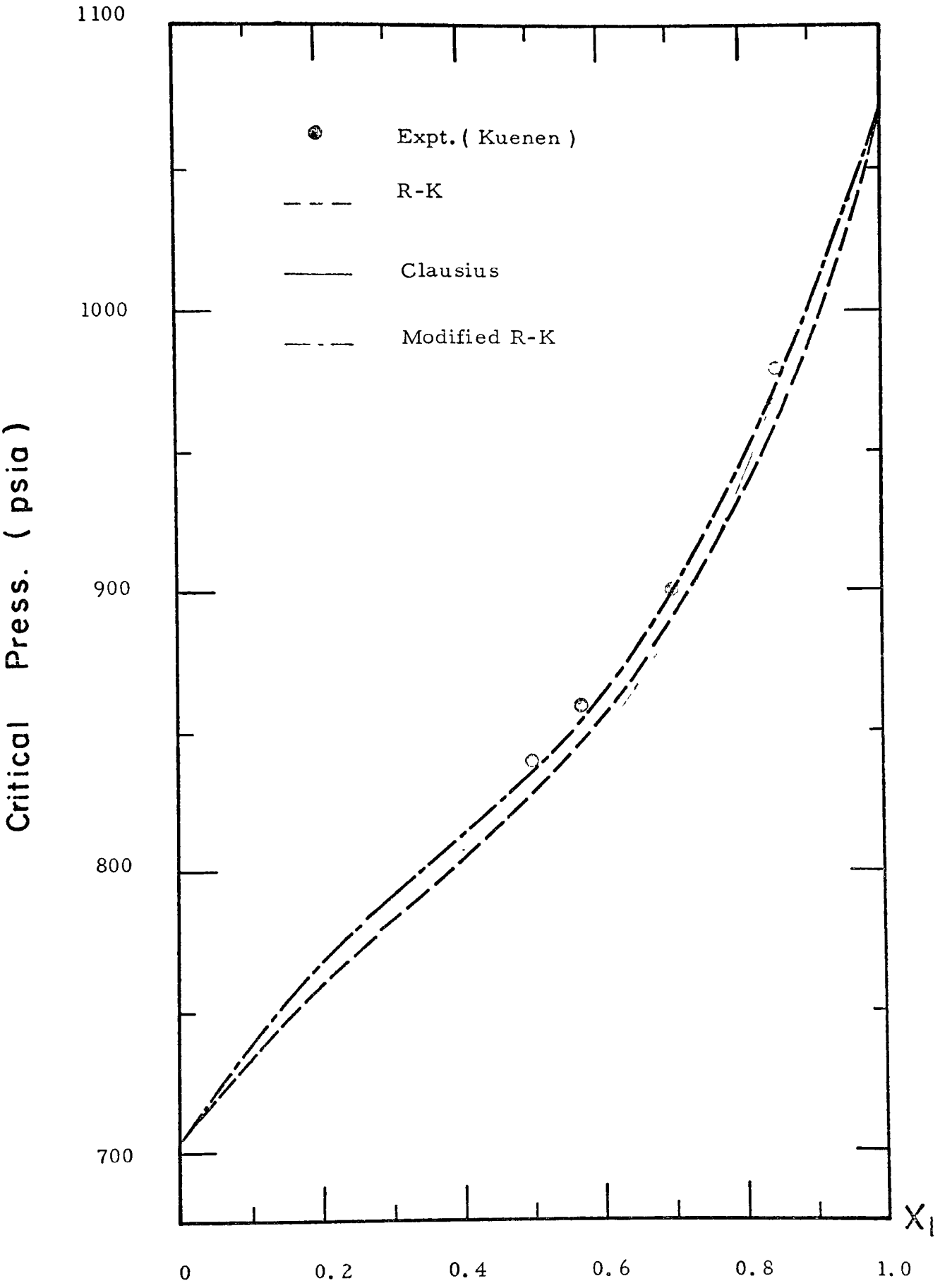


Figure 4.44 Critical Pressures for the Carbon Dioxide (1)-Ethane(2) Mixtures.

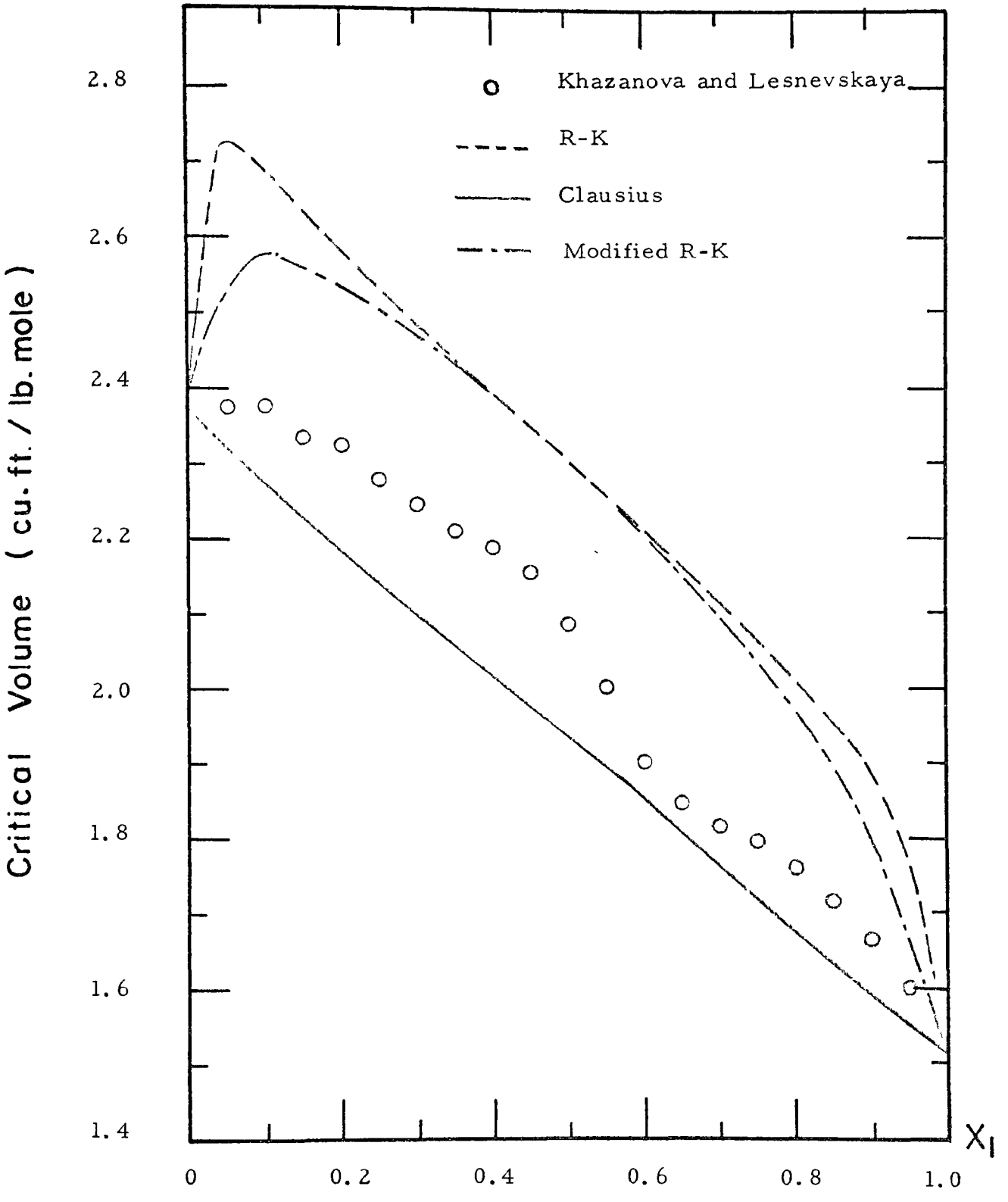


Figure 4.45 Critical Volumes for the Carbon Dioxide (1)-Ethane Mixtures.

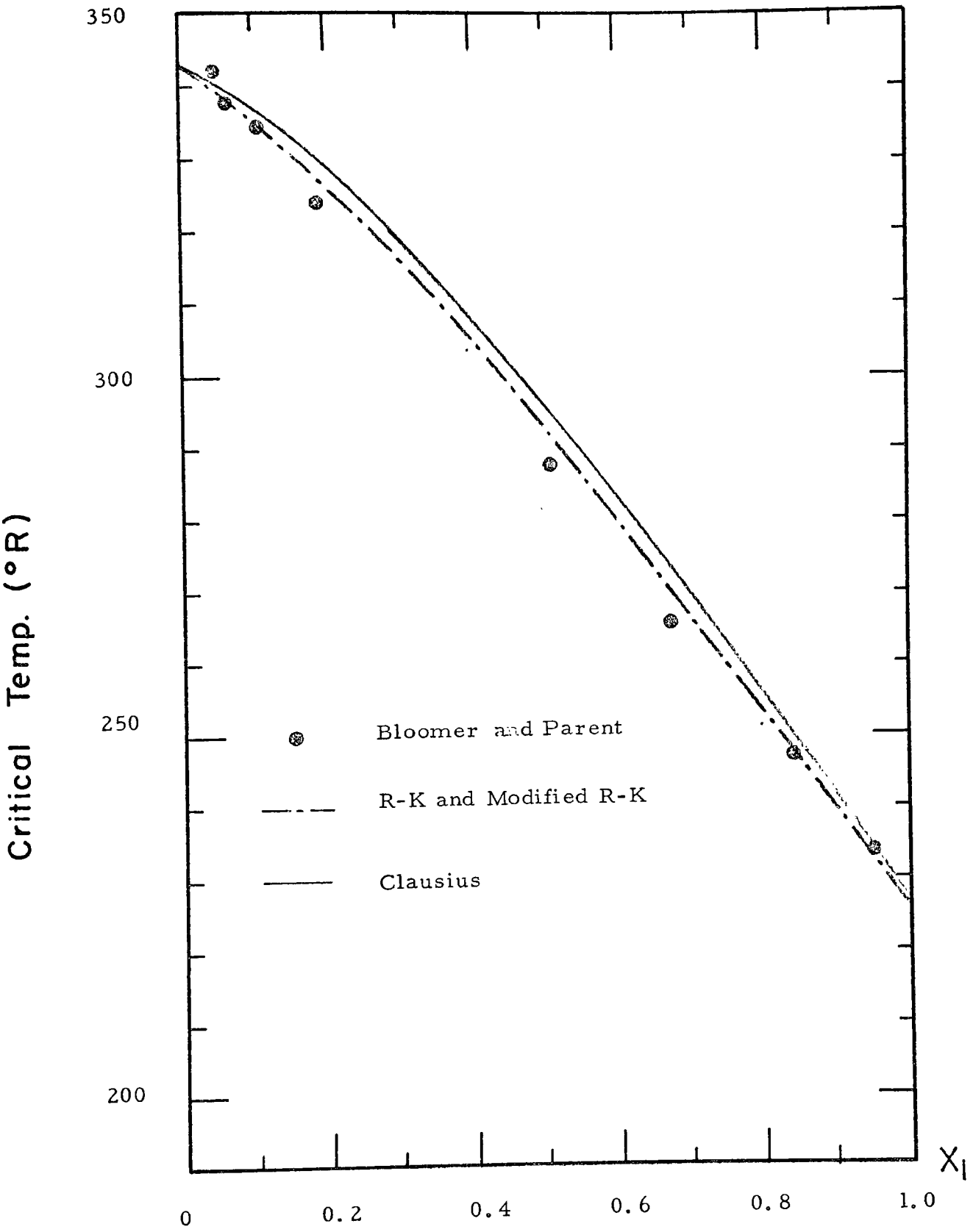


Figure 4.46 Critical Temperatures for the Nitrogen Methane Mixtures (Evaluated from different equations)

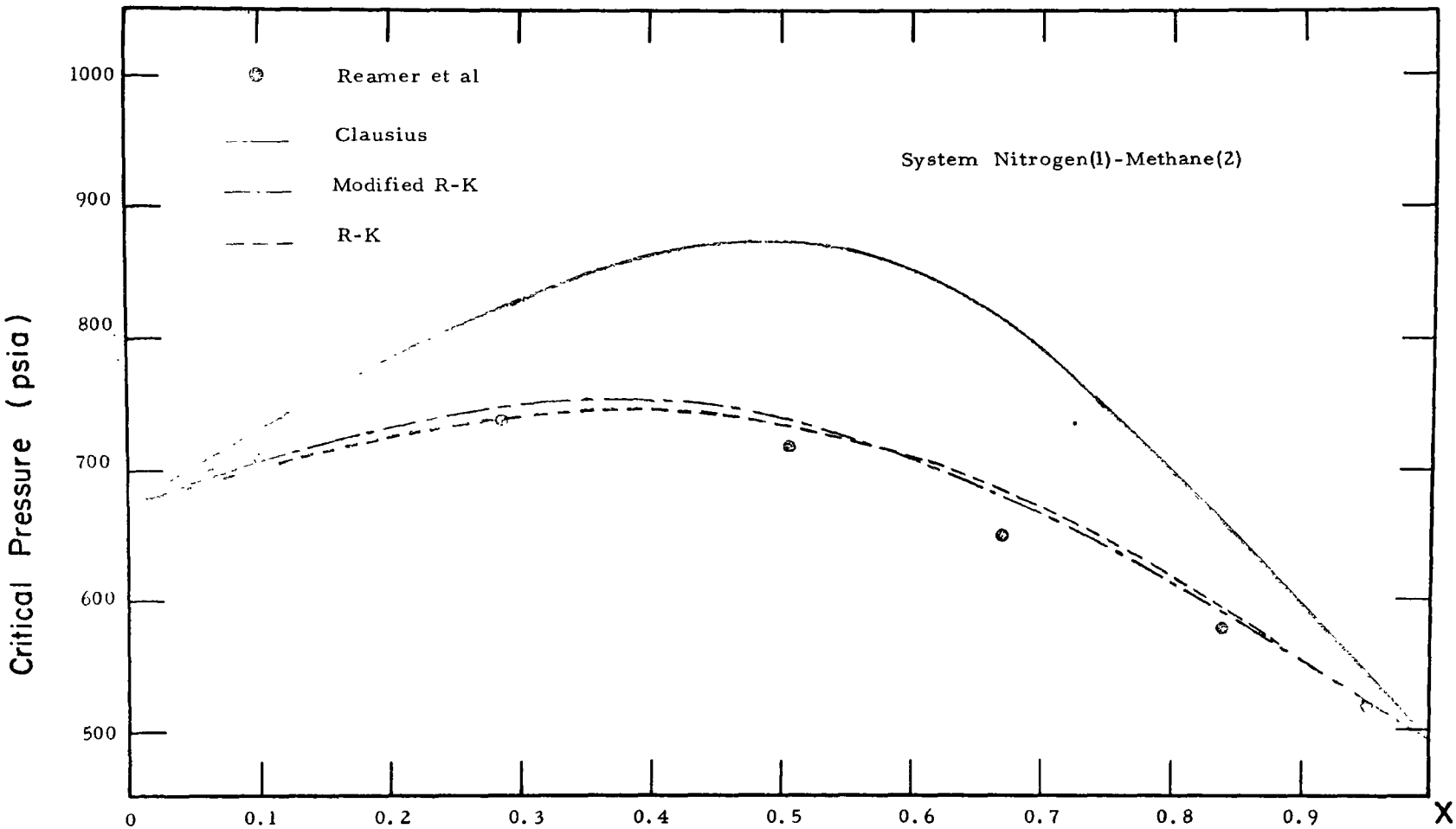


Figure 4.48 Critical Pressures for the Nitrogen(1)-Methane(2) Mixtures.

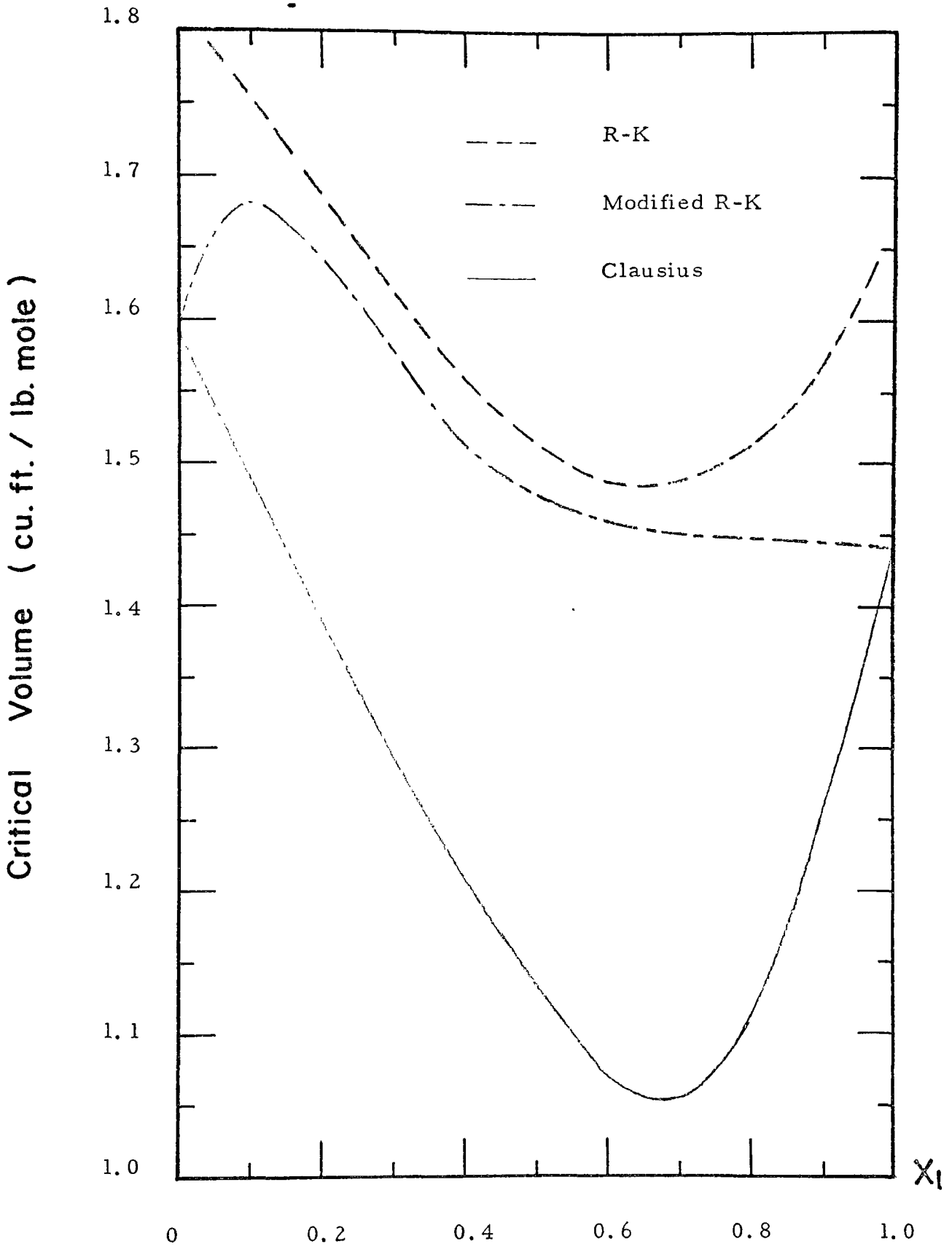


Figure 4.48 Critical Volumes for the Nitrogen-Methane Mixtures (Evaluated from different equations)

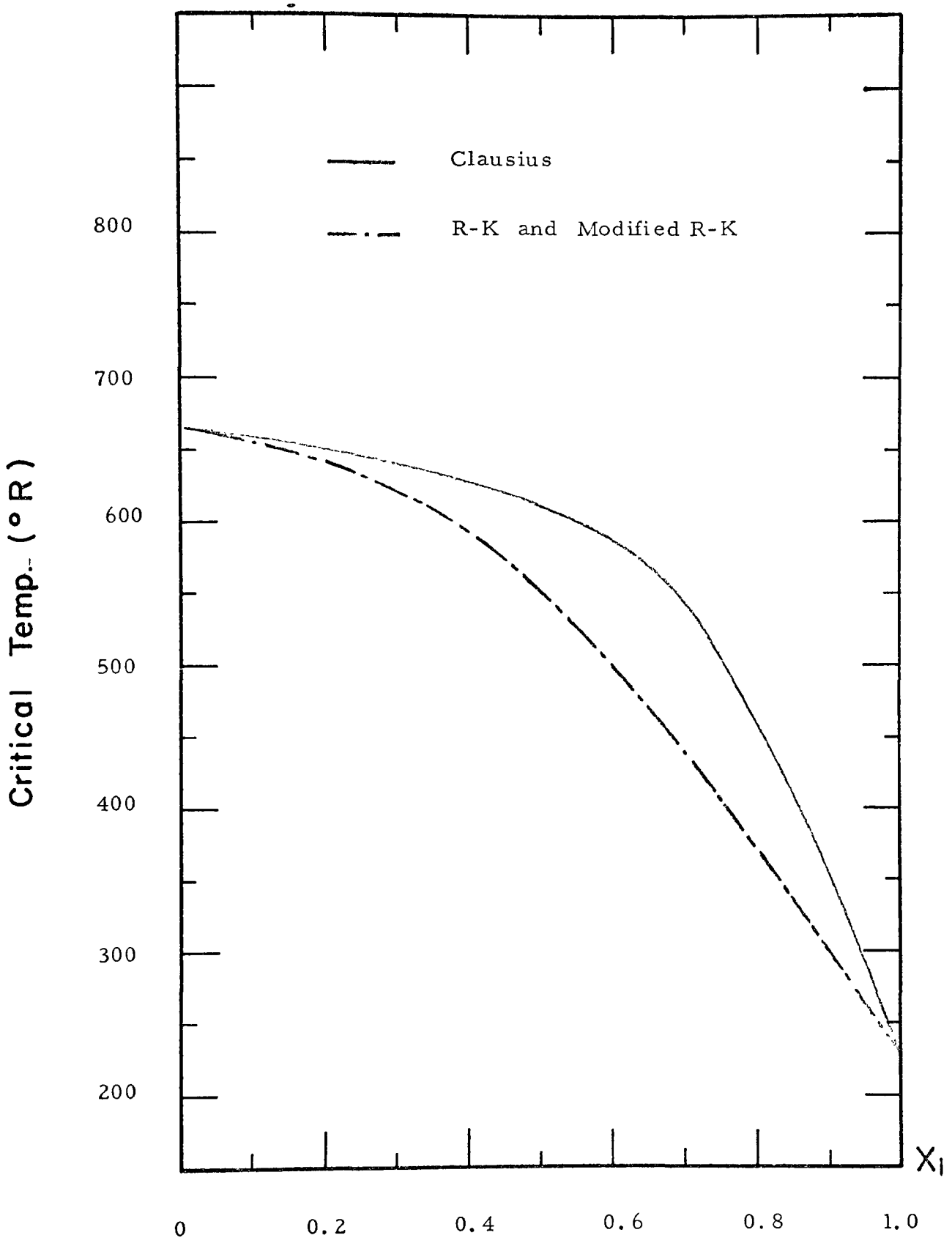


Figure 4.49 Critical Temperatures for the Nitrogen-Propane Mixtures (Evaluated from different equations)

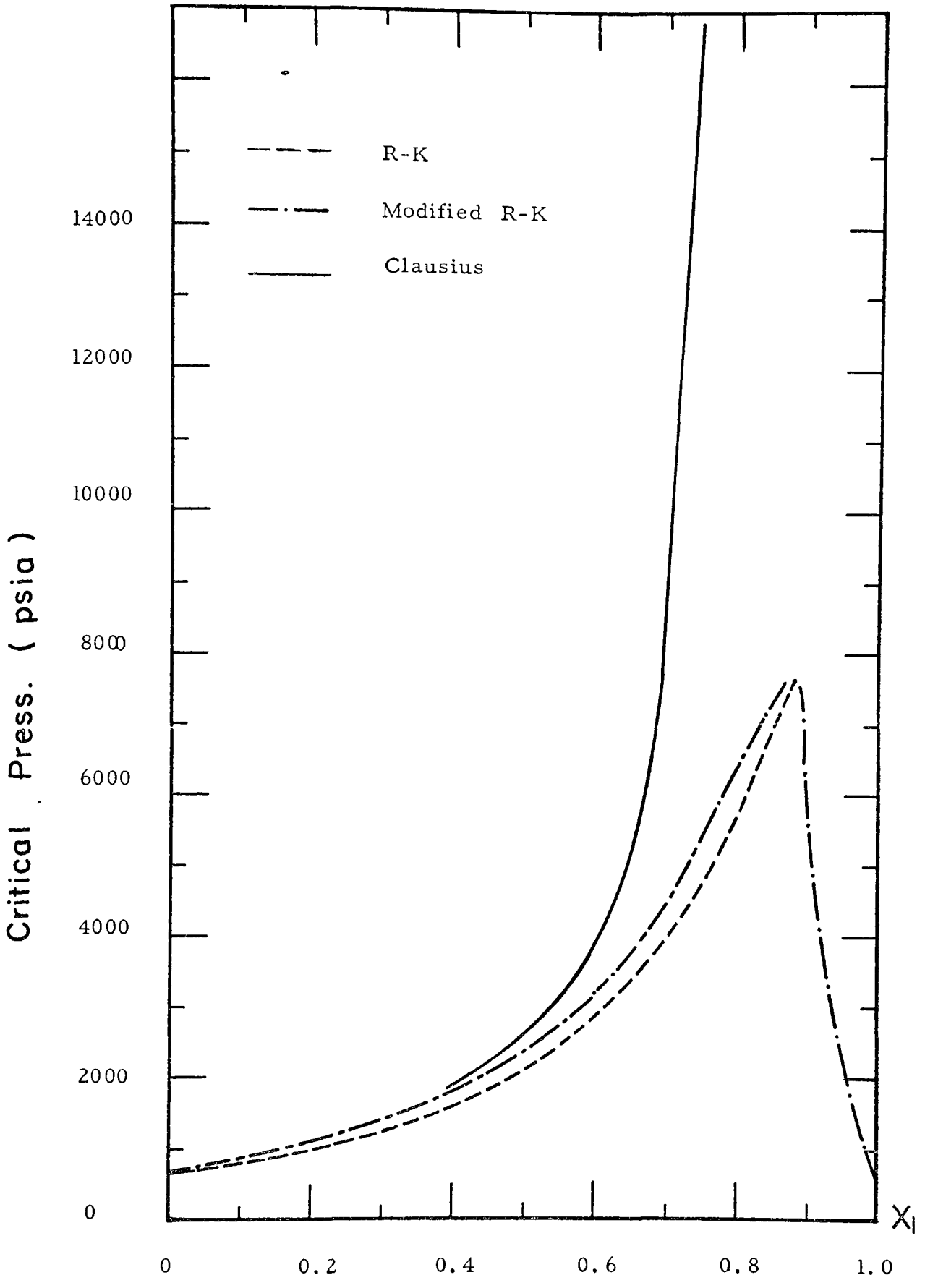


Figure 4.50 Critical Pressures for the Nitrogen-Propane Mixtures (Evaluated from different equations)

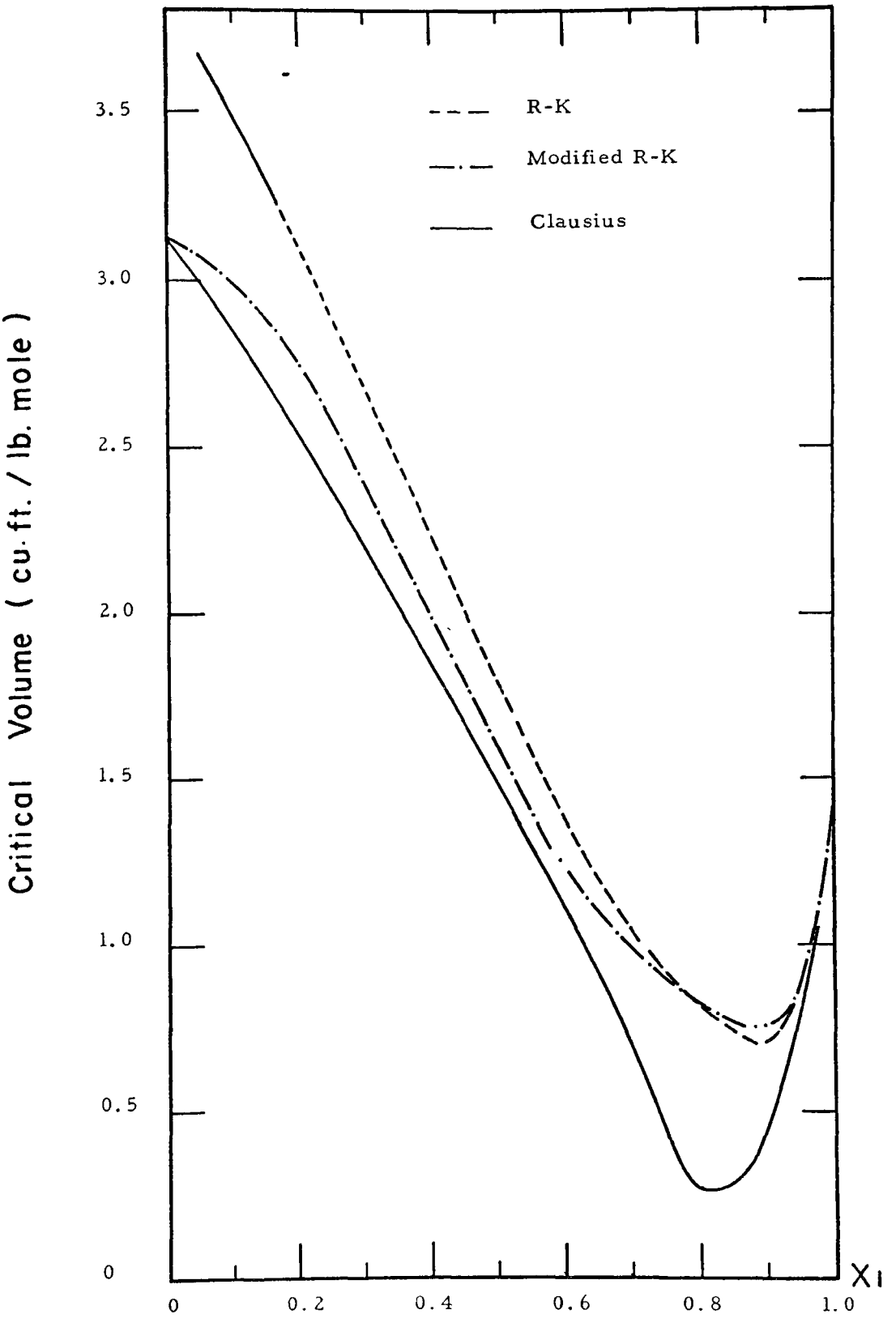


Figure 4.51 Critical Volumes for the Nitrogen-Propane Mixtures (Evaluated from different equations)

CHAPTER 5

SUMMARY AND CONCLUSIONS

The results of the experimental determination for the system nitrogen-propane show that the existence of partial miscibility is confirmed in the temperature range of 112.8 to 125.15 K. It is found that the nitrogen - rich liquid phase contains more than 0.9977 mole fraction of nitrogen; and the propane-rich liquid phase contains more than 0.9158 mole fraction of propane. In all cases, the amount of propane in the vapor phase is negligible. It is also found that the extrapolated liquid composition deviates from the experimental measurement to a value as high as 25%.

Experimental vapor-liquid equilibrium data of the system methane-propane show that at 114.05 to 122.24 K, the vapor phase contains more than 0.9976 mole fraction of methane. It is also found that a consistent trend is indicated between these data and those of Wichterle and Kobayashi.

From the experimental results of the vapor-liquid equilibrium and vapor-liquid-liquid equilibrium data for the ternary system nitrogen-methane-propane, it is found that the vapor phase contains less than 0.0005 mole fraction of propane, which is less than the experimental error. It is also found that in the temperature range of 114.05 to 122.24 K, the critical solution points locate in the vicinity of 0.35 and 0.45 mole fractions of nitrogen and methane respectively. The binodal curves of the liquid-liquid equilibria differ from each other only in the vicinity of the plait points. It is also found that the tie-lines are horizontal and the slopes change only in the vicinity of the plait points.

The phenomenon of liquid phase inversion has been investigated for the binary system nitrogen-ethane, and ternary system nitrogen-methane-ethane [1] [2]. It was found that the occurrence of the phenomenon was related to the behavior of the densities of the pure components and that of the mixtures.

Liquid activity coefficients have been evaluated for the vapor-liquid equilibrium data. It was found that the activity coefficients evaluated through gas phase fugacity was not suitable for systems with one component almost absent in the vapor phase. The calculation directly involved the vapor composition, the amount of which was so small in this case that the experimental error would give a value of a few hundred percent off the true values. Therefore the liquid activity coefficients were calculated through liquid phase fugacity in this investigation.

The Redlich-Kwong equation of state, with the parameters Ω_a and Ω_b considered as temperature dependent at the conditions of subcritical and supercritical temperatures, has been used to predict total pressures and vapor compositions. Vapor compositions have been predicted to within experimental error; and total pressures have been predicted to within 2% for binary systems, and within 4% for ternary systems. The same equation has been used to predict liquid-liquid equilibrium, to within 1%.

Different equations of state have been used to predict the temperatures, pressures, and volumes of a binary mixture at the critical state. The Clausius and Wohl equations have been used, in hope that with a third constant, the critical state may be predicted more accurately. However, it is found that the modified Redlich-Kwong equation of state yields the best results, and these results indicate improvement over the existing methods. For the system methane-propane,

the predicted critical temperatures are within 0.5%, the critical pressures are within 0.7%, and the critical volumes are within 2.3%. Tested systems are: nitrogen-methane, nitrogen-ethane, nitrogen-propane, methane-ethane, methane-propane, ethane-propane, carbon dioxide-n-butane, and carbon dioxide-ethane.

As a summary, this investigation can be outlined in the following:

A. Experimental

1) System nitrogen-propane: P-T liquid-liquid locus, vapor-liquid-liquid equilibrium compositions at saturation pressures, vapor-pressure curves for the liquid region which is rich in propane.

2) System methane-propane: vapor-liquid equilibria at isothermal conditions of 114.05, 118.32, and 122.24 K.

3) System nitrogen-methane-propane: vapor-liquid equilibria and vapor-liquid-liquid equilibria at three isothermal conditions.

4) System nitrogen-methane-ethane: liquid phase inversion.

B. Correlation and prediction

The modified Redlich-Kwong equation of state has been applied in predicting vapor composition and total pressure for vapor-liquid equilibria, in predicting total pressure and liquid composition in liquid-liquid equilibria, and in predicting critical properties of a binary mixture.

