

ABSTRACT

Phase equilibrium compositions were measured for the mixtures of nitrogen, methane and ethane at fourteen isotherms from 94.3° to 133.3° K and at pressures up to 591 psia. A forced-recirculation apparatus was employed for the determinations. Two liquid phases were present at low temperatures for the nitrogen-ethane binary and the nitrogen-methane-ethane ternary systems. Inversion phenomena for the liquid phases were also observed for these systems between 109.1° and 113.4° K. The two liquid phases and liquid-phase inversion phenomena may provide useful information to the development of processes for separating the constituents of natural gases.

In the data reduction procedure, liquid-phase activity coefficients for the binary and ternary vapor-liquid equilibria were evaluated by means of a modified Redlich-Kwong equation of state and correlated by the Redlich-Kister equations. Liquid-liquid equilibrium compositions were correlated in terms of distribution coefficients and a solubility function.

The liquid densities of LNG(Liquefied Natural Gas) mixtures were predicted from a Redlich-Kwong equation of state. Its applicability was tested on five binary and two ternary systems.

The Regula-falsi method was modified and extended to multivariable systems, and was employed for the prediction of liquid-liquid-vapor equilibria.

The success of the proposed method was demonstrated

by predicting the liquid-liquid-vapor equilibria for the binary nitrogen-ethane and the ternary nitrogen-methane-ethane systems investigated in this study and the liquid-liquid equilibria for the n-octane-octene-1-nitroethane system at 273.1° K.

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NOMENCLATURE

A	=	binary constant in the Wilson equation
A, B, a, b	=	parameters in the Redlich-Kwong equation of state
A, B, C, E	=	constants in the Francis equation
A, B, D	=	constants in the Martin equation
A', B'	=	Binary parameters (equations(2-91) and (2-92))
A ₀ , B ₀ , C ₀	=	constants in the Benedict-Webb-Rubin equation of state
a, b, c, α , γ	=	
a, b	=	liquid mole fraction
B, C, D	=	coefficients in the virial equation of state
B, C, D	=	constants in the Redlich-Kister equation
BL	=	bottom liquid phase
C	=	constant in the Harmens formula
c	=	interaction constant for the modified Redlich-Kwong equation of state
E	=	empirical parameter (equation(2-51))
F	=	generalized function (equation(2-9))
F, U	=	functions
f	=	fugacity
G	=	Gibbs free energy
G, g, α , $\mathcal{J}$	=	parameters in the Non-Random Two-Liquid equation

h	=	dummy parameter in the Redlich-Kwong of state
K	=	equilibrium ratio
K'	=	distribution coefficient
k	=	binary interaction parameter in the Redlich-Kwong equation of state
M	=	molecular weight
N, M	=	constants (equations(2-28) and (2-29))
P	=	pressure
P_{ov}	=	convergence pressure of the system
Q	=	excess free energy function
R	=	gas constant
R	=	constant (equation(2-1))
T	=	temperature
TL	=	top liquid phase
V	=	molal volume
x	=	liquid mole fraction
y	=	vapor mole fraction
Z	=	compressibility factor
z	=	mole fraction (liquid or vapor)
α	=	self-interaction constant (equation(2-94))
β	=	adjustable constant of the modified B-W-R equation of state (equation(2-30))
γ	=	activity coefficient

Δ	=	difference
δ	=	solubility parameter
η	=	dilation constant (equation(2-82))
ϕ	=	fugacity coefficient
Φ	=	volume fraction (equation(2-91))
λ	=	interaction energy (equation(2-67))
ρ	=	density
θ	=	temperature parameter for the modified Redlich-Kwong equation of state
μ	=	chemical potential
ν	=	liquid fugacity coefficient (equation(2-79))
Ω_a, Ω_b	=	parameters of the Redlich-Kwong equation of state
ω	=	acentric factor

Superscripts

E	=	excess
L ₁	=	liquid phase one
L ₂	=	liquid phase two
M	=	mixture
r	=	reference state
o	=	reference state
V	=	vapor phase
$\wedge$	=	mixture property
-	=	partial molal quantity

∞ = infinite dilution property
* = unsymmetric convention of normalization
for activity coefficient
1, 2, 3, n = number of iteration process

Subscripts

a, b, i, j, = component identification
k, 1, 1, 2, 3
c = critical property
H = total hydrocarbons
r = reduced state

CHAPTER I

INTRODUCTION

Methane and ethane are two of the major raw materials for synthesising petrochemical products. Ethane is the most desirable feedstock for ethylene manufacture because of the small quantities of by-products that are obtained as compared to other feedstocks. The total Canadian consumption of ethylene was 80 million lbs. in 1970(1). Methane is a better starting material for the manufacture of ammonia and urea than other hydrocarbons, since it contains a higher proportion of hydrogen. Ammonia and urea are the raw materials for manufacturing fertilizer. By the end of the 1970's, more than 60,000 million cubic metres of methane and ethane will be required all over the world(2).

The low-temperature approach to the separation of methane and ethane from natural gas is an attractive proposition on its own merits. The existence of partial miscibility between nitrogen, methane and ethane at low-temperature is particularly useful to the petroleum industries. The separation of natural gases into components can be facilitated by taking advantage of composition differences of the two liquid phases.

The design of industrial equipment for separation

processes requires information on liquid-liquid-vapor equilibrium data of the system concerned. The necessary information on phase equilibrium data is the composition of each phase under specific conditions of temperature and pressure. The phase equilibrium data may be obtained from experimental determinations. However, high cost and the amount of time consumed in experimental investigation prevent us from making numerous laboratory measurements.

For rational design, therefore the liquid-liquid-vapor equilibrium data should be evaluated by methods other than direct experimental determinations. The prediction methods may employ a rigorous thermodynamic approach from the properties of pure components or from binary phase equilibrium data.

Unfortunately, the methods available in the literature have not been accurate enough to predict the phase equilibrium data needed for the design of solvent extraction equipment.

In this investigation, the following attempts are made:

- (1) to determine experimentally phase equilibrium data at low-temperature for nitrogen-methane-ethane systems for the purpose of completing and extending the available data,

- (2) to correlate the experimental equilibrium data,
- (3) to develop a new method for predicting binary and ternary liquid-liquid-vapor equilibria, and
- (4) to apply the method to the available liquid-liquid-vapor equilibrium data.

CHAPTER II

LITERATURE SURVEY

This chapter is a review of the general background and some previous studies pertinent to this work, and is divided into four parts. In the first part, a review of the direct determination methods of the equilibrium composition of the liquid and vapor phases of the system is presented. In the second part, the available phase equilibrium and liquid density data for the systems containing nitrogen, methane, ethane and propane are collected. In the third part, the correlation methods for phase equilibria and liquid density are presented. Finally, the equation of state, the activity coefficient equation and the methods for predicting phase equilibria at low temperatures are presented.

A. EXPERIMENTAL METHODS

A bibliography for experimental methods has been presented by Hala, Pick, Fried and Vilim in their book entitled " Vapor-Liquid Equilibrium " (3). These methods can be classified as follows:

(1) Distillation Method

The oldest method for the direct determination of vapor-liquid equilibrium data is the distillation method

in which a small amount of liquid is distilled off from the boiling flask containing a large charge. This method is very simple but has marked disadvantages and generated large errors in determining the temperature, pressure, and compositions.

(2) Static Method

In this method, the liquid solutions are placed in the equilibrium cell which is rotated or shaken until equilibrium is established between the liquid and its vapor. Then the samples are taken and analyzed.

This method is simple only apparently since removing the gas sample for analysis causes great difficulties. At low pressures, the amount of vapor required for analysis is of the same order as the total amount of the vapor phase in the equilibrium cell. Therefore, the removal of a sample causes a marked disturbance of the equilibrium.

To overcome this restriction, Prausnitz(4) and Scatchard etc.(5) developed the static and total pressure method. The vapor compositions are calculated directly from the thermodynamic relationships based on the liquid composition and total pressure. This method is useful for high or moderate pressure and high or low temperature systems(6,7).

(3) Dew and Bubble Point method

This method was employed by Sage and Lacey(8,9)

for determining phase equilibrium data of light hydrocarbons in the temperature range of 20° to 100°C. This method was also applied by the IGT (Institute of Gas Technology) group at low temperatures for the nitrogen-methane(10), nitrogen-ethane(11) and methane-ethane(12) systems, and by Kurata and his associates for the nitrogen-propane(13) system.

In this method, the liquids of known composition are fed into the equilibrium cell which is maintained at a constant temperature. The pressure at which the liquid first started to vaporize is termed the bubble-point pressure and that at complete vaporization, or initial condensation, the dew-point pressure.

The dew-point and bubble-point pressures are determined by direct measurement. The results are plotted on the pressure-composition curve at constant temperature, and on the temperature-pressure curve at constant composition.

The advantage of this method is that the composition of the gases are predetermined. Therefore, vapor and liquid samples need not be analyzed.

(4) Flow Method

A gas mixture is passed under steady-state condition into the equilibrium cell where it is cooled and partially liquified. The vapor, which is in equilibrium with the liquid formed from condensation, is separated and

removed continuously to storage for analysis. The samples are withdrawn and analyzed continuously.

This method was utilized by Steckel and Zinn(14) and by Ruhemann and Zinn(15) for determining phase equilibrium data and by Stutzman and Brown(16) for natural gas at low temperatures.

The disadvantage of this method lies in the maintenance of constant pressure and temperature during rapid condensation.

(5) Forced-recirculation Method

The vapor, formed by the vaporization of the liquid, is recirculated through the liquid by means of a recirculation pump. In this way the liquid is stirred and equilibrium reached by continually bringing the vapor into contact with the liquid.

The forced-recirculation method was developed by Inglis(17) and modified into practical use by Dodge and Dunber(18) for the oxygen-nitrogen system. It was used by Torocheshuikov(19) for determining equilibria of the carbon monoxide-nitrogen system and by Aroyan and Katy(20) for studying equilibria of the methane-hydrogen system. Further modification of the equipment was made by DAVIS, Rodewald and Kurata(21), Harvey(22), (rice and Kobayashi (23). They introduced a transparent equilibrium cell and a liquid bath

in the cryostat in the study of the systems containing methane, ethane and propane. A similar apparatus was employed by Brandt, Strand and Deaton(24), Stein, Sterner and Geist(25) and by Rogers and Prausnitz(26).

It is probably the most accurate and reliable one of all the existing methods and is widely used at present. The advantages of the forced-recirculation method are as follows:

- (1) the equilibrium is reached very quickly,
and
- (2) vapor and liquid samples can be withdrawn
almost without disturbing the equilibrium.

For these reasons, this method is utilized in the present investigation.

B. AVAILABLE PHASE EQUILIBRIUM DATA

This section is to review the experimental vapor-liquid equilibrium data pertinent to this work. The available data, which covers the period up to 1966, containing nitrogen, methane and ethane at low temperatures are listed as follows:

TABLE 2-1Available Phase Equilibrium Data

<u>System</u>	<u>Pressure Range (atm)</u>	<u>Temp. Range (°K)</u>	<u>Ref.</u>
Nitrogen-Methane	1.4-4.5	100-173	27
	1.0	89-106	28
	1.0-10.0	117-156	29
	2.0-16.5	83-158	30
	1.0-10.0	17-133	31
	34.5	129-179	32
	0.12-3.8	90.67	33
	1.0-48.5	94-187	10
Nitrogen-Ethane	7.0-137	83-305	11
Methane-Ethane	75-65	173-273	12
	5-20	143-263	34
	40-70	144-283	23
	5-60	195	35
Nitrogen-Methane-Ethane	35-69	144-200	36

The experimental works from 1966 to date on vapor-liquid equilibria for systems containing nitrogen, methane and ethane at cryogenic temperatures are briefly reviewed as follows:

The equilibrium data reported in 1967 by Chang and Lu(37) were determined at temperatures of 121.9° to 171.3° K.

Ellington et. al.(11) reported that two liquid phases were measured from nitrogen-ethane binary system at temperatures lower than 133° K by the dew point-bubble point method. Unfortunately, the compositions of two liquid phases obtained by the dew point-bubble point method are only approximate to 5% of ethane in top liquid phase and 70% of ethane in bottom liquid phase.

Chang and Lu(37) measured the liquid-liquid equilibrium data for the nitrogen-methane-ethane ternary system at 121.9° K. Yu, Elshayal and Lu(38) reported liquid-liquid-vapor equilibrium data for the nitrogen-ethane binary and nitrogen-methane-ethane ternary systems from 113.3° to 133.1° K and Yu and Lu(39) for the same systems from 94.3° to 109.1° K.

In 1972, Wichterle and Kobayashi(40) reported the vapor-liquid equilibrium data for the methane-ethane binary system from 130.4° to 199.9° K over a pressure range of 25 to 800 psia at twelve isotherms.

C. AVAILABLE LIQUID DENSITY DATA

The liquid density data containing nitrogen, methane and ethane were required for accurate calculation of the quantity of LNG(Liquefied Natural Gas) in storage, in transit or upon delivery to the terminal.

However few liquid density data for these mixtures are available in the literature. The available data are summarized in Table 2-2:

TABLE 2-2

Available Liquid Density data

<u>System</u>	<u>Pressure Range (atm)</u>	<u>Temp. Range (°K)</u>	<u>Ref.</u>
Nitrogen	0.15-33.5	63.15-126.2	41,34
Methane	0.12-45.4	90.67-190.5	42,43
Ethane	0.00-45.4	88.56-305.4	41,42
Propane	0.00-42.0	88.56-369.8	41,42
Nitrogen-Methane	2.60-45.8	109.6-188.8	10
Nitrogen-Ethane	7.10-46.5	101.7-221.1	9
Methane-Ethane	6.00-60.5	140.3-279.2	12

TABLE 2-2 (continued...)

System	Pressure Range (atm)	Temp. Range (°K)	Ref.
Methane- Ethane	0.20-0.76	108.2	44
	-	102.5-114.9	42
Methane- Propane	34.0-340	123.2-310.9	45
	0.32-0.69	108.2	44
Ethane- Propane	-	108.2	44
Nitrogen- Methane- Ethane	9.00-45.1	144.8-188.7	10
Methane- Ethane- Propane	0.39-0.62	108.2	44
	-	103.9-116.7	42

Data which were obtained by the IGT group(10,11,12) were calculated from vapor-liquid equilibrium data by means of the BWR equation of state(46). Data presented by Klosek and McKinley(42) were obtained at different compositions and temperatures. Therefore, it is difficult to compare these experimental results directly. However, Huebler et. al. (47) reported that those liquid densities data obtained by Klosek and McKinley(42) were the best data presently available in the literature, because Kloseks' correlation represented their data to an accuracy of $\pm 0.3\%$.

D. CORRELATION OF PHASE EQUILIBRIUM DATA

Several methods are available in the literature for the correlation of experimental data of vapor-liquid and liquid-liquid equilibrium, and are given as follows:

(1) The Convergence Pressure Method

The concept of convergence pressure arises from the observation that for mixtures of light hydrocarbons, isothermal component K-values appear to converge to unity when plotted against pressure. Two typical diagrams are shown in Figures 2-1 and 2-2 for binary and ternary systems, respectively.

The pressure at which K-values converge to unity is the convergence pressure of the system, P_{ov} . The

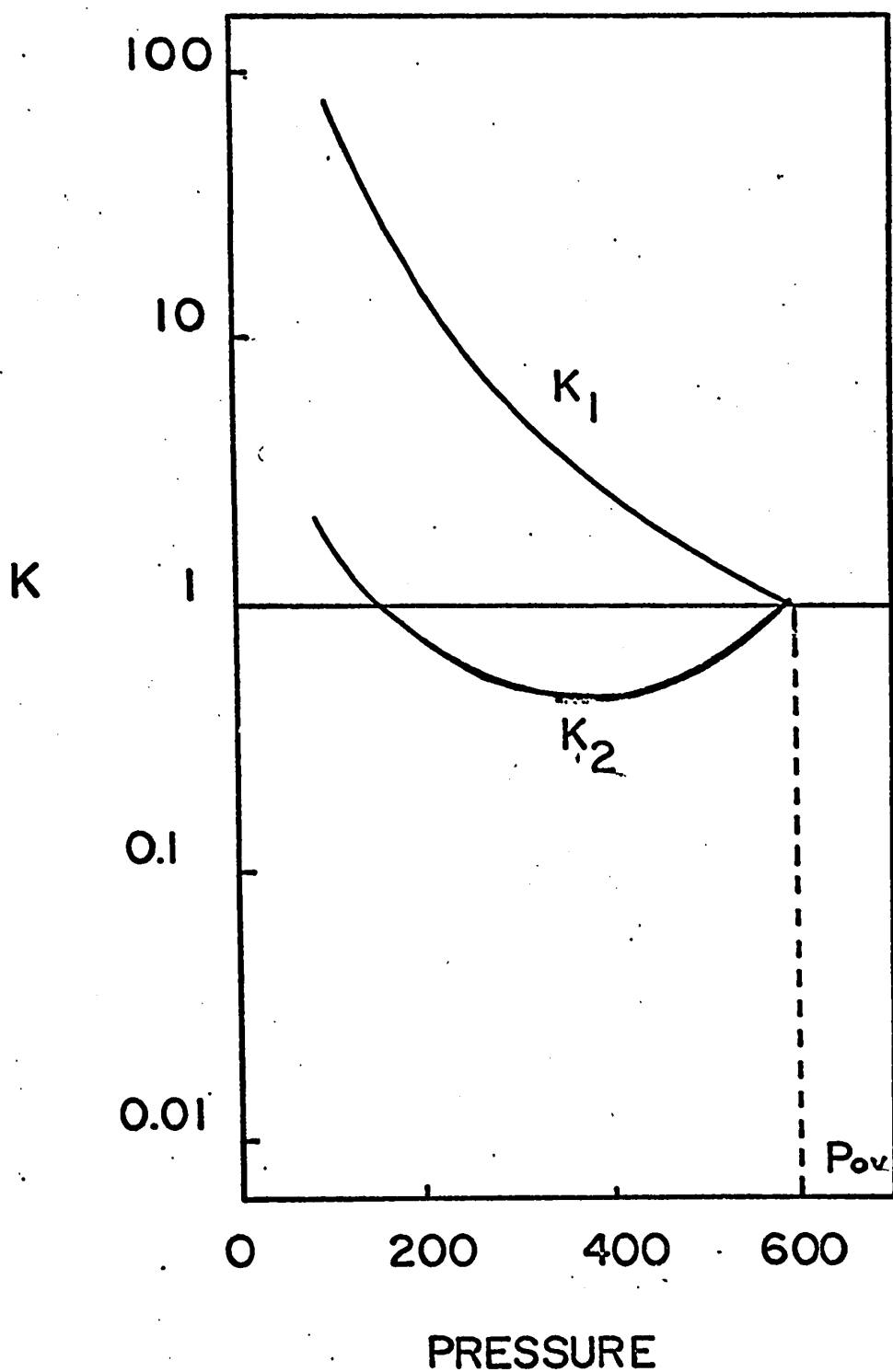


Figure 2-1 An Example of P-K Diagram for Binary system

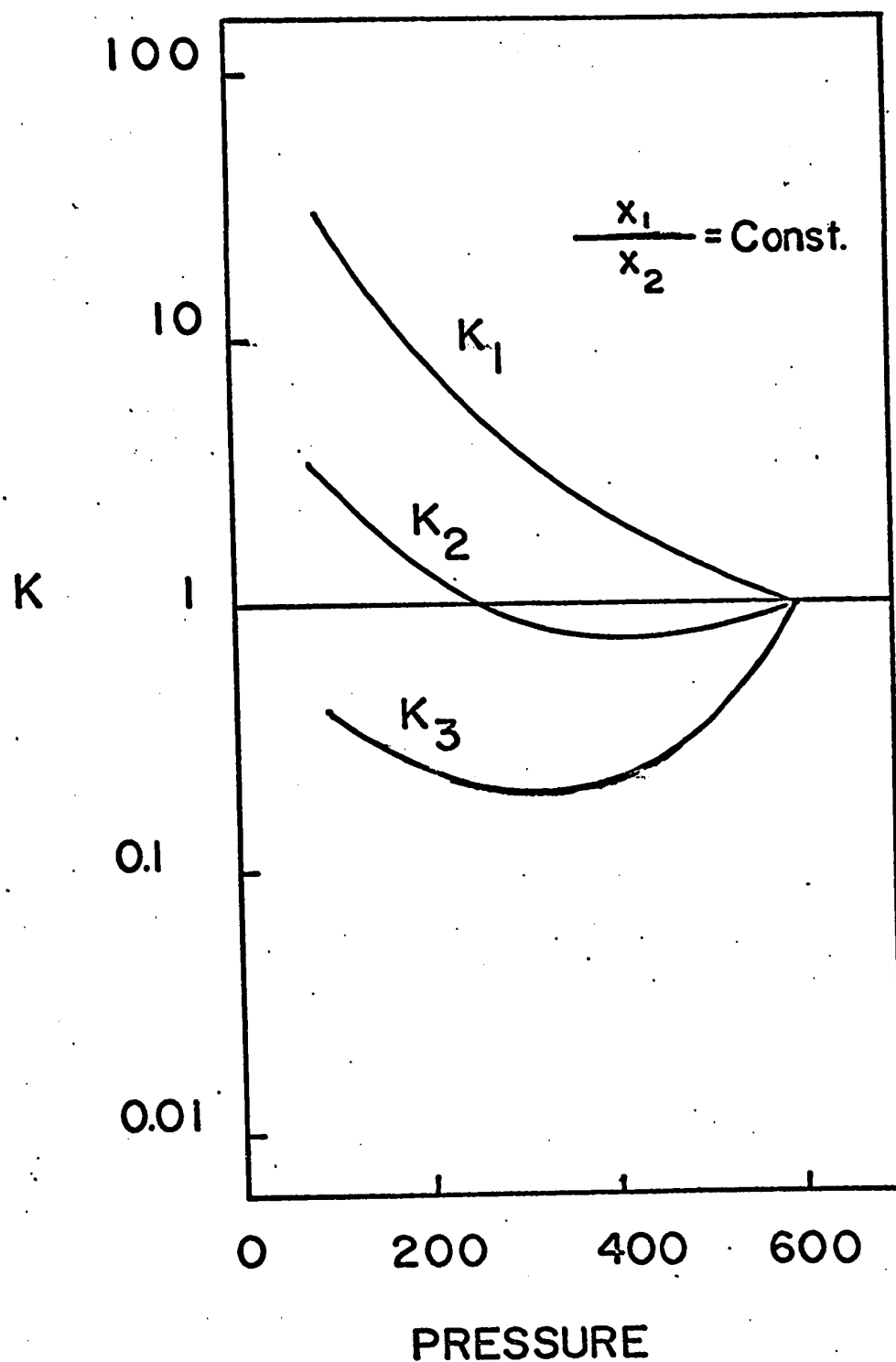


Figure 2-2 An Example of P-K Diagram for Ternary System

convergence pressure is in turn a function of the system composition for ternary mixtures.

The convergence-pressure method had been extensively employed in the data book of the Natural Gas Processors Suppliers Association (NGPSA) (48). In the same book a set of charts for twelve hydrocarbons and nitrogen was published. Equilibrium ratios for individual components were presented as functions of temperature, pressure and the convergence-pressure of the mixture.

(2) Kellogg Charts

A set of 324 charts was published by the M. W. Kellogg Company in 1950. These charts were drawn by means of the B-W-R equation of state (46).

These charts had been prepared for twelve paraffin hydrocarbons, ranging from methane to heptane. Equilibrium ratios and fugacities were expressed as functions of temperature and molal average boiling points (MABP) of the liquid and the vapor phases. These charts can be used to estimate the equilibrium constant from the temperature, pressure, and MABP of each phase.

Linear or nearly linear relations between the two fugacity functions $\hat{f}_i^L / P x_i$ and $P y_i / \hat{f}_i^V$, and pressure were found by Depriester (49). Therefore, the Kellogg charts were condensed into a more manageable form.

(3) Lenoir Diagram

The Lenoir diagram was published in 1960 by Canjander, Hipin, and Lenoir(50). The diagrams gave K-values at a pressure of 10 psia as a function of temperature. The temperature range covered was from 133° to 466.5°K. The nomograph gave the pressure correction which depended on an effective boiling point which was a composition-dependent parameter..

The above mentioned correlations are applicable to calculate K-values of light hydrocarbon mixtures up to twelve components within the range of pressure, temperature and MABP of the charts with satisfactory results.

However when these correlations are applied to systems containing nonhydrocarbons large errors are obtained in the predicted K-values.

(4) Hand Method For Correlation of The Liquid-Liquid Solubility Curves

For most of the liquid-liquid ternary systems, the solubility curves were unsymmetrical. The tie-lines were not parallel to the base of the triangular diagram as shown in Figure 2-3.

Hand(51) had indicated that tie-lines could be made horizontal by plotting in properly selected units for one of the immiscible components as shown in Figure 2-4.

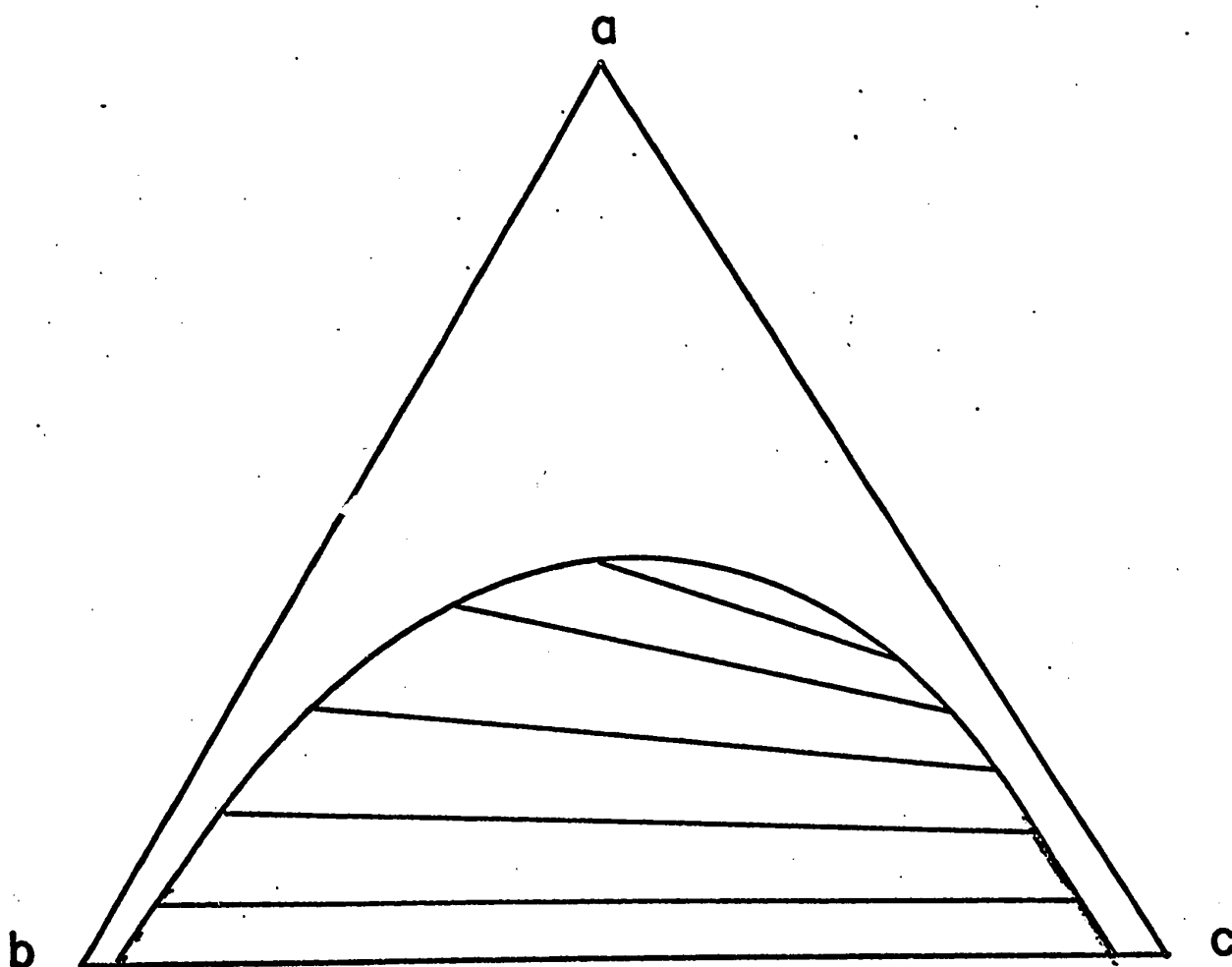


Figure 2-3 Illustration of Ternary Solubility Curve

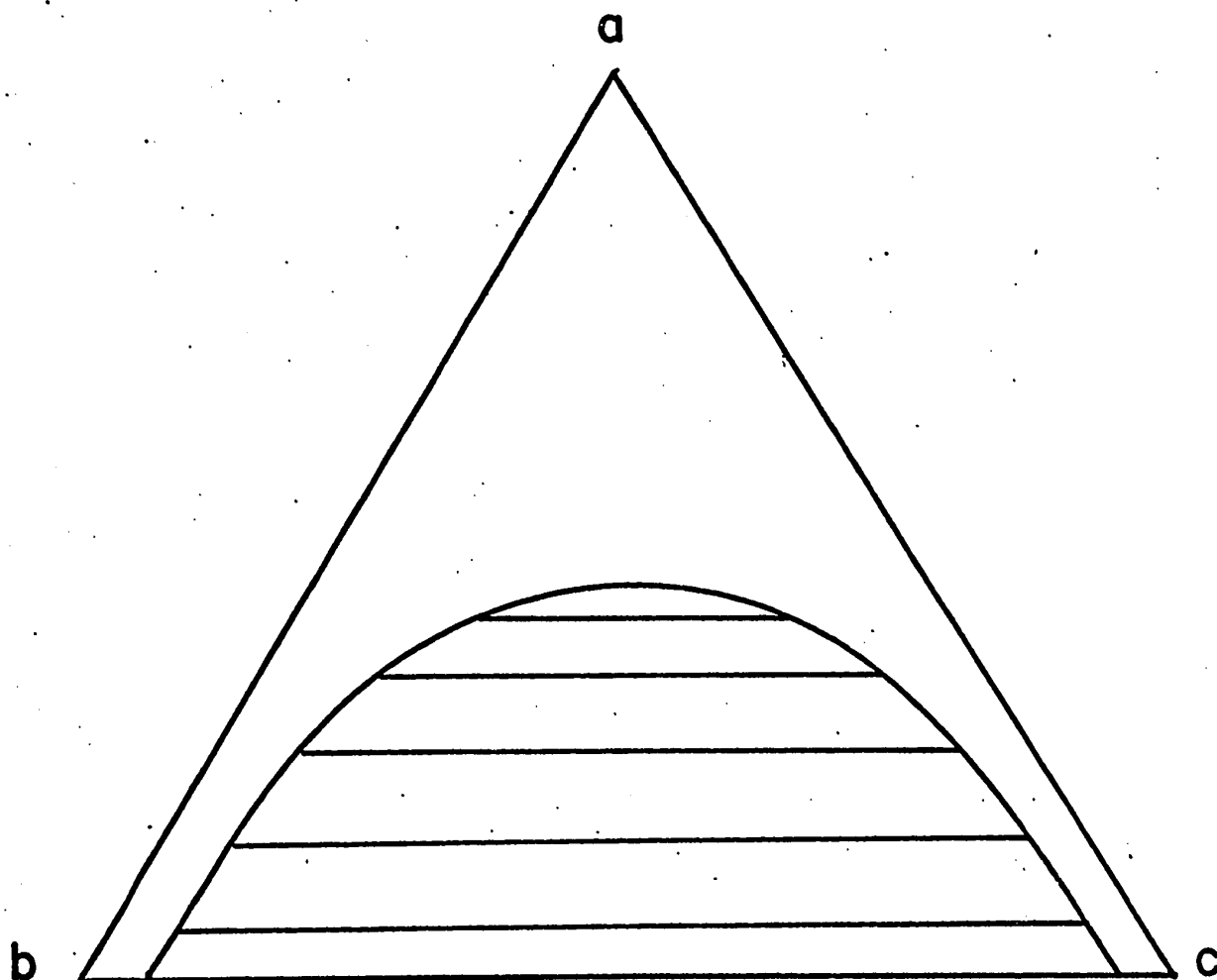


Figure 2-4 Illustration of Hand Method

The distribution equation is expressed by the following relation.

$$\frac{\frac{X_{a1}}{X_{b1} + RX_{c1}}}{\frac{X_{a2}}{X_{b2} + RX_{c2}}} = \frac{X_{a2}}{X_{b2} + RX_{c2}} \quad 2-1$$

where a, b and c represent the mole or weight fractions of the diluent, the solute and the solvent, respectively, R is an empirical constant, and the subscripts denote the top and bottom liquid phases.

Hand(48) obtained very good results for the acetic acid(a)-benzene(b)-water(c) system using a R value of 9.

(5) Black and Hartvig Correlation

A simple ternary diagram for a system composed of components a, b and c is shown in Figure 2-3.

Black and Hartvig (52) presented a correlation method for the distribution coefficients between two liquid phases of this ternary system. The distribution coefficient for component i is given by $K'_i = x_i(BL)/x_i(TL)$.

A solubility function K'_H is defined as the distribution

coefficient for the total nonsolvent material between the two liquid phases, $K'_H = (1-x_c)(BL)/(1-x_c)(TL)$, in which BL refers to the bottom liquid phase and TL refers to the top liquid phase. The quantities K'_a , K'_H and K'_b are plotted

against K'_c on log-log scales at constant temperature. An example is shown in Figure 2-5. K'_H becomes identical with K'_b at point PPb in Figure 2-5 as the b-c binary is reached.

When only one binary system is partially miscible in a ternary system, K'_c as well as K'_a , K'_H and K'_b approaches unity at the plait point. These two points may be applied to test the experimental liquid-liquid equilibrium data.

This correlation for two liquid phase equilibrium data is chosen in the present study, because the changes of K'_H , K'_a and K'_b with temperature at constant K'_c values can be obtained from these plots. From these figures, the quantities K'_H , K'_a and K'_b may be obtained at a given values of K'_c and a given temperature. These quantities provide the required information for calculating complete ternary liquid-liquid equilibrium data.

E. CORRELATION OF SATURATED LIQUID DENSITY

Several methods are available in the literature for correlation of saturated liquid densities of pure components and their mixtures, which are given as follows:

(1) Francis Equation

Experimental density data for pure liquids at

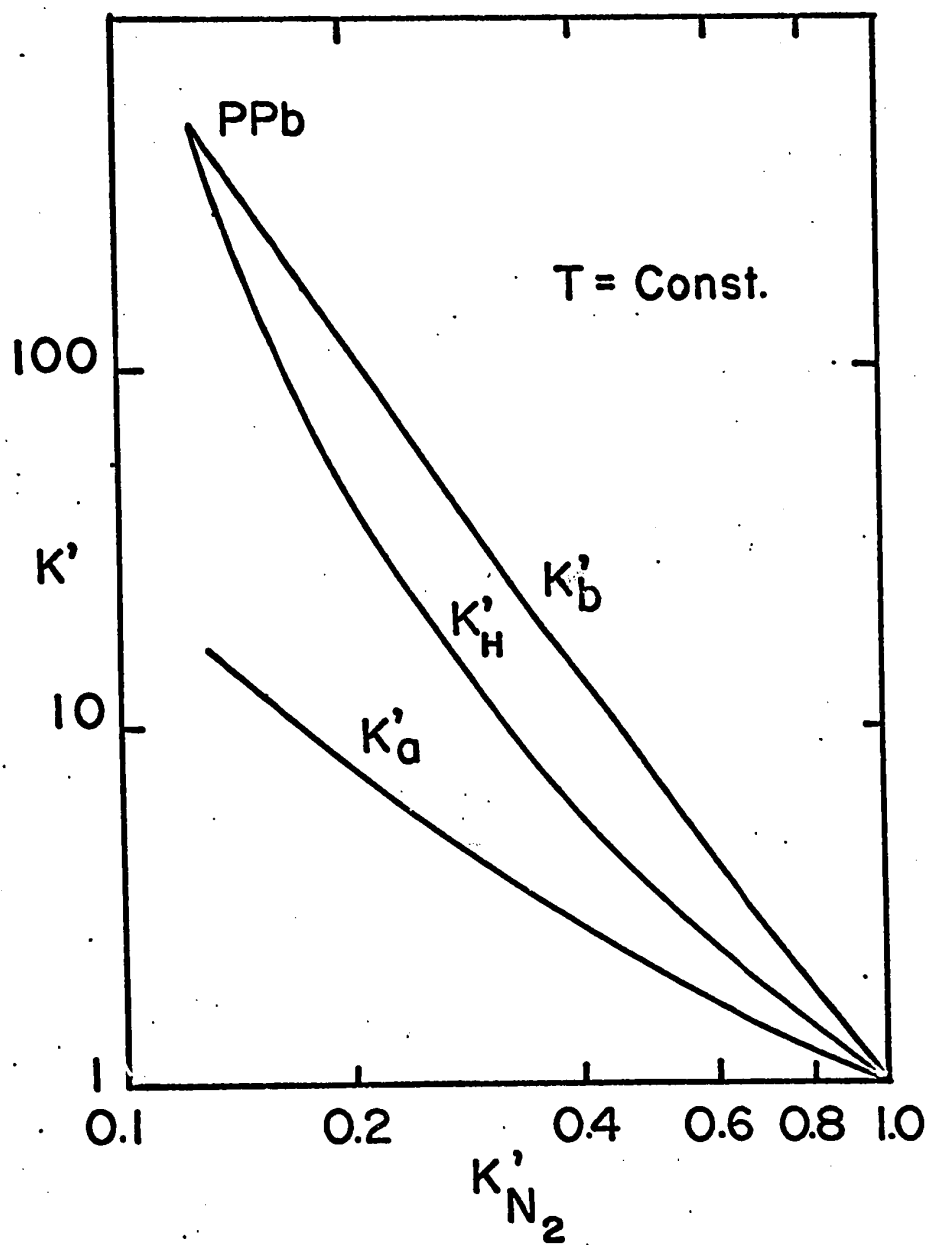


Figure 2-5 Illustration of Black and Hartvig Method

saturation states are abundant and have been subjected to various treatments. Francis(53,54) has fitted the following equation to the experimental liquid density data with an accuracy of about 2 to 5%.

$$\rho = A - Bt - \frac{C}{E - t} \quad 2-2$$

where ρ refers to the liquid density, A, B, C and E refer to the coefficients, and t refers to temperature.

(2) Martin Equation

Martin(55) and Yen and Woods(56) have suggested the following equation which holds up to temperatures near the critical point.

$$\rho_r = \frac{\rho}{\rho_c} = 1 + A(1-T_r)^{1/3} + B(1-T_r)^{2/3} + D(1-T_r)^{4/3} \quad 2-3$$

where ρ_r refers to reduced liquid density, ρ_c refers to liquid density at critical temperature, and A, B and D refer to coefficients.

For liquid mixture densities, Yen(56) suggested that the following mixing rule of Prausnitz and Gunn be used(57).

$$T_c = \sum_i X_i T_{ci} \quad 2-4$$

$$V_c = \sum_i X_i V_{ci} \quad 2-5$$

$$Z_c = \sum_i X_i Z_{ci} \quad 2-6$$

$$P_c = Z_c RT_c / V_c \quad 2-7$$

(3) Lu's Generalized Chart

If all critical values are known, the density of pure liquid can be estimated directly by calculation from the generalized chart which was prepared by Lu(58).

A value of ρ was known, the chart was used with the equation:

$$\frac{K_1}{\rho_1} = \frac{K_2}{\rho_2} \quad 2-8$$

where K_1 is read at T_r and P_r of the known density value

ρ_1 and K_2 is read at T_r and P_r of the desired density

ρ_2 .

This method is not reliable if the estimated ρ indicates a Z less than 0.24.

(4) Harmens Formula

Liquid densities of pure hydrocarbons of low molecular weight can be calculated with the formula by Harmen(59).

$$\rho_r = CF(T_r) \quad 2-9$$

The values of the generalized function $F(T_r)$ were prepared in tabulated form. The quantity C is

an empirical constant which is different for each component. This formula can also be applied to a mixture of hydrocarbons.

(5) Klosek and Mckinley Chart

This chart(42) employed a correction factor for the nonideality of a mixture to the molar volume of an ideal mixture. For paraffinic hydrocarbon systems, the nonideal behavior was due to the decrease in volume on mixing. Klosek and Mckinley assumed that methane was the leading contributor to the nonideal behavior, because of the unique structure of its molecules relative to the higher hydrocarbons in the paraffin series.

A chart was prepared for the relationship between molar volume reduction and molecular weight of mixture to cover the temperature range from 88.5° to 133°K. However, this method is accepted for pure hydrocarbons mixtures with average molar molecular weights ≤ 33.0 .

(6) Gunn and Yamada Correlation

Gunn and Yamada(60) presented a corresponding states correlation for the prediction of the saturated liquid densities ρ of nonpolar compounds. This correlation has the following form:

$$\frac{\rho_{sc}}{\rho} = \frac{1}{\rho_r(0)} \left(1.0 - \frac{w}{\rho_r(1)} \right) \quad 2-10$$

The generalized functions $\rho_r(0)$ and $\rho_r(1)$ which are dependent only upon the reduced temperature, are given as follows:

For $0.2 < T_r < 0.8$

$$\frac{1}{\rho_r(0)} = 0.33593 - 0.33953T_r + 1.51941T_r^2 - 2.02502T_r^3 + 1.11422T_r^4 \quad 2-11$$

For $0.8 < T_r < 1.0$

$$\frac{1}{\rho_r(0)} = 1.0 + 1.3(1 - T_r)^{1/2} \log(1 - T_r) - 0.50879(1 - T_r) - 0.91534(1 - T_r)^2 \quad 2-12$$

For $0.2 < T_r < 1.0$

$$\frac{1}{\rho_r(1)} = 0.29607 - 0.09045T_r - 0.4842T_r^2 \quad 2-13$$

The scaling density ρ_{sc} , is defined by the following equation:

$$\rho_{sc} = \rho_{0.6} (0.3862 - 0.0866\omega) \quad 2-14$$

The quantity $\rho_{0.6}$ is the saturated liquid density at a reduced temperature of 0.6.

This correlation is valid over the entire useful range of reduced temperatures from 0.2 to 1.0:

Methods for prediction of the saturated liquid density, studied in this section, were satisfactory for

hydrocarbon components and hydrocarbon mixtures only.

P. EQUATIONS OF STATE

A large number of equations of state have been suggested in the past hundred years. Among the many available equations of state(61,62,63), three were widely used for calculating equilibrium data at low temperatures (64). These are the virial equation, the eight-constant Benedict-Webb-Rubin(B-W-R) equation(65) and the simple two constant Redlich-Kwong(R-K) equation(66).

(1) The Virial Equation

The virial equation of state is of the following form:

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad 2-15$$

where B, C, D etc are known as the virial coefficients.

These virial coefficients are functions of temperature alone for pure components. In principle, virial coefficients can be evaluated directly from intermolecular forces(67). For example, the second virial coefficient, B, accounts for interactions between pairs of molecules. Many theories and experimental data are available for second virial coefficients but rather little is known about the third virial coefficient. Knowledge of fourth and higher coefficients is practically nonexistent.

For mixtures, the virial coefficients are functions of composition as follows:

$$B = \sum_i \sum_j y_i y_j B_{ij} \quad 2-16$$

and

$$C = \sum_i \sum_j \sum_k y_i y_j y_k C_{ijk} \quad 2-17$$

For pure non-polar gases, an excellent correlation has been given for B_{ii} by Pitzer and Gurl(68). It is of the form:

$$\frac{P_{ci} B_{ii}}{R T_{ci}} = f_B^0(T_r) + \omega_i f_B^1(T_r) \quad 2-18$$

A generalized correlation for the third virial coefficient C which is applicable to quantum and non-polar gases for the reduced temperatures above 1.4, were presented by Chueh and Prausnitz(69).

(2) The Benedict-Webb-Rubin Equation (B-W-R)

Benedict-Webb-Rubin(46) presented an equation of state as follows:

$$P = \frac{RT}{V} + \frac{B_0 RT - A_0 - C_0/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{6V} + \frac{c}{3VT^2} \left(1 + \frac{r}{2} \right) e^{-r/V^2} \quad 2-19$$

where A_0 , B_0 , C_0 , a , b , c , α and r are constants.

The procedure for determining these constants is available in the literature(46). Tabulated values of

all these coefficients for 38 components were presented by Cooper and Goldfrank(70).

For application of this equation of state to mixtures, the following mixing rules were proposed by Benedict, Webb and Rubin in 1942(46).

$$A_0 = \left[\sum_i Z_i (A_{0,i})^{1/2} \right]^2 \quad 2-20$$

$$B_0 = \sum_i Z_i B_{0,i} \quad 2-21$$

$$C_0 = \left[\sum_i Z_i (C_{0,i})^{1/2} \right]^2 \quad 2-22$$

$$a = \left[\sum_i Z_i (a_i)^{1/3} \right]^3 \quad 2-23$$

$$b = \left[\sum_i Z_i (b_i)^{1/3} \right]^3 \quad 2-24$$

$$c = \left[\sum_i Z_i (c_i)^{1/3} \right]^3 \quad 2-25$$

$$\alpha = \left[\sum_i Z_i (\alpha_i)^{1/3} \right]^3 \quad 2-26$$

$$r = \left[\sum_i Z_i (r_i)^{1/2} \right]^2 \quad 2-27$$

where Z_i is the mole fraction of component i either in the vapor or in the liquid phase.

This equation specifically describes behavior of light hydrocarbons and their mixtures at reduced temperatures greater than 0.6(71). Its limitations, particularly in the critical and low temperature regions have been studied by many authors(72,73,74,75,76,77).

Some modifications of this equation of

state may be briefly presented as follows:

Benedict and Stotler(72) suggested that the constant C. was temperature-dependent when predicting K-values for the mixtures of nitrogen-methane at low temperatures. They have also made an attempt to modify the mixing rule for constant A.,

$$A_o = \sum_i^2 Z_i^2 A_{oi} + \sum_j^2 Z_j^2 A_{oj} + N \sum_{i,j} Z_i Z_j \quad 2-28$$

Orye(78) suggested that this be replaced by

$$A_o = \sum_i Z_i A_{oi} + \sum_{\substack{i,j \\ j \neq i \\ j > i}} \sum M_{ij} Z_i Z_j A_{oi}^{1/2} A_{oj}^{1/2} \quad 2-29$$

where N_{ij} and M_{ij} were determined from experimental phase equilibrium data. Lin and Naphtali(75) modified the B-W-R equation of state into the following form:

$$P = \frac{RT}{V} + \frac{B \cdot RT - A_o - C_o / T^\rho}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{V^3 T^2} \left(1 + \frac{r}{2} \right) e^{-r/V^2} \quad 2-30$$

In this expression, a constant ρ was introduced. Gullen and Kobe(79) indicated that the lack of success in certain cases outside of the hydrocarbons was thought to be caused by the increased interaction of the molecules in the liquid phase. Therefore, one or more constants were likely required in some cases to give a good overall representation of a binary

mixtures with the B-W-R equation of state.

Schiller and Caniar(80) applied the B-W-R equation of state to predict vapor-liquid equilibrium data for the nitrogen-carbon monoxide system with satisfactory results. However, the prediction of the K-values for mixtures of nitrogen-methane(72), propane-carbon dioxide(79) and light hydrocarbons containing hydrogen(81) were found to be far from satisfactory.

(3) The Redlich-Kwong Equation (R-K)

The equation proposed by Redlich and Kwong (66) is of the following form:

$$P = \frac{RT}{V-b} + \frac{a}{T^{0.5} V(V+b)} \quad 2-31$$

where a and b are constants.

This two-constant equation offered advantages over the B-W-R equation by saving both the computing time and storage requirement.

Redlich and Kwong(66) obtained the values of the constants a and b by setting the first and second isothermal derivatives of pressure with respect to volume equal to zero at the critical point. These are

$$\left(\frac{\partial P}{\partial V} \right)_{T_c} = 0 \quad 2-32$$

and

$$\left(\frac{\partial^2 P}{\partial V^2} \right)_{T_c} = 0 \quad 2-33$$

For pure component i

$$a_i = \frac{0.4278 R^2 T^{2.5} c_i}{P_{ci}} \quad 2-34$$

and

$$b_i = \frac{0.0867 R T c_i}{P_{ci}} \quad 2-35$$

For application to mixtures, the following mixing rules were proposed by Redlich and Kwong(66).

$$b = \sum_i y_i b_i \quad 2-36$$

$$a = a_{11} y_1^2 + a_{22} y_2^2 + \dots + 2a_{12} y_1 y_2 + \dots \quad 2-37$$

$$a_{12} = (a_{11} a_{22})^{1/2} \quad 2-38$$

The Redlich-Kwong equation of state has been chosen and modified by many workers to represent the nonideality of fluid mixtures. It led to many well-known methods of prediction of vapor-liquid equilibrium data(82, 83,84,85,86,67). The prediction methods of vapor-liquid equilibria and the modified Redlich-Kwong equation of state will be discussed in section H of this chapter.

In summary, the virial equation of state applied for pure components and mixtures at moderate pressure and at low densities. The B-W-R equation of state applied to light paraffinic and olefinic hydrocarbons and their mixtures.

The B-W-R equation of state failed at low temperatures(88).

The R-K equation of state has the following advantages:

- (1) There are only two parameters.
- (2) It can be applied to normal fluids. (The definition of normal fluids is that given by Pitzer(89))
- (3) It can offer over the B-W-R and virial equations of state a saving in computing time.
- (4) Only the saturated liquid properties are required to determine the parameters for pure substances.
- (5) It can give more accurate results when applied to a pure component at low temperature, high density and liquid regions.
- (6) The binary interaction constants are easily introduced.

For these reasons, the Redlich-Kwong equation of state is chosen in this study.

G. THE ACTIVITY COEFFICIENT EQUATIONS

At isothermal condition, the liquid phase activity coefficients depend on the liquid phase composition

and also on total pressure.

At low or moderate pressures, the liquid activity coefficients are slightly dependent on pressure, and as a result, it has been customary to assume that, for practical purposes, activity coefficient depends only on temperature and composition. Hence, the isothermal and isobaric Gibbs-Duhem equation can be used. However, it can lead to serious error when this assumption is applied to the case of high-pressure phase equilibria. Therefore, for effective thermodynamic analysis and correlation of high-pressure phase equilibrium data, it is important to separate the effect of pressure from that of composition, and it is necessary to adjust the liquid activity coefficient in the following manner.

The activity coefficient of component i in the liquid mixture at the system temperature T and reference pressure P^R may be defined by:

$$\gamma_i(P^R, T, x) = \frac{\hat{f}_i^L(P^R, T, x)}{x_i f_i^{OL}(P^R, T)} \quad 2-39$$

$\gamma_i \rightarrow 1 \quad \text{as } x_i \rightarrow 1$

where f_i^{OL} is the reference fugacity of component i at T and reference pressure, P^R . The fugacity of any component i of solution, $\hat{f}_i$, is defined by the following equation:

$$\mu_i = \mu_i^0 + RT \ln \hat{f}_i \quad 2-40$$

$$\frac{\hat{f}_i}{P} \rightarrow 1 \quad \text{as } P \rightarrow 0$$

Partial differentiating Equation(2-40) with respect to pressure gives the pressure dependence of the fugacity:

$$\begin{aligned} \left(\frac{\partial \ln \hat{f}_i}{\partial P} \right)_{T,x} &= \frac{1}{RT} \left(\frac{\partial u_i}{\partial P} \right)_{T,x} \\ &= \frac{\bar{V}_i}{RT} \end{aligned} \quad 2-41$$

Integrating Equation(2-41) from system pressure P to P^R gives:

$$\hat{f}_i^L(P, T, x) = \hat{f}_i^L(P^R, T, x) \exp \int_P^{P^R} \frac{\bar{V}_i}{RT} dP \quad 2-42$$

where $\bar{V}_i$ is the partial molal volume of component i in the liquid mixture. Combining Equation(2-39) and (2-42) gives:

$$\gamma_i(P^R, T, x) = \frac{\hat{f}_i^L(P, T, x)}{x_i \hat{f}_i^{oL}(P^R, T)} \exp \int_P^{P^R} \frac{\bar{V}_i}{RT} dP \quad 2-43$$

$\gamma_i \rightarrow 1 \quad \text{as} \quad x_i \rightarrow 1$

This expression is similar to that given by Prausnitz(91).

At equilibrium, the fugacities of component i in both the liquid and the vapor phases are identical:

$$\hat{f}_i^L = \hat{f}_i^V \quad 2-44$$

since

$$\hat{f}_i^V = \hat{\phi}_i^V y_i P \quad 2-45$$

Equation(2-43) may be rearranged as follows:

$$\gamma_i = \frac{y_i^V \hat{Q}_i^V P}{x_i f_i^{oL}} \exp \int_P^{P^r} \frac{\bar{V}_i}{RT} dP \quad 2-46$$

Equation(2-46) may be employed to calculate constant-pressure activity coefficients. Thus the activity coefficients satisfy the isothermal, isobaric Gibbs-Duhem equation.

The variation of activity coefficient equations with composition are expressed as follows:

(1) The Hildebrand's Regular Solution Model

Hildebrand(92) assumed that for a regular solution,

$$\Delta S^E = 0 \quad 2-47$$

and

$$\Delta V^E = 0 \quad 2-48$$

Therefore for a binary solution,

$$\log \gamma_i = \frac{V_i^L (\bar{\delta} - \delta_i)^2}{RT} \quad 2-49$$

where

$$\bar{\delta} = \frac{\sum_i x_i V_i^L \delta_i}{\sum_i x_i V_i^L} \quad 2-50$$

δ_i is solubility parameter, and V_i^L is the liquid

molar volume.

Chao-Seader(93) used the original Hildebrand equation(50) for correlation the liquid phase. Modification of this equation have been presented by Van Horn and Kobayashi(94) for hydrocarbon mixtures at low temperatures and high pressures as follows:

$$\log \gamma_i = \frac{E_i}{RT} (\bar{v} - \delta_i)^2 \quad 2-51$$

where E_i is an empirical parameter calculated from infinite dilution data.

(2) The Redlich-Kister Equation

Redlich and Kister(95) used a power series expansion for the excess free energy of mixing of a binary system at constant T and P.

$$\frac{\Delta G^E}{RT} = x_1 x_2 \left[B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots \right] \quad 2-52$$

The resulting binary activity coefficient equations are:

$$\ln \gamma_1 = x_2^2 \left(B + C(1 - 4x_1) + D(1 - 8x_1 - 12x_1)^2 + \dots \right) \quad 2-53$$

and

$$\ln \gamma_2 = x_1^2 \left(B + C(1 - 4x_2) + D(1 - 8x_2 - 12x_2)^2 + \dots \right) \quad 2-54$$

These equations are frequently used in the literature for correlating various binary data.

The liquid activity coefficient of the ternary system was correlated by the following equation which was also proposed by Redlich and Kister(95).

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1 x_2 x_3 \left[C + \frac{D_1}{2} (x_2 - x_3) + \frac{D_2}{2} (x_3 - x_1) + \frac{D_3}{2} (x_1 - x_2) + \dots \right] \quad 2-55$$

where

$$Q_{123} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3 \quad 2-56$$

$$Q_{12} = x_1 x_2 \left[B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2 \right] \quad 2-57$$

$$Q_{23} = x_2 x_3 \left[B_{23} + C_{23} (x_2 - x_3) + D_{23} (x_2 - x_3)^2 \right] \quad 2-58$$

$$Q_{31} = x_3 x_1 \left[B_{31} + C_{31} (x_3 - x_1) + D_{31} (x_3 - x_1)^2 \right] \quad 2-59$$

The individual activity coefficients of the ternary system can be obtained by differentiating Equation(2-55), yielding Equations(2-60), (2-61) and (2-62).

$$\begin{aligned}
\ln r_1 = & B_{12} x_1 (1-x_1) + C_{12} x_1 (2x_1 - x_2 - 2x_1^2 + 2x_1 x_2) \\
& + D_{12} x_1 (3x_1^2 - 3x_1^3 + 6x_1^2 x_2 - 4x_1 x_2 - 3x_1 x_2^3 + x_2^2) \\
& - B_{23} x_2 x_3 - 2C_{23} x_2 x_3 (x_2 - x_3) - 3D_{23} (x_2 - x_3)^2 \\
& + B_{31} x_3 (1-x_3) + C_{31} x_3 (x_3 - 2x_1 x_3 + 2x_1 - 2x_1^2) \\
& + D_{31} x_3 (x_3^2 + 6x_1^2 x_3 - 4x_1 x_3 - 3x_1 x_3^2 + 3x_1^2 - 3x_1^3) \\
& + D_{12} x_1 x_2 (x_2 - x_3 - 3x_1 x_2 + 3x_1 x_3) \\
& + D_{23} x_2 x_3 (x_3 - 2x_1 - 3x_1 x_3 + 3x_1^2) \\
& + D_{31} x_3 x_1 (2x_1 - x_2 - 3x_1^2 + 3x_1 x_2) \\
& + C_{123} x_1 x_2 (1-2x_1)
\end{aligned}$$

2-60

$$\begin{aligned}
\ln r_2 = & B_{12} x_1 (1-x_1) + C_{12} x_1 (x_1 - 2x_2 - 2x_1 x_2 + 2x_1^2) \\
& + D_{12} x_1 (x_1^2 - 4x_1 x_2 + 3x_1^2 x_2 + 6x_1 x_2^2 - 3x_2^3 + 3x_2^2) \\
& + B_{23} x_2 x_3 (1-x_2) + C_{23} x_2 x_3 (2x_2 - x_3 - 2x_2^2 + 2x_2 x_3) \\
& + D_{23} x_2 x_3 (x_2^2 + 3x_2^2 - 4x_2 x_3 - 3x_2^3 + 6x_2^2 x_3 - 3x_2 x_3)
\end{aligned}$$

$$\begin{aligned}
& - B_{31} x x - 2C_{31} x x (x_3 - x_1) \\
& - 3D_{31} x x (x_3 - x_1)^2 + C_{123} x x (1 - 2x_2) \\
& + D_{113} x x (2x_2 - x_3 - 3x_2^2 + 3x_2 x_3) \\
& + D_{213} x x (x_3 - x_1 + 3x_1 x_2 - 3x_2 x_3) \\
& + D_{313} x x (x_1 - 2x_2 - 3x_1 x_2 + 3x_2^2) \quad 2-61
\end{aligned}$$

$$\begin{aligned}
\ln r_3 = & - B_{12} x x - 2C_{12} x x (x_1 - x_2) \\
& - 3D_{12} x x (x_1 - x_2)^2 + B_{23} x (1 - x_3) \\
& + C_{23} x (x_2 - 2x_3 - 2x_2 x_3 + 2x_3^2) \\
& + D_{23} x (x_2^2 - 4x_2 x_3 + 3x_3^2 + 3x_2^2 x_3 + 6x_2 x_3^2 - 3x_3^3) \\
& + B_{31} x (1 - x_3) + C_{31} x (2x_3 - x_1 - 2x_3^2 + 2x_1 x_3) \\
& + D_{31} x (x_1^2 + 3x_3^2 - 4x_1 x_3 - 3x_3^3 + 6x_1 x_3^2 - 3x_1^2 x_3) \\
& + C_{123} x x (1 - 2x_3)
\end{aligned}$$

$$\begin{aligned}
& + D_{112} x_1 x_2 (x_2 - 2x_3 - 3x_2 x_3 + 3x_3^2) \\
& + D_{212} x_2 x_1 (-x_1 + 2x_3 - 3x_3^2 + 3x_1 x_2) \\
& + D_{312} x_3 x_1 (x_1 - x_2 - 3x_1 x_3 + 3x_2 x_3) \quad 2-62
\end{aligned}$$

(3) The Flory-Huggins Equation

Flory(96) assumed that for an athermal solution.

$$\Delta H^E = 0 \quad 2-63$$

Therefore the Flory-Huggins equation for an athermal mixture is given as follows:

$$\frac{\Delta G^E}{RT} = \sum_i x_i \ln \frac{v_i}{x_i} \quad 2-64$$

where v_i is the volume fraction of i , and x_i is the mole fraction of i . These are related by

$$v_i = \frac{x_i V_i^L}{\sum_i x_i V_i} \quad 2-65$$

where V_i^L is the molar liquid volume of pure component i .

Flory and Huggins introduced Equation (2-64) for studying high polymer solutions. This approach is the basis of the Wilson equation(97) and the Non-Random Two-

Liquid(NRTL)(98) equation.

(4) The Wilson Equation

Wilson(97) proposed a semiempirical extension of the Flory-Huggins equation for the effect of molecular size on the entropy of mixing and arrived at the following equation for the excess free energy of mixing.

$$\frac{\Delta G^E}{RT} = -\sum_i x_i \ln \left[\sum_j x_j A_{ij} \right] \quad 2-66$$

where A_{ij} 's are binary constants,

$$A_{ij} = \frac{V_j^L}{V_i^L} \exp \left[- \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right] \quad 2-67$$

where λ_{ij} and λ_{ii} are proportional to the 1-2 and 1-1 interaction energies, respectively.

The resulting Wilson activity coefficient equation is

$$\ln \gamma_k = 1 - \ln \left[\sum_j x_j A_{kj} \right] - \sum_i \left(\frac{x_i A_{ik}}{\sum_j x_j A_{ij}} \right) \quad 2-68$$

The Wilson activity coefficient equation contains only binary constants and will allow the prediction of multicomponent data using only binary equilibrium data (99).

The Wilson equation has the disadvantage of not being suitable for partially miscible systems. The

condition for partial miscibility is

$$\left(\frac{\partial^2 \Delta G^M}{\partial x_i^2} \right)_{T,P} = 0 \quad 2-69$$

which can not be satisfied by the Wilson equation. Therefore, Wilson modified Equation(2-67) as follows(100):

$$\frac{\Delta G^E}{RT} = - C \sum_i x_i \ln \left[\sum_j x_j A_{ij} \right] \quad 2-70$$

An example of the use of Equation(2-70) was presented by Scatchard and Wilson(99) where the results agreed qualitatively, but not quantitatively, with the experimental results. In order to overcome these limitations of Wilson's equation, the so called the Non-Random Two-Liquid(NRTL) equation was developed(98).

(4) The Non-Random Two-Liquid(NRTL) Equation

Renon and Prausnitz(98,101) presented an activity coefficient equation based on an expression for the excess free energy of mixing. The excess free energy of mixing was derived by applying Scott's two-liquid theory to a nonrandomly distributed mixture.

The resulting activity coefficient equation has the following form for a binary system:

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} \right] \quad 2-71$$

and

$$\ln \gamma_2 = x_1^2 \left(\frac{\tau_{12}^G}{(x_2 + x_1 G_{12})^2} + \frac{\tau_{21}^G}{(x_1 + x_2 G_{21})^2} \right) \quad 2-72$$

where

$$\tau_{12} = (g_{12} - g_{22}) / RT \quad 2-73$$

$$\tau_{21} = (g_{21} - g_{11}) / RT \quad 2-74$$

with

$$g_{12} = g_{21} \quad 2-75$$

$$G_{12} = \exp(-\alpha \tau_{12}) \quad 2-76$$

$$G_{21} = \exp(-\alpha \tau_{21}) \quad 2-77$$

where α is the nonrandomness parameter; $(g_{12} - g_{22})$ and

$(g_{21} - g_{11})$ are the temperature-dependent parameters

This equation gives much better representation than the Wilson equation for strongly non-ideal mixtures. For multicomponent systems, the NRTL equation is

$$\ln \gamma_k = \frac{\sum_j \tau_{kj} G_{kj}}{\sum_l G_{kl}} + \sum_j \frac{\tau_{jk} G_{jk}}{\sum_l G_{jl}} \left(\tau_{ij} - \frac{\sum_r \tau_{ir} G_{ir}}{\sum_l G_{il}} \right) \quad 2-78$$

In this section, a brief discussion of the most commonly used activity coefficient equations, is presented and among these equations, the NRTL equation was recommended by Joy(102) for predicting liquid-liquid equilibria. However the NRTL equation needs binary vapor-liquid equilibrium data and limited ternary liquid-liquid equilibrium data to calculate the parameters α_{ij} .

H. METHOD FOR PREDICTING PHASE EQUILIBRIA AT LOW TEMPERATURES

Many methods have been proposed for predicting vapor-liquid equilibrium data at low temperatures which utilize an equation of state for fugacity coefficient and an activity coefficient equation for activity coefficient. These methods may be presented as follows:

(1) The Chao-Seader Method

Chao and Seader(93) calculated K-values from the following equation.

$$K_i = \frac{y_i}{x_i} = \frac{(f_i^0/P) r_i}{\hat{Q}_i^V} = \nu_i^0 f_i / \hat{Q}_i^V \quad 2-79$$

The quantity ν_i^0 is the liquid fugacity coefficient of the pure component i. The liquid fugacity coefficients are

correlated according to:

$$\log \nu_i^{(0)} = \log \nu_i^{(0)} + \omega_i \log \nu_i^{(1)} \quad 2-80$$

The quantities $\nu_i^{(0)}$ and $\nu_i^{(1)}$ are presented as functions of reduced temperature and reduced pressure. The quantity $\nu_i^{(0)}$

is given by:

$$\begin{aligned} \log \nu_i^{(0)} = & A_0 + A_1/T_r + A_2 T_r + A_3 T_r^2 + A_4 T_r^3 + \\ & (A_5 + A_6 T_r + A_7 T_r^2) P_r + (A_8 + A_9 T_r) P_r^2 - \\ & \log P_r \end{aligned} \quad 2-81$$

The quantity $\nu_i^{(1)}$ is given by:

$$\begin{aligned} \log \nu_i^{(1)} = & -4.23893 + 8.65808 T_r - 1.22060/T_r - \\ & 3.15224 T_r^3 - 0.025 (P_r - 0.6) \end{aligned} \quad 2-82$$

The liquid activity coefficient, r_i , was calculated from the theory of regular solutions of Hildebrand(92).

The vapor-phase fugacity coefficient of component i, $\hat{\phi}_i$, was calculated using the original Redlich-Kwong equation of state(66).

The correlation was applied to hydrocarbons of various molecular types, including paraffins and olefins.

The correlation was successful at high temperatures but failed at low temperatures. Extensions and modification of this correlation have been presented by Grayson and Streed(103), Shelton(104) and Shelton and Wood (105).

(2) The Wilson Method

Wilson(83,84) proposed a method to predict vapor-liquid equilibrium data for the nitrogen-methane and hydrogen-helium systems by means of the Redlich-Kwong equation of state with a modified procedure.

The equation for the fugacity of a component is given as follows:

$$\ln \hat{f}_i = \ln \frac{RTZ_i}{V-b_i} + \frac{b_i}{b} \left(\frac{PV}{RT} - 1 \right) - \frac{a}{RT^{3/2}b} \left(\frac{\sum_j Z_j a_{ij}}{a} - \frac{b_i}{b} \right) \ln \left(1 - \frac{b_i}{V} \right)$$

2-83

where

$$b_i = \frac{\sum_j \Omega_j \frac{RT}{P} c_{ij}}{c_i}$$

2-84

$$\Omega_b = 0.0687$$

2-85

$$a_i = 4.934RT^{1.5}b_i \left[1 + (1.45 + 1.62\omega_i) \left(\frac{1}{Tr} - 1 \right) \right] \left(\frac{1}{Tr} \right)$$

2-86

$$a_{ij} = \theta_{ij} a_i + (1 - \theta_{ij}) a_j \quad 2-87$$

where θ_{ij} is temperature-independent parameter.

Wilson successfully applied his method to the hydrogen-nitrogen system; for some other systems, especially those containing large hydrocarbons, agreement was less satisfactory.

(3) The Prausnitz-Orye Method

The method proposed by Prausnitz and Orye(99) was mainly based on the following equation:

$$\hat{\phi}_{i,i}^V P = r_{i,i} \times f_{i,i}^{o(P_o)} \exp\left(\frac{V_i^L P}{RT}\right) \quad 2-88$$

where $\hat{\phi}_i^V$ is the vapor-phase fugacity coefficient and $f_i^{o(P_o)}$

is the fugacity of pure liquid i at the temperature of solution and at an arbitrarily fixed reference pressure.

The fugacity coefficient was given by the virial equation truncated after the second virial coefficient.

$$\ln \hat{\phi}_i^V = \frac{2}{V} \sum_j y_j B_{ij} - \ln Z_{\text{mix}} \quad 2-89$$

The partial molar liquid volume $\bar{V}_i^L$ was taken to be equal to the pure liquid molar volume V_i^L . The reference fugacity, $f_i^{o(P_o)}$, based on a three-parameter theorem of

corresponding state, was from the generalized table of Lyckman et. al.(106).

The activity coefficient was obtained from the Wilson's equation(97).

This procedure was restricted to moderate pressures and to a completely miscible liquid phase.

(4) The Prausnitz-Chueh Method

Chueh and Prausnitz(82) presented a method for reducing binary vapor-liquid equilibrium data to thermodynamically significant binary parameters and predicted the phase equilibria of multicomponent mixture by using these binary parameters.

This approach was based on the following equation:

$$\hat{\phi}_i^V y_i P = \gamma_i x_i \hat{f}_i^0 \quad 2-90$$

The vapor phase fugacity coefficient was evaluated by means of the Prausnitz-Chueh modification of the Redlich-Kwong equation of state(82)

The dilated Van Lear equation(82) was expressed for the liquid phase activity coefficients at constant pressure.

$$\ln \gamma_i^{(P_0)} = A' \phi_2^2 + B' \phi_2^4 \quad 2-91$$

$$\ln \gamma_2^{*(P_0)} = a \left(\frac{V_{c2}}{V_{c1}} \right) \left(\phi_2^2 - 2\phi_2 \right) + B' \left(\frac{V_{c2}}{V_{b1}} \right) \left(\phi_2^4 - 4\phi_2^3 \right)$$

2-92

where

$$\bar{V}_2 = \frac{x_2 V_{c2}}{x_1 V_{c1} + x_2 V_{c2}} \quad 2-93$$

$$A' = \alpha_{22(1)} V_{c1} \quad 2-94$$

$$B' = 3\eta_{2(1)} \alpha_{22(1)} V_{c1} \quad 2-95$$

and subscript 1 refers to the condensable and subscript 2 to the noncondensable component, and the asterisk * in Equation(2-91) indicates that the unsymmetric convention has been used for normalization of the activity coefficients. $\alpha_{22(1)}$ is called the self-interaction constant and $\eta_{2(1)}$ is called the dilation constant.

