VAPOR-LIQUID PHASE EQUILIBRIA AT LOW TEMPERATURES

by

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ABSTRACT

Vapor-liquid phase equilibrium compositions were measured for the nitrogen-methane, methane-ethane and nitrogen-ethane binary mixtures at 169.9 K and 130.0 K and nitrogen-methane-ethane ternary mixture at 130.0 K, and at pressures up to 795 psia.

A modified forced-recirculation apparatus was employed for the determination of phase equilibrium. Vapor was circulated through the liquid in a transparent equilibrium cell by means of a magnetic pump which was submerged in the cooling bath.

In an effort to reduce the experimental work, an attempt was made to predict the vapor phase compositions and total pressures by means of a modified Redlich-Kwong equation of state.

In the data reduction, liquid phase activity coefficients for the binary and ternary vapor-liquid equilibria were evaluated from a modified Redlich-Kwong equation of state and further correlated by the Redlich-Kister equations.

The equilibrium data for the binary systems were tested and considered to be thermodynamically consistent.

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NOMENCLATURE

A = Helmholtz free energy

A_0 B_0, a, b, c = constants of the Beattie-Bridgeman equation

A_0, B_0, C_0, a, b, c, α, γ, ρ = constants of the Benedict-Webb-Rubin equation

A_2, A_3, A_4, B_2, B_3, B_4, C_2, C_3, b = constants of the Martin-Hou equation

A , B , C , D , E , a, b, c, d,α ,γ ,ρ = constants of the Cox-Bono-Kwok-Starling equation

a, b = constants of the van der Waals equation

a, b = constants of the Redlich-Kwong equation

a, b, c = constants of the Clausius equation

$a_0^{(0)}$, $a_1^{(0)}$, $a_2^{(0)}$, $a_0^{(1)}$, $a_1^{(0)}$, $a_0^{(2)}$ = coefficients of the generalized correlation of the dimensionless parameter θ

a, b, c, d, e, f, g = constants of the Sugie-Lu equation

B, C, D, $\cdots\cdot$ = virial coefficients of the virial equation

B_{12}, C_{12}, D_{12}, B_{23}, C_{23}, D_{23} = constants of the Redlich-Kister equation in the binary system

B_{31}, C_{31}, D_{31}

C_{123}, D_1, D_2, D_3 = constants of the Redlich-Kister equation in the ternary system

f = fugacity of pure component

$\hat{f}$ = fugacity of a component in mixture

G = Gibbs free energy

G^E = excess Gibbs free energy

G^{id} = Gibbs free energy at ideal state

H = enthalpy

K = (y/x) equilibrium constant

K_{ij} = binary interaction constant

N = number of molecules

N = number of components

n = number of moles

P = pressure

Q = ($G^E/2.303RT$)excess Gibbs free energy function

R = universal gas constant

S = entropy

T = temperature

U = internal energy

V = volume

$\bar{V}$ = partial molar volume

v = molar volume

x = mole fraction in the liquid phase

y = mole fraction in the vapor phase

Z = compressibility factor

Ωa, Ωb = parameters of the Redlich-Kwong equation

ϕ = fugacity coefficient of pure omcponent

$\hat{\phi}$ = fugacity coefficient of a component in mixture

θ = (T/T_c) dimensionless parameter

μ = chemical potential

γ = activity coefficient

ω = acentric factor

Superscripts:

L = liquid phase

V = Vapor phase

o = standard state

$*$ = apparent value

r = reference value

∞ = infinite dilution

Subscripts:

AV = average value

c = critical property

i, j = component identification

r = reduced property

1, 2, 3 = component identification

12, 23, 31, 123 = mixture identification

CHAPTER 1

INTRODUCTION

Cheaper and better stagewise separation techniques are strongly demanded in the ever growing petrochemical industry and space technology. The main concern in the stagewise operation is the physical equilibrium. The equilibrium compositions in different phases are often very much different and it is precisely this difference which enables us to separate mixtures by distillation, extraction, and other phase-contacting operations.

Since vapor-liquid equilibrium relations of many systems cannot yet be predicted from theoretical consideration, they can only be determined experimentally.

The experimental investigation of vapor-liquid phase equilibrium consists of the determination of the compositions of both the vapor and the liquid phases at equilibrium conditions. These determinations can be carried out either at constant temperature or at constant pressure. And since for systematic exploration of the field of phase equilibrium, isothermal measurements are far more useful than isobaric determination for data treatment, so isothermal measurements were carried out in this study.

The Gibbs-Duham equation is the basic equation to test the consistency of the phase equilibrium data. With simplifying assumptions many semi-empirical equations (1-8) have been proposed as the special forms of this equation. They are applicable to many systems. The equation proposed by Redlich and Kister (7) appears to be flexible and adequate for representing the vapor-liquid equilibrium data.

Due to the rapidly decreasing amount of petroleum oil and the ever growing demand for it, some other sources of energy must be applied instead. The natural gas, of which the nitrogen, methane and ethane are the major components, draws much attention and will surely play an important role in the energy field for some future years. The present investigation consists of determining the equilibrium pressure and compositions of the vapor and liquid phase for the three major components of natural gas at low temperatures. Measurements were made at 169.9 K and 130.0 K for the binary mixtures of nitrogen, methane and ethane, and at 130.0 K for the ternary mixtures. The two temperatures were chosen as part of the continuing work in this laboratory.

An equilibrium cell with modified recirculating systems was used. Temperatures were measured by means of a calibrated thermocouple and pressures were measured by means of calibrated Heise Gauges. The equilibrium compositions were determined by a gas chromatograph which was calibrated against composition known mixtures.

The Redlich-Kwong equation of state is one of the most commonly used equations in engineering due to its accuracy and simplicity. For the purpose of comparison, the equilibrium vapor phase compositions and total pressures were predicted by means of a modified Redlich-Kwong equation of state. The agreements between the experimental and calculated results are very satisfactory.

CHAPTER 2

LITERATURE SURVEY

A brief review of the literature covering only those points which are of interest to this study, such as the experimental methods, available phase equilibrium data and some important equations of state is presented as follows.

2.1 EXPERIMENTAL METHODS

In their book entitled "Vapor-Liquid Equilibrium" Hala et al (9) presented a bibliography for experimental methods which can be classified as follows:

2.1.1 Distillation Method

This method is the oldest one for the direct determination of vapor-liquid equilibrium data. It involves the distillation of a small amount of liquid from the boiling flask containing a large charge. The method is very simple but has marked disadvantages and generates large errors (8) in determining the equilibrium temperature, pressure and compositions.

2.1.2 Static Method

In this method, the liquid solution is charged into a closed equilibrium cell which is rotated or shaken until equilibrium is reached between the two phases. Then the samples are taken and analyzed.

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

To overcome this restriction, Prausnitz (10) and Scatchard et al. (11) developed the static and total pressure method in which the vapor phase compositions are calculated directly from the thermodynamic relationships based on the liquid phase compositions and total pressure. This method is useful for high or moderate pressure and high or low temperature systems (12,13).

2.1.3 Dew and Bubble Point Method

A method employing apparatus similar to the static method but omitting the analyses, is the dew and bubble point method. A liquid of known composition is introduced into the equilibrium cell which is maintained at a constant temperature. The pressure at which the liquid first starts to vaporize is the so called 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 solution is predetermined. Therefore, vapor and liquid samples need not be analyzed.

This method was employed by Sage and Lacey (14,15) for determining equilibrium data of light hydrocarbons in the temperature range of 20°C to 100°C. This method was also applied by I.G.T. (Institute of Gas Technology) group at low temperatures for the nitrogen-methane (16), nitrogen-ethane (17) and methane-ethane (18) systems, and by Kurata and his associates for the nitrogen-propane (19) system.

2.1.4 Flow Method

The flow method is used for measuring equilibrium data in systems of limited miscibility in the liquid phase. 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.

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

2.1.5 Forced-Recirculation Method

In this 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 (20) and modified to practical use by Dodge and Dunber (21) for the oxygen-nitrogen system. It was used by Torocheshuikov (22) for determining equilibria of the carbon monoxide-nitrogen system and by Aroyan and Katz (23) for studying equilibria of the methane-hydrogen system. Futher modification of the equipment was made by Davis, Rodewald and Kurata (24), Harvey (25), Price and Kobayashi (26). They introduced a transparent equilibrium cell and a liquid bath in the cryostat for studying systems containing methane, ethane and propane. A similar apparatus was employed by Brandt, Stroud and Deaton (27), Sterner and Geist (28) and by Rogers and Prausnitz (29).

Because of its marked advantage that the equilibrium can be reached very quickly and that the vapor and liquid samples can be withdrawn almost without disturbing the equilibrium it is probably the most accurate and reliable method and is widely used at present. This method has been used extensively in our laboratory (e.g. 43···). In the present study it has also been chosen.

2.2 AVAILABLE PHASE EQUILIBRIUM DATA

This section gibes a brief review of the experimental vapor-liquid phase equilibrium data pertinent to this work. The available data, which covers the period up to 1977 containing nitrogen, methane and ethane at low temperatures are listed in Tables 2.1 to 2.4.

TABLE 2.1

Vapor-Liquid Equilibrium Data Available in the Literature for the Nitrogen-Methane Binary System

Investigators	Year Reported	Temperature	Pressure
McTaggart & Edwards (30)	1919	-306 to -268°F	1 atm
Rysakov et al. (31)	1934	72.63 to 149.5 K	0.5 to 10 atm
Steckel & Zinn (32)	1939	-266°F	10 atm
Torocheshnikov & Levius (33)	1939	-295 to -220°F	0 to 24 atm
Torocheshnikov & Levius (34)	1941	17 to 133 K	1.0 to 10 atm
Booth & Martin	1943	89 to 106 K	1.0 atm
Vellinger & Pons (36)	1943	-183°C	0 to 1 atm
Bloomer & Parent (37)	1952	-290 to -125°F	14.7 to 7000 psia
Cines et al. (38)	1953	-280 to -150°F	1.4 to 4.5 atm
Fastovskii & Petrovskii (39)	1957	-312 to -189°F	below 16 atm
Brandt & Stroud (40)	1958	-213 to -145°F	500 psia
Chung & Wang (41)	1964	-296 to -236°F	below 5 atm
Sprow & Prausnitz (42)	1966	113 to 183 K	1 to 50 atm

TABLE 2.1 (continued)

Vapor-Liquid Equilibrium Data Available in the Literature for the Nitrogen-Methane Binary System

Investigators	Year Reported	Temperature	Pressure
Chang & Lu (43)	1967	-151.1 & -240°F	50.7 to 721.7 psia
Fuks & Bellemans (44)	1967	91 K	756.9 to 2165.5 mmHg
Skripka et al. (45)	1970	-256°F	----
Miller et al. (46)	1973	112 K	2 to 13 atm
Parrish & Hiza (47)	1974	95 to 120 K	0 to 25 atm
Stryjek & Kobayashi (48)	1974	-240 to -130°F	1 to 50 atm
Wilson (49)	1975	-260°F	14.0 to 223.0 psia
Kidnay et al. (50)	1975	130 to 180 K	4 to 48 atm

TABLE 2.2

Vapor-Liquid Equilibrium Data Available in the Literature for the Methane-Ethane Binary System

Investigators	Year Reported	Temperature	Pressure
Uehara (51)	1932	139 to 161 K	1 atm
Michels & Nederbragt (52)	1939	0 to 50°C	9 to 60 atm
Ruhemann (53)	1939	-130 to -10°C	5 to 20 atm
Guter et al. (54)	1940	169 to 273 K	3 to 65 atm
Levitskaya (55)	1941	178 to 188 K	30 and 40 atm
Bloomer, Gami & Parent (56)	1953	-200 to 50°F	100 to 800 psia
Ellington et al. (57)	1959	142 to 300 K	7 to 64 atm
Moran (58)	1959	99 to 193 K	0 to 2 atm
Price & Kobayashi (26)	1959	-200 to 0°F	100 to 900 psia
Chang & Lu (43)	1967	-151.1 & -240°F	31.7 to 301.7 psia
Skripka et al. (45)	1970	-150 to -120°C	0.31 to 12.18 atm
Wichterle (59)	1970	-225 to -100°F	25.8 psia to critical
Hsi & Lu (60)	1971	-173.1°F	below 22 atm
Wilson (49)	1975	-260°F	2.38 to 14.0 psia
Miller et al. (61)	1977	150 to 190 K	0.0276 to 2.516 MPa

TABLE 2.3

Vapor-Liquid Equilibrium Data Available in the Literature for the Nitrogen-Ethane

Investigators	Year Reported	Temperature	Pressure
Eakin et al. (17)	1955	-300 to 90°F	50 to 1850 psia
Ellington et al. (57)	1959	101 to 302 K	7 to 126 atm
Cheung & Wang (41)	1964	92.8 K	below 1 atm
Chang & Lu (43)	1967	-151.1 & -240°F	3 to 34 atm
Cannon et al. (62)	1968	144 to 228 K	20 to 48 atm
Yu et al. (63)	1969	-255 to -220°F	260 to 591 psia
Stryjek et al. (64)	1974	-210 to -110°F	0.5 to 1953 psia
Wilson (49)	1975	-260°F	28.5 to 223.7 psia

TABLE 2.4

Vapor-Liquid Equilibrium Data Available in the Literature for the Nitrogen-Methane-Ethane Ternary System

Investigators	Year Reported	Temperature	Pressure
Cosway & Katz (65)	1959	-100°F	500 & 1000 psia
Chang & Lu (43)	1967	-151.1 & -240°F	25.3 to 406.5 psia
Yu et al. (63)	1969	-255 to -227.6°F	222 to 513.9 psia
Lu et al. (66)	1969	-257.8°F	203.5 psia
Lu et al. (67)	1970	-255.4 to -263.6°F	189.8 to 213 psia

2.3 EQUATIONS OF STATE

Several hundred equations of state have been proposed since van der Waals first introduced his equation in 1873 and achieved success in qualitatively describing some important features of the volumetric properties of real fluids. From a practical point of view, the usefulness of a reliable equation exceeds by far the mere description of the P-V-T behavior, for it leads directly to departure from ideal-gas value of thermodynamic properties such as enthalpy, entropy and free energy. As a result, fugacity, vapor pressure, heat of vaporization, activity coefficients and phase equilibrium in fluid mixtures can all be derived.

There are many kinds of equation of state which can vary greatly in complexity and generality. Some very complex equations may be designed to describe only one substance. For instance, one equation containing more than forty constants accurately describe the properties of steam, and indeed the latest steam tables (68) were generated from it. Other equations may be intended only for a restricted range of conditions. Still others may be very generally applicable, but not highly accurate. However, all existing equations are practical modifications of either the virial equation or the hard-core equation or both (69).

2.3.1 Virial Equation of State

The virial equation of state for gases has a sound theoretical basis and is free of arbitrary assumptions. The virial equation gives the compressibility factor as a power series in the reciprocal molar volume 1 / v:

$$Z = \frac{P\,v}{R\,T} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots \tag{2.1}$$

In Equation (2.1), B is the second virial coefficient, C is the third virial coefficient, D is the fourth, and so on. All the virial coefficients are independent of pressure or density and for pure components they are functions only of the temperature.

The virial equation was initially used by Kammerlingh-Onnes and co-workers for fitting experimental data. It was subsequently discovered in the development of the molecular theory of imperfect gases (70) that the virial coefficients are precisely related to the interaction of molecules in clusters of various sizes. For instance, the second virial coefficient is related to the interaction of molecules in pairs and the third virial coefficient is related to that of molecules in tripletes. Furthermore, in a gaseous mixture, the virial coefficients depend on the composition in an exact and particularly simple manner.

The second and third virial coefficients are properly evaluated from low pressure P-V-T data by means of the following equations:

$$B = \lim_{\rho \to 0} \left(\frac{\partial Z}{\partial \rho} \right)_T \tag{2.2}$$

$$C = \lim_{\rho \to 0} \frac{1}{2} \left(\frac{\partial^2 Z}{\partial \rho^2} \right)_T \tag{2.3}$$

For a mixture of N components the second and third virial coefficients are given by:

$$B_{mixture} = \sum_i \sum_j y_i \, y_j \, B_{ij} \qquad (B_{ii} = B_i) \qquad (2.4)$$

$$C_{mixture} = \sum_i \sum_j \sum_k y_i \, y_j \, y_k \, C_{ijk} \qquad (C_{iii} = C_i) \qquad (2.5)$$

where y_i is the mole fraction of component i in mixture and B_{ij} and C_{ijk} are the cross virial coefficients.

2.3.2 Hard Sphere Equation of State

Theoretical development of equations of state is greatly simplified when the molecules are treated as behaving like hard cores. No molecules are truly just hard cores, but the simplication makes it possible to obtain useful descriptions that are particularly valuable at high densities and pressures, for the structure of dense fluids is primarily dependent on the order of packing of the hard cores.

An ultrasimplified view of an assembly of hard spheres (71) is shown in Figure 2.1. N molecules of diameter d are inserted one at a time into a cubical box of volume V. This leads to the ultrasimplified hard-sphere equation of state:

$$P \, (v - b) = R \, T \qquad (2.6)$$

in which the covolume b is given by (2/3) $N\pi d^3$, and is equal to N/2 times the volume of the dashed sphere in Figure 2.1.

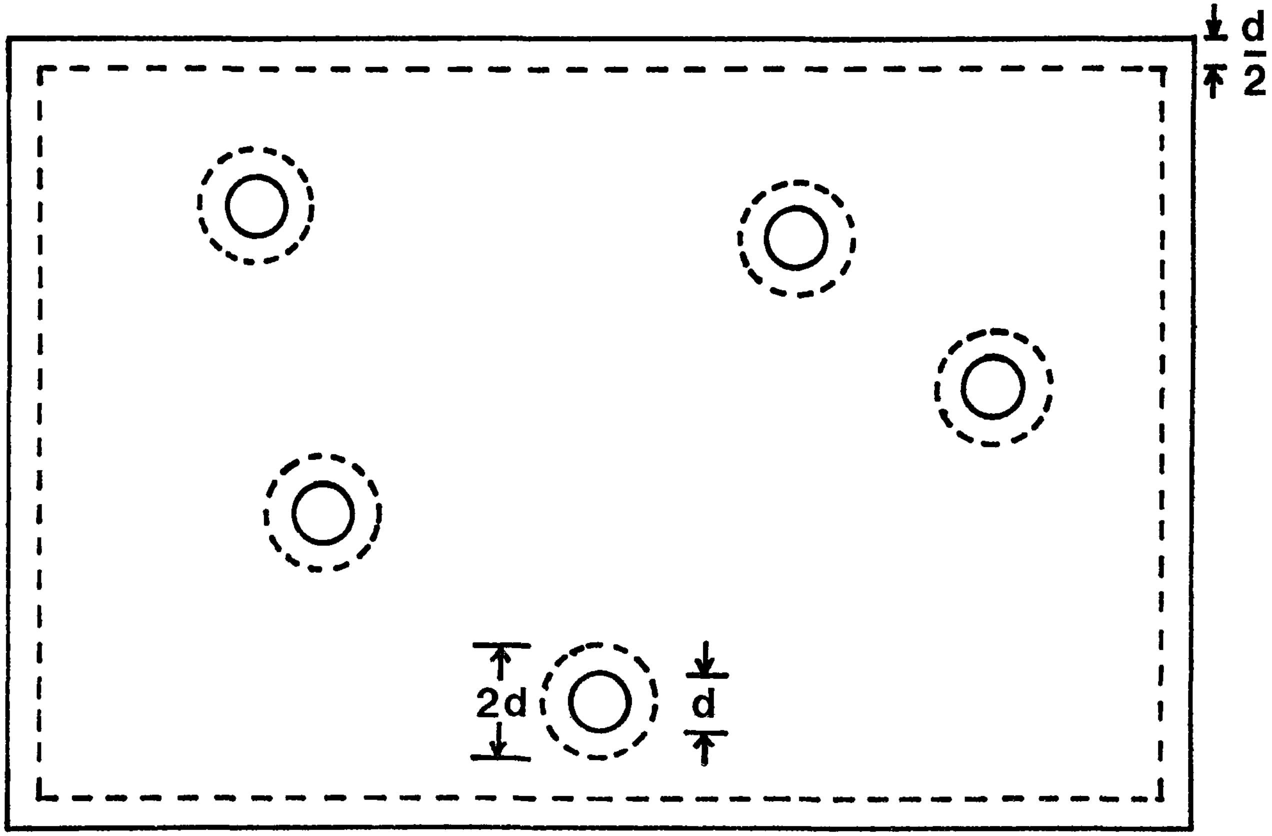


Figure 2.1 An Ultrasimplified View of Hard Sphere Molecules

2.3.3 Empirical Equations of State

Empirical equations of state are practical modifications of the virial equation or the hard-sphere equation or both and are designed for the range of conditions of interest and fitted to experimental data. The van der Waals equation is of much historical interest:

$$\left(P + \frac{a}{v^2}\right)(v - b) = R\,T \tag{2.7}$$

where a and b are constants, characteristic of the particular gas. The van der Waals equation can be rewritten in the virial form:

$$Z = 1 + \frac{\left(b - \frac{a}{R\,T}\right)}{v} + \frac{b^2}{v^2} + \frac{b^3}{v^3} + \ldots. \tag{2.8}$$

The virial coefficients are therefore given by:

$$B = b - \frac{a}{R\,T} \tag{2.9}$$

$$C = b^2 \tag{2.10}$$

$$D = b^3 \tag{2.11}$$

. . . .

The constants a and b are related to critical properties by solving the two expressions:

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 \tag{2.12}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 \tag{2.13}$$

and the results obtained are:

$$a = \frac{27 R^2 T_c^2}{64 P_c} \qquad (2.14)$$

$$b = \frac{R T_c}{8 P_c} \qquad (2.15)$$

2.3.4 Development of Empirical Equations

A large number of empirical equations of state have been developed since the van der Waals equation. One procedure that receives much attention is to add more terms of greater complexity. Examples of this development are as follows:

1. Clausius Equation (72) (3 constants)

$$P = \frac{R T}{v - b} - \frac{a}{T (v + c)^2} \qquad (2.16)$$

2. Beattie-Bridgeman Equation (73) (5 constants)

$$P v^2 = R T [v + B_0 (1 - \frac{b}{v})] (1 - \frac{c}{v T^3}) - A_0 (1 - \frac{a}{v}) \qquad (2.17)$$

3. Benedict-Webb-Rubin Equation (74) (8 constants)

$$P = R T\rho + (B_0 R T - A_0 - \frac{C_0}{T^2})\rho^2 + (b R T - a)\rho^3 + \alpha a\rho^6 + \frac{c\rho^3}{T^2} (1 + \gamma\rho^2) \exp(-\gamma\rho^2) \qquad (2.18)$$

4. Martin-Hou Equation (75) (9 constants)

$$P = \frac{R\ T}{v - b} + \frac{A_2 + B_2\ T + C_2 \exp\ (-5.475\ T/T_c)}{(v - b)^2}$$

$$+ \frac{A_3 + B_3\ T + C_3 \exp\ (-5.475\ T/T_c)}{(v - b)^3}$$

$$+ \frac{A_4}{(v - b)^4} + \frac{B_5}{(v - b)^5} \tag{2.19}$$

5. Cox-Bono-Kwok-Starling Equation (76) (11 constants)

$$P = R\ T\rho + (B_0\ R\ T - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4})\ \rho^2$$

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

$$+ \frac{C\rho^3}{T^2}\ (1 + \gamma\rho^2)\ \exp\ (-\gamma\rho^2) \tag{2.20}$$

Many other useful equations have been proposed. Some of the examples are those by Vennix and Kobayashi (77), Baner and Adler (78,79), and Lee and Edmister (80).

Sugie and Lu (81) developed a generalized equation of state for vapors and liquids as follows:

$$P = \frac{R\ T}{v - b + c} - \frac{a}{T^{0.5}\ (v + c)\ (v + b + c)}$$

$$+ \frac{d\ T^2}{v^2} + \sum_{j=1}^{5} \frac{e_j + f_j\ T + g_j\ T^{-2}}{v^{j+1}} \tag{2.21}$$

A somewhat different approach is to write the equations based on the principles of corresponding states. The equation can be of great complexity, but no new constants are required to be evaluated in order for the equation to apply to a new substance, provided the critical properties are known. The Redlich-Kwong equation of state (82) has been used as a starting point by several authors for the development. This equation is an effective modification of the van der Waals equation and is as follows:

$$P = \frac{R\ T}{v-b} - \frac{a}{T^{0.5}\ v\ (\ v + b\ )} \tag{2.22}$$

And it is used in the form:

$$Z = \frac{1}{1 - h} - \frac{A^2\ h}{B\ (1 + h)} \tag{2.23}$$

where

$$Z = \frac{P\ v}{R\ T} \tag{2.24}$$

$$A^2 = \frac{a}{R^2\ T^{2.5}} \tag{2.25}$$

$$B = \frac{b}{R\ T} \tag{2.26}$$

$$h = \frac{B\ P}{Z} \tag{2.27}$$

Furthermore,

$$a = \frac{\Omega_a\ R^2\ T_c^{\ 2.5}}{P_c} \tag{2.28}$$

$$b = \frac{\Omega_b R T_c}{P_c} \qquad (2.29)$$

Redlich and Kwong considered the parameters Ω_a and Ω_b universal constants with the values of 0.42748 and 0.08664 respectively.

The fugacity coefficient is calculated according to:

$$\ln \phi = \int_0^P \frac{(Z-1)}{P} dP$$

$$= Z - 1 - \ln (Z - BP) - (\frac{A^2}{B}) \ln (1 + \frac{B P}{Z}) \qquad (2.30)$$

For gaseous mixtures Redlich and Kwong suggested the following mixing rules:

$$b_{mixture} = \sum_i y_i b_i \qquad (2.31)$$

$$a_{mixture} = \sum_i \sum_j y_i y_j a_{ij} \qquad (2.32)$$

and $$a_{ij} = (a_i a_j)^{0.5} \qquad (2.33)$$

2.4 THE ADVANTAGE OF THE VIRIAL, B-W-R AND R-K EQUATIONS

Of all the equations mentioned above, three were widely used for calculating equilibrium data at low temperatures (83). They are the virial equation, the eight-constant Benedict-Webb-Rubin (B-W-R) equation and the simple two-constant Redlich-Kwong (R-K) equation.

The virial equation of state is applicable to pure components and mixtures at moderate pressure and at low densities. The B-W-R equation of state is applicable to light paraffinic and olefinic hydrocarbons and their mixtures.

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

1. It is very simple with only two constants.
2. It can be applied to normal fluids.
3. It saves computing time over the virial and B-W-R equations because of its simplicity.
4. It can give more accurate results when applied to a pure component at low temperature, high density and liquid regions, if Ω_a and Ω_b are considered to be temperature and substance dependent.
5. It permits quantitative predictions through recent modifications (84-99). For calculating mixture properties, the binary interaction constant K_{ij}, which will be mentioned later in Chapter 5, is easily introduced.

In fact, the R-K equation is one of the most frequently used equation of state for estimating system properties (100). It is for these reasons that the Redlich-Kwong equation of state is chosen in this investigation.

CHAPTER 3

THEORETICAL CONSIDERATION

Several important equilibrium variables such as chemical potential μ, fugacity f, liquid phase activity coefficient γ , and fugacity coefficient ϕ are defined or briefly derived.

The liquid phase activity coefficient is evaluated by means of an equation of state (Redlich-Kwong equation) and correlated by the Redlich-Kister equation.

Binary isothermal equilibrium data are thermodynamically tested following a method proposed by Redlich and Kister.

3.1 DEFINITIONS OF μ, f, γ AND ϕ

The chemical potential of component i in a homogeneous phase is given by:

$$\mu_i = \left[\frac{\partial U}{\partial n_i}\right]_{S,V,n_j} = \left[\frac{\partial H}{\partial n_i}\right]_{S,P,n_j} = \left[\frac{\partial A}{\partial n_i}\right]_{V,T,n_j} = \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_j} \tag{3.1}$$

where the subscripts n_j indicate constancy of all mole numbers other than n_i. The variables U,H,A,G,S, and V are the toal internal energy, enthalpy, Helmholtz free energy, Gibbs free energy, entropy and volume of the mixture, respectively.

Though the chemical potential is of great importance, it can't be used conveniently. Therefore , two other important variables, fugacity f and activity coefficient γ are defined. The definitions are as follows:

1. For single gas:

(perfect) $\mu_i = \mu_i^o + RT \ln P$ (3.2)

(imperfect) $\mu_i = \mu_i^o + RT \ln f_i$ (3.3)

$f_i / P \rightarrow 1$ as $P \rightarrow 0$

2. For gas mixture

(perfect) $\mu_i = \mu_i^o + RT \ln \overline{P}_i$ (3.4)

$\overline{P}_i = y_i P$ (3.5)

(Imperfect) $\mu_i = \mu_i^o + RT \ln \hat{f}_i$ (3.6)

$\hat{f}_i / \overline{P}_i \rightarrow 1$ as $P \rightarrow 0$

3. For solution

(ideal) $\mu_i = \mu_i^* + RT \ln x_i$ (3.7)

(non-ideal) $\mu_i = \mu_i^* + RT \ln \gamma_i x_i$ (3.8)

$\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$

In the above definitions R is the gas constant and T the temperature. P is the pressure of a single gas or total pressure of a gas mixture and $\overline{P}_i$ is the partial pressure of i. The mole fraction of component i in a gas mixture is y_i and that in a solution is x_i. The activity coefficient γ_i approaches 1 as x_i approaches 1. The chemical potential constant μ_i^o is a function of T only while μ_i^* is a function of both T and P.

When two phases are in equilibrium, the following conditions must be satisfied.

$$\mu_i^L = \mu_i^V \qquad i = 1, \cdots\cdots, N \qquad (3.9)$$

or

$$\hat{f}_i^L = \hat{f}_i^V \qquad i = 1, \cdots\cdots, N \qquad (3.10)$$

in which N is the total number of components in the mixture with L refers to the liquid phase and V the vapor phase.

The fugacity coefficient $\hat{\phi}_i$ is defined by

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{y_i P} \qquad (3.11)$$

and it is readily calculated from PVT data. The equations are given by (101)

$$\ln \hat{\phi}_i = \frac{1}{RT} \int_o^P [(\frac{\partial V}{\partial n_i})_{T,P,n_j} - \frac{RT}{P}] \, dP \qquad (3.12)$$

or

$$\ln \hat{\phi}_i = \frac{1}{RT} \int_V^\infty [(\frac{\partial P}{\partial n_i})_{T,V,n_j} - \frac{RT}{V}] \, dV - \ln Z \qquad (3.13)$$

With an adequate equation of state, which represents not only for the pure components but also for the mixtures, the calculation of fugacity coeeficients can be computerized and thus save both labor and time. For instance, if R-K equation (Equation 2.22) and the accompanied mixing rules (Equations 2.31 and 2.32) are applied, the resulting equation is (102):

$$\ln \hat{\phi}_i = \ln \frac{v}{v-b} + \frac{b_i}{v-b} - \frac{2 \sum_{j=1} y_i a_{ij}}{RT^{3/2} b} \ln \frac{v+b}{v} + \frac{ab_i}{RT^{3/2} b^2} [\ln \frac{v+b}{v} - \frac{b}{v+b}] - \ln Z \qquad (3.14)$$

Practically all the fugacities are evaluated by first calculating the fugacity coefficients. In Equation 3.10 $\hat{f}_i^L$ is a function of x_i, P and T, and $\hat{f}_i^V$ is a function of y_i, P and T. With this equation one can obtain y_i's and T or P from a knowledge of x_i's and P or T, or vice versa.

3.2 EVALUATION OF LIQUID PHASE ACTIVITY COEFFICIENTS

The fugacity of component i in a liquid solution is most conveniently related to the mole fraction x_i by an equation of the form:

$$\hat{f}_i^{L} = \gamma_i x_i f_i^{oL} \qquad (3.15)$$

where γ_i is the activity coefficient and f_i^{oL} is the fugacity of i at the same arbitrary condition known as the standard state. At any composition, the activity coefficient depends on the choice of standard state and the numerical value of γ_i has no significance unless the numerical value of f_i^{oL} ia also specified.

At a constant temperature T and a constant reference pressure P^r, the activity coeffficient can be expressed as

$$\gamma_i = \frac{y_i \hat{\phi}_i^{V} P}{x_i f_i^{oL}} e^{\int_P^{P^r} \frac{\bar{V}_i}{RT} dP} \qquad (3.16)$$

where $\bar{V}_i$ is the partial molar volumes of the liquid.

It is usually normalized as follows:

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 \qquad (3.17)$$

By normalization we mean a specification of state wherein the acitivity coefficient is unity. If all the activity coeffients are normalized according to Equation 3.17, the normaliztion of activity coefficient is said to follow the symmetric convention.

Values of $\hat{\phi}_i^{V}$ and f_i^{oL} together with $\bar{V}_i$ can be evaluated from the modified Redlich-Kwong equation of state (103), which will be mentioned later in Chapter 5.

The equation for the calculation of $\bar{V}_i$'s is as follow:

$$\overline{V}_i = \frac{\frac{RT}{v-b}\left(1+\frac{b_i}{v-b}\right) - \frac{2\left(\sum_{j=1}^{N} x_j a_{ij}\right) - \frac{ab_i}{(v+b)}}{v\,(v+b)\,T^{0.5}}}{\frac{RT}{(v-b)^2} - \frac{a\,(2v+b)}{T^{0.5}v^2\,(v+b)^2}} \qquad (3.18)$$

The quantity f_i^{oL} for subcritical component i is the fugacity for the pure component i at the system temperature T and a reference pressure p^r. For component i with temperature T above its critical temperature T_{ci}, the f_i^{oL} is then the hypothetical standard state fugacity of i at that temperature T and reference pressure P^r.

3.3 CORRELATION OF DATA

A number of integrated forms of the Gibbs-Duhem equation are available for correlating activity coefficients for a binary system. Some of the examples are the van Laar equations (7,104), the Margules equations (105) and the Redlich-Kister equations (106).

The Redlich-Kister equations are probably the most commonly used equations for relating the liquid activity coefficients with the liquid compositions. Redlich and Kister started the derivation of these equations from the molar excess Gibbs free energy.

An excess Gibbs free energy is defined as the difference between an actual Gibbs free energy and the Gibbs free energy that would be calculated under the same conditions of T, P and x by the equations for an ideal solution. Thus by definition:

$$G^E = G - G^{id} \qquad (3.19)$$

or in another form (107)

$$G^E = RT\Sigma(x_i \ln\gamma_i) \tag{3.20}$$

Redlich and Kister defined a new function

$$Q = \frac{G^E}{2.303\ RT} \tag{3.21}$$

For a binary system, one obtains

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 \tag{3.22}$$

where x_1 and x_2 denote the mole fractions and γ_1 and γ_2 the activity coefificients. The function Q, according to Equation 3.22, has zero values for $x_1=0$ and $x_1=1$. In this application, the usual convention $\gamma_1=1$ for $x_1=1$ and $\gamma_2=1$ for $x_2=1$ is adopted. Redlich and Kister proposed a series expansion of Q as follow:

$$Q = x_1\, x_2\, [B_{12} + C_{12}\,(x_1 - x_2) + D_{12}\,(x_1 - x_2)^2 + \cdots] \quad \text{(const. T, P)} \tag{3.23}$$

where the constants B_{12}, C_{12}, D_{12} $\cdots$ depend only on the temperature.