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APPENDIX A

Experimental Data

and

Results of Calculation

TABLE 3.1

P-T liquid-liquid locus for the system Nitrogen (1)-Propane (2)

Pressure (psia)	Temperature (K)
443.8	124.2
415.9	122.5
389.5	121.7
361.5	119.6
329.2	117.9
308.6	116.5
283.7	115.0
249.8	112.8

TABLE 3.2

Vapor-liquid- equilibrium compositions at saturation pressures for the system Nitrogen (1) - Propane (2)

Temperature (K)	Pressure (psia)	x_1	x_2	x_1'	x_2'
113.22	246.7	0.0842	0.9158	0.9984	0.0016
115.15	275.5	0.0844	0.9156	0.9982	0.0018
116.80	301.1	0.0841	0.9159	0.9981	0.0019
117.92	351.8	0.0859	0.9141	0.9983	0.0017
121.34	384.0	0.0876	0.9124	0.9978	0.0022
123.51	425.4	0.0902	0.9098	0.9977	0.0023
123.71	430.0	0.0903	0.9097	0.9977	0.0023
125.15	460.8	0.0933	0.9067	0.9981	0.0019

TABLE 3.3

Vapor-pressure data for the liquid region which is rich in propane for the system nitrogen(1)-propane(2) at 114.05 K

P (psia)	X1	X2	Y1	Y2
21.80	0.0075	0.9925	0.9999	0.0001
23.60	0.0086	0.9914	0.9999	0.0001
49.50	0.0169	0.9831	0.9999	0.0001
95.40	0.0335	0.9665	0.9999	0.0001
145.20	0.0486	0.9514	0.9999	0.0001
199.10	0.0640	0.9360	0.9999	0.0001
232.50	0.0736	0.9264	0.9999	0.0001
239.60	0.0773	0.9227	0.9999	0.0001
258.00	0.0842	0.9158	0.9999	0.0001
261.00	0.0845	0.9155	0.9999	0.0001

TABLE 3.4

Vapor-pressure data for the liquid region which is rich in propane for the system nitrogen(1)-propane(2) at 118.32 K

P (psia)	X1	X2	Y1	Y2
27.20	0.0079	0.9921	0.9995	0.0005
61.80	0.0175	0.9825	0.9994	0.0006
107.35	0.0321	0.9679	0.9996	0.0004
145.25	0.0433	0.9567	0.9996	0.0004
177.50	0.0511	0.9489	0.9998	0.0002
188.20	0.0557	0.9443	0.9998	0.0002
215.80	0.0621	0.9379	0.9998	0.0002
280.00	0.0760	0.9240	0.9999	0.0001
297.50	0.0801	0.9199	0.9992	0.0008
312.20	0.0854	0.9146	0.9999	0.0001

TABLE 3.5

Vapor-pressure data for the liquid region which is rich in propane for the system nitrogen(1)-propane(2) at 122.24 K

P (psia)	X1	X2	Y1	Y2
44.00	0.0107	0.9893	0.9989	0.0011
51.80	0.0133	0.9867	0.9989	0.0011
100.80	0.0254	0.9746	0.9992	0.0008
150.60	0.0380	0.9620	0.9994	0.0006
166.10	0.0410	0.9590	0.9995	0.0005
202.90	0.0486	0.9514	0.9996	0.0004
280.10	0.0672	0.9328	0.9999	0.0001
341.70	0.0812	0.9188	0.9999	0.0001
369.50	0.0858	0.9142	0.9999	0.0001
400.00	0.0869	0.9131	0.9999	0.0001
400.00	0.0885	0.9115	0.9998	0.0002
406.00	0.0888	0.9112	0.9998	0.0002

TABLE 3.6

Vapor-liquid equilibrium data for the system methane(1)-propane(2) at 114.05 K

P (psia)	X1	X2	Y1	Y2
6.06	0.1812	0.8188	0.9990	0.0010
8.60	0.2911	0.7089	0.9995	0.0005
11.17	0.4102	0.5898	0.9997	0.0003
13.96	0.6647	0.3353	0.9998	0.0002
13.00	0.5488	0.4512	1.0000	0.0
16.20	0.8812	0.1188	1.0000	0.0

TABLE 3.7

Vapor-liquid equilibrium data for the system methane(1)-propane(2) at 118.32 K

P (psia)	X1	X2	Y1	Y2
7.88	0.1775	0.8225	0.9986	0.0014
10.95	0.2717	0.7283	0.9993	0.0007
14.12	0.3909	0.6091	0.9997	0.0003
17.63	0.5714	0.4286	0.9992	0.0008
19.60	0.6540	0.3460	0.9999	0.0001
20.60	0.7399	0.2601	1.0000	0.0
22.90	0.9031	0.0969	1.0000	0.0
24.70	1.0000	0.0	1.0000	0.0

TABLE 3.8

Vapor-liquid equilibrium data for the system methane(1)-propane(2) at 122.24 K

P (psia)	X1	X2	Y1	Y2
7.06	0.1130	0.8870	0.9976	0.0024
9.05	0.1409	0.8591	0.9986	0.0014
13.06	0.2219	0.7781	0.9996	0.0004
13.50	0.2253	0.7747	0.9996	0.0004
18.78	0.3701	0.6299	0.9999	0.0001
23.10	0.5297	0.4703	0.9999	0.0001
26.90	0.7090	0.2910	0.9999	0.0001
28.76	0.8095	0.1905	1.0000	0.0
31.04	0.8910	0.1090	1.0000	0.0
33.20	1.0000	0.0	1.0000	0.0

TABLE 3.9

Vapor-liquid equilibrium data for the system nitrogen(1)-methane(2)-propane(3) at 114.05 K

P (psia)	X1	X2	X3	Y1	Y2	Y3
70.88	0.0245	0.0161	0.9594	0.9886	0.0112	0.0002
127.20	0.0446	0.0159	0.9395	0.9901	0.0098	0.0001
193.40	0.0637	0.0136	0.9228	0.9932	0.0067	0.0001
82.80	0.0388	0.2624	0.6988	0.8986	0.1013	0.0001
124.50	0.0620	0.2606	0.6774	0.9314	0.0685	0.0001
65.80	0.0562	0.6126	0.3312	0.7851	0.2149	0.0
101.38	0.0989	0.5779	0.3232	0.8644	0.1356	0.0
124.05	0.1797	0.5525	0.2679	0.9074	0.0926	0.0
43.40	0.0503	0.8352	0.1145	0.6241	0.3759	0.0
41.80	0.0525	0.8657	0.0818	0.6057	0.3942	0.0001
77.60	0.1270	0.7679	0.1051	0.7902	0.2098	0.0
131.70	0.2999	0.6180	0.0821	0.8866	0.1134	0.0
158.30	0.4184	0.5117	0.0699	0.9145	0.0855	0.0
173.00	0.5072	0.4373	0.0555	0.9283	0.0716	0.0
185.30	0.6106	0.3566	0.0328	0.9353	0.0647	0.0
220.80	0.8059	0.1800	0.0141	0.9593	0.0407	0.0
233.70	0.8644	0.1248	0.0108	0.9699	0.0301	0.0
253.70	0.9415	0.0547	0.0038	0.9811	0.0189	0.0
260.60	0.9750	0.0247	0.0003	0.9922	0.0078	0.0

TABLE 3.10

Vapor-liquid equilibrium data for the system nitrogen(1)-methane(2)-propane(3) at 118.32 K

P (psia)	X1	X2	X3	Y1	Y2	Y3
50.75	0.0559	0.9126	0.0314	0.5299	0.4700	0.0
89.60	0.1501	0.8217	0.0282	0.7490	0.2509	0.0
127.10	C.2509	C.7187	0.0304	0.8279	0.1721	0.0
155.90	0.3559	0.6287	0.0154	0.8633	0.1367	0.0
175.80	C.4403	0.5481	0.0116	0.8896	0.1104	0.0
191.50	0.4954	0.4979	0.0067	0.8938	0.1062	0.0
214.40	0.5946	0.4007	0.0047	0.9156	0.0844	0.0
48.80	C.0207	0.4689	0.5104	0.6498	0.3501	0.0001
78.80	0.0399	0.4499	0.5102	0.7845	0.2154	0.0001
142.00	0.0820	0.4169	0.5011	0.8815	0.1184	0.0001
178.60	0.1221	0.3954	0.4825	0.9022	0.0977	0.0001
106.80	0.0970	0.6262	0.2768	0.8147	0.1852	0.0
150.50	0.1683	0.5672	0.2646	0.8791	0.1209	0.0
169.70	0.2258	0.5226	0.2516	0.8969	0.1031	0.0
193.80	0.2843	0.4869	0.2289	0.9122	0.0877	0.0
200.70	0.3033	0.4792	0.2175	0.9044	0.0956	0.0
59.00	0.0227	0.2826	0.6947	0.8067	0.1931	0.0002
102.20	C.0470	0.2713	0.6817	0.8836	0.1154	0.0010
123.70	0.0601	0.2631	0.6768	0.9098	0.0892	0.0011
24.55	0.0071	0.0628	0.9301	0.8782	0.1217	0.0001
64.30	0.0199	0.0603	0.9199	0.9505	0.0494	0.0001
105.30	0.0324	0.0578	0.9098	0.9671	0.0328	0.0001
140.75	0.0443	0.0558	0.8998	0.9795	0.0204	0.0001

TABLE 3.11

Vapor-liquid equilibrium data for the system nitrogen(1)-methane(2)-propane(3) at 122.24 K

P (psia)	X1	X2	X3	Y1	Y2	Y3
30.60	0.0080	0.0501	0.9419	0.8948	0.1048	0.0004
64.80	0.0190	0.0458	0.9352	0.9564	0.0434	0.0003
67.30	0.0203	0.2628	0.7169	0.7711	0.2288	0.0001
108.60	0.0360	0.2462	0.7178	0.8591	0.1409	0.0
145.20	0.0500	0.2388	0.7111	0.8951	0.1048	0.0001
186.80	0.0767	0.2327	0.6906	0.9207	0.0793	0.0001
48.30	0.0156	0.4876	0.4968	0.5374	0.4625	0.0001
88.75	0.0378	0.4576	0.5046	0.7492	0.2508	0.0
173.80	0.0823	0.4073	0.5103	0.8680	0.1319	0.0001
240.30	0.1443	0.3789	0.4768	0.8875	0.1124	0.0001
51.80	0.0215	0.6813	0.2972	0.4699	0.5301	0.0
79.40	0.0450	0.6528	0.3022	0.6528	0.3472	0.0
199.20	0.1699	0.5419	0.2882	0.8696	0.1304	0.0
83.80	0.0846	0.8225	0.0929	0.6484	0.3516	0.0
137.30	0.1853	0.7294	0.0853	0.7908	0.2092	0.0
185.10	0.3532	0.6102	0.0367	0.8561	0.1438	0.0
255.10	0.5875	0.4019	0.0106	0.9023	0.0967	0.0010
327.40	0.8468	0.1510	0.0022	0.9497	0.0503	0.0

TABLE 3.12

Vapor-liquid-liquid equilibrium data for the system nitrogen(1)-methane(2)-propane(3) at 114.05 K

P (psia)	X1	X2	X3	Y1	Y2	Y3	X1	X2	X3
254.40	0.0977	0.0145	0.8879	0.9921	0.0078	0.0001	C.9854	0.0136	0.0010
245.40	0.0935	0.0352	0.8713	0.9886	0.0113	0.0001	0.9588	0.0396	0.0016
238.95	0.1003	0.0607	0.8390	0.9829	0.0169	0.0001	0.9404	0.0569	0.0027
230.00	0.0983	0.0895	0.8122	0.9779	0.0220	0.0001	0.9022	0.0903	0.0075
219.95	0.1075	0.1316	0.7609	0.9693	0.0306	0.0001	0.8651	0.1258	0.0091
207.00	0.1150	0.1830	0.7020	0.9613	0.0386	0.0001	0.7958	0.1890	0.0152
195.26	0.1250	0.2420	0.6330	0.9530	0.0469	0.0001	0.7290	0.2480	0.0230
183.50	0.1361	0.2941	0.5698	0.9446	0.0554	0.0001	0.5254	0.4190	0.0555
178.25	0.1491	0.3300	0.5209	0.9416	0.0583	0.0001	0.4877	0.4450	0.0672
167.70	0.1694	0.3984	0.4323	0.9345	0.0655	0.0	0.4015	0.4819	0.1166
165.40	0.1755	0.4222	0.4024	0.9337	0.0662	0.0	0.6523	0.3147	0.0329

TABLE 3.13

Vapoe-liquid-loquid equilibrium data for the system nitrogen(1)-methane(2)-propane(3) at 118.32 K

P (psia)	X1	X2	X3	Y1	Y2	Y3	X1	X2	X3
309.00	0.0907	0.0433	0.8660	0.9845	0.0154	0.0002	0.9555	0.0426	0.0019
283.23	C.1127	0.1209	0.7664	0.9670	0.0329	0.0001	0.8804	0.1149	0.0047
269.30	0.1170	0.1649	0.7181	0.9596	0.0403	0.0001	0.8396	0.1540	0.0064
257.70	0.1281	0.2053	0.6666	0.9520	0.0479	0.0001	0.7915	0.1980	0.0105
257.70	0.1280	0.2051	0.6669	0.9520	0.0479	0.0001	0.7924	0.1971	0.0105
244.30	0.1351	0.2481	0.6168	0.9429	0.0570	0.0001	0.7370	0.2451	0.0178
228.50	C.1545	0.3171	0.5284	0.9349	0.0650	0.0	0.6481	0.3219	0.0300
216.53	0.1746	0.3710	0.4544	0.9275	0.0724	0.0	0.5836	0.3718	0.0446
206.50	0.2176	0.4306	0.3518	0.9214	0.0785	0.0	0.4793	0.4434	0.0773
204.50	0.2341	0.4377	0.3282	0.9206	0.0793	0.0	0.4667	0.4457	0.0875

TABLE 3.14

Vapor-liquid-liquid equilibrium data for the system nitrogen(1)-methane(2)-propane(3) at 122.24 K

P (psia)	X1	X2	X3	Y1	Y2	Y3	X1 '	X2 '	X3 '
386.50	0.0953	0.0227	0.8820	0.9880	0.0115	0.0005	0.9776	0.0211	0.0013
346.85	0.1036	0.0993	0.7970	0.9638	0.0361	0.0001	0.8954	0.1023	0.0023
330.00	0.1146	0.1422	0.7432	0.9545	0.0454	0.0001	0.8467	0.1513	0.0020
296.85	0.1444	0.2304	0.6252	0.9356	0.0643	0.0001	0.7418	0.2497	0.0085
260.80	0.2051	0.3577	0.4372	0.9147	0.0853	0.0	0.5837	0.3765	0.0398
250.20	0.2451	0.4090	0.3459	0.9083	0.0917	0.0	0.4891	0.4423	0.0686
245.12	0.2829	0.4372	0.2799	0.9057	0.0943	0.0			

TABLE 3.15

Phase inversion temperature and liquid-liquid equilibrium compositions for the system nitrogen(1)-methane(2)-ethane(3)

Temp. K	Pressure psia	Liquid phase I(B.L.) N_2	C_1	C_2	Liquid phase II (T.L.) N_2	C_1	C_2
109.10	190.0	0.2014		0.7986	0.9453		0.0547
	189.8	0.9238		0.0762	0.2228		0.7772
111.72	200.8	0.2824	0.0960	0.6216	0.8396	0.0737	0.0867
	200.6	0.8276	0.0747	0.0977	0.2759	0.0938	0.6303
113.39	208.5	0.3511	0.1487	0.5002	0.7443	0.1258	0.1299
	208.3	0.7382	0.1271	0.1337	0.3401	0.1463	0.5126
113.67	213.0	0.4829	0.1850	0.3318	0.6324	0.1651	0.2025
	212.3	0.6266	0.1662	0.2072	0.4829	0.1848	0.3223

TABLE 4.1

Liquid activity coefficients for the binary systems nitrogen(1)-propane(2) and methane(1)-propane(2)

T = 114.05 K System Nitrogen(1)-Propane(2)

P (psia)	X1	GA1	GA2	LN G1	LN G2	Q12
21.80	0.0075	14.8415	0.9999	2.6974	-0.0001	0.0202
23.60	0.0086	14.8034	1.0000	2.6949	0.0	0.0232
49.50	0.0169	14.5180	1.0002	2.6754	0.0002	0.0454
95.40	0.0335	13.9588	1.0012	2.6361	0.0012	0.0895
145.20	0.0486	13.4633	1.0028	2.6000	0.0028	0.1290
199.10	0.0640	12.9707	1.0051	2.5627	0.0050	0.1687
232.50	0.0736	12.6703	1.0068	2.5393	0.0067	0.1931
239.60	0.0773	12.5557	1.0075	2.5302	0.0075	0.2025
258.00	0.0842	12.3442	1.0090	2.5132	0.0090	0.2198
261.00	0.0845	12.3351	1.0091	2.5124	0.0090	0.2206

T = 118.32 K System Nitrogen(1)-Propane(2)

P (psia)	X1	GA1	GA2	LN G1	LN G2	Q12
27.20	0.0079	14.2206	0.9999	2.6547	-0.0001	0.0208
61.80	0.0175	13.9103	1.0002	2.6326	0.0002	0.0462
107.35	0.0321	13.4474	1.0010	2.5988	0.0010	0.0844
145.25	0.0433	13.0995	1.0020	2.5726	0.0020	0.1133
177.50	0.0511	12.8610	1.0030	2.5542	0.0030	0.1333
188.20	0.0557	12.7218	1.0036	2.5433	0.0036	0.1450
215.80	0.0621	12.5298	1.0045	2.5281	0.0045	0.1612
280.00	0.0760	12.1198	1.0070	2.4948	0.0070	0.1961
297.50	0.0801	12.0007	1.0079	2.4850	0.0078	0.2063
312.20	0.0854	11.8480	1.0090	2.4722	0.0090	0.2194

TABLE 4.1 (continued)

T = 122.24 K System Nitrogen(1)-Propane(2)

P (psia)	X1	GA1	GA2	LN G1	LN G2	Q12
44.00	0.0107	13.9575	1.0001	2.6360	0.0001	0.0283
51.80	0.0133	13.8751	1.0001	2.6301	0.0001	0.0351
100.80	0.0254	13.4963	1.0007	2.6024	0.0007	0.0667
150.60	0.0380	13.1093	1.0016	2.5733	0.0016	0.0993
166.10	0.0410	13.0183	1.0019	2.5664	0.0019	0.1071
202.90	0.0486	12.7893	1.0028	2.5487	0.0027	0.1265
280.10	0.0672	12.2422	1.0055	2.5049	0.0055	0.1734
341.70	0.0812	11.8409	1.0082	2.4716	0.0081	0.2082
369.50	0.0858	11.7111	1.0092	2.4605	0.0091	0.2195
400.00	0.0869	11.6802	1.0094	2.4579	0.0094	0.2222
400.00	0.0885	11.6354	1.0098	2.4540	0.0097	0.2261
406.00	0.0888	11.6270	1.0099	2.4533	0.0098	0.2268

T = 114.05 K System Methane(1)-Propane(2)

P (psia)	X1	GA1	GA2	LN G1	LN G2	Q12
6.06	0.1812	1.8300	1.0147	0.6043	0.0146	0.1214
8.60	0.2911	1.6716	1.0437	0.5138	0.0428	0.1799
11.17	0.4102	1.5093	1.1035	0.4116	0.0985	0.2269
13.96	0.6647	1.2087	1.4455	0.1896	0.3684	0.2495
13.00	0.5488	1.3362	1.2363	0.2898	0.2121	0.2548
16.20	0.8812	1.0348	2.5296	0.0342	0.9281	0.1404

TABLE 4.1 (continued)

T = 118.32 K System Methane(1)-Propane(2)

P (psia)	X1	GA1	GA2	LN G1	LN G2	Q12
7.88	0.1775	1.8461	1.0141	0.6131	0.0140	0.1203
10.95	0.2717	1.7076	1.0374	0.5351	0.0367	0.1721
14.12	0.3909	1.5410	1.0921	0.4324	0.0881	0.2227
17.63	0.5714	1.3132	1.2708	0.2725	0.2397	0.2584
19.60	0.6540	1.2219	1.4251	0.2004	0.3542	0.2536
20.60	0.7399	1.1383	1.6792	0.1295	0.5183	0.2307
22.90	0.9031	1.0242	2.7852	0.0239	1.0243	0.1208
24.70	1.0000	1.0000	4.5659	0.0	1.5186	0.0

T = 122.24 K System Methane(1)-Propane(2)

P (psia)	X1	GA1	GA2	LN G1	LN G2	Q12
7.06	0.1130	1.9729	1.0054	0.6795	0.0054	0.0816
9.05	0.1409	1.9287	1.0087	0.6568	0.0087	0.1000
13.06	0.2219	1.8029	1.0240	0.5894	0.0237	0.1493
13.50	0.2253	1.7977	1.0249	0.5865	0.0246	0.1512
18.78	0.3701	1.5846	1.0821	0.4603	0.0789	0.2201
23.10	0.5297	1.3716	1.2201	0.3160	0.1989	0.2609
26.90	0.7090	1.1705	1.5894	0.1574	0.4634	0.2465
28.76	0.8095	1.0828	2.0375	0.0796	0.7117	0.2000
31.04	0.8910	1.0306	2.7067	0.0301	0.9957	0.1354
33.20	1.0000	1.0000	4.7086	0.0	1.5494	0.0

TABLE 4.2

Results of the Correlation of Liquid Activity Coefficients for the Binary Systems

Temp (°K)	System	Redlich-Kister Constants B_{12}	C_{12}	D_{12}	Avg. abs. dev. in γ_1 and γ_2	Avg. abs. % dev. in γ_1 and γ_2
114.05	*	0.7845			0.0188	0.92
	N_2-C_1	0.7845	0.0490		0.0004	0.02
		0.7845	0.0490	0.0010	0.0003	0.01
		1.0395			0.1327	6.46
	C_1-C_3	0.9762	0.3528		0.0279	1.11
		0.9959	0.3396	0.1036	0.0048	0.18
		2.8433			0.6550	4.37
	N_2-C_3	3.5157	0.8311		0.0107	0.07
		3.6287	1.0946	0.1528	0.0044	0.03
118.32	*	0.7557			0.0202	1.01
	N_2-C_1	0.7557	0.0538		0.0012	0.05
		0.7559	0.0538	0.0041	0.0005	0.03
		1.0344			0.1533	6.56
	Cl-C_3	0.9819	0.3794		0.3370	1.23
		1.0046	0.3469	0.1164	0.0061	0.21
		2.8106			0.5293	3.43
	N_2-C_3	3.4724	0.8275		0.0109	0.08
		3.6494	1.2400		0.0015	0.02
122.24	*	0.7463			0.0238	1.19
	N_2 - C_1	0.7463	0.0634		0.0027	0.12
		0.7468	0.0634	0.0096	0.0010	0.05
		0.9999			0.1522	5.63
	C_1-C_3	1.0129	0.3445		0.0327	1.16
		1.0222	0.3482	0.1176	0.0070	0.27
		2.8202			0.0608	4.40
	N_2-C_3	3.4773	0.8407		0.0113	0.08
		3.6778	1.3178	0.2830	0.0019	0.02

* using smoothed values from the literature (4)

TABLE 4.3

Liquid activity coefficients evaluated from gas phase fugacity coefficients

T = 114.05 K System Nitrogen(1)-Propane(2)

P (psia)	X1	GE1	GE2	LN GE1	LN GE2
21.80	0.0075	15.7426	0.1880	2.7564	-1.6716
23.60	0.0086	14.8280	0.2010	2.6965	-1.6043
49.50	0.0169	15.2992	0.3498	2.7278	-1.0504
95.40	0.0335	13.9826	0.4725	2.6378	-0.7498
145.20	0.0486	13.6733	0.4622	2.6154	-0.7717
199.10	0.0640	13.1253	0.3526	2.5745	-1.0423
232.50	0.0736	12.6200	0.2548	2.5353	-1.3672
239.60	0.0773	12.2325	0.2319	2.5041	-1.4616
258.00	0.0842	11.6970	0.1640	2.4593	-1.8078
261.00	0.0845	11.7237	0.1506	2.4616	-1.8931

T = 118.32 K System Nitrogen(1)-Propane(2)

P (psia)	X1	GE1	GE2	LN GE1	LN GE2
27.20	0.0079	14.9916	1.1513	2.7075	0.1409
61.80	0.0175	14.7359	2.5054	2.6903	0.9184
107.35	0.0321	13.1775	2.1169	2.5785	0.7499
145.25	0.0433	12.5792	2.1393	2.5320	0.7605
177.50	0.0511	12.4721	0.9968	2.5235	-0.0032
188.20	0.0557	11.9533	0.9597	2.4810	-0.0412
215.80	0.0621	11.8208	0.8343	2.4699	-0.1812
280.00	0.0760	11.3492	0.2203	2.4291	-1.5128
297.50	0.0801	11.0861	0.9698	2.4057	-0.0306
312.20	0.0854	10.2884	0.1570	2.3310	-1.8516

TABLE 4.3 (continued)

T = 122.24 K System Nitrogen(1)-Propane(2)

P (psia)	X1	GE1	GE2	LN GE1	LN GE2
44.00	0.0107	14.9798	3.7768	2.7067	1.3289
51.80	0.0133	14.0592	4.2502	2.6433	1.4470
100.80	0.0254	13.5197	4.4624	2.6041	1.4957
150.60	0.0380	12.7029	3.5855	2.5418	1.2769
166.10	0.0410	12.7352	2.9476	2.5444	1.0810
202.90	0.0486	12.5165	2.1616	2.5270	0.7709
280.10	0.0672	11.2349	0.3492	2.4190	-1.0520
341.70	0.0812	9.9892	0.1767	2.3015	-1.7335
369.50	0.0858	9.2887	0.1959	2.2288	-1.6304
400.00	0.0869	9.0612	0.1946	2.2040	-1.6368
400.00	0.0885	8.8935	0.3882	2.1853	-0.9463
406.00	0.0888	8.8458	0.3857	2.1799	-0.9526

T = 114.05 K System Methane(1)-Propane(2)

P (psia)	X1	GE1	GE2	LN GE1	LN GE2
6.06	0.1812	1.9435	0.6785	0.6645	-0.3878
8.60	0.2911	1.7069	0.5360	0.5347	-0.6236
11.17	0.4102	1.5635	0.4836	0.4470	-0.7266
13.96	0.6647	1.1976	0.6799	0.1803	-0.3859
13.00	0.5488	1.3543	0.0	0.3033	0.0
16.20	0.8812	1.0426	0.0	0.0417	0.0

TABLE 4.3 (continued)

T = 118.32 K System Methane(1)-Propane(2)

P (psia)	X1	GE1	GE2	LN GE1	LN GE2
7.88	0.1775	1.8655	1.2172	0.6236	0.1966
10.95	0.2717	1.6830	0.9196	0.5206	-0.0839
14.12	0.3909	1.4982	0.5841	0.4042	-0.5377
17.63	0.5714	1.2688	2.6386	0.2381	0.9703
19.60	0.6540	1.2277	0.4435	0.2051	-0.8131
20.60	0.7399	1.1380	0.0	0.1293	0.0
22.90	0.9031	1.0309	0.0	0.0305	0.0
24.70	1.0000	1.0000	0.0	0.0	0.0

T = 122.24 K System Methane(1)-Propane(2)

P (psia)	X1	GE1	GE2	LN GE1	LN GE2
7.06	0.1130	1.9845	1.7700	0.6854	0.5710
9.05	0.1409	2.0338	1.3379	0.7099	0.2911
13.06	0.2219	1.8499	0.5833	0.6151	-0.5390
13.50	0.2253	1.8816	0.6027	0.6321	-0.5064
18.78	0.3701	1.5763	0.2432	0.4551	-1.4140
23.10	0.5297	1.3423	0.3815	0.2944	-0.9637
26.90	0.7090	1.1583	0.6872	0.1470	-0.3751
28.76	0.8095	1.0805	0.0	0.0774	0.0
31.04	0.8910	1.0542	0.0	0.0528	0.0
33.20	1.0000	1.0000	0.0	0.0	0.0

TABLE 4.4

Comparison of liquid activity coefficients evaluated from Equation(4.13) to those evaluated from Equation(4.8), for binary systems. GA1, GA2 were obtained from Eq.(4.8), and GE1, GE2 were obtained from Eq.(4.13).

T = 114.05 K System Nitrogen(1)-Propane(2)

X1	GA1	GE1	% DG1	GA2	GE2	% DG2
0.0075	14.8415	15.7426	-6.0714	0.9999	0.1680	81.2037
0.0036	14.8034	14.3280	-0.1661	1.0000	0.2010	79.8973
0.0169	14.5180	15.2992	-5.3807	1.0002	0.3498	65.0261
0.0335	13.9588	13.9826	-0.1705	1.0012	0.4725	52.8117
0.0486	13.4633	13.6733	-1.5600	1.0028	0.4622	53.9057
0.0640	12.9707	13.1253	-1.1913	1.0051	0.3526	64.9140
0.0736	12.6703	12.6200	0.3963	1.0068	0.2548	74.6904
0.0773	12.5557	12.2325	2.5745	1.0075	0.2319	76.9854
0.0842	12.3442	11.6970	5.2426	1.0090	0.1640	83.7459
0.0845	12.3351	11.7237	4.9563	1.0091	0.1506	85.0753

T = 118.32 K System Nitrogen(1)-Propane(2)

X1	GA1	GE1	% DG1	GA2	GE2	% DG2
0.0079	14.2206	14.9916	-5.4213	0.9999	1.1513	-15.1428
0.0175	13.9103	14.7359	-5.9347	1.0002	2.5054	-150.4952
0.0321	13.4474	13.1775	2.0070	1.0010	2.1169	-111.4680
0.0433	13.0955	12.5792	3.9725	1.0020	2.1393	-113.4976
0.0511	12.8610	12.4721	3.0237	1.0030	0.9968	0.6172
0.0557	12.7218	11.9533	6.0408	1.0036	0.9597	4.3768
0.0621	12.5298	11.8208	5.6584	1.0045	0.8343	16.9452
0.0760	12.1198	11.3492	6.3581	1.0070	0.2203	78.1245
0.0801	12.0007	11.0861	7.6215	1.0079	0.9698	3.7751
0.0854	11.8480	10.2884	13.1630	1.0090	0.1570	84.4413

TABLE 4.4 (continued)

T = 122.24 K System Nitrogen(1)-Propane(2)

X1	GA1	GE1	% DG1	GA2	GE2	% DG2
0.0107	13.9575	14.9798	-7.3246	1.0001	3.7768	-277.6470
0.0133	13.8751	14.0592	-1.3266	1.0001	4.2502	-324.9646
0.0254	13.4963	13.5197	-0.1734	1.0007	4.4624	-345.9502
0.0380	13.1093	12.7029	3.1002	1.0016	3.5855	-257.9705
0.0410	13.0183	12.7352	2.1747	1.0019	2.9476	-194.1927
0.0486	12.7898	12.5165	2.1372	1.0028	2.1616	-115.5681
0.0672	12.2422	11.2349	8.2282	1.0055	0.3492	65.2663
0.0812	11.8409	9.9892	15.6385	1.0082	0.1767	82.4764
0.0858	11.7111	9.2887	20.6842	1.0092	0.1959	80.5925
0.0869	11.6802	9.0612	22.4227	1.0094	0.1946	80.7212
0.0885	11.6354	8.8935	23.5647	1.0098	0.3882	61.5609
0.0888	11.6270	8.8458	23.9197	1.0099	0.3857	61.8032

T = 114.05 K System Methane(1)-Propane(2)

X1	GA1	GE1	% DG1	GA2	GE2	% DG2
0.1812	1.8300	1.9435	-6.2052	1.0147	0.6785	33.1286
0.2911	1.6716	1.7069	-2.1130	1.0437	0.5360	48.6429
0.4102	1.5093	1.5635	-3.5970	1.1035	0.4836	56.1812
0.6647	1.2087	1.1976	0.9217	1.4455	0.6799	52.9655
0.5488	1.3362	1.3543	-1.3547	1.2363	0.0	100.0000
0.8812	1.0348	1.0426	-0.7574	2.5296	0.0	100.0000

TABLE 4.4 (continued)

T = 118.32 K System Methane(1)-Propane(2)

X1	GA1	GE1	% DG1	GA2	GE2	% DG2
0.1775	1.8461	1.8655	-1.0520	1.0141	1.2172	-20.0326
0.2717	1.7076	1.6830	1.4395	1.0374	0.9196	11.3593
0.3909	1.5410	1.4982	2.7786	1.0921	0.5841	46.5191
0.5714	1.3132	1.2688	3.3830	1.2708	2.6386	-107.6283
0.6540	1.2219	1.2277	-0.4710	1.4251	0.4435	68.8790
0.7399	1.1383	1.1380	0.0278	1.6792	0.0	100.0000
0.9031	1.0242	1.0309	-0.6570	2.7852	0.0	100.0000
1.0000	1.0000	1.0000	-0.0003	4.5659	0.0	100.0000

T = 122.24 K System Methane(1)-Propane(2)

X1	GA1	GE1	% DG1	GA2	GE2	% DG2
0.1130	1.9729	1.9845	-0.5871	1.0054	1.7700	-76.0394
0.1409	1.9287	2.0338	-5.4478	1.0087	1.3379	-32.6303
0.2219	1.8029	1.8499	-2.6060	1.0240	0.5833	43.0380
0.2253	1.7977	1.8816	-4.6673	1.0249	0.6027	41.1967
0.3701	1.5846	1.5763	0.5265	1.0821	0.2432	77.5269
0.5297	1.3716	1.3423	2.1370	1.2201	0.3815	68.7338
0.7090	1.1705	1.1583	1.0384	1.5894	0.6872	56.7632
0.8095	1.0828	1.0805	0.2184	2.0375	0.0	100.0000
0.8910	1.0306	1.0542	-2.2958	2.7067	0.0	100.0000
1.0000	1.0000	1.0000	0.0005	4.7086	0.0	100.0000

TABLE 4.5

Properties of Pure Components

	T_c (°K)	P_c (psia)	V_c (ft^2/lb mole)	Reference
Nitrogen	126.2	492.5	1.44	95
Methane	190.55	667.8	1.59	106
Ethane	305.43	707.8	2.37	106
Propane	369.82	616.3	3.26	106
n-Butane	425.16	550.7	4.08	106
Carbon Dioxide	304.19	1070.6	1.51	106

TABLE 4.6

Comparison of experimental values to vapor compositions predicted by the modified Redlich-Kwong equation of state for the binary systems nitrogen(1)-propane(2) and methane(1)-propane(2).

T = 114.05 K System Nitrogen(1)-Propane(2)

P (psia)	X1	Y1 EXP	Y1 CAL	Y2 EXP	Y2 CAL
21.80	0.0075	0.9999	1.0000	0.0001	0.0
23.60	0.0086	0.9999	1.0000	0.0001	0.0
49.50	0.0169	0.9999	1.0000	0.0001	0.0
95.40	0.0335	0.9999	1.0000	0.0001	0.0
145.20	0.0486	0.9999	1.0000	0.0001	0.0
199.10	0.0640	0.9999	1.0000	0.0001	0.0
232.50	0.0736	0.9999	1.0000	0.0001	0.0
239.60	0.0773	0.9999	1.0000	0.0001	0.0
258.00	0.0842	0.9999	1.0000	0.0001	0.0
261.00	0.0845	0.9999	1.0000	0.0001	0.0

T = 118.32 K System Nitrogen(1)-Propane(2)

P (psia)	X1	Y1 EXP	Y1 CAL	Y2 EXP	Y2 CAL
27.20	0.0079	0.9995	1.0000	0.0005	0.0
61.80	0.0175	0.9994	1.0000	0.0006	0.0
107.35	0.0321	0.9996	1.0000	0.0004	0.0
145.25	0.0433	0.9996	1.0000	0.0004	0.0
177.50	0.0511	0.9998	1.0000	0.0002	0.0
188.20	0.0557	0.9998	1.0000	0.0002	0.0
215.80	0.0621	0.9998	1.0000	0.0002	0.0
280.00	0.0760	0.9999	1.0000	0.0001	0.0
297.50	0.0801	0.9992	1.0000	0.0008	0.0
312.20	0.0854	0.9999	1.0000	0.0001	0.0

TABLE 4.6 (continued)

T = 118.32 K System Methane(1)-Propane(2)

P (psia)	X1	Y1 EXP	Y1 CAL	Y2 EXP	Y2 CAL
7.88	0.1775	0.9986	1.0000	0.0014	0.0
10.95	0.2717	0.9993	1.0000	0.0007	0.0
14.12	0.3909	0.9997	1.0000	0.0003	0.0
17.63	0.5714	0.9992	1.0000	0.0008	0.0
19.60	0.6540	0.9999	1.0000	0.0001	0.0
20.60	0.7399	1.0000	1.0000	0.0	0.0
22.90	0.9031	1.0000	1.0000	0.0	0.0
24.70	1.0000	1.0000	1.0000	0.0	0.0

T = 122.24 K System Methane(1)-Propane(2)

P (psia)	X1	Y1 EXP	Y1 CAL	Y2 EXP	Y2 CAL
7.06	0.1130	0.9976	0.9999	0.0024	0.0001
9.05	0.1409	0.9986	0.9999	0.0014	0.0001
13.06	0.2219	0.9996	1.0000	0.0004	0.0
13.50	0.2253	0.9996	1.0000	0.0004	0.0
18.78	0.3701	0.9999	1.0000	0.0001	0.0
23.10	0.5297	0.9999	1.0000	0.0001	0.0
26.90	0.7090	0.9999	1.0000	0.0001	0.0
28.76	0.8095	1.0000	1.0000	0.0	0.0
31.04	0.8910	1.0000	1.0000	0.0	0.0
33.20	1.0000	1.0000	1.0000	0.0	0.0

TABLE 4.6 (continued)

T = 122.24 K System Nitrogen(1)-Propane(2)

P (psia)	X1	Y1 EXP	Y1 CAL	Y2 EXP	Y2 CAL
44.00	0.0107	0.9989	1.0000	0.0011	0.0
51.80	0.0133	0.9989	1.0000	0.0011	0.0
100.80	0.0254	0.9992	1.0000	0.0008	0.0
150.60	0.0380	0.9994	1.0000	0.0006	0.0
166.10	0.0410	0.9995	1.0000	0.0005	0.0
202.90	0.0486	0.9996	1.0000	0.0004	0.0
280.10	0.0672	0.9999	1.0000	0.0001	0.0
341.70	0.0812	0.9999	1.0000	0.0001	0.0
369.50	0.0858	0.9999	1.0000	0.0001	0.0
400.00	0.0869	0.9999	1.0000	0.0001	0.0
400.00	0.0885	0.9998	1.0000	0.0002	0.0
406.00	0.0888	0.9998	1.0000	0.0002	0.0

T = 114.05 K System Methane(1)-Propane(2)

P (psia)	X1	Y1 EXP	Y1 CAL	Y2 EXP	Y2 CAL
6.06	0.1812	0.9990	1.0000	0.0010	0.0
8.60	0.2911	0.9995	1.0000	0.0005	0.0
11.17	0.4102	0.9997	1.0000	0.0003	0.0
13.96	0.6647	0.9998	1.0000	0.0002	0.0
13.00	0.5488	1.0000	1.0000	0.0	0.0
16.20	0.8812	1.0000	1.0000	0.0	0.0

TABLE 4.7

Comparison of experimental values to predicted pressures and vapor compositions by the modified Redlich-Kwong equation of state for the systems nitrogen(1)-propane(2) and methane(1)-propane(2).

