This item was submitted to Loughborough's Research Repository by the author.
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

The calculation of thermodynamic properties and phase equilibria using a new cubic equation of state

PLEASE CITE THE PUBLISHED VERSION

PUBLISHER

© Navin C. Patel

LICENCE

CC BY-NC-ND 4.0

REPOSITORY RECORD

Patel, Navin C.. 2012. “The Calculation of Thermodynamic Properties and Phase Equilibria Using a New Cubic Equation of State”. figshare. https://hdl.handle.net/2134/11044.

Loughborough University

This item was submitted to Loughborough University as a PhD thesis by the author and is made available in the Institutional Repository (https://dspace.lboro.ac.uk/) under the following Creative Commons Licence conditions.

creative commons

COMMONS DEED

Attribution-NonCommercial-NoDerivs 2.5

You are free:

- to copy, distribute, display, and perform the work

Under the following conditions:

Attribution. You must attribute the work in the manner specified by the author or licensor.

Noncommercial. You may not use this work for commercial purposes.

No Derivative Works. You may not alter, transform, or build upon this work.

- For any reuse or distribution, you must make clear to others the license terms of this work.
- Any of these conditions can be waived if you get permission from the copyright holder.

Your fair use and other rights are in no way affected by the above.

This is a human-readable summary of the Legal Code (the full license).

Disclaimer

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/

BLL ID NO: D35744/81

LOUGHBOROUGH
UNIVERSITY OF TECHNOLOGY
LIBRARY

AUTHOR/FILING TITLE
PATEL, N

ACCESSION/COPY NO.
120510/02

VOL. NO. | CLASS MARK
FOR REFERENCE ONLY

LOAN COPY

08 JUN 81

18 NOV 2000

FOR REFERENCE ONLY

-5. JUL 1985

-3. JUL 1987

31 OCT 1996

012 0510 02

THE CALCULATION OF THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIA USING A NEW CUBIC EQUATION OF STATE

by

Navin Chhotubhai Patel, B.Sc. (D.I.S)

A Doctoral Thesis Submitted in Partial Fulfilment
of the Requirements for the Award of
Doctor of Philosophy of the
Loughborough University of Technology

October 1980

Supervisor: Dr A S Teja

© by Navin C Patel, 1980

Loughborough University
of Technology Library
Date Jan 81
Class
Acc. No 120510/02

ABSTRACT

A new three constant equation of state for fluids and fluid mixtures has been proposed. The equation contains three constants and is a more general form of the Peng-Robinson equation. In addition to the critical temperature and the critical pressure, two parameters are required to characterize a particular fluid. These parameters have been evaluated by minimizing the deviation in the saturated liquid densities while simultaneously satisfying the equilibrium criteria (equality of fugacities) along the saturation curve. Thus, prediction of volumetric properties in the saturation region and other regions of the phase diagram is improved, while accuracy in the prediction of vapour-liquid equilibrium is maintained. Parameters for hydrocarbons and non-hydrocarbons of importance to the synthetic fuel industry are presented. The new equation is extended to mixtures by using mixing rules similar to those used by Peng and Robinson. Only one binary interaction coefficient is sufficient for the accurate prediction of vapour-liquid equilibria. Optimum values of the binary interaction coefficients for hydrocarbon-hydrocarbon and hydrocarbon-non-hydrocarbon systems have been obtained using the new equation, the Peng-Robinson equation and the Soave modification of the Redlich-Kwong equation. The criterion used for selecting the optimum interaction coefficient is the minimization of deviations in bubble point pressures. The new equation has been tested for the prediction of volumetric behaviour of pure fluids and the phase and volumetric behaviour of binary, ternary and multicomponent systems. Comparisons with conventional equations (P-R, S-R-K, R-K and B-W-R-S) are shown.

The applicability of van-der-Waals one fluid model to generalised equations of state is demonstrated. The equations of Han and Starling, Simonet and Behar and Chaudron et al have been compared for volumetric predictions. The Han and Starling equation has also been used with two sets of mixing rules to predict vapour-liquid equilibrium. The van-der-Waals one fluid model has been

shown to be a simple and effective method of applying the complicated equations of state to the prediction of thermodynamic properties of mixtures.

A generalised form of the corresponding states principle using two non-spherical reference fluids is presented. This represents an alternative method of extending the equation of state approach to fluids and fluid mixtures when experimental data are not available.

ACKNOWLEDGEMENTS

I should like to express my sincere appreciation to the following:

DR A S TEJA for his unfailing friendship, encouragement and patient supervision of all the work presented in this thesis and for his invaluable guidance and help.

MR R H BERESFORD, MR J GLOVER and DR P RICE for their helpful discussions.

Staff of the Advisory Office of the University Computer Centre, for their constant advice, guidance and encouragement.

Mrs Janet Smith for typing this thesis.

All my friends who, in one way or another, contributed towards the making of this thesis, and above all my brother and parents for their years of patience and encouragement.

	Page
TITLE PAGE	i
ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
CONTENTS	
LIST OF PRINCIPAL SYMBOLS AND ABBREVIATIONS	viii

CONTENTS

1.	INTRODUCTION	1
2.	LITERATURE REVIEW: EQUATIONS OF STATE AND THE CORRESPONDING STATES PRINCIPLE	5
	2.1 Equations of State	5
	2.1.1 The Ideal Gas Equation of State	8
	2.1.2 The van der Waals Equation of State (1873)	9
	2.1.3 The Virial Equation of State	14
	2.1.4 The Redlich-Kwong Equation of State (1949)	16
	2.1.5 Modifications of the Redlich-Kwong Equation	20
	2.1.6 A Modified Redlich-Kwong Equation by Chaudron, Asselineau and Renon (1973)	22
	2.1.7 A Modified Redlich-Kwong Equation by Simonet and Behar (1976)	26
	2.1.8 The Soave-Redlich-Kwong Equation (1972)	28
	2.1.9 The Peng and Robinson Equation of State (1976)	31
	2.1.10 A Modified Peng and Robinson Equation of State by Heyen (1980)	34
	2.1.11 A Modified van der Waals Type Equation of State by Schmidt and Wenzel (1980)	38
	2.1.12 The Han-Starling Equation of State (1972)	41
	2.2 The Corresponding States Principle	46
	2.2.1 CSP and Two-Parameter Equations of State	48
	2.2.2 Extension of the CSP	49
	2.2.3 Extension to Mixtures	51
3.	CHOICE OF AN EQUATION OF STATE	56
4.	A NEW CUBIC EQUATION OF STATE	61

		Page
4.1	Evaluation of the Parameters	62
4.2	Pure Component Calculations	69
4.2.1	Density	69
4.2.2	Vapour Pressure	83
4.2.3	The Enthalpy Departure	87
4.2.4	The Entropy Departure	91
4.3	Extension to New Substances	92
4.4	Extension to New Substances via the Generalized Corresponding States Principle	96
4.5	Comparison of the Methods Used for Generalizing the Equation of State	103
4.6	Use of the Exponential Temperature Function	104
5.	PHASE EQUILIBRIUM IN MIXTURES	113
5.1	Thermodynamic Considerations	114
6.	CALCULATION OF MIXTURE PROPERTIES	121
6.1	Extension of the New Equation of State to Mixtures	122
6.2	Evaluation of the Binary Interaction Coefficient	125
6.3	Vapour-Liquid Equilibrium (VLE) Calculations	130
6.3.1	Calculation of the Bubble Point Pressure	130
6.3.2	Calculation of the Bubble Point Temperature	134
6.3.3	Calculation of the Equilibrium Ratios (K values)	134
6.3.4	Effect of Temperature and Pressure on ξ_{ijopt}	135
6.4	Calculation of the Mixture Density	135
6.5	Prediction of Saturated Liquid Volumes	137
7.	THE VAN DER WAALS ONE FLUID MODEL AND GENERALIZED EQUATIONS OF STATE	156
7.1	Mixture Density	157
7.2	VLE Calculations	157
7.2.1	Predictions of Bubble Point Pressure	158

	Page
7.2.2 Predictions of the Equilibrium Ratios	159
7.2.3 Volumes and Fugacities of Co-existing Phases	161
7.3 Comparison of Computer Time	161
8. SUMMARY OF RESULTS AND CONCLUSIONS	178
8.1 Conclusions	182
8.2 Suggestions for Future Work	184
GRAPHS (Figures 6.1 to 6.113)	190
REFERENCES	305
REFERENCES OF SATURATION DATA	314
REFERENCES OF VOLUMETRIC DATA	315
REFERENCES OF VAPOUR-LIQUID EQUILIBRIUM DATA	319

APPENDICES:

A. Parameters for the New Equation of State	329
B. Critical Properties of Pure Components.	331
Conversion Factors.	332
C. Constants Used in the Equations of State.	
Generalized Coefficients $d_i^{(K)}$ and $g_i^{(K)}$ in Chaudron Equation	333
Values of Parameters A_i and B_j in the Generalized Han and Starling Equation	334
Optimized Coefficients for the Chaudron Equation	335
Individually Fitted Constants for the Han and Starling Equation	336
D. Analytic Solution of A Cubic Equation.	337
E. Expressions for the Enthalpy and the Entropy Departures.	340
F. Calculation of Pure Component Fugacity.	347
Fugacity of Component i in a Fluid Mixture.	349
Fugacity of the ith component in a Fluid Mixture Using Han and Starling Equation.	359
Differentials of Pseudo Critical Constants.	367
G. Algorithms for Vapour-Liquid Equilibrium Calculations.	
Prediction of the Vapour Pressure.	371
Prediction of the Bubble Point Pressure.	372
Prediction of the Bubble Point Temperature.	375
Prediction of the Equilibrium Ratios.	377
H. Listings of Computer Programs.	381

LIST OF PRINCIPAL SYMBOLS AND ABBREVIATIONS

Roman Capitals

A	Molar Helmholtz free energy. Constant in Equation of State; may be Function of Temperature.
B	Second Virial Coefficient Constant in Equation of State; may be Function of Temperature.
C	Third Virial Coefficient. ~~Binary Interaction Parameter.~~ Constant in Equation of State; may be Function of Temperature. ~~Specific Heat Capacity.~~
D	Constant in Equation of State.
E	Constant in Equation of State; may be Function of Temperature.
F	Constant in Equation of State; may be Substance Dependent.
G	Molar Gibbs Free Energy.
H	Molar Enthalpy. Henry's Constant.
K	Constant in Equation of State; may be Substance Dependent. Equilibrium Ratio.
M	Constant
N	Constant
P	Pressure. Constant.

Q — Constant.

R — Molar Gas Constant.
Constant.
Initial Estimate of Equilibrium Ratio.

S — Molar Entropy.
Sum to be Minimized.

T — Absolute Temperature.

U — Molar Internal Energy.

V — Molar Volume.

X — Mole Fraction in Liquid Phase.
Variable.

Y — Mole Fraction in Vapour Phase.
Variable.

Z — Compressibility Factor.
Parameter in the New Equation of State.
Feed Composition.

Roman Lower Case

a — Constant in Equation of State; may be Function of Temperature.

b — Constant in Equation of State.

c — Constant in Equation of State.

d — Optimized Coefficient in Chaudron Equation.
Constant in Equation of State

e — Constant in Equation of State.

f	Fugacity.
g	Optimized Coefficient in Chaudron Equation.
k	Binary Interaction Parameter.
m	Constant; may be Substance Dependent.
n	No. of moles; No. of Components; No. of Carbon Atoms; No. of Data Points; Constant.
q	Constant. A Thermodynamic Function.
r	Constant.
u	Constant in Equation of State.
w	Constant in Equation of State.
x	Mole Fraction in Liquid Phase. Variable.
y	Mole Fraction in Vapour Phase. Variable.

Greek Symbols

α	Riedel Parameter. Constant in Equation of State; may be Function of Temperature.
β	Constant in Equation of State; may be Function of Temperature.
γ	Constant in Equation of State. Activity Coefficient.
δ	Binary Interaction Parameter.
ζ	Predicted Compressibility.

η	Binary Interaction Parameter for Volume.
θ	Substance Dependent Constant.
μ	Chemical Potential.
ξ	Binary Interaction Parameter for Temperature.
ρ	Molar Density.
ϕ	Conversion Factor; Angle in Degrees; Constant; Fugacity Coefficient.
ω	Pitzer's Acentric Factor.
Ω	Dimensionless Coefficient.

Subscripts

a,b	Refers to corresponding constants.
ab	Ratio of the values corresponding to a and b.
c	Critical property.
c_i	Critical property of component i.
calc.	Calculated.
CPR	Critical value from Peng and Robinson Equation.
CRK	Critical value from Redlich-Kwong Equation.
CvdW	Critical value from van der Waals Equation.
cm	Pseudo Critical Property.
D	Deviation Function.
exp	Experimental.
HS	Value from Han-Starling Equation.

i,j,k	Component Identification.
m	Mixture Property; Minimum or Maximum Value.
n	Constant Composition.
o	Constant Value.
opt	Optimum Value.
P	Constant Pressure.
r	Reduced Property.
s	Saturation Property.
S	Constant Entropy.
T	Constant Temperature.
V	Constant Volume.
1,2,3	Generalized Coefficients in Han-Starling Equation. Roots of Cubic Equation; Used to Identify Different Constants.
-	Total Quantity.

Superscripts

CH	Refers to Hydrocarbon.
i,j,k	Optimized Coefficients in Chaudron Equation.
L	Liquid Phase.
o	Reference State; Simple Fluid; Standard State; Ideal Gas State.
r	Reference Fluid.
r1,r2	Reference Fluid 1, Reference Fluid 2.
S	Solid Phase.

V	Vapour Phase.
α,β,γ	Different Phases.
-	Partial Molar Quantity.
'	Used to Differentiate between two Quantities Represented by the Same Symbol. Differential of Given Quantity.
0,1,2	Reference Fluids in Generalized Corresponding States Principle. Generalized Coefficients in Simonet-Behar Equation.

Abbreviations

AAD	Absolute Average Deviation.
CSP	Corresponding States Principle.
GCSP	Generalized Corresponding States Principle.
H-S	Han and Starling Equation.
M-P-R	Modified Peng and Robinson Equation (the New Equation presented in this work).
P-R	Peng and Robinson Equation.
P-V-T	Pressure-Volume-Temperature.
R-K	Redlich-Kwong Equation.
S-R-K	Soave-Redlich-Kwong Equation.
vdW	van der Waals Equation.
VLE	Vapour-Liquid Equilibrium.

CHAPTER 1

INTRODUCTION

Knowledge of accurate thermodynamic properties is an essential requirement of design work in the chemical industry. Failure of a particular design can often be directly attributed to a lack of accurate data.

The design of experiments to provide thermodynamic data is a cumbersome and often inaccurate process. It is also difficult to reproduce in a small scale laboratory experiment the conditions that will prevail in an actual industrial set-up. These difficulties have contributed to the formulation of different methods for the prediction of unmeasured properties. Currently available methods of correlation and prediction can be divided into three main categories:

i) The Corresponding States Principle (CSP) and its extensions.

ii) Methods based on an empirical equation of state.

iii) Activity coefficient methods.

Activity coefficient methods are at best, empirical correlations of data and are not considered further in this work. Of the first two methods, the Corresponding States Principle is the oldest and within certain limits, has the strongest theoretical basis. Historically, the CSP was introduced by van der Waals (1873), and it can be said that the principle is the most useful by product of the van der Waals equation of state. One of the limitations of the statistical mechanical CSP is its restriction to simple pure substances. Many proposals have been made for overcoming these difficulties (Rowlinson, 1954; Pitzer, 1939; Riedel, 1954; Viswanath and Su, 1965). The most widely used method of extending the sets of substances over which the (extended) principle can be used is the introduction of the

acentric factor by Pitzer (1939). The CSP can also be extended to mixtures by means of a one-fluid model whereby the properties of a given mixture can be represented by those of a single hypothetical pure fluid.

Equations of state can either be theoretical or semi-theoretical. Theoretical equations are based on either kinetic theory or statistical mechanics involving intermolecular forces while semitheoretical equations combine theory with a limited amount of experimental data. Semitheoretical equations of state have had the greatest success in representing data and in the calculation of derived properties.

When combined with appropriate thermodynamic relations, a well behaved equation of state can give accurate predictions of isothermal changes in heat capacity, enthalpy, entropy, fugacity, vapour pressure, latent heat of vaporization, activity coefficients and vapour-liquid equilibrium (VLE) in mixtures. The main advantage of using an equation of state procedure compared to the method using activity coefficients for VLE calculations, is that it avoids defining different reference states for the activity coefficients when one or more components are supercritical and, therefore, non existent as liquids at the given pressure and temperature. Equations of state on the other hand, may be applied to gases, liquids and solids, whether pure or mixed. For the above reasons, the search for simple and accurate equations of state continues to be of importance.

Since the time of van der Waals (1873), a large number of equations of state have appeared in the literature. These have ranged from simple expressions with one or two constants to complicated forms with more than 50 constants. The longer equations have been utilized for high precision work and one can find in the literature many interesting and useful forms such as the Benedict-Webb-Rubin (1940), the Strobridge (1962), the Virial form of Onnes (1901), the Martin-Stanford (1974) and the Han-Starling (1972) equations. Although these long and complex equations are desirable for the

precise representation of PVT data and calculation of thermodynamic properties, they are not generally preferred for involved thermodynamic calculations such as those for vapour pressures, latent heat of vaporization and multicomponent vapour-liquid equilibrium ratios because they require tedious manipulation and excessive computer storage in lengthy iterative calculations. The application of these long equations is frequently limited by the inaccessibility of the constants for the PVT conditions of interest. Establishing these constants is usually a lengthy process, requiring curve fitting, careful weighting of the experimental data and trial and error procedures. What appears to be limiting is the fact that extensive PVT data of the substance must be available in order to begin establishing these constants. In addition, some thermodynamic properties, such as the vapour pressure, must also be known.

The attractiveness of the shorter equations of state lies in their simplicity of calculation. Many of these short equations are cubic in volume and these include such well known forms as the van der Waals (1873), Clausius (1880), Berthelot (1899), Redlich-Kwong (1949), Wilson (1964), Soave (1972), Chaudron et al (1973), Simonet-Behar (1976), Peng-Robinson (1976) and Fuller (1976). To increase the accuracy of prediction, the cubic equations are often designed for the calculation of a specific thermodynamic property. No cubic equation has yet been found which can represent both low and high pressure volumetric behaviour and give accurate prediction of VLE. One of the most successful of the cubic equations has been the modified Redlich-Kwong equation proposed by Peng and Robinson (1976). This equation has been used with considerable success for the prediction of vapour-liquid equilibrium (Peng and Robinson, 1976; API, 1977), three phase equilibria (Peng and Robinson, 1976) and critical states of multicomponent mixtures (Peng and Robinson, 1977). Although the Peng and Robinson equation gives very good representation of VLE, the liquid phase density predicted by this equation is not reliable. One of the objectives of this research

was therefore to modify the Peng and Robinson equation in order to improve the prediction of liquid phase density while maintaining the accuracy in the prediction of VLE.

A second objective was to examine alternative ways of extending the resulting equation to the calculation of phase equilibria and phase densities of mixtures. Simple equations of state may be extended to mixtures either by means of the van der Waals one fluid model and the extended corresponding states principle (Teja, 1980; Teja and Sandler, 1980; Teja, Sandler and Patel, 1980) or by means of arbitrary mixing rules whereby their constants are replaced by composition dependent terms. Both approaches have been followed in this work. Wherever possible, comparisons with other equations and with alternative approaches will be shown and the relative advantages of each method will be outlined.

CHAPTER 2

LITERATURE REVIEW: EQUATIONS OF STATE AND THE CORRESPONDING STATES PRINCIPLE

2.1 Equations of State

An equation of state attempts to express in an analytical form the relationship existing between pressure (P) - Volume (V) - Temperature (T) and composition (x or y) in the absence of special field forces. Via this relationship for pure components and mixtures with fixed composition, it becomes possible to express an otherwise complicated three dimensional relationship or surface in terms of two dimensions by keeping one variable constant and varying the other two. The general form of this relationship is given by:

$$f\ [P,V,T,x] = 0 \qquad (2.1)$$

Two approaches to the development of an equation of state have been followed in the past. One is the theoretical approach based on either kinetic theory or statistical mechanics involving intermolecular forces. This is exemplified by such equations as those of van der Waals (1873), Lennard-Jones and Devonshire (1937), Flory, Orwall and Vrij (1964), Carnahan and Starling (1972), Beret and Prausnitz (1975) and De Santis, Gironi and Marrelli (1976). The other approach is empirical or at best only semi-theoretical. This is exemplified by equations such as those of Clausius (1880), Beattie and Bridgeman (1928), Benedict, Webb and Rubin (1940), Redlich and Kwong (1949), Bender (1973), Han and Starling (1972) and Peng and Robinson (1976).

The widespread activity in the field of equations of state over an extended period of time since the introduction of the van der Waals equation can be attributed to the exceptional power

and utility of an equation of state. In addition to P-V-T data smoothing and interpolation, an equation of state can be used to calculate derived thermodynamic properties through various thermodynamic relationships. When combined with appropriate thermodynamic relations, a well behaved equation of state can predict with high precision thermodynamic properties commonly needed in process engineering, such as:

1) Isothermal entropy and enthalpy departures.
2) Heats of mixing.
3) Isothermal changes in heat capacities.
4) Fugacities of liquid and vapour phases.
5) Vapour pressures.
6) Densities.
7) Latent heats of vaporization.

But the utility of an equation of state extends far beyond the the prediction of the above-mentioned thermodynamic properties. An equation of state even offers assistance in transport property calculations. Perhaps the most important industrial applications of equations of state lie in phase-equilibrium predictions and in calculations listed below.

a) Vapour-liquid equilibrium - bubble point, dew point and flash calculations.

b) Liquid-liquid equilibrium calculations.

c) Liquid-vapour-solid equilibria and freeze-out problems.

d) Simultaneous phase and chemical reaction equilibria.

Even the simple operations of compression and expansion of gases and liquids often involve vapour-liquid equilibrium.

Equations of state have been used for the prediction of critical points and the critical locus of a mixture (Joffe and Zudkevitch, 1967; Spear et al, 1969; Hissong and Kay, 1970) and in the calculation of data charts, particularly K value charts for

vapour-liquid equilibrium. Equations of state can also be used to predict and interpret results for thermodynamic anomalies e.g. multiple bubble points.

The enormous and varied potential and utility of equations of state has resulted in incorporating such equations in computerised flow sheet calculations for entire processes and in design calculations involving heat exchangers, distillation columns, storage tanks etc.

More recently, the scope of research in the field of equations of state has broadened to cover more than just improvements in P-V-T representation. The emphasis today is more towards the needs of industries. Modern research aspects of equations of state can be summarized as follows (Adler et al, 1977):

1. Development of completely new equations.
2. Improvement of existing equations.
3. Testing of existing equations for successes and failures.
4. Applications to mixtures via:
   a) new models
   b) new interaction constants.
5. Extension of given equations of state to other properties.
6. Extension to cryogenic conditions.
7. Calculation of constants for more and more substances.
8. Extension of usefulness of equations of state to new applications.
   a) addition to minimization of free energy technique.
   b) solution of freeze-out problems.
9. Development of a whole new approach - combining existing equations: one for the liquid phase and one for the vapour phase, and even one for pure liquid fugacity.

2.1.1 The Ideal Gas Equation of State

Attempts to describe the volumetric properties of gases date back at least to the time of Boyle, 300 years ago. These attempts led to the ideal gas laws which yield the simplest equation of state of the form:

$$PV = n\,RT \tag{2.2}$$

where n is no. of moles.

Equation (2.2) describes the behaviour of an ideal gas at any pressure, or the limiting behaviour of a real gas as the pressure tends to zero. Equation (2.2) is highly deficient in the representation of real gas behaviour such as the process of condensation at subcritical temperatures - a phenomenon which is not implicit in equation (2.2). From equation (2.2) it follows that for one mole of gas:

$$Z = \frac{PV}{RT} = 1 \tag{2.3}$$

where Z is the compressibility factor.

Thus, the compressibility factor Z predicted by the ideal gas equation of state is 1, and is independent of temperature and pressure. But for a real gas, Z is a function of these variables, as shown by Figure 2.1.

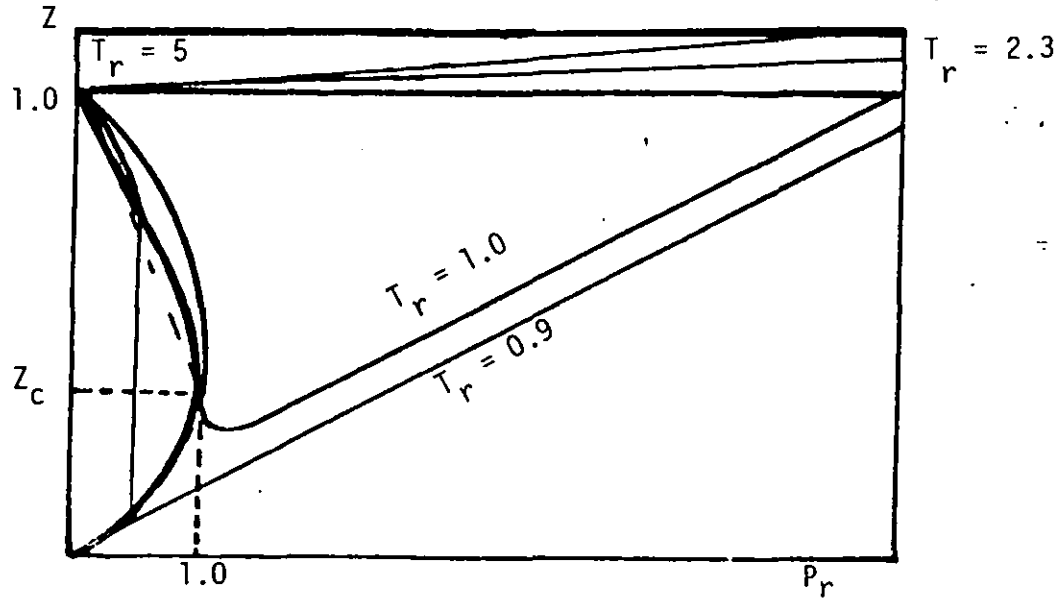


FIGURE 2.1 Generalized compressibility chart

2.1.2 The van der Waals Equation of State (1873)

It was not until van der Waals (1873) published his classical equation of state that systematic efforts were made to describe the occurrence of two phases and the equilibrium properties of real gases. Van der Waals took into account correction factors for the intermolecular forces of attraction and repulsion as well as the finite volume of the molecules. The van der Waals (vdW) equation is written in the following form:

$$(P + \frac{a}{V^2})\ (V - b) = RT \qquad (2.4)$$

where P is pressure; T is the absolute temperature; V is the molar volume and R the universal gas constant.

The constants a and b have an approximate physical meaning. 'a' provides a rough measure of the attraction forces between the molecules while 'b' is related to the molecular size.

The standard procedure for evaluating a and b is as follows.

Because the critical point on a P-V plot is a point of inflection the usual first two pressure-volume derivatives are set to zero:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \frac{-RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \qquad (2.5)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = \frac{2\ RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0 \qquad (2.6)$$

Since equation (2.4) holds in general, it holds at the critical point, so there are three equations available to solve for the two constants a and b. If P_c, V_c, and T_c are known, any two equations can be chosen for the solution. Usually equation (2.5) and equation (2.6) are used. In this case a and b are obtained in terms of T_c and V_c. Rearranging equations (2.5) and (2.6) and dividing one by the other we have:

$$\frac{2a}{V_c^3} \times \frac{V_c^4}{6a} = \frac{RT_c}{(V_c - b)^2} \times \frac{(V_c - b)^3}{2\ RT_c} \qquad (2.7)$$

hence: $V_c = 3b$ or $b = \frac{V_c}{3}$ (2.8)

By substituting for b into equation (2.5) or equation (2.6), we get:

$$a = \frac{9}{8}\ RT_c\ V_c \qquad (2.9)$$

When values of a and b are put into equation (2.4), a value

of P_c at V_c and T_c is predicted to be:

$$P_c = \frac{3}{8} \frac{RT_c}{V_c} \quad \text{or} \quad Z_{cvdW} = \frac{P_c V_c}{RT_c} = 0.375 \tag{2.10}$$

Thus, the predicted critical compressibility is higher than the experimental value which is less than 0.30 for common substances. Using equation (2.10), it is possible to write three different expressions for a, and two different expressions for b, depending on which pair of independent quantities is used from P_c, V_c, and T_c. These expressions are:

$$a\ [V_c, T_c] = \frac{9\ R\ T_c\ V_c}{8} \tag{2.11}$$

$$a\ [P_c, T_c] = \frac{27\ R^2\ T_c^{\ 2}}{64\ P_c} \tag{2.12}$$

$$a\ [P_c, V_c] = 3\ P_c\ V_c^{\ 2} \tag{2.13}$$

$$b\ [V_c] = \frac{V_c}{3} \tag{2.14}$$

$$b\ [P_c, T_c] = \frac{R\ T_c}{8\ P_c} \tag{2.15}$$

If the same pair of independent variables is employed in calculating a and b, three different equations of state result:

$$P\ [V_c, T_c] = \frac{RT}{V - \frac{V_c}{3}} - \frac{9\ RT_c\ V_c}{8\ V^2} \tag{2.16}$$

$$P\ [P_c, V_c] = \frac{RT}{V - \frac{V_c}{3}} - \frac{3\ P_c\ V_c^{\ 2}}{V^2} \tag{2.17}$$

$$P\ [P_c, T_c] = \frac{RT}{V - \frac{RT_c}{8P_c}} - \frac{27\ R^2\ T_c^{\ 2}}{64\ P_c\ V^2} \tag{2.18}$$

These are all perfectly valid equations based on the van der Waals development. The critical isotherms of these equations are shown in Figure 2.2 along with the true curve for Argon (see Martin, 1967). As can be seen, only equation (2.18) has a general appearance of the true curve. In fact, equation (2.18) is the most common form of the van der Waals equation which has been quoted in many textbooks. With reduced parameters defined by

$$P_r = \frac{P}{P_c}, \quad V_r = \frac{V}{V_c}, \quad T_r = \frac{T}{T_c}$$

equation (2.18) becomes

$$P_r = \frac{T_r}{Z_c V_r - \frac{1}{8}} - \frac{27}{64\ Z_c^{\ 2}\ V_r^{\ 2}} \tag{2.19}$$

Substituting $Z_c = \frac{3}{8}$ from equation (2.10)

$$P_r = \frac{8\ T_r}{3\ V_r - 1} - \frac{3}{V_r^{\ 2}} \tag{2.20}$$

This reduced equation of state implies that all gases, when held at equal values of P_r and T_r, should have equal values of V_r.

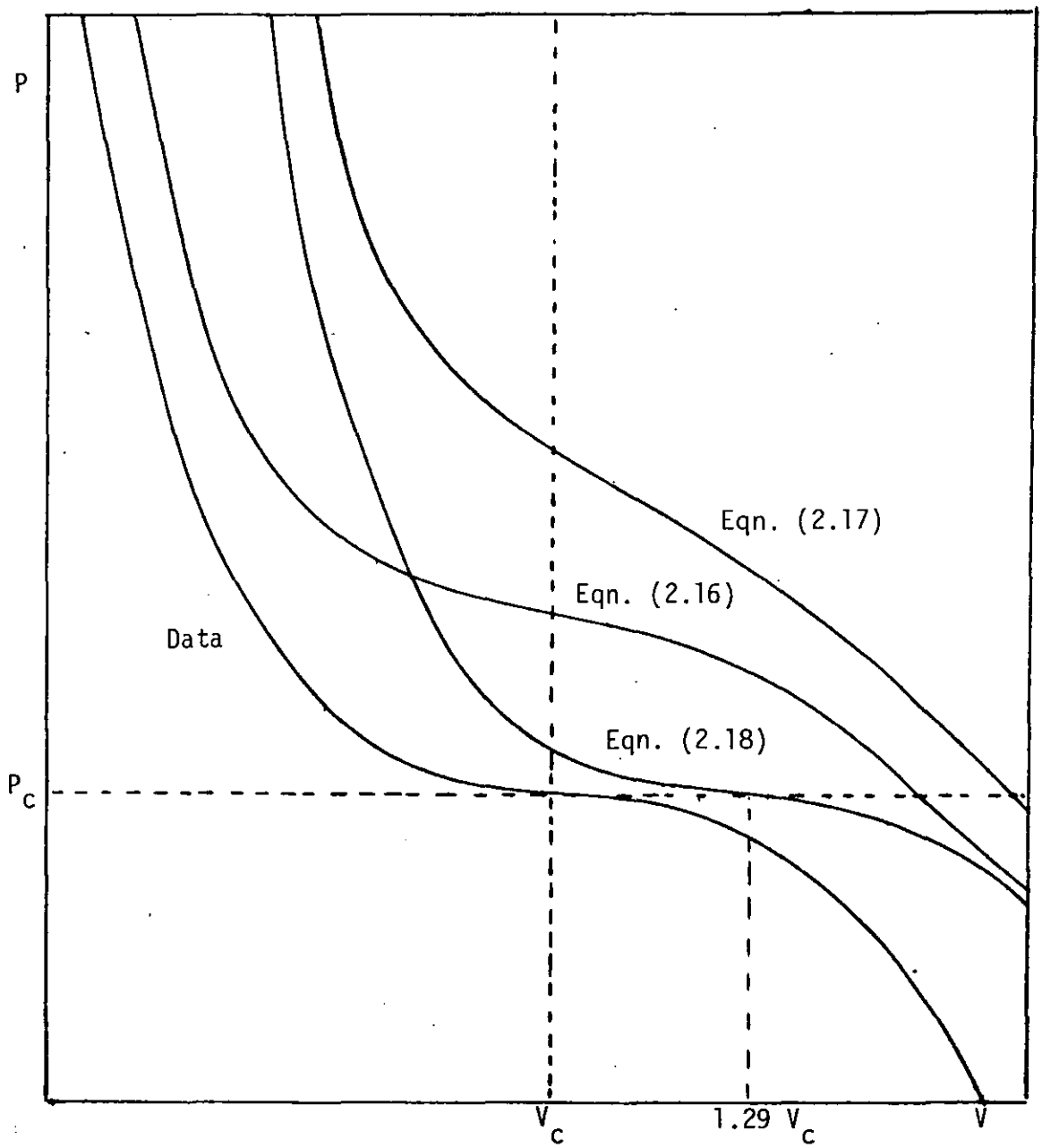


FIGURE 2.2 Critical isotherms of three van der Waals equations

This theorem, known as the corresponding states principle, has provided the basis for many theories of the fluid state and is discussed later in this chapter.

Van der Waals used the following mixing rules to extend his equation of state to mixtures:

$$a_m = \sum_i \sum_j y_i \, y_j \, a_{ij} \tag{2.21}$$

$$b_m = \sum_i \sum_j y_i \, y_j \, b_{ij} \tag{2.22}$$

$$a_{ij} = (a_{ii} \, a_{jj})^{\frac{1}{2}} \tag{2.23}$$

$$b_{ij} = \tfrac{1}{2} \, (b_{ii} + b_{jj}) \tag{2.24}$$

Although the vdW equation of state is rarely used in industrial applications nowadays, it is of considerable interest since it is the forerunner of the so called Redlich-Kwong type of equations which are so commonly used. The vdW equation is the simplest equation that gives a qualitatively adequate account of the process of condensation and the properties of co-existing phases. It is easy to manipulate and never yields physically absurd results. The poor agreement with experiment, particularly at the critical point and below, can be attributed to the simplicity of the equation and the fact that the predicted critical compressibility Z_{cvdW} is higher than the actual Z_c.

2.1.3 The Virial Equation of State

Most of the equations of state that have been proposed since the time of van der Waals are empirical in nature - there being

little theoretical justification for the constants appearing in them. In contrast to these equations, the virial equation of state has a sound theoretical foundation. The virial equation gives the compressibility factor as a power series:

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots\ldots \tag{2.25}$$

or $$Z = 1 + B\rho + C\rho^2 + \ldots\ldots\ldots \tag{2.26}$$

where: $\rho = 1/V$

or $$Z = 1 + B'P + C'P^2 + \ldots\ldots\ldots \tag{2.27}$$

The two, volume and pressure-implicit forms of the above equation are frequently called the Leiden and Berlin forms in recognition of the work done in the two cities. The constants B, B', C, C', D, D' .... etc. are termed the second, third and fourth virial coefficients etc. and it may be shown that they are independent of pressure and molar density. The virial coefficients are functions of temperature only and have a direct relationship to intermolecular forces. For simple molecules the second virial coefficient can be accurately calculated from pair interaction potentials. One of the most important advantages of this approach is that virial coefficients for mixtures are given by the rigorous relationships.

$$B_{mixture} = \sum_i \sum_j y_i \, y_j \, B_{ij} \tag{2.28}$$

$$C_{mixture} = \sum_i \sum_j \sum_k y_i \, y_j \, y_k \, C_{ijk} \tag{2.29}$$

Virial coefficients can be obtained from derivatives of the compressibility factor but the results obtained for the higher order (third, fourth, etc) coefficients are not accurate as errors are introduced by repeated differentiations. By far the most realistic method for calculating virial coefficients is that proposed by Lennard-Jones (1924).

Except in the case of hard sphere molecules with no attractive forces, virials beyond the third are largely unknown. With three virials, the gaseous region compressibility factors of simple molecules can be predicted accurately to the saturation line at reduced temperatures below about 0.9. At higher reduced temperatures the equation truncated after the third virial is accurate for V_r values greater than approximately 2. With only two virials, the equation is accurate at V_r values greater than about 8. For densities above the critical density approaching the liquid region, the virial equation gives poor results (Leland et al, 1968).

2.1.4 The Redlich-Kwong Equation of State (1949)

Redlich and Kwong proposed a two constant equation based on several theoretical and practical considerations. Their proposed equation is:

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}}\, V\,(V+b)} \qquad (2.30)$$

where the constants a and b are obtained by equating the two pressure-volume derivatives to zero at the critical point, as in the case of the vdW equation. In terms of T_c and P_c, a and b are

$$a = 0.42748\ \frac{R^2\, T_c^{\,2.5}}{P_c} \qquad (2.31)$$

$$b = 0.08664\ \frac{R\, T_c}{P_c} \qquad (2.32)$$

An important theoretical consideration in the derivation of Redlich-Kwong (R-K) equation was the experimental observation that the volume of all gases approaches a limiting value at high pressures. Redlich and Kwong assumed a value given by:

$$b = 0.26\ V_c \tag{2.33}$$

Redlich and Kwong stated that equation (2.30) furnishes satisfactory results above the critical temperature for any pressure. This was also concluded by Thodos and Shah (1965) who used the equation for the prediction of P-V-T properties of argon. Thodos and Shah found that for argon, the R-K equation predicted accurate densities over a wide range of temperature and pressure and was valid for both the gaseous and liquid regions.

The RK equation can be written in the following reduced form:

$$P_r = \frac{T_r}{Z_c\left(V_r - \frac{0.08664}{Z_c}\right)} - \frac{0.42748}{T_r^{\frac{1}{2}}\ V_r\ Z_c^{\ 2}\left(V_r + \frac{0.08664}{Z_c}\right)^2} \tag{2.34}$$

At the critical point, $P_r = 1$, $T_r = 1$, $V_r = 1$ and substituting into equation (2.34), a gas obeying the R-K equation has a critical compressibility of

$$Z_{CRK} = 0.3333 \tag{2.35}$$

If the actual critical compressibility of a fluid is used in equation (2.34), prediction of densities in the critical region is improved (Leland et al, 1968).

Equation (2.30) can also be written as a cubic in the compressibility Z,

$$Z^3 - Z^2 + (A - B^2 - B)\ Z - AB = 0 \qquad (2.36)$$

where: $$A = \frac{aP}{R^2\ T^{2.5}} = \Omega_a \frac{P_r}{T_r^{2.5}} \qquad (2.37)$$

$$B = \frac{bP}{RT} = \Omega_b \frac{P_r}{T_r} \qquad (2.38)$$

and $\Omega_a = 0.42748$
$\Omega_b = 0.08664$

To extend the application of the equation to mixtures, the following mixing rules for a and b are recommended:

$$a_m = \sum_i \sum_j y_i\ y_j\ a_{ij} \qquad (2.39)$$

$$b_m = \sum_i y_i\ b_i \qquad (2.40)$$

where: a_m and b_m are mixture constants.
y_i, y_j are mole fractions.

There are no sound theoretical reasons for the mixing rules given here. However, b is related to the limiting volume, and therefore depends linearly on the mole fractions, while a is related to the second virial coefficient and must therefore be quadratic in the mole fractions. The cross-terms a_{ij} in equation (2.39) can be obtained from the following geometric mean rule:

$$a_{ij} = (a_{ii}\ a_{jj})^{\frac{1}{2}} \tag{2.41}$$

For mixtures containing physically and chemically similar molecules, equation (2.41) gives adequate representation of P-V-T properties. However, for mixtures containing chemically and physically dissimilar molecules, a correction factor commonly known as the binary interaction coefficient must be used. Thus we may write

$$a_{ij} = \xi_{ij}\ (a_{ii}\ a_{jj})^{\frac{1}{2}} \tag{2.42}$$

where ξ_{ij} is a binary interaction coefficient which must be obtained from experimental data for the mixture.

The R-K equation is a marked improvement over the vdW equation, with a greater numerical accuracy and providing the best two parameter equation of state for the gas phase volumetric properties of simple fluids and fluid mixtures. It is remarkably simple and can be employed in all property calculations. It has achieved wide application and acceptance in chemical engineering practice, its justification resting mainly on the good degree of approximation obtained by comparatively simple means. Like the vdW equation, it is a well behaved function which can be used to represent gas phase properties over a wide range of pressures. Although it provides a superior fit to real gas behaviour than the vdW equation, it is no better in the critical region. However, it is doubtful whether this region can be represented by any single cubic equation or, indeed, any analytical equation of state (Sengers et al, 1968). Nevertheless, the representation in the critical region is more realistic than that of the more complicated equation of Benedict, Webb and Rubin (1940), which exhibits erratic and unusual behaviour in this region. The R-K equation is desirable in mixture calculations because of the ease and simple manner in which binary interactions can be introduced into it.

Nevertheless, like any other equations of state, the R-K equation has its shortcomings. It cannot give accurate predictions for widely different types of fluid over extensive ranges of temperature, pressure and density conditions. The original R-K equation was proposed for non-polar fluids in the gaseous state only and hence, its application to polar fluids and their mixtures and for the liquid state is not recommended. The fundamental criterion of the equality of fugacities is not implicit in the equation and therefore it should not be strictly applied for the calculation of vapour-liquid equilibrium.

The inherent inadequacies of the R-K equation are related to the fact that it contains only two parameters and predicts a universal critical compressibility which is much higher than the actual experimental value for any fluid.

2.1.5 Modifications of the Redlich-Kwong Equation

Since its introduction in 1949, the R-K equation has been modified in many different ways in an attempt to improve its accuracy in P-V-T representation and in the prediction of thermodynamic properties and phase equilibria. The corresponding states principle suggests that the equation should have at least three parameters to describe satisfactorily the behaviour of substances which are not simple fluids. Two possibilities for the third parameter are the actual critical compressibility Z_c and Pitzer's acentric factor, ω. The acentric factor has been used widely and it permits the influence of the molecular size and shape to be taken into account. It is defined by:

$$\omega = - \log P_r - 1.0 \qquad (2.43)$$

where P_r is the reduced vapour pressure at $T_r = 0.7$.

Efforts have also been made to extend the R-K equation to polar substances (Fuller, 1976; Chaudron et al, 1973) and their mixtures and to the critical region. It is interesting to note that Redlich himself has proposed a number of variations in the hope of achieving more accurate representation (Redlich et al, 1963; 1965; 1970). Horvath (1974) presented a shorter communication giving a list of 112 references containing a comprehensive collection of the published works on the R-K equation. Since 1974 more than 20 modifications have appeared in the literature. The fact that the R-K equation has become the most modified equation of state in the history of applied thermodynamics reflects the need for a simple equation of state. The multiplicity of variations can also be explained by the general difficulty of developing a reasonable compact equation of state applicable over a wide range of substances and conditions.

Any modifications to the R-K equation and in general to any cubic equations will involve two kinds of compromise:

1. Accuracy versus complexity.
2. Accuracy in one region versus inaccuracy in another.

The modifications made to date can be conveniently classified under the following categories:

1. Temperature dependence of the parameters a and/or b (Chaudron et al, 1973).

2. Addition of a correction term such as a deviation function to the original function; thus

$$Z = Z_{RK} + Z_D \qquad \text{(Redlich et al, 1970)}$$

3. Use of additional constraints to determine constants (Soave; 1972).

4. Changing the expression to determine a and b (Peng and Robinson; 1976).

5. Addition of new parameters (Simonet and Behar; 1976).

6. Use of hard sphere repulsion theory (De Santis et al; 1976).

7. Improvements and new suggestions on mixing rules. This includes the introduction of binary interaction coefficient (Graboski and Daubert; 1978).

Perhaps the most successful modifications of the R-K equation, which are widely used in industries for vapour-liquid equilibria are those proposed by Soave (1972) and Peng and Robinson (1976). Modifications by Simonet and Behar (1976) and Chaudron et al (1973) have been shown to give excellent predictions of pure component density over a wide range of conditions. However, the most important application of equations of state in industry is probably in the calculation of vapour-liquid equilibria and, for such calculations, the equations of Soave (1972) and Peng and Robinson (1976) have achieved eminence.

2.1.6 A Modified Redlich-Kwong Equation by Chaudron, Asselineau and Renon (1973)

In this modification, the two parameters of the original R-K equation were taken as temperature dependent. Constants a and b were written in terms of critical temperature and critical pressure in the usual manner:

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c} \tag{2.44}$$

$$b = \Omega_b \frac{R T_c}{P_c} \tag{2.45}$$

However, in contrast to the other modifications of the R-K equation, Ω_a and Ω_b were not evaluated by applying the classical constraints at the critical point. They were represented by the

following analytical forms:

$$\Omega_a = \sum_i \frac{C_{a,i}}{T_r^{\,i}} \qquad i = 0, 1, 2 \tag{2.46}$$

$$\Omega_b = \sum_j C_{b,j} \cdot T_r^{\,j} \qquad j = 0, 1, 2 \tag{2.47}$$

$C_{a,i}$ and $C_{b,j}$ are optimised coefficients which were obtained by minimizing the relative deviation between experimental and computed values of volume for all data available. Chaudron et al (1973) obtained $C_{a,i}$ and $C_{b,j}$ for 25 substances including hydrocarbons up to n-decane and some polar substances such as water and ammonia.

For non-polar substances in reduced temperature range $0.65 < T_r < 1.5$, Ω_a and Ω_b have been correlated in the following way:

$$\Omega_a \sqrt{T_c} = \Omega_a^{(0)} + \omega \Omega_a^{(1)} \tag{2.48}$$

$$\Omega_b = \Omega_b^{(0)} + \omega\, \Omega_b^{(1)} \tag{2.49}$$

and $$\Omega_a^{(K)} = \sum_i \frac{d_i^{(K)}}{T_r^{\,i}} \qquad i = 0, 1, 2 \tag{2.50}$$

$$\Omega_b^{(K)} = \sum_j g_j^{(K)}\, T_r^{\,j} \qquad j = 0, 1, 2 \tag{2.51}$$

$d_i^{(K)}$ and $g_j^{(K)}$ are generalised coefficients and they have

been obtained by fitting values of Ω_a and Ω_b from equations (2.46) and (2.47) at a few reduced temperature values for all substances considered.

To extend the proposed modification to the calculations of mixture properties, a new set of mixing rules were used. A new parameter F was defined as:

$$F_{ii} = \frac{a_{ii}^{2/3}}{b_{ii}} \tag{2.52}$$

$$F_{mix} = \sum_i \sum_j x_i \, x_j \, F_{ij} \tag{2.53}$$

$$F_{mix} = \frac{a_{mix}^{2/3}}{b_{mix}} \tag{2.54}$$

$$b_{mix} = \sum_i x_i \, b_i \tag{2.55}$$

Based on the experimental partial volume data of 19 binary mixtures, the following correlation for F_{ij} was obtained:

$$F_{ij} = \frac{\Omega_{ai}^{2/3} \, [T_m] . \, R^{2/3} . Z_{ci}^{1/3} \, T_{cij}}{\Omega_{b,i} \, [T_m] . \, V_{ci}^{1/3}} \tag{2.56}$$

where: $$T_{cij} = (T_{ci} . T_{cj})^{\frac{1}{2}} \, (1 - C_{ij}) \tag{2.57}$$

$$T_m = T/T_{cij} \tag{2.58}$$

$$Z_{ci} = 0.291 - 0.08\,\omega_i \tag{2.59}$$

where, i is the most volatile component ($T_{ci} < T_{cj}$). The interaction coefficient, C_{ij} for different systems was given by:

For hydrocarbon mixtures:

$$C_{ij} = 1 - \frac{\sqrt{V_{ci}^{1/3}\,V_{cj}^{1/3}}}{\frac{1}{2}(V_{ci}^{1/3} + V_{cj}^{1/3})} \tag{2.60}$$

For paraffin-carbon dioxide systems:

$$C_{ij} = \frac{0.25\,V_c^{CH} - 7}{V_c^{CH} + 31.5} \tag{2.61}$$

where V_c^{CH} is the critical volume of the paraffin.

For paraffin-hydrogen sulfide systems:

$$C_{ij} = 1.0 \tag{2.62}$$

For other mixtures, some experimental data are needed to obtain F_{ij}.

The above mixing rules were recommended for the calculation of partial molal volumes and vapour phase fugacity coefficients. For the calculation of liquid phase fugacity, activity coefficients were used and the influence of pressure on liquid fugacity was calculated using the modified equation with given mixing rules.

In view of the number of equations involved and the requirement of additional parameters, the use of this modification for vapour-liquid equilibrium (VLE) calculations presents a more difficult task compared with the use of the Soave (1972) or the Peng-Robinson (1976) equations. Accurate predictions of VLE were made by Chaudron et al but they did not follow the easier single equation of state approach.

In general, this modification using equations (2.46) and (2.47), gives very accurate predictions of density over a wide range of pressures and temperatures. Results obtained were as good as and in some cases better than those obtained using the eight constant equation of Benedict, Webb and Rubin (1940). Other volumetric properties can also be predicted with a good degree of accuracy.

The prediction of mixture density can be made through the mixing rules given by equations (2.52) - (2.62). But it is not necessary to use this set of mixing rules. Accurate predictions of mixture density have also been obtained by Teja et al (1978) using the relatively simple mixing rules of van der Waals.

2.1.7 A Modified Redlich-Kwong Equation by Simonet and Behar (1976)

In this modification, the parameters of the original R-K equation were treated as functions of temperature and acentric factor. The equation was written as:

$$P = \frac{RT}{V-b} - \frac{a\ [T]}{V(V+b)} \tag{2.63}$$

with the constants a and b being given by:

$$a = \Omega_a \frac{R^2\ T_c^2}{P_c} \tag{2.64}$$

$$b = \Omega_b \frac{R\ T_c}{P_c} \tag{2.65}$$

From equations (2.64) and (2.65):

$$\frac{a}{b} = \frac{\Omega_a}{\Omega_b} RT_c = \Omega_{ab}\ RT_c \tag{2.66}$$

Ω_a and Ω_b were obtained by minimizing the root mean square deviation between the experimental and computed values of volume for all data available. The temperature range of data was $0.5 < T_r < 1.5$. Ω_{ab} was correlated with the acentric factor and reduced temperature in the following way:

$$\Omega_{ab} = \Omega_{ab}^0 + \omega\ \Omega_{ab}^1 \tag{2.67}$$

$$\Omega_{ab}^0 = 5.06364 \tag{2.68}$$

$$\Omega_{ab}^1 = -8.10914 + 8.81715/T_r \tag{2.69}$$

Ω_b was correlated as:

$$\Omega_b = \Omega_b^0 + \Omega_b^1 \, |T_r - 1| + \Omega_b^2 \, |T_r - 1|^2 \qquad (2.70)$$

$$\Omega_b^0 = 0.0826 - 0.0122.\omega \qquad (2.71)$$

$$\Omega_b^1 = 0.0220 - 0.0127.\omega \qquad (2.72)$$

$$\Omega_b^2 = -0.0072 - 0.02905.\omega \qquad (2.73)$$

This generalized form of the equation has been tested in the liquid, gas and hypercritical regions for normal alkanes up to n-decane. Experimental volumes were reproduced within 1% but the critical region ($0.96 < T_r < 1.1$) was avoided. This equation also gave accurate predictions for heavy hydrocarbons: from n-decane to n-hexadecane. Results obtained from this equation were as good as and in some cases better than those obtained from the equation of Chaudron et al (1973) and the equation of Benedict, Webb and Rubin (1940). Accurate predictions for the enthalpy departures have also been obtained.

This equation has been used with the van der Waals one-fluid model to predict mixture densities (Teja et al; 1978). Their results indicated that accurate predictions of mixture density can be made using simple mixing rules.

Equation (2.63) should not be used for the calculation of saturation properties because the fundamental criterion of the equality of fugacities for saturation phases is not satisfied.

2.1.8 The Soave-Redlich-Kwong Equation (1972)

Soave modified the original R-K equation for vapour-liquid equilibrium (VLE) calculations. He surmised that the R-K equation

gave poor predictions for VLE because the influence of temperature was not represented adequately. His work was based on the assumption that an improvement in reproducing saturation conditions of pure substances also leads to an improvement for mixtures. The term $a/T^{\frac{1}{2}}$ in equation (2.30) was replaced by a more general temperature-dependent term a[T].

$$P = \frac{RT}{V-b} - \frac{a[T]}{V\,(V+b)} \tag{2.74}$$

In terms of the compressibility factor, Z, the R-K-S equation is identical to the R-K equation

$$Z^3 - Z^2 + (A - B^2 - B)\,Z - AB = 0 \tag{2.75}$$

where: $$A = \frac{a[T]\,P}{R^2\,T^2} = \Omega_a \frac{P_r}{T_r^{\,2}}\,\alpha[T] \tag{2.76}$$

$$B = \frac{bP}{RT} = \Omega_b \frac{P_r}{T_r} \tag{2.77}$$

$$b = \Omega_b \frac{RT_c}{P_c}$$

$$\Omega_a = 0.42748; \quad \Omega_b = 0.08664 \tag{2.78}$$

At the critical point the S-R-K equation is identical to the R-K equation and the predicted critical compressibility factor is 0.333. At temperatures other than the critical, constant a[T] is

given by:

$$a[T] = a_c.\alpha[T] \tag{2.79}$$

where: $$a_c = \Omega_a . \frac{R^2 \; T_c^{\;2}}{P_c} \tag{2.80}$$

A set of values of $\alpha[T]$ for a number of hydrocarbons were obtained by satisfying the criterion of the equality of fugacities

$$f^L = f^V \tag{2.81}$$

When values of $\alpha[T]^{\frac{1}{2}}$ were plotted against $T_r^{\frac{1}{2}}$, almost straight lines were obtained. As all lines must pass through the same point ($T_r = \alpha[T] = 1.0$), we can write:

$$\alpha[T]^{\frac{1}{2}} = 1 + m\,(1 - T_r^{\frac{1}{2}}) \tag{2.82}$$

The slopes of these lines, m, were correlated with the acentric factor by Soave to give

$$m = 0.480 + 1.57\,\omega - 0.176\,\omega^2 \tag{2.83}$$

The acentric factor, ω, was used as a third parameter to extend the original R-K equation to heavier hydrocarbons.

Soave calculated the vapour pressures of a number of hydrocarbons ranging from ethylene to n-decane.

From the results presented by him, the modification appears to be a vast improvement over the original R-K equation not only in the prediction of vapour pressures but also in VLE predictions. Mixing rules used for a and b were the same as those used for the original R-K equation.

Soave concluded that larger deviations were obtained for systems containing carbon dioxide, hydrogen sulfide and polar compounds. For these systems use of the binary interaction coefficient was recommended. No binary interaction coefficients were used for hydrocarbon-hydrocarbon systems.

In general, saturated liquid densities calculated from the Soave equation are lower than the experimental values. This is true except for small molecules like argon, nitrogen and methane at very low temperatures where the predicted values of liquid density are slightly higher. Saturated vapour densities are predicted accurately (Peng and Robinson, 1976).

2.1.9 The Peng and Robinson Equation of State (1976)

This equation can be written in the following form, which is different to that of the R-K equation:

$$P = \frac{RT}{V-b} - \frac{a[T]}{V(V+b) + b(V-b)} \qquad (2.84)$$

In terms of the compressibility factor, it can be written as:

$$Z^3 - (1-B)\,Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \qquad (2.85)$$

where: $$A = \frac{aP}{R^2\ T^2} \tag{2.86}$$

$$B = \frac{bP}{RT} \tag{2.87}$$

$$Z = \frac{PV}{RT} \tag{2.88}$$

Equating the two pressure derivatives to zero to describe the critical point, we have

$$a[T_c] = 0.45724\ \frac{R^2\ T_c^{\ 2}}{P_c} \tag{2.89}$$

$$b[T_c] = 0.07780\ \frac{RT_c}{P_c} \tag{2.90}$$

$$Z_{CPR} = 0.3074$$

At temperatures other than the critical:

$$a[T] = a[T_c].\ \ \alpha[T_r,\omega] \tag{2.92}$$

$$b[T] = b[T_c] \tag{2.93}$$

where: $\alpha[T_r,\omega]$ is a dimensionless function of reduced temperature and acentric factor and equals unity at the critical temperature. Equation (2.92) was also used by Soave (1972).

The functional form of $\alpha[T_r,\omega]$ was determined by using experimental vapour pressures and satisfying the equilibrium condition of the equality of fugacities along the vapour pressure curve. The relationship between α and T_r was given by:

$$\alpha^{\frac{1}{2}} = 1 + K\,(1 - T_r^{\frac{1}{2}}) \qquad (2.94)$$

where: K is a constant characteristic of each substance and was given by:

$$K = 0.37464 + 1.54226\omega - 0.26992\,\omega^2 \qquad (2.95)$$

The value of K for each pure component was obtained by linearizing the $\alpha^{\frac{1}{2}}\,[T_r,\omega]$ vs $T_r^{\frac{1}{2}}$ relationship between the normal boiling point and the critical point. This is slightly different than the method of Soave (1972) which assumed a linear relationship from $T_r = 1.0$ to $T_r = 0.7$.

The influence of ω and K was obtained by a least squares fit of the data for all components of interest.

Equation (2.84) was extended to mixtures using the same mixing rules as those used for a and b in the original R-K equations. Use of an experimentally determined binary interaction coefficient was recommended for VLE calculations of systems containing weakly polar components such as carbon dioxide and hydrogen sulfide.

Comparison with the Soave equation shows that both equations predict bubble point pressures and equilibrium ratios with the same accuracy. However, equation (2.84) is superior in the representation of vapour pressures and saturated liquid densities. In general, both equations predict vapour phase properties equally

well but equation (2.84) is superior for liquid phase properties, except in the case of very light components such as argon for which it gives poor predictions in the region away from the critical ($T_r < 0.8$). The fact that equation (2.84) predicts a universal critical compressibility factor of 0.3074 as compared with Soave's 0.333 has improved the predictions in the critical region for those components whose critical compressibility factor is close to 0.3074. For heavy hydrocarbons and highly polar substances, for which the value of the critical compressibility factor lies below 0.26 (and therefore far from 0.3074), equation (2.84) does not give good predictions. The applicability of equation (2.84) can be extended to a wide range of substances and conditions if a way can be found to make the predicted critical compressibility factor a substance dependent parameter. It is not necessary to reproduce the actual critical compressibility factor as indicated by the results obtained from equation (2.84), but the value of the predicted critical compressibility factor should be sufficiently close to the experimental value for the overall results to be acceptable.

2.1.10 A Modified Peng and Robinson Equation of State by Heyen (1980)

In this modification, a third parameter has been added to the two parameter equation of state proposed by Peng-Robinson (1976). The experimental value of the critical compressibility factor is reproduced exactly. The form of this equation is given by:

$$P = \frac{RT}{V-e} - \frac{a}{V^2 + (b+e)\,V - be} \qquad (2.96)$$

where a and e are temperature dependent. Equation (2.96) reduces to the Peng-Robinson equation by setting b=e. In terms of the compressibility, Z, it can be written as:

$$Z^3 + (B-1)Z^2 + (A-B-E-2BE-E^2)Z + (BE^2+BE-AE) = 0 \qquad (2.97)$$

where: $Z = \frac{PV}{RT}$; $B = \frac{bP}{RT}$

$A = \frac{aP}{R^2T^2}$; $E = \frac{eP}{RT}$

As explained by Martin and Hou (1955), values of A, B and E at the critical temperature are obtained by noting that equation (2.97) has 3 equal roots Z_c. Hence:

$$B_c = 1 - 3Z_c \qquad (2.98)$$

$$E_c^3 + (2 - 3Z_c)E_c^2 + 3Z_c^2 E_c - Z_c^3 = 0 \qquad (2.99)$$

$$A_c = B_c + E_c + 2B_c E_c + E_c^2 + 3Z_c^2 \qquad (2.100)$$

To solve equation (2.99) Newton's method is recommended with an initial value of E_c given by:

$$E_c \sim 0.32429\ Z_c - 0.022005 \qquad (2.101)$$

Since equation (2.99) is cubic, it can also be solved analytically, as indicated in Appendix (D). At temperatures other than the critical, a, b and e were given by:

$$a = A_c \cdot \frac{R^2\ T_c^2}{P_c} \cdot \alpha[T_r] \qquad (2.102)$$

$$b = B_c \cdot \frac{RT_c}{P_c} \tag{2.103}$$

$$e = E_c \cdot \frac{RT_c}{P_c} \cdot \beta[T_r] \tag{2.104}$$

Values of $\alpha[T_r]$ and $\beta[T_r]$ have been calculated by forcing the equation of state to match experimental vapour pressures and saturated liquid volumes. α is a monotonically decreasing function of T_r. The form selected by Soave (1972) and Peng-Robinson (1976) is not appropriate, since it predicts that α vanishes, then starts increasing at high T_r. A new form for α was suggested by Heyen. This is given by:

$$\alpha[T_r] = \exp\left(K\left(1 - T_r^{\,n}\right)\right) \tag{2.105}$$

Values of β decrease from a maximum asymptotic value at low T_r, to unity at $T_r = 1$, and can be correlated by:

$$\beta[T_r] = 1 + m\,\frac{1 - \exp\left(\theta(T_r - 1)\right)}{1 + \exp\left(\theta(T_r - 1)\right)} \tag{2.106}$$

Parameters K, n, m and θ have been evaluated for polar and non polar components. For normal fluids, K, n, m and θ have been correlated with acentric factor, as follows:

$$K = 0.47614 + 0.51455\omega - 0.19072\omega^2 \tag{2.107}$$

$$n = 1.589 + 1.188\omega \tag{2.108}$$

$$m = 0.2311 - 0.0421\omega + 0.39068\omega^2 \tag{2.109}$$

$$\theta = 6.8635 + 13.982\omega + 7.8829\omega^2 \tag{2.110}$$

To extend equation (2.96) to mixture calculations, the following mixing rules were used:

$$a_m = \sum_i \sum_j x_i \, x_j \sqrt{a_i \, a_j} \, (1 - \delta_{ij}) \tag{2.111}$$

$$b_m = \sum_i x_i \, b_i \tag{2.112}$$

$$e_m = \sum_i x_i \, e_i \tag{2.113}$$

Equation (2.111) is the same as equation (2.39) and equation (2.42) put together. The binary interaction coefficient δ_{ij} in equation (2.111) is related to the previously defined value of ξ_{ij} by the following equation:

$$\xi_{ij} = 1 - \delta_{ij} \tag{2.114}$$

Equation (2.96) gives accurate predictions of saturated liquid densities and vapour pressures for the reduced temperature range, $T_r = 0.5$ to $T_r = 1.0$. No results are given for saturated vapour phase densities. Accurate predictions of vapour-liquid equilibria have been made for systems containing polar and non-polar components.

The predictive capabilities of equation (2.96) have not been tested in the regions away from the critical and for the vapour phase in particular. It is possible that the accuracy in the representation of the liquid phase densities is achieved at the expense of the accuracy in the vapour phase.

Equation (2.96) is used in this study for comparison purposes (see Chapter 4).

2.1.11 A Modified van der Waals Type Equation of State by Schmidt and Wenzel (1980)

The equation of state proposed is a generalised form of the van der Waals equation. It has the following form:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2} \qquad (2.115)$$

where: $a = a[T]$ is a function of temperature and u, w and b are independent of temperature. To avoid the condition that $V^2 + ubV + wb^2 = 0$ for $V \geqslant b$, it has been shown that u and w must satisfy the following constraints:

$$w > -u - 1 \quad \text{for } u \geqslant -2$$

$$w > \frac{u^2}{4} \quad \text{for } u \leqslant -2 \qquad (2.116)$$

As shown in Table 2.1, equation (2.115) can be reduced to some of the well known equations of state by selecting a particular pair of values for u and w.

TABLE 2.1

Values of u and w from equation (2.115) and corresponding equation of state

u	w	Equation of state
0	0	van der Waals (1873)
1	0	Redlich-Kwong (1949), Soave (1972)
2	-1	Peng-Robinson (1976)
3	-2	Harmens (1977)
u	$u^2/4$	Clausius (1880)

The parameters are given by:

$$u + w = 1 \quad \text{and} \quad w = -3.\omega \tag{2.117}$$

Using equation (2.117), application of the classical critical conditions to equation (2.115) yields:

$$b = \Omega_b\ [\omega].\ \frac{R.T_c}{P_c} \tag{2.118}$$

$$a_c = \Omega_a\ [\omega].\ \frac{R^2.T_c^{\ 2}}{P_c} \tag{2.119}$$

with $\Omega_b = \beta_c.\ \zeta_c$ (2.120)

$$\Omega_a = [1 - \zeta_c\ (1 - \beta_c)]^3 \tag{2.120}$$

where β_c is given as the solution of the cubic equation

$$(6\omega + 1)\ \beta_c^{\ 3} + 3\beta_c^{\ 2} + 3\beta_c - 1 = 0 \tag{2.121}$$

and $\zeta_c = \dfrac{1}{3(1 + \beta_c\omega)}$ (2.122)

The smallest positive root of equation (2.121) should be taken.

The temperature dependence of a[T] has been selected in a way similar to that of R-K-S.

$$a[T] = a_c \cdot \alpha[T_r, m] \tag{2.123}$$

where $\alpha(T_r,m)$ is given as a function of reduced temperature T_r by:

$$\alpha^{\frac{1}{2}} [T_r,m] = 1 + m [T_r,m_o] (1 - T_r^{\frac{1}{2}}) \tag{2.124}$$

with

$$m[T_r,m_o] = m_o + \frac{(5\ T_r - 3\ m_o - 1)^2}{70} \quad \text{for } T_r \leq 1 \tag{2.125}$$

and

$$m\ [T_r,m_o] = m[1,m_o] \quad \text{for } T_r > 1 \tag{2.126}$$

and

$$m_o = 0.465 + 1.347\omega - 0.528\omega^2 \tag{2.127}$$

Unlike Soave's expression, m has been treated as temperature dependent.

The resulting values of ζ_c (the predicted critical compressibility) are always greater than the experimental values of the critical compressibility, Z_c.

At low reduced temperatures, molar liquid volumes have been reproduced within two percent of the experimental values. Accurate predictions of vapour pressures have also been made (Schmidt and Wenzel, 1980). Compared to the Peng-Robinson (1976) equation and the S-R-K equation, equation (2.115) gives better representation of the vapour-pressure in the low pressure region. In the critical region large deviations in liquid volume occur because the experimental critical volume is not accurately reproduced. These limitations appear to be inherent in cubic equations of state (Abbott, 1973). Accurate predictions for the

saturated vapour compressibility factors have also been made. VLE calculations have been successfully carried out but no results have yet been reported.

2.1.12 The Han-Starling Equation of State (1972)

This is a modification of the B-W-R (Benedict, Webb and Rubin, 1940) equation of state. The original B-W-R equation of state is:

$$P = \rho RT + (BRT - A - \frac{C}{T^2})\rho^2 + (bRT - a)\rho^3$$

$$+ a\alpha\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \qquad (2.128)$$

where B, A, C, b, a, γ, c, α are constants. The B-W-R equation of state has been found to be very inaccurate at low temperatures. The modified equation of state by Han and Starling has added constants which improves the behaviour at low temperatures. The modified equation of state is the following function of temperature, T, and molar density, ρ

$$P = \rho RT + (B_oRT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4})\rho^2$$

$$+ (bRT - a - \frac{d}{T})\rho^3 + \alpha(a + \frac{d}{T})\rho^6$$

$$+ \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \qquad (2.129)$$

where A_o, B_o, C_o, D_o, E_o, a, b, c, d, α, γ are constants.

Equation (2.129) is capable of predicting thermodynamic properties at reduced temperatures as low as $T_r = 0.3$ and reduced densities as great as $\rho V_r = 3.0$. It can be used for light hydrocarbons in the cryogenic liquid region in addition to higher temperature regions.

To ensure consistency between predicted properties, available experimental PVT, enthalpy and vapour pressure data have been used simultaneously in a multiproperty analysis to determine the constants for individual components. Due to the lack of extensive data, the individual constants have been reported for only light hydrocarbons up to n-octane and components commonly found in the petroleum industry such as carbon dioxide and hydrogen sulfide. However, the 11 constants in equation (2.116) have been generalised using data for the normal paraffin hydrocarbons methane through n-octane and are expressed as the following functions of the component acentric factor, ω_i, critical temperature, T_{ci}, and critical density, ρ_{ci}.

$$\rho_{ci} B_{oi} = A_1 + B_1 \omega_i \tag{2.130}$$

$$\frac{\rho_{ci} A_{oi}}{RT_{ci}} = A_2 + B_2 \omega_i \tag{2.131}$$

$$\frac{\rho_{ci} C_{oi}}{RT_{c}{}^{3}{}_{i}} = A_3 + B_3 \omega_i \tag{2.132}$$

$$\rho_{ci}^2 \gamma_i = A_4 + B_4 \omega_i \tag{2.133}$$

$$\rho_{ci}^2 b_i = A_5 + B_5 \omega_i \tag{2.134}$$

$$\frac{\rho_{ci}^2 a_i}{RT_{ci}} = A_6 + B_6 \omega_i \tag{2.135}$$

$$\rho_{ci}^3 \alpha_i = A_7 + B_7 \omega_i \tag{2.136}$$

$$\frac{\rho_{ci}^2 c_i}{RT_{ci}^3} = A_8 + B_8 \omega_i \tag{2.137}$$

$$\frac{\rho_{ci} D_{oi}}{RT_{ci}^4} = A_9 + B_9 \omega_i \tag{2.138}$$

$$\frac{\rho_{ci}^2 d_i}{RT_{ci}^2} = A_{10} + B_{10} \omega_i \tag{2.139}$$

$$\frac{\rho_{ci} E_{oi}}{RT_{ci}^5} = A_{11} + B_{11} \omega_i \exp(-3.8 \omega_i) \tag{2.140}$$

The parameters A_j and B_j ($j = 1, 2, \ldots 11$) have been evaluated by Starling (1973). They are given in Appendix C. For consistency in thermodynamic property prediction calculations, the values of T_{ci}, ρ_{ci}, and ω_i should be taken as those values reported by Starling (1973).

The generalised equation has been extended to mixtures using the following mixing rules for the 11 constants:

$$B_{om} = \sum_i x_i B_{oi} \tag{2.141}$$

$$A_{om} = \sum_i \sum_j x_i x_j A_{oi}^{\frac{1}{2}} A_{oj}^{\frac{1}{2}} (1 - k_{ij}) \tag{2.142}$$

$$C_{om} = \sum_i \sum_j x_i x_j C_{oi}^{\frac{1}{2}} C_{oj}^{\frac{1}{2}} (1 - k_{ij})^3 \tag{2.143}$$

$$\gamma_m = [\sum_i x_i \gamma_i^{\frac{1}{2}}]^2 \tag{2.144}$$

$$b_m = [\sum_i x_i b_i^{1/3}]^3 \tag{2.145}$$

$$a_m = [\sum_i x_i a_i^{1/3}]^3 \tag{2.146}$$

$$\alpha_m = [\sum_i x_i \alpha_i^{1/3}]^3 \tag{2.147}$$

$$c_m = [\sum_i x_i c_i^{1/3}]^3 \tag{2.148}$$

$$D_{om} = \sum_i \sum_j x_i x_j D_{oi}^{\frac{1}{2}} D_{oj}^{\frac{1}{2}} (1 - k_{ij})^4 \tag{2.149}$$

$$d_m = [\sum_i x_i d_i^{1/3}]^3 \tag{2.150}$$

$$E_{om} = \sum_i \sum_j x_i x_j E_{oi}^{\frac{1}{2}} E_{oj}^{\frac{1}{2}} (1 - k_{ij})^5 \tag{2.160}$$

In equations (2.141) through (2.160), A_{om}, B_{om}, C_{om}, D_{om}, E_{om}, a_m, b_m, c_m, d_m, α_m, γ_m are mixture parameters, i and j are indices for the components and the summations range from i = 1 to i = n and j = 1 to j = n, where n is the total number of components. B_{oi}, A_{oi} etc. are the pure component equation of state parameters for the ith component, given by equations (2.130) through (2.140). x_i is the mole fraction of the ith component. k_{ij} is the binary interaction parameter and it is a measure of deviations from ideal solution behaviour for interactions between the ith and jth components. k_{ij} values for a large number of binaries have been reported by Starling (1973).

Equation (2.129) with generalised parameters have been used by Han and Starling (1972) for predicting thermodynamic properties of 23 pure fluids. These fluids include polar and non-polar components, paraffin, olefin, naphthalene, and aromatic hydrocarbons and non-hydrocarbons. Densities were predicted with an absolute average deviation of 1.38 per cent for 971 data points. Enthalpy departures were predicted with an absolute average deviation of 1.74 Btu/lb for 620 data points. Saturated liquid fugacities were predicted with an absolute average deviation of 1.08 per cent from saturated vapour fugacities, for 663 data points. Vapour pressures can also be predicted accurately because the equality of fugacities criterion is satisfied (Han and Starling, 1972).

The consistent accuracy with which predictions were made showed that the generalised equation can be used for non-polar fluids with confidence. In addition, the equation of state is thermodynamically consistent, since density, enthalpy and vapour pressure can be predicted accurately using the same constants. Thus, entropy, heat capacities, Joule-Thomson coefficients, etc. can also be predicted with confidence.

The generalised equation of state gave accurate predictions of densities, enthalpies, and entropies for both gas and liquid mixtures. Vapour-liquid equilibria were also predicted accurately but the use of binary interaction parameters was recommended. It must be pointed out that the use of the generalised equation of state for vapour-liquid equilibrium prediction involves tedious manipulation. It requires a trial and error procedure to calculate density at a given P and T, while the shorter equations such as the Soave (1972), and the Peng-Robinson (1976) are amenable to analytical solution and may be solved rapidly. Predictions of bubble point pressures and temperatures, and equilibrium ratios made by simple equations of state are comparable to those made by the generalised Han-Starling equation (Chapter 8). Because of their simplicity, the shorter

equations are preferred for the prediction of vapour-liquid equilibria.

The generalised equation of state has also been used with the van der Waals mixing rules to give accurate predictions of mixture density (Teja et al, 1978). In this study (Chapter 7) use of the van der Waals mixing rules is extended to the prediction of vapour-liquid equilibria.

2.2 The Corresponding States Principle

The principle of corresponding states was first proposed by van der Waals on the basis of his well known equation of state. The main application of the corresponding states principle (CSP) is the prediction of unknown properties of many fluids from the known properties of a few. It also makes possible the utilization of some important developments in statistical mechanics which would otherwise be prohibited by computational difficulties.

From the principle of continuity of the gaseous and liquid phases, van der Waals showed that at the critical point

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0; \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \qquad (2.161)$$

The relations led to the general result of van der Waals that for variables V, T and P there exists a universal function F such that:

$$F\left[\frac{V}{V_c}, \frac{T}{T_c}, \frac{P}{P_c}\right] = 0 \qquad (2.162)$$

is valid for all members of a given set of substances. When this is applied to the van der Waals equation, we obtain

$$[\frac{P}{P_c} + \frac{3}{(\frac{V}{V_c})^2}][3(\frac{V}{V_c}) - 1] - 8(\frac{T}{T_c}) = 0 \qquad (2.163)$$

Equation (2.162) can be written in terms of the compressibility factor as:

$$Z = F[\frac{T}{T_c}, \frac{V}{V_c}] \qquad (2.164)$$

A similar function can be written in terms of P/P_c instead of V/V_c.

It can be shown, however, that this result is not strictly tied to any particular equation but can be applied to any equation of state containing two arbitrary constants in addition to the gas constant, R. Equation (2.164) is the simplest form of the corresponding states principle and is often called the two parameter law of corresponding states, since knowledge of only two parameters is required for its application.

According to the simple law of corresponding states, two fluids at the same reduced temperature and reduced pressure will have the same reduced volume. They will also have the same value for the compressibility factor, and indeed for any dimensionless property which is calculable solely from P-V-T data, e.g. fugacity coefficient, residual enthalpy and residual entropy.

In general, the accuracy with which a given substance obeys the simple law is greatest in the gas phase, poorer in the liquid phase and very poor in the solid phase. The accuracy is also better for temperatures higher than the critical temperature.

The simple form of the two parameter CSP is applicable to restricted sets of substances, e.g. the heavy inert gases commonly known as simple fluids.

2.2.1 CSP and Two-Parameter Equations of State

An important consequence ~~of~~ for the CSP is that the parameters in any empirical two-parameter equation of state can always be expressed in terms of critical constants. For example, any empirical two-parameter equation of state may be represented by:

$$Z = f\ [T,\ V,\ a,\ b] \qquad (2.165)$$

where a and b are two parameters independent of T and V, whose values are adjusted to fit various fluids. When equation (2.165) and equation (2.161) are solved simultaneously, a and b are obtained in terms of critical constants for each fluid and, in addition, a universal constant value of Z_c for all fluids is also obtained. Substituting these values into equation (2.165) leads to a generalized equation of state which can be rearranged in the form of equation (2.164).

In general, if the equation of state can be expressed as an nth-order polynomial in the volume or compressibility factor, then a total of (n-1) adjustable parameters can be found in terms of critical constants. It is thus possible to apply the CSP to certain kinds of equations of state of greater complexity than equation (2.165). As an example, consider the equation:

$$Z = f\ [a,\ b,\ c,\ \ldots.,\ T,\ V] \qquad (2.166)$$

which can be rearranged in a polynomial in V,

$$V^n + f_1\ [a, b, c, \ldots, T_c, P_c, Z_c]\ V^{n-1} +$$

$$f_2\ [a, b, c, \ldots, T_c, P_c, Z_c]\ V^{n-2} + \ldots = 0 \qquad (2.167)$$

where a, b, c, ... are equation of state constants adjustable for various fluids. At the critical point, ~~all~~ m real volume roots of equation (2.167) must become identical and the polynomial form must approach:

$$(V - V_c)^m = 0 \qquad (2.168)$$

Equating coefficients of like powers of V in equations (2.167) and (2.168) will then determine (m-1) parameters a, b, c, ... in terms of critical properties. If only (m-1) parameters are present in the equation, a universal constant value will also be predicted for Z_c. With this procedure, an equation with many constants can be expressed in reduced form according to the CSP. This procedure is identical with the simultaneous solution of equations (2.165) and (2.161), for two constant equations of state.

2.2.2 Extension of the CSP

The set of substances over which the simple form of the two parameter law applies can be extended by introducing a third parameter.

The most widely used parameter is the acentric factor proposed by Pitzer (1958) and is defined by equation (2.43).

The three parameter law of corresponding states which results may be defined by:

$$Z = f\left[\frac{T}{T_c}, \frac{V}{V_c}, \omega\right] \tag{2.169}$$

This definition implies that all substances with the same value of ω have the same reduced equation of state. Pitzer has shown that equation (2.169) can be expanded about a zero ω value to give:

$$Z = Z^0 + \left(\frac{\partial Z}{\partial \omega}\right)_{\omega=0} \omega + \ldots. \tag{2.170}$$

The function Z^0 is the value predicted by the simple CSP. Pitzer and Curl (1957) have shown that within the range of applicability of three parameters, the higher derivatives in equation (2.170) can usually be neglected. Moreover, other reduced properties which measure deviations from ideal gas behaviour have also been expressed as linear functions of ω as in equation (2.170). For a molecule such as argon, $\omega = 0$ and the three-parameter equation reduces to the simple law of corresponding states.

The acentric factor has had a great deal of significance for the development of analytical reduced equations of state. In principle any of the simple fluid equations could be modified according to equation (2.170). Most investigators, however, have provided for the non-linear dependence of ω.

All fluids obeying the three parameter CSP should lie on a single line in plots of ω against the critical compressibility factor. In practice, however, there is a great deal of scatter in such plots. This scatter is greater than that which can be

attributed to errors in the experimental values of the critical volume. This clearly indicates the need for more than three parameters in the principle. However, the three parameter law is obeyed by many substances with sufficient accuracy and it remains the most widely used extension of the principle of corresponding states.

A useful form of the three parameter law has been proposed by Leland et al (1962) who have introduced shape factors. Lee and Kesler (1975) modified equation (2.170) and used B-W-R type equation of state to represent Z, Z^o etc. Further modifications have been presented by Teja et al (1980) and also in Chapter 4.

2.2.3 Extension to Mixtures

The simplest way of extending the CSP and equations of state to mixtures is to assume that the mixture can be represented by a hypothetical equivalent substance whose parameters are composition averages of all the binary interactions in the mixture. The most successful recipe for obtaining the parameters is the van der Waals approximation (Leland et al, 1968) which can be written as:

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \qquad (2.171)$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \qquad (2.172)$$

where, T_{cm} and V_{cm} are respectively the critical temperature and the critical volume of the equivalent substance. T_{cm} and V_{cm} replaces T_c and V_c in the pure component equation of state. Thus equation (2.164) for mixture becomes:

$$Z_m = F\left[\frac{T}{T_{cm}}, \frac{V}{V_{cm}}\right] \tag{2.173}$$

where Z_m is the compressibility factor of the mixture.

The use of a single equivalent substance to represent the mixture is often called the one fluid model or the "pseudo-critical" approach. It may be extended to the development of "multi fluid" models in which each component of the mixture is replaced by an equivalent substance and the equivalent substances are then assumed to mix ideally to form the mixture.

Multi-fluid models are discussed by Lelands, Rowlinson, Sather and Watson (1969). There is no advantage in using multi-fluid models for the prediction of phase-equilibria. Because of its simplicity, the one-fluid model is widely used. The following discussion is, therefore, restricted to the development of the one fluid model only.

The van der Waals approximation can be used to obtain the thermodynamic properties of a mixture provided values can be assigned to the cross-parameters T_{cij} and V_{cij} $(i \neq j)$. This problem is usually solved via the modified Lorentz-Berthelot mixing rules:

$$T_{cij} = \xi_{ij}\,(T_{cii}\,T_{cjj})^{\frac{1}{2}} \tag{2.174}$$

$$V_{cij} = \eta_{ij}\,(V_{cii}^{1/3} + V_{cjj}^{1/3})^3/8 \tag{2.175}$$

where ξ_{ij} and η_{ij} are binary interaction coefficients. If no experimental data are available for the binary system i-j, then the Lorentz-Berthelot assumptions are adopted, with

$$\xi_{ij} = 1 \tag{2.176}$$

$$\eta_{ij} = 1 \tag{2.197}$$

In most cases, it is sufficient to use one adjustable coefficient to characterize each binary system and it is usual to assume $\eta_{ij} = 1$, with ξ_{ij} being calculated from the experimental data for the binary system (Teja, 1978). When complex equations of state are used, however, it is better to assume $\xi_{ij} = 1$ and calculate η_{ij} from the experimental data (Chapter 7). No further information is required to predict the properties of ternary and higher mixtures.

The values of ξ_{ij} have been estimated from corresponding states correlations of vapour-liquid equilibria and related properties (Gunning and Rowlinson, 1973), critical and azeotropic states (Teja and Rowlinson, 1973) and saturated liquid densities (Mollerup and Rowlinson, 1974). These values agree very well with each other (Mollerup and Rowlinson, 1974) and with values found by Chueh and Prausnitz (1967) who used a modified Redlich-Kwong equation to correlate thermodynamic properties and phase equilibria. The above mentioned studies have also shown that to a good approximation, ξ_{ij} is independent of temperature, density and composition. Typical values of ξ_{ij} have been given by Teja (1978).

There have been many attempts to relate ξ_{ij} and η_{ij} to physical properties using theory (Hudson and McCoubery, 1960; Munn, 1961; Good and Hope, 1970; Prausnitz and Gunn, 1958). Teja (1978) has given the following correlations for methane-n-alkane, ethane-n-alkane and CO_2-n-alkane binaries.

For methane-n-alkane binaries:

$$\xi_{ij} = 1.0 - 0.02\ (n - 2) \tag{2.178}$$

For ethane-higher alkane binaries:

$$\xi_{ij} = 1.0 - 0.01\ (n - 3) \tag{2.179}$$

For CO_2-n-alkane binaries:

$$\xi_{ij} = 1.0 - 0.04n \tag{2.180}$$

where n is the number of carbon atoms in the (higher) n-alkane of the binary pair.

In terms of the critical volumes, ξ_{ij} was correlated as:

$$\xi_{ij} = (V_{cii}\ V_{cjj})^{\frac{1}{2}}/V_{cij} \tag{2.181}$$

where V_{cij} is given by equation (2.175), with $\eta_{ij} = 1$.

When a three-parameter generalised equation of state is used, an additional mixing rule is required for the third parameter. In most cases, the third parameter is either Pitzer's acentric factor ω or the critical compressibility factor Z_c. For these parameters, the following mixing rules have been successfully used (Teja et al, 1978; Joffe, 1976; Plöcker et al, 1978).

$$\omega_m = \sum_i x_i\ \omega_i \tag{2.182}$$

$$Z_{cm} = \sum_i x_i\ Z_{ci} \tag{2.183}$$

where ω_m and Z_{cm} refers to the equivalent substance.

One of the main advantages of the one-fluid model is in the application of complex equations of state to the prediction of mixture properties. For example a modified B-W-R equation by Hans and Starling (1972) has 11 constants. Application of this equation to mixtures requires 11 arbitrary mixing rules and in view of this complexity, introduction of the binary interaction coefficient is a formidable task. If the van der Waals one-fluid model is used, then mixing rules for only the critical constants and the acentric factor are required. Differentials of the mixing rules are required for derived thermodynamic properties and these can be easily obtained for the van der Waals mixing rules (Appendix F). In general, use of the van der Waals mixing rules increases the speed of calculation and reduces computation involved for the prediction of the derived thermodynamic property (see Chapter 7).

CHAPTER 3

CHOICE OF AN EQUATION OF STATE

A large number of equations of state can be found in the literature. Each equation has its strengths and weaknesses. To date, no single equation of state has been found which is truly valid over a wide range of temperature, pressure, density and can be applied to a variety of components. There are many characteristics of the phase diagram of a fluid which an equation of state should be able to predict. These can be summarized as follows (Rowlinson, 1965; Teja and Singh, 1977):

1. The critical point of the fluid. This is the limit of the vapour-liquid phase boundary and is important in the application of the corresponding states principle. At the critical point, the equation of state should give:

$$P_c = P\ [T_c,\ V_c] \tag{3.1}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \tag{3.2}$$

and $$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \tag{3.3}$$

2. The slope of the vapour pressure curve at the critical point. The importance of this has been suggested by the work of Riedel (1954). The slope is given by:

$$\alpha_c = \left(\frac{T}{P_s} \times \frac{dP_s}{dT}\right)_c \tag{3.4}$$

where α_c is the Riedel parameter.

3. The vapour-liquid and liquid-solid phase boundaries. The equality of fugacity criterion for saturated phases must be satisfied:

$$f^V = f^L; \quad f^L = f^S \tag{3.5}$$

$$\text{and } \ln \frac{f}{P} = \int_0^P \left(\frac{V}{RT} - \frac{1}{P}\right) dP \tag{3.6}$$

4. The virial coefficients. The availability of second virial coefficient data of sufficient accuracy allows us to include the residual second virial coefficient function in the evaluation of the constants.

5. The loci of the vanishing of various derivatives:

(a) The Amagat curve or Joule inversion locus:

$$\text{where } \left(\frac{\partial Z}{\partial T}\right)_V = 0 \quad \text{and} \quad \left(\frac{\partial U}{\partial T}\right)_T = 0 \tag{3.7}$$

(b) The Boyle curve, along which

$$\left(\frac{\partial Z}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial Z}{\partial P}\right)_T = 0 \tag{3.8}$$

(c) The Joule-Thompson inversion locus where

$$\left(\frac{\partial Z}{\partial T}\right)_P = 0 \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_T = 0 \tag{3.9}$$

(d) The loci of maxima or minima in the heat capacities where

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0 \quad \text{and} \quad \left(\frac{\partial C_V}{\partial V}\right)_T = 0 \tag{3.10}$$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0 \quad \text{and} \quad \left(\frac{\partial C_p}{\partial P}\right)_T = 0 \tag{3.11}$$

6. The deviation from linearity of the lines of constant volume.

7. The intersections with the P = 0 axis of the curves generated by equating the derivatives in (5) to zero. These intersections determine some important values of the second virial coefficient and the nature of its variation with temperature.

Even for simple fluids, no equation of state exists which can possibly account for all the features outlined above and give accurate numerical values for the compressibility factor over the entire P-V-T region. It is a usual practice to select a few important features and include them in the development of an equation of state. In selecting the particular features, five main considerations are made initially:

1. The thermodynamic properties to be predicted.
2. The complexity of the required equation.
3. The amount and kind of experimental data that will be required and are available to evaluate the parameters of the equation.
4. The range of pressure, density and temperature as well as the nature of the components.
5. The precision with which the P-V-T data are to be represented, or the thermodynamic property calculated.

For some applications, it is desirable to have an equation which can be obtained from a minimum of data such as the critical temperature, pressure and volume, or the boiling point or some molecular parameter. In other instances, an equation of state is sought which will represent a large amount of experimental P-V-T data within experimental uncertainty.

In general an equation with two or three constants will suffice for low densities but a many constant equation will be required if coverage is to include both low and high densities. From present knowledge, high precision equations have many arbitrary constants whose number depends primarily upon the density range. These constants reflect the non-idealities of a real fluid. The fact that there is a need at all for any constants follows from the existence of intermolecular forces. The evaluation of a large number of constants involves a lengthy process requiring curve-fitting and, trial and error procedures. Extensive data on some thermodynamic properties are required in order to begin establishing these constants.

Reliable and thermodynamically consistent data exist for the more common substances but are scarce for binary mixtures. The problem is even more acute for multicomponent mixtures. Considering the large number of systems involved, it is an impossible task to obtain experimental data for even a small fraction of these systems under varying conditions of pressure and temperature.

The shorter equations of state, having only two or three constants have been overlooked, largely because of their lack of sophistication. This is consistent with the false common notion that an equation of state with more constants should predict results that are consistent with the experimental behaviour of a fluid.

One of the most attractive features of simple, two or three constant equations of state is that they do not require vast amounts of experimental data for the evaluation of these constants. Using only limited experimental data such as P_c, T_c, V_c, Z_c etc. they allow predictions of thermodynamic properties at other temperatures and pressures. Simple equations can be easily linked to theory via the corresponding states principle.

The interpretation and prediction of vapour-liquid equilibrium data at high pressures are everyday necessities in the design of separation processes. With simple two or three constant equations, which yield direct analytical expressions for the compressibility factor and densities, vapour-liquid equilibrium calculations can be performed with ease and simplicity. On a practical basis, the simple equations also afford ease of adaptation to the techniques of computer-aided design used so commonly today. Although direct comparisons between simple equations and multi-constant equations are rarely found, comparable results have been obtained for vapour-liquid equilibria with both types of equations when a binary interaction coefficient is used in the calculations (Peng and Robinson, 1976; Soave, 1972; Han and Starling, 1972).

The greatest limitation of simple equations of state is their inability to give simultaneously accurate representation of both the liquid phase and the vapour phase densities while maintaining accuracy in VLE calculations. Because of attractiveness of such equations, it seems more fruitful to try and overcome this limitation than to consider multi-constant equations of state.

CHAPTER 4

A NEW CUBIC EQUATION OF STATE

In an effort to find a cubic equation of state suitable for representing low- and high-pressure behaviour and vapour-liquid equilibria, a new three constant equation of state is proposed in this work. The new equation has the following form:

$$P = \frac{RT}{V-b} - \frac{a[T]}{V(V+b) + c(V-b)} \tag{4.1}$$

where: R is the universal gas constant, a is a function of temperature and b and c are constants. By choosing particular values for the constants, two well known cubic equations of state can easily be obtained from equation (4.1). When c=b equation (4.1) reduces to the Peng and Robinson equation (1976) and when c=0, it reduces to the Redlich and Kwong (1949) or Soave (1972) equations.

Acceptable prediction of both low and high pressure behaviour requires at the very least that the critical compressibility factor implied by the equation of state be treated as an empirical parameter different in general from the experimental value of Z_c (Abbott, 1973; Leland, 1966). It is also well known that the predicted value of the critical compressibility factor (denoted by Z_m below) is not an important indicator of the overall performance of any reduced equation of state (Leland et al, 1968). For these reasons, the new equation of state is constrained to satisfy one more condition, in addition to the two classical conditions at the critical point. The three conditions satisfied by the new equation are:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \tag{4.2}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \tag{4.3}$$

and $$\frac{P_c V_c}{RT_c} = Z_m \tag{4.4}$$

Instead of letting Z_m have a value equal to the experimental value of the critical compressibility factor, an arbitrary value is chosen. Thus, Z_m is an empirical parameter. If Z_m is set equal to 0.3074, equation (4.1) together with equations (4.2) and (4.3) reduce to the Peng and Robinson equation. Similarly if Z_m is set equal to 1/3 equation (4.1) reduce to the Redlich and Kwong or Soave equations.

4.1 Evaluation of the Parameters

Constants a, b and c in equation (4.1) are given by:

$$a[T] = \alpha[T_r] \cdot \Omega_a \cdot \frac{R^2 . T_c^{\,2}}{P_c} \tag{4.5}$$

$$b = \Omega_b \cdot \frac{R . T_c}{P_c} \tag{4.6}$$

$$c = \Omega_c \cdot \frac{R . T_c}{P_c} \tag{4.7}$$

where: $\alpha[T_r]$ is a function of reduced temperature which has the same form as that used by Peng and Robinson (1976) and Soave (1972). It is given by:

$$\alpha^{\frac{1}{2}} = 1 + F\,(1 - T_r^{\frac{1}{2}}) \tag{4.8}$$

$$T_r = T/T_c \tag{4.9}$$

where: T_r is a reduced temperature and Ω_a, Ω_b, Ω_c and F are constants for a given substance.

Equation (4.1) can be written as:

$$Z^3 + (C-1)\ Z^2 - (2BC + B^2 + B + C - A)Z$$

$$+ B^2C - AB + BC = 0 \tag{4.10}$$

where: $$A = \frac{aP}{R^2T^2} = \alpha[T_r] \cdot \Omega_a \cdot \frac{P_r}{T_r^{\ 2}} \tag{4.11}$$

$$B = \frac{bP}{RT} = \Omega_b \cdot \frac{P_r}{T_r} \tag{4.12}$$

$$C = \frac{cP}{RT} = \Omega_c \cdot \frac{P_r}{T_r} \tag{4.13}$$

$$Z = \frac{PV}{RT} \tag{4.14}$$

$$P_r = P/P_c \tag{4.15}$$

At the critical point, $P_r = 1$, $T_r = 1$, $\alpha[T_r] = 1$ and $A = \Omega_a$, $B = \Omega_b$, $C = \Omega_c$ and $Z = Z_c$. Therefore equation (4.10) becomes:

$$Z_c^3 + (\Omega_c - 1)\, Z_c^2 - (2\,\Omega_b\Omega_c + \Omega_b^2 + \Omega_b + \Omega_c - \Omega_a)\, Z_c$$

$$+ \Omega_b^2\,\Omega_c - \Omega_a\Omega_b + \Omega_b\Omega_c = 0 \qquad (4.16)$$

To develop the stability criterion, we note that at $T < T_c$ there are three real roots of V (volume); for $T > T_c$ there is only one real root for V corresponding to the gas phase; and at $T = T_c$ there are three equal real roots for V. Thus, at $T = T_c$ there are also three equal roots for Z. If we call these Z_m, then we can write:

$$(Z_c - Z_m)^3 = Z_c^3 - 3Z_m\, Z_c^2 + 3Z_m^2\, Z_c - Z_m^3 = 0 \qquad (4.17)$$

Equation (4.17) is a requirement equivalent to equations (4.2), (4.3) and (4.4). Comparing equation (4.17) with equation (4.16), we obtain the following three equations relating Ω_a, Ω_b and Ω_c to the empirical parameter Z_m

$$-\,3Z_m = \Omega_c - 1 \qquad (4.18)$$

$$+\,3Z_m^2 = -\,(2\,\Omega_b\Omega_c + \Omega_b^2 + \Omega_b + \Omega_c - \Omega_a) \qquad (4.19)$$

$$-Z_m^3 = \Omega_b^2\Omega_c - \Omega_a\Omega_b + \Omega_b\Omega_c \qquad (4.20)$$

From equation (4.18):

$$\underline{\Omega_c = 1 - 3Z_m} \qquad (4.21)$$

Substituting for Ω_c into equation (4.19) and rearranging, we get:

$$\underline{\Omega_a = 3Z_m^2 + 3\,(1 - 2Z_m)\,\Omega_b + \Omega_b^2 + 1 - 3Z_m} \tag{4.22}$$

Substituting for Ω_a and Ω_c into equation (4.20), we get

$$\underline{C_1\,\Omega_b^3 + C_2\,\Omega_b^2 + C_3\,\Omega_b + C_4 = 0} \tag{4.23}$$

where: $C_1 = 1.0$
$C_2 = 2 - 3\,Z_m$
$C_3 = 3\,Z_m^2$
$C_4 = -\,Z_m^3$

Equation (4.23) can be solved analytically as shown in Appendix D. Only the smallest positive root is meaningful and should be used. Once Ω_b is found, Ω_a can be obtained from equation (4.22). However, before Ω_a, Ω_b and Ω_c can be found, a value must be assigned to Z_m. To obtain Z_m and F, the following trial and error procedure is used.

Initially, Z_m is set equal to 0.307 or 1.1 Z_c whichever is closer to the experimental critical compressibility Z_c. Ω_a, Ω_b and Ω_c are calculated using equations (4.23), (4.22) and (4.21). Using these values of Ω_a, Ω_b and Ω_c, a value for α is obtained for each temperature such that the equilibrium condition

$$f^L = f^V \tag{4.24}$$

is satisfied along the saturation curve. For this, an expression for the fugacity of a pure component is required. The fugacity

of a pure component is given by the following thermodynamic relationship

$$\ln \frac{f}{P} = \int_0^P \left(\frac{V}{RT} - \frac{1}{P}\right) dP \tag{4.25}$$

Using equation (4.25) with the new equation of state the following expression for the fugacity is obtained (for derivation see Appendix F)

$$\ln \frac{f}{P} = Z - 1 - \ln (Z-B) + \frac{a}{2\,RT\,N} \ln \frac{(Z+M)}{(Z+Q)} \tag{4.26}$$

where: $N = \sqrt{bc + \left(\frac{b+c}{2}\right)^2}$ (4.26a)

$M = \left(\frac{b+c}{2} - N\right) \frac{P}{RT}$ (4.26b)

$Q = \left(\frac{b+c}{2} + N\right) \frac{P}{RT}$ (4.26c)

A computer program for evaluating α for each temperature is given in Appendix H. Equation (4.8) is fitted using a least square technique to sets of α values corresponding to each T_r. The following sum is minimised:

$$S = \sum_{i=1}^{n} (\alpha_{i,calc} - \alpha_{i,exp})^2 \tag{4.27}$$

Here $\alpha_{i,calc} = [1 + F(1 - T_{r,i}^{\frac{1}{2}})]^2$

$T_{r,i} = T_i/T_c$

$\alpha_{i,exp}$ is the value obtained by applying equation (4.24)

n is the total no. of data points.

Thus: $$S = \sum_{i=1}^{n} [\{1 + F(1 - T_{r,i}^{\frac{1}{2}})\}^2 - \alpha_{i,exp}]^2 \tag{4.28}$$

For a minimum

$$\left(\frac{\partial S}{\partial F}\right) = 0 = 2[\sum_{i=1}^{n} \{1 + F(1 - T_{r,i}^{\frac{1}{2}})\}^2 - \alpha_{i,exp}]$$

$$X\ [2\ \{1 + F(1 - T_{r,i}^{\frac{1}{2}})\}]\ X\ (1 - T_{r,i}^{\frac{1}{2}}) \tag{4.29}$$

Simplifying equation (4.29) leads to

$$C_1 F^3 + C_2 F^2 + C_3 F + C_4 = 0 \tag{4.30}$$

where: $$C_1 = \sum_{i=1}^{n} (1 - T_{r,i}^{\frac{1}{2}})^4 \tag{4.30a}$$

$$C_2 = 3 \sum_{i=1}^{n} (1 - T_{r,i}^{\frac{1}{2}})^3 \tag{4.30b}$$

$$C_3 = 3 \sum_{i=1}^{n} (1 - T_{r,i}^{\frac{1}{2}})^2 - \sum_{i=1}^{n} \alpha_{i,exp}\ (1 - T_{r,i}^{\frac{1}{2}})^2 \tag{4.30c}$$

$$C_4 = \sum_{i=1}^{n} (1 - T_{r,i}^{\frac{1}{2}}) - \sum_{i=1}^{n} \alpha_{i,exp}\ (1 - T_{r,i}^{\frac{1}{2}}) \tag{4.30d}$$

Equation (4.30) is a cubic in F and can be solved analytically as shown in Appendix D. Only the smallest positive root is meaningful and should be used. Using the values of Ω_a, Ω_b, Ω_c and F, saturated liquid densities are calculated and compared with experimental values obtained from the literature. The absolute average deviation is noted. The value of Z_m is changed by 0.001 and new values of Ω_c, Ω_b, Ω_a and F are obtained by solving equations (4.21),

(4.23), (4.22) and (4.30) respectively. The absolute average deviation in saturated liquid densities is obtained once again. This procedure is repeated until a minimum value of the absolute average deviation is obtained. After the first iteration, it becomes clear whether the value of Z_m should be increased or decreased by 0.001. A typical set of results obtained for n-decane is given in Table 4.1.

TABLE 4.1

Evaluation of Z_m and F for n-Decane

Saturated pressures and temperatures from API (1973).
Saturated liquid densities from a modified Rackett equation (Spencer and Adler, 1978).
No. of points = 27.
T_r range = 0.5356 - 0.7706

Z_m	F	Sat. liq. A.A.D. (%)
0.295	1.011969	0.9783
0.296	1.016983	0.7669
0.297	1.021919	0.6166
0.298	1.026949	0.9442
0.299	1.031881	1.4383
0.300	1.036873	1.9803

$$\text{A.A.D. (\%)} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{\rho^S_{exp} - \rho^S_{cal}}{\rho^S_{exp}} \right| \times 100$$

The optimum values of Z_m and F correspond to the minimum deviation in saturated liquid densities and the equilibrium condition of equality of fugacities as implied by equation (4.24). The new equation using optimum values of Z_m and F is therefore expected to give accurate prediction of liquid phase densities

and vapour-liquid equilibria. Optimum values of Z_m and F have been evaluated for 38 pure components including polar substances and are given in Appendix A. Experimental values of the saturation pressure, saturation temperature and saturated liquid densities were used for evaluating Z_m and F.

4.2 Pure Component Calculations

The new equation of state has been used to calculate the thermodynamic properties of pure components. Density, vapour pressure, the enthalpy departure and the entropy departure have been calculated and compared with experimental values (when available) and with the values calculated using other equations of state.

4.2.1 Density

The prediction of density at a given temperature and pressure requires a solution of equation (4.1). This equation is first transformed into a cubic equation in Z as given by equation (4.10) and solved analytically as shown in Appendix D.

In the region where vapour and liquid phases co-exist, there are three real roots of Z. The largest Z value is for the saturated vapour state, while the smallest is for the saturated liquid state. The third Z value has no physical meaning.

Saturated liquid and vapour densities have been calculated for 38 components for which values of Z_m and F have been evaluated. The new equation is compared with the Peng and Robinson (P-R) equation (1976), the Heyen equation (1980), the Redlich and Kwong (R-K) equation (1949) and the Han and Starling (H-S) equation (1972). Calculation of the density using the H-S equation requires a trial and error procedure as outlined by Starling (1973). Their procedure is followed in this work. Absolute average deviations obtained in saturated liquid densities and

vapour densities are given in Tables 4.2 to 4.5.

The R-K equation was designed for the vapour-phase only. This is evident from the results obtained. Very accurate predictions of the saturated vapour densities are obtained for light components. For polar components and heavy hydrocarbons absolute average deviations of the order of 5% are obtained for vapour densities. The overall average deviation for 24 components was found to be 3.35% (Table 4.3). Deviations in the small region near the critical point ($0.9 < T_r < 1.0$) are shown in Table 4.5. Accurate predictions of saturated vapour densities have been obtained in the critical region for light components. For heavy hydrocarbons and polar components deviations of the order of 10% were obtained in this region. The overall average deviation is 5.66% (Table 4.5). Predictions of saturated liquid densities are very poor. Even for light components deviations of the order of 10-15% were obtained. For heavy hydrocarbons and polar components deviations of the order of 30-50% were obtained (Table 4.2). Predictions of saturated liquid densities in the critical region are very poor. The overall average deviation was found to be 34.15% (Table 4.4)

The new equation of state gives absolute average deviations which are lower than the P-R and the R-K equations, for both saturated liquid and saturated vapour densities. The overall average deviation for saturated vapour densities was found to be 1.44% for the new equation compared to 1.89% for the P-R equation and 3.35% for the R-K equation (Table 4.3). For saturated liquid densities the overall average deviation for the new equation was found to be 2.94% compared with 7.75% for the P-R equation and 20.02% for the R-K equation. In the critical region ($0.9 < T_r < 1.0$), large deviations for saturated liquid densities were obtained from the three equations (Table 4.4) but saturated vapour densities are predicted accurately. The overall average deviation for saturated vapour densities was found to be 2.32% for the new equation, 3.78% for the P-R equation and 5.66% for the R-K equation (Table 4.5). For heavy hydrocarbons and polar compo-

nents, the new equation gives consistently better predictions than the P-R and the R-K equations. Deviations between experimental and calculated saturated liquid densities are plotted against reduced temperature for methane, n-pentane, n-decane, n-eicosane, hydrogen sulfide, carbon dioxide, ammonia and water in Figures 4.1 to 4.8. Except in the region close to the critical point, the new equation of state gives accurate predictions of saturated liquid densities. The superiority of the new equation over the P-R equation for heavy hydrocarbons and polar components is clearly shown in Figures4.3, 4.4, 4.7 and 4.8.

The Heyen equation has been designed to represent saturated liquid densities and this is reflected in the small deviations obtained for this property. However, the predictions of vapour phase densities are worse than the R-K equation. The overall average deviation for saturated liquid densities was found to be 2.98% (Table 4.2) and for saturated vapour densities 4.14% (Table 4.3). Because the experimental value of the critical compressibility factor is reproduced by this equation, accurate predictions of saturated liquid densities in the region near the critical point are obtained. The overall average deviation for saturated liquid densities in the critical region was found to be 3.69% (Table 4.4). The overall average deviation for the saturated vapour densities was 9.9% (Table 4.5).

The Han and Starling equation gives excellent predictions of both saturated liquid and saturated vapour densities. However, surprisingly large deviations were obtained for saturated liquid densities of n-octane. The use of this equation is limited to normal alkanes from methane to n-octane, for which the eleven equation of state constants have been reported (Starling, 1973).

Although the overall predictions obtained from the new equation are better than those obtained from the other cubic equations considered in this study, results for the saturated

liquid densities in the critical region are very poor (Table 4.4). To improve the predictions in the critical region, the predicted value of the critical compressibility factor (Z_m), is made a linear function of temperature between $T_r = 0.9$ and $T_r = 1.0$. That is $Z_m' = f\,[T_r]$ is given by

$$Z_m' = f[T_r] = Z_m - \frac{Z_m - Z_c}{0.10}\,(T_r - 0.9) \qquad (4.31)$$

where Z_m' is the predicted critical compressibility as a function of T_r.

According to equation (4.31) at $T_r = 1.0$, $Z_m' = Z_c$ and hence the experimental value of the critical compressibility is reproduced. This resulted in the improvement of the predictions for saturated liquid densities. The overall average deviation for saturated liquid densities was reduced from 11.56% to 3.04% (Table 4.4) through the use of equation (4.31) in the critical region. However, this also resulted in a loss of accuracy for the saturated vapour densities. The overall average deviation for the saturated vapour densities increased from 2.32% to 5.37% (Table 4.5). Nevertheless the use of equation (4.31) is a good compromise between the accuracy in the saturated liquid and the saturated vapour phase densities. As can be seen from Tables 4.4 and 4.5, no cubic equation can give accurate predictions of both saturated liquid and saturated vapour densities in the critical region. Accuracy in saturated liquid densities always results in a loss of accuracy in saturated vapour densities and vice versa. However, better agreement between the predicted and the experimental values of the saturated liquid and vapour densities can be obtained if the temperature dependence of Z_m' represented by equation (4.31) is improved. The results obtained through the use of equation (4.31) are also presented in Tables 4.2 and 4.3. It must be remembered that equation (4.31) is only used in the region $0.9 < T_r < 1.0$. In the region where $T_r < 0.90$, $Z_m' = Z_m$ is used.

TABLE 4.2

Comparison of Saturated Liquid Densities

Component	No. of Points	T_r Range	NEW EQ. $Z'_m=Z_m$ AAD (%)	NEW EQ. $Z'_m=f[T_r]$ AAD (%)	Heyen AAD (%)	P-R AAD (%)	R-K AAD (%)	H-S AAD (%)	Sat. Data Ref.
Argon	34	0.556-0.981	4.27	2.45	1.80	8.72	5.06	-	1,4
Nitrogen	32	0.501-0.983	4.10	2.32	1.20	8.88	4.76	-	4
Oxygen	36	0.530-0.983	4.30	2.37	1.99	8.16	5.74	-	4
Methane	32	0.524-0.976	4.59	3.03	1.52	7.66	5.72	0.50	6
Ethane	28	0.563-0.982	6.25	3.63	2.65	7.12	13.32	0.09	9
Ethylene	24	0.550-0.983	4.82	2.72	1.46	6.07	11.79	-	9
Propane	33	0.570-0.984	5.58	2.86	1.63	5.98	14.51	0.23	9
Propylene	27	0.563-0.974	4.35	2.27	5.99	7.17	9.97	-	9
Acetylene	21	0.624-0.972	4.91	1.83	2.40	5.30	24.91	-	5
n-Butane	28	0.627-0.980	5.57	3.39	2.26	5.61	19.36	0.13	9
i-Butane	29	0.578-0.980	2.29	2.61	3.82	3.40	15.64	-	9
1-Butene	26	0.651-0.966	3.80	1.45	1.19	4.52	16.88	-	5
n-Pentane	30	0.638-0.981	3.96	3.11	5.22	4.00	20.12	0.05	9
i-Pentane	21	0.579-0.965	4.83	2.24	1.91	5.43	23.66	-	9
n-Hexane	32	0.613-0.974	3.11	2.24	0.62	3.22	24.02	0.12	9
n-Heptane	23	0.637-0.987	4.44	2.04	3.23	4.69	29.56	0.15	9
n-Octane	23	0.586-0.972	3.91	1.34	3.96	6.55	31.40	5.58	10
n-Nonane	27	0.525-0.760	0.53	0.53	-	3.62	-	-	8,3

TABLE 4.2 continued.

Component	No. of Points	T_r Range	NEW EQ. $Z'_m=Z_m$ AAD (%)	NEW EQ. $Z'_m=f[T_r]$ AAD (%)	Heyen AAD (%)	P-R AAD (%)	R-K AAD (%)	H-S AAD (%)	Sat. Data Ref.
n-Decane	27	0.536-0.771	0.62	0.62	-	5.85	-	-	8,3
n-Undecane	27	0.545-0.781	0.63	0.63	-	5.81	-	-	8,3
n-Dodecane	27	0.576-0.790	0.70	0.70	-	7.47	-	-	8,3
n-Tridecane	27	0.563-0.799	0.70	0.70	2.41	6.81	-	-	8,3
n-Tetradecane	27	0.569-0.806	0.76	0.76	1.11	8.95	-	-	8,3
n-Heptadecane	27	0.592-0.832	0.94	0.94	1.76	14.82	-	-	8,3
n-Octadecane	27	0.598-0.839	1.07	1.07	-	18.89	-	-	8,3
n-Eicosane	27	0.615-0.850	1.04	1.04	-	18.42	-	-	8,3
Carbon dioxide	44	0.712-0.987	4.48	1.78	5.70	5.22	23.00	-	2
Carbon monoxide	21	0.542-0.960	3.81	2.10	2.70	8.48	4.97	-	5
Sulfur dioxide	33	0.593-0.989	4.46	1.71	1.70	4.49	35.14	-	5
Hydrogen sulfide	29	0.565-0.982	3.47	1.57	0.83	5.84	10.29	-	9
Water	29	0.546-0.978	3.99	1.57	2.69	26.33	64.88	-	7
Ammonia	22	0.698-0.986	3.21	2.44	6.19	15.90	45.83	-	5
Benzene	39	0.553-0.988	3.87	1.69	0.77	4.05	20.95	-	5
Methanol	22	0.588-0.695	0.51	0.51	0.55	20.05	-	-	8,3
Ethanol	26	0.575-0.719	0.51	0.51	0.96	4.33	-	-	8,3
Propan-1-01	30	0.536-0.726	0.66	0.66	7.09	3.06	-	-	8,3
Butan-1-01	23	0.609-0.730	0.28	0.28	10.09	2.18	-	-	8,3
Pentan-1-01	30	0.542-0.736	0.53	0.53	7.11	1.32	-	-	8,3
Overall Average (%)			2.94	1.69	2.98	7.75	20.02	0.86	

TABLE 4.3

Comparison of saturated vapour densities

Component	NEW EQ. $Z'_m=Z_m$ AAD (%)	NEW EQ. $Z'_m=f[T_r]$ AAD (%)	Heyen AAD (%)	P-R AAD (%)	R-K AAD (%)	H-S AAD (%)
Argon	0.36	1.15	4.32	1.42	0.33	-
Nitrogen	0.55	1.32	3.32	1.20	0.75	-
Oxygen	0.70	1.23	3.58	0.91	0.94	-
Methane	0.88	1.50	4.20	1.66	0.51	0.58
Ethane	0.99	2.12	4.03	1.38	1.97	0.20
Ethylene	0.71	1.60	3.72	1.04	1.70	-
Propane	0.86	2.22	4.03	1.23	2.91	0.22
Propylene	2.43	2.71	3.10	1.68	3.91	-
Acetylene	2.09	2.11	2.86	1.87	5.05	-
n-Butane	0.73	1.62	3.98	0.78	3.23	0.15
i-Butane	1.30	2.30	4.39	1.73	1.30	-
1-Butene	1.41	2.31	4.84	1.71	2.65	-
n-Pentane	0.59	1.78	5.27	0.62	3.30	0.14
i-Pentane	0.88	1.99	4.01	1.13	1.97	-
n-Hexane	0.87	1.70	3.48	0.88	4.10	-
n-Heptane	0.67	1.32	3.54	0.63	3.54	-
n-Octane	2.46	3.08	3.85	2.86	4.62	-
Carbon dioxide	0.71	2.13	6.20	2.00	4.53	-

TABLE 4.3 (Continued)

Component	NEW EQ.		Heyen	P-R	R-K	H-S
	$Z'_m=Z_m$ AAD (%)	$Z'_m=f[T_r]$ AAD (%)	AAD (%)	AAD (%)	AAD (%)	AAD (%)
Carbon monoxide	3.93	3.24	3.39	3.45	4.14	-
Sulfur dioxide	1.04	2.00	3.70	1.11	5.11	-
Hydrogen sulfide	2.58	3.38	6.37	3.38	1.27	-
Water	1.26	2.36	4.47	3.76	7.11	-
Ammonia	4.48	3.00	3.64	6.81	11.31	-
Benzene	2.18	3.27	4.80	2.23	4.21	-
Overall average (%)	1.44	2.14	4.14	1.89	3.35	0.26

No. of points, temperature range and saturation data reference are same as those given in Table 4.2.

TABLE 4.4

Comparison in the critical region $0.90 < T_r < 1.0$

Predictions of saturated liquid densities

Component	NEW EQ. $Z_m'=Z_m$ AAD (%)	NEW EQ. $Z_m'=f[T_r]$ AAD (%)	Heyen AAD (%)	P-R AAD (%)	R-K AAD (%)
Argon	11.39	2.41	1.28	3.84	13.86
Oxygen	12.47	2.55	1.36	3.69	15.65
Nitrogen	12.19	2.72	1.32	3.25	14.85
Methane	12.90	4.56	2.08	4.75	17.16
Ethane	14.18	5.09	6.23	10.80	26.63
Ethylene	14.44	4.36	2.68	8.98	25.37
Propane	11.16	2.88	3.26	6.33	24.86
Propylene	13.62	2.39	3.19	5.17	23.09
Acetylene	13.35	2.03	2.86	11.86	39.60
n-Butane	12.51	3.79	5.80	11.68	33.02
i-Butane	3.99	5.45	2.52	0.50	22.69
1-Butene	11.55	1.38	6.02	7.70	28.18
n-Pentane	8.74	5.10	4.37	8.43	31.75
i-Pentane	16.59	2.37	3.36	13.10	46.79
n-Hexane	7.94	3.96	1.43	9.26	35.09
n-Heptane	14.52	3.51	7.08	15.90	55.06
Carbon dioxide	9.38	1.47	7.95	4.78	36.43
Carbon monoxide	11.15	1.72	4.55	2.96	15.06
Sulfur dioxide	11.38	2.28	2.40	12.26	48.71
Hydrogen sulfide	10.61	1.51	1.59	4.42	20.40
Water	12.69	2.31	3.95	37.82	123.41
Ammonia	6.91	4.52	7.85	21.54	54.87
Benzene	12.11	1.48	1.75	10.84	32.87
Overall average (%)	11.56	3.04	3.69	9.56	34.15

For saturation data reference see Table 4.2.

TABLE 4.5

Comparison in the critical region $0.90 < T_r < 1.0$

Predictions of saturated vapour densities

Component	NEW EQ. $Z'_m = Z_m$ AAD (%)	NEW EQ. $Z'_m = f[T_r]$ AAD (%)	Heyen AAD (%)	P-R AAD (%)	R-K AAD (%)
Argon	0.68	4.50	9.83	4.16	1.00
Oxygen	0.89	3.64	9.13	2.60	2.01
Nitrogen	0.27	4.33	9.57	3.76	1.06
Methane	2.25	5.58	11.28	4.98	0.97
Ethane	1.31	5.24	9.21	3.03	2.62
Ethylene	0.86	5.11	10.40	2.66	2.90
Propane	0.56	4.63	9.06	2.13	4.40
Propylene	2.23	3.74	9.66	0.82	5.86
Acetylene	3.16	3.24	6.96	2.64	9.66
n-Butane	1.00	4.55	9.44	1.25	5.64
i-Butane	3.89	8.41	11.34	5.22	1.95
1-Butene	2.04	5.95	10.44	2.90	4.00
n-Pentane	1.09	6.19	11.94	1.18	6.38
i-Pentane	2.48	8.63	9.47	3.65	3.93
n-Hexane	0.44	4.20	9.45	0.19	7.36
n-Heptane	1.93	4.91	9.07	1.79	9.11
Carbon dioxide	0.59	4.46	10.30	3.58	-
Carbon monoxide	9.77	5.98	7.28	7.58	10.78
Sulfur dioxide	1.47	4.63	7.99	1.61	10.22
Hydrogen sulfide	7.51	11.39	15.98	9.66	3.96
Water	0.72	5.45	11.58	8.32	-
Ammonia	6.43	1.76	6.88	11.29	19.70
Benzene	1.68	6.98	11.42	2.09	5.45
Overall average (%)	2.32	5.37	9.90	3.78	5.66

For saturation data reference see Table 4.2.

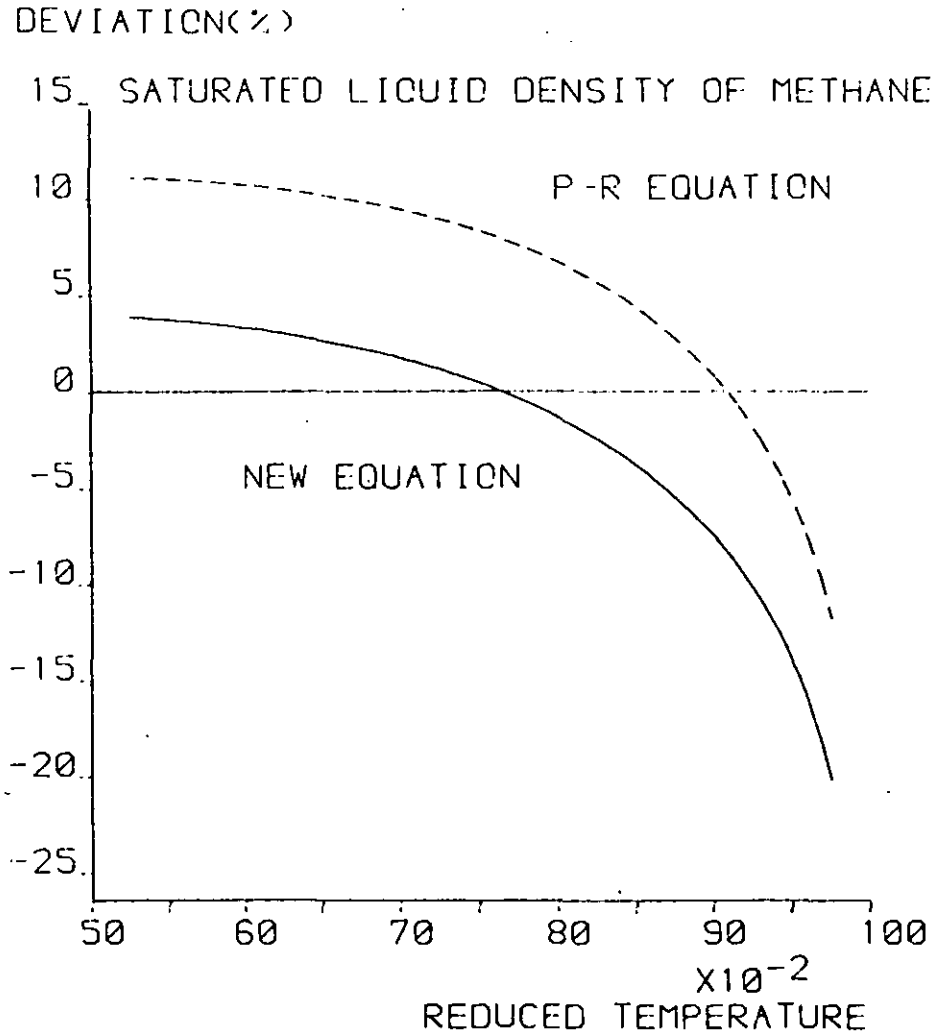


FIGURE 4.1 Comparison of predicted densities for saturated methane.

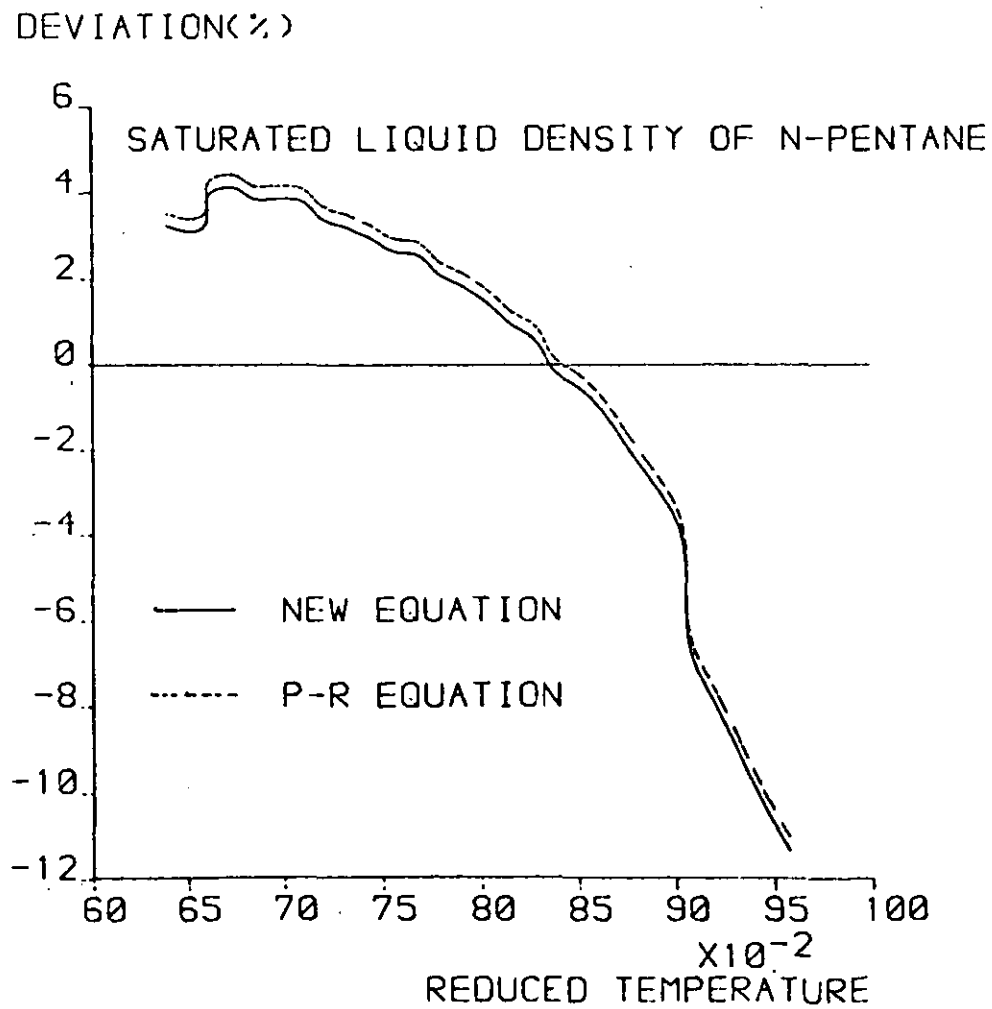


FIGURE 4.2 Comparison of predicted densities for saturated n-Pentane

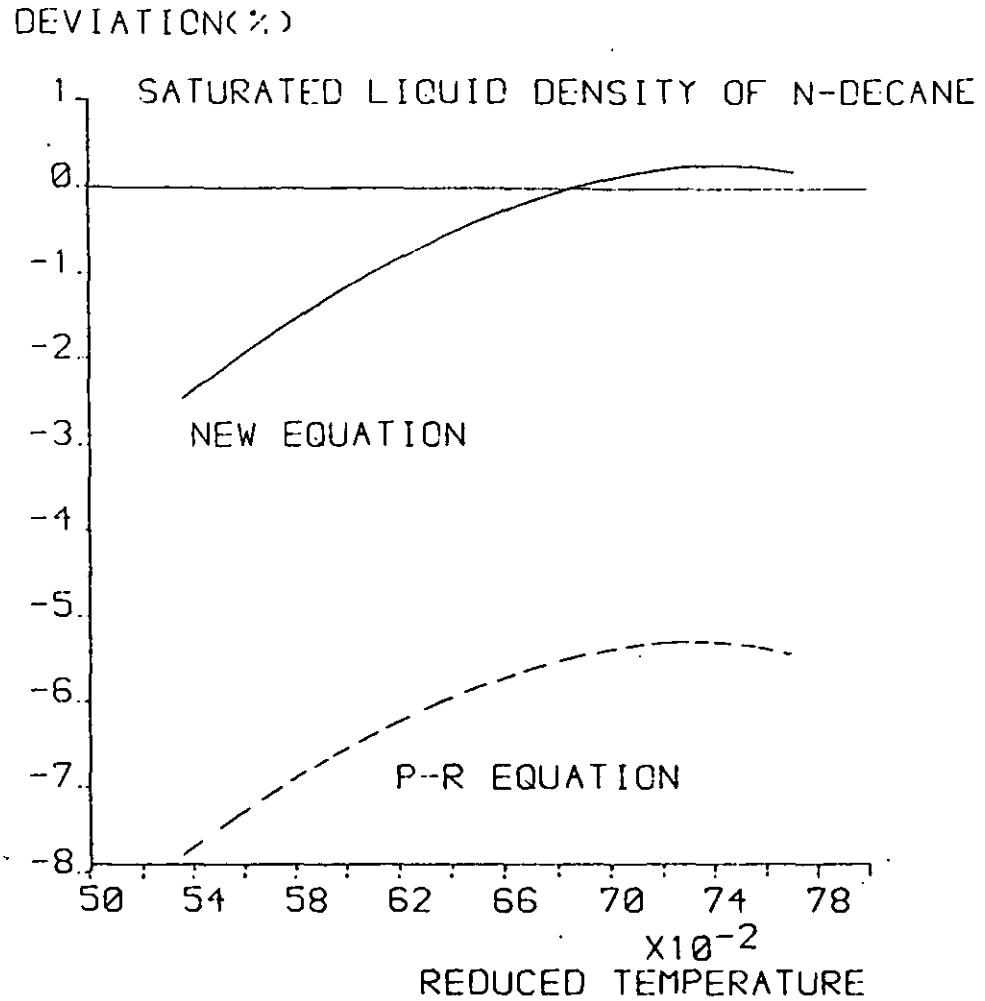


FIGURE 4.3 Comparison of predicted densities for saturated n-Decane

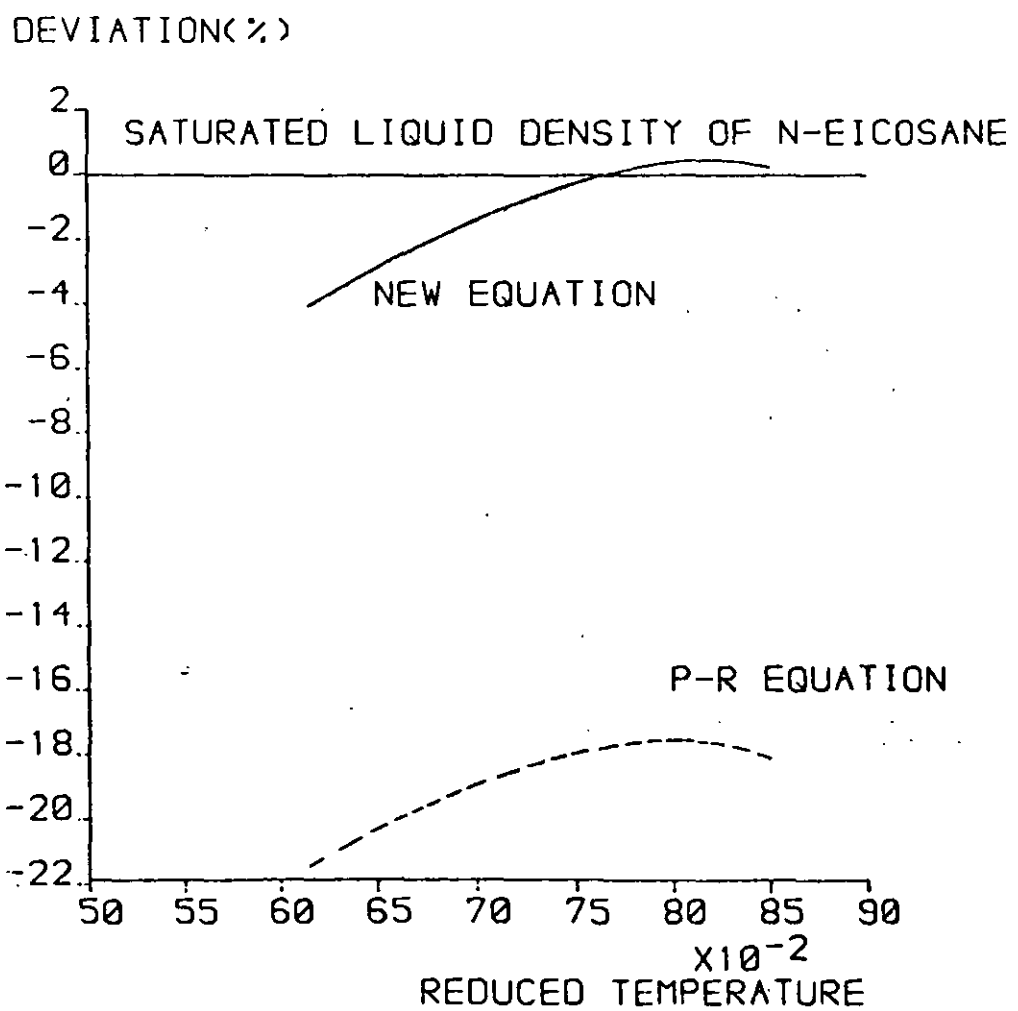


FIGURE 4.4 Comparison of predicted densities for saturated n-Eicosane

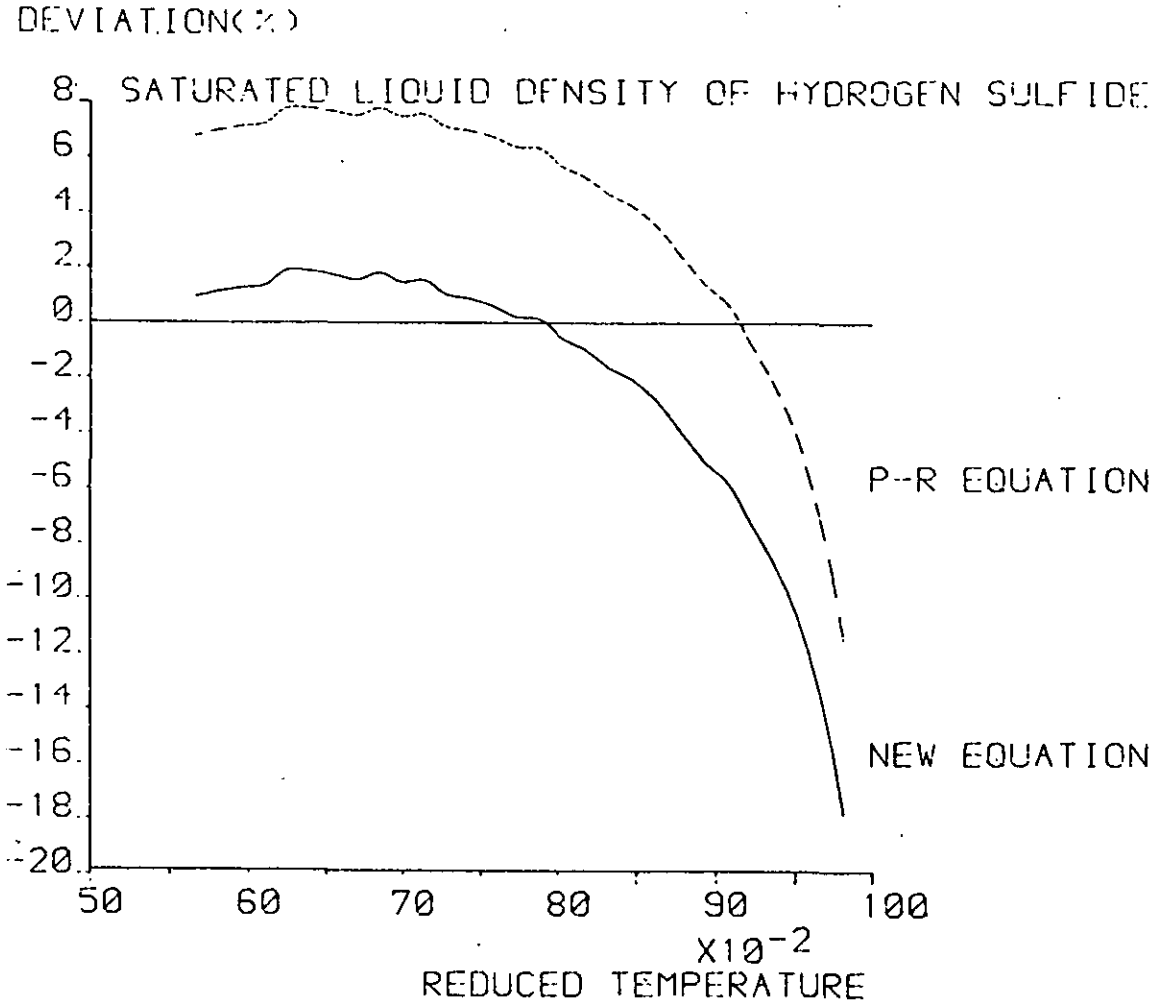


FIGURE 4.5 Comparison of predicted densities for saturated hydrogen sulfide

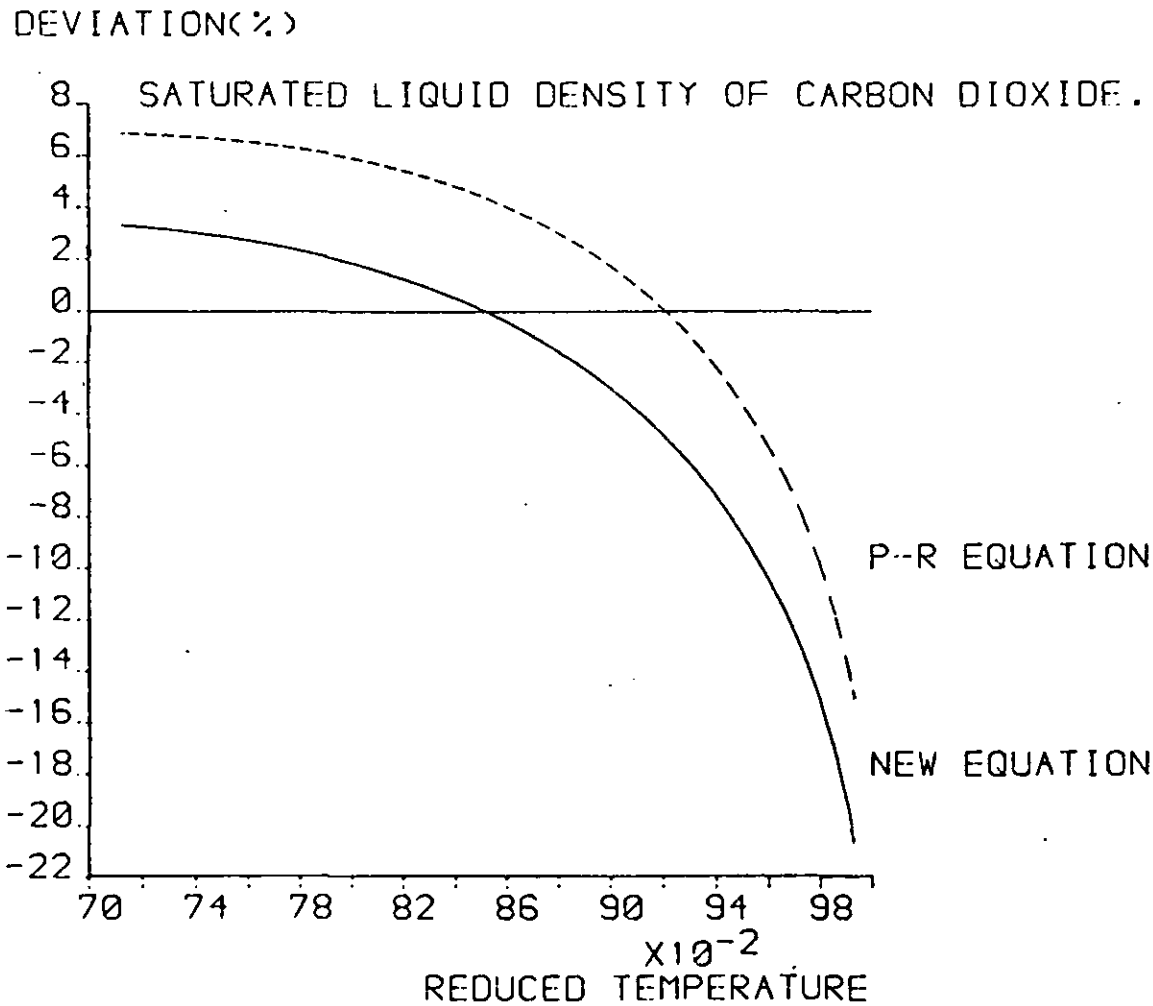


FIGURE 4.6 Comparison of predicted densities for saturated carbon dioxide

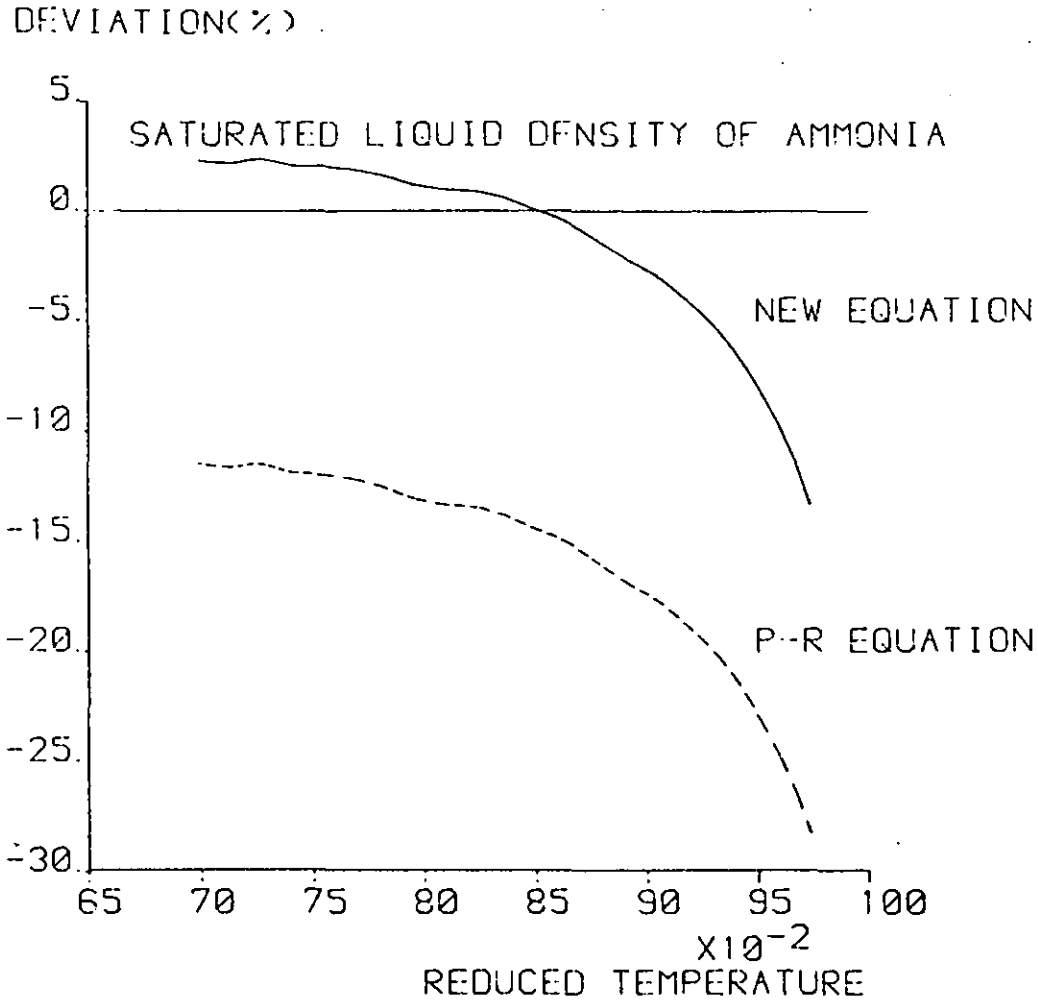


FIGURE 4.7 Comparison of predicted densities for saturated ammonia.

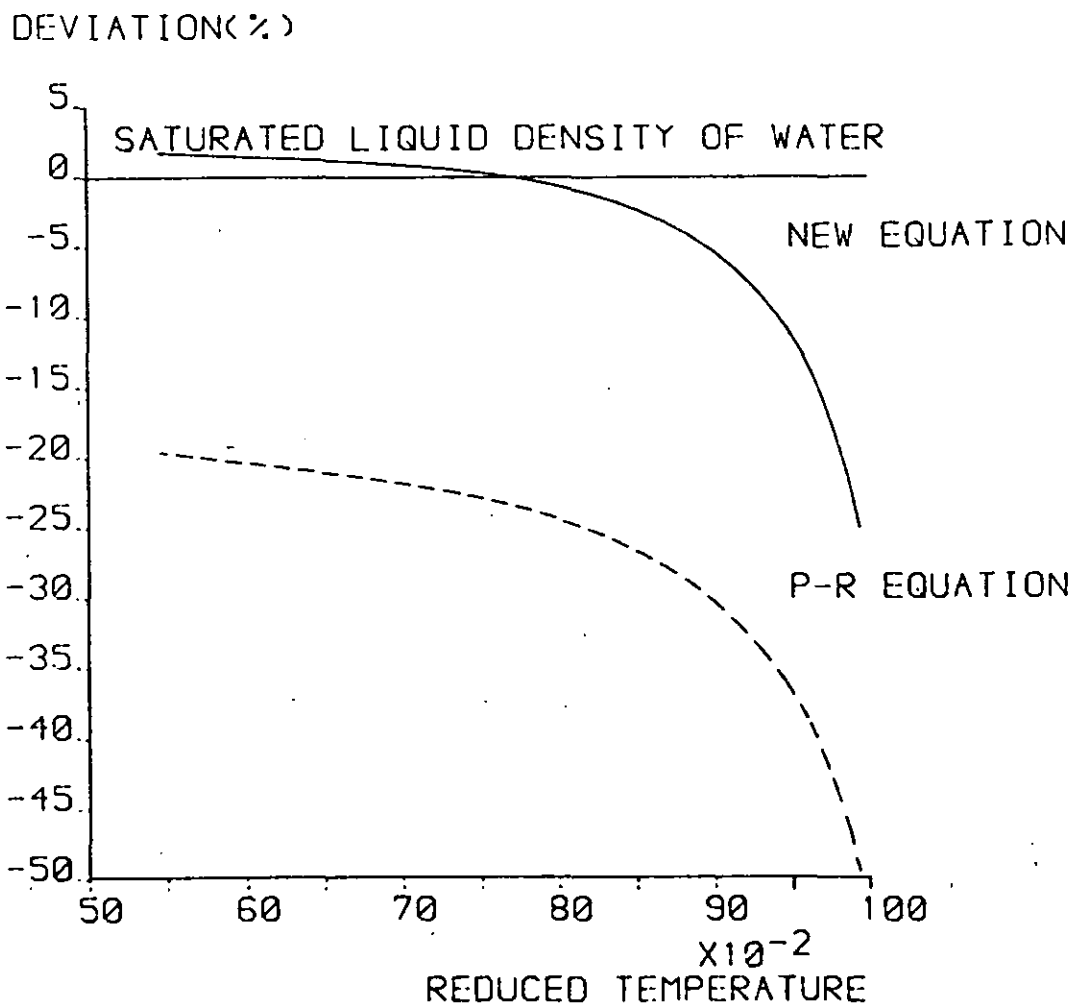


FIGURE 4.8 Comparison of predicted densities for saturated water

Densities in regions other than the saturation region have also been calculated. Results are given in Table 4.6. For light hydrocarbons, sulfur dioxide and benzene, the new equation and the P-R equation give similar predictions but for heavy hydrocarbons, better predictions were obtained with the new equation. As expected, the Han and Starling equation gives very accurate predictions of density. The individually fitted constants were used (Starling, 1973). These constants are given in Appendix C. The Heyen equation gave very poor predictions of density. The absolute average deviation obtained from the Heyen equation was of the order of 5-10%, compared with 2-3% for the new equation and the P-R equation.

4.2.2 Vapour Pressure

One of the most important considerations for any equation of state that is to be used for vapour-liquid equilibrium calculations is whether or not it can accurately predict the vapour pressure of pure substances. The calculation of the vapour pressure P_s at a given temperature requires the simultaneous solution of the following equations for vapour-liquid equilibrium (Benedict et al, 1940)

$$P^L = P^V = P_s \quad \text{and} \quad f^L = f^V \tag{4.32}$$

where: L and V refer to the liquid and vapour respectively.

The procedure used for calculating the vapour pressure is described in Appendix G. A computer program for the prediction of the vapour pressure at a given temperature is given in Appendix H.

Excellent predictions of vapour pressures were obtained for 38 components using the new equation of state. Results are given in Table 4.7. Only the three alcohols - propan-1-ol,

TABLE 4.6

Comparison of pure component densities

Substance	No. of Data	T_r Range	P_r Range	New Eq. AAD (%)	P-R AAD (%)	Heyen AAD (%)	H-S AAD (%)	Vol.Data Ref.
Methane	570	0.601-3.271	0.150-10.682	3.77	4.81	5.68	1.79	1, 2, 3
Ethane	336	0.894-1.713	0.021-14.129	2.32	3.05	6.31	1.02	4, 5, 6, 7
Propane	419	0.796-1.483	0.024-16.225	2.19	2.96	6.54	0.71	8, 9, 10
n-Butane	244	0.693-1.348	0.018-18.160	3.43	3.64	8.36	1.26	11, 12, 13, 14, 15
n-Pentane	440	0.662-1.221	0.030-20.465	3.45	3.51	9.01	1.46	11, 12, 16, 17, 18
n-Hexane	159	0.613-1.080	0.188-22.327	3.96	3.38	7.87	1.57	19, 20, 21
n-Heptane	102	0.514-0.946	0.045-25.273	2.12	3.53	4.38	1.24	22
n-Octane	93	0.656-0.964	0.204-12.225	2.19	3.18	3.50	4.15	23
n-Nonane	75	0.523-0.860	0.103-29.968	1.40	3.15	-	-	24
n-Decane	214	0.503-0.827	0.656-32.778	1.71	5.24	-	-	25
Sulfur dioxide	170	0.593-1.212	0.001-3.935	1.67	1.68	-	-	12
Benzene	353	0.553-2.233	0.001-4.223	1.06	1.05	-	-	12
Overall average (%)				2.44	3.27	6.46	1.65	

P-R - Peng and Robinson equation (1976)

H-S - Han and Starling equation (1973)

TABLE 4.7

Vapour pressures from the new equation of state

(For data reference, see Table 4.2)

Component	No. of Points	T_r Range	p^S AAD (%)
Argon	34	0.556-0.981	0.64
Nitrogen	32	0.501-0.983	0.51
Oxygen	36	0.530-0.983	0.88
Methane	32	0.524-0.976	0.88
Ethane	28	0.563-0.982	0.46
Ethylene	24	0.550-0.983	1.04
Propane	33	0.570-0.984	0.59
Propylene	27	0.563-0.974	0.56
Acetylene	21	0.624-0.972	0.90
n-Butane	28	0.627-0.980	0.25
i-Butane	29	0.578-0.980	0.50
i-Butene	26	0.651-0.966	0.50
n-Pentane	30	0.638-0.981	0.26
i-Pentane	21	0.579-0.965	0.34
n-Hexane	32	0.613-0.974	0.67
n-Heptane	23	0.637-0.987	0.61
n-Octane	23	0.586-0.972	0.92
n-Nonane	27	0.525-0.760	1.49
n-Decane	27	0.536-0.771	1.50
n-Undecane	27	0.545-0.781	1.18
n-Dodecane	27	0.576-0.790	1.36
n-Tridecane	27	0.563-0.799	0.94
n-Tetradecane	27	0.569-0.806	2.58
n-Heptadecane	27	0.592-0.832	0.94
n-Octadecane	27	0.598-0.839	2.07
n-Eicosane	27	0.615-0.850	2.75
Carbon dioxide	43	0.712-0.987	0.23
Carbon monoxide	21	0.542-0.960	0.58
Sulfur dioxide	33	0.593-0.989	0.30
Hydrogen sulfide	29	0.565-0.982	0.67

TABLE 4.7 (Continued)

Component	No. of Points	T_r Range	p^S AAD (%)
Water	29	0.546-0.978	0.64
Ammonia	22	0.698-0.986	0.73
Benzene	39	0.553-0.988	0.53
Methanol	22	0.588-0.695	0.77
Ethanol	26	0.575-0.719	0.52
Propan-1-Ol	30	0.536-0.726	4.06*
Butan-1-Ol	23	0.609-0.730	3.53*
Pentan-1-Ol	30	0.542-0.736	6.97*
Overall average (%)			0.865

* These points are not included in the overall average deviation.

Butan-1-Ol and Pentan-1-Ol showed absolute average deviations of the order of 5%. For light components (hydrocarbons up to n-octane), the predictions were within 1% of the experimental values. For heavy hydrocarbons (up to n-eicosane), the predictions were within 2% of the experimental values. For polar components - such as water, ammonia and the lower alcohols - the predictions were within 1% of the experimental values.

4.2.3 The Enthalpy Departure

The enthalpy departure is required in the calculation of the enthalpy of a compound by the following equation:

$$H = (H - H^{o}) + (H^{o} - H_{o}^{o}) + H_{o}^{o} \qquad (4.33)$$

where H_{o}^{o} is the standard enthalpy of formation of the compound from the elements at zero pressure and zero temperature and which can be obtained from API (1953); $(H^{o} - H_{o}^{o})$ is the difference in the enthalpy of the compound in the ideal gas state at the temperature of interest and the reference state of zero temperature. This quantity can also be obtained from API (1953); $(H - H^{o})$ is the enthalpy departure or the difference in the enthalpy of the compound at the temperature-pressure conditions of interest and the enthalpy of the compound in the ideal gas state at the same temperature.

The enthalpy departure is related to the equation of state by the following equation:

$$\phi(H - H^{o}) = RT\ (Z - 1) + \int_{\infty}^{V} [T\ (\frac{\partial P}{\partial T})_{V} - P]dv \qquad (4.34)$$

where ϕ is a conversion factor.

The equation of state expression for the enthalpy departure (derived in Appendix E) has the following form when the new equation of state given in equation (4.1) is substituted in equation (4.34).

$$\phi(H - H^{o}) = RT\ (Z - 1) - (T\ \frac{\partial a}{\partial T} - a)\ [\frac{1}{2N}\ \ln\ \frac{(Z+M)}{(Z+Q)}] \tag{4.35}$$

where N, M and Q are given by equations:

(4 - 26a); (4 - 26b), and (4 - 26c)

For self-consistency, the value of Z used in equation (4.35) must be determined by the solution of equation (4.10), for the temperature-pressure condition of interest.

Instead of the actual enthalpy H, the enthalpy departures were calculated using the new equation, the P-R equation and the H-S equation. The H-S equation predicts the enthalpy departures and the entropy departures within the experimental errors. The percentage deviation from the experimental value is less than 1 per cent for methane, ethane, propane and n-butane. For n-pentane and n-hexane the deviation is slightly greater than 1 percent and for n-heptane and n-octane predictions are within 3 per cent of the experimental values (Starling, 1973). The expressions of the enthalpy departure from the Peng-Robinson and the Han-Starling equation are given in Appendix E.

The values of the enthalpy departures obtained from the new equation and the P-R equation are compared with the values obtained from the H-S equation. Results are given in Table 4.8. The new equation predicts the enthalpy departures of pure components with the same accuracy as the P-R equation. Absolute average deviations of the order of ~~4~~ 2-5% were obtained. Enthalpy departures of saturated liquid have ~~also~~ been calculated with ~~the~~ better ~~same~~ accuracy (%). Results are given in Table 4.9.

TABLE 4.8

Comparison of enthalpy and entropy departures

Substance	No. of Points	T_r Range	P_r Range	ΔH		ΔS	
				New Eq. AAD (%)	P-R AAD (%)	New Eq. AAD (%)	P-R AAD (%)
Methane	570	0.601-3.271	0.150-10.682	3.80	5.21	1.01	0.98
Ethane	336	0.894-1.713	0.021-14.129	5.57	6.96	0.62	0.61
Propane	419	0.796-1.483	0.024-16.225	5.21	5.78	0.62	0.57
n-Butane	244	0.693-1.348	0.018-18.160	4.07	4.10	0.67	0.65
n-Pentane	440	0.662-1.221	0.030-20.465	2.73	2.74	0.49	0.49
n-Hexane	159	0.613-1.080	0.188-22.327	2.16	2.28	1.19	1.16
n-Heptane	102	0.514-0.946	0.045-25.273	2.49	2.42	1.58	1.53
n-Octane	93	0.656-0.964	0.204-12.225	1.37	1.31	0.89	0.95
Overall average (%)				3.43	3.85	0.88	0.87

$$\text{AAD in } \Delta S = \frac{1}{N} \sum \frac{|\Delta S_{HS} - \Delta S_{CALC}|}{\Delta S_{HS}} \times 100 \qquad \text{AAD in } \Delta H = \frac{1}{N} \sum \frac{|\Delta H_{HS} - \Delta H_{CALC}|}{\Delta H_{HS}} \times 100$$

ΔH_{HS}, ΔS_{HS} are enthalpy and entropy departures calculated from the Han and Starling equation.

TABLE 4.9

Enthalpy and entropy departures of saturated liquid

Substance	No. of Points	T_r Range	ΔH New Eq. AAD (%)	ΔS New Eq. AAD (%)
Methane	32	0.524-0.976	2.11	1.07
Ethane	28	0.563-0.982	2.53	1.16
Propane	33	0.570-0.984	2.52	1.21
n-Butane	28	0.627-0.980	2.41	1.24
n-Pentane	30	0.638-0.981	1.70	0.92
n-Hexane	32	0.613-0.974	2.55	1.44
n-Heptane	23	0.637-0.987	1.53	0.85
n-Octane	24	0.586-0.972	1.13	0.79
Overall average (%)			2.06	1.09

ΔH, ΔS as defined in Table 4.8.

4.2.4 The Entropy Departure

The entropy of a compound is calculated using the equation

$$S = (S - S^o) + S^o \tag{4.36}$$

This equation is analogous to equation (4.33) for the enthalpy except that the entropy of formation at zero temperature, S_o^o is zero by virtue of the third law of thermodynamics (Canjar et al, 1967). S^o is the entropy of the compound in the ideal gas state at unit pressure (Canjar et al, 1967) and can be obtained from API (1953); $(S - S^o)$ is the entropy departure or the difference in the entropy of the compound at the temperature-pressure conditions of interest and the entropy of the compound in the ideal gas state at the same temperature and unit pressure. The entropy departure is related to the equation of state by the following equation:

$$\phi(S - S^o) = -R \ln \frac{RT}{V} - \int_{\infty}^{V} [\frac{R}{V} - (\frac{\partial P}{\partial T})_V] dV \tag{4.37}$$

When the new equation of state is used with equation (4.37), the following expression for the entropy departure is obtained (Appendix E)

$$\phi(S - S^o) = -R \ln \frac{P}{Z-B} - \frac{\partial a}{\partial T} [\frac{1}{2N} \ln \frac{(Z+M)}{(Z+Q)}] \tag{4.38}$$

where ϕ is a conversion factor. M, N and Q are given by equations (4.26a), (4.26b) and (4.26c).

The value of Z used in equation (4.38) must be determined by the solution of equation (4.10), for the temperature-pressure conditions of interest.

The entropy departures have been calculated using the new equation, the P-R equation and the H-S equation. The entropy departure expressions for the P-R equation and the H-S equation are given in Appendix E. The entropy departures obtained with the new equation and the P-R equation are compared with the entropy departures obtained from the H-S equation. As mentioned earlier in the text, the H-S equation predicts entropy departures within the experimental errors.

Results are given in Table 4.8. The new equation predicts the entropy departures of pure components with the same accuracy as the P-R equation. Absolute average deviations of the order of 1 to 2% were obtained. Entropy departures of saturated liquid have also been calculated with the same accuracy. Results are given in Table 4.9.

4.3 Extension to New Substances

One way of extending any equation of state to new substances is to generalise the equation of state constants. In order to apply the new equation of state to the prediction of thermodynamic properties of substances not covered in this work, the values of the parameters Z_m and F have been correlated with the acentric factors as shown in Figure 4.9 and Figure 4.10. The resulting equations are given by:

$$F = 0.452413 + 1.30982\,\omega - 0.295937\,\omega^2 \qquad (4.39)$$

$$Z_m = 0.329032 - 0.0767992\omega + 0.0211947\,\omega^2 \qquad (4.40)$$

These expressions were obtained using mini-max polynomial fitting (NAG routine E02ACF, Loughborough University Computer Centre). Equations (4.39) and (4.40) are shown by a solid line in Figures 4.10 and 4.9 respectively. As can be seen excellent correlations have been obtained.