Differentiating Equation 3.22 with respect to x_1 gives

$$\frac{dQ}{dx_1} = \log\,(\gamma_1/\gamma_2) \tag{3.24}$$

Rearrange Equations 3.22 and 3.24, one obtains

$$\log \gamma_1 = Q + x_2 \frac{dQ}{dx_1} \tag{3.25}$$

$$\log \gamma_2 = Q - x_1 \frac{dQ}{dx_1} \tag{3.26}$$

Substituting Equation 3.23 into Equations 3.25 and 3.26 gives

$$\log \gamma_1 = x_2^2\, [B_{12} + C_{12}\,(3x_1 - x_2) + D_{12}\,(x_1 - x_2)(5x_1 - x_2) + \cdots] \tag{3.27}$$

$$\log \gamma_2 = x_1^2 \,[B_{12} + C_{12}\,(x_1 - 3x_2) + D_{12}(x_1-x_2)(x_1-5x_2)+\cdots] \qquad (3.28)$$

In most applications the quantity

$$\begin{aligned}\log\,(\gamma_1/\gamma_2) &= dQ/dx_1 \\ &= B_{12}(x_2-x_1) + C_{12}(\,x_1x_2-1) \qquad (3.29)\\ &\quad +D_{12}(x_2-x_1)(1-8x_1x_2)+\cdots\end{aligned}$$

is used.

According to Redlich, Kister and Turnquist (108) only the first term of the equations is required for a nearly perfect solution, and only very accurate measurements for an extremely imperfect solution require four terms. This is further supported by Ho et al. (109) that three-term Redlich-Kister equations such as Equations 3.27 and 3.28 are adequate for representing liquid activity coefficients for most systems.

The series used for binary systems can be extended without difficulty to multicomponent systems. For a ternary system the function Q is now represented by

$$Q_{123} = x_1 \log {}_1 + x_2 \log {}_2 + x_3 \log {}_3 \qquad (3.30)$$

and

$$\log(\gamma_i/\gamma_j) = \frac{\partial Q_{123}}{\partial x_i} - \frac{\partial Q_{123}}{\partial x_j} \qquad (3.31)$$

which offers the same advantage as the function defined in Equation 3.24. The following three equations may also be obtained conveniently.

$$\log \gamma_1 = Q_{123} + \frac{\partial Q_{123}}{\partial x_1} - \left(x_1 \frac{Q_{123}}{\partial x_1} + x_2 \frac{\partial Q_{123}}{\partial x_2} + x_3 \frac{\partial Q_{123}}{\partial x_3}\right) \qquad (3.32)$$

$$\log \gamma_2 = Q_{123} + \frac{\partial Q_{123}}{\partial x_2} - \left(x_1 \frac{\partial Q_{123}}{\partial x_1} + x_2 \frac{\partial Q_{123}}{\partial x_2} + x_3 \frac{\partial Q_{123}}{\partial x_3}\right) \quad (3.33)$$

$$\log \gamma_3 = Q_{123} + \frac{\partial Q_{123}}{\partial x_3} - \left(x_1 \frac{\partial Q_{123}}{\partial x_1} + x_2 \frac{\partial Q_{123}}{\partial x_2} + x_3 \frac{Q_{123}}{\partial x_3}\right) \quad (3.34)$$

The function Q_{123} can be represented as the sum of Equation 3.23 for all binary systems involved plus additional terms. Thus the Q function is expressed as follows:

$$\begin{aligned} Q_{123} = {} & Q_{12} + Q_{23} + Q_{31} + \qquad\qquad (3.35) \\ & x_1x_2x_3 \; [\, C_{123} + D_3 \,(x_1-x_2) + D_1(x_2-x_3) + D_2(x_3-x_1) + \ldots] \end{aligned}$$

where Q_{12}, Q_{23} and Q_{31} are evaluated from the mole fractions x_1, x_2, and x_3 of the ternary system.

Formulation of individual activity coefficients of the ternary system is obtained by differentiating and substituting of Equation 3.25 into Equations 3.32, 3.33 and 3.34 respectively.

$$\begin{aligned} \log \gamma_1 = {} & B_{12}x_2 \;(1-x_1) + C_{12}x_2 \;(2x_1-x_2-2x_1^2 + 2x_1x_2) \\ & + D_{12}x_2 \;(3x_1^2 - 3x_1^3 + 6x_1^2x_2 - 4x_1x_2 - 3x_1x_2^2 + x_2^2) \\ & - B_{23}\, x_2x_3 - 2\, C_{23}\, x_2x_3 \;(x_2 - x_3) - 3D_{23}\;(x_2 - x_3)^2 \\ & + B_{31}\, x_3 \;(1 - x_1) + C_{31}\, x_3 \;(x_3 - 2x_1x_3 + 2x_1^2 - 2x_1) \\ & + D_{31}\, x_3 \;(x_3^2 + 6x_1^2x_3 - 4x_1x_3 - 3x_2x_3^2 + 3x_1^2 - 3x_1^3) \\ & + C_{123}\, x_2x_3 \;(1 - 2x_1) \\ & + D_1\, x_2x_3 \;(x_2 - x_3 - 3x_1x_2 + 3x_1x_3) \\ & + D_2\, x_2x_3 \;(x_3 - 2x_1 - 3x_1x_3 + 3x_1^2) \\ & + D_3\, x_2x_3 \;(2x_1 - x_2 - 3x_1^2 + 3x_1x_2) \qquad (3.36) \end{aligned}$$

$$\begin{aligned}
\log \gamma_2 = {} & B_{12}\, x_1\, (1-x_2) + C_{12}\, x_1\, (x_1-2x_2-2x_1x_2 + 2x_2^2) \\
& + D_{12}\, x_1\, (x_1^2 - 4x_1x_2 + 3x_2^2 - 3x_1^2x_2 + 6x_1x_2^2 - 3x_2^3) \\
& + B_{23}\, x_3\, (1 - x_2) + C_{23}\, x_3\, (2x_2 - x_3 - 2x_2^2 + 2x_2x_3) \\
& + D_{23}\, x_3\, (x_3^2 + 3x_2^2 - 4x_2x_3 - 3x_2^3 + 6x_2^2x_3 - 3x_2x_3) \\
& - B_{31}\, x_1x_3 - 2C_{31}\, x_1x_3\, (x_3 - x_1) \\
& - 3D_{31}\, x_1x_3\, (x_3 - x_1) + C_{123}\, x_1x_3\, (1 - 2x_2) \\
& + D_1\, x_1x_3\, (2x_2 - x_3 - 3x_2^2 + 3x_2x_3) \\
& + D_2\, x_1x_3\, (x_3 - x_1 + 3x_1x_2 - 3x_2x_3) \\
& + D_3\, x_1x_3\, (x_1 - 2x_2 - 3x_1x_2 + 3x_2^2)
\end{aligned} \qquad (3.37)$$

$$\begin{aligned}
\log \gamma_3 = {} & - B_{12}\, x_1x_2 - 2C_{12}\, x_1x_2\, (x_1 - x_2) \\
& - 3D_{12}\, x_1x_2\, (x_1 - x_2)^2 + B_{23}\, x_2\, (1 - x_3) \\
& + C_{23}\, x_2\, (x_2 - 2x_3 - 2x_2x_3 + 2x_3^2) \\
& + D_{23}\, x_2\, (x_2^2 - 4x_2x_3 + 3x_3^2 + 3x_2^2x_3 + 6x_2x_3^2 - 3x_3^3) \\
& + B_{31}\, x_1\, (1 - x_3) + C_{31}\, x_1\, (2x_3 - x_1 - 2x_3^2 + 2x_1x_3) \\
& + D_{31}\, x_1\, (x_1^2 + 3x_3^2 - 4x_1x_3 - 3x_3^3 + 6x_1x_3^2 - 3x_1^2x_3) \\
& + C_{123}\, x_1x_2\, (1 - 2x_3) \\
& + D_1\, x_1x_2\, (x_2 - 2x_3 - 3x_2x_3 + 3x_3^2) \\
& + D_2\, x_1x_2\, (- x_1 + 2x_3 - 3x_3^2 + 3x_1x_3) \\
& + D_3\, x_1x_2\, (x_1 - x_2 - 3x_1x_3 + 3x_2x_3)
\end{aligned} \qquad (3.38)$$

3.4 THERMODYNAMIC CONSISTENCY TEST OF THE BINARY ISOTHERMAL DATA

3.4.1 Data Cover the Whole Concentration Range

Redlich and Kister (106) developed a simple and general thermodynamic consistency test obtained by integrating Equation 3.24. Since Q is zero for both $x_1 = 0$ and $x_1 = 1$, according to the definition of Q and the normalization of γ, they proposed the following relationship:

$$\int_0^1 \log(\gamma_1/\gamma_2)\, dx_1 = 0 \quad \text{(const. T, P)} \tag{3.39}$$

provided that $\log(\gamma_1/\gamma_2)$ is a continuous function of x_1.

When $\log(\gamma_1/\gamma_2)$ is plotted against x_1 from $x_1 = 0$ to $x_1 = 1$, the net area between the curve and x_1-axis is equal to zero.

3.4.2 Data Cover a Limited Concentration Range from $x_1 = a$ to $x_1 = b$

For a binary system at constant temperature T and reference pressure P^r, the Gibbs-Duhem equation can be expressed as

$$x_1\, d\log\gamma_1 + x_2\, d\log\gamma_2 = 0 \tag{3.40}$$

Rearrange and one obtains

$$d\log\gamma_2 = -\, x_1\, d\log(\gamma_1/\gamma_2) \tag{3.41}$$

since $x_1 + x_2 = 1$

Thus for binary equilibrium data cover a limited range from $x_1 = a$ to $x_1 = b$, we can integrate Equation 3.41 from $x_1 = a$ to $x_1 = b$ and get

$$\log \frac{\gamma_2\ (\text{at } x_1 = b)}{\gamma_2\ (\text{at } x_1 = a)}$$

$$= -\int_{\log(\gamma_1/\gamma_2)(\text{at } x_1 = a)}^{\log(\gamma_1/\gamma_2)(\text{at } x_1 = b)} x_1\, d\log(\gamma_1/\gamma_2) \tag{3.42}$$

When $\log(\gamma_1/\gamma_2)$ is plotted against x_1 , the net area between the curve and the $\log(\gamma_1/\gamma_2)$ axis from $\log\,(\gamma_1/\gamma_2)$ at $x_1 = b$ to $\log\,(\gamma_1/\gamma_2)$ at $x_1 = a$ is equal to the value of

$$\log\,(\gamma_2(\text{at } x_1 = b)/\gamma_2(\text{at } x_1 = a)).$$

CHAPTER 4

EXPERIMENTAL DETAILS AND RESULTS

Vapor-liquid phase equilibrium data were measured for the binary systems containing nitrogen, methane and ethane at 130.0 K and 169.9 K and nitrogen-methane-ethane ternary system at 130.0 K, and at pressures up to 795 psia.

4.1 APPARATUS

A forced-recirculation apparatus used previously in this laboratory was modified in this study. While the details of the previous design are available (43), the only significant change made in this study is in the vapor circulation loop. A brief description of the whole system in this study is given here. Essentially, it consists of a charging unit, a transparent equilibrium cell, a cryostat with the temperature control system, a recirculation loop with an effective magnetic pump, sampling facilities, temperature and pressure measuring devices and a coolant supply. A schematic flow diagram of the modified apparatus is shown in Figure 4.1.

4.1.1 Equilibrium Cell

A 100 ml Jerguson transparent gauge with stainless steel body was used as an equilibrium cell. A schematic diagram of the cell and the cryostat, into which the cell was immersed, is shown in Figure 4.2.

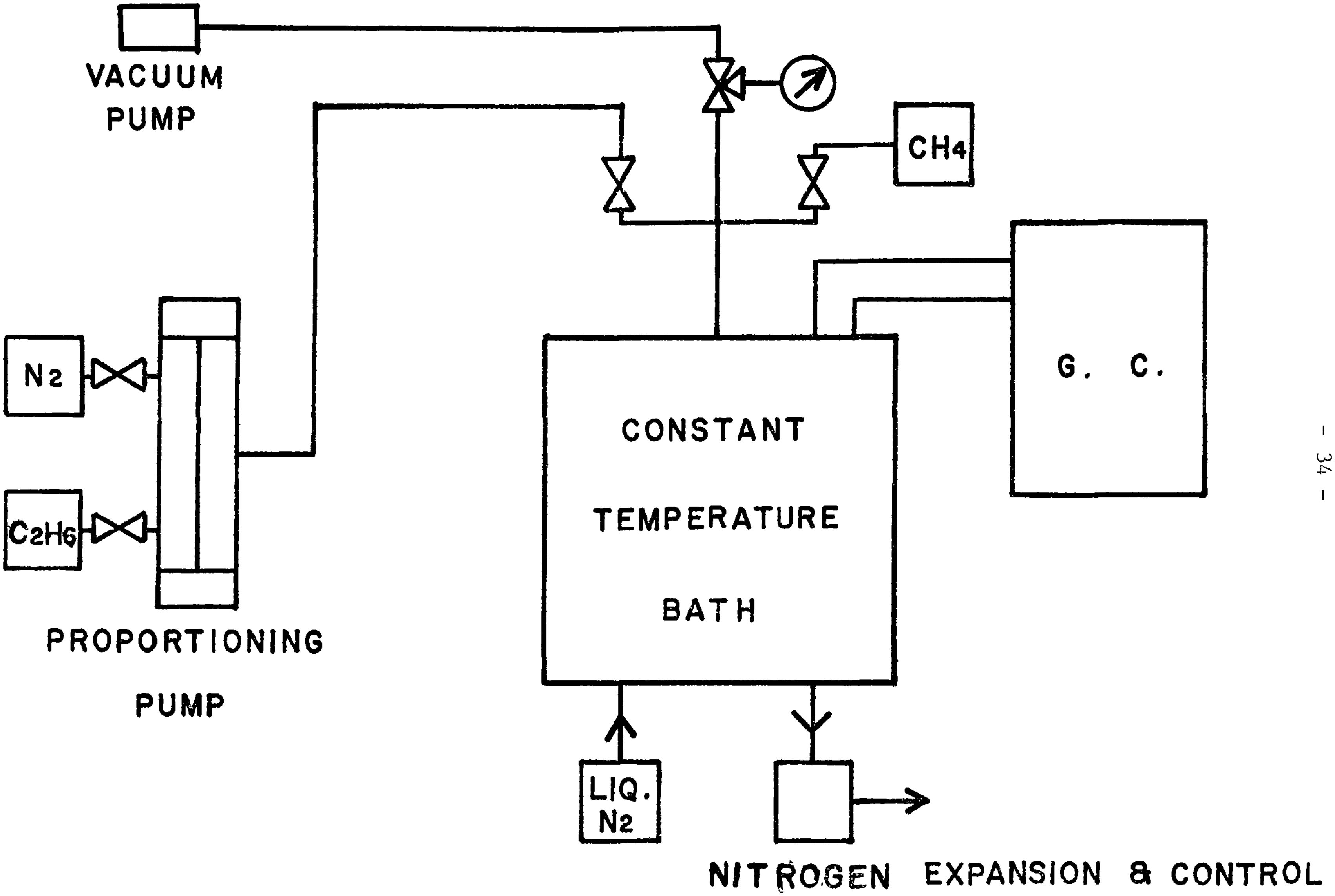
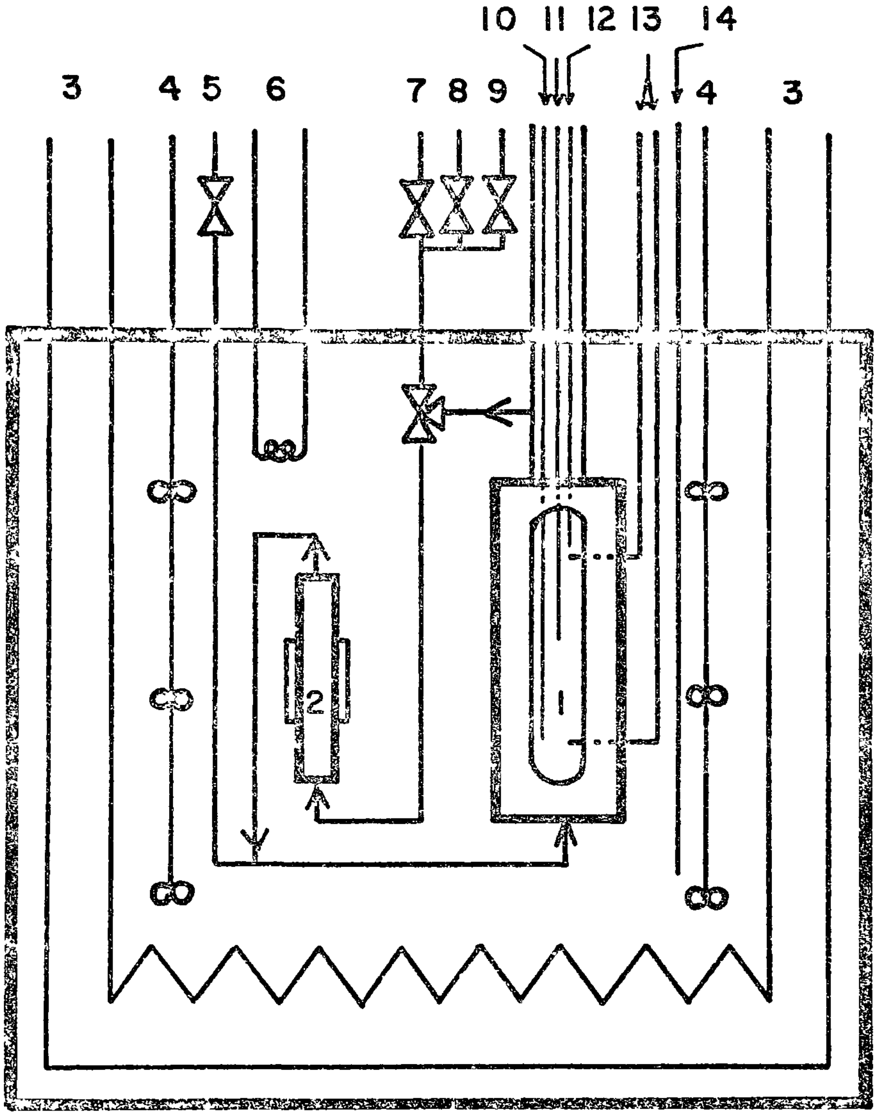


Figure 4.1 A Flow Diagram of Experimental Apparatus



1. Equilibrium Cell
2. Magnetic Pump
3. Cooling System
4. Stirrer
5. Ventilation
6. Heating System
7. Charging System
8. Charging System
9. Vacuum
10. Liquid Sampling
11. Liquid Sampling
12. Vapor Sampling
13. Thermocouple
14. Sensing Probe

Figure 4.2 A Schematic View of Constant Temperature Bath

The top of the cell was fitted with a 1/2-in. National Pipe thread connector, into which the vapor outlet tube and two 1/16-in. liquid sampling tubings were inserted. A 1/8-in. Autoclave joint was welded to the connector at the bottom of the cell, which was connected to the vapor inlet line.

4.1.2 Cryostat and Temperature Control Assembly

A Dewar flask of 18-liter capacity was employed as the cryostat into which the equilibrium cell was submerged, with isopentane used as the bath liquid. The cryostat was equipped with refrigeration coil for liquid nitrogen, two stirrers, one heating element, and a resistance type temperature sensing element. In the down stream line of the liquid nitrogen refrigeration coil a buffer tank and a needle valve were situated to keep the flow rate of nitrogen approximately constant. In addition to these elements, the cryostat was equipped with a Bayley precision temperature controller, Model 250.

4.1.3 Vapor Recirculation Loop

The vapor recirculation loop as shown in Figure 4.2 consisted of a magnetic pump, which was not employed previously in this laboratory, was constructed by the Department of Chemical Engineering, University of Ottawa, following the design of Ruska (110). An external magnet was operated up and down by means of a crank and connecting rod actuated by a Zero-Max motor installed outside the liquid bath, hence the recirculation loop was always kept at constant temperature.

4.1.4 Charging System

When the system pressure was low, nitrogen, methane and ethane were charged directly from the cylinders through a Ruska proportioning pump in the order of component with the lowest vapor pressure first. For instance, ethane, which has the lowest vapor pressure, was first introduced followed by methane and nitrogen. The most volatile component, say, nitrogen, was charged into the Ruska proportioning pump, which was disconnected from the equilibrium cell by closing a valve in the line, when the system pressure was higher than the pressure in the supply cylinder. The lightest component was then compressed by driving the proportioning pump until the pressure in this pump was much higher than the system pressure. Finally, the component in the proportioning pump was charged into the equilibrium cell. The above procedure was repeated until the desired system pressure was approximately obtained.

4.1.5 Sampling System

The vapor sample was entrapped within the vapor sampling tube. The liquid sample was withdrawn from one of the two liquid sampling tubes (1/16-in. in diameter). Both of these tubes passed through the outlet vapor chamber and extended into the equilibrium cell at different levels. A 250 mm. long and 10 mm. O.D. stainless steel tube which contained a loosely fitting soft iron core was added to the liquid sampling tube externally. Manual mixing of the liquid phase sample was achieved by occasionally moving a ring magnet along the stainless steel tube, which produced a uniform composition liquid phase sample.

4.1.6 Temperature and Pressure Measuring Devices

Two protected type copper-constantan thermocouples were installed in the equilibrium cell, one of which was located at one-quarter of the height, and the other one three-quarters of the height of the cell. The system temperature measurements were made by means of a Leeds and Northrup 7555 type K-5 potentiometer. In addition, two calibrated Heise gauges with ranges of 0 to 500 and 0 to 1,000 psia, and with 0.5 and 1.0 psia subdivisions, respectively, were also provided for measurement of the system pressure. The uncertainties involved in the temperature and the pressure measurements are believed to be ± 0.1 K and ±1 psia respectively.

4.1.7 Coolant Supply System

One liquid nitrogen tank was stationed nearby to supply the needed coolant for the system operated at low temperature.

4.1.8 Analytical Equipment

A Hewlett Packard 5700 A gas chromatograph with a Hewlett Packard valve timer was used for analysis. A Westronics Model MT 21 recorder and a Hewlett Packard 3373 B integrator were used to record and integrate the chromatographic curves.

4.2 MATERIALS USED

The materials used in this study were obtained from Matheson of Canada Limited, Whilby, Ontario with their indicated minimum purities as follows:

Component	Minimum Purity, Mole %
Nitrogen	99.9995
Methane	99.99
Ethane	99.96

These materials were used in this study without any further purification.

4.3 EXPERIMENTAL PROCEDURES

4.3.1 Temperature Control of Cryostat

Since temperature is one of the variables, its control therefore becomes an important step in this study. A good technique is required to build up a delicated balance between the heat supply by the heating element and the heat removal from the evaporation of liquid nitrogen. A system for controlling the temperature generally consists of a sensing element, a temperature controller, a cooling coil, a heating element and a liquid bath.

In this study one proportional type temperature controller of Bayley, Model 250 was used throughout. The instruction manual (111) supplied by the company was closely followed. Besides, the information described in the following paragraph was also found to be very useful.

The system temperature was brought down by evaporating liquid nitrogen through the coil inside the bath. The evaporating rate was adjusted to bring the bath temperature slightly lower than the desired by making sure that the heat removed by the evaporation of liquid nitrogen was just sufficient so that the bath temperature would decrease slowly. The temperature controller was turned on for about 10 minutes to bring the unit to full sensitivity. The temperature controller was set according to the procedures given in the instruction manual to allow the controller to increase the bath temperature.

The proportional band width of this type of controller is used to match the sensitivity of the controller to the requirements of the system, i.e. the degree of control accuracy needed, the amount of heat employed, the type of circulation, and the size of the controlled bath, etc. One of the drawbacks of this type of controller is that it produces proportional offset for load change, such as the change in room temperature, liquid nitrogen evaporation rate, vapor circulation rate, stirrer speed, etc. The band width adjustment is used to reduce the sensitivity of the controller and to prevent oscillation during the operation. The narrower the band width, the smaller the offset produced. The sensitivity of this controller at full band width is about $2^{o}C$ and at zero band width is approximately $0.01^{o}C$. Therefore, the band width setting is very critical for the temperature control. The procedure for obtaining the best band width setting is available in the instruction manual (111).

4.3.2 Pressure Control

The pressure was controlled by means of a Ruska proportioning pump made by the Ruska Instrument Corp. rated up to 12,000 psia. The initial adjustment of the pressure within 5 psia was made manually by the addition of the most volatile component, say nitrogen, from the high pressure supply cylinder. This initial charge of nitrogen to the equilibrium cell also filled the volume of the proportioning pump (see Figure 4.1), which was not in operation during the charging procedure. The nitrogen supply was cut off and the final fine adjustment of the pressure was achieved by changing the volume of this reservoir of nitrogen. The pump could be either motor driven or hand operated depending on the pressure change desired. A complete piston displacement discharged a volume of 500 ml. This pump was connected directly to the equilibrium section and pressure gauges.

4.3.3 Preparation of the Equipment

The construction and calibration of the equipment required the usual care for high precision equilibrium measurements. The entire apparatus required cleaning to remove oil, solid particles, and any other contaminants. The general method to achieve the desired cleanliness was a multiple series of flushing with solvents, evacuation, flushing with room air, evacuation, etc. A multiple flushing and evacuation of the entire system with main component from the supply cylinder was required. After that the system was always maintained at a pressure higher than 1 atm to prevent air from entering the system.

4.3.4 Vapor-Liquid Equilibrium Measurements

When the desired bath temperature was reached the individual components were charged into the cell directly in order of increasing vapor pressure, i.e. the least volatile component first. The amounts being charged were roughly estimated by observing the liquid level in the equilibrium cell. The desired pressure was set approximately by the addition of nitrogen (from the high pressure cylinder), with fine adjustment achieved by means of the proportioning pump. The vapor recirculation pump was turned on during the charging process to circulate the vapor phase from the equilibrium cell. Further adjustments of the pressure had to be made during the early stage of circulation.

As the equilibrium pressure was approached, the vapor sampling line was partially opened to allow the withdrawal of an extremely small amount of the vapor phase from the cell. With the slight but continuous withdrawal of vapor, the composition of the vapor in the sampling line could be assumed to be the same as that of the vapor phase in the equilibrium cell. The flow rate of the gas phase was checked by bubbling the vapor through a small column of water. The flow rate was adjusted to one bubble per 5 to 15 seconds, which had been determined as an optimal rate. A higher flow rate would cause excessive pressure drop in the equilibrium cell; a lower flow rate would not fill up the sample loop. Above a certain pressure (in the range of 200 to 600 psia determined by temperature), the amount of vapor phase withdrawn did not affect the pressure much in the cell. At lower pressures, very small amounts of nitrogen had been added by manual operation of the proportioning pump to compensate for pressure drop in the cell.

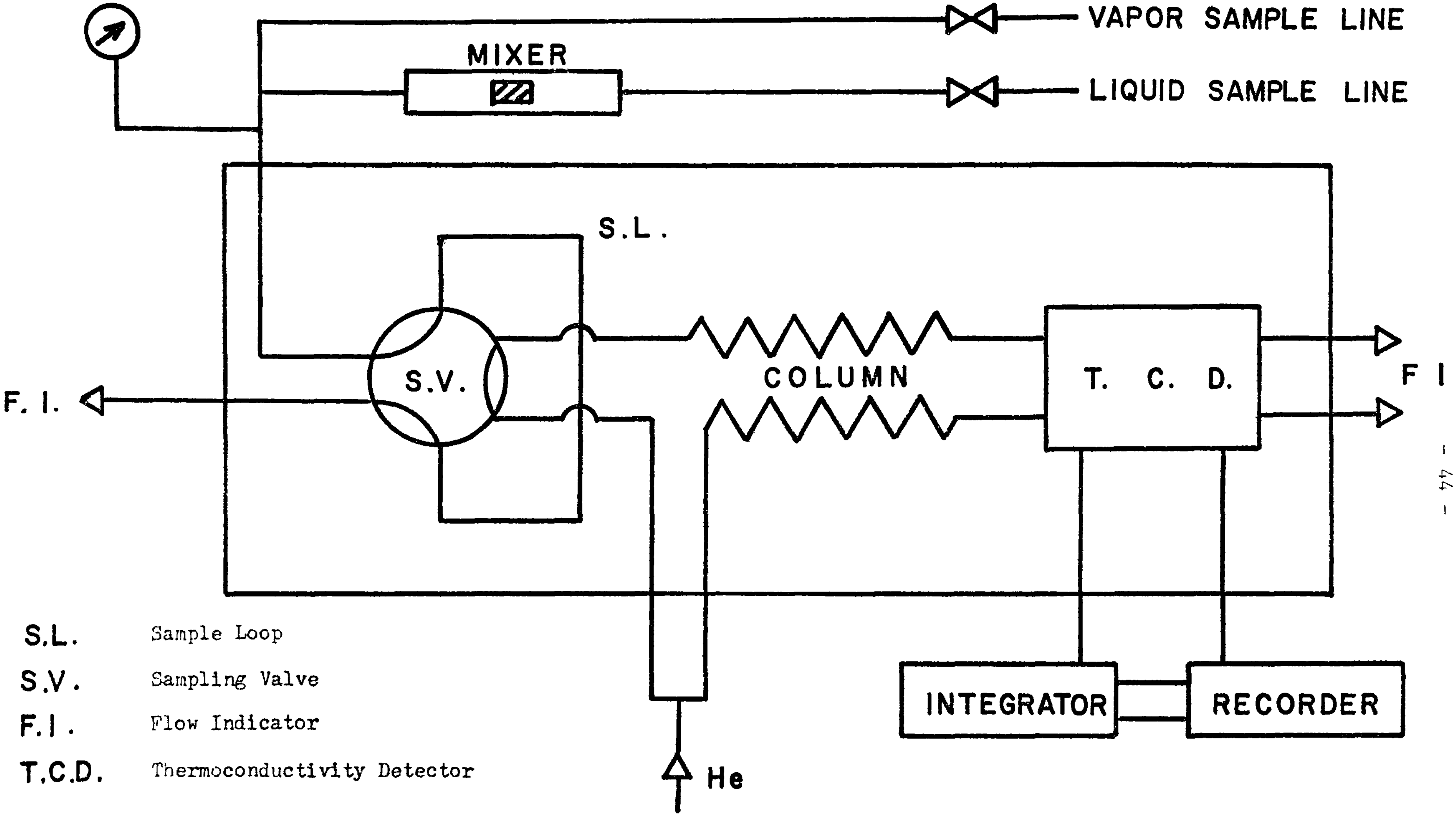
No change of the concentration was observed from the possibility that some drops of the liquid phase had entered into the vapor sampling line. Measurements of the vapor phase compositions from samples taken with the recycle pump in operation were identical with those from samples taken after the pump was stopped and no drops were visible in the vapor phase

The circulation of the vapor phase continued until the pressure was constant for at least 10 minutes, after which the analysis of the vapor phase was made. On completion of the vapor phase analysis the recycle pump was stopped and the vapor phase sampling valve was closed. The liquid sampling system had to be evacuated and purged with room air several times to assure the removal of the previous sample, due to the relatively large volume of the mixer (see Figure 4.3). The flow rate for the liquid phase sample was about 10 times that for the vapor phase; it was also monitored by bubbling the gasified-liquid phase through a water column. For the first five minutes no manual mixing was carried out to ensure that the air in the mixer was principally replaced by the new sample. Intermittent mixing to make the composition of the gasified-liquid sample uniform was done and the analysis of the liquid phase was made.

At least six analyses were made for each phase. When both phases had been analyzed the pressure was adjusted for the next run.

4.3.5 Composition Analysis

All compositions were analyzed gas-chromatographically through a 10 feet long, 1/8-in. diameter stainless steel column, packed with Porapak Q, mesh 80-100. Along with the Hewlett Packard 5700 A gas chromatograph were a Hewlett Packard valve timer, a Hewlett Packard



S.L.	Sample Loop
S.V.	Sampling Valve
F.I.	Flow Indicator
T.C.D.	Thermoconductivity Detector

Figure 4.3 Connection of the Sampling System to the Gas Chromatography System

3373 B integrator and a Westronics MT 21 recorder. The gas chromatograph was equipped with dual columns and a thermal conductivity detector. In this study only one column was used and was found very stable throughout the study. Helium was used as the carrier gas at a flow rate of 40 ml./min. A retention time of 3.5 minutes was required to separate the three components at an oven temperature 50°C, and detector temperature 100°C. The peaks were well spaced and separated in the sequence of nitrogen, methane and ethane.

The gas chromatograph's responses were calibrated against the synthetic samples of known compositions. The results of the calibration were plotted graphically as composition ratio versus peak area ratio of first component to second component as well as the reciprocal ratio (see Figures 4.4 to 4.6) in order to cover the whole range of the concentration. The ratio plot was believed to be superior to the absolute quantity plot since the former was relatively insensitive to any change in detector current, temperature, column pressure, carrier gas flow rate, sample quantity, recorder sensitivity, etc.

4.4 EXPERIMENTAL RESULTS

Equilibrium measurements were made at the following conditions:

Nitrogen-Methane	169.9 & 130.0 K
Methane-Ethane	169.9 & 130.0 K
Nitrogen-Ethane	169.9 & 130.0 K
Nitrogen-Methane-Ethane	130.0 K

All the experimental pressure values are reported in psia (pounds per square inch, absolute). The unit of psia can be converted to SI unit pascal ($Pa = N \cdot m^{-2}$) by multiplying a factor 6,894.757.

The numerical values of the experimental results are listed in Tables 4.1 to 4.7. The experimental data for three binary systems at both temperatures are plotted in Figures 4.7 to 4.11.

For the nitrogen-methane-ethane ternary system experimental data were measured at 130.0 K and at four constant pressures (100, 200, 300 and 400 psia). A smoothed liquid phase composition diagram for the four constant pressures is shown in Figure 4.12, while the corresponding vapor phase composition curves are omitted because of the overlap of the four curves.

Vapor-liquid equilibriums were observed for all the binary systems and for the ternary system at the above mentioned temperatures. At the lower temperature two liquid phases were observed in the nitrogen-ethane binary and the nitrogen-methane-ethane ternary systems. The ethane concentration was found richer in the bottom layer (BL) than that in the top layer (TL).

