SC

PHASE EQUILIBRIA OF NON-IDEAL SOLUTIONS

BY

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ABSTRACT

In this investigation new and more efficient means for obtaining, processing and screening the urgently needed vapor-liquid equilibrium data were proposed.

Experimental vapor-liquid equilibrium data for the binary and ternary mixtures of the components nitrogen, methane and ethane were obtained at -240° F by means of a modified forced-recirculation apparatus. Liquid-liquid-vapor equilibrium data of the ternary system were also obtained at the same temperature.

Two methods were proposed for computing vapor phase compositions from total pressure and liquid composition data. One was for low and medium pressure conditions, in which a hypothetical component concept was employed and thus extended the method for binary systems to ternary systems at isothermal condition. The proposed method was successfully applied to the ternary system nitrogen-argon-oxygen. The other was proposed for high pressure systems in which an adjusted activity coefficient was introduced in conjunction with the appropriate symmetric and unsymmetric conventions. As a result, the indirect method was generalized and extended to the high pressure and multicomponent systems. Moreover a nonlinear regression technique was introduced making possible the evaluation of the adjustable parameters. Three binary systems were used to illustrate the proposed method with good results.

A general thermodynamic consistency test method which permits a point-by-point evaluation of the vapor-liquid equilibrium data was proposed and the maximum experimental error bounds were also established analytically. Vapor-liquid equilibrium data of one ternary and five binary systems were effectively evaluated by the proposed method.

In addition, the total pressure method of Barker was generalized, the composition resolution method of Van Ness was extended to the ternary systems and a five-junction copper-constantan thermopile was built and its calibration table was also prepared.

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NOMENCLATURE

NOTATION

A, B, a, b = adjustable parameter, or constant

D = deviation

E = measuring error

f = fugacity

F = degree of freedom

G = Gibbs' free energy

h = enthalpy of pure component or variable (Eq. 2.37)

H = enthalpy

$\mathcal{H}$ = Henry's law coefficient

I = intercept

J = pure number

K = y/x, equilibrium vaporization constant, or so called equilibrium ratio, or K-values

k = pure number

m = number of terms or adjustable parameters used in the series expansion

n = number of component

N = number of mole

p = number of phase

P = pressure

r = molecular size ratio

R = universal gas constant

S = entropy

T = temperature

v = molal volume

V = total volume or molal volume (Chapter 6)

W = weight

x = mole fraction in liquid phase

X = functional group Eq. 2.43

y = mole fraction in vapor phase

z = number of the nearest neighbor, or mole fraction either in the vapor phase or in the liquid phase

Z = compressibility factor

GREEK LETTERS

α = relative volatility

β = second virial coefficient

γ = activity coefficient

δ = solubility parameter (Eq. 2.14) or function of the second virial coefficient (Eq. 4.3)

Δ = difference or property change on mixing

$\triangle$ = deviation

ϵ = electromotive force, e.m.f.

θ = volume fraction (Eq. 2.13)

μ = chemical potential

ξ = functional group (Eq. 7.11 or 7.12)

ϕ = fugacity coefficient

ψ = functional group (Eq. 4.2)

ω = acentric factor

SUPERCRIPTS

ath = athermal (Eq. 2.40)

E = excess property

* = perfect gas state or unsymmetric convention (Chap. 5)

id = ideal behavior

M = mixing

$^\circ$ = reference state

s = saturated property

th = thermal (Eq. 2.42)

vap = vaporization

— = partial molar quantity

∞ = infinitive dilution

, = hypothetical or pure number identification

$\wedge$ = fugacity of component i in the solution

SUBSCRIPTS

a, b = experimental point identification

A, B = component identification

c = critical property

comp = computed

cv = convergence

i, ii, ij
or 1, 2 = component identification

L = liquid phase

m = last adjustable parameter identification

obs = observed

pc = pseudocritical property

r = reduced property

V = vapor phase

CHAPTER 1

INTRODUCTION

THE OBJECTIVES OF THE STUDY

The ever growing petrochemical industry and space technology demand cheaper and better stagewise separation techniques. The concept of the stagewise separation is mainly dependent on the physical equilibria. Therefore, practical necessities require more and better prediction methods as well as better experimental determinations of vapor-liquid equilibrium data.

According to Scatchard (88) there are three schools of thought among students of the vapor-liquid equilibrium. The first examines the temperature, pressure, liquid and vapor compositions; the second considers the pressure measurement relatively inaccurate and therefore requires knowledge only of the other three; and the third considers that the vapor composition is difficult to measure and works with temperature, pressure and liquid composition. The first two schools express the experimental data in terms of excess free energy and relative volatility, $\alpha = y_1x_2/x_1y_2$, respectively. Meanwhile, the third school faces more difficult problems which have not been satisfactorily solved, although they have received considerable attention for many years. This statement is still true even today if one likes to combine the K-values correlation with relative volatility as a group.

To meet these needs, attempts were made in this study to combine the advantages and to remove the disadvantages of all available methods by making full use of modern techniques, such as gas chromatography and automatic computation, to investigate:

i) some new means for obtaining the urgently needed data,
ii) more efficient methods for processing the experimental data,
iii) better methods of thermodynamic consistency test for screening the existing data.

The prediction and correlation methods were also reviewed briefly.

CHAPTER 2

LITERATURE REVIEW AND DISCUSSION

A complete literature survey up to October 1, 1959 was reported by Flynn (35). It gaves a bibliography of the physical equilibria and related properties of cryogenic fluids such as hydrocarbon, helium, nitrogen, carbon dioxide, carbon monoxide, methane, ethane, and propane. Another bibliography of vapor-liquid equilibria has been recently prepared by the British Institute of Chemical Engineers (85). In this survey, which covers the period up to 1966, low temperature vapor-liquid systems are classified into eight categories, namely:

1. Atmospheric gases (26 refs.)
2. Systems containing carbon dioxide (16 refs.)
3. Systems containing hydrogen sulfide (8 refs.)
4. Systems containing hydrocarbons only (31 refs.)
5. Systems containing hydrogen and hydrocarbons (18 refs.)
6. Systems containing nitrogen and/or carbon monoxide with hydrogen and/or hydrocarbons (22 refs.)
7. Systems containing helium and/or neon (18 refs.)
8. Miscellaneous (8 refs.).

Pressure and temperature ranges of each system are given in this survey. Besides these bibliographies the book of Hala, Pick, Fried and Vilim, entitled "Vapor-Liquid Equilibrium (42)" also provides useful references. In the first part of this book theoretical principles and methods of calculation at equilibrium conditions from various experimental data are discussed. In the second part, elements of measuring technique and a systematic review of instruments for the direct determination of the equilibrium compositions of the liquid and vapor phases of the system are presented. In the third part of this book a review of the literature up to July, 1965 is given.

In view of the fact that the bibliographies available are quite exhaustive and up to date, only a brief review of the literature will be made in this thesis, covering only those points which are of interest to this study, such as the experimental methods, prediction methods, and correlation methods. In addition, current publications will be quoted accordingly.

2.1 EXPERIMENTAL METHODS

In the literature, various methods have been proposed for investigation of the vapor-liquid equilibrium. The acceptable methods may be classified as follows:

FORCED-RECIRCULATION METHOD

The forced-recirculation method was first developed by Dodge and Dunber (29) into a practical use. The vapor distilled from the liquid was recirculated back through the liquid by means of a mercury pump. In this way the liquid was stirred thoroughly and the equilibrium was achieved by continuously bringing the vapor into contact with the liquid. These authors used this apparatus in the study of the oxygen-nitrogen systems with great success. It is probably the most accurate and reliable one among all the existing methods and has been widely adopted. Aroyan and Katz (4) studied the methane-hyrogen system by means of this method and modified the circulation process by introducing an electromagnetic pump. Further modification was made by Harvey (43), Price and Kobayashi (77). They introduced a transparent equilibrium cell and a bath liquid in the cryostat in the study of the systems containing methane, ethane and propane (77). A similar apparatus was also constructed by Brandt, Straud, and Deaton (10), and by Stein, Sterner and Geist (92). In the present study, the forced-recirculation method has also been chosen.

STATIC AND TOTAL PRESSURE (OR BUBBLE POINT PRESSURE) METHODS

In the static and total pressure methods a mixture is introduced into the equilibrium cell which is maintained at constant temperature and is agitated, either by shaking the container or using a magnetic stirrer. After a certain period of time the mixture is assumed to be in equilibrium. The operating conditions are then recorded. In a static method, (28) portions of vapor and liquid samples are withdrawn and their compositions are analyzed experimentally; whereas in the total pressure method, the vapor phase compositions are calculated directly from the thermodynamic relationships based on the liquid composition and total pressure data (45, 89).

Both the static and the total pressure methods are useful for high or moderate pressure, high or low temperature systems. Rigorously, these are the only methods which can reach the true equilibrium state. However, in the present state of the static method, there is no provision made for keeping the pressure constant during the sampling procedure. A drop in the pressure during the sampling, of course, disturbs the equilibrium. Moreover, in the total pressure method the existing means of calculation are far from perfect, especially under the high pressure and low temperature conditions.

In this study, new methods of calculation of the vapor phase composition from total pressure and liquid composition data both for low and high pressure are developed which enable us to remove the barrier in obtaining data by means of the total pressure method.

DEW-POINT AND BUBBLE-POINT METHOD

This method consists of introducing a known amount of gas mixture into a stirred transparent or an opaque equilibrium cell maintained at constant temperature. The contents of the cell are brought through the gas-phase region to the dew-point and then through the two-phase region to the bubble point, by adding measured increments of gas to the cell, thereby increasing the pressure. The dew-point and bubble-point pressures are determined by direct observation (or detected by certain sensing devices if an opaque cell is used) and from the plots of the pressure-mass of gas data and the liquid volume-pressure data at constant temperature. This procedure is repeated at different temperatures to define the constant composition liquid-vapor phase boundary or dew-point and bubble-point loop of the mixture for several mixtures. The results are plotted and the equilibrium conditions are then determined through the intersection of the dew-point curve of one composition with the bubble-point curve of the other composition.

This method has been developed for many years and has frequently been employed. It was developed to a considerable perfection by Sage and Lacey (87) who used it for mixtures of light hydrocarbons chiefly above the room temperature. It was also employed by the IGT group in the studies of the cryogenic vapor-liquid equilibrium (7-9, 30, 32) for the systems of nitrogen-methane (8), nitrogen-ethane (32), and methane-ethane (32).

The advantage of this method is that the mixtures may be prepared with predetermined composition. Therefore the phase compositions need not be analyzed. However, it must be applied with great care, since to detect the minute drop of liquid formed or the disappearance of the last gas bubble demands a highly trained technique. Moreover, it cannot be used to study multi-component systems.

FLOW METHOD

In the flow method a gas mixture is passed steadily into the equilibrium cell where it is cooled and partially liquified. The vapor in equilibrium with the liquid formed from condensation is separated and removed continuously to the storage for analysis. A continuous analysis of the sample is also possible.

This method was employed by Steckel (91) for the carbon monoxide-nitrogen system, and frequently used by Ruhemann and co-workers for systems such as methane-ethane (84), methane-ethylene system (38). Later, it was also employed in the United States by Stutzman and Brown (93) to study natural gas systems.

The advantages of this method are that large quantities of samples of vapor and liquid can be obtained with a small experimental assembly and the intimate contact between the vapor and the liquid during condensation provides a rapid approach to the equilibrium. The drawback of the method is the difficulty in controlling the pressure and temperature inside the cell while rapid condensation takes place. Moreover, the separation of the two phases becomes difficult in the critical region.

DISTILLATION TOWER METHOD

In the development of the distillation tower method, Chu et al. (21) studied the system of acetone-water and showed that the equilibrium condition could be attained on a distillation tray consisting of one bubble cap and operating under the total reflux condition. Based on their idea, Wang (102) constructed a still of several number of sieve plates in which the separation on each tray was expected to be equivalent to the performance of one theoretical plate. Wang studied the argon-oxygen system (102) by means of this apparatus, and found that the reproducibility of the data was within ± 2% on the logarithm of the relative volatility over the entire composition range. The overall accuracy of this method was estimated to be ± 3%, prior to any correction.

Indeed, this is not an accurate method from the theoretical standpoint; however, it does provide a quick investigation method which should draw much more attention from a practical point of view. Nevertheless, it may be used to study the vapor-liquid equilibrium, either by modifying the tower or by taking the tray efficiency into account to obtain the correct data, thus enables one to speed up the accumulation of data and to shorten the gap between the theoretical scientists and engineers. This would be a good topic for future studies.

2.2 PREDICTION METHOD BASED ON AN EQUATION OF STATE

When two phases are in equilibrium and if μ_i and $\hat{f}_i$ are the chemical potential and the fugacity in two phases the condition for equilibrium is

$$\mu_{iL} = \mu_{iV}$$

or

$$\hat{f}_{iL} = \hat{f}_{iV}$$

The fugacity coefficient ϕ_i of component i in any phase of a binary or a multicomponent system can be expressed as

$$RT \ln \phi_i = \int_0^P \left[\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} - \frac{RT}{P} \right] dP \qquad 2.1$$

or

$$RT \ln \phi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} - \frac{RT}{V} \right] dV - RT \ln Z \qquad 2.2$$

where V is the total volume of the fluid mixture, and Z is the compressibility factor of the fluid mixture at T and P. Since most equations of state are explicit in pressure, it is therefore more convenient to use Eq. 2.2. In order to evaluate the fugacity coefficient from either Eq. 2.1 or Eq. 2.2, it requires an equation of state which can be used to represent not only for the pure components but also for their mixtures including composition as one of their independent variables, that is,

$$\phi_{iL}(x_i, P, T) = \phi_{iV}(y_i, P, T) \qquad i = 1, m \qquad 2.3$$

Equation 2.3 enables one to obtain y_i's from a knowledge of x_i's, or vice versa.

CRITERIA OF THE VALIDITY OF AN EQUATION OF STATE FOR THE PREDICTION OF VAPOR-LIQUID EQUILIBRIA

In practice, none of the existing equations of state can be used to predict the vapor-liquid equilibria without any restriction. The necessary but not sufficient conditions for an equation of state to predict the equilibrium properties of the mixture are

$$P^s_L = P^s_V \qquad 2.4$$

and

$$f^\circ_L = f^\circ_V \qquad 2.5$$

The first condition, Eq. 2.4, can be easily satisfied. The second condition can be satisfied by adjusting a parameter in an empirical equation of state (109), but in doing so, the first condition is usually sacrificed. As an alternative, the author would like to call attention to one of the oldest relationships - the Maxwell condition (63).

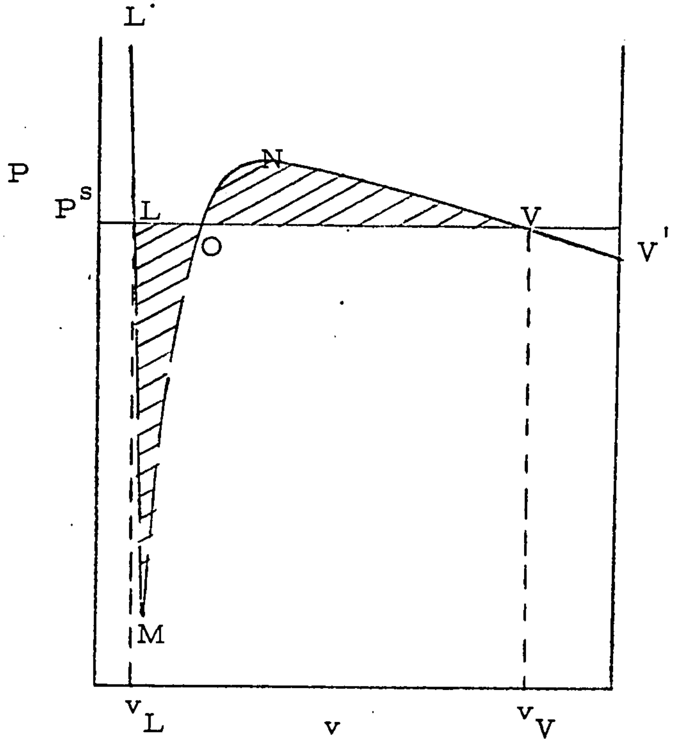


Figure 2.1 Illustration of Maxwell Condition.

Referring to figure 2.1, which shows the continuity of a P-v isotherm, one sees that at a given temperature the substance can be brought from the liquid state to the gaseous state or conversely through the path denoted by L'LMONVV'. The Maxwell condition states that the two shaped surfaces LMO and ONV are of equal area. The proof of this relationship is straightforward.

The effect of the pressure on the fugacity of a pure component is given by

$$\frac{\partial \ln f^{\circ}}{\partial P} = \frac{v}{RT} \qquad 2.6$$

Integrating this equation from the saturated gaseous state, V, to the saturated liquid state, L, at constant temperature yields

$$\ln(f^{\circ}_{L}/f^{\circ}_{V}) = \frac{1}{RT}\int_{V}^{L} vdP \qquad 2.7$$

At equilibrium,

$$f^{\circ}_{L} = f^{\circ}_{V} \qquad 2.5$$

therefore,

$$\int_{V}^{L} vdP = 0 \qquad 2.8$$

2.3 PREDICTION METHOD BASED ON THE SOLUTION THEORY

Many solution models based on the microscopic consideration have been proposed in the literature. The solution theory may be considered as the only rigorous way to solve the problem. An extensive review of the literature in such a large field is beyond the scope of this study. The present discussion will be restricted to two simple models : one is a regular solution and the other is an athermal mixing theory.

2.3.1 REGULAR SOLUTION THEORY : SCATCHARD-HILDEBRAND'S EQUATION (46)

The relationship between the excess Gibbs free energy, the excess enthalpy and the excess entropy is given by

$$\Delta G^E = \Delta H^E - T\ \Delta S^E \quad \cdots\cdots\cdots \qquad 2.11$$

Hildebrand assumed that for a regular solution $\Delta S^E = 0$, $\Delta v^E = 0$. Therefore, for a binary solution

$$\Delta G^E = \Delta H^E = \Delta E^E = \theta_1\ \theta_2\ v(\delta_1 - \delta_2)^2 \quad \cdots\cdots \qquad 2.12$$

where $$\theta_i = N_i v_i / \sum_i N_i v_i \quad \cdots\cdots\cdots \qquad 2.13$$

$$\delta_i = \left(\frac{\Delta H^{vap} - RT}{v_i}\right)^{1/2} \quad \cdots\cdots\cdots \qquad 2.14$$

Differentiating Eq. 2.11 with respect to N_i and combining with Eq. 2.15,

$$\left(\frac{\partial NG^E}{\partial N_i}\right)_{T,P,N_j} = RT \ln \gamma_i \quad \cdots\cdots \qquad 2.15$$

gives

$$RT \ln \gamma_1 = v_1 \theta_2^2 (\delta_2 - \delta_1)^2 \quad \cdots\cdots\cdots \quad 2.16$$

Equation 2.16 is being used as a basis for many prediction methods.

2.3.2 ATHERMAL MIXING THEORY —— FLORY - HUGGIN'S EQUATION (33, 34, 49)

Flory and Huggins assumed a model of an athermal solution, in which $\Delta H^M = 0$, $\Delta v^M = 0$. Thus the Gibbs free energy of mixing may then be represented by:

$$\Delta G^M = - T \Delta S^M \quad \cdots\cdots\cdots \quad 2.17$$

Since for an athermal mixing (33, 49),

$$\Delta S^M = - R \sum_i x_i \ln \theta_i \quad \cdots\cdots\cdots \quad 2.18$$

therefore

$$\Delta G^M = RT \sum_i x_i \ln \theta_i \quad \cdots\cdots\cdots \quad 2.19$$

For an ideal solution,

$$(\Delta S^M) \text{ ideal} = - R \sum_i x_i \ln \theta_i \quad \cdots\cdots\cdots \quad 2.20$$

hence

$$\Delta G^E = RT \sum_i x_i \ln (\theta_i / x_i) \quad 2.21$$

For the case when random mixing is predominant this model is found to be useful and is applied to polymer solutions frequently.

2.3.3 APPLICATIONS OF REGULAR SOLUTION AND ATHERMAL MIXING THEORIES

CHAO AND SEADER METHOD (17)

Chao and Seader rearranged Eq. 1.13 to correlate the K-value through a combination of three factors:

$$K_i = y_i/x_i = (\overset{\circ}{f}_{iL}/P)(\gamma_i)/(\phi_i) \quad \cdots\cdots\cdots \qquad 2.22$$

Following the three-parameter law of corresponding states of Pitzer (17), the liquid fugacity coefficient of pure component i or $(\overset{\circ}{f}_{iL}/P)$, can be expressed as

$$\log(\overset{\circ}{f}_i/P) = \log(\overset{\circ}{f}_i/P)^{\circ} + \omega \log(\overset{\circ}{f}_i/P)^{1} \quad \cdots\cdots \qquad 2.23$$

The quantities $(\overset{\circ}{f}_i/P)^{\circ}$ and $(\overset{\circ}{f}_i/P)^{1}$ depend upon the reduced temperatures and reduced pressures. Both of these quantities have been fitted with the following empirical functions:

$$\begin{aligned}\log(\overset{\circ}{f}_i/P)^{\circ} &= (A_{\circ} + A_1/T_r + A_2T_r + A_3T_r^2 + A_4T_r^3)\\ &\quad + (A_5 + A_6T_r + A_7T_r^2)P_r\\ &\quad + (A_8 + A_9T_r)P_r^2 - \log P_r \quad \cdots\cdots \qquad 2.24\end{aligned}$$

$$\begin{aligned}\log(\overset{\circ}{f}_i/P)^{1} &= -4.23893 + 8.65806\,T_r - 1.22060/T_r\\ &\quad - 3.15224\,T_r^3 - 0.025\,(P_r - 0.06) \quad \cdots\cdots \qquad 2.25\end{aligned}$$

The activity coefficient was calculated from the Scatchard-Hildebrand equation with the regular solution assumption. Instead of calculating the solubility parameter from heat of vaporization and liquid molar volume, the necessary parameters of forty-three hydrocarbons and hydrogen, were determined from the experimental vapor-liquid data. The vapor phase fugacity coefficients ϕ_i were calculated from the Redlich-Kwong equation of state. The correlation could be applied to hydrocarbons of various molecular types including paraffins, olefins, aromatics and naphthlenes. Hydrogen in hydrocarbon mixtures was also correlated. The correlation was successful in predicting K-values of hydrocarbons at relatively high temperatures but failed badly at low temperatures.

CHANG, CHAPPELLAR AND KOBAYASHI'S CORRELATION (13)

Chang, Chappellar and Kobayashi correlated K-values of methane in paraffinic and aromatic solvents at low temperature and high pressure. They expressed K-values by an equation similar to the work of Chao and Seader,

$$K_i = y_i/x_i = (f^{\circ}_{iL}/P)\,(\gamma_i)/(\phi_i) \quad \cdots\cdots\cdots \qquad 2.26$$

where the (f°_{iL}/P) term was taken from Chao and Seader's work (17). The vapor phase fugacity coefficient was evaluated from the modified form of Redlich-Kwong equation of state (104, 105), and the liquid phase activity coefficient was taken as a sum of the athermal and thermal effects.

For the vapor phase fugacity the Redlich-Kwong equation was rearranged as follows:

$$\frac{Pv}{RT} = \frac{v}{v-b} - \left(\frac{a}{b\,RT^{1.5}}\right)\left(\frac{b}{b+v}\right) \quad \cdots\cdots \qquad 2.27$$

This equation was modified by Wilson (104, 105) by assuming that

$$a/(b\,RT^{1.5}) = F(Tc/T, \omega) = D_1 + D_2/T \quad \cdots\cdots\cdots \qquad 2.28$$

to yield the following relationships:

$$F(T/T_c, \omega) = 4.934 \left[1 + (1.45 + 1.62\omega)(T_c/T - 1.0)\right] (T_c/T)^{0.12} \quad 2.29$$

The constants for pure component were given as

$$a_i = F(T_{c_i}/T, \omega) b_i RT^{1.5} \quad 2.30$$

$$b_i = 0.0867 \; RT_{c_i}/P_{c_i} \quad 2.31$$

or

$$A_i^2 = a_i/R^2T^{2.5} \quad 2.32$$

$$B_i = b_i/RT \quad 2.33$$

The constants for mixtures were given as

$$A^2 = \sum_i y_i A_i \quad 2.34$$

$$B = \sum_i x_i B_i \quad 2.35$$

The vapor phase fugacity was then evaluated through Eq. 2.36

$$\log \phi = 0.4343 (Z - 1) (B_i/B) - \log (Z - BA) - (A^2/B) (2A_i/A - B_i/B) \log (1 + BP/Z) \quad 2.36$$

where

$$Z = \left(\frac{1}{1 - h}\right) - \frac{A^2}{B} \left(\frac{h}{1 + h}\right) \quad 2.37$$

and

$$h = BP/Z \quad 2.38$$

The compressibility factor Z of the vapor mixture was calculated by a trial and error procedure utilizing Eq. 2.36 and Eq. 2.37

The activity coefficient was written in the form

$$\ln \gamma_i = \ln \gamma_i^{ath} + \ln \gamma_i^{th} \tag{2.39}$$

with the γ_i^{ath} given by Miller-Guggenheim (37, 66) as

$$\ln \gamma_1^{ath} = \ln \left[(1 - \theta_2)/x_1 \right] - z/2 \ln \left[1 - (1 - 1/r_1)\, 2\,\theta_2/z \right] \quad \ldots\ldots\ldots \tag{2.40}$$

with

$$\theta_2 = r_1 x_2/(x_1 + r_1 x_2) \quad \ldots\ldots\ldots\ldots \tag{2.41}$$

In Eq. 2.40 r_1 is the molecular size ratio, z is the number of the nearest neighbour. In Eq. 2.39, the γ^{th}-term was taken the form similar to the Scatchard-Hildebrand equation,

$$\ln \gamma_1^{th} = X\, \theta_2^n \quad \ldots\ldots\ldots\ldots \tag{2.42}$$

but instead of 2, n was taken to be 2.6 and X was determined experimentally through the equation

$$X = \left[\ln (K_1 \cdot \Phi) - \ln (f_1^{\circ}/P) - \ln \gamma_1^{ath} \right] \theta_2^{-n} \quad \ldots\ldots \tag{2.43}$$

Chang, Chappelear and Kobayashi correlated K-values of methane in hydrocarbon solvent based on the foregoing discussion in which the liquid fugacity was taken from Chao and Seader's work (17), the molecular size ratio was taken as the molar volume of liquid at 25°C and z, the number of the nearest neighbour was taken to be 12.

The correlated results were in good agreement with K-values of methane with a relative deviation of ± 5%, except in the vicinity of the critical point. However, for the heavier components the results were not so successful. The relative deviations involved were in the range + 20 to - 200%. The failure of the correlation was attributed to the unsuccessful description of the non-ideality of the heavier component in the vapor phase by the approximate Redlich-Kwong equation of state.

CORRELATION OF ORENTILICHER AND PRAUSNITZ FOR THE SOLUBILITY OF HYDROGEN (67)

Based on the previous work of Prausnitz (71), the Krichevsky-Kasarnovsky's equation was modified by Orentilicher and Prausnitz (67). By defining,

$$\mathcal{H} = \lim_{x_2 \to 0} \hat{f}_2/x_2 \qquad 2.43$$

$$\ln \gamma_1 = \frac{A}{RT} x_2^2 \qquad 2.44$$

$$\ln \gamma_2^* = \frac{A}{RT} (x_1^2 - 1) \qquad 2.45$$

and, when combining with,

$$\hat{f}_2 = x_2 \gamma_2^* \mathcal{H} \qquad 2.46$$

gives

$$\ln \hat{f}_2/x_2 = \ln \mathcal{H} + \frac{A}{RT} (x_1^2 - 1) + \frac{\bar{v}_2^{\infty} (P - P_1^s}{RT} \qquad 2.47$$

Equation 2.47 is similar to the Krichevsky-Kasarnovsky's equation (54) except that the former equation takes into account the effects of the deviations of composition and pressure. For a small value of x_2, Eq. 2.47 becomes

$$\ln \hat{f}_2/x_2 = \ln \mathcal{H} + \left[\bar{v}_2^{\infty} - \frac{2A}{(\mathcal{H}/\phi_2^s) - P_1^s} \right] \left(\frac{P - P_1^s}{RT} \right) \qquad 2.48$$

Thus a semilogarithmic plot of the ratio $\hat{f}_2/x_2$ at constant temperature against total pressure should give a straight line for small values of x_2, which is justifiable from the solubility data of hydrogen. The constant A and the Henry's Law constant in Eq. 2.47 were evaluated for the following solvents: A, CO, N_2, CH_4, C_2H_6, C_3H_8, C_3H_6, and C_6H_{14}. The partial molar volume of hydrogen was approximated by the following relationship

$$\bar{v}_2^{\infty} = b_2 + RT/\delta_1^2 \quad \ldots\ldots\ldots\ldots \qquad 2.49$$

where b is the van der Waals covolume, taken to be 26.6 $cm.^3$ /g-mole for hydrogen.

CORRELATION OF VAN HORN AND KOBAYASHI FOR HYDROCARBONS (97)

Extending the work of Orentlicher-Prausnitz (67), van Horn and Kobayashi correlated liquid fugacity coefficients by an equation similar to Eq. 2.47 as follows:

$$\ln \hat{f}_{1L}/x_1 = \ln \gamma_1^{\infty} \mathcal{H} + \frac{\bar{v}_1^{\infty}}{RT} (P - P^{\circ}) \quad \ldots\ldots\ldots \qquad 2.50$$

in which subscript 1 is assigned to the lighter component methane, and P° is the reference pressure, taken to be 1 atm. By combining Eq. 25 with the solubility parameter, they generalized the correlation to the following form

$$\begin{aligned}\ln(\hat{f}_{1L}/x_1) = {} & (A_1 + B_1\, Tc_1/T) + (A_2 + B_2\, Tc_1/T)(\delta_1 - \delta_2)^2 \\ & + (C_1 + C_2/v_2)\, x_1\, Tc_1/T \\ & + (D_1 + D_2\, T/\delta_2^{\,2})(P - P^\circ)/RT \quad \ldots\ldots \qquad 2.51\end{aligned}$$

where constants A, B, C, D together with v are given in the original paper (97). By combining Eq. 2. 51 with the vapor phase fugacity, evaluated from the Benedict-Webb-Rubin's equation of state, the K-value was found to be

$$K_i = (\hat{f}_{iL}/x_iP)/(\hat{f}_{iV}/y_iP) \quad \ldots\ldots\ldots\ldots \qquad 2.52$$

The liquid activity coefficients for ethane and propane were calculated by using the Scatchard-Hildebrand equation; however, they were modified empirically by using infinite dilution data in the determination of the adjustable parameter.

Excellent agreement of K-values was obtained in the correlation. It should be mentioned, however, that for the intermediate component, K-values at infinite dilution, required in the calculation, are not always available.

2. 4 CORRELATION METHODS

According to the phase rule,

$$p + F = n + 2 \quad \ldots\ldots\ldots\ldots \qquad 2.53$$

where F = number of degrees of freedom in the system,

n = number of components in the system,

p = number of phases present in the system.

The number of degrees of freedom of a two-phase system is equal to the number of components.

The composition or a composition variable may be chosen in addition to the T and P for describing the ternary system. The composition variables employed in the literature may be summarized as follows:

$$P_{cv} = \text{convergence pressure} \quad \ldots\ldots \quad 2.54$$

$$K_i = y_i/x_i \quad \ldots\ldots \quad 2.55$$

$$MABP = \sum_{i=1}^{n} z_i \,(NBP)_i \quad \ldots\ldots \quad 2.56$$

$$AM = \sum_{i=1}^{n} z_i \, M_i \quad \ldots\ldots \quad 2.57$$

$$P_{pc} = \sum_{i=1}^{n} z_i \, Pc_i \quad \ldots\ldots \quad 2.58$$

$$T_{pc} = \sum_{i=1}^{n} z_i \, Tc_i \quad \ldots\ldots \quad 2.59$$

where K_i is the equilibrium ratio or K-value, z_i is the mole fraction, x_i is the mole fraction in the liquid pahse, y_i is the mole fraction in the vapor phase and M is the molecular weight of component i. MABP is the molal average boiling point, AM is the average molecular weight, P_{pc} is the pseudo critical pressure, T_{pc} is the pseudo critical temperature, and n represents the total number of components.

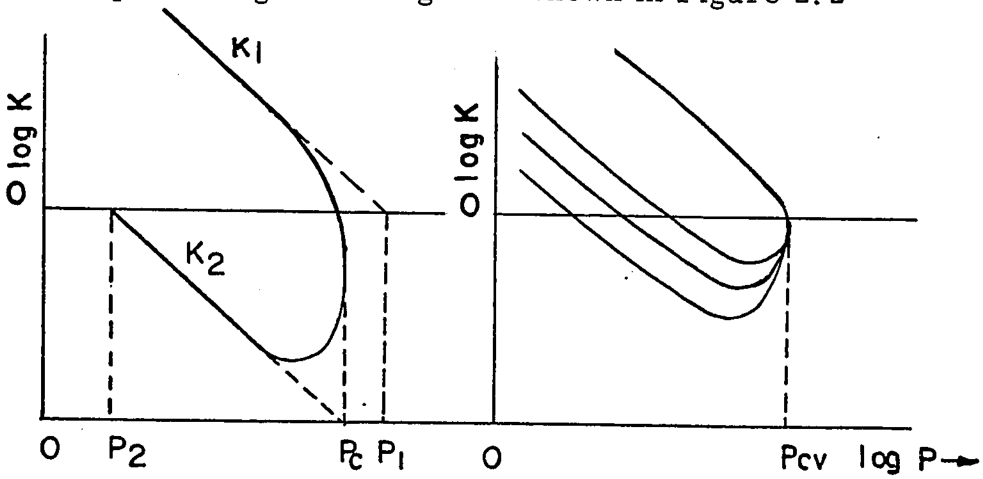
The functional relationship for a n -component system may be generalized as follows:

$$\Phi_i (\theta_i , P, T) = 0 \qquad \dots\dots\dots\dots\dots \qquad 2.60$$

where θ_i denotes the (n - 2) composition variables. When Henry's law is applicable for the system concerned, one variable may be deducted accordingly.

CONVERGENCE PRESSURE METHOD

One of the most important composition variables is the convergence pressure, which is defined as the pressure at which the K-value appears to converge to unity on an isothermal plot of log K vs log P as shown in Figure 2.2



Binary system, T= Const·   Complex system, T= Const·

Figure 2.2

The dotted lines in the plot for a binary system indicate the situation when Raoult's law is obeyed. The solid lines indicate the typical behavior of hydrocarbons in which the K-value approaches unity, when pressure approaches Pc or Pc v. This phenomenon was first noted by Katz (51). For a complex system, a similar behavior was also observed by the same author. The convergence pressure has been found to be a function of composition and has been therefore suggested (103) as a parameter to represent the effect of composition at higher pressures when the ideal solution approximation is not valid. Several schemes have been proposed (39, 55, 68, 86) for the prediction of convergence pressure as a function of composition.

The most recent correlations based on the use of the convergence pressure are the following:

1. The N. G. P. S. A. chart – This set of charts for twelve hydrocarbons (and nitrogen) was published by the N. G. P. S. A. (the Natural Gas Producers' Supplier Association of Tulsa, Oklahoma) in its 1966 Engineering Data Book. It supersedes the earlier set of diagrams in the 1957 N. G. S. M. A. Engineering Data Book which, however, is still being widely used. In this book new diagrams were derived from more recent and more plentiful basic data, particularly for the low temperature region. Therefore, they contain many valuable improvements over the earlier works. The K-values are presented as a function of temperature, pressure and convergence pressure. The latter parameter which represents the dependence of the K-values on liquid mixture composition was introduced by Hadden in 1953 (40).
2. The Hadden and Grayson nomographs - Hadden and Grayson gave a new set of diagrams in 1961 (41) for more accurate determination of convergence pressure. With the aid of this convergence pressure, K-values can be read from a nomograph. Two nomographs for different temperature ranges are given. One of them goes down to - 260° F.

LENOIR DIAGRAM

The Lenoir-diagrma was published by Canjander, Hipkin and Lenoir in 1960 (11). This method also employs a set of diagrams and a nomograph. The diagrams give K-values at a pressure of 10 psia as a function of temperature only. The lowest temperature given is -220° F. The nomograph gives the pressure correction which depends on an effective boiling point as the composition dependent parameter.

Another set of diagrams also prepared by Lenoir (55) for carbon-dioxide rich hydrocarbon systems, which is consistent with those mentioned above, describes the effect of the particular non-ideality on the hydrocarbon K-values caused by the presence of carbon dioxide. A diagram for the carbon dioxide K-values at 10 psia is also given. The temperature range covered is from -60° F to 100° F.

KELLOGG CHARTS

A set of 324 charts was published in 1950 by the M. W. Kellogg Company, entitled "Liquid-Vapor Equilibria in Mixtures of Light Hydrocarbons, MWK Equilibrium Constants, Polyco Data". These charts were prepared based on the Benedict-Webb-Rubin equation of state. The molar average boiling point (MABP) expressed in degrees Fahrenheit was chosen as the composition dependent parameter. It covers the temperature range from -100° F to 400° F, a range of MABP from -255° F to 180° F and lists values at 26 different pressures between 14.7 and 3600 psia for twelve hydrocarbons: methane, ethylene, ethane, propylene, propane, i-butane, i-butylene, n-butane, i-pentane, n-pentane, n-hexane and n-heptane.

CHAPTER 3

EXPERIMENTAL STUDY OF VAPOR-LIQUID EQUILIBRIA: NITROGEN, METHANE, AND ETHANE SYSTEMS

3.1 EXPERIMENTAL DETAILS

3.1.1 APPARATUS

A forced-recirculation apparatus used in previous work (14) was modified in the present study. The details of the design are available (16). A brief description is given here. A schematic diagram of the modified apparatus is shown in figure 3.1. Essentially, it consists of a feed preparation and charging unit, a transparent equilibrium cell, a cryostat and associated temperature control system, an electromagnetic pump, a recirculation loop, sampling facilities, temperature and pressure measuring devices, and a coolant supply system.

FEED PREPARATION AND CHARGING UNIT

Three gas tanks, installed with individual pressure regulators were connected to the system for storing the pure gases. Additional three gas tanks, one of 2-liter capacity and two of 300-ml. capacity, respectively, and a calibrated pressure gauge were also connected in parallel. These tanks together with the evacuation facilities comprised the system for preparation of the gas feed mixtures.

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 cryostat, into which the cell is immersed, is shown in figure 3. 2. 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 cooling coil, the vapor inlet pipe line.

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 coils, one for freon and the other for liquid nitrogen, two stirrers, two heating elements, and a resistance type temperature sensing element. In the down stream line of the liquid nitrogen refrigeration coil a buffer tank, a flow indicator and a needle valve to keep the nitrogen flowrate constant were situated. In addition to these elements, the cryostat was equipped with a Bayley temperature controller, model 250. A complete description of the temperature control problem is given later.

ELECTROMAGNETIC PUMP

The electromagnetic pump, designed and built in the course of a previous study (14), was further modified to eliminate the noise and sparking during operation. In the modification the mechanical relays were eliminated from the circuit.

The new circuit and a cross section of a portion of the pump are shown in figure 3. 3. The major part of the circuit, shown in the middle portion of the figure, is a symmetric Flip-Flop circuit producing a square wave-output. On the left side of the figure is a power supply system which may be adjusted through a variable resistence R to give a minimum of 1. 5 milli-second and a maximum of 1 sec. per cycle.

VAPOR RECIRCULATION LOOP

The vapor recirculation loop, as depicted in figure 3. 1, consisted of an electromagnetic pump, a volume regulator, a cooling coil, an equilibrium cell and a vapor sampling tube.

SAMPLING FACILITIES

The vapor sample was entrapped within either the vapor sampling tube or the volume regulator. The liquid sample was withdrawn from one of three liquid sampling tubings of 1/16 - in. diameter, all of which passed through the outlet vapor chamber and extended into the equilibrium cell at different levels. A needle valve and a three-way valve were installed between the liquid sampling bulb and the equilibrium cell.

TEMPERATURE AND PRESSURE MEASURING DEVICES

Two protected type copper-constantan thermocouples were installed in the equilibrium cell at two different levels, one located one-quarter of the height, and the other three-quarters of the height of the cell, measured from the bottom of the cell. The system temperature measurements were made by means of a Leeds and Northrup K-3 potentiometer and a Tinsley SRI galvanometer. In addition, three calibrated "Test Gauges" with ranges of 0 to 200, 0 to 600 and 0 to 1500 psig and with 1, 2, and 5 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°F and 1 psi respectively.

COOLANT SUPPLY SYSTEM

One freon refrigerator was provided to bring the unit a little cooler than the room temperature. In addition, one liquid nitrogen tank was stationed nearby to supply the needed coolant for the system operated at lower temperature.

3.1.2 EXPERIMENTAL PROCEDURES

At room temperature the system was first evacuated and maintained under the vacuum of 0.1 mm. Hg. or less. The freon refrigerator was turned on to cool down the cryostat and the equilibrium cell. The Dewar flask was filled with isopentane as the bath liquid. During idling period, for safety precaution, the freon refrigerator was always kept on to prevent the hazard which might arise from the evaporation of the isopentane into the air. After the starting period, the freon refrigerator was turned off, both stirrers were turned on and the liquid nitrogen tank was pressurized by compressed nitrogen gas to 10 psig or less. By adjusting the needle valve after the buffer tank the evaporating rate of liquid nitrogen was regulated. The approximate evaporating rate could be watched from the flow indicator which consisted of a Venturi tube and a manometer. In the starting period, the vaporization rate was preferably large, in order to reduce the temperature rapidly to a point slightly below the desired level. The temperature of the bath could be maintained near the desired value by regulating the nitrogen evaporating rate through the needle valve and simultaneously checking the system temperature.

For a binary system study, the heavier component was simply introduced into the storage tank. However, for a tenary system study, two heavier components were premixed at the desired ratio in the feed preparation unit and kept overnight. The heavier component of the system studied could then be charged into the equilibrium cell by opening the stop valve after isolating the vacuum pump from the system. As the pressure reached the saturation point, the liquid was formed. The charge was stopped until the liquid level had risen to half of the cell capacity. The temperature controller was then turned on and the temperature was adjusted. As the electromagnetic pump was started, the vapor was withdrawn from the cell. The vapor was warmed up when passed through the vapor sampling tube, volume regulator, and to the electromagnetic pump. Then it was recirculated back through the cooling coil. The vapor was thus cooled down again and returned back to the equilibrium cell by bubbling through the liquid phase. In this manner frequent gas liquid contact was provided. From continuous analyses of the vapor sample for one or more runs the minimum time required to reach equilibrium was established. In this study, the minimum time required was found to be less than an hour. In practice, the vapor was recirculated for two hours. Then the vapor sample was trapped as soon as the pump was stopped, and the pressure and temperature were recorded. Then the liquid sampling valve was opened, and the sample was withdrawn. However, when studying the liquid-liquid-vapor equilibria, the samples were withdrawn only after one hour settling period. The liquid sampling pipe line was thus purged by the first portion of sample through the needle valve and three-way valve to the bottle filled with water. The sampling rate could be regulated by adjusting the needle valve in line and counting bubbles through the bottle. After the sampling rate was appropriately adjusted, the three-way valve was then switched to the liquid sampling bulb which was pre-evacuated. Ten to twenty minutes were required to collect 10-ml. of the sample at room temperature and at a pressure of 20-psig. If the system pressure dropped while sampling, the pressure of the system could be maintained constant by adjusting the volume regulator. The analysis work was followed and the first experimental point was obtained.

The procedure required to obtain the second point was much simpler. After adjusting valves of the system the more volatile component could be fed to the system by bubbling it through the liquid and then passing to the other part of the system. The charging process should be kept as slow as possible. This could be done by simply adjusting a needle valve between the tanks and the system. Recirculation was resumed and the second point was thus obtained. If the pressure was far below the critical value, this process could be repeated two or three times without affecting the constant ratio of the two heavy components in the liquid phase. In this manner three points could be collected for each run. The time required for each run was about 15 hours including analysis work. Then the pressure of the system was relieved and vented to the air outside of the building. The system was evacuated overnight and ready for the next run.

3.1.3 TEMPERATURE CONTROL OF CRYOSTAT

Since temperature is one of the variables, its control therefore becomes an important step in this type of study. A good technique is required to build up a delicate balance between heat removal from the evaporation of liquid nitrogen and the heat supply by the heating elements. A system for controlling the temperature generally consists of a sensing element, a temperature controller, a cooling coil, heating elements and a liquid bath. For securing good results it is necessary that all factors are correct.

In this study one proportional type temperature controller of Bayley, Model 250 was used throughout. The instructions (6) given by the company should be followed closely. In addition, the information described in the following paragraphs was also found to be very useful.

The system temperature was brought down by evaporating liquid nitrogen through the coil inside the cryostat. The evaporating rate was adjusted to bring the bath temperature slightly lower than desired by making sure that the evaporation of liquid nitrogen or the removal of heat was just sufficient so that the bath temperature was tending to drop 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 manual (6) to allow the controller to increase the bath temperature.

The proportional band width adjustment 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 size of heaters employed, the type of circulation, and the size of the controlled bath, etc. One major drawback of this type of controller is that it produces proportional offset for a 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 proportional band width, the smaller is the offset produced. The sensitivity of this controller at full band width is about 2°C and at zero band width is approximately 0.01°C. Therefore, the band width setting is very critical for the temperature control. The procedures for obtaining a best band width setting are available in the manual (6).

3.1.4 MATERIALS

The materials used in this study were obtained from Matheson of Canada Limited, Whitby, Ontario. Their minimum purities were reported as follows:

	Minimum Purity, mol %
Nitrogen	99.999
Methane	99.99
Ethane	99.9

These materials were used in this study without any further purification. No impurity was found from the analysis by means of gas-chromatography.

3.1.5 ANALYSIS

All compositions were analyzed gas-chromatographically through a type - J column, 6 feet long, along with a Fisher gas partitioner of Model 25 and a Texas Instrument potentiorecorder of Model SERVO RITER II with one milivolt span. The gas partitioner was of dual columns and a double-detector design. In this study the first column was left empty and only the second 6-ft. long column was packed with 28-30 mesh silica gel. This was found to be extraordinarily stable throughout the study. Helium was used as a carrier gas at a flowrate of 41 ml./min. A retention time of six to eight minutes was required for separating the three components at the temperature 50° C. and the pressure 11.5 psig. The peaks were very well spaced and completely separated in the sequence of nitrogen, methane and ethane.

The gas partitioner's responses were calibrated against the known synthetic samples. The peak area and peak height responses were compared and it was found that the peak height response was simpler and more reliable. The results of the calibration were plotted graphically as composition ratio versus peak height ratio of first component to second component as well as the reciprocal ratio in order to cover the whole range of the concentration. The ratio plot was believed to be superior over the absolute quantity plot since the former was relatively insensitive to any change in detector current, temperature, column pressure, carrier gas flowrate, sample quantity, recorder sensitivity, etc. However, for extremely low concentration such as nitrogen in the liquid phase and ethane in the vapor phase it was found necessary to plot the absolute quantity instead of the relative ratio for better results.

The reproducibility of the analysis in general was good to 0.003 mole fraction. The good accuracy was obtained by repeating the analysis four to five times for each sample before the average was taken. For samples of an extreme concentration region extra care was taken in the analysis as well as in the calibration so that reproducibility was improved to 0.001 mole fraction.

3.2 EXPERIMENTAL RESULTS

Equilibrium measurements were made at -240° F as follows:

For vapor-liquid equilibria

nitrogen - methane
nitrogen - ethane
methane - ethane
nitrogen - methane - ethane

and For liquid-liquid-vapor equilibria

nitrogen-methane-ethane

Numerical values are presented in Tables 3.1 to 3.4.

NITROGEN-METHANE MIXTURES

For the binary system of nitrogen-methane, the pressure composition data obtained in this investigation are compared with literature data in figure 3.4. Previous work (14) is also included. In the critical region of the -151.1° F isotherm the present data agrees well with the values reported by Bloomer and Parent (8, 9) at -150° F, but not with the data reported by Cines et al. (26) at -150° F. The -240° F isotherm obtained in this investigation also disagrees with that reported by Cines et al. (26) at the same temperature. The present data gave higher K-values for nitrogen.

NITROGEN-ETHANE MIXTURES

At -240° F., two liquid phases were observed in equilibrium with the vapor phase for overall nitrogen concentration between

0.2945 and 0.9566 mole fraction in the liquid phase. The ethane concentration was found to be richer in the bottom liquid layer (BL) than in the top liquid layer (TL). The three-phase bubble point pressure was in between the vapor pressure of two pure components. The agreement between the present data and those reported by Elington et al. (30, 32) is very good at low pressures as shown in figure 3.5. However, discrepancy between the two sets of data was found at high pressure.

METHANE-ETHANE MIXTURES

The pressure-composition data obtained at -240° F are shown in figure 3.6. The -151.1° F isotherm previously obtained (14) is also included. The pressure-liquid composition curves obtained at these two isotherms are almost linear in a large nitrogen concentration region, indicating the near ideal behavior of the system in the liquid phase.

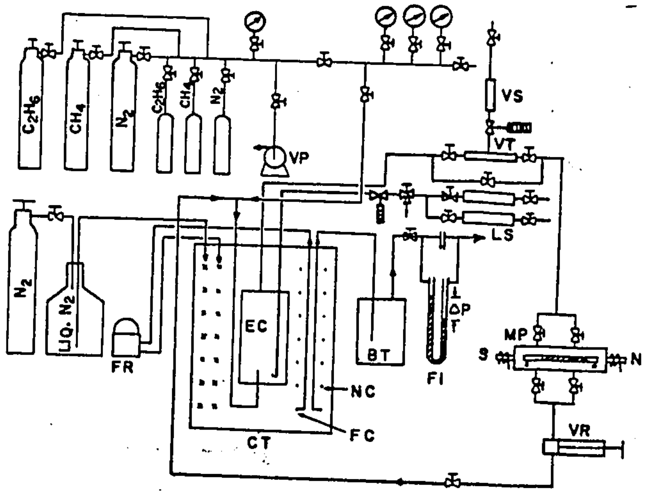
NITROGEN-METHANE-ETHANE MIXTURES

Equilibrium vapor-liquid compositions for the ternary mixtures were determined at -240° F. At this temperature two liquid phases were observed in equilibrium with the vapor phase when methane concentration was lower than 0.15 mole fraction. The binodal curve is shown in figure 3.7. Along the ethane-rich portion of the curve, it was observed that the pressure of the system decreases with increase of nitrogen concentration in the liquid. At -240° F., an attempt was made to determine the equilibrium compositions along constant x_i/x_j lines. Experimental data were smoothed and interpolated to obtain equilibrium composition diagrams at three constant pressures. They are shown in figures 3.8 to 3.10 for the pressures 100, 200, and 300 psia respectively. Furthermore, K-values for the components in the ternary system were correlated as a function of pressure and composition. The correlations are shown in figures 3.11 with $x_{CH_4}/(x_{CH_4} + x_{C_2H_6})$ used as the parameter. The partially miscible region is not, however, included in the correlation.

The results suggest that at constant temperature, K-values of nitrogen always decrease with the increase of pressure, and the K-values of methane and ethane decrease first with the increase of pressure. As the total pressure approaches the vapor pressure of nitrogen or the critical pressure, K-values of methane and ethane increase with the increase of the total pressure.

The separation of nitrogen from natural gases rich in nitrogen may be facilitated by taking advantage of the presence of two liquid phases at the lower temperature. A liquefied natural gas stream may be blended with a hydrocarbon-rich stream so that the overall composition falls within the partially miscible region. Hydrocarbons may be recovered from the hydrocarbon-rich bottom liquid layer, a part of which may be recycled.

Further analysis of the experimental data are given in Chapters 5 and 6.



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

Fig.3.1 Schematic diagram of experimental apparatus.

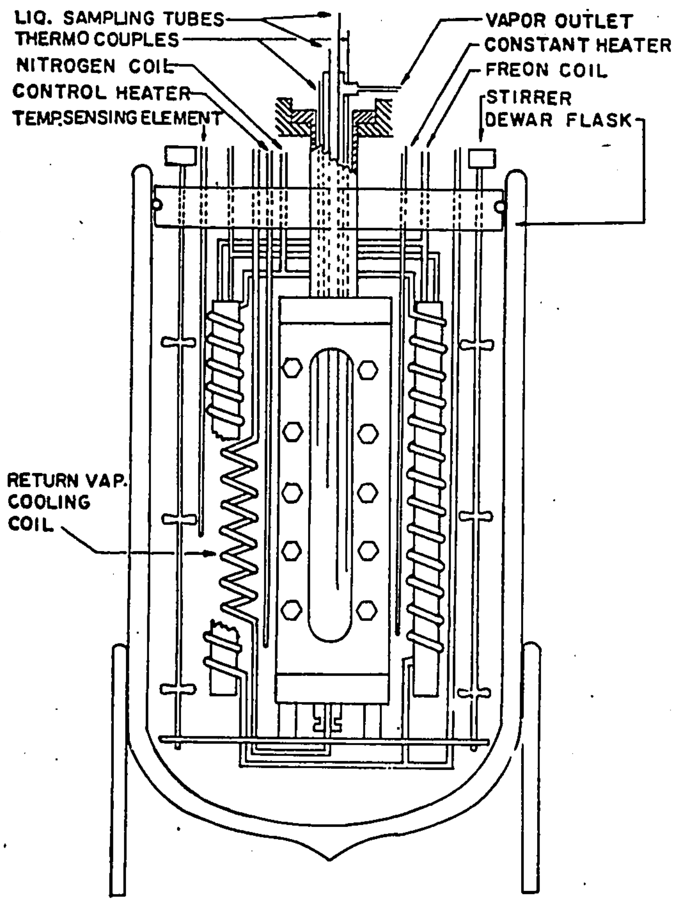


Fig. 3.2 Equilibrium cell and cryostat.