At constant temperature, the activity coefficients were calculated with the aid of the partial molal volumes using the following equation:

$$\left(\frac{\partial \ln r_i}{\partial P} \right)_{T,X} = \frac{V_i}{RT} \quad 2-96$$

$$r_i \rightarrow 1 \quad \text{as} \quad x_i \rightarrow 1$$

The reference state was taken at a fixed pressure. The partial molal volumes were evaluated also by means of the modified Redlich-Kwong equation of state(82). The parameters Ω_a and Ω_b , of the equation were obtained by fitting the Redlich-Kwong equation of state to the P-V-T data of the saturated vapor for each pure component.

For a solvent component at equilibrium conditions, the pure liquid fugacity at zero pressure was:

$$f_1^{oL} = f_{\text{pure } 1}^{(o)} \exp\left(\int_0^P \frac{\bar{V}_1^L}{RT} dP\right) \quad 2-97$$

For a solute component, the standard-state fugacity was Henry's constant in the mixed solvent corrected to zero pressure.

$$f_2^{oL} = H_{2,1}^{(o)} \exp\left(\int_0^P \frac{\bar{V}_2}{RT} dP\right) \quad 2-98$$

In general, this method can be applied to the systems containing nonpolar (or slightly polar) components and will give satisfactory results.

(5) The Zudkevitch-Joffe Method

Zudkevitch and Joffe(84) followed the approach of Wilson(81,82) and considered Ω_b as a temperature-dependent parameter. Zudkevitch and Joffe(84) have evaluated Ω_a and Ω_b of the Redlich-Kwong equation of state separately for the saturated vapor phase and the saturated liquid phase. In the establishment of the values Ω_a and Ω_b , the values of fugacity coefficient were obtained from the generalized correlation of Lyckman, Eckert and Prausnitz(106).

$$\log \Omega = (\log \Omega)^{(o)} + \omega (\log \Omega)^{(1)} \quad 2-99$$

where $(\log \Omega)^{(o)}$ and $(\log \Omega)^{(1)}$ are functions of the

reduced temperature, tabulated by Lyckman et. al.(106)

The parameters of pure components were combined to give that of a mixture in the form of the following relation:

$$a_{ij} = (1 - c_{ij}) \sqrt{a_i a_j} \quad i \neq j \quad 2-100$$

where the quantity c_{ij} was established from experimental data.

The K-values for each component were then calculated from the fugacity coefficient in both phases

$$K_i = \hat{q}_i^L / \hat{q}_i^V \quad 2-101$$

The values of $\hat{q}_i^V$ and $\hat{q}_i^L$ were obtained from P-T-x-y data

by means of the modified Redlich-Kwong equation of state(86)

(6) The Lu-Chang Method

The partial molal volumes of normal fluid mixtures were predicted from the modified Redlich-Kwong equation of state by Chang and Lu(85).

The parameters Ω_a and Ω_b of the Redlich-Kwong equation of state were treated as temperature-dependent. The values of these parameters were obtained from saturated P-V-T data for each pure component through a fundamental condition of equilibrium state,

$$\hat{q}_i^V = \hat{q}_i^L \quad 2-102$$

The values of $\bar{V}_i$ for normal fluid mixtures can be successfully predicted by employing the modified Redlich-Kwong equation of state(85). Therefore the modified Redlich-Kwong equation of state was invited further to correlate vapor-liquid equilibrium data at low temperatures(107).

(7) The Prausnitz-Renon Method

Renon and Prausnitz(98,101) proposed a method for predicting multicomponent equilibrium data from binary equilibrium data. They employed the NRTL activity coefficient equation and applied it to the prediction of ternary and quaternary vapor-liquid and liquid-liquid equilibrium data.

Phase equilibrium data were therefore predicted by using their NRTL activity coefficient equations by the following basic relation:

$$\left(\gamma_i x_i \right)^{L_1} = \left(\gamma_i x_i \right)^{L_2} \quad 2-103$$

In general, this method can be applied to the systems containing polar components at low pressures and it will give a satisfactory result.

In summary, the conventional methods to predict phase equilibrium data should satisfy the following criteria:

- (1) It can be applied to the supercritical, the subcritical, the high pressure and the low pressure regions.

- (2) The method utilizes a minimum experimental data of mixture for predicting the equilibrium data.

The Redlich-Kwong equation of state which was modified by Lu and Chang(85) appears to meet the above mentioned criteria. Therefore, their modified Redlich-Kwong equation of state is employed in this study.

CHAPTER III

EXPERIMENTAL DETAILS

In order to separate methane and ethane from natural gases, phase equilibrium data are required for the process design.

Experimental study of phase equilibria for the mixtures containing nitrogen, methane and ethane at low-temperature and high-pressure conditions was carried out in this study.

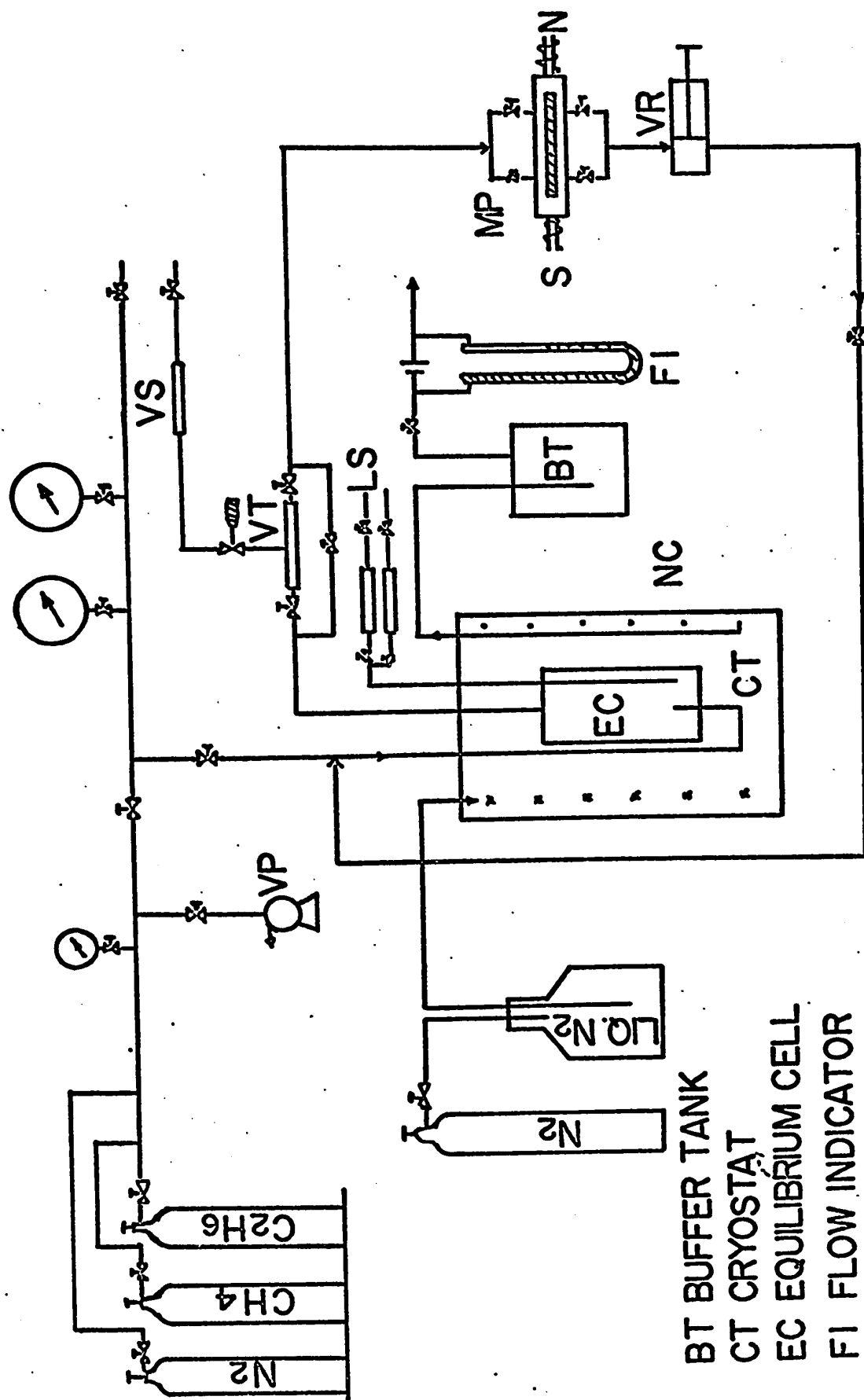
A. THE APPARATUS

A forced-recirculation apparatus was built and used in the present study(?).

A schematic diagram of the apparatus is shown in Figure 3-1. It consists of the following sections: an equilibrium cell, an electro-magnetic pump, two pressure gauges for the pressure measurement, a temperature control system, a temperature measurement system, and a set of sampling facilities.

(1) Equilibrium Cell

A 100 ml. Jerguson transparent level gauge with stainless steel body was used as the equilibrium cell. To the top end was connected a 4 inch long $\frac{1}{2}$ inch stainless steel pipe nipple, through which the vapor outlet line and three $\frac{3}{16}$ inch stainless steel liquid sampling tubes were inserted.



BT BUFFER TANK
 CT CRYOSTAT
 EC EQUILIBRIUM CELL
 FI FLOW INDICATOR
 LS LIQUID SAMPLING BULB
 MP MAGNETIC PUMP
 NC N₂ VAPORIZATION COIL
 VP VACUUM PUMP
 VR VOLUME REGULATOR

VS VAPOR SAMPLING BULB
 VT VAPOR SAMPLING TUBE

Figure 3-1 A Schematic Flow Diagram of the Force-recirculation Apparatus

To the bottom end was connected a $\frac{1}{2}$ inch long $\frac{1}{2}$ inch stainless steel pipe nipple, and a $\frac{1}{8}$ inch Autoclave adapter used to connect to the cooling coil of the vapor inlet line. A sprayer with twenty tiny holes was used to spray the vapor inside the equilibrium cell. Two screens, one near the top and the other near the bottom, were used to reduce entrainment and to distribute the vapor. Two copper-constantan thermocouples of $\frac{1}{16}$ inch in diameter with protective stainless steel sheaths were introduced into the cell, through two horizontal holes located $1\frac{1}{2}$ inch from the top and the bottom end of the cell housing. The tips of the thermocouples were extended to the center of the cell. A detailed diagram of the equilibrium cell is shown in Figure 3-2.

(2) Electromagnetic Pump

For the recirculation of the vapor, an electromagnetic pump was used. The pump had a double-acting piston. It moved to and fro due to the induced magnetic field. Its frequency could be used to regulate the flow rate of the vapor from 0 to 56 c.c. per minute. The developed head was 7.8 psi. The electric circuit of the electromagnetic pump is shown in Figure 3-3.

(3) Pressure Measurements

Equilibrium pressure was measured by means of two certified Heise Bourdon Gauges. The ranges of the gauges

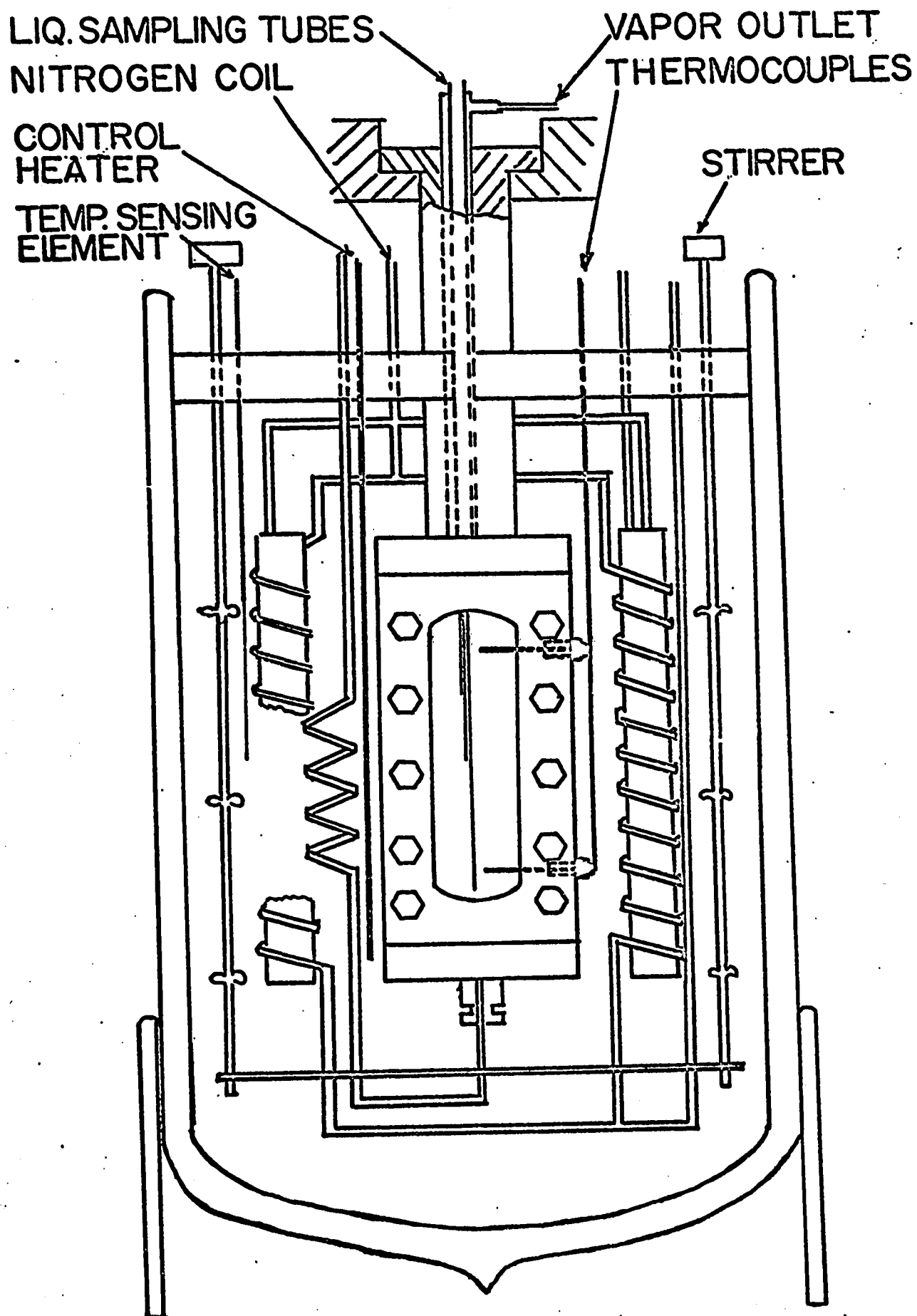


Figure 3-2 A Schematic Diagram of Equilibrium Cell and the Cryostat

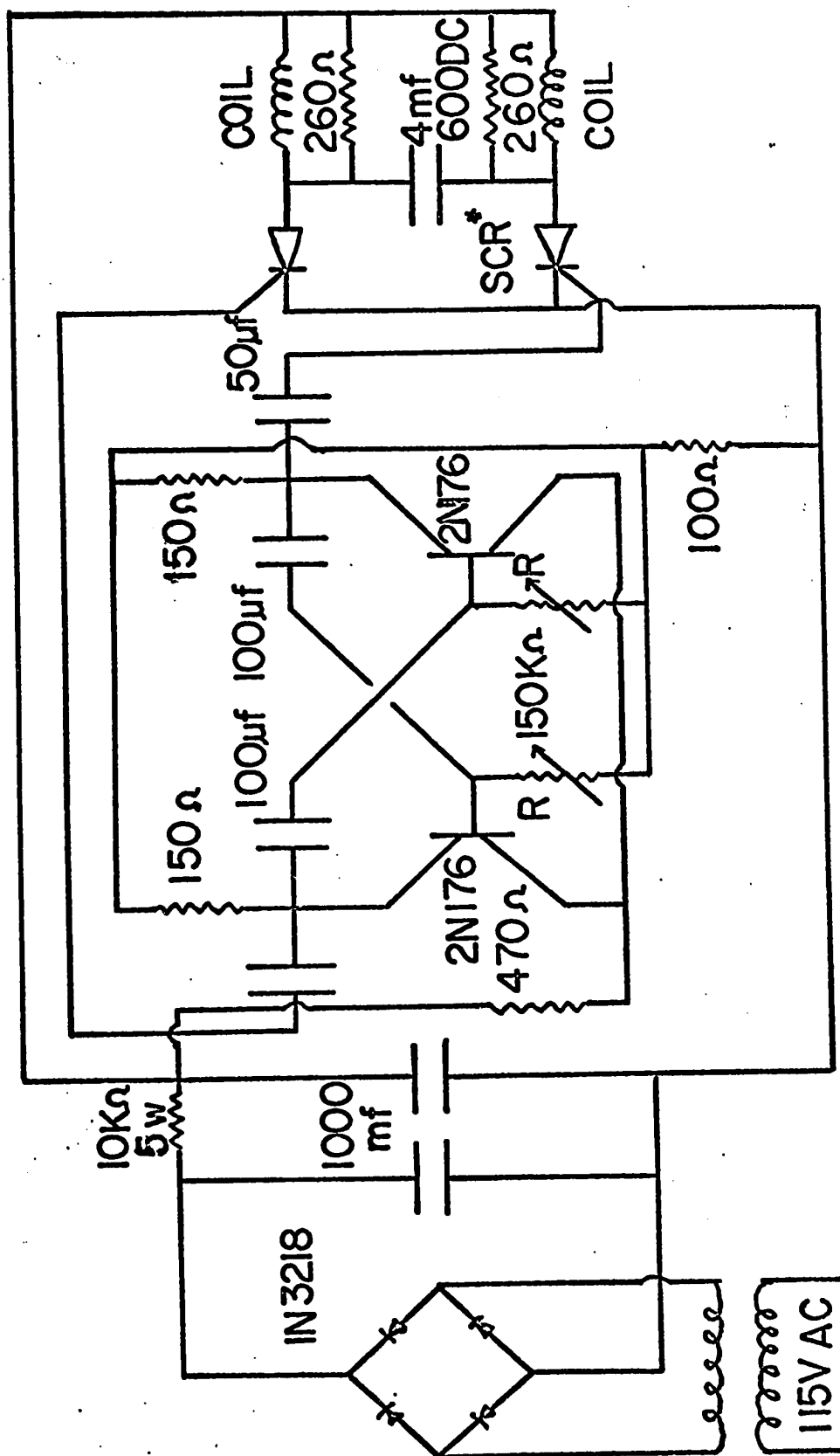


Figure 3-3 Electric Circuit of the Electromagnetic Pump

are 0 to 500, and 0 to 1000 psia with 0.5 and 1.0 psi per division, respectively.

(4) Temperature Control System and Temperature Measurement System

A Dewar flask having a capacity of about 20 liters was employed as the cryostat, into which the equilibrium cell was immersed. In this investigation, isopentane and propane were used as the bath liquid in the cryostat.

Inside the cryostat, a refrigeration coil, two stirrers, two heating elements and a resistance type temperature sensing element were installed. Liquid nitrogen was used as the refrigerant which was supplied under pressure through the refrigerant coil. The refrigerant-nitrogen, after vaporization, was let through a five-gallon buffer tank, a needle valve and a manometer and then was let into the air. The evaporation rate of liquid nitrogen was controlled by the needle valve and the manometer.

The bath was heated by a pair of heating elements which were connected to the power source through a powerstat. One of them was used as a controlling heater which was connected through the temperature controller.

The other was used as a constant heater. Two stirrers with variable speed were used to stir the bath liquid.

A proportional-type Bayley temperature con-

troller, model 250, with a resistance-type temperature sensing element was used to control the temperature. The sensing probe detected temperature fluctuations from the set temperature-range dial position.

Equilibrium temperatures were measured by means of two protective-type thermocouples in conjunction with a Leeds and Northrup K-3 potentiometer and a Tinsley SRI galvanometer. One of the thermocouples was located in the vapor phase and the other in the liquid phase.

The thermocouples were calibrated against the vapor pressure of research grade methane(108). Results of the calibration are presented in Appendix VI.

(5) Sampling Facilities

Three 3/16 inch-diameter liquid sampling tubes were extended into the equilibrium cell to three different positions, the top, the middle and the bottom of the cell. At different levels the liquid sample can be taken by different tubes. The sampling bulbs are of 10 ml. capacity. The vapor sample was trapped in the vapor sampling bulb through the sampling tube.

B. EXPERIMENTAL PROCEDURES

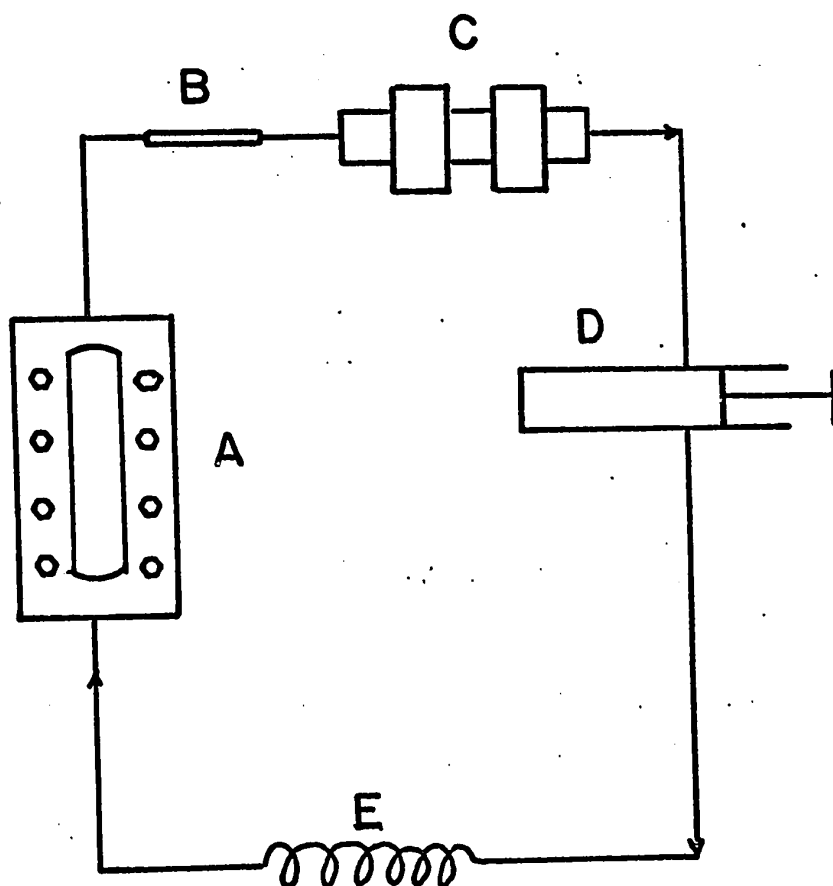
At room temperature, the system was purged and evacuated to a pressure of 0.01 mm. Hg or less. The Dewar flask was filled with isopentane as the bath liquid. Liquid nitrogen was pressurized by compressed nitrogen gas through

the nitrogen coil. The pressure regulator of compressed nitrogen gas was adjusted to 10 psig. By adjusting the needle valve after the buffer tank, the evaporating rate of liquid nitrogen was regulated. In the starting period, the needle valve was fully open to reduced the temperature very rapidly. After cooling for two hours, propane gas, if necessary, was introduced into the isopentane bath.

After the bath was cooled to the required temperature, mixtures under study were synthesized and liquefied within the equilibrium cell. The heavier component was first charged into the cell. Then followed by the lighter component. As soon as the desired pressure and liquid level were reached, the electromagnetic pump was started. The vapor was recirculated within the recirculation loop. The recirculation loop consisted of the electromagnetic pump, the equilibrium cell, the volume regulator, the vapor sampling tube and the cooling coil.

Schematic diagram of the recirculation loop is shown in Figure 3-4.

After two or more hours of operation, the circulation was stopped for recording the equilibrium temperature and pressure. When there were two liquid phases in equilibrium with the vapor, the liquid phases were allowed to settle for more than one hour before any samples were withdrawn from the equilibrium cell. The sampling system



- A EQUILIBRIUM CELL
- B VAPOR SAMPLING BLUB
- C ELECTROMAGNETIC PUMP
- D VOLUME REGULATOR
- E CONDENSATION COIL

Figure 3-4 Schematic Diagram of the Recirculation Loop

was evacuated to 0.001 mm. Hg before collecting each sample from the equilibrium system.

The vapor sample was trapped in the vapor sampling bulb through the sampling tube. Then the liquid samples were withdrawn. The first portion of the liquid sample was totally vaporized to purge the line and to estimate the sampling rate. The rate was regulated by two valves in series; the one adjacent to the high pressure side was partially opened, whereas, the other was kept tightly closed. A total gas pressure of 20 psia was sufficient to provide at least three gas samples. If the system pressure dropped while sampling, the pressure of the system could be kept constant by adjusting the volume regulator.

The vapor and liquid samples were analyzed by a Fisher Gas Partitioner Model 25V in conjunction with a Texas Instruments Incorporated recorder. Helium gas was used as the carrier gas. The column was 6½ feet long by ¼ inch O.D. packed with 28-30 mesh silica gel. The helium flow rate through the gas partitioner was 85 ml. per minute at the pressure of 20 psig. The column temperature was 40 °C. The chart speed of the recorder was ½ inch per minute. A retention time of 6 to 8 minutes was required to separate the three components, nitrogen, methane and ethane. A typical analysis chromatogram is shown in Figure 3-5.

C. MEASUREMENT ERRORS

RUN 3144

 N_2 CH_4 C_2H_6

Figure 3-5 Chromatogram of Run 3144

The principal errors in the measurement of phases equilibria can be attributed to the inaccuracy in the temperature and pressure measurements, and the errors involved in the analysis of the vapor and the liquid samples.

In this investigation temperature fluctuations of the cryostat were controllable to ± 0.01 °K(109), and the uncertainty involved in the temperature measurement was believed to be ± 0.1 °K.

The uncertainty involved in the measurement of pressure was $\pm 0.1\%$ of the full scale of the pressure gauge. For instance, ± 0.5 psi and ± 1.0 psi uncertainties were involved for the " 0-500 psia " and the " 0-1000 psia " gauges, respectively.

The reproducibility of the analysis in general was good to 0.003 mole fraction.

D. MATERIALS

Research grade gases, supplied by the Matheson of Canada, Ltd., were used in this investigation without any further purification. Specified minimum purities of these gases were as follows:

<u>Gases</u>	<u>Minimum purity, mole %</u>
Nitrogen	99.999
Methane	99.99
Ethane	99.9

E. EXPERIMENTAL RESULTS

A summary of the experimental determination is given in the following table:

TABLE 3-1

A SUMMARY OF THE EXPERIMENTAL DETERMINATION

<u>System</u>	<u>Phases</u>	<u>Temperature °K</u>	<u>Pressure psia</u>	<u>No. of points</u>
Nitrogen- Methane	V-L	130.1	123.5-435.5	8
Nitrogen- Ethane	V-L	130.1	62.0-500.0	6
Methane- Ethane	V-L	130.1	8.3-46.3	21
Nitrogen- Methane- Ethane	V-L	130.1	50.0-422.0	30
Nitrogen- Ethane	L ₁ -L ₂ -V	113.6-133.1	68.2-591.0	13
Nitrogen- Methane- Ethane	L ₁ -L ₂ -V	113.5-133.3	217.0-558.6	55
Nitrogen- Methane- Ethane	L ₂ -L ₁ -V	94.3-109.1	61.1-165.7	24
Nitrogen- Methane- Ethane	L ₁ -L ₂ -V and L ₂ -L ₁ -V	109.1-113.3	167.1-213.0	12

In this table L_1 refers to the liquid rich in ethane; L_2 refers to the liquid phase rich in nitrogen; V refers to the vapor phase.

(1) Nitrogen-Methane System

The pressure-composition data obtained in this investigation for the nitrogen-methane system are compared with values reported in literature in Figure 3-6. Vapor-liquid equilibrium data for this system were reported by Bloomer and Parent(10). Graphically interpolated values from their data at 130.1 °K were compared with those obtained in this investigation.

(2) Nitrogen-Ethane System

For the binary system nitrogen-ethane, the 130.1 °K isotherm obtained in this investigation disagrees with the data reported by Ellington et. al.(12) at 130.3 °K but it agrees fairly with that reported by Cosway et. al. (36) at 132.8 °K. The pressure-composition data measured at 130.1 °K are shown in Figure 3-7.

For this system, two liquid phases were obtained in equilibrium with vapor phase at temperatures lower than 133 K. The compositions of the three coexisting phases are plotted as functions of equilibrium temperature in Figure 3-13. The agreement between these data and those reported by Ellington et. al.(12) was very good at lower

temperatures. However, higher temperatures the data obtained in this investigation disagree with that reported by Ellington et. al.(12).

The concentration of ethane in the bottom liquid layer was always higher than in the top liquid layer at the temperatures above 109.1 °K. It appears from Figure 3-13 that the nitrogen-rich phase(top liquid phase) became identical with the vapor at temperature somewhat higher than 133.1 °K.

(3) Methane-Ethane System

For the binary methane-ethane system, the pressure-composition data obtained at 130.1 °K are shown in Figure 3-8. The present data agrees very well with the graphically interpolated data at this temperature. These literature values were reported by Bloomer et. al.(10) for the temperatures above 155 °K and by Chang and Lu(37) at 122.1° and 171.4 °K.

(4) Nitrogen-Methane-Ethane System

Equilibrium vapor-liquid compositions for the nitrogen-methane-ethane ternary system were determined at 130.1 °K. Isothermal vapor-liquid compositions for the ternary mixtures are shown in Figures 3-9 to 3-12. At this temperature, 130.1 °K, the equilibrium compositions were determined along the constant x_{c1}/x_{c2} lines of liquid phase.

The compositions and pressures of the two liquid phases in equilibrium with the vapor phase were measured for the nitrogen-methane-ethane system at eleven isotherms from 94.3° to 133.3 °K. It was observed that a liquid phase inversion took place between the temperatures 109.1° and 113.5 °K, the bottom liquid layer being nitrogen-rich phase at 109.1 °K and the ethane-rich phase at 113.5 °K.

The experimental equilibrium results for the ternary mixtures are shown in Figures 3-14 to 3-24, and presented in Appendix I.

At the conditions that three phases coexist, it is seen in Figures 3-14 to 3-24 that the partially miscible region increases with the decrease of temperature, and from experimental equilibrium data, the system pressure decreases with the decrease of temperature. Along the ethane-rich portion of the curve at all temperatures investigated, the pressure of system decreases with the increase of methane concentration in the liquid phase, and the concentration of methane in ethane-rich liquid phase is always greater than in the equilibrium nitrogen-rich liquid phase regardless of the liquid phase inversion behavior. Equilibrium vapor compositions are found to be extremely rich in the nitrogen ($y_{N_2} \geq 0.96$) at all the temperatures investigated.

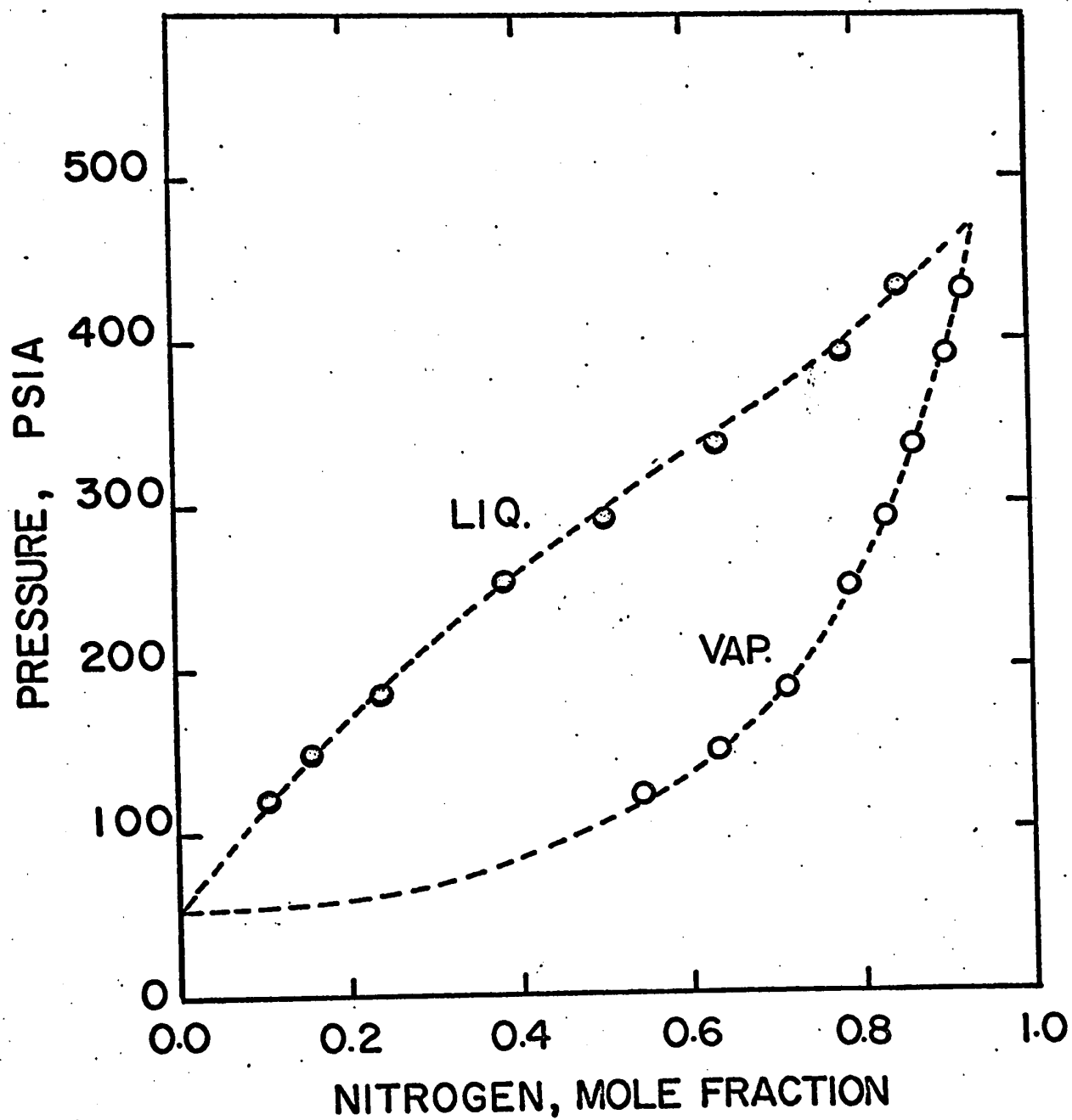


Figure 3-6 Vapor-Liquid Equilibrium Data for the Nitrogen-Methane System at 130.1 °K

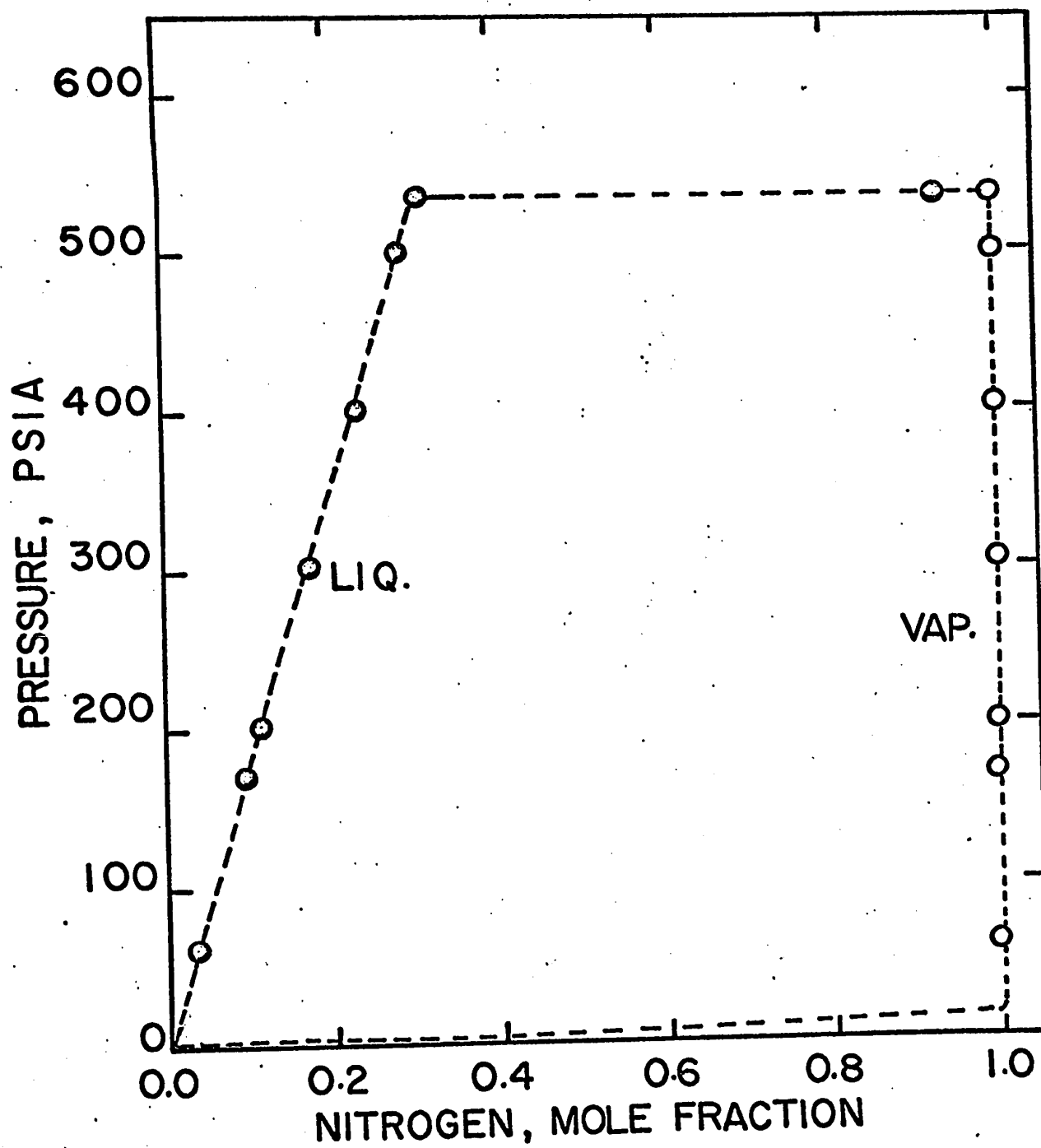


Figure 3-7 Vapor-Liquid Equilibrium Data for the Nitrogen-Ethane System at 130.1 °K

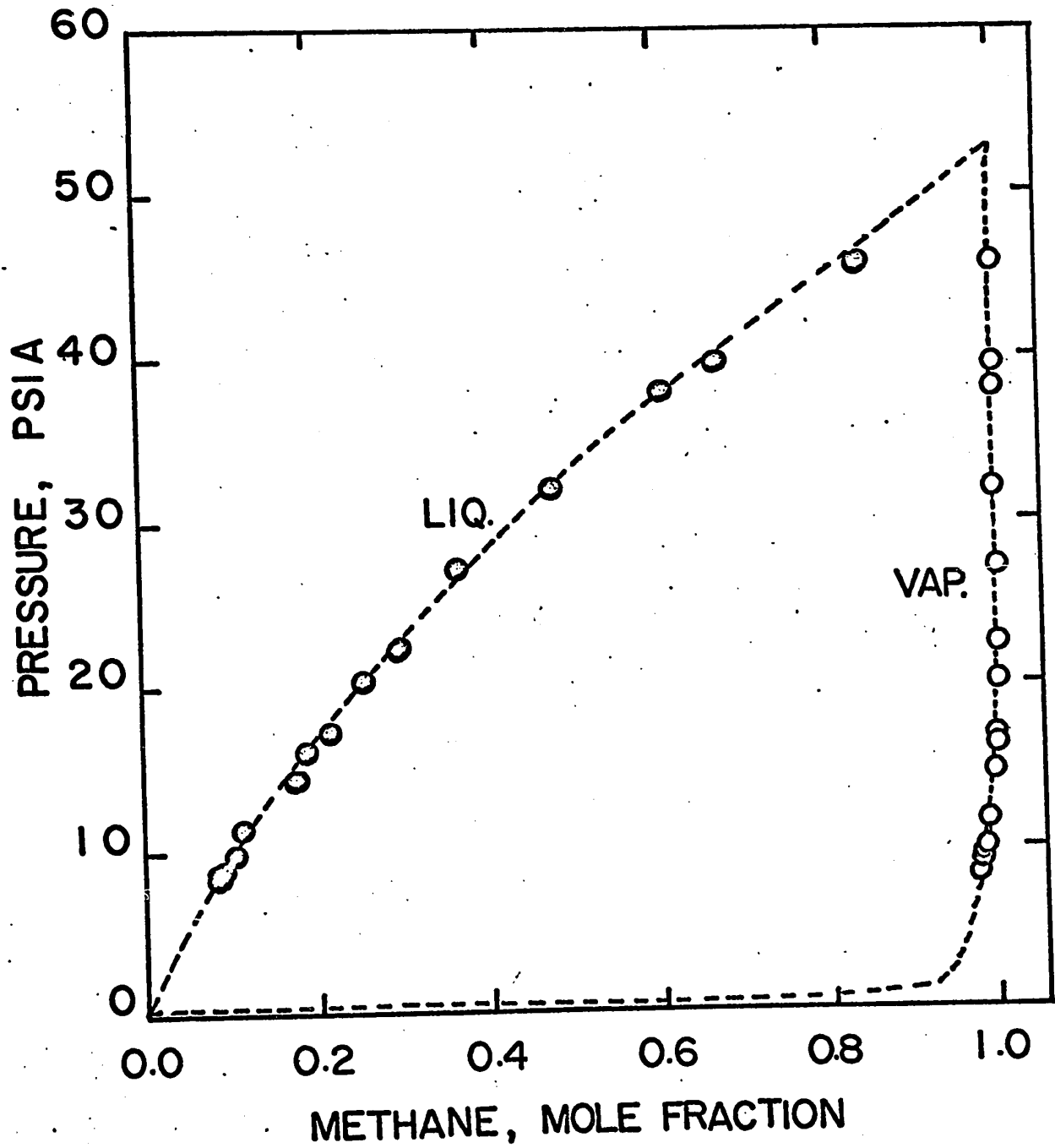


Figure 3-8 Vapor-Liquid Equilibrium Data for the Methane-Ethane System at 130.1 °K