T = 114.05 K System Nitrogen(1)-Propane(2)

X1	DY1	DY2	P EXP (psia)	P CAL (psia)	% DP
0.0075	0.0001	-0.0001	21.8000	21.35	-2.08
0.0086	0.0001	-0.0001	23.6000	24.50	3.83
0.0169	0.0001	-0.0001	49.5000	48.57	-1.88
0.0335	0.0001	-0.0001	95.4000	98.22	2.96
0.0486	0.0001	-0.0001	145.2000	145.75	0.38
0.0640	0.0001	-0.0001	199.1000	197.71	-0.70
0.0736	0.0001	-0.0001	232.5000	232.87	0.16
0.0773	0.0001	-0.0001	239.5999	247.25	3.19
0.0842	0.0001	-0.0001	257.9998	275.92	6.95
0.0845	0.0001	-0.0001	260.9998	277.23	6.22

AVE. ABS. % DEV. IN PRESSURE %DP = 2.83 (%)

AVE. ABS. DEV. IN VAPOR COMP. = 0.0001 (MOLE FRACTION)

TABLE 4.7 (continued)

T = 118.32 K System Nitrogen(1)-Propane(2)

X1	DY1	DY2	P EXP (psia)	P CAL (psia)	% DP
0.0079	0.0005	-0.0005	27.2000	25.63	-5.76
0.0175	0.0006	-0.0006	61.8000	57.47	-7.01
0.0321	0.0004	-0.0004	107.3500	107.65	0.28
0.0433	0.0004	-0.0004	145.2500	148.01	1.90
0.0511	0.0002	-0.0002	177.5000	177.38	-0.07
0.0557	0.0002	-0.0002	188.2000	195.30	3.77
0.0621	0.0002	-0.0002	215.8000	221.15	2.48
0.0760	0.0001	-0.0001	279.9998	282.47	0.88
0.0801	0.0008	-0.0008	297.4998	302.60	1.71
0.0854	0.0001	-0.0001	312.1995	330.93	6.00

AVE. ABS. % DEV. IN PRESSURE %DP = 2.99 (%)
AVE. ABS. DEV. IN VAPOR COMP. = 0.0003 (MOLE FRACTION)

T = 122.24 K System Nitrogen(1)-Propane(2)

X1	DY1	DY2	P EXP (psia)	P CAL (psia)	% DP
0.0107	0.0011	-0.0011	44.0000	39.53	-10.16
0.0133	0.0011	-0.0011	51.8000	49.32	-4.78
0.0254	0.0008	-0.0008	100.8000	96.01	-4.75
0.0380	0.0006	-0.0006	150.6000	147.02	-2.38
0.0410	0.0005	-0.0005	166.1000	159.61	-3.91
0.0486	0.0004	-0.0004	202.9000	192.44	-5.16
0.0672	0.0001	-0.0001	280.0994	280.69	0.21
0.0812	0.0001	-0.0001	341.6995	360.85	5.61
0.0858	0.0001	-0.0001	369.4998	393.05	6.37
0.0869	0.0001	-0.0001	399.9998	401.68	0.42
0.0885	0.0002	-0.0002	399.9998	415.43	3.86
0.0888	0.0002	-0.0002	405.9998	418.11	2.98

AVE. ABS. % DEV. IN PRESSURE %DP = 4.22 (%)
AVE. ABS. DEV. IN VAPOR COMP. = 0.0004 (MOLE FRACTION)

TABLE 4.7 (continued)

T = 114.05 K System Methane(1)-Propane(2)

X1	DY1	DY2	P EXP (psia)	P CAL (psia)	% DP
0.1812	0.0010	-0.0010	6.0600	5.81	-4.07
0.2911	0.0005	-0.0005	8.6000	8.57	-0.33
0.4102	0.0003	-0.0003	11.1700	10.95	-2.00
0.6647	0.0002	-0.0002	13.9600	14.26	2.17
0.5488	0.0	0.0	13.0000	13.00	0.01
0.8812	0.0	0.0	16.2000	16.21	0.08

AVE. ABS. % DEV. IN PRESSURE %DP = 1.44 (%)
AVE. ABS. DEV. IN VAPOR COMP. = 0.0003 (MOLE FRACTION)

T = 118.32 K System Methane(1)-Propane(2)

X1	DY1	DY2	P EXP (psia)	P CAL (psia)	% DP
0.1775	0.0014	-0.0014	7.8800	7.91	0.36
0.2717	0.0007	-0.0007	10.9500	11.27	2.89
0.3909	0.0003	-0.0003	14.1200	14.72	4.22
0.5714	0.0008	-0.0008	17.6300	18.44	4.58
0.6540	0.0001	-0.0001	19.6000	19.67	0.34
0.7399	0.0	0.0	20.6000	20.75	0.73
0.9031	0.0	0.0	22.9000	22.84	-0.27
1.0000	0.0	0.0	24.7000	24.78	0.31

AVE. ABS. % DEV. IN PRESSURE %DP = 1.71 (%)
AVE. ABS. DEV. IN VAPOR COMP. = 0.0004 (MOLE FRACTION)

TABLE 4.7 (continued)

T = 122.24 K System Methane(1)-Propane(2)

X1	DY1	DY2	P EXP (psia)	P CAL (psia)	% DP
0.1130	0.0023	-0.0023	7.0600	6.98	-1.11
0.1409	0.0013	-0.0013	9.0500	8.53	-5.69
0.2219	0.0004	-0.0004	13.0600	12.66	-3.05
0.2253	0.0004	-0.0004	13.5000	12.82	-5.02
0.3701	0.0001	-0.0001	18.7800	18.77	-0.05
0.5297	0.0001	-0.0001	23.1000	23.44	1.48
0.7090	0.0001	-0.0001	26.9000	26.91	0.04
0.8095	0.0	0.0	28.7600	28.47	-1.00
0.8910	0.0	0.0	31.0400	29.88	-3.75
1.0000	0.0	0.0	33.2000	32.69	-1.54

AVE. ABS. % DEV. IN PRESSURE %DP = 2.27 (%)

AVE. ABS. DEV. IN VAPOR COMP. = 0.0005 (MOLE FRACTION)

TABLE 4.8

Comparison of experimental values to the predicted values of liquid-liquid equilibrium for the system nitrogen(1)-propane(2).

TEMP K	BOTTOM LIQUID PHASE				TOP LIQUID PHASE		
	P EXP / P CAL / DP	X1 EXP / X1 CAL / DX1	X2 EXP / X2 CAL / DX2	X3 EXP / X3 CAL / DX3	X1 EXP / X1 CAL / DX1	X2 EXP / X2 CAL / DX2	X3 EXP / X3 CAL / DX3
113.22	246.60	0.0	0.0842	0.9158	0.0	0.9984	0.0016
	236.87	0.0	0.0846	0.9154	0.0	0.9984	0.0016
	-9.73	0.0	-0.0004	0.0004	0.0	0.0	0.0
115.15	275.40	0.0	0.0844	0.9156	0.0	0.9982	0.0018
	263.92	0.0	0.0849	0.9151	0.0	0.9982	0.0018
	-11.48	0.0	-0.0005	0.0005	0.0	0.0	0.0
116.80	301.00	0.0	0.0841	0.9159	0.0	0.9981	0.0019
	289.74	0.0	0.0842	0.9158	0.0	0.9981	0.0019
	-11.26	0.0	-0.0001	0.0001	0.0	0.0	0.0
117.92	320.70	0.0	0.0834	0.9166	0.0	0.9981	0.0019
	308.22	0.0	0.0836	0.9164	0.0	0.9981	0.0019
	-12.48	0.0	-0.0002	0.0002	0.0	0.0	0.0
119.72	351.70	0.0	0.0859	0.9141	0.0	0.9983	0.0017
	339.36	0.0	0.0863	0.9137	0.0	0.9983	0.0017
	-12.34	0.0	-0.0004	0.0004	0.0	0.0	0.0

TABLE 4.8 (continued)

TEMP K	BOTTOM LIQUID PHASE				TOP LIQUID PHASE		
	P EXP / P CAL / DP	X1 EXP / X1 CAL / DX1	X2 EXP / X2 CAL / DX2	X3 EXP / X3 CAL / DX3	X1 EXP / X1 CAL / DX1	X2 EXP / X2 CAL / DX2	X3 EXP / X3 CAL / DX3
121.34	383.90	0.0	0.0876	0.9124	0.0	0.9978	0.0022
	365.65	0.0	0.0874	0.9126	0.0	0.9978	0.0022
	-18.25	0.0	0.0002	-0.0002	0.0	0.0	0.0
123.51	425.30	0.0	0.0902	0.9098	0.0	0.9977	0.0023
	407.60	0.0	0.0906	0.9094	0.0	0.9977	0.0023
	-17.70	0.0	-0.0004	0.0004	0.0	0.0	0.0
123.71	429.90	0.0	0.0903	0.9097	0.0	0.9977	0.0023
	416.44	0.0	0.0908	0.9092	0.0	0.9977	0.0023
	-13.46	0.0	-0.0005	0.0005	0.0	0.0	0.0
125.15	460.80	0.0	0.0933	0.9067	0.0	0.9981	0.0019
	447.44	0.0	0.0939	0.9061	0.0	0.9981	0.0019
	-13.36	0.0	-0.0006	0.0006	0.0	0.0	0.0

TABLE 4.9

List of parameters used in the application of the modified Redlich-Kwong equation to predict vapor-liquid equilibrium

Temp. K	N_2		C_1		C_3	
	Ω_a	Ω_b	Ω_a	Ω_b	Ω_a	Ω_b
114.05	0.41835	0.08250	0.40480	0.08623	0.38350	0.08020
118.32	0.41875	0.08220	0.40635	0.08600	0.38723	0.08035
122.24	0.41717	0.08185	0.40770	0.08579	0.39070	0.08053

Temp. K	k_{ij} $(N_2 - C_1)$	k_{ij} $(C_1 - C_3)$	k_{ij} $(N_2 - C_3)$
115.04	0.0320	0.0132	0.0840
118.32	0.0310	0.0145	0.0870
122.24	0.0304	0.0162	0.0910

TABLE 4.10

Liquid activity coefficients for the ternary system nitrogen(1)-methane(2)-propane(3) evalued from vapor-liquid equilibrium data.

T = 114.04 K

P	X1	GA1	GA2	GA3	LN GA1	LN GA2	LN GA3	Q123
70.88	0.0245	13.9571	2.0146	1.0012	2.6360	0.7004	0.0012	0.0771
127.20	0.0446	13.3034	1.9629	1.0035	2.5880	0.6744	0.0035	0.1294
193.40	0.0637	12.7399	1.9179	1.0063	2.5447	0.6512	0.0063	0.1767
82.80	0.0388	9.3257	1.6226	1.0578	2.2328	0.4841	0.0562	0.2529
124.50	0.0620	8.7590	1.5738	1.0751	2.1701	0.4535	0.0724	0.3018
65.80	0.0562	4.4925	1.1752	1.5362	1.5024	0.1614	0.4293	0.3255
101.38	0.0989	4.1769	1.1477	1.6318	1.4296	0.1377	0.4897	0.3792
124.05	0.1797	3.3164	1.0737	2.0690	1.1989	0.0711	0.7271	0.4495
43.40	0.0503	2.6861	1.0215	2.8301	0.9881	0.0212	1.0403	0.1865
41.80	0.0525	2.4610	1.0093	3.2888	0.9006	0.0092	1.1905	0.1527
77.60	0.1270	2.3732	1.0072	3.4679	0.8642	0.0072	1.2435	0.2459
131.70	0.2999	1.8167	1.0126	6.1752	0.5970	0.0125	1.8205	0.3362
158.30	0.4184	1.5524	1.0509	9.8771	0.4398	0.0496	2.2902	0.3695
173.00	0.5072	1.3795	1.1100	15.6387	0.3217	0.1043	2.7497	0.3615
185.30	0.6106	1.2095	1.2367	31.4872	0.1902	0.2125	3.4496	0.3050
220.80	0.8059	1.0503	1.6066	117.4054	0.0491	0.4741	4.7656	0.1921
233.70	0.8644	1.0258	1.7670	179.0534	0.0255	0.5693	5.1877	0.1491
253.70	0.9415	1.0047	2.0646	345.9551	0.0047	0.7249	5.8463	0.0662
260.60	0.9750	1.0008	2.2320	475.6299	0.0008	0.8029	6.1646	0.0222

TABLE 4.10 (continued)

T = 118.32 K

P	X1	GA1	GA2	GA3	LN GA1	LN GA2	LN GA3	Q123
50.75	0.0559	2.0772	1.0003	4.3735	0.7310	0.0003	1.4756	0.0875
89.60	0.1501	1.8423	1.0051	5.7728	0.6110	0.0051	1.7531	0.1453
127.10	0.2509	1.6561	1.0219	7.7363	0.5045	0.0217	2.0459	0.2044
155.90	0.3559	1.4367	1.0715	12.7322	0.3623	0.0691	2.5441	0.2115
175.80	0.4403	1.3200	1.1250	18.5379	0.2777	0.1178	2.9198	0.2207
191.50	0.4954	1.2489	1.1761	24.9434	0.2222	0.1622	3.2166	0.2124
214.40	0.5946	1.1583	1.2806	41.1042	0.1470	0.2473	3.7161	0.2040
48.80	0.0207	6.5436	1.3972	1.1826	1.8785	0.3345	0.1677	0.2813
78.80	0.0399	6.3956	1.3834	1.1948	1.8556	0.3245	0.1780	0.3109
142.00	0.0820	5.9807	1.3440	1.2347	1.7885	0.2957	0.2109	0.3756
178.60	0.1221	5.5010	1.2977	1.2933	1.7049	0.2606	0.2572	0.4353
106.80	0.0970	3.6389	1.1112	1.8121	1.2917	0.1054	0.5945	0.3559
150.50	0.1683	3.2417	1.0764	2.0572	1.1761	0.0736	0.7214	0.4305
169.70	0.2258	2.9354	1.0516	2.3316	1.0768	0.0503	0.8466	0.4824
193.80	0.2843	2.5960	1.0274	2.7901	0.9540	0.0270	1.0261	0.5192
200.70	0.3033	2.4716	1.0199	3.0239	0.9049	0.0197	1.1065	0.5246
59.00	0.0227	9.0598	1.6393	1.0554	2.2038	0.4943	0.0539	0.2272
102.20	0.0470	8.6301	1.6001	1.0683	2.1553	0.4701	0.0661	0.2739
123.70	0.0601	8.4365	1.5824	1.0750	2.1326	0.4590	0.0723	0.2979
24.55	0.0071	13.1060	2.0026	1.0021	2.5731	0.6945	0.0021	0.0638
64.30	0.0199	12.7572	1.9731	1.0035	2.5461	0.6796	0.0035	0.0947
105.30	0.0324	12.4208	1.9444	1.0052	2.5194	0.6650	0.0052	0.1248
140.75	0.0443	12.1004	1.9169	1.0072	2.4932	0.6507	0.0072	0.1533

TABLE 4.10 (continued)

T = 122.24 K

P	X1	GA1	GA2	GA3	LN GA1	LN GA2	LN GA3	Q123
30.60	0.0080	13.1228	2.0859	1.0016	2.5744	0.7352	0.0016	0.0590
64.80	0.0190	12.8660	2.0625	1.0025	2.5546	0.7239	0.0025	0.0839
67.30	0.0203	9.2334	1.7125	1.0481	2.2228	0.5380	0.0469	0.2201
108.60	0.0360	9.0962	1.6994	1.0515	2.2079	0.5303	0.0502	0.2461
145.20	0.0500	8.8665	1.6770	1.0579	2.1823	0.5170	0.0563	0.2727
186.80	0.0767	8.3304	1.6238	1.0755	2.1199	0.4848	0.0728	0.3256
48.30	0.0156	6.2424	1.4043	1.2036	1.8314	0.3396	0.1853	0.2862
88.75	0.0378	6.1838	1.3989	1.2087	1.8219	0.3357	0.1895	0.3180
173.80	0.0823	5.9510	1.3755	1.2317	1.7836	0.3188	0.2084	0.3831
240.30	0.1443	5.1948	1.2962	1.3325	1.6477	0.2595	0.2870	0.4729
51.80	0.0215	4.0558	1.1702	1.6206	1.4001	0.1572	0.4828	0.2807
79.40	0.0450	3.9854	1.1637	1.6438	1.3836	0.1516	0.4970	0.3114
199.20	0.1699	3.3416	1.0995	1.9674	1.2065	0.0949	0.6767	0.4514
83.80	0.0846	2.2814	1.0094	3.5248	0.8248	0.0093	1.2598	0.1945
137.30	0.1853	1.9972	1.0012	4.6322	0.6918	0.0012	1.5330	0.2599
185.10	0.3532	1.4928	1.0443	10.8489	0.4006	0.0433	2.3841	0.2553
255.10	0.5875	1.1717	1.2383	38.0513	0.1584	0.2138	3.6389	0.2177
327.40	0.8468	1.0241	1.7026	192.4386	0.0239	0.5321	5.2598	0.1121

TABLE 4.11

Liquid activity coefficients for the ternary system nitrogen(1)-methane(2)-propane(3) evalued from vapor-liquid-liquid equilibrium data. The nitrogen-rich liquid phase is considered in equilibrium with the vapor phase.

T = 114.05 K

P	X1	GA1	GA2	GA3	LN GA1	LN GA2	LN GA3	Q123
254.40	0.9854	1.0005	2.2658	504.5979	0.0005	0.8179	6.2238	0.0178
245.90	0.9588	1.0022	2.1515	409.7139	0.0022	0.7661	6.0155	0.0421
238.95	0.9404	1.0045	2.0711	350.6543	0.0045	0.7281	5.8598	0.0616
230.00	0.9022	1.0135	1.9001	244.5254	0.0134	0.6419	5.4993	0.1113
219.85	0.8651	1.0241	1.7817	185.8155	0.0238	0.5775	5.2248	0.1406
207.00	0.7958	1.0560	1.5791	108.4595	0.0545	0.4568	4.6864	0.2010
195.26	0.7290	1.1023	1.4207	65.5257	0.0974	0.3512	4.1824	0.2545
167.70	0.5254	1.3569	1.1215	16.8326	0.3052	0.1147	2.8233	0.3651
165.40	0.4877	1.4411	1.0843	12.9822	0.3654	0.0809	2.5636	0.3866
160.20	0.4015	1.7651	1.0194	6.5855	0.5682	0.0192	1.8849	0.4572
183.50	0.6523	1.1744	1.2820	38.4095	0.1608	0.2484	3.6483	0.3032

TABLE 4.11 (continued)

T = 118.32 K

P	X1	GA1	GA2	GA3	LN GA1	LN GA2	LN GA3	Q123
309.00	0.9555	1.0026	2.0828	394.6741	0.0026	0.7337	5.9781	0.0449
283.23	C.8804	1.0168	1.8131	218.2011	J.J166	J.595J	5.3854	J.1J83
269.30	C.8396	1.0296	1.6939	161.4224	0.C292	0.5270	5.0840	0.1383
257.70	0.7915	1.0518	1.5623	111.2767	C.0505	0.4462	4.7120	0.1778
257.70	C.7924	1.0515	1.5640	111.8317	0.0502	0.4472	4.7170	0.1775
244.30	0.7370	1.0881	1.4285	72.0858	0.0845	0.3566	4.2779	0.2258
228.50	C.6481	1.1682	1.2665	38.1404	J.1555	J.2362	3.6413	J.2861
216.53	C.5836	1.2568	1.1704	23.7064	0.2286	0.1574	3.1657	0.3331
206.50	0.4793	1.4718	1.0620	11.3510	C.3865	0.0601	2.4293	0.3997
204.50	C.4667	1.5242	1.0482	9.9624	0.4214	0.0471	2.2988	0.4189

T = 122.24 K

386.50	0.9776	1.0009	2.1334	522.5496	0.0009	0.7577	6.2587	0.0251
346.85	C.8954	1.0122	1.8342	269.5752	J.J122	J.6J66	5.5968	J.J857
330.00	0.8467	1.0240	1.7041	193.2765	0.0237	0.5331	5.2641	0.1111
296.85	0.7418	1.J719	1.4494	88.9187	J.J695	0.3712	4.4877	0.1824
260.80	0.5837	1.2403	1.1654	25.8163	0.2153	0.1530	3.2510	0.3126
250.20	0.4891	1.4204	1.0664	13.0856	0.3509	0.0643	2.5715	0.3765

TABLE 4.12

Liquid activity coefficients for the ternary system nitrogen(1)-methane(2)-propane(3) evaluated from vapor-liquid-liquid equilibrium data. The propane-rich liquid phase is considered in equilibrium with the vapor.

T = 114.05 K

P	X1	GA1	GA2	GA3	LN GA1	LN GA2	LN GA3	Q123
254.40	0.0977	11.6937	1.8329	1.0148	2.4590	0.6059	0.0147	0.2619
245.40	0.0935	11.4674	1.8133	1.0173	2.4395	0.5951	0.0171	0.2639
238.95	0.1003	10.8522	1.7611	1.0253	2.3844	0.5659	0.0250	0.2944
230.00	0.0983	10.4427	1.7254	1.0320	2.3459	0.5455	0.0315	0.3050
219.85	0.1075	9.5394	1.6469	1.0512	2.2554	0.4989	0.0499	0.3462
207.00	0.1150	8.5899	1.5624	1.0803	2.1506	0.4463	0.0773	0.3832
195.26	0.1250	7.5371	1.4669	1.1286	2.0198	0.3832	0.1210	0.4218
183.50	0.1361	6.6287	1.3828	1.1916	1.8914	0.3241	0.1753	0.4527
178.25	0.1491	5.9449	1.3189	1.2598	1.7825	0.2768	0.2310	0.4774
167.70	0.1694	4.8466	1.2149	1.4371	1.5783	0.1947	0.3626	0.5016
165.40	0.1755	4.5145	1.1835	1.5186	1.5073	0.1685	0.4178	0.5037

TABLE 4.12 (continued)

T = 118.32

P	X1	GA1	GA2	GA3	LN GA1	LN GA2	LN GA3	Q123
309.00	0.0907	10.9915	1.8207	1.0176	2.3971	0.5992	0.0174	0.2584
283.23	0.1127	9.2273	1.6598	1.0500	2.2222	0.5067	0.0488	0.3490
269.30	0.1170	8.4935	1.5908	1.0723	2.1393	0.4643	0.0698	0.3769
257.70	0.1281	7.6912	1.5144	1.1058	2.0401	0.4150	0.1006	0.4136
257.70	0.1280	7.6952	1.5148	1.1056	2.0406	0.4153	0.1004	0.4134
244.30	0.1351	6.9905	1.4465	1.1462	1.9446	0.3691	0.1364	0.4384
228.50	0.1545	5.7983	1.3289	1.2536	1.7576	0.2844	0.2260	0.4812
216.53	0.1746	4.8881	1.2380	1.3955	1.5868	0.2135	0.3332	0.5077
206.50	0.2176	3.7306	1.1240	1.7554	1.3166	0.1169	0.5627	0.5348
204.50	0.2341	3.4697	1.0996	1.8944	1.2441	0.0950	0.6389	0.5425

T = 122.24 K

386.50	0.0953	11.0736	1.8962	1.0153	2.4046	0.6399	0.0152	0.2570
346.85	0.1036	9.6473	1.7572	1.0379	2.2667	0.5637	0.0372	0.3205
330.00	0.1146	8.7471	1.6676	1.0611	2.1687	0.5114	0.0593	0.3654
296.85	0.1444	6.9127	1.4797	1.1470	1.9334	0.3918	0.1371	0.4552
260.80	0.2051	4.4724	1.2199	1.4821	1.4979	0.1987	0 3934	0.5503
250.20	0.2451	3.5035	1.1179	1.8605	1.2538	0.1114	0.6209	0.5676
245.12	0.2829	2.8853	1.0582	2.3631	1.0596	0.0566	0.8600	0.5652

TABLE 4.13

Summary of correlation results of γ values for the system nitrogen (1)-methane (2)-propane (3)

Temperature (K)	C_{123}	D_3	D_1	D_2	Av. Abs. % dev. of Q_{123}
	–				9.7%
	2.9448				8.3%
114.05	4.0356	5.6942			7.7%
	4.2459	7.3324	3.9421		4.3%
	4.2459	-5.5248	-8.9151	-12.8571	4.3%
	–				11.0%
	2.8912				5.4%
	4.0440	5.9450			5.2%
118.32	4.1322	7.3565	3.7107		2.0%
	4.1322	66.0236	62.3774	58.6667	2.0%
	–				13.0%
	2.7080				4.8%
122.24	3.2047	2.5760			4.9%
	3.7845	5.8471	3.6925		1.9%
	3.7841	-88.1546	-90.3078	-94.0	1.9%

TABLE 4.14

Comparison of liquid activity coefficients evaluated from gas fugacity coefficient to those evaluated from Equation (4.8), for the system nitrogen(1)-methane(2)-propane(3).
(GA1 refers to activity coefficient of component 1 evaluated from Eq. (4.8), and
GE1 refers to activity coefficient of component 1 evaluated from gas fugacity coeff.)
T=114.05 K

X1	GA1	GE1	% DG1	GA2	GE2	% DG2	GA3	GE3	% DG3
0.0245	13.9571	14.5095	-3.9577	2.0146	2.5033	-24.2602	1.0012	1.2506	-24.9013
0.0446	13.3034	13.2612	0.3173	1.9629	3.4783	-77.2045	1.0035	1.3866	-38.1838
0.0637	12.7399	12.8458	-0.8310	1.9179	3.5186	-83.4611	1.0063	1.7596	-74.8579
0.0388	9.3257	9.5849	-2.7794	1.6226	1.5642	3.5999	1.0578	1.0796	-2.0615
0.0620	8.7590	8.8216	-0.7144	1.5738	1.4477	8.0102	1.0751	1.2286	-14.2832
0.0562	4.4925	4.7047	-4.7227	1.1752	1.1697	0.4701	1.5362	0.0010	99.9329
0.0989	4.1769	4.3199	-3.4243	1.1477	1.1084	3.4182	1.6318	0.0015	99.9089
0.1797	3.3164	2.9574	10.8245	1.0737	0.9179	14.5142	2.0690	0.0021	99.9003
0.0503	2.6861	2.8435	-5.8568	1.0215	1.0400	-1.8197	2.8301	0.0021	99.9264
0.0525	2.4610	2.5525	-3.7171	1.0093	1.0171	-0.7788	3.2888	2.3645	28.1059
0.1270	2.3732	2.4333	-2.5315	1.0072	1.0435	-3.6017	3.4679	0.0037	99.8925
0.2999	1.8167	1.8187	-0.1099	1.0126	1.0418	-2.8858	6.1752	0.0070	99.8863
0.4184	1.5524	1.5548	-0.1579	1.0509	1.0625	-1.1027	9.8771	0.0092	99.9072
0.5072	1.3795	1.3919	-0.8998	1.1100	1.0929	1.5321	15.6387	0.0121	99.9229
0.6106	1.2095	1.2243	-1.2248	1.2367	1.2494	-1.0267	31.4872	0.0210	99.9332
0.8059	1.0503	1.0712	-1.9898	1.6066	1.6546	-2.9861	117.4054	0.0513	99.9563
0.8644	1.0258	1.0459	-1.9593	1.7670	1.7778	-0.6157	179.0534	0.0671	99.9625
0.9415	1.0047	1.0176	-1.2798	2.0646	2.5264	-22.3654	345.9551	0.1881	99.9456
0.9750	1.0008	1.0075	-0.6643	2.2320	2.3009	-3.0867	475.6299	2.8091	99.4093

TABLE 4.14 (continued)

T = 118.32 K

X1	GA1	GE1	% DG1	GA2	GE2	% DG2	GA3	GE3	% DG3
0.0559	2.0772	2.0446	1.5675	1.0003	1.0002	0.0112	4.3735	5.9499	-36.0448
0.1501	1.8423	1.8078	1.8686	1.0051	0.9645	4.0376	5.7728	5.3626	7.1051
0.2509	1.6561	1.6143	2.5260	1.0219	0.9867	3.4414	7.7363	6.4331	16.8454
0.3559	1.4367	1.4008	2.4998	1.0715	1.0266	4.1947	12.7322	14.5077	-13.9454
0.4403	1.3200	1.2803	3.0074	1.1250	1.0217	9.1878	18.5379	20.5539	-10.8751
0.4954	1.2489	1.2186	2.4268	1.1761	1.1294	3.9760	24.9434	37.0914	-48.7021
0.5946	1.1583	1.1268	2.7180	1.2806	1.1728	8.4134	41.1042	27.7313	32.5342
0.0207	6.5436	6.5124	0.4762	1.3972	1.4045	-0.5268	1.1826	0.6137	48.1068
0.0399	6.3956	6.3416	0.8443	1.3834	1.3664	1.2296	1.1948	0.9264	22.4655
0.0820	5.9807	5.7555	3.7653	1.3440	1.2687	5.6029	1.2347	1.0450	15.3635
0.1221	5.5010	4.7369	13.8902	1.2977	1.2675	2.3273	1.2933	1.2394	4.1697
0.0970	3.6389	3.5458	2.5592	1.1112	1.0743	3.3196	1.8121	1.2458	31.2532
0.1683	3.2417	2.9324	9.5423	1.0764	0.9874	8.2661	2.0572	1.2339	40.0214
0.2258	2.9354	2.4498	16.5407	1.0516	0.9829	6.5257	2.3316	1.3931	40.2533
0.2843	2.5960	2.1854	15.8157	1.0274	0.9634	6.2237	2.7901	1.0922	60.8550
0.3033	2.4716	2.0833	15.7096	1.0199	1.0803	-5.9209	3.0239	1.1651	61.4698
0.0227	9.0598	8.7893	2.9851	1.6393	1.5275	6.8178	1.0554	1.1347	-7.5093
0.0470	8.6301	7.6297	11.5917	1.6001	1.5039	6.0139	1.0683	11.5857	-984.4590
0.0601	8.4365	7.2343	14.2499	1.5824	1.3835	12.5744	1.0750	14.8492	-1281.3787
0.0071	13.1060	13.2539	-1.1287	2.0026	1.9413	3.0625	1.0021	0.2013	79.9101
0.0199	12.7572	12.8042	-0.3677	1.9731	1.9856	-0.6345	1.0035	0.6113	39.0834
0.0324	12.4208	12.4200	0.0067	1.9444	2.0655	-6.2274	1.0052	0.9216	8.3146
0.0443	12.1004	11.7379	2.9956	1.9169	1.6431	14.2835	1.0072	0.9141	9.2440

TABLE 4.14 (continued)

T = 122.24 K

X1	GA1	GE1	% DG1	GA2	GE2	% DG2	GA3	GE3	% DG3
0.0080	13.1228	12.6637	3.4984	2.0859	1.9555	6.2514	1.0016	1.1044	-10.2600
0.0190	12.8660	11.6280	9.6221	2.0625	1.7610	14.6181	1.0025	1.5870	-58.3094
0.0203	9.2334	9.0927	1.5242	1.7125	1.6609	3.0126	1.0481	0.4167	60.2401
0.0360	9.0962	8.7579	3.7188	1.6994	1.6253	4.3649	1.0515	0.3694	64.8711
0.0500	8.8665	8.3961	5.3053	1.6770	1.5452	7.8548	1.0579	1.3756	-30.0271
0.0767	8.3304	6.8758	17.4616	1.6238	1.4076	13.3166	1.0755	0.9190	14.5555
0.0156	6.2424	6.0560	2.9859	1.4043	1.3418	4.4521	1.2036	1.0832	10.0070
0.0378	6.1838	6.1044	1.2851	1.3989	1.3172	5.8393	1.2087	0.0009	99.9259
0.0823	5.9510	5.7146	3.9726	1.3755	1.2733	7.4356	1.2317	1.2018	2.4274
0.1443	5.1948	4.2249	18.6708	1.2962	1.3574	-4.7230	1.3325	1.4973	-12.3704
0.0215	4.0558	4.1167	-1.5019	1.1702	1.1703	-0.0077	1.6206	0.0010	99.9406
0.0450	3.9894	4.0423	-1.3261	1.1637	1.1613	0.2076	1.6438	0.0014	99.9166
0.1699	3.3416	3.0783	7.8789	1.0995	1.0185	7.3693	1.9674	0.0027	99.8609
0.0846	2.2814	2.2436	1.6550	1.0094	0.9757	3.3374	3.5248	0.7893	77.6067
0.1853	1.9972	1.9162	4.0594	1.0012	0.9609	4.0217	4.6322	1.2510	72.9941
0.3532	1.4928	1.3802	7.5443	1.0443	0.9583	8.2297	10.8489	3.5018	67.7218
0.5875	1.1717	1.0987	6.2305	1.2383	1.1227	9.3330	38.0513	1309.4468	-3341.2703
0.8468	1.0241	0.8902	13.0759	1.7026	1.5365	9.7522	192.4386	0.3794	99.8029

TABLE 4.14 (continued)

(top liquid phase is considered in equilibrium with the vapor phase)

T =114.05 K

X1	GA1	GE1	% DG1	GA2	GE2	% DG2	GA3	GE3	% DG3
0.9854	1.0005	0.9848	1.5726	2.2658	4.2116	-85.8761	504.5979	1659.5503	-228.8855
0.9588	1.0022	0.9900	1.2184	2.1515	2.1112	1.8707	409.7139	975.2676	-138.0362
0.9404	1.0045	0.9872	1.7228	2.0711	2.2117	-6.7920	350.6543	574.2476	-63.7645
0.9022	1.0135	1.0006	1.2755	1.9001	1.8052	4.9955	244.5254	177.3857	27.4571
0.8651	1.0241	1.0056	1.8133	1.7817	1.7861	-0.2516	185.8155	106.5762	42.6441
0.7958	1.0560	1.0423	1.2971	1.5791	1.4746	6.6191	108.4595	70.6058	34.9012
0.7290	1.1023	1.0842	1.6463	1.4207	1.3354	6.0070	65.5257	40.7358	37.8323
0.5254	1.3569	1.3213	2.6247	1.1215	1.0279	8.3440	16.8326	7.9630	52.6929
0.4877	1.4411	1.4076	2.3211	1.0843	0.9720	10.3577	12.9822	6.5298	49.7022
0.4015	1.7651	1.6613	5.8780	1.0194	0.9391	7.8802	6.5855	1.8587	71.7752
0.6523	1.1744	1.1493	2.1438	1.2820	1.2096	5.6499	38.4095	24.4053	36.4603

TABLE 4.14 (continued)

T = 118.32 K

0.9555	1.0026	0.8986	10.3779	2.0828	2.0634	0.9281	394.6741	1019.6951	-158.3637
0.8804	1.0168	0.9540	6.1692	1.8131	1.6418	9.4484	218.2011	330.5015	-51.4666
0.8396	1.0296	0.9659	6.1884	1.6939	1.5284	9.7736	161.4224	207.1418	-28.3228
0.7915	1.0518	0.9909	5.7946	1.5623	1.4141	9.4838	111.2767	101.7506	8.5608
0.7924	1.0515	0.9899	5.8600	1.5640	1.4195	9.2362	111.8317	101.6751	9.0821
0.7370	1.0881	1.0201	6.2539	1.4285	1.3506	5.4506	72.0858	52.3911	27.3213
0.6481	1.1682	1.1018	5.6905	1.2665	1.1534	8.9232	38.1404	17.5858	53.8920
0.5836	1.2568	1.1706	6.8590	1.1704	1.0927	6.6439	23.7064	8.7416	63.1254
0.4793	1.4718	1.3701	6.9122	1.0620	0.9745	8.2330	11.3510	4.9614	56.2913
0.4667	1.5242	1.3963	8.3915	1.0482	0.9755	6.9332	9.9624	47.4492	-376.2832

T = 122.24 K

X1	GA1	GE1	% DG1	GA2	GE2	% DG2	GA3	GE3	% DG3
0.9776	1.0009	0.7947	20.6037	2.1334	2.6156	-22.6058	522.5496	1771.0269	-238.9201
0.8954	1.0122	0.8498	16.0473	1.8342	1.6456	10.2831	269.5752	732.2029	-171.6135
0.8467	1.0240	0.8955	12.5453	1.7041	1.3889	18.4987	193.2765	706.4307	-265.5022
0.7418	1.0719	0.9861	8.0076	1.4494	1.2125	16.3473	88.9187	101.4789	-14.1254
0.5837	1.2403	1.1345	8.5269	1.1654	1.0650	8.6097	25.8163	7.3040	71.7077
0.4891	1.4204	1.3094	7.8116	1.0664	0.9645	9.5569	13.0856	2.1011	83.9435

TABLE 4.14 (continued)

(Bottom liquid phase is considered in equilibrium with the vapor phase)

T = 114.05 K

X1	GA1	GE1	% DG1	GA2	GE2	% DG2	GA3	GE3	% DG3
0.0977	11.6937	9.9364	15.0278	1.8329	3.9554	-115.8029	1.0148	1.8692	-84.1989
0.0935	11.4674	10.1410	11.5665	1.8133	2.3784	-31.1646	1.0173	1.7918	-76.1445
0.1003	10.8522	9.2595	14.6762	1.7611	2.0712	-17.6074	1.0253	1.8685	-82.2373
0.0983	10.4427	9.1805	12.0865	1.7254	1.8217	-5.5808	1.0320	1.6380	-58.7230
0.1075	9.5394	8.0894	15.1999	1.6469	1.7083	-3.7267	1.0512	1.7414	-65.6606
0.1150	8.5899	7.2129	16.0305	1.5624	1.5231	2.5206	1.0803	1.5288	-41.5139
0.1250	7.5371	6.3214	16.1288	1.4669	1.3684	6.7124	1.1286	1.4828	-31.3807
0.1361	6.6287	5.5063	16.9324	1.3828	1.2946	6.3840	1.1916	1.4109	-18.4069
0.1491	5.9449	4.9092	17.4210	1.3189	1.1987	9.1133	1.2598	1.3074	-3.7777
0.1694	4.8466	4.0993	15.4196	1.2149	1.0812	11.0036	1.4371	1.0224	28.8554
0.1755	4.5145	3.9128	13.3283	1.1835	1.0246	13.4272	1.5136	1.0909	28.1611