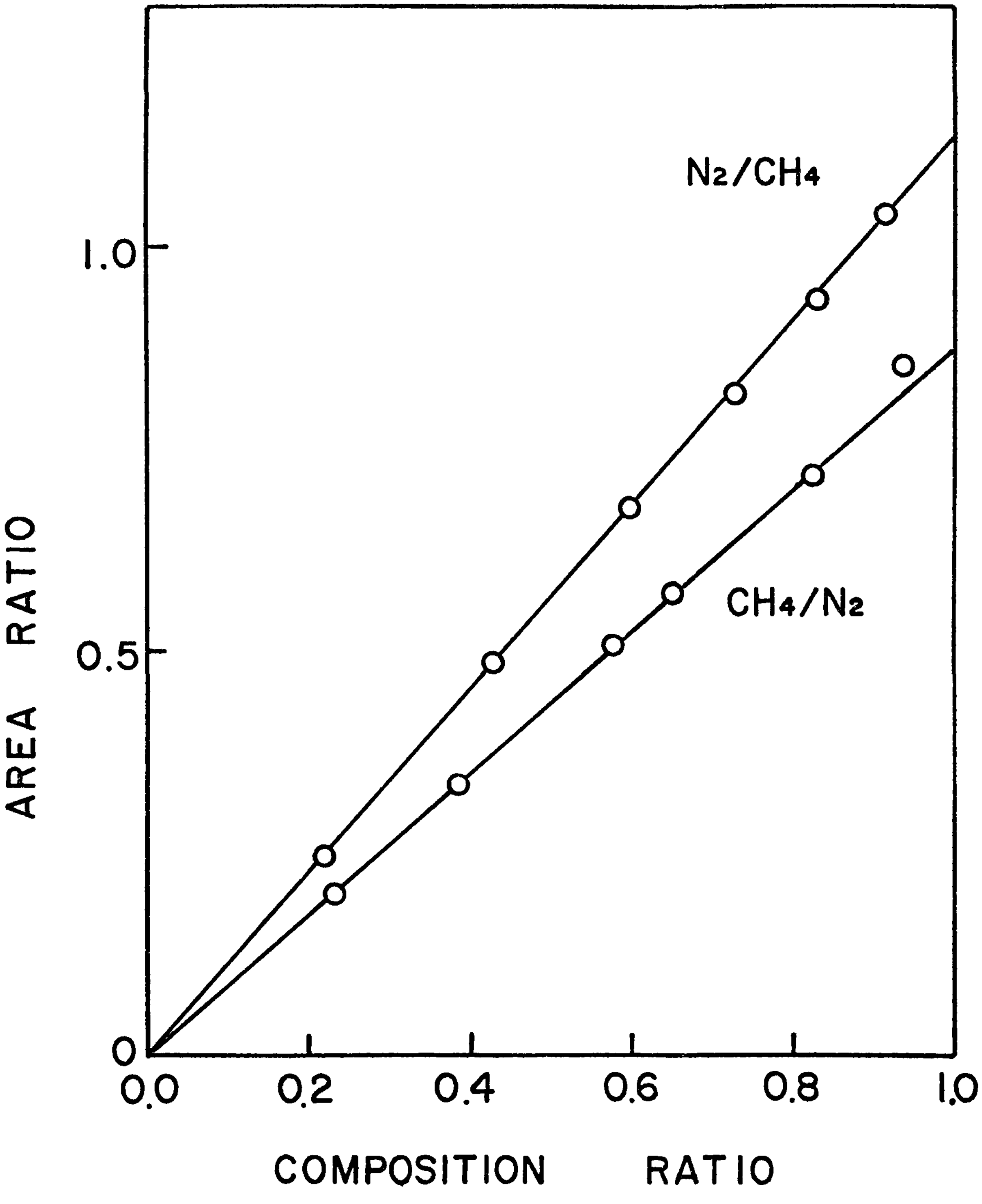


Figure 4.4 Calibration Results for the Gas Chromatograph for the Nitrogen-Methane System

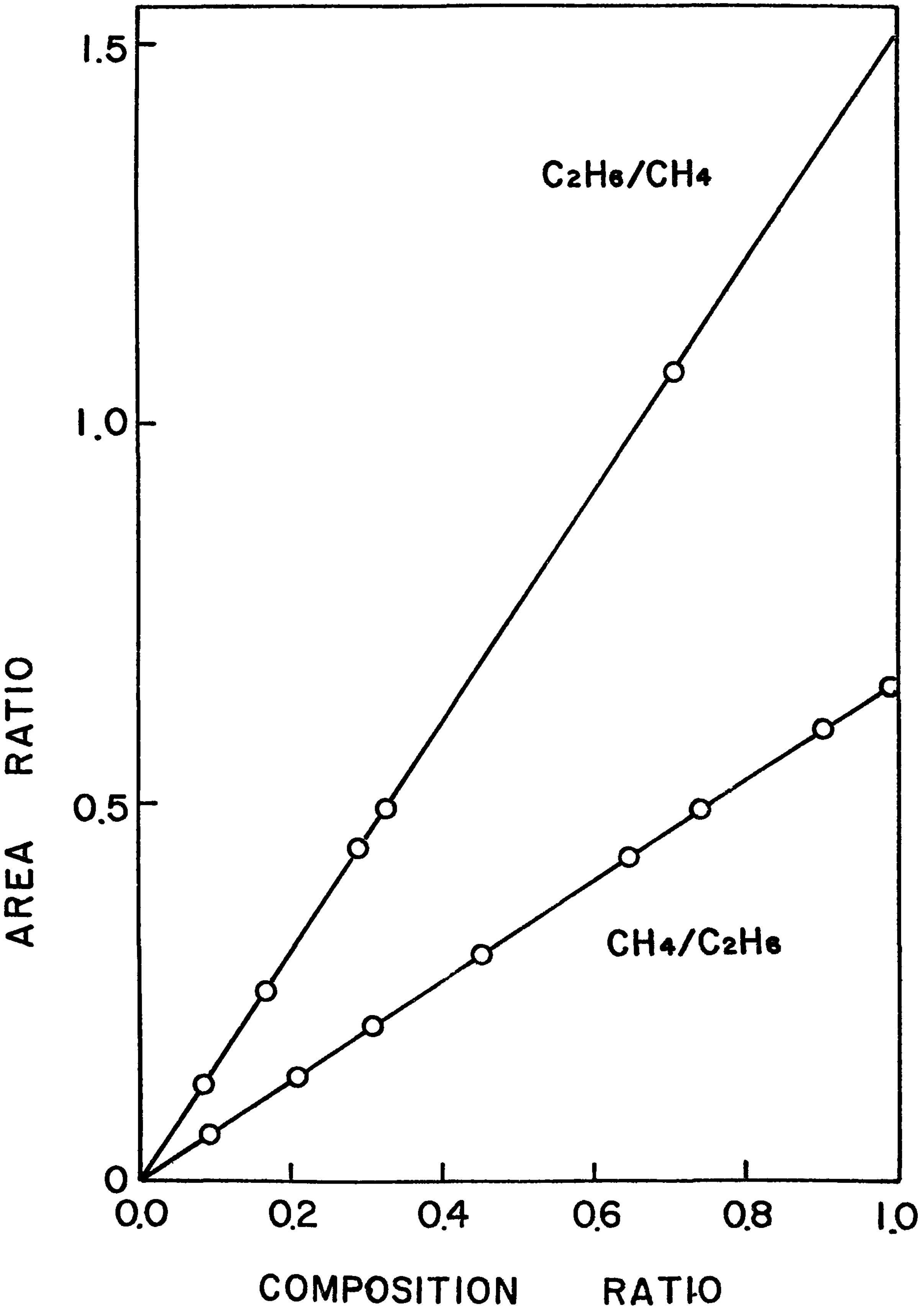


Figure 4.5 Calibration Results for the Gas Chromatograph for the Methane-Ethane System

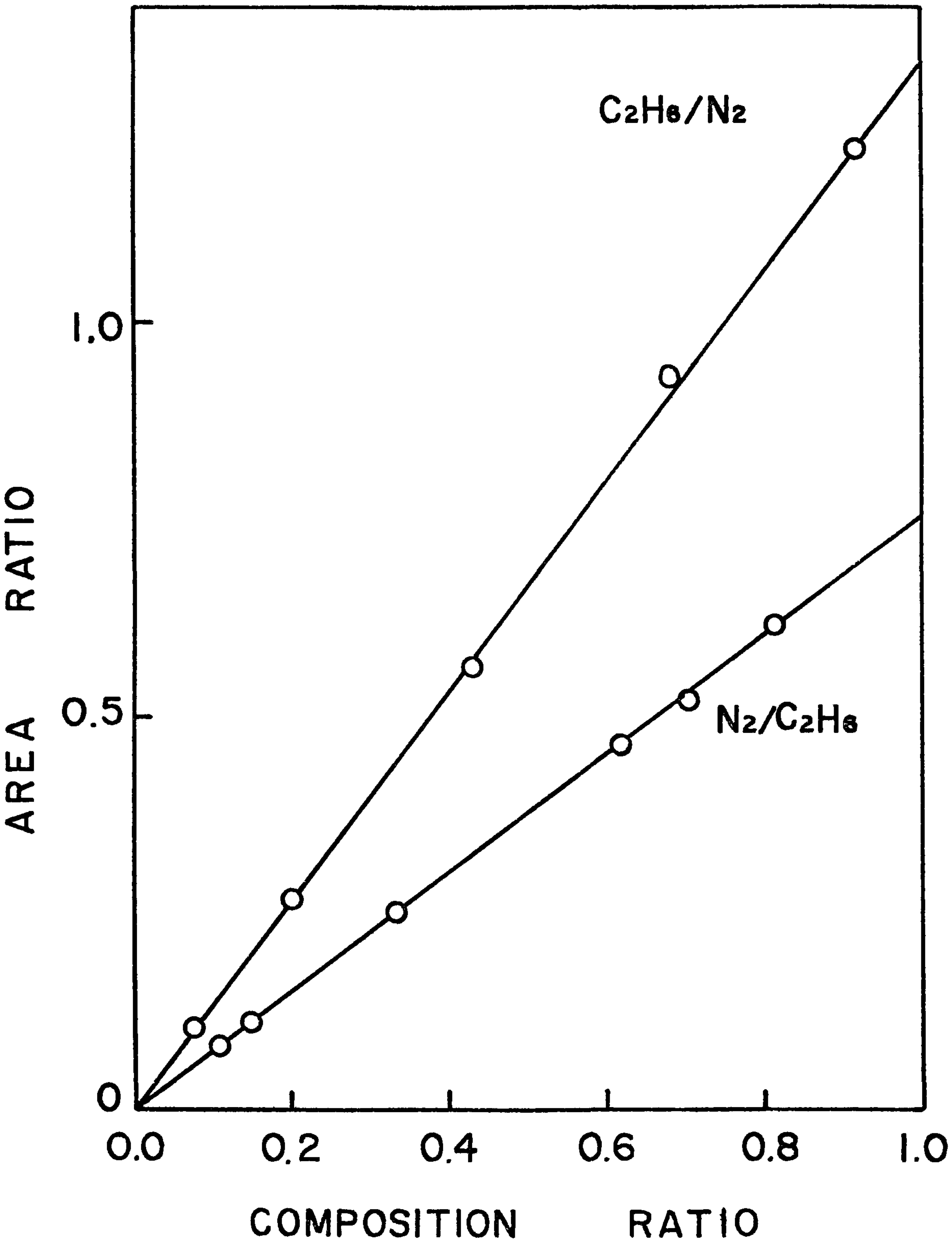


Figure 4.6 Calibration Results for the Gas Chromatograph for the Nitrogen-Ethane System

TABLE 4.1

Vapor-Liquid Equilibrium Data for the Nitrogen(1)-Methane(2) System at 169.9 K

Run	Total Pressure psia	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Equilibrium Constant K=y/x	
				K_1	K_2
1	361.6	0.0231	0.0770	3.333	0.9448
2	373.5	0.0301	0.0993	3.299	0.9287
3	402.1	0.0579	0.1485	2.565	0.9038
4	458.6	0.0888	0.2298	2.588	0.8453
5	500.7	0.1183	0.7248	2.326	0.8221
6	559.8	0.1632	0.3275	2.007	0.8037
7	640.0	0.2352	0.3790	1.611	0.8119
8	671.0	0.2683	0.3875	1.444	0.8371
9	687.0	0.2885	0.4235	1.468	0.8103
10	702.0	0.3057	0.3970	1.299	0.8685
11	703.0	0.3032	0.3962	1.307	0.8665
12	714.0	0.3159	0.3836	1.214	0.9010

TABLE 4.2

Vapor-Liquid Equilibrium Data for the Nitrogen(1)-Methane(2) System at 130.0 K

Run	Total Pressure psia	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Equilibrium Constant K=y/x	
				K_1	K_2
1	108.6	0.0756	0.4946	6.542	0.5467
2	148.0	0.1623	0.6436	3.966	0.4255
3	204.7	0.2745	0.7406	2.698	0.3576
4	252.3	0.3790	0.7900	2.084	0.3382
5	302.1	0.5022	0.8343	1.661	0.3329
6	347.2	0.6052	0.8614	1.423	0.3511
7	382.0	0.6600	0.8805	1.334	0.3515
8	405.7	0.7111	0.8931	1.256	0.3700
9	443.8	0.8222	0.9125	1.110	0.4921
10	462.0	0.8447	0.9198	1.089	0.5164
11	482.3	0.8750	0.9326	1.066	0.5392

TABLE 4.3

Vapor-Liquid Equilibrium Data for the Methane(1)-Ethane(2) System at 169.9 K

Run	Total Pressure psia	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Equilibrium Constant K=y/x	
				K_1	K_2
1	20.8	0.0388	0.6724	17.33	0.3410
2	66.8	0.1855	0.9118	4.915	0.1083
3	100.5	0.2820	0.9449	3.351	0.07674
4	143.1	0.4038	0.9624	2.383	0.06307
5	181.2	0.5213	0.9726	1.866	0.05724
6	215.5	0.6731	0.9835	1.461	0.05047
7	249.1	0.7775	0.9861	1.268	0.06247
8	284.0	0.8638	0.9927	1.149	0.05360
9	310.9	0.9308	0.9909	1.065	0.1315

TABLE 4.4

Vapor-Liquid Equilibrium Data for the Methane(1)-Ethane(2) System at 130.0 K

Run	Total Pressure psia	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Equilibrium Constant K=y/x	
				K_1	K_2
1	18.2	0.3119	0.9915	3.179	0.01235
2	19.3	0.3067	0.9941	3.241	0.008510
3	26.0	0.4589	0.9973	2.173	0.004990
4	29.3	0.5015	0.9965	1.987	0.007021
5	34.5	0.5996	0.9978	1.664	0.005495
6	39.4	0.6938	0.9985	1.439	0.004899
7	44.0	0.8027	0.9992	1.245	0.004055
8	47.8	0.8571	0.9998	1.166	0.001400

TABLE 4.5

Vapor-Liquid Equilibrium Data for the Nitrogen(1)-Ethane(2) System at 169.9 K

Run	Total Pressure psia	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Equilibrium Constant K=y/x K_1	K_2
1	51.1	0.0125	0.8708	69.66	0.1308
2	111.0	0.0214	0.9407	43.96	0.06060
3	207.7	0.0402	0.9645	23.99	0.03699
4	302.8	0.0751	0.9727	12.95	0.02952
5	411.1	0.0960	0.9760	10.17	0.02655
6	493.0	0.1132	0.9773	8.633	0.02560
7	577.0	0.1330	0.9765	7.342	0.02710
8	667.2	0.1422	0.9754	6.859	0.02868
9	734.2	0.1898	0.9743	5.133	0.03172
10	795.5	0.1772	0.9737	5.495	0.03196

TABLE 4.6

Vapor-Liquid Equilibrium Data for the Nitrogen(1)-Ethane(2) System at 130.0 K

Run	Total Pressure psia	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Equilibrium Constant K=y/x	
				K_1	K_2
1	49.0	0.0219	0.9868	45.06	0.01350
2	124.0	0.0569	0.9982	17.54	0.001909
3	210.3	0.1033	0.9988	9.669	0.001338
4	263.4	0.1370	0.9988	7.291	0.001390
5	282.8	0.1357	0.9988	7.360	0.001388
6	295.1	0.1545	0.9903	6.410	0.01147
7	328.6	0.1469	0.9989	6.800	0.001289
8	358.4	0.1678	0.9987	5.952	0.001562
9	395.3	0.1844	0.9981	5.413	0.002330
10	425.5	0.1899	0.9887	5.206	0.01395
11	525.5	0.2770 (BL) 0.9559 (TL)	0.9903	3.561	0.01895

TABLE 4.7

Vapor-Liquid Equilibrium Data for the Nitrogen (1)-Methane(2)-Ethane(3) System at 130.0 K

Run	Total Pressure psia	Liquid Mole Fraction		Vapor Mole Fraction		Equilibrium Constant K=y/x		
		x_1	x_2	y_1	y_2	K_1	K_2	K_3
1	100.0	0.0705	0.7168	0.5869	0.4126	8.325	0.5756	0.002351
2	100.2	0.0669	0.4646	0.7543	0.2441	11.28	0.5254	0.003415
3	100.7	0.0649	0.5409	0.6708	0.3278	10.34	0.6060	0.003551
4	101.3	0.0511	0.1613	0.8801	0.1167	17.22	0.7235	0.004063
5	101.4	0.0646	0.5064	0.7013	0.2971	10.86	0.5867	0.003730
6	101.5	0.0544	0.3820	0.7565	0.2423	13.91	0.6343	0.002129
7	101.8	0.0650	0.5300	0.6781	0.3142	10.43	0.5928	0.01901
8	199.3	0.1215	0.3642	0.8685	0.1298	7.148	0.3564	0.003305
9	200.0	0.1224	0.3896	0.8690	0.1299	7.100	0.3334	0.002254
10	200.3	0.2163	0.6485	0.7817	0.2176	3.614	0.3355	0.005178
11	200.8	0.1628	0.4986	0.8384	0.1604	5.150	0.3217	0.003544
12	200.8	0.1018	0.1673	0.9357	0.0635	9.192	0.3796	0.001095
13	300.1	0.2660	0.3123	0.9141	0.0850	3.436	0.2722	0.002134
14	300.1	0.2525	0.3323	0.9120	0.0871	3.612	0.2621	0.002168
15	301.1	0.2169	0.1836	0.9459	0.0532	4.361	0.2898	0.001501

TABLE 4.7 (continued)

Vapor-Liquid Equilibrium Data for Nitrogen(1)-Methane(2)-Ethane(3) System at 130.0 K

Run	Total Pressure psia	Liquid Mole Fraction		Vapor Mole Fraction		Equilibrium Constant K=y/x		
		x_1	x_2	y	y_2	K_1	K_2	K_3
16	301.1	0.4038	0.4796	0.8604	0.1394	2.131	0.2907	0.001715
17	302.5	0.3078	0.3729	0.8771	0.1167	2.850	0.3130	0.01942
18	400.0	0.3762	0.2352	0.9375	0.0611	2.492	0.2598	0.003603
19	402.3	0.3039	0.1540	0.9583	0.0399	3.153	0.2591	0.003320
20	403.0	0.6957	0.2792	0.9096	0.0897	1.502	0.3213	0.02789
21	403.2	0.5601	0.2416	0.9314	0.0668	1.663	0.2765	0.009077
22	505.5	0.9181	0.0177 (TL)	0.9844	0.0086			
		0.2820	0.0164 (BL)			3.491	0.5244	0.009977

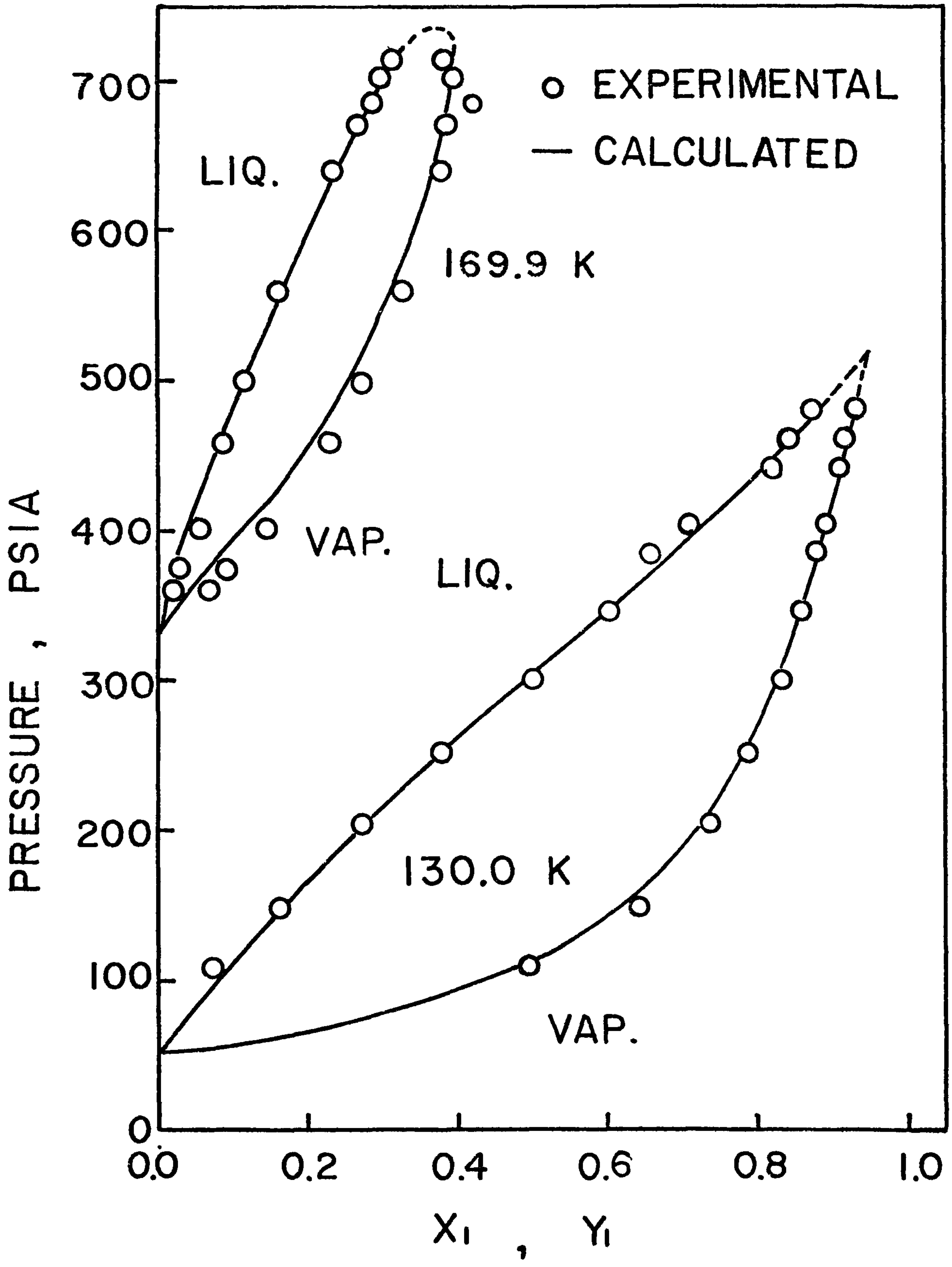


Figure 4.7 Vapor-Liquid Equilibrium Data for the Nitrogen(1)-Methane(2) System at 169.9 & 130.0 K

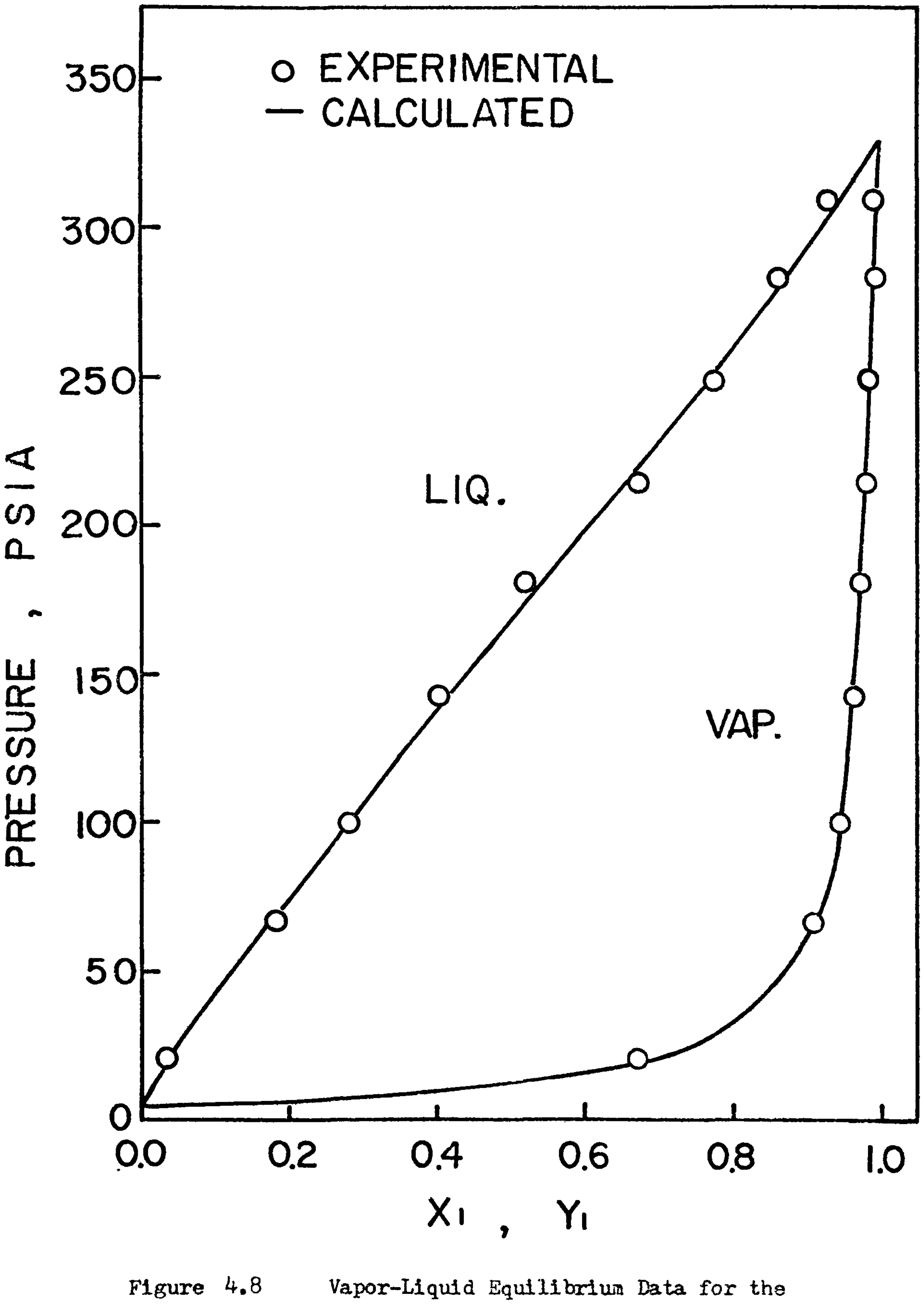


Figure 4.8 Vapor-Liquid Equilibrium Data for the Methane(1)-Ethane(2) System at 169.9 K

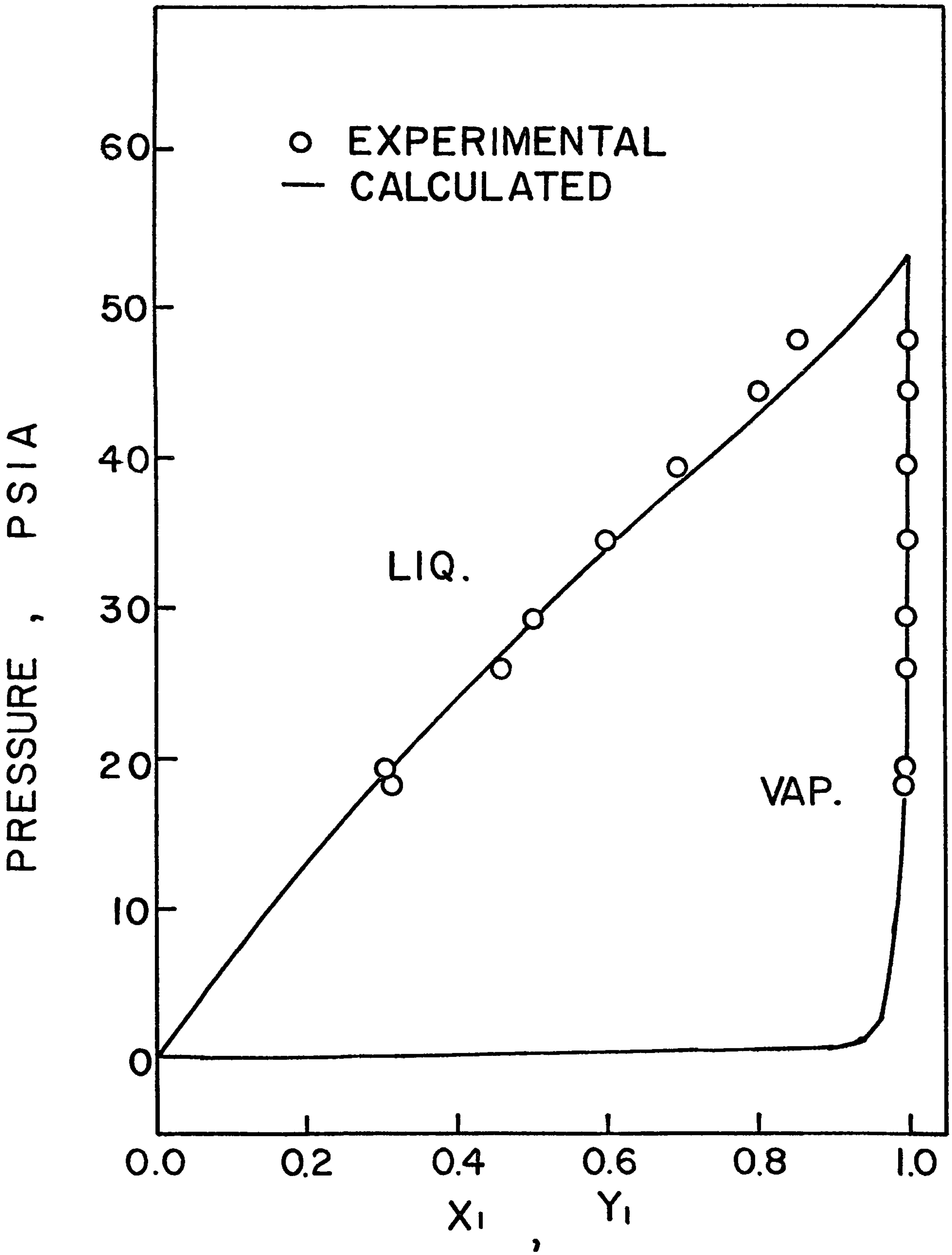


Figure 4.9 Vapor-Liquid Equilibrium Data for the Methane(1)-Ethane(2) System at 130.0 K

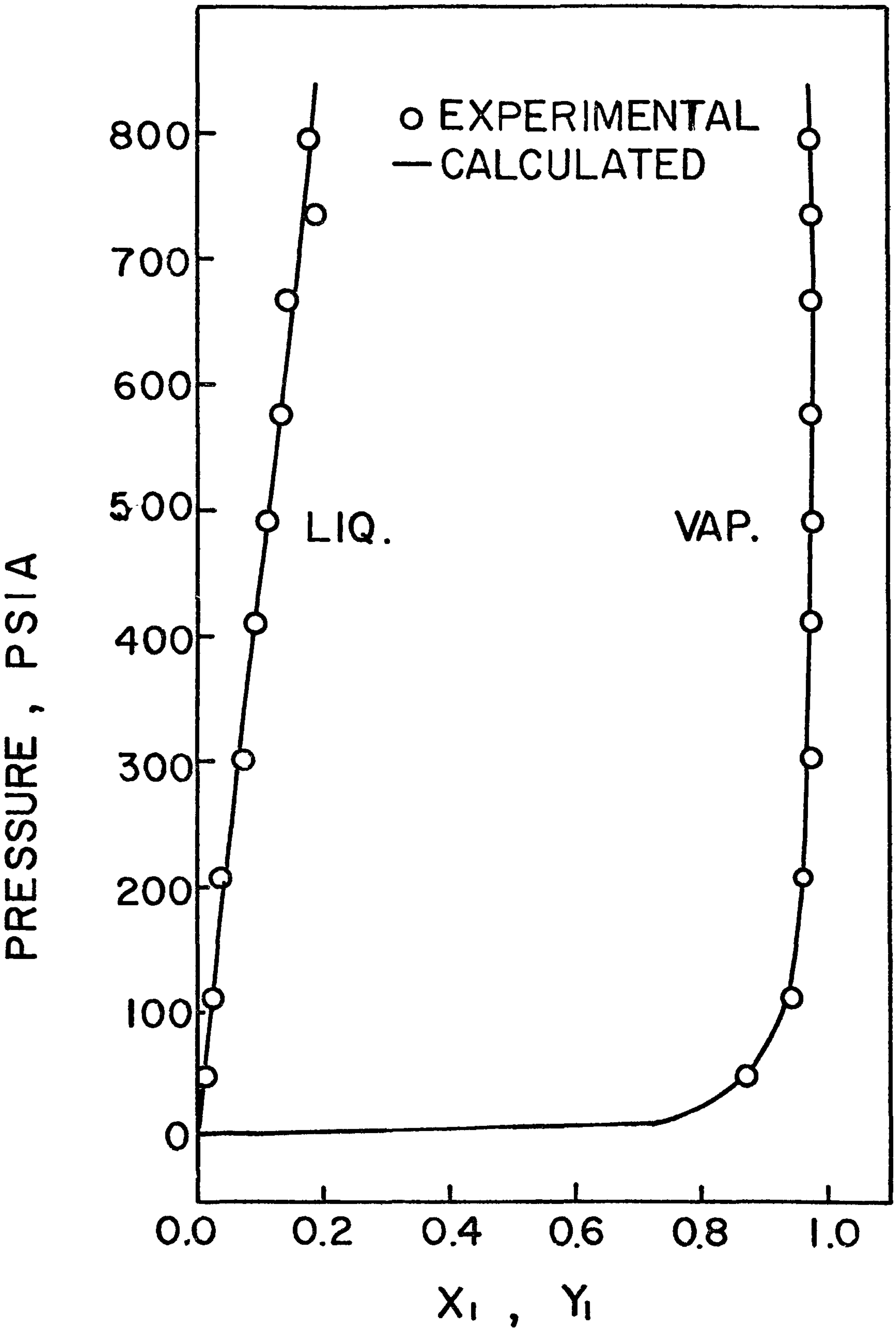


Figure 4.10 Vapor-Liquid Equilibrium Data for the Nitrogen(1)-Ethane(2) System at 169.9 K

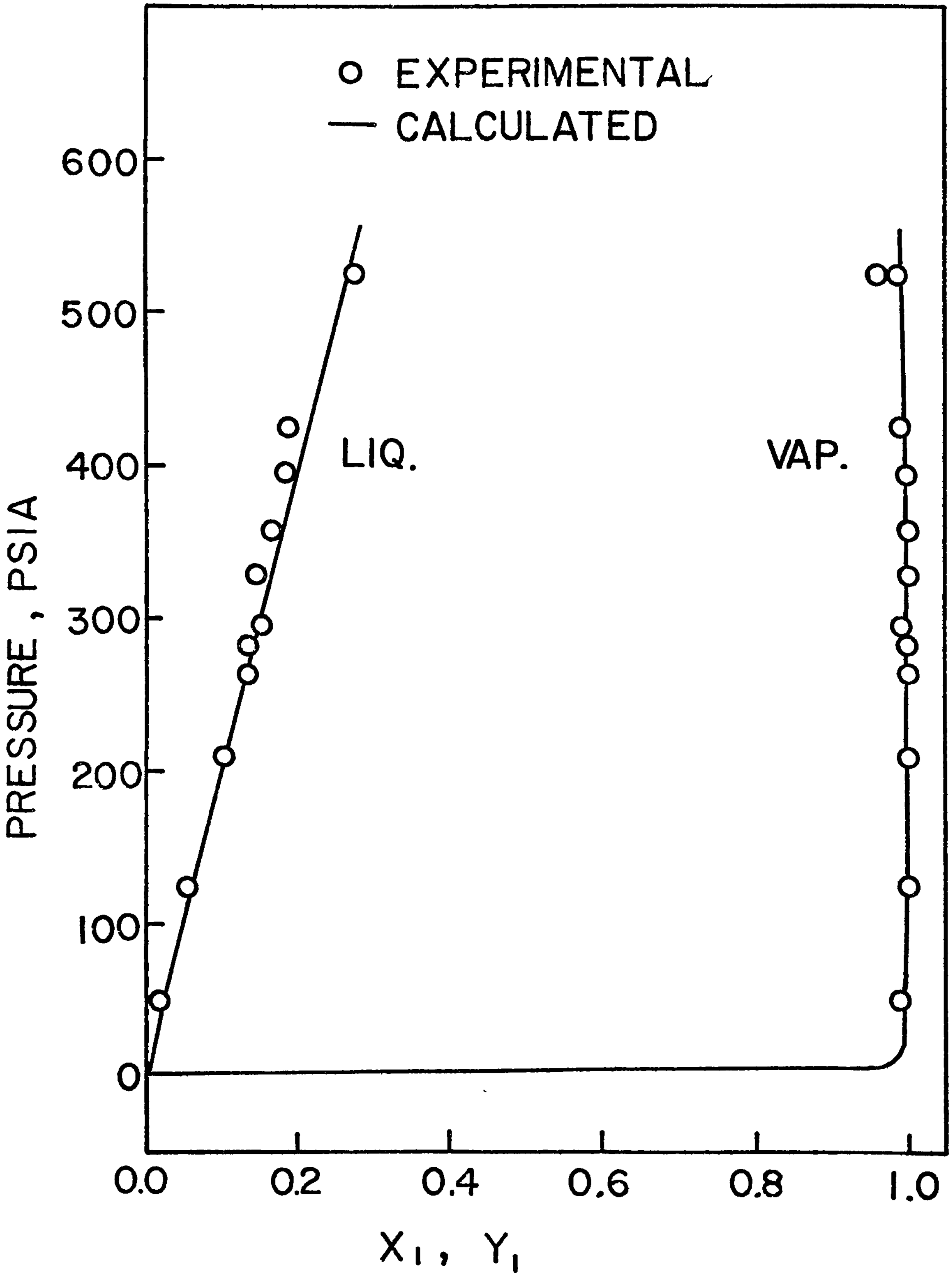


Figure 4.11 Vapor-Liquid Equilibrium Data for the Nitrogen(1)-Ethane (2) System at 130.0 K