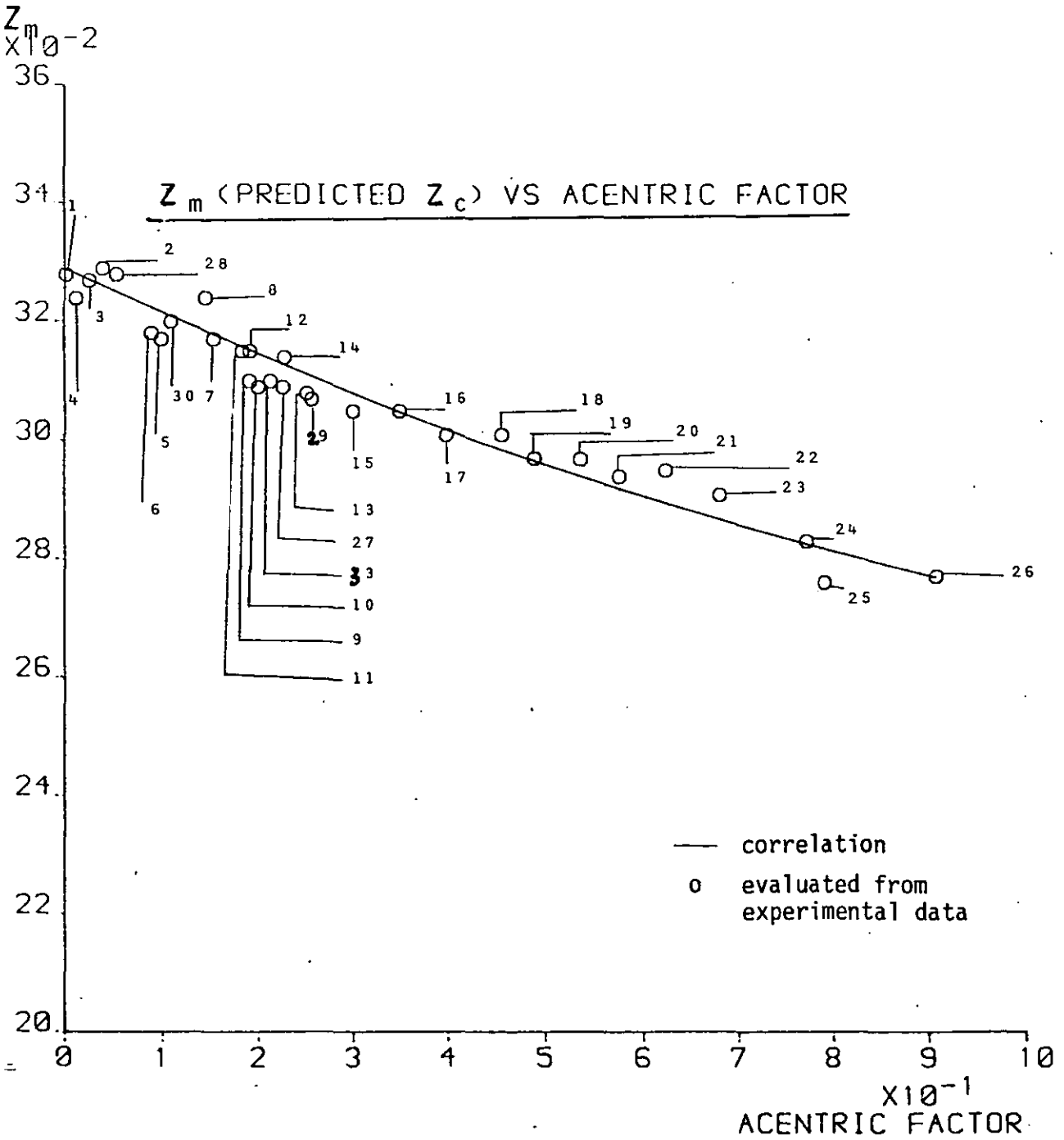


FIGURE 4.9 Relationship between predicted critical compressibilities (Z_m) and acentric factors (ω).
Each value is marked with an identification number (see Appendix A)

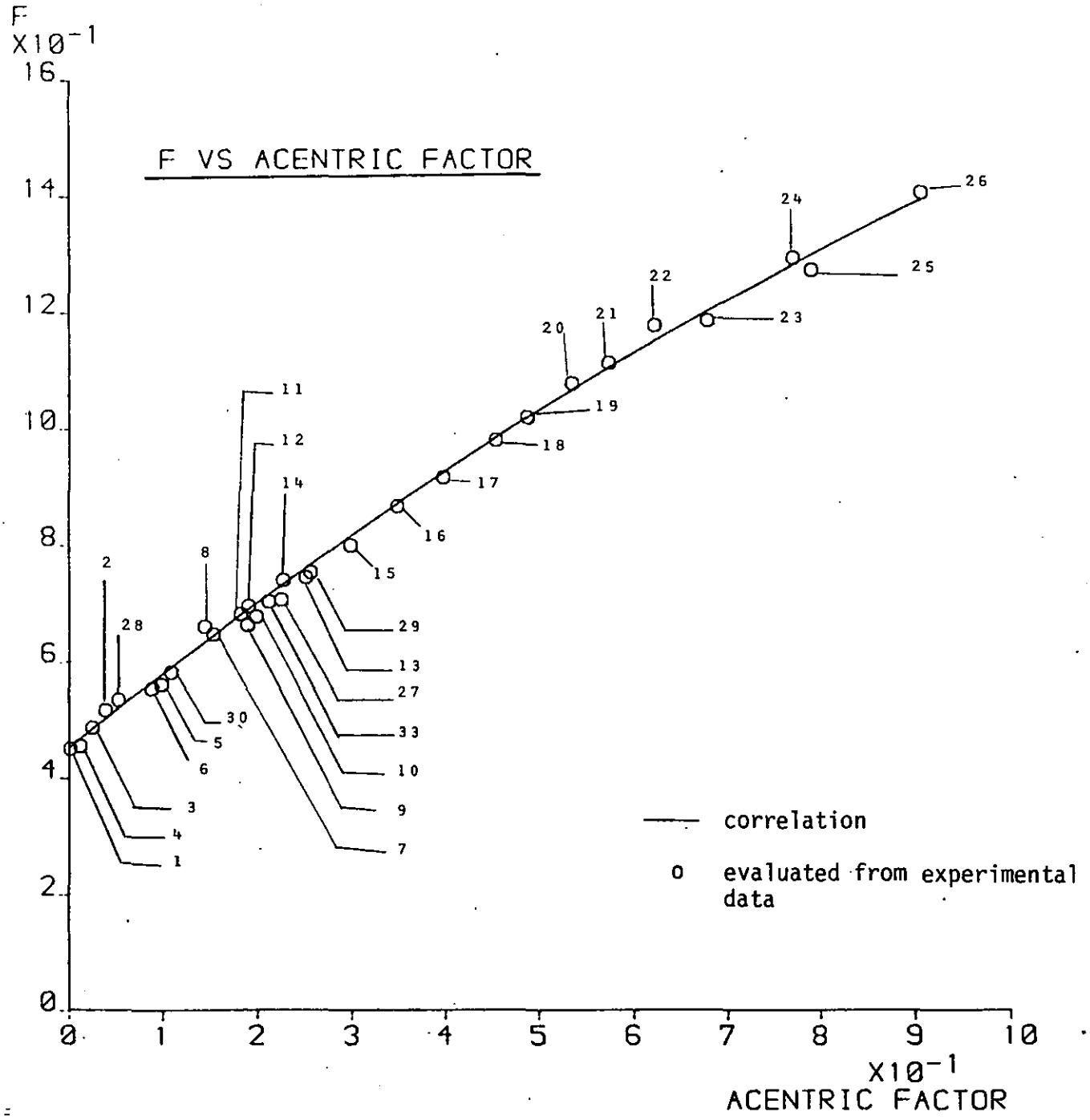


FIGURE 4.10 Relationship between characterization constants (F) and acentric factors (ω)

Each value is marked with an identification number (see Appendix A).

As expected the generalised equations apply to non-polar substances only (3 parameter CSP). Water, ammonia and alcohols are not included in Figures (4.9) and (4.10). The values of Z_m and F for these components are very different from those obtained by using equations (4.39) and (4.40).

To test the validity of equations (4.39) and (4.40), saturated liquid densities and vapour pressures have been calculated for methane, n-pentane, n-decane and n-eicosane. Results are summarized in Table 4.10. Equations (4.39) and (4.40) give results which are as good as those obtained by using Z_m and F values evaluated from experimental data (Appendix A). Equations (4.39) and (4.40) are most useful for components for which saturation data are not easily available. However, for accurate work it is necessary to evaluate Z_m and F from saturation data as described in Section 4.1.

TABLE 4.10

Saturated liquid densities and vapour pressures from generalized correlations

Component	No.of Points	T_r Range	ρ_s^L AAD (%) *	ρ_s^L AAD (%) **	P_s AAD (%) *	P_s AAD (%) **
Methane	32	0.524-0.976	4.86	4.59	0.96	0.88
n-pentane	30	0.638-0.981	3.92	3.96	0.42	0.26
n-decane	27	0.536-0.771	0.66	0.62	1.58	1.50
n-eicosane	27	0.615-0.850	1.03	1.04	2.97	2.75
Overall average (%)			2.62	2.55	1.48	1.35

* Generalized constants

** Individual constants

Results have also been obtained for compressibilities of normal alkanes using the generalized form of the new equation (see Table 4.12).

4.4 Extension to New Substances via the Generalized Corresponding States Principle

The three parameter corresponding states principle was originally proposed by Pitzer et al (1955), who showed that the compressibility factor (expressed as a function of reduced temperature and reduced pressure) can be written as a power series in the acentric factor as follows:

$$Z = Z^{(0)} + \omega Z^{(1)} + \ldots. \tag{4.41}$$

where, $Z^{(0)}$, $Z^{(1)}$, etc. are each functions of reduced temperature (T_r) and reduced pressure (P_r). $Z^{(0)}$ is the compressibility factor of a simple fluid with zero acentric factor at the same reduced temperature and pressure and $Z^{(1)}$, $Z^{(2)}$ etc. are complicated deviation functions.

The first two terms in equation (4.41), are usually sufficient for moderate and high temperatures ($T_r > 0.8$) and Z is then given by:

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{4.42}$$

Expressions for other thermoydnamic properties can be written in a similar way. In particular, Pitzer et al (1955) showed that the vapour pressures of pure substances can be expressed in the form:

$$\ln P_r = \ln P_r^{(0)} + \omega \ln P_r^{(1)} \tag{4.43}$$

and Gunn and Yamada (1971) showed that the saturated liquid volumes of pure substances can be expressed as:

$$V_r = V_r^{(0)} + \omega V_r^{(1)} \tag{4.44}$$

where: $\ln P_r^{(0)}$, $\ln P_r^{(1)}$, $V_r^{(0)}$ and $V_r^{(1)}$, which are saturated fluid properties, are complicated functions of reduced temperature only.

The three parameter corresponding states principle of Pitzer et al (1955) and the subsequent modifications by other workers (Lu et al 1973; Hsi and Lu, 1974; Gunn and Yamada, 1971) have been used extensively for the prediction of volumetric and thermodynamic properties needed for process design. However, most of these correlations are in tabular or graphical form, difficult to use on the computer. Since the calculation of derived properties and phase equilibria requires differentiation and integration of the compressibility function and often involves iterative calculations, it is desirable to have the correlations in analytical form which can be used on a digital computer.

With improvements in equations of state for pure substances, it has been possible to provide an analytical framework for the three parameter corresponding states principle. This was done by Lee and Kesler (1975) who showed that equation (4.42) can also be written as

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}} [Z^{(r)} - Z^{(0)}] \tag{4.45}$$

where the compressibility of any fluid of acentric factor ω is expressed in terms of the compressibility factor of a simple fluid $Z^{(0)}$ and the compressibility factor of a (heavy) reference fluid $Z^{(r)}$. Lee and Kesler used mainly the properties of argon to obtain an analytic B-W-R type expression for $Z^{(0)}$ and mainly the properties of n-octane to obtain a similar expression for $Z^{(r)}$. The Lee-Kesler correlation is accurate for the estimation of the thermodynamic properties of non-polar fluids (Reid et al,

1977). Lin and Daubert (1979) have expressed the saturated liquid volumes in a similar fashion

$$V_r = V_r^{(0)} + \frac{\omega}{\omega^{(r)}} [V_r^{(r)} - V_r^{(0)}] \qquad (4.46)$$

A similar approach is used to represent analytically other derived thermodynamic functions, such as fugacity and the departures of enthalpy, entropy and isobaric and isochoric heat capacities from the ideal gas state. (Lee and Kesler, 1975).

Both equations (4.45) and (4.46) have retained Pitzer's original proposal of a Taylor series expansion of a thermodynamic property about that property of a simple reference fluid of zero acentric factor. The extended corresponding states equation proposed by Teja (1980) and Teja and Sandler (1980) no longer retains the simple fluid as one of the references. The Lee-Kesler form is rewritten as:

$$Z = Z^{(r1)} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} [Z^{(r2)} - Z^{(r1)}] \qquad (4.47)$$

where the superscripts r1 and r2 refer to two reference fluids which are chosen so that they are similar to the pure component of interest or, in the case of mixtures, to the key components of interest. If one of the references chosen is a simple fluid of zero acentric factor, equation (4.47) reduces to equation (4.45).

Equation (4.47) provides a method for generalizing equations of state using the known equations of two pure components. In this work, the new equation of state (equation 4.1) is generalized by choosing ethane and n-decane as two reference fluids. Following the work of Lee and Kesler (1975), the compressi-

bility of the fluid of interest at a given T and P is calculated as follows:

i) Values of T_r (= T/T_c) and P_r (= P/P_c) are first calculated using the critical properties of the fluid.

ii) From Appendix A, the values of Z_m and F for the reference fluid, r1 (ethane) are used to solve for Z in equation (4.10). The smallest root is used if liquid compressibility is calculated and the largest root is used if vapour compressibility is calculated. The value of Z obtained in this step is the value of $Z^{(r1)}$ in equation (4.47).

iii) From Appendix A, the values of Z_m and F for the reference fluid, r2 (n-decane) are used and equation (4.10) is solved for Z. The value of Z obtained in this step is the value of $Z^{(r2)}$ in equation (4.47).

iv) From $Z^{(r1)}$ and $Z^{(r2)}$, the compressibility factor Z is determined using equation (4.47). If volumes are required, they are obtained from:

$$V_r = \frac{Z}{Z_c} \cdot \frac{T_r}{P_r} \qquad (4.48)$$

where Z is obtained from equation (4.47).

If vapour pressures and saturated liquid densities at a given T, are to be calculated from the generalized equation (4.47), then the state of vapour-liquid equilibrium must be established (as described in Appendix G) prior to carrying out the procedure described above. The following equation, similar to equation (4.47), can be written for other thermodynamic functions:

$$q = q^{(r1)} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} \left[q^{(r2)} - q^{(r1)}\right] \qquad (4.49)$$

where q is the thermodynamic function of interest.

For saturated liquid densities

$$q = V_r = \frac{V^L}{(RT_c/P_c)} \tag{4.50}$$

The reduction of the volume is carried out with RT_c/P_c instead of V_c, as the former is likely to be more readily available in practice.

For vapour pressures

$$q = \ln P_r = \ln (P_s/P_c) \tag{4.51}$$

For fugacity coefficient

$$q = \ln \phi = \ln (\frac{f}{P}) \tag{4.52}$$

For enthalpy departures

$$q = \frac{H - H^o}{RT_c} \tag{4.53}$$

For entropy departures

$$q = \frac{S - S^o}{R} + \ln (\frac{P}{P^o}) \tag{4.54}$$

For isochoric heat capacity departures

$$q = \frac{C_v - C_v{}^o}{R} \tag{4.55}$$

For isobaric heat capacity departures

$$q = \frac{C_p - C_p{}^o}{R} \tag{4.56}$$

Table 4.11 compares the results obtained using the generalised equation (4.47) with those of the individually fitted constants. The extension of the Redlich and Kwong equation by Chaudron et al (1973) is used for comparison purposes, because it is simple, predicts accurate compressibilities both for the gas and liquid phases (except in the region around the critical point) and individually fitted constants are available for a number of substances (a description of this equation is given in Chapter 2).

Results obtained by the method of equation (4.47) are in good agreement with experiment and the deviations from experimental data are comparable to those obtained from the individually fitted equations. The predicted values from both these methods were compared with the same experimental data. Better agreement with experiment could be obtained if a more accurate reference equation is chosen. Both equations used in this work give large deviations in the vicinity of the critical point and these deviations are included in the overall results presented in Table 4.11.

The effect of changing reference fluids is shown by the results obtained using argon and n-octane as the two reference fluids. For the hydrocarbons considered, argon and n-octane appear to be better reference fluids than ethane and n-decane. This is due mainly to the fact that the range of pressures and temperatures of the experimental data used to evaluate equation of state constants, is greater for argon and n-octane than for ethane and n-decane. The other reason is that, the acentric factors of the hydrocarbons considered are within the range covered by argon and n-octane. However, one of the main advantages of using equation (4.47) is in the flexibility of choosing the two reference fluids. Thus, for the prediction of the thermodynamic properties of hydrocarbons heavier than n-decane, one reference fluid can be chosen as n-decane and the other reference fluid can be chosen as the heaviest hydrocarbon for which the equation of state constants are available.

TABLE 4.11

Compressibilities of pure components

Pressure range)
Temperature range) Same as in Table 4.6
No. of points)

Component	New Equation AAD (%)			CRK Equation AAD (%)			Volumetric Data Reference
	*	** C_2-C_{10}	*** Ar-C_8	*	** C_2-C_{10}	*** Ar-C_8	
Methane	3.77	5.32	4.30	2.5	6.71	-	
Ethane	2.32	-	4.21	-	-	-	
Propane	2.20	2.48	2.27	1.72	2.13	1.95	SAME AS
n-Butane	3.43	3.57	2.77	1.86	3.07	3.01	
n-Pentane	3.45	3.55	3.29	3.90	6.44	5.98	TABLE 4.6
n-Hexane	3.96	4.00	3.25	5.58	3.23	-	
n-Heptane	2.12	3.45	2.22	1.96	3.74	3.22	
n-Octane	2.19	2.10	-	0.73	1.49	-	
n-Nonane	-	-	-	2.56	2.06	1.42	
Overall average(%)	2.93	3.35	3.06	2.60	3.61	3.12	

* Individual constants

$$AAD\ (\%) = 100 \sum |(Z_{calc} - Z_{exp})| / Z_{exp}) \div \text{No. of points}$$

** Generalized with Ethane as Ref. 1 and n-Decane as Ref. 2

*** Generalized with Argon as Ref. 1 and n-Octane as Ref. 2.

4.5 Comparison of the Methods Used for Generalizing the Equation of State

Two methods are used in this work to generalize the new equation of state (equation 4.1). One method (Section 4.3) uses the correlations given in terms of the acentric factor by equation (4.39) and equation (4.40) to calculate the equation of state parameters F and Z_m respectively. The second method (Section 4.4) uses the generalized corresponding states principle (GCSP) with two reference fluids. In both methods the critical temperature, the critical pressure and the acentric factor are required as input parameters for the calculation of thermodynamic properties of a fluid of interest. The advantage of using the GCSP is that it requires the equation of state constants for only the two reference fluids. Thus, experimental data of only two reference fluids are required compared with the other method in which experimental data on many pure components are required in order to obtain the correlations such as those given by equations (4.39) and (4.40). If an equation of state with a large number of constants is employed, then generalizing the parameters presents a more severe problem. The second advantage of the GCSP is that it is more closely tied to theory and so can be safely extrapolated to new regions of pressure and temperature. The disadvantage of using the GCSP method is that it involves steps in which the equation of state has to be solved twice (for two reference fluids) in order to get the final result. In general, the method using the correlations for Z_m and F (or for any other parameters in the equation of state) is easier and requires less computer time. Both methods give similar predictions for the compressibilities of hydrocarbons. Table 4.12 compares the results obtained using the GCSP method with argon and n-octane as the two reference fluids and the method using correlations for F and Z_m. A major disadvantage of the two methods is their restriction to relatively simple fluids.

TABLE 4.12

Comparison of the two methods used for generalizing the new equation of state; prediction of compressibilities

Component	No. of Points	GCSP * AAD (%)	New equation Generalized ** AAD (%)
Methane	570	4.30	4.42
Ethane	336	4.21	2.70
Propane	419	2.27	2.18
n-Butane	244	2.77	2.86
n-Pentane	440	3.29	3.34
n-Hexane	159	3.25	3.25
n-Heptane	102	2.22	2.17
n-Octane	93	2.19	2.09
Overall average (%)		3.06	2.88

* Argon as ref. 1 and n-octane as ref. 2.
Results are taken from Table 4.11.

** Using Z_m and F given by equations (4.40) and (4.39).

4.6 Use of the Exponential Temperature Function

It has been pointed out by many authors (Adler et al, 1977; Heyen, 1980) that the temperature function used by Soave (1972) and Peng and Robinson (1976) for the constant 'a' does not reproduce the correct temperature behaviour at very high temperatures. This is mainly because at a finite value of the reduced temperature, $T_{r,m}$, the function becomes zero and then starts to rise with temperature. This is not in accordance with what is observed in practice. At high temperatures, the real gas behaviour approaches that of an ideal gas and, if the constant 'a' is assumed to represent the attraction between molecules,

the function should become zero as the temperature approaches infinity. The value of $T_{r,m}$ is given by

$$T_{r,m} = (1 + \frac{1}{F})^2 \tag{4.57}$$

This is obtained by equating α from equation (4.8) to zero. $T_{r,m}$ represents the maximum temperature for which equation (4.8) is valid.

Heyen (1980) proposed the following exponential function

$$\alpha[T_r] = e^{K(1-T_r^n)} \tag{4.58}$$

This temperature function has the required characteristics. It becomes unity when $T_r = 1$ and it approaches zero as the temperature approaches infinity. However, equation (4.58) contains two arbitrary constants K and n, compared with only one constant F in equation (4.8). Constants, K, n and F have been evaluated for 38 components from saturation data and are given in Appendix A.

Both temperature functions are plotted for methane and n-decane as shown in Figure 4.11 and Figure 4.12. For temperatures up to $T_r = 12$ for methane, both functions show a similar trend but at high temperatures, the exponential function assumes zero value while the function given by equation (4.8) increases with temperature. Similarly for n-decane both functions show similar trend up to $T_r \approx 2$; after that the exponential function approaches zero while the other function increases with temperature. The results obtained for saturated liquid and vapour densities and densities in other regions are presented in Table 4.13 and Table 4.14. As can be expected, identical results

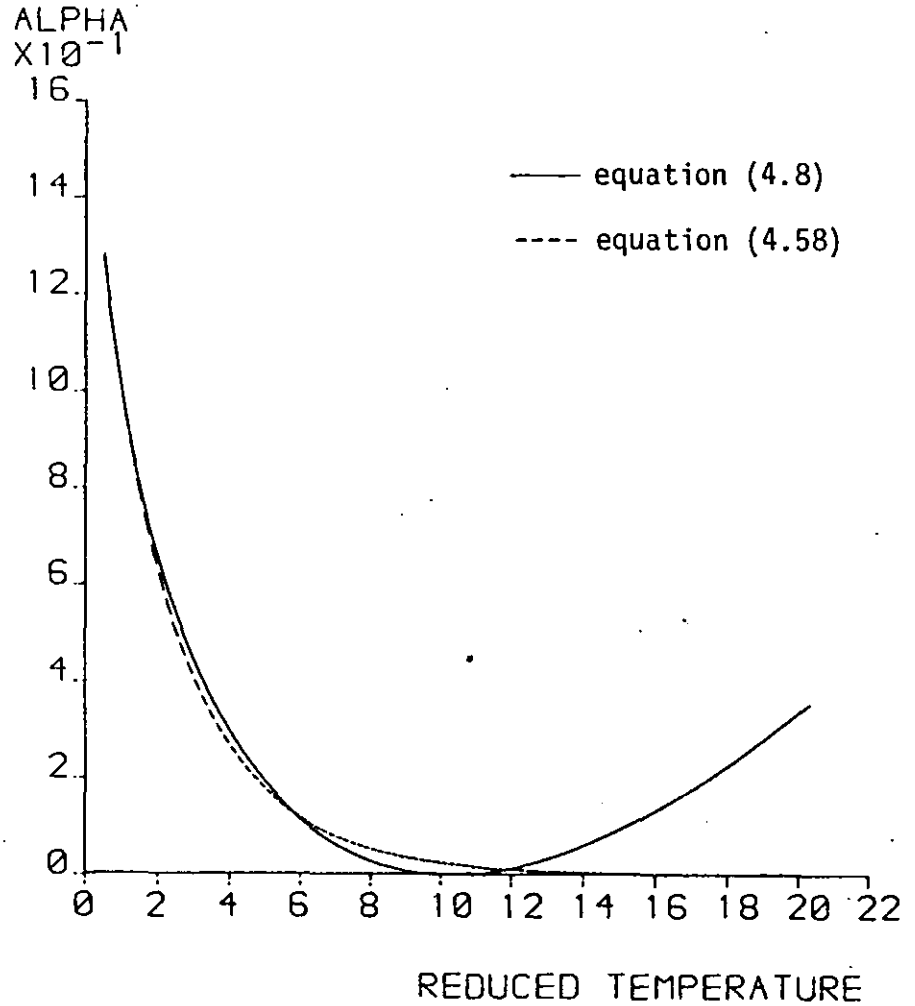


FIGURE 4.11 Comparison of the two temperature functions for methane

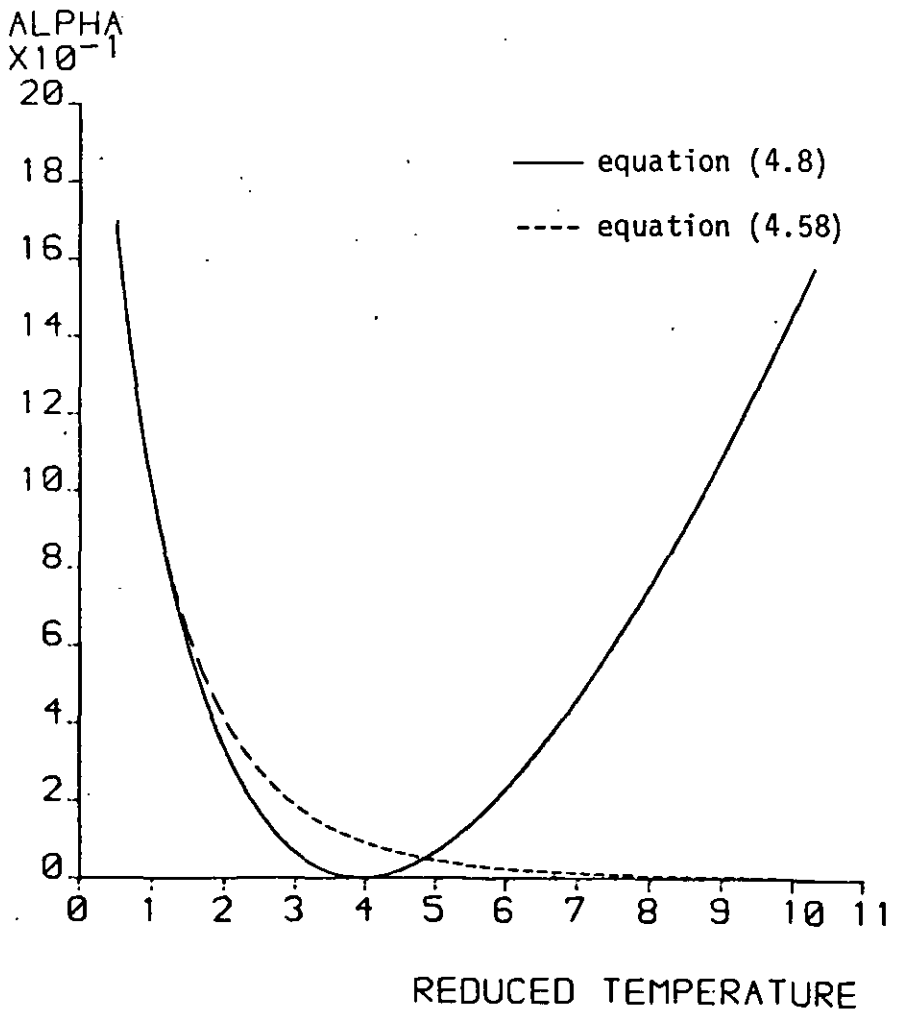


FIGURE 4.12 Comparison of the two temperature functions for n-Decane

TABLE 4.13

Comparison of the temperature functions.

Predictions of saturated liquid and vapour densities.

1. $\alpha[T] = [1 + F(1 - T_r^{\frac{1}{2}})]^2$

2. $\alpha[T] = e^{K(1-T_r^n)}$

Component	LIQUID		VAPOUR	
	1* AAD (%)	2 AAD (%)	1** AAD (%)	2 AAD (%)
Argon	4.27	4.15	0.36	0.40
Methane	4.59	4.45	0.88	0.94
Propane	5.58	5.52	0.86	0.87
n-Pentane	3.96	3.93	0.59	0.60
n-Heptane	4.44	4.35	0.67	0.69
n-Decane	0.62	0.56	-	-
n-Dodecane	0.70	0.63	-	-
n-Tetradecane	0.76	0.68	-	-
n-Octadecade	1.07	0.96	-	-
n-Eicosane	1.04	0.90	-	-
Carbon dioxide	4.48	4.48	0.71	0.71
Caron monoxide	3.81	3.76	3.93	3.92
Sulfur dioxide	4.46	4.43	1.04	1.02
Hydrogen sulfide	3.47	3.56	2.58	2.55
Water	3.99	4.10	1.26	1.32
Ammonia	3.21	3.40	4.48	4.60
Benzene	3.87	3.88	2.18	2.18
Methanol	0.51	0.54	-	-
Ethanol	0.51	0.51	-	-
Propanol	0.66	0.65	-	-
Butan-1-01	0.28	0.31	-	-
Pentan-1-01	0.53	0.29	-	-
Overall average (%)	2.58	2.55	1.63	1.65

* Taken from Table 4.2

** Taken from Table 4.3.

For temperature range, no. of data points and saturation data reference see Table 4.2 and Table 4.3.

TABLE 4.14

Comparison of the temperature functions.
Predictions of pure component densities

1. $\alpha[T] = [1 + F(1 - T_r^{\frac{1}{2}})]^2$

2. $\alpha[T] = e^{K(1 - T_r^n)}$

Component	1* AAD (%)	2 AAD (%)
Methane	3.77	4.11
Ethane	2.32	2.33
Propane	2.19	2.24
n-Butane	3.43	3.42
n-Pentane	3.45	3.47
n-Hexane	3.96	3.98
n-Heptane	2.12	2.13
n-Octane	2.19	2.20
n-Nonane	1.40	1.39
n-Decane	1.71	1.67
Sulfur dioxide	1.67	1.67
Benzene	1.06	1.05
Overall average (%)	2.44	2.47

* Taken from Table 4.6

For temperature range, pressure range, no. of data points and volumetric data references see Table 4.6.

are obtained. This is mainly due to the fact that the temperature range of all the experimental data used is well below $T_{r,m}$. Comparisons of the two functions are made here to show that there is no definite improvement in the prediction of thermodynamic properties in regions of interest when the exponential function is used. In vapour-liquid equilibrium predictions we are concerned with low reduced temperatures (except for mixtures containing hydrogen) and therefore the use of the exponential function is unlikely to lead to an improvement in accuracy.

When constants K and n are correlated with the acentric factors using minimax polynomial fitting, the following equations are obtained:

$$K = 0.594707 + 1.16337\ \omega \tag{4.59}$$

$$n = 0.823795 + 0.117995\,\omega \tag{4.60}$$

The straight lines given by equations (4.59) and (4.60) are shown in Figures 4.13 and 4.14 where the values of K and n from Appendix A are plotted. As can be seen, the straight line approximation is acceptable for K but not for n. In fact no reliable correlation could be found between n and the acentric factor. This means that equation (4.58) cannot be generalized as easily as equation (4.8). The constant F in equation (4.8) has been correlated with the acentric factor in Figure 4.10 and the correlation is given by equation (4.39). As can be seen in Figure 4.10, there is an excellent correlation between F and ω .

In general, the exponential function is useful for reduced temperatures greater than, $T_{r,m}$, but in practice such temperatures are usually not encountered in vapour-liquid equilibrium calculations.

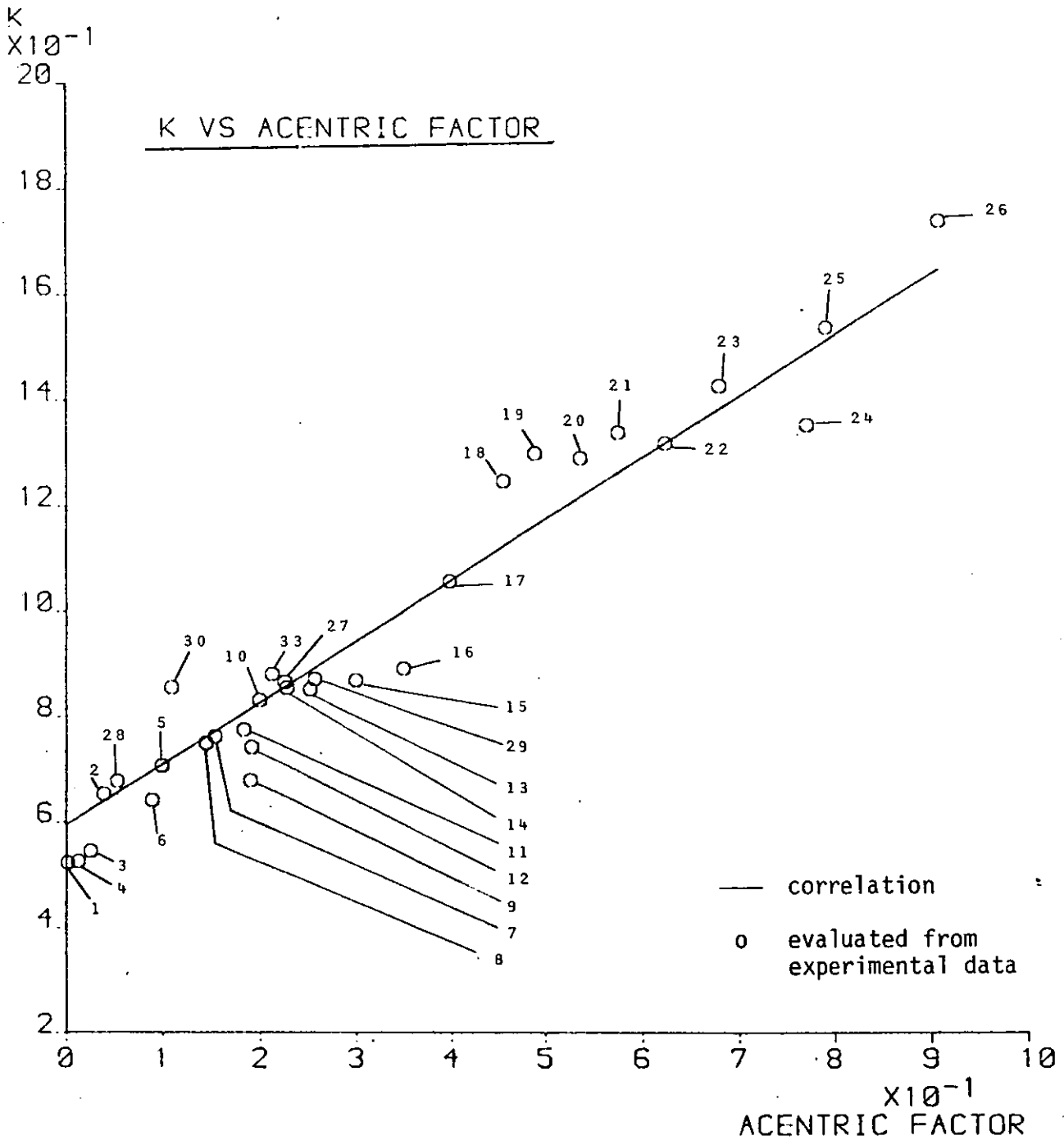


FIGURE 4.13 Relationship between K (used in the exponential temperature function) and acentric factors (ω). For component identification see Appendix A.

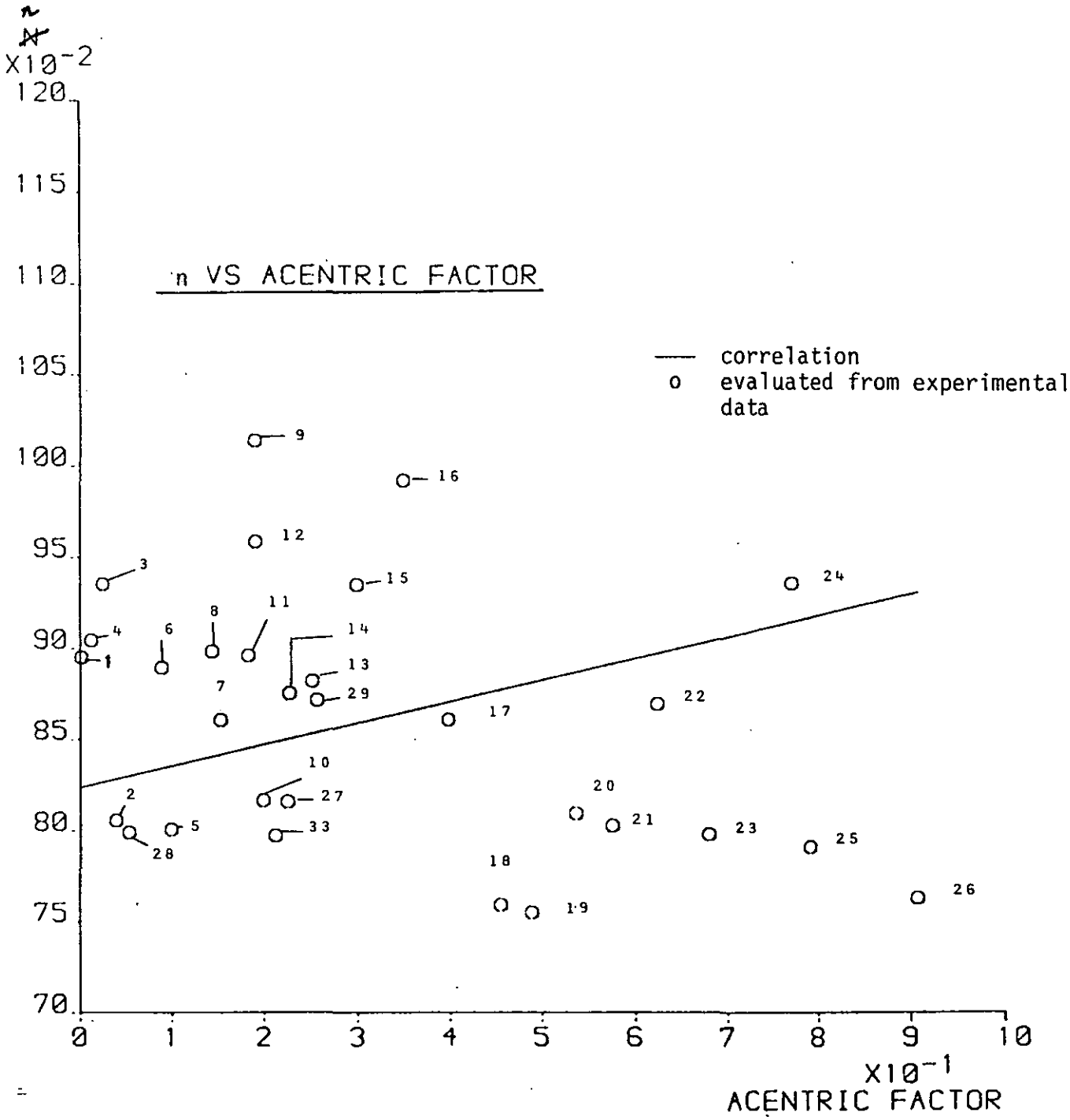


FIGURE 4.14 Relationship between n (used in the exponential temperature function) and acentric factors (ω). For component identification see Appendix A.

In most cases when the reduced temperature exceeds $T_{r,m}$, it is easier to use an equation of state such as the R-K equation (this equation is valid at high temperatures) than to use the exponential temperature function with equation (4.1). In view of this and the shortcomings outlined above, the use of the exponential temperature function for α was not pursued further in this study.

CHAPTER 5

PHASE EQUILIBRIUM IN MIXTURES

A phase is any part of the system or quantity of matter, that is homogeneous in composition, temperature and pressure. The term 'phase equilibrium' implies a condition of equilibrium between two or more phases. When two phases are in contact with each other, an exchange of the constituents between the phases will occur until a constant value of the composition in each phase has been attained. At this stage, there will then be no tendency towards change of the physical properties and composition with time. The system is then considered to be in equilibrium.

Although the equipment in a plant or laboratory rarely operates at a state of equilibrium between the phases, a knowledge of the relationship between the phases at equilibrium is essential to the understanding of the process. The thermodynamics of phase equilibrium is of fundamental importance in chemical engineering, since so many unit operations rely on phase contacting e.g. distillation, absorption, leaching etc. In particular, vapour-liquid equilibrium (VLE) operations are extensively used in the chemical industries. The most prominent of VLE operations is undoubtedly the classic distillation process, which relies on favourable distribution between vapour and liquid phases. Other operations of importance involving vapour-liquid equilibrium are gas absorption, azeotropic distillation, flashing of liquid mixtures, to quote a few. In addition, many chemical reactions are carried out with a gas or vapour in intimate contact with a liquid phase. Even the simple operations of compression and expansion of gases and liquids frequently involve vapour-liquid equilibrium.

5.1 Thermodynamic Considerations

In 1875, Gibbs proposed that for different phases to co-exist in equilibrium the following conditions must hold:

$$\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} \quad \text{for chemical equilibrium} \qquad (5.1)$$

$$P^{\alpha} = P^{\beta} = P^{\gamma} \quad \text{for mechanical equilibrium} \qquad (5.2)$$

$$T^{\alpha} = T^{\beta} = T^{\gamma} \quad \text{for thermal equilibrium} \qquad (5.3)$$

where μ_i^{α} is the chemical potential of component i in phase α, P^{α} is the pressure in phase α, T^{α} is the temperature in phase α and α, β, γ are different phases.

The chemical potential μ_i is defined in terms of the partial quantities as

$$\mu_i = \overline{G}_i = \overline{H}_i = \overline{A}_i = \overline{U}_i \qquad (5.4)$$

or

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j} \qquad (5.5)$$

where: G = Gibbs free energy
H = Enthalpy
A = Helmholtz free energy
U = Internal energy
S = Entropy
n_i = no. of moles of component i in a mixture.

The evaluation of the chemical potential is the central problem

in phase equilibrium thermodynamics. However, the chemical potential cannot easily be computed and must first be transformed into another quantity which is easier to evaluate using readily available data.

In terms of the chemical potential, the differential equations for the four thermodynamic potentials U, H, A and G become:

$$dU = T\,dS - P\,dV + \sum_i \mu_i\,dn_i \tag{5.6}$$

$$dH = T\,dS + V\,dP + \sum_i \mu_i\,dn_i \tag{5.7}$$

$$dA = -S\,dT - P\,dV + \sum_i \mu_i\,dn_i \tag{5.8}$$

$$dG = -S\,dT + V\,dP + \sum_i \mu_i\,dn_i \tag{5.9}$$

Any of these equations can be used to obtain the Gibbs-Duhem equation (Edmister, 1961):

$$V\,dp - S\,dT = \sum n_i\,d\mu_i \tag{5.10}$$

For a pure component i we can write,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = V_i \tag{5.11}$$

For an ideal gas V_i is given by

$$V_i = \frac{RT}{P} \tag{5.12}$$

and we obtain,

$$\mu_i - \mu_i^o = RT \ln \frac{P}{P^o} \tag{5.13}$$

where superscript 'o' denotes a standard state.

The above equation can only apply to an ideal gas. This observation led Lewis (1923) to define a pressure-related function known as the fugacity. Thus, for any real substance, whether pure or mixed, whether solid, liquid or gas, we have:

$$\mu_i - \mu_i^o = RT \ln \frac{f_i}{f_i^o} \tag{5.14}$$

Furthermore, it can be observed that at very low pressures and high temperatures, when all substances tend to behave like ideal gases

$$f_i = P \quad \text{for pure substances} \tag{5.15}$$

or

$$f_i = y_i P \quad \text{for component i in a mixture} \tag{5.16}$$

where $y_i P$ is the partial pressure in a mixture. The above definitions are all at constant temperature and it is therefore essential that all standard states, denoted by superscript 'o' be defined at the same temperature.

This possibility of expressing the chemical potential in terms of the more physically definable fugacity, allows us to calculate the conditions that must be satisfied in order that equilibrium be maintained. If the standard states are carefully

defined to be the same at any particular temperature, then it can be shown (Dodge, 1944; Prausnitz et al, 1967) that for different phases, α, β and γ we can write

$$f_i^{\alpha} = f_i^{\beta} = f_i^{\gamma} \text{ at equilibrium} \tag{5.17}$$

Equation (5.17) forms the basis for the calculation of phase equilibria in pure fluids and mixtures.

It may be shown (Edmister, 1961) that the fugacity of a pure component is given by:

$$RT \ln \frac{f}{P} = \int_0^P \left(V - \frac{RT}{P}\right) dP \tag{5.18}$$

Equation (5.18) is in a form convenient for use with a volume explicit equation of state. However, many useful equations are pressure explicit. For such equations of state, the following expression for the fugacity of a pure component can be easily derived from equation (5.18).

$$\ln \frac{f}{P} = Z - 1 - \ln Z - \int_{\infty}^{V} \left(\frac{P}{RT} - \frac{1}{V}\right) dV \tag{5.19}$$

where: $$Z = \frac{PV}{RT} \tag{5.20}$$

It may also be shown that the fugacity of component i in a multicomponent mixture is given by the following expression (Prausnitz, 1959)

$$RT \ln \left(\frac{f_i}{y_i P}\right) = \int_0^P \left(\overline{V}_i - \frac{RT}{P}\right) dP \qquad (5.21)$$

where: y_i = mole fraction of component i in a liquid or vapour phase.

$\overline{V}_i$ = is the partial molar volume

$$= \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} \qquad (5.22)$$

Equation (5.21) is not suitable for use with a pressure explicit equation of state. A more suitable fugacity expression for such equations can be derived from equation (5.8) and is given by (Beattie, 1949):

$$RT \ln \frac{f_i}{y_i P} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,\underline{V},n_j} - \frac{RT}{\underline{V}}\right] d\underline{V} - RT \ln Z \qquad (5.23)$$

where: $\underline{V}$ is the total volume = nV

and V is molar volume.

Using equation (5.23) with an equation of state capable of representing both liquid and vapour phase behaviour, it is possible to calculate fugacity in liquid and vapour phases and thereby carry out VLE calculations. However, equations of state are rarely valid for the liquid phase of mixtures containing one or more strongly polar or hydrogen-bonding components. In this case, activity coefficients are used to evaluate liquid phase fugacity (Wilson, 1964) and the vapour phase fugacity is calculated from the equation of state (Prausnitz and Chueh, 1968;

Prausnitz et al, 1967). When activity coefficients are used, the liquid phase fugacity is calculated from:

$$f_i^L = \gamma_i X_i f_i^o \tag{5.24}$$

where: X_i = liquid phase mole fraction of component i.

f_i^o = standard state fugacity.

γ_i = activity coefficient of component i.

An activity coefficient has no significance unless there is a clear definition of the standard state to which it refers. The standard state is commonly taken as the pure liquid at the system temperature and pressure.

A common problem in multicomponent phase equilibrium calculations is that the system temperature is often such that one or more components do not exist as liquids. It is possible to introduce the concept of a pure, hypothetical supercritical liquid and to evaluate its fugacity by extrapolation provided the component in question is not excessively above its critical temperature. However, for a highly supercritical component (e.g. H_2, N_2, CH_4, etc. at room temperature) the concept of a hypothetical liquid is of little use since the extrapolation of pure liquid fugacity is so excessive as to lose all its physical significance.

The only satisfactory procedure for the evaluation of the activity coefficients of supercritical components is the use of Henry's constant as the standard state fugacity (Prausnitz, 1977; Prausnitz et al, 1967; O'Connell, 1977). Henry's constant H_i, for component i in a pure (reference) solvent r which is a constituent of the solvent mixture is defined by:

$$H_i \text{ (in pure r)} \equiv \lim_{\substack{x_i \to 0 \\ x_r \to 1}} \frac{f_i^L}{x_i} \tag{5.25}$$

Henry's constants are not hypothetical but are experimentally accessible. Moreover, they can, in principle, be calculated from an equation of state (Prausnitz, 1977). However, the use of Henry's constants is only convenient for dilute solutions and for binary mixtures. At high concentration unsymmetrically normalized activity coefficients are needed and because they depend on both the solute and the solvent, difficulties are encountered when several solvents are present as in the case of multicomponent systems.

The only simple approach for mixtures containing highly supercritical components is the one using an equation of state for all fluid phases. In this approach the problem of specifying a standard state is avoided and information on pure components and their binary mixtures is sufficient to calculate equilibria in multicomponent mixtures (Peng and Robinson, 1976; Soave, 1972).

CHAPTER 6

CALCULATION OF MIXTURE PROPERTIES

In the process industries, the problem of calculating mixture properties occurs more often than the calculation of pure component properties. In particular, phase equilibria at high pressures are of great interest to chemical engineers involved with petroleum, cryogenic and related industries. Mixture densities are often required in the design of equipment involving mass transfer while enthalpies and heat capacities are required for the design of equipment involving heat transfer.

The development of an equation of state that can accurately represent phase equilibria has been one of the success stories of physical chemistry and chemical engineering in the past two decades. At present, two methods are widely used for the calculation of vapour-liquid equilibria. Both methods start from the equilibrium criterion of the equality of fugacities. In one method, however, an equation of state is used to calculate the fugacities in both phases. In the other method, an equation of state is used only for calculating the vapour phase fugacity and activity coefficients are used for calculating condensed phase fugacities. One of the main advantages of using an equation of state for all fluid phases is that the same standard states are also used for all phases and the method is self-consistent. If separate standard states are defined for different phases, then problems may arise with multicomponent mixtures where at least one component is super-critical and, therefore, non existent as liquid at a given pressure and temperature. In that event, the choice of a properly defined activity coefficient and standard state introduces formal difficulties which are often mathematically inconvenient and for practical implementation, require parameters from experimental data that are rarely available. Since the method using activity coefficients relies on separate equations to represent liquid and gas phases, it cannot guarantee consistency for all properties and may not predict phase equilibrium

under certain conditions at all. Moreover, this method only describes vapour-liquid equilibria and other equations are needed for other thermodynamic properties.

From a strictly thermodynamic point of view, using an equation of state is more efficient than using activity coefficients. If an equation of state is applicable to all phases of interest, we can calculate not only the fugacities but also all other configurational properties such as the enthalpy, entropy and volume change on mixing. However, the method relying on the equation of state has hitherto been limited to mixtures containing simple non-polar and weakly polar components only. To calculate vapour-liquid equilibria for mixtures containing one or more strongly polar or hydrogen bonding components, we have had to resort to the use of activity coefficients and standard state fugacities in the past.

In the present work, the new equation of state given by equation (4.1) was used to calculate densities and vapour-liquid equilibria of mixtures containing light and heavy hydrocarbons as well as non-polar, weakly polar and some polar components. The Peng and Robinson (1976) and the Soave (1972) equations were used for comparison purposes. In Chapter 4, it has already been shown that the new equation of state gives better representation of pure component saturated liquid densities than the Peng and Robinson (P-R) equation, specially for heavy hydrocarbons and polar substances. This feature of the new equation is likely to improve the prediction of saturated liquid densities of mixtures containing heavy hydrocarbons and polar substances.

6.1 Extension of the New Equation of State to Mixtures

By replacing a, b and c in equation (4.1) with a_m, b_m and c_m respectively, the new equation of state for mixtures is written in the following form:

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V(V + b_m) + c_m (V - b_m)} \tag{6.1}$$

where a_m, b_m and c_m are mixture constants.

In order to apply equation (6.1) to the calculation of mixture properties, it is necessary to devise a mixture model so that a_m, b_m and c_m for the mixture of interest can be calculated from the knowledge of constants a_i, b_i and c_i for the pure components and the mole fractions. The following mixture model is proposed:

$$a_m = \sum_i \sum_j X_i X_j a_{ij} \tag{6.2}$$

$$b_m = \sum_i X_i b_i \tag{6.3}$$

$$c_m = \sum_i X_i c_i \tag{6.4}$$

The choice of this model is completely arbitrary, the only justification being the success with which analogous equations have been applied to other cubic equations of state such as the P-R and the S-R-K equations. It is also possible to reduce equation (6.1) to the P-R equation and the S-R-K equation by setting $c_m = b_m$ and $c_m = 0$ respectively as in the case of pure components. This is not possible if a different mixture model is used. By using equations (6.2) - (6.4), the method of comparison becomes consistent and the amount of computing involved is reduced considerably. A computer program written for equation (6.1) can also be used for the P-R equation and the S-R-K equation. Appropriate values for the constants used to describe the temperature dependence of a_i have to be specified in each case.

To use equation (6.2), the cross-term a_{ij} needs to be evaluated and this is done by the following mixing rule.

$$a_{ij} = \xi_{ij} \, (a_{ii} \, a_{jj})^{\frac{1}{2}} \tag{6.5}$$

where ξ_{ij} is a correction factor for the geometric mean rule assumption. ξ_{ij} is known as the binary interaction coefficient. Although empirical in practice, the interaction coefficient ξ_{ij} is a measure of deviations from ideal solution behaviour for interactions between i^{th} and j^{th} components (Prausnitz and Chueh, 1968; Bishnoi and Robinson, 1972). Thus ξ_{ij} is 1.0 when i equals j (pure fluid interaction) and ξ_{ij} is nearly 1.0 for component pairs which form nearly ideal solutions (for example paraffin hydrocarbon pairs heavier than propane). The numerical values of ξ_{ij} differs considerably from 1.0 when the component pair forms highly non-ideal solutions. Thus, accurate values of ξ_{ij} are required when i or j is a light hydrocarbon or a non-hydrocarbon (for example methane with hydrocarbons heavier than n-butane, CO_2-hydrocarbon, H_2S-hydrocarbon and N_2-hydrocarbon mixtures).

Compared with vapour-liquid equilibrium (VLE) predictions, the sensitivity of predicted bulk mixture properties such as density and enthalpy to the value of ξ_{ij} is small (Han and Starling, 1973). Therefore it is a common practice to use binary vapour-liquid equilibrium data for the determination of ξ_{ij} values.

In this study, the values of ξ_{ij} have been determined from isothermal VLE data. Equation (6.1), the P-R equation and the S-R-K equation are used. The binaries considered are mainly those of importance to the synthetic fuel industry.

6.2 Evaluation of the Binary Interaction Coefficient

A number of criteria may be chosen for selecting the optimum value of the binary interaction coefficient. Two useful criteria using VLE data are (Graboski and Daubert, 1978):

1. Minimizing the deviation in the bubble point pressure.
2. Minimizing the deviation in the flash volume.

The first criterion uses the experimental values of liquid phase compositions, total pressure and temperature to determine ξ_{ij}. Since all these quantities can be accurately determined by experiment, this criterion has an advantage over the second criterion. Because the bubble point pressure is sensitive to the most volatile component, the first criterion will most accurately correlate that equilibrium ratio. The second criterion utilizes the experimental liquid and vapour phase compositions for an isothermal flash calculation to optimize the material balance as predicted by the correlation. The material balance (called flash) criterion is very sensitive to K values which are close to unity.

Graboski and Daubert (1978) have used both criteria with the S-R-K equation and found that no difficulty in convergence is encountered with the bubble point procedure making it useful for the determination of the binary interaction coefficient. However, some problems were encountered with the flash procedure because, for close boiling mixtures, the correct value of the interaction coefficient was needed in advance to "find" the two phase region. Their results indicate that the minimization of bubble point pressures is the better criterion for obtaining the interaction coefficient because it will produce good results for both the flash and bubble point calculations.

In this study, the optimum value of the binary interaction coefficient was obtained by minimizing the absolute average deviation in the bubble point pressures at a selected temperature.

The absolute average deviation is defined as:

$$P\ (\%) = \frac{1}{n} \sum_{i}^{n} \left| \frac{P_{exp} - P_{calc}}{P_{exp}} \right| \times 100 \qquad (6.6)$$

Generally, ξ_{ij} is assumed to be independent of temperature, pressure, density and compositions. (Plöcker, Knapp and Prausnitz, 1978; Grabosky and Daubert, 1978; Chueh and Prausnitz, 1967). However, in practice this is not always true. Therefore, ξ_{ij} values should be determined at temperatures and pressures where they will find the most usage. No attempt was made in this work to correlate ξ_{ij} with temperature or pressure but the temperature at which the optimum value of ξ_{ij} is evaluated, was selected carefully to lie in the middle range of the reported experimental data. Optimum values of ξ_{ij} have been evaluated using three different equations. The Peng and Robinson equation (1976) and the Soave equation (1972) were used for evaluating optimum values of ξ_{ij} of 32 binaries containing a light hydrocarbon as one of the components with the other component being either a light hydrocarbon, carbon dioxide, or hydrogen sulfide. Equation (6.1) was used to evaluate optimum ξ_{ij} for 52 binaries including those used with the P-R and the S-R-K equations. Some binaries containing heavy hydrocarbons, nitrogen, water and alcohols were also included.

Where all three equations had been used for a particular binary at a given temperature, the same set and number of experimental data were used. Data points were selected to cover the maximum available composition range, including the critical region where possible.

The precision to which the optimum value of ξ_{ij} had been evaluated was restricted to three decimal places for two reasons. Firstly, since a reliable convergence criterion is not available, the procedure adopted for evaluating the optimum value of ξ_{ij} is

a trial and error method taking a long time to reach the final solution. Secondly, there is no justification in increasing the precision because in all cases considered, it was found that the difference in the absolute average deviations of the bubble point pressures between neighbouring values of ξ_{ij} is small.

The following trial and error method was used. Initially, the value of ξ_{ij} is set at 1.0 and then decreased in large intervals of 0.1 or 0.01 depending on the magnitude of the absolute average deviation of the bubble point pressures. If the predicted values of the bubble point pressures were found to be consistently greater than the experimental values for all compositions then the value of ξ_{ij} was increased in large intervals. Once the region of the optimum ξ_{ij} had been detected and bracketed, the interval was decreased to 0.001 and the optimum value of ξ_{ij} corresponding to the minimum deviation in the bubble point pressures was evaluated.

The optimum values of ξ_{ij} obtained from the three equations of state are given in Table 6.1. Corresponding values of the absolute average deviations in bubble point pressures and vapour phase mole fractions are given in Table 6.3. The results obtained from equation (6.1) for systems containing heavy hydrocarbons, nitrogen, water and alcohols are given in Table 6.2. This table also contains results of some binaries with light hydrocarbons.

As can be seen from Table 6.1, the optimum values of ξ_{ij} obtained from the three equations are close to each other except for binaries containing methane. The anomolous behaviour of methane is well known since it tends to form highly non-ideal solutions with hydrocarbons heavier than propane. In general the Soave and the Peng and Robinson equations give very similar values of ξ_{ij}. The optimum values of ξ_{ij} obtained in this study can be summarised as follows for the different groups of binaries considered.

a) Hydrocarbon-Hydrocarbon (up to n-decane)

Except for binaries containing methane and the binary system ethylene-n-butane, the binary interaction coefficient ξ_{ij} for all other hydrocarbon-hydrocarbon mixtures was found to be very close to unity. This is true for all three equations used in this study and is in accordance with Soave's conclusion that no binary interaction coefficients are needed for VLE predictions in hydrocarbon-hydrocarbon systems. For binaries containing methane, equation (6.1) gives ξ_{ij} values which are close to unity but ξ_{ij} values obtained from the P-R and the S-R-K equations are significantly different from unity. The value of ξ_{ij} for ethylene-n-butane appears to be inconsistent with other ethylene-hydrocarbon binaries and is probably due to the inconsistency of the experimental data. There is no consistent trend in the values of ξ_{ij} obtained but in general the ξ_{ij} values from equation (6.1) are closer to unity than those obtained from the other two equations.

b) Hydrocarbon (light) - Hydrocarbon (heavier than n-nonane)

These systems include binaries such as methane-n-eicosane, ethane-n-dodecane, ethane-n-eicosane etc. For these binaries only equation (6.1) has been used and the optimum values of ξ_{ij} obtained are given in Table 6.2. Most of the ξ_{ij} optimum values are in the range 1.0 - 1.08.

c) Carbon dioxide - Hydrocarbon (up to n-decane)

The optimum values of ξ_{ij} obtained from the three equations are slightly different from each other and are usually in the range 0.90 ÷ 0.84. These values are given in Tables 6.1 and 6.2.

d) Hydrogen sulfide - Hydrocarbon

Slightly different values of ξ_{ij} optimum are obtained from the three equations. The optimum values of ξ_{ij} are given in

Table 6.1 and Table 6.2 and they are found to be in the range 0.91 - 1.0.

e) Nitrogen - Hydrocarbon (up to n-heptane)

Only equation (6.1) has been used to evaluate ξ_{ij} optimum for these binaries. The optimum values obtained are given in Table 6.2. Most of the values are found to be in the range 0.97 - 0.91.

f) Alcohol - Water

Only equation (6.1) has been used to evaluate optimum value of ξ_{ij} for these binaries. Only two binaries have been considered. They are methanol-water and ethanol-water. For methanol-water the optimum ξ_{ij} was found to be 1.083 and for ethanol-water ξ_{ij} optimum was found to be 1.075. For other alcohol-water binaries similar values of ξ_{ij} optimum can be expected.

In Table 6.4, the optimum values of ξ_{ij} obtained in this study from the Soave equation are compared with those obtained by Graboski and Daubert (1978) using the same equation and the same criterion for optimizing the binary interaction coefficients. The slight disagreement in results is mainly due to the temperature dependence of ξ_{ij}. In this study, isothermal VLE data were used to evaluate ξ_{ij}, whereas Graboski and Daubert used VLE data at different temperatures. Nevertheless, in many cases the optimum values of ξ_{ij} are in good agreement and therefore the procedure used in this study for evaluating the binary interaction coefficient is valid.

Further discussion on the optimum values of ξ_{ij} will be presented later when the predictions of bubble point pressures are discussed.

6.3 Vapour-Liquid Equilibrium (VLE) Calculations

There are three basic categories of VLE calculations which are extensively used in design:

1. Estimation of equilibrium temperature, T and vapour or liquid phase compositions, y or x, at constant pressure (bubble point or dew point temperature calculations).

2. The prediction of the system pressure, P, and vapour or liquid compositions, y or x under isothermal conditions (bubble and dew point pressure calculations).

3. The evaluation of the phase compositions, x, y or K-values at a given temperature and pressure (flash calculations).

Other, more complex, VLE calculations exist but they can generally be broken into a combination of the three basic types indicated above. In this study computer programs have been devised for the three types of calculation. In cases 1 and 2 above, only the bubble point calculations are considered. Algorithms necessary for these calculations are presented in Appendix G.

6.3.1 Calculation of the Bubble Point Pressure

A computer program for the prediction of bubble point pressure is given in Appendix H. Results obtained for 52 binaries containing hydrocarbons, carbon dioxide, hydrogen sulfide, nitrogen, carbon monoxide, alcohols and water have been summarized in Tables 6.2 and 6.3. The absolute average deviations in bubble point pressures and vapour phase mole fractions have been obtained using the optimum values of the binary interaction coefficients evaluated in this study. Results have also been obtained without the use of the binary interaction coefficients ($\xi_{ij} = 1.0$).

As can be seen, excellent predictions have been obtained by using the optimum values of the binary interaction coefficients. This is expected since the minimization of the bubble point pressure deviations has been used as the criterion for optimizing the interaction coefficients. Equation (6.1) has been used for all 52 binaries and the P-R and the S-R-K equations have been used for 32 binaries. Results obtained from the three equations are very similar. To date, the P-R and the S-R-K equations have not been used for the binaries containing heavy hydrocarbons.

Results are also presented in the form of phase diagrams which include plots of pressure (P) versus mole fractions (x,y) and the mole fractions in the vapour phase (y) versus the mole fractions in the liquid phase (x). These are given in Figures 6.1 to 6.113. The dotted lines represent results obtained without using the binary interaction coefficient and the solid lines represent results obtained using the optimum value of ξ_{ij} from Tables 6.1 or 6.2. The 52 binaries considered in this work can be conveniently grouped under the following headings:

a) Hydrocarbon - Hydrocarbon

Results for these binaries are given in Tables 6.2 and 6.3, and the phase diagrams are shown in Figures 6.1 to 6.56. With the exception of binaries containing methane, there is very little improvement in the accuracy of predictions through the use of the optimum values of ξ_{ij} for light hydrocarbon binaries. This is clearly shown in the phase diagrams where the dotted line (ξ_{ij} = 1.0) is very close to the solid line ($\xi_{ij} = \xi_{ij\ opt}$) and in some cases the two lines coincide.. In such cases the optimum values of ξ_{ij} are very close to unity and there is little or no advantage offered by the optimum value of ξ_{ij}.

For binaries containing methane, the accuracy of predictions can be improved considerably through the use of the optimum value of ξ_{ij}. Large deviations are obtained with ξ_{ij} = 1.0.

This is clearly shown in the phase diagrams where the dotted lines are further from the experimental points than the solid line.

For binaries containing light hydrocarbon with a heavy hydrocarbon (above n-decane), the predictions made with $\xi_{ij} = 1.0$ can produce deviations of the order of 30 or 40 percent. In these cases, use of the optimum ξ_{ij} is necessary. In most cases considered, the optimum values of ξ_{ij} have been found to be greater than unity. This is in contrast to light component binaries where ξ_{ij} is always less than unity. Results for the binaries with heavy hydrocarbons are given in Table 6.2 and are shown in Figure 6.14, and Figures 6.28 to 6.30.

b) Carbon dioxide - Hydrocarbon

Results for these binaries are given in Tables 6.2 and 6.3. Deviations of the order of 20% were obtained with $\xi_{ij} = 1.0$. These deviations can be reduced to approximately 1% by the use of optimum values of ξ_{ij}. The optimum values are significantly different from unity and are usually below 0.9.

Results obtained with the three equations are almost identical and this can be clearly seen in the phase diagrams obtained (Figures 6.57 to 6.78).

c) Hydrogen sulfide - hydrocarbon

Results of these binaries are given in Tables 6.2 and 6.3. Deviations of the order of 15 to 20% were obtained with $\xi_{ij} = 1.0$. These deviations can be reduced to approximately 2% by using optimum values of ξ_{ij}. The optimum values of ξ_{ij} were found to be significantly different from unity.

The similarity in results obtained from the three equations can be seen from the phase diagrams (Figures 6.80 to 6.93).

d) Nitrogen - Hydrocarbon

Results are given in Table 6.2 and are shown in Figures 6.94 to 6.97. Deviations of the order of 10% were obtained with ξ_{ij} = 1.0. These deviations can be reduced to approximately 3% by the use of optimum values of ξ_{ij}.

e) Alcohol - Water

Results are given in Table 6.2 and are shown in Figures 6.98 and 6.99. As can be seen, deviations of the order of 25% were obtained with ξ_{ij} = 1.0. These deviations can be reduced to approximately 1% by using the optimum values of ξ_{ij}. The optimum values of ξ_{ij} were found to be greater than unity.

In all the binaries considered (Figures 6.1 to 6.113), improvement in the prediction of bubble point pressures with the use of the optimum value of ξ_{ij} also resulted in improvement in the prediction of the vapour phase mole fractions (y).

In Table 6.5, results are given for the methane-ethane-propane system. Acceptable predictions have been obtained with ξ_{ij} = 1.0. When the optimum values of ξ_{ij} were used, equation (6.1) gave predictions which were less accurate than those obtained with ξ_{ij} = 1.0. The Peng and Robinson equation gave better predictions with the optimum values of ξ_{ij}. The results are very similar and it is difficult to say which equation is superior. Results obtained for the methane-propane-decane system are shown in Table 6.6. No binary interaction coefficients were used (ξ_{ij} = 1.0). The results indicate the superiority of equation (6.1) at high pressures.

To test the applicability of the equation (6.1) and also of the computer program for the predictions of VLE in multicomponent systems, a system containing methane, ethane, propane,

n-pentane and n-hexane was chosen. Results obtained are given in Table 6.7. Three equations of state have been used. The S-R-K and the P-R equations give very similar predictions. Overall deviation in the bubble point pressure is of the order of 3.5% for all three equations.

6.3.2 Calculation of the Bubble Point Temperature

A computer program for the prediction of bubble point temperature is given in Appendix H. The carbon dioxide-n-pentane system was used to demonstrate the predictive capabilities of equation (6.1). The P-R equation was used for comparison purposes. Results are given in Table 6.8. As can be seen, both equations gave accurate predictions of the bubble point temperature if the optimum value of the binary interaction coefficient, ξ_{ij} was used. Optimum values of ξ_{ij} are given in Tables 6.1 and 6.2. In general, accurate predictions of the bubble point temperature can be obtained for any system provided the optimum values of the binary interaction coefficients are available.

6.3.3 Calculation of the Equilibrium Ratios (K values)

A computer program for the prediction of K values is given in Appendix H. Two binaries were used to show the predictive capabilities of equation (6.1). The P-R equation was used for comparison purposes. The results obtained for the n-butane-n-decane system are presented in Table 6.9. As can be seen, both equations gave accurate predictions of the K values. Predictions from the two equations are very similar although the optimum values of ξ_{ij} are different. Results for the carbon dioxide-n-decane system are given in Table 6.10. Equation (6.1) gave consistently better predictions compared with the P-R equation for the K values of carbon dioxide. For the K values of n-decane, both equations gave similar predictions. The optimum value of

ξ_{ij} for equation (6.1) was taken from Table 6.2. For the P-R equation the same value of ξ_{ij} was used and this is probably the cause of the poor predictions for the K values of carbon dioxide.

6.3.4 Effect of Temperature and Pressure on ξ_{ijopt}

Because of the nature of the systems considered, it is impossible to separate the effects of temperature and pressure. In other words, a high temperature data set is also a high pressure data set. Results obtained by Graboski and Daubert (1978) have clearly shown that for many systems the binary interaction coefficients are essentially independent of temperature and pressure. This is confirmed by the results obtained in this study. Results have been obtained at different temperatures using the optimum values of ξ_{ij} from Tables 6.1 and 6.2. The binaries considered are ethane-n-decane, ethane-n-dodecane, ethylene-n-dodecane, propane-benzene, carbon dioxide-n-decane, hydrogen sulfide-n-heptane, n-heptane-nitrogen, methanol-water and ethanol-water. These results are given in the form of phase diagrams in Figures 6.100 to 6.113. With the exception of ethane-n-decane (at 499.67^{o}R) and methanol-water (761.67^{o}R), excellent predictions of the bubble point pressure were obtained for all binaries. Even for the two binaries mentioned here the results are within the acceptable limits of accuracy.

6.4 Calculation of the Mixture Density

A computer program for the prediction of mixture density is given in Appendix H. Equation (6.1) has been used to calculate the mixture density using two different approaches. In one approach, equation (6.1) was transformed into a cubic in the compressibility Z, and was then solved at a given P, T and x

(mole fractions). In this case, the mixture parameters are evaluated using equations (6.2) to (6.5). In the second approach, the generalized corresponding states principle (GCSP) presented in Chapter 4 (Section 4.4) was used. The GCSP with two non-spherical reference fluids is given by equation (4.47). The procedure for calculating the compressibility of pure component is given in Chapter 4. The same procedure can be used for mixtures if the critical properties T_c, V_c, Z_c, P_c and ω of the pure component can be replaced by the pseudocritical properties T_{cm}, V_{cm}, Z_{cm}, P_{cm} and ω_m of a hypothetical equivalent substance. This is achieved via the van der Waals one fluid model given by equations (2.171), (2.172) and (2.175), together with equations (2.182) and (2.183). The following combining rule is used for T_{cij} V_{cij}

$$T_{cij} V_{cij} = \xi_{ij} \quad (T_{cii} V_{cii} T_{cjj} V_{cjj})^{\frac{1}{2}} \tag{6.7}$$

and P_{cm} is given by

$$P_{cm} = Z_{cm}.R.T_{cm}/V_{cm} \tag{6.8}$$

Two cases were considered. In one case, ethane was used as the reference fluid 1 and n -decane was used as reference fluid 2. In the second case, component 1 was used as reference fluid 1 and component 2 was used as reference fluid 2.

The equation of Chaudron et al (1973) was used for comparison purposes. This equation is simple, the individually fitted constants are available for a large number of substances and has been known to give accurate predictions of density for both pure components and mixtures (Chaudron et al, 1973; Teja et al

1978). The Chaudron equation was used with the mixture model given by equations (6.2), (6.3) and (6.5) and in the case of the GCSP with the van der Waals one fluid model.

The results are given in Table 6.11. Binary interaction coefficients were not used (ξ_{ij} = 1.0, η_{ij} = 1.0). Very similar predictions were obtained with the two equations used. A total of five binary systems were considered and the overall average deviation of the order of 2% was obtained using equation (6.1) compared with 1.74% using the Chaudron equation with individually fitted constants. When the two equations were used with the GCSP (ethane and n-decane as the reference fluids), the overall average deviation obtained was of the order of 3.51% with equation (6.1) as the reference equation compared to 3.04% with the Chaudron equation as the reference equation. If component 1 is used as reference 1 and component 2 as reference 2, then the overall average deviation obtained from equation (6.1) is decreased to 3%. In general predictions obtained with the Chaudron equation were slightly better than those obtained using equation (6.1). This is not surprising because the Chaudron equation contains six constants per substance evaluated from the P-V-T data covering a wide range of conditions. However, the results obtained using equation (6.1) are adequate for many design calculations. The loss of accuracy in the method using the GCSP is mainly due to the generalization.

6.5 Prediction of Saturated Liquid Volumes

The main advantage of using the new equation of state proposed in this work is that it gives accurate predictions of the saturated liquid volumes as well as other properties of the equilibrium phases. In Chapter 4, it has been shown that the new equation is superior to the Peng and Robinson and the Soave equations in the representation of saturated liquid densities of pure components. The improvement in the accuracy of predictions

is greater for heavy hydrocarbons and polar substances. For mixtures, the improvement in the predictions of saturated liquid volumes is likely to be a direct consequence of the improvement in the saturated liquid volumes of pure components. Results for the n-butane-n-decane system are shown in Figure 6.114. The dotted line represents the predictions of the Peng and Robinson equation and the solid line represents the predictions obtained from equation (6.1). As can be seen, the new equation is superior to the Peng and Robinson equation. Saturated liquid volumes were obtained by using the equilibrium criterion of the equality of fugacities for saturated phases.

From the results obtained in this chapter it can be said with confidence that equation (6.1) is capable of giving accurate and consistent predictions of the thermodynamic properties of mixtures. The most interesting feature of equation (6.1) is its applicability to mixtures containing heavy hydrocarbons and polar substances and the fact that it is cubic and thus easy to handle. It can reproduce with sufficient accuracy the liquid and vapour phase densities (except in the region around the critical point) and give very accurate VLE predictions. Comparisons have shown that equation (6.1) is as good as and in many cases better than the well known equations of Soave and Peng and Robinson.

The generalized form of equation (6.1) is not used in this chapter but similar predictions can be expected since excellent results have been obtained for pure components (Chapter 4) using the generalized correlations for F and Z_m given by equations (4.39) and (4.40).

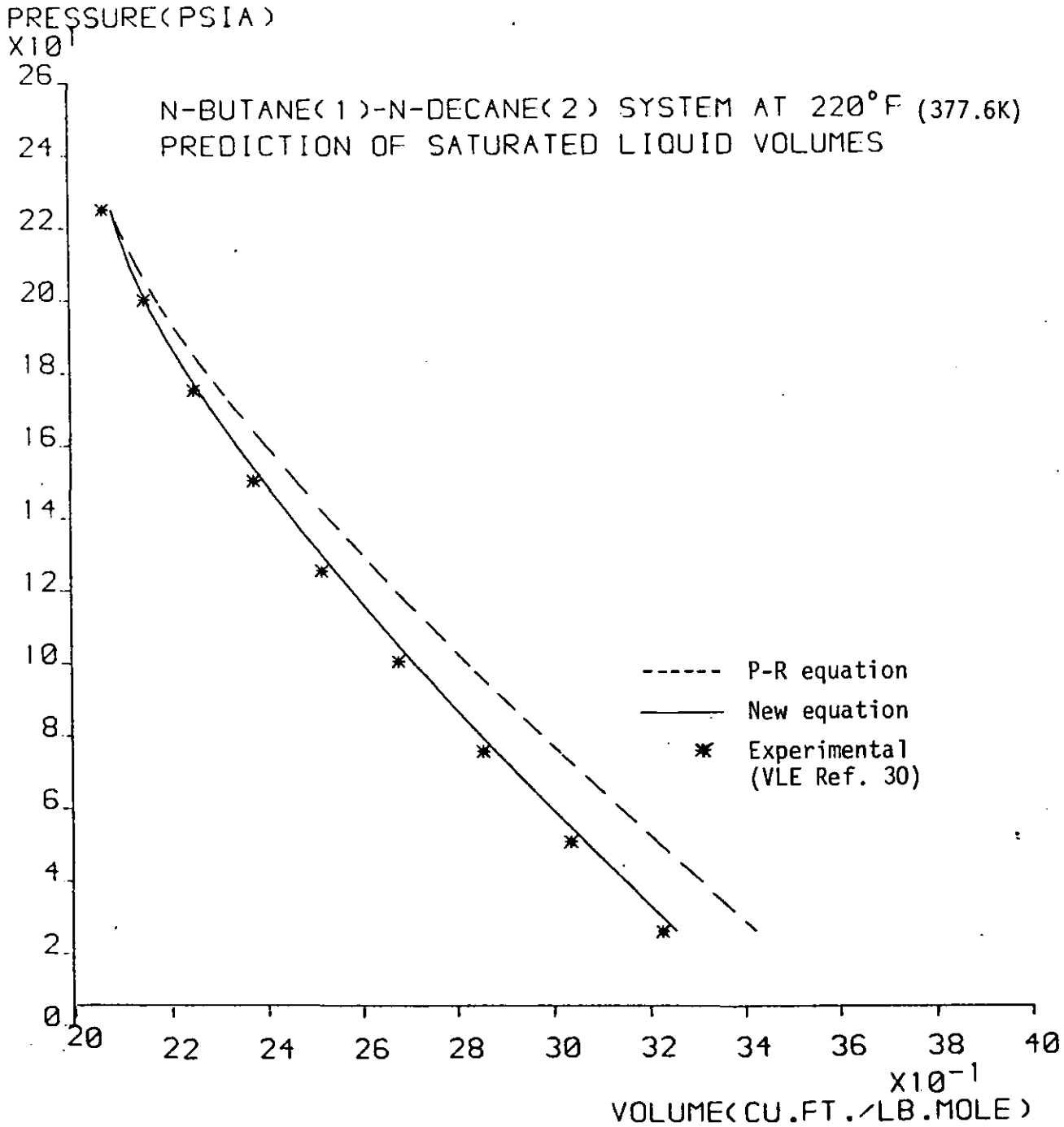


FIGURE 6.114 Comparison of predicted saturated liquid volumes for n-Butane-n-Decane system

TABLE 6.1

Optimum values of ξ_{ij} from three different equations of state

No.	System	No. of Points	Temperature		Optimum ξ_{ij}			VLE Ref.
			(^{o}R)	(K)	EQ.(6.1)	P-R	S-R-K	
1.	Methane-Ethane	6	450.02	250.0	0.995	0.989	0.991	1
2.	Methane-n-Butane	8	379.73	211.0	1.008	0.986	1.000	3
3.	Methane-i-Butane	7	559.69	311.0	0.986	0.976	0.977	4
4.	Methane-n-Pentane	9	491.69	273.2	0.980	0.959	0.964	5
5.	Methane-n-Hexane	9	671.69	373.2	0.990	0.954	0.952	6
6.	Ethane-Propane	7	499.61	277.6	0.996	0.994	0.998	9
7.	Ethane-Propylene	6	509.69	283.2	0.994	0.992	0.997	10
8.	Ethane-n-Butane	9	558.65	310.4	0.999	0.994	0.997	11
9.	Ethane-n-Pentane	10	559.73	311.0	1.001	0.994	0.998	13
10.	Ethane-n-Heptane	5	659.68	366.5	1.015	0.999	0.999	14
11.	Ethylene-Methane	9	270.02	150.0	0.974	0.971	0.973	18
12.	Ethylene-Ethane	9	459.67	255.4	0.992	0.990	0.994	19
13.	Ethylene-Propane	10	491.53	273.1	0.981	0.979	0.982	20
14.	Ethylene-n-Butane	7	579.61	322.0	0.938	0.932	0.930	21
15.	Propane-i-Butane	10	539.69	299.8	0.987	0.987	0.944	23
16.	Propane-n-Pentane	11	649.73	361.0	0.987	0.976	0.979	24
17.	Propane-i-Pentane	10	671.69	373.2	0.979	0.978	0.980	25
18.	Propylene-Propane	9	559.71	311.0	0.970	0.993	1.000	28

TABLE 6.1 (continued)

No.	System	No. of Points	Temperature		Optimum ξ_{ij}			VLE Ref.
			(^{o}R)	(K)	EQ.(6.1)	P-R	S-R-K	
19.	Propylene-1-Butene	7	529.67	294.3	1.002	0.998	1.000	29
20.	n-Butane-n-Decane	9	679.67	377.6	0.995	0.986	0.988	30
21.	1-Butene-n-Butane	9	739.69	411.0	1.003	1.000	1.000	31
22.	CO_2-Methane	8	434.63	241.5	0.907	0.902	0.899	32
23.	CO_2-Ethane	10	455.33	253.0	0.872	0.870	0.870	33
24.	CO_2-Ethylene	10	416.81	231.6	0.943	0.942	0.944	34
25.	CO_2-Propane	9	529.67	294.3	0.869	0.874	0.868	35
26.	CO_2-n-Butane	10	491.69	273.2	0.891	0.875	0.886	36
27.	CO_2-i-Butane	9	559.67	311.0	0.873	0.884	0.874	37
28.	CO_2-n-Pentane	9	679.69	377.6	0.865	0.866	0.849	38
29.	H_2S-Methane	8	499.61	277.6	0.920	0.927	0.931	41
30.	H_2S-Ethane	9	509.69	283.2	0.911	0.910	0.909	42
31.	H_2S-i-Butane	8	619.89	344.4	0.954	0.952	0.950	43
32.	H_2S-n-Heptane	9	559.69	311.0	0.947	0.936	0.928	44

TABLE 6.2

Values of the deviations in bubble point pressures and vapour phase mole fractions with $\xi_{ij} = 1.0$ and $\xi_{ij} = \xi_{ijopt}$ from equation 6.1.

No.	System	No of Points	Temp		$\xi_{ij} = 1.0$		ξ_{ijopt}	$\xi_{ij} = \xi_{ijopt}$		VLE REF
			^oR	K	ΔP (%)	ΔY_1		ΔP (%)	ΔY_1	
1.	Methane-propane	5	499.67	277.6	2.65	0.0059	0.989	0.68	0.0048	2
2.	Methane-benzene	7	609.75	338.8	2.45	0.0064	0.991	0.92	0.0054	8
3.	Methane-n-Eicosane	5	563.67	313.2	29.26	0.0000	1.080	1.09	0.0000	7
4.	Ethane-i-butane	8	560.27	311.8	3.57	0.0072	1.018	1.62	0.0038	12
5.	Ethane-n-decane	8	679.67	377.6	4.81	0.0455	1.019	0.60	0.0426	15
6.	Ethane-n-dodecane	9	581.67	323.2	5.58	0.0009	1.016	2.26	0.0008	16
7.	Ethane-n-Eicosane	7	599.67	333.2	41.01	0.0002	1.070	9.15	0.0000	17
8.	Ethylene-n-dodecane	8	536.67	298.2	2.92	0.0002	1.006	1.10	0.0000	22
9.	Propane-benzene	10	679.67	377.6	3.58	0.0101	0.988	1.86	0.0086	27
10.	Propane-n-decane	7	679.67	377.6	8.63	0.0008	1.024	0.79	0.0004	26
11.	Nitrogen-methane	10	279.65	155.4	4.22	0.0299	0.968	0.71	0.0217	46
12.	Nitrogen-propane	6	536.67	298.2	11.00	0.0269	0.926	3.80	0.0161	47
13.	Nitrogen-n-butane	6	559.71	311.0	10.83	0.0146	0.969	8.73	0.0151	48
14.	Nitrogen-n-heptane	5	634.67	352.6	17.14	0.0032	0.911	3.30	0.0018	49
15.	H_2S-n-heptane	5	634.67	352.6	10.97	0.0027	0.956	3.41	0.0018	44
16.	H_2S-n-decane	7	619.67	344.3	0.62	0.0004	0.999	0.53	0.0004	45

TABLE 6.2 (continued)

No.	System	No. of Points	Temp.		$\xi_{ij} = 1.0$		ξ_{ij} opt	$\xi_{ij} = \xi_{ijopt}$		VLE REF
			^oR	K	ΔP (%)	ΔY_1		ΔP (%)	ΔY_1	
17.	CO_2-n-decane	7	619.67	344.3	24.74	0.0003	0.903	2.24	0.0020	39
18.	CO-propane	8	491.67	273.2	7.11	0.0170	0.979	6.11	0.0151	40
19.	Methanol-water	10	671.67	373.2	27.45	0.0750	1.083	1.75	0.0081	50
20.	Ethanol-water	10	761.67	423.2	23.75	0.0847	1.075	2.04	0.0213	51

TABLE 6.3

Values of the deviations in bubble point pressures and vapour phase mole fractions with ξ_{ij} = 1.0 and $\xi_{ij} = \xi_{ijopt}$ from three different equations

Refer to Table 6.1 for optimum ξ_{ij}, temperature, no. of points and data.ref.

No.	System	ξ_{ij} = 1.0						$\xi_{ij} = \xi_{ij\ opt.}$					
		EQ. (6.1)		P-R		S-R-K		EQ. (6.1)		P-R		S-R-K	
		ΔP (%)	ΔY_1	ΔP (%)	ΔY_1	ΔP (%)	ΔY_1	ΔP (%)	ΔY_1	ΔP (%)	ΔY_1	ΔP (%)	ΔY_1
1.	Methane-ethane	0.91	0.0044	1.74	0.0056	1.25	0.0036	0.59	0.0039	0.45	0.0044	0.65	0.0038
2.	Methane-n-butane	9.13	0.0191	9.30	0.0188	8.30	0.0195	8.65	0.0190	8.31	0.0189	8.30	0.0195
3.	Methane-i-butane	2.36	0.0108	4.67	0.0195	3.90	0.0203	0.43	0.0067	0.63	0.0117	0.58	0.0149
4.	Methane-n-pentane	7.94	0.0022	12.97	0.0048	11.29	0.0034	6.16	0.0015	4.97	0.0025	5.41	0.0021
5.	Methane-n-hexane	2.44	0.0150	8.91	0.0185	8.56	0.0129	0.88	0.0150	0.56	0.0149	0.47	0.0073
6.	Ethane-propane	0.84	0.0083	1.09	0.0031	0.57	0.0026	0.42	0.0019	0.46	0.0023	0.53	0.0020
7.	Ethane-propylene	0.76	0.0051	0.97	0.0046	0.43	0.0048	0.34	0.0036	0.24	0.0026	0.44	0.0040
8.	Ethane-n-butane	2.21	0.0093	2.30	0.0092	2.29	0.0092	2.20	0.0093	2.19	0.0093	2.24	0.0093
9.	Ethane-n-pentane	1.16	0.0039	1.96	0.0046	1.29	0.0046	1.02	0.0040	1.02	0.0039	1.12	0.0044
10.	Ethane-n-heptane	2.66	0.0052	1.13	0.0039	1.20	0.0015	1.31	0.0038	1.15	0.0040	1.21	0.0015
11.	Ethylene-methane	9.54	0.0120	11.01	0.0156	10.04	0.0130	1.36	0.0043	0.97	0.0060	1.26	0.0040
12.	Ethylene-ethane	1.03	0.0061	1.47	0.0060	0.69	0.0058	0.22	0.0056	0.18	0.0053	0.33	0.0053
13.	Ethylene-propane	3.60	0.0067	3.96	0.0074	3.09	0.0066	0.21	0.0020	0.32	0.0014	0.18	0.0019
14.	Ethylene-n-butane	13.33	0.0334	14.74	0.0352	14.25	0.0317	1.37	0.0237	1.41	0.0241	1.34	0.0184
15.	Propane-i-butane	2.07	0.0037	2.25	0.0032	1.26	0.0038	0.90	0.0075	0.96	0.0072	0.60	0.0048

TABLE 6.3 (continued)

No.	System	$\xi_{ij} = 1.0$						$\xi_{ij} = \xi_{ij\ opt.}$					
		EQ. (6.1)		P-R		S-R-K		EQ. (6.1)		P-R		S-R-K	
		ΔP (%)	ΔY_1	ΔP (%)	ΔY_1	ΔP (%)	ΔY_1	ΔP (%)	ΔY_1	ΔP (%)	ΔY_1	ΔP (%)	ΔY_1
16.	Propane-n-pentane	3.27	0.0112	4.13	0.0126	3.26	0.0119	0.46	0.0141	0.49	0.0144	0.51	0.0129
17.	Propane-i-pentane	2.28	0.0162	3.22	0.0163	2.54	0.0161	0.63	0.0166	0.60	0.0168	0.80	0.0166
18.	Propylene-propane	5.27	0.0089	0.97	0.0032	0.41	0.0034	1.51	0.0132	0.25	0.0029	0.41	0.0034
19.	Propylene-1- butene	0.48	0.0028	0.42	0.0007	0.43	0.0017	0.44	0.0021	0.18	0.0013	0.43	0.0017
20.	n-butane-n-decane	1.73	0.0010	3.36	0.0023	3.23	0.0013	1.24	0.0007	0.94	0.0030	1.86	0.0006
21.	1-butene-n-butane	0.48	0.0163	0.39	0.0013	0.76	0.0013	0.14	0.0161	0.39	0.0013	0.76	0.0013
22.	CO_2-methane*	22.49	0.0593	24.29	0.0622	23.06	0.0597	3.26	0.0145	3.19	0.0129	3.27	0.0118
23.	CO_2-ethane	18.17	0.0588	18.47	0.0582	17.68	0.0585	1.15	0.0066	1.17	0.0070	1.18	0.0074
24.	CO_2-ethylene	8.73	0.0258	9.22	0.0258	8.36	0.0259	0.39	0.0107	0.50	0.0122	0.50	0.0095
25.	CO_2-propane	16.41	0.0398	16.00	0.0384	15.61	0.0391	0.67	0.0048	0.70	0.0050	0.55	0.0045
26.	CO_2-n-butane	26.29	0.0466	26.43	0.0462	26.25	0.0464	1.77	0.0084	3.81	0.0082	3.19	0.0085
27.	CO_2-i-butane	20.47	0.0471	16.81	0.0442	16.88	0.0455	1.23	0.0036	1.11	0.0038	0.99	0.0039
28.	CO_2-n-pentane	17.25	0.0664	22.19	0.0663	22.64	0.0666	2.64	0.0270	2.70	0.0271	2.43	0.0242
29.	H_2S-methane*	19.59	0.0352	20.86	0.0373	18.78	0.0308	2.76	0.0138	3.00	0.0122	3.51	0.0129
30.	H_2S-ethane*	12.08	0.0431	12.71	0.0428	12.04	0.0456	0.67	0.0099	0.78	0.0102	0.76	0.0095
31.	H_2S-i-butane	5.54	0.0297	5.99	0.0304	5.98	0.0314	0.99	0.0205	0.90	0.0210	0.97	0.0210
32.	H_2S-n-heptane	13.77	0.0051	16.57	0.0059	17.85	0.0059	3.27	0.0019	2.92	0.0020	3.27	0.0018

* ΔY_1 refers to hydrocarbon. $\Delta Y_1 = \frac{1}{n} \sum |y_{1,exp} - y_{1,calc.}|$

TABLE 6.4

Comparison of the optimum values of ξ_{ij} obtained from the Soave equation

System	Optimum ξ_{ij}	
	This Work	Graboski*
CO_2 - methane	0.899	0.903
CO_2 - ethane	0.870	0.865
CO_2 - propane	0.868	0.898
CO_2 - n-butane	0.886	0.853
CO_2 - n-pentane	0.849	0.872
H_2S - methane	0.931	0.915
H_2S - ethane	0.909	0.911
H_2S - n-heptane	0.928	0.926
Nitrogen - methane	0.968	0.968
Nitrogen - propane	0.926	0.919
CO - propane	0.979	0.980

* Graboski and Daubert (1978)

TABLE 6.5

Predictions of bubble point pressures

Ternary system: Methane (1) - Ethane (2) - Propane (3)

T = 359.67°R (199.8K); VLE data reference (52)

Component	EXPERIMENTAL			CALCULATED WITH ξ_{ij} = 1.0				CALCULATED WITH $\xi_{ij}=\xi_{ij}$ opt.			
				NEW EQ.		P-R EQ.		NEW EQ.		P-R EQ.	
	P (psia)	X	Y	P (psia)	Y	P (psia)	Y	P (psia)	Y	P (psia)	Y
1	100	0.1180	0.9186	100.28	0.9228	95.44	0.9188	105.90	0.9243	103.86	0.9219
2		0.1440	0.0472		0.0502		0.0523		0.0498		0.0510
1	100	0.1100	0.7916	103.43	0.7905	99.68	0.7838	106.45	0.7936	105.31	0.7911
2		0.5800	0.1940		0.1980		0.2041		0.1949		0.1969
1	200	0.2350	0.9615	194.15	0.9590	185.43	0.9527	204.01	0.9594	200.30	0.9582
2		0.1210	0.0228		0.0254		0.0262		0.0253		0.0259
1	200	0.2360	0.8926	198.40	0.8917	191.40	0.8888	203.89	0.8927	201.63	0.8913
2		0.4830	0.0983		0.1012		0.1038		0.1001		0.1013
1	400	0.4920	0.9630	399.21	0.9650	388.15	0.9645	409.37	0.9646	404.96	0.9639
2		0.1750	0.0266		0.0270		0.0273		0.0273		0.0277
1	400	0.5191	0.9321	408.13	0.9341	400.31	0.9338	413.16	0.9337	411.14	0.9331
2		0.3860	0.0630		0.0633		0.0635		0.0635		0.0640

TABLE 6.5 (continued)

Component	EXPERIMENTAL			CALCULATED WITH ξ_{ij} = 1.0				CALCULATUED WITH $\xi_{ij}=\xi_{ij}$ opt.			
				NEW EQ.		P-R EQ.		NEW EQ.		P-R EQ.	
	P (psia)	X	Y	P (psia)	Y	P (psia)	Y	P (psia)	Y	P (psia)	Y
1	600	0.7450	0.9775	598.70	0.9813	591.84	0.9815	604.84	0.9807	601.74	0.9803
2		0.0520	0.0119		0.0097		0.0097		0.0100		0.0101
1	600	0.7647	0.9583	595.25	0.9617	591.13	0.9621	597.45	0.9608	596.03	0.9604
2		0.1612	0.0366		0.0342		0.0339		0.0348		0.0352

TABLE 6.6

Predictions of bubble point pressures

Ternary System: Methane (1) - Propane (20) - n-Decane (3)

T = 739.67°R (410.93K); VLE data reference (53)

Component	EXPERIMENTAL			CALCULATED WITH ξ_{ij} = 1.0			
				NEW EQ.		P-R EQ	
	P (psia)	X	Y	P (psia)	Y	P (psia)	Y
1	400	0.0632	0.5872	432.55	0.6113	382.56	0.6013
2		0.1874	0.3925		0.3673		0.3757
1	400	0.0251	0.2081	426.64	0.2152	392.29	0.2103
2		0.3900	0.7702		0.7614		0.7661
1	1000	0.0791	0.1808	982.11	0.1732	962.83	0.1759
2		0.7367	0.7883		0.7937		0.7943
1	1000	0.1941	0.7973	1058.76	0.8157	929.20	0.8128
2		0.1612	0.1881		0.1668		0.1697
1	2000	0.3791	0.8871	2070.25	0.8790	1826.43	0.8811
2		0.1242	0.0942		0.0966		0.0963
1	2000	0.3472	0.6311	1995.40	0.6131	1874.63	0.6216
2		0.3917	0.3333		0.3457		0.3421
1	3000	0.5381	0.8971	3055.03	0.8902	2723.99	0.8964
2		0.0924	0.0676		0.0697		0.0684

TABLE 6.7

Multicomponent results: Predictions of bubble point pressures

Methane (1) - Ethane (2) - Propane (3) - n-Pentane (4) - n-Hexane (5) system

T = 559.67°R (310.93°K); VLE data reference (55)

Component	EXPERIMENTAL			CALCULATED WITH ξ_{ij} = 1.0					
				NEW EQ.		P-R EQ.		S-R-K EQ.	
	P (psia)	X	Y	P (psia)	Y	P (psia)	Y	P (psia)	Y
Methane		0.3042	0.7801		0.7731		0.7715		0.7765
Ethane	1040	0.1311	0.1102	1099.2	0.1156	1046.1	0.1168	1057.5	0.1155
Propane		0.2026	0.0787		0.0837		0.0846		0.0826
n-Pentane		0.2021	0.0223		0.0197		0.0195		0.0183
n-Hexane		0.1600	0.0087		0.0087		0.0077		0.0071
Methane		0.3472	0.8040		0.7786		0.7781		0.7836
Ethane	1235	0.1325	0.1039	1250.4	0.1124	1193.5	0.1132	1205.6	0.1119
Propane		0.1893	0.0700		0.0803		0.0807		0.0786
n-Pentane		0.1613	0.0140		0.0183		0.0179		0.0168
n-Hexane		0.1697	0.0081		0.0105		0.0100		0.0092
Methane		0.3858	0.7645		0.7818		0.7824		0.7883
Ethane	1419	0.1314	0.1169	1383.2	0.1092	1324.4	0.1098	1337.1	0.1083
Propane		0.1755	0.0836		0.0775		0.0775		0.0753
n-Pentane		0.1449	0.0215		0.0192		0.0187		0.0174
n-Hexane		0.1624	0.0135		0.0123		0.0117		0.0107

TABLE 6.7 (continued)

Component	EXPERIMENTAL			CALCULATED WITH ξ_{ij} = 1.0					
				NEW EQ.		P-R EQ.		S-R-K EQ.	
	P (psia)	X	Y	P (psia)	Y	P (psia)	Y	P (psia)	Y
Methane		0.4512	0.7853		0.7807		0.7829		0.7899
Ethane	1639	0.1306	0.1022	1607.4	0.1076	1548.4	0.1077	1562.3	0.1061
Propane		0.1490	0.0764		0.0727		0.0721		0.0699
n-Pentane		0.1256	0.0198		0.0226		0.0218		0.0202
n-Hexane		0.1436	0.0163		0.0164		0.0154		0.0139
Methane		0.5574	0.7647		0.7471		0.7522		0.7616
Ethane	1822	0.1222	0.1022	1909.2	0.1064	1866.4	0.1060	1844.1	0.1044
Propane		0.1369	0.0779		0.0881		0.0867		0.0837
n-Pentane		0.0851	0.0309		0.0309		0.0295		0.0272
n-Hexane		0.0984	0.0243		0.0275		0.0257		0.0232
ABS. AVE. DEV. (%) IN P =				3.235		3.717		3.585	

TABLE 6.8

Predictions of bubble point temperatures

Carbon dioxide (1) - n-Pentane (2) system

VLE data reference (38)

EXPERIMENTAL				CALCULATED			
				NEW EQ. ξ_{ij} = 0.865		P-R EQ. ξ_{ij} = 0.866	
P (psia)	T (^oR)	X	Y	T (^oR)	Y	T (^oR)	Y
160	499.8	0.1834	0.9709	499.65	0.9686	500.57	0.9680
501	499.8	0.8998	0.9862	497.80	0.9910	498.05	0.9911
230	559.9	0.1689	0.9202	553.55	0.9265	554.37	0.9255
986	559.9	0.8763	0.9701	559.87	0.9603	559.87	0.9604
127	619.5	0.0444	0.6420	625.63	0.6031	625.99	0.6016
1202	619.5	0.6830	0.9045	616.84	0.8902	616.89	0.8903
341	679.7	0.1115	0.6668	682.43	0.6421	682.72	0.6412
1286	679.7	0.5601	0.8000	680.29	0.7837	680.23	0.7838

TABLE 6.9

Predictions of 'K' values

n-Butane (1) - n-Decane (2) system

T = 679.67 ^{o}R (377.59K): VLE data reference (30)

P (psia)	EXPERIMENTAL		CALCULATED			
			NEW EQ.		P-R EQ.	
			ξ_{ij} = 0.995		ξ_{ij} = 0.986	
	K_1	K_2	K_1	K_2	K_1	K_2
25	8.4970	0.0706	8.3072	0.0733	8.3625	0.0749
50	4.2660	0.0399	4.2159	0.0411	4.2403	0.0419
75	2.8530	0.0303	2.8500	0.0309	2.8638	0.0315
100	2.1470	0.0264	2.1658	0.0263	2.1764	0.0268
125	1.7300	0.0250	1.7580	0.0242	1.7635	0.0247
150	1.4590	0.0247	1.4861	0.0236	1.4891	0.0240
175	1.2760	0.0249	1.2944	0.0242	1.2957	0.0246
200	1.1450	0.0255	1.1550	0.0261	1.1552	0.0266
225	1.0500	0.0267	1.0535	0.0297	1.0532	0.0304

TABLE 6.10

Predictions of 'K' values

Carbon dioxide (1) - n-Decane (2) system

T = 619.67 °R (344.26K); VLE data reference (39)

P (psia)	EXPERIMENTAL		CALCULATED			
			NEW EQ.		P-R EQ.	
			ξ_{ij} = 0.903		ξ_{ij} = 0.903	
	K_1	K_2	K_1	K_2	K_1	K_2
200	8.910	0.0044	8.857	0.0034	8.250	0.0034
400	4.688	0.0036	4.613	0.0029	4.312	0.0030
600	3.242	0.0036	3.198	0.0034	2.997	0.0035
800	2.501	0.0040	2.488	0.0046	2.339	0.0047
1000	2.046	0.0047	2.059	0.0069	1.943	0.0072
1250	1.662	0.0070	1.711	0.0131	1.618	0.0140
1500	1.394	0.0202	1.471	0.0300	1.389	0.0336

TABLE 6.11

Comparison of density predictions of binary mixtures

Mixture	No. of Points	Temp. Range (°R)	Pressure Range (psia)	X_1	EQ.(6.1) *** AAD (%)	C-H *** AAD (%)	GCSP			VLE DATA REF.
							EQ.(6.1)* AAD (%)	C-H* AAD (%)	EQ.(6.1)* AAD (%)	
Ethane-propene	174	470-858	15-10000	0.4958	2.37	1.88	3.42	2.83	2.72	10
Ethane-n-pentane	152	498-920	200-10000	0.5000	3.72	3.13	5.64	3.45	4.75	13
Propane-n-pentane	44	619-800	20-500	0.2480	0.67	1.27	0.72	0.50	0.71	24
Propane-n-pentane	28	619-709	20-500	0.6511	0.66	0.37	0.64	1.01	0.60	24
Propene-propane	268	470-858	15-10000	0.6289	1.92	1.79	2.75	2.13	1.91	28
H_2S-n-pentane	123	498-800	200-10000	0.6123	2.95	2.01	7.88	8.32	7.29	58
OVERALL AVERAGE =					2.05	1.74	3.51	3.04	3.00	

C-H Chaudron et al (1973) equation with fitted constants

* GCSP with Ethane as ref. 1 and n-Decane as ref. 2.

** GCSP with Component 1 as ref. 1 and Component 2 as ref. 2.

*** Using the given equation with mixing rules given by equations (6.2) to (6.5).

$$\text{AAD (\%)} = \frac{1}{n} \sum \frac{|\rho_{exp} - \rho_{calc}|}{\rho_{exp}} \times 100$$

CHAPTER 7

THE VAN DER WAALS ONE FLUID MODEL AND GENERALIZED EQUATIONS OF STATE

Vera and Prausnitz (1971) have discussed the application of the van der Waals one-fluid model to the calculation of vapour-liquid equilibria in mixtures containing simple fluids. They assumed the validity of a two parameter principle of corresponding states. For more complex mixtures, a generalized equation with a third parameter such as Pitzer's acentric factor, is necessary. The van der Waals one-fluid model has been used with slight modifications by many workers (Joffe, 1976; Plöcker et al, 1978; Teja et al, 1980).

In this chapter, the van der Waals model is applied to the generalized equations of Han and Starling (1972), Simonet and Behar (1976) and Chaudron et al (1973). These equations have been used previously with the one-fluid model to predict the densities of mixtures containing mainly hydrocarbons (Teja et al, 1978). Mixtures containing carbon dioxide and hydrocarbons are used in this work.

As shown in Chapter 2, one of the main advantages of using the van der Waals one-fluid model is the simplicity with which it can be applied to the complex equations of state. The main objective of the present work was to show the effectiveness of the one-fluid model when used with the modified B-W-R equation of Han and Starling (1972) to predict vapour-liquid equilibria. Results obtained from the one-fluid model are compared with those obtained by using the eleven arbitrary mixing rules recommended by Han and Starling (see Chapter 2).

A description of the equations used and the one-fluid model can be found in Chapter 2. Only the results and discussion of the results are presented in this Chapter.

7.1 Mixture Density

Calculations of mixture densities have been made for three binaries, methane-propane, propane-CO_2 and n-butane-CO_2. The results are summarized in Table 7.1. The optimum values of ξ_{ij} have been taken from the literature (Teja, 1978). As can be seen accpetable predictions have been obtained using the Han and Starling equation for methane-propane and propane-CO_2 systems. For the n-butane-CO_2 system, it is necessary to adjust the binary interaction coefficient, ξ_{ij}, from the reported value of 0.84 to 0.90 for accurate density predictions. In Table 7.2, results obtained for n-butane-CO_2 systems with different values of ξ_{ij} are presented. The results indicate the necessity of using the optimum value of ξ_{ij} for density predictions. In general, for binaries with ξ_{ij} values which are significantly different from unity it is necessary to use the optimum ξ_{ij} value for accurate predictions of density.

The results obtained using Simonet and Behar equation are within 7% of the experimental values. In the case of the generalized equation of Chaudron et al (1973), better predictions have been obtained for methane-propane systems by taking the coefficients $d_3^{(K)}$ (in equation (2.50)) and $g_2^{(K)}$ (in equation (2.51)) as negative constants. However, this adjustment is only effective for methane-propane systems. For other systems large deviations are obtained. In the previous study by Teja et al (1978) excellent predictions of mixture densities were obtained using the individually fitted constants reported by Chaudron et al (1973). In view of the large deviations obtained in this study, the generalized form of the Chaudron equation is not recommended for the prediction of mixture density.

7.2 VLE Calculations

Bubble point pressures and equilibrium ratios (K values) for mixtures containing hydrocarbons and carbon dioxide have been calculated to demonstrate the genuinely predictive capa-

bilities of the van der Waals one fluid model and the ease with which it can be applied to generalized multi-constant equations of state. Han and Starling (1972) have used a set of arbitrary mixing rules (given in Section 2.1.12) to obtain accurate predictions of vapour-liquid equilibria in systems containing members of the alkane and alkene homologous series and components such as nitrogen, carbon dioxide, hydrogen sulfide, etc. commonly found in the petroleum industry. The Han and Starling mixing rules have been used here for comparison purposes only.

VLE calculations are very sensitive to the binary interaction coefficients k_{ij} (in Han and Starling mixing rules), η_{ij} and ξ_{ij} (in the van der Waals model). Optimum values of k_{ij} for various systems have been reported by Starling (1973). His values have been used in this study. For the van der Waals model, optimum values of ξ_{ij} were obtained from Teja (1978). Setting $\eta_{ij} = 1.0$ and $\xi_{ij} = \xi_{ijopt}$ failed to achieve accurate predictions of vapour-liquid equilibria for systems containing dissimilar hydrocarbons. It was found that better predictions could be obtained by setting $\xi_{ij} = 1.0$ and $\eta_{ij} = \xi_{ijopt}$. In this study accurate predictions of vapour-liquid equilibria were obtained by assigning η_{ijopt} the value of ξ_{ijopt} reported by Teja (1978). Results obtained using the van der Waals model are as good as and in some cases better than those obtained using the Han and Starling mixing rules.

The fugacity expressions necessary for VLE calculations are given in Appendix F.

7.2.1 Predictions of Bubble Point Pressure

Bubble point pressures have been predicted for four binaries - ethane-propene, propene-propane, methane-propane and methane-n-pentane. The results are given in Tables 7.3 and 7.4. For ethane-propene and propene-propane systems, no binary interaction coefficients are needed. The results obtained using the van der

Waals one-fluid model are in close agreement with the results obtained using the Han and Starling mixing rules. In both cases accurate predictions of bubble point pressures have been obtained.

For the methane-propane system, no binary interaction coefficients were used with the van der Waals model but an optimum value of k_{ij} equal to 0.023 was used in the Han and Starling mixing rules. Results are given in Table 7.4. As can be seen, predictions using the van der Waals model are consistently better than those obtained using the Han and Starling mixing rules.

For the methane-n-pentane system, optimum values of the binary interaction coefficient are needed to obtain accurate predictions of bubble point pressures. For the van der Waals model, η_{ij} was taken as 0.94 and for the Han and Starling mixing rules, k_{ij} was taken as 0.041. Results are given in Table 7.4. The Han and Starling mixing rules give acceptable predictions at low pressures (below 1000 psia) but at high pressures the predictions are very poor. On the other hand the van der Waals model gives excellent predictions at high pressures but at low pressures the predictions are poor.

7.2.2 Predictions of the Equilibrium Ratios

Predictions of equilibrium ratios (K-values) have been made for six binaries, propene-propane, methane-ethane, methane-propane, methane-n-pentane, methane-n-heptane and propane-carbon dioxide. The results obtained for these binaries are given in Tables 7.5 to 7.10.

For the propene-propane system, binary interaction coefficients are not needed. Predictions obtained using the van der Waals model were similar to those obtained using the Han and Starling mixing rules. In both cases the predictions were within

10% of the experimental 'K' values. These large deviations are mainly due to the fact that most 'K' values are close to unity and therefore there is little difference between the liquid phase mole fractions and the vapour phase mole fractions. In these cases, the equation of state fails to recognise the existence of two different phases and hence poor results are obtained.

For the methane-ethane system, optimum values of the binary interaction coefficients are not needed for the van der Waals model but for the Han and Starling mixing rules, k_{ij} has been taken as 0.01. Very similar results were obtained for both sets of mixing rules over a wide range of temperatures (346.6 ^{o}R to 539.67 ^{o}R). Results are given in Table 7.6.

For the methane-propane system, predictions were made with k_{ij} = 0.023 and η_{ij} = 0.98 over a wide range of temperatures (351.27 ^{o}R to 649.67 ^{o}R). Results are given in Table 7.7. There is no consistent trend in the predictions but generally the van der Waals model gives better predictions at high pressures while the Han and Starling mixing rules give better predictions at low pressures.

For the methane-n-pentane system, predictions over a wide range of temperatures (499.67 ^{o}R to 819.67 ^{o}R) were obtained with k_{ij} = 0.041 and η_{ij} = 0.94. Results are given in Table 7.8. Both sets of mixing rules are only useful at low pressures; at high pressures large deviations from the experimental 'K' values were obtained. Overall the van der Waals model gives better predictions than the Han and Starling mixing rules.

For the methane-n-heptane system, predictions were made over a wide range of temperatures (359.67 ^{o}R to 919.67 ^{o}R) using k_{ij} = 0.06 and η_{ij} = 0.90. Acceptable predictions were obtained at low pressures only.

For the propane-carbon dioxide system, predictions were obtained using ξ_{ij} = 0.89, η_{ij} = 1.0 and k_{ij} = 0.045. Very similar

results were obtained from the two sets of mixing rules. The predicted 'K' values were within 4% of the experimental values. At low pressures, the predicted 'K' values were usually lower than the experimental values.

7.2.3 Volumes and Fugacities of Co-existing Phases

Volumes and Fugacities of co-existing phases have been calculated for two binaries, methane-propane and propane-carbon dioxide. For the methane-propane system, a wide range of temperatures was covered (499.67 ^{o}R to 649.67 ^{o}R). For the propane-carbon dioxide system, results have been obtained at 529.67 ^{o}R. only. The results are presented in Tables 7.11 to 7.14. As can be seen, very accurate predictions of vapour and liquid phase volumes were obtained from the two sets of mixing rules. Except at very high pressures, the predicted volumes for the liquid phase were lower than the experimental values. Fugacities obtained from the van der Waals model were similar to those obtained from the Han and Starling mixing rules.

7.3 Comparison of Computer Time

It has been pointed out before that the van der Waals model is simple to use and requires less mathematical manipulation. In deriving the fugacity expression there is an additional advantage of using van der Waals model because the differentials of the mixing rules can be easily computed. Although time comparison for only binary mixtures are presented in Table 7.15, it can be confidently said that for multicomponent systems the use of van der Waals model will require less computer time than the use of the Han and Starling mixing rules. In VLE valculations the use of van der Waals model will offer even greater advantage for multicomponent systems. In Table 7.15, the computer time is

given in mill units (1 mill unit ≈ 0.5 sec. on ICL 1900 computer). The same experimental data have been used for both sets of mixing rules and the same algorithm has been followed for the 'K' value prediction (see Appendix G). As can be seen, the use of the van der Waals model reduced the computer time by a factor of nearly 4. This may be a direct consequence of the fact that in the van der Waals model, mixing rules for only the critical temperature, the critical volume and the acentric factor are required compared to eleven mixing rules in the Han and Starling equation. The ratio of the time taken by the two sets of mixing rules (1155/309) is approximately the same as the ratio of the number of mixing rules involved (11/3). We may conclude from this that the simpler equations with fewer mixing rules offer a large saving in computer time and storage in VLE calculations, and that the use of the van der Waals model with the complex generalized equations of state offers one way of reducing the time penalty.

TABLE 7.1

Density predictions of binary mixtures

System	ξ_{12}	No. of Data N	Mol. Frac. X_1	Temp. Range (°R)	Press. Range (psia)	*AV. ABSOLUTE DEV. (%)			VLE REF
						Han	Chaudron	Simonet	
Methane-propane	0.98	170	0.200	500-920	200-10000	1.41	5.13	5.51	2
		64	0.500			1.74	4.19	5.17	
		37	0.800			2.27	3.04	5.79	
n-Butane-CO_2	0.84	154	0.169	560-900	200-10000	3.59	13.44	5.58	36
		154	0.498			5.15	10.65	5.03	
		154	0.827			7.38	7.31	4.38	
Propane-CO_2	0.89	173	0.206	500-920	200-10000	1.89	14.56	7.13	35
		171	0.412			1.86	13.22	7.16	
		173	0.804			4.79	11.48	6.47	
OVERALL AVERAGE						3.34	9.22	5.80	

$$* \text{ AV. ABSOLUTE DEV. } (\%) = \frac{1}{N} \sum_{i}^{N} \left| \frac{\rho_{exp} - \rho_{cal}}{\rho_{exp}} \right| \times 100$$

TABLE 7.2

Effect of ξ_{ij} on density predictions

Pressure range, temperature range, no. of data points and data reference are same as those given in Table 7.1

System	Mole Frac. X_1	ξ_{ij}	* AV. ABSOLUTE DEV.(%)		
			Han	Chaudron	Simonet
n-Butane-CO_2	0.169	1.00	5.10	19.39	11.65
		0.90	1.36	15.55	7.96
		0.89	1.42	15.18	7.18
		0.84	3.59	13.44	5.58
	0.498	1.00	6.17	17.84	11.46
		0.90	2.81	13.23	6.72
		0.89	2.82	12.83	6.39
		0.84	5.15	10.65	5.03
	0.827	1.00	3.36	9.28	4.83
		0.90	5.81	7.97	4.36
		0.89	6.03	7.86	4.35
		0.84	7.38	7.31	4.38

* Defined as in Table 7.1

TABLE 7.3

Predictions of the bubble point pressure

Ethane (1) - Propene (2) System

T = 499.67 ^{o}R (277.59K)

VLE Reference (10)

EXPERIMENTAL			CALCULATED			
			van der Waals Model η_{ij} = 1.0; ξ_{ij} = 1.		Han-Starling Mixing Rules k_{ij} = 0.0	
P (psia)	X_1	Y_1	P (psia)	Y_1	P (psia)	Y_1
100	0.014	0.045	98.31	0.0434	98.17	0.0423
150	0.209	0.452	147.19	0.4458	145.85	0.4421
200	0.390	0.646	194.24	0.6492	192.70	0.6482
250	0.568	0.775	242.82	0.7826	241.60	0.7832
300	0.739	0.873	292.71	0.8793	291.96	0.8802
350	0.896	0.951	342.65	0.9539	342.37	0.9543
Propene (1) - Propane (2) System T = 469.67 ^{o}R (260.93K) VLE Reference (28)						
49.55	0.1818	0.2168	47.41	0.2124	47.48	0.2133
50.00	0.2053	0.2503	47.67	0.2383	47.74	0.2396
51.99	0.3768	0.4344	49.53	0.4238	49.65	0.4243
52.20	0.4136	0.4653	49.95	0.4619	50.07	0.4622
54.12	0.5557	0.6048	51.55	0.6038	51.66	0.6037
54.80	0.6480	0.6945	52.59	0.6919	52.68	0.6914
56.32	0.7924	0.8050	54.23	0.8234	54.30	0.8228
56.50	0.8468	0.8642	54.85	0.8711	54.91	0.8705

TABLE 7.4

Predictions of the bubble point pressure

Methane (1) - Propane (2) System

T = 407.67 ^{o}R (226.48K)

VLE Reference (2)

EXPERIMENTAL			CALCULATED			
			van der Waals Model η_{ij} = 1.0; ξ_{ij} = 1.		Han-Starling Mixing Rules k_{ij} = 0.0	
P (psia)	X_1	Y_1	P (psia)	Y_1	P(psia)	Y_1
200	0.136	0.915	203.79	0.9307	184.3	0.9252
300	0.208	0.937	299.53	0.9481	285.2	0.9468
400	0.284	0.946	397.89	0.9567	398.9	0.9572
500	0.361	0.952	496.36	0.9613	521.3	0.9622
600	0.440	0.960	598.21	0.9638	653.4	0.9639
700	0.522	0.964	706.96	0.9646	795.9	0.9625
800	0.605	0.963	822.61	0.9637	943.2	0.9566
Methane (1) - n-Pentane (2) System T = 491.69 ^{o}R (273.16K) VLE Reference (5)						
			η_{ij}=0.94	ξ_{ij}=1.0	k_{ij} = 0.041	
200.2	0.0909	0.9758	238.2	0.9808	213.2	0.9792
400.2	0.1653	0.9839	446.1	0.9869	413.2	0.9864
600	0.2320	0.9855	644.3	0.9883	621.9	0.9883
800	0.2920	0.9856	832.7	0.9883	837.1	0.9885
1000	0.3481	0.9839	1018.9	0.9875	1068.5	0.9876
1200	0.4005	0.9818	1203.0	0.9861	1317.9	0.9857
1400	0.4480	0.9782	1380.2	0.9841	1579.1	0.9827
1600	0.4980	0.9722	1578.5	0.9811	1898.7	0.9779
1800	0.5501	0.9623	1800.0	0.9766	2288.8	0.9707
2000	0.6117	0.9450	2080.6	0.9692	2828.8	0.9595

TABLE 7.5

Predictions of 'K' values

Propene (1) - Propane (2) System

T = 469.67 ^{o}R (260.93K)

VLE Reference (6)

P (psia)	EXPERIMENTAL		CALCULATED			
			van der Waals Model $\eta_{ij} = 1.0$ $\xi_{ij} = 1.0$		Han-Starling Mixing Rules $k_{ij} = 0.0$	
	K_1	K_2	K_1	K_2	K_1	K_2
48.56	1.2695	0.9701	1.1447	0.9420	1.1495	0.9426
49.90	1.2229	0.9443	1.1179	0.9188	1.1212	0.9200
51.56	1.1805	0.9226	1.0939	0.8979	1.0960	0.8998
52.31	1.1425	0.9050	1.0727	0.8796	1.0741	0.8823
52.36	1.1092	0.8908	1.0541	0.8635	1.0549	0.8670
54.33	1.0807	0.8789	1.0375	0.8490	1.0378	0.8534
55.26	1.0562	0.8689	1.0220	0.8356	1.0221	0.8409
56.16	1.0350	0.8600	1.0074	0.8229	1.0074	0.8291

TABLE 7.6

Predictions of 'K' values

Methane (1) - Ethane (2) System

VLE Reference (1)

P (psia)	T (°R)	EXPERIMENTAL		CALCULATED van der Waals model $\eta_{ij}=1.0$ $\xi_{ij}=1.0$		CALCULATED Han-Starling Mixing Rules $k_{ij} = 0.01$	
		K_1	K_2	K_1	K_2	K_1	K_2
160	346.60	3.740	0.181	3.893	0.177	3.671	0.177
350		1.700	0.140	1.707	0.133	1.742	0.129
600		1.066	0.290	1.070	0.246	1.071	0.261
100	379.67	8.596	0.5408	8.9190	0.5322	8.1798	0.5347
300		2.764	0.2585	2.9264	0.2451	2.8858	0.2464
600		1.448	0.2665	1.4790	0.2427	1.5102	0.2420
800		1.085	0.5595	1.1416	0.4099	1.1431	0.4358
300	419.67	3.658	0.4899	3.9943	0.4676	3.9060	0.4724
600		1.865	0.4037	2.0146	0.3658	2.0370	0.3712
950		1.099	0.7827	1.2453	0.5489	1.2401	0.5852
400	479.67	3.563	0.8248	3.7715	0.8146	3.7594	0.8174
700		1.944	0.6888	2.1535	0.6578	2.1446	0.6703
950		1.194	0.8521	1.4538	0.7252	1.3907	0.7700
600	519.67	2.259	0.9281	2.3956	0.9209	2.4100	0.9227
800		1.482	0.9012	1.6138	0.8832	1.5314	0.8998
850		1.081	0.9769	1.4067	0.9029	1.0811	0.9769
750	539.67	1.686	0.9769	1.5860	0.9774	1.5723	0.9786

TABLE 7.7

Predictions of 'K' values

Methane (1) - Propane (2) System

VLE Reference (1,2)

P (psia)	T (^oR)	EXPERIMENTAL		CALCULATED van der Waals model $\eta_{ij}=0.98, \xi_{ij}=1.0$		CALCULATED Han-Starling Mixing Rules $k_{ij}=0.023$	
		K_1	K_2	K_1	K_2	K_1	K_2
30.5	351.27	24.50	0.0786	29.93	0.0746	21.74	0.0751
200		3.87	0.0208	4.22	0.0177	3.71	0.0178
600		1.17	0.0614	1.18	0.0453	1.27	0.0390
51.5	384.67	19.70	0.1350	23.16	0.1325	18.83	0.1339
500		2.13	0.0443	2.22	0.0387	2.30	0.0380
700		1.49	0.0711	1.56	0.0560	1.71	0.0523
150	499.67	13.680	0.5754	13.813	0.5646	13.573	0.5712
700		2.870	0.2602	3.120	0.2309	3.215	0.2414
1300		1.424	0.4206	1.675	0.3237	1.750	0.3467
250	559.67	8.500	0.8022	8.877	0.8059	9.154	0.8098
700		3.010	0.4920	3.406	0.4524	3.463	0.4758
1200		1.604	0.5578	1.903	0.4881	1.877	0.5459
500	619.67	3.590	0.8832	3.895	0.8773	4.045	0.8821
700		2.488	0.7973	2.807	0.7732	2.770	0.7953
950		1.549	0.8291	1.886	0.7661	1.557	0.8544
600	649.67	2.396	0.9519	2.207	0.9661	2.243	0.9681
700		1.894	0.9237	1.709	0.9444	1.339	0.9709
750		1.429	0.9458	1.350	0.9575	1.003	0.9995

TABLE 7.8

Predictions of 'K' values

Methane (1) - n-Pentane (2) System

VLE Data Reference (5)

P (psia)	T (^oR)	EXPERIMENTAL		CALCULATED van der Waals model $\eta_{ij}=0.94;\xi_{ij}=1.0$		CALCULATED Han-Starling Mixing Rules $k_{ij}=0.041$	
		K_1	K_2	K_1	K_2	K_1	K_2
400	499.67	6.28	0.0313	6.77	0.0196	6.38	0.0197
2400		1.18	0.4020	1.45	0.1299	1.74	0.0752
100	539.67	26.50	0.1320	28.47	0.1171	27.39	0.1194
600		4.75	0.0557	5.14	0.0374	5.24	0.0375
2200		1.38	0.2540	1.69	0.1085	1.96	0.0838
80	579.67	36.470	0.3125	38.134	0.2972	38.637	0.3038
600		5.082	0.0933	5.529	0.0705	5.835	0.0717
2000		1.588	0.2260	1.937	0.1184	2.199	0.1052
160	659.67	19.170	0.5062	20.434	0.5089	22.106	0.5224
800		3.962	0.2225	4.561	0.1796	4.993	0.1901
1800		1.725	0.3567	2.190	0.2118	2.423	0.2197
400	739.67	6.902	0.6100	7.784	0.5826	8.413	0.6088
1000		2.750	0.4680	3.405	0.3799	3.543	0.4303
1400		1.724	0.5868	2.449	0.3879	2.452	0.4646
600	819.67	2.400	0.8830	2.5512	0.8767	1.9937	0.9201
800		1.260	0.9500	1.2600	0.9495	-	-

TABLE 7.9

Predictions of 'K' values

Methane (1) - n-Heptane (2) System

VLE Data Reference (57)

P (psia)	T (^oR)	EXPERIMENTAL		CALCULATED van der Waals model η_{ij}=0.90;ξ_{ij}=1.0		CALCULATED Han-Starling Mixing Rules k_{ij} = 0.06	
		K_1	K_2	K_1	K_2	K_1	K_2
600	359.67	2.170	0.0001	2.802	0.0000	2.000	0.0000
1000		1.600	0.0004	3.392	0.0025	1.784	0.0008
100	459.67	22.440	0.0015	18.895	0.0009	17.240	0.0009
1000		2.640	0.0026	3.210	0.0009	2.820	0.0008
2500		1.360	0.0520	1.718	0.0192	1.920	0.0055
200	559.67	15.416	0.0143	15.368	0.0109	15.829	0.0107
1000		3.487	0.0126	3.841	0.0073	4.018	0.0064
2500		1.640	0.0757	1.922	0.0275	2.252	0.0145
400	739.67	9.403	0.1511	9.804	0.1418	11.771	0.1473
1000		3.956	0.1167	4.324	0.0954	5.178	0.0928
2000		2.079	0.1763	2.438	0.1126	2.934	0.0948
400	859.67	7.796	0.5120	8.394	0.4944	9.644	0.5345
1000		3.026	0.3982	3.798	0.3061	4.234	0.3509
1750		1.448	0.6152	2.311	0.3134	2.485	0.3671
400	919.67	5.443	0.7735	5.307	0.8069	5.681	0.8343
800		2.435	0.6595	3.390	0.5574	2.672	0.6986
1000		1.703	0.7282	2.820	0.5219	-	-

TABLE 7.10

Predictions of 'K' Values

Propane (1) - Carbon Dioxide (2) System

T = 529.67°R (294.26K)

VLE Reference (35).

P (psia)	EXPERIMENTAL		CALCULATED			
			Van der Waals model $\eta_{ij}=1.0$ $\xi_{ij}=0.89$		Han-Starling Mixing Rules k_{ij} = 0.045	
	K_1	K_2	K_1	K_2	K_1	K_2
150	0.8593	6.600	0.8521	5.5261	0.8532	5.7316
200	0.6925	4.840	0.6823	4.2474	0.6876	4.3249
250	0.5945	3.780	0.5809	3.4456	0.5906	3.4623
300	0.5347	3.070	0.5156	2.8933	0.5294	2.8782
350	0.4969	2.573	0.4721	2.4874	0.4901	2.4546
400	0.4720	2.204	0.4434	2.1746	0.4657	2.1334
450	0.4544	1.918	0.4260	1.9245	0.4528	1.8805
500	0.4469	1.692	0.4182	1.7185	0.4500	1.6763
550	0.4533	1.509	0.4199	1.5461	0.4574	1.5075
600	0.4700	1.363	0.4324	1.3999	0.4762	1.3674
650	0.4980	1.245	0.4578	1.2769	0.5085	1.2518
700	0.5340	1.155	0.4997	1.1759	0.5575	1.1583
750	0.5730	1.089	0.5613	1.0974	0.6243	1.0867
800	0.6110	1.041	0.6450	1.0411	0.7021	1.0373
850	0.6400	1.007	0.7605	1.0050	0.7955	1.0049

TABLE 7.11

Predictions of volumes of coexisting phases

Methane (1) - Propane (2) System

VLE Data Reference (2)

P (psia)	T (^oR)	EXPERIMENTAL VOLUME (Cu.ft/Lb.Mole)		CALCULATED van der Waals model η_{ij}=0.98 ξ_{ij}=1.0		CALCULATED Han-Starling Mixing Rules k_{ij} = 0.023	
		Vapour	Liquid	Vapour	Liquid	Vapour	Liquid
150	499.67	32.800	1.841	32.150	1.321	31.868	1.323
700		5.930	1.260	6.129	1.233	6.062	1.250
1300		2.436	1.343	2.657	1.204	2.581	1.226
250	559.67	18.60	1.478	19.197	1.459	18.793	1.461
700		6.30	1.448	6.544	1.416	6.353	1.434
1200		3.13	1.606	3.278	1.427	3.053	1.462
500	619.67	8.80	1.806	8.422	1.723	8.216	1.729
700		5.47	1.864	5.896	1.751	5.541	1.775
950		3.44	2.062	3.952	1.857	3.258	1.999
600	649.67	5.60	2.324	5.471	2.156	5.320	2.180
700		4.29	2.629	4.491	2.376	3.963	2.830
750		3.63	2.901	4.020	2.792	3.706	3.692

TABLE 7.12

Predictions of volumes of coexisting phases

Propane (1) - Carbon Dioxide (2) System

T = 529.67°R (294.26K)

VLE Data Reference (35)

P (psia)	EXPERIMENTAL VOLUME (Cu.ft/Lb.mole)		CALCULATED van der Waals model η_{ij} = 1.0 ξ_{ij}=0.89		CALCULATED Han-Starling Mixing Rules k_{ij} = 0.045	
	Vapour	Liquid	Vapour	Liquid	Vapour	Liquid
150	31.80	1.4040	31.73	1.377	31.54	1.379
200	23.33	1.3860	23.61	1.346	23.31	1.351
250	18.27	1.3680	18.59	1.315	18.26	1.323
300	14.89	1.3480	15.17	1.286	14.84	1.295
350	12.47	1.3260	12.68	1.257	12.35	1.267
400	10.64	1.3020	10.78	1.228	10.47	1.238
450	9.22	1.2770	9.29	1.199	8.97	1.210
500	8.08	1.2500	8.07	1.171	7.76	1.183
550	7.14	1.2210	7.05	1.144	6.74	1.156
600	6.35	1.1900	6.19	1.117	5.87	1.130
650	5.67	1.1570	5.44	1.092	5.12	1.109
700	5.07	1.1190	4.78	1.070	4.46	1.094
750	4.52	1.0750	4.21	1.049	3.91	1.085
800	4.00	1.0180	3.72	1.021	3.49	1.064
850	3.51	0.9427	3.38	0.958	3.32	0.970

TABLE 7.13

Predictions of fugacities of coexisting phases

Methane (1) - Propane (2) System

VLE Data Reference (2)

P (psia)	T (°R)	CALCULATED van der Waals model $\eta_{ij} = 0.98$ $\xi_{ij} = 1.0$		CALCULATED Han-Starling Mixing Rules $k_{ij} = 0.023$	
		f_1 (psia)	f_2 (psia)	f_1 (psia)	f_2 (psia)
150	499.67	69.06	67.71	68.14	67.71
700	499.67	528.26	60.62	525.39	60.99
1300	499.67	925.03	54.01	916.83	55.95
250	559.67	58.81	121.36	56.79	151.62
700	559.67	436.66	143.26	429.05	144.68
1200	559.67	800.02	135.45	784.62	139.09
500	619.67	100.04	278.86	94.43	279.79
700	619.67	263.83	274.22	251.06	276.59
950	619.67	455.55	268.90	432.90	273.49
600	649.67	57.92	360.51	53.37	361.39
700	649.67	140.51	357.28	128.88	359.51
750	649.67	180.75	355.69	168.77	357.67

TABLE 7.14

Predictions of fugacities of coexisting phases

Propane (1) - Carbon Dioxide (2) System

T = 529.67°R (294.26K)

VLE Data Reference (35)

P (psia)	CALCULATED			
	van der Waals model η_{ij} = 1.0 ξ_{ij} = 0.89		Han-Starling Mixing Rules k_{ij} = 0.045	
	f_1 (psia)	f_2 (psia)	f_1 (psia)	f_2 (psia)
150	102.74	26.48	102.86	25.76
200	97.93	73.79	98.34	71.77
250	93.23	119.22	93.79	116.15
300	88.55	162.92	89.19	158.93
350	83.86	204.97	84.50	200.21
400	79.11	245.43	79.73	239.96
450	74.25	289.39	74.81	278.30
500	69.15	322.06	69.69	315.32
550	63.89	358.31	64.21	351.31
600	58.24	393.49	58.48	386.12
650	51.97	427.95	52.12	420.40
700	44.75	462.22	44.80	454.82
750	35.96	497.31	35.83	490.74
800	24.34	535.24	24.34	530.00
850	6.00	581.87	6.22	580.08

TABLE 7.15

Comparison of computer time

Prediction of 'K' Values

System	No. of Points	T_{vdw}* mill units	T_{Han}** mill units
Methane-Ethane	17	63	222
Methane-Propane	18	61	293
Methane-n-Pentane	15	60	230
Methane-n-Heptane	17	80	296
Propane-CO_2	15	45	114
TOTAL	82	309	1155

1 mill unit = 0.5 sec (on ICL 1900 computer)

* T_{vdw} is time taken using van der Waals model

** T_{Han} is time taken using Han and Starling mixing rules

CHAPTER 8

SUMMARY OF RESULTS AND CONCLUSIONS

A new cubic equation of state has been proposed in this study. The results obtained with this equation are presented and discussed in Chapters 4, 6 and 7. In Chapter 4, results obtained for pure components are given. The new equation predicts saturated liquid densities within 2% of their experimental values (except in the region $0.9 < T_r < 1.0$), saturated vapour densities within 1.5% and vapour pressures within 1% of their experimental values (Tables 4.2, 4.3 and 4.7). Comparisons with the P-R, the R-K, the Heyen and the Han and Starling equations are also shown (Tables 4.2 to 4.6). The overall absolute average deviation (including the critical region) for saturated liquid densities of pure components (polar components included) was found to be 2.94% for the new equation, 2.98% for the Heyen equation, 7.75% for the P-R equation and 20.02% for the R-K equation (Table 4.2). The improvement is greater for the heavy hydrocarbons (above n-Octane) and polar substances. This improvement is achieved by making the predicted critical compressibility (denoted by Z_m) a substance dependent parameter in general different from the experimental value of the critical compressibility (denoted by Z_c). A generalised correlation for Z_m has been obtained in terms of the acentric factor (equation 4.40). For all components considered, Z_m is found to be greater than Z_c. This was also found by Schmidt and Wenzel (1980) who made use of a modified van der Waals type equation of state (Section 2.1.11). In Table 8.1, Z_m values obtained in this work are compared with those given by Schmidt and Wenzel. As can be seen very similar values are obtained.

TABLE 8.1

Comparison of predicted critical compressibilities

ω	Z_m	
	This work	Schmidt-Wenzel
0.000	0.329	0.333
0.100	0.321	0.325
0.200	0.314	0.317
0.300	0.308	0.310
0.400	0.302	0.303
0.500	0.296	0.296

A plot of Z_m versus the acentric factor is shown in Figure 4.9. This plot summarizes the characteristics of the new equation. For light components ($\omega = 0$; $Z_m = 0.329$) the new equation is comparable to the S-R-K equation and for components whose acentric factor is approximately 0.3 ($Z_m = 0.307$), it is comparable to the P-R equation. Thus, characteristics of both the S-R-K and the P-R equations are implicit in the new equation. However, the application of the new equation extends to heavy hydrocarbons (up to n-Eicosane) and polar substances for which the S-R-K and the P-R equations are inadequate.

The new equation of state, like many other cubic equations, fails to give accurate representation of the liquid phase densities in the small region ($0.9 < T_r < 1.0$) near the critical point. An overall absolute average deviation of 11.56% was obtained in this region (Table 4.4). This is mainly due to the fact that the experimental value of the critical compressibility is not reproduced by the new equation. However, the overall absolute average deviation was reduced from 11.56% to 3.04% by assuming the predicted critical compressibility to be a temperature dependent parameter in the

critical region (Table 4.4). The temperature dependency is given by equation (4.31). Use of equation (4.31) is equivalent to making constants a, b and c temperature dependent in the critical region.

Densities in the regions away from the saturation envelope are predicted within 2.5% of their experimental values (Table 4.6). Entropy departures are predicted within 2% and enthalpy departures within 3.5% of the values predicted by the eleven constant equation of Han and Starling (Table 4.8).

In Chapter 6, results obtained for mixtures are given. Predictions of vapour-liquid equilibria and mixture densities are obtained for a variety of systems containing hydrocarbons (up to n-Eicosane), non-hydrocarbons (CO_2, CO, N_2, H_2S) and polar components (water, ammonia, alcohols). It is necessary to use the optimum value of the binary interaction coefficient for systems containing methane, heavy hydrocarbons, non-hydrocarbons and polar components. Optimum values of ξ_{ij} are evaluated for 52 binaries using the new equation. Comparisons with the S-R-K and the P-R equations are given for 32 binaries (Tables 6.1, 6.2 and 6.3). As can be seen, excellent predictions for the bubble point pressure and the vapour phase mole fractions are obtained. Bubble point pressures for most of the systems are predicted within 2% of their experimental values. Results are summarised in Tables 6.2 and 6.3 and are shown in the form of the phase diagrams in Figures 6.1 to 6.113. The predictions obtained using the new equation, the S-R-K equation and the P-R equation are very similar (Table 6.3). Accurate predictions for ternary and multicomponent systems are obtained without using the binary interaction coefficient (Tables 6.5 to 6.7).

Using the optimum values of ξ_{ij} from Tables 6.1 and 6.2, accurate predictions of bubble point temperatures and equilibrium ratios can also be obtained (Tables 6.8 to 6.10). Thus, the values of ξ_{ijopt} given in Tables 6.1 and 6.2 can be confidently used for predicting other thermodynamic properties of the saturated phases.

Accurate predictions of mixture densities can be obtained using the new equation; results are shown in Table 6.11. The overall absolute average deviation for five binaries (containing mainly hydrocarbons) was found to be 2.05% for the new equation and 1.74% for the individually fitted Chaudron equation (1973).

The improvement in the representation of saturated liquid densities of mixtures is a direct consequence of the improvement in pure components saturated liquid densities. Predictions of saturated liquid volumes are shown in Figure 6.114 for the n-Butane-n-Decane system. As can be seen, better predictions are obtained from the new equation than the Peng and Robinson equation.

In Chapter 7, the generalized Han and Starling equation is used with~~in~~ the van der Waals one fluid model to obtain accurate predictions of mixture densities and vapour-liquid equilibria. Predictions of mixture densities for three binaries (methane-propane, propane-CO_2, n-butane-CO_2) are given in Table 7.1. The overall absolute average deviation was found to be 3.34% for the Han and Starling equation, 9.22% for the generalized Chaudron equation and 5.8% for the Simonet-Behar equation. Predictions of bubble point pressures and equilibrium ratios are given in Tables 7.3 to 7.10. Results obtained using the one fluid model are compared with those obtained using the eleven arbitrary mixing rules given by Han and Starling. Predictions obtained using the one fluid model are as good as those obtained using the Han and Starling mixing rules for mixtures containing light components. For mixtures containing dissimilar molecules, the van der Waals model gives better predictions at high pressures (Table 7.4). One of the main advantages of the van der Waals one fluid model is the ease and speed with which VLE calculations can be made. A comparison of computer times is presented in Table 7.15. The ratio of the computer time taken by using the Han and Starling mixing rules to that taken by using the one fluid model is approximately the same as the ratio of the number of mixing rules involved in each case (11/3).

Some of the results given in Chapters 6 and 7 are reproduced in Table 8.2 to show a comparison between the results obtained from

the new equation and those obtained from the eleven constant Han and Starling equation. As can be seen, for the Ethane-Propene system better predictions of bubble point pressures are obtained with the new equation. For the Methane-n-Pentane system, both equations give similar predictions at low pressures, but at high pressures, the Han and Starling equation with the van der Waals model gives better predictions. It is interesting to note that predictions obtained using the Han and Starling mixing rules are less accurate than those obtained from the new equation (Tables 7.3, 7.4 and 8.2). In general, for vapour liquid equilibrium predictions, the new equation and other simple equations (the S-R-K, the P-R) can give predictions which are as accurate as and sometimes better than those obtained from a multi constant equation of state. In Figures 8.1 to 8.4, results obtained from the new equation, the S-R-K, the P-R equation and the Han and Starling equation (with two sets of mixing rules) for Propane-Carbon dioxide system are shown. As can be seen, except for the liquid phase volumes, all other properties are predicted very accurately and the predictions obtained using all the equations are very similar. Solid lines in Figures 8.2 to 8.4 depict the experimental values. At low pressures, the predictions of liquid phase volumes obtained using the new equation are superior to those obtained using the other equations but as the critical region is approached, the P-R equation and the new equation tend to give poor predictions, while the Han and Starling equation gives accurate predictions in this region. As expected the S-R-K equation gives very poor predictions of the liquid phase volumes (Figure 8.4).

8.1 Conclusions

A new three constant equation of state is proposed in this study to improve the representation of the liquid phase densities while maintaining the accuracy in the prediction of vapour-liquid equilibrium. Only saturation data (T_s, P_s, V^L) are used for the evaluation of the equation of state parameters Z_m and F. In addition to the critical temperature and the critical pressure, only two

parameters (Z_m and F) are required to characterize a particular fluid. These parameters are evaluated by minimizing the deviation in the saturated liquid densities while simultaneously satisfying the equilibrium criterion (equality of fugacities) along the saturation curve. The new equation has been tested for 38 pure components including hydrocarbons (up to n-Eicosane), non-hydrocarbons (CO_2, H_2S, SO_2, N_2, O_2, A_r, CO) and polar components (water, ammonia, alcohols). The use of the new equation is strongly recommended for heavy hydrocarbons and polar components for which other cubic equations (P-R, S-R-K) are inadequate. For non polar and weakly polar components, generalized correlations for Z_m and F are obtained in terms of the acentric factor. Thus, only T_c, P_c and ω are required to characterize a fluid. The new equation of state is also used with the generalized form of the corresponding states principle based on two non-spherical reference fluids.

The new equation of state is extended to mixtures by using mixing rules similar to those used by Peng and Robinson. Only one binary interaction coefficient is sufficient for the accurate prediction of vapour-liquid equilibria. Optimum values of the binary interaction coefficients are obtained for 52 binaries (including polar components). For 32 binaries, comparisons with the Soave and the Peng and Robinson equations are shown. Comparisons with the Han and Starling equation are also shown. The criterion used for selecting the optimum interaction coefficient is the minimization of deviations in bubble point pressures. The new equation is also tested for the prediction of vapour-liquid equilibria in ternary and multicomponent systems. Apart from the liquid phase volumes for which the new equation gives better predictions, similar results for VLE are obtained from the new equation, the Soave equation and the Peng and Robinson equation.

The genuinely predictive capabilities of the van der Waals one fluid model and the ease and speed with which VLE predictions can be obtained from a multiconstant equation of state are demonstrated. The Han and Starling generalized equation is used. Results obtained from the one fluid model are compared with those obtained from the

eleven arbitrary mixing rules given by Han and Starling. Mixture densities are calculated using the one fluid model with the equations of Han and Starling, Chaudron et al and Simonet and Behar. The van der Waals one fluid model is shown to be a simple and effective method of extending complex equations of state to the prediction of thermodynamic properties of mixtures.

8.2 Suggestions for Future Work

The new equation of state has been extended in the critical region by assuming the predicted critical compressibility to be a temperature dependent parameter in the region $0.9 < T_r < 1.0$. Further improvements could be made by using a different temperature function for the predicted critical compressibility. Although such temperature dependency improves the representation of the liquid phase densities, its effect on other thermodynamic properties needs to be evaluated.

An exponential temperature function for α was suggested by Heyen (1980) but it has two arbitrary constants K and n and, as found in this study, a generalized correlation for n cannot be obtained. It may be possible to overcome this problem by assuming a constant value for n and evaluating K. From the results obtained in this study (Appendix A) it would seem appropriate to take n between 0.8 and 0.85. This may result in a good correlation for K in terms of the acentric factor.

The use of the new equation could be extended to hydrocarbon-water systems and to the predictions of liquid-liquid equilibria, liquid-vapour-solid and freeze-out problems. Because of the improvement in the liquid phase densities, the new equation is likely to give better predictions of liquid-liquid equilibria than other simple equations of state.

Finally, the generalized corresponding states principle with two non-spherical reference fluids could be extended to predict phase equilibrium in multicomponent systems using the van der Waals one fluid model and accurate equations for the reference fluids.

TABLE 8.2

Predictions of bubble point pressures

Ethane (1) - Propene (2) System

T = 499.67°R (277.59K) VLE Reference (10)

EXPERIMENTAL			CALCULATED			
			Han-Starling Eq. van der Waals model $\eta_{ij}=1.0$ $\xi_{ij}=1.0$		New Equation $\xi_{ij} = 1.0$	
P(psia)	X_1	Y_1	P(psia)	Y_1	P(psia)	Y_1
100	0.014	0.045	98.31	0.0434	100.27	0.0424
150	0.209	0.452	147.19	0.4458	148.98	0.4423
200	0.390	0.646	194.24	0.6492	196.73	0.6477
250	0.568	0.775	242.82	0.7826	246.66	0.7823
300	0.739	0.873	292.71	0.8793	298.31	0.8793
350	0.896	0.951	342.65	0.9539	350.34	0.9538

Methane (1) - n-Pentane (2) System

T = 491.69°R (273.16K) VLE Reference (5)

			$\eta_{ij}=0.94$ $\xi_{ij}=1.0$		$\xi_{ij} = 0.98$	
200.2	0.0909	0.9758	238.2	0.9808	238.5	0.9788
400.2	0.1653	0.9839	446.1	0.9869	443.3	0.9846
600	0.2320	0.9855	644.3	0.9883	637.4	0.9857
800	0.2920	0.9856	832.7	0.9883	821.0	0.9852
1000	0.3481	0.9839	1018.9	0.9875	1000.6	0.9838
1200	0.4005	0.9818	1203.0	0.9861	1175.5	0.9816
1400	0.4480	0.9782	1380.2	0.9841	1339.6	0.9787
1600	0.4980	0.9722	1578.5	0.9811	1517.7	0.9745
1800	0.5501	0.9623	1800.0	0.9766	1707.5	0.9683
2000	0.6117	0.9450	2080.6	0.9692	1933.7	0.9578

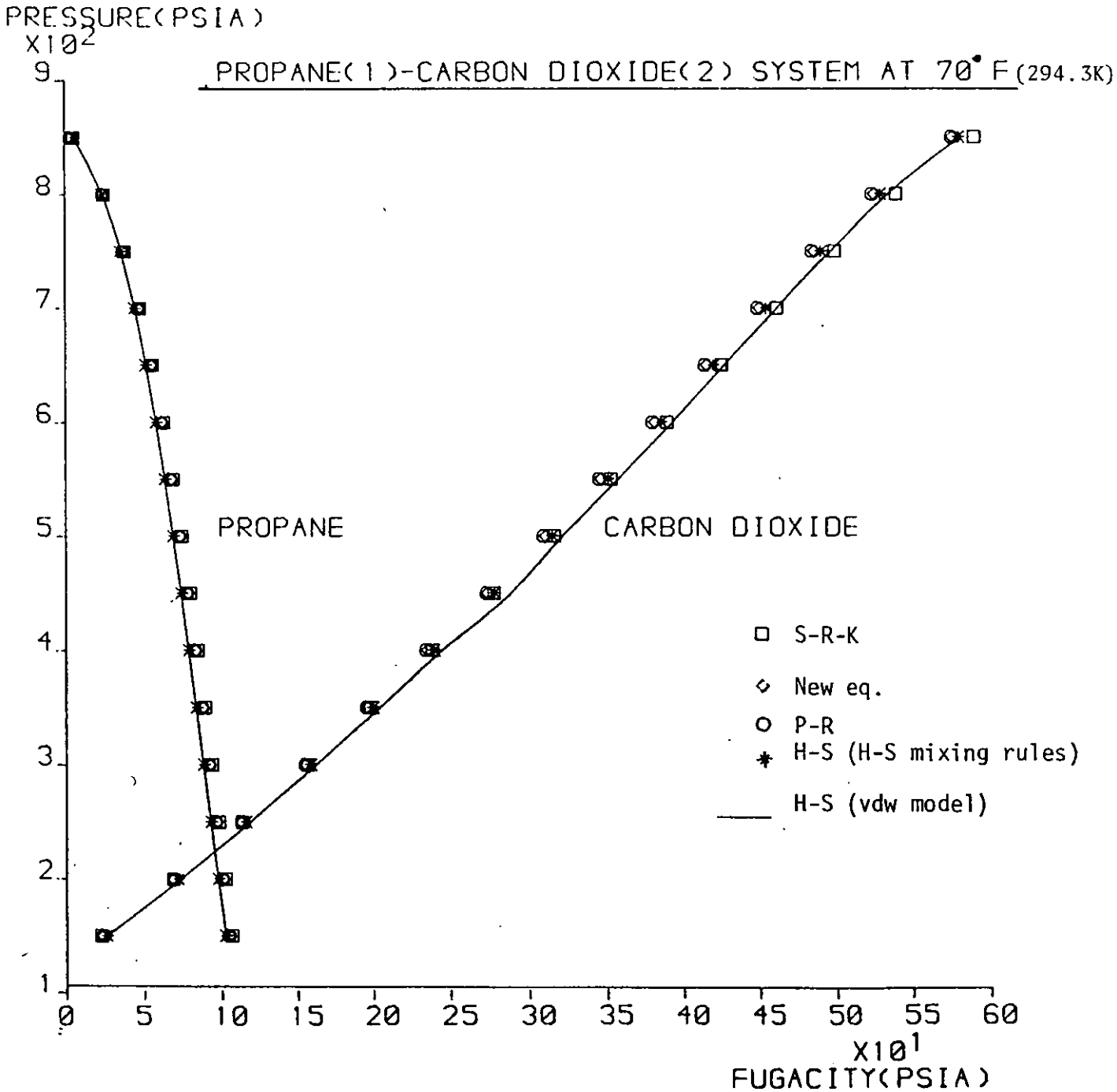


FIGURE 8.1 Comparison of predicted fugacities for propane-carbon dioxide system

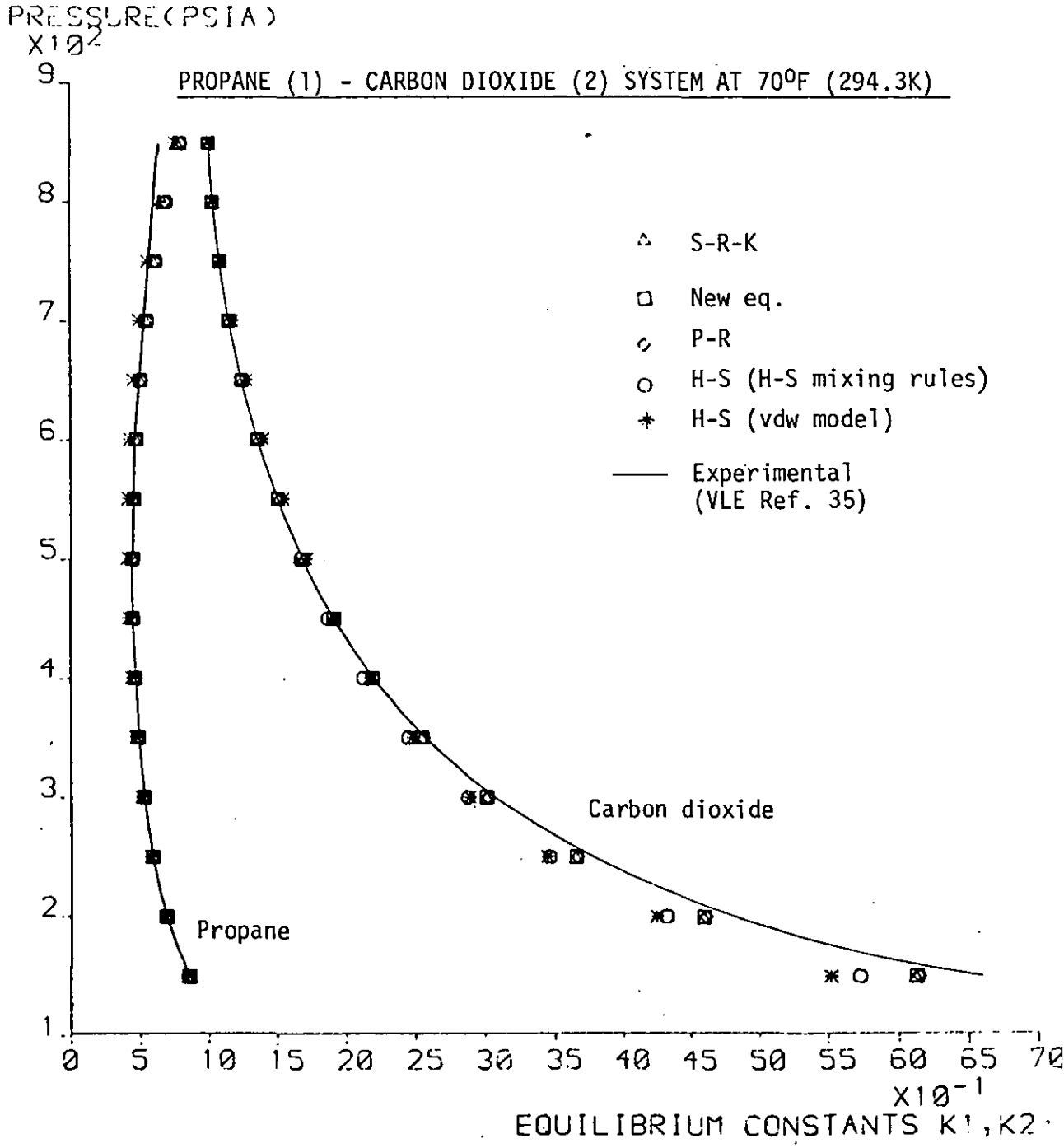


FIGURE 8.2 Comparison of predicted 'K' values for propane-carbon dioxide system

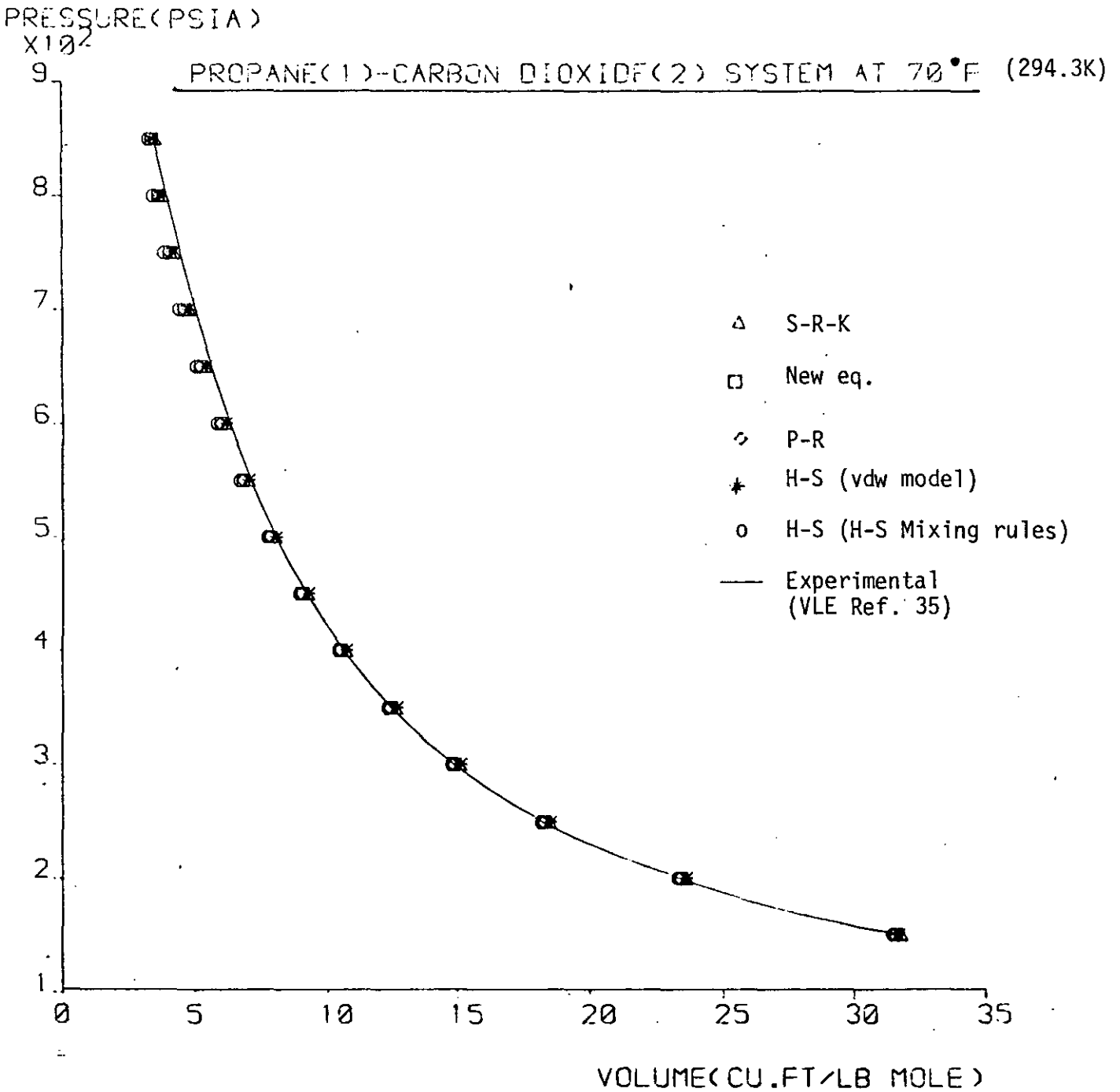


FIGURE 8.3 Comparison of predicted vapour phase volumes for propane-carbon dioxide system

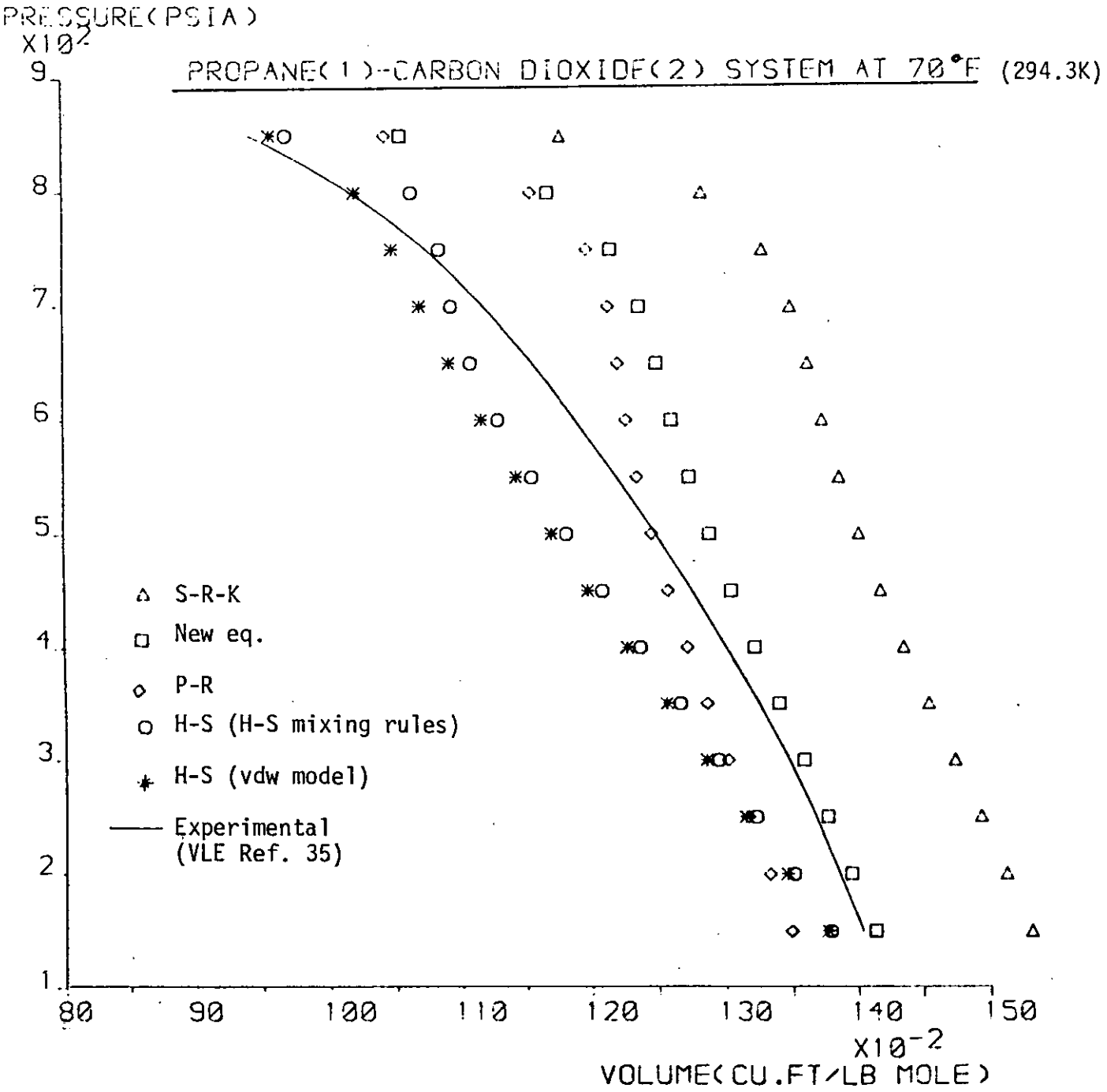


FIGURE 8.4 Comparison of predicted liquid phase volumes for propane-carbon dioxide system

NOTE ON GRAPHS

In Figures 6.1 to 6.113:

1. Solid lines depict curves predicted using the optimum value of the binary interaction coefficient given in Tables 6.1 and 6.2.

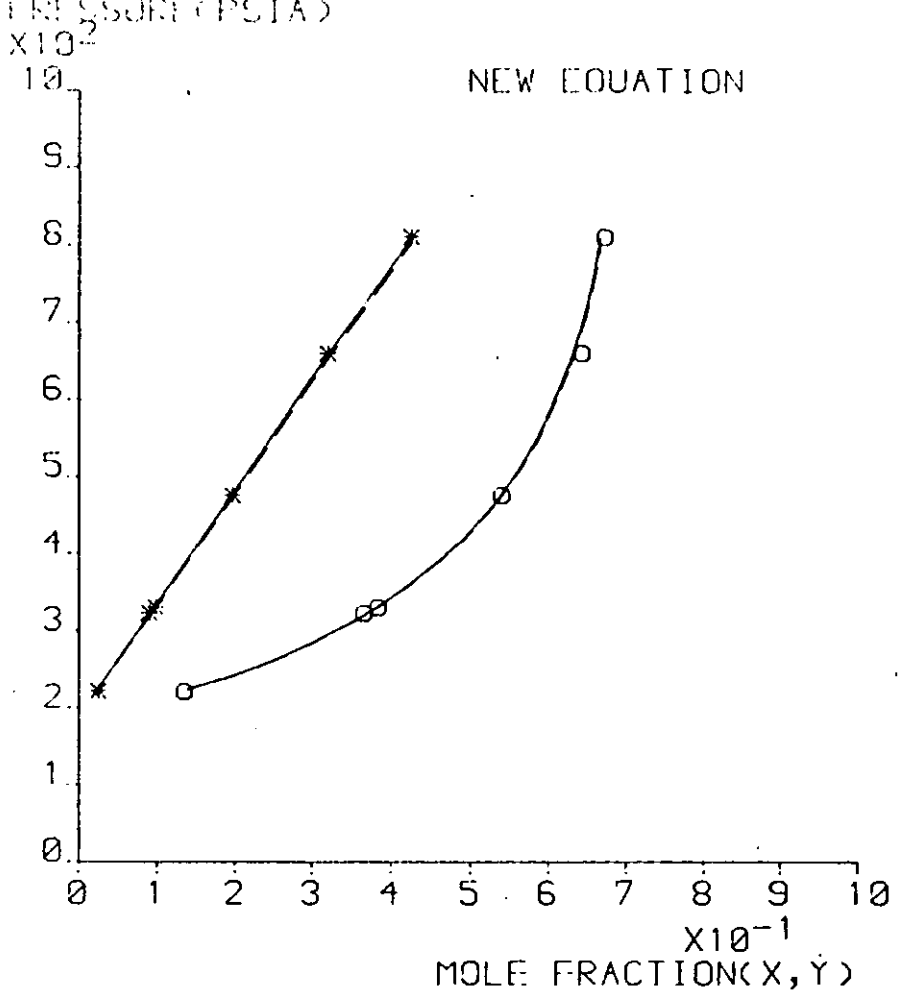
2. Dotted lines depict curves predicted without using the binary interaction coefficient (ξ_{ij} = 1.0).

3. Experimental points are represented by asterisks or circles and the corresponding references are listed, under "References of vapour-liquid equilibrium data".

4. P, X and Y refer to the pressure (psia), the mole-fraction of the first named component in the liquid phase and the mole-fraction of the first named component in the vapour phase.

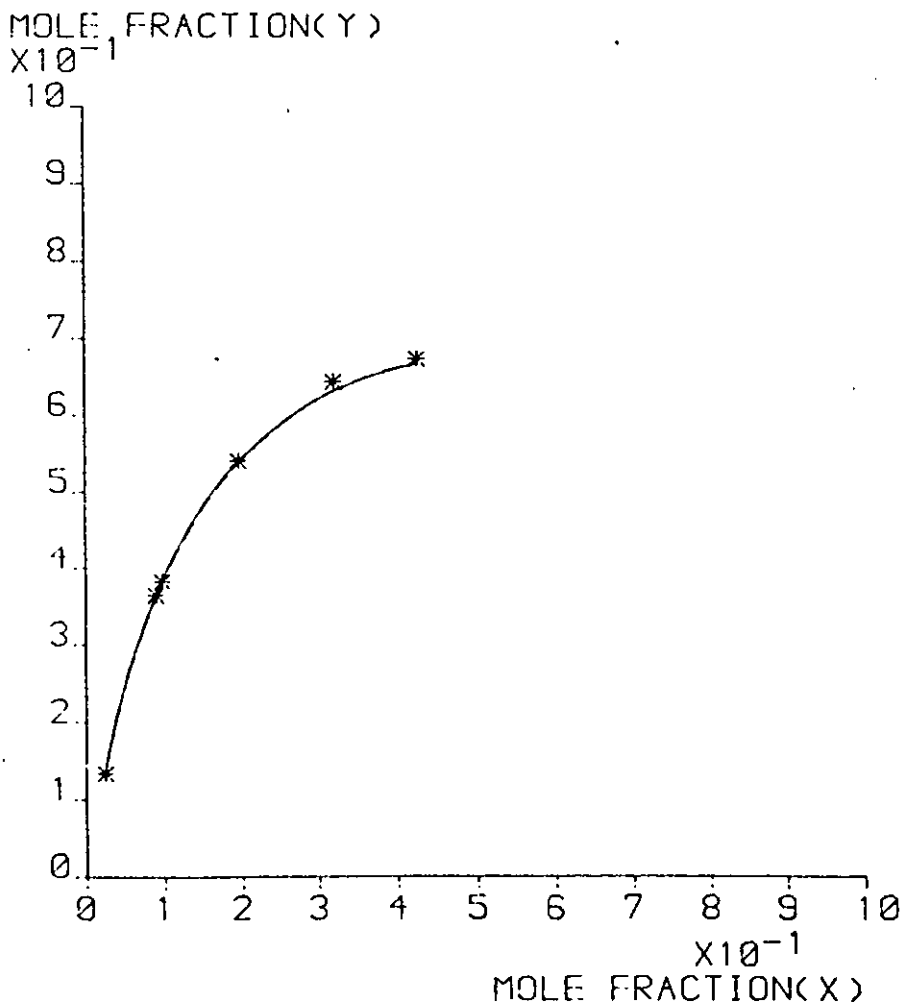
5. In pressure vs mole fraction (X,Y) graphs, circles represent the vapour phase while asterisks represent the liquid phase.