TABLE 4.14 (continued)

T = 118.32 K

0.0907	10.9915	9.4698	13.8440	1.8207	2.0305	-11.5255	1.0176	2.1901	-115.2201
0.1127	9.2273	7.4545	19.2124	1.6598	1.5608	5.9634	1.0500	2.0268	-93.0279
0.1170	8.4935	6.9336	18.3654	1.5908	1.4277	10.2544	1.0723	1.8460	-72.1563
0.1281	7.6912	6.1231	20.3874	1.5144	1.3635	9.9652	1.1058	1.6027	-44.9390
0.1280	7.6952	6.1256	20.3962	1.5148	1.3644	9.9289	1.1056	1.6009	-44.7991
0.1351	6.9905	5.5661	20.3769	1.4465	1.3344	7.7495	1.1462	1.5120	-31.9110
0.1545	5.7983	4.6214	20.2969	1.3289	1.1709	11.8897	1.2536	0.9985	20.3542
0.1746	4.8881	3.9133	19.9418	1.2380	1.0950	11.5511	1.3955	0.8579	38.5198
0.2176	3.7306	3.0180	19.1015	1.1240	1.0034	10.7282	1.7554	1.0900	37.9040
0.2341	3.4697	2.7830	19.7907	1.0996	0.9933	9.6705	1.8944	1.1663	38.4331

T = 122.24 K

X1	GA1	GE1	% DG1	GA2	GE2	% DG2	GA3	GE3	% DG3
0.0953	11.0736	8.1532	26.3726	1.8962	2.3741	-25.2020	1.0153	7.0944	-598.7522
0.1036	9.6473	7.3410	23.9060	1.7572	1.6958	3.4955	1.0379	2.0854	-100.9310
0.1146	8.7471	6.6142	24.3841	1.6676	1.4782	11.3589	1.0611	1.8726	-76.4794
0.1444	6.9127	5.0648	26.7322	1.4797	1.3142	11.1861	1.1470	1.3829	-20.5709
0.2051	4.4724	3.2289	27.8041	1.2199	1.1209	8.1136	1.4821	0.6646	55.1541
0.2451	3.5035	2.6128	25.4242	1.1179	1.0430	6.6971	1.8605	0.4168	77.5958
0.2829	2.8853	2.2269	22.8197	1.0582	0.9979	5.7013	2.3631	0.5126	78.3099

TABLE 4.15

Correlation of the liquid-liquid equilibrium data with the method of Black and Hartwig for the system nitrogen (s) - methane (i) - propane(r) at 114.05 K

P (psia)	x_s	y_s	K_s	K_i	K_r	K_H	y'_i	x'_i
254.4	0.9754	0.0977	0.1001	1.0648	887.9	36.70	–	–
245.9	0.9588	0.0935	0.0975	0.8880	544.6	21.98	0.0388	0.9612
238.9	0.9404	0.1003	0.1066	1.0679	307.3	15.09	0.0675	0.9542
230.0	0.9022	0.0983	0.1090	0.9644	161.8	9.22	0.0992	0.9487
219.9	0.8651	0.1075	0.1243	1.0456	84.0	6.62	0.1474	0.9328
207.0	0.7958	0.1150	0.1445	0.9682	46.2	4.33	0.2068	0.9256
195.3	0.7289	0.1250	0.1715	0.9758	27.5	3.23	0.2766	0.0950
183.5	0.6524	0.1362	0.2087	0.9361	15.7	2.48	0.3371	0.8949
178.3	0.6141	0.1491	0.2428	0.9568	12.7	2.20	0.3878	0.8938
167.7	0.5253	0.1693	0.3223	0.9507	7.8	1.75	0.4798	0.8831
165.4	0.4879	0.1755	0.3598	0.9486	6.0	1.61	0.5519	0.8688
160.2	0.4015							

$a = -1.7407$

$b = 0.0384$

$c = -0.4582$

p.pt : $x_s = 0.3142$, $x_i = 0.4944$, $x_r = 0.1914$

Table 4.15 (continued)

T = 118.32 K

P (psia)	x_s	y_s	K_s	K_i	K_r	K_H	y'_i	x'_i
326.4	0.9981	0.0850	0.0851	–	486.7	486.7	–	–
309.0	0.9555	0.0907	0.0949	1.0162	456.6	20.4	0.0476	0.9574
283.2	0.8804	0.1127	0.1280	1.0519	163.1	7.4	0.1363	0.0967
269.3	0.8396	0.1170	0.1393	1.0705	112.2	5.5	0.1867	0.9601
257.7	0.7924	0.1280	0.1616	1.0404	63.5	4.2	0.2352	0.9494
257.7	0.7915	0.1281	0.1618	1.0371	63.5	4.2	0.2355	0.9496
244.3	0.7371	0.1351	0.1833	1.0122	34.6	3.3	0.2869	0.9323
228.5	0.6438	0.1535	0.2384	0.9851	17.6	2.4	0.3751	0.9148
216.5	0.5836	0.1746	0.2991	1.1529	10.2	2.0	0.5282	0.9082
206.5	0.4793	0.2176	0.4540	0.9712	4.5	1.5	0.5504	0.8516
204.5	0.4668	0.2342	0.5017	0.9819	3.7	1.4	0.5715	0.8539
199.5	0.3728							
201.6		0.2934						

a = -1.9242
b = 0.0396
c = -0.5139

ppt

x_s = 0.3395
x_i = 0.4743
x_r = 0.1862

Table 4.15 (continued)

T = 122.24 K

P psia)	x_s	y_s	K_s	K_i	K_r	K_H	y'_i	x'_i
386.5	0.9776	0.0953	0.0974	1.0743	678.5	40.32	0.0251	0.9421
346.9	0.8954	0.1037	0.1158	0.9704	351.1	8.57	0.1108	0.9783
330.0	0.8467	0.1146	0.1354	0.9396	379.2	5.78	0.1606	0.9872
296.9	0.7418	0.1444	0.1947	0.9226	73.4	3.31	0.2693	0.9670
260.8	0.5837	0.2051	0.3514	0.9502	10.8	1.91	0.4494	0.9031
250.2	0.4891	0.2451	0.5012	0.9247	5.0	1.48	0.5418	0.8657
245.1								
406.0	0.9981	0.0888	0.0890		479.6	479.6		

a = -2.3293

b = 0.0633

c = -0.5679

ppt

x_s = 0.3622

x_i = 0.4695

x_r = 0.1683

TABLE 4.16

Comparison of experimental values to vapor composition predicted by the modified Redlich-Kwong equation of state for the system nitrogen(1)-methane(2)-propane(3) at 114.05 K.

P (psia)	X1	Y1 EXP	Y1 CAL	P2 EXP	Y2 CAL	Y3 EXP	Y3 CAL
70.88	0.0245	C.9886	0.9908	0.0112	0.0092	0.0002	0.0
127.20	0.0446	0.9901	0.9946	0.0098	0.0054	0.0001	0.0
193.40	0.0637	0.9932	0.9965	0.0067	0.0035	0.0001	0.0
82.80	0.0388	0.8986	0.8946	0.1013	0.1054	0.0001	0.0
124.50	0.0620	C.9314	0.9270	0.0685	0.0730	0.0001	0.0
65.80	0.0562	C.7851	0.7799	0.2149	0.2201	0.0	0.0
101.38	0.0989	0.8644	0.8592	0.1356	0.1408	0.0	0.0
124.05	0.1797	0.9074	0.9041	0.0926	0.0959	0.0	0.0
43.40	0.0503	0.6241	0.6187	0.3759	0.3813	0.0	0.0
41.80	0.0525	0.6057	0.6024	0.3942	0.3976	0.0001	0.0
77.60	0.1270	C.7902	0.7955	0.2098	0.2045	0.0	0.0
131.70	0.2999	0.8866	0.8925	0.1134	0.1075	0.0	0.0
158.30	0.4184	C.9145	0.9184	0.0855	0.0816	0.0	0.0
173.00	0.5072	0.9283	0.9299	0.0716	0.0701	0.0	0.0
185.30	0.6106	C.9353	0.9385	0.0647	0.0615	0.0	0.0
220.80	C.8059	C.9593	0.9626	0.0407	0.0373	0.0	0.0
233.70	0.8644	0.9699	0.9721	0.0301	0.0279	0.0	0.0
253.70	0.9415	C.9811	0.9860	0.0189	0.0140	0.0	0.0
260.60	0.9750	C.9922	0.9932	0.0078	0.0068	0.0	0.0

TABLE 4.16 (continued)

Comparison of experimental values to vapor composition predicted by the modified Redlich-Kwong equation of state for the system nitrogen(1)-methane(2)-propane(3) at 118.32 K.

P (psia)	X1	Y1 EXP	Y1 CAL	P2 EXP	Y2 CAL	Y3 EXP	Y3 CAL
50.75	0.0559	0.5299	0.5269	0.4700	0.4731	0.0	0.0
89.60	0.1501	0.7490	0.7401	0.2509	0.2599	0.0	0.0
127.10	0.2509	0.8279	0.8239	0.1721	0.1761	0.0	0.0
155.90	0.3559	0.8633	0.8597	0.1367	0.1403	0.0	0.0
175.80	0.4403	0.8896	0.8819	0.1104	0.1181	0.0	0.0
191.50	0.4954	0.8938	0.8922	0.1062	0.1078	0.0	0.0
214.40	0.5946	0.9156	0.9113	0.0844	0.0887	0.0	0.0
48.80	0.0207	0.6498	0.6473	0.3501	0.3527	0.0001	0.0
78.80	0.0399	0.7845	0.7805	0.2154	0.2195	0.0001	0.0
142.00	0.0820	0.8815	0.8777	0.1184	0.1223	0.0001	0.0
178.60	0.1221	0.9022	0.9099	0.0977	0.0901	0.0001	0.0
106.80	0.0970	0.8147	0.8107	0.1852	0.1893	0.0	0.0
150.50	0.1683	0.8791	0.8778	0.1209	0.1222	0.0	0.0
169.70	0.2258	0.8969	0.9032	0.1031	0.0968	0.0	0.0
193.80	0.2843	0.9122	0.9172	0.0877	0.0828	0.0	0.0
200.70	0.3033	0.9044	0.9198	0.0956	0.0802	0.0	0.0
59.00	0.0227	0.8067	0.7967	0.1931	0.2033	0.0002	0.0
102.20	0.0470	0.8836	0.8876	0.1154	0.1124	0.0010	0.0
123.70	0.0601	0.9098	0.9092	0.0892	0.0908	0.0011	0.0
24.55	0.0071	0.8782	0.8711	0.1217	0.1289	0.0001	0.0
64.30	0.0199	0.9505	0.9497	0.0494	0.0503	0.0001	0.0
105.30	0.0324	0.9671	0.9685	0.0328	0.0315	0.0001	0.0
140.75	0.0443	0.9795	0.9765	0.0204	0.0235	0.0001	0.0

TABLE 4.16 (continued)

Comparison of experimental values to vapor composition predicted by the modified Redlich-Kwong equation of state for the system nitrogen(1)-methane(2)-propane(3) at 122.24 K.

P (psia)	X1	Y1 EXP	Y1 CAL	P2 EXP	Y2 CAL	Y3 EXP	Y3 CAL
30.60	0.0080	0.8948	0.8922	0.1048	0.1078	0.0004	0.0
64.80	0.0190	0.9564	0.9539	0.0434	0.0461	0.0003	0.0
67.30	0.0203	0.7711	0.7682	0.2288	0.2318	0.0001	0.0
108.60	0.0360	0.8591	0.8579	0.1409	0.1421	0.0	0.0
145.20	0.0500	0.8951	0.8922	0.1048	0.1078	0.0001	0.0
186.80	0.0767	0.9207	0.9216	0.0793	0.0784	0.0001	0.0
48.30	0.0156	0.5374	0.5330	0.4625	0.4670	0.0001	0.0
88.75	0.0378	0.7492	0.7397	0.2508	0.2603	0.0	0.0
173.80	0.0823	0.8680	0.8639	0.1319	0.1361	0.0001	0.0
240.30	0.1443	0.8875	0.9072	0.1124	0.0928	0.0001	0.0
51.80	0.0215	0.4699	0.4657	0.5301	0.5343	0.0	0.0
79.40	0.0450	0.6528	0.6491	0.3472	0.3509	0.0	0.0
199.20	0.1699	0.8696	0.8696	0.1304	0.1304	0.0	0.0
83.80	0.0846	0.6484	0.6422	0.3516	0.3578	0.0	0.0
137.30	0.1853	0.7908	0.7893	0.2092	0.2107	0.0	0.0
185.10	0.3532	0.8561	0.8530	0.1438	0.1470	0.0	0.0
255.10	0.5875	0.9023	0.9004	0.0967	0.0996	0.0010	0.0
327.40	0.8468	0.9497	0.9518	0.0503	0.0482	0.0	0.0

TABLE 4.17

Comparison of experimental values to vapor composition predicted by the modified Redlich-Kwong equation of state for top liquid phase in equilibrium with vapor phase for the system nitrogen(1)-methane(2)-propane(3).

T = 114.05 K

P	X1	Y1 EXP	Y1 CAL	P2 EXP	Y2 CAL	Y3 EXP	Y3 CAL
254.40	C.9854	C.9921	0.9962	0.0078	0.0038	0.0001	0.0
245.90	C.9588	C.9886	0.9895	0.0113	0.0105	0.0001	0.0
238.95	C.9404	C.9829	0.9854	0.0169	0.0146	0.0001	0.0
230.00	0.9022	0.9779	0.9786	0.0220	0.0214	0.0001	0.0
219.85	0.8651	0.9693	0.9716	0.0306	0.0284	0.0001	0.0
207.00	0.7958	0.9613	0.9613	0.0386	0.0387	0.0001	0.0
195.26	0.7290	0.9530	0.9532	0.0469	0.0467	0.0001	0.0
167.70	0.5254	C.9345	0.9330	0.0655	0.0670	0.0	0.0
165.40	0.4877	0.9337	0.9305	0.0662	0.0695	0.0	0.0
160.20	0.4015	0.9295	0.9296	0.0705	0.0704	0.0	0.0
183.50	0.6523	0.9446	0.9450	0.0554	0.0550	0.0001	0.0

TABLE 4.17 (continued)

T = 118.32 K

P	X1	Y1 EXP	Y1 CAL	P2 EXP	Y2 CAL	Y3 EXP	Y3 CAL
309.00	C.9555	C.9845	0.9865	0.0154	0.0135	0.0002	0.0
283.23	0.8804	0.9670	0.9679	0.0329	0.0321	0.0001	0.0
269.30	0.8396	0.9596	0.9594	0.0403	0.0406	0.0001	0.0
257.70	0.7915	0.9520	0.9513	0.0479	0.0487	0.0001	0.0
257.70	0.7924	0.9520	0.9515	0.0479	0.0485	0.0001	0.0
244.30	C.7370	C.9429	0.9441	0.0570	0.0559	0.0001	0.0
228.50	C.6481	C.9349	0.9332	0.0650	0.0668	0.0	0.0
216.53	0.5836	C.9275	0.9276	0.0724	0.0724	0.0	0.0
206.50	0.4793	0.9214	0.9200	0.0785	0.0800	0.0	0.0
204.50	0.4667	C.9203	0.9210	0.0793	0.0790	0.0003	0.0

T = 122.24 K

P	X1	Y1 EXP	Y1 CAL	P2 EXP	Y2 CAL	Y3 EXP	Y3 CAL
386.50	0.9776	0.9880	0.9777	0.0118	0.0210	0.0002	0.0013
346.85	0.8954	C.9638	0.9648	0.0361	0.0352	0.0001	0.0
330.00	0.8467	0.9545	0.9516	0.0454	0.0484	0.0001	0.0
296.85	0.7418	C.9356	0.9313	0.0643	0.0687	0.0001	0.0
260.80	C.5837	C.9147	0.9145	0.0853	0.0854	0.0	0.0
250.20	0.4891	0.9083	0.9068	0.0917	0.0932	0.0	0.0

TABLE 4.18

Comparison of experimental values to vapor compositions predicted by the modified Redlich-Kwong equation of state for bottom liquid phase in equilibrium with vapor phase for the system nitrogen(1)-methane(2)-propane(3).

T = 114.05 K

P	X1	Y1 EXP	Y1 CAL	P2 EXP	Y2 CAL	Y3 EXP	Y3 CAL
254.40	0.0977	0.9921	0.9832	0.0078	0.0129	0.0001	0.0039
245.40	C.C935	C.9886	0.9923	0.0113	0.0077	0.0001	0.0
238.95	0.1003	0.9829	0.9868	0.0169	0.0132	0.0001	0.0
230.00	0.0983	0.9779	0.9813	0.0220	0.0187	0.0001	0.0
219.85	C.1C75	C.9693	0.9736	0.0306	0.0264	0.0001	0.0
207.00	0.1150	C.9613	0.9650	0.0386	0.0350	0.0001	0.0
195.26	0.1250	C.9530	0.9560	0.0469	0.0440	0.0001	0.0
183.50	0.1361	0.9446	0.9489	0.0554	0.0511	0.0001	0.0
178.25	0.1491	0.9416	0.9449	0.0583	0.0551	0.0001	0.0
167.70	C.1694	C.9345	0.9364	0.0655	0.0636	0.0	0.0
165.40	0.1755	C.9337	0.9331	0.0662	0.0669	0.0	0.0

TABLE 4.18 (continued)

T = 118.32 K

P	X1	Y1 EXP	Y1 CAL	P2 EXP	Y2 CAL	Y3 EXP	Y3 CAL
309.00	0.0907	0.9845	0.9881	0.0154	0.0119	0.0002	0.0
283.23	0.1127	0.9670	0.8729	0.0329	0.1194	0.0001	0.0077
269.30	0.1170	0.9596	0.9586	0.0403	0.0414	0.0001	0.0
257.70	0.1281	0.9520	0.9504	0.0479	0.0496	0.0001	0.0
257.70	0.1280	0.9520	0.9505	0.0479	0.0495	0.0001	0.0
244.30	0.1351	0.9429	0.9444	0.0570	0.0556	0.0001	0.0
228.50	0.1545	0.9349	0.9349	0.0650	0.0651	0.0	0.0
216.53	0.1746	0.9275	0.9284	0.0724	0.0716	0.0	0.0
206.50	0.2176	0.9214	0.9234	0.0785	0.0766	0.0	0.0
204.50	0.2341	0.9206	0.9239	0.0793	0.0761	0.0	0.0

T = 122.24 K

P	X1	Y1 EXP	Y1 CAL	P2 EXP	Y2 CAL	Y3 EXP	Y3 CAL
386.50	0.0953	0.9830	0.9757	0.0115	0.0213	0.0005	0.0030
346.85	0.1036	0.9638	0.8955	0.0361	0.0992	0.0001	0.0053
330.00	0.1146	0.9545	0.8444	0.0454	0.1470	0.0001	0.0086
296.85	0.1444	0.9356	0.7357	0.0643	0.2443	0.0001	0.0200
260.80	0.2051	0.9147	0.5709	0.0853	0.3745	0.0	0.0546
250.20	0.2451	0.9083	0.9141	0.0917	0.0859	0.0	0.0
245.12	0.2829	0.9057	0.9141	0.0943	0.0859	0.0	0.0

TABLE 4.19

Comparison of experimental values to predicted pressures and vapor compositions by the modified Redlich-Kwong equation of state for vapor-liquid equilibrium, for the system nitrogen(1)-methane(2)-propane(3) at 114.05, 118.32, and 122.24 K.

T = 114.05 K

X1	DY1	DY2	DY3	P EXP (psia)	P CAL (psia)	% DP
0.0245	0.0022	-0.0020	-0.0002	70.88	70.13	-1.06
0.0446	0.0045	-0.0044	-0.0001	127.20	130.36	2.48
0.0637	0.0033	-0.0032	-0.0001	193.40	192.53	-0.45
0.0388	-0.0040	0.0041	-0.0001	82.80	83.09	0.35
0.0620	-0.0044	0.0045	-0.0001	124.50	127.05	2.05
0.0562	-0.0052	0.0052	0.0	65.80	64.62	-1.79
0.0989	-0.0052	0.0052	0.0	101.38	100.37	-1.00
0.1797	-0.0032	0.0032	0.0	124.05	145.93	17.64
0.0503	-0.0054	0.0054	0.0	43.40	42.13	-2.92
0.0525	-0.0034	0.0034	0.0	41.80	41.30	-1.21
0.1270	0.0053	-0.0053	0.0	77.60	76.45	-1.48
0.2999	0.0059	-0.0059	0.0	131.70	132.80	0.84
0.4184	0.0039	-0.0039	0.0	158.30	159.65	0.85
0.5072	0.0016	-0.0016	0.0	173.00	173.05	0.03
0.6106	0.0032	-0.0032	0.0	185.30	183.60	-0.92
0.8059	0.0034	-0.0034	0.0	220.80	213.76	-3.19
0.8644	0.0022	-0.0022	0.0	233.70	225.32	-3.58
0.9415	0.0049	-0.0049	0.0	253.70	243.09	-4.18
0.9750	0.0011	-0.0011	0.0	260.60	252.39	-3.15

AVE. ABS. % DEV. IN PRESSURE %DP = 2.59 (%)

AVE. ABS. DEV. IN VAPOR COMP. = 0.0025 (MOLE FRACTION)

TABLE 4.19 (continued)

T = 118.32 K

X1	DY1	DY2	DY3	P EXP (psia)	P CAL (psia)	% DP
0.0559	-0.0030	0.0031	0.0	50.75	50.30	-0.88
0.1501	-0.0089	0.0090	0.0	89.60	89.36	-0.27
0.2509	-0.0040	0.0040	0.0	127.10	126.20	-0.71
0.3559	-0.0035	0.0036	0.0	155.90	153.84	-1.32
0.4403	-0.0077	0.0077	0.0	175.80	174.94	-0.49
0.4954	-0.0016	0.0016	0.0	191.50	186.76	-2.47
0.5946	-0.0043	0.0043	0.0	214.40	209.34	-2.36
0.0207	-0.0025	0.0026	-0.0001	48.80	48.40	-0.82
0.0399	-0.0040	0.0041	-0.0001	78.80	78.19	-0.77
0.0820	-0.0038	0.0039	0.0	142.00	144.12	1.49
0.1221	0.0077	-0.0076	0.0	178.60	204.47	14.48
0.0970	-0.0041	0.0041	0.0	106.80	107.18	0.36
0.1683	-0.0013	0.0013	0.0	150.50	163.61	8.71
0.2258	0.0063	-0.0062	0.0	169.70	202.63	19.40
0.2843	0.0050	-0.0050	0.0	193.80	230.01	18.68
0.3033	0.0154	-0.0154	0.0	200.70	234.28	16.73
0.0227	-0.0100	0.0102	-0.0001	59.00	60.72	2.92
0.0470	0.0040	-0.0030	-0.0010	102.20	114.09	11.64
0.0601	-0.0005	0.0016	-0.0011	123.70	144.02	16.42
0.0071	-0.0071	0.0072	-0.0001	24.55	24.25	-1.23
0.0199	-0.0008	0.0009	-0.0001	64.30	63.09	-1.89
0.0324	0.0014	-0.0013	-0.0001	105.30	102.60	-2.56
0.0443	-0.0030	0.0031	-0.0001	140.75	141.69	0.67

AVE. ABS. % DEV. IN PRESSURE %DP = 5.53 (%)

AVE. ABS. DEV. IN VAPOR COMP. = 0.0032 (MOLE FRACTION)

TABLE 4.19 (continued)

T = 122.24 K

X1	DY1	DY2	DY3	P EXP (psia)	P CAL (psia)	% DP
0.0080	-0.0026	0.0030	-0.0003	30.60	31.08	1.57
0.0190	-0.0025	0.0027	-0.0002	64.80	70.18	8.30
0.0203	-0.0029	0.0030	0.0	67.30	66.79	-0.75
0.0360	-0.0011	0.0012	0.0	108.60	109.26	0.61
0.0500	-0.0029	0.0030	-0.0001	145.20	148.11	2.01
0.0767	0.0010	-0.0009	0.0	186.80	223.94	19.88
0.0156	-0.0044	0.0045	-0.0001	48.30	49.23	1.93
0.0378	-0.0095	0.0095	0.0	88.75	88.56	-0.22
0.0823	-0.0041	0.0042	0.0	173.80	174.10	0.17
0.1443	0.0197	-0.0196	0.0	240.30	287.70	19.73
0.0215	-0.0042	0.0042	0.0	51.80	50.36	-2.79
0.0450	-0.0037	0.0037	0.0	79.40	76.60	-3.53
0.1699	0.0	0.0	0.0	199.20	207.99	4.41
0.0846	-0.0062	0.0062	0.0	83.80	83.24	-0.67
0.1853	-0.0015	0.0015	0.0	137.30	137.45	0.11
0.3532	-0.0032	0.0032	0.0	185.10	191.20	3.30
0.5875	-0.0019	0.0029	-0.0010	255.10	251.81	-1.29
0.8468	0.0020	-0.0020	0.0	327.40	327.47	0.02

AVE. ABS. % DEV. IN PRESSURE %DP = 3.96 (%)

AVE. ABS. DEV. IN VAPOR COMP. = 0.0028 (MOLE FRACTION)

TABLE 4.20

Comparison of experimental values to predicted pressures and vapor compositions by the modified Redlich-Kwong equation of state. Top liquid phase being considered in equilibrium with the vapor phase for the system nitrogen(1)-methane(2)-propane(3) at 114.05, 118.32, and 122.24 K.

T = 114.05 K

X1	DY1	DY2	DY3	P EXP (psia)	P CAL (psia)	% DP
0.9854	0.0041	-0.0040	-0.0001	254.40	255.39	0.39
0.9588	0.0009	-0.0008	-0.0001	245.90	247.73	0.74
0.9404	0.0025	-0.0024	-0.0001	238.95	242.76	1.59
0.9022	0.0007	-0.0006	-0.0001	230.00	233.52	1.53
0.8651	0.0023	-0.0023	-0.0001	219.85	225.19	2.43
0.7958	0.0	0.0001	-0.0001	207.00	212.00	2.42
0.7290	0.0002	-0.0001	-0.0001	195.26	201.56	3.23
0.5254	-0.0015	0.0016	0.0	167.70	176.67	5.35
0.4877	-0.0032	0.0033	0.0	165.40	173.98	5.19
0.4015	0.0002	-0.0001	0.0	160.20	176.09	9.92
0.6523	0.0004	-0.0003	-0.0001	183.50	191.15	4.17

AVE. ABS. % DEV. IN PRESSURE %DP = 3.36 (%)

AVE. ABS. DEV. IN VAPOR COMP. = 0.0010 (MOLE FRACTION)

TABLE 4.20 (continued)

T = 118.32 K

X1	DY1	DY2	DY3	P EXP (psia)	P CAL (psia)	% DP
0.9555	0.0020	-0.0018	-0.0001	309.00	305.31	-1.19
0.8804	0.0009	-0.0008	-0.0001	283.23	281.17	-0.73
0.8396	-0.0002	0.0003	-0.0001	269.30	269.82	0.19
0.7915	-0.0007	0.0008	-0.0001	257.70	258.19	0.19
0.7924	-0.0006	0.0006	-0.0001	257.70	258.41	0.27
0.7370	0.0012	-0.0012	-0.0001	244.30	247.26	1.21
0.6481	-0.0017	0.0018	0.0	228.50	231.71	1.41
0.5836	0.0	0.0	0.0	216.53	223.78	3.35
0.4793	-0.0015	0.0015	0.0	206.50	214.81	4.03
0.4667	0.0006	-0.0003	-0.0003	204.50	217.06	6.14

AVE. ABS. % DEV. IN PRESSURE %DP = 1.87 (%)
AVE. ABS. DEV. IN VAPOR COMP. = 0.0006 (MOLE FRACTION)

T = 122.24 K

X1	DY1	DY2	DY3	P EXP (psia)	P CAL (psia)	% DP
0.9776	-0.0103	0.0092	0.0011	386.50	246.50	-36.22
0.8954	0.0010	-0.0009	-0.0001	346.85	345.47	-0.40
0.8467	-0.0029	0.0030	-0.0001	330.00	327.39	-0.79
0.7418	-0.0044	0.0044	-0.0001	296.85	295.45	-0.47
0.5837	-0.0001	0.0001	0.0	260.80	266.06	2.02
0.4891	-0.0016	0.0016	0.0	250.20	255.17	1.99

AVE. ABS. % DEV. IN PRESSURE %DP = 6.98 (%)
AVE. ABS. DEV. IN VAPOR COMP. = 0.0023 (MOLE FRACTION)

TABLE 4.21

Comparison of experimental values to predicted pressures and vapor compositions by the modified Redlich-Kwong equation of state. Bottom liquid phase being considered in equilibrium with the vapor phase for the system nitrogen(1)-methane(2)-propane(3) at 114.05, 118.32, and 122.24 K.

T = 114.05 K

X1	DY1	DY2	DY3	P EXP (psia)	P CAL (psia)	% DP
0.0977	-0.0089	0.0051	0.0038	254.40	2473.16	872.15
0.0935	0.0036	-0.0035	-0.0001	245.40	295.18	20.28
0.1003	0.0039	-0.0038	-0.0001	238.95	306.58	28.30
0.0983	0.0034	-0.0033	-0.0001	230.00	278.79	21.21
0.1075	0.0043	-0.0042	-0.0001	219.85	281.95	28.25
0.1150	0.0037	-0.0036	-0.0001	207.00	268.40	29.66
0.1250	0.0030	-0.0029	-0.0001	195.26	252.47	29.30
0.1361	0.0043	-0.0042	-0.0001	183.50	238.97	30.23
0.1491	0.0032	-0.0032	-0.0001	178.25	233.97	31.26
0.1694	0.0019	-0.0019	0.0	167.70	212.16	26.51
0.1755	-0.0007	0.0007	0.0	165.40	202.89	22.67

AVE. ABS. % DEV. IN PRESSURE %DP = 103.62 (%)

AVE. ABS. DEV. IN VAPOR COMP. = 0.0025 (MOLE FRACTION)

TABLE 4.21 (continued)

T = 118.32 K

X1	DY1	DY2	DY3	P EXP (psia)	P CAL (psia)	% DP
0.0907	0.0036	-0.0035	-0.0001	309.00	327.01	5.83
0.1127	-0.0941	0.0866	0.0076	283.23	2630.41	828.72
0.1170	-0.0010	0.0011	-0.0001	269.30	343.94	27.72
0.1281	-0.0016	0.0017	-0.0001	257.70	343.91	33.45
0.1280	-0.0016	0.0017	-0.0001	257.70	343.97	33.48
0.1351	0.0015	-0.0015	-0.0001	244.30	321.69	31.68
0.1545	-0.0001	0.0001	0.0	228.50	299.15	30.92
0.1746	0.0009	-0.0009	0.0	216.53	279.79	29.22
0.2176	0.0020	-0.0019	0.0	206.50	261.47	26.62
0.2341	0.0032	-0.0032	0.0	204.50	261.65	27.95

AVE. ABS. % DEV. IN PRESSURE %DP = 107.56 (%)
AVE. ABS. DEV. IN VAPOR COMP. = 0.0073 (MOLE FRACTION)

T = 122.24 K

X1	DY1	DY2	DY3	P EXP (psia)	P CAL (psia)	% DP
0.0953	-0.0123	0.0098	0.0025	386.50	1078.27	178.98
0.1036	-0.0683	0.0631	0.0052	346.85	1411.51	306.95
0.1146	-0.1101	0.1016	0.0085	330.00	2299.78	596.90
0.1444	-0.1999	0.1800	0.0199	296.85	5485.43	1747.88
0.2051	-0.3438	0.2892	0.0546	260.80	13846.45	5209.23
0.2451	0.0058	-0.0058	0.0	250.20	354.68	41.76
0.2829	0.0084	-0.0084	0.0	245.12	325.63	32.84

AVE. ABS. % DEV. IN PRESSURE %DP =1159.22 (%)
AVE. ABS. DEV. IN VAPOR COMP. = 0.0713 (MOLE FRACTION)

TABLE 4.22

Comparison between predicted and experimental values of the liquid-liquid equilibrium for the system nitrogen(1)-methane(2)-propane(3).

	BOTTOM LIQUID PHASE			TOP LIQUID PHASE		
TEMP	P EXP P CAL	X1 EXP X1 CAL	X2 EXP X2 CAL	X3 EXP X3 CAL	X1 EXP X1 CAL	X2 EXP X2 CAL	X3 EXP X3 CAL
K	D P	DX1	DX2	DX3	DX1	DX2	DX3
114.05	254.40	0.0977	0.0145	0.8879	0.9854	0.0136	0.0010
	254.51	0.0974	0.0142	0.8884	0.9854	0.0135	0.0010
	0.11	0.0003	0.0003	-0.0006	0.0	0.0	0.0
114.05	245.90	0.0935	0.0352	0.8713	0.9588	0.0395	0.0016
	246.17	0.0935	0.0353	0.8712	0.9588	0.0395	0.0016
	0.27	-0.0001	-0.0001	0.0001	0.0	0.0	0.0
114.05	238.95	0.1003	0.0607	0.8390	0.9404	0.0569	0.0027
	239.60	0.1002	0.0603	0.8395	0.9404	0.0569	0.0027
	0.65	0.0001	0.0004	-0.0005	0.0	0.0	0.0
114.05	219.85	0.1075	0.1316	0.7609	0.8651	0.1258	0.0091
	220.82	0.1066	0.1305	0.7630	0.8651	0.1259	0.0090
	0.97	0.0010	0.0011	-0.0021	0.0	-0.0001	0.0001
114.05	207.00	0.1150	0.1830	0.7020	0.7958	0.1890	0.0152
	207.90	0.1153	0.1834	0.7013	0.7958	0.1890	0.0152
	0.90	-0.0003	-0.0004	0.0007	0.0	0.0	0.0

TABLE 4.22 (continued)

114.05	195.26	0.1250	0.2420	0.6330	0.7290	0.2480	0.0230
	196.39	0.1251	0.2402	0.6347	0.7290	0.2482	0.0228
	1.13	-0.0001	0.0018	-0.0017	0.0	-0.0002	0.0002
114.05	183.50	0.1361	0.2941	0.5698	0.6523	0.3147	0.0329
	184.81	0.1356	0.2920	0.5724	0.6523	0.3151	0.0326
	1.31	0.0005	0.0021	-0.0026	0.0	-0.0003	0.0003
114.05	178.25	0.1491	0.3300	0.5209	0.6141	0.3449	0.0410
	179.64	0.1485	0.3298	0.5217	0.6141	0.3450	0.0409
	1.59	0.0006	0.0002	-0.0007	0.0	-0.0001	0.0001
114.05	167.70	0.1694	0.3984	0.4323	0.5254	0.4190	0.0555
	169.04	0.1692	0.3968	0.4340	0.5254	0.4194	0.0551
	1.34	0.0002	0.0016	-0.0018	0.0	-0.0004	0.0004
114.05	165.40	0.1755	0.4222	0.4024	0.4877	0.4450	0.0672
	166.64	0.1744	0.4220	0.4037	0.4877	0.4453	0.0670
	1.24	0.0011	0.0002	-0.0013	0.0	-0.0002	0.0002
114.02	160.20	0.1755	0.4222	0.4024	0.4015	0.4819	0.1166
	163.28	0.1842	0.4259	0.3899	0.4015	0.4730	0.1205
	3.08	-0.0088	-0.0037	0.0125	0.0	0.0038	-0.0038
118.32	204.50	0.2341	0.4377	0.3282	0.4667	0.4457	0.0875
	205.31	0.2357	0.4350	0.3293	0.4567	0.4464	0.0868
	0.81	-0.0016	0.0027	-0.0011	0.0	-0.0007	0.0007
118.32	206.50	0.2176	0.4306	0.3518	0.4793	0.4434	0.0773
	206.83	0.2188	0.4289	0.3523	0.4793	0.4437	0.0769
	0.33	-0.0012	0.0017	-0.0005	0.0	-0.0004	0.0004

TABLE 4.22 (continued)

118.32	216.53	0.1746	0.3710	0.4544	0.5836	0.3718	0.0446
	217.49	0.1754	0.3673	0.4573	0.5836	0.3724	0.0440
	0.96	-0.0008	0.0037	-0.0029	0.0	-0.0005	0.0006
118.32	228.50	0.1545	0.3171	0.5284	0.6481	0.3219	0.0300
	228.80	0.1558	0.3134	0.5308	0.6481	0.3223	0.0296
	0.30	-0.0013	0.0037	-0.0024	0.0	-0.0004	0.0004
118.32	244.30	0.1351	0.2481	0.6168	0.7370	0.2451	0.0178
	244.70	0.1351	0.2439	0.6211	0.7370	0.2455	0.0174
	0.40	0.0	0.0043	-0.0043	0.0	-0.0004	0.0004
118.32	257.70	0.1281	0.2053	0.6666	0.7915	0.1980	0.0105
	257.45	0.1274	0.2011	0.6716	0.7915	0.1982	0.0102
	-0.25	0.0007	0.0042	-0.0050	0.0	-0.0003	0.0003
118.32	257.70	0.1280	0.2051	0.6669	0.7924	0.1971	0.0105
	257.68	0.1280	0.2030	0.6690	0.7924	0.1973	0.0104
	-0.02	0.0001	0.0021	-0.0022	0.0	-0.0001	0.0001
118.32	269.30	0.1170	0.1649	0.7181	0.8396	0.1540	0.0064
	269.29	0.1169	0.1646	0.7185	0.8396	0.1541	0.0064
	-0.01	0.0001	0.0003	-0.0004	0.0	0.0	0.0
118.32	283.23	0.1127	0.1209	0.7664	0.8804	0.1149	0.0047
	280.68	0.1128	0.1197	0.7675	0.8804	0.1150	0.0046
	-2.55	-0.0001	0.0012	-0.0011	0.0	-0.0001	0.0001
118.32	309.00	0.0907	0.0433	0.8660	0.9555	0.0426	0.0019
	304.80	0.0908	0.0436	0.8656	0.9555	0.0425	0.0019
	-4.20	-0.0001	-0.0003	0.0004	0.0	0.0	0.0

TABLE 4.22 (continued)

122.24	386.50	0.0953	0.0227	0.8820	0.9776	0.0211	0.0013
	380.43	0.0950	0.0227	0.8823	0.9776	0.0211	0.0013
	-6.07	0.0002	0.0	-0.0002	0.0	0.0	0.0
122.24	346.85	0.1036	0.0993	0.7970	0.8954	0.1023	0.0023
	344.87	0.1003	0.0980	0.8016	0.8954	0.1024	0.0022
	-1.98	0.0033	0.0013	-0.0046	0.0	0.0	0.0
122.24	330.00	0.1146	0.1422	0.7432	0.8467	0.1513	0.0020
	326.76	0.1150	0.1445	0.7405	0.8467	0.1513	0.0020
	-3.24	-0.0003	-0.0024	0.0027	0.0	0.0	0.0
122.24	296.85	0.1444	0.2304	0.6252	0.7418	0.2497	0.0085
	294.82	0.1446	0.2449	0.6104	0.7418	0.2490	0.0093
	-2.03	-0.0002	-0.0146	0.0148	0.0	0.0007	-0.0007
122.24	260.80	0.2051	0.3577	0.4372	0.5837	0.3765	0.0398
	260.88	0.2055	0.3558	0.4387	0.5837	0.3768	0.0395
	0.08	-0.0004	0.0019	-0.0015	0.0	-0.0003	0.0003
122.24	250.20	0.2451	0.4090	0.3459	0.4891	0.4423	0.0686
	243.68	0.2449	0.4105	0.3447	0.4891	0.4419	0.0690
	-6.52	0.0002	-0.0015	0.0012	0.0	0.0004	-0.0004

TABLE 4.23

Compositions of the plait points evaluated from the method of Black and Hartwig compared with the results predicted by the modified Redlich-Kwong equation of state for the system nitrogen(1)-methane(2)-propane(3).