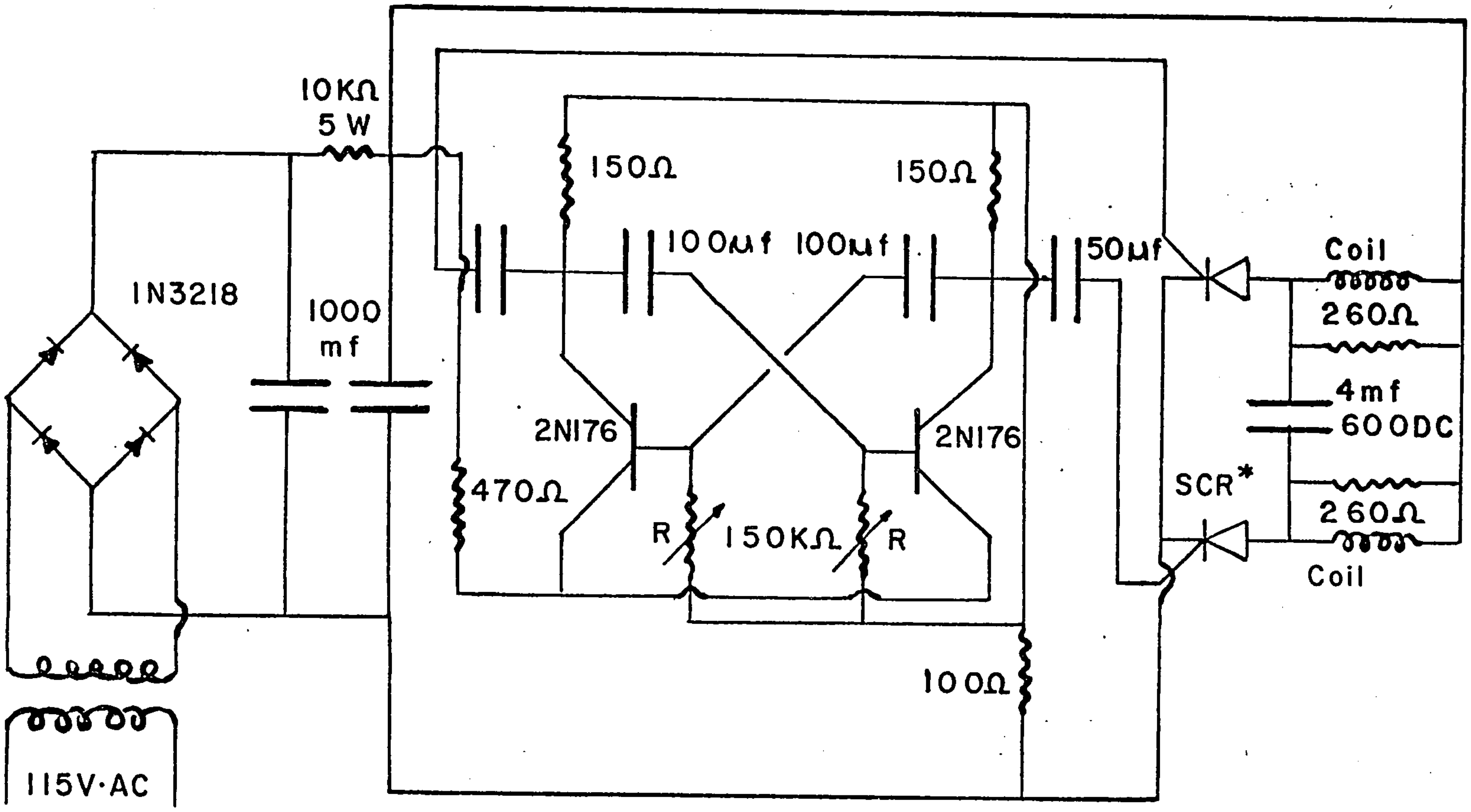
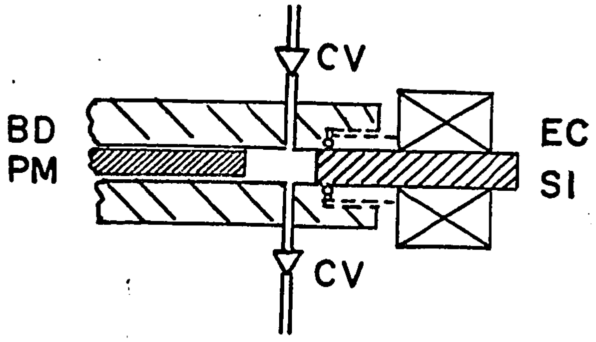


Figure 3.3 a

Electric Circuit of the Electromagnetic Pump



EC	ELECTROMAGNETIC COIL
SI	SOFT IRON ROD
CV	CHECK VALVE
PM	PERMANENT MAGNETIC PISTON ROD
BD	PUMP BODY

Figure 3.3B

Cross Section of the Electromagnetic Pump

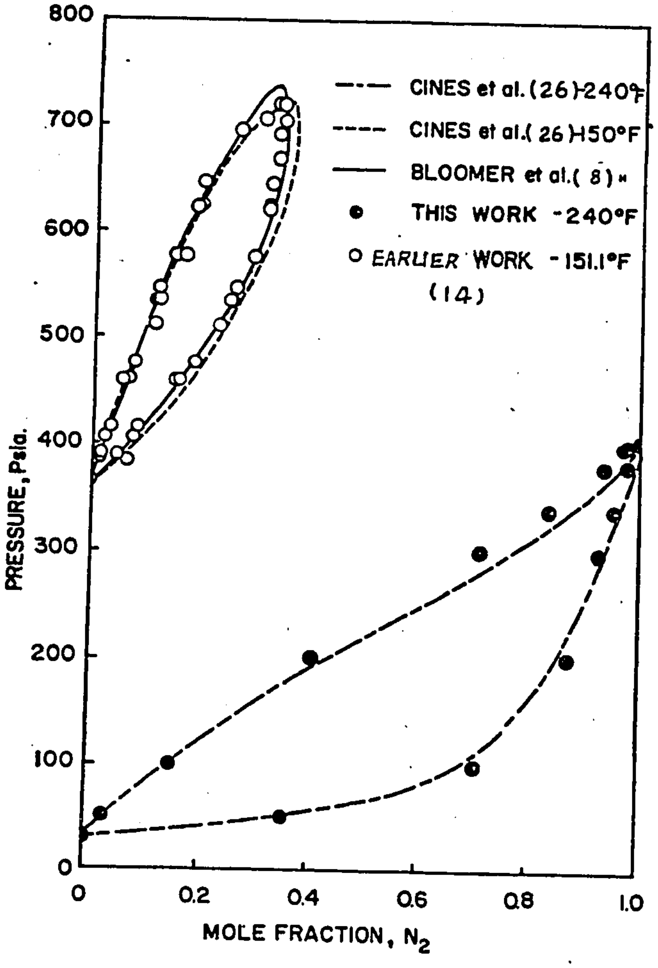


Fig. 3.4 Pressure-composition diagram for nitrogen-methane system.

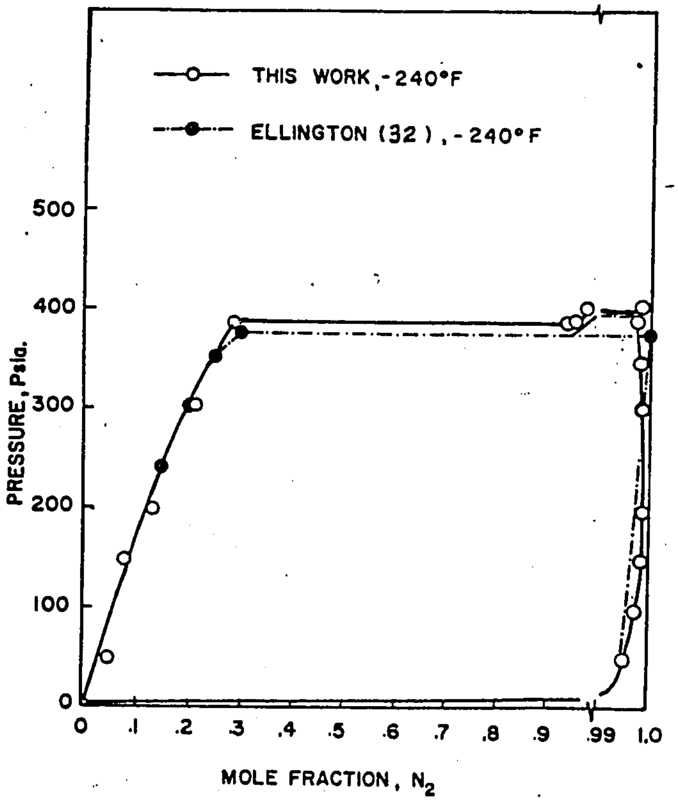


Fig. 3.5 Pressure-composition diagram for nitrogen-ethane system at −240°F.

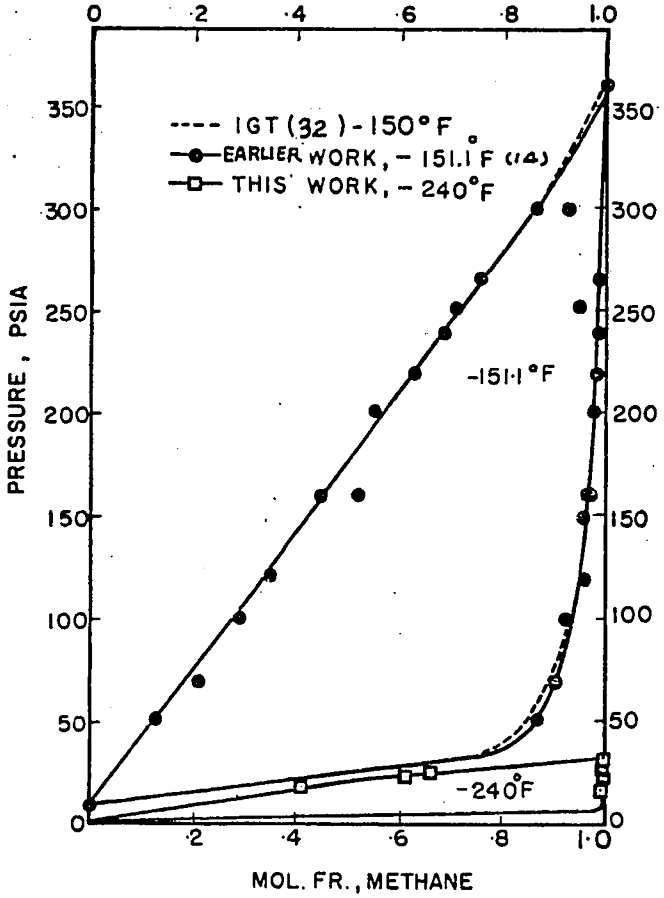


Fig. 3.6 Pressure-composition diagram for methane-ethane system.

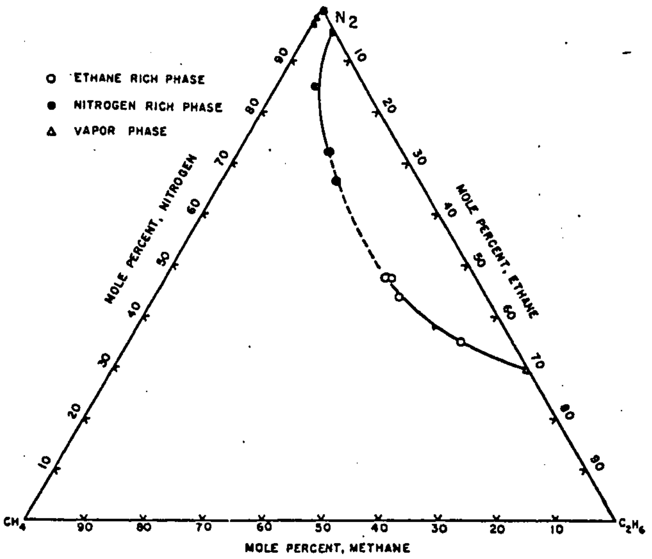


Fig. 3.7 Partial miscible region of the ternary system at −240 °F.

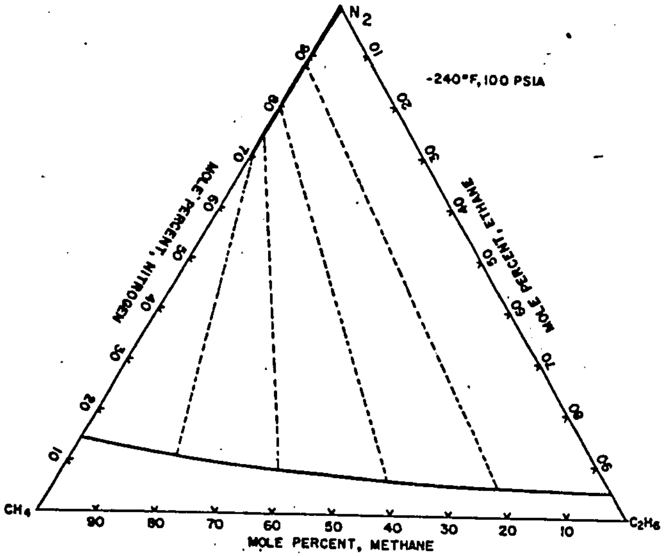


Fig. 3.8 Smoothed equilibrium-composition diagram for nitrogen-methane-ethane system at −240 °F. and 100 lb./sq. in. abs.

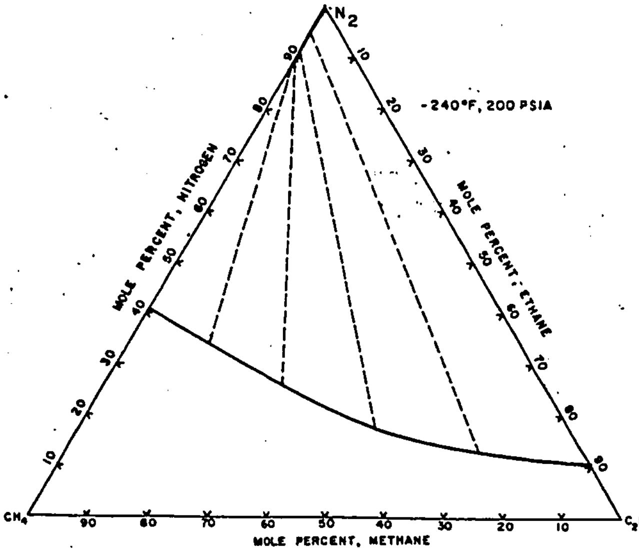


Fig. 3.9 Smoothed equilibrium-composition diagram for nitrogen-methane-ethane system at −240 °F. and 200 lb./sq. in. abs.

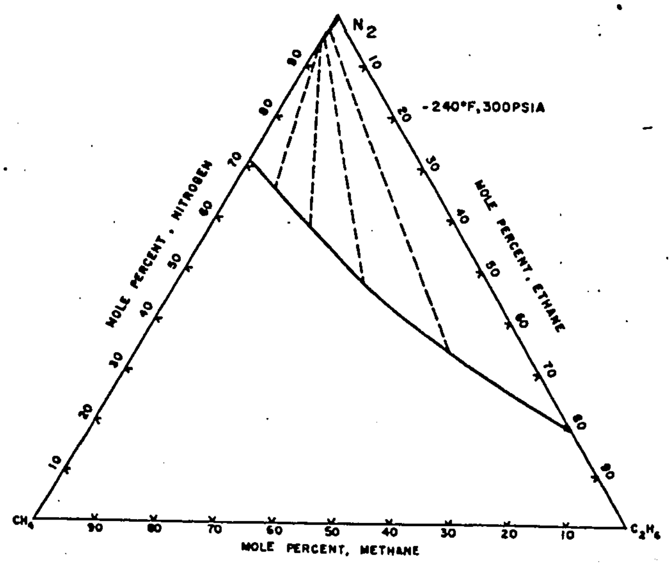


Fig. 3·10 Smoothed equilibrium-composition diagram for nitrogen-methane-ethane system at $-240\,^{\circ}$F. and 300 lb./sq. in. abs.

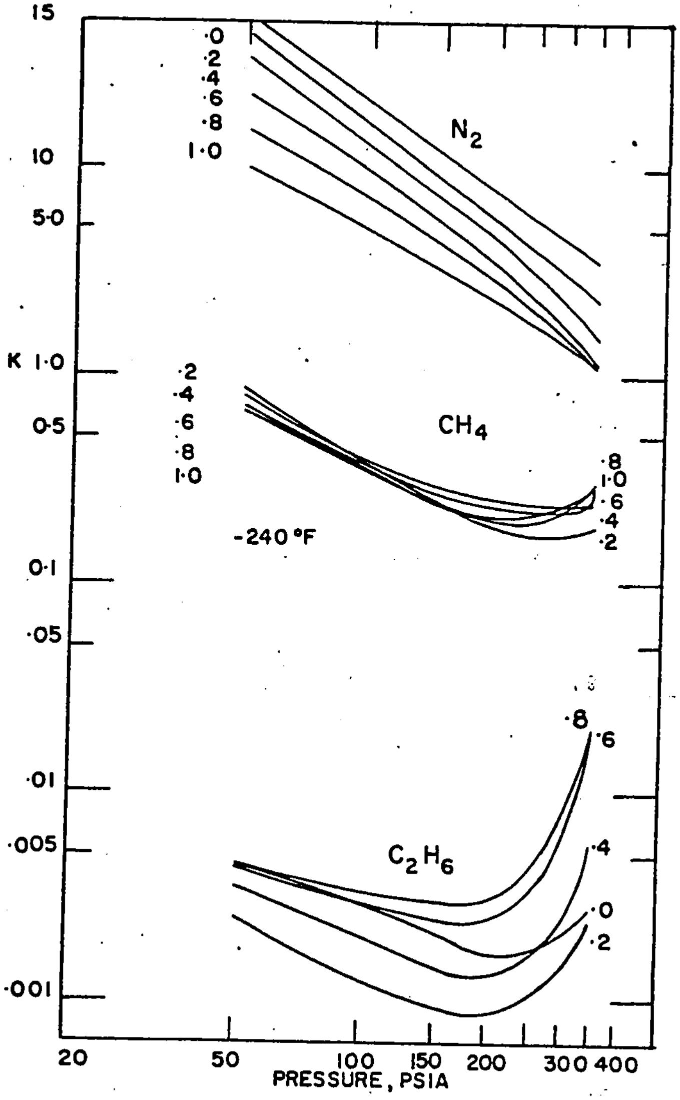


Fig. 3.11 K value-pressure diagram for nitrogen-methane-ethane system at − 240 °F., with $x_{CH_4}/(x_{CH_4} + x_{C_2H_6})$ used as parameter.

CHAPTER 4

CALCULATION OF TERNARY EQUILIBRIUM VAPOR COMPOSITIONS FROM TOTAL PRESSURE-LIQUID COMPOSITION DATA

Various methods have been proposed for the direct (60) and indirect (5, 12, 20, 47, 57, 64, 75, 76, 78, 82, 94, 107) calculation of equilibrium vapor compositions from total pressure (or bubble-point pressure) and liquid composition (p - x) measurements. For the indirect method, an analytical expression for the activity coefficient in terms of liquid composition is required in the calculation. Usually some forms of the integrated Gibbs-Duhem equation are used for this purpose. The method offers a simple and convenient way of calculation. Moreover, it demands fewer experimental points than the direct method. The disadvantage of this method is that there is no criterion in the selection of a model to represent the activity coefficients. A wrong choice of the model may overshadow the quality of the data. However, this difficulty may be overcome by selecting a flexible type, integrated form of the Gibbs-Duhem equation. A modified version of Barker's method (5) using the flexible Redlich-Kister equation from one to five terms is suitable for this purpose and is considered in this study. Details of this modified method are given in Chapter 7. In the direct method the vapor compositions are obtained by direct integration of the coexisting equation without involving the selection of any physical model which is the major advantage of this method. However, in order to evaluate the quantities dP/dx the total pressure data in general must be correlated as a function of liquid composition. For a highly non-ideal system, many terms are needed for such a correlation.

In addition the errors are accumulated from the step-by-step numerical integration procedure. In turn, it may diverge the result of the calculation.

The purpose of this chapter is to formulate a method to extend the existing calculation method for binary systems to ternary systems. By introducing a new concept of Hypothetical component in conjunction with a novel graphical technique of interpolation makes this extension possible.

4.1 EQUATIONS FOR BINARY SYSTEMS

At moderate densities (low and medium pressures), the virial equation of state truncated to the second term gives a good representation of the volumetric properties of vapor mixtures (73). Under these conditions, the equation for the direct evaluation of equilibrium vapor compositions for binary systems at constant temperature is given as (60),

$$\frac{dy_1}{dP} = \frac{\psi - (1 - 2y_1)(y_1 - x_1)(\delta/RT)}{[(y_1 - x_1)/y_1(1 - y_1)] - (y_1 - x_1)(2P\delta/RT)} \qquad 4.1$$

in which

$$\psi = \frac{y_1 y_2 \delta - v_L + x_1\beta_{11} + x_2\beta_{22}}{RT} + \frac{1}{P} \qquad 4.2$$

and

$$\delta = 2\beta_{12} - \beta_{11} - \beta_{22} \qquad 4.3$$

The usefulness of Eq. 4.1 has been demonstrated in the literature (60). Methods for evaluating second virial coefficients β_{ii} of the pure components and the cross coefficient β_{ij} of the mixtures are available in the literature (73).

Since the estimation of δ, v_L, β_{11} and β_{12} does not require high accuracy, two additional simplifications are made in this investigation (60): namely, $v_L = x_1 v_{1L} + x_2 v_{2L}$ and $\delta = 0$. However, these two simplifications should not be considered as restrictions of the method. They are introduced only for the sake of convenience. The errors associated with these assumptions are in general insensitive in the overall calculations. Hence, Eq. 4.1 is reduced to

$$\frac{dy_1}{dP} = \frac{\psi y_1(1 - y_1)}{y_1 - x_1} \qquad 4.4$$

which may be rearranged to give

$$\frac{dy_1}{dx_1} = \frac{\psi y_1(1 - y_1)}{(y_1 - x_1)} \frac{dP}{dx_1} \qquad 4.5$$

The total vapor pressure-liquid composition values may be correlated by means of the excess total vapor pressure as follows:

$$P^E = P - x_1 P_1^s - x_2 P_2^s = x_1(1 - x_1) \sum_{J=0}^{m-1} A_J(2x_1 - 1)^J \qquad 4.6$$

or simply by

$$P = \sum_{J=o}^{m-1} A_J x_1^J \quad \ldots\ldots\ldots\ldots\ldots \quad 4.7$$

The quantity (dP/dx_1) of Eq. 4.5 may be obtained from these equations and the choice of these two equations will be given in a later section. These are the basic working equations employed in this investigation.

4.2 EXTENSION TO TERNARY SYSTEMS

In order to extend the above working equations to ternary systems, one additional restriction must be made. In this investigation, ternary mixtures along any constant liquid mole fraction ratio line are treated as binary mixtures, considering the constant liquid mole fraction ratio mixture in the actual binary as a hypothetical "pure" component in the treatment. It may be seen from figure 4.1a that if component A is considered as the component 1 along the line Aa, the binary mixture B-C as represented by the point a is considered as the hypothetical "pure" component 2. Equilibrium vapor compositions of A, or of component 1, along the line Aa may be evaluated using Eq. 4.5. The vapor pressure of a is given by the P-x measurements of the binary B-C. In the integration of Eq. 4.5, the properties of the hypothetical pure component may be approximated as follows for the evaluation of the quantity ψ :

$$v_{aL} = x_B v_{BL} + x_C v_{CL} = v_{2L} \quad \ldots\ldots\ldots \quad 4.8$$

$$\beta_a = y_B^2 \beta_{BB} + 2 y_B y_C \beta_{BC} + y_C^2 \beta_{CC} = \beta_{22}' \ldots \quad 4.9$$

and

$$\beta_{BC} \doteq (\beta_{BB} \cdot \beta_{CC})^{0.5} \quad \ldots\ldots\ldots \quad 4.10$$

In Eq. 4.9, y_B and y_C (= 1 - y_B) are the equilibrium vapor compositions corresponding to the liquid composition at point a. Similarly, equilibrium vapor compositions of B may be evaluated by means of Eq. 4.5 along the line Bb, and equilibrium vapor compositions of C, along the line Cc. Therefore, at point I in figure 4.1a equilibrium vapor compositions for the three components A, B and C may be evaluated along the lines Aa, Bb, and Cc respectively.

Numerical integration of Eq. 4.5 may proceed either from $x_1 = 0$ to $x_1 = 1$ or from $x_1 = 1$ to $x_1 = 0$ for y_1. In this investigation, an approximation has been used for the initial step of the integration

$$\frac{dy_1}{dx_1} = \frac{\Delta y_1}{\Delta x_1} \quad \ldots\ldots\ldots\ldots\ldots \quad 4.11$$

If the integration starts at $x_1 = 0$, then

$$\Delta y_1 = (y_1)_{x_1 = h} - (y_1)_{x_1 = 0} = (y_1)_{x_1 = h} \quad \ldots \quad 4.12$$

and h is the size of the integration step. With this approximation, the y_1 value at the end of the initial step can be solved algebraically

$$(y_1)_{x_1 = h} = \left\{ \frac{x_1 \left[1 + \left(\frac{dP}{dx_1} \right) \right] \psi}{1 + x_1 \left(\frac{dP}{dx_1} \right) \psi} \right\}_{x_1 = h} \quad \ldots\ldots\ldots\ldots \quad 4.13$$

The subsequent points can be integrated conveniently by using the Runge-Kutta method.

4.3 APPLICATION TO THE NITROGEN-ARGON-OXYGEN TERNARY

Extensive vapor-liquid equilibrium data for the ternary system nitrogen-argon-oxygen were experimentally determined by Wilson, Silverberg, and Zellner (106). Smoothed experimental results , reported at constant temperatures in the order of increasing liquid mole fraction ratio $x_A/(x_A + x_{0_2})$, are suitable for testing the applicability of the proposed method. The reported isothermal data of the ternary at 180° R were employed for this purpose, and the following calculation procedure was followed:

1. Along a constant $x_A/(x_A + x_{0_2})$ line, $P - x_{N_2}$ data were correlated by means of Eq. 4.6 or 4.7.
2. Along the same line, equilibrium vapor composition of N_2 was obtained by integrating Eq.4.5 numerically from $x_{N_2} = 0$ to $x_{N_2} = 1$.
3. Steps 1 and 2 were repeated for other constant $x_A/(x_A + x_{0_2})$ lines. The evaluated y_{N_2} values together with the $P - x_{N_2}$ values were employed for constructing the total vapor pressure-composition diagram as shown in figure 4.2, in which the liquid mole fraction ratio $x_A/(x_A + x_{0_2})$ was used as the paremeter.
4. In order to calculate y_A along constant $x_{N_2}/(x_{N_2} + x_{0_2})$ lines, total vapor pressure values at all intersection points

of the selected lines of constant $x_A/(x_A + x_{O_2})$ and $x_{N_2}/(x_{N_2} + x_{O_2})$ were evaluated by interpolation. The lines were selected at 0.1 intervals. The interpolated total vapor pressure values were correlated and then employed for evaluating the equilibrium vapor composition y_A. In other words, steps 1 and 2 were repeated for each constant liquid mole fraction ratio $x_{N_2}/(x_{N_2} + x_{O_2})$ line for the evaluation of y_A. Total vapor pressure - y_A plot was then constructed as shown in figure 4.3, using the liquid mole fraction $x_{N_2}/(x_{N_2} + x_{O_2})$ as the parameter.

5. The total vapor pressure - composition y_A lines along the constant ratio $x_A/(x_A + x_{O_2})$ were constructed by drawing a smooth curve through the points of intersection of the horizontal lines (not shown in figure 4.3) and the corresponding total vapor pressure - composition y_A line of constant ratio $x_{N_2}/(x_{N_2} + x_{O_2})$ obtained from step 4. The horizontal lines represent the values of total vapor pressure which were obtained from the points of intersection of the constant ratio lines of $x_{N_2}/(x_{N_2} + x_{O_2})$ and $x_A/(x_A + x_{O_2})$, also from step 4.
6. Similarly, figure 4.4 was constructed for component O_2.

4.4 RESULTS OF CALCULATIONS

From figures 4.3 and 4.4, equilibrium vapor compositions of A and O_2 were evaluated along constant $x_A/(x_A + x_{O_2})$ lines and at 0.1 intervals of x_{N_2}. These values, together with the equilibrium vapor composition values of nitrogen obtained in step 2, are compared with smoothed experimental values in Table 4.1 and 4.2. In Table 4.1, calculated results are compared with the experimental values in details along the constant ratio $x_A/(x_A + x_{O_2})$ lines, and in Table 4.2, a summary of average and maximum Δy values for the ternary at 180° R is presented.

Calculations were performed by means of an IBM 360 Model 40 digital computer with double precision. It was found that the average absolute deviations obtained by using Eq. 4.6 for correlating the total vapor pressure data were lower than those using Eq. 4.7. On the other hand, the reverse was observed for the maximum deviations. Since it was desirable to have low maximum deviations for obtaining smooth interpolated total vapor pressure values, Eq. 4.7 was favoured. The results reported in Tables 1 and 2 were those obtained by using Eq. 4.7. The average absolute deviations obtained were in general less than 0.002 in y values indicating the usefulness of the proposed method.

4.5 MINIMUM EXPERIMENTAL DETERMINATIONS

It appears that Eq. 4.7 is a useful tool for correlating total vapor pressure-liquid composition data. If the validity of a four-term Eq. 4.7 is accepted, as observed in this investigation for the ternary system nitrogen-argon-oxygen, measurement of total vapor pressure for two ternary liquid mixtures, along a constant liquid mole fraction line suffices for calculation along one constant mole fraction ratio line. It may be seen from figure 4.1b that for ternary systems over the complete concentration range, in addition to the properties of the pure components and the three binaries, a minimum of three experimental points is required.

If the validity of a five-term Eq. 4.7 is accepted, a minimum of seven experimental points is required. This is shown in figure 4.1c.

4.6 SUMMARY

In conclusion, a simple and direct method has been proposed for evaluating ternary vapor-liquid equilibrium compositions from P - x measurements along constant liquid mole fraction ratio lines. Based on the new concept of "hypothetical component" and a new graphical technique, an extension of the method for binary calculation to ternary systems, has been made possible. The proposed method takes into account the ternary effect in the liquid solution as no assumption is involved . Although the procedures outlined are limited to low or medium-pressures, the proposed method can be extended to high pressures when a suitable equation of state or P-V-T data of the pure components and their vapor mixtures are available. Rigorous equation for the direct evaluation of equilibrium vapor compositions for binary systems is available (60), which can be extended to ternary systems following a similar procedure as outlined in this investigation. Furthermore, although only direct method is demonstrated in the foregoing discussions, but with this new concept and graphical technique (figure 4.3 or 4.4) any method for binary calculation can be extended to ternary system.

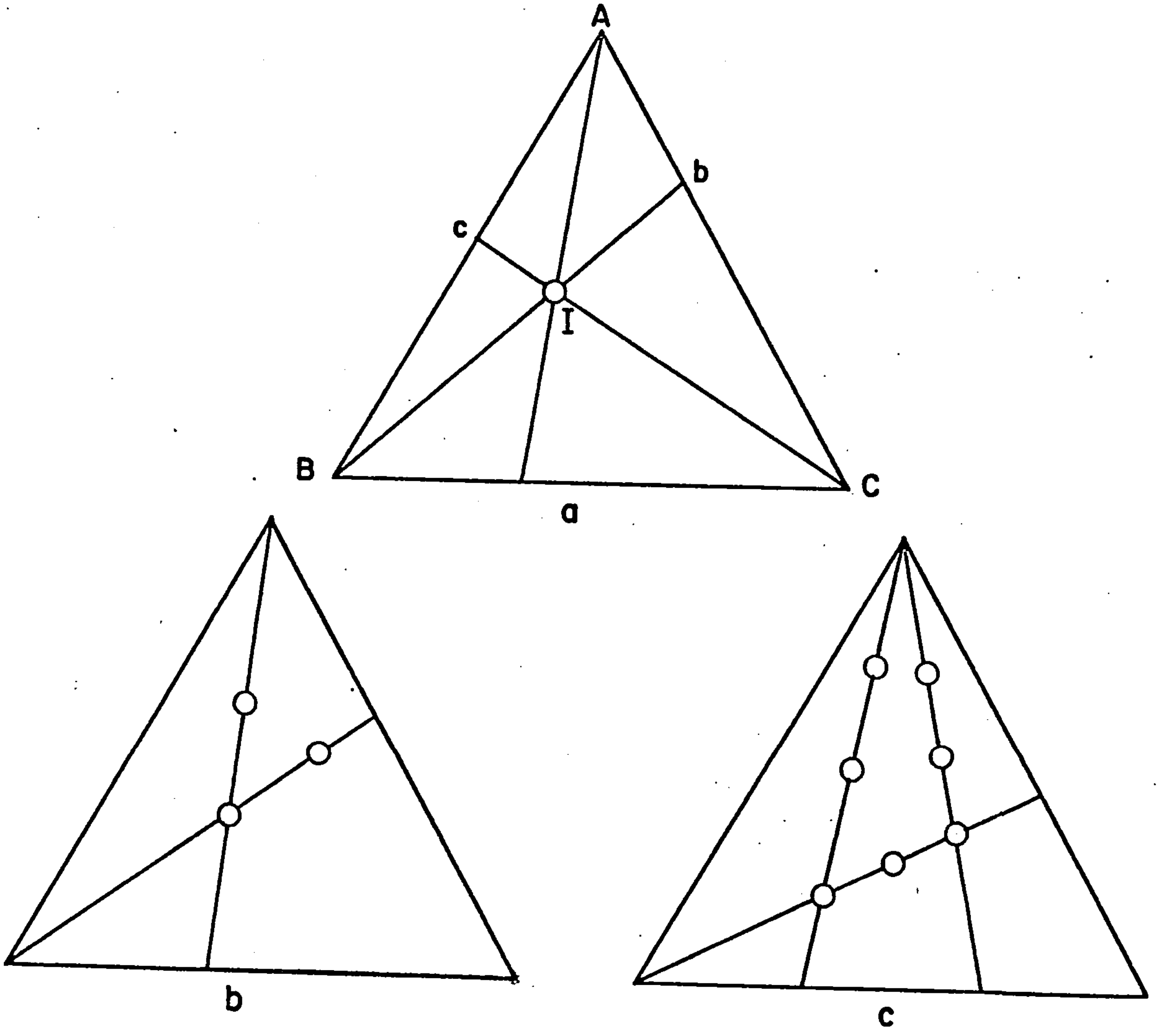


Figure 4.1 Illustration of the Proposed Method

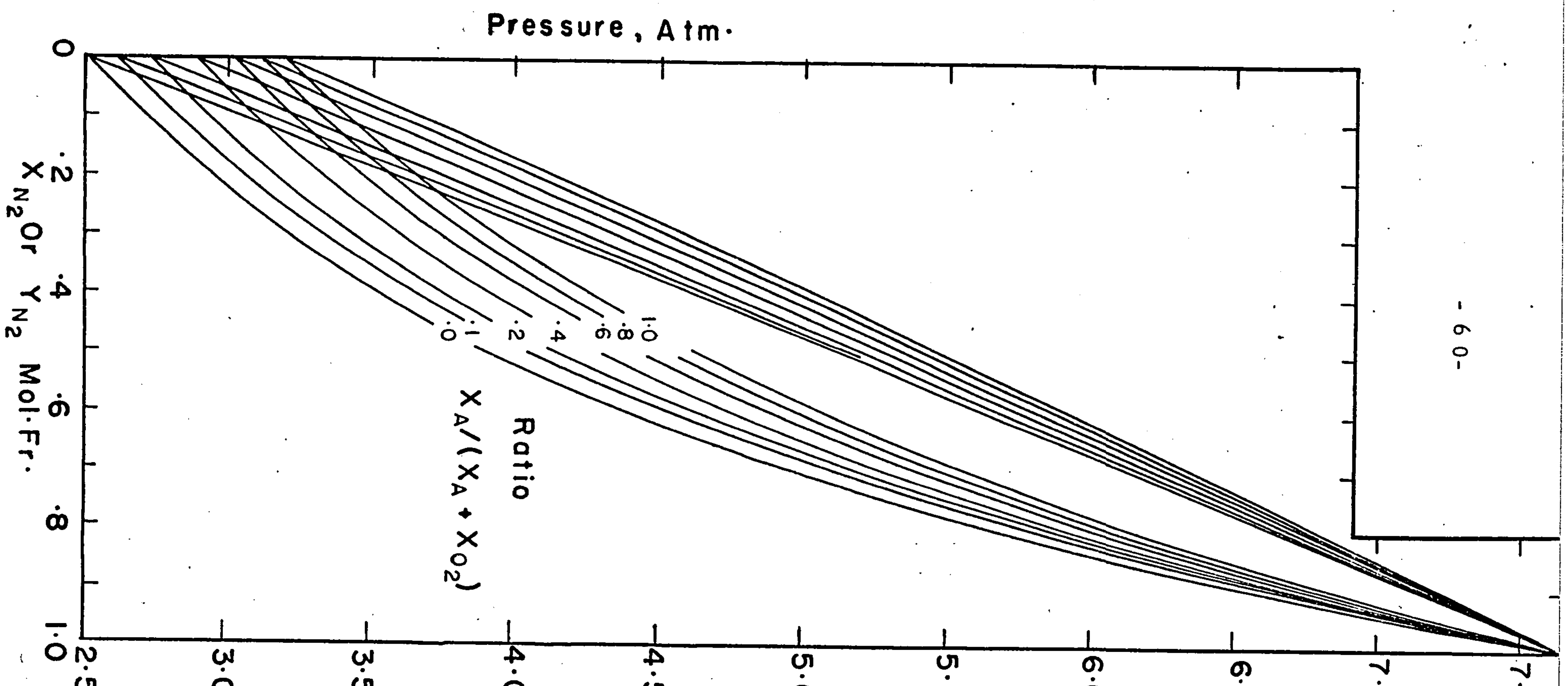


Figure 4.2 Total Pressure-Composition Diagram for Nitrogen in the System Nitrogen-Argon-Oxygen at 180° R.

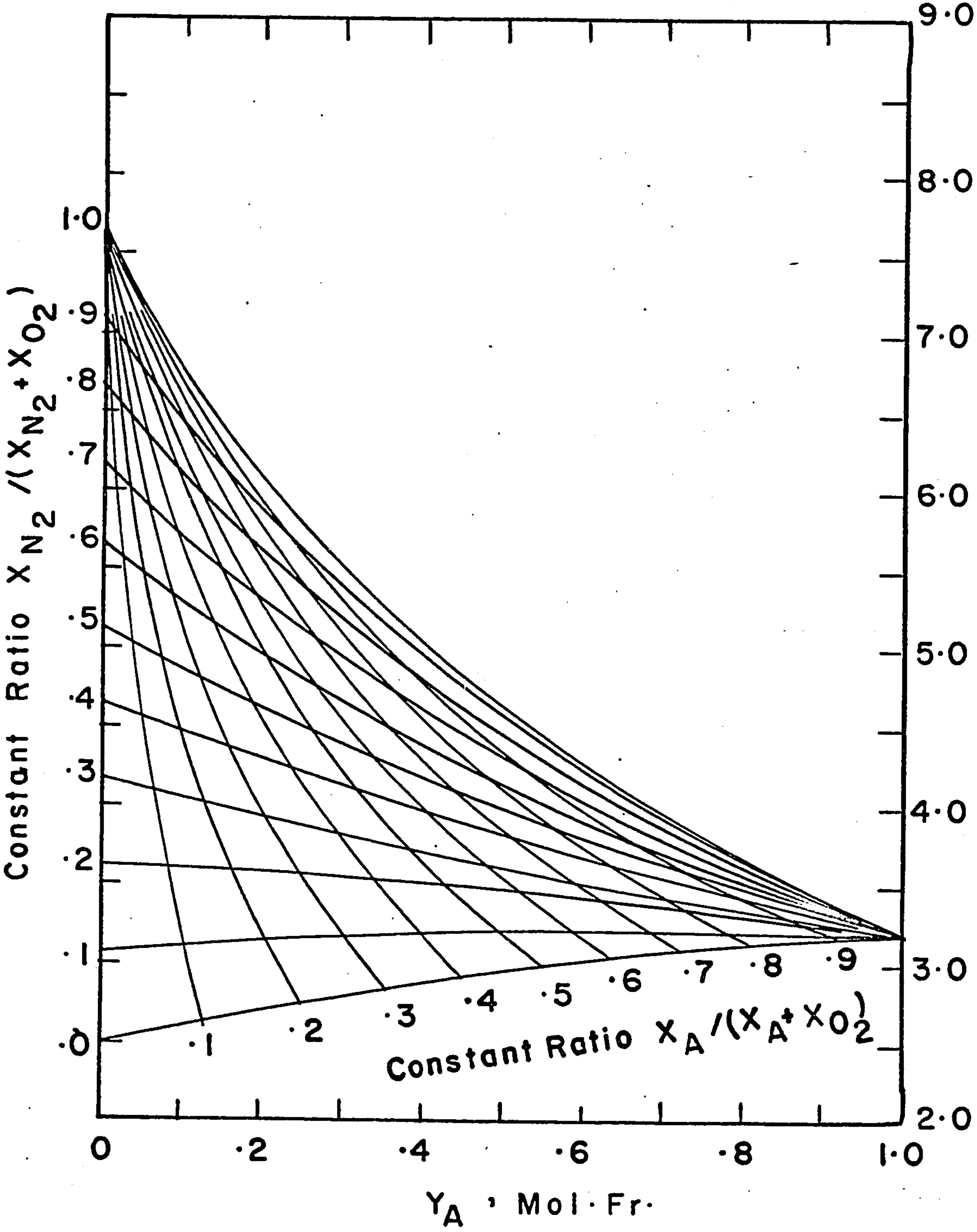


Figure 4.3

Total Vapor Pressure-Composition Diagram for Argon in the System Nitrogen-Argon-Oxygen at 180° R.

Total Vapor Pressure-Composition Diagram for Oxygen in the System Nitrogen-Argon-Oxygen at 180° R.

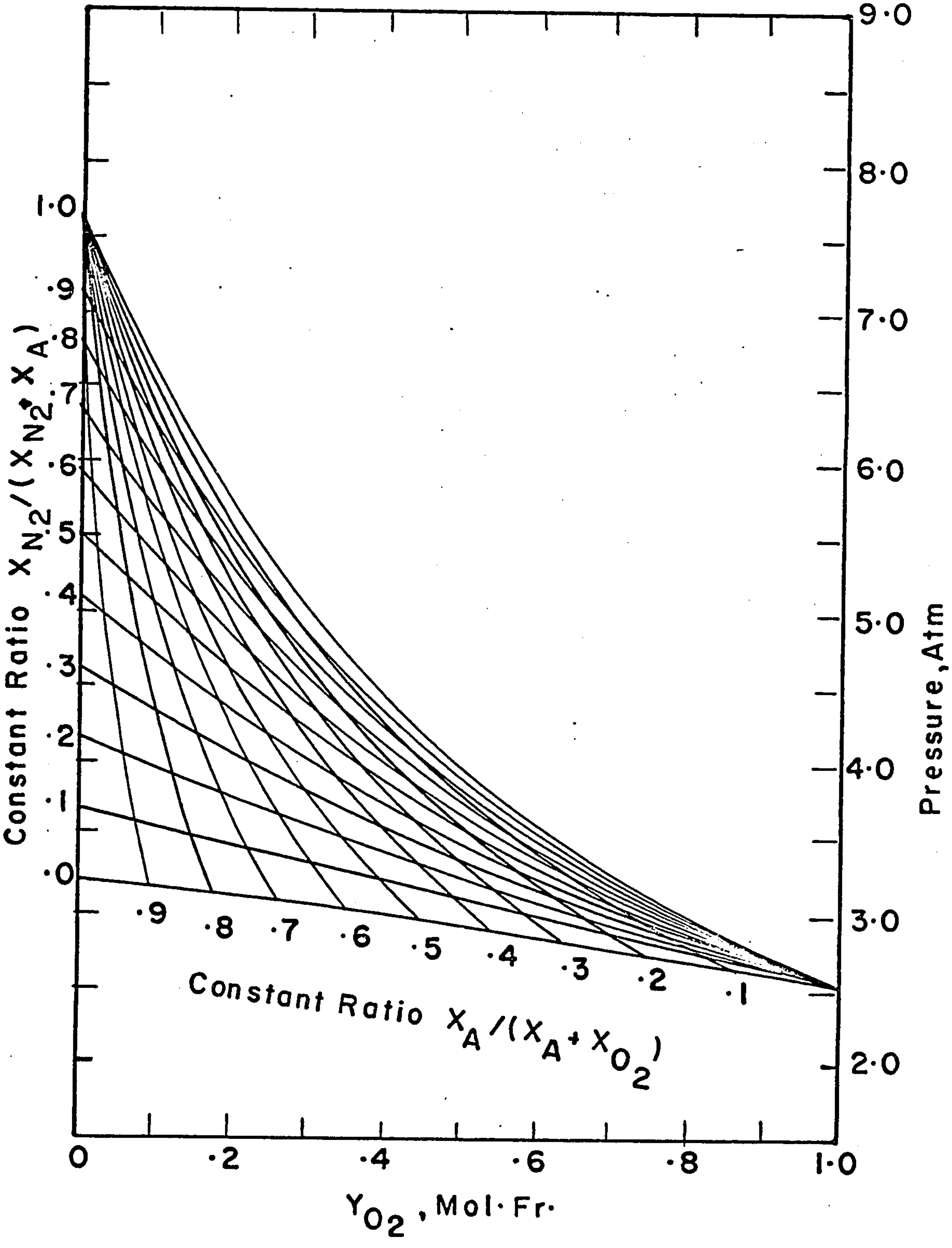


Figure 4.4

CHAPTER 5

DEVELOPMENT OF THE TOTAL PRESSURE METHOD FOR SYSTEMS AT HIGH PRESSURES

At high pressures the effect of pressure on the activity coefficient,

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{x,\ T} = \frac{\bar{v}_i}{RT} \qquad 5.1$$

is not negligible hence the Gibbs-Duhem equation,

$$\sum_{i=1}^{n} x_i \, d \ln \gamma_i = 0 \qquad 5.2$$

should be used only under isobaric and isothermal conditions. Therefore, it is necessary to devise an adjusted activity coefficient to be used under such restrictions. If the system temperature is above the critical temperature of any one constituent, the traditional reference state for either the activity coefficient or the fugacity is usually unattainable or hypothetical. This makes the thermodynamic analysis difficult. In such a case an unsymmetric convention of the activity coefficient, introduced for the lighter component taking into account the deviation from Henry's law rather than from Raoult's law, is more convenient.

Based on these considerations, a general and rigorous indirect method is developed for calculating vapor phase compositions from total pressure and liquid composition data at high pressures and isothermal conditions. Both the equations derived and the method for evaluating adjustable parameters are formulated for multicomponent systems in a general manner.

5.1 DERIVATION OF EQUATIONS

At system temperature T and reference pressure P° the activity coefficient of component i in the liquid phase can be conveniently defined as

$$\gamma_i(P°,\ T,\ x) = \hat{f}_{iL}(P°,\ T,\ x)/x_i f°_{iL}(P°,\ T) \qquad 5.3$$

where $\hat{f}_{iL}$ and x are the fugacity and composition of component i in the liquid mixtures, and $f°_{iL}$ is the reference fugacity of component i at the reference pressure P°. The pressure effect on the fugacity coefficient is

$$\frac{\partial \ln \hat{f}_{iL}}{\partial P} = \frac{\bar{v}_i}{RT} \qquad 5.4$$

Combining Eqs. 5.3 and 5.4, the definition of the adjusted activity coefficient is then given as

$$\gamma_i(P°, T, x) = \hat{f}_{iL}(P, T, x) \ / \ x_i f°_{iL}(P°, T)\ \exp \int_P^{P°} \frac{\bar{v}_i}{RT}\, dP \qquad 5.5$$

This equation may be rewritten as

$$\gamma_i = \frac{\hat{f}_i}{x_i f°_i} \ \exp \int_P^{P°} \frac{\bar{v}_i}{RT}\, dP \qquad 5.6$$

with the subscript L omitted for the purpose of simplicity. This result is similar to the definition given by Prausnitz (71). The convention is chosen to normalize the activity coefficient as $\gamma_i \rightarrow 1$ when $x_i \rightarrow 1$ for the subcritical component i or as $\gamma_j \rightarrow 1$ when $x_j \rightarrow 0$ for the supercritical component j. Therefore for a subcritical component the reference fugacity f_i° is simply the liquid fugacity of the pure component i at system temperature T and reference pressure P°. However, for a supercritical component j the reference fugacity is defined by

$$f_j^\circ\ (P^\circ,\ T) = \mathcal{H}(P^\circ,\ T) = \left[\lim_{x_j \rightarrow 0} \frac{\hat{f}_j}{x_j}\right] \exp - \int_{P_M^s}^{P^\circ} \frac{\bar{v}_j^{\infty}\ dP}{RT} \quad ..5.6A$$

In this expression, $\mathcal{H}(P^\circ,\ T)$ is the constant - pressure Henry's law coefficient for the supercritical component j in the solute-free mixture and P_M^s is the bubble point pressure of the solute-free mixture.

It can be easily shown that Eq. 5.6 satisfies the Gibbs-Duhem equation. Since the general form of the Gibbs-Duhem equation for a system at isothermal condition is given by

$$\sum_{i=1}^{n} x_i\ d\,\mu_i = v dP \qquad 5.7$$

where μ_i is the chemical potential of the component i, and v is the molar volume of the liquid mixture, the chemical potential at composition x and total pressure P is given by

$$\mu_i\ (P,\ T,\ x) = \mu_i^\circ\ (P^\circ,\ T) + RT \ln \frac{\hat{f}_i\ (P,\ T,\ x)}{f_{iL}^\circ\ (P^\circ,\ T)} \quad \cdots\cdots \qquad 5.8$$

From Eq. 5.6

$$\hat{f}_i = x_i\ \gamma_i\ f_i^\circ\ \ \exp \int_{P^\circ}^{P} \frac{\bar{v}_i}{RT}\ dP \quad \cdots\cdots\cdots \qquad 5.9$$

thus, Eq. 5.8 becomes

$$\mu_i (P, T, x) = \mu_i^\circ (P^\circ, T) + RT \ln \gamma_i x_i + \int_{P^\circ}^{P} \bar{v}_i \, dP \cdots \qquad 5.10$$

The above equation can be expressed into the following differentail form

$$d\mu_i = RT \, d \ln \gamma_i + RT \, d \ln x_i + \bar{v}_i \, dP + \left(\int_{P^\circ}^{P} dP \right) d\bar{v}_i \qquad 5.11$$

Substituting this equation into Eq. 5.7 gives

$$\sum_{i=1}^{n} x_i \, d \ln \gamma_i + \int_{P^\circ}^{P} \left[\sum_{i=1}^{n} x_i \, d \bar{v}_i \right]_{T, P} dP = 0 \qquad 5.12$$

The second term of Eq. 5.12 is equal to zero, thus the equation reduces to Eq. 5.2.

At equilibrium the fugacities of component i in both phases should be identical namely:

$$\hat{f}_{iL} = \hat{f}_{iv} \quad \cdots\cdots\cdots\cdots \qquad 5.13$$

Since

$$\hat{f}_{iv} = y_i \, \phi_i \, P \quad \cdots\cdots\cdots\cdots \qquad 5.14$$

Eq. 5.6 thus becomes

$$\gamma_i = \frac{y_i \, \phi_i \, P}{x_i \, f_i^\circ} \exp \int_{P}^{P^\circ} \frac{\bar{v}_i \, dP}{RT} \quad \cdots\cdots\cdots \qquad 5.15$$

or

$$Py_i = \frac{\gamma_i \, x_i \, f_i^\circ}{\phi_i} \exp \int_{P^\circ}^{P} \frac{\bar{v}_i \, dP}{RT} \quad \cdots\cdots\cdots \qquad 5.16$$

Summing up Eq. 5.16 for n components gives

$$P = \sum_{i=1}^{n} \frac{\gamma_i \, x_i \, f_i^\circ}{\phi} \exp \int_{P^\circ}^{P} \frac{\bar{v}_i \, dP}{RT} \quad \cdots\cdots \qquad 5.17$$

where γ_i standing for activity coefficient using either the symmetric or the unsymmetric convention depends upon the system's condition. A summary of the integrated forms of the Gibbs-Duhem equation is available in the literature (42). In general, it can be expressed as

$$\gamma_i = \gamma_1 (x, P, B_1, B_2 \cdots B_m)_T \cdots\cdots\cdots \qquad 5.18$$

Substituting Eq. 5.18 back to the Eq. 5.17 gives

$$P = \sum_{i=1}^{n} \frac{\gamma_i (x , P, B_1, B_2 \cdots B_m)_T \; x_i f_i^\circ}{\phi_i} \exp \int_{P^\circ}^{P} \frac{\bar{v}_i \, dP}{RT} \qquad 5.19$$

Thus, the system pressure is related to the compositions x , with the exception that ϕ_i is dependent on the vapor composition. From Eqs. 5.16 and 5.19 vapor compositions can then be related to the P and x as

$$y_i = \frac{\gamma_i (x , P, B_1, B_2, \cdots B_m)_T \, x_i f_i^\circ}{\phi_i} \exp \int_{P^\circ}^{P} \frac{\bar{v}_i \, dP}{RT} \Bigg/ \sum_{i=1}^{n} \frac{\gamma_i (x , P, B_1, B_2, \cdots B_m)_T \; x_i f_i^\circ}{\phi_i} \exp \int_{P^\circ}^{P} \frac{\bar{v}_i \, dP}{RT} \quad \cdots\cdots\cdots\cdots\cdots \qquad 5.20$$

Equations 5.19 and 5.20 are the general and basic equations for computing vapor compositions from total pressure P and liquid composition data at isothermal conditions. Methods for evaluating the supporting properties such as ϕ_i and $\bar{v}_i$ are available (23, 25). The rest of the problem is to develop a practical method to evaluate the adjustable parameters B_j's from experimental data.

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5.2 EVALUATION OF THE ADJUSTABLE PARAMETER B_j's

Assuming that ϕ_i's are a set of known quantities then Eq. 5.19 can be written in a simple form

$$P_{icomp} = P_{icomp}\,(x,\ B_1,\ \cdots\ B_j,\ \cdots\ B_m) \quad \cdots\cdots\cdots \qquad 5.21$$

The sum of the deviation squares is defined as

$$S = \sum_{i=1}^{nobs} W_i \left[P_{iobs} - P_{icomp}\,(x,\ B_1,\ \cdots\ B_j,\ \cdots\ B_m) \right]^2 \qquad 5.22$$

where the subscript 'comp' is referred to as a computed and 'obs' an observed value ; and W_i denotes the weights associated with the experimental data. Heavier weight may be given to the experimental point of higher accuracy. For instance, if $W_i = (1/P_{iobs})^2$, Eq. 5.22 thus becomes a sum of the percentage deviation squares rather than a sum of the absolute deviation squares.

The sum of the deviation squares may be minimized by setting

$$\frac{\partial S}{\partial B_j} = 0, \quad (j = 1,\ m) \quad \cdots\cdots\cdots\cdots\cdots \qquad 5.23$$

This gives a set of m simultaneous equations from which m number of unknowns B_j's, in principle, can be solved. However, since these equations are nonlinear in B_j thus making the solution impossible. To overcome this difficulty, the function P_i may be linearized first by expanding it into a Taylor series about the point o, that is,

$$P_{io} = P_i \left(x_o \quad B_{1o}, \cdots, \ B_{jo} \cdots \ B_{mo} \right)$$

where B_{jo}'s are the estimated values corresponding to B_j's at the first interation, such that the function $\widetilde{P}_{icomp}$ is linear in ΔB_j, or

$$\widetilde{P}_{icomp} = P_{io} + \left(\frac{\partial P_{io}}{\partial B_1} \right) \Delta B_1 + \left(\frac{\partial P_{io}}{\partial B_2} \right) \Delta B_2 + \cdots$$

$$+ \left(\frac{\partial P_{io}}{\partial B_m} \right) \Delta B_m \qquad \cdots\cdots\cdots\cdots\cdots \qquad 5.24$$

where $\Delta B_j = B_j - B_{jo}$, and $\widetilde{P}_{icomp}$ is the approximated value of P_{icomp}. The S in Eq. 5.22 is then replaced by $\widetilde{S}$ or

$$\widetilde{S} = \sum_{i=1}^{nobs} W_i \left(P_{iobs} - \widetilde{P}_{icomp} \right)^2 \qquad \cdots\cdots\cdots \qquad 5.25$$

Differentiating $\widetilde{S}$ with respect to each ΔB_j and setting the derivatives equal to zero gives a set of m equations,

$$\sum_{i=1}^{nobs} W_i \left(\frac{\partial P_{io}}{\partial B_j} \right) \left(\frac{\partial P_{io}}{\partial B_1} \right) \Delta B_1 + \qquad \cdots\cdots\cdots\cdots$$

$$+ \sum_{i=1}^{nobs} W_i \left(\frac{\partial P_{io}}{\partial B_1} \right) \left(\frac{\partial P_{io}}{\partial B_m} \right) \Delta B_m$$

$$= \sum_{i=1}^{nobs} W_i \quad \left(P_{iobs} - P_{io} \right) \left(\frac{\partial P_{io}}{\partial B_j} \right) \cdots\cdots\cdots \qquad 5.26$$

which are linear in ΔB_j and can be solved simultaneously for ΔB_j's. The new values of B_j's can be calculated by $B_j = B_{jo} + \Delta B_j$. These new values are then used as the starting values for the next interation. Repeat these procedures until ΔB_j's become less than the specified tolerance, then the next nest of iteration is followed to calculate the correct values of Φ_i. As soon as B_j's are established, y_i's can be calculated directly from Eq. 5.20.

5.3 BINARY SYSTEM CONTAINING SUBCRITICAL COMPONENTS

For a binary system containing subcritical component Eq. 5.19 may be reduced to

$$P = \frac{\gamma_1 x_1 f_1^\circ}{\Phi_i} \exp \int_{P^\circ}^{P} \frac{\bar{v}_1 \, dP}{RT} + \frac{\gamma_2 x_2 f_2^\circ}{\Phi_2} \exp \int_{P^\circ}^{P} \frac{\bar{v}_2 dP}{RT} \quad \cdot\cdot \; 5.27$$

It is most convenient and attainable to choose the saturated pressure of more volatile component as a reference pressure, thus avoiding a hypothetical reference state. If the Redlich-Kister equation is used to express the activity coefficients, one obtains

$$\ln \gamma_1 = x_2^2 \Big[B_1 + B_2 (4x_1 - 1) + B_3 (6x_1 - 1)(2x_1 - 1) + B_4 (8x_1 - 1) (2x_1 - 1)^2 + B_5 (10x_1 - 1)(2x_1 - 1)^3 + \cdots \Big] \quad 5.28$$

$$\ln \gamma_2 = x_1^2 \Big[B_1 + B_2 (4x_1 - 3) + B_3 (6x_1 - 5)(2x_1 - 1) + B_4 (8x_1 - 7)(2x_1 - 1)^2 + B_5 (10x_1 - 9)(2x_1 - 1)^3 + \cdots \Big] \quad 5.29$$

Differentiate Eq. 5.27 partially with respect to B_j to give

$$\frac{\partial P}{\partial B_j} = \left(x \; f_1^{\circ} \; \exp \int_{P^{\circ}}^{P} \frac{\bar{v}_1 \, dP}{RT} \Big/ \phi_1 \right) \frac{\partial \gamma_1}{\partial B_j}$$

$$+ \left(x_2 \, f_2^{\circ} \; \exp \int_{P^{\circ}}^{P} \frac{v_2 \, dP}{RT} \Big/ \phi_2 \right) \frac{\partial \gamma_2}{\partial B_j} \qquad \ldots\ldots\ldots \qquad 5.30$$

where $\frac{\partial \gamma_1}{\partial B_j}$ and $\frac{\partial \gamma_2}{\partial B_j}$ can be obtained from Eq. 5.28 and from Eq. 5.29 respectively.