In Figures 6.100 to 6.113 results obtained for temperatures other than at which the optimum value of ξ_{ij} is evaluated, are shown.

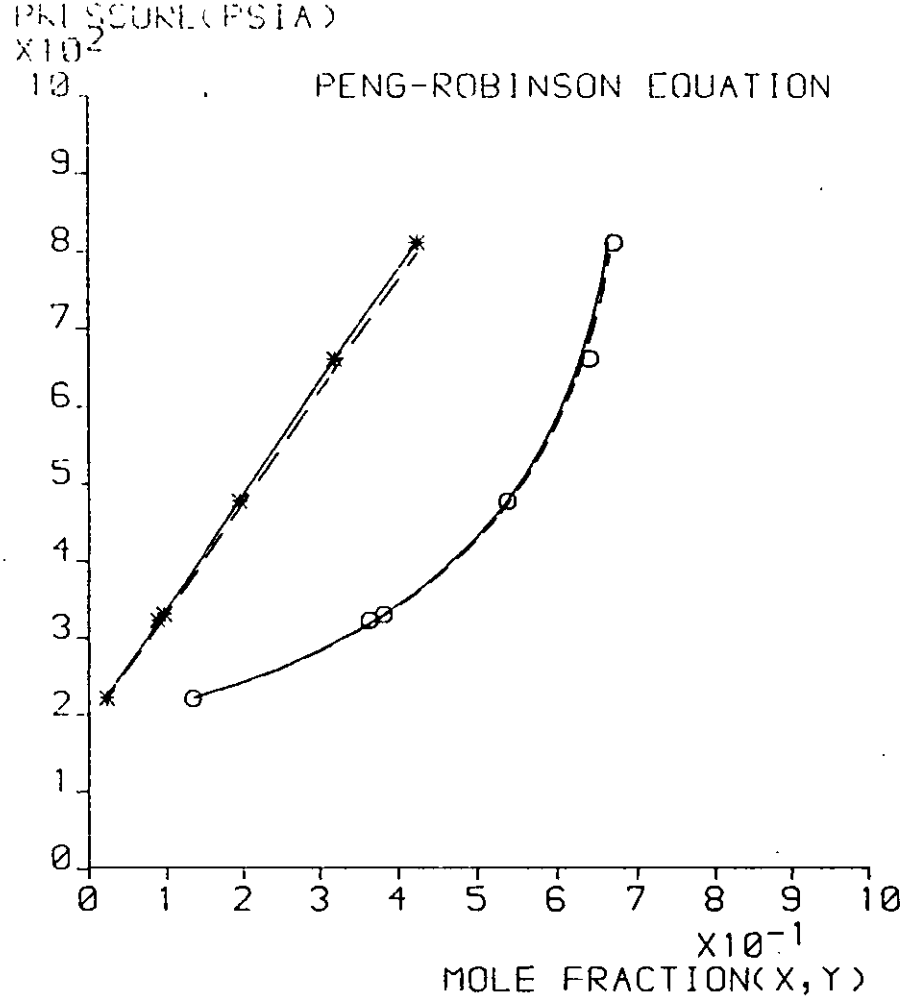


(a)

FIGURE 6.1 Methane-Ethane System at 450.02°R (250K)

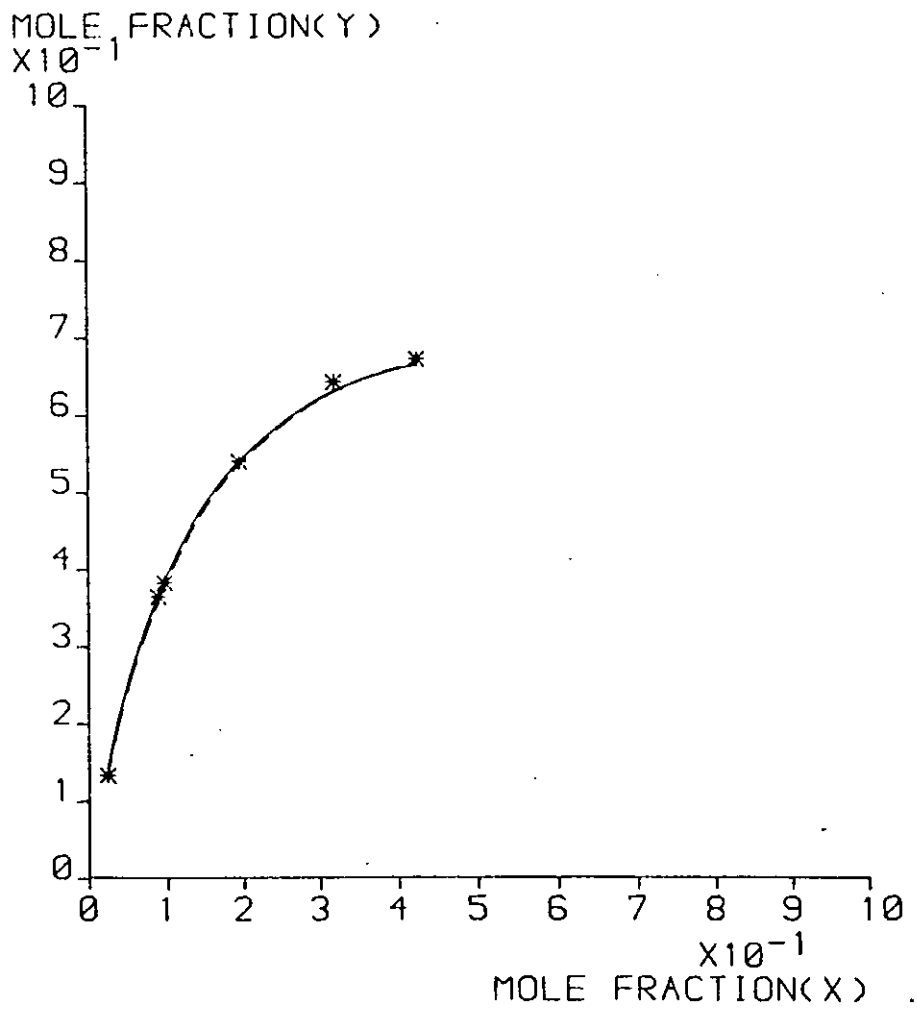


(b)

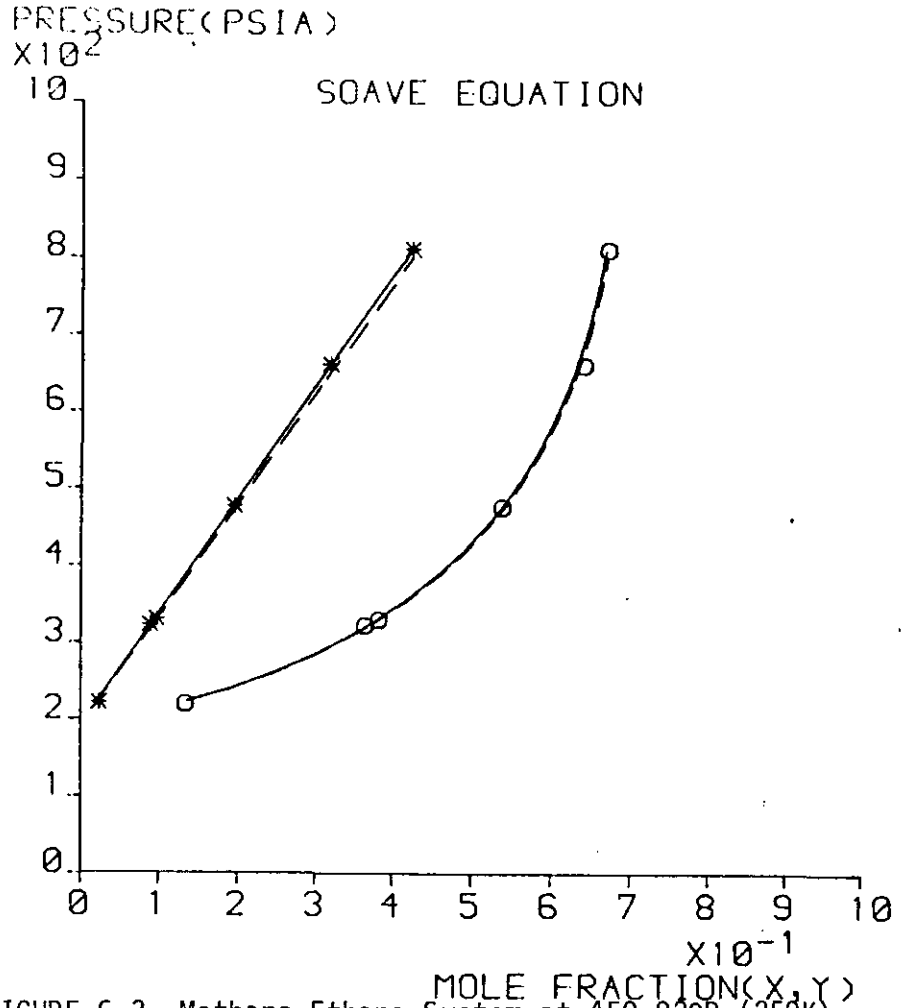


(a)

FIGURE 6.2 Methane-Ethane System at 450.02°R (250K)

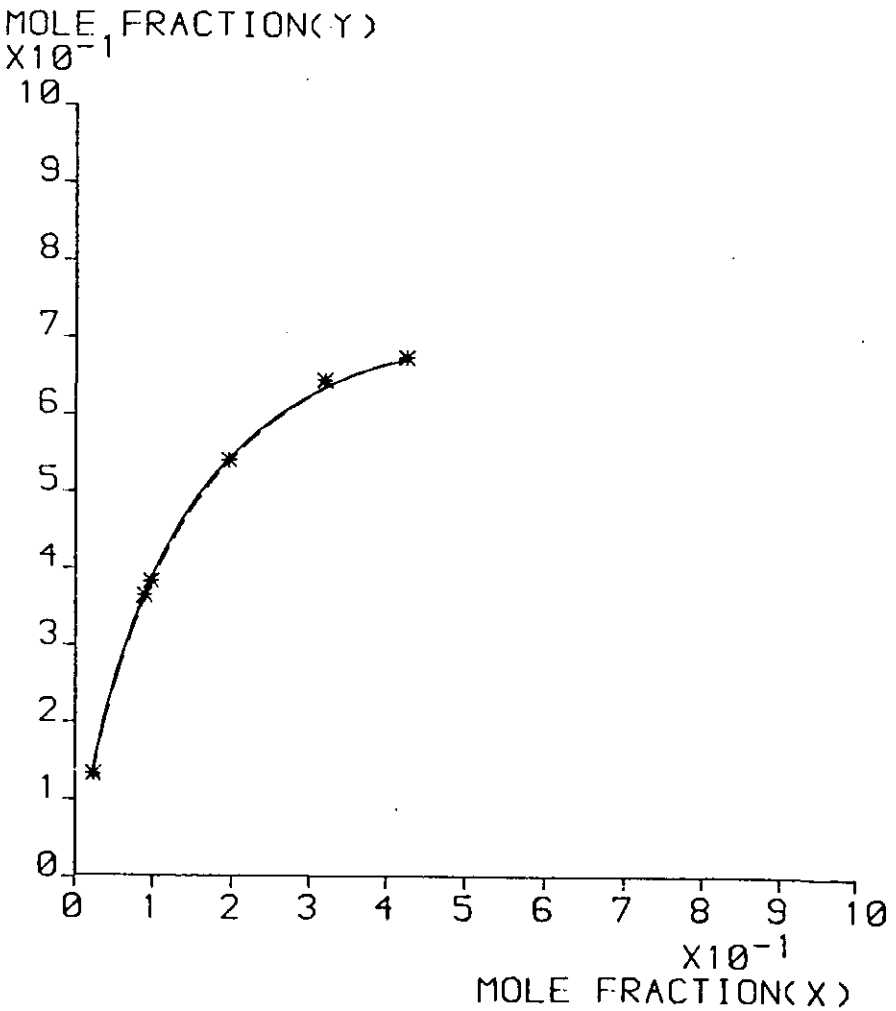


(b)

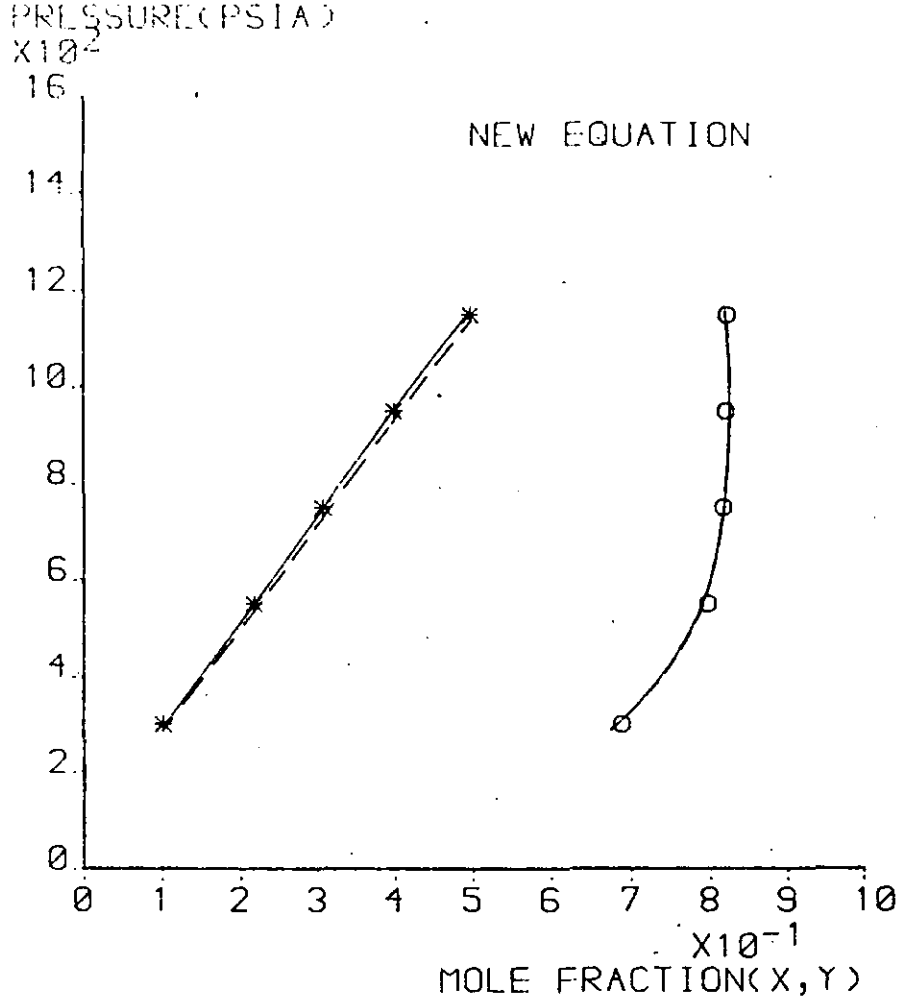


(a)

FIGURE 6.3 Methane-Ethane System at 450.02°R (250K)

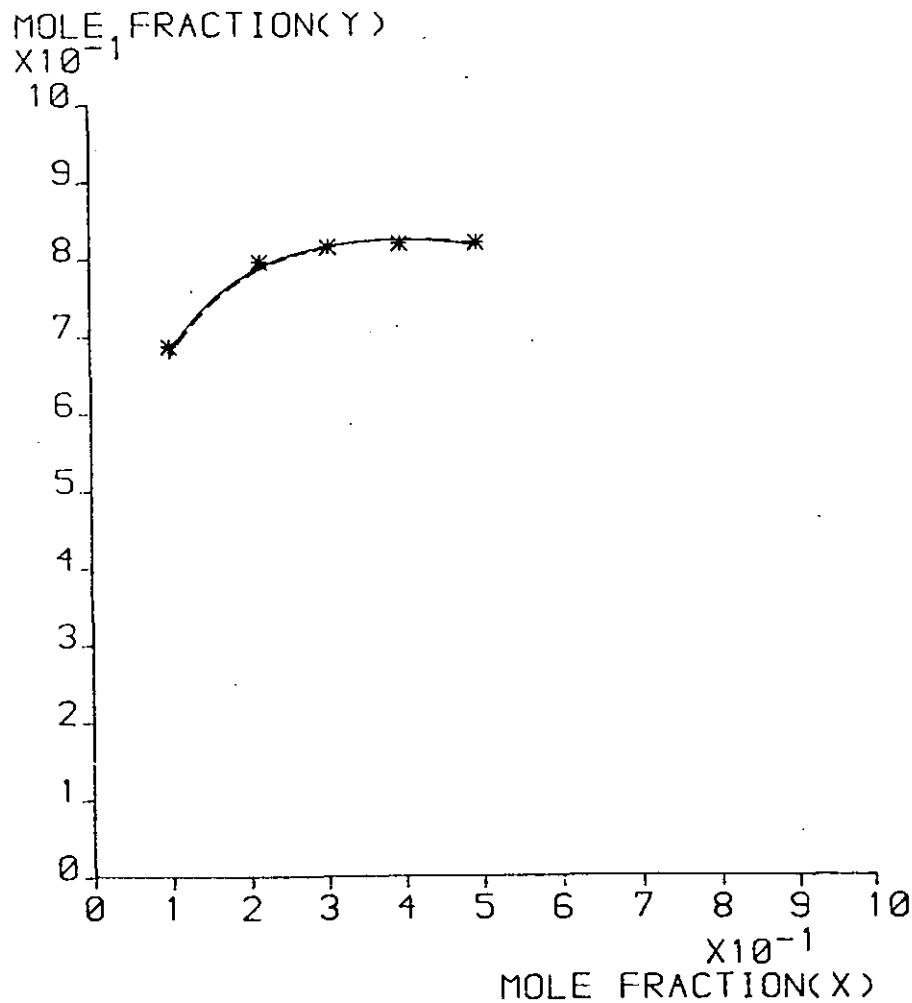


(b)

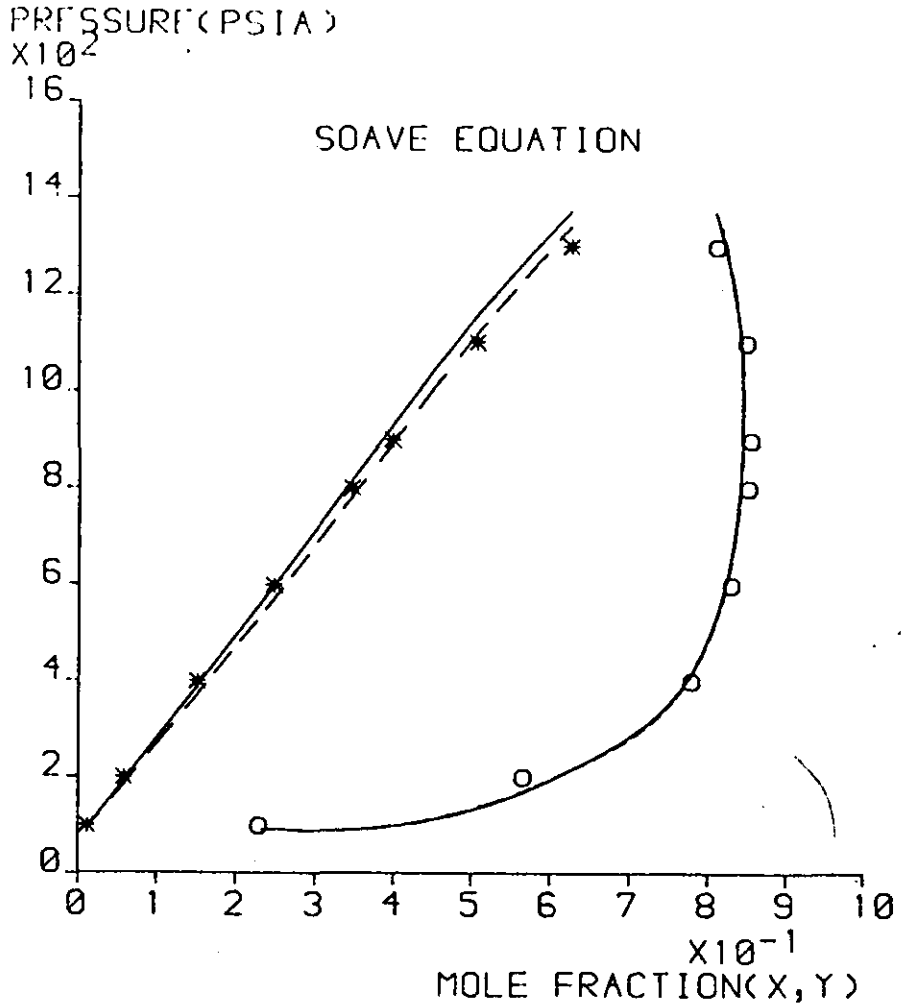


(a)

FIGURE 6.4 Methane-Propane System at 499.67°R (277.6K)

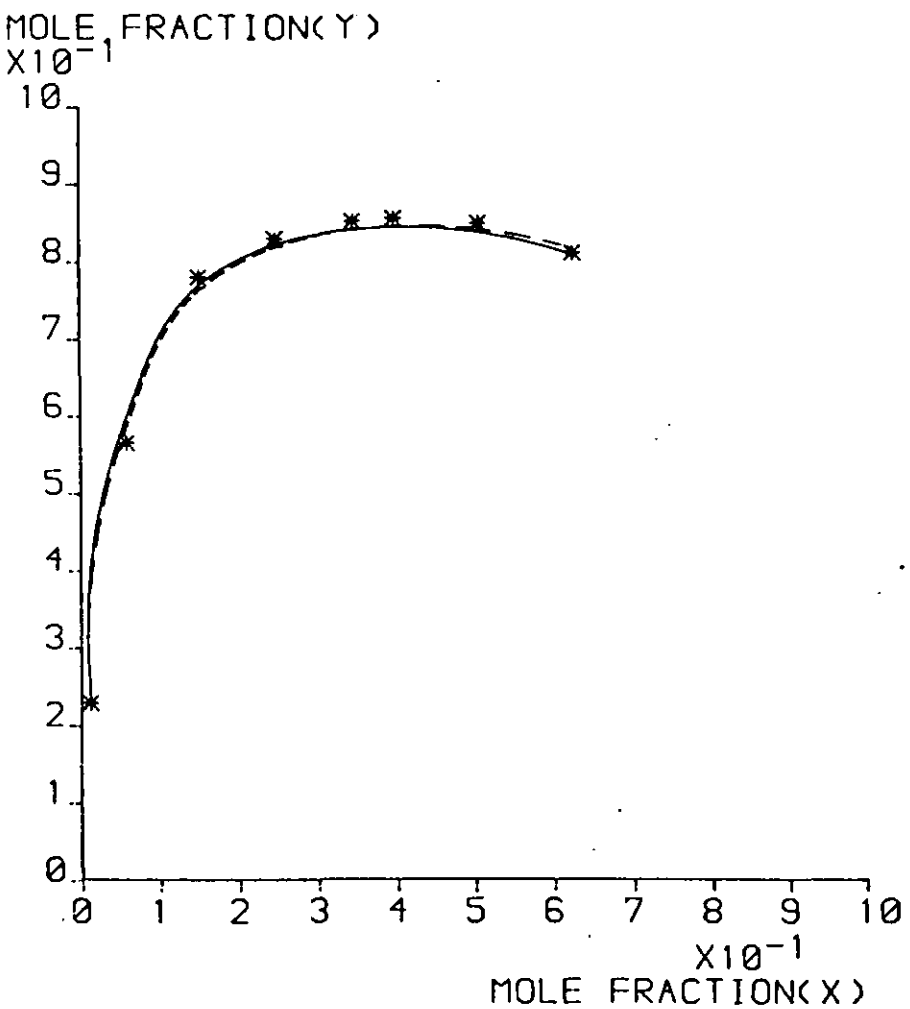


(b)

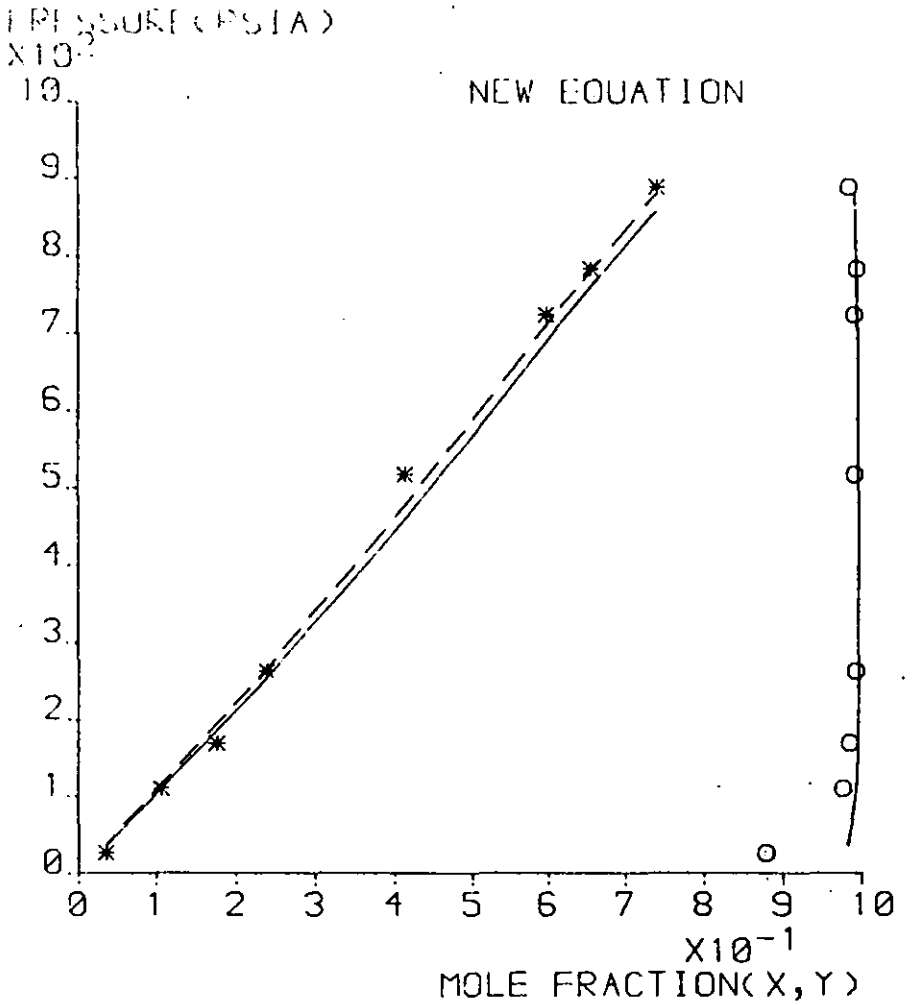


(c)

FIGURE 6.4 Methane-Propane System at 499.67°R (277.6K)

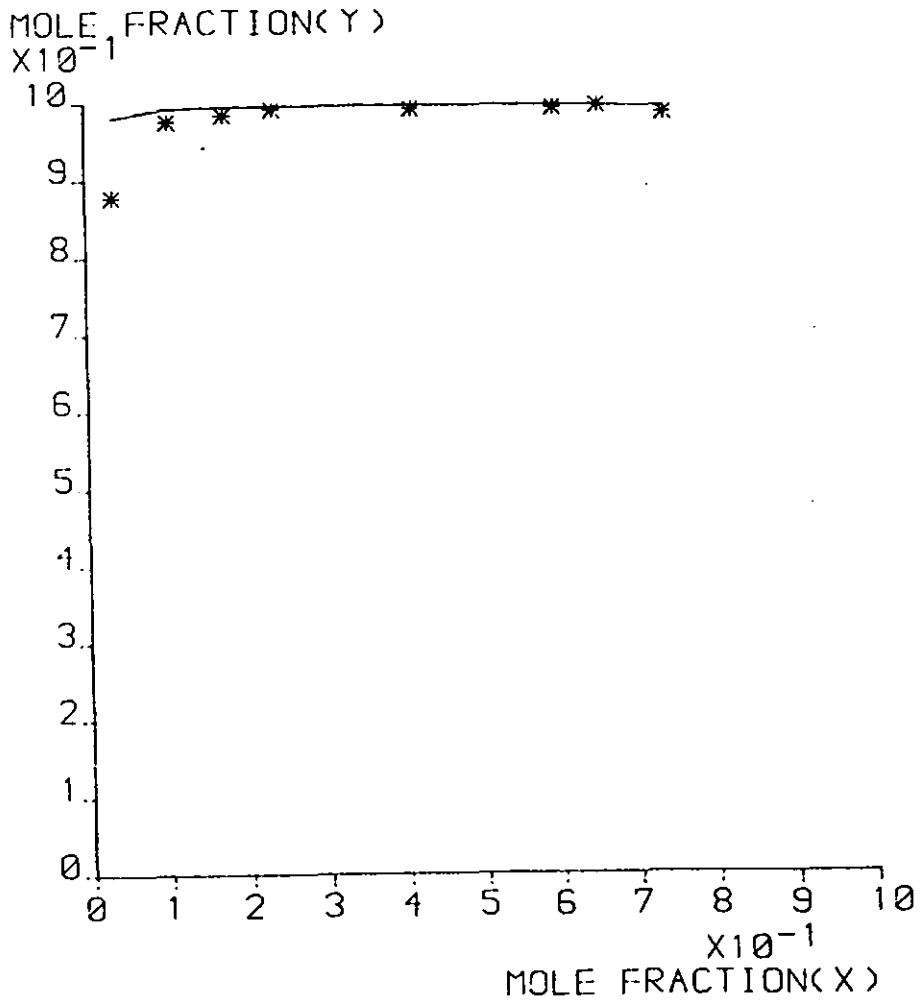


(d)

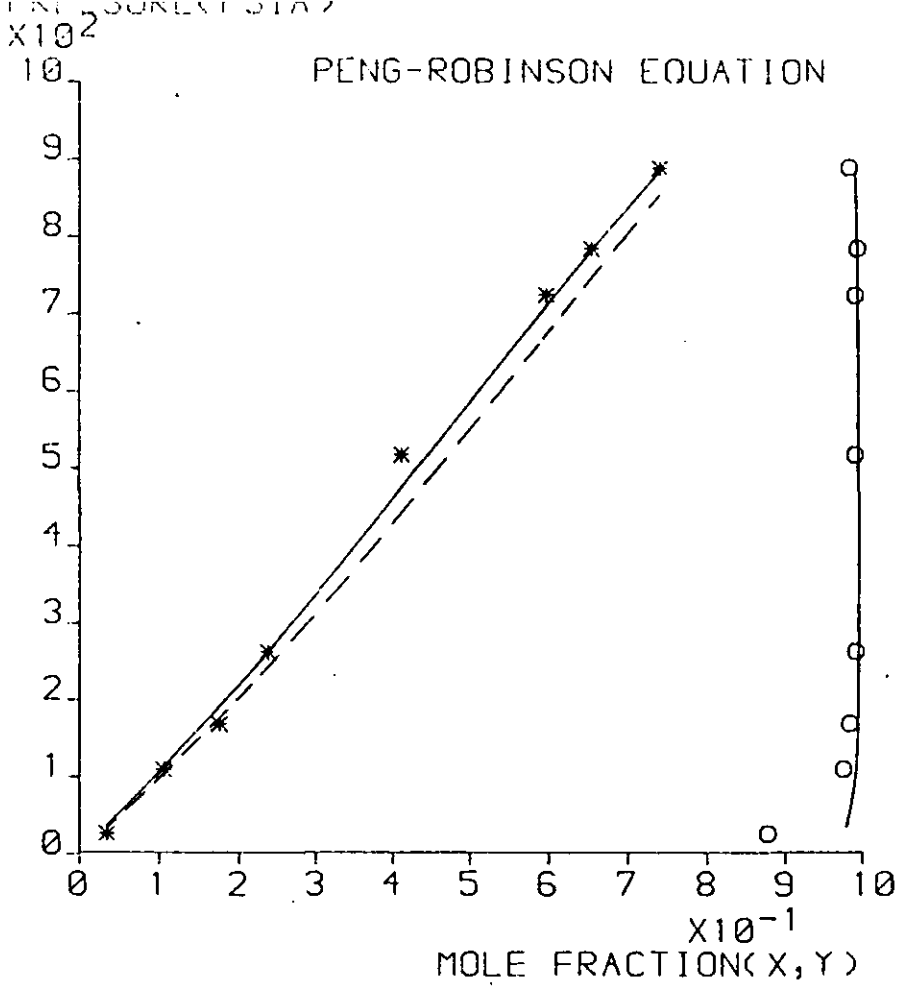


(a)

FIGURE 6.5 Methane-n-Butane System at 379.93°R (211K)

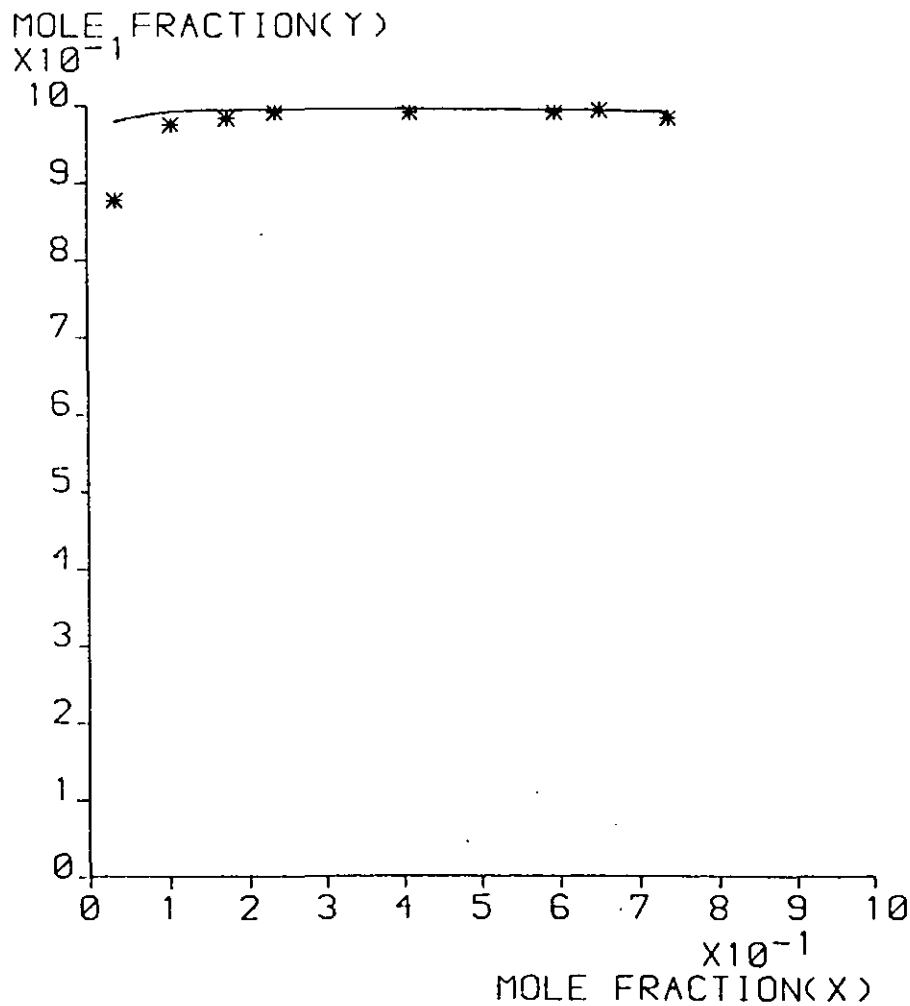


(b)

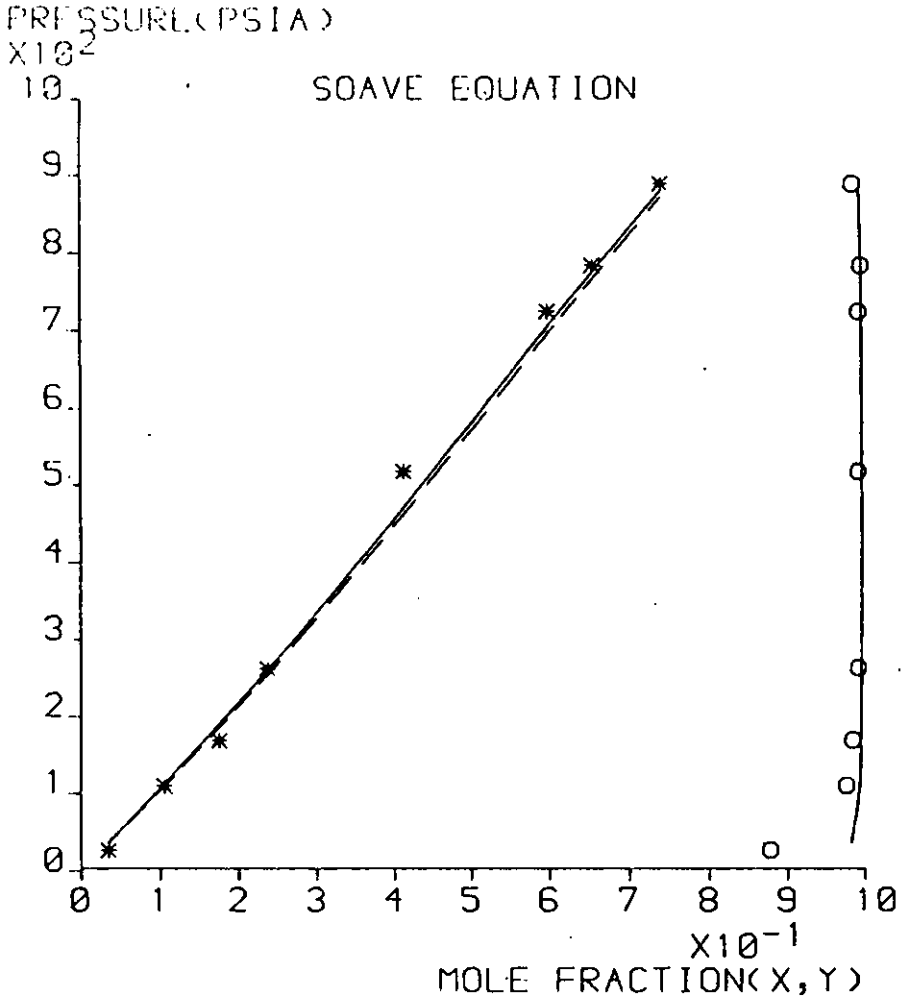


(a)

FIGURE 6.6 Methane-n-Butane System at 379.93°R (211K)

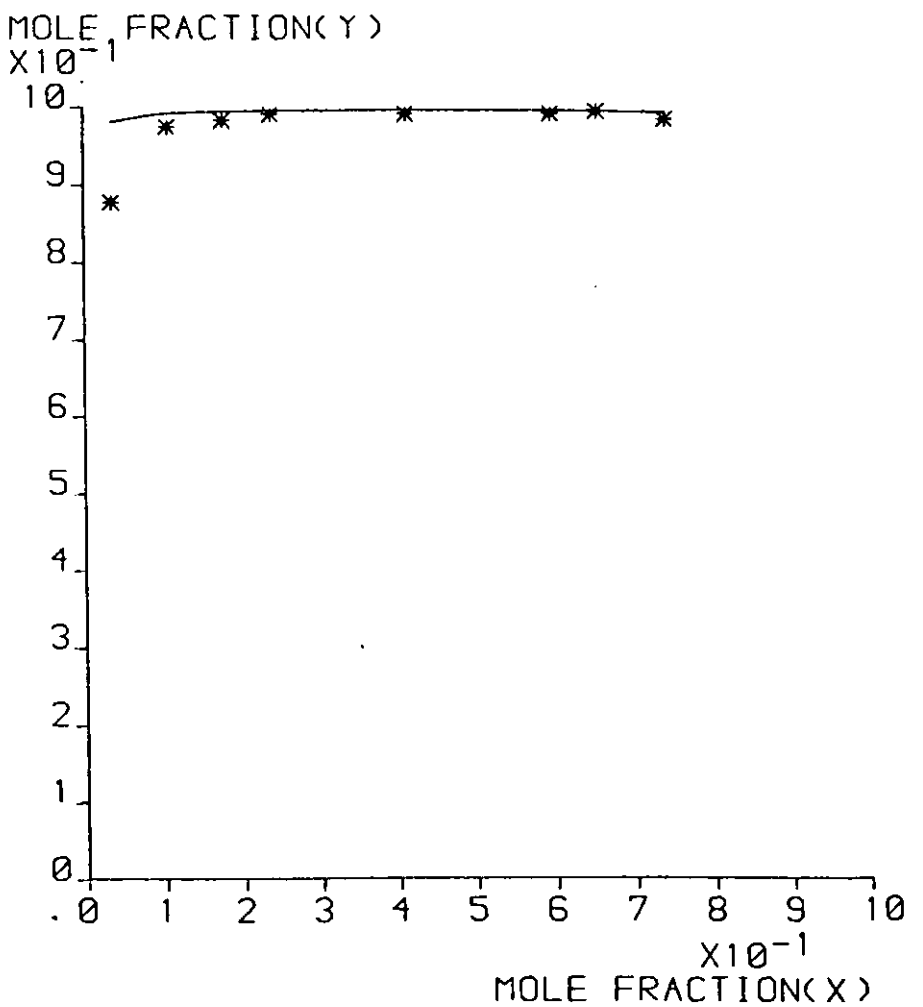


(b)

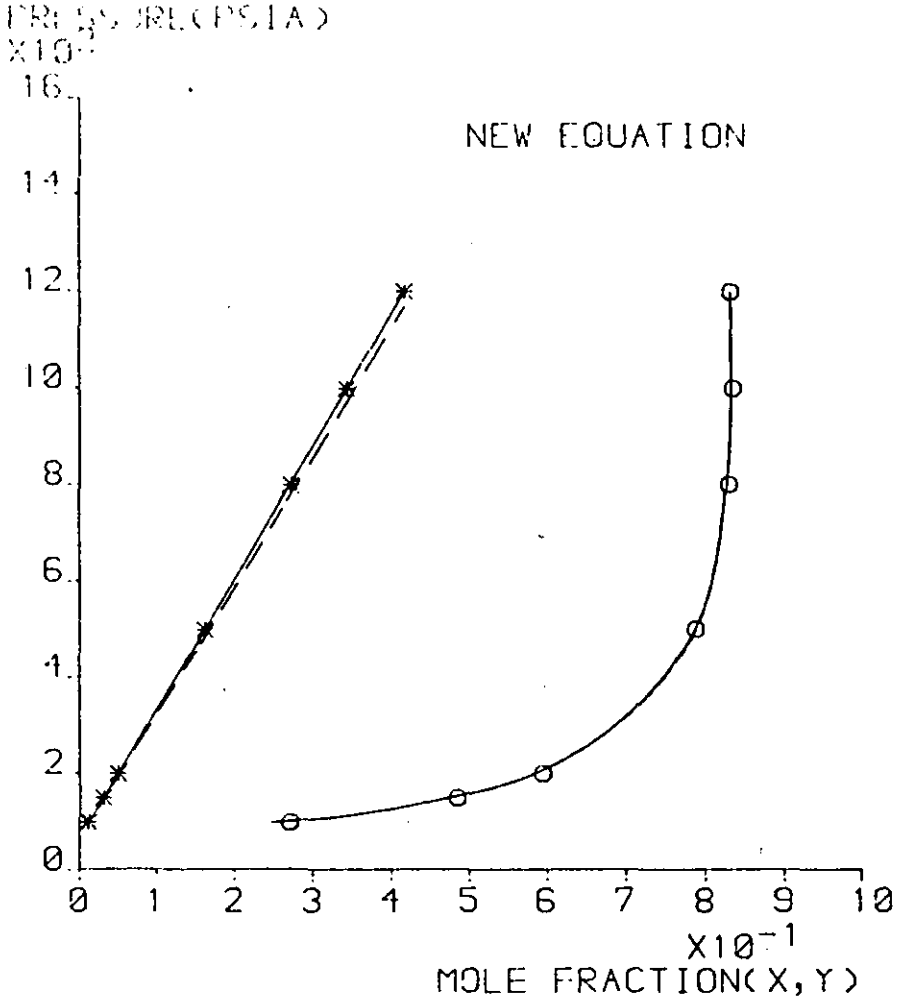


(a)

FIGURE 6.7 Methane-n-Butane System at 379.93°R (211K)

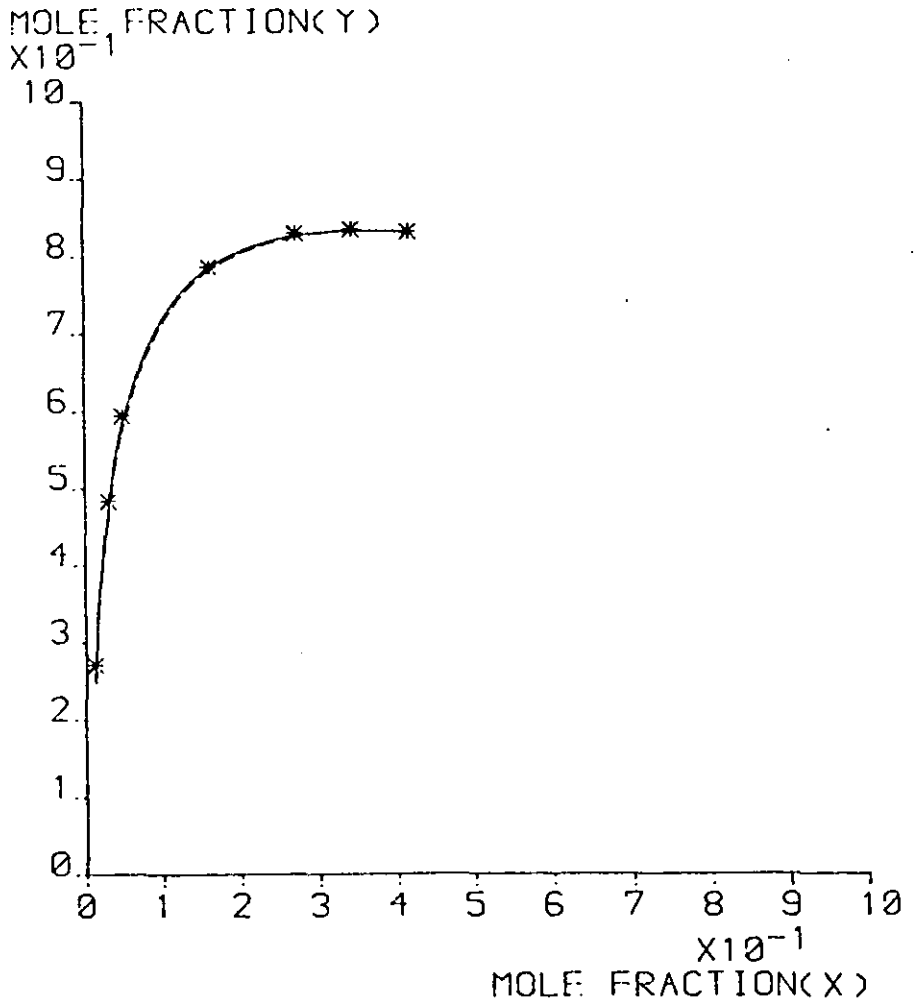


(b)

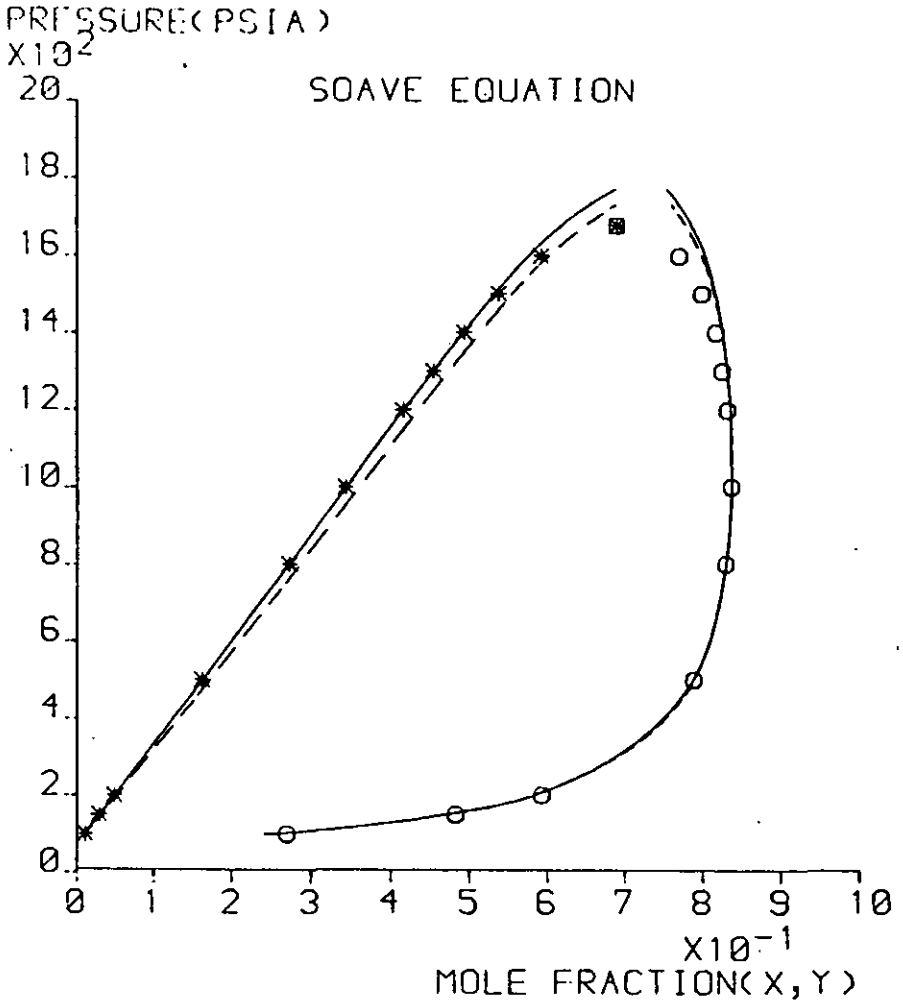


(a)

FIGURE 6.8 Methane-i-Butane System at 559.69°R (311K)

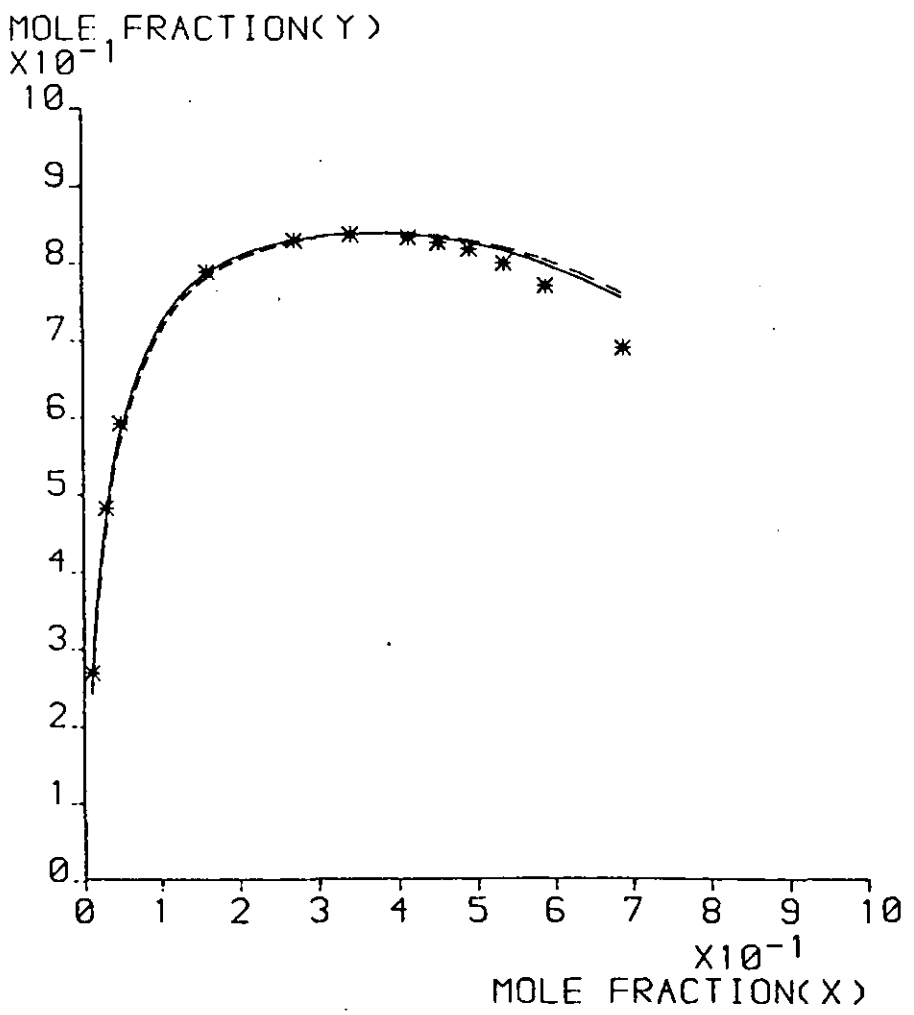


(b)

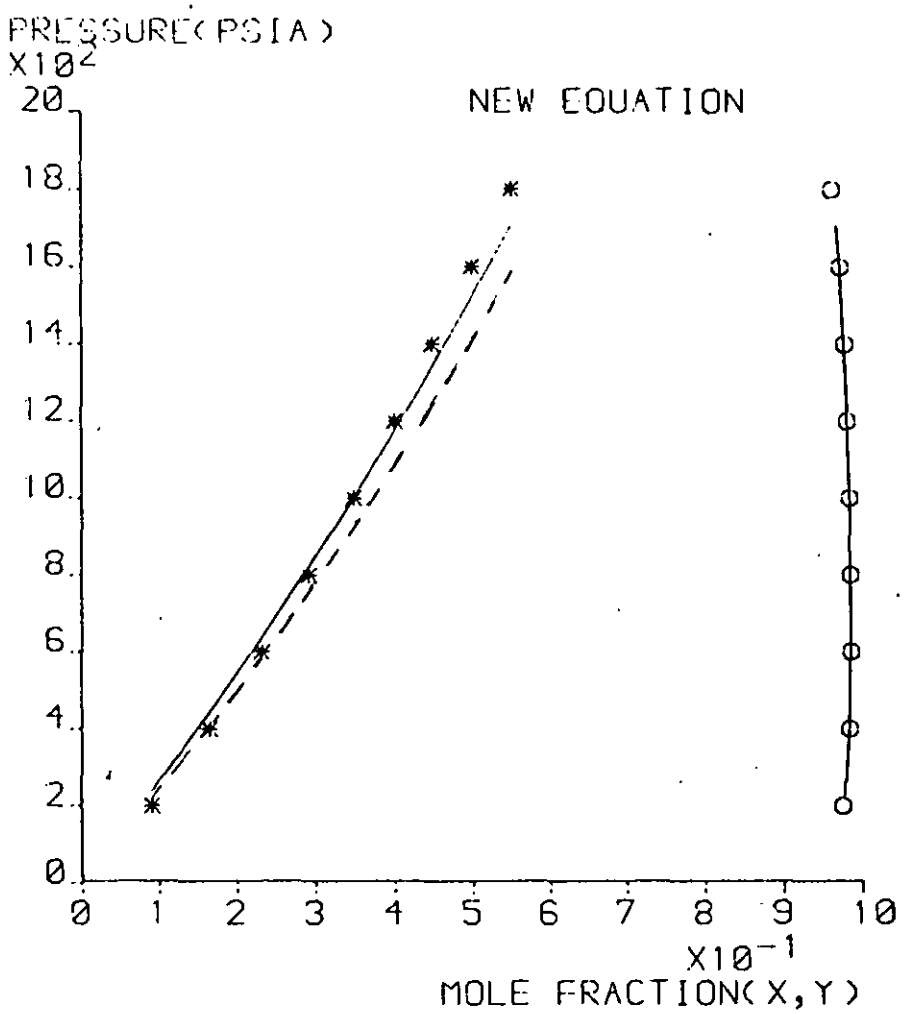


(a)

FIGURE 6.9 Methane-i-Butane System at 559.69°R (311K)

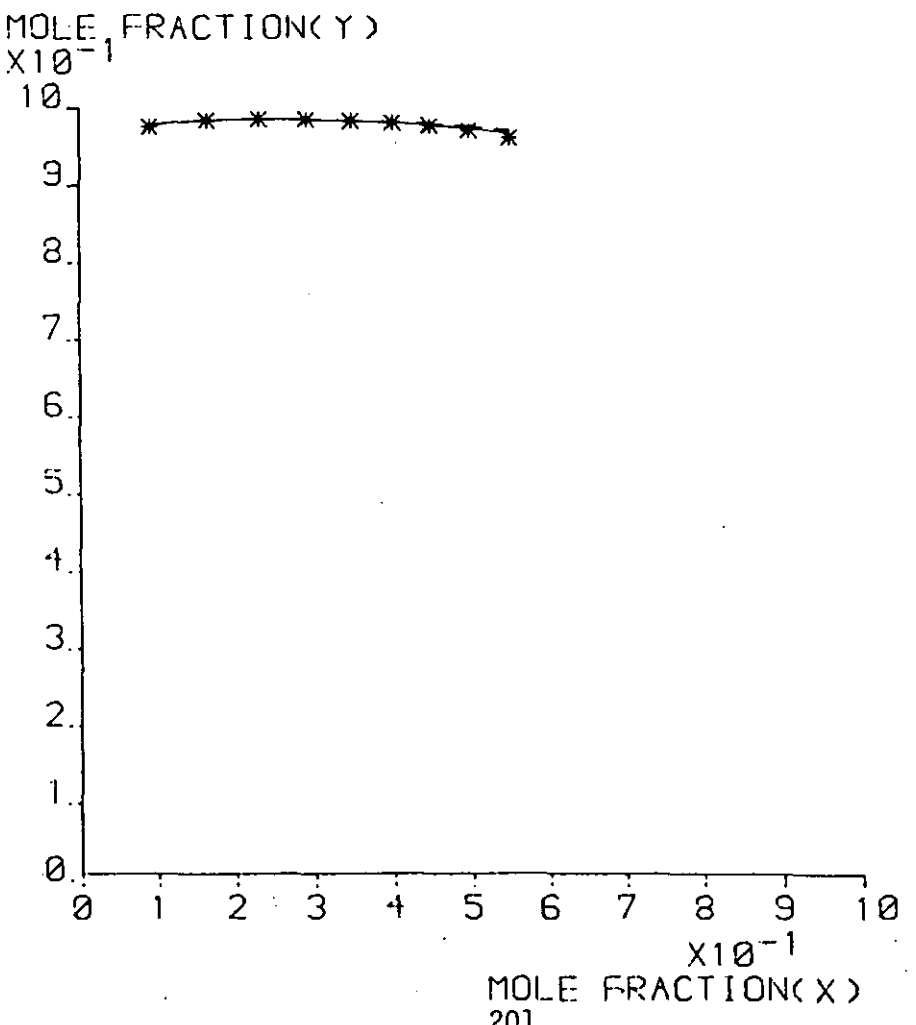


(b)

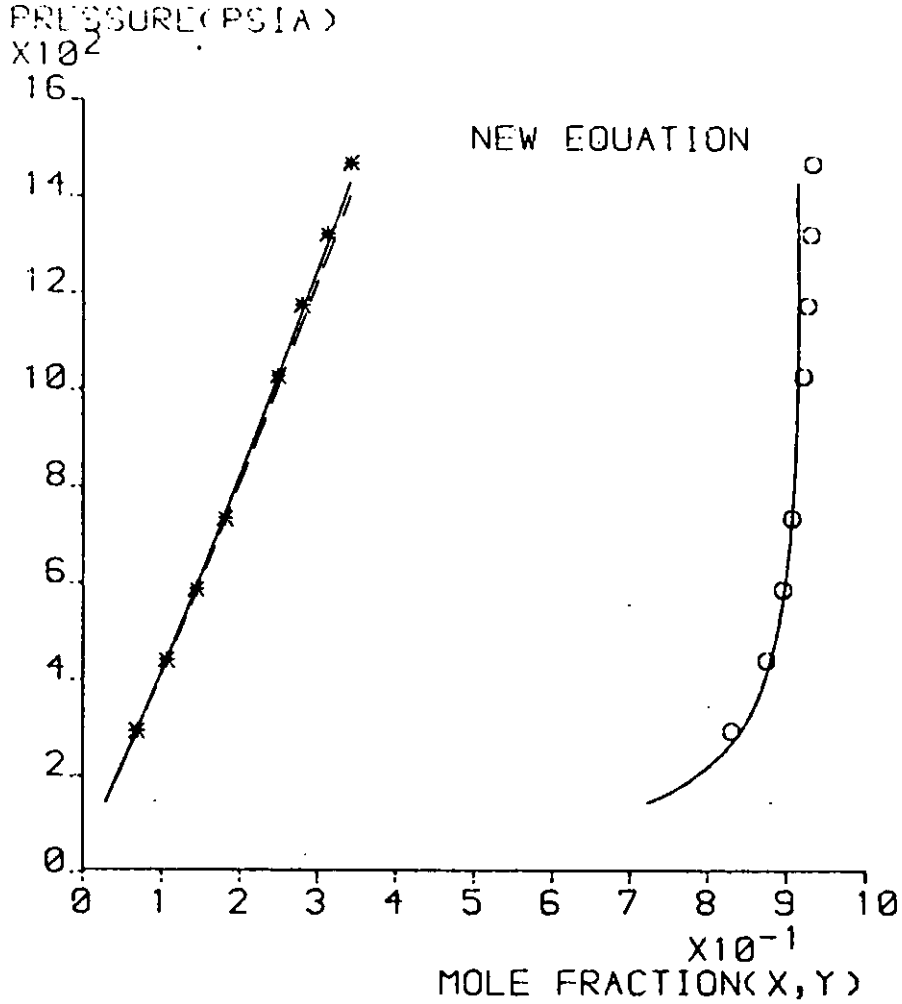


(a)

FIGURE 6.10 Methane-n-Pentane System at 491.69°R (273.2K)

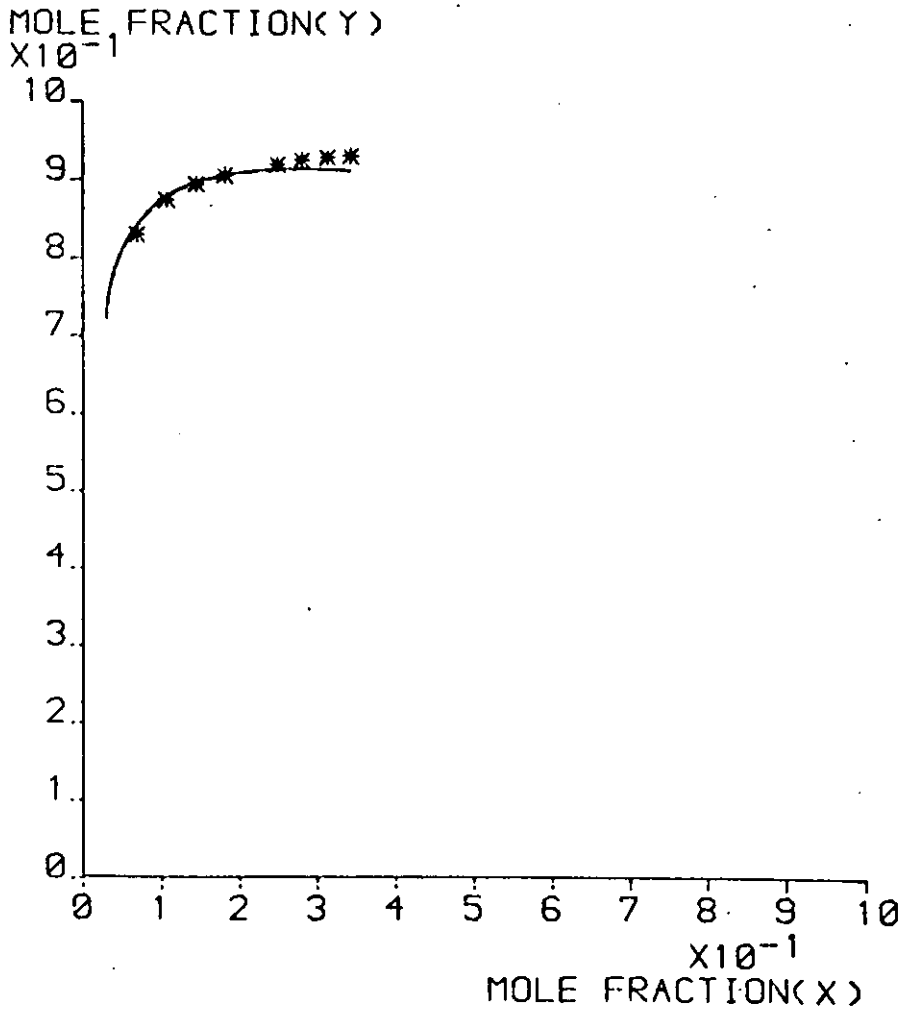


(b)

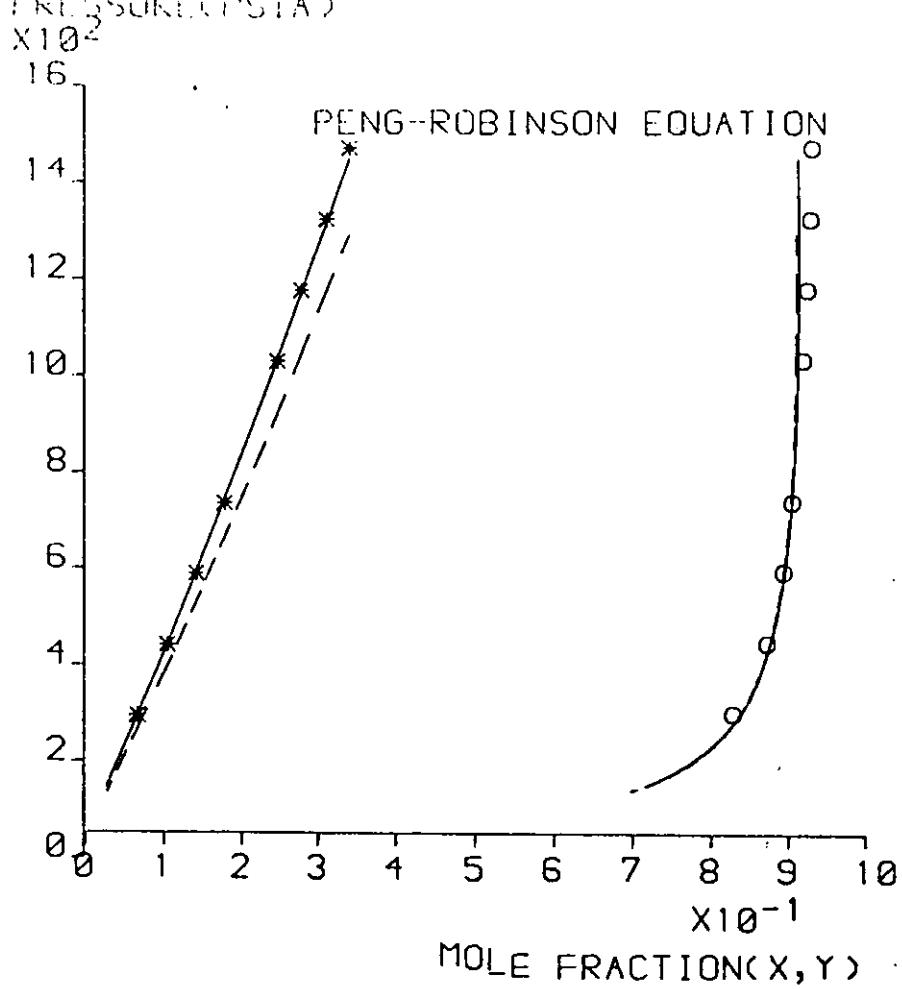


(a)

FIGURE 6.11 Methane-n-Hexane System at 671.69°R (373.2K)

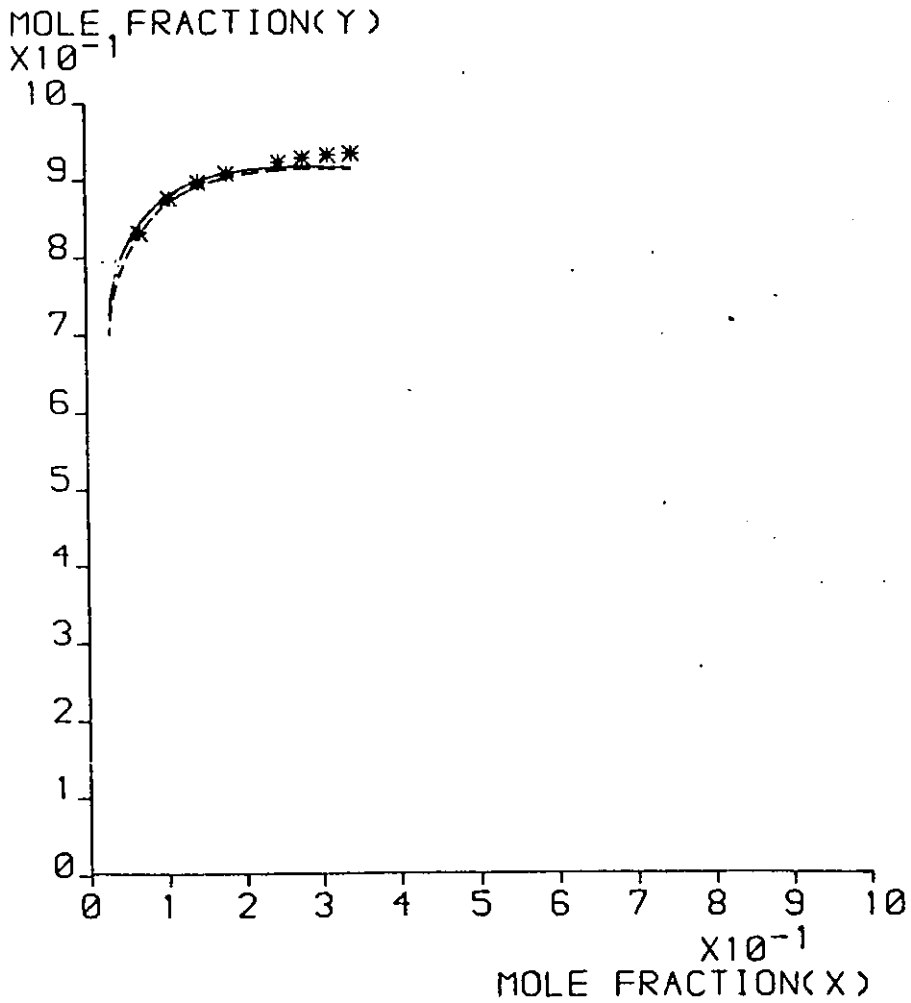


(b)

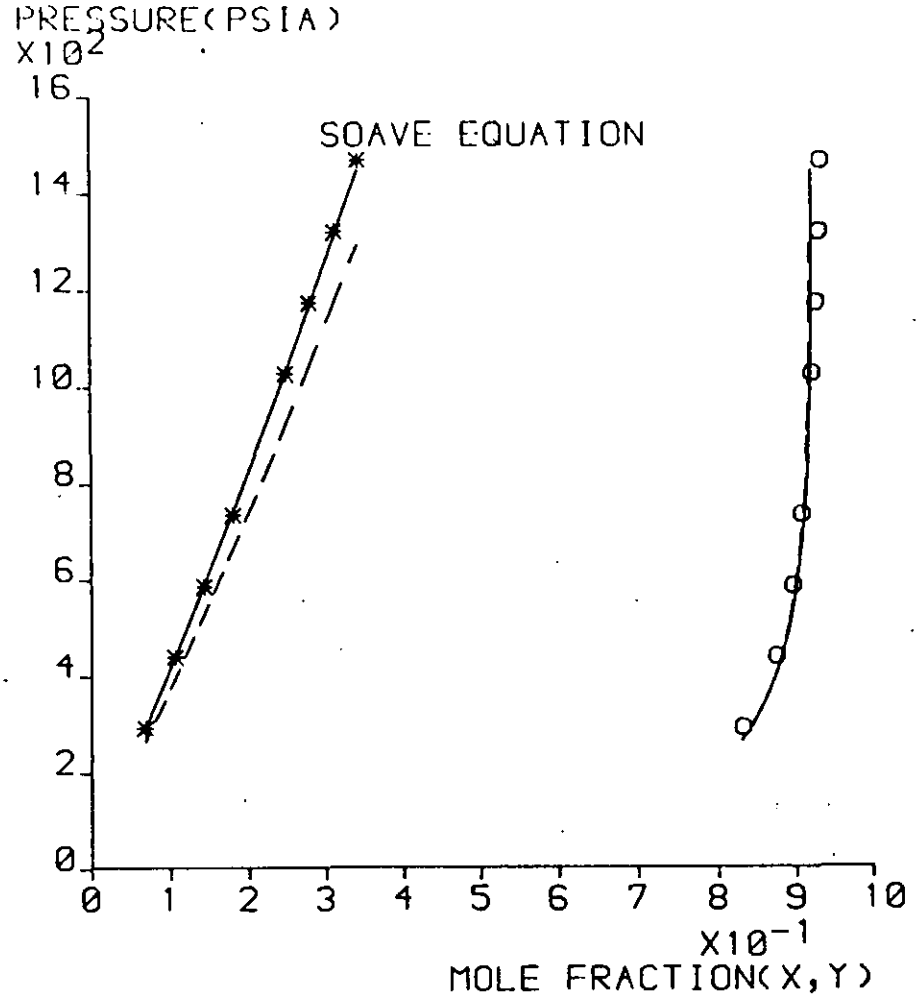


(a)

FIGURE 6.12 Methane-Hexane System at 671.69°R (373.2K)

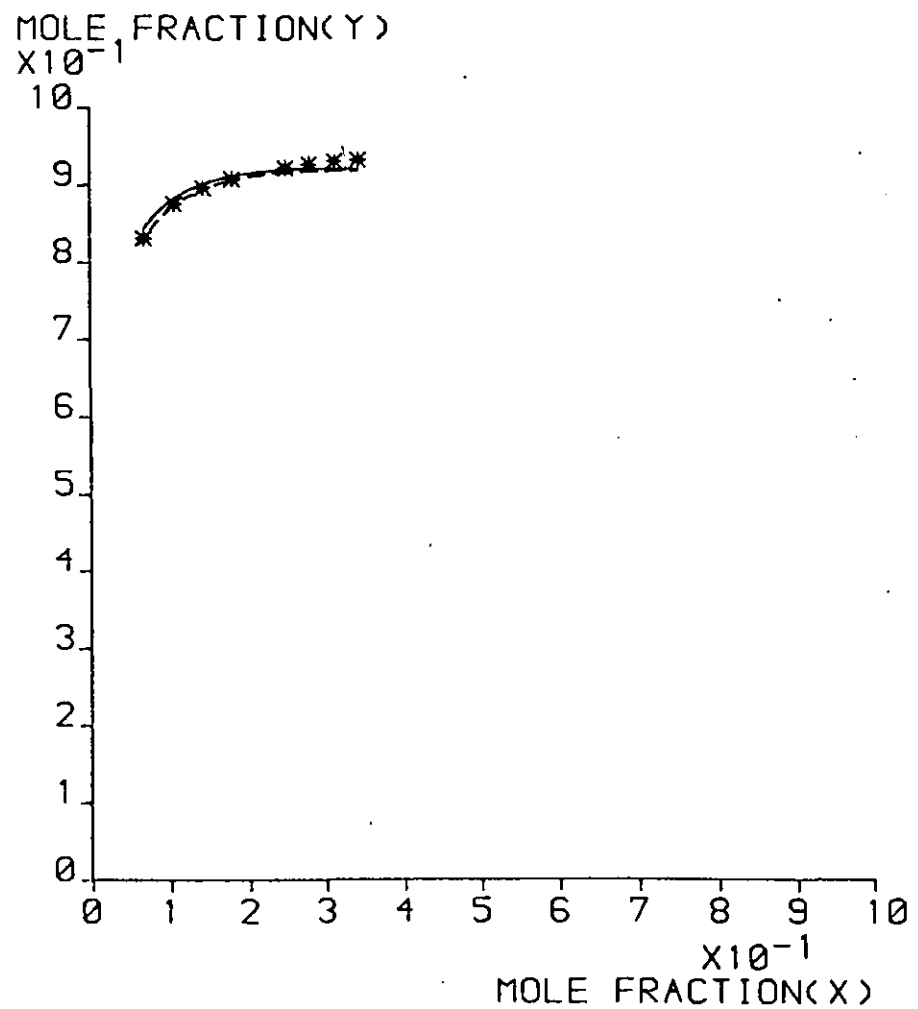


(b)

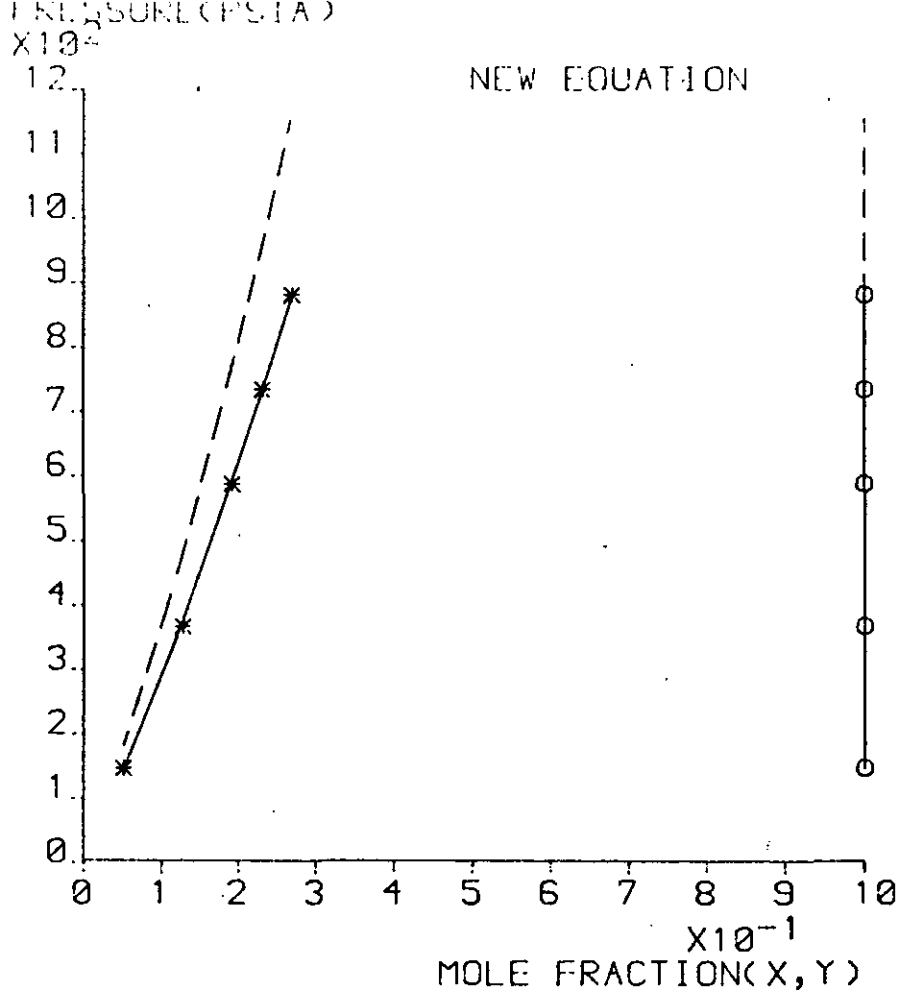


(a)

FIGURE 6.13 Methane-Hexane System at 671.69°R (373.2K)

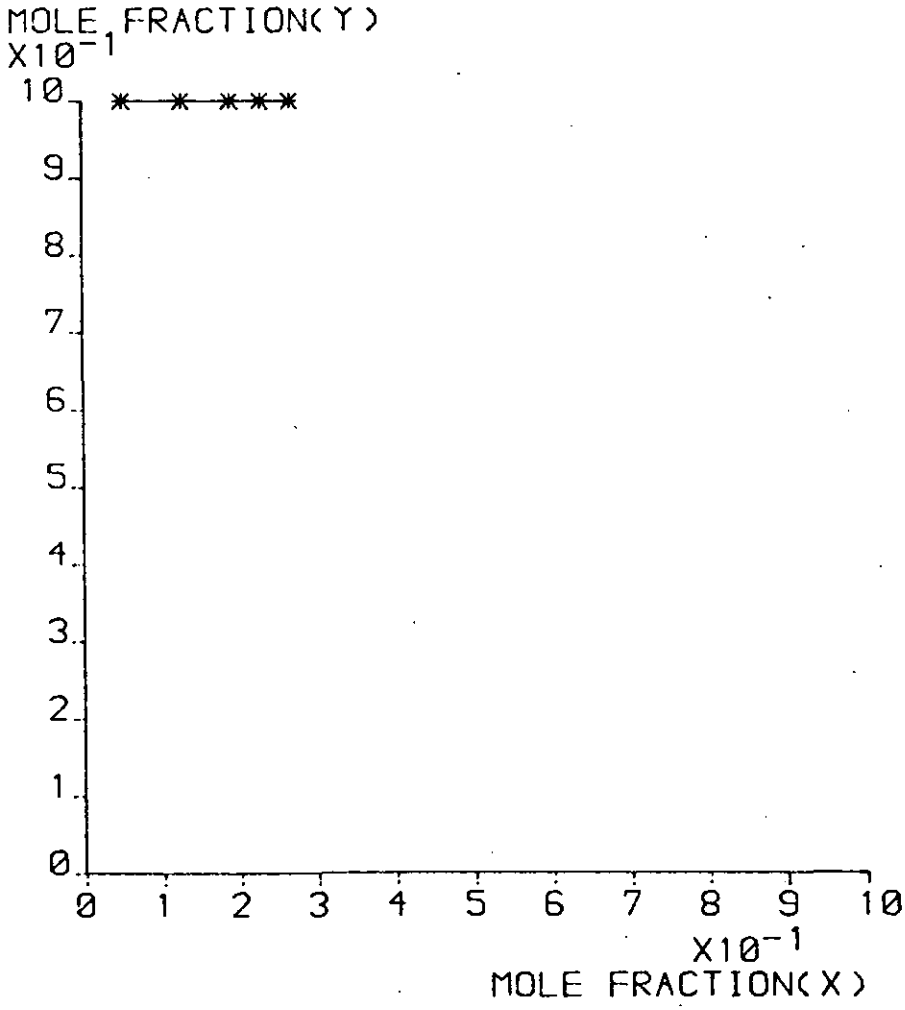


(b)

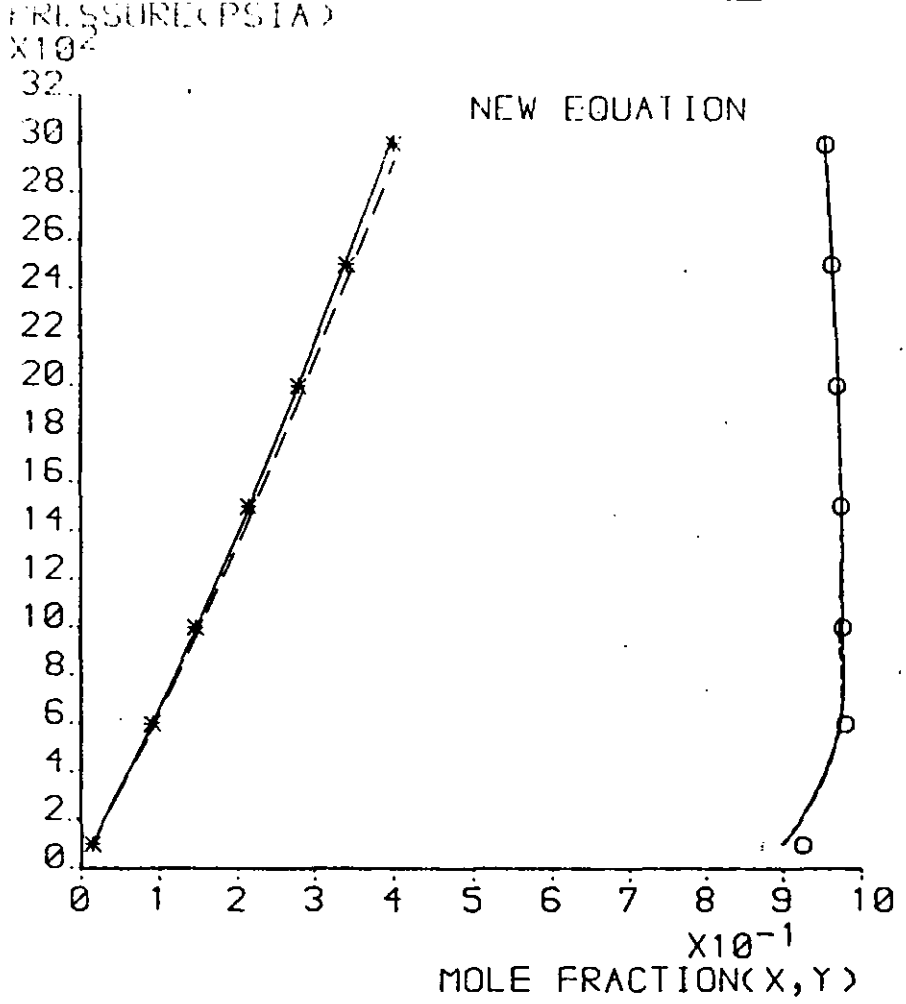


(a)

FIGURE 6.14 Methane-n-Eicosane System at 563.67°R (313.2K)

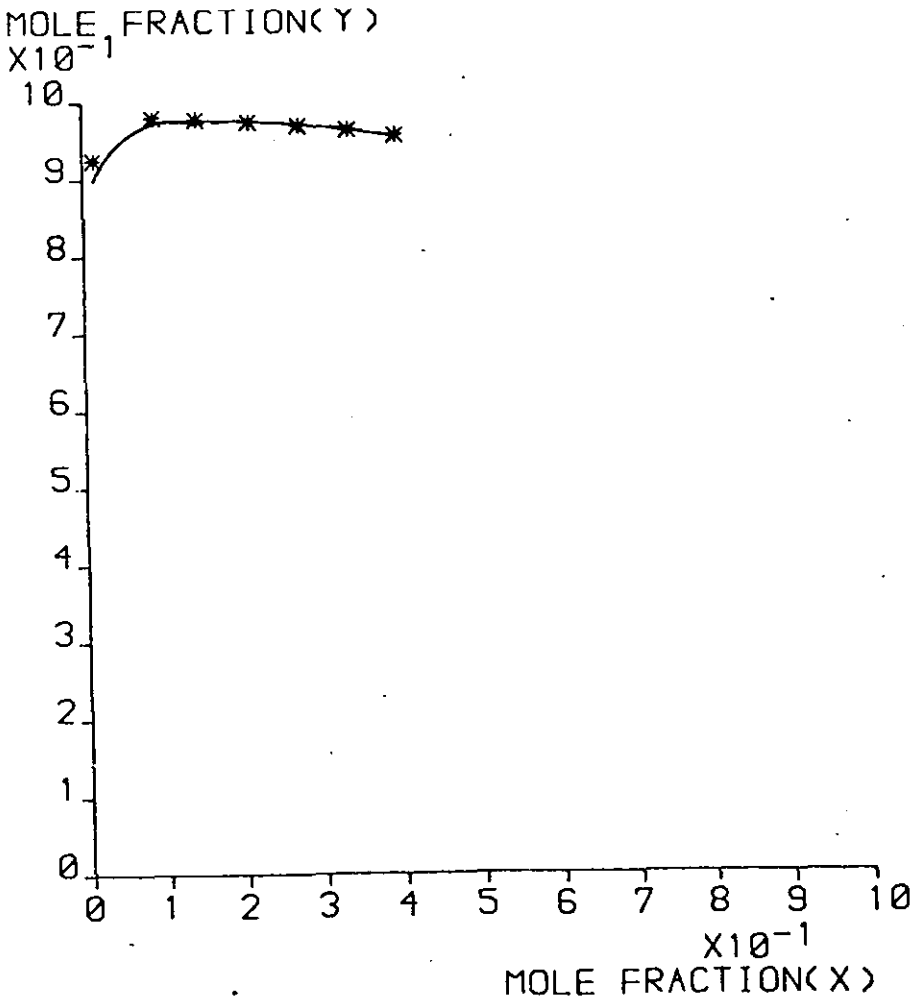


(b)

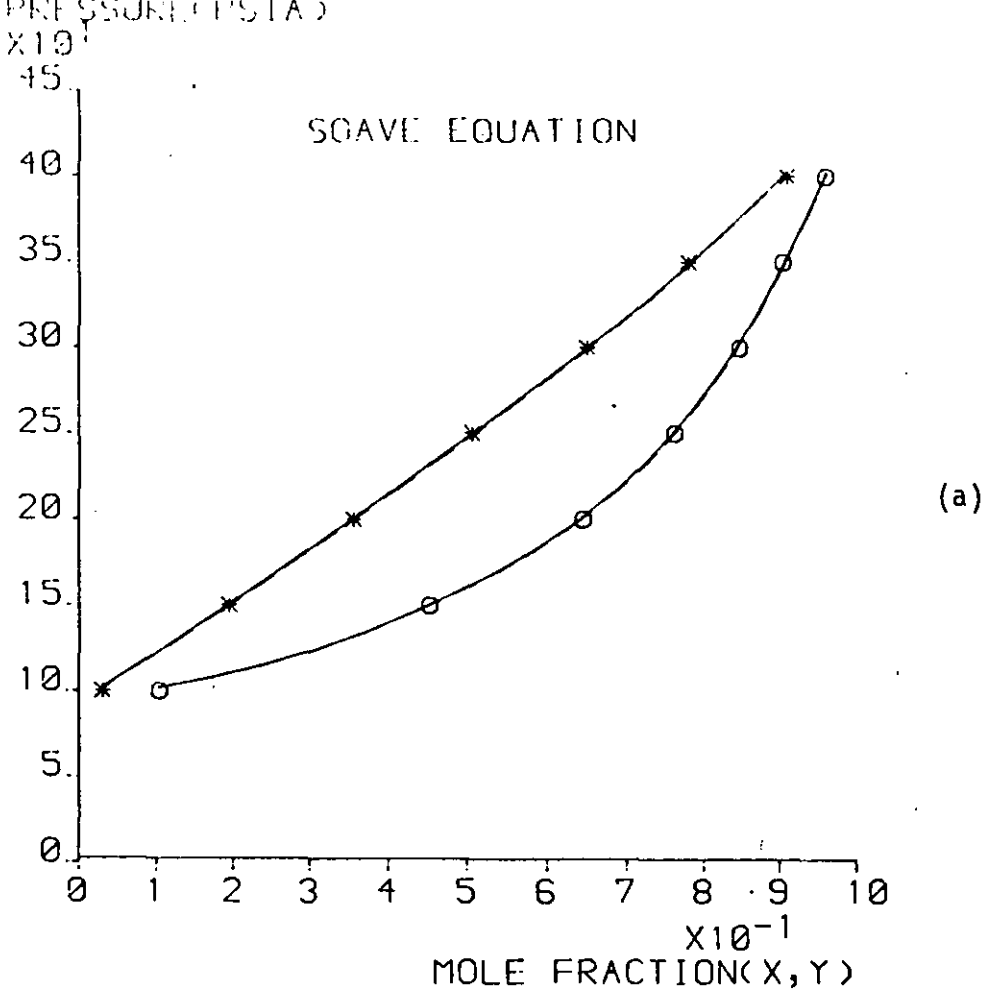


(a)

FIGURE 6.15 Methane-Benzene System at 609.75°R (338.8K)

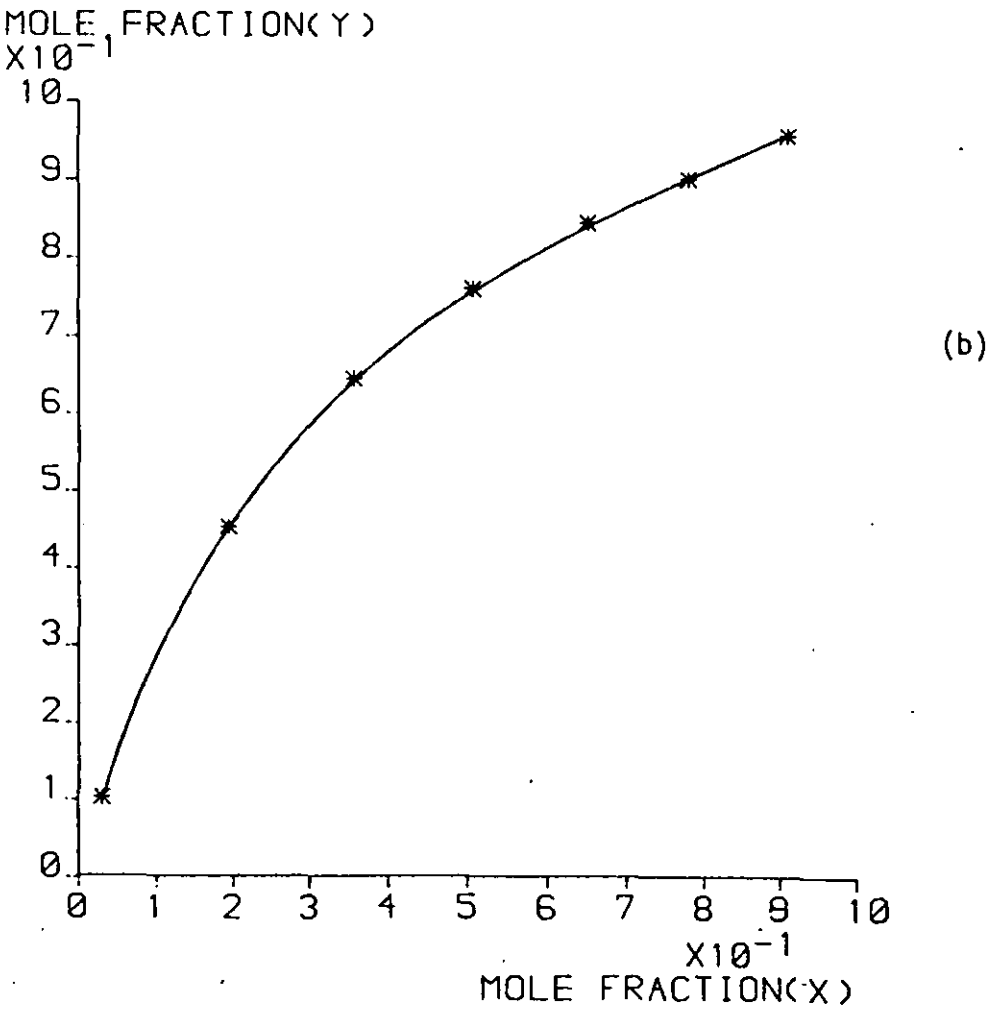


(b)

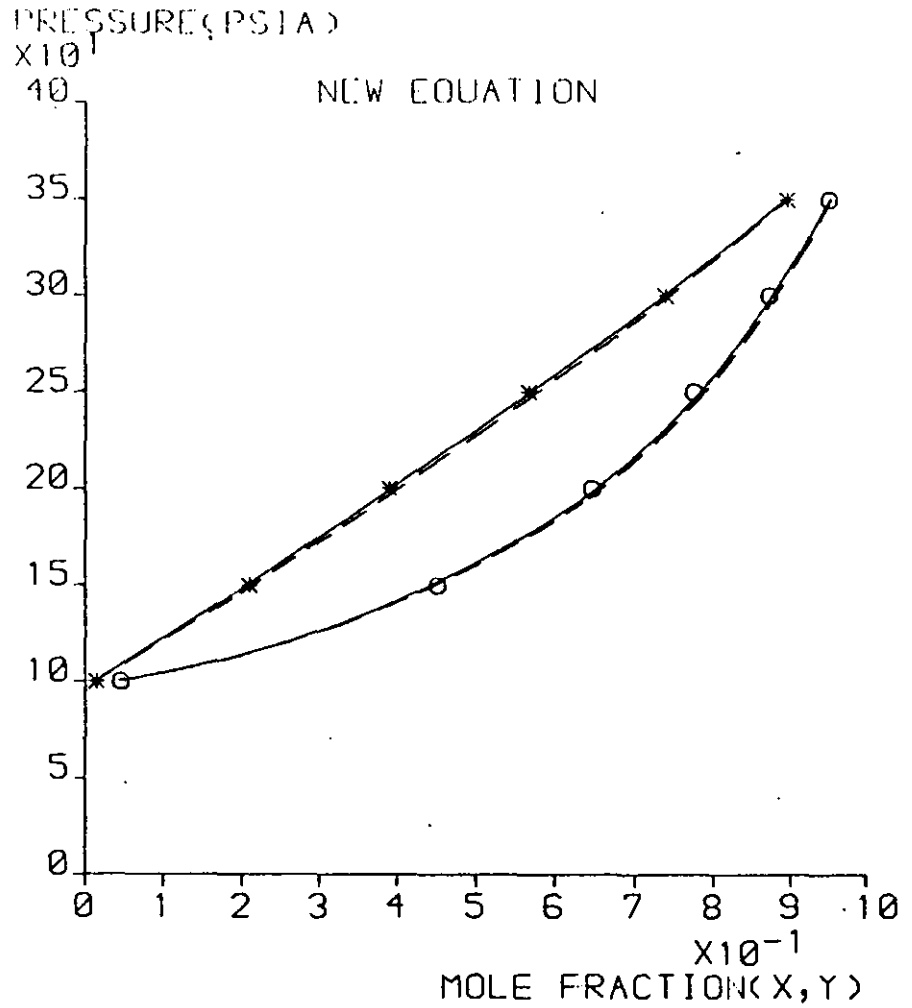


(a)

FIGURE 5.16 Ethane-Propane System at 491.61°R (277.6K)

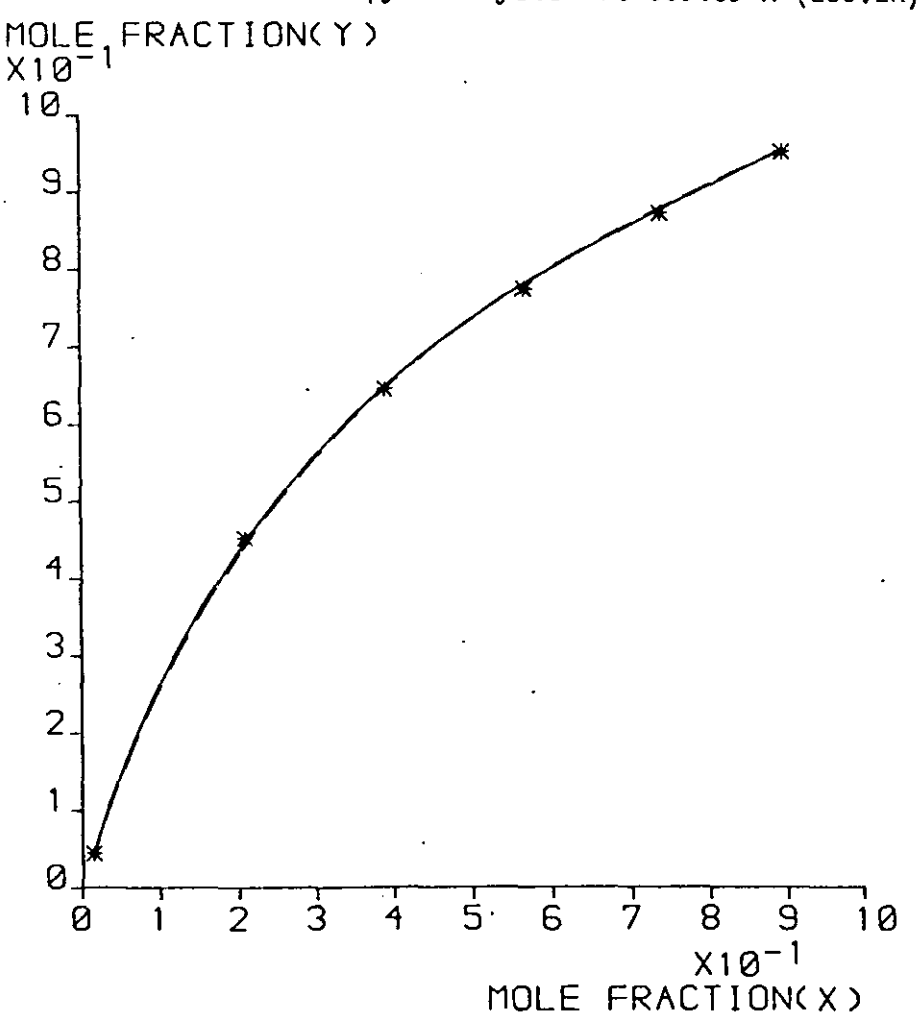


(b)

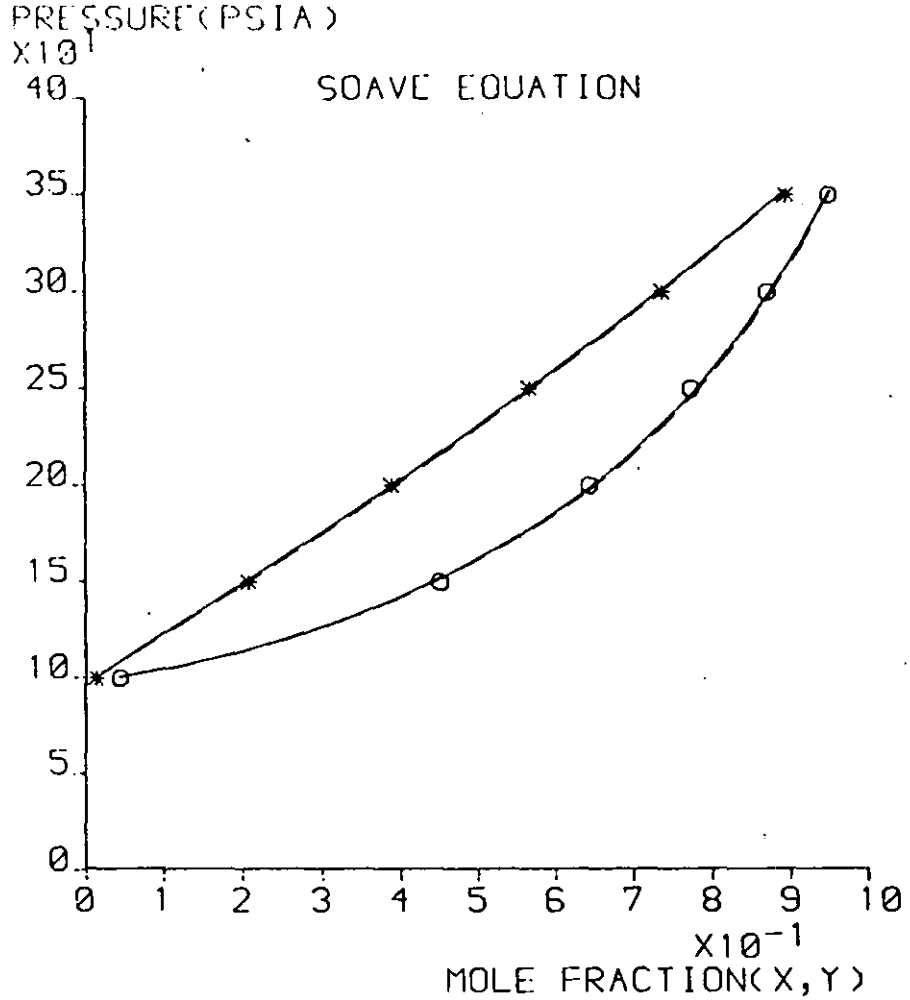


(a)

FIGURE 6.17 Ethane-Propylene System at 509.69°R (283.2K)

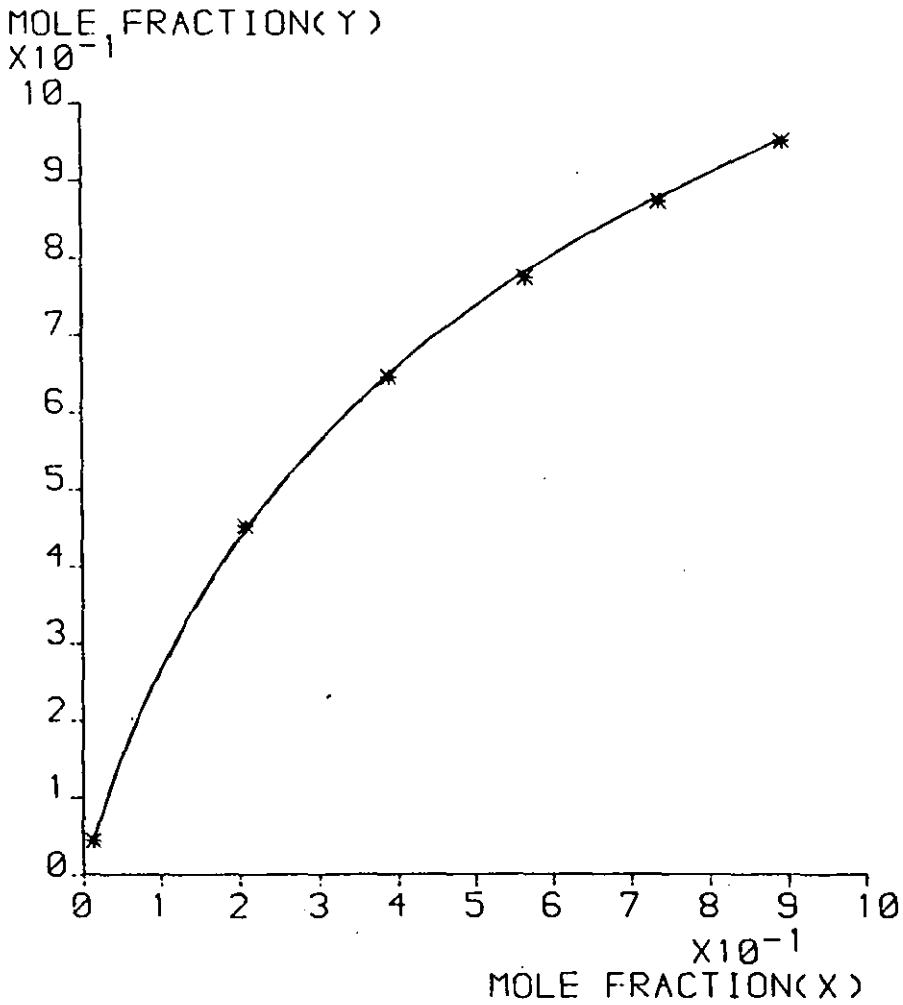


(b)

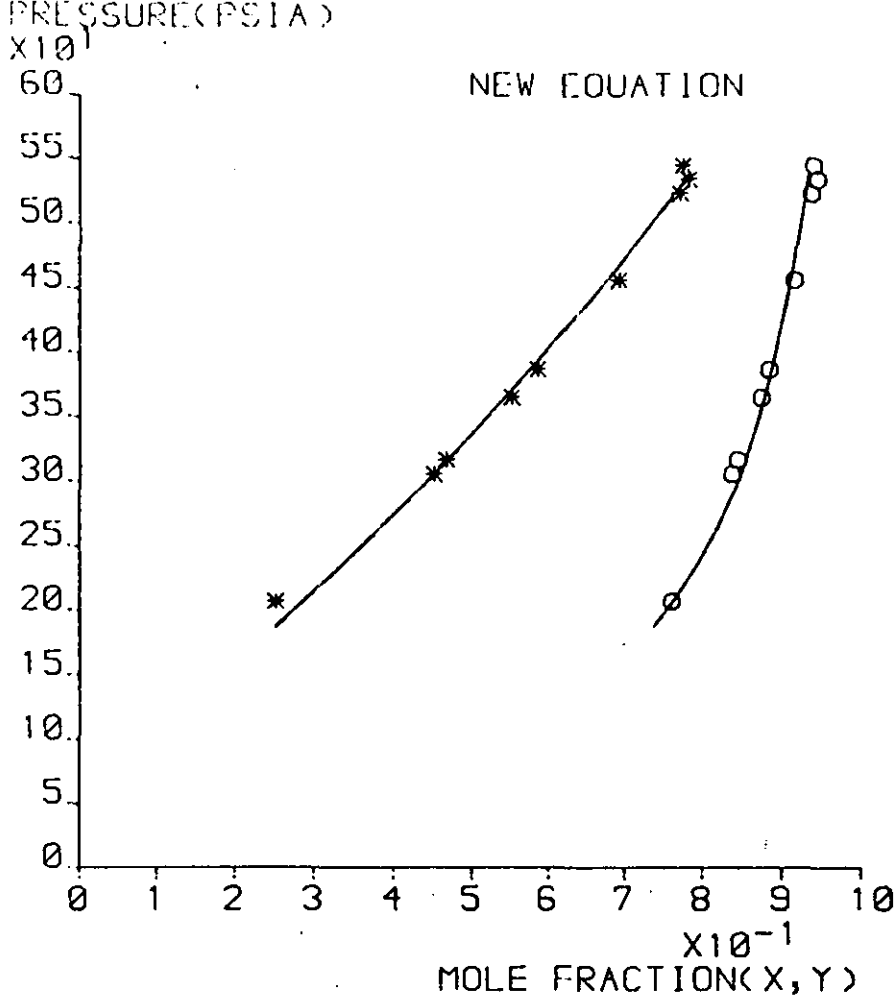


(a)

FIGURE 6.18 Ethane-Propylene System at 509.69^{0}R (283.2K)

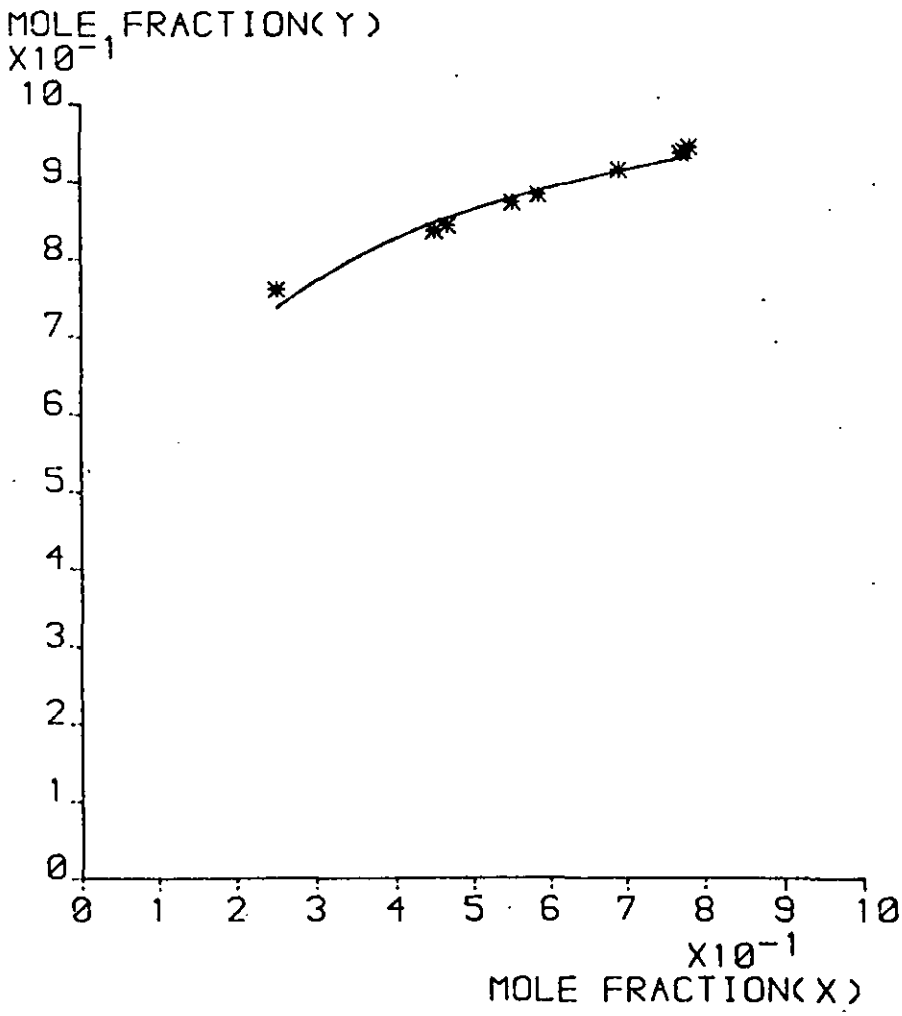


(b)

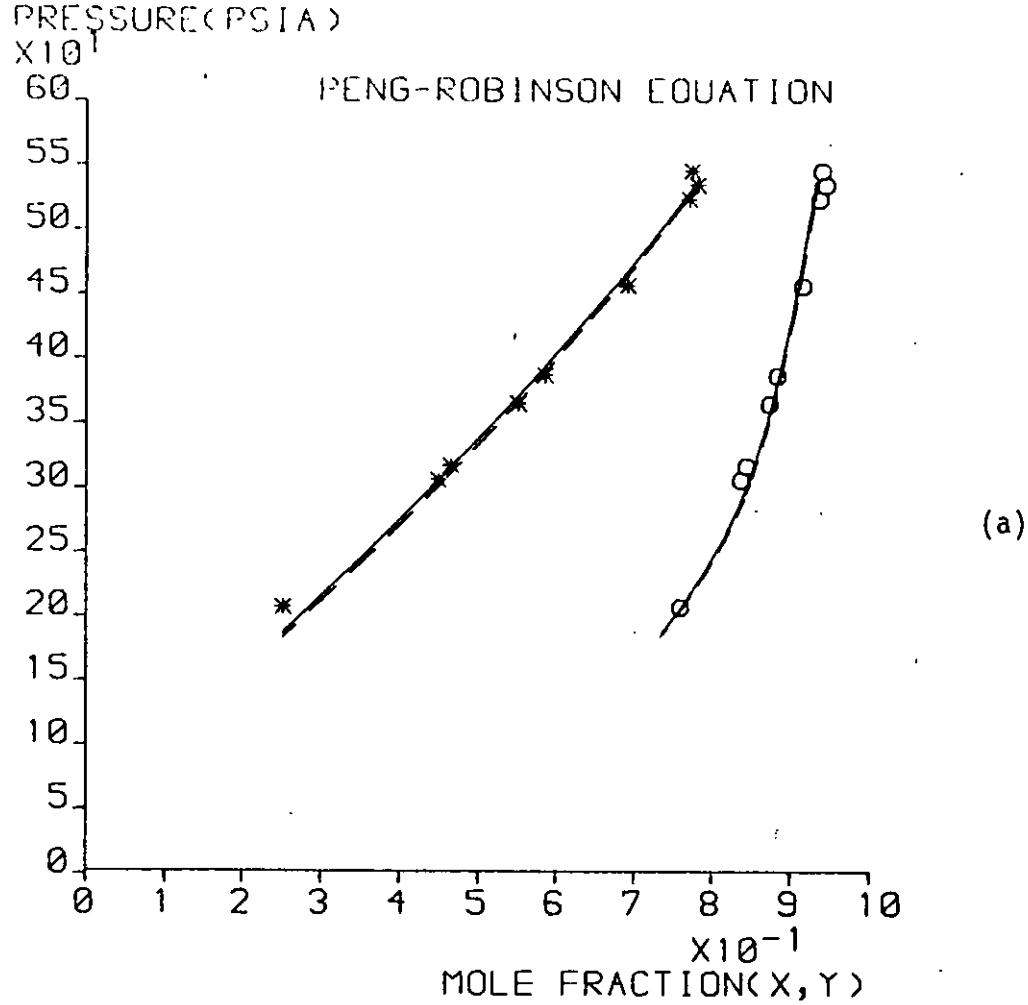


(a)

FIGURE 6.19 Ethane-n-Butane System at 558.65°R (310.4K)

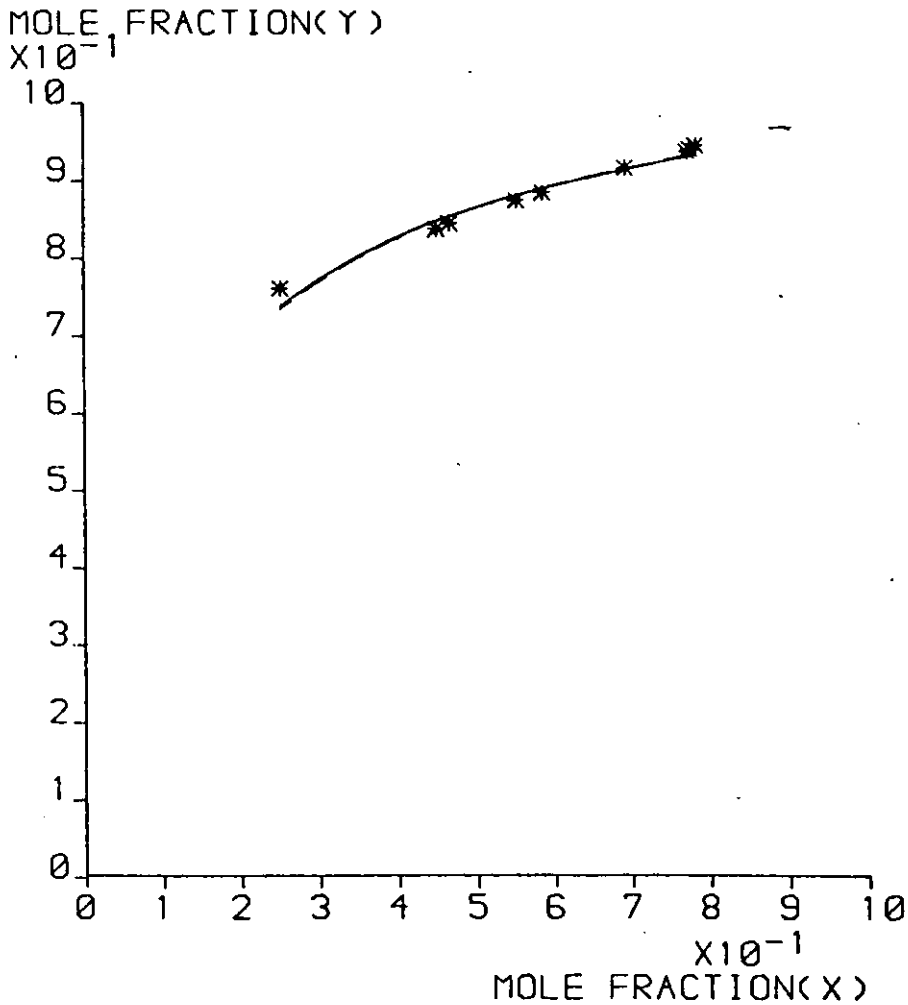


(b)

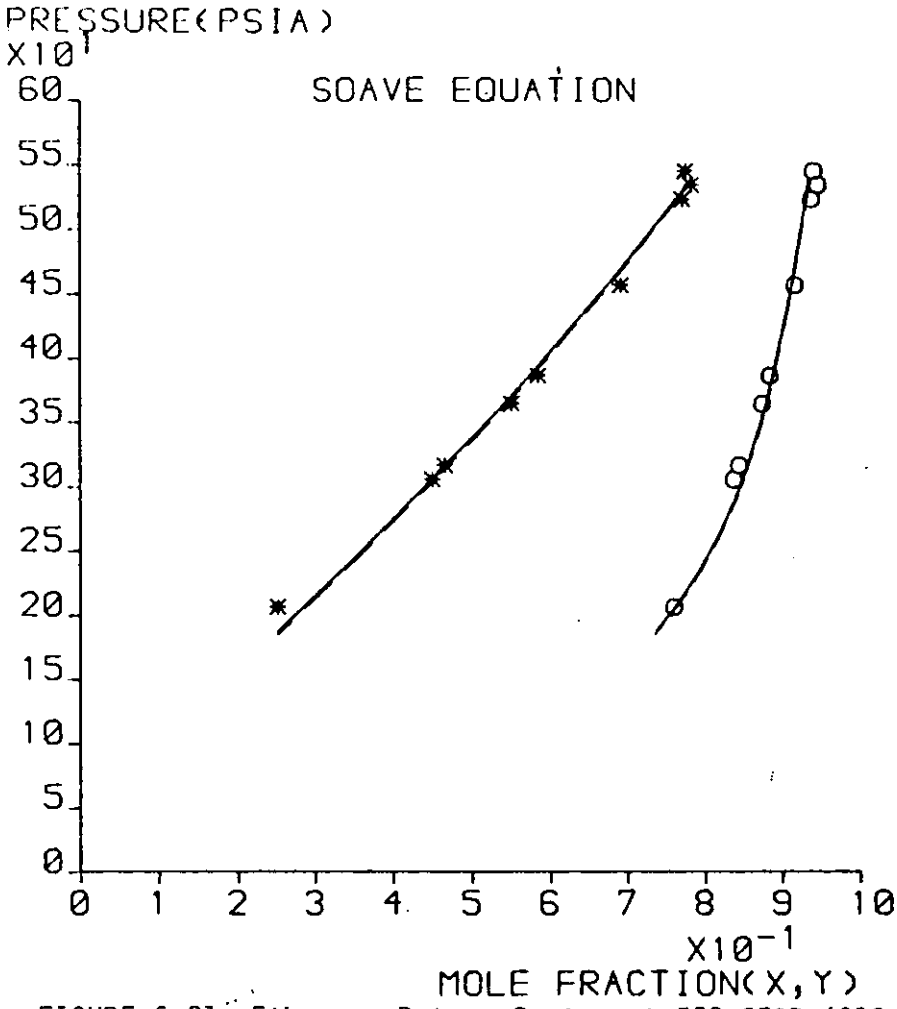


(a)

FIGURE 6.20 · Ethane-n-Butane System at 558.65°R (310.4K)

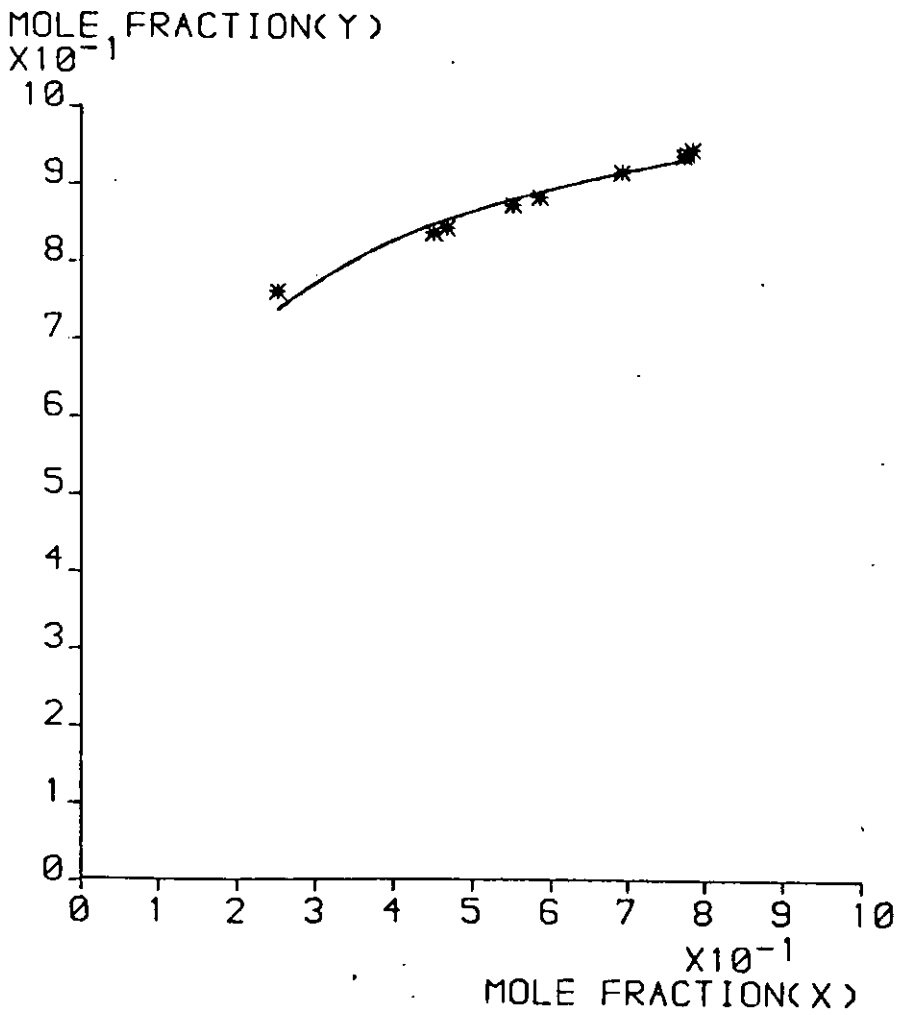


(b)



(a)

FIGURE 6.21 Ethane-n-Butane System at 558.65°R (310.4K)



(b)

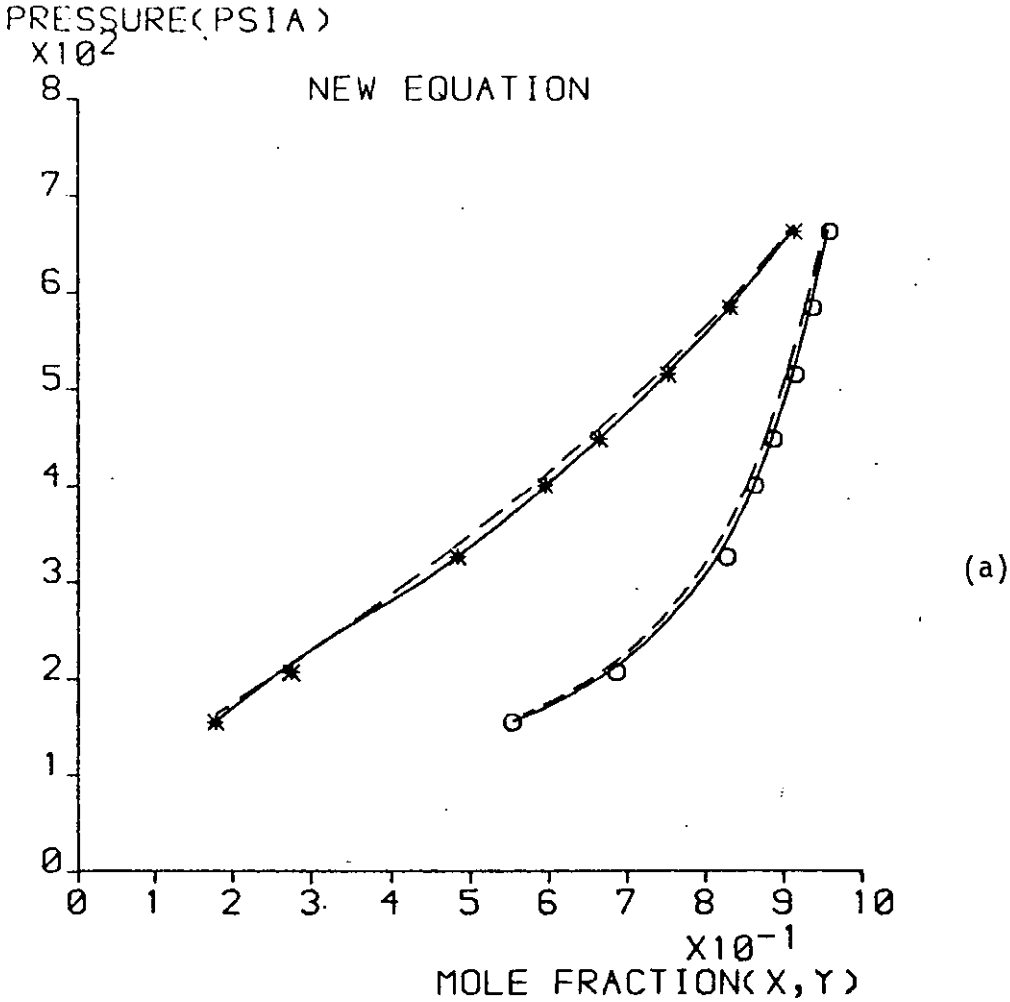
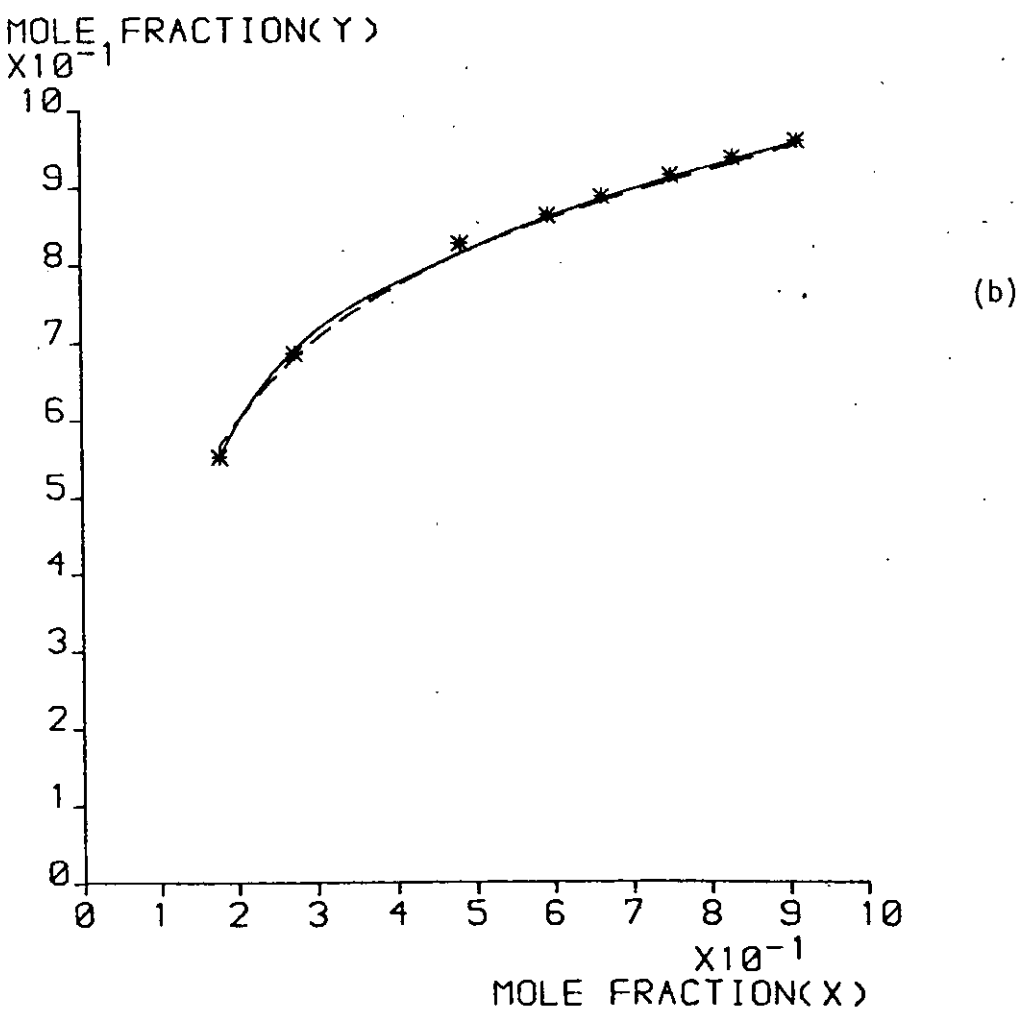
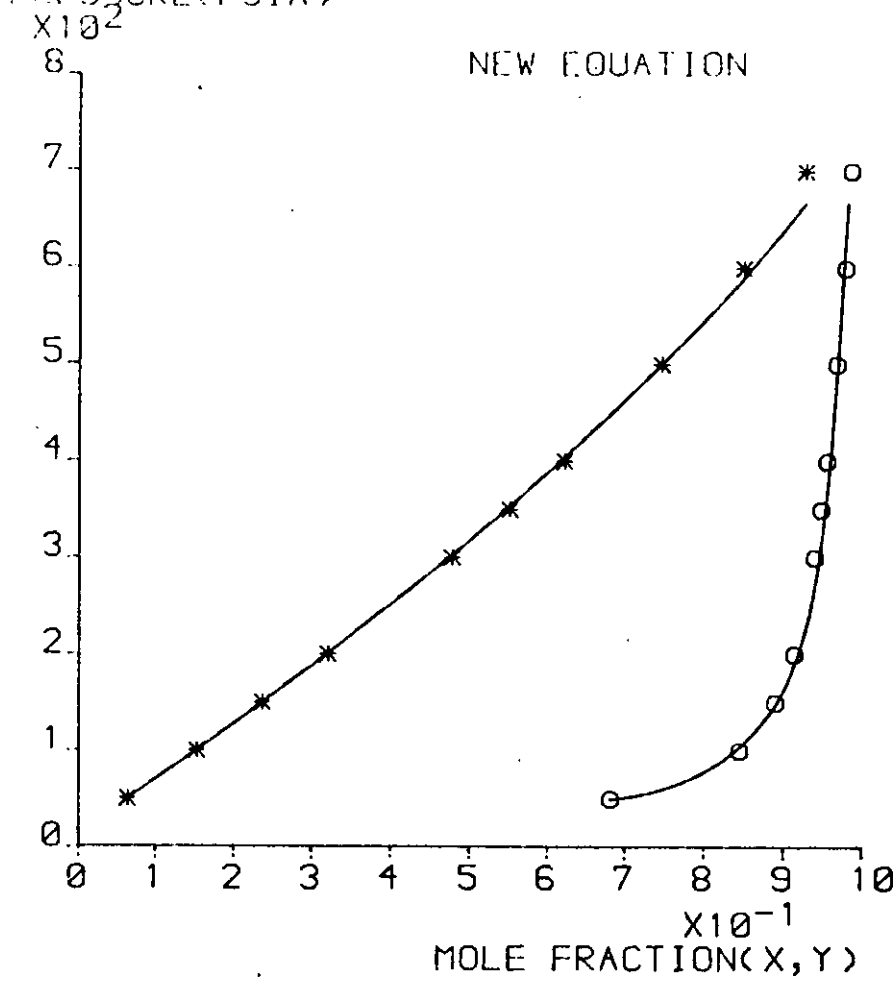


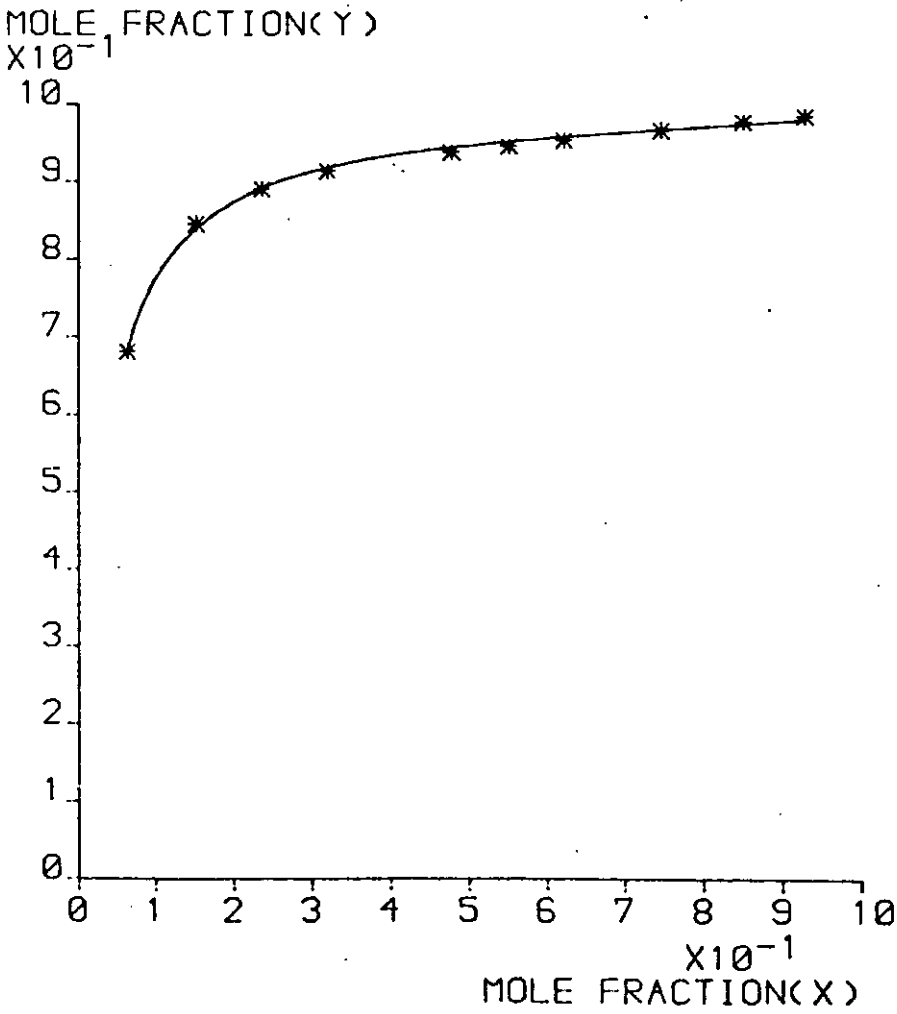
FIGURE 6.22 Ethane-i-Butane System at 560.27°R (311.8K)



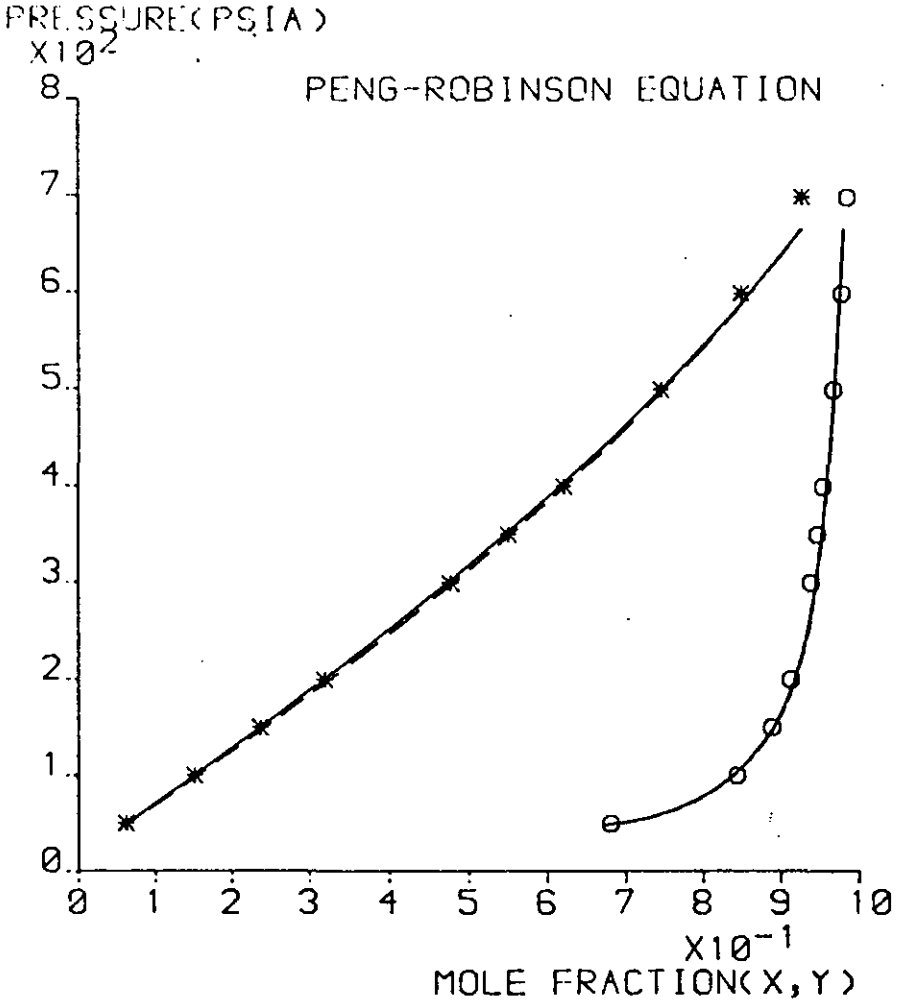


(a)

FIGURE 6.23 Ethane-n-Pentane System at 559.73°R (311K)

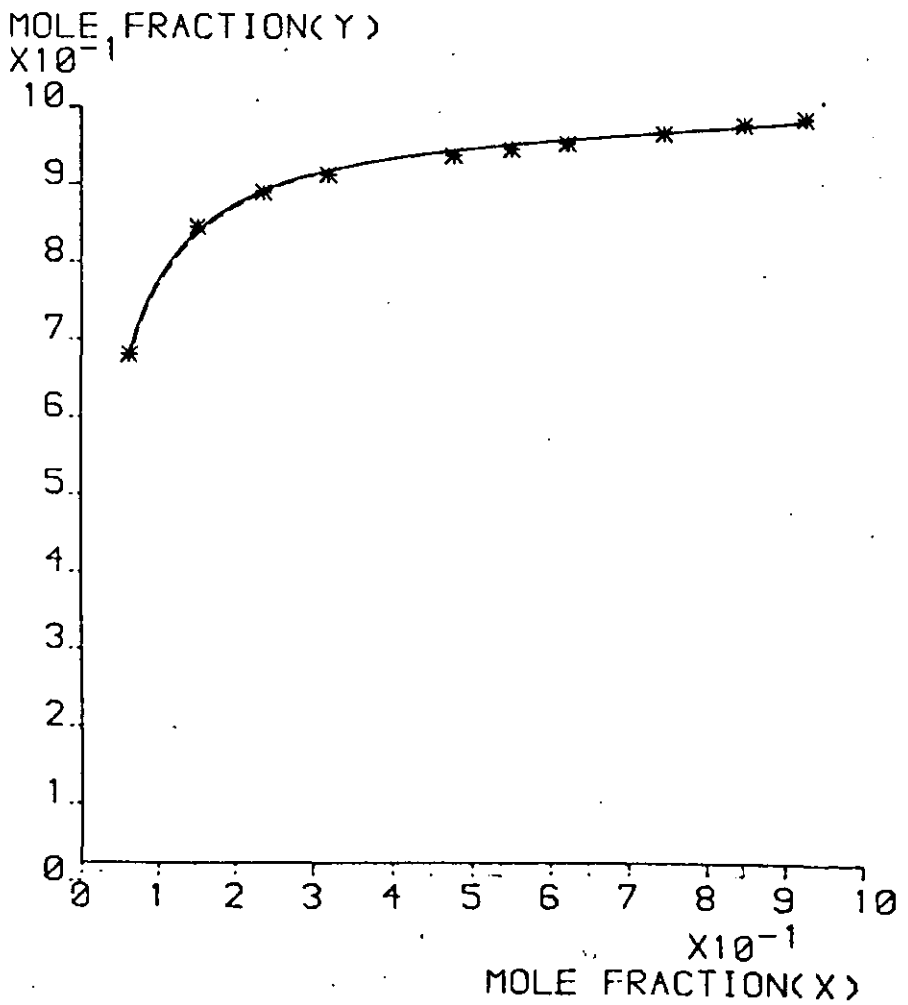


(b)

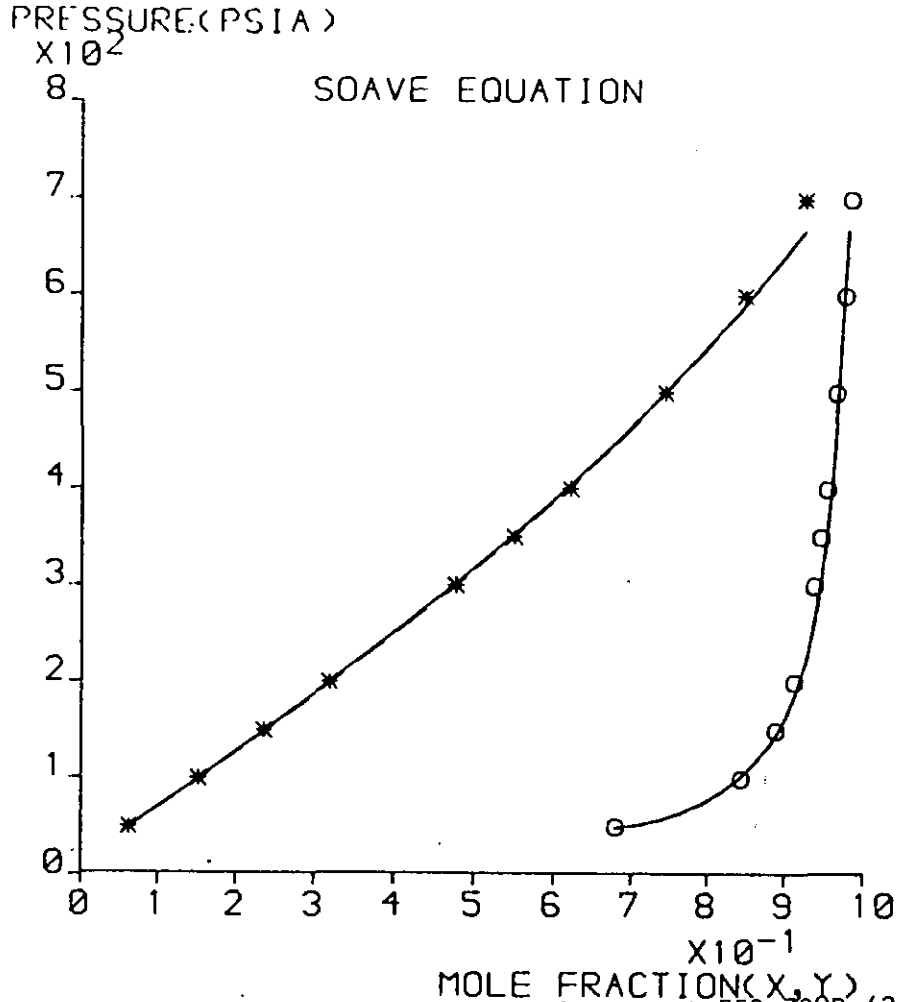


(a)

FIGURE 6.24 Ethane-n-Pentane System at 559.73°R (311K)

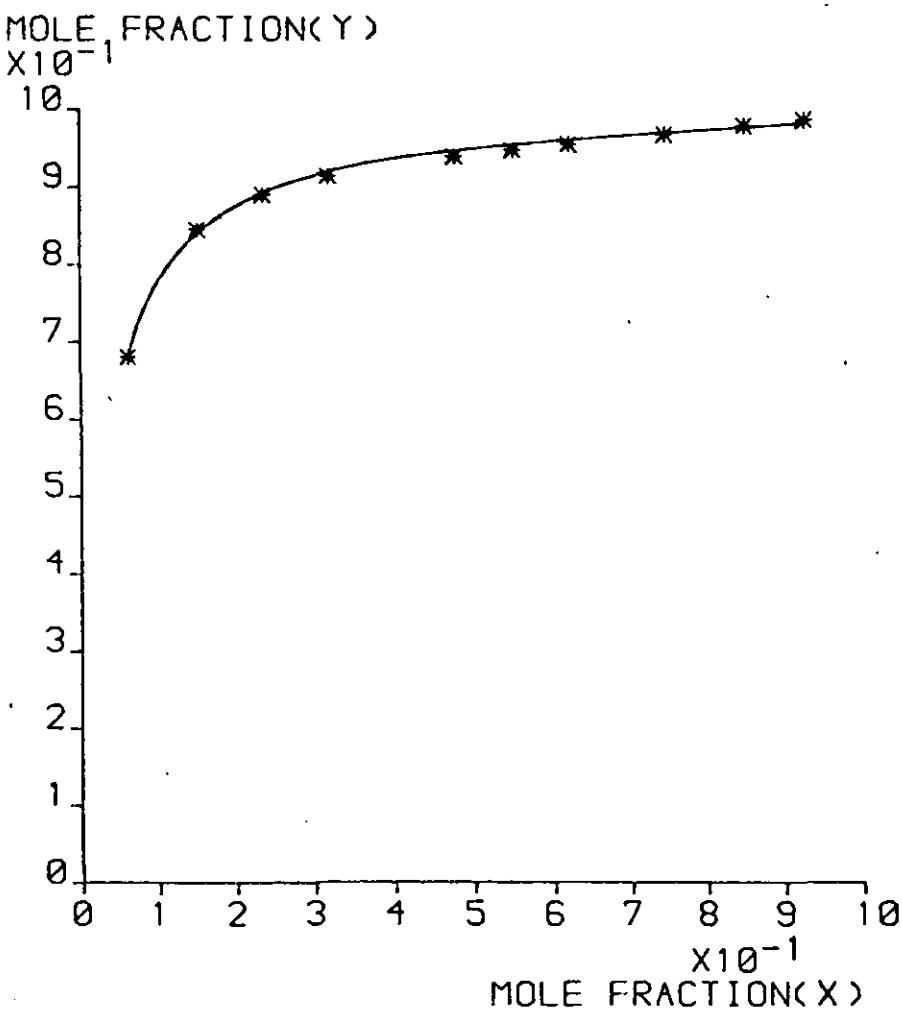


(b)



(a)

FIGURE 6.25 Ethane-n-Pentane System at 559.73°R (311K)



(b)

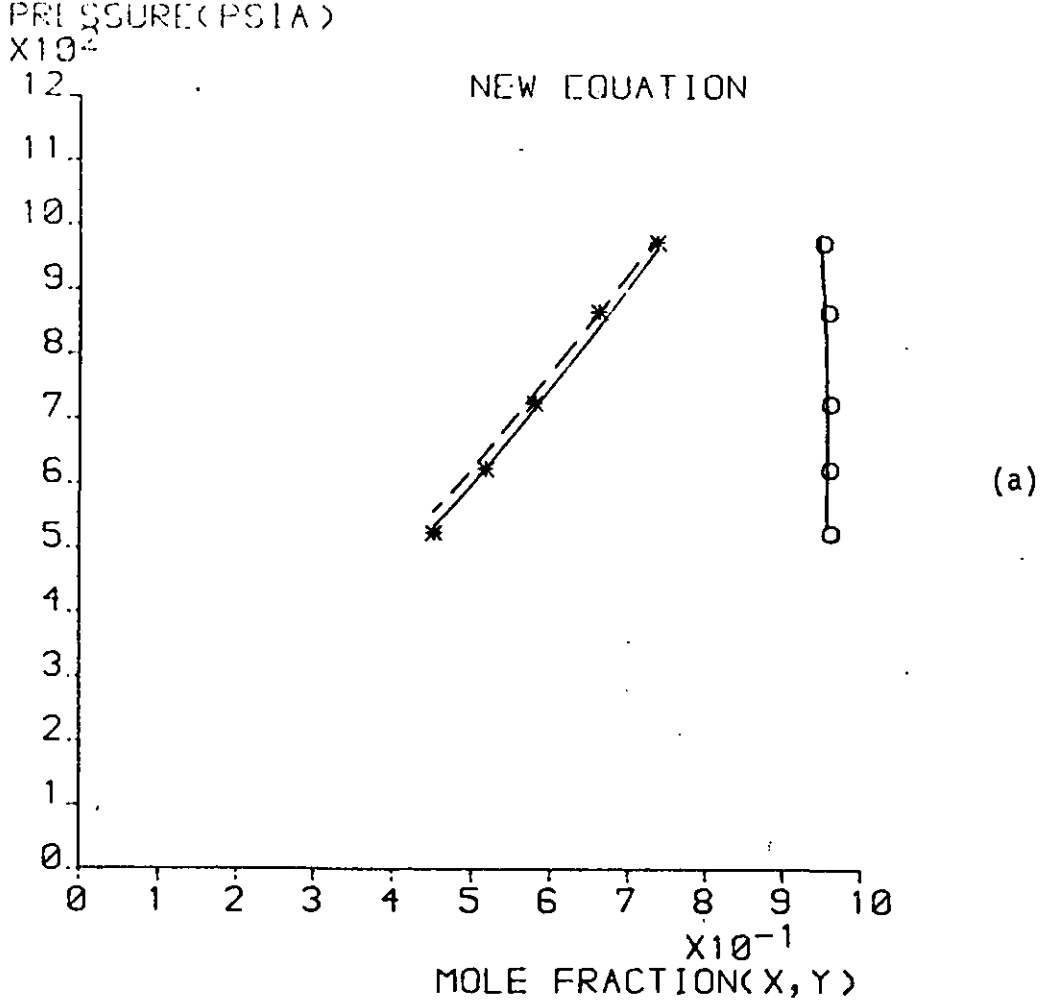
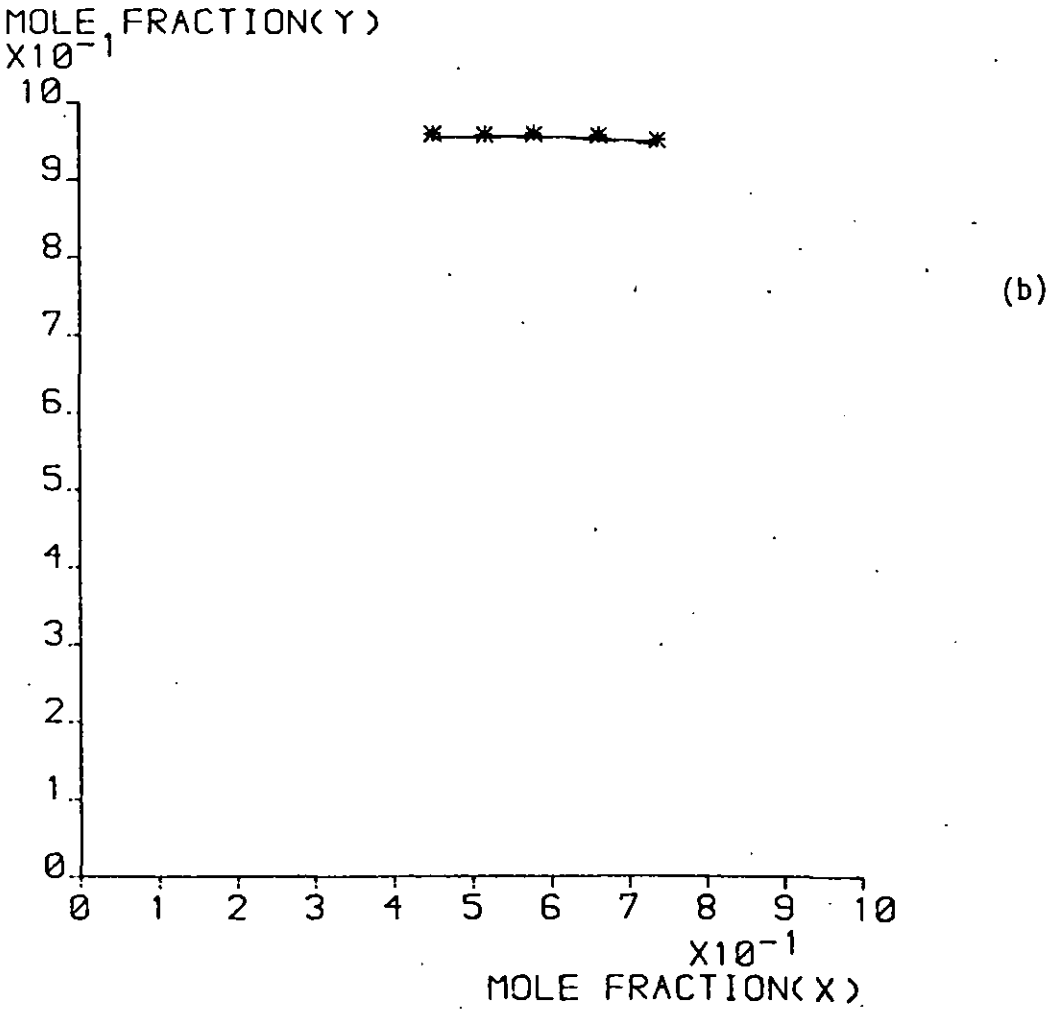


FIGURE 6.26 Ethane-n-Heptane System at 659.68°R (366.8K)



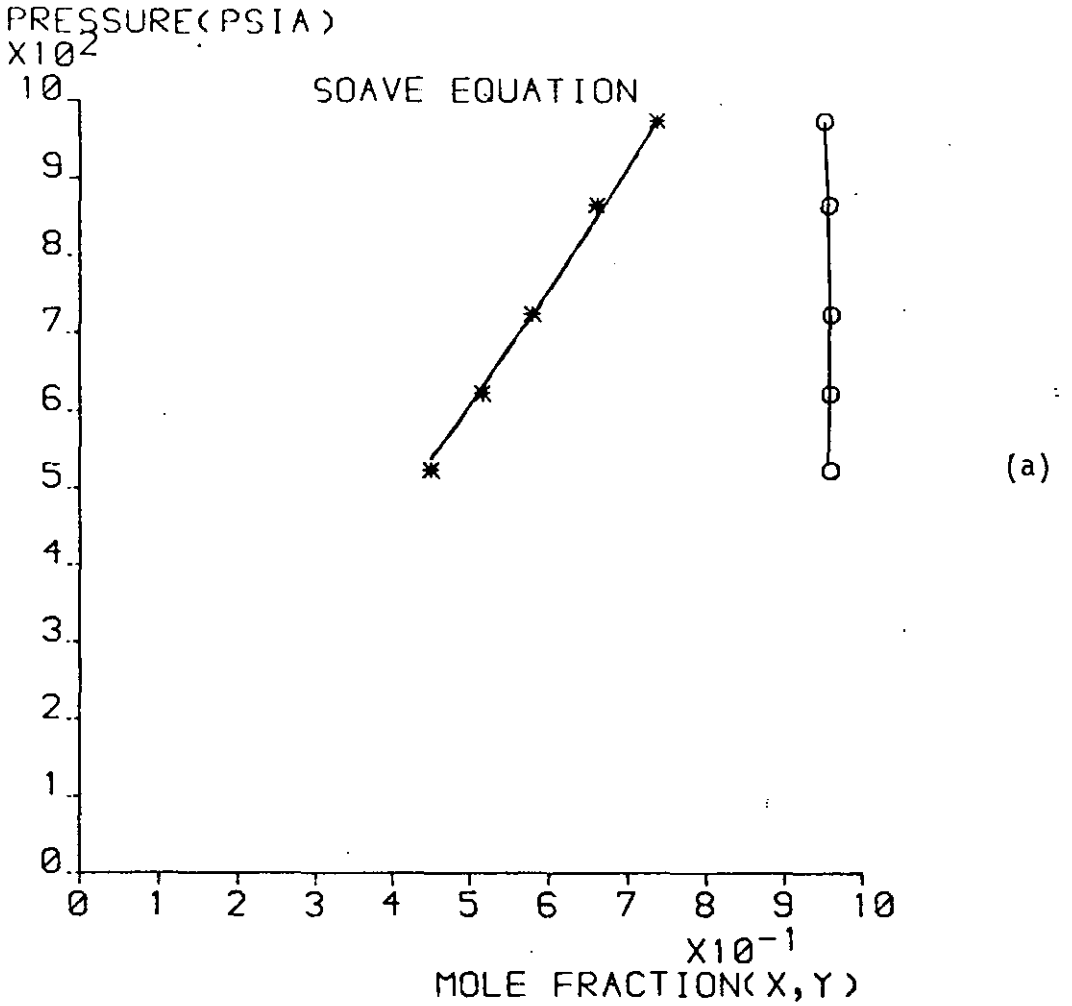
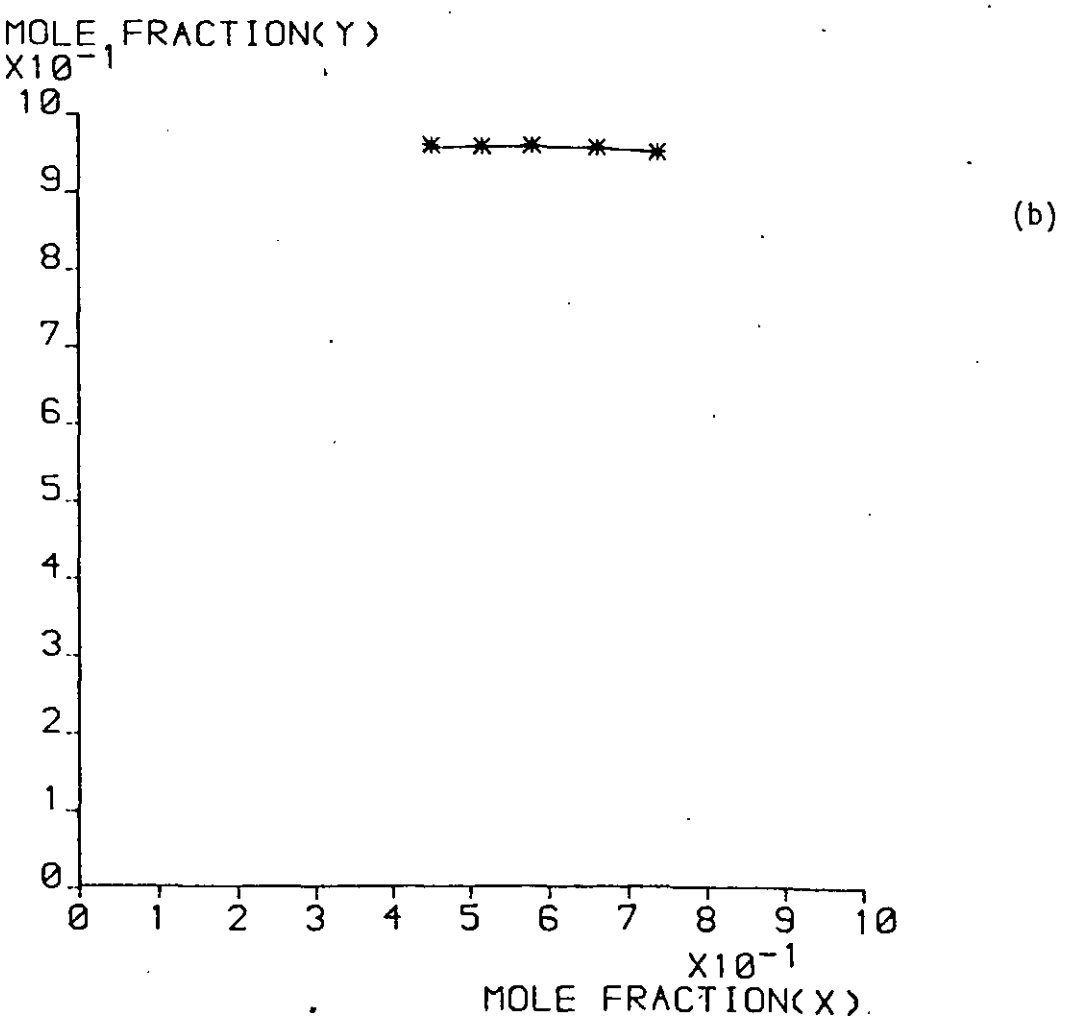
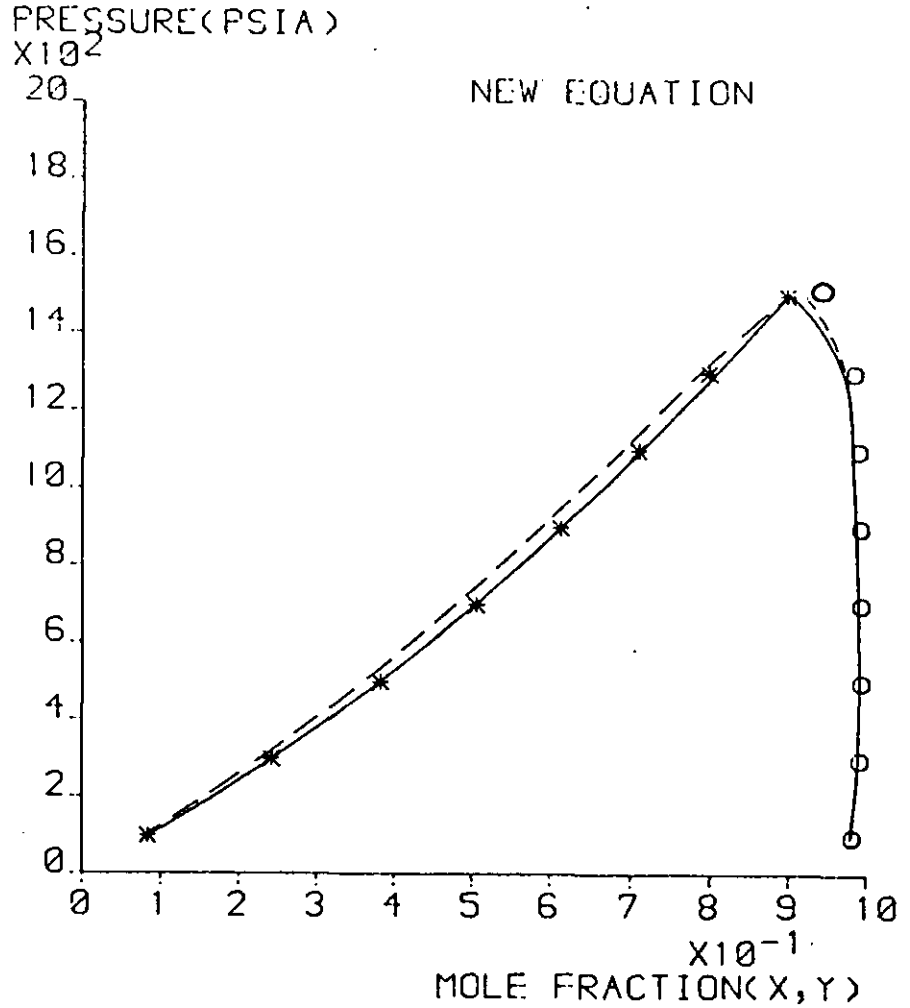