TEMP K	BOTTOM LIQUID PHASE				TOP LIQUID PHASE		
	P EXP / P CAL / DP	X1 EXP / X1 CAL / DX1	X2 EXP / X2 CAL / DX2	X3 EXP / X3 CAL / DX3	X1 EXP / X1 CAL / DX1	X2 EXP / X2 CAL / DX2	X3 EXP / X3 CAL / DX3
114.05	157.00	0.3142	0.4944	0.1914	0.3142	0.4944	0.1914
	161.57	0.3142	0.4944	0.1914	0.3142	0.4944	0.1914
	4.57	0.0	0.0	0.0	0.0	0.0	0.0
118.32	198.00	0.3395	0.4743	0.1862	0.3395	0.4743	0.1862
	203.64	0.3395	0.4743	0.1862	0.3395	0.4743	0.1862
	5.64	0.0	0.0	0.0	0.0	0.0	0.0
122.24	241.00	0.3622	0.4695	0.1683	0.3622	0.4695	0.1683
	244.36	0.3622	0.4695	0.1683	0.3622	0.4695	0.1683
	3.36	0.0	0.0	0.0	0.0	0.0	0.0

APPENDIX B

The Electric Circuit of the Electromagnetic Pump

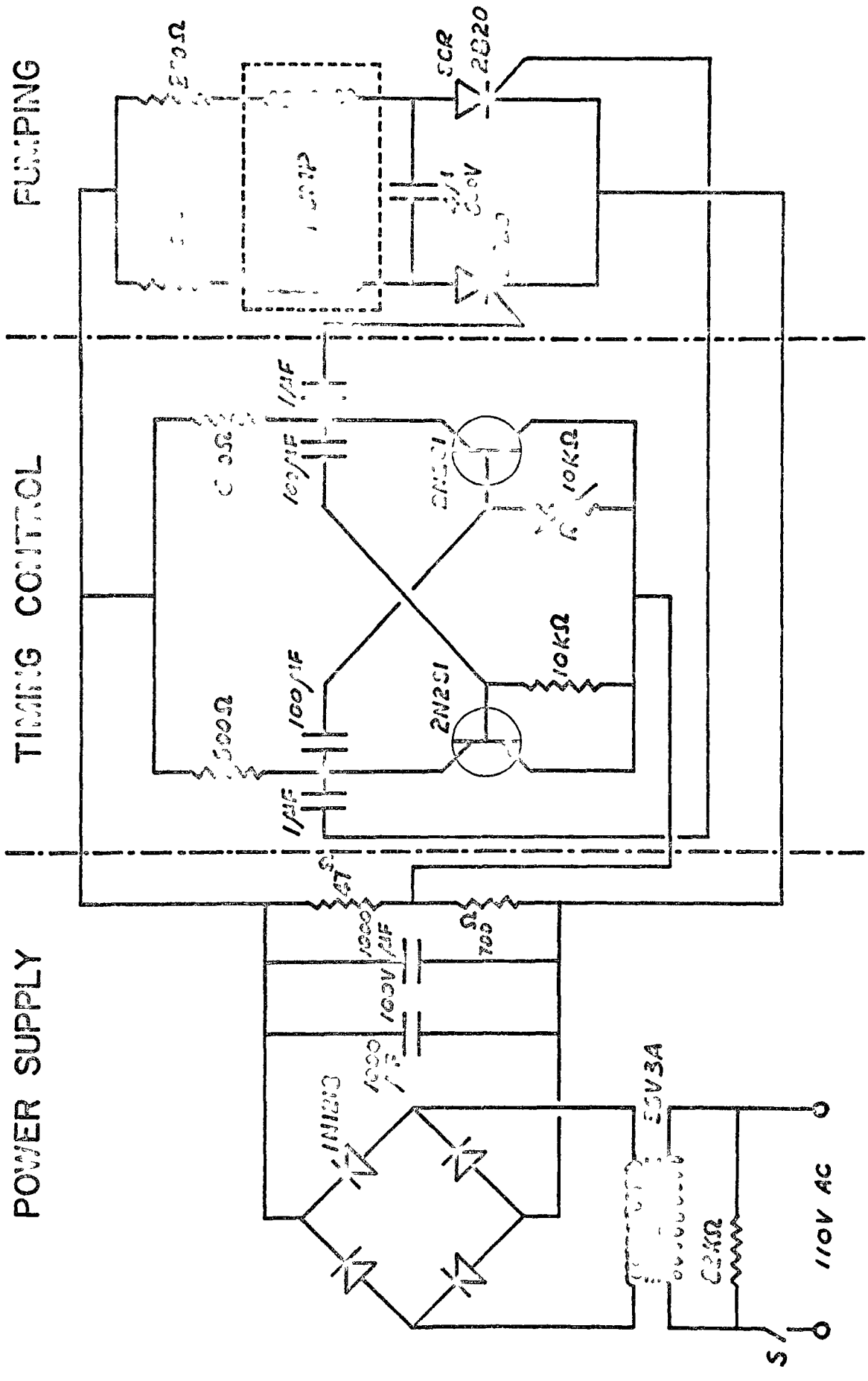
The circuit consists of three sections:

(1) the power supply section

(2) the timing control section

(3) the pumping section

The major part of the circuit is similar to that of a Flip-Flop circuit to produce a square wave-output. The action of the pump is within the range of 1.5 millisecond to 1 second per cycle and can be adjusted through a variable resistance.