Thus

$$\frac{\partial \gamma_1}{\partial B_1} = \gamma_1 \, x_2^2$$

$$\frac{\partial \gamma_1}{\partial B_2} = \gamma_1 \, x_2^2 \; (4x_1 - 1)$$

$$\frac{\partial \gamma_1}{\partial B_3} = \gamma_1 \, x_2^2 \; (6x_1 - 1) \; (2x_1 - 1)$$

$$\frac{\partial \gamma_1}{\partial B_4} = \gamma_1 \, x_2^2 \; (8x_1 - 1) \; (2x_1 - 1)^2$$

$$\frac{\partial \gamma_1}{\partial B_5} = \gamma_1 \, x_2^2 \; (10x_1 - 1) \; (2x_1 - 1)^3$$

$$\ldots\ldots\ldots\ldots \qquad 5.31A$$

and

$$\frac{\partial \gamma_2}{\partial B_1} = \gamma_2 \, x_1^{\,2}$$

$$\frac{\partial \gamma_2}{\partial B_2} = \gamma_2 \, x_1^{\,2}(4x_1 - 3)$$

$$\frac{\partial \gamma_2}{\partial B_3} = \gamma_2 \, x_1^{\,2}(6x_1 - 5)(2x_1 - 1)$$

$$\frac{\partial \gamma_2}{\partial B_4} = \gamma_2 \, x_1^{\,2}(8x_1 - 7)(2x_1 - 1)^2$$

$$\frac{\partial \gamma_2}{\partial B_5} = \gamma_2 \, x_1^{\,2}(10x_1 - 9)(2x_1 - 1)^3$$

$$\cdots\cdots\cdots\cdots \qquad 5.31\,B$$

Substituting Eqs. 5.28 to 5.31 into Eq. 5.26 gives m equations which can be solved simultaneously for B_j's according to the method described in Section 5.2. Details of the computing technique and computer program are given in Appendix VI.

5.4 BINARY SYSTEM CONTAINING ONE SUPERCRITICAL COMPONENT

For a binary system containing one supercritical component, Eq. 5.19 is reduced to

$$P = \frac{\gamma_1 x_1 f_1^{\circ}(P^{\circ})}{\phi_1} \exp \int_{P^{\circ}}^{P} \frac{\bar{v}_1}{RT} dP + \frac{\gamma_2^{*} \, x_2 \, \mathscr{H}(P^{\circ})}{\phi_2} \exp \int_{P^{\circ}}^{P} \frac{\bar{v}_2}{RT} dP \qquad \cdots\cdots\cdots \; 5.32$$

in which liquid activity coefficients are defined by the following conventions

$$\gamma_1 = 1 \quad \text{at} \quad x_1 = 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 5.33$$

and

$$\gamma_2^* = 1 \quad \text{at} \quad x_2 = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 5.34$$

where

$$f_1^\circ (P^\circ) = f_1^\circ (P^s) \exp - \int_{P^\circ}^{P^s} \frac{v_1}{RT} \, dP \quad \ldots\ldots\ldots \quad 5.35$$

$$\mathcal{H}(P_1^s) = \lim_{x_2 \to 0} \frac{\hat{f}_2}{x_2} \quad \ldots\ldots\ldots \quad 5.36$$

and

$$\mathcal{H}(P^\circ) = \mathcal{H}(P_1^s) \exp - \int_{P^\circ}^{P^s} \frac{\bar{v}_2^\infty dP}{RT} \quad \ldots\ldots\ldots \quad 5.37$$

The subscript 2 is referred to the supercritical component; the supercript * is referred to the unsymmetric convention. For component 1 Eq. 5.28 can be used to represent the activity coefficient. However, for the unsymmetric convention the activity coefficient of the component 2 can be derived as follows:

At reference pressure P° and system temperature T the Gibbs-Duhem equation takes the form

$$x_1 \, d \ln \gamma_1 + (1 - x_1) \, d \ln \gamma_2^* = 0$$

which can be rearranged and integrated to give

$$\int_{x_1 = 1}^{x_1 = x} d \ln \gamma_2^* = \int_{x_1 = 1}^{x_1 = x} - \frac{x_1}{1 - x_1} \, d \ln \gamma_1 \quad \ldots \quad 5.38$$

Substituting Eq. 5.28 into Eq. 5.38 and combining with the limiting condition,

$$\gamma_2^{*} = 1 \quad \text{at} \quad x_2 = 0 \qquad 5.39$$

it can be shown that

$$\ln \gamma_2^{*} = B_1 (x_1^2 - 1) + B_2 (x_1^2 (4x_1 - 3) - 1) + B_3 (x_1^2 (6x_1 - 5) (2x_1 - 1) - 1) + B_4 (x_1^2 (8x_1 - 7) (2x_1 - 1)^2 - 1) + B_5 (x_1^2 (10x_1 - 9) (2x_1 - 1)^3 - 1) + \quad \ldots\ldots\ldots\ldots\ldots\ldots \qquad 5.40$$

This is a new equation of the Redlich-Kister type which can be used to represent activity coefficient of unsymmetric convention. Differentiating Eq. 5.32 with respect to B_j gives

$$\frac{\partial P}{\partial B_j} = \left(x_1 f_1^{\circ} \exp\int_{P^r}^{P} \frac{\bar{v}_1 \, dP}{RT} \Big/ \phi_1\right) \frac{\partial \gamma_1}{\partial B_j} + \left(x_2 \mathcal{H} \exp\int_{P^r}^{P} \frac{\bar{v}_2 \, dP}{RT} \Big/ \phi_2\right) \frac{\partial \gamma_2^{*}}{\partial B_j} \quad \ldots\ldots\ldots \qquad 5.41$$

where $\dfrac{\partial \gamma_1}{\partial B_j}$ may be calculated from Eq. 5.31A,

and $\dfrac{\partial \gamma_2^{*}}{\partial B_j}$ can be obtained from Eq. 5.40

Hence

$$\frac{\partial \gamma_2^{*}}{\partial B_1} = \gamma_2 (x_1^2 - 1)$$

$$\frac{\partial \gamma_2^*}{\partial B_2} = \gamma_2 (x_1^2 (4x_1 - 3) - 1)$$

$$\frac{\partial \gamma_2^*}{\partial B_3} = \gamma_2 (x_1^2 (6x_1 - 5) (2x_1 - 1) - 1)$$

$$\frac{\partial \gamma_2^*}{\partial B_4} = \gamma_2 (x_1^2 (8x_1 - 7) (2x_1 - 1)^2 - 1)$$

$$\frac{\partial \gamma_2^*}{\partial B_5} = \gamma_2 (x_1^2 (10x_1 - 9) (2x_1 - 1)^3 - 1)$$

$$\ldots\ldots \qquad 5.42$$

The equations resulted by substituting Eqs. 5.31A, 5.42 and 5.41 into Eq. 5.32 can be solved simultaneously for $B_j^{'}s$. The Henry's constant $\mathcal{H}$ which is a reference fugacity and is different from the symmetric convention and must be determined by the trial-and-error procedure.

5.5 SAMPLE CALCULATIONS AND DISCUSSIONS

Sample calculations for testing the proposed method were carried out for four binary systems. Summary of the test results of each system is presented in a table as well as in a graph.

Methane-Ethane at -151.1°F (14)

A summary of the test results is shown in Figure 5.1 and Table 5.1. The calculated vapor phase compositions agree well with the experimental data (14). The average deviation in vapor phase composition is only 0.5%.

Nitrogen-Methane at -240° F

Experimental data obtained in this study together with that reported by Cines et al. (26) were tested. The results of the calculation are compared in Figure 5.2 and are also shown in Tables 5.2 and 5.3. The percentage deviations obtained are summarized as follows

	This work	Cines et al. (26)
Average % Dev. in Pressure	0.5	1.6
Average Dev. in y, mol. fr.	0.0112	0.159

It is seen that the experimental data of this study are more self-consistent than those reported by Cines et al. (26).

Argon-Methane at 123.53° K

A smoothed set of data obtained in this laboratory by Gravelle (36) was also tested. A summary of the test results is presented in Figure 5.3 and Table 5.4. A good agreement is obtained by comparing with the experimental data as indicated by an average % deviation in pressure of 0.5% and average deviation in vapor phase composition of 0.01 mole fraction.

Details of the sample calculations as presented in Tables 5.5 to 5.8 are available in the appendix for the four systems tested. Each table consists of six parts. In part A of each table, the data tested are given in the first three columns; the supporting data used in the calculation are given in the columns 4 and 5 (partial molar volumes) and columns 10 and 11 (fugacity coefficients); the pressure effects on the activity coefficient or the values of the exponential term in Eq. 5.15 are given in the 6th and 7th columns; the adjusted activity coefficients according to Eq. 5.15 are given in the 8th and 9th columns. The remaining parts (B to F) of each table show the test results of each system concerned. The observed pressure, the computed pressure, and their differences are given in the first three columns, the liquid composition is given in the 4th column, the vapor phase compositions of observed and computed in the 5th and 6th columns, the logarithm of the adjusted activity coefficients in the 7th and 8th columns, and pressure effects on the activity coefficient in the last two columns. Parts B to F show the differences between the correlations using different number of adjustable constants in the Redlich-Kister equation.

All data tested were obtained from the forced-recirculation method. Their composition analyses were carried out either by means of the gas chromatography or by the density measurement (26). Their measuring errors in the compositions were of the range 0.003 to 0.005 mole fraction. The pressure measuring errors are 1 psi.

In general, the test results show that the maximum deviation is usually associated with data at low pressure region, which is not purprising. It is known that at low pressure the propagation of the measuring error in pressure on the composition of the vapor phase is larger than that in the liquid phase. The reverse is also true. Therefore, the same accuracy of pressure correlation will give different results in different regions. However, this problem is not difficult to overcome. If data were taken from total pressure measurements of which the composition analyses could be avoided., it would give more precise data in composition than those obtained from other methods.

In conclusion, a method was proposed to calculate vapor phase compositions at high pressure for multicomponent systems. The method was tested only for one limiting case of a few systems due to the lack of suitable experimental data. The test results were consistent with those derived from rigorous considerations. Such good results were really surprising since the quality of the data tested as mentioned above was not ideally suited for this purpose and the supporting properties used in the calculation were evaluated by means of the two-constant Redlich-Kwong equation of state (23, 25).

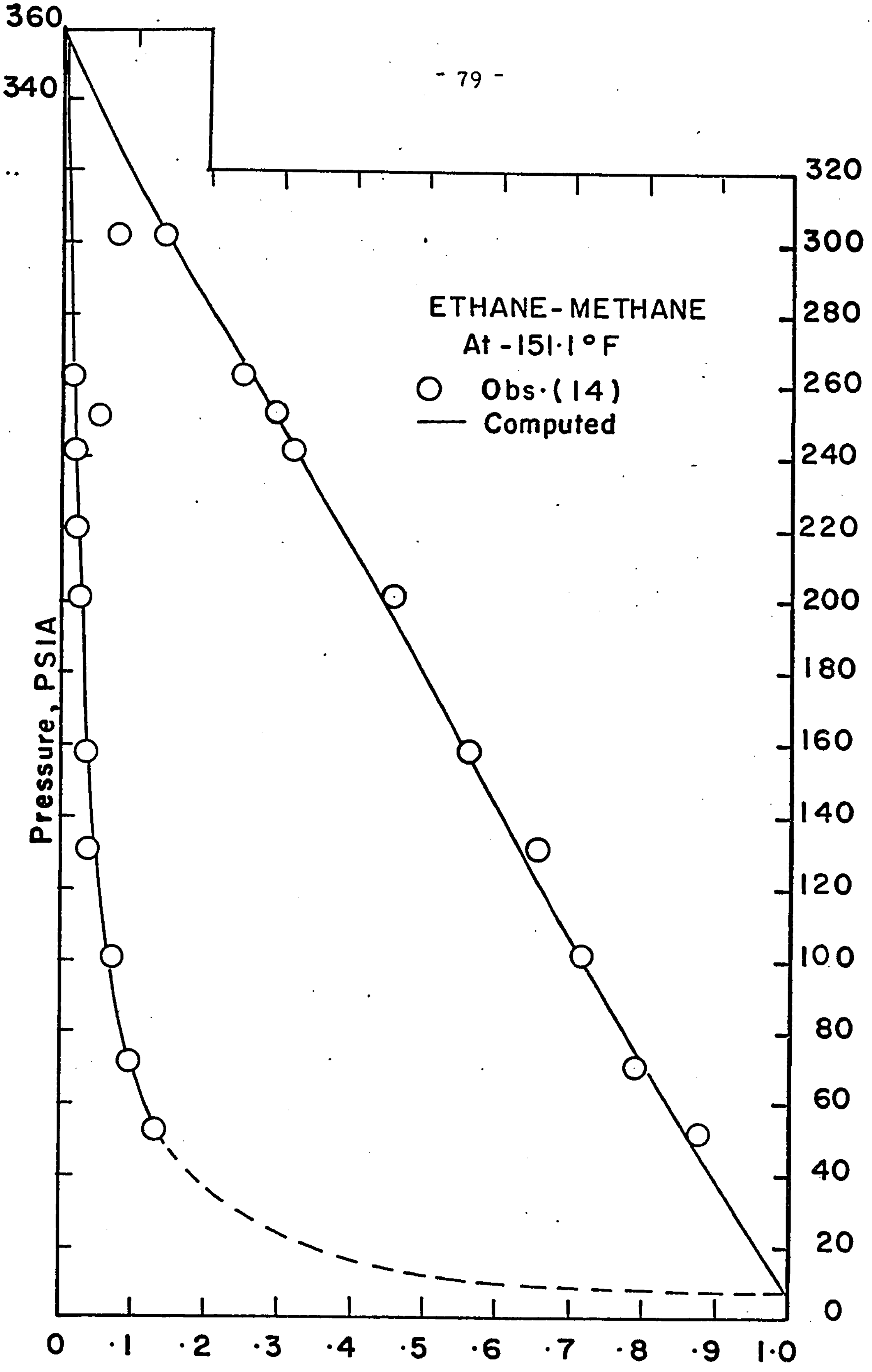

Figure 5.1 Pressure-Composition Diagram of Ethane-Methane System at -151.1°F.

TABLE 5.1

Summary of the Test Results of Methane-Ethane System at -151.1°F (14)

Redlich - Kister Constants					Pressure Correlation			
B	C	D	E	F	Std. Dev.** psi	Max. Dev. psi	Av. % Dev.	Av. Dev.* in y mol. fr.
.4008					10.7	16.5	5.3	.0070
.4027	.2360				4.8	6.2	3.2	.0065
.4165	.2237	.2698			4.3	5.6	2.3	.0055
.4790	.2840	.2629	-.4683		4.9	6.9	2.1	.0048
.5755	.1620	.0254	-.4682	.9977	3.9	6.14	1.4	.0055

* Excluding experimental points 9th and 11st which were obviously off.

** St. Dev. = $\sqrt{\sum_i (P_{i\,obs} - P_{i\,comp})^2 / (\text{No. of obs. - No. of adjustable consts.})}$

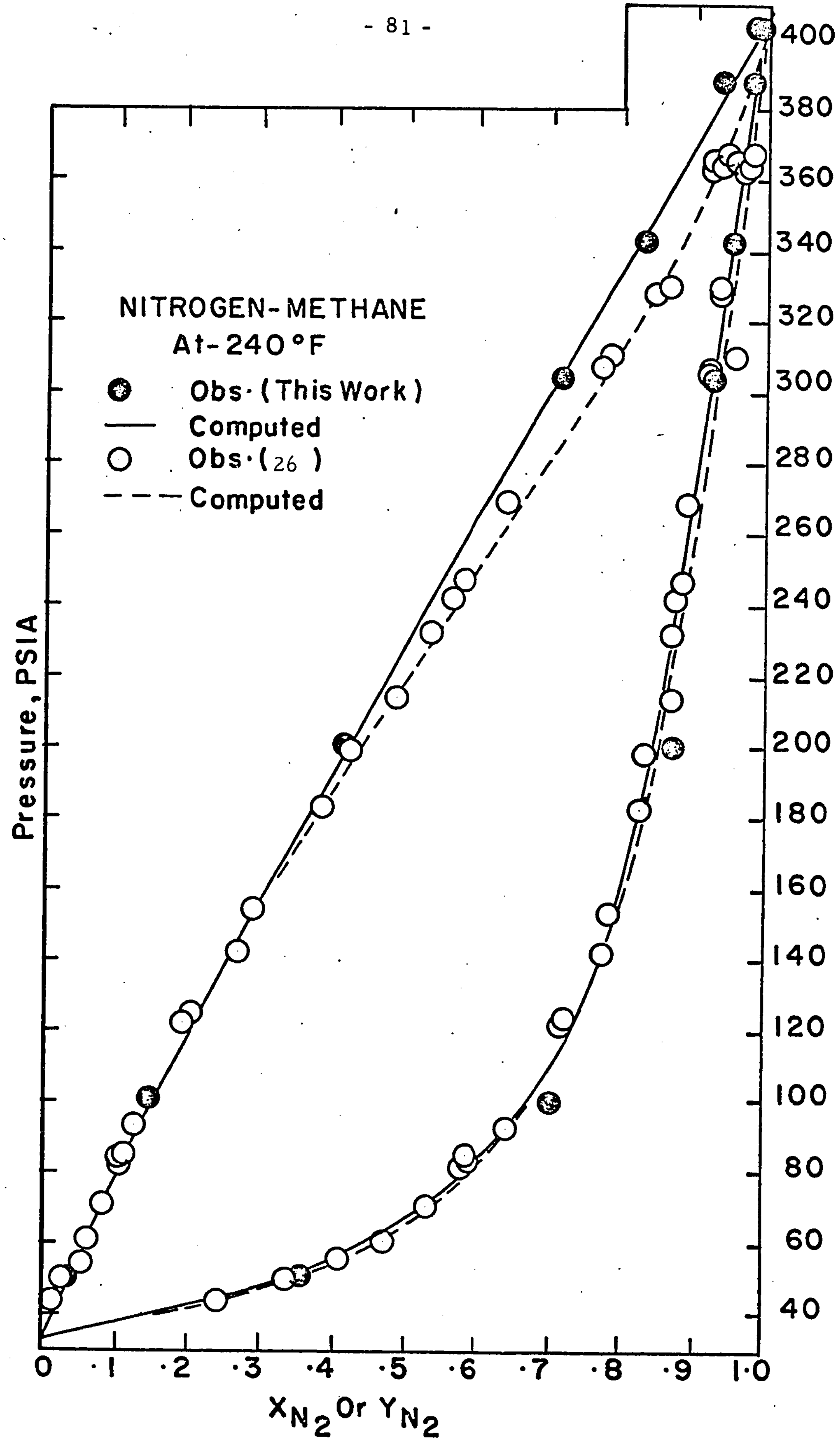

Figure 5.2 Pressure-Composition Diagram of Nitrogen-Methane System at -240° F

TABLE 5.2

Summary of the Test [illegible] Results of Nitrogen Methane System at -240°F (This work)

Redlich-Kister Constants					Pressure Correlation			
B	C	D	E	F	Std. Dev. psi	Max. Dev. psi	Av. % Dev.	Av. Dev. in y mol. fr.
.7558					7.4	12.0	2.2	.0111
.7924	-.1331				4.4	5.6	1.5	.0127
.7694	-.1983	.2063			1.9	2.4	0.5	.0112
.7757	-.2254	.1816	.0812		2.1	3.2	0.3	.0114
.7794	-.1637	.0680	-.0451	.0202	1.3	1.6	.11	.0107

TABLE 5.3

Summary of the Test Results of Nitrogen-Methane System at -240° F (26)

Redlich-Kister Constants					Pressure Correlation			Av. Dev. in y mol. fr.
B	C	D	D	E	Std. Dev. psi	Max. Dev. psi	Av. % Dev.	
.6988					2.8	6.7	1.7	.0158
.7110	-.0405				2.5	4.5	1.6	.0161
.7088	-.0485	.0237			2.6	6.0	1.6	.0159
.7128	-.0587	.0004	.0531		2.5	4.8	1.6	.0155
.7148	-.0517	-.0207	.0360	.0468	2.7	5.4	1.7	.0154

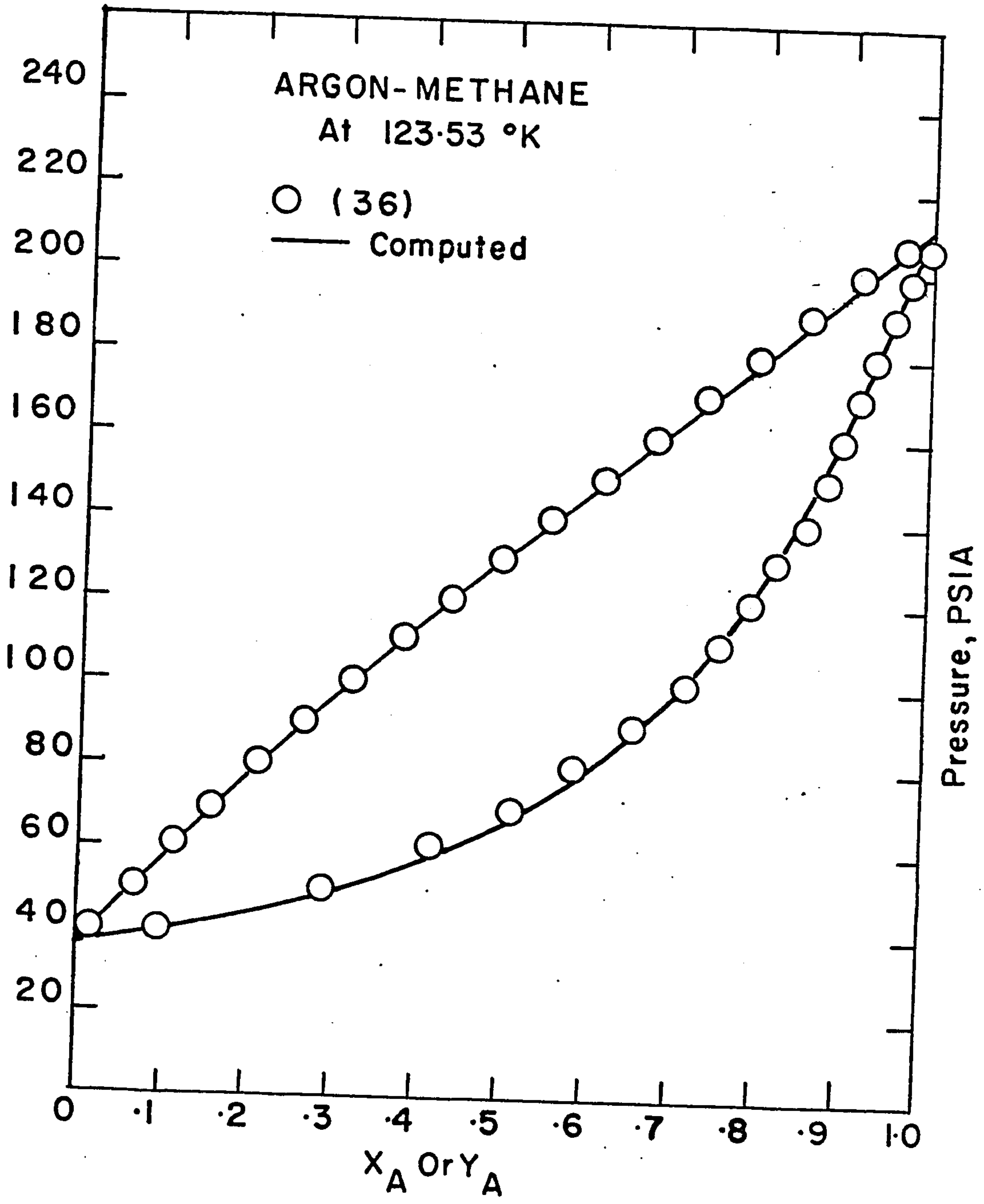

Figure 5.3

Pressure-Composition Diagram of Argon-Methane System at 123.53° K

TABLE 5.4

Summary of the Test Results of Argon-Methane System at 123.53°K (36)

Redlich-Kister Constants					Pressure Correlation			
B	C	D	E	F	Std. Dev. psi	Max, Dev. psi	Av. % Dev.	Av. Dev. in y mol. fr.
.3922					1.4	2.5	0.8	.0118
.3929	-.0475				1.0	2.3	0.6	.0110
.3892	-.0550	.0679			0.7	2.1	0.4	.0103
.3863	-.0445	.0774	-.0508		0.6	2.0	0.3	.0101
.3887	-.0354	.0444	-.0716	.0822	0.6	1.8	0.3	.0101

CHAPTER 6

THERMODYNAMIC CONSISTENCY TEST OF VAPOR-LIQUID EQUILIBRIUM DATA

6.1 BACKGROUND OF THE TESTING METHOD

When the number of the measuring variables is greater than the number of the independent variables which are needed to define a vapor-liquid equilibrium system, in principle, such data can always be tested for internal consistency provided that the supporting physical properties are available. All methods published in the literature are based on either the integrated or the differential form of the Gibbs-Duhem equation. Experimental data are said to be consistent if this equation is satisfied. Good reviews on the testing methods are available (31, 99).

Tao (95) proposed a method which is suitable for testing the local and over-all consistency of linear paths in binary and multicomponent systems. It is restricted, however, to the situation when the system temperature is below the critical temperature of the pure components.

Adler, Friend, Pigford and Rosselli (2) developed a method for testing binary vapour-liquid equilibrium data when the system temperature is above the critical temperature of the more volatile component. This method was subsequently extended to multicomponent systems by Robinson (83). These authors employed the Lewis-Randall rule to overcome the difficulty encountered in the evaluation of vapour-phase fugacity coefficients. However, errors introduced by this approximation are often vary large. According to Ibl and Dodge (50) and Hougen and Watson (48), this rule can only serve as a first approximation up to the reduced pseudocritical pressure of 0.8.

The method of Adler et al. (2) was further modified by Thompson and Edmister (96). They avoided the Lewis-Randall rule and developed a rigorous equation for testing isothermal binary data. Chueh, Muirbrook and Prausnitz (24) extended the area test method of Redlich and Kister (81) and of Herington (44) to isothermal high-pressure data. This extension is suitable for testing binary and multicomponent data along linear paths.

The object of this work is to unify some of the available concepts and to present a practical test method which is general and rigorous. In the development of the proposed method, both symmetric and unsymmetric conventions of the liquid activity coefficient, γ, were employed. All the γ values were adjusted to the state of isothermal and isobaric conditions. The quantity γ, however, does not appear in the two final expressions in the chapter , one of which is for isothermal data and the other for isobaric data.

The proposed method permits a point-by-point evaluation of the data along any arbitrary path. It is suitable for binary and multicomponent systems and is applicable to all conditions including the situation when the system temperature is above the critical temperature of the more volatile component. The only limitation placed on the proposed method is that experimental points should not be widely separated.

6.2 DEVELOPMENT OF BASIC EQUATIONS

ISOTHERMAL CASE

At constant temperature and pressure, the Gibbs-Duhem equation is:

$$\sum_{i=1}^{n} x_i \, d\ln \gamma_i = 0 \qquad 6.1$$

Integrating Eq. 6.1 from point a to its adjacent point b by the trapezoidal rule gives:

$$\sum_{i=1}^{n} (x_{ia} + x_{ib}) \; (\ln \gamma_{ib} - \ln \gamma_{ia}) = 0 \qquad 6.2$$

The assumption involved here is that all the $\ln\gamma$ vs. $\dot{x}$ curves can be approximated by segments of straight lines connecting the points. This approach is identical to that employed by Li and Lu (59) and by McDermott and Ellis (65).

In the following development, liquid activity coefficients are adjusted to a constant reference pressure, P°, so that the conditions of Eq. 6.1 are exactly followed. The constant-pressure liquid activity coefficient of component i in the mixture is defined by

$$\gamma_i (P^\circ, T, x) = \frac{\hat{f}_{iL} (P, T, x)}{x_i \, f_{iL}^{\circ} (P^\circ, T)} \; \exp \int_{P}^{P^\circ} \frac{\bar{V}_{iL}}{RT} \, dP \qquad 6.3$$

In Eq. 6.3, f_{iL} (P, T, x) represents the fugacity of component i in the liquid mixture at the system temperature T and the pressure P, and f_{iL}° (P°, T) represents the standard-state fugacity of component i. The exponential term represents the pressure adjustment.

For a subcritical component i (the critical temperature of the component is well above the system temperature).

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

and the fugacity of pure component i in the liquid state at the system temperature T and at the reference pressure P° is chosen as the standard-state fugacity.

For a supercritical component j (the critical temperature of the component is near or below the system temperature),

$$\gamma_j \to 1 \quad \text{as} \quad x_j \to 0$$

and the standard-state fugacity of the component j is defined by

$$f_{jL}^{\circ}(P^{\circ}, T) = \mathcal{H}_j(P^{\circ}, T)$$

$$= \left[\lim_{x_j \to 0} \frac{\hat{f}_{jL}(P, T, x)}{x_j} \right] \exp \int_{P_M^{s}}^{P^{\circ}} \frac{\overline{V}_{jL}^{\infty} \, dP}{RT} \qquad 6.4$$

In this expression, $\mathcal{H}_j(P^{\circ}, T)$ is the constant-pressure Henry's law coefficient for the supercritical component j in the solute-free mixture and P_M^{s} is the bubble point pressure of the solute-free mixture.

At equilibrium,

$$\hat{f}_{iL}(P, T, x) = \hat{f}_{iV}(P, T, x) \qquad 6.5$$

and in the vapour phase,

$$\hat{f}_{iV} = y_i \, \phi_i \, P \qquad 6.6$$

Hence,

$$\gamma_i(P^{\circ}, T, x) = \frac{y_i \, \phi_i \, P}{x_i \, f_{iL}^{\circ}} \quad \exp \int_{P}^{P^{\circ}} \frac{\overline{V}_{iL}}{RT} \, dP \qquad 6.7$$

The quantity ϕ_i is the fugacity coefficient of component i in the vapour mixture. Substituting Eq. 6.7 into Eq. 6.2 gives:

$$\sum_{i=1}^{n} (x_{ib} + x_{ia}) \ln \frac{K_{ib}}{K_{ia}} = \sum_{i=1}^{n} (x_{ib} + x_{ia}) \ln \frac{\phi_{ia} \, P_a}{\phi_{ib} \, P_b} +$$

$$\sum_{i=1}^{n} (x_{ib} + x_{ia}) \int_{P_a}^{P_b} \frac{\overline{V}_{iL} \, dP}{RT} \qquad 6.8$$

in which $K_i = y_i/x_i$. The left-hand side of this equation contains only the experimental equilibrium composition data. The quantities

ϕ_i and $\overline{V}_{iL}$ of the right-hand side of this equation may be evaluated from a suitable equation of state or obtained from experimental measurements. Equation 6. 8 is the basic equation for testing isothermal data.

ISOBARIC CASE

The temperature dependence of the liquid activity coefficient is given by:

$$\frac{\partial \ln \gamma_i}{\partial T} = \frac{h_i - \overline{H}_i}{RT^2} \qquad 6.9$$

for the case $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$, or

$$\frac{\partial \ln \gamma_i}{\partial T} = \frac{\overline{H}_i^{\infty} - \overline{H}_i}{RT^2} \qquad 6.10$$

for the case $\gamma_i \rightarrow 1$ as $x_i \rightarrow 0$. In these expressions, h_i represents the molal enthalpy of pure component i in the liquid state; $\overline{H}_i^{\infty}$ and $\overline{H}_i$ represent the partial molal enthalpy of component i at infinite dilution and in the solution respectively. In the following development, liquid activity coefficients are adjusted to a constant reference temperature so that the constant temperature condition of the Gibbs-Duhem equation is satisfied. For the isobaric case, the quantity γ is defined by

$$\gamma_i (P, T, x) = \hat{f}_{iL} (P, T, x) \;/\; x_i \, f^{\circ}_{iL} \; (P, T) \qquad 6.11$$

Therefore, at the reference temperature T°,

$$\gamma_i (P, T^{\circ}, x) = \frac{\hat{f}_{iL} (P, T, x)}{x_i \, f^{\circ}_{iL} \; (P, T)} \; \exp \int_{T}^{T^{\circ}} - \frac{\Delta \overline{H}_{iL}}{RT^2} \, dT \qquad 6.12$$

In Eq. 6.12,

$$\Delta\overline{H}_{iL} = -(h_{iL} - \overline{H}_{iL}) \qquad 6.13$$

for the case $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$, and

$$\Delta\overline{H}_{iL} = -(\overline{H}_{iL}^{\infty} - \overline{H}_{iL}) \qquad 6.14$$

for the case $\gamma_i \rightarrow 1$ as $x_i \rightarrow 0$. Substituting Eqs. 6.5, 6.6 and 6.12 into Eq. 6.2 gives:

$$\sum_{i=1}^{n} (x_{ib} + x_{ia}) \ln \frac{K_{ib}}{K_{ia}} = \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left[\ln \frac{\phi_{ia} P_a}{\phi_{ib} P_b} \right.$$

$$\left. + \ln \frac{f^{\circ}_{iL}(T_b, P)}{f^{\circ}_{iL}(T_a, P)} - \int_{T^{\circ}}^{T_b} \frac{\Delta\overline{H}_{iL}}{RT^2} dT + \int_{T^{\circ}}^{T_a} \frac{\Delta\overline{H}_{iL}}{RT^2} dT \right] \qquad 6.15$$

However,

$$\frac{\partial \ln f_{iL}^{\circ}}{\partial T} = \frac{h_{iV}^{*} - h_{iL}}{RT^2} \qquad 6.16$$

for the case $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$. The quantity $h_{iV}^{*} - h_{iL}$ is the ideal heat of vaporization. For the case $\gamma_i \rightarrow 1$ as $x_i \rightarrow 0$,

$$\frac{\partial \ln f_{iL}^{\circ}}{\partial T} = \frac{h_{iV}^{*} - \overline{H}_{iL}^{\infty}}{RT^2} \qquad 6.17$$

Evaluating the quantities $f_{iL}^{\circ}(T_a, P)$ and $f_{iL}^{\circ}(T_b, P)$ from the reference temperature T° by means of Eqs. 6.16 and 6.17, substituting the results into Eq. 6.15 and rearranging gives

$$\sum_{i=1}^{n} (x_{ib} + x_{ia}) \ln \frac{K_{ib}}{K_{ia}} = \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left[\ln \frac{\phi_{ia} P_a}{\phi_{ib} P_b} \right.$$

$$\left. + \int_{T_a}^{T_b} \frac{h_{iV}^{*} - \overline{H}_{iL}}{RT^2} dT \right] \qquad 6.18$$

This is the basic equation for testing isobaric data.

6.3 ESTABLISHMENT OF ERROR BOUNDS

In order to make a test conclusive, maximum experimental error bounds must be established. As all measured results have experimental errors, it is necessary to determine whether or not the data are consistent within the error bounds, and it is also useful to determine the conditions under which the data are consistent.

For isothermal data, the overall deviation resulting from experimental errors of the tested pair may be obtained by rearranging Eq. 6.8 as follows:

$$\triangle = \sum_{i=1}^{n} (x_{ib} + x_{ia}) \; (\ln \frac{K_{ib}}{K_{ia}} - \ln \frac{\Phi_{ia} \, P_a}{\Phi_{ib} \, P_b} - \int_{P_a}^{P_b} \frac{\overline{V}_{iL}}{RT} \, dP) \qquad 6.19$$

Considering that all the supporting quantities, $\overline{V}_{iL}$, Φ_i and f°_{iL} are free from error, the total differential of $\triangle$ is given by

$$\begin{aligned} d\,\triangle = & \sum_{i=1}^{n} (dx_{ib} + dx_{ia}) \; (\ln \frac{K_{ib}}{K_{ia}} - \ln \frac{\Phi_{ia} \, P_a}{\Phi_{ib} \, P_b} - \int_{P_a}^{P_b} \frac{\overline{V}_{iL}}{RT} \, dP) \\ & + \sum_{i=1}^{n} (x_{ib} + x_{ia}) \; \{ (\frac{dy_{ib}}{y_{ib}} - \frac{dx_{ib}}{x_{ib}} + \frac{dx_{ia}}{x_{ia}} - \frac{dy_{ia}}{y_{ia}}) \\ & + (- \frac{dP_a}{P_a} + \frac{dP_b}{P_b} - \frac{\partial}{\partial P} \left[\int_{P_a}^{P_b} \frac{\overline{V}_{iL}}{RT} \, dP \right] dP \\ & + \frac{\partial}{\partial P} [\int_{P_a}^{P_b} \frac{\overline{V}_{iL}}{RT} \, dP) \} \end{aligned}$$

In the above expression, ± dP, ± dT and ± dx are replaced by the measuring errors, E(P), E(T) and E(x), respectively, for obtaining the maximum experimental error bounds. This approach follows that of Tao (95). Hence

$$
\begin{aligned}
\left| D \right|_{\max} = {} & \sum_{i=1} (x_{ib} + x_{ia}) \Bigg[\left(\frac{1}{y_{ib}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{x_{ia}} \right) \\
& + 2 \left| \left(\ln \frac{K_{ib}}{K_{ia}} - \ln \frac{\Phi_{ia} P_a}{\Phi_{ib} P_b} - \int_{P_a}^{P_b} \frac{\overline{V}_{iL}}{RT} \, dP \right) \right| \Bigg] E(x) \\
& + \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left(\frac{1}{P_a} + \frac{1}{P_b} + \left| \frac{\partial}{\partial P} \int_{P_a}^{P_b} \frac{\overline{V}_{iL} \, dP}{RT} \right| \right) E(P) \\
& + \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left| \left(\frac{\partial}{\partial T} \int_{P_a}^{P_b} \frac{\overline{V}_{iL} \, dP}{RT} \right) \right| E(T) \qquad 6.20
\end{aligned}
$$

where

$E(x)$ = error in composition x or y measurement
$E(P)$ = error in pressure measurement
$E(T)$ = error in temperature measurement

Similarly, the overall deviation for the isobaric case may be expressed by:

$$
\Delta = \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left[\ln \frac{K_{ib}}{K_{ia}} + \ln \frac{\Phi_b P_b}{\Phi_a P_a} - \int_{T_a}^{T_b} \frac{h_{iV}^{*} - \overline{H}_{iL}}{RT^2} \, dP \right] \qquad 6.21
$$

the total differential of Δ is given by

$$
\begin{aligned}
d\Delta = {} & \sum_{i=1}^{n} (dx_{ib} + dx_{ia}) \left(\ln \frac{K_{ib}}{K_{ia}} + \ln \frac{\Phi_b P_b}{\Phi_a P_a} - \int_{T_a}^{T_b} \frac{h_{iV}^{*} - \overline{H}_{iL}}{RT^2} \, dT \right) \\
& + \sum_{i=1}^{n} (x_{ib} + x_{ia}) \Bigg[\left(\frac{dy_{ib}}{y_{ib}} - \frac{dy_{ia}}{y_{ia}} - \frac{dx_{ib}}{x_{ib}} + \frac{dx_{ia}}{x_{ia}} \right)
\end{aligned}
$$

$$+ \left(\frac{dP_b}{P_b} - \frac{dP_a}{P_a} + \frac{\partial}{\partial T} \left[\int_{T_a}^{T_b} \frac{h_{iV}^* - \overline{H}_{iL}}{RT^2} \, dT \right] dT \right) \Bigg]$$

and the maximum experimental error bounds for isobaric data may be represented by:

$$\left| D \right|_{max} = \sum_{i=1}^{n} \Bigg[(x_{ib} + x_{ia}) \left(\frac{1}{y_{ib}} + \frac{1}{x_{ib}} + \frac{1}{y_{ia}} + \frac{1}{x_{ia}} \right)$$

$$+ 2 \left| \left(\ln \frac{K_{ib}}{K_{ia}} - \ln \frac{\Phi_{ia}}{\Phi_{ib}} - \int_{T_a}^{T_b} \frac{h_{iV}^* - \overline{H}_{iL}}{RT^2} \, dT \right) \right| \Bigg] \; E(x)$$

$$+ \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left(\frac{2}{P} \right) \quad E(P)$$

$$+ \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left| \left(\frac{\partial}{\partial T} \int_{T_a}^{T_b} \frac{h_{iV}^* - \overline{H}_{iL}}{RT^2} \, dT \right) \right| \; E(T) \qquad 6.22$$

Experimental data can be arranged along any arbitrary path, and tested in pairs by means of Eqs. 6.19 - 6.20 or Eqs. 6.21 - 6.22 for isothermal and isobaric data respectively. The only restriction is that the experimental points should not be widely separated. In the test, each experimental point appears twice, except the first and the last points of the chosen path. An experimental point is considered inconsistent if the values of the quantity Δ consisting this point are greater than the experimental error bounds, represented by $\left| D \right|_{max}$. In so doing, a point-by-point evaluation of the data is achieved.

6.4 PROCEDURE

The procedure employed in this investigation may be briefly outlined as follows:

1. Group experimental points along an arbitrary path in such a manner that the liquid composition of an experimental point is not too far away from its adjacent points.
2. Evaluate the necessary supporting data. The computer programs of Prausnitz and Chueh (72) were employed in this study for evaluating the values of ϕ_i, $\overline{V}_{iL}$ and $\overline{V}_{iL}^{\infty}$. These programs were written basing on a modified Redlich-Kwong equation of state (79). The quantity $(h_{iV}^* - \overline{H}_{iL})$ was approximated as follows:

$$h_{iV}^* - \overline{H}_{iL} = (h_{iV}^* - h_{iL}) - \left[- (h_{iL} - \overline{H}_{iL}) \right] \qquad 6.23$$

$$\fallingdotseq \Delta H_i^{vap} - \Delta \overline{H}_{iL} \qquad 6.24$$

For a supercritical component, $\overline{H}_{iL}^{\infty}$ should be used instead of h_{iL} in Eq. 6.24. The quantity ΔH_i^{vap} may be evaluated from the correlation of Chen (19) and the quantity $\Delta \overline{H}_{iL}$ may be estimated by means of the Scatchard-Hildebrand equation (46). If more than one set of isobaric data is available, the quantity $h_{iV}^* - \overline{H}_{iL}$ may be obtained from a $\ln \hat{f}_{iL}$ vs. 1/T plot according to the expression

$$\left(\frac{\partial \ln \hat{f}_{iL}}{\partial T} \right)_{P,x} = \frac{h_{iV}^* - \overline{H}_{iL}}{RT^2} \qquad 6.25$$

3. Calculate the quantity Δ by means of Eqs. 6.19 or 6.21. In the evaluation, the integral terms are approximated as follows:

$$\int_{P_a}^{P_b} \frac{\overline{V}_{iL}}{RT}\, dP = \frac{\left[(\overline{V}_{iL})_a + (\overline{V}_{iL})_b\right] (P_b - P_a)}{2\ RT}$$

$$\int_{T_a}^{T_b} \frac{h_{iV}^{*} - \overline{H}_{iL}}{RT^2}\, dT = \left(\frac{(h_{iV}^{*} - \overline{H}_{iL})_b + (h_{iV}^{*} - \overline{H}_{iL})_a}{2R} \right) \left(\frac{1}{T_a} - \frac{1}{T_b} \right)$$

4. Evaluate the quantity $| D |$ max, by means of Eqs. 6.20 or 6.22.
5. Screen the data.

6.5 EXAMPLES

Five examples are given to illustrate the proposed method, four for the isothermal case and one for the isobaric case. Systems chosen for the test contain components of air and natural gas which are related to the current interests of this study.

Isothermal Data: Experimental results for one ternary and three binary systems were tested. Namely,

System Methane - Propane
System Nitrogen - Methane
System Methane - Ethane
System Carbon Dioxide - Oxygen - Nitrogen

The measuring errors in the calculation were arbitrarily set as follows:

$E\ (P)\ +\ \pm\ 1$ psi
$E\ (T)\ =\ \pm\ 0.2°F$
$E\ (x)\ =\ \pm\ 0.0005;\ \pm\ 0.0010;\ \pm\ 0.0020$ mole fraction

As measuring errors usually occur in the compositions even for well designed apparatus, three levels of E (x) were selected.

Results of the test are presented in figures 6.1 to 6.6 and Tables 6.1 to 6. Each experimental point appears twice in the pair test with the exception of the first and the last points. Experimental deviations, Δ , are represented by the circles in these figures. Maximum experimental error bounds are represented by the solid lines for the three levels of E(x). An experimental point is considered inconsistent if the two pairs containing this point are located outside the selected maximum experimental error bounds.

System Methane-Propane: Isothermal data for this system reported by Reamer et al. (80) at 160° F are used to show the systematic trend of the distribution of experimental deviations, reflecting the fact that the authors have smoothed the data (80). In figure 6.1, the pair average pressure. the absissa, is the average system pressure of the two adjacent experimental points. The test results indicate that the quality of the data is excellent. The data are consistent within the bounds indicated by $E(x) = 0.0005$ as shown in figure 6.1. For the purpose of identification, experimental data and numerical test results are summarized in Table 6.1.

System Nitrogen-Methane: Two sets of isothermal data of this system, one taken from this work, another reported by Cines et al. (17), both at - 240° F are used to show the random distribution of experimental deviations. The results of the first set, presented in figure 6.2, show that all experimental points are consistant within error bounds indicated by $E(x) = 0.002$ except point 2. The results of the second set, shown in figure 6.3, indicate that majority of the experimental points is consistent within the bounds indicated by $E(x) = 0.0005$. The experimental points 9, 15, 16, 19, 22 and 27 are inconsistent. If the maximum error bounds indicated by $E(x) = 0.0020$ are used as the criterion, only points 9, 16 and 22 are inconsistent. Experimental data and numerical test results of first and second sets are summarized in Tables 6. 2 and 6. 3 respectively.

Methane-Ethane System: Experimental data of this system taken from earlier work (14) were tested. As shown in figure 6. 4 and Table 6. 4, there are four pairs located outside error bounds of $E(x) = 0.001$ mole fraction. The common experimental points 3 and 9 of these four pairs are therefore considered to be inconsistent. Nevertheless, for the pair such as 10-11, containing the end point, the criterion established earlier can not by itself give a conclusive judgement either on point 10 or on point 11. In this case other information may help in the screening process. By referring to the P-x-y data as shown in figure 5. 1, it shows that point 11 is obviously off and therefore is inconsistent.

System Carbon Dioxide-Nitrogen-Oxygen: Isothermal data for this system reported by Zenner and Dana (108) at 40. 2°C and 51 atm. are used to show the application of the proposed method to a multicomponent system. In figure 6. 5 experimental deviations of the pairs tested are plotted against the average mole ratios of $x_{O_2}/(x_{O_2} + x_{N_2})$. All experimental points may be considered consistent with the bounds established by $E(x) = 0.0005$. Numerical results are presented in Table 6. 5.

Isobaric Data: Experimental data reported by Cockett (27) for the nitrogen-oxygen system at 1. 3158 atm. were tested. The measuring errors in the calculation were set as follows:

$E(P) = \pm 1$ mm. Hg.
$E(T) = \pm 0.1°K$
$E(x) = \pm 0.0005, \pm 0.0010, \pm 0.0020$ mole fraction.

The solubility parameter values for nitrogen and oxygen were taken as 5. 96 and 7. 14 $(\text{cal./mole})^{0.5}$, respectively. These values which agree well with those given by Hildebrand and Scott (46) were used in the evaluation of ΔH values by means of the Scatchard-Hildebrand equation,

$$\Delta H = \theta_1 \ \theta_2 \ (\delta_1 - \delta_2)^2 \ V_L$$

in which

$$V_L = x_1 V_{L_1} + x_2 V_{L_2}$$

and

$$\theta_1 = x_1 V_{L_1} / V_L$$

The quantity V_{L_i} was evaluated from Lyckman's generalization (62). The good agreement between the calculated ΔH values and the experimental values reported by Knobler et al. (52) at 77°K is shown in figure 6. 7. The calculated experimental deviations are compared with the maximum error bounds in figure 6. 6, in which the absissa is the average system temperature of the two adjacent experimental points. It is seen that the quantity of the experimental data is excellent. There is only one inconsistent point (No. 10) which is outside of the maximum error bounds indicated by $E(x) = 0.0010$.

In conclusion, a rigorous and general consistency test is proposed. It is independent of the reference state chosen for the calculations. The equations developed involve no activity coefficient terms. Any errors inherited from the assumptions made in the calculation appear both in the Δ and $|D|_{max}$ terms, hence there is a mutual cancellation effect. The proposed method is sensitive to errors in the composition measurements. It is also useful in determining the conditions under which the data are consistent.

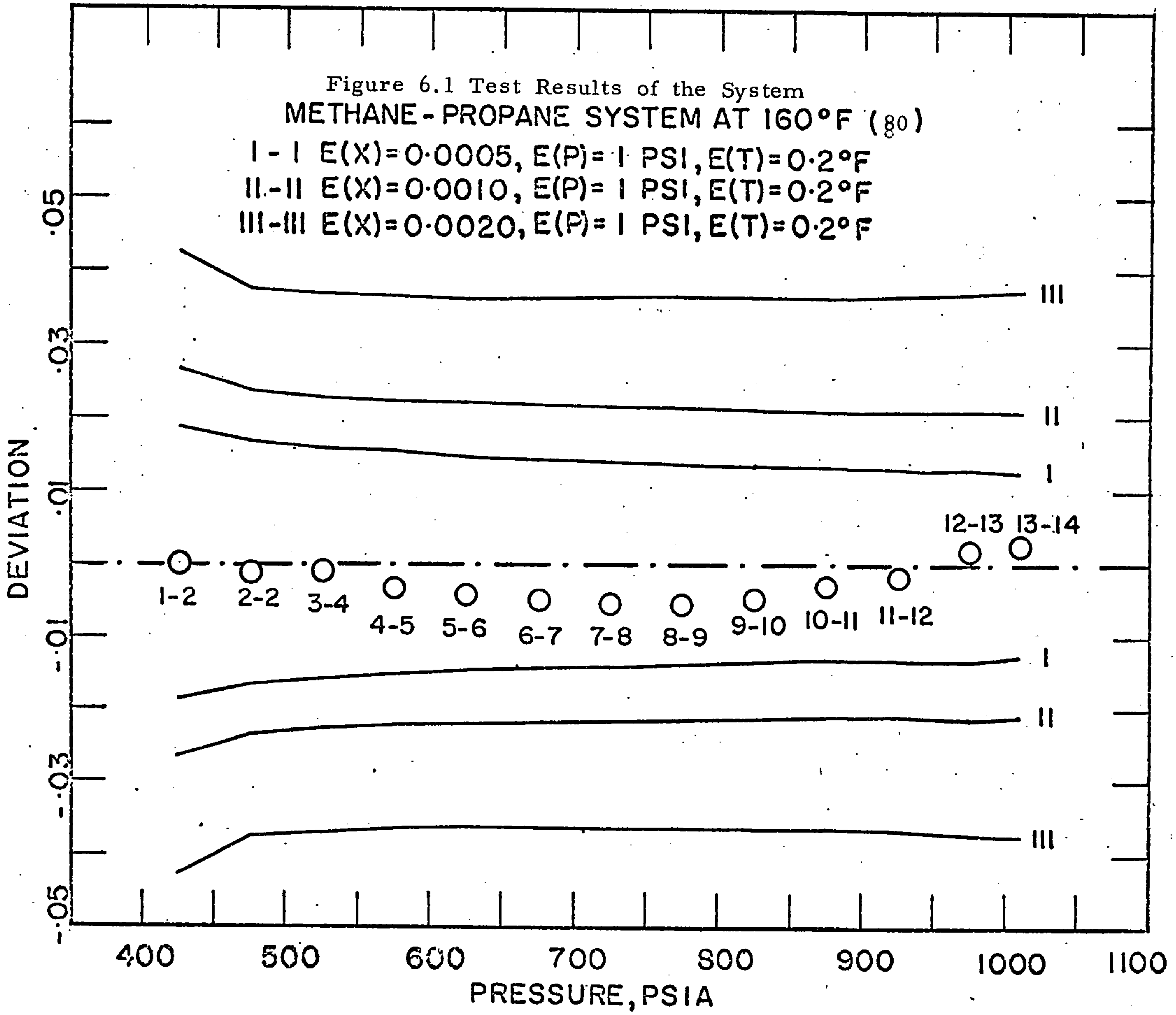

Figure 6.1 Test Results of the System

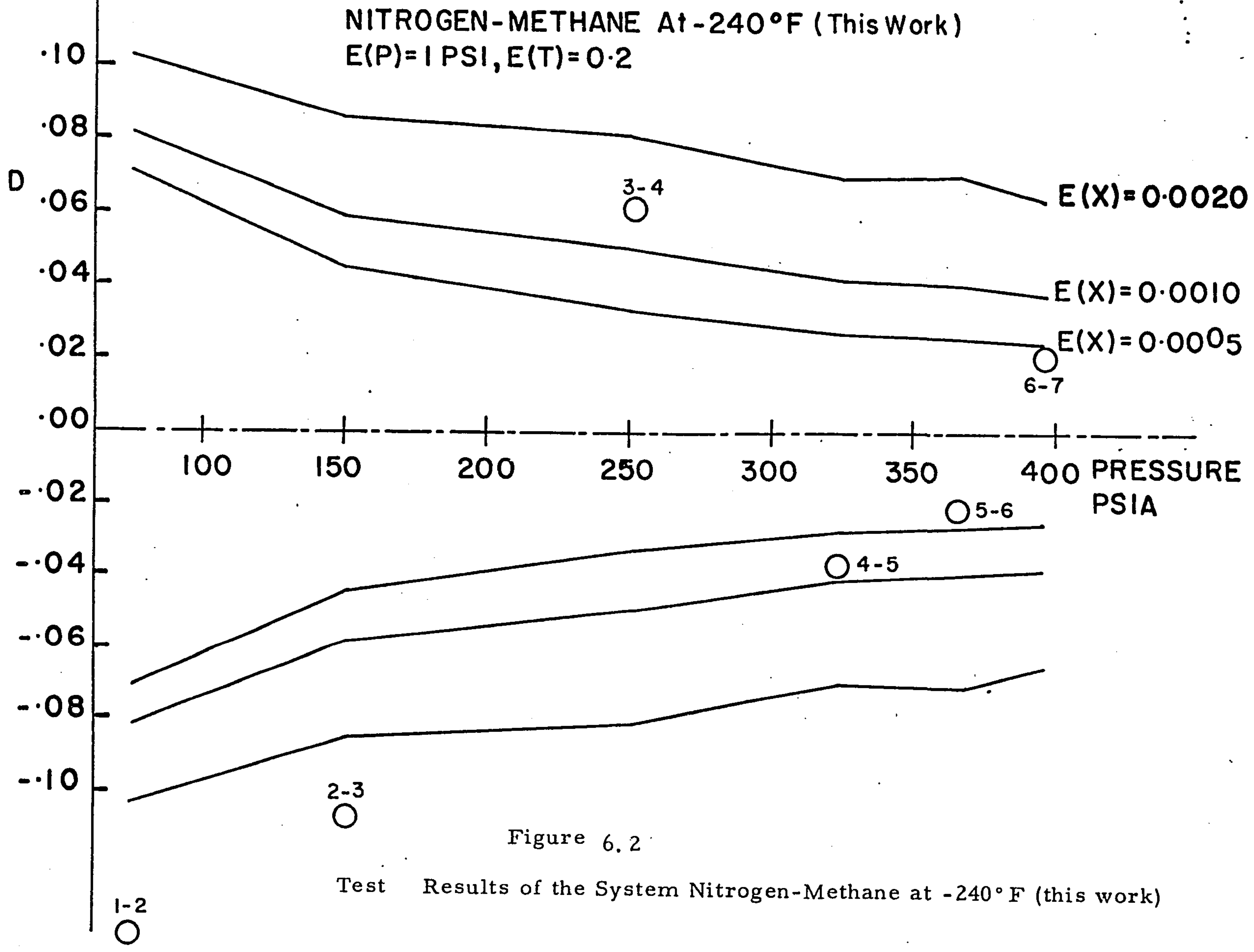

Figure 6.2

Test Results of the System Nitrogen-Methane at -240° F (this work)

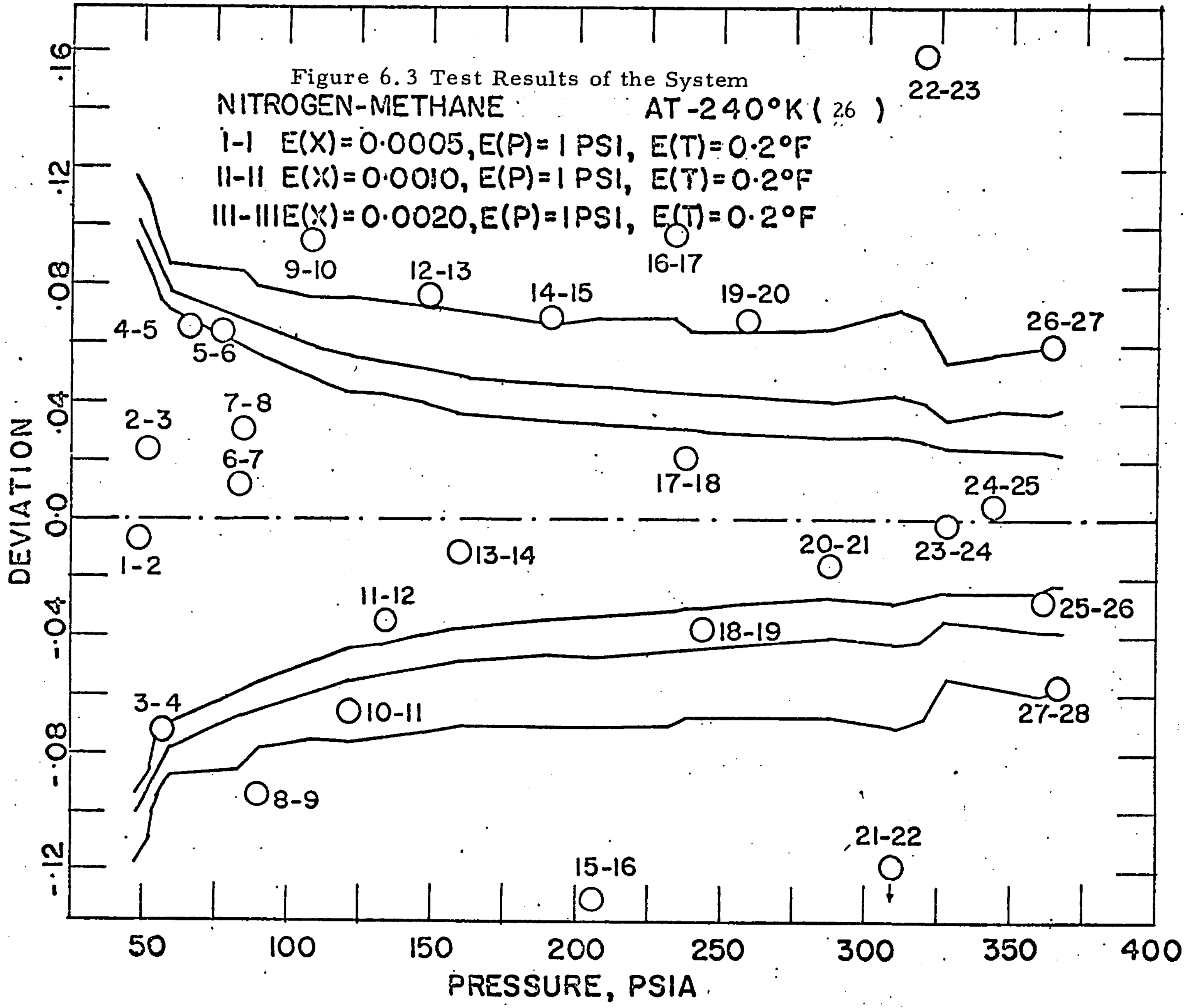

Figure 6.3 Test Results of the System

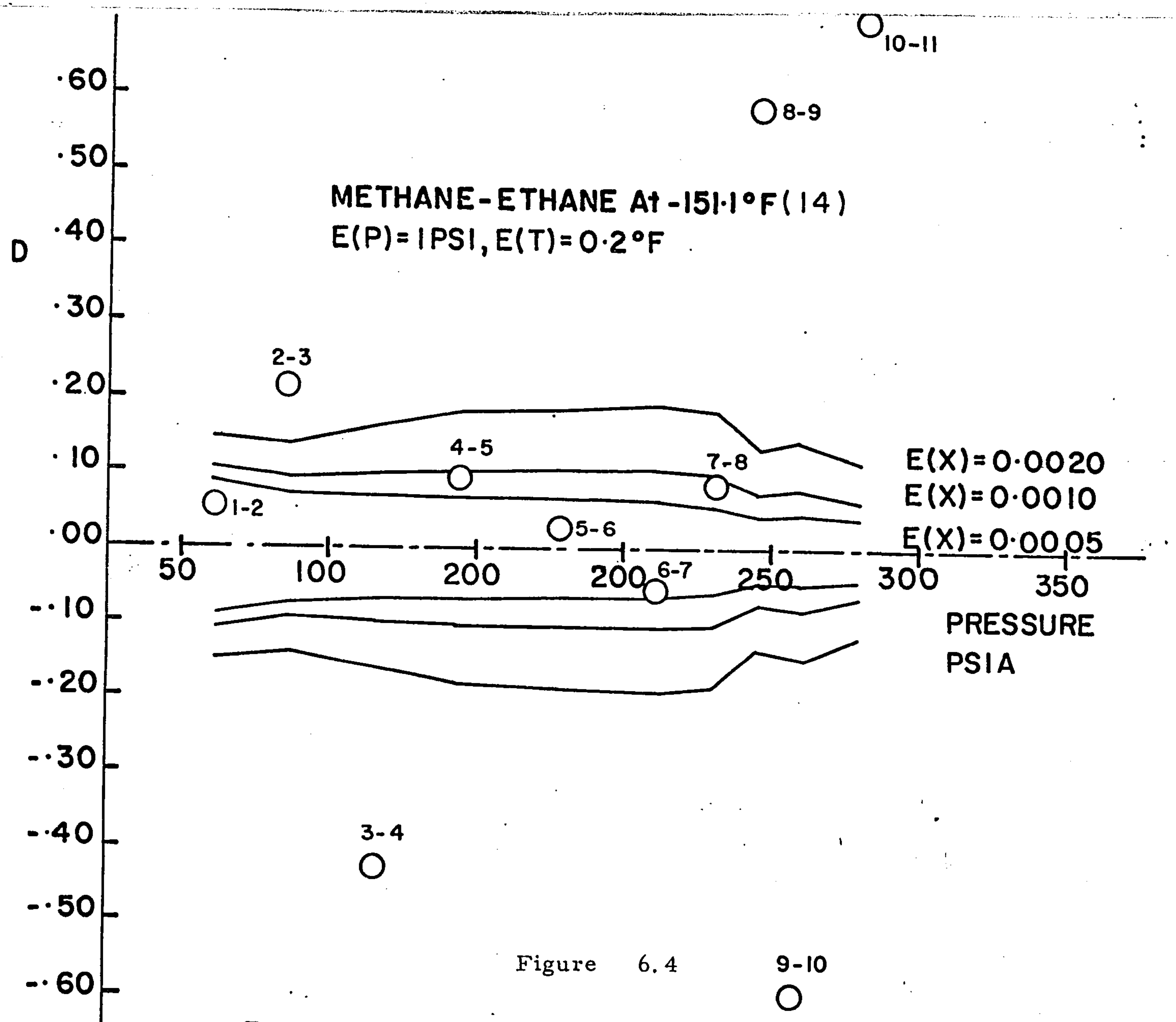

Figure 6.4

Test Results of the System Methane-Ethane at -151.1° F.