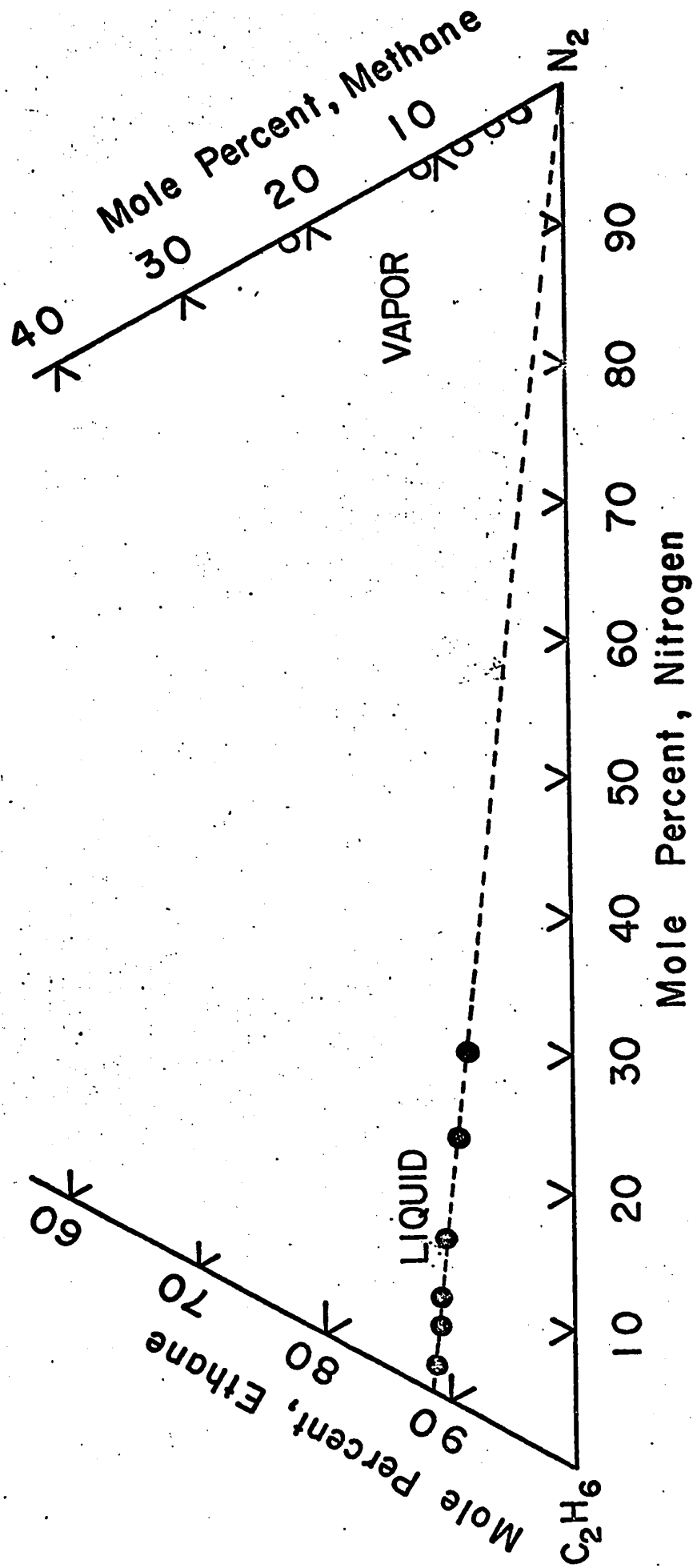


Figure 3-9 The Triangular Composition Diagram for the Nitrogen-Methane-Ethane

System at 130.1 K and $x_{C1}/x_{C2} = 0.14$

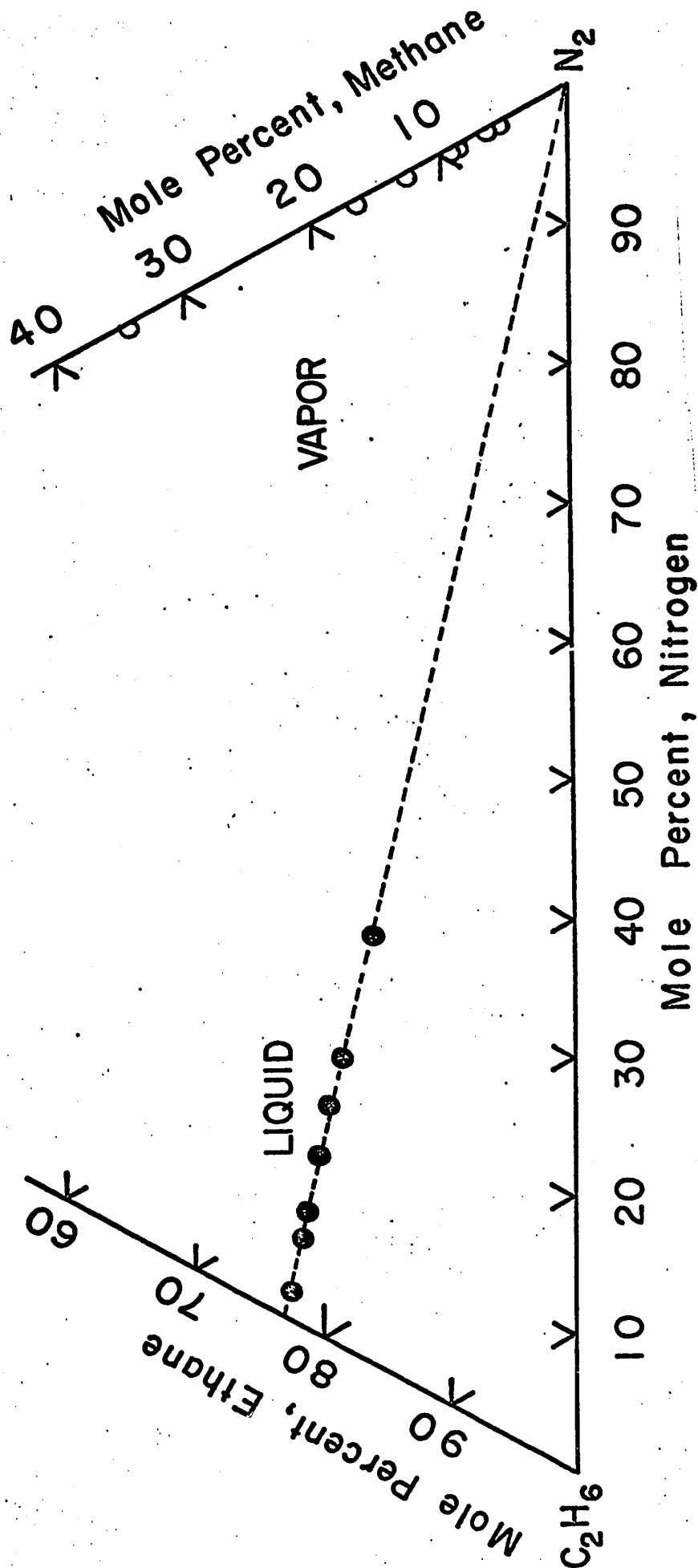


Figure 3-10 The Triangular Composition Diagram for the Nitrogen-Methane-Ethane

System at $130.1^\circ K$ and $x_{C1}/x_{C2} = 0.30$

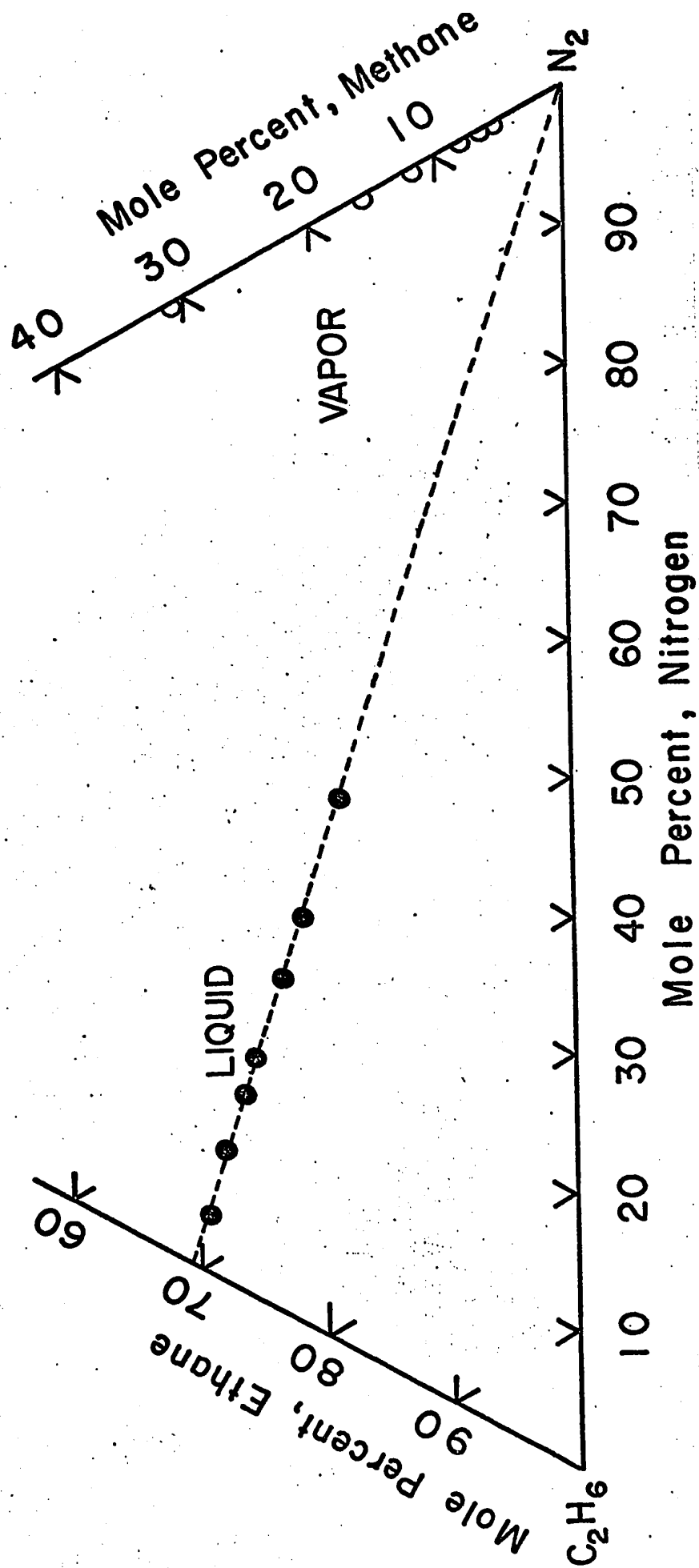


Figure 3-11 The Triangular Composition Diagram for the Nitrogen-Methane-Ethane

System at 130.1 °K and $x_{C_1}/x_{C_2} = 0.47$

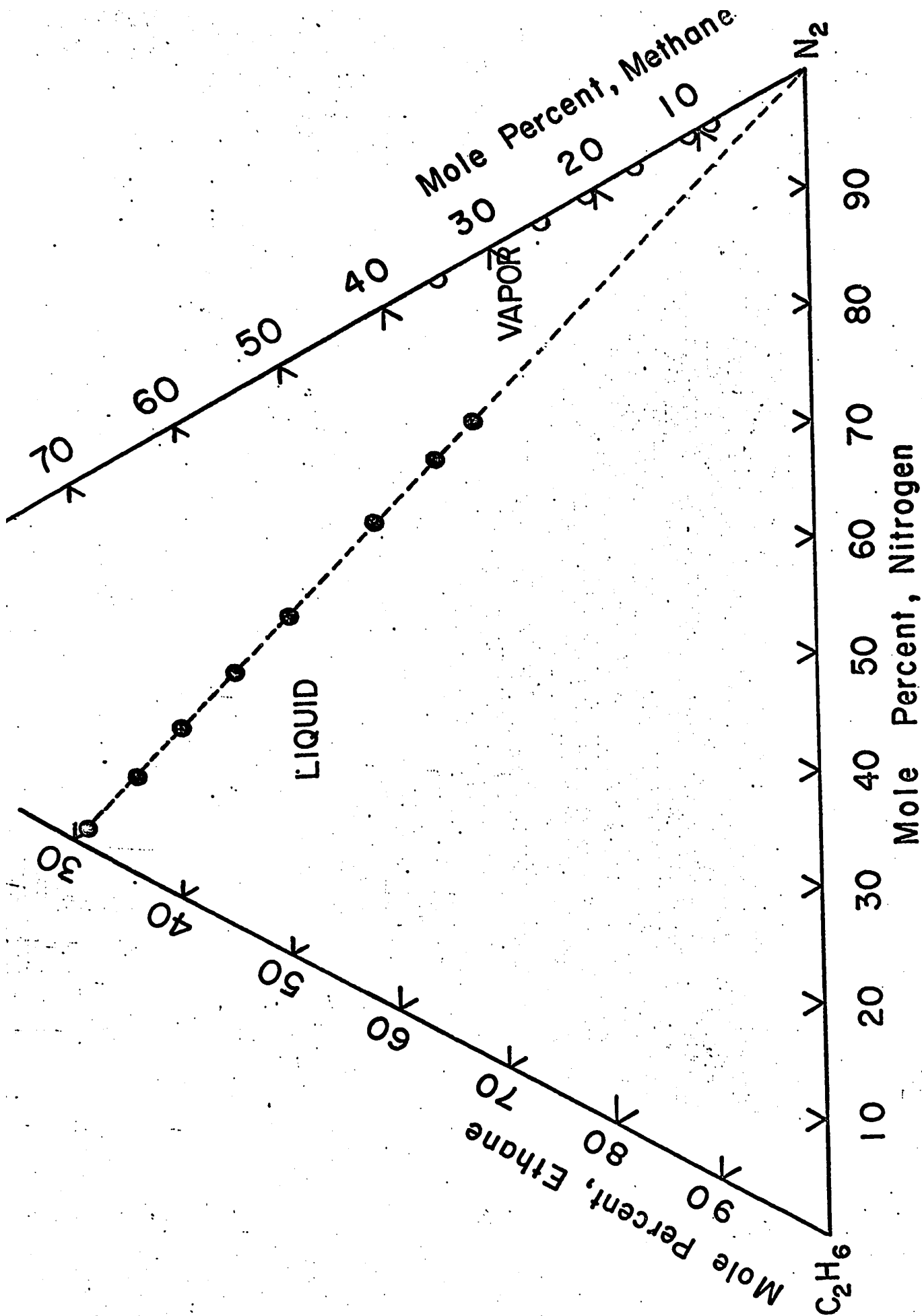


Figure 3-12 The Triangular Composition Diagram for the Nitrogen-Methane-Ethane

System at 130.1°K and $x_{\text{C}_1}/x_{\text{C}_2} = 2.33$

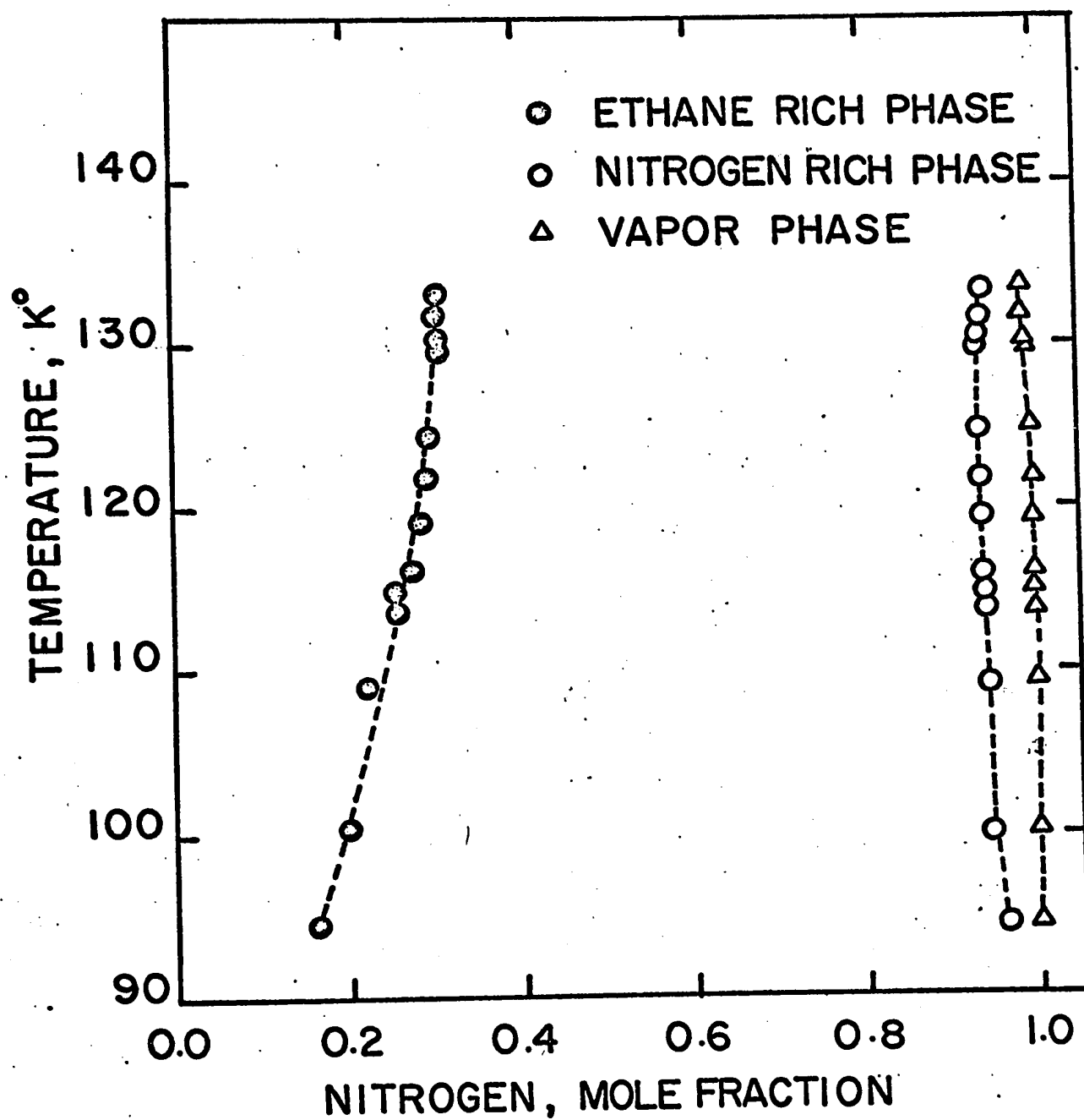


Figure 3-13 Liquid-Liquid-Vapor Equilibrium Data for the Nitrogen-Ethane System

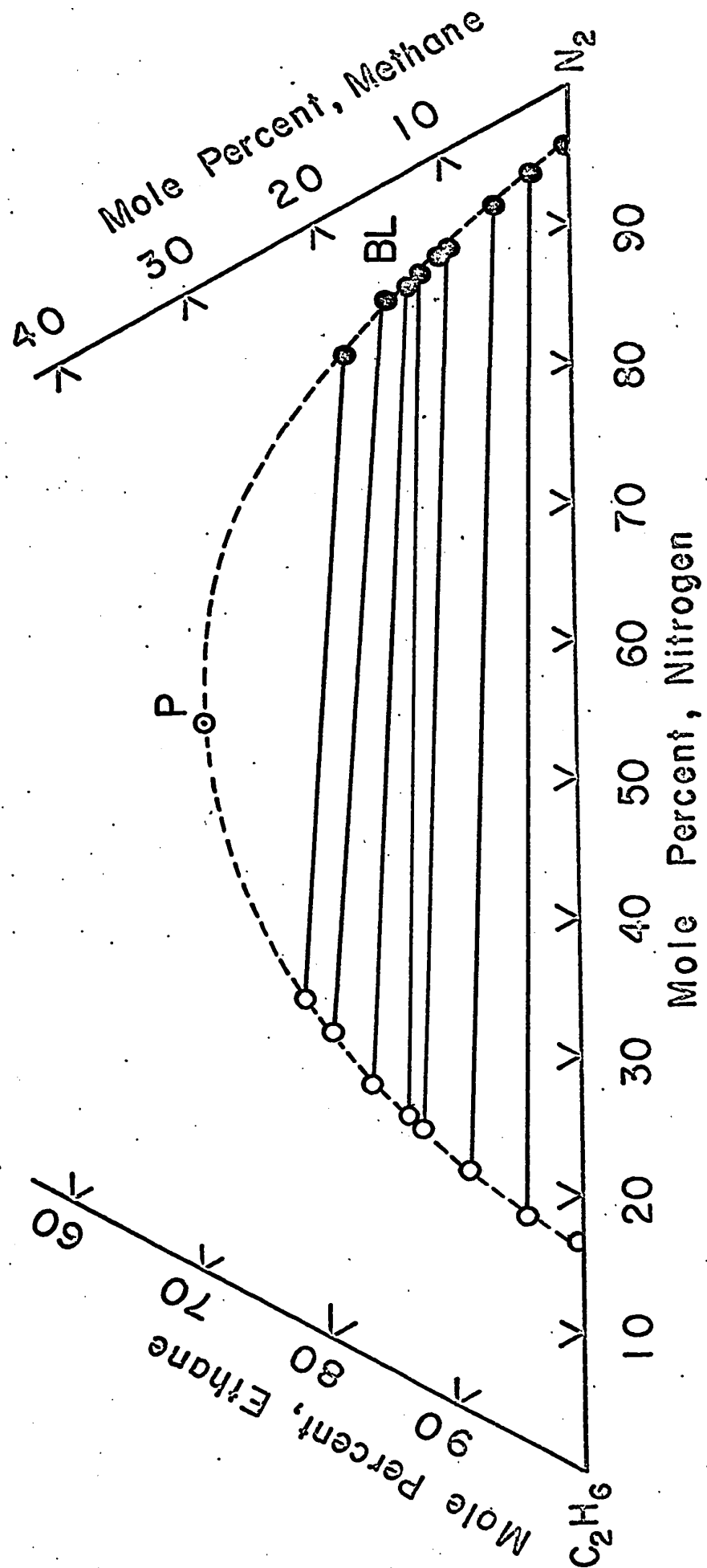


Figure 3-14 Partial Miscible Region of Ternary System at 94.3°K

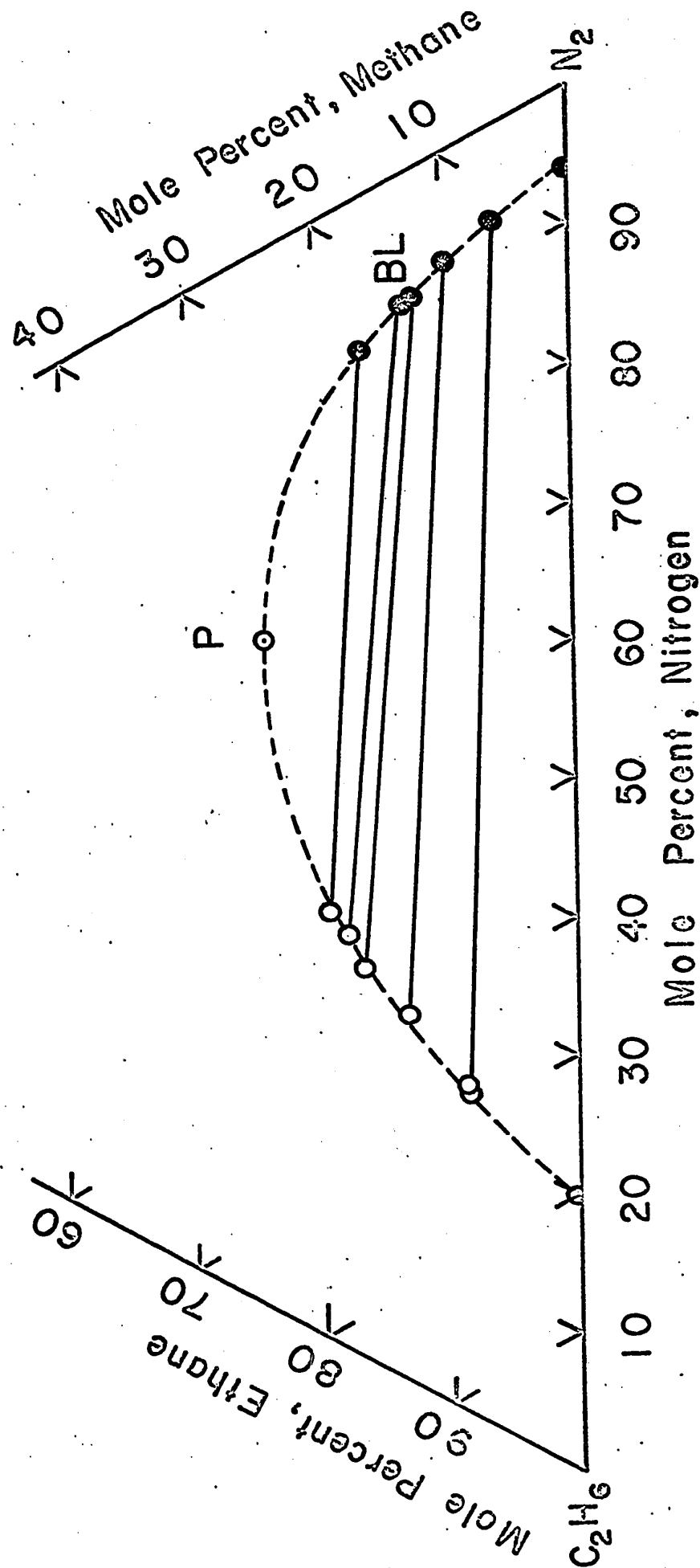


Figure 3-15 Partial Miscible Region of Ternary System at 101.5°K

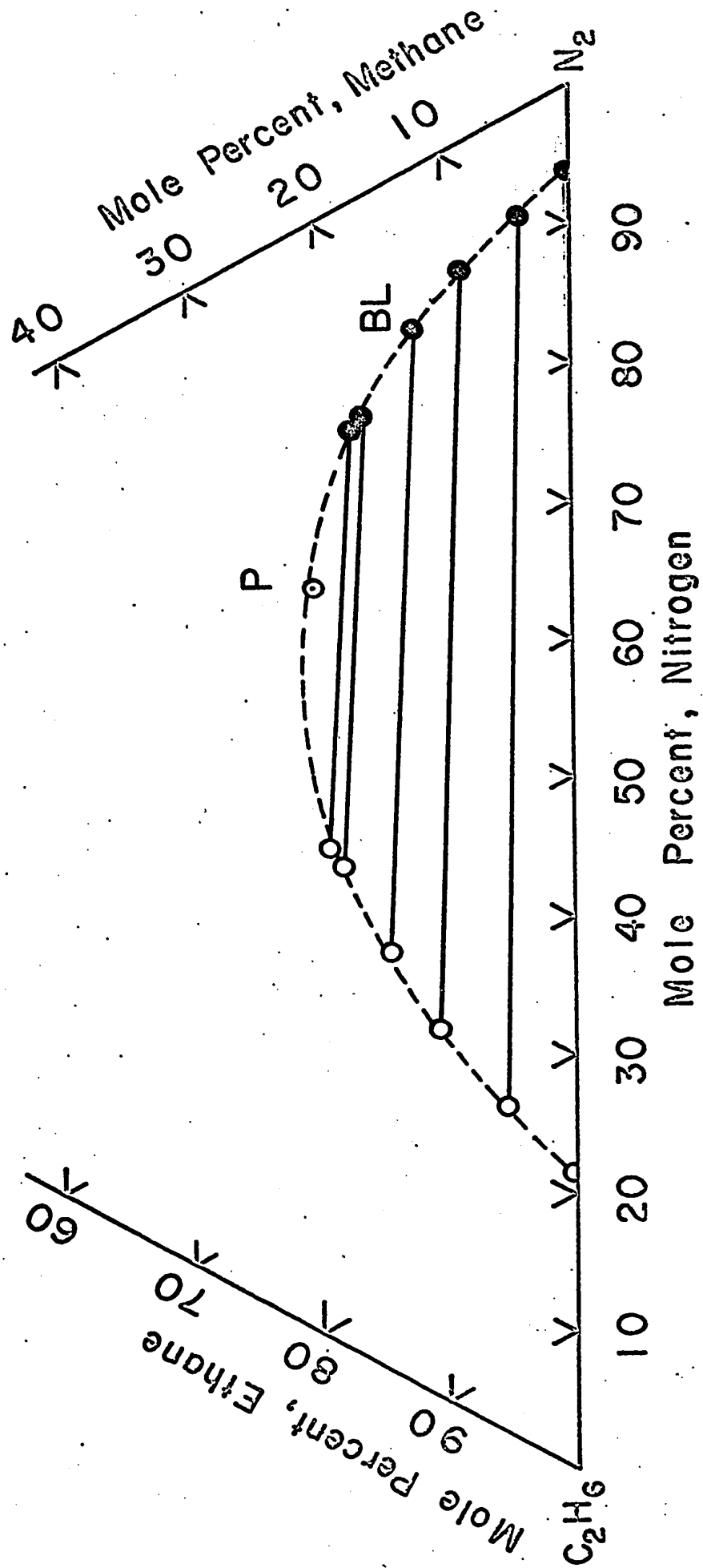


Figure 3-16 Partial Miscible Region of Ternary System at 109.1 °K

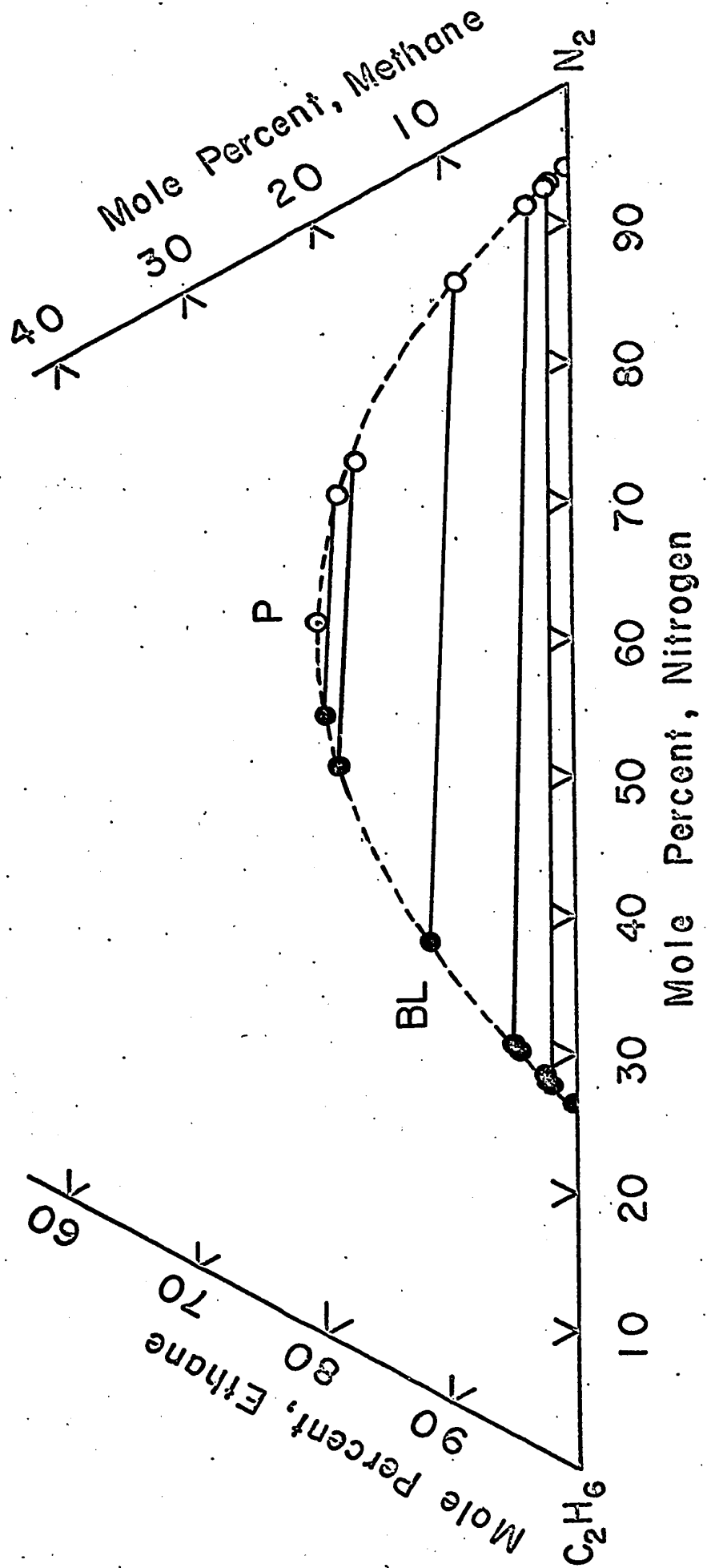


Figure 3-17 Partial Miscible Region of Ternary System at 113.4°K

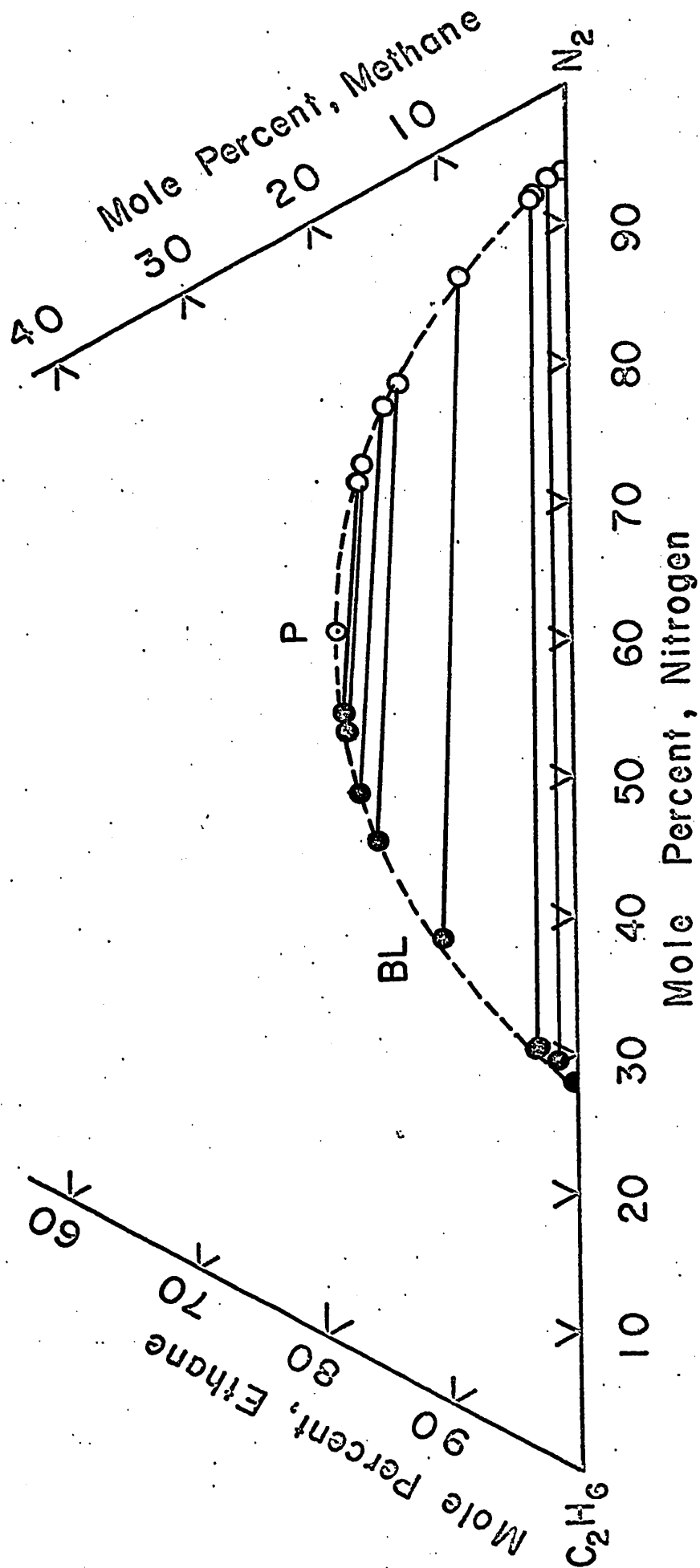


Figure 3-18 Partial Miscible Region of Ternary System at 115.2°K

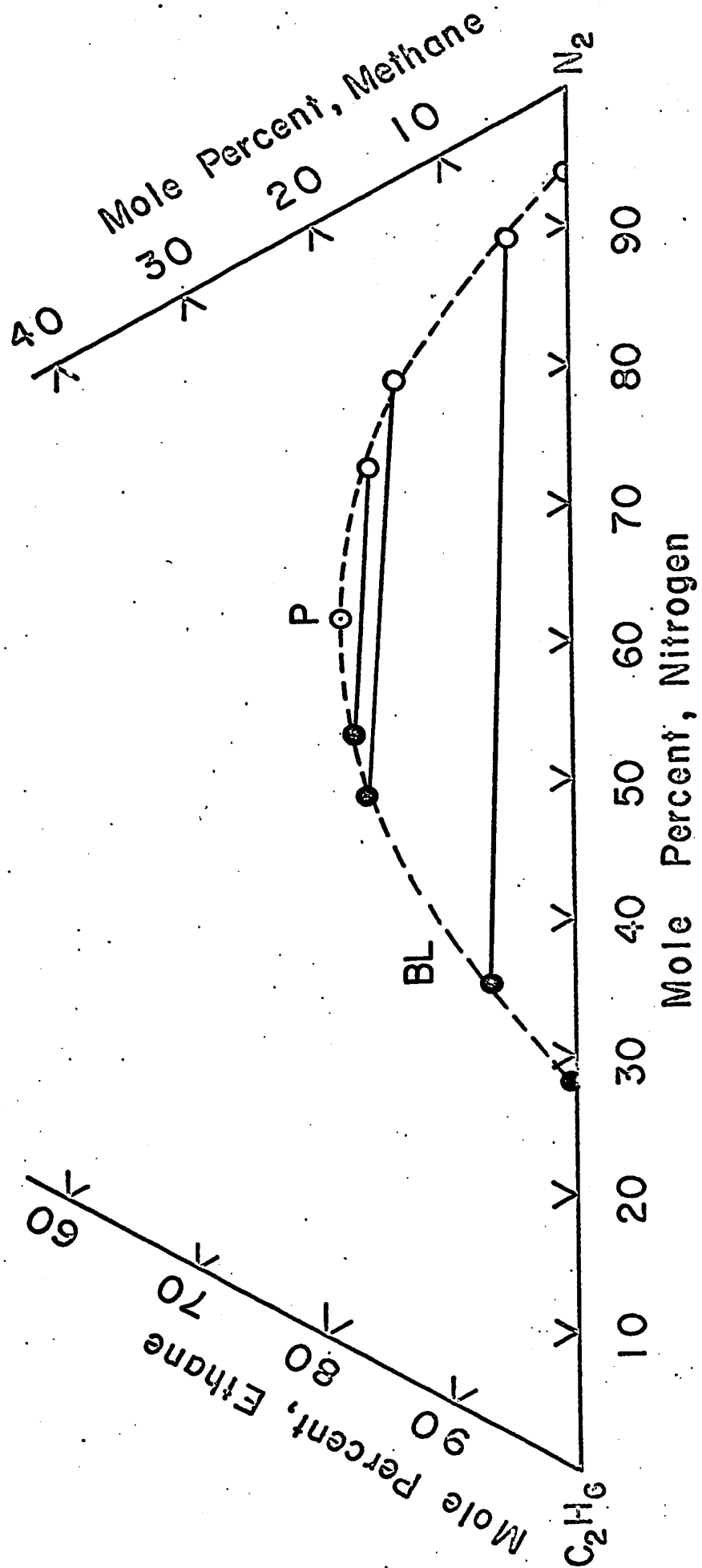


Figure 3-19 Partial Miscible Region of Ternary System at 116.3 °K

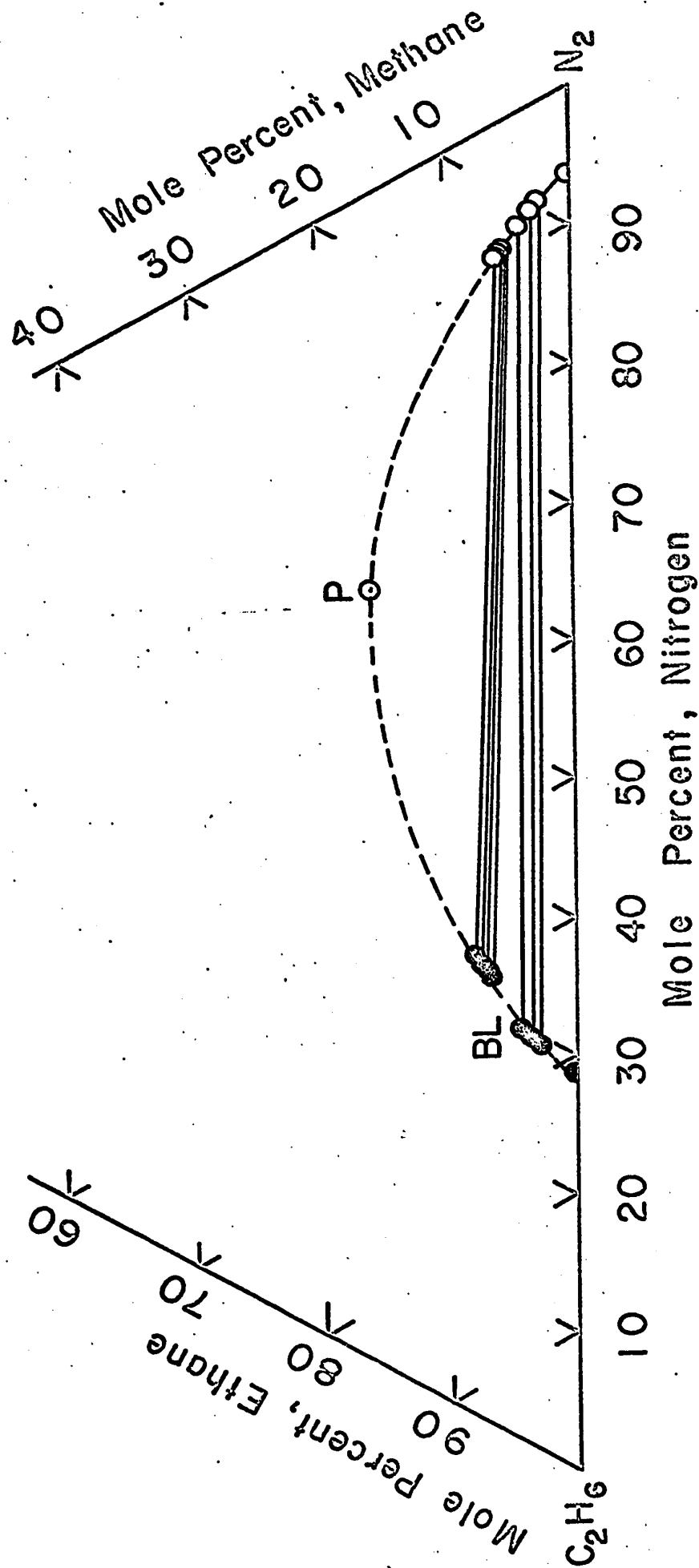


Figure 3-20 Partial Miscible Region of Ternary System at 119.3°K

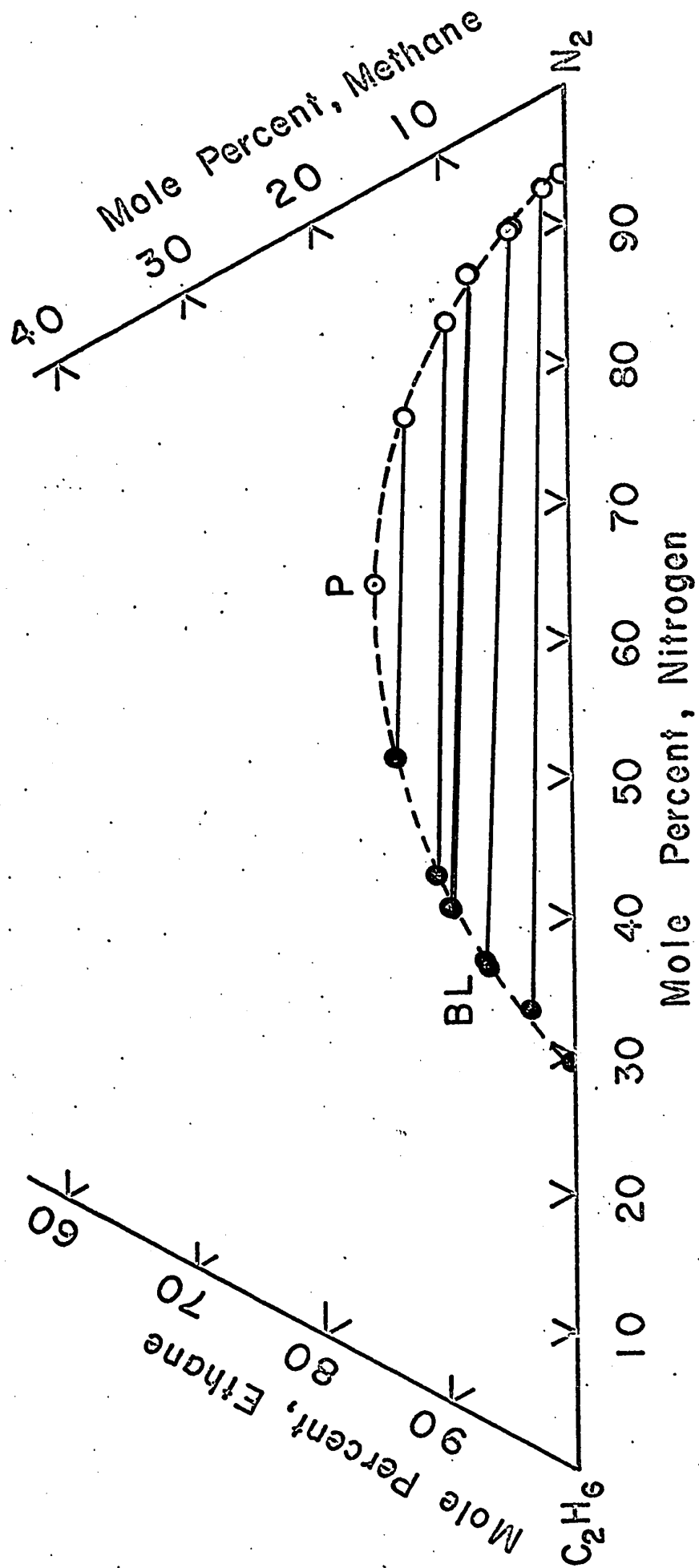


Figure 3-21 Partial Miscible Region of Ternary System at 123.4°K

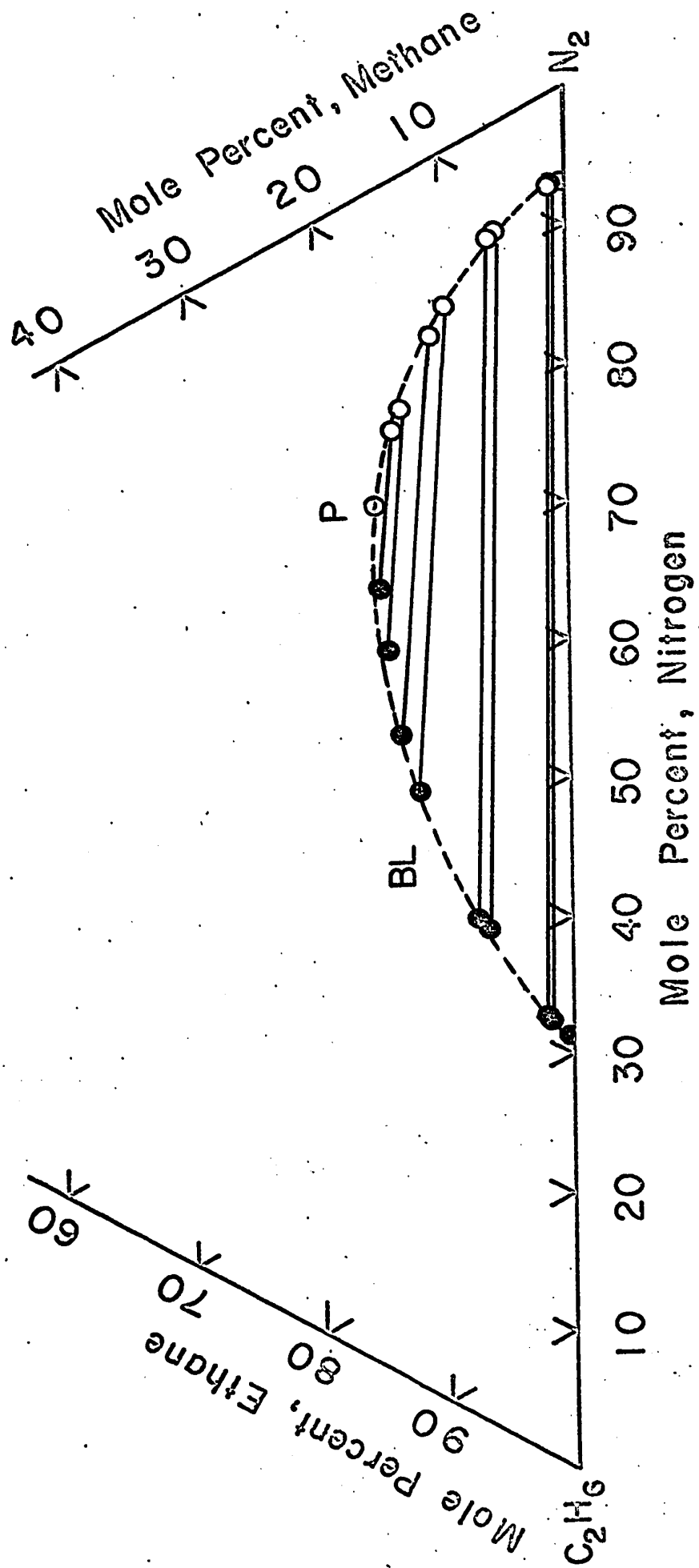


Figure 3-22 Partial Miscible Region of Ternary System at 128.8 °K

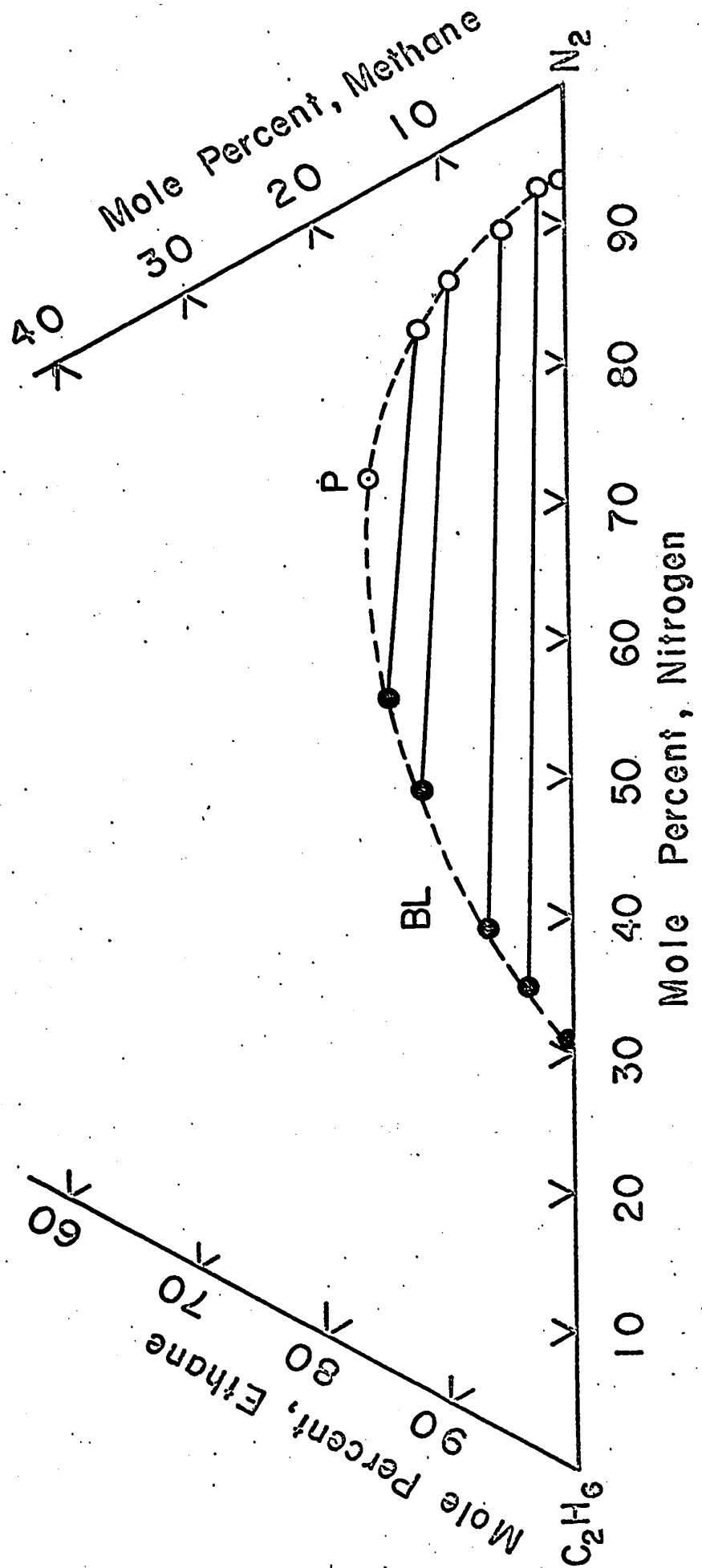


Figure 3-23 Partial Miscible Region of Ternary System at 130.1 °K

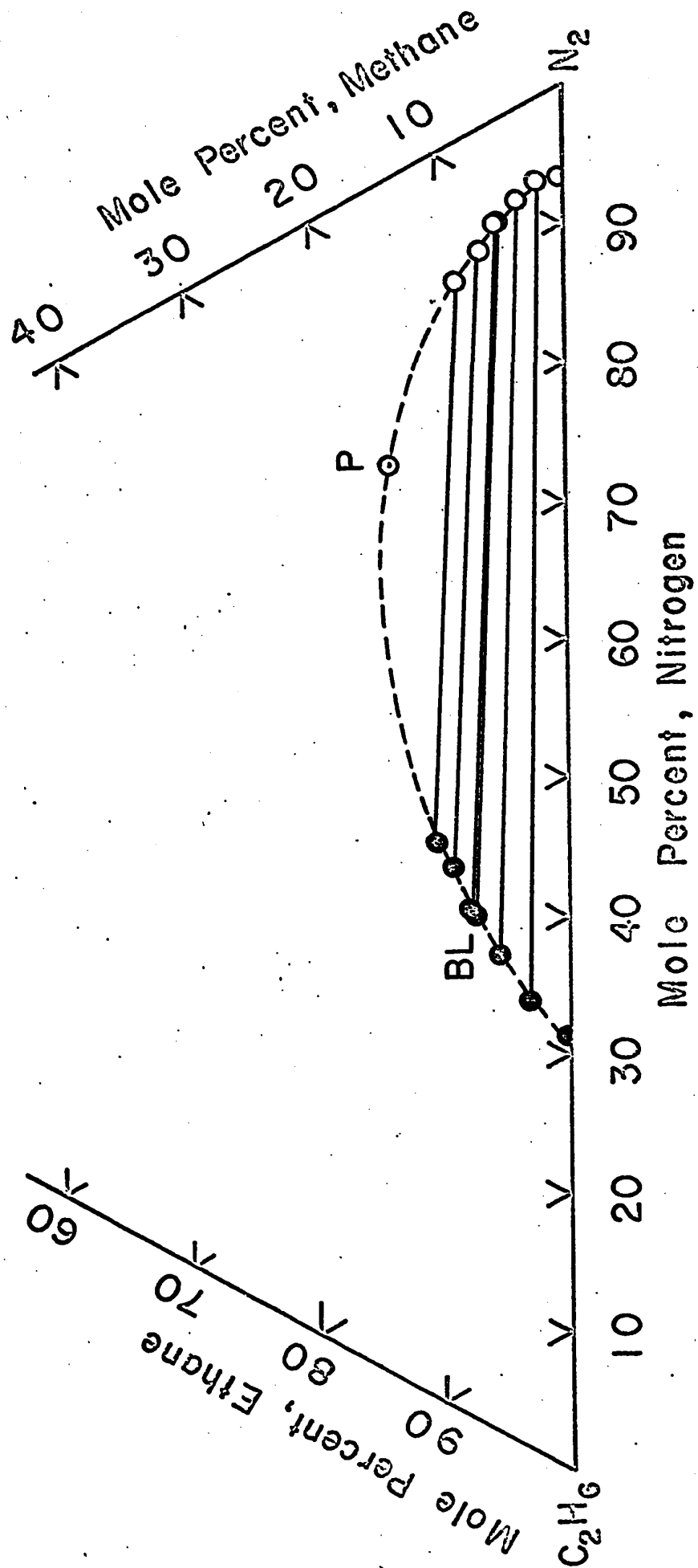


Figure 3-24 Partial Miscible Region of Ternary System at 133.3 °K

CHAPTER IV

CORRELATION OF VAPOR-LIQUID

AND

LIQUID LIQUID VAPOR EQUILIBRIUM DATA

The experimental vapor-liquid equilibrium data which were obtained in this investigation, were correlated by the available method as follows:

First, the liquid activity coefficients were evaluated at constant temperature and constant pressure conditions.

Secondly, the calculated activity coefficients were correlated with the Redlich-Kister equation(95).

A. EVALUATION OF ACTIVITY COEFFICIENT

From Chapter II, the liquid activity coefficient of component i at a constant temperature and at a reference pressure P^r is given by:

$$\gamma_i(P^r, T, x) = \frac{y_i \hat{\phi}_i^V}{x_i f_i^{OL}(P^r, T)} \exp \int_P^{P^r} \frac{\bar{V}_i}{RT} dP \quad 2-46$$

It is normalized as follows:

$$\gamma_i \rightarrow 1 \quad \text{when} \quad x_i \rightarrow 1$$

Values of $\hat{\phi}_i^V$ and f_i^{OL} together with $\bar{V}_i$ were evaluated from the modified Redlich-Kwong equation of state(82).

The partial molal volumes, $\bar{V}_i$'s were evaluated from

Equation(4-1)

$$\bar{V}_i = \frac{\frac{RT}{V-b} \left(1 + \frac{b_i}{V-b}\right) - \frac{2(\sum_j x_{ij} a_{ij}) - ab_i}{V(V+b)T^{0.5}}}{\frac{RT}{(V-b)^2} - \frac{a}{T^{0.5}} - \frac{2V+b}{V(V+b)^2}} \quad 4-1$$

By definition,

$$f_i^{OL} = \phi_i^{OL} P^r \quad 4-2$$

The quantity ϕ_i^{OL} is fugacity coefficient for the pure component at a reference pressure P^r .

B. THERMODYNAMIC CONSISTENCY TEST OF THE BINARY ISOTHERMAL DATA

The thermodynamic consistency of the binary equilibrium data at constant temperature and at a reference pressure P^r may be conveniently tested by the equation(95).

$$\int_{x_1=0}^{x_1=1.0} \frac{r_1(P^r)}{r_2(P^r)} dx_1 = 0 \quad 4-3$$

When $\ln \frac{r_1(P^r)}{r_2(P^r)}$ is plotted against x_1 from 0.0 to 1.0, the net

area between the curve and x-axis is equal to zero.

If the vapor-liquid equilibrium data is measured for a limited concentration range from $x_1 = a$ and $x_1 = b$, the experimental data can be tested for the thermodynamic consistency by the following equation(12):

$$\ln \frac{r_{2b}^{(Pr)}}{r_{2a}^{(Pr)}} = - \int_a^b \left[\frac{r_1^{(Pr)}}{r_2^{(Pr)}} \right] x_1 d \left(\ln \frac{r_1^{(Pr)}}{r_2^{(Pr)}} \right) \quad 4-4$$

When $\ln \frac{r_1^{(Pr)}}{r_2^{(Pr)}}$ is plotted against x_1 the net area between

the curve and $\ln \frac{r_1^{(Pr)}}{r_2^{(Pr)}}$ axis from $\left(\frac{r_1^{(Pr)}}{r_2^{(Pr)}} \right)_b$ to

$\left(\frac{r_1^{(Pr)}}{r_2^{(Pr)}} \right)_a$ is equal to the value of $\ln \frac{r_{2b}^{(Pr)}}{r_{2a}^{(Pr)}}$.

C. CORRELATION OF LIQUID-LIQUID-VAPOR EQUILIBRIUM

In order to smooth the liquid-liquid equilibrium data, the experimental tie lines were graphically correlated, interpolated, and extrapolated.

In Figure 4-1, if DE is a tie line. Line DG may

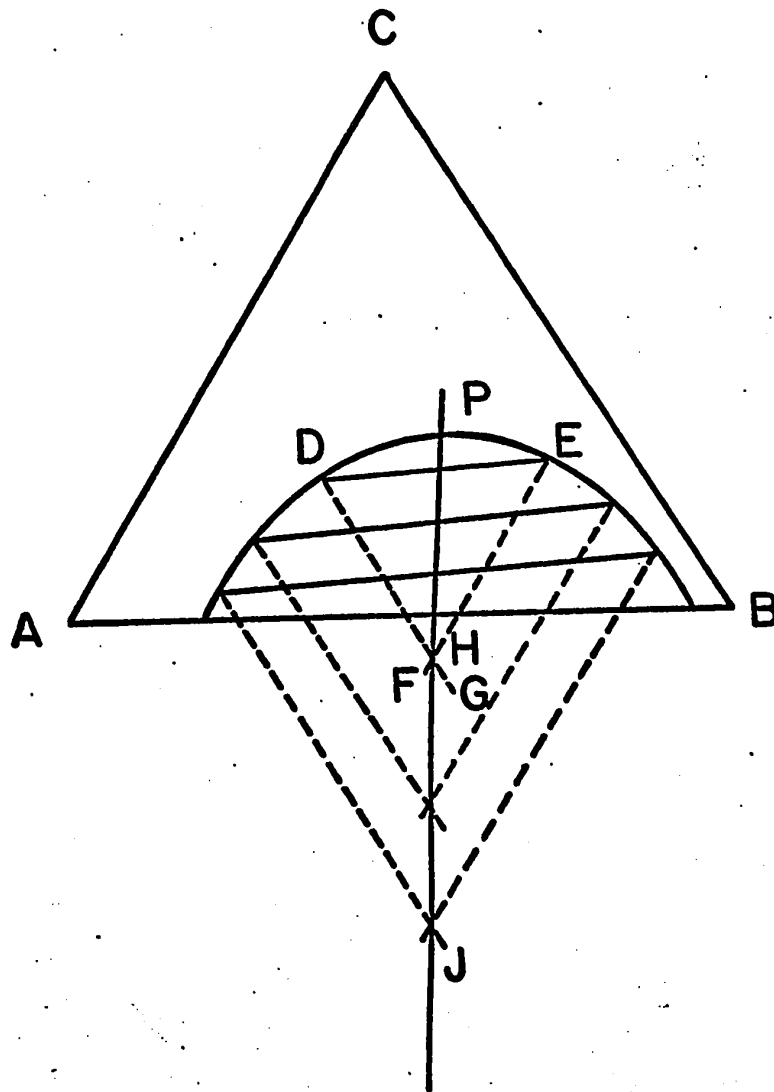


Figure 4-1 Graphical Interpolation of Tie Lines

be drawn parallel to CB, and EF parallel to AC. The two constructed lines intersect at H. A tie-line correlation curve or conjugation line PHJ is then drawn through several such intersections obtained from the known tie lines. From any point on the tie-line correlation curve, two lines drawn parallel to AC and BC will intersect the solubility curve at concentrations corresponding to the equilibrium solutions.

Although the curvature is ordinarily small, the curve PHJ is not straight, and it necessarily passes through the plait point, P. The position of the plait point can be found by extrapolation provided that tie lines very close to the plait point are known.

The smoothed liquid-liquid equilibrium compositions were correlated in terms of the distribution coefficients. The distribution coefficient for nitrogen K'_{N_2} is defined by

$$K'_{N_2} = x_{N_2}(\text{BL})/x_{N_2}(\text{TL}) \quad 4-5$$

in which BL refers to the bottom liquid phase and TL, the top liquid phase. Similarly the distribution coefficients for methane, ethane and the total hydrocarbon material (K'_{C_1} ,

K'_{C_2} and K'_H) are defined.

The equilibrium composition data were correlated in

terms of the equilibrium ratio K_{N_2} , which is defined as the ratio of nitrogen concentration in the vapor phase to the nitrogen concentration in the liquid phase.

D. RESULTS AND DISCUSSIONS

In this study, the reference pressure was chosen to be 1000 psia which is above the highest saturation pressure encountered in this work. The liquid activity coefficients of the components in the binary systems nitrogen-methane, nitrogen-ethane and methane-ethane were evaluated by means of Equation(2-46).

The fitted constants for all the binary systems, which were obtained by the least-squares method for the three-constant Redlich-Kister equation, are presented in Table 4-1. The experimental and calculated liquid activity coefficients are compared in Figures 4-2 to 4-4 and in Tables I-III of Appendix II.

TABLE 4-1Summary of The Correlation Results forThe Binary Systems at 130.1 °K

System	B_{12}	C_{12}	D_{12}	r_1^∞	r_2^∞
Nitrogen(1)-Methane(2)	0.7738	-0.0015	0.0039	2.1798	2.1732
Nitrogen(1)-Ethane(2)	2.2428	0.5935	0.1177	5.8537	19.185
Methane(1)-Ethane(2)	0.7868	0.1496	0.0261	2.0002	3.9846

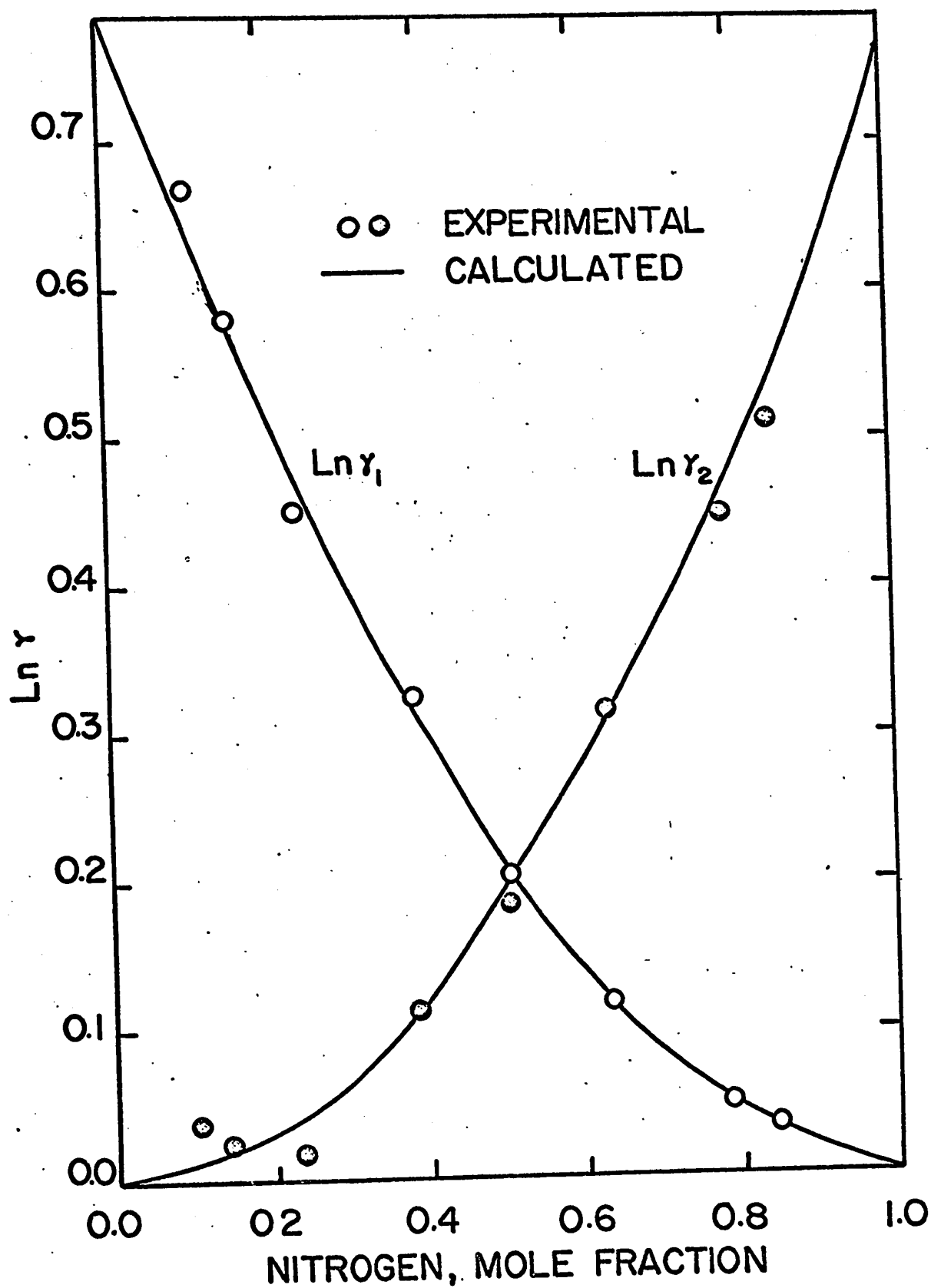


Figure 4-2 Comparison of Experimental and Calculated γ Values for the Nitrogen-Methane System at 130.1 °K

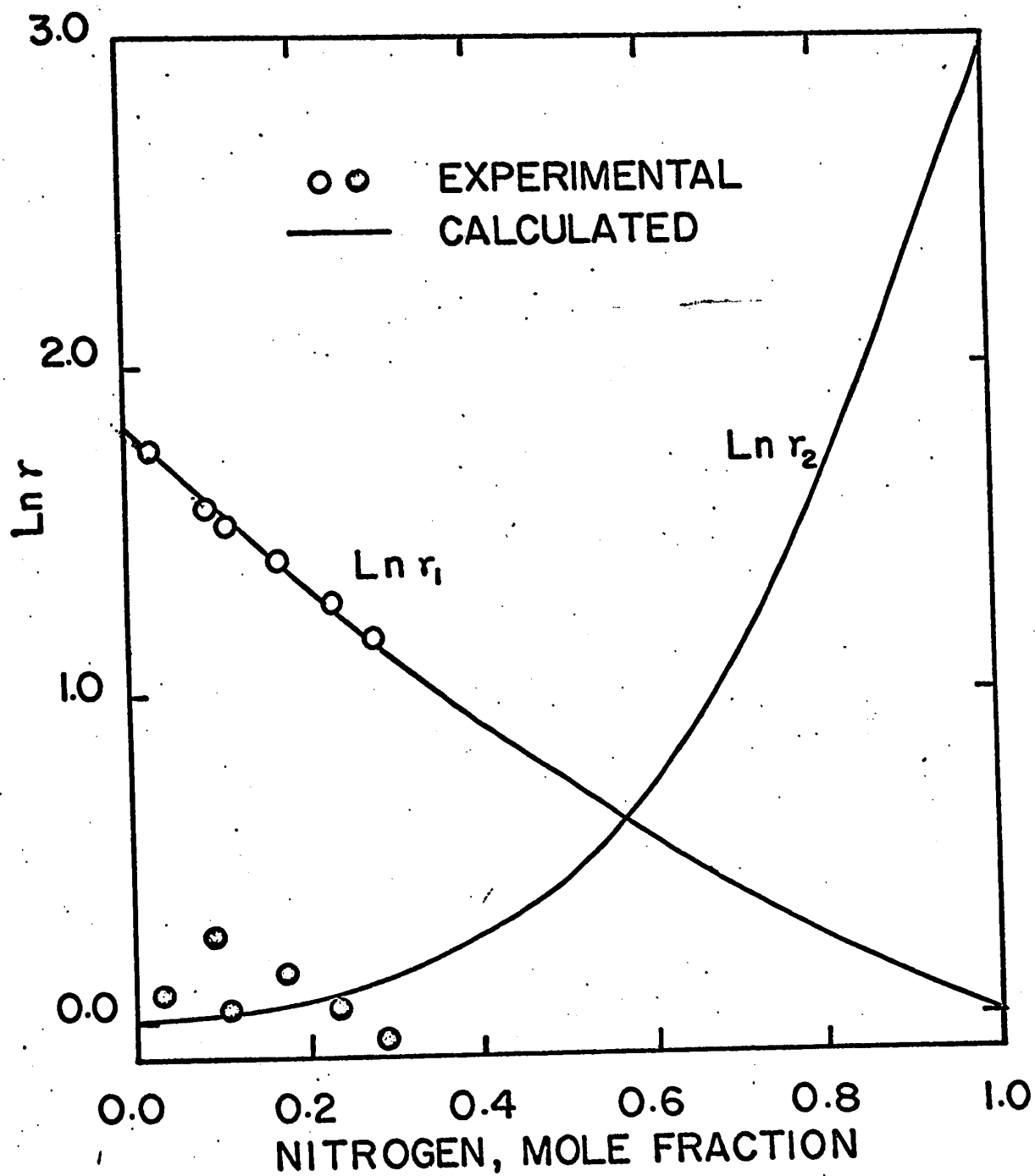


Figure 4-3 Comparison of Experimental and Calculated r Values for the Nitrogen-Ethane System at 130.1 K

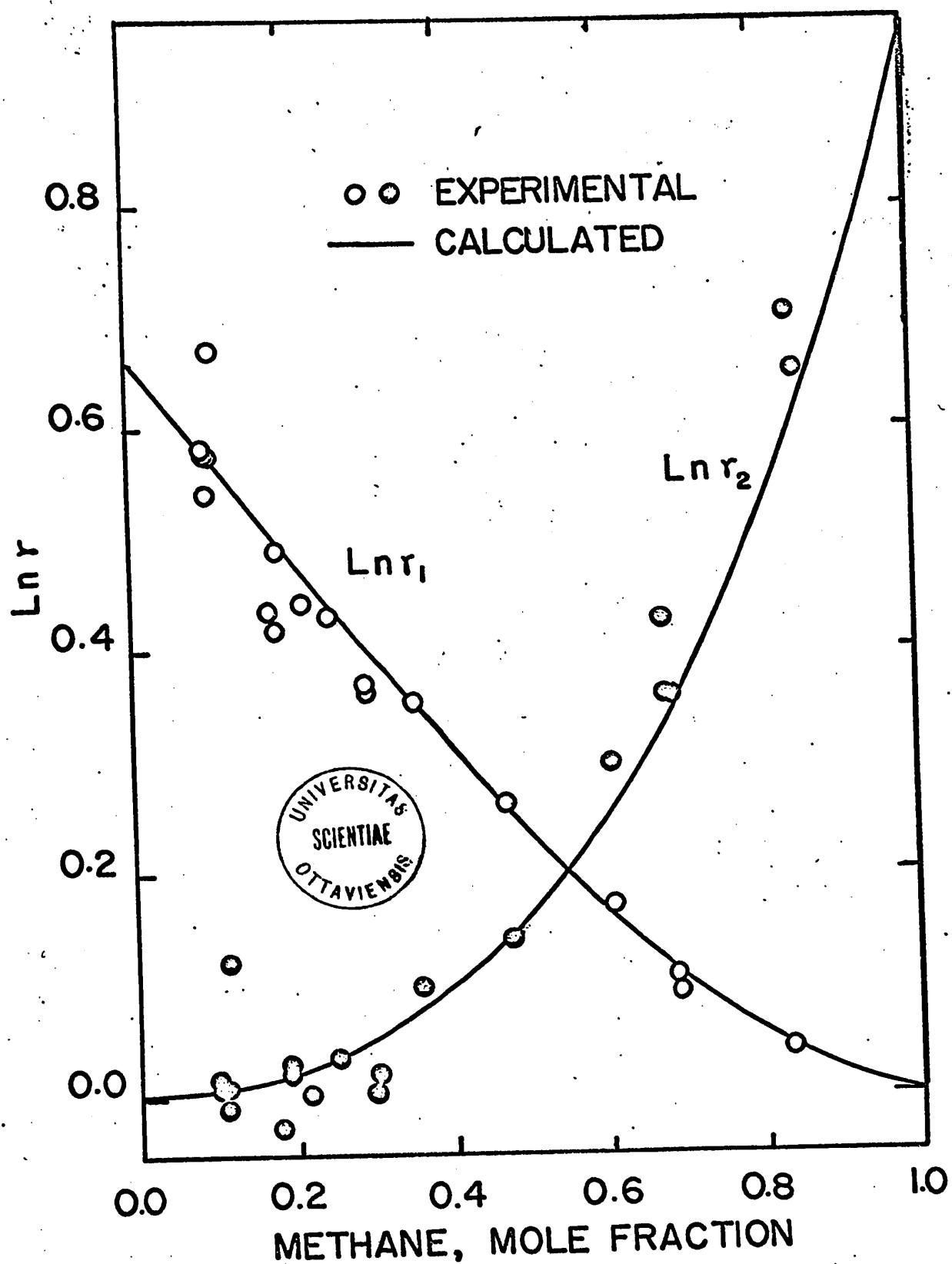


Figure 4-4 Comparison of Experimental and Calculated r Values for the Methane-Ethane System at 130.1 °K

The liquid activity coefficients of the components in the ternary system nitrogen-methane-ethane at 130.1 °K were also evaluated by means of Equation(2-46) and then correlated by Equation(2-55) with the assumption that there was no third component effect. The calculated $\ln \gamma$ values of the components in the ternary system, nitrogen-methane-ethane, at 130.1 °K are compared with experimental values in Table IV of Appendix II. The average absolute deviation between the experimental and calculated values is 0.0698.

For the systems of nitrogen-methane vapor-liquid equilibria at 130.1 °K, the net area of the $\ln \gamma_1 / \gamma_2$ versus x_1 plot is 0.0001 units indicating that the data is consistent.

For the system of nitrogen-ethane at 130.1 °K, the vapor-liquid equilibria from $x_1 = 0.0314$ to $x_2 = 0.2853$ were tested by Equation(4-4). The value on the left hand side was 0.1083 units and the value on the right hand side was 0.1085 units also indicating that the data is consistent.

For the system of methane-ethane at 130.1 °K, the net area of the $\ln \gamma_1 / \gamma_2$ versus x_1 plot is 0.0002 units which may be considered thermodynamically consistent for this binary vapor-liquid equilibria.

The $\ln \gamma_1 / \gamma_2$ versus composition diagrams for the binary systems nitrogen-methane, nitrogen-ethane and methane-

ethane at 130.1 °K are shown in Figures 4-5, 4-6 and 4-7 respectively.

The average absolute deviations between the experimental $\ln r$ -values and values predicted by the modified Redlich-Kwong equation of state are given in Table 4-2.

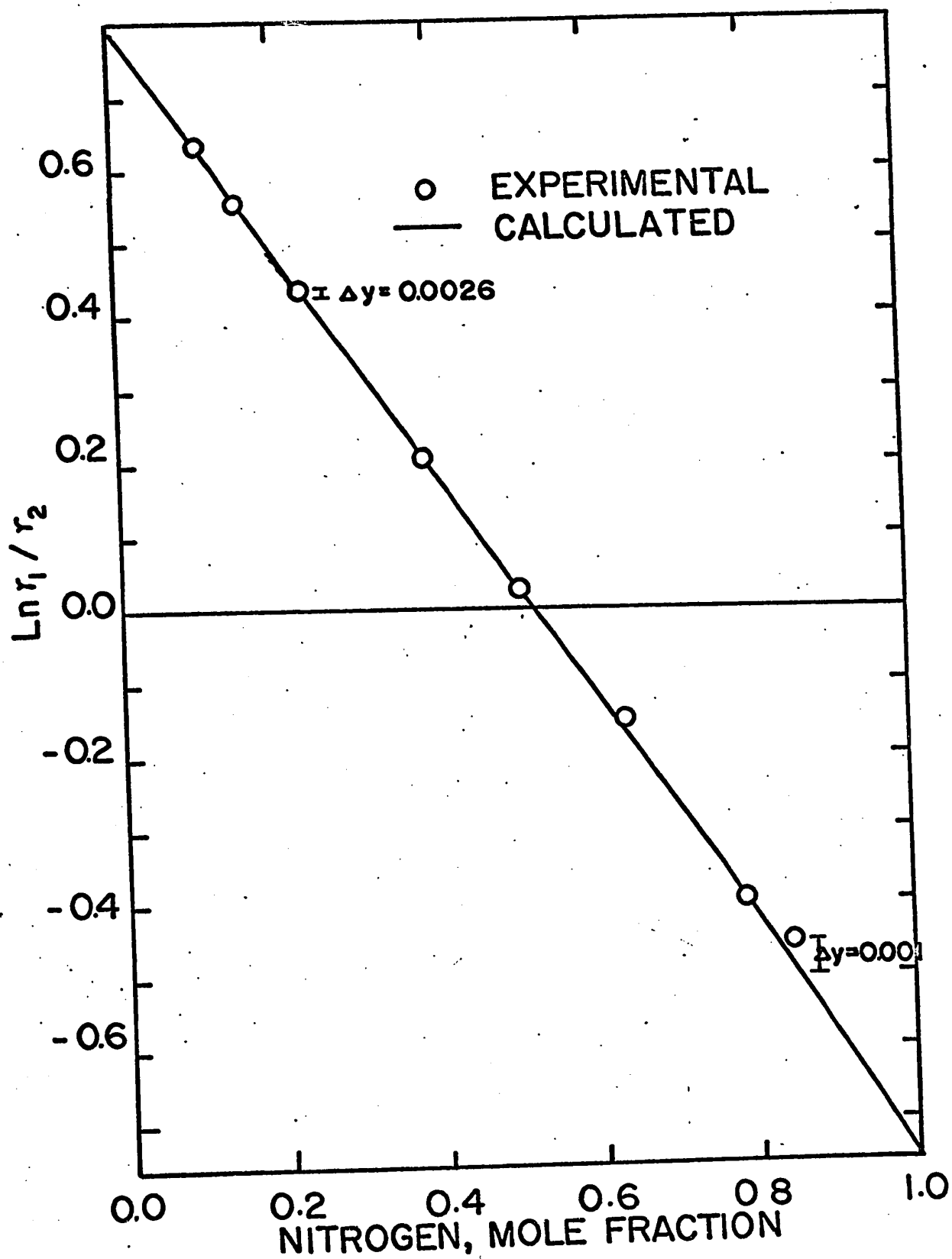


Figure 4-5 Area-test for the Nitrogen-Methane System at 130.1 °K

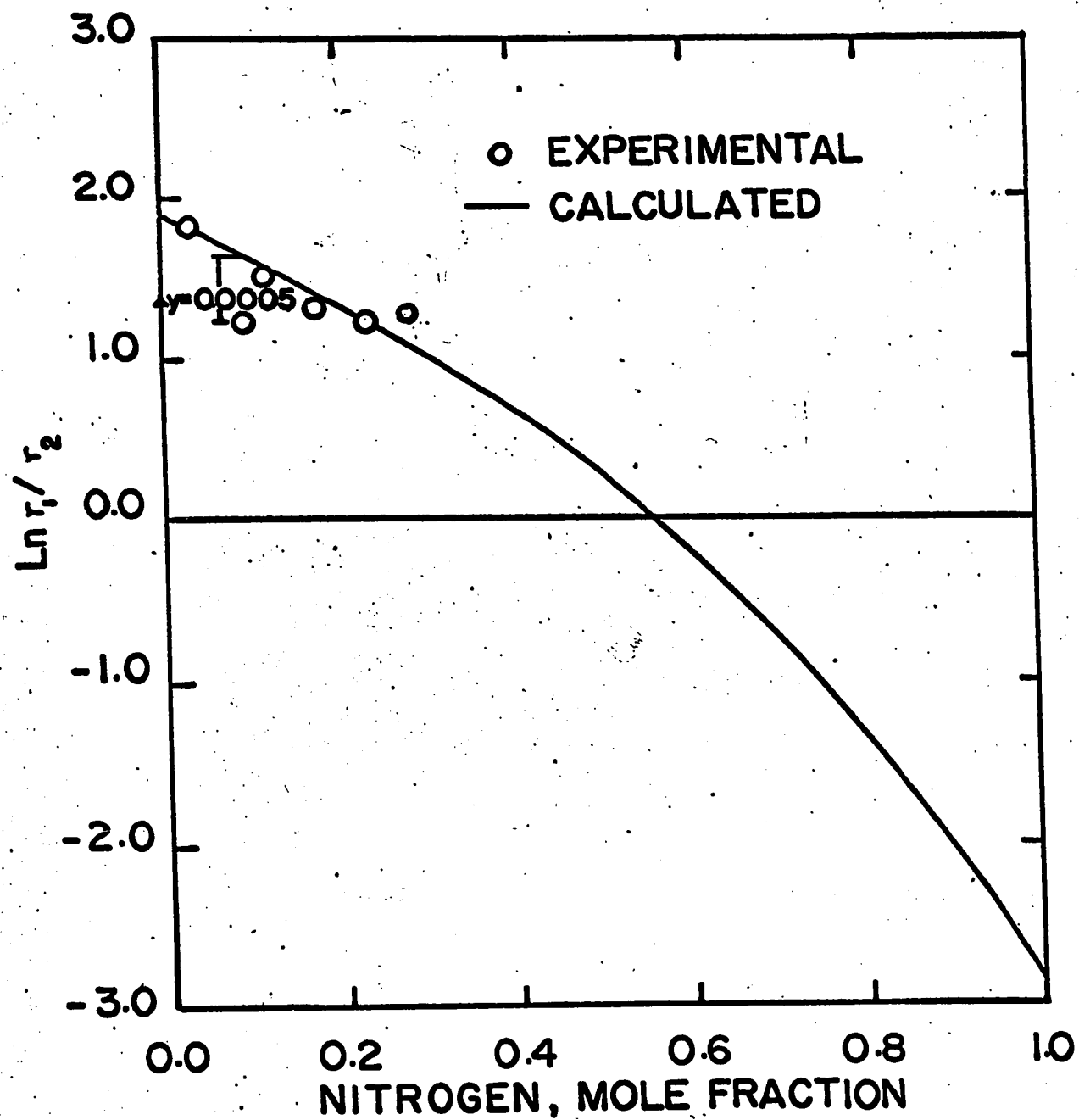


Figure 4-6 Area-test for the Nitrogen-Ethane System at 130.1 °K

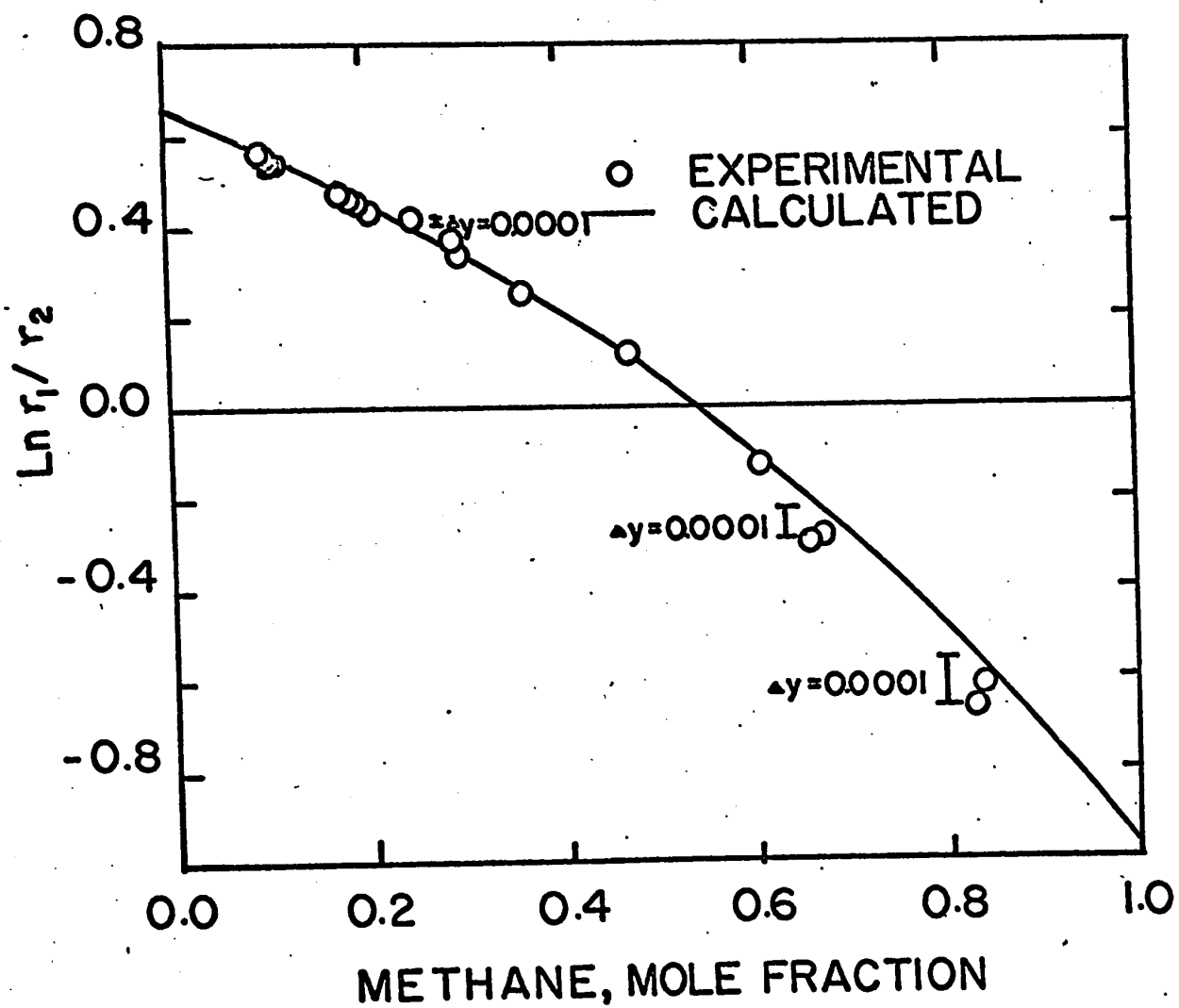


Figure 4-7 Area-test for the Methane-Ethane System at 130.1 °K

TABLE 4-2The Average Absolute Deviations BetweenThe Experimental and Calculated $\ln \gamma$

System	Average Absolute Deviation		
	$\Delta \ln \gamma$ 1	$\Delta \ln \gamma$ 2	$\Delta \ln \gamma$ 3
Nitrogen(1)-Methane(2)	0.0120	0.0167	
Nitrogen(1)-Ethane(2)	0.0759		0.2429
Methane(2)-Ethane(3)		0.0269	0.0442
Nitrogen(1)-Methane(2) -Ethane(3)	0.0280	0.0351	0.1464

Values of K'_H , K'_{c_1} and K'_{c_2} were plotted against K'_{N_2} for liquid-liquid equilibrium data on log-log scales over the temperature range from 94° to 133° K in Figures 4-8, 4-9 and 4-10 respectively. From these plots, changes of K'_H , K'_{c_1} and K'_{c_2} with temperature, at constant K'_{N_2} values were obtained. These values are plotted in Figures 4-13 to 4-18. Since the curves of K'_H , K'_{c_1} and K'_{c_2} at constant K'_{N_2} were discontinuous at the temperature higher and lower than the liquid-phase inversion temperature, each plot was separated into two figures, one at the temperature higher than the liquid-phase inversion temperature, the another at the temperature low than the liquid-phase inversion temperature. From these figures, it can be seen that at constant K'_{N_2} , values of K'_H , K'_{c_1} and K'_{c_2} tend to decrease with the decrease in temperature, at temperatures higher than the liquid-phase inversion temperature. However, at temperatures lower than the liquid-phase inversion temperature, values of K'_H and K'_{c_2} increase with the decrease in temperature, and the values of K'_{c_1} increase with the increase in temperature at constant K'_{N_2} values.

In Figures 4-11 and 4-12, values of K'_{N_2} and K'_{c_1} were

plotted as functions of pressure. As concentration of ethane is extremely low in the vapor phase, any small variation of the ethane concentration in vapor phase composition would considerably affect the K_{c_2} values. For this reason, no correlation was made for K_{c_2} .

In the separation of methane and ethane from natural gases, it is desirable to design a separation process at low temperatures. The necessary information for calculating ternary liquid-liquid-vapor equilibrium data may be derived from Figures 4-8 to 4-18.