Electric Circuit of Electromagnetic Pump

APPENDIX C

Computer programs

Programs

Subroutines

```
C       PREDICTION OF CRITICAL LOCI FOR BINARY MIXTURES
C       DAVID POON  (SEPTEMBER 1970).
C       SUBROUTINE NEEDED, ONE OF THE FOLLOWINGS :
C       RK,CLAUS,WOHL, OR SUGLU.
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION  A(5,5),F(5,5), C1RKL(5),C2RKL(5),TC(5),PC(5),VC(5),
       1    TCIJ(5,5),WIJ(5,5),W(5),Y(5 ),CORRL(5,5) ,TITLE(19),
       2 C1RKV(5),C2RKV(5),C3RKL(5)
        DIMENSION VV(50),C(5,5)
  800   READ(1,5)(TITLE(I),I=1,19)
        WRITE(3,6)(TITLE(I),I=1,19)
    5   FORMAT(19A4)
    6   FORMAT(1H1,19A4)
        READ(1,510) T,ET
        READ(1,510) VI,EV
        DT=(ET-T)/15.0D0
        DV=(EV-VI)/20.0D0
        DO 600 I=1,20
  600   VV(I)=VI+FLOAT(I-1)*DV
        READ(1,500) NCOMP,NEQ,IJK,R
        IF(NCOMP.LE.0) GO TO 900
        DO 400 I=1,NCOMP
        READ(1,510) PC(I),VC(I),TC(I),W(I),C1RKL(I),C2RKL(I),C3RKL(I)
  400   WRITE(3,515) PC(I),VC(I),TC(I),W(I),C1RKL(I),C2RKL(I),C3RKL(I)
        CORRL(NCOMP,NCOMP)=0.0
        NCOMP1=NCOMP-1
        DO 101 I=1,NCOMP1
        I1=I+1
        DO 101 J=I1,NCOMP
  101   READ(1,520) CORRL(I,J)
        WRITE(3,200) CORRL(I,J)
        READ(1,525) (Y(J),J=1,NCOMP)
        WRITE(3,515) (Y(J),J=1,NCOMP)
        CALL RK       (PC,VC,TC,W,C1RKL,C2RKL,C3RKL,NCOMP,CORRL,Y,ET)
        GO TO 800
  200   FORMAT(5X,5D20.9)
  510   FORMAT(8F10.5)
  515   FORMAT( /1H /,7D12.5)
  520   FORMAT(3F10.5)
  525   FORMAT(3F10.5)
  900   STOP
  500   FORMAT(3I5,F10.4)
  901   RETURN
        END
```

```
C      DAVID POON  (OCTOBER,1970)
C      EVALUATION OF LIQUID ACTIVITY COEEFICIENTS
C      (1) FROM LIQUID FUGACITY COEFFICIENTS (REDLICH-KWONG EQUATION OF
C      (2) FROM GAS FUGACITY COEFFICIENTS (VIRIAL EQUATION OF STATE)
C      SUBROUTINES NEEDED :   SEXP,FUGRK,CUBEQN,VOLPAR, AND EQNRK.
C1 EXPT   2  BARKER   3   POLY, FITTING
       DIMENSION PHI(5),X(5), F( 5),GAMMA(5),FREFER(5),PVOL(5),Y(5),
      1 PC(5),VC(5),TC(5),W(5),C1RKV(5),C2RKV(5),C1RKL(5),C2RKL(5),
      2 AMOLWT(5),COMPA(5),COMPB(5),CORRV(5,5),CORRL(5,5),GAMALN(5),
      3 A(4),Z(3),TITLE(20),D(5),PCO(5),VCO(5),TCO(5),PHIV(5),FREF(5),
      4PP(50),XX(50,3),YY(50,3),PS(5),PPVOL(4),YCAL(3)
       DIMENSION ARKV(5,5),ARKL(5,5),BRKV(5),BRKL(5)
       DIMENSION GEMA(5),PREF(5),VOL(5),DGMA(5),PDGMA(5)
       DIMENSION REQ(5)
       DIMENSION RAQ(5)
       DIMENSION GEMALN(5),Q(50)
       COMMON  /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NONTUM
      1   /SECOND/ Z,A,MTYPE
      1   /THIRD/ ARKV,ARKL,BRKV,BRKL,ZL,ZV,AMRKV,AMRKL,BMRKV,BMRKL
       EXTERNAL CUBEQN
C        MM   TO END READING PXYGIGII  ON CARD OUTPUT
  800  MM=1
C      WRITE(2,1005)  MM
 1005  FORMAT(50X,I1)
       READ(1,5) (TITLE(I),I=1,19)
C 800  READ(1,5)(TITLE(I),I=1,19)
    6  FORMAT(19A4)
    5  FORMAT(    19A4)
       WRITE(3,927)
       WRITE(3,6)(TITLE(I),I=1,19)
       WRITE(2,6) (TITLE(I),I=1,19)
       WRITE(2,500) NCOMP
C      WRITE(2,5)(TITLE(I),I=1,19)
       READ(1,500)NCOMP,NONTUM,IJK,R
       IF(NCOMP.LE.0) GO TO 900
C      WRITE(3,505)
       DO 210 I=1,NCOMP
       READ(1,510)PCO(I),VCO(I),TCO(I),W(I),C1RKV(I),C2RKV(I),
      1   C1RKL(I),C2RKL(I),AMOLWT(I),COMPA(I),COMPB(I)
       READ(1,510)  C1RKL(I),C2RKL(I)
       READ(1,510) PREF(I),VOL(I)
       C1RKV(I)=C1RKL(I)
       C2RKV(I)=C2RKL(I)
  210  CONTINUE
C 210  WRITE(3,515)PCO(I),VCO(I),TCO(I),W(I),
C     1   C1RKL(I),C2RKL(I),AMOLWT(I),COMPA(I),COMPB(I)
       CORRL(NCOMP,NCOMP)=0.0
       NCOMP1=NCOMP-1
C      WRITE(3,519)
  519  FORMAT(/10X,12HINPUT DATA ://4X,1HP,8X,2HX1,8X,2HX2,9X,1HT,7X,3HR
      11,7X,3HRB1,7X,3HRA2,7X,3HRB2//)
       WRITE(3,920)
  920  FORMAT(1H1/////)
       IF(NCOMP.EQ.2) GO TO 995
       WRITE(3,518)
       GO TO 994
  995  WRITE(3,993)
  994  CONTINUE
```

```
  518 FORMAT(///11X,1HP,9X,2HX1,8X,2HX2,8X,2HX3,8X,2HY1,8X,2HY2,8X,2HY3
  993     FORMAT(///11X,1HP,9X,2HX1,8X,2HX2,8X,2HY1,8X,2HY2)
      DO 9 I=1,NCOMP1
      I1=I+1
      DO 9 J=I1,NCOMP
    9 READ(1,520)CORRL(I,J)
      I=0
C        M=1   PRESSURE IS IN CM  HG
      READ(1,1000) M
 1000 FORMAT(I1)
 1003 FORMAT(3F21.0)
   10 I=I+1
      SX=0.0
      SY=0.0
      IF(M.EQ.0.OR.M.EQ.1) GO TO 1001
      GO TO 1002
C1001 READ(1,520) PP(I),(XX(I,J),J=1,NCOMP1),(YY(I,J),J=1,NCOMP1)
 1001 READ(1,520) PP(I),(XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
      IF(M.EQ.0) GO TO 1002
      PP(I)=PP(I)*14.696/760.
C     PP(I)=PP(I)*14.696/76.
 1002 CONTINUE
      DO 15 J=1,NCOMP1
      SY=SY+YY(I,J)
   15 SX=SX+ XX(I,J)
      XX(I,NCOMP)=1.0-SX
      YY(I,NCOMP)=1.0-SY
      IF(R.LT.11.0) GO TO 16
C     PP(I)=PP(I)/14.697
   16 IF(PP(I).LT.0.0) GO TO 20
      WRITE(3,523)
  523 FORMAT(/)
      WRITE(3,521) PP(I),(XX(I,J),J=1,NCOMP ),(YY(I,J),J=1,NCOMP )
      IF(PP(I).GE.0) GO TO 10
   20 NOBS=I-1
C     WRITE(2,525)NOBS, NQNTUM,R
      READ(1,520)TTT,PS0,(PS(I),I=1,NCOMP)
      I=(R.LT.11.0) GO TO 21
      PS0=PS0/14.697
   21 CONTINUE
C  21 WRITE(3,520)TTT,PS0,(PS(I),I=1,NCOMP)
      READ(1,525)IJK,KIJ,CINI,CFIN
  525 FORMAT(2I5,2F10.4)
   30 KIJ=KIJ+1
      IF(KIJ.GE.2) GO TO 800
      K=0
C     WRITE(3,525)IJK,KIJ,CINI,CFIN
      KK=0
      KK=20
  280 CONTINUE
C     WRITE(3,6)(TITLE(I),I=1,19)
      WRITE(3,924)
  924 FORMAT(/)
      KK=KK+1
      DO 220 I=1,NCOMP1
C     WRITE(3,516)
      DO 220 I=1,NCOMP1
      CORRL(I,I)=0.0
```

```
      I1=I+1
      DO 220 J=I1,NCOMP
      IF(KK.GT.20) GO TO 214
      CORRL(I,J)=CINI+(KK-1)*(CFIN-CINI)/10.
C 214 WRITE(3,530)I,J,CORRL(I,J)
  214 CONTINUE
      CORRL(J,I)=CORRL(I,J)
  220 CONTINUE
      K=0
      SSDY=0.0
  219 CONTINUE
      IF(NQNTUM.GE.1) GO TO 223
      DO 221 I=1,NCOMP
      PC(I)=PCO(I)
      VC(I)=VCO(I)
  221 TC(I)=TCO(I)
  120 T=TTT
      RT=R*T
      DO 226 I=1,NCOMP
      DO 224 J=1,NCOMP
      X(J)=0.0
  224 CONTINUE
      X(I)=1.0
      P=PSO
      LV=1
      CALL FUGRK( PHI,X,C1RKV,C2RKV,CORRL,CUBEQN,  KIJ, LV)
      CALL VOLPAR(C1RKL,C2RKL,CORRL,X,CUBEQN,F,PVOL,IJK)
      FREF(I)=F(I)*X(I)*PSO
      FREFER(I)=PHI(I)*X(I)*PSO
  226 D(I)=PVOL(I)
C     WRITE(3,521)T,PSO,(FREFER(I),I=1,NCOMP),(D(I),I=1,NCOMP)
C    1   ,(FREF(I),I=1,NCOMP)
C 521 FORMAT(//5X,2F10.2,11F 9.4//)
      WRITE(3,927)
  927 FORMAT(1H1////////)
      IF (NCOMP.EQ.2) GO TO 892
      WRITE(3,535)
C 535 FORMAT(//6X,1HP,7X,2HX1,9X,2HX2,8X,2HX3,8X,2HY1,
C    123X,2HY2,23X,2HY3//)
  535 FORMAT(//'1234567890123456789012345678901234567890123456789012345
     1789012345678901234567890123456789012345678901234567890')
C 535 FORMAT(//20X,       2HX1,4X,'GAMMA1',3X,'GEMA1',4X,'%DEV.G1',3X,
C    1  'GAMMA2',4X,'GEMA2',3X,'%DEV.G2',4X,'GAMMA3',4X,'GEMA3',3X,
C    2  '%DEV.G3'//)
C     WRITE(3,6)(TITLE(I),I=1,19)
  536 FORMAT(    ///11X,2HX1,8X,2HX2,7X,2HG1,9X,2HG2,7X,2HG3,7X,
     15HLN G1,5X,5HLN G2,5X,5HLN G3 )
C     WRITE(3,536)
      GO TO 223
  892 WRITE(3,891)
  891 FORMAT(//'1234567890123456789012345678901234567890123456789012345
     1789012345678901234567890')
C 891 FORMAT(//6X,1HP,9X,2HX1,7X,2HY1,                    8X,4HGAM1,6X,4HGE
C    11,6X,4H%DG1,6X,4HGAM2,6X,4HGEM2,6X,4H%DG2//)
C 891 FORMAT(//6X,1HP,7X,2HX1,9X,2HX2,8X,2HX3,8X,2HY1,8X,2HY2,8X,2HY3//
C     WRITE(3,6)(TITLE(I),I=1,19)
C     WRITE(3,893)
  893 FORMAT(    ///11X,2HX1,8X,2HX2,7X,2HG1,9X,2HG2,
```

```
     17X,5HLN G1,5X,5HLN G2 )
C 535 FORMAT(1H1,'SUPPORTING DATA ARE LISTED IN THE FOLLOWING ORDER:
C     1ARGON=1, METHANE=2), P,X1,Y1,PV1,PV2,FL1,FL2,FV1,FV2....'///)
C 535 FORMAT(/26X,9HCOMPONENT,1X,1HX,7X,4HYCAL,4X,4HYOBS,4X,
C     1   6HGAMALN,2X,5HGAMMA,5X,4HV(P),6X,5HV(P0),5X,4HPHIL,6X,
C     1   4HPHIV,6X,5HPHILL/)
  223 CONTINUE
      K=K+1
      DO 234 J=1,NCOMP
      Y(J)=YY(K,J)
  234 X(J)=XX(K,J)
      III=0
  230 III=III+1
      IF(III.GT.1)GO TO 236
      P=PS0
      CALL VOLPAR(C1RKL,C2RKL,CORRL,X,CUBEQN,F,PVOL,IJK)
      DO 233 J=1,NCOMP
      PPVOL(J)=PVOL(J)
  233 CONTINUE
      GO TO 230
  236 P=PP(K)
      CALL VOLPAR(C1RKL,C2RKL,CORRL,X,CUBEQN,F,PVOL,IJK)
      LV=1
C     CALL FUGRK(PHIV,Y,C1RKV,C2RKV,CORRL,CUBEQN,KIJ,LV)
      CALL FUGRK( PHI,X,C1RKV,C2RKV,CORRL,CUBEQN,  KIJ, LV)
      DO 235 J=1,NCOMP
C     GAMALN(J)=ALOG(PHI(J)*P/FREFER(J)      )
C     GAMALN(J)=(Y(J)*PHIV(J)*P)/(X(J)*FREFER(J))
      GAMALN(J)=ALOG(   F(J)*P/FREFER(J)      )
     1    +(PPVOL(J)+PVOL(J))*(PS0-P)/2.0/RT
      PHIV(J)=1.0
  235 GAMMA(J)= EXP(GAMALN(J) )
      ITER=0
      LV=0
C     CALL FUGRK(PHIV,Y,C1RKV,C2RKV,CORRL,CUBEQN, KIJ,  LV)
      RATIO=PHIV(1)*Y(1)/PHI(1)/X(1)
  240 ITER=ITER+1
      SDY=0.0
      IF(ITER-20)242,242,260
  242 DO 245 J=1,NCOMP
      YCAL(J)=PHI(J)/PHIV(J)*X(J)
      SDY=SDY+YCAL(J)
  245 CONTINUE
      DO 246 J=1,NCOMP
      IF(ITER.LE.1) GO TO 250
  246 YCAL(J)=YCAL(J)/SDY
      DO 247 J=1,NCOMP
      IF(ABS(YCAL(J)-Y(J)) .GT.0.00001) GO TO 250
  247 CONTINUE
      GO TO 260
  250 DO 255 J=1,NCOMP
  255 Y(J)=YCAL(J)
      LV=0
      CALL FUGRK(PHIV,Y,C1RKV,C2RKV,CORRL,CUBEQN, KIJ,  LV)
      GO TO 240
  260 SDY=0.0
      DO 265 J=1,NCOMP
  265 SDY    =SDY    +ABS(YCAL(J)-YY(K,J))
```

```
      SSDY=SSDY+SDY
      IF(R.LT.11.) GO TO 266
      P=P*14.697
C 266 WRITE(2,540)P,(X(J),J=1,NCOMP1),(YCAL(J),J=1,NCOMP1)
C 265 WRITE(3,540)P,(X(J),J=1,NCOMP1),(YY(K,J),J=1,NCOMP1)
C     1   ,(GAMALN(J),J=1,NCOMP)
C     WRITE(2,540)P,(X(J),J=1,NCOMP1),(YY(K,J),J=1,NCOMP1)
      P=P/14.697
  266 CONTINUE
      DO 267 J=1,NCOMP
      Y(J)=YY(K,J)
  267 X(J)=XX(K,J)
      CALL SEXP(TC,PC,VC,W,T,P,R,X,Y,GEMA,PREF,VOL,NCOMP,CORRL,BD)
  888 DO 999 I=1,NCOMP
      IF (GEMA(I).LE.0.0) GO TO 998
  999 GEMALN(I)=ALOG(GEMA(I))
      GO TO 869
  998 GEMALN(I)=0.0
  869 CONTINUE
C     DO 869 J=1,NCOMP
C 869 GEMA(J)=GEMA(J)/EXP( (PPVOL(J)+PVOL(J))*(PSO-P)/2.0/RT)
  540 FORMAT(8F10.4)
C     WRITE(3,611)  P,X(I),YY(K,1),PPVOL(1),PPVOL(2),PHI(1),PHI(2),PHIV(
C    11),PHIV(2)
      DO 268 I=1,NCOMP
      DGMA(I)=GAMMA(I)-GEMA(I)
  268 PDGMA(I)=DGMA(I)/GAMMA(I)*100.0
      DO 896 I=1,NCOMP
  896 REO(I)=X(I)*GEMA(I)
      RAO(I)=X(I)*GAMMA(I)
      WRITE(3,879)
  879 FORMAT(/)
      IF (NCOMP.EQ.3) GO TO 899
C     WRITE(3,520)  P,X(1),X(2),X(3),Y(1),Y(2),Y(3)
C     WRITE(3,521)  X(1),X(2),GAMMA(1),GAMMA(2),GAMALN(1),GAMALN(2)
  925 FORMAT(F10.2,4F10.4,F10.2,2F10.4,F10.2)
  926 FORMAT(       3F8.4 ,F 8.2,2F10.4,F10.2,2F10.4,F10.2)
      Q(K)=X(1)*GAMALN(1)+X(2)*GAMALN(2)
      WRITE(2,935)  PP(K),(XX(K,J),J=1,NCOMP),(YY(K,J),J=1,NCOMP)
      WRITE(3,931)  P,X(1),Y(1),GAMMA(1),GAMMA(2),GAMALN(1),GAMALN(2),Q(K
     1)
      WRITE(2,935)                GAMMA(1),GAMMA(2),GAMALN(1),GAMALN(2),Q(K
     1)
      WRITE(2,935)              GEMA(1),GEMA(2),GEMALN(1),GEMALN(2)
  931 FORMAT(5X,F8.2,4F8.4,3F10.4)
      WRITE(2,935)               GAMMA(1),GEMA(1),PDGMA(1),GAMMA(2),GEMA(2
     1),PDGMA(2)
C     WRITE(3,521)  X(1),X(2),GEMA(1),GEMA(2),GEMALN(1),GEMALN(2)
C     WRITE(3,925)  P,X(1),Y(1),GAMMA(1),GEMA(1),PDGMA(1),GAMMA(2),GEMA(2
C    1),PDGMA(2)
      GO TO 270
C 899 WRITE(3,520)  P,REO(1),REO(2),REO(3)
C     WRITE(3,520)  P,RAO(1),RAO(2),RAO(3)
C 899 WRITE(3,520)  P,X(1),X(2),X(3),Y(1),Y(2),Y(3)
  899 CONTINUE
      Q(K)=X(1)*GAMALN(1)+X(2)*GAMALN(2)+X(3)*GAMALN(3)
      WRITE(3,932)  X(1),X(2),GAMMA(1),GAMMA(2),GAMMA(3),
     1 GAMALN(1),GAMALN(2),GAMALN(3),Q(K)
```

```
      WRITE(2,935) PP(K),(XX(K,J),J=1,NCOMP),(YY(K,J),J=1,NCOMP)
      WRITE(2,935)          GAMMA(1),GAMMA(2),GAMMA(3),
     1 GAMALN(1),GAMALN(2),GAMALN(3),Q(K)
      WRITE(2,935)          GEMA(1),GEMA(2),GEMA(3),
     1GEMALN(1),GEMALN(2),GEMALN(3)
C     WRITE(3,521) X(1),X(2),GEMA(1),GEMA(2),GEMA(3),
C    1GEMALN(1),GEMALN(2),GEMALN(3)
  932 FORMAT(5X,4F8.4,5F10.4)
      WRITE(2,935)          GAMMA(1),GEMA(1),PDGMA(1),GAMMA(2),
     1   GEMA(2),PDGMA(2),GAMMA(3),GEMA(3)
      WRITE(2,935) PDGMA(3)
C     WRITE(3,926)    X(1),GAMMA(1),GEMA(1),PDGMA(1),GAMMA(2),
C    1   GEMA(2),PDGMA(2),GAMMA(3),GEMA(3),PDGMA(3)
  611 FORMAT(1H0,F10.2,2F10.3,10X,6F10.4//)
C     WRITE(3,600)T,P ,RATIO
C     DO 300 J=1,NCOMP
C 300 WRITE(3,610)COMPA(J),COMPB(J),X(J),YCAL(J),YY(K,J),GAMALN(J),
C    1    GAMMA(J),PVOL(J),PPVOL(J),PHI(J),PHIV(J),F(J),ITER
  600 FORMAT(3X,3HT= ,F8.2,5H  P= ,F10.4,8H  RATIO=,F8.4)
  610 FORMAT(27X,2A4,5F8.4,5F10.4,I5)
  270 IF(K-NOBS)223,650,850
  850 CONTINUE
      STAR=-1.0
      WRITE(2,510) STAR
C     WRITE(3,620)SSDY
  620 FORMAT (/ 10X,'ACCUM. SUM OF DEV. IN Y IS',E12.4//)
      IF(KK-10)280,30,30
  900 STOP
  500 FORMAT (3I5,F10.4)
  505 FORMAT(1H0,4X,2HPC,10X,2HVC,6X,2HTC,10X,1HW,7X,5HC1RKL,5X,5HC2RKL
     15X,5HMOLWT,4X,9HCOMPONENT//)
  510 FORMAT(4F8.4,     5F8.4,2A4)
  515 FORMAT(1H ,4F10.3,3F10.4,3X,2A4)
  516 FORMAT(1H , /1H ,16X,3HKIJ                    / )
  520 FORMAT(1F10.2,12F10.5)
C 521 FORMAT(5X,12F10.4)
C 521 FORMAT(5X,F10.2,F10.4,2F10.4,F10.2,2F10.4,F10.2,2F10.4,F10.2)
  521 FORMAT(5X,F10.2,F10.4,2F10.4,F10.4,2F10.4,F10.2,2F10.4,F10.2)
  530 FORMAT(1H ,6X,2I2,F10.3,2F10.4)
  562 FORMAT(45X,2A4,3F10.4)
  935 FORMAT(10F10.4)
      END
```

```
C       SUPPLIED BY S.D.CHANG
C       MODIFIED BY DAVID POON  (APRIL,1971).
C       EVALUATION OF BINARY AND TERNARY CONSTANTS FROM ACTIVITY COEFFICI
C       SUBROUTINE NEEDED : RKFIT.
        DIMENSION TITLE(20),P(90),X1(90),X2(90),X3(90),Y1(90),Y2(90),
       1Y3(90),GI(90),GII(90),GIII(90),Q12(50),Q23(50),Q31(50),EXCESS(90)
      6 READ(1,1,END=5)(TITLE(I),I=1,20)
      1 FORMAT(20A4)
        WRITE(3,9)(TITLE(I),I=1,20)
      9 FORMAT(1H1,20A4///)
C       READ(1,11)B12,C12,D12
C        READ(1,11)B23,C23,D23
C       READ(1,11)B31,C31,D31
     11 FORMAT(3F10.6)
C       WRITE(3,20)B12,C12,D12,B23,C23,D23,B31,C31,D31
     20 FORMAT(10X,'B12=',F10.4,'C12=',F10.4,'D12=',F10.4/10X,'B23=',F10.4
       1,'C23=',F10.4,'D23=',F10.4/10X,'B31=',F10.4,'C31=',F10.4,'D31= ',
       2F10.4///)
        WRITE(3,8)
      8 FORMAT(1H0,' J          P          X1          X2          Y1
       1 Y2          G1          GII          GIII          GE'///)
        I=1
C     4 READ(1,2)P(I),X1(I),X2(I),Y1(I),Y2(I),GI(I),GII(I),GIII(I),J
      4 READ(1,2)P(I),X1(I),X2(I),Y1(I),Y2(I),GI(I),GII(I),GIII(I)
C     2 FORMAT(F10.0,7F8.4,I1)
      2 FORMAT(8F10.4)
C       IF(J.EQ.1)GO TO 3
        IF(P(I).LE.0.0) GO TO 3
        X3(I)=1.0-X1(I)-X2(I)
        EXCESS(I)=X1(I)*GI(I)+X2(I)*GII(I)+(1.0-X1(I)-X2(I))*GIII(I)
C       Q12(I)=X1(I)*X2(I)*(B12+C12*(X1(I)-X2(I))+D12*(X1(I)-X2(I))**2)
C       Q23(I)=X2(I)*X3(I)*(B23+C23*(X2(I)-X3(I))+D23*(X2(I)-X3(I))**2)
C       Q31(I)=X3(I)*X1(I)*(B31+C31*(X3(I)-X1(I))+D31    *(X3(I)-X1(I))**2
        WRITE(3,7)I,P(I),X1(I),X2(I),Y1(I),Y2(I),GI(I),GII(I),GIII(I),
       1 EXCESS(I)
      7 FORMAT(1H ,I2,5X,F10.2,8F10.4)
        I=I+1
        GO TO 4
      3 N=I-1
        CALL RKFIT(TITLE,N,P,X1,X2,GI,GII,GIII,EXCESS,Q12,Q23,Q31)
        GO TO 6
      5 RETURN
        END
```

```
C       PROGRAM SUPPLIED BY S.D.CHANG
C       MODIFIED BY DAVID POON  (JULY 1970).
C       CORRELATION OF ACTIVITY COEFFICIENTS BY THE REDLICH-KISTER EQUATI
C       SUBROUTINES NEED  :  SOLVE,SECOND.
        DIMENSION GAMAI(50),GAMAII(50),A( 5,6),H(5,6),F(6)
        DIMENSION P(50),X(50),Y(50),GI(50),GII(50)
        DIMENSION TITLE(20)
        COMMON PCI,PCJ,VCI,VCJ,TCI,TCJ,WI,WJ,PI,PJ,VI,VJ,BI,BJ,R,BIJ,DIJ
     1    ,WIJ,PCIJ,TCIJ
      1 READ(1,102)(TITLE(I),I=1,20)
    102 FORMAT(20A4)
        DO 10 I=1,5
        DO 10 J=1,6
     10 H(I,J)=0.0
        WRITE(3,103)(TITLE(I),I=1,20)
    103 FORMAT(//1H1,20A4//)
        READ(1,101)NOBS,IJK,R
    101 FORMAT(2I5,F10.4)
        IF(NOBS.LE.0) GO TO 800
        IF(IJK.EQ.0) GO TO 2
        READ(1,100)TT,PJ,PI,VJ,VI,BI,BJ,DIJ
        BI=BI/62.4
        BJ=BJ/62.4
        DIJ=BIJ/62.4
        RT=R*TT
        IF(IJK.EQ.1) GO TO 2
        READ(1,100)PCI,VCI,TCI,WI
        READ(1,100)PCJ,VCJ,TCJ,WJ
        CALL SECOND(TT)
      2 DO 20 I=1,NOBS
        READ(1,100)P(I),X(I),Y(I),GI(I),GII(I)
        P(I)=P(I)/14.699
        IF(IJK.EQ.0) GO TO 3
        GI1=ALOG(Y(I)*P(I)/X(I)/PI)
        GI2=(BI-VI)*(P(I)-PI)/RT
        GI3=P(I)*DIJ*(1.0-Y(I))**2/RT
        GI(I)=GI1+GI2+GI3
        GJ1=ALOG((1.0-Y(I))*P(I)/(1.0-X(I))/PJ)
        GJ2=(BJ-VJ)*(P(I)-PJ)/RT
        GJ3=P(I)*DIJ*Y(I)**2/RT
        GII(I)=GJ1+GJ2+GJ3
      3 WRITE(3,104)P(I),X(I),Y(I),GI(I),GII(I)
    100 FORMAT(8F10.0)
        XIJ=X(I)*(1.-X(I))
        F(1)=-(2.0*X(I)-1.0)
        F(2)=6.0*XIJ-1.0
        F(3)=-F(1)*(8.0*XIJ-1.0)
        F(4)=F(1)*F(1)*(10.0*XIJ-1.0)
        F(5)=-F(1)**3*(12.0*XIJ-1.0)
        F(6)=GI(I)-GII(I)
C       F(6)=ALOG(GI(I)/GII(I))
        DO 20 L=1,5
        DO 20 J=L,6
     20 H(L,J)=H(L,J)+F(L)*F(J)
        DO 16 I=1,5
        DO 16 J=I,5
     16 H(J,I)=H(I,J)
        DO 12 I=1,NOBS
```

```
    6 GI(I)= EXP(GI(I))
   11 GII(I)= EXP(GII(I))
   12 CONTINUE
      NEQ=1
   17 DO 15 I=1,5
      DO 15 J=1,6
   15 A(I,J)=0.0
      NEQ1=NEQ+1
      DO 18 I=1,NEQ
      A(I,NEQ1)=H(I,6)
      DO 18 J=1,NEQ
   18 A(I,J)=H(I,J)
      CALL SOLVE(NEQ,A,INDIC)
      WRITE(3,103)(TITLE(I),I=1,20)
      WRITE(3,106)(A(I,NEQ1),I=1,NEQ)
  106 FORMAT(5X,4H B= ,F8.4,4H C= ,F8.4,4H D= ,F8.4,4H E= ,F8.4,4H F= ,
     1F8.4///)
      WRITE(3,105)
  105 FORMAT(3X,1HP,7X,1HX,7X,1HY,7X //)
      SSI=0.0
      SSJ=0.0
      SI=0.0
      SJ=0.0
      DO 30 I=1,NOBS
      FF=2.*X(I)-1.
      GAMAI(I)=(1.0-X(I))**2*(A(1,NEQ1)+A(2,NEQ1)*(2.0*FF+1.0)
     1    +A(3,NEQ1)*(3.0*FF+2.0)*FF+A(4,NEQ1)*(4.*FF+3.0)*FF**2
     3    +A(5,NEQ1)*(5.0*FF+4.0)*FF**3)
      GAMAII(I)=X(I)**2*(A(1,NEQ1)+A(2,NEQ1)*(2.*FF-1.)
     1    +A(3,NEQ1)*(3.*FF-2.)*FF+A(4,NEQ1)*(4.*FF-3.)*FF*FF
     2    +A(5,NEQ1)*(5.0*FF-4.0)*FF**3)
      AI= EXP(GAMAI(I))
      AII= EXP(GAMAII(I))
   46 DGI=  AI     -GI(I)
      DGJ=  AII    -GII(I)
      SSI=SSI+DGI*DGI
      SSJ=SSJ+DGJ*DGJ
      SI=SI+100.0*ABS(DGI/ GI(I))
      SJ=SJ+100.0*ABS(DGJ/GII(I))
      WRITE(3,104) P(I),X(I),Y(I),  AI    ,GI(I),DGI,   AII    ,GII(I),
     1    DGJ,GAMAI(I),GAMAII(I)
  104 FORMAT(1H ,F8.1,11F8.4)
   30 CONTINUE
      SSDI=(SSI/(NOBS-NEQ))**0.5
      SSDJ=(SSJ/(NOBS-NEQ))**0.5
      SDI=SI/NOBS
      SDJ=SJ/NOBS
      WRITE(3,300)SSDI,SSDJ,SDI,SDJ,NOBS,NEQ
  300 FORMAT(/1H ,55H ST.DEV.OF GAMMA VALUES OF THE 1ST & 2ND COMPONENTS
     1 ARE,F15.4,4H AND,F15.4/1H ,58H  AV.% DEV.OF GAMMA VALUES OF THE 1
     2ST & 2ND COMPONENTS ARE,F15.4,4H AND,F15.4/
     2                                    20H NO.OF OBSERVATION =,I5/
     1    31H NO. OF ADJUSTABLE PARAMETERS =,I5/)
      NEQ=NEQ1
      IF(NEQ.GT.5) GO TO 1
      GO TO 17
  800 RETURN
      END
```

```
C       PREDICT P-X-Y CURVE
C       MODIFIED REDLICH-KWONG EQUATION OF STATE IS USED
C       FOR MULTICOMPONENT  SYSTEMS CALCULATION
C       FROM THE PURE COMPONENT PROPERTIES
C       ONE OF THE COMPONENTS IS AT ITS HYPERCRITICAL STATE
C       WRITTEN BY CHU HSI ,CHEMICAL ENGINEERING DEPARTMENT, UNIV. OF OIC
C       SUBROUTINES SORT,CONRK, CUBEQN ARE SUPPLIED BY S.D.CHANG
C       FALSI-POSITION METHOD IS EMPLOYED
C       MAY 28,1971
C       MODIFIED BY DAVID EDUN  (SEPTEMBER,1971).
        DIMENSION PHI(5),X(5), F( 5),GAMMA(5),FREFFR(5),PVOL(5),Y(5),
       1 PC(5),VC(5),TC(5),W(5),C1RKV(5),C2RKV(5),C1RKL(5),C2RKL(5),
       2 AMOLWT(5),COMPA(5),COMPB(5),CORRV(5,5),CORRL(5,5),GAMALN(5),
       3 A(4),Z(3),TITLE(20),K(5),PCO(5),VCO(5),TCO(5),PHIV(5),FREF(5),
       4 PS(5),PP(50),XX(50,5),YY(50,5),YCAL(5),PPVOL(5),DC1DT(5),DC2DT(5
       5,YD(5),RATIO(5),VVL(80),ZZL(80),ZZV(80),YI(5),G(5),YO(5)
        DIMENSION EV(50,5),PDEV(50,5)
        DIMENSION DEV(50,5)
        DIMENSION VLM(50)
        DIMENSION FVLM(50)
        DIMENSION PDVLM(50)
        DIMENSION RKA(5,5),DVLM(50)
        COMMON   /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NONTUM,ZZZL, ZZZV
       1    /SECOND/ Z,A,MTYPE
  800   READ(1,5)(TITLE(I),I=1,19)
    6   FORMAT(1H1,19A4)
    5   FORMAT(     19A4)
        WRITE(3,6)(TITLE(I),I=1,19)
        READ(1,500)NCOMP,NONTUM,IJK,R
        IF(NCOMP.LE.0) GO TO 900
        WRITE(3,505)
        DO 210 I=1,NCOMP
        READ(1,510)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),
       1                                 COMPA(I),COMPB(I)
        C1RKV(I)=C1RKL(I)
        C2RKV(I)=C2RKL(I)
  210   WRITE(3,515)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),
       1                                 COMPA(I),COMPB(I)
        CORRL(NCOMP,NCOMP)=0.0
        NCOMP1=NCOMP-1
        WRITE(3,519)
  519   FORMAT(/10X,12HINPUT DATA :///4X,1HP,8X,2HX1,8X,2HX2,9X,1HT,7X,3HF
       11,7X,3HRB1,7X,3HRA2,7X,3HRB2//)
        DO 9 I=1,NCOMP1
        I1=I+1
        DO 9 J=I1,NCOMP
    9   READ(1,520)CORRL(I,J)
        READ(1,520) TTT,PSI,(YI(J),J=1,NCOMP)
        PSI=PSI/14.697
        PSII=PSI
C       PSI=PSI/760.
        I=0
   10   I=I+1
        SX=0.0
        SY=0.0
C       READ(1,520)TTT,PP(I),(XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
C     1 ,VVL(I)
        READ( 1,520) PP(I),(XX(I,J),J=1,NCOMP ),(YY(I,J),J=1,NCOMP )
```

```
     1,VVL(I)
       DO 15 J=1,NCOMP1
       SY=SY+YY(I,J)
  15   SX=SX+ XX(I,J)
       XX(I,NCOMP)=1.0-SX
       YY(I,NCOMP)=1.0-SY
       IF(R.LT.11.0) GO TO 16
C      PP(I)=PP(I)/760.
       PP(I)=PP(I)/14.697
  16   WRITE(3,520) PP(I),(XX(I,J),J=1,NCOMP ),(YY(I,J),J=1,NCOMP )
C     1 ,VVL(I)
       IF(PP(I).GE.0) GO TO 10
  20   NOBS=I-1
       READ(1,525)IJK,KIJ,CINI,CFIN
 525   FORMAT(2I5,2F10.4)
  30   KIJ=KIJ+1
       IF(KIJ.GE.2) GO TO 800
       WRITE(3,525)IJK,KIJ,CINI,CFIN
       K=0
       KK=0
       KK=20
 280   CONTINUE
       WRITE(3,6)(TITLE(I),I=1,19)
       KK=KK+1
       WRITE(3,516)
       DO 220 I=1,NCOMP1
       CORRL(I,I)=0.0
       I1=I+1
       DO 220 J=I1,NCOMP
       IF(KK.GE.20) GO TO 214
       CORRL(I,J)=CINI+(KK-1)*(CFIN-CINI)/10.
       PSI=PSII
 214   WRITE(3,530)I,J,CORRL(I,J)
       CORRL(J,I)=CORRL(I,J)
 220   CONTINUE
       K=0
       SDVLM=0.0
       SPDP=0.0
       SDP=0.0
       SDV=0.0
       SSYD=0.0
       IF(NONTUM.GT.1) GO TO 223
       DO 221 I=1,NCOMP
       PC(I)=PCO(I)
       VC(I)=VCO(I)
 221   TC(I)=TCO(I)
 120   T=TTT
       RT=R*T
       WRITE(3,6)(TITLE(I),I=1,19)
       IF(NCOMP.EQ.2) GO TO 534
       WRITE(3,531)
 531   FORMAT(///16X,2HX1,8X,3HDY1,7X,3HDY2,7X,3HDY3)
       GO TO 532
 534   WRITE(3,533)
 533   FORMAT(///16X,2HX1,8X,3HDY1,7X,3HDY2)
 532   CONTINUE
C      WRITE(3,535)
 535   FORMAT(///16X,2HX1,7X,4HPEXT,6X,4HPCAL,7X,2HDP,9X,3H%DP/)
```

```
223 CONTINUE
    NIP=0
    MIP=0
    P=PSI
    K=K+1
    ZZZV=ZZV(K)
    ZZZL=ZZL(K)
    DO 39 J=1,NCOMP
 39 PHIV(J)=1.0
 54 CONTINUE
    DO 40 J=1,NCOMP
 40 X(J)=XX(K,J)
 42 CALL SUPT(VL,PHI,PPVOL,C1RKL,C2RKL,CORRL,X,1,KIJ)
    JY=0
 63 IF(JY.GT.20) GO TO 61
    SUMY=0.
    DO 50 J=1,NCOMP
    Y(J)=PHI(J)*X(J)/PHIV(J)
    WRITE(3,600) Y(J)
 50 SUMY=SUMY+Y(J)
    IF(JY)60,45,60
 60 IF(ABS((SUMYO-SUMY)/SUMY).LE.0.0005) GO TO 61
 45 SUMYO=SUMY
    JY=JY+1
    DO 62 J=1,NCOMP
 62 Y(J)=Y(J)/SUMY
    CALLSUPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
    GO TO 63
 61 CONTINUE
    DY=SUMY-1.0
    IF(ABS(DY).LE.0.0001) GO TO 110
    IF(NIP.GT.100) GO TO 105
    IF(MIP.GT.20) GO TO 105
    IF(MIP)52,52,56
 52 IF(NIP.LE.0) GO TO 51
    IF((DY*DDY).LT.0.0) GO TO 55
 51 NIP=NIP+1
    IF(NIP-1)91,91,92
 91 POLD=P
    DDY=DY
    P=P+0.01
    GO TO 70
 92 SLOPE=(P-POLD)/(DY-DDY)
    DELP=SLOPE*DY
    IF(ABS(DELP)-1.0)79,79,78
 78 DELP=SIGN(1.0,DELP)
 79 POLD=P
    DDY=DY
    P=P-DELP
    GO TO 70
 56 IF((DY*DDY).LT.0.0)GO TO 55
    IF((DY*DYO).LT.0.0) GO TO 57
 55 IF(ABS((P-POLD)/P).LE.0.0001) GO TO 105
    PN=(DY*POLD-DDY*P)/(DY-DDY)
    GO TO 58
 57 IF(ABS((P-PO)/P).LE.0.0001) GO TO 105
    PN=(DY*PO-DYO*P)/(DY-DYO)
    GO TO 59
```

```
      58 PO=POLD
         DYO=DDY
      59 POLD=P
         DDY=DY
         P=PN
         MIP=MIP+1
      70 DO 53 J=1,NCOMP
      53 Y(J)=Y(J)/SUMY
         CALL SUPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
         GO TO 54
     105 IF(ABS(DY).LE.0.005) GO TO 110
      96 WRITE(3,601)
     110 P=P*14.697
         PP(K)=PP(K)*14.697
         DP=P-PP(K)
         PDP=ABS(DP)/PP(K) *100.
         SDP=SDP+ABS(DP)
         SPDP=SPDP+ABS(PDP)
C        WRITE(3,600) X(1),PP(K),P,DP,PDP
         PP(K)=PP(K)/14.697
C 600 FORMAT(/10X,F10.4,3F10.2,F10.2)
         DO 111 J=1,NCOMP
         SYD=0.0
         WRITE(3,600) Y(J)      ,YY(K,J)
         YD(J)=Y(J)-YY(K,J)
         SYD=SYD+ABS(YD(J))
         SSYD=SSYD+SYD
     111 CONTINUE
         IF (NCOMP.EQ.2) GO TO 992
         WRITE(3,600)X(1),YD(1),YD(2),YD(3)
         GO TO 991
     992 WRITE(3,600) X(1),YD(1),YD(2)
     991 CONTINUE
     600 FORMAT(/10X,8E10.4)
     902 FORMAT(/,12F10.3)
         DV=VL-VVL(K)
         SDV=SDV+ABS(DV)
C        WRITE(3,901)VL,VVL(K),DV
     901 FORMAT(15X,4HVL= ,F10.4,5HVVL= ,F10.4,4HDV= ,F10.4)
     610 FORMAT(10X,2A4,4E12.4,4F10.4,F3.4,2I5)
     601 FORMAT(1H0,37HFAILED TO CONVERGE, RESULTS BELOW ARE NOT RELIABLE
        1= SUMY IS MUCH DIFFERENT FROM UNITY)
         PSI=P
         PSI=PSI/14.697
         IF(K-NOBS) 223, 850,850
     850 CONTINUE
     903 FORMAT(/,10X,2F10.5)
         FNOBS=FLOAT(NOBS)
         IF(NCOMP.EQ.2) GO TO 999
         ASSYD=SSYD/3./FNOBS
         GO TO 998
     999 ASSYD=SSYD/2./FNOBS
     998 CONTINUE
         WRITE(3,620) ASSYD
         WRITE(3,620)FNOBS
         ASDP=SDP/NOBS
         ASPDP=SPDP/NOBS
C        WRITE(3,620) ASPDP
```

```
C       WRITE(3,620)SDP,SSYD,SDV
  620 FORMAT(//15X,'AVERAGE ABSOLUTE DEVIATION IN VAPOR COMPOSITION IS
     1 DY =',F7.4)
C 620 FORMAT(//15X,'AVERAGE ABSOLUTE PERCENTAGE DEVIATION IN PRESSURE
C     1',F10.2,'  %')
      IF(KK-11)280,30,30
   900 STOP
   500 FORMAT (3I5,F10.4)
   505 FORMAT(1H0,4X,2HPC,10X,2HVC,6X,2HTC,10X,1HW,7X,5HC1RKL,5X,5HC2RK
     15X,5HMOL WT,4X,9HCOMPONENT//)
   510 FORMAT(4F8.4,2F6.4,2A4)
   515 FORMAT(1H ,6E12.5,3X,2A4)
   516 FORMAT(1H , /1H ,10X,3HKIJ                    / )
   520 FORMAT(14F10.5)
   530 FORMAT(1H ,6X,2I2,F10.4,2F10.4)
       END
```

```
C       PROGRAM SUPPLIED BY P.YU
C       MODIFIED BY DAVID POON  (JANUARY,1972).
C       PREDICTION OF LIQUID-LIQUID EQUILIBRIUM
C       SUBROUTINES NEED  :  SNPT,CUBEQN,EQNRK.
C       INPUT OF DATA: TEMP. K, PRESSURE PSIA
C       INPUT OF DATA: BINARY SYSTEM ASSUMED XX(1,1)AND XX(1,2)  EQUAL
C       TO 0.0000
C      6 ,A2I(3),BI(3),AIRKL(3)
C      7 ,PP(10),BRKL(3)
C      8,PHI(3)
C      9 ,PHY1(3),PHY2(3)
C      9,J(3),XP(3)
C       R : GAS CONSTANT 10.73
C       CORRL(I,J) : TEMP. DEPENDENT
C       RKA(L,I)    : TEMP. DEPENDENT
C       RKB(L,I)    : TEMP. DEPENDENT
C       SOLVE THE SIMULTANEOUS NON-LINEAR EQUATION BY THE MODIFIED
C       FALSE POSITION METHOD
        DIMENSION PHV1(3),PHV2(3),X1(3),X2(3),X10(3),X20(3),PHI1(3),
       2 PHI2(3),Y1(3),Y2(3),   YP1(3),YP2(3),U1(3),U2(3)
       1 ,ARKL(3,3),BRKL(3),  RKA(10,3),RKB(10,3),WIJ(3,3),TCOIJ(3,3)
       2,TCIJ(3,3),C1RKL(3),C2RKL(3),PVOL(3),CORRL(3,3),ZC(3),LLV(10)
       3          , TC(3),PC(3),VC(3),WW(3),AM(3),VCC(3),TCC(3),PCC(3)
        DIMENSION A2I(3),BI(3),AIRKL(3),PP(10),BRKL(3),PHI(3),PHY1(3),PH
       1(3),U(3),XP(3)
       1 ,PHI1(3),PHI2(3)        ,DX1(3),DX2(3)
       1,SUMYN(10)
       4 ,XX(3,2),Q(3),G(4),D(3),E(3),ZZ(3),PHIV(3),RATIO(3)
        COMMON /FIRST/
       1                    TC,PC,VC,WW,AMOLWT,   P,R,NCOMP,NQNTUM
       2 ,T
        COMMON
       1 /SECOND/D,G,MTYPE
      11 READ(1,101) M
        IF(M.EQ.0) GO TO 800
        READ(1,102)(TC(I),I=1,M)
        READ(1,102)(PC(I),I=1,M)
        READ(1,102)(VC(I),I=1,M)
        READ(1,102)(AM(I),I=1,M)
        READ(1,102)(WW(I),I=1,M)
        READ(1,102)R,RR
        READ(1,115)CORRL(1,2),CORRL(2,3),CORRL(1,3)
C       DO 50 K=1,M
C  50   READ(1,115)(CORRL(K,I),I=1,M)
        L=1
        READ(1,103) LLV(L),PP(L)
  103   FORMAT(I6,F5.0)
        READ(1,110)(RKA(L,I),I=1,M),(RKB(L,I),I=1,M)
        DO 153 I=1,M
        C1RKL(I)= RKA(L,I)
        C2RKL(I)=RKB(L,I)
  153   ZC(I)=PC(I)*VC(I)/R/TC(I)
        P=PP(L)
        WRITE(3,403)
        WRITE(3,404)  (TC(I),PC(I),VC(I),AM(I),WW(I),ZC(I),I=1,M)
        WRITE(3,311)          R,RR
        WRITE(3,112)  CORRL(1,2),CORRL(2,3),CORRL(1,3)
        WRITE(3,112)  (C1RKL(I),I=1,3),(C2RKL(I),I=1,3)
```

```
      READ(1,102) T
      IF(P.LT.10) GO TO 33
   32 T=T*1.8
C     IF((T-124.0*1.8).GT.0.0) GO TO 29
   33 READ(1,102)(XX(I,1),I=1,3)
      READ(1,102)(XX(I,2),I=1,3)
      XX(3,1)=1.0-XX(1,1)-XX(2,1)
      XX(3,2)=1.0-XX(1,2)-XX(2,2)
      GO TO 338
   29 READ(1,102)(XX(I,2),I=1,3)
      READ(1,102)(XX(I,1),I=1,3)
      XX(3,1)=1.0-XX(1,1)-XX(2,1)
      XX(3,2)=1.0-XX(1,2)-XX(2,2)
  333 WRITE(3,112)(XX(I,1),I=1,3),(XX(I,2),I=1,3)
      WRITE(2,600)P,T,(XX(I,1),I=1,3),(XX(I,2),I=1,3)
C     WRITE(2,911) P,T,(XX(I,1),I=1,3),(XX(I,2),I=1,3)
  911 FORMAT(2F10.1,6F10.4)
  331 WRITE(3,110)P       ,T
      KIJ=0
      SUMY1=0.0
      SUMY2=0.0
  333 P=PP(L)
      DO 80 I=1,3
      PHV1(I)=1.0
      PHV2(I)=1.0
      PHY1(I)=1.0
      PHY2(I)=1.0
      PHT1(I)=1.0
      PHT2(I)=1.0
      X1(I)=XX(I,1)
   80 X2(I)=XX(I,2)
C  86 DO 82 LJK=1,50
   86 DO 82 LJK=1,20
      P01=P
      SUMY2=SUMY1
      DO 81 I=1,3
      X10(I)=X1(I)
   81 X20(I)=X2(I)
      CALL SNPT(VL,PHI1 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X1)
      CALL SNPT(VL,PHI2 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X2)
      IF(X2(1).EQ.0.0000) GO TO 90
   94 DO 30 I=1,3
      PHY1(I)=PHI1(I)*X1(I)
   30 PHY2(I)=PHI2(I)*X2(I)
      DO 40 I=1,3
      U1(I)=(PHY2(I)/PHY1(I))*X1(I)
   40 U2(I)=(PHY1(I)/PHY2(I))*X2(I)
      GO TO 68
   90 DO 98 I=2,3
      PHY1(I)=PHI1(I)*X1(I)
   98 PHY2(I)=PHI2(I)*X2(I)
      U1(1)=0.0
      U2(1)=0.0
      DO 92 I=2,3
      U1(I)=(PHY2(I)/PHY1(I))*X1(I)
   92 U2(I)=(PHY1(I)/PHY2(I))*X2(I)
   68 SUMU1=0.0
      DO 60 I=1,3
```

```
      60 SUMU1=SUMU1+U1(I)
         DO 61 I=1,3
      61 X1(I)=(U1(I)/SUMU1+X10(I))/2.0
         SUMU2=U2(2)+U2(3)
         BATA=(1.0-X2(1))/SUMU2
         X2(2)=(BATA*U2(2)+X20(2))/2.0
         X2(3)=(BATA*U2(3)+X20(3))/2.0
         SUMXY1=0.0
         SUMXY2=0.0
         IF(T.LT. 400) GO TO 400
         DO 401 I=1,3
         CALL SNPT(VL,PHI1 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X1)
         CALL SNPT(VL,PHI2 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X2)
         PHT1(I)=PHI1(I)*X1(I)
         PHT2(I)=PHI2(I)*X2(I)
         SUMXY1=SUMXY1+(ABS(PHY1(I)-PHT1(I))          )
     401 SUMXY2=SUMXY2+(ABS(PHY2(I)-PHT2(I)))
         DL=(SUMXY1+SUMXY2)/ 5.0
         IF(DL. LT. 0.001) GO TO 201
         GO TO 86
     400 DO 91 I=1,3
         CALL SNPT(VL,PHI1 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X1)
         CALL SNPT(VL,PHI2 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X2)
         PHT1(I)=PHI1(I)*X1(I)
         PHT2(I)=PHI2(I)*X2(I)
         SUMXY1=SUMXY1+(ABS(PHY1(I)-PHT1(I))          )
      91 SUMXY2=SUMXY2+(ABS(PHY2(I)-PHT2(I)))
         DL=(SUMXY1+SUMXY2)/ 5.0
         IF(DL.LT.0.0001) GO TO 201
      82 CONTINUE
     201 DO 44 LIJ=1,15
C        IF((T-400).GT.0.0) GO TO 25
C 600 IF((T-124.0*1.8).GT.0.0) GO TO 27
      25 DO 23 I=1,3
      23 Y1(I)=PHI2(I)*X2(I)/PHV1(I)
C     27 DO  28 I=1,3
C     28 Y1(I)=PHI1(I)*X1(I)/PHV1(I)
         SUMY1=0.0
         DO 24 I=1,3
      24 SUMY1=SUMY1+Y1(I)
       7 DO 45 I=1,3
      45 Y1(I)=Y1(I)/SUMY1
         CALL SNPT(VL,PHV1,PVOL,C1RKL,C2RKL,CORRL,0,KIJ,Y1)
      44 CONTINUE
         IF (SUMY1.EQ.1.0000) GO TO 910
     190 IF(P.LT.1.0) GO TO 910
      89 PU=P/SUMY1
         PO=P-PU
         IF(PO-0.1 ) 71,70,72
      71 P=P-0.3*(ABS(PO))
      84 DP=P01-P
         IF(SUMY1.LT.1.0000) GO TO 903
         IF(DP.LT.0.3 ) GO TO 922
     903 P=P-0.1
     930 GO TO 86
     922 PUU=P01
         PLL=P
         WRITE(3,120)PUU,PLL, SUMY1,SUMY2
```

```
      DO 908 J=1,5
      PSU=PUU*(SUMY1-1.0000)
      PSL=PLL*(SUMY2-1.0000)
      SUMY12=SUMY1-SUMY2
      P02=(PSU-PSL)/SUMY12
      PUU=P02
  908 CONTINUE
      GO TO 910
   70 GO TO 910
   72 P=P+0.3*P0
   85 DP=P01-P
      IF(SUMY2.GT.1.0000) GO TO 904
      IF(DP.LT.0.3) GO TO 923
  904 P=P+0.1
  920 GO TO 86
  923 PUU=P
      PLL=P01
      WRITE(3,120)PUU,PLL, SUMY1,SUMY2
      DO 918 J=1,5
      PSU=PUU*(SUMY2-1.0000)
      PSL=PLL*(SUMY1-1.0000)
      SUMY12=SUMY2-SUMY1
      P02=(PSU-PSL)/SUMY12
      PUU=P02
  918 CONTINUE
      GO TO 910
  910 T=T/1.3
      WRITE(2,600) P,T,(X1(I),I=1,3),(X2(I),I=1,3)
C     WRITE(2,911) P,T,(X1(I),I=1,3),(X2(I),I=1,3)
      WRITE(3,110) P,T,(X1(I),I=1,3),(X2(I),I=1,3)    ,P02
      WRITE(3,119)
      DO 77 I=1,3
      DX1(I)=XX(I,1)-X1(I)
   77 DX2(I)=XX(I,2)-X2(I)
      DP=P-PP(1)
      WRITE(3,120)DP, (DX1(I),I=1,3),(DX2(I),I=1,3)
      WRITE(2,600) DP,T,(DX1(I),I=1,3),(DX2(I),I=1,3)
  600 FORMAT(2F12.2,6F10.4)
      WRITE(3,112)(Y1(I),I=1,3)
C     WRITE(2,222)(Y1(I),I=1,3)
  222 FORMAT(3F10.4)
      WRITE(3,500) P,T,(X1(I),I=1,3),(X2(I),I=1,3)
      WRITE(3,501) P,T,(XX(I,1),I=1,3),(XX(I,2),I=1,3)
  500 FORMAT(///5X,2F10.2,6F14.6)
  501 FORMAT(/5X,2F10.2,6F14.6)
      GO TO 11
  110 FORMAT(2F12.1,6F12.4,F12.1)
  101 FORMAT(318)
  311 FORMAT(10X,'R=',F8.3,'RR=',F8.3)
  403 FORMAT(1H1,//13X,'TC',5X,'PC',5X,'VC',6X,'M',
     16X,'W',6X,'ZC',/)
  404 FORMAT(10X,2F7.1,F7.3,F7.2,2F8.4)
  102 FORMAT(8F8.0)
  115 FORMAT(6F10.0)
  116 FORMAT(6F10.0)
  112 FORMAT(6F12.4)
  120 FORMAT(F12.1,6F12.4)
  119 FORMAT(//9X,'DP',
     1          9X,'DX1',9X,'DX2',9X,'DX3',9X,'DX1',
     1 9X,'DX2',9X,'DX3',/)
  989 FORMAT(/5X,10E12.5)
  800 STOP
      END
```

```
C  EVALUATION OF R-K PARAMETERS FROM MOLAR VOLUME DATA
C      MODIFIED BY DAVID POON  (SEPTEMBER,1971).
C      SUBROUTINE USED :  SUPT,CUBEQN.
C      PREDICT P-X-Y CURVE
C      MODIFIED REDLICH-KWONG EQUATION OF STATE IS USED
C      FOR MULTICOMPONENT  SYSTEMS CALCULATION
C      FROM THE PURE COMPONENT PROPERTIES
C      ONE OF THE COMPONENTS IS AT ITS HYPERCRITICAL STATE
C      WRITTEN BY CHU HSI ,CHEMICAL ENGINEERING DEPARTMENT, UNIV. OF OTT
C      SUBROUTINES SUPT,EQNRK, CUBEQN ARE SUPPLIED BY S.C.CHANG
C      FALSI-POSITION METHOD IS EMPLOYED
C      MAY 28,1971
       DIMENSION PHI(5),X(5), F( 5),GAMMA(5),FREFER(5),PVOL(5),Y(5),
      1 PC(5),VC(5),TC(5),W(5),C1RKV(5),C2RKV(5),C1RKL(5),C2RKL(5),
      2 AMOLWT(5),COMPA(5),COMPB(5),CORRV(5,5),CORRL(5,5),GAMALN(5),
      3 A(4),Z(3),TITLE(20),D(5),PCO(5),VCO(5),TCO(5),PHIV(5),FREF(5),
      4 PS(5),PP(80),XX(80,5),YY(80,5),YCAL(5),PPVOL(5),DC1DT(5),DC2DT(5
      5,YD(5),RATIO(5),VVL(80),ZZL(80),ZZV(80),YI(5),G(5),YD(5)
       DIMENSION EV(50,5),PDEV(50,5)
       DIMENSION DEV(50,5)
       DIMENSION VLM(50)
       DIMENSION EVLM(50)
       DIMENSION PDVLM(50)
       DIMENSION RKA(5,5),DVLM(50)
       COMMON  /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM,ZZZL,ZZZV
      1    /SECOND/ Z,A,MTYPE
  800  READ(1,5)(TITLE(I),I=1,19)
    6  FORMAT(1H1,19A4)
    5  FORMAT(     19A4)
       WRITE(3,6)(TITLE(I),I=1,19)
       READ(1,500)NCOMP,NQNTUM,IJK,R
       IF(NCOMP.LE.0) GO TO 900
       WRITE(3,505)
       DO 210 I=1,NCOMP
       READ(1,510)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),
      1                                 COMPA(I),COMPB(I)
       C1RKV(I)=C1RKL(I)
       C2RKV(I)=C2RKL(I)
  210  WRITE(3,515)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),
      1                                 COMPA(I),COMPB(I)
       CORRL(NCOMP,NCOMP)=0.0
       NCOMP1=NCOMP-1
       WRITE(3,519)
  519  FORMAT(/10X,12HINPUT DATA ://4X,1HP,8X,2HX1,8X,2HX2,9X,1HT,7X,3HR
      11,7X,3HRB1,7X,3HRA2,7X,3HRB2//)
       DO 9 I=1,NCOMP1
       II=I+1
       DO 9 J=II,NCOMP
    9  READ(1,520)CORRL(I,J)
       READ(1,520) TTT,PSI,(YI(J),J=1,NCOMP)
       PSI=PSI/14.697
       PSII=PSI
       I=0
   10  I=I+1
       SX=0.0
       SY=0.0
       READ( 1,520) PP(I),(XX(I,J),J=1,NCOMP ),(YY(I,J),J=1,NCOMP )
      1,VVL(I)
```

```
      READ(1,520) (EV(I,J),J=1,NCOMP) ,EVLM(I)
      DO 15 J=1,NCOMP1
      SY=SY+YY(I,J)
   15 SX=SX+ XX(I,J)
      XX(I,NCOMP)=1.0-SX
      YY(I,NCOMP)=1.0-SY
      IF(R.LT.11.0) GO TO 16
      PP(I)=PP(I)/14.697
   16 WRITE(3,520) PP(I),(XX(I,J),J=1,NCOMP ),(YY(I,J),J=1,NCOMP )
      IF(PP(I).GE.0) GO TO 10
   20 NOBS=I-1
      READ(1,525)IJK,KIJ,CINI,CFIN
  525 FORMAT(2I5,2F10.4)
      JJ=0
   30 KIJ=KIJ+1
      IF(KIJ.GE.2) GO TO 800
      WRITE(3,525)IJK,KIJ,CINI,CFIN
      K=0
      KK=0
      KK=20
  280 CONTINUE
      WRITE(3,6)(TITLE(I),I=1,19)
      KK=KK+1
      WRITE(3,516)
      DO 220 I=1,NCOMP1
      CORRL(I,I)=0.0
      I1=I+1
      DO 220 J=I1,NCOMP
      IF(KK.GE.20) GO TO 214
      CORRL(I,J)=CINI+(KK-1)*(CFIN-CINI)/10.
      PSI=PSII
  214 WRITE(3,530)I,J,CORRL(I,J)
      CORRL(J,I)=CORRL(I,J)
  220 CONTINUE
   31 JJ=JJ+1
      IF(JJ.GT.11) GO TO 800
      DO 35 L=1, NOBS
      RKA(L,1)=CINI+(JJ-1)*(CFIN-CINI)/10.0
      C2RKL(2)=RKA(L,1)
   35 CONTINUE
      K=0
      SDVLM=0.0
      SDP=0.0
      SDV=0.0
      SSYD=0.0
      IF(NQNTUM.GE.1) GO TO 223
      DO 221 I=1,NCOMP
      PC(I)=PCO(I)
      VC(I)=VCO(I)
  221 TC(I)=TCO(I)
  120 T=TTT
      RT=R*T
      WRITE(3,535)
  535 FORMAT(/5X,1HX,9X,4HEPV1,5X,3HPV1,6X,4HDEV1,7X,5H%DEV1,5X,
     1 4HEPV2,8X,3HPV2,8X,4HDPV2,5X,4H%DV2,5X,3HVLM,8X,4HEVLM,
     2 7X,5H%DVLM)
  223 CONTINUE
      NIP=0
```

```
      MIP=0
      P=PSI
      K=K+1
      ZZZV=ZZV(K)
      ZZZL=ZZL(K)
      DO 39 J=1,NCOMP
   39 PHIV(J)=1.0
   54 CONTINUE
      DO 40 J=1,NCOMP
   40 X(J)=XX(K,J)
   42 CALL SUPT(VL,PHI,PPVOL,C1RKL,C2RKL,CORRL,X,1,KIJ)
      JY=0
   63 IF(JY.GT.20) GO TO 61
      SUMY=0.
      DO 50 J=1,NCOMP
      Y(J)=PHI(J)*X(J)/PHIV(J)
   50 SUMY=SUMY+Y(J)
      IF(JY)60,45,60
   60 IF(ABS((SUMYO-SUMY)/SUMY).LE.0.0005) GO TO 61
   45 SUMYO=SUMY
      JY=JY+1
      DO 62 J=1,NCOMP
   62 Y(J)=Y(J)/SUMY
      CALLSUPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
      GO TO 63
   61 CONTINUE
      DY=SUMY-1.0
      IF(ABS(DY).LE.0.0001) GO TO 110
      IF(NIP.GT.100) GO TO 105
      IF(NIP.GT.20) GO TO 105
      IF(MIP)52,52,56
   52 IF(NIP.LE.0) GO TO 51
      IF((DY*DDY).LT.0.0) GO TO 55
   51 NIP=NIP+1
      IF(NIP-1)91,91,92
   91 POLD=P
      DDY=DY
      P=P+0.01
      GO TO 70
   92 SLOPE=(P-POLD)/(DY-DDY)
      DELP=SLOPE*DY
      IF(ABS(DELP)-1.0)79,79,78
   78 DELP=SIGN(1.0,DELP)
   79 POLD=P
      DDY=DY
      P=P-DELP
      GO TO 70
   56 IF((DY*DDY).LT.0.0)GO TO 55
      IF((DY*DYO).LT.0.0) GO TO 57
   55 IF(ABS((P-POLD)/P).LE.0.0001) GO TO 105
      PN=(DY*POLD-DDY*P)/(DY-DDY)
      GO TO 58
   57 IF(ABS((P-PO)/P).LE.0.0001) GO TO 105
      PN=(DY*PO-DYO*P)/(DY-DYO)
      GO TO 59
   58 PO=POLD
      DYO=DDY
   59 POLD=P
```

```
      DDY=DY
      P=PN
      MIP=MIP+1
   70 DO 53 J=1,NCOMP
   53 Y(J)=Y(J)/SUMY
      CALL SUPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
      GO TO 54
  105 IF(ABS(DY).LE.0.005) GO TO 110
   96 WRITE(3,601)
  110 P=P*14.697
      PP(K)=PP(K)*14.697
      DP=P-PP(K)
      SDP=SDP+ABS(DP)
      PP(K)=PP(K)/14.697
  600 FORMAT(3X,3HT= ,F8.2,5H  P= ,F10.4,7HPP(K)= ,F10.4,4HDP= ,F10.4)
      SYD=0.0
      DO 111 J=1,NCOMP
      YD(J)=Y(J)-YY(K,J)
      SYD=SYD+ABS(YD(J))
      SSYD=SSYD+SYD
      DEV(K,J)=( ABS(EV(K,J))-ABS(PPVOL(J)))
  111 PDEV(K,J)=( ABS(EV(K,J))-ABS(PPVOL(J)))/ABS(EV(K,J))*100.
      VL1(K)=X(1)*PPVOL(1)+X(2)*PPVOL(2)
      DVLM(K)=EVL1(K)-VLM(K)
      SDVLM=SDVLM+ABS(DVLM(K))
      PDVLM(K)=( ABS(EVL1(K))-ABS(VLM(K)))/ABS(EVLM(K))*100.0
      WRITE(3,902) X(1),EV(K,1),PPVOL(  1),DEV(K,1),PDEV(K,1)
     1,EV(K,2),PPVOL(2),DEV(K,2),PDEV(K,2),VLM(K) ,EVLM(K),PDVLM(K)
  902 FORMAT(/,12F10.3)
      DV=VL-VVL(K)
      SDV=SDV+ABS(DV)
  901 FORMAT(15X,4HVL= ,F10.4,5HVVL= ,F10.4,4HDV= ,F10.4)
  610 FORMAT(10X,2A4,4E12.4,4F10.4,F8.4,2I5)
  601 FORMAT(1H0,87HFAILED TO CONVERGE, RESULTS BELOW ARE NOT RELIABLE
     1IF SUMY IS MUCH DIFFERENT FROM UNITY)
      PSI=P
      PSI=PSI/14.697
      IF(K-NO3S) 223, 850,850
  850 CONTINUE
      WRITE(3,903) C1RKL(1),C2RKL(1),C1RKL(2),C2RKL(2)
      WRITE(3,903) SDVLM
  903 FORMAT(/,10X,2F10.5)
  620 FORMAT(/10X,'ACCUM. SUM OF DEV. IN P IS ',E12.4,'ACCUM. SUM OF
     1DEV. IN Y IS ',E12.4,'SDV IS ',E12.4/)
      IF(KK-11)280,31,31
  900 STOP
  500 FORMAT (3I5,F10.4)
  505 FORMAT(1H0,4X,2HPC,10X,2HVC,6X,2HTC,10X,1HW,7X,5HC1RKL,5X,5HC2RKL
     15X,5HMOLWT,4X,9HCOMPONENT//)
  510 FORMAT(4F8.4,2F8.4,2A4)
  515 FORMAT(1H ,6E12.5,3X,2A4)
  516 FORMAT(1H , /1H ,16X,3HKIJ                    / )
  520 FORMAT(14F10.5)
  530 FORMAT(1H ,6X,2I2,F10.4,2F10.4)
      END
```

```
      SUBROUTINE RK  (PC,VC,TC,W,C1RKL,C2RKL,C3RKL,NCOMP,CORRL,Y,ET)
C     DAVID POON, OCTOBER,1971.
C     SUBROUTINE FOR THE CALCULATION OF CRITICAL LOCI FOR BINARY MIXTURES
C     REDLICH-KWONG OR MODIFIED REDLICH-KWONG EQUATION OF STATE IS USED
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION  A(5,5),B(5,5), C1RKL(5),C2RKL(5),TC(5),PC(5),VC(5),
     1   TCIJ(5,5),WIJ(5,5),W(5),Y(5 ),CORRL(5,5) ,TITLE(19),
     2 C1RKV(5),C2RKV(5),C3RKL(5)
      DIMENSION VV(50),C(5,5)
   91 DO 100 I=1,2
      A(I,I)=C1RKL(I)*R*R*(TC(I)**2.5)/PC(I)
  100 B(I,I)=C2RKL(I)*R*TC(I)/PC(I)
      I=1
      I1=I+1
      DO 102 J=I1,2
      TCIJ(I,J)=( TC(I)*TC(J) ) **0.5D0*(1.0D0-CORRL(I,J) )
      TCIJ(J,I)=TCIJ(I,J)
      WIJ(I,J)=( W(I)+W(J) )*0.5D0
      ZCIJ=0.291D0-0.08DC*WIJ(I,J)
      VCIJ=(VC(I)**(1.D0/3.D0)+VC(J)**(1.D0/3.D0))**3/8.0D0
      PCIJ=ZCIJ*R*TCIJ(I,J)/VCIJ
      A(I,J)=( C1RKL(I)+C1RKL(J) )*0.5D0*R*R*(TCIJ(I,J)**2.5)/PCIJ
      B(I,J)=( C2RKL(I)+C2RKL(J) )*0.5D0*R*TCIJ(I,J)/PCIJ
      A(J,I)=A(I,J)
  102 B(J,I)=B(I,J)
  902 T=T+DT
      IF(T.GT.ET) GO TO 800
      WRITE(3,201) T
  201 FORMAT(/1H /,8X,4D20.9)
      DO 801 I=1,40
      V=VV(I)
      RT=R*T
      Y1=Y(1)
      Y2=Y(2)
      A11=A(1,1)
      A22=A(2,2)
      A12=A(1,2)
      B11=B(1,1)
      B22=B(2,2)
      B12=B(1,2)
      AM=Y1**2*A11  +  Y2**2*A22  +  2.0D0*Y1*Y2*A12
      BM=Y1**2*B11  +  Y2**2*B22  +  2.0D0*Y1*Y2*B12
      F1=V+BM
      F2=V-BM
      F3=B11+B22-2.0D0*B12
      F4=A11+A22-2.0D0*A12
      F5=Y1*B11+Y2*B12-Y1*B12-Y2*B22
      F6=Y1*A11+Y2*A12-Y1*A12-Y2*A22
      F7=DSQRT(T)
      BIGA=-2.0D0*RT*F3/F2-4.0D0*RT*F5*F5/(F2)**2+(2.0D0*AM/(F7))*F3
     1    *(1.0D0/BM/F1-1.0D0/(BM)**2*DLOG(F1/V) )
     2  -8.0D0*AM/F7/((BM)**3)*F5**2*((V+2.0D0*BM)**2/2.D0/F1**2-.5D0
     3   -DLOG ( F1/V) )
     4   +2.0D0/F7/BM*F4*DLOG(F1/V)
     5    +8.0D0/F7*F5*F6*(1.D0/BM/F1-1.D0/(BM)**2*DLOG(F1/V))
      BIGB= 2.0D0*RT/(F2)**2*F5+2.D0*AM/F7/V/F1**2*F5-2.D0/F7/V/F1*F6
      BIGC= -RT/(F2)**2 +AM/F7/V/(F1)**2 +AM/( F7*V**2*F1)
      DAADY=2.0D0*F6
```

```
      D2AADY=2.0D0*F4
      D3BDY=2.0D0*F5
      D2BBDY=2.0D0*F3
      DVDY=-(BIGB)/(BIGC)
      D3DY= RT/(F2)**2*(D2BBDY) -2.0D0*RT/(F2)**3 *(DBBDY)
     1    *( (DVDY) -(DBBDY) )+1.D0/(F7*V*(F1)**2)*(DAADY)*(DBBDY)
     2    +AM/( F7*V*(F1)**2 ) *(D2BBDY)-2.D0*AM/( F7*V*(F1)**3 ) *DBBD
     4    *( (DVDY)+(DBBDY) ) -AM/( F7*V*V*(F1)**2) *(DBBDY)*(DVDY)
     5   -1.D0/( F7*V*(F1) ) *D2AADY+1.D0/( F7*V*V*F1) *(DAADY)*(DVDY)
     6   +1.D0/(F7*V*(F1)**2) *(DAADY)*( (DVDY)+(DBBDY) )
      DCDY=2.D0*RT/(F2)**3 *( (DVDY)-(DBBDY) )+1.D0/( F7*V*(F1)**2 )
     1    *(DAADY) -AM/( F7*V*V*(F1)**2 ) *(DVDY)-2.D0*AM/( F7*V*(F1)**
     2    *( (DVDY)+(DBBDY) ) +1.D0/(F7*V*V*F1) *(DAADY)-2.D0*AM/
     3    (F7*V**3*F1) *(DVDY) -AM/( F7*V*V*(F1)**2) *((DVDY)+(DBBDY) )
      D2VDY=-(D3DY)/(BIGC) +(DCDY)*(BIGB)/(BIGC)**2
      EIGD=-3.D0*RT/(F2)**2*(DBBDY)*(D2BBDY)-2.D0*RT/(F2)**3 *(DBBDY)*
     1   +3.D0/F7/BM *(DAADY)*(D2BBDY)*(1.D0/F1-1.D0/BM*DLOG(F1/V) )
     2-6.D0*AM/F7/(BM)**3*(DBBDY)*(D2BBDY)*((V+2.D0*BM)**2/2.D0/(F1)**
     3-.5D0-DLOG(F1/V))-6.D0/(F7*BM**3)*DAADY*DBBDY**2*((V+2.D0*BM)**2
     4 /2.D0/(F1)**2- .5D0-DLOG(F1/V))
      E=6.D0*AM/F7/BM*(DBBDY)**3*(1.D0/(3.D0*(F1)**3)+1.D0/(BM)**3
     7   *( (V+2.D0*BM)**2/2.D0/(F1)**2 -DLOG(F1/V)))
     8   +3.D0/F7/BM *(DBBDY)*(D2AADY)*(1.D0/F1-1.D0/BM *DLOG(F1/V) )
      BIGD=EIGD+E
      BIGE=RT/(F2)**2 *(D2BBDY) +2.D0*RT/(F2)**3 *(DBBDY)**2
     1    +AM/( F7*V*(F1)**2 ) *(D2BBDY)-2.D0*AM/( F7*V*(F1)**3 )*(DBBD
     3    **2+2.D0/( F7*V*(F1)**2 ) *(DBBDY)*(DAADY)
     4   -1.D0/( F7*V*F1) *(D2AADY)
      BIGG=-2.D0*RT/(F2)**3*(DBBDY) -AM/( F7*V*V*(F1)**2 )*(DBBDY)
     1   -2.D0*AM/( F7*V*(F1)**3 ) *(DBBDY)+1.D0/( F7*V*V*F1 ) *
     2    (DAADY) +1.D0/( F7*V*(F1)**2 ) *(DAADY)
      HRS10=RT/(Y1*Y2)
      HLS10=(BIGA)-(BIGB)**2/(BIGC)
      HRS11=RT*(Y1-Y2)/(Y1*Y2)**2
      HLS11=BIGD +2.D0*(BIGE)*(DVDY)+(BIGG)*(DVDY)**2+(BIGB)*(D2VDY)
      DD=(HLS10)-(HRS10)
      DS=(HLS11)-(HRS11)
  801 WRITE(3,200) V,DD,DS
      GO TO 902
  900 STOP
  200 FORMAT(5X,5D20.9)
  500 FORMAT(3I5,F10.4)
  901 RETURN
      END
```

```
      SUBROUTINE CLAUS (PC,VC,TC,W,C1RKL,C2RKL,C3RKL,NCOMP,CORRL,Y,ET)
C     DAVID POON, OCTOBER,1971.
C     SUBROUTINE FOR THE CALCULATION OF CRITICAL LOCI FOR BINARY MIXTURES
C     THE CLAUSIUS EQUATION OF STATE IS USED
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(5,5),B(5,5), C1RKL(5),C2RKL(5),TC(5),PC(5),VC(5),
     1    TCIJ(5,5),WIJ(5,5),W(5),Y(5 ),CORRL(5,5) ,TITLE(19),
     2 C1RKV(5),C2RKV(5),C3RKL(5)
      DIMENSION VV(50),C(5,5)
   91 DO 100 I=1,2
      A(I,I)=C1RKL(I)*R*R*(TC(I)**3)/PC(I)
      B(I,I)=VC(I)-R*TC(I)/PC(I)*C2RKL(I)
  100 C(I,I)=C3RKL(I)*R*TC(I)/PC(I)-VC(I)
      I=1
      II=I+1
      DO 102 J=II,2
      TCIJ(I,J)=( TC(I)*TC(J) ) **0.5D0*(1.0D0-CORRL(I,J) )
      TCIJ(J,I)=TCIJ(I,J)
      WIJ(I,J)=( W(I)+W(J) )*0.5D0
      ZCIJ=0.291D0-0.08D0*WIJ(I,J)
      VCIJ=(VC(I)**(1.D0/3.D0)+VC(J)**(1.D0/3.D0))**3/8.0D0
      PCIJ=ZCIJ*R*TCIJ(I,J)/VCIJ
      A(I,J)=( C1RKL(I)+C1RKL(J) )*0.5D0*R*R*(TCIJ(I,J)**3 )/PCIJ
      B(I,J)=VCIJ-R*TCIJ(I,J)/PCIJ*((C2RKL(I)+C2RKL(J))*0.5D0)
      C(I,J)=(C3RKL(I)+C3RKL(J))*0.5D0*R*TCIJ(I,J)/PCIJ-VCIJ
      A(J,I)=A(I,J)
      B(J,I)=B(I,J)
  102 C(J,I)=C(I,J)
  902 T=T+DT
      IF(T.GT.ET) GO TO 800
      WRITE(3,201) T
      DO 801 I=1,20
      V=VV(I)
      RT=R*T
      Y1=Y(1)
      Y2=Y(2)
      A11=A(1,1)
      A22=A(2,2)
      A12=A(1,2)
      B11=B(1,1)
      B22=B(2,2)
      B12=B(1,2)
      C11=C(1,1)
      C22=C(2,2)
      C12=C(1,2)
      AM=Y1**2*A11 + Y2**2*A22 + 2.0D0*Y1*Y2*A12
      BM=B11*Y1+B22*Y2
      CM=C11*Y1+C22*Y2
      F1=V+BM
      F2=V-BM
      F3=B11+B22-2.0D0*B12
      F4=A11+A22-2.0D0*A12
      F5=Y1*B11+Y2*B22-Y1*B12-Y2*B22
      F6=Y1*A11+Y2*A12-Y1*A12-Y2*A22
      F7=DSQRT(T)
      F8=Y1*C11-Y2*C22+Y2*C12-Y1*C12
      F9=C11+C22-2.0D0*C12
      F10=V+CM
```

```
      DAADY=2.0D0*F6
      D2AADY=2.0D0*F4
      DBBDY=B11-B22
      DCCDY=C11-C22
      D2BBDY=0.0D0
      D2CCDY=0.0D0
      BIGA  =  -RT*(DBBDY)**2/(F2)**2  +(D2AADY)/T/(F10)-2.0D0*(DAADY)
     1   (DCCDY)/T/(F10)**2  +2.0D0*AM*(DCCDY)**2/T/(F10)**3
      BIGB=RT/(F2)**2*(DBBDY)-1.0D0/T/(F10)**2*(DAADY) +2.0D0*AM/T/(F1
     1   **3*(DCCDY)
      BIGC= -RT/(F2)**2+2.0D0*AM/T/(F10)**3
      DVDY=-(BIGB)/(BIGC)
      DBDY=RT/(F2)**2*(D2BBDY)-2.0D0*RT/(F2)**3*(DBBDY)*((DVDY)-(DBBDY
     1  -1.0D0/T/(F10)**2*(D2AADY) +2.0D0/T/(F10)**3*(DCCDY)*(DAADY)
     2  +2.0D0/T/(F10)**3*(DAADY)*((DVDY)+(DCCDY))+2.0D0*AM/T/(F10)**3
     3  *(D2CCDY)-6.0D0*AM/T/(F10)**4*(DCCDY)*((DVDY)+(DCCDY))
      DCDY=2.0D0*RT/(F2)**3 *((DVDY)-(DBBDY))+2.0D0/T/(F10)**3*(DAADY)
     1  6.0D0*AM/T/(F10)**4 *((DVDY)+(DCCDY))
      D2VDY=-(DBDY)/(BIGC)+(DCDY)*(BIGB)/(BIGC)**2
      BIGD=-3.0D0*RT  /(F2)**2 *(DBBDY)*(D2BBDY)-2.0D0*RT/(F2)**3 *(DBB
     1   )**3-3.0D0/T/(F10)**2*(D2AADY)*(DCCDY)-3.0D0/T/(F10)**2*(DAA)
     2   *(D2CCDY)+6.0D0/T/(F10)**3*(DAADY)*(DCCDY)**2+6.0D0/T/(F10)**
     3   (DCCDY)*(D2CCDY)*AM -6.0D0*AM/T/(F10)**4*(DCCDY)**3
      BIGE= RT/(F2)**2*(D2BBDY)+2.0D0*RT/(F2)**3*(DBBDY)**2-1.0D0/T/(F
     1   )**2*(D2AADY)+4.D0/T/(F10)**3*(DAADY)*(DCCDY)+2.0D0*AM/T
     2   /(F10)**3*(D2CCDY)-6.D0*AM/T/(F10)**4*(DCCDY)**2
      BIGG=-2.0D0*RT/(F2)**3*(DBBDY)+2.0D0/T/(F10)**3*(DAADY)-6.D0*AM/
     1   (F10)**4*(DCCDY)
      HRS10=(RT)/(Y1*Y2)
      HLS10=(BIGA)-(BIGB)**2/(BIGC)
      HRS11=RT*(Y1-Y2)/(Y1*Y2)**2
      HLS11=(BIGD)+2.0D0*(BIGE)*(DVDY)+(BIGG)*(DVDY)**2+(BIGB)*(D2VDY)
      DD=(HLS10)-(HRS10)
      DS=(HLS11)-(HRS11)
  801 WRITE(3,200) V,DD,DS
  201 FORMAT(/1H /,8X,4D20.9)
      RETURN
      END
```

```
      SUBROUTINE WOHL  (PC,VC,TC,W,C1RKL,C2RKL,C3RKL,NCOMP,CORRL,Y,ET)
C     DAVID POON, APRIL,1972.
C     SUBROUTINE FOR THE CALCULATION OF CRITICAL LOCI FOR BINARY MIXTURES
C     THE WOHL EQUATION OF STATE IS USED
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION  A(5,5),B(5,5), C1RKL(5),C2RKL(5),TC(5),PC(5),VC(5),
     1    TCIJ(5,5),WIJ(5,5),W(5),Y(5 ),CORRL(5,5) ,TITLE(19),
     2 C1RKV(5),C2RKV(5),C3RKL(5)
      DIMENSION VV(50),C(5,5)
   91 DO 100 I=1,2
      VC(I)=R*TC(I)/PC(I)/3.75D0
      A(I,I)=C1RKL(I)*TC(I)*PC(I)*VC(I)**2
      B(I,I)=C2RKL(I)*VC(I)
  100 C(I,I)=C3RKL(I)*PC(I)*TC(I)**2*VC(I)**3
      I=1
      I1=I+1
      DO 102 J=I1,2
      TCIJ(I,J)=( TC(I)*TC(J) ) **0.5D0*(1.0D0-CORRL(I,J) )
      TCIJ(J,I)=TCIJ(I,J)
      WIJ(I,J)=( W(I)+W(J) )*0.5D0
      ZCIJ=0.291D0-0.08D0*WIJ(I,J)
      VCIJ=(VC(I)**(1.D0/3.D0)+VC(J)**(1.D0/3.D0))**3/8.0D0
      PCIJ=ZCIJ*R*TCIJ(I,J)/VCIJ
      A(I,J)=( C1RKL(I)+C1RKL(J) )*0.5D0*PCIJ*TCIJ(I,J)*VCIJ**2
      B(I,J)=( C2RKL(I)+C2RKL(J) )*0.5D0*VCIJ
      C(I,J)=( C3RKL(I)+C3RKL(J) )*0.5D0*PCIJ*TCIJ(I,J)**2*VCIJ**3
      A(J,I)=A(I,J)
      B(J,I)=B(I,J)
  102 C(J,I)=C(I,J)
  902 T=T+DT
      IF(T.GT.ET) GO TO 800
      WRITE(3,201) T
  201 FORMAT(/1H /,8X,4D20.9)
      DO 801 I=1,20
      VM=VV(I)
      RT=R*T
      Y1=Y(1)
      Y2=Y(2)
      A11=A(1,1)
      A22=A(2,2)
      A12=A(1,2)
      B11=B(1,1)
      B22=B(2,2)
      B12=B(1,2)
      C11=C(1,1)
      C22=C(2,2)
      C12=C(1,2)
      AM=Y1**2*A11 + Y2**2*A22 + 2.0D0*Y1*Y2*A12
      BM=Y1**2*B11 +Y2**2*B22 +2.0D0*Y1*Y2*B12
      CM=Y1**2*C11 +Y2**2*C22 +2.0D0*Y1*Y2*C12
      F2=VM-BM
      F3=B11+B22-2.0D0*B12
      F4=A11+A22-2.0D0*A12
      F5=Y1*B11+Y2*B12-Y1*B12-Y2*B22
      F6=Y1*A11+Y2*A12-Y1*A12-Y2*A22
      F7=DSQRT(T)
      F8=Y1*C11-Y2*C22+Y2*C12-Y1*C12
      F9=C11+C22-2.0D0*C12
```

```
      DAADY=2.0D0*F6
      D2AADY=2.0D0*F4
      DBBDY=2.0D0*F5
      D2BBDY=2.0D0*F3
      DCCDY=2.0D0*F8
      D2CCDY=2.0D0*F9
      D3BBDY=0.0D0
      D3CCDY=0.0D0
      D3AADY=0.0D0
      BIGA=  -RT*(D2BBDY)/(F2)  -RT*(DBBDY)**2/(F2)**2  -(D2AADY)/T
     1  *(DLOG((VM-BM)/VM)/BM)  -(AM*(D2BBDY) +2.0D0*(DAADY)*(DBBDY))
     3  * (-1.0D0/BM/(F2)-DLOG((VM-BM)/VM)/BM/BM)/T  -(DBBDY)**2*2.0D0
     4   AM/T*(1.0D0/BM/BM/(F2)  -0.5D0/BM/(F2)**2  +DLOG((VM-BM)/VM)/
     5  (BM)**3)  -(D2CCDY)/2.0D0/T/T/(VM)**2
      BIGB=  RT*(DBBDY)/(F2)**2  -(DAADY)/T/VM/(F2)  -AM*(DBBDY)
     1  /T/VM/(F2)**2  +(DCCDY)/T/T/(VM)**3
      BIGC=  -RT/(F2)**2  +AM*(2.0D0*VM-BM)/T/(VM)**2/(F2)**2
     1  -3.0D0*CM/T/T/(VM)**4
      DVDY=-(BIGB)/(BIGC)
      DBDY=  RT*(D2BBDY)/(F2)**2  -2.0D0*RT*(DBBDY)*(DVDY-DBBDY)/(F2)*
     2  -(D2AADY)/T/VM/(F2)  -(AM*D2BBDY  -DAADY*DVDY  +2.0D0*DAADY
     3  *DBBDY)/T/VM/(F2)**2  +2.0D0*DBBDY*(AM*(DVDY-DBBDY))/T/VM
     1/(F2)**3  +(DAADY)*(DVDY)/T/VM/VM/(F2)  +AM*(DBBDY)*(DVDY)
     4  /T/VM/VM/(F2)**2  +(D2CCDY)/T/T/(VM)**3  -3.0D0*(DCCDY)*(DVDY)/
     5  /T/(VM)**4
      DCDY=  2.0D0*RT*(DVDY-DBBDY)/(F2)**3  +(AM*(2.0D0*DVDY-DBBDY)
     1 +(2.0D0*VM-BM)*(DAADY))/T/VM/VM/(F2)**2  -2.0D0*AM*(2.0D0*VM
     3  -BM)*(DVDY-DBBDY)/T/VM/VM/(F2)**3  -2.0D0*AM*(DVDY)*(2.0D0
     3  *VM-BM)/T/(VM)**3/(F2)**2  -3.0D0*(DCCDY)/T/T/(VM)**4  +12.0D0
     4  *CM*(DVDY)/T/T/(VM)**5
      D2VDY=-(DBDY)/(BIGC)+(DCDY)*(BIGB)/(BIGC)**2
      BIGD  =  -RT*(D3BBDY)/(F2)  -3.0D0*RT*(DBBDY)*(D2BBDY)/(F2)**2
     1  2.0D0*RT*(DBBDY)**3/(F2)**3  -(D3AADY)/T*(DLOG((VM-BM)/VM)/BM)
     2  -(AM*(D3BBDY)+3.0D0*(DAADY)*(D2BBDY)+3.0D0*(D2AADY)*(DBBDY))/T
     3  *(-1.0D0/BM/(F2)  -DLOG((VM-BM)/VM)/BM/BM)  -6.0D0/T*(AM*
     3  (DBBDY)*(D2BBDY)+(DAADY)*(DBBDY)**2)*(1.0D0/BM/BM/(F2)-0.5D0
     5  /BM/(F2)**2  +DLOG((VM-BM)/VM)/(BM)**3)  +5.0D0*AM/T*(DBBDY)
     6 **3*(1.0D0/(BM)**3/F2-0.5D0/BM/BM/(F2)**2  +DLOG((VM-BM)/VM)/(B
     6  **4  +1.0D0/3.0D0/BM/(F2)**3)
      BIGE=  RT*(D2BBDY)/(F2)**2  +2.0D0*RT*(DBBDY)**2/(F2)**3  -(D2AA
     1  )/T/VM/(F2)  -(AM*(D2BBDY)+2.0D0*(DAADY)*(DBBDY))/T/VM/(F2)**2
     2  -2.0D0*AM*(DBBDY)**2/T/VM/(F2)**3  +(D2CCDY)/T/T/(VM)**3
      BIGG=  -2.0D0*RT*(DBBDY)/(F2)**3  +(DAADY)*(2.0D0*VM-BM)/T/(VM)
     1  **2/(F2)**2  +AM*(3.0D0*VM-BM)  *(DBBDY)/T/VM/VM/(F2)**3
     3  -3.0D0*(DCCDY)/T/T/(VM)**4
      HRS10=(RT)/(Y1*Y2)
      HLS10=(BIGA)-(BIGB)**2/(BIGC)
      HRS11=RT*(Y1-Y2)/(Y1*Y2)**2
      HLS11=(BIGD)+2.0D0*(BIGE)*(DVDY)+(BIGG)*(DVDY)**2+(BIGB)*(D2VDY)
      DD=(HLS10)-(HRS10)
      DS=(HLS11)-(HRS11)
  801 WRITE(3,200)  VM,DD,DS
      GO TO 902
  800 CONTINUE
  200 FORMAT(5X,5D20.9)
  500 FORMAT(3I5,F10.4)
  901 RETURN
      END
```

```
      SUBROUTINE SEXP(TC,PC,VC,W,T,P,R,X,Y,GEMA,PREF,VOL,NCOMP,CORRL,BD
      DIMENSION TEF(5),TET(5)
      DIMENSION TC(5),PC(5),VC(5),W(5),X(5),Y(5),B(5),GEMA(5),TCIJ(5,5)
     1   ,PCIJ(5,5),VCIJ(5,5),WIJ(5,5),ZCIJ(5,5),TRIJ(5,5),VRIJ(5,5),PRI
     2   (5,5),BIJ(5,5),FLN(5),F(5),BR(5),BRIJ(5,5),FRLN(5),FR(5),
     3   PREF(5),VOL(5),CORRL(5,5),TR(5),PR(5),VPU(5)
      DO 99 I=1,NCOMP
      TR(I)=T/TC(I)
   99 PR(I)=P/PC(I)
      NCOMP1=NCOMP-1
      DO 100 I=1,NCOMP1
      I1=I+1
      DO 100 J=I1,NCOMP
      TCIJ(I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
      TCIJ(J,I)=TCIJ(I,J)
      WIJ(I,J)=(W(I)+W(J))*0.5
      WIJ(J,I)=WIJ(I,J)
      ZCIJ(I,J)=0.291-0.08*WIJ(I,J)
      ZCIJ(J,I)=ZCIJ(I,J)
      VCIJ(I,J)=(VC(I)**(1./3.)+VC(J)**(1./3.))**3/8.0
      VCIJ(J,I)=VCIJ(I,J)
      PCIJ(I,J)=ZCIJ(I,J)*R*TCIJ(I,J)/VCIJ(I,J)
      PCIJ(J,I)=PCIJ(I,J)
      TRIJ(I,J)=T/TCIJ(I,J)
      TRIJ(J,I)=TRIJ(I,J)
      PRIJ(I,J)=P/PCIJ(I,J)
      PRIJ(J,I)=PRIJ(I,J)
  100 CONTINUE
      DO 101 I=1,NCOMP
  101 B(I)=( (.1445 +.073*W(I) )-( .33 -.46*W(I) )/TR(I)
     1   -( .1385 +.5*W(I) )/TR(I)/TR(I)  -( .0121 +.097*W(I) )/(TR(I)**
     2   )  -.0073 *W(I)/(TR(I)**8))*R*TC(I)/PC(I)
      DO 102 I=1,NCOMP1
      I1=I+1
      DO 102 J=I1,NCOMP
      BIJ(I,J)=( (.1445+.073*WIJ(I,J))-(.33-.46*WIJ(I,J))/TRIJ(I,J)
     1-(.1385+.5*WIJ(I,J) )/TRIJ(I,J)/TRIJ(I,J) -(.0121+.097*WIJ(I,J)
     2  )/(TRIJ(I,J)**3) -.0073*WIJ(I,J)/(TRIJ(I,J)**8))*R*TCIJ(I,J)
     3  /PCIJ(I,J)
  102 BIJ(J,I)=BIJ(I,J)
      IF(NCOMP.EQ.3) GO TO 132
      BM=Y(1)*Y(1)*B(1)+2.*Y(1)*Y(2)*BIJ(1,2)+Y(2)*Y(2)*B(2)
      GO TO 133
  132 BM=   Y(1)*Y(1)*B(1)   +Y(2)*Y(2)*B(2)   +Y(3)*Y(3)*B(3)
     1   +2.*Y(1)*Y(2)*BIJ(1,2)   +2.*Y(1)*Y(3)*BIJ(1,3)   +2.*Y(2)*Y(3)*
     2   BIJ(2,3)
  133 TAI=R*R*T*T
      TAF=4.0*R*T*P*BM
      TAT=TAI-TAF
      IF (TAT.LT.0.0) GO TO 144
C     V=   (R*T +SQRT (R*R*T*T+4.*P*R*T*BM))   /2./P
C     V=R*T/P  +BM
      V=   (R*T   +SQRT(ABS(R*R*T*T+4.*R*T*P*BM)))/2./P
      GO TO 145
C 144 V=R*T/P  +BM
  144 V=   (R*T   +SQRT(ABS(R*R*T*T+4.*R*T*P*BM)))/2./P
  145 CONTINUE
      DO 103 I=1,NCOMP
```

```
C 104 FLN(I)=2.0/V *(Y(I)*B(I)+(1.0-Y(I))*BCR      )-ALOG(P*V/R/T)
  104 FLN(I)=2.0/V *(Y(I)*B(I)+(1.0-Y(I))*BIJ(1,2))-ALOG(P*V/R/T)
  103 F(I)=EXP(FLN(I))
      DO 113 I=1,NCOMP
      TEI=R*R*T*T
      TEF(I)=4.0*R*T*PREF(I)*B(I)
      TET(I)=TEI-TEF(I)
      IF (TET(I).LT.0.0) GO TO 134
C     VPU(I)=(R*T +SQRT(R*R*T*T +4.0*R*T*B(I)*PREF(I)) )/2.0/PREF(I)
C     VPU(I)=R*T/(PREF(I))  +B(I)
      VPU(I)=(R*T+SQRT(ABS(R*R*T*T+4.*R*T*B(I)*PREF(I))))/2./PREF(I)
      GO TO 135
C 134 VPU(I)=R*T/(PREF(I))  +B(I)
  134 VPU(I)=(R*T+SQRT(ABS(R*R*T*T+4.*R*T*B(I)*PREF(I))))/2./PREF(I)
  135 CONTINUE
C     FRLN(I)=B(I)*PREF(I)/R/T
      FRLN(I)= -ALOG(1.0+B(I)/VPU(I) ) +2.0*B(I)/VPU(I)
  113 FR(I)=EXP(FRLN(I))
      DO 121 I=1,NCOMP
  121 GEMA(I)=P*Y(I)*F(I)/(PREF(I)*FR(I)*X(I)*EXP(VOL(I)*(P-PREF(I))
     1/R/T))
C     WRITE(3,700) B(1),B(2),B(3) ,BIJ(1,2),BIJ(1,3),BIJ(2,3)
  700 FORMAT(5X,8E12.5)
      RETURN
      END
```

```
      SUBROUTINE CUBEQN(INDEX,LI,LJ)
C     SOLVING EQN F(Z)=A(1)*Z**3+A(2)*Z**2+A(3)*Z+A(4)=0
C     BY SHINN-DER CHANG ( DEPT OF CHEM ENG , UNIV OF OTTAWA )
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*4 LI(4),LJ(3)
      DIMENSION A(4),Z(3)
      DO 15 I=1,4
   15 A(I)=LI(I)
      DO 25 I=1,3
   25 Z(I)=LJ(I)
      P=(A(3)-A(2)**2/A(1)/3.0D0)/A(1)
      Q=2.0D0*(A(2)/3.0D0/A(1))**3-A(3)*A(2)/3.0D0/A(1)**2+A(4)/A(1)
      DE=(P/3.0D0)**3+(Q/2.0D0)**2
      T=A(2)/3.0D0/A(1)
      IF(DE.GE.0.0D0) GO TO 5
      THI=DARCOS(-(Q/2.0D0)/DSQRT(-(P/3.0D0)**3))
      R=2.0D0*DSQRT(-P/3.0D0)*DCOS(THI/3.0D0)
      GO TO 8
    5 S=(-(Q/2.0D0)+DSQRT(DE))
      U=(-Q/2.0D0-DSQRT(DE))
      IF(S) 6,7,8
    6 S=S/DABS(S)*(S*S)**(1.0D0/6.0D0)
    7 IF(U) 9,11,9
    9 U=U/DABS(U)*(U*U)**(1.0D0/6.0D0)
   11 R=S+U
    8 DISC=R*R-4.0D0*(P+R*R)
      IF(DISC)40,10,30
   10 INDEX=0
      Z(1)=R-T
      Z(2)=-R/2.0D0-T
      Z(3)=Z(2)
      GO TO 26
   30 INDEX=-1
      Z(1)=R-T
      Z(2)=-R/2.0D0+DSQRT(DISC)/2.0D0-T
      Z(3)=-R/2.0D0-DSQRT(DISC)/2.0D0-T
      GO TO 26
   40 INDEX=1
      Z(1)=R-T
      DB=DSQRT(DABS(DISC))/2.0D0
      DA=-R/2.0D0-T
      Z(2)=Z(1)
      Z(3)=Z(1)
C     WRITE(3,100)DA,DB
  100 FORMAT( /'THERE ARE TWO CONJUGATE ROOTS , REAL PART= ',E15.6
     1 /27X,'IMAG. PART= ',E15.6/)
   26 DO 27 I=1,3
   27 LJ(I)=Z(I)
      RETURN
      END
```

```
      SUBROUTINE FUGRK(PHI,Y,C1RKV,C2RKV,CORRV,CUBEQN,KIJ,LV)
C     FROM PRAUSNITZ, MODIFIED BY S.D.CHANG.
C    CALCULATE VAPOR-PHASE FUGACITY COEFFICIENTS USING REVISED REDLICH
C    AND KWONG EQUATION
C      JULY 7, 1969
      DIMENSION TC(5),PC(5),VCO(5),W(5),AMOLWT(5)  ,AIRKV(5),ARKV(5,5)
     1 BRKV(5),WIJ(5,5), VCIJ(5,5),ZCIJ(5,5),PHILN(5),A(4),Z(3),
     2 TCOIJ(5,5),C1RKV(5),C2RKV(5),          Y(5),PHI(5),AMWTIJ(5,5)
     3   ,CORRV(5,5)
      DIMENSION ARKL(5,5),BRKL(5)
      COMMON  /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM
     1   /SECOND/ Z,A,MTYPE
     1   /THIRD/ ARKV,ARKL,BRKV,BRKL,ZL,ZV,AMRKV,AMRKL,BMRKV,BMRKL
C     LV=0,FOR VAPOR PHASE
C     LV=1,FOR LIQUID PHASE
C     KIJ=0, TCIJ=SQRT(TCI*TCJ)(1.-CORRV)
C     KIJ GT 0, AIJ=SQRT(AI*AJ)(1.0-CORRV)
    1 CONTINUE
      RT=R*T
      DO 90 I=1,NCOMP
      ARKV(I,1)=C1RKV(I)*R*R      *(TC(I)**2.5)/PC(I)
      BRKV(I)=C2RKV(I)*   R *TC(I)/PC(I)
   90 CONTINUE
      DO 100 I=1,NCOMP
      TCOIJ(I,1)=TC(I)
      IF(I.EQ.NCOMP) GO TO 110
      I1=I+1
      DO 100 J=I1,NCOMP
      IF(KIJ. GT.1) GO TO 97
      TCOIJ(I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRV(I,J))
      AMWTIJ(I,J)=2.0*AMOLWT(I)*AMOLWT(J)/(AMOLWT(I)+AMOLWT(J))
      TCOIJ(J,I)=TCOIJ(I,J)
      WIJ(I,J)=(W(I)+W(J))*0.5
      ZCOIJ=0.291-0.08*WIJ(I,J)
      ZCIJ(I,J)=ZCOIJ
   94 VCOIJ=(VCO(I)**(1./3.)+VCO(J)**(1./3.))**3/8.0
      VCIJ(I,J)=VCOIJ
   96 PCOIJ=ZCOIJ*  R   *TCOIJ(I,J)/VCOIJ
      IF(NQNTUM.GE.1) GO TO 92
      PCIJ=PCOIJ
      GO TO 95
   92 PCIJ=PCOIJ/(1.0+44.2*1.8/(AMWTIJ(I,J)*T))
   95 ARKV(I,J)=
     1          (C1RKV(I)+C1RKV(J))*R/2. *(TC(I)*TC(J)*(1.-CORRV(I,J))
     1 2.0)**0.75*VCIJ(I,J)/ZCIJ(I,J)
      GO TO 98
   97 ARKV(I,J)=(ARKV(I,I)*ARKV(J,J))**0.5*(1.0-CORRV(I,J))
   98 ARKV(J,I)=ARKV(I,J)
  100 CONTINUE
  110 CONTINUE
      AMRKV=0.0
      BMRKV=0.0
      DO 120 I=1,NCOMP
      AIRKV(I)=0.0
      BMRKV=BMRKV+Y(I)*BRKV(I)
      DO 120 J=1,NCOMP
      AIRKV(I)=AIRKV(I)+Y(J)*ARKV(I,J)
  120 AMRKV=AMRKV+Y(I)*Y(J)*ARKV(I,J)
```

```
      A2=AMRKV/RT**2/T**0.5
      B=BMRKV/RT
      A(1)=1.0
      A(2)=-1.0
      PBRT=P*BMRKV/RT
      ABRT=AMRKV/(BMRKV* R    *T**1.5)
      A(3)=PBRT*(ABRT-1.0-PBRT)
      A(4)=-ABRT*(PBRT**2.0)
      CALL CUBEQN
      IF(MTYPE)13 ,140,140
  130 IF (LV) 125,135,125
  125 ZV=AMIN1(Z(1),Z(2),Z(3))
      GO TO 150
  135 ZV=AMAX1(Z(1),Z(2),Z(3))
      GO TO 150
  140 ZV=Z(1)
  150 H=B*P/ZV
      CALL EQNRK(A2,B,P,H,ZV,LV)
      VV=ZV*RT/P
      QVVB=ALOG(VV/(VV-BMRKV))
      Q1VB=1.0/(VV-BMRKV)
      Q2RTB=2.0/( R    *T**1.5*BMRKV)
      QVBV=ALOG((VV+BMRKV)/VV)
      QARTB=AMRKV/( R    *T**1.5*BMRKV**2.0)
      QBVB=BMRKV/(VV+BMRKV)
      DO 160 I=1,NCOMP
      PHILN(I)=QVVB+BRKV(I)*Q1VB-ARKV(I)*Q2RTB*QVBV+BRKV(I)*QARTB*(QV
     1 -QBVB)-ALOG(ZV)
  160 PHI(I)=EXP(PHILN(I))
      RETURN
      END
```

```
      SUBROUTINE VOLPAR(C1RKL,C2RKL,CORRL,X,CUBEQN,PHI, PVOL,IJK)
C     FROM PRAUSNITZ, MODIFIED BY S.D.CHANG.
C     CALCULATE PARTIAL MOLAR VOLUMES IN A MULTICOMPONENT LIQUID MIXTU
      DIMENSION TC(5),PC(5),VCO(5),W(5),AMOLWT(5)  ,ARKL(5,5),BRKL(5),
     1  WIJ(5,5),TCOIJ(5,5),TCIJ(5,5),A(4),Z(3),C1RKL(5),C2RKL(5),
     1  PVOL(5),PHI(5),CORRL(5,5),X(5),A2I(5),BI(5) ,AMWTIJ(5,5)
     3  ,AIRKL(5)
      DIMENSION ARKV(5,5),BRKV(5)
      COMMON  /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM
     1  /SECOND/ Z,A,MTYPE
     1  /THIRD/ ARKV,ARKL,BRKV,BRKL,ZL,ZV,AMRKV,AMRKL,BMRKV,BMRKL
      RT=R*T
   91 DO 100 I=1,NCOMP
      ARKL(I,I)=C1RKL(I)* R*R     *(TC(I)**2.5)/PC(I)
      BRKL(I)=C2RKL(I)* R    *TC(I)/PC(I)
      IF(I.EQ.NCOMP) GO TO 110
      I1=I+1
      DO 100 J=I1,NCOMP
      AMWTIJ(I,J)=2.0*AMOLWT(I)*AMOLWT(J)/(AMOLWT(I)+AMOLWT(J))
      TCOIJ(I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
      TCOIJ(J,I)=TCOIJ(I,J)
      TCIJ(I,J)=TCOIJ(I,J)
      WIJ(I,J)=(W(I)+W(J))*0.5
      ZCOIJ=0.291-0.08*WIJ(I,J)
C     IF(IJK.GE.2) GO TO 94
C     VCOIJ=(VCO(I)+VCO(J))*0.5
C     GO TO 96
   94 VCOIJ=(VCO(I)**(1./3.)+VCO(J)**(1./3.))**3/8.0
   96 PCOIJ=ZCOIJ* R    *TCOIJ(I,J)/VCOIJ
      IF(NQNTUM.GE.1) GO TO 92
      PCIJ=PCOIJ
      GO TO 95
   92 PCIJ=PCOIJ/(1.0+44.2*1.8/(AMWTIJ(I,J)*T))
   95 ARKL(I,J)=(C1RKL(I)+C1RKL(J))*0.5* R    **2*TCIJ(I,J)**2.5/PCIJ
      ARKL(J,I)=ARKL(I,J)
  100 CONTINUE
  110 CONTINUE
      AMRKL=0.0
      BMRKL=0.0
      DO 120 I=1,NCOMP
      A2I(I)=ARKL(I,I)/RT**2/T**0.5
      BI(I)=BRKL(I)/RT
      BMRKL=BMRKL+X(I)*BRKL(I)
      AIRKL(I)=0.0
      DO 120 J=1,NCOMP
      AIRKL(I)=AIRKL(I)+X(J)*ARKL(I,J)
  120 AMRKL=AMRKL+X(I)*X(J)*ARKL(I,J)
      A2=AMRKL/RT**2/T**0.5
      B=BMRKL/RT
      A(1)=1.0
      A(2)=-1.0
      A(3)=B*P*(A2/B-1.0-B*P)
      A(4)=-(A2/B)*(B*P)**2
      CALL CUBEQN
      IF(MTYPE)135,140,140
  135 ZL=AMIN1(Z(1),Z(2),Z(3))
      GO TO 150
  140 ZL=Z(1)
```

```
  150 H=B*P/ZL
      CALL EQNRK(A2,B,P,H,ZL,LV)
      VL=RT*B/H
  123 CONTINUE
      QD=(T**0.5)*VL*(VL+BMRKL)
      QH=(AMRKL/(T**0.5))*
     1                    ((2.0*VL+BMRKL)/(VL**2  *(VL+BMRKL)**2  ))
      QK=RT/((VL-BMRKL)**2  )
      DO 130 I=1,NCOMP
      PHILN =(ZL-1.0)*BI(I)/B-ALOG(ZL)-ALOG(1.0-H)
C     1   -(A2/B)*(2.0*(AAI(I)/A2)**0.5-BI(I)/B)*ALOG(1.0+H)
     1   -(A2/B)*(2.0*AIRKL(I)/AMRKL  -BI(I)/B)*ALOG(1.0+H)
      PHI(I)= EXP(PHILN )
      QE1=0.0
      DO 125 J=1,NCOMP
  125 QE1=QE1+X(J)*ARKL(I,J)
      QE=2.0*QE1-AMRKL*BRKL(I)/(VL+BMRKL)
      QG=(RT/(VL-BMRKL))*(1.0+BRKL(I)/(VL-BMRKL))
      PVOL(I)=((QL/QD)-QG)/(QH-QK)
  130 CONTINUE
  300 RETURN
      END
```

```
      SUBROUTINE RKFIT(TITLE,NOBS,P,X1,X2,GI,GII,GIII,EXCESS,Q12,Q23,
     1)
C     DAVID POON  (OCTOBER,1970).
C     FIT REDLICH KISTER EQUATION FOR TERNARY SYSTEM
      DIMENSION EXCESS(90),Q12(50),Q23(50),Q31(50)
      DIMENSION H(10,11),F(11),A(10,11),TITLE(20),Q123(90)
      DIMENSION P(90),X1(90),X2(90),X3(90),GI(90),GII(90),GIII(90)
   90 CONTINUE
      DO 10 I=1,10
      DO 10 J=1,11
   10 H(I,J)=0.0
  801 FORMAT(1H ,11F11.4)
C 801 FORMAT(1H ,6E15.4)
      DO 20 I=1,NOBS
      X3(I)=1.0-X1(I)-X2(I)
      F(1)= (X1(I)*X2(I))
      F(2)= (X1(I)*X2(I))*(X1(I)-X2(I))
      F(3)= (X1(I)*X2(I))*(X1(I)-X2(I))**2
      F(4)= (X2(I)*X3(I))
      F(5)= (X2(I)*X3(I))*(X2(I)-X3(I))
      F(6)= (X2(I)*X3(I))*(X2(I)-X3(I))**2
      F(7)= (X3(I)*X1(I))
      F(8)= (X3(I)*X1(I))*(X3(I)-X1(I))
      F(9)= (X3(I)*X1(I))*(X3(I)-X1(I))**2
      F(10)=(X1(I)*X2(I)*X3(I))
      F(11)= EXCESS(I)
      H(1 ,1 )=H(1 ,1 )+F(1 )*F(1 )
      H(1 ,2 )=H(1 ,2 )+F(1 )*F(2 )
      H(1 ,3 )=H(1 ,3 )+F(1 )*F(3 )
      H(1 ,4 )=H(1 ,4 )+F(1 )*F(4 )
      H(1 ,5 )=H(1 ,5 )+F(1 )*F(5 )
      H(1 ,6 )=H(1 ,6 )+F(1 )*F(6 )
      H(1 ,7 )=H(1 ,7 )+F(1 )*F(7 )
      H(1 ,8 )=H(1 ,8 )+F(1 )*F(8 )
      H(1 ,9 )=H(1 ,9 )+F(1 )*F(9 )
      H(1 ,10)=H(1 ,10)+F(1 )*F(10)
      H(1 ,11)=H(1 ,11)+F(1 )*F(11)
      H(2 ,2 )=H(2 ,2 )+F(2 )*F(2 )
      H(2 ,3 )=H(2 ,3 )+F(2 )*F(3 )
      H(2 ,4 )=H(2 ,4 )+F(2 )*F(4 )
      H(2 ,5 )=H(2 ,5 )+F(2 )*F(5 )
      H(2 ,6 )=H(2 ,6 )+F(2 )*F(6 )
      H(2 ,7 )=H(2 ,7 )+F(2 )*F(7 )
      H(2 ,8 )=H(2 ,8 )+F(2 )*F(8 )
      H(2 ,9 )=H(2 ,9 )+F(2 )*F(9 )
      H(2 ,10)=H(2 ,10)+F(2 )*F(10)
      H(2 ,11)=H(2 ,11)+F(2 )*F(11)
      H(3 ,3 )=H(3 ,3 )+F(3 )*F(3 )
      H(3 ,4 )=H(3 ,4 )+F(3 )*F(4 )
      H(3 ,5 )=H(3 ,5 )+F(3 )*F(5 )
      H(3 ,6 )=H(3 ,6 )+F(3 )*F(6 )
      H(3 ,7 )=H(3 ,7 )+F(3 )*F(7 )
      H(3 ,8 )=H(3 ,8 )+F(3 )*F(8 )
      H(3 ,9 )=H(3 ,9 )+F(3 )*F(9 )
      H(3 ,10)=H(3 ,10)+F(3 )*F(10)
      H(3 ,11)=H(3 ,11)+F(3 )*F(11)
      H(4 ,4 )=H(4 ,4 )+F(4 )*F(4 )
      H(4 ,5 )=H(4 ,5 )+F(4 )*F(5 )
```