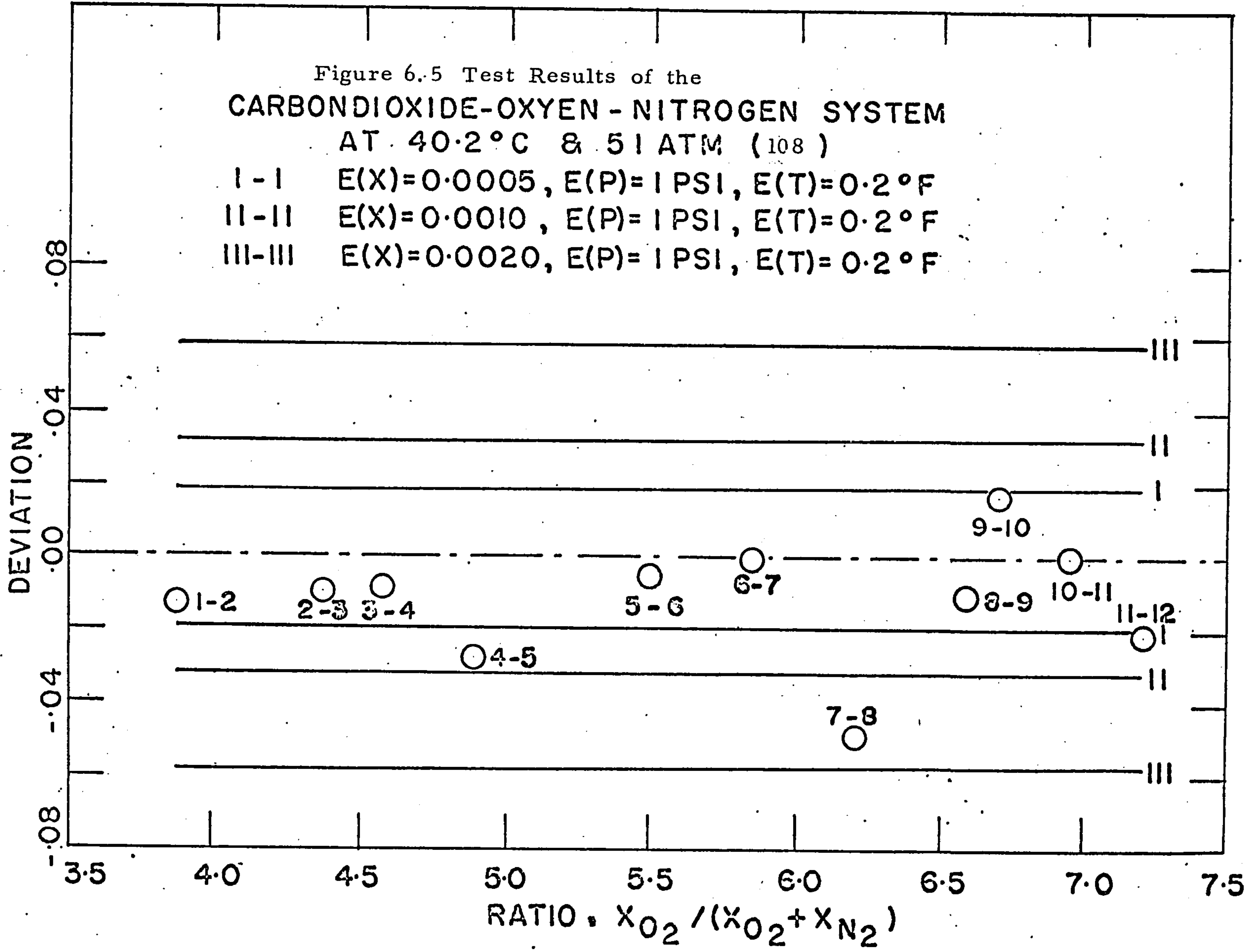

Figure 6.5 Test Results of the CARBONDIOXIDE-OXYEN - NITROGEN SYSTEM AT 40·2°C & 51 ATM (108)

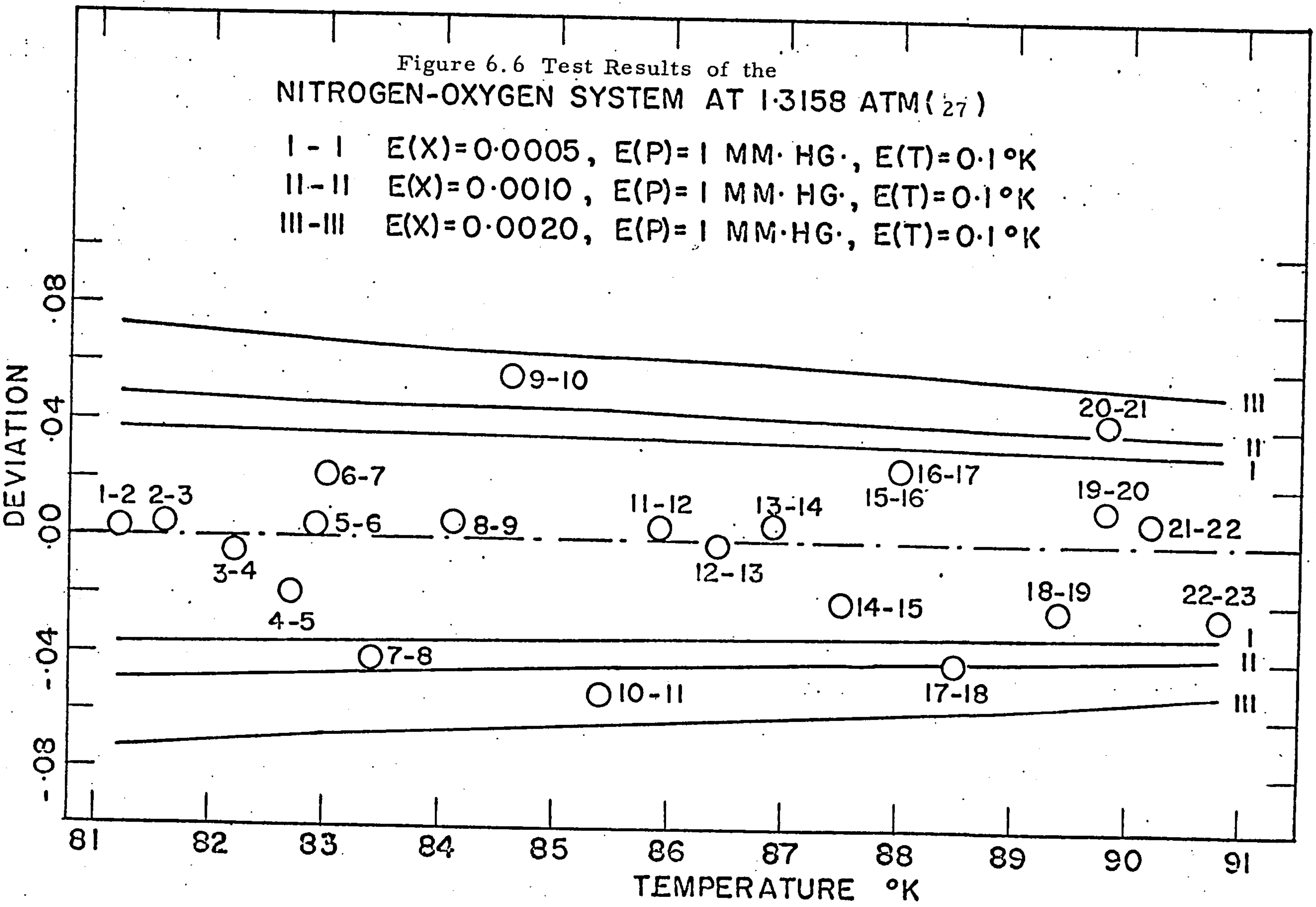

Figure 6.6 Test Results of the NITROGEN-OXYGEN SYSTEM AT 1·3158 ATM(27)

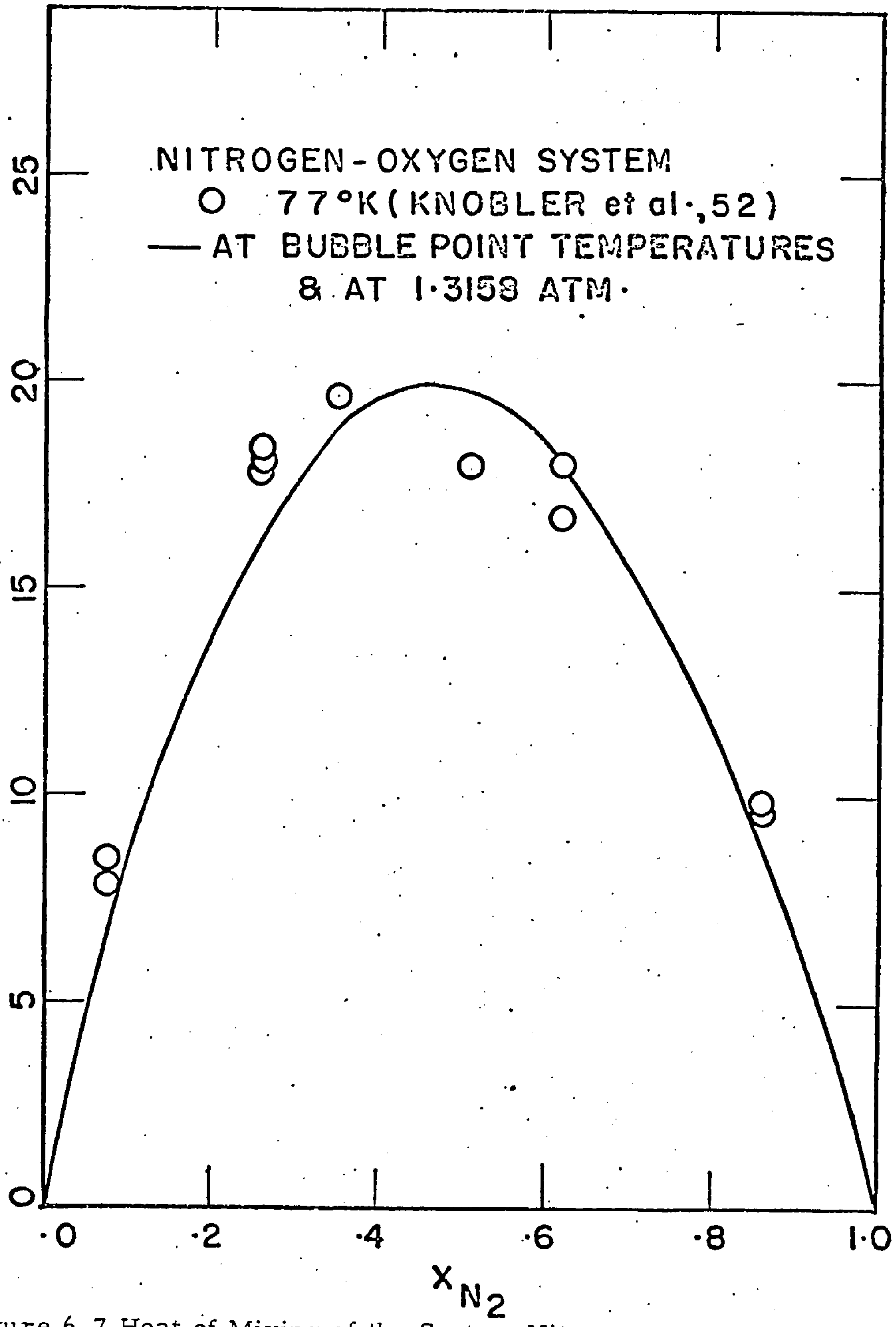

Figure 6.7 Heat of Mixing of the System Nitrogen-Oxygen at Bubble-Point Temperatures and 1.3158 atm.

CHAPTER 7

MISCELLANEOUS WORKS

7.1 GENERALIZED BARKER'S METHOD FOR CALCULATING VAPOR COMPOSITIONS FROM TOTAL PRESSURE MEASUREMENTS AND LIQUID COMPOSITION DATA

FORMULATION AND TESTING OF THE METHOD

For a system at low pressure the activity coefficients, in general, can be calculated by the equation,

$$\ln \gamma_{iL} = \ln \frac{y_i P}{x_i P_i^s} + \frac{(\beta_{ii} - v_{iL})(P - P_i^s)}{RT} + \ln \gamma_{iV} \qquad 7.1$$

The details of the derivation of this equation is available (100). It can be rearranged to give

$$Py_i = \frac{x_i \gamma_{iL} P_i^s}{\gamma_{iV}} \exp\left[- \frac{(\beta_{ii} - v_{iL})(P - P_i^s)}{RT} \right] \qquad 7.2$$

Summing up this equation for n-components gives

$$P = \sum_{i=1}^{n} \frac{x_i \gamma_{iL} P_i^s}{\gamma_{iV}} \exp\left[- \frac{(\beta_{ii} - v_{iL})(P - P_i^s)}{RT} \right] \qquad 7.3$$

The last two equations are the basic and general relationships for calculating vapor compositions from total pressure measurements and liquid composition data. Similar to the method described in Chapter 5, an integrated Gibbs-Duhem equation is needed in the calculation. For a limiting case of a binary system using a three-term Redlich-Kister equation, the method is reduced to Barker's case (5). In this study, one binary system, acetone-methanol (90), was chosen to demonstrate the proposed method in which the flexible-type Redlich-Kister equation of one to five terms was used. The method used for evaluating adjustable parameters was similar to that described in Chapter 5. The computer program written in FORTRAN IV is presented in Appendix VI. In the calculation, the vapor phase activity coefficients were approximated as

$$\ln \gamma_{1V} = P\delta_{12} y_2^2 / RT \qquad 7.4$$

and

$$\ln \gamma_{2V} = P\delta_{12} y_1^2 / RT \qquad 7.5$$

This approximation was originally proposed by Van Ness (100). The second virial coefficients were evaluated by the method of Pitzer and Curl (70) and their cross coefficient δ_{12} was evaluated based on the work of Prausnitz and O'Connell (74). The computed results of the highly non-ideal system acetone-methanol at 50° C are shown in figure 7.1 and Table 7.1. The calculated vapor phase compositions agreed well with those obtained from the recirculation method (90).

APPLICATION

Vapor pressures of mixtures of benzene-n-octane system obtained in this laboratory by Cheh (18) were processed by the proposed method. The summary of the computation is given in Table 7.2 and figure 7.2. The four-term Redlich-Kister equation was employed in the calculation. The results are shown in Tables 7.3 to 7.7 for isotherms of 25, 35, 45, 55, and 65° C, respectively.

It is usually difficult to obtain vapor-liquid equilibrium data of the system containing one more volatile component such as benzene in n-octane by using a recirculation still. However, there is no limitation in using the total pressure method for such study. Therefore the total pressure method is shown to be a good alternative for obtaining vapor-liquid equilibrium data.

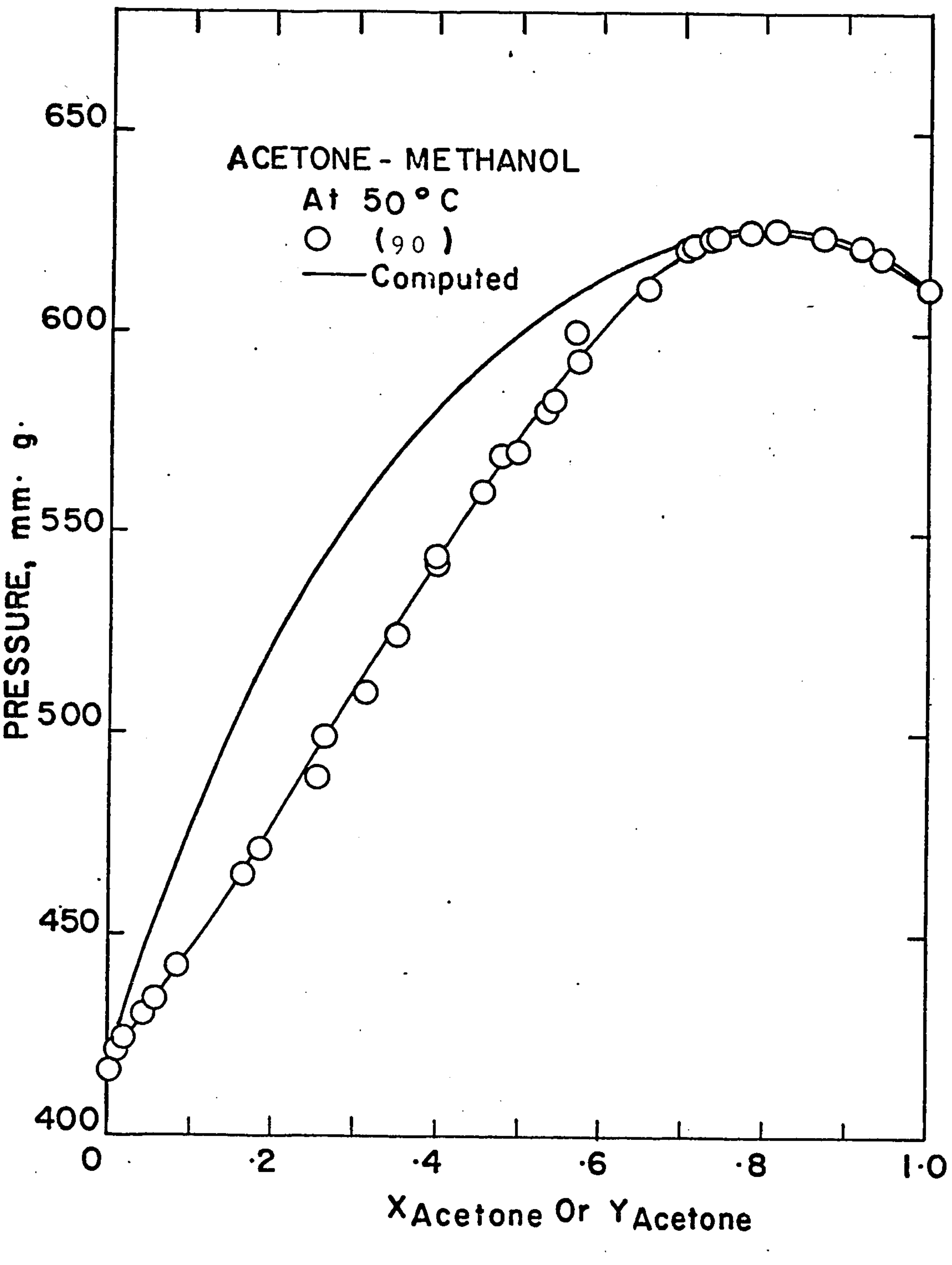

Figure 7.1

Pressure-Composition Diagram of the System Acetone-Methanol at 50 ° C.

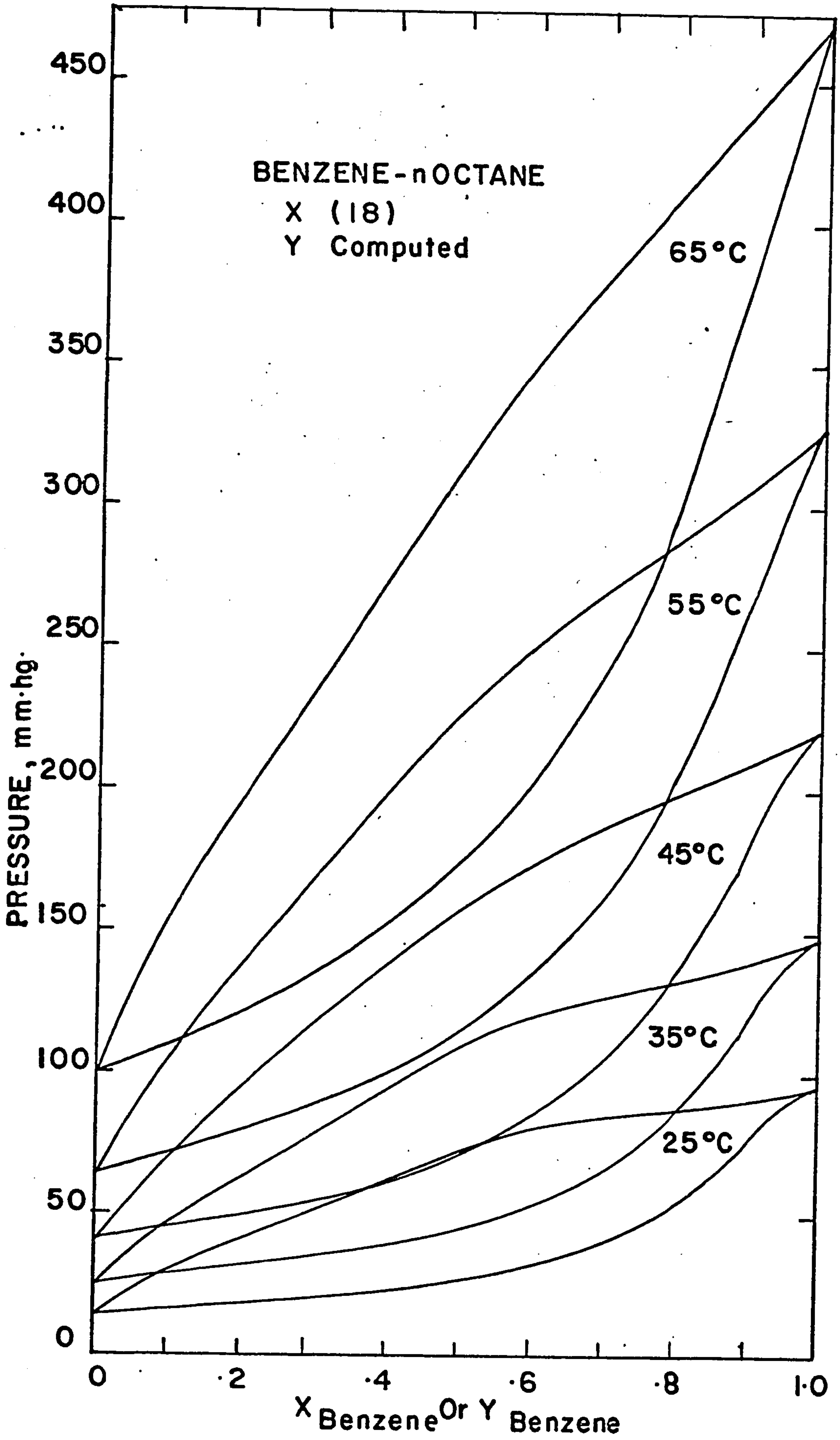

Figure 7.2 Pressure-Composition Diagram of the System Benzene- Octane at 25, 35, 45, 55 and 65° C

7.2 ON THE THERMODYNAMIC CONSISTENCY TEST OF TERNARY VAPOR-LIQUID EQUILIBRIUM DATA

When experimental data for a ternary system are available along linear paths, point-by-point evaluation of such data may be made by the "composition-resolution" test which was originally proposed by Van Ness (98) for testing binary vapor-liquid equilibrium data.

Extension of Van Ness' Method to test the ternary data along a linear path is straightforward. As it has apparently not been discussed before, a brief presentation is given as follows.

Along a linear path of constant mole ratio of $x_2/(x_2 + x_3) = k$, the quantities, $(\Delta G^E - (1 - x_1)\, \Delta G^E_{23})/RT$, may be plotted against x_1 as shown in figure 8.3, in which ΔG^E_{23} has a constant value, i.e., the excess Gibbs free energy of mixing per mole of the binary solution 2-3 of the concentration at the constant mole ratio of $x_2/(x_2 + x_3) = k$. The quantity ΔG^E is the excess ternary Gibbs free energy of mixing per mole of the mixture. At $x_1 = x_{1A}$, the composition at which an experimental point is measured, $(\Delta G^E - (1 - x_1)\, \Delta G^E_{23})/RT = A$. Draw a tangent to the curve at A. The tangent is shown intersecting the ordinates at $x_1 = 0$ and $x_1 = 1$ at points labelled I_0 and I_1 respectively. From the following relationships:

$$\Delta G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3 \quad \ldots\ldots\ldots \quad 7.6$$

$$d\left(\frac{\Delta G^E}{RT}\right) = \frac{\Delta v}{RT}\, dP - \frac{\Delta H}{RT^2}\, dT + \sum_i \ln \gamma_i \, dx_i \quad \ldots\ldots \quad 7.7$$

and

$$d\,x_3/d\,x_1 = -\,x_3/(1 - x_1) \quad \ldots\ldots\ldots\ldots\ldots \quad 7.8$$

and from the geometry, it may be readily shown that the slope of the tangent is equal to:

$$\xi + \quad (\Delta \overline{G}_1^{\,E} - \Delta G^E) / (1 - x_1) + \Delta G^E{}_{23} \quad /RT \quad \ldots\ldots \quad 7.9$$

and the intercept $I_1 = \ln \gamma_1 + (1 - x_1)\, \xi$ 7.10

where $\xi = \left(\frac{\Delta v}{RT}\right)\left(\frac{dP}{dx_1}\right)$ for isothermal data 7.11

and $\xi = -\left(\frac{\Delta H}{RT^2}\right)\left(\frac{dT}{dx_1}\right)$ for isobaric data 7.12

If the $\ln\gamma_1$ values obtained in this manner agree with the values directly calculated from the experimental data then these γ values are consistent.

The intercept I_0 involves both $\ln\gamma_2$ and $\ln\gamma_3$ terms and cannot be used explicitly for testing $\ln\gamma_2$ and $\ln\gamma_3$ values. In order to test $\ln\gamma_2$ values in the above described manner, linear paths must be chosen so that x_1/x_3 or $x_1/(x_1 + x_3) = k'$.

Similarly, $\ln\gamma_3$ values must be tested along x_1/x_2 or $x_1/(x_1 + x_2) = k''$ paths. Cross-plotting and interpolation of $\ln\gamma$ values along these linear paths may be carried out by following a procedure outlined elsewhere for a similar situation (15). It should be mentioned that the method of Van Ness and Mrazek (101) may be used for obtaining the intercepts.

This method of testing is particularly useful when the distance between points along the linear paths is relatively large. It is most convenient for testing isothermal data as it is generally satisfactory to take ξ as zero.

It may also be mentioned that when ΔP (for isothermal data) or ΔT (for isobaric data) is small, the minimum number of precisely measured experimental points required for a ternary system is only four (61).

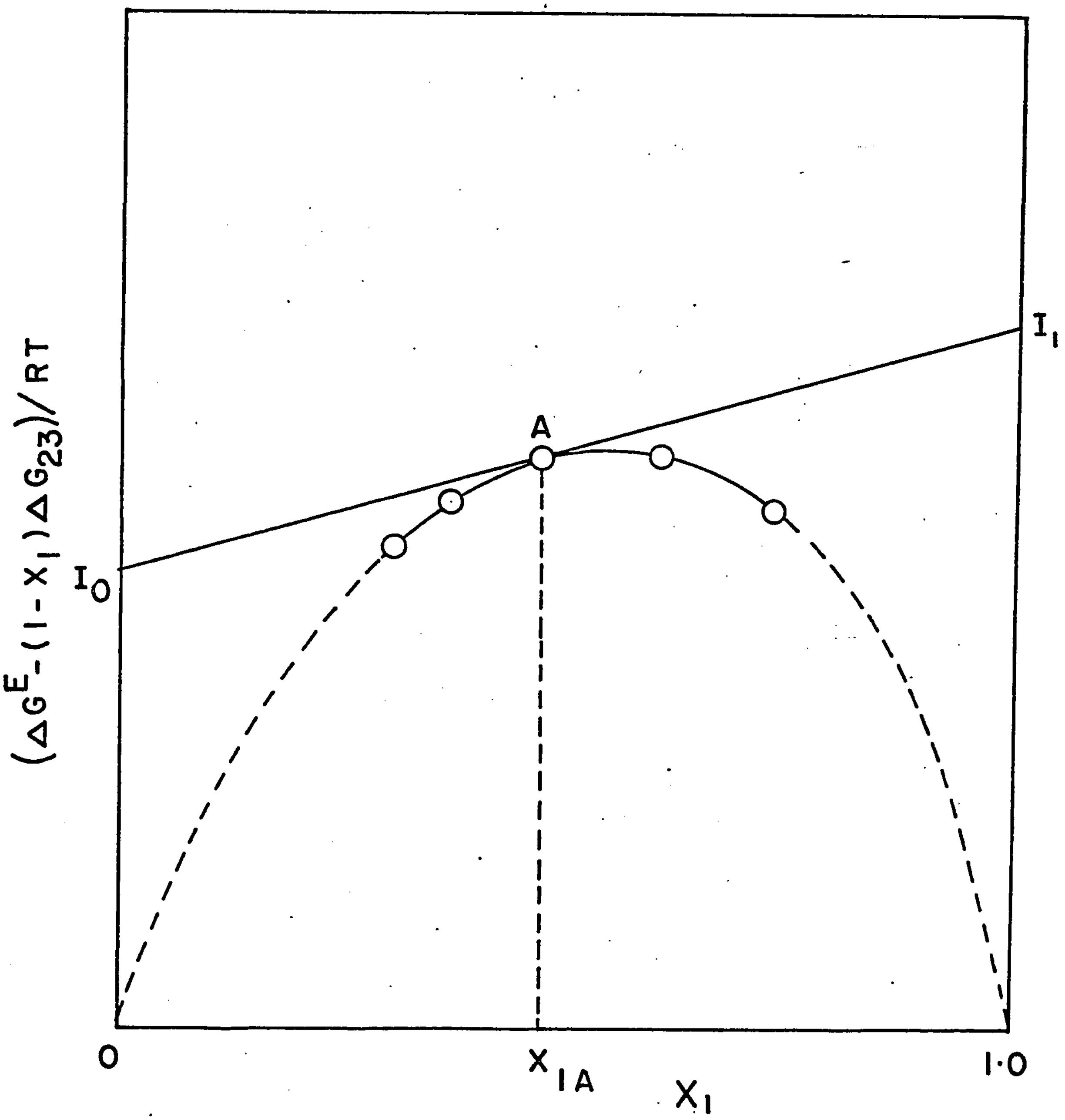

Figure 7.3

Illustration of the Composition Resolution Method for a Ternary System.

7.3 COPPER-CONSTANTAN THERMOPILE

A five-junction copper-constantan thermopile was built. Thermocouple wires of Type-T, 30 B. S. Gauge, catalogue no. 9B1C5 with varnished fiber glass insulation used in the construction were purchased from Honeywell Company., Philadelphia, Pa.

The calibration of the thermocouple was carried out by measuring the vapor pressure of water from 44 to 100° C. The temperature conversion is based on the available steam table (69).

In the correlation, an equation of Adam's type (1) was chosen in the form of

$$\mathcal{E} = At + B(1 - \exp(-Ct))$$

where $\mathcal{E}$ = e.m.f. in microvolt,

t = temperature in ° C.,

A, B and C = adjustable constants.

The standard deviation of the correlation, which was defined as the square root of the sum of the deviation squares over the degrees of the freedom or

$$\text{St. Dev.} = \sum_{i}^{nobs} \sqrt{(\mathcal{E}(\text{comp}) - \mathcal{E}(\text{obs}))^2/(\text{nobs} - 3)}$$

was found to be 3.2 microvolts and the average percentage deviation was 0.018%. The adjustable constants were determined to be A = 385.570, B = -80815.2, and C = .00237785. Details of the correlations are presented in Table 7.8. The calibration table for the five-junction copper constantan thermopile with reference junction of 0° C was also prepared in the temperature range of 0 to 100° C and at the interval of 0.1° C. The complete table is presented in Table 7.9. The reliability of the table prepared is within ± 0.03° C.

CHAPTER 8

SUMMARY AND CONCLUSIONS

Attempts were made in this study to investigate some new means and more efficient methods to obtain and to process the experimental data and to screen the existing data as well. A summary and conclusions of the results are as follow :

EXPERIMENTAL WORK

A forced-recirculation apparatus was redesigned and constructed for the experimental study of the vapor-liquid equilibrium problem at low temperature and high pressure conditions. Provisions were made to study the liquid-liquid-vapor equilibria.

Experimental vapor-liquid equilibrium data for the binary and ternary mixtures of the components nitrogen, methane and ethane were obtained at -240° F by means of the modified apparatus.

Partially miscible liquid phases were found and liquid-liquid-vapor equilibrium data of the ternary mixtures of nitrogen-methane-ethane were also obtained at -240° F. The partially miscible phenomenon of this system could lead to a new liquid phase separation technique for nitrogen. In addition to the work mentioned above the experimental data of the same systems were obtained at -151° F and reported earlier (14).

From the nature of the present experimental work it may be concluded that the forced-recirculation apparatus with the modification made in this study is the most suitable one for obtaining multicomponent liquid-liquid-vapor equilibrium data. It should also be mentioned that the accuracy of the data obtained by this method is limited to the accuracy of the analysis. If the method of the gas chromatography is employed and the analysis of each sample is repeated for four to five times then the reproducibility is ± 0.001 mole fraction. Under isothermal condition, when the difference of the vapor pressure between the pure components is too large or at conditions when the presence of the heavier component in the vapor phase is extremely low the existing method of the analysis should be replaced by a better one, for example, mass spectrometry.

CALCULATION OF VAPOR COMPOSITIONS FROM TOTAL PRESSURE-LIQUID COMPOSITION DATA

A new hypothetical component concept has been introduced in conjunction with a new graphical interpolation technique from which a simple and direct method has been proposed for evaluating ternary vapor-liquid equilibrium composition from measurements of the total vapor pressure exerted by the liquid phase along lines of constant liquid mole ratio. The proposed method accounts for ternary effect in the liquid solution because no assumption is involved. Although the procedures used in this work are limited to low or medium pressures, the proposed method can be extended to high pressures when a suitable equation of state or P-V-T data of pure components and their vapor mixtures are available. An application has been successfully made to the ternary system, nitrogen-argon-oxygen at 180°R.

DEVELOPMENT OF TOTAL PRESSURE METHOD FOR THE SYSTEMS AT HIGH PRESSURES

At high pressure the effect of the pressure on the activity coefficient is not negligible and the original form of the Gibbs-Duhem equation should be used only under isobaric and isothermal conditions. To meet these restrictions an adjusted activity coefficient was introduced in conjunction with the appropriate symmetric and unsymmetric conventions. As a consequence, a general and rigorous indirect method has been proposed for calculating the vapor compositions from total pressure and liquid composition data at high pressure and isothermal conditions. The derived equations and the method for evaluating adjustable parameters are general and suitable for multicomponent systems. Owing to the the lack of adequate experimental data, examples were given only for binary systems.

The total pressure method available in the literature is inadequate for processing data of multicomponent systems or at the conditions of the high pressure. This major drawback has now been overcome by the proposed method.

Data of three simple systems: methane-ethane, nitrogen-ethane, and argon-methane have been successfully used in testing the proposed method. γ-values were obtained in the evaluation indicating that none of the systems obeys the regular solution theory. Failures of some prediction methods as reviewed in this study probably are due to the wrong choice of the physical model such as the Scatchard-Hildebrand's equation.

THERMODYNAMIC CONSISTENCY TEST OF VAPOR-LIQUID EQUILIBRIUM DATA

If the number of the measuring variables is greater than the independent variables for defining a vapor-liquid equilibrium system, in principle such data can always be tested for internal consistency provided that the supporting physical properties are available. Based on the adjusted activity coefficient and the original form of the Gibbs-Duhem equation a rigorous and general method of the thermodynamic consistency test has been developed for examining experimental binary and multicomponent vapor-liquid equilibrium data. However, the equations developed involve no activity coefficient terms and are applicable to all conditions including the situation when the more volatile component(s) is (are) above its (their) critical temperature. The proposed method permits a point-by-point evaluation of data provided that the tested data are fairly well spaced. In order to establish the consistency of the data within the tolerable experimental error, error bounds have been established analytically. Sample calculations for four isothermal and one isobaric systems were presented. Data tested have been taken from this work and from the literature.

It may be suggested that in order to improve the quality of data the experimental results should be tested and screened as soon as they are obtained. Furthermore, the experiment should be well designed for obtaining data at well spaced distance to take advantage of the proposed testing method.

COMPUTER PROGRAMS

A number of numerical techniques have been developed for supporting the research work mentioned above. More than a dozen computer programs have been written using the FORTRAN language. Details of three most important programs are included.

It may be mentioned that without extensive use of the modern computing technique it would not be possible to have this work completed.

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APPENDIX I

TABLES 3.1 TO 3.4 FOR CHAPTER 3

Table 3.1 Experimental Equilibrium Data for Nitrogen-Methane System

Temperature - 240° F

Pressure, lb. sq. in. abs.	Composition, mole fraction				Equilibrium ratio	
	Vapor		Liquid			
	N_2	CH_4	N_2	CH_4	K_{N_2}	K_{CH_4}
50.7	0.3599	0.6401	0.03371	0.9663	10.68	0.6624
100.9	0.7070	0.2930	0.1503	0.8497	4.704	0.3448
200.6	0.8731	0.1269	0.4045	0.5955	2.158	0.2131
303.9	0.9269	0.07311	0.7122	0.2878	1.301	0.2540
343.9	0.9526	0.04736	0.8303	0.1797	1.159	0.2795
388.5	0.9784	0.02165	0.9366	0.06344	1.045	0.3407
403.4	0.9874	0.01264	0.9861	0.01391	1.001	0.9065

Table 3.2 Experimental Equilibrium Data for Nitrogen-Ethane System

Temperature - 240° F.

Pressure, lb./sq. in. abs.	Composition, mole fraction				Equilibrium ratio	
	Vapor		Liquid			
	N_2	C_2H_6	N_2	C_2H_6	K_{N_2}	$K_{C_2H_6}$
49.9	0.9958	0.004150	0.04956	0.9504	20.09	0.004367
98.9	0.9972	0.002848	0.005040	0.9496	19.79	0.002999
146.7	0.9980	0.002017	0.07889	0.9211	12.65	0.002190
199.3	0.9985	0.001468	0.1317	0.8683	7.582	0.001691
298.8	0.9982	0.001789	0.1529	0.8471	6.528	0.002112
302.2	0.9981	0.001917	0.2124	0.7876	4.699	0.002434
349.3	0.9979	0.002141	0.2446	0.7554	4.079	0.002834
386.9	0.9973	0.002743*	(BL) 0.2854	0.7146	3.494	0.003839
			(TL) 0.9376	0.06236	1.064	0.004399
388.5	0.9982	0.001786	(BL) 0.2945	0.7055	3.389	0.002532
			(TL) 0.9566	0.04342	1.043	0.04113
389.5	0.9971	0.002883	0.9543	0.04573	1.045	0.06304
389.5	0.9982	0.001770	0.9485	0.05154	1.052	0.03434
400.5	0.9986	0.001415	0.9727	0.02734	1.027	0.05176

* Sample was taken before 1-hr. settling period.

Table 3.3 Experimental Equilibrium Data for Methane-Ethane System

Temperature -240° F.

Pressure, lb./sq. in. abs.	Composition, mole fraction				Equilibrium ratio	
	Vapor		Liquid			
	CH_4	C_2H_6	CH_4	C_2H_6	K_{CH_4}	$K_{C_2H_6}$
0.07	0.000	1.000	0.000	1.000	-----	1.000
18.2	0.9968	0.003173	0.4181	0.5819	2.384	0.005454
23.1	0.9978	0.002236	0.6140	0.3859	1.625	0.00574
26.7	0.9977	0.002266	0.6664	0.3336	1.497	0.006793
32.4	1.000	0.000	1.000	0.000	1.000	-------

TABLE 3.4 EXPERIMENTAL EQUILIBRIUM DATA FOR NITROGEN-METHANE-ETHANE SYSTEM

Temperature −240°F

Pressure, lb./sq. in. abs.	Composition, mole fraction: Vapor N_2	Vapor CH_4	Vapor C_2H_6	Liquid N_2	Liquid CH_4	Liquid C_2H_6	Equilibrium ratio K_{N_2}	K_{CH_4}	$K_{C_2H_6}$
45.95	0.6249	0.3712	0.001856	0.03356	0.5000	0.4663	18.62	0.7424	0.004254
114.5	0.8409	0.1574	0.001740	0.09687	0.3638	0.5393	8.681	0.4327	0.003226
189.7	0.9026	0.09737	0.000696	0.1646	0.3556	0.4800	5.484	0.2738	0.001450
260.7	0.9313	0.06777	0.00095	0.3188	0.2966	0.3846	2.921	0.2285	0.002470
323.1	0.9597	0.04133	0.00112	0.5940	0.1779	0.2281	1.612	0.2323	0.004910
342.9	0.9729	0.02598	0.00115	0.7605	0.1078	0.1317	1.279	0.2410	0.008732
381.2	0.9873	0.01144	0.001276	0.9358	0.03627	0.02793	1.055	0.3154	0.04569
27.9	0.04142	0.9537	0.004872	0.07798	0.3348	0.5871	0.5312	2.849	0.008298
82.6	0.8446	0.1521	0.00335	0.09513	0.3405	0.5643	8.878	0.4467	0.005936
146.6	0.7817	0.2169	0.001316	0.08766	0.2419	0.6705	8.9174	0.8967	0.001963
230.7	0.9242	0.07415	0.001652	0.1659	0.2413	0.5928	5.571	0.3073	0.002787
288.7	0.9529	0.04571	0.001380	0.2772	0.1863	0.5365	3.4376	0.2453	0.002572
308.1	0.9582	0.03966	0.002098	(BL) 0.4219	0.1458	0.4323	2.2712	0.2720	0.004853
				*(TL) 0.5322	0.1529	0.3149	1.8005	0.2594	0.00662
327.1	0.9700	0.02891	0.001710	0.5450	0.1644	0.2906	1.7798	0.1759	0.005884
332.5	0.9722	0.02661	0.001161	(BL) 0.4715	0.1513	0.3772	2.0619	0.1759	0.003078
				(TL) 0.6628	0.1418	0.1954	1.4668	0.1877	0.005941
348.89	0.9807	0.01880	0.0005356	0.6996	0.07831	0.2221	1.4018	0.2401	0.002411
355.8	0.9837	0.01510	0.001157	0.7509	0.06091	0.1882	1.3100	0.2479	0.006184
33.3	0.7110	0.2867	0.002279	0.02279	0.2783	0.6989	31.1979	1.0302	0.003261

TABLE 3.4 EXPERIMENTAL EQUILIBRIUM DATA FOR NITROGEN-METHANE-ETHANE SYSTEM (CONT'D)

Temperature −240°F.

Pressure, lb./sq. in. abs.	Composition, mole fraction						Equilibrium ratio		
	Vapor			Liquid					
	N_2	CH_4	C_2H_6	N_2	CH_4	C_2H_6	K_{N_2}	K_{CH_4}	$K_{C_2H_6}$
31.2	0.7914	0.2086	0.003105	0.03949	0.2750	0.6855	20.0405	0.7585	0.004529
70.8	0.9582	0.04112	0.0006961	0.1095	0.2642	0.6263	8.7507	0.1556	0.001111
147.6	0.9571	0.04216	0.0006863	0.1026	0.1672	0.7302	9.3285	0.2522	0.0009399
195.7	0.9673	0.03206	0.0006209	0.1507	0.1629	0.6864	6.4187	0.1968	0.0009046
249.2	0.9715	0.02675	0.0006855	0.2048	0.1469	0.6482	4.7437	0.1821	0.001058
316.2	0.9780	0.02107	0.0008995	0.3158	0.1260	0.5582	3.125	0.1672	0.001611
351.5	0.9809	0.01785	0.001251	(BL) 0.3658	0.1025	0.5317	2.6815	0.1741	0.002353
				*(TL) 0.7047	0.07117	0.2241	1.3919	0.2508	0.005582
365.8	0.9901	0.008430	0.001499	0.8971	0.03577	0.06715	1.1037	0.2357	0.02232
25.3	0.09370	0.9045	0.001847						
49.35	0.5256	0.4731	0.001238	0.03182	0.6916	0.2766	16.5179	0.6841	0.004476
99.15	0.7535	0.2456	0.0009046	0.09313	0.6348	0.2680	8.0908	0.3869	0.003375
203.0	0.8888	0.1106	0.0006336	0.3072	0.4874	0.2054	2.8932	0.2269	0.003085
333.0	0.9625	0.03672	0.0007767	0.8206	0.1318	0.04758	1.1729	0.2786	0.01632
338.9	0.9641	0.03515	0.0007576	0.8396	0.1171	0.04330	1.1483	0.3002	0.1750
395.6	0.9872	0.01229	0.0005563	0.9605	0.02907	0.01039	1.0278	0.4228	0.05354
406.5	0.9920	0.007547	0.0004530	0.8523	0.1429	0.004819	1.1639	0.05281	0.09400
358.3	0.9853	0.01352	0.001279	(BL) 0.3500	0.08683	0.5632	2.815	0.1557	0.002271
				(TL) 0.8496	0.06764	0.08278	1.160	0.1999	0.001545
340.5	0.9770	0.02171	0.001226	(BL) 0.4389	0.1464	0.4147	2.226	0.1483	0.002956
				(TL) 0.7208	0.1228	0.1564	1.355	0.1768	0.007839
339.0	0.9742	0.02312	0.001278	(BL) 0.4731	0.1439	0.3830	2.059	0.1607	0.00337
				(TL) 0.7217	0.1233	0.1551	1.350	0.1875	0.008240

*Sample was taken before 1-hr. settling period.