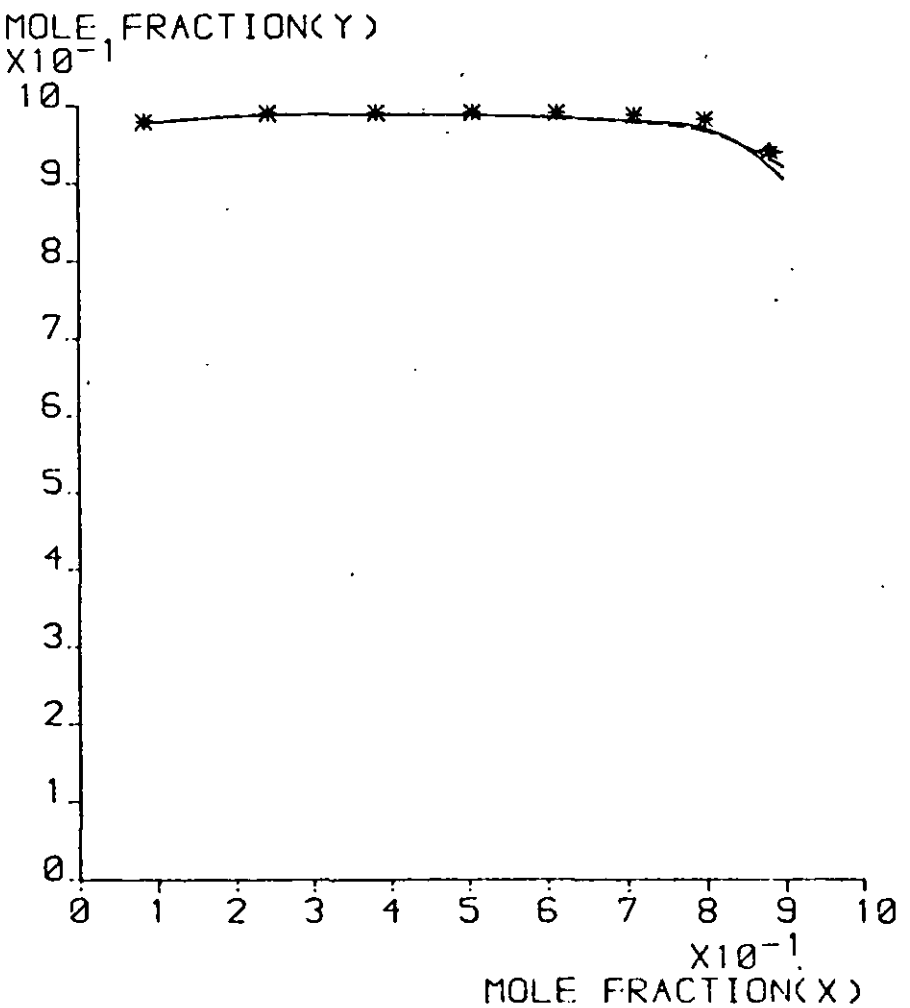
FIGURE 6.27 Ethane-n-Heptane System ay 659.68°R (366.8K)



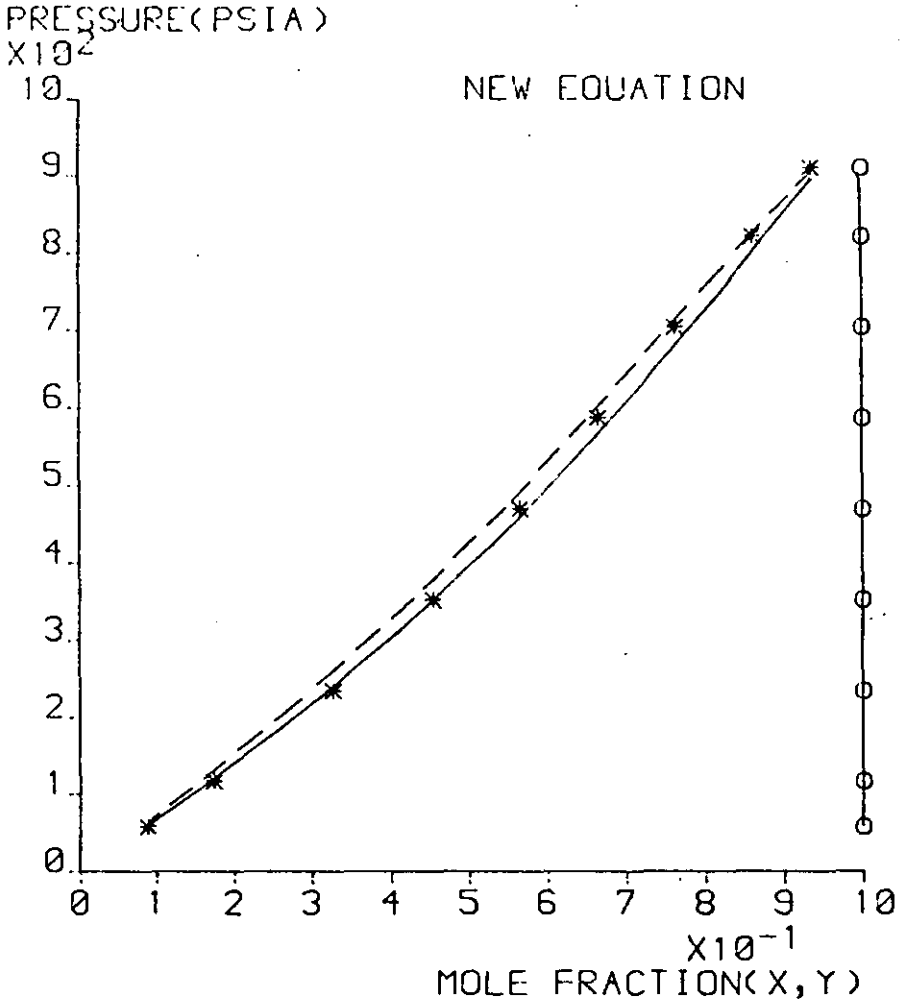


(a)

FIGURE 6.28 Ethane-n-Decane System at 679.67°R (377.6K)

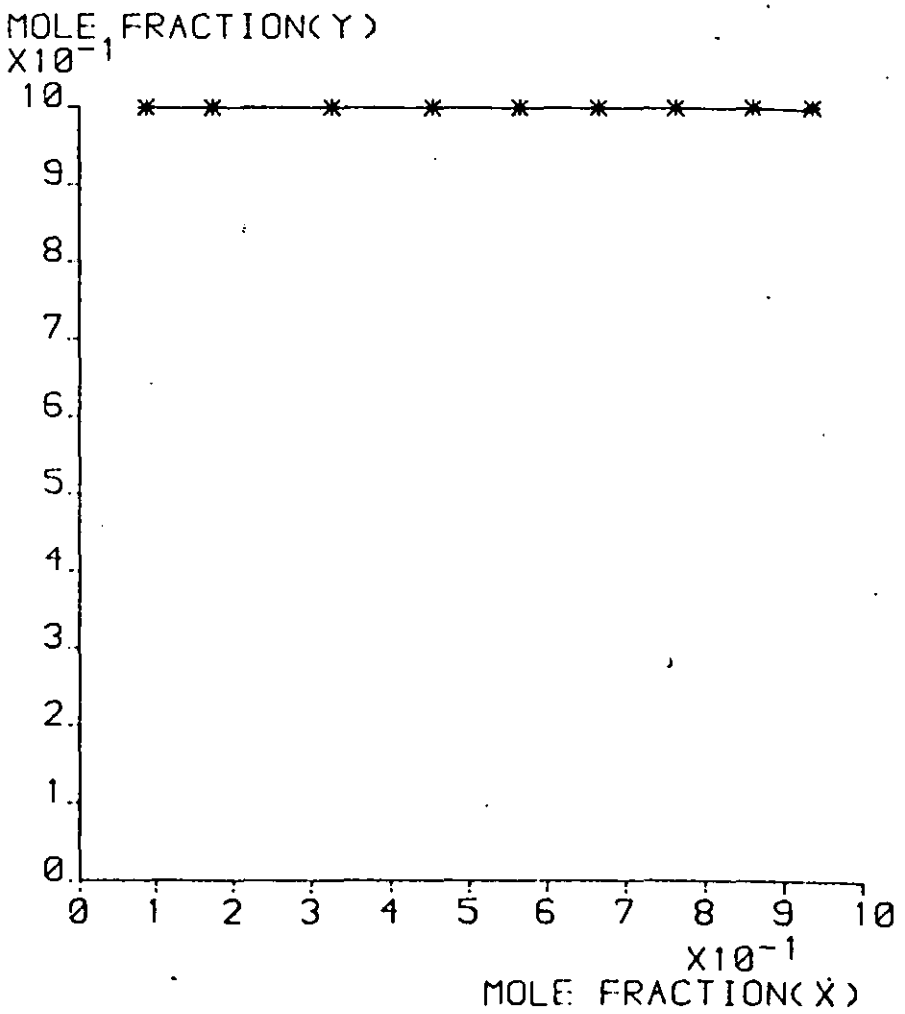


(b)

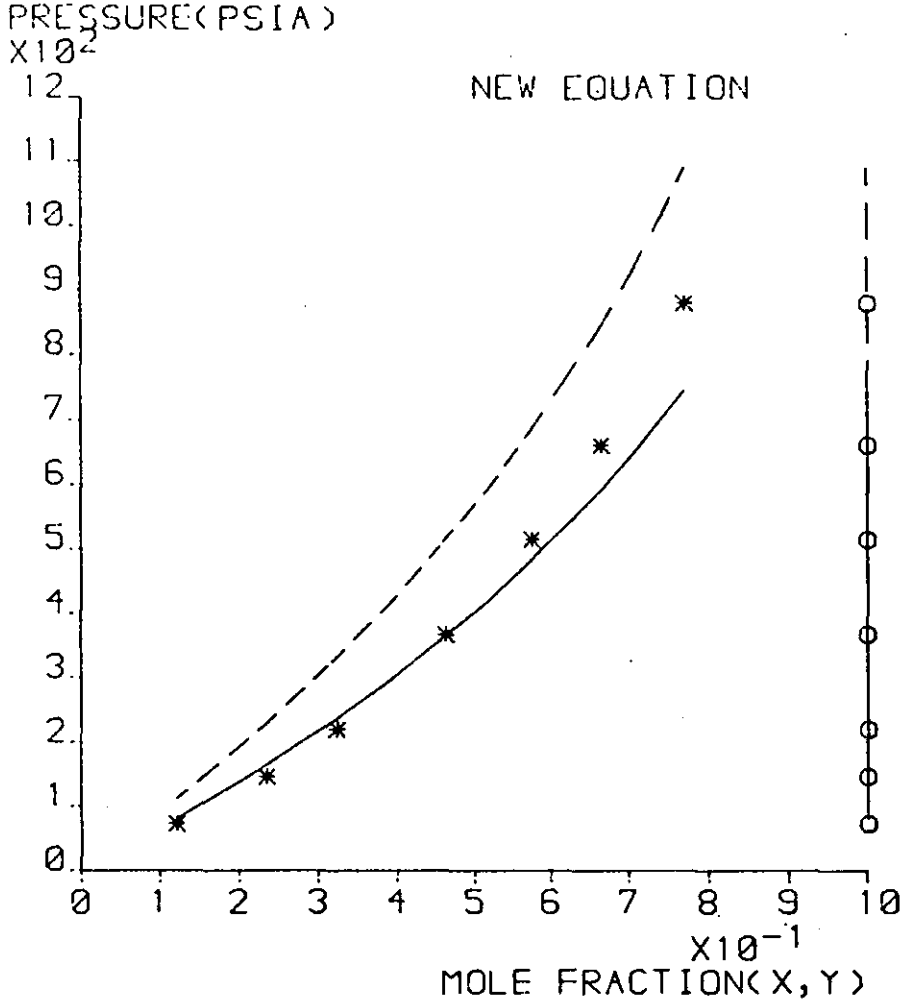


(a)

FIGURE 6.29 Ethane-n-Dodecane System at 581.67°R (323.2K)

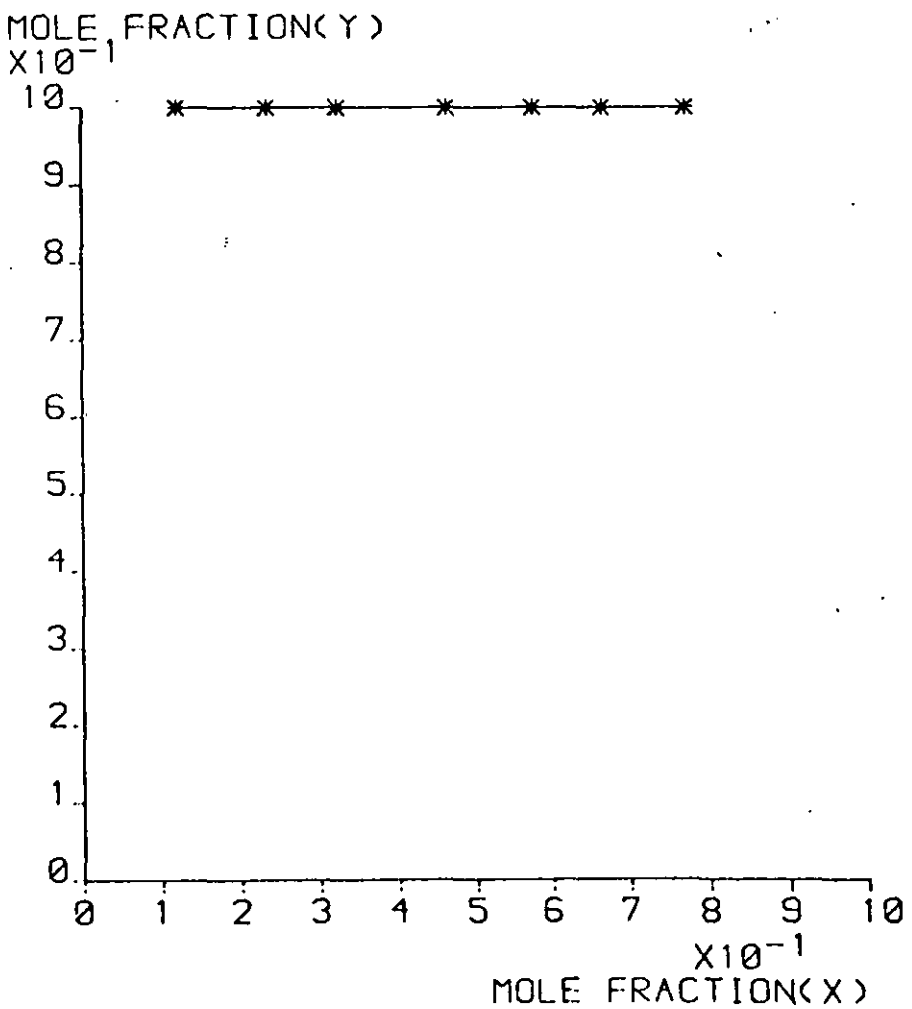


(b)

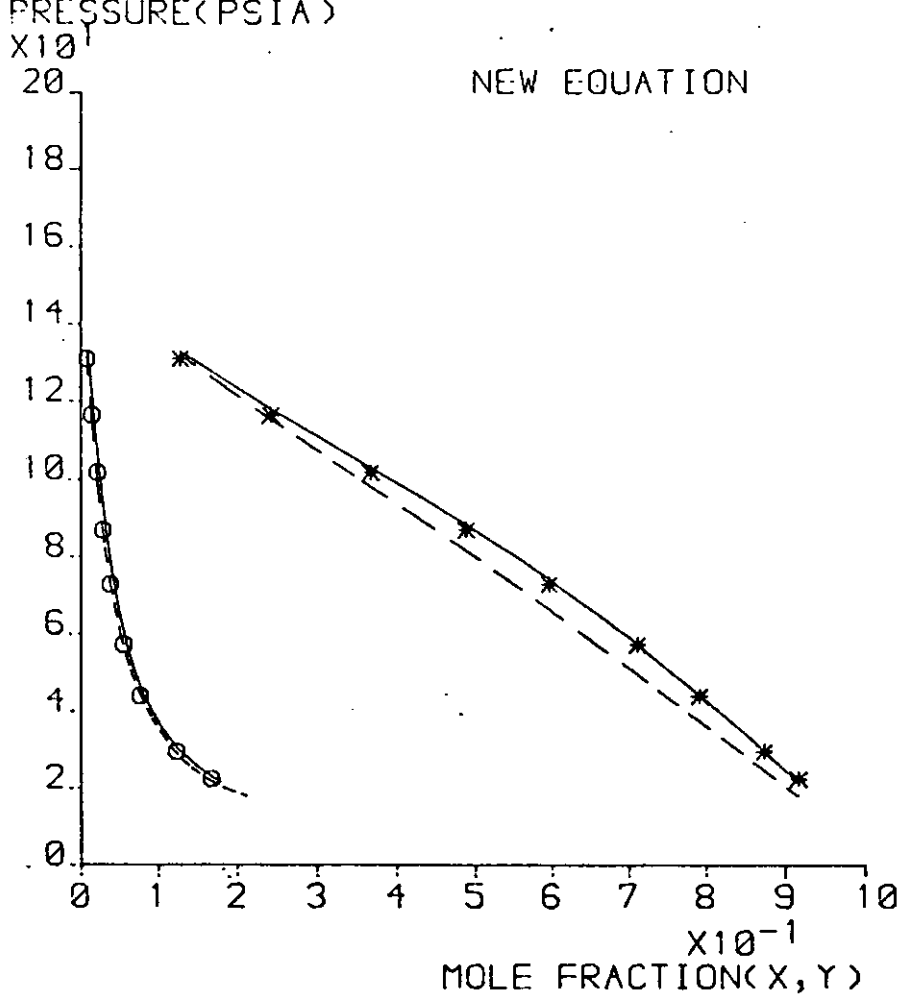


(a)

FIGURE 6.30 Ethane-n-Eicosane System at 599.67°R (333.2K)

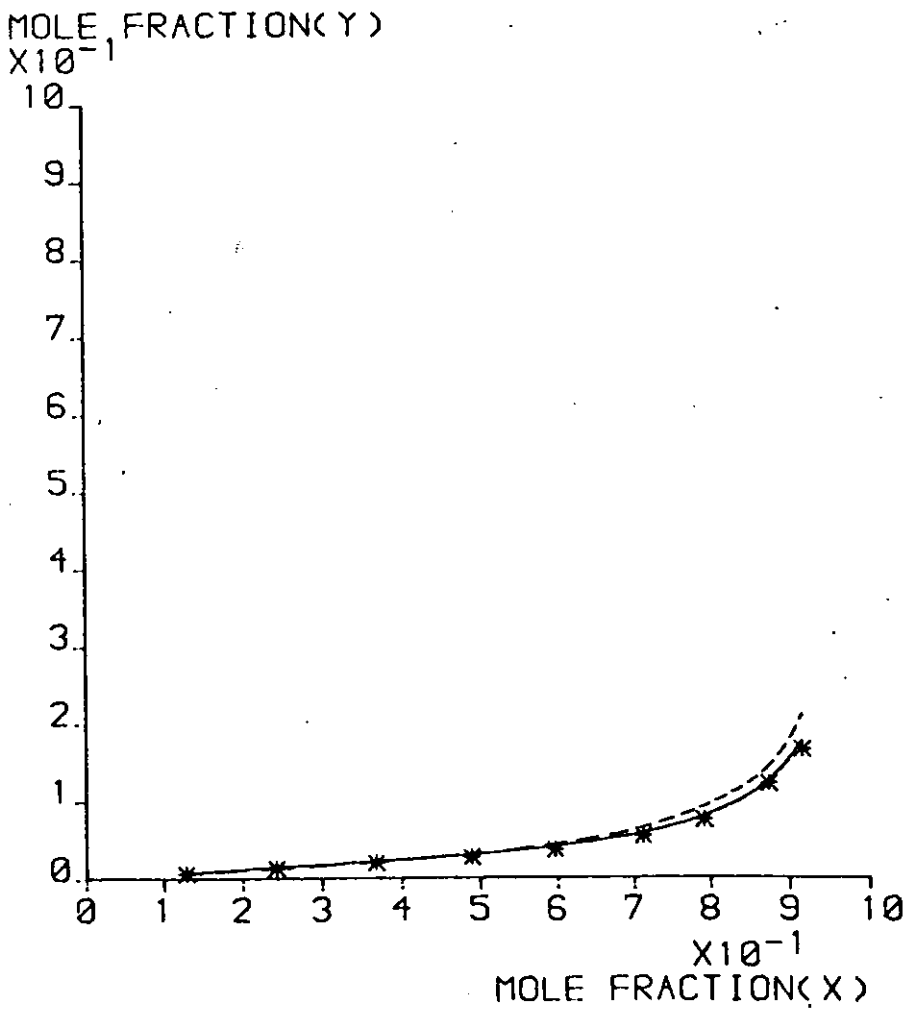


(b)

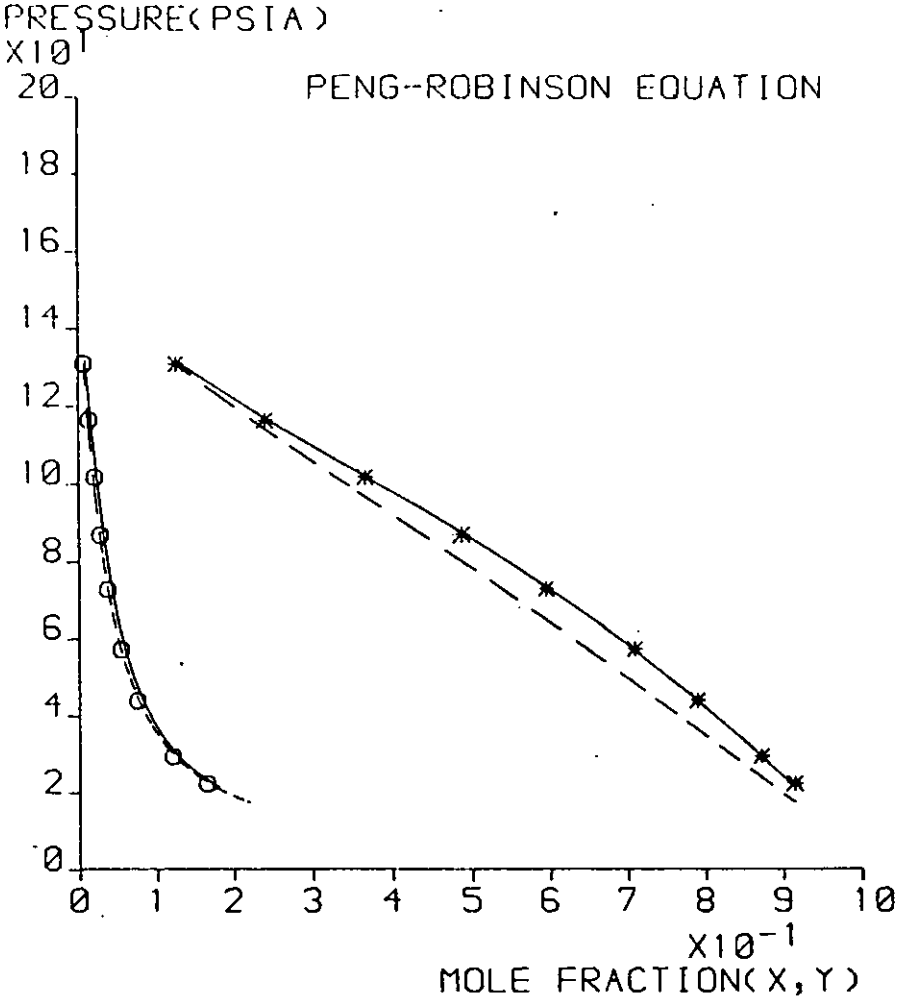


(a)

FIGURE 6.31 Ethylene-Methane System at 270.02°R (150K)

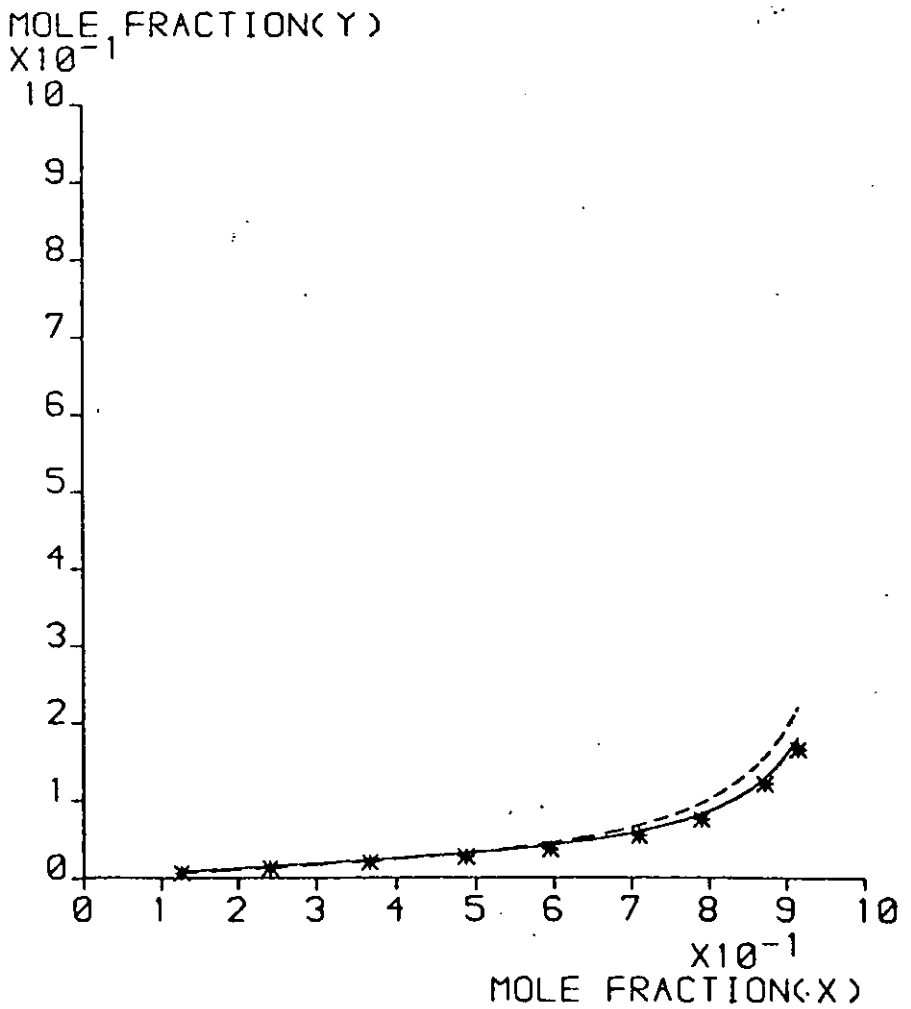


(b)

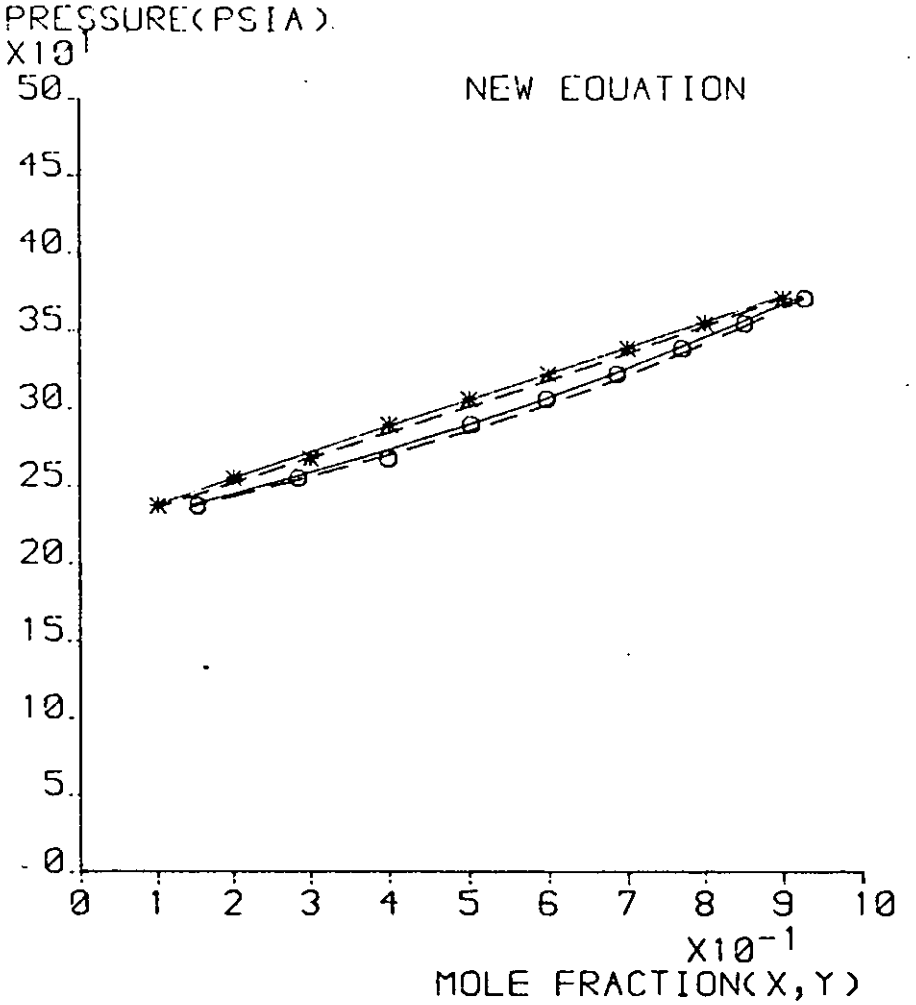


(a)

FIGURE 6.32 Ethylene-Methane System at 270.02°R (150K)

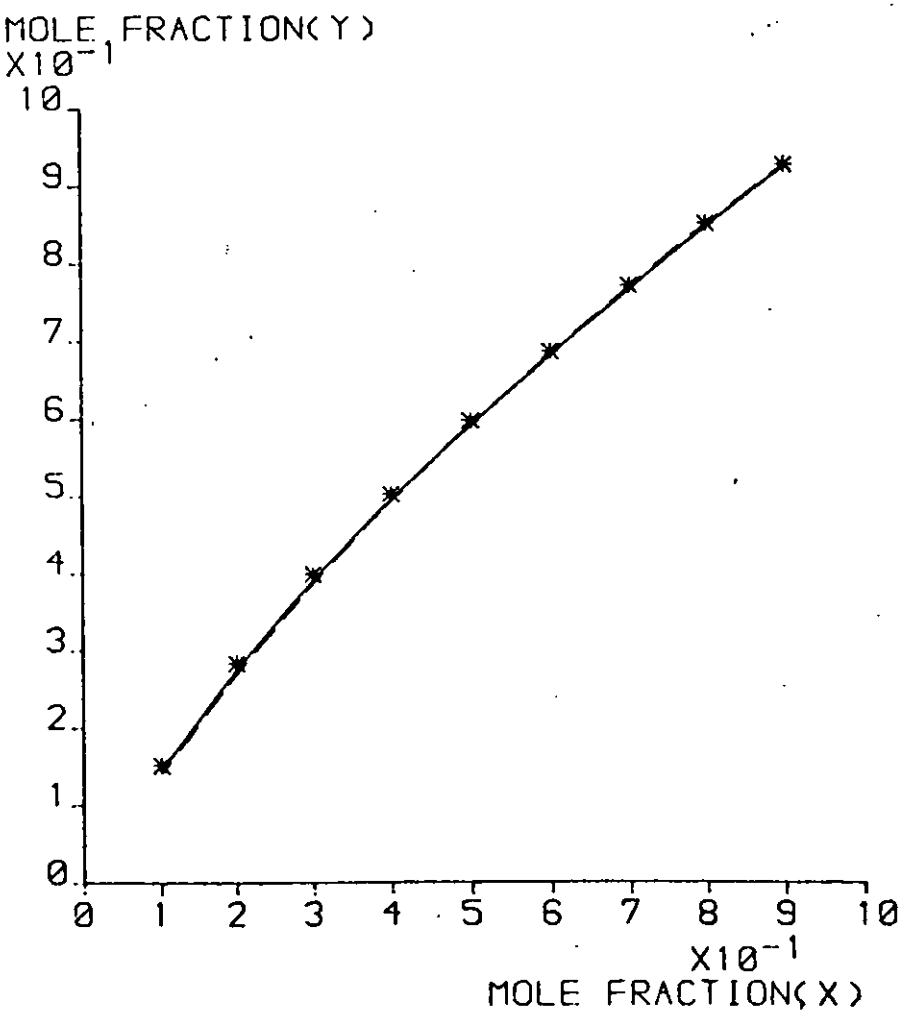


(b)

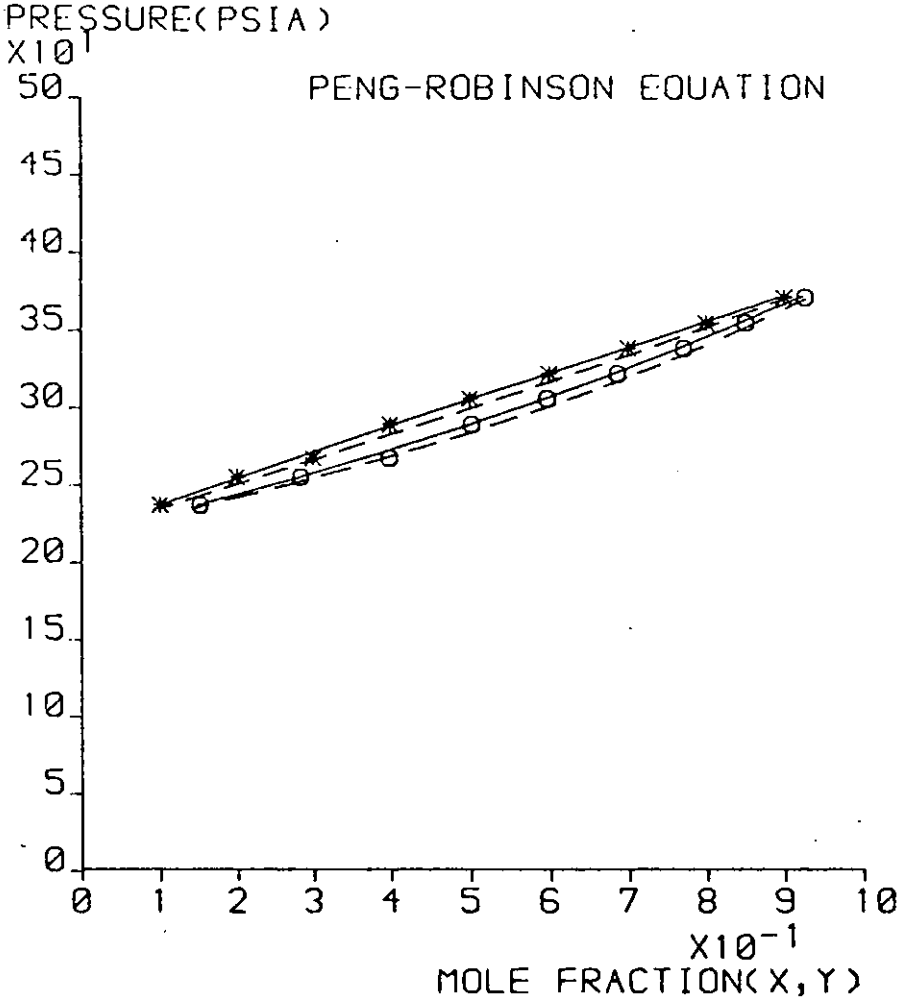


(a)

FIGURE 6.33 Ethylene-Ethane System at 459.67°R (255.4K)

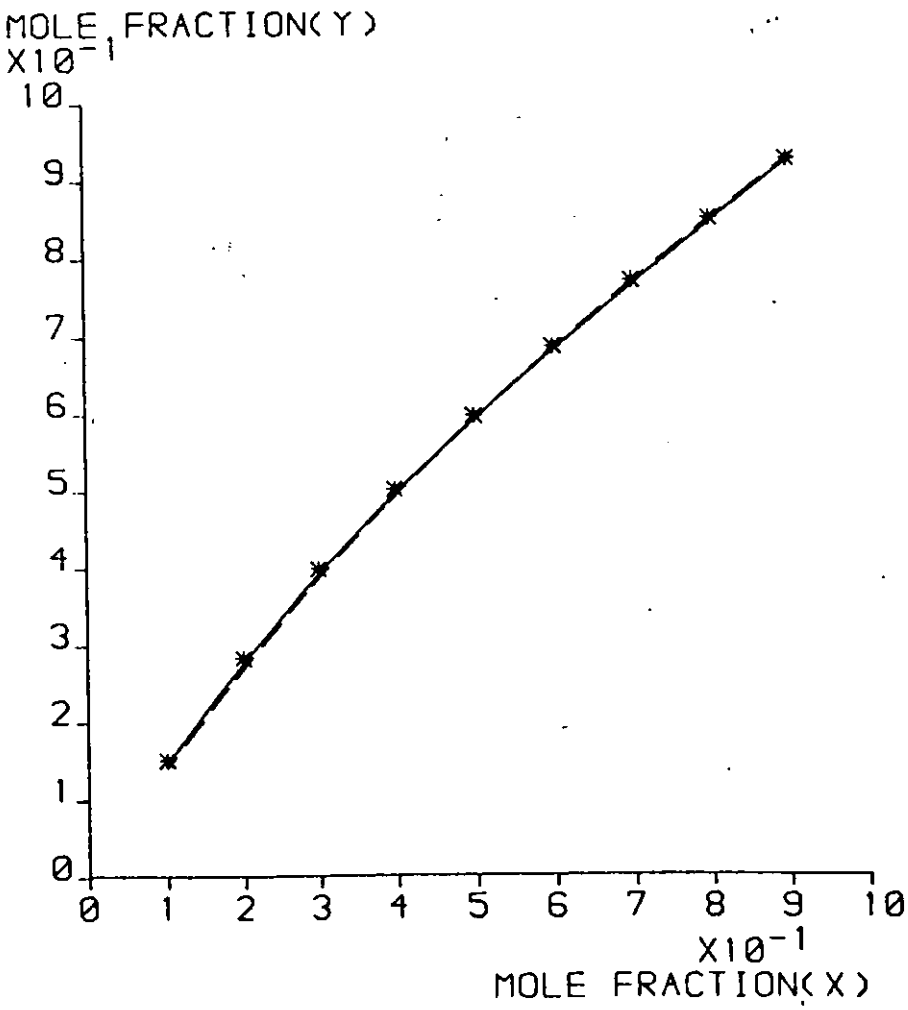


(b)

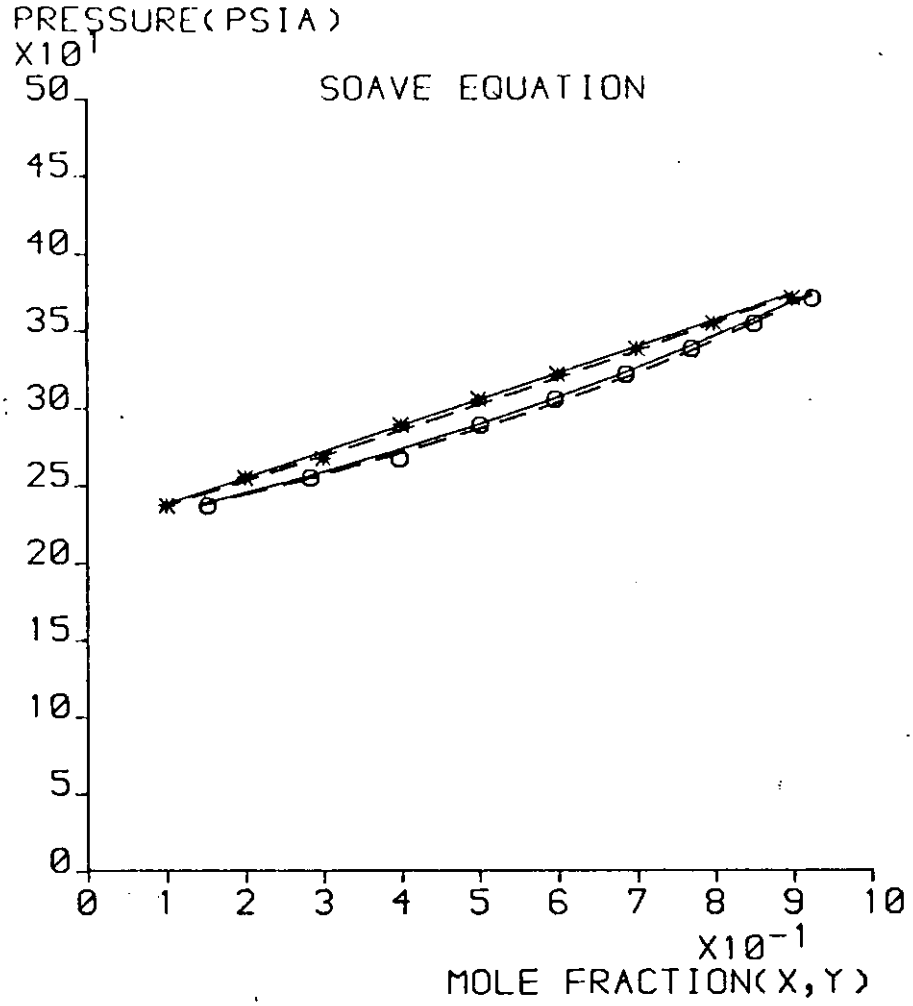


(a)

FIGURE 6.34 Ethylene-Ethane System at 459.67°R (255.4K)

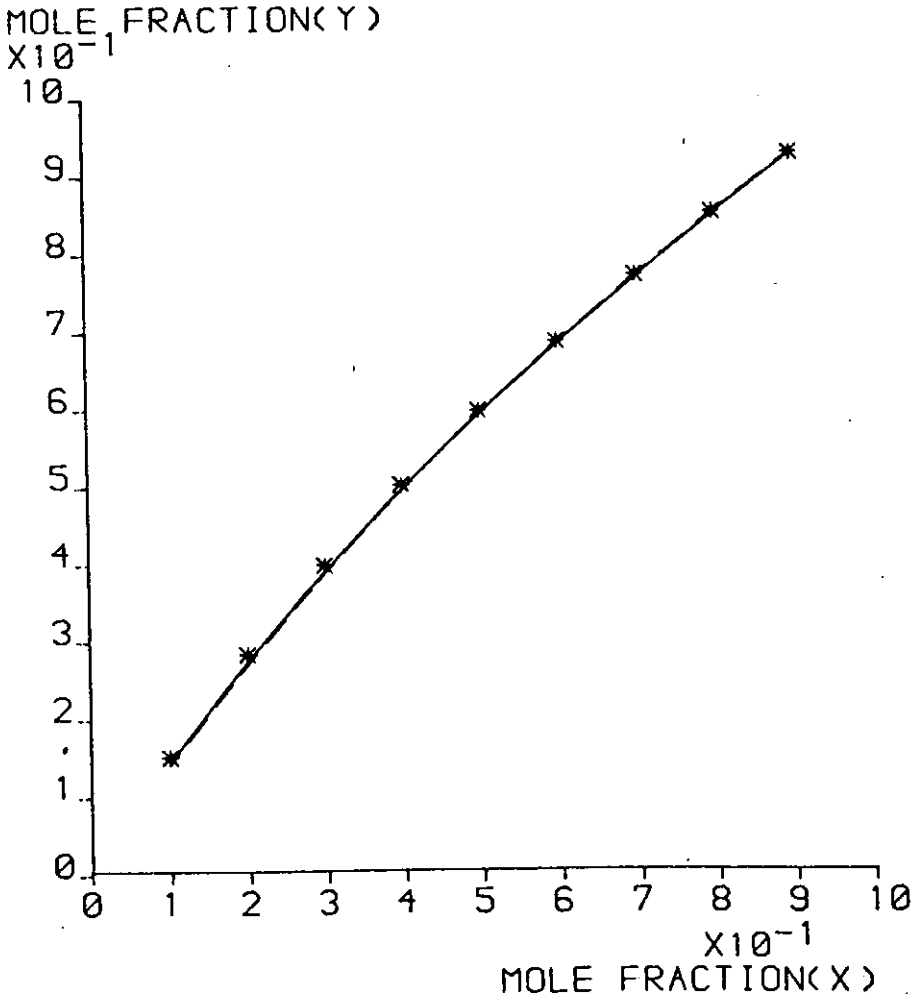


(b)

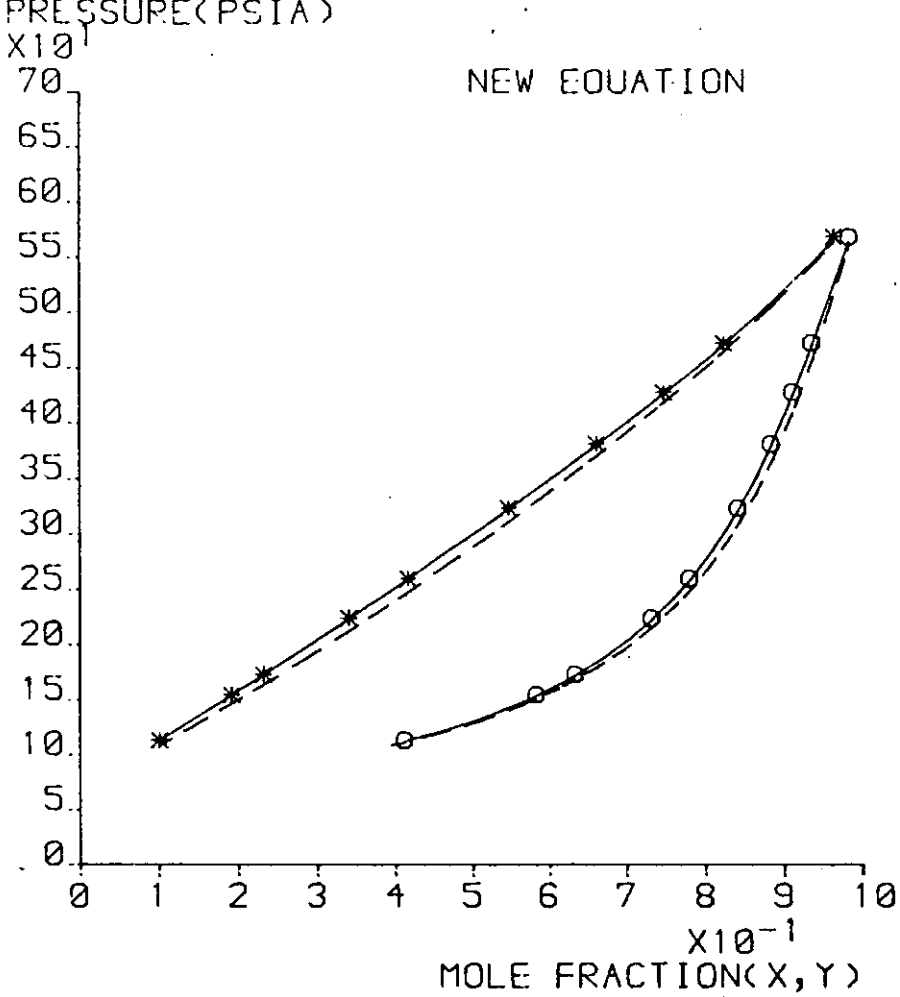


(a)

FIGURE 6.35 Ethylene-Ethane System at 459.67°R (255.4K)

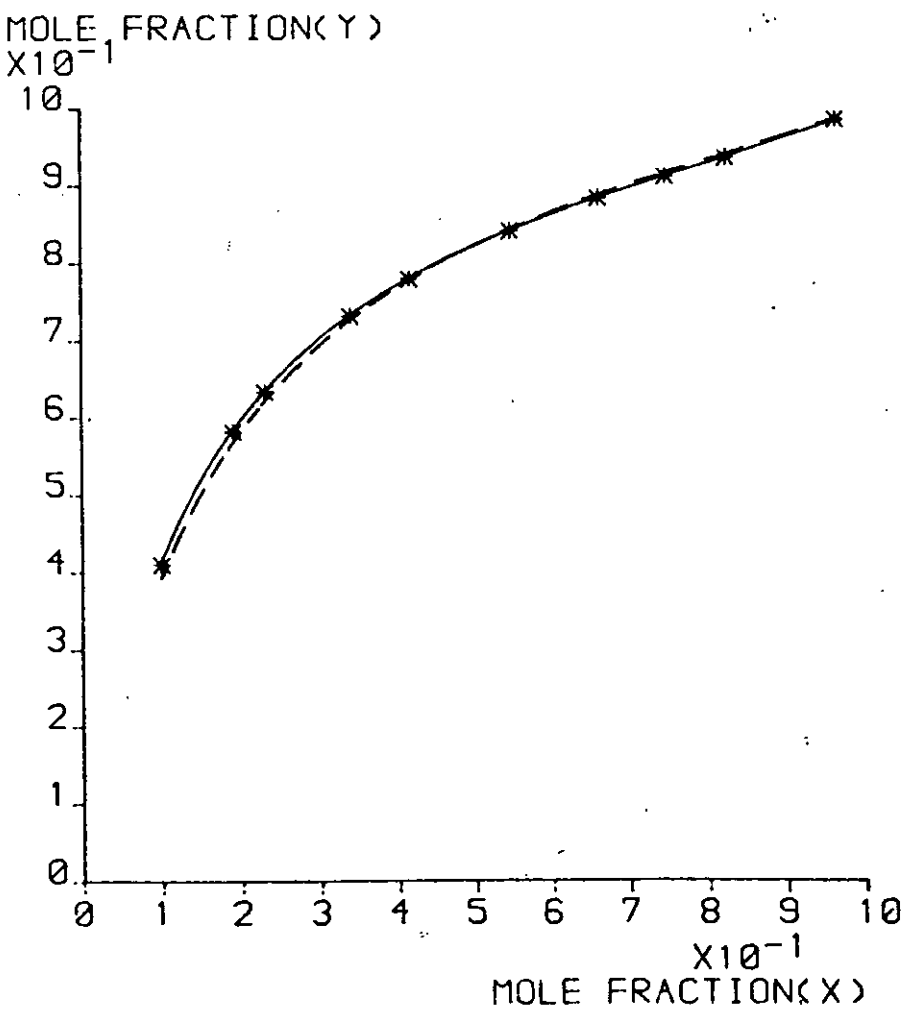


(b)

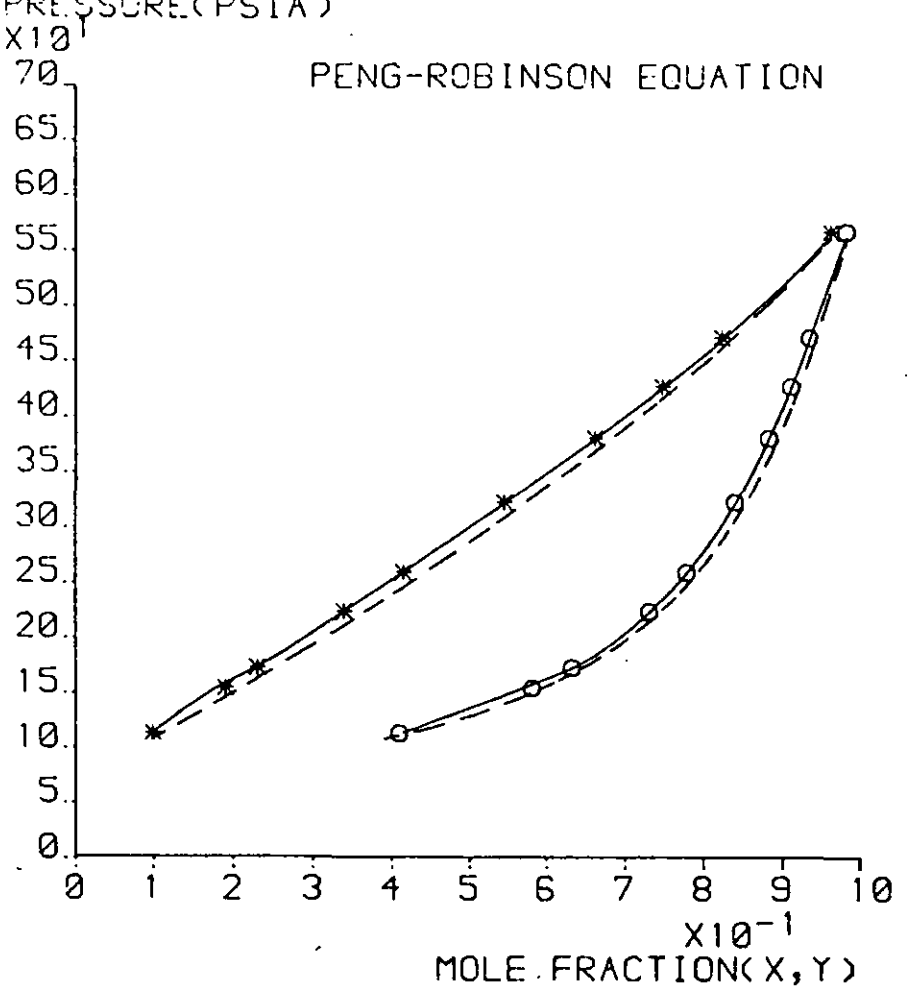


(a)

FIGURE 6.36 Ethylene-Propane System at 491.53°R (273.1K)

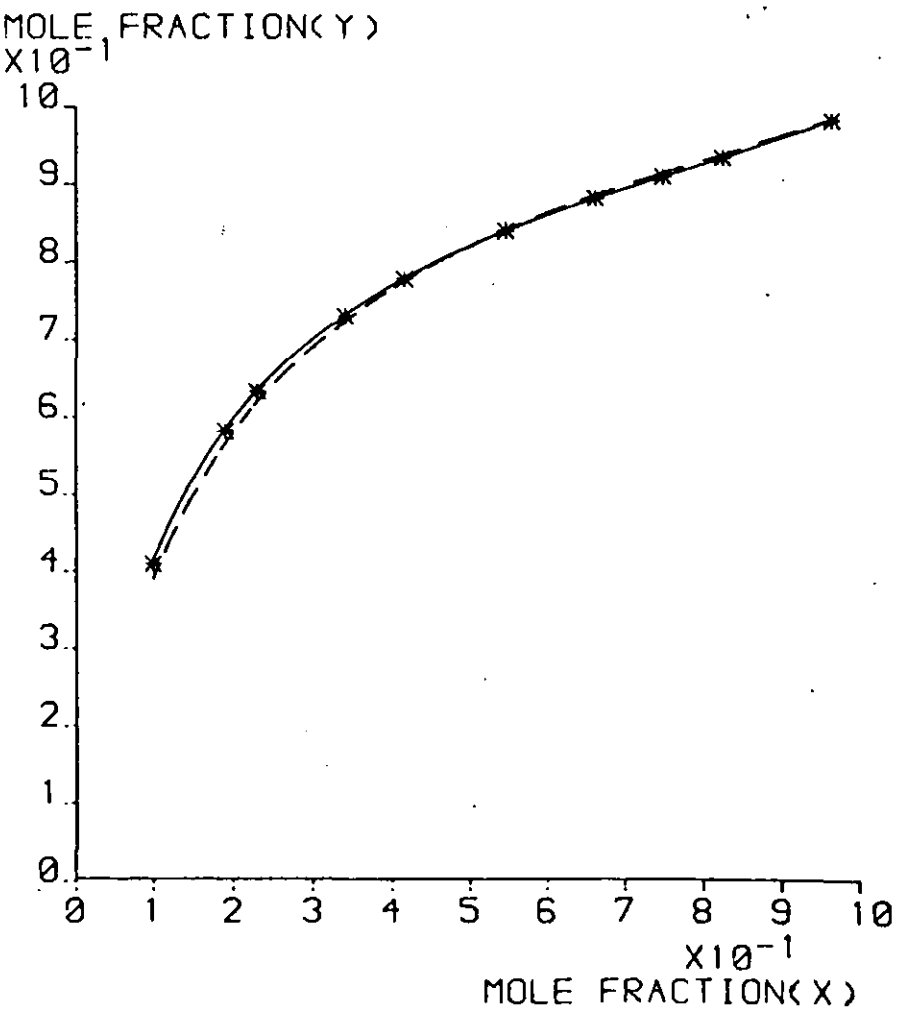


(b)



(a)

FIGURE 6.37 Ethylene-Propane System at 491.53°R (273.1K)



(b)

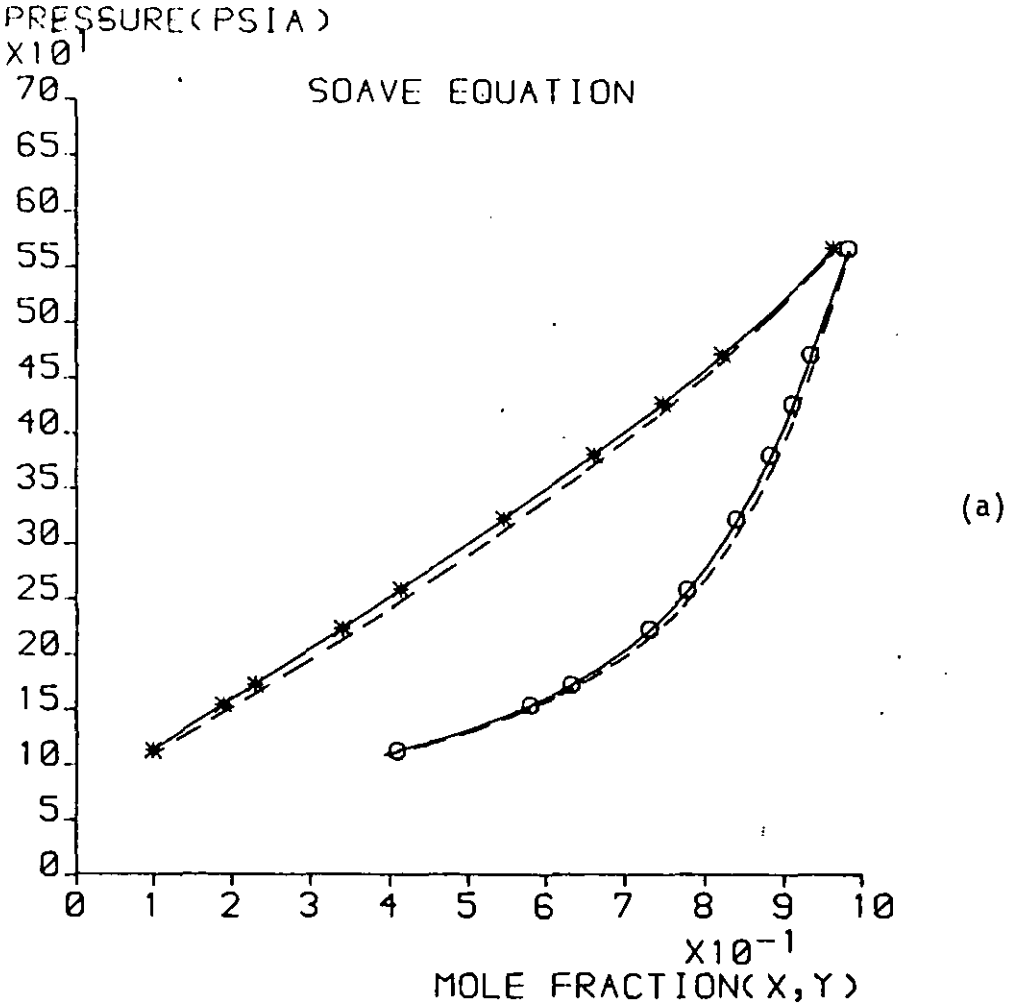
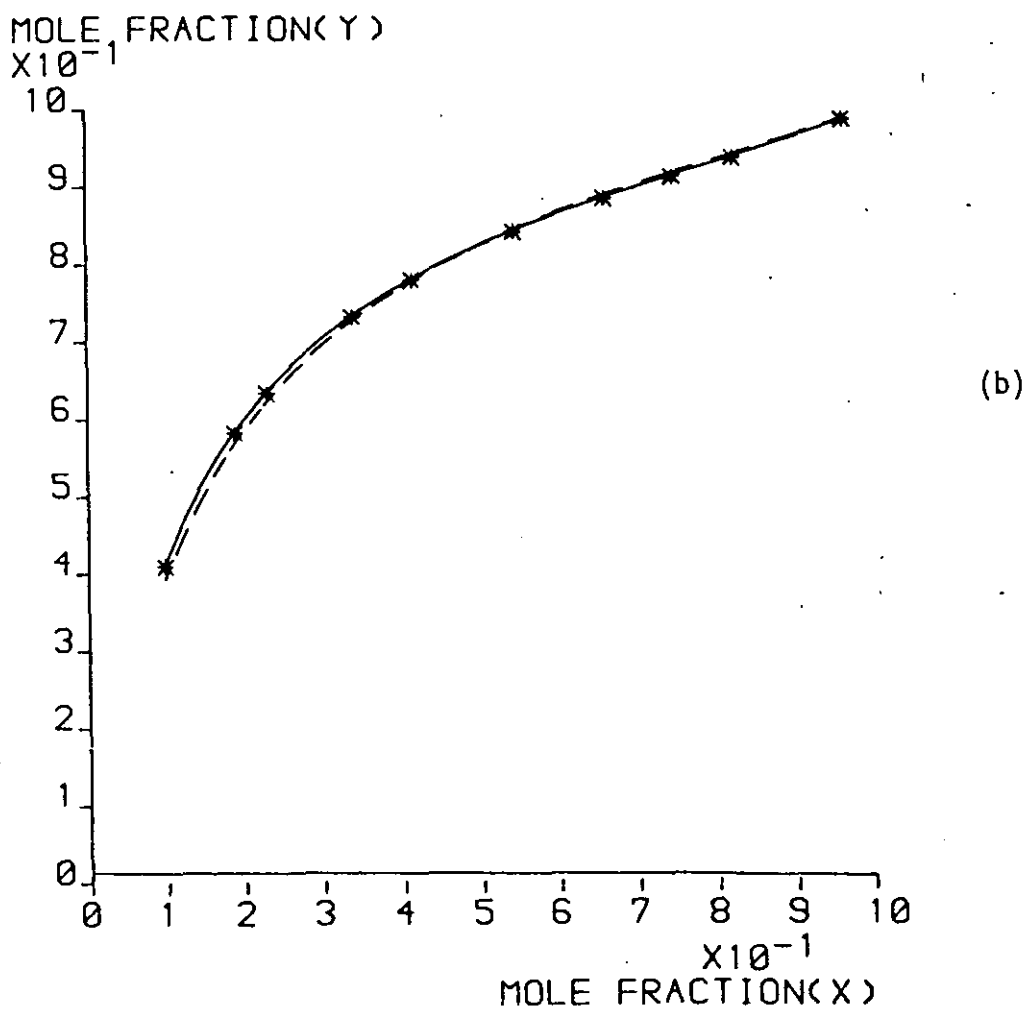
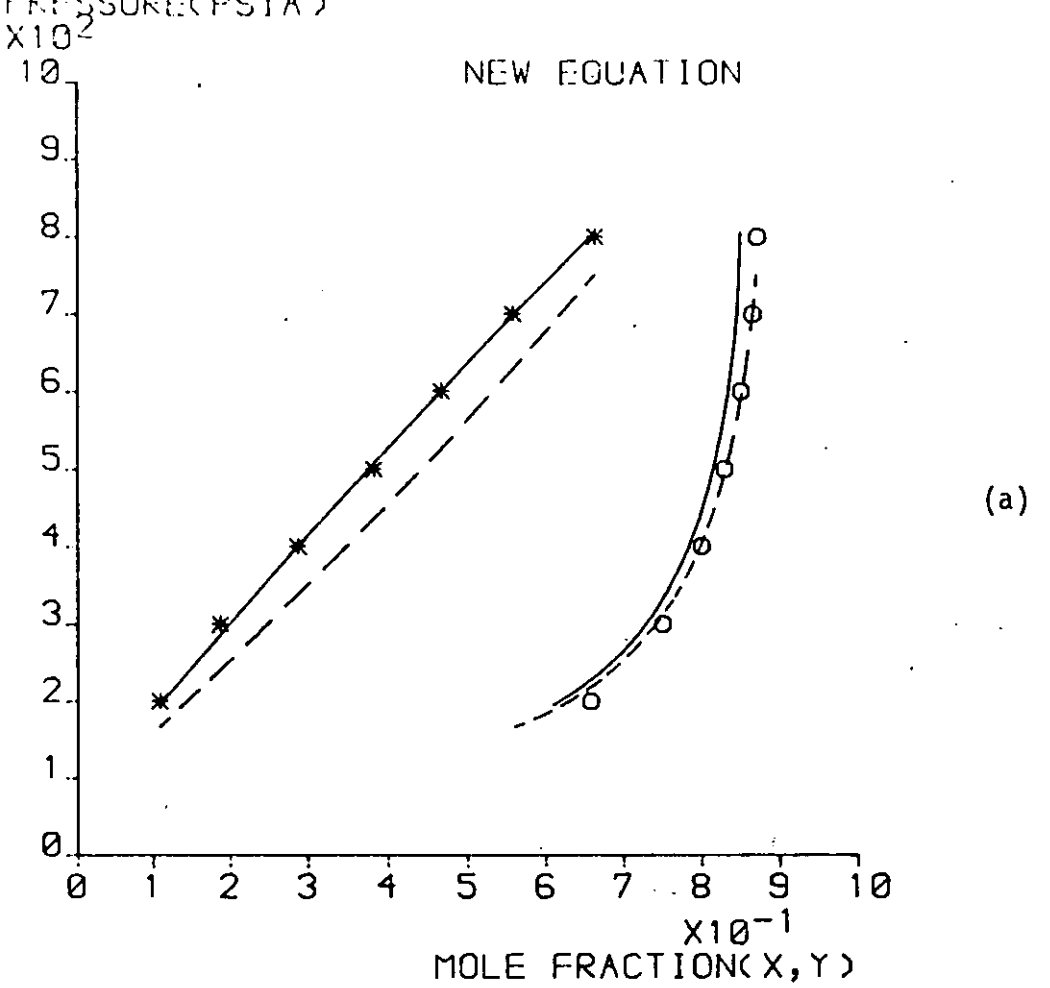


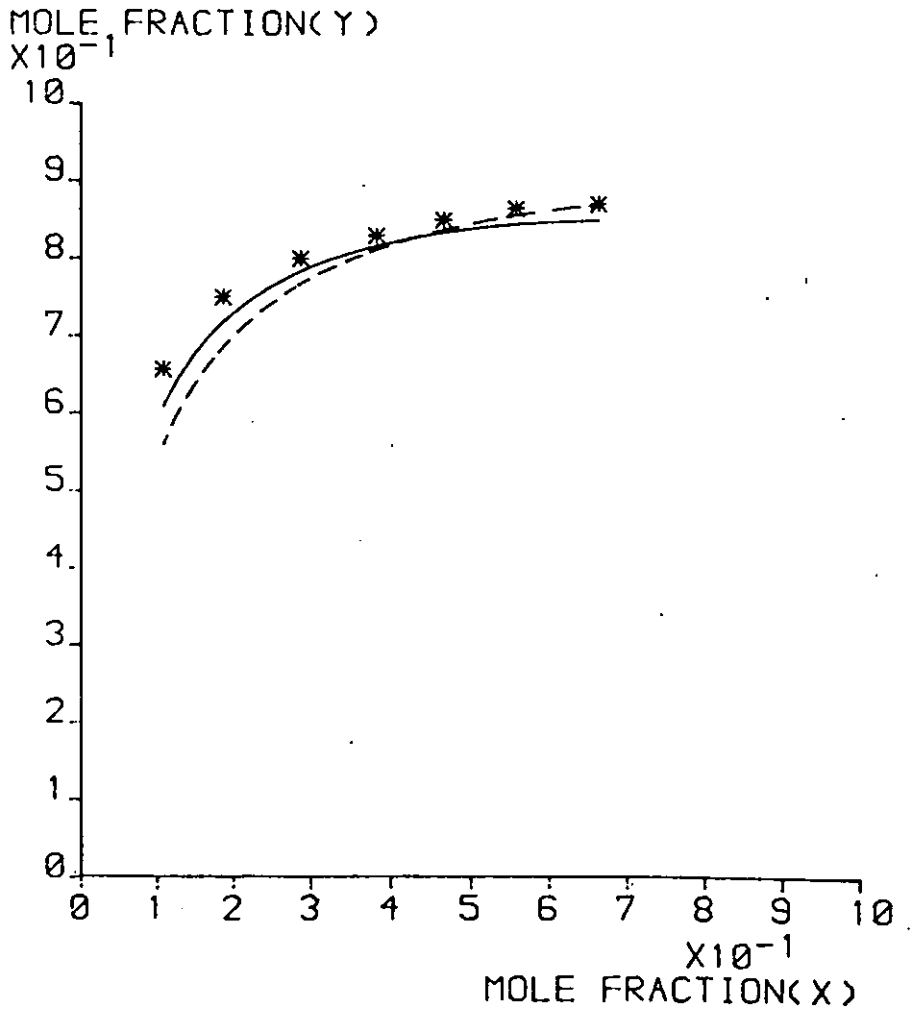
FIGURE 6.38 Ethylene-Propane System at 491.53°R (273.1K)



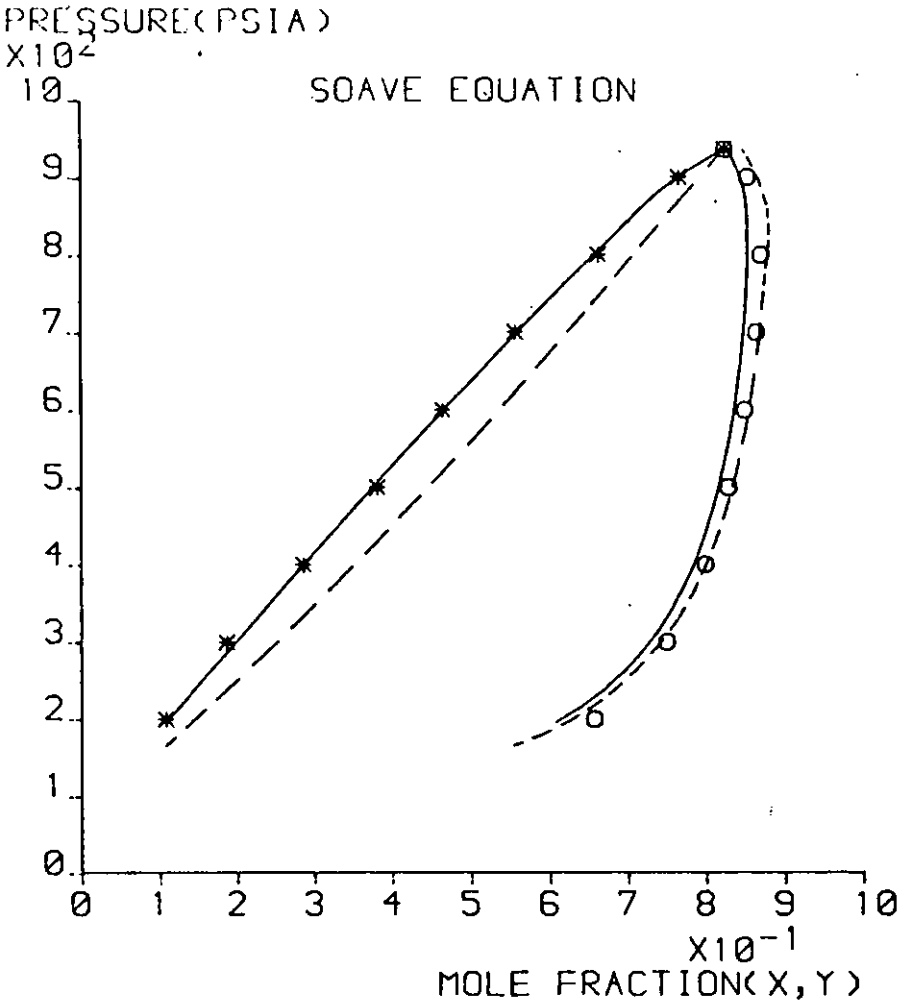


(a)

FIGURE 6.39 Ethylene-n-Butane System at 579.61°R (322K)

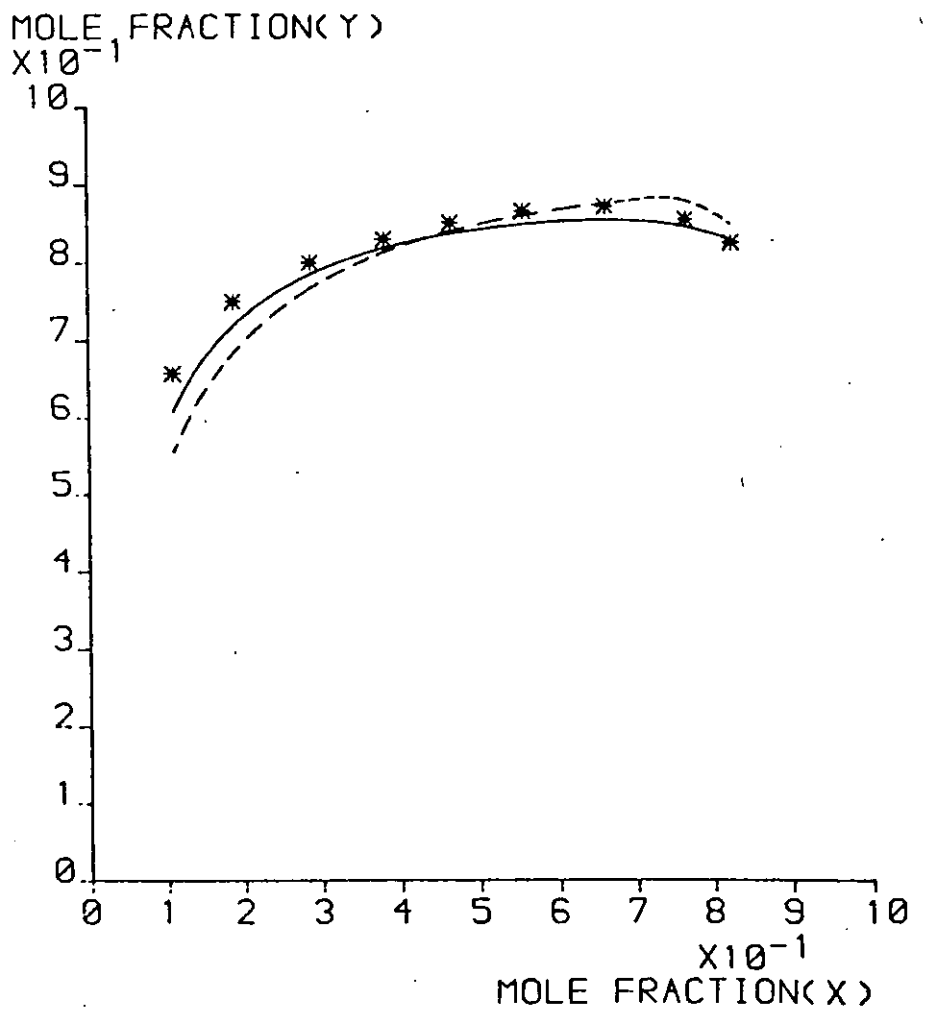


(b)



(a)

FIGURE 6.40 Ethylene-n-Butane System at 579.61°R (322K)



(b)

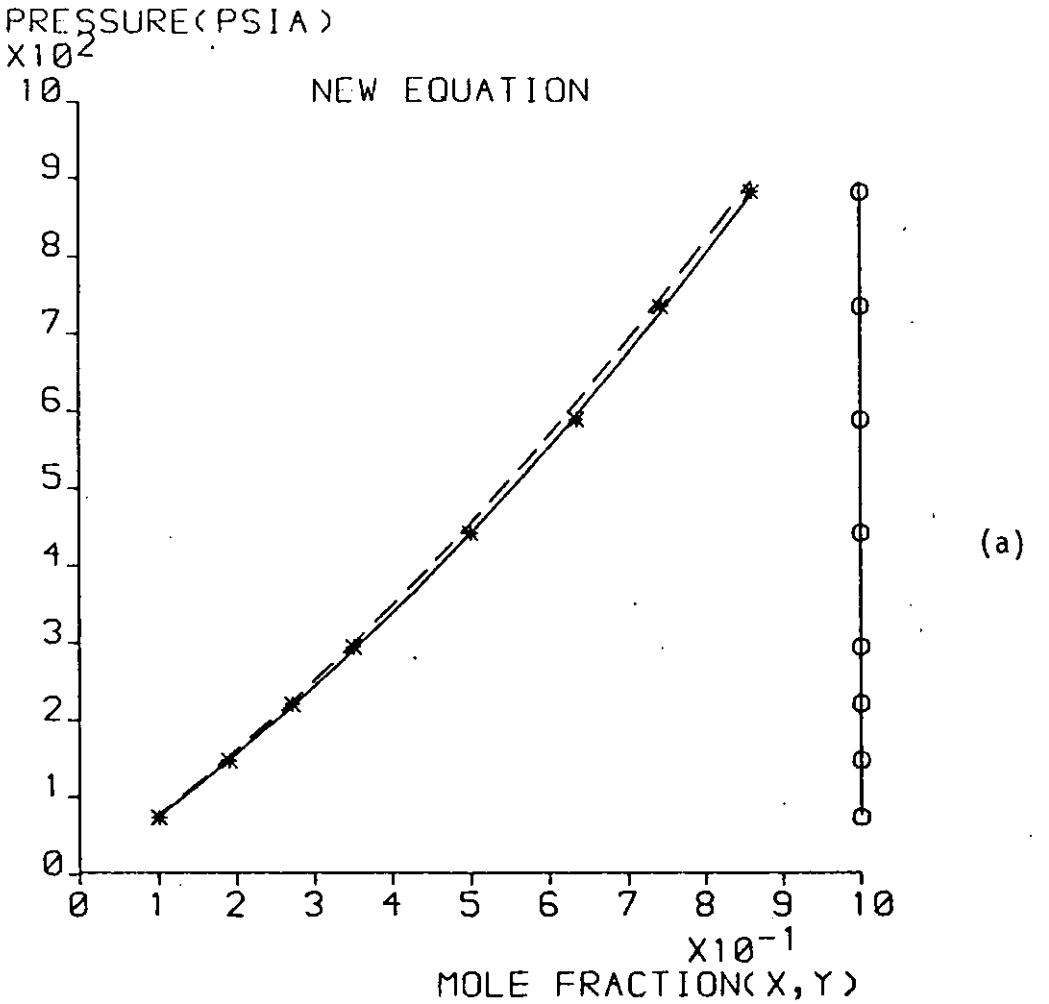
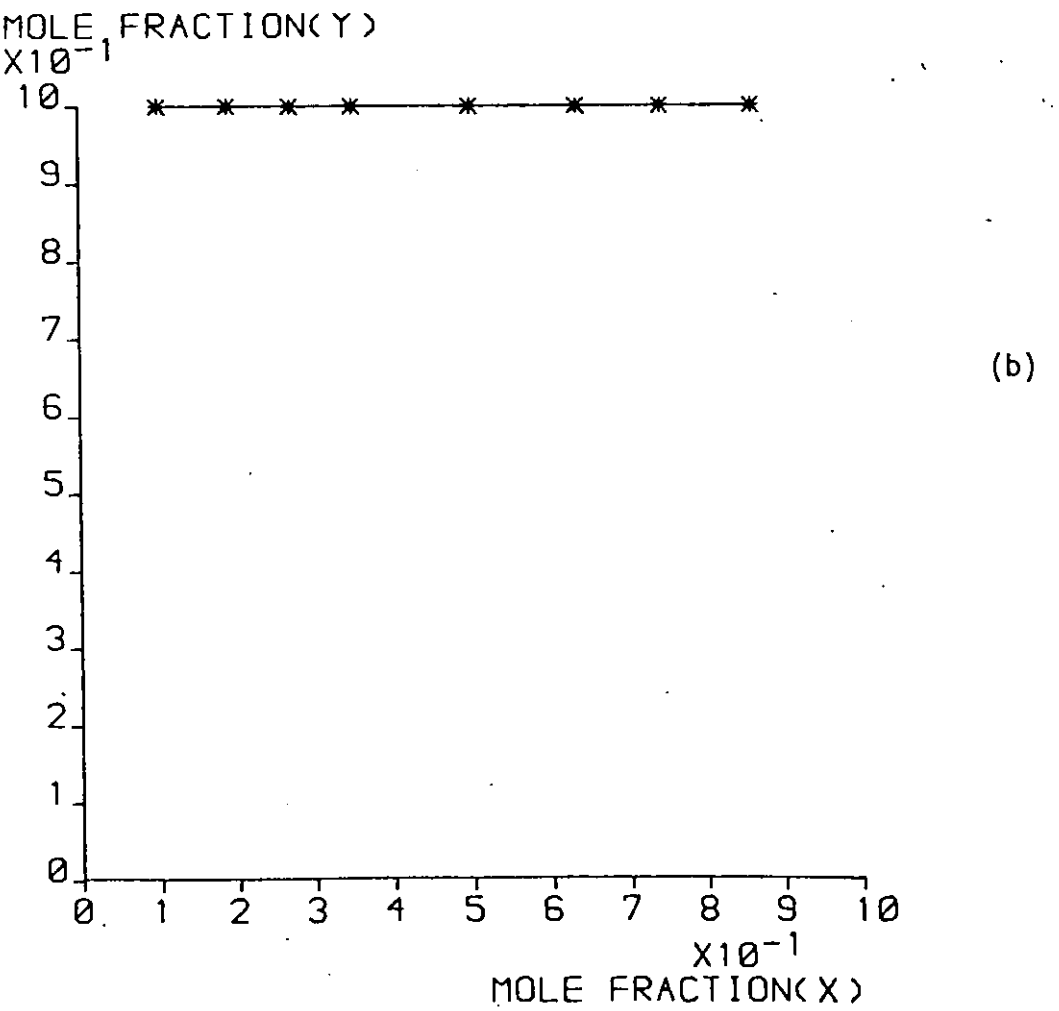
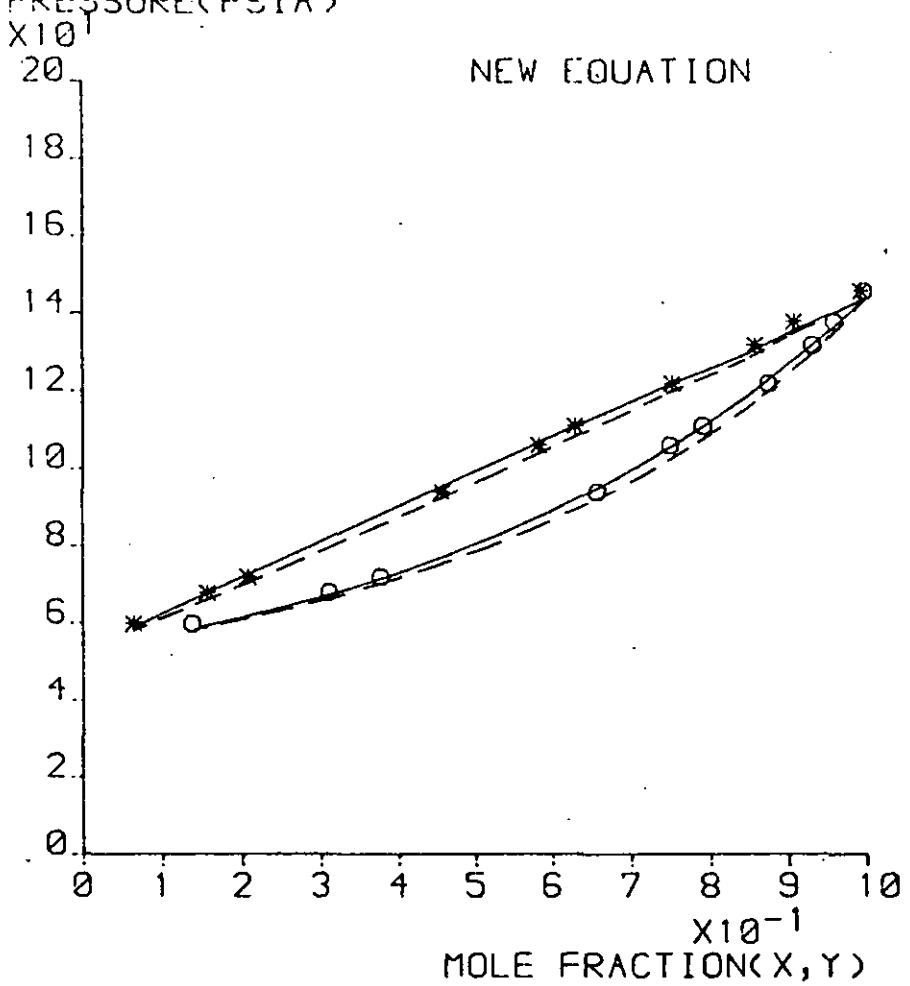


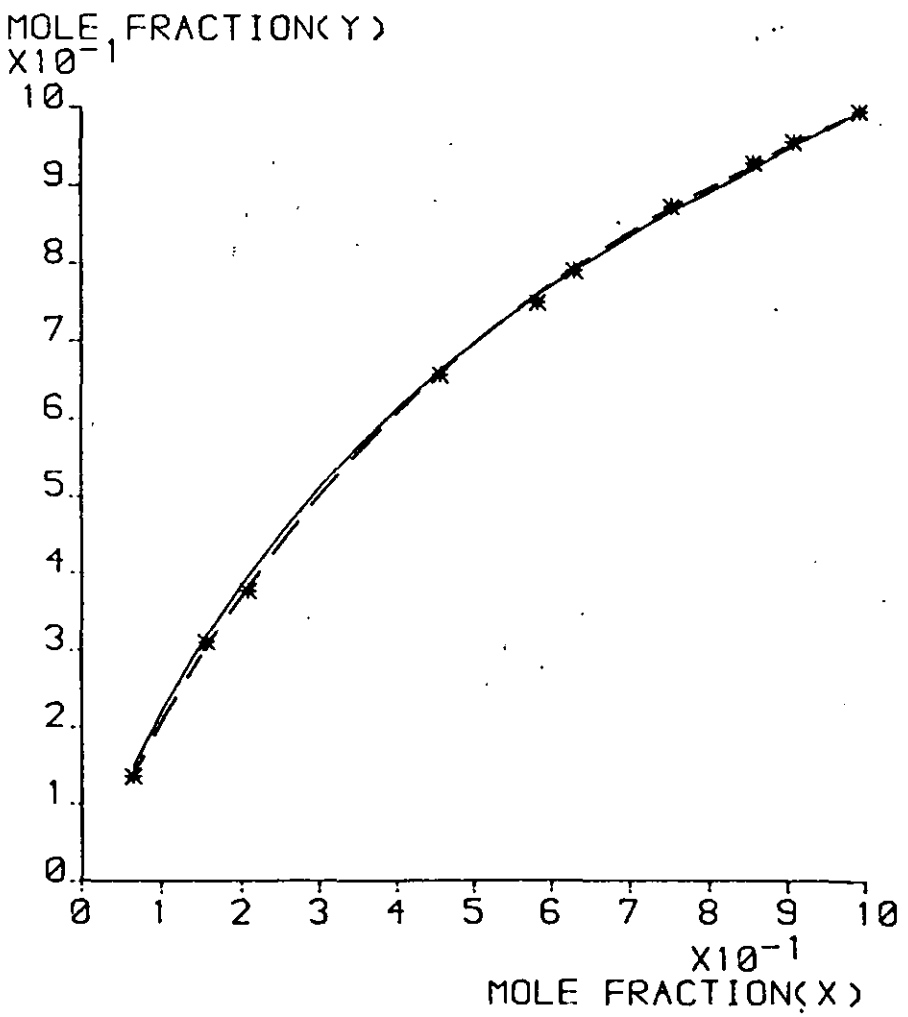
FIGURE 6.41 Ethylene-n-Dodecane System at 536.67°R (298.2K)



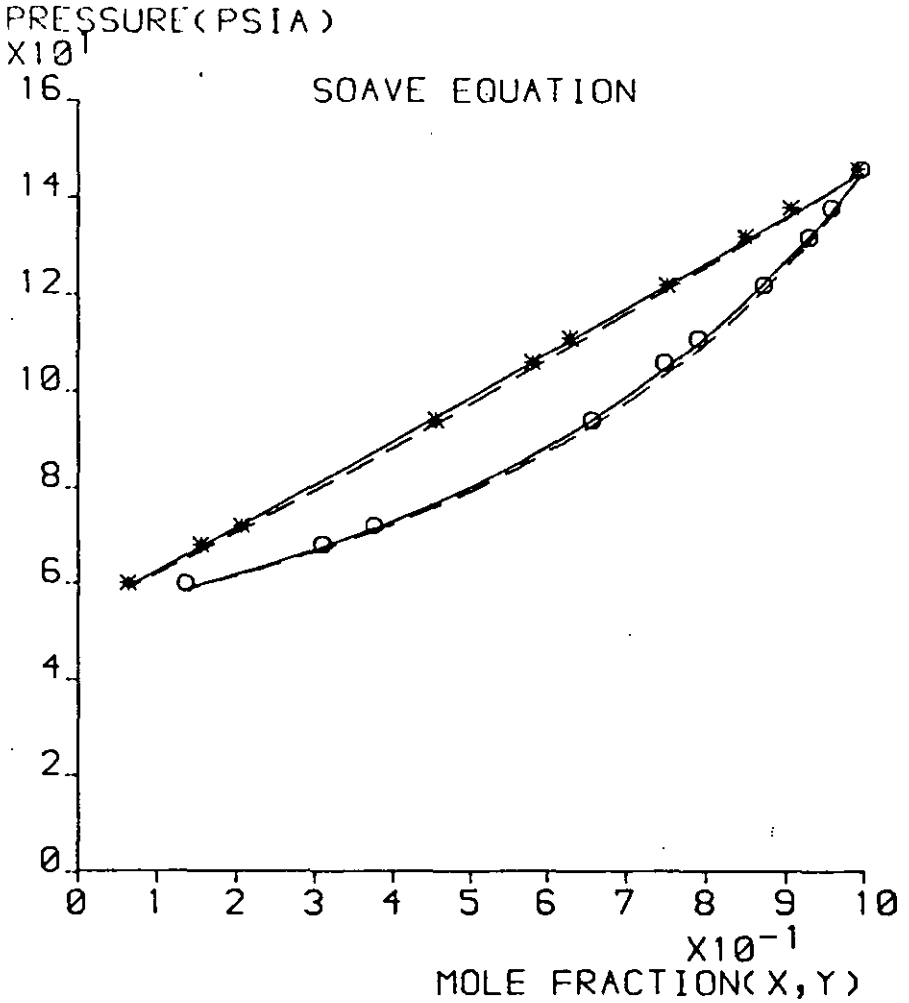


(a)

FIGURE 6.42 Propane-i-Butane System at 539.69°R (299.8K)

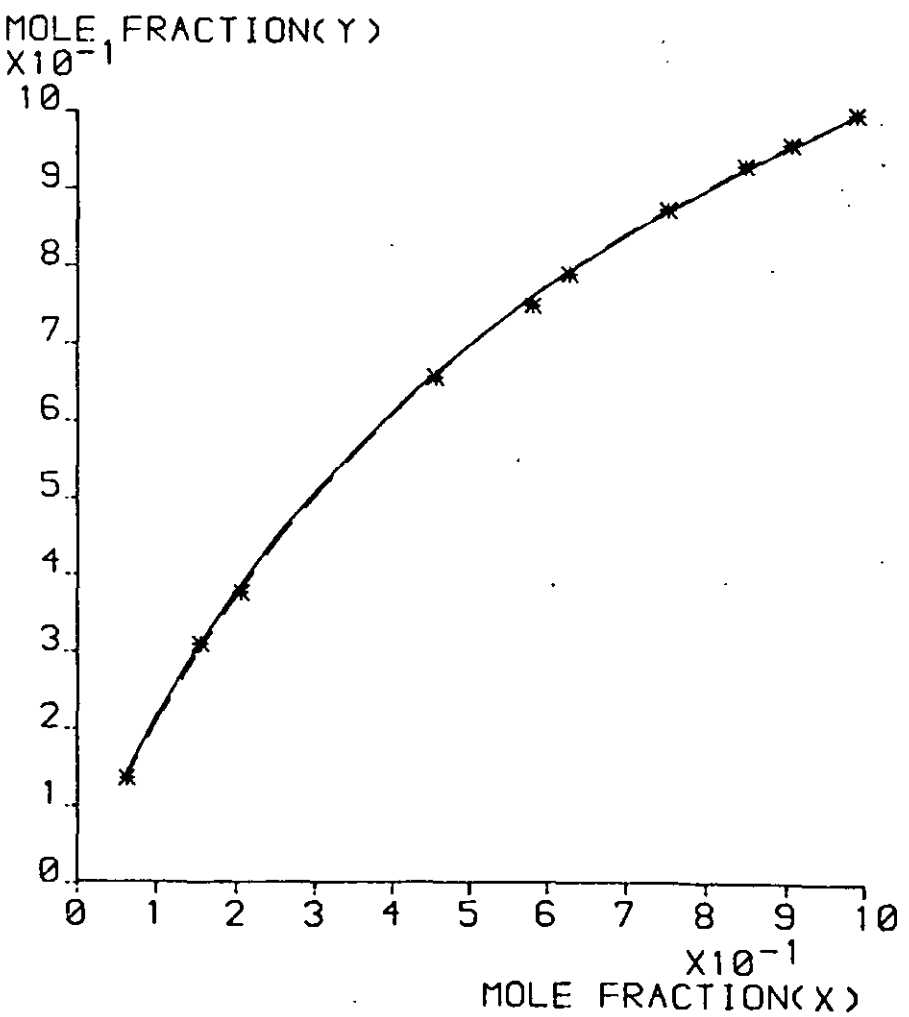


(b)

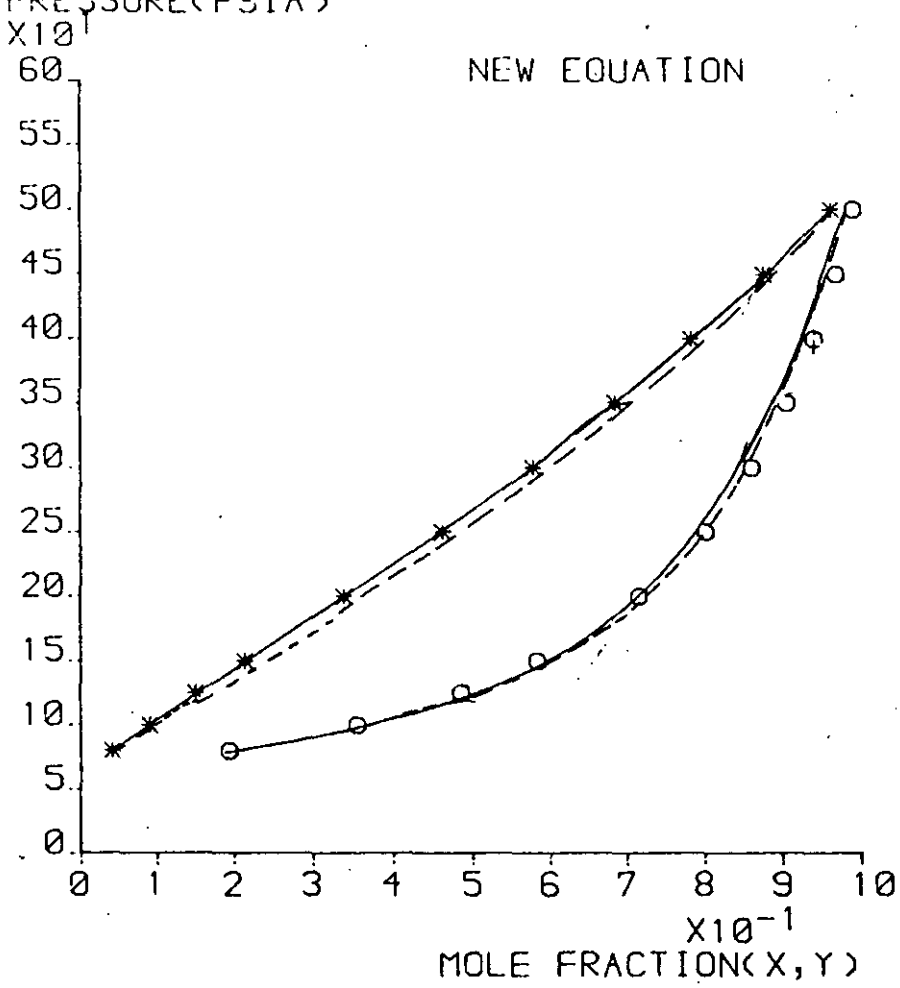


(a)

FIGURE 6.43 Propane-i-Butane System at 539.69°R (299.8K)

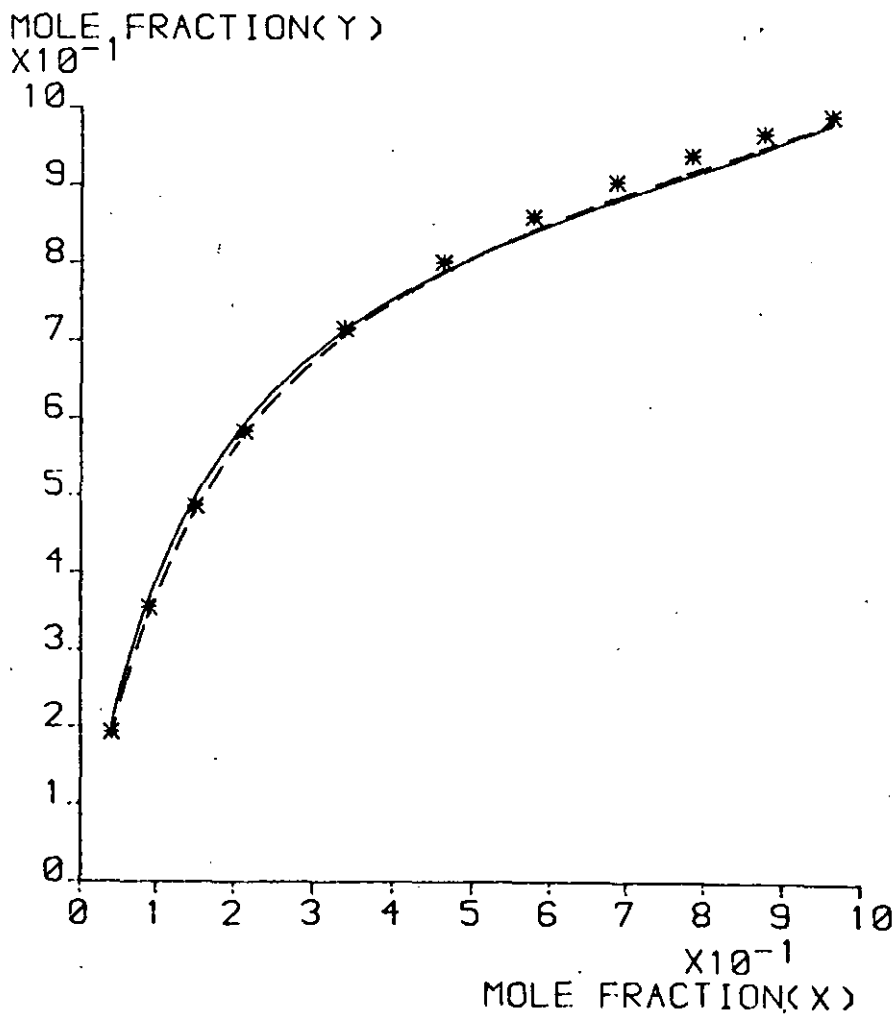


(b)

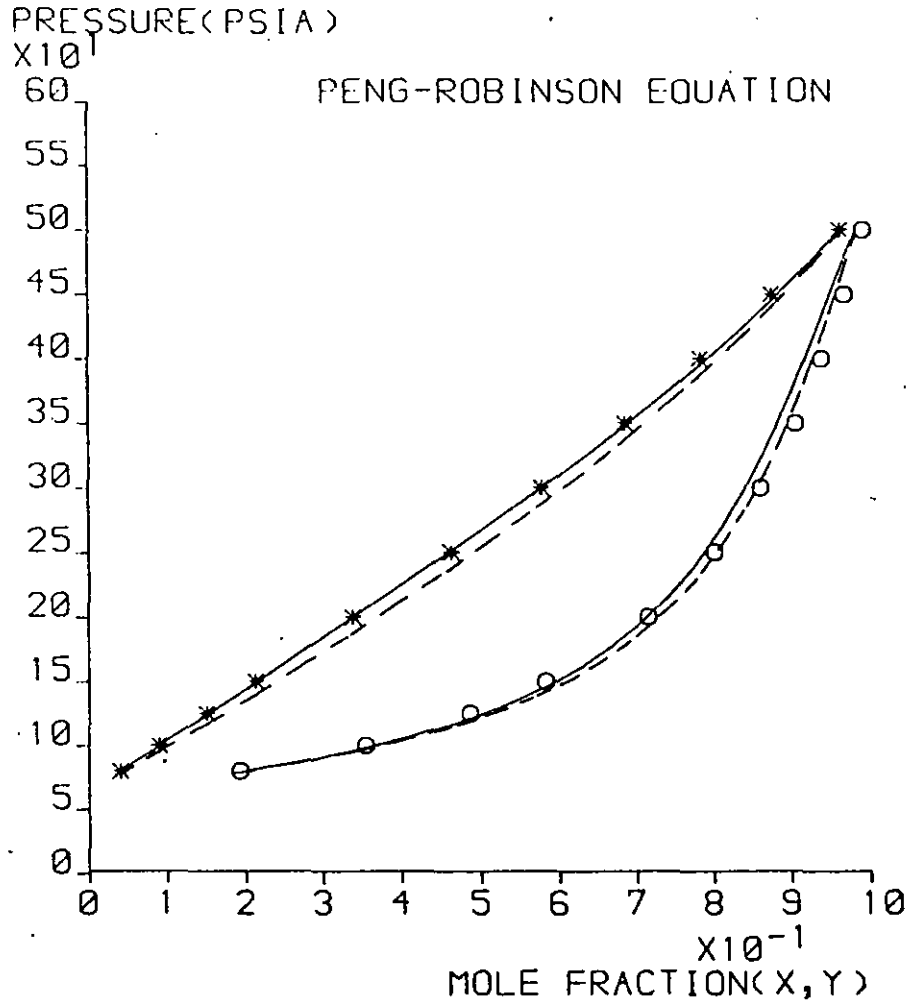


(a)

FIGURE 6.44 Propane-n-Pentane System at 649.73°R (361K)

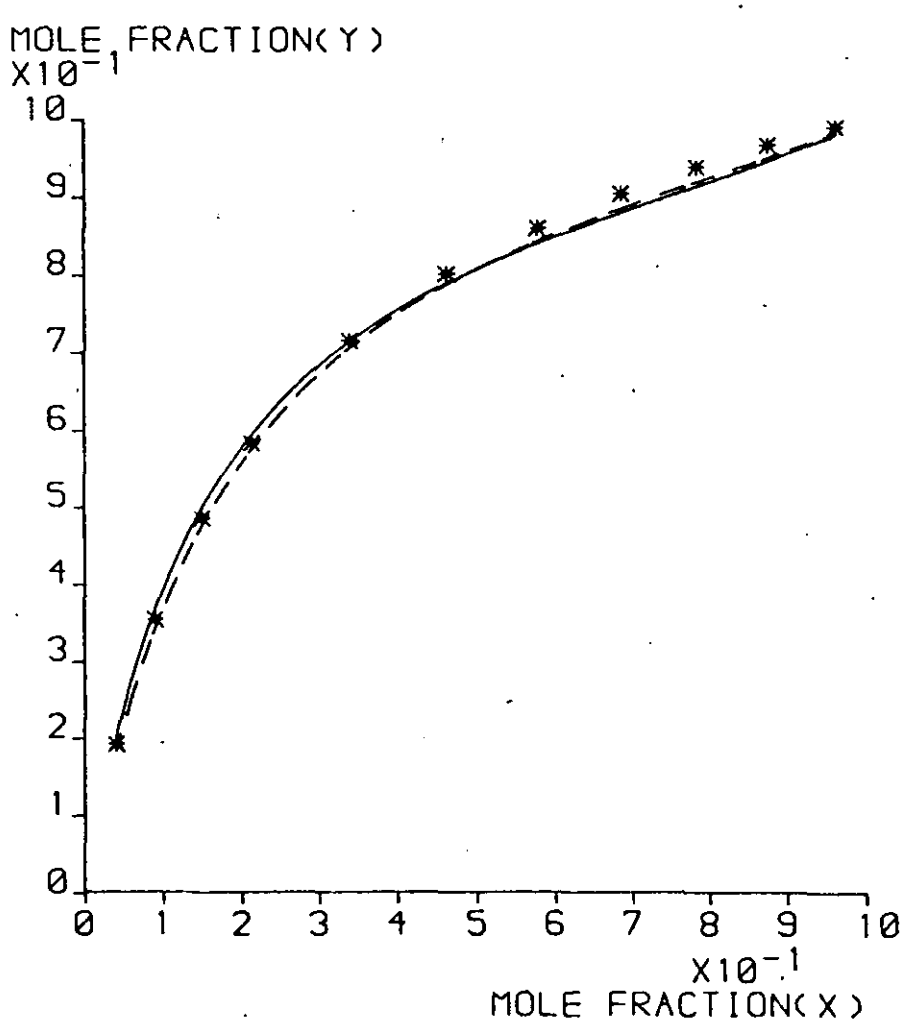


(b)



(a)

FIGURE 6.45 Propane-n-Pentane System at 649.73°R (361K)



(b)

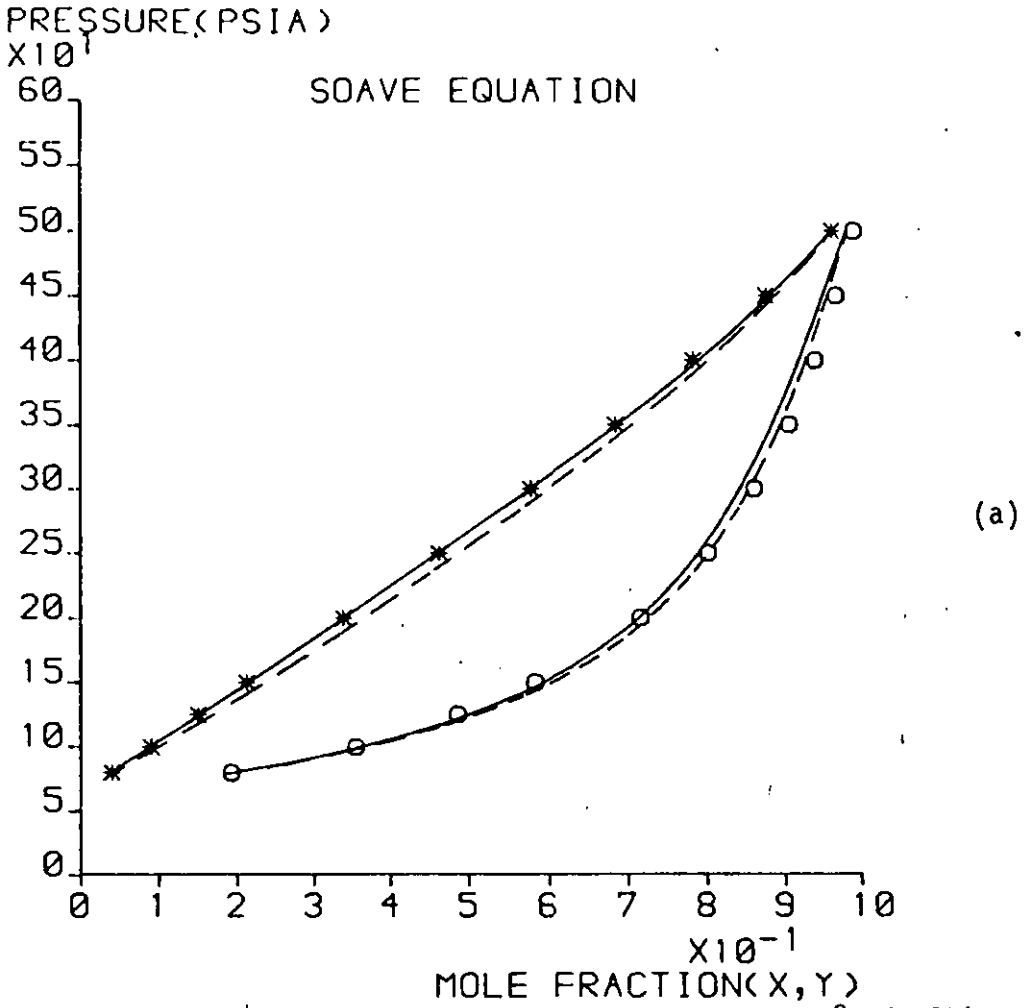
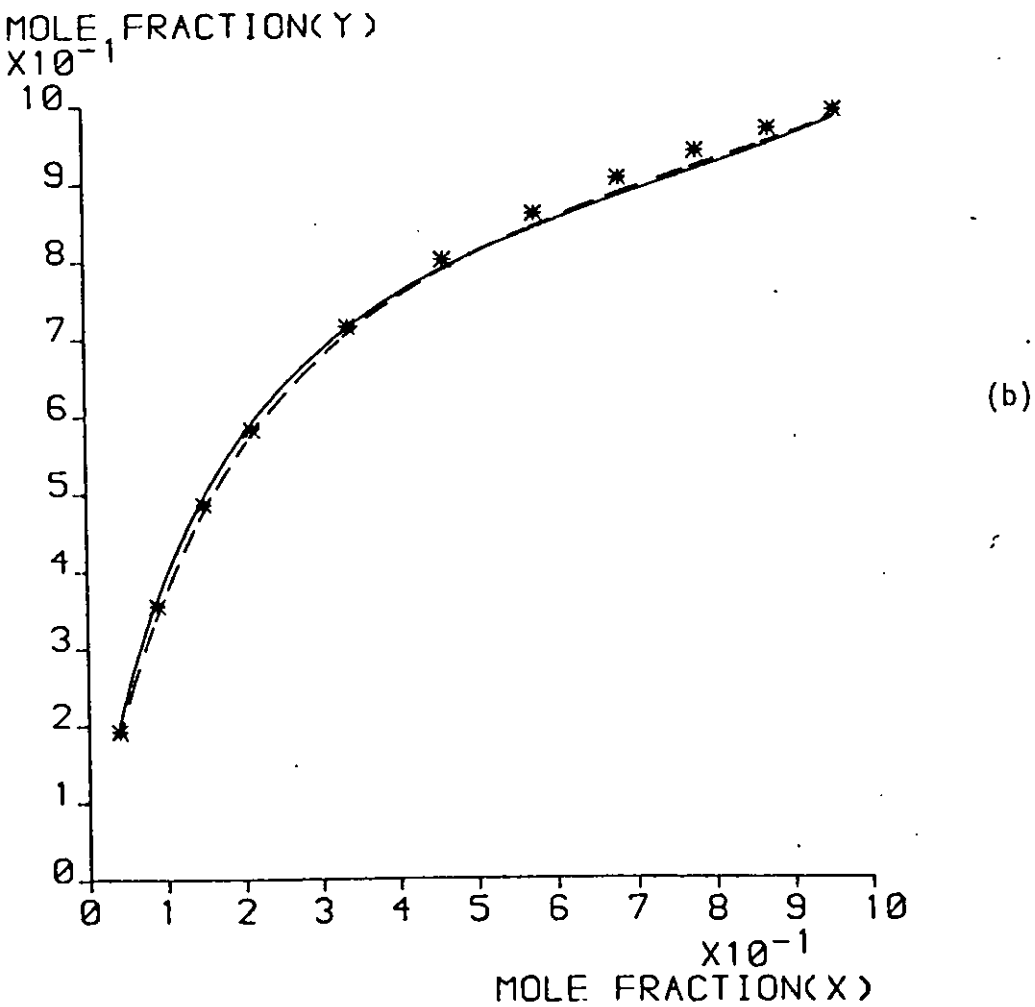
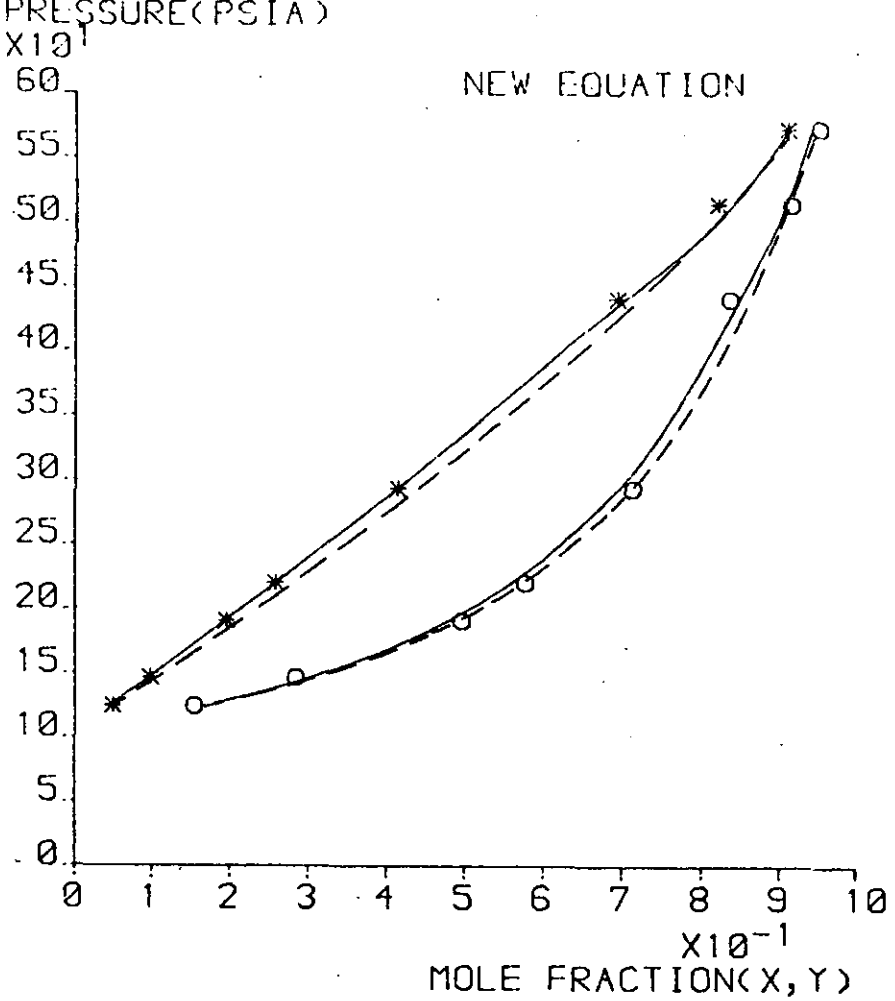


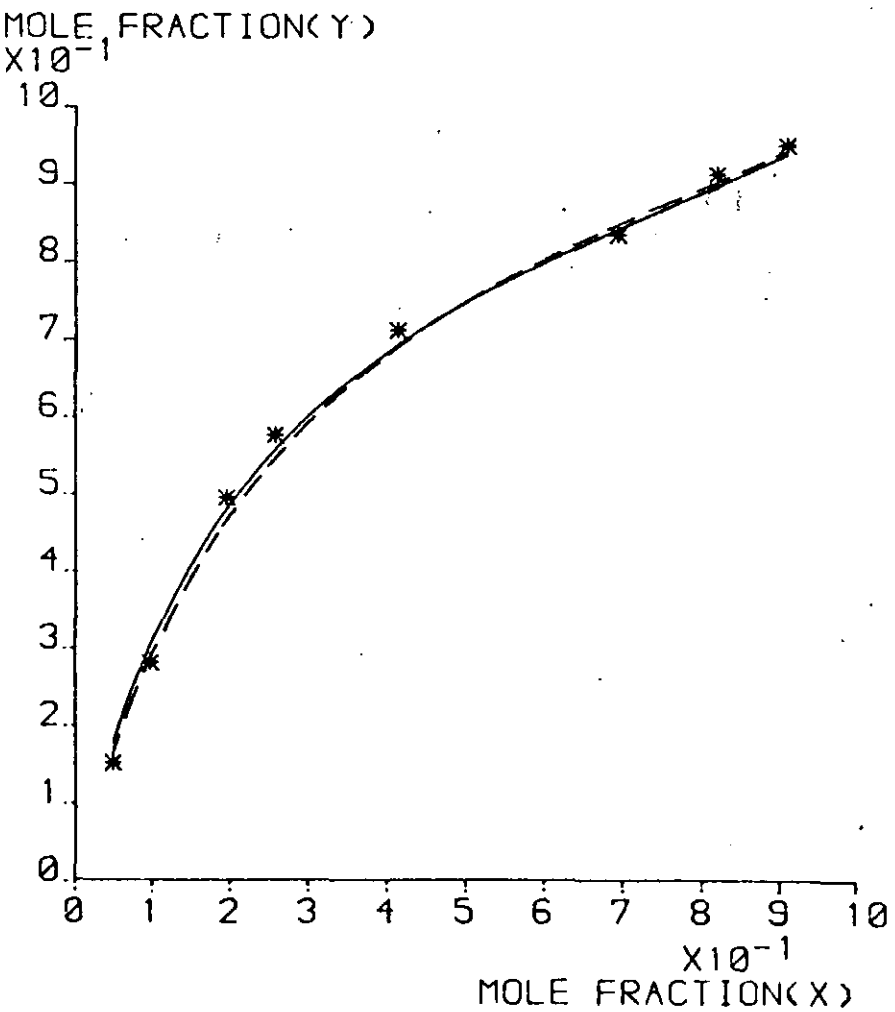
FIGURE 6.46 Propane-n-Pentane System at 649.73°R (361K)



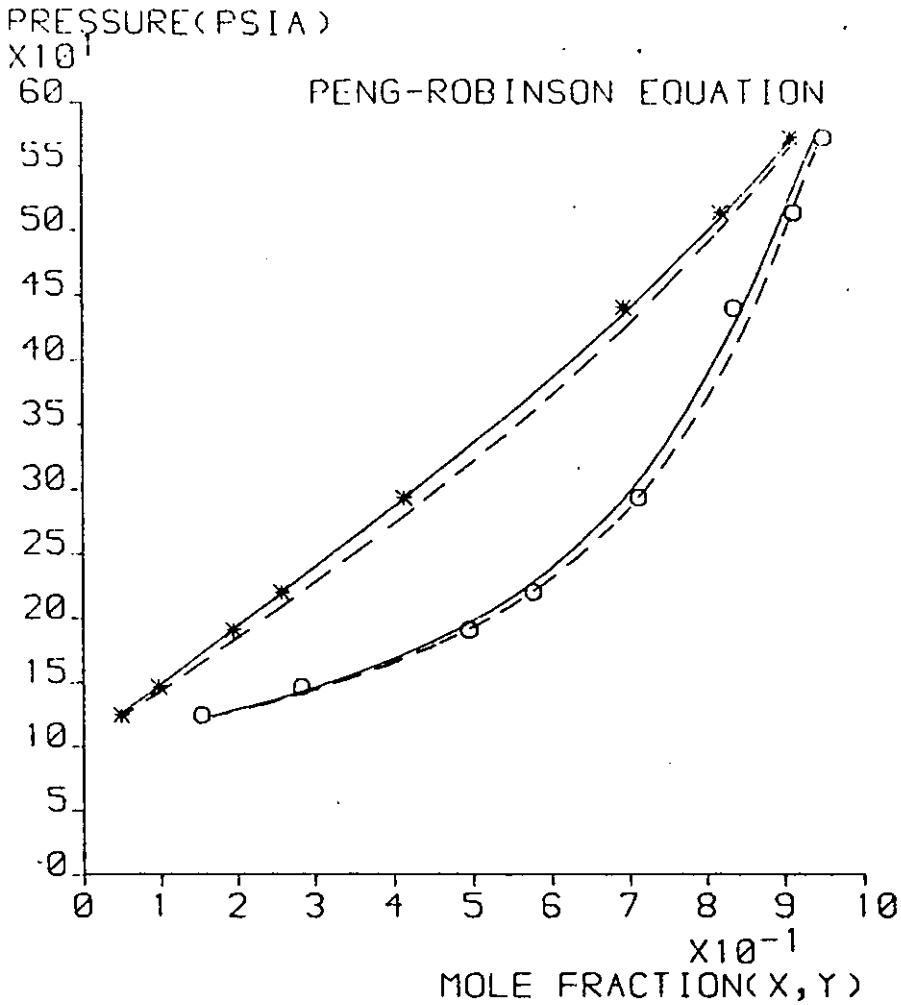


(a)

FIGURE 6.47 Propane-i-Pentane System at 671.69°R (373.2K)

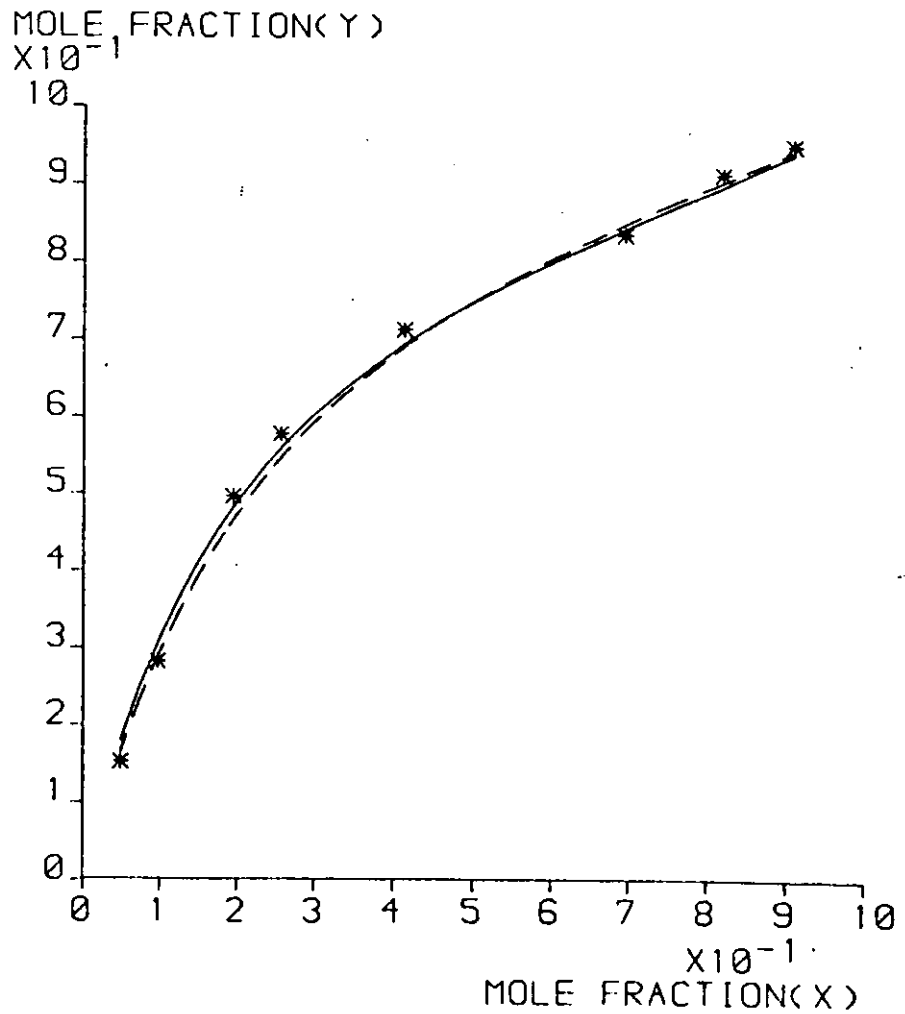


(b)

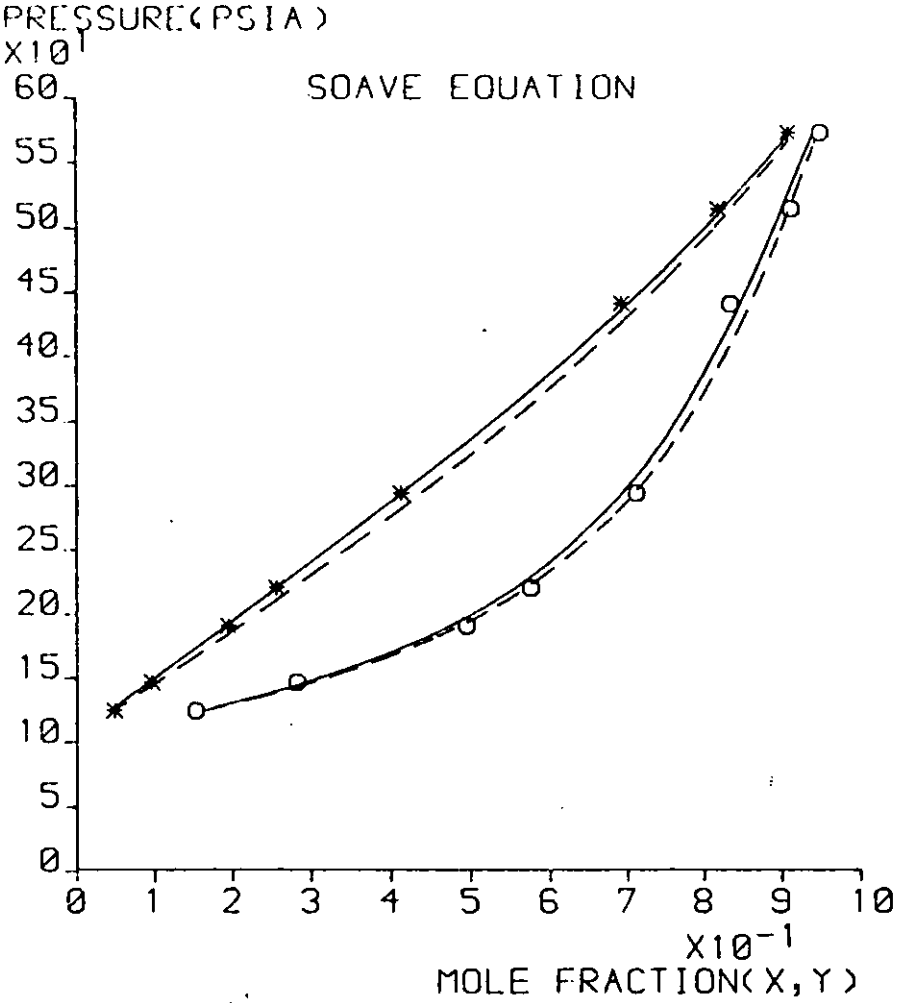


(a)

FIGURE 6.48 Propane-i-Pentane System at 671.69°R (373.2K)

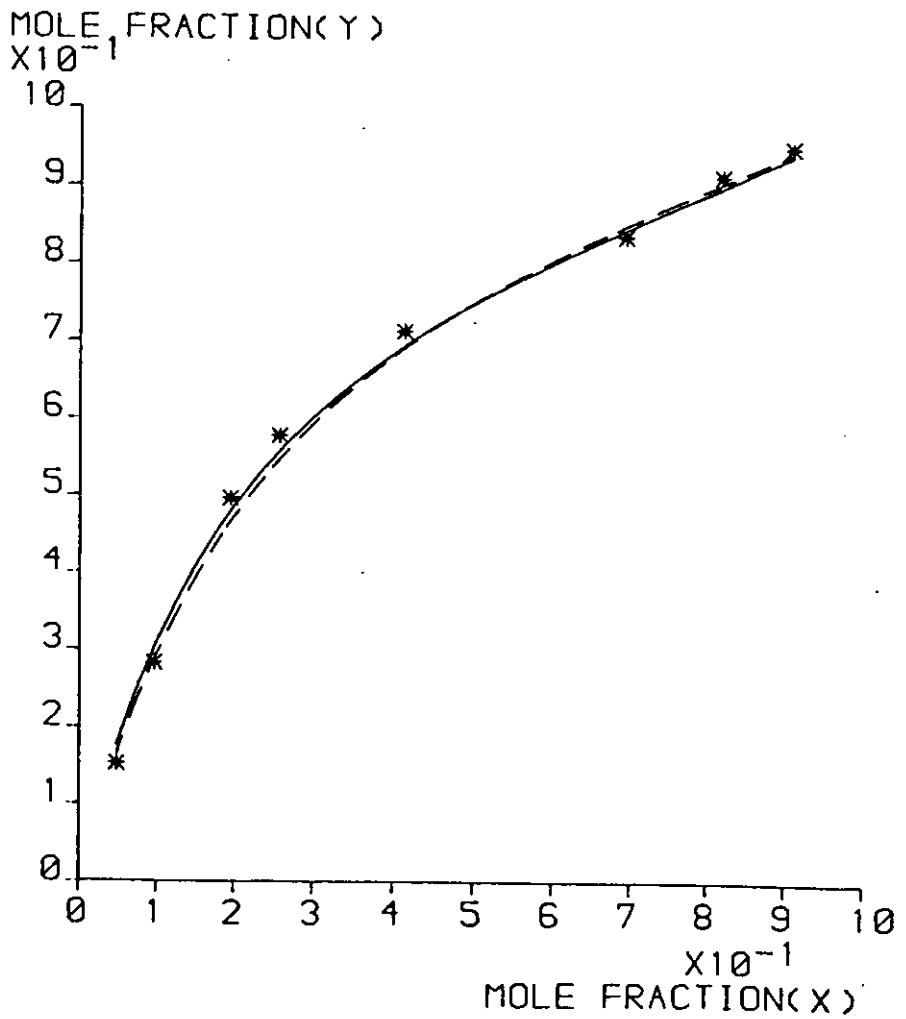


(b)



(a)

FIGURE 6.49 Propane-i-Pentane System at 671.69°R (373.2K)



(b)

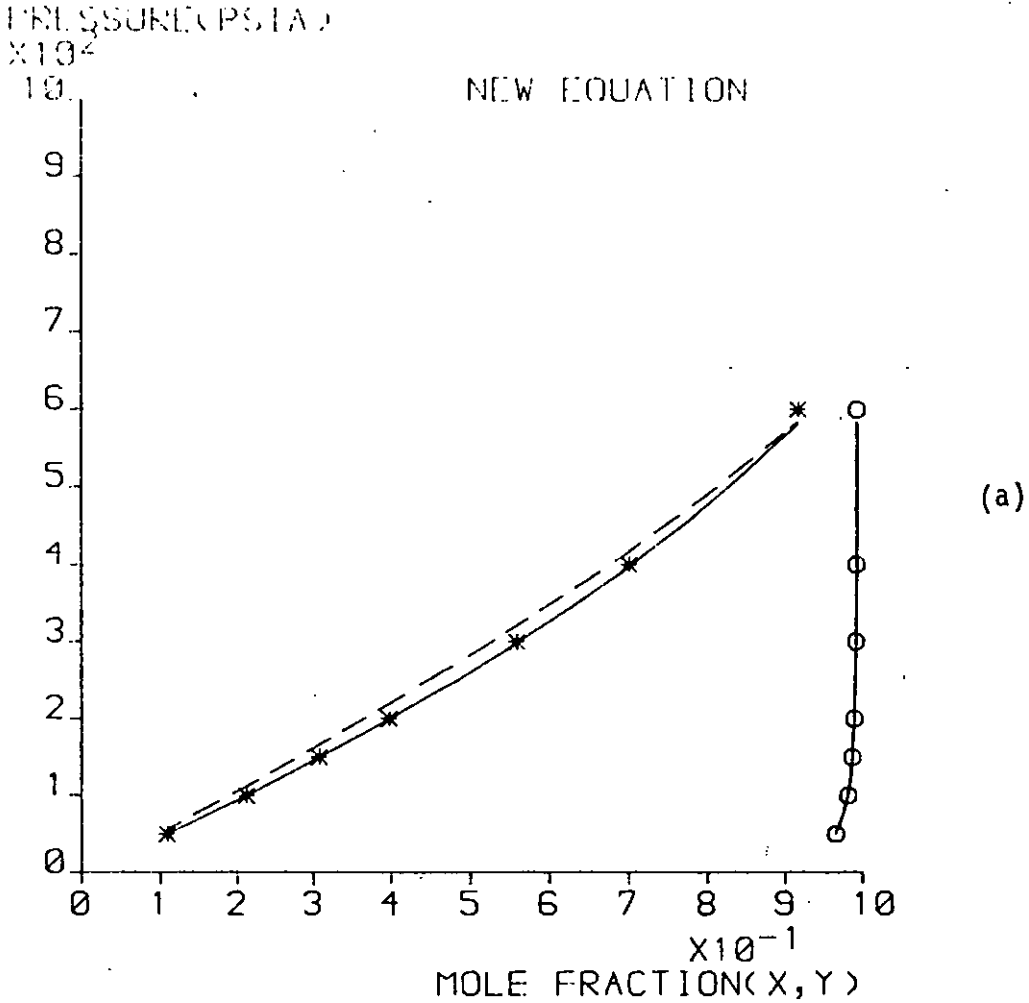
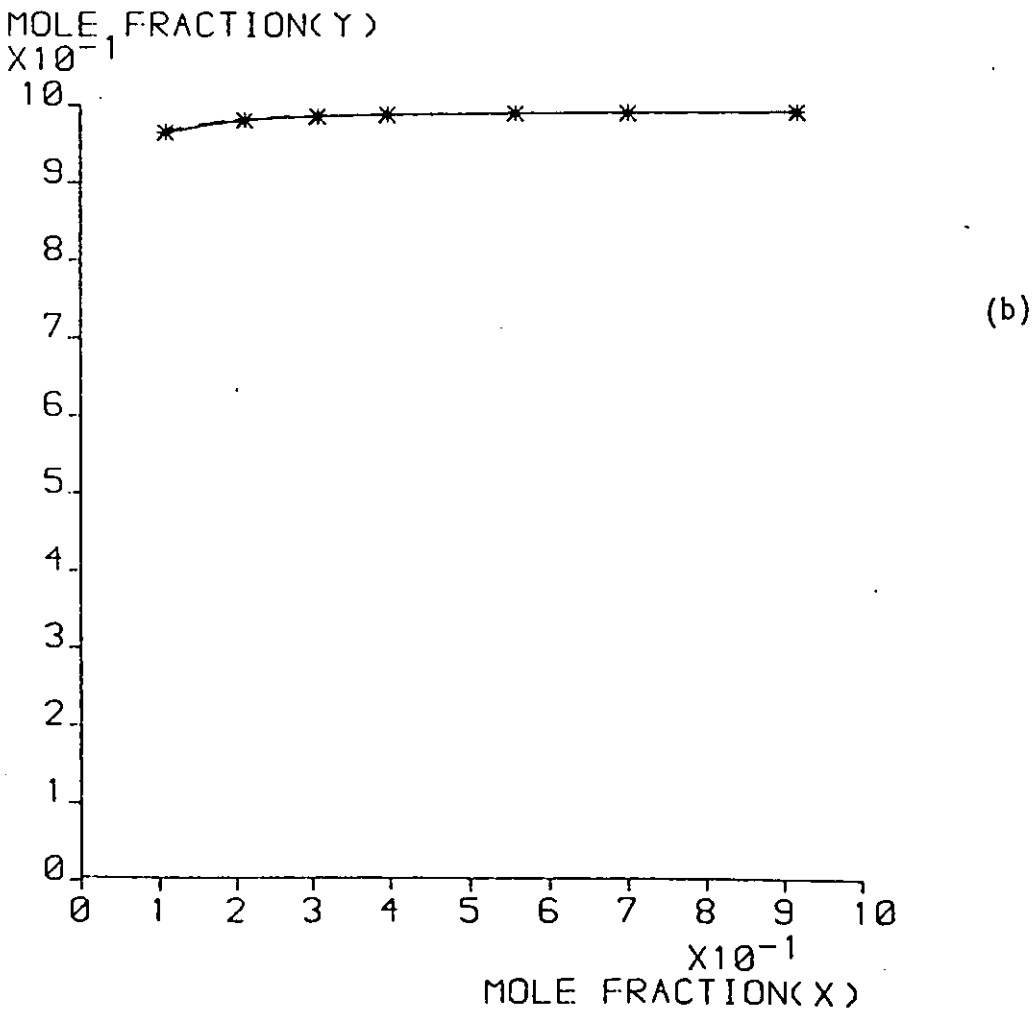
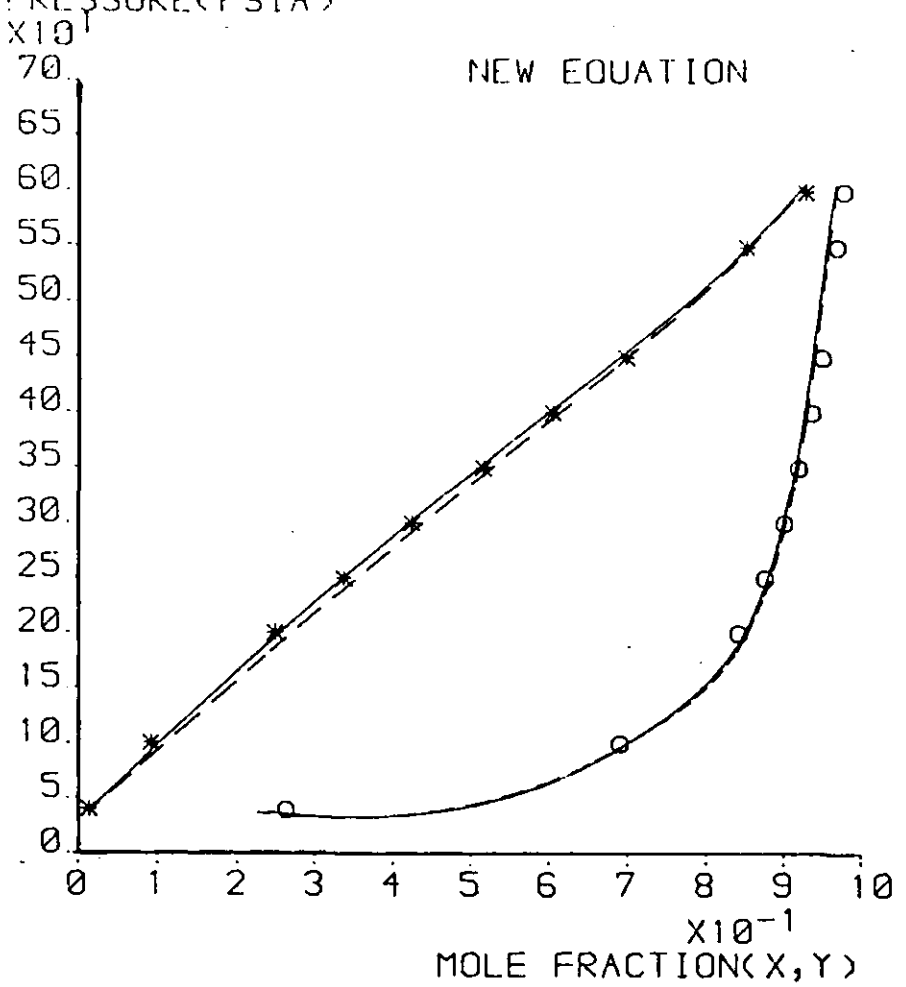


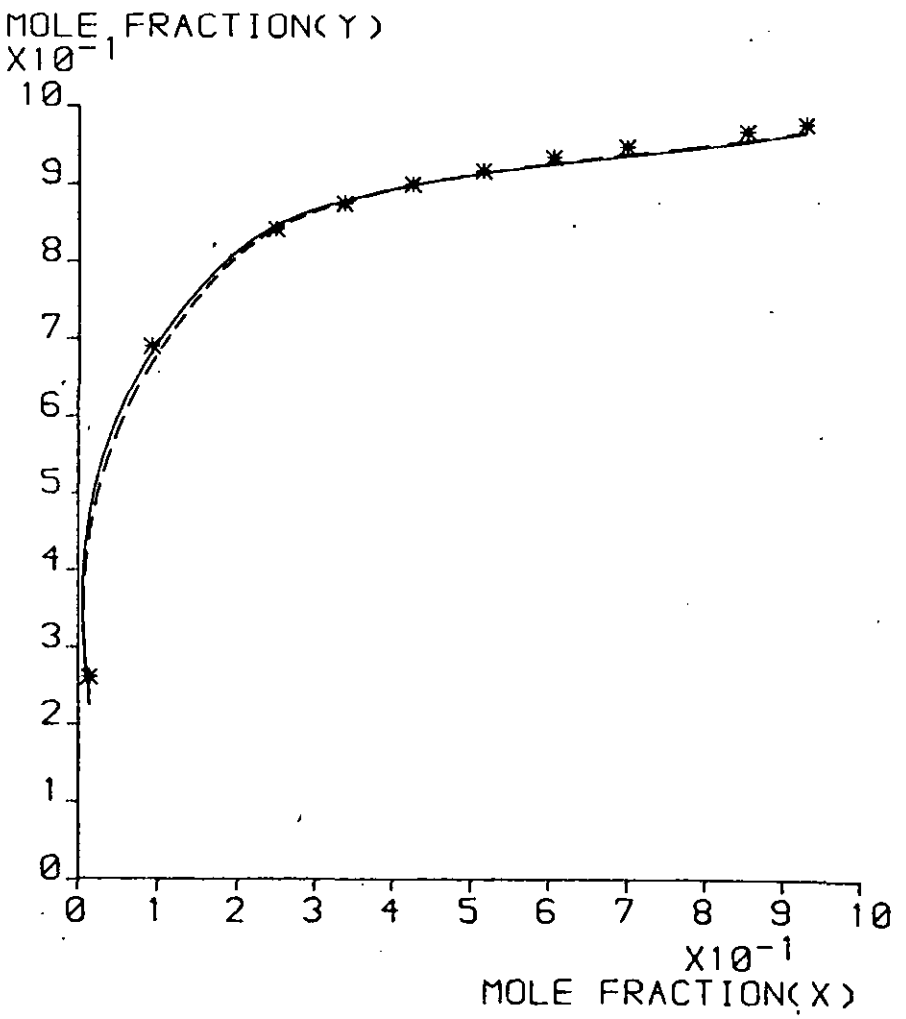
FIGURE 6.50 Propane-n-Decane System at 679.67°R (377.6K)



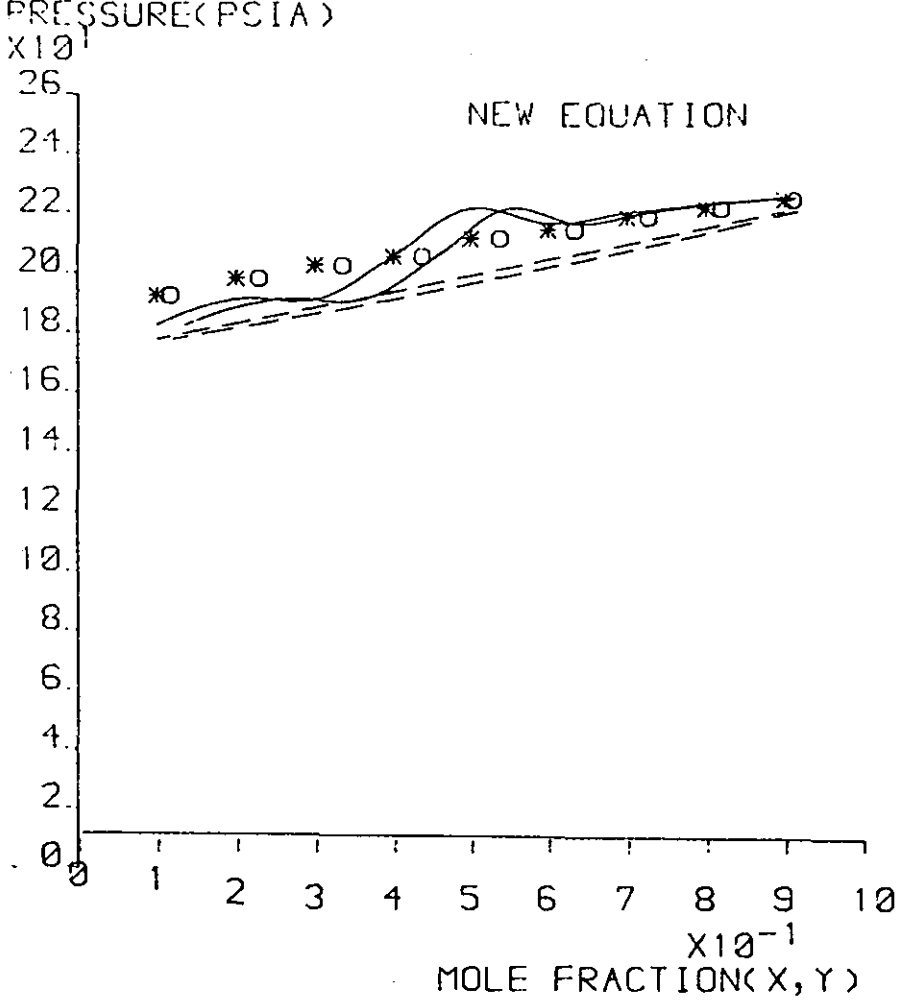


(a)

FIGURE 6.51 Propane-Benzene System at 679.67°R (377.6K)

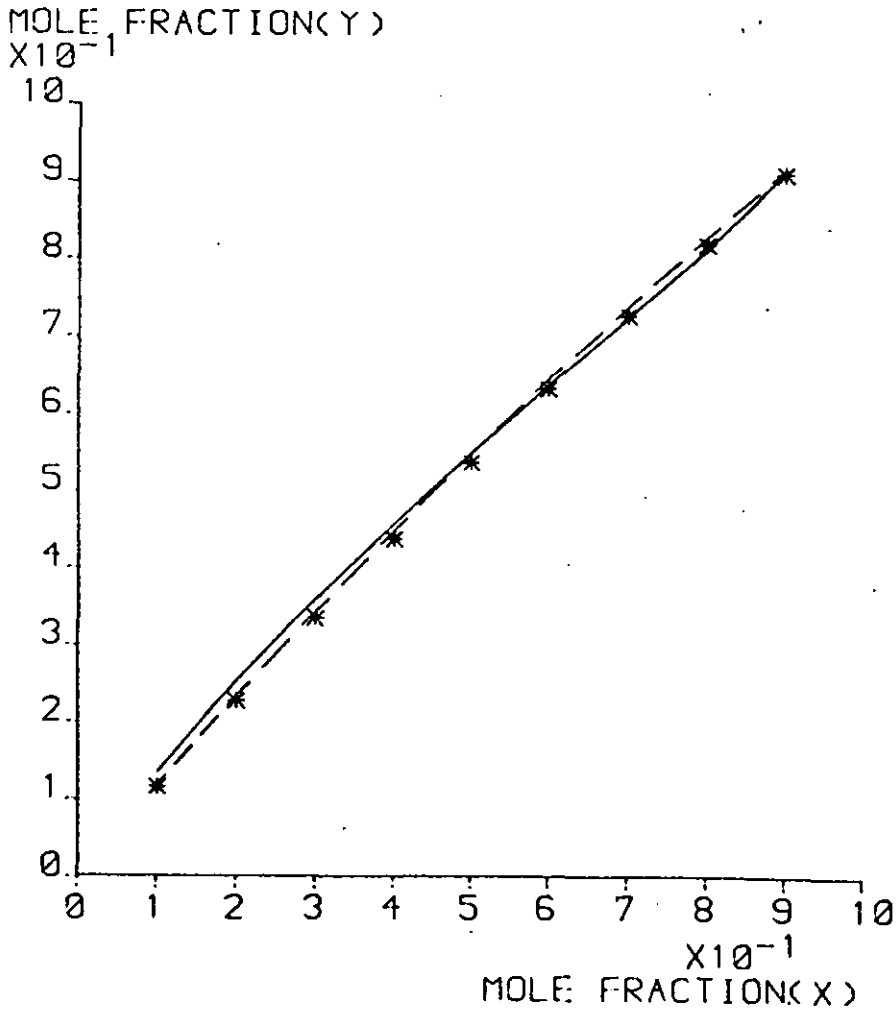


(b)

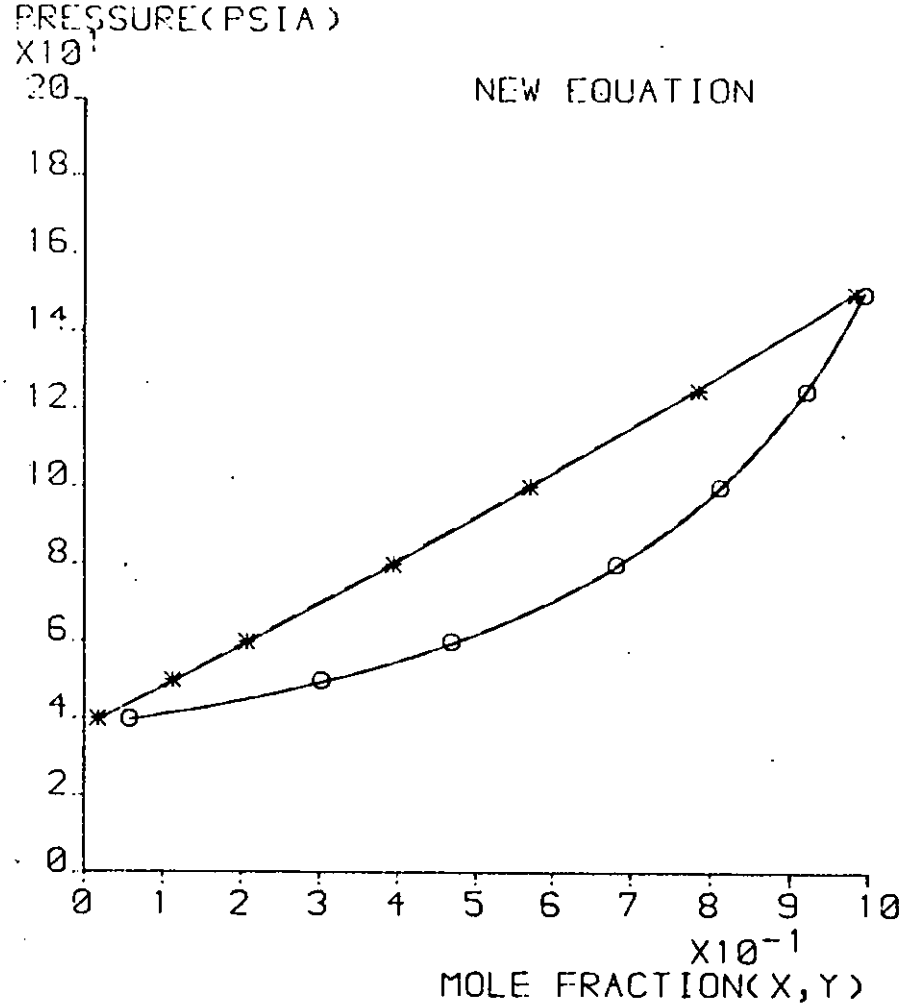


(a)

FIGURE 6.52 Propylene-Propane System at 559.71°R (311K)

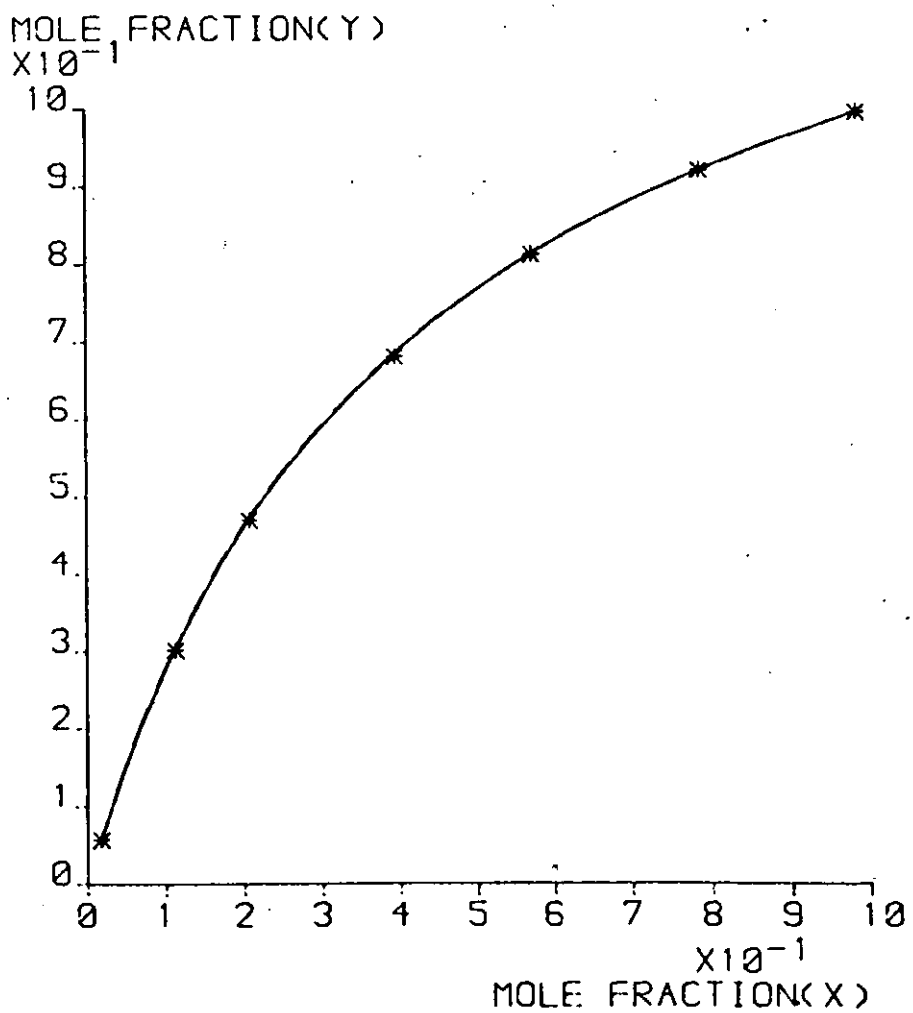


(b)

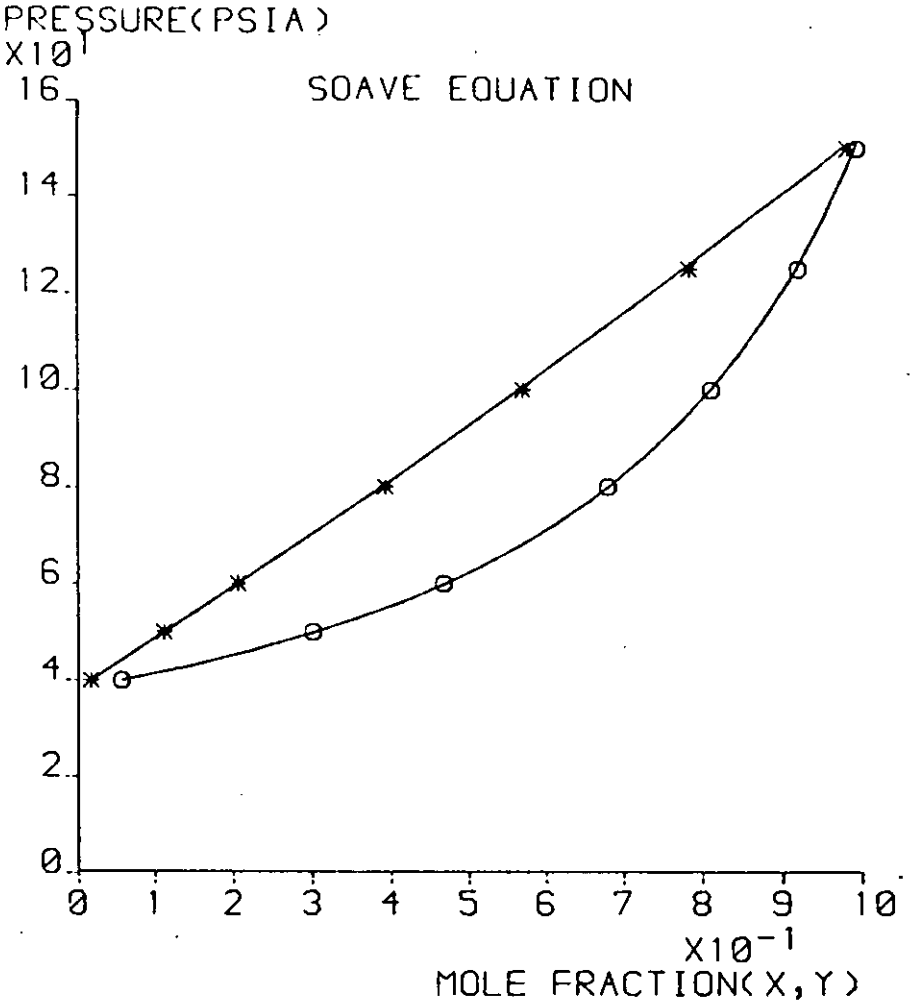


(a)

FIGURE 6.53 Propylene-1-Butene System at 529.67°R (294.3K)

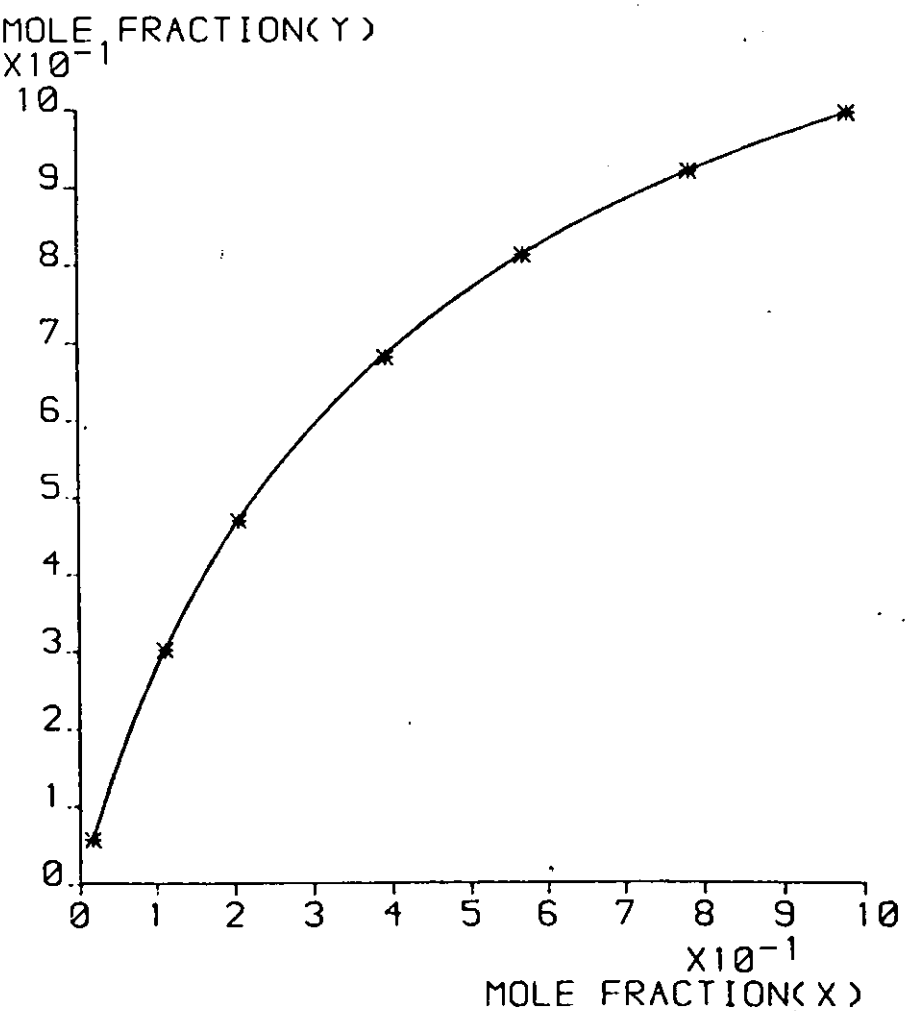


(b)

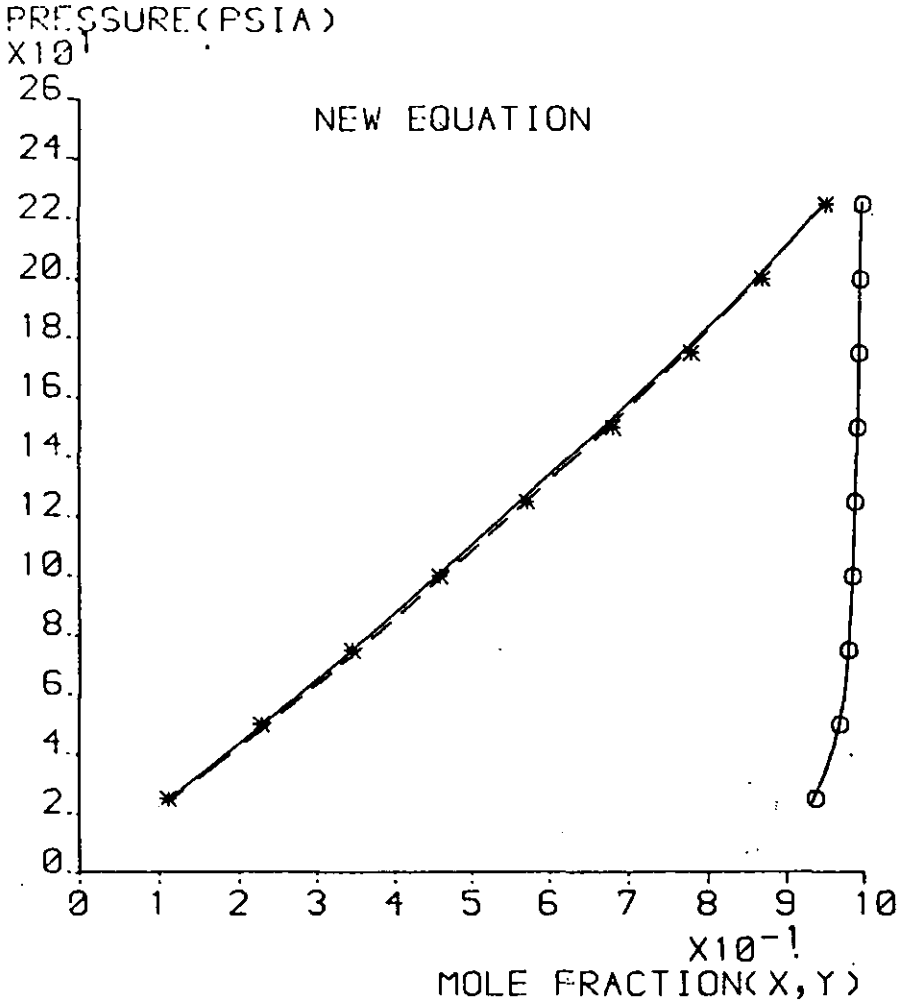


(a)

FIGURE 6.54 Propylene-1-Butene System at 539.67°R (294.3K)