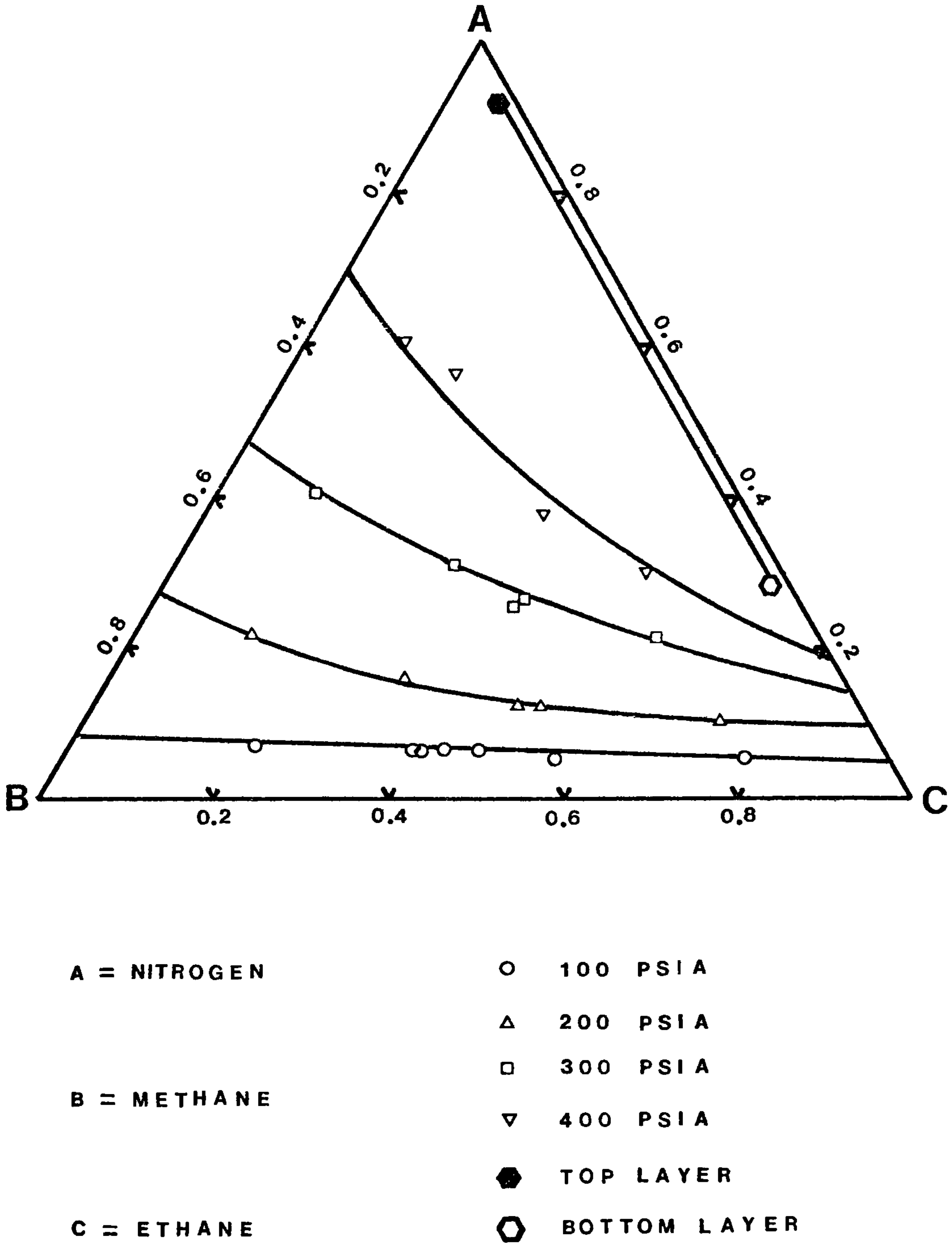


Figure 4.12 Smoothed Liquid Phase Composition Diagram for the Nitrogen-Methane-Ethane System at 130.0 K

CHAPTER 5

PREDICTION OF VAPOR-LIQUID PHASE EQUILIBRIUM BASED ON THE REDLICH-KWONG EQUATION OF STATE

One of the common methods of predicting mixture properties is to select a suitable equation of state together with appropriate thermodynamic relationships and mixing rules. The Redlich-Kwong equation of state (82) draws special attention for this purpose because of its simplicity. Many modifications of the R-K equation have been proposed recently, Some of these modificatons involve the determination and correlation of its characteristic parameters of the pure components. Others involve the improvements of the mixing rules, such as the introduction of an interaction coefficient.

5.1 MODIFIED REDLICH-KWONG EQUATION OF STATE

It is now generally accepted that the original parameters of the R-K equation are not universal constants but substance- and temperature-dependent (88).

Kato et al. (84) proposed two pure-component parameters for improving the representation of the original R-K equation in the critical region. However, these pure-component parameters can only be determined at $T \leq T_c$, and are useful for calculating vapor-liquid equilibrium data when all components are in the subcritical region. In this study of vapor liquid equilibrium, two temperatures 169.9 K and 130.0 K were selected and both temperatures are above the critical temperature of nitrogen, which is one of the component of interest. In an effort to improve the temperature restriction, Kato et al. (103) proposed a one-parameter method which is suitable for calculating vapor liquid equilibrium data without the restriction $T \leq T_c$. A generalization of the new parameter was also made in the new modification.

The new modification (one-parameter method) (103) is based on the previously proposed modified parameters for the R-K equation of state, the apparent critical temperature T_c^* and the apparent critical pressure P_c^* (84). These parameters are related to the R-K equation, which is represented by

$$P = \frac{R\,T}{v - b} - \frac{a}{T^{0.5}\, v\,(v + b)} \tag{2.22}$$

where

$$a = \Omega_a^{o}\, R^2 T_c^{2.5} / P_c \tag{5.1}$$

$$b = \Omega_b^{o}\, R\, T_c / P_c \tag{5.2}$$

$$\Omega_a^{o} = 0.42748 \tag{5.3}$$

$$\Omega_b^{o} = 0.08664 \tag{5.4}$$

and in the previous modification (84), the relationships are:

$$a_i = \Omega_a^{\,o} R^2 (T_{c_i}*)^{2.5} / P_{c_i}* \qquad (5.5)$$

$$b_i = \Omega_b^{\,o} R T_{c_i}* / P_{c_i}* \qquad (5.6)$$

In the new modification they proposed that the apparent critical pressure P_c* be arbitrarily treated as equal to the critical pressure P_c. Consequently, the apparent critical temperature T_c^* is the only parameter which is adjustable. A dimensionless parameter is defined by

$$\theta = \frac{T_c^*}{T_c} \qquad (5.7)$$

Therefore, the quantities a_i and b_i of Equations (5.5) and (5.6) are modified to give:

$$a_i = \Omega_a^{\,o} R^2 \theta_i^{2.5} T_{c_i}^{\;2.5} / P_{c_i} \qquad (5.8)$$

$$b_i = \Omega_b^{\,o} R \theta_i T_{c_i} / P_{c_i} \qquad (5.9)$$

The proposed mixing rules for calculating mixture properties are as follows:

$$b_{\text{mixture}} = \sum_i y_i b_i \qquad (5.10)$$

$$a_{\text{mixture}} = \sum_i \sum_j y_i y_j a_{ij} \quad (a_{ii} = a_i) \qquad (5.11)$$

$$a_{ij} = \Omega_a^{\,o} R^2 (T_{c_{ij}}^{\;*})^{2.5} / P_{c_{ij}} \qquad (5.12)$$

$$v_{c_{ij}}^{\;*} = \{0.5[(v_{c_i}^{\;*})^{1/3} + (v_{c_j}^{\;*})^{1/3}]\}^3 \qquad (5.13)$$

$$v_{c_i}^{\;*} = Z_{c_i}^{\;*} R T_{c_i}^{\;*} / P_{c_i} \qquad (5.14)$$

$$T_{c_{ij}}^{*} = (T_{c_i}^{*} \; T_{c_j}^{*})^{0.5} \; (1 - K_{ij}) \tag{5.15}$$

$$Z_{c_i}^{*} = Z_{c_{ij}}^{*} = 1/3 \tag{5.16}$$

Equations (5.10) and (5.11) are identical to those (Equations (2.31) and (2.32)) originally proposed by Redlich and Kwong, while Equations (5.12) to (5.15) are very similar to those proposed by Chueh and Prausnitz (87). In the above expressions, the superscript ' $*$ ' indicates the apparent mathematical value. The proposed mixing rules are equally applicable to the liquid and the vapor phases.

The parameter θ is related to the conventional temperature-dependent parameters Ω_a and Ω_b as follows:

$$\Omega_a = \Omega_a^{o} \; \theta^{2.5} \tag{5.17}$$

$$\Omega_b = \Omega_b^{o} \; \theta \tag{5.18}$$

Therefore

$$\theta = (\Omega_a / \Omega_a^{o})^{2/3} \; (\Omega_b^{o} / \Omega_b)^{2/3} \tag{5.19}$$

As the quantity θ is to be determined from vapor pressure of the pure component by equating fugacity coefficients of the liquid and vapor phases, it varies with temperature.

In Equation (5.15) the binary interaction constant K_{ij}, which is very similar to the characteristic binary constant k_{ij} used by Chueh and Prausnitz (87), represents the deviation from the geometric mean for $T_{c_{ij}}^{*}$. Though k_{ij} values are frequently considered, to a good approximation, to be molecular constants independent of temperature, composition and density (112) there is evidence that k_{ij} values obtained from different excess thermodynamic properties are different

(89-93), and that k_{ij} values vary with temperature.

5.2 EVALUATION OF θ AND ITS GENERALIZED CORRELATIONS

The R-K equation may be expressed in terms of compressibility factor in the form:

$$Z^3 - Z^2 + (\Omega_a - \Omega_b - \Omega_b^2)\,Z - \Omega_a\,\Omega_b = 0 \tag{5.20}$$

where Ω_a and Ω_b are represented by Equations (5.17) and (5.18) respectively. At the true critical temperature, $\theta = 1$. At temperatures less than T_c, the iteration procedures for the calculation of θ may be described as follows:

1. Assume T_c as the initial value of T_c^* ($\theta = 1$).
2. Calculate Ω_a and Ω_b from Equations (5.17) and (5.18) respectively.
3. Calculate Z from Eq. (5.20) which has three real roots of Z generally. The largest value of Z is treated as Z^V while the smallest value of Z as Z^L. If only one real root is obtained the value of θ is multiplied by 0.999 or 1.001 depending whether the Z value is greater or smaller than 1/3, and repeat from Step 2 until three roots are obtained.
4. Calculate the fugacity coefficients ϕ^V and ϕ^L by means of the equation

$$\ln\phi = (Z - 1) - \ln Z - \ln\,(1 - \Omega_b/\,Z) - (\Omega_a/\Omega_b)\,\ln\,(1+\Omega_b/Z) \tag{5.21}$$

and note the difference between these two quantities in terms of $\Delta\ln\phi$ ($= \ln\phi^V - \ln\phi^L$).

5. It is unlikely that $\Delta\ln\phi = 0$ in the first instance. The value of θ is then multiplied by 0.999 or 1.001 depending on whether the quantity $\Delta\ln\phi$ is positive or negative, and the calculation moves to Step 2. This calculation is repeated until the sign of the quantity $\Delta\ln\phi$ is changed. Subsequently, the desired value of θ is obtained by means of the conventional regular-falsi method.

In the correlation of binary isothermal data, the binary interaction coefficient K_{12} of Eq. (5.15) can be determined by minimizing the sum of the absolute deviations between the calculated and experimental P values.

For the correlation of binary vapor-liquid equilibria data when the system temperature is above the critical temperature of the light component (component 1), the calculation of θ_1 cannot be carried out in the manner described above, due to the nonexistence of pure liquid of the component in the supercritical region. However, the K_{12} values obtained at lower temperature permit their use in the supercritical region because of their nearly temperature-independent characteristics, which is shown in Figure 1 of Kato et al. (103). The average K_{12} value obtained is used for the evaluation of θ_1 in the supercritical region by minimizing the sum of absolute deviations between the calculated and experimental P values.

The θ values of normal paraffin hydrocarbons from methane to n-nonane were evaluated and correlated by Kato et al. (103) in terms of reduced temperature T_r and acentric factor ω for $T = T_c$:

$$\theta = \theta^{(0)} + \omega\,\theta^{(1)} + \omega^2\,\theta^{(2)} \tag{5.22}$$

where

$$\theta^{(0)} = 1 + (1 - T_r)[a_0^{(0)} + a_1^{(0)}(1 - T_r) + a_2^{(0)}(1-T_r)^2] \tag{5.23}$$

$$\theta^{(1)} = (1-T_r)[a_0^{(1)} + a_1^{(1)}(1-T_r)] \tag{5.24}$$

$$\theta^{(2)} = a_0^{(2)}(1-T_r) \tag{5.25}$$

The ω values were taken from those reported by Passut and Danner (113). The coefficients of these equations are as follows:

$$a_0^{(0)} = 0.0201 \tag{5.26}$$

$$a_1^{(0)} = -0.1769 \tag{5.27}$$

$$a_2^{(0)} = -0.1497 \tag{5.38}$$

$$a_0^{(1)} = 0.8225 \tag{5.29}$$

$$a_1^{(1)} = 0.3079 \tag{5.30}$$

$$a_0^{(2)} = -0.0950 \tag{5.31}$$

For temperature above the critical point a new set of coefficients were also proposed by Kato et al. (103):

$$a_0^{(0)} = -0.0314 \tag{5.32}$$

$$a_1^{(0)} = -0.1181 \tag{5.33}$$

$$a_2^{(0)} = -0.1740 \tag{5.34}$$

$$a_0^{(1)} = 1.1404 \tag{5.35}$$

$$a_1^{(1)} = 0.1815 \tag{5.36}$$

$$a_0^{(2)} = -0.5636 \tag{5.37}$$

By applying Equations (5.22) to (5.31), Equations (5.17) and (5.18), the Ω_a and Ω_b values of nitrogen, methane and ethane were evaluated and shown in Figures 5.1 and 5.2, respectively.

In this study, the first set of coefficients (Equations 5.26-5.31) was used in the methane-ethane binary system while the second set of coefficients (Equations 5.32-5.37) was used for the other systems containing nitrogen which was at its supercritical region.

5.3 COMPARISON OF THE PREDICTED VALUES AND THE EXPERIMENTAL RESULTS

Vapor-liquid phase equilibria were predicted by applying the above mentioned methods of Kato et al. (103). The prediction was made for the binary and ternary systems containing nitrogen, methane, and ethane, and the predicted values are compared with the experimental results obtained in this study and from other sources (50,59).

5.3.1 Nitrogen-Methane System

Vapor-liquid equilibria for the nitrogen-methane binary system were predicted at 169.9 and 130.0 K. The predicted values are compared with the experimental results obtained in this study at the same two temperatures, respectively. The comparisons are listed in Tables 5.1 and 5.2. At 169.9 K, $|\Delta P|_{AV}$=6.3 psia, $|\Delta P/P|_{AV}$x100%=1.5%, $|\Delta y|_{AV}$=0.0129, and K_{12}=0.023; at 130.0 K, $|\Delta P|_{AV}$=3.8 psia, $|\Delta P/P|_{AV}$ x100%=1.4%, $|\Delta y|_{AV}$0.0135, and K_{12}=0.010. As shown in Figure 4.7, the agreements are quite good, especially at the lower temperature.

The present data of the nitrogen-methane binary system at 169.9 and 130.0 K are compared with those of Kidnay et al. (50) at

TABLE 5.1

Comparison of the Experimental and Calculated Results
for the Nitrogen(1)-Methane(2) System at 169.9 K

x_1	P (psia)		ΔP	y_1		Δy_1
	Expt.	Calc.		Expt.	Calc.	
0.0231	361.6	378.5	16.9	0.0770	0.0697	-0.0073
0.0301	373 5	388.0	44.5	0.0993	0.0883	-0.0110
0.0579	402.1	425.2	23.1	0.1485	0.1530	0.0045
0.0888	458.6	465.3	6.7	0.2298	0.2110	-0.0188
0.1183	500.7	502.6	1.9	0.2752	0.2557	-0.0195
0.1632	559.8	557.0	-2.8	0.3275	0.3088	-0.0187
0.2352	640.0	637.7	-2.3	0.3790	0.3652	-0.0138
0.2683	671.0	671.1	0.1	0.3875	0.3814	-0.0061
0.2885	687.0	689.9	2.9	0.4235	0.3882	-0.0353
0.3032	703.0	702.7	-0.3	0.3962	0.3917	-0.0045
0.3057	702.0	704.8	2.8	0.3970	0.3922	-0.0048
0.3159	714.0	712.9	-1.1	0.3836	0.3936	0.0100

TABLE 5.2

Comparison of the Experimental and Calculated Results
for the Nitrogen(1)-Methane(2) System at 130.0 K

x_1	P (psia)		ΔP	y_1		Δy_1
	Expt.	Calc.		Expt.	Calc.	
0.0756	108.6	101.6	-7.0	0.4846	0.4309	-0.0637
0.1623	148.0	148.3	0.3	0.6436	0.6133	-0.0303
0.2745	204.7	204.1	-0.6	0.7406	0.7241	-0.0165
0.3790	252.3	252.2	-0.1	0.7900	0.7824	-0.0076
0.5022	302.1	306.1	4.0	0.8343	0.8285	-0.0058
0.6052	347.2	350.2	3.0	0.8614	0.8583	-0.0031
0.6600	382.0	374.2	-7.8	0.8805	0.8725	-0.0080
0.7111	405.7	397.1	-8.6	0.8931	0.8855	-0.0076
0.8222	443.8	450.9	7.1	0.9125	0.9147	0.0022
0.8447	462.4	463.0	0.6	0.9198	0.9211	0.0013
0.8750	482.3	480.0	-2.3	0.9326	0.9301	-0.0025

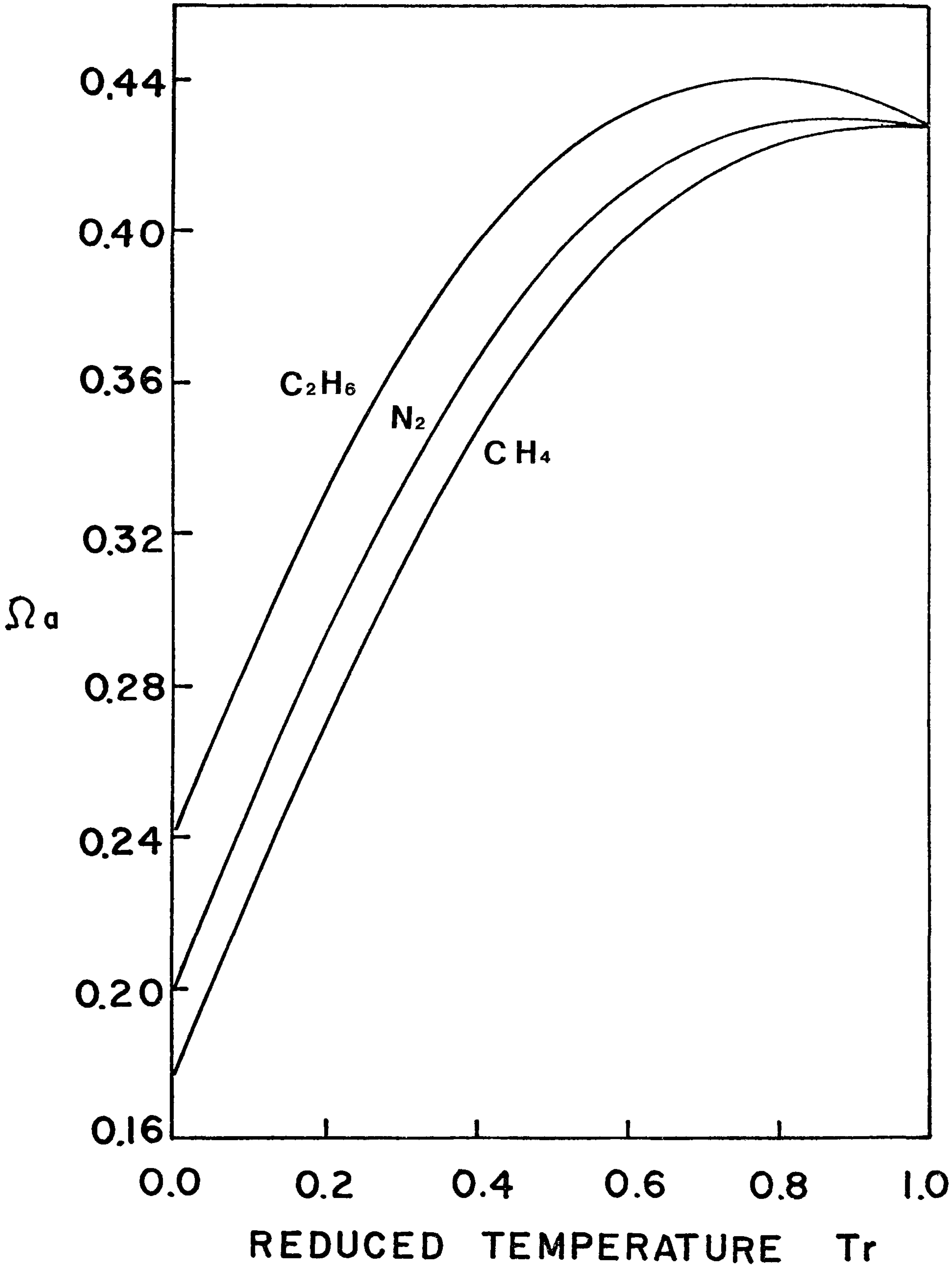


Figure 5.1 Values of Ω_a for Nitrogen, Methane and Ethane

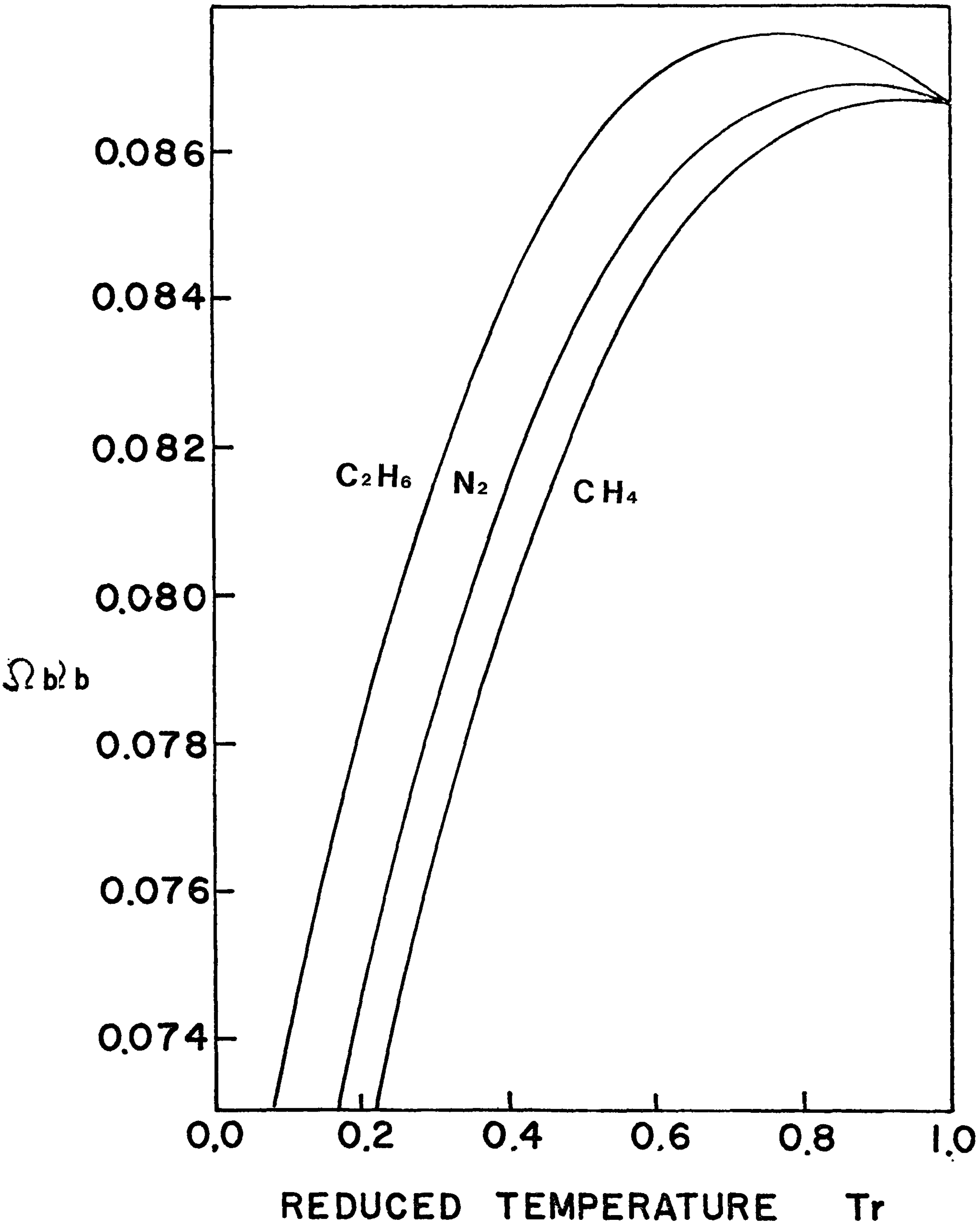


Figure 5.2 Values of Ω_b for Nitrogen, Methane and Ethane

170.0 and 130.0 K. As shown in Figure 5.3, the agreement between these two sets of data is very satisfactory.

For the same system, vapor-liquid equilibria were also predicted at 170.0 and 130.0 K. The predicted values are compared satisfactorily with the experimental values of Kidnay et al. (50) at these two temperatures. The results are shown in Tables A.1, A.2, A.4, and in Figure A.1.

5.3.2 Methane-Ethane System

For the methane-ethane binary system, the comparisons of the predicted values and the experimental results obtained in this study at 169.9 and 130.0 K are listed in Tables 5.3 and 5.4, and shown in Figures 4.8 and 4.9. At 169.9 K, $|\Delta P|_{AV}=3.4$ psia, $|\Delta P/P|_{AV}\text{x}100\%=2.4\%$, $|\Delta y|_{AV}=0.0026$, and $K_{12}=0.006$; at 130.0 K, $|\Delta P|_{AV}=1.0$ psia, $|\Delta P/P|_{AV}\text{x}100\%=3.1\%$, $|\Delta y|_{AV}=0.0010$, and $K_{12}=0.007$.

The present data of this system at 169.9 and 130.0 K are compared with those of Wichterle (59) at 172.04 and 130.37 K. It can be seen in Figure 5.4 that the data obtained at 169.9 K are lower than those of Wichterle at 172.04 K. The difference is greater at high nitrogen concentration. The agreement between the 130.0 K and 130.37 K is fairly good as can be seen in Figure 5.5.

The experimental values of Wichterle (59) are compared with the predicted values at 172.04 and 130.37 K. The comparisons are listed in Tables A.3, A.4, and shown in Figures A.2 and A.3.

It is seen clearly that the prediction of the vapor-liquid equilibria for the methane-ethane binary system are very successful.

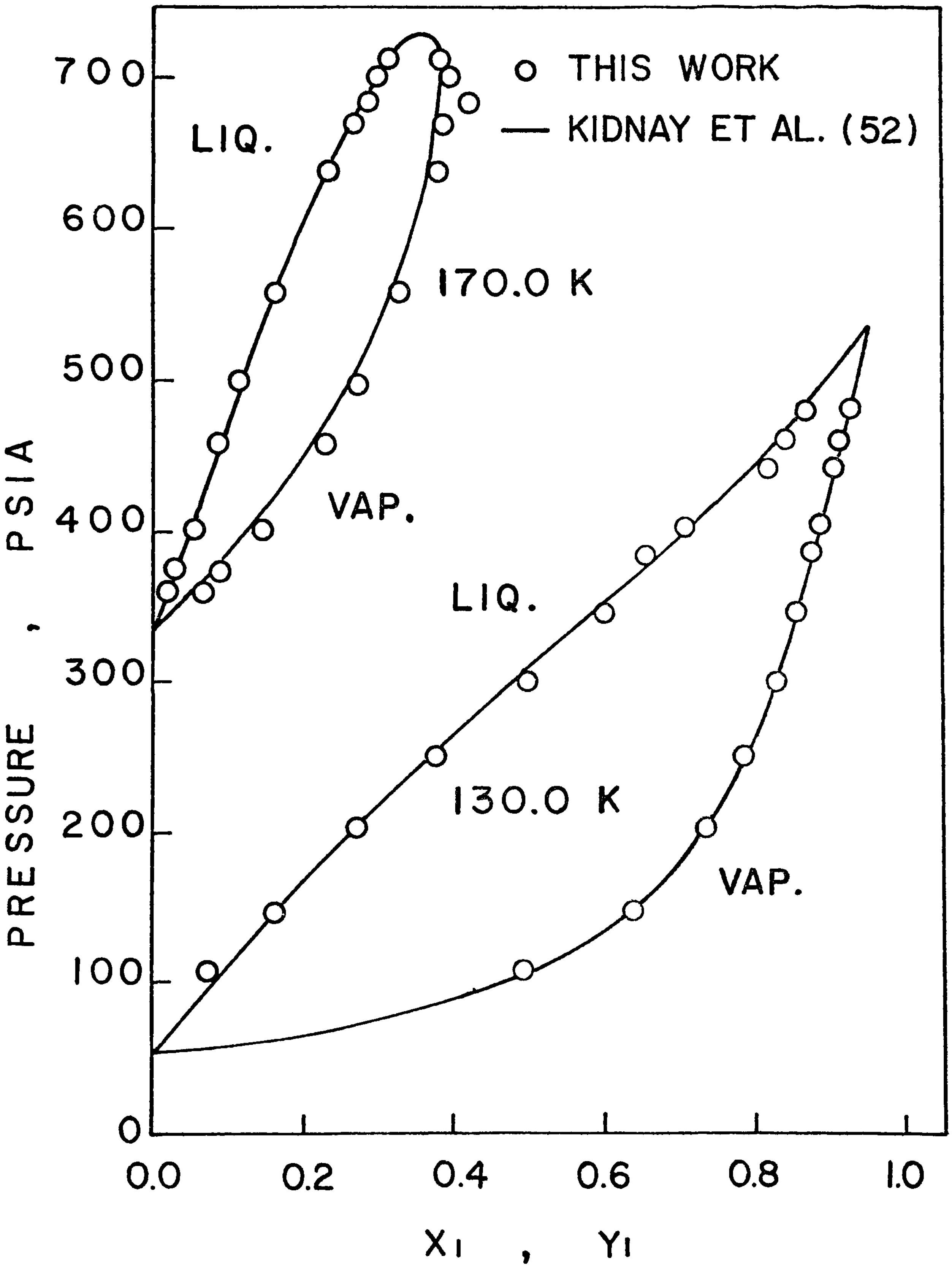


Figure 5.3 Comparison of the Results in This Study at 169.9 and 130.0 K for the Nitrogen(1)-Methane(2) System with those Reported by Kidnay et al. (50) at 170.0 and 130.0 K

TABLE 5.3

Comparison of the Experimental and Calculated Results
for the Methane (1)-Ethane (2) System at 169.9 K

x_1	P (psia)		ΔP	y_1		Δy_1
	Expt.	Calc.		Expt.	Calc.	
0.0388	20.8	19.6	-1.2	0.6724	0.6815	0.0091
0.1855	66.8	69.0	2.2	0.9118	0.9134	0.0016
0.2820	100.5	100.6	0.1	0.9449	0.9428	-0.0021
0.4038	143.1	139.3	-3.8	0.9624	0.9612	-0.0012
0.5213	181.2	175.5	-5.7	0.9726	0.9716	-0.0010
0.6731	215.5	221.2	5.7	0.9835	0.9810	-0.0025
0.7775	249.1	253.1	4.0	0.9861	0.9816	-0.0045
0.8638	284.0	281.3	-2.7	0.9927	0.9906	-0.0021
0.9308	310.9	305.9	-5.0	0.9909	0.9945	0.0036

TABLE 5.4

Comparison of the Experimental and Calculated Results
for the Methane (1)-Ethane (2) System at 130.0 K

x_1	P (psia)		ΔP	y_1		Δy_1
	Expt.	Calc.		Expt.	Calc.	
0.3067	19.3	19.3	0.0	0.9941	0.9923	-0.0018
0.3119	18.2	19.5	1.3	0.9915	0.9926	0.0011
0.4589	26.0	27.2	1.2	0,9973	0.9955	-0.0018
0.5015	29.3	29.3	0.0	0.9965	0.9960	-0.0005
0.5996	34.5	33.9	-0.6	0.9978	0.9970	-0.0008
0.6938	39.4	38.2	1.2	0.9985	0.9978	-0.0007
0.8027	44.4	43.0	-1.4	0.9992	0.9986	-0.0006
0.8571	47.8	45.3	-2.3	0.9998	0.9989	-0.0009