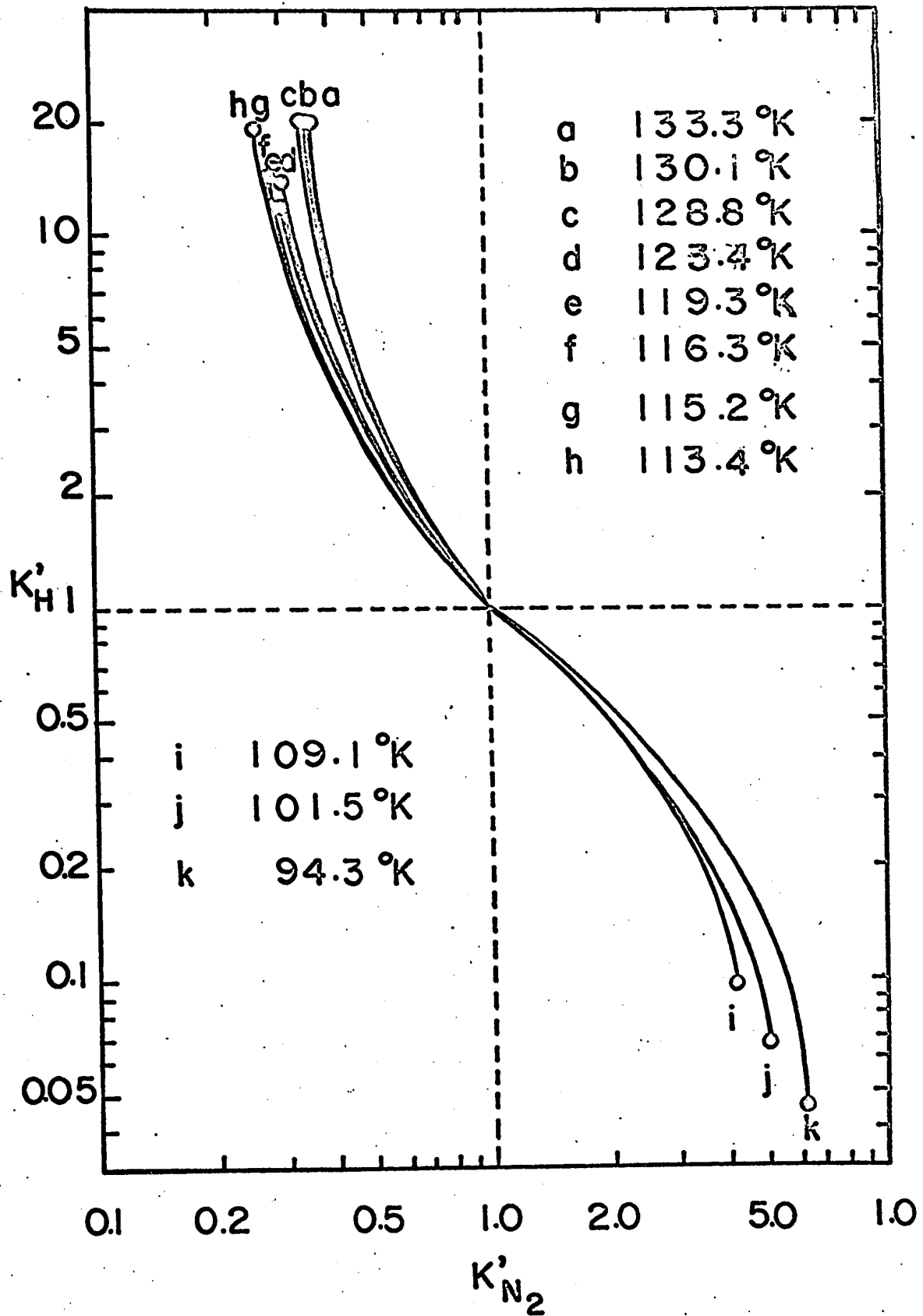


Figure 4-8 Correlation of K'_H with K'_{N_2}

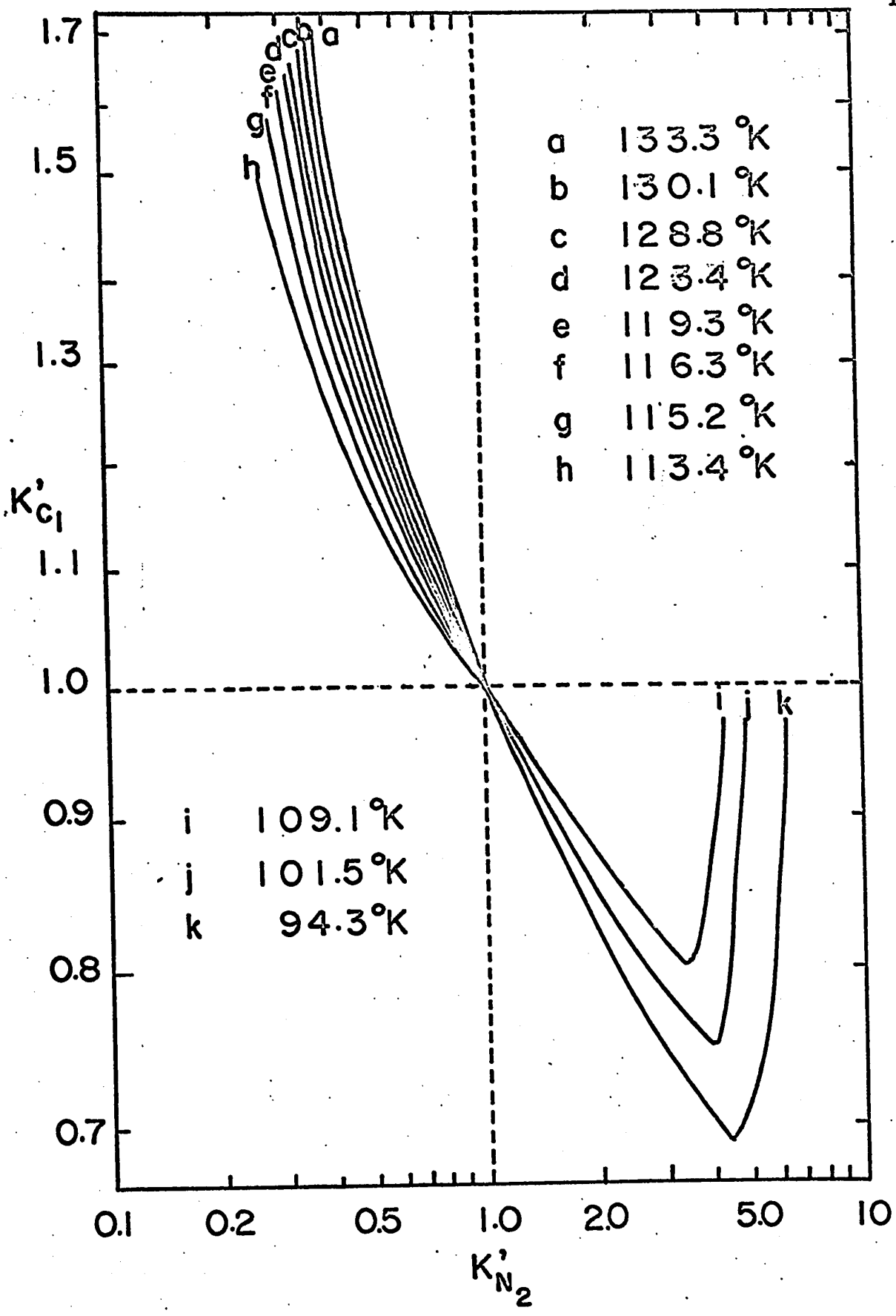


Figure 4-9 Correlation of K'_{c1} with K'_{N2}

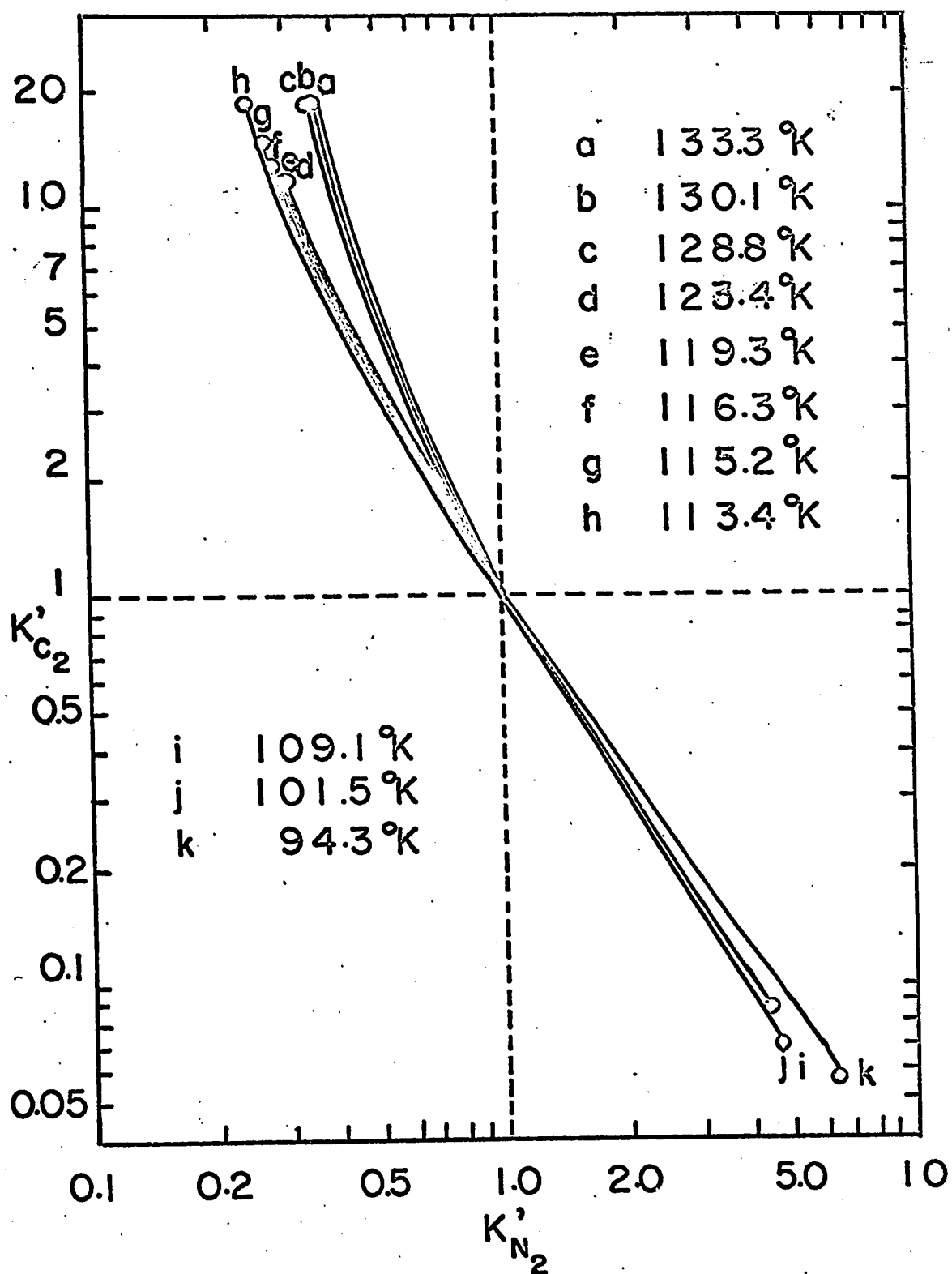


Figure 4-10 Correlation of K'_{c2} with K'_{N2}

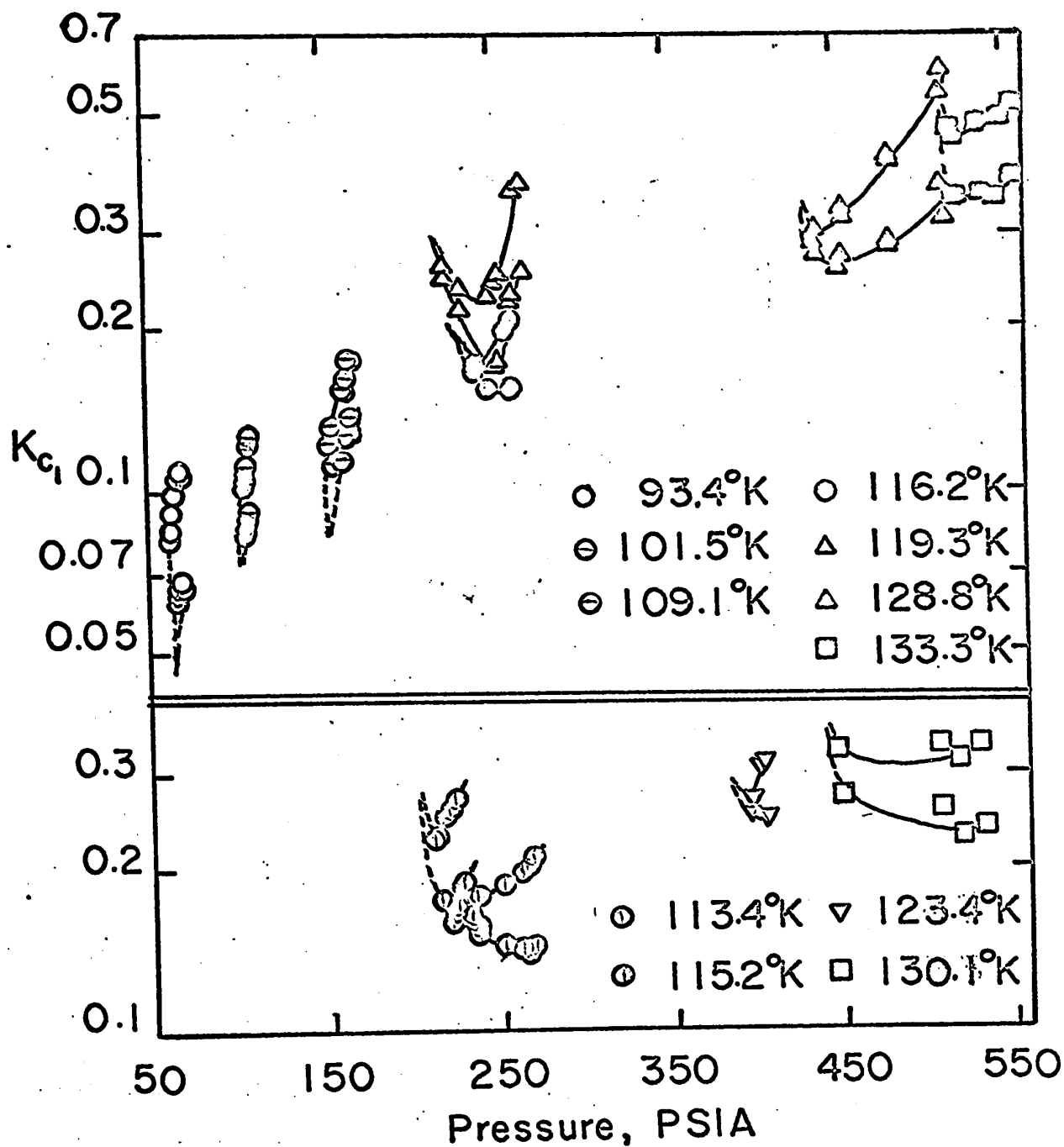


Figure 4-11 Correlation of K_{c1} with Pressure

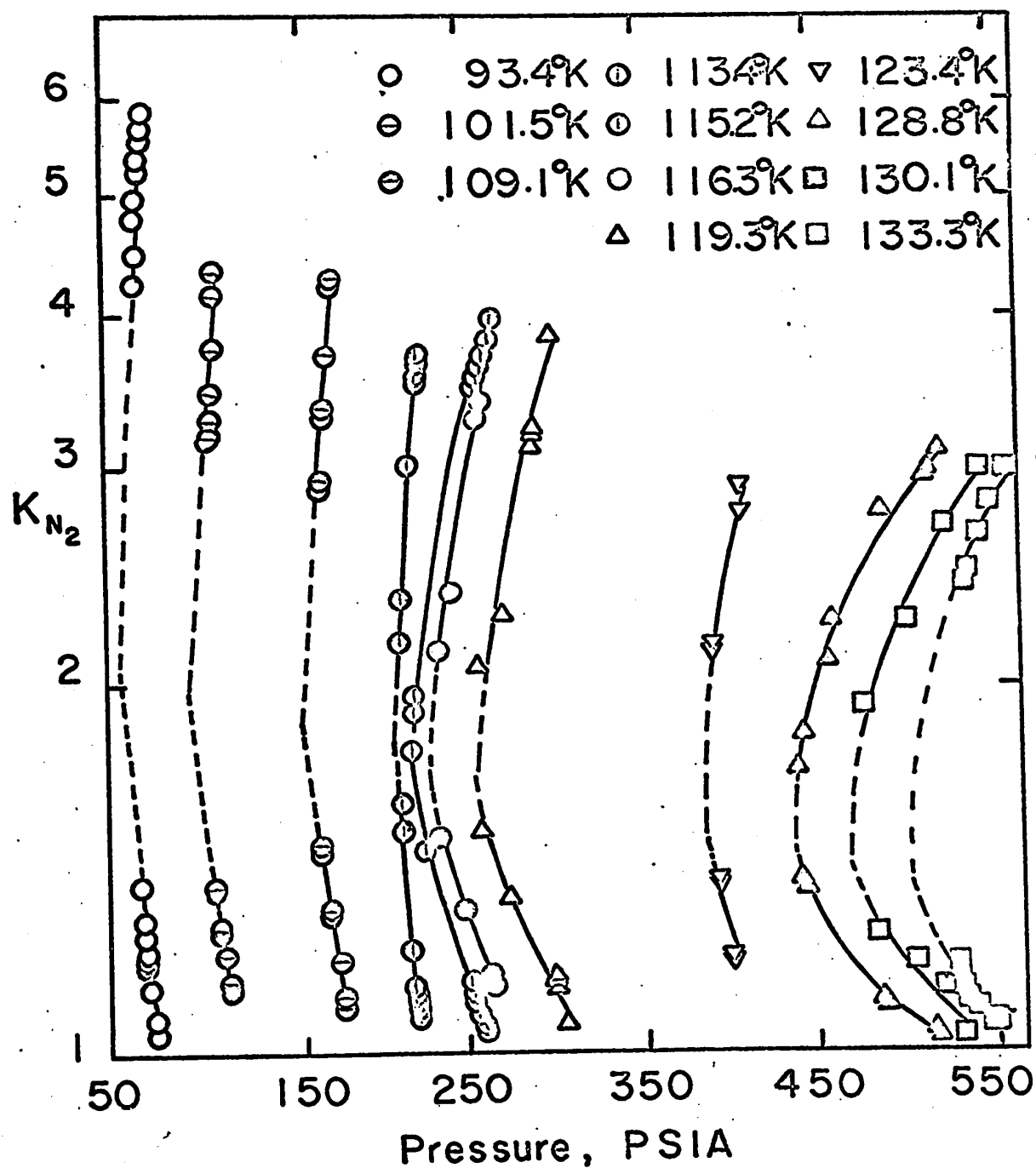


Figure 4-12 Correlation of K_{N_2} with Pressure

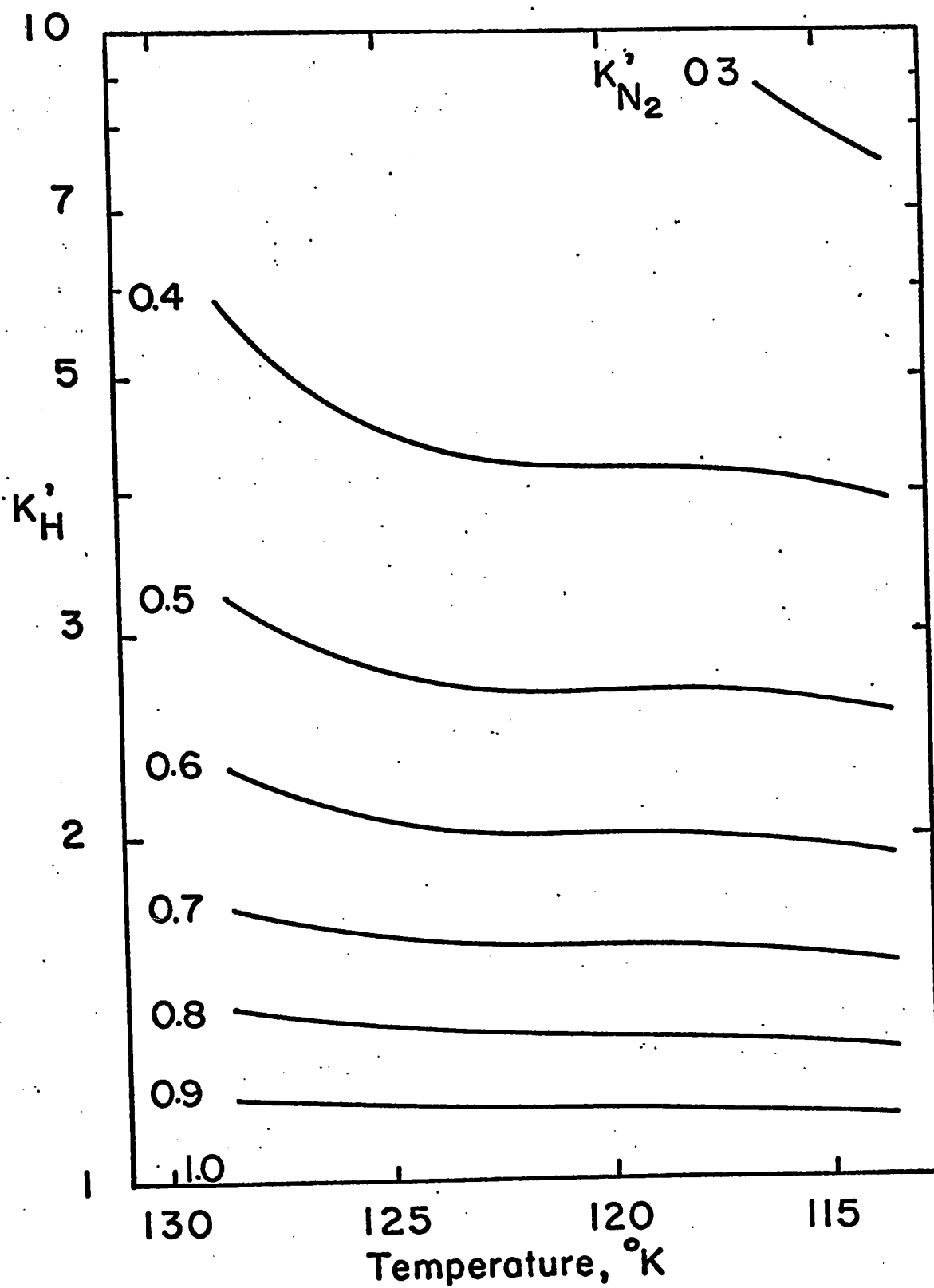


Figure 4-13 Correlation of K'_H with Temperature

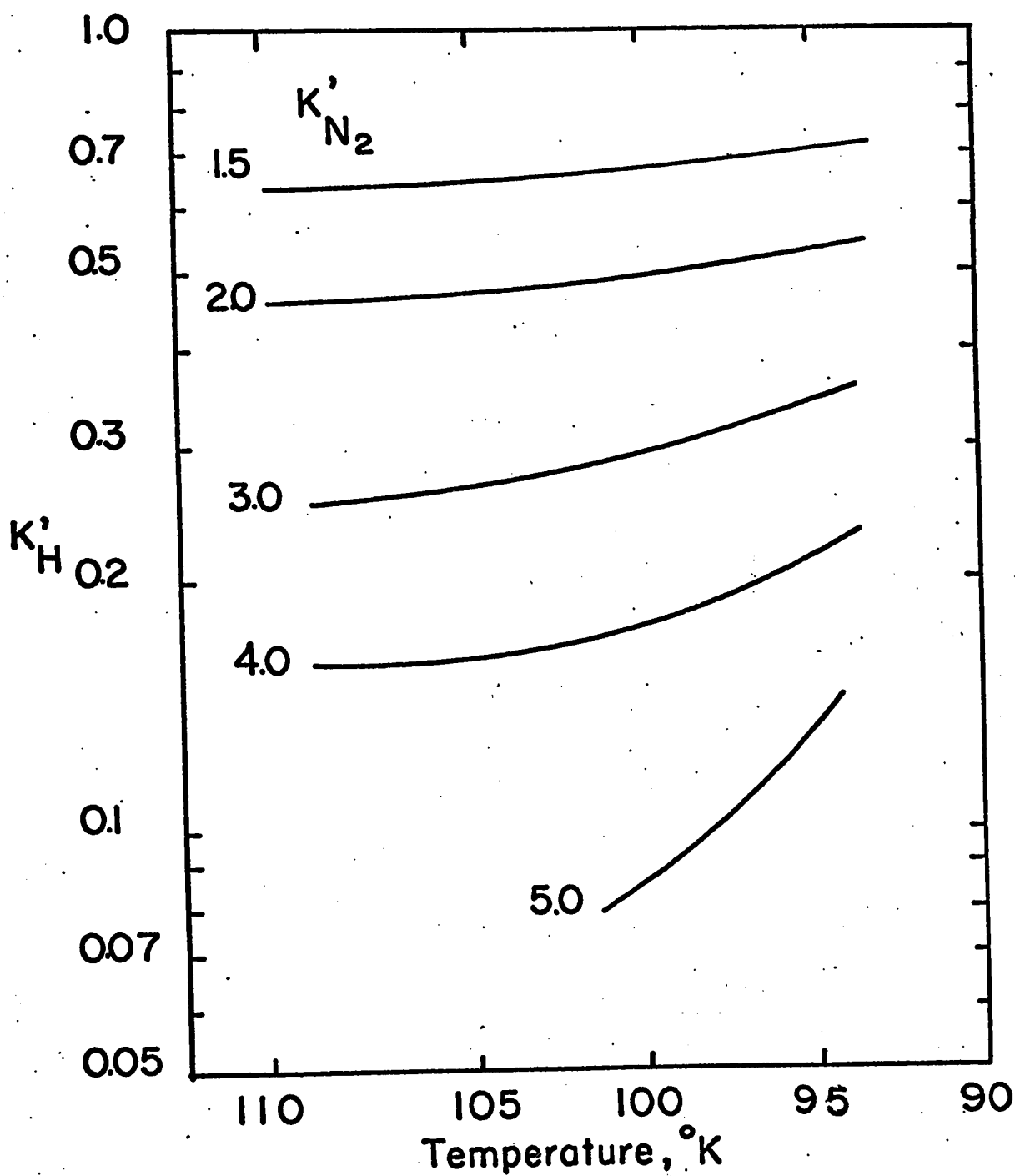


Figure 4-14 Correlation of K'_H with Temperature

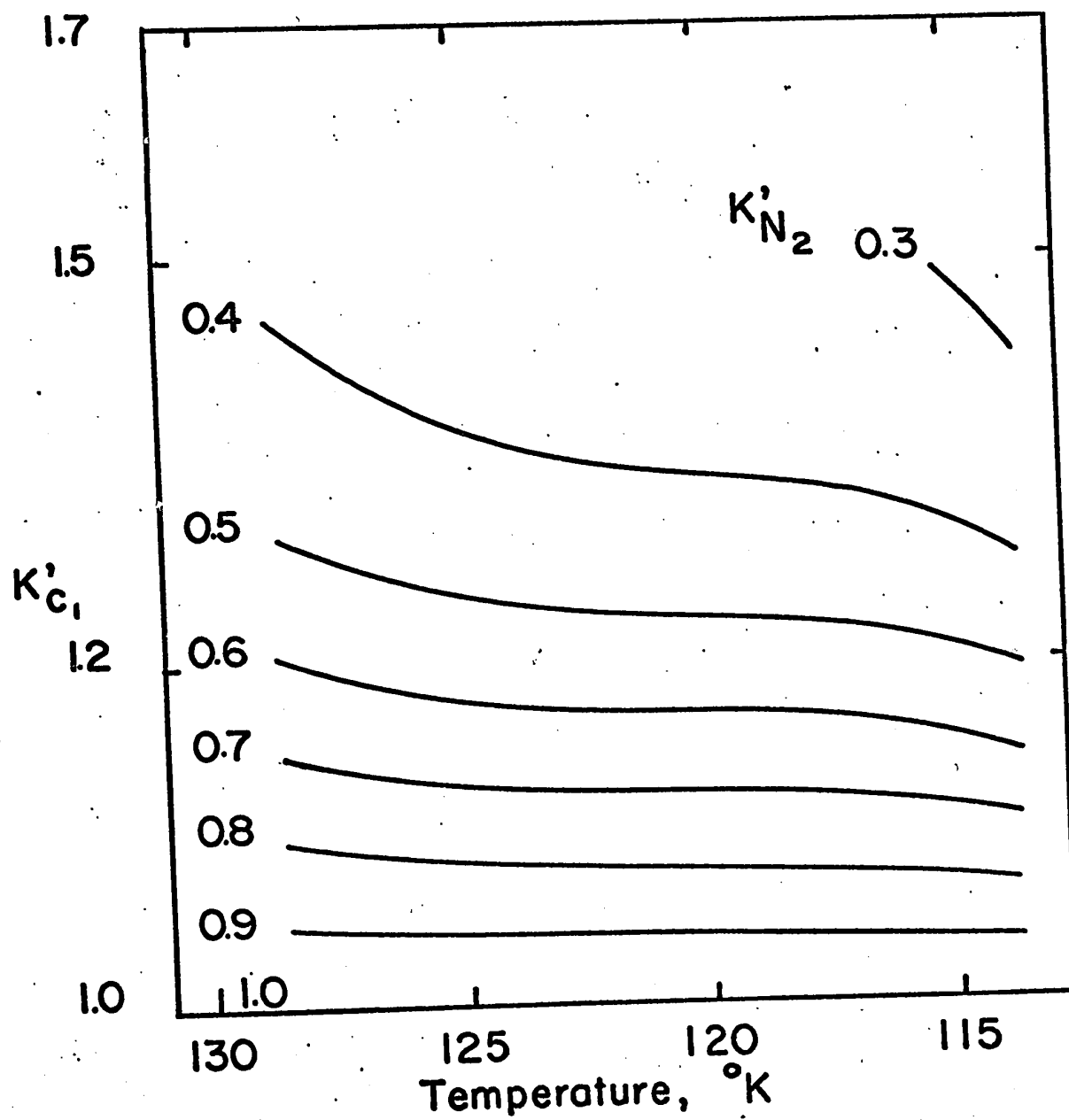


Figure 4-15 Correlation of K'_{c1} with Temperature

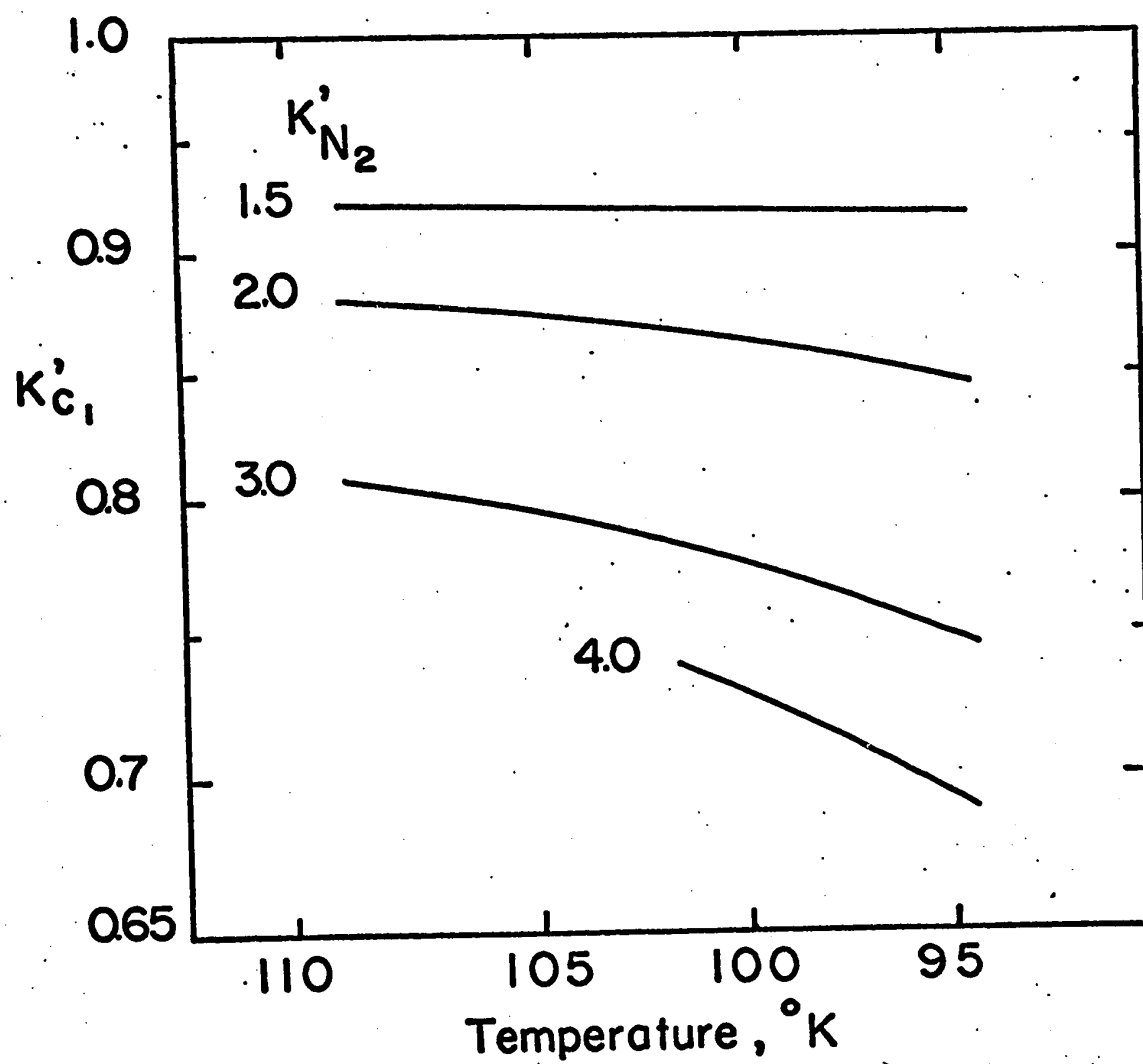


Figure 4-16 Correlation of K'_{c1} with Temperature

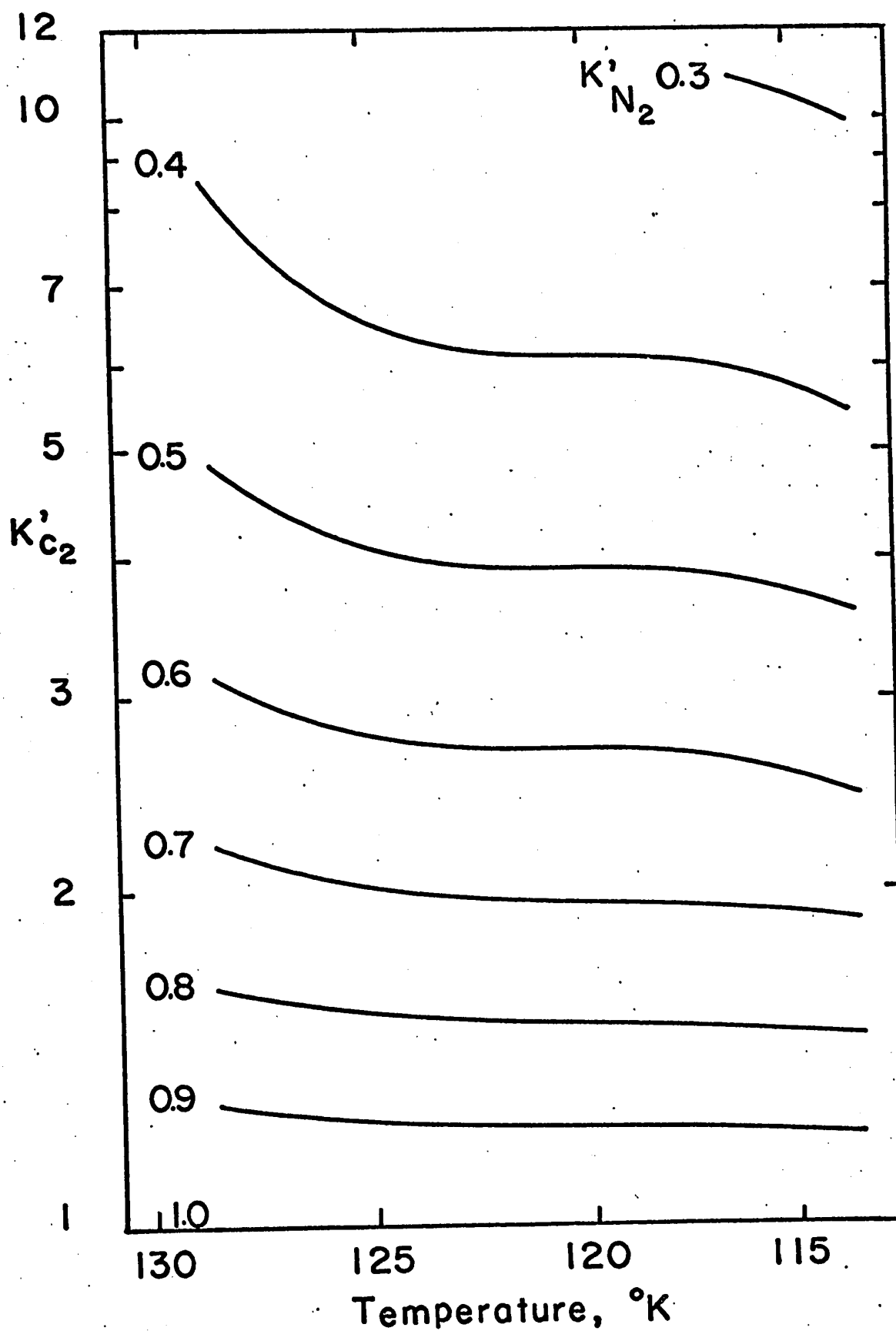


Figure 4-17 Correlation of K'_{c2} with Temperature

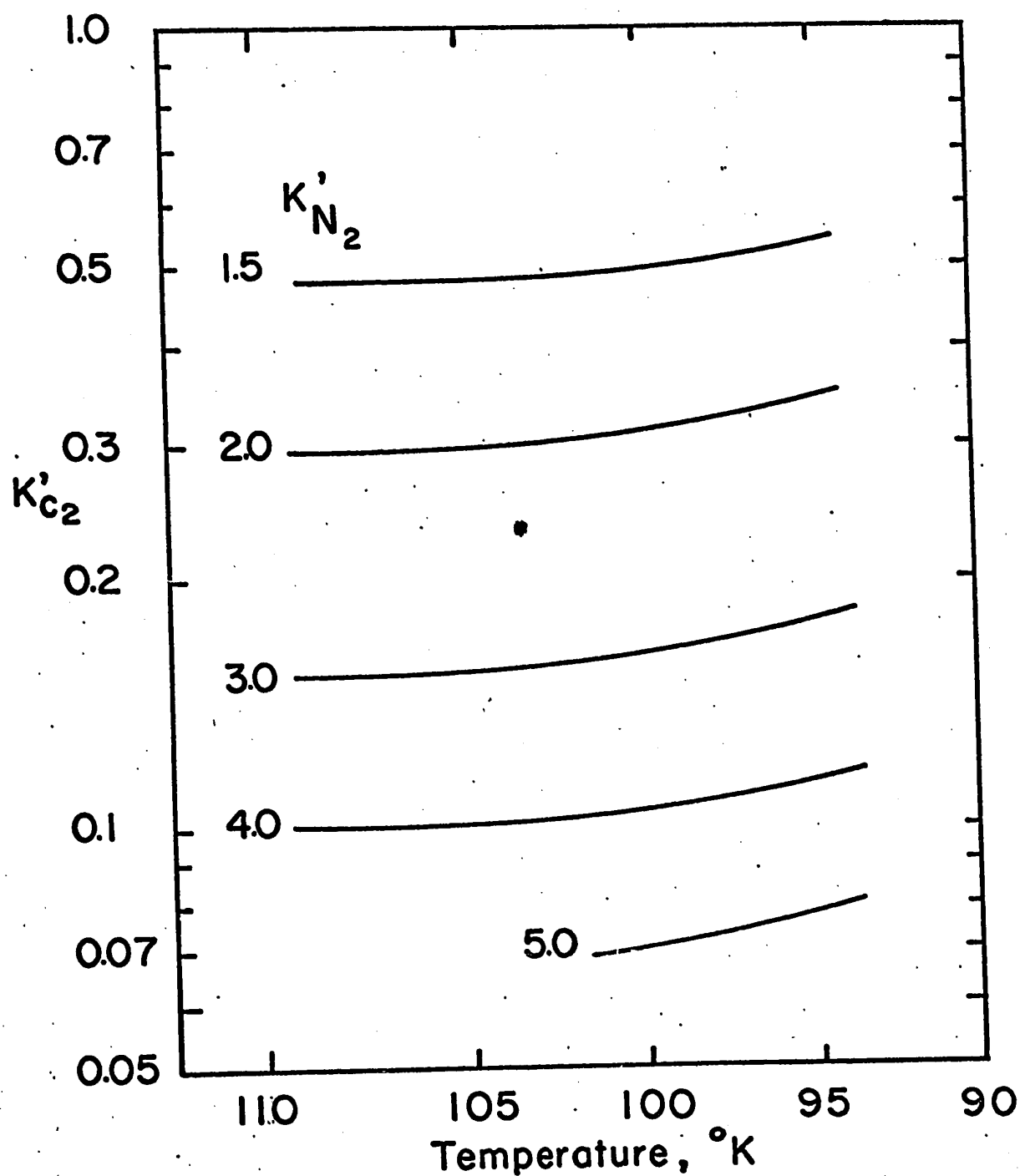


Figure 4-18 Correlation of K'_{c_2} with Temperature

CHAPTER V

LIQUID-LIQUID-VAPOR EQUILIBRIA

AT

THE CONDITIONS OF LIQUID INVERSION

A. INTRODUCTION

At a temperature of 111.4 °K and a pressure of 201.2 psia, a liquid-phase inversion occurred for the nitrogen-methane-ethane system. At this temperature and pressure, the recirculated vapor, which was condensed before re-entering the cell, rose slowly along the cell in large bubbles. Then the bottom liquid layer crept upwards along the walls of the cell and eventually formed a middle phase(layer 2 in Figure 5-1) which had the least surface tension as indicated by its concave meniscus. The formation of the liquid-phase inversion is depicted in sequence in Figure 5-1. This phenomena appeared also with the binary system of nitrogen-ethane.

At inversion temperatures, a slight adjustment of the fine temperature control dial of the precision controller would produce the desired phase inversion effect. Adjustment of the fine temperature control dial by one division made a temperature difference of ± 0.001 °K. So the change in tem-

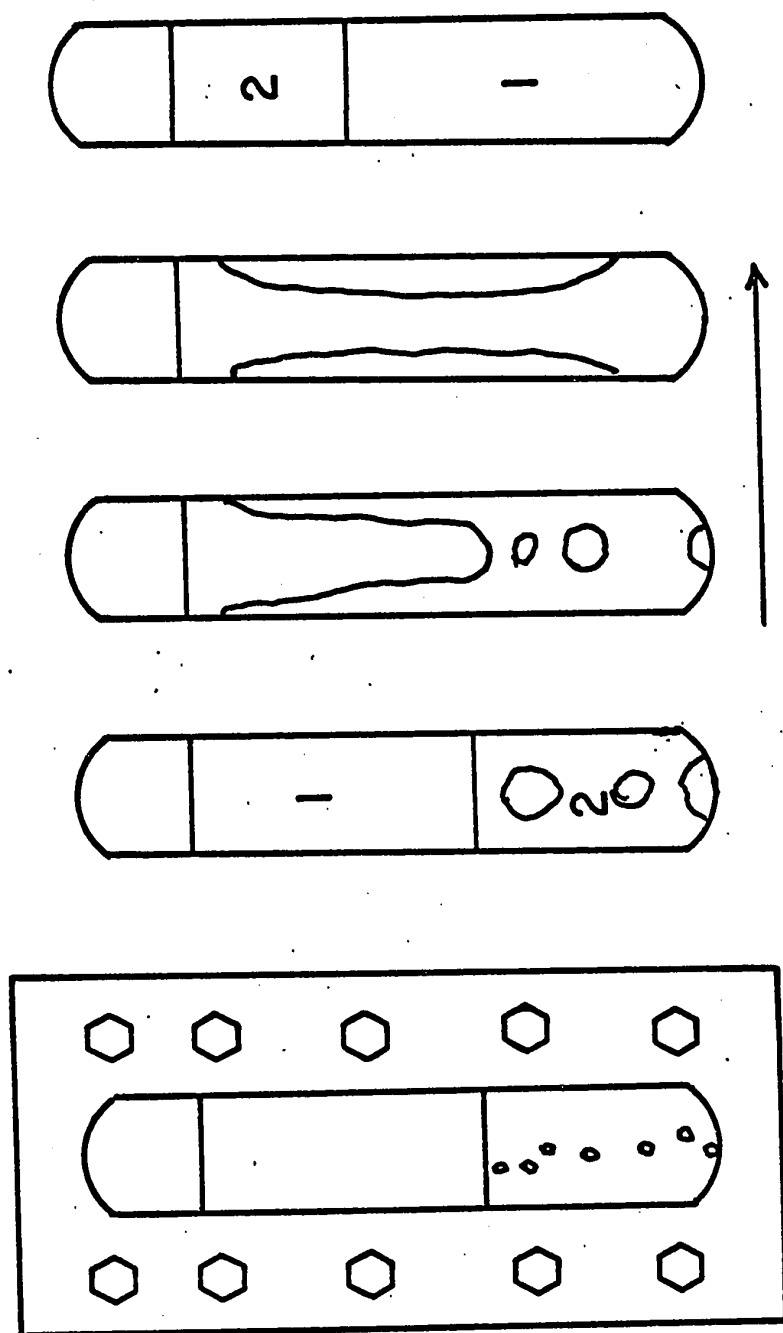


Figure 5-1 Sequence of Formation of the Liquid Phase Inversion in the Nitrogen-Methane-Ethane System

perature was much less than the experimental error, which was $\pm 0.1^\circ\text{K}$. Therefore the formation of liquid-phase inversion, which is shown in Figure 5-1, could be considered at the same temperature.

The liquid-phase inversion temperatures together with equilibrium compositions which were obtained in the investigation, are shown in Figure 5-2.

In order to understand the liquid-phase inversion phenomena, one must investigate the change of liquid densities with temperature and composition. In the literature, some experimental data of liquid densities of nitrogen methane, ethane and propane and their mixtures were reported. The purpose of this study is to propose a method for predicting liquid densities of the mixtures of this investigation and turn these available data to test the validity of the proposed method.

B. DENSITY OF PURE NITROGEN, METHANE AND ETHANE

A survey of liquid densities of pure components revealed that the decrease of nitrogen density(41) with the increase of temperature is faster than that for the paraffins (41,42,110). As shown in Figure 5-3, at temperatures below 109.1°K the density of nitrogen is higher than that of ethane and at temperatures above 109.1°K , the reverse is true.

From Figure 5-3, the density curve of pure liquid

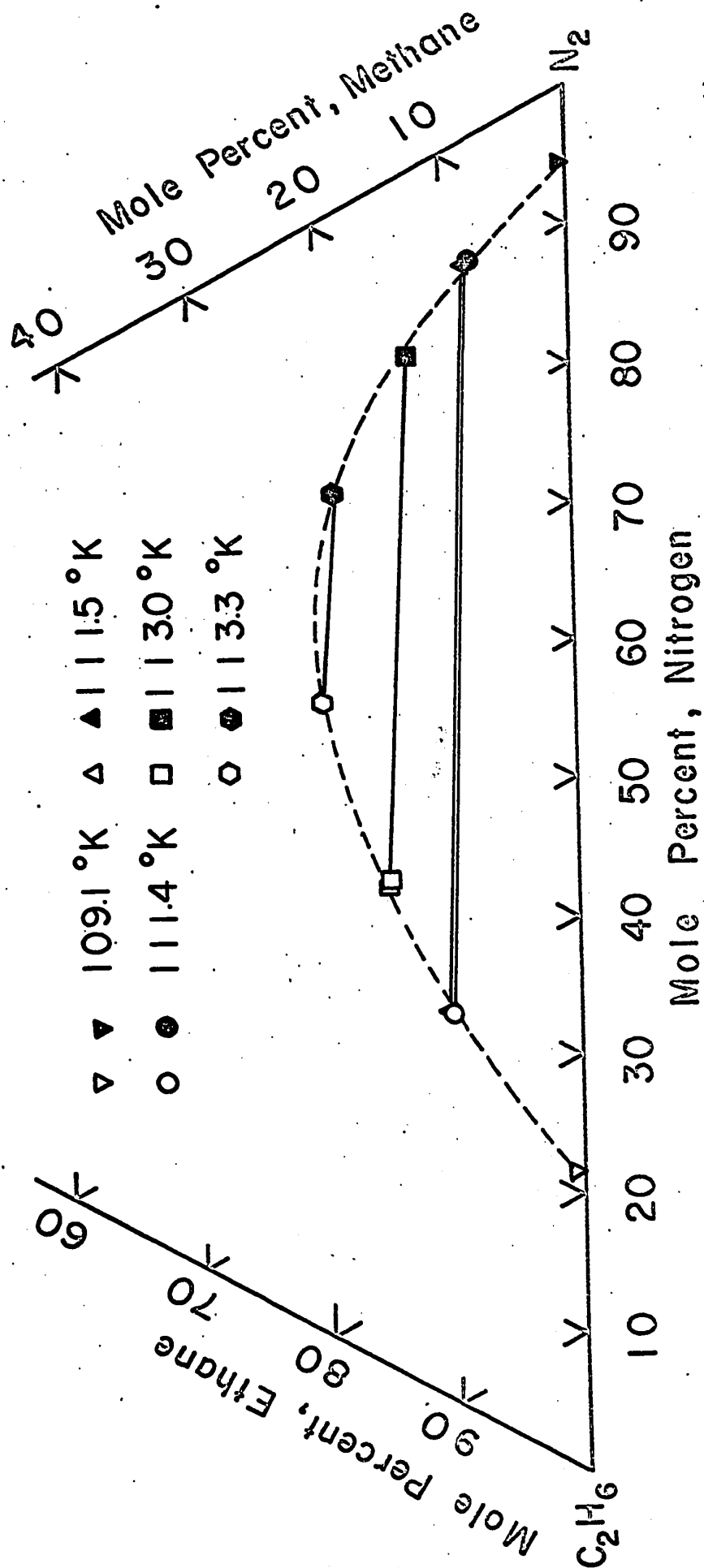


Figure 5-2 Nitrogen-Methane-Ethane System at Liquid Phase Inversion Condition

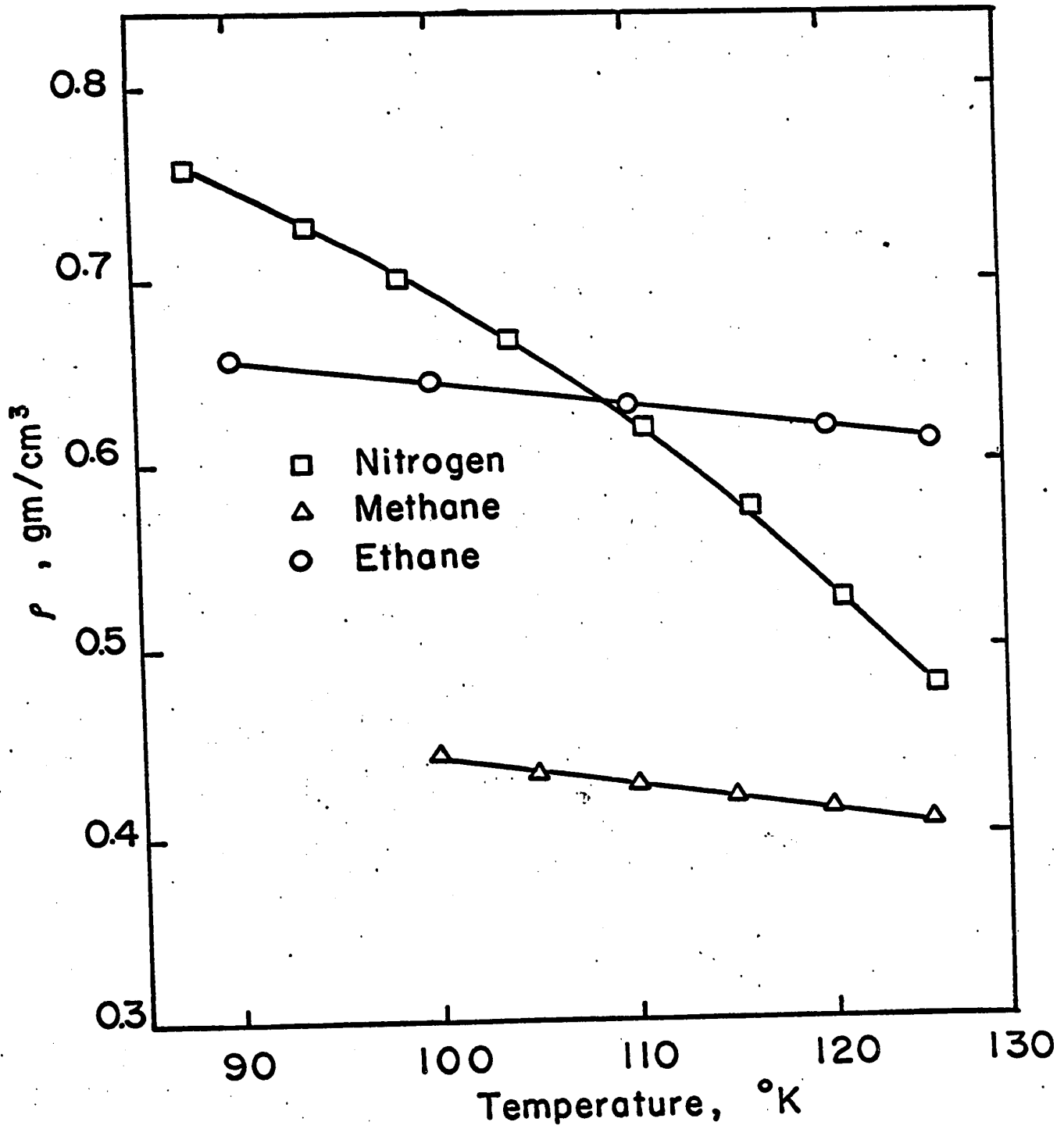


Figure 5-3 Liquid Densities of Pure Components

ethane crosses that of nitrogen at 109.1 °K. This implies that the density of liquid nitrogen is identical to the density of ethane at 109.1 °K. Further investigation of experimental equilibrium data for the binary system of nitrogen-ethane was conducted at temperatures lower than 113 °K. The reversal of the liquid phases for this system also took place in the vicinity of 109.1 °K. The bottom phase changed from the ethane-rich liquid to the nitrogen-rich liquid. It was of interest to note that the liquid-phase inversion for the nitrogen-ethane binary system took place at the temperature at which both pure nitrogen and ethane had the same liquid density.

However, one liquid phase only was observed in this investigation for the nitrogen-methane system.

C. PREDICTION OF LIQUID DENSITY BY THE REDLICH-KWONG EQUATION OF STATE

The purpose of this section is to formulate a method to predict liquid densities by the modified Redlich-Kwong equation of state(80).

(1) The Original Redlich-Kwong Equation of State

The original Redlich-Kwong equation of state(63) is of the following form:

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

5-1

$$h = BP/Z \quad 5-2$$

$$A^2 = \Omega_{a,c} T^{2.5} / P T^{2.5} = a/R T^{2.5} \quad 5-3$$

$$B = \Omega_{b,c} T / P T = b/RT \quad 5-4$$

$$\Omega_a = 0.4278 \quad 5-5$$

$$\Omega_b = 0.0867 \quad 5-6$$

where Z is $\frac{PV}{RT}$, compressibility factor; a and b are parameters.

The values of Ω_a and Ω_b were obtained originally by setting the first and second partial derivatives of pressure with respect to volume equal to zero at the critical point.

Namely, $(\frac{\partial P}{\partial V})_{T_c} = 0$ and $(\frac{\partial^2 P}{\partial V^2})_{T_c} = 0$. In this investigation, following up the approach of Chang and Lu(83), Ω_a and Ω_b are treated as temperature-dependent, below its critical temperature, from the pressure-volume-temperature of the pure liquid. The procedure to calculate Ω_a and Ω_b is presented in section 3.

(2) Pressure-Volume-Temperature Data of Saturated Liquid

The P-V-T data of the saturated liquid are available in the literature for pure nitrogen, methane, ethane and propane.

Most of these P-V-T data are presented in the book by Din(41,110).

In this study, the sources of pure component P-T and V-T data were taken from the National Bureau of Standard(NBS) of America, Washington D.C,(108,111), Din (41,110),Kloskey(42) and Roche(43). The sources are listed in Table 5-1. The critical constants are listed in Table 5-2.

TABLE 5-1The Sources of Pressure-Volume-TemperatureData at Saturated Condition

<u>Component</u>	<u>Temp. Range (°K)</u>	<u>Properties</u>	<u>Sources</u>
Nitrogen	63.15-122.55	P-V-T	111
	88.56-133.1	T-V	42
Methane	90.00-112.0	T-V	43
	91.00-190.0	P-T	108
	88.56-133.1	T-V	42
Ethane	89.88-305.5	P-T-V	41
	88.56-133.1	T-V	42
Propane	88.45-370.0	P-V-T	110
	88.56-133.0	T-V	42

TABLE 5-2The Critical Constants of Pure Component

Component	V_c cc./g-mole	P_c psia	T_c °K	Z_c	Ref.
Nitrogen	90.094	492.45	126.20	0.226	41
Methane	99.258	667.8	190.56	0.288	112
Ethane	147.95	707.8	305.44	0.285	112
Propane	203.51	616.3	369.83	0.281	112

(3) Procedure to Evaluate ρ_a and ρ_b (85)

The method developed by Chang and Lu(85) for evaluation of temperature-dependent parameters, ρ_a and ρ_b of the Redlich-Kwong equation of state in the subcritical region is presented as follows:

At equilibrium,

$$\rho^L = \rho^V \quad 5-7$$

The fugacity coefficient ϕ for a pure component is evaluated from the Redlich-Kwong equation of state by means of the following equation:

$$\ln \phi^L = Z^L - 1 - \ln Z^L - \ln(1-h^L) - (A^2/B) \ln(1+h^L) \quad 5-8$$

similarly

$$\ln \phi^V = Z^V - 1 - \ln Z^V - \ln(1-h^V) - (A^2/B) \ln(1+h^V) \quad 5-9$$

It may be readily shown that substituting Equations(5-8), (5-9), (5-1) and (5-2) into Equation(5-7) gives:

$$\ln Z^L \phi^V + 1 - Z^L + \ln(1-h^L) + \frac{(1-Z^L)(1-h^L)}{h^L(1-h^L)} \ln(1+h^L) = 0 \quad 5-10$$

These equations were employed in the evaluation of ρ_a and ρ_b .

The calculation procedure can be briefly outlined as follows:

- (1) For a given value of Z^L , and an assumed value of Q^V , the value of h^L can be obtained from Equation(5-10).
- (2) Calculate B by means of Equation(5-2) and A by means of Equation(5-1).
- (3) Substitute A and B values obtained from step 2 into Equations(5-1) and (5-2) and solve simultaneously for Z^V and h^V .
- (4) Calculate Q^V from Equation(5-9).
- (5) Obtain new h^L value from Equation(5-10) and compare it with that obtained in step 1. If they differ by more than a small tolerance, repeat the steps 1-5 using the new value of Q^V obtained from step 4.

An iteration loop is thus built up until the change of h^L value is less than the specified tolerance. The final set of A and B values are used to obtain Ω_a and Ω_b values from Equations(5-3) and (5-4), respectively. The tolerance used in this investigation is 0.00001.

The temperature-dependent parameters Ω_a and Ω_b , were evaluated for the pure components nitrogen, methane, ethane and propane. The calculated results are presented graphically in Figures 5-5 to 5-12 and the numerical values

are listed in Table I of Appendix III.

The schematic diagram for evaluating Ω_a and Ω_b by equalizing Q^V and Q^L is shown in Figure 5-4. The curve represents the modified Redlich-Kwong equation of state(85) with temperature parameters Ω_a and Ω_b , so as to give equal areas enclosed by the curve on both sides of the horizontal vapor pressure line. Equality that the fugacity coefficients of vapor and liquid for pure component are equal.

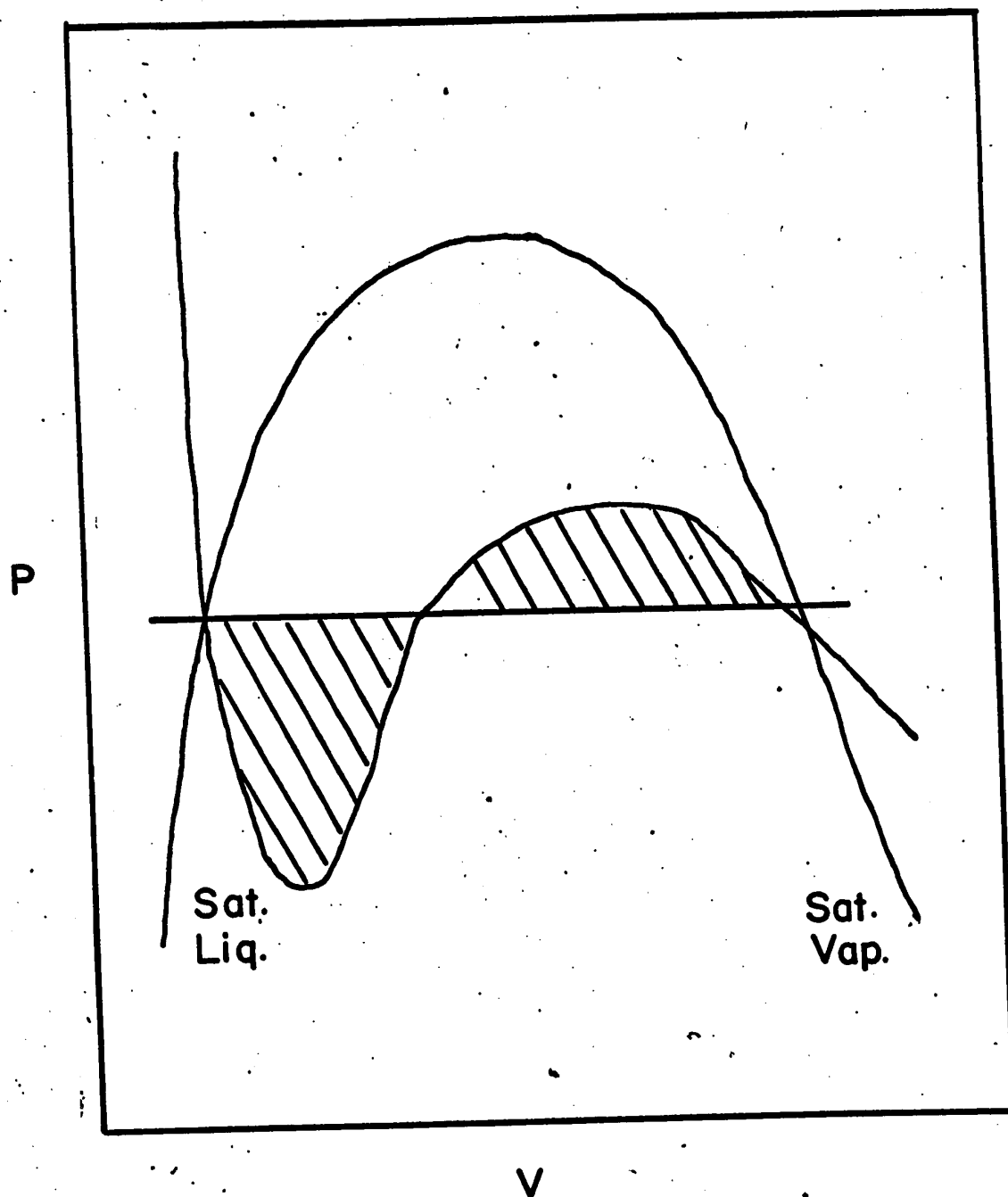


Figure 5-4 The Modified Redlich-Kwong Equation of State with Temperature Parameters