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      H(4 ,6 )=H(4 ,6 )+F(4 )*F(6 )
      H(4 ,7 )=H(4 ,7 )+F(4 )*F(7 )
      H(4 ,8 )=H(4 ,8 )+F(4 )*F(8 )
      H(4 ,9 )=H(4 ,9 )+F(4 )*F(9 )
      H(4 ,10)=H(4 ,10)+F(4 )*F(10)
      H(4 ,11)=H(4 ,11)+F(4 )*F(11)
      H(5 ,5 )=H(5 ,5 )+F(5 )*F(5 )
      H(5 ,6 )=H(5 ,6 )+F(5 )*F(6 )
      H(5 ,7 )=H(5 ,7 )+F(5 )*F(7 )
      H(5 ,8 )=H(5 ,8 )+F(5 )*F(8 )
      H(5 ,9 )=H(5 ,9 )+F(5 )*F(9 )
      H(5 ,10)=H(5 ,10)+F(5 )*F(10)
      H(5 ,11)=H(5 ,11)+F(5 )*F(11)
      H(6 ,6 )=H(6 ,6 )+F(6 )*F(6 )
      H(6 ,7 )=H(6 ,7 )+F(6 )*F(7 )
      H(6 ,8 )=H(6 ,8 )+F(6 )*F(8 )
      H(6 ,9 )=H(6 ,9 )+F(6 )*F(9 )
      H(6 ,10)=H(6 ,10)+F(6 )*F(10)
      H(6 ,11)=H(6 ,11)+F(6 )*F(11)
      H(7 ,7 )=H(7 ,7 )+F(7 )*F(7 )
      H(7 ,8 )=H(7 ,8 )+F(7 )*F(8 )
      H(7 ,9 )=H(7 ,9 )+F(7 )*F(9 )
      H(7 ,10)=H(7 ,10)+F(7 )*F(10)
      H(7 ,11)=H(7 ,11)+F(7 )*F(11)
      H(8 ,8 )=H(8 ,8 )+F(8 )*F(8 )
      H(8 ,9 )=H(8 ,9 )+F(8 )*F(9 )
      H(8 ,10)=H(8 ,10)+F(8 )*F(10)
      H(8 ,11)=H(8 ,11)+F(8 )*F(11)
      H(9 ,9 )=H(9 ,9 )+F(9 )*F(9 )
      H(9 ,10)=H(9 ,10)+F(9 )*F(10)
      H(9 ,11)=H(9 ,11)+F(9 )*F(11)
      H(10,10)=H(10,10)+F(10)*F(10)
      H(10,11)=H(10,11)+F(10)*F(11)
   20 CONTINUE
      H(2 ,1 )=H(1 ,2 )
      H(3 ,1 )=H(1 ,3 )
      H(3 ,2 )=H(2 ,3 )
      H(4 ,1 )=H(1 ,4 )
      H(4 ,2 )=H(2 ,4 )
      H(4 ,3 )=H(3 ,4 )
      H(5 ,1 )=H(1 ,5 )
      H(5 ,2 )=H(2 ,5 )
      H(5 ,3 )=H(3 ,5 )
      H(5 ,4 )=H(4 ,5 )
      H(6 ,1 )=H(1 ,6 )
      H(6 ,2 )=H(2 ,6 )
      H(6 ,3 )=H(3 ,6 )
      H(6 ,4 )=H(4 ,6 )
      H(6 ,5 )=H(5 ,6 )
      H(7 ,1 )=H(1 ,7 )
      H(7 ,2 )=H(2 ,7 )
      H(7 ,3 )=H(3 ,7 )
      H(7 ,4 )=H(4 ,7 )
      H(7 ,5 )=H(5 ,7 )
      H(7 ,6 )=H(6 ,7 )
      H(8 ,1 )=H(1 ,8 )
      H(8 ,2 )=H(2 ,8 )
      H(8 ,3 )=H(3 ,8 )
```