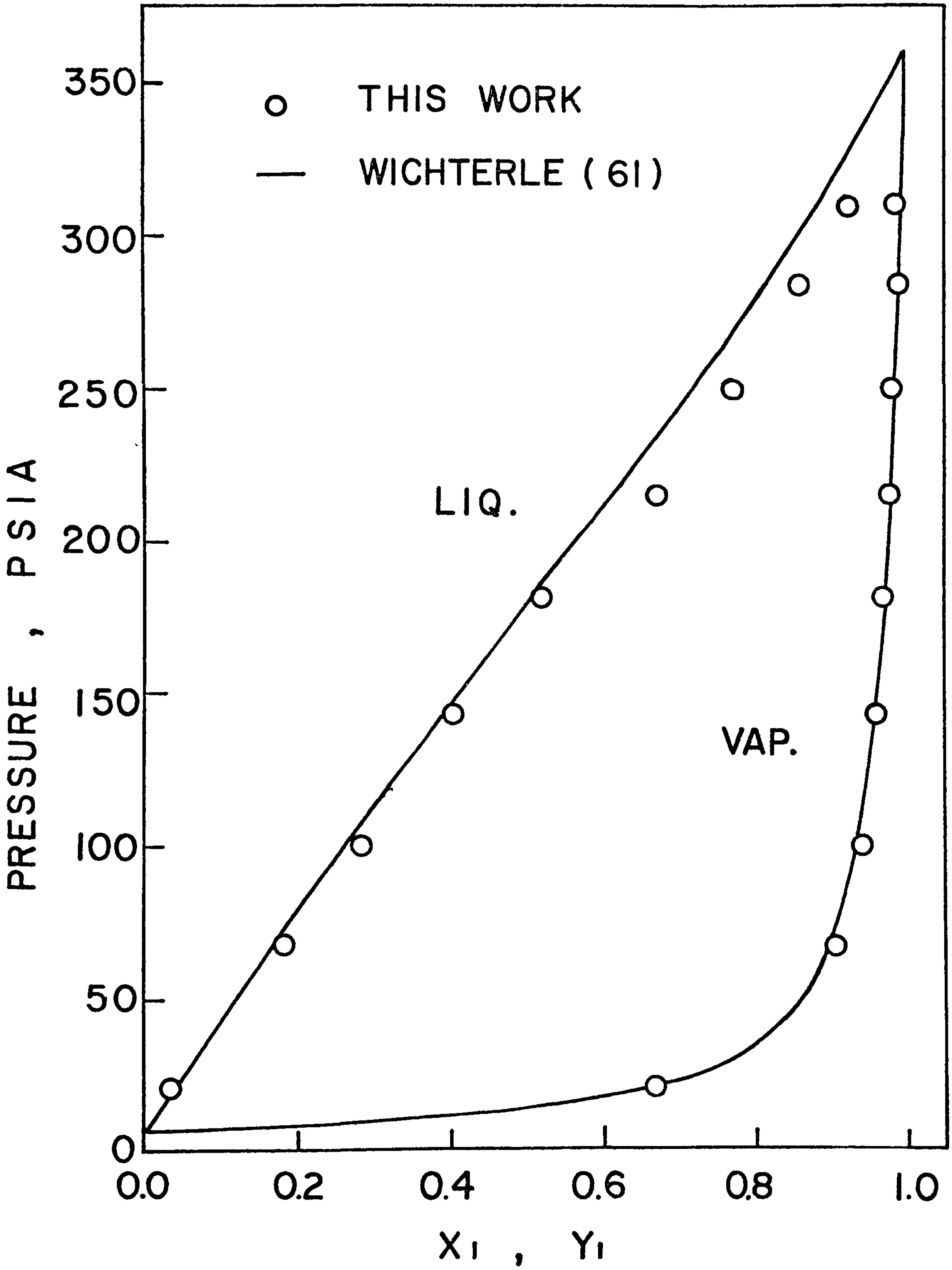


Figure 5.4 Comparison of the Results in This Study at 169.9 K for the Methane(1)-Ethane(2) System with Those Reported by Wichterle (59) at 172.04 K

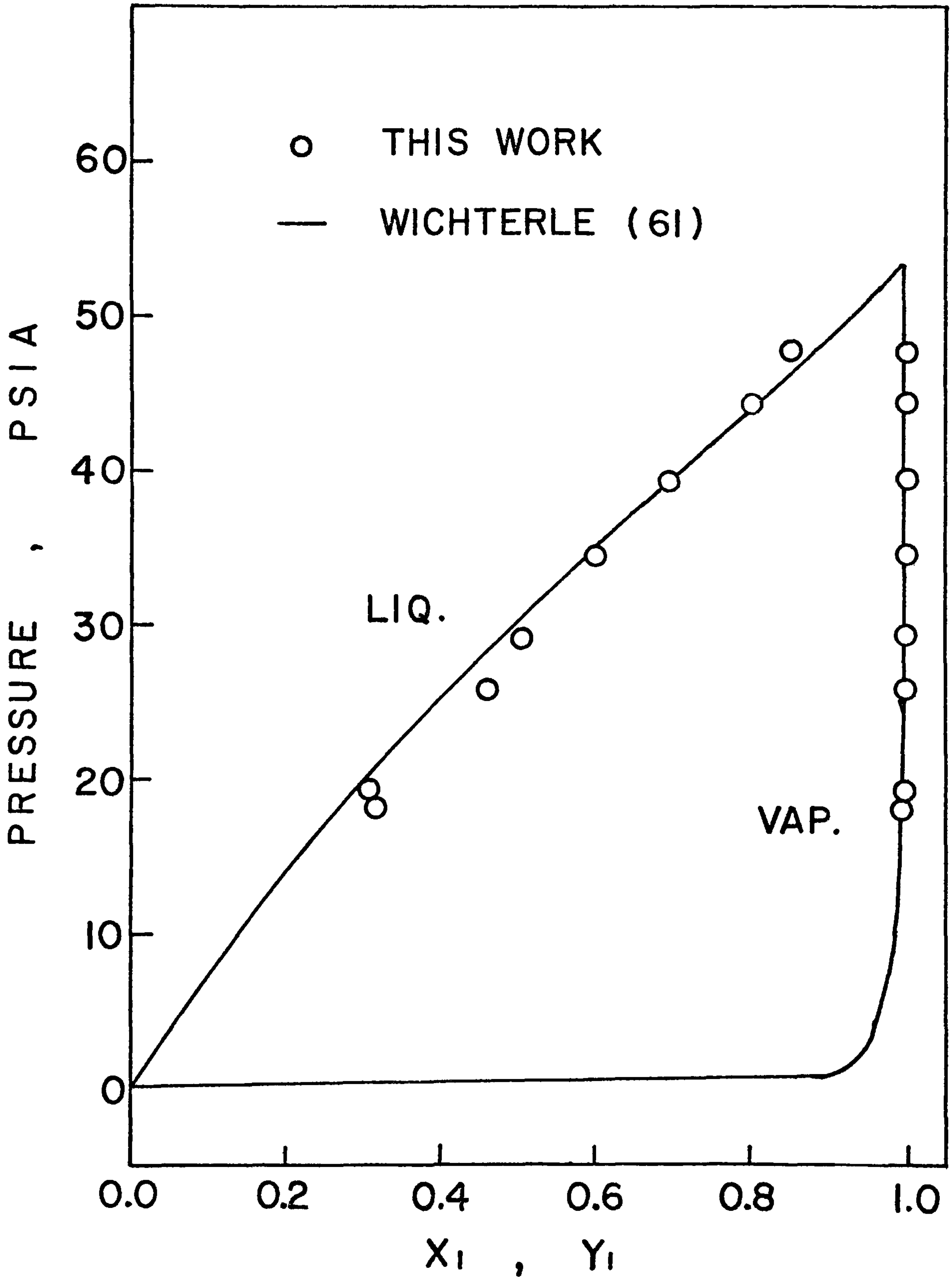


Figure 5.5 Comparison of the Results in This Study at 130.0 K for the Methane(1)-Ethane(2) System with Those Reported by Wichterle (59) at 130.37 K

5.3.3 Nitrogen-Ethane System

Vapor-liquid phase equilibria data for the nitrogen-ethane binary system in this study are compared with predicted values at 169.9 and 130.0 K. The results are listed in Tables 5.5 and 5.6, and shown in Figures 4.10 and 4.11. At 169.9 K, $|\Delta P|_{AV}$=25.2 psia, $|\Delta P/P|_{AV}$x100%=7.6%, $|\Delta y|_{AV}$=0.0067, and K_{12}=0.058; at 130.0 K, $|\Delta P|_{AV}$=22.1 psia, $|\Delta P/P|_{AV}$x100%=7.2%, $|\Delta y|_{AV}$=0.0030, and K_{12}=0.034. As can be seen in the two diagrams that the predicted values agree with the experimental values.

5.3.4 Nitrogen-Methane-Ethane System

The values of K_{ij} obtained from the above three binary systems at 130.0 K were applied to predict vapor-liquid phase equilibria for the nitrogen-methane-ethane ternary system at the same temperature. The final results are listed in Table 5.7. The averaged $|\Delta P|$ is 13.2 psia, $|\Delta P/P|_{AV}$x100%=5.3, and averaged $|\Delta y|$ is 0.0129. These results are considered to be satisfactory.

The calculated vapor-liquid equilibrium results such as $|\Delta P|_{AV}$, $|\Delta P/P|_{AV}$x100%, $|\Delta y|_{AV}$, K_{ij}, Ω_a, Ω_b of this study for all the binary and ternary systems are summarized in Table 5.8 and those of the other two sources (50,59) are summarized in Table A.5.

5.4 CORRELATION OF LIQUID PHASE ACTIVITY COEFFICIENTS

In this study, the liquid phase activity coefficients γ of the components in the binary and ternary systems were evaluated by means of Equation (3.16). The reference pressure P^r was chosen to be 1,000

TABLE 5.5

Comparison of the Experimental and Calculated Results for the Nitrogen(1)- Ethane(2) System at 169.9 K

x_1	P (psia)		ΔP	y_1		Δy_1
	Expt.	Calc.		Expt.	Calc.	
0.0125	51.1	58.8	7.7	0.8708	0.8778	0.0070
0.0214	111.0	96.0	-15.0	0.9407	0.9213	-0.0194
0.0402	207.7	175.2	-32.5	0.9645	0.9518	-0.0127
0.0751	302.8	323.8	21.0	0.9727	0.9677	-0.0051
0.0960	411.1	414.2	3.1	0.9760	0.9709	-0.0051
0.1132	493.0	489.6	-3.4	0.9773	0.9722	-0.0051
0.1330	577.0	577.4	0.4	0.9765	0.9728	-0.0037
0.1422	667.2	618.8	-48.4	0.9754	0.9728	-0.0026
0.1772	795.5	799.8	-15.7	0.9737	0.9713	-0.0024
0.1898	734.2	839.3	105.1	0.9743	0.9704	-0.0039

TABLE 5.6

Comparison of the Experimental and Calculated Results
for the Nitrogen(1)- Ethane(2) System at 130.0 K

x_1	P (psia)		ΔP	y_1		Δy_1
	Expt.	Calc.		Expt.	Calc.	
0.0219	49.0	44.3	-4.7	0.9868	0.9949	0.0080
0.0569	124.0	113.9	-10.1	0.9982	0.9975	-0.0007
0.1033	210.3	204.4	-5.9	0.9988	0.9981	-0.0007
0.1357	282.8	266.5	-16.3	0.9988	0.9982	-0.0006
0.1370	263.4	269.0	5.6	0.9988	0.9984	-0.0004
0.1469	328.6	287.9	-40.7	0.9989	0.9982	-0.0007
0.1545	295.1	302.2	7.1	0.9903	0.9984	0.0081
0.1844	395.3	358.9	-36.4	0.9981	0.9981	0.0000
0.1678	358.4	327.5	-30.9	0.9987	0.9982	-0.0005
0.1899	425.5	369.3	-56.2	0.9887	0.9981	0.0094
0.2770	525.5	554.2	28.7	0.9863	0.9901	0.0038

TABLE 5.7.A

Comparison of the Experimental and Calculated Results for the Nitrogen(1)-Methane(2)-Ethane(3) System at 130.0 K

	x_1	x_2	P(psia)		ΔP
			Expt.	Calc.	
1.	0.0511	0.1613	101.3	98.8	-2.5
2.	0.0544	0.3820	101.5	97.6	-3.9
3.	0.0646	0.5064	101.4	104.7	3.3
4.	0.0649	0.5409	100.7	103.7	3.0
5.	0.0650	0.5300	101.8	104.2	2.4
6.	0.0669	0.4646	100.2	109.0	8.8
7.	0.0705	0.7168	100.0	102.0	2.0
8.	0.1018	0.1673	200.8	178.9	-21.1
9.	0.1215	0.3642	199.3	176.9	-22.4
10.	0.1224	0.3896	200.0	174.2	-25.8
11.	0.1628	0.4986	200.0	191.5	-9.3
12.	0.2163	0.6485	200.3	194.6	-5.7
13.	0.2169	0.1836	301.1	329.0	27.9
14.	0.2525	0.3323	300.1	299.8	-0.2
15.	0.2660	0.3123	300.1	316.9	16.8
16.	0.2820	0.0164	505.0	543.2	38.2
17.	0.3039	0.1540	402.3	436.4	34.1
18.	0.3078	0.3729	302.5	312.9	10.4
19.	0.3762	0.2352	400.0	418.0	18.0
20.	0.4038	0.4796	301.1	295.9	-5.2
21.	0.5601	0.2416	403.2	424.6	21.4
22.	0.6057	0.2792	403.0	396.5	-6.5

TABLE 5.7.B

Comparison of the Experimental and Calculated Results for the Nitrogen(1)-Methane(2)-Ethane(3) System at 130.0 K

	y_1		Δy_1	y_2		Δy_2
	Expt.	Calc.		Expt.	Calc.	
1.	0.8801	0.8699	-0.0102	0.1167	0.1277	0 0110
2.	0.7565	0.7198	-0.0367	0.2423	0.2783	0.0360
3.	0.7013	0.6695	-0.0318	0.2971	0.3291	0.0320
4.	0.6708	0.6484	-0.0224	0.4278	0.3503	-0.0775
5.	0.6781	0.6556	-0.0225	0.3142	0.3430	0.0288
6.	0.7543	0.7023	-0.0520	0.2441	0.2962	0.0521
7.	0.5869	0.5531	-0.0338	0.4126	0.4460	0.0334
8.	0.9357	0.9189	-0.0168	0.0635	0.0795	0.0160
9.	0.8685	0.8392	-0.0293	0.1298	0.1595	0.0287
10.	0.8690	0.8279	-0.0411	0.1299	0.1708	0.0409
11.	0.8384	0.8053	-0.0331	0.1604	0.1937	0.0333
12.	0.7817	0.7570	-0.0247	0.2176	0.2424	0.0248
13.	0.9459	0.9417	-0.0042	0.0532	0.0569	0.0037
14.	0.9120	0.8984	-0.0136	0.0871	0.1003	0.0132
15.	0.9141	0.9067	-0.0074	0.0850	0.0922	0.0072
16.	0.9844	0.9874	0.0030	0.0086	0.0063	-0.0023
17.	0.9583	0.9537	-0.0046	0.0399	0.0443	0.0044
18.	0.8771	0.8910	0.0139	0.1167	0.1080	-0.0087
19.	0.9375	0.9337	-0.0038	0.0611	0.0647	0.0036
20.	0.8604	0.8532	-0.0072	0.1394	0.1461	0.0067
21.	0.9314	0.9299	-0.0015	0.0668	0.0685	0.0017
22.	0.9096	0.9140	0.0044	0.0897	0.0846	-0.0051

TABLE 5.8

A Summary of the Calculated Results

System	T (K)	$\lvert\Delta P\rvert_{AV}$ (psia)	$\lvert\Delta P/P\rvert_{AV}$ X100%	$\lvert\Delta y\rvert_{AV}$	K_{12}	Ω_a	Ω_b
Nitrogen(1)-Methane(2)	169.9	6.3	1.5	0.0129	0.023	0.41616 0.42309	0.08571 (1) 0.08628 (2)
	130.0	3.8	1.4	0.0135	0.010	0.42695 0.40149	0.08660 (1) 0.09449 (2)
Methane(1)-Ethane(2)	169.9	3.4	2.4	0.0026	0.006	0.42809 0.42687	0.08669 (1) 0.08659 (2)
	130.0	1.0	3.1	0.0010	0.007	0.41248 0.40297	0.08541 (1) 0.08462 (2)
Nitrogen(1)-Ethane(2)	169.9	25.2	7.6	0.0067	0.058	0.41616 0.42189	0.08571 (1) 0.08618 (2)
	130.0	22.1	7.2	0.0030	0.034	0.42695 0.39847	0.08660 (1) 0.08424 (2)
Nitrogen(1)-Methane(2) -Ethane(3)	130.0	13.2	5.3	0.0129		0.42695 0.40149 0.42695	0.08571 (1) 0.08628 (2) 0.08424 (3)

psia which is above the highest saturation pressure encountered in this work.

For all the binary systems the liquid phase activity coefficients obtained were further correlated by the three-constant Redlich-Kister equations. The fitted constants, which were obtained by a least-squares method, are presented in Table 5.9. The experimental and calculated γ values for all the binary systems are shown in Figures 5.6 to 5.11 and listed in Tables 5.10 to 5.15.

The liquid phase activity coeficients of the ternary system at 130.0 K were correlated by means of the Redlich-Kister equations (Equations (3.35) to (3.38)). The fitted constants C_{123}, D_1, D_2 and D_3 are all found to be zero. The experimental and calculated values are listed in Table 5.16.

The log (γ_1/γ_2) versus composition diagrams for the binary nitrogen-methane, methane-ethane and nitrogen-ethane systems at the temperatures of 169.9 and 130.0 K are shown in Figures 5.12 to 5.17, respectively.

For the nitrogen-methane binary system at 130.0 K, the net area of the log (γ_1/γ_2) versus composition plot (see Figure 5.13, the area under the dashed line) is 0.013. This value is somewhat higher to indicate the consistency of the data, though the averaged $|\Delta y|$ value is 0.0135, which is considered acceptable in this study. The net area of the log (γ_1/γ_2) versus composition plot (Figures 5.14 and 5.15) for the methane-ethane binary system at 169.9 and 130.0 K are all found to be zero indicating the consistency of the data.

TABLE 5.9

A Summary of the Correlation Results for the Binary and Ternary Systems

System	Temperature (K)	B_{12}	C_{12}	D_{12}	γ_1^∞	γ_2^∞
Nitrogen(1)-Methane(2)	169.9	0.3639	0.1069	0.0468	2.013	3.292
	130.0	0.1731	-0.0430	0.0827	1.990	1.632
Methane(1)-Ethane(2)	169.9	0.1817	0.0518	0.0152	1.397	1.773
	130.0	0.1853	0.0402	0.0123	1.437	1.729
Nitrogen(1)-Ethane(2)	169.9	1.109	0.3612	0.0763	6.676	35.23
	130.0	0.9814	0.2905	0.0679	5.739	21.87

		C_{123}	D_1	D_2	D_3
Nitrogen(1)-Methane(2) -Ethane(3)	130.0	0.0000	0.0000	0.0000	0.0000

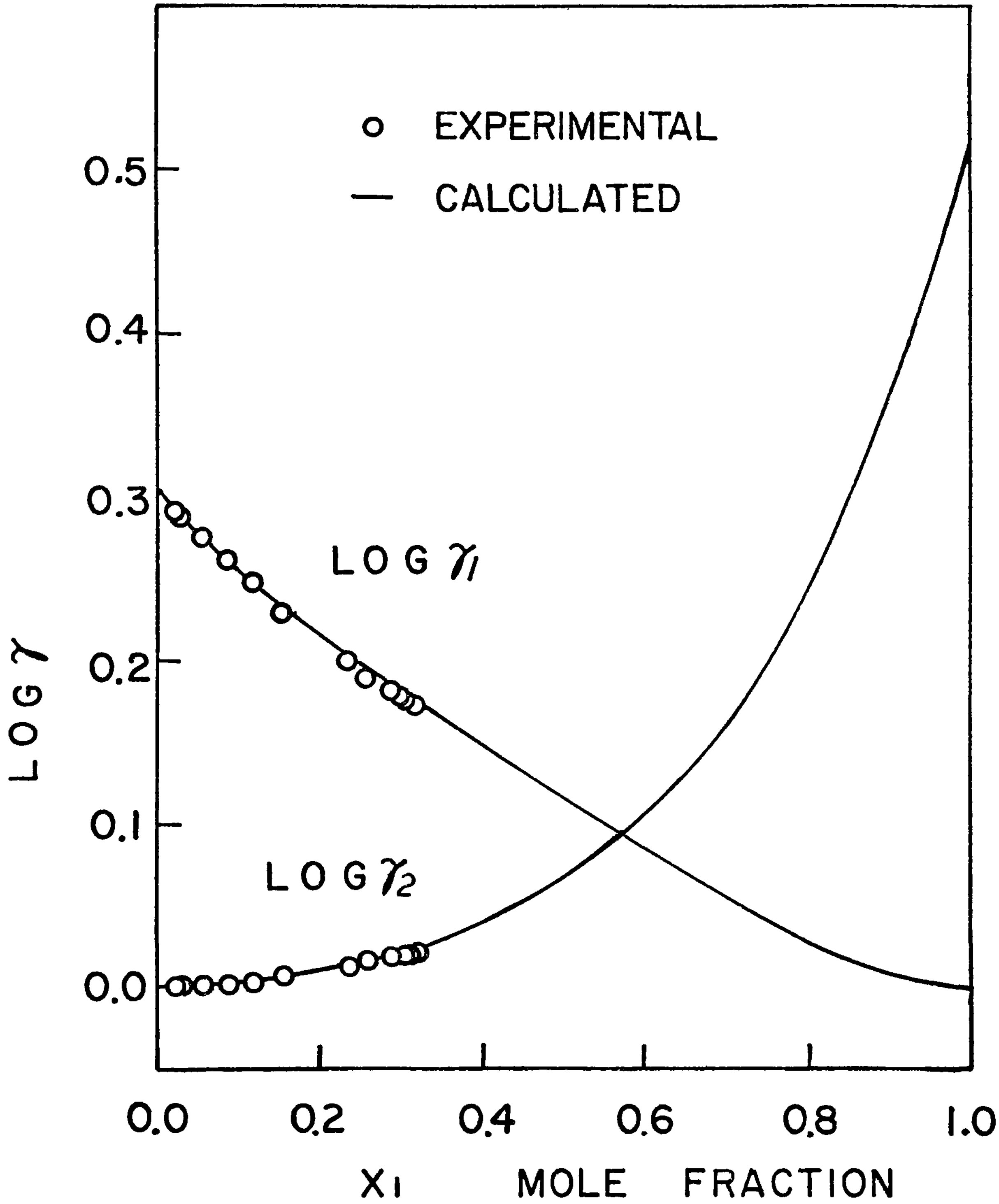


Figure 5.6 Comparison of the Experimental and Calculated γ Values for the Nitrogen(1)-Methane System at 169.9 K

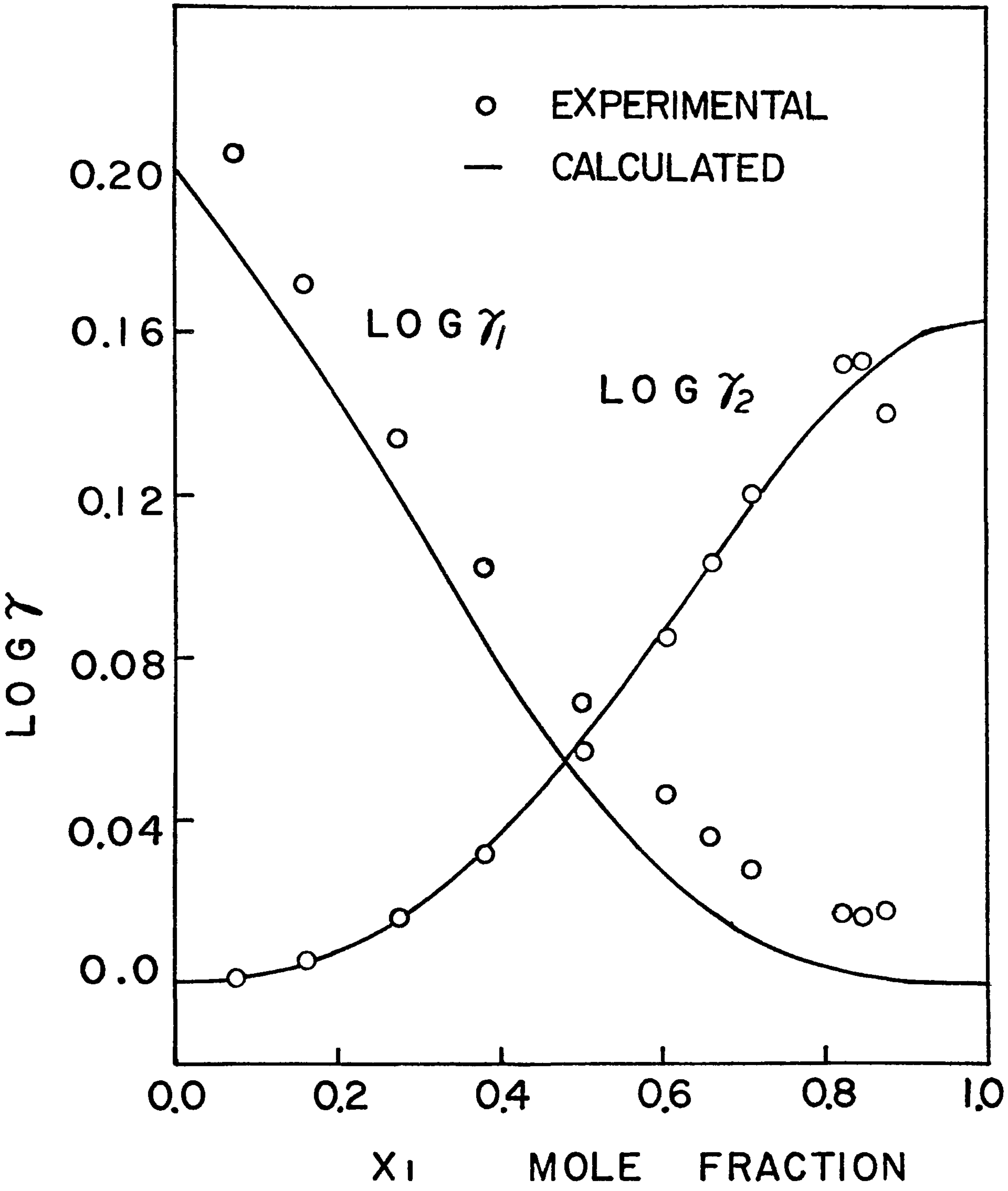


Figure 5.7 Comparison of the Experimental and Calculated γ Values for the Nitrogen(1)-Methane(2) System at 130.0 K

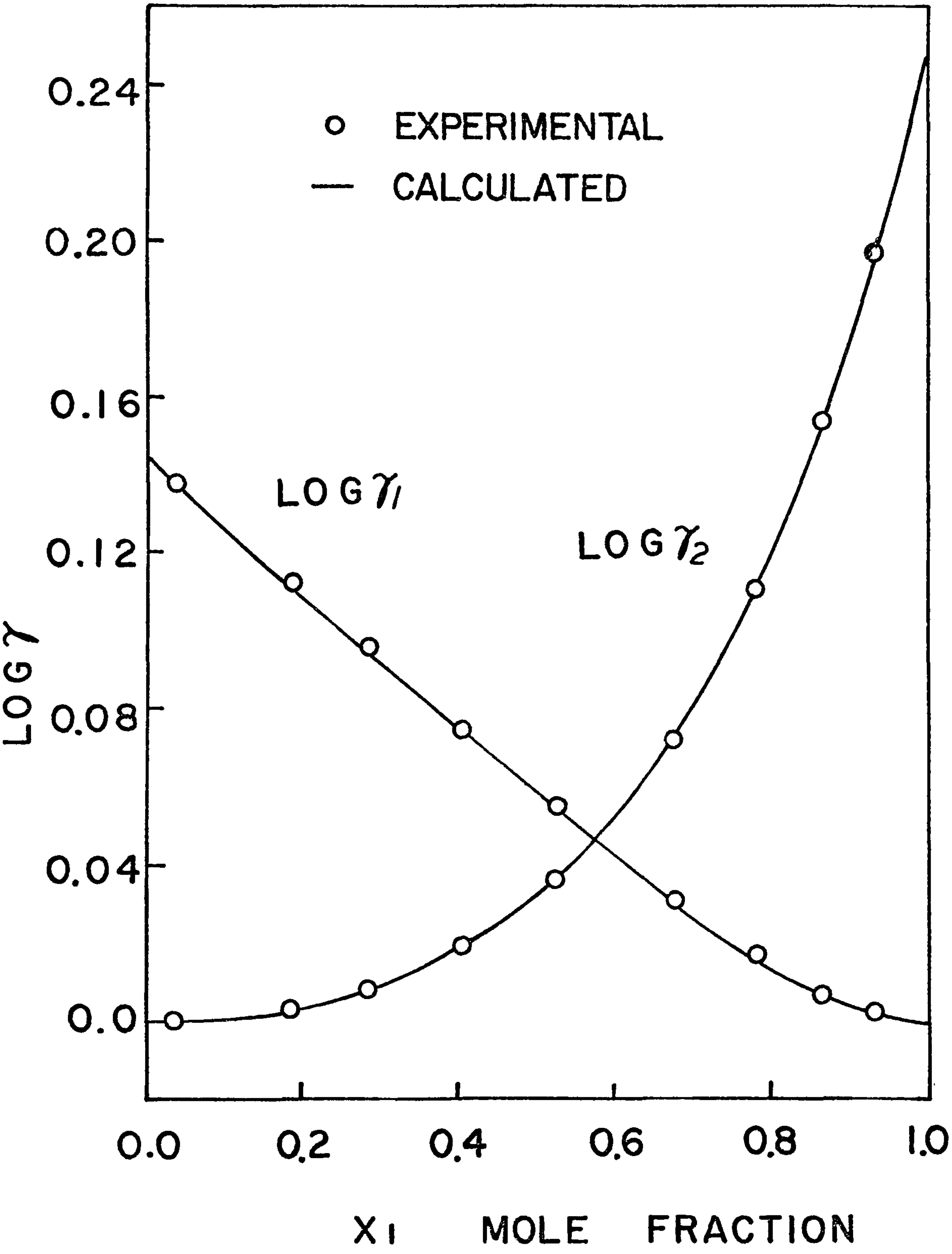


Figure 5.8 Comparison of the Experimental and Calculated γ Values for the Methane(1)-Ethane(2) System at 169.9 K

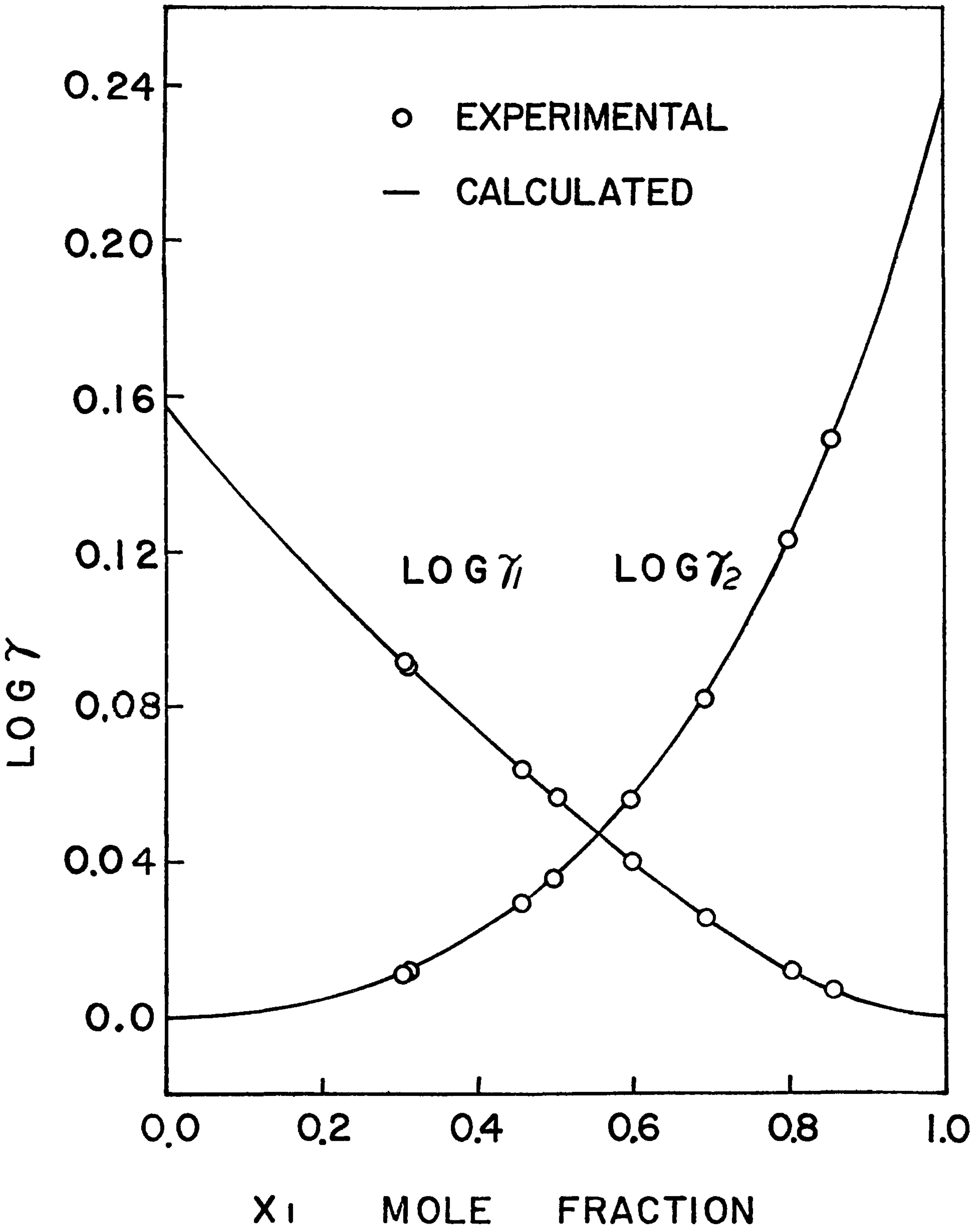


Figure 5.9 Comparison of the Experimental and Calculated γ Values for the Methane(1)-Ethane(2) System at 130.0 K

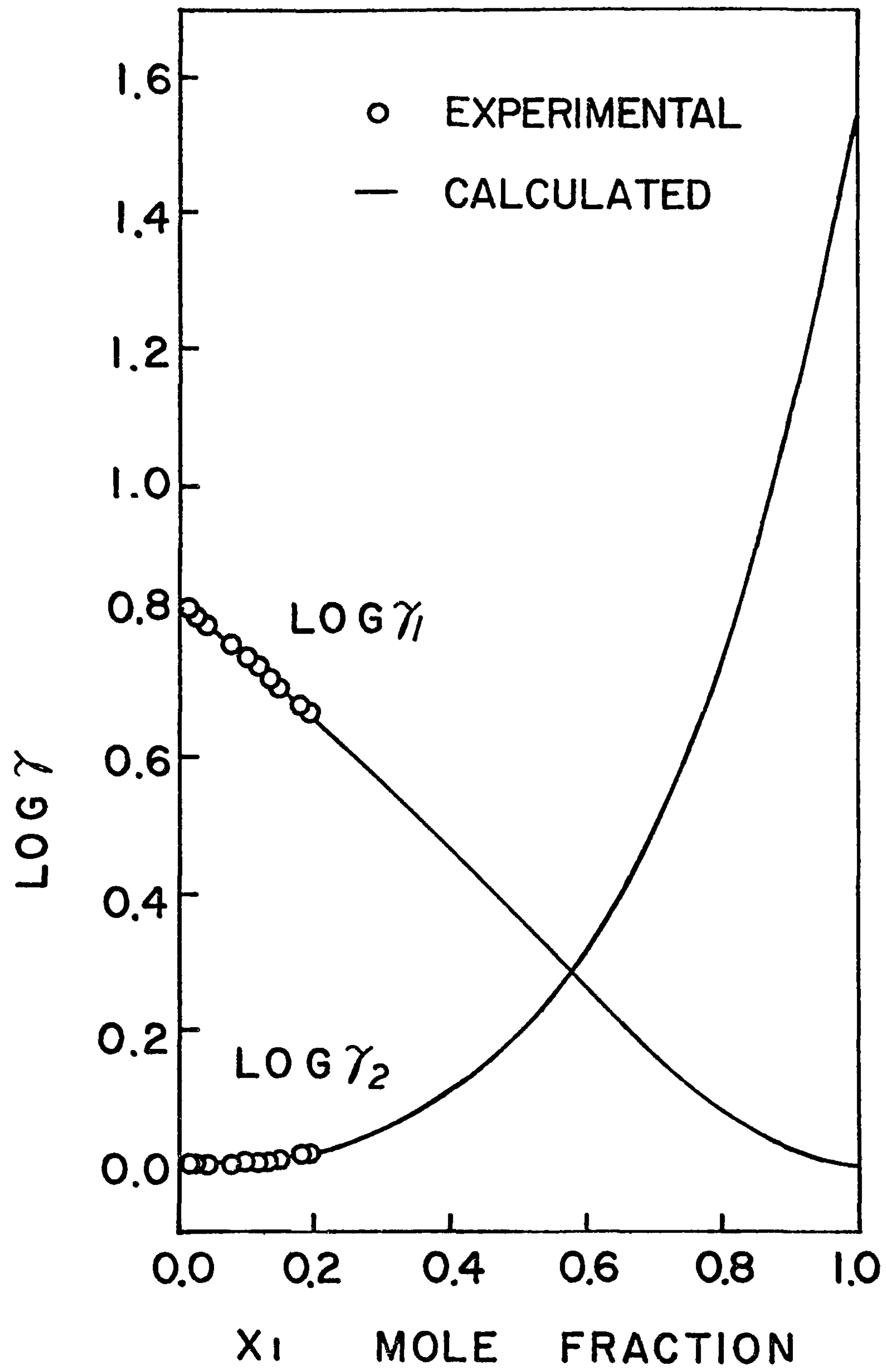


Figure 5.10 Comparison of the Experimental and Calculated γ Values for the Nitrogen(1)-Ethane(2) System at 169.9 K