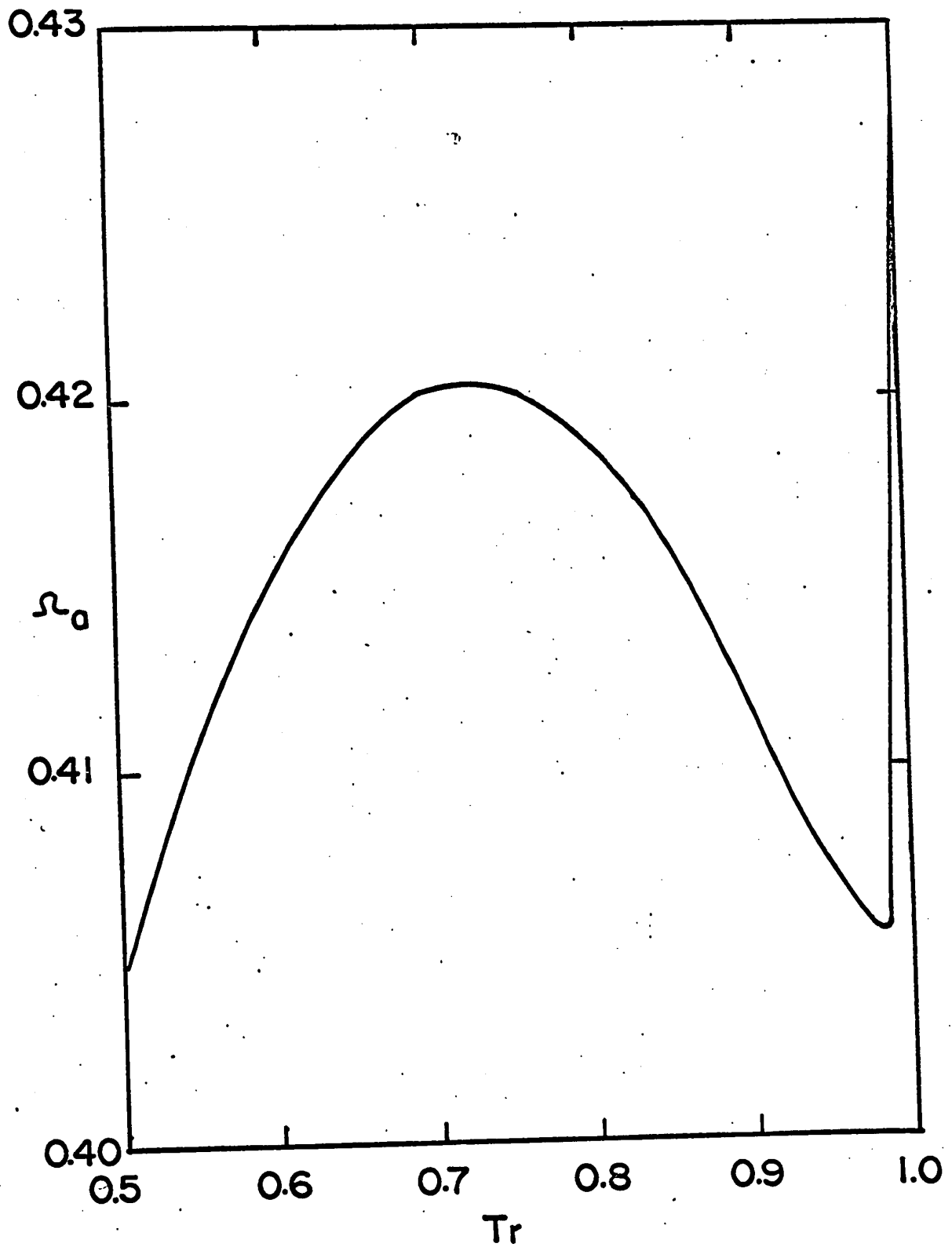


Figure 5-5 Ω_a Values for Nitrogen

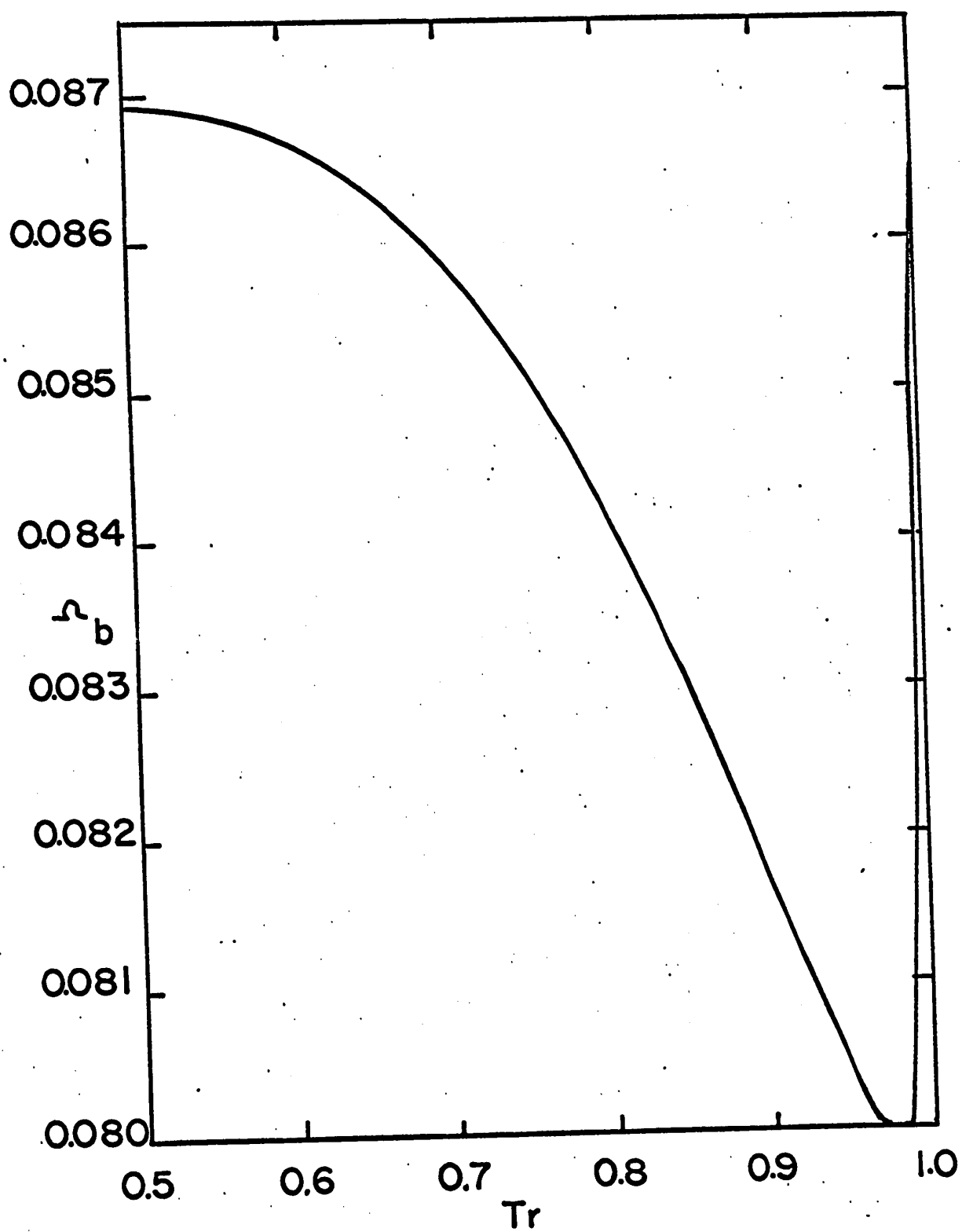


Figure 5-6 Ω_b Values for Nitrogen

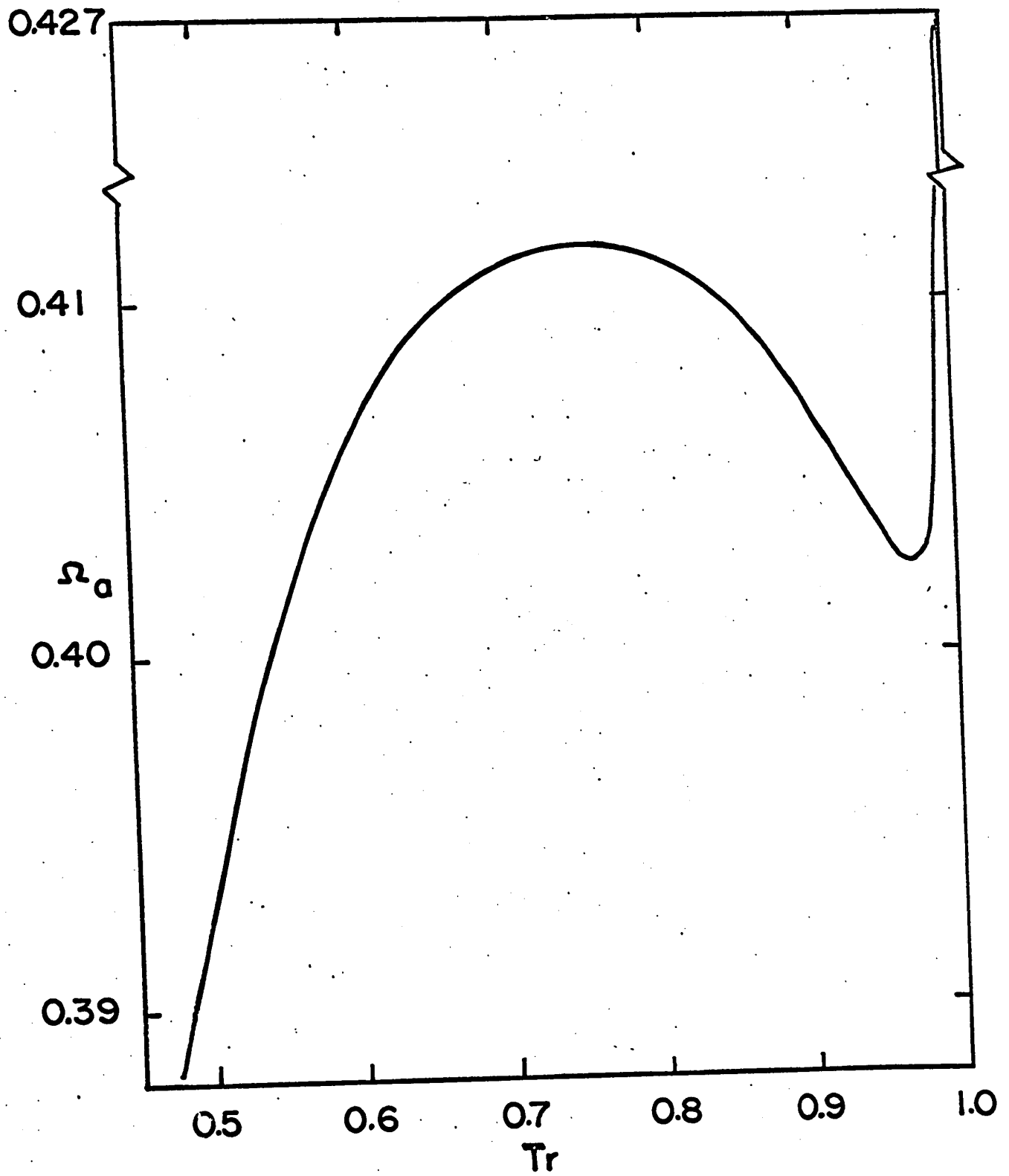


Figure 5-7 Ω_a Values for Methane

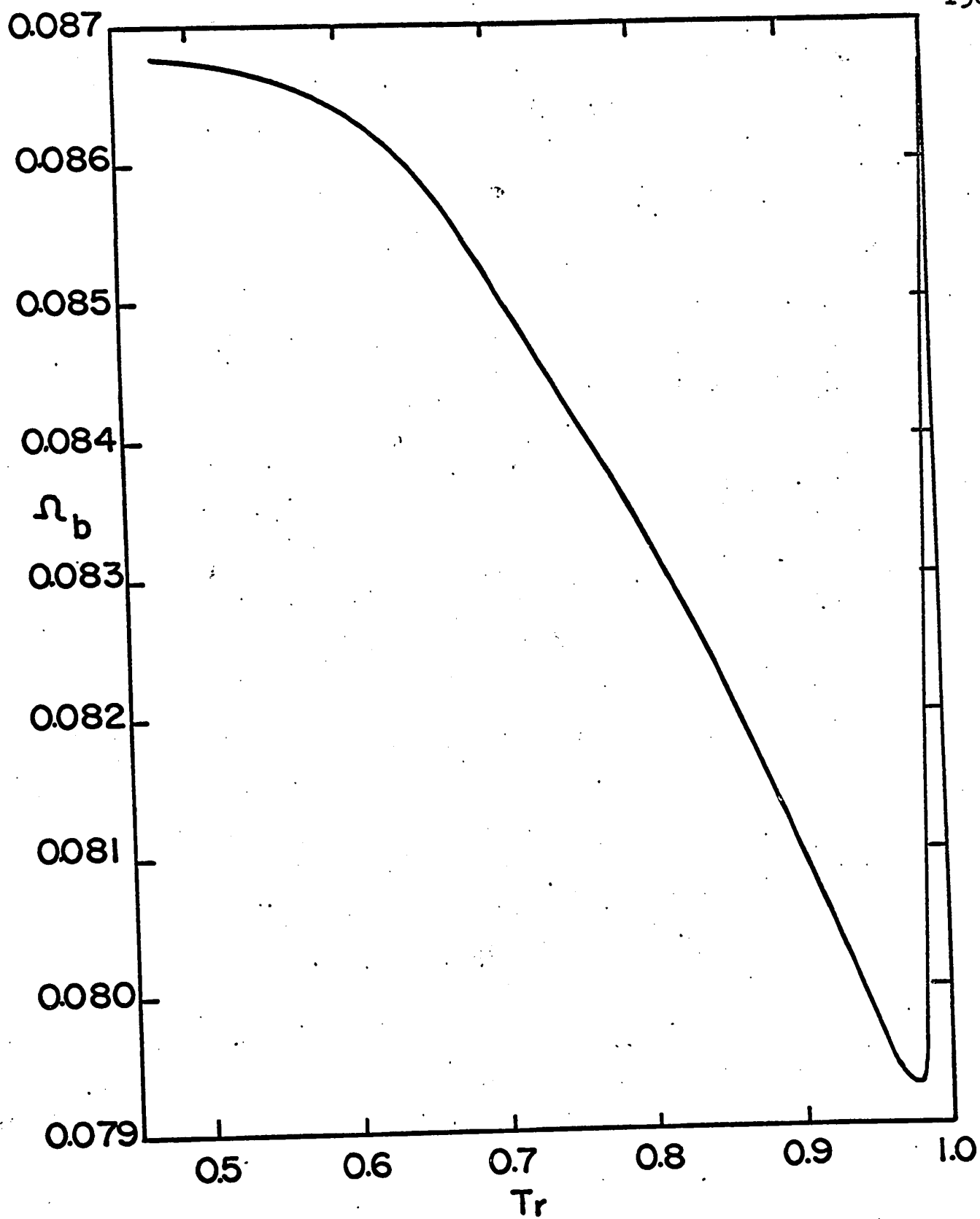


Figure 5-8 Ω_b Values for Methane

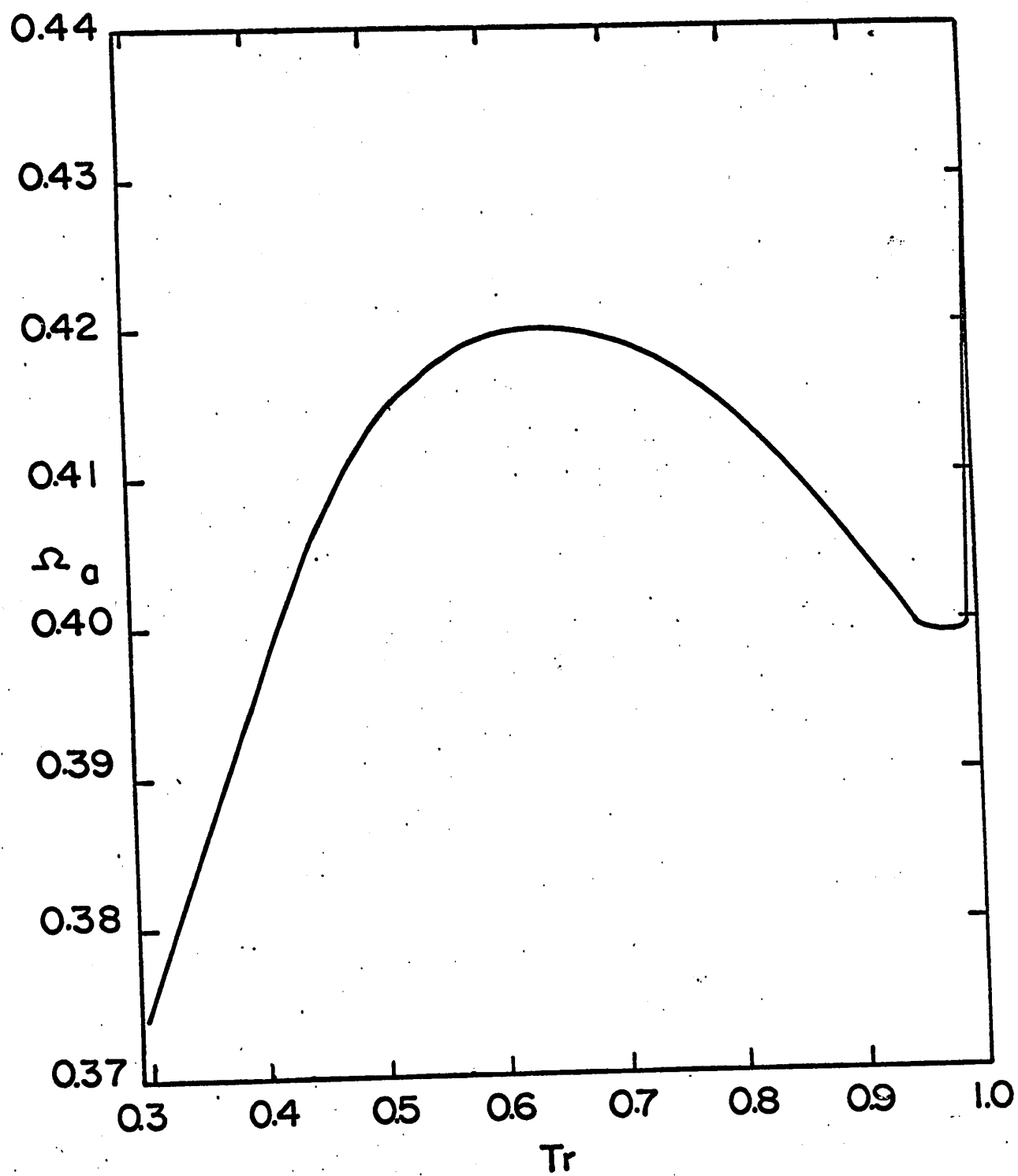


Figure 5-9 Ω_a Values for Ethane

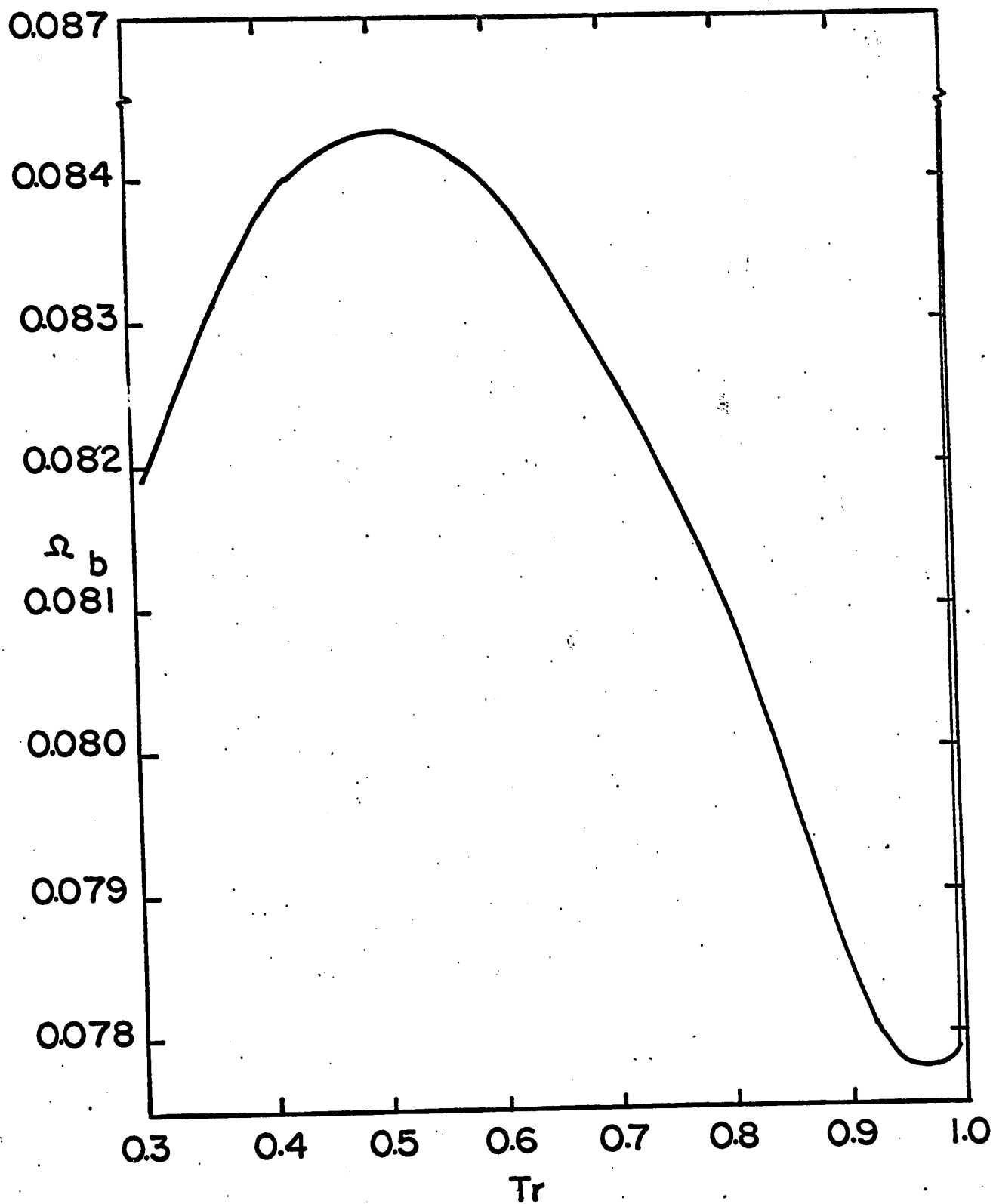


Figure 5-10 Ω_b Values for Ethane

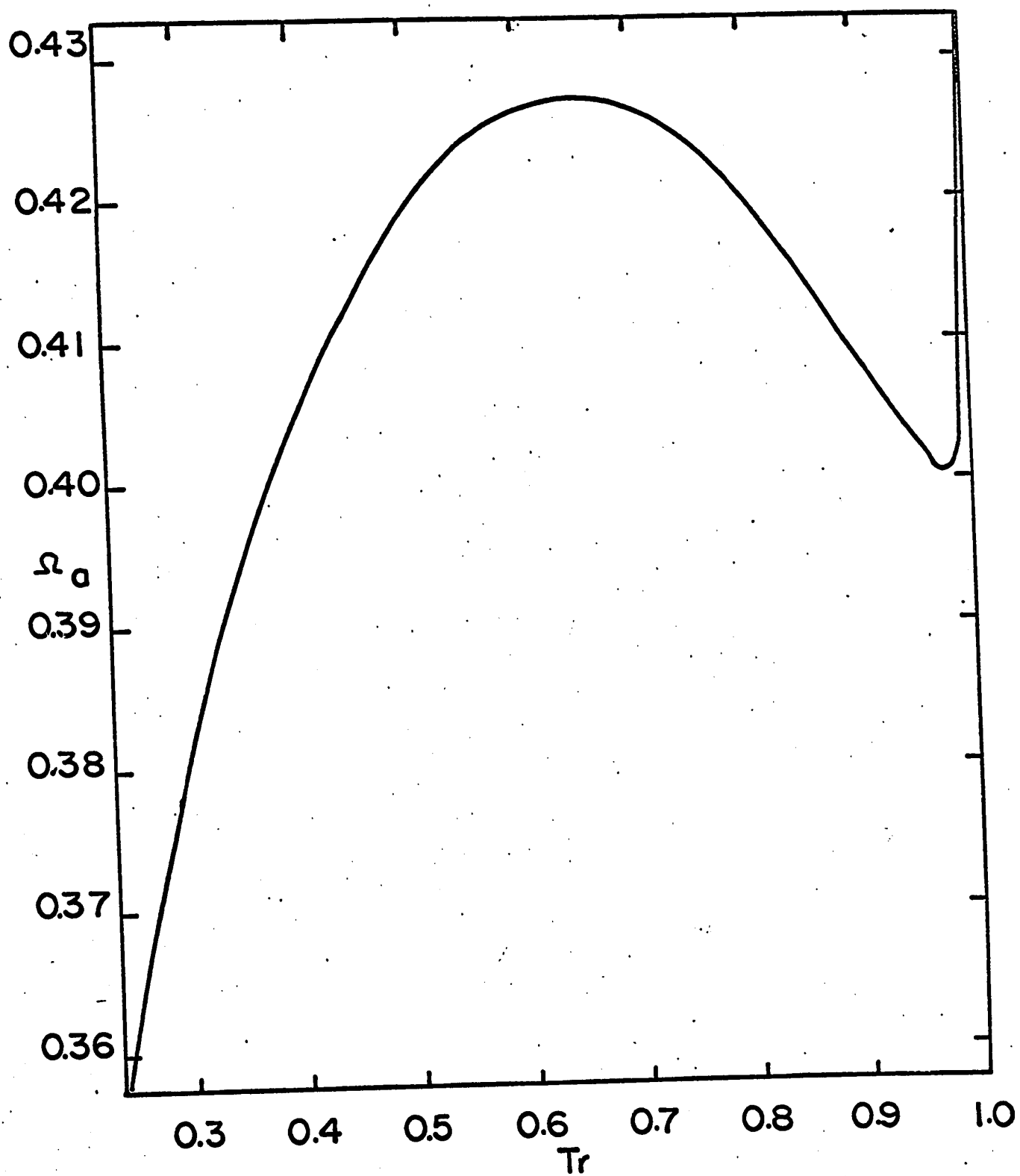


Figure 5-11 Ω_a Values for Propane

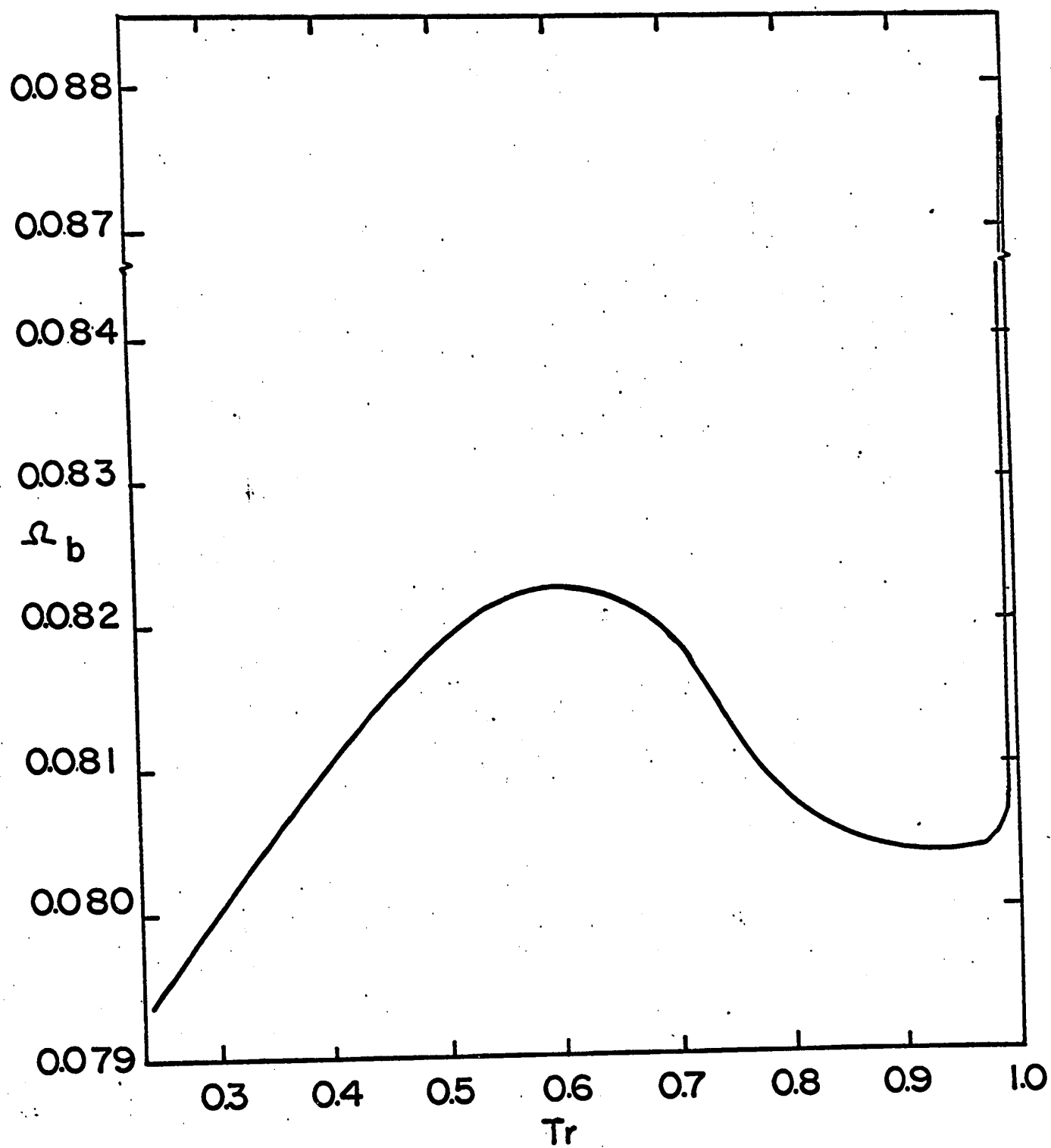


Figure 5-12 Ω_b Values for Propane

(4) Correlation of k_{12} From Available Experimental

Data

When the modified Redlich-Kwong equation of state is applied to mixtures, the following mixing rules are used(83,113):

$$a = \sum_i \sum_j Z_i Z_j a_{ij} \quad 5-11$$

$$a_{ij} = \left(\frac{a_{ii} a_{jj}}{Z_i Z_j} \right)^{\frac{1}{2}}$$

$$b = \sum_i Z_i b_i \quad 5-12$$

where Z_i represents the mole fraction of component i either in the vapor or in the liquid phase. The quantities a_{ij} and b_i are defined by:

$$a_{ij} = \Omega_{aij}^2 \frac{R^2 T_{cij}^{2.5}}{P_{cij}} \quad 5-13$$

$$b_i = \Omega_{bii} \frac{RT_{cii}}{P_{cii}} \quad 5-14$$

in which

$$T_{cij} = (T_{ci} T_{cj})^{0.5} (1 - k_{ij}) \quad 5-15$$

$$P_{cij} = Z_{cij} \frac{R T_{cij}}{V_{cij}} \quad 5-16$$

$$V_{cij} = \left(0.5(V_{ci}^{1/3} + V_{cj}^{1/3}) \right)^3 \quad 5-17$$

$$z_{cij} = 0.291 - 0.08 \left(\frac{\omega_i + \omega_j}{2} \right) \quad 2-18$$

$$\rho_{aij} = 0.5 (\rho_{a ii} + \rho_{a jj}) \quad 5-19$$

$$\omega_{ij} = 0.5 (\omega_i + \omega_j) \quad 5-20$$

The quantity k_{ij} in Equation(5-15) is the binary interaction constant. The values of k_{ij} were obtained from experimental vapor-liquid equilibrium data for the systems of interest.

Prausnitz and Gunn(57) calculated the k_{12} from the second virial coefficients B_{ij} data. Chueh and Prausnitz (113) calculated k_{12} for 115 binary systems.

The coefficient, k_{12} , was reported as being a constant characteristic(113,114,115) for each binary system. It was assumed to be independent of the temperature, density and composition. However, different values of k_{12} were reported by the Prausnitz and his associates(113,116,117,118) as shown in the following Table:

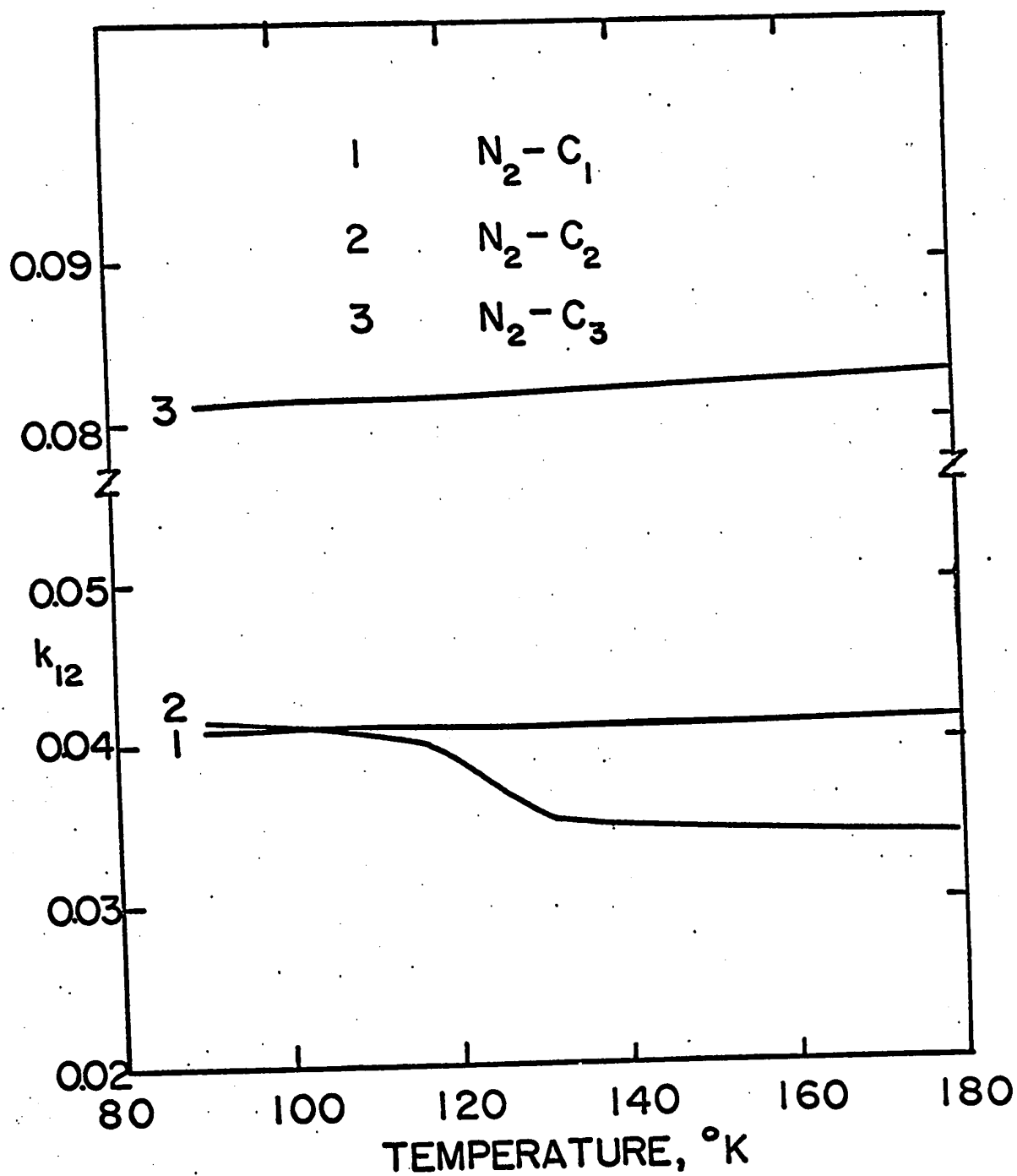
TABLE 5-3Values of Interaction Constant

<u>System</u>	<u>k₁₂</u>	<u>Sources</u>
Nitrogen-Methane	0.03	113
	0.24	116
Methane-Ethane	0.01	113
	-0.001	116
Methane-Propane	0.02	113
	-0.0018	116
Helium-Methane	0.46	113
	0.40	117
Helium-Ethane	0.05±0.01	113
	0.40	118

From Table 5-3, it is obvious that k_{12} value may not be a constant.

In this study, the presented k_{12} values were considered to be temperature-dependent only. Values of k_{12} were obtained from the minimum sum of squares of the deviations of y or P . The deviation is defined as the difference between the experimental value and the calculated value.

The values of k_{12} are presented graphically in Figures 5-13 to 5-15 for the binary systems methane-ethane, methane-propane, ethane-propane, nitrogen-methane, nitrogen-ethane and nitrogen-propane.

Figure 5-13 Values of k_{12}

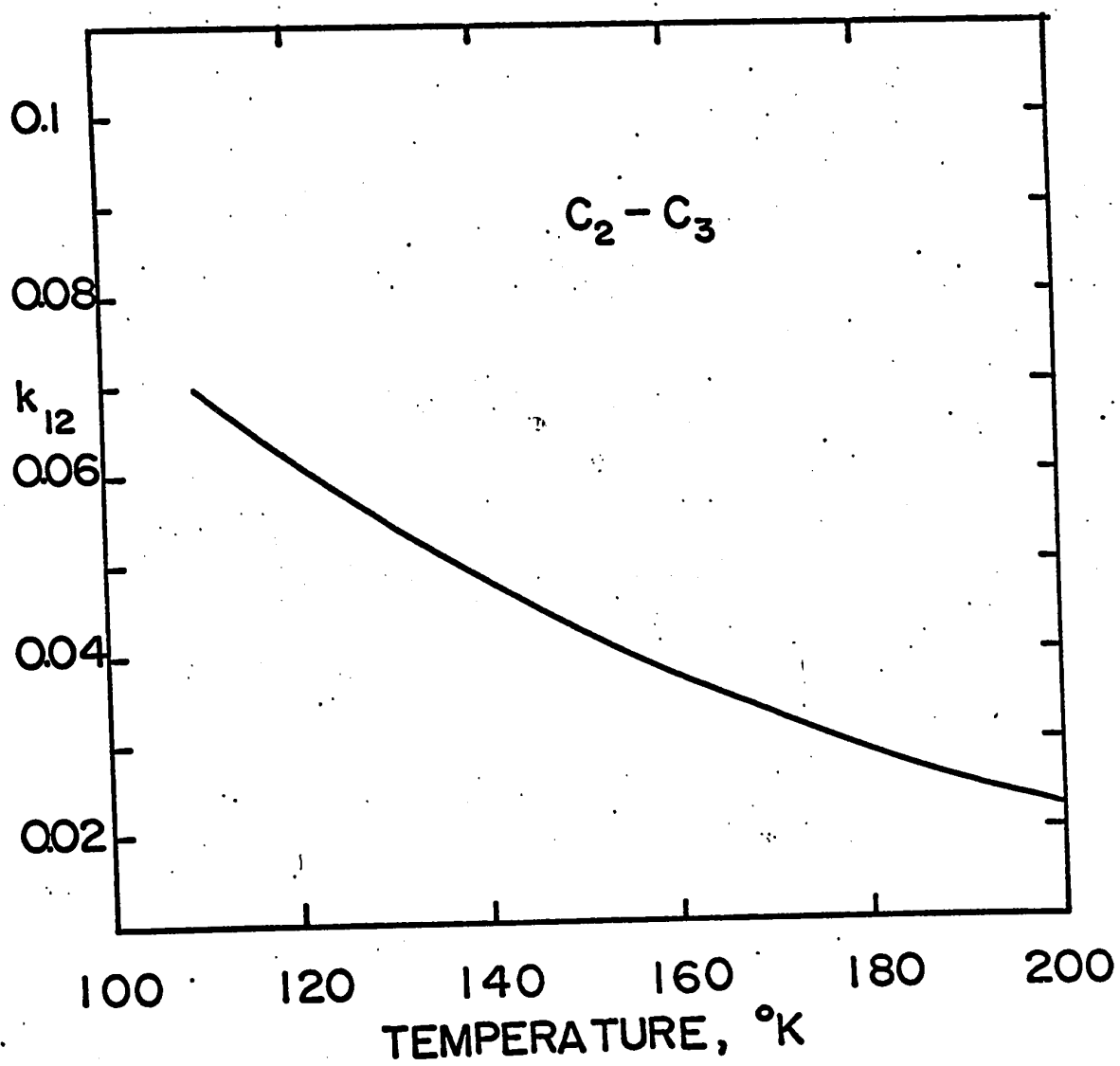


Figure 5-14 Values of k_{12}

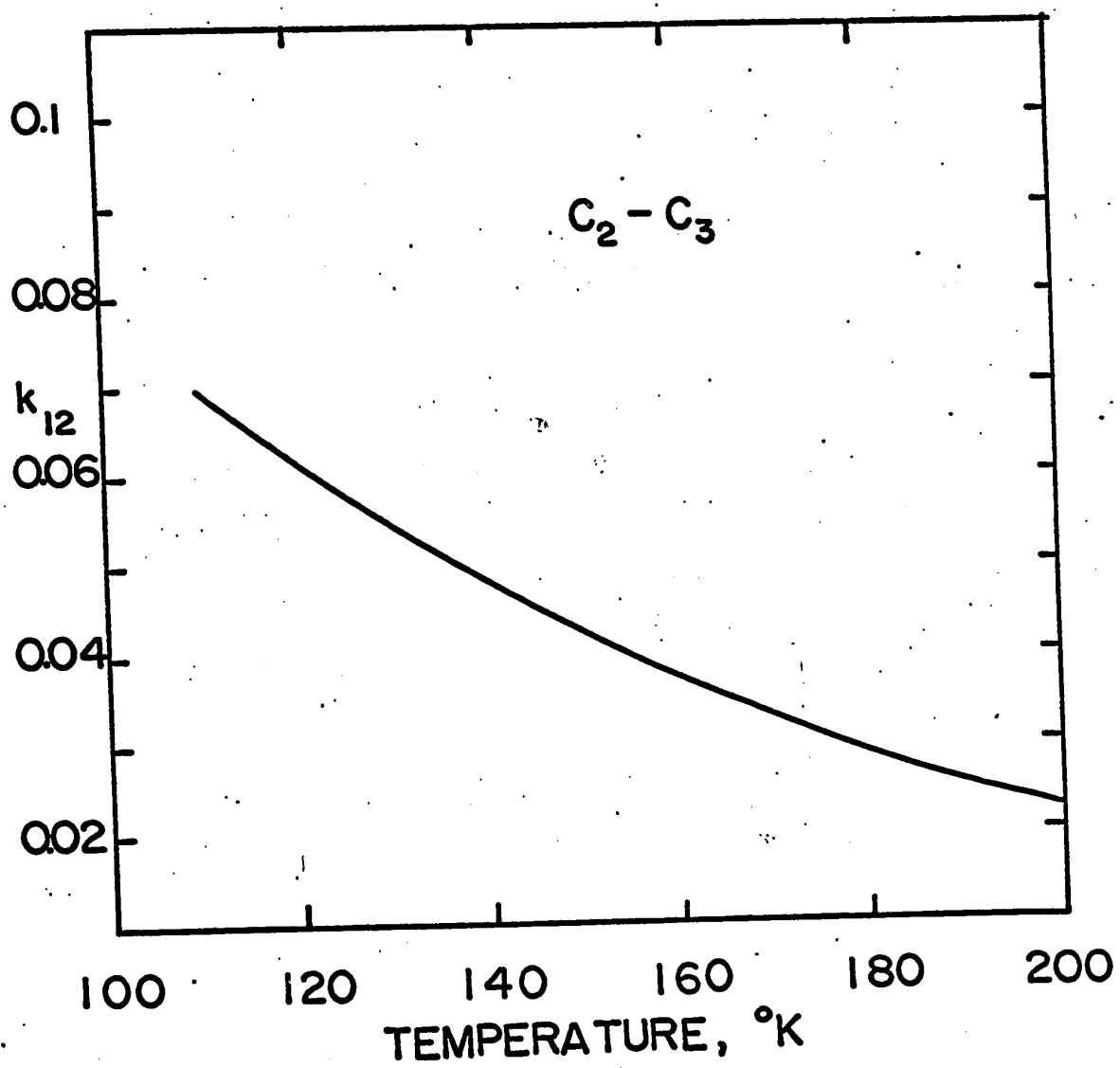


Figure 5-14 Values of k_{12}

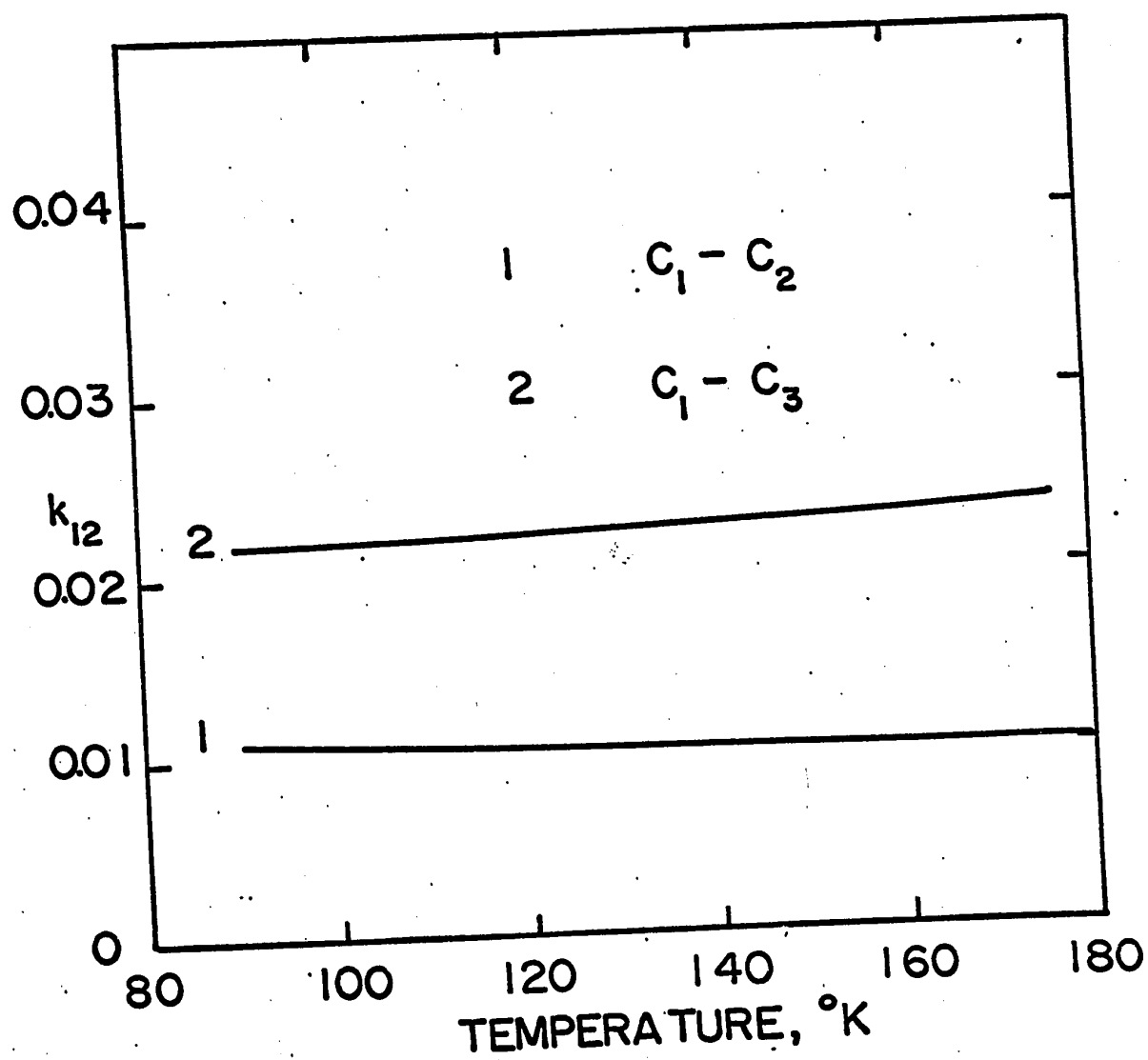


Figure 5-15 Values of k_{12}

(5) Calculation of Liquid Density by the Modified Redlich-Kwong Equation of State(83)

Liquid densities were calculated by means of the modified Redlich-Kwong equation of state(83). The calculation procedure may be briefly given as follows:

- (1) Substitute the values of a , b and k_{12} into

Equations(5-11) to (5-20) for the given temperature and composition.

- (2) The molal volume can be obtained from Equation(5-1), which is a cubic equation in molal volume. As there are three roots of V , the smallest real root was considered as the molal volume of the liquid mixture.
- (3) Calculate M , the mean molecular weight, of the liquid mixture from the following equation,

$$M = \sum_i x_i M_i \quad 5-21$$

where M_i refers to the molecular weight of pure component.

- (4) Obtain the liquid density, ρ , of mixture from Equation(5-22)

$$\rho = M/V \quad 5-22$$

A flow diagram of the computation is given in Figure 5-16. The computer program is given in Appendix VII.

In order to establish the reliability of the calculations, calculation results for five binary systems and two ternary systems were compared with the literature values:

Methane-Ethane System

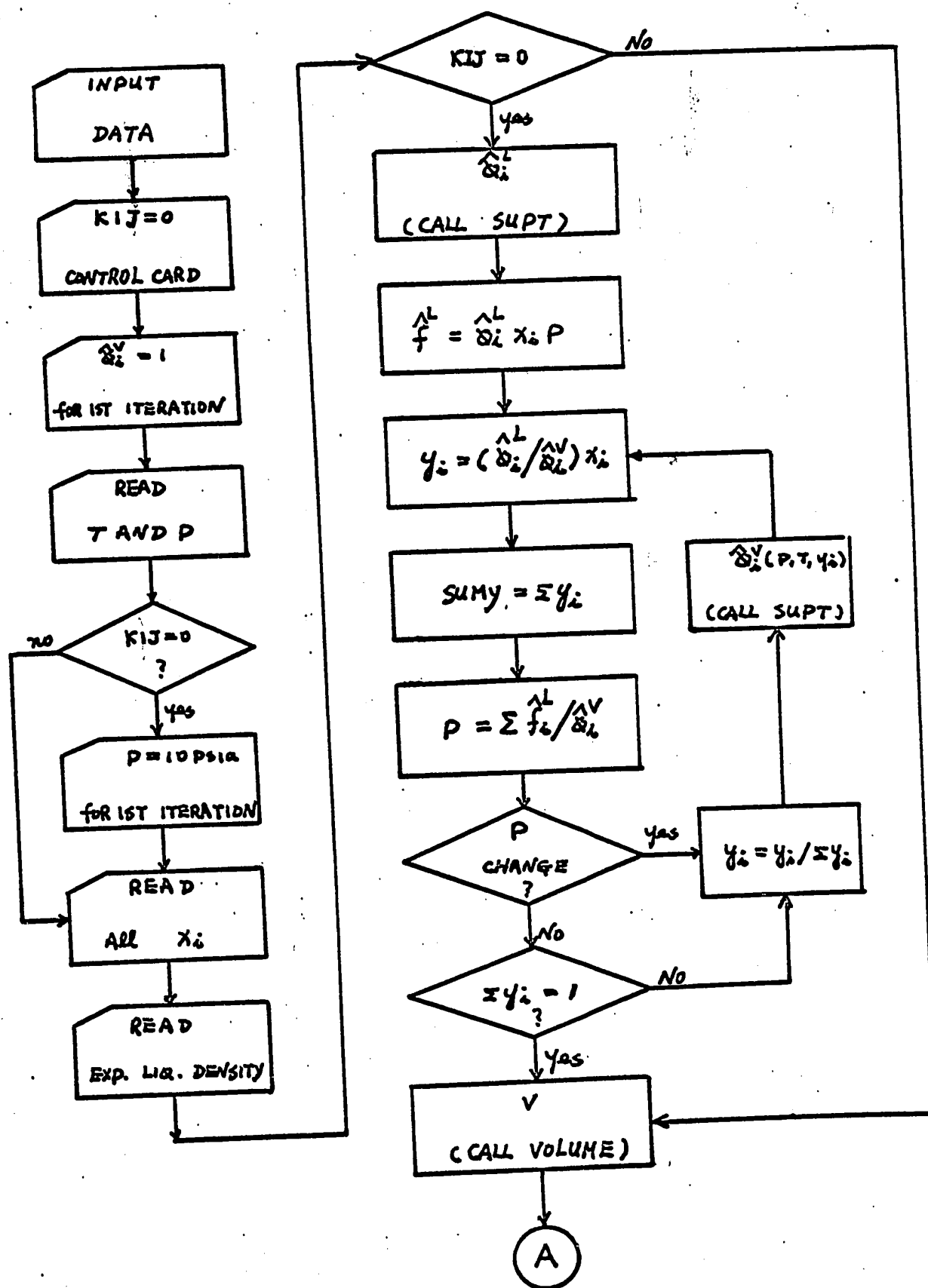
Two sets of data of this system(42,44) were tested.

The tested results, excess volume $V^E = \frac{1}{\rho^E} = V_m - \sum_i x_i V_i^0$,

are presented in Figures 5-17 and 5-18, and numerical values of liquid density are reported in Table II in Appendix III. The calculated liquid densities agree very well with the experimental results(42,44). The average absolute deviation and the maximum absolute deviation in the calculated liquid density are 0.001 g/cc. and 0.002 g/cc., respectively. The average percentage deviation is 0.07%!

Nitrogen-Methane System

Liquid density data for this binary system were reported by Bloomer and Parent(10). Four experimental data points have been tested by Harmens(59) for this system. The same experimental data points were also used. The calculated results are compared with the experimental data in Table III of Appendix III. The average absolute deviation in the calculated



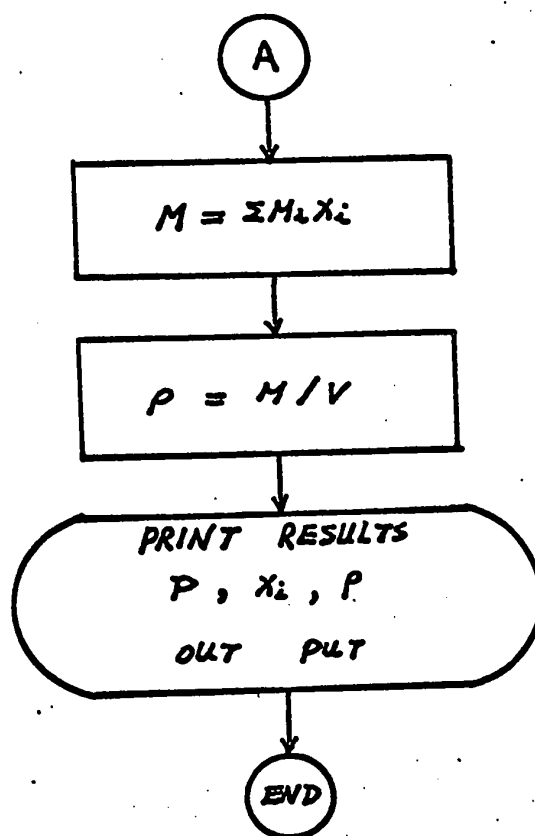


Figure 5-16 A Flow Diagram of Computer Program for Calculation of Liquid Density

liquid density is 0.006 g/cc. and the average percentage deviation is 0.6%.

Ethane-Propane System

The liquid density data of ethane-propane was measured by Shana'a(44) at 108.1 °K. In Figure 5-19 and Table IV of Appendix III, the experimental and calculated results are presented. The average absolute deviation and maximum absolute deviation are 0.003 g/cc. and 0.005 g./cc., respectively. The average percentage deviation is 0.4%.

Nitrogen-Ethane System

The five experimental measurements reported by Eakin(11) were chosen to test this method. The results are shown in Table V of Appendix III. Eakin et. al.(11) stated that the liquid density data were calculated from the phase equilibrium data by means of the B-W-R equation of state, which were measured by a Dew point and Bubble point apparatus. Therefore the maximum absolute deviation is 0.043 g/cc. The average absolute deviation is 0.016 g/cc. and the average percentage deviation is 3.3%.

Methane-Propane System

Isothermal data for this system was also measured by Shana'a(44) at 108.1 °K. The comparison of experimental and calculated results is given in Figure 5-20 and Table VI

of Appendix III. It can be seen that very good agreement is obtained. The average absolute deviation is 0.001 g/cc. The average percentage deviation is 0.22%.

Methane-Ethane-Propane System

Two sets of experimental data for this system were reported in the literature(42,44). The calculated liquid density was agreed reasonably well with both experimental results. The average absolute deviation is less than 0.001 g/cc.. The tested results are shown in Figure 5-21 and Table VII of Appendix III.

Nitrogen-Methane-Ethane System

In the literature, there was only one set of data for this system reported by Bloomer and Parent(10). The calculation results are listed in Table VIII of Appendix III. The average absolute deviation obtained between the experimental and calculated values is 0.003g/cc.. The maximum absolute deviation is 0.006 g/cc.. The average percentage deviation is 0.7%.

In summary, the proposed method was successfully applied to the prediction of liquid density for seven systems containing nitrogen, methane, ethane and propane. The average deviation in the calculated liquid densities is only 0.55%.

D. APPLICATION OF THE PROPOSED METHOD FOR CALCULATING LIQUID DENSITIES TO THE NITROGEN-METHANE-ETHANE SYSTEM AT LIQUID-PHASE INVERSION CONDITIONS

The densities of the mixtures of nitrogen, methane and ethane at the condition of liquid-phase inversion were calculated by the proposed method.

The densities, calculated from the results obtained in this investigation, were compared for both the liquid phases. The calculation results for four isothermals were tabulated in Table IX of Appendix III. A summary is given as follows:

<u>Temp. (°K)</u>	<u>Pressure (psia)</u>	<u>Dev. (g/c.c.)</u>	<u>No. of Points</u>
111.4	200.8	0.012	4
111.5	201.4	0.009	4
113.1	208.5	0.012	4
113.3	213.0	0.005	4

The average absolute deviation of the liquid density between the two liquid phases at inversion condition is 0.009 g/cc.. The average percentage deviation is 1.2%.

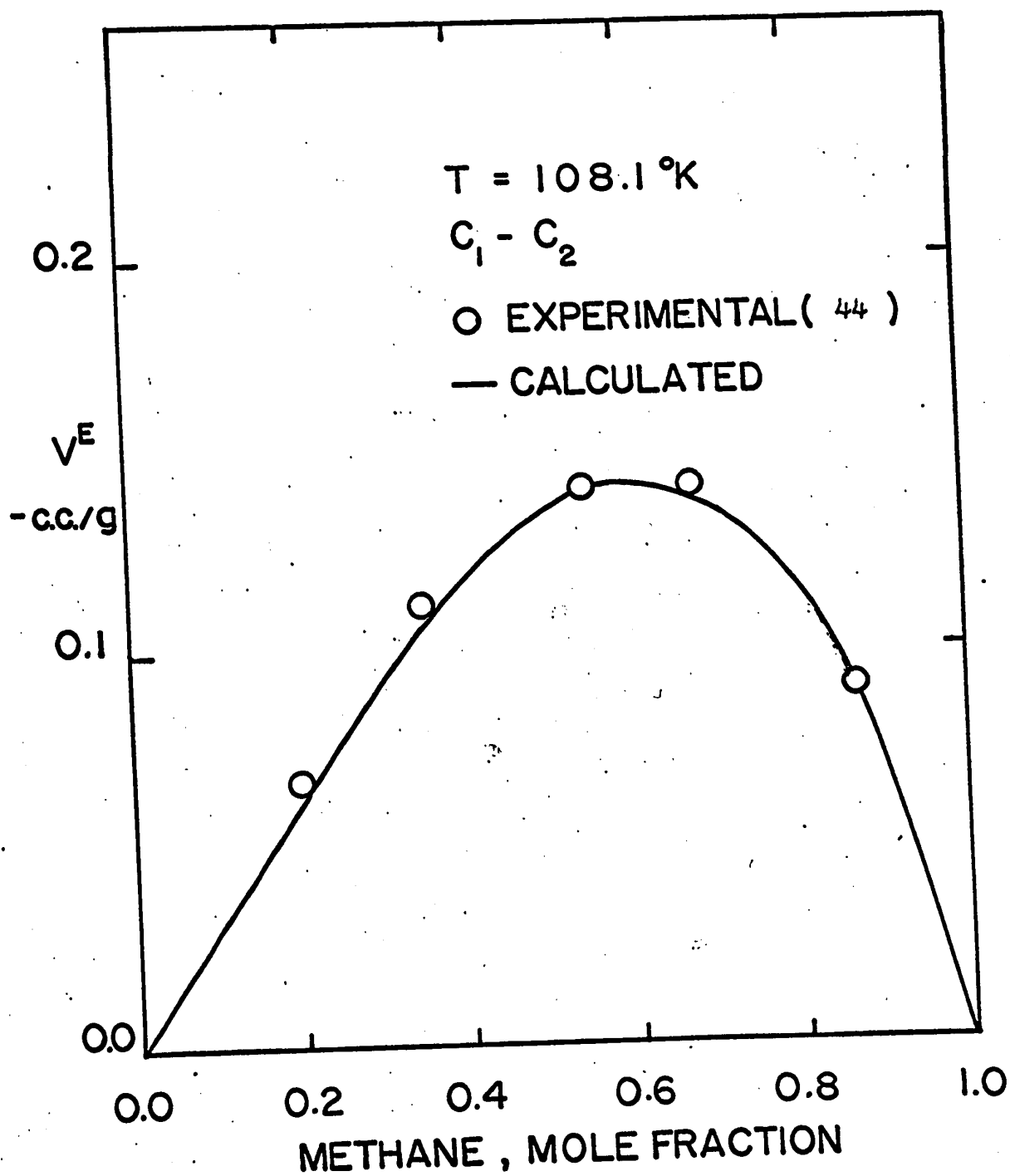


Figure 5-17 Comparison of Calculated and Experimental Excess Volumes for the Methane-Ethane system

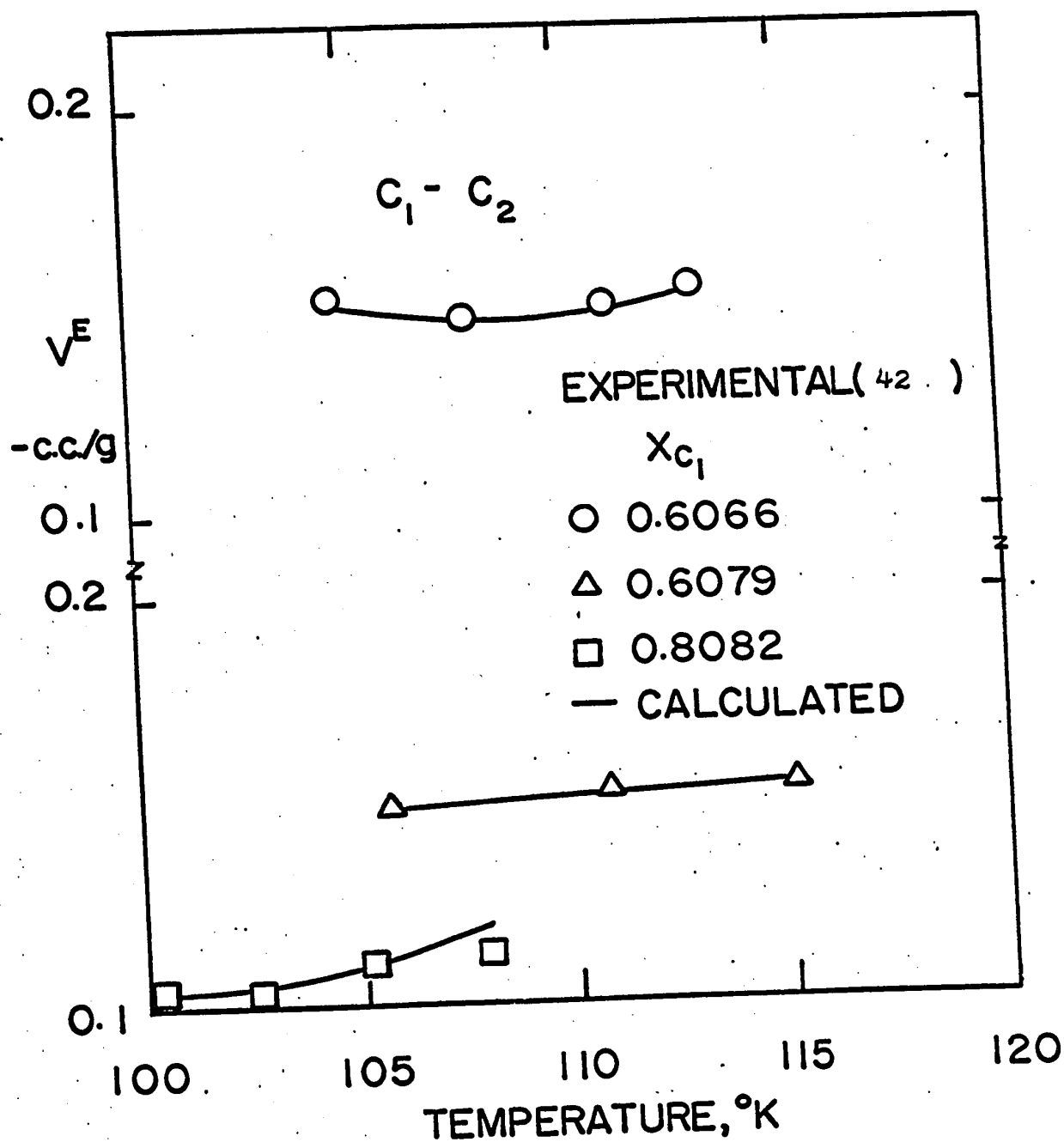


Figure 5-18 Comparison of Calculated and Experimental Excess Volumes for the Methane-Ethane System

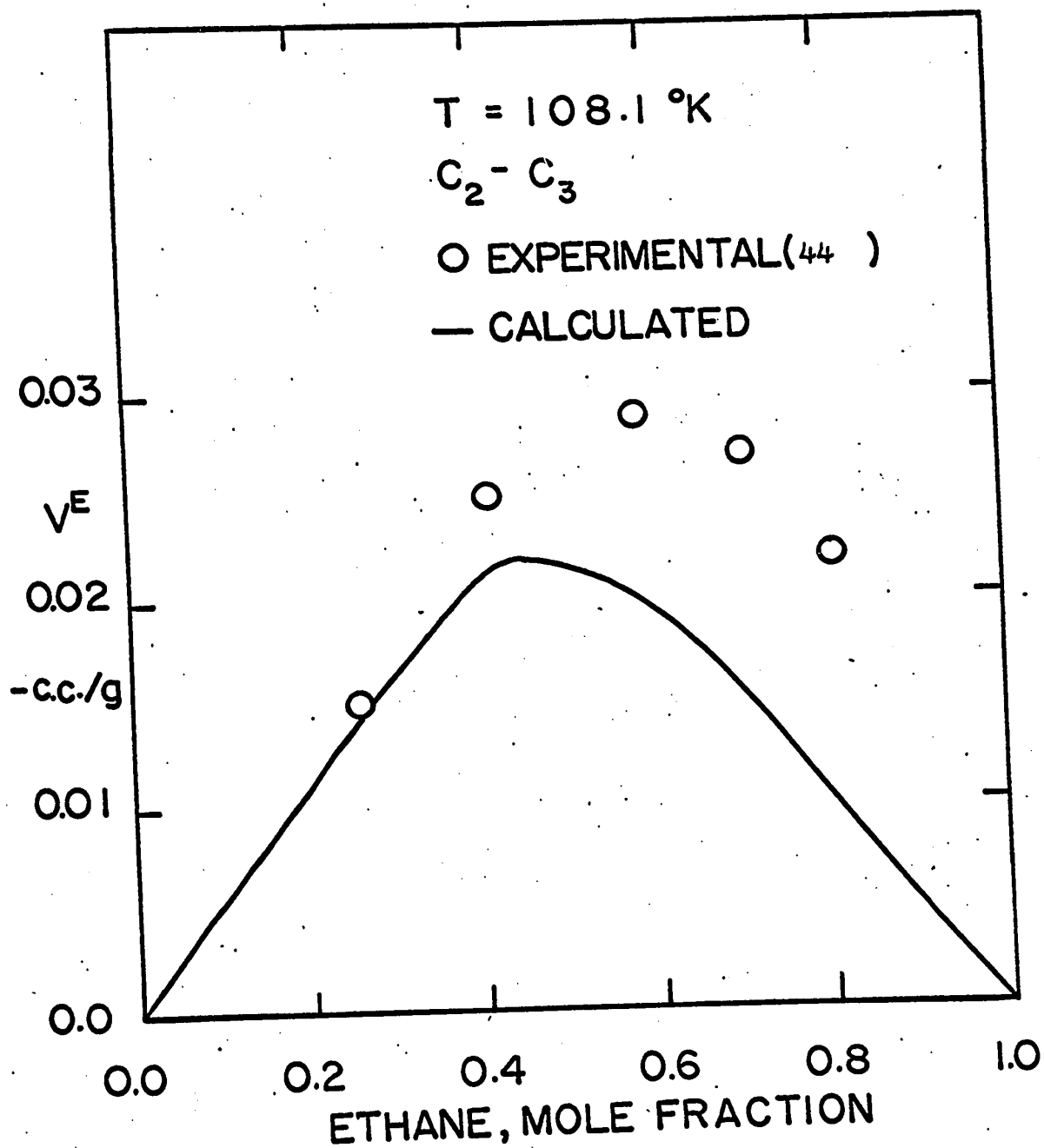


Figure 5-19 Comparison of Calculated and Experimental Excess Volumes for the Ethane-Propane System

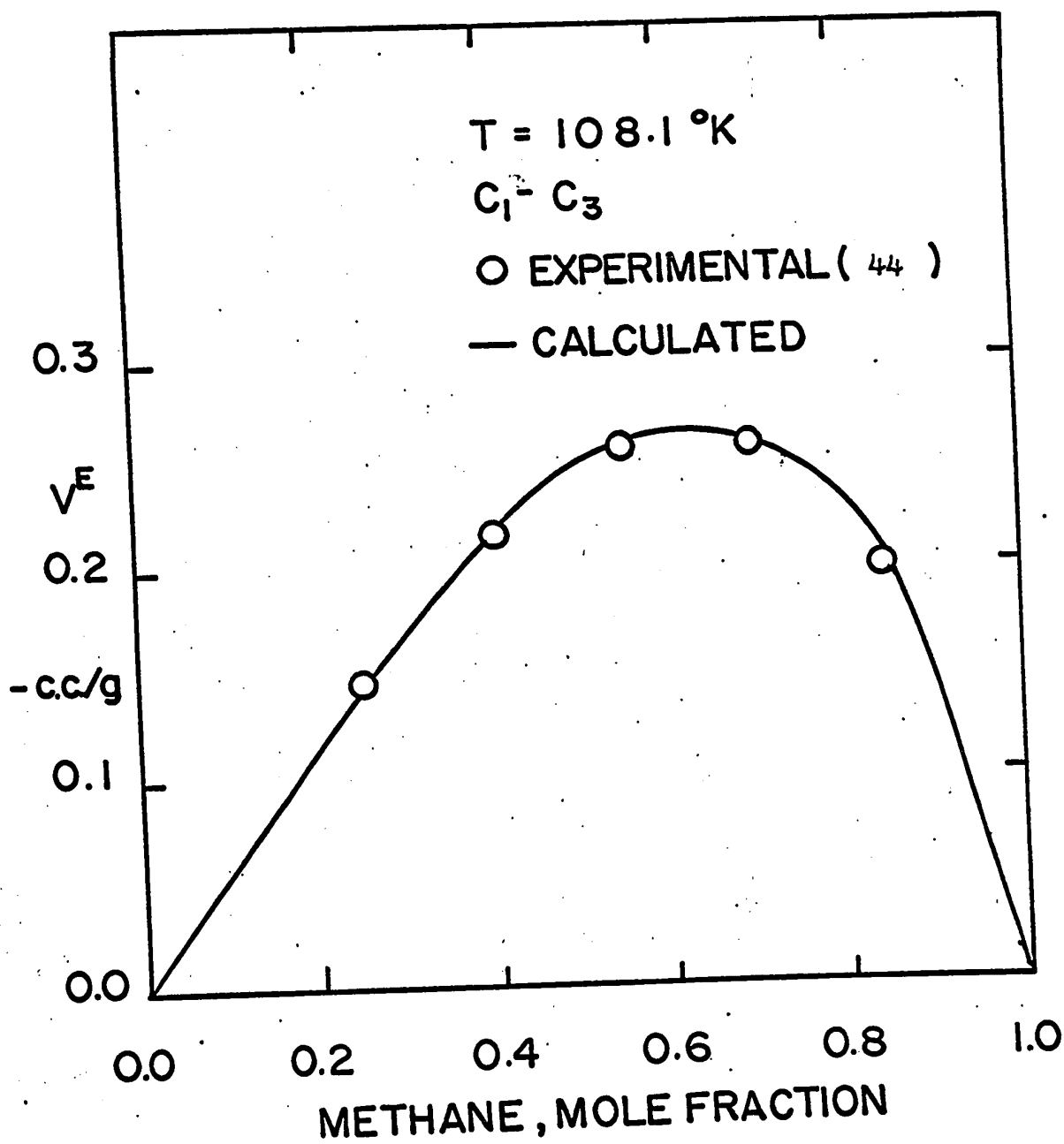


Figure 5-20 Comparison of Calculated and Experimental Excess Volumes for the Methane-Propane System

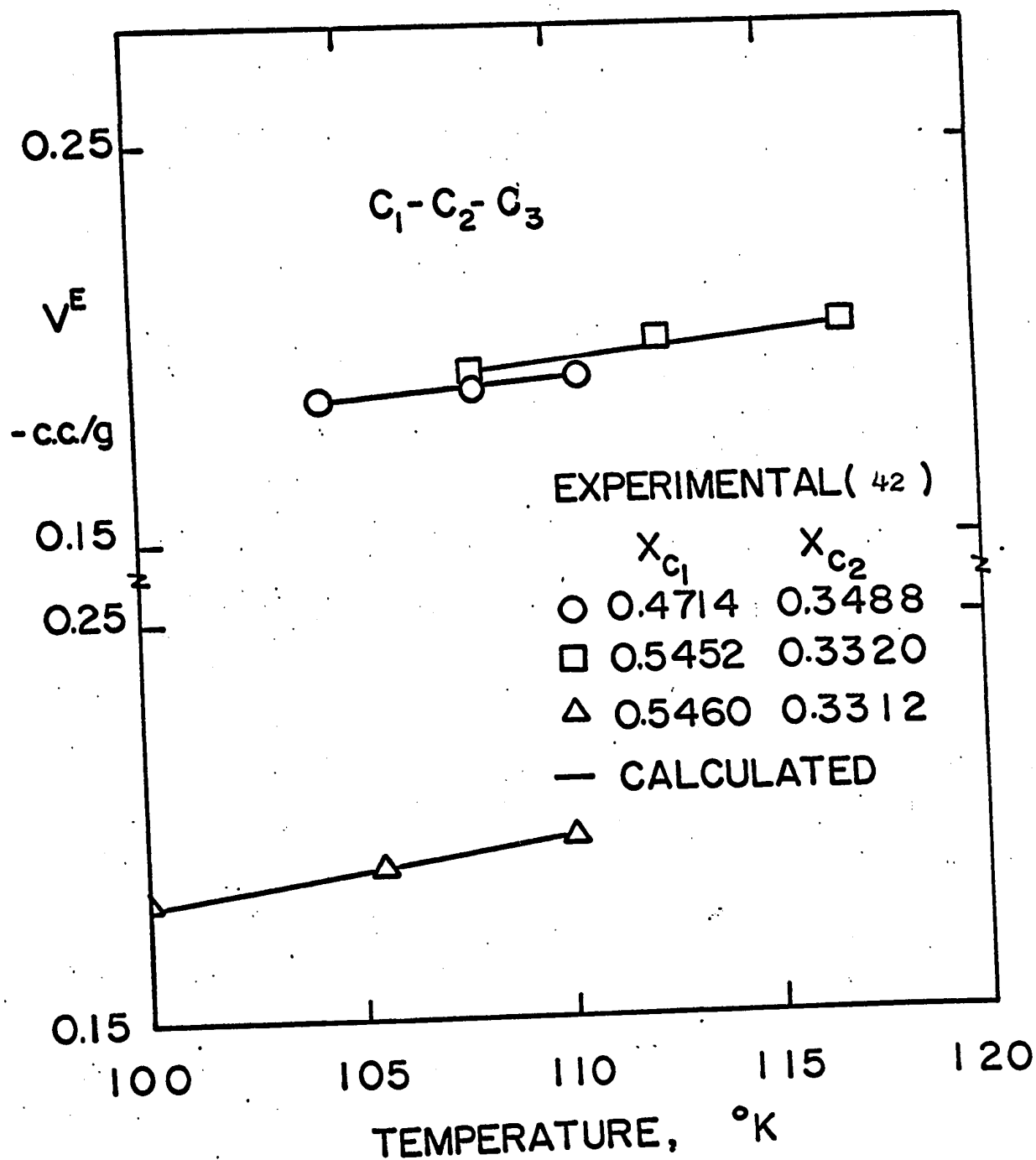


Figure 5-21 Comparison of Calculated and Experimental Excess Volumes for the Methane-Ethane-Propane System

CHAPTER VI

PREDICTION OF LIQUID-LIQUID-VAPOR

EQUILIBRIUM DATA AT LOW TEMPERATURES

A. INTRODUCTION

Accurate liquid-liquid-vapor equilibrium data are required for the design of separation processes. The experimental determination of the liquid-liquid-vapor equilibria over a range of conditions is expensive and time consuming.

In the chemical industry, it is most desirable, if liquid-liquid-vapor equilibrium data could be predicted without experimental determinations.

Recently, Renon and Prausnitz(98,101) employed their NRTL equation to predict ternary liquid-liquid equilibrium data for the temperature range from 245° to 360 °K.

The calculation of equilibrium data was performed with the NRTL equation by assigning a value α_{12} for each binary system in accordance with their rules. The two remaining parameters, $(g_{12}-g_{22})$ and $(g_{21}-g_{11})$ were evaluated from experimental binary phase equilibrium data by means of the NRTL equation.

However, the calculated and experimental ternary liquid-liquid equilibrium data can not match each other, except by adjusting α_{12} for the partially miscible binary

system.

For this reason, there is a need to develop a new method to predict liquid-liquid-vapor equilibrium data.

B. PREDICTION OF LIQUID-LIQUID-VAPOR EQUILIBRIUM DATA

The purpose of this investigation is to propose a simple, direct and reliable method for predicting liquid-liquid-vapor equilibrium data from the conditions of equilibrium and an equation of state without involving the calculation or correlation of activity coefficients.

The conditions for a system having two liquid phases in equilibrium with a vapor phase require that

$$\hat{f}_i^{L1} = \hat{f}_i^{L2} = \hat{f}_i^V \quad 6-1$$

since:

$$\hat{f}_i = \hat{Q}_i x_i P \quad 6-2$$

The fugacity coefficient of component i in the mixture, $\hat{Q}_i$, is rigorously related to the volumetric properties of the mixture(82,119) through the following equation:

$$\ln \hat{Q}_i = \frac{1}{RT} \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right) dV - \ln Z \quad 6-3$$

where n_i represents the number of moles of component i , V

is the total volume of the mixture, and Z is the compressibility factor of the mixture. The total pressure is designated by P , and the absolute temperature by T . The subscript n_j signifies that all mole numbers with the exception of n_i must be held constant.

The quantity $\hat{Q}_i$ could be evaluated from modified Redlich-Kwong equation of state(82) in this investigation, because of its simplicity and validity of representing the P-V-T properties of normal fluids.