APPENDIX II

TABLES 4.1 AND 4.2 FOR CHAPTER 4

Table 4.1 Comparison of Calculated and Experimental Vapour Compositions for the System Nitrogen-Argon-Oxygen at 180° R

P	x_{N_2}	y exptl, (106)			y calcd.			y calcd - y exptl		
atm	mol. fr.	N_2	A	O_2	N_2	A	O_2	N_2	A	O_2
$x_A/(x_A + x_{0_2}) = 0.0$										
3.08	.1	.2536		.7464	.2546		.7454	.0010		.0010
3.62	.2	.4241		.5759	.4255		.5745	.0014		.0014
4.15	.3	.5490		.4510	.5508		.4492	.0018		.0018
4.66	.4	.6462		.3538	.6483		.3517	.0021		.0021
5.16	.5	.7254		.2746	.7277		.2723	.0022		.0022
5.65	.6	.7927		.2073	.7947		.2053	.0020		.0020
6.14	.7	.8513		.1487	.8533		.1467	.0020		.0020
6.64	.8	.9045		.0955	.9059		.0941	.0014		.0014
7.14	.9	.9537		.0463	.9543		.0457	.0018		.0018
							Avg.	.0018		.0018
$x_A/(x_A + x_{0_2}) = 0.1$										
3.17	.1	.2436	.0999	.6565	.2439	.1030	.6565	.0006	.0021	.0000
3.70	.2	.4123	.0766	.5112	.4126	.0780	.5120	.0003	.0014	.0008
4.21	.3	.5379	.0594	.4028	.5387	.0590	.4020	.0014	.0004	.0008
4.70	.4	.6367	.0461	.3174	.6380	.0440	.3175	.0013	.0021	.0001
5.19	.5	.7180	.0353	.2470	.7195	.0340	.2450	.0015	.0013	.0020
5.68	.6	.7871	.0263	.1870	.7887	.0250	.1860	.0016	.0013	.0010

P	x_{N_2}	y exptl,			y calcd.			y calcd - y exptl		
atm	mol. fr.	N_2	A	O_2	N_2	A	O_2	N_2	A	O_2
6.17	.7	.8475	.0185	.1340	.8492	.0170	.1340	.0017	.0015	.0000
6.66	.8	.9022	.0117	.0862	.9035	.0110	.0845	.0013	.0007	.0011
7.15	.9	.9527	.0056	.0419	.9533	.0040	.0415	.0006	.0016	.0004
							Avg.	.0011	.0037	.0007
$x_A/(x_A + x_{O_2}) = 0.2$										
3.25	.1	.2354	.1914	.5732	.2355	.1950	.5720	.0006	.0036	.0012
3.76	.2	.4021	.1482	.4497	.4022	.1480	.4480	.0001	.0002	.0017
4.26	.3	.5282	.1158	.3561	.5289	.1150	.3585	.0006	.0008	.0024
4.75	.4	.6284	.0904	.2815	.6296	.0880	.2820	.0011	.0016	.0005
5.23	.5	.7112	.0696	.2195	.7128	.0662	.2200	.0014	.0034	.0005
5.71	.6	.7821	.0520	.1663	.7837	.0520	.1660	.0016	.0000	.0003
6.19	.7	.8440	.0368	.1193	.8457	.0362	.1180	.0018	.0006	.0013
6.67	.8	.9001	.0234	.0767	.9014	.0240	.0750	.0013	.0006	.0017
7.16	.9	.9517	.0112	.0373	.9523	.0100	.0370	.0006	.0012	.0003
							Avg.	.0014	.0013	.0011
$x_A/(x_A + x_{O_2}) = 0.3$										
3.32	.1	.2286	.2763	.4951	.2291	.2780	.4980	.0005	.0017	.0029
3.82	.2	.3935	.2158	.3907	.3942	.2150	.3920	.0007	.0008	.0013
4.31	.3	.5198	.1698	.3106	.5210	.1700	.3110	.0012	.0002	.0004
4.79	.4	.6210	.1332	.2461	.6227	.1340	.2470	.0017	.0008	.0009
5.26	.5	.7052	.1030	.1922	.7071	.1040	.1930	.0019	.0010	.0008
5.73	.6	.7774	.0773	.1457	.7793	.0790	.1450	.0019	.0017	.0007

P	x_{N_2}	y exptl.			y calcd.			y calcd - y exptl		
atm	mol. fr.	N_2	A	O_2	N_2	A	O_2	N_2	A	O_2
6.21	.7	.8407	.0549	.1045	.8426	.0560	.1030	.0019	.0011	.0015
6.69	.8	.8980	.0349	.0672	.8994	.0350	.0660	.0014	.0001	.0012
7.17	.9	.9508	.0168	.0326	.9514	.0016	.0310	.0006	.0008	.0016
							Avg.	.0013	.0009	.0011
$x_A/(x_A + x_{O_2}) = 0.4$										
3.39	.1	.2231	.3561	.4209	.2235	.3530	.4230	.0004	.0031	.0021
3.88	.2	.3863	.2802	.3336	.3870	.2770	.3345	.0007	.0012	.0009
4.36	.3	.5126	.2217	.2659	.5138	.2220	.2660	.0012	.0017	.0001
4.83	.4	.6146	.1747	.2110	.6162	.1740	.2110	.0016	.0007	.0000
5.30	.5	.6998	.1355	.1649	.7017	.1360	.1650	.0019	.0005	.0001
5.76	.6	.7732	.1021	.1251	.7751	.1030	.1250	.0019	.0009	.0001
6.23	.7	.8377	.0727	.0897	.8396	.0730	.0880	.0019	.0003	.0017
6.70	.8	.8961	.0464	.0577	.8975	.0460	.0570	.0014	.0004	.0007
7.18	.9	.9499	.0223	.0280	.9505	.0220	.0280	.0006	.0003	.0000
							Avg.	.0013	.0010	.0006
$x_A/(x_A + x_{O_2}) = 0.5$										
3.45	.1	.2185	.4323	.3493	.2186	.4350	.3480	.0001	.0027	.0013
3.93	.2	.3803	.3421	.2777	.3808	.3430	.2770	.0005	.0009	.0007
4.40	.3	.5065	.2719	.2217	.5077	.2720	.2220	.0012	.0001	.0003
4.87	.4	.6090	.2151	.1761	.6109	.2150	.1770	.0019	.0001	.0009
5.33	.5	.6951	.1674	.1378	.6973	.1670	.1390	.0022	.0004	.0011
5.79	.6	.7695	.1265	.1045	.2716	.1270	.1040	.0021	.0005	.0005
6.25	.7	.8349	.0903	.0749	.8370	.0910	.0740	.0021	.0007	.0009

P	x_{N_2}	y exptl.			y calcd.			y calcd - y exptl		
atm	mol.fr.	N_2	A	O_2	N_2	A	O_2	N_2	A	O_2
6.72	.8	.8943	.0577	.0481	.8957	.0570	.0470	.0014	.0007	.0011
7.18	.9	.9490	.0279	.0233	.9496	.0270	.0230	.0005	.0009	.0003
							Avg.	.001	.0008	.0007
$x_A/(x_A + x_{O_2}) = 0.6$										
3.50	.1	.2150	.5057	.2794	.2152	.4940	.2750	.0002	.0017	.0044
3.98	.2	.3755	.4021	.2225	.3761	.3990	.2220	.0016	.0022	.0005
4.45	.3	.5015	.3208	.1778	.5028	.3140	.1780	.0013	.0014	.0002
4.91	.4	.6043	.2546	.1414	.6062	.2550	.1430	.0019	.0004	.0016
5.37	.5	.6910	.1988	.1106	.6932	.1990	.1120	.0022	.0002	.0016
5.82	.6	.7661	.1505	.0838	.7683	.1500	.0840	.0017	.0005	.0002
6.27	.7	.8323	.1077	.0601	.8345	.1060	.0590	.0013	.0017	.0011
6.73	.8	.8926	.0690	.0386	.8941	.0670	.0390	.0015	.0020	.0004
7.19	.9	.9481	.0334	.0187	.9488	.0310	.0190	.0007	.0024	.0003
							Avg.	.0014	.0014	.0011
$x_A/(x_A + x_{O_2}) = 0.7$										
3.55	.1	.2123	.5774	.2103	.2133	.5680	.2090	.0010	.0094	.0013
4.03	.2	.3718	.4607	.1676	.3732	.4560	.1660	.0014	.0047	.0016
4.49	.3	.4975	.3687	.1340	.4995	.3660	.1330	.0020	.0027	.0010
4.95	.4	.6004	.2933	.1065	.6029	.2920	.1060	.0025	.0013	.0005
5.40	.5	.6875	.2296	.0832	.6901	.2290	.0840	.0026	.0006	.0008
5.85	.6	.7631	.1742	.0631	.7656	.1740	.0640	.0025	.0002	.0009
6.30	.7	.8300	.1249	.0452	.8323	.1240	.0450	.0023	.0009	.0002

P	x_{N_2}	y exptl.			y calcd.			y calcd - y exptl		
atm	mol. fr.	N_2	A	O_2	N_2	A	O_2	N_2	A	O_2
6.75	.8	.8910	.0802	.0290	.8926	.0790	.0290	.0016	.0012	.0000
7.20	.9	.9473	.0389	.0140	.9480	.0390	.0140	.0007	.0012	.0000
							Avg.	.0019	.0023	.0005
$x_A/(x_A + x_{O_2}) = 0.8$										
3.60	.1	.2105	.6483	.1413	.2111	.6390	.1400	.0006	.0093	.0013
4.07	.2	.3691	.5185	.1125	.3703	.5160	.1120	.0012	.0025	.0005
4.53	.3	.4944	.4158	.0899	.4964	.4150	.0890	.0020	.0008	.0009
4.98	.4	.5974	.3315	.0714	.5999	.3310	.0710	.0025	.0005	.0004
5.43	.5	.6846	.2599	.0558	.6874	.2600	.0560	.0028	.0001	.0002
5.87	.6	.7606	.1976	.0422	.7632	.1960	.0420	.0026	.0016	.0002
6.32	.7	.8229	.1419	.0302	.8304	.1400	.0300	.0024	.0019	.0002
6.76	.8	.8895	.0913	.0194	.8911	.0910	.0190	.0016	.0003	.0004
7.21	.9	.9465	.0443	.0094	.9471	.0430	.0090	.0006	.0013	.0004
							Avg.	.0018	.0020	.0005
$x_A/(x_A + x_{O_2}) = 0.9$										
3.64	.1	.2095	.7192	.0714	.2100	.7150	.0710	.0005	.0042	.0004
4.11	.2	.3674	.5759	.0568	.3685	.5780	.0570	.0010	.0021	.0002
4.57	.3	.4923	.4625	.0453	.4943	.4640	.0450	.0020	.0015	.0003
5.02	.4	.5950	.3692	.359	.5976	.3700	.0360	.0026	.0008	.0001
5.46	.5	.6823	.2900	.0280	.6851	.2890	.0270	.0028	.0010	.0010
5.90	.6	.7584	.2208	.0212	.7610	.2190	.0200	.0026	.0018	.0012
6.34	.7	.8261	.1589	.0152	.8284	.1570	.0150	.0023	.0019	.0002
6.78	.8	.8881	.1024	.0097	.8896	.1020	.0090	.0015	.0008	.0007

P	x_{N_2}	y exptl.			y calcd.			y calcd - y exptl		
atm	mol. fr.	N_2	A	O_2	N_2	A	O_2	N_2	A	O_2
7.21	.9	.9457	.0458	.0047	.9463	.0520	.0042	.0006	.0072	.0005
							Avg.	.0018	.0015	.0005
$x_A/(x_A + x_{0_2}) = 1.0$										
3.67	.1	.2092	.7908		.2098	.7902		.0006	.0006	
4.14	.2	.3666	.5334		.3677	.6323		.0011	.0011	
4.60	.3	.4911	.5089		.4928	.5072		.0017	.0017	
5.05	.4	.5935	.4065		.5957	.4043		.0022	.0022	
5.49	.5	.6806	.3194		.6829	.3171		.0023	.0023	
5.93	.6	.7567	.2433		.7589	.2411		.0022	.0022	
6.36	.7	.8245	.1755		.8266	.1734		.0021	.0021	
6.79	.8	.8868	.1132		.8883	.1117		.0015	.0015	
7.22	.9	.9450	.0550		.9456	.0544		.0006	.0006	
							Avg.	.0016	.0016	

Table 4. 2 Summary of Average and Maximum Δy Values for the System Nitrogen-Argon-Oxygen at 180° R

		$\lvert y \text{ calcd} - y \text{ exptl} \rvert$ Avg.			$\lvert y \text{ calcd} - y \text{ exptl} \rvert$ Max.		
$x_A/(x_A + x_{O_2})$	Press. Range atm.	N_2	A_r	O_2	N_2	A_r	O_2
0	2.51 - 7.646	.0018	------	------	.0023	------	------
.1	2.62 - 7.646	.0011	.0014	.0007	.0017	.0021	.0020
.2	2.72 - 7.646	.0014	.0013	.0011	.0018	.0036	.0024
.3	2.80 - 7.46	.0013	.0009	.0011	.0019	.0017	.0029
.4	2.88 - 7.646	.0013	.0010	.0006	.0019	.0031	.0031
.5	2.95 - 7.646	.0011	.0008	.0007	.0022	.0027	.0013
.6	3.01 - 7.646	.0014	.0014	.0011	.0022	.0022	.0044
.7	3.06 - 7.646	.0019	.0023	.0005	.0026	.0094	.0016
.8	3.11 - 7.646	.0018	.0020	.0005	.0028	.0093	.0013
.9	3.15 - 7.646	.0018	.0015	.0005	.0023	.0072	.0010
1.0	3.18 - 7.646	.0016	------	------	.0023	------	------

APPENDIX III

TABLES 5.5 TO 5.8 FOR CHAPTER 5

Table 5.5 Methane- Ethane System at -151.1° F

A. Tested Data and Supporting Properties

```
K12(V)= 0.010   K12(L)= 0.005   DTR= 0.0      DVR= 0.0

TEMP=   3C8.9C
PS1=  358.2C0        FREFER(1)=  249.573
PS2=    7.112        FREFER(2)=    6.993
PS0=    7.112

   P       X2      Y2     PVOL1   PVOL2   POYNT1  PCYNT2  GAMA1   GAMA2    PHI1    PHI2

  51.7C  0.8756  C.1310  0.7030  0.8328  1.0095  1.0113  1.3842  0.9857  0.9656  0.9012
  70.2C  0.7892  0.0976  0.7095  0.8295  1.0136  1.0159  1.1323  1.0621  0.9531  0.8691
 1C1.20  0.7128  0.0745  0.7163  0.8255  1.0205  1.0237  1.1938  1.2057  0.9324  0.8160
 13C.9C  0.6509  0.0397  0.7225  0.8212  1.0274  1.0311  1.2814  0.8521  C.9124  0.7696
 158.20  0.5547  0.0339  0.7337  0.8115  1.0340  1.0377  1.1895  0.9667  0.8943  0.7256
 2C1.5C  0.4514  0.0248  0.7481  0.7948  1.0449  1.0477  1.1891  0.9946  0.8657  0.6583
 219.70  0.3749  C.0201  0.7604  0.7752  1.0500  1.0510  1.1219  1.0114  0.8536  0.6310
 242.2C  0.3147  0.0189  0.7713  0.7528  1.0562  1.0548  1.1033  1.1769  0.8387  0.5968
 251.7C  0.2907  0.0506  0.7759  0.7415  1.0589  1.0562  1.0619  3.3977  C.8330  0.5728
 263.20  0.2456  0.0133  0.7849  0.7152  1.0625  1.0568  1.0708  1.0929  0.8248  0.5667
 301.70  0.1398  0.0758  0.8081  0.6108  1.0745  1.0558  0.9685 10.7061  0.8012  0.4832
```

Table 5.5 B Test Results by Using One-Term Redlish-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln \gamma_2$	$\ln \gamma_1$	Z_2	Z_1
51.70	51.05	0.65	0.876	0.135	0.131	0.0062	0.3073	1.011	1.010
70.20	78.38	-8.18	0.789	0.084	0.098	0.0178	0.2496	1.016	1.014
101.20	102.64	-1.44	0.713	0.063	0.074	0.0331	0.2036	1.024	1.021
130.90	122.66	8.24	0.651	0.052	0.040	0.0488	0.1698	1.031	1.027
158.20	151.36	6.84	0.555	0.040	0.034	0.0795	0.1233	1.038	1.034
201.50	184.99	16.51	0.451	0.031	0.025	0.1206	0.0817	1.048	1.045
219.70	208.12	11.58	0.375	0.025	0.020	0.1566	0.0563	1.051	1.050
242.20	228.80	13.40	0.315	0.021	0.019	0.1882	0.0397	1.055	1.056
251.70	237.45	14.25	0.291	0.019	0.051	0.2016	0.0339	1.056	1.059
263.20	252.50	10.70	0.246	0.016	0.013	0.2281	0.0242	1.057	1.063
301.70	293.60	8.10	0.140	0.009	0.076	0.2966	0.0078	1.056	1.074

```
B=    0.40079    C=
NO.OF OBSERVATIONS =          11
NO.OF CONSTANTS =          1
SYSTEM TEMPERATURE AT     308.90DEG
ST.DEV. OF CORRELATION IS      10.74PSIA
AV.% DEV OF CORRELATION IS       5.25
```

Table 5.5 C Test Results by Using Two-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln \gamma_2$	$\ln \gamma_1$	Z_2	Z_1
51.70	47.21	4.49	0.876	0.145	0.131	-0.0029	0.2179	1.011	1.010
70.20	76.68	-6.48	0.789	0.084	0.098	-0.0047	0.2278	1.016	1.014
101.20	104.24	-3.04	0.713	0.060	0.074	-0.0028	0.2225	1.024	1.021
130.90	127.17	3.73	0.651	0.048	0.040	0.0030	0.2103	1.031	1.027
158.20	159.61	-1.41	0.555	0.036	0.034	0.0228	0.1806	1.038	1.034
201.50	195.35	6.15	0.451	0.027	0.025	0.0640	0.1395	1.048	1.045
219.70	218.31	1.39	0.375	0.022	0.020	0.1113	0.1064	1.051	1.050
242.20	238.02	4.18	0.315	0.019	0.019	0.1605	0.0806	1.055	1.056
251.70	246.09	5.61	0.291	0.018	0.051	0.1833	0.0707	1.056	1.059
263.20	259.78	3.42	0.246	0.016	0.013	0.2316	0.0530	1.057	1.063
301.70	297.13	4.57	0.140	0.010	0.076	0.3750	0.0191	1.056	1.074

```
B=    0.40273    C=    0.23596    D=
NO.OF OBSERVATIONS =          11
NO.OF CONSTANTS =          2
SYSTEM TEMPERATURE AT    308.90DEG
ST.DEV. OF CORRELATION IS       4.81PSIA
AV.% DEV OF CORRELATION IS       3.22
```

Table 5.5 D Test Results by Using Three-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
51.70	49.58	2.12	0.876	0.140	0.131	0.0111	0.2726	1.011	1.010
70.20	75.75	-5.55	0.789	0.087	0.098	0.0230	0.2118	1.016	1.014
101.20	100.98	0.22	0.713	0.064	0.074	0.0312	0.1863	1.024	1.021
130.90	123.33	7.57	0.651	0.051	0.040	0.0359	0.1763	1.031	1.027
158.20	157.59	0.61	0.555	0.037	0.034	0.0422	0.1667	1.038	1.034
201.50	197.62	3.88	0.451	0.027	0.025	0.0576	0.1515	1.048	1.045
219.70	223.69	-3.99	0.375	0.021	0.020	0.0861	0.1318	1.051	1.050
242.20	244.99	-2.79	0.315	0.018	0.019	0.1267	0.1106	1.055	1.056
251.70	253.39	-1.69	0.291	0.017	0.051	0.1489	0.1010	1.056	1.059
263.20	267.07	-3.87	0.246	0.015	0.013	0.2023	0.0815	1.057	1.063
301.70	301.81	-0.11	0.140	0.010	0.076	0.4043	0.0346	1.056	1.074

```
B=   0.41652   C=   0.22366   D=   0.26983   E=
NO.OF OBSERVATIONS =        11
NO.OF CONSTANTS =        3
SYSTEM TEMPERATURE AT    308.90DEG
ST.DEV. OF CORRELATION IS      4.32PSIA
AV.% DEV OF CORRELATION IS      2.31
```

Table 5.5 E Test Results by Using Four-Term Redlish-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
51.70	50.80	0.90	0.876	0.140	0.131	0.0340	0.2972	1.011	1.010
70.20	73.71	-3.51	0.789	0.093	0.098	0.0563	0.1785	1.016	1.014
101.20	99.42	1.78	0.713	0.067	0.074	0.0593	0.1678	1.024	1.021
130.90	124.04	6.86	0.651	0.052	0.040	0.0528	0.1814	1.031	1.027
158.20	162.17	-3.97	0.555	0.036	0.034	0.0434	0.1964	1.038	1.034
201.50	202.34	-0.84	0.451	0.027	0.025	0.0656	0.1756	1.048	1.045
219.70	224.82	-5.12	0.375	0.022	0.020	0.1225	0.1361	1.051	1.050
242.20	242.26	-0.06	0.315	0.020	0.019	0.1956	0.0979	1.055	1.056
251.70	249.17	2.53	0.291	0.019	0.051	0.2312	0.0824	1.056	1.059
263.20	260.62	2.58	0.246	0.017	0.013	0.3059	0.0551	1.057	1.063
301.70	294.93	6.77	0.140	0.011	0.076	0.4909	0.0104	1.056	1.074

```
B=    0.47896    C=    0.28395    D=    0.26292    E=   -0.46830    F=
NO.OF OBSERVATIONS =          11
NO.OF CONSTANTS =          4
SYSTEM TEMPERATURE AT     308.90DEG
ST.DEV. OF CORRELATION IS       4.85PSIA
AV.% DEV OF CORRELATION IS       2.12
```

Table 5.5 F Test Results by Using Five-Term Redlish-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln \gamma_2$	$\ln \gamma_1$	Z_2	Z_1
51.70	51.44	0.26	0.876	0.145	0.131	0.0792	0.3044	1.011	1.010
70.20	71.55	-1.35	0.789	0.101	0.098	0.1086	0.1400	1.016	1.014
101.20	100.04	1.16	0.713	0.069	0.074	0.0974	0.1716	1.024	1.021
130.90	127.18	3.72	0.651	0.052	0.040	0.0815	0.2062	1.031	1.027
158.20	164.34	-6.14	0.555	0.037	0.034	0.0813	0.2088	1.038	1.034
201.50	198.84	2.66	0.451	0.029	0.025	0.1352	0.1556	1.048	1.045
219.70	220.07	-0.37	0.375	0.024	0.020	0.1963	0.1126	1.051	1.050
242.20	240.31	1.89	0.315	0.021	0.019	0.2413	0.0887	1.055	1.056
251.70	249.18	2.52	0.291	0.019	0.051	0.2568	0.0820	1.056	1.059
263.20	264.96	-1.76	0.246	0.016	0.013	0.2834	0.0722	1.057	1.063
301.70	305.78	-4.08	0.140	0.010	0.076	0.3923	0.0479	1.056	1.074

```
B=   0.57554    C=   0.16198    D=   0.02539    E=  -0.46820    F=    0.99765

NO.OF OBSERVATIONS =          11
NO.OF CONSTANTS =          5
SYSTEM TEMPERATURE AT    308.90DEG
ST.DEV. OF CORRELATION IS       3.91PSIA
AV.% DEV OF CORRELATION IS       1.41
```

Table 5.6 Nitrogen (2) - Methane (1) System at -240° F

A. Tested Data and the Supporting Properties

```
K12(V)= 0.030    K12(L)= 0.030    DTR= 0.0198    DVR=-0.0700

TEMP=    220.00
PS1=     32.400        FREFER(1)=    33.816
PS2=    408.700        FREFER(2)=   283.821
PS0=    408.700

     P       X2       Y2      PVOL1     PVOL2    POYNT1   POYNT2   GAMA1    GAMA2    PHI1     PHI2

   50.70   0.0337   0.3599   0.6243   0.7189   0.9097   0.8967   0.9994   2.0588   0.9153   0.9680
  100.90   0.1503   0.7070   0.6175   0.7308   0.9226   0.9091   0.9410   1.7050   0.8438   0.9269
  200.60   0.4045   0.8731   0.5876   0.7691   0.9495   0.9345   0.9445   1.3906   0.7094   0.8518
  303.90   0.7122   0.9269   0.4603   0.8340   0.9798   0.9637   1.3277   1.1216   0.5699   0.7756
  343.90   0.8303   0.9526   0.3233   0.8633   0.9912   0.9766   1.4788   1.0611   0.5160   0.7454
  388.50   0.9366   0.9784   0.0404   0.8897   0.9997   0.9924   1.7620   1.0243   0.4500   0.7109
  403.40   0.9861   0.9874  -0.2973   0.9037   1.0007   0.9980   4.5883   0.9967   0.4246   0.6989
```

Table 5.6 B. Test Results by Using One-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	$YCOMP_2$	Y_2	$\ln \gamma_2$	$\ln \gamma_1$	Z_2	Z_1
50.7C	50.45	0.25	0.034	0.356	0.360	0.7057	0.0009	0.897	0.910
1C0.9C	104.17	-3.27	0.150	0.693	0.707	0.5457	0.0171	0.909	0.923
200.60	195.17	5.43	0.404	0.843	0.873	0.2680	0.1237	0.934	0.950
303.90	291.93	11.97	0.712	0.915	0.927	0.0626	0.3834	0.964	0.980
343.90	334.09	9.81	0.830	0.944	0.953	0.0218	0.5210	0.977	0.991
388.50	381.47	7.03	0.937	0.976	0.978	0.0030	0.6630	0.992	1.000
403.4C	402.03	1.37	0.986	0.994	0.987	0.0001	0.7349	0.998	1.001

```
B=    C.7558C    C=
NO.OF OBSERVATIONS =           7
NO.OF CONSTANTS =          1
SYSTEM TEMPERATURE AT    220.00DEG
ST.DEV. OF CORRELATICN IS        7.43PSIA
AV.% DEV OF CORRELATION IS       2.23
```

Table 5.6 C. Test Results by Using Two-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
50.70	49.17	1.53	0.034	0.339	0.360	0.6324	0.0005	0.897	0.910
100.90	103.11	-2.21	0.150	0.692	0.707	0.5338	0.0107	0.909	0.923
200.60	201.53	-0.93	0.404	0.852	0.873	0.3102	0.0996	0.934	0.950
303.90	298.47	5.43	0.712	0.917	0.927	0.0860	0.3917	0.964	0.980
343.90	338.29	5.61	0.830	0.942	0.953	0.0317	0.5757	0.977	0.991
388.50	383.25	5.25	0.937	0.973	0.978	0.0047	0.7822	0.992	1.000
403.40	402.46	0.94	0.986	0.993	0.987	0.0002	0.8927	0.998	1.001

```
B=    0.79238    C=   -0.13307    D=
NO.OF OBSERVATIONS =            7
NO.OF CONSTANTS =            2
SYSTEM TEMPERATURE AT     220.00DEG
ST.DEV. OF CORRELATION IS        4.42PSIA
AV.% DEV OF CORRELATION IS        1.54
```

Table 5.6 D. Test Results by Using Three-Term Redlich-Kister Equation

PCBS	PCOMP	DP	X_2	$YCOMP_2$	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
50.70	50.39	0.31	0.034	0.355	0.360	0.7015	0.0013	0.897	0.910
100.90	101.63	-0.73	0.150	0.684	0.707	0.5086	0.0200	0.909	0.923
200.60	199.11	1.49	0.404	0.850	0.873	0.2963	0.0976	0.934	0.950
303.90	306.12	-2.22	0.712	0.923	0.927	0.1178	0.3428	0.964	0.980
343.90	344.44	-0.54	0.830	0.943	0.953	0.0510	0.5726	0.977	0.991
388.50	386.08	2.42	0.937	0.969	0.978	0.0086	0.9026	0.992	1.000
403.40	403.19	0.21	0.986	0.992	0.987	0.0005	1.1089	0.998	1.001

```
B=    0.76935    C=  -0.19828    D=    0.20627    E=
NO.OF OBSERVATIONS =           7
NO.OF CONSTANTS =            3
SYSTEM TEMPERATURE AT     220.00DEG
ST.DEV. OF CORRELATION IS       1.87PSIA
AV.% DEV OF CORRELATION IS       0.52
```

Table 5.6 E. Test Results by Using Four-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln \gamma_2$	$\ln \gamma_2$	Z_2	Z_1
50.70	50.67	0.03	0.034	0.358	0.360	0.7164	0.0016	0.897	0.910
100.90	100.99	-0.09	0.150	0.681	0.707	0.4983	0.0223	0.909	0.923
200.60	200.36	0.24	0.404	0.852	0.873	0.3046	0.0924	0.934	0.950
303.90	305.39	-1.49	0.712	0.921	0.927	0.1140	0.3574	0.964	0.980
343.90	343.00	0.90	0.830	0.941	0.953	0.0454	0.5919	0.977	0.991
388.50	385.27	3.23	0.937	0.970	0.978	0.0069	0.8874	0.992	1.000
403.40	402.97	0.43	0.986	0.992	0.987	0.0003	1.0523	0.998	1.001

```
B=    0.77568    C=  -0.22542    D=    0.18157    E=    0.08118    F=
NO.OF OBSERVATIONS =          7
NO.OF CONSTANTS =          4
SYSTEM TEMPERATURE AT    220.00DEG
ST.DEV. OF CORRELATION IS        2.14PSIA
AV.% DEV OF CORRELATION IS        0.28
```

Table 5.6 F. Test Results by Using Five-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
50.7C	50.70	-0.00	0.034	0.358	0.360	0.7175	0.0020	0.897	C.910
1C0.90	10C.90	0.00	0.150	0.681	0.707	0.4970	0.0220	0.909	0.923
200.6C	200.62	-0.02	0.404	0.852	0.873	0.3055	0.0961	0.934	0.950
303.9C	303.71	0.19	0.712	0.921	0.927	0.1085	0.3520	0.964	C.980
343.9C	344.78	-0.88	0.830	0.945	0.953	0.0540	0.5401	0.977	0.991
388.50	386.89	1.61	0.937	C.970	0.978	0.0115	0.8813	0.992	1.000
4C3.4C	403.46	-0.06	0.986	0.991	0.987	0.0007	1.1596	0.998	1.001

```
B=    C.77939    C=  -0.16371    D=    0.06804    E=  -0.04513    F=    0.20225

NO.OF OBSERVATIONS =          7
NO.OF CONSTANTS =          5
SYSTEM TEMPERATURE AT     220.00DEG
ST.DEV. OF CORRELATICN IS        1.30PSIA
AV.% DEV OF CORRELATION IS        0.11
```

Table 5.7 Nitrogen (2) - Methane (1) System at -240° F (26)

A. Tested Data and the Supporting Properties

K12(V)= 0.030   K12(L)= 0.030   DTR= 0.0198   DVR=-0.0700

TEMP= 220.00
PS1= 32.400   FREFER(1)= 33.816
PS2= 408.700   FREFER(2)= 283.821
PS0= 408.700

P	X2	Y2	PVOL1	PVOL2	POYNT1	POYNT2	GAMA1	GAMA2	PHI1	PHI2
44.00	0.0170	0.2460	0.6252	0.7176	0.9079	0.8951	1.0174	2.4420	0.9256	0.9743
50.00	0.0290	0.3380	0.6246	0.7185	0.9095	0.8966	1.0156	2.2189	0.9163	0.9689
56.00	0.0540	0.4020	0.6233	0.7207	0.9111	0.8979	1.0423	1.5767	0.9071	0.9638
61.00	0.0640	0.4750	0.6227	0.7216	0.9124	0.8992	0.9981	1.7015	0.9000	0.9591
71.00	0.0850	0.5330	0.6216	0.7237	0.9149	0.9017	1.0366	1.6549	0.8850	0.9513
82.00	0.1040	0.5820	0.6205	0.7256	0.9177	0.9045	1.0709	1.6853	0.8687	0.9427
84.00	0.1060	0.5920	0.6204	0.7258	0.9182	0.9050	1.0690	1.7190	0.8658	0.9412
85.00	0.1160	0.5890	0.6197	0.7269	0.9185	0.9051	1.0995	1.5801	0.8642	0.9405
93.00	0.1290	0.6480	0.6189	0.7283	0.9206	0.9072	1.0306	1.6941	0.8536	0.9337
122.00	0.1950	0.7180	0.6141	0.7363	0.9281	0.9145	1.1060	1.5780	0.8122	0.9117
125.00	0.2050	0.7380	0.6133	0.7376	0.9289	0.9152	1.0607	1.5750	0.8088	0.9091
142.00	0.2700	0.7780	0.6071	0.7468	0.9337	0.9191	1.0749	1.4055	0.7859	0.8961
154.00	0.2900	0.7850	0.6049	0.7498	0.9368	0.9223	1.1315	1.4131	0.7687	0.8873
183.00	0.3850	0.8270	0.5912	0.7656	0.9450	0.9294	1.1756	1.2898	0.7298	0.8655
199.00	0.4280	0.8340	0.5829	0.7734	0.9495	0.9336	1.2722	1.2496	0.7073	0.8539
214.00	0.4900	0.8700	0.5679	0.7853	0.9542	0.9373	1.1663	1.2029	0.6899	0.8422
232.00	0.5350	0.8700	0.5541	0.7945	0.9594	0.9423	1.3277	1.1698	0.6641	0.8292
242.00	0.5680	0.8750	0.5421	0.8015	0.9624	0.9450	1.3993	1.1424	0.6503	0.8219
247.00	0.5840	0.8860	0.5356	0.8049	0.9640	0.9464	1.3390	1.1412	0.6448	0.8180
269.00	0.6420	0.8910	0.5073	0.8177	0.9704	0.9528	1.5318	1.1072	0.6137	0.8020
307.00	0.7720	0.9240	0.4034	0.8485	0.9828	0.9641	1.7384	1.0386	0.5645	0.7734
310.00	0.7850	0.9550	0.3881	0.8518	0.9839	0.9650	1.1072	1.0610	0.5677	0.7705
328.00	0.8450	0.9340	0.2974	0.8672	0.9899	0.9708	2.2328	0.9970	0.5351	0.7577
330.00	0.8680	0.9370	0.2522	0.8725	0.9916	0.9713	2.5030	0.9771	0.5329	0.7562
361.00	0.9240	0.9680	0.0920	0.8864	0.9981	0.9822	2.2243	0.9934	0.4939	0.7323
364.00	0.9370	0.9790	0.0387	0.8898	0.9993	0.9833	1.7714	0.9945	0.4933	0.7298
365.00	0.9220	0.9580	0.0995	0.8859	0.9982	0.9837	2.8124	0.9908	0.4830	0.7295
367.00	0.9430	0.9810	0.0107	0.8914	0.9998	0.9844	1.7703	0.9941	0.4893	0.7275

Table 5.7 B. Test Results by Using One-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2^{COMP}	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
44.00	41.32	2.68	0.017	0.211	0.246	0.6753	0.0002	0.895	0.908
50.00	47.33	2.67	0.029	0.311	0.338	0.6589	0.0006	0.897	0.909
56.00	58.88	-2.88	0.054	0.454	0.402	0.6254	0.0020	0.898	0.911
61.00	63.59	-2.59	0.064	0.494	0.475	0.6122	0.0029	0.899	0.912
71.00	73.20	-2.20	0.085	0.561	0.533	0.5851	0.0050	0.902	0.915
82.00	81.88	0.12	0.104	0.606	0.582	0.5610	0.0076	0.904	0.918
84.00	82.88	1.12	0.106	0.610	0.592	0.5585	0.0079	0.905	0.918
85.00	86.78	-1.78	0.116	0.631	0.589	0.5461	0.0094	0.905	0.919
93.00	92.58	0.42	0.129	0.653	0.648	0.5301	0.0116	0.907	0.921
122.00	119.25	2.75	0.195	0.732	0.718	0.4528	0.0266	0.914	0.928
125.00	122.89	2.11	0.205	0.741	0.738	0.4417	0.0294	0.915	0.929
142.00	144.93	-2.93	0.270	0.787	0.778	0.3724	0.0509	0.919	0.934
154.00	152.71	1.29	0.290	0.797	0.785	0.3523	0.0588	0.922	0.937
183.00	182.70	0.30	0.385	0.837	0.827	0.2643	0.1036	0.929	0.945
199.00	196.46	2.54	0.428	0.850	0.834	0.2286	0.1280	0.934	0.950
214.00	213.84	0.16	0.490	0.868	0.870	0.1818	0.1678	0.937	0.954
232.00	228.44	3.56	0.535	0.879	0.870	0.1511	0.2000	0.942	0.959
242.00	238.27	3.73	0.568	0.887	0.875	0.1304	0.2255	0.945	0.962
247.00	243.11	3.89	0.584	0.890	0.886	0.1209	0.2383	0.946	0.964
269.00	262.30	6.70	0.642	0.903	0.891	0.0896	0.2880	0.953	0.970
307.00	303.60	3.40	0.772	0.933	0.924	0.0363	0.4165	0.964	0.983
310.00	307.59	2.41	0.785	0.936	0.955	0.0323	0.4306	0.965	0.984
328.00	328.47	-0.47	0.845	0.952	0.934	0.0168	0.4990	0.971	0.990
330.00	334.44	-4.44	0.868	0.958	0.937	0.0122	0.5265	0.971	0.992
361.00	362.65	-1.65	0.924	0.974	0.968	0.0040	0.5966	0.982	0.998
364.00	367.28	-3.28	0.937	0.978	0.979	0.0028	0.6135	0.983	0.999
365.00	364.31	0.69	0.922	0.973	0.958	0.0043	0.5940	0.984	0.998
367.00	370.31	-3.31	0.943	0.980	0.981	0.0023	0.6214	0.984	1.000

```
B=    0.69881    C=
NO.OF OBSERVATIONS =          28
NO.OF CONSTANTS =           1
SYSTEM TEMPERATURE AT     220.00DEG
ST.DEV. OF CORRELATION IS       2.83PSIA
AV.% DEV OF CORRELATION IS       1.77
```

Table 5.7 C. Test Results by Using Two-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
44.00	41.11	2.89	0.017	0.206	0.246	0.6506	0.0002	0.895	0.908
50.00	47.00	3.00	0.029	0.306	0.338	0.6366	0.0005	0.897	0.909
56.00	58.41	-2.41	0.054	0.449	0.402	0.6079	0.0017	0.898	0.911
61.00	63.09	-2.09	0.064	0.490	0.475	0.5965	0.0025	0.899	0.912
71.00	72.68	-1.68	0.085	0.558	0.533	0.5729	0.0044	0.902	0.915
82.00	81.39	0.61	0.104	0.604	0.582	0.5518	0.0066	0.904	0.918
84.00	82.40	1.60	0.106	0.609	0.592	0.5496	0.0068	0.905	0.918
85.00	86.33	-1.33	0.116	0.630	0.589	0.5387	0.0082	0.905	0.919
93.00	92.20	0.80	0.129	0.652	0.648	0.5245	0.0102	0.907	0.921
122.00	119.34	2.66	0.195	0.733	0.718	0.4550	0.0236	0.914	0.928
125.00	123.07	1.93	0.205	0.743	0.738	0.4448	0.0262	0.915	0.929
142.00	145.72	-3.72	0.270	0.789	0.778	0.3806	0.0462	0.919	0.934
154.00	153.70	0.30	0.290	0.799	0.785	0.3617	0.0535	0.922	0.937
183.00	184.48	-1.48	0.385	0.839	0.827	0.2772	0.0966	0.929	0.945
199.00	198.50	0.50	0.428	0.853	0.834	0.2421	0.1207	0.934	0.950
214.00	216.12	-2.12	0.490	0.870	0.870	0.1950	0.1606	0.937	0.954
232.00	230.81	1.19	0.535	0.881	0.870	0.1637	0.1935	0.942	0.959
242.00	240.64	1.36	0.568	0.888	0.875	0.1423	0.2199	0.945	0.962
247.00	245.47	1.53	0.584	0.892	0.886	0.1324	0.2333	0.946	0.964
269.00	264.55	4.45	0.642	0.904	0.891	0.0993	0.2858	0.953	0.970
307.00	305.22	1.78	0.772	0.933	0.924	0.0414	0.4259	0.964	0.983
310.00	309.13	0.87	0.785	0.936	0.955	0.0369	0.4416	0.965	0.984
328.00	329.60	-1.60	0.845	0.951	0.934	0.0194	0.5187	0.971	0.990
330.00	335.40	-5.40	0.868	0.958	0.937	0.0141	0.5501	0.971	0.992
361.00	363.22	-2.22	0.924	0.973	0.968	0.0047	0.6311	0.982	0.998
364.00	367.76	-3.76	0.937	0.977	0.979	0.0033	0.6508	0.983	0.999
365.00	364.91	0.09	0.922	0.972	0.958	0.0050	0.6281	0.984	0.998
367.00	370.75	-3.75	0.943	0.979	0.981	0.0027	0.6601	0.984	1.000

```
B=    0.71100    C=  -0.04049    D=
NO.OF OBSERVATIONS =          28
NO.OF CONSTANTS =          2
SYSTEM TEMPERATURE AT    220.00DEG
ST.DEV. OF CORRELATION IS       2.49PSIA
AV.% DEV OF CORRELATION IS       1.64
```

Table 5.7 D. Test Results by Using Three-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2^{COMP}	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
44.00	41.20	2.80	0.017	0.208	0.246	0.6610	0.0002	0.895	0.908
50.00	47.13	2.87	0.029	0.308	0.338	0.6452	0.0006	0.897	0.909
56.00	58.55	-2.55	0.054	0.451	0.402	0.6130	0.0020	0.898	0.911
61.00	63.22	-2.22	0.064	0.491	0.475	0.6005	0.0027	0.899	0.912
71.00	72.77	-1.77	0.085	0.559	0.533	0.5747	0.0048	0.902	0.915
82.00	81.42	0.58	0.104	0.604	0.582	0.5519	0.0072	0.904	0.918
84.00	82.42	1.58	0.106	0.608	0.592	0.5496	0.0075	0.905	0.918
85.00	86.32	-1.32	0.116	0.629	0.589	0.5379	0.0089	0.905	0.919
93.00	92.13	0.87	0.129	0.651	0.648	0.5229	0.0110	0.907	0.921
122.00	119.02	2.98	0.195	0.732	0.718	0.4508	0.0250	0.914	0.928
125.00	122.72	2.28	0.205	0.741	0.738	0.4404	0.0276	0.915	0.929
142.00	145.26	-3.26	0.270	0.788	0.778	0.3762	0.0476	0.919	0.934
154.00	153.23	0.77	0.290	0.799	0.785	0.3575	0.0548	0.922	0.937
183.00	184.19	-1.19	0.385	0.839	0.827	0.2753	0.0967	0.929	0.945
199.00	198.37	0.63	0.428	0.853	0.834	0.2415	0.1199	0.934	0.950
214.00	216.28	-2.28	0.490	0.871	0.870	0.1962	0.1583	0.937	0.954
232.00	231.18	0.82	0.535	0.881	0.870	0.1660	0.1901	0.942	0.959
242.00	241.16	0.84	0.568	0.889	0.875	0.1452	0.2156	0.945	0.962
247.00	246.05	0.95	0.584	0.893	0.886	0.1356	0.2287	0.946	0.964
269.00	265.32	3.68	0.642	0.905	0.891	0.1030	0.2803	0.953	0.970
307.00	306.05	0.95	0.772	0.933	0.924	0.0445	0.4222	0.964	0.983
310.00	309.94	0.06	0.785	0.936	0.955	0.0399	0.4386	0.965	0.984
328.00	330.25	-2.25	0.845	0.951	0.934	0.0214	0.5201	0.971	0.990
330.00	335.96	-5.96	0.868	0.957	0.937	0.0157	0.5540	0.971	0.992
361.00	363.57	-2.57	0.924	0.973	0.968	0.0054	0.6433	0.982	0.998
364.00	368.05	-4.05	0.937	0.977	0.979	0.0037	0.6654	0.983	0.999
365.00	365.27	-0.27	0.922	0.972	0.958	0.0057	0.6399	0.984	0.998
367.00	371.01	-4.01	0.943	0.979	0.981	0.0031	0.6759	0.984	1.000

```
B=    0.70879   C=  -0.04853   D=   0.02365   E=
NO.OF OBSERVATIONS =        28
NO.OF CONSTANTS =        3
SYSTEM TEMPERATURE AT    220.00DEG
ST.DEV. OF CORRELATION IS      2.57PSIA
AV.% DEV OF CORRELATION IS      1.63
```

Table 5.7 E. Test Results by Using Four-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	$YCOMP_2$	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
44.00	41.35	2.65	0.017	0.211	0.246	0.6777	0.0003	0.895	0.908
50.00	47.32	2.68	0.029	0.311	0.338	0.6576	0.0007	0.897	0.909
56.00	58.71	-2.71	0.054	0.452	0.402	0.6185	0.0024	0.898	0.911
61.00	63.34	-2.34	0.064	0.492	0.475	0.6037	0.0033	0.899	0.912
71.00	72.78	-1.78	0.085	0.558	0.533	0.5743	0.0057	0.902	0.915
82.00	81.33	0.67	0.104	0.603	0.582	0.5493	0.0083	0.904	0.918
84.00	82.32	1.68	0.106	0.607	0.592	0.5468	0.0086	0.905	0.918
85.00	86.16	-1.16	0.116	0.628	0.589	0.5343	0.0102	0.905	0.919
93.00	91.91	1.09	0.129	0.650	0.648	0.5186	0.0124	0.907	0.921
122.00	118.68	3.32	0.195	0.731	0.718	0.4464	0.0263	0.914	0.928
125.00	122.39	2.61	0.205	0.740	0.738	0.4363	0.0288	0.915	0.929
142.00	145.17	-3.17	0.270	0.788	0.778	0.3753	0.0478	0.919	0.934
154.00	153.25	0.75	0.290	0.799	0.785	0.3578	0.0546	0.922	0.937
183.00	184.75	-1.75	0.385	0.840	0.827	0.2793	0.0946	0.929	0.945
199.00	199.07	-0.07	0.428	0.854	0.834	0.2460	0.1175	0.934	0.950
214.00	216.94	-2.94	0.490	0.871	0.870	0.2000	0.1565	0.937	0.954
232.00	231.66	0.34	0.535	0.882	0.870	0.1684	0.1898	0.942	0.959
242.00	241.43	0.57	0.568	0.889	0.875	0.1463	0.2169	0.945	0.962
247.00	246.20	0.80	0.584	0.893	0.886	0.1360	0.2310	0.946	0.964
269.00	264.97	4.03	0.642	0.904	0.891	0.1009	0.2866	0.953	0.970
307.00	304.81	2.19	0.772	0.932	0.924	0.0392	0.4356	0.964	0.983
310.00	308.67	1.33	0.785	0.935	0.955	0.0346	0.4519	0.965	0.984
328.00	329.02	-1.02	0.845	0.950	0.934	0.0170	0.5292	0.971	0.990
330.00	334.84	-4.84	0.868	0.957	0.937	0.0120	0.5592	0.971	0.992
361.00	362.83	-1.83	0.924	0.973	0.968	0.0036	0.6308	0.982	0.998
364.00	367.43	-3.43	0.937	0.978	0.979	0.0024	0.6469	0.983	0.999
365.00	364.51	0.49	0.922	0.972	0.958	0.0038	0.6283	0.984	0.998
367.00	370.45	-3.45	0.943	0.980	0.981	0.0020	0.6542	0.984	1.000

```
B=    0.71280    C=  -0.05865   D=    0.00043    E=    0.05310    F=
NO.OF OBSERVATIONS =        28
NO.OF CONSTANTS =        4
SYSTEM TEMPERATURE AT     220.00DEG
ST.DEV. OF CORRELATION IS       2.52PSIA
AV.% DEV OF CORRELATION IS       1.64
```

Table 5.7 F. Test Results by Using Five-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
44.00	41.44	2.56	0.017	0.213	0.246	0.6886	0.0003	0.895	0.908
50.00	47.43	2.57	0.029	0.312	0.338	0.6650	0.0009	0.897	0.909
56.00	58.78	-2.78	0.054	0.452	0.402	0.6205	0.0028	0.898	0.911
61.00	63.37	-2.37	0.064	0.492	0.475	0.6043	0.0038	0.899	0.912
71.00	72.74	-1.74	0.085	0.558	0.533	0.5728	0.0063	0.902	0.915
82.00	81.23	0.77	0.104	0.603	0.582	0.5469	0.0090	0.904	0.918
84.00	82.22	1.78	0.106	0.607	0.592	0.5443	0.0093	0.905	0.918
85.00	86.04	-1.04	0.116	0.627	0.589	0.5317	0.0109	0.905	0.919
93.00	91.78	1.22	0.129	0.649	0.648	0.5160	0.0131	0.907	0.921
122.00	118.64	3.36	0.195	0.731	0.718	0.4458	0.0266	0.914	0.928
125.00	122.38	2.62	0.205	0.740	0.738	0.4362	0.0290	0.915	0.929
142.00	145.39	-3.39	0.270	0.789	0.778	0.3774	0.0473	0.919	0.934
154.00	153.53	0.47	0.290	0.799	0.785	0.3602	0.0540	0.922	0.937
183.00	185.03	-2.03	0.385	0.840	0.827	0.2812	0.0944	0.929	0.945
199.00	199.21	-0.21	0.428	0.854	0.834	0.2467	0.1180	0.934	0.950
214.00	216.81	-2.81	0.490	0.871	0.870	0.1990	0.1585	0.937	0.954
232.00	231.36	0.64	0.535	0.881	0.870	0.1665	0.1927	0.942	0.959
242.00	241.03	0.97	0.568	0.889	0.875	0.1441	0.2203	0.945	0.962
247.00	245.78	1.22	0.584	0.892	0.886	0.1337	0.2344	0.946	0.964
269.00	264.59	4.41	0.642	0.904	0.891	0.0991	0.2893	0.953	0.970
307.00	305.05	1.95	0.772	0.933	0.924	0.0404	0.4307	0.964	0.983
310.00	308.97	1.03	0.785	0.936	0.955	0.0360	0.4461	0.965	0.984
328.00	329.54	-1.54	0.845	0.951	0.934	0.0191	0.5206	0.971	0.990
330.00	335.38	-5.38	0.868	0.958	0.937	0.0140	0.5509	0.971	0.992
361.00	363.26	-2.26	0.924	0.973	0.968	0.0049	0.6300	0.982	0.998
364.00	367.80	-3.80	0.937	0.978	0.979	0.0034	0.6498	0.983	0.999
365.00	364.95	0.05	0.922	0.972	0.958	0.0051	0.6271	0.984	0.998
367.00	370.79	-3.79	0.943	0.979	0.981	0.0028	0.6592	0.984	1.000

```
B=    0.71479   C=  -0.05173   D=  -0.02068   E=    0.03601   F=    0.04678

NO.OF OBSERVATIONS =        28
NO.OF CONSTANTS =         5
SYSTEM TEMPERATURE AT    220.00DEG
ST.DEV. OF CORRELATION IS       2.72PSIA
AV.% DEV OF CORRELATION IS       1.67
```

Table 5.8 Argon (2) - Methane (1) System at 123.53°K

A. Tested Data and Supporting Properties

```
K12(V)= C.0      K12(L)= C.0      DTR= 0.0      DVR= 0.0

TEMP=   222.35
PS1=   35.500        FREFER(1)=    34.887
PS2=  212.860        FREFER(2)=   174.587
PSO=  212.860

   P       X2       Y2     PVOL1    PVOL2   POYNT1   POYNT2   GAMA1    GAMA2    PHI1     PHI2

  40.0C  0.018C  C.1000  0.5963  0.5035  0.9577  0.9642  1.0233  1.2850  0.9327  0.9734
  50.0C  0.0650  0.2930  0.5972  0.5055  0.9601  0.9661  1.0348  1.2872  0.9167  0.9633
  60.00  0.1150  0.4200  C.5982  0.5078  0.9624  0.9680  1.0557  1.2367  0.9C14  0.9538
  70.00  0.16CC  C.5150  0.5990  0.5099  0.9648  0.9699  1.0645  1.2567  0.8865  0.9445
  80.00  0.214C  0.5850  C.6000  0.5124  0.9671  0.9719  1.0914  1.2057  0.8718  0.9355
  90.C0  0.2670  0.655C  C.6C09  0.5150  0.9695  0.9738  1.0741  1.2C29  0.8577  0.9263
 1CC.00  0.325C  0.7150  C.6C18  0.5180  0.9719  0.9758  1.0508  1.1846  0.8439  0.9173
 110.0C  0.3820  0.7550  C.6C25  0.5209  0.9744  0.9778  1.0647  1.1571  C.8299  0.9085
 120.C0  0.4390  C.7900  0.6C32  0.5239  0.9768  0.9798  1.0758  1.1359  0.8161  0.8998
 130.0C  0.498C  0.8210  0.6037  0.5272  0.9793  0.9819  1.0888  1.1142  0.8025  0.8912
 140.00  0.5560  0.8540  0.6C39  0.5305  0.9817  0.9839  1.0609  1.1046  0.7893  0.8825
 15C.00  0.616C  0.8760  0.6C39  0.5340  0.9842  0.9860  1.0943  1.0828  0.7757  0.8739
 160.0C  0.6780  0.8970  C.6C35  0.5377  0.9867  0.9882  1.1334  1.0617  0.7623  0.8653
 170.0C  0.7360  0.9210  0.6C28  0.5413  0.9892  0.9903  1.1046  1.C541  0.7494  0.8567
 180.0C  0.795C  0.9350  C.6C14  0.5450  0.9918  0.9925  1.2139  1.C363  0.7359  0.8482
 190.00  0.8560  0.955C  C.5992  0.5489  0.9943  0.9948  1.2377  1.0249  0.7231  0.8397
 2CC.00  0.9190  0.9750  C.5957  0.5530  0.9968  0.997C  1.2611  1.0132  0.7105  0.8311
 209.99  0.9670  0.9950  0.5920  0.5562  0.9993  0.9993  0.6371  1.0188  0.6981  0.8226
```

Table 5. 8 B. Test Result by Using One-Term Redlich-Kister Equation

PCBS	PCOMP	DP	X_2	Y_2^{COMP}	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
40.00	39.73	0.27	0.018	0.114	0.100	0.3782	0.0001	0.964	0.958
50.00	50.25	-0.25	0.065	0.319	0.293	0.3429	0.0017	0.966	0.960
60.00	60.84	-0.84	0.115	0.456	0.420	0.3072	0.0052	0.968	0.962
70.00	70.05	-0.05	0.160	0.540	0.515	0.2767	0.0100	0.970	0.965
80.00	80.43	-0.43	0.214	0.615	0.585	0.2423	0.0180	0.972	0.967
90.00	90.23	-0.23	0.267	0.671	0.655	0.2107	0.0280	0.974	0.970
100.00	100.44	-0.44	0.325	0.719	0.715	0.1787	0.0414	0.976	0.972
110.00	110.18	-0.18	0.382	0.757	0.755	0.1498	0.0572	0.978	0.974
120.00	119.69	0.31	0.439	0.789	0.790	0.1234	0.0756	0.980	0.977
130.00	129.30	0.70	0.498	0.818	0.821	0.0988	0.0973	0.982	0.979
140.00	138.69	1.31	0.556	0.843	0.854	0.0773	0.1212	0.984	0.982
150.00	148.30	1.70	0.616	0.867	0.876	0.0578	0.1488	0.986	0.984
160.00	158.20	1.80	0.678	0.890	0.897	0.0407	0.1803	0.988	0.987
170.00	167.69	2.31	0.736	0.910	0.921	0.0273	0.2125	0.990	0.989
180.00	177.46	2.54	0.795	0.930	0.935	0.0165	0.2479	0.993	0.992
190.00	187.70	2.30	0.856	0.951	0.955	0.0081	0.2874	0.995	0.994
200.00	198.48	1.52	0.919	0.972	0.975	0.0026	0.3312	0.997	0.997
209.99	207.55	2.44	0.967	0.989	0.995	0.0004	0.3667	0.999	0.999

```
B=    0.39220    C=
NO.OF OBSERVATIONS =        18
NO.OF CONSTANTS =         1
SYSTEM TEMPERATURE AT     222.35DEG
ST.DEV. OF CORRELATION IS       1.44PSIA
AV.% DEV OF CORRELATION IS       0.78
```

Table 5. 8 C. Test Results by Using Two-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
40.00	39.54	0.46	0.018	0.110	0.100	0.3364	0.0001	0.964	0.958
50.00	49.76	0.24	0.065	0.313	0.293	0.3128	0.0011	0.966	0.960
60.00	60.25	-0.25	0.115	0.451	0.420	0.2877	0.0036	0.968	0.962
70.00	69.52	0.48	0.160	0.538	0.515	0.2652	0.0072	0.970	0.965
80.00	80.10	-0.10	0.214	0.615	0.585	0.2385	0.0133	0.972	0.967
90.00	90.16	-0.17	0.267	0.673	0.655	0.2128	0.0215	0.974	0.970
100.00	100.69	-0.70	0.325	0.722	0.715	0.1855	0.0330	0.976	0.972
110.00	110.73	-0.73	0.382	0.760	0.755	0.1596	0.0471	0.978	0.974
120.00	120.50	-0.50	0.439	0.793	0.790	0.1350	0.0643	0.980	0.977
130.00	130.31	-0.31	0.498	0.821	0.821	0.1109	0.0856	0.982	0.979
140.00	139.81	0.19	0.556	0.846	0.854	0.0889	0.1101	0.984	0.982
150.00	149.45	0.55	0.616	0.869	0.876	0.0682	0.1394	0.986	0.984
160.00	159.30	0.70	0.678	0.891	0.897	0.0492	0.1743	0.988	0.987
170.00	168.66	1.34	0.736	0.911	0.921	0.0338	0.2114	0.990	0.989
180.00	178.26	1.74	0.795	0.930	0.935	0.0209	0.2537	0.993	0.992
190.00	188.27	1.73	0.856	0.950	0.955	0.0105	0.3026	0.995	0.994
200.00	198.80	1.20	0.919	0.971	0.975	0.0034	0.3589	0.997	0.997
209.95	207.68	2.31	0.967	0.988	0.995	0.0006	0.4059	0.999	0.999

```
B=    0.39292    C=  -0.04745    D=
NO.OF OBSERVATIONS =          18
NO.OF CONSTANTS =          2
SYSTEM TEMPERATURE AT     222.35DEG
ST.DEV. OF CORRELATICN IS       1.04PSIA
AV.% DEV OF CORRELATION IS      0.58
```

Table 5.8 D. Test Results by Using Three-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
40.00	39.75	0.25	0.018	0.115	0.100	0.3824	0.0002	0.964	0.958
50.00	50.16	-0.16	0.065	0.318	0.293	0.3362	0.0022	0.966	0.960
60.00	60.52	-0.52	0.115	0.452	0.420	0.2943	0.0063	0.968	0.962
70.00	69.54	0.46	0.160	0.536	0.515	0.2619	0.0114	0.970	0.965
80.00	79.80	0.20	0.214	0.612	0.585	0.2287	0.0190	0.972	0.967
90.00	89.63	0.37	0.267	0.669	0.655	0.2009	0.0278	0.974	0.970
100.00	100.07	-0.07	0.325	0.718	0.715	0.1745	0.0389	0.976	0.972
110.00	110.19	-0.19	0.382	0.758	0.755	0.1518	0.0513	0.978	0.974
120.00	120.18	-0.18	0.439	0.792	0.790	0.1313	0.0656	0.980	0.977
130.00	130.33	-0.33	0.498	0.822	0.821	0.1117	0.0829	0.982	0.979
140.00	140.20	-0.20	0.556	0.848	0.854	0.0935	0.1032	0.984	0.982
150.00	150.20	-0.20	0.616	0.871	0.876	0.0755	0.1287	0.986	0.984
160.00	160.30	-0.30	0.678	0.893	0.897	0.0578	0.1613	0.988	0.987
170.00	169.77	0.23	0.736	0.913	0.921	0.0422	0.1990	0.990	0.989
180.00	179.31	0.69	0.795	0.931	0.935	0.0277	0.2464	0.993	0.992
190.00	189.11	0.89	0.856	0.950	0.955	0.0150	0.3070	0.995	0.994
200.00	199.30	0.70	0.919	0.971	0.975	0.0052	0.3847	0.997	0.997
209.99	207.88	2.11	0.967	0.987	0.995	0.0009	0.4561	0.999	0.999

```
B=    0.38917    C=  -0.05496    D=    0.06789    E=
NO.OF OBSERVATIONS =         18
NO.OF CONSTANTS =          3
SYSTEM TEMPERATURE AT    222.35DEG
ST.DEV. OF CORRELATION IS      0.70PSIA
AV.% DEV OF CORRELATION IS      0.37
```

Table 5.8 E. Test Results by Using Four-Term Redlich-Kister Equation

POBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
40.00	39.64	0.37	0.018	0.112	0.100	0.3579	0.0001	0.964	0.958
50.00	50.02	-0.02	0.065	0.316	0.293	0.3287	0.0014	0.966	0.960
60.00	60.52	-0.52	0.115	0.453	0.420	0.2963	0.0046	0.968	0.962
70.00	69.67	0.33	0.160	0.538	0.515	0.2674	0.0092	0.970	0.965
80.00	80.00	0.00	0.214	0.614	0.585	0.2342	0.0168	0.972	0.967
90.00	89.79	0.21	0.267	0.670	0.655	0.2042	0.0263	0.974	0.970
100.00	100.09	-0.09	0.325	0.718	0.715	0.1749	0.0386	0.976	0.972
110.00	110.04	-0.04	0.382	0.758	0.755	0.1497	0.0524	0.978	0.974
120.00	119.91	0.09	0.439	0.791	0.790	0.1279	0.0676	0.980	0.977
130.00	130.02	-0.02	0.498	0.821	0.821	0.1083	0.0848	0.982	0.979
140.00	139.96	0.04	0.556	0.847	0.854	0.0913	0.1038	0.984	0.982
150.00	150.13	-0.13	0.616	0.871	0.876	0.0753	0.1265	0.986	0.984
160.00	160.47	-0.47	0.678	0.894	0.897	0.0597	0.1552	0.988	0.987
170.00	170.14	-0.14	0.736	0.914	0.921	0.0455	0.1895	0.990	0.989
180.00	179.81	0.19	0.795	0.932	0.935	0.0315	0.2354	0.993	0.992
190.00	189.60	0.40	0.856	0.951	0.955	0.0181	0.2995	0.995	0.994
200.00	199.62	0.38	0.919	0.971	0.975	0.0067	0.3904	0.997	0.997
209.99	208.02	1.97	0.967	0.987	0.995	0.0013	0.4820	0.999	0.999

```
B=    0.38628    C=  -0.04446    D=    0.07740    E=  -0.05084    F=
NO.OF OBSERVATIONS =          18
NO.OF CONSTANTS =          4
SYSTEM TEMPERATURE AT     222.35DEG
ST.DEV. OF CORRELATICN IS        0.60PSIA
AV.% DEV OF CORRELATION IS        0.26
```

Table 5.8 F. Test Results by Using Five-Term Redlich-Kister Equation

PCBS	PCOMP	DP	X_2	Y_2COMP	Y_2	$\ln\gamma_2$	$\ln\gamma_1$	Z_2	Z_1
40.00	39.75	0.25	0.018	0.115	0.100	0.3833	0.0002	0.964	0.958
50.00	50.10	-0.09	0.065	0.317	0.293	0.3313	0.0024	0.966	0.960
60.00	60.43	-0.43	0.115	0.451	0.420	0.2907	0.0064	0.968	0.962
70.00	69.52	0.48	0.160	0.536	0.515	0.2617	0.0110	0.970	0.965
80.00	79.92	0.08	0.214	0.613	0.585	0.2320	0.0178	0.972	0.967
90.00	89.86	0.14	0.267	0.670	0.655	0.2055	0.0262	0.974	0.970
100.00	100.29	-0.29	0.325	0.719	0.715	0.1780	0.0378	0.976	0.972
110.00	110.25	-0.25	0.382	0.758	0.755	0.1524	0.0518	0.978	0.974
120.00	120.00	0.00	0.439	0.791	0.790	0.1287	0.0683	0.980	0.977
130.00	129.91	0.09	0.498	0.820	0.821	0.1067	0.0876	0.982	0.979
140.00	139.68	0.32	0.556	0.846	0.854	0.0882	0.1083	0.984	0.982
150.00	149.80	0.21	0.616	0.871	0.876	0.0721	0.1311	0.986	0.984
160.00	160.26	-0.26	0.678	0.894	0.897	0.0580	0.1569	0.988	0.987
170.00	170.19	-0.19	0.736	0.914	0.921	0.0462	0.1856	0.990	0.989
180.00	180.14	-0.14	0.795	0.933	0.935	0.0343	0.2246	0.993	0.992
190.00	190.10	-0.10	0.856	0.952	0.955	0.0216	0.2854	0.995	0.994
200.00	200.04	-0.04	0.919	0.971	0.975	0.0090	0.3874	0.997	0.997
209.99	208.21	1.78	0.967	0.987	0.995	0.0018	0.5083	0.999	0.999

B= 0.38874 C= -0.03543 D= 0.04439 E= -0.07162 F= 0.08225

NO.OF OBSERVATIONS = 18
NO.OF CONSTANTS = 5
SYSTEM TEMPERATURE AT 222.35DEG
ST.DEV. OF CORRELATION IS 0.56PSIA
AV.% DEV OF CORRELATION IS 0.26

APPENDIX IV

TABLES 6.1 TO 6.6 FOR CHAPTER 6

Table 6.1 A Tested Data of Methane-Propane System at 160° F.

```
 TESTED DATA OF  METHANE-PROPANE SYSTEM AT 160 DEG F (SAGE)
                      (1)        (2)

       1 2      0.02       0.02      0.1775   -0.3653

 620.0000 1020.0000 1020.0000    0.0        0.0        0.0        0.0

 IC    P psia   x2        x1         y2        y1

  1    400.0   0.9937   0.0063   0.9724   0.0276
  2    450.0   0.9751   0.0249   0.9019   0.0981
  3    500.0   0.9567   0.0433   0.8450   0.1550
  4    550.0   0.9378   0.0622   0.7993   0.2007
  5    600.0   0.9187   0.0813   0.7608   0.2392
  6    650.0   0.8998   0.1002   0.7288   0.2712
  7    700.0   0.8801   0.1199   0.7017   0.2983
  8    750.0   0.8598   0.1402   0.6785   0.3215
  9    800.0   0.8382   0.1618   0.6586   0.3414
 10    850.0   0.8180   0.1820   0.6434   0.3566
 11    900.0   0.7919   0.2081   0.6344   0.3656
 12    950.0   0.7625   0.2375   0.6322   0.3678
 13   1000.0   0.7200   0.2800   0.6442   0.3558
 14   1020.0   0.6712   0.3288   0.6712   0.3288
```

Table 6.1 B Supporting Data for Testing Methane-Propane System at 160° F.