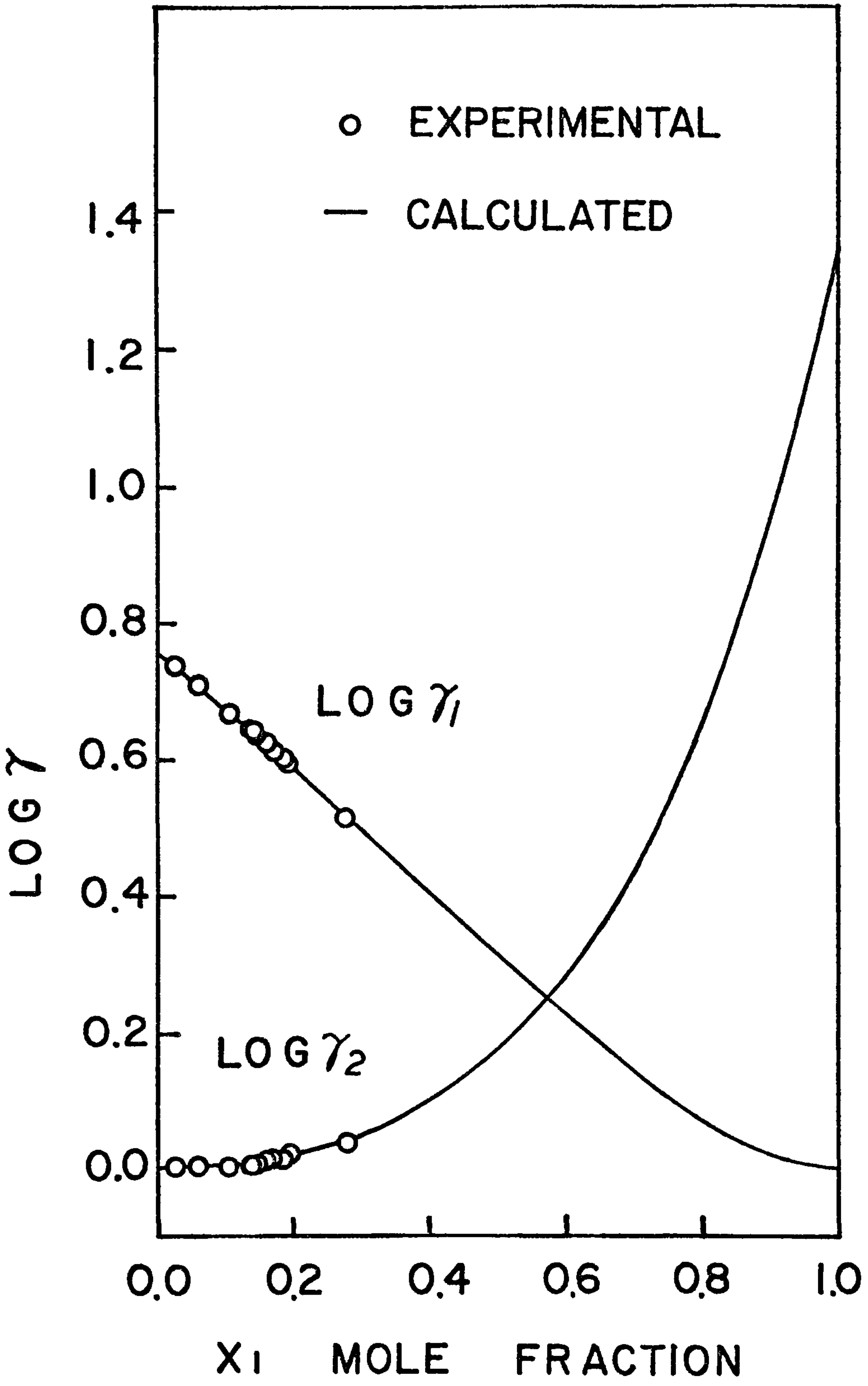


Figure 5.11 Comparison of the Experimental and Calculated γ Values for the Nitrogen(1)-Ethane(2) System at 130.0 K

TABLE 5.10

Comparison of the Experimental and Calculated γ Values for the Nitrogen(1)-Methane(2) System at 169.9 K

P(psia)	x_1	γ_1		$\Delta\gamma_1$	γ_2		$\Delta\gamma_2$
		Expt.	Calc.		Expt.	Calc.	
361.6	0.0231	1.9584	1.9561	-0.0023	1.0014	1.0002	-0.0012
373.5	0.0301	1.9436	1.9400	-0.0036	1.0014	1.0005	-0.0009
402.1	0.0579	1.8871	1.8797	-0.0074	1.0025	1.0021	-0.0004
458.6	0.0888	1.8268	1,8193	-0.0075	1.0044	1.0046	0.0002
500.7	0.1183	1.7612	1.7669	0.0057	1.0074	1.0081	0.0007
559.8	0.1632	1.6939	1.6955	0.0016	1.0139	1.0148	0.0009
640.0	0.2352	1.5823	1.5966	0.0143	1.0287	1.0301	0.0014
671.0	0.2683	1.5385	1.5556	0.0171	1.0368	1.0392	0.0024
687.0	0.2885	1.5153	1.5318	0.0165	1.0416	1.0454	0.0038
703.0	0.3032	1.5007	1.5150	0.0143	1.0450	1.0503	0.0053
702.0	0.3057	1.4983	1.5122	0.0139	1.0454	1.0510	0.0056
714.0	0.3159	1.4900	1.5007	0.0107	1.0474	1.0546	0.0072

TABLE 5.11

Comparison of the Experimental and Calculated γ Values for the Nitrogen(1)-Methane(2) System at 130.0 K

P(psia)	x_1	γ_1		$\Delta\gamma_1$	γ_2		$\Delta\gamma_2$
		Expt.	Calc.		Expt.	Calc.	
108.6	0.0756	1.5995	1.6080	0.0085	1.0028	1.0081	0.0053
148.0	0.1623	1.4863	1.3586	-0.1277	1.0127	1.0306	0.0179
204.7	0.2745	1.3614	1.1918	-0.1696	1.0380	1.0681	0.0301
252.3	0.3790	1.2647	1.1176	-0.1471	1.0757	1.1013	0.0256
302.1	0.5022	1.1727	1.0772	-0.0955	1.1413	1.1329	-0.0084
347.2	0.6052	1.1127	1.0583	-0.0544	1.2179	1.1582	-0.0597
382.0	0.6600	1.0869	1.0493	-0.0376	1.2676	1.1752	-0.0924
405.7	0.7111	1.0668	1.0406	-0.0262	1.3186	1.1965	-0.1221
443.8	0.8222	1.0404	1.0209	-0.0195	1.4197	1.2770	-0.1427
462.4	0.8447	1.0392	1.0169	-0.0223	1.4220	1.3020	-0.1200
482.3	0.8750	1.0418	1.0118	-0.0300	1.3823	1.3425	-0.0398

TABLE 5.12

Comparison of the Experimental and Calculated γ Values
or the Methane(1)-Ethane(2) System at 169.9 K

P(psia)	x_1	γ_1		$\Delta\gamma_1$	γ_2		$\Delta\gamma_2$
		Expt.	Calc.		Expt.	Calc.	
20.8	0.0388	1.3729	1.3720	-0.0009	1.0003	1.0004	0.0001
66.8	0.1855	1.2962	1.6911	-0.0051	1.0078	1.0081	0.0003
100.5	0.2820	1.2474	1.2437	-0.0037	1.0197	1.0197	0.0000
143.1	0.4038	1.1886	1.1870	-0.0016	1.0460	1.0451	-0.0009
181.2	0.5213	1.1355	1.1346	-0.0009	1.0882	1.0868	-0.0014
215.5	0.6731	1.0745	1.0728	-0.0017	1.1823	1.1825	0.0002
249.1	0.7775	1.0397	1.0374	-0.0023	1.2905	1.2929	0.0024
284.0	0.8638	1.0175	1.0153	-0.0022	1.4257	1.4279	0.0022
310.9	0.9308	1.0059	1.0042	-0.0017	1.5754	1.5723	-0.0031

TABLE 5.13

Comparison of the Experimental and Calculated γ Values
for the Methane(1)-Ethane(2) System at 130.0 K

P(psia)	x_1	γ_1		$\Delta\gamma_1$	γ_2		$\Delta\gamma_2$
		Expt.	Calc.		Expt.	Calc.	
19.3	0.3067	1.2352	1.2346	-0.0006	1.0263	1.0283	0.0020
18.2	0.3119	1.2324	1.2318	-010006	1.0273	1.0294	0.0021
26.0	0.4589	1.1584	1.1576	-0.0008	1.0684	1.0706	0.0022
29.3	0.5015	1.1386	1.1379	-0.0007	1.0856	1.0877	0.0021
34.5	0.5996	1.0964	1.0958	-0.0006	1.1373	1.1394	0.0021
39.4	0.6938	1.0610	1.0604	-0.0006	1.2079	1.2103	0.0024
44.4	0.8027	1.0281	1.0275	-0.0006	1.3274	1.3303	0.0029
47.8	0.8571	1.0157	1.0151	-0.0006	1.4090	1.4115	0.0025

TABLE 5.14

Comparison of the Experimental and Calculated γ Values for the Nitrogen(1)-Ethane(2) System at 169.9 K

P(psia)	x_1	γ_1		$\Delta\gamma_1$	γ_2		$\Delta\gamma_2$
		Expt.	Calc.		Expt.	Calc.	
51.1	0.0125	6.5223	6.5208	-0.0015	1.0002	1.0002	0.0000
111.0	0.0214	6.4150	6.4136	-0.0014	1.0005	1.0005	0.0000
207.7	0.0402	6.1944	6.1916	-0.0028	1.0016	1.0016	0.0000
302.8	0.0751	5.8010	5.7996	-0.0014	1.0055	0.0055	0.0000
411.1	0.0960	5.5744	5.5744	0.0000	1.0093	1.0093	0.0000
493.0	0.1132	5.3939	5.3939	0.0000	1.0132	1.0132	0.0000
577.0	0.1330	5.1916	5.1928	0.0012	1.0186	1.0186	0.0000
667.2	0.1422	5.1004	5.1015	0.0011	1.0216	1.0216	0.0000
795.5	0.1772	4.7621	4.7621	0.0000	1.0351	1.0349	-0.0002
734.2	0.1898	4.6452	4.6441	-0.0011	1.0406	1.0409	0.0003

TABLE 5.15

Comparison of the Experimental and Calculated γ Values
for the Nitrogen(1)-Ethane(2) System at 130.0 K

P(psia)	x_1	γ_1		$\Delta\gamma_1$	γ_2		$\Delta\gamma_2$
		Expt.	Calc.		Expt.	Calc.	
49.0	0.0219	5.4853	5.4853	0.0000	1.0005	1.0005	0.0000
124.0	0.0569	5.1204	5.1109	-0.0095	1.0032	1.0035	0.0003
210.3	0.1033	4.6698	4.6612	-0.0086	1.0113	1.0116	0.0003
282.8	0.1357	4.3762	4.3732	-0.0030	1.0205	1.0202	-0.0003
263.4	0.1370	4.3642	4.3621	-0.0021	1.0207	1.0207	0.0000
328.6	0.1469	4.2786	4.2776	-0.0010	1.0242	1.0240	-0.0002
295.1	0.1545	4.2131	4.2140	0.0009	1.0268	1.0268	0.0000
358.4	0.1678	4.1020	4.1049	0.0029	1.0323	1.0320	0.0003
395.3	0.1844	3.9655	3.9728	0.0073	1.0399	1.0392	-0.0007
425.5	0.1899	3.9219	3.9301	0.0082	1.0426	1.0418	-0.0008
525.5	0.2770	3.2825	3.3029	0.0104	1.0917	1.0988	0.0071

TABLE 5.16.A

Comparison of the Experimental and Calculated γ Values for the Nitrogen(1)-Methane(2)-Ethane(3) System at 130.0 K

	P(psia)	x_1	x_2	γ_1		$\Delta\gamma_1$
				Expt.	Calc.	
1.	101.3	0.0511	0.1613	4.3912	7.6584	3.2672
2.	101.5	0.0544	0.3820	3.4070	4.1773	0.7703
3.	101.4	0.0646	0.5064	2.8655	2.9951	0.1296
4.	100.7	0.0649	0.5409	2.7425	2.7785	0.0360
5.	101.8	0.0650	0.5300	2.7798	2.8424	0.0626
6.	100.2	0.0669	0.4646	3.0017	3.2495	0.2478
7.	100.0	0.0705	0.7168	2.1528	1.9251	-0.2277
8.	200.8	0.1018	0.1673	3.9273	5.4348	1.5075
9.	199.3	0.1215	0.3642	3.0049	3.1571	0.1522
10.	200.0	0.1224	0.3896	2.9086	2.9900	0.0814
11.	200.0	0.1628	0.4986	2.3224	2.1235	-0.1989
12.	200.3	0.2163	0.6485	1.6979	1.5042	-0.1937
13.	301.1	0.2169	0.1836	3.0256	2.9267	-0.0989
14.	300.1	0.2525	0.3323	2.3473	2.0489	-0.2984
15.	300.1	0.2660	0.3123	2.3363	2.0188	-0.3175
16.	505.0	0.2820	0.0164	3.1902	2.9281	-0.2621
17.	402.3	0.3039	0.1540	2.6045	2.1996	-0.4049
18.	302.5	0.3078	0.3729	1.9812	1.6757	-0.3055
19.	400.0	0.3762	0.2352	2.0292	1.6346	-0.3946
20.	301.1	0.4038	0.4796	1.4242	1.2714	-0.1528
21.	403.2	0.5601	0.2416	1.3957	1.1871	-0.2086
22.	403.0	0.6057	0.2792	1.2381	1.1149	-0.1232

TABLE 5.16.B

Comparison of the Experimental and Calculated γ Values for The Nitrogen(1)-Methane(2)-Ethane(3) System at 130.0 K

	γ_2		$\Delta\gamma_2$	γ_3		$\Delta\gamma_3$
	Expt.	Calc.		Expt.	Calc.	
1.	1.2587	1.1512	-0.1075	1.0192	1.0483	0.0291
2.	1.1454	1.0836	-0.0618	1.0812	1.1334	0.0522
3.	1.0848	1.0426	-0.0422	1.1595	1.2283	0.0688
4.	1.0718	1.0356	-0.0362	1.1855	1.2556	0.0701
5.	1.0757	1.0375	-0.0382	1.1772	1.2471	0.0699
6.	1.0993	1.0484	-0.0509	1.1352	1.2040	0.0688
7.	1.0177	1.0051	-0.0126	1.3976	1.4616	0.0640
8.	1.2009	1.0405	-0.1604	1.0414	1.1109	0.0695
9.	1.0959	1.0055	-0.0904	1.1380	1.2507	0.1127
10.	1.0855	1.0037	-0.0818	1.1553	1.2704	0.1151
11.	1.0264	0.9818	-0.0446	1.3282	1.4717	0.1435
12.	0.9969	0.9906	-0.0063	1.8519	1.8866	0.0347
13.	1.0909	0.9222	-0.1687	1.1379	1.3349	0.1970
14.	1.0230	0.9464	-0.0766	1.3253	1.5607	0.2354
15.	1.0212	0.9417	-0.0795	1.3307	1.5813	0.2506
16.	1.1010	0.8409	-0.2601	1.1058	1.3597	0.2539
17.	1.0419	0.8936	-0.1483	1.2351	1.5403	0.3052
18.	0.9963	0.9625	-0.0338	1.5483	1.7933	0.2450
19.	0.9941	0.9422	-0.0519	1.5151	1.8731	0.3580
20.	1.0196	1.0368	0.0172	2.5871	2.3914	-0.1957
21.	1.0196	1.0848	0.0652	2.7492	2.7465	-0.0027
22.	1.0860	1.1539	0.0679	3.8817	3.0956	-0.7861

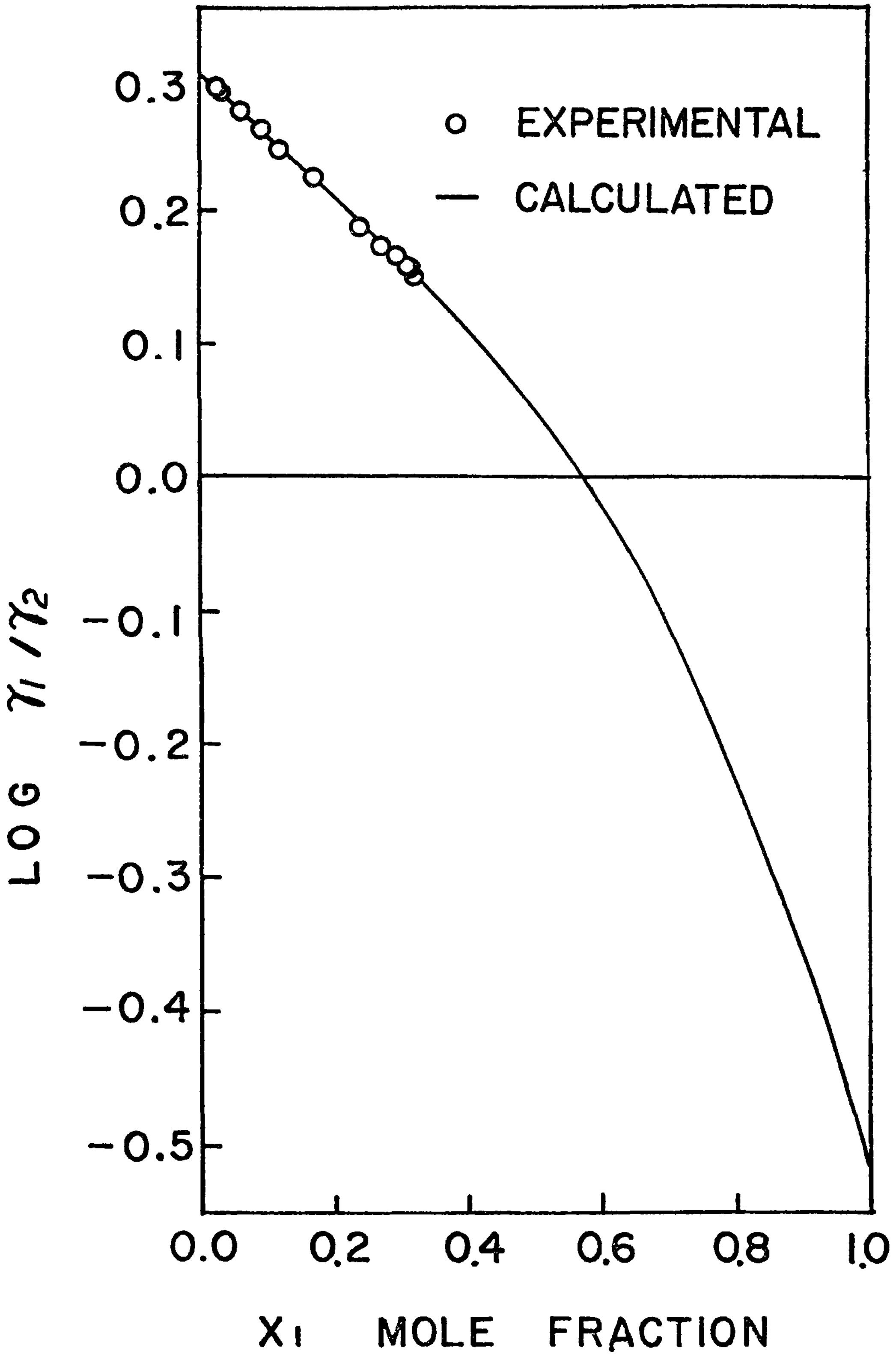


Figure 5.12 Area-Test for the Nitrogen(1)-Methane(2) System at 169.9 K

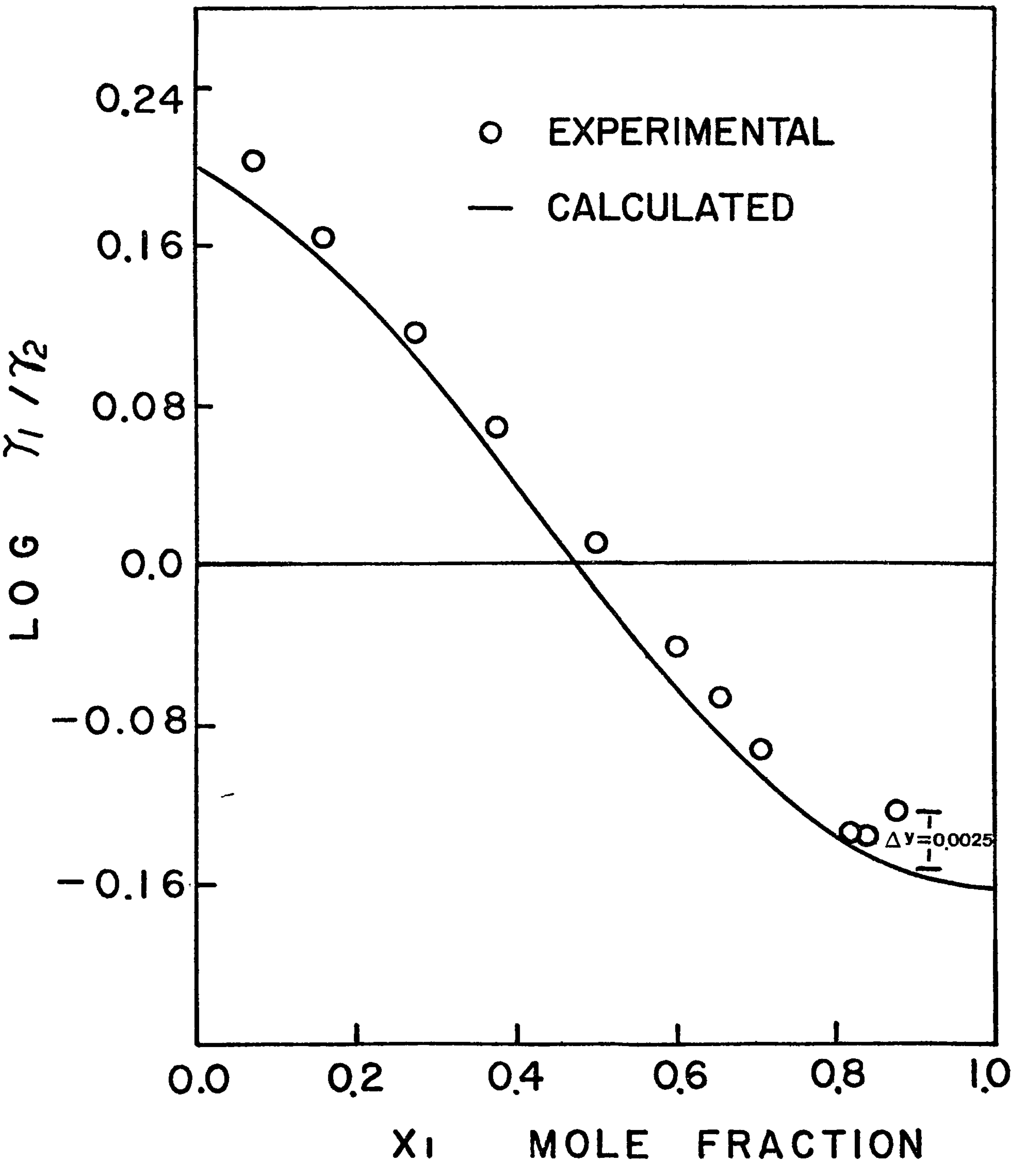


Figure 5.13 Area-Test for the Nitrogen(1)-Methane(2) System at 130.0 K

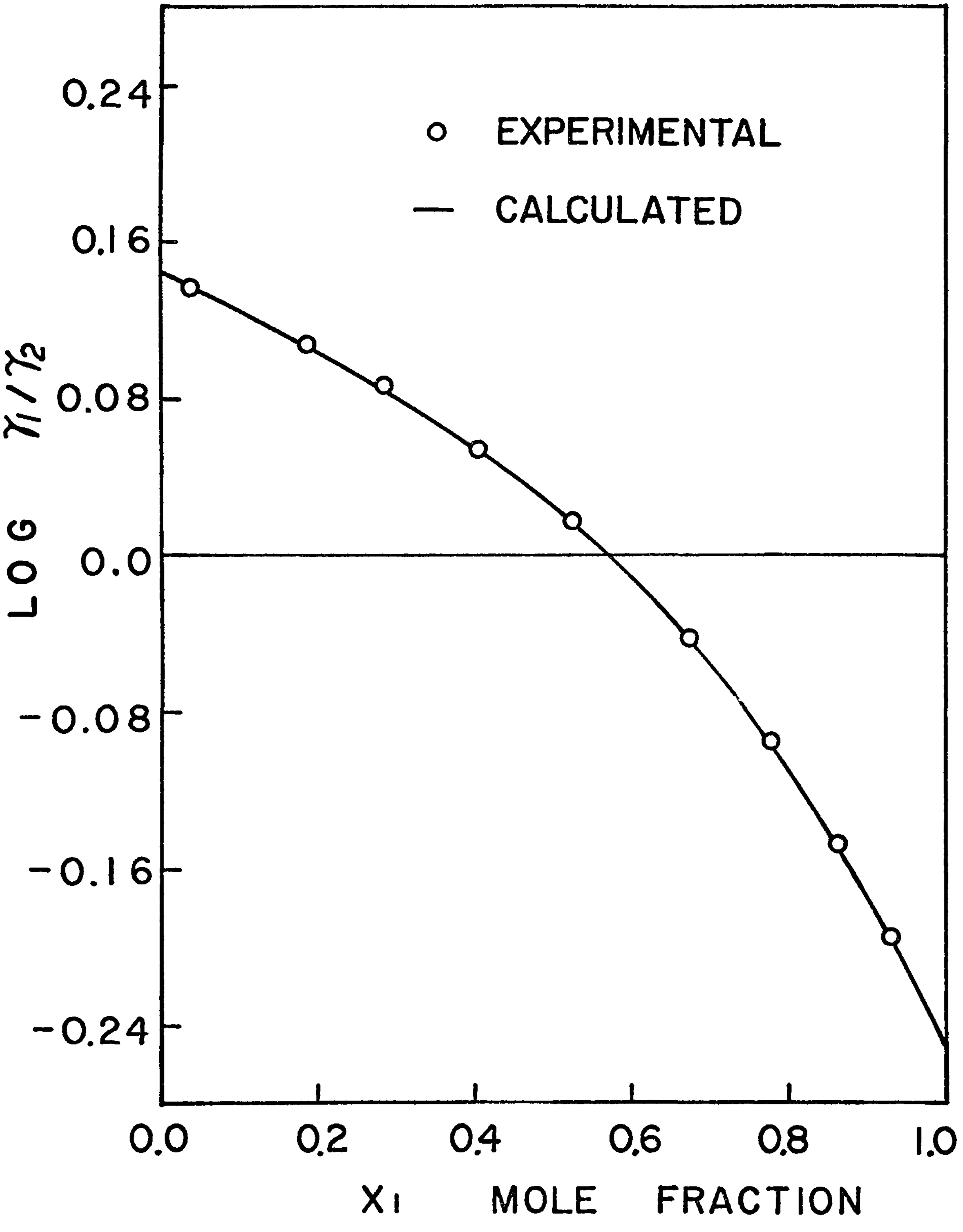


Figure 5.14 Area-Test for the Methane(1)-Ethane(2) System at 169.9 K

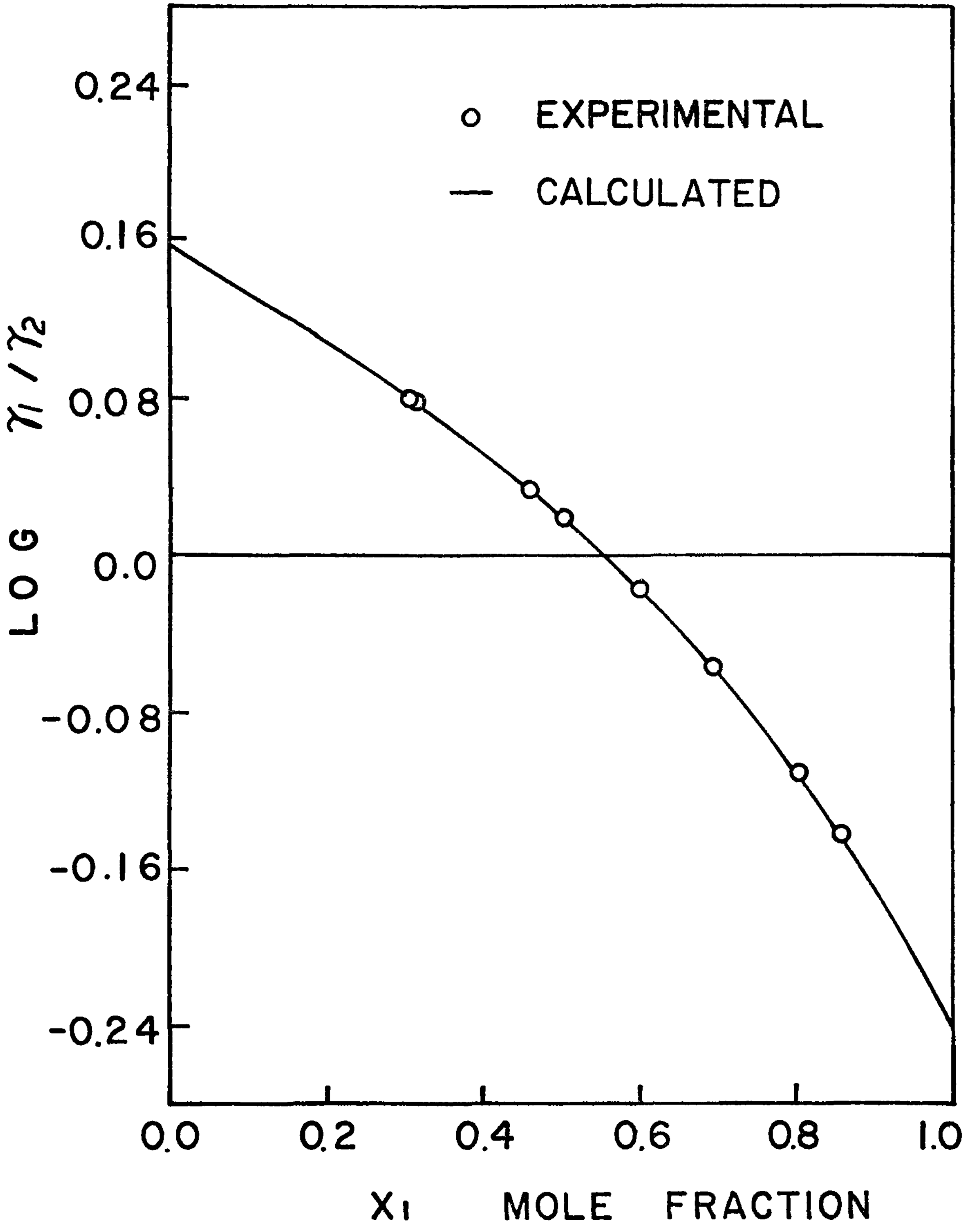


Figure 5.15 Area-Test for the Methane(1)-Ethane(2) System at 130.0 K

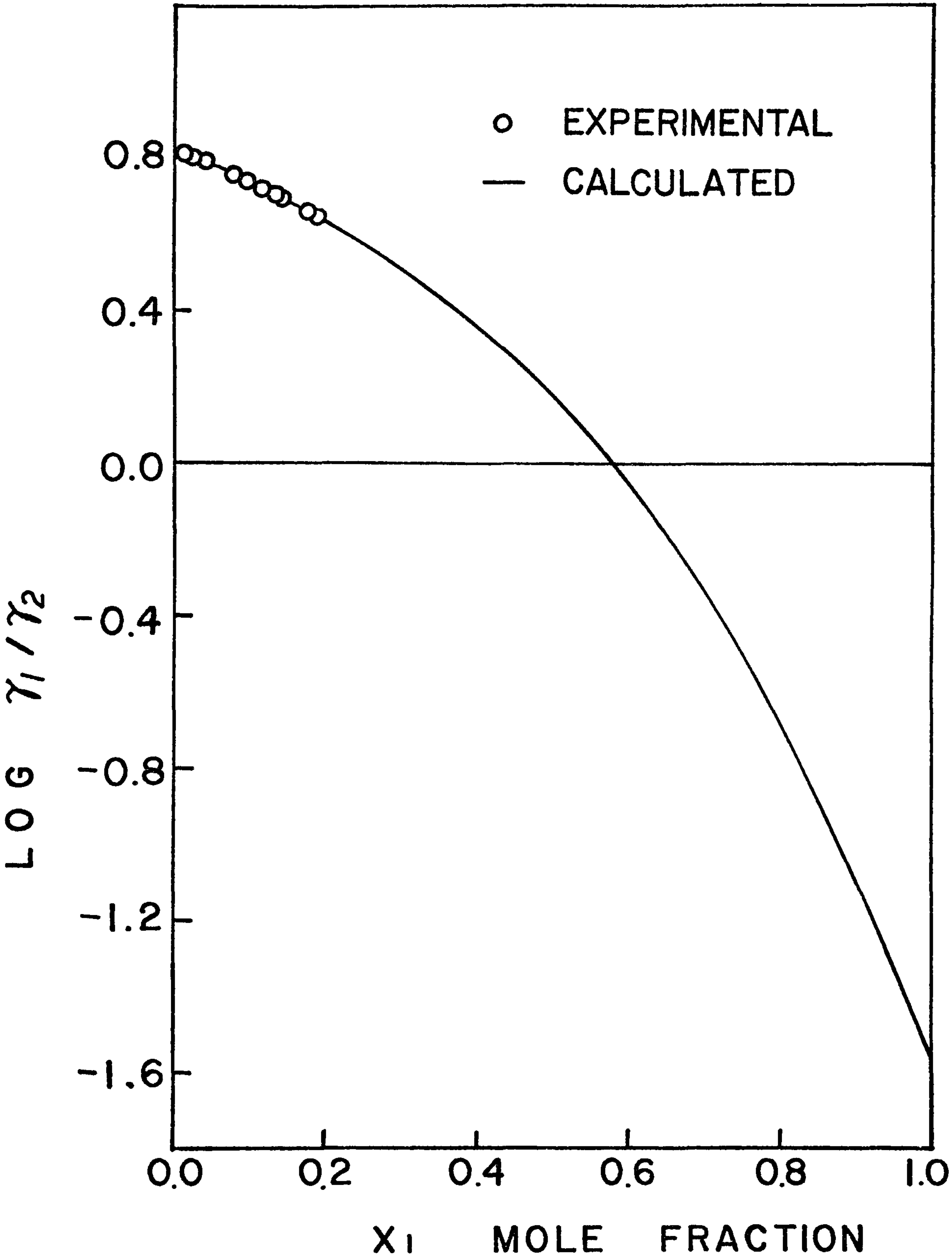


Figure 5.16 Area-Test for the Nitrogen(1)-Ethane(2) System at 169.9 K

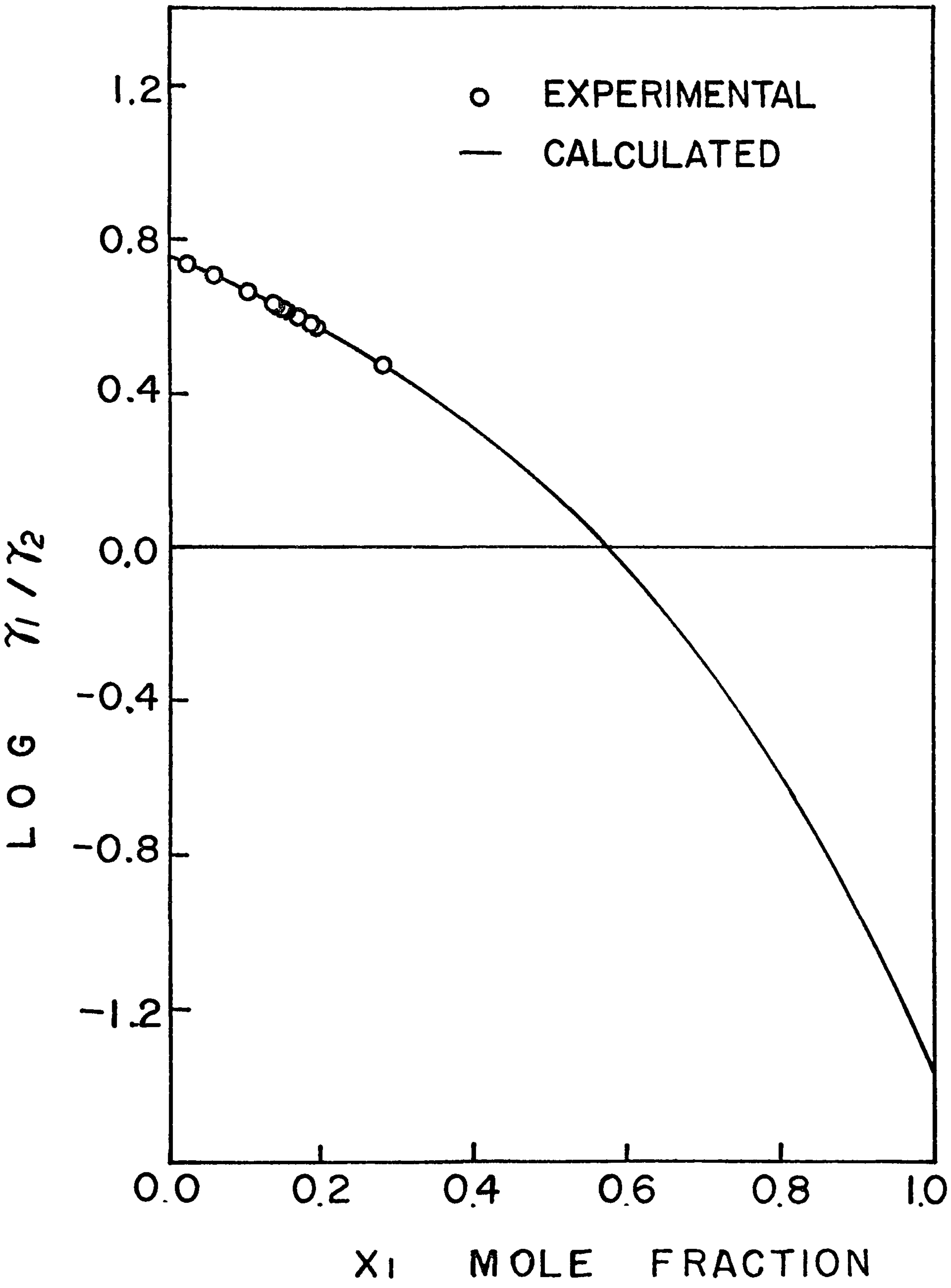


Figure 5.17 Area-Test for the Nitrogen(1)-Ethane(2) System at 130.0 K

For the binary nitrogen-methane system at 169.9 K and the nitrogen-ethane system at 169.9 and 130.0 K, the vapor-liquid phase equilibria were tested by Equation (3.42). The numerical values obtained of the left hand side and right hand side of Equation (3.42) for the above systems are as follows:

System	L.H.S.	R.H.S.
Nitrogen-Methane at 169.9 K	0.0230	0.0230
Nitrogen-Ethane at 169.9 K	0.0173	0.0173
Nitrogen-Ethane at 130.0 K	0.0407	0.0407

The above listed results confirm the consistency of the data for the nitrogen-methane system at 169.9 K and the nitrogen-ethane system at both temperatures.

CHAPTER 6

SUMMARY AND CONCLUSIONS

Vapor-liquid phase equilibria were measured at 169.9 and 130.0 K for the nitrogen-methane, methane-ethane and nitrogen-ethane binary systems and at 130.0 K for the nitrogen-methane-ethane ternary system by means of a modified recirculation apparatus. A modified Redlich-Kwong equation of state proposed by Kato et al. (103) was applied to predict the vapor-liquid equilibria.

6.1 EXPERIMENTAL WORKS

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

The magnetic pump newly introduced in the circulation loop, which was completely submerged in the liquid bath thus always kept at constant temperature, was essentially the same as that used by Kobayashi and coworkers (59) at Rice University and was so effective that the equilibrium could be approached within half an hour. In addition to reducing the time needed to achieve equilibrium, accurate equilibrium data can be secured because of the constant temperature recirculation of the vapor.

A mixer of 250 mm long and 10 mm O.D. was also added to the liquid sampling line. Manual mixing of the liquid phase was achieved by occasionally moving a ring magnet along the stainless steel, which kept the composition of the gasified-liquid for the liquid phase sample uniform.

The vapor and liquid samples were analyzed by a gas chromatograph with a thermal conductivity detector. The gas chromatograph was calibrated against mixtures with known compositions before the analyses.

Experimental vapor-liquid equilibrium data for the nitrogen-methane, methane-ethane, nitrogen-ethane binary systems at 169.9 and 130.0 K and the nitrogen-methane-ethane ternary system at 130.0 K were obtained by means of the modified equipment. The pressure range was from 18.2 to 795.5 psia.

Two liquid phases were observed in the nitrogen-ethane binary and the nitrogen-methane-ethane ternary systems at 130.0 K. The ethane concentration was found to be richer in the bottom layer (BL) than in the top layer (TL). This phenomenon is of considerable importance to the separation of the main components from the natural gas.

The experimental data of the nitrogen-methane and methane-ethane binary systems obtained in this study are compared with those of Kidnay et al. (50) and Wichterle and Kobayashi (59). It has been shown in Figure 5.3 that the agreement between these data is quite good. As shown in Figures 5.4 and 5.5, the present data are lower than those of Wichterle (59). These are very reasonable because the temperatures in this study, 169.9 and 130.0 K, are lower than those of Wichterle, 172.04 and 130.37 K. Though there is no comparison of the nitrogen-ethane binary equilibrium results with other data, it is believed that the present data are quite reasonable ($|\Delta y|_{AV} = 0.0067$ at 169.9 K and $|\Delta y|_{AV} = 0.0030$ at 130.0 K).

It is seen from Chapter 2, the forced-recirculation apparatus is suitable for obtaining phase equilibrium data at low temperatures and high pressures.

6.2 PREDICTION AND CORRELATION OF EQUILIBRIUM DATA

The modified Redlich-Kwong equation of state can successfully predict the vapor-liquid composition as well as the total pressure at given temperature. It has been shown that the method is applicable to the nitrogen-methane, methane-ethane, nitrogen-ethane and nitrogen-methane-ethane systems at low temperatures.

The simplicity of the R-K equation, which is a very important factor to be considered for applying it in computer work, and the ability to predict mixture properties by knowing pure component properties and binary interaction constants K_{ij} make it the most commonly used and valuable equation of state.

The liquid phase activity coefficients were calculated by means of the modified R-K equation. They were further correlated by the Redlich-Kister equations. The data were tested and were thermodynamically consistent.

Future work on the nitrogen-ethane system can be done at higher pressures to obtain experimental data covering all the possible concentration range.

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APPENDIX I

COMPARISON OF THE CALCULATED RESULTS WITH THE DATA FROM LITERATURES (50,59)

TABLE A.1

Comparison of the Calculated Results with the Experimental Data Reported by Kidnay et al. (50) for the Nitrogen(1)-Methane(2) System at 170.0 K

x_1	P (psia)		y_1	
	Expt.	Calc.	Expt.	Calc.
0.0082	352.0	359.5	0.0291	0.0264
0.0189	368.3	374.3	0.0652	0.0582
0.0276	380.1	386.3	0.0889	0.0820
0.0399	398.4	403.0	0.1219	0.1130
0.0495	412.4	416.0	0.1458	0.1352
0.0688	440.3	441.6	0.1875	0.1752
0.1115	499.4	496.8	0.2593	0.2463
0.1562	559.7	551.8	0.3135	0.3012
0.2001	616.7	603.1	0.3519	0.3406
0.2469	671.7	653.4	0.3743	0.3698
0.2729	701.0	679.6	0.3784	0.3808
0.2915	710.0	695.9	0.3798	0.3877
0.3066	716.3	708.5	0.3801	0.3901

TABLE A.2

Comparison of the Calculated Results with the Experimental Data Reported by Kidnay et al. (50) for the Nitrogen(1)-Methane(2) System at 130.0 K

x_1	P (psia)		y_1	
	Expt.	Calc.	Expt.	Calc.
0.0097	60.3	64.0	0.1098	0.0944
0.0186	66.0	69.0	0.1862	0.1660
0.0292	72.9	76.1	0.2640	0.2372
0.0641	95.6	97.1	0.4339	0.4019
0.0926	113.1	113.6	0.5201	0.4895
0.1547	148.0	148.1	0.6316	0.6097
0.2188	182.5	181.5	0.7018	0.6837
0.2941	218.1	218.4	0.7508	0.7402
0.3822	258.9	258.8	0.7932	0.7849
0.4512	289.0	288.9	0.8166	0.8112
0.5516	331.4	331.4	0.8463	0.8422
0.7077	402.3	398.3	0.8860	0.8826
0.7828	439.6	433.2	0.9054	0.9018
0.8676	487.1	477.5	0.9285	0.9259
0.9017	505.0	497.6	0.9393	0.9368

TABLE A.3

Comparison of the Calculated Results with the Experimental Data Reported by Wichterle (59) for the Methane(1)-Ethane(2) System at 172.04 and 130.37 K

T (K)	x_1	P (psia)		y_1	
		Expt.	Calc.	Expt.	Calc.
172.04	0.0685	30.8	32.4	0.7681	0.7804
	0.1087	45.5	47.1	0.8469	0.8502
	0.2050	81.0	81.6	0.9161	0.9159
	0.3164	120.0	120.4	0.9434	0.9454
	0.5024	180.0	182.7	0.9656	0.9676
	0.7082	247.5	249.5	0.9788	0.9809
	0.8609	299.0	301.9	0.9878	0.9892
	0.9175	324.0	324.1	0.9921	0.9928
	0.9513	339.5	338.9	0.9953	0.9954
130.37	0.4319	28.0	26.5	0.9948	0.9949
	0.5989	35.0	34.7	0.9965	0.9969
	0.7788	43.3	42.9	0.9984	0.9984
	0.8935	48.6	48.3	0.9992	0.9992

TABLE A.4

A Summary of the Calculated Results for the Binary Systems from Other Works (50, 59)

System	T (K)	$\lvert\Delta P\rvert_{AV}$ (psia)	$\lvert\Delta P/P\rvert$ X100%	$\lvert\Delta y\rvert_{AV}$	K_{12}	Ω_a	Ω_b
Nitrogen(1)-Methane(2)	170.0	8.8421	1.593	0.0084	0.025	0.41614	0.08571 (1)
Kidnay (52)						0.42312	0.08629 (2)
	130.0	2.7306	1.627	0.0137	0.015	0.42695	0.08660 (1)
						0.40149	0.08449 (2)
Methane(1)-Ethane(2)	172.04	1.3900	1.482	0.0027	0.0007	0.42827	0.08670 (1)
Wichterle (61)						0.42780	0.08667 (2)
	130.37	0.9472	6.575	0.0037	0.007	0.41274	0.08543 (1)
						0.40325	0.08464 (2)

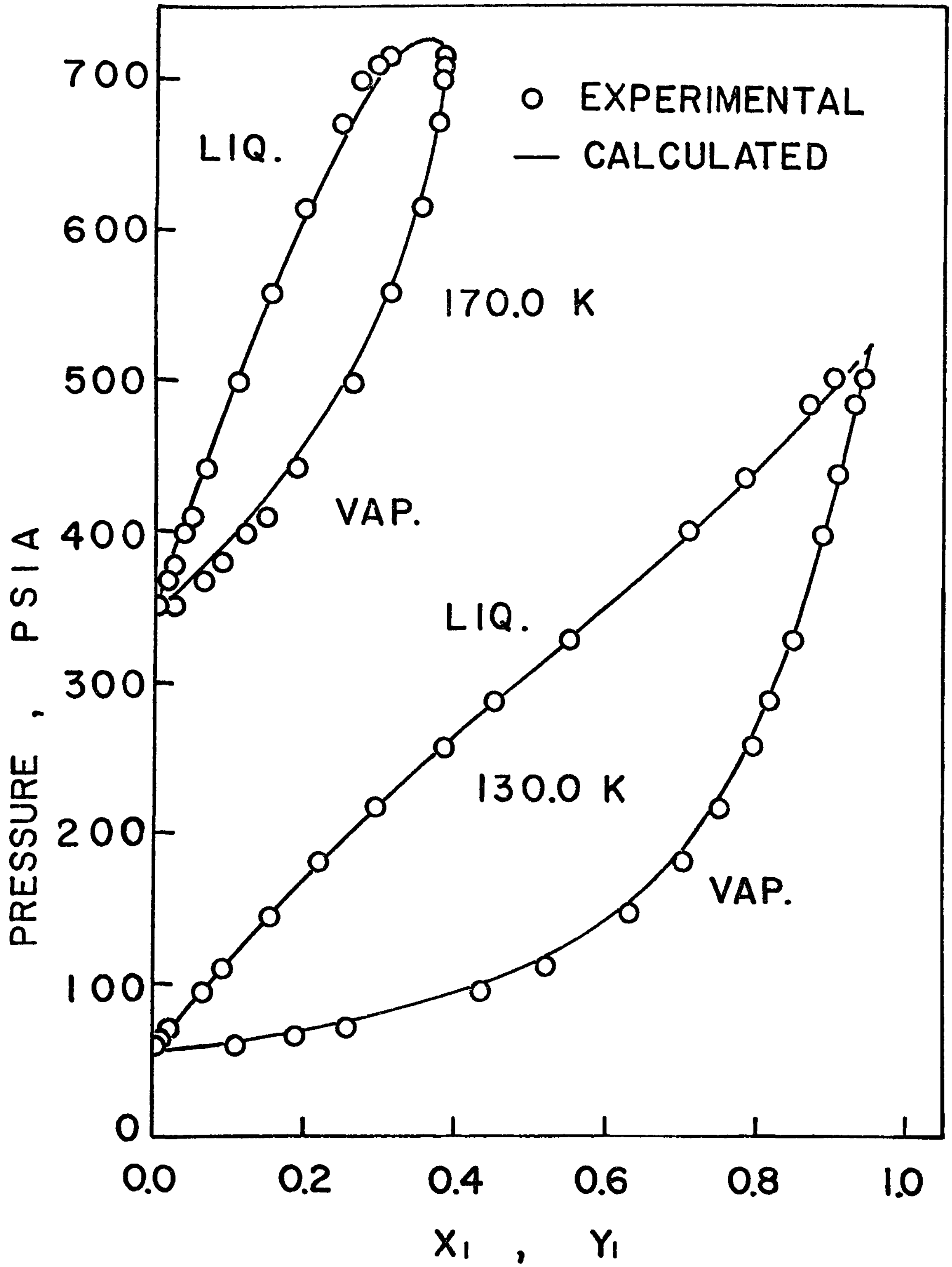

Figure A.1 Comparison of the Calculated Results with the Experimental Data Reported by Kidnay et al. (50) for the Nitrogen(1)-Methane(2) System at 170.0 and 130.0 K

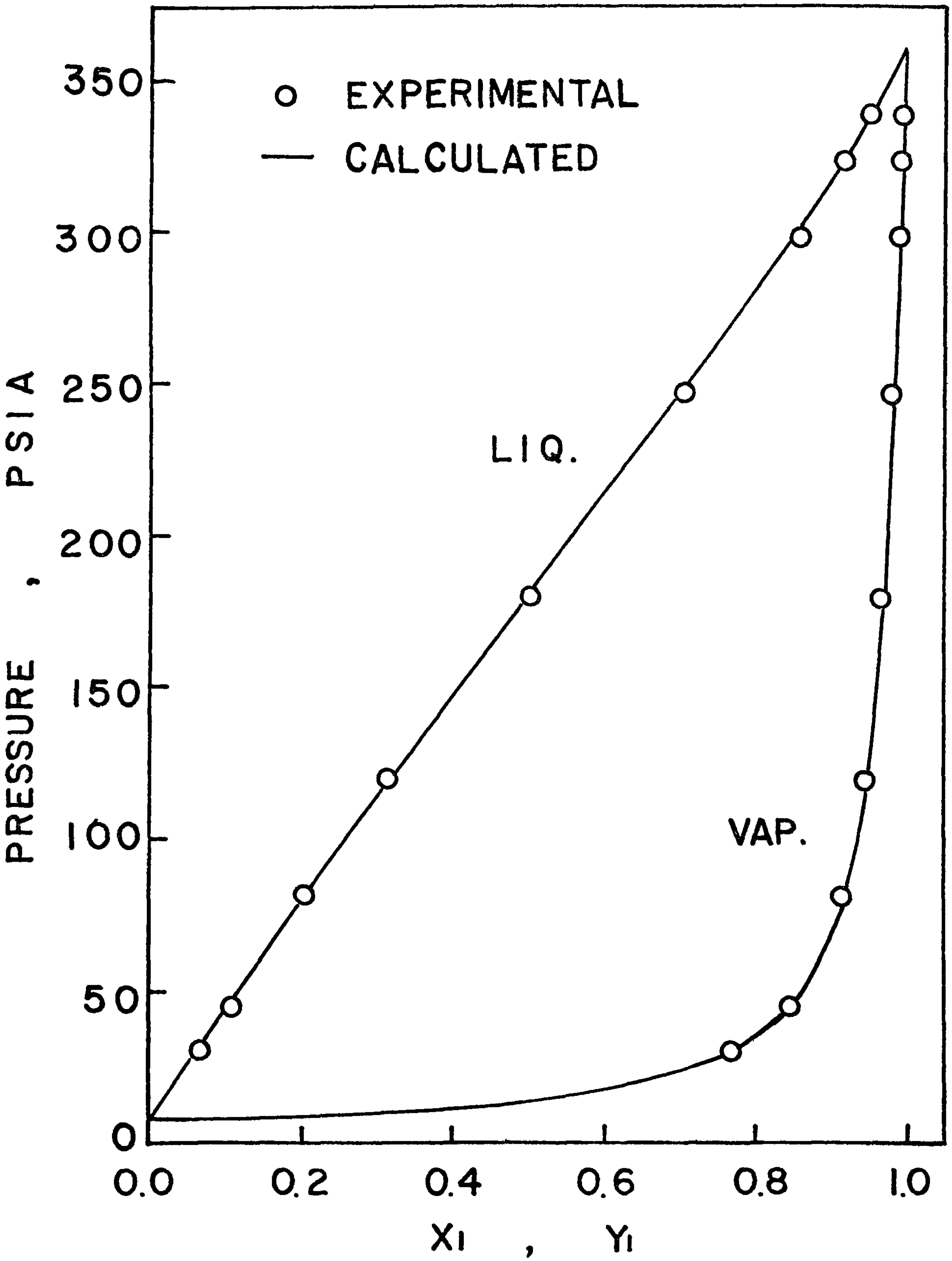

Figure A.2 Comparison of the Calculated Results with the Experimental Data Reported by Wichterle (59) for the Methane(1)-Ethane(2) System at 172.04 K

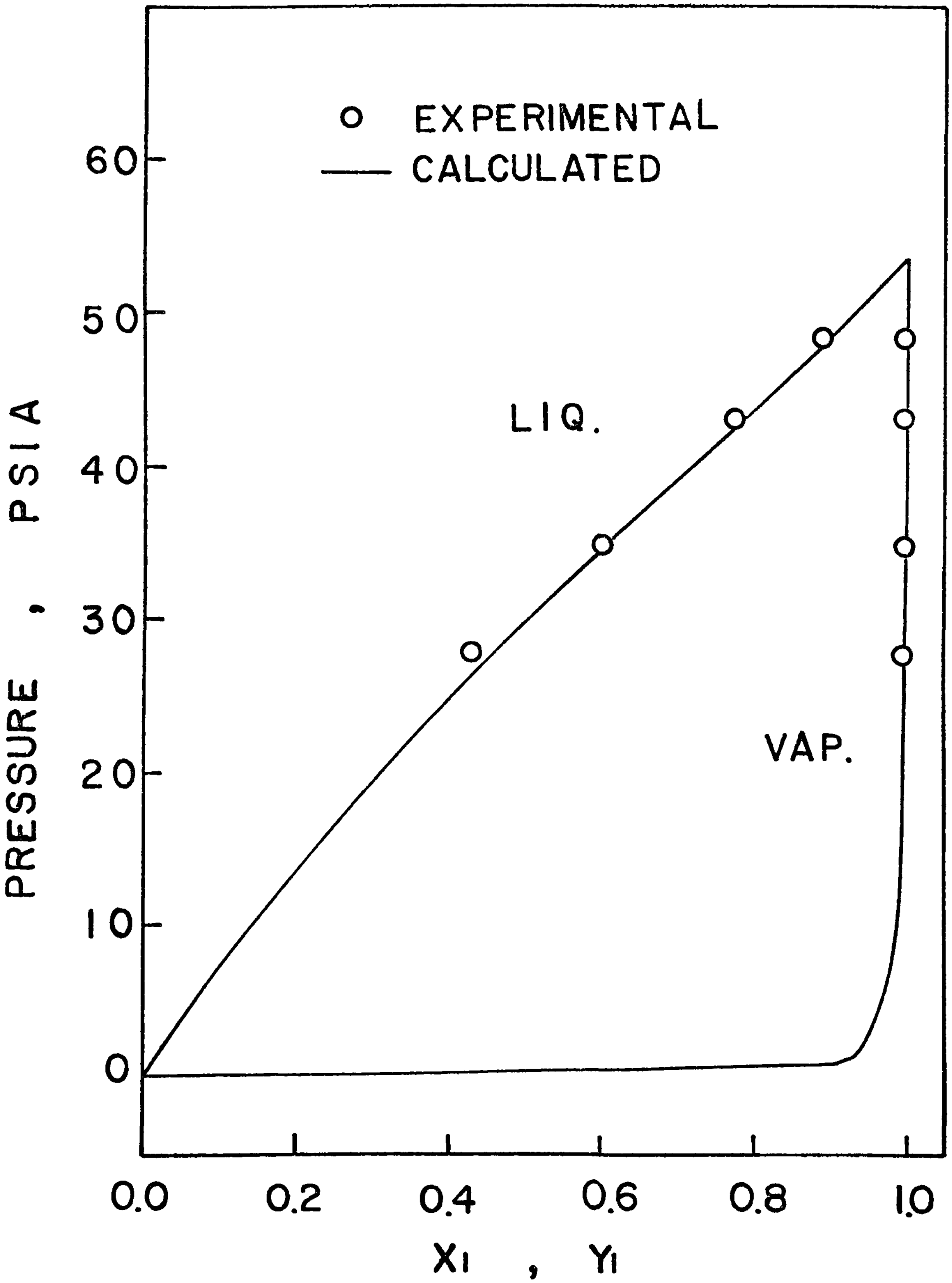

Figure A.3 Comparison of the Calculated Results with the Experimental Data Reported by Wichterle (59) for the Methane(1)-Ethane(2) System at 130.37 K