Upon substituting Equations(5-1), (5-11) to (5-20) and the mixing rules into Equation(6-3), the fugacity coefficients of component i in a multicomponent mixture may be expressed by the following Equation(6-4):

$$\ln \hat{Q}_i = (Z - 1) \frac{B_i}{B} - \ln(Z)(1 - h) - \left(\frac{A^2}{B} \right) \left(\frac{2 \sum_j Z A_{ji}}{A^2} - \frac{B_i}{B} \right) \ln(1 + h) \quad 6-4$$

The compressibility factor Z is one of three roots of Equation (5-1) rearranged in the following form:

$$f(Z) = Z^3 - Z^2 + BP \left(\frac{A^2}{B} - 1 - BP \right) Z - \frac{A^2}{B} (BP)^2 = 0 \quad 6-5$$

The smallest root is taken as the compressibility factor of the saturated liquid, and the largest root is taken as that of

the saturated vapor.

For liquid-liquid-vapor equilibria of a three component system, the variables of interest are the system temperature, total pressure, two liquid-phase mole fractions in each of the liquid phases, and two vapor-phase mole fractions. Therefore, there are eight variables in total.

According to the phase rule, when a ternary system which contains two separate liquid phases reaches equilibrium with a vapor phase, the number of degrees of freedom is two.

By selecting the system temperature and mole fraction of nitrogen in one of liquid phases as the known variables, it should be possible to calculate the remaining six unknowns with the aid of Equation(6-1). These six simultaneous equations may be solved by a trial-and-error procedure.

From the given T and x_1^{L1} or x_1^{L2} , the liquid-phase compositions are calculated by:

$$\hat{Q}_i^{L1} x_i^{L1} = \hat{Q}_i^{L2} x_i^{L2} \quad 6-6$$

Arbitrary values of P , x_2^{L1} , x_1^{L2} and x_2^{L2} are assumed for the first iteration.

In order to solve these simultaneous cubic equations, the modified Regula-falsi method was employed. The modified Regula-falsi method is presented in Appendix V.

After evaluating the liquid-liquid equilibrium data using Equation(6-6) at an assumed total pressure, the vapor

phase may be calculated by:

$$y_i = (\hat{Q}_i^{L1} / \hat{Q}_i^V) x_i^{L1} \quad 6-7$$

For the first iteration, $\hat{Q}_i^V$ may be assumed to be equal to unity. Values of y_i are evaluated by means of Equation(6-7).

Using these y_i values, new $\hat{Q}_i^V$ values are evaluated by means of Equation(6-4). The iteration procedure is repeated until y_i values are no longer changed. Then the summation of y_i is tested. If $\sum y_i > 1$ the assumed total pressure would increase, $\sum y_i < 1$ the assumed total pressure would decrease, since the total pressure has large effect on the vapor-phase compositions than the liquid-phase compositions.

Then the liquid-liquid-vapor equilibrium compositions were calculated with the newly assumed total pressure, until Equations(6-1) and the condition the $\sum y_i = 1$ are satisfied.

A flow diagram of computation is shown in Figure 6-1.

C. CALCULATION RESULTS

The applicability of the proposed method was tested. The systems were nitrogen-ethane, nitrogen-methane-ethane and n-octane-octene-1-nitroethane.

(1) Nitrogen-Ethane System

The liquid-liquid-vapor equilibria for the binary system nitrogen-ethane were predicted by the proposed method

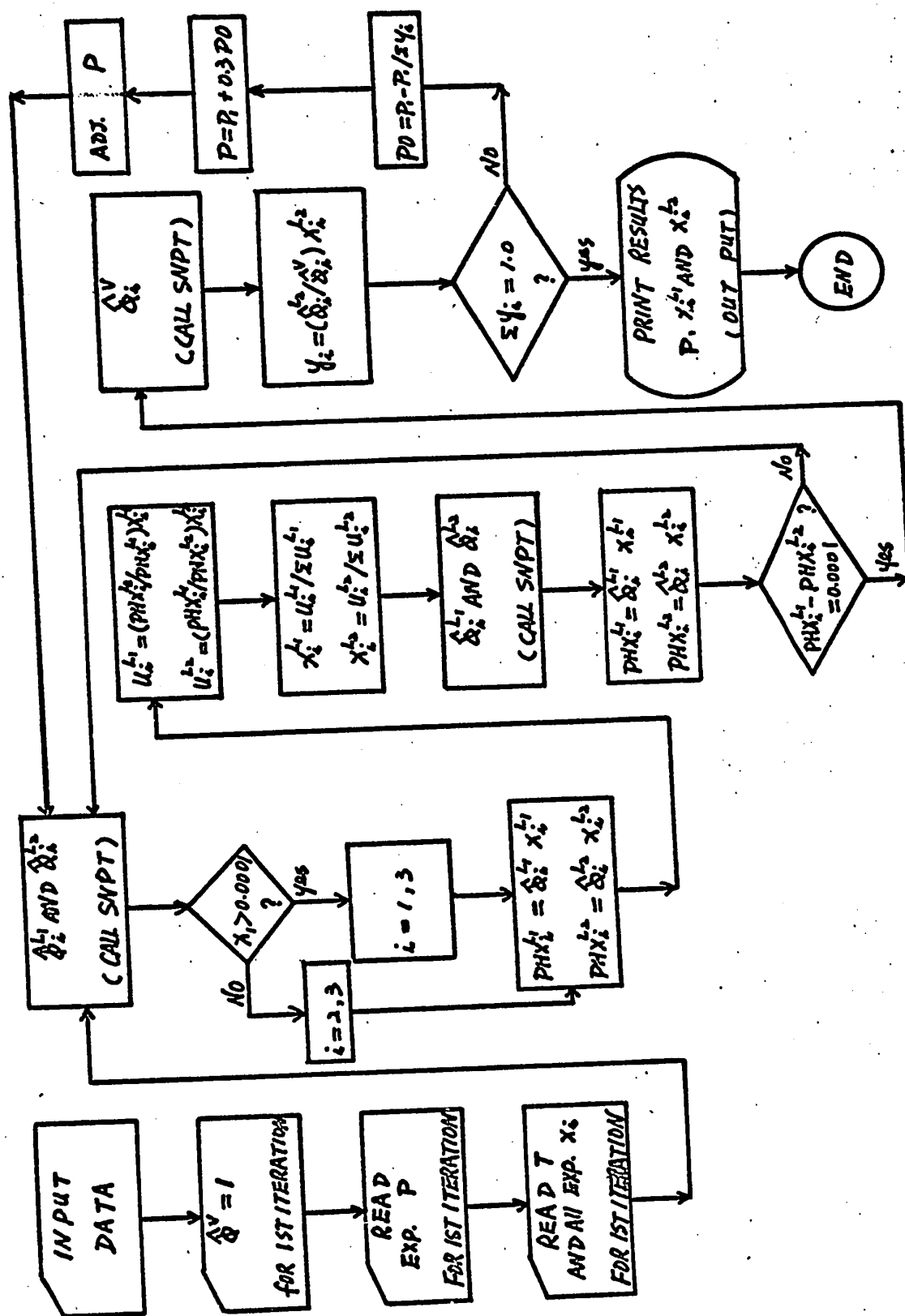


Figure 6-1 A Flow Diagram of the Computer Program

from 94.3° to 133.3 °K for thirteen isotherms and the pressure up to 591 psia. The predicted values are compared satisfactorily with the experimental results obtained in this study. The results are shown in Table I of Appendix IV and Figure 6-2. The average deviation of bottom liquid phase was 0.0002 mole fraction, the top liquid phase was 0.0004, and the pressure was 1.0 psia. The comparison of the calculated and experimental equilibrium data are shown in Table II of Appendix IV.

(2) Nitrogen-Methane-Ethane System

Liquid-liquid-vapor equilibrium data were obtained for nitrogen-methane-ethane system at eleven isotherms from 94.3° to 133.3 °K in this laboratory.

The calculated results were compared with the experimental equilibrium data. The agreement is very good. The comparison of the calculated and experimental equilibrium data in Figures 6-3 to 6-13. The calculated equilibrium data are shown in Table III of Appendix III. In Table IV of Appendix III, the absolute deviation and absolute average deviation are shown. The average deviation of the bottom liquid phase and the top liquid phase is 0.0005 mole fraction and the pressure is 1.8 psia.

A summary of the comparison is given as follows:

Pressure psia	Bottom Liquid Phase		Top liquid Phase	
	Δx_{c1}	Δx_{c2}	Δx_{c1}	Δx_{c2}
1.8	0.0003	0.0006	0.0003	0.0006

(3) Liquid-Liquid Equilibrium Data for the N-octane-Octene-1-Nitroethane System at 273.1 °K

Liquid-liquid equilibria for the ternary system n-octane-octene-1-nitroethane at 273.1 °K were also predicted by the proposed method. The predicted values are compared with the experimental values which were reported by Hwa et. al.(120), and with the calculated results obtained by means of the NRTL equation in Figure 6-14, in which the success of the proposed method is indicated. The average deviation of the bottom liquid phase was 0.012 and the top liquid phase was 0.006 mole fraction.

Values of the binary interaction parameter, k_{12} , and the pure component parameters Ω_a and Ω_b , employed in this investigation are listed in Table 6-1 and 6-2, respectively.

TABLE 6-1Binary Interaction Parameters k_{12}

System		Temperature	k_{12}
1	2	$^{\circ}\text{K}$	
Nitrogen	Methane	94.3	0.0415
		101.5	0.0415
		109.1	0.0414
		113.4	0.0414
		115.2	0.0414
		116.3	0.0414
		119.3	0.0413
		123.4	0.0415
		128.8	0.0415
		130.1	0.0415
		133.3	0.0415
Methane	Ethane	94.3	0.0110
		101.5	0.0110
		109.1	0.0110
		113.4	0.0100
		115.2	0.0100
		116.3	0.0100
		119.3	0.0100

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TABLE 6-1 (continue....)

System		Temperature	k_{12}
1	2	°K	
Methane	Ethane	123.4	0.0100
		128.8	0.0100
		130.1	0.0100
		133.3	0.0100
Nitrogen	Ethane	94.3	0.0410
		101.5	0.0410
		109.1	0.0410
		113.4	0.0400
		115.2	0.0400
		116.3	0.0400
		119.3	0.0385
		123.4	0.0380
		128.8	0.0350
N-octane	Octene-1	130.1	0.0350
		133.3	0.0350
		273.1	0.0000
N-octane	Nitroethane	273.1	0.0215
Octene-1	Nitroethane	273.1	0.0190

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TABLE 6-2

Values of Ω_a and Ω_b

<u>Component</u>	<u>T °K</u>	<u>Ω_a</u>	<u>Ω_b</u>
Nitrogen	94.3	0.41683	0.08498
	101.5	0.41972	0.08409
	109.1	0.41505	0.08252
	113.4	0.41182	0.08173
	115.2	0.41124	0.08102
	116.3	0.41058	0.08089
	119.3	0.40561	0.08032
	123.4	0.40561	0.07997
	128.8	0.45525	0.08675
	130.1	0.45088	0.08687
	133.3	0.45632	0.08755
Methane	94.3	0.38969	0.08674
	101.5	0.39778	0.08660
	109.1	0.40356	0.08660
	113.4	0.40559	0.08672
	115.2	0.40533	0.08633
	116.3	0.40668	0.08630
	119.3	0.40767	0.08618
	123.4	0.40872	0.08596

TABLE 6-2 (continue....)

Component	T °K	Ω_a	Ω_b
Methane	128.8	0.41015	0.08562
	130.1	0.41032	0.08353
	133.3	0.41189	0.08557
Ethane	94.3	0.35979	0.08203
	101.5	0.36691	0.08226
	109.1	0.38348	0.08321
	113.4	0.38662	0.08334
	115.2	0.39042	0.08345
	116.3	0.39058	0.08349
	119.3	0.39407	0.08369
	123.4	0.39515	0.08879
	128.8	0.40030	0.08393
	130.1	0.40130	0.08413
	133.3	0.40325	0.08412
N-octane	273.1	0.45359	0.07386
Octene-1	273.1	0.48210	0.07419
Nitroethane(121)	273.1	0.38312	0.06471

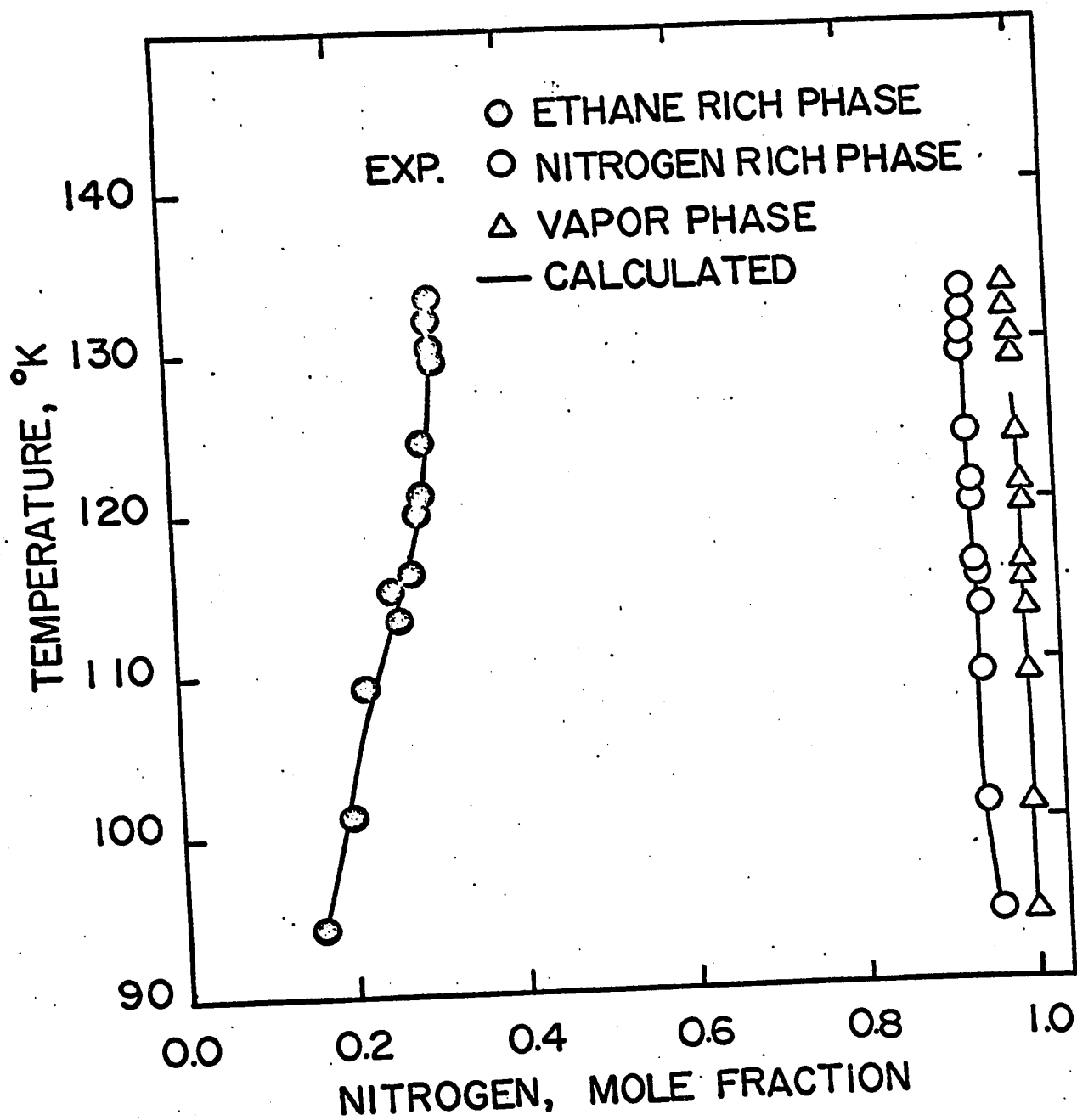


Figure 6-2 Comparison of Calculated and Experimental Liquid-Liquid-Vapor Equilibria for Nitrogen-Ethane System

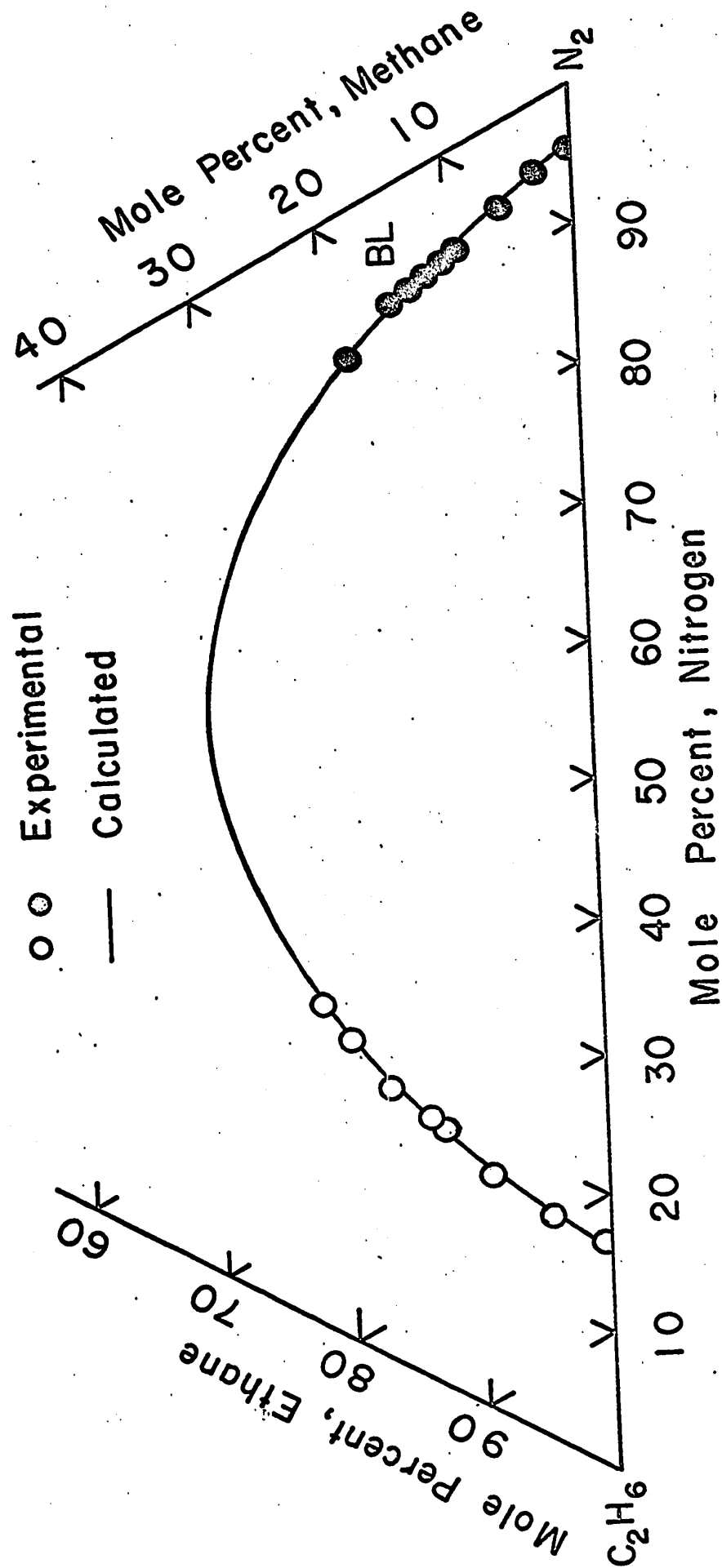


Figure 6-3 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 94.3°K

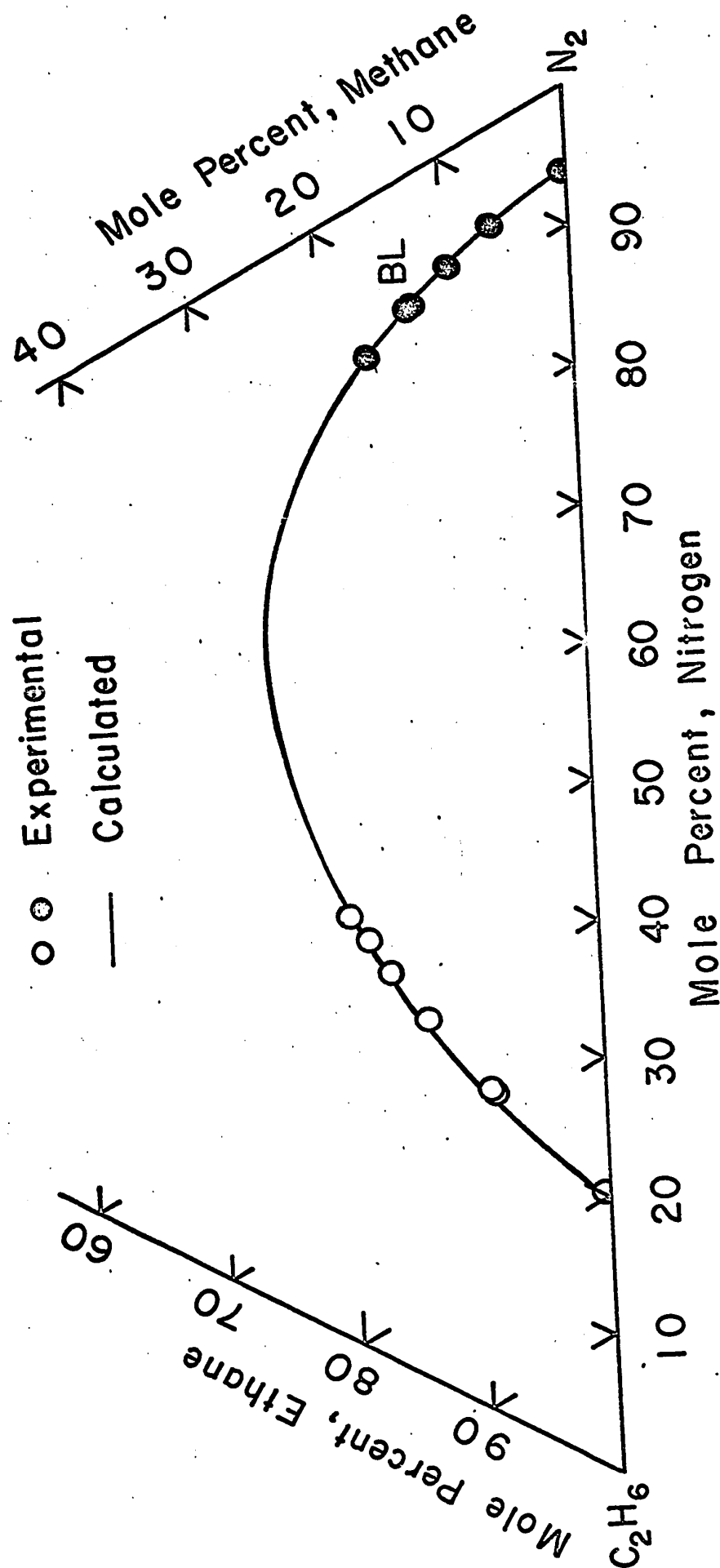


Figure 6-4 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 101.5°K

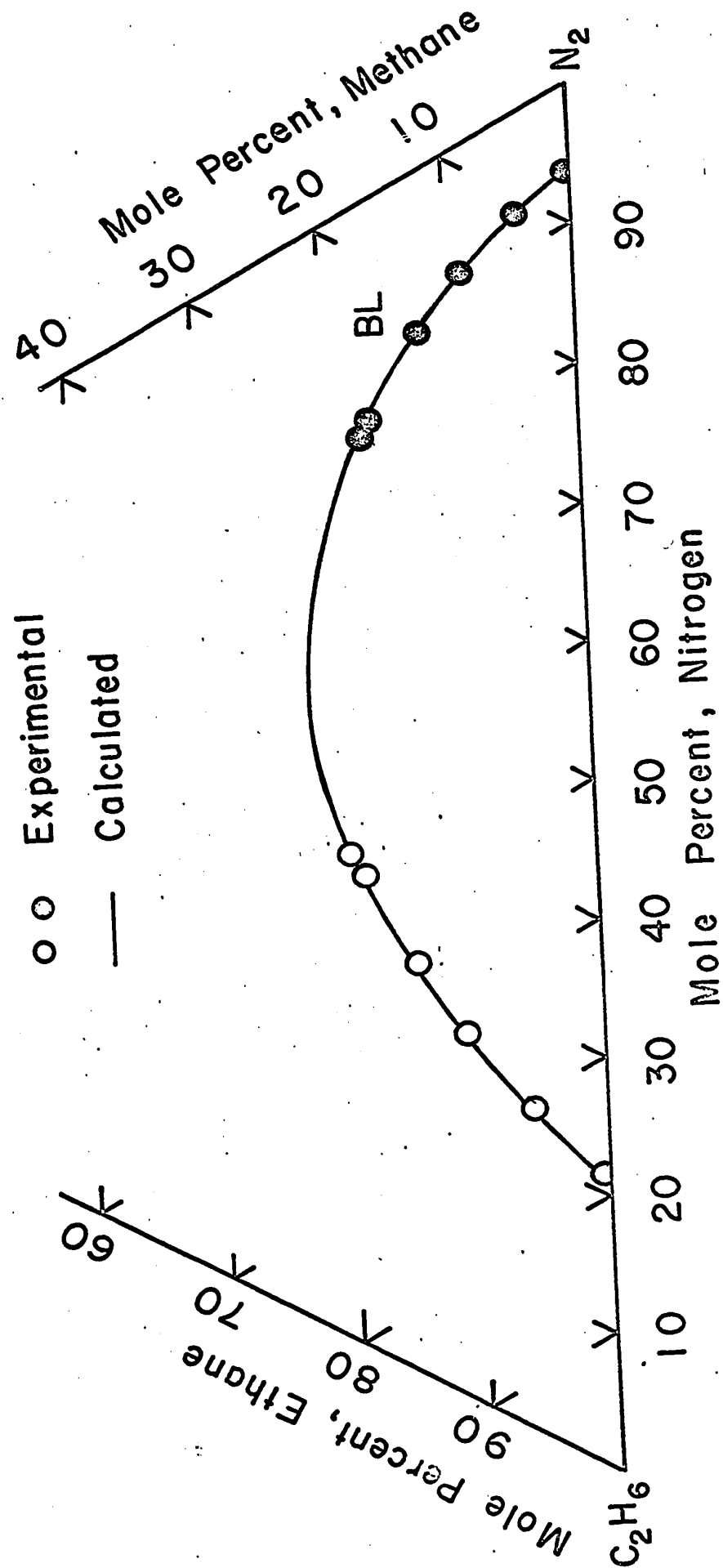


Figure 6-5 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 109.1°K

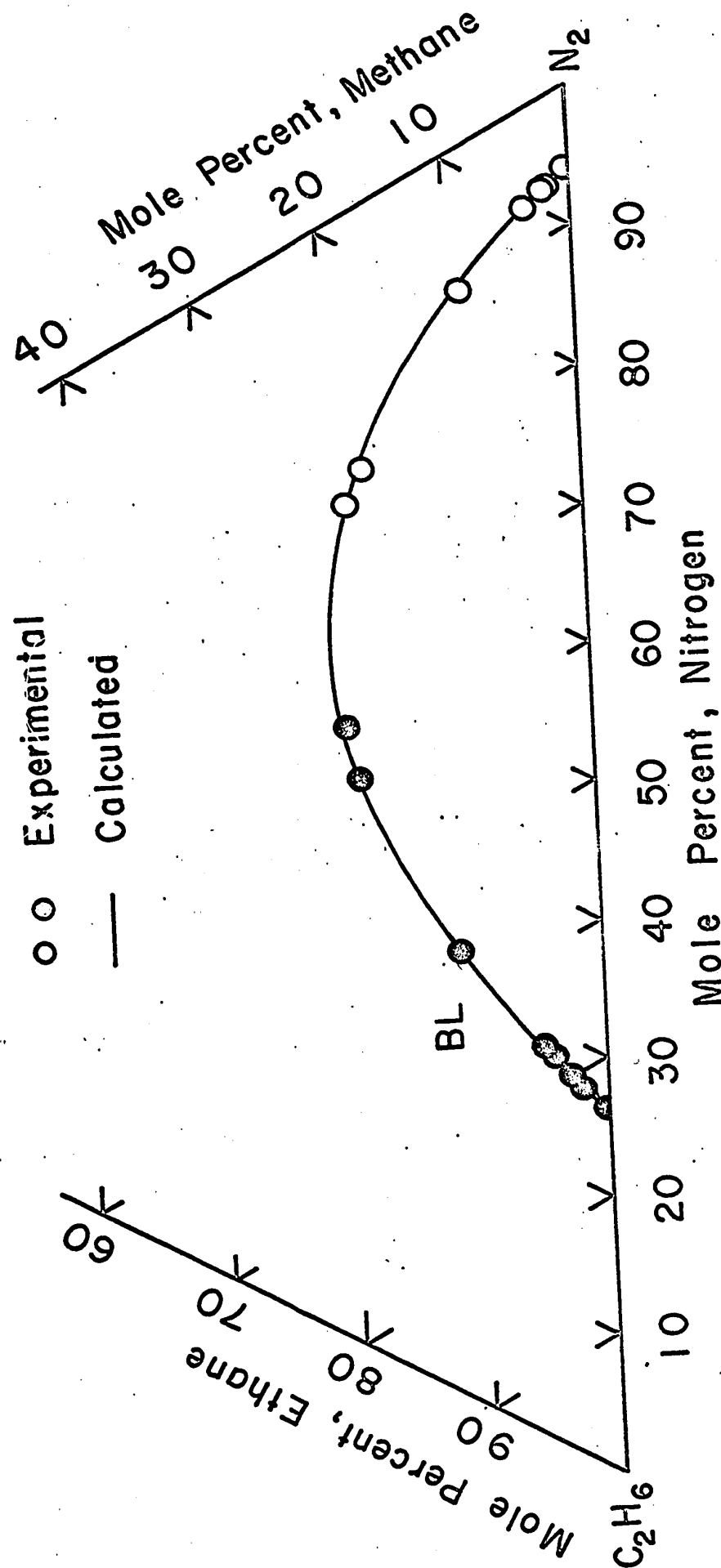


Figure 6-6 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 113.4°K

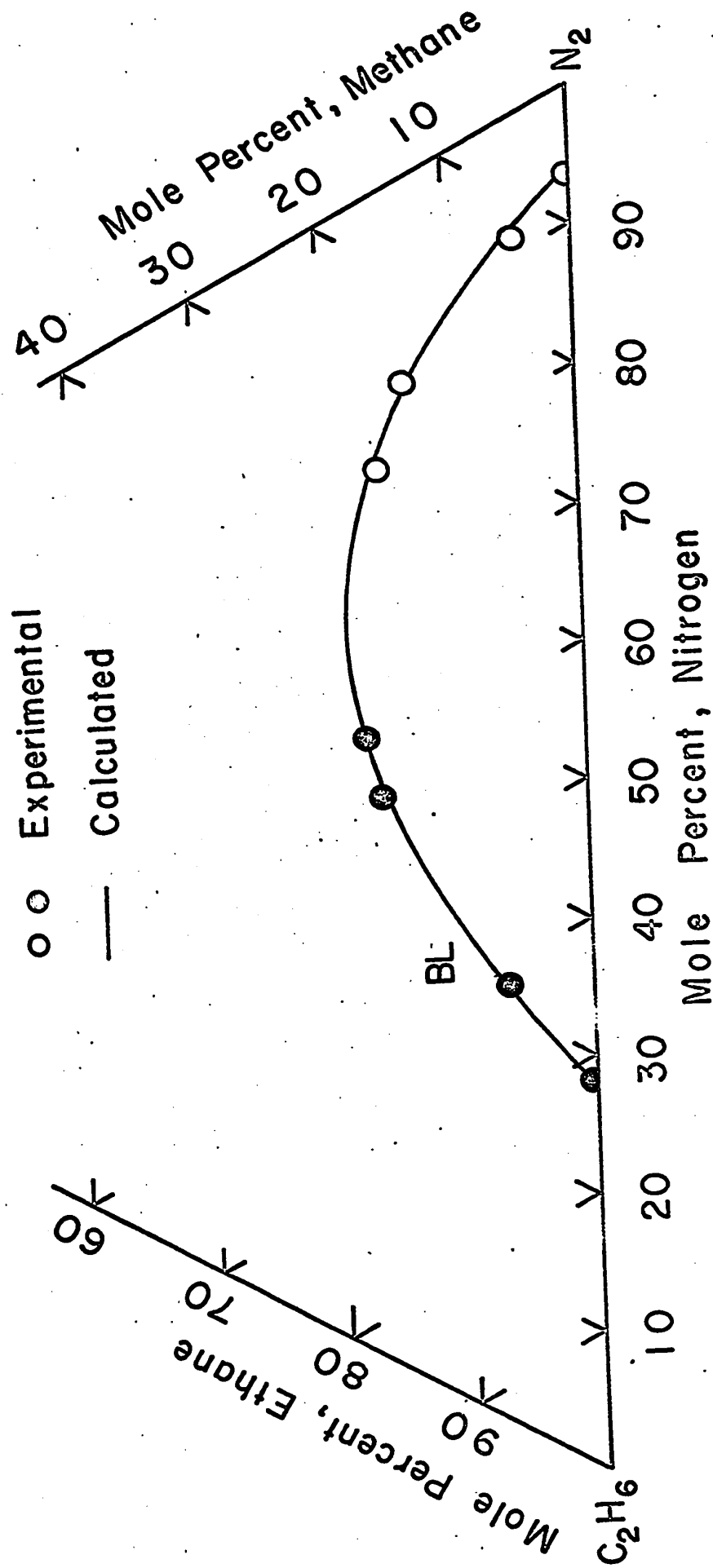


Figure 6-8 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 116.3 K

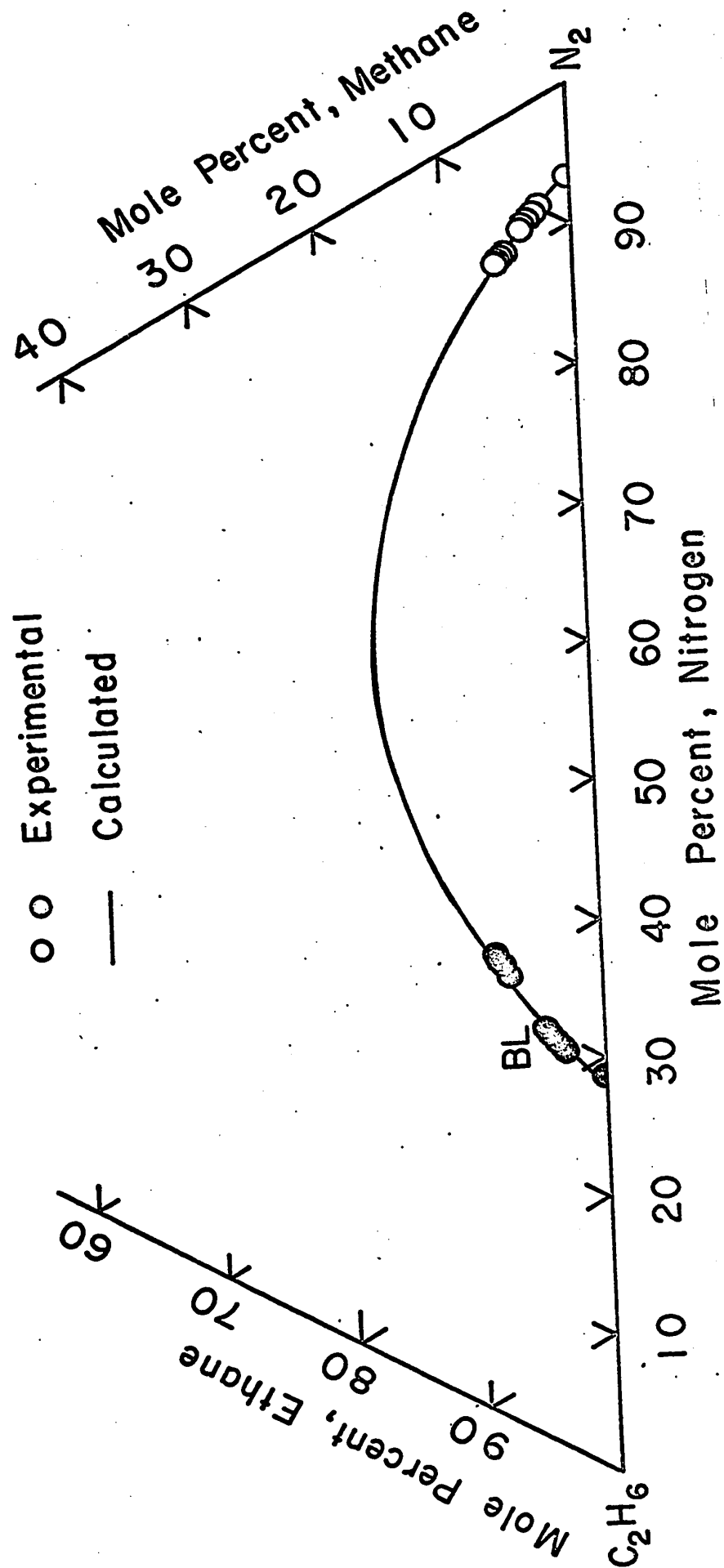


Figure 6-9 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 119.3 K

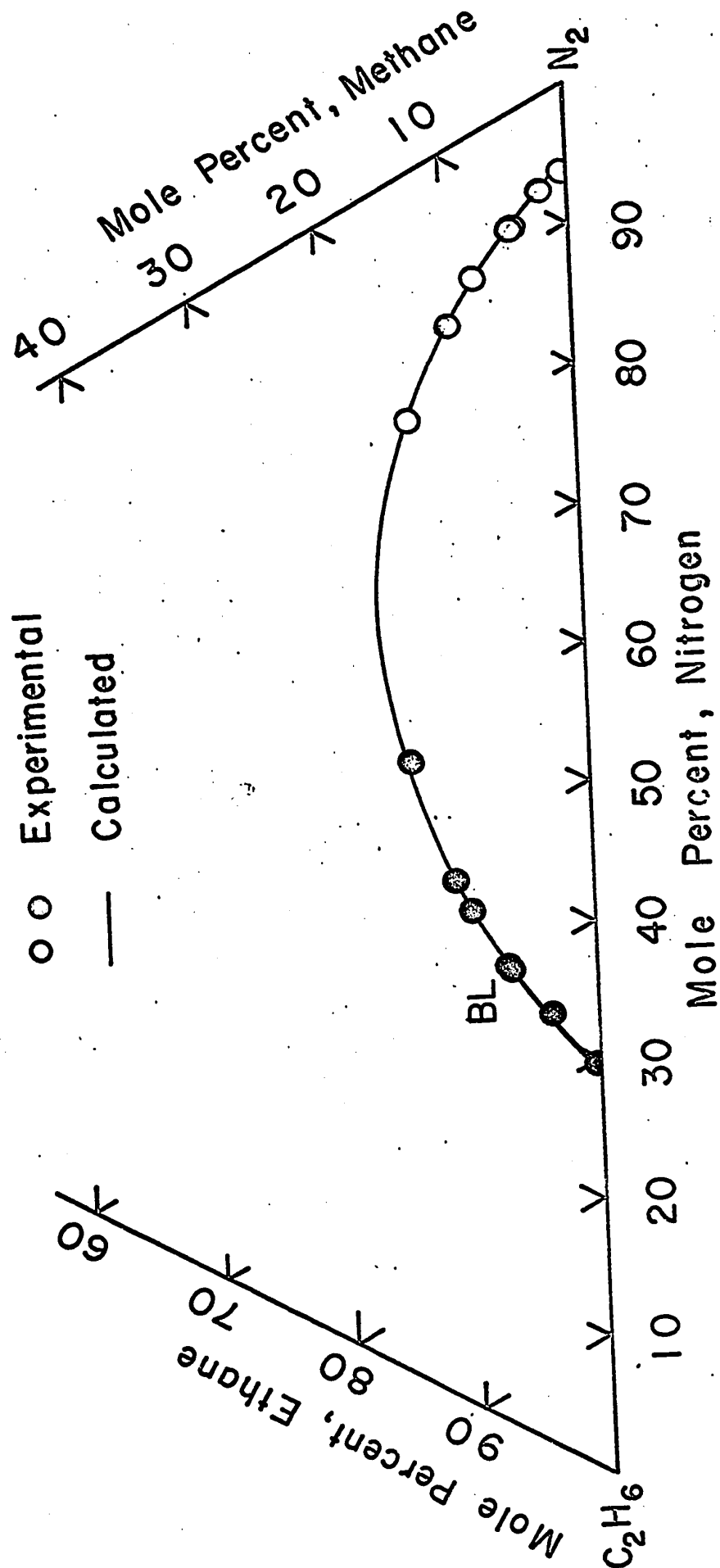


Figure 6-10 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 123.4°K

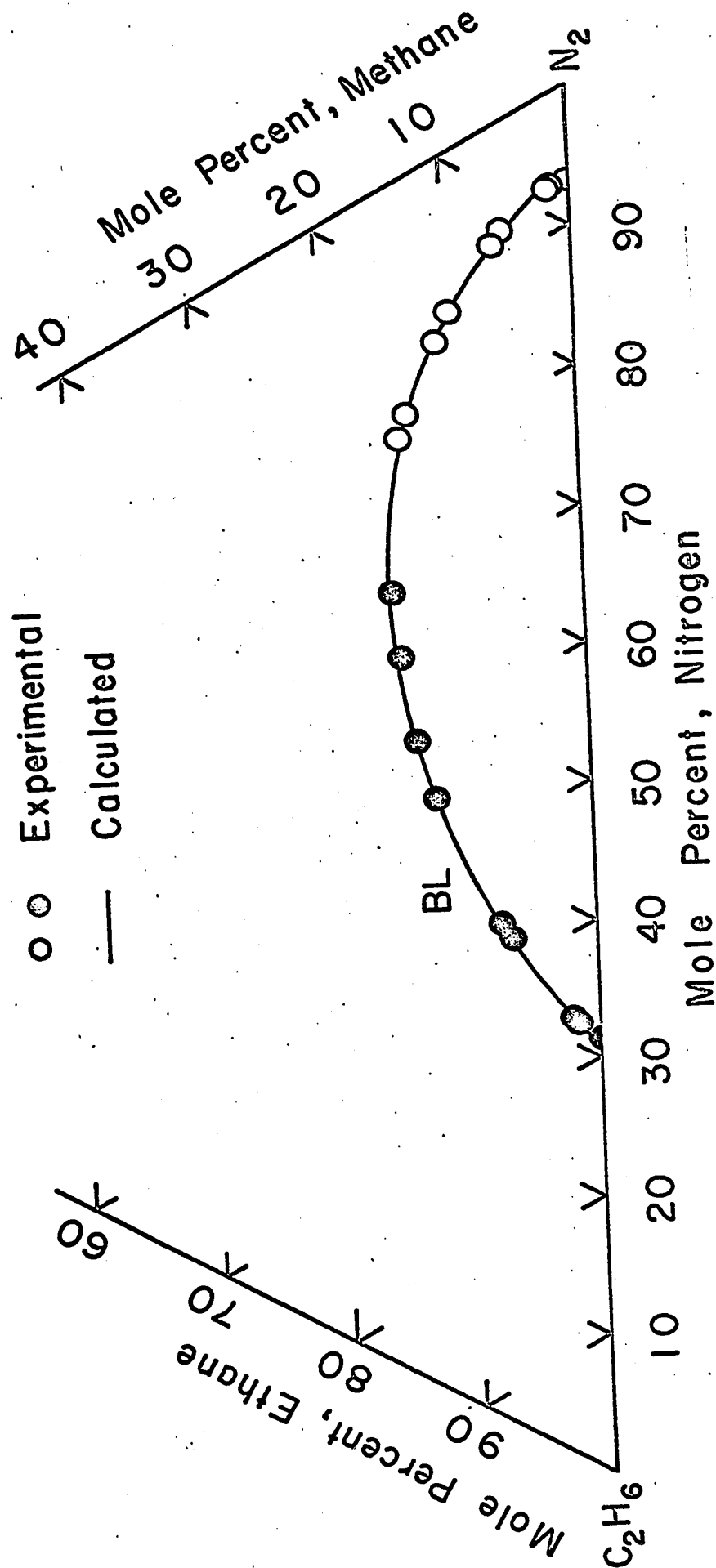


Figure 6-11 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 128.8°K

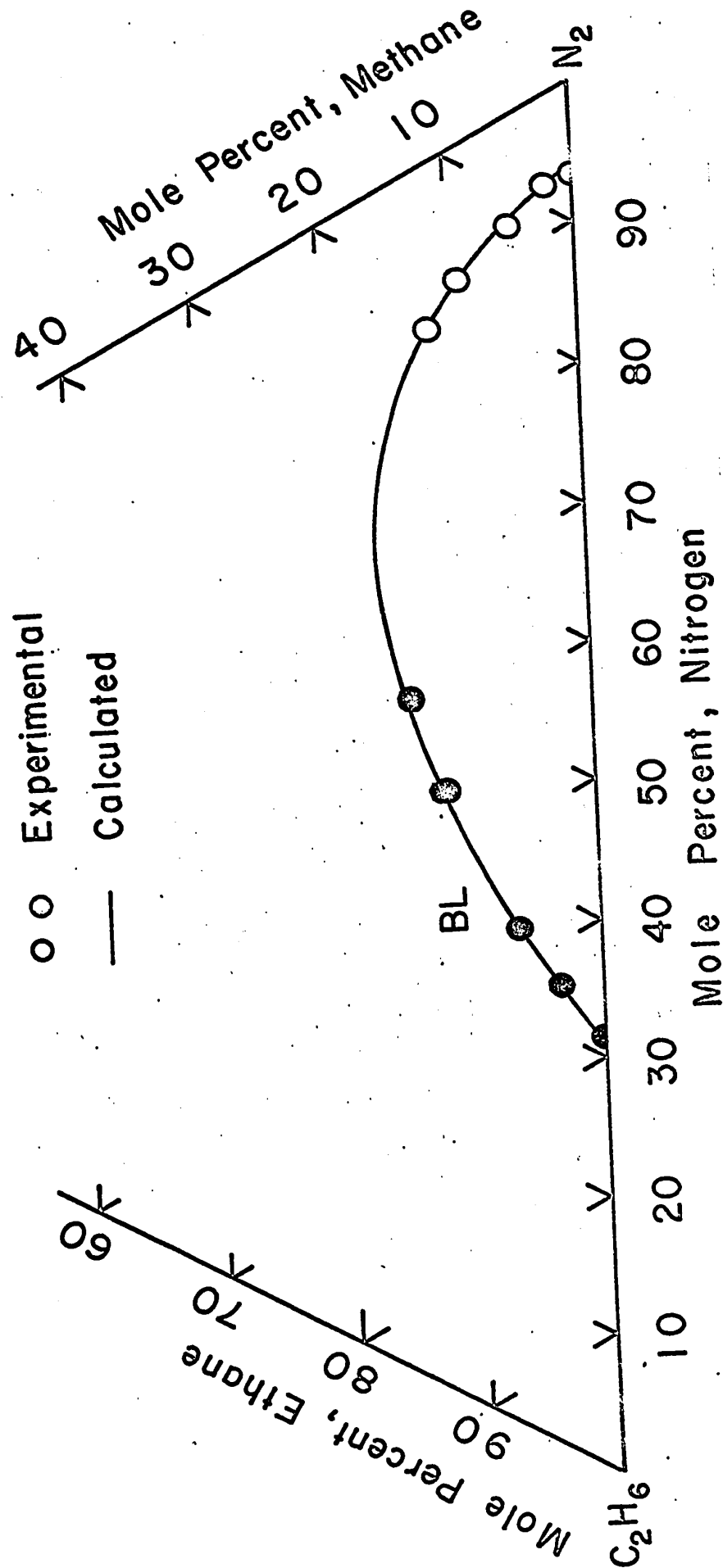


Figure 6-12 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 130.1 °K

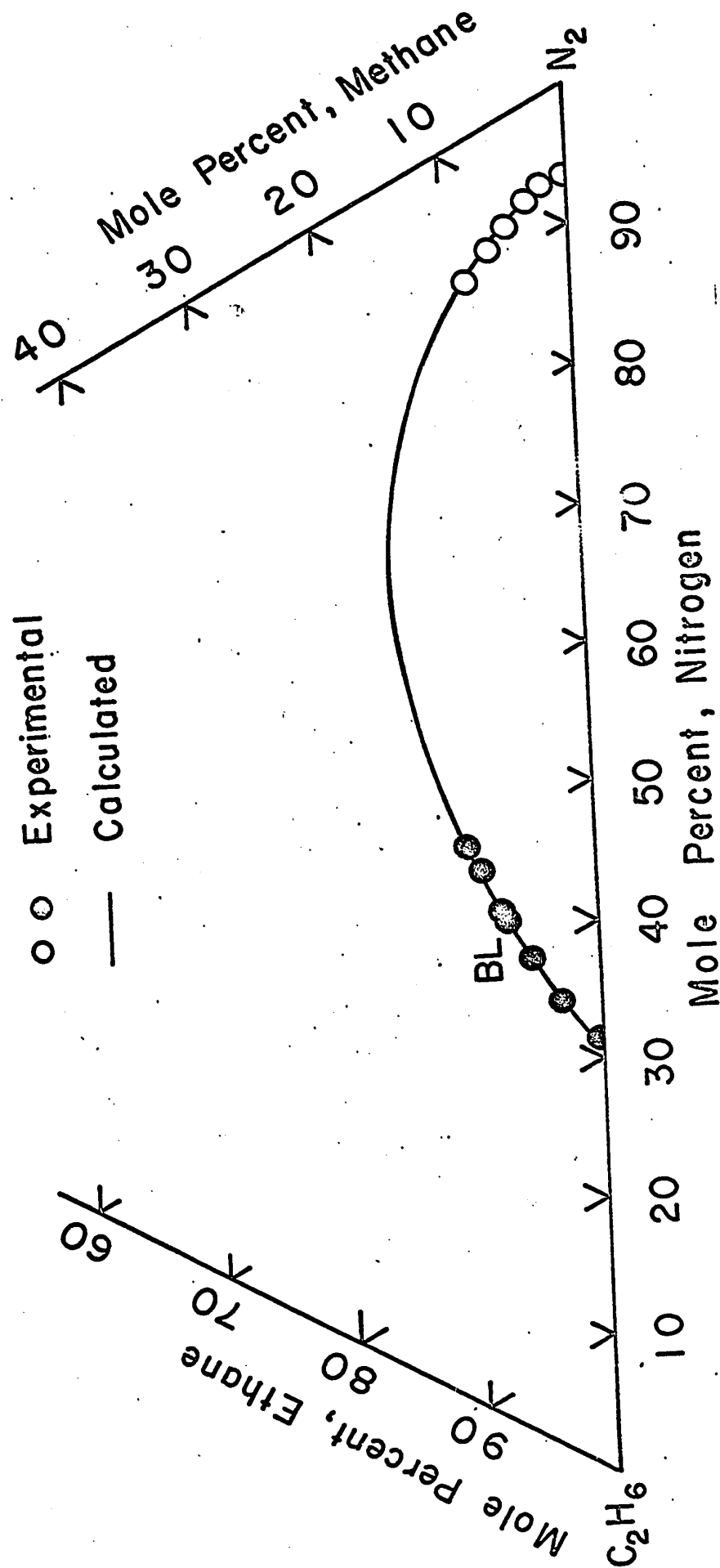


Figure 6-13 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the Nitrogen-Methane-Ethane System at 133.3 K

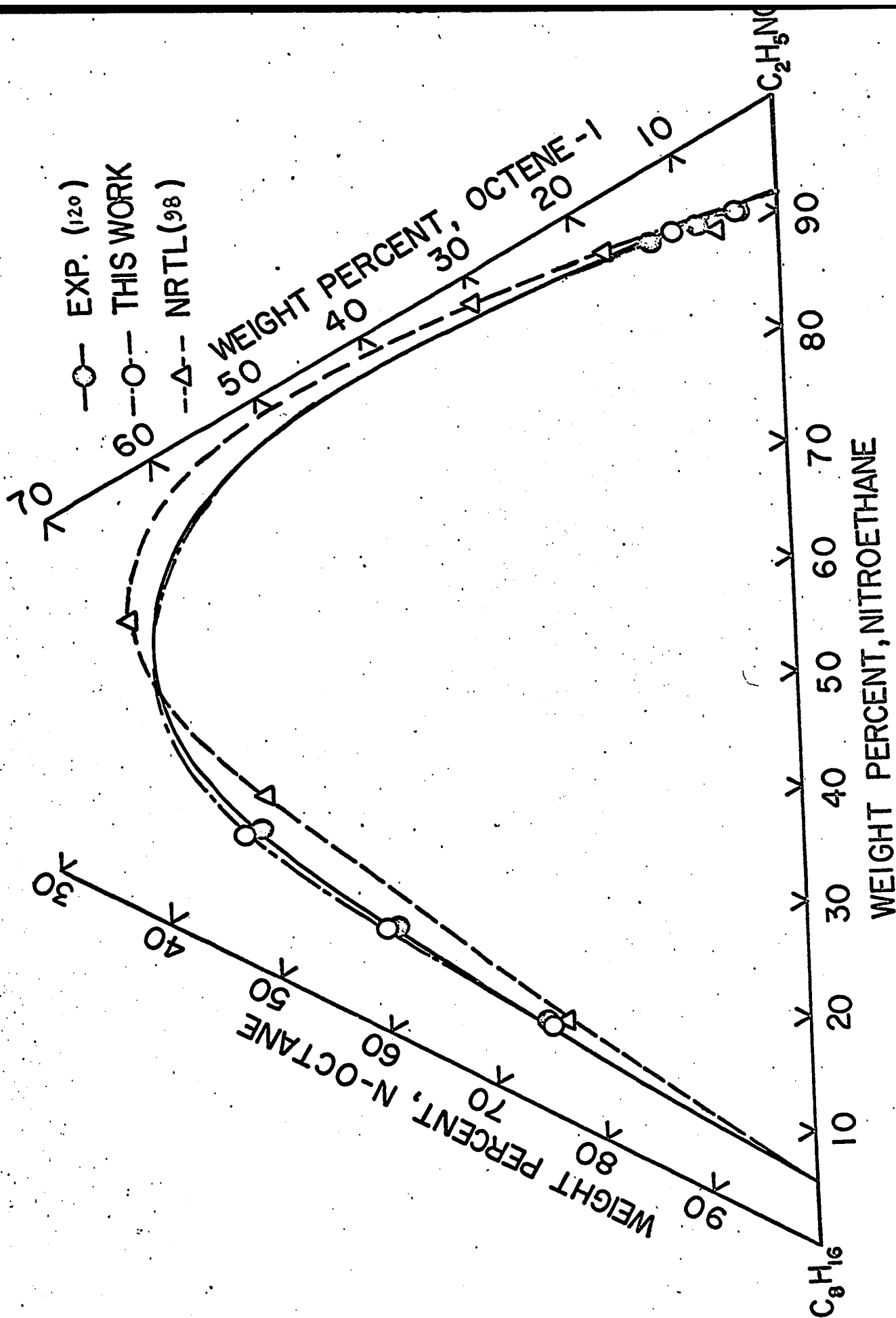


Figure 6-14 Comparison of Calculated and Experimental Liquid-Liquid Equilibria for the N-octane-Octene-1-Nitroethane System at 273.1 °K

CHAPTER VII

SUMMARY AND CONCLUSIONS

A. EXPERIMENTAL WORK

A forced-recirculation apparatus was modified and built for obtaining the phase equilibrium data at low temperatures and high pressures.

The existence of two liquid phases between nitrogen and low-molecular weight paraffins at low temperatures is of interest, because this system consists of the three major components of natural gases and separation of nitrogen from natural gases rich in nitrogen may be facilitated by taking advantage of the composition difference of the two liquid phases. The liquid-phase inversion phenomenon is found for the nitrogen-ethane and nitrogen-methane-ethane systems in the temperature range from 109° to 113 °K.

Equilibrium data for two liquid phases were obtained at eight isotherms above the liquid phase inversion temperature and at three isotherms below the phase inversion temperature over the temperature range of 93° to 133 °K.

It is seen from Chapter II, the forced-recirculation apparatus is suitable for obtaining phase equilibrium data at low temperatures and high pressures.

The experimental results obtained in this investigation were compared with the values reported in literature(10,12,

37,38). The agreement is very good.

The experimental results for the binary systems obtained in this investigation satisfy the area-test for thermodynamic consistency.

In all the cases investigated, the nitrogen concentration in the vapor phase was more than 96 mole percent.

At the condition that three-phase coexist, the partially miscible region increases with the decrease of temperature; and the concentration of methane in the ethane-rich phase is always greater than that in the equilibrium nitrogen-rich liquid phase regardless of the liquid-phase inversion behavior.

B. CORRELATION OF VAPOR-LIQUID AND LIQUID-LIQUID-VAPOR EQUILIBRIUM DATA

The constant-pressure and constant-temperature liquid activity coefficients were evaluated from the experimental data of the systems containing nitrogen, methane and ethane by means of Equation(2-46).

In the calculations, the modified Redlich-Kwong equation of state was employed to evaluate the necessary thermodynamic functions $\hat{G}_i^V$, f_i^{Lo} , and $\bar{V}_i$. The reference pressure was taken as 1000 psia.

The γ values were then correlated by means of the Redlich-Kister equation for both the binary and ternary

systems. The calculated activity coefficients deviate from the experimental values within 2% for the binary systems and within 3% for the ternary system.

It was found in this investigation that a small difference in vapor-phase composition would give a large difference in activity coefficient for the less volatile component, because the vapor phase was extremely rich in the volatile component nitrogen. For instance, a change of ethane composition from 0.0036 to 0.0038 mole fraction would cause a change of r value for ethane from 0.2873 to 1.1101 for the nitrogen-ethane binary system at 130.1 °K and 500 psia. Therefore, the activity coefficient for the less volatile component would show a large scattering although the absolute deviation in vapor composition is not very significant.

Ternary liquid-liquid-vapor equilibrium data were correlated in terms of the distribution coefficients. For the liquid-liquid-vapor equilibria, the K'_{N_2} values decrease with the increase of temperature. At constant K'_H , K'_{C_1} , or K'_{C_2} the lower the temperature, the lower K'_{N_2} values (ie. the lower the concentration of nitrogen in the ethane-rich liquid phase) at temperatures higher than the liquid-phase inversion temperature. However at temperatures lower than the liquid-phase inversion temperature, the lower the temperature, the

higher the K'_{N_2} values.

C. LIQUID-DENSITY AND LIQUID-PHASE INVERSION

In order to understand how the liquid-phase inversion phenomenon. The values of liquid are required.

The available methods were not adequate to calculate liquid densities for this system. Therefore, the new calculation method was proposed. The liquid densities were calculated by means of the modified Redlich-Kwong equation of state with temperature-dependent parameters k_{12} , Ω_a and Ω_b . The proposed method has been successfully applied to the systems containing nitrogen, methane, ethane and propane.

The overall average absolute deviation is less than 0.003g/cc.. The average absolute deviation of the liquid density between the two liquid phases at inversion condition is less than 0.01g/cc..

D. PREDICTION OF LIQUID-LIQUID-VAPOR EQUILIBRIUM DATA

The Renon's method of predicting liquid-liquid equilibria has the following disadvantages:

- (1) The parameters (α_{12} , $g_{12}-g_{22}$ and $g_{21}-g_{11}$) for the

binary systems were evaluated from the experimental

binary vapor-liquid and limited points of ternary liquid-liquid equilibrium data. Then using these binary parameters, the ternary binodal curves of calculated and experimental at the same temperature may be calculated from the NRTL equation(122).

- (2) Joy and Kyle(123) pointed out that an error of 0.05 in the estimated activity coefficients from the NRTL equation would produce a completely different binodal curve. Therefore the average absolute deviation in mole fraction was 0.019(101).

For these reasons, the proposed method was developed. In the prediction procedure, the modified Redlich-Kwong equation of state was again employed for evaluation of $\hat{Q}_i$.

The modified Regula-Falsi method in conjunction with the modified Redlich-Kwong equation can successfully predict the liquid-liquid-vapor compositions and total pressure at the given temperature. It has been shown that the method is applicable to the systems nitrogen-ethane, nitrogen-methane-ethane and n-octane-octene-1-nitroethane. It was also shown that the knowledge of thermodynamic properties of pure component and binary vapor-liquid equilibrium data was adequate to predict the liquid-liquid-vapor equilibrium data.

Perhaps the modified Redlich-Kwong equation of state works better at low temperatures, therefore the

calculated vapor compositions disagree with the experimental vapor compositions at temperatures above the critical temperature of nitrogen.

The proposed method uses simple algebraic equation does not involve derivatives of any functions. It produces fast results in relatively few iterations. It is general and suitable for solving simultaneous high-order equations.

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APPENDIX I

EXPERIMENTAL EQUILIBRIUM DATA
OF THE SYSTEMS CONTAINING
NITROGEN, METHANE AND ETHANE

TABLE I

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR

THE SYSTEM NITROGEN(1)-METHANE(2) AT 130.1°K

P	X	X	Y	Y
PSIA	1	2	1	2
123.5	0.1023	0.8977	0.5437	0.4563
149.0	0.1527	0.8473	0.6318	0.3682
183.0	0.2356	0.7644	0.7167	0.2833
254.0	0.3821	0.6179	0.7905	0.2095
291.0	0.5032	0.4968	0.8311	0.1689
336.5	0.6329	0.3671	0.8623	0.1377
390.0	0.7853	0.2147	0.9063	0.0937
435.5	0.8433	0.1567	0.9234	0.0766

TABLE II
EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR
THE SYSTEM NITROGEN(1)-ETHANE(2) AT 130.1 °K

<u>P</u> <u>PSIA</u>	<u>X</u> <u>1</u>	<u>X</u> <u>2</u>	<u>Y</u> <u>1</u>	<u>Y</u> <u>2</u>
62.0	0.0314	0.9686	0.9960	0.0040
170.0	0.0945	0.9055	0.9977	0.0023
202.0	0.1142	0.8858	0.9983	0.0017
303.0	0.1720	0.8280	0.9982	0.0018
400.0	0.2327	0.7673	0.9981	0.0019
500.0	0.2853	0.7147	0.9964	0.0036

TABLE III

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR

THE SYSTEM METHANE(1)-ETHANE(2) AT 130.1°K

P	X	X	Y	Y
PSIA	1	2	1	2
46.3	0.8362	0.1638	0.9984	0.0016
46.5	0.8386	0.1614	0.9984	0.0016
38.4	0.6666	0.3334	0.9972	0.0028
39.2	0.6679	0.3321	0.9971	0.0029
38.1	0.6064	0.3936	0.9969	0.0031
38.2	0.6069	0.3931	0.9969	0.0031
32.4	0.4778	0.5222	0.9960	0.0040
27.1	0.3646	0.6354	0.9945	0.0055
22.2	0.2985	0.7015	0.9935	0.0065
22.2	0.3016	0.6984	0.9934	0.0066
20.1	0.2514	0.7486	0.9922	0.0078

TABLE III (CONTINUE.....)

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR

THE SYSTEM METHANE(1)-ETHANE(2) AT 130.1°K

P PSIA	X 1	X 2	Y 1	Y 2
17.1	0.2134	0.7866	0.9906	0.0094
16.0	0.1888	0.8112	0.9894	0.0106
14.2	0.1813	0.8187	0.9890	0.0110
14.1	0.1769	0.8231	0.9889	0.0111
11.3	0.1114	0.8886	0.9824	0.0176
9.8	0.1070	0.8930	0.9817	0.0183
8.8	0.0996	0.9004	0.9806	0.0194
8.7	0.0935	0.9065	0.9796	0.0204
8.4	0.0915	0.9085	0.9786	0.0214
8.3	0.0882	0.9118	0.9781	0.0219

TABLE IV
EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR
THE SYSTEM NITROGEN(1)-METHANE(2)-ETHANE(3) AT 130.1°K

P	X			Y		
	1	2	3	1	2	3
73.7	0.0413	0.2976	0.6611	0.6805	0.3174	0.0021
150.0	0.0965	0.2805	0.6230	0.8371	0.1513	0.0015
200.0	0.1430	0.2661	0.5909	0.8768	0.1220	0.0012
229.0	0.1726	0.2569	0.5705	0.8967	0.1022	0.0011
300.0	0.2456	0.2342	0.5202	0.9170	0.0819	0.0011
345.0	0.2945	0.2191	0.4864	0.9283	0.0702	0.0015
415.0	0.3943	0.1881	0.4176	0.9400	0.0582	0.0018
50.0	0.0123	0.6928	0.2949	0.2217	0.7760	0.0023
112.5	0.0846	0.6421	0.2733	0.6489	0.3500	0.0011
160.0	0.1483	0.5974	0.2543	0.7437	0.2553	0.0010
213.5	0.2187	0.5481	0.2332	0.7880	0.2111	0.0009
248.5	0.2898	0.4982	0.2120	0.8305	0.1687	0.0008
320.0	0.4128	0.4119	0.1753	0.8694	0.1297	0.0009
350.0	0.4918	0.3565	0.1517	0.8879	0.1111	0.0010
400.0	0.5396	0.3230	0.1374	0.9065	0.0923	0.0012

TABLE V
EXPERIMENTAL LIQUID-LIQUID-VAPOR EQUILIBRIUM DATA FOR
THE SYSTEM NITROGEN(1)-ETHANE(3)

T °K	P PSIA	TOP			BOTTOM			VAPOR		
		X			X			Y		
		1	3	1	1	3	3	1	3	3
94.3	68.2	0.1695	0.8305	0.9588	0.0412	1.0000	0.0000	0.0000	0.0000	0.0000
101.5	104.9	0.1987	0.8013	0.9401	0.0599	1.0000	0.0000	0.0000	0.0000	0.0000
109.1	167.1	0.2139	0.7861	0.9413	0.0587	0.9999	0.0001	0.9999	0.0001	0.0001
113.4	225.0	0.9416	0.0584	0.2645	0.7355	0.9997	0.0003	0.9997	0.0003	0.0003
115.2	244.7	0.9475	0.0525	0.2486	0.7514	0.9996	0.0004	0.9996	0.0004	0.0004
116.3	251.7	0.9374	0.0626	0.2796	0.7204	0.9995	0.0005	0.9995	0.0005	0.0005
119.3	291.3	0.9351	0.0649	0.2865	0.7135	0.9995	0.0005	0.9995	0.0005	0.0005
121.9	320.0	0.9355	0.0645	0.2910	0.7090	0.9981	0.0019	0.9981	0.0019	0.0019
124.7	433.2	0.9343	0.0657	0.2925	0.7075	0.9935	0.0065	0.9935	0.0065	0.0065
129.7	542.6	0.9290	0.0710	0.3151	0.6849	0.9927	0.0073	0.9927	0.0073	0.0073
130.1	534.6	0.9307	0.0693	0.3104	0.6896	0.9899	0.0101	0.9899	0.0101	0.0101
132.3	588.0	0.9318	0.0682	0.3061	0.6939	0.9848	0.0152	0.9848	0.0152	0.0152
133.3	591.0	0.9319	0.0681	0.3109	0.6891					

TABLE IV (CONTINUE.....)

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR									
THE SYSTEM NITROGEN(1)-METHANE(2)-ETHANE(3) AT 130.1°K									
P	X			Y			Y		
	1	2	3	1	2	3	1	2	3
55.0	0.0232	0.2270	0.7498	0.6527	0.3436	0.0037	0.6527	0.3436	0.0037
104.3	0.0684	0.2165	0.7151	0.8315	0.1665	0.0020	0.8315	0.1665	0.0020
156.0	0.0896	0.2113	0.6991	0.8697	0.1286	0.0017	0.8697	0.1286	0.0017
202.0	0.1308	0.2020	0.6672	0.9021	0.0954	0.0015	0.9021	0.0954	0.0015
250.0	0.1721	0.1924	0.6355	0.9199	0.0787	0.0014	0.9199	0.0787	0.0014
300.0	0.2181	0.1817	0.6002	0.9358	0.0528	0.0014	0.9358	0.0528	0.0014
422.0	0.3189	0.1583	0.5228	0.9459	0.0524	0.0017	0.9459	0.0524	0.0017
51.5	0.0242	0.1123	0.8635	0.7797	0.2164	0.0039	0.7797	0.2164	0.0039
101.0	0.0525	0.1090	0.8385	0.8851	0.1125	0.0024	0.8851	0.1125	0.0024
151.0	0.0767	0.1061	0.8172	0.9195	0.0786	0.0019	0.9195	0.0786	0.0019
197.0	0.1176	0.1015	0.7809	0.9458	0.0526	0.0016	0.9458	0.0526	0.0016
200.0	0.1194	0.1013	0.7793	0.9458	0.0527	0.0015	0.9458	0.0527	0.0015
290.0	0.1913	0.0930	0.7157	0.9606	0.0378	0.0016	0.9606	0.0378	0.0016
300.0	0.1946	0.0926	0.7128	0.9617	0.0367	0.0016	0.9617	0.0367	0.0016
400.0	0.2662	0.0844	0.6494	0.9695	0.0287	0.0018	0.9695	0.0287	0.0018

TABLE VI

EXPERIMENTAL LIQUID-LIQUID-VAPOR EQUILIBRIUM DATA
FOR THE SYSTEM NITROGEN(1)-METHANE(2)-ETHANE(3)

T °K	P PSIA	TOP						BOTTOM						VAPOR					
		1		2		3		1		2		3		1		2		3	
		X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
94.3	67.4	0.1767	0.0394	0.7839	0.9285	0.0253	0.0462	0.9974	0.0026	0.0000	0.0000	0.0000	0.0000	0.9922	0.0078	0.0000	0.0000	0.0000	0.0000
94.3	62.8	0.1843	0.1249	0.6908	0.8300	0.0951	0.0749	0.9901	0.0099	0.0000	0.0000	0.0000	0.0000	0.9848	0.0152	0.0000	0.0000	0.0000	0.0000
94.3	61.9	0.2008	0.1615	0.6377	0.7889	0.1263	0.0848	0.9879	0.0121	0.0000	0.0000	0.0000	0.0000	0.9834	0.0166	0.0000	0.0000	0.0000	0.0000
94.3	62.0	0.2232	0.1910	0.5858	0.7718	0.1448	0.0834	0.9966	0.0034	0.0000	0.0000	0.0000	0.0000	0.9966	0.0034	0.0000	0.0000	0.0000	0.0000
94.3	65.1	0.1716	0.0438	0.7846	0.9217	0.0291	0.0492	0.9947	0.0053	0.0000	0.0000	0.0000	0.0000	0.9947	0.0053	0.0000	0.0000	0.0000	0.0000
94.3	64.2	0.1770	0.0842	0.7388	0.8815	0.0596	0.0724	0.9912	0.0088	0.0000	0.0000	0.0000	0.0000	0.9912	0.0088	0.0000	0.0000	0.0000	0.0000
94.3	62.9	0.1902	0.1314	0.6784	0.8293	0.0983	0.0753	0.9882	0.0118	0.0000	0.0000	0.0000	0.0000	0.9882	0.0118	0.0000	0.0000	0.0000	0.0000
94.3	62.0	0.2066	0.1601	0.6333	0.8060	0.1187	0.0753	0.9854	0.0146	0.0000	0.0000	0.0000	0.0000	0.9854	0.0146	0.0000	0.0000	0.0000	0.0000
94.3	61.1	0.2320	0.2151	0.5529	0.7181	0.1759	0.1060	0.9922	0.0078	0.0000	0.0000	0.0000	0.0000	0.9922	0.0078	0.0000	0.0000	0.0000	0.0000
94.3	62.9	0.1828	0.1233	0.6939	0.8301	0.0949	0.0750	0.9924	0.0076	0.0000	0.0000	0.0000	0.0000	0.9924	0.0076	0.0000	0.0000	0.0000	0.0000
101.5	104.0	0.2296	0.0821	0.6883	0.8652	0.0595	0.0753	0.9924	0.0076	0.0000	0.0000	0.0000	0.0000	0.9924	0.0076	0.0000	0.0000	0.0000	0.0000

TABLE VI (CONTINUE.....)