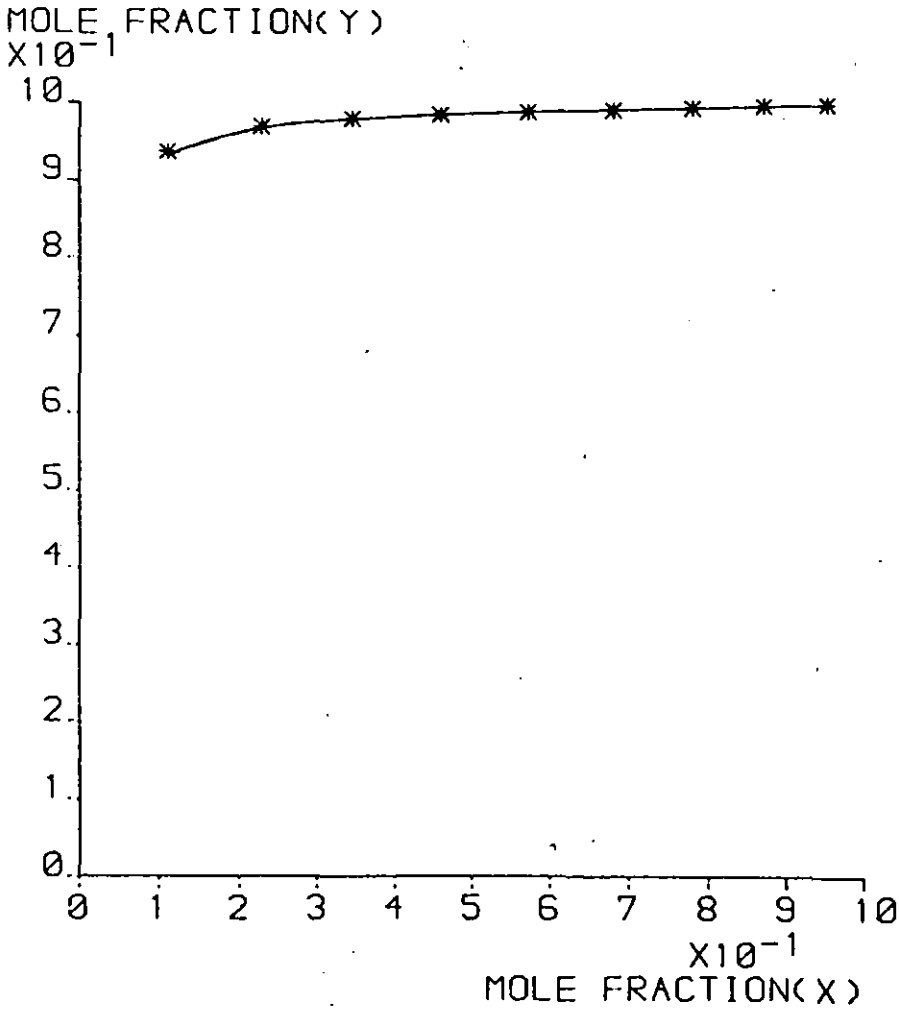


(b)

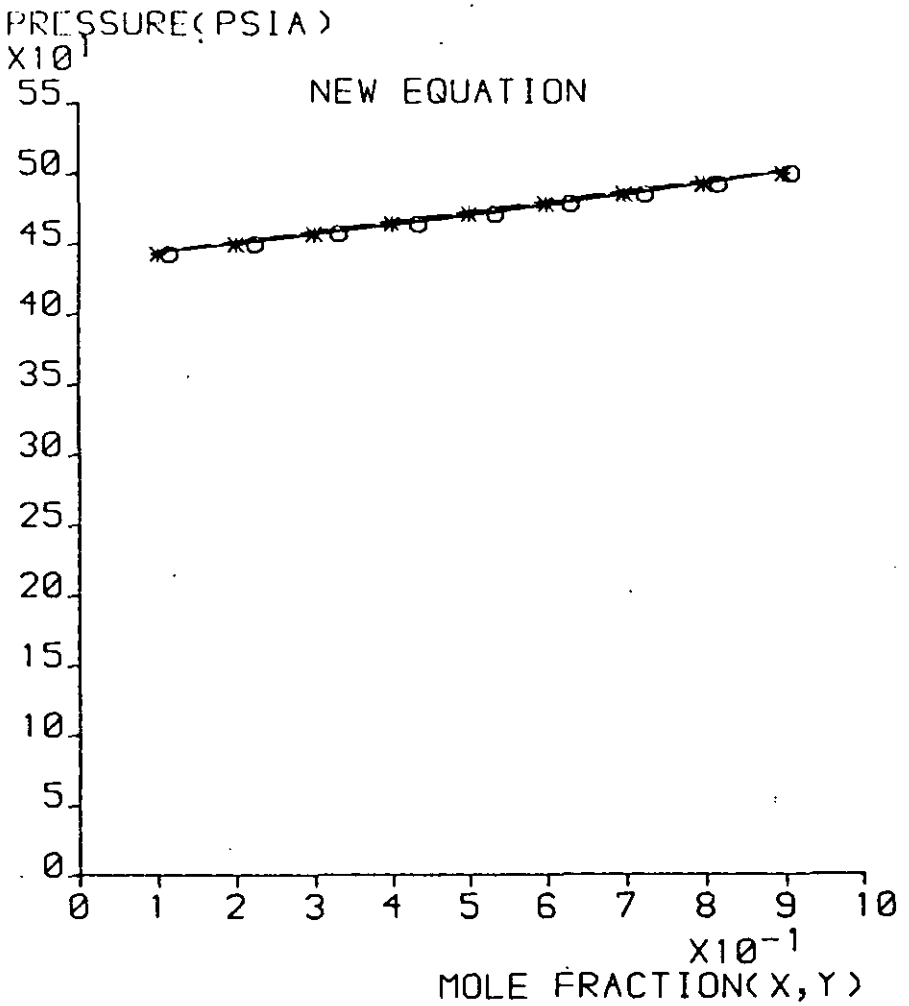


(a)

FIGURE 6.55 n-Butane-n-Decane System at 679.67°R (377.6K)

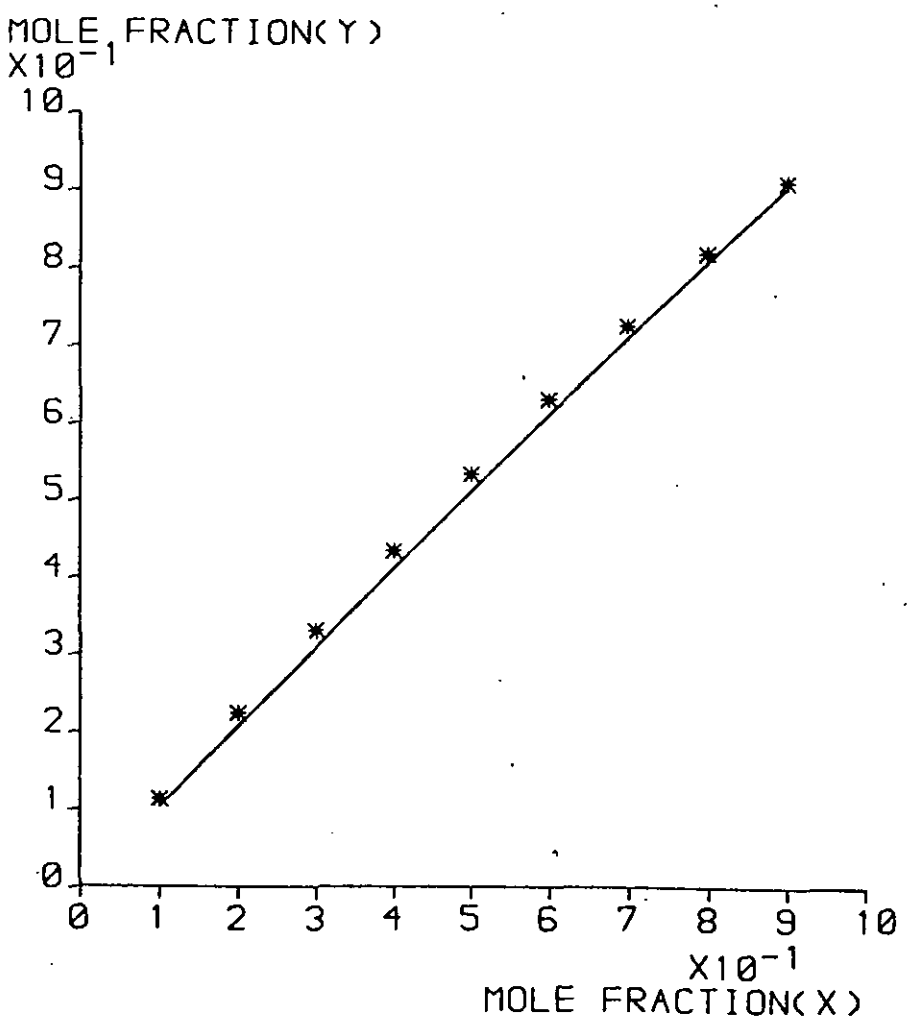


(b)

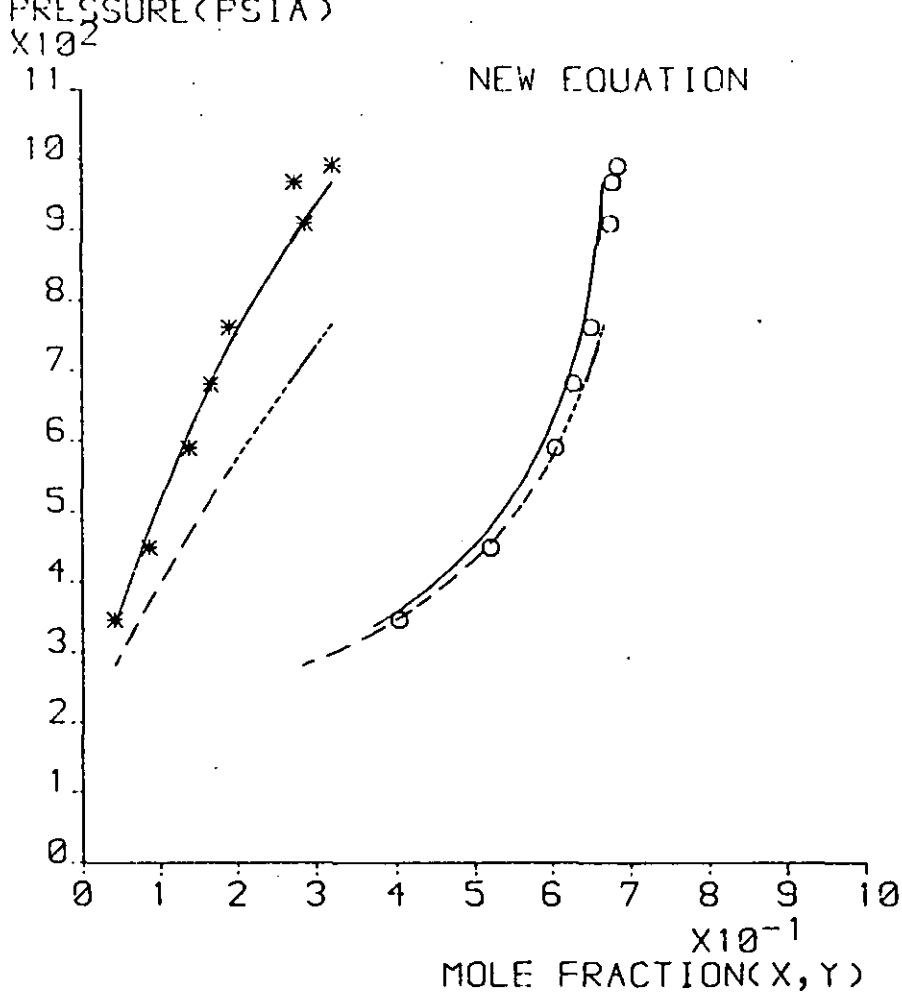


(a)

FIGURE 6.56 1-Butene-n-Butane System at 739.69°R (411K)

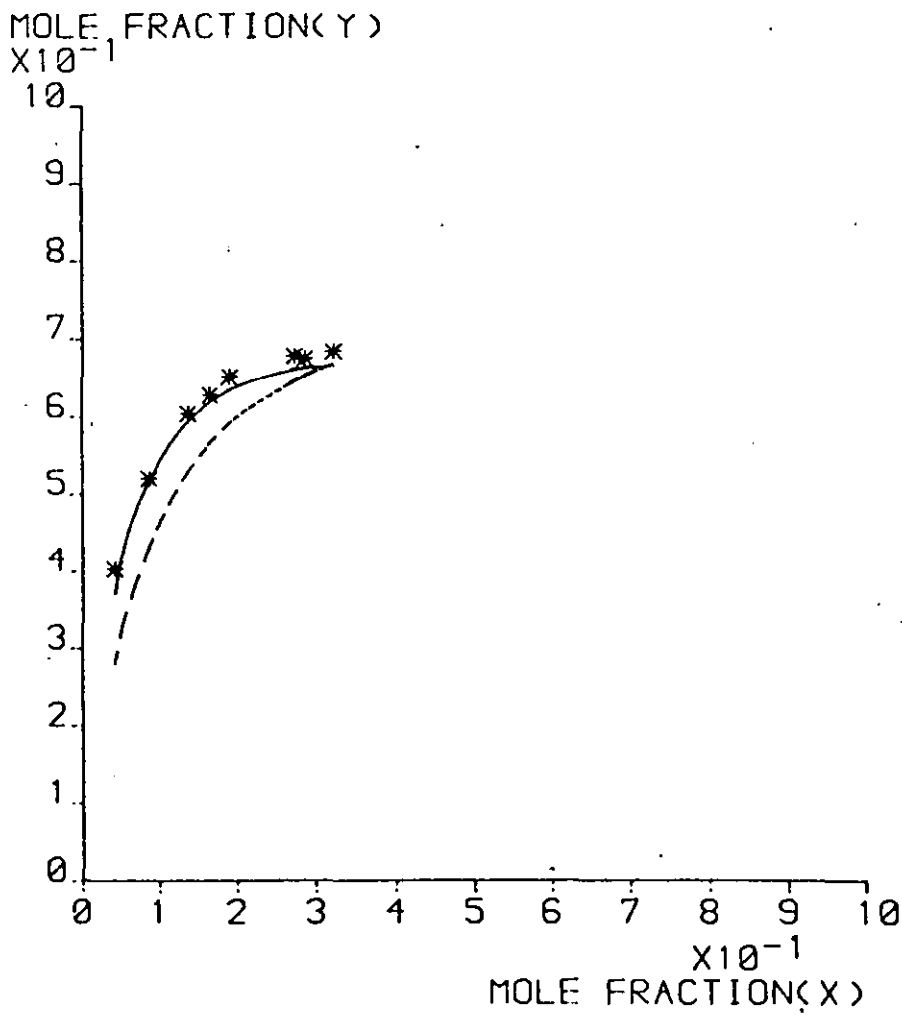


(b)

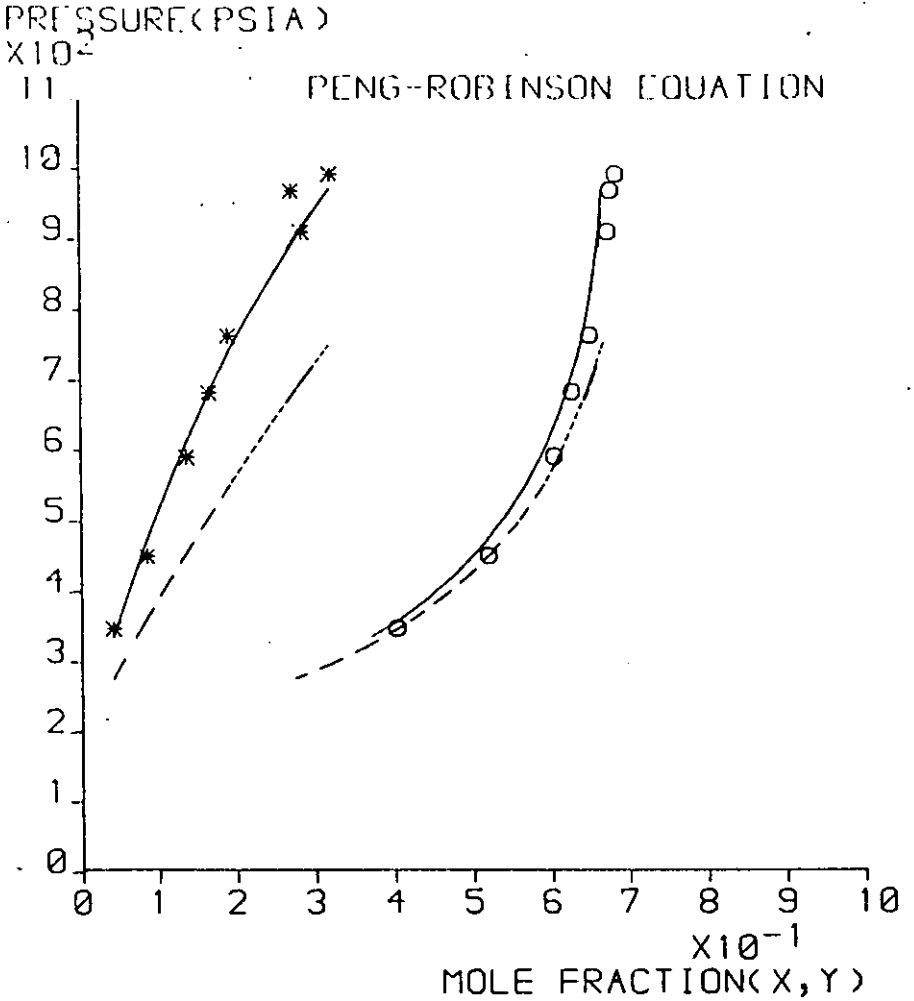


(a)

FIGURE 6.57 Methane-CO_2 System at 434.63°R (241.5K)

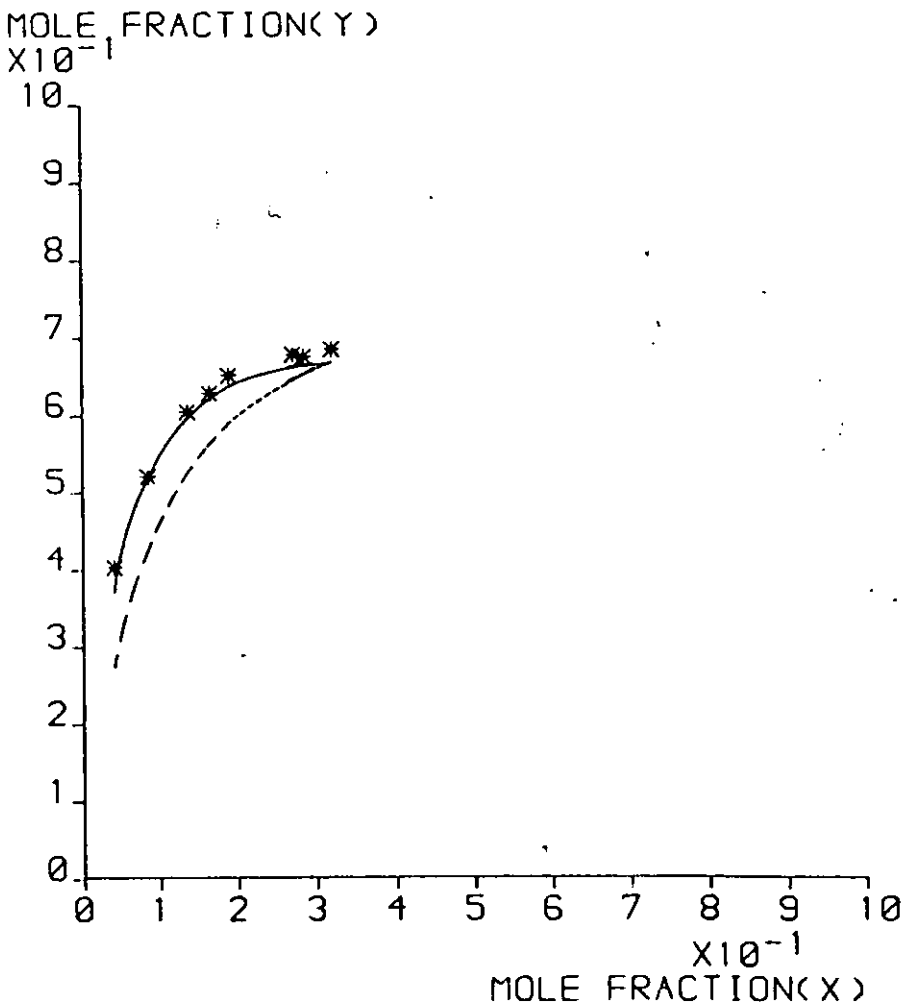


(b)

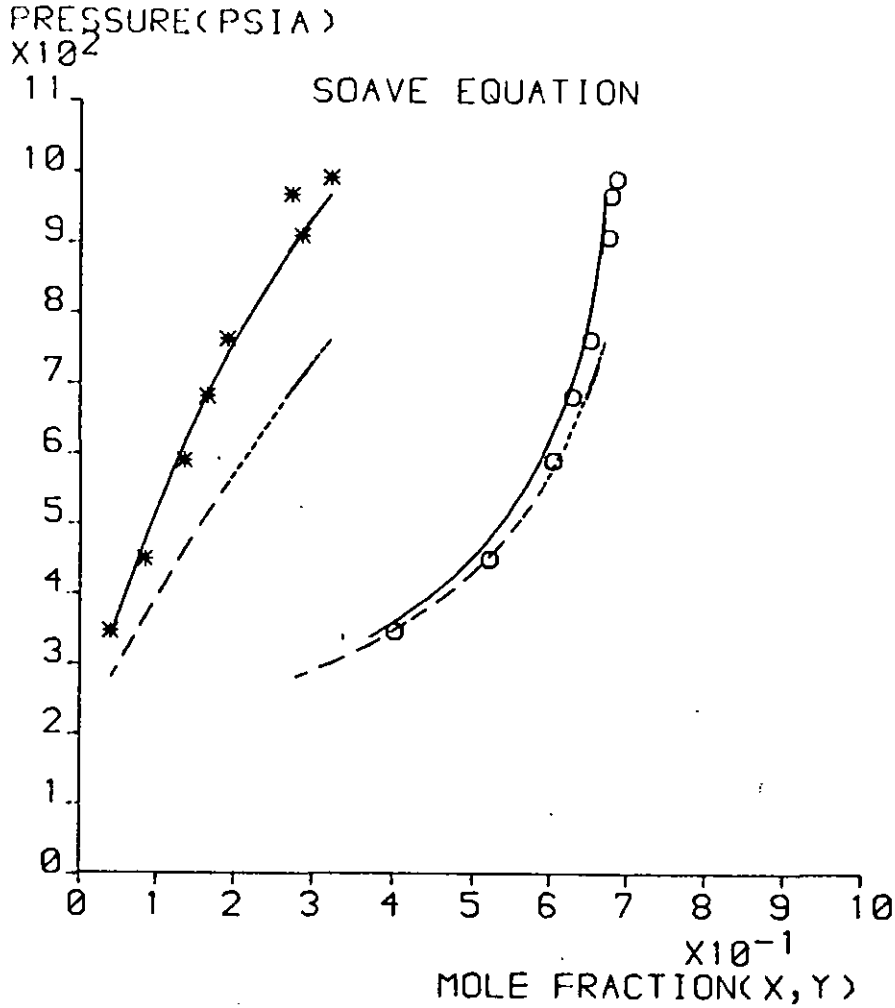


(a)

FIGURE 6.58 Methane-CO_2 System at 434.63°R (241.5K)

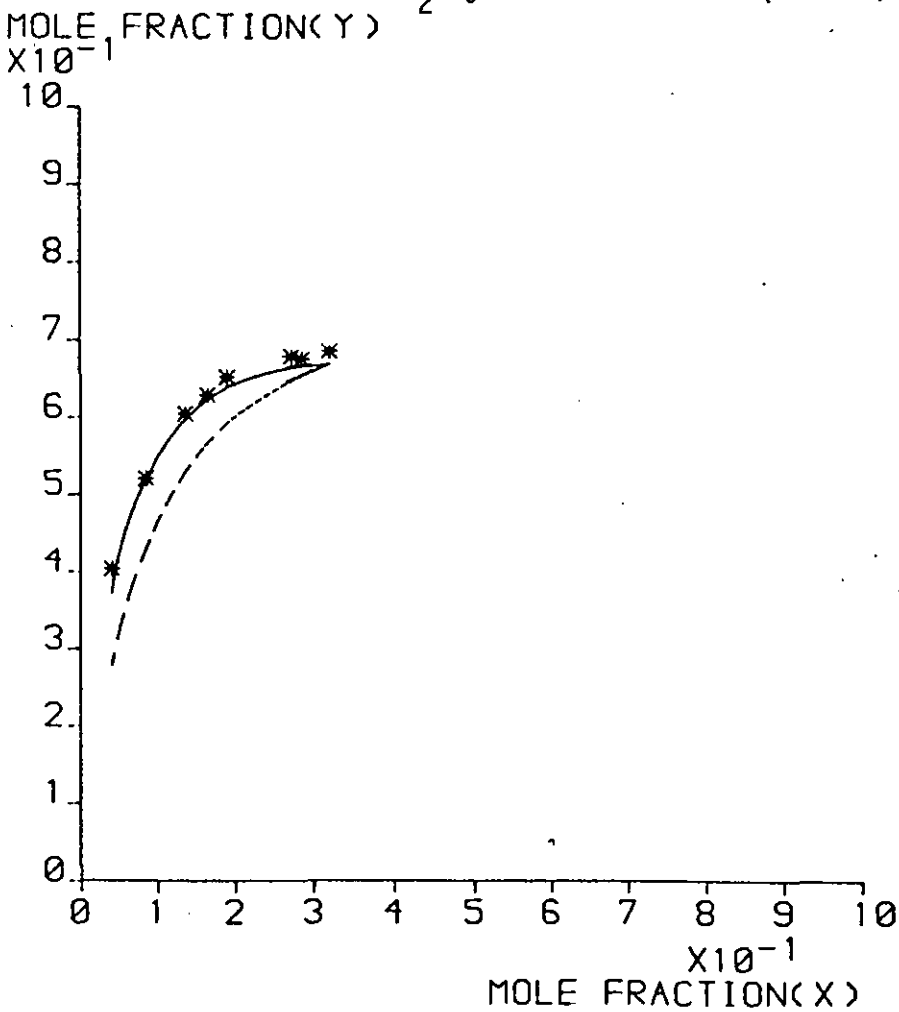


(b)

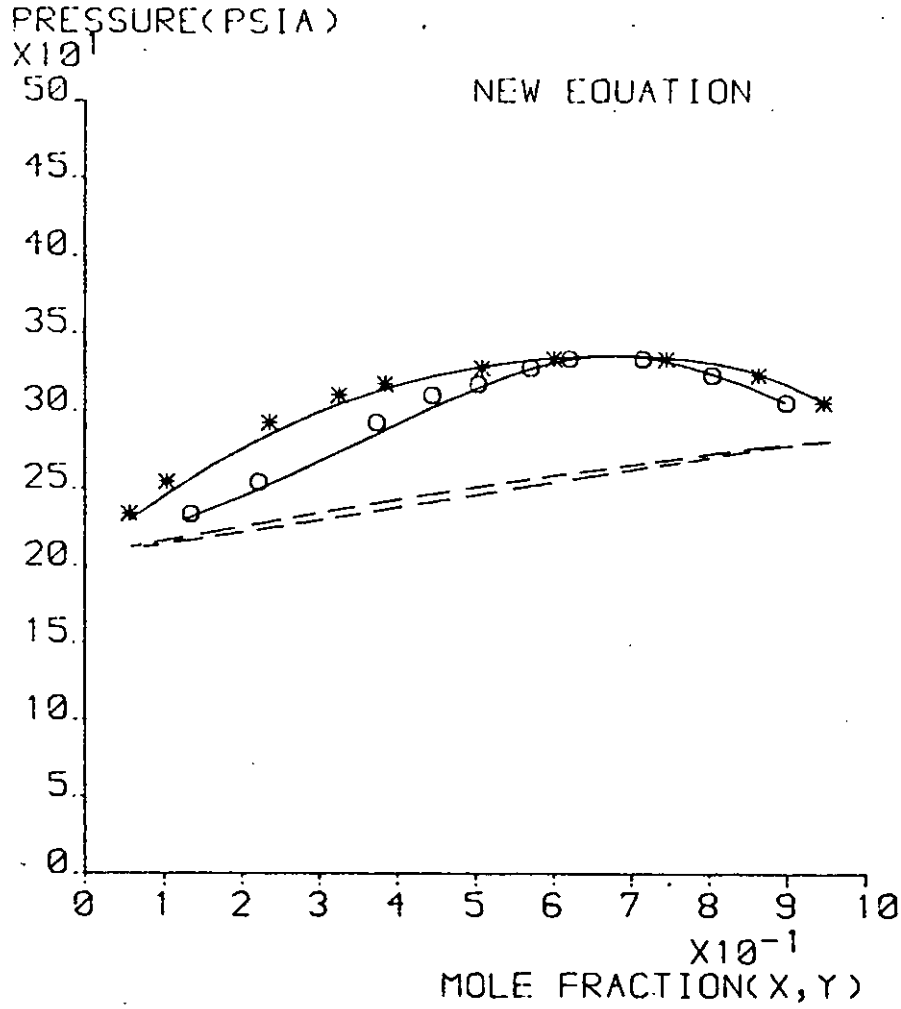


(a)

FIGURE 6.59 Methane-CO_2 System at 434.63°R (241.5K)

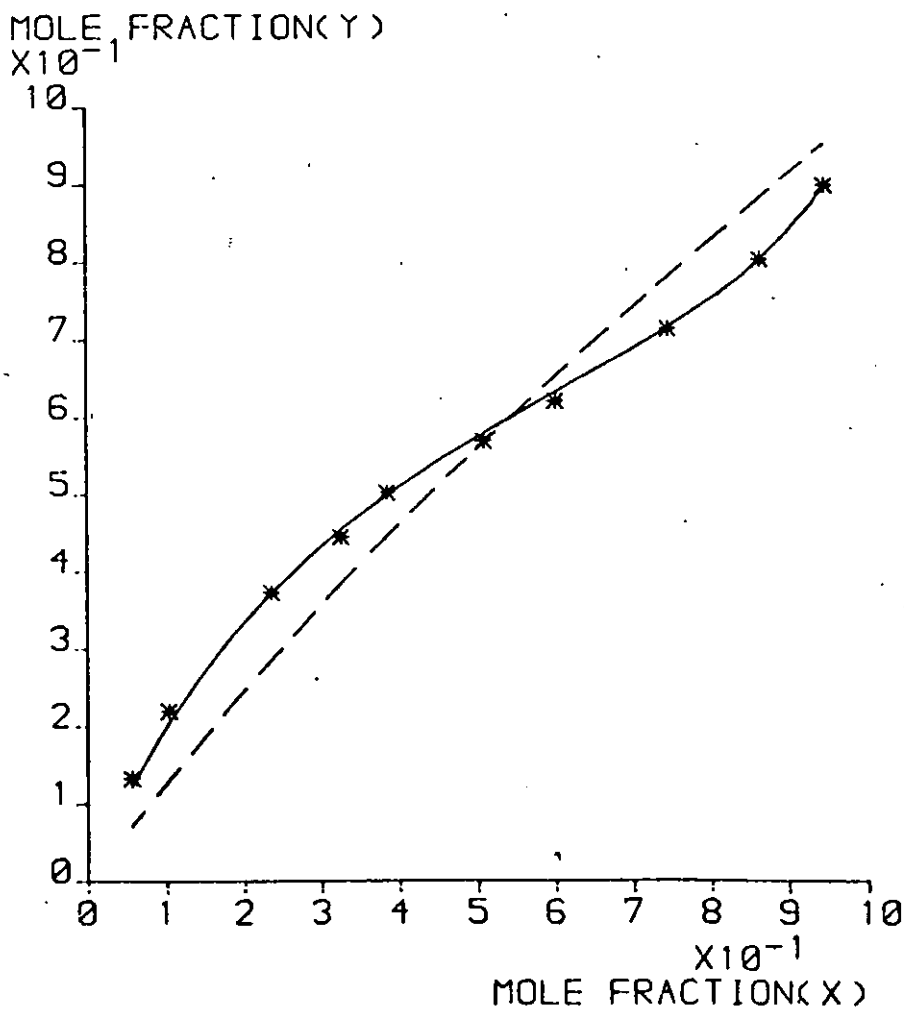


(b)

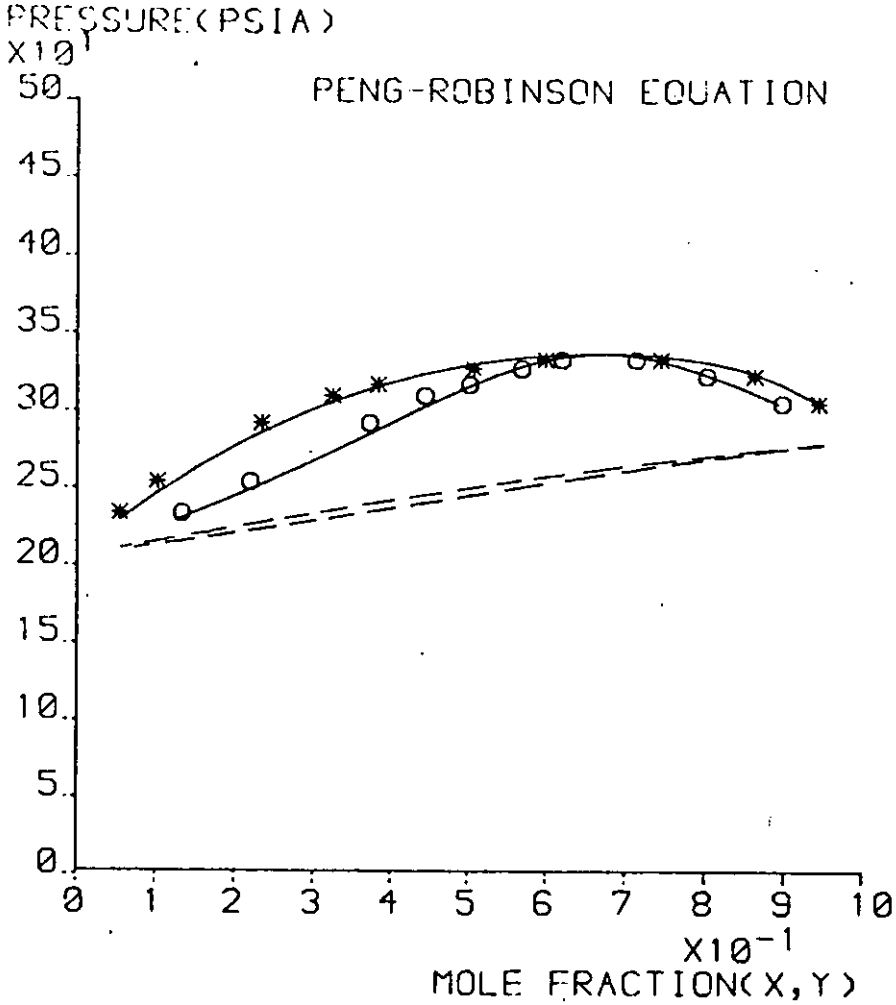


(a)

FIGURE 6.60 CO_2-Ethane System at 455.33°R (253K)

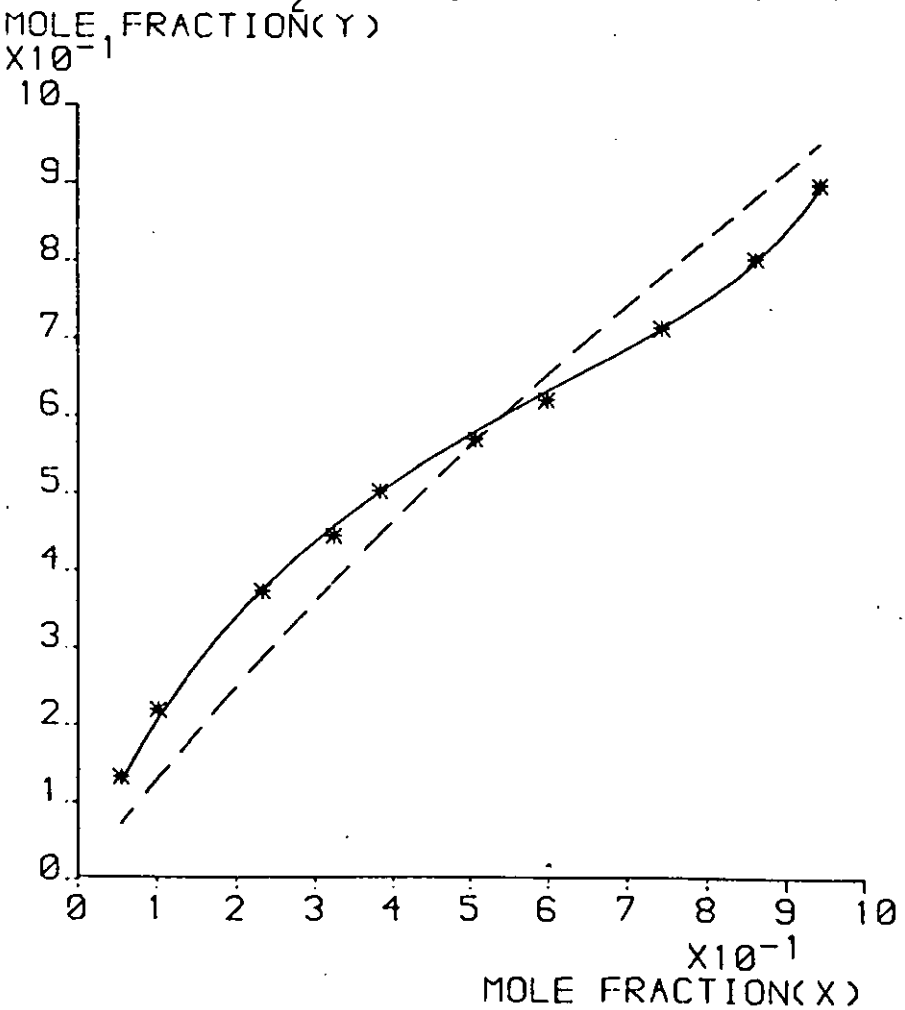


(b)

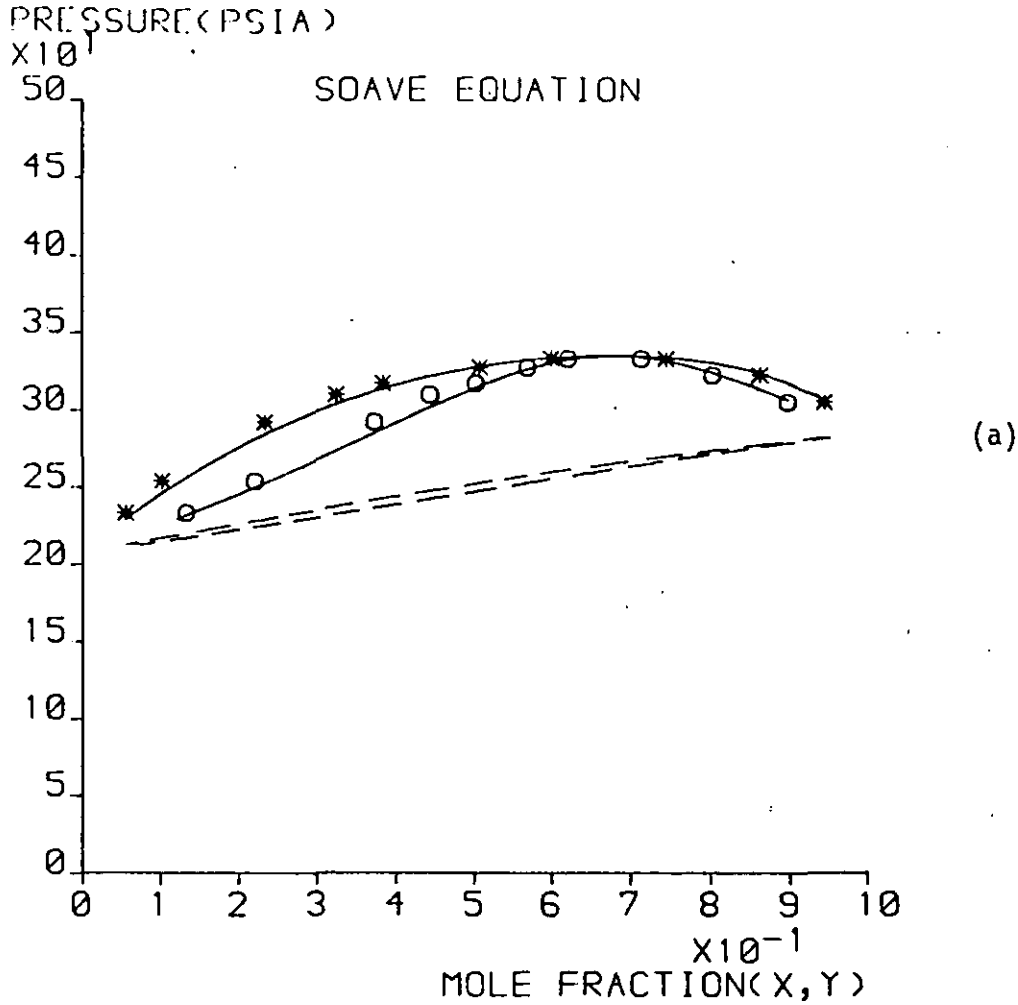


(a)

FIGURE 6.61 CO_2-Ethane System at 455.33°R (253K)

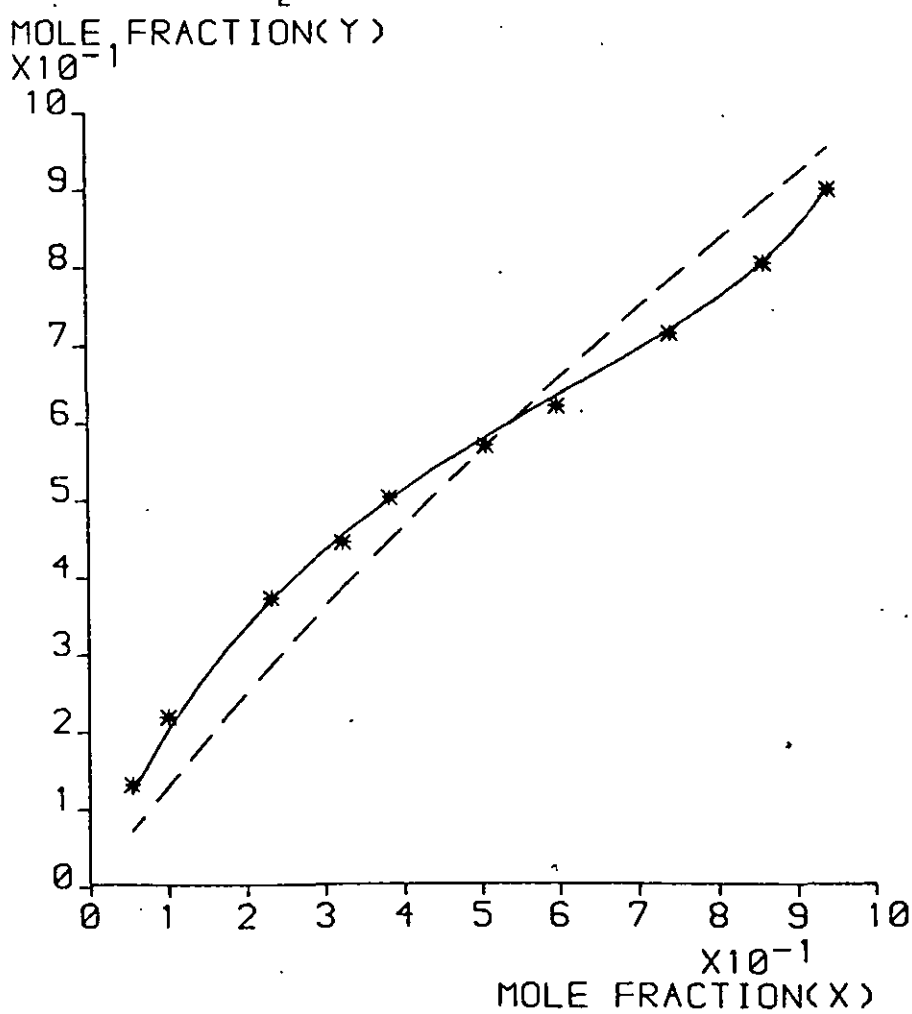


(b)



(a)

FIGURE 6.62 · CO_2-Ethane System at 455.53°R (253K)



(b)

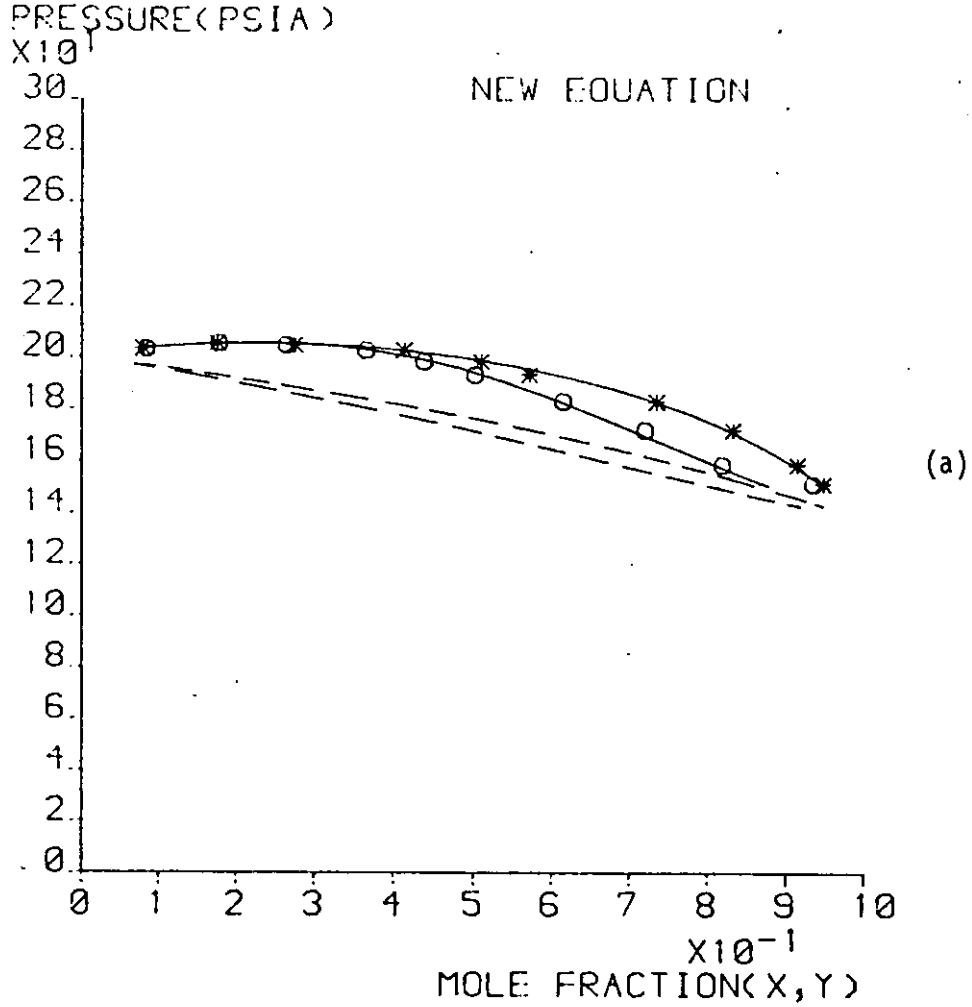
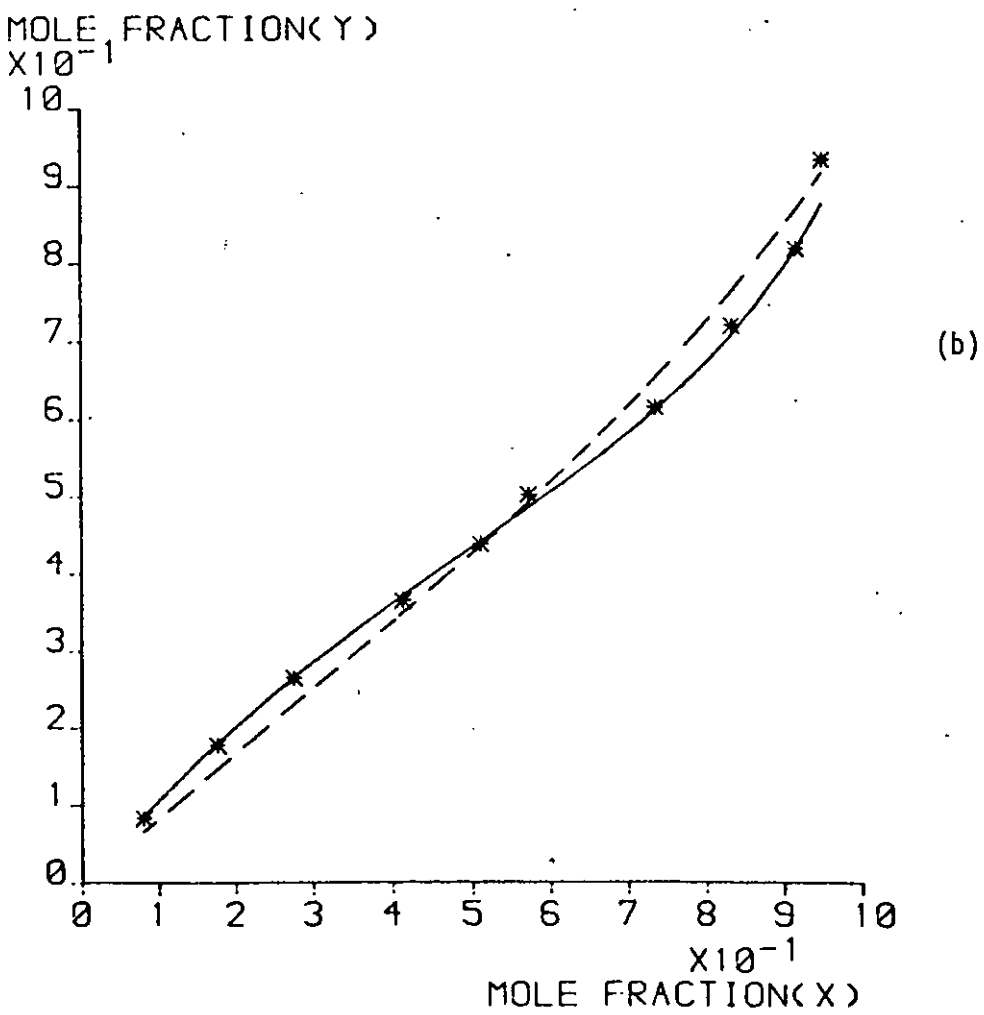


FIGURE 6.63 CO_2-Ethylene System at 416.81°R (231.6K)



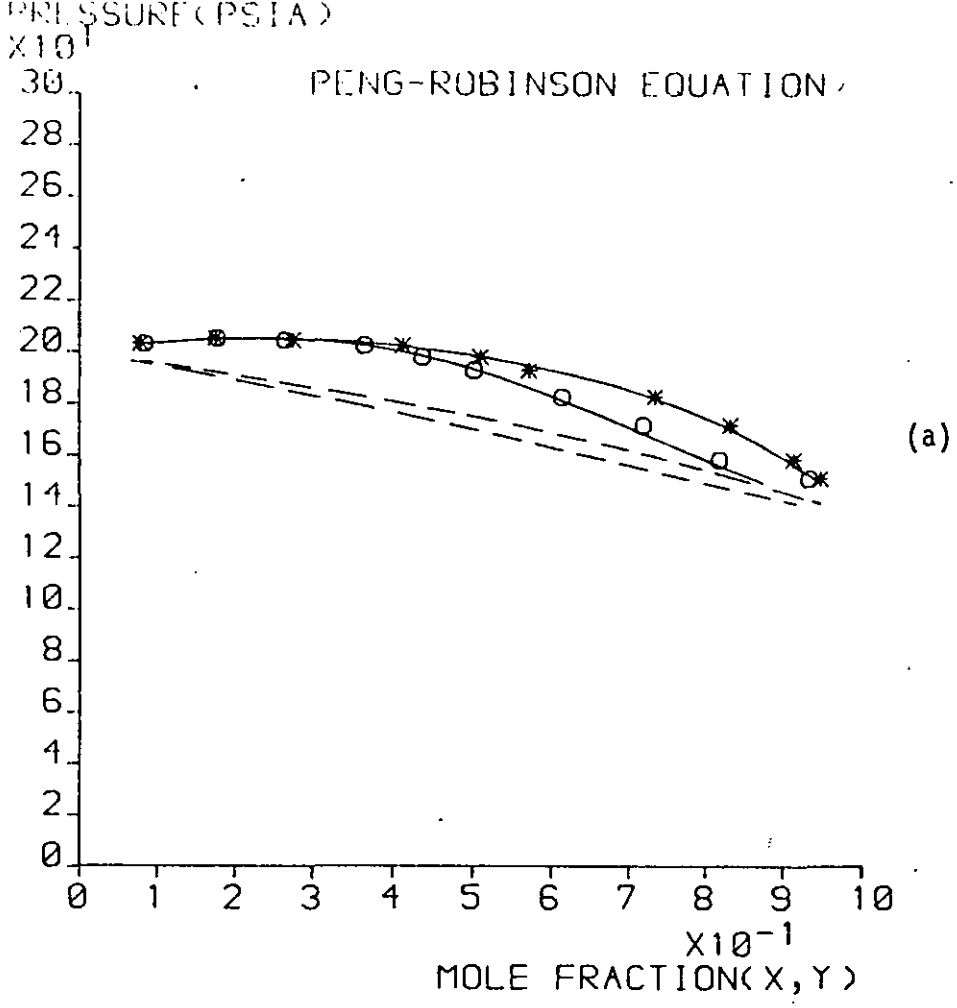
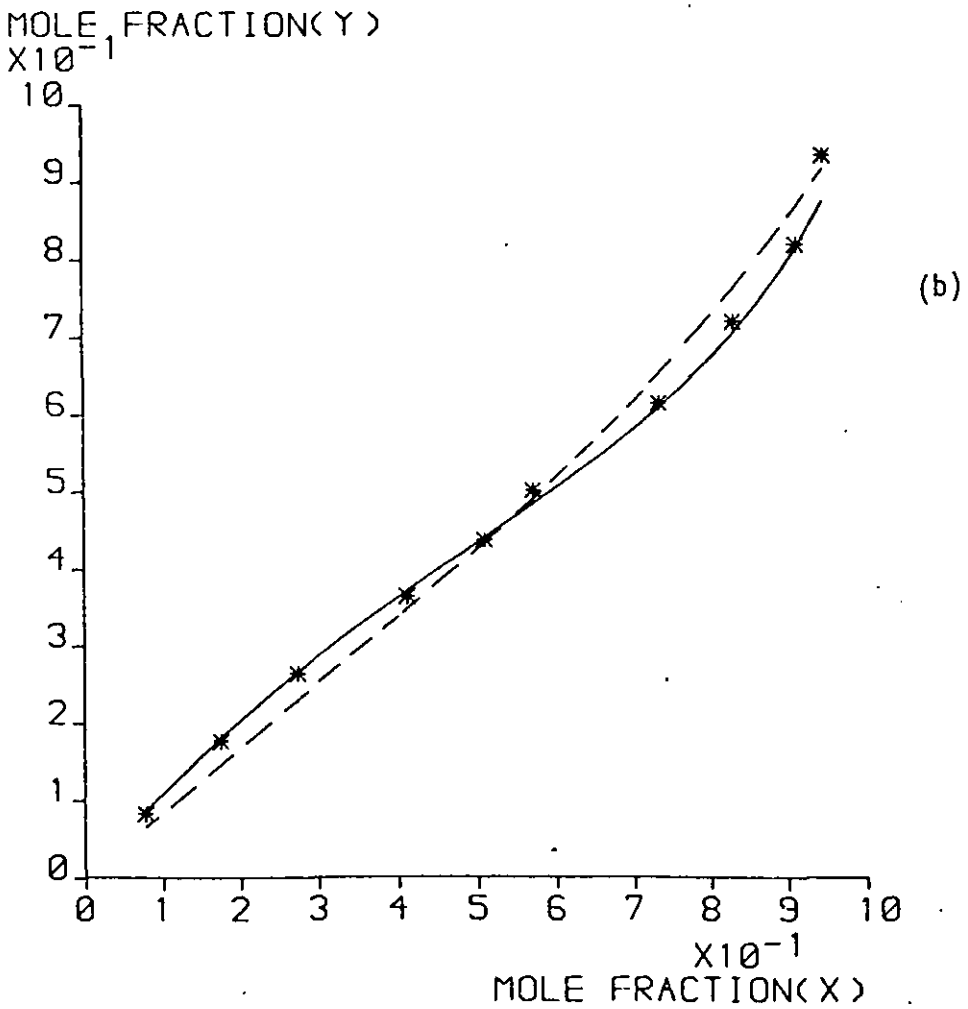
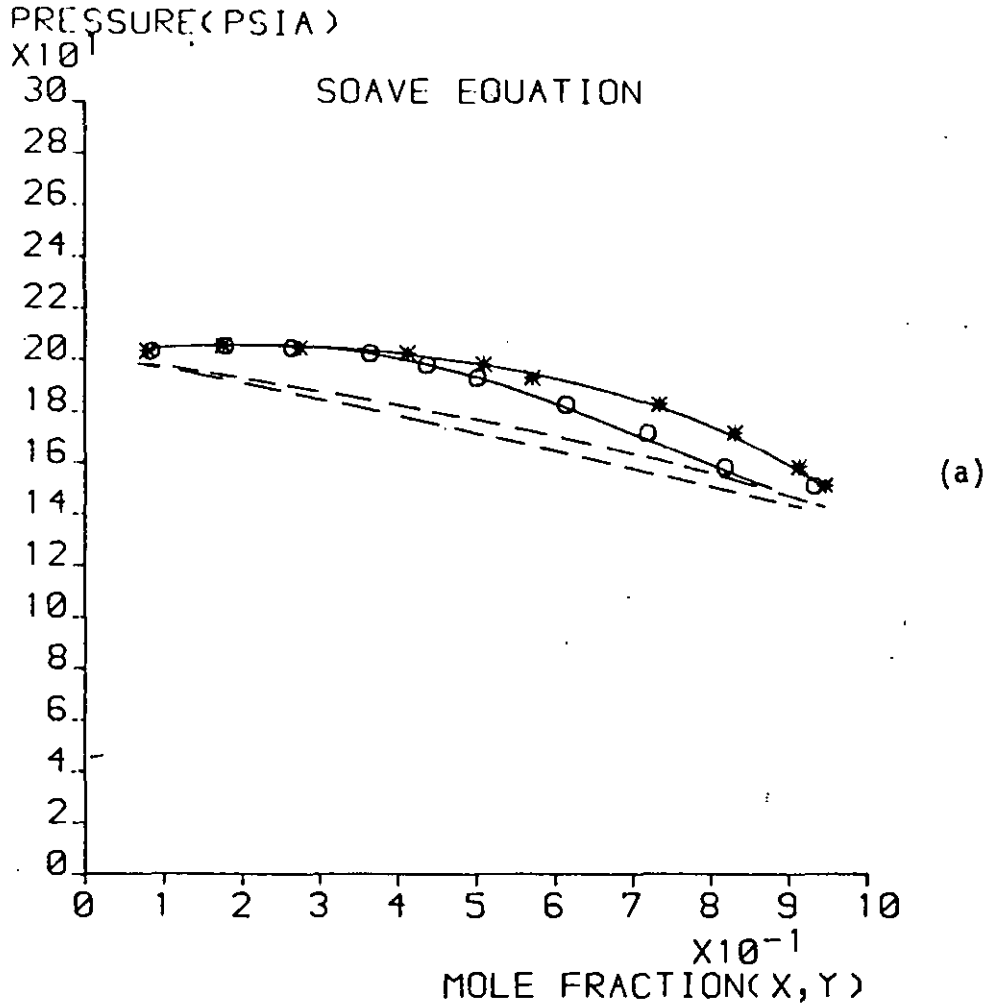


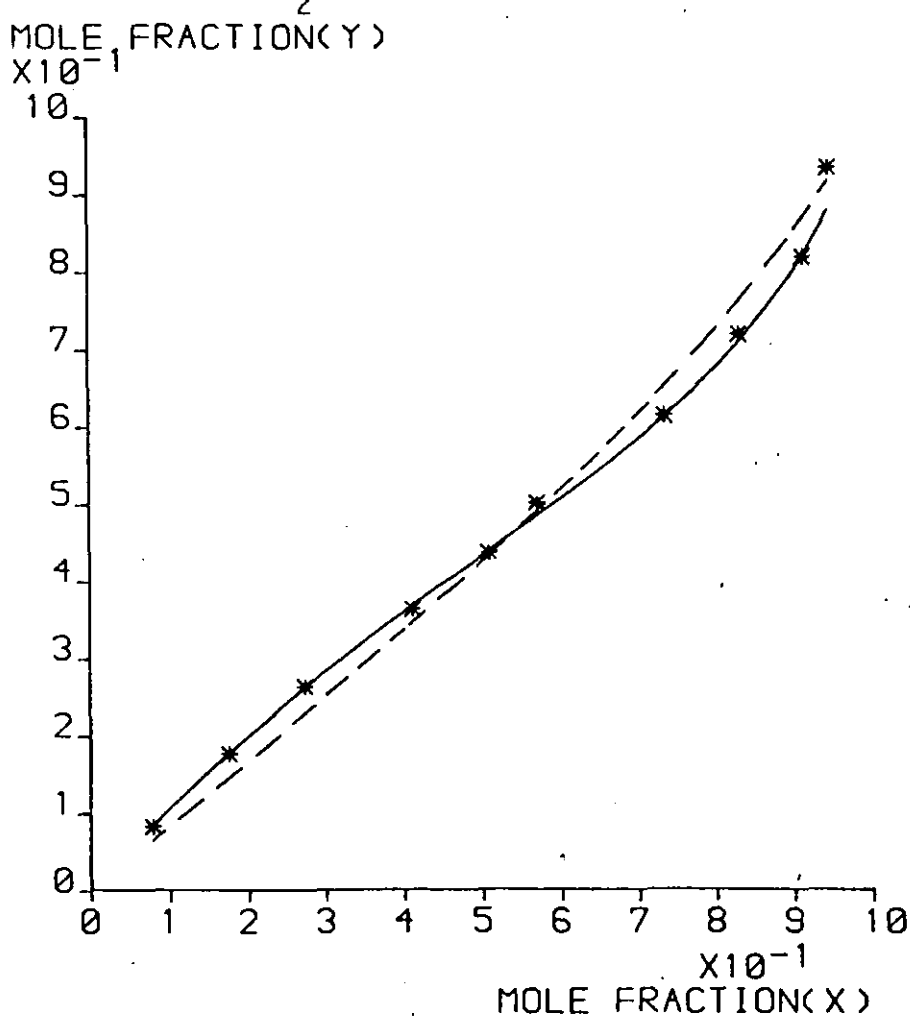
FIGURE 6.64 CO_2-Ethylene System at 416.81°R (231.6K)



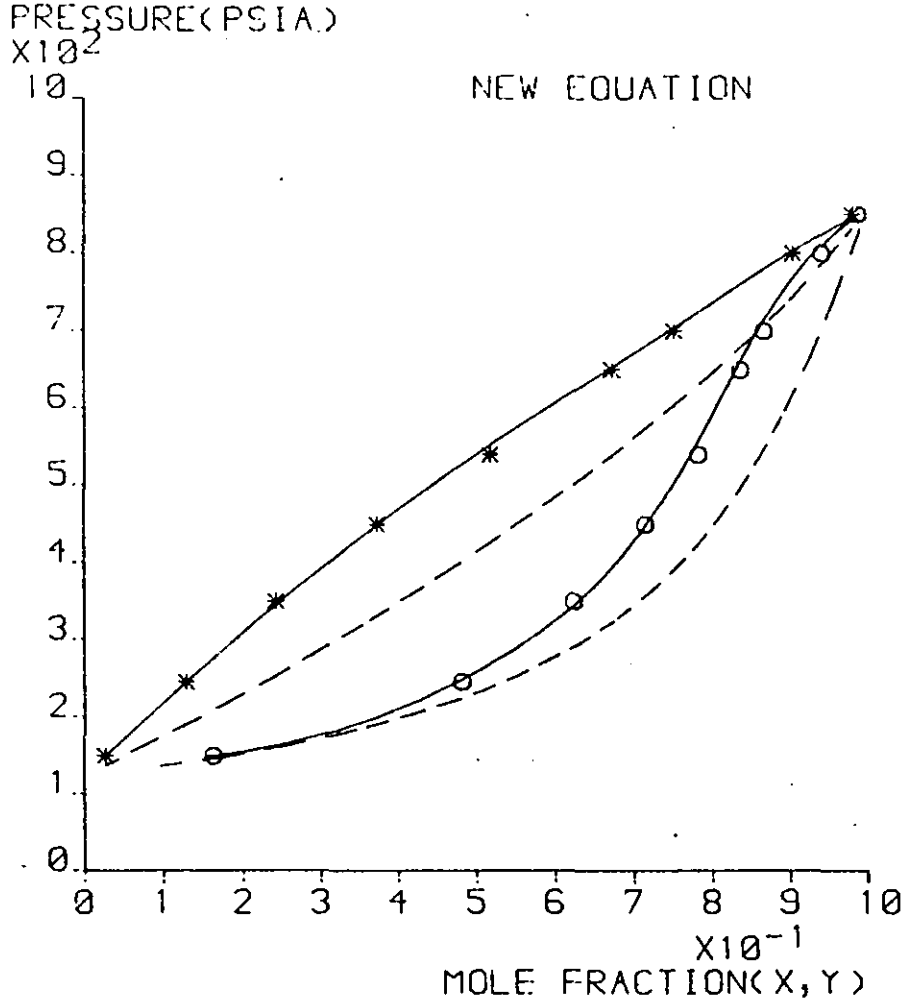


(a)

FIGURE 6.65 CO_2-Ethylene System at 416.81°R (231.6K)

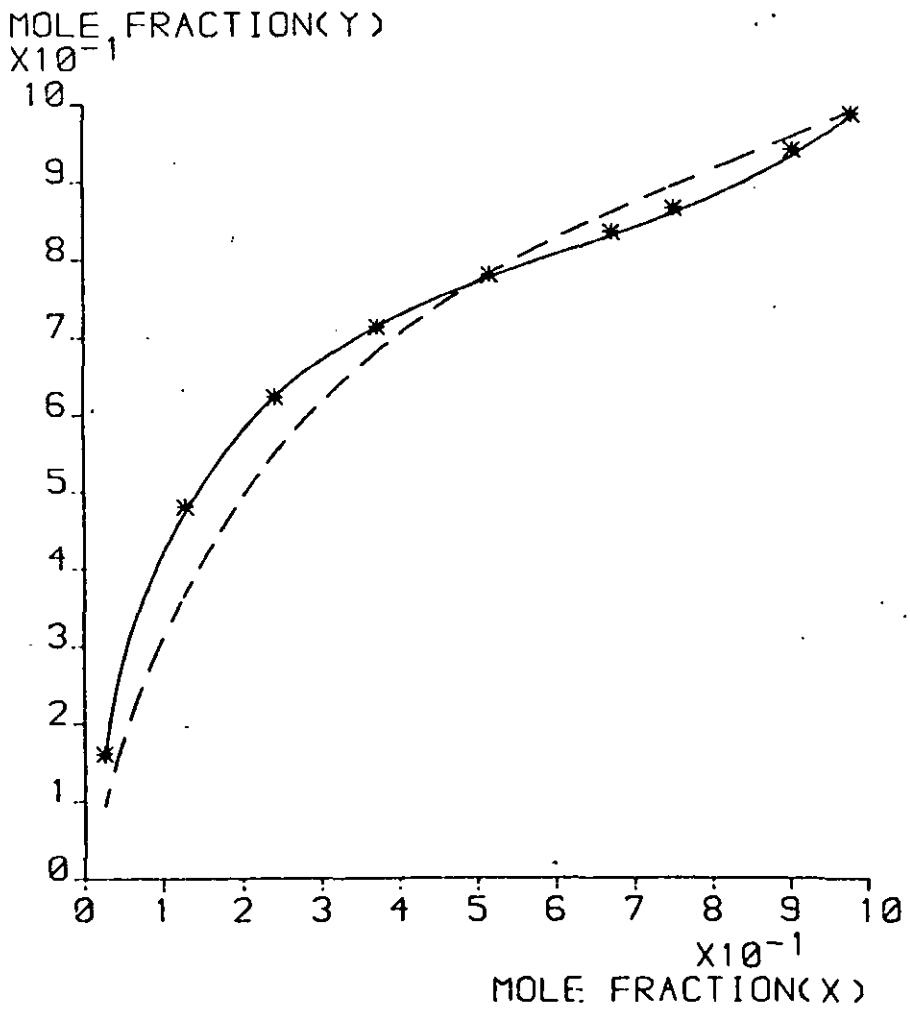


(b)

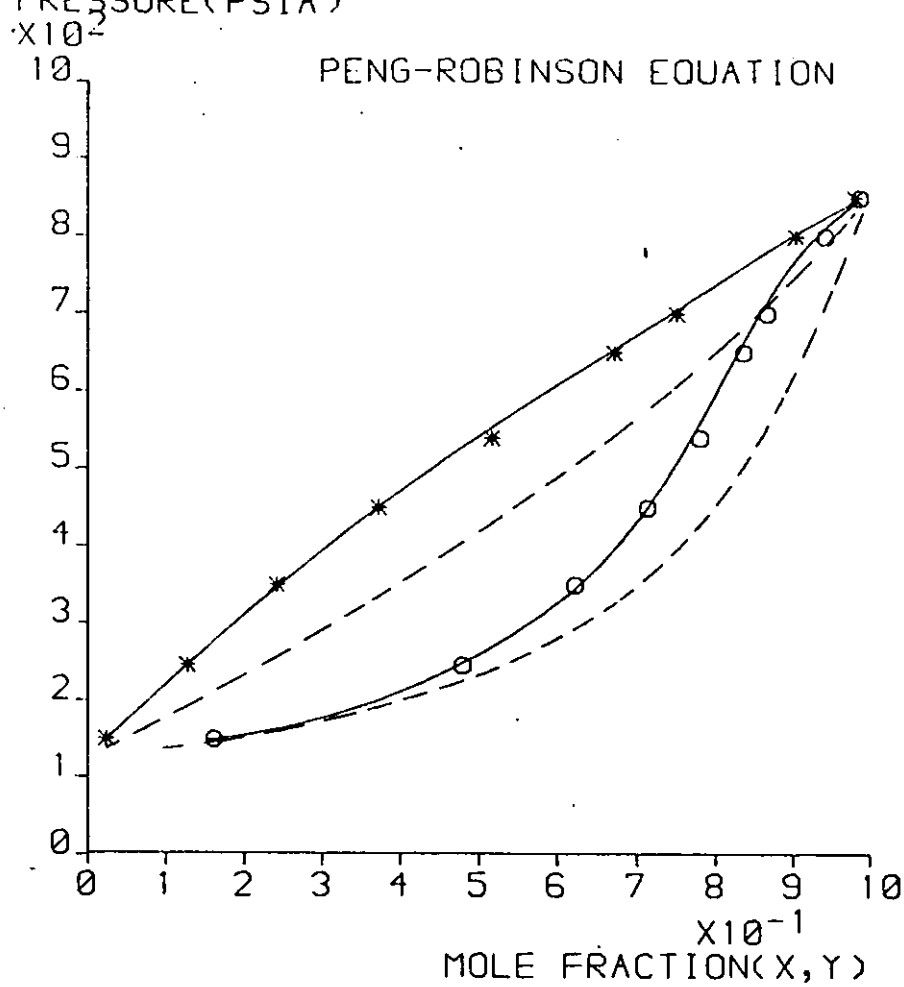


(a)

FIGURE 6.66 CO_2-Propane System at 529.67°R (294.3K)

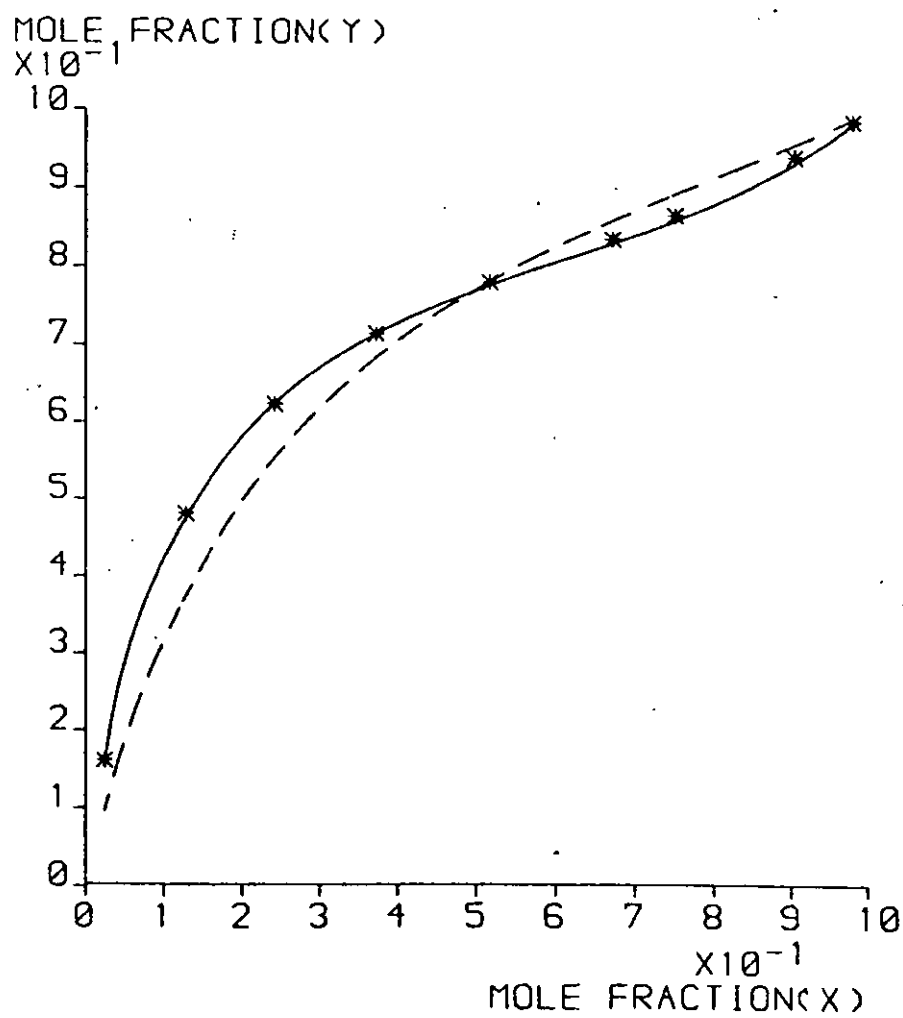


(b)



(a)

FIGURE 6.67 CO_2-Propane System at 529.67°R (294.3K)



(b)

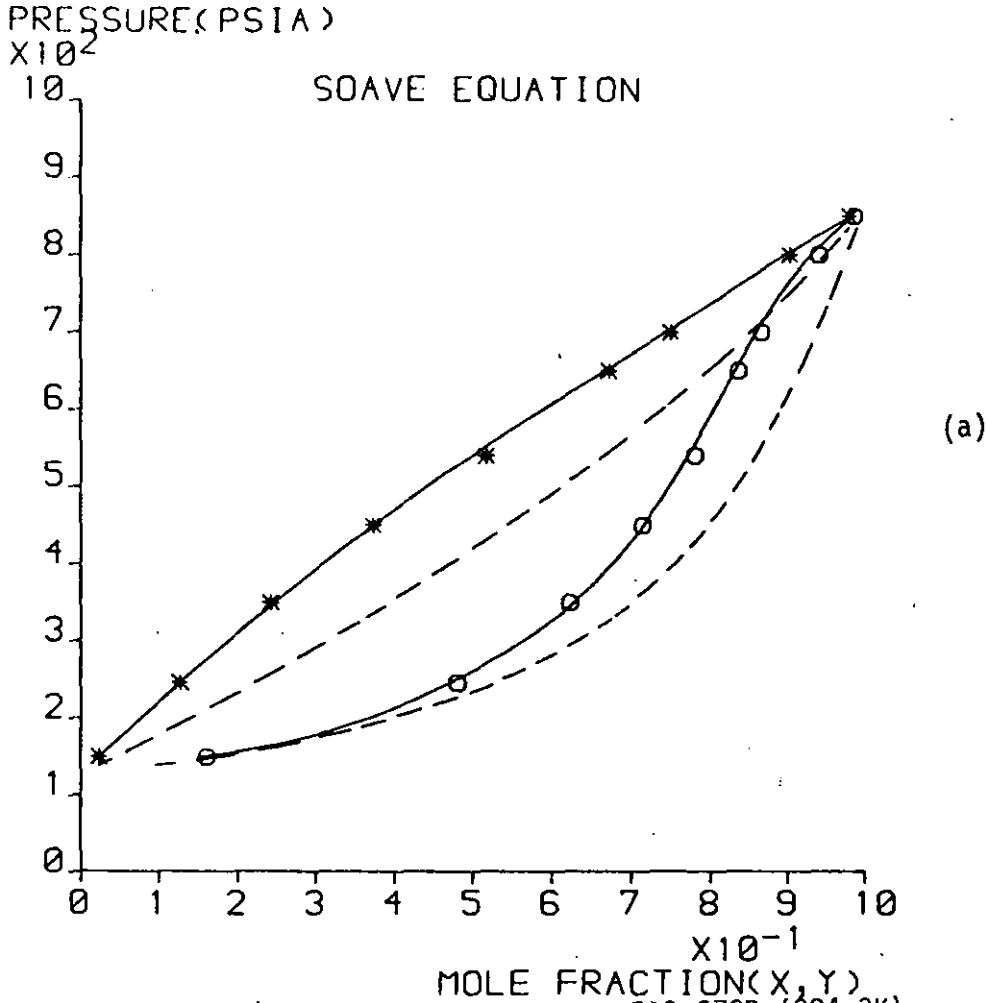
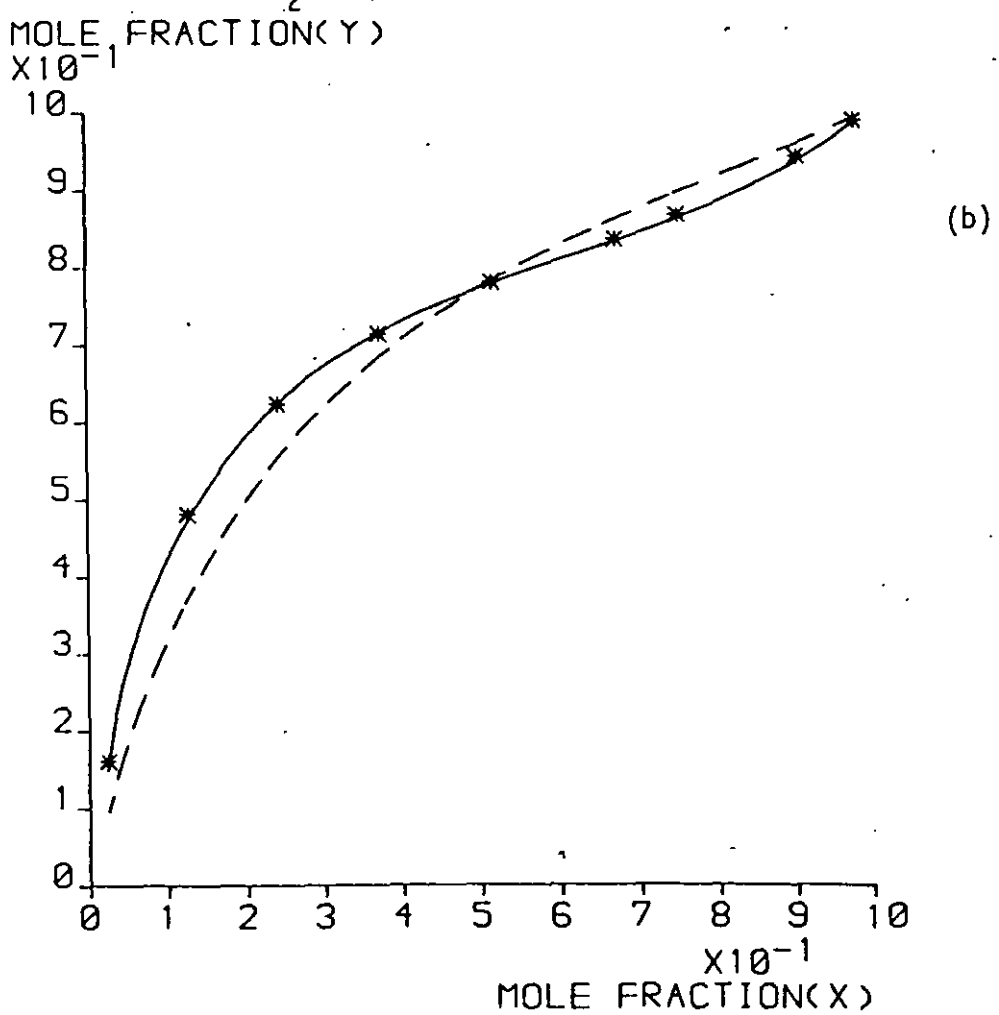
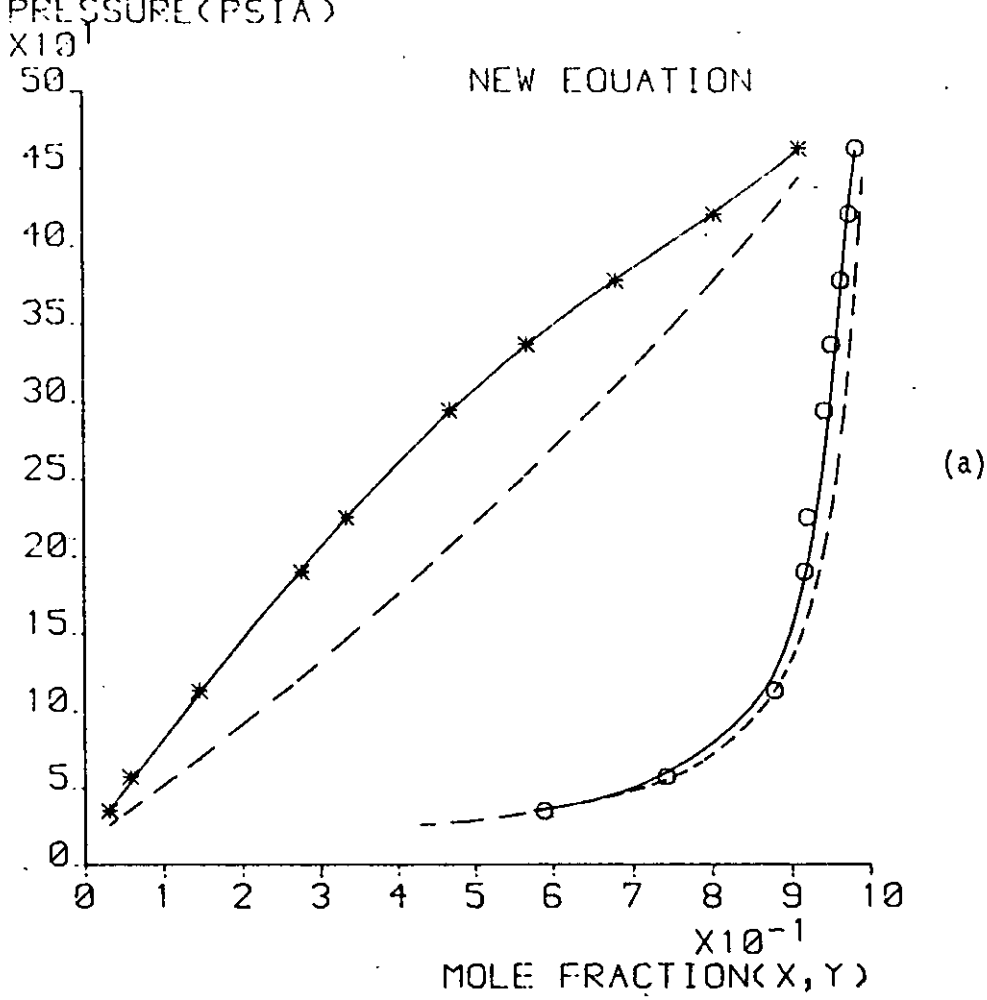


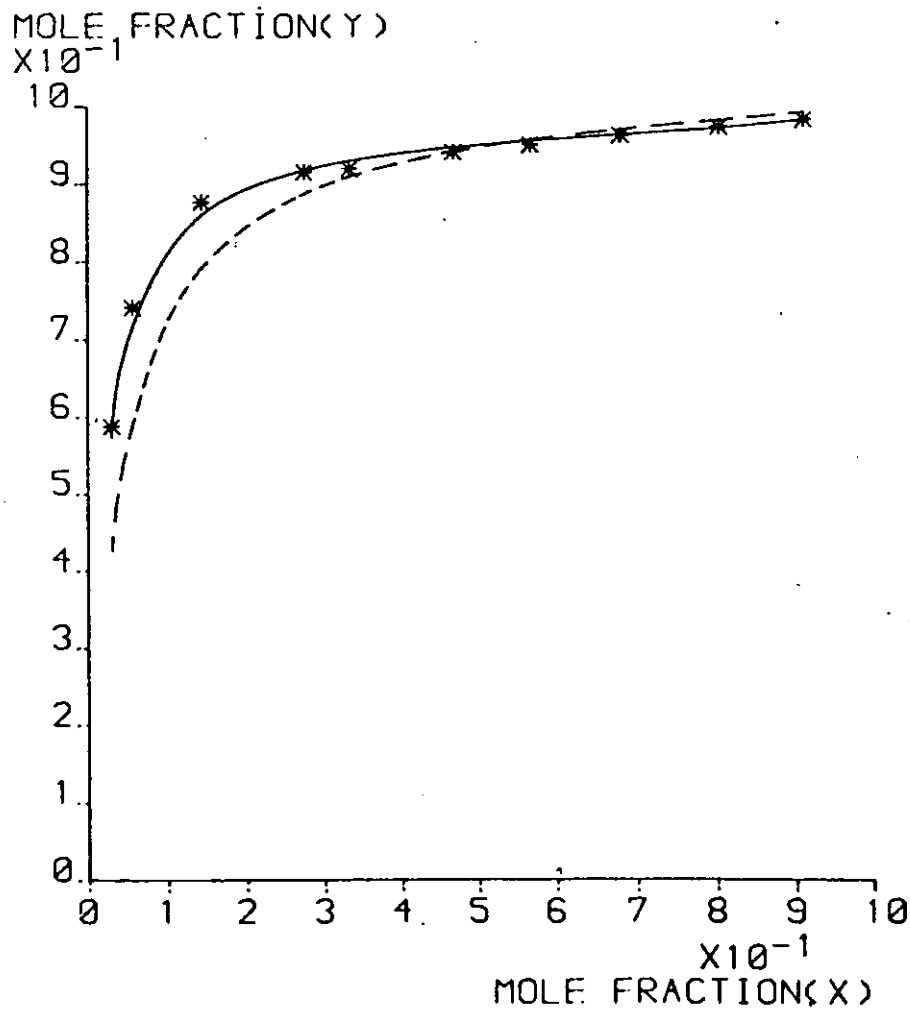
FIGURE 6.68 CO_2-Propane System at 529.67°R (294.3K)



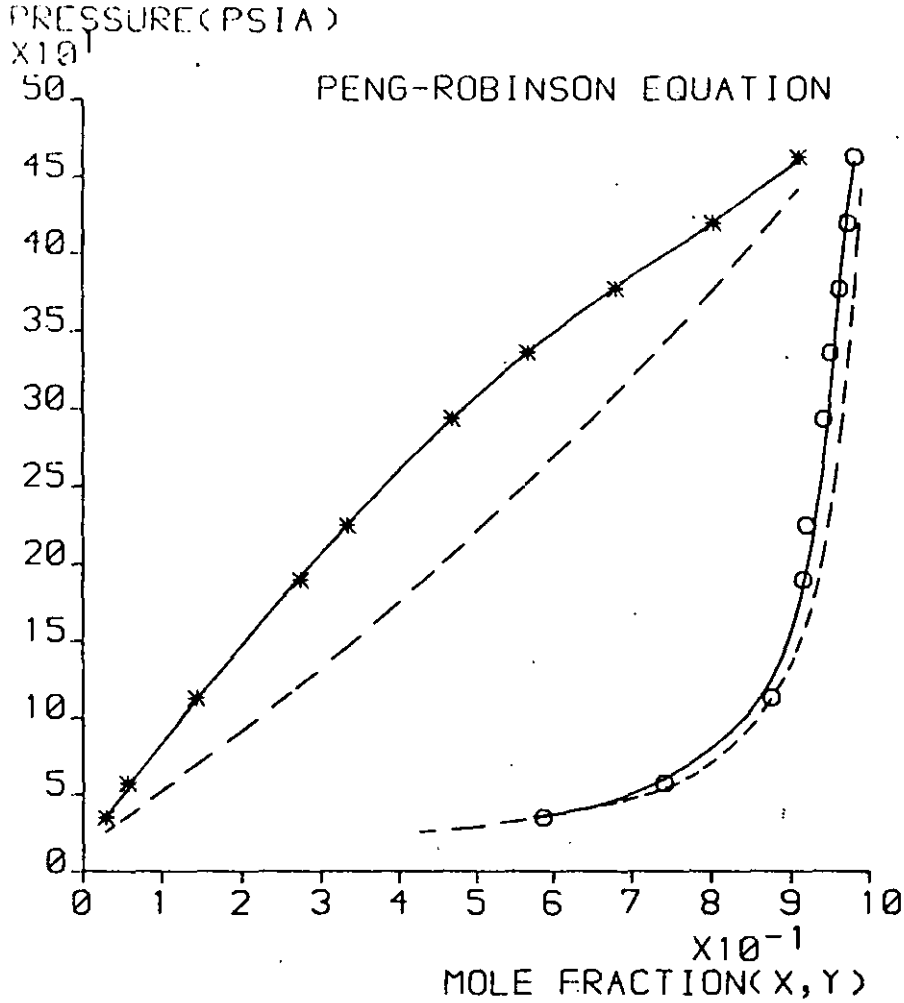


(a)

FIGURE 6.69 CO_2-n-Butane System at 491.69°R (273.2K)

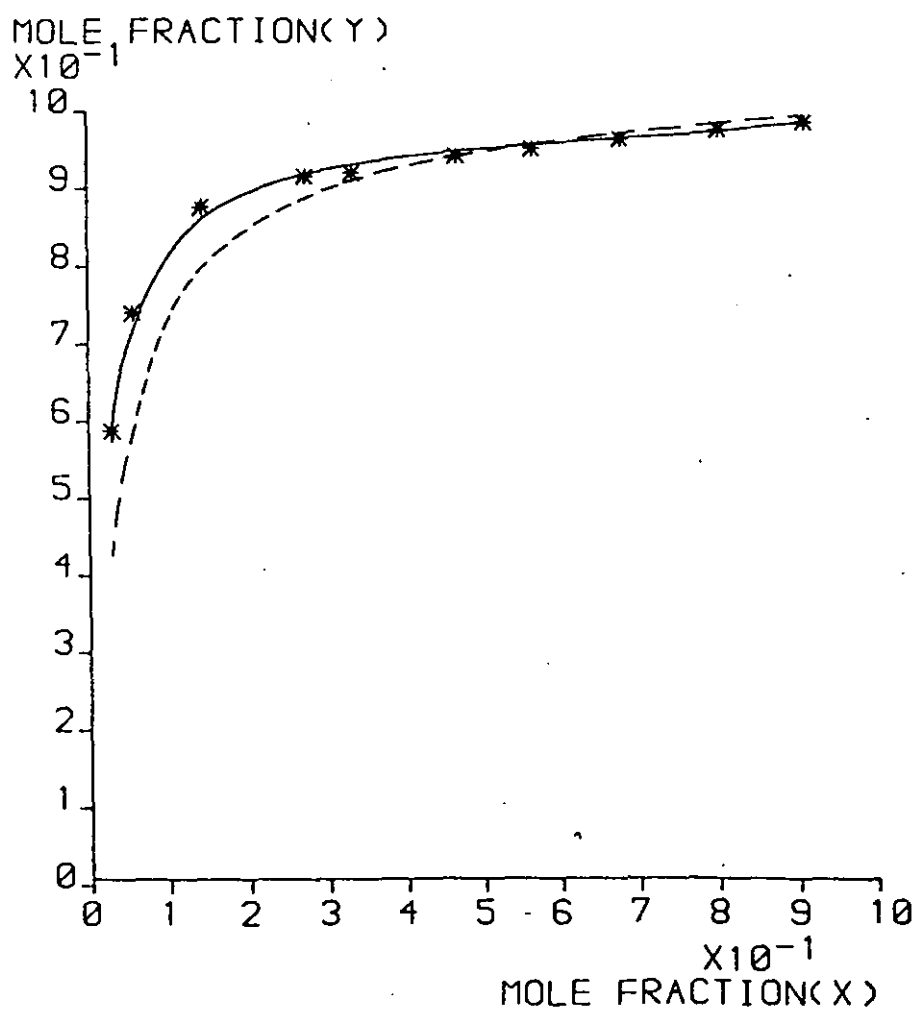


(b)

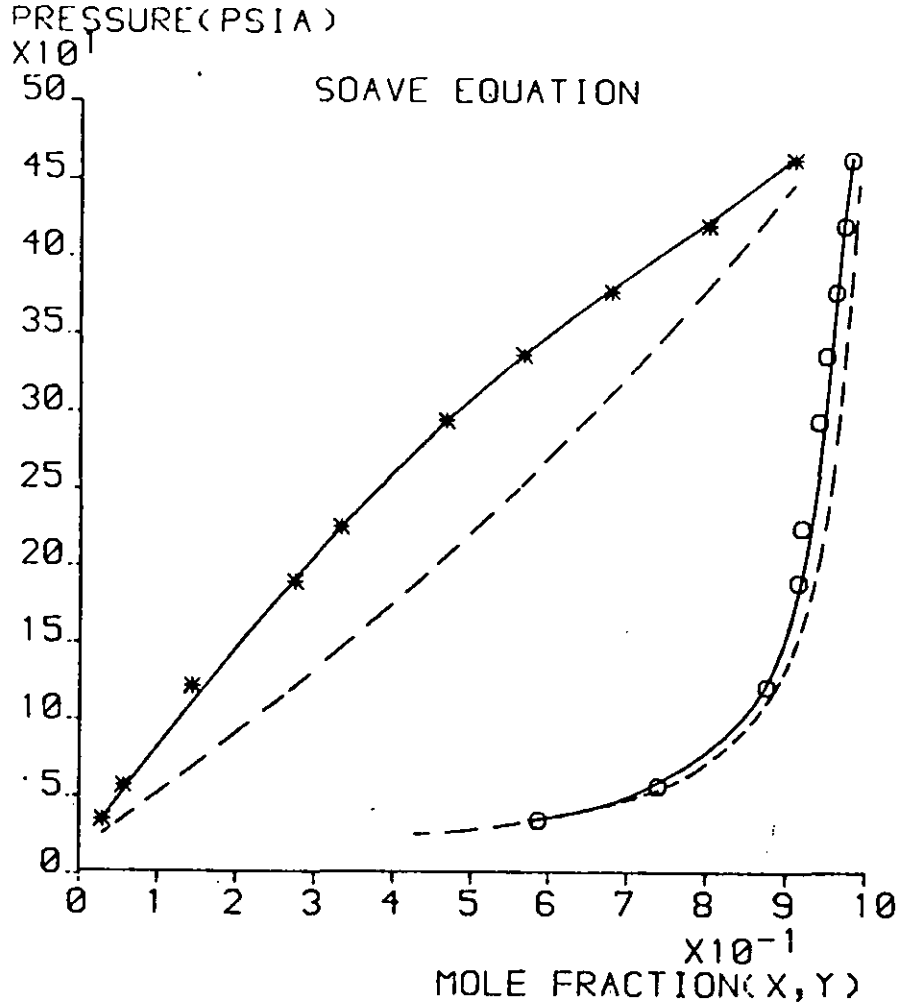


(a)

FIGURE 6.70 CO_2-n-Butane System at 491.69°R (273.2K)

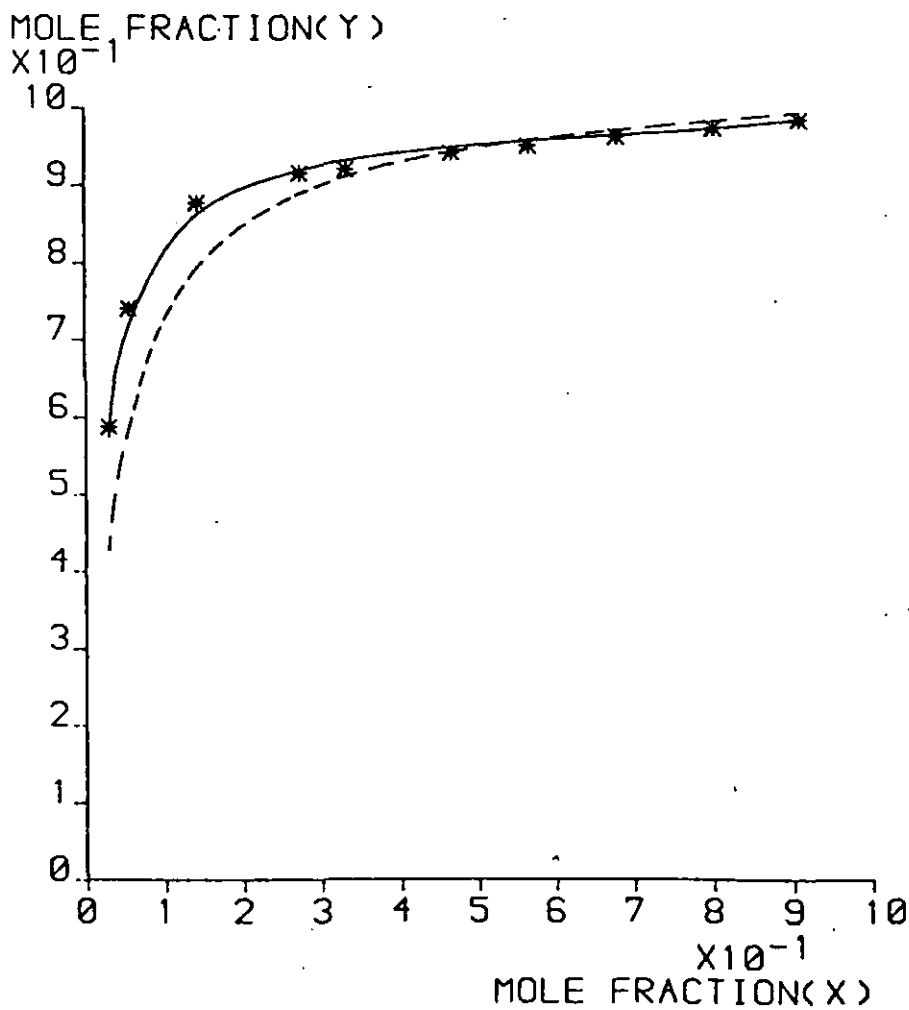


(b)

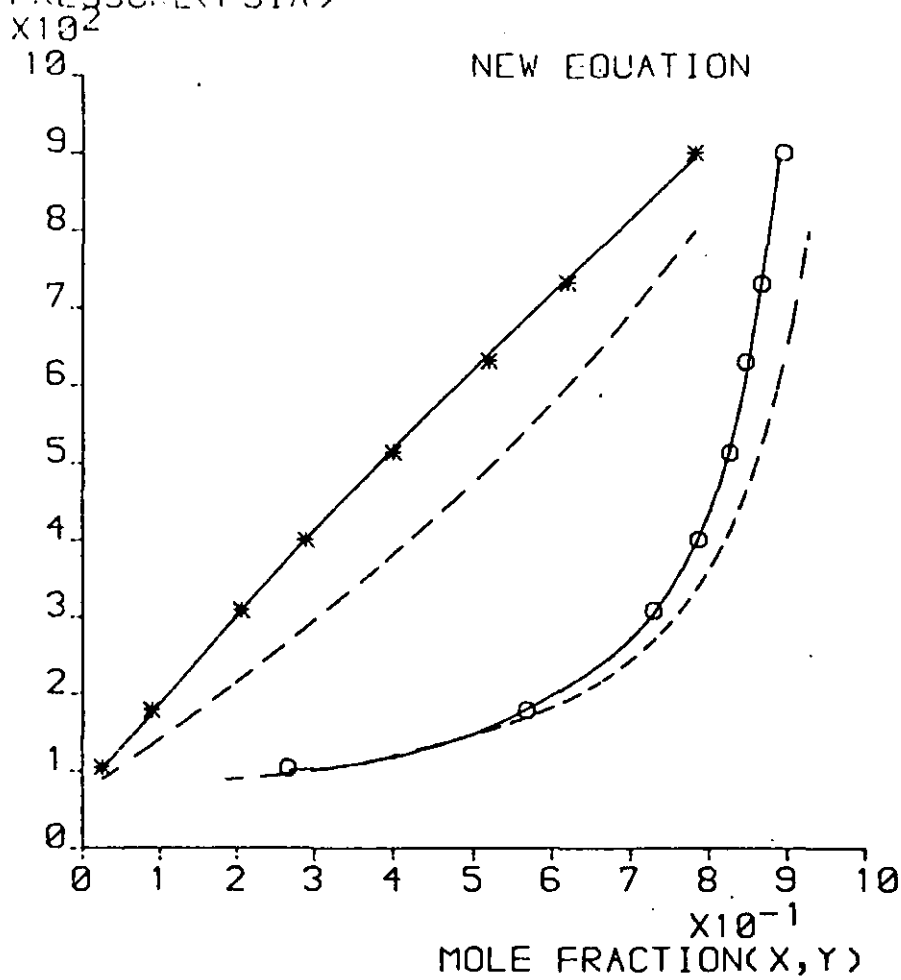


(a)

FIGURE 6.71. CO_2-n-Butane System at 491.69°R (273.2K)

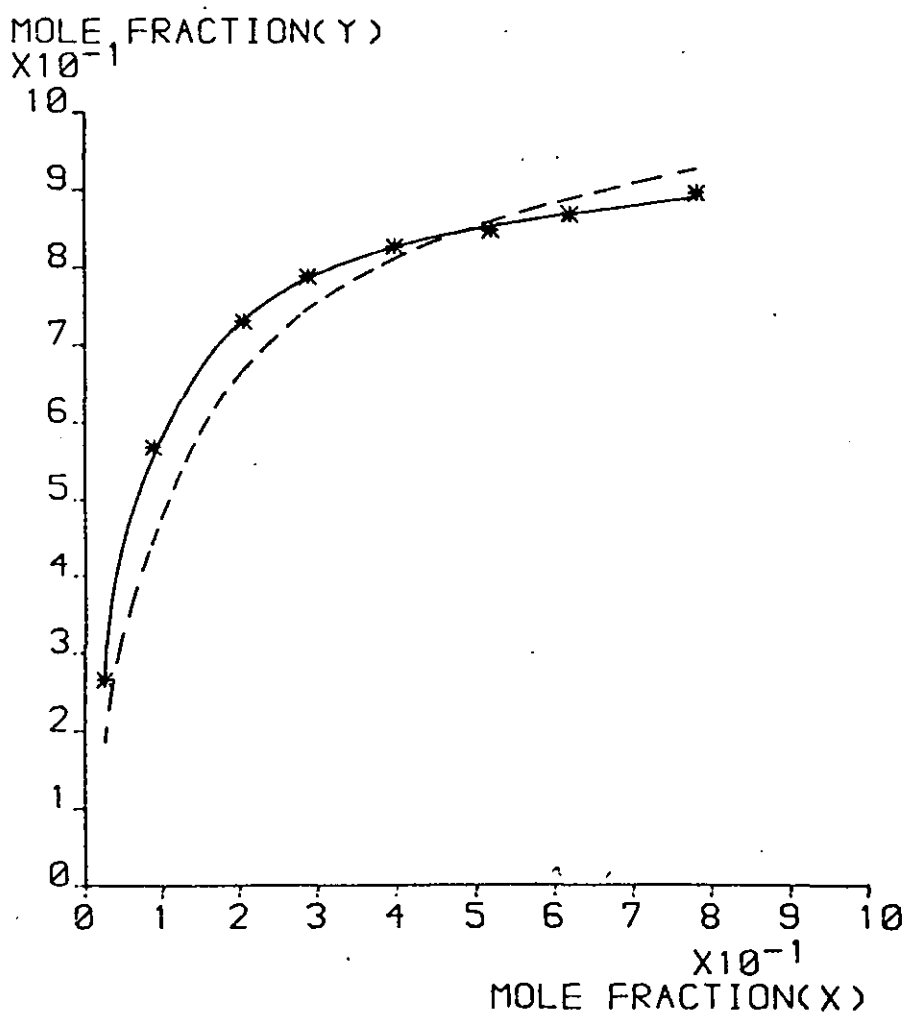


(b)

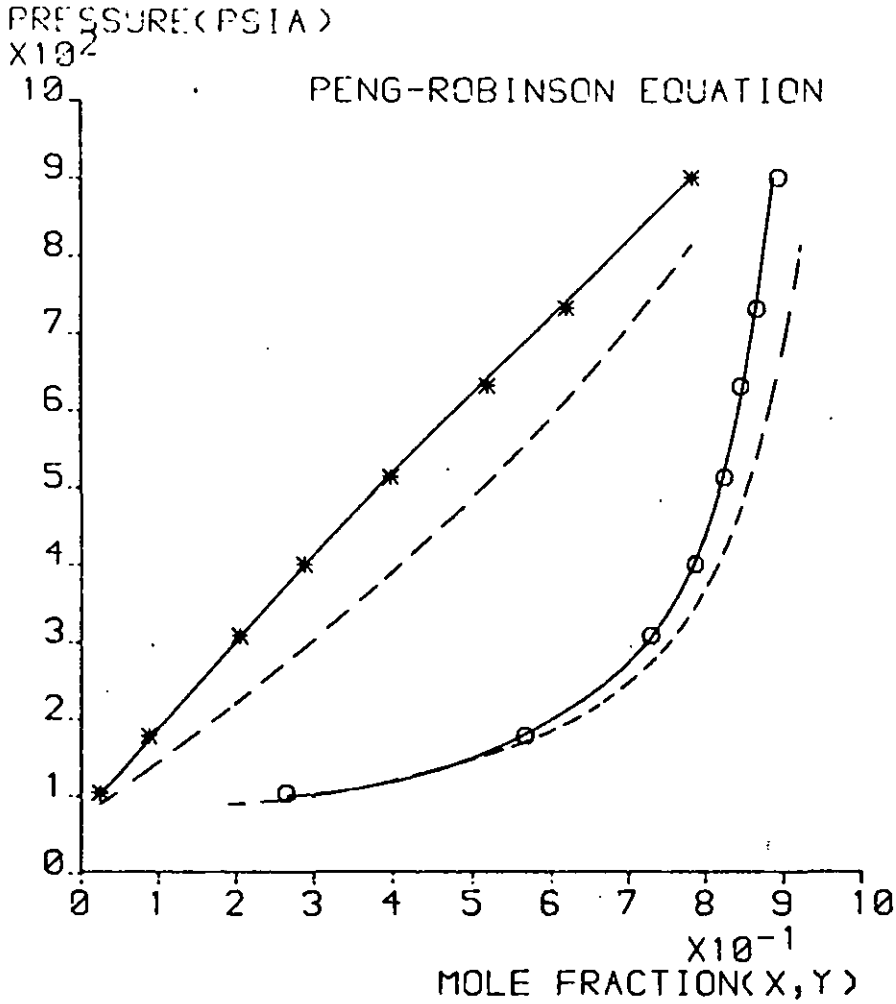


(a)

FIGURE 6.72 CO_2-i-Butane System at 559.67°R (311K)

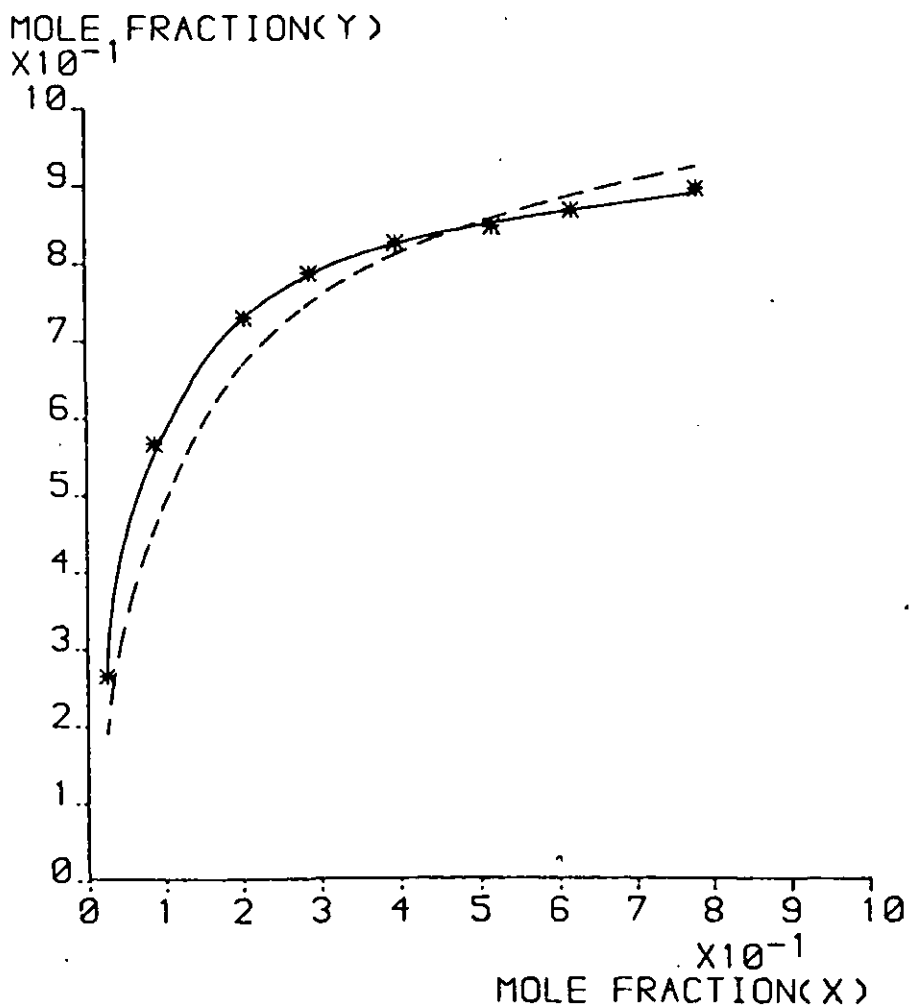


(b)

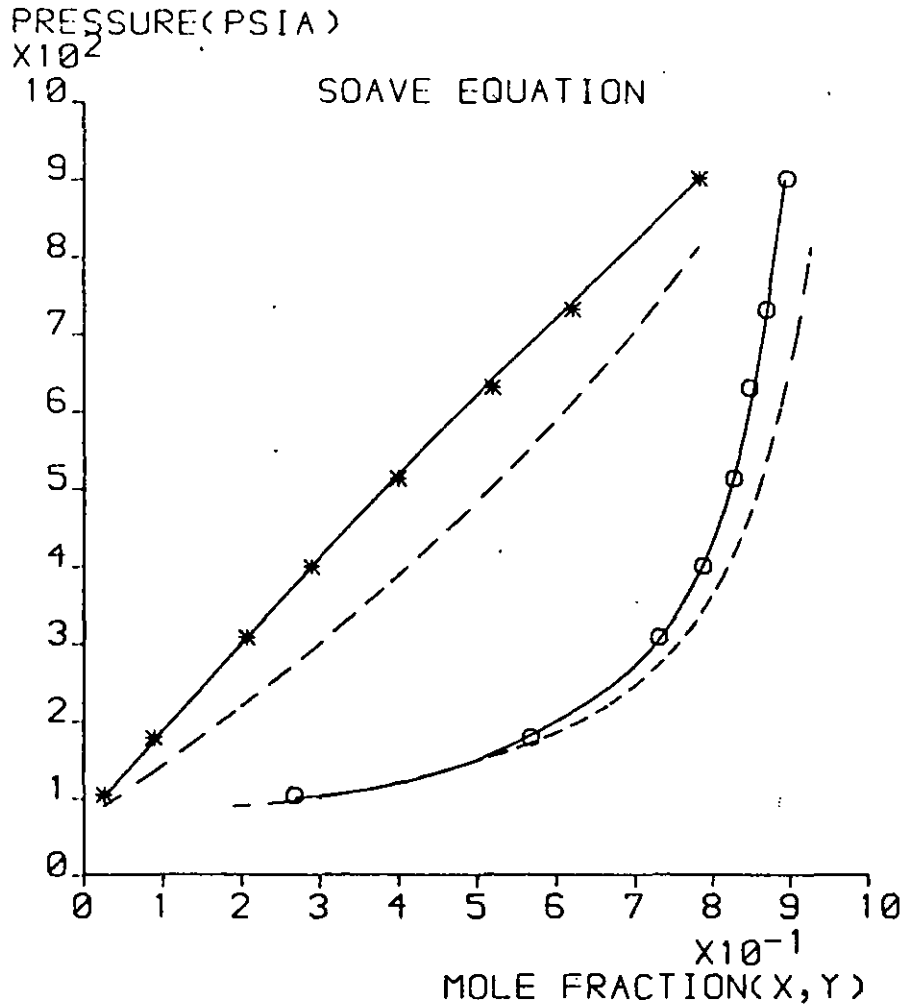


(a)

FIGURE 6.73. CO_2-i-Butane System at 559.67°R (311K)

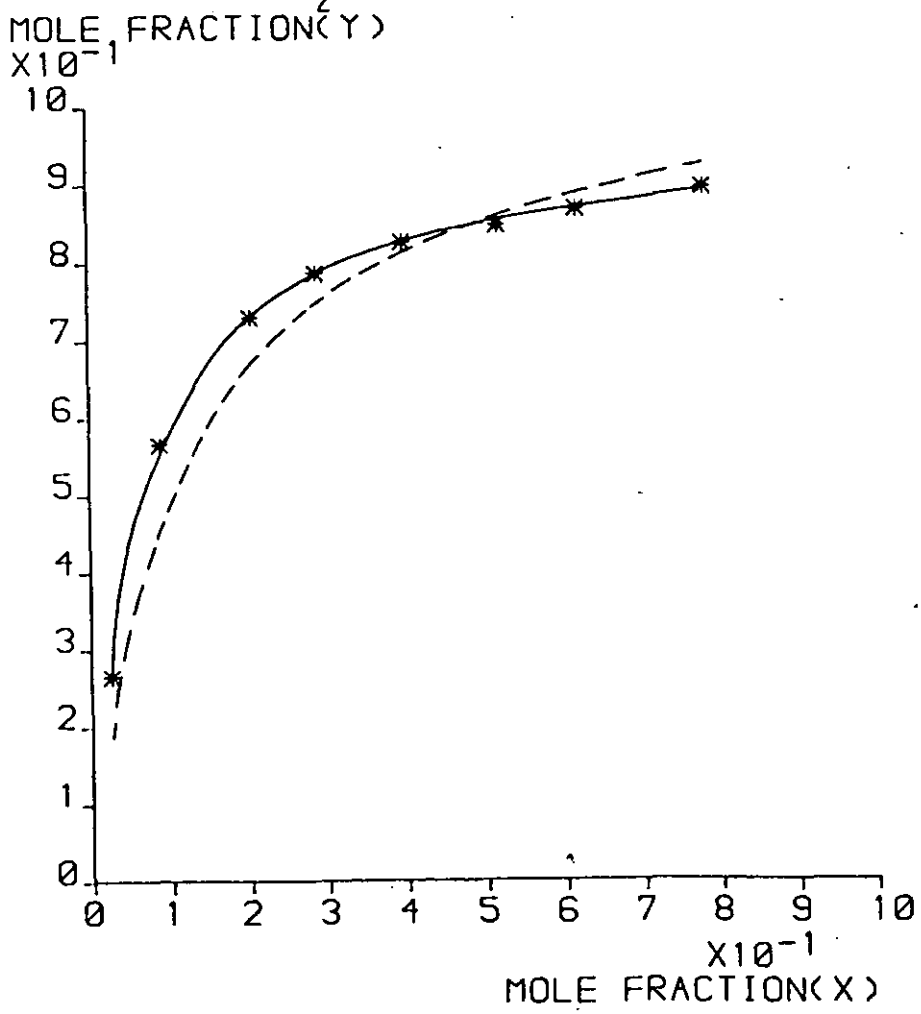


(b)

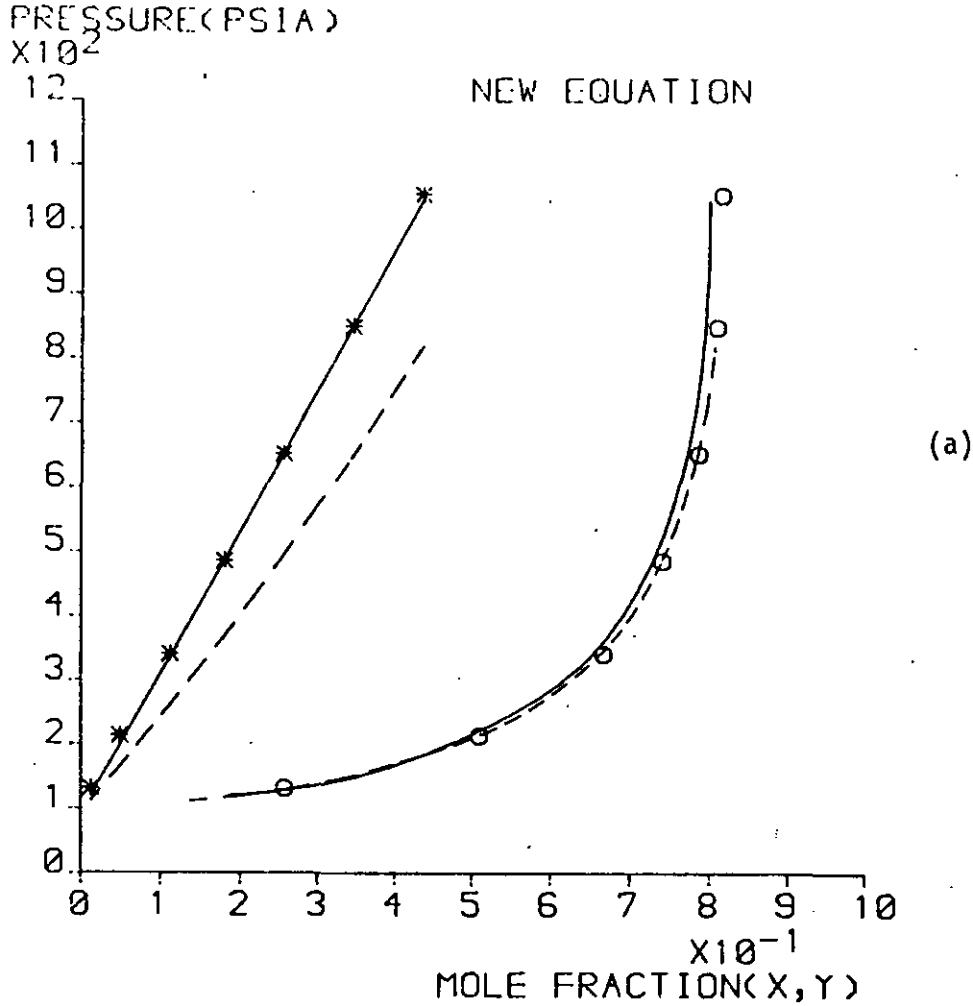


(a)

FIGURE 6.74 CO_2-i-Butane System at 559.67°R (311K)

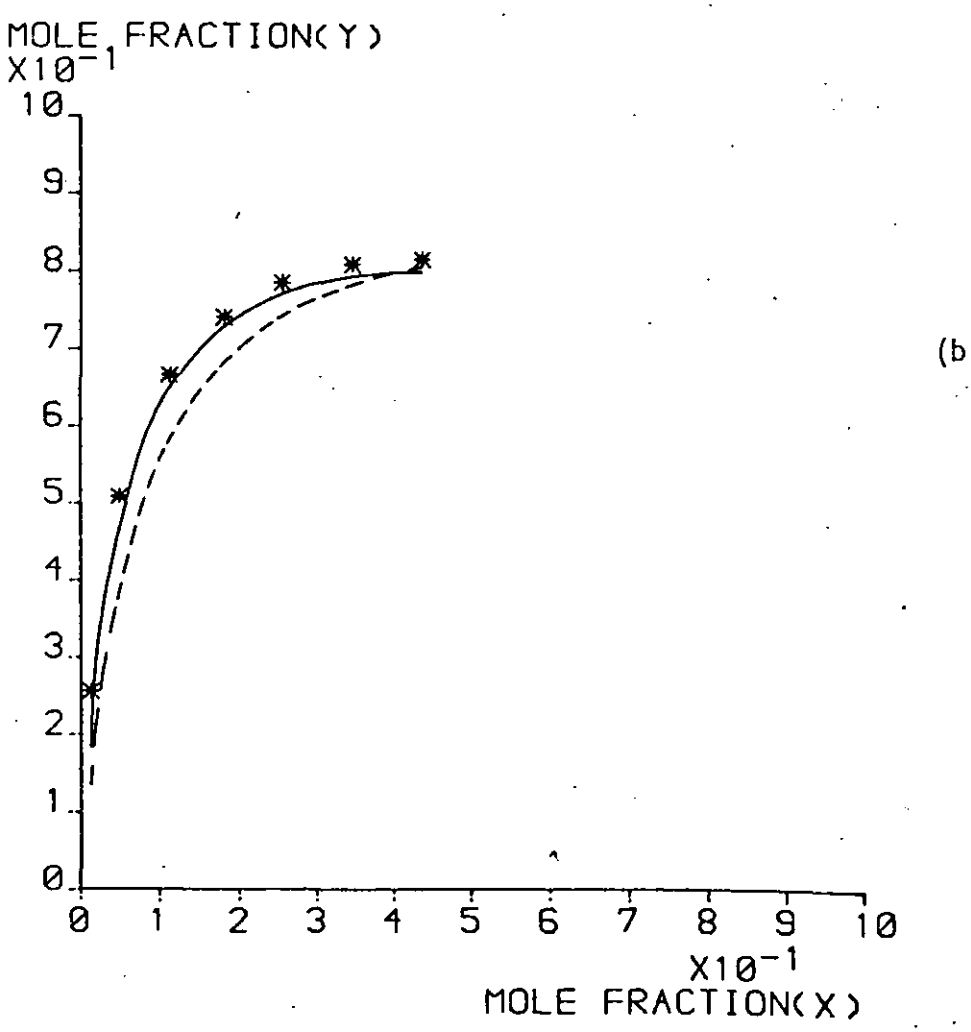


(b)

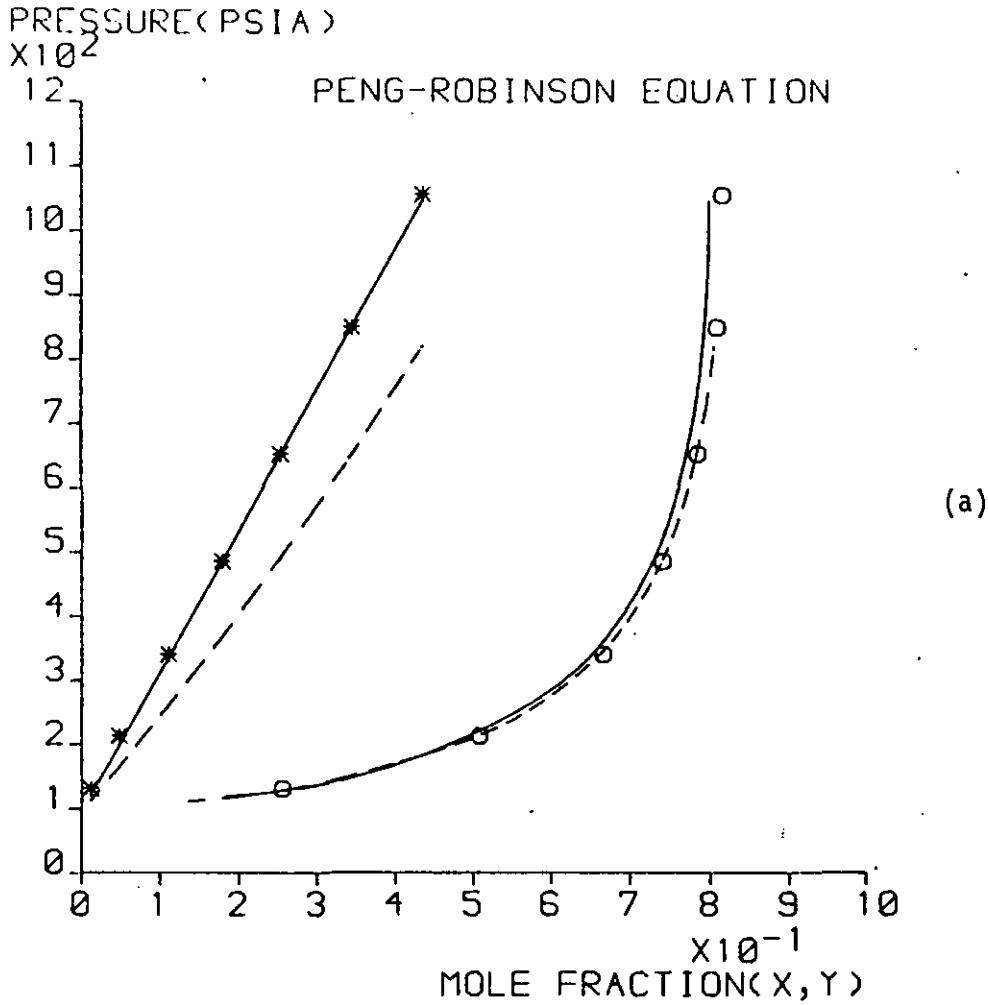


(a)

FIGURE 6.75. CO_2-n-Pentane System at 679.69°R (377.6K)

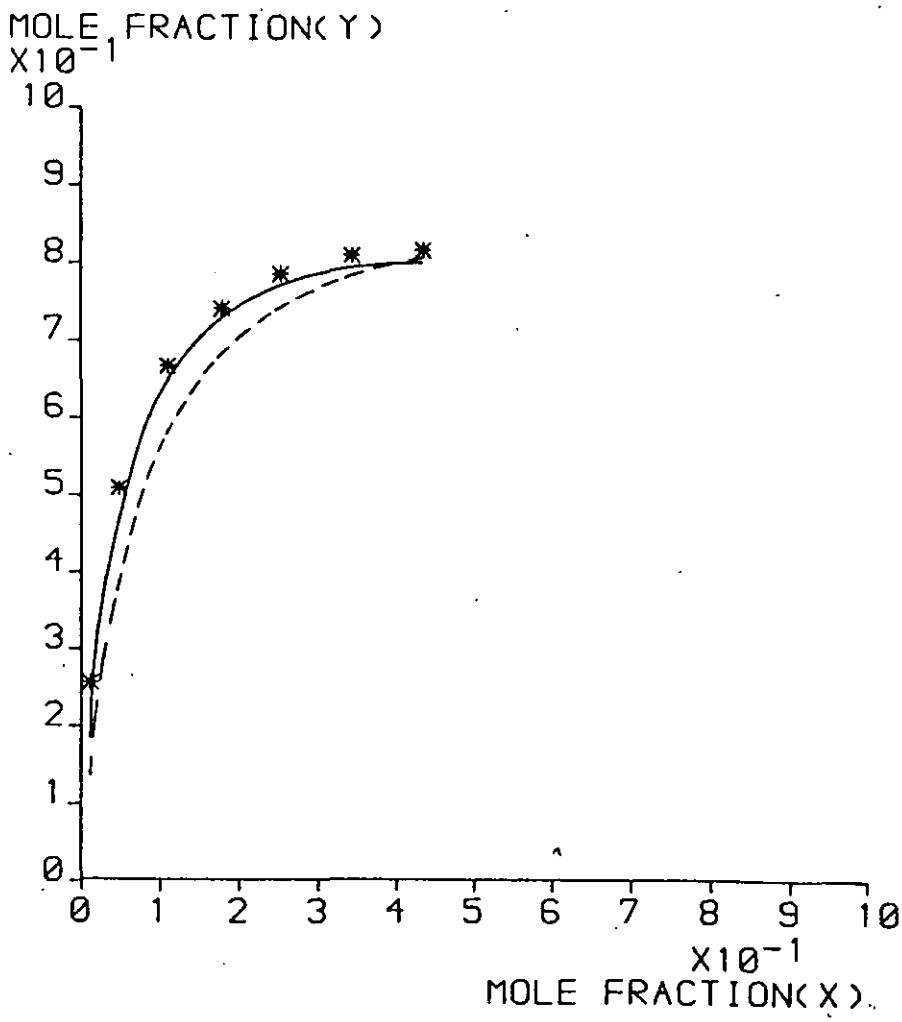


(b)

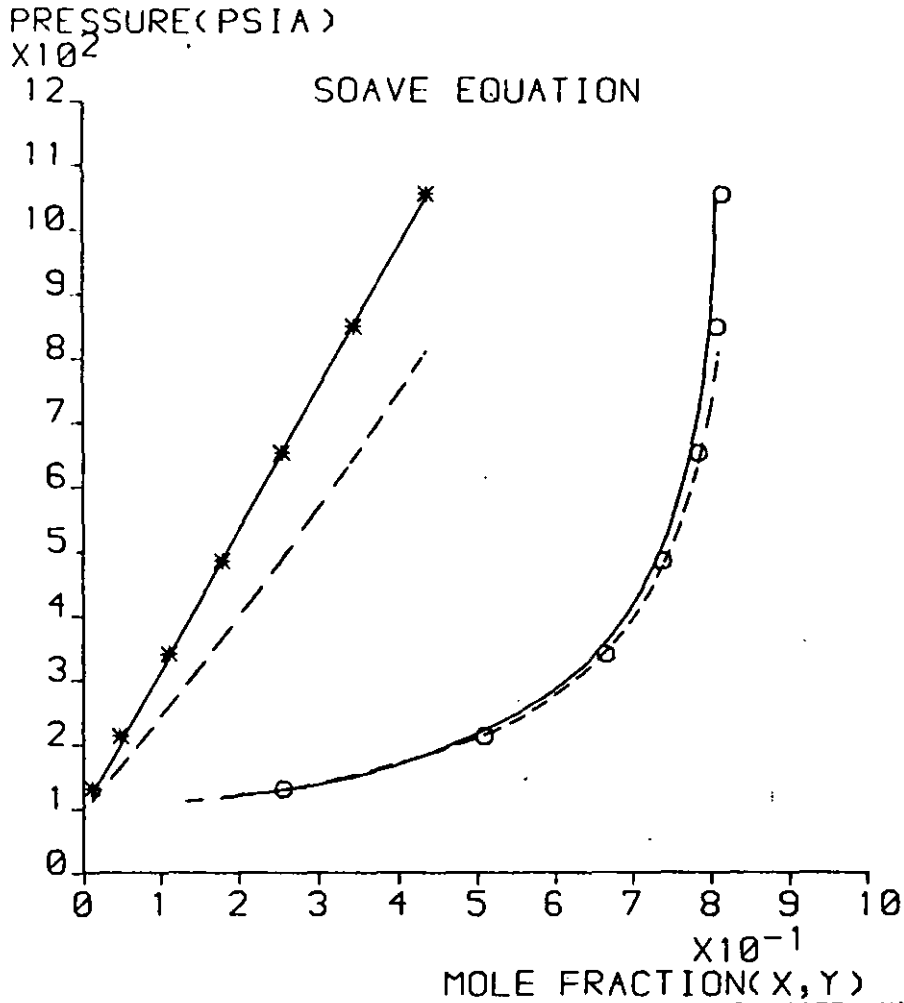


(a)

FIGURE 6.76 CO_2-n-Pentane System at 679.69°R (377.6K)

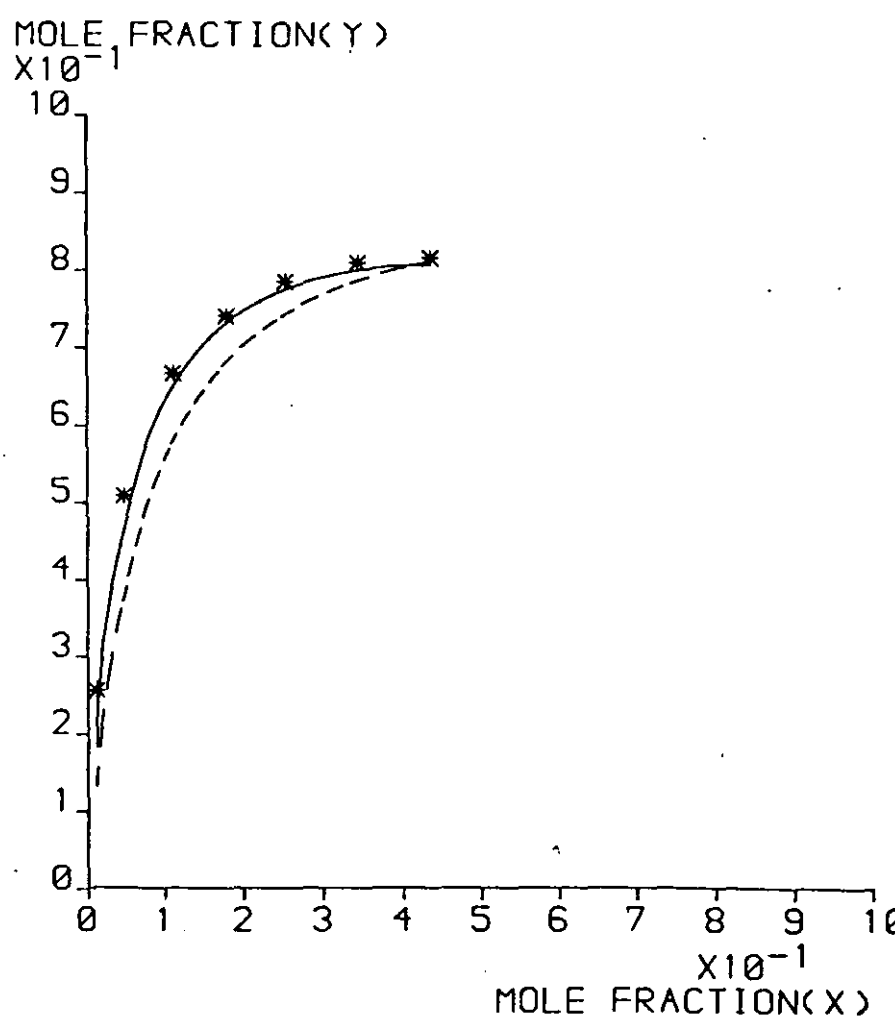


(b)

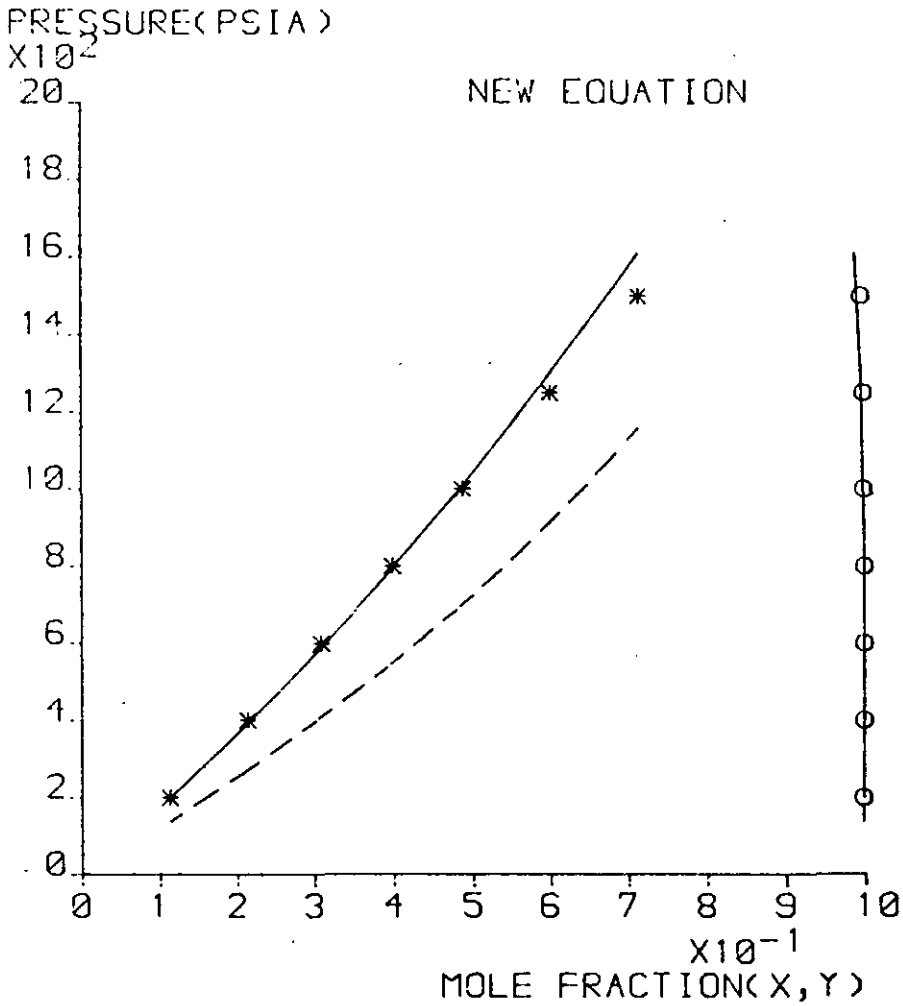


(a)

FIGURE 6.77 CO_2-n-Pentane System at 679.69°R (377.6K)

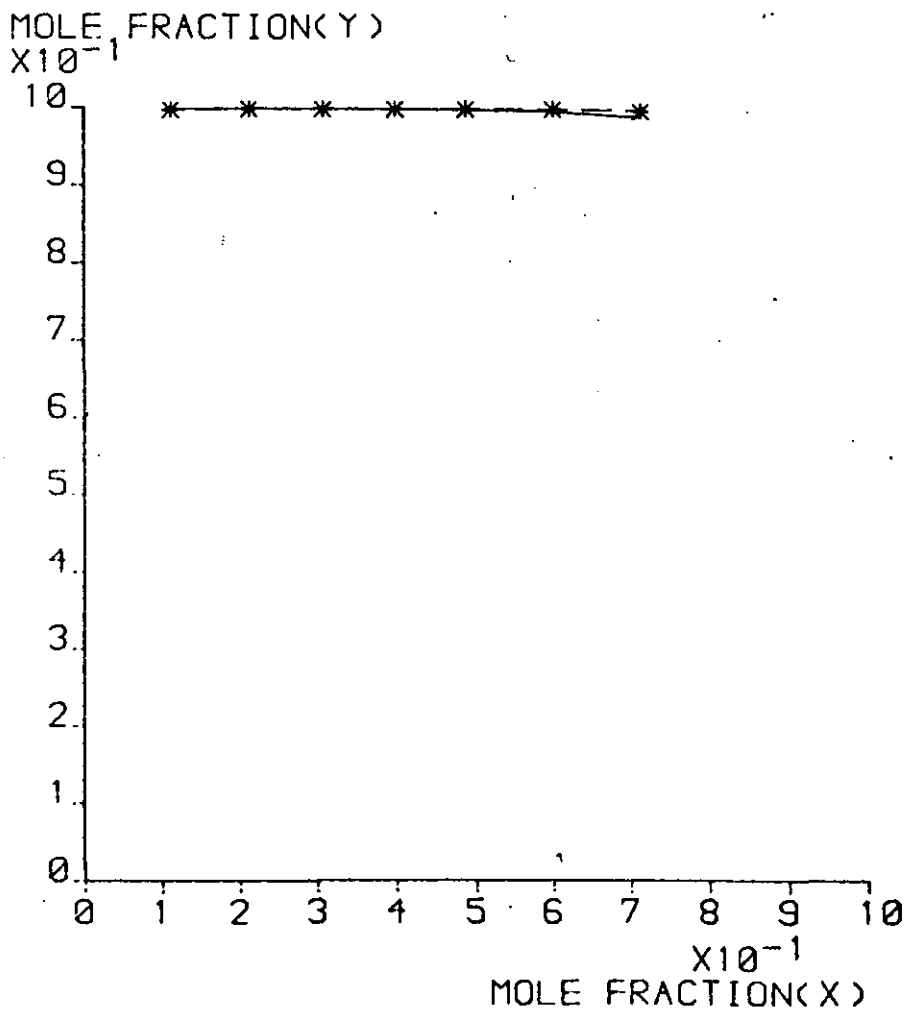


(b)

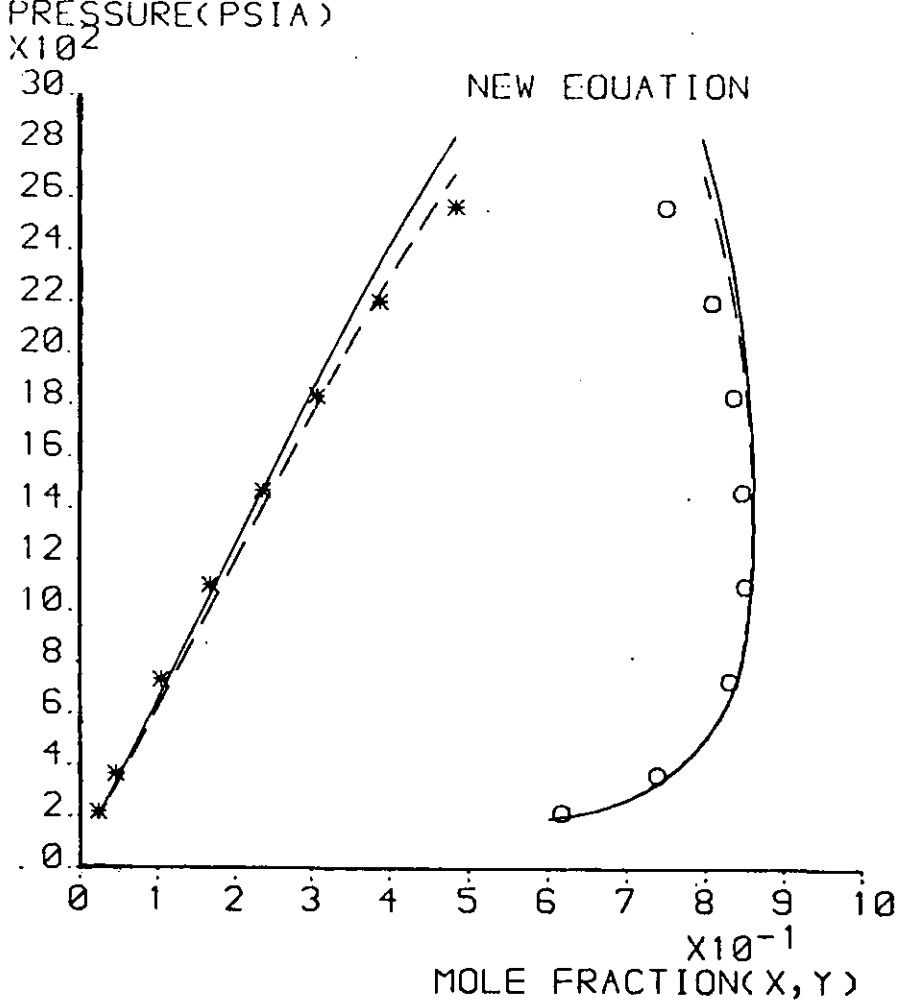


(a)

FIGURE 6.78 CO_2-n-Decane System at 619.67°R (344.3K)

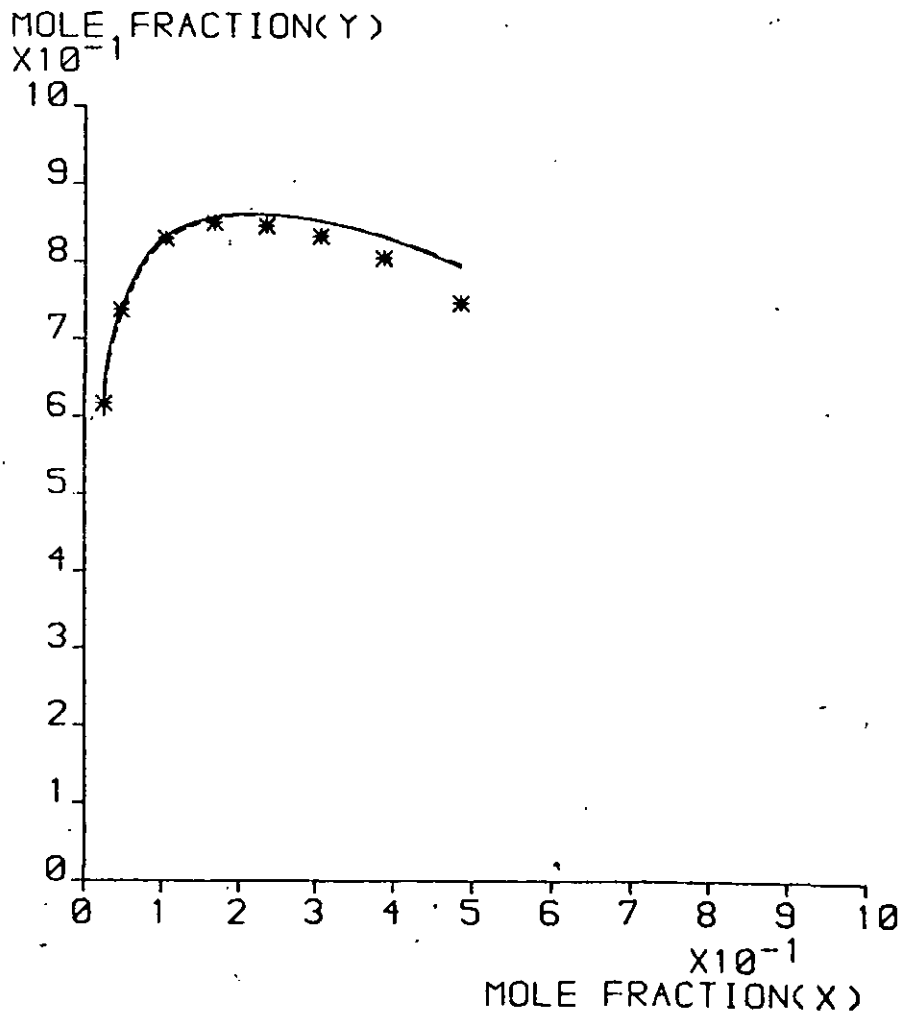


(b)

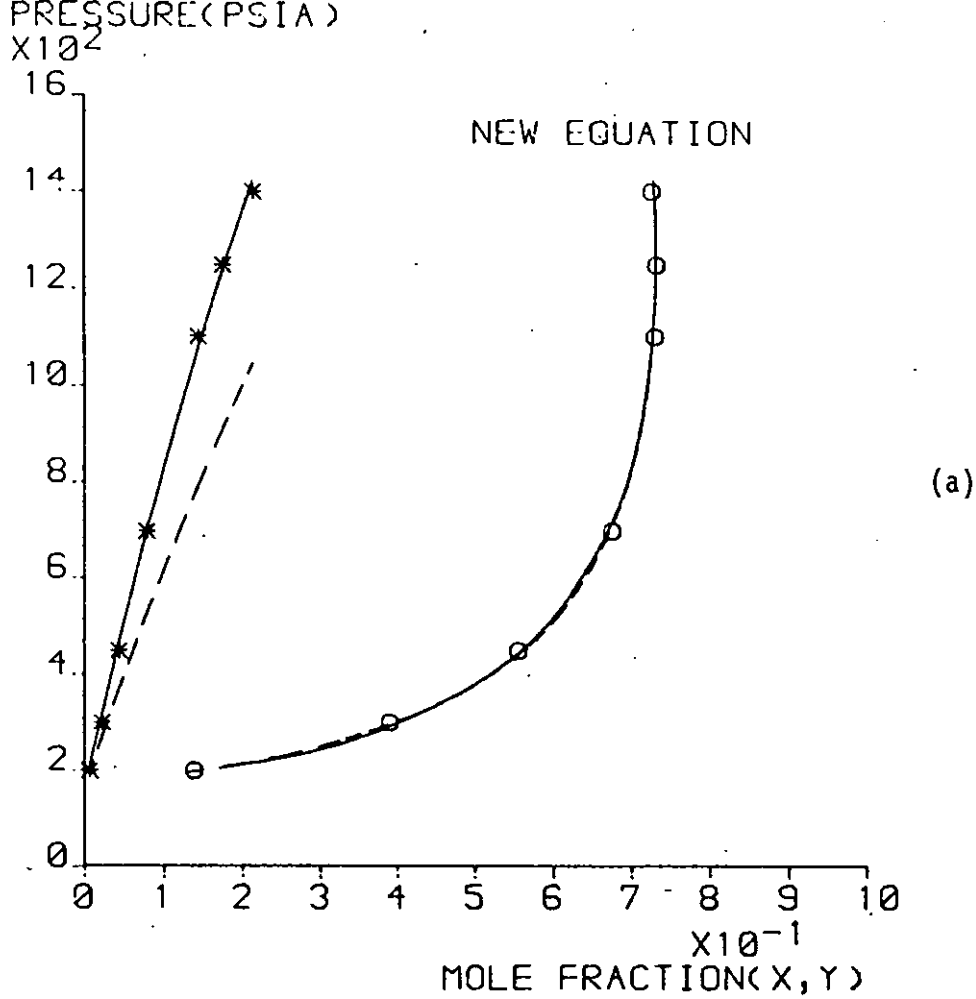


(a)

FIGURE 6.79 CO_2- Propane System at 491.67°R (273.2K)

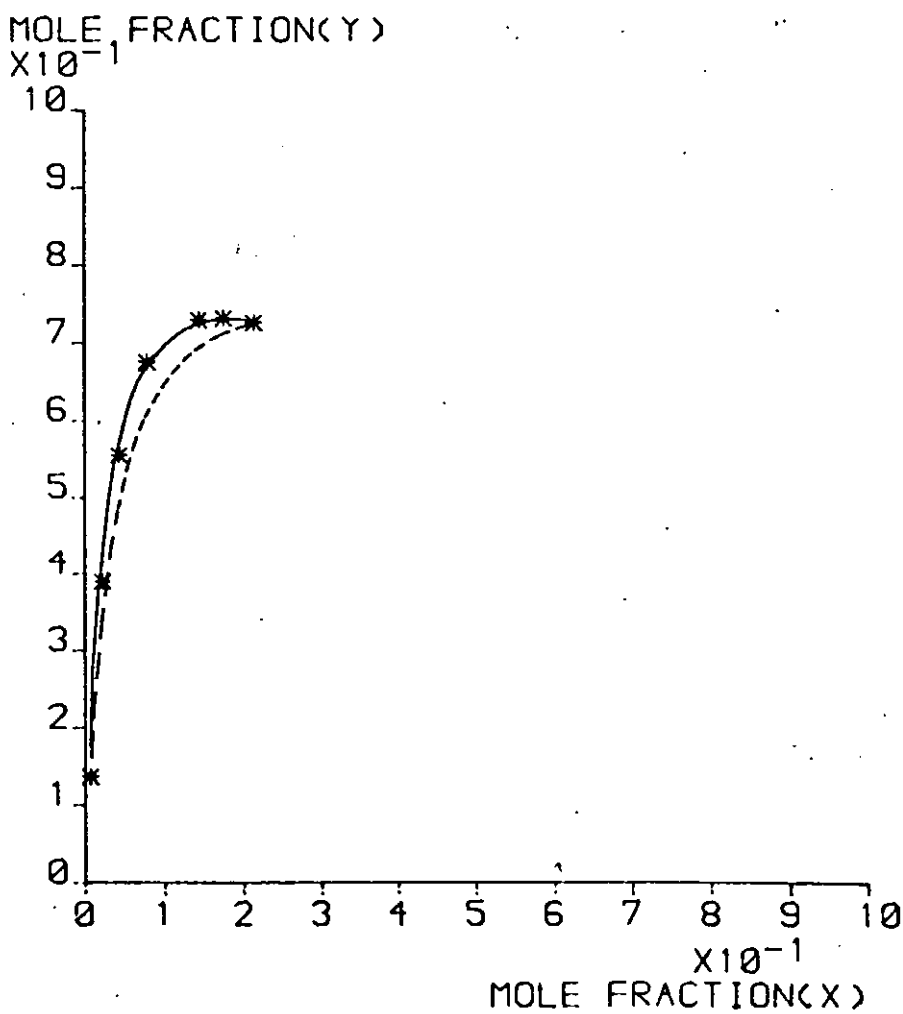


(b)

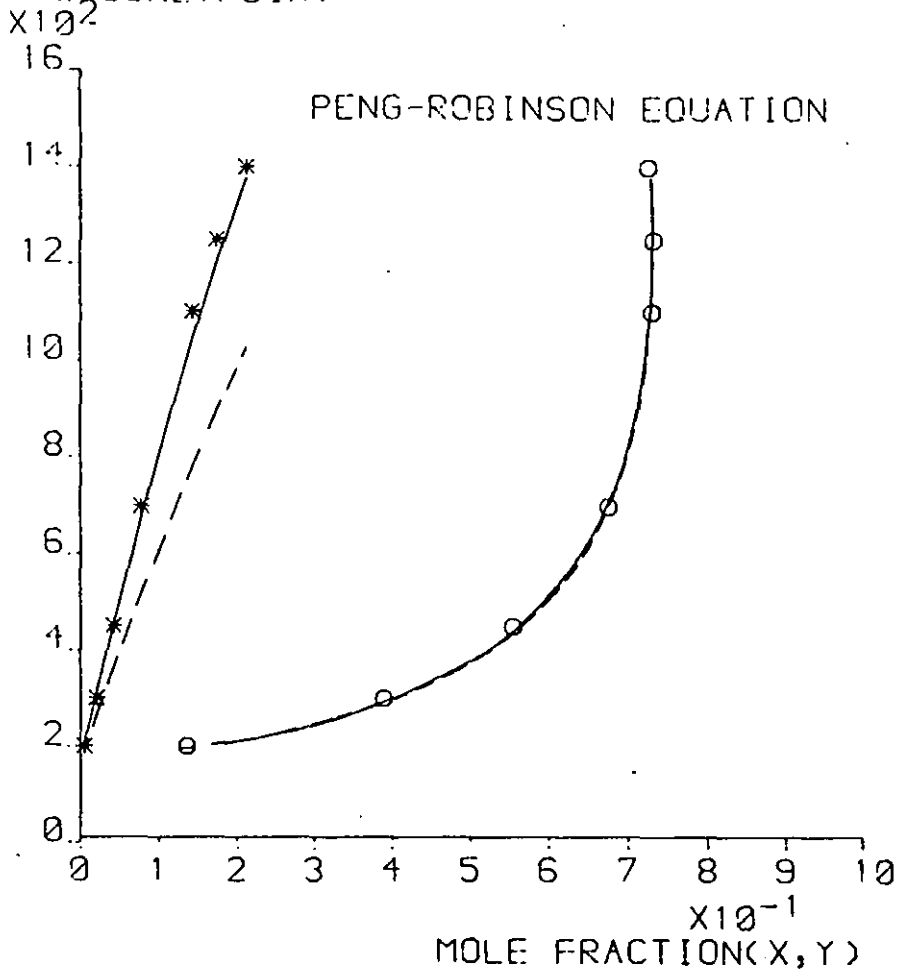


(a)

FIGURE 6.80 Methane- H_2S System at 499.61°R (277.6K)

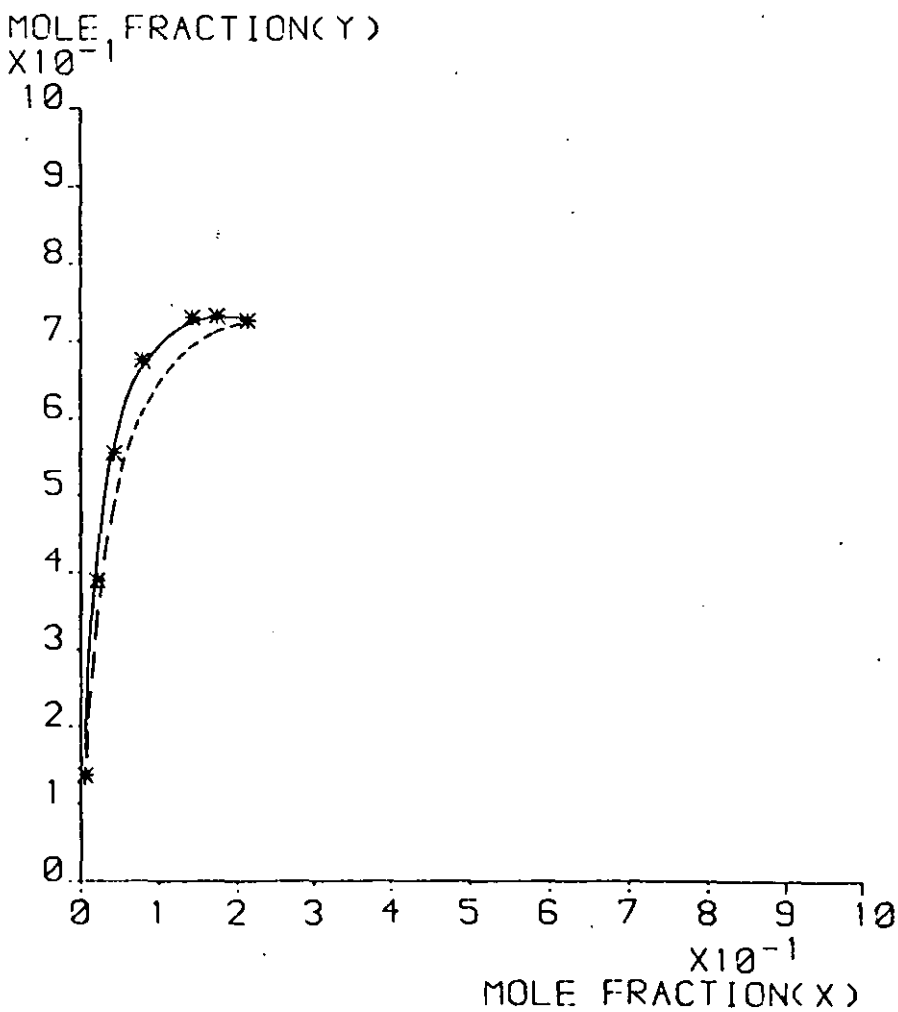


(b)



(a)

FIGURE 6.81 Methane-H_2S System at 499.61°R (277.6K)



(b)

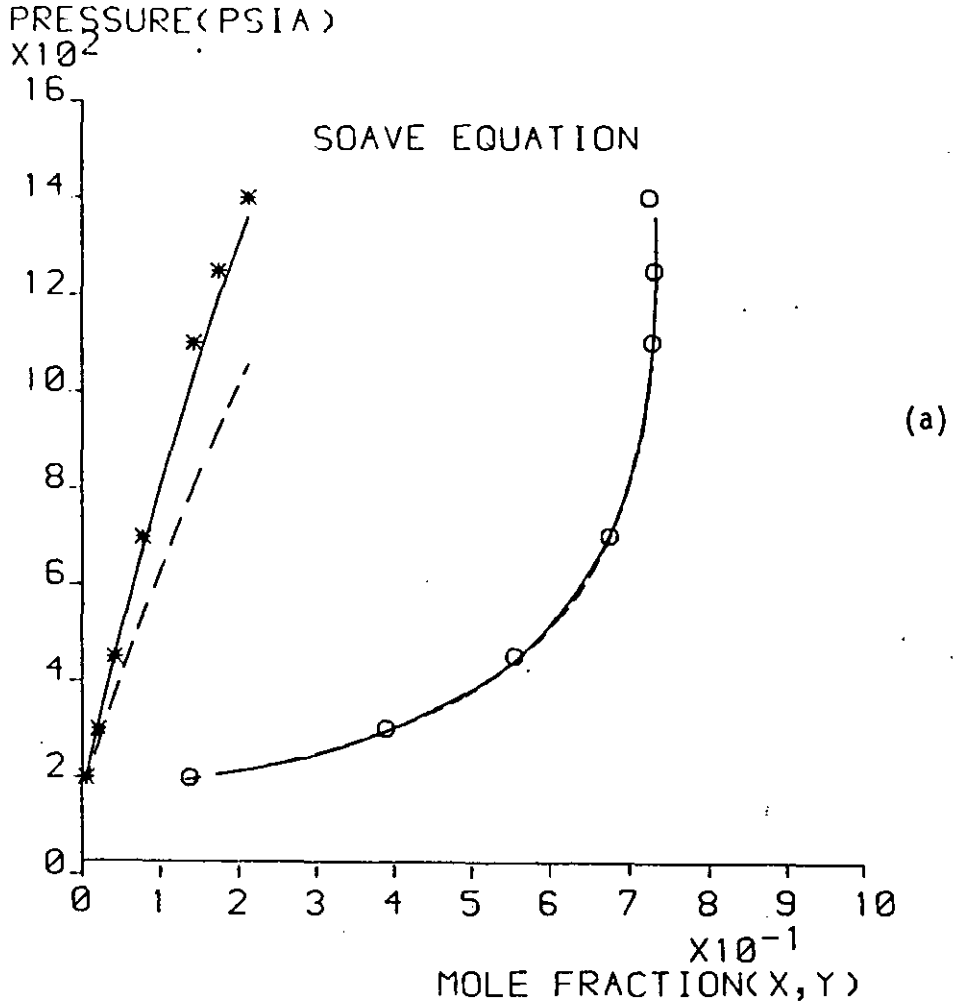
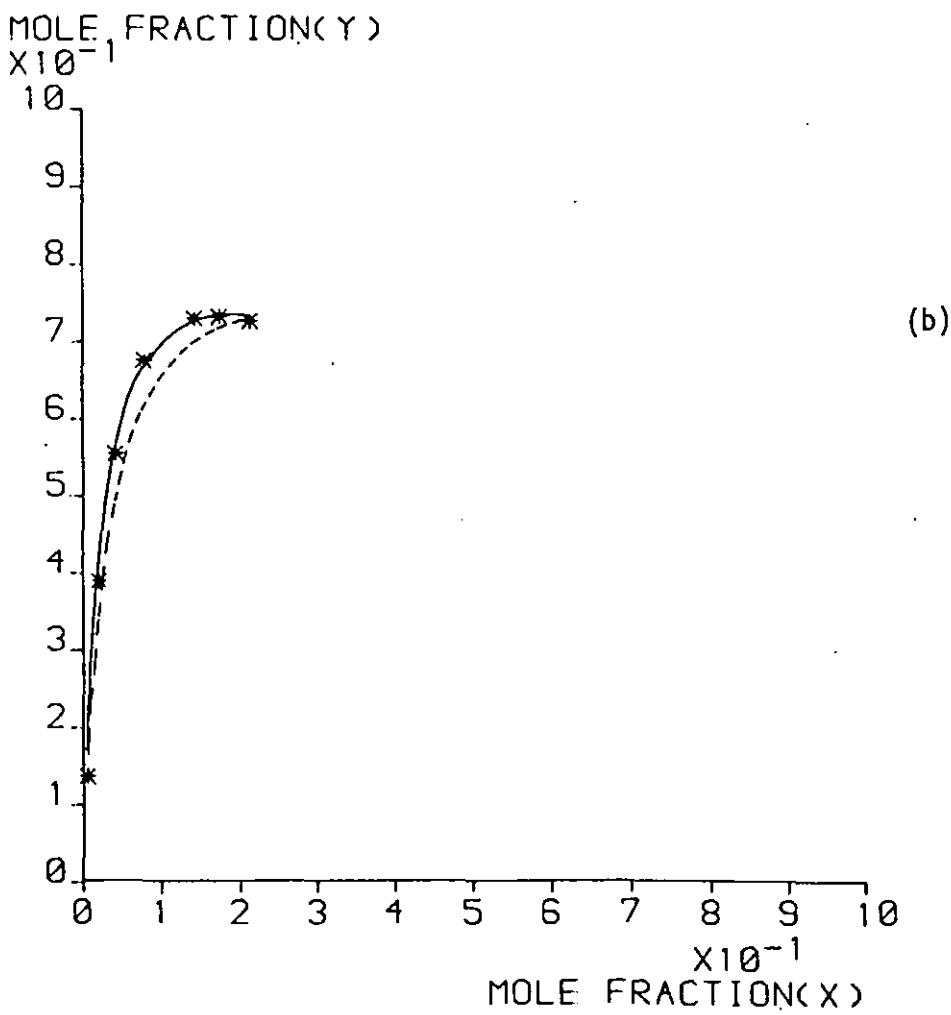
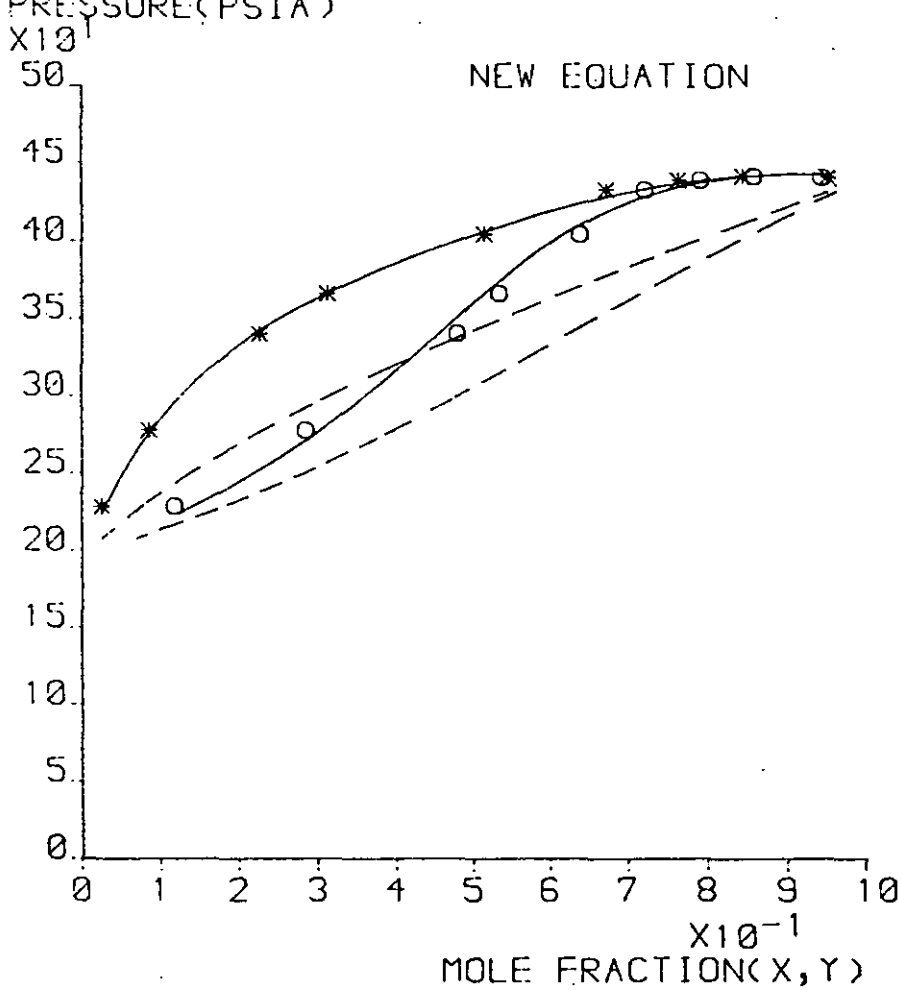