SUPPORTING DATA FOR TESTING METHANE-PROPANE SYSTEM AT 160 DEG F (SAGE)
(1) (2)

ID	P, psia	TRMIX	VL	ϕ_2	ϕ_1	$\bar{V}_2$	$\bar{V}_1$
1	400.0	0.9327	1.7757	0.7204	1.2403	1.7701	2.6691
2	450.0	0.9378	1.7809	0.6868	1.2296	1.7564	2.7406
3	500.0	0.9428	1.7874	0.6558	1.2224	1.7407	2.8203
4	550.0	0.9481	1.7956	0.6266	1.2196	1.7215	2.9126
5	600.0	0.9534	1.8058	0.5991	1.2179	1.6984	3.0200
6	650.0	0.9587	1.8181	0.5728	1.2186	1.6706	3.1430
7	700.0	0.9642	1.8341	0.5478	1.2206	1.6348	3.2966
8	750.0	0.9698	1.8544	0.5239	1.2234	1.5880	3.4886
9	800.0	0.9757	1.8823	0.5012	1.2265	1.5215	3.7513
10	850.0	0.9810	1.9155	0.4787	1.2346	1.4361	4.0704
11	900.0	0.9872	1.9697	0.4553	1.2523	1.2751	4.6129
12	950.0	0.9926	2.0451	0.4303	1.2837	0.9995	5.4020
13	1000.0	0.9972	2.2156	0.4002	1.3544	0.2181	7.3519
14	1020.0	0.9996	2.4473	0.3788	1.4569	-0.9157	9.3124

Table 6.1 C Test. Results of Methane-Propane System at 160° F with (E(x) = 0.0005

```
TESTED RESULTS OF  METHANE-PROPANE SYSTEM AT 160 DEG F (SAGE)

   EX=  0.0005  EP=  1.0000  ET=  0.2000

PAIR NO    P (Av.)  I         II         III      D         |DMAX|   DX       DP       DT

  1- 2     425.0 -0.1143 -0.1412   0.0289 -0.0020   0.0187  0.0079  0.0105  0.0002
  2- 3     475.0 -0.0956 -0.1211   0.0289 -0.0034   0.0167  0.0070  0.0095  0.0002
  3- 4     525.0 -0.0785 -0.1041   0.0289 -0.0033   0.0159  0.0070  0.0087  0.0002
  4- 5     575.0 -0.0667 -0.0905   0.0289 -0.0051   0.0153  0.0071  0.0081  0.0002
  5- 6     625.0 -0.0555 -0.0787   0.0289 -0.0057   0.0148  0.0072  0.0075  0.0001
  6- 7     675.0 -0.0466 -0.0690   0.0290 -0.0066   0.0145  0.0073  0.0070  0.0001
  7- 8     725.0 -0.0391 -0.0611   0.0291 -0.0071   0.0141  0.0074  0.0066  0.0001
  8- 9     775.0 -0.0325 -0.0546   0.0293 -0.0072   0.0139  0.0075  0.0063  0.0001
  9-10     825.0 -0.0237 -0.0474   0.0294 -0.0058   0.0136  0.0076  0.0060  0.0001
 10-11     875.0 -0.0130 -0.0391   0.0302 -0.0041   0.0135  0.0077  0.0057  0.0001
 11-12     925.0 -0.0028 -0.0316   0.0312 -0.0024   0.0133  0.0078  0.0055  0.0000
 12-13     975.0  0.0105 -0.0228   0.0326  0.0007   0.0133  0.0079  0.0054  0.0000
 13-14    1010.0  0.0089 -0.0074   0.0144  0.0020   0.0128  0.0082  0.0047  0.0000
```

Table 6.1 D Test Results of Methane-Propane System at 160° F with E(x) = 0.0010.

```
TESTED RESULTS OF  METHANE-PROPANE SYSTEM AT 160 DEG F (SAGE)


EX=   0.0010  EP=   1.0000  ET=   0.2000

PAIR NO    P (Av.)   I          II        III        D        |DMAX|    DX       DP       DT

 1- 2      425.0 -0.1143 -0.1412   0.0289 -0.0020   0.0266  0.0159  0.0105  0.0002
 2- 3      475.0 -0.0956 -0.1211   0.0289 -0.0034   0.0236  0.0139  0.0095  0.0002
 3- 4      525.0 -0.0785 -0.1041   0.0289 -0.0033   0.0229  0.0140  0.0087  0.0002
 4- 5      575.0 -0.0667 -0.0905   0.0289 -0.0051   0.0224  0.0142  0.0081  0.0002
 5- 6      625.0 -0.0555 -0.0787   0.0289 -0.0057   0.0220  0.0144  0.0075  0.0001
 6- 7      675.0 -0.0466 -0.0690   0.0290 -0.0066   0.0218  0.0146  0.0070  0.0001
 7- 8      725.0 -0.0391 -0.0611   0.0291 -0.0071   0.0215  0.0148  0.0066  0.0001
 8- 9      775.0 -0.0325 -0.0546   0.0293 -0.0072   0.0214  0.0150  0.0063  0.0001
 9-10      825.0 -0.0237 -0.0474   0.0294 -0.0058   0.0212  0.0151  0.0060  0.0001
10-11      875.0 -0.0130 -0.0391   0.0302 -0.0041   0.0212  0.0154  0.0057  0.0001
11-12      925.0 -0.0028 -0.0316   0.0312 -0.0024   0.0211  0.0155  0.0055  0.0000
12-13      975.0  0.0105 -0.0228   0.0326  0.0007   0.0213  0.0159  0.0054  0.0000
13-14     1010.0  0.0089 -0.0074   0.0144  0.0020   0.0210  0.0163  0.0047  0.0000
```

Table 6.1 E Test Results of Methane-Propane System at 160° F with E(x) = 0.0020.

```
TESTED RESULTS OF  METHANE-PROPANE SYSTEM AT 160 DEG F (SAGE)


   EX=  0.0020  EP=  1.0000  ET=  0.2000

PAIR NO   P (Av.)  I       II        III      D        |DMAX|   DX       DP       DT

  1- 2     425.0 -0.1143 -0.1412  0.0289 -0.0020  0.0425  0.0318  0.0105  0.0002
  2- 3     475.0 -0.0956 -0.1211  0.0289 -0.0034  0.0375  0.0278  0.0095  0.0002
  3- 4     525.0 -0.0785 -0.1041  0.0289 -0.0033  0.0369  0.0280  0.0087  0.0002
  4- 5     575.0 -0.0667 -0.0905  0.0289 -0.0051  0.0366  0.0284  0.0081  0.0002
  5- 6     625.0 -0.0555 -0.0787  0.0289 -0.0057  0.0364  0.0288  0.0075  0.0001
  6- 7     675.0 -0.0466 -0.0690  0.0290 -0.0066  0.0364  0.0292  0.0070  0.0001
  7- 8     725.0 -0.0391 -0.0611  0.0291 -0.0071  0.0363  0.0296  0.0066  0.0001
  8- 9     775.0 -0.0325 -0.0546  0.0293 -0.0072  0.0364  0.0300  0.0063  0.0001
  9-10     825.0 -0.0237 -0.0474  0.0294 -0.0058  0.0363  0.0303  0.0060  0.0001
 10-11     875.0 -0.0130 -0.0391  0.0302 -0.0041  0.0365  0.0307  0.0057  0.0001
 11-12     925.0 -0.0028 -0.0316  0.0312 -0.0024  0.0367  0.0311  0.0055  0.0000
 12-13     975.0  0.0105 -0.0228  0.0326  0.0007  0.0372  0.0318  0.0054  0.0000
 13-14    1010.0  0.0089 -0.0074  0.0144  0.0020  0.0373  0.0326  0.0047  0.0000
```

Table 6.2 A Test Data of Nitrogen-Methane System at -240° F (this work)

```
  TESTED DATA OF  NITRCCEN-METHANE SYSTEM AT -240 CEG F(CHANG'S DATA )
                    (1)        (2)

     1 2      0.03      C.03     0.0       0.0

22C.COCC  408.7CCC  4C8.7CCC   C.0       0.0       0.0       0.0

IC   P, psia  X2       X1       Y2       Y1

 1     5C.7  0.9663  0.0337  0.6401  0.3599
 2    10C.9  0.8497  0.15C3  C.293C  0.7070
 3    2CC.6  0.5955  C.4C45  0.1269  0.8731
 4    3C3.9  0.2878  C.7122  0.C731  0.9269
 5    343.9  0.1697  0.83C3  0.C474  0.9526
 6    388.5  0.0634  0.9366  0.0216  0.9784
 7    4C3.4  0.0139  0.9861  0.C126  0.9874
```

Table 6.2 B Supporting Data for Testing Nitrogen-Methane System at -240° F.

SUPPORTING DATA FOR TESTING NITROGEN$_{(1)}$-METHANE$_{(2)}$ SYSTEM AT -240 DEG F(CHANG'S DATA)

ID	P,psia	TRMIX	VL	ϕ_2	ϕ_1	$\bar{V}_2$	$\bar{V}_1$
1	50.7	0.6514	0.6275	0.9153	0.9680	0.6243	0.7189
2	100.9	0.6817	0.6345	0.8438	0.9269	0.6175	0.7308
3	200.6	0.7550	0.6610	0.7094	0.8518	0.5876	0.7691
4	303.9	0.8581	0.7265	0.5699	0.7756	0.4603	0.8340
5	343.9	0.9019	0.7717	0.5160	0.7454	0.3233	0.8633
6	388.5	0.9427	0.8367	0.4500	0.7109	0.0352	0.8909
7	403.4	0.9627	0.8875	0.4246	0.6989	-0.3025	0.9043

Table 6.2 C Test Results of Nitrogen-Methane System at -240°F with E(x) = 0.0005

```
TESTED RESULTS OF  NITROGEN-METHANE SYSTEM AT -240 DEG F(CHANG'S DATA )
                      (1)      (2)

   EX=  0.0005  EP=  1.0000  ET=  0.2000

PAIR NO   P(Av.)  I        II       III      D        ±DMAX    DX       DP       DT

  1- 2      75.8 -1.3364 -1.2206  0.0283 -0.1441  0.0712  0.0105  0.0603  0.0003
  2- 3     150.7 -1.1278 -1.0769  0.0567 -0.1076  0.0448  0.0137  0.0309  0.0003
  3- 4     252.2 -0.4099 -0.5326  0.0621  0.0607  0.0336  0.0158  0.0177  0.0002
  4- 5     323.9 -0.1510 -0.1407  0.0258 -0.0362  0.0277  0.0139  0.0137  0.0001
  5- 6     366.2 -0.1193 -0.1281  0.0304 -0.0216  0.0268  0.0144  0.0123  0.0001
  6- 7     395.9 -0.0058 -0.0380  0.0108  0.0214  0.0248  0.0132  0.0116  0.0000
```

Table 6.2 D Test Results of Nitrogen-Methane System at -240°F with E(x) = 0.0010

```
TESTED RESULTS OF  NITROGEN-METHANE SYSTEM AT -240 DEG F(CHANG'S DATA )

 EX=  0.0010  EP=  1.0000  ET=  0.2000

PAIR NO   P(Av.)  I        II        III      D        ±DMAX    DX       CP       DT

  1- 2     75.8 -1.3364 -1.2206   0.0283 -0.1441   0.0817  0.0210  0.0603  0.0003
  2- 3    150.7 -1.1278 -1.0769   0.0567 -0.1076   0.0585  0.0273  0.0309  0.0003
  3- 4    252.2 -0.4099 -0.5326   0.0621  0.0607   0.0494  0.0315  0.0177  0.0002
  4- 5    323.9 -0.1510 -0.1407   0.0258 -0.0362   0.0416  0.0278  0.0137  0.0001
  5- 6    366.2 -0.1193 -0.1281   0.0304 -0.0216   0.0412  0.0289  0.0123  0.0001
  6- 7    395.9 -0.0058 -0.0380   0.0108  0.0214   0.0380  0.0264  0.0116  0.0000
```

Table 6.2 E Test Results of Nitrogen-Methane System at -240°F with E(x) = 0.0020

```
TESTED RESULTS OF  NITROGEN-METHANE SYSTEM AT -240 DEG F(CHANG'S DATA )


  EX=  0.0020  EP=  1.0000  ET=  0.2000

PAIR NO   P (Av.)  I         II        III      D         ±DMAX    DX       CP       DT

 1- 2      75.8 -1.3364 -1.2206  0.0283 -0.1441  0.1027  0.0420  0.0603  0.0003
 2- 3     150.7 -1.1278 -1.0769  0.0567 -0.1076  0.0858  0.0547  0.0309  0.0003
 3- 4     252.2 -0.4099 -0.5326  0.0621  0.0607  0.0809  0.0630  0.0177  0.0002
 4- 5     323.9 -0.1510 -0.1407  0.0258 -0.0362  0.0694  0.0557  0.0137  0.0001
 5- 6     366.2 -0.1193 -0.1281  0.0304 -0.0216  0.0701  0.0577  0.0123  0.0001
 6- 7     395.9 -0.0058 -0.0380  0.0108  0.0214  0.0644  0.0528  0.0116  0.0000
```

Table 6.3 A. Test Data of Nitrogen-Methane System at -240°F (ref. 26).

1 2 0.03 0.03 0.0198 -0.0700

220.0000 408.7000 408.7000 0.0 0.0 0.0

ID	P, psia	x_2	x_1	y_2	y_1
1	44.0	0.9830	0.0170	0.7540	0.2460
2	50.0	0.9710	0.0290	0.6620	0.3380
3	56.0	0.9460	0.0540	0.5980	0.4020
4	61.0	0.9360	0.0640	0.5250	0.4750
5	71.0	0.9150	0.0850	0.4670	0.5330
6	82.0	0.8960	0.1040	0.4180	0.5820
7	84.0	0.8940	0.1060	0.4080	0.5920
8	85.0	0.8840	0.1160	0.4110	0.5890
9	93.0	0.8710	0.1290	0.3520	0.6480
10	122.0	0.8050	0.1950	0.2820	0.7180
11	125.0	0.7950	0.2050	0.2620	0.7380
12	142.0	0.7300	0.2700	0.2220	0.7780
13	154.0	0.7100	0.2900	0.2150	0.7850
14	183.0	0.6150	0.3850	0.1730	0.8270
15	199.0	0.5720	0.4280	0.1660	0.8340
16	214.0	0.5100	0.4900	0.1300	0.8700
17	232.0	0.4650	0.5350	0.1300	0.8700
18	242.0	0.4320	0.5680	0.1250	0.8750
19	247.0	0.4160	0.5840	0.1140	0.8860
20	269.0	0.3580	0.6420	0.1090	0.8910
21	307.0	0.2280	0.7720	0.0760	0.9240
22	310.0	0.2150	0.7850	0.0450	0.9550
23	328.0	0.1550	0.8450	0.0660	0.9340
24	330.0	0.1320	0.8680	0.0630	0.9370
25	361.0	0.0760	0.9240	0.0320	0.9680
26	364.0	0.0630	0.9370	0.0210	0.9790
27	365.0	0.0780	0.9220	0.0420	0.9580
28	367.0	0.0570	0.9430	0.0190	0.9810

Table 6.3 B Supporting Data for Testing Nitrogen-Methane System at -240° F.

IC	P, psia	TRMIX	VL	ϕ_2	ϕ_1	$\overline{V}_2$	$\overline{V}_1$
1	44.0	0.6473	0.6267	0.9256	0.9743	0.6252	0.7176
2	50.0	0.6503	0.6273	0.9163	0.9689	0.6246	0.7185
3	56.0	0.6566	0.6285	0.9071	0.9638	0.6233	0.7207
4	61.0	0.6591	0.6291	0.9000	0.9591	0.6227	0.7216
5	71.0	0.6645	0.6303	0.8850	0.9513	0.6216	0.7237
6	82.0	0.6654	0.6314	0.8687	0.9427	0.6205	0.7256
7	84.0	0.6700	0.6315	0.8658	0.9412	0.6204	0.7258
8	85.0	0.6726	0.6322	0.8642	0.9405	0.6197	0.7269
9	93.0	0.6760	0.6330	0.8536	0.9337	0.6189	0.7283
10	122.0	0.6938	0.6380	0.8122	0.9117	0.6141	0.7363
11	125.0	0.6966	0.6388	0.8088	0.9091	0.6133	0.7376
12	142.0	0.7149	0.6448	0.7859	0.8961	0.6071	0.7468
13	154.0	0.7207	0.6469	0.7687	0.8873	0.6049	0.7498
14	183.0	0.7490	0.6583	0.7298	0.8655	0.5912	0.7656
15	199.0	0.7623	0.6644	0.7073	0.8539	0.5829	0.7734
16	214.0	0.7820	0.6744	0.6899	0.8422	0.5679	0.7853
17	232.0	0.7967	0.6827	0.6641	0.8292	0.5541	0.7945
18	242.0	0.8078	0.6894	0.6503	0.8219	0.5421	0.8015
19	247.0	0.8132	0.6929	0.6448	0.8180	0.5356	0.8049
20	269.0	0.8331	0.7066	0.6137	0.8020	0.5073	0.8177
21	307.0	0.8800	0.7471	0.5645	0.7734	0.4034	0.8485
22	310.0	0.8848	0.7521	0.5677	0.7705	0.3881	0.8518
23	328.0	0.9075	0.7789	0.5351	0.7577	0.2974	0.8672
24	330.0	0.9161	0.7906	0.5329	0.7562	0.2522	0.8725
25	361.0	0.9376	0.8260	0.4939	0.7323	0.0920	0.8864
26	364.0	0.9427	0.8362	0.4933	0.7298	0.0387	0.8898
27	365.0	0.9369	0.8246	0.4830	0.7295	0.0995	0.8859
28	367.0	0.9451	0.8412	0.4893	0.7275	0.0107	0.8914

Table 6.3 C Test Results of Nitrogen-Methane System at -240°F with $E(x) = 0.0005$

EX= 0.0005 EP= 1.0000 ET= 0.2000

PAIR NO	P (Av.)	I	II	III	D	±DMAX	DX	DP	DT
1- 2	47.0	-0.2402	-0.2357	0.0034	-0.0079	0.0940	0.0072	0.0865	0.0003
2- 3	53.0	-0.1821	-0.2069	0.0035	0.0212	0.0850	0.0078	0.0768	0.0003
3- 4	58.5	-0.2254	-0.1558	0.0028	-0.0724	0.0777	0.0078	0.0696	0.0003
4- 5	66.0	-0.1998	-0.2713	0.0056	0.0658	0.0705	0.0081	0.0620	0.0003
5- 6	76.5	-0.1843	-0.2527	0.0061	0.0624	0.0625	0.0085	0.0536	0.0003
6- 7	83.0	-0.0398	-0.0419	0.0011	0.0011	0.0583	0.0087	0.0493	0.0003
7- 8	84.5	0.0119	-0.0201	0.0007	0.0313	0.0576	0.0088	0.0484	0.0003
8- 9	89.0	-0.2486	-0.1565	0.0044	-0.0965	0.0556	0.0092	0.0461	0.0003
9-10	107.5	-0.3402	-0.4518	0.0163	0.0953	0.0493	0.0101	0.0390	0.0003
10-11	123.5	-0.1067	-0.0407	0.0017	-0.0677	0.0442	0.0105	0.0335	0.0003
11-12	133.5	-0.2283	-0.2044	0.0098	-0.0338	0.0426	0.0111	0.0312	0.0003
12-13	148.0	-0.0411	-0.1248	0.0067	0.0769	0.0398	0.0114	0.0282	0.0003
13-14	168.5	-0.2537	-0.2596	0.0168	-0.0109	0.0372	0.0119	0.0250	0.0002
14-15	191.0	-0.0422	-0.1194	0.0093	0.0679	0.0344	0.0121	0.0221	0.0002
15-16	206.5	-0.2258	-0.1058	0.0090	-0.1289	0.0334	0.0126	0.0205	0.0002
16-17	223.0	0.0000	-0.1083	0.0107	0.0977	0.0322	0.0128	0.0191	0.0002
17-18	237.0	-0.0289	-0.0559	0.0060	0.0210	0.0306	0.0124	0.0180	0.0002
18-19	244.5	-0.0637	-0.0282	0.0030	-0.0385	0.0302	0.0125	0.0175	0.0002
19-20	258.0	-0.0277	-0.1081	0.0134	0.0670	0.0294	0.0125	0.0167	0.0002
20-21	288.0	-0.1562	-0.1641	0.0241	-0.0163	0.0277	0.0124	0.0152	0.0001
21-22	308.5	-0.1808	-0.0161	0.0020	-0.1666	0.0283	0.0140	0.0142	0.0001
22-23	319.0	0.1065	-0.0637	0.0120	0.1582	0.0274	0.0135	0.0138	0.0001
23-24	329.0	-0.0078	-0.0074	0.0015	-0.0018	0.0240	0.0104	0.0135	0.0001
24-25	345.5	-0.0798	-0.1062	0.0214	0.0050	0.0241	0.0111	0.0130	0.0001
25-26	362.5	-0.0374	-0.0101	0.0021	-0.0294	0.0241	0.0116	0.0124	0.0001
26-27	364.5	0.0573	-0.0017	0.0007	0.0583	0.0239	0.0114	0.0124	0.0001
27-28	366.0	-0.0625	-0.0076	0.0014	-0.0563	0.0240	0.0116	0.0123	0.0001

Table 6.3 D Test Results of Nitrogen-Methane System at -240°F with $E(x) = 0.0010$

EX= 0.0010 EP= 1.0000 ET= 0.2000

PAIR NO	P (Av.)	I	II	III	D	±DMAX	DX	CP	DT
1- 2	47.0	-0.2402	-0.2357	0.0034	-0.0079	0.1012	0.0144	0.0865	0.0003
2- 3	53.0	-0.1821	-0.2069	0.0035	0.0212	0.0928	0.0157	0.0768	0.0003
3- 4	53.5	-0.2254	-0.1558	0.0028	-0.0724	0.0854	0.0155	0.0696	0.0003
4- 5	66.0	-0.1998	-0.2713	0.0056	0.0658	0.0787	0.0163	0.0620	0.0003
5- 6	76.5	-0.1843	-0.2527	0.0061	0.0624	0.0710	0.0170	0.0536	0.0003
6- 7	83.0	-0.0398	-0.0419	0.0011	0.0011	0.0670	0.0174	0.0493	0.0003
7- 8	84.5	0.0119	-0.0201	0.0007	0.0313	0.0664	0.0177	0.0484	0.0003
8- 9	89.0	-0.2486	-0.1565	0.0044	-0.0965	0.0647	0.0183	0.0461	0.0003
9-10	107.5	-0.3402	-0.4518	0.0163	0.0953	0.0594	0.0201	0.0390	0.0003
10-11	123.5	-0.1067	-0.0407	0.0017	-0.0677	0.0547	0.0210	0.0335	0.0003
11-12	133.5	-0.2283	-0.2044	0.0098	-0.0338	0.0537	0.0223	0.0312	0.0003
12-13	148.0	-0.0411	-0.1248	0.0067	0.0769	0.0512	0.0227	0.0282	0.0003
13-14	168.5	-0.2537	-0.2596	0.0168	-0.0109	0.0491	0.0239	0.0250	0.0002
14-15	191.0	-0.0422	-0.1194	0.0093	0.0679	0.0465	0.0242	0.0221	0.0002
15-16	206.5	-0.2258	-0.1058	0.0090	-0.1289	0.0460	0.0253	0.0205	0.0002
16-17	223.0	0.0000	-0.1083	0.0107	0.0977	0.0450	0.0257	0.0191	0.0002
17-18	237.0	-0.0289	-0.0559	0.0060	0.0210	0.0430	0.0248	0.0180	0.0002
18-19	244.5	-0.0637	-0.0282	0.0030	-0.0385	0.0426	0.0249	0.0175	0.0002
19-20	258.0	-0.0277	-0.1081	0.0134	0.0670	0.0419	0.0250	0.0167	0.0002
20-21	288.0	-0.1562	-0.1641	0.0241	-0.0163	0.0401	0.0248	0.0152	0.0001
21-22	308.5	-0.1308	-0.0161	0.0020	-0.1666	0.0423	0.0279	0.0142	0.0001
22-23	319.0	0.1065	-0.0637	0.0120	0.1582	0.0409	0.0269	0.0138	0.0001
23-24	329.0	-0.0078	-0.0074	0.0015	-0.0018	0.0344	0.0209	0.0135	0.0001
24-25	345.5	-0.0798	-0.1062	0.0214	0.0050	0.0352	0.0222	0.0130	0.0001
25-26	362.5	-0.0374	-0.0101	0.0021	-0.0294	0.0358	0.0233	0.0124	0.0001
26-27	364.5	0.0573	-0.0017	0.0007	0.0583	0.0353	0.0229	0.0124	0.0001
27-28	366.0	-0.0625	-0.0076	0.0014	-0.0563	0.0356	0.0232	0.0123	0.0001

Table 6.3 E Test Results of Nitrogen-Methane System at -240°F with $E(x) = 0.0020$

EX= 0.0020 EP= 1.0000 ET= 0.2000

PAIR NO	P (Av.)	I	II	III	D	±DMAX	DX	DP	DT
1- 2	47.0	-0.2402	-0.2357	0.0034	-0.0079	0.1156	0.0287	0.0865	0.0003
2- 3	53.0	-0.1821	-0.2069	0.0035	0.0212	0.1085	0.0314	0.0768	0.0003
3- 4	58.5	-0.2254	-0.1558	0.0028	-0.0724	0.1010	0.0311	0.0696	0.0003
4- 5	66.0	-0.1998	-0.2713	0.0056	0.0658	0.0949	0.0326	0.0620	0.0003
5- 6	76.5	-0.1843	-0.2527	0.0061	0.0624	0.0880	0.0341	0.0536	0.0003
6- 7	83.0	-0.0398	-0.0419	0.0011	0.0011	0.0844	0.0349	0.0493	0.0003
7- 8	84.5	0.0119	-0.0201	0.0007	0.0313	0.0841	0.0353	0.0484	0.0003
8- 9	89.0	-0.2486	-0.1565	0.0044	-0.0965	0.0831	0.0367	0.0461	0.0003
9-10	107.5	-0.3402	-0.4518	0.0163	0.0953	0.0795	0.0402	0.0390	0.0003
10-11	123.5	-0.1067	-0.0407	0.0017	-0.0677	0.0757	0.0419	0.0335	0.0003
11-12	133.5	-0.2283	-0.2044	0.0098	-0.0338	0.0760	0.0446	0.0312	0.0003
12-13	148.0	-0.0411	-0.1248	0.0067	0.0769	0.0739	0.0455	0.0282	0.0003
13-14	168.5	-0.2537	-0.2596	0.0168	-0.0109	0.0730	0.0477	0.0250	0.0002
14-15	191.0	-0.0422	-0.1194	0.0093	0.0679	0.0707	0.0484	0.0221	0.0002
15-16	206.5	-0.2258	-0.1058	0.0090	-0.1289	0.0713	0.0506	0.0205	0.0002
16-17	223.0	0.0000	-0.1083	0.0107	0.0977	0.0707	0.0514	0.0191	0.0002
17-18	237.0	-0.0289	-0.0559	0.0060	0.0210	0.0678	0.0495	0.0180	0.0002
18-19	244.5	-0.0637	-0.0282	0.0030	-0.0385	0.0676	0.0499	0.0175	0.0002
19-20	258.0	-0.0277	-0.1081	0.0134	0.0670	0.0669	0.0500	0.0167	0.0002
20-21	288.0	-0.1562	-0.1641	0.0241	-0.0163	0.0650	0.0497	0.0152	0.0001
21-22	308.5	-0.1808	-0.0161	0.0020	-0.1666	0.0702	0.0559	0.0142	0.0001
22-23	319.0	0.1065	-0.0637	0.0120	0.1582	0.0678	0.0538	0.0138	0.0001
23-24	329.0	-0.0078	-0.0074	0.0015	-0.0018	0.0553	0.0417	0.0135	0.0001
24-25	345.5	-0.0798	-0.1062	0.0214	0.0050	0.0573	0.0443	0.0130	0.0001
25-26	362.5	-0.0374	-0.0101	0.0021	-0.0294	0.0591	0.0466	0.0124	0.0001
26-27	364.5	0.0573	-0.0017	0.0007	0.0583	0.0582	0.0458	0.0124	0.0001
27-28	366.0	-0.0625	-0.0076	0.0014	-0.0563	0.0588	0.0464	0.0123	0.0001

Table 6.4 A Test Data of Methane-Ethane System at -151.1°F.

```
  TESTED DATA OF  METHANE-ETHANE SYSTEM AT  -151.1 DEG F (CHANG'S DATA)
                       (1)      (2)

      1 2     0.01      0.01    0.0      0.0

308.6999  358.2000  358.2000   7.1120    0.0      0.0      0.0

 ID    P, psia   x1       x2       y1       y2

  1     51.7   0.1244   0.8756   0.8690   0.1310
  2     70.2   0.2108   0.7892   0.9024   0.0976
  3    101.2   0.2872   0.7128   0.9255   0.0745
  4    130.9   0.3491   0.6509   0.9603   0.0397
  5    158.2   0.4453   0.5547   0.9661   0.0339
  6    201.5   0.5486   0.4514   0.9752   0.0248
  7    219.7   0.6251   0.3749   0.9799   0.0201
  8    242.2   0.6853   0.3147   0.9811   0.0189
  9    251.7   0.7093   0.2907   0.9494   0.0506
 10    263.2   0.7544   0.2456   0.9867   0.0133
 11    301.7   0.8602   0.1398   0.9242   0.0758
```

Table 6.4 B Supporting Data for Testing Methane-Ethane System at -151.1° F.

SUPPORTING DATA FOR TESTING METHANE-ETHANE SYSTEM AT -151.1 DEG F (CHANG'S DATA)
(1) (2)

ID	P, psia	TRMIX	VL	ϕ_1	ϕ_2	$\bar{V}_1$	$\bar{V}_2$
1	51.7	0.5842	0.8166	0.9656	0.9012	0.7030	0.8328
2	70.2	0.6016	0.8042	0.9531	0.8691	0.7095	0.8295
3	101.2	0.6186	0.7941	0.9324	0.8160	0.7163	0.8255
4	130.9	0.6335	0.7867	0.9124	0.7696	0.7225	0.8212
5	158.2	0.6591	0.7769	0.8943	0.7256	0.7337	0.8115
6	201.5	0.6905	0.7692	0.8657	0.6583	0.7481	0.7948
7	219.7	0.7167	0.7660	0.8536	0.6310	0.7604	0.7752
8	242.2	0.7396	0.7655	0.8387	0.5968	0.7713	0.7528
9	251.7	0.7493	0.7659	0.8330	0.5728	0.7759	0.7415
10	263.2	0.7685	0.7678	0.8248	0.5667	0.7849	0.7152
11	301.7	0.8195	0.7805	0.8012	0.4832	0.8081	0.6108

Table 6.4 C Test Results of Methane-Ethane System at -151.1F with E(x) = 0.0005.

```
TESTED RESULTS OF  METHANE-ETHANE SYSTEM AT  -151.1 DEG F (CHANG'S DATA)


    EX=  0.0005  EP=  1.0000  ET=  0.2000

PAIR NO    P (Av.)  I         II       III      D        ±DMAX    DX       CP       DT

 1- 2       60.9 -0.4812 -0.5471  0.0093  0.0566  0.0880  0.0197  0.0682  0.0002
 2- 3       85.7 -0.3942 -0.6259  0.0152  0.2165  0.0719  0.0226  0.0492  0.0002
 3- 4      116.0 -0.8352 -0.4210  0.0143 -0.4285  0.0676  0.0314  0.0360  0.0001
 4- 5      144.5 -0.1862 -0.2919  0.0130  0.0927  0.0670  0.0380  0.0289  0.0001
 5- 6      179.8 -0.3052 -0.3535  0.0203  0.0280  0.0638  0.0402  0.0235  0.0001
 6- 7      210.6 -0.1678 -0.1216  0.0085 -0.0546  0.0626  0.0425  0.0200  0.0001
 7- 8      230.9 -0.0406 -0.1335  0.0104  0.0825  0.0593  0.0409  0.0183  0.0001
 8- 9      246.9  0.5504 -0.0425  0.0044  0.5885  0.0457  0.0285  0.0171  0.0001
 9-10      257.4 -0.6600 -0.0692  0.0053 -0.5962  0.0487  0.0321  0.0165  0.0001
10-11      282.4  0.5703 -0.1648  0.0180  0.7172  0.0405  0.0253  0.0152  0.0000
```

Table 6.4 D Test. Results of Methane-Ethane System at -151.1°F with E(x) = 0.0010

```
TESTED RESULTS OF  METHANE-ETHANE SYSTEM AT  -151.1 DEG F (CHANG'S DATA)


   EX=  0.0010  EP=  1.0000  ET=  0.2000

PAIR NO   P (Av.)  I          II        III      D        ±DMAX    DX       DP       DT

 1- 2      60.9 -0.4812 -0.5471  0.0093  0.0566  0.1077  0.0394  0.0682  0.0002
 2- 3      85.7 -0.3942 -0.6259  0.0152  0.2165  0.0945  0.0451  0.0492  0.0002
 3- 4     116.0 -0.8352 -0.4210  0.0143 -0.4285  0.0990  0.0629  0.0360  0.0001
 4- 5     144.5 -0.1862 -0.2919  0.0130  0.0927  0.1051  0.0761  0.0289  0.0001
 5- 6     179.8 -0.3052 -0.3535  0.0203  0.0280  0.1040  0.0804  0.0235  0.0001
 6- 7     210.6 -0.1678 -0.1216  0.0085 -0.0546  0.1051  0.0850  0.0200  0.0001
 7- 8     230.9 -0.0406 -0.1335  0.0104  0.0825  0.1002  0.0818  0.0183  0.0001
 8- 9     246.9  0.5504 -0.0425  0.0044  0.5885  0.0743  0.0571  0.0171  0.0001
 9-10     257.4 -0.6600 -0.0692  0.0053 -0.5962  0.0808  0.0643  0.0165  0.0001
10-11     282.4  0.5703 -0.1648  0.0180  0.7172  0.0657  0.0505  0.0152  0.0000
```

Table 6.4 E Test. Results of Methane-Ethane System at -151.1°F with E(x) = 0.0020.

```
  TESTED RESULTS OF  METHANE-ETHANE SYSTEM AT  -151.1 DEG F (CHANG'S DATA)

    EX=  0.0020  EP=  1.0000  ET=  0.2000

 PAIR NO  P(Av.)  I        II       III      D       ±DMAX    DX      DP      DT

  1- 2     60.9 -0.4812 -0.5471  0.0093  0.0566  0.1471  0.0787  0.0682  0.0002
  2- 3     85.7 -0.3942 -0.6259  0.0152  0.2165  0.1396  0.0902  0.0492  0.0002
  3- 4    116.0 -0.8352 -0.4210  0.0143 -0.4285  0.1619  0.1258  0.0360  0.0001
  4- 5    144.5 -0.1862 -0.2919  0.0130  0.0927  0.1811  0.1521  0.0289  0.0001
  5- 6    179.8 -0.3052 -0.3535  0.0203  0.0280  0.1845  0.1609  0.0235  0.0001
  6- 7    210.6 -0.1678 -0.1216  0.0085 -0.0546  0.1901  0.1700  0.0200  0.0001
  7- 8    230.9 -0.0406 -0.1335  0.0104  0.0825  0.1820  0.1637  0.0183  0.0001
  8- 9    246.9  0.5504 -0.0425  0.0044  0.5885  0.1314  0.1142  0.0171  0.0001
  9-10    257.4 -0.6600 -0.0692  0.0053 -0.5962  0.1451  0.1285  0.0165  0.0001
 10-11    282.4  0.5703 -0.1648  0.0180  0.7172  0.1163  0.1011  0.0152  0.0000
```

Table 6.5 A   Tested Data of Carbon Dioxide-Nitrogen-Oxygen System at -40° C and 51 atm.

SUPPORTING DATA FOR TESTING CARBONDIOXIDE-NITROGEN-OXYGEN SYSTEM AT -40

ID	P, psia	TRMIX	VL	ϕ_1	ϕ_2	ϕ_3	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_3$
1	749.7	0.7987	0.6618	0.7068	1.7118	0.9397	0.4969	3.8462	0.5150
2	749.7	0.7991	0.6629	0.7031	1.7172	0.9395	0.5097	4.0081	0.5417
3	749.7	0.8012	0.6647	0.6976	1.7257	0.9394	0.5124	4.0475	0.5480
4	749.7	0.8028	0.6658	0.6973	1.7261	0.9394	0.5102	4.0107	0.5426
5	749.7	0.8017	0.6657	0.6943	1.7312	0.9394	0.5247	4.2763	0.5802
6	749.7	0.8022	0.6667	0.6871	1.7443	0.9396	0.5342	4.5085	0.6101
7	749.7	0.8047	0.6687	0.6854	1.7478	0.9397	0.5329	4.4697	0.6058
8	749.7	0.8080	0.6719	0.6793	1.7606	0.9402	0.5413	4.7138	0.6363
9	749.7	0.8067	0.6710	0.6779	1.7637	0.9403	0.5456	4.8593	0.6532
10	749.7	0.8070	0.6713	0.6763	1.7674	0.9405	0.5465	4.8918	0.6571
11	749.7	0.8080	0.6726	0.6699	1.7828	0.9413	0.5532	5.1533	0.6872
12	749.7	0.8085	0.6731	0.6694	1.7842	0.9414	0.5556	5.2584	0.6991

Table 6.5 B Supporting Data for Testing Carbon Dioxide-Nitrogen-Oxygen System at -40° C and 51 atm

TESTED DATA OF CARBONDIOXIDE-NITROGEN-OXYGEN SYSTEM AT -40 DEG C (ZENNER'S DATA)
(1) (2) (3)

1 2 0.0 0.0 -0.0054 0.0

1 3 0.0 0.0 -0.0005 0.0

2 3 0.0 0.0 -0.0163 0.0

0.0 749.7000 749.7000 0.0 0.0 0.0 0.0

ID	P	x_1	x_2	x_3	y_1	y_2	y_3	$x_{O_2}/(x_{O_2}+x_{N_2})$
1	749.7	0.9240	0.0491	0.0269	0.2828	0.5035	0.2137	.3540
2	749.7	0.9250	0.0435	0.0315	0.2820	0.4717	0.2463	.4200
3	749.7	0.9216	0.0427	0.0357	0.2823	0.4297	0.2880	.4550
4	749.7	0.9183	0.0441	0.0376	0.2810	0.4256	0.2934	.4593
5	749.7	0.9226	0.0370	0.0404	0.2776	0.3978	0.3246	.5220
6	749.7	0.9230	0.0325	0.0445	0.2794	0.3492	0.3714	.5780
7	749.7	0.9182	0.0336	0.0482	0.2800	0.3380	0.3820	.5900
8	749.7	0.9136	0.0300	0.0564	0.2744	0.2893	0.4363	.6520
9	749.7	0.9166	0.0277	0.0557	0.2732	0.2789	0.4479	.6680
10	749.7	0.9162	0.0273	0.0565	0.2765	0.2731	0.4504	.6740
11	749.7	0.9154	0.0242	0.0604	0.2790	0.2373	0.4837	.7140
12	749.7	0.9149	0.0231	0.0620	0.2758	0.2299	0.4943	.7280

Table 6.5 C Test. Results of Carbon Dioxide-Nitrogen-Oxygen System at -40° C and 51 atm with E(x) = 0.0005

```
 TESTED RESULTS OF  CARBONDIOXIDE-NITROGEN-OXYGEN SYSTEM  AT -40 DEG C (ZENNE

    EX=  0.0005  EP=  1.0000  ET=  0.2000

PAIR NO    P         I        II      III       D      ±DMAX    DX       DP      DT

  1- 2    749.7 -0.0030  0.0096  0.0    -0.0126  0.0184  0.0131  0.0053  0.0
  2- 3    749.7  0.0044  0.0140  0.0    -0.0095  0.0184  0.0131  0.0053  0.0
  3- 4    749.7 -0.0080  0.0007  0.0    -0.0087  0.0184  0.0131  0.0053  0.0
  4- 5    749.7 -0.0200  0.0078  0.0    -0.0277  0.0186  0.0132  0.0053  0.0
  5- 6    749.7  0.0143  0.0186  0.0    -0.0043  0.0185  0.0131  0.0053  0.0
  6- 7    749.7  0.0044  0.0045  0.0    -0.0002  0.0185  0.0131  0.0053  0.0
  7- 8    749.7 -0.0330  0.0159  0.0    -0.0489  0.0185  0.0132  0.0053  0.0
  8- 9    749.7 -0.0072  0.0035  0.0    -0.0107  0.0186  0.0132  0.0053  0.0
  9-10    749.7  0.0215  0.0043  0.0     0.0172  0.0185  0.0131  0.0053  0.0
 10-11    749.7  0.0176  0.0168  0.0     0.0008  0.0184  0.0131  0.0053  0.0
 11-12    749.7 -0.0200  0.0014  0.0    -0.0214  0.0184  0.0131  0.0053  0.0
```

Table 6.5 D Test Results of Carbon Dioxide-Nitrogen-Oxygen System at -40° C and 51 atm with E(x) = 0.0010

```
TESTED RESULTS OF  CARBONDIOXIDE-NITROGEN-OXYGEN SYSTEM  AT -40 DEG C (ZENNE


   EX=  0.0010  EP=  1.0000  ET=  0.2000

PAIR NO   P        I         II       III      D        ±DMAX    DX       DP       DT

  1- 2    749.7 -0.0030   0.0096   0.0    -0.0126   0.0315   0.0262   0.0053   0.0
  2- 3    749.7  0.0044   0.0140   0.0    -0.0095   0.0315   0.0262   0.0053   0.0
  3- 4    749.7 -0.0080   0.0007   0.0    -0.0087   0.0315   0.0261   0.0053   0.0
  4- 5    749.7 -0.0200   0.0078   0.0    -0.0277   0.0318   0.0264   0.0053   0.0
  5- 6    749.7  0.0143   0.0186   0.0    -0.0043   0.0316   0.0262   0.0053   0.0
  6- 7    749.7  0.0044   0.0045   0.0    -0.0002   0.0316   0.0263   0.0053   0.0
  7- 8    749.7 -0.0330   0.0159   0.0    -0.0489   0.0317   0.0263   0.0053   0.0
  8- 9    749.7 -0.0072   0.0035   0.0    -0.0107   0.0318   0.0265   0.0053   0.0
  9-10    749.7  0.0215   0.0043   0.0     0.0172   0.0316   0.0263   0.0053   0.0
 10-11    749.7  0.0176   0.0168   0.0     0.0008   0.0315   0.0261   0.0053   0.0
 11-12    749.7 -0.0200   0.0014   0.0    -0.0214   0.0315   0.0262   0.0053   0.0
```

Table 6.5 E Test Results of Carbon Dioxide-Nitrogen-Oxygen System at -40° C and 51 atm with E(x) = 0.0020

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TESTED RESULTS OF  CARBONDIOXIDE-NITROGEN-OXYGEN SYSTEM  AT -40 DEG C (ZENNER