		TOP			BOTTOM			VAPOR		
T	P	X	X	X	X	X	X	Y	Y	Y
°K	PSIA	1	2	3	1	2	3	1	2	3
101.5	103.9	0.2382	0.0835	0.6783	0.8722	0.0589	0.0689	0.9928	0.0072	0.0000
101.5	103.8	0.2514	0.1306	0.6080	0.8224	0.0947	0.0829	0.9890	0.0110	0.0000
101.5	103.7	0.2893	0.1685	0.5422	0.7860	0.1237	0.0903	0.9859	0.0141	0.0000
101.5	103.6	0.3003	0.1773	0.5224	0.7795	0.1299	0.0906	0.9853	0.0147	0.0000
101.5	103.1	0.3077	0.1996	0.4927	0.7273	0.1591	0.1136	0.9832	0.0168	0.0000
101.5	102.1	0.3027	0.1988	0.4985	0.7226	0.1596	0.1178	0.9832	0.0168	0.0000
109.1	165.7	0.2340	0.0513	0.7147	0.8799	0.0406	0.0795	0.9930	0.0070	0.0000
109.1	165.6	0.2364	0.0511	0.7125	0.8829	0.0400	0.0771	0.9932	0.0068	0.0000
109.1	164.9	0.2675	0.1051	0.6274	0.8245	0.0842	0.0913	0.9866	0.0134	0.0000
109.1	164.7	0.2952	0.1461	0.5587	0.7532	0.1242	0.1226	0.9814	0.0186	0.0000
109.1	163.8	0.2956	0.1465	0.5579	0.7530	0.1245	0.1225	0.9813	0.0187	0.0000
109.1	162.2	0.3447	0.1883	0.4670	0.6739	0.1676	0.1585	0.9792	0.0208	0.0000
109.1	161.5	0.3505	0.1928	0.4567	0.6670	0.1725	0.1605	0.9781	0.0219	0.0000

TABLE VI (CONTINUE.....)

T °K	P PSIA	TOP						BOTTOM						VAPOR					
		X		X		X		X		X		X		Y		Y		Y	
		1	2	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	
128.8	484.3	0.9095	0.0110	0.0795	0.3338	0.0151	0.6511	0.9777	0.0167	0.0056									
128.8	455.2	0.7937	0.0935	0.1128	0.4302	0.1188	0.4510	0.9637	0.0326	0.0037									
128.8	449.6	0.7696	0.1064	0.1240	0.4638	0.1307	0.4055	0.9529	0.0338	0.0033									
128.8	440.7	0.6994	0.1293	0.1713	0.5268	0.1442	0.3290	0.9581	0.0393	0.0026									
128.8	438.6	0.6875	0.1354	0.1771	0.5638	0.1463	0.2899	0.9577	0.0398	0.0025									
130.1	535.2	0.9132	0.0216	0.0652	0.3287	0.0314	0.6399	0.9884	0.0068	0.0048									
130.1	528.6	0.8708	0.0494	0.0798	0.3570	0.0688	0.5742	0.9768	0.0158	0.0074									
130.1	512.0	0.8117	0.0909	0.0974	0.4312	0.1208	0.4480	0.9633	0.0315	0.0052									
130.1	463.0	0.7800	0.1127	0.1073	0.4847	0.1433	0.3720	0.9582	0.0398	0.0020									
133.3	525.0	0.8459	0.0668	0.0873	0.3892	0.0892	0.5216	0.9645	0.0298	0.0057									
133.3	535.3	0.8730	0.0543	0.0727	0.3625	0.0755	0.5620	0.9580	0.0264	0.0056									
133.3	549.0	0.8974	0.0371	0.0655	0.3440	0.0522	0.6038	0.9766	0.0176	0.0058									
133.3	558.6	0.9173	0.0209	0.0618	0.3194	0.0293	0.6513	0.9817	0.0108	0.0075									

TABLE VI (CONTINUE.....)

		TOP			BOTTOM			VAPOR		
T	P	X	X	X	X	X	X	Y	Y	Y
°K	PSIA	1	2	3	1	2	3	1	2	3
133.3	534.5	0.8758	0.0515	0.0727	0.3609	0.0724	0.5667	0.9587	0.0248	0.0065
133.3	515.1	0.8183	0.0830	0.0987	0.3996	0.1062	0.4942	0.9603	0.0357	0.0040

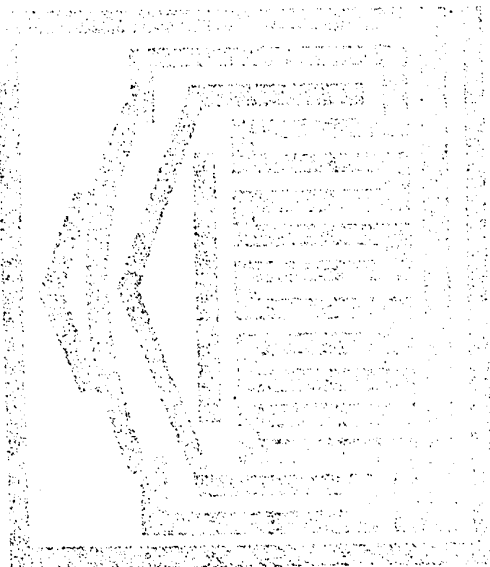


TABLE VII

PHASE INVERSION TEMPERATURES AND LIQUID-LIQUID-VAPOR EQUILIBRIUM

DATA FOR THE SYSTEM NITROGEN(1)-METHANE(2)-ETHANE(3)

		TOP			BOTTOM			VAPOR		
T	P	X	X	X	X	X	X	Y	Y	Y
°K	PSIA	1	2	3	1	2	3	1	2	3
111.4	200.8	0.8396	0.0737	0.0867	0.2851	0.0921	0.6228	0.9888	0.0112	0.0000
111.4	200.6	0.2831	0.0938	0.6231	0.8340	0.0831	0.0829	0.9896	0.0104	0.0000
111.5	201.4	0.8269	0.0876	0.0855	0.2878	0.0978	0.6144	0.9874	0.0126	0.0000
111.5	200.8	0.2912	0.0980	0.6108	0.8341	0.0874	0.0785	0.9873	0.0127	0.0000
113.0	208.5	0.7483	0.1301	0.1216	0.3609	0.1503	0.4888	0.9796	0.0204	0.0000
113.0	208.3	0.3426	0.1466	0.5108	0.7499	0.1282	0.1219	0.9796	0.0204	0.0000
113.3	213.0	0.6182	0.1896	0.1922	0.4576	0.2011	0.3413	0.9746	0.0254	0.0000
113.3	212.3	0.4584	0.2013	0.3403	0.6172	0.1899	0.1929	0.9743	0.0257	0.0000

APPENDIX II

CORRELATION OF VAPOR-LIQUID AND
LIQUID-LIQUID-VAPOR EQUILIBRIUM DATA

TABLE I
COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED Y AND Y VALUES FOR
THE SYSTEM NITROGEN(1)-METHANE(2) AT 130.1°K

P	X	EXP		CAL		EXP		CAL	
		Y	1	Y	1	Y	2	Y	2
	1	1	1	1	1	1	2	1	2
PSIA									
123.5	0.1023	0.5437	0.5441	1.9490	1.0368	1.8908	1.0080		
149.0	0.1527	0.6318	0.6315	1.7870	1.0252	1.7690	1.0178		
183.0	0.2356	0.7167	0.7141	1.5646	1.0140	1.5868	1.0432		
254.0	0.3821	0.7905	0.7901	1.3826	1.1275	1.3634	1.1195		
291.0	0.5032	0.8311	0.8286	1.2250	1.1993	1.2251	1.2185		
336.5	0.6329	0.8623	0.8625	1.1220	1.3710	1.1208	1.3689		
390.0	0.7853	0.9063	0.9037	1.0498	1.5649	1.0478	1.6065		
435.5	0.8433	0.9234	0.9224	1.0534	1.6639	1.0337	1.6973		

TABLE III
COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED Y AND Y VALUES FOR
THE SYSTEM METHANE(1)-ETHANE(2) AT 130.1°K

P PSIA	X	EXP		CAL		EXP		CAL	
		Y	1	Y	1	Y	1	Y	1
46.3	0.8362	0.9984	0.9985	1.0390	1.9514	1.0335	1.7960	1.0325	1.8042
46.5	0.8386	0.9984	0.9985	1.0402	1.4509	1.1257	1.3814	1.1248	1.3836
38.4	0.6666	0.9972	0.9974	1.0914	1.5348	1.1704	1.2902	1.1700	1.2908
39.2	0.6679	0.9971	0.9974	1.1104	1.3543	1.2854	1.1539	1.4078	1.0796
38.1	0.6064	0.9969	0.9970	1.1893	1.1498	1.4884	1.0502	1.4845	1.0513
38.2	0.6069	0.9969	0.9970	1.1913	1.1119	1.5499	1.0341	1.0216	1.5432
32.4	0.4778	0.9960	0.9960	1.2919	0.9948	0.9948	0.9948	0.9948	0.9948
27.1	0.3646	0.9945	0.9946	1.4238	1.0146	1.4845	1.0513	1.4845	1.0513
22.2	0.2985	0.9935	0.9934	1.4334	1.0146	1.4845	1.0513	1.4845	1.0513
22.2	0.3016	0.9934	0.9934	1.4186	1.0146	1.4845	1.0513	1.4845	1.0513
20.1	0.2514	0.9922	0.9921	1.5432	1.0216	1.5499	1.0341	1.0216	1.5432

TABLE III (CONT INUE.....)

COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED Y AND Y VALUES FOR
THE SYSTEM METHANE(1)-ETHANE(2) AT 130.1°K

P PSIA	X	EXP				CAL			
		Y		1		Y		1	
		1	2	1	2	1	2	1	2
17.1	0.2134	0.9906	0.9908	1.5510	1.0089	1.6020	1.0238		
16.0	0.1888	0.9894	0.9896	1.6407	1.0368	1.6369	1.0183		
14.2	0.1813	0.9890	0.9891	1.5201	0.9529	1.6477	1.0168		
14.1	0.1769	0.9889	0.9889	1.5469	0.9500	1.6541	1.0159		
11.3	0.1114	0.9824	0.9825	1.9628	1.1306	1.7528	1.0060		
9.8	0.1070	0.9817	0.9818	1.7753	1.0205	1.7597	1.0055		
8.8	0.0996	0.9806	0.9805	1.7134	0.9672	1.7713	1.0048		
8.7	0.0935	0.9796	0.9793	1.8027	0.9991	1.7810	1.0042		
8.4	0.0915	0.9786	0.9788	1.7776	1.0109	1.7842	1.0040		
8.3	0.0882	0.9781	0.9780	1.8214	1.0189	1.7894	1.0037		

TABLE IV
COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED Y AND Y VALUES FOR
THE SYSTEM NITROGEN(1)-METHANE(2)-ETHANE(3) AT 130.1°K

P PSIA	EXP						CAL					
	X		Y		3		Y		2		Y	
	1	2	1	2	1	2	1	2	1	2	1	2
73.7	0.0413	0.2976	3.5749	1.4090	0.9555	3.9149	1.4311	1.0714	1.4311	1.0714	1.4311	1.0714
150.0	0.0965	0.2805	3.5656	1.3749	1.2080	3.5306	1.3796	1.1014	1.3796	1.1014	1.3796	1.1014
200.0	0.1430	0.2661	3.2044	1.3480	1.0566	3.2368	1.3409	1.1349	1.3409	1.1349	1.3409	1.1349
229.0	0.1726	0.2569	3.0228	1.2763	1.0254	3.0633	1.3187	1.1607	1.3187	1.1607	1.3187	1.1607
300.0	0.2456	0.2342	2.6527	1.2913	1.0762	2.6765	1.2716	1.2426	1.2716	1.2426	1.2716	1.2426
345.0	0.2945	0.2191	2.4589	1.2423	1.4335	2.4472	1.2464	1.3155	1.2464	1.3155	1.2464	1.3155
415.0	0.3943	0.1881	2.0766	1.2168	1.5130	2.0468	1.2128	1.5270	1.2128	1.5270	1.2128	1.5270
50.0	0.0123	0.6928	2.7809	1.0439	1.6827	2.7707	1.0988	1.4577	1.0988	1.4577	1.0988	1.4577
112.5	0.0846	0.6421	2.5054	1.0361	1.5736	2.4692	1.0807	1.5458	1.0807	1.5458	1.0807	1.5458
160.0	0.1483	0.5974	2.2286	1.0703	1.8336	2.2374	1.0713	1.6480	1.0713	1.6480	1.0713	1.6480
213.5	0.2187	0.5481	2.0317	1.1737	1.9303	2.0135	1.0685	1.7950	1.0685	1.7950	1.0685	1.7950
248.5	0.2898	0.4982	1.8200	1.1312	1.8968	1.8183	1.0745	1.9902	1.0745	1.9902	1.0745	1.9902
320.0	0.4128	0.4119	1.6065	1.1788	2.3366	1.5431	1.1093	2.9766	1.1093	2.9766	1.1093	2.9766
350.0	0.4918	0.3565	1.4640	1.1975	2.7614	1.4022	1.1509	3.3651	1.1509	3.3651	1.1509	3.3651
400.0	0.5396	0.3230	1.4733	1.1082	2.9793	1.3290	1.1851		1.1851		1.1851	

TABLE IV (CONTINUE.....)

COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED Y AND Y VALUES FOR

THE SYSTEM NITROGEN(1)-METHANE(2)-ETHANE(3) AT 130.1°K

P PSIA	EXP						CAL					
	X	X	Y	Y	Y	Y	X	X	Y	Y	Y	Y
	1	2	1	2	3	1	1	2	3	1	2	3
55.0	0.0232	0.2270	4.6185	1.5347	1.1835	4.3915	1.5471	1.0352				
104.3	0.0684	0.2165	3.6158	1.3753	1.0828	4.0260	1.4942	1.0519				
156.0	0.0896	0.2113	4.1115	1.5002	1.1717	3.8661	1.4713	1.0616				
202.0	0.1308	0.2020	3.6208	1.4148	1.1824	3.5701	1.4285	1.0850				
250.0	0.1721	0.1924	3.3143	1.3826	1.1816	3.2972	1.3897	1.1145				
300.0	0.2181	0.1817	3.0365	1.2802	1.2042	3.0182	1.3510	1.1558				
422.0	0.3189	0.1583	2.5906	1.2990	1.1135	2.4905	1.2833	1.2874				
51.5	0.0242	0.1123	4.9453	1.8411	1.0344	4.9464	1.7095	1.0159				
101.0	0.0525	0.1090	4.8484	1.7977	1.0936	4.6756	1.6669	1.0225				
151.0	0.0767	0.1061	4.9175	1.7863	1.1172	4.4555	1.6321	1.0374				
197.0	0.1176	0.1015	4.1207	1.5166	1.0875	4.1040	1.5762	1.0382				
200.0	0.1194	0.1013	4.1084	1.5380	1.0253	4.0892	1.5739	1.0780				
290.0	0.1913	0.0930	3.4560	1.4897	1.1897	3.5377	1.4864	1.0803				
300.0	0.1946	0.0926	3.4823	1.4747	1.1804	3.5142	1.4827	1.1421				
400.0	0.2662	0.0844	3.0759	1.3623	1.1218	3.0409	1.4091					

TABLE V

EXPERIMENTAL VALUES OF EQUILIBRIUM RATIOS AND DISTRIBUTION COEFFICIENTS

FOR THE SYSTEM NITROGEN(1)-METHANE(2)-ETHANE(3)

T °K	P PSIA	TOP						BOTTOM						K'					
		K		K		K		K		K		K		K		K		K	
		1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
94.3	67.4	5.6446	0.0660	0.0000	1.0742	0.1028	0.0000	5.2547	0.6421	0.0589	0.0868	0.0000	4.5035	0.7614	0.1084	0.2084	0.0000	4.5035	0.7614
94.3	62.8	5.3835	0.0624	0.0000	1.1954	0.0820	0.0000	3.9288	0.7820	0.1330	0.2641	0.0000	3.9288	0.7820	0.1330	0.2641	0.0000	3.9288	0.7820
94.3	61.9	4.9308	0.0613	0.0000	1.2550	0.0784	0.0000	3.4579	0.7581	0.1424	0.2938	0.0000	3.4579	0.7581	0.1424	0.2938	0.0000	3.4579	0.7581
94.3	62.0	4.4261	0.0634	0.0000	1.2800	0.0836	0.0000	5.3712	0.6644	0.0627	0.0945	0.0000	5.3712	0.6644	0.0627	0.0945	0.0000	5.3712	0.6644
94.3	65.1	5.8077	0.0776	0.0000	1.0813	0.1168	0.0000	4.9802	0.7078	0.0797	0.1440	0.0000	4.9802	0.7078	0.0797	0.1440	0.0000	4.9802	0.7078
94.3	64.2	5.6198	0.0629	0.0000	1.1284	0.0889	0.0000	4.3601	0.7481	0.1067	0.2108	0.0000	4.3601	0.7481	0.1067	0.2108	0.0000	4.3601	0.7481
94.3	62.9	5.2114	0.0670	0.0000	1.1952	0.0895	0.0000	3.9013	0.7414	0.1189	0.2445	0.0000	3.9013	0.7414	0.1189	0.2445	0.0000	3.9013	0.7414
94.3	62.0	4.7832	0.0737	0.0000	1.2261	0.0994	0.0000	3.0953	0.8178	0.1917	0.3671	0.0000	3.0953	0.8178	0.1917	0.3671	0.0000	3.0953	0.8178
94.3	61.1	4.2474	0.0679	0.0000	1.3722	0.0830	0.0000	4.5410	0.7697	0.1081	0.2079	0.0000	4.5410	0.7697	0.1081	0.2079	0.0000	4.5410	0.7697
94.3	62.9	5.4278	0.0633	0.0000	1.1953	0.0822	0.0000	3.7683	0.7247	0.1094	0.1750	0.0000	3.7683	0.7247	0.1094	0.1750	0.0000	3.7683	0.7247
101.5	104.0	4.3223	0.0926	0.0000	1.1470	0.1277	0.0000					0.0000							

TABLE V (CONTINUE.....)														
TOP										BOTTOM				
T •K	P	PSIA	K			K			K			K'		
			1	2	3	1	2	3	1	2	3	1	2	3
101.5	103.9	4.1679	0.0862	0.0000	0.0000	1.1383	0.1222	0.0000	3.6616	0.7054	0.1016	0.1678		
101.5	103.8	3.7835	0.0842	0.0000	0.0000	1.2026	0.1162	0.0000	3.1461	0.7251	0.1363	0.2405		
101.5	103.7	3.4079	0.0837	0.0000	0.0000	1.2543	0.1140	0.0000	2.7169	0.7341	0.1565	0.3011		
101.5	103.6	3.2811	0.0829	0.0000	0.0000	1.2640	0.1132	0.0000	2.5957	0.7327	0.1734	0.3151		
101.5	103.1	3.1953	0.0842	0.0000	0.0000	1.3518	0.1056	0.0000	2.3637	0.7971	0.2306	0.3939		
101.5	102.1	3.2481	0.0845	0.0000	0.0000	1.3606	0.1053	0.0000	2.3872	0.8028	0.2363	0.3978		
109.1	165.7	4.2435	0.1365	0.0000	0.0000	1.1285	0.1724	0.0000	3.7348	0.7828	0.1082	0.1534		
109.1	165.6	4.2014	0.1331	0.0000	0.0000	1.1249	0.1700	0.0000	3.0822	0.8011	0.1455	0.2396		
109.1	164.9	3.6882	0.1275	0.0000	0.0000	1.1966	0.1591	0.0000	2.5515	0.8501	0.2194	0.3502		
109.1	164.7	3.3245	0.1273	0.0000	0.0000	1.3030	0.1498	0.0000	2.5474	0.8498	0.2196	0.3507		
109.1	163.8	3.3197	0.1276	0.0000	0.0000	1.3032	0.1502	0.0000	1.9550	0.8901	0.3394	0.4976		
109.1	162.2	2.8407	0.1105	0.0000	0.0000	1.4530	0.1241	0.0000	1.9030	0.8947	0.3514	0.5127		
109.1	161.5	2.7906	0.1136	0.0000	0.0000	1.4664	0.1270	0.0000						

TABLE V (CONTINUE.....)

T °K	P PSIA	TOP						BOTTOM						K'					
		K		K		K		K		K		K		K'		K'		K'	
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
115.2	231.5	1.3987	0.1744	0.0044	2.4116	0.1526	0.0016	0.5800	1.1430	2.7227	1.9625								
115.2	230.4	1.5085	0.1638	0.0047	2.1916	0.1508	0.0024	0.5883	1.0859	1.9714	1.5653								
115.2	229.7	1.5315	0.1631	0.0045	2.1480	0.1507	0.0024	0.7130	1.0825	1.8417	1.4989								
116.3	248.5	1.1407	0.2021	0.0060	3.1620	0.1519	0.0008	0.3608	1.3299	7.4195	5.1888								
116.3	248.3	1.1431	0.2085	0.0059	3.1807	0.1602	0.0008	0.3594	1.3016	7.3322	5.1189								
116.3	247.1	1.5069	0.1744	0.0045	2.1819	0.1601	0.0023	0.6906	1.0895	1.9340	1.5618								
116.3	246.3	1.3556	0.1768	0.0042	2.4121	0.1512	0.0014	0.5620	1.1695	3.0313	2.1230								
119.3	284.6	1.0986	0.2543	0.0055	3.2148	0.1879	0.0006	0.3417	1.3534	9.1217	7.2346								
119.3	284.3	1.1032	0.2500	0.0054	3.1756	0.1875	0.0006	0.3474	1.3333	8.8721	6.8799								
119.3	284.2	1.1125	0.2208	0.0052	3.1408	0.1631	0.0006	0.3542	1.3539	8.3620	6.3559								
119.3	282.5	1.1026	0.2548	0.0054	3.1847	0.1886	0.0006	0.3462	1.3514	8.8871	6.9235								
119.3	281.3	1.1376	0.2416	0.0060	2.9813	0.1823	0.0008	0.3816	1.3256	7.2169	5.0844								
119.3	280.0	1.1564	0.2252	0.0044	2.9580	0.1756	0.0007	0.3909	1.2829	6.5468	4.5512								

TABLE V (CONTINUE.....)

		TOP						BOTTOM						K'					
		K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	H
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	3	3	H
T	P																		
°K	PSIA																		
133.3	534.5	1.1061	0.4816	0.0894	2.6841	0.3425	0.0115	0.4121	1.4058	7.7951	5.1457								
133.3	515.1	1.1735	0.4301	0.0405	2.4032	0.3362	0.0081	0.4883	1.2795	5.0071	3.3043								

APPENDIX III

THE Ω VALUES AND THE OBSERVED
AND CALCULATED LIQUID DENSITIES

TABLE I

THE Ω_a AND Ω_b VALUES FOR PURE COMPONENT OF
NITROGEN, METHANE, ETHANE AND PROPANE

Tr	Ω_a			Ω_b				
	N_2	C_1	C_2	C_3	N_2	C_1	C_2	C_3
1.00	0.42759	0.42577	0.43042	0.43284	0.08005	0.08607	0.08709	0.08764
0.95	0.40639	0.40272	0.40016	0.40153	0.08032	0.07949	0.07756	0.07782
0.90	0.41140	0.40706	0.40465	0.40819	0.08163	0.08092	0.07842	0.07884
0.85	0.41559	0.41001	0.40990	0.41460	0.08308	0.08225	0.07968	0.07891
0.80	0.41788	0.41135	0.41434	0.41952	0.08417	0.08343	0.08073	0.08069
0.75	0.41685	0.41156	0.41754	0.42229	0.08489	0.08420	0.08181	0.08114
0.70	0.41633	0.41122	0.41811	0.42584	0.08566	0.08516	0.08211	0.08182
0.65	0.41623	0.40640	0.42028	0.42752	0.08628	0.08575	0.08329	0.08223
0.60	0.41303	0.40624	0.41981	0.42679	0.08660	0.08643	0.08384	0.08230
0.55	0.40961	0.39951	0.41744	0.42339	0.08706	0.08660	0.08417	0.08207
0.50	0.40200	0.39157	0.41272	0.41929	0.08679	0.08676	0.08428	0.08186
0.45			0.40566	0.41439			0.08420	0.08154
0.40			0.39585	0.40496			0.08376	0.08113
0.35				0.39407				0.08065
0.30				0.38012				0.08010
0.25				0.36185				0.07950

TABLE II

COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED
LIQUID DENSITIES FOR MIXTURES OF METHANE(1)-PROPANE(2)

T, °K	X ₁	DENSITY, G/C.C.		
		EXP	CAL	DEV
108.1	0.2575	0.666	0.668	-0.002
108.1	0.4068	0.636	0.637	-0.001
108.1	0.5504	0.600	0.601	-0.001
108.1	0.6924	0.557	0.559	-0.002
108.1	0.8484	0.499	0.500	-0.001
AVE. 0.001				

TABLE III

COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED
LIQUID DENSITIES FOR MIXTURES OF NITROGEN(1)-ETHANE(2)

T, °K	X ₁	DENSITY, G/C.C.		
		EXP	CAL	DEV
117.0	0.1501	0.641	0.643	-0.002
101.8	0.1501	0.661	0.663	-0.002
123.2	0.3169	0.660	0.661	-0.001
106.5	0.9802	0.583	0.614	-0.031
132.6	0.9490	0.411	0.454	-0.043

AVE. 0.015

TABLE IV

COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED
LIQUID DENSITIES FOR MIXTURES OF ETHANE(1)-PROPANE(2)

T, °K	X ₁	DENSITY, G/C.C.		
		EXP	CAL	DEV
108.1	0.2619	0.695	0.595	0.000
108.1	0.4120	0.687	0.685	0.002
108.1	0.7036	0.665	0.660	0.005
108.1	0.5852	0.675	0.671	0.004
108.1	0.8087	0.655	0.650	0.005

AVE. 0.003

TABLE V
COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED
LIQUID DENSITIES FOR MIXTURES OF NITROGEN(1)-METHANE(2)

T, °K	X ₁	DENSITY, G/C.C.		
		EXP	CAL	DEV
122.8	0.1002	0.433	0.435	-0.002
109.7	0.2879	0.506	0.509	-0.003
120.0	0.2879	0.483	0.483	0.000
141.6	0.1002	0.387	0.381	0.006
				AVE. 0.003

TABLE VI

COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED
LIQUID DENSITIES FOR MIXTURES OF METHANE(1)-PROPANE(2)

T, °K	X ₁	DENSITY, G/C.C.		
		EXP	CAL	DEV
108.1	0.1902	0.603	0.601	0.002
108.1	0.3426	0.578	0.576	0.002
108.1	0.5454	0.539	0.539	0.000
108.1	0.6767	0.512	0.511	0.001
108.1	0.8686	0.465	0.465	0.000
113.8	0.6095	0.520	0.519	0.001
104.7	0.6066	0.533	0.532	0.001
107.8	0.6066	0.528	0.528	0.000
111.0	0.6066	0.525	0.525	0.000
113.0	0.6066	0.523	0.521	0.002
105.7	0.6079	0.531	0.531	0.000
110.8	0.6079	0.524	0.524	0.000
115.1	0.6079	0.519	0.519	0.000
100.4	0.8082	0.490	0.490	0.000
102.6	0.8082	0.487	0.487	0.000
105.2	0.8082	0.484	0.486	-0.002
107.9	0.8082	0.480	0.482	-0.002

AVE. 0.000

TABLE VII

COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED

LIQUID DENSITIES FOR MIXTURES OF METHANE(1)-ETHANE(2)-PROPANE(3)

T, °K	X		DENSITY, G/C.C.		DEV
	1	2	EXP	CAL	
108.1	0.3884	0.3216	0.607	0.608	-0.001
108.1	0.7238	0.1668	0.521	0.524	-0.003
108.0	0.5452	0.3320	0.562	0.561	0.001
112.5	0.5452	0.3320	0.556	0.555	0.001
116.9	0.5452	0.3320	0.551	0.551	0.000
99.7	0.5460	0.3312	0.571	0.571	0.000
105.5	0.5460	0.3312	0.564	0.564	0.000
110.1	0.5460	0.3312	0.558	0.558	0.000
104.2	0.4714	0.3488	0.586	0.587	-0.001
108.0	0.4714	0.3488	0.582	0.582	0.000
110.5	0.4714	0.3488	0.578	0.579	-0.001
AVE.					0.000

TABLE VIII
COMPARISON OF THE EXPERIMENTAL AND THE CALCULATED

LIQUID DENSITIES FOR MIXTURES OF NITROGEN(1)-METHANE(2)-ETHANE(3)

T, °K	X		DENSITY, G/C.C.		
	1	2	EXP	CAL	DEV
145.0	0.0140	0.9858	0.367	0.373	-0.006
161.1	0.0140	0.9858	0.335	0.337	-0.002
172.8	0.0140	0.9858	0.303	0.303	0.000
			AVE. 0.003		

TABLE IX

CALCULATED LIQUID PHASES DENSITY AT INVERSION CONDITION

FOR THE SYSTEM OF NITROGEN(1)-METHANE(2)-ETHANE(3)

T K	P PSIA	DENSITY, G/ C.C.	
		TOP	BOTTOM
111.4	200.8	0.657	0.670
111.4	200.6	0.667	0.656
111.5	201.4	0.656	0.667
111.5	200.8	0.664	0.656
113.1	208.5	0.667	0.656
113.1	208.3	0.654	0.667
113.3	213.0	0.660	0.655
113.3	212.3	0.655	0.660

APPENDIX IV

COMPARISON OF THE EXPERIMENTAL AND THE
CALCULATED LIQUID-LIQUID-VAPOR
EQUILIBRIUM DATA

TABLE I
CALCULATED LIQUID-LIQUID-VAPOR EQUILIBRIUM DATA FOR
THE SYSTEM NITROGEN(1)-ETHANE(3)

T K	P PSIA	TOP			BOTTOM			VAPOR		
		X	X	X	X	X	X	Y	Y	Y
		1	3	3	1	3	3	1	3	3
94.3	67.4	0.1696	0.8304	0.8304	0.9588	0.0412	1.0000	1.0000	0.0000	0.0000
101.5	103.4	0.1984	0.8016	0.8016	0.9402	0.0598	1.0000	1.0000	0.0000	0.0000
109.1	165.6	0.2135	0.7865	0.7865	0.9414	0.0586	0.9999	0.9999	0.0001	0.0001
113.4	220.0	0.9417	0.0583	0.0583	0.2642	0.7358	0.9998	0.9998	0.0002	0.0002
115.2	238.1	0.9397	0.0603	0.0603	0.2770	0.7230	0.9997	0.9997	0.0003	0.0003
116.3	250.8	0.9379	0.0621	0.0621	0.2811	0.7189	0.9997	0.9997	0.0003	0.0003
119.3	286.7	0.9351	0.0649	0.0649	0.2867	0.7133	0.9995	0.9995	0.0005	0.0005
121.9	317.7	0.9356	0.0644	0.0644	0.2907	0.7093	0.9994	0.9994	0.0006	0.0006
124.7	429.7	0.9343	0.0657	0.0657	0.2924	0.7076	0.9986	0.9986	0.0014	0.0014
129.7	542.3	0.9287	0.0713	0.0713	0.3160	0.6840	0.9287	0.9287	0.0713	0.0713
130.1	534.2	0.9296	0.0704	0.0704	0.3140	0.6860	0.9296	0.9296	0.0704	0.0704
132.3	587.7	0.9314	0.0686	0.0686	0.3074	0.6926	0.9314	0.9314	0.0686	0.0686
133.3	590.6	0.9315	0.0685	0.0685	0.3124	0.6876	0.9315	0.9315	0.0685	0.0685

TABLE II
COMPARISON THE EXPERIMENTAL AND THE CALCULATED LIQUID-LIQUID-VAPOR EQUILIBRIA

FOR THE SYSTEM NITROGEN(1)-ETHANE(2)

T K	DP PSIA	TOP			BOTTOM			VAPOR		
		DX			DX			DY		
		1	3		1	3		1	3	
94.3	0.8	-0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
101.5	1.5	0.0003	-0.0003	-0.0001	-0.0001	0.0001	0.0001	0.0000	0.0000	0.0000
109.1	1.5	0.0004	-0.0004	-0.0001	-0.0001	0.0001	0.0001	0.0000	0.0000	0.0000
113.4	5.0	-0.0001	0.0001	0.0003	0.0003	-0.0003	-0.0003	0.0001	-0.0001	-0.0001
115.2	6.6	0.0078	-0.0078	-0.0284	-0.0284	0.0284	0.0284	0.0000	0.0000	0.0000
116.3	0.9	-0.0005	0.0005	0.0016	0.0016	-0.0016	-0.0016	-0.0001	0.0001	0.0001
119.3	4.6	0.0000	0.0000	-0.0002	-0.0002	0.0002	0.0002	0.0000	0.0000	0.0000
121.9	2.3	-0.0001	0.0001	0.0003	0.0003	-0.0003	-0.0003	0.0001	-0.0001	-0.0001
124.7	3.5	0.0000	0.0000	0.0000	0.0001	-0.0001	-0.0001	-0.0005	0.0005	0.0005
129.7	0.3	0.0003	-0.0003	-0.0009	-0.0009	0.0009	0.0009	0.0648	-0.0648	-0.0648
130.1	0.4	0.0011	-0.0011	-0.0036	-0.0036	0.0036	0.0036	0.0631	-0.0631	-0.0631
132.3	0.3	0.0004	-0.0004	-0.0013	-0.0013	0.0013	0.0013	0.0585	-0.0585	-0.0585
133.3	0.4	0.0004	-0.0004	-0.0015	-0.0015	0.0015	0.0015	0.0533	-0.0533	-0.0533
AVE	2.2	0.0009	0.0009	0.0030	0.0030	0.0030	0.0030	0.0185	0.0185	0.0185

TABLE III

CALCULATED LIQUID-LIQUID-VAPOR EQUILIBRIUM DATA
FOR THE SYSTEM NITROGEN(1)-METHANE(2)-ETHANE(3)

		TOP						BOTTOM						VAPOR					
T	P	X	X	X	X	X	X	X	X	X	X	X	X	Y	Y	Y	Y	Y	Y
°K	PSIA	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
94.3	66.0	0.1771	0.0395	0.7834	0.9285	0.0252	0.0463	0.9971	0.0029	0.0000	0.0000	0.0000	0.0000	0.9971	0.0029	0.0000	0.0000	0.0000	0.0000
94.3	61.1	0.1839	0.1245	0.6917	0.8300	0.0953	0.0747	0.9908	0.0092	0.0000	0.0000	0.0000	0.0000	0.9908	0.0092	0.0000	0.0000	0.0000	0.0000
94.3	61.3	0.2006	0.1615	0.6379	0.7889	0.1263	0.0848	0.9886	0.0114	0.0000	0.0000	0.0000	0.0000	0.9886	0.0114	0.0000	0.0000	0.0000	0.0000
94.3	62.1	0.2231	0.1910	0.5859	0.7718	0.1448	0.0834	0.9871	0.0129	0.0000	0.0000	0.0000	0.0000	0.9871	0.0129	0.0000	0.0000	0.0000	0.0000
94.3	64.5	0.1721	0.0439	0.7840	0.9217	0.0291	0.0492	0.9967	0.0033	0.0000	0.0000	0.0000	0.0000	0.9967	0.0033	0.0000	0.0000	0.0000	0.0000
94.3	62.7	0.1774	0.0843	0.7383	0.8815	0.0595	0.0590	0.9937	0.0063	0.0000	0.0000	0.0000	0.0000	0.9937	0.0063	0.0000	0.0000	0.0000	0.0000
94.3	61.8	0.1900	0.1313	0.6787	0.8293	0.0983	0.0724	0.9905	0.0095	0.0000	0.0000	0.0000	0.0000	0.9905	0.0095	0.0000	0.0000	0.0000	0.0000
94.3	62.1	0.2065	0.1599	0.6336	0.8060	0.1188	0.0752	0.9889	0.0111	0.0000	0.0000	0.0000	0.0000	0.9889	0.0111	0.0000	0.0000	0.0000	0.0000
94.3	61.2	0.2320	0.2152	0.5529	0.7181	0.1759	0.1060	0.9856	0.0144	0.0000	0.0000	0.0000	0.0000	0.9856	0.0144	0.0000	0.0000	0.0000	0.0000
94.3	60.9	0.1829	0.1234	0.6936	0.8301	0.0948	0.0751	0.9909	0.0091	0.0000	0.0000	0.0000	0.0000	0.9909	0.0091	0.0000	0.0000	0.0000	0.0000
101.5	103.1	0.2300	0.0822	0.6877	0.8652	0.0594	0.0754	0.9921	0.0079	0.0000	0.0000	0.0000	0.0000	0.9921	0.0079	0.0000	0.0000	0.0000	0.0000

TABLE III (CONTINUE.....)

T °K	P PSIA	TOP						BOTTOM						VAPOR					
		1			2			1			2			1			2		
		X	X	X	X	X	X	X	X	X	X	X	X	Y	Y	Y	Y	Y	Y
113.4	218.5	0.9262	0.0113	0.0625	0.2691	0.0158	0.7151	0.9973	0.0025	0.0002	0.0002	0.0002	0.0002	0.9973	0.0025	0.0002	0.0002	0.0002	0.0002
113.4	216.6	0.9190	0.0154	0.0656	0.2679	0.0214	0.7108	0.9964	0.0034	0.0002	0.0002	0.0002	0.0002	0.9964	0.0034	0.0002	0.0002	0.0002	0.0002
113.4	215.3	0.8945	0.0327	0.0728	0.2768	0.0442	0.6790	0.9928	0.0070	0.0002	0.0002	0.0002	0.0002	0.9928	0.0070	0.0002	0.0002	0.0002	0.0002
113.4	216.5	0.8945	0.0339	0.0716	0.2805	0.0461	0.6734	0.9926	0.0072	0.0002	0.0002	0.0002	0.0002	0.9926	0.0072	0.0002	0.0002	0.0002	0.0002
113.4	219.5	0.9232	0.0142	0.0626	0.2729	0.0200	0.7070	0.9956	0.0032	0.0002	0.0002	0.0002	0.0002	0.9956	0.0032	0.0002	0.0002	0.0002	0.0002
113.4	212.4	0.6441	0.1698	0.1861	0.4138	0.1863	0.3999	0.9733	0.0265	0.0002	0.0002	0.0002	0.0002	0.9733	0.0265	0.0002	0.0002	0.0002	0.0002
113.4	212.8	0.6122	0.1807	0.2071	0.4486	0.1935	0.3579	0.9724	0.0275	0.0002	0.0002	0.0002	0.0002	0.9724	0.0275	0.0002	0.0002	0.0002	0.0002
113.4	214.5	0.8162	0.0875	0.0963	0.3193	0.1117	0.5689	0.9831	0.0167	0.0002	0.0002	0.0002	0.0002	0.9831	0.0167	0.0002	0.0002	0.0002	0.0002
115.2	240.8	0.9254	0.0125	0.0621	0.2910	0.0178	0.6912	0.9967	0.0030	0.0002	0.0002	0.0002	0.0002	0.9967	0.0030	0.0002	0.0002	0.0002	0.0002
115.2	237.0	0.9110	0.0211	0.0679	0.2898	0.0291	0.6812	0.9948	0.0049	0.0002	0.0002	0.0002	0.0002	0.9948	0.0049	0.0002	0.0002	0.0002	0.0002
115.2	235.5	0.9066	0.0233	0.0701	0.2882	0.0317	0.6801	0.9944	0.0054	0.0002	0.0002	0.0002	0.0002	0.9944	0.0054	0.0002	0.0002	0.0002	0.0002
115.2	233.6	0.8218	0.0819	0.0963	0.3332	0.1043	0.5625	0.9830	0.0168	0.0002	0.0002	0.0002	0.0002	0.9830	0.0168	0.0002	0.0002	0.0002	0.0002
115.2	231.3	0.7175	0.1327	0.1498	0.3779	0.1521	0.4700	0.9760	0.0238	0.0002	0.0002	0.0002	0.0002	0.9760	0.0238	0.0002	0.0002	0.0002	0.0002

TABLE III (CONTINUE.....)

T °K	P PSIA	TOP						BOTTOM						VAPOR					
		1		2		3		1		2		3		1		2		3	
		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
115.2	231.1	0.6962	0.1466	0.1572	0.4026	0.1668	0.4307	0.9740	0.9740	0.0258	0.0002								
115.2	230.8	0.6445	0.1630	0.1924	0.4428	0.1773	0.3799	0.9727	0.9727	0.0271	0.0002								
115.2	230.3	0.6348	0.1652	0.2000	0.4518	0.1783	0.3699	0.9726	0.9726	0.0272	0.0002								
116.3	248.5	0.8676	0.0487	0.0837	0.3123	0.0642	0.6236	0.9888	0.9888	0.0109	0.0003								
116.3	247.7	0.8654	0.0493	0.0853	0.3106	0.0645	0.6249	0.9887	0.9887	0.0110	0.0003								
116.3	247.1	0.6449	0.1570	0.1981	0.4433	0.1705	0.3862	0.9728	0.9728	0.0270	0.0002								
116.3	245.5	0.7194	0.1370	0.1436	0.4035	0.1602	0.4364	0.9742	0.9742	0.0256	0.0002								
119.3	285.9	0.9045	0.0232	0.0723	0.3089	0.0314	0.6597	0.9935	0.9935	0.0061	0.0004								
119.3	285.7	0.9001	0.0263	0.0736	0.3119	0.0354	0.6527	0.9928	0.9928	0.0068	0.0004								
119.3	285.6	0.8924	0.0310	0.0766	0.3151	0.0414	0.6435	0.9917	0.9917	0.0079	0.0004								
119.3	284.2	0.9006	0.0259	0.0735	0.3114	0.0349	0.6537	0.9929	0.9929	0.0067	0.0004								
119.3	283.5	0.8685	0.0478	0.0837	0.3309	0.0628	0.6063	0.9878	0.9878	0.0118	0.0004								
119.3	282.1	0.8536	0.0555	0.0909	0.3334	0.0713	0.5953	0.9863	0.9863	0.0133	0.0004								

TABLE III (CONT INUE.....)

		TOP			BOTTOM			VAPOR		
T °K	P PSIA	X 1	X 2	X 3	X 1	X 2	X 3	Y 1	Y 2	Y 3
133.3	534.4	0.8743	0.0523	0.0734	0.3609	0.0720	0.5671	0.8753	0.0521	0.0726
133.3	514.8	0.8229	0.0815	0.0956	0.3996	0.1051	0.4953	0.8236	0.0813	0.0951

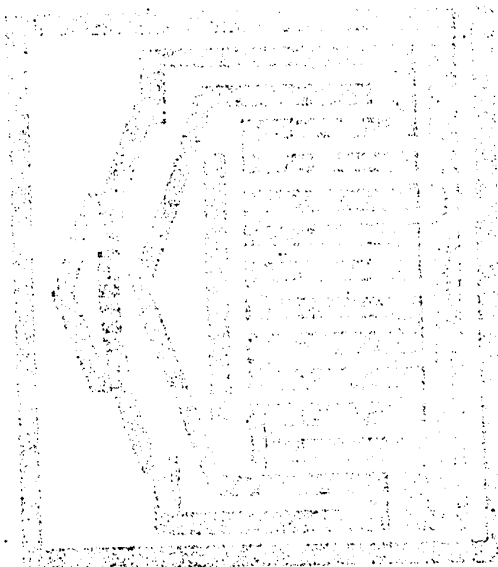


TABLE IV (CONTINUE.....)

TOP				BOTTOM			VAPOR				
T	P	DP	EX	EX	DX	DX	DX	DY	DY	DY	
°K	PSIA	PSIA	1	2	3	1	2	3	1	2	3
101.5	104.0	0.9-0.0004-0.0001	0.0006	0.0000	0.0001-0.0001	0.0003-0.0003	0.0003	0.0000	0.0007	0.0007	0.0000
101.5	103.9	-0.3-0.0017-0.0009	0.0026	0.0000	0.0005-0.0005	0.0007-0.0007	0.0007	0.0000	0.0007	0.0007	0.0000
101.5	103.8	0.0 0.0002	0.0001-0.0003	0.0000-0.0001	0.0001	0.0009-0.0009	0.0009	0.0000	0.0009	0.0009	0.0000
101.5	103.7	0.1 0.0001	0.0003-0.0003	0.0000-0.0001	0.0001	0.0008-0.0008	0.0008	0.0000	0.0008	0.0008	0.0000
101.5	103.6	-0.1 0.0002	0.0001-0.0003	0.0000-0.0001	0.0001	0.0008-0.0008	0.0008	0.0000	0.0008	0.0008	0.0000
101.5	103.1	1.4 0.0002-0.0008	0.0006	0.0000	0.0004-0.0004	0.0008-0.0008	0.0008	0.0000	0.0008	0.0008	0.0000
101.5	102.1	0.6-0.0006-0.0001	0.0006	0.0000	0.0001-0.0001	0.0007-0.0007	0.0007	0.0000	0.0007	0.0007	0.0000
AVE			0.5 0.0005	0.0003	0.0008	0.0000	0.0002	0.0002	0.0007	0.0007	0.0000

TABLE IV (CONTINUE.....)

		TOP						BOTTOM						VAPOR					
		P	DP	DX	DX	DX	DX	DX	DX	DX	DX	DX	DX	DX	DX	DX	DX	DX	DX
T	°K	PSIA	PSIA	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	3
119.3	284.6	-1.3	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	-0.0002	0.0002	-0.0002	-0.0002	0.0002	-0.0002	0.0000				
119.3	284.3	-1.4	0.0000	0.0001	-0.0001	0.0001	0.0008	-0.0002	-0.0006	0.0002	-0.0002	-0.0002	0.0000						
119.3	284.2	-1.4	0.0000	0.0002	0.0002	0.0002	0.0010	0.0003	-0.0013	0.0011	-0.0011	0.0000							
119.3	282.5	-1.7	0.0000	0.0000	0.0000	0.0004	0.0004	0.0001	-0.0005	0.0001	-0.0001	0.0000							
119.3	281.3	-2.2	0.0000	-0.0002	0.0002	0.0002	0.0005	0.0003	-0.0008	0.0002	-0.0003	0.0001							
119.3	280.0	-2.1	0.0000	0.0000	0.0000	0.0003	-0.0001	-0.0002	0.0002	0.0008	-0.0008	0.0000							
119.3	279.5	-2.2	0.0000	-0.0001	0.0001	0.0004	0.0004	0.0002	-0.0006	0.0003	-0.0004	0.0001							
119.3	278.4	-2.4	0.0000	0.0000	0.0000	0.0004	0.0004	-0.0001	-0.0003	0.0005	0.0005	0.0001							
119.3	278.2	-2.5	0.0000	-0.0002	0.0002	0.0004	0.0004	0.0002	-0.0007	-0.0001	-0.0001	0.0002							
AVE		1.9	0.0000	0.0001	0.0001	0.0005	0.0002	0.0002	0.0006	0.0004	0.0004	0.0001							

TABLE IV (CONTINUE.....)

		TOP						BOTTOM						VAPOR					
T °K	P PSIA	DP PSIA	DX			1	DX			2	DX			1	DX			2	3
			1	2	3		1	2	3		1	2	3		1	2	3		
123.4	358.0	0.3	0.0000	0.0001	0.0001	-0.0012	0.0000	0.0000	0.0012	0.0008	-0.0009	0.0000	0.0000						
123.4	356.3	0.3	0.0000	0.0001	0.0001	-0.0017	0.0002	0.0015	0.0002	-0.0002	0.0002	0.0002	0.0000						
123.4	359.7	1.4	0.0000	0.0001	0.0001	-0.0009	0.0000	0.0009	0.0002	0.0002	0.0002	0.0002	0.0000						
123.4	354.3	1.4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0002	-0.0002	-0.0001	0.0001						
123.4	357.2	1.0	0.0000	0.0000	0.0000	-0.0001	0.0001	0.0000	-0.0002	0.0003	0.0003	0.0000	0.0000						
123.4	353.6	-0.3	0.0000	0.0000	0.0000	0.0002	0.0000	-0.0002	0.0003	-0.0003	-0.0003	0.0000	0.0000						
123.4	350.0	0.5	0.0000	0.0000	0.0000	0.0001	0.0000	-0.0001	0.0003	-0.0003	-0.0003	0.0000	0.0000						
123.4	342.3	-2.6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	-0.0002	0.0000	0.0000						
AVE		1.0	0.0000	0.0000	0.0000	0.0005	0.0000	0.0005	0.0003	0.0003	0.0003	0.0000	0.0000						

TABLE IV (CONTINUE.....)

TOP										BOTTOM						VAPOR					
T		P	CP	FX	EX	DX	DX	DX	DX	DX	DX	DX	DY	DY	DY	DY	DY	DY	DY		
°K		PSIA	PSIA	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	3		
128.8		513.9	0.3	0.0065-0.0005-0.0060	0.0005-0.0060	0.0060	0.0000-0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0881-0.0080-0.0801								
128.8		512.4	0.8	0.0085-0.0006-0.0079	0.0006-0.0079	0.0079	0.0000-0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0933-0.0092-0.0841								
128.8		484.3	0.1	0.0017-0.0002-0.0014	0.0002-0.0014	0.0014	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0695-0.0055-0.0750								
128.8		455.2	0.3	0.0042-0.0017-0.0025	0.0017-0.0025	0.0025	0.0000-0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.1732-0.0624-0.1108								
128.8		449.6	0.3	0.0004	0.0000	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.1910-0.0722-0.1188								
128.8		440.7	0.6	0.0076	0.0022	0.0054	0.0000	0.0000	0.0015-0.0015	0.0015	0.0015	0.0015	0.2249-0.0836-0.1413								
128.8		438.6	0.6	0.0089	0.0031	0.0057	0.0000	0.0000	0.0009-0.0009	0.0009	0.0009	0.0009	0.2303-0.0875-0.1429								
AVE			0.4	0.0054	0.0012	0.0042	0.0000	0.0000	0.0006	0.0006	0.0006	0.0006	0.1529	0.0469	0.1076						

TABLE IV (CONTINUE.....)

		TOP						BOTTOM						VAPOR					
		P	DP	CX	CX	DX	DX	DX	DX	DX	DX	DX	DX	DY	DY	DY	DY	DY	DY
T	°K	PSIA	PSIA	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	3
133.3	525.0		0.2-0.0046	0.0012	0.0034	0.0000	0.0017-0.0017	0.0017	0.1135-0.0357	0.0778									
133.3	535.3		0.1	0.0013-0.0005	-0.0008	0.0000	0.0000-0.0001	0.0001	0.0954-0.0283	0.0671									
133.3	549.0		0.1	0.0017-0.0004	-0.0014	0.0000	0.0000-0.0005	0.0005	0.0806-0.0198	0.0608									
133.3	558.6		0.2	0.0036-0.0005	-0.0031	0.0000	0.0000-0.0007	0.0007	0.0679-0.0106	0.0573									
133.3	534.5		0.1	0.0015-0.0008	-0.0007	0.0000	0.0000-0.0004	0.0004	0.0934-0.0273	0.0661									
133.3	515.1		0.3-0.0046	0.0015	0.0031	0.0000	0.0011-0.0011	0.0011	0.1367-0.0456	0.0911									
AVE			0.2	0.0029	0.0008	0.0021	0.0000	0.0008	0.0008	0.0979	0.0279	0.0700							

APPENDIX V

THE MODIFIED REGULA-FALSI METHOD

The Modified Regula-Falsi Method

With the help of the numerical method, c unknowns can be solved in the c simultaneous equations, namely Equations (6-6) and (6-7). The Newton-Raphson method was one of the numerical methods.

The Newton-Raphson method can be applied for equations with complex roots as well as real roots, and the iterations converge rapidly provided the initial estimated for the roots are close enough. However, when there is a point of inflection or horizontal tangent in the vicinity of the roots, the Newton-Raphson method does not converge. The other demerit of the Newton-Raphson method is that the more complicated the equation, the harder it is to obtain a first derivative equation.

In this investigation, a modified Regula-falsi iteration method was proposed for solving simultaneous high order equations. It was developed using the principles of the original Regula-falsi method for a single variable(124).

The principles of the original Regula-falsi method may be given as follows:

Let the root x_0 of equation $F(x)=0$ be isolated between x_1 and x_2 . Then, in the interval (x_1, x_2) , the graph of $y=F(x)$ has the appearance shown in Figure A-1.

If the points y_1 and y_2 in Figure A-1 are jointed by a straight line, it will cut the x -axis at the point x_3 .

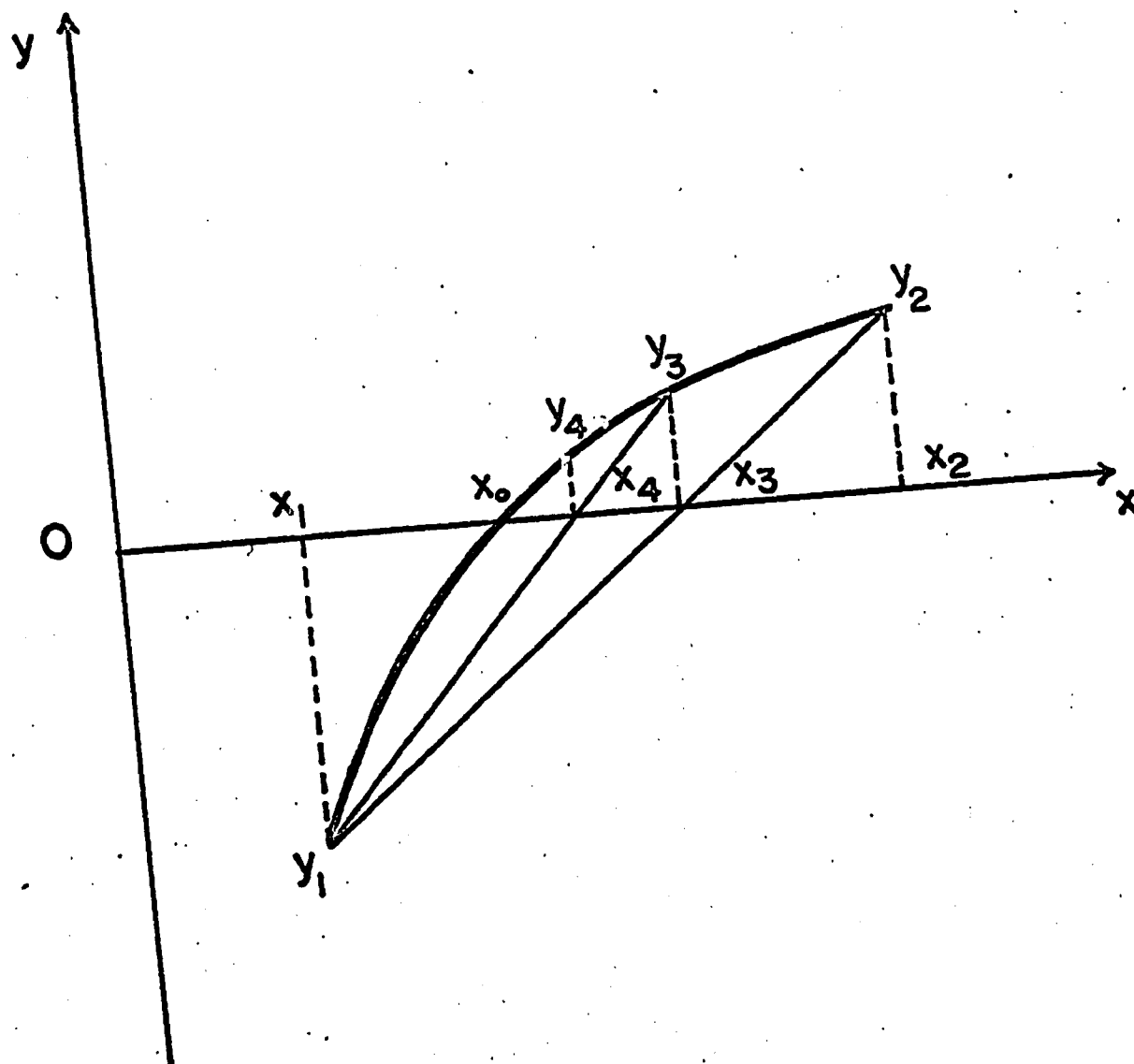


Figure A-1 An Example of the Original Regula-Falsi Method

$$x_3 = (x_1 y_2 - x_2 y_1) / (y_2 - y_1) \quad A-1$$

In general, this procedure can be repeated to obtain the succeeding approximations until the desired degree of accuracy is reached. The convergence solution x_0 is given by:

$$x_0 = x_{n+1} = (x_1 y_n - x_n y_1) / (y_n - y_1) \quad A-2$$

From this logic, the modified Regula-falsi method may be shown as follows:

As mentioned earlier, the quantities $\hat{\theta}_i^{L1}$ and $\hat{\theta}_i^{L2}$ are functions of x_i^{L1} and x_i^{L2} respectively. Hence, Equation (6-6) may be represented by:

$$U(a_i) = U(b_i) \quad A-3$$

where $a_i = x_i^{L1}$ and $b_i = x_i^{L2}$. Now define two additional functions $F(a_i)$ and $F(b_i)$ as follows:

$$F(a_i) = U(a_i) / U(b_i) \quad A-4$$

$$F(b_i) = U(b_i) / U(a_i) \quad A-5$$

and set them to satisfy the limiting conditions:

$$\lim_{a_i \rightarrow 0} F(a_i) = 0 \quad A-6$$

$$\text{and} \quad \lim_{b_i \rightarrow 0} F(b_i) = 0 \quad A-7$$

When $F(a) = 1$ and $F(b) = 1$, the values of a_i and b_i are the solutions of Equation(A-3).

In order to explain the logic of the modified Regula-falsi method two cases of extrapolation and interpolation are depicted in Figures A-2 and A-3 respectively.

After selecting an initial value a_i^1 (or b_i^1) by guessing, the straight line op^1 will cut the $F(a_i) = 1$ or $F(b_i) = 1$ line at the point h^1 . From the two similar triangles $Op^1a_i^1$ and $Oh^1a_i^2$ in Figure A-3, the Equation(A-8) is obtained:

$$0a_i^1/0a_i^2 = p^1a_i^1/h^1a_i^2 \quad A-8$$

but $0a_i^1 = a_i^1$, $0a_i^2 = a_i^2$, $p^1a_i^1 = F(a_i^1)$ and $h^1a_i^2 = 1$

therefore

$$a_i^2 = a_i^1/F(a_i^1) \quad A-9$$

a_i^2 or b_i^2 is closer to the root. Then this procedure is repeated for the succeeding approximations until the desired degree of accuracy is reached. The $(n+1)$ approximation may be represented by,

$$a_i^{n+1} = a_i^n/F(a_i^n) \quad A-10$$

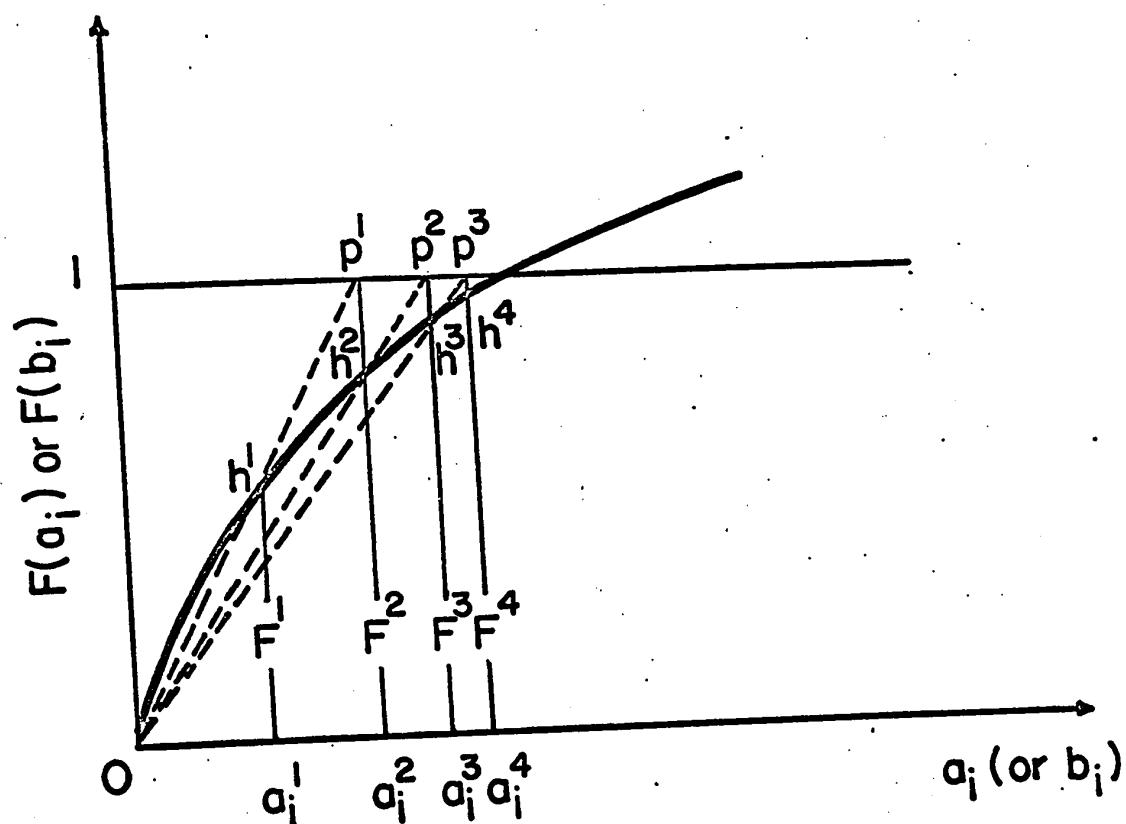


Figure A-2 A Graphical Representation of the Modified Regula-Falsi Method for a Case of Extrapolation

$$\left(\frac{\partial^2 F}{\partial a_i^2} < 0 \right)$$

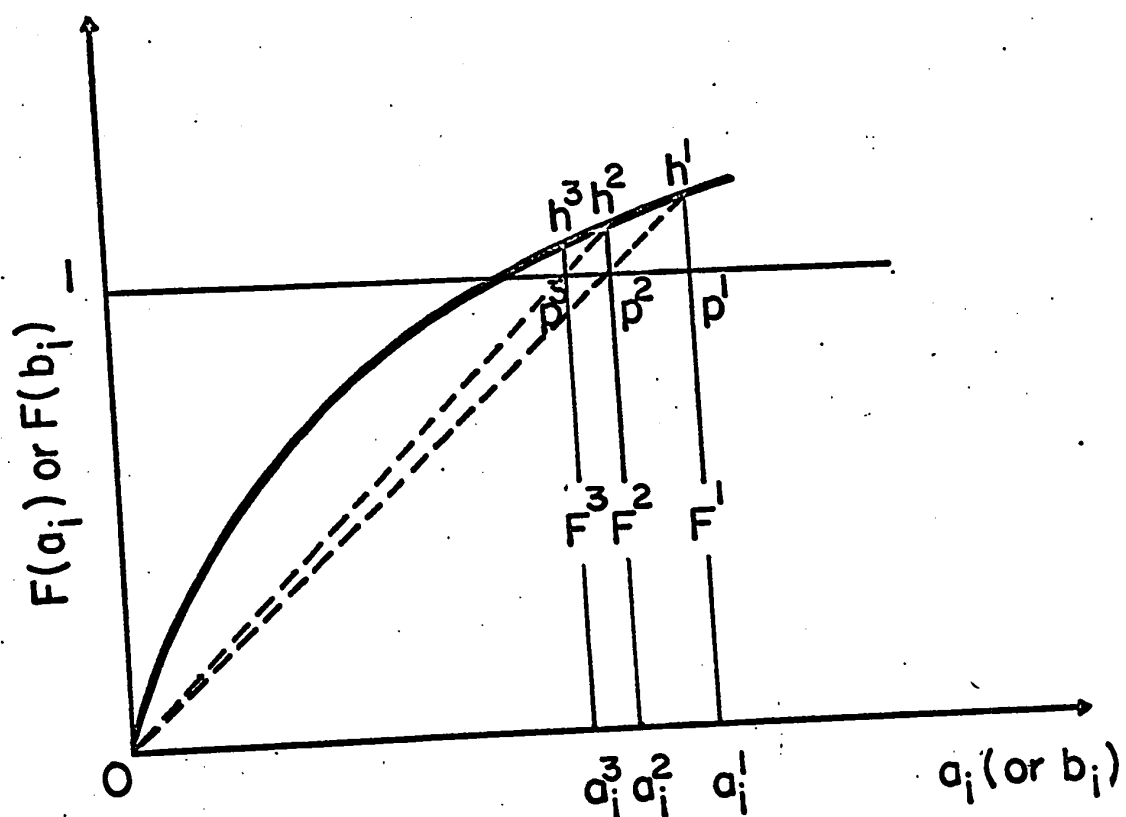


Figure A-3 A Graphical Representation of the Modified Regula-Falsi Method for a case of Interpolation

$$\left(\frac{\partial^2 F}{\partial a_i^2} < 0 \right)$$

and

$$b_i^{n+1} = b_i^n / F(b_i^n) \quad A-11$$

Substituting Equations(A-4) and (A-5) into Equations(A-10) and (A-11) respectively, gives,

$$a_i^{n+1} = U(b_i^n) a_i^n / U(a_i^n) \quad A-12$$

and

$$b_i^{n+1} = U(a_i^n) b_i^n / U(b_i^n) \quad A-13$$

In general, the values of a_i^{n+1} and b_i^{n+1} obtained would not satisfy the conditions of Equations(A-14) and (A-15)

$$\sum_i a_i^{n+1} = 1 \quad A-14$$

and

$$\sum_i b_i^{n+1} = 1 \quad A-15$$

It is therefore necessary to normalized these values as follows:

$$a_i^{n+1} = a_i^{n+1} / \sum_i a_i^{n+1} \quad A-16$$

and

$$b_i^{n+1} = b_i^{n+1} / \sum_i b_i^{n+1} \quad A-17$$

On the other hand, the mole fraction of one of the components in one of the liquid phases has been specified. Let this quantity be a_j , which can not be adjusted. Therefore, Equation A-16 should be replaced by the relationship:

$$a_i^{n+1} = (1-a_j)a_i^{n+1} / \sum_{i \neq j} a_i^{n+1} \quad A-18$$

Similarly, if the mole fraction specified is the quantity b_k , the normalization of b_i^{n+1} should be given by:

$$b_i^{n+1} = (1-b_k)b_i^{n+1} / \sum_{i \neq k} b_i^{n+1} \quad A-19$$

Figures A-2 and A-3 are examples of the convergence solution obtained by extrapolation and interpolation for

the cases having $\frac{\partial^2 F}{\partial a_i^2} < 0$ and $\frac{\partial^2 F}{\partial b_i^2} < 0$ in the

vicinity of the roots.

For the situations where $\frac{\partial^2 F}{\partial a_i^2} > 0$ and $\frac{\partial^2 F}{\partial b_i^2} > 0$

in the vicinity of the roots the iteration process may be convergent as shown in Figure A-4, or divergent as shown in Figure A-5.