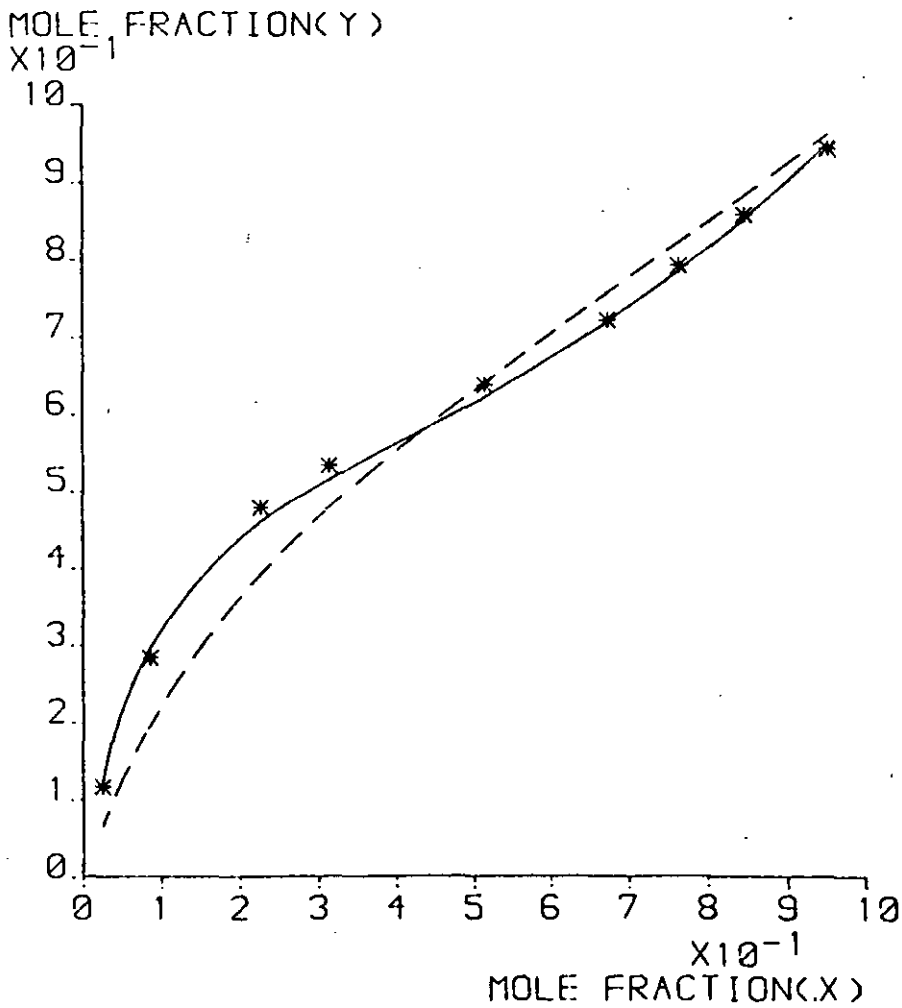
FIGURE 6.82 Methane-H_2S System at 499.61°R (277.6K)



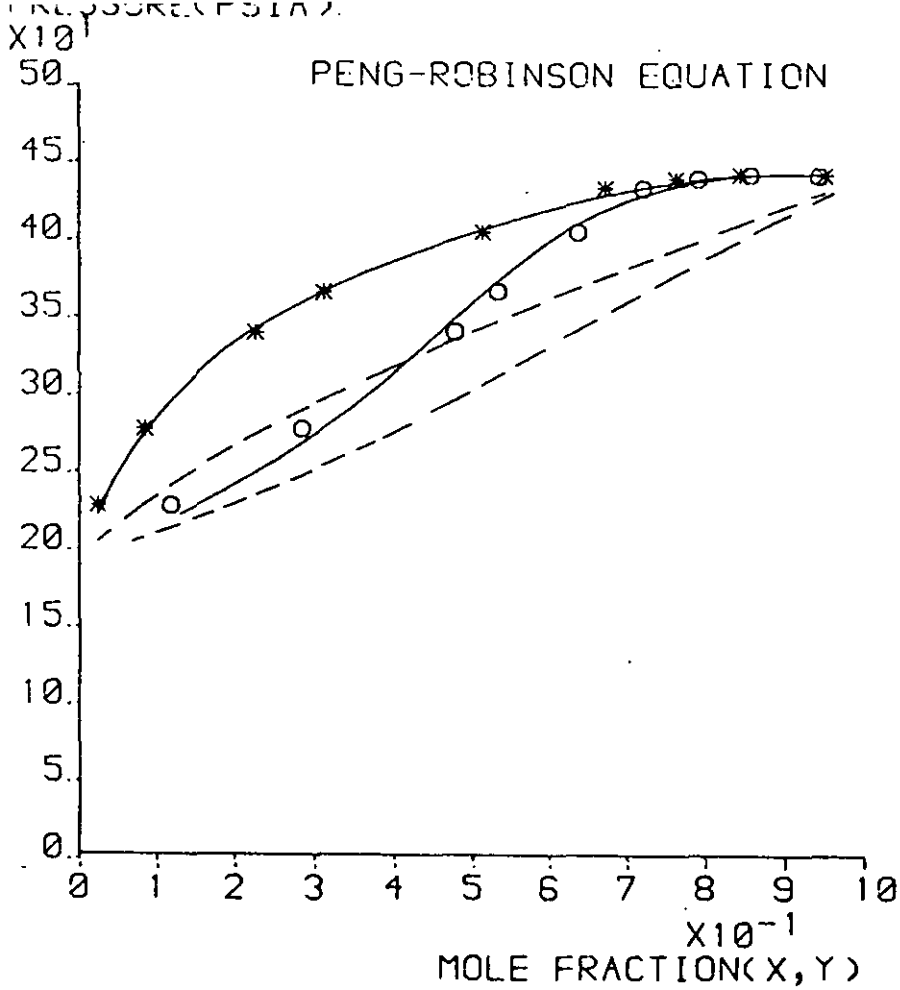


(a)

FIGURE 6.83 Ethane-H_2S System at 509.69°R (283.2K)

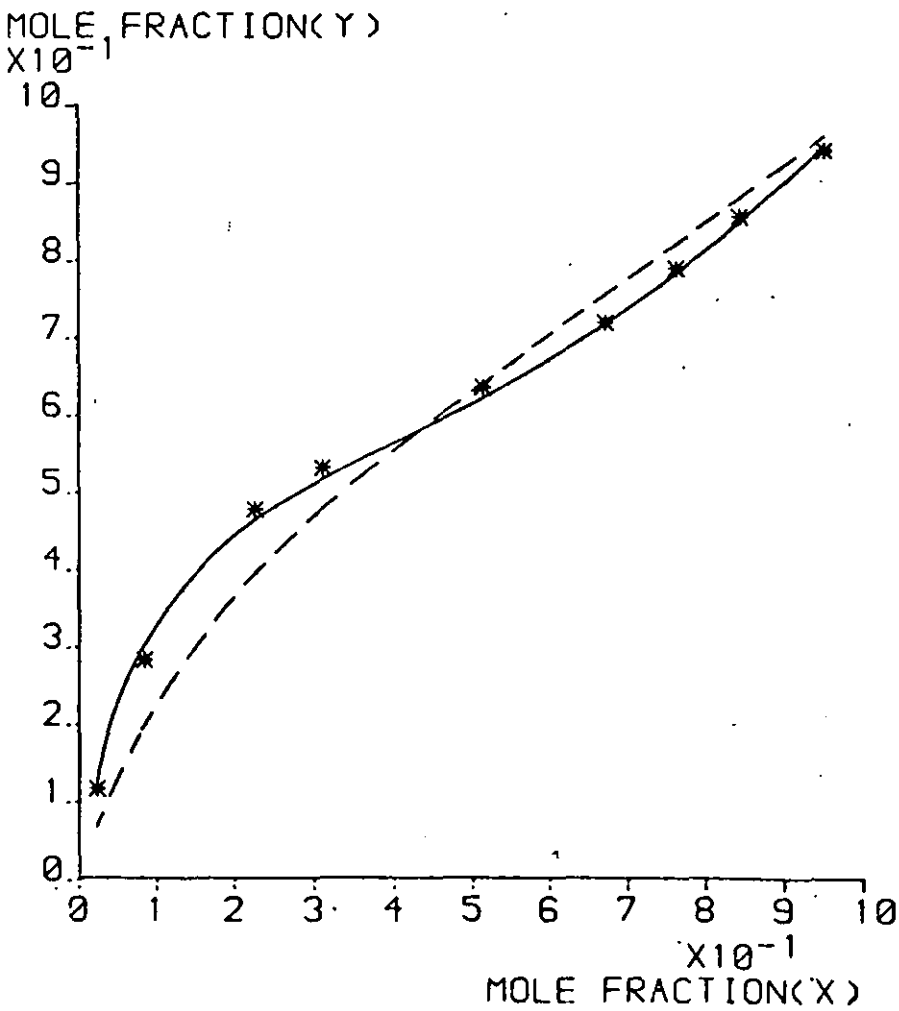


(b)

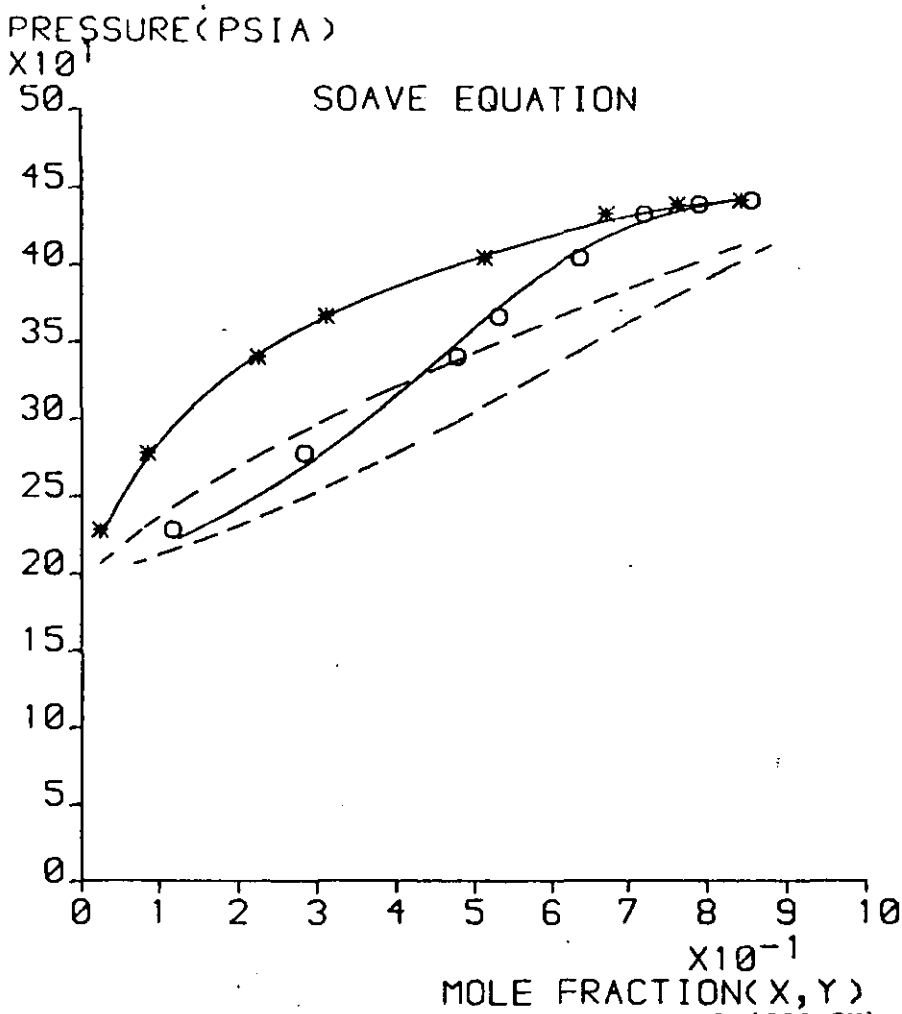


(a)

FIGURE 6.84 Ethane-H_2S System at 509.69°R (283.2K)

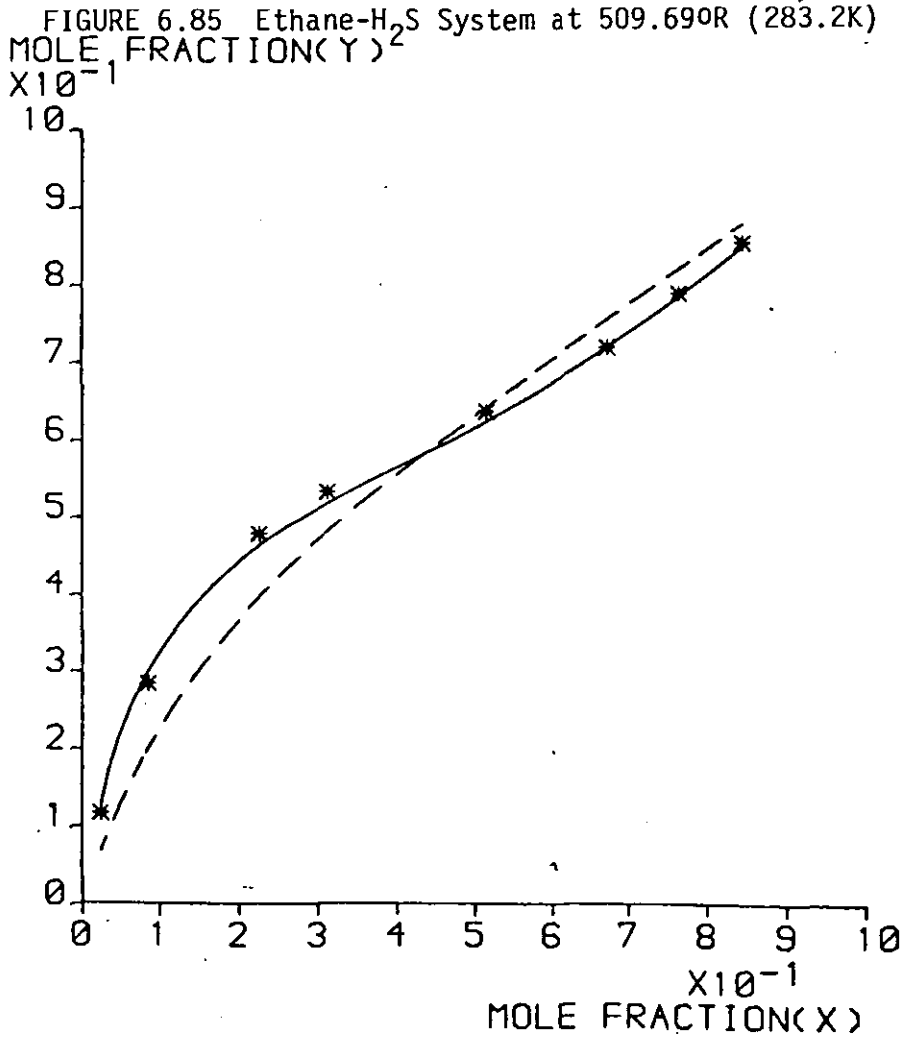


(b)



(a)

FIGURE 6.85 Ethane-H_2S System at 509.69°R (283.2K)



(b)

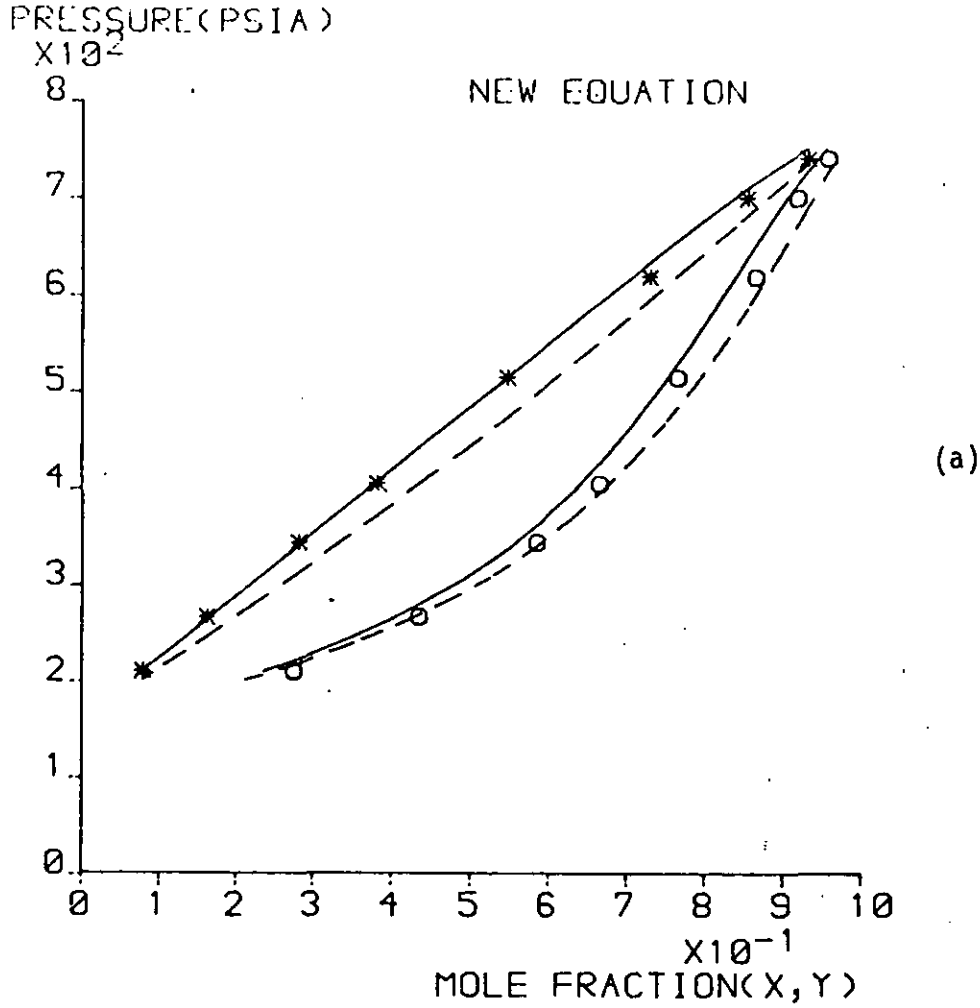
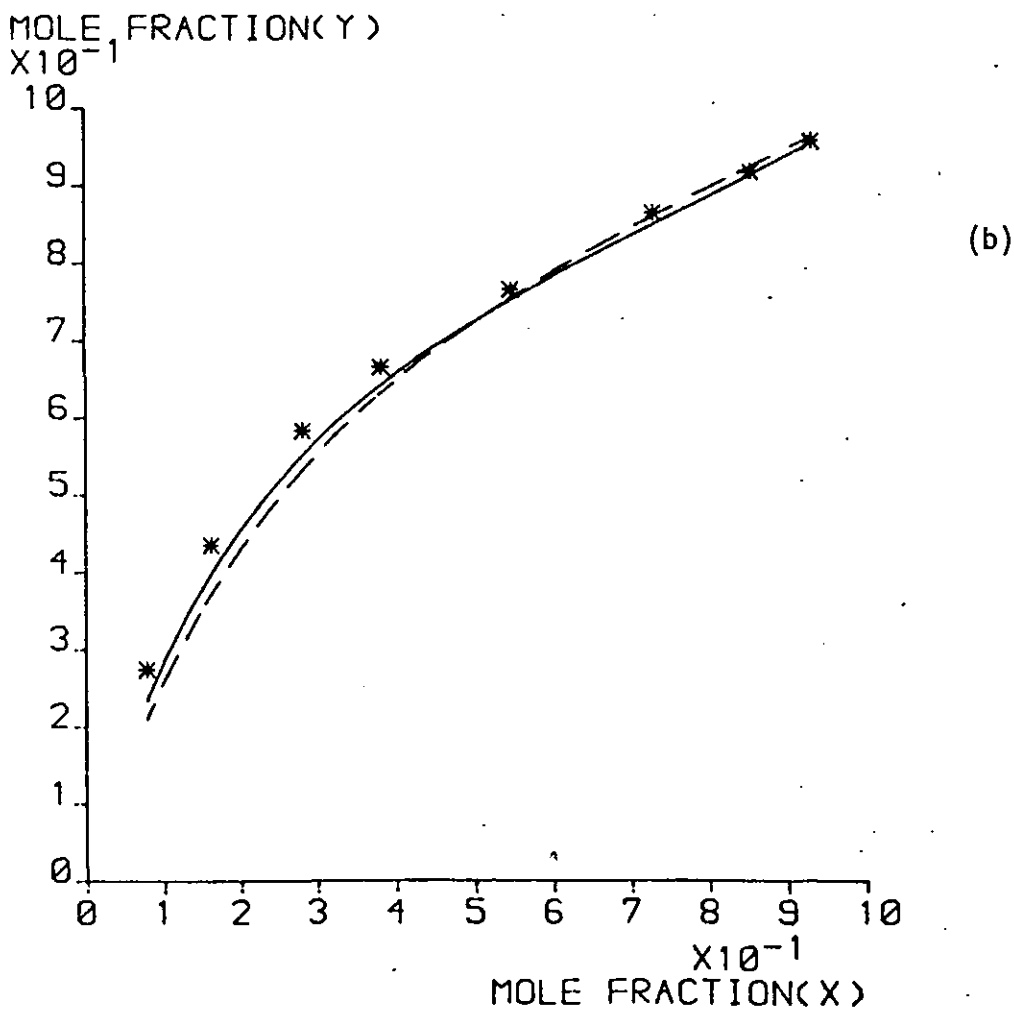
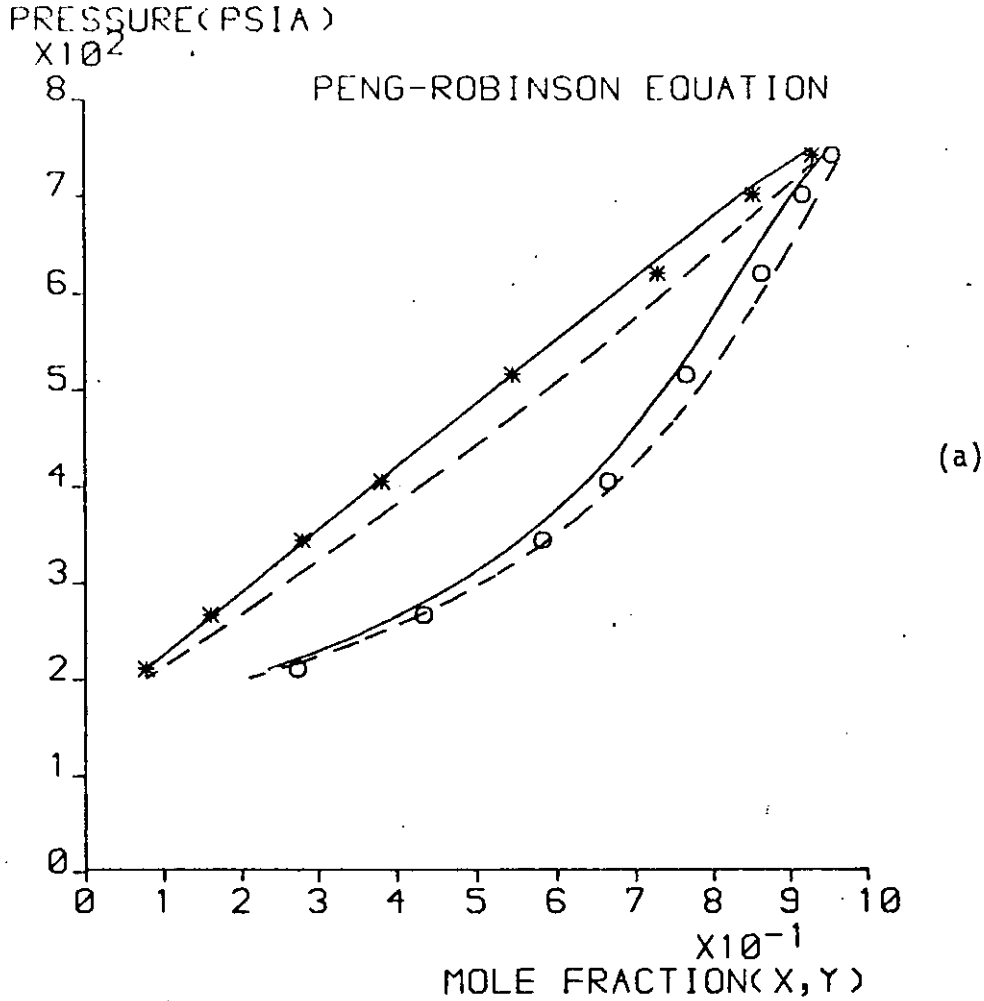


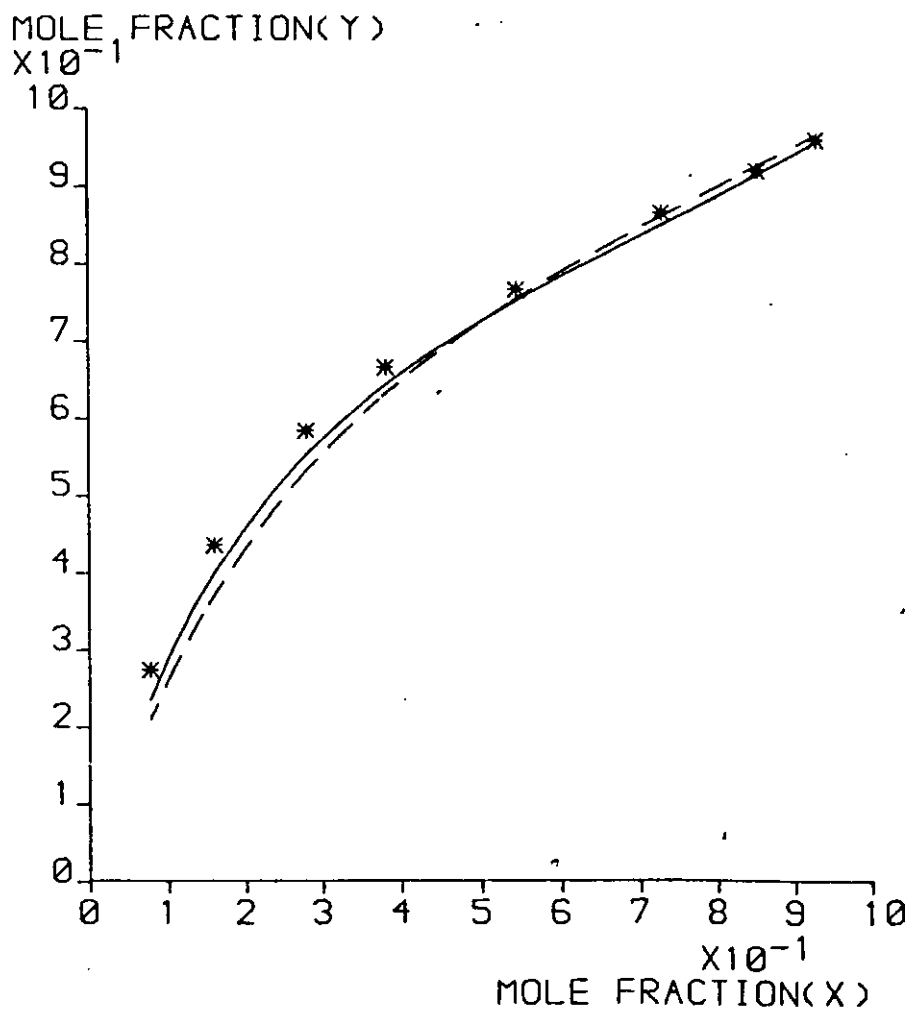
FIGURE 6.86 : H_2S-i-Butane System at 619.89°R (344.4K)



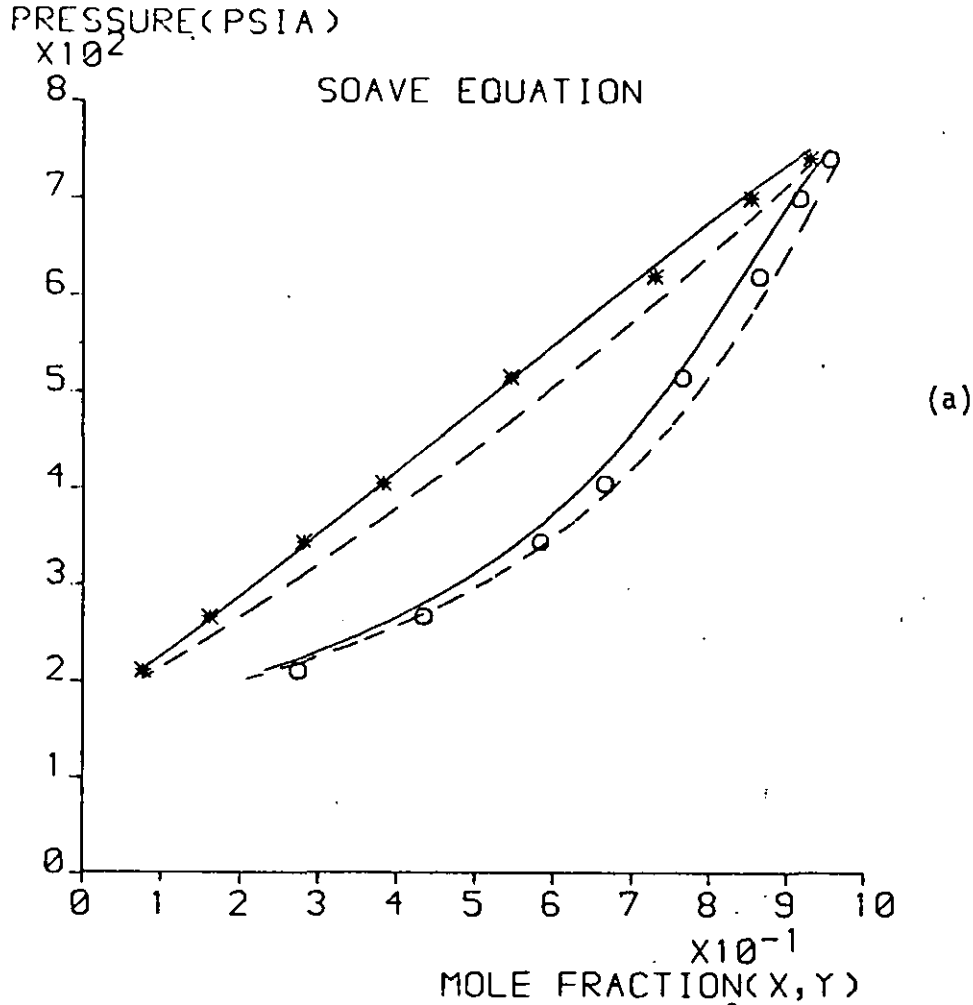


(a)

FIGURE 6.87 H_2S-i-Butane System at 619.89°R (344.4K)

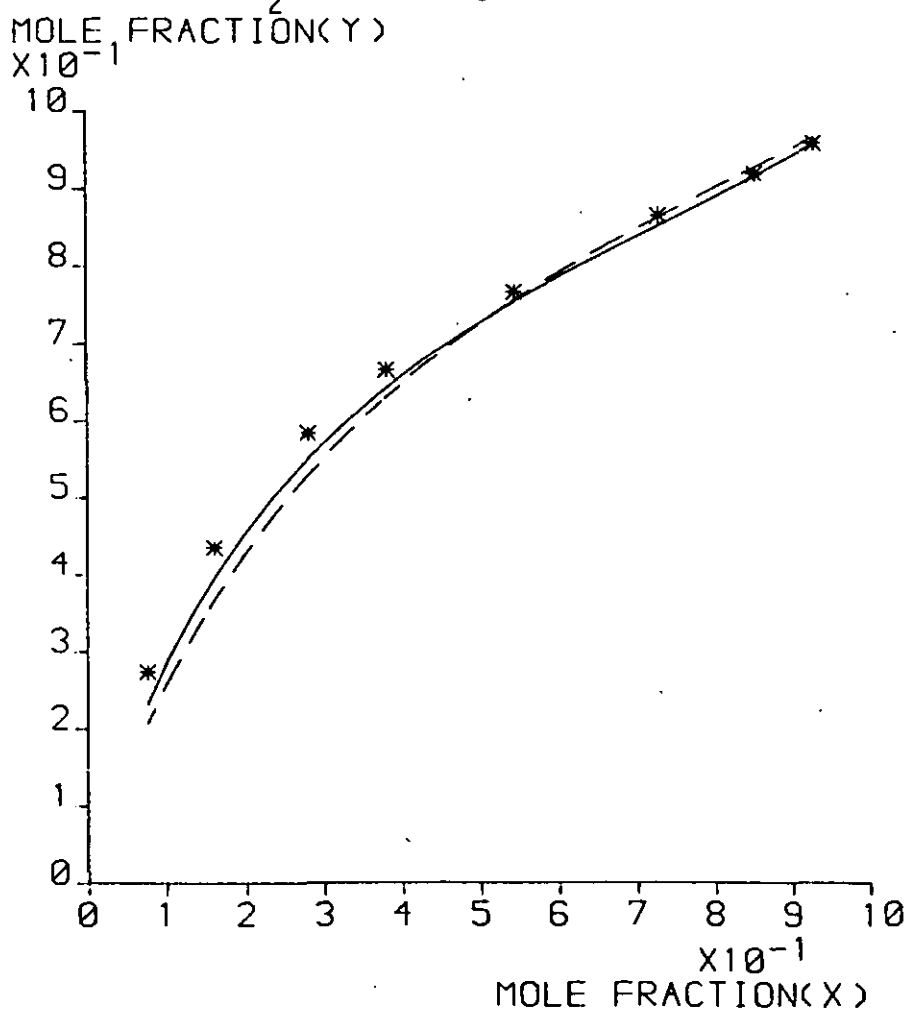


(b)

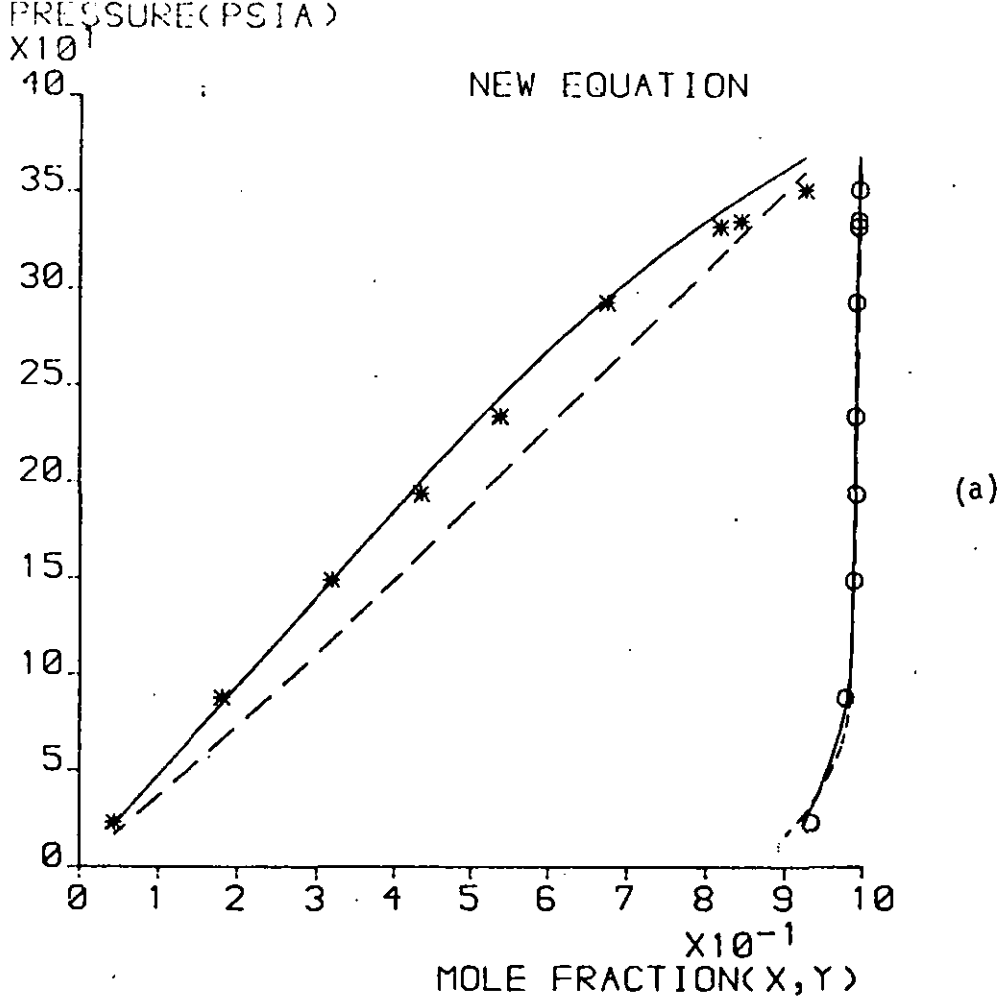


(a)

FIGURE 6.88 H_2S-i-Butane System at 619.89°R (344.4K)

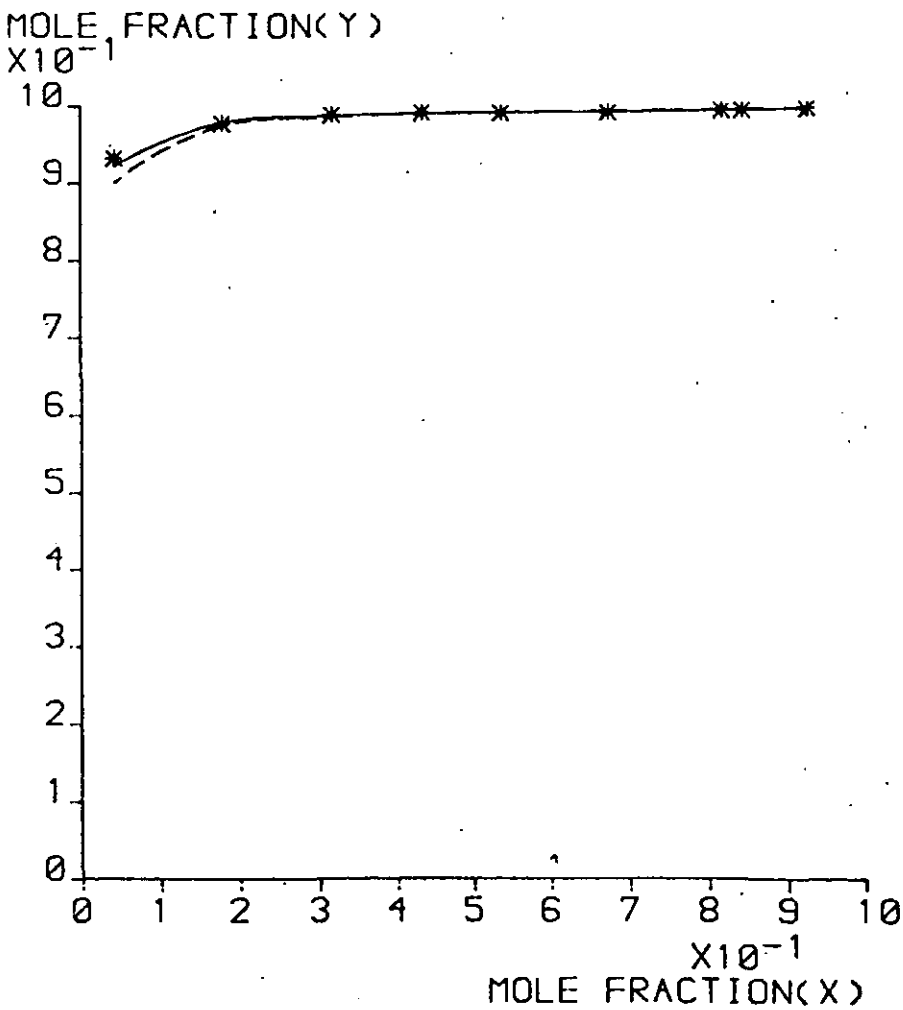


(b)

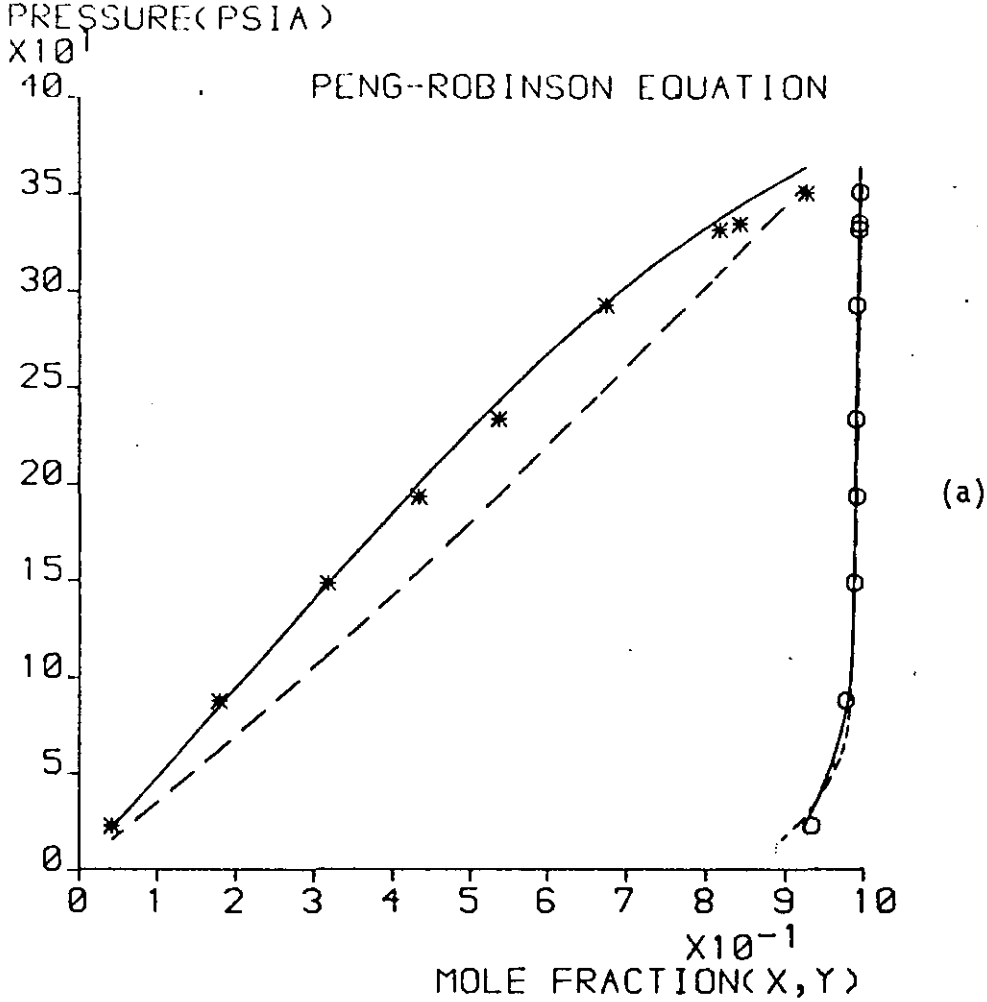


(a)

FIGURE 6.89 H_2S-n-Heptane System at 559.69°R (311K)

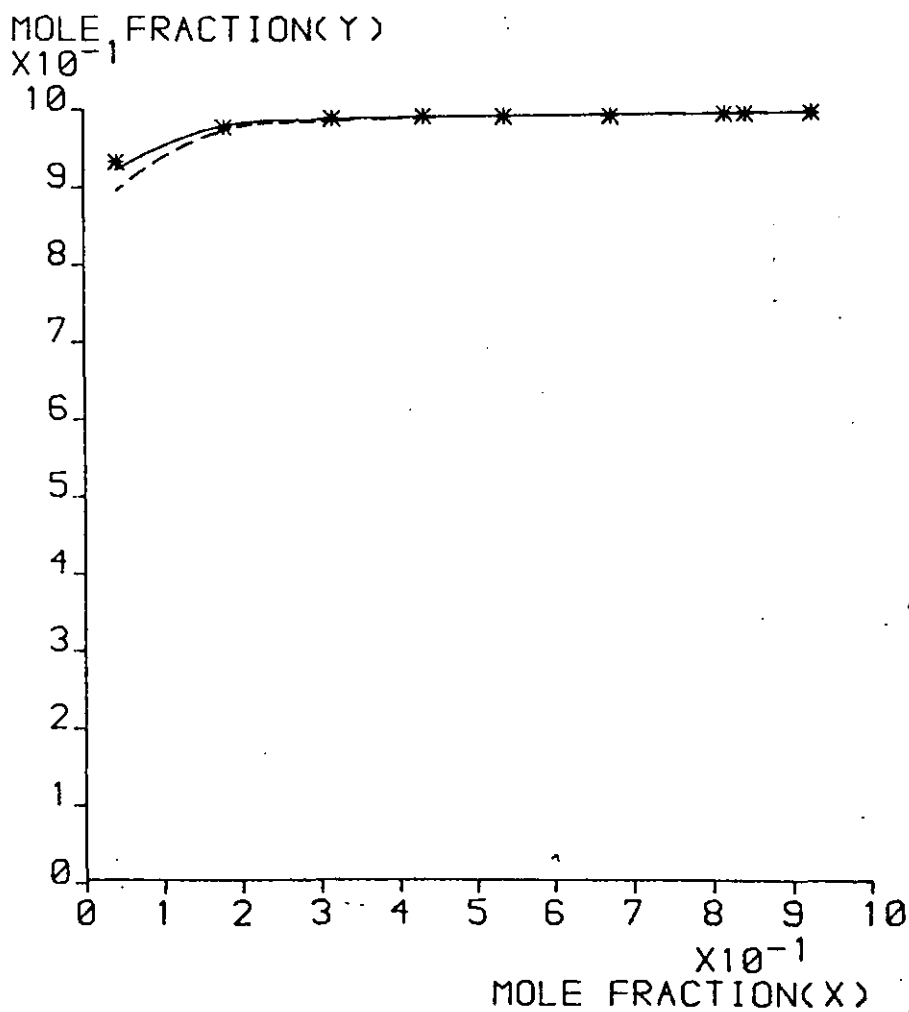


(b)

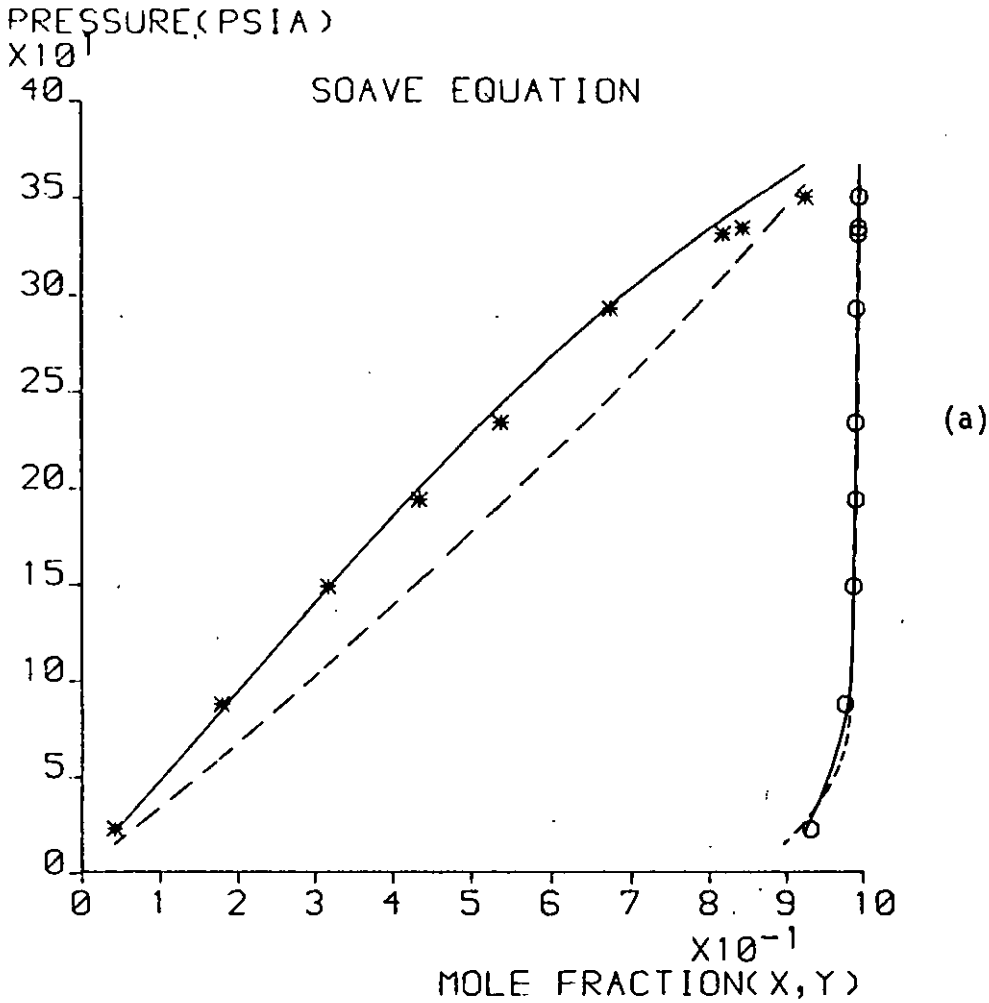


(a)

FIGURE 6.90 H_2S-n-Heptane System at 559.69oR (311K)

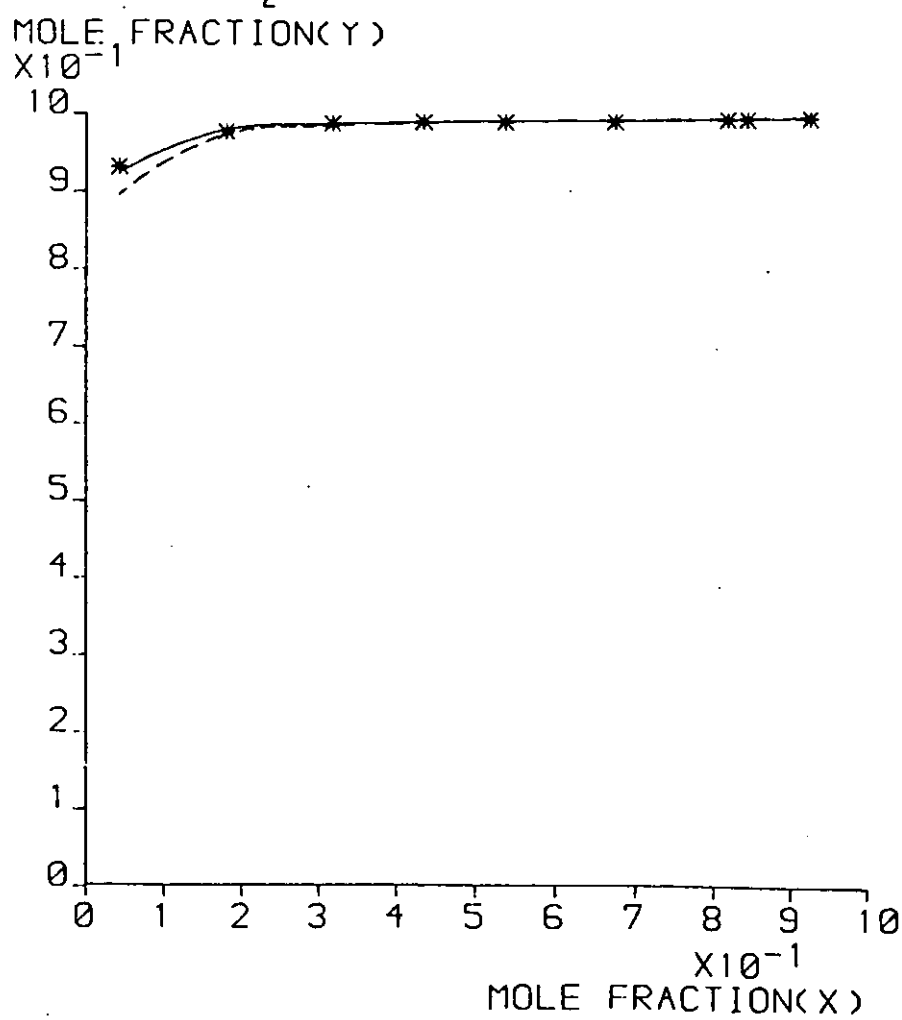


(b)

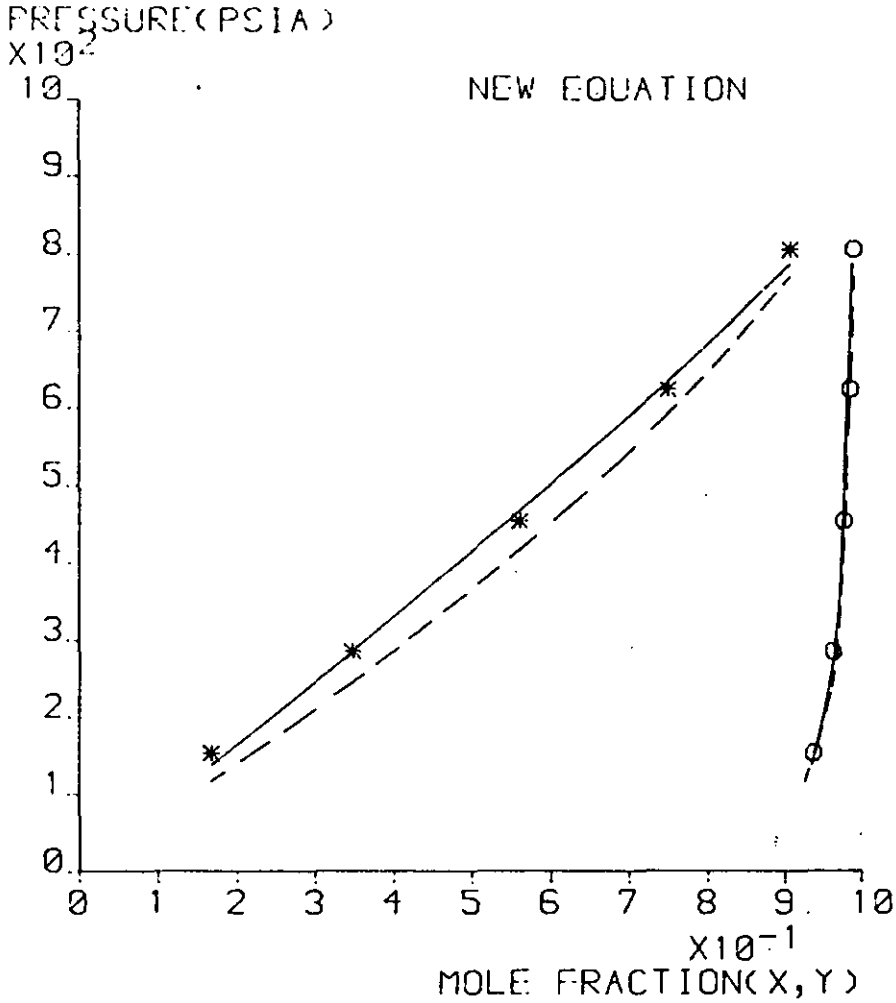


(a)

FIGURE 6.91 H_2S-n-Heptane System at 559.69°R (311K)

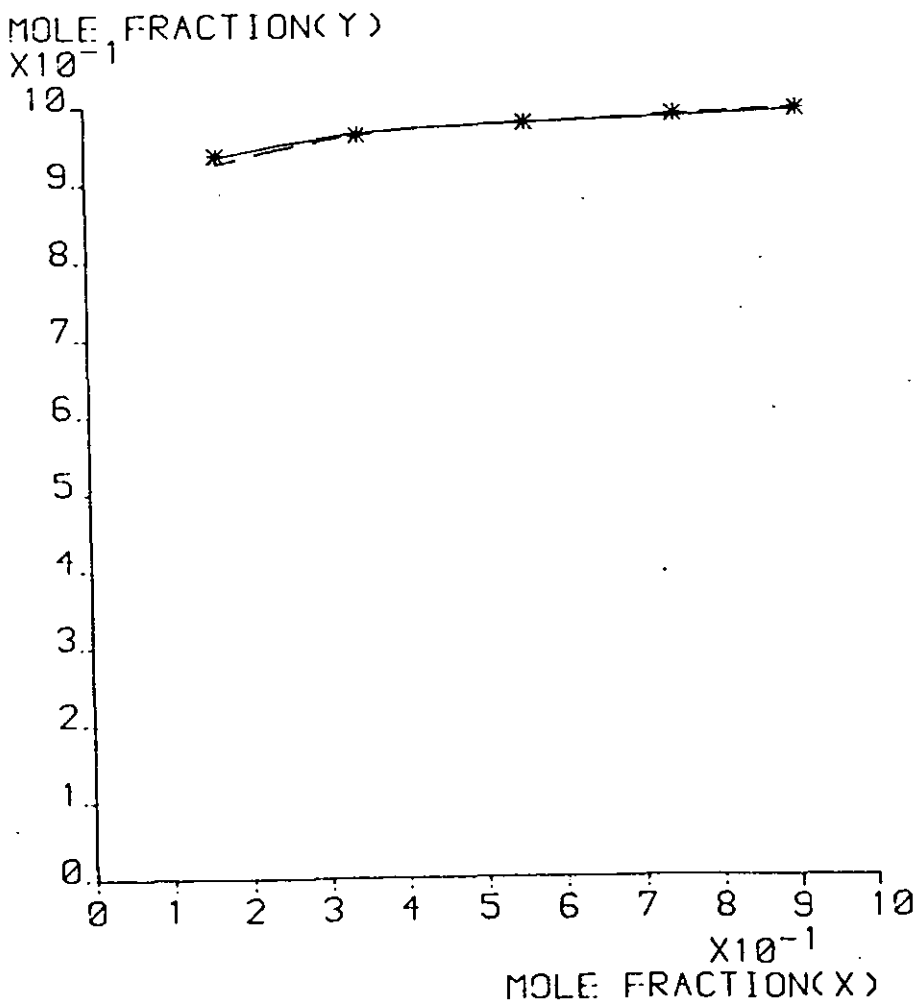


(b)

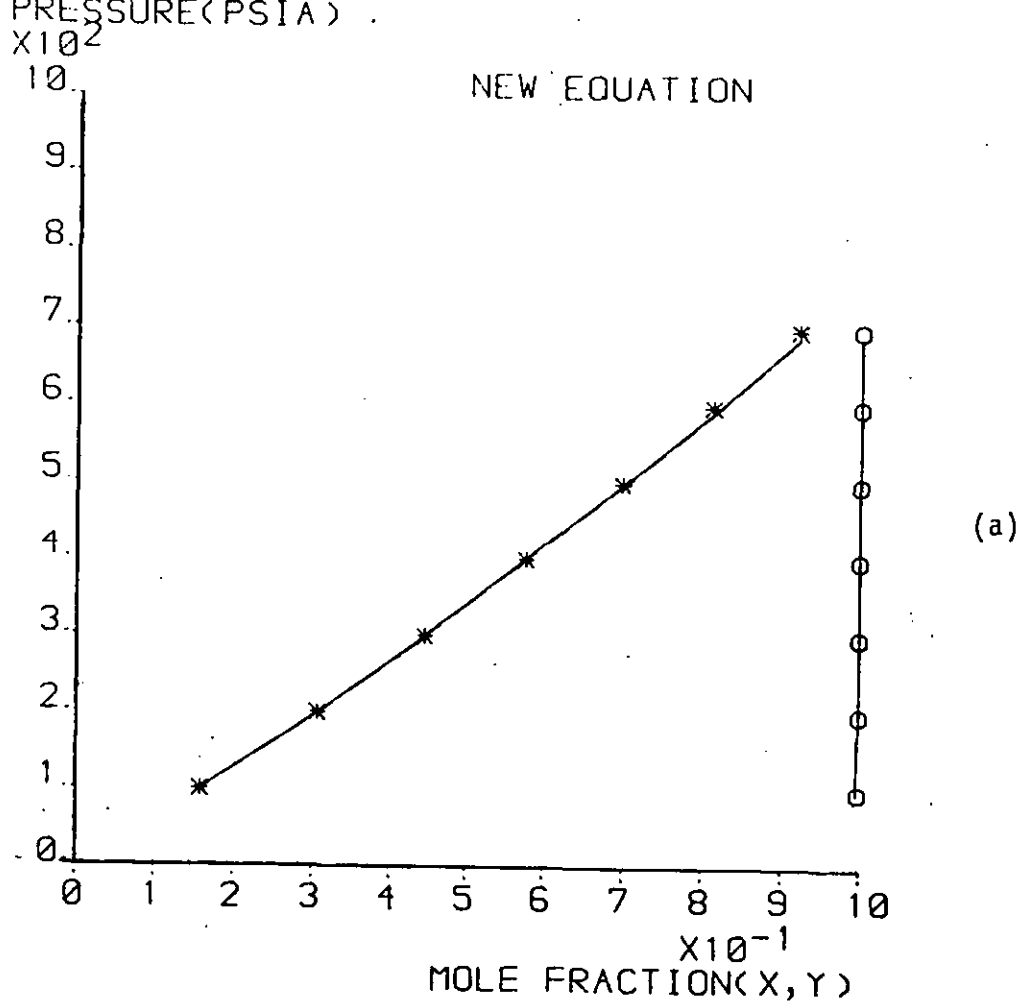


(a)

FIGURE 6.92 H_2S-n-Heptane System at 634.67°R (352.6K)

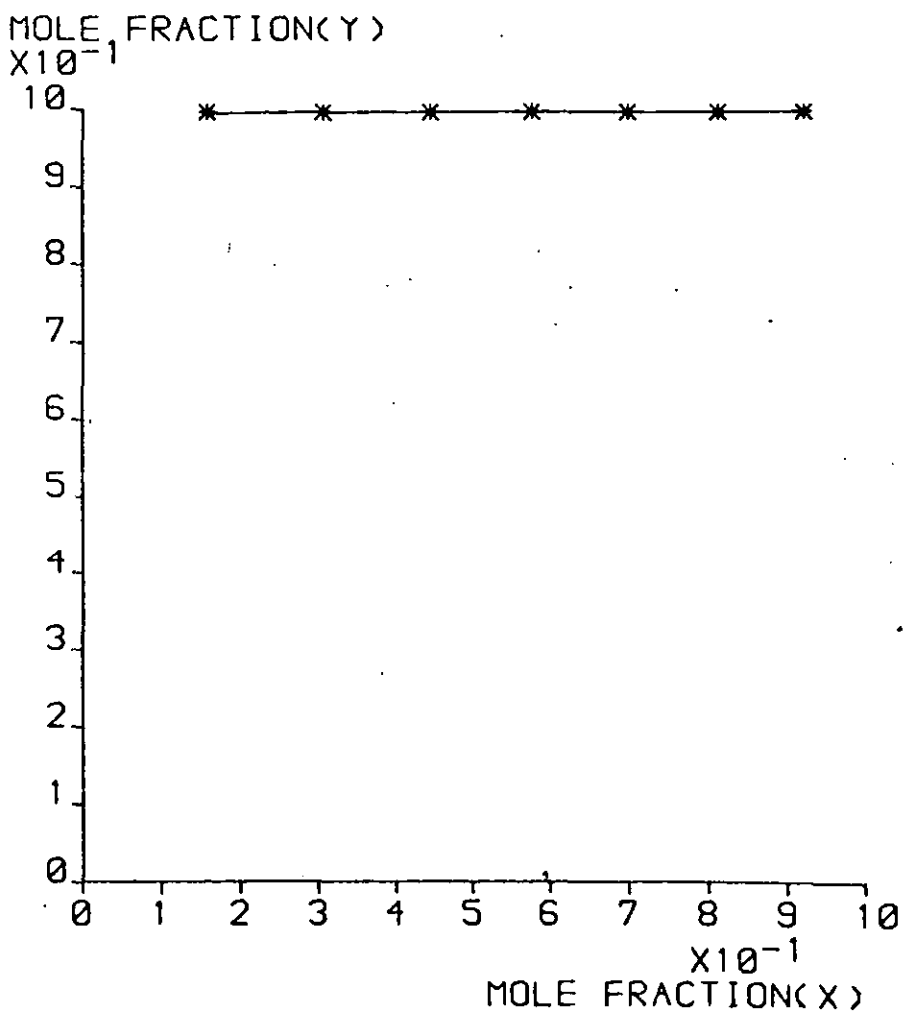


(b)

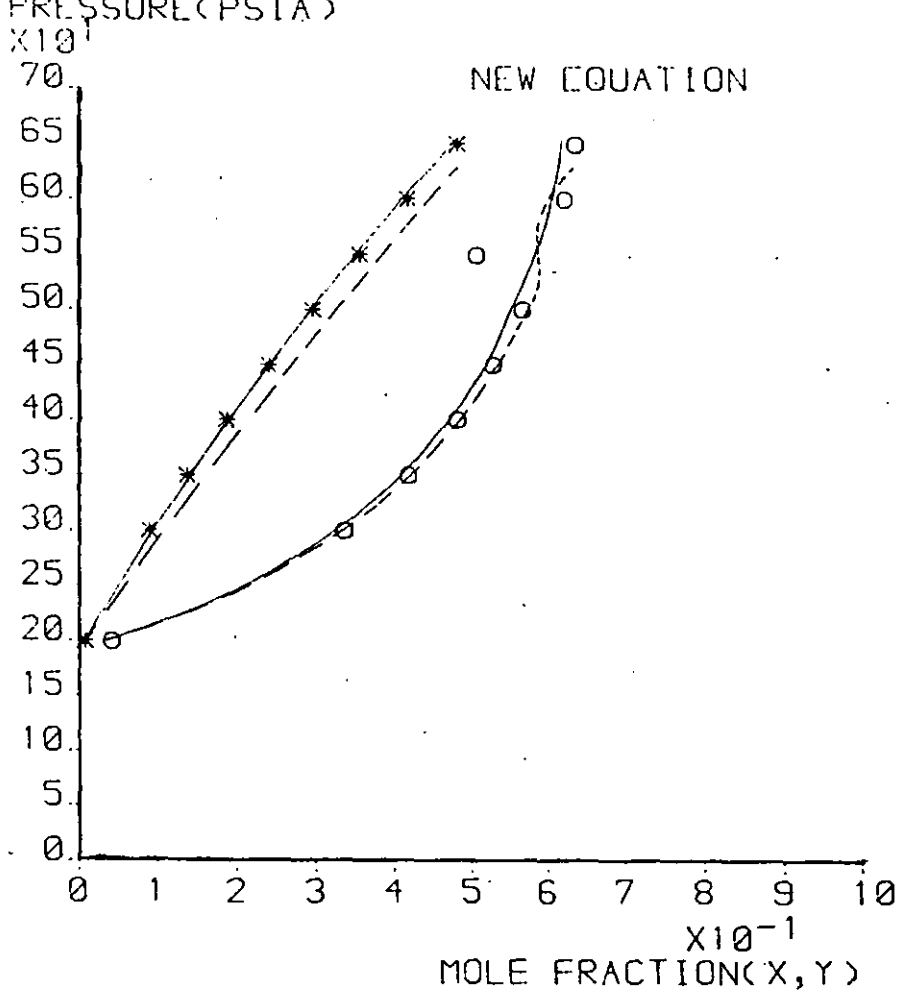


(a)

FIGURE 6.93 H_2S-n-Decane System at 619.67°R (344.3K)

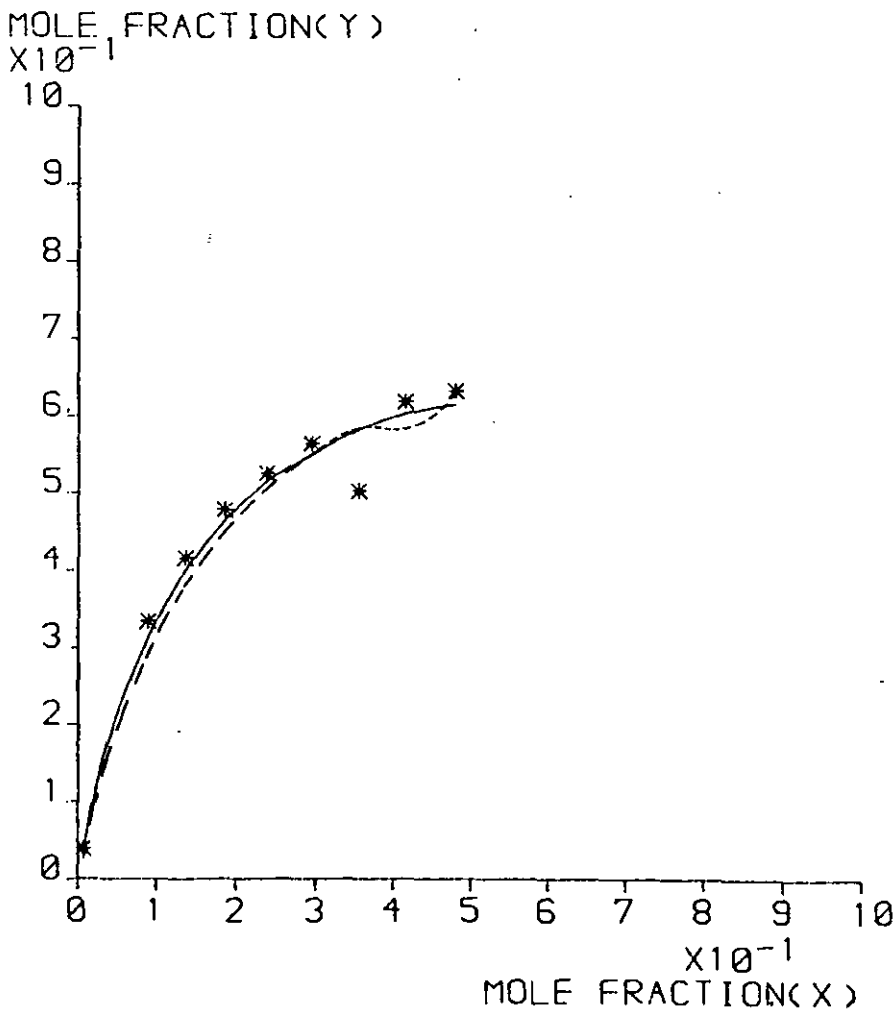


(b)

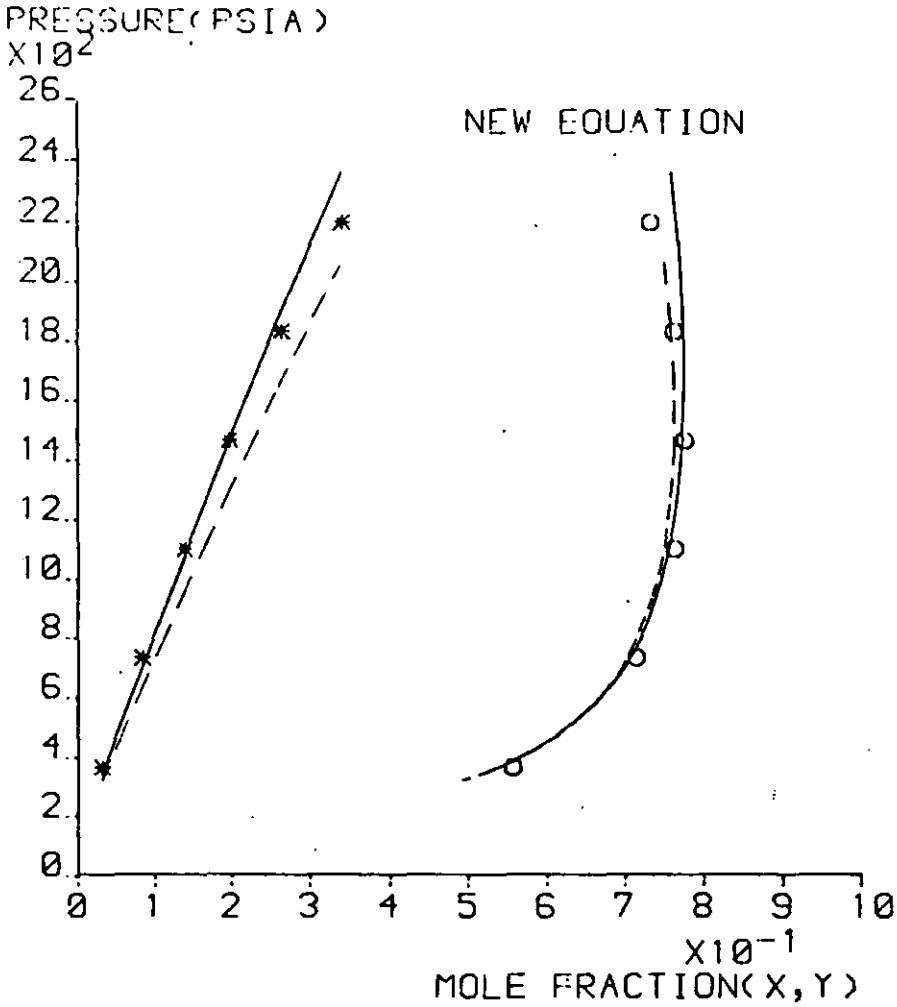


(a)

FIGURE 6.94 Nitrogen-Methane System at 279.65°R (155.4K)

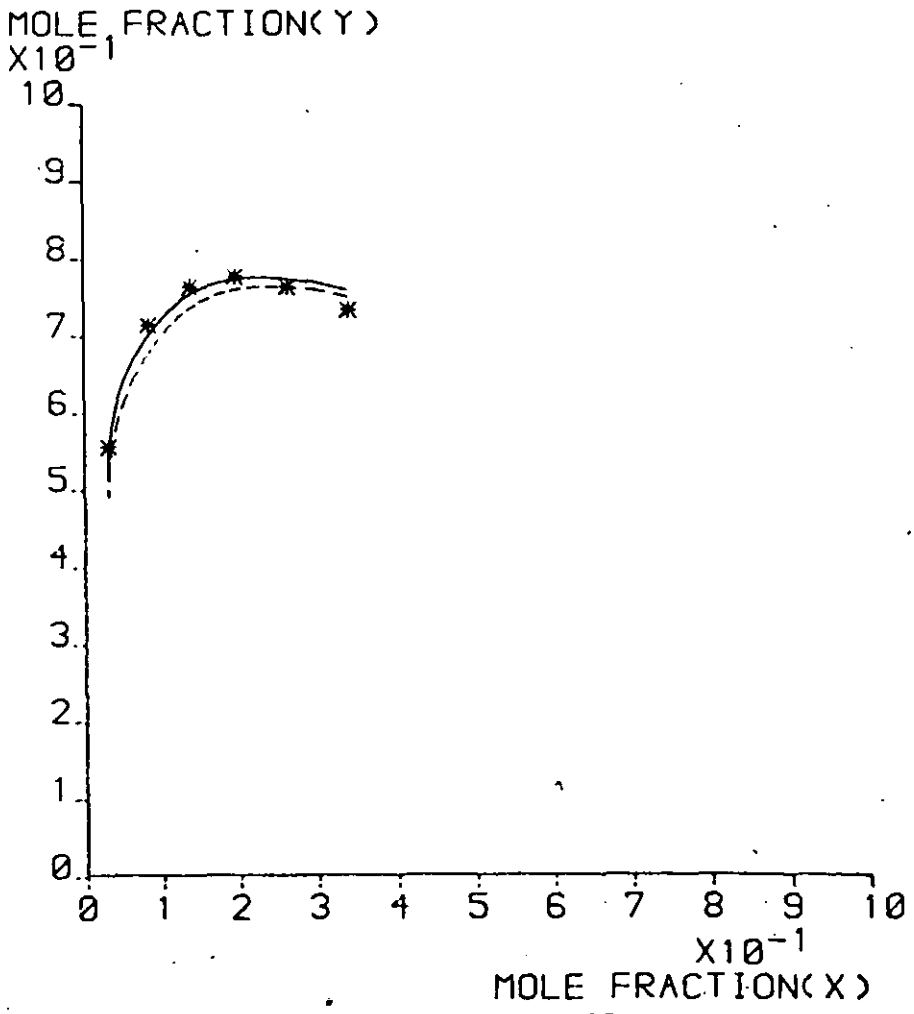


(b)

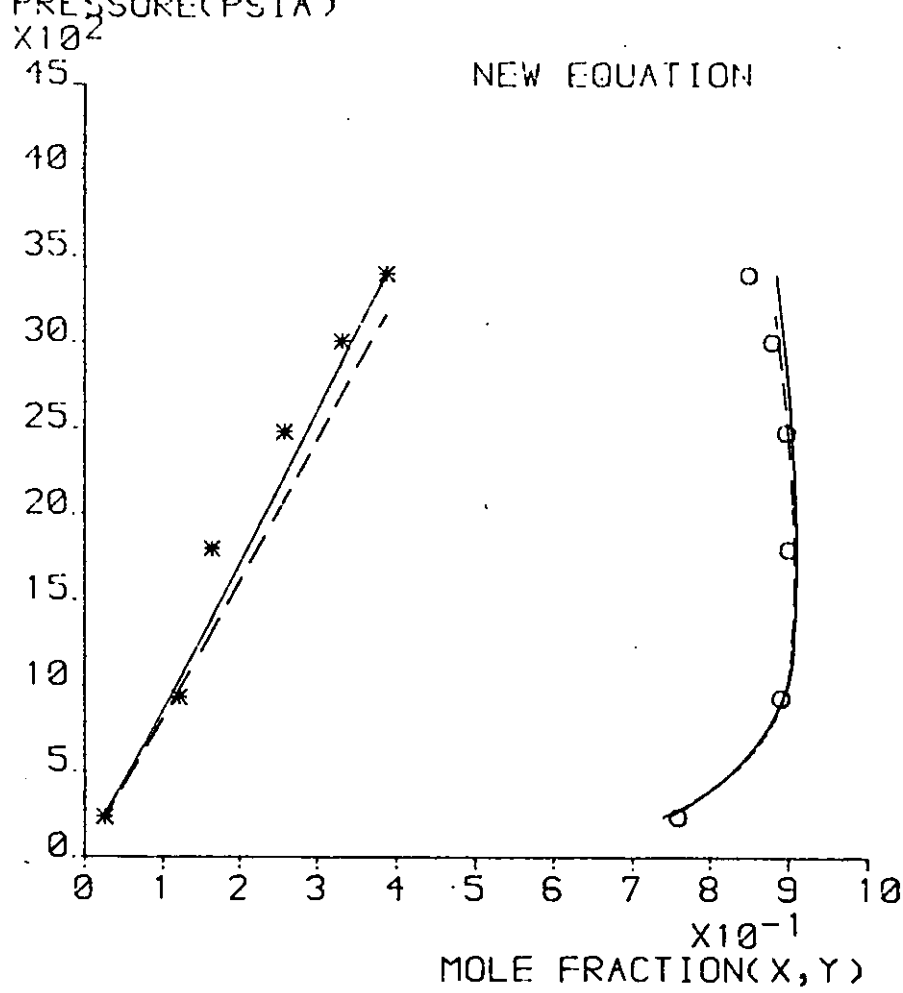


(a)

FIGURE 6.95 Nitrogen-Propane System at 536.67°R (298.2K)

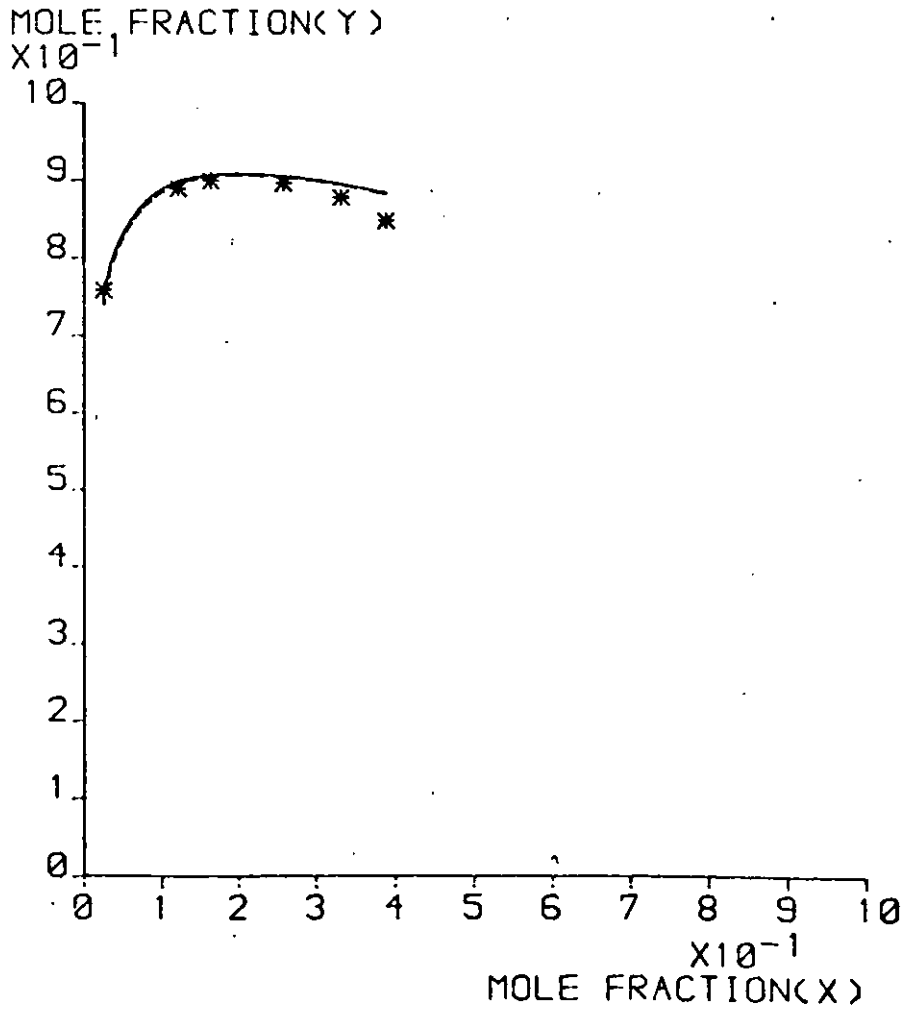


(b)

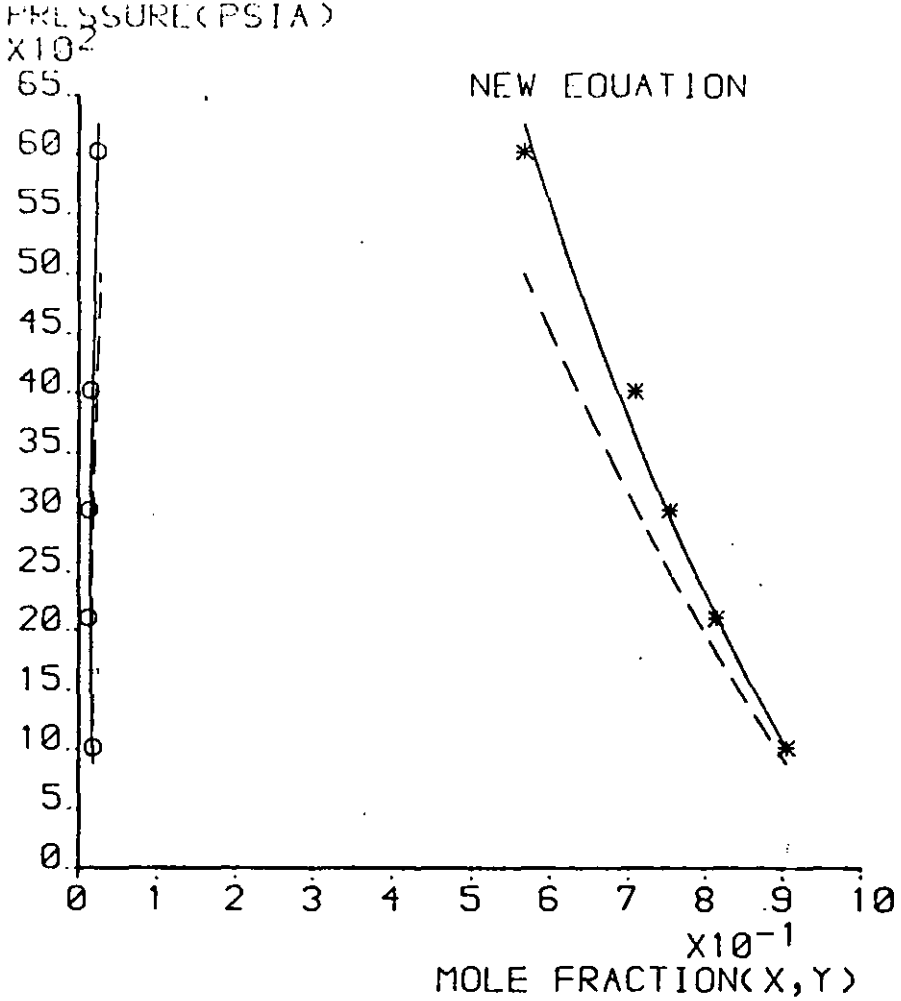


(a)

FIGURE 6.96 Nitrogen-n-Butane System at 559.71°R (311.0K)

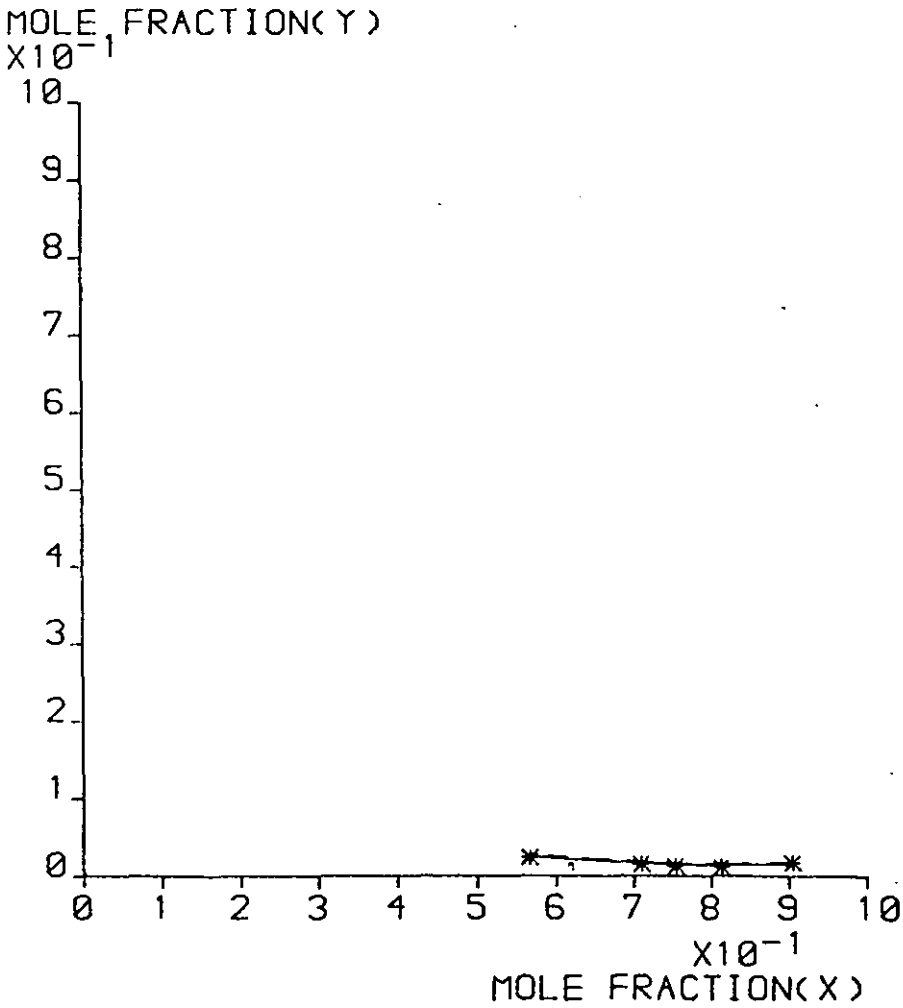


(b)

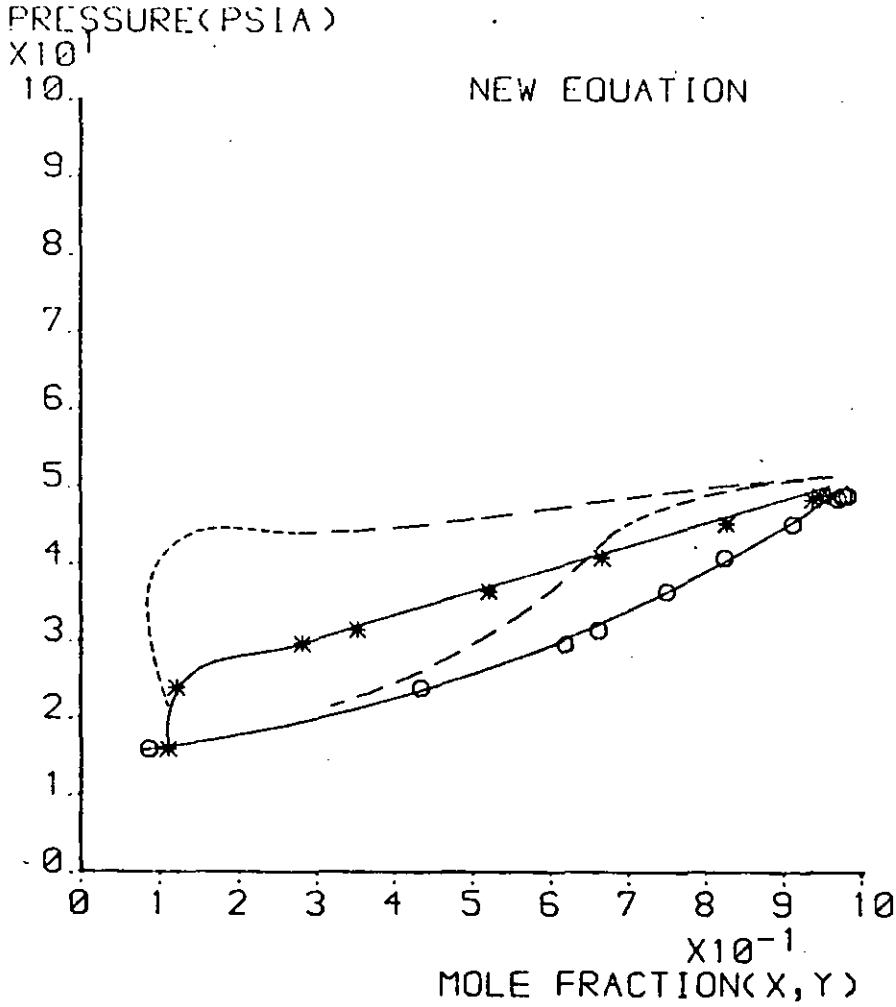


(a)

FIGURE 6.97 Nitrogen-n-Heptane System at 634.67°R (352.6K)

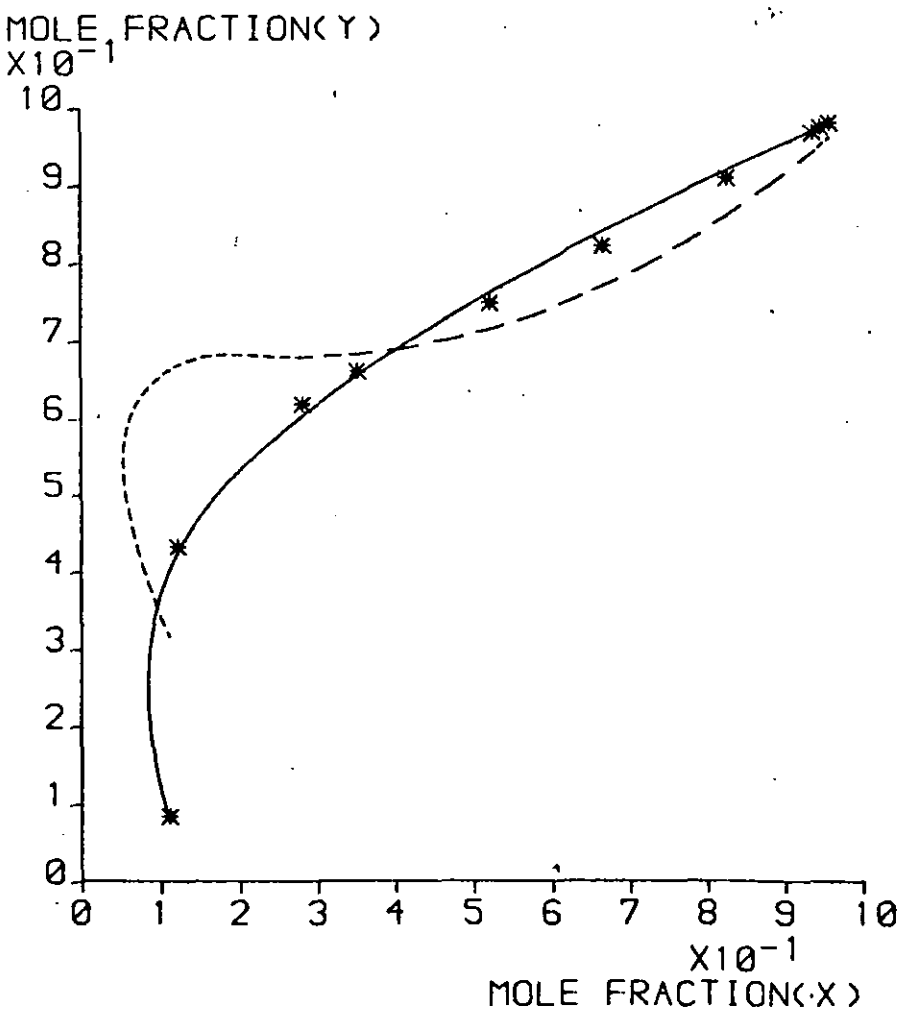


(b)

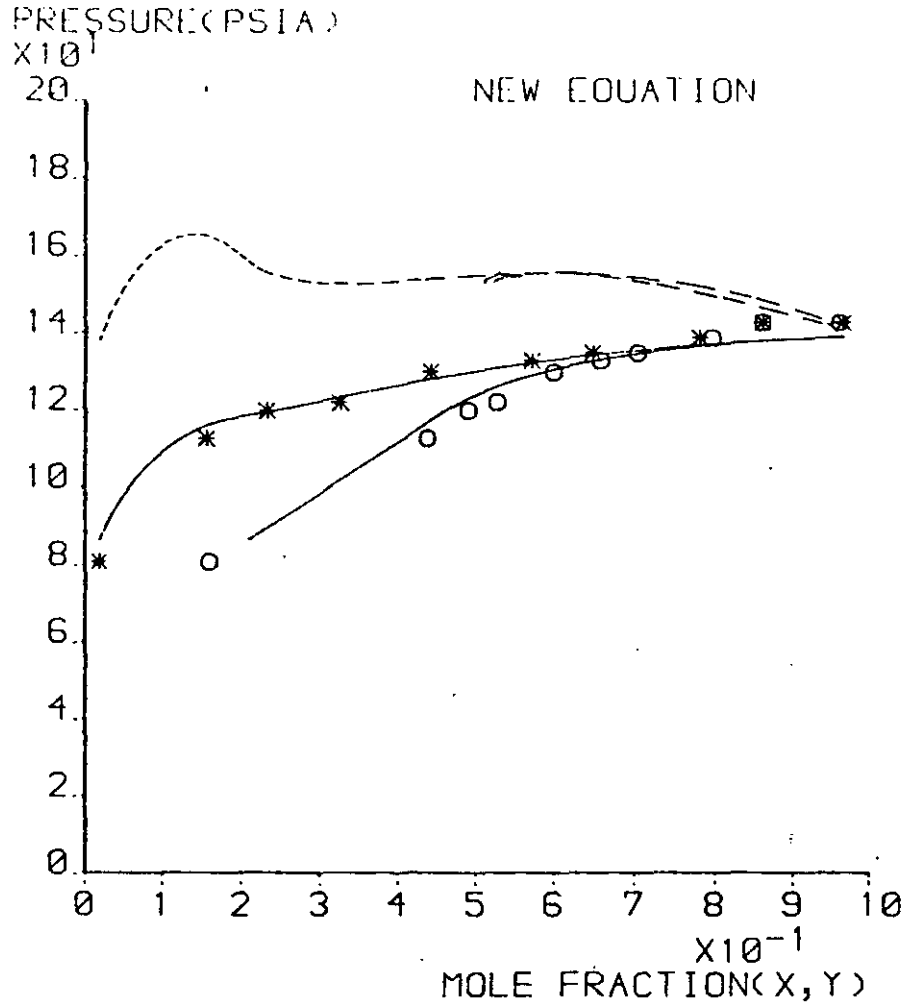


(a)

FIGURE 6.98 Methanol-Water System at 671.67°R (373.2K)

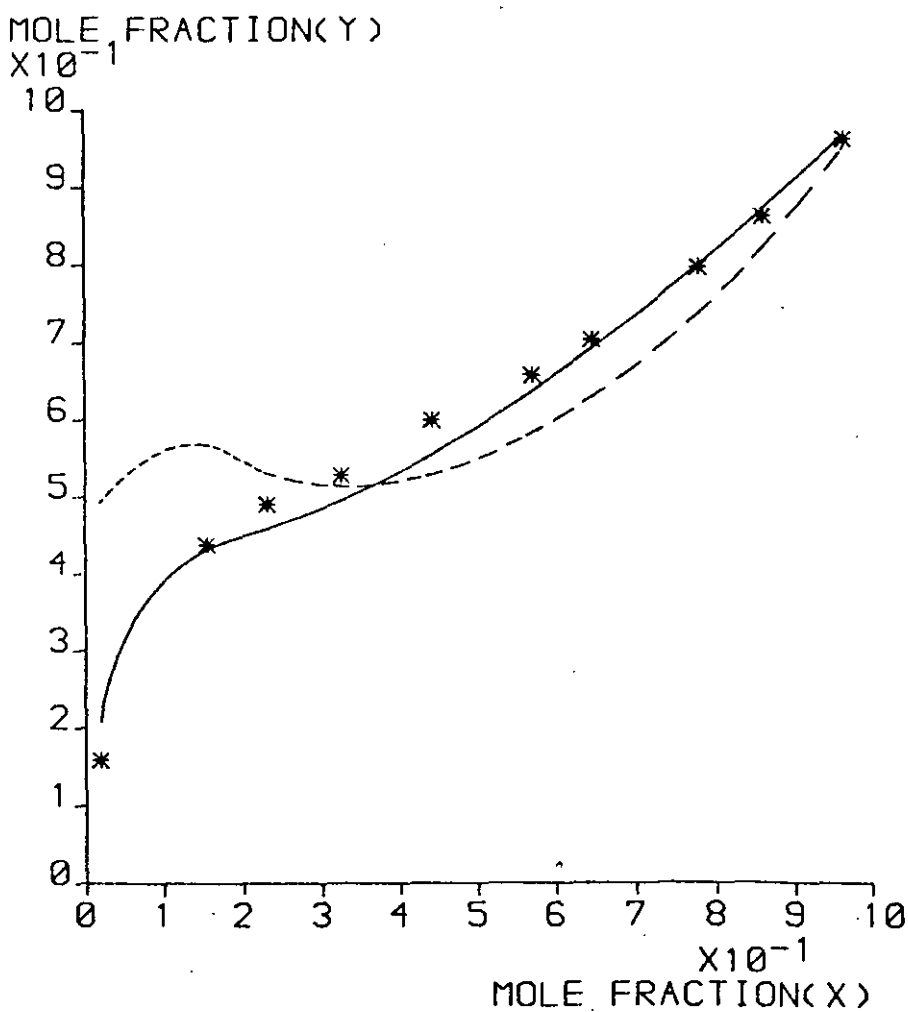


(b)

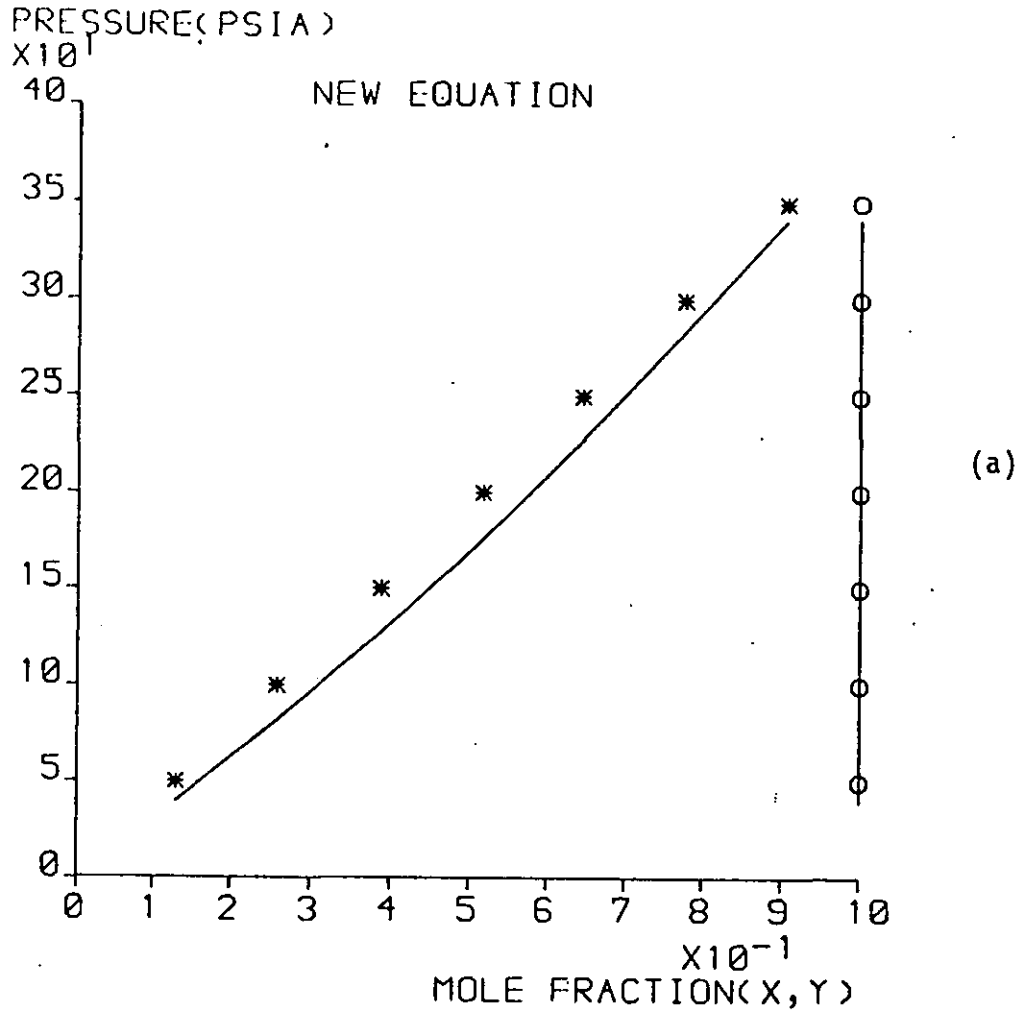


(a)

FIGURE 6.99 Ethanol-Water System at 761.67°R (423.2K)

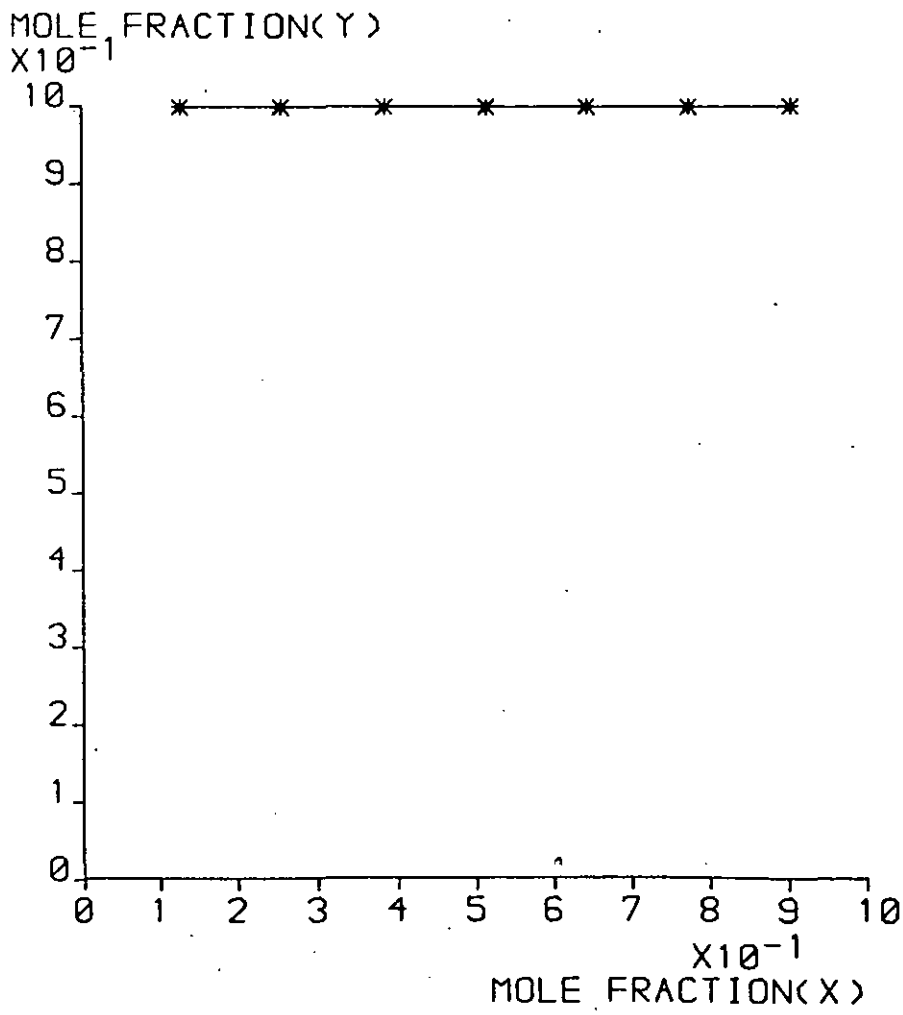


(b)

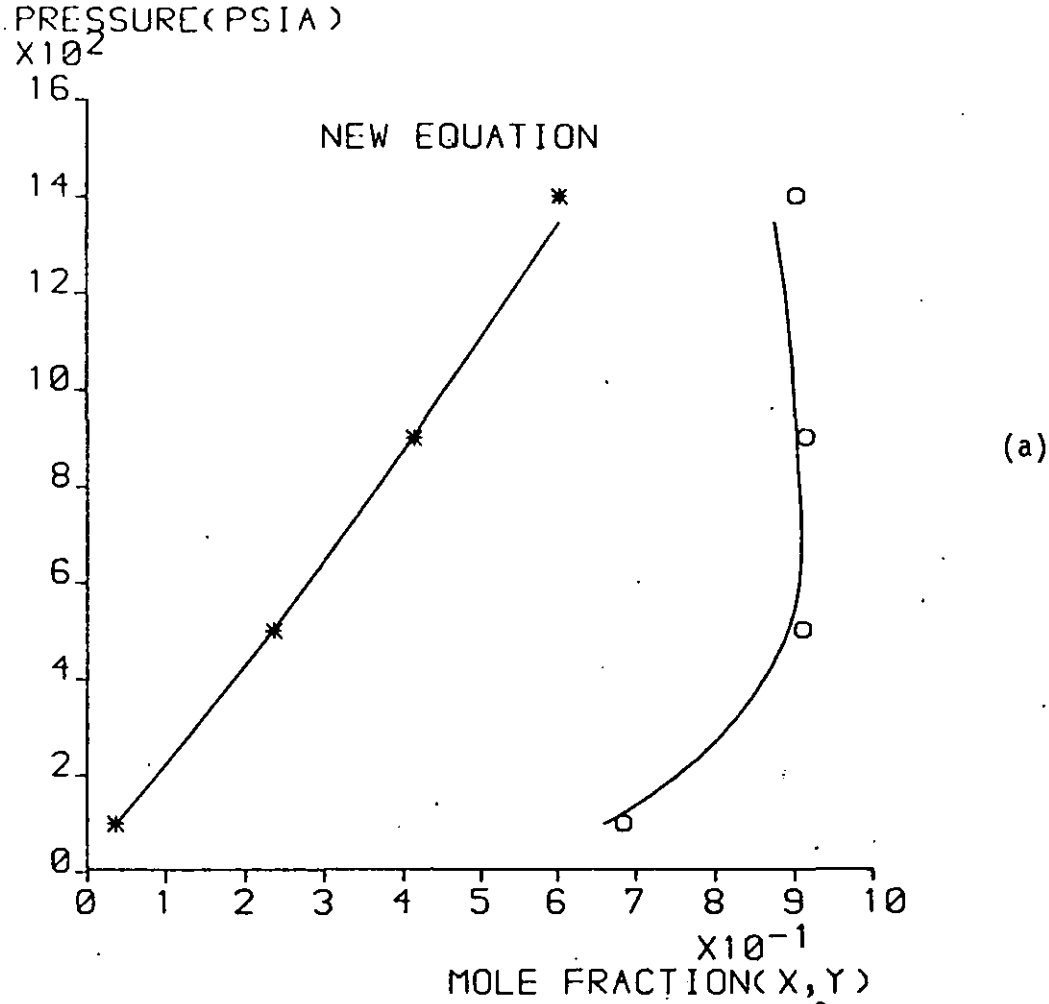


(a)

FIGURE 6.100 Ethane-n-Decane System at 499.67°R (277.59K)

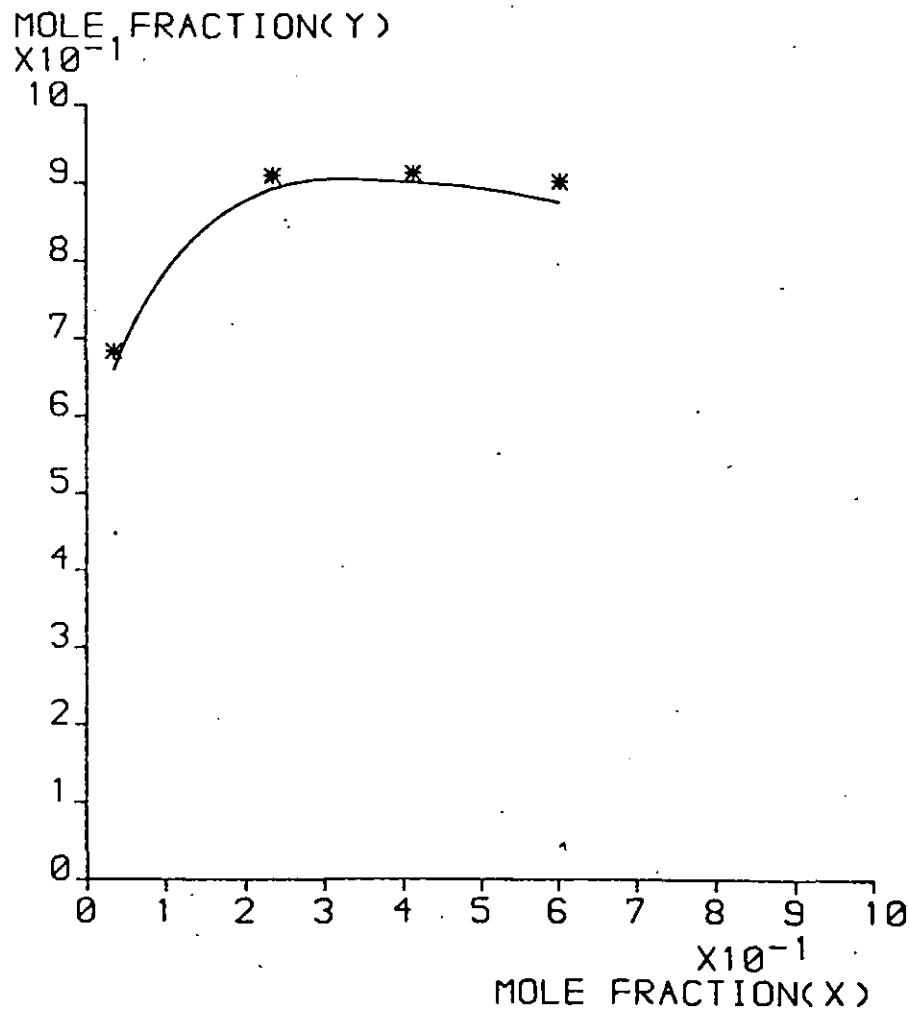


(b)

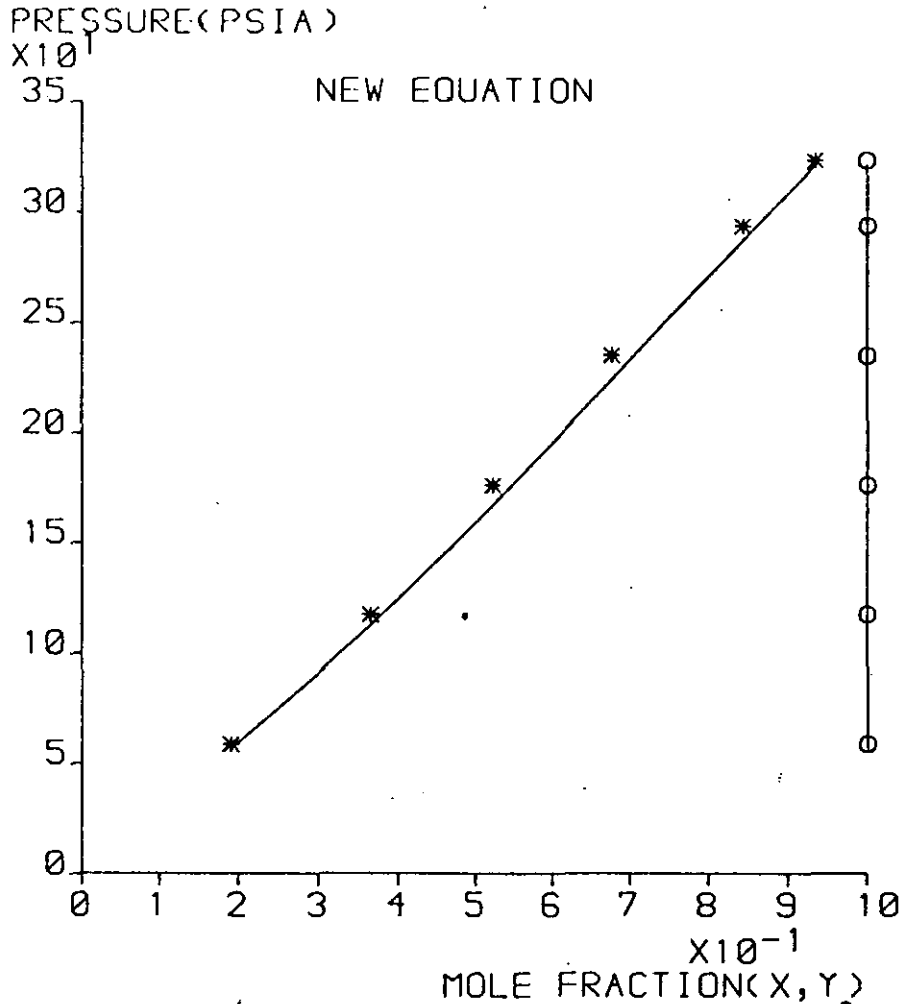


(a)

FIGURE 6.101 Ethane-n-Decane System at 859.67°R (477.59K)

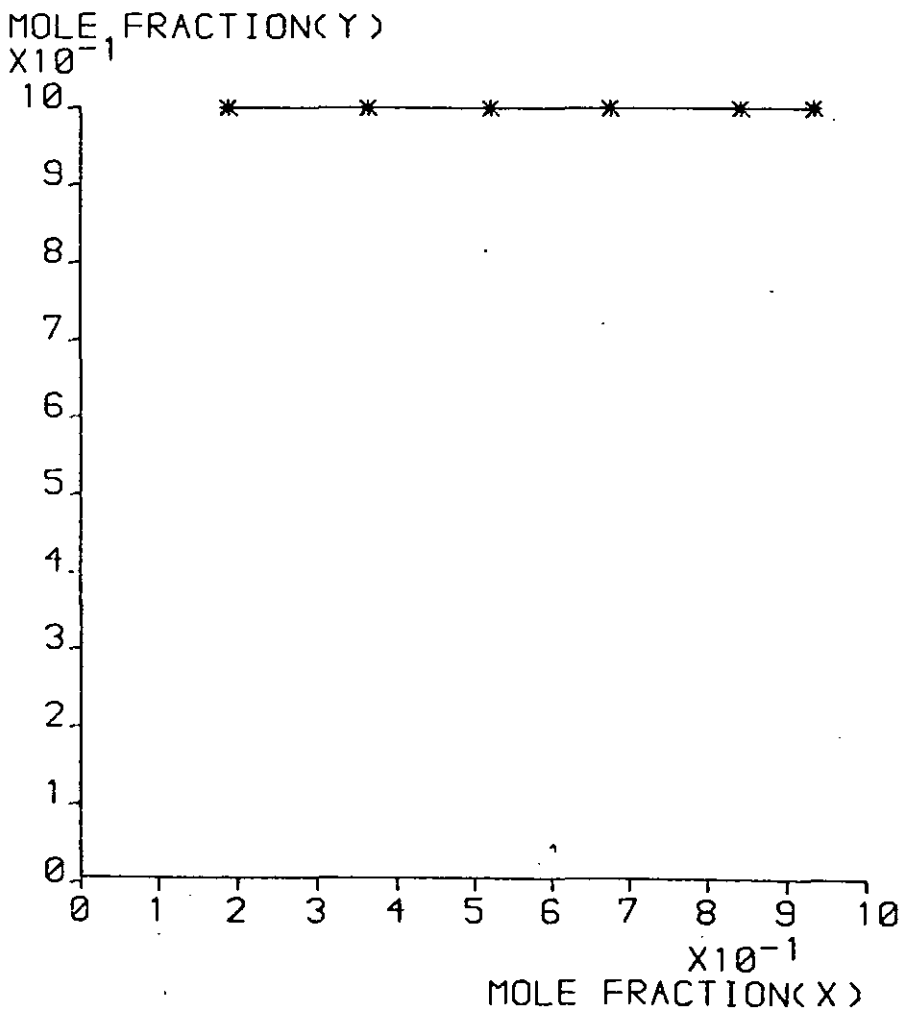


(b)

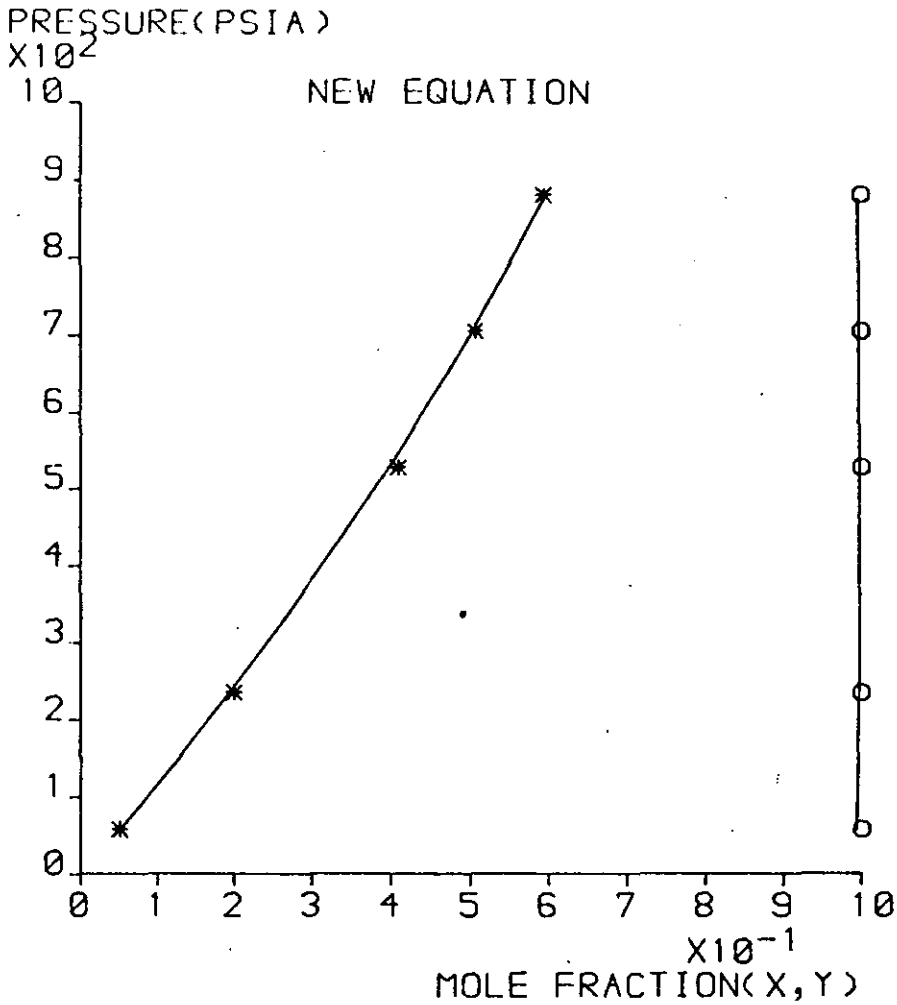


(a)

FIGURE 6.102 Ethane-n-Dodecane System at 491.67°R (273.15K)

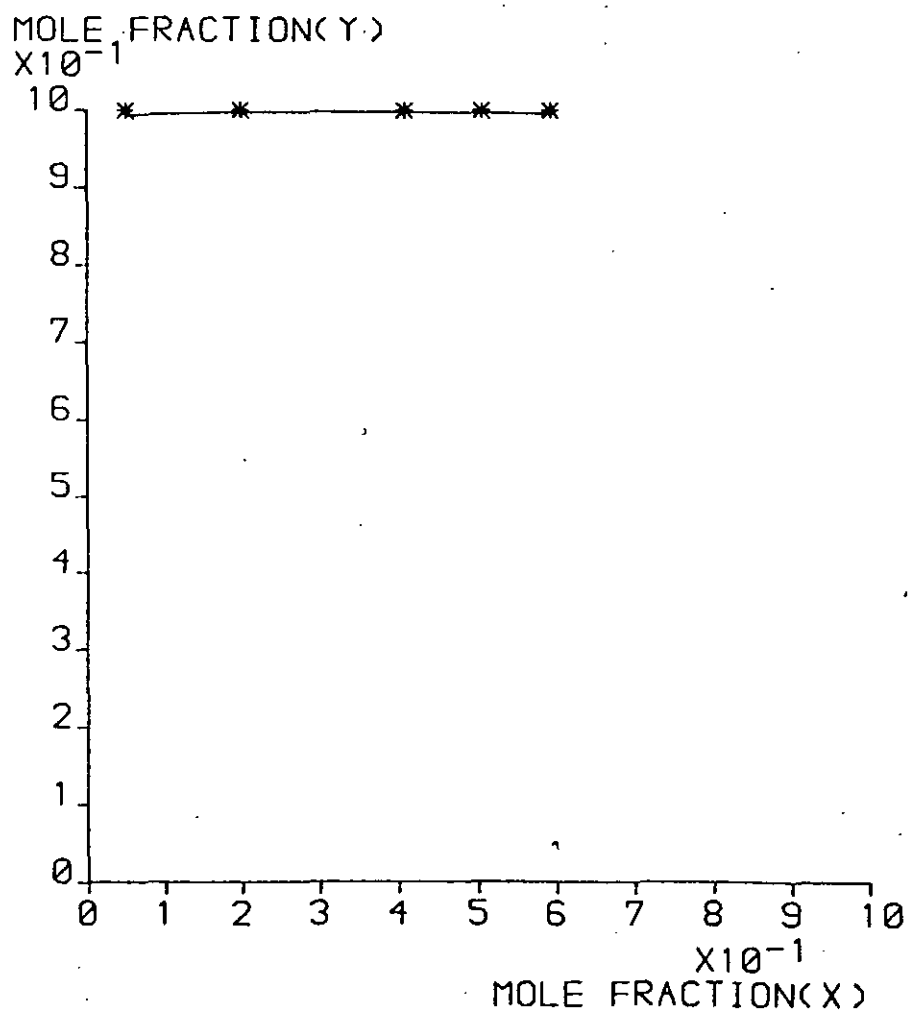


(b)

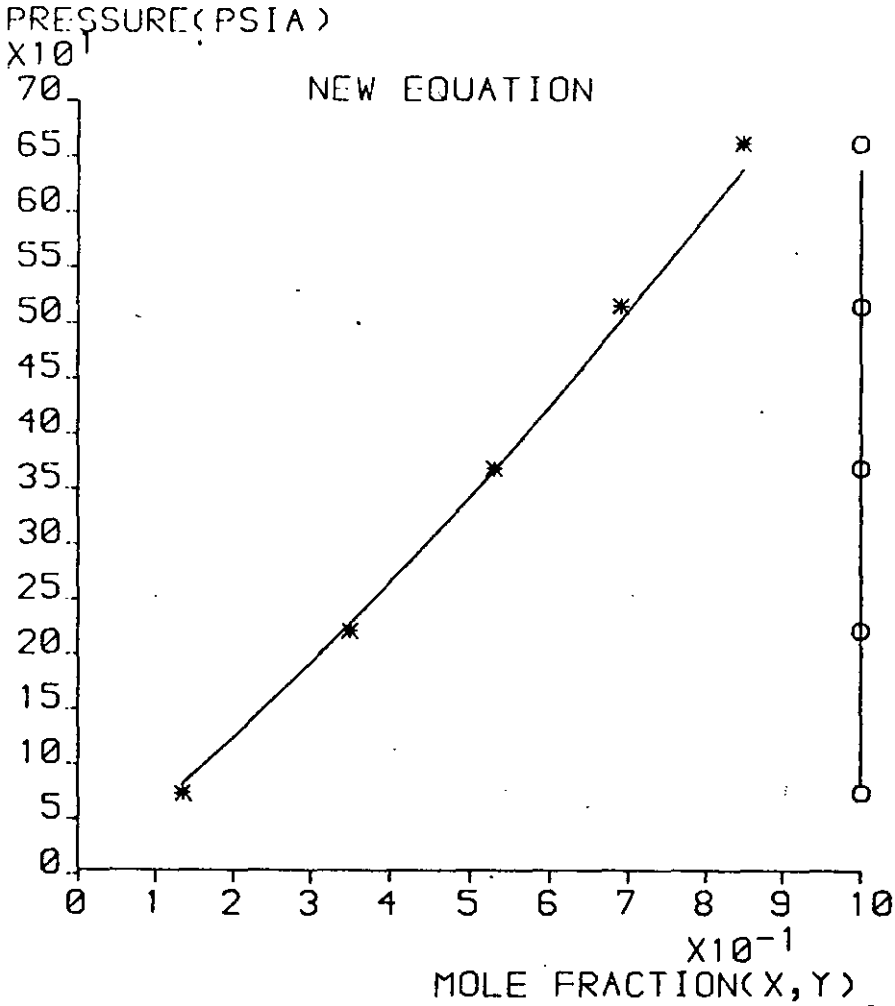


(a)

FIGURE 6.103 Ethane-n-Dodecane System at 671.67°R (373.15K)

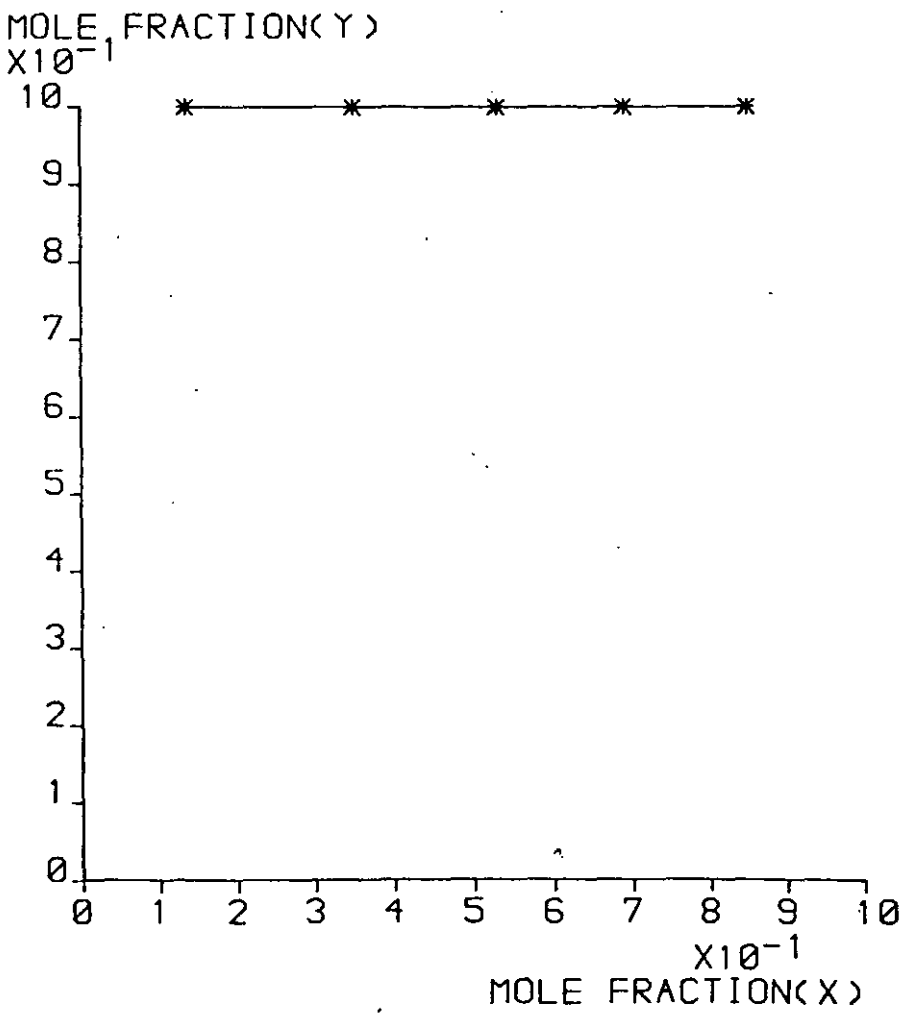


(b)

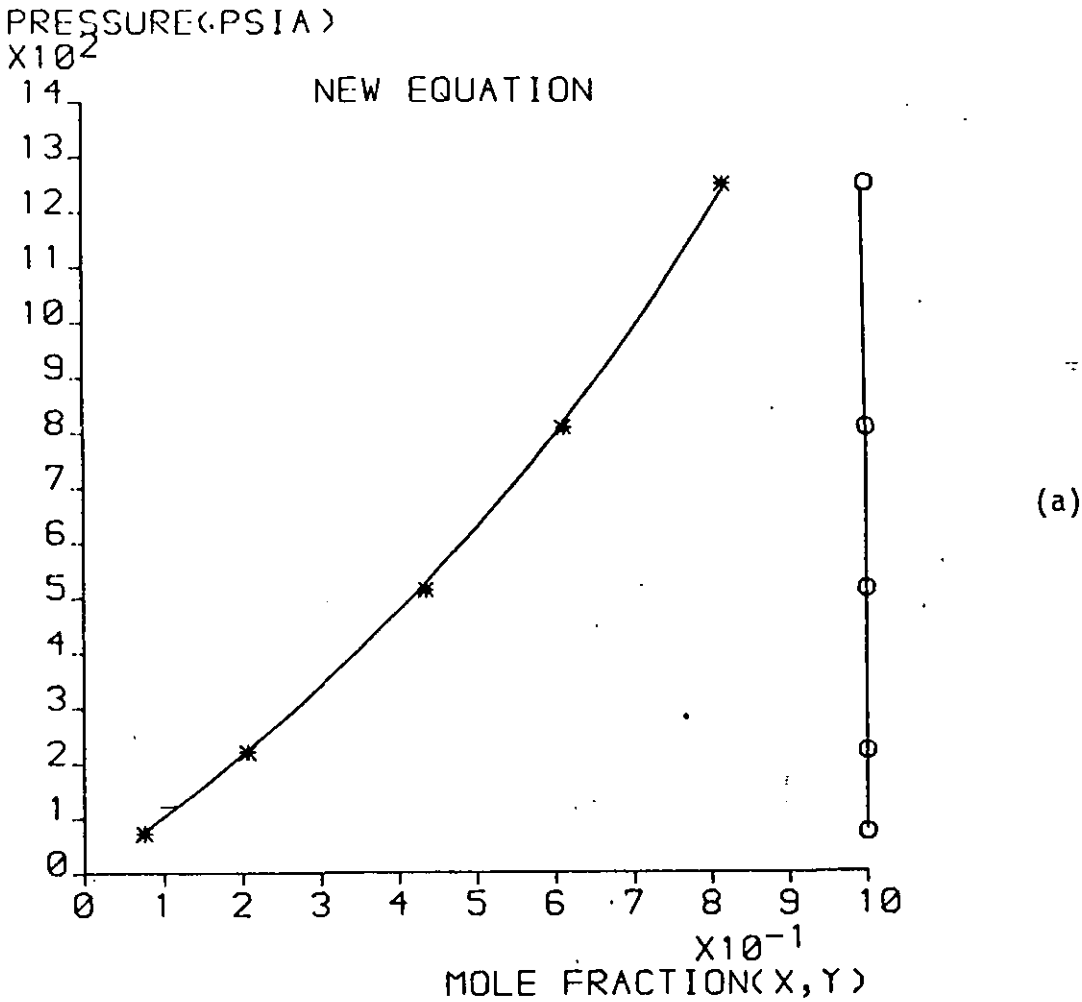


(a)

FIGURE 6.104 Ethylene-n-Dodecane System at 509.67°R (283.15K)

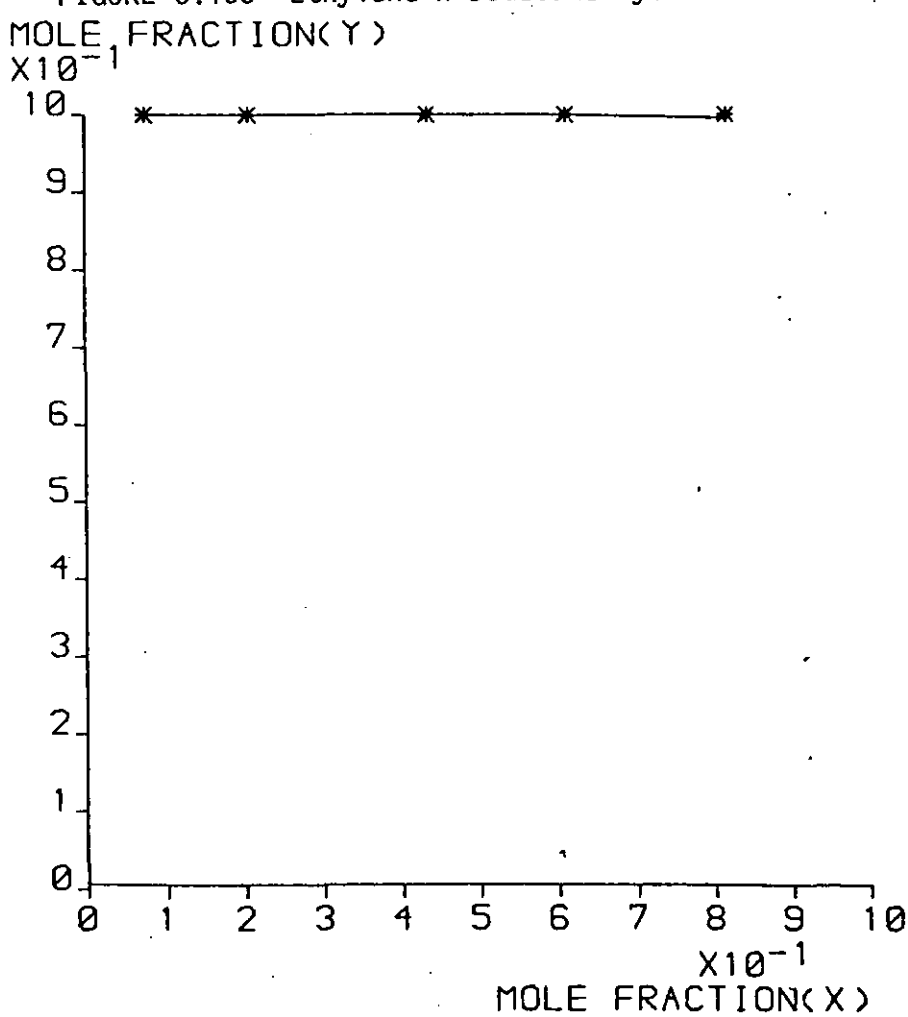


(b)

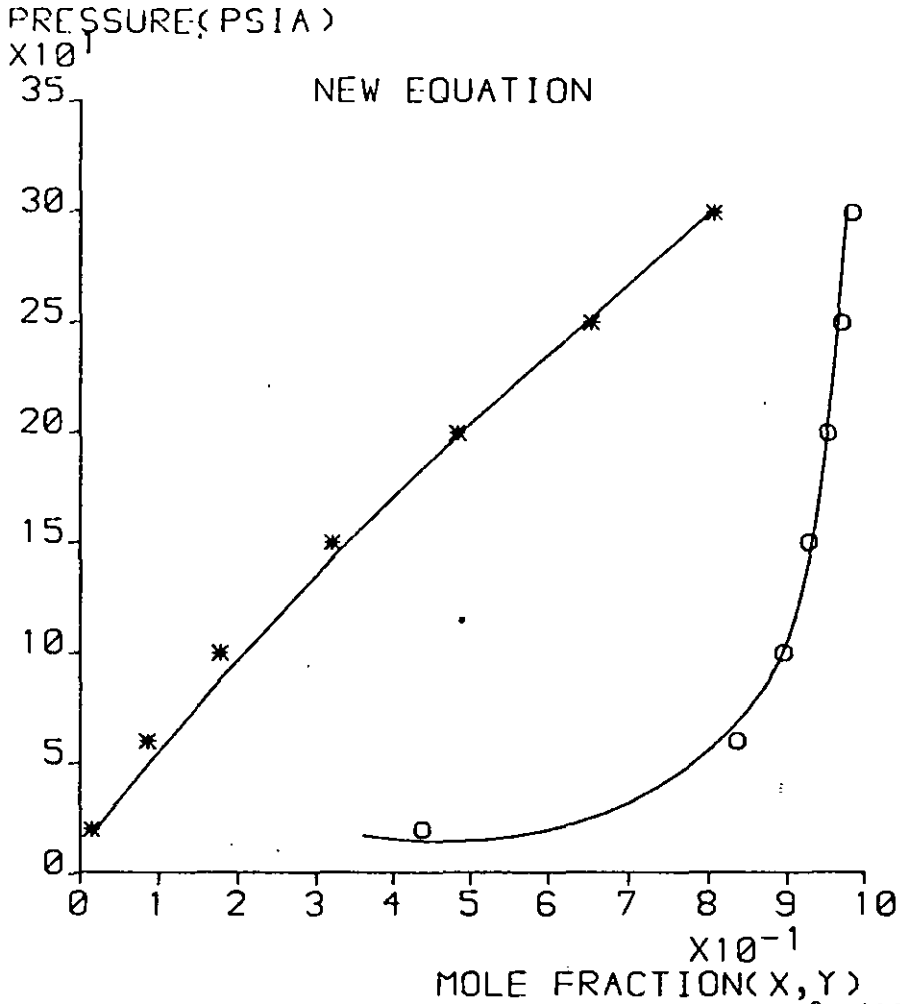


(a)

FIGURE 6.105 Ethylene-n-Dodecane System at 581.67°R (323.15K)

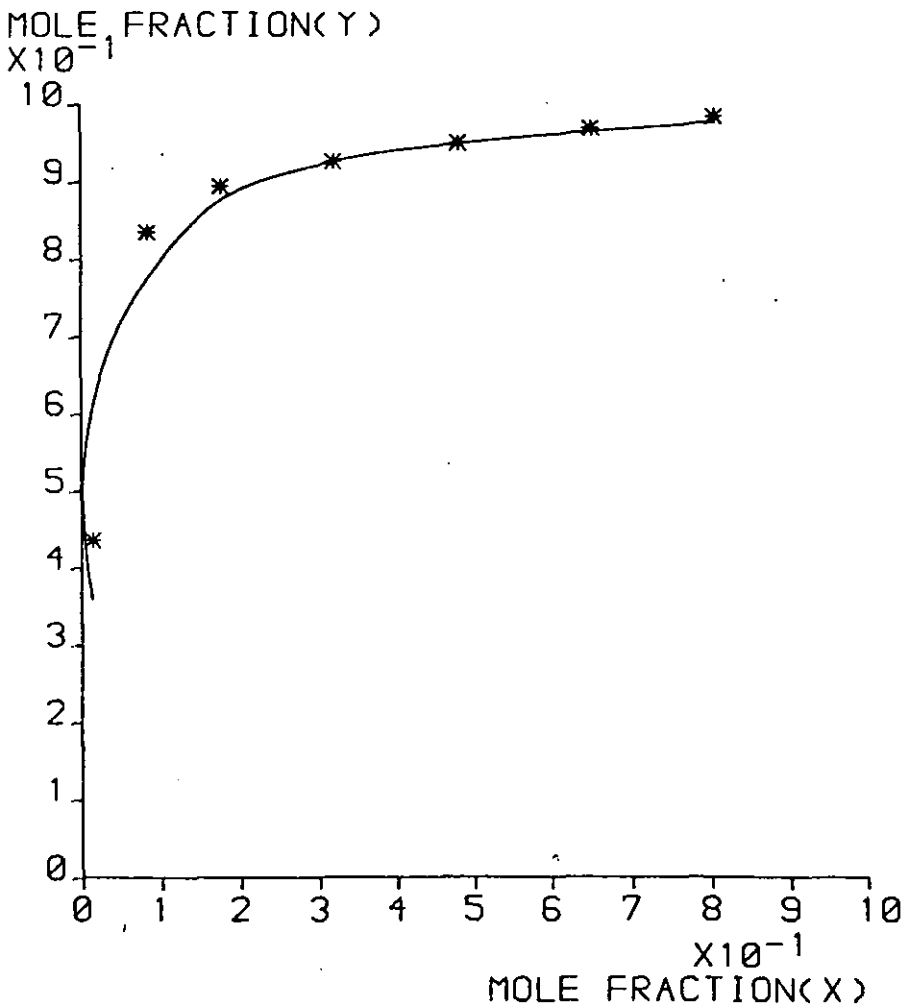


(b)

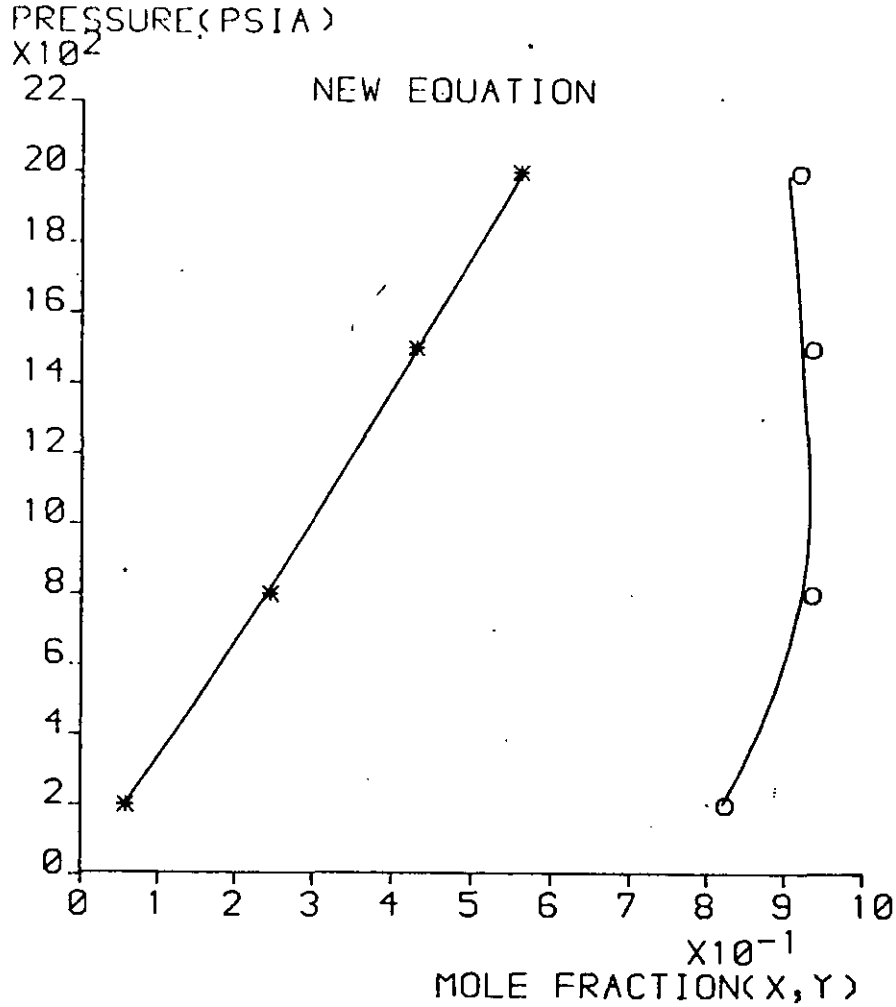


(a)

FIGURE 6.106 Propane-Benzene System at 619.65°R (344.25K)

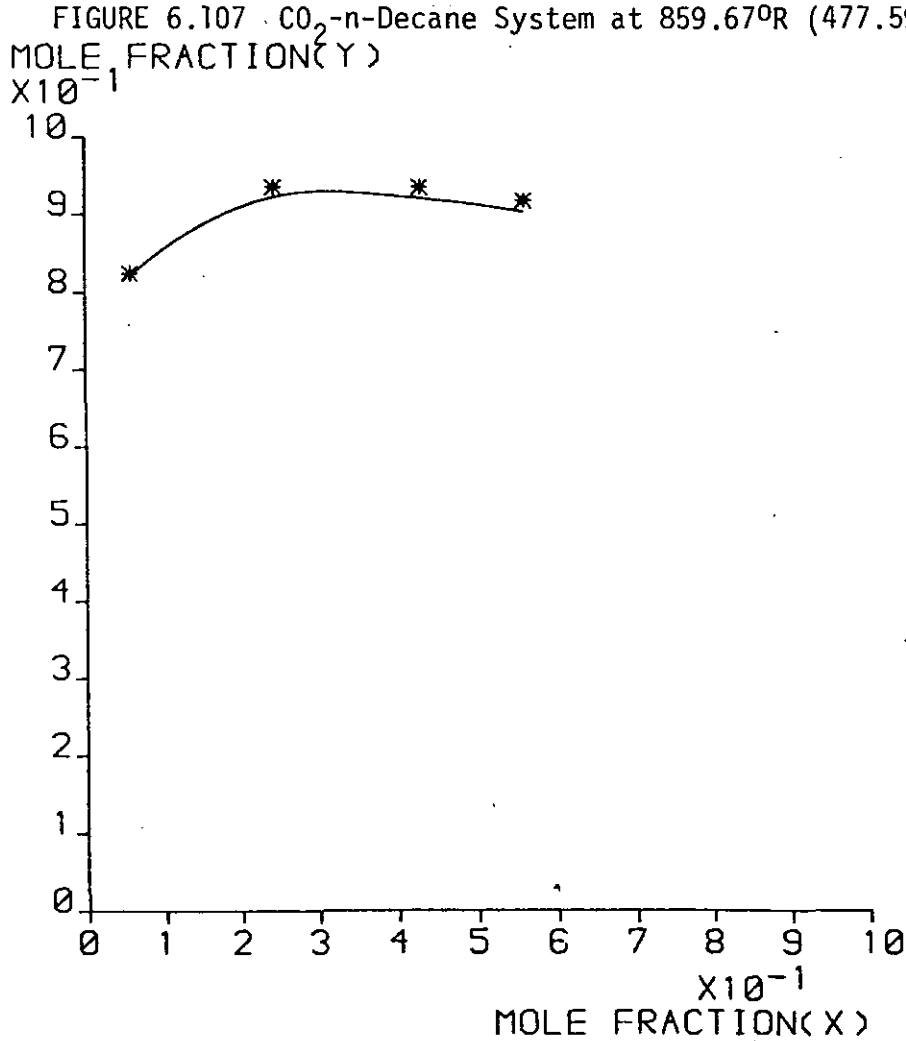


(b)

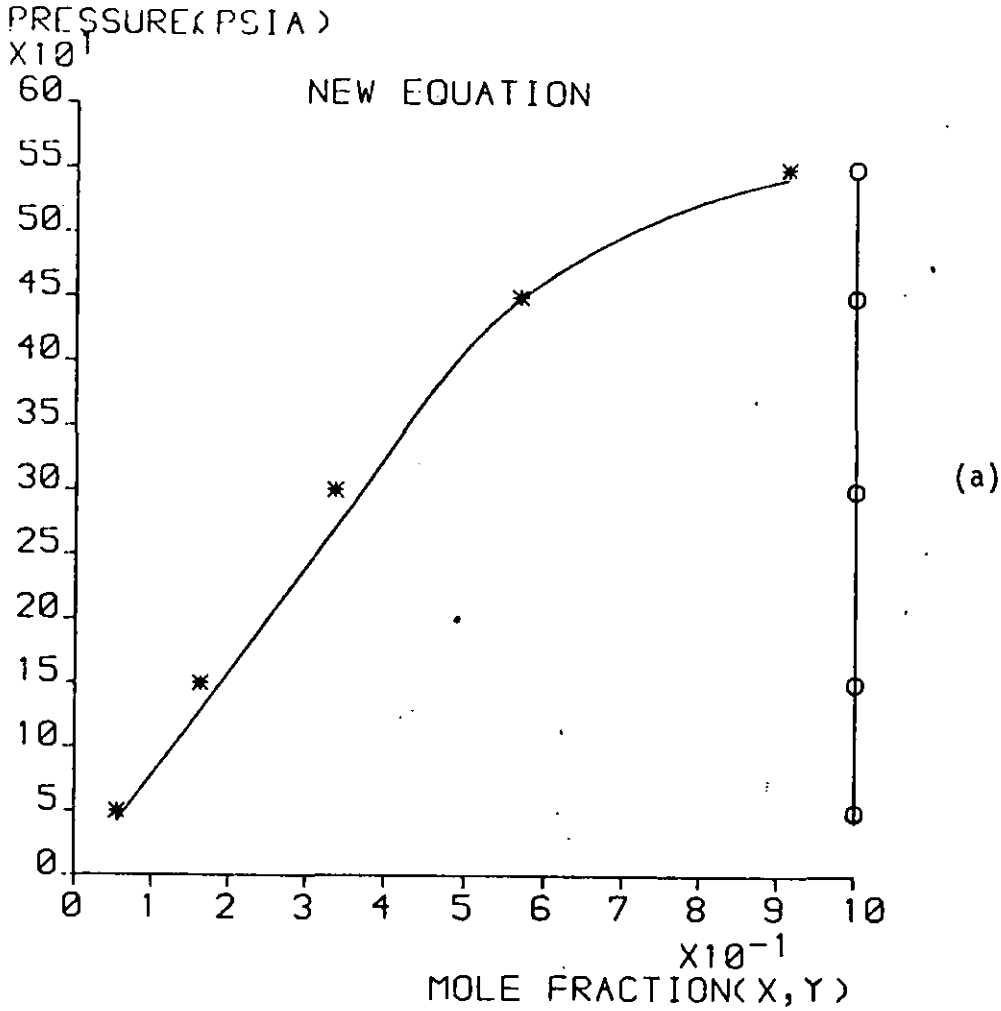


(a)

FIGURE 6.107 CO_2-n-Decane System at 859.67°R (477.59K)

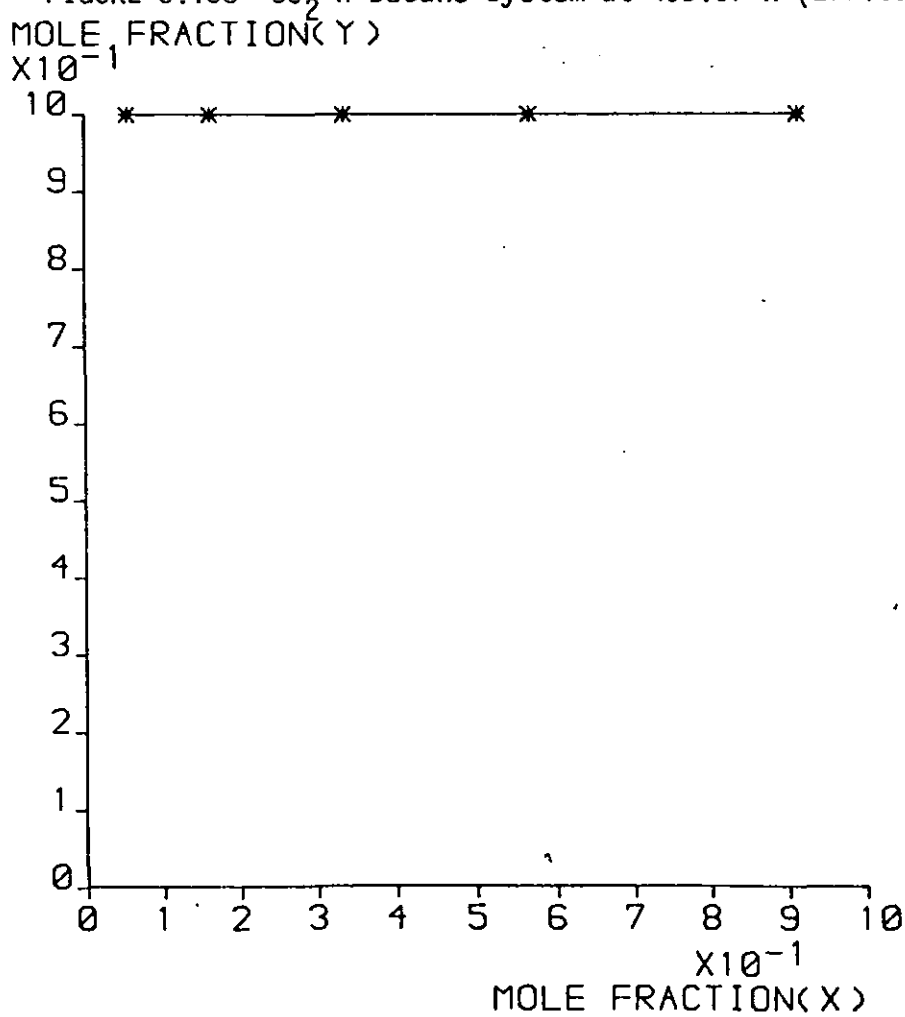


(b)



(a)

FIGURE 6.108 CO_2-n-Decane System at 499.67°R (277.59K)



(b)

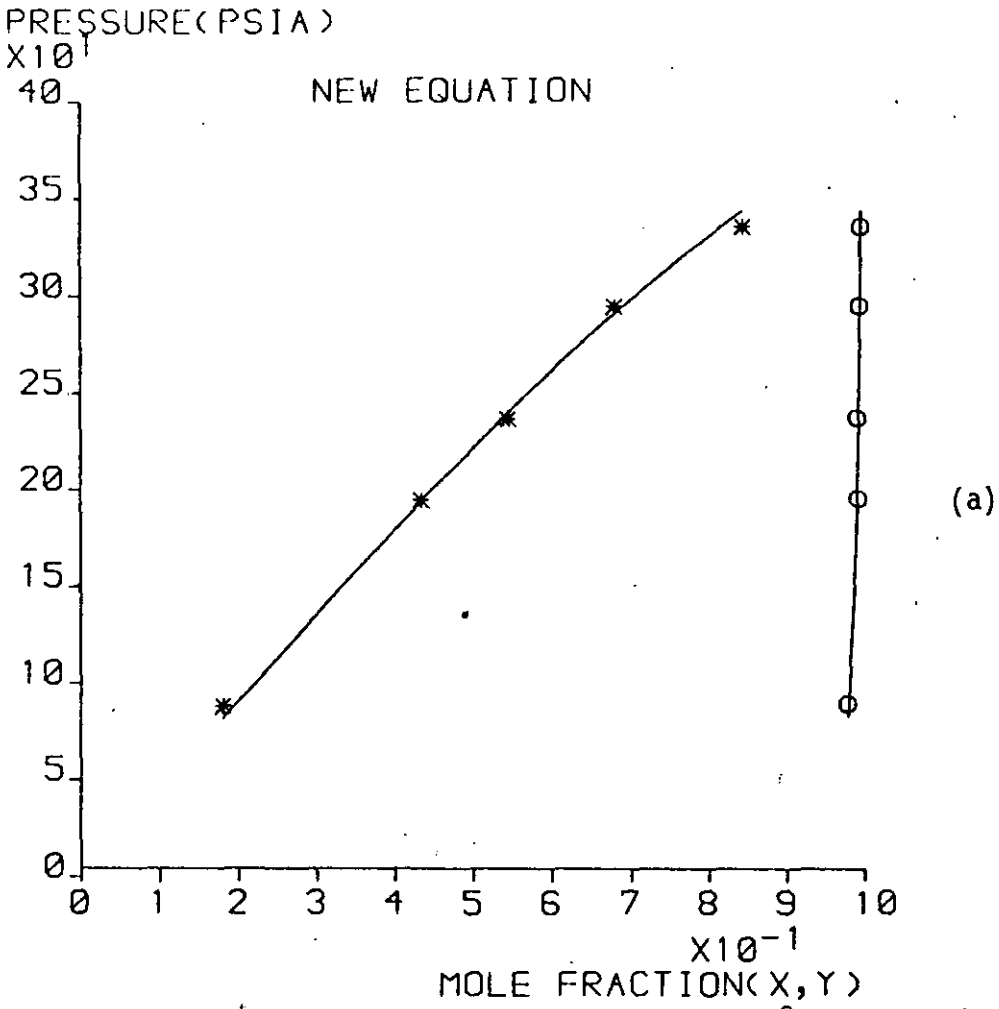
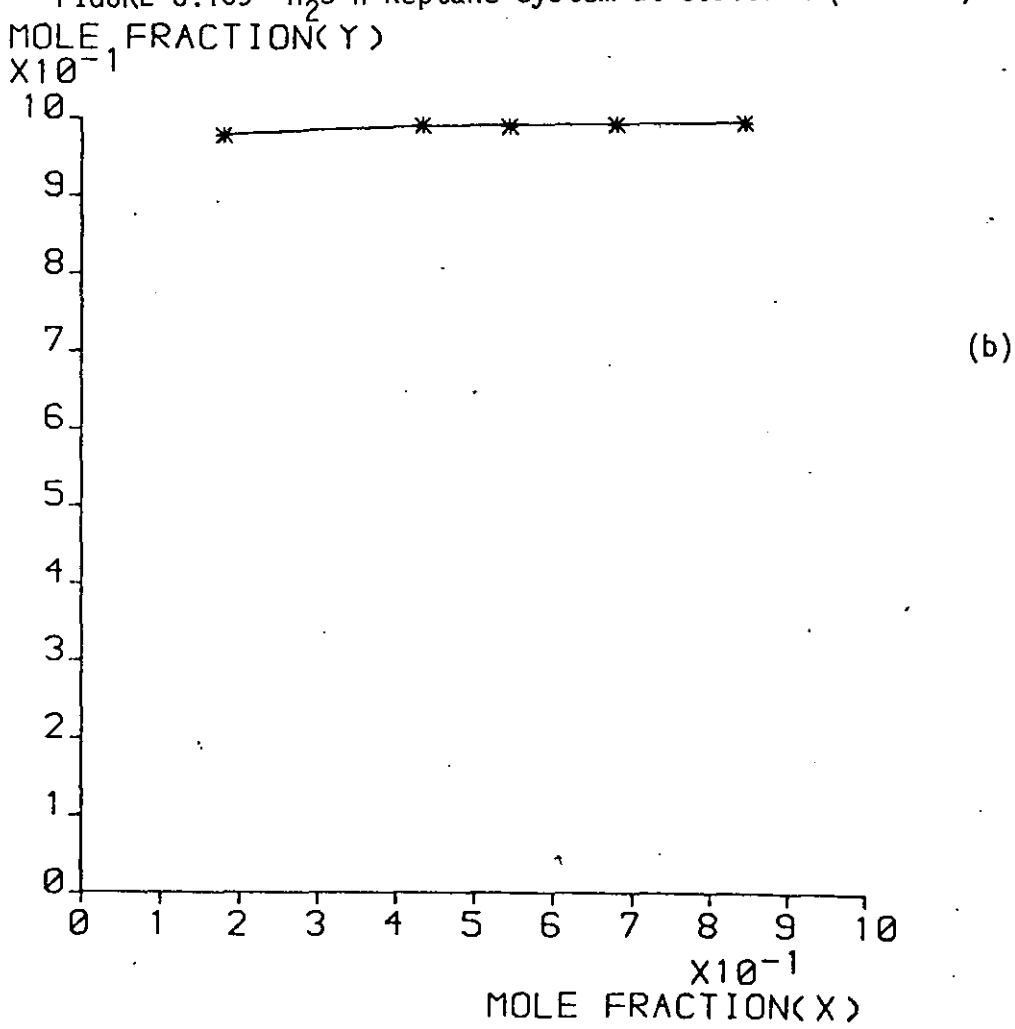
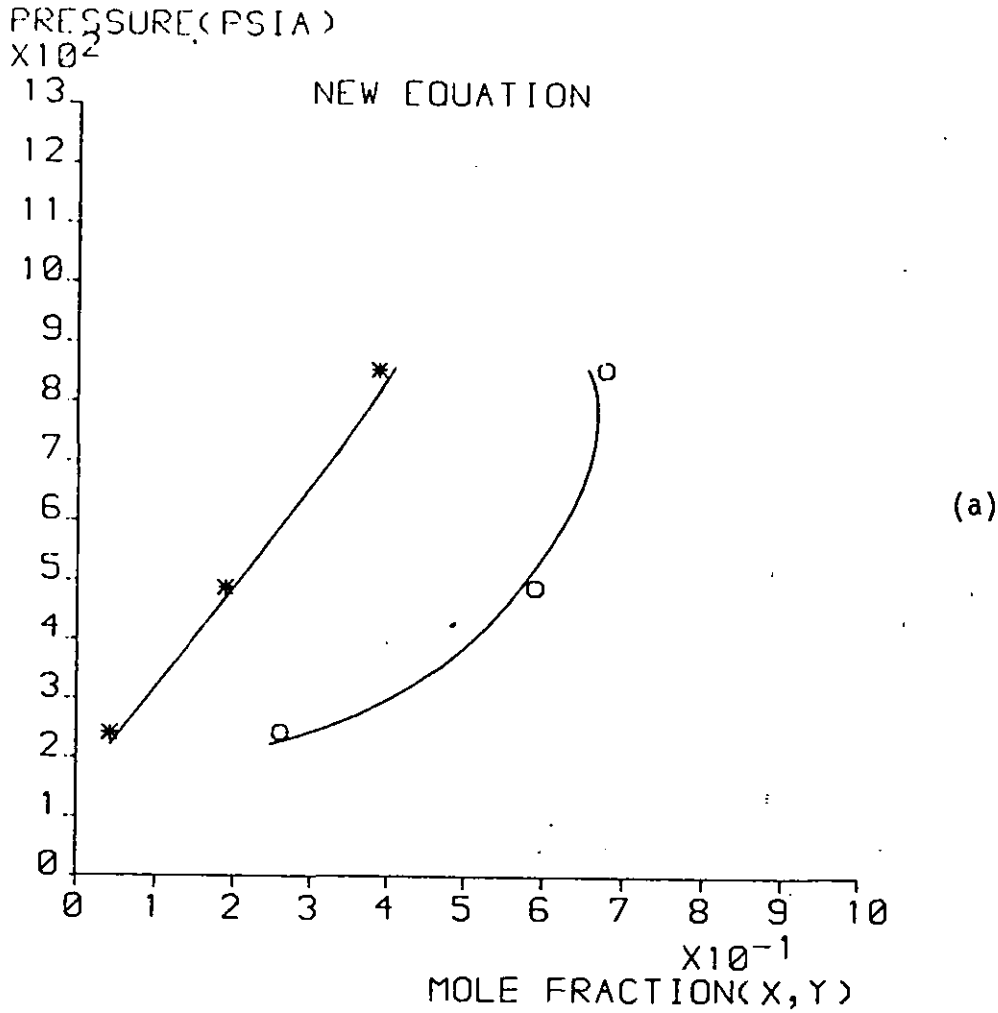


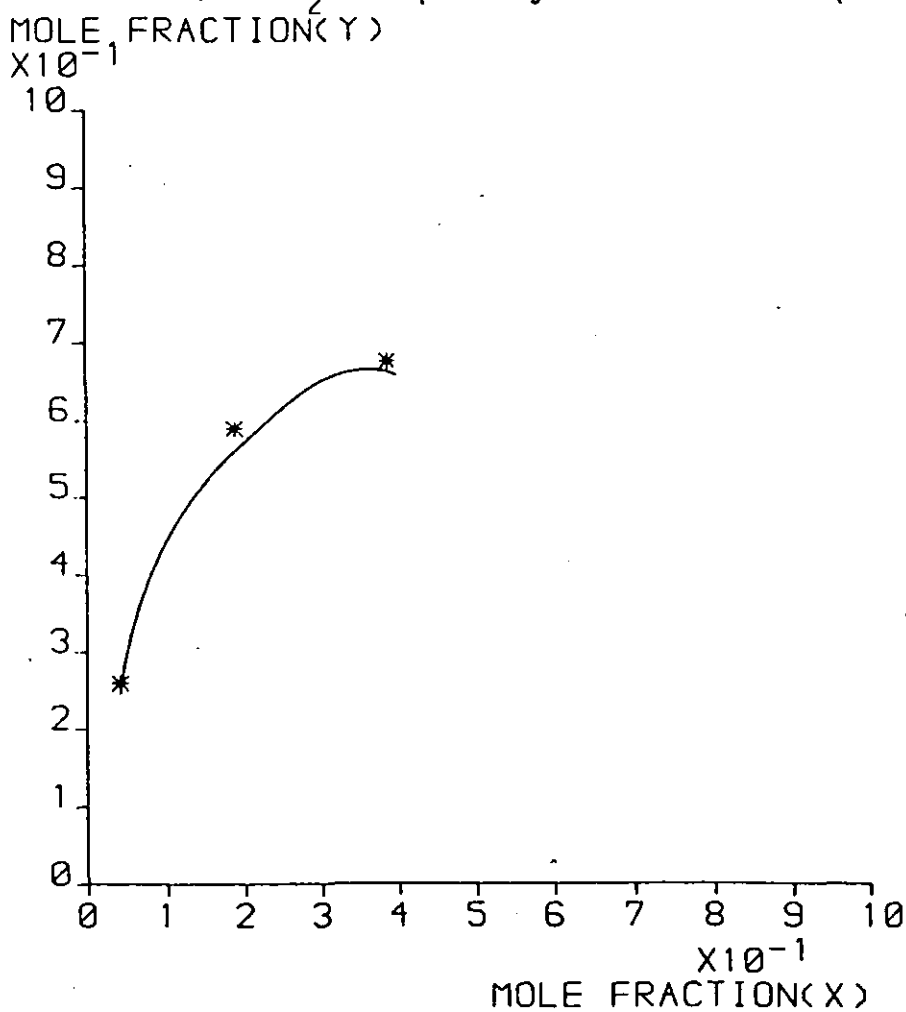
FIGURE 6.109 H_2S-n-Heptane System at 559.67°R (310.93K)



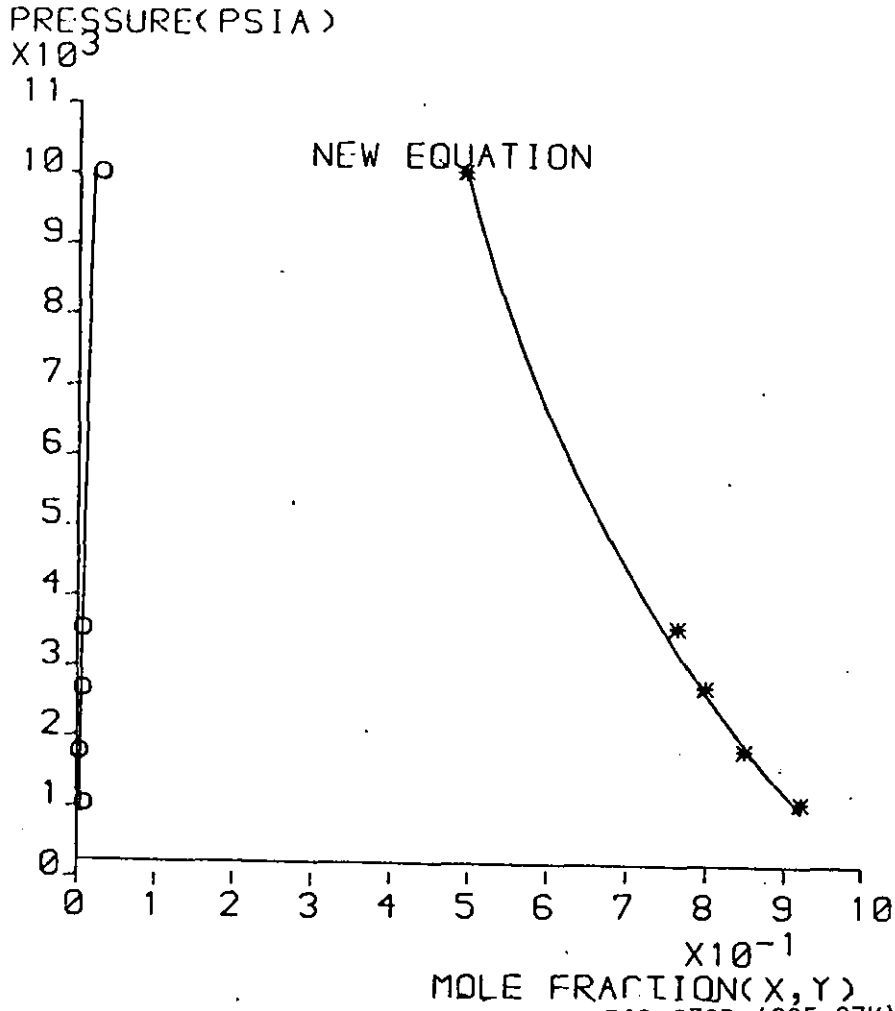


(a)

FIGURE 6.110 H_2S-n-Heptane System at 859.67°R (477.59K)

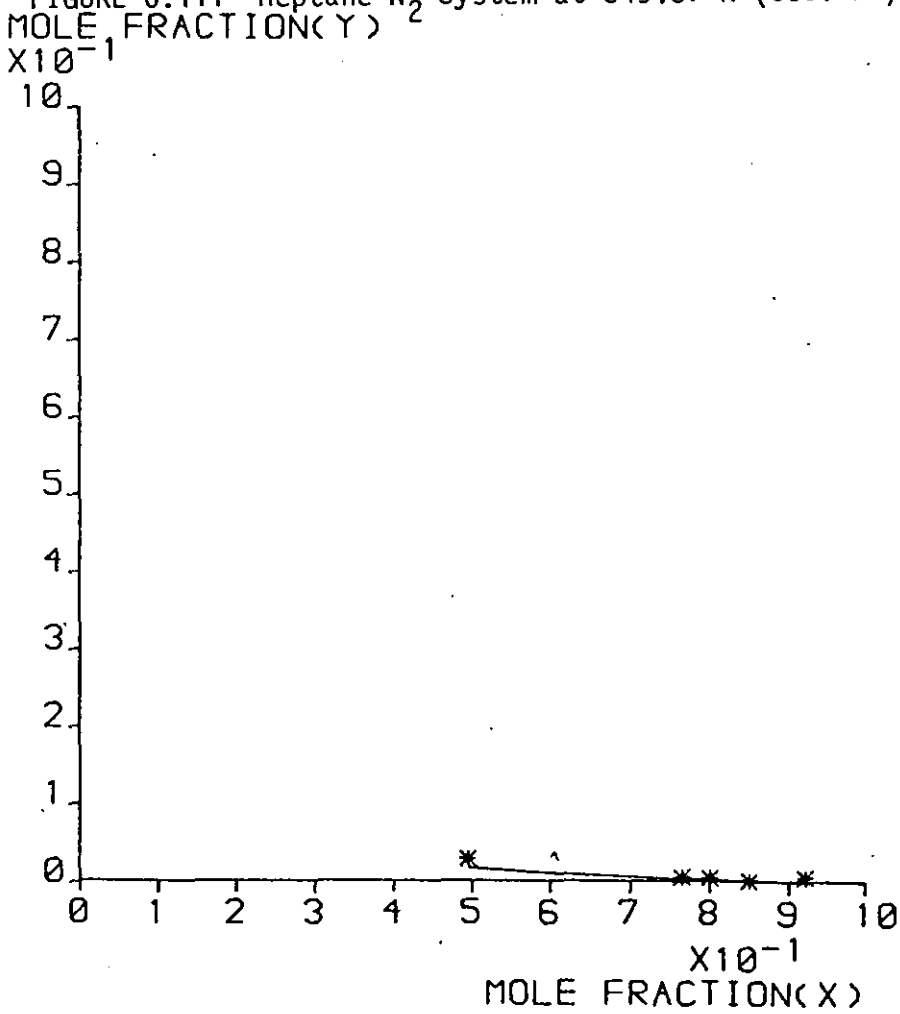


(b)

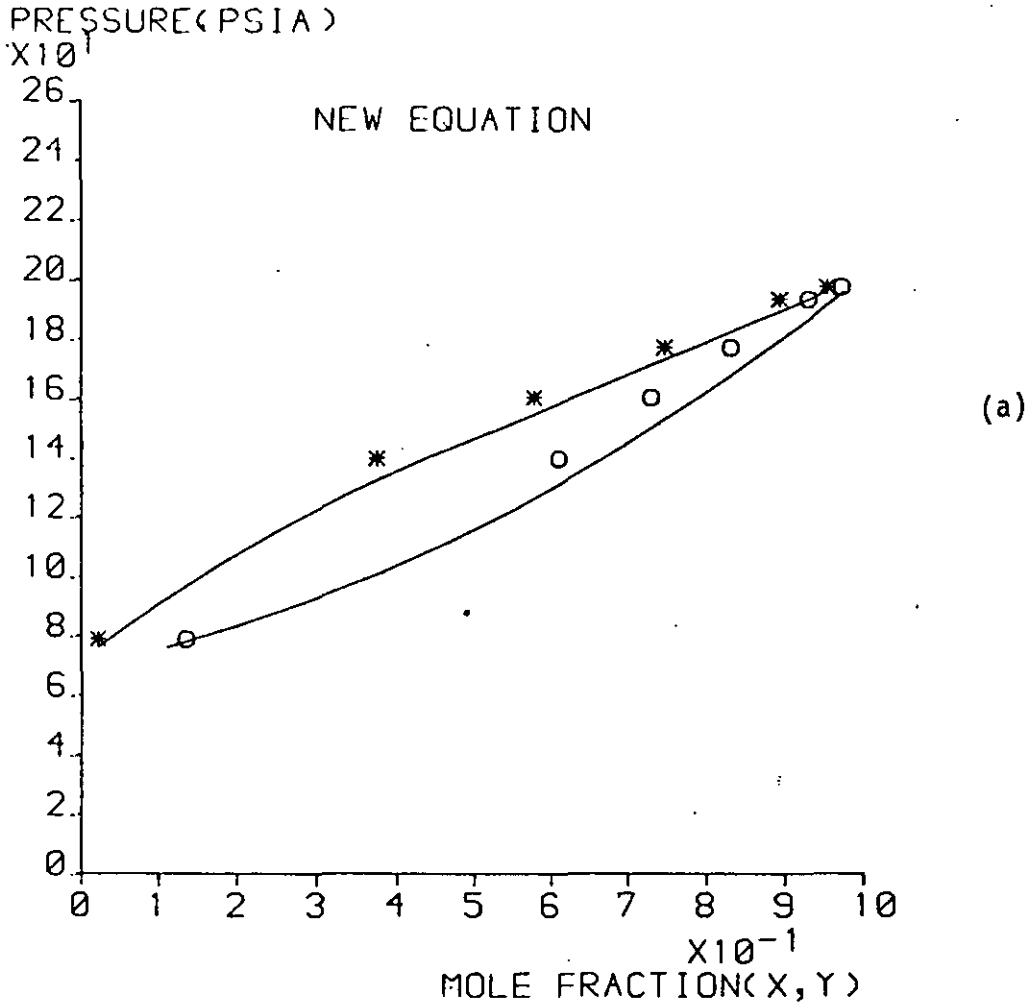


(a)

FIGURE 6.111 Heptane-N_2 System at 549.67°R (305.37K)

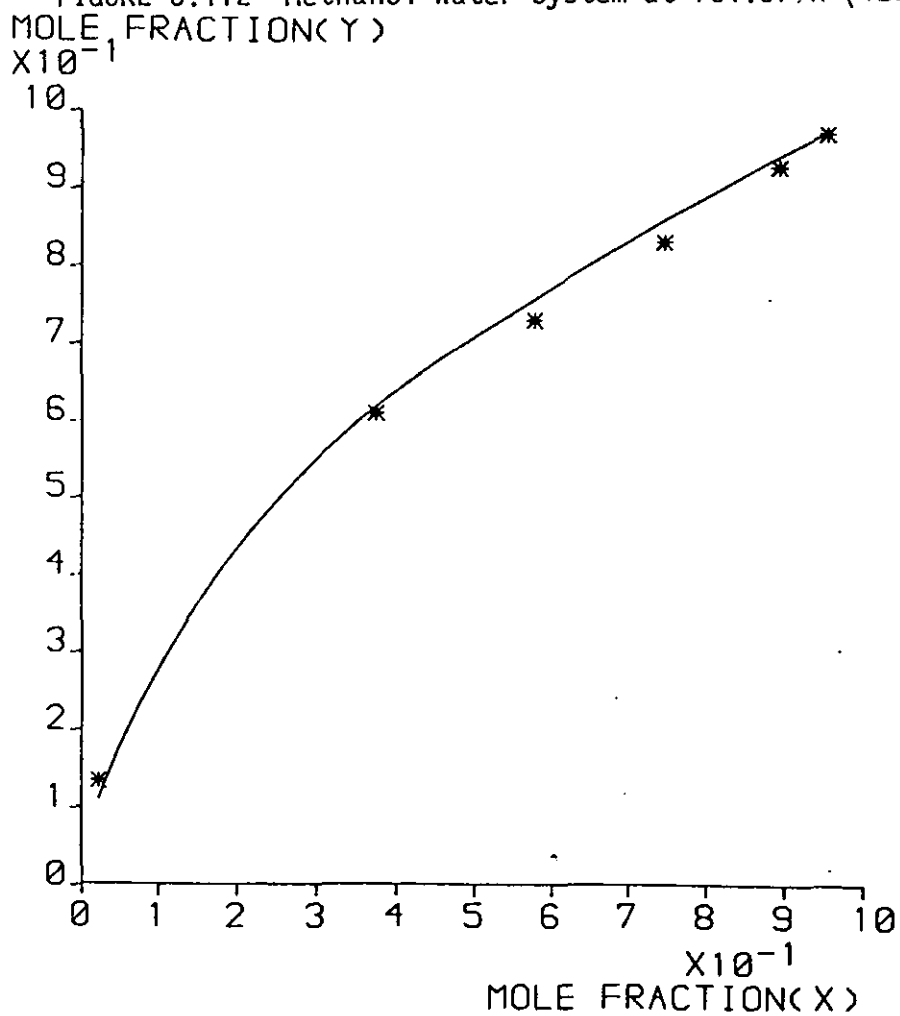


(b)

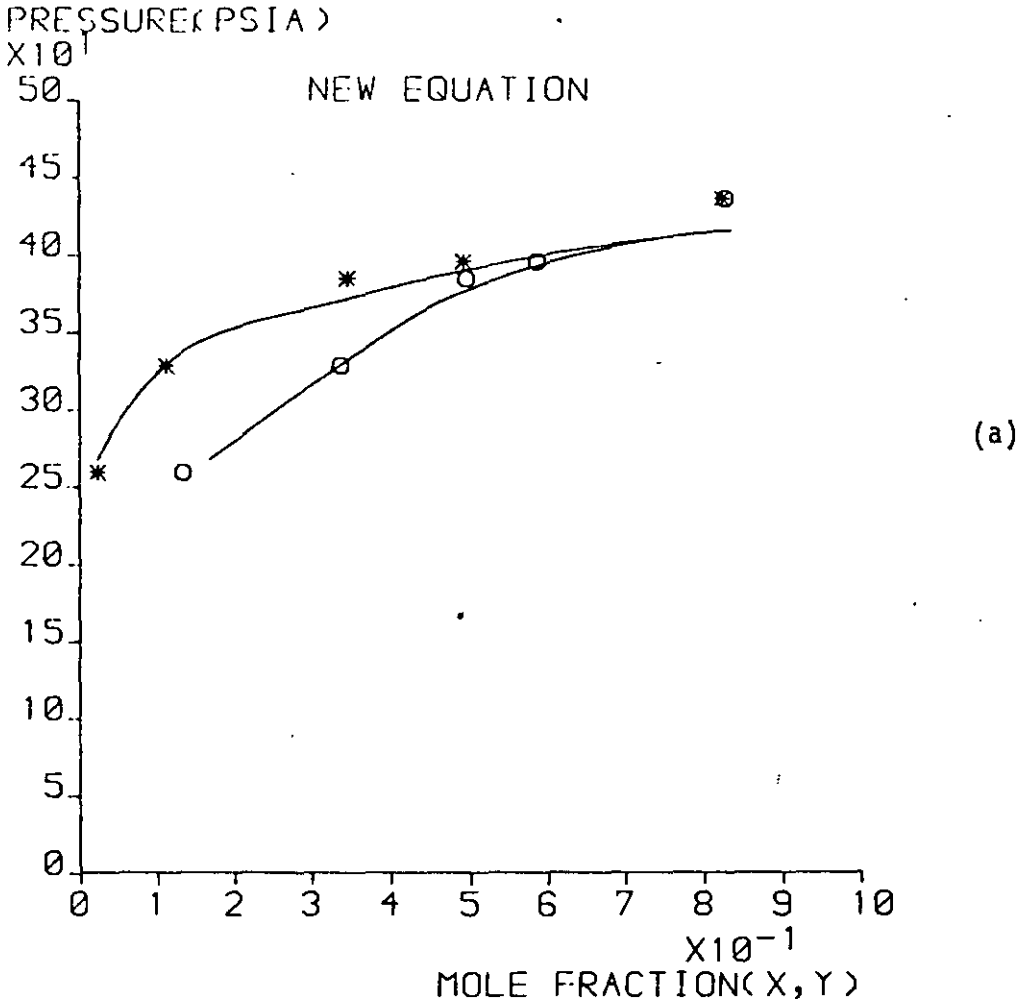


(a)

FIGURE 6.112 Methanol-Water System at 761.67°R (423.15K)

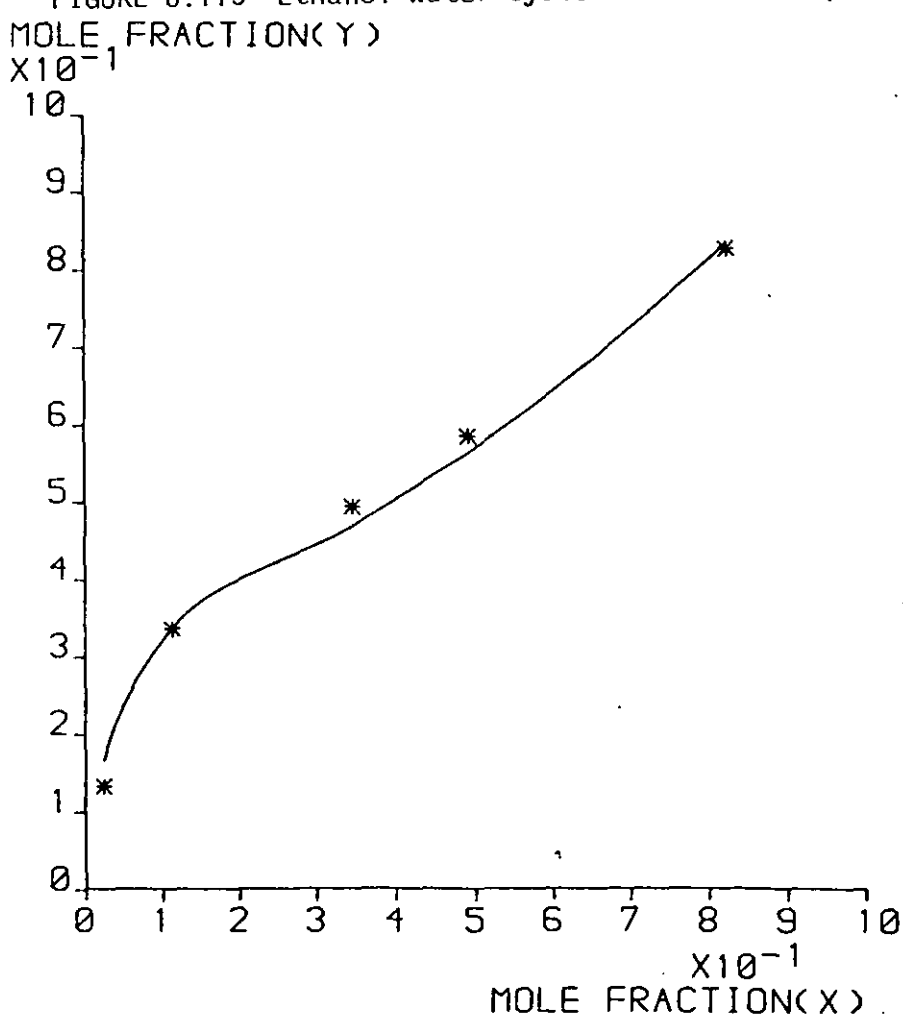


(b)



(a)

FIGURE 6.113 Ethanol-Water System at 851.67°R (473.15K)



(b)

REFERENCES

1. ABBOTT, M M, "Cubic Equations of State", AIChEJ., 19, No. 3, 596 (1973).

2. ADLER, S B, SPENCER, C F, OZKARDESH, H and KUO C M, "Industrial Uses of Equations of State: A State-of-the-Art Review", refer to Storvick and Sandler (1977).