APPENDIX II

PRESSURE CONVERSIONS TO SI UNITS

1 psia = 6894.757 Pa

1 atm = 101,325 Pa

1 bar = 100,000 Pa

1 torr = 133.3244 Pa

where

Pa = N m^{-2}

psia = pound/in^2

atm = atmosphere

torr = (1/760) atm

APPENDIX III

COMPUTER PROGRAM USED IN THIS STUDY

```
C      *********************************************************************
C
C      THIS PROGRAM IS USED TO CALCULATE ALL THE RELATED PARAMETERS AND
C      TO PREDICT THE T-P-X-Y RELATIONSHIP
C
C      GOLDEN SECTION SEARCH TECHNIQUE IS APPLIED TO FIND THE K12 VALUE
C
C      CORRELATED COEFFICIENTS AND GENERALIQED EQUATIONS ARE APPLIED TO
C      FIND THE WAII,WBII.
C
C
C      NING-WU WANG
C      DEPARTMENT OF CHEMICAL ENGINEERING
C      UNIVERSITY OF OTTAWA
C      JUNE 1977
C      SUBROUTINES PYINIT, PCALC, YVCALC, SUPT, CUBEQN AND EQNRK ARE REQUIRE
C
C      *********************************************************************
       DIMENSION TITLE (20) ,PCII(5),VCII(5),TCII(5),W(5),WAII(5), WBII(5
     1),COMPA(5), COMPB(5), COMPC(5), FREFER(5), PHI(5), PHIV(5),
     2 PHIJ(5), PHIK(5), P1(5), PTVOL(5), PPVOL(5), VVV(5), CORRL(5,5),
     3 X(5), Y(5),          VC(5), TC(5), INDEXS(5),      EXG(5), EXGF(5),
     4 YX(5), VVL(5), DY(5), PVOL(5), GAMMB(5), GAMMA(5), AMOLWT(5)
     5 , PC(5), XX(50, 5), YY(50,5) ,PP(50), EXG1(5), COMPD(5)
            DIMENSION A0(20),A1(20),A2(20),A3(20),B(20),TR(5) ,S(5)
       DIMENSION EDYAV(5),DYAV(5) ,EDY(5), INDEX(5),DK(5),EDK(5)
       DIMENSION  AC0(5),AC1(5),AC2(5),AC3(5),CC0(5),CC1(5),CC2(5),
     1CC3(5),BC0(5),BC1(5),BC2(5),DC0(5),DC1(5),DC2(5),RKE(5),RKC(5)
       COMMON /FIRST/ TC, PC, VCII, W, AMOLWT, T, P, R, NCOMP, NQNTUM,TR
     1    /SECOND/ Z, A, MTYPE
     2 / THIRD/ PCII, TCII, WAII, WBII, PSI, PP, XX, YY, IJK, KIJ, NOI,
     3 ITER,K, CORRL, EXGT, PPVUL, PHI, PHIV, VV, VVL1, DV, P1, PPP, Y
     4  / FOURTH / SDP, EP, DP, SSDY, SDY, SDV,        PHIK, GAMMA, EXG,
     5 X, SUMY, GAMMB, PG, RT, PF, FREFER, YX, DY, EXG1,SLNA12,SLNB12
     6 / FIFTH / DPAV,EDYAV,EDY, EDP, EDPAV, DYAV
     7/ SIXTH / PN
       M=2
       M1=M+2
       M2=M+1
       M4=2*(M1+M2)
       A00= 0.0201
       A10=-0.1769
       A20=-0.1497
       A01= 0.8255
       A11= 0.3079
       A02=-0.0950
       READ(5,9102)(A0(I),A1(I),A2(I),A3(I), I=1,M4)
 9102  FORMAT(4F15.8)
    1  READ (5,100) (TITLE (I), I = 1, 19)
 100   FORMAT (19A4)
       WRITE (6,200) (TITLE (I), I = 1, 19)
  200  FORMAT (1H1, 19A4)
       READ (5,101) NCOMP, NQNTUM, IJK, R
  101  FORMAT (3I5, F10.4)
       IF ( NCOMP .LE. 0) GO TO 1
C      NCOMP MUST BE GREATER THAN ZERO
C      NCOMP: NO. OF COMPONENTS IN THE MIXTURE
C      R: GAS CONSTANT
```

```
C     IJK: CONTROL VARIABLF
C     WRITE HEADINGS
      WRITE (6, 203)
  203 FORMAT (1H0, 'INPUT DATA:'//)
      WRITE ( 6, 201)
  201 FORMAT ( 1H0,6X, 'PCII', 8X, 'VCII', 8X, 'TCII', 8X, 'W', 11X, 'WAI
     1I', 8X, 'WBII', 4X, 'COMPONENT'//)
      DO 2 I = 1, NCOMP
      READ (5, 102) PCII(I), VCII(I), TCII(I), W(I), WAII(I), WBII(I),
     1COMPA(I), COMPB(I), COMPC(I),COMPD(I)
  102 FORMAT (4F8.4,F8.5,F9.6,4A4)
    2 WRITE (6,202) PCII(I), VCII(I), TCII(I), W(I), WAII(I), WBII(I),
     1COMPA(I), COMPB(I), COMPC(I),COMPD(I)
  202 FORMAT (1H , 6F12.6, 3X, 4A4)
C     IT         T
C     0          DEGREE K
C     1          DEGREE F
C     2          DEGREE C
      READ (5, 106) T, PSI, IT
  106 FORMAT(2F10.4, 5I2)
      IF ( IT .EQ. 1) T = (T - 32.)*5./9. + 273.15
      IF ( IT .EQ. 2) T = T + 273.15
  707 WRITE(6, 204) T, PSI
  204 FORMAT(1H0,'T=', F5.1, 1X, 'K', 3X, 'PSI=', F7.2, 1X, 'PSIA'//
     1 7X, 'PRESSURE', 8X, 'X1', 10X, 'X2', 10X, 'Y1', 10X, 'Y2'//)
C     IJK            P
C      0             PSIA
C      1             ATM
      READ (5, 104) IJK, KIJ, CINI, CFIN
  104 FORMAT (2I5, 2F10.4)
      READ(5,115)  FR
  115 FORMAT(F10.4)
C     PP IS EXPFRIMENTAL VALUE OF PRESSURE
      NCOMP1 = NCOMP - 1
      NOI = 1
   32 READ (5, 105) PP(NOI),(XX(NOI,J),J=1,NCOMP1),(YY(NOI,J),J=1,NCOMP1
     1)
C 105 FORMAT(6F10.0)
  105 FORMAT(6F10.0)
C 105 FORMAT(F14.8,F10.9,F14.13)
C     IF NONTUM IS DIFFERENT FROM ZERO, XX IS K VALUE, X = Y/K
      IF ( NONTUM .NE. 0) XX(NOI,1) = YY(NOI,1)/XX(NOI,1)
      IF ( IJK .EQ. 1) PP(NOI) = PP(NOI)*14.697
      SX = 0.0
      SY = 0.0
      IF (PP(NOI)) 33, 34, 34
   34 DO 4 J = 1, NCOMP1
      SY = SY + YY(NOI, J)
    4 SX = SX + XX(NOI, J)
      XX(NOI, NCOMP) = 1.0 - SX
      YY(NOI, NCOMP) = 1.0 -SY
      WRITE (6, 205) NOI, PP(NOI), (XX(NOI,J),J=1,NCOMP),(YY(NOI,J),
     1 J = 1, NCOMP)
  205 FORMAT(1H ,I3,2X,F8.2,1X,6(6X,F6.4))
      NOI = NOI + 1
      GO TO 32
   33 NOI = NOI - 1
  400 READ (5, 151) BK6
```

```
  151 FORMAT(5F10.4)
      READ(5,685) AC0(1),AC1(1),AC2(1),AC3(1),BC0(1),BC1(1),BC2(1),
     1CC0(1),CC1(1),CC2(1),CC3(1),DC0(1),DC1(1),DC2(1)
      READ(5,685) AC0(2),AC1(2),AC2(2),AC3(2),BC0(2),BC1(2),BC2(2),
     1CC0(2),CC1(2),CC2(2),CC3(2),DC0(2),DC1(2),DC2(2)
  685 FORMAT(4F20.8)
          DO 1218 I = 1, NCOMP
      TR(I)=T/TCII(I)
      IF(TR(I).LE.0.85) INDEX(I)=1
      IF(TR(I).GT.0.85.AND.TR(I).LE.1.0) INDEX(I)=2
      IF(TR(I).GT.1.0.AND.TR(I).LE.1.6) INDEX(I)=3
      IF(TR(I).GT.1.6) INDEX(I)=4
      INDEX(I)=3
 1218 INDEXS(I)=INDEX(I)
          WRITE (6, 1245) (TR(I), I = 1, NCOMP)
 1245 FORMAT(1H0,'TR(1)=',F6.4,'   TR(2)=',F6.4,'   TR(3)=',F6.4)
      WRITE (6, 209)
  209 FORMAT (1H0, 'RESULT:'///
     11X,'**************************************************************
     2*********************************************************')
      DO 671 I = 1, NOI
      IF ( XX(NOI,1) .LT. .0 .OR. XX(NUI,1) .GT. 1.0) GO TC 1
  671 CONTINUE
      ITG=0
 9999 ICG=0
      IF(ICG.EQ.0)  GO TO 3100
 2400 WRITE(6,681)
  681 FORMAT(1H0,'FIND WAII, WBII USING GENERALIZED EQUATIONS'//1X,
     1********************************************')
      DO  2111  JJJ= 1, NCOMP
      IAX=INDEX(JJJ)
      GO TO (2500,2600,2700,2800),IAX
 2500 II=2*(M+2)+1
      IFF=2*(M+2)+(M+1)
      WAII(JJJ)=0.0
      WBII(JJJ)=0.0
      DO 2490 IN=II,IFF
      I=IN-II+1
      B(I)=A0(IN)+A1(IN)*W(JJJ)+A2(IN)*W(JJJ)**2
      JN=M+1+IN
      J=M+1+I
 2490 B(J)=A0(JN)+A1(JN)*W(JJJ)+A2(JN)*W(JJJ)**2
      DO 2480 I=1,M2
      JJ=I-1
      J=I+3
      WAII(JJJ)=WAII(JJJ)+B(I)*TR(JJJ)**JJ
 2480 WBII(JJJ)=WBII(JJJ)+B(J)*TR(JJJ)**JJ
      GO TO 2000
 2600 II=1
      IFF=M1
      DO 2590 IN=II,IFF
      I=IN-II+1
      B(I)=A0(IN)+A1(IN)*W(JJJ)+A2(IN)*W(JJJ)**2+A3(IN)*W(JJJ)**3
      JN=M+2+IN
      J=M+2+I
 2590 B(J)=A0(JN)+A1(JN)*W(JJJ)+A2(JN)*W(JJJ)**2+A3(JN)*W(JJJ)**3
      TR1=1.-TR(JJJ)
      WAII(JJJ)=B(1)+B(2)*TR1+B(3)*TR1**(1./3.)+B(4)*TR1**(2./3.)
```

```
      WBII(JJJ)=B(5)+B(6)*TR1+B(7)*TR1**(1./3.)+B(8)*TR1**(2./3.)
      GO TO 2000
 2700 TR1=1.-TR(JJJ)
      S0=1.+TR1*(A00+A10*TR1+A20*TR1**2)
      S1=TR1*(A01+A11*TR1)
      S2=TR1*A02
      Q=S0+S1*W(JJJ)+S2*W(JJJ)**2
      WAII(JJJ)=0.42748*Q**2.5
      WBII(JJJ)=0.08664*Q
      JJJ1=JJJ+1
      INDEX(JJJ1)=3
      KIJ=5
      GO TO 2000
 2800 Q=10.**((1.-SQRT(TR(JJJ)))*(0.28+0.665*W(JJJ)-0.2*(1.-TR(JJJ))))
      WAII(JJJ)=0.42748*Q**2.5
      WBII(JJJ)=0.08664*Q
 2000 CONTINUE
      WRITE(6,677) JJJ,WAII(JJJ),JJJ,WBII(JJJ),JJJ,INDEX(JJJ)
  677 FORMAT(1H0,'WAII(',I1,')=',F7.5,5X,'WBII(',I1,')=',F7.5,5X,'INDEX(
     1',I1,')=',I1)
 2111 CONTINUE
      ICG=ICG+1
      GO TO 98
 3100 WRITE(6,682)
  682 FORMAT(1H0,'FIND WAII, WBII USING CORRELATED COEFFICIENTS'//1X,
     1******************************************')
      DO 3111  JJJ=1,NCOMP
      IAX=INDEX(JJJ)
      GO TO (3200,3300,3400,3500), IAX
 3200 WAII(JJJ)=BC0(JJJ)+BC1(JJJ)*TR(JJJ)+BC2(JJJ)*TR(JJJ)**2
      WBII(JJJ)=DC0(JJJ)+DC1(JJJ)*TR(JJJ)+DC2(JJJ)*TR(JJJ)**2
      GO TO 3110
 3300 TR1=1.0-TR(JJJ)
      WAII(JJJ)=AC0(JJJ)+AC1(JJJ)*TR1+AC2(JJJ)*TR1**(1./3.)
     1+AC3(JJJ)*TR1**(2./3.)
      WBII(JJJ)=CC0(JJJ)+CC1(JJJ)*TR1+CC2(JJJ)*TR1**(1./3.)
     1+CC3(JJJ)*TR1**(2./3.)
      GO TO 3110
 3400 TR1=1.0-TR(JJJ)
      S0=1.+TR1*(A00+A10*TR1+A20*TR1**2)
      S1=TR1*(A01+A11*TR1)
      S2=TR1*A02
      Q=S0+S1*W(JJJ)+S2*W(JJJ)**2
      WAII(JJJ)=0.42748*Q**2.5
      WBII(JJJ)=0.08664*Q
      JJJ1=JJJ+1
      INDEX(JJJ1)=3
      ICG=1
      KIJ=5
      GO TO 3110
 3500 Q=10.**((1.-SQRT(TR(JJJ)))*(0.28+0.665*W(JJJ)-0.2*(1.-TR(JJJ))))
      WAII(JJJ)=0.42748*Q**2.5
      WBII(JJJ)=0.08664*Q
 3110 WRITE(6,677) JJJ,WAII(JJJ),JJJ,WBII(JJJ),JJJ,INDEX(JJJ)
 3111 CONTINUE
      ICG=ICG+1
   98 KIJ=KIJ-5
      DO 599 I=1,NCOMP
```

```
  589 INDEX(I)=INDEXS(I)
   99 KIJ = KIJ + 5
      IF ( KIJ .GE. 6) GO TO 1
  401 WRITE (6, 207) IJK, KIJ, CINI, CFIN
  207 FORMAT (1H0, 3X, 'IJK=', I1, 3X, 'KIJ=', I1, 3X, 'CINI=', F7.4
     1 3X, 'CFIN=', F 7.4 //)
C
C     GOLDEN SECTION SEARCH TECHNIQUE FOR FINDING THE VALUE K12 SUCH
C     THAT SDP IS MINIMUM
C
      TOL = .00005
      TOL = .0001
      I1 = 0
      I2 = 0
      I3 = 0
      I4 = 0
      BK4 = CFIN
      BK1 = CINI
      NOS = 1
      IF (I1 .EQ. 1) GO  TO 4002
      PPP = PSI
      CALL PYINIT (BK1)
      DO 510 K = 1, NOI
      CALL PCALC
  510 CONTINUE
      PSI = PPP
      DP1 = SDP
      DY1 = SSDY
      I1 = 1
 4002 IF (I2 .EQ. 1) GO TO 3002
      BK2 = BK1 + (3.0 - SQRT(5.0))/2.0*(BK4-BK1)
      PPP = PSI
      CALL PYINIT (BK2)
      DO 501  K = 1, NOI
      CALL PCALC
  501 CONTINUE
      PSI = PPP
      DP2 = SDP
      DY2 = SSDY
      I2 = 1
C3002 IF (ABS(DP2 - DP1).LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7001
C3002 IF (ABS(DY2 - DY1).LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7001
 3002 IF (ABS(DP2 - DP1).LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7001
C5000 IF (DP2 .GT. DP1) GO TO 4001
 5000 IF (DP2 .GT. DP1) GO TO 4001
 4000 IF (I3 .EQ. 1) GO TO 3003
      BK3 = BK4 - (3.0 - SQRT(5.0))/2.0 * (BK4 - BK1)
      PPP = PSI
      CALL PYINIT (BK3)
      DO 503  K = 1, NOI
      CALL PCALC
  503 CONTINUE
      PSI = PPP
      DP3 = SDP
      DY3 = SSDY
      I3 = 1
C3003 IF (ABS(DP3 - DP2).LE. TOL .OR. ABS(BK3-BK2) .LE. TOL) GO TO 7002
C3003 IF (ABS(DY3 - DY2).LE. TOL .OR. ABS(BK3-BK2) .LE. TOL) GO TO 7002
```

```
 3003 IF (ABS(DP3 - DP2).LE. TOL .OR. ABS(BK3-BK2) .LE. TOL) GO TO 7002
C     IF (DP3 .GT. DP2) GO TO 4003
      IF (DP3 .GT. DP2) GO TO 4003
      IF (I4 .EQ. 1) GO TO 3004
      PPP = PSI
      CALL PYINIT ( BK4 )
      DO 504  K = 1, NOI
      CALL PCALC
  504 CONTINUE
      PSI = PPP
      DP4 = SDP
      DY4 = SSDY
      I4 = 1
C3004 IF (ABS(DP4 - DP3).LE. TOL .OR. ABS(BK4-BK3) .LE. TOL) GO TO 7003
C3004 IF (ABS(DY4 - DY3).LE. TOL .OR. ABS(BK4-BK3) .LE. TOL) GO TO 7003
 3004 IF (ABS(DP4 - DP3).LE. TOL .OR. ABS(BK4-BK3) .LE. TOL) GO TO 7003
C     IF (DP3 .GT. DP4) GO TO 4004
      IF (DP3 .GT. DP4) GO TO 4004
      BK1 = BK2
      DP1 = DP2
      DY1 = DY2
      BK2 = BK3
      DP2 = DP3
      DY2 = DY3
      I3 = 0
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 4000
 4001 BK4 = BK2
         DP4 = DP2
      DY4 = DY2
      I4 = 1
      I2 = 0
      I3 = 0
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 4002
 4003 BK4 = BK3
      DP4 = DP3
      DY4 = DY3
      BK3 = BK2
      DP3 = DP2
      DY3 = DY2
      I4 = 1
      I2 = 0
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 4002
 4004 BK1 = BK3
      DP1 = DP3
      DY1 = DY3
      I2 = 0
      I3 = 0
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 4002
 7001 BK4 = BK2
      DP4 = DP2
```

```
      DY4 = DY2
      I4 = 1
      I3 = 0
 5001 BK2 = BK1 + (3.0 - SQRT(5.0))/2.0 * (BK4 - BK1)
      PPP = PSI
      CALL PYINIT (BK2)
      DO 502  K = 1, NOI
      CALL PCALC
  502 CONTINUE
      PSI = PPP
      DP2 = SDP
      DY2 = SSDY
      I2 = 1
C     IF (ABS(DP2 - DP1).LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7000
C     IF (ABS(DY2 - DY1).LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7000
      IF (ABS(DP2 - DP1).LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7000
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 5000
 7002 BK1 = BK2
      DP1 = DP2
      DY1 = DY2
      I1 = 1
      BK4 = BK3
      DP4 = DP3
      DY4 = DY3
      I4 = 1
      I3 = 0
      GO TO 5001
 7003 BK1 = BK3
      DP1 = DP3
      DY1 = DY3
      I1 = 1
      I3 = 0
      GO TO 5001
 8000 WRITE (6, 2004) BK1,BK2,BK3,BK4,DP1,DP2,DP3,DP4,DY1,DY2,DY3,DY4
 2004 FORMAT(1H0,'K12 DID NOT CONVERGE,  THE FOLLOWING RESULT IS NOT OPT
     1IMUM '/8(2X,E13.7)/4(2X,E13.7))
 7000 WRITE ( 6, 2005) BK4, DP4, DY4, NOS
 2005 FORMAT (1H0,' THE VALUE OF K12 IS ', F10.8, '    THE CORRESPONDING
     1 D.P. IS ',E14.8/' AND THE CORRESPONDING D.Y. IS ',E14.8, ' NO. OF
     2 ITERATIONS = ', I4//1X,'----------------------------------------
     3--------------------------------')
      ITA=0
  298 CALL PYINIT(BK4)
          WRITE(6, 301) ((CORRL(I,J), I =1, NCOMP),J=1, NCOMP)
  301 FORMAT (1H0,'CORRL(I)=',5X,9F10.5///)
      EDYAV(3)=0.0
      DYAV(3) = 0.0
      EDPAV = 0.0
      DPAV = 0.0
      EDYAV(1) = 0.0
      EDYAV(2) = 0.0
      DYAV(1) = 0.0
      DYAV(2)=0.0
       SDP=0.0
       SSDY=0.0
       SDV=0.0
```

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LEVEL  21                        MAIN                  DATE = 77203            11/47/21

      DO 500  K=1,NOI
      WRITE(6,228)  K,PP(K)
  228 FORMAT(1H0,I2,' RUN', F10.1,' PSIA',5X,'=========================
     1==============================================================')
      CALL PCALC
      IF ( YY(K, 1) .LE. 0.0) GO TO 500
      WRITE(6,210) T,PP(K), P, DP, EDP
  210 FORMAT(1H0, T18,'T=',F5.1,' K', T39,'PP=', F5.1,' PSIA', T62,'P=',
     1       F5.1,' PSIA', T83,'DP=',F8.4, T102,'EDP=',E12.6,'%')
      CALL YVCALC
      DO 40 I=1,NCOMP
   40 WRITE(6,226) I,X(I), I,YY(K,I), I,Y(I),I,DY(I),I,EDY(I)
  226 FORMAT(1H0,T15,'X(',I1,')=',F6.4,T36,'YY(',I1,')=',F6.4,T59,'Y(',I
     1       1,')=',F6.4,T80,'DY(',I1,')=',F6.4,T99,'EDY(',I1,')=',E12.6
     2       ,'%')
      DO 41 I=1,NCOMP
      RKE(I)=YY(K,I)/X(I)
      RKC(I)=Y(I)/X(I)
      DK(I) =RKC(I)-RKE(I)
      EDK(I)=DK(I)/RKE(I)*100.0
   41 WRITE(6,211) I,RKE(I),I,RKC(I),I,DK(I),I,EDK(I)
  211 FORMAT(1H0,T36,'KK(',I1,')=',F8.5, T59,'K(',I1,')=',F8.5, T80,
     1       'DK(',I1,')=',F8.5,T99,'EDK(',I1,')=',E12.6,'%')
      DO 26 I=1,NCOMP
   26 WRITE(6,214) I,PPVOL(I),I,PHI(I),I,PHIV(I),I,PHIK(I)
  214 FORMAT(1H0,T11,'PPVOL(',I1,')=',F9.4,T35,'PHI(',I1,')=',F7.4, T56,
     1       'PHIV(',I1,')=',F7.4,T78,'PHIK(',I1,')=',F7.4)
      DO 29 I=1,NCOMP
   29 WRITE(6,217) I,GAMMA(I),I,EXG(I),I,GAMMB(I),I,EXG1(I)
  217 FORMAT(1H0,T14,'GA(',I1,')=',E14.7,T55,'LN GA(',I1,')=',E14.7,
     1//     T14,'GB(',I1,')=',E14.7,T55,'LN GB(',I1,')=',E14.7)
      WRITE(6,229) SLNB12, VV, SUMY, ITER, SLNA12
  229 FORMAT(1H0, T15,'LN GB(1)/GB(2)=', E14.7, T61, 'VV=', F9.4, T81,
     1       'SUMY=', F6.4, T101, 'ITER=', I2//T15,'LN GA(1)/GA(2)=',
     2       E14.7)
      WRITE(6,225)  EXGT
  225 FORMAT(1H0, T15,'8.314*T*(X(1)*LN GB(1)+X(2)*LN GB(2)+X(3)*LN GB(3
     1))=',  E14.7)
  500 CONTINUE
      WRITE(6,306) SDP,DPAV,EDPAV
  306 FORMAT(1H0,'STATISTICS OF THE SYSTEM',  5X,'++++++++++++++++++++++
     1++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++'
     2       /// T38,'SDP=',F5.1, T81,'DPAV=',F8.4, T100,'EDPAV=',E12.6,
     3       '%')
      DO 31 I=1,NCOMP
   31 WRITE(6,218) I,DYAV(I),I,EDYAV(I)
  218 FORMAT(1H0, T78,'DYAV(',I1,')=',F8.6, T97,'EDYAV(',I1,')=',E12.6,
     1       '%')
            SSDY = SSDY/NOI /NCOMP
      SSDYA = SSDY*NOI
      WRITE(6,300)  BK4,SSDY,SSDYA
  300 FORMAT(1H0,T11,'K12=',F8.6,T81,'DYAV=',F8.6,T97,'SUM OF DY=',F8.6/
     2       //1X,'****************************************************
     3*****************************************************************
     4')
      PSI = PPP
      ITA=ITA+1
      IF(ITA.EQ.1) GO TO 297
```

```
LEVEL  21                        MAIN                  DATE = 77203            11/47/21

      IF(ICG.EQ.1) GO TO 2400
      GO TO 99
  297 WRITE(6,224)
  224 FORMAT(1H0,'CALCULATION WITH KNOWN INTERACTION CONSTANT  K12:'//1X
     1,'------------------------------------------------')
      BK4=BK6
      GO TO 298
        END
```

```
C
C     ******************************************************************
      SUBROUTINE PYINIT ( BK )
C
C     ******************************************************************
C     PREDICT P-X-Y CURVE
C     MODIFIED REDLICH-KWUNG EQUATION OF STATE IS USED FOR MULTI-
C     COMPONENT SYSTEMS CALCULATION FROM THE PURE COMPONENT PROPERTIES
C     ONE OF THE COMPCNENTS IS AT ITS HYPERCRITICAL STATE
C     ******************************************************************
C     DECEMBER 10, 1974
C     WHO KEE CHUNG, DEPT. OF CHEMICAL ENGINEERING, U. OF C.
      DIMENSION TITLE (20) ,PCII(5),VCII(5),TCII(5),W(5),WAII(5), WBII(5
     1),COMPA(5), COMPB(5), COMPC(5), FREFER(5), PHI(5), PHIV(5),
     2 PHIJ(5), PHIK(5), P1(5), PTVOL(5), PPVOL(5), VVV(5), CORRL(5,5),
     3 X(5), Y(5),        VC(5), TC(5), TR(5),         EXG(5), EXGF(5),
     4 YX(5), VVL(5), DY(5), PVOL(5), GAMMB(5), GAMMA(5), AMOLWT(5)
     5 , PC(5), XX(50, 5), YY(50,5) ,PP(50), EXG1(5), COMPD(5)
      COMMON /FIRST/ TC, PC, VCII, W, AMOLWT, T, P, R, NCOMP, NONTUM,TR
     1   /SECOND/ Z, A, MTYPE
     2 / THIRD/ PCII, TCII, WAII, WBII, PSI, PP, XX, YY, IJK, KIJ, NOI,
     3 ITER,K, CORRL, EXGT, PPVOL, PHI, PHIV, VV, VVL1, DV, P1, PPP, Y
     4 / FOURTH / SDP, EP, DP, SSDY, SDY, SDV,       PHIK, GAMMA, EXG,
     5 X, SUMY, GAMMB, PG, RT, PF, FREFER, YX, DY, EXG1,SLNA12,SLNB12
      SDP = 0.0
      SDV = 0.0
      SSDY = 0.0
C     PF=REFERENCE PRESSURE IN PSIA
C     1 ATM = 14.697 PSIA
      PF=1000./14.697
  111 PPP=PSI
      PSI = PSI/14.697
        DO 3 I = 1, NCOMP
    3 CORRL(I,I) = 0.0
      CORRL(1, 2) = BK
      CORRL(2,1) = CORRL(1,2)
C     SET UP THE NECESSARY INFORMATION FOR THE SUPPORT SUBROUTINE
      RETURN
      END
```

```
C     ***************************************************************
      SUBROUTINE  PCALC
C     ***************************************************************
      DIMENSION TITLE (20) ,PCII(5),VCII(5),TCII(5),W(5),WAII(5), WBII(5
     1),COMPA(5), COMPB(5), COMPC(5), FREFER(5), PHI(5), PHIV(5),
     2 PHIJ(5), PHIK(5), P1(5), PTVOL(5), PPVOL(5). VVV(5), CORRL(5.5),
     3 X(5), Y(5),          VC(5), TC(5),                EXG(5), EXGF(5),
     4 YX(5), VVL(5), DY(5), PVOL(5), GAMMB(5), GAMMA(5), AMULWT(5)
     5 , PC(5), XX(50, 5), YY(50,5) ,PP(50), EXG1(5), COMPD(5)
      DIMENSION EDYAV(5),DYAV(5) ,EDY(5)
      COMMON /FIRST/ TC, PC, VCII, W, AMOLWT, T, P, R, NCOMP. NONTUM
     1   /SECOND/ Z, A, MTYPE
     2 / THIRD/ PCII, TCII, WAII, WBII, PSI, PP, XX, YY, IJK, KIJ, NJI,
     3 ITER,K, CORRL, EXGT, PPVOL, PHI, PHIV, VV, VVL1, DV, P1, PPP, Y
     4 / FOURTH / SDP, EP. DP. SSDY, SDY, SDV,          PHIK, GAMMA, EXG,
     5 X, SUMY, GAMMB, PG, RT, PF, FREFER, YX, DY, EXG1,SLNA12,SLNB12
     6 / FIFTH / DPAV,EDYAV,EDY, EDP, EDPAV, DYAV
     7/ SIXTH / PN
      ITER = 0
      DO 8 I = 1, NCOMP
      PC(I) = PCII(I)
       VC(I) = VCII(I)
    8 TC(I) = TCII(I)
      RT = R * T
      P = PF
C     USE TO CALCULATE THE MOLAL VOLUMN VL, FUGACITY COEFFICIENT PHI,
C     PARTIAL MOLAL VOLUMN PPVOL AND FUGACITY FREFER OF LIQUID PHASE
C     FOR PURE COMPONENT AT REFERENCE PRESSURE
   35 DO 9 I = 1, NCOMP
      DO 10 J = 1, NCOMP
   10 X(J) = 0.0
      X(I) = 1.0
      CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
    9 FREFER(I) = PHI(I) * P
C     *****************************
C     USE TO CALCULATE VAPORMOLE FRACTIONS Y(I) FOR MIXTURE ASSUMING
C     CORRESPONDING FUGACITY COEFFICIENTS PHIV(I) ARE 1. ( INITIAL GUESS)
      P=PP(K)/14.697*1.02
       DO 7 J = 1, NCOMP
       PHIV(J) = 1.0
    7 X(J) = XX(K,J)
      SUMY = 0.0
      CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL. X, 1, KIJ)
      DO 37 I = 1, NCOMP
      Y(I) = PHI(I) * X(I)/PHIV(I)
   37 SUMY = SUMY + Y(I)
C     *************************
      DO 11 I = 1, NCOMP
   11 Y(I) = Y(I) / SUMY
      SUMY1 = SUMY
      CALL SUPT (VV, PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
C     SET UP THE LOOP TO FIND Y(I), SUCH THAT SUMY IS EQUAL TO SUMY1
C     ,THE SUMY OBTAINED IN IMMEDIATE PRECEDING CALCULATION, I. E. TEST
C     FOR STABILITY BY CHANGING Y(I) AND TEST FOR SUMY = 1.0
   25 CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL. X, 1, KIJ)
   17 SUMY = 0.0
      DO 12 J = 1, NCOMP
      Y(J) = PHI(J) * X(J) / PHIV(J)
```

```
   12 SUMY = SUMY + Y(J)
      DO 13  I = 1, NCOMP
   13 Y(I) = Y(I)/SUMY
      IF( ABS(SUMY1 - SUMY) - 1.0E-5) 14, 14, 15
C     FIND A NEW VALUE OF Y(I) AND SUMY USING Y(I) IF SUMY1 IS DIFFERENT
C     FROM SUMY
   15 IF (ITER -100) 16, 21, 21
C  15 IF (ITER - 50) 16, 21, 21
   16 ITER = ITER + 1
      SUMY1 = SUMY
      CALL SUPT(VV,PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
      GO TO 17
C     Y(I) IS STABLE. NOW WE HAVE TO TEST FOR SUMY = 1. BY CHANGING P
C     CHANGE P
   14 SUMP =0.0
      DO 18 I = 1, NCOMP
      PHIJ(I) = PHI(I) * X(I)
      PHIK(I) = PHIV(I) * Y(I)
      P1(I) = P * Y(I)
      P1(I) = PHIJ(I) * P1(I)/PHIK(I)
   18 SUMP = SUMP + P1(I)
      P = SUMP
C      ***********************************
      CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
      CALL SUPT (VV, PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
      SUMY = 0.0
      DO 20 I = 1, NCOMP
      Y(I) = PHI(I) * X(I)/PHIV(I)
   20 SUMY = SUMY + Y(I)
      IF ( ABS (SUMY - 1.0) - 1.0E-4) 21, 21, 22
   22 IF (ITER - 100) 23, 21, 21
C  22 IF (ITER -  50) 23, 21, 21
   23 DO 24 I = 1, NCOMP
   24 Y(I) = Y(I)/SUMY
      ITER = ITER + 1
      SUMY1 = SUMY
      CALL SUPT(VV, PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
      GO TO 25
C     GATHER STATISTICS AND PRINT OUT RESULTS
   21 P = P * 14.697
      DP = P - PP( K)
      EDP = (DP/PP(K))*100.
      SDP = SDP + ABS(DP)
      DPAV = (DPAV*(K-1) + ABS(DP))/K
      EDPAV = (EDPAV*(K-1) + ABS(EDP))/K
      EP = (DP/PP(K))*100.
      RETURN
      END
```

```
C       ******************************************************************
        SUBROUTINE YVCALC
C       ******************************************************************
        DIMENSION TITLE (20) ,PCII(5),VCII(5),TCII(5),W(5),WAII(5), WBII(5
       1),COMPA(5), COMPB(5), COMPC(5), FREFER(5), PHI(5), PHIV(5),
       2 PHIJ(5), PHIK(5), P1(5), PTVCL(5), PPVOL(5), VVV(5), CORRL(5,5),
       3 X(5), Y(5),          VC(5), TC(5),                 EXG(5), EXGF(5),
       4 YX(5), VVL(5), DY(5), PVOL(5), GAMMB(5), GAMMA(5), AMOLWT(5)
       5 , PC(5), XX(50, 5), YY(50,5) ,PP(50), EXG1(5), COMPD(5)
        DIMENSION EDYAV(5),DYAV(5) ,EDY(5)
        COMMON /FIRST/ TC, PC, VCII, W, AMOLWT, T, P, R, NCOMP, NONTUM
       1   /SECOND/ Z, A, MTYPE
       2 / THIRD/ PCII, TCII, WAII, WBII, PSI, PP, XX, YY, IJK, KIJ, NOI,
       3 ITFR,K, CORRL, EXGT, PPVOL, PHI, PHIV, VV, VVL1, DV, P1, PPP, Y
       4 / FOURTH / SDP, EP, DP, SSDY, SDY, SDV.         PHIK, GAMMA, EXG,
       5 X, SUMY, GAMMB, PG, RT, PF, FREFER, YX, DY, EXG1,SLNA12,SLNB12
       6 / FIFTH / DPAV,EDYAV,EDY, EDP. EDPAV, DYAV
        P = P/14.697
        PP(K) = PP(K)/14.697
        PG = P
        CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
        CALL SUPT(VV, PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
        P = PF
        CALL SUPT (VL, PHI, PTVOL, WAII, WBII, CORRL, X, 1, KIJ)
        P = PG
        DO 26 J = 1, NCOMP
        VVV(J) = (PTVOL(J) + PPVOL(J)) * (PF - P)/2./RT
        FREFER(J) = FREFER(J) * X(J)
        GAMMB(J) = ALOG(PHIV(J) * P * Y(J)/FREFER(J)) + VVV(J)
     26 GAMMB(J) = EXP(GAMMB(J))
        SEXGF = 0.0
        DO 27 I = 1, NCOMP
        EXG1(I)= ALOG(GAMMB(I))
         EXGF(I) = X(I) * EXG1(I)
     27 SEXGF = SEXGF + EXGF(I)
        SLNB12=EXG1(1)-EXG1(2)
        EXGT = 8.314* T * SEXGF
        DO 28 J = 1, NCOMP
     28 YX(J) = YY(K,J)
        P = PP(K)
        CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
        CALL SUPT (VV, PHIV, PVOL, WAII , WBII, CORRL, YX, 0, KIJ)
        DO 29 J = 1, NCOMP
        VVL(J) = (PTVOL(J) + PPVOL(J)) * (PF - P)/2./RT
        GAMMA(J) = ALOG(PHIV(J) * P * YX(J)/FREFER(J)) + VVL(J)
     29 GAMMA(J) = EXP(GAMMA(J))
        SEXGT = 0.0
        DO 30 I = 1, NCOMP
        EXG(I) = ALOG(GAMMA(I))
        EXGF(I) = X(I) * EXG(I)
     30 SEXGT = SEXGT + EXGF (I)
        SLNA12=EXG(1)-EXG(2)
C         GATHER ANOTHER STATISTICS
        DO 31 J = 1, NCOMP
        SDY = 0.0
        DY(J) = Y(J) - YY( K ,J)
        SDY = SDY + ABS(DY(J))
        EDY(J) = (DY(J)/YY(K,J))*100.
```

```
      EDYAV(J) = (EDYAV(J)*(K-1) + ABS(EDY(J)))/K
      DYAV(J) = ( DYAV(J)*(K-1) + ABS( DY(J)))/K
   31  SSDY = SSDY + SDY
      VVL1 = 0.0
      DO 39 I = 1, NCOMP
   39 VVL1 = VVL1 + VVL(I)
      DV = VV - VVL1
      SDV = SDV + ABS(DV)
      PSI = P
      PP(K) = PP(K) * 14.697
      RETURN
      END
```

```
LEVEL  21                       MAIN                 DATE = 77203            11/47/21
C        ******************************************************************
         SUBROUTINE CUBEQN
C    SOLVES CUBIC EQUATION OF REDLICH-KWONG EQUATION
C        FOR COMPRESSIBILITY FACTORS
C        ******************************************************************
         DIMENSION A(4),Z(3) ,B(3)
         COMMON /SECOND/ Z,A,MTYPE
    1    CONTINUE
         B(1)=A(2)/A(1)
         B1OV3=B(1)/3.0
         B(2)=A(3)/A(1)
         B(3)=A(4)/A(1)
         ALF=B(2)-B(1)*B1OV3
         BET=2.0*B1OV3**3  -B(2)*B1OV3+B(3)
         BETOV2=BET/2.0
         ALFOV3=ALF/3.0
         CUAOV3=ALFOV3**3
         SQBOV2=BETOV2**2
         DEL=SQBOV2+CUAOV3
         IF(DEL)40,20,30
   20    MTYPE=0.0
         GAM=SQRT(-ALFOV3)
         IF(BET)22,22,21
   21    Z(1)=-2.0*GAM-B1OV3
         Z(2)=GAM-B1OV3
         Z(3)=Z(2)
         GO TO 50
   22    Z(1)=2.0*GAM-B1OV3
         Z(2)=-GAM-B1OV3
         Z(3)=Z(2)
         GO TO 50
   30    MTYPE=1
         EPS=SQRT(DEL)
         TAU=-BETOV2
         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    R=SIR*(SIR*RCU)**0.33333333
         S=SIS*(SIS*SCU)**0.33333333
         Z(1)=R+S-B1OV3
         Z(2)=-(R+S)/2.0-B1OV3
         Z(3)=0.86602540*(R-S)
         GO TO 50
   40    MTYPE=-1
         QUOT=SQBOV2/CUAOV3
         ROOT=SQRT(-QUOT)
         IF(BET)42,41,41
   41    PEI=(1.5707963+ATAN(ROOT/SQRT(1.0-ROOT**2)))/3.0
         GO TO 43
   42    PEI=ATAN(SQRT(1.0-ROOT**2)/ROOT)/3.0
   43    FACT=2.0*SQRT(-ALFOV3)
         Z(1)=FACT*COS(PEI)-B1OV3
         PEI2=PEI+2.0943951
```

```
LEVEL  21                       CUBEQN               DATE = 77203            11/47/21

         Z(2)=FACT* COS(PEI2)         -B1OV3
         PEI4=PEI+4.1887902
           Z(3)=FACT* COS(PEI4)          -B1OV3
   50    RETURN
         END
```

```
LEVEL  21                    MAIN                DATE = 77203          11/47/21
C     ******************************************************************
      SUBROUTINE SUPT(VL,PHI, PVOL  ,C1RKL,C2RKL,CORRL,X,LV,KIJ)
C
C     ******************************************************************
C     EVALUTION OF SUPPORTING PROPERTIES.THE FUGACITY AND THE
C     PARTIAL MOLAL VOLUME OF FLUID MIXTURES.
C     SHINN-DER CHANG, DEPT.OF CHEM.ENG., UNIV. OF OTTAWA.
      DIMENSION TC(5),PC(5),VCO(5),W(5),AMOLWT(5)   ,ARKL(5,5),BRKL(5),
     1  WIJ(5,5),TCOIJ(5,5),TCIJ(5,5),A(4),Z(3),C1RKL(5),C2RKL(5),
     1  PVOL(5),PHI(5),CORRL(5,5),X(5),A2I(5),BI(5),AIRKL(5)
      DIMENSION ZZ(3)
      DIMENSION TC1(5), VC1(5), PC1(5), TC11(5,5),VC11(5,5),WAII(5),WBII
     1(5),PCII(5), TCII(5)
      COMMON  /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NONTUM
     1    /SECOND/ Z,A,MTYPE
     2 / THIRD / PCII, TCII, WAII, WBII
C     LV=0, FOR VAPOR PHASE.
C     LV=1, FOR LIQUID PHASE.
C     KIJ=1, TCIJ=SQRT(TCI*TCJ)*(1.-KIJ)
C     KIJ=2, AIJ=SQRT(AI*AJ)*(1.-KIJ)
C     KIJ=3, AIJ=(AI*KIJ+(1.-KIJ)*AJ)/2.
      RT=R*T
      WAO = 0.42748
      WBO = 0.08664
   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)=(W(I)+W(J))*0.5
      ZCOIJ=0.291-0.08*WIJ(I,J)
   94 VCOIJ=(VCO(I)**(1./3.)+VCO(J)**(1./3.))**3/8.0
   96 PCOIJ=ZCOIJ* R    *TCIJ( I,J)/VCOIJ
      PCIJ=PCOIJ
   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 IF (KIJ .GT. 3) GO TO 998
      ARKL(I,J) = (ARKL(I,I)*CORRL(I,J)+(1.-CORRL(I,J))*ARKL(J,J))
      GO TO 98
  998 DO 1 II = 1, NCOMP
      TC1(II) = (WAII(II)/WAO*WBO/WBII(II))**(2./3.)*TCII(II)
    1 PC1(II) = (WAII(II)/WAO)**(2./3.)*(WBO/WBII(II))**(5./3.)*PCII(II)
      VC1(I) = (1./3.)*R*TC1(I)/PC1(I)
      VC1(J) = (1./3.)*R*TC1(J)/PC1(J)
      TC11(I,J)= (1.-CORRL(I,J))*(TC1(I)*TC1(J))**0.5
      IF (KIJ .GT. 4) GO TO 999
      VC11(I,J)= (1./2.)*(VC1(I)+VC1(J))
  997 ARKL(I,J) = WAO*R*R*TC11(I,J)**2.5/((1./3.)*R*TC11(I,J)/VC11(I,J))
      GO TO 98
  999 VC11(I,J)= (1./8.)*(VC1(I)**(1./3.)+VC1(J)**(1./3.))**3.0
      GO TO 997
```

```
   98 ARKL(J,I)=ARKL(I,J)
  100 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
      BI(I)=BRKL(I)/RT
      BMRKL=BMRKL+X(I)*BRKL(I)
      AIRKL(I)=0.0
      DO 120 J=1,NCOMP
      AIRKL(I)=AIRKL(I)+X(J)*ARKL(I,J)
  120 AMRKL=AMRKL+X(I)*X(J)*ARKL(I,J)
      A2=AMRKL/RT**2/T**0.5
      B=BMRKL/RT
      A(1)=1.0
      A(2)=-1.0
      A(3)=B*P*(A2/B-1.0-B*P)
      A(4)=-(A2/B)*(B*P)**2
      CALL CUBEQN
      IF(MTYPE)115,140,140
  115 IF(LV.EQ.0) GO TO 145
C     ZL=AMIN1(Z(1),Z(2),Z(3))
      ZL=AMIN1(Z(1),Z(2),Z(3))
C     JJ=0
C     DO 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(Z(1),Z(2),Z(3))
      GO TO 150
  140 ZL=Z(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)
  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+X(J)*ARKL(I,J)
      QE=2.0*QE1-AMRKL*BRKL(I)/(VL+BMRKL)
      QG=(RT/(VL-BMRKL))*(1.0+BRKL(I)/(VL-BMRKL))
```

```
      PVOL(I)=((QE/QD)-QG)/(QH-QK)
  130 CONTINUE
  300 RETURN
      END
```

```
C     *****************************************************************
      SUBROUTINE EQNRK(A2,B,P,E,Z,LV)
C     *****************************************************************
      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)
      DFE=B*P /E**2 +1./(1.-E)**2-(A2/B)/(1.+E)**2
C     WRITE(3,592)E,FE,DFE,LV
C 592 FORMAT(20X,3E12.4,5X,I2)
C     IF(ABS(DFE).LT.1.0E-20) DFE=DFE/ABS(DFE)*1.0E-20
      TEST=FE/DFE
      E=E-TEST
      IF(IJ.GT.60)GO TO 48
      IF( ABS(TEST/E).GT.TOL) GO TO 45
   48 Z  =B*P/E
      RETURN
      END
```