```
      H(8 ,4 )=H(4 ,8 )
      H(8 ,5 )=H(5 ,8 )
      H(8 ,6 )=H(6 ,8 )
      H(8 ,7 )=H(7 ,8 )
      H(9 ,1 )=H(1 ,9 )
      H(9 ,2 )=H(2 ,9 )
      H(9 ,3 )=H(3 ,9 )
      H(9 ,4 )=H(4 ,9 )
      H(9 ,5 )=H(5 ,9 )
      H(9 ,6 )=H(6 ,9 )
      H(9 ,7 )=H(7 ,9 )
      H(9 ,8 )=H(8 ,9 )
      H(10,1 )=H(1 ,10)
      H(10,2 )=H(2 ,10)
      H(10,3 )=H(3 ,10)
      H(10,4 )=H(4 ,10)
      H(10,5 )=H(5 ,10)
      H(10,6 )=H(6 ,10)
      H(10,7 )=H(7 ,10)
      H(10,8 )=H(8 ,10)
      H(10,9 )=H(9 ,10)
      H(11,1 )=H(1 ,11)
      H(11,2 )=H(2 ,11)
      H(11,3 )=H(3 ,11)
      H(11,4 )=H(4 ,11)
      H(11,5 )=H(5 ,11)
      H(11,6 )=H(6 ,11)
      H(11,7 )=H(7 ,11)
      H(11,8 )=H(8 ,11)
      H(11,9 )=H(9 ,11)
      H(11,10)=H(10,11)
      NEQ=1
C     DO 21 L=1,10
C     DO 21 J=L,11
C  21 H(L,J)=H(L,J)+F(L)*F(J)
C     DO 16 I=1,10
C     DO 16 J=I,10
C  16 H(J,I)=H(I,J)
   17 DO 15 I=1,10
      DO 15 J=1,11
   15 A(I,J)=0.0
C     IF(NEQ.EQ.2) GO TO 809
      NEQ1=NEQ+1
C     GO TO 802
C 809 NEQ1=NEQ+2
  802 DO 18 I=1,NEQ
      A(I,NEQ1)=H(I,11)
      WRITE(3,801) A(I,NEQ1)
      DO 18 J=1,NEQ
      A(I,J)=H(I,J)
   18 WRITE(3,801) A(I,J)
      CALL SOLVE(NEQ,A,INDIC)
      WRITE(3,103)(TITLE(I),I=1,20)
  103 FORMAT(1H1, 'REDLICH-KISTER EQUATION REPRESENTATION OF ',20A4//
      WRITE(3,106)(A(I,NEQ1),I=1,NEQ)
  106 FORMAT(5X,'B12=',F8.4,3X,'C12=',F8.4,3X,'D12=',F8.4,3X,'B23=',F
     1,3X,'C23=',F8.4,3X,'D23=',F8.4,3X,'B31=',F8.4,3X,'C31=',F8.4,3X
     25X,'D31=',F8.4,3X,'C123=',F8.4///)
```

```
      WRITE(3,105)
  105 FORMAT(2X,1HJ,5X,1HP,5X,2HX1,7X,2HX2,6X,5HQ(EX),5X,6HQ(CAL),7X,
     1GI//)
      SSI=0.0
      SI=0.0
      DO 30 I=1,NOBS
      Q123(I)=
     1                                  (   X1(I)*X2(I)   )   *   (   A(1,NEQ1)
     1A(2,NEQ1)*( X1(I)-X2(I) )   +     A(3,NEQ1)*( X1(I)-X2(I) )**2   )
     1                                  (   X2(I)*X3(I)   )   *   (   A(4,NEQ1)
     1A(5,NEQ1)*( X2(I)-X3(I) )   +     A(6,NEQ1)*( X2(I)-X3(I) )**2   )
     1                                  (   X3(I)*X1(I)   )   *   (   A(7,NEQ1)
     1A(8,NEQ1)*( X3(I)-X1(I) )   +     A(9,NEQ1)*( X3(I)-X1(I) )**2   )
     1A(10,NEQ1)*X1(I)*X2(I)*X3(I)
      AI=Q123(I)
   46 DGI=AI-EXCESS(I)
      DDGI=(DGI/(EXCESS(I) ))*100.
   48 SSI=SSI+(AI*0.05)**2
   47 SSI=SSI+DGI*DGI
   49 SI=SI+100.0*ABS(DGI/EXCESS(I))
      WRITE(3,104) I,P(I),X1(I),X2(I),AI,EXCESS(I),DGI,DDGI
  104 FORMAT(1H ,I2,F10.2,6F10.4//)
   30 CONTINUE
      SSDI=(SSI/(NOBS-NEQ))**0.5
      SDI=SI/NOBS
      WRITE(3,300)SSDI,      SDI,      NOBS,NEQ
  300 FORMAT(/1H ,'ST. DEV. OF Q123 VALUES IS',F15.4/1H ,'AV. % DEV. (
     1 Q123 VALUES IS',F15.4/1H ,'NO. OF OBSERVATION=',I5/1H ,'NO. OF
     2 ADJUSTABLE PARAMETERS =',I5/)
      NEQ=NEQ1
      IF(NEQ.GT.10) GO TO 800
      GO TO 17
  800 RETURN
      END
```

```
      SUBROUTINE SOLVE( NA,A,INDIC)
C     SUBROUTINE SUPPLIED BY S.D. CHANG
      DIMENSION A(5,6)
      NA1=NA+1
      DO 205 I=1,NA
      IF(A(I,I))200,206,200
  200 P=1./A(I,I)
      DO 201 J=I,NA1
  201 A(I,J)=P*A(I,J)
      DO 202 K=1,NA
      IF (I-K) 203,202,203
  203 Q=A(K,I)
      DO 204 J=I,NA1
  204 A(K,J)=A(K,J)-Q*A(I,J)
  202 CONTINUE
  205 CONTINUE
      INDIC=0
      RETURN
  206 IF(NA-1) 300,304,300
  300 I1 = I+1
      DO 303 L=I1,NA
      IF(A(L,I)) 301,303,301
  301 DO 302 J=1,NA1
      HOLD=A(I,J)
      A(I,J)=A(L,J)
  302 A(L,J)=HOLD
      GO TO 200
  303 CONTINUE
      INDIC=1
  304 WRITE(3,207)I
  207 FORMAT(//25H DIAGONAL ELEMENT IN EQN ,I4,40H IS ZERO TRANSPOSE EQN
     1 WITH PREVIOUS ONE//)
      RETURN
      END
```

```
      SUBROUTINE SUPT(VL,PHI, PVCL ,C1RKL,C2RKL,CORRL,X,LV,KIJ)
C     EVALUATES SUPERCRITICAL PROPERTIES,THE FUGACITY AND THE
C     PARTIAL MOLAL VOLUME OF FLUID MIXTURES.
C     SHINN-LEE CHANG, DEPT.OF CHEM.ENG., UNIV. OF OTTAWA.
      DIMENSION T( ),P( ),V( ),Z(5),A(5),T(5)  ,ARKL(5,5),BRKL( )
     1  ,TCIJ(5,5),TCIJ(5,5),TCIJ(5,5),X(5),Z(3),C1RKL(5),C2RKL( ),
     1  PVCL( ),PHI( ),C1RKL( ,5),X( ),A2I(5),BI(5),AIRKL(5)
      DIMENSION Z( )
      COMMON /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM,ZZZL,ZZZV
     1  /SECOND/ Z,AMIXTURE
C     LV=0, FOR VAPOR PHASE.
C     LV=1, FOR LIQUID PHASE.
C     KIJ=1, TCIJ=SQRT(TCI*TCJ)*(1.-KIJ)
C     KIJ=2, AIJ=SQRT(AI*AJ)*(1.-KIJ)
C     KIJ=3, AIJ=(AI*KIJ+(1.-KIJ)*AJ)/2.
      RT=R*T
   91 DO 100 I=1,NCOMP
      ARKL(I,I)=C1RKL(I)*R*R*(TC(I)**2.5)/PC(I)
      BRKL(I)=C2RKL(I)*R*TC(I)/PC(I)
      IF(I.EQ.NCOMP) GO TO 1
      II=I+1
      DO 100 J=II,NCOMP
      IF(KIJ.GT.1) GO TO 97
      TCIJ(I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
      TCIJ(J,I)=TCIJ(I,J)
      WIJ(I,J)=(W(I)+W(J))*0.5
      ZCOIJ=0.291-0.08*WIJ(I,J)
   94 VCOIJ=(VCO(I)**(1./3.)+VCO(J)**(1./3.))**3/8.0
   96 PCOIJ=ZCOIJ*R*R*TCIJ(I,J)/VCOIJ
      PCIJ=PCOIJ
   95 ARKL(I,J)=(C1RKL(I)+C1RKL(J))*0.5*R*R**2*TCIJ(I,J)**2.5/PCIJ
      GO TO 98
   97 IF(KIJ.GT.2) GO TO 99
      ARKL(I,J)=(ARKL(I,I)*ARKL(J,J))**0.5*(1.0-CORRL(I,J))
      GO TO 98
   99 ARKL(I,J)=(ARKL(I,I)*CORRL(I,J)+(1.-CORRL(I,J))*ARKL(J,J))
   98 ARKL(J,I)=ARKL(I,J)
  100 CONTINUE
      AMRKL=0.0
      BMRKL=0.0
      DO 120 I=1,NCOMP
      A2I(I)=ARKL(I,1)/RT**2/T**0.5
      BI(I)=BRKL(I)/RT
      BMRKL=BMRKL+X(I)*BRKL(I)
      AIRKL(I)=0.0
      DO 120 J=1,NCOMP
      AIRKL(I)=AIRKL(I)+X(J)*ARKL(I,J)
  120 AMRKL=AMRKL+X(I)*X(J)*ARKL(I,J)
      A2=AMRKL/RT**2/T**0.5
      B=BMRKL/RT
C     WRITE(3,711)C1RKL,       R,R,T,P
  711 FORMAT(3X,5 12.5)
      A(1)=1.0
      A(2)=-1.0
      A(3)=R*P*(A2/B-1.0-B*P)
      A(4)=-(A2/B)*(B*P)**2
      CALL CUBEQN(ITYPE,A,Z)
      IF(ITYPE)115,140,140
```

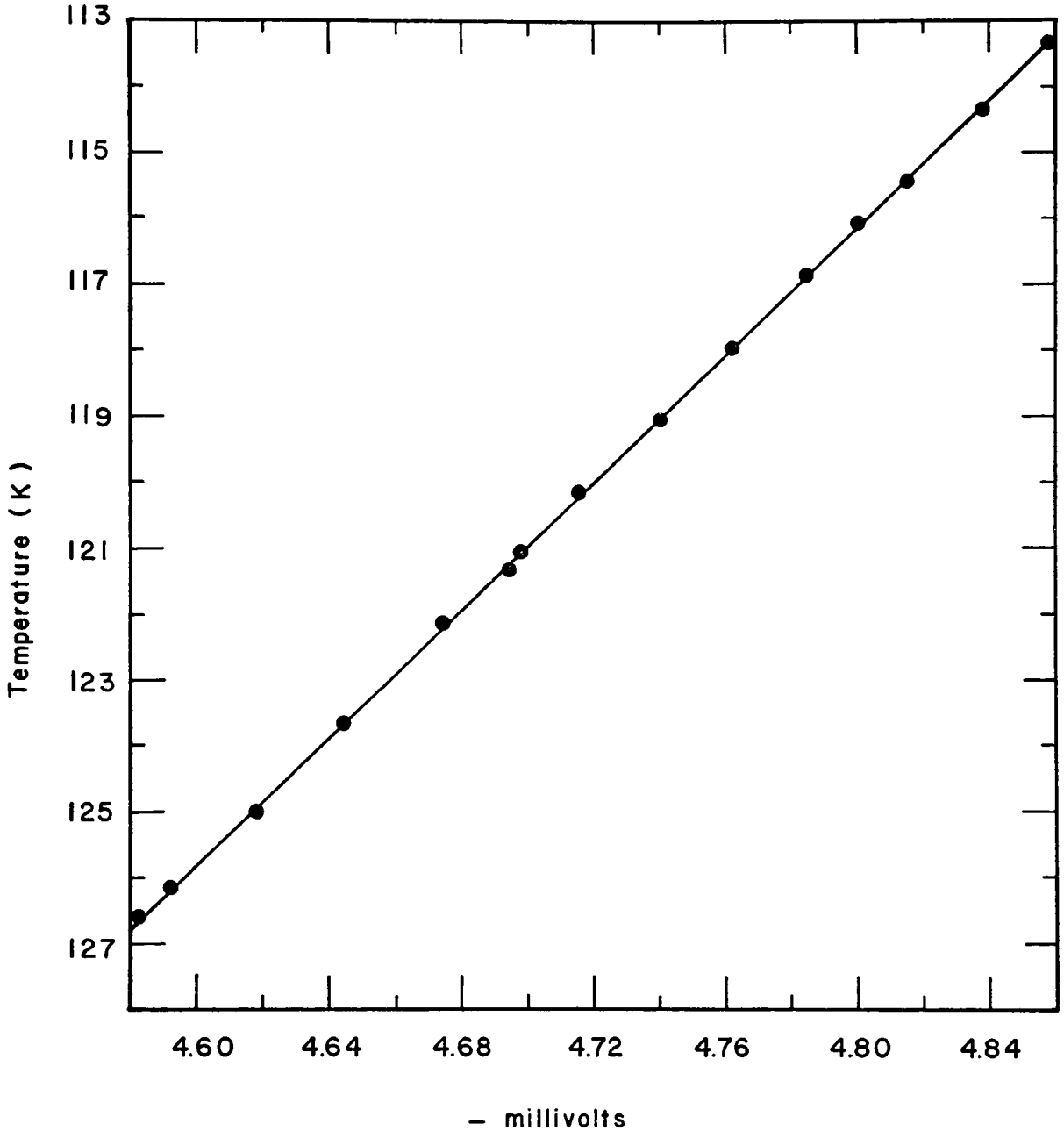
```
  115 IF(LV.EQ.0) GO TO 145
C     ZL=AMIN1(Z(1),Z(2),Z(3))
      ZL=AMIN1(Z(1),Z(2),Z(3))
C     JJ=0
C     DO 140 I=1,3
C     ZZ(I)=9999.
C     JJ=JJ+1
C     IF(Z(I).LT.0.0) GO TO 146
C     ZZ(JJ)=Z(I)
C 140 CONTINUE
C     ZL=AMIN1(ZZ(1),ZZ(2),ZZ(3))
      GO TO 150
  145 ZL=AMAX1(Z(1),Z(2),Z(3))
      GO TO 150
  146 ZL=Z(1)
C     IF(ZL.GT.0.0) GO TO 126
C     ZL=ZZZL
C 126 IF(ZL.LE.1000.) GO TO 123
C     ZL=ZZZV
  123 CONTINUE
  150 H=B*P/ZL
      IF(1.0-H) 127,127,128
  127 IF(LV.EQ.0) GO TO 124
      H=0.98
      GO TO 128
  124 H=0.02
  128 IF(1.0+H)129,129,131
  129 IF(LV.EQ.0) GO TO 132
      H=0.98
      GO TO 131
  132 H=0.02
  131 CONTINUE
      VL=RT*B/H
C     WRITE(3,710)LV,ZL,VL,B,H,MTYPE
  710 FORMAT(3X,'LV= ',I3,2X,'ZL= ',E12.5,2X,'VL= ',E12.5,2X
     1,'B= ',E12.5,2X,'H= ',E12.5,2X,'MTYPE= ',I3)
C     CALL EQNRK(A2,B,P,H,ZL,LV)
      IF(LV.EQ.0) GO TO 135
      QD=(T**0.5)*VL*(VL+BMRKL)
      QH=(AMRKL/(T**0.5))*((2.*VL+BMRKL)/(VL**2*(VL+BMRKL)**2))
      QK=RT/((VL-BMRKL)**2   )
  135 DO 130 I=1,NCOMP
C     WRITE(3,591)ZL,H
      PHILN =(ZL-1.0)*BI(I)/B-ALOG(ZL)-ALOG(1.0-H)
     1    -(A2/B)*(2.**AIRKL(I)/AMRKL   -BI(I)/B)*ALOG(1.0+H)
      PHI(I)= EXP(PHILN )
C     WRITE(3,592)PHI(I),LV
  592 FORMAT(/3X,E12.5,2X,I3)
      IF(LV.EQ.0) GO TO 130
      QE1=0.0
      DO 125 J=1,NCOMP
  125 QE1=QE1+X(J)*ARKL(I,J)
      QE=2.0*QE1-AMRKL*BRKL(I)/(VL+BMRKL)
      QG=(RT/(VL-BMRKL))*(1.0+BRKL(I)/(VL-BMRKL))
      PVOL(I)=((QE/QD)-QG)/(QH-QK)
  130 CONTINUE
  300 RETURN
      END
```

```
      SUBROUTINE FGAMA(X,SGM,FGAMA)
C     DAVID KLEIN  (DECEMBER 8, 1982)
C  EVALUATION OF GAMMA VALUES FROM PEDLICH-KISTLER CONSTANTS
C     FORMULATION FOLLOWING EXACTLY FROM JEAN FU' THESIS
      DIMENSION X(5), SGM(5), FGAMA(5)
      COMMON/ELEMENTS/A1,A2,A3,A4,A5,A6,A7,A8,A9,A10,A11,A12,A13
      S1=X(1)*X(1)
      S2=X(2)*X(2)
      S3=X(3)*X(1)
      S4=X(1)-X(2)
      S5=X(2)-X(3)
      S6=X(3)-X(1)
      S7=X(1)
      S8=X(2)
      S9=X(3)
      SGM(   1)=  A1*S6*(1.-S7)
     1       +A2*S8*( 2.*S7-S6-2.*S7*S7+2.*S1 )
     2     +A3*S9*( 3.*S7*S7-3.*(S7)**3+6.*S7*S7*S8-4.*S1-3.*S1*S5+(S3)**
     3       2 )
C    4       -A4*S2 -2.*A5*S2*S5-3.*A6*(S5)**2
     4       -A4*S2 -2.*A5*S2*S5-3.*A6*(S5)**2  *S5*S9
     5       +A7*S7*(1.-S7)
     7       +A8*S9*( S7-2.*S3+2.*S7*S7-2.*S7 )
C    8   +A9*S9*( S9*S9+6.*S7*S2-4.*S5-3.*S2*S9+3.*S7*S7-3.*(S7)**3 )
     8   +A9*S9*( S9*S9+6.*S7*S3-4.*S3-3.*S3*S9+3.*S7*S7-3.*(S7)**3 )
     X       +A10*S2*(1.-2.*S7)  +A11*S2*( S8-S9-3.*S1+3.*S3 )
     9       +A12*S2*( S9-2.*S7-3.*S3+3.*S7*S7 )
     9       +A13*S2*( 2.*S7-S8-3.*S7*S7+3.*S1 )
      SGM(   2)= A1*S7*(1.-S8)  + A2*S7*( S7-2.*S8-2.*S1+2.*S3*S8 )
     1       +A3*S7*( S7*S7-4.*S1+6.*S3*S8-3.*S7*S7*S8+6.*S1*S5-3.*(S5)**
     2       )  + A4*S9*(1.-S8) +A5*S9*(2.*S8-S9-2.*S8*S8+2.*S2)
C    3       +A6*S9*( S9*S9+3.*S8*S8-4.*S2-3.*(S8)**3+6.*S2*S8-3.*S2)
     3       +A6*S9*( S9*S9+3.*S8*S8-4.*S2-3.*(S8)**3+6.*S2*S8-3.*S2*S9)
     4       -A7*S3 - 2.*A8*S3*( S6) - 3.*A9*S3*( S6)**2 + A10*S3*(1.-2.*
     5     S8)  +A11*S5*( 2.*S8-S9-3.*S8*S8+3.*S2) + A12*S3*( S5-S7+3.*S1
     7       3.*S2) + A13*S3*( S7-2.*S8-3.*S1+3.*S8*S8)
      SGM(   3)=  -A1*S1 -2.*A2*S1*S4 - 3.*A3*S1*(S4)**2 + A4*S8*(1.-S9)
     1       +A5*S9*( S8-2.*S9-2.*S2+2.*S9*S9) + A6*S8*( S5*S8-4.*S2
C    3       +3.*S9*S9+3.*S8*S2+6.*S2*S9-3.*S9*S9) + A7*S7*(1.-S9)
     3       +3.*S9*S9-3.*S8*S2+6.*S2*S9-3.*S9*S9) + A7*S7*(1.-S9)
     5       + A8*S7*( 2.*S9-S7-2.*S9*S9+2.*S3) + A9*S7*( S7*S7+3.*S9*S9
     7       -4.*S3-3.*(S9)**3+6.*S3*S9-3.*S3*S7) + A10*S1*(1.-2.*S9)
     7       +A11*S1*(S8-2.*S9-3.*S2+3.*S9*S9) + A12*S1*( -S7+2.*S9-3.*S9
     8       S9+3.*S3) + A13*S1*( S7-S8-3.*S3+3.*S2)
      FGAMA(1)=EXP(SGM(1))
      FGAMA(2)=EXP(SGM(2))
      FGAMA(3)=EXP(SGM(3))
      RETURN
      END
```

```
      SUBROUTINE CONFR(A2,B,P,E,Z,LV)
      TOL=1.0E-6
      IH=0
      IJ=0
   45 IF(LV.LT.1) GO TO 47
      IF(E.LT.1.0) GO TO 45
      E=0.12
      IH=IH+1
      IF(IH.LT.20) GO TO 45
      E=0.98
      GO TO 46
   47 IF(E.GT.0.0) GO TO 46
      E=E+0.01
      IH=IH+1
      IF(IH.LT.20)GO TO 47
      E=0.02
   46 IJ=IJ+1
      FE=-5*B /E+1./(1.0-E)-(A2/B)*E/(1.+E)
      DFE=5*B /E**2 +1./(1.-E)**2-(A2/B)/(1.+E)**2
C     WRITE(3,592)E,FE,DFE,LV
C592  FORMAT(20X,3E12.4,5X,I2)
C     IF(ABS(DFE).LT.1.0E-20) DFE=DFE/ABS(DFE)*1.0E-20
      TEST=FE/DFE
      E=E-TEST
      IF(IJ.GT.60)GO TO 48
      IF( ABS(TEST/E).GT.TOL) GO TO 45
   48 Z   =B*P/E
      RETURN
      END
```

APPENDIX D

The calibration curve of thermocouple # 2


113
115
117
119
121
123
125
127
Temperature (K)
4.60
4.64
4.68
4.72
4.76
4.80
4.84
– millivolts