3. American Petroleum Institute (API) Research Project No. 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Carnegie Institute of Technology, Pittsburgh, Pa., (1953).

4. API Research Project 44, Data "Selected Values of Properties of Hydrocarbons and Related Compounds", Texas A and M University, College Station, Texas (1973).

5. API, Technical Data Book - Petroleum Refining, 2nd Edition, Chapters 4, 7 and 8, Washington, D.C. (1977).

6. BEATTIE, J A "The Computation of the Thermodynamic Properties of Real Gases and Mixtures of Real Gases", Chem. Rev., 44, 141 (1949).

7. BEATTIE, J A, BRIDGEMAN, O C, Proc. Am. Acad. Arts Sci., 63, 229 (1928).

8. BENDER, E, "An Equation of State for Predicting Vapour-Liquid Equilibria of the System N_2-A_r-O_2", Cryogenics, 13, 11 (1973).

9. BENEDICT, M., WEBB, G W and RUBIN, L C, "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures", I. Methane, Ethane, Propane and n-Butane", J. Chem. Phys. 8, 334 (1940).

10. BERET, S and PRAUSNITZ, J M, "Perturbed Hard-Chain Theory: An Equation of State for Fluids Containing Small or Large Molecules", AIChEJ, 21, 1123 (1975).

11. BERTHELOT, D J, J Phys., 8, 263 (1899).

12. BISHNOI, P R, and ROBINSON, D B, "New Mixing Rules for the BWR Parameters to Predict Mixture Properties", Can. J. Chem. Eng., 50, 101 (1972).

13. CANJAR, L N and MANNING, F S, "Thermodynamic Properties and Reduced Correlations for Gases", Gulf Publishing Company, Houston, Texas, (1967).

14. CARNAHAN, N F and STARLING, K E, "Intermolecular Repulsions and the Equation of State for Fluids", AIChEJ, 18, 1184 (1972).

15. CHAUDRON, J., ASSELINEAU, L and RENON, H., "A New Modification of the Redlich-Kwong Equation of State Based on the Analysis of a Large Set of Pure Component Data", Chem. Eng. Sci., 28, 839 (1973).

16. CHUEH, P L and PRAUSNITZ, J M, "Vapor-Liquid Equilibria at High Pressures. Vapor-Phase Fugacity Coefficients in Non-polar and Quantum-Gas Mixtures", Ind. Eng. Chem. Fundam., 6, No. 4, 492 (1967).

17. CLAUSIUS, R., Ann. Phys., 9, 337 (1880).

18. DE SANTIS, R., GIRONI, F and MARRELLI, L, "Vapor-Liquid Equilibrium From a Hard-Sphere Equation of State", Ind. Eng. Chem. Fundam., 15, No. 3, 183 (1976).

19. DODGE, B F., "Chemical Engineering Thermodynamics", New York, N.Y. McGraw Hill Book Company Inc., 1944.

20. EDMISTER, W C., "Applied Hydrocarbon Thermodynamics. Vol. 1", Gulf Publishing Company, Houston, Texas (1961).

21. FLORY, P J, ORWALL, R A and VRIJ, A., "Statistical Thermodynamics of Chain Molecule Liquids, I. An Equation of State for Normal Paraffin Hydrocarbons. II. Liquid Mixtures of Normal Paraffin Hydrocarbons", J. Am. Chem. Soc., 86, 3507 (1964).

22. FULLER, G G, "A Modified Redlich-Kwong-Soave Equation of State Capable of Representing the Liquid State", Ind. Eng. Chem. Fundam., 15, No. 4, 254 (1976).

23. GOOD, R J and HOPE, C J, "New Combining Rule for Intermolecular Distances in Intermolecular Potential Functions", J. Chem. Phys., 53, 540 (1970).

24. GRABOSKI, M S and DAUBERT, T E, "A Modified Soave Equation of State for Phase Equilibrium Calculations. 1. Hydrocarbon Systems. 2. Systems Containing CO_2, H_2S, N_2 and CO", Ind. Eng. Chem. Process Des. Dev., 17, No. 4, 443 (1978).

25. GUNNING, A J and ROWLINSON, J S, "The Prediction of the Thermodynamic Properties of Fluids and Fluid Mixtures - III. Applications", Chem. Eng. Sci., 28, 521 (1973).

26. GUNN, R D and YAMADA, T, "Corresponding States Correlation of Saturated Liquid Volumes", AIChEJ, 17, 1341 (1971).

27. HAN, M S and STARLING, K E, "Thermo Data Refined for LPG. Part 14: Mixtures", Hydrocarbon Processing, 51, No. 5, 129 (1972).

28. HARMENS, A, "A Cubic Equation of State for the Prediction of N_2-A_r-O_2 Phase Equilibrium", Cryogenics, 17, 519 (1977).

29. HEYEN, G, "Liquid and Vapor Properties from a Cubic Equation of State", EFCE Publication Series No. 11. 'Phase Equilibria and Fluid Properties in the Chemical Industry', 2nd International Conference Berlin (West), 17-21 March, Proceedings, Part 1. Manuscripts of Poster Papers, DECHEMA, Frankfur t/Main (1980).

30. HISSONG, D W and KAY, W B, "The Calculation of the Critical Locus Curve of a Binary Hydrocarbon System", AIChEJ, 16, No. 4, 580 (1970).

31. HORVATH, A L, "Redlich-Kwong Equation of State: Review for Chemical Engineering Calculations", Chem. Eng. Sci., 29, 1334 (1974).

32. HSI, C, and LU, B C Y, "Generalised f/p, Z_T and Z_p Values for Liquids at Low Reduced Temperatures", AIChEJ, 20, 109 (1974).

33. HUDSON, G H and McCOUBERY, J C, "Intermolecular Forces Between Unlike Molecules. A More Complete Form of the Combining Rules", Trans. Faraday Soc., 56, 761 (1960).

34. JOFFE, J, "Vapor-Liquid Equilibria by the Pseudo-Critical Method", Ind. Eng. Chem. Fundam., 15, No. 4, 298 (1976).

35. JOFFE, J, and ZUDKEVITCH, D, "Prediction of Critical Properties of Mixtures: Rigorous Procedure for Binary Mixtures", Chem. Eng. Prog. Symp. Ser. 63, No. 81, 43, (1967).

36. LEE, B and KESLER, M G, "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States", AIChEJ, 21, No. 3, 510 (1975).

37. LENNARD-JONES, J E, Proc. Roy. Soc. (London) A106, 463 (1924).

38. LENNARD-JONES, J E, and DEVONSHIRE, A F, Proc. Roy. Soc. London, A163, 53 (1937).

39. LELAND, T W, Jr, "Note on the Use of Z_c as a Third Parameter with the Corresponding States Principle", AIChEJ, 12, No. 6, 1227 (1966).

40. LELAND, T W, CHAPPEL EAR, P S and GAMSON, B W, "Prediction of Vapor-Liquid Equilibria from the Corresponding States Principle", AIChE J, 8, No. 4, 482 (1962).

41. LELAND, T W, Jr, and CHAPPELEAR, P S, "The Corresponding States Principle. A Review of Current Theory and Practice", Ind. Eng. Chem., 60, No. 7, 15 (1968).

42. LELAND, T W, ROWLINSON, J S and SATHER, G A, "Statistical Thermodynamics of Mixtures of Molecules of Different Sizes", Trans. Faraday Soc., 64, 1447 (1968).

43. LELAND, T W, ROWLINSON, J S, SATHER, G A and WATSON, I D, "Statistical Thermodynamics of Two-Fluid Models of Mixtures", Trans. Faraday Soc., 65, 2034 (1969).

44. LIN, C T and DAUBERT, T E, "Prediction of Partial Molar Volume from the Lee-Kesler Equation of State", AIChEJ, 25, 365 (1979).

45. LEWIS, G N and RANDALL, M, "Thermodynamics", New York, N.Y: McGraw Hill Book Company, Inc., 1923.

46. LU, B C Y, HSI, C, CHANG, S D and TSANG, A, "Volumetric Properties of Normal Fluids at Low Temperatures: An Extension of Pitzer's Generalized Correlation", AIChEJ, 19, 748 (1973).

47. MOLLERUP, J and ROWLINSON, J S, "The Prediction of the Densities of Liquified Natural Gas and of Lower Molecular Weight Hydrocarbons", Chem. Eng. Sci., 29, 1373 (1974).

48. MARTIN, J J, "Equations of State", Ind. Eng. Chem., 59, No. 12, 37 (1967).

49. MARTIN, J J and HOU, Y C, "Development of an Equation of State for Gases", AIChEJ, 1, No. 2, 142 (1955).

50. MARTIN, J J and STANFORD, T G, "Development of High Precision Equations of State for Wide Ranges of Density Utilizing a Minimum of Input Information: Example - Argon", AIChE Symp. Ser. 70, No. 140, 1 (1974).

51. MUNN, R J, "Intermolecular Forces in Perfluorocarbon + Hydrocarbon and Hydrocarbon + Hydrocarbon Mixtures, Using an Improved Dispersion-Forces Combining Rule", Trans. Faraday Soc., 57, 187 (1961).

52. O'CONNELL, J P, "Some Aspects of Henry's Constants and Unsymmetric Convention Activity Coefficients", Refer to Storvick and Sandler, (1977).

53. ONNES, H K, Commun. Phys. Lab., Leiden, Holland, 71 (1901).

54. PENG, D Y and ROBINSON, D B, "A New Two-Constant Equation of State", Ind. Eng. Chem. Fundam., 15, No. 1, 59 (1976).

55. PENG, D Y and ROBINSON, D B, "Two and Three Phase Equilibrium Calculations for SystemsContaining Water", Can. J. Chem. Eng., 54, 595 (1976).

56. PENG, D Y and ROBINSON, D B, "A Rigorous Method for Predicting the Critical Properties of Multicomponent Systems Using an Equation of State", AIChEJ, 23, 137 (1977).

57. PITZER, K S, "Corresponding States for Perfect Liquids", J.Chem.Phys., 7, 583 (1939).

58. PITZER, K S, LIPPMANN, D Z, CURL, R F, Jr, HUGGINS, C M and PETERSON D E, "The Volumetric and Thermodynamic Properties of Fluids II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization", J. Am. Chem. Soc., 77, 3433 (1955).

59. PITZER, K S and CURL, R F, "Volumetric and Thermodynamic Properties of Fluids - Enthalpy, Free Energy and Entropy", Ind. Eng. Chem., 50, No, 2, 265 (1958).

60. PITZER, K S and CURL, R F, Jr, "The Volumetric and Thermodynamic properties of Fluids. III. Empirical Equation for the Second Virial Coefficient", J. Am. Chem. Soc., 79, 2369 (1957).

61. PLOCKER, H, KNAPP, H, and PRAUSNITZ, J, "Calculation of High-Pressure Vapor-Liquid Equilibria from a Corresponding-States Correlation with Emphasis on Asymmetric Mixtures", Ind. Eng. Chem. Process Des. Dev., 17, 324 (1978).

62. PRAUSNITZ, J M, "Fugacities in High-Pressure Equilibria and in Rate Processes", Am. Inst. Chem. Eng., J, 5, 3 (1959).

63. PRAUSNITZ, J M, "State-of-the-Art Review of Phase Equilibria", Refer to Storvick and Sandler (1977).

64. PRAUSNITZ, J M and CHUEH P L, "Computer Calculations for High-Pressure Vapor-Liquid Equilibria", Englewood Cliffs, N.J.: Prentice-Hall, Inc., (1968).

65. PRAUSNITZ, J M and GUNN, R D,"Volumetric Properties of Nonpolar Gaseous Mixtures", AIChE J., 4, No. 4, 430, 494 (1958).

66. PRAUSNITZ, J M, ECKERT, C A, ORYE R V and O'CONNELL, J P, "Computer Calculations for Multicomponent Vapor-Liquid Equilibria", Englewood Cliffs, N.J.: Prentice-Hall, Inc. (1967).

67. REDLICH, O, and KWONG, J N S, "On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions", Chem. Rev. 44, 233 (1949).

68. REDLICH, O and DUNLOP, A K, "Thermodynamics of Solutions. VIII. An Improved Equation of State", Chem. Eng. Prog. Symp. Ser., 59, No. 44, 95 (1963).

69. REDLICH, O, ACKERMAN, F J, GUNN, R D, JACOBSON, M and LAU, S, "Thermodynamics of Solutions. Equation of State and Vapor Pressure", Ind. Eng. Chem. Fundam., 4, 369 (1965).

70. REDLICH, O, and NGO, V B T, "An Improved Equation of State", Ind. Eng. Chem. Fundam, 9, 287 (1970).

71. REID, R C, PRAUSNITZ, J M and SHERWOOD, T K, "The Properties of Gases and Liquids", 3rd Edition, McGraw-Hill, New York, (1977).

72. RIEDEL, E, Chemie.-Ing. Techn,, 26, 83, 259 (1954).

73. ROWLINSON, J S, "The Equilibrium Properties of Assemblies of Non-Spherical Molecules", Trans. Faraday Soc. 50, 647 (1954).

74. ROWLINSON, J S, "The Equation of State of Dense Systems", Rept. Prog. Phys. 28, 169 (1965).

75. SCHMIDT, G and WENZEL, H, "A Modified van der Waals Type Equation of State", Chem. Eng. Sci., 35, 1503 (1980).

76. SENGERS, J V and SENGERS, A L, "The Critical Region", Chem. Eng. News, 46, 104 (1968).

77. SIMONET, R, and BEHAR, E, "A Modified Redlich-Kwong Equation of State for Accurately Representing Pure Components Data", Chem. Eng. Sci., 31, 37 (1976).

78. SOAVE, G, "Equilibrium Constants from a Modified Redlich-Kwong Equation of State", Chem. Eng. Sci., 27, 1197 (1972).

79. SPEAR, R R, ROBINSON, R L and CHAO, K C, "Critical States of Mixtures and Equations of State", Ind. Eng. Chem. Fundam. 8, 2 (1969).

80. SPENCER, C F and ADLER, S B, "A Critical Review of Equations for Predicting Saturated Liquid Density", J. Chem. Eng. Data, 23, No. 1, 82 (1978).

81. STARLING, K E, "Fluid Thermodynamic Properties for Light Petroleum Systems", Gulf Publishing Co., Houston, Texas (1973).

82. STORWICK, T S and SANDLER, S I, "Phase Equilibria and Fluid Properties in the Chemical Industry. Estimation and Correlation", ACS Symposium Series 60, American Chemical Society, Washington, D.C. (1977).

83. STROBRIDGE, T R, Natl. Bur. Stds., Tech. Note, 129 (1962).

84. TEJA, A S, "Binary Interaction Coefficients for Mixtures Containing the n-Alkanes", Chem. Eng. Sci., 33, 609 (1978).

85. TEJA, A S, "A Corresponding States Equation for Saturated Liquid Densities. I. Applications to LNG", AIChE J, 26, 337 (1980).

86. TEJA, A S, PATEL, N C and NG, N H , "The van der Waals One-Fluid Model for Mixtures and Generalised Equations of State", Chem. Eng. Sci., 33, 624 (1978).

87. TEJA, A S and SANDLER, S I, "A Corresponding States Equation for Saturated Liquid Densities. II. Applications to the Calculation of Swelling Factors of CO_2 - Crude Oil Systems", AIChE J., 26, 341 (1980).

88. TEJA, A S, SANDLER, S I and PATEL, N C, "A Generalisation of the Corresponding States Principle using Two Nonspherical Reference Fluids", Chem. Eng. J. (1980) - in press.

89. TEJA, A S and SINGH, A, "Equations of State for Ethane, Propane and n-Butane", Cryogenics, 17, No. 11, 591 (1977).

90. TEJA, A S and ROWLINSON, J S, "The Prediction of the Thermodynamic Properties of Fluids and Fluid Mixtures", Chem. Eng. Sci., 29, 529 (1973).

91. THODOS, G and SHAH, K K, "A Comparison of Equations of State". Ind. Eng. Chem. 57, No. 3, 30 (1965).

92. VAN DER WAALS, J D, Doctoral Dissertation, Leiden, Holland (1873).

93. VERA, J H and PRAUSNITZ, J M, "Van der Waals One Fluid Theory of Mixtures for High-Pressure Vapor-Liquid Equilibria", Chem. Eng. Sci., 26, 1772 (1971).

94. VISWANATH, D S and SU, G J, "Generalized Thermodynamic Properties of Real Gases. Part 1. Generalized PVT Behaviour of Real Gases. Part 2. Generalized Benedict-Webb-Rubin Equation of State for Real Gases", AIChE J., 11, No. 2, 202 (1965).

95. WILSON, G M, "Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing", J. Am. Chem. Soc., 86, 127 (1964).

96. WILSON, G M, "Vapor-Liquid Equilibria, Correlation by Means of a Modified Redlich-Kwong Equation of State", Adv. Cryogenic Eng., 9, 168 (1964).

REFERENCES OF SATURATION DATA

1. ANGUS, S, and ARMSTRONG, B, "IUPAC Thermodynamic Tables of the Fluid State - Argon 1971", Butterworths, London (1972).

2. ANGUS, S, ARMSTRONG, B and DE REUCK, K M, "IUPAC International Thermodynamic Tables of the Fluid State - 3 Carbon Dioxide", Pergamon, Oxford (1973).

3. API (1973) - see Text Reference No. 4.

4. BENDER, E, "Die Berechnung von Phasengleichgewitchten mit der Thermischen Zustandsgleichungdargestellt an den Reinen Fluiden Argon, Stickstoff, Sauerstoff und an Ihern Gemischen", English Translation: "The Calculation of Phase Equilibria from a Thermal Equation of State", Verlag, C.F. Muller, Karlsruhe (1973).

5. CANJAR, L N and MANNING, F S (1967) - see Text Reference No. 13.

6. MATTHEWS, C S and HURD, C O, "Thermodynamic Properties of Methane", Trans. Am. Inst. Chem. Eng., 42, No. 4, 55 (1946).

7. POLLAK, R, "Thermodynamic Properties of Water up to 1200K and 3000 Bar", English Translation, IUPAC Thermodynamics Project Centre, Imperial College, London (1976).

8. SPENCER, C F and ADLER, S B (1978) - see Text Reference No. 80.

9. STARLING, K E, (1973) - see Text Reference No. 81.

10. Young, S, "Vapor Pressures, Specific Volumes and Critical Constants of Normal Octane", JCS, Vol. LXXVII, 1145 (1900).

11. YOUNG, S, Sci. Proc. Royal Dublin Soc., 12, 374 (1910).

REFERENCES OF VOLUMETRIC DATA

METHANE

1. DOUSLIN, D R, HARRISON, R H, MOORE, R T and McCULLOUGH, J P, "P-V-T Relations for Methane", J. Chem. Eng. Data, 9, No. 3, 358 (1964).

2. VAN ITTERBEEK, A, VERBEKE, O B and STATES, K, "Measurements on the Equation of State of Liquid Argon and Methane up to 300 kg cm^{-2} at Low Temperatures", Physica, 29, 742 (1963).

3. GOODWIN, R D, "The Thermophysical Properties of Methane, from 90 to 500K at Pressures to 700 Bar", National Bureau of Standards. Report No. NBSIR 73-342 (1973).

ETHANE

4. DATE, K, WATANABE, K and VEMATSU, M, "Evaluation of P-V-T Properties Data. The Most Probable Values of Compressibility Factor of Gaseous Ethane and Ethene", Review Phys. Chem. Japan, 43, No. 2, 93 (1973).

5. BEATTIE, J A, HADLOCK, C and POFFENBERGER, N, "The Compressibility of and an Equation of State for Gaseous Ethane", J. Chem. Phys., 3, 93 (1935).

6. REAMER, H H, OLDS, R H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric Behaviour of Ethane", Ind. Eng. Chem., 36, 956 (1944).

7. SAGE, B H, WEBSTER, D C and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. XVIII. Thermodynamic Properties of Ethane", Ind. Eng. Chem., 29, 658 (1937).

PROPANE

8. BEATTIE, J A, KAY, W C and KAMINSKY, J, "The Compressibility of and an Equation of State for Gaseous Propane", J. Am. Chem. Soc., 59, 1589 (1937).

9. SAGE, B H, SCHAAFSMA, J G and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems V. Pressure-Volume-Temperature Relations and Thermal Properties of Propane", Ind. Eng. Chem., 26, 1218 (1934).

10. REAMER, H H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric Behaviour of Propane", Ind. Eng. Chem., 41, 483 (1949).

n-BUTANE

11. API (1953) - see Text Reference No.3.

12. CANJAR, L N, and MANNING, F S (1967), See Text Reference No. 13.

13. SAGE, B H, WEBSTER, D C and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. XIX. Thermodynamic Properties of n-Butane", Ind. Eng. Chem., 29, 1188 (1937).

14. OLDS, R H, REAMER, H H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric Behaviour of n-Butane", Ind. Eng. Chem., 36, 282 (1944).

15. KAY, W B, "Pressure-Volume-Temperature Relations for n-Butane", Ind. Eng. Chem., 32, 358 (1940).

n-Pentane

(Text Reference No. 3 and 13)

16. BEATTIE, J A, LEVINE, S W and DOUSLIN, D R, "The Compressibility of and an Equation of State for Gaseous Normal Pentane", J. Am. Chem. Soc., 74, 4778 (1952) and 73, 4431 (1951).

17. BRYDON, J W, WALEN, N and CANJAR, L N, "Thermodynamic Properties of n-Pentane", Chem. Eng. Symp. Ser., 49, No. 7, 151 (1953).

18. SAGE, B H, and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Thermodynamic Properties of n-Pentane", Ind. Eng. Chem., 34, No. 6, 730 (1942).

n-Hexane

19. WEBER, J H, "Thermodynamic Properties of n-Hexane", AIChE J., 2, No. 4, 514 (1956).

20. STEWART, D E, SAGE, B H and LACEY, W N, "Volumetric Behaviour of n-Hexane in Liquid Phase", Ind. Eng. Chem., 46, No. 12, 2529 (1954).

21. KELSO, E A, and FELSING, W A, "The Pressure-Volume-Temperature Relations of n-Hexane and of 2-Methyl Pentane", J. Am. Chem. Soc., 62, 3132 (1940).

n-HEPTANE

22. NICHOLS, W B, REAMER, H H and SAGE, B H, "Phase Equilibria in Hydorcarbon Systems. Volumetric Behaviour of n-Heptane", Ind. Eng. Chem., 47, 2219 (1955).

n-OCTANE

23. FELSING, W A and WATSON, G M, "The Compressibility of Liquid n-Octane", J. Am. Chem. Soc., 64, 1822 (1942).

n-NONANE

24. CARMICHAEL, L T, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric Behaviour of n-Nonane", Ind. Eng. Chem., 45, 2697 (1953).

n-DECANE

25. REAMER, H H, OLDS, R H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Methane-Decane System", Ind. Eng. Chem., 34, No. 12, 1526 (1942).

SULFUR DIOXIDE AND BENZENE

26. CANJAR, L N, and MANNING, F S (1967) see Text Reference No. 13.

REFERENCES OF VAPOUR-LIQUID EQUILIBRIUM

1. Methane-Ethane

DAVALOS, J, ANDERSON, W R, PHELPS, R E and KIDNAY, A J, "Liquid-Vapor Equilibria at 250.00K for Systems Containing Methane, Ethane and Carbon Dioxide", J. Chem. Eng. Data, 21, 82 (1976).

BLOOMER, O T, GAMI, D C, and PARENT, J D, Inst. Gas. Tech. Research Bull. 22 (July 1953).

WIGHTERLE, I and KOBAYASHI, R, "Low Temperature Vapor-Liquid Equilibria in the Methane-Ethane-Propane Ternary and Associated Binary Methane Systems with Special Consideration of the Equilibria in the Vicinity of the Critical Temperature of Methane", Monograph, Rice University, Houston, Texas, August 31 (1970).

2. Methane-Propane

REAMER, H H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of the Methane-Propane System", Ind. Eng. Chem., 42, 534 (1950).

AKERS, W W, BURNS, J F and FAIRCHILD, W W, "Low-Temperature Phase Equilibria. Methane-Propane System", Ind. Eng. Chem., 46, 2531 (1954).

3. Methane-n-Butane

ROBERTS, L, WANG, R, AZARNOOSH, A and McKETTA, J, "Methane-n-Butane System in the Two-Phase Region", J. Chem. Eng. Data, 7, 484 (1962).

4. Methane-i-Butane

OLDS, R H, SAGE, B H and LACEY, W N, "Methane-i-Butane System", Ind. Eng. Chem., 34, 1008 (1942).

5. Methane-n-Pentane

CHU, T C, CHEN, R J, CHAPPELEAR, P S and KOBAYASHI, R, Vapor-Liquid Equilibrium of Methane-n-Pentane System at Low Temperatures and High Pressures", J. Chem. Eng. Data, 21, No. 1, 41 (1976).

BERRY, V M and SAGE, B H, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. 32 (June 1970).

6. Methane-n-Hexane

SHIM, J and KOHN, J, "Multiphase and Volumetric Equilibria of Methane-n-Hexane Binary System at Temperatures Between -110° and 150°C", J. Chem. Eng. Data, 7, 3 (1962).

7. Methane-n-Eicosane

PURI, S and KOHN, J P, "Solid-Liquid-Vapor Equilibrium in the Methane-n-Eicosane and Ethane-Eicosane Binary Systems", J. Chem. Eng. Data, 15, No. 3, 373 (1970).

8. Methane-Benzene

ELBISHLAWI, M, and SPENCER, J R, "Equilibrium Relations of Two Methane-Aromatic Binary Systems at 150°F", Ind. Eng. Chem., 43, 1811 (1951).

9. Ethane-Propane

MATSCHKE, D E and THODOS, G, "Vapor-Liquid Equilibria for the Ethane-Propane System", J. Chem. Eng. Data, 7, 232, (1962).

10. Ethane-Propylene

McKAY, R A, REAMER, H H, SAGE, B H and LACEY, W N, "Volumetric and Phase Behaviour in the Ethane-Propene System", Ind. Eng. Chem., 43, No. 9, 2112 (1951).

11. Ethane-n-Butane

DINGRANI, J, and THODOS, G, "Vapor-Liquid Equilibria Behaviour of the Ethane-n-Butane-n-Hexane System", Can. J. Chem. Eng., 56, 616 (1978).

12. Ethane-i-Butane

BESSERER, G J and ROBINSON, D B, "Equilibrium-Phase Properties of i-Butane-Ethane System", J. Chem. Eng. Data, 18, No. 3, 301 (1973).

13. Ethane-n-Pentane

REAMER, H H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of Ethane-n-Pentane System", J. Chem. Eng. Data, 5, 44 (1960).

14. Ethane-n-Heptane

MEHRA, V S and THODOS G, "Vapor-Liquid Equilibrium in the Ethane-n-Heptane System", J. Chem. Eng. Data, 10, 211 (1965).

15. Ethane-n-Decane

REAMER, H H and SAGE, B H, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of the Ethane-n-Decane System", J. Chem. Eng. Data, 7, No. 2, 161 (1962).

16. Ethane-n-Dodecane

LEE, K H and KOHN, J P, "Heterogeneous Phase Equilibrium in the Ethane-n-Dodecane System", J. Chem. Eng. Data, 14, 292, (1969).

17. Ethane-n-Eicosane

Same as Ref. 7.

18. Ethylene-Methane

MILLER, R C, KIDNAY, A J and HIZA, M J, "Liquid + Vapor Equilibria in Methane + Ethene and in Methane + Ethane from 150.00K to 190.00K", J. Chem. Thermod., 9, 167 (1977).

19. Ethylene-Ethane

HANSON, G H, HOGAN, R J, RUEHLEN, F N and CINES, M R, "Ethane-Ethylene System. Vapor-Liquid Equilibria at 0°, -40°, and $-100^{o}F$", Chem. Eng. Progr. Symp. Ser. 49, 37 (1953).

20. Ethylene-Propane

ELSHAYAL, I M and LU, B C Y, "Measurement of Total Pressures for Ethylene-Propane Mixtures", Can. J. Chem. Eng., 53, 86 (1975).

21. Ethylene-n-Butane

CHU, Ju Chin, "Vapor-Liquid Equilibrium Data", Edward (1954).

22. Ethylene-n-Dodecane

RIBERIO, J V, SUSU, A A and KOHN, J P, "Heterogeneous-Phase Equilibrium in Ethylene-n-Dodecane System", J. Chem. Eng. Data, 17, No. 3, 279 (1972).

23. Propane-i-Butane

HIPKIN, H, "Experimental Vapor-Liquid Equilibrium Data for Propane-Isobutane", AIChE J., 12, No. 3, 484 (1966).

24. Propane-n-Pentane

SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Propane-n-Pentane System", Ind. Eng. Chem., 32, 992 (1940).

25. Propane-i-Pentane

VOUGHAN, W E and COLLINS, F C, "P-V-T-x Relations of the System Propane-Isopentane", Ind. Eng. Chem., 34, 885 (1942).

26. Propane-n-Decane

REAMER, H H, and SAGE, B H, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of the Propane-n-Decane System", J. Chem. Eng. Data, 11, No. 1, 17 (1966).

27. Propane-Benzene

GLANVILLE, J W, SAGE, B H and LACEY, W N, "Volumetric and Phase Behaviour of Propane-Benzene System", Ind. Eng. Chem., 42, 508 (1950).

28. Propylene-Propane

REAMER, H H and SAGE, B H, "Volumetric and Phase Behaviour of Propene-Propane System" Ind. Eng. Chem., 43, No. 7, 1628 (1951).

29. Propylene-1-Butane

GOFF, G H, FARRINGTON, P S and SAGE, B H, "Volumetric and Phase Behaviour of Propene-1-Butene System", Ind. Eng. Chem., 42, 735 (1950).

30. n-Butane-n-Decane

REAMER, H H and SAGE, B H, "Phase Equilibria in Hydrocarbon Systems. Phase Behaviour in the n-Butane-n-Decane System", J. Chem. Eng. Data, 9, No. 1, 24 (1964).

31. 1-Butene-n-Butane

LAWRENCE, D and SWIFT, G W, "Vapor-Liquid Equilibria in Three Binary and Ternary Systems Composed of n-Butane, Butene-1 and Butadiene-1,3", J. Chem. Eng. Data, 19,No. 1, 64 (1964).

32. Carbon dioxide-Methane

DONNELLY, H G and KATZ, D L, "Phase Equilibria in the Carbon dioxide-Methane System", Ind. Eng. Chem., 46, 511 (1954).

33. Carbon dioxide-Ethane

NAGAHAMA, K, KONISHI, H, HOSHINO, D and HIRATA, M, "Binary Vapor-Liquid Equilibria of Carbon dioxide - Light Hydrocarbons at Low Temperature", J. Chem. Eng., Japan, 7, No. 5, 323 (1974).

34. Carbon dioxide-Ethylene

See Ref. 33.

35. Carbon dioxide-Propane

See Ref. 33.

REAMER, H H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of the Propane-Carbon dioxide System", Ind. Eng. Chem., 43, No. 11, 2515 (1951).

36. Carbon dioxide-n-Butane

See Ref. 33.

OLDS, R H, REAMER, H H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. The n-Butane-Carbon dioxide System", Ind. Eng. Chem., 41, 475 (1949).

37. Carbon dioxide-i-Butane

BESSERER, G J, and ROBINSON, D B , "Equilibrium-Phase Properties of i-Butane-Carbon dioxide System", J.Chem. Eng. Data, 18, 298 (1973).

38. Carbon dioxide-n-Pentane

BESSERER, G J and ROBINSON, D B, "Equilibrium-Phase Properties of n-Pentane-Carbon dioxide System", J. Chem. Eng. Data, 18, No. 4, 417 (1973).

39. Carbon dioxide-n-Decane

REAMER, H H and SAGE, B H, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of the n-Decane-CO_2 System", J. Chem. Eng. Data, 8, 508 (1963).

40. Carbon monoxide-Propane

BOLSHAKOV, P E and LINSHITS, L R, TR.GIAP, 3, 18 (1954).

41. Hydrogen sulfide-Methane

REAMER, H H, SAGE, B H and LACEY, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of the Methane-Hydrogen sulfide System", Ind. Eng. Chem., 43, 976 (1951).

42. Hydrogen sulfide-Ethane

KALRA, H, ROBINSON, D B and KRISHNAN, T R, "The Equilibrium Phase Properties of the Ethane-Hydrogen Sulfide System at Sub-ambient Temperatures", J. Chem. Eng. Data, 22, No. 1, 86 (1977).

43. Hydrogen sulfide-i-Butane

BESSERER, G J, and ROBINSON, D B, "The Equilibrium Phase Properties of the i-Butane-Hydrogen Sulfide System", J.Chem. Eng. Japan, 8, No. 1, 13 (1975).

44. Hydrogen sulfide-n-Heptane

NG, H J, KALRA, H, ROBINSON, D B and KUBOTA, H, "Equilibrium Phase Properties of the Toluene-Hydrogen Sulfide and n-Heptane-Hydrogen Sulfide Binary Systems", J. Chem. Eng. Data, 25, No. 1, 51 (1980).

45. Hydrogen sulfide-n-Decane

REAMER, H H, SELLECK, F T, SAGE, BH and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of Decane-Hydrogen Sulfide System", Ind. Eng. Chem., 45, No. 8, 1810 (1953).

46. Nitrogen-Methane

CINES, M R, ROACH, J T, HOGAN, R J and ROLAND, C H, "Nitrogen-Methane-Vapor-Liquid Equilibria", Chem. Eng. Progr. Symp. Ser., 49, No. 6, 1 (1953).

47. Nitrogen-Propane

BOLSHAKOV, P E and LINSHITS, L R, T.R. GIAP, 3, 18 (1954).

48. Nitrogen-n-Butane

ROBERTS, L R and MACKETTA, J J, "Vapor-Liquid Equilibrium in the n-Butane-Methane-Nitrogen System", J.Chem.Eng. Data, 8, 161 (1963).

49. Nitrogen-n-Heptane

AKERS, W W, KEHN, D M and KILGORE, C H, "Volumetric and Phase Behaviour of Nitrogen-Hydrocarbon Systems. Nitrogen-n-Heptane System", Ind. Eng. Chem., 46, No. 12, 2536 (1954))

50. Methanol-Water

GRISWOLD, J and WONG, S Y, "Phase-Equilibria of the Acetone-Methanol-Water System from 100°C in to the Critical Region", Chem. Eng. Prog. Symp. Ser. 48, No. 3, 18 (1952).

51. Ethanol-Water

BARR-DAVID, F and DODGE, B F, "Vapor-Liquid Equilibrium at High Pressures. The Systems Ethanol-Water and 2-Propanol-Water", J. Chem. Eng. Data, 4, 107 (1959).

52. Methane-Ethane-Propane

PRICE, A R and KOBAYASHI, R, "Low Temperature Vapor-Liquid Equilibrium in Light Hydrocarbon Mixtures: Methane-Ethane-Propane System", J. Chem. Eng. Data, 4, No. 1, 40 (1959).

53. Methane-Propane-n-Decane

WIESE, H C, REAMER, H H and SAGE, B H, "Phase Equilibria in Hydrocarbon Systems. Phase Behaviour in the Methane-Propane-n-Decane System", J. Chem. Eng. Data, 15, No. 1, 75 (1970).

54. Methane-n-Butane-n-Decane

REAMER, H H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon System. Methane-n-Butane-Decane System", Ind. Eng. Chem., 39, No. 1, 77 (1947).

55. Methane-Ethane-Propane-n-Pentane-n-Hexane

HANSON, G H, and BROWN, G G, "Vapor-Liquid Equilibria in Mixtures of Volatile Paraffins", Ind. Eng. Chem., 37, 821 (1945).

56. Methane-Ethane-Propane-n-Butane-n-Pentane

DE PRIESTER, "Light-Hydrocarbon Vapor-Liquid Distribution Coefficients. Pressure-Temperature-Composition Charts and Pressure-Temperature Nomographs", Chem. Eng. Prog. Symp. Seires, 49, No. 7, 1 (1953).

57. Methane-n-Heptane

CHANG, H L, HURT, L J and KOBAYASHI, R, "Vapor-Liquid Equilibria of Light Hydrocarbons at Low Temperatures and High Pressures. The Methane-n-Heptane System", AIChE J, 12, 1212 (1966).

REAMER, H H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of the Methane-n-Heptane System", Chem. Eng. Data. Ser. 1, 29 (1956).

58. Hydrogen Sulfide-n-Pentane

REAMER, H H, SAGE, B H and LACEY, W N, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behaviour of n-Pentane-Hydrogen Sulfide System", Ind. Eng. Chem., 45, No. 8, 1805 (1953).

APPENDIX A

TABLE A.1

Parameters for the new equation of state

Constants F, K and n are required in the following temperature functions:

1. $\alpha[T_r] = [1 + F\,(1 - T_r^{\frac{1}{2}})]^2$

2. $\alpha[T_r] = e^{K(1-T_r^{n})}$

No.	Component	Z_m	F	K	n
1	Argon	0.328	0.450751	0.524130	0.895275
2	Nitrogen	0.329	0.516798	0.673567	0.805805
3	Oxygen	0.327	0.487035	0.545990	0.935180
4	Methane	0.324	0.455336	0.526324	0.904570
5	Ethane	0.317	0.561567	0.708265	0.800910
6	Ethylene	0.318	0.554369	0.642236	0.889410
7	Propane	0.317	0.648049	0.763276	0.860655
8	Propylene	0.324	0.661305	0.750739	0.898305
9	Acetylene	0.310	0.664179	0.659602	1.013775
10	n-Butane	0.309	0.678389	0.831715	0.816840
11	i-Butane	0.315	0.683133	0.775633	0.896125
12	1-Butene	0.315	0.696423	0.742573	0.958385
13	n-Pentane	0.308	0.746470	0.851904	0.882260
14	i-Pentane	0.314	0.741095	0.854607	0.875455
15	n-Hexane	0.305	0.801605	0.868581	0.934715
16	n-Heptane	0.305	0.868856	0.890894	0.992105
17	n-Octane	0.301	0.918544	1.057530	0.861175
18	n-Nonane	0.301	0.982750	1.247160	0.759605
19	n-Decane	0.297	1.021919	1.299741	0.755210
20	n-Undecane	0.297	1.080416	1.291079	0.809660
21	n-Dodecane	0.294	1.115585	1.339256	0.802980
22	n-Tridecane	0.295	1.179982	1.319388	0.869635
23	n-Tetradecane	0.291	1.188785	1.427823	0.798090
24	n-Heptadecane	0.283	1.297054	1.354358	0.935665

TABLE A.1 continued.

No.	Component	Z_m	F	K	n
25	n-Octadecane	0.276	1.276058	1.538739	0.791235
26	n-Eicosane	0.277	1.409671	1.741225	0.763255
27	Carbon dioxide	0.309	0.707727	0.865847	0.816080
28	Carbon monoxide	0.328	0.535060	0.678260	0.799145
29	Sulfur-dioxide	0.307	0.754966	0.871496	0.871745
30	Hydrogen-sulfide	0.320	0.583165	0.855553	0.669095
31	Water	0.269	0.689803	0.987468	0.680260
32	Ammonia	0.282	0.627090	1.425590	0.418730
33	Benzene	0.310	0.704657	0.880833	0.797500
34	Methanol	0.272	0.972708	0.939465	1.064985
35	Ethanol	0.300	1.230395	1.221152	1.001250
36	Propan-1-01	0.303	1.241347	1.806248	0.629465
37	Butan-1-01	0.304	1.199787	3.503814	0.298255
38	Pentan-1-01	0.311	1.242855	2.811893	0.384015

APPENDIX B

Table B.1

Critical Properties of Pure Components

Component	T_c (°R)	P_c (PSIA)	ω	Mol.Wt.	V_c (Ft^3/lb.mol)	Z_c
Argon	271.44	706.874	0.001	39.95	1.2014	0.291
Nitrogen	227.16	492.313	0.039	28.01	1.4257	0.290
Oxygen	278.244	731.416	0.025	32.00	1.1694	0.288
Methane	343.044	667.782	0.012	16.04	1.5859	0.288
Ethane	549.76	707.755	0.099	30.07	2.3708	0.285
Ethylene	508.212	730.828	0.089	28.05	2.0825	0.280
Propane	665.68	616.347	0.153	44.10	3.2519	0.281
Propylene	656.73	667.341	0.144	42.08	2.8994	0.274
Acetylene	554.99	890.425	0.190	26.04	1.8101	0.270
n-Butane	765.32	550.656	0.199	58.12	4.0848	0.274
i-Butane	734.67	529.053	0.183	58.12	4.2130	0.283
1-Butene	755.226	583.428	0.191	56.11	3.8446	0.277
n-Pentane	845.46	488.639	0.251	72.15	4.8698	0.268
i-Pentane	828.77	490.403	0.227	72.15	4.9018	0.270
n-Hexane	913.50	436.909	0.299	86.18	5.9270	0.264
n-Heptane	972.54	396.789	0.349	100.21	6.9202	0.263
n-Octane	1023.89	360.638	0.398	114.23	7.8813	0.259
n-Nonane	1070.28	331.834	0.455	128.26	8.7784	0.260
n-Decane	1111.86	305.087	0.489	142.29	9.6595	0.247
n-Undecane	1149.84	285.100	0.536	156.31	-	-
n-Dodecane	1184.76	264.526	0.575	170.34	11.4225	0.240
n-Tridecane	1216.44	249.830	0.623	184.367	12.4948	0.240
n-Tetra-decane	1249.20	235.135	0.679	198.394	13.2958	0.230
n-Hepta-decane	1319.40	191.047	0.770	240.475	16.0190	0.220
n-Octa-decane	1341.00	174.881	0.790	254.502	-	-
n-Eicosane	1380.60	161.655	0.907	282.556	-	-
Carbon dioxide	547.38	1069.715	0.225	44.01	1.5058	0.274

Continued....

TABLE B.1 (continued)

Component	T_c (^oR)	P_c (PSIA)	ω	Mol.Wt.	V_c (Ft^3/lb.mol)	Z_c
Carbon monoxide	239.24	507.45	0.053	28.01	1.4898	0.295
Sulfur dioxide	775.44	1143.489	0.256	64.06	1.9543	0.269
Hydrogen sulfide	671.76	1296.180	0.109	34.08	1.5699	0.284
Water	1164.852	3197.83	0.328	18.02	0.8971	0.231
Ammonia	729.90	1645.94	0.250	17.03	1.1534	0.244
Benzene	1011.888	710.40	0.212	78.11	4.1489	0.271
Methanol	922.752	1173.622	0.556	32.04	1.8902	0.224
Ethanol	925.056	890.137	0.644	46.07	2.6752	0.240
Propan-1-ol	966.204	749.790	0.623	60.10	3.5082	0.253
Butan-1-Ol	1013.49	641.480	0.593	74.12	4.4052	0.259
Pentan-1-Ol	1058.67	566.972	0.579	88.15	5.2222	0.261

These properties have been taken mainly from Ambrose and Townsend (1978)* Values for higher alkanes have been taken from Reid, Prausnitz and Sherwood (1977).

* AMBROSE, D and TOWNSEND, R, "Vapour-Liquid Critical Properties", NPL Report Inst. Chem. Engnrs., London (1978).

TABLE B.2

Conversion factors

Units used in this work		SI Units	Reciprocal
Pressure 1 PSIA	=	6.894757×10^3 Pa (N/m^2)	1.450377×10^{-4}
Volume 1 ft^3/lb. mol.	=	$6.2426 \times 10^{-5} m^3$/g.mol	1.6019×10^4
Temperature 1^oR	=	$\frac{5}{9}$ K	1.8

The universal gas constant was taken as:

$$R = 10.7335 \text{ PSIA ft}^3/\text{lb. mole } ^oR.$$

APPENDIX C

CONSTANTS USED IN THE EQUATIONS OF STATE

TABLE C.1

Generalized coefficients $d_i^{(K)}$ and $g_i^{(K)}$ in the Chaudron equation (Chaudron et al, 1973).

$d_1^{(0)}$	=	0.56718556×10
$d_2^{(0)}$	=	0.74164072
$d_3^{(0)}$	=	0.71094087
$d_1^{(1)}$	=	0.16679287×10^2
$d_2^{(1)}$	=	0.67454796×10
$d_3^{(1)}$	=	0.77929031×10
$g_1^{(0)}$	=	$0.81958137 \times 10^{-1}$
$g_2^{(0)}$	=	$0.74299534 \times 10^{-2}$
$g_3^{(0)}$	=	$0.70756935 \times 10^{-2}$
$g_1^{(1)}$	=	$0.35656367 \times 10^{-1}$
$g_2^{(1)}$	=	0.14087820
$g_3^{(1)}$	=	0.11159947

$d_3^{(0)}$, $d_3^{(1)}$, $g_2^{(0)}$ and $g_2^{(1)}$ were taken as negative constants.

TABLE C.2

Values of parameters A_j and B_j in the generalized Han and Starling equation (Starling, 1973).

Parameter subscript (j)	Parameter Value	
	A_j	B_j
1	0.443690	0.115449
2	1.284380	-0.920731
3	0.356306	1.70871
4	0.544979	-0.270896
5	0.528629	0.349261
6	0.484011	0.754130
7	0.0705233	-0.044448
8	0.504087	1.32245
9	0.0307455	0.179433
10	0.0732828	0.463492
11	0.006450	-0.022143

TABLE C.3

Optimized coefficients for the Chaudron equation (Chaudron et al, 1973)

Component	$C_{a,1}$	$C_{a,2}$	$C_{a,3}$	$C_{b,1}$	$C_{b,2}$	$C_{b,3}$
Methane	0.40967470	0.22458091E-01	-0.91956459E-02	0.88023049E-01	-0.52911710E-02	0.19177828E-02
Ethane	0.78866631	-0.8537238	0.47932892	0.14329590	-0.12171415	0.59102997E-01
Propane	0.43590488	-0.17353137E-01	0.64985006E-02	0.10015148	-0.4604456E-01	0.27707769E-01
Propene	0.47766385	-0.25176058	0.19929708	0.14625807	-0.10421069	0.41906842E-01
n-Butane	0.27387763E-01	0.6441934	-0.25200684	0.5803150E-01	0.54847368E-01	-0.31640223E-01
n-Pentane	0.45907634	-0.50429213E-01	0.16830703E-01	0.13701341	-0.14607899	0.91826751E-01
n-Hexane	0.46073222	-0.31919533E-01	0.49562734E-02	0.10964856	-0.98488547E-01	0.76020935E-01
n-Heptane	-0.27451394	0.11752720E+01	-0.42302919	0.44787026E-01	0.82135816E-01	-0.44797952E-01
n-Octane	-0.19457486	0.11008389E+01	-0.42560414	0.64435102E-01	0.18707489E-01	0.84749789E-03
n-Nonane	0.16428597	0.3458626~~4~~	-0.1655586E-03	0.68801827E-01	0.16780767E-01	-0.15390650E-04
Hydrogen Sulfide	0.32354017	0.1640353	-0.65736106E-01	0.93086018E-01	-0.18007459E-01	0.75856515E-02

TABLE C.4

Individually fitted constants for the Han and Starling equation (Starling, 1973)

Component	B_o	A_o	C_o	D_o	E_o	b
Methane	0.723251	7520.29	271092×10^3	107737×10^5	301122×10^5	0.925404
Ethane	0.826059	13439.30	295195×10^4	257477×10^6	146819×10^8	3.112060
Propane	0.964762	18634.70	796178×10^4	453708×10^6	256053×10^8	5.462480
n-Butane	1.56588	32544.70	137436×10^5	333159×10^6	230902×10^7	9.140660
n-Pentane	2.44417	51108.20	223931×10^5	101769×10^7	390860×10^8	16.607000
n-Hexane	2.66233	45333.10	526067×10^5	552158×10^7	626433×10^9	29.498300
n-Heptane	3.60493	77826.90	615662×10^5	777123×10^7	636251×10^7	27.441500
n-Octane	4.86965	81690.60	996546×10^5	790575×10^7	346419×10^8	10.590700
	a	d	α	c	γ	
Methane	2574.89	47489.1	0.468828	437222×10^3	1.48640	
Ethane	22404.50	702189.0	0.909681	681826×10^4	2.99656	
Propane	40066.40	150520×10^2	2.014020	274461×10^5	4.56182	
n-Butane	71181.80	364238×10^2	4.009850	700044×10^5	7.54122	
n-Pentane	162185.00	388521×10^2	7.067020	135286×10^6	11.85930	
n-Hexane	434517.00	327460×10^2	9.702300	318412×10^6	14.87200	
n-Heptane	359087.00	8351150.0	21.878200	374876×10^6	24.76040	
n-Octane	131646.00	185906×10^3	34.512400	642053×10^6	21.98880	

APPENDIX D
ANALYTICAL SOLUTION OF A CUBIC EQUATION

A general cubic equation can be written as:

$$C_1 x^3 + C_2 x^2 + C_3 x + C_4 = 0 \qquad (D.1)$$

or

$$x^3 + px^2 + qx + r = 0 \qquad (D.2)$$

where:

$$p = \frac{C_2}{C_1}; \quad q = \frac{C_3}{C_1}; \quad r = \frac{C_4}{C_1} \qquad (D.3)$$

Equation (D.2) can be transformed as follows by putting:

$$x = y - \frac{p}{3}; \quad A = \frac{1}{3}(3q - p^2) \qquad (D.4)$$

$$B = \frac{1}{27}(2p^3 - 9\,pq + 27\,r) \qquad (D.5)$$

$$y^3 + A\,y + B = 0 \qquad (D.6)$$

The procedure for solving equation (D.6) depends on the sign of the discriminant.

$$D = \frac{A^3}{27} + \frac{B^2}{4}$$

D may be zero , greater than zero or less than zero. These three cases and their solutions are discussed below.

Case 1 $D > 0$

In this case there is only one real root, which is given by:

$$y_1 = M + N \tag{D.7}$$

where: $$M = \left(-\frac{B}{2} + \sqrt{D}\right)^{1/3} \tag{D.8}$$

$$N = \left(-\frac{B}{2} - \sqrt{D}\right)^{1/3} \tag{D.9}$$

Imaginary roots are given by:

$$y_2 = -\tfrac{1}{2}(M + N) + \frac{\sqrt{3}}{2}(M - N)i \tag{D.10}$$

$$y_3 = -\tfrac{1}{2}(M + N) - \frac{\sqrt{3}}{2}(M - N)i \tag{D.11}$$

Case 2 $D = 0$

In this case there are three real roots and at least two are equal. Since both A and B can be positive as well as negative, D can become zero either by A and B simultaneously becoming zero, or by $(A^3/27)$ and $(B^2/4)$ cancelling out. If A and B are both zero then we have three equal roots. This occurs at the critical point in the case of a cubic equation of state. Three roots are given by:

$$y_1 = M + N \tag{D.12}$$

$$y_2 = -\tfrac{1}{2}(M + N) \tag{D.13}$$

$$y_3 = -\tfrac{1}{2}(M + N) \tag{D.14}$$

In some cases multiple roots are not detected even if they are known to exist. To avoid this problem we note that three roots in case 1 and case 2 are similar except the imaginary parts in equations (D.10) and (D.11). Imaginary parts are first calculated and if they are less than a given tolerance (negligible compared to the real part), then multiple roots are assumed.

Case 3 $D < 0$

In this case there are three real roots which are given by:

$$y_i = 2\left(\sqrt{-\frac{A}{3}}\right) \cos\left(\frac{\phi}{3} + 120k\right) \tag{D.15}$$

$k = 0, 1, 2$
$i = 1, 2, 3$

where: $$\phi = \cos^{-1}\left[\pm\sqrt{\frac{B^2}{4} / \left(-\frac{A^3}{27}\right)}\right] \tag{D.16}$$

ϕ is in degrees
The minus sign applies when $B > 0$.
The positive sign applies when $B < 0$.

The corresponding roots of equation (D.2) are given by:

$$x_i = y_i - \frac{p}{3} \tag{D.17}$$

Equation (D.17) is valid for all three cases.

APPENDIX E

EXPRESSIONS FOR THE ENTHALPY AND THE ENTROPY DEPARTURES

The enthalpy departure

The enthalpy departure is related to the equation of state by the following equation:

$$H - H^{o} = PV - RT + H_1 \tag{E.1}$$

where: $$H_1 = \int_{\infty}^{V} T \left(\frac{\partial P}{\partial T}\right)_V - P \tag{E.2}$$

H_1 can be calculated from any equation of state. Using the new equation of state (equation 4.1) we have:

$$H_1 = \int_{\infty}^{V} \left[\frac{RT}{V-b} - \frac{T\frac{\partial a}{\partial T}}{V(V+b) + c(V-b)} - \frac{RT}{V-b} + \frac{a}{V(V+b) + c(V-b)}\right] dV \tag{E.3}$$

$$H_1 = \int_{\infty}^{V} - \left(T\frac{\partial a}{\partial T} - a\right) \frac{dV}{V(V+b) + c\,(V-b)} \tag{E.4}$$

$$H_1 = \int_{\infty}^{V} - \left(T\frac{\partial a}{\partial T} - a\right) \frac{dV}{\left[\left(V + \frac{b+c}{2}\right)^2 - \left\{\sqrt{\left(\frac{b+c}{2}\right)^2 + bc}\right\}^2\right]} \tag{E.5}$$

If we let $\left(\frac{b+c}{2}\right)^2 + bc = n^2$ (E.6)

and $V + \frac{b+c}{2} = x$ (E.7)

Then $dV = dx$ (E.8)

Combining equations (E.6), (E.7) and (E.8) with equation (E.5):

$$H_1 = -\left(T\frac{\partial a}{\partial T} - a\right)\int \frac{dx}{x^2 - n^2} \qquad (E.9)$$

$$H_1 = -\left(T\frac{\partial a}{\partial T} - a\right)\frac{1}{2n} \cdot \ln\left(\frac{x-n}{x+n}\right) \qquad (E.10)$$

Substituting for x and evaluating the limits of integration in equation (E.10) we have:

$$H_1 = -\left(T\frac{\partial a}{\partial T} - a\right) . \frac{1}{2n} \cdot \ln\left(\frac{V + \frac{b+c}{2} - n}{V + \frac{b+c}{2} + n}\right) \qquad (E.11)$$

Let $\frac{b+c}{2} - n = m$ (E.12)

and $\frac{b+c}{2} + n = q$ (E.13)

combining equations (E.11), (E.12) and (E.13) with equation (E.1) yields:

$$H - H^0 = PV - RT - \left(T\frac{\partial a}{\partial T} - a\right) . \frac{1}{2n} \cdot \ln\left(\frac{V+m}{V+q}\right) \qquad (E.14)$$

This equation can also be written as:

$$H - H^0 = RT\,(Z - 1) - \left(T\frac{\partial a}{\partial T} - a\right) . \frac{1}{2n} . \ln\left(\frac{Z+M}{Z+Q}\right) \qquad (E.15)$$

where: $M = \frac{mP}{RT}$; $Z = \frac{PV}{RT}$

$$Q = \frac{qP}{RT} \tag{E.16}$$

For the Peng and Robinson equation

By setting b = c in equation (4.1) we have $n^2 = 2b^2$; $n = \sqrt{2}\,b$; $m = b - \sqrt{2}b = -0.414b$; $q = b + \sqrt{2}b = 2.414b$; $M = -0.414B$ and $Q = 2.414B$.

Therefore equation (E.15) reduces to:

$$H - H^0 = RT\,(Z - 1) - (T\,\frac{\partial a}{\partial T} - a).\,\frac{1}{2\sqrt{2}b}\,\ln\left(\frac{Z - 0.414B}{Z + 2.414B}\right) \tag{E.17}$$

For the Redlich and Kwong equation and the Soave equation

By setting c = 0, we have $n = b/2$; $m = 0$; $q = b$; $M = 0$; and $Q = B$.

Therefore equation (E.15) reduces to:

$$H - H^0 = RT\,(Z - 1) - (T\,\frac{\partial a}{\partial T} - a).\,\frac{1}{b}\,.\,\ln\left(\frac{Z}{Z+B}\right) \tag{E.18}$$

For the Chaudron equation

$$H - H^0 = PV - RT - \frac{RT^2}{V-b}\,\frac{db}{dT} - (T^{\frac{1}{2}}\,\frac{da}{dT} - \frac{3a}{2\sqrt{T}} - \frac{aT^{\frac{1}{2}}}{b}\,\frac{db}{dT})\,\frac{1}{b}\,\ln\left(\frac{V}{V+b}\right)$$

$$+ \frac{a}{b}\,\frac{T^{\frac{1}{2}}}{(V+b)}\,\frac{db}{dT} \tag{E.19}$$

For the Simonet and Behar equation

$$H - H^o = PV - RT + \frac{1}{b} \ln \frac{V}{V+b} \left(a - T \frac{\partial a}{\partial T}\right)$$

$$+ \left[\frac{aT}{b} \left(\frac{1}{b} \ln \frac{V}{V+b} + \frac{1}{V+b}\right) - \frac{RT^2}{V-b}\right] \frac{db}{dT} \qquad (E.20)$$

For the Han and Starling equation

$$H - H^o = C_1 \rho + C_2 \rho^2 + C_3 \rho^5 + f[\rho] \qquad (E.21)$$

where: $$C_1 = B_o RT - 2A_o - \frac{4C_o}{T^2} + \frac{5D_o}{T^3} - \frac{6E_o}{T^4} \qquad (E.22)$$

$$C_2 = \tfrac{1}{2} \left(2b\ RT - 3a - \frac{4d}{T}\right) \qquad (E.23)$$

$$C_3 = \frac{\alpha}{5} \left(6a + \frac{7d}{T}\right) \qquad (E.24)$$

$$f[\rho] = \frac{c}{\gamma T^2} \left[3 - \left(3 + \tfrac{1}{2} \gamma \rho^2 - \gamma^2 \rho^4\right) \exp\left(-\gamma\rho^2\right)\right] \qquad (E.25)$$

The entropy departure

The entropy departure is related to the equation of state by the following equation:

$$S - S^o = -R \ln \left(\frac{RT}{V}\right) - \int_{\infty}^{V} \left[\frac{R}{V} - \left(\frac{\partial P}{\partial T}\right)_V\right] dV \qquad (E.26)$$

Let $$S_1 = \int_{\infty}^{V} \left[\frac{R}{V} - \left(\frac{\partial P}{\partial T}\right)_V\right] dV \qquad (E.27)$$

Using the new equation of state:

$$S_1 = \int_{\infty}^{V} \left[\frac{R}{V} - \frac{R}{V-b} + \frac{\frac{\partial a}{\partial T}}{V(V+b) + c(V-b)} \right] dV \qquad (E.28)$$

$$= R \ln \left(\frac{V}{V-b}\right) + \frac{\partial a}{\partial T} \cdot \frac{1}{2n} \cdot \ln \left(\frac{V+m}{V+q}\right) \qquad (E.29)$$

where m and q are given by equations (E.12) and (E.13) respectively. Combining equation (E.29) with equation (E.26) yields:

$$S - S^o = -R \ln \left(\frac{RT}{V}\right) - R \ln \left(\frac{V}{V-b}\right) - \frac{\partial a}{\partial T} \cdot \frac{1}{2n} \cdot \ln \left(\frac{V+m}{V+q}\right) \qquad (E.30)$$

$$S - S^o = -R \ln \left(\frac{RT}{V-b}\right) - \frac{\partial a}{\partial T} \cdot \frac{1}{2n} \cdot \ln \left(\frac{V+m}{V+q}\right) \qquad (E.31)$$

This equation can also be written as:

$$S - S^o = -R \ln \frac{P}{Z-B} - \frac{\partial a}{\partial T} \cdot \frac{1}{2n} \cdot \ln \left(\frac{Z+M}{Z+Q}\right) \qquad (E.32)$$

where M, Q and Z are given by equation (E.16).

For the Peng and Robinson equation

The following expression for the entropy departure is obtained by setting c = b in equation (4.1).

$$S - S^{o} = -R \ln \frac{P}{Z-B} - \frac{\partial a}{\partial T} \cdot \frac{1}{2\sqrt{2}\, b} \cdot \ln \left(\frac{Z - 0.414B}{Z + 2.414B}\right) \qquad (E.33)$$

For the R-K and S-R-K equations

c = 0 in equation (4.1).

$$S - S^{o} = -R \ln \frac{P}{Z-B} - \frac{\partial a}{\partial T} \cdot \frac{1}{b} \ln \left(\frac{Z}{Z+B}\right) \qquad (E.34)$$

For the Han and Starling equation

$$S - S^{o} = -R \ln (\rho RT) - S_1 - S_2 + S_3 + S_4 \qquad (E.35)$$

where: $$S_1 = \left(B_o R + \frac{2C_o}{T^3} - \frac{3D_o}{T^4} + \frac{4E_o}{T^5}\right)\rho \qquad (E.36)$$

$$S_2 = \tfrac{1}{2} \left(b\, R + \frac{d}{T^2}\right)\rho^2 \qquad (E.37)$$

$$S_3 = \frac{\alpha\, d\, \rho^5}{5T^2} \qquad (E.38)$$

$$S_4 = \frac{2c}{\gamma T^3} \left[1 - \left(1 + \tfrac{1}{2}\gamma\, \rho^2\right) \exp\left(-\gamma\rho^2\right)\right] \qquad (E.39)$$

Evaluation of $\frac{\partial a}{\partial T}$ for the new equation

$$\text{Since } a = \Omega_a \cdot \frac{R^2 T_c^{\,2}}{P_c} \cdot \alpha[T_r] \tag{E.40}$$

$$\frac{\partial a}{\partial T} = \Omega_a \cdot \frac{R^2 T_c^{\,2}}{P_c} \cdot \frac{\partial \alpha}{\partial T} \tag{E.41}$$

$$\alpha = [1 + F\,(1 - T_r^{\frac{1}{2}})]^2 \tag{E.42}$$

$$\therefore \quad \frac{\partial \alpha}{\partial T} = - \frac{F[1 + F(1 - T_r^{\frac{1}{2}})]^2}{T_c^{\frac{1}{2}}\, T^{\frac{1}{2}}} = - \frac{F\alpha}{T_c^{\frac{1}{2}}\, T^{\frac{1}{2}}} = \frac{-F\,\alpha\, T_r^{-\frac{1}{2}}}{T_c} \tag{E.43}$$

Combining equation (E.43) with equation (E.41) yields:

$$\frac{\partial a}{\partial T} = \Omega_a \cdot \frac{R^2 T_c}{P_c} \cdot -F\,\alpha\, T_r^{-\frac{1}{2}} \tag{E.44}$$

Expressions similar to equation (E.44) can be obtained for the P-R equation and the R-K equation.

APPENDIX F

CALCULATION OF PURE COMPONENT FUGACITY

The fugacity of a pure component is related to the equation of state by the following equation:

$$\ln \frac{f}{P} = Z-1 - \ln Z - \int_{\infty}^{V} \left(\frac{P}{RT} - \frac{1}{V}\right) dV \qquad (F.1)$$

Using the new equation of state

$$\frac{P}{RT} = \frac{1}{V-b} - \frac{a/RT}{V(V+b) + c(V-b)} \qquad (F.2)$$

$$\int_{\infty}^{V} \left(\frac{P}{RT} - \frac{1}{V}\right) dV = \int_{\infty}^{V} \left[\frac{1}{V-b} - \frac{1}{V}\right] dV - \frac{a}{RT} \int_{\infty}^{V} \frac{dV}{V(V+b) + c(V-b)} \qquad (F.3)$$

$$= \ln \left(\frac{V-b}{V}\right) - \frac{a}{2RTn} \ln \left(\frac{V+m}{V+q}\right) \qquad (F.4)$$

$$= \ln \left(\frac{Z-B}{Z}\right) - \frac{a}{2RTn} \ln \left(\frac{Z+M}{Z+Q}\right) \qquad (F.5)$$

Hence: $$\ln \frac{f}{P} = Z-1 - \ln Z - \ln \left(\frac{Z-B}{Z}\right) + \frac{a}{2RTn} \ln \left(\frac{Z+M}{Z+Q}\right) \qquad (F.6)$$

where m, q, M, Q, Z, B and n are the same variables defined in Appendix E. Equation (F.6) can be written as:

$$\ln \frac{f}{P} = Z-1 - \ln (Z-B) + \frac{a}{2RTn} \ln \left(\frac{Z+M}{Z+Q}\right) \qquad (F.7)$$

By setting c = b (for the Peng and Robinson equation).

$$\ln \frac{f}{P} = Z-1 - \ln (Z-B) + \frac{a}{2\sqrt{2}\, b\, RT} \ln \left(\frac{Z - 0.414B}{Z + 2.414B}\right) \qquad (F.8)$$

By setting c = 0 (for the Soave equation)

$$\ln \frac{f}{P} = Z-1 - \ln (Z-B) + \frac{a}{bRT} \ln \left(\frac{Z}{Z+B}\right) \qquad (F.9)$$

<u>For the Han and Starling equation (Starling 1973)</u>

$$RT \ln f = \ln (\rho RT) + 2C_1\rho + \frac{3}{2} C_2 \rho^2 + \frac{6}{5} C_3 \rho^5$$

$$+ C_4 \left[1 - \left(1 - \frac{1}{2} \gamma \rho^2 + \gamma^2\rho^4\right) e^{-\gamma\rho^2}\right] \qquad (F.10)$$

where: $C_1 = B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}$

$$C_2 = bRT - a - \frac{d}{T}$$

$$C_3 = \alpha\left(a + \frac{d}{T}\right)$$

$$C_4 = \frac{c}{\gamma T^2}$$

Fugacity of component i in a fluid mixture

The fugacity of component in in a multicomponent mixture is given by:

$$RT \ln \left(\frac{f_i}{x_i P}\right) = \int_{\underline{V}}^{\infty} \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,\underline{V},n_j} - \frac{RT}{\underline{V}}\right] d\underline{V} - RT \ln Z \qquad (F.11)$$

$$\underline{V} = nV$$

where: $\underline{V}$ is the total volume; V is the molar volume and n is the total number of moles. x_i is the mole fraction of the ith component in the liquid or vapour phase.

Using the new equation of state:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + (b+c)\,V - bc} \qquad (F.12)$$

$$= \frac{RT}{\frac{\underline{V}}{n} - b} - \frac{a}{\left(\frac{\underline{V}^2}{n^2} + (b+c)\,\frac{\underline{V}}{n} - bc\right)} \qquad (F.13)$$

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,\underline{V},n_j} = RT \frac{\partial}{\partial n_i}\left(\frac{\underline{V}}{n} - b\right)^{-1} - \frac{\partial}{\partial n_i}\left(\frac{a}{\frac{\underline{V}^2}{n^2} + (b+c)\,\frac{\underline{V}}{n} - bc}\right) \qquad (F.14)$$

$$RT \frac{\partial}{\partial n_i}\left(\frac{\underline{V}}{n} - b\right)^{-1} = \frac{RT\left(\frac{\underline{V}}{n^2} + b'\right)}{\left(\frac{\underline{V}}{n} - b\right)^2} = A \qquad (E.15)$$

$$\frac{\partial}{\partial n_i}\left(\frac{a}{q}\right) = \frac{a'q - a\,q'}{q^2} \tag{F.16}$$

where: $$q = \frac{\underline{V}^2}{n^2} + (b+c)\,\frac{\underline{V}}{n} - bc \tag{F.17}$$

$$q' = \left(\frac{\partial q}{\partial n_i}\right)_{T,\underline{V},n_j} = -\frac{2\underline{V}^2}{n^3} - \frac{(b+c)}{n^2}\,\underline{V} + \frac{\underline{V}}{n}\,(b'+c') - bc' - cb' \tag{F.18}$$

$$a' = \left(\frac{\partial a}{\partial n_i}\right)_{T,\underline{V},n_j}\ ;\quad b' = \left(\frac{\partial b}{\partial n_i}\right)_{T,\underline{V},n_j};\quad c' = \left(\frac{\partial c}{\partial n_i}\right)_{T,\underline{V},n_j}$$

$$\frac{\partial}{\partial n_i}\left(\frac{a}{q}\right) = \frac{a'}{q} - \frac{aq'}{q^2}$$

$$\therefore\quad \ln\left(\frac{f}{x_i p}\right) = \int_{\underline{V}}^{\infty}\left[\left(A - \frac{a'}{q} + \frac{aq'}{q^2}\right) - \frac{RT}{\underline{V}}\right]d\underline{V} - RT\ \ln Z \tag{F.19}$$

$$\int_{V}^{\infty} A\ d\underline{V} = RT\int \frac{\underline{V} + n^2b'}{(\underline{V} - bn)^2}\,d\underline{V} \tag{F.20}$$

$$= RT\ \left[\int \frac{\underline{V}}{(\underline{V} - bn)^2}\,d\underline{V} + \int \frac{n^2b'}{(\underline{V} - bn)^2}\,d\underline{V}\right] \tag{F.21}$$

$$= RT\ \left[\left(\ln\,(\underline{V} - bn) - \frac{bn}{(\underline{V} - bn)}\right) - n^2b'\,\frac{1}{(\underline{V} - bn)}\right]_{V}^{\infty} \tag{F.22}$$

$$\int \frac{a'}{q}\, d\underline{V} = n^2 a' \int_{\underline{V}}^{\infty} \frac{d\underline{V}}{\underline{V}^2 + (b+c)\, n\underline{V} - bcn^2} \tag{F.23}$$

$$= n^2 a' \int \frac{d\underline{V}}{(\underline{V} + \alpha)^2 - \beta^2} \tag{F.24}$$

$$\alpha = \frac{(b+c)n}{2}\ ; \qquad \beta^2 = (bc + \frac{(b+c)^2}{4})n^2 \tag{F.25}$$

$$\int \frac{a'}{q}\, d\underline{V} = n^2 a' \int \left[\frac{-\frac{1}{2\beta}}{(\underline{V} + \alpha + \beta)} + \frac{\frac{1}{2\beta}}{(\underline{V} + \alpha - \beta)} \right] d\underline{V} \tag{F.26}$$

$$= \frac{n^2 a'}{2\beta} \left[\ln \left(\frac{\underline{V} + \alpha - \beta}{\underline{V} + \alpha + \beta} \right) \right]_{\underline{V}}^{\infty} \tag{F.27}$$

$$\int_{\underline{V}}^{\infty} \frac{aq'}{q^2}\, d\underline{V}$$

$$= an \int \frac{-2[\underline{V}^2 + (b+c)n\underline{V} - bcn^2] + n^2(b'+c')\underline{V} - (bc'+cb')n^3 + (b+c)n\underline{V} - 2bcn^2}{q^2}\, d\underline{V}$$

(F.28)

$$= an \int [\ \frac{-2q + \phi\, V - (bc' + cb')n^3 - 2bcn^2}{q^2}\ d\underline{V} \tag{F.29}$$

$$= an \int \frac{-2}{q} + \frac{\frac{\phi}{2}(2\underline{V} + (b+c)n) - (bc'+cb')n^3 - 2bcn^2 - \frac{\phi(b+c)n}{2}}{q^2}\ d\underline{V}$$

$$= an \int \left(E_1 + E_2 + E_3\right) d\underline{V} \tag{F.30}$$

where: $$E_1 = \frac{-2}{q} \tag{F.31}$$

$$E_2 = \frac{\frac{\phi}{2}\,(2\underline{V} + (b+c)n)}{q^2} \tag{F.32}$$

$$\phi = n^2\,(b' + c') + (b+c)n \tag{F.33}$$

$$E_3 = \frac{\gamma}{q^2} \tag{F.34}$$

$$\gamma = -\,(bc' + cb')n^3 - 2bcn^2 - \frac{\phi(b+c)n}{2} \tag{F.35}$$

$$\int_{\underline{V}}^{\infty} E_1\, d\underline{V} = -2 \int_{\underline{V}}^{\infty} \frac{d\underline{V}}{(\underline{V}^2 + (b+c)n\underline{V} - bcn^2)} \tag{F.36}$$

$$= -\frac{1}{\beta}\,[\ln\,(\frac{\underline{V} + \alpha - \beta}{\underline{V} + \alpha + \beta})]_{\underline{V}}^{\infty} \quad \text{as derived earlier.} \tag{F.37}$$

$$\int_{\underline{V}}^{\infty} E_2\, d\underline{V} = \frac{\phi}{2} \int_{\underline{V}}^{\infty} \frac{2\underline{V} + (b+c)n}{(\underline{V}^2 + (b+c)n\underline{V} - bcn^2)^2}\, d\underline{V} \tag{F.38}$$

$$= \frac{\phi}{2}\,[\frac{-1}{(\underline{V}^2 + (b+c)n\underline{V} - bcn^2)}]_{\underline{V}}^{\infty} \tag{F.39}$$

$$\int_{\underline{V}}^{\infty} E_3 \, d\underline{V} = \gamma \int \frac{R_1}{(\underline{V}+\alpha+\beta)^2} + \frac{R_2}{(\underline{V}+\alpha+\beta)} + \frac{R_3}{(\underline{V}+\alpha-\beta)^2} + \frac{R_4}{(\underline{V}+\alpha-\beta)} \, d\underline{V} \qquad (F.40)$$

R_1, R_2, R_3 and R_4 can be obtained by expanding the numerator and equating coefficients. Thus:

$$R_1 = \frac{1}{4\beta^2}; \qquad R_3 = \frac{1}{4\beta^2}$$

$$R_2 = \frac{1}{4\beta^3}; \qquad R_4 = -\frac{1}{4\beta^3} \qquad (F.41)$$

$$\therefore \int E_3 \, d\underline{V} = \frac{\gamma}{4\beta^3} \left[\frac{-\beta}{(\underline{V}+\alpha+\beta)} + \ln(\underline{V}+\alpha+\beta) - \frac{\beta}{(\underline{V}+\alpha-\beta)} - \ln(\underline{V}+\alpha-\beta)\right]_{\underline{V}}^{\infty} \qquad (F.42)$$

$$= \frac{\gamma}{4\beta^2} \left[\ln\left(\frac{\underline{V}+\alpha+\beta}{\underline{V}+\alpha-\beta}\right) - \beta\left(\frac{1}{\underline{V}+\alpha+\beta} + \frac{1}{\underline{V}+\alpha-\beta}\right)\right]_{\underline{V}}^{\infty} \qquad (F.43)$$

Hence:

$$RT \ln \frac{f_i}{x_i P} = RT\left[\ln(\underline{V} - bn) - \frac{bn}{(\underline{V}\ bn)} - n^2 b' \frac{1}{(\underline{V} - bn)}\right]_{\underline{V}}^{\infty}$$

$$- \frac{n^2}{2\beta} a' \ln\left(\frac{\underline{V} + \alpha - \beta}{\underline{V} + \alpha + \beta}\right)\Big]_{\underline{V}}^{\infty} + an \left\{- \frac{1}{\beta} \ln\left(\frac{\underline{V} + \alpha - \beta}{\underline{V} + \alpha + \beta}\right)\right.$$

$$- \frac{\phi}{2} \left(\frac{1}{\underline{V}^2 + (b+c)\, n\underline{V} - bcn^2}\right) + \frac{\gamma}{4\beta^3} \left[\ln\left(\frac{\underline{V} + \alpha + \beta}{\underline{V} + \alpha - \beta}\right)\right.$$

$$- \frac{2\beta\ (\underline{V} + \alpha)}{(\underline{V}+\alpha)^2 - \beta^2}\ ]\}_{\underline{V}}^{\infty} - RT[\ln \underline{V}]_{\underline{V}}^{\infty} - RT \ln Z \qquad (F.44)$$

From the mixing rules:

$$a = \sum \sum x_i\ x_j\ a_{ij} \qquad (F.45)$$

$$= \frac{1}{n^2} \sum \sum n_i\ n_j\ a_{ij} \qquad (F.46)$$

$$a' = - \frac{2}{n^3}\ \sum \sum n_i\ n_j\ a_{ij} + \frac{1}{n^2}\ 2 \sum n_j\ a_{ij} \qquad (F.47)$$

$$= \frac{2}{n}\ [\sum x_j\ a_{ij} - a] \qquad (F.48)$$

$$b = \sum x_i\ b_i = \frac{1}{n} \sum n_i\ b_i \qquad (F.49)$$

$$b' = \frac{n\ b_i - \sum n_i\ b_i}{n^2} = \frac{1}{n}\ (b_i - b) \qquad (F.50)$$

$$c = \sum x_i\ c_i = \frac{1}{n} \sum n_i\ c_i \qquad (F.51)$$

$$c' = \frac{1}{n}\ (b_i - b) \qquad (F.52)$$

Let $d = \frac{\beta}{n}$ (F.53)

$$X = \frac{1}{n}\ (\underline{V} + \alpha) \qquad (F.54)$$

For n = 1,

$$\underline{V} + \alpha + \beta = X + d$$

$$\underline{V} + \alpha - \beta = X - d$$

$$\underline{V} + \alpha = X$$

$$\therefore \quad (\underline{V} + \alpha)^2 - \beta^2 = X^2 - d^2$$

$$\phi = b' + c' + b + c$$

$$\gamma = -\frac{1}{2}(3bc' + 3b'c + 6bc + bb' + cc' + b^2 + c^2)$$

Taking limits and writing the fugacity expression in terms of molar volumes. For one mole:

$$RT \ln \left(\frac{f_i}{x_i P}\right) = -RT \ln \left(\frac{V-b}{V}\right) - RT \ln Z + RT \left(\frac{b}{V-b} + \frac{b'}{V-b}\right)$$

$$+ \frac{a'}{2d} \ln \left(\frac{X-d}{X+d}\right) + \frac{a}{d} \ln \left(\frac{X-d}{X+d}\right)$$

$$+ \frac{a(b' + c' + b + c)}{2(X^2 - d^2)} + \frac{a}{8d^3}(3bc' + 3b'c + 6bc + bb' + cc'$$

$$+ b^2 + c^2) \left[\ln \left(\frac{X+d}{X-d}\right) - \frac{2Xd}{X^2 - d^2}\right] \qquad \text{(F.55)}$$

$$RT \ln\left(\frac{f_i}{x_i P}\right) =$$

$$= RT \cancel{\ln\left(\frac{f_i}{x_i P}\right)}(Z-B) + RT\,\frac{b+b'}{(V-b)} - \left(\frac{a'}{2d} + \frac{a}{d}\right) \ln\left(\frac{X+d}{X-d}\right)$$

$$+ \frac{a(b' + c' + b + c)}{2(X^2 - d^2)} - \frac{a}{8d^3}\,[(b' + c')(b+c) + (b+c)^2$$

$$+ 2\,(cb' + bc') + 4bc]\,\left[\frac{2Xd}{X^2 - d^2} - \ln\left(\frac{X+d}{X-d}\right)\right] \qquad \text{(F.56)}$$

$$= -RT \ln (Z-B) + RT\,\frac{b_i}{(V-b)} - \frac{\sum x_j\, a_{ij}}{d} \ln\left(\frac{X+d}{X-d}\right)$$

$$+ \frac{a(b_i + c_i)}{2(X^2 - d^2)} + \frac{a}{8d^3}\,[3b\,(c_i - c) + 3c\,(b_i - b) + 6\,bc$$

$$+ bb_i + cc_i]\,\left[\ln\left(\frac{X+d}{X-d}\right) - \frac{2Xd}{X^2 - d^2}\right] \qquad \text{(F.57)}$$

<u>Conversion to Peng and Robinson equation</u>

By setting c = b, equation (F.57) reduces to:

$$\ln \frac{f_i}{x_i P} = -\ln (Z-B) + \frac{b_i}{V-b} - \frac{\sum x_j\, a_{ij}}{\sqrt{2}\;RTb} \ln\left(\frac{V + 2.414b}{V - 0.414b}\right)$$

$$+ \frac{ab_i}{[(V+b)^2 - 2b^2]RT} + \frac{a}{8 \times 2\sqrt{2}\, b^3\, RT}\,(8bb_i)\left[\ln\left(\frac{V+2.414b}{V-0.414b}\right) - \right.$$

$$\left. - \frac{2\sqrt{2}b\,(V+b)}{(V+b)^2 - 2b^2}\right] \qquad \text{(F.58)}$$

$$= -\ln (Z-B) - \frac{a}{2\sqrt{2}\, bRT} \left[\frac{2\sum x_j\, a_{ij}}{a} - \frac{b_i}{b} \right] \ln \left(\frac{V + 2.414b}{V - 0.414b}\right)$$

$$+ \frac{b_i}{b} \left\{ \frac{b}{V-b} - \frac{aV/RT}{[(V+b)^2 - 2b^2]} \right\}$$

From the equation of state:

$$Z = \frac{Z}{Z-B} - \frac{aV/RT}{(V+b)^2 - 2b^2} \qquad \text{(F.59)}$$

$\therefore$ The last term in equation (F.58) becomes:

$$\frac{b_i}{b} \left(\frac{B}{Z-B} + Z - \frac{Z}{Z-B} \right)$$

$$= \frac{b_i}{b} (Z-1)$$

$$\therefore \quad \ln \left(\frac{f_i}{x_i P}\right) = -\ln (Z-B) - \frac{a}{2\sqrt{2}\, bRT} \left[\frac{2\sum x_j\, a_{ij}}{a} - \frac{b_i}{b} \right] \ln \left(\frac{V + 2.414b}{V - 0.414b}\right)$$

$$+ \frac{b_i}{b} (Z-1) \qquad \text{(F.60)}$$

$$= - \ln (Z-B) - \frac{A}{2\sqrt{2}\, B} \left[\frac{2\sum x_j\, a_{ij}}{a} - \frac{b_i}{b} \right] \ln \left(\frac{Z + 2.414B}{Z - 0.414B}\right)$$

$$+ \frac{b_i}{b} (Z-1) \qquad \text{(F.61)}$$

Conversion to Soave equation

By setting c = 0, equation (F.57) reduces to:

$$\ln\left(\frac{f_i}{x_i P}\right) = -\ln(Z-B) + \frac{b_i}{V-b} - \frac{2\sum x_j a_{ij}}{bRT}\ln\left(\frac{V+b}{V}\right)$$

$$+ \frac{ab_i}{2V(V+b)RT} + \frac{a}{b^3RT}(bb_i)\left[\ln\left(\frac{V+b}{V}\right) - \frac{b(V+\frac{b}{2})}{V(V+b)}\right] \qquad (F.62)$$

$$= -\ln(Z-B) + \frac{b_i}{V-b} - \frac{aV/RT}{V(V+b)}\frac{b_i}{b}$$

$$- \frac{a}{bRT}\left[\frac{2\sum x_j a_{ij}}{a} - \frac{b_i}{b}\right]\ln\left(1+\frac{b}{V}\right) \qquad (F.63)$$

The Soave equation is:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \qquad (F.64)$$

$$Z = \frac{PV}{RT} = \frac{V}{V-b} - \frac{aV/RT}{V(V+b)} \qquad (F.65)$$

$$Z = \frac{Z}{Z-B} - \frac{aV/RT}{V(V+b)} \qquad (F.66)$$

$$\therefore \quad \ln\left(\frac{f_i}{x_i P}\right) = -\ln(Z-B) + \frac{b_i}{b}(Z-1)$$

$$- \frac{A}{B}\left[\frac{2\sum x_j a_{ij}}{a} - \frac{b_i}{b}\right]\ln\left(1+\frac{B}{Z}\right) \qquad (F.67)$$

Fugacity of the ith component in a fluid mixture using Han and Starling equation

As before we need to evaluate $\left(\frac{\partial P}{\partial n_i}\right)_{T,\underline{V},n_j}$

$$P = \frac{nRT}{\underline{V}} + C_1 \frac{n^2}{\underline{V}^2} + C_2 \frac{n^3}{\underline{V}^3} + C_3 \frac{n^6}{\underline{V}^6}$$

$$+ \frac{cn^3}{T^2\underline{V}^3}\left(1 + \gamma \frac{n^2}{\underline{V}^2}\right) e^{-\gamma \frac{n^2}{\underline{V}^2}} \qquad (F.68)$$

where: $$C_1 = B_oRT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4} \qquad (F.69)$$

$$C_2 = bRT - a - \frac{d}{T} \qquad (F.70)$$

$$C_3 = \alpha\left(a + \frac{d}{T}\right) \qquad (F.71)$$

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,\underline{V},n_j} = \frac{RT}{\underline{V}} + (2C_1+nC_1')\frac{n}{\underline{V}^2} + (3C_2+nC_2')\frac{n^2}{\underline{V}^3}$$

$$+ (6C_3+nC_3')\frac{n^5}{\underline{V}^6} + \left(\frac{c'n^3}{T^2\underline{V}^3} + \frac{3n^2c}{T^2\underline{V}^3}\right)\left[\left(1 + \frac{\gamma n^2}{\underline{V}^2}\right) e^{-\gamma \frac{n^2}{\underline{V}^2}}\right]$$

$$+ \frac{cn^3}{T^2\underline{V}^3}\left[\left(\frac{2n\gamma}{\underline{V}^2} + \frac{n^2\gamma'}{\underline{V}^2}\right) e^{-\gamma \frac{n^2}{\underline{V}^2}} - \left(1 + \frac{\gamma n^2}{\underline{V}^2}\right)\left(\frac{2n\gamma}{\underline{V}^2} + \frac{n^2\gamma'}{\underline{V}^2}\right) e^{-\gamma \frac{n^2}{\underline{V}^2}}\right] \qquad (F.72)$$

The last term

$$= \frac{cn^3}{T^2\underline{V}^3} \left[\left(\frac{2n\gamma}{\underline{V}^2} + \frac{n^2\gamma'}{\underline{V}^2}\right)\left(\frac{-\gamma n^2}{\underline{V}^2}\right) e^{-\frac{\gamma n^2}{\underline{V}^2}} \right]$$

where C_1', C_2' etc are the differentials of these constants with respect to the number of moles of component i.

i.e $C_1' = \left(\frac{\partial C_1}{\partial n_i}\right)_{T,V,n_j}$

$$C_1' = B_o' RT - A_o' - \frac{C_o'}{T^2} + \frac{D_o'}{T^3} - \frac{E_o'}{T^4} \qquad (F.73)$$

$$C_2' = b'RT - a' - \frac{d'}{T} \qquad (F.74)$$

$$C_3' = \alpha' \left(a + \frac{d}{T}\right) + \alpha\left(a' + \frac{d'}{T}\right) \qquad (F.75)$$

In equation (F.72) only the last two terms contain exp $\left(-\frac{\gamma n^2}{\underline{V}^2}\right)$.

The last two terms can be expanded as follows:

$$\text{Last two terms} = C_5 \frac{1}{\underline{V}^3} e^{-\frac{\gamma n^3}{\underline{V}^2}} + C_6 \frac{1}{\underline{V}^5} e^{-\frac{\gamma n^2}{\underline{V}^2}} + C_7 \frac{1}{\underline{V}^7} e^{-\frac{\gamma n^2}{\underline{V}^2}} \qquad (F.76)$$

Integrating w.r.t. $\underline{V}$

$$\int = C_5 \int \frac{1}{\underline{V}^3} e^{-\frac{\gamma n^2}{\underline{V}^2}} dV + C_6 \int \frac{1}{\underline{V}} e^{-\frac{\gamma n^2}{\underline{V}^2}} dV + C_7 \int \frac{1}{\underline{V}^7} e^{-\frac{\gamma n^2}{\underline{V}^2}} dV \qquad (F.77)$$

where:

$$C_5 = \frac{1}{T^2}\,(c'n^3 + 3\,cn^2) \tag{F.78}$$

$$C_6 = C_5 \cdot \gamma n^2 \tag{F.79}$$

$$C_7 = -\,\frac{cn^3}{T^2}\,(2n\gamma + n^2\gamma')\;\gamma n^2 \tag{F.80}$$

Since $$\frac{\partial}{\partial \underline{V}}\left(e^{-\frac{\gamma n^2}{\underline{V}^2}}\right) = \frac{2\gamma n^2}{\underline{V}^3}\; e^{-\frac{\gamma n^2}{\underline{V}^2}} \tag{F.81}$$

$$\therefore \quad \int \frac{1}{\underline{V}^3}\, e^{-\frac{\gamma n^2}{\underline{V}^2}}\, d\underline{V} = \frac{1}{2\gamma n^2}\, e^{-\frac{\gamma n^2}{\underline{V}^2}} \tag{F.82}$$

$$\int \frac{1}{\underline{V}^5}\, e^{-\frac{\gamma n^2}{\underline{V}^2}}\, dV = \int \frac{1}{\underline{V}^2} \cdot \frac{1}{\underline{V}^3}\, e^{-\frac{\gamma n^2}{\underline{V}^2}}\, dV \tag{F.83}$$

Integrating by parts:

$$\int = \left[\frac{1}{\underline{V}^3} \cdot \frac{1}{2\gamma n^2}\; e^{-\frac{\gamma n^2}{\underline{V}^2}}\right] - \int \frac{1}{2\gamma n^2}\, e^{-\frac{\gamma n^2}{\underline{V}^2}} \cdot \frac{-2}{\underline{V}^3}\, d\underline{V} \tag{F.84}$$

$$= \frac{1}{2\gamma n^2}\left[\frac{1}{\underline{V}^2} + \frac{1}{\gamma n^2}\right] e^{-\frac{\gamma n^2}{\underline{V}^2}} \tag{F.85}$$

Similarly:

Similarly:

$$\int \frac{1}{\underline{V}^7} e^{-\frac{\gamma n^2}{\underline{V}^2}} dV = \int \frac{1}{\underline{V}^2} \cdot \frac{1}{\underline{V}^5} e^{-\frac{\gamma n^2}{\underline{V}^2}} d\underline{V} \qquad (F.86)$$

$$\int = \{[\frac{1}{\underline{V}^2} (\frac{1}{2\gamma n^2} (\frac{1}{\underline{V}^2} + \frac{1}{\gamma n^2}) e^{-\frac{\gamma n^2}{\underline{V}^2}})] - \int \frac{-2}{\underline{V}^3} \cdot \frac{1}{2\gamma n^2} (\frac{1}{\underline{V}^2} + \frac{1}{\gamma n^2}) e^{-\frac{\gamma n^2}{\underline{V}^2}} dV\}$$

(F.87)

$$= \frac{1}{2\gamma n^2} [(\frac{1}{\underline{V}^2} + \frac{1}{\gamma n^2})^2 + (\frac{1}{\gamma n^2})^2] e^{-\frac{\gamma n^2}{\underline{V}^2}} \qquad (F.88)$$

Substituting these integrated terms (equations (F.88), (F.85) and (F.82)) with limits into equation (F.77):

$$\int = \{\frac{C_5}{2\gamma n^2} e^{-\frac{\gamma n^2}{\underline{V}^2}} + \frac{C_6}{2\gamma n^2} [\frac{1}{\underline{V}^2} + \frac{1}{\gamma n^2}] e^{-\frac{\gamma n^2}{\underline{V}^2}}$$

$$+ \frac{C_7}{2\gamma n^2} [(\frac{1}{\underline{V}^2} + \frac{1}{\gamma n^2})^2 + (\frac{1}{\gamma n^2})^2] e^{-\frac{\gamma n^2}{\underline{V}^2}} \}_{\underline{V}}^{\infty} \qquad (F.89)$$

$$= \frac{C_5}{2\gamma n^2} (1 - e^{-\frac{\gamma n^2}{\underline{V}^2}}) + \frac{C_6}{2\gamma n^2} [- \frac{e^{-\frac{\gamma n^2}{\underline{V}^2}}}{\underline{V}^2} + \frac{1}{\gamma n^2} (1 - e^{-\frac{\gamma n^2}{\underline{V}^2}})]$$

$$+ \frac{C_7}{2\gamma n^2} [- \frac{e^{-\frac{\gamma n^2}{\underline{V}^2}}}{\underline{V}^4} - \frac{2e^{-\frac{\gamma n^2}{\underline{V}^2}}}{\underline{V}^2 \gamma n^2} + \frac{2}{(\gamma n^2)^2} (1 - e^{-\frac{\gamma n^2}{\underline{V}^2}})] \qquad (F.90)$$

$$\int = \frac{C_5}{2\gamma n^2} [2 - (2 + \frac{\gamma n^2}{\underline{V}^2}) e^{-\frac{\gamma n^2}{\underline{V}^2}}]$$

$$- \frac{C_7}{2(\gamma n^2)^3} \{[(\frac{n^2\gamma}{\underline{V}^2})^2 + \frac{2\gamma n^2}{\underline{V}^2} + 2] e^{-\frac{\gamma n^2}{\underline{V}^2}} - 2\} \qquad (F.91)$$

Now consider other terms in equation

$$\therefore \quad \int[(\frac{\partial P}{\partial n_i})_{T,\underline{V},n_j} - \frac{RT}{\underline{V}}] \, d\underline{V} = (2C_1 + nC_1') \int \frac{-n}{\underline{V}^2} dV$$

$$+ (3C_2 + nC_2') \int \frac{n^2}{\underline{V}^3} d\underline{V} + (6C_3 + nC_3') \quad \frac{n^5}{\underline{V}^6} d\underline{V}$$

$$+ \text{equation (F.91)} \qquad (F.92)$$

$$\int = (2C_1 + nC_1') \; [\frac{-n}{V}]_{\underline{V}}^{\infty} + (3C_2 + nC_2') \; [\frac{-n^2}{2V^2}]_{\underline{V}}^{\infty}$$

$$+ (6C_3 + nC_3') \; [- \frac{n^5}{5\underline{V}^5}]_{\underline{V}}^{\infty} + \text{Equation (F.91)} \qquad (F.93)$$

$$= (2C_1 + nC_1')\frac{n}{V} + (3C_2 + nC_2')\frac{n^2}{V^2} + (6C_3 + nC_3')\frac{n^5}{V^5}$$

$$+ \text{Equation (F.91)} \qquad \text{(F.94)}$$

The expression for the fugacity is obtained by using equation (F.11)

$$RT \ln \frac{f_i}{x_i P} = (2C_1 + nC_1')\frac{n}{V} + (3C_2 + nC_2')\frac{n^2}{V^2} + (6C_3 + nC_3')\frac{n^5}{V^5}$$

$$+ \text{Equation (F.91)} - RT \ln Z \qquad \text{(F.95)}$$

Substituting for C_1, C_2, C_3, C_1', C_2', C_3' and $\rho = \frac{n}{V}$

$$RT \ln \frac{f_i}{x_i P} = [RT\,(nB_o' + 2B_o) - (nA_o' + 2A_o) - \frac{1}{T^2}(nC_o' + 2C_o)$$

$$+ \frac{1}{T^3}(nD_o' + 2D_o) - \frac{1}{T^4}(nE_o' + 2E_o)]\rho$$

$$+ [\frac{RT}{2}(nb' + 3b) - \frac{1}{2}(na' + 3a) - \frac{1}{2T}(nd' + 3d)]\rho^2$$

$$+ \left[\frac{1}{5}\left(a + \frac{d}{T}\right)(n\alpha' + 6\alpha) + \frac{n\alpha}{5}\left(a' + \frac{d'}{T}\right)\right]\rho^5$$

$$+ \frac{(c'n^3 + 3cn^2)}{2\gamma n^2 T^2}\left[2 - (2 + \gamma\rho^2)\, e^{-\gamma\rho^2}\right]$$

$$+ \frac{cn^3}{2T^2\,(n^2\gamma)^2}\,(2n\gamma + n^2\gamma')\,\left\{\left[(\rho^2\gamma)^2 + 2\gamma\rho^2 + 2\right]e^{-\gamma\rho^2} - 2\right\}$$

$$- RT \ln Z \qquad \text{(F.96)}$$

<u>Differentials B_o', C_o' etc. are obtained in terms of the differentials of critical constants as follows:</u>

$$B_o = V_{cm}\,(A_1 + B_1\,\omega_m) \qquad \text{(F.97)}$$

$$B_o' = V_{cm}'\,(A_1 + B_1\,\omega_m) + V_{cm}\,B_1\,\omega_m' \qquad \text{(F.98)}$$

$$A_o = R\,T_{cm}\,V_{cm}\,(A_2 + B_2\,\omega_m) \qquad \text{(F.99)}$$

$$A_o' = R\,\left[(T_{cm}\,V_{cm})'\,(A_2 + B_2\,\omega_m) + T_{cm}\,V_{cm}\,B_2\,\omega_m'\right] \qquad \text{(F.100)}$$

$$C_o = R.T_{cm}\,V_{cm}\,T_{cm}^2\,(A_3 + B_3\,\omega_m) \qquad \text{(F.101)}$$

$$C_o' = R.\,\left\{\left[(T_{cm}\,V_{cm})'\,T_{cm}^2 + 2T_{cm}\,T_{cm}'\,(T_{cm}\,V_{cm})\right](A_3 + B_3\omega_m)\right.$$

$$+ V_{cm} T_{cm}^3 B_3 \omega_m'\} \tag{F.102}$$

$$\gamma = V_{cm}^2 (A_4 + B_4 \omega_m) \tag{F.103}$$

$$\gamma' = 2 V_{cm} V_{cm}' (A_4 + B_4 \omega_m) + V_{cm}^2 B_4 \omega_m' \tag{F.104}$$

$$b = V_{cm}^2 (A_5 + B_5 \omega_m) \tag{F.105}$$

$$b' = 2 V_{cm} V_{cm}' (A_5 + B_5 \omega_m) + V_{cm}^2 B_5 \omega_m' \tag{F.106}$$

$$a = R T_{cm} V_{cm}^2 (A_6 + B_6 \omega_m) \tag{F.107}$$

$$a' = R \{[(T_{cm} V_{cm})' V_{cm} + T_{cm} V_{cm} V_{cm}'] (A_6 + B_6 \omega_m) + T_{cm} V_{cm}^2 B_6 \omega_m'\} \tag{F.108}$$

$$\alpha = V_{cm}^3 (A_7 + B_7 \omega_m) \tag{F.109}$$

$$\alpha' = 3 V_{cm}^2 V_{cm}' (A_7 + B_7 \omega_m) + V_{cm}^3 B_7 \omega_m' \tag{F.110}$$

$$c = R (T_{cm} V_{cm})^2 T_{cm} (A_8 + B_8 \omega_m) \tag{F.111}$$

$$c' = R \{[2 (T_{cm} V_{cm})(T_{cm} V_{cm})' T_{cm} + (T_{cm} V_{cm})^2 T_{cm}'] (A_8 + B_8 \omega_m)$$

$$+ (T_{cm} V_{cm})^2 T_{cm} B_8 \omega_m'\} \tag{F.112}$$

$$D = R\ (T_{cm}\ V_{cm})\ T_{cm}^{3}\ (A_9 + B_9\ \omega_m) \tag{F.113}$$

$$D' = R\ \{[(T_{cm}\ V_{cm})'\ T_{cm}^{3} + 3T_{cm}^{2}\ T_{cm}'\ (T_{cm}\ V_{cm})](A_9 + B_9\ \omega_m)$$

$$+ (T_{cm}\ V_{cm})\ T_{cm}^{3}\ B_9\ \omega_m'\} \tag{F.114}$$

$$d = R\ (T_{cm}\ V_{cm})^2\ (A_{10} + B_{10}\ \omega_m) \tag{F.115}$$

$$d' = R[2(T_{cm}V_{cm})(T_{cm}V_{cm})'(A_{10}+B_{10}\omega_m) + (T_{cm}V_{cm})^2 B_{10}\omega_m'] \tag{F.116}$$

$$E_o = R.V_{cm}\ T_{cm}^{5}\ [A_{11} + B_{11}\ \omega_m\ \exp\ (-3.8\ \omega_m)] \tag{F.117}$$

$$E' = R\ T_{cm}^{4}\ \{[(T_{cm}V_{cm})' + 4\ V_{cm}T_{cm}'][A_{11}+B_{11}\ \omega_m\ \exp(-3.8\ \omega_m)]$$

$$+ \omega_m'\ T_{cm}V_{cm}\ B_{11}\ \exp\ (-3.8\ \omega_m)\ [1-3.8\ \omega_m]\} \tag{F.118}$$

<u>The differential of the critical constants are derived as follows:</u>

$$T_{cm}V_{cm} = \sum_i \sum_j x_i\ x_j\ T_{cij}\ V_{cij} = \frac{1}{n^2} \sum_i \sum_j n_i\ n_j\ T_{cij}\ V_{cij} \tag{F.119}$$

where n = total number of moles.

$$\therefore \quad (T_{cm} V_{cm})' = \frac{-2}{n^3} \sum_i \sum_j n_i n_j T_{cij} V_{cij} + \frac{1}{n^2} 2 \sum_j n_j T_{cij} V_{cij} \tag{F.120}$$

$$= \frac{2}{n} [\sum_j x_j T_{cij} V_{cij} - T_{cm} V_{cm}] \tag{F.121}$$

$$\text{(For one mole)} = 2 (\sum_j x_j T_{cij} V_{cij} - T_{cm} V_{cm}) \tag{F.122}$$

$$(T_{cm} V_{cm})' = \frac{\partial}{\partial n_i} (T_{cm} V_{cm})_{T,V,n_j} \tag{F.123}$$

Similarly,

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \tag{F.124}$$

$$V_{cm}' = 2 (\sum_j x_j V_{cij} - V_{cm}) \tag{F.125}$$

$$T_{cm}' = (\frac{T_{cm} V_{cm}}{V_{cm}})' = \frac{1}{V_{cm}} (T_{cm} V_{cm})' - \frac{T_{cm} V_{cm}}{(V_{cm})^2} V_{cm}' \tag{F.126}$$

$$= \frac{1}{V_{cm}} [(T_{cm} V_{cm})' - T_{cm} (V_{cm})'] \tag{F.127}$$

$$\text{(For one mole)} = \frac{2}{V_{cm}} [\sum_j x_j T_{cij} V_{cij} - T_{cm} \sum_j x_j V_{cij}] \tag{F.128}$$

$$Z_{cm} = \sum_i Z_{ci} x_i = \frac{1}{n} \sum n_i Z_{ci} \tag{F.129}$$

$$Z'_{cm} = \frac{Z_{ci}}{n} - \frac{\sum_i Z_{ci}\, n_i}{n^2} \tag{F.130}$$

$$= \frac{1}{n}\,(Z_{ci} - Z_{cm}) \tag{F.131}$$

$\underline{(\text{For one mole}) = Z_{c_i} - Z_{cm}}$

$$\omega_m = \sum_i x_i\, \omega_i \tag{F.132}$$

$$\omega_m' = \frac{1}{n}\,(\omega_i - \omega_m) \tag{F.133}$$

$\underline{(\text{For one mole}) = \omega_i - \omega_m}$

When Han and Starling mixing rules are used, the following expression for the fugacity is obtained (Starling, 1973).

$$\begin{aligned}
RT \ln f_i &= RT \ln (\rho\, RT\, x_i) + \rho\,(B_{oi} + B_o)RT \\
&+ 2\rho \sum_j x_j \left[-(A_{oi}A_{oj})^{\frac{1}{2}}\,(1 - k_{ij}) - \frac{(C_{oi}\, C_{oj})^{\frac{1}{2}}}{T^2}\,(1 - k_{ij})^3\right. \\
&\left. + \frac{(D_{oi}\, D_{oj})^{\frac{1}{2}}}{T^3}\,(1 - k_{ij})^4 - \frac{(E_{oi}\, E_{oj})^{\frac{1}{2}}}{T^4}\,(1 - k_{ij})^5\right] \\
&+ \frac{\rho^2}{2}\left[3(b^2 b_i)^{1/3}\, RT - 3(a^2 a_i)^{1/3} - \frac{3(d^2 d_i)^{1/3}}{T}\right] \\
&+ \frac{\alpha\, \rho^5}{5}\left[3(a^2 a_i)^{1/3} + \frac{3(d^2 d_i)^{1/3}}{T}\right] + \frac{3\rho^5}{5}\,(a + \frac{d}{T})(\alpha^2 \alpha_i)^{1/3}
\end{aligned}$$

$$+ \frac{3(c^2 c_i)^{1/3} \rho^2}{T^2} \left[\frac{1 - \exp(-\gamma\rho^2)}{\gamma\rho^2} - \frac{\exp(-\gamma\rho^2)}{2} \right]$$

$$- \frac{2c}{\gamma T^2} \left(\frac{\gamma_i}{\gamma}\right)^{\frac{1}{2}} \{1 - \exp(-\gamma\rho^2) [1 + \gamma\rho^2 + \frac{1}{2}\gamma^2\rho^4]\} \qquad (F.134)$$

APPENDIX G

ALGORITHMS FOR VAPOUR-LIQUID EQUILIBRIUM CALCULATIONS

Prediction of the vapour pressure

The calculation of the vapour pressure P_s at a given temperature requires the simultaneous solution of the following equations for vapour-liquid equilibrium (Benedict et al, 1940).

$$P^L = P^V = P_s \qquad (G.1)$$

$$f^L = f^V \qquad (G.2)$$

where L and V refer to the liquid and vapour respectively.

The steps in the algorithm for the prediction of vapour pressure are as follows:

1. Initial estimate of the vapour pressure P_s is made and P^L and P^V are set equal to P_s.

2. Liquid and vapour densities are calculated by solving for the largest and smallest roots satisfying the equation of state with $P = P_s$ and $T = T$ (given).

3. Liquid and vapour densities are used to calculate the liquid and vapour fugacities using the fugacity expression derived from an equation of state.

4. A new estimate for P_s is obtained as follows:

$$P_{s,i} = 0.999 \times P_{s,initial} \text{ for } i = 2 \qquad (G.3)$$

$$P_{s,i} = P_{s,i-1} - \frac{(P_{s,i} - P_{s,i-1}) \times |f^V - f^L|_i}{|f^V - f^L|_i - |f^V - f^L|_{i-1}} \text{ for } i > 2 \qquad (G.4)$$

where i refers to the number of iterations.

5. Steps 2 to 4 are repeated until equation (G.2) is satisfied within a specified tolerance or $|1 - f^L/f^V|$ is less than 0.001.

Usually 3 to 4 iterations are required to obtain the vapour pressure. The computer program is given in Appendix H.

Prediction of the bubble point pressure

This algorithm sets out a method for calculating the bubble point pressure and vapour phase compositions given isothermal condition and liquid phase compositions. If vapour phase compositions are given then this algorithm can be easily changed to predict liquid phase compositions. The steps are as follows:

1. Set the temperature, T and liquid phase compositions x_i.

2. Guess a value of P and set the fugacity coefficients, ϕ_i's to 1.0.

3. Use mixing rules to evaluate mixture parameters and transform the equation of state into the form $F[\rho] = 0$. Solve the resulting equation for the maximum root corresponding to the liquid phase density, ρ^L.

4. ρ^L is used with the fugacity expression derived from the equation of state (see Appendix F) to calculate the liquid phase fugacity, f_i^L for each component.

5. Calculate vapour phase compositions y_i's using:

$$y_i = \frac{f_i^L}{\phi_i P} \qquad (G.5)$$

and store their sum as SUM 1. Thus:

$$SUM1 = \sum y_i \qquad (G.6)$$

6. Normalize y_i's.

$$y_i = \frac{y_i}{SUM1} \qquad (G.7)$$

Using these y_i's calculate the vapour phase density ρ^V by solving $F[\rho] = 0$ for the minimum root. Calculate the vapour phase fugacity, f_i^V for each component using the fugacity expression derived from the equation of state and ρ^V.

7. Calculate new y_i's from $y_{i,new} = \frac{f_i^L}{f_i^V} y_{i,old}$ (G.8)

and store their sum as SUM 2.

$$SUM2 = \sum y_{i,new} \qquad (G.9)$$

Calculate partial pressures P_i's and store their sum as SUMP.

$$P_i = y_{i,new} P \qquad SUMP = \sum P_i \qquad (G.10)$$

8. Use $y_{i,new}$ to calculate ρ^V and f_i^V for each component. Repeat this with step 7 until the following condition is satisfied for each component

$$\left|1 - \frac{f_i^L}{f_i^V}\right| < 0.0001 \qquad (G.11)$$

9. Transfer the value of SUMP to P and repeat steps 2 to 8 until the following condition is satisfied:

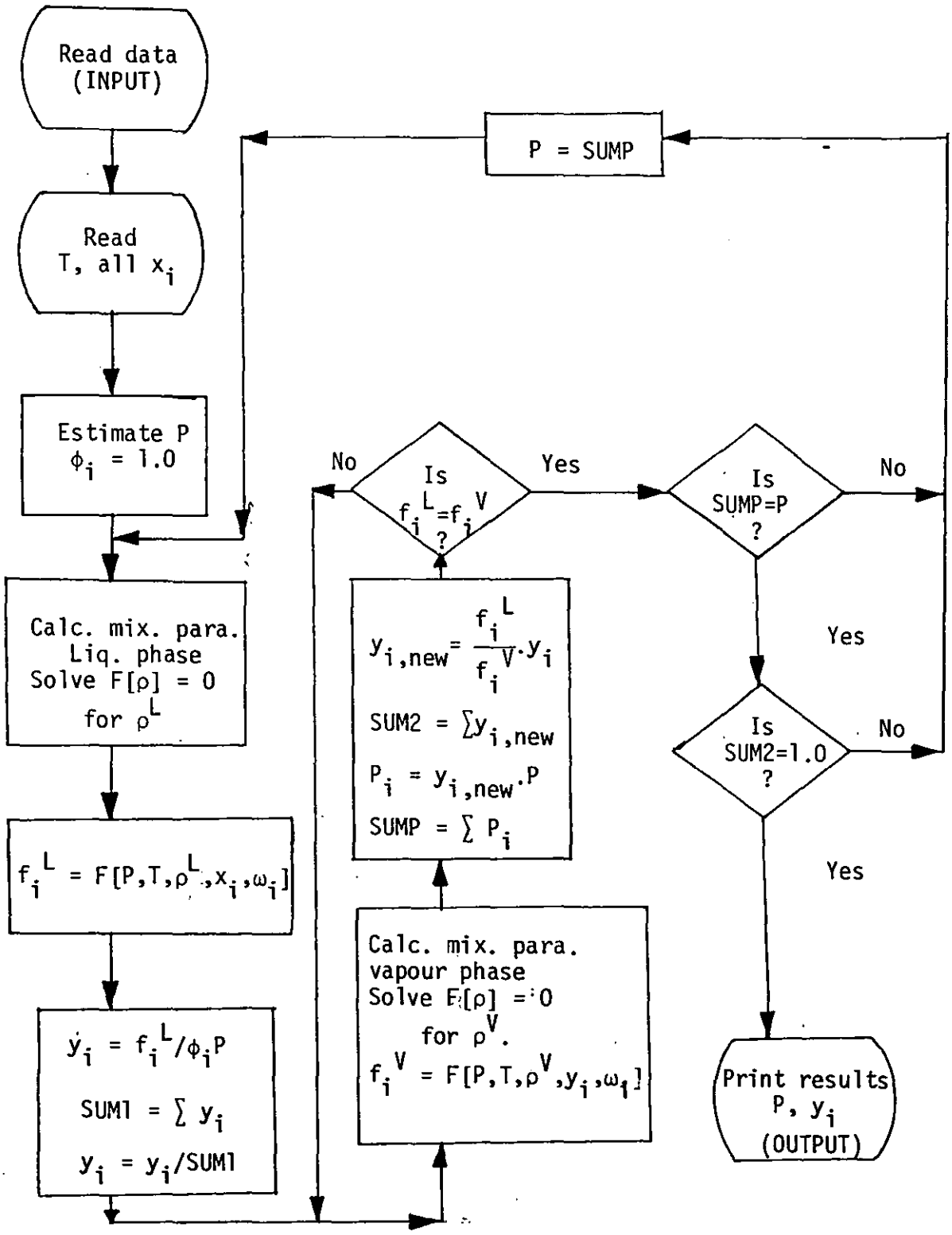


FIGURE G.1 Flow diagram for the prediction of the bubble point pressure

$$\left|\frac{SUMP - P}{SUMP}\right| < 0.00001 \qquad (G.12)$$

$$\text{Check if } |SUM2 - 1| < 0.00001 \qquad (G.13)$$

When equations (G.11), (G.12) and (G.13) are satisfied, the calculated pressure P is the bubble point pressure (see Appendix H for the computer program).

Prediction of the bubble point temperature

The steps in the algorithm for the prediction of the bubble point temperature are as follows:

1. Set the pressure P and liquid phase compositions x_i.

2. Guess the temperature T and set the fugacity coefficients ϕ_i's to 1.0.

3. Evaluate mixture parameters using appropriate mixing rules and transform the equation of state into the form $F[\rho] = 0$. Solve the resulting equation for the maximum root corresponding to the liquid phase density, ρ^L.

4. Calculate the liquid phase fugacity, f_i^L for each component using ρ^L in the fugacity expression derived from the equation of state (Appendix F).

5. Calculate vapour phase compositions y_i's using equation (G.5) and store their sum as SUM1.

6.. Normalize y_i's using equation (G.7). Using these y_i's repeat steps 3 and 4 for the vapour phase (Calculate ρ^V and f_i^V).

7. Calculate new y_i's from equation (G.8) and store their sums as SUM2.

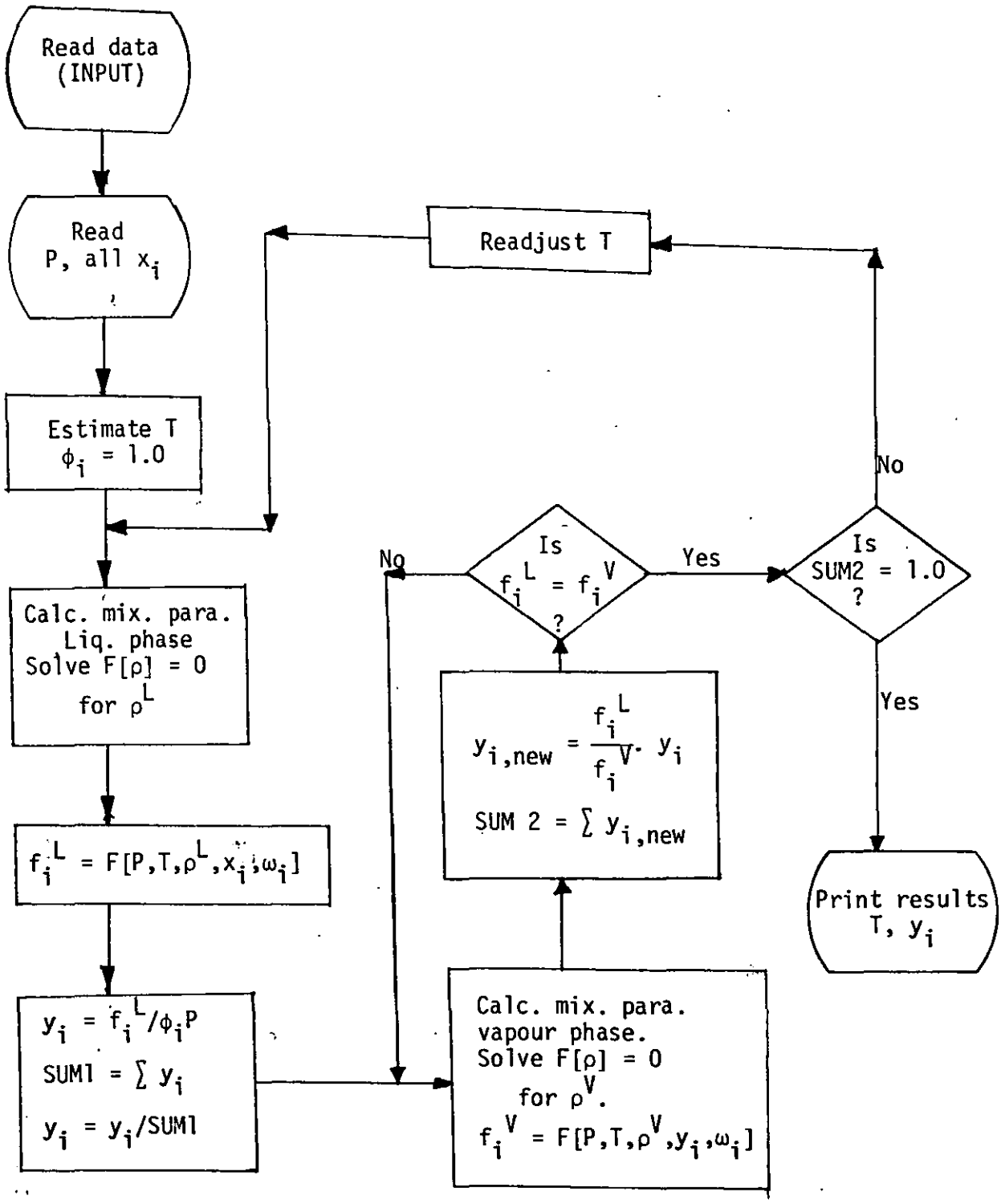


FIGURE G.2 Flow diagram for the prediction of the bubble point temperature.

8. Use $y_{i,new}$ to calculate ρ^V and f_i^V (for each component). Repeat this with step 7 until the condition defined by equation (G.11) is satisfied.

9. Check if equation (G.13) is satisfied. If it is not satisfied then adjust the temperature, T as follows:

$$\left.\begin{array}{ll} \text{If SUM2} > 1.0 & T_{new} = 0.98T \\ \text{If SUM2} < 1.0 & T_{new} = 1.02T \end{array}\right\} \text{for N1} = 2 \qquad \text{(G.14)}$$

$$\text{For N1} > 2 \qquad T_{new} = T - \Delta \qquad \text{(G.15)}$$

$$\text{where } \Delta = \text{SLOPE} \times (\text{SUM2} - 1) \qquad \text{(G.16)}$$

$$\text{SLOPE} = \frac{T - T_{old}}{\text{SUM2} - \text{SUMY P}} \qquad \text{(G.17)}$$

N1 is the number of "full" iterations and SUMY P is the sum of y_i's for the previous iteration. To avoid diverging iteration, it is necessary to use a control statement so that the magnitude of Δ does not exceed 10% of the current temperature (see Appendix H for the computer program).

Prediction of the equilibrium ratios

This algorithm sets out a method for calculating the equilibrium ratios or 'K' values (y_i/x_i) at a given pressure P and temperature T.

1. Set the temperature T and pressure P.

2. Guess values of the equilibrium ratios R_i. So called ideal K values (the ratio of vapour pressure to system pressure).

can be conveniently used as first estimates of R_i.

3. Calculate x_i's and y_i's using R_i's.

$$x_i = \frac{Z_i}{R_i V + 1 - V} \tag{G.18}$$

$$y_i = R_i X_i \tag{G.19}$$

where Z_i's are compositions of feed and V is the amount of vapour (lb.moles) obtained from one lb.mole of the feed mixture at equilibrium. V is obtained by solving the following equation.

$$\sum_{i=1}^{i=n} \frac{Z_i (1 - R_i)}{R_i V + (1 - V)} = 0 \tag{G.20}$$

For binary mixture:

$$x_1 = \frac{1 - R_2}{R_1 - R_2} \tag{G.21}$$

$$x_2 = 1 - x_1 \tag{G.22}$$

4. Calculate mixture parameters and solve the equation of state for the liquid phase density, ρ^L.

5. Calculate the liquid phase fugacity, f_i^L for each component using ρ^L in the fugacity expression derived from the equation of state.

6. Calculate vapour phase compositions, y_i's using equation (G.5) and store their sum as SUM1 (equation G.6).

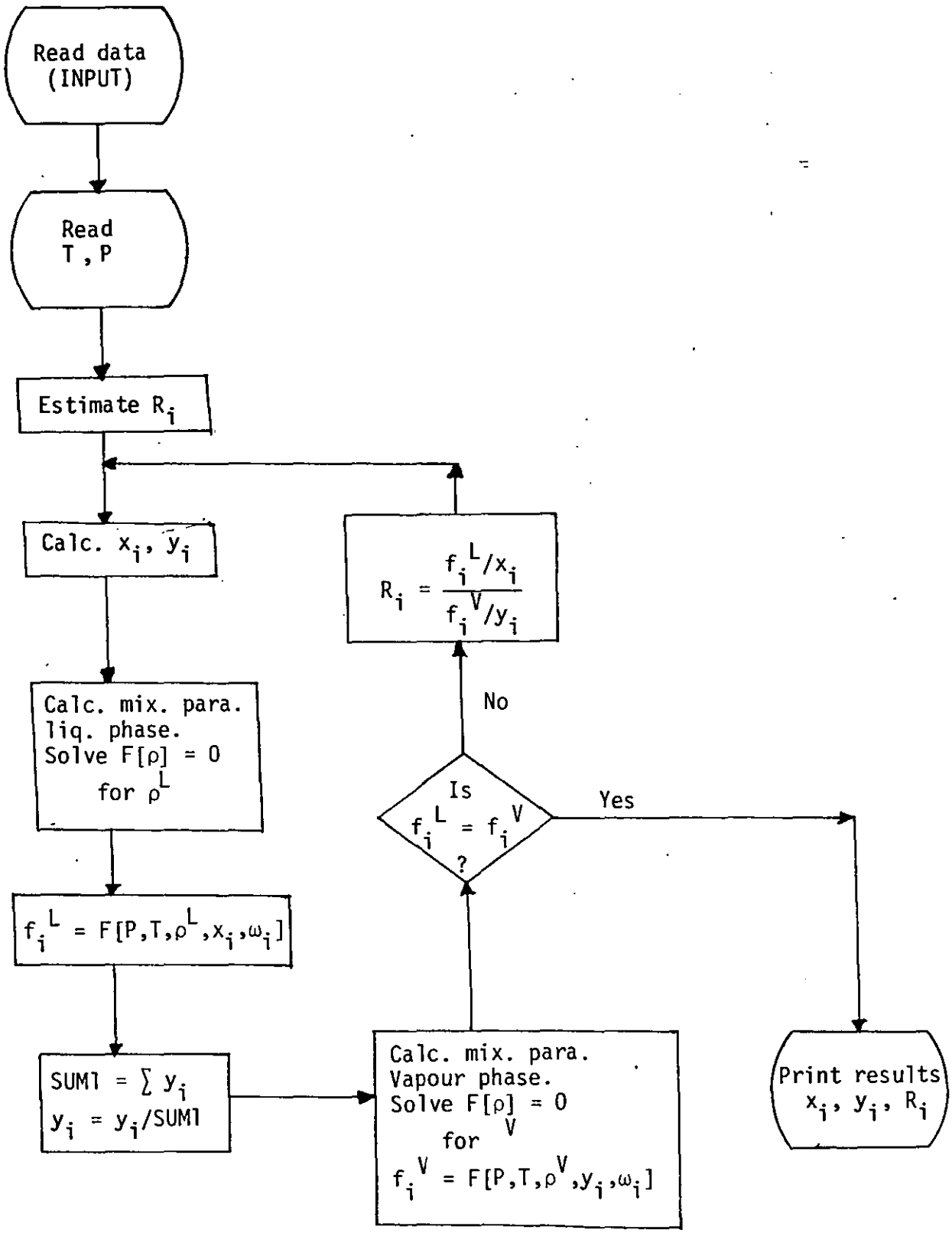


FIGURE G.3 Flow diagram for the prediction of the equilibrium ratios

7. Normalize y_i's using equation (G.7). Using the normalized y_i's calculate mixture parameters and solve the equation of state for the vapour phase density, ρ^V. Calculate the vapour phase fugacity, f_i^V for each component.

8. New values of R_i's are given by:

$$R_i = \frac{f_i^L/x_i}{f_i^V/y_i} \tag{G.23}$$

Repeat steps (3) to (7) with new values of R_i given by equation (G.23) until equation (G.11) is satisfied.

(See Appendix H for the computer program).