   EX=  0.0020  EP=  1.0000  ET=  0.2000

PAIR NO   P        I         II       III      D       ±DMAX    DX       DP       DT

  1- 2     749.7 -0.0030   0.0096   0.0    -0.0126   0.0577   0.0524   0.0053   0.0
  2- 3     749.7  0.0044   0.0140   0.0    -0.0095   0.0577   0.0524   0.0053   0.0
  3- 4     749.7 -0.0080   0.0007   0.0    -0.0087   0.0576   0.0523   0.0053   0.0
  4- 5     749.7 -0.0200   0.0078   0.0    -0.0277   0.0582   0.0529   0.0053   0.0
  5- 6     749.7  0.0143   0.0186   0.0    -0.0043   0.0578   0.0525   0.0053   0.0
  6- 7     749.7  0.0044   0.0045   0.0    -0.0002   0.0579   0.0526   0.0053   0.0
  7- 8     749.7 -0.0330   0.0159   0.0    -0.0489   0.0580   0.0527   0.0053   0.0
  8- 9     749.7 -0.0072   0.0035   0.0    -0.0107   0.0583   0.0530   0.0053   0.0
  9-10     749.7  0.0215   0.0043   0.0     0.0172   0.0579   0.0526   0.0053   0.0
 10-11     749.7  0.0176   0.0168   0.0     0.0008   0.0576   0.0523   0.0053   0.0
 11-12     749.7 -0.0200   0.0014   0.0    -0.0214   0.0577   0.0523   0.0053   0.0
```

Table 6.6 A Tested Data of Nitrogen-Oxygen System at 1.3158 atm

ID	T°R	x_{N_2}	x_{O_2}	y_{N_2}	y_{O_2}
1	145.9	0.8109	0.1891	0.9400	0.0600
2	146.4	0.7846	0.2154	0.9281	0.0719
3	147.3	0.7151	0.2849	0.9001	0.0999
4	148.7	0.6307	0.3693	0.8633	0.1367
5	149.1	0.6113	0.3887	0.8555	0.1445
6	149.3	0.5980	0.4020	0.8475	0.1525
7	149.5	0.5840	0.4160	0.8362	0.1638
8	150.7	0.5299	0.4701	0.8081	0.1919
9	151.9	0.4593	0.5407	0.7682	0.2318
10	152.7	0.4049	0.5951	0.7227	0.2773
11	154.7	0.3396	0.6604	0.6670	0.3330
12	154.7	0.3381	0.6619	0.6665	0.3335
13	156.3	0.2748	0.7252	0.5997	0.4003
14	156.4	0.2744	0.7256	0.5946	0.4054
15	158.5	0.2071	0.7929	0.5089	0.4911
16	158.5	0.2022	0.7978	0.5011	0.4989
17	158.5	0.1905	0.8095	0.4868	0.5132
18	160.2	0.1575	0.8425	0.4210	0.5790
19	161.7	0.1254	0.8746	0.3583	0.6417
20	161.7	0.1196	0.8804	0.3514	0.6486
21	161.5	0.1124	0.8876	0.3373	0.6627
22	163.2	0.0724	0.9276	0.2396	0.7604
23	163.8	0.0717	0.9283	0.2191	0.7809

Table 6.6 B Supporting Data for Testing Nitrogen-Oxygen System at 1.3158 atm

ID	VL	ϕ_1	ϕ_2	$\Delta\overline{H}_2$	$\Delta\overline{H}_2$	ΔH	H_1^{vap}	H_2^{vap}
1	0.5421	0.9545	0.9461	2.1565	50.0715	11.2172	2349.8	3131.0
2	0.5393	0.9548	0.9466	2.8296	47.4488	12.4406	2344.9	3126.4
3	0.5317	0.9556	0.9476	5.1033	40.7186	15.2501	2333.8	3116.0
4	0.5226	0.9567	0.9489	8.9109	33.0079	17.8099	2318.7	3101.8
5	0.5207	0.9570	0.9493	9.9621	31.3211	18.2643	2313.8	3097.3
6	0.5193	0.9572	0.9496	10.7228	30.1773	18.5435	2311.1	3094.8
7	0.5177	0.9573	0.9498	11.5592	28.9838	18.8078	2309.1	3092.8
8	0.5124	0.9582	0.9509	15.1576	24.5688	19.5818	2294.8	3079.5
9	0.5049	0.9591	0.9520	20.7775	19.1737	19.9103	2281.5	3067.0
10	0.4991	0.9596	0.9528	25.8887	15.3539	19.6194	2272.1	3058.3
11	0.4931	0.9609	0.9545	33.0712	11.2510	18.6611	2249.7	3037.6
12	0.4929	0.9609	0.9545	33.2460	11.1593	18.6268	2250.1	3037.9
13	0.4868	0.9619	0.9559	41.4083	7.6766	16.9460	2230.9	3020.2
14	0.4868	0.9620	0.9560	41.4687	7.6581	16.9357	2230.2	3019.5
15	0.4806	0.9632	0.9576	51.6446	4.5707	14.3197	2205.7	2997.0
16	0.4800	0.9631	0.9576	52.4203	4.3677	14.0839	2206.4	2997.6
17	0.4786	0.9632	0.9577	54.3329	3.9035	13.5103	2205.8	2997.0
18	0.4762	0.9641	0.9590	60.2610	2.7424	11.8016	2185.9	2978.8
19	0.4735	0.9648	0.9600	66.4536	1.7845	9.8940	2169.6	2964.0
20	0.4729	0.9648	0.9600	67.5728	1.6290	9.5159	2169.4	2963.8
21	0.4719	0.9647	0.9599	68.9464	1.4439	9.0311	2170.9	2965.2
22	0.4685	0.9655	0.9611	77.5619	0.6193	6.1900	2151.6	2947.8
23	0.4689	0.9658	0.9614	77.8701	0.6097	6.1492	2145.0	2941.8

Table 6.6 C Test Results of Nitrogen-Oxygen System at 1.3158 atm with E(x)=0.0005

EX= 0.0005 EP= 0.0194 ET= 0.1800

PAIR NO	T	I	II	III	D	DMAX	DX	DP	DT
1- 2	81.2	0.0528	-0.0008	0.0503	0.0032	0.0373	0.0120	0.0040	0.0212
2- 3	81.6	0.1178	-0.0018	0.1148	0.0048	0.0372	0.0119	0.0040	0.0213
3- 4	82.2	0.1483	-0.0024	0.1555	-0.0049	0.0370	0.0115	0.0040	0.0214
4- 5	82.7	0.0308	-0.0008	0.0503	-0.0187	0.0362	0.0109	0.0040	0.0213
5- 6	82.9	0.0312	-0.0004	0.0276	0.0041	0.0360	0.0108	0.0040	0.0212
6- 7	83.0	0.0426	-0.0003	0.0212	0.0217	0.0359	0.0107	0.0040	0.0212
7- 8	83.4	0.1022	-0.0021	0.1465	-0.0422	0.0360	0.0106	0.0040	0.0213
8- 9	84.1	0.1409	-0.0020	0.1368	0.0061	0.0356	0.0104	0.0040	0.0212
9-10	84.6	0.1509	-0.0014	0.0958	0.0565	0.0351	0.0099	0.0040	0.0212
10-11	85.4	0.1703	-0.0032	0.2278	-0.0543	0.0349	0.0096	0.0040	0.0212
11-12	85.9	0.0015	0.0001	-0.0033	0.0048	0.0338	0.0090	0.0040	0.0208
12-13	86.4	0.1889	-0.0027	0.1926	-0.0010	0.0342	0.0092	0.0040	0.0210
13-14	86.9	0.0137	-0.0001	0.0074	0.0064	0.0332	0.0085	0.0040	0.0207
14-15	87.5	0.2171	-0.0033	0.2418	-0.0215	0.0336	0.0088	0.0040	0.0208
15-16	88.0	0.0187	0.0001	-0.0069	0.0256	0.0324	0.0080	0.0040	0.0203
16-17	88.0	0.0341	-0.0001	0.0063	0.0278	0.0324	0.0080	0.0040	0.0204
17-18	88.5	0.1489	-0.0026	0.1939	-0.0424	0.0326	0.0081	0.0040	0.0205
18-19	89.4	0.1312	-0.0020	0.1562	-0.0229	0.0320	0.0079	0.0040	0.0201
19-20	89.8	0.0140	-0.0000	0.0020	0.0121	0.0313	0.0074	0.0040	0.0198
20-21	89.8	0.0285	0.0002	-0.0145	0.0429	0.0313	0.0074	0.0040	0.0198
21-22	90.2	0.1877	-0.0023	0.1816	0.0084	0.0317	0.0077	0.0040	0.0200
22-23	90.8	0.0365	-0.0008	0.0619	-0.0247	0.0308	0.0072	0.0040	0.0196

Table 6.6D Test Results of Nitrogen-Oxygen System at 1.3158 atm with E(x)= 0.0010

EX= 0.0010 EP= 0.0194 ET= 0.1800

PAIR NO	T	I	II	III	D	DMAX	DX	DP	DT
1- 2	81.2	0.0528	-0.0008	0.0503	0.0032	0.0493	0.0241	0.0040	0.0212
2- 3	81.6	0.1178	-0.0018	0.1148	0.0048	0.0491	0.0238	0.0040	0.0213
3- 4	82.2	0.1483	-0.0024	0.1555	-0.0049	0.0485	0.0231	0.0040	0.0214
4- 5	82.7	0.0308	-0.0008	0.0503	-0.0187	0.0471	0.0218	0.0040	0.0213
5- 6	82.9	0.0312	-0.0004	0.0276	0.0041	0.0469	0.0216	0.0040	0.0212
6- 7	83.0	0.0426	-0.0003	0.0212	0.0217	0.0465	0.0213	0.0040	0.0212
7- 8	83.4	0.1022	-0.0021	0.1465	-0.0422	0.0466	0.0213	0.0040	0.0213
8- 9	84.1	0.1409	-0.0020	0.1368	0.0061	0.0460	0.0207	0.0040	0.0212
9-10	84.6	0.1509	-0.0014	0.0958	0.0565	0.0451	0.0198	0.0040	0.0212
10-11	85.4	0.1703	-0.0032	0.2278	-0.0543	0.0445	0.0193	0.0040	0.0212
11-12	85.9	0.0015	0.0001	-0.0033	0.0048	0.0428	0.0180	0.0040	0.0208
12-13	86.4	0.1889	-0.0027	0.1926	-0.0010	0.0434	0.0184	0.0040	0.0210
13-14	86.9	0.0137	-0.0001	0.0074	0.0064	0.0417	0.0171	0.0040	0.0207
14-15	87.5	0.2171	-0.0033	0.2418	-0.0215	0.0424	0.0176	0.0040	0.0208
15-16	88.0	0.0187	0.0001	-0.0069	0.0256	0.0404	0.0161	0.0040	0.0203
16-17	88.0	0.0341	-0.0001	0.0063	0.0278	0.0405	0.0160	0.0040	0.0204
17-18	88.5	0.1489	-0.0026	0.1939	-0.0424	0.0407	0.0163	0.0040	0.0205
18-19	89.4	0.1312	-0.0020	0.1562	-0.0229	0.0398	0.0157	0.0040	0.0201
19-20	89.8	0.0140	-0.0000	0.0020	0.0121	0.0387	0.0149	0.0040	0.0198
20-21	89.8	0.0285	0.0002	-0.0145	0.0429	0.0386	0.0148	0.0040	0.0199
21-22	90.2	0.1877	-0.0023	0.1816	0.0084	0.0393	0.0153	0.0040	0.0200
22-23	90.8	0.0365	-0.0008	0.0619	-0.0247	0.0379	0.0143	0.0040	0.0196

Table 6.6 E Test Results Of Nitrogen-Oxygen System at 1.3158 atm with E(x)= 0.0020

EX= 0.0020 EP= 0.0194 ET= 0.1800

PAIR NO	T	I	II	III	D	DMAX	DX	DP	DT
1- 2	81.2	0.0528	-0.0008	0.0503	0.0032	0.0733	0.0481	0.0040	0.0212
2- 3	81.6	0.1178	-0.0018	0.1148	0.0048	0.0729	0.0476	0.0040	0.0213
3- 4	82.2	0.1483	-0.0024	0.1555	-0.0049	0.0716	0.0462	0.0040	0.0214
4- 5	82.7	0.0308	-0.0008	0.0503	-0.0187	0.0690	0.0437	0.0040	0.0213
5- 6	82.9	0.0312	-0.0004	0.0276	0.0041	0.0685	0.0432	0.0040	0.0212
6- 7	83.0	0.0426	-0.0003	0.0212	0.0217	0.0678	0.0426	0.0040	0.0212
7- 8	83.4	0.1022	-0.0021	0.1465	-0.0422	0.0679	0.0425	0.0040	0.0213
8- 9	84.1	0.1409	-0.0020	0.1368	0.0061	0.0667	0.0415	0.0040	0.0212
9-10	84.6	0.1509	-0.0014	0.0958	0.0565	0.0649	0.0397	0.0040	0.0212
10-11	85.4	0.1703	-0.0032	0.2278	-0.0543	0.0638	0.0386	0.0040	0.0212
11-12	85.9	0.0015	0.0001	-0.0033	0.0048	0.0608	0.0360	0.0040	0.0208
12-13	86.4	0.1889	-0.0027	0.1926	-0.0010	0.0617	0.0367	0.0040	0.0210
13-14	86.9	0.0137	-0.0001	0.0074	0.0064	0.0588	0.0342	0.0040	0.0207
14-15	87.5	0.2171	-0.0033	0.2418	-0.0215	0.0600	0.0352	0.0040	0.0208
15-16	88.0	0.0187	0.0001	-0.0069	0.0256	0.0565	0.0321	0.0040	0.0203
16-17	88.0	0.0341	-0.0001	0.0063	0.0278	0.0565	0.0321	0.0040	0.0204
17-18	88.5	0.1489	-0.0026	0.1939	-0.0424	0.0570	0.0325	0.0040	0.0205
18-19	89.4	0.1312	-0.0020	0.1562	-0.0229	0.0555	0.0314	0.0040	0.0201
19-20	89.8	0.0140	-0.0000	0.0020	0.0121	0.0536	0.0298	0.0040	0.0198
20-21	89.8	0.0285	0.0002	-0.0145	0.0429	0.0534	0.0296	0.0040	0.0198
21-22	90.2	0.1877	-0.0023	0.1816	0.0084	0.0547	0.0307	0.0040	0.0200
22-23	90.8	0.0365	-0.0008	0.0619	-0.0247	0.0522	0.0286	0.0040	0.0196

APPENDIX

TABLES 7.1 TO 7.9 FOR CHAPTER 7

Table 7.1 A Test Results of Acetone-Methanol System at 50° C by Using Two-Term Redlich-Kister Equation

ACETONE(1)-METHANOL(3) AT 50C

POBS mm.Hg.	PCOMP mm.Hg.	DP mm.Hg.	X_1	Y_1	Y_1OBS	GAMMA1 $\ln \gamma_1$	GAMMA2 $\ln \gamma_2$
421.00	420.19	0.81	0.003	0.008	0.0086	0.6092	0.0000
424.00	423.11	0.89	0.007	0.019	0.0203	0.6040	0.0000
430.00	429.19	0.81	0.016	0.041	0.0452	0.5931	0.0002
434.00	433.13	0.87	0.022	0.056	0.0603	0.5858	0.0003
442.00	440.78	1.22	0.034	0.083	0.0910	0.5716	0.0007
465.00	463.05	1.95	0.071	0.158	0.1690	0.5279	0.0031
471.00	468.53	2.47	0.081	0.175	0.1890	0.5167	0.0041
489.00	489.40	-0.40	0.121	0.241	0.2560	0.4717	0.0091
499.00	496.54	2.46	0.136	0.263	0.2660	0.4555	0.0115
510.00	510.30	-0.30	0.167	0.304	0.3150	0.4229	0.0173
524.00	525.89	-1.89	0.206	0.350	0.3520	0.3837	0.0263
544.00	543.73	0.27	0.257	0.403	0.3900	0.3354	0.0408
542.00	544.70	-2.70	0.260	0.406	0.4000	0.3327	0.0418
560.00	561.31	-1.31	0.316	0.456	0.4550	0.2837	0.0616
569.00	567.13	1.87	0.338	0.475	0.4790	0.2655	0.0704
570.00	571.87	-1.87	0.357	0.490	0.4990	0.2503	0.0785
580.00	580.81	-0.81	0.396	0.519	0.5330	0.2206	0.0965
581.00	582.73	-1.73	0.405	0.526	0.5380	0.2140	0.1009
583.00	584.20	-1.20	0.412	0.531	0.5430	0.2089	0.1044
593.00	591.99	1.01	0.452	0.559	0.5740	0.1812	0.1255
602.00	600.48	1.52	0.502	0.594	0.5700	0.1494	0.1545
613.00	610.97	2.03	0.578	0.644	0.6580	0.1070	0.2043
621.00	619.37	1.63	0.662	0.701	0.7000	0.0684	0.2672
615.00	620.30	-5.30	0.674	0.709	0.7280	0.0636	0.2768
623.00	620.52	2.48	0.677	0.711	0.7110	0.0625	0.2793
624.00	621.49	2.51	0.691	0.721	0.7180	0.0571	0.2908
623.00	621.81	1.19	0.696	0.724	0.7280	0.0553	0.2950
624.00	623.24	0.76	0.721	0.742	0.7460	0.0465	0.3163
621.00	623.94	-2.94	0.736	0.753	0.7540	0.0416	0.3294
625.00	625.01	-0.01	0.767	0.776	0.7820	0.0324	0.3573
624.00	625.54	-1.54	0.798	0.800	0.8160	0.0243	0.3864
626.00	625.59	0.41	0.812	0.812	0.8100	0.0211	0.3998
625.00	623.93	1.07	0.881	0.872	0.8710	0.0084	0.4695
623.00	621.11	1.89	0.924	0.914	0.9170	0.0034	0.5157
619.00	618.73	0.27	0.949	0.940	0.9410	0.0015	0.5435

```
B=    0.60776    C=   -0.00534    D=
NO.OF OBSERVATIONS =          35
NO.OF CONSTANTS =          2
SYSTEM TEMPERATURE AT     323.16DEG K
ST.DEV. OF CORRELATION IS       1.86MM.HG.
AV.% DEV OF CORRELATION IS      0.27
```

Table 7.1 B Test Results of Acetone-Methanol System at 50°C by Using Three-Term Redlich-Kister Equation

ACETONE(1)-METHANOL(3) AT 50C

POBS mm.Hg.	PCOMP mm.Hg.	DP mm.Hg.	X_1	Y_1	Y_1OBS	GAMMA1 $\ln \gamma_1$	GAMMA2 $\ln \gamma_2$
421.00	420.28	0.72	0.003	0.008	0.0086	0.6350	0.0000
424.00	423.32	0.68	0.007	0.020	0.0203	0.6287	0.0000
430.00	429.61	0.39	0.016	0.042	0.0452	0.6153	0.0002
434.00	433.67	0.33	0.022	0.057	0.0603	0.6066	0.0004
442.00	441.51	0.49	0.034	0.084	0.0910	0.5895	0.0009
465.00	464.04	0.96	0.071	0.159	0.1690	0.5383	0.0037
471.00	469.53	1.47	0.081	0.177	0.1890	0.5254	0.0048
489.00	490.25	-1.25	0.121	0.241	0.2560	0.4746	0.0104
499.00	497.29	1.71	0.136	0.263	0.2660	0.4566	0.0131
510.00	510.79	-0.79	0.167	0.303	0.3150	0.4212	0.0194
524.00	526.04	-2.04	0.206	0.349	0.3520	0.3796	0.0289
544.00	543.48	0.52	0.257	0.401	0.3900	0.3297	0.0440
542.00	544.43	-2.43	0.260	0.404	0.4000	0.3269	0.0449
560.00	560.75	-0.75	0.316	0.454	0.4550	0.2777	0.0648
569.00	566.50	2.50	0.338	0.472	0.4790	0.2598	0.0735
570.00	571.20	-1.20	0.357	0.488	0.4990	0.2450	0.0814
580.00	580.11	-0.11	0.396	0.518	0.5330	0.2162	0.0988
581.00	582.04	-1.04	0.405	0.524	0.5380	0.2098	0.1030
583.00	583.50	-0.50	0.412	0.530	0.5430	0.2050	0.1064
593.00	591.35	1.65	0.452	0.559	0.5740	0.1785	0.1265
602.00	599.97	2.03	0.502	0.593	0.5700	0.1482	0.1541
613.00	610.72	2.28	0.578	0.645	0.6580	0.1079	0.2015
621.00	619.45	1.55	0.662	0.702	0.7000	0.0708	0.2621
615.00	620.43	-5.43	0.674	0.710	0.7280	0.0661	0.2715
623.00	620.66	2.34	0.677	0.713	0.7110	0.0650	0.2739
624.00	621.69	2.31	0.691	0.722	0.7180	0.0597	0.2852
623.00	622.03	0.97	0.696	0.726	0.7280	0.0579	0.2893
624.00	623.56	0.44	0.721	0.744	0.7460	0.0492	0.3105
621.00	624.32	-3.32	0.736	0.755	0.7540	0.0443	0.3236
625.00	625.51	-0.51	0.767	0.778	0.7820	0.0349	0.3520
624.00	626.14	-2.14	0.798	0.801	0.8160	0.0266	0.3820
626.00	626.24	-0.24	0.812	0.813	0.8100	0.0232	0.3961
625.00	624.72	0.28	0.881	0.872	0.8710	0.0096	0.4711
623.00	621.84	1.16	0.924	0.913	0.9170	0.0040	0.5230
619.00	619.34	-0.34	0.949	0.940	0.9410	0.0018	0.5551

B= 0.60470 C= -0.00721 D= 0.02785 E=

NO.OF OBSERVATIONS = 35

NO.OF CONSTANTS = 3

SYSTEM TEMPERATURE AT 323.16DEG K

ST.DEV. OF CORRELATION IS 1.79MM.HG.

AV.% DEV OF CORRELATION IS 0.24

Table 7.1 C Test Results of Acetone-Methanol System at 50° C by Using Four-Term Redlich-Kister Equation

ACETONE(1)-METHANOL(3) AT 50C

POBS	PCOMP	DP	X_1	Y_1	Y_1OBS	GAMMA1	GAMMA2
m.m. Hg.	m.m. Hg.	m.m. Hg.				$\ln \gamma_1$	$\ln \gamma_2$
421.00	420.39	0.61	0.003	0.009	0.0086	0.6658	0.0000
424.00	423.57	0.43	0.007	0.020	0.0203	0.6572	0.0001
430.00	430.09	-0.09	0.016	0.043	0.0452	0.6393	0.0003
434.00	434.25	-0.25	0.022	0.058	0.0603	0.6278	0.0005
442.00	442.23	-0.23	0.034	0.085	0.0910	0.6056	0.0011
465.00	464.71	0.29	0.071	0.159	0.1690	0.5424	0.0046
471.00	470.11	0.89	0.081	0.177	0.1890	0.5271	0.0059
489.00	490.37	-1.37	0.121	0.240	0.2560	0.4698	0.0123
499.00	497.23	1.77	0.136	0.261	0.2660	0.4505	0.0151
510.00	510.42	-0.42	0.167	0.301	0.3150	0.4136	0.0217
524.00	525.42	-1.42	0.206	0.347	0.3520	0.3720	0.0312
544.00	542.81	1.19	0.257	0.399	0.3900	0.3242	0.0456
542.00	543.77	-1.77	0.260	0.402	0.4000	0.3216	0.0465
560.00	560.31	-0.31	0.316	0.454	0.4550	0.2758	0.0650
569.00	566.20	2.80	0.338	0.472	0.4790	0.2592	0.0731
570.00	571.02	-1.02	0.357	0.488	0.4990	0.2454	0.0804
580.00	580.19	-0.19	0.396	0.519	0.5330	0.2183	0.0968
581.00	582.17	-1.17	0.405	0.526	0.5380	0.2123	0.1008
583.00	583.68	-0.68	0.412	0.531	0.5430	0.2076	0.1040
593.00	591.74	1.26	0.452	0.560	0.5740	0.1820	0.1235
602.00	600.53	1.47	0.502	0.595	0.5700	0.1520	0.1509
613.00	611.34	1.66	0.578	0.646	0.6580	0.1103	0.1999
621.00	619.86	1.14	0.662	0.702	0.7000	0.0705	0.2649
615.00	620.79	-5.79	0.674	0.710	0.7280	0.0654	0.2751
623.00	621.01	1.99	0.677	0.712	0.7110	0.0642	0.2777
624.00	621.98	2.02	0.691	0.721	0.7180	0.0585	0.2900
623.00	622.30	0.70	0.696	0.725	0.7280	0.0565	0.2944
624.00	623.70	0.30	0.721	0.742	0.7460	0.0472	0.3171
621.00	624.39	-3.39	0.736	0.753	0.7540	0.0420	0.3312
625.00	625.40	-0.40	0.767	0.776	0.7820	0.0321	0.3610
624.00	625.84	-1.84	0.798	0.799	0.8160	0.0236	0.3917
626.00	625.84	0.16	0.812	0.811	0.8100	0.0202	0.4058
625.00	623.89	1.11	0.881	0.871	0.8710	0.0074	0.4758
623.00	620.89	2.11	0.924	0.914	0.9170	0.0028	0.5184
619.00	618.47	0.53	0.949	0.940	0.9410	0.0012	0.5421

```
B=    0.60577   C=    0.00678    D=    0.02336    E=   -0.04997    F=
NO.OF OBSERVATIONS =          35
NO.OF CONSTANTS =          4
SYSTEM TEMPERATURE AT     323.16DEG K
ST.DEV. OF CORRELATION IS       1.75MM.HG.
AV.% DEV OF CORRELATION IS       0.21
```

Table 7.1 D Test Results of Acetone-Methanol System at 50° C by Using Five-Term Redlich-Kister Equation

ACETONE(1)-METHANOL(3) AT 50C

POBS mm.Hg.	PCOMP mm.Hg.	DP mm.Hg.	X_1	Y_1	Y_1OBS	GAMMA1 $\ln \gamma_1$	GAMMA2 $\ln \gamma_2$
421.00	420.49	0.51	0.003	0.009	0.0086	0.6933	0.0000
424.00	423.79	0.21	0.007	0.021	0.0203	0.6818	0.0001
430.00	430.48	-0.48	0.016	0.044	0.0452	0.6585	0.0003
434.00	434.72	-0.72	0.022	0.059	0.0603	0.6438	0.0006
442.00	442.76	-0.76	0.034	0.086	0.0910	0.6160	0.0014
465.00	464.98	0.02	0.071	0.159	0.1690	0.5412	0.0055
471.00	470.27	0.73	0.081	0.176	0.1890	0.5241	0.0069
489.00	490.12	-1.12	0.121	0.239	0.2560	0.4631	0.0137
499.00	496.87	2.13	0.136	0.260	0.2660	0.4435	0.0166
510.00	509.95	0.05	0.167	0.300	0.3150	0.4074	0.0230
524.00	524.98	-0.98	0.206	0.345	0.3520	0.3681	0.0320
544.00	542.62	1.38	0.257	0.399	0.3900	0.3236	0.0454
542.00	543.59	-1.59	0.260	0.402	0.4000	0.3212	0.0463
560.00	560.45	-0.45	0.316	0.454	0.4550	0.2778	0.0638
569.00	566.43	2.57	0.338	0.473	0.4790	0.2616	0.0717
570.00	571.31	-1.31	0.357	0.489	0.4990	0.2480	0.0789
580.00	580.54	-0.54	0.396	0.520	0.5330	0.2207	0.0954
581.00	582.52	-1.52	0.405	0.526	0.5380	0.2146	0.0995
583.00	584.03	-1.03	0.412	0.532	0.5430	0.2098	0.1028
593.00	592.03	0.97	0.452	0.561	0.5740	0.1833	0.1230
602.00	600.67	1.33	0.502	0.595	0.5700	0.1518	0.1517
613.00	611.22	1.78	0.578	0.645	0.6580	0.1086	0.2024
621.00	619.60	1.40	0.662	0.701	0.7000	0.0690	0.2670
615.00	620.52	-5.52	0.674	0.709	0.7280	0.0641	0.2769
623.00	620.74	2.26	0.677	0.711	0.7110	0.0629	0.2794
624.00	621.71	2.29	0.691	0.721	0.7180	0.0575	0.2910
623.00	622.04	0.96	0.696	0.724	0.7280	0.0557	0.2952
624.00	623.46	0.54	0.721	0.742	0.7460	0.0469	0.3166
621.00	624.17	-3.17	0.736	0.753	0.7540	0.0420	0.3296
625.00	625.25	-0.25	0.767	0.776	0.7820	0.0329	0.3572
624.00	625.79	-1.79	0.798	0.801	0.8160	0.0250	0.3857
626.00	625.85	0.15	0.812	0.812	0.8100	0.0218	0.3988
625.00	624.29	0.71	0.881	0.872	0.8710	0.0093	0.4681
623.00	621.51	1.49	0.924	0.914	0.9170	0.0040	0.5168
619.00	619.12	-0.12	0.949	0.940	0.9410	0.0019	0.5482

B= 0.60701 C= 0.00519 D= -0.00259 E= -0.04479 F= 0.05793

NO.OF OBSERVATIONS = 35

NO.OF CONSTANTS = 5

SYSTEM TEMPERATURE AT 323.16DEG K

ST.DEV. OF CORRELATION IS 1.75MM.HG.

AV.% DEV OF CORRELATION IS 0.21

TABLE 7. 2

Summary of the Data Reduction for the System Benzene (1) - n-Octane (2)

No. of terms	B	C	D	E	F	$\ln\gamma_1$	$\ln\gamma_2$	Pressure Correlation St. Dev. mm. Hg.	Av. %Dev.	Max. % Dev.
25° C										
2	.7678	.4849				.2830	1.2527	1.87	3.65	4.3
3	.7908	.4188	.2685			.6404	1.4781	1.52	2.42	2.9
4	.8181	.4865	.2879	-.3603		.9798	1.2321	1.17	1.07	2.0
5	.8184	.4857	.2815	-.3593	.0141	.9877	1.2404	1.26	1.06	2.0
35° C										
2	.6801	.3483				.3318	1.0284	2.37	2.88	4.3
3	.6944	.2962	.2197			.6179	1.2104	1.96	1.99	2.9
4	.7182	.3645	.2388	-.3396		.9321	.9818	1.39	0.83	2.3
5	.7180	.3648	.2420	-.3401	-.0070	.9282	.9778	1.49	0.83	2.3
45° C										
2	.5899	.2408				.3491	.8307	3.03	2.30	8.3
3	.5989	.1968	.1884			.5905	.9841	2.55	1.65	4.0
4	.6189	.2629	.2080	-.3105		.8744	.7793	1.77	.68	2.6
5	.6179	.2650	.2269	-.3125	-.0402	.8520	.7569	1.88	.69	2.4

								Pressure Correlation		
No. of terms	B	C	D	E	F	$\ln\gamma_1$	$\ln\gamma_2$	St. Dev. mm. Hg.	Av. % Dev.	Max. % Dev.
55° C										
2	.5009	.1358				.3652	.6367	3.71	1.82	6.1
3	.5055	.0990	.1619			.5684	.7664	3.12	1.23	4.7
4	.5194	.1520	.1793	-.2364		.7831	.6142	2.49	.594	4.8
5	.5180	.1545	.2040	-.2382	-.0522	.7534	.5860	2.65	.634	5.0
65° C										
2	.3892	.0486				.3406	.4378	4.58	1.45	7.7
3	.3911	.0173	.1321			.5060	.5406	4.05	1.02	7.0
4	.4030	.0702	.1523	-.2251		.7103	.4004	3.23	0.38	8.1
5	.4018	.0720	.1736	-.2258	-.0444	.6848	.3772	3.44	.36	8.3

Table 7.3 Computed Results of the System Benzene-n Octane System at 25° C.

POBS m.m.Hg.	PCOMP m.m.Hg.	DP m.m.Hg.	X_1	Y_1	GAMMA1 $\ln \gamma_1$	GAMMA2 $\ln \gamma_2$	ZI	ZII
95.19	95.19	0.0	1.000	1.000	0.0	1.2321	1.000	1.016
93.76	93.28	0.48	0.959	0.981	0.0024	1.1211	1.000	1.016
87.90	88.79	-0.89	0.849	0.947	0.0409	0.7681	0.999	1.015
86.60	86.52	0.08	0.776	0.936	0.0925	0.5437	0.999	1.015
83.20	82.04	1.16	0.635	0.921	0.2232	0.2233	0.999	1.014
69.60	71.59	-1.99	0.478	0.888	0.3369	0.0726	0.998	1.012
61.20	59.18	2.02	0.364	0.839	0.3625	0.0525	0.997	1.009
46.70	47.26	-0.56	0.265	0.768	0.3664	0.0509	0.996	1.007
37.97	38.44	-0.47	0.187	0.688	0.3986	0.0420	0.995	1.005
26.40	26.09	0.31	0.073	0.492	0.6199	0.0123	0.994	1.003
20.10	20.08	0.02	0.030	0.316	0.8029	0.0026	0.993	1.001
14.10	14.10	0.0	0.0	0.0	0.9798	0.0	0.993	1.000

```
B=    0.81807    C=    0.48649    D=    0.28789    E=  -0.36034    F=
NO.OF OBSERVATIONS =          12
NO.OF CONSTANTS =           4
SYSTEM TEMPERATURE AT     298.16DEG K
ST.DEV. OF CORRELATION IS      1.17MM.HG.
AV.% DEV OF CORRELATION IS      1.07
```

Table 7.4 Computed Results of the System Benzene-n Octane System at 35° C.

POBS m.m.Hg	PCOMP m.m.Hg.	DP m.m.Hg.	X_1	Y_1	GAMMA1 $\ln\gamma_1$	GAMMA2 $\ln\gamma_2$	ZI	ZII
147.90	147.90	0.0	1.000	1.000	0.0	0.9818	1.000	1.022
145.40	144.50	0.90	0.959	0.983	0.0015	0.9153	1.000	1.021
135.20	136.40	-1.20	0.849	0.948	0.0300	0.6576	0.999	1.020
132.10	132.00	0.10	0.776	0.933	0.0714	0.4783	0.999	1.019
124.80	123.38	1.42	0.635	0.911	0.1808	0.2108	0.998	1.018
104.70	107.03	-2.33	0.478	0.871	0.2805	0.0791	0.997	1.015
91.50	89.25	2.25	0.364	0.817	0.3072	0.0584	0.995	1.012
71.86	72.42	-0.56	0.265	0.741	0.3186	0.0534	0.994	1.009
59.30	59.84	-0.54	0.187	0.658	0.3581	0.0424	0.993	1.007
42.10	41.75	0.35	0.073	0.459	0.5827	0.0120	0.992	1.003
32.80	32.82	-0.02	0.030	0.288	0.7612	0.0025	0.991	1.002
24.00	24.00	0.0	0.0	0.0	0.9321	0.0	0.990	1.000

```
B=     0.71822    C=     0.36447    D=     0.23877     F=   -0.33961     F=
NO.OF OBSERVATIONS =              12
NO.OF CONSTANTS =              4
SYSTEM TEMPERATURE AT      308.16DEG K
ST.DEV. OF CORRELATION IS         1.39MM.HG.
AV.% DEV OF CORRELATION IS         0.83
```

Ta

Table 7.5 Computed Results of the System Benzene-n Octane System at 45° C.

POBS m.m.Hg.	PCOMP mm.Hg.	DP m.m.Hg.	X_1	Y_1	GAMMA1 $\ln \gamma_1$	GAMMA2 $\ln \gamma_2$	ZI	ZII
223.10	223.10	0.0	1.000	1.000	0.0	0.7793	1.000	1.028
219.80	217.52	2.28	0.959	0.984	0.0009	0.7416	1.000	1.028
202.30	204.01	-1.71	0.849	0.948	0.0221	0.5534	0.999	1.026
196.10	196.31	-0.21	0.776	0.930	0.0549	0.4112	0.998	1.025
183.20	181.21	1.99	0.635	0.902	0.1448	0.1918	0.997	1.022
153.50	156.19	-2.69	0.478	0.854	0.2289	0.0309	0.995	1.019
133.40	131.15	2.25	0.364	0.793	0.2539	0.0618	0.994	1.015
107.50	107.93	-0.43	0.265	0.713	0.2701	0.0546	0.992	1.011
89.95	90.46	-0.51	0.187	0.627	0.3146	0.0421	0.991	1.008
65.10	64.78	0.32	0.073	0.426	0.5388	0.0115	0.989	1.004
51.90	51.99	-0.09	0.030	0.260	0.7111	0.0024	0.988	1.002
39.50	39.50	0.0	0.0	0.0	0.8744	0.0	0.987	1.000

```
B=    0.61885    C=    0.26293    D=    0.20802    E=  -0.31050    F=
NO.OF OBSERVATIONS =          12
NO.OF CONSTANTS =           4
SYSTEM TEMPERATURE AT     318.16DEG K
ST.DEV. OF CORRELATION IS       1.77MM.HG.
AV.% DEV OF CORRELATION IS        0.68
```

Table 7.6 Computed Results of the System Benzene-n Octane System at 55° C

POBS m.m.Hg.	PCOMP m.m.Hg.	DP m.m.Hg.	X_1	Y_1	GAMMA1 $\ln\gamma_1$	GAMMA2 $\ln\gamma_2$	ZI	ZII
328.10	328.10	0.0	1.000	1.000	0.0	0.6142	1.000	1.036
324.30	319.44	4.86	0.959	0.985	0.0007	0.5852	0.999	1.035
295.80	298.01	-2.21	0.849	0.949	0.0166	0.4434	0.998	1.033
284.10	285.13	-1.03	0.776	0.929	0.0413	0.3367	0.997	1.031
262.40	259.54	2.86	0.635	0.892	0.1089	0.1717	0.996	1.027
219.30	222.22	-2.92	0.478	0.835	0.1750	0.0850	0.993	1.022
189.90	188.41	1.49	0.364	0.769	0.2012	0.0654	0.991	1.018
158.30	157.67	0.63	0.265	0.686	0.2269	0.0539	0.989	1.014
133.20	134.06	-0.86	0.187	0.598	0.2783	0.0393	0.988	1.010
97.95	97.88	0.07	0.073	0.393	0.4896	0.0102	0.985	1.005
80.10	79.95	0.15	0.030	0.231	0.6418	0.0021	0.984	1.003
63.10	63.10	0.0	0.0	0.0	0.7831	0.0	0.983	1.000

```
B=    0.51939    C=    0.15198    D=    0.17928    E=   -0.23643    F=
NO.OF OBSERVATIONS =          12
NO.OF CONSTANTS =            4
SYSTEM TEMPERATURE AT     328.16DEG K
ST.DEV. OF CORRELATION IS       2.49MM.HG.
AV.% DEV OF CORRELATION IS       0.59
```

Table 7.7 Computed Results of the System Benzene-n Octane System at 65° C

POBS mm.Hg.	PCOMP m.m.Hg.	DP mm.Hg.	X_1	Y_1	GAMMA1 $\ln\gamma_1$	GAMMA2 $\ln\gamma_2$	ZI	ZII
472.10	472.10	0.0	1.000	1.000	0.0	0.4004	1.000	1.046
466.70	458.59	8.11	0.959	0.986	0.0000	0.4042	0.999	1.044
422.70	424.61	-1.91	0.849	0.949	0.0085	0.3340	0.997	1.041
401.80	403.95	-2.15	0.776	0.927	0.0250	0.2627	0.996	1.038
366.40	363.73	2.67	0.635	0.883	0.0744	0.1427	0.994	1.033
308.30	309.71	-1.41	0.478	0.817	0.1235	0.0782	0.991	1.027
263.60	263.79	-0.19	0.364	0.743	0.1432	0.0635	0.988	1.021
223.70	223.04	0.66	0.265	0.654	0.1669	0.0530	0.986	1.016
191.90	191.92	-0.02	0.187	0.564	0.2177	0.0385	0.984	1.012
143.90	143.96	-0.06	0.073	0.359	0.4253	0.0099	0.981	1.006
119.90	120.18	-0.28	0.030	0.205	0.5734	0.0020	0.979	1.003
97.95	97.95	0.0	0.0	0.0	0.7103	0.0	0.978	1.000

```
B=    0.40296    C=    0.07018    D=    0.15237    E=   -0.22513    F=
NO.OF OBSERVATIONS =          12
NO.OF CONSTANTS =           4
SYSTEM TEMPERATURE AT     338.16DEG K
ST.DEV. OF CORRELATION IS       3.23MM.HG.
AV.% DEV OF CORRELATION IS       0.38
```

Table 7.8 Correlation Results of the Five-Junction Copper Constantan Thermopile

ε_{obs}	ε_{comp}	$\Delta\varepsilon$	$\%\Delta\varepsilon$	t°
μv.	μv.	μv.		°C
21463.4	21462.8	0.6	0.00	99.93
21438.8	21441.8	-3.0	-0.01	99.84
21437.5	21439.4	-1.9	-0.01	99.83
21427.3	21425.4	1.9	0.01	99.77
21384.7	21380.9	3.8	0.02	99.58
20266.4	20263.6	2.8	0.01	94.79
19140.6	19145.5	-4.9	-0.03	89.96
19107.0	19104.0	3.0	0.02	89.78
15721.0	15724.8	-3.8	-0.02	74.94
15718.0	15721.5	-3.5	-0.02	74.93
15716.0	15718.1	-2.1	-0.01	74.91
13480.5	13480.9	-0.4	-0.00	64.88
13467.2	13464.3	2.9	0.02	64.81
13465.2	13462.1	3.1	0.02	64.80
11296.0	11299.3	-3.3	-0.03	54.93
11248.0	11249.3	-1.3	-0.01	54.70
9063.0	9060.3	2.7	0.03	44.52
9042.1	9039.0	3.1	0.03	44.42

0 A=385.569580 B=-80815.187500 C=0.002374

STANDARD DEVIATION OF CURVE-FITTING IS 3.16960621 μv.
AVERAGE O/O DEVIATION IS 0.01775086
NO.OF OBSERVATION = 18

Table 7.9 Calibration Table of the Five-Junction Copper Constantan Thermopile

CALIBRATION TABLE FOR 5-JUNCTION COPPER CONSTNTAN THERMOPILE

t°C	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	1·0	t°C
1	194.	213.	233.	252.	272.	291.	311.	330.	349.	369.	388.	1
2	388.	408.	427.	447.	466.	486.	505.	525.	544.	564.	583.	2
3	583.	603.	622.	642.	661.	681.	700.	720.	739.	759.	779.	3
4	779.	798.	818.	837.	857.	876.	896.	915.	935.	955.	974.	4
5	974.	994.	1013.	1033.	1053.	1072.	1092.	1112.	1131.	1151.	1171.	5
6	1171.	1190.	1210.	1229.	1249.	1269.	1288.	1308.	1328.	1347.	1367.	6
7	1367.	1387.	1406.	1426.	1446.	1466.	1485.	1505.	1525.	1544.	1564.	7
8	1564.	1584.	1604.	1623.	1643.	1663.	1683.	1702.	1722.	1742.	1762.	8
9	1762.	1782.	1801.	1821.	1841.	1861.	1881.	1900.	1920.	1940.	1960.	9
10	1960.	1980.	1999.	2019.	2039.	2059.	2079.	2099.	2119.	2138.	2158.	10
11	2158.	2178.	2198.	2218.	2238.	2258.	2278.	2297.	2317.	2337.	2357.	11
12	2357.	2377.	2397.	2417.	2437.	2457.	2477.	2497.	2517.	2536.	2556.	12
13	2556.	2576.	2596.	2616.	2636.	2656.	2676.	2696.	2716.	2736.	2756.	13
14	2756.	2776.	2796.	2816.	2836.	2856.	2876.	2896.	2916.	2936.	2956.	14
15	2956.	2977.	2997.	3017.	3037.	3057.	3077.	3097.	3117.	3137.	3157.	15
16	3157.	3177.	3197.	3217.	3237.	3258.	3278.	3298.	3318.	3338.	3358.	16
17	3358.	3378.	3398.	3419.	3439.	3459.	3479.	3499.	3519.	3540.	3560.	17
18	3560.	3580.	3600.	3620.	3640.	3661.	3681.	3701.	3721.	3741.	3762.	18
19	3762.	3782.	3802.	3822.	3843.	3863.	3883.	3903.	3924.	3944.	3964.	19
20	3964.	3984.	4005.	4025.	4045.	4065.	4086.	4106.	4126.	4147.	4167.	20
21	4167.	4187.	4208.	4228.	4248.	4268.	4289.	4309.	4329.	4350.	4370.	21
22	4370.	4391.	4411.	4431.	4452.	4472.	4492.	4513.	4533.	4554.	4574.	22
23	4574.	4594.	4615.	4635.	4655.	4676.	4696.	4717.	4737.	4758.	4778.	23
24	4778.	4798.	4819.	4839.	4860.	4880.	4901.	4921.	4942.	4962.	4983.	24
25	4983.	5003.	5024.	5044.	5064.	5085.	5105.	5126.	5146.	5167.	5188.	25

t°C	0	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0	t°C
26	5188.	5208.	5229.	5249.	5270.	5290.	5311.	5331.	5352.	5372.	5393.	26
27	5393.	5413.	5434.	5455.	5475.	5496.	5516.	5537.	5558.	5578.	5599.	27
28	5599.	5619.	5640.	5661.	5681.	5702.	5722.	5743.	5764.	5784.	5805.	28
29	5805.	5826.	5846.	5867.	5888.	5908.	5929.	5950.	5970.	5991.	6012.	29
30	6012.	6032.	6053.	6074.	6095.	6115.	6136.	6157.	6177.	6198.	6219.	30
31	6219.	6240.	6260.	6281.	6302.	6323.	6343.	6364.	6385.	6406.	6426.	31
32	6426.	6447.	6468.	6489.	6510.	6530.	6551.	6572.	6593.	6614.	6634.	32
33	6634.	6655.	6676.	6697.	6718.	6739.	6759.	6780.	6801.	6822.	6843.	33
34	6843.	6864.	6885.	6905.	6926.	6947.	6968.	6989.	7010.	7031.	7052.	34
35	7052.	7072.	7093.	7114.	7135.	7156.	7177.	7198.	7219.	7240.	7261.	35
36	7261.	7282.	7303.	7324.	7345.	7366.	7387.	7408.	7429.	7449.	7470.	36
37	7470.	7491.	7512.	7533.	7554.	7575.	7596.	7617.	7638.	7660.	7681.	37
38	7681.	7702.	7723.	7744.	7765.	7786.	7807.	7828.	7849.	7870.	7891.	38
39	7891.	7912.	7933.	7954.	7975.	7996.	8017.	8039.	8060.	8081.	8102.	39
40	8102.	8123.	8144.	8165.	8186.	8207.	8229.	8250.	8271.	8292.	8313.	40
41	8313.	8334.	8355.	8377.	8398.	8419.	8440.	8461.	8483.	8504.	8525.	41
42	8525.	8546.	8567.	8589.	8610.	8631.	8652.	8673.	8695.	8716.	8737.	42
43	8737.	8758.	8780.	8801.	8822.	8843.	8865.	8886.	8907.	8928.	8950.	43
44	8950.	8971.	8992.	9013.	9035.	9056.	9077.	9099.	9120.	9141.	9163.	44
45	9163.	9184.	9205.	9227.	9248.	9269.	9291.	9312.	9333.	9355.	9376.	45
46	9376.	9397.	9419.	9440.	9461.	9483.	9504.	9526.	9547.	9568.	9590.	46
47	9590.	9611.	9633.	9654.	9675.	9697.	9718.	9740.	9761.	9782.	9804.	47
48	9804.	9825.	9847.	9868.	9890.	9911.	9933.	9954.	9975.	9997.	10018.	48
49	10018.	10040.	10061.	10083.	10104.	10126.	10147.	10169.	10190.	10212.	10233.	49
50	10233.	10255.	10277.	10298.	10320.	10341.	10363.	10384.	10406.	10427.	10449.	50

t°c	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	1.0	t°c
51	10449.	10470.	10492.	10514.	10535.	10557.	10578.	10600.	10621.	10643.	10665.	51
52	10665.	10686.	10708.	10729.	10751.	10773.	10794.	10816.	10838.	10859.	10881.	52
53	10881.	10902.	10924.	10946.	10967.	10989.	11011.	11032.	11054.	11076.	11097.	53
54	11097.	11119.	11141.	11163.	11184.	11206.	11228.	11249.	11271.	11293.	11314.	54
55	11314.	11336.	11358.	11380.	11401.	11423.	11445.	11467.	11488.	11510.	11532.	55
56	11532.	11554.	11575.	11597.	11619.	11641.	11662.	11684.	11706.	11728.	11750.	56
57	11750.	11771.	11793.	11815.	11837.	11859.	11881.	11902.	11924.	11946.	11968.	57
58	11968.	11990.	12012.	12033.	12055.	12077.	12099.	12121.	12143.	12165.	12186.	58
59	12186.	12208.	12230.	12252.	12274.	12296.	12318.	12340.	12362.	12383.	12405.	59
60	12405.	12427.	12449.	12471.	12493.	12515.	12537.	12559.	12581.	12603.	12625.	60
61	12625.	12647.	12669.	12691.	12713.	12735.	12757.	12779.	12801.	12823.	12845.	61
62	12845.	12867.	12889.	12911.	12933.	12955.	12977.	12999.	13021.	13043.	13065.	62
63	13065.	13087.	13109.	13131.	13153.	13175.	13197.	13219.	13241.	13263.	13285.	63
64	13285.	13307.	13330.	13352.	13374.	13396.	13418.	13440.	13462.	13484.	13506.	64
65	13506.	13528.	13551.	13573.	13595.	13617.	13639.	13661.	13683.	13706.	13728.	65
66	13728.	13750.	13772.	13794.	13816.	13838.	13861.	13883.	13905.	13927.	13949.	66
67	13949.	13972.	13994.	14016.	14038.	14060.	14083.	14105.	14127.	14149.	14172.	67
68	14172.	14194.	14216.	14238.	14260.	14283.	14305.	14327.	14349.	14372.	14394.	68
69	14394.	14416.	14439.	14461.	14483.	14505.	14528.	14550.	14572.	14595.	14617.	69
70	14617.	14639.	14662.	14684.	14706.	14729.	14751.	14773.	14796.	14818.	14840.	70
71	14840.	14863.	14885.	14907.	14930.	14952.	14974.	14997.	15019.	15041.	15064.	71
72	15064.	15086.	15109.	15131.	15153.	15176.	15198.	15221.	15243.	15266.	15288.	72
73	15288.	15310.	15333.	15355.	15378.	15400.	15423.	15445.	15467.	15490.	15512.	73
74	15512.	15535.	15557.	15580.	15602.	15625.	15647.	15670.	15692.	15715.	15737.	74
75	15737.	15760.	15782.	15805.	15827.	15850.	15872.	15895.	15917.	15940.	15962.	75

t°C	0	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0	t°C
76	15962.	15985.	16007.	16030.	16053.	16075.	16098.	16120.	16143.	16165.	16188.	76
77	16188.	16211.	16233.	16256.	16278.	16301.	16323.	16346.	16369.	16391.	16414.	77
78	16414.	16437.	16459.	16482.	16504.	16527.	16550.	16572.	16595.	16618.	16640.	78
79	16640.	16663.	16686.	16708.	16731.	16754.	16776.	16799.	16822.	16844.	16867.	79
80	16867.	16890.	16912.	16935.	16958.	16980.	17003.	17026.	17049.	17071.	17094.	80
81	17094.	17117.	17140.	17162.	17185.	17208.	17231.	17253.	17276.	17299.	17322.	81
82	17322.	17344.	17367.	17390.	17413.	17435.	17458.	17481.	17504.	17527.	17549.	82
83	17549.	17572.	17595.	17618.	17641.	17663.	17686.	17709.	17732.	17755.	17778.	83
84	17778.	17800.	17823.	17846.	17869.	17892.	17915.	17938.	17960.	17983.	18006.	84
85	18006.	18029.	18052.	18075.	18098.	18121.	18144.	18166.	18189.	18212.	18235.	85
86	18235.	18258.	18281.	18304.	18327.	18350.	18373.	18396.	18419.	18442.	18464.	86
87	18464.	18487.	18510.	18533.	18556.	18579.	18602.	18625.	18648.	18671.	18694.	87
88	18694.	18717.	18740.	18763.	18786.	18809.	18832.	18855.	18878.	18901.	18924.	88
89	18924.	18947.	18970.	18993.	19016.	19039.	19063.	19086.	19109.	19132.	19155.	89
90	19155.	19178.	19201.	19224.	19247.	19270.	19293.	19316.	19339.	19362.	19386.	90
91	19386.	19409.	19432.	19455.	19478.	19501.	19524.	19547.	19570.	19594.	19617.	91
92	19617.	19640.	19663.	19686.	19709.	19732.	19756.	19779.	19802.	19825.	19848.	92
93	19848.	19871.	19895.	19918.	19941.	19964.	19987.	20011.	20034.	20057.	20080.	93
94	20080.	20103.	20127.	20150.	20173.	20196.	20219.	20243.	20266.	20289.	20312.	94
95	20312.	20336.	20359.	20382.	20405.	20429.	20452.	20475.	20498.	20522.	20545.	95
96	20545.	20568.	20592.	20615.	20638.	20662.	20685.	20708.	20731.	20755.	20778.	96
97	20778.	20801.	20825.	20848.	20871.	20895.	20918.	20941.	20965.	20988.	21011.	97
98	21011.	21035.	21058.	21082.	21105.	21128.	21152.	21175.	21198.	21222.	21245.	98
99	21245.	21269.	21292.	21315.	21339.	21362.	21386.	21409.	21432.	21456.	21479.	99

APPENDIX VI

COMPUTER PROGRAMS

APPENDIX VI

COMPUTER PROGRAMS

VI.1 FITTING BINARY ISOTHERMAL TOTAL PRESSURE AND LIQUID COMPOSITION DATA AT HIGH PRESSURES TO THE SYMMETRIC ONE- TO FIVE-TERM REDLICH-KISTER EQUATION

VI.1.1 GENERAL INFORMATION

PURPOSE - Calculating vapor phase composition from total pressure measurement and liquid composition data for the systems at high pressure and isothermal condition.

LANGUAGE - FORTRAN IV in G level.

SUBROUTINES REQUIRED - VOLPAR (Refs. 22, 23)

PHIMIX (Refs. 22, 25), CUBEQN (Ref. 22) and SOLVEJ .

INPUT AND OUTPUT COMMANDS:

Input - READ (1, FORMAT's statement number)
Print - WRITE (3, FORMAT's statement number)
Card output - WRITE (2, FORMAT's statement number)
Printing control:
  Single space - blank in first column
  Double space - 0 in first column
  Starting a new page - 1 in first column

VI.1.2 INPUT and OUTPUT

INPUT:

Card 1 : The title of the problem can be entered into the card from columns 1 to 80.

Card 2 : It bears the control variables which are distributed as follows:

Column	
1 - 5	N DATA, the number of observations
6 - 10	NZ, the minimum number of terms desired in the Redlich-Kister equation
11 - 15	MAX, the maximum number of terms desired in the Redlich-Kister equation
16 - 20	weight option if 0, WT = 1 1, $WT = 1/P_{obs}^2$

Cards 3 and 4 : They bear the pure component properties which are required in the evaluation of the supporting quantities, one card per each component. Their distributions are:

Column	
1 - 8	P_c, psia
9 - 16	V_c, cu. ft. per pound mole
17 - 24	T_c, °R
25 - 30	Acentric factor, dimensionless,

Card 5 : It bears the information of the system temperature, and saturation pressures of pure components, and also the gas constant.

Column	
1 - 10	T, system temperature, °R
11 - 20	P_1^s, vapor pressure of the first component, psia

21 - 30	P_2^s, vapor pressure of the second compoent, psia
31 - 40	Gas constant, 10.73 $(ft^3)(lb)/(in^2)(lb\text{-}mole)(°R)$

Card 6 : It bears the initial estimation of the adjustable parameters in Redlich-Kister equation, in F-FORMAT, 10 columns per field.

Cards 7 to (nobs + 6) : They bear the experimental data in F-FORMAT, one card per point.

Column	
1 - 10	Pressure, psia
11 - 20	x_2
21 - 30	y_2 (option)

OUTPUT : see flow diagram

VI. 1. 3 FLOW DIAGRAM (see figure VI. 1)

Figure VI.1

Flow Diagram of the Program "Fitting Binary Isothermal Total Pressure and Liquid Composition Data at High Pressure to the Symmetric One- to Five-Term Redlich-Kister Equation

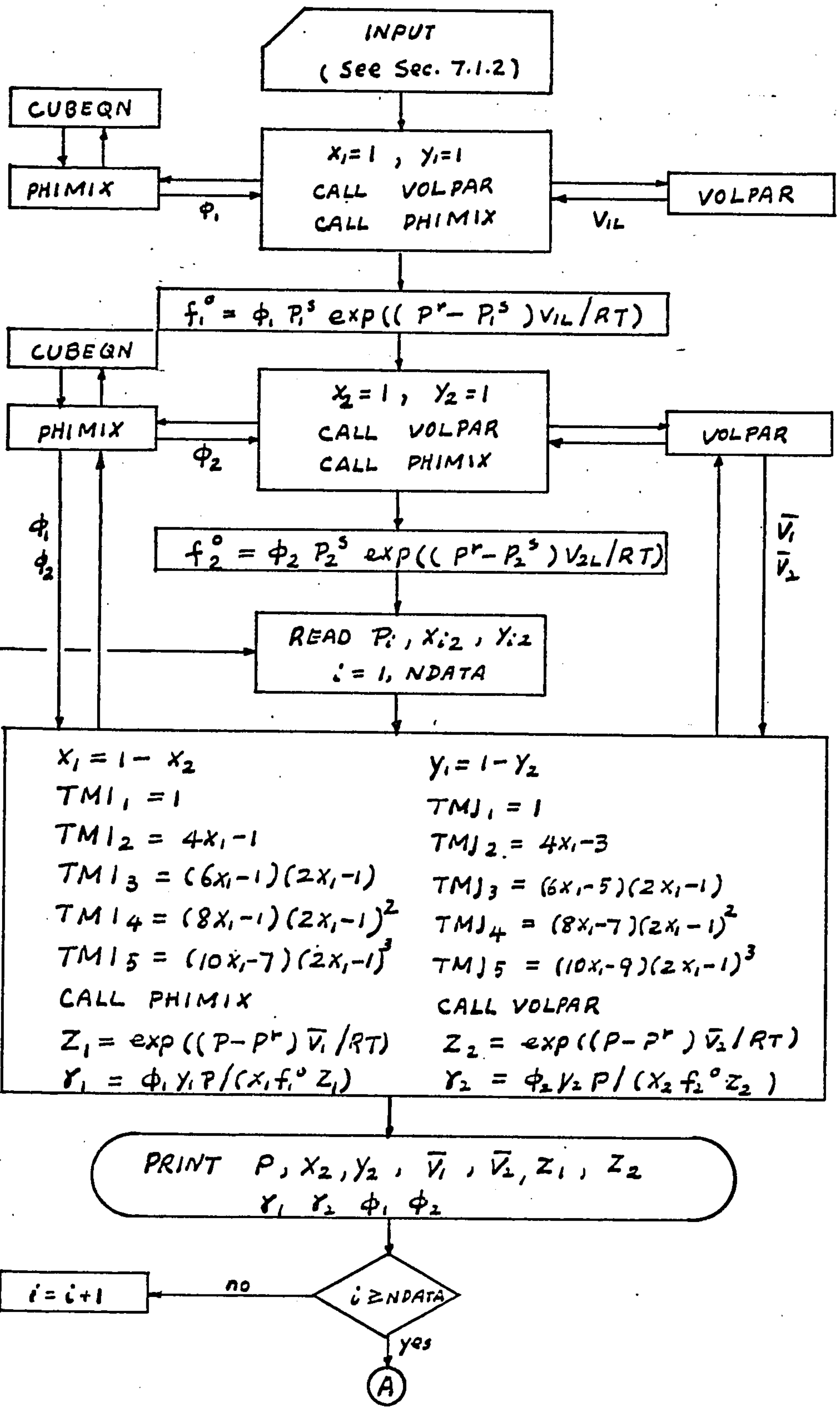


Figure VI. 1 (continued)

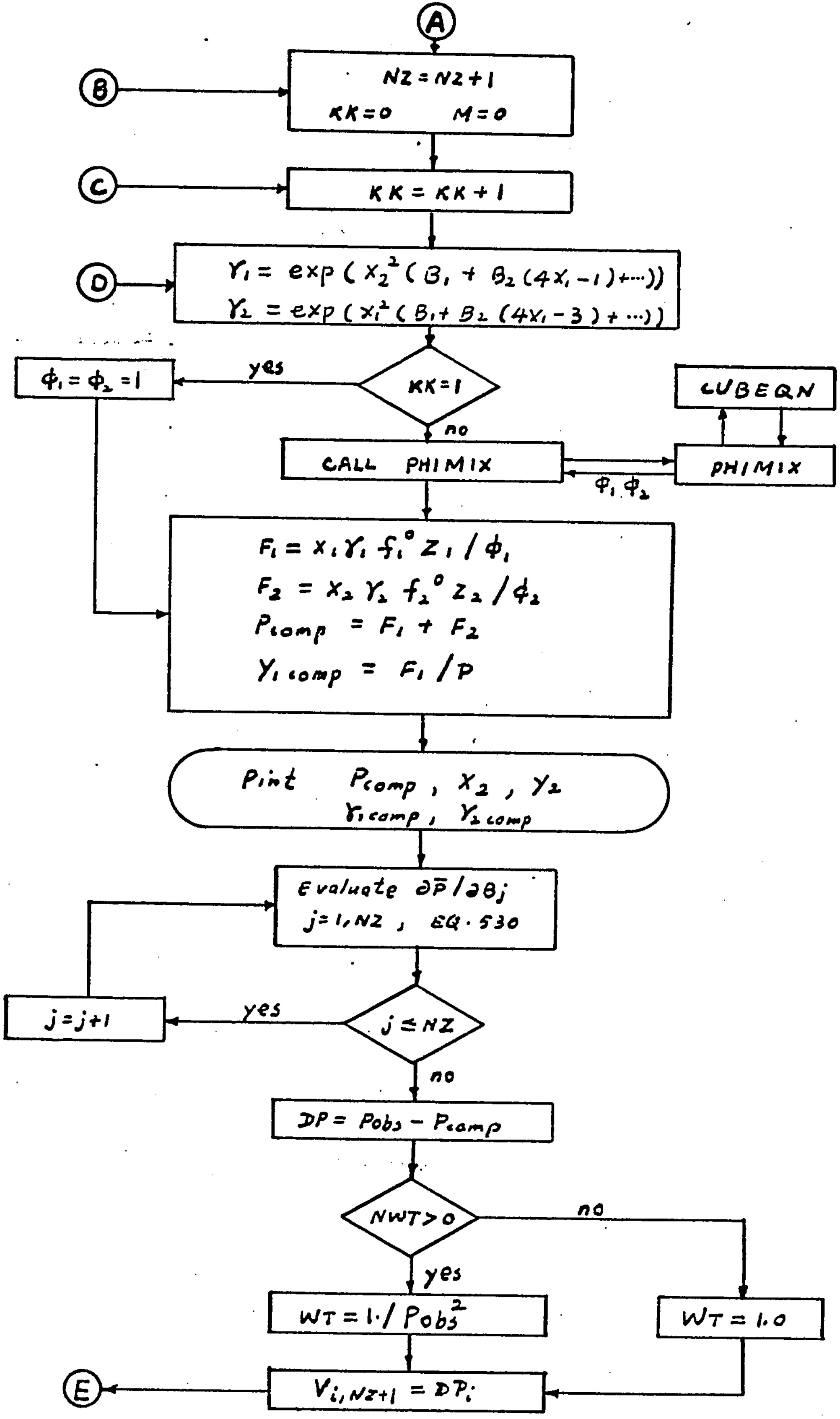


Figure VI. 1 (continued)

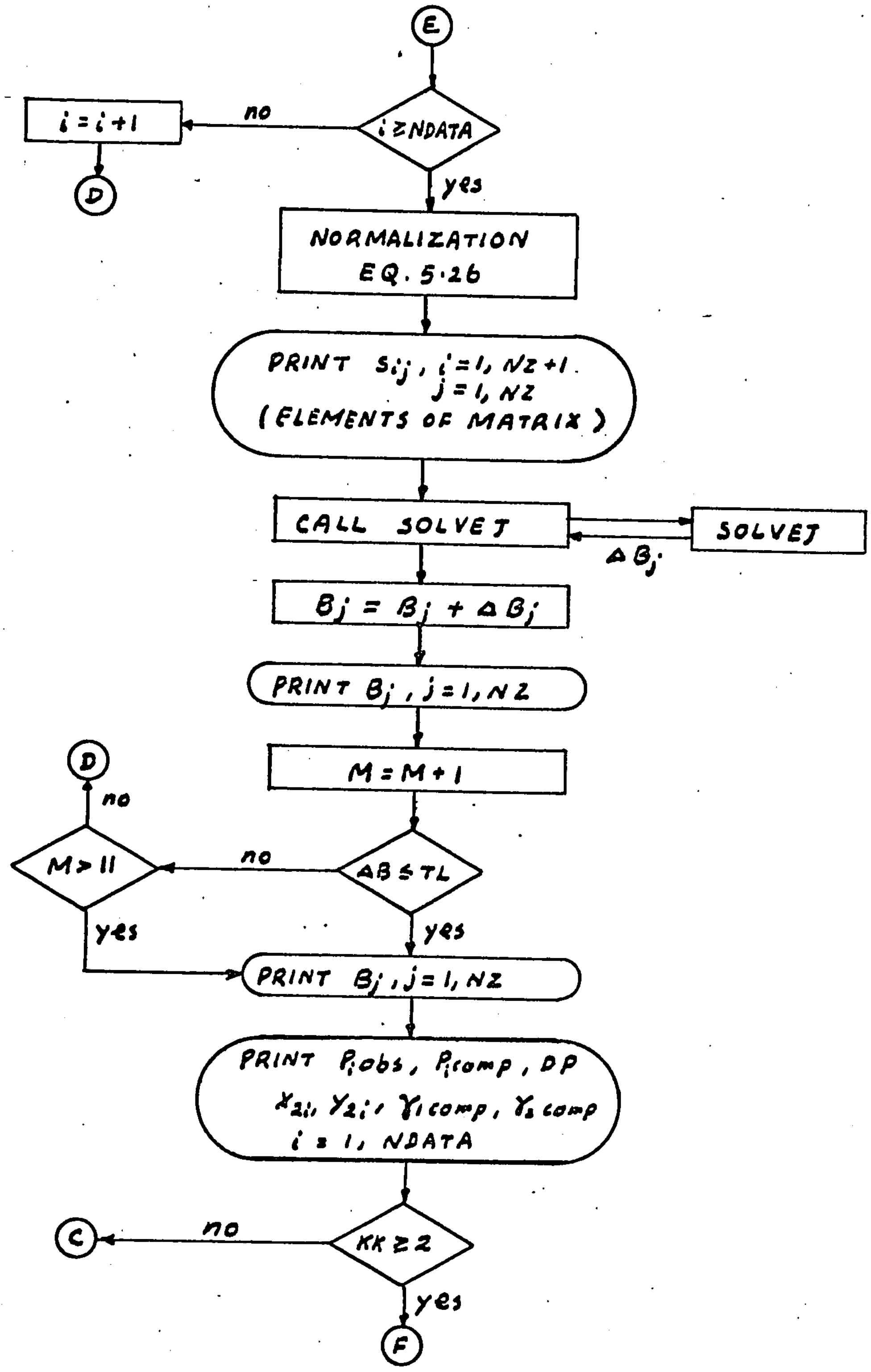
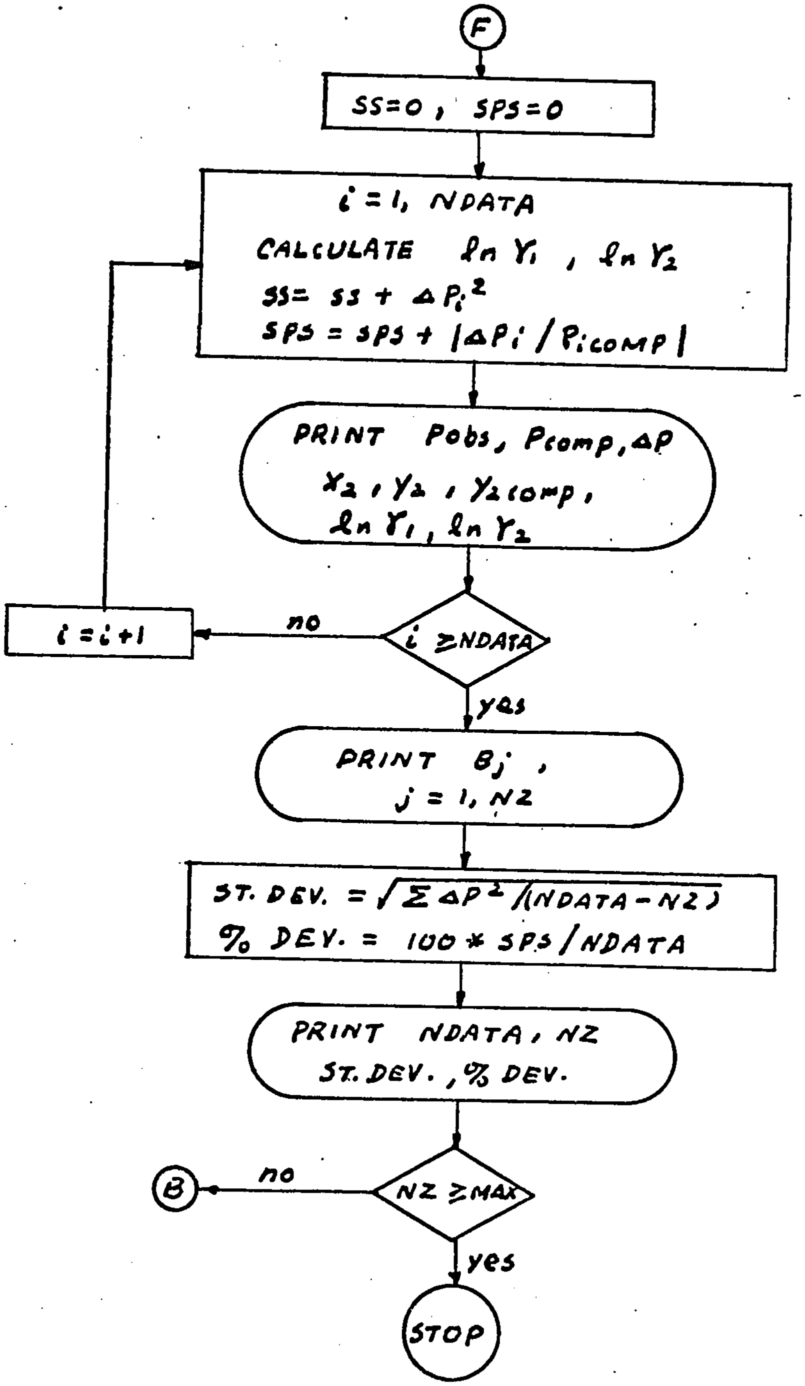


Figure VI.1 (continued)



VI. 1. 4 COMPUTER PROGRAM.