To change a diverging process into a converging one, the following procedure is suggested:

$$a_i^{n+1} = \frac{1}{2} (a_i^{(n+1)} + a_i^n) \quad A-20$$

and

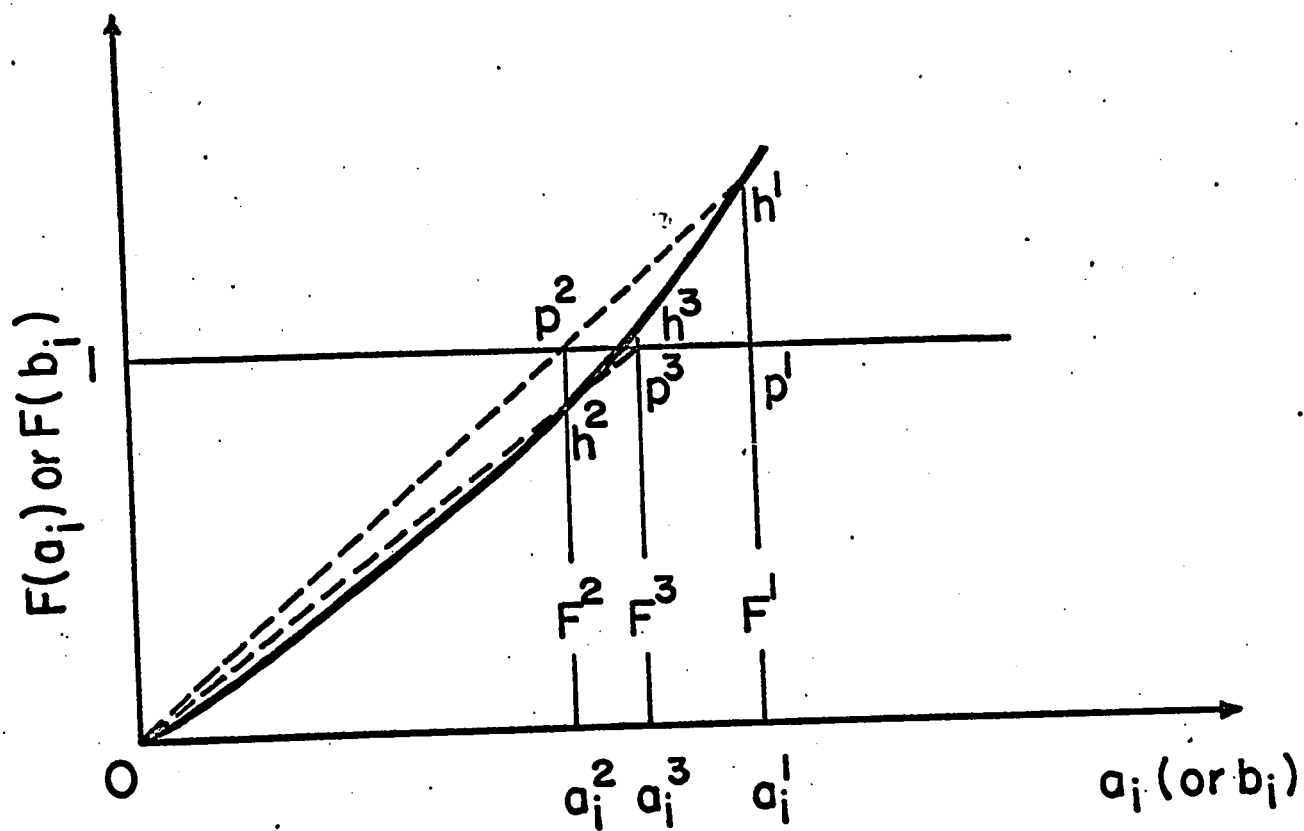


Figure A-4 A Convergence Process ($\frac{\partial^2 F}{\partial a_i^2} > 0$) .

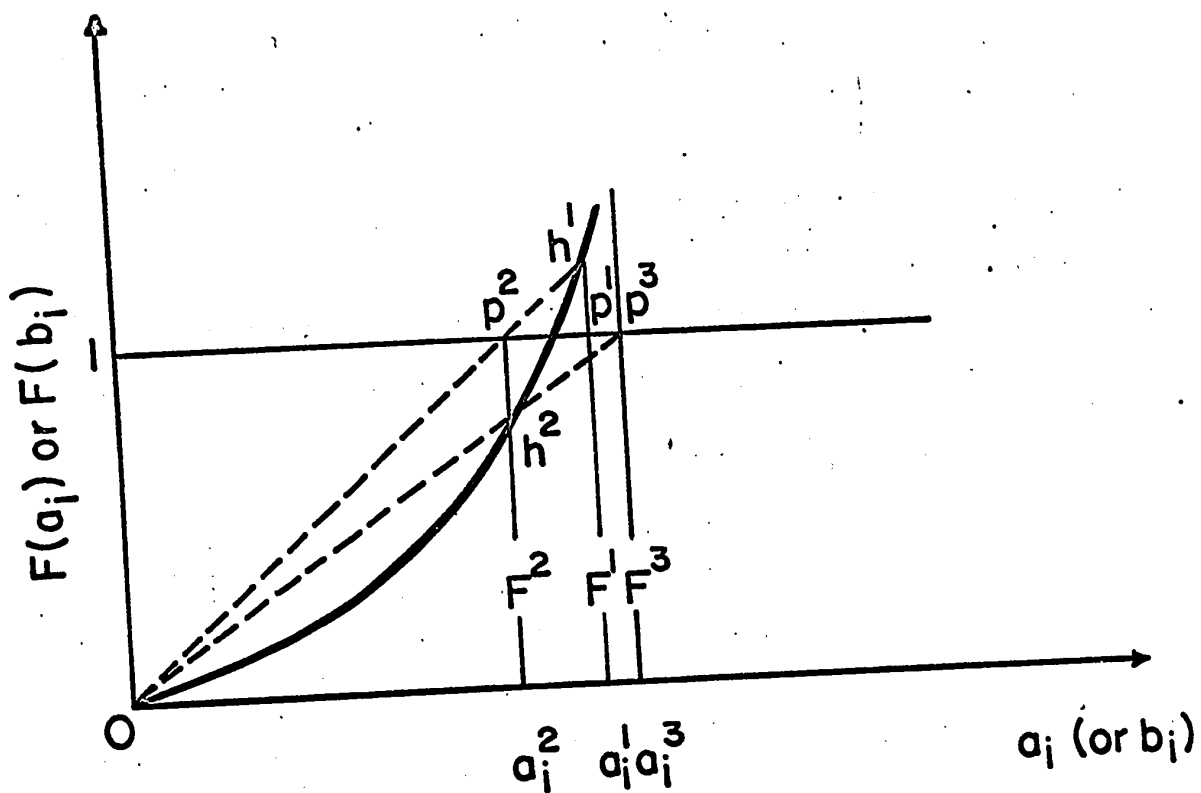


Figure A-5 A Divergence Process ($\frac{\partial^2 F}{\partial a_i^2} > 0$)

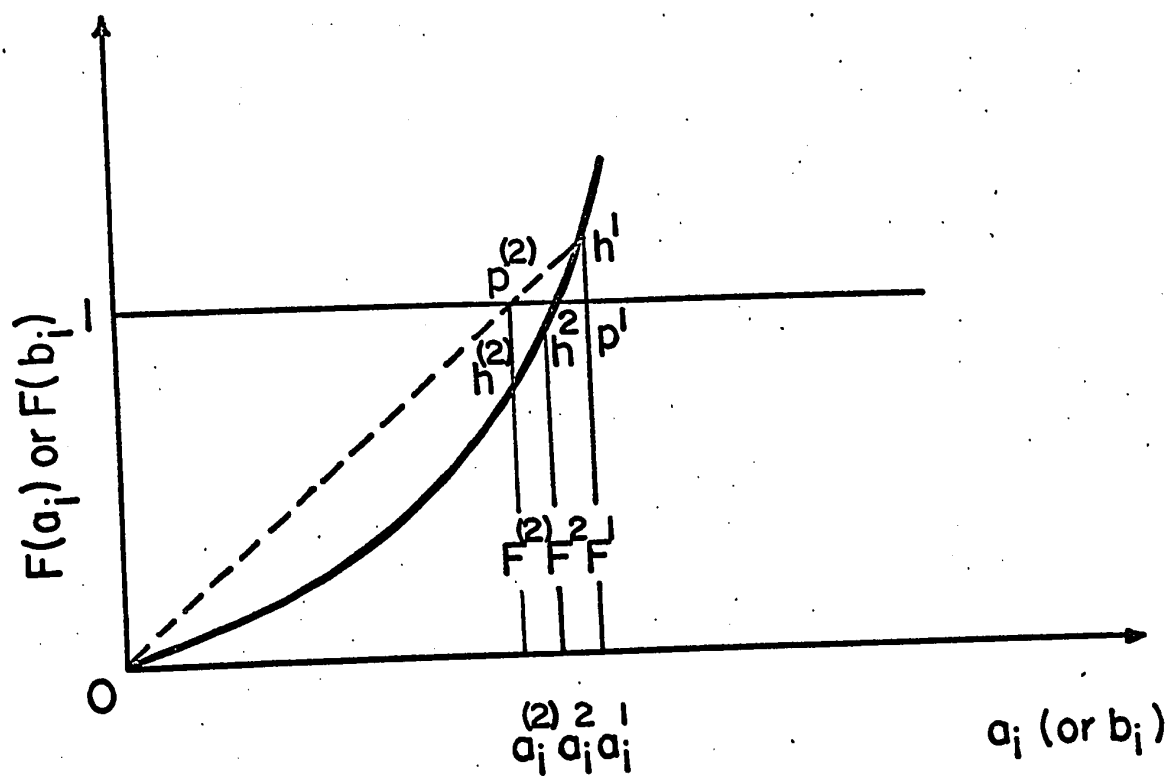


Figure A-6 A Proposed Modification for Changing a Diverging into a Converging Process

$$b_i^{n+1} = \frac{1}{2} (b_i^{(n+1)} + b_i^n) \quad \text{A-21}$$

In other words, the mean value of the n-th approximation and the value of the interception of the straight line Op^n with $F=1$ is used as the (n+1) th approximation. The improved convergence process is depicted in Figure A-6. Therefore Equations A-12 and A-13 are modified to give:

$$a_i^{n+1} = \frac{1}{2} \left(\frac{F(b_i^{(n)})}{F(a_i^{(n)})} + 1 \right) a_i^n \quad \text{A-22}$$

and

$$b_i^{n+1} = \frac{1}{2} \left(\frac{F(a_i^{(n)})}{F(b_i^{(n)})} + 1 \right) b_i^n \quad \text{A-23}$$

As the curvature of the function F is unknown before hand, it is recommended that Equations(A-22) and (A-23) be used in all cases.

APPENDIX VI

CALIBRATION RESULTS FOR THE THERMOCOUPLE

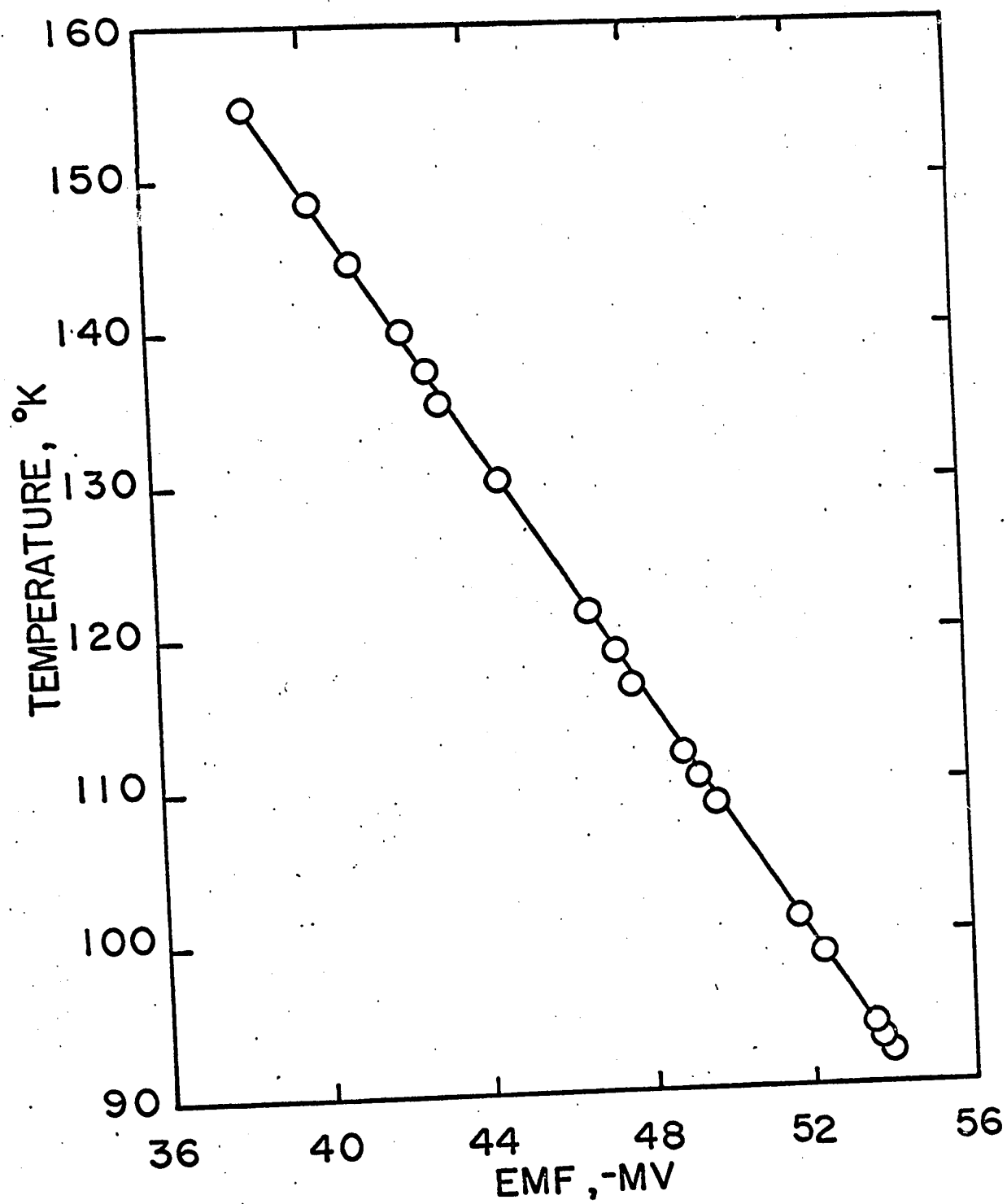


Figure A-7 Calibration Results for the Thermocouple

APPENDIX VII

COMPUTER PROGRAMS

C-1 Calculation Liquid Density

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DIMENSION ZZ(5),
2 ARKL(5,5),BRKL(5),      RKA(50,5),RKB(50,5),
3 WIJ(5,5),TCGIJ(5,5),TCIJ(5,5),      CIRKL(5),C2RKL(5),
3 PVCL(5),PHI(5),CORRL(5,5)
4,ZC(3)  ,LLV(50),YY(50,5)      ,PP(50)  ,PS(50,5)
6      ,      WW(5),VC(5),TC(5),PC(5),AM(5)
7 ,VCC(5),TCC(5),PCC(5)      ,DMK(50)
8,DEX(5,2)
9 TITLE(20)  ,Q(5)  ,C(4),D(3),E(3)
1 ,AMOLWT(5)      ,X(50,5),XX(5)      ,DEXE(50)
1 ,PHIV(5),XP(5),Y(5),RATIO(5)
CGMVCN /FIRST/
1      TC,PC,VC,WW,AMOLWT,T,P,R,NCOMP,NQNTUM
1 /SECOND/C,C,MTYPE
C      KIJ=0 PRESSURE CALCULATED FROM LIQUID COMPOSITION
C      KIJ=2 PRESSURE IS ONE OF INPUT DATA
      READ(1,101) KIJ
163 READ(1,417)(TITLE(I),I=1,19)
      READ(1,101) III
      READ(1,101) M,NC
      READ(1,102)(TC(I),I=1,M)
      READ(1,102)(PC(I),I=1,M)
      READ(1,102)(VC(I),I=1,M)
      READ(1,102)(AM(I),I=1,M)
      READ(1,102)(WW(I),I=1,M)
      READ(1,102) R,RR
      READ(1,102) T      ,PSI
      NCOMP=M
      NQNTUM=0
      DO 50 K=1,M
50 READ(1,115)(CORRL(K,I),I=1,M)
      L=1
26 READ(1,116)(RKA(L,I),I=1,M),(RKB(L,I),I=1,M)
      DO 153 I=1,M
153 ZC(I)=PC(I)*VC(I)/R/TC(I)
      WRITE(3,403)
      WRITE(3,404)(TC(I),PC(I),VC(I),AM(I),WW(I),ZC(I),I=1,M)
      WRITE(3,311) R,RR
      WRITE(3,418)(TITLE(I),I=1,19)
      M1=M-1
      L=0
33 L=L+1
      IF(M.GT.3) GO TO 444

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      IF(M.GT.2) GO TO 266
      READ(1,113)LLV(L),PP(L), X(L,1)          ,DEXE(L)
      X(L,M)=1.0-X(L,M1)
      IF(LLV(L).LE.0.0) GO TO 163
      GO TO 57
266  READ(1,113)LLV(L),PP(L),(X(L,J),J=1,M1),DEXE(L)
      M2=M-2
      X(L,M)=1.0-X(L,M1)-X(L,M2)
      IF(LLV(L).LE.0.0) GO TO 163
      GO TO 57
444  READ(1,113)LLV(L),PP(L),(X(L,J),J=1,M1),DEXE(L)
      M2=M-2
      M3=M-3
      X(L,M)=1.0-X(L,M1)-X(L,M2)-X(L,M3)
      IF(LLV(L).LE.0.0) GO TO 163
      GO TO 57
      57 DO 25 I=1,M
      25 XX(I)=X(L,I)
      IF(R.GT.11) GO TO 166
      333 P=PP(L)
      GO TO 411
      166 P=PP(L)/14.696
      411 LV=LLV(L)
      IF(R.GT.11) GO TO 195
      T=1.8*T
      GO TO 197
      195 T=T
      197 RT=R*T
      DO 224 J=1,N
      C1RKL(J)=RKA(1,J)
      C2RKL(J)=RKB(1,J)
      224 CONTINUE
      IF(KIJ.GT.0.0) GO TO 91
C    CALCULATION OF PRESSURE FROM TEMP -X DATA
      KIJ=0
      IF(KIJ.GT.0.0) GO TO 91
      NIY=0
      ITER=0
      22 P=PSI
      K=K+1
      DO 40 J=1,NCOMP
      PHIV(J)=1.0
      AMOLWT(J)=AM(J)

```

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40 XP(J)=XX(J)
42 CALL SUPT(VL,PHI,PPVOL,C1RKL,C2RKL,CORRL,XP,1,KIJ)
41 SUMY=0.0
   SUMP=0.0
   DO 77 J=1,NCOMP
     Y(J)=PHI(J)*XP(J)/PHIV(J)
     SUMY=SUMY+Y(J)
77 SUMP=SUMP+P*Y(J)
   DO 52 J=1,NCCMP
     Y(J)=Y(J)/SUMY
     IF(XP(J).EQ.0.0) GO TO 51
     RATIC(J)=Y(J)/XP(J)
     GO TO 52
51 RATIC(J)=0.0
52 CONTINUE
   DY=SUMY-1.0
   PCLD=P
   P=SUMP
   ITER=ITER+1
   IF(ABS((PCLD-P)/P)-1.0E-4) 90,90,72
72 IF(ITER.GT.150)GO TO 76
   IF(ITER.LE.10) GO TO 80
   IF (ABS(CY).GT.ABS(CYOLD)) GO TO 76
80 DYGLD=DY
   CALL SLPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
   GC TO 42
90 IF(ABS(SUMY-1.0)-1.0E-4) 910,910, 70
70 NIY=NIY+1
   IF(NIY-1)>71,71,92
71 P=P+0.01
   GO TO 93
92 SLCPE=(P-PO)/(SUMY-SYC)
   DELP=SLCPE*DDY
   IF(ABS(DELP)-1.0 ) 79,79,78
78 DELP=SIGN(1.0 ,DELP)
79 P=P-DELP
93 DO 74 J=1,NCCMP
74 Y(J)=Y(J)/SUMY
   PO=P
   SYC=SUMY
   DDY=SUMY-1.0
   IF(NIY.LE.30) GO TO 75
   IF(ABS(CCY).LE.0.005) GO TO 910

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75 CALL SUPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
  GO TO 42
76 IF(ABS(DY).LE.0.005) GC TC 910
910 P=P
91 DO 100 I=1,M
  ARKL(I,I)=C1RKL(I)* R*R      *(TC(I)**2.5)/PC(I)
  BRKL(I)=C2RKL(I)* R      *TC(I)/PC(I)
  IF(I.EQ. M ) GO TO 100
  I1=I+1
  DO 100 J=I1,M
    TCIJ( I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
    DO 211 K=1,M
      PCO(K)=PC(K)
      TCO(K)=TC(K)
211 VCO(K)=VC(K)
      TCIJ( J,I)=TCIJ( I,J)
      WIJ(I,J)=(Ww(I)+Ww      (J))*0.5
      ZCCIJ=0.291-0.08*WIJ(I,J)
94 VCOIJ=(1.0/8.0)*(VCO(I)**(1./3.)+VCO(J)**(1./3.))**3.0
96 PCCIJ=ZCCIJ* R      *TCIJ( I,J)/VCCIJ
      PCIJ=PCCIJ
95 ARKL(I,J)=(C1RKL(I)+C1RKL(J))*0.5* R      **2*TCIJ(I,J)**2.5/PCIJ
98 ARKL(J,I)=ARKL(I,J)
100 CONTINUE
  AMRKL=0.0
  BMRKL=0.0
  DO 220 I=1,M
    BMRKL=BMRKL+XX(I) *BRKL(I)
  DO 220 J=1,M
220 AMRKL=AMRKL+XX(I)*XX(J) * ARKL(I,J)
    IF(LV-1) 501,502,502
501 U=R*T/P/1.2
    GO TO 503
502 U=BMRKL*1.2
    AMRKL=AMRKL/T**0.5
503 CALL VOLUME(R,T,AMRKL,BMRKL,P,U,KR)
    VRLT=U
    XMT=0.0
    DO 760 I=1,M
760 XMT=XMT+AM(I)*XX(I)
    IF(R.GT.11) GO TO 192
    DXRT=XMT/VRLT
    DXRT=DXRT/62.426

```

IV G LEVEL 19

MAIN

DATE = 72025

14/00/29

GG TC 851

192 DXRT=XMT/VRLT

851 DEXEC=DEXE(L)

DEXEC=DEXEC/62.426

AVE=(DEXEC-DXRT)

PX=PP(L)

T=T/1.8

WRITE(3,852)

WRITE(3,217) DXRT,DEXEC,(XX(I),I=1,M) ,T ,PX ,P,CORRL(1,2)

WRITE(3,850) AVE

56 CONTINUE

GG TO 33

217 FORMAT(12F10.5)

101 FORMAT(5I8)

102 FORMAT(8F8.0)

113 FORMAT(13,6F10.0)

115 FORMAT(6F10.0)

116 FORMAT(8F10.0)

404 FORMAT(10X,2F7.1,F7.3,F7.2,2F8.4)

403 FORMAT(1H1,/,13X,'TC',5X,'PC',5X,'VC',6X,'M',
16X,'W',6X,'ZC',/)

417 FORMAT(19A4)

418 FORMAT(1H1,19A4)

311 FORMAT(10X,'R=',F8.3,'RR=',F8.3)

850 FORMAT(/,10X,'AVE =',F8.4

852 FORMAT(/,' CXRT CEXEC
1X PC ',/)

,/)

X(1)

X(2)

T

PE

END

IV G LEVEL 19

VOLUME

DATE = 72025

14/00/2

SUBROUTINE VOLUME(R,T,A,B,P,V,KK)

KK=0

10 C=R*T/(V-B)

KK=KK+1

IF(KK.GT.50) GO TO 12

D=A/(V*(V+B))

PN=C-D

PDV=-C/(V-B)+C/V+D/(V+B)

H=(P-PN)/PDV

V=V+H

G=V*1.E-5

IF(V.GT.B) GO TO 11

V=(V-H+B)/2.

11 IF(ABS(H).GT.G) GO TO 10

12 RETURN

END

IV G LEVEL 19

CUBEQN

DATE = 72025

14/00/2

SUBROUTINE CUBEQN

C SOLVES CUBIC EQUATION OF REDLICH-KWONG EQUATION FOR COMPRESSESSIBILI
C FACTORS

DIMENSION C(4),D(3),E(3)

COMMON

1 /SECONDD/D,C,MTYPE

1 CONTINUE

E(1)=C(2)/C(1)

B1OV3=E(1)/3.0

E(2)=C(3)/C(1)

E(3)=C(4)/C(1)

ALF=E(2)-E(1)*B1OV3

BET=2.0*B1OV3**3 -E(2)*B1OV3+E(3)

BETOV2=BET/2.0

ALFOV3=ALF/3.0

CUACV3=ALFCV3**3

SQBOV2=BETCV2**2

DEL=SQBOV2+CUAOV3

IF(DEL)40,20,30

20 MTYPE=0.0

GAM=SQRT(-ALFOV3)

IF(BET)22,22,21

21 D(1)=-2.0*GAM-B1OV3

D(2)=GAM-B1OV3

D(3)=D(2)

GO TO 50

22 D(1)=2.0*GAM-B1OV3

D(2)=-GAM-B1OV3

D(3)=D(2)

GO TO 50

30 MTYPE=1

EPS=SQRT(DEL)

TAU=-BETCV2

RCU=TAU+EPS

SCU=TAU-EPS

SIR=1.0

SIS=1.0

IF(RCU)31,32,32

31 SIR=-1.0

32 IF(SCU)33,34,34

33 SIS=-1.0

34 A=SIR*(SIR*RCU)**0.33333333

S=SIS*(SIS*SCU)**0.33333333

IV G LEVEL 19

CUBEQN

DATE = 72025

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 $D(1) = A + S - B1GV3$ $D(2) = -(A + S) / 2.0 - B1GV3$ $D(3) = 0.86602540 * (A - S)$

GO TO 50

40 MTYPE=-1

 $QUOT = SQBCV2 / CUACV3$ $RCCT = SQRT(-QUOT)$

IF(BET)42,41,41

41 $PEI = (1.5707963 + ATAN(RCCT / SQRT(1.0 - RCCT**2))) / 3.0$

GO TO 43

42 $PEI = ATAN(SQRT(1.0 - RCCT**2) / RCCT) / 3.0$ 43 $FACT = 2.0 * SQRT(-ALFOV3)$ $D(1) = FACT * COS(PEI) - B1GV3$ $PEI2 = PEI + 2.0943951$ $D(2) = FACT * COS(PEI2)$

-B1GV3

 $PEI4 = PEI + 4.1887902$ $D(3) = FACT * COS(PEI4)$

-B1GV3

50 RETURN

END

IV G LEVEL 19

SUPT

DATE = 72025

14/00/

```

SUBROUTINE SUPT(VL,PHI, PVOL ,C1RKL,C2RKL,CORRL,Q,LV,KIJ)
C EVALUTON OF SUPPCRTING PROPERTIES,THE FUGACITY AND THE
C PARTIAL MOLAL VCLUME CF FLUID MIXTURES.
DIMENSION TC(5),PC(5),VC(5),WW(5),AMCLWT(5) ,ARKL(5,5),BRKL(5),
3 WIJ(5,5),TCOIJ(5,5),TCIJ(5,5),C(4),D(3),C1RKL(5),C2RKL(5),
3 PVOL(5),PHI(5),CORRL(5,5) ,A2I(5),BI(5),AIRKL(5),Q(5)
DIMENSION ZZ(5)
COMMON /FIRST/
1 TC,PC,VC,WW,AMOLWT,T,P,R,NCOMP,NQNTUM
1 /SECOND/D,C,MTYPE
C LV=0, FOR VAPOR PHASE.
C LV=1, FOR LIQUID PHASE.
C KIJ=1, TCIJ=SQRT(TCI*TCJ)*(1.-KIJ)
C KIJ=2, AIJ=SQRT(AI*AJ)*(1.-KIJ)
C KIJ=3, AIJ=(AI*KIJ+(1.-KIJ)*AJ)/2.
R=10.73
NQNTUM=0
RT=R*T
91 DO 100 I=1,NCOMP
ARKL(I,I)=C1RKL(I)* R*R *(TC(I)**2.5)/PC(I)
BRKL(I)=C2RKL(I)* R *TC(I)/PC(I)
IF(I.EQ.NCOMP) GO TO 100
I1=I+1
DO 100 J=I1,NCOMP
IF(KIJ.GT.1) GO TO 97
TCIJ( I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
TCIJ( J,I)=TCIJ( I,J)
WIJ(I,J)=(WW(I)+WW(J))*0.5
ZCOIJ=0.291-0.08*WIJ(I,J)
94 VCCIJ=(VC (I)**(1./3.))+VC (J)**(1./3.))**3/8.0
96 PCCIJ=ZCCIJ* R *TCIJ( I,J)/VCCIJ
PCIJ=PCCIJ
95 ARKL(I,J)=(C1RKL(I)+C1RKL(J))*0.5* R **2*TCIJ(I,J)**2.5/PCIJ
GO TO 98
97 IF(KIJ.GT.2) GO TO 99
ARKL(I,J)=(ARKL(I,I)*ARKL(J,J))**0.5*(1.0-CORRL(I,J))
GO TO 98
99 ARKL(I,J)=(ARKL(I,I)*CORRL(I,J)+(1.-CORRL(I,J))*ARKL(J,J))
98 ARKL(J,I)=ARKL(I,J)
100 CONTINUE
AMRKL=0.0
BMRKL=C.0
DO 120 I=1,NCOMP

```

IV G LEVEL 19

SUPT

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```

      A2I(I)=ARKL(I,I)/RT**2/T**0.5
      BI(I)=BRKL(I)/RT
      BMRKL=BMRKL+Q(I)*BRKL(I)
      AIRKL(I)=0.0
      DO 120 J=1,NCCMP
      AIRKL(I)=AIRKL(I)+Q(J)*ARKL(I,J)
120  AMRKL=AMRKL+Q(I)*Q(J)*ARKL(I,J)
      A2=AMRKL/RT**2/T**0.5
      B=BMRKL/RT
      C(1)=1.0
      C(2)=-1.0
      C(3)=B*P*(A2/B-1.0-B*P)
      C(4)=-((A2/B)*(B*P)**2)
      CALL CUBEGN
      IF(MTYPE)115,140,140
115  IF(LV.EQ.0) GO TO 145
      C      ZL=AMIN1(D(1),D(2),C(3))
      C      ZL=AMIN1(D(1),D(2),D(3))
      C      JJ=0
      C      DO 146 I=1,3
      C      ZZ(I)=9999.
      C      JJ=JJ+1
      C      IF(Z(I).LT.0.0) GO TO 146
      C      ZZ(JJ)=Z(I)
      C 146  CCNTINUE
      C      ZL=AMIN1(ZZ(1),ZZ(2),ZZ(3))
      C      GO TO 150
145  ZL=AMAX1(C(1),C(2),C(3))
      C      GO TO 150
140  ZL=C(1)
150  H=B*P/ZL
      C      WRITE (3,591) H,ZL,B,Z(1),Z(2),Z(3),LV
      C 591  FORMAT(5X,6E12.4,I2)
      C      CALL FGNRK(A2,B,P,H,ZL,LV)
      VL=RT*B/H
123  CCNTINUE
      IF(LV.EQ.0) GO TO 135
      QD=(T**0.5)*VL*(VL+BMRKL)
      QH=(AMRKL/(T**0.5))*((2.*VL+BMRKL)/(VL**2*(VL+BMRKL)**2))
      QK=RT/((VL-BMRKL)**2)
135  DO 130 I=1,NCOMP
      C      WRITE(3,591) ZL,H
      PHILN=(ZL-1.0)*BI(I)/B-ALCG(ZL)-ALCG(1.0-H)

```

IV G LEVEL 19

SUPT

DATE = 72025

14/00

```
1  -(A2/B)*(2.0*AIRKL(I)/AMRKL  -BI(I)/B)*ALOG(1.0+H)
  PHI(I)= EXP(PHILN )
  IF(LV.EC.0) GO TC 130
  QE1=0.0
  DO 125 J=1,NCCMP
125 QE1=QE1+Q(J)*ARKL(I,J)
  QE=2.0*QE1-AMRKL*BRKL(I)/(VL+BMRKL)
  QG=(RT/(VL-BMRKL))*(1.0+BRKL(I)/(VL-BMRKL))
  PVOL(I)=((CE/QC)-CG)/(QH-QK)
130 CONTINUE
300 RETURN
  END
```

IV G LEVEL 19

EQNRK

DATE = 72025

14/00

SUBROUTINE EQNRK(A2,B,P,E,Z,LV)

TOL=1.0E-6

IH=0

IJ=0

45 IF(LV.LT.1) GO TO 47
 IF(E.LT.1.0) GO TO 46
 E=E-0.02

IH=IH+1
 IF(IH.LT.20) GO TO 45
 E=0.98

GO TO 46
 47 IF(E.GT.0.0) GO TO 46
 E=E+0.01

IH=IH+1
 IF(IH.LT.20) GO TO 47
 E=0.02

46 IJ=IJ+1
 $FE = -B * P / E + 1. / (1.0 - E) - (A2 / B) * E / (1. + E)$
 $CFE = B * P / E ** 2 + 1. / (1. - E) ** 2 - (A2 / B) / (1. + E) ** 2$

C WRITE(3,592)E,FE,CFE,LV

C 592 FORMAT(20X,3E12.4,5X,I2)

C IF(ABS(CFE).LT.1.0E-20) CFE=CFE/ABS(CFE)*1.0E-20

TEST=FE/CFE

E=E-TEST

IF(IJ.GT.60) GO TO 48

IF(ABS(TEST/E).GT.TOL) GO TO 45

48 Z = B * P / E

RETURN

END

C-2 Prediction of Liquid-Liquid-Vapor Equilibria

IV G LEVEL 20

MAIN

DATE = 72133

21/19/

```

C INPUT OF DATA: TEMP. K, PRESSURE PSIA
C INPUT OF DATA: BINARY SYSTEM ASSUMED XX(1,1) AND XX(1,2) EQUAL
C TO 0.0000
C R : GAS CONSTANT 10.73
C CORRL(I,J) : TEMP. DEPENDENT
C RKA(L,I) : TEMP. DEPENDENT
C RKB(L,I) : TEMP. DEPENDENT
C SOLVE THE SIMULTANEOUS NON-LINEAR EQUATION BY THE MODIFIED
C FALSE POSITION METHOD
  DIMENSION PHV1(3),PHV2(3),X1(3),X2(3),X10(3),X20(3),PHI1(3),
1 PH12(3),Y1(3),Y2(3), YP1(3),YP2(3),U1(3),U2(3)
1 ,ARKL(3,3),RRKL(3), RKA(10,3),RKB(10,3),WIJ(3,3),TCOIJ(3,3)
2,TCIJ(3,3),C1RKL(3),C2RKL(3),PVOL(3),CJRRL(3,3),ZC(3),LLV(10)
  DIMENSION TC(3),PC(3),VC(3),WW(3),AM(3),VCO(3),TCO(3),PCO(3)
4 ,XX(3,2),Q(3),G(4),D(3),E(3),ZZ(3),PHIV(3),RATIO(3)
6 ,A2I(3),B1(3),AIRKL(3)
7 ,PP(10),BRKL(3)
  DIMENSION PHI(3)
9 ,PHY1(3),PHY2(3)
9,U(3),XP(3)
1 ,PHT1(3),PHT2(3) ,DX1(3),DX2(3)
1,SUMYN(10)
  COMMON /FIRST/
1
2 ,T
  COMMON
1 /SECOVD/D,G,MTYPE
11 READ(1,101) M
  IF(M.EQ.0) GO TO 800
  READ(1,102)(TC(I),I=1,M)
  READ(1,102)(PC(I),I=1,M)
  READ(1,102)(VC(I),I=1,M)
  READ(1,102)(AM(I),I=1,M)
  READ(1,102)(WW(I),I=1,M)
  READ(1,102)R,RR
  DO 50 K=1,M
50 READ(1,115)(CORRL(K,I),I=1,M)
  L=1
  READ(1,103) LLV(L),PP(L)
103 FORMAT(I8,F8.0)
  READ(1,116)(RKA(L,I),I=1,M),(RKB(L,I),I=1,M)
  DO 153 I=1,M
  C1RKL(I)= RKA(L,I)

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STÉ D'OTTA A
INFORMATION

C-2 Prediction of Liquid-Liquid-Vapor Equilibria

I IV G LEVEL 20

MAIN

DATE = 72133

21/19/

```

C INPUT OF DATA: TEMP. K, PRESSURE PSIA
C INPUT OF DATA: BINARY SYSTEM ASSUMED XX(1,1) AND XX(1,2) EQUAL
C TO 0.0000
C R : GAS CONSTANT 10.73
C CORRRL(I,J) : TEMP. DEPENDENT
C RKA(L,I) : TEMP. DEPENDENT
C RKB(L,I) : TEMP. DEPENDENT
C SOLVE THE SIMULTANEOUS NON-LINEAR EQUATION BY THE MODIFIED
C FALSE POSITION METHOD
C DIMENSION PHV1(3),PHV2(3),X1(3),X2(3),X10(3),X20(3),PH11(3),
2 PH12(3),Y1(3),Y2(3), YP1(3),YP2(3),U1(3),U2(3)
1 ,ARKL(3,3),RRKL(3), RKA(10,3),RKB(10,3),WIJ(3,3),TCOIJ(3,3)
2,TCIJ(3,3),C1RKL(3),C2RKL(3),PVOL(3),CJRRL(3,3),ZC(3),LLV(10)
C DIMENSION TC(3),PC(3),VC(3),WW(3),AM(3),VCO(3),TCO(3),PCO(3)
4 ,XX(3,2),Q(3),G(4),D(3),E(3),ZZ(3),PHIV(3),RATIO(3)
6 ,A2I(3),BI(3),AIRKL(3)
7 ,PP(10),BRKL(3)
C DIMENSION PHI(3)
9 ,PHY1(3),PHY2(3)
9,U(3),XP(3)
1 ,PHT1(3),PHT2(3) ,DX1(3),DX2(3)
1 ,SUMYN(10)
COMMON /FIRST/ TC,PC,VC,WW,AMOLWT, P,R,NCJMP,NQNTUM
1
2 ,T
COMMON
1 /SECOND/D,G,MTYPE
11 READ(1,101) M
IF(M.EQ.0) GO TO 800
READ(1,102)(TC(I),I=1,M)
READ(1,102)(PC(I),I=1,M)
READ(1,102)(VC(I),I=1,M)
READ(1,102)(AM(I),I=1,M)
READ(1,102)(WW(I),I=1,M)
READ(1,102)R,RR
DO 50 K=1,M
50 READ(1,115)(CORRL(K,I),I=1,M)
L=1
READ(1,103) LLV(L),PP(L)
103 FORMAT(I8,F8.0)
READ(1,116)(RKA(L,I),I=1,M),(RKB(L,I),I=1,M)
DO 153 I=1,M
C1RKL(I)=RKA(L,I)

```

IV G LEVEL 20

MAIN

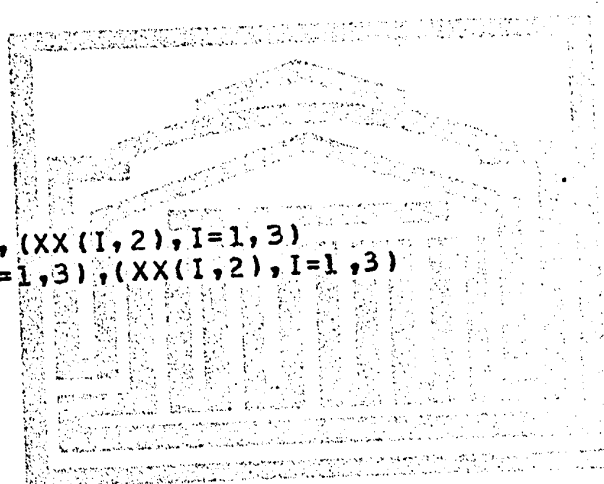
DATE = 72133

21/19/

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      C2RKL(I)=RKB(L,I)
153  ZC(I)=PC(I)*VC(I)/R/TC(I)
      P=PP(L)
      WRITE(3,403)
      WRITE(3,404) (TC(I),PC(I),VC(I),AM(I),WW(I),ZC(I),I=1,M)
      WRITE(3,311)      R,RR
      WRITE(3,112) CORRL(1,2),CORRL(2,3),CORRL(1,3)
      WRITE(3,112) (C1RKL(I),I=1,3),(C2RKL(I),I=1,3)
      READ(1,102) T
      IF(R.LT.10) GO TO 33
32   T=T*1.8
      IF((T-124.0*1.8).GT.0.0) GO TO 29
33   READ(1,102)(XX(I,1),I=1,3)
      READ(1,102)(XX(I,2),I=1,3)
      XX(3,1)=1.0-XX(1,1)-XX(2,1)
      XX(3,2)=1.0-XX(1,2)-XX(2,2)
      GO TO 338
29   READ(1,102)(XX(I,2),I=1,3)
      READ(1,102)(XX(I,1),I=1,3)
      XX(3,1)=1.0-XX(1,1)-XX(2,1)
      XX(3,2)=1.0-XX(1,2)-XX(2,2)
338  WRITE(3,112)(XX(I,1),I=1,3),(XX(I,2),I=1,3)
      WRITE(2,911) P,T,(XX(I,1),I=1,3),(XX(I,2),I=1,3)
911  FORMAT(2F10.1,6F10.4)
331  WRITE(3,110) P      ,T
      KIJ=0
      SUMY2=0.0
      SUMY1=0.0
333  P=PP(L)
      DO 80 I=1,3
      PHV1(I)=1.0
      PHV2(I)=1.0
      PHY1(I)=1.0
      PHY2(I)=1.0
      PHT1(I)=1.0
      PHT2(I)=1.0
      X1(I)=XX(I,1)
80   X2(I)=XX(I,2)
86   DO 82 LJK=1,50
      P01=P
      SUMY2=SUMY1
      DO 81 I=1,3
      X10(I)=X1(I)

```



SITE D'OTTA - 4
THE INFORMATION

IV G LEVEL 20

MAIN

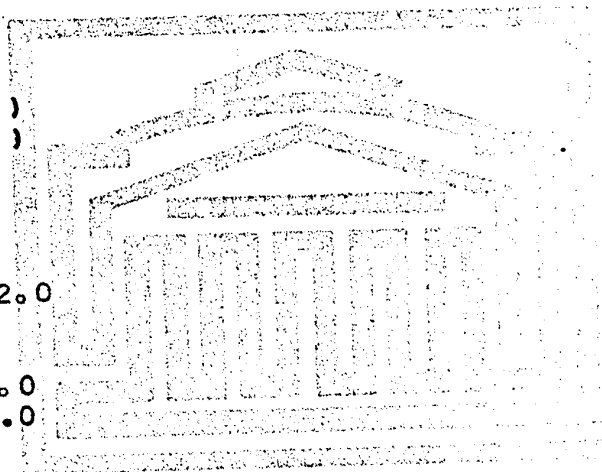
DATE = 72133

21/19/

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81 X20(I)=X2(I)
   CALL SNPT(VL,PHI1 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X1)
   CALL SNPT(VL,PHI2 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X2)
   IF(X2(1).EQ.0.0000) GO TO 90
94 DO 30 I=1,3
   PHY1(I)=PHI1(I)*X1(I)
30 PHY2(I)=PHI2(I)*X2(I)
   DO 40 I=1,3
   U1(I)=(PHY2(I)/PHY1(I))*X1(I)
40 U2(I)=(PHY1(I)/PHY2(I))*X2(I)
   GO TO 68
90 DO 98 I=2,3
   PHY1(I)=PHI1(I)*X1(I)
98 PHY2(I)=PHI2(I)*X2(I)
   U1(I)=0.0
   U2(I)=0.0
   DO 92 I=2,3
   U1(I)=(PHY2(I)/PHY1(I))*X1(I)
92 U2(I)=(PHY1(I)/PHY2(I))*X2(I)
68 SUMU1=0.0
   DO 60 I=1,3
60 SUMU1=SUMU1+U1(I)
   DO 61 I=1,3
61 X1(I)=(U1(I)/SUMU1+X10(I))/2.0
   SUMU2=U2(2)+U2(3)
   BATA=(1.0-X2(1))/SUMU2
   X2(2)=(BATA*U2(2)+X20(2))/2.0
   X2(3)=(BATA*U2(3)+X20(3))/2.0
   SUMXY1=0.0
   SUMXY2=0.0
   IF(T.LT. 400) GO TO 400
   DO 401 I=1,3
   CALL SNPT(VL,PHI1 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X1)
   CALL SNPT(VL,PHI2 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X2)
   PHT1(I)=PHI1(I)*X1(I)
   PHT2(I)=PHI2(I)*X2(I)
   SUMXY1=SUMXY1+(ABS(PHY1(I)-PHT1(I)))
401 SUMXY2=SUMXY2+(ABS(PHY2(I)-PHT2(I)))
   DL=(SUMXY1+SUMXY2)/ 5.0
   IF(DL. LT. 0.001) GO TO 201
   GO TO 86
400 DO 91 I=1,3
   CALL SNPT(VL,PHI1 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X1)

```



SITE D'OTTA

TIC INFORMATION

IV G LEVEL 20

MAIN

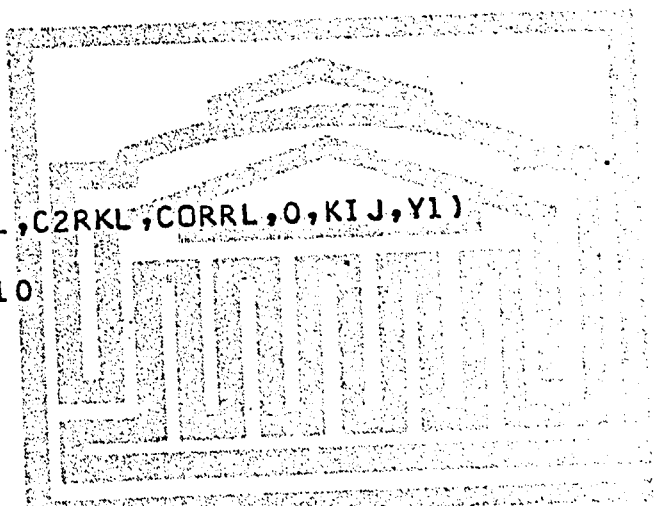
DATE = 72133

21/197

```

CALL SNPT(VL,PHI2 ,PVOL,C1RKL,C2RKL,CORRL, 1,KIJ ,X2)
PHT1(I)=PHI1(I)*X1(I)
PHT2(I)=PHI2(I)*X2(I)
SUMXY1=SUMXY1+(ABS(PHY1(I)-PHT1(I)))
91 SUMXY2=SUMXY2+(ABS(PHY2(I)-PHT2(I)))
DL=(SUMXY1+SUMXY2)/ 5.0
IF(DL.LT.0.0001) GO TO 201
.82 CONTINUE
201 DO 44 LIJ=1,15
    IF((T-400).GT.0.0) GO TO 25
600 IF((T-124.0*1.8).GT.0.0) GO TO 27
25 DO 23 I=1,3
23 Y1(I)=PHI2(I)*X2(I)/PHV1(I)
27 DO 28 I=1,3
28 Y1(I)=PHI1(I)*X1(I)/PHV1(I)
    SUMY1=0.0
    DO 24 I=1,3
24 SUMY1=SUMY1+Y1(I)
7 DO 45 I=1,3
45 Y1(I)=Y1(I)/SUMY1
    CALL SNPT(VL,PHV1,PVOL,C1RKL,C2RKL,CORRL,0,KIJ,Y1)
44 CONTINUE
    IF(SUMY1.EQ.1.0000) GO TO 910
190 IF(P.LT. 1.0) GO TO 910
89 PU=P/SUMY1
    PO=P-PU
    IF(PO-0.1 ) 71,70,72
71 P=P-0.3*(ABS(PO))
84 DP=PO1-P
    IF(SUMY1.LT.1.0000) GO TO 903
    IF(DP.LT.0.3 ) GO TO 922
903 P=P-0.1
930 GO TO 86
922 PUU=PO1
    PLL=P
    WRITE(3,120)PUU,PLL, SUMY1,SUMY2
    DO 908 J=1,5
    PSU=PUU*(SUMY1-1.0000)
    PSL=PLL*(SUMY2-1.0000)
    SUMY12=SUMY1-SUMY2
    PO2=(PSU-PSL)/SUMY12
    PUU=PO2
908 CONTINUE

```



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      GO TO 910
70  GO TO 910
72  P=P+0.3*PJ
85  DP=PO1-P
      IF(SUMY2.GT.1.0000) GO TO 904
      IF(DP.LT.0.3) GO TO 923
904  P=P+0.1
920  GO TO 86
923  PUU=P
      PLL=PO1
      WRITE(3,120)PUU,PLL, SUMY1,SUMY2
      DO 918 J=1,5
      PSU=PUU*(SUMY2-1.0000)
      PSL=PLL*(SUMY1-1.0000)
      SUMY12=SUMY2-SUMY1
      PO2=(PSU-PSL)/SUMY12
      PUU=PO2
918  CONTINUE
      GO TO 910
910  T=T/1.8
      WRITE(2,911) P,T,(X1(I),I=1,3),(X2(I),I=1,3)
      WRITE(3,110) P,T,(X1(I),I=1,3),(X2(I),I=1,3),PO2
      WRITE(3,119)
      DO 77 I=1,3
      DX1(I)=XX(I,1)-X1(I)
77  DX2(I)=XX(I,2)-X2(I)
      DP=P-PP(1)
      WRITE(3,120)DP,(DX1(I),I=1,3),(DX2(I),I=1,3)
      WRITE(3,112)(Y1(I),I=1,3)
      WRITE(2,222)(Y1(I),I=1,3)
222  FORMAT(3F10.4)
      GO TO 11
110  FORMAT(2F12.1,6F12.4,F12.1)
101  FORMAT(3I8)
311  FORMAT(10X,'R=',F8.3,'RR=',F8.3)
403  FORMAT(1H1,/,13X,'TC',5X,'PC',5X,'VC',5X,'M',
      15X,'W',6X,'ZC',/)
404  FORMAT(10X,2F7.1,F7.3,F7.2,2F8.4)
102  FORMAT(8F8.0)
115  FORMAT(6F10.0)
116  FORMAT(6F10.0)
112  FORMAT(6F12.4)
120  FORMAT(F12.1,6F12.4)

```

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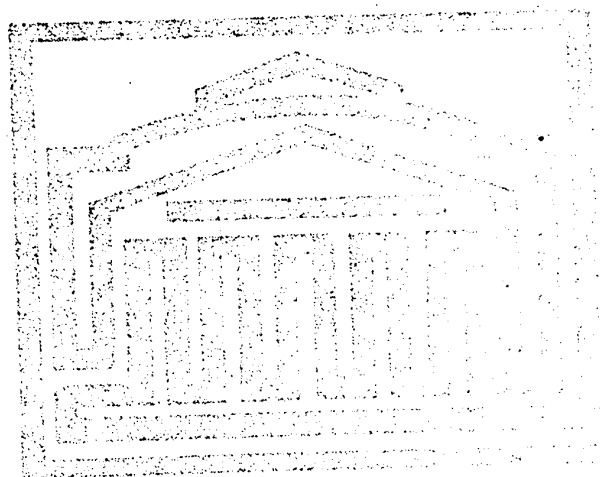
119 FORMAT (//9X,'DP',

1 9X,'DX1',9X,'DX2',9X,'DX3',9X,'DX1',

1 9X,'DX2',9X,'DX3',/)

800 STOP

END

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SUBROUTINE SNPT(VL, PHI, PVOL, C1RKL, C2RKL, CORRL, LV, KIJ, Q)
C EVALUATION OF SUPPORTING PROPERTIES, THE FUGACITY AND THE
C PARTIAL MOLAL VOLUME OF FLUID MIXTURES.
DIMENSION PHV1(3), PHV2(3), X1(3), X2(3), X10(3), X20(3), PHI1(3),
2 PHI2(3), Y1(3), Y2(3), YP1(3), YP2(3), U1(3), U2(3)
1 , ARKL(3,3), RRKL(3), RKA(10,3), RKB(10,3), WIJ(3,3), TCOIJ(3,3)
2, TCIJ(3,3), C1RKL(3), C2RKL(3), PVOL(3), CORRL(3,3), ZC(3), LLV(10)
DIMENSION TC(3), PC(3), VC(3), WW(3), AM(3), VCO(3), TCO(3), PCO(3)
4 , XX(3,2), Q(3), G(4), D(3), E(3), ZZ(3), PHIV(3), RATIO(3)
6 , A2I(3), BI(3), AIRKL(3)
7 , PP(10), BRKL(3)
DIMENSION PHI(3)
9 , PHY1(3), PHY2(3)
9, U(3), XP(3)
COMMON /FIRST/ TC, PC, VC, WW, AMOLWT, P, R, NCOMP, NQNTUM
1
2 , T
COMMON
1 /SECOND/D, G, MTYPE
C LV=0, FOR VAPOR PHASE.
C LV=1, FOR LIQUID PHASE.
C KIJ=1, TCIJ=SQRT(TCI*TCJ)*(1.-KIJ)
C KIJ=2, AIJ=SQRT(AI*AJ)*(1.-KIJ)
C KIJ=3, AIJ=(AI*KIJ+(1.-KIJ)*AJ)/2.
R=10.73
NCOMP=3
NQNTUM=0
RT=R*T
91 CONTINUE
DO 100 I=1, NCOMP
  ARKL(I,I)=C1RKL(I)* R*R *(TC(I)**2.5)/PC(I)
  BRKL(I)=C2RKL(I)* R *(TC(I)/PC(I)
  IF(I.EQ.NCOMP) GO TO 101
  I1=I+1
  DO 100 J=I1, NCOMP
    IF(KIJ.GT.1) GO TO 97
    TCIJ( I,J)=(TC(I)*TC(J))**0.5*(1.-CORRL(I,J))
    TCIJ( J,I)=TCIJ( I,J)
    WIJ(I,J)=(WW(I)+WW(J))*0.5
    ZCOIJ=0.291-0.08*WIJ(I,J)
94 VCOIJ=(VC(I)**(1./3.))+VC(J)**(1./3.))**3/8.0
96 PCOIJ=ZCOIJ* R *(TCIJ( I,J)/VCOIJ
  PCIJ=PCOIJ

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SNPT

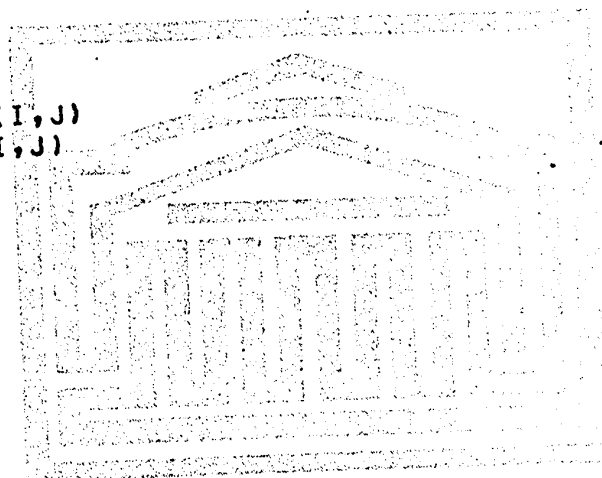
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95 ARKL(I,J)=(C1RKL(I)+C1RKL(J))*0.5* R **2*TCIJ(I,J)**2.5/PCIJ
GO TO 98
97 IF(KIJ.GT.2) GO TO 99
ARKL(I,J)=(ARKL(I,I)*ARKL(J,J))*0.5*(1.0-CORRL(I,J))
GO TO 98
99 ARKL(I,J)=(ARKL(I,I)*CORRL(I,J)+(1.0-CORRL(I,J))*ARKL(J,J))
98 ARKL(J,I)=ARKL(I,J)
100 CONTINUE
101 CONTINUE
AMRKL=0.0
BMRKL=0.0
DO 120 I=1,NCOMP
A2I(I)=ARKL(I,I)/RT**2/T**0.5
BI(I)=BRKL(I)/RT
BMRKL=BMRKL+Q(I)*BRKL(I)
AIRKL(I)=0.0
DO 120 J=1,NCOMP
AIRKL(I)=AIRKL(I)+Q(J)*ARKL(I,J)
120 AMRKL=AMRKL+Q(I)*Q(J)*ARKL(I,J)
A2=AMRKL/RT**2/T**0.5
B=BMRKL/RT
G(1)=1.0
G(2)=-1.0
G(3)=B*P*(A2/B-1.0-B*P)
G(4)=- (A2/B)*(B*P)**2
CALL CUBEQN
IF(MTYPE)115,140,140
115 IF(LV.EQ.0) GO TO 145
C ZL=AMIN1(D(1),D(2),D(3))
C ZL=AMIN1(D(1),D(2),D(3))
C JJ=0
C DO 146 I=1,3
C ZZ(I)=9999.
C JJ=JJ+1
C IF(Z(I).LT.0.0) GO TO 146
C ZZ(JJ)=Z(I)
C 146 CONTINUE
C ZL=AMIN1(ZZ(1),ZZ(2),ZZ(3))
GO TO 150
145 ZL=AMAX1(D(1),D(2),D(3))
GO TO 150
140 ZL=D(1)
150 H=B*P/ZL

```



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C WRITE (3,591) H,ZL,B,Z(1),Z(2),Z(3),LV

C 591 FORMAT(5X,6E12.4,I2)

CALL EQNRK(A2,B,P,H,ZL,LV)

VL=RT*B/H

123 CONTINUE

IF(LV.EQ.0) GO TO 135

QD=(T**0.5)*VL*(VL+BMRKL)

QH=(AMRKL/(T**0.5))*((2.*VL+BMRKL)/(VL**2*(VL+BMRKL)**2))

QK=RT/((VL-BMRKL)**2)

135 DO 130 I=1,NCOMP

C WRITE(3,591) ZL,H

PHILN =(ZL-1.0)*BI(I)/B-ALOG(ZL)-ALOG(1.0-H)

1 -(A2/B)*(2.0*AIRKL(I)/AMRKL -BI(I)/B)*ALOG(1.0+H)

PHI(I)= EXP(PHILN)

IF(LV.EQ.0) GO TO 130

QE1=0.0

DO 125 J=1,NCOMP

125 QE1=QE1+Q(J)*ARKL(I,J)

QE=2.0*QE1-AMRKL*BRKL(I)/(VL+BMRKL)

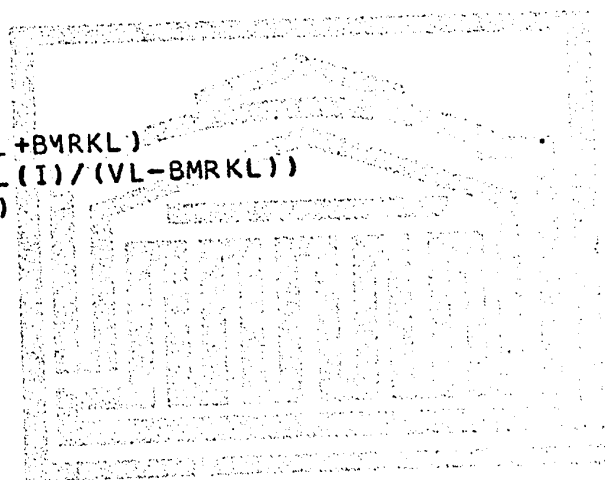
QG=(RT/(VL-BMRKL))*(1.0+BRKL(I)/(VL-BMRKL))

PVOL(I)=((QE/QD)-QG)/(QH-QK)

130 CONTINUE

300 RETURN

END



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INFORMATION

APPENDIX VIII

CALIBRATION RESULTS OF THE GAS PARTITIONER

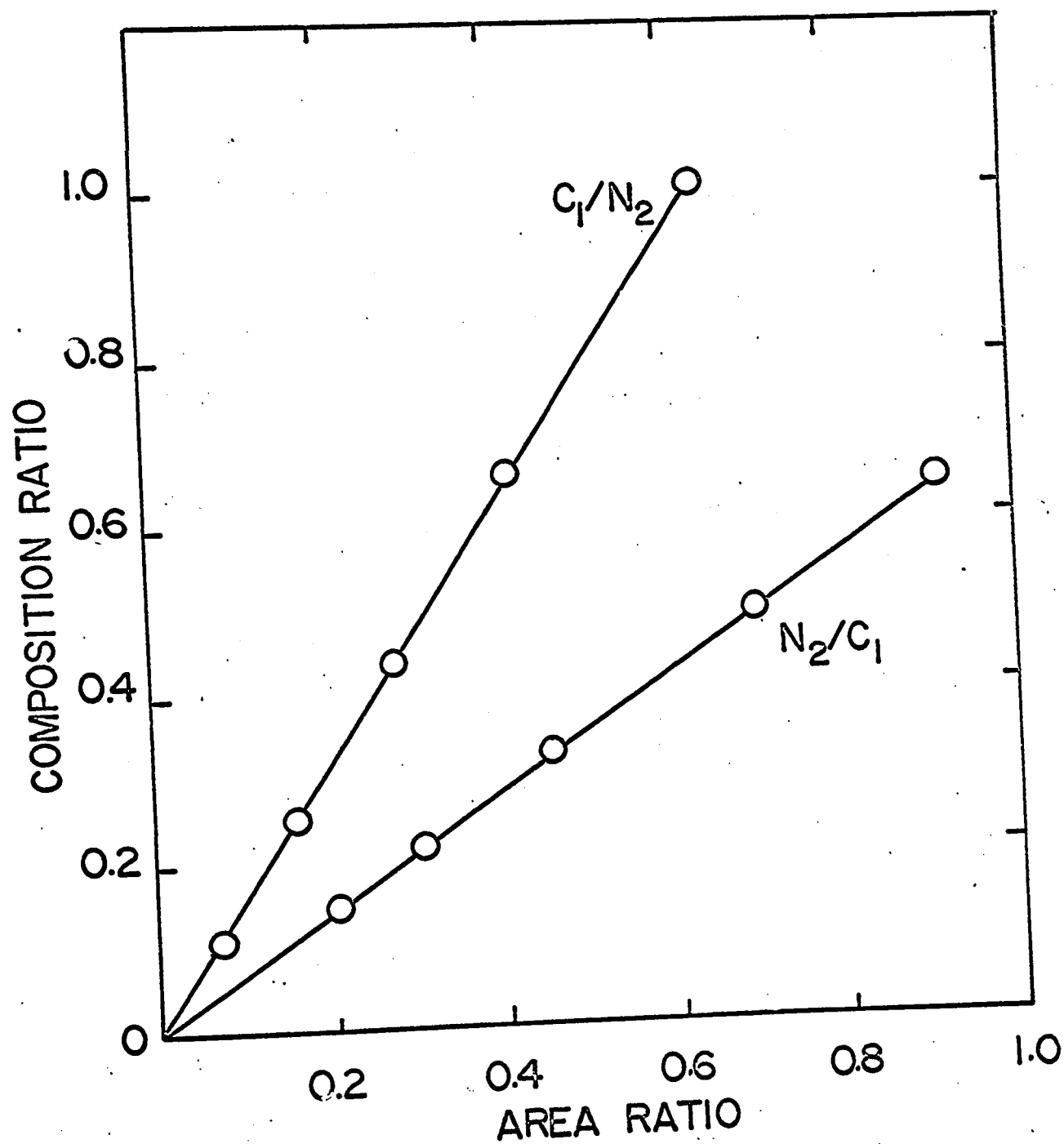


Figure A-8 Calibration Results for the Gas Partitioner
for the Nitrogen-Methane System

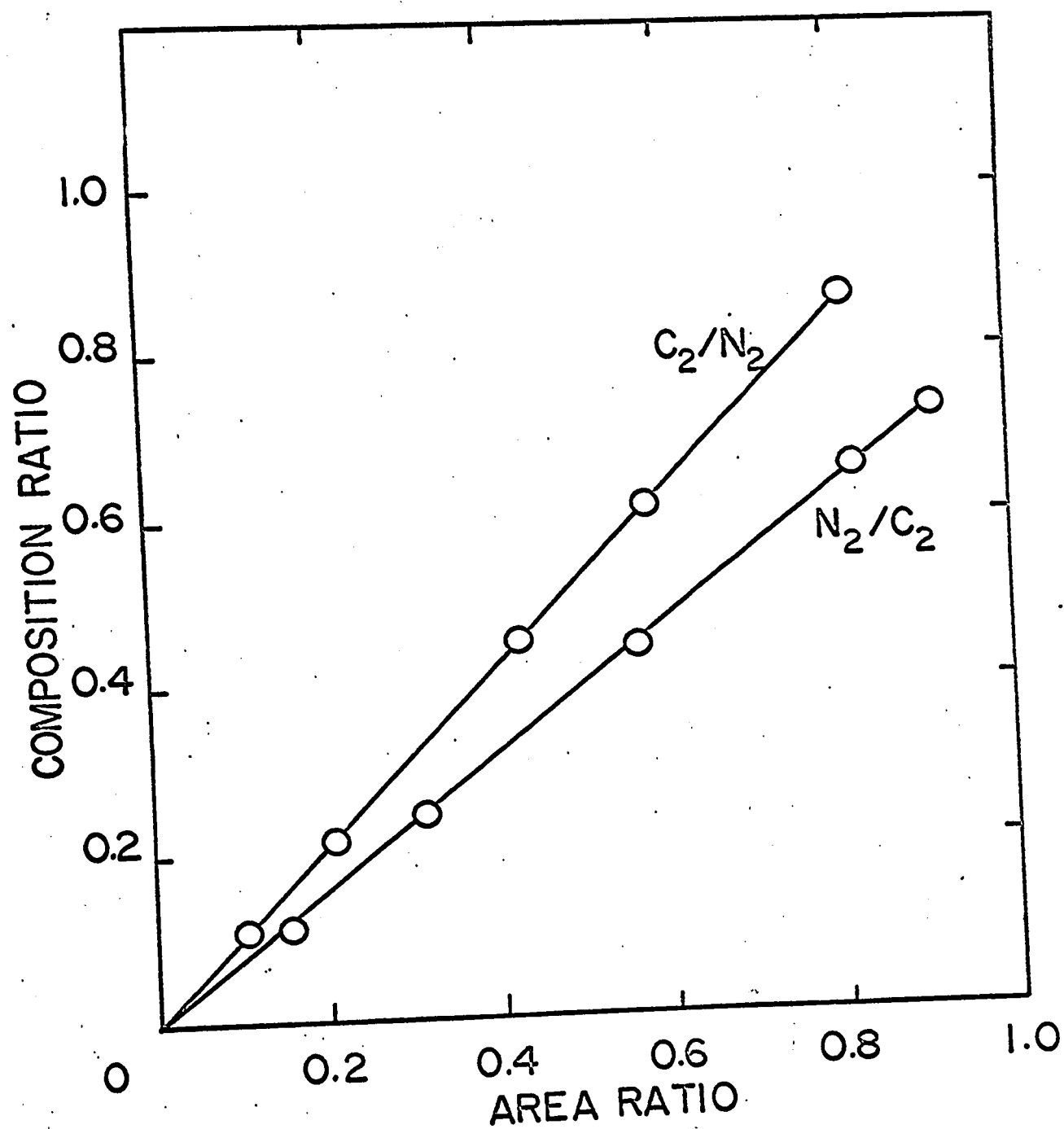


Figure A-9 Calibration Results for the Gas Partitioner
for the Nitrogen-Ethane System

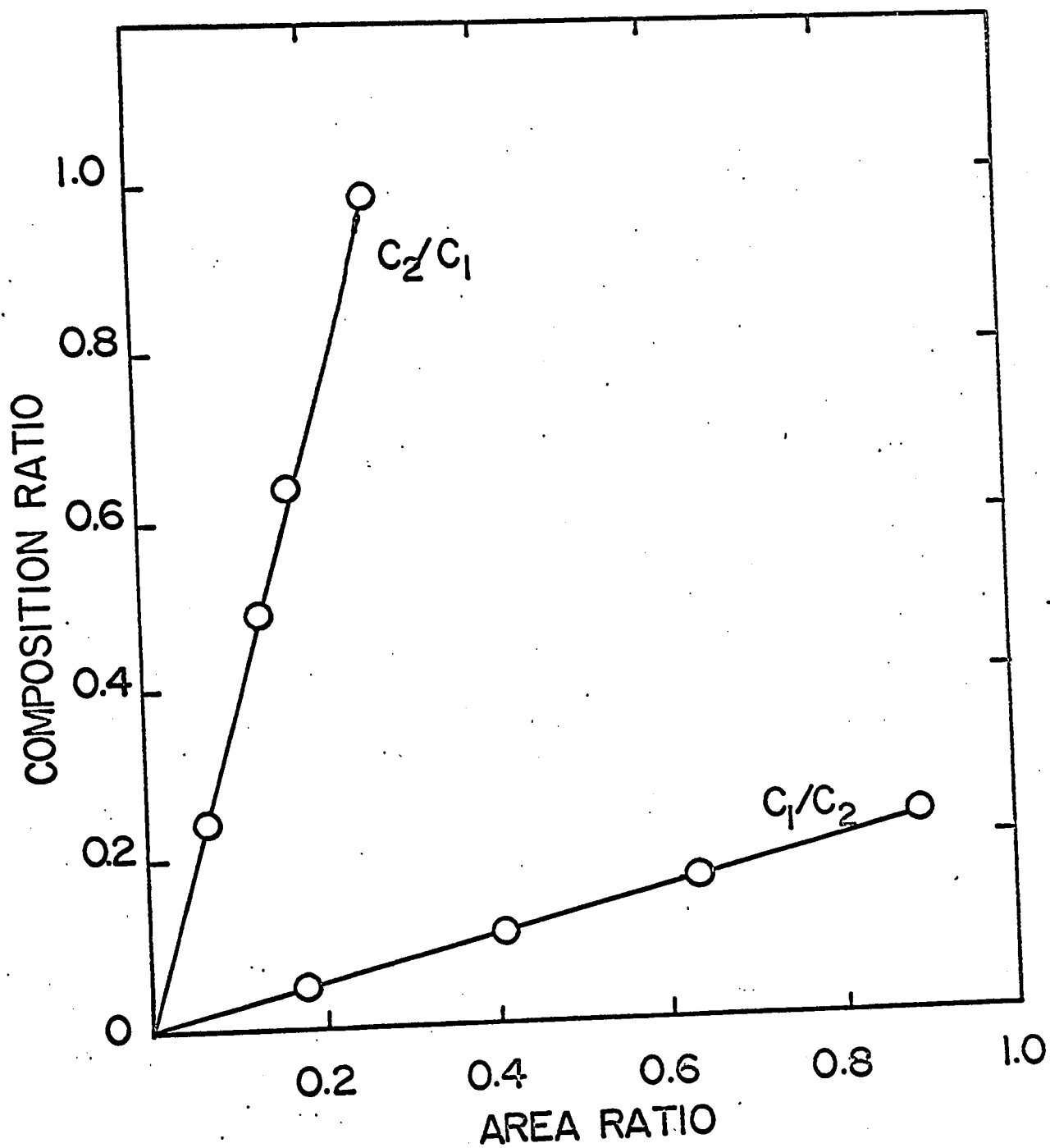


Figure A-10 Calibration Results for the Gas Partitioner for the Methane-Ethane System