APPENDIX H

LISTINGS OF COMPUTER PROGRAMS

The following computer programs are listed in this Appendix:

		Page
1.	Program for evaluating constants F, K and n required in the temperature functions.	382
2.	Program for the prediction of equilibrium pressure and vapour phase mole fractions using the modified Peng-Robinson (M-P-R) equation, the Peng-Robinson (P-R) equation and the Soave (S-R-K) equation.	387
3.	Program for the prediction of equilibrium temperature and vapour phase mole fractions using the M-P-R, the P-R and the S-R-K equations.	395
4.	Program for the prediction of equilibrium ratios using the M-P-R, the P-R and the S-R-K equations.	402
5.	Program for the prediction of equilibrium pressure and vapour phase mole fractions using the Han and Starling equation with van der Waals mixing rules.	408
6.	Same as (5) but Han and Starling mixing rules are used.	414
7.	Program for the prediction of compressibility using the generalized versions of the M-P-R equation.	419
8.	Program for the prediction of vapour pressure.	424
9.	Program for the prediction of pure component density using the M-P-R, the P-R and the R-K equations.	428
10.	Program for the prediction of mixture density using the M-P-R equation.	432

```
C****
      MASTER FITTING          PROGRAM NO.1
C*****************************************************************
C**** THIS PROGRAM EVALUATES CONSTANTS F,K AND N REQUIRED FOR DESCRIBING
C**** THE TEMPERATURE DEPENDENCY OF CONSTANT A IN THE MODIFIED PR
C**** EQUATION.   THE FOLLOWING TWO TEMP. FUNCTIONS ARE FITTED BY
C**** LEAST SQUARE.
C**** 1. ALPHA=(1+F*(1-TR**0.5))**2
C**** 2. ALPHA=EXP(K*(1-TR**N))
C**** EXPERIMENTAL VALUES OF SATURATION PRESSURES AND TEMPERATURES ARE
C**** USED.
C*****************************************************************
      DIMENSION C(5),VGG(50),VLL(50)
      COMMON/BL1/X,XX,N3,TRR(50),P(50),T(50),OMEGA(50),S(10),C1
      WRITE(2,296)
      WRITE(2,298)
      WRITE(2,295)
  106 CONTINUE
      READ(1,177)U
C****
C**** U IS USED TO IDENTIFY UNITS OF TEMP. AND PRESSURE
C**** IF T IN FAHRENHEIT AND P IN PSIA U=1
C**** IF T IN KELVIN AND P IN BARS U=3
C**** IF T IN CENTIGRADE AND P IN MM HG  U= ANY NO.
C****
      READ(1,150)N3
C**** N3 IS NO. OF DATA POINTS
C**** INPUT CRITICAL CONSTANTS
      READ(1,114)TC,PC,WC,W1,R
      CONST=0.37464+1.54226*WC-0.26992*WC*WC
C****
C**** CONST IS PR CONSTANT K . THIS IS USED TO EVALUATE INITIAL ESTIMATE
C**** OF ALPHA
C****
      READ(1,150)M
C**** M IS NO. OF ZM VALUES FOR WHICH F,K AND N ARE TO BE EVALUATED
C****
C**** INPUT SATURATION DATA
      READ(1,113)(T(I),P(I),VGG(I),VLL(I),I=1,N3)
      L=1
  105 CONTINUE
      IF(L.GT.M)GO TO 106
      READ(1,130)ZEXP
C****
C**** INPUT VALUES OF ZM (CALLED ZEXP) FOR WHICH F,K AND N ARE TO BE
C**** EVALUATED
C****
C**** OMAC,OMB AND OMC ARE EVALUATED
      C(1)=1.0
      C(2)=2.0-3.0*ZEXP
      C(3)=3.0*ZEXP*ZEXP
      C(4)=-ZEXP**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION
      OMB=ZMAX
      OMC=1.0-3.0*ZEXP
      OMAC=3.0*ZEXP*ZEXP+3.0*(1-2.0*ZEXP)*OMB+OMB*OMB+OMC
      BB=OMB*R*TC/PC
      CC=OMC*R*TC/PC
      WRITE(2,240)TC,PC,WC,W1,R
```

```
      WRITE(2,350)ZEXP,OMAC,OMB,OMC,CONST
      WRITE(2,296)
      WRITE(2,51)
      WRITE(2,296)
      DO 60 I=1,N3
      IF(I.GT.1)GO TO 58
      IF(II.EQ.1)GO TO 600
      IF(II.EQ.3)GO TO 69
      P(I)=P(I)*14.695916/760.0
      T(I)=(T(I)+273.16)*9.0/5.0
      TRR(I)=T(I)/TC
      GO TO 58
   69 T(I)=T(I)*1.8
      P(I)=P(I)*14.5037
      TRR(I)=T(I)/TC
      GO TO 58
  600 T(I)=T(I)+459.67
      TRR(I)=T(I)/TC
   58 CONTINUE
      VGG(I)=VGG(I)*W1
      VLL(I)=VLL(I)*W1
C**** INITIAL ESTIMATE OF ALPHA(CALLED OMEGAA) IS OBTAINED
      OMEGAA=(1.0+CONST*(1-TRR(I)**0.5))**2
      D2=SQRT(BB*CC+0.25*(BB+CC)**2)
      D1=0.5*(BB+CC)-D2
      D3=0.5*(BB+CC)+D2
      PR=P(I)/PC
      B=BB*P(I)/R/T(I)
      CCC=CC*P(I)/R/T(I)
      C(1)=1.0
      C(2)=CCC-1.0
      N=0
  710 CONTINUE
      N=N+1
      AA=OMAC*OMEGAA*R*R*TC*TC/PC
      A=AA*P(I)/(R*R*T(I)*T(I))
      C(3)=A-2*B*CCC-B*B-B-CCC
      C(4)=B*B*CCC-A*B*B*CCC
C****
C**** EQUATION OF STATE IS SOLVED FOR COMPRESSIBILITIES OF LIQUID AND
C**** VAPOUR PHASES
C****
      CALL SOLVE(ZMIN,ZMAX,C)
      ZL=ZMIN
      ZV=ZMAX
      IF(ABS(1.0-ZL/ZV).LE.0.01)GO TO 800
      VLE=ZL*R*T(I)/P(I)
      VVE=ZV*R*T(I)/P(I)
C**** LIQUID AND VAPOUR FUGACITIES ARE CALCULATED
      FL1=(AA/(2.0*R*T(I)*D2))*ALOG((VLE+D1)/(VLE+D3))
      FL2=ALOG(ZL-B)
      FV1=(AA/(2.0*R*T(I)*D2))*ALOG((VVE+D1)/(VVE+D3))
      FV2=ALOG(ZV-B)
      ZZL=ZL-1.0-FL2+FL1
      ZZV=ZV-1.0-FV2+FV1
      FL=P(I)*EXP(ZZL)
      FV=P(I)*EXP(ZZV)
      FVFI=ABS(FV-FL)
C****
C**** EQUALITY OF FUGACITY FOR BOTH PHASES IS DEFINED BY THE FOLLOWING
```

```
C**** STATEMENT
C****
      IF(ABS(1.0-FL/FV).LT.0.0001)GO TO 700
      IF(N.GT.1)GO TO 280
      OMEGAA1=OMEGAA
      FVFL1=FVFL
      OMEGAA=OMEGAA*0.999
      GO TO 710
  800 OMEGAA=OMEGAA*0.999
      GO TO 710
  280 CONTINUE
C**** THE FOLLOWING CONVERGENCE CRITERION IS USED
      SLOPE=(OMEGAA-OMEGAA1)/(FVFL-FVFL1)
      DELT=SLOPE*FVFL
      OMEGAA1=OMEGAA
      FVFL1=FVFL
      OMEGAA=OMEGAA-DELT
      GO TO 710
  700 CONTINUE
      OMEGA(I)=OMEGAA
      VG=VGG(I)
      VL=VLL(I)
      WRITE(2,50)P(I),T(I),OMEGAA,VVE,VG,VLE,VL,N
   60 CONTINUE
      WRITE(2,296)
      CALL SUM
C****
C**** SUBROUTINE SUM EVALUATES SUM OF THE NECCESSARY TERMS FOR LEAST
C**** SQUARE FITTING OF PR FUNCTION
C****
      C(1)=S(4)
      C(2)=3.0*S(3)
      C(3)=3.0*S(2)-S(5)
      C(4)=S(1)-S(6)
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION
      C1=ZMAX
      CALL NONLINEAR(C)
C****
C**** SUBROUTINE NON LINEAR SOLVES THE NON LINEAR EQUATION FOR
C**** LEAST SQUARE FITTING OF EXPONENTIAL FUNCTION FOR ALPHA
C****
      WRITE(2,25)C1,X,XX
      CALL DEVA
C****
C**** SUBROUTINE DEVA CALCULATES DEVIATIONS OF PREDICTED ALPHA VALUES
C**** (USING TWO FITTED FUNCTIONS) FROM THE ACTUAL VALUE OF ALPHA
C**** OBTAINED BY EQUATING FUGACITY.
C****
      L=L+1
      GO TO 105
C*********************************************************************
   25 FORMAT(/1H ,'CONSTANT F=',F9.6,5X,'N=',F9.6,5X,'K=',F9.6)
   50 FORMAT(1H ,7(F12.6),2X,I3)
   51 FORMAT(1H ,6X,'P',10X,'T',10X,'ALPHA',10X,'VG',6X,'VGEXP',7X,'VL',
     110X,'VLEXP',7X,'NO. ITER.')
  113 FORMAT(4F0.0)
  114 FORMAT(5F0.0)
  130 FORMAT(F0.0)
  150 FORMAT(I0)
```

```
177 FORMAT(F0.0)
240 FORMAT(1H ,'TC=',F6.4,2X,'PC=',F6.2,2X,'ACE.FAC.=',F6.4,2X,'MOL WT
   1=',F6.3,2X,'R=',F8.5)
295 FORMAT(1H ,'P IN PSIA; V IN CU.FT./LB.MOLE ; T IN RANKINE ')
296 FORMAT(1H ,'-----------------------------------------------------------
   1-----------------------------------------------------------')
298 FORMAT(1H ,'EVALUATION OF CONSTANTS F , K , AND N IN THE FOLLOWING
   1EQUATIONS '/1H ,'(1) ALPHA=(1+F*(1-TR**0.5))**2'/1H ,'(2) ALPHA=
   2EXP(K*(1-TR**N))')
350 FORMAT(1H ,'Z=',F6.4,5X,'OMAC=',F9.7,5X,'OMB=',F9.7,5X,'OMC=',F9.7
   1,5X,'PR CONSTANT K=',F9.7)
C**** ****************** ***********************************************
      STOP
      END
```

INPUT FOR PROGRAM NO. 1

```
C**** ***************************************************************
C**** DATA INPUT FOR METHANE
C**** ***************************************************************
DOC DATA
1                                          U
10                                         NO. OF DATA POINTS
343.044   667.782 0.012 16.04 10.7335      TC  PC  WC  MOL WT  R
1                                          NO. OF ZM VALUES
-235 39 3.57 0.03956                       T  P  VG  VL
-240 32.4 4.24 0.03915
-245 26.6 5.09 0.03876
-250 21.71 6.13 0.03839
-255 17.4 7.52 0.03801
-260 13.8 9.31 0.03766
-265 10.82 11.63 0.03732
-270 8.44 14.61 0.03698
-275 6.47 18.64 0.03666
-280 4.9 24.04 0.03635
0.324                                      ZM
****
```

EVALUATION OF CONSTANTS F , K , AND N IN THE FOLLOWINGEQUATIONS
(1). ALPHA=(1+F*(1-TR**0.5))**2
(2). ALPHA=EXP(K*(1-TR**N))
P IN PSIA: V IN CU.FT /LB.MOLE ; T IN RANKINE
TC=*343.0440 PC=667.78 ACE.FAC.=0.0120 MOL WT=16.040 R=10.73350
Z=0.3240 OMAC=0.4379945 OMB=0.0834332 OMC=0.0280000 PR CONSTANT K=0.3931083

P	T	ALPHA	VG	VGEXP	VL	VLEXP	NO. ITER.
4.900000	179.670000	1.264428	388.133359	385.601600	0.560926	0.583054	5
6.470000	184.670000	1.255433	301.111088	298.985600	0.566045	0.588026	5
8.440000	189.670000	1.245952	236.137333	234.344400	0.571475	0.593159	5
10.820000	194.670000	1.237154	188.202069	186.545200	0.577084	0.598613	5
13.800000	199.670000	1.226946	150.547069	149.332400	0.583193	0.604066	5
17.400000	204.670000	1.216656	121.647985	120.620800	0.589656	0.609680	5
21.710000	209.670000	1.206268	99.194239	98.325200	0.596513	0.615776	5
26.600000	214.670000	1.197547	82.280072	81.643600	0.603459	0.621710	5
32.400000	219.670000	1.188152	68.549256	68.009600	0.610947	0.627966	5
39.000000	224.670000	1.179484	57.719691	57.262800	0.618731	0.634542	5

CONSTANT F= 0.452295 N= 0.656060 K= 0 681648

TR	ALPHA	ALP CALC EXP	DEV(%)	ALP CALC PR	DEV(%)
0.523752	1.264428	1.265787	-0.107505	1.265548	-0.088599
0.538327	1.255433	1.255572	-0.011053	1.255392	0.003284
0.552903	1.245952	1.245532	0.033741	1.245412	0.043392
0.567478	1.237154	1.235662	0.120622	1.235601	0.125519
0.582054	1.226946	1.225956	0.080672	1.225954	0.080808
0.596629	1.216656	1.216408	0.020384	1.216464	0.015790
0.611204	1.206268	1.207014	-0.061885	1.207126	-0.071134
0.625780	1.197547	1.197769	-0.018498	1.197933	-0.032266
0.640355	1.188152	1.188667	-0.043284	1.188882	-0.061413
0.654931	1.179484	1.179704	-0.018680	1.179967	-0.040957

A.A.D EXP FORM =0.0515 A.A.D PR FORM =0.0563

OUTPUT FOR PROGRAM NO.1

PROGRAM NO.2

```
      MASTER BUBBLE PRESSURE
C****
C**** ******************************************************************
C**** PREDICTION OF PRESSURE  AND VAPOUR PHASE MOLE FRAC. USING MODIFIED
C**** PENG-ROBINSON EQUATION OF STATE
C**** THIS PROGRAM CAN ALSO BE USED FOR PENG-ROBINSON EQUATION AND
C**** SOAVE EQUATION BY SPECIFYING THE PARAMETER ES=2 AND ES=3
C**** RESPECTIVELY.
C**** THIS PROGRAM CAN BE USED FOR MULTICOMPONENT SYSTEM.
C**** ******************************************************************
C****
      DIMENSION EXPR1(10),DEV(10),DEVR1(10)
      DIMENSION R1(10),ALP(10),F(10)
      DIMENSION X(10),Y(10),FL(10),FV(10),PHIV(10),PHIL(10)
      DIMENSION ZM(10),TC(10),PC(10),WC(10),W1(10),TR(10),C(5),OMB(10)
      DIMENSION OMC(10),OMAC(10),E1(10),E2(10),E3(10),E4(10)
      COMMON/BL1/A1(10),B1(10),C1(10),AIJ(10,10),DIA(10)
      COMMON/BL2/AM,BM,CM,NUM,ZETA(10,10)
      COMMON/BL3/DAM(10),DBM(10),DCM(10)
      WRITE(2,225)
C****
C**** ES=1 IF MODIFIED PR EQUATION IS TO BE USED.
C**** ES=2 IF PR EQUATION IS TO BE USED.
C**** ES=3 IF SOAVE EQUATION IS TO BE USED.
C****
      READ(1,55)ES
C****
C**** INPUT GS=1.0 IF GENERALISED FORM OF THE MODIFIED PENG ROBINSON
C**** EQUATION IS TO BE USED WITH ALL THE INTERACTION CO EFFICIENTS
C**** ASSUMED TO BE 1.0. THIS IS NECCESSARY FOR A MIXTURE CONTAINING
C**** COMPONENTS WHOSE ZM AND F PARAMETERS ARE NOT AVAILABLE AND
C**** INTERACTION CO EFFICIENTS ARE NOT KNOWN.
C****
      READ(1,55)GS
      IF(ES.EQ.1)WRITE(2,295)
      IF(ES.EQ.2)WRITE(2,296)
      IF(ES.EQ.3)WRITE(2,297)
      READ(1,4)NUM,FC,R
C****
C**** NUM IS NO. OF COMPONENTS; R IS THE UNIVERSAL GAS CONSTANT.
C**** FC IS THE INITIAL ESTIMATE OF THE VAPOUR PHASE FUGACITY COEFFICIENTS
C**** THE VALUE OF R CORRESPONDS TO P(PSIA), V(CU.FT./LB.MOLE),
C**** T(RANKINE).
C****
      WRITE(2,210)R
C**** INPUT CRITICAL CONSTANTS
      READ(1,8)(TC(I),PC(I),WC(I),W1(I),I=1,NUM)
      IF(GS.EQ.1.0)GO TO 750
C****
C**** INPUT INTERACTION CO EFFICIENTS IN THIS ORDER ZETA(1,2),ZETA(1,3)
C**** ZETA(1,4),ZETA(2,3),ZETA(2,4),ZETA(3,4) FOR 4 COMPONENTS.
C****
      DO 500 I=1,NUM
      DO 550 J=1,NUM
      IF(I.GE.J)GO TO 550
      READ(1,22)ZETA(I,J)
      ZETA(J,I)=ZETA(I,J)
      WRITE(2,23)I,J,ZETA(I,J)
  550 CONTINUE
  500 CONTINUE
```

```
C**** INPUT EQUATION OF STATE PARAMETERS ZM AND F FOR EACH COMPONENT
      READ(1,6)(ZM(I),F(I),I=1,NUM)
      GO TO 770
  750 CONTINUE
      DO 560 I=1,NUM
      DO 570 J=1,NUM
      ZETA(I,J)=1.0
  570 CONTINUE
C**** GENERALISED CORRELATONS FOR ZM AND F.
      ZM(I)=0.329032-0.0767992*WC(I)+0.0211947*WC(I)*WC(I)
      F(I)=0.452413+1.30982*WC(I)-0.295937*WC(I)*WC(I)
  560 CONTINUE
  770 CONTINUE
C**** INPUT THE TEMPERATURE OF THE SYSTEM IN RANKINE.
      READ(1,10)T
      READ(1,12)M
C**** M IS THE NO. OF EXPERIMENTAL POINTS
      WRITE(2,300)
C****
C**** THIS LOOP CALCULATES PURE COMPONENT CONSTANTS USING CRITICAL
C**** PROPERTIES AND ZM.
C****
      DO 14 I=1,NUM
      IF(FS.EQ.2)GO TO 700
      IF(FS.EQ.3)GO TO 710
      C(1)=1.0
      C(2)=2.0-3.0*ZM(I)
      C(3)=3.0*ZM(I)*ZM(I)
      C(4)=-ZM(I)**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION.
      OMB(I)=ZMAX
      OMC(I)=1.0-3.0*ZM(I)
      OMAC(I)=3.0*ZM(I)*ZM(I)+3.0*(1-2.0*ZM(I))*OMB(I)+OMB(I)*OMB(I)+OMC
     1(I)
      GO TO 720
  700 ZM(I)=0.3074
      F(I)=0.37464+1.54226*WC(I)-0.26992*WC(I)*WC(I)
      OMC(I)=1.0-3.0*ZM(I)
      OMB(I)=OMC(I)
      OMAC(I)=3.0*ZM(I)*ZM(I)+3.0*(1-2.0*ZM(I))*OMB(I)+OMB(I)*OMB(I)+OMC
     1(I)
      GO TO 720
  710 ZM(I)=0.333
      F(I)=0.48+1.574*WC(I)-0.176*WC(I)*WC(I)
      OMC(I)=0.0
      OMB(I)=0.08664
      OMAC(I)=0.42747
  720 CONTINUE
      B1(I)=OMB(I)*R*TC(I)/PC(I)
      C1(I)=OMC(I)*R*TC(I)/PC(I)
      TR(I)=T/TC(I)
      ALP(I)=(1+F(I)*(1-TR(I)**0.5))**2.0
      A1(I)=OMAC(I)*ALP(I)*R*R*TC(I)*TC(I)/PC(I)
      WRITE(2,995)I,ZM(I),I,OMAC(I),I,OMB(I),I,OMC(I),I,F(I)
      WRITE(2,40)I,TC(I),I,PC(I),I,WC(I),I,W1(I)
   14 CONTINUE
      WRITE(2,225)
      DO 900 L=1,M
C****
```

```
C**** INPUT A GUESS VALUE OF PRESSURE(PSIA)
C**** EXPERIMENTAL VALUE IS USED FOR COMPARISON PURPOSE.FINAL DEVIATION
C**** IN PRESSURE IS OBTAINED WITH RESPECT TO THIS VALUE.
C****
      READ(1,2)P
C****
C**** INPUT MOLE FRACTIONS IN LIQUIDPHASE IN THIS ORDER X(1),X(2),X(3),...
C**** ....X(NUM-1). EACH MOLE FRAC. ON SEPARATE CARD.
C****
      READ(1,2)(X(I),I=1,NUM-1)
      SUMX=0.0
      DO 525 I=1,NUM-1
  525 SUMX=SUMX+X(I)
      X(NUM)=1-SUMX
      POLD=P
      N1=0
    3 N1=N1+1
      ITN=1
      ITNM=50
      CALL SUMMATION(X)
C****
C**** SUBROUTINE SUMMATION IS USED TO CALCULATE MIXTURE PARAMETERS
C**** FROM PURE COMPONENT PARAMETERS FOR LIQUID PHASE.
C****
      CMM=CM*P/R/T
      BMM=BM*P/R/T
      AMM=AM*P/(R*R*T*T)
      C(1)=1.0
      C(2)=CMM-1.0
      C(3)=AMM-2*BMM*CMM-BMM*BMM-BMM-CMM
      C(4)=BMM*BMM*CMM-AMM*BMM+BMM*CMM
C**** EQUATION OF STATE IS SOLVED FOR LIQUID PHASE.
      CALL SOLVE(ZMIN,ZMAX,C)
      ZL=ZMIN
      IF(ZL.LT.0)ZL=ZMAX
      VL=ZL*R*T/P
      Z=ZL
C**** LIQUID PHASE FUGACITY IS CALCULATED.
      D=SQRT(((BM+CM)/2.0)**2.0+BM*CM)
      XX=VL+(BM+CM)/2.0
      XD2=XX**2.0-D**2.0
      AXD=ALOG((XX+D)/(XX-D))
      G1=-ALOG(Z-BMM)
      G2=XX/XD2-AXD/(2.0*D)
      DO 20 K=1,NUM
      E1(K)=(DBM(K)+BM)/(VL-BM)
      E2(K)=-(2.0+AM+DAM(K))*AXD/(2.0*D*R*T)
      E3(K)=AM*(DBM(K)+BM+DCM(K)+CM)/(2.0*XD2*R*T)
      E4(K)=-AM*((DBM(K)+DCM(K))*(BM+CM)*(BM+CM)**2.0+2*(CM*DBM(K)+BM*DC
     1M(K))+4.0*BM*CM)*G2/(4.0*R*T*D**2.0)
   20 CONTINUE
      SUM1=0.0
      DO 75 K=1,NUM
      PHIL(K)=G1+E1(K)+E2(K)+E3(K)+E4(K)
      PHIL(K)=EXP(PHIL(K))
      FL(K)=PHIL(K)*X(K)*P
      Y(K)=FL(K)/FC/P
C****
C**** INITIAL ESTIMATES OF THE VAPOUR PHASE FUGACITY CO EFFICIENTS
C**** FC=1.0 ARE USED.
```

```
C****
      SUM1=SUM1+Y(K)
   75 CONTINUE
      DO 80 I=1,NUM
   80 Y(I)=Y(I)/SUM1
C****
C**** NORMALISE VAPOUR MOLE FRACTIONS TO AVOID SUM OF THE MOLE FRACTIONS
C**** INCREASING BEYOND 1.0
C****
   90 CALL SUMMATION(Y)
C**** MIXTURE PARAMETERS ARE EVALUATED FOR VAPOUR PHASE.
      AMM=AM*P/(R*R*T*T)
      BMM=BM*P/R/T
      CMM=CM*P/R/T
      C(1)=1.0
      C(2)=CMM-1.0
      C(3)=AMM-2*BMM*CMM-BMM*BMM-BMM-CMM
      C(4)=BMM*BMM*CMM-AMM*BMM*BMM*CMM
C**** EQUATION OF STATE IS SOLVED FOR VAPOUR PHASE.
      CALL SOLVE(ZMIN,ZMAX,C)
      ZV=ZMAX
      VV=ZV*R*T/P
      Z=ZV
C**** VAPOUR PHASE FUGACITY IS CALCULATED.
      G1=-ALOG(Z-BMM)
      D=SQRT(((BM+CM)/2.0)**2.0+BM*CM)
      XX=VV+(BM+CM)/2.0
      XD2=XX**2.0-D**2.0
      AXD=ALOG((XX+D)/(XX-D))
      G2=XX/XD2-AXD/(2.0*D)
      SUM2=0.0
      SUMP=0.0
      DO 100 K=1,NUM
C****
C**** IF THE MOLE FRACTION OF ANY COMPONENT IN VAPOUR PHASE BECOMES
C**** 1.0 THEN PURE COMPONENT FUGACITY EXPRESSION MUST BE USED.
C****
      IF(ABS(1.0-Y(K)).LE.0.00001)GO TO 333
      E1(K)=(DBM(K)+BM)/(VV-BM)
      E2(K)=-(2.0*AM+DAM(K))*AXD/(2.0*D*R*T)
      E3(K)=AM*(DBM(K)+BM+DCM(K)+CM)/(2.0*XD2*R*T)
      E4(K)=-AM*((DBM(K)+DCM(K))*(BM+CM)+(BM+CM)**2.0+2*(CM*DBM(K)+BM*DC
     1M(K))+4.0*BM*CM)*G2/(4.0*R*T*D**2.0)
      PHIV(K)=G1+E1(K)+E2(K)+E3(K)+E4(K)
      PHIV(K)=EXP(PHIV(K))
      FV(K)=PHIV(K)*Y(K)*P
      GO TO 334
  333 CONTINUE
      Y(K)=1.0
      D1=SQRT(((BM+CM)/2.0)**2+BM*CM)
      D2=(BM+CM)/2.0-D1
      D3=(BM+CM)/2.0+D1
C**** PURE COMPONENT FUGACITY IS EVALUATED.
      PHIV(K)=Z-1.0-ALOG(Z)-ALOG((VV-BM)/VV)*(AM/(2.0*R*T*D1))*ALOG((VV+
     1D2)/(VV+D3))
      PHIV(K)=EXP(PHIV(K))
      FV(K)=PHIV(K)*P
  334 CONTINUE
      IF(FV(K).LE.0.00001)Y(K)=0.0
      IF(FV(K).LE.0.00001)FL(K)=FV(K)
```

```
      IF(FV(K).LE.0.00001)GO TO 100
      Y(K)=FL(K)*Y(K)/FV(K)
      SUMP=SUMP+Y(K)*P
      SUM2=SUM2+Y(K)
  100 CONTINUE
      DO 151 K=1,NUM
      IF(FL(K).LE.0.00001)GO TO 151
C**** EQUALITY OF FUGACITY IS DEFINED BY THE FOLLOWING STATEMENT.
      IF(ABS(FL(K)/FV(K)-1.0)-0.001)151,151,149
  151 CONTINUE
      GO TO 200
  149 ITN=ITN+1
      IF(ITNM-ITN)51,11,11
   51 WRITE(2,52)
      GO TO 220
   11 CONTINUE
      GO TO 90
  200 CONTINUE
C****
C**** THE SUM OF PARTIAL PRESSURES IS EQUATED TO TOTAL PRESSURE WITHIN A
C**** SPECIFIED LIMIT DEFINED BY THE FOLLOWING STATEMENT.
C****
      IF(ABS((SUMP-P)/SUMP).LE.0.00001)GO TO 185
      P=SUMP
      GO TO 3
  185 SUM1=SUM2
   99 SUMY=SUM1-1.0
C****
C**** WITHIN A SPECIFIED TOLERANCE AS DEFINED BY THE FOLLOWING
C**** STATEMENT THE SUM OF THE VAPOUR PHASE MOLE FRACTIONS MUST ADD UP
C**** TO 1.0
C****
      IF(ABS(SUMY).LE.0.00001)GO TO 220
      GO TO 90
  220 CONTINUE
C**** RESULTS ARE PRINTED
      WRITE(2,19)POLD
      WRITE(2,65)P,T
      WRITE(2,61)VL,VV
      WRITE(2,225)
      WRITE(2,29)
      WRITE(2,225)
      DO 50 I=1,NUM
C**** EQUILIBRIUM RATIOS ARE CALCULATED.
      R1(I)=Y(I)/X(I)
      WRITE(2,27)I,X(I),Y(I),FL(I),R1(I),EXPR1(I)
   50 CONTINUE
C**** DEVIATION IS CALCULATED
      DEVV=(POLD-P)*100/POLD
      ADEV=ADEV+ABS(DEVV)
      WRITE(2,36)DEVV
      WRITE(2,35)N1
      WRITE(2,62)
  900 CONTINUE
      L=L-1
      ADEV=ADEV/L
      WRITE(2,925)ADEV
C**** ***********************************************************************
    2 FORMAT(F0.0)
    4 FORMAT(I0,2F0.0)
```

```
    6 FORMAT(2F0.0)
    8 FORMAT(4F0.0)
   10 FORMAT(F0.0)
   12 FORMAT(I0)
   19 FORMAT(1H ,'EXPERIMENTAL PRESSURE=',F7.3)
   22 FORMAT(F0.0)
   23 FORMAT(1H ,'INTERACTION CO EFFICIENT ZETA(',I2,',',I2,')=',F6.4)
   27 FORMAT(1H ,4X,I2,14X,F6.4,10X,F6.4,13X,F9.4,10X,F7.4,10X,F7.4)
   29 FORMAT(1H ,'COMPONENT      LIQUID MOLE FRAC.      VAP. MOLE FRAC.
     1  FUGACITY      EQUILIBRIUM RATIO      EXP.EQUI. RATIO ')
   35 FORMAT(1H ,'NO. OF ITER.=',I3)
   36 FORMAT(1H ,'DEVIATION IN PRESSURE=',F6.4,'(%)')
   40 FORMAT(1H ,'TC(',I2,')=',F9.3,5X,'PC(',I2,')=',F9.4,5X,'ACE.FAC.('
     1,I2,')=',F6.4,5X,'MOL.WT.(',I2,')=',F9.3)
   52 FORMAT(1H ,'PHASE CALCULATION FAILED TO CONVERGE',/)
   55 FORMAT(F0.0)
   61 FORMAT(1H ,'VOLUME OF LIQUID PHASE=',F8.5,5X,'VOLUME OF VAPOUR PHA
     1SE =',F8.5)
   62 FORMAT(1H ,'*****************************************************
     1*****************************************************',/)
   65 FORMAT(1H ,'CALCULATED PRESSURE=',F8.3,5X,'TEMPERATURE=',F7.2)
  210 FORMAT(1H ,'GAS CONSTANT=',F8.4)
  225 FORMAT(/1H ,'-----------------------------------------------------
     1-----------------------------------------------------',/)
  295 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
     1 USING MODIFIED PENG-ROBINSON EQUATION')
  296 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
     1USING PENG-ROBINSON EQUATION')
  297 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
     1USING SOAVE EQUATION')
  300 FORMAT(1H ,'PRESSURE IN P.S.I.A.     VOLUME IN CU.FT.PER LB.MOLE
     1TEMPERATURE IN DEGREES RANKINE',//)
  925 FORMAT(1H ,'ABSOLUTE AVERAGE DEVIATION=',F6.4,'(%)')
  995 FORMAT(1H ,'ZM(',I2,')=',F9.7,5X,'OMAC(',I2,')=',F9.7,5X,'OMB(',I2
     1,')=',F9.7,5X,'OMC(',I2,')=',F9.7,5X,'F(',I2,')=',F9.7)
C*********************************************************************
      STOP
      END
```

INPUT FOR PROGRAM NO.2

```
C*****************************************************************************
C**** A TYPICAL DATA INPUT FOR METHANE(1)-ETHANE(2)-PROPANE(3) SYSTEM
C**** ****************** ***************************************************
DOCUMENT DATA
1.0                                          ES SPECIFIES EQUATION
2.0                                          GS
3 1.0 10.7335                                NUM  FC  R
343.044 667.782 0.012 16.04                  TC  PC  WC  W1
549.76 707.755 0.099 30.07
665.68 616.347 0.153 44.10
1.0                                           INTERACTION COEFFICIENT
1.0                                           INTERACTION COEFFICIENT
1.0                                           INTERACTION COEFFICIENT
0.324 0.455336                               ZM  F
0.317 0.561567
0.317 0.648049
359.67                                       TEMPERATURE
1                                            NO. OF EXPERIMENTAL POINTS
100.0                                        PRESSURE
0.118                                        MOLE FRACTION X(1)
0.144                                        MOLE FRACTION X(2)
****
```

```
PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA  USING MODIFIED PENG-ROBINSON EQUATION
GAS CONSTANT= 10.7335
INTERACTION CO EFFICIENT ZETA( 1, 2)=1.0000
INTERACTION CO EFFICIENT ZETA( 1, 3)=1.0000
INTERACTION CO EFFICIENT ZETA( 2, 3)=1.0000
PRESSURE IN P.S.I.A.    VOLUME IN CU.FT.PER LB.MOLE   TEMPERATURE IN DEGREES RANKINE

ZM( 1)=0.3240000     OMAC( 1)=0.4379945     OMB( 1)=0.0834332     OMC( 1)=0.0280000     F( 1)=0.4553360
TC( 1)=  343.044     PC( 1)= 667.7820     ACE.FAC.( 1)=0.0120     MOL.WT.( 1)=   16.040
ZM( 2)=0.3170000     OMAC( 2)=0.4460231     OMB( 2)=0.0810453     OMC( 2)=0.0490000     F( 2)=0.5615670
TC( 2)=  549.760     PC( 2)= 707.7550     ACE.FAC.( 2)=0.0990     MOL.WT.( 2)=   30.070
ZM( 3)=0.3170000     OMAC( 3)=0.4460231     OMB( 3)=0.0810453     OMC( 3)=0.0490000     F( 3)=0.6480490
TC( 3)=  665.680     PC( 3)= 616.3470     ACE.FAC.( 3)=0.1530     MOL.WT.( 3)=   44.100

EXPERIMENTAL PRESSURE=100.000
CALCULATED PRESSURE= 100.282     TEMPERATURE= 359.67
VOLUME OF LIQUID PHASE= 1.04127     VOLUME OF VAPOUR PHASE =36.29746
```

COMPONENT	LIQUID MOLE FRAC.	VAP. MOLE FRAC.	FUGACITY	EQUILIBRIUM RATIO	EXP.EQUI. RATIO
1	0.1180	0.9228	88.3114	7.8202	
2	0.1440	0.0502	4.3718	0.3485	
3	0.7380	0.0270	2.1756	0.0366	

```
DEVIATION IN PRESSURE=-.2820(%)
NO. OF ITER.=  4
**********************************************************************************************

ABSOLUTE AVERAGE DEVIATION=0.2820(%)
```

PROGRAM NO.3

```
      MASTER TEMPERATURE
C****
C*****************************************************************
C     PREDICTION OF TEMPERATURE AND VAP. PHASE MOLE FRACTIONS USING
C     MODIFIED PENG-ROBINSON EQUATION OF STATE
C**** THIS PROGRAM CAN ALSO BE USED FOR PENG-ROBINSON EQUATION AND
C**** SOAVE EQUATION BY SPECIFYING THE PARAMETER ES=2 AND ES=3
C**** RESPECTIVELY.
C**** ****************** ***********************************************
C****
      DIMENSION EXPR1(10),DEV(10),DEVR1(10)
      DIMENSION R1(10),ALP(10),F(10)
      DIMENSION ZM(10),TC(10),PC(10),WC(10),W1(10),TR(10),C(5),OMB(10)
      DIMENSION OMC(10),OMAC(10),E1(10),E2(10),E3(10),E4(10)
      DIMENSION X(10),Y(10),FL(10),FV(10),PHIV(10),PHIL(10)
      COMMON/BL1/A1(10),B1(10),C1(10),AIJ(10,10),DIA(10)
      COMMON/BL2/AM,BM,CM,NUM,ZETA(10,10)
      COMMON/BL3/DAM(10),DBM(10),DCM(10)
      WRITE(2,225)
C**** ES=1 IF MODIFIED PR EQUATION IS TO BE USED.
C**** ES=2 IF PR EQUATION IS TO BE USED.
C**** ES=3 IF SOAVE EQUATION IS TO BE USED.
C****
      READ(1,55)ES
      READ(1,55)GS
C****
C**** INPUT GS=1.0 IF GENERALISED FORM OF THE MODIFIED PENG ROBINSON
C**** EQUATION IS TO BE USED WITH ALL THE INTERACTION CO EFFICIENTS
C**** ASSUMED TO BE 1.0. THIS IS NECCESSARY FOR A MIXTURE CONTAINING
C**** COMPONENTS WHOSE ZM AND F PARAMETERS ARE NOT AVAILABLE AND
C**** INTERACTION CO EFFICIENTS ARE NOT KNOWN.
C****
      IF(ES.EQ.1)WRITE(2,295)
      IF(ES.EQ.2)WRITE(2,296)
      IF(ES.EQ.3)WRITE(2,297)
      READ(1,4)NUM,FC,R
C****
C**** NUM IS NO. OF COMPONENTS; R IS THE UNIVERSAL GAS CONSTANT.
C**** THE VALUE OF R CORRESPONDS TO P(PSIA), V(CU.FT./LB.MOLE),
C**** T(RANKINE).
C**** FC IS THE INITIAL ESTIMATE OF THE VAPOUR PHASE FUGACITY COEFFICIEN
C****
      WRITE(2,210)R
C****
C**** INPUT CRITICAL CONSTANTS
C****
      READ(1,8)(TC(I),PC(I),WC(I),W1(I),I=1,NUM)
      IF(GS.EQ.1.0)GO TO 750
C****
C**** INPUT INTERACTION CO EFFICIENTS IN THIS ORDER ZETA(1,2),ZETA(1,3)
C**** ZETA(1,4),ZETA(2,3),ZETA(2,4),ZETA(3,4) FOR 4 COMPONENTS.
C****
      DO 500 I=1,NUM
      DO 550 J=1,NUM
      IF(I.GE.J)GO TO 550
      READ(1,22)ZETA(I,J)
      ZETA(J,I)=ZETA(I,J)
      WRITE(2,23)I,J,ZETA(I,J)
  550 CONTINUE
  500 CONTINUE
```

```
C**** INPUT EQUATION OF STATE PARAMETERS ZM AND F FOR EACH COMPONENT
      READ(1,6)(ZM(I),F(I),I=1,NUM)
      GO TO 770
  750 CONTINUE
      DO 560 I=1,NUM
      DO 570 J=1,NUM
      ZETA(I,J)=1.0
  570 CONTINUE
C**** GENERALISED CORRELATONS FOR ZM AND F.
      ZM(I)=0.329032-0.0767992*WC(I)+0.0211947*WC(I)*WC(I)
      F(I)=0.452413+1.30982*WC(I)-0.295937*WC(I)*WC(I)
  560 CONTINUE
  770 CONTINUE
      WRITE(2,300)
      READ(1,12)M
C**** M IS THE NO. OF EXPERIMENTAL POINTS
C****
C**** THIS LOOP CALCULATES PURE COMPONENT CONSTANTS USING CRITICAL
C**** PROPERTIES AND ZM.
C****
      DO 14 I=1,NUM
      IF(FS.EQ.2)GO TO 700
      IF(FS.EQ.3)GO TO 710
      C(1)=1.0
      C(2)=2.0-3.0*ZM(I)
      C(3)=3.0*ZM(I)*ZM(I)
      C(4)=-ZM(I)**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION.
      OMB(I)=ZMAX
      OMC(I)=1.0-3.0*ZM(I)
      OMAC(I)=3.0*ZM(I)*ZM(I)+3.0*(1-2.0*ZM(I))*OMB(I)+OMB(I)*OMB(I)+OMC
     1(I)
      GO TO 720
  700 ZM(I)=0.3074
      F(I)=0.37464+1.54226*WC(I)-0.26992*WC(I)*WC(I)
      OMC(I)=1.0-3.0*ZM(I)
      OMB(I)=OMC(I)
      OMAC(I)=3.0*ZM(I)*ZM(I)+3.0*(1-2.0*ZM(I))*OMB(I)+OMB(I)*OMB(I)+OMC
     1(I)
      GO TO 720
  710 ZM(I)=0.333
      F(I)=0.48+1.574*WC(I)-0.176*WC(I)*WC(I)
      OMC(I)=0.0
      OMB(I)=0.08664
      OMAC(I)=0.42747
  720 CONTINUE
      B1(I)=OMB(I)*R*TC(I)/PC(I)
      C1(I)=OMC(I)*R*TC(I)/PC(I)
      WRITE(2,995)I,ZM(I),I,OMAC(I),I,OMB(I),I,OMC(I),I,F(I)
      WRITE(2,40)I,TC(I),I,PC(I),I,WC(I),I,W1(I)
   14 CONTINUE
      WRITE(2,225)
      DO 900 L=1,M
      READ(1,10)P,T
C**** INPUT EXPERIMENTAL PRESSURE AND A GUESS VALUE OF TEMPERATURE
C**** EXPERIMENTAL VALUE OF  T IS USED WHEN AVAILABLE
C****
C**** INPUT MOLE FRACTIONS IN LIQUIDPHASE IN THIS ORDER X(1),X(2),X(3)..
C**** ....X(NUM-1). EACH MOLE FRAC. ON SEPARATE CARD.
```

```
C****
      READ(1,2)(X(I),I=1,NUM-1)
      SUMX=0.0
      DO 525 I=1,NUM-1
  525 SUMX=SUMX+X(I)
      X(NUM)=1-SUMX
      TIN=T
      N1=0
      ITN=1
      ITNM=50
    3 N1=N1+1
      DO 15 I=1,NUM
      TR(I)=T/TC(I)
      ALP(I)=(1+F(I)*(1-TR(I)**0.5))**2.0
      A1(I)=OMAC(I)*ALP(I)*R*R*TC(I)*TC(I)/PC(I)
   15 CONTINUE
      CALL SUMMATION(X)
C****
C**** SUBROUTINE SUMMATION IS USED TO CALCULATE MIXTURE PARAMETERS
C**** FROM PURE COMPONENT PARAMETERS FOR LIQUID PHASE.
C****
      CMM=CM*P/R/T
      BMM=BM*P/R/T
      AMM=AM*P/(R*R*T*T)
      C(1)=1.0
      C(2)=CMM-1.0
      C(3)=AMM-2*BMM*CMM-BMM*BMM-BMM-CMM
      C(4)=BMM*BMM*CMM-AMM*BMM+BMM*CMM
C**** EQUATION OF STATE IS SOLVED FOR LIQUID PHASE.
      CALL SOLVE(ZMIN,ZMAX,C)
      ZL=ZMIN
      VL=ZL*R*T/P
      Z=ZL
C**** LIQUID PHASE FUGACITY IS CALCULATED.
      D=SQRT(((BM+CM)/2.0)**2.0+BM*CM)
      XX=VL+(BM+CM)/2.0
      XD2=XX**2.0-D**2.0
      AXD=ALOG((XX+D)/(XX-D))
      G1=-ALOG(Z-BMM)
      G2=XX/XD2-AXD/(2.0*D)
      DO 20 K=1,NUM
      E1(K)=(DBM(K)+BM)/(VL-BM)
      E2(K)=-(2.0*AM+DAM(K))*AXD/(2.0*D*R*T)
      E3(K)=AM*(DBM(K)+BM+DCM(K)+CM)/(2.0*XD2*R*T)
      E4(K)=-AM*((DBM(K)+DCM(K))*(BM+CM)+(BM+CM)**2.0+2*(CM*DBM(K)+BM*DC
     1M(K))+4.0*BM*CM)*G2/(4.0*R*T*D**2.0)
   20 CONTINUE
      SUM1=0.0
      DO 75 K=1,NUM
      PHIL(K)=G1+E1(K)+E2(K)+E3(K)+E4(K)
      PHIL(K)=EXP(PHIL(K))
      FL(K)=PHIL(K)*X(K)*P
      Y(K)=FL(K)/FC/P
      SUM1=SUM1+Y(K)
   75 CONTINUE
      DO 80 I=1,NUM
   80 Y(I)=Y(I)/SUM1
C**** MIXTURE PARAMETERS ARE EVALUATED FOR VAPOUR PHASE.
   90 CALL SUMMATION(Y)
      AMM=AM*P/(R*R*T*T)
```

```
      BMM=BM*P/R/T
      CMM=CM*P/R/T
      C(1)=1.0
      C(2)=CMM-1.0
      C(3)=AMM-2*BMM*CMM-BMM*BMM-BMM-CMM
      C(4)=BMM*BMM*CMM-AMM*BMM+BMM*CMM
C**** EQUATION OF STATE IS SOLVED FOR VAPOUR PHASE.
      CALL SOLVE(ZMIN,ZMAX,C)
      ZV=ZMAX
      VV=ZV*R*T/P
      Z=ZV
C**** VAPOUR PHASE FUGACITY IS CALCULATED.
      G1=-ALOG(Z-BMM)
      D=SQRT(((BM+CM)/2.0)**2.0+BM*CM)
      XX=VV+(BM+CM)/2.0
      XD2=XX**2.0-D**2.0
      AXD=ALOG((XX+D)/(XX-D))
      G2=XX/XD2-AXD/(2.0*D)
      DO 30 K=1,NUM
      E1(K)=(DBM(K)+BM)/(VV-BM)
      E2(K)=-(2.0*AM+DAM(K))*AXD/(2.0*D*R*T)
      E3(K)=AM*(DBM(K)+BM+DCM(K)+CM)/(2.0*XD2*R*T)
      E4(K)=-AM*((DBM(K)+DCM(K))*(BM+CM)+(BM+CM)**2.0+2*(CM*DBM(K)+BM*DC
     1M(K))+4.0*BM*CM)*G2/(4.0*R*T*D**2.0)
   30 CONTINUE
      SUM2=0.0
      DO 100 K=1,NUM
      PHIV(K)=G1+E1(K)+E2(K)+E3(K)+E4(K)
      PHIV(K)=EXP(PHIV(K))
      FV(K)=PHIV(K)*Y(K)*P
      R1(K)=FL(K)*Y(K)/FV(K)/X(K)
      Y(K)=R1(K)*X(K)
      SUM2=SUM2+Y(K)
  100 CONTINUE
      DO 151 K=1,NUM
C**** EQUALITY OF FUGACITY IS DEFINED BY THE FOLLOWING STATEMENT.
      IF(ABS(FL(K)/FV(K)-1.0)-0.001)151,151,149
  151 CONTINUE
      GO TO 200
  149 ITN=ITN+1
      IF(ITNM-ITN)51,11,11
   51 WRITE(2,52)
      GO TO 220
   11 CONTINUE
      GO TO 90
  200 SUMY=SUM2-1.0
C**** SUM OF THE VAPOUR PHASE MOLE FRACTIONS MUST BE UNITY
      IF(ABS(SUMY).LE.0.0001)GO TO 220
      IF(N1.EQ.1)GO TO 260
      GO TO 280
  260 TPREV=T
      IF(SUM2.LT.1.0)GO TO 270
      T=0.99*T
      SUMVP=SUM2
      GO TO 3
  270 T=1.01*T
      SUMVP=SUM2
      GO TO 3
  280 IF((SUM2-SUMVP).EQ.0.0)GO TO 260
C**** NEW VALUE OF THE TEMP. IS OBTAINED AS FOLLOWS AFTER THE FIRST
```

```
C**** ITERATION
      SLOPE=(T-TPREV)/(SUM2-SUMYP)
      DELT=SLOPE*SUMY
      IF(ABS(DELT).GT.0.1*T)DELT=DELT*0.1*T/ABS(DELT)
      TPREV=T
      SUMYP=SUM2
      T=T-DELT
      GO TO 3
  220 CONTINUE
      WRITE(2,19)TIN
      WRITE(2,65)P,T
      WRITE(2,61)VL,VV
      WRITE(2,225)
      WRITE(2,29)
      WRITE(2,225)
      DO 50 I=1,NUM
      R1(I)=Y(I)/X(I)
      WRITE(2,27)I,X(I),Y(I),FL(I),R1(I),EXPR1(I)
   50 CONTINUE
      WRITE(2,35)N1
      WRITE(2,62)
  900 CONTINUE
C*********************************************************************
    2 FORMAT(F0.0)
    4 FORMAT(I0,2F0.0)
    6 FORMAT(2F0.0)
    8 FORMAT(4F0.0)
   10 FORMAT(2F0.0)
   12 FORMAT(I0)
   19 FORMAT(1H ,'EXPERIMENTAL TEMPERATURE =',F6.1)
   22 FORMAT(F0.0)
   23 FORMAT(1H ,'INTERACTION CO EFFICIENT ZETA(',I2,',',I2,')=',F6.4)
   27 FORMAT(1H ,4X,I2,14X,F6.4,10X,F6.4,13X,F9.4,10X,F7.4,10X,F7.4)
   29 FORMAT(1H ,'COMPONENT      LIQUID MOLE FRAC.      VAP. MOLE FRAC.
     1  FUGACITY      EQUILIBRIUM RATIO      EXP.EQUI. RATIO ')
   35 FORMAT(1H ,'NO. OF ITER.=',I3)
   40 FORMAT(1H ,'TC(',I2,')=',F9.3,5X,'PC(',I2,')=',F9.4,5X,'ACE.FAC.('
     1,I2,')=',F6.4,5X,'MOL.WT.(',I2,')=',F9.3)
   52 FORMAT(1H ,'PHASE CALCULATION FAILED TO CONVERGE',/)
   55 FORMAT(F0.0)
   61 FORMAT(1H ,'VOLUME OF LIQUID PHASE=',F8.5,5X,'VOLUME OF VAPOUR PHA
     1SE =',F8.5)
   62 FORMAT(1H ,'*********************************************************
     1*********************************************************',/)
   65 FORMAT(1H ,'PRESSURE=',F7.2,5X,'CALCULATED TEMPERATURE=',F7.2)
  210 FORMAT(1H ,'GAS CONSTANT=',F8.4)
  225 FORMAT(/1H ,'-------------------------------------------------------
     1-------------------------------------------------------',/)
  295 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
     1 USING MODIFIED PENG-ROBINSON EQUATION')
  296 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
     1USING PENG-ROBINSON EQUATION')
  297 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
     1USING SOAVE EQUATION')
  300 FORMAT(1H ,'PRESSURE IN P.S.I.A.     VOLUME IN CU.FT.PER LB.MOLE
     1TEMPERATURE IN DEGREES RANKINE ',//)
  995 FORMAT(1H ,'ZM(',I2,')=',F9.7,5X,'OMAC(',I2,')=',F9.7,5X,'OMB(',I2
     1,')=',F9.7,5X,'OMC(',I2,')=',F9.7,5X,'F(',I2,')=',F9.7)
C*********************************************************************
      STOP
      END
```

INPUT FOR PROGRAM NO.3

```
C*****************************************************************
C**** A TYPICAL DATA INPUT FOR METHANE(1)-ETHANE(2)-PROPANE(3) SYSTEM
C*****************************************************************
DOC DATA
1.0                                          ES
2.0                                          GS
 3 1.0 10.7335                               NUM  FC  R
343.044 667.782 0.012 16.04                  TC   PC  WC  W1
549.76 707.755 0.099 30.07                   TC   PC  WC  W1
665.68 616.347 0.153 44.10                   TC   PC  WC  W1
1.0                                          INTERACTION CO-EFFICIENT
1.0                                          INTERACTION CO-EFFICIENT
1.0                                          INTERACTION CO-EFFICIENT
0.324 0.455336                               ZM   F
0.317 0.561567                               ZM   F
0.317 0.648049                               ZM   F
1                                            NO. OF DATA POINTS
100.0 509.67                                 P    T(GUESS)
0.0022                                       X(1)
0.008                                        X(2)
****
```

OUTPUT FOR PROGRAM NO.3

```
PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA  USING MODIFIED PENG-ROBINSON EQUATION
GAS CONSTANT= 10 7335
INTERACTION CO EFFICIENT ZETA( 1, 2)=1.0000
INTERACTION CO EFFICIENT ZETA( 1, 3)=1.0000
INTERACTION CO EFFICIENT ZETA( 2, 3)=1.0000
PRESSURE IN P.S.I.A.    VOLUME IN CU.FT.PER LB.MOLE   TEMPERATURE IN DEGREES RANKINE

ZM( 1)=0.3240000     OMAC( 1)=0.4379945     OMB( 1)=0.0834332     OMC( 1)=0.0280000     F( 1)=0.4553360
TC( 1)=  343.044     PC( 1)= 667.7820     ACE.FAC.( 1)=0.0120     MOL.WT.( 1)=   16.040
ZM( 2)=0.3170000     OMAC( 2)=0.4460231     OMB( 2)=0.0810453     OMC( 2)=0.0490000     F( 2)=0.5615670
TC( 2)=  549.760     PC( 2)= 707.7550     ACE.FAC.( 2)=0.0990     MOL.WT.( 2)=   30.070
ZM( 3)=0.3170000     OMAC( 3)=0.4460231     OMB( 3)=0.0810453     OMC( 3)=0.0490000     F( 3)=0.6480490
TC( 3)=  665.680     PC( 3)= 616.3470     ACE.FAC.( 3)=0.1530     MOL.WT.( 3)=   44.100

EXPERIMENTAL TEMPERATURE = 509.7
PRESSURE= 100.00     CALCULATED TEMPERATURE= 510.30
VOLUME OF LIQUID PHASE= 1.36623     VOLUME OF VAPOUR PHASE =47.59638
```

COMPONENT	LIQUID MOLE FRAC.	VAP. MOLE FRAC.	FUGACITY	EQUILIBRIUM RATIO	EXP.EQUI. RATIO
1	0.0022	0.0413	4.3094	18.7896	
2	0.0080	0.0267	2.5314	3.3391	
3	0.9898	0.9319	81.5506	0.9415	

NO. OF ITER.= 3

****

PROGRAM NO.4

```
      MASTER EQUILIBRIUM RATIOS
C****
C**** ****************** ***********************************************
C**** PREDICTION OF K VALUES USING MODIFIED PENG-ROBINSON EQUATION
C**** THIS PROGRAM CAN ALSO BE USED FOR PENG-ROBINSON EQUATION AND
C**** SOAVE EQUATION BY SPECIFYING THE PARAMETER ES=2 AND ES=3
C**** RESPECTIVELY.
C**** BINARY MIXTURES ONLY
C**** ****************** ***********************************************
C****
      DIMENSION EXPR1(10),DEV(10),DEVR1(10)
      DIMENSION R1(10),ALP(10),F(10)
      DIMENSION X(10),Y(10),FL(10),FV(10),PHIV(10),PHIL(10)
      DIMENSION ZM(10),TC(10),PC(10),WC(10),W1(10),TR(10),C(5),OMB(10)
      DIMENSION OMC(10),OMAC(10),E1(10),E2(10),E3(10),E4(10)
      COMMON/BL1/A1(10),B1(10),C1(10),AIJ(10,10),DIA(10)
      COMMON/BL2/AM,BM,CM,NUM,ZETA(10,10)
      COMMON/BL3/DAM(10),DBM(10),DCM(10)
C****
C**** ES=1 IF MODIFIED PR EQUATION IS TO BE USED.
C**** ES=2 IF PR EQUATION IS TO BE USED.
C**** ES=3 IF SOAVE EQUATION IS TO BE USED.
C****
      READ(1,55)ES
      WRITE(2,225)
      IF(ES.EQ.2)WRITE(2,296)
      IF(ES.EQ.3)WRITE(2,297)
      IF(ES.EQ.1)WRITE(2,295)
      READ(1,22)ZETA(1,2)
C**** ZETA IS THE BINARY INTERACTION CO-EFFICIENT.
      NUM=2
      R=10.7335
C**** NUM IS NO. OF COMPONENTS; R IS THE UNIVERSAL GAS CONSTANT.
C****
C**** THE VALUE OF R CORRESPONDS TO P(PSIA), V(CU.FT./LB.MOLE),
C**** T(RANKINE).
C****
C**** INPUT EQUATION OF STATE PARAMETERS ZM AND F FOR EACH COMPONENT
C****
      READ(1,6)(ZM(I),F(I),I=1,NUM)
C**** INPUT CRITICAL CONSTANTS
C****
      READ(1,8)(TC(I),PC(I),WC(I),W1(I),I=1,NUM)
      WRITE(2,210)R,ZETA(1,2)
      WRITE(2,300)
      READ(1,12)M
C**** M IS THE NO. OF EXPERIMENTAL POINTS
      DEVR1(1)=0.0
      DEVR1(2)=0.0
C****
C**** THIS LOOP CALCULATES PURE COMPONENT CONSTANTS USING CRITICAL
C**** PROPERTIES AND ZM.
C****
      DO 14 I=1,NUM
      IF(ES.EQ.2)GO TO 700
      IF(ES.EQ.3)GO TO 710
      C(1)=1.0
      C(2)=2.0-3.0*ZM(I)
      C(3)=3.0*ZM(I)*ZM(I)
      C(4)=-ZM(I)**3.0
```

```
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION.
      OMB(I)=ZMAX
      OMC(I)=1.0-3.0*ZM(I)
      OMAC(I)=3.0*ZM(I)*ZM(I)+3.0*(1-2.0*ZM(I))*OMB(I)+OMB(I)*OMB(I)+OM
     1(I)
      GO TO 720
  700 ZM(I)=0.3074
      F(I)=0.37464+1.54226*WC(I)-0.26992*WC(I)*WC(I)
      OMC(I)=1.0-3.0*ZM(I)
      OMB(I)=OMC(I)
      OMAC(I)=3.0*ZM(I)*ZM(I)+3.0*(1-2.0*ZM(I))*OMB(I)+OMB(I)*OMB(I)+OM
     1(I)
      GO TO 720
  710 ZM(I)=0.333
      F(I)=0.48+1.574*WC(I)-0.176*WC(I)*WC(I)
      OMC(I)=0.0
      OMB(I)=0.08664
      OMAC(I)=0.42747
  720 CONTINUE
      B1(I)=OMB(I)*R*TC(I)/PC(I)
      C1(I)=OMC(I)*R*TC(I)/PC(I)
      WRITE(2,995)I,ZM(I),I,OMAC(I),I,OMB(I),I,OMC(I),I,F(I)
      WRITE(2,40)I,TC(I),I,PC(I),I,WC(I),I,W1(I)
   14 CONTINUE
      WRITE(2,225)
      DO 900 L=1,M
C****
C**** INPUT P(PSIA),T(RANKINE) AND GUESSES FOR 'K' VALUES.EXPERIMENTAL
C**** VALUES ARE USED FOR COMPARISON PURPOSE.
C****
      READ(1,10)P,T,R1(1),R1(2)
      EXPR1(1)=R1(1)
      EXPR1(2)=R1(2)
      DO 15 I=1,NUM
      TR(I)=T/TC(I)
      ALP(I)=(1+F(I)*(1-TR(I)**0.5))**2.0
      A1(I)=OMAC(I)*ALP(I)*R*R*TC(I)*TC(I)/PC(I)
   15 CONTINUE
      N1=0
      ITN=1
      ITNM=50
    3 N1=N1+1
      X(1)=(1-R1(2))/(R1(1)-R1(2))
      X(2)=1-X(1)
      CALL SUMMATION(X)
C**** SUBROUTINE SUMMATION IS USED TO CALCULATE MIXTURE PARAMETERS
C**** FROM PURE COMPONENT PARAMETERS FOR LIQUID PHASE.
      CMM=CM*P/R/T
      BMM=BM*P/R/T
      AMM=AM*P/(R*R*T*T)
      C(1)=1.0
      C(2)=CMM-1.0
      C(3)=AMM-2*BMM*CMM-BMM*BMM-BMM-CMM
      C(4)=BMM*BMM*CMM-AMM*BMM+BMM*CMM
C**** EQUATION OF STATE IS SOLVED FOR LIQUID PHASE.
      CALL SOLVE(ZMIN,ZMAX,C)
      ZL=ZMIN
      VL=ZL*R*T/P
      Z=ZL
```

```
C**** LIQUID PHASE FUGACITY IS CALCULATED.
      D=SQRT(((BM+CM)/2.0)**2.0+BM*CM)
      XX=VL+(BM+CM)/2.0
      XD2=XX**2.0-D**2.0
      AXD=ALOG((XX+D)/(XX-D))
      G1=-ALOG(Z-BMM)
      G2=XX/XD2-AXD/(2.0*D)
      DO 20 K=1,NUM
      E1(K)=(DBM(K)+BM)/(VL-BM)
      E2(K)=-(2.0*AM+DAM(K))*AXD/(2.0*D*R*T)
      E3(K)=AM*(DBM(K)+BM+DCM(K)+CM)/(2.0*XD2*R*T)
      E4(K)=-AM*((DBM(K)+DCM(K))*(BM+CM)+(BM+CM)**2.0+2*(CM*DBM(K)+BM*D
     1M(K))+4.0*BM*CM)*G2/(4.0*R*T*D**2.0)
   20 CONTINUE
      SUM1=0.0
      DO 75 K=1,NUM
      PHIL(K)=G1+E1(K)+E2(K)+E3(K)+E4(K)
      PHIL(K)=EXP(PHIL(K))
      FL(K)=PHIL(K)*X(K)*P
      Y(K)=R1(K)*X(K)
      SUM1=SUM1+Y(K)
   75 CONTINUE
      DO 80 I=1,NUM
   80 Y(I)=Y(I)/SUM1
C**** MIXTURE PARAMETERS ARE EVALUATED FOR VAPOUR PHASE.
   90 CALL SUMMATION(Y)
      AMM=AM*P/(R*R*T*T)
      BMM=BM*P/R/T
      CMM=CM*P/R/T
      C(1)=1.0
      C(2)=CMM-1.0
      C(3)=AMM-2*BMM*CMM-BMM*BMM-BMM-CMM
      C(4)=BMM*BMM*CMM-AMM*BMM+BMM*CMM
C**** EQUATION OF STATE IS SOLVED FOR VAPOUR PHASE.
      CALL SOLVE(ZMIN,ZMAX,C)
      ZV=ZMAX
      VV=ZV*R*T/P
      Z=ZV
C**** VAPOUR PHASE FUGACITY IS CALCULATED.
      G1=-ALOG(Z-BMM)
      D=SQRT(((BM+CM)/2.0)**2.0+BM*CM)
      XX=VV+(BM+CM)/2.0
      XD2=XX**2.0-D**2.0
      AXD=ALOG((XX+D)/(XX-D))
      G2=XX/XD2-AXD/(2.0*D)
      DO 30 K=1,NUM
      E1(K)=(DBM(K)+BM)/(VV-BM)
      E2(K)=-(2.0*AM+DAM(K))*AXD/(2.0*D*R*T)
      E3(K)=AM*(DBM(K)+BM+DCM(K)+CM)/(2.0*XD2*R*T)
      E4(K)=-AM*((DBM(K)+DCM(K))*(BM+CM)+(BM+CM)**2.0+2*(CM*DBM(K)+BM*D
     1M(K))+4.0*BM*CM)*G2/(4.0*R*T*D**2.0)
   30 CONTINUE
      DO 100 K=1,NUM
      PHIV(K)=G1+E1(K)+E2(K)+E3(K)+E4(K)
      PHIV(K)=EXP(PHIV(K))
      FV(K)=PHIV(K)*Y(K)*P
      R1(K)=FL(K)*Y(K)/FV(K)/X(K)
  100 CONTINUE
      DO 151 K=1,NUM
C**** EQUALITY OF FUGACITY IS DEFINED BY THE FOLLOWING STATEMENT.
```

```
      IF(ABS(FL(K)/FV(K)-1.0)-0.001)151,151,149
  151 CONTINUE
      GO TO 200
  149 ITN=ITN+1
      IF(ITNM-ITN)51,11,11
   51 WRITE(2,52)
   52 FORMAT(1H ,'PHASE CALCULATION FAILED TO CONVERGE',/)
      GO TO 200
   11 CONTINUE
      GO TO 3
  200 CONTINUE
      WRITE(2,65)P,T
      WRITE(2,61)VL,VV
      WRITE(2,225)
      WRITE(2,29)
      WRITE(2,225)
      DO 50 I=1,NUM
      R1(I)=Y(I)/X(I)
C****
C     DEVIATIONS ARE CALCULATED.
C****
      DEV(I)=(EXPR1(I)-R1(I))*100/EXPR1(I)
      DEVR1(I)=DEVR1(I)+ABS(DEV(I))
      WRITE(2,27)I,X(I),Y(I),FL(I),R1(I),EXPR1(I)
   50 CONTINUE
      WRITE(2,36)DEV(1),DEV(2)
      WRITE(2,35)N1
      WRITE(2,62)
  900 CONTINUE
      L=L-1
      DEVR1(1)=DEVR1(1)/L
      DEVR1(2)=DEVR1(2)/L
      WRITE(2,925)L,DEVR1(1),DEVR1(2)
C*****************************************************************
    6 FORMAT(2F0.0)
    8 FORMAT(4F0.0)
   10 FORMAT(4F0.0)
   12 FORMAT(I0)
   22 FORMAT(F0.0)
   27 FORMAT(1H ,4X,I2,14X,F6.4,10X,F6.4,13X,F9.4,10X,F7.4,10X,F7.4)
   29 FORMAT(1H ,'COMPONENT      LIQUID MOLE FRAC.      VAP. MOLE FRAC.
     1  FUGACITY      EQUILIBRIUM RATIO      EXP.EQUI. RATIO ')
   35 FORMAT(1H ,'NO. OF ITER.=',I3)
   36 FORMAT(/1H ,'DEVIATION K(1)=',F6.3,5X,'K(2)=',F6.3,/)
   40 FORMAT(1H ,'TC(',I2,')=',F9.3,5X,'PC(',I2,')=',F9.4,5X,'ACE.FAC.(
     1,I2,')=',F6.4,5X,'MOL.WT.(',I2,')=',F9.3)
   55 FORMAT(F0.0)
   61 FORMAT(1H ,'VOLUME OF LIQUID PHASE=',F8.5,5X,'VOLUME OF VAPOUR PH
     1SE =',F8.5)
   62 FORMAT(1H ,'*****************************************************
     1*****************************************************',/)
   65 FORMAT(1H ,'PRESSURE=',F7.2,5X,'TEMPERATURE=',F7.2)
  210 FORMAT(/1H ,'GAS CONSTANT=',F8.4,10X,'INTERACTION COEFFICIENT=',F
     1.4,/)
  225 FORMAT(/1H ,'-----------------------------------------------------
     1-----------------------------------------------------',/)
  295 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
     1 USING MODIFIED PENG-ROBINSON EQUATION')
  296 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
     1USING PENG-ROBINSON EQUATION')
```

```
297 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
   1USING SOAVE EQUATION')
300 FORMAT(1H ,'PRESSURE IN P.S.I.A.     VOLUME IN CU.FT.PER LB.MOLE
   1TEMPERATURE IN DEGREES RANKINE',//)
925 FORMAT(//1H ,'AVERAGE DEVIATIONS(',I2,'POINTS)=',5X,'K(1)=',F5.2,
   1 % ',5X,'K(2)=',F5.2,'%')
995 FORMAT(1H ,'ZM(',I2,')=',F9.7,5X,'OMAC(',I2,')=',F9.7,5X,'OMB(',I
   1,')=',F9.7,5X,'OMC(',I2,')=',F9.7,5X,'F(',I2,')=',F9.7)
C*****************************************************************
      STOP
      END
```

INPUT FOR PROGRAM NO.4

```
C*****************************************************************
C*****A TYPICAL DATA INPUT  FOR METHANE(1)-PENTANE(2) SYSTEM *********
C*****************************************************************
DOCUMENT DATA
1.0                                        THIS SPECIFIES THE EQUATION
0.98                                       INTERACTION CO EFFICIENT
0.324   0.455336                           ZM  F  VALUES FOR METHANE
0.308   0.74647                            ZM  F  VALUES FOR PENTANE
343.044   667.782   0.012   16.04          TC  PC  WC  W1  FOR METHANE
845.460   488.639   0.251   72.15          TC  PC  WC  W1  FOR PENTANE
1                                          NO. OF EXPERIMENTAL DATA
1000.0 491.69   2.8540   0.02457           P  T  K1  K2
****
C*****************************************************************
```

PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA USING MODIFIED PENG-ROBINSON EQUATION

GAS CONSTANT= 10.7335 INTERACTION COEFFICIENT=0.9800

PRESSURE IN P.S.I.A. VOLUME IN CU.FT.PER LB.MOLE TEMPERATURE IN DEGREES RANKINE

ZM(1)=0.3240000	OMAC(1)=0.4379945	OMB(1)=0.0834332	OMC(1)=0.0280000	F(1)=0.4553360
TC(1)= 343.044	PC(1)= 667.7820	ACE.FAC.(1)=0.0120	MOL.WT.(1)= 16.040	
ZM(2)=0.3080000	OMAC(2)=0.4565202	OMB(2)=0.0779979	OMC(2)=0.0760000	F(2)=0.7464700
TC(2)= 845.460	PC(2)= 488.6390	ACE.FAC.(2)=0.2510	MOL.WT.(2)= 72.150	

PRESSURE=1000.00 TEMPERATURE= 491.69
VOLUME OF LIQUID PHASE= 1.44121 VOLUME OF VAPOUR PHASE = 4.30662

COMPONENT	LIQUID MOLE FRAC.	VAP. MOLE FRAC.	FUGACITY	EQUILIBRIUM RATIO	EXP.EQUI. RATIO
1	0.3477	0.9838	829.2008	2.8297	2.8540
2	0.6523	0.0162	3.3773	0.0248	0.0246

DEVIATION K(1)= 0.852 K(2)=-1.005

NO. OF ITER.= 3

AVERAGE DEVIATIONS(1POINTS)= K(1)= 0.85 % K(2)= 1.00%

PROGRAM NO.5

```
      MASTER HAN-STARLING        VAN DER WAALS
C*********************************************************************
C     V.L.E. PREDICTION USING HAN-STARLING EQUATION
C**** PREDICTION OF PRESSURE AND VAPOUR PHASE MOLE FRACTIONS
C**** GIVEN VALUES OF TEMPERATURE AND LIQUID PHASE MOLE FRACTIONS
C**** VAN DER WAALS MIXING RULES ARE USED
C*********************************************************************
C****
      REAL MOLW(10)
      DIMENSION TCIJ(10,10),VCIJ(10,10),TCVCIJ(10,10),DITV(10),DIV(10)
      DIMENSION X(10),Y(10),FL(10),Y1(10),G(10),H1(10),D(10),C(5)
      DIMENSION AB(11),A(11),B(11),FUL(10),FUG(10),R1(10)
      DIMENSION DBOM(10),DAOM(10),DCOM(10),DGAM(10),DBM(10),DAM(10)
      DIMENSION DALM(10),DCM(10),DDOM(10),DDM(10),DEOM(10),F(10),E(10)
      COMMON/BL1/TC(10),VC(10),WC(10),ZC(10)
      COMMON/BL2/DTCM(10),DVCM(10),DWCM(10),DZCM(10),DTCVCM(10)
      COMMON/BL3/NUM,TCVCM,VCM,ZCM,WCM
      COMMON/BL4/ZETA(10,10),ETA(10,10)
      WRITE(2,62)
      WRITE(2,230)
      WRITE(2,295)
      WRITE(2,296)
      WRITE(2,300)
      READ(1,4)NUM,FC,R
C****
C**** NUM=NO. OF COMPONENTS
C**** FC=INITIAL ESTIMATE OF FUGACITY CO EFFICIENT FOR VAPOUR PHASE
C**** R=10.7335  UNIVERSAL GAS CONSTANT
C****
C****
C**** INPUT INTERACTION CO EFFICIENTS IN THE FOLLOWING ORDER
C**** ZETA(1,2),ETA(1,2),ZETA(1,3),ETA(1,3)------ZETA(2,3),ETA(2,3)---
C**** ONE VALUE OF ZETA AND ETA ON EACH CARD
C****
      DO 500 I=1,NUM
      DO 550 J=1,NUM
      IF(I.GE.J)GO TO 550
      READ(1,22)ZETA(I,J),ETA(I,J)
      ZETA(J,I)=ZETA(I,J)
      ETA(J,I)=ETA(I,J)
      WRITE(2,23)I,J,ZETA(I,J),I,J,ETA(I,J)
  550 CONTINUE
  500 CONTINUE
C**** INPUT CRITICAL CONSTANTS OF EACH COMPONENT
      READ(1,14)(TC(I),VC(I),WC(I),ZC(I),MOLW(I), I=1,NUM)
C**** INPUT EQUATION OF STATE PARAMETERS
      DO 15 I=1,11
      READ(1,7)A(I),B(I)
   15 CONTINUE
      WRITE(2,210)R
C**** INPUT TEMPERATURE IN RANKINE
      READ(1,24)T
      READ(1,95)M
C**** M IS THE NO. OF DATA POINTS
      WRITE(2,62)
      DO 600 L=1,M
C****
C**** INPUT A GUESS VALUE OF PRESSURE(PSIA)
C**** EXPERIMENTAL VALUE IS USED FOR COMPARISON PURPOSE. FINAL DEVIATION
C**** IN PRESSURE IS OBTAINED WITH RESPECT TO THIS VALUE.
```

```
C****
      READ(1,2)P
C****
C**** INPUT LIQUID PHASE MOLE FRACTIONS IN THIS ORDER X(1),X(2) ....
C**** ......X(NUM-1). EACH MOLE FRAC ON SEPARATE CARD
C****
      READ(1,2)(X(I),I=1,NUM-1)
      SUMX=0.0
      DO 525 I=1,NUM-1
  525 SUMX=SUMX+X(I)
      X(NUM)=1-SUMX
      PEXP=P
      N1=0.0
    3 N1=N1+1
      ITN=1
      ITNM=50
    6 T=ABS(T)
      CALL VDWMX(X)
C****
C**** SUBROUTINE VDWMX CALCULATES MIXTURE PARAMETERS USING
C**** VAN DER WAALS MIXING RULES
C****
      FL(1)=0
   25 TCM=TCVCM/VCM
      TR=T/TCM
      DO 30 I=1,10
      AB(I)=(A(I)+B(I)*WCM)
   30 CONTINUE
      BOM=AB(1)*VCM
      AOM=AB(2)*R*TCVCM
      COM=AB(3)*R*VCM*TCM**3
      GAM=AB(4)*VCM**2
      BM=AB(5)*VCM**2
      AM=AB(6)*R*TCM*VCM**2
      ALM=AB(7)*VCM**3
      CM=AB(8)*R*TCM*TCVCM**2
      DOM=AB(9)*R*VCM*TCM**4
      DM=AB(10)*R*TCVCM**2
      EXPW=EXP(-3.8*WCM)
      AB(11)=A(11)+B(11)*WCM*EXPW
      EOM=AB(11)*R*VCM*TCM**5
    5 C(1)=R*T*BOM-AOM-COM/(T**2)+DOM/(T**3)-EOM/(T**4)
      C(2)=BM*R*T-AM-DM/T
      C(3)=ALM*(AM+DM/T)
      C(4)=R*T
      C(5)=CM/(T**2)
      DO 70 K=1,NUM
      DBOM(K)=AB(1)*DVCM(K)+B(1)*DWCM(K)*VCM
      DAOM(K)=R*(AB(2)*DTCVCM(K)+B(2)*DWCM(K)*TCVCM)
      DCOM(K)=R*((DTCVCM(K)*TCM**2+2*TCM*TCVCM*DTCM(K))*AB(3)+B(3)*DWCM(
     1K)*VCM*TCM**3)
      DGAM(K)=2*VCM*DVCM(K)*AB(4)+B(4)*DWCM(K)*VCM**2
      DBM(K)=2*VCM*DVCM(K)*AB(5)+B(5)*DWCM(K)*VCM**2
      DAM(K)=R*((VCM*DTCVCM(K)+TCVCM*DVCM(K))*AB(6)+B(6)*TCM*DWCM(K)*VCM*
     1**2)
      DALM(K)=3*DVCM(K)*AB(7)*VCM**2+B(7)*DWCM(K)*VCM**3
      DCM(K)=R*((2*TCVCM*TCM*DTCVCM(K)+DTCM(K)*TCVCM**2)*AB(8)+B(8)*DWCM(
     1(K)*TCM*TCVCM**2)
      DDOM(K)=R*((DTCVCM(K)*TCM**3+3*TCVCM*DTCM(K)*TCM**2)*AB(9)+B(9)*DW
     1CM(K)*TCVCM*TCM**3)
```

```
      DDM(K)=R*(2*TCVCM*DTCVCM(K)*AB(10)+B(10)*DWCM(K)*TCVCM**2)
      DEOM(K)=((DTCVCM(K)+4*VCM*DTCM(K))*AB(11)+B(11)*EXPW*DWCM(K)*TCVCM
     1*(1-3.8*WCM))*R*TCM**4
      F(K)=0.5*(R*T*(DBM(K)+3*BM)-(DAM(K)+3*AM)-(DDM(K)+3*DM)/T)
      G(K)=0.2*((AM+DM/T)*(DALM(K)+6*ALM)+ALM*(DAM(K)+DDM(K)/T))
      D(K)=CM*(2*GAM+DGAM(K))/(2*GAM*GAM*T*T)
      H1(K)=(DCM(K)+3*CM)/(2*GAM*T**2)
      E(K)=R*T*(DBOM(K)+2*BOM)-(DAOM(K)+2*AOM)-(1/T**2)*(DCOM(K)+2*COM)+
     1(1/(T**3))*(DDOM(K)+2*DOM)-(1/T**4)*(DEOM(K)+2*EOM)
   70 CONTINUE
      IF(FL(1).NE.0)GOTO 350
      RO=2.5
      E1=0.0
      H=-0.05
      CALL DEN(RO,E1,H,C,GAM,P)
C**** SUBROUTINE DEN CALCULATES DENSITY OF LIQUID OR VAPOUR PHASE
C**** BY SOLVING THE HAN-STARLING EQUATION OF STATE
      IF(RO.LE.0.0)GOTO 800
      VL=1/RO
C**** LIQUID PHASE FUGACITY IS CALCULATED
      GR2=GAM*RO*RO
      EXPG=EXP(-GR2)
      RR=2-(2+GR2)*EXPG
      RS=(GR2**2+2*GR2+2)*EXPG-2
      SUM1=0.0
      DO 75 K1=1,NUM
      FL(K1)=(E(K1)*RO+F(K1)*RO*RO+G(K1)*RO**5+H1(K1)*RR+D(K1)*RS)/(R*T)
      FL(K1)=X(K1)*RO*R*T*EXP(FL(K1))
      FUL(K1)=FL(K1)
      Y(K1)=FUL(K1)/FC/P
      SUM1=SUM1+Y(K1)
   75 CONTINUE
C**** VAPOUR PHASE MOLE FRACTIONS ARE NORMALISED
      Y(1)=Y(1)/SUM1
      Y(2)=Y(2)/SUM1
   90 CALL VDWMX(Y)
      GO TO 25
  350 RO=0.0
      E1=2.5
      DH=0.1*P/R/T
      IF(DH.LT.0.01)GOTO 12
      H=0.01
      GOTO 13
   12 H=DH
   13 CONTINUE
      CALL DEN(RO,E1,H,C,GAM,P)
C**** SUBROUTINE DEN CALCULATES DENSITY OF LIQUID OR VAPOUR PHASE
C**** BY SOLVING THE HAN-STARLING EQUATION OF STATE
      IF(RO.GE.2.5)GOTO 810
      V=1/RO
C**** VAPOUR PHASE FUGACITY IS CALCULATED
      GR2=GAM*RO*RO
      EXPG=EXP(-GR2)
      RR=2-(2+GR2)*EXPG
      RS=(GR2**2+2*GR2+2)*EXPG-2
      SUM2=0.0
      SUMP=0.0
      DO 100 K1=1,NUM
      FL(K1)=(E(K1)*RO+F(K1)*RO*RO+G(K1)*RO**5+H1(K1)*RR+D(K1)*RS)/(R*T)
      FL(K1)=Y(K1)*RO*R*T*EXP(FL(K1))
```

```
      FUG(K1)=FL(K1)
      R1(K1)=FUL(K1)*Y(K1)/FUG(K1)/X(K1)
      Y(K1)=R1(K1)*X(K1)
      SUMP=SUMP+Y(K1)*P
      SUM2=SUM2+Y(K1)
  100 CONTINUE
      DO 151 K1=1,NUM
      IF(ABS(FUL(K1)/FUG(K1)-1.0)-0.001)151,151,49
C****
C     THE CONDITION OF THE EQUALITY OF FUGACITY FOR BOTH PHASES IS
C    1DEFINED BY THIS STATEMENT
C****
  151 CONTINUE
      GO TO 200
   49 ITN=ITN+1
      IF(ITNM-ITN)51,11,11
   51 WRITE(2,52)
      GOTO 220
   11 CONTINUE
      GOTO 90
  200 CONTINUE
C**** SUM OF THE PARTIAL PRESSURES MUST BE EQUAL TO THE TOTAL PRESSURE
      IF((ABS(SUMP-P)/SUMP).LE.0.0001)GO TO 185
      P=SUMP
      GO TO 3
  185 SUM1=SUM2
   99 SUMV=SUM1-1.0
C**** SUM OF THE VAPOUR PHASE MOLE FRACTIONS MUST BE 1.0
      IF(ABS(SUMV).LE.0.0001)GO TO 220
      GO TO 90
  220 CONTINUE
      WRITE(2,19)PEXP
      WRITE(2,65)P,T
      WRITE(2,61)VL,V
      WRITE(2,225)
      WRITE(2,29)
      WRITE(2,225)
      DO 50 I=1,NUM
      WRITE(2,27)I,X(I),Y(I),FL(I),R1(I)
   50 CONTINUE
      DELP=PEXP-P
      DEVP=DELP*100/PEXP
      WRITE(2,240)DEVP
      WRITE(2,35)N1
      GO TO 890
  800 WRITE(2,85)
      GO TO 890
  810 WRITE(2,86)
  890 WRITE(2,62)
  900 CONTINUE
    2 FORMAT(F0.0)
    4 FORMAT(I0,2F0.0)
    7 FORMAT(2F0.0)
   14 FORMAT(5F0.0)
   19 FORMAT(1H ,'EXP. PRESSURE =',F7.1)
   22 FORMAT(2F0.0)
   23 FORMAT(1H ,'ZETA(',I2,',',I2,')=',F6.4,3X,'ETA(',I2,',',I2,')=',F6
     1.4)
   24 FORMAT(F0.0)
   27 FORMAT(1H ,4X,I2,14X,F6.4,10X,F6.4,13X,F9.4,10X,F7.4)
```

```
 29 FORMAT(1H ,'COMPONENT      LIQUID MOLE FRAC.      VAP. MOLE FRAC.
   1  FUGACITY      EQUILIBRIUM RATIO  ')
 35 FORMAT(1H ,'NO.OF ITER.=',I3)
 52 FORMAT(1H ,'PHASE CALCULATION FAILED TO CONVERGE',/)
 61 FORMAT(1H ,'VOLUME OF LIQUID PHASE=',F8.5,5X,'VOLUME OF VAPOUR PHA
   1SE=',F8.5)
 62 FORMAT(1H ,'*************************************************************
   1*************************************************************')
 65 FORMAT(1H ,'CALC. PRESSURE=',F7.2,5X,'TEMPERATURE=',F7.2)
 85 FORMAT(1H ,28HNO ROOT FOR VOLUME OF LIQUID)
 86 FORMAT(1H ,28HNO ROOT FOR VOLUME OF VAPOUR)
 95 FORMAT(I0)
111 FORMAT(3F0.0)
210 FORMAT(1H ,'GAS CONSTANT=',F8.4)
225 FORMAT(1H ,'-------------------------------------------------------------
   1-------------------------------------------------------------')
230 FORMAT(/1H ,'ETHANE(1)-PROPENE(2) SYSTEM ',/)
240 FORMAT(1H ,'DEVIATION IN PRESSURE =',F6.3)
295 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
   1 USING HAN-STARLING EQUATION ')
296 FORMAT(1H ,'VAN DER WAALS MIXING RULES ARE USED ')
300 FORMAT(1H ,'PRESSURE IN P.S.I.A.     VOLUME IN CU.FT.PER LB.MOLE
   1TEMPERATURE IN DEGREES RANKINE',//)
    STOP
    END
```

INPUT FOR PROGRAM NO.5

```
****
C*********************************************************************
C**** A TYPICAL DATA INPUT FOR PROPENE(1)-PROPANE(2) SYSTEM  **********
C*********************************************************************
DOCUMENT DATA
 2 1.0 10.7335                                  NUM  FC  R
C**** THE FOLLOWING CARD MUST CONTAIN ZETA AND ETA FOR VDW MIXING RULES
0.0                                             CKIJ   OR  ZETA  ETA FOR VDWMX
549.76 2.370812 0.099 0.285 30.07                 TC  VC  WC  ZC  MOL WT
656.73 2.899439 0.144 0.274 42.08                 TC  VC  WC  ZC  MOL WT
C**** EQUATION OF STATE CONSTANTS FOR HAN-STARLING EQUATION
0.44369 0.115449
1.28438 -0.920731
0.356306 1.70871
0.544979 -0.270896
0.528629 0.349261
0.484011 0.75413
0.0705233 -0.044448
0.504087 1.32245
0.0307452 0.179433
0.0732828 0.463492
0.00645 -0.022143
500                                             TEMPERATURE(RANKINE)
1                                               NO. OF DATA POINTS
100                                             GUESS PRESSURE (PSIA)
0.014                                           X(1)
****
```

```
*****************************************************************************

ETHANE(1)-PROPENE(2) SYSTEM


   PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA  USING HAN-STARLING EQUATION
VAN DER WAALS MIXING RULES ARE USED
PRESSURE IN P.S.I.A.    VOLUME IN CU.FT.PER LB.MOLE   TEMPERATURE IN DEGREES RANKINE


ZETA( 1, 2)=1.0000   ETA( 1, 2)=1.0000
GAS CONSTANT= 10.7335
*****************************************************************************
EXP. PRESSURE =  100.0
CALC. PRESSURE= 100.08     TEMPERATURE= 500.00
VOLUME OF LIQUID PHASE= 1.22191     VOLUME OF VAPOUR PHASE=46.44666
-----------------------------------------------------------------------------
COMPONENT     LIQUID MOLE FRAC.     VAP. MOLE FRAC.     FUGACITY     EQUILIBRIUM RATIO
-----------------------------------------------------------------------------
     1              0.0140              0.0426              4.0507          3.0457
     2              0.9860              0.9574             84.1792          0.9710
DEVIATION IN PRESSURE =-0.078
NO.OF ITER.=  3
*****************************************************************************
EXP. PRESSURE =  150.0
CALC. PRESSURE= 148.80     TEMPERATURE= 500.00
VOLUME OF LIQUID PHASE= 1.20562     VOLUME OF VAPOUR PHASE=30.28387
-----------------------------------------------------------------------------
COMPONENT     LIQUID MOLE FRAC.     VAP. MOLE FRAC.     FUGACITY     EQUILIBRIUM RATIO
-----------------------------------------------------------------------------
     1              0.2090              0.4418             59.8718          2.1139
```

PROGRAM NO.6

```
      MASTER HAN-STARLING
C*****************************************************************
C     V.L.E. PREDICTION USING HAN-STARLING EQUATION
C**** PREDICTION OF PRESSURE AND VAPOUR PHASE MOLE FRACTIONS
C**** GIVEN VALUES OF TEMPERATURE AND LIQUID PHASE MOLE FRACTIONS
C**** HAN-STARLING MIXING RULES ARE USED
C*****************************************************************
      DIMENSION EXPR1(10),DEV(10),DEVR1(10)
      DIMENSION X(10),F(10),F1(10),F2(10),F3(10),F4(10),F5(10),F6(10)
      DIMENSION Y(10),Y1(10),FL(10),FUL(10),FUG(10),R1(10),C(5),W1(10)
      COMMON/BL1/AO(10),BO(10),CO(10),DO(10),EO(10),A1(10),B1(10)
      COMMON/BL2/C1(10),D1(10),AL(10),GA(10)
      COMMON/BL3/A(11),B(11),TC(10),VC(10),WC(10),ZC(10)
      COMMON/BL4/R,T,AM,BM,CM,DM,AOM,BOM,COM,DOM,EOM,ALM,GAM,NUM
      COMMON/BL5/CKIJ(10,10)
      WRITE(2,225)
      WRITE(2,230)
      WRITE(2,295)
      WRITE(2,296)
      WRITE(2,300)
      READ(1,4)NUM,FC,R
C****
C**** NUM=NO. OF COMPONENTS
C**** FC=INITIAL ESTIMATE OF FUGACITY CO EFFICIENT FOR VAPOUR PHASE
C**** R=10.7335  UNIVERSAL GAS CONSTANT
C****
C****
C**** INPUT INTERACTION CO EFFICIENTS IN THE FOLLOWING ORDER
C**** CKIJ(1,2),CKIJ(1,3),----CKIJ(2,3),---
C**** EACH VALUE OF CKIJ ON SEPARATE CARD
C****
      DO 500 I=1,NUM
      DO 550 J=1,NUM
      IF(I.GE.J)GO TO 550
      READ(1,22)CKIJ(I,J)
      CKIJ(J,I)=CKIJ(I,J)
      WRITE(2,23)I,J,CKIJ(I,J)
  550 CONTINUE
  500 CONTINUE
C**** INPUT CRITICAL CONSTANTS OF EACH COMPONENT
      READ(1,8)(TC(I),VC(I),WC(I),ZC(I),W1(I),I=1,NUM)
      DO 15 I=1,11
C**** INPUT EQUATION OF STATE PARAMETERS
      READ(1,7)A(I),B(I)
   15 CONTINUE
      WRITE(2,210)R
C**** INPUT TEMPERATURE IN RANKINE
      READ(1,22)T
      READ(1,95)M
C**** M IS THE NO. OF DATA POINTS
      DO 900 L=1,M
C****
C**** INPUT A GUESS VALUE OF PRESSURE(PSIA)
C**** EXPERIMENTAL VALUE IS USED FOR COMPARISON PURPOSE. FINAL DEVIATIC
C**** IN PRESSURE IS OBTAINED WITH RESPECT TO THIS VALUE.
C****
      READ(1,2)P
C****
C**** INPUT LIQUID PHASE MOLE FRACTIONS IN THIS ORDER X(1),X(2) ....
C**** ......X(NUM-1). EACH MOLE FRAC ON SEPARATE CARD
```

```
C****
      READ(1,2)(X(I),I=1,NUM-1)
      SUMX=0.0
      DO 525 I=1,NUM-1
  525 SUMX=SUMX+X(I)
      X(NUM)=1-SUMX
      POLD=P
      N1=0.0
    3 N1=N1+1
      ITN=1
      ITNM=50
    6 T=ABS(T)
      CALL MIXP(X)
C****
C**** SUBROUTINE MIXP CALCULATES MIXTURE PARAMETERS USING HAN-STARLING
C**** MIXING RULES
C****
      FL(1)=0
    5 C(1)=R*T*BOM-AOM-COM/(T**2)+DOM/(T**3)-EOM/(T**4)
      C(2)=BM*R*T-AM-DM/T
      C(3)=ALM*(AM+DM/T)
      C(4)=R*T
      C(5)=CM/(T**2)
      IF(FL(1).NE.0.0)GOTO 350
      RO=2.5
      E1=0.0
      H=-0.05
      CALL DEN(RO,E1,H,C,GAM,P)
C****
C**** SUBROUTINE DEN CALCULATES DENSITY OF LIQUID OR VAPOUR PHASE
C**** BY SOLVING THE HAN-STARLING EQUATION OF STATE
C****
      IF(RO.LE.0.0)GOTO 800
      VL=1/RO
      SUM1=0.0
      CALL FUGA(X,FL,RO)
C****
C     SUBROUTINE FUGA CALCULATES THE FUGACITY OF EACH COMPONENT IN A
C     GIVEN MIXTURE
C****
      DO 75 K1=1,NUM
      FUL(K1)=FL(K1)
      Y(K1)=FUL(K1)/FC/P
      SUM1=SUM1+Y(K1)
   75 CONTINUE
C**** VAPOUR PHASE MOLE FRACTIONS ARE NORMALISED
      Y(1)=Y(1)/SUM1
      Y(2)=Y(2)/SUM1
   90 CALL MIXP(Y)
      GO TO 5
  350 RO=0.0
      E1=2.5
      DH=0.1*P/R/T
      IF(DH.LT.0.01)GOTO 12
      H=0.01
      GOTO 13
   12 H=DH
   13 CONTINUE
      CALL DEN(RO,E1,H,C,GAM,P)
C****
```

```
C**** SUBROUTINE DEN CALCULATES DENSITY OF LIQUID OR VAPOUR PHASE
C**** BY SOLVING THE HAN-STARLING EQUATION OF STATE
C****
      IF(RO.GE.2.5)GOTO 810
      V=1/RO
      SUM2=0.0
      SUMP=0.0
      CALL FUGA(Y,FL,RO)
      DO 100 K1=1,NUM
      FUG(K1)=FL(K1)
      Y(K1)=FUL(K1)*Y(K1)/FUG(K1)
      SUMP=SUMP+Y(K1)*P
      SUM2=SUM2+Y(K1)
  100 CONTINUE
      DO 151 K1=1,NUM
      IF(ABS(FUL(K1)/FUG(K1)-1.0)-0.001)151,151,49
C****
C     THE CONDITION OF THE EQUALITY OF FUGACITY FOR BOTH PHASES IS
C    1DEFINED BY THIS STATEMENT
C****
  151 CONTINUE
      GO TO 200
   49 ITN=ITN+1
      IF(ITNM-ITN)51,11,11
   51 WRITE(2,52)
      GO TO 220
   11 CONTINUE
      GOTO 90
  200 CONTINUE
C**** SUM OF THE PARTIAL PRESSURES MUST BE EQUAL TO THE TOTAL PRESSURE
      IF(ABS((SUMP-P)/SUMP).LE.0.00001)GO TO 185
      P=SUMP
      GO TO 3
  185 SUM1=SUM2
   99 SUMY=SUM1-1.0
C**** SUM OF THE VAPOUR PHASE MOLE FRACTIONS MUST BE 1.0
      IF(ABS(SUMY).LE.0.00001)GO TO 220
      GO TO 90
  220 CONTINUE
C**** RESULTS ARE PRINTED
      WRITE(2,19)POLD
      WRITE(2,65)P,T
      WRITE(2,61)VL,V
      WRITE(2,225)
      WRITE(2,29)
      WRITE(2,225)
      DO 50 I=1,NUM
C**** EQUILIBRIUM RATIOS ARE CALCULATED.
      R1(I)=Y(I)/X(I)
      WRITE(2,27)I,X(I),Y(I),FL(I),R1(I),EXPR1(I)
   50 CONTINUE
C**** DEVIATION IS CALCULATED
      DEVV=(POLD-P)*100/POLD
      ADEV=ADEV+ABS(DEVV)
      WRITE(2,36)DEVV
      WRITE(2,35)N1
      GO TO 890
  800 WRITE(2,85)
      GO TO 890
  810 WRITE(2,86)
```

```
  890 WRITE(2,62)
  900 CONTINUE
      L=L-1
      ADEV=ADEV/L
      WRITE(2,925)ADEV
C**** ***********************************************************************
    2 FORMAT(F0.0)
    4 FORMAT(I0,2F0.0)
    7 FORMAT(2F0.0)
    8 FORMAT(5F0.0)
   19 FORMAT(1H ,'EXPERIMENTAL PRESSURE=',F7.3)
   22 FORMAT(F0.0)
   23 FORMAT(1H ,'INTERACTION CO EFFICIENT CKIJ(',I2,',',I2,')=',F6.4)
   27 FORMAT(1H ,4X,I2,14X,F6.4,10X,F6.4,13X,F9.4,10X,F7.4,10X,F7.4)
   29 FORMAT(1H ,'COMPONENT      LIQUID MOLE FRAC.      VAP. MOLE FRAC.
     1  FUGACITY      EQUILIBRIUM RATIO      EXP.EQUI. RATIO ')
   35 FORMAT(1H ,'NO. OF ITER.=',I3)
   36 FORMAT(1H ,'DEVIATION IN PRESSURE=',F6.4,'(%)')
   52 FORMAT(1H ,'PHASE CALCULATION FAILED TO CONVERGE',/)
   61 FORMAT(1H ,'VOLUME OF LIQUID PHASE=',F8.5,5X,'VOLUME OF VAPOUR PHA
     1SE =',F8.5)
   62 FORMAT(1H ,'*****************************************************
     1*****************************************************',/)
   65 FORMAT(1H ,'CALCULATED PRESSURE=',F8.3,5X,'TEMPERATURE=',F7.2)
   85 FORMAT(1H ,28HNO ROOT FOR VOLUME OF LIQUID)
   86 FORMAT(1H ,28HNO ROOT FOR VOLUME OF VAPOUR)
   95 FORMAT(I0)
  210 FORMAT(1H ,'GAS CONSTANT=',F8.4)
  225 FORMAT(/1H ,'-----------------------------------------------------
     1-----------------------------------------------------',/)
  230 FORMAT(/1H ,'ETHANE(1)-PROPENE(2) SYSTEM ',/)
  295 FORMAT(1H ///1H ,3X,'PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA
     1 USING HAN-STARLING EQUATION ')
  296 FORMAT(1H ,'HAN-STARLING MIXING RULES ARE USED')
  300 FORMAT(1H ,'PRESSURE IN P.S.I.A.     VOLUME IN CU.FT.PER LB.MOLE
     1TEMPERATURE IN DEGREES RANKINE',//)
  925 FORMAT(1H ,'ABSOLUTE AVERAGE DEVIATION=',F6.4,'(%)')
C*****Z*********************************************************************
      STOP
      END
```

INPUT FOR PROGRAM NO.6 (SAME AS PROGRAM NO.5)

OUTPUT FOR PROGRAM NO.6

```
ETHANE(1)-PROPENE(2) SYSTEM


   PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM DATA  USING HAN-STARLING EQUATION
HAN-STARLING MIXING RULES ARE USED
PRESSURE IN P.S.I.A.    VOLUME IN CU.FT.PER LB.MOLE   TEMPERATURE IN DEGREES RANKINE

INTERACTION CO EFFICIENT CKIJ( 1, 2)=0.0000
GAS CONSTANT= 10 7335
EXPERIMENTAL PRESSURE=100.000
CALCULATED PRESSURE=  99.949      TEMPERATURE= 500.00
VOLUME OF LIQUID PHASE= 1.22189     VOLUME OF VAPOUR PHASE =46.50110
```

COMPONENT	LIQUID MOLE FRAC.	VAP. MOLE FRAC.	FUGACITY	EQUILIBRIUM RATIO	EXP.EQUI. RATIO
1	0.0140	0.0416	3.9381	2.9742	
2	0.9860	0.9584	84.1768	0.9720	

```
DEVIATION IN PRESSURE=0.0509(%)
NO. OF ITER.=  4
```

PROGRAM NO.7

```
      MASTER GENERALISED
C****
C**** ***************************************************************
C**** THIS PROGRAM COMPARES TWO METHODS USED FOR GENERALISING THE
C**** MODIFIED PENG-ROBINSON EQUATION.
C**** PREDICTION OF DENSITIES(OR COMPRESSIBILITIES)
C**** METHOD 1  USES THE GENERALISED CORRESPONDING STATES PRINCIPLE
C**** WITH TWO NON-SPHERICAL REFERENCE FLUIDS
C**** METHOD 2 USES THE GENERALISED EQUATION OF STATE PARAMETERS IN
C**** TERMS OF THE ACENTRIC FACTORS
C**** ***************************************************************
C****
      DIMENSION C(5)
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL2/PR,TR,VRE,TR2,VHE,ZHE
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL4/PC,F,ZM,OMAC,OMB,OMC
      COMMON/BL5/AUTHOR,W1,DL
      WRITE(2,227)
      WRITE(2,225)
C**** INPUT THE ACENTRIC FACTORS OF TWO REFERENCE FLUIDS
      READ(1,150)AC1,AC2
C**** INPUT CRITICAL CONSTANTS OF THE FLUID OF INTEREST
      READ(1,114)TC,VC,ZC,AC,W1
      R=10.7335
C****
C**** INPUT THE EQUATION OF STATE PARAMETERS ZM AND F FOR THE TWO
C**** REFERENCE FLUIDS
C****
      READ(1,116)ZM1,F1
      READ(1,116)ZM2,F2
      WRITE(2,220)TC,VC,ZC,AC,W1,R
      ADEV=0.0
      ADEV1=0.0
      READ(1,130)U
C****
C**** U IS USED TO IDENTIFY THE COMPONENT SO THAT THE EXPERIMENTAL
C**** DATA FOR THE PARTICULAR COMPONENT CAN BE CONVERTED INTO APPROPRIA
C**** UNITS CONSISTENT WITH THIS PROGRAM
C****
      READ(1,125)N1
C**** N1 IS THE NO. OF DATA POINTS USED
      ZCE=ZC
      WC=AC
      ZC=ZM1
C**** EVALUATION OF OMAC,OMB,OMC FROM ZM FOR REF. FLUID 1
      C(1)=1.0
      C(2)=2.0-3.0*ZC
      C(3)=3.0*ZC*ZC
      C(4)=-ZC**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION
      OMB=ZMAX
      OMC=1.0-3.0*ZC
      OMAC=3.0*ZC*ZC+3.0*(1.0-2.0*ZC)*OMB+OMB*OMB+OMC
      OMAC1=OMAC
      OMB1=OMB
      OMC1=OMC
      ZC=ZM2
C**** EVALUATION OF OMAC,OMB,OMC FROM ZM FOR REF. FLUID 2
```

```
      C(1)=1.0
      C(2)=2.0-3.0*ZC
      C(3)=3.0*ZC*ZC
      C(4)=-ZC**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
      OMB=ZMAX
      OMC=1.0-3.0*ZC
      OMAC=3.0*ZC*ZC+3.0*(1.0-2.0*ZC)*OMB+OMB*OMB+OMC
      OMAC2=OMAC
      OMB2=OMB
      OMC2=OMC
C**** GENERALISED CORRELATIONS FOR ZM AND F
      F=0.452413+1.30982*WC-0.295937*WC*WC
      ZM=0.329032-0.0767992*WC+0.0211947*WC*WC
      ZC=ZM
C**** EVALUATION OF OMAC,OMB,OMC FROM ZM FOR THE FLUID OF INTEREST
      C(1)=1.0
      C(2)=2.0-3.0*ZC
      C(3)=3.0*ZC*ZC
      C(4)=-ZC**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
      OMB=ZMAX
      OMC=1.0-3.0*ZC
      OMAC=3.0*ZC*ZC+3.0*(1.0-2.0*ZC)*OMB+OMB*OMB+OMC
      WRITE(2,117)OMAC,OMB,OMC,F,ZM
      WRITE(2,227)
      WRITE(2,250)
      WRITE(2,227)
      ZC=ZCE
      DO 90 I=1,N1
C****
C**** INPUT EXPERIMENTAL DATA. THE VALUE OF THE PARAMETER AUTHOR GIVES
C**** INFORMATION REGARDING THE UNITS OF P,VEXP AND T.
C****
      READ(1,111)AUTHOR,P,VEXP,T
C****
C**** CALL TO THE FOLLOWING ROUTINES IS NECCESSARY FOR THE CONVERSION
C**** OF UNITS
C****
      IF(U.EQ.1)CALL UNMET
      IF(U.EQ.2)CALL UNETH
      IF(U.EQ.3)CALL UNPR
      IF(U.EQ.4)CALL UNBU
      IF(U.EQ.5)CALL UNPE
      IF(U.EQ.6)CALL UNHE
      IF(U.EQ.7)CALL UNHEP
      IF(U.EQ.8)CALL UNOCT
      IF(U.EQ.9)CALL UNNO
      IF(U.EQ.10)CALL UNDE
      TR=T/TC
      TR2=TR*TR
      PC=ZC*R*TC/VC
      PR=P/PC
      ALP1=(1.0+F1*(1.0-SQRT(TR)))**2.0
      A=OMAC1*ALP1*PR/TR2
      B=OMB1*PR/TR
      CC=OMC1*PR/TR
C**** EQUATION OF STATE IS SOLVED FOR REF. FLUID 1
      C(1)=1.0
      C(2)=CC-1.0
```

```
      C(3)=-(2.0*B*CC+B*B+B+CC-A)
      C(4)=B*B*CC-A*B+B*CC
      CALL SOLVE(ZMIN,ZMAX,C)
      IF(VEXP.LT.VC)GO TO 55
      Z1=ZMAX
      GO TO 56
   55 Z1=ZMIN
   56 CONTINUE
      ALP2=(1.0+F2*(1.0-SQRT(TR)))**2.0
      A=OMAC2*ALP2*PR/TR2
      B=OMB2*PR/TR
      CC=OMC2*PR/TR
C**** EQUATION OF STATE IS SOLVED FOR REF. FLUID 2
      C(1)=1.0
      C(2)=CC-1.0
      C(3)=-(2.0*B*CC+B*B+B+CC-A)
      C(4)=B*B*CC-A*B+B*CC
      CALL SOLVE(ZMIN,ZMAX,C)
      IF(VEXP.LT.VC)GO TO 65
      Z2=ZMAX
      GO TO 75
   65 Z2=ZMIN
   75 CONTINUE
C****
C**** THE GCSP USING TWO NON-SPHERICAL REF FLUIDS IS DEFINED BY THE
C**** FOLLOWING EQUATION
C****
      Z=Z1+(AC-AC1)*(Z2-Z1)/(AC2-AC1)
      V=Z*R*T/P
      VR=V/VC
      VRE=VEXP/VC
      DEV=(VRE-VR)*100/VRE
C**** DEVIATION FROM EXPERIMENTAL VALUE IS CALCULATED.
      ADEV=ADEV+ABS(DEV)
      CALL NCP
C****
C**** SUBROUTINE NCP IS USED TO SOLVE EQUATION OF STATE USING ZM AND
C**** F FROM GENERALISED CORRELATIONS.ZHE IS THE COMPRESSIBILITY
C**** OBTAINED FROM THIS ROUTINE
C****
      VHE=ZHE*R*T/P
      VRHE=VHE/VC
      DEVHE=(VRE-VRHE)*100/VRE
      ADEV1=ADEV1+ABS(DEVHE)
      WRITE(2,32)I,PR,TR,VRE,VR,DEV,VRHE,DEVHE,AUTHOR
   90 CONTINUE
      AADEV=ADEV/N1
      AADEV1=ADEV1/N1
      WRITE(2,35)AADEV
      WRITE(2,38)AADEV1
   32 FORMAT(1H ,I3,4X,7(F10.6,4X),4X,F3.1)
   35 FORMAT(///1H ,'ABS. AVE. DEV(%) GCSP =',F10.5)
   38 FORMAT(/1H ,'ABS.AVE. DEV.(%) NCP CORRELATIONS  =',F10.5)
  111 FORMAT(4F0.0)
  114 FORMAT(5F0.0)
  116 FORMAT(2F0.0)
  117 FORMAT(1H ,'OMAC=',F12.9,2X,'OMB=',F12.9,2X,'OMC=',F12.9,2X,'F=',
     112.9,2X,'Z=',F6.4)
  125 FORMAT(I0)
  130 FORMAT(F0.0)
```

```
150 FORMAT(2F0.0)
220 FORMAT(1H ,'TC=',F8.2,4X,'VC=',F9.6,4X,'ZC=',F6.4,4X,'ACE.FAC.=',F
   16.4,4X,'MOL.WT.=',F8.4,4X,'GAS CONST=',F8.4)
225 FORMAT(/1H ,'PREDICTION OF PURE COMPONENT DENSITIES USING GENERALI
   1SED PR(MODIFIED) EQUATION OF STATE')
227 FORMAT(1H ,'*****************************************************
   1*****************************************************')
250 FORMAT(1H ,' NO',8X,'PR',12X,'TR',11X,'VREXP',10X,'VRLK',9X,'DEV(X
   1)',7X,'VRNCP',9X,'DEVNCP(X)',7X,'REF')
    STOP
    END
```

INPUT FOR PROGRAM NO.7

```
C
C
C**** ***********************************************************************
C**** ***********  A TYPICAL DATA INPUT FOR N-OCTANE  ******************
C**** ***********************************************************************
0.001 0.398                                ACENTRIC FACTORS AC1  AC2
1023.89 7.881348 0.259 0.398 114.23         TC  VC  ZC  AC  W1 FOR N-OCTANE
0.328 0.450751                             ZM1  F1  FOR REF. FLUID 1
0.301 0.918544                             ZM2  F2  FOR REF. FLUID 2
8                                          U  IDENTIFICATION FOR N- OCTANE
20                                         NO. OF PVT DATA USED.
C  PVT DATA FILE INCLUDED  P  V  T  AUTHOR
****
C***********************************************************************
```

REDICTION OF PURE COMPONENT DENSITIES USING GENERALISED PR(MODIFIED) EQUATION OF STATE

C= 1023.89 VC= 7.881348 ZC=0.2590 ACE.FAC.=0.3980 MOL.WT.=114.2300 GAS CONST= 10.7335

MAC= 0.463861351 OMB= 0.075921453 OMC= 0.094530269 F= 0.926843755 Z=0.3018

NO	PR	TR	VREXP	VRLK	DEV(%)	VRNCP	DEVNCP(%)
1	0.203456	0.655998	0.364282	0.360973	0.908509	0.362309	0.541596
2	0.406913	0.655998	0.363121	0.360380	0.754852	0.361714	0.387604
3	0.610369	0.655998	0.362425	0.359802	0.723719	0.361132	0.356587
4	0.813825	0.655998	0.361961	0.359237	0.752487	0.360564	0.385690
5	1.017281	0.655998	0.361496	0.358634	0.777799	0.360009	0.411318
6	1.220738	0.655998	0.361032	0.358144	0.799782	0.359466	0.433601
7	2.034563	0.655998	0.359174	0.356097	0.856750	0.357409	0.491612
8	4.069125	0.655998	0.355227	0.351642	1.009459	0.352930	0.646710
9	6.103688	0.655998	0.351513	0.347913	1.024022	0.349183	0.662859
10	8.138251	0.655998	0.348494	0.344726	1.081430	0.345979	0.721775
11	10.172814	0.655998	0.345708	0.341956	1.085465	0.343195	0.726938
12	12.207376	0.655998	0.342922	0.339517	0.992954	0.340744	0.635053
13	0.203456	0.699948	0.378213	0.374100	1.087460	0.375491	0.719739
14	0.406913	0.699948	0.377052	0.373251	1.008107	0.374637	0.640364
15	0.610369	0.699948	0.376123	0.372427	0.982723	0.373809	0.615154
16	0.813825	0.699948	0.375427	0.371627	1.012194	0.373005	0.644998
17	1.017281	0.699948	0.374962	0.370849	1.097094	0.372223	0.730470
18	1.220738	0.699948	0.374266	0.370092	1.115234	0.371463	0.748930
19	2.034563	0.699948	0.371944	0.367257	1.260085	0.368614	0.895278
20	4.069125	0.699948	0.366836	0.361254	1.521739	0.362581	1.160003

BS. AVE. DEV(%) GCSP = 0.99259

BS.AVE. DEV.(%) NCP CORRELATIONS = 0.62781

OUTPUT FOR PROGRAM NO.7

PROGRAM NO.8

```
      MASTER VAPOUR PRESSURE
C*****************************************************************;
C**** THIS PROGRAM CALCULATES VAPOUR PRESSURE OF A PURE COMPONENT AT
C**** A GIVEN TEMPERATURE USING MODIFIED PENG-ROBINSON EQUATION OF STATE
C**** EQUILIBRIUM IS ESTABLISHED BY THE EQUALITY OF FUGACITY CRITERION
C*****************************************************************;
      DIMENSION C(5),T(50),P(50)
      COMMON/BL1/TRR(50),OMEGA(50),S(10),C1,N3
  108 CONTINUE
      READ(1,250)U
C****
C**** U IS USED TO IDENTIFY VARIOUS UNITS
C**** U=0 WILL CONVERT TEMP FROM CENTIGRADE TO RANKINE AND P FROM MM HG
C**** TO PSIA. U=3  WILL CONVERT T FROM KELVIN TO RANKINE AND P FROM
C**** BARS TO PSIA.  U=OTHER NO  WILL ASSUME T IN DEGREES FAHRENHEIT
C**** AND P IN PSIA.
C****
C**** INPUT CRITICAL CONSTANTS OF THE FLUID
      READ(1,114)TC,PC,WC,W1,R
C**** T IN RANKINE, P IN PSIA       R=10.7335
      READ(1,150)N3
C**** N3 IS THE NO OF DATA POINTS
      READ(1,150)N4
C**** N4 IS THE NO OF ZM AND F VALUES FOR WHICH CALCULATIONS ARE TO BE
C**** REPEATED. WHEN ONLY OPTIMUM ZM AND F ARE USED  N4=1
      L=1
      READ(1,113)(T(I),P(I),I=1,N3)
C**** INPUT SATURATION TEMPERATURE AND A GUESS VALUE OF PRESSURE
  105 CONTINUE
      IF(L.GT.N4)GO TO 108
C**** INPUT EQUATION OF STATE PARAMETERS ZM AND F
      READ(1,135)ZM,CONST
C**** CALCULATION OF OMAC,OMB,OMC
      C(1)=1.0
      C(2)=2.0-3.0*ZM
      C(3)=3.0*ZM*ZM
      C(4)=-ZM**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
      OMB=ZMAX
      OMC=1.0-3.0*ZM
      OMAC=3.0*ZM*ZM+3.0*(1.0-2.0*ZM)*OMB+OMB*OMB+OMC
      ZEXP=ZM
      BB=OMB*R*TC/PC
      CC=OMC*R*TC/PC
      WRITE(2,500)
      WRITE(2,277)
      WRITE(2,351)
      WRITE(2,450)
      WRITE(2,240)TC,PC,WC,W1,R
      WRITE(2,350)ZEXP,OMAC,OMB,OMC,CONST
      WRITE(2,351)
      WRITE(2,300)
      WRITE(2,351)
      DO 60 I=1,N3
      IF(U.EQ.0)GO TO 600
      IF(U.EQ.3)GO TO 606
      T(I)=T(I)+459.67
      TRR(I)=T(I)/TC
      GO TO 58
  606 P(I)=P(I)*14.5037
```

```
      T(I)=T(I)*1.8
      TRR(I)=T(I)/TC
      GO TO 58
  600 P(I)=P(I)*14.696/760.0
      T(I)=(T(I)+273.15)*1.8
      TRR(I)=T(I)/TC
   58 CONTINUE
      PS=0.98*P(I)
      OMEGAA=(1.0+CONST*(1-TRR(I)**0.5))**2
      AA=OMAC*OMEGAA*R*R*TC*TC/PC
      D2=SQRT(BB*CC+0.25*(BB+CC)**2)
      D1=0.5*(BB+CC)-D2
      D3=0.5*(BB+CC)+D2
      N=0
  710 CONTINUE
      N=N+1
      B=BB*PS/R/T(I)
      CCC=CC*PS/R/T(I)
      A=AA*PS/(R*R*T(I)*T(I))
      C(1)=1.0
      C(2)=CCC-1.0
      C(3)=A-2*B*CCC-B*B-B-CCC
      C(4)=B*B*CCC-A*B+B*CCC
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION OF STATE
      ZV=ZMAX
C**** ZV IS VAPOUR PHASE COMPRESSIBILITY
      ZL=ZMIN
C**** ZL IS LIQUID PHASE COMPRESSIBILITY
      IF(ABS(1.0-ZL/ZV).LE.0.01)GO TO 800
      VLE=ZL*R*T(I)/PS
      VVE=ZV*R*T(I)/PS
C**** FUGACITY FOR BOTH PHASES ARE CALCULATED
      FL1=(AA/(2.0*R*T(I)*D2))*ALOG((VLE+D1)/(VLE+D3))
      FL2=ALOG(ZL-B)
      FV1=(AA/(2.0*R*T(I)*D2))*ALOG((VVE+D1)/(VVE+D3))
      FV2=ALOG(ZV-B)
      ZZL=ZL-1.0-FL2+FL1
      ZZV=ZV-1.0-FV2+FV1
      FL=PS*EXP(ZZL)
      FV=PS*EXP(ZZV)
      FVFL=ABS(FV-FL)
C**** EQUALITY OF FUGACITY FOR BOTH PHASES IS DEFINED BY THE FOLLOWING
C**** STATEMENT
      IF(ABS(1.0-FL/FV).LT.0.001)GO TO 700
      IF(N.GT.1)GO TO 280
      PS1=PS
      FVFL1=FVFL
      PS=PS*0.999
      GO TO 710
  800 PS=PS*0.99
      GO TO 710
  280 CONTINUE
C**** THE FOLLOWING CONVERGENCE CRITERION IS USED
      SLOPE=(PS-PS1)/(FVFL-FVFL1)
      DELT=SLOPE*FVFL
      PS1=PS
      FVFL1=FVFL
      PS=PS-DELT
      GO TO 710
```

```
  700 CONTINUE
C**** DEVIATION IS CALCULATED
      DPS=(P(I)-PS)*100/P(I)
      ADPS=ADPS+ABS(DPS)
      WRITE(2,50)P(I),PS,DPS,T(I),N,I
   60 CONTINUE
      ADPS=ADPS/N3
      WRITE(2,70)ADPS
      WRITE(2,351)
      L=L+1
      GO TO 105
C*********************************************************************
   50 FORMAT(1H ,2(F12.6,2X),8X,2(F12.6,2X),5X,I3,5X,I3)
   70 FORMAT(//1H ,'ABS. AVE. DEV(%) IN PS=',F6.4)
  113 FORMAT(2F0.0)
  114 FORMAT(5F0.0)
  135 FORMAT(2F0.0)
  150 FORMAT(I0)
  240 FORMAT(1H ,'TC=',F6.4,2X,'PC=',F6.2,2X,'ACE.FAC.=',F6.4,2X,'MOL WT
     1=',F6.3,2X,'R=',F8.5)
  250 FORMAT(F0.0)
  277 FORMAT(1H ,////)
  300 FORMAT(1H ,'   PEXP',11X,'PCALC',17X,'DEV(%)',6X,'TEMP',12X,'NO. I
     1TER.',3X,'NO.')
  350 FORMAT(1H ,'ZM=',F6.4,5X,'OMAC=',F9.7,5X,'OMB=',F9.7,5X,'OMC=',F9.
     17,5X,'CONSTANT F=',F9.7)
  351 FORMAT(1H ,'*************************************************
     1*************************************************')
  450 FORMAT(1H ,'PRESSURE IN PSIA: TEMPERATURE IN DEGREES RANKINE; VOLU
     1ME IN CU.FT./LB.MOLE.')
  500 FORMAT(1H1,' ')
C*********************************************************************
      STOP
      END
```

INPUT FOR PROGRAM NO.8

```
C*****************************************************************
C**** DATA INPUT FOR ETHANE
C*****************************************************************
DOCUMENT DATA
1                                          U
549.76 707.755 0.099 30.07 10.7335         TC  PC  WC  MOL WT  R
15                                          NO. OF DATA POINTS
1                                          NO. OF COMPONENTS
-150.0 7.099  15.2322  0.0286              T  P  VG  VL
-140.0  9.952  11.1461  0.029
-130.0  13.64  8.3269  0.0294
-127.8  14.696  7.7618  0.0295
-120.0  18.48  6.2762  0.0298
-110.0  24.35  4.8566  0.0303
-100.0 31.55  3.8142  0.0307
-90.0  40.27  3.0342  0.0311
-80.0  50.66  2.4442  0.0316
-70.0  62.97  1.9882  0.0321
-60.0 77.37  1.6826  0.0326
-50.0  94.13  1.3507  0.0331
-40.0  113.4  1.1258  0.0337
-30.0  135.5  0.9436  0.0342
-20.0  160.6  0.7951  0.0349
0.317  0.561567                            ZM   F
****
```

```
*****************************************************************************
PRESSURE IN PSIA; TEMPERATURE IN DEGREES RANKINE; VOLUME IN CU.FT./LB.MOLE.
TC=*549.7600  PC=707.76  ACE.FAC.=0.0990  MOL WT=30.070  R=10.73350
ZM=0.3170     OMAC=0.4460231     OMB=0.0810453     OMC=0.0490000     CONSTANT F=0.5615670
*****************************************************************************
```

PEXP	PCALC	DEV(%)	TEMP	NO. ITER.	NO.
7.099000	7.130232	-0.439950	309.670000	3	1
9.952000	9.958427	-0.366025	319.670000	3	2
13.640000	13.682348	-0.310468	329.670000	3	3
14.696000	14.622524	0.499974	331.870000	3	4
18.480000	18.367778	0.607263	339.670000	3	5
24.350000	24.211353	0.569391	349.670000	3	6
31.550000	31.390474	0.505628	359.670000	3	7
40.270000	40.091628	0.442940	369.670000	3	8
50.660000	50.509379	0.297316	379.670000	3	9
62.970000	62.845784	0.197262	389.670000	3	10
77.370000	77.309141	0.078659	399.670000	3	11
94.130000	94.113939	0.017062	409.670000	3	12
113.400000	113.479329	-0.069955	419.670000	3	13
135.500000	135.630305	-0.096166	429.670000	3	14
160.600000	160.795456	-0.121704	439.670000	3	15

```
ABS. AVE. DEV(%) IN PS=0.3080
*****************************************************************************
```

PROGRAM NO.9

```
      MASTER COMPARISON
C****
C*****************************************************************
C**** THIS PROGRAM COMPARES THREE EQUATIONS OF STATE FOR THE PREDICTION
C**** OF DENSITIES AT A GIVEN P AND T.
C**** 1. MODIFIED PENG-ROBINSON EQUATION  SUBROUTINE MPR
C**** 2. PENG-ROBINSON EQUATION  SUBROUTINE PENG
C**** 3. REDLICH-KWONG EQUATION  SUBROUTINE RK
C*****************************************************************
C****
      DIMENSION C(5)
      COMMON/BL1/F,ZM,OMAC,OMB,OMC
      COMMON/BL2/VGNCP,VGRK,VGPE,VLNCP,VLRK,VLPE
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL4/PC,R,T,P,TC,WC,CO(10)
      R=10.7335
C**** R IS A GAS CONSTANT
      READ(1,112)N1
C**** N1 IS NO.OF DATA POINTS
C**** INPUT CRITICAL CONSTANTS
      READ(1,114)TC,PC,WC,W1
C**** INPUT EQUATION OF STATE PARAMETERS ZM AND F FOR MODIFIED PR EQ.
      READ(1,50)ZM,F
C**** EVALUATION OF OMAC,OMB,OMC FOR MODIFIED PR EQ.
      C(1)=1.0
      C(2)=2.0-3.0*ZM
      C(3)=3.0*ZM*ZM
      C(4)=-ZM**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION.
      OMB=ZMAX
      OMC=1.0-3.0*ZM
      OMAC=3.0*ZM*ZM+3.0*(1-2.0*ZM)*OMB+OMB*OMB+OMC
      WRITE(2,250)
      WRITE(2,300)
      WRITE(2,230)
      WRITE(2,295)
      WRITE(2,118)TC,PC,WC,W1
      WRITE(2,117)ZM,OMAC,OMB,OMC,F
      WRITE(2,250)
      WRITE(2,225)
      WRITE(2,250)
      ADPE=0.0
      ADRK=0.0
      ADNCP=0.0
      DO 99 I=1,N1
      READ(1,126)T,P
      AUTHOR=1.0
C**** AUTHOR IS USED TO IDENTIFY DIFFERENT SOURCES OF EXP DATA
      P=P*14.696/760.0
C**** CONVERSION OF UNITS
      T=(T+273.15)*1.8
      ZRK=0.22811
      TR=T/TC
      VEXP=(R*TC/PC)*(ZRK**(1.0+(1.0-TR)**(2.0/7.0)))
C****
C**** SATURATED LIQUID DENSITY FOR N-EICOSANE IS OBTAINED FROM
C**** MODIFIED RACKETT EQUATION BY SPENCER AND DANNER(1972)
C****
      CALL MPR
```

```
C****
C**** SUBROUTINE MPR CALCULATES DENSITY USING MODIFIED PR EQ.
C**** DEVIATION BETWEEN EXPERIMENTAL AND CALCULATED VALUE IS OBTAINED.
C****
      CALL PENG
C****
C**** SUBROUTINE PENG CALCULATES DENSITY USING PR EQUATION
C**** DEVIATION BETWEEN EXPERIMENTAL AND CALCULATED VALUE IS OBTAINED.
C****
      CALL RK
C****
C**** SUBROUTINE RK CALCULATES DENSITY USING RK EQUATION
C**** DEVIATION BETWEEN EXPERIMENTAL AND CALCULATED VALUE IS OBTAINED.
C****
      ADNCP=ADNCP+ABS(DNCP)
      ADRK=ADRK+ABS(DRK)
      ADPE=ADPE+ABS(DPE)
      WRITE(2,275)I,P,T,VEXP,VGNCP,DNCP,VGRK,DRK,VGPE,DPE,AUTHOR
   99 CONTINUE
C**** ABS AVE DEVIATIONS ARE CALCULATED
      AADPE=ADPE/N1
      AADRK=ADRK/N1
      AADNCP=ADNCP/N1
      WRITE(2,51)
      WRITE(2,145)AADNCP,AADRK,AADPE
      WRITE(2,51)
C*****************************************************************;
   50 FORMAT(2F0.0)
   51 FORMAT(1H ,'*****************************************************
     1*****************************************************')
  112 FORMAT(10)
  114 FORMAT(4F0.0)
  117 FORMAT(1H ,'ZM=',F6.4,3X,'OMAC=',F8.5,3X,'OMB=',F8.5,3X,'OMC=',F8.
     15,3X,'F=',F9.6)
  118 FORMAT(1H ,'TC=',F7.2,3X,'PC=',F8.3,3X,'WC=',F6.4,3X,'MOL WT=',F7.
     13)
  126 FORMAT(2F0.0)
  145 FORMAT(1H ,'A.A.D.NCP=',F6.4,5X,'A.A.D.RK=',F6.4,5X,'A.A.D.PR=',F6
     1.4)
  225 FORMAT(1H ,' NO',4X,'P(PSIA)',3X,'T(R)',7X,'VEXP',5X,'VNCP',6X,'DN
     1CP',6X,'VRK',8X,'DRK',6X,'VPR',6X,'DPR',7X,'AUT')
  230 FORMAT(1H ,'N-EICOSANE---N-EICOSANE ')
  250 FORMAT(1H ,'-----------------------------------------------------
     1-----------------------------------------------------')
  275 FORMAT(1H ,I3,2X,F8.3,2X,F7.2,2X,7(F9.4,1X),2X,F3.1)
  295 FORMAT(1H ,'P IN PSIA ; V IN CU. FT./LB. MOLE ; T IN RANKINE')
  300 FORMAT(1H ,'***** CALCULATION OF PURE COMPONENT DENSITIES AT A GIV
     1EN P AND T ****')
C*****************************************************************;
      STOP
      END
```

INPUT FOR PROGRAM NO.9

```
C*****************************************************************************
C**** DATA INPUT FOR N-EICOSANE
C*****************************************************************************
DOCUMENT DATA
27                                          NO. OF DATA POINTS
1380.6 161.655 0.907 282.556                TC  PC  WC  MOL WT
0.277  1.409671                             ZM  F
379.0 1500                                  T   P
367.0 1200
357.0 1000
352.10 900
346.30 800
345.00 780
344.40 770
343.80 760
343.10 750
342.50 740
341.20 720
339.80 700
332.6 600
324.4 500
314.60 400
302.70 300
295.45 250
286.91 200
276.39 150
262.43 100
255.15 80
246.10 60
240.70 50
234.10 40
226.10 30
215.30 20
198.30 10
****
```

***** CALCULATION OF PURE COMPONENT DENSITIES AT A GIVEN P AND T ****

N-EICOSANE---N-EICOSANE

P IN PSIA ; V IN CU. FT./LB. MOLE ; T IN RANKINE

TC=1380.60 PC= 161.655 WC=0.9070 MOL WT=282.556

ZM=0.2770 OMAC= 0.49436 OMB= 0.06771 OMC= 0.16900 F= 1.409671

NO	P(PSIA)	T(R)	VEXP	VNCP	DNCP	VRK	DRK	VPR	DPR	AUT
1	29.005	1173.87	8.8567	8.8352	0.2424	14.0084	-58.1678	10.4612	-18.1168	1.0
2	23.204	1152.27	8.6402	8.6039	0.4197	13.5471	-56.7913	10.1786	-17.8051	1.0
3	19.337	1134.27	8.4745	8.4340	0.4776	13.2037	-55.8064	9.9697	-17.6442	1.0
4	17.403	1125.45	8.3975	8.3575	0.4768	13.0492	-55.3944	9.8754	-17.5991	1.0
5	15.469	1115.01	8.3097	8.2716	0.4576	12.8743	-54.9314	9.7693	-17.5657	1.0
6	15.083	1112.67	8.2904	8.2531	0.4507	12.8362	-54.8316	9.7463	-17.5611	1.0
7	14.889	1111.59	8.2816	8.2446	0.4470	12.8189	-54.7872	9.7358	-17.5596	1.0
8	14.696	1110.51	8.2728	8.2362	0.4431	12.8017	-54.7434	9.7254	-17.5584	1.0
9	14.503	1109.25	8.2626	8.2264	0.4385	12.7816	-54.6910	9.7133	-17.5568	1.0
10	14.309	1108.17	8.2539	8.2181	0.4342	12.7646	-54.6483	9.7030	-17.5561	1.0
11	13.923	1105.83	8.2352	8.2003	0.4242	12.7279	-54.5554	9.6809	-17.5551	1.0
12	13.536	1103.31	8.2152	8.1813	0.4126	12.6888	-54.4562	9.6573	-17.5549	1.0
13	11.602	1090.35	8.1150	8.0877	0.3359	12.4956	-53.9820	9.5411	-17.5739	1.0
14	9.668	1075.59	8.0061	7.9886	0.2178	12.2893	-53.5004	9.4176	-17.6311	1.0
15	7.735	1057.95	7.8826	7.8795	0.0387	12.0600	-52.9956	9.2812	-17.7436	1.0
16	5.801	1036.53	7.7413	7.7589	-0.2279	11.8037	-52.4767	9.1300	-17.9382	1.0
17	4.834	1023.48	7.6595	7.6912	-0.4135	11.6581	-52.2044	9.0447	-18.0844	1.0
18	3.867	1008.11	7.5669	7.6162	-0.6522	11.4958	-51.9223	8.9502	-18.2808	1.0
19	2.901	989.17	7.4579	7.5305	-0.9734	11.3082	-51.6264	8.8418	-18.5555	1.0
20	1.934	964.04	7.3213	7.4267	-1.4403	11.0780	-51.3122	8.7101	-18.9699	1.0
21	1.547	950.94	7.2533	7.3766	-1.7002	10.9655	-51.1801	8.6464	-19.2063	1.0
22	1.160	934.65	7.1717	7.3178	-2.0377	10.8323	-51.0435	8.5714	-19.5180	1.0
23	0.967	924.93	7.1244	7.2844	-2.2461	10.7561	-50.9758	8.5288	-19.7128	1.0
24	0.773	913.05	7.0680	7.2452	-2.5076	10.6660	-50.9061	8.4787	-19.9594	1.0
25	0.580	898.65	7.0016	7.2000	-2.8343	10.5612	-50.8401	8.4208	-20.2705	1.0
26	0.387	879.21	6.9151	7.1427	-3.2916	10.4267	-50.7816	8.3473	-20.7108	1.0
27	0.193	848.61	6.7857	7.0605	-4.0495	10.2301	-50.7592	8.2413	-21.4511	1.0

A.A.D.NCP=1.0404 A.A.D.RK=+53.3448 A.A.D.PR=+18.4163

OUTPUT FOR PROGRAM NO.9

PROGRAM NO.10

```
      MASTER MIXTURE DENSITY
C****
C*****************************************************************
C**** THIS PROGRAM CALCULATES DENSITY OF A MULTICOMPONENT MIXTURE
C**** METHOD 1. THE GCSP WITH TWO NON-SPHERICAL REFERENCE FLUIDS.
C**** VAN DER WAALS ONE FLUID MODEL IS USED.
C**** METHOD 2. COMBINATION OF PURE COMPONENT CONSTANTS WITH A SET
C**** OF EMPIRICAL MIXING RULES.
C*****************************************************************
C****
      DIMENSION X(10),C(5),ALP(10),AA(10),BB(10),CCC(10),AIJ(10,10)
      DIMENSION TCIJ(10,10),VCIJ(10,10),TCVCIJ(10,10),DITV(10),DIV(10)
      COMMON/BL1/TC(10),VC(10),WC(10),ZC(10)
      COMMON/BL2/DTCM(10),DVCM(10),DWCM(10),DZCM(10),DTCVCM(10)
      COMMON/BL3/NUM,TCVCM,VCM,ZCM,WCM
      COMMON/BL4/ZETA(10,10),ETA(10,10)
      COMMON/BL5/OMA(10),OB(10),OC(10)
      COMMON/BL6/PR,TR,TR2,VEXP,ZCH
      COMMON/BL7/R,T,P,W(10),ZM(10),F(10)
      WRITE(2,227)
      WRITE(2,225)
C**** INPUT ACENTRIC FACTORS OF TWO REFERENCE FLUIDS
      READ(1,116)AC1,AC2
C****
C**** INPUT EQUATION OF STATE PARAMETERS ZM AND F FOR TWO REFERENCE
C**** FLUIDS.
C****
      READ(1,116)ZM1,F1
      READ(1,116)ZM2,F2
      READ(1,16)NUM
C**** NUM IS NO. OF COMPONENTS IN A MIXTURE.
      R=0.083143
C**** R IS A GAS CONSTANT.
C****
C**** INPUT INTERACTION COEFFICIENTS IN THE FOLLOWING ORDER
C**** ZETA(1,2),ETA(1,2),ZETA(1,3),ETA(1,3),---ZETA(2,3),ETA(2,3)---
C**** ONE VALUE OF ZETA AND ETA ON EACH CARD.
C****
      DO 600 I=1,NUM
      DO 650 J=1,NUM
      IF(I.GE.J)GO TO 650
      READ(1,22)ZETA(I,J),ETA(I,J)
      ETA(J,I)=ETA(I,J)
      ZETA(J,I)=ZETA(I,J)
      WRITE(2,23)I,J,ZETA(I,J),I,J,ETA(I,J)
  650 CONTINUE
  600 CONTINUE
C**** INPUT CRITICAL CONSTANTS OF EACH COMPONENT
      READ(1,114)(TC(I),VC(I),WC(I),ZC(I),W(I),I=1,NUM)
C**** INPUT EQUATION OF STATE PARAMETERS ZM AND F FOR EACH COMPONENT.
      READ(1,120)(ZM(I),F(I),I=1,NUM)
   89 CONTINUE
      READ(1,226)N1
C**** N1 IS NO. OF DATA POINTS.
C****
C**** INPUT MOLE FRACTIONS IN THIS ORDER X(1), X(2)---X(NUM-1).
C**** EACH MOLE FRACTION ON A SEPARATE CARD.
C****
      READ(1,2)(X(I),I=1,NUM-1)
      SUMX=0.0
```

```
      DO 525 I=1,NUM-1
  525 SUMX=SUMX+X(I)
      X(NUM)=1-SUMX
      READ(1,112)REF
C**** REF IS USED TO IDENTIFY UNITS OF EXPERIMENTAL P V T DATA.
      CALL VDWMX(X)
C****
C**** SUBROUTINE VDWMX CALCULATES MIXTURE PARAMETERS USING
C**** VAN DER WAALS MIXING RULES.
C****
      TCM=TCVCM/VCM
      PCM=ZCM*R*TCM/VCM
      AC=WCM
      ADEV=0.0
      ADEV1=0.0
      ZCC=ZM1
C**** EVALUATION OF OMAC,OMB,OMC FOR REFERENCE FLUID 1
      C(1)=1.0
      C(2)=2.0-3.0*ZCC
      C(3)=3.0*ZCC*ZCC
      C(4)=-ZCC**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION.
      OMB=ZMAX
      OMC=1.0-3.0*ZCC
      OMAC=3.0*ZCC*ZCC+3.0*(1.0-2.0*ZCC)*OMB+OMB*OMB+OMC
      OMAC1=OMAC
      OMB1=OMB
      OMC1=OMC
      ZCC=ZM2
C**** EVALUATION OF OMAC,OMB,OMC FOR REFERENCE FLUID 2
      C(1)=1.0
      C(2)=2.0-3.0*ZCC
      C(3)=3.0*ZCC*ZCC
      C(4)=-ZCC**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION.
      OMB=ZMAX
      OMC=1.0-3.0*ZCC
      OMAC=3.0*ZCC*ZCC+3.0*(1.0-2.0*ZCC)*OMB+OMB*OMB+OMC
      OMAC2=OMAC
      OMB2=OMB
      OMC2=OMC
      DO 70 I=1,NUM
      ZCC=ZM(I)
C**** EVALUATION OF OMAC,OMB,OMC FOR EACH COMPONENT.
      C(1)=1.0
      C(2)=2.0-3.0*ZCC
      C(3)=3.0*ZCC*ZCC
      C(4)=-ZCC**3.0
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION.
      OMB=ZMAX
      OMC=1.0-3.0*ZCC
      OMAC=3.0*ZCC*ZCC+3.0*(1.0-2.0*ZCC)*OMB+OMB*OMB+OMC
      OMA(I)=OMAC
      OB(I)=OMB
      OC(I)=OMC
   70 CONTINUE
      WRITE(2,260)AC1,AC2
```

```
      WRITE(2,270)ZM1,OMAC1,OMB1,OMC1
      WRITE(2,271)ZM2,OMAC2,OMB2,OMC2
      WRITE(2,220)(I,TC(I),I,VC(I),I,ZC(I),I,WC(I),I,W(I),I=1,NUM)
      WRITE(2,280)(I,ZM(I),I,OMA(I),I,OB(I),I,OC(I),I=1,NUM)
      WRITE(2,275)(I,X(I),I=1,NUM)
      WRITE(2,227)
      WRITE(2,500)
      WRITE(2,227)
      DO 90 I=1,N1
C**** INPUT EXPERIMENTAL P V T .
      READ(1,111)P,VEXP,T
      T=273.16+(T-32)*5.0/9.0
      P=P/14.5037
      IF(REF.EQ.1)GO TO 85
      VEXP=VEXP*R*T/P
      GO TO 86
   85 VEXP=VEXP*0.062426
   86 CONTINUE
      TR=T/TCM
      TR2=TR*TR
      PR=P/PCM
C**** EQUATION OF STATE IS SOLVED FOR REFERENCE FLUID 1.
      ALP1=(1.0+F1*(1.0-SQRT(TR)))**2.0
      A=OMAC1*ALP1*PR/TR2
      B=OMB1*PR/TR
      CC=OMC1*PR/TR
      C(1)=1.0
      C(2)=CC-1.0
      C(3)=-(2.0*B*CC+B*B+B+CC-A)
      C(4)=B*B*CC-A*B+B*CC
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION.
      IF(VEXP.LT.VCM)GO TO 55
      Z1=ZMAX
      GO TO 56
   55 Z1=ZMIN
   56 CONTINUE
C**** EQUATION OF STATE IS SOLVED FOR REFERENCE FLUID 2.
      ALP2=(1.0+F2*(1.0-SQRT(TR)))**2.0
      A=OMAC2*ALP2*PR/TR2
      B=OMB2*PR/TR
      CC=OMC2*PR/TR
      C(1)=1.0
      C(2)=CC-1.0
      C(3)=-(2.0*B*CC+B*B+B+CC-A)
      C(4)=B*B*CC-A*B+B*CC
      CALL SOLVE(ZMIN,ZMAX,C)
C**** SUBROUTINE SOLVE IS USED TO SOLVE THE CUBIC EQUATION.
      IF(VEXP.LT.VCM)GO TO 65
      Z2=ZMAX
      GO TO 75
   65 Z2=ZMIN
   75 CONTINUE
C****
C**** THE GCSP USING TWO NON-SPHERICAL REF FLUIDS IS DEFINED BY THE
C**** FOLLOWING STATEMENT.
C****
      Z=Z1+(AC-AC1)*(Z2-Z1)/(AC2-AC1)
      V=Z*R*T/P
      VR=V/VCM
```

```
      VRE=VEXP/VCH
C**** DEVIATION FROM EXPERIMENTAL VALUE IS CALCULATED.
      DEV=(VRE-VR)*100/VRE
      ADEV=ADEV+ABS(DEV)
      CALL NCPMIX(X)
C****
C**** SUBROUTINE NCPMIX CALCULATES DENSITY OF MIXTURE USING PURE
C**** COMPONENT CONSTANTS AND A SET OF EMPIRICAL MIXING RULES.
C****
      VCH=ZCH*R*T/P
      VRCH=VCH/VCH
      DEVCH=(VRE-VRCH)*100/VRE
      ADEV1=ADEV1+ABS(DEVCH)
      WRITE(2,32)I,PR,TR,VRE,VR,DEV,VRCH,DEVCH,AUTHOR
   90 CONTINUE
      WRITE(2,510)
      AADEV=ADEV/N1
      AADEV1=ADEV1/N1
      WRITE(2,35)AADEV
      WRITE(2,38)AADEV1
      WRITE(2,510)
      GO TO 89
C*********************************************************************
    2 FORMAT(F0.0)
   16 FORMAT(I0)
   22 FORMAT(2F0.0)
   23 FORMAT(1H ,'ZETA(',I2,',',I2,')=',F6.4,3X,'ETA(',I2,',',I2,')=',F6
     1.4)
   32 FORMAT(1H ,I3,2X,7(F10.6,1X),2X,F3.1)
   35 FORMAT(//1H ,'ABS AVE DEV(%) GCSP=',F10.5)
   38 FORMAT(/1H ,'ABS AVE DEV(%)  NCP =',F10.5)
  111 FORMAT(3F0.0)
  112 FORMAT(F0.0)
  114 FORMAT(5F0.0)
  116 FORMAT(2F0.0)
  120 FORMAT(2F0.0)
  220 FORMAT(1H ,'TC(',I2,')=',F6.2,3X,'VC(',I2,')=',F8.5,3X,'ZC(',I2,')
     1=',F6.4,3X,'ACE.FAC.(',I2,')=',F6.4,3X,'MOL WT.(',I2,')=',F6.2)
  225 FORMAT(1H ,'PREDICTION OF DENSITIES OF MIXTURE USING GCSP WITH MOD
     1IFIED PR EQUATION OF STATE')
  226 FORMAT(I0)
  227 FORMAT(1H ,'*********************************************************
     1*********************************************************')
  260 FORMAT(1H ,'ACE.FAC.REF.1=',F6.4,5X,'ACE.FAC.REF.2=',F6.4)
  270 FORMAT(1H ,'ZM1=',F6.4,3X,'OMAC1=',F8.6,3X,'OMB1=',F8.6,3X,'OMC1='
     1,F8.6)
  271 FORMAT(1H ,'ZM2=',F6.4,3X,'OMAC2=',F8.6,3X,'OMB2=',F8.6,3X,'OMC2='
     1,F8.6)
  275 FORMAT(1H ,'X(',I2,')=',F6.4)
  280 FORMAT(1H ,'ZM(',I2,')=',F6.4,3X,'OMA(',I2,')=',F8.6,3X,'OB(',I2,'
     1)=',F8.6,3X,'OC(',I2,')=',F8.6)
  500 FORMAT(1H ,' NO',6X,'PR',9X,'TR',8X,'VREXP',6X,'VRGCSP',5X,'DEV',6
     1X,'VRNCP',7X,'DEV',5X,'REF')
  510 FORMAT(1H ,'---------------------------------------------------------
     1-----------------------------------------------------------')
C*********************************************************************
      STOP
      END
```

INPUT FOR PROGRAM NO.10

```
C*****************************************************************************
C**** DATA INPUT FOR  PROPANE(1)-PENTANE(2) SYSTEM  ***************
C*****************************************************************************
DOC DATA
0.099   0.489                                   AC1   AC2
0.317   0.561567                                ZM1   F1
0.297   1.021919                                ZM2   F2
2                                               NO. OF COMPONENTS
1.0 1.0                                         ZETA(1,2)  ETA(1,2)
369.82 0.203 0.153 0.281 44.094                 TC  VC  WC  ZC  MOL WT
469.7 0.304 0.251 0.263 72.146                  TC VC WC ZC MOL WT
0.317 0.648049                                  ZM(1)  F(1)
0.308 0.746470                                  ZM(2)  F(2)
10                                              NO. OF DATA POINTS
0.6511                                          X(1)
2.0                                             REF
20      0.983          160                      P  V  T
40      0.954          160
60      0.931          160
80      0.906          160
100     0.880          160
20      0.986          190
40      0.963          190
60      0.945          190
80      0.926          190
100     0.906          190
****
```

```
*****************************************************************************************
PREDICTION OF DENSITIES OF MIXTURE USING GCSP WITH MODIFIED PR EQUATION OF STATE
ZETA( 1, 2)=1.0000    ETA( 1, 2)=1.0000
ACE.FAC.REF.1=0.0990      ACE.FAC.REF.2=0.4890
ZM1=0.3170    OMAC1=0.446023    OMB1=0.081045    OMC1=0.049000
ZM2=0.2970    OMAC2=0.469657    OMB2=0.074309    OMC2=0.109000
TC( 1)=369.82    VC( 1)= 0.20300    ZC( 1)=0.2810    ACE.FAC.( 1)=0.1530    MOL WT.( 1)= 44.09
TC( 2)=469.70    VC( 2)= 0.30400    ZC( 2)=0.2630    ACE.FAC.( 2)=0.2510    MOL WT.( 2)= 72.15
ZM( 1)=0.3170    OMA( 1)=0.446023    OB( 1)=0.081045    OC( 1)=0.049000
ZM( 2)=0.3080    OMA( 2)=0.456529    OB( 2)=0.077998    OC( 2)=0.076000
X( 1)=0.6511
X( 2)=0.3489
*****************************************************************************************
```

NO	PR	TR	VREXP	VRGCSP	DEV	VRNCP	DEV	REF
1	0.035026	0.843844	86.204826	85.792008	0.478880	85.788553	0.482888	2.0
2	0.070053	0.843844	41.830826	41.914573	-0.200204	41.911236	-0.192227	2.0
3	0.105079	0.843844	27.214884	27.266532	-0.189777	27.263346	-0.178073	2.0
4	0.140105	0.843844	19.863065	19.923542	-0.304469	19.920554	-0.289426	2.0
5	0.175131	0.843844	15.434435	15.500270	-0.426549	15.497544	-0.408888	2.0
6	0.035026	0.884696	90.653950	90.201845	0.498716	90.200493	0.500207	2.0
7	0.070053	0.884696	44.269652	44.209375	0.136159	44.208162	0.138899	2.0
8	0.105079	0.884696	28.961455	28.862435	0.341902	28.861383	0.345533	2.0
9	0.140105	0.884696	21.284371	21.175534	0.511346	21.174671	0.515401	2.0
10	0.175131	0.884696	16.659732	16.551359	0.650509	16.550719	0.654348	2.0

ABS AVE DEV(%) GCSP= 0.37385

ABS AVE DEV(%) NCP = 0.37059

```
      SUBROUTINE DEN(RO,E1,H,C,GAM,P)
C*********************************************************************
C     THIS SUBROUTINE CALCULATES THE DENSITY OF VAPOUR AND LIQUID PHASE
C      BY USING A BASIC ITERATION TECHNIQUE TO LOCATE THE ROOTS OF A
C     POLYNOMIAL
C*********************************************************************
      DIMENSION C(5)
      E2=0.00001
    5 Y=ST(RO,C,P,GAM)
      K=2
      IF(Y.LT.0) K=1
   10 RO=RO+H
      Y=ST(RO,C,P,GAM)
      IF(Y.EQ.0.0)GO TO 72
      IF(Y.LT.0.AND.K.EQ.2.OR.Y.GT.0.AND.K.EQ.1)GOTO 55
      IF(H.LT.0)GOTO 30
      IF(RO.LT.E1)GOTO 10
      GO TO 72
   30 IF(RO.GT.E1)GOTO 10
      GO TO 72
   55 IF(ABS(H).GT.E2)GO TO 70
      GO TO 72
   70 E1=RO
      RO=RO-H
      H=H/10
      GO TO 5
   72 RETURN
      END
```

```
      SUBROUTINE DEVA
C**** ***********************************************************************
C****THIS SUBROUTINEA CALCULATES DEVIATIONS OF PREDICTED ALPHA VALUES
C**** (USING TWO FITTED FUNCTIONS) FROM THE ACTUAL VALUE OF ALPHA
C**** OBTAINED BY EQUATING FUGACITY.
C**** ***********************************************************************
      COMMON/BL1/X,XX,N3,TRR(50),P(50),T(50),OMEGA(50),S(10),C1
      ADEV=0.0
      ADEV1=0.0
      WRITE(2,296)
      WRITE(2,80)
      WRITE(2,296)
      DO 60 I=1,N3
      TRTR=1.0-TRR(I)**0.5
      STR=1.0-TRR(I)**X
      ALPH=EXP(XX*STR)
      ALPH1=(1.0+C1*TRTR)**2
      DEV=(OMEGA(I)-ALPH)*100/OMEGA(I)
      DEV1=(OMEGA(I)-ALPH1)*100/OMEGA(I)
      ADEV=ADEV+ABS(DEV)
      ADEV1=ADEV1+ABS(DEV1)
      WRITE(2,70)TRR(I),OMEGA(I),ALPH,DEV,ALPH1,DEV1
   70 FORMAT(1H ,6(F12.6))
   80 FORMAT(1H ,3X,'TR',7X,'ALPHA',7X,'ALP CALC EXP',2X,'DEV(%)',4X,'AL
     1P CALC PR',2X,'DEV(%)')
   60 CONTINUE
      WRITE(2,296)
      ADEV=ADEV/N3
      ADEV1=ADEV1/N3
      WRITE(2,50)ADEV,ADEV1
   50 FORMAT(1H ,'A.A.D EXP FORM =',F6.4,5X,'A.A.D PR FORM =',F6.4)
      WRITE(2,296)
  296 FORMAT(1H ,'-----------------------------------------------------
     1-----------------------------------------------------------')
      RETURN
      END
```

```
      SUBROUTINE FUGA(X,FL,RO)
C*****************************************************************
C     THIS SUBROUTINE CALCULATES THE FUGACITY OF EACH COMPONENT
C*****************************************************************
      DIMENSION FL(10)
      DIMENSION X(10),F(10),F1(10),F2(10),F3(10),F4(10),F5(10),F6(10)
      COMMON/BL1/AO(10),BO(10),CO(10),DO(10),EO(10),A1(10),B1(10)
      COMMON/BL2/C1(10),D1(10),AL(10),GA(10)
      COMMON/BL3/A(11),B(11),TC(10),VC(10),WC(10),ZC(10)
      COMMON/BL4/R,T,AM,BM,CM,DM,AOM,BOM,COM,DOM,EOM,ALM,GAM,NUM
      COMMON/BL5/CKIJ(10,10)
      DO 5 I=1,NUM
      F(I)=(BO(I)+BOM)*R*T
      F1(I)=0.0
      DO 25 J=1,NUM
      IF(I.EQ.J)CKIJ(I,J)=0.0
      F1(I)=F1(I)+X(J)*(-SQRT(AO(J)*AO(I))*(1-CKIJ(I,J))-(SQRT(CO(J)*CO(
     1I))*(1-CKIJ(I,J))**3)/(T*T)+(SQRT(DO(J)*DO(I))*(1-CKIJ(I,J))**4)/(T*
     2T**3)-(SQRT(EO(J)*EO(I))*(1-CKIJ(I,J))**5)/(T**4))
   25 CONTINUE
      F2(I)=0.5*(3*R*T*(BM*BM*B1(I))**(1.0/3.0)-3*(AM*AM*A1(I))**(1.0/3.0)
     10)-(3.0/T)*(DM*DM*D1(I))**(1.0/3.0))
      F3(I)=(ALM/5.0)*(3*(AM*AM*A1(I))**(1.0/3.0)+(3.0/T)*(DM*DM*D1(I))**
     1*(1.0/3.0))
      F4(I)=0.6*(AM+DM/T)*(ALM*ALM*AL(I))**(1.0/3.0)
      F5(I)=(3.0/(T*T))*(CM*CM*C1(I))**(1.0/3.0)
      F6(I)=-(2*CM/(GAM*T*T))*SQRT(GA(I)/GAM)
      GAM2=GAM*RO*RO
      EXPG=EXP(-GAM2)
      FL(I)=(1.0/(R*T))*(F(I)*RO+F1(I)*RO*2.0+F2(I)*RO*RO+F3(I)*RO**5+F4(I
     1(I)*RO**5+F5(I)*RO*RO*((1-EXPG)/GAM2-EXPG/2.0)+F6(I)*(1-EXPG*(1+GA
     2M2+(GAM2)**2/2.0)))
      EXPFL=EXP(FL(I))
      FL(I)=R*T*X(I)*RO*EXPFL
    5 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE MIXP(X)
!*****************************************************************
!     THIS SUBROUTINE CALCULATES MIXTURE PARAMETERS USING THE MIXING RULES
!      GIVEN BY HAN-STARLING
!*****************************************************************
      DIMENSION X(5)
      COMMON/BL1/AO(10),BO(10),CO(10),DO(10),EO(10),A1(10),B1(10)
      COMMON/BL2/C1(10),D1(10),AL(10),GA(10)
      COMMON/BL3/A(11),B(11),TC(10),VC(10),WC(10),ZC(10)
      COMMON/BL4/R,T,AM,BM,CM,DM,AOM,BOM,COM,DOM,EOM,ALM,GAM,NUM
      COMMON/BL5/CKIJ(10,10)
      BOM=0.0
      BM=0.0
      GAM=0.0
      AM=0.0
      ALM=0.0
      CM=0.0
      DM=0.0
      DO 5 I=1,NUM
      BO(I)=(A(1)+B(1)*WC(I))*VC(I)
      AO(I)=(A(2)+B(2)*WC(I))*R*TC(I)*VC(I)
      CO(I)=(A(3)+B(3)*WC(I))*R*VC(I)*TC(I)**3
      GA(I)=(A(4)+B(4)*WC(I))*VC(I)*VC(I)
      B1(I)=(A(5)+B(5)*WC(I))*VC(I)*VC(I)
      A1(I)=(A(6)+B(6)*WC(I))*R*TC(I)*VC(I)**2
      AL(I)=(A(7)+B(7)*WC(I))*VC(I)**3
      C1(I)=(A(8)+B(8)*WC(I))*R*TC(I)*(VC(I)*TC(I))**2
      DO(I)=(A(9)+B(9)*WC(I))*R*VC(I)*TC(I)**4
      D1(I)=(A(10)+B(10)*WC(I))*R*(VC(I)*TC(I))**2
      EO(I)=(A(11)+B(11)*WC(I)*EXP(-3.8*WC(I)))*R*VC(I)*TC(I)**5
      BOM=BOM+BO(I)*X(I)
      GAM=GAM+X(I)*SQRT(GA(I))
      AM=AM+X(I)*A1(I)**(1.0/3.0)
      BM=BM+X(I)*B1(I)**(1.0/3.0)
      CM=CM+X(I)*C1(I)**(1.0/3.0)
      DM=DM+X(I)*D1(I)**(1.0/3.0)
      ALM=ALM+X(I)*AL(I)**(1.0/3.0)
    5 CONTINUE
      GAM=GAM*GAM
      BM=BM**3
      AM=AM**3
      ALM=ALM**3
      CM=CM**3
      DM=DM**3
      AOM=0.0
      COM=0.0
      DOM=0.0
      EOM=0.0
      DO 15 I=1,NUM
      DO 20 J=1,NUM
      IF(I.EQ.J)CKIJ(I,J)=0.0
      AOM=AOM+(1-CKIJ(I,J))*SQRT(AO(I)*AO(J))*X(I)*X(J)
      COM=COM+SQRT(CO(I)*CO(J))*X(I)*X(J)*(1-CKIJ(I,J))**3
      DOM=DOM+X(I)*X(J)*SQRT(DO(I)*DO(J))*(1-CKIJ(I,J))**4
      EOM=EOM+X(I)*X(J)*SQRT(EO(I)*EO(J))*(1-CKIJ(I,J))**5
   20 CONTINUE
   15 CONTINUE
      RETURN
      END
```

```
C****
      SUBROUTINE MPR
C*********************************************************************
C**** THIS SUBROUTINE CALCULATES DENSITY AT A GIVEN P AND T USING
C**** MODIFIED PENG-ROBINSON EQUATION
C**** DEVIATION BETWEEN EXPERIMENTAL AND CALCULATED VALUE IS OBTAINED.
C**** OMAC,OMB,OMC AND F FOR THE FLUID OF INTEREST ARE SUPPLIED BY
C**** THE MAIN PROGRAM
C*********************************************************************
      DIMENSION C(5)
      COMMON/BL1/F,ZM,OMAC,OMB,OMC
      COMMON/BL2/VGNCP,VGRK,VGPE,VLNCP,VLRK,VLPE
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL4/PC,R,T,P,TC,WC,CO(10)
      TR=T/TC
      ALP=(1+F*(1-SQRT(TR)))**2.0
      AC=OMAC*R*R*TC*TC/PC
      BC=OMB*R*TC/PC
      CC=OMC*R*TC/PC
      AA=AC*ALP
      BB=BC
      A=AA*P/(R*R*T*T)
      B=BB*P/(R*T)
      CCC=CC*P/(R*T)
      C(1)=1.0
      C(2)=CCC-1.0
      C(3)=-(2.0*B*CCC+B*B+B+CCC-A)
      C(4)=B*B*CCC-A*B+B*CCC
      CALL SOLVE(ZMIN,ZMAX,C)
      Z=ZMAX
      VNCP=Z*R*T/P
      VGNCP=VNCP
      DNCP=(VEXP-VGNCP)*100/VEXP
      IF(ABS(DNCP).LT.50.0)GO TO 72
      Z=ZMIN
      VLNCP=Z*R*T/P
      VGNCP=VLNCP
      DNCP=(VEXP-VGNCP)*100/VEXP
   72 RETURN
      END
```

```
C****
C**** ******************************************************************
      SUBROUTINE NCP
C**** THIS ROUTINE CALCULATES COMPRESSIBILITY AT A GIVEN T AND P USING
C**** MODIFIED P-R EQUATION OF STATE.F,OMAC,OMB AND OMC ARE SUPPLIED
C**** BY THE MAIN PROGRAM.
C******************************************************************
C****
      DIMENSION C(5)
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL2/PR,TR,VRE,TR2,VHE,ZHE
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL4/PC,F,ZM,OMAC,OMB,OMC
      COMMON/BL5/AUTHOR,W1,DL
      TR=T/TC
      ALP=(1+F*(1-SQRT(TR)))**2
      AC=OMAC*R*R*TC*TC/PC
      BC=OMB*R*TC/PC
      CC=OMC*R*TC/PC
      AA=AC*ALP
      BB=BC
      A=AA*P/(R*R*T*T)
      B=BB*P/(R*T)
      CCC=CC*P/(R*T)
      C(1)=1.0
      C(2)=CCC-1.0
      C(3)=-(2.0*B*CCC+B*B+B*CCC-A)
      C(4)=B*B*CCC-A*B+B*CCC
      CALL SOLVE(ZMIN,ZMAX,C)
      IF(VEXP.LT.VC.AND.ZMIN.GT.0)GO TO 55
      ZHE=ZMAX
      GO TO 56
   55 ZHE=ZMIN
   56 CONTINUE
      RETURN
      END
```

```
C****
      SUBROUTINE NCPMIX(X)
C*********************************************************************
C**** THIS SUBROUTINE CALCULATES DENSITY OF A MULTICOMPONENT MIXTURE
C**** USING THE MODIFIED PR EQUATION AND A SET OF EMPIRICAL MIXING RULES.
C*********************************************************************
C****
      DIMENSION X(10),C(5),ALP(10),AA(10),BB(10),CCC(10),AIJ(10,10)
      COMMON/BL1/TC(10),VC(10),WC(10),ZC(10)
      COMMON/BL3/NUM,TCVCM,VCM,ZCM,WCM
      COMMON/BL4/ZETA(10,10),ETA(10,10)
      COMMON/BL5/OMA(10),OB(10),OC(10)
      COMMON/BL6/PR,TR,TR2,VEXP,ZCH
      COMMON/BL7/R,T,P,W(10),ZM(10),F(10)
      DO 50 I=1,NUM
      ALP(I)=(1.0+F(I)*(1.0-SQRT(TR)))**2.0
      AA(I)=OMA(I)*ALP(I)*R*TC(I)*VC(I)/ZC(I)
      BB(I)=OB(I)*VC(I)/ZC(I)
      CCC(I)=OC(I)*VC(I)/ZC(I)
   50 CONTINUE
      AM=0.0
      BM=0.0
      CM=0.0
      DO 500 I=1,NUM
      DO 550 J=1,NUM
      IF(I.EQ.J)GO TO 600
      AIJ(I,J)=ZETA(I,J)*SQRT(AA(I)*AA(J))
      GO TO 650
  600 AIJ(I,J)=AA(I)
  650 AM=AM+X(I)*X(J)*AIJ(I,J)
  550 CONTINUE
      BM=BM+BB(I)*X(I)
      CM=CM+CCC(I)*X(I)
  500 CONTINUE
      A=AM*P/(R*R*T*T)
      B=BM*P/R/T
      CC=CM*P/R/T
      C(1)=1.0
      C(2)=CC-1.0
      C(3)=-(2.0*B*CC+B*B+B+CC-A)
      C(4)=B*B*CC-A*B+B*CC
      CALL SOLVE(ZMIN,ZMAX,C)
      IF(VEXP.LT.VCM.AND.ZMIN.GT.0)GO TO 55
      ZCH=ZMAX
      GO TO 56
   55 ZCH=ZMIN
   56 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE NONLINEAR(C)
C**** ***********************************************************************
C**** THIS SUBROUTINE SOLVES THE NON LINEAR EQUATION RESULTING FROM
C**** LEAST SQUARE FITTING OF EXPONENTIAL FUNCTION. BASIC ITERATION
C**** TECHNIQUE IS USED
C**** ***********************************************************************
      DIMENSION C(5)
      COMMON/BL1/X,XX,N3,TRR(50),P(50),T(50),OMEGA(50),S(10),C1
      Z=3.0
C**** Z IS UPPER LIMIT OF N
      E1=-10.0
C**** E1 IS LOWER LIMIT OF N
      H=-0.5
C**** H IS STEP SIZE
      E2=0.00001
C**** E2 IS REQUIRED DECIMAL POINT ACCURACY IN N
    5 X=Z
      IF(X.EQ.0)X=H
      CALL SUMMA(C)
      Y=C(1)+C(2)+C(3)
      K=2
      IF(Y.LT.0)K=1
   10 Z=Z+H
      X=Z
      IF(X.EQ.0)X=H
      CALL SUMMA(C)
      Y=C(1)+C(2)+C(3)
      IF(Y.EQ.0.0)GO TO 72
      IF(Y.LT.0.AND.K.EQ.2.OR.Y.GT.0.AND.K.EQ.1)GO TO 55
      IF(H.LT.0)GO TO 30
      IF(Z.LT.E1)GO TO 10
      GO TO 72
   30 IF(Z.GT.E1)GO TO 10
      GO TO 72
   55 IF(ABS(H).GT.E2)GO TO 70
      GO TO 72
   70 E1=Z
      Z=Z-H
      H=H/10
      GO TO 5
   72 RETURN
      END
```

```
C****
      SUBROUTINE PENG
C*****************************************************************;
C**** THIS SUBROUTINE CALCULATES DENSITY AT A GIVEN P AND T USING
C**** PENG-ROBINSON EQUATION
C**** DEVIATION BETWEEN EXPERIMENTAL AND CALCULATED VALUE IS OBTAINED.
C*****************************************************************;
      DIMENSION C(5)
      COMMON/BL4/PC,R,T,P,TC,WC,CO(10)
      COMMON/BL2/VGNCP,VGRK,VGPE,VLNCP,VLRK,VLPE
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      TR=T/TC
      F=0.37464+1.54226*WC-0.26992*WC*WC
      ALP=(1+F*(1-SQRT(TR)))**2
      BC=R*TC/PC
      AC=0.45724*R*TC*BC
      BB=0.0778*BC
      AA=AC*ALP
      A=AA*P/(R*R*T*T)
      B=BB*P/(R*T)
      C(1)=1.0
      C(2)=B-1
      C(3)=A-3*B*B-2*B
      C(4)=B*B*B+B*B-A*B
      CALL SOLVE(ZMIN,ZMAX,C)
      Z=ZMAX
      VPENG=Z*R*T/P
      VGPE=VPENG
      DPE=(VEXP-VGPE)*100/VEXP
      IF(ABS(DPE).LT.50.0)GO TO 72
      Z=ZMIN
      VLPE=Z*R*T/P
      VGPE=VLPE
      DPE=(VEXP-VGPE)*100/VEXP
   72 RETURN
      END
```

```
C****
      SUBROUTINE RK
C*****************************************************************
C**** THIS SUBROUTINE CALCULATES DENSITY AT A GIVEN P AND T USING
C**** USING REDLICH-KWONG EQUATION
C**** DEVIATION BETWEEN EXPERIMENTAL AND CALCULATED VALUE IS OBTAINED.
C*****************************************************************
      DIMENSION C(5)
      COMMON/BL4/PC,R,T,P,TC,WC,CO(10)
      COMMON/BL2/VGNCP,VGRK,VGPE,VLNCP,VLRK,VLPE
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      BC=R*TC/PC
      AC=RC*R*TC**1.5
      AO=0.42748*AC
      BO=0.08664*BC
      A=AO*P/(R*R*T**2.5)
      B=BO*P/(R*T)
      C(1)=1.0
      C(2)=-1
      C(3)=A-B-B*B
      C(4)=-A*B
      CALL SOLVE(ZMIN,ZMAX,C)
      Z=ZMAX
      VRK=Z*R*T/P
      VGRK=VRK
      DRK=(VEXP-VGRK)*100/VEXP
      IF(ABS(DRK).LT.50.0)GO TO 72
      Z=ZMIN
      VLRK=Z*R*T/P
      VGRK=VLRK
      DRK=(VEXP-VGRK)*100/VEXP
   72 RETURN
      END
```

```
      SUBROUTINE SOLVE(ZMIN,ZMAX,C)
C
C     ******************************************************************
C     THIS ROUTINE SOLVES CUBIC EQUATION ANALYTICALLY AND DIFFERENTIATE
C     BETWEEN MINIMUM AND MAXIMUM ROOTS
C     ******************************************************************
C
      DIMENSION C(5)
      C(2)=C(2)/C(1)
      C(3)=C(3)/C(1)
      C(4)=C(4)/C(1)
      A=(3.0*C(3)-C(2)*C(2))/3.0
      B=(2.0*C(2)*C(2)*C(2)-9.0*C(2)*C(3)+27.0*C(4))/27.0
      AA=A*A*A/27.0
      BB=B*B/4.0
      SUM=BB+AA
      IF(SUM.GE.0)GO TO 500
      X=-BB/AA
      CX=SQRT(X)
      PHI=ACOS(CX)
      IF(B.GT.0)PHI=ACOS(-CX)
      XX1=PHI/3.0
      XX2=PHI/3.0+2.094395
      XX3=PHI/3.0+2.094395*2.0
      XX=2.0*SQRT(-A/3.0)
      X1=XX*COS(XX1)-C(2)/3.0
      X2=XX*COS(XX2)-C(2)/3.0
      X3=XX*COS(XX3)-C(2)/3.0
  660 CONTINUE
      IF(X1.EQ.X2.AND.X1.LT.X3)GO TO 10
      IF(X1.EQ.X2.AND.X1.GT.X3)GO TO 20
      IF(X1.EQ.X3.AND.X1.LT.X2)GO TO 30
      IF(X1.EQ.X3.AND.X1.GT.X2)GO TO 40
      IF(X1.GT.X2.AND.X1.GT.X3)GO TO 50
      IF(X1.GT.X2.AND.X1.LT.X3)GO TO 60
      IF(X1.EQ.X2.AND.X1.EQ.X3)GO TO 70
      IF(X1.LT.X2.AND.X1.LT.X3)GO TO 80
      IF(X1.LT.X2.AND.X1.GT.X3)GO TO 90
      GO TO 72
   10 ZMAX=X3
      ZMIN=X1
      GO TO 72
   20 ZMAX=X1
      ZMIN=X3
      GO TO 72
   30 ZMAX=X2
      ZMIN=X1
      GO TO 72
   40 ZMAX=X1
      ZMIN=X2
      GO TO 72
   50 ZMAX=X1
      IF(X2.GT.X3)GO TO 501
      ZMIN=X2
      GO TO 72
  501 ZMIN=X3
      GO TO 72
   60 ZMAX=X3
      ZMIN=X2
      GO TO 72
```

```
 70 ZMAX=X1
    ZMIN=X1
    GO TO 72
 80 ZMIN=X1
    IF(X2.GT.X3)GO TO 801
    ZMAX=X3
    GO TO 72
801 ZMAX=X2
    GO TO 72
 90 ZMAX=X2
    ZMIN=X3
    GO TO 72
500 XX1=-B/2.0+SQRT(SUM)
    XX2=-B/2.0-SQRT(SUM)
    XXX1=(ABS(XX1))**(1.0/3.0)
    XXX2=(ABS(XX2))**(1.0/3.0)
    IF(XX1.LT.0)XXX1=-XXX1
    IF(XX2.LT.0)XXX2=-XXX2
    X1=XXX1+XXX2-C(2)/3.0
    SU=XXX1-XXX2
    SU=SU*0.866025
    IF(SU.LT.0.00001)GO TO 600
    X3=X1
    X2=X1
    ZMAX=X1
    ZMIN=X1
    GO TO 72
600 X2=-(XXX1+XXX2)/2.0-C(2)/3.0
    X3=X2
    GO TO 660
 72 CONTINUE
    RETURN
    END
```

```
      SUBROUTINE SUM
C**** ***********************************************************************
C**** SUBROUTINE SUM EVALUATES SUM OF THE NECCESSARY TERMS FOR LEAST
C**** SQUARE FITTING OF PR FUNCTION
C**** ***********************************************************************
      COMMON/BL1/X,XX,N3,TRR(50),P(50),T(50),OMEGA(50),S(10),C1
      DO 50 I=1,10
   50 S(I)=0.0
      DO 60 I=1,N3
      STR=1.0-TRR(I)**0.5
      STR2=STR*STR
      STR3=STR2*STR
      STR4=STR2*STR2
      S(1)=S(1)+STR
      S(2)=S(2)+STR2
      S(3)=S(3)+STR3
      S(4)=S(4)+STR4
      S(5)=S(5)+OMEGA(I)*STR2
      S(6)=S(6)+OMEGA(I)*STR
   60 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE SUMMA(C)
C**** ***********************************************************************
C**** SUBROUTINE SUMMA EVALUATES ALL THE NECCESSARY SUMMATIONS FOR THE
C**** LEAST SQUARE FITTING OF EXPONENTIAL FUNCTION
C**** ***********************************************************************
      DIMENSION C(5)
      COMMON/BL1/X,XX,N3,TRR(50),P(50),T(50),OMEGA(50),S(10),C1
      DO 50 I=1,10
   50 S(I)=0.0
      DO 60 I=1,N3
      STR=TRR(I)**X
      STR2=STR*STR
      STR3=ALOG(TRR(I))
      STR4=ALOG(OMEGA(I))
      S(1)=S(1)+STR*STR3*STR4
      S(2)=S(2)+STR*STR3
      S(3)=S(3)+STR2*STR3
      S(4)=S(4)+(1.0-STR)**2
      S(5)=S(5)+STR4
      S(6)=S(6)+STR*STR4
   60 CONTINUE
      XX=S(1)/(S(2)-S(3))
      C(1)=XX*S(4)
      C(2)=-S(5)
      C(3)=S(6)
      RETURN
      END
```

```
      SUBROUTINE SUMMATION(X)
C
C     ******************************************************************
C     THIS SUBROUTINE CALCULATES MIXTURE PARAMETERS USING MIXING RULES
C     FOR THE EQUATION OF STATE CONSTANTS.ZETA(I,J) IS THE
C     INTERACTION CO EFFICIENT.DIFFERENTIALS OF THE MIXTURE PARAMETERS
C     DAM,DBM,DCM REQUIRED FOR FUGACITY ARE ALSO EVALUATED.
C     ******************************************************************
C
      DIMENSION X(10),Y(10),FL(10),FV(10),PHIV(10),PHIL(10)
      COMMON/BL1/A1(10),B1(10),C1(10),AIJ(10,10),DIA(10)
      COMMON/BL2/AM,BM,CM,NUM,ZETA(10,10)
      COMMON/BL3/DAM(10),DBM(10),DCM(10)
      AM=0.0
      BM=0.0
      CM=0.0
      DO 500 I=1,NUM
      DIA(I)=0.0
      DO 550 J=1,NUM
      IF(I.EQ.J)GO TO 600
      ZETA(J,I)=ZETA(I,J)
      AIJ(I,J)=ZETA(I,J)*SQRT(A1(I)*A1(J))
      GO TO 650
  600 AIJ(I,J)=A1(I)
  650 AM=AM+X(I)*X(J)*AIJ(I,J)
      DIA(I)=DIA(I)+X(J)*AIJ(I,J)
  550 CONTINUE
  500 CONTINUE
      DO 700 I1=1,NUM
      BM=BM+B1(I1)*X(I1)
      CM=CM+C1(I1)*X(I1)
  700 CONTINUE
      DO 16 I1=1,NUM
      DAM(I1)=2*(DIA(I1)-AM)
      DBM(I1)=B1(I1)-BM
      DCM(I1)=C1(I1)-CM
   16 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE VDWMX(X)
C*********************************************************************
C     THIS SUBROUTINE CALCULATES MIXTURE PARAMETERS USING VAN DER WAALS
C    1MIXING RULES FOR THE LIQUID AND VAPOUR PHASES
C*********************************************************************
      DIMENSION X(10)
      DIMENSION TCIJ(10,10),VCIJ(10,10),TCVCIJ(10,10),DITV(10),DIV(10)
      COMMON/BL1/TC(10),VC(10),WC(10),ZC(10)
      COMMON/BL2/DTCM(10),DVCM(10),DWCM(10),DZCM(10),DTCVCM(10)
      COMMON/BL3/NUM,TCVCM,VCM,ZCM,WCM
      COMMON/BL4/ZETA(10,10),ETA(10,10)
      TCVCM=0.0
      VCM=0.0
      DO 500 I=1,NUM
      DITV(I)=0.0
      DIV(I)=0.0
      DO 550 J=1,NUM
      IF(I.EQ.J)GOTO 600
      TCIJ(I,J)=ZETA(I,J)*SQRT(TC(I)*TC(J))
      TCIJ(J,I)=TCIJ(I,J)
      VCIT=0.5*(VC(I)**(1.0/3.0)+VC(J)**(1.0/3.0))
      VCIJ(I,J)=VCIT**3
      VCIJ(I,J)=ETA(I,J)*VCIJ(I,J)
      VCIJ(J,I)=VCIJ(I,J)
      TCVCIJ(I,J)=TCIJ(I,J)*VCIJ(I,J)
      GOTO 650
  600 TCVCIJ(I,J)=TC(I)*VC(I)
      VCIJ(I,J)=VC(I)
  650 TCVCM=TCVCM+X(I)*X(J)*TCVCIJ(I,J)
      VCM=VCM+X(I)*X(J)*VCIJ(I,J)
      DITV(I)=DITV(I)+X(J)*TCVCIJ(I,J)
      DIV(I)=DIV(I)+X(J)*VCIJ(I,J)
  550 CONTINUE
  500 CONTINUE
      WCM=0.0
      DO 700 I1=1,NUM
      WCM=WCM+WC(I1)*X(I1)
  700 CONTINUE
      ZCM=0.0
      DO 750 J1=1,NUM
      ZCM=ZCM+ZC(J1)*X(J1)
  750 CONTINUE
      DO 50 I2=1,NUM
      DTCVCM(I2)=2*(DITV(I2)-TCVCM)
      DTCM(I2)=(2/VCM)*(DITV(I2)-(TCVCM*DIV(I2)/VCM))
      DVCM(I2)=2*(DIV(I2)-VCM)
      DWCM(I2)=(WC(I2)-WCM)
      DZCM(I2)=(ZC(I2)-ZCM)
   50 CONTINUE
      RETURN
      END
```

```
C****
C**** ******************************************************************
C**** THE FOLLOWING ROUTINES ARE USED TO CONVERT PVT DATA INTO
C**** APPROPRIATE UNITS
C**** ******************************************************************
C****
C**** ******************************************************************
      SUBROUTINE UNMET
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR METHANE   PVT DATA
C**** ******************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      T=T*1.8
      IF(AUTHOR.EQ.6)GO TO 30
      IF(AUTHOR.EQ.7)GO TO 40
      P=P*14.5037
      VEXP=16.019/VEXP
      GO TO 95
   30 P=P*14.695916
      VEXP=16.019/VEXP
      GO TO 95
   40 P=P*14.223
      VEXP=VEXP*0.016019
   95 RETURN
      END
C**** ******************************************************************
      SUBROUTINE UNETH
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR ETHANE    PVT DATA
C**** ******************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      IF(AUTHOR.EQ.2)GO TO 20
      IF(AUTHOR.EQ.3)GO TO 30
      IF(AUTHOR.EQ.4)GO TO 40
      IF(AUTHOR.EQ.5)GO TO 50
      P=P*14.695916
      VEXP=16.019/VEXP
      T=T*1.8+491.67
      GO TO 95
   20 P=P*100.0
      T=T+459.67
      VEXP=VEXP*R*T/P
      GO TO 95
   30 VEXP=VEXP*W1
      T=T+459.67
      GO TO 95
   40 P=P*100.0
      VEXP=VEXP*W1
      T=T+459.67
      GO TO 95
   50 P=P*14.695916
      T=T*1.8
      VEXP=VEXP*R*T/P
   95 RETURN
      END
```

```
C**** ***********************************************************************
      SUBROUTINE UNPR
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR PROPANE   PVT DATA
C**** ***********************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      IF(AUTHOR.EQ.3)GO TO 25
      T=T+459.67
      IF(AUTHOR.EQ.1)GO TO 95
      VEXP=VEXP*W1
      GO TO 95
   25 P=P*14.69586
      VEXP=16.019/VEXP
      T=T*9.0/5.0+492
   95 RETURN
      END
C**** ***********************************************************************
      SUBROUTINE UNBU
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR N-BUTANE  PVT DATA
C**** ***********************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      IF(AUTHOR.EQ.3.OR.AUTHOR.EQ.8)GO TO 25
      IF(AUTHOR.EQ.2)GO TO 30
      VEXP=VEXP*W1
      T=T+459.67
      GO TO 95
   25 P=P*14.69586
      VEXP=0.016019*W1/VEXP
      T=(T-273.15)*9.0/5.0+491.67
      GO TO 95
   30 P=P*14.69586
      VEXP=16.019/VEXP
      T=T*9.0/5.0+491.67
   95 RETURN
      END
C**** ***********************************************************************
      SUBROUTINE UNPE
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR N-PENTANE PVT DATA
C**** ***********************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      IF(AUTHOR.EQ.4)GO TO 25
      T=T+459.67
      IF(AUTHOR.EQ.5)GO TO 30
      GO TO 95
   25 P=P*14.69586
      VEXP=16.019/VEXP
      T=T*9.0/5.0+491.67
      GO TO 95
   30 VEXP=1.0/VEXP
   95 RETURN
      END
```

```
C**** ***********************************************************************
      SUBROUTINE UNHE
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR N-HEXANE  PVT DATA
C**** ***********************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      IF(AUTHOR.EQ.4)GO TO 25
      IF(AUTHOR.EQ.2.OR.AUTHOR.EQ.3)GO TO 30
      T=T+491.67
      GO TO 95
   25 P=P*14.69586
      VEXP=VEXP*1.477*0.016019*W1
      T=T*9.0/5.0+491.67
      GO TO 95
   30 P=P*14.69586
      VEXP=16.019/VEXP
      T=T*9.0/5.0+491.67
   95 RETURN
      END
C**** ***********************************************************************
      SUBROUTINE UNHEP
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR N-HEPTANE PVT DATA
C**** ***********************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      VEXP=VEXP*W1
      T=T+459.67
      RETURN
      END
C**** ***********************************************************************
      SUBROUTINE UNOCT
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR N-OCTANE  PVT DATA
C**** ***********************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      T=T*9.0/5.0+491.67
      P=P*14.69586
      IF(AUTHOR.EQ.1)GO TO 25
      IF(AUTHOR.EQ.3)GO TO 30
      VEXP=0.016019*W1/VEXP
      GO TO 95
   25 VEXP=VEXP*W1*0.016019
      GO TO 95
   30 VEXP=VEXP*1.3918*W1*0.016019
   95 RETURN
      END
C**** ***********************************************************************
      SUBROUTINE UNNO
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR N-NONANE  PVT DATA
C**** ***********************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      T=T+459.67
   95 RETURN
      END
```

```
C**** ***********************************************************************
      SUBROUTINE UNDE
C**** THIS ROUTINE IS USED TO CONVERT UNITS FOR N-DECANE  PVT DATA
C**** ***********************************************************************
      COMMON/BL1/R,T,P,VC,ZC,TC,WC,CO(10)
      COMMON/BL3/DNCP,DRK,DPE,VEXP
      COMMON/BL5/AUTHOR,W1,DL
      T=T+459.67
      P=P*10.0
      VEXP=VEXP*W1/100000.0
      RETURN
      END
C
```

```
      FUNCTION ST(RO,C,P,GAM)
C***********************************************************************
C     THIS DEFINDS A FUNCTION TO BE SOLVED TO FIND DENSITY OF LIQUID
C     AND VAPOUR PHASES
C***********************************************************************
      DIMENSION C(5)
      RO2=RO*RO
      RO3=RO2*RO
      RO6=RO3*RO3
      EXPG=EXP(-GAM*RO2)
      ST=C(4)*RO+C(1)*RO2+C(2)*RO3+C(3)*RO6+C(5)*RO3*(1+GAM*RO2)*EXPG-P
      RETURN
      END
```