```
C     S.D.CHANG(CHEM.ENG.)
C      FITTING BINARY TOTAL PRESSURE AND LIQUID COMPOSITION DATA TO
C      SYMMETRIC REDLICH-KISTER'S EQUATION OF ONE TO FIVE TERMS.
C      NEEDS SUBROUTINES PHIMIX,VOLPAR,CUBEQN AND SOLVEJ.
       DIMENSION PHI(10),X(10),F(10),GAMMA(10),FREFER(10),PVOL(10),Y(10),
     1PC(10),VC(10),TC(10),W(10),C1RKV(10),C2RKV(10),C1RKL(10),C2RKL(10)
     2,AMOLWT(10),COMPA(10),COMPB(10),CORRV(10,10),CORRL(10,10),
     3ALFA(10,10),TS(10,10),VOLFR(10),GAMALN(10),A(4),Z(3),ZCIJ(10,10)
     4,WIJ(10,10),VCIJ(10,10),TITLE(20),ESTAR(10),HENRY(10,10),
     5GAMSLN(10),DTR(10,10),DVR(10,10),C1FREF(10),
     6X1(30),X2(30),Y1(30),Y2(30),Q(30),UJ(30),U(30),YY(30),
     7          GI(30),GJ(30),TMI(30,5),TMJ(30,5),V(30,6),PM(5),S(6,6),
     8 ZI(30),ZII(30),PT(30),GAMA1(30),GAMA2(30) ,DP(30),WT(30)
      COMMON P,NCOMP,PHI,T,X,RT,TOLD,TITLE,F,GAMMA,FREFER,PVOL,SUMY,Y,
     1VL,NSOLV,PC,VC,TC,W,C1RKV,C2RKV,C1RKL,C2RKL,AMOLWT,COMPA,COMPB,
     2CORRV,CORRL,ALFA,TS,VOLFR,GAMALN,A,MTYPE,Z,ZCIJ,WIJ,VCIJ,VCX,
     3ESTAR,HENRY,GAMSLN,DTR,DVR,TRV,TRTRU,TRMIX
      EQUIVALENCE (UJ,X2),        (U,X1)
C     EQUIVALENCE (UJ,X2),(YY,Y2),(U,X1)
      EXTERNAL CUBEQN
    1 READ(1,501,END=800)(TITLE(I),I=1,20)
      WRITE(3,505)(TITLE(I),I=1,20)
      READ(1,510)NDATA,NZ,MAX,NWT
      NCOMP=2
      DO 10  I=1, NCOMP
   10 READ(1,520)PC(I),VC(I),TC(I),W(I),C1RKV(I),C2RKV(I),C1RKL(I),
     1C2RKL(I),AMOLWT(I),COMPA(I),COMPB(I)
      VC1=VC(1)
      VC2=VC(2)
      DO 20 I=1,NCOMP
      CORRV(I,I)=0.0
      CORRL(I,I)=0.0
      DTR(I,I)=0.0
   20 DVR(I,I)=0.0
      READ(1,530)CORRV(1,2),CORRL(1,2),DTR(1,2),DVR(1,2)
      WRITE(3,531)CORRV(1,2),CORRL(1,2),DTR(1,2),DVR(1,2)
      CORRV(2,1)=CORRV(1,2)
      CORRL(2,1)=CORRL(1,2)
      DTR(2,1)=DTR(1,2)
      DVR(2,1)=DVR(1,2)
      READ(1,530)T,PS1,PS2,R
      READ(1,101)(PM(I),I=1,5)
      T=T*1.8
```

```
      PS1=PS1*14.7
      PS2=PS2*14.7
      PS0=PS2
      X(1)=1.0
      X(2)=0.0
      Y(1)=1.0
      Y(2)=0.0
      P=PS1
      RT=R*T
      VCX=VC1
      VOLFR(1)=1.0
      VOLFR(2)=0.0
      CALL VCLPAR
      CALL  PHIMIX(CUBEQN)
      IF(PS0-PS1)30,35,40
   30 FREF1=PHI(1)*PS1/EXP((PS1-PS0)*VL/RT)
      GO TO 45
   35 FREF1=PHI(1)*PS1
      GO TO 45
   40 FREF1=PHI(1)*PS1*EXP((PS0-PS1)*VL/RT)
   45 X(2)=1.0
      X(1)=0.0
      Y(2)=1.0
      Y(1)=0.0
      P=PS2
      VCX=VC2
      VOLFR(2)=1.0
      VOLFR(1)=0.0
      CALL VCLPAR
      CALL  PHIMIX(CUBEQN)
      IF(PS0-PS2)50,55,60
   50 FREF2=PHI(2)*PS2/EXP((PS2-PS0)*VL/RT)
      GO TO 65
   55 FREF2=PHI(2)*PS2
      GO TO 65
   60 FREF2=PHI(2)*PS2*EXP((PS0-PS2)*VL/RT)
   65 WRITE(3,535)T,PS1,FREF1,PS2,FREF2,PS0
      WRITE(3,540)
      TL=0.00001
      FACT=1.0E0
      DO 298 I=1,NDATA
C     READ(1,101)Q(I),UJ(I)
      READ(1,101)Q(I),UJ(I),YY(I)
```

```
      Q(I)=Q(I)*14.7
      U(I)=1.0-UJ(I)
       XX=2.0*U(I)-1.0
      TMI(I,1)=1.0E0
      TMI(I,2)=4.0*U(I)-1.0
      TMI(I,3)=(6.0*U(I)-1.0)*XX
      TMI(I,4)=(8.0*U(I)-1.0)*XX**2
      TMI(I,5)=(10.0*U(I)-1.0)*XX**3
      TMJ(I,1)=1.0E0
      TMJ(I,2)=TMI(I,2)-2.0
      TMJ(I,3)=TMI(I,3)-4.0*XX
      TMJ(I,4)=TMI(I,4)-6.0*XX**2
      TMJ(I,5)=TMI(I,5)-8.0*XX**3
      Y2(I)=YY(I)
      Y1(I)=1.0-YY(I)
      X(1)= U(I)
      X(2)=UJ(I)
      P=Q(I)
      Y(1)=Y1(I)
      Y(2)=Y2(I)
      VCX=X(1)*VC1+X(2)*VC2
      VOLFR(1)=X(1)*VC1/VCX
      VOLFR(2)=1.0-VOLFR(1)
      CALL VOLPAR
      CALL PHIMIX(CUBEGN)
      POYNT1=(Q(I)-PSO)*PVOL(1)/RT
      POYNT2=(Q(I)-PSO)*PVOL(2)/RT
      ZI(I)=POYNT1
      ZII(I)=POYNT2
      IF(ZI(I))304,305,306
  304 ZI(I)=1.00/ EXP(-ZI(I))
      GO TO 307
  305 ZI(I)=1.00
      GO TO 307
  306 ZI(I)= EXP(ZI(I))
  307 IF(ZII(I))309,310,311
  309 ZII(I)=1.00/ EXP(-ZII(I))
      GO TO 312
  310 ZII(I)=1.00
      GO TO 312
  311 ZII(I)= EXP(ZII(I))
  312 CONTINUE
      POYNT1=ZI(I)
```

```
      POYNT2=ZII(I)
      GAMA1(I)=PHI(1)*Y1(I)* Q(I)/(X1(I)*FREF1*POYNT1)
      GAMA2(I)=PHI(2)*Y2(I)* Q(I)/(X2(I)*FREF2  *POYNT2)
      WRITE(3,550)Q(I),X2(I),Y2(I),           PVOL(1),PVOL(2),POYNT1,
     1POYNT2,GAMA1(I),GAMA2(I),PHI(1),PHI(2)
  298 CONTINUE
      WRITE(3,505)(TITLE(I),I=1,20)
      DO 6 I=1,5
    6 PM(I)=0.0
      WRITE(3,102)TL,(PM(I),I=1,5)
  297 NZ=NZ+1
      NZ1=NZ+1
      KK=0
  299 KK=KK+1
      M=0
  300 DO 410 I=1,NDATA
      X1(I)=1.0-X2(I)
      Y1(I)=1.0-Y2(I)
      X(1)=X1(I)
      X(2)=X2(I)
      Y(1)=Y1(I)
      Y(2)=Y2(I)
      P= Q(I)
      VCX=X(1)*VC1+X(2)*VC2
      VOLFR(1)=X(1)*VC1/VCX
      VOLFR(2)=1.0-VOLFR(1)
      GI(I)=0.0
      GJ(I)=0.0
      DO 320 J=1,NZ
      GI(I)=GI(I)+PM(J)*TMI(I,J)
  320  GJ(I)=GJ(I)+PM(J)*TMJ(I,J)
      GI(I)=EXP(UJ(I)*UJ(I)*GI(I))
      GJ(I)= EXP(U(I)*U(I)*GJ(I))
C
      IF(KK-1)301,302,301
  302 Y(2)=YY(I)
      Y(1)=1.0-YY(I)
C 302 PHI(1)=1.0
C     PHI(2)=1.0
C     GO TO 303
  301 Y(1)=Y1(I)
      Y(2)=Y2(I)
      CALL PHIMIX(CUBEQN)
```

```
  303 FI=X(1)*GI(I)*FREF1*ZI(I)/PHI(1)
      FJ=X(2)*GJ(I)*FREF2*ZII(I)/PHI(2)
      PT(I)=FI+FJ
      Y1(I)=FI/PT(I)
      Y2(I)=1.0-Y1(I)
C     WRITE(3,550)PT(I),X2(I),Y2(I),GI(I),GJ(I),PHI(1),PHI(2)
      DO 400 J=1,NZ
      V(I,J)=FI*(1.0-U(I))*(1.0-U(I))*TMI(I,J)
     1   +FJ*U(I)*U(I)*TMJ(I,J)
  400 CONTINUE
      DP(I)=Q(I)-PT(I)
      IF(NWT.GT.0)GO TO 401
      WT(I)=1.0
      GO TO 402
  401 WT(I)=1.0/Q(I)/Q(I)
  402 V(I,NZ1)=       DP(I)
  410 CONTINUE
  500 DO 508 I=1,NZ1
      DO 508 J=1,NZ1
      SUM=0.0
      DO 509 K=1,NDATA
  509 SUM=SUM+V(K,I)*V(K,J) *WT(K)
      S(I,J)=SUM
      S(J,I)=S(I,J)
  508 CONTINUE
      DO 511 I=1,NZ
  511  WRITE(3,102)(S(I,J),J=1,NZ1)
      CALL SOLVEJ(NZ,S,INDIC)
C
      DO 600 I=1,NZ
  600 PM(I)=PM(I)+S(I,NZ1)*FACT
      WRITE(3,102)(S(I,NZ1),I=1,NZ)
      M=M+1
      DO 612 I=1,NZ
      IF( ABS(S(I,NZ1))-TL)612,612,616
  616 IF(M-11)622,622,632
  622 GO TO 300
  612 CONTINUE
  632 WRITE(3,104)M,(PM(I),I=1,NZ)
C
      DO 633 I=1,NDATA
  633 WRITE(3,102)Q(I),PT(I), DP(I)  ,UJ(I),Y2(I),GI(I),GJ(I),ZI(I),
     1   ZII(I)
```

```
      IF(KK-2)299,700,700
C
C     EVALLATION
C
  700 WRITE(3,105)
      WRITE(3,505)(TITLE(I),I=1,20)
      WRITE(3,906)
  906 FORMAT(1H ,4X,4HPOBS,4X,5HPCCMP,3X,2HDP,6X,1HX,7X,5HYCOMP,3X,1HY7X
     1,6H      ,2X,6H      ,2X,2HZ ,6X,3HZ  ////)
      FI=0.0
      FJ=0.0
      DO 750 I=1,NDATA
      GI(I)=ALCG(GI(I))
      GJ(I)=ALOG(GJ(I))
      FI=FI+DP(I)*DP(I)
      FJ=FJ+ABS(V(I,NZ1)/PT(I))
      WRITE(3,902)Q(I),PT(I),   DP(I),UJ(I),Y2(I),YY(I),GJ(I),GI(I),
     1   ZII(I),ZI(I)
  750 CONTINUE
      WRITE(3,105)
      WRITE(3,922)(PM(I),I=1,NZ)
  922 FORMAT(1H ,2HB=,F10.5,3X,2HC=,F10.5,3X,2HD=,F10.5,3X,2HE=,F10.5,3X
     1,2HF=,F10.5/)
      FI=(FI/(NDATA-NZ))**0.5
      FJ=FJ/NDATA*100.
  902 FORMAT(1H ,3F8.2,3F8.3,2F8.4,2F8.3)
      WRITE(3,907)NDATA,NZ,T,FI,FJ
  907 FORMAT(21H NO.OF OBSERVATIONS =,I10/
     1 18H NO.CF CCNSTANTS =,I10/
     2 22H SYSTEM TEMPERATURE AT,F10.2,5HDEG  /
     3 26H ST.DEV. OF CORRELATICN IS,F10.2,6HPSIA  /
     4 27H AV.% DEV CF CORRELATION IS,F10.2/   )
      WRITE(3,505)(TITLE(I),I=1,20)
      IF(NZ-MAX)297,760,760
  101 FORMAT (8F10.0)
  102 FORMAT(1H ,9E14.6)
  104 FORMAT(//I5,5E15.7/)
  105 FORMAT(//)
  501 FORMAT(20A4)
  505 FORMAT(1H1,20A4// )
  510 FORMAT(4I5)
  520 FORMAT(9F8.4,2A4)
  530 FORMAT(8F10.4)
```

```
 531 FORMAT(1H ,7HK12(V)=,F6.3,3X,7HK12(L)=,F6.3,3X,4HDTR=,F7.4,3X,
    14HDVR=,F7.4//    )
 535 FORMAT(1H ,5HTEMP=,F9.2/1H ,4HPS1=,F9.3,7X,10HFREFER(1)=,F9.3/1H ,
    14HPS2=,F9.3,7X,10HFREFER(2)=,F9.3/1H ,4HPS0=, F9.3//)
 540 FORMAT(1H ,4X,1HP, 6X,2HX2,6X,2HY2,4X,5HPVOL1,3X,5HPVOL2,
    1 3X,6HPOYNT1,2X,6HPCYNT2,2X,5HGAMA1,3X,5HGAMA2,3X,4HPHI1,4X,4HPHI2
    1,/)
 550 FORMAT(1H ,F8.2,2F8.4,8F8.4)
 760 GO TO 1
 800 RETURN
     END
```

```
      SUBROUTINE SOLVEJ(NA,A,INDIC)
      DIMENSION A(6,6)
      NA1=NA+1
      DO 205 I=1,NA
      IF(A(I,I))200,206,200
  200 P=1./A(I,I)
      DO 201 J=I,NA1
  201 A(I,J)=P*A(I,J)
      DO 202 K=1,NA
      IF (I-K) 203,202,203
  203 Q=A(K,I)
      DO 204 J=I,NA1
  204 A(K,J)=A(K,J)-Q*A(I,J)
  202 CONTINUE
  205 CONTINUE
      INDIC=0
      RETURN
  206 IF(NA-1) 300,304,300
  300 I1 = I+1
      DO 303 L=I1,NA
      IF(A(L,I)) 301,303,301
  301 DO 302 J=I,NA1
      HOLD=A(I,J)
      A(I,J)=A(L,J)
  302 A(L,J)=HOLD
      GO TO 200
  303 CONTINUE
      INDIC=1
  304 WRITE(3,207)I
  207 FORMAT(//25H DIAGONAL ELEMENT IN EQN ,I4,40H IS ZERO TRANSPOSE EQN
     1 WITH PREVIOUS ONE//)
      RETURN
      END
```

```
      SUBROUTINE PHIMIX(CUBEQN)
C     CALCULATE VAPOR-PHASE FUGACITY COEFFICIENTS USING REVISED REDLICH
C     AND KWONG EQUATION
      DIMENSION PHI(10),X(10),F(10),GAMMA(10),FREFER(10),PVOL(10),Y(10),
     1PC(10),VC(10),TC(10),W(10),C1RKV(10),C2RKV(10),C1RKL(10),C2RKL(10)
     2,AMOLWT(10),COMPA(10),COMPB(10),CORRV(10,10),CORRL(10,10),
     3ALFA(10,10),TS(10,10),VOLFR(10),GAMALN(10),A(4),Z(3),ZCIJ(10,10)
     4,WIJ(10,10),VCIJ(10,10),TITLE(20),ESTAR(10),HENRY(10,10),
     5GAMSLN(10),DTR(10,10),DVR(10,10),C1FREF(10),C2FREF(10),C3FREF(10),
     6C4FREF(10), C5FREF(10),C6FREF(10),C1HNRY(10,10),C2HNRY(10,10),
     7C3HNRY(10,10),C4HNRY(10,10),C5HNRY(10,10),C6HNRY(10,10),
     8C1ALFA(10,10),C2ALFA(10,10),C3ALFA(10,10),C4ALFA(10,10),
     9C5ALFA(10,10),C6ALFA(10,10),
     9 ARKV(10,10),BRKV(10)    ,AIRKV(10),PHILN(10)
      COMMON P,NCOMP,PHI,T,X,RT,TOLD,TITLE,F,GAMMA,FREFER,PVOL,SUMY,Y,
     1VL,NSOLV,PC,VC,TC,W,C1RKV,C2RKV,C1RKL,C2RKL,AMOLWT,COMPA,COMPB,
     2CORRV,CORRL,ALFA,TS,VOLFR,GAMALN,A,MTYPE,Z,ZCIJ,WIJ,VCIJ,VCX,
     3ESTAR,HENRY,GAMSLN,DTR,DVR,TRV,TRTRU,TRMIX,C1FREF,C2FREF,C3FREF,
     4C4FREF,C5FREF,C6FREF,C1HNRY,C2HNRY,C3HNRY,C4HNRY,C5HNRY,C6HNRY,
     6C1ALFA,C2ALFA,C3ALFA,C4ALFA,C5ALFA,C6ALFA,IPRINT
      DO 100 I=1,NCOMP
      ARKV(I,I)=C1RKV(I)*115.1329*(TC(I)**2.5)/PC(I)
      BRKV(I)=C2RKV(I)*10.73*TC(I)/PC(I)
      IF(I.EQ.NCOMP) GO TO 110
      I1=I+1
      DO 100 J=I1,NCOMP
      ARKV(I,J)=
     1          (C1RKV(I)+C1RKV(J))*5.365*(TC(I)*TC(J)*(1.-CORRV(I,J))**
     1 2.0)**0.75*VCIJ(I,J)/ZCIJ(I,J)
      ARKV(J,I)=ARKV(I,J)
  100 CONTINUE
  110 CONTINUE
      AMRKV=0.0
      BMRKV=0.0
      DO 120 I=1,NCOMP
      AIRKV(I)=0.0
      BMRKV=BMRKV+Y(I)*BRKV(I)
      DO 120 J=1,NCOMP
      AIRKV(I)=AIRKV(I)+Y(J)*ARKV(I,J)
  120 AMRKV=AMRKV+Y(I)*Y(J)*ARKV(I,J)
      A(1)=1.0
      A(2)=-1.0
      PBRT=P*BMRKV/RT
```

```
      ABRT=AMRKV/(BMRKV*10.73*T**1.5)
      A(3)=PBRT*(ABRT-1.0-PBRT)
      A(4)=-ABRT*(PBRT**2.0)
      CALL CUBEQN
      IF(MTYPE)130,140,140
  130 ZV=AMAX1(Z(1),Z(2),Z(3))
      GO TO 150
  140 ZV=Z(1)
  150 VV=ZV*RT/P
      QVVB=ALOG(VV/(VV-BMRKV))
      Q1VB=1.0/(VV-BMRKV)
      Q2RTB=2.0/(10.73*T**1.5*BMRKV)
      QVBV=ALOG((VV+BMRKV)/VV)
      QARTB=AMRKV/(10.73*T**1.5*BMRKV**2.0)
      QBVB=BMRKV/(VV+BMRKV)
      DO 160 I=1,NCOMP
      PHILN(I)=QVVB+BRKV(I)*Q1VB-AIRKV(I)*Q2RTB*QVBV+BRKV(I)*QARTB*(QVBV
     1 -QBVB)-ALOG(ZV)
  160 PHI(I)=EXP(PHILN(I))
      RETURN
      END
```

```
      SUBROUTINE VOLPAR
C     CALCULATE PARTIAL MOLAR VOLUMES IN A MULTICOMPONENT LIQUID MIXTURE
      DIMENSION PHI(10),X(10),F(10),GAMMA(10),FREFER(10),PVOL(10),Y(10),
     1PC(10),VC(10),TC(10),W(10),C1RKV(10),C2RKV(10),C1RKL(10),C2RKL(10)
     2,AMOLWT(10),COMPA(10),COMPB(10),CORRV(10,10),CORRL(10,10),
     3ALFA(10,10),TS(10,10),VOLFR(10),GAMALN(10),A(4),Z(3),ZCIJ(10,10)
     4,WIJ(10,10),VCIJ(10,10),TITLE(20),ESTAR(10),HENRY(10,10),
     5GAMSLN(10),DTR(10,10),DVR(10,10),C1FREF(10),C2FREF(10),C3FREF(10),
     6C4FREF(10), C5FREF(10),C6FREF(10),C1HNRY(10,10),C2HNRY(10,10),
     7C3HNRY(10,10),C4HNRY(10,10),C5HNRY(10,10),C6HNRY(10,10),
     8C1ALFA(10,10),C2ALFA(10,10),C3ALFA(10,10),C4ALFA(10,10),
     9C5ALFA(10,10),C6ALFA(10,10),
     9AFR(10),ARKL(10,10),BRKL(10)
      COMMON P,NCOMP,PHI,T,X,RT,TOLD,TITLE,F,GAMMA,FREFER,PVOL,SUMY,Y,
     1VL,NSOLV,PC,VC,TC,W,C1RKV,C2RKV,C1RKL,C2RKL,AMOLWT,COMPA,COMPB,
     2CORRV,CORRL,ALFA,TS,VOLFR,GAMALN,A,MTYPE,Z,ZCIJ,WIJ,VCIJ,VCX,
     3ESTAR,HENRY,GAMSLN,DTR,DVR,TRV,TRTRU,TRMIX,C1FREF,C2FREF,C3FREF,
     4C4FREF,C5FREF,C6FREF,C1HNRY,C2HNRY,C3HNRY,C4HNRY,C5HNRY,C6HNRY,
     6C1ALFA,C2ALFA,C3ALFA,C4ALFA,C5ALFA,C6ALFA,IPRINT
      VCX=0.0
      DO 1 I=1,NCOMP
    1 VCX=VCX+X(I)*VC(I)
      DO 2 I=1,NCOMP
    2 VOLFR(I)=X(I)*VC(I)/VCX
      TCV=0.0
      DO 10 I=1,NCOMP
      DO 10 J=1,NCOMP
   10 TCV=TCV+VOLFR(I)*VOLFR(J)*(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
      WMIX=0.0
      DO 11 I=1,NCOMP
   11 WMIX=WMIX+VOLFR(I)*W(I)
      TRV=T/TCV
      IF(TRV-0.91)12,13,13
   12 TRMIX=TRV
      VCMIX=VCX
      GO TO 80
   13 VC23X=0.0
      DO 14 I=1,NCOMP
   14 VC23X=VC23X+X(I)*VC(I)**(2.0/3.0)
      DO 15 I=1,NCOMP
   15 AFR(I)=X(I)*VC(I)**(2.0/3.0)/VC23X
      VCAFR=0.0
      TCAFR=0.0
```

```
      DO 16 I=1,NCOMP
      VCAFR=VCAFR+AFR(I)*VC(I)
   16 TCAFR=TCAFR+AFR(I)*TC(I)
      DVCAFR=0.0
      DTCAFR=0.0
      DO 17 I=1,NCOMP
      DO 17 J=1,NCOMP
      DVCAFR=DVCAFR+AFR(I)*AFR(J)*DVR(I,J)*(VC(I)+VC(J))*0.5
      DTCAFR=DTCAFR+AFR(I)*AFR(J)*DTR(I,J)*(TC(I)+TC(J))*0.5
   17 CONTINUE
      VCTRU=VCAFR+DVCAFR
      TCTRU=TCAFR+DTCAFR
      TRTRU=T/TCTRU
      IF(TRTRU-1.0)20,18,18
   18 VRMIX=1.0
      TRMIX=1.0
      VCMIX=VCTRU
      GO TO 90
   20 CONTINUE
      TRM0=1.0
      TRM1=0.9
      FTRM0=(TRV-1.0)-(TRV/TRTRU-1.0)
      FTRM1=(TRV/0.9-1.0)-(TRV/TRTRU-1.0)/EXP(6.019)
   25 TRM2=(TRM0*FTRM1-TRM1*FTRM0)/(FTRM1-FTRM0)
      IF(ABS(TRM2-TRM1).LT.0.0001) GO TO 40
      FTRM2=(TRV/TRM2-1.0)-(TRV/TRTRU-1.0)/EXP((1.0-TRM2)*(2901.01
     1-5738.921*TRM2+2849.854*TRM2**2+1.741266/(1.01-TRM2)))
      SIGN=FTRM2*FTRM0
      IF(SIGN)35,40,30
   30 TRM0=TRM1
      FTRM0=FTRM1
   35 TRM1=TRM2
      FTRM1=FTRM2
      GO TO 25
   40 CONTINUE
      TRMIX=TRM2
      VCMIX=VCX+(VCTRU-VCX)/EXP((1.0-TRMIX)*(2901.01-5738.921*TRMIX
     1+2849.854*TRMIX**2+1.741266/(1.01-TRMIX)))
   60 IF(TRMIX-0.995)80,70,70
   70 VR995=0.79202-WMIX*0.21798+WMIX**2.0*0.36129
      VR990=0.7327-WMIX*0.1604+WMIX**2.0*0.2032
      COFCVR=20000.0*(1.0+VR990-2.0*VR995)
      COFBVR=200.0*(1.0-VR995)-1.995*COFCVR
```

```
      COFAVR=1.0-COFBVR-COFCVR
      VRMIX=(COFAVR+COFBVR*TRMIX+COFCVR*TRMIX**2)*(0.978+4159.0*(TRMIX
     1-0.9977)**2)
      GO TO 90
   80 QLN1TR=ALOG(1.0-TRMIX)
      VROF=0.11917+0.009513*TRMIX+0.21091*TRMIX**2.-0.06922*TRMIX**3.0+
     10.0748/TRMIX-0.084476*QLN1TR
      VR1F=0.98465-1.60378*TRMIX+1.82484*TRMIX**2.0-0.61432*TRMIX**3.0
     1-0.34546/TRMIX+0.087037*QLN1TR
      VR2F=-0.55314-0.15793*TRMIX-1.01601*TRMIX**2.0+0.34095*TRMIX**3.0
     1+.46795/TRMIX-0.239938*QLN1TR
      IF(TRMIX-0.9925)85,85,81
   81 VRMIX=(VROF+WMIX*VR1F+WMIX**2*VR2F)*(1.0+(TRMIX-0.9925)*2.4)
      GO TO 90
   85 VRMIX=VROF+WMIX*VR1F+WMIX**2.0*VR2F
   90 VL=VRMIX*VCMIX
      DO 100 I=1,NCOMP
      ARKL(I,I)=C1RKL(I)*115.1329*(TC(I)**2.5)/PC(I)
      BRKL(I)=C2RKL(I)*10.73*TC(I)/PC(I)
      IF(I.EQ.NCOMP) GO TO 110
      I1=I+1
      DO 100 J=I1,NCOMP
      WIJ(I,J)=(W(I)+W(J))*0.5
      ZCIJ(I,J)=0.291-0.08*WIJ(I,J)
      VCIJ(I,J)=(VC(I)+VC(J))*0.5
      ARKL(I,J)=(C1RKL(I)+C1RKL(J))*5.365*(TC(I)*TC(J)*(1.0-CORRL(I,J))
     1**2.0)**0.75*VCIJ(I,J)/ZCIJ(I,J)
      ARKL(J,I)=ARKL(I,J)
  100 CONTINUE
  110 CONTINUE
      AMRKL=0.0
      BMRKL=0.0
      DO 120 I=1,NCOMP
      BMRKL=BMRKL+X(I)*BRKL(I)
      DO 120 J=1,NCOMP
  120 AMRKL=AMRKL+X(I)*X(J)*ARKL(I,J)
      QD=(T**0.5)*VL*(VL+BMRKL)
      QH=(AMRKL/(T**0.5))*
     1                      ((2.0*VL+BMRKL)/(VL**2.0*(VL+BMRKL)**2.0))
      QK=RT/((VL-BMRKL)**2.0)
      DO 130 I=1,NCOMP
      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))
  130 PVOL(I)=((QE/QD)-QG)/(QH-QK)
  300 RETURN
      END
```

```
      SUBROUTINE CUBEQN
C    SOLVES CUBIC EQUATION OF REDLICH-KWONG EQUATION FOR COMPRESSESSIBILIT
C    FACTORS
      DIMENSION PHI(10),X(10),F(10),GAMMA(10),FREFER(10),PVOL(10),Y(10),
     1PC(10),VC(10),TC(10),W(10),C1RKV(10),C2RKV(10),C1RKL(10),C2RKL(10)
     2,AMOLWT(10),COMPA(10),COMPB(10),CORRV(10,10),CORRL(10,10),
     3ALFA(10,10),TS(10,10),VOLFR(10),GAMALN(10),A(4),Z(3),ZCIJ(10,10)
     4,WIJ(10,10),VCIJ(10,10),TITLE(20),ESTAR(10),HENRY(10,10),
     5GAMSLN(10),CTR(10,10),DVR(10,10),C1FREF(10),C2FREF(10),C3FREF(10),
     6C4FREF(10), C5FREF(10),C6FREF(10),C1HNRY(10,10),C2HNRY(10,10),
     7C3HNRY(10,10),C4HNRY(10,10),C5HNRY(10,10),C6HNRY(10,10),
     8C1ALFA(10,10),C2ALFA(10,10),C3ALFA(10,10),C4ALFA(10,10),
     9C5ALFA(10,10),C6ALFA(10,10), B(10)
      COMMON P,NCOMP,PHI,T,X,RT,TOLC,TITLE,F,GAMMA,FREFER,PVOL,SUMY,Y,
     1VL,NSOLV,PC,VC,TC,W,C1RKV,C2RKV,C1RKL,C2RKL,AMOLWT,COMPA,COMPB,
     2CORRV,CORRL,ALFA,TS,VOLFR,GAMALN,A,MTYPE,Z,ZCIJ,WIJ,VCIJ,VCX,
     3ESTAR,HENRY,GAMSLN,CTR,DVR,TRV,TRTRU,TRMIX,C1FREF,C2FREF,C3FREF,
     4C4FREF,C5FREF,C6FREF,C1HNRY,C2HNRY,C3HNRY,C4HNRY,C5HNRY,C6HNRY,
     6C1ALFA,C2ALFA,C3ALFA,C4ALFA,C5ALFA,C6ALFA,IPRINT
      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
      Z(2)=FACT* COS(PEI2)         -B1OV3
      PEI4=PEI+4.1887902
      Z(3)=FACT* COS(PEI4)         -B1OV3
   50 RETURN
      END
```

VI. 2 GENERAL THERMODYNAMIC CONSISTENCY TEST

VI. 2. 1 GENERAL INFORMATION

PURPOSE - Testing thermodynamic consistency point-by-point of the multicomponent vapor-liquid equilibrium data at isothermal condition.

LANGUAGE - FORTRAN IV in G level

SUBROUTINES REQUIRED - VOLPAR (Refs. 22, 23) PHIMIX (Refs. 22, 25), and CUBEQN (Ref. 22)

INPUT AND OUTPUT COMMANDS:

Input - READ (1, FORMAT's statement number)
Print - WRITE (3, FORMAT's statement number)
Card output - WRITE (2, FORMAT's statement number)

Printing Control:

Single space - blank in first column
Double space - 0 in first column
Starting a new page - 1 in the first column

VI. 2. 2 INPUT and OUTPUT

INPUT:

Card 1	The title of the problem can be entered into the card from columns 1 to 80.
Card 2	It contains NCOMP, NOBS

Column	
1 - 5	NCOMP, number of components present in the system, in F-FORMAT
6 - 10	NOBS, number of observations, in F-FORMAT

Cards 3 to (2 + NCOMP): They bear the basic properties which are required for evaluating the supporting data such as fugacity and partial molar volume by using the modified Redlich-Kwong equation of state (Ref. 23, 25). One card is required for each component.

Column	
1 - 8	P_c, psia
9 - 16	V_c, cu. ft. per lb-mole
17 - 24	T_c, °R
25 - 32	ω, acentric factor, dimensionless
33 - 40	C1RKV, the first constant of R-K equation of state in vapor phase
41 - 48	C2RKV, the second constant of R-K equation of state in vapor phase
49 - 56	C1RKL, the first constant of R-K equation of state in liquid phase
57 - 64	C2RKL, the second constant of R-K equation of state in liquid phase
65 - 72	AMLWT, molecular weight
72 - 80	The name of the component

Cards (3 + NCOMP) to (3 + 2 NCOMP) : They bear the cross constants for mixtures of the modified R-K equation of state.

Column	
1 - 10	CORRV (or k_{12} of Ref. 25) in vapor phase
11 - 20	CORRL (or k_{12} of Ref. 23) in liquid phase
21 - 30	Critical region correction factor (Ref. 23) for temperature
31 - 40	Critical region correction factor (Ref. 23) for volume

Card (4 + 2 NCOMP) : It bears the system temperature and saturation pressure (if any) of each component in F-FORMAT, 10 columns per field.

Card (5 + 2 NCOMP) : It bears the measuring errors

Column	
1 - 10	E(x), the measuring error of the composition
11 - 20	E(P), the measuring error of the pressure
21 - 30	E(T), the measuring error of the temperature

Cards (6 + 2 NCOMP) to (6 + 2 NCOMP + NOBS) : They bear the data to be tested in F-FORMAT, 10 columns per field. Data are read in the order of T, P, (x_j, j = 1, NCOMP) and (y_j, j = 1, NCOMP).

- OUTPUT : see flow diagram

VI. 2. 3 FLOW DIAGRAM (see figure VI. 2)

Figure VI. 2 Flow Diagram of the Program "General Thermodynamic Consistency Test".

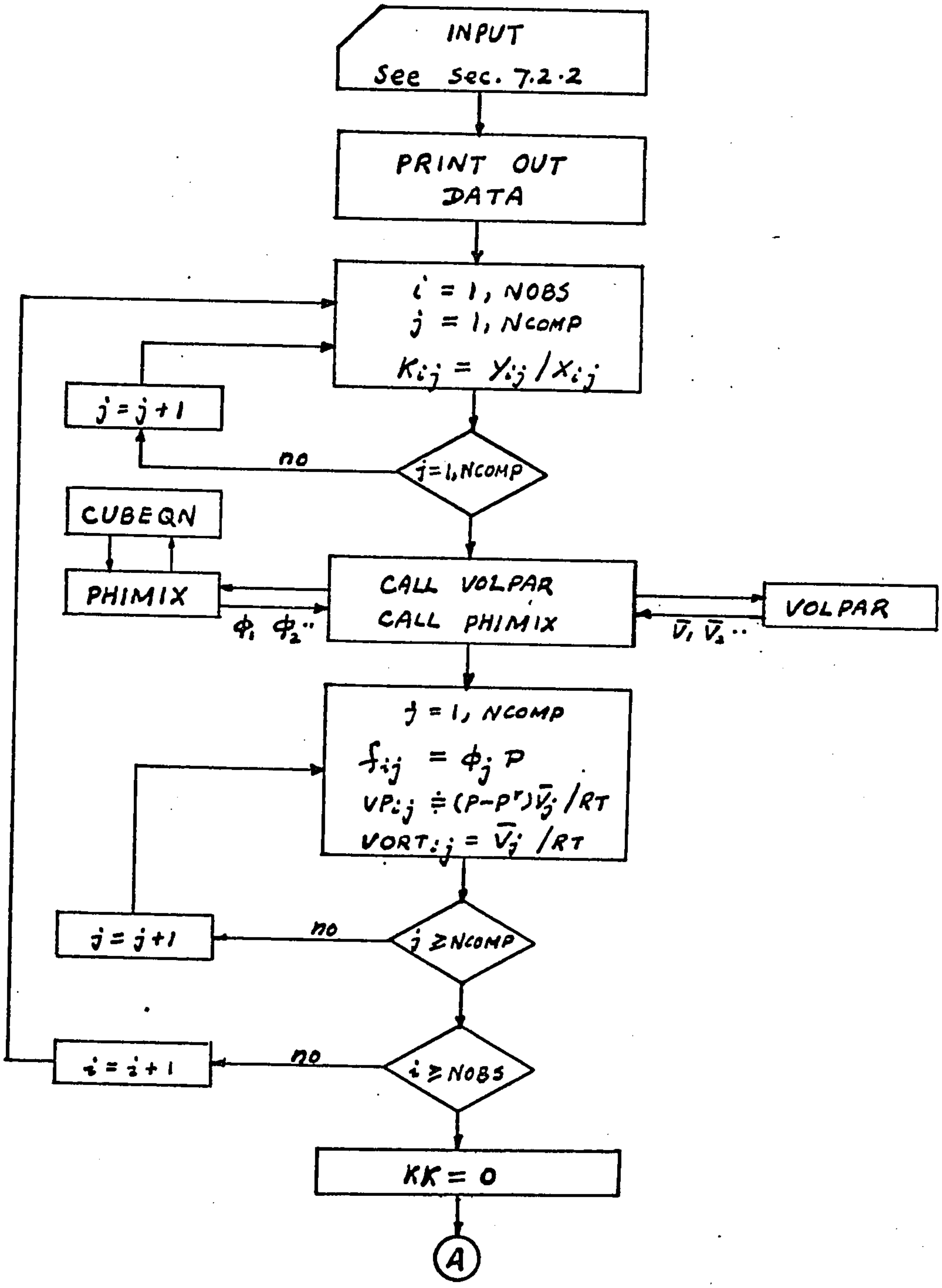


Figure VI. 2(continued)

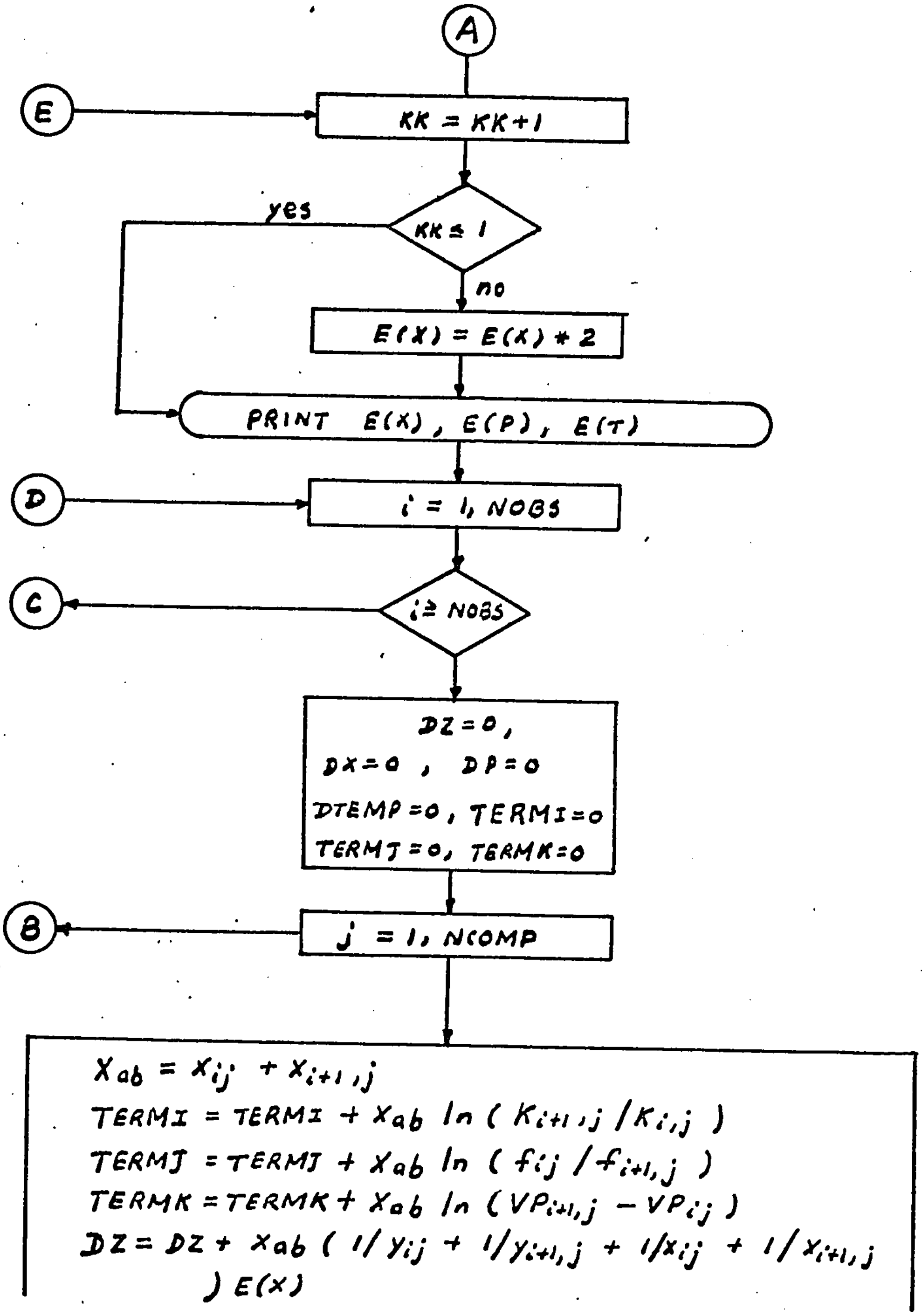
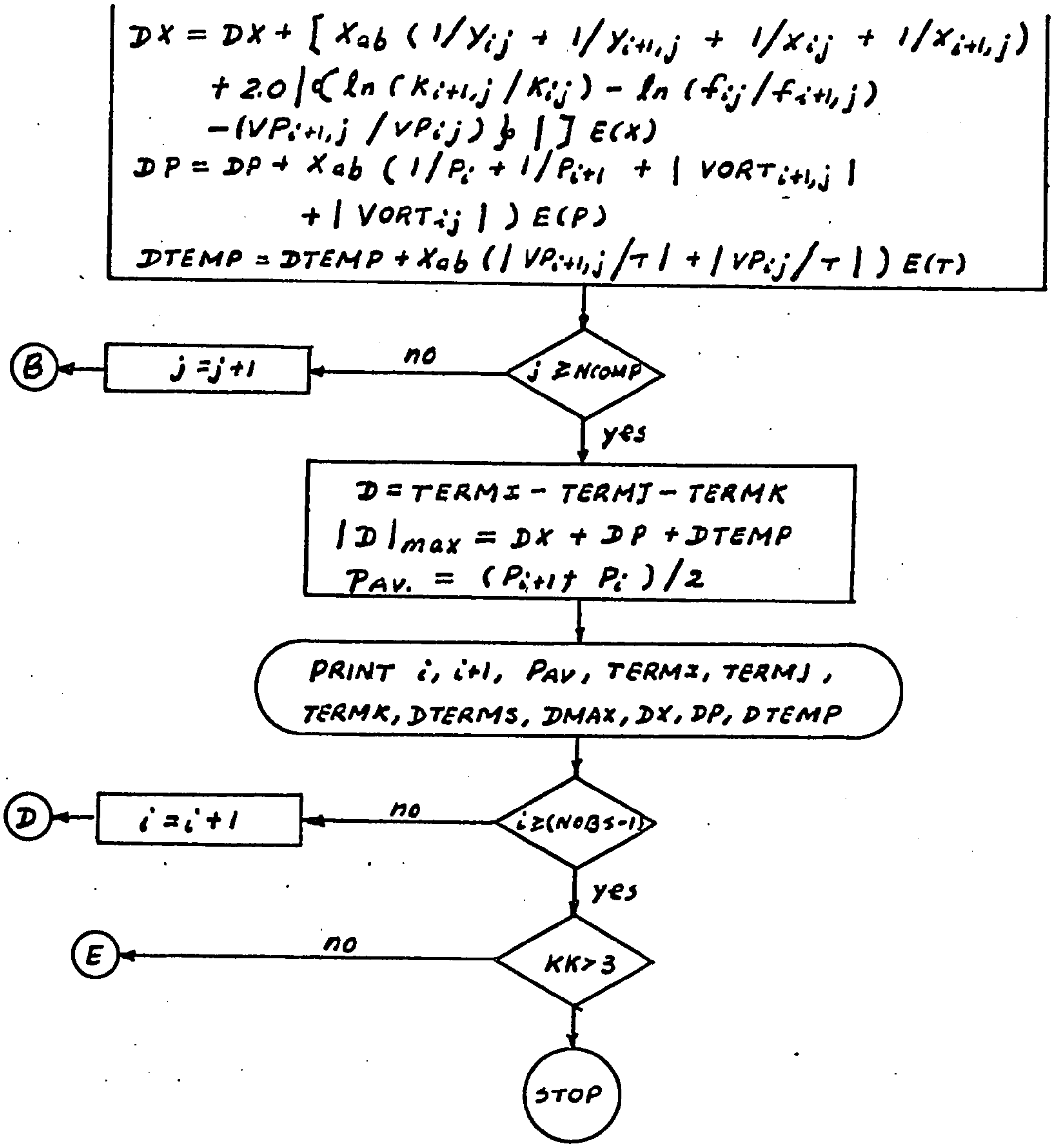


Figure VI. 2(continued)



VI. 2. 4 COMPUTER PROGRAM

```
C     TESTING THERMODYNAMIC CONSISTENCY OF THE HIGH PRESSURE MULTI-
C     COMPONENT VAPOR-LIQUID EQUILIBRIUM DATA AT ISOTHERMAL CONDITION.
C     NEEDS SUBROUTINES VOLPAR,PHIMIX AND CUBEQN.
C     CHANG,S.-D. AND BENJAMIN C.-Y. LU,JULY 2,1968
C     MODIFIED VERSION SEPT.3,1968,BY CHANG
      DIMENSION PHI(10),X(10),F(10),GAMMA(10),FREFER(10),PVOL(10),Y(10),
     1PC(10),VC(10),TC(10),W(10),C1RKV(10),C2RKV(10),C1RKL(10),C2RKL(10)
     2,AMOLWT(10),COMPA(10),COMPB(10),CORRV(10,10),CORRL(10,10),
     3ALFA(10,10),TS(10,10),VOLFR(10),GAMALN(10),A(4),Z(3),ZCIJ(10,10),
     4WIJ(10,10),TITLE(20),ESTAR(10),HENRY(10,10),GAMSLN(10),
     5DTR(10,10),DVR(10,10),VCIJ(10,10),
     6 PP( 50), XX( 50,3),YY( 50,3),C( 50,3),FP( 50,3),VP( 50,3),TT( 50)
     7  ,PVOLR(4),DTM(50),VORT(50,3)
      COMMON P,NCOMP,PHI,T,X,RT,TOLD,TITLE,F,GAMMA,FREFER,PVOL,SUMY,Y,
     1VL,NSOLV,PC,VC,TC,W,C1RKV,C2RKV,C1RKL,C2RKL,AMOLWT,COMPA,COMPB,
     2CORRV,CORRL,ALFA,TS,VOLFR,GAMALN,A,MTYPE,Z,ZCIJ,WIJ,VCIJ,VCX,
     3ESTAR,HENRY,GAMSLN,DTR,DVR,TRV,TRTRU,TRMIX
      EXTERNAL CUBEQN
  600 READ(1,500,END=800)(TITLE(I),I=1,20)
      WRITE(3,540)(TITLE(I),I=1,20)
      READ(1,590)NCOMP,NOBS
      NCOMP1=NCOMP-1
      DO 10 I=1,NCOMP
   10 READ(1,520)PC(I),VC(I),TC(I),W(I),C1RKV(I),C2RKV(I),C1RKL(I),
     1 C2RKL(I),AMOLWT(I),COMPA(I),COMPB(I)
      CORRV(NCOMP,NCOMP)=0.0
      CORRL(NCOMP,NCOMP)=0.0
      DTR(NCOMP,NCOMP)=0.0
      DVR(NCOMP,NCOMP)=0.0
      DO 20 I=1,NCOMP1
      CORRV(I,I)=0.0
      CORRL(I,I)=0.0
      DTR(I,I)=0.0
      DVR(I,I)=0.0
      I1=I+1
      DO 20 J=I1,NCOMP
      READ(1,530)CORRV(I,J),CORRL(I,J),DTR(I,J),DVR(I,J)
      WRITE(3,510)I,J,CORRV(I,J),CORRL(I,J),DTR(I,J),DVR(I,J)
      WRITE(3,549)
      CORRV(J,I)=CORRV(I,J)
      CORRL(J,I)=CORRL(I,J)
      DTR(J,I)=DTR(I,J)
      DVR(J,I)=DVR(I,J)
```

```
   20 CONTINUE
  700 READ(1,530)T,PS1,PS2,PS3,PS4,PS5
      READ(1,550)EX,EP,ET,ETHI,EV
      PS0=PS1
  540 FORMAT(1H1,//// 5X,15HTESTED DATA OF ,20A4///)
      WRITE(3,550)T,PS0,PS1,PS2,PS3,PS4,PS5
      WRITE(3,549)
  549 FORMAT(//)
      WRITE(3,541)
  541 FORMAT(1H ,2X,2HID,3X,1HP,7X,        1HX,7X,1HX,7X,//)
      DO 30 I=1,NOBS
      READ(1,550)TT(I),PP(I),(XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
      WRITE(3,570)I,PP(I),        (XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
   30 CONTINUE
      WRITE(3,542)(TITLE(I),I=1,20)
  542 FORMAT(1H1,//// 5X,28HSUPPORTING DATA FOR TESTING ,20A4///)
      WRITE(3,543)
  543 FORMAT(1H ,2X,2HID,3X,1HP,7X,5HTRMIX,3X,2HVL,6X//)
      DO 35 I=1,NOBS
      T=TT(I) +460.
      RT=10.73*T
      P=PP(I)
   22 DO 25 J=1,NCOMP
      C(I,J)=(YY(I,J)/XX(I,J))
      X(J)=XX(I,J)
      Y(J)=YY(I,J)
   25 CONTINUE
      CALL VOLPAR
      CALL PHIMIX(CUBEQN)
      DO 26 J=1,NCOMP
      FP(I,J)=PHI(J)*P
      VP(I,J)=(P-PS0)*PVOL(J)/RT
      VORT(I,J)=PVOL(J)/RT
   26 CONTINUE
      WRITE(3,570)I,P,TRMIX,VL,(PHI(J),J=1,NCOMP),(PVOL(J),J=1,NCOMP)
   35 CONTINUE
      KK=0
   36 KK=KK+1
      WRITE(3,545)(TITLE(I),I=1,20)
  545 FORMAT(1H1,///5X,  18HTESTED RESULTS OF 20A4///)
      IF(KK.LE.1)GO TO 37
      EX=EX*2.0
   37 WRITE(3,551)EX,EP,ET
```

```
  551 FORMAT(5X,5H  EX=,F8.4,5H  EP=,F8.4,5H  ET=,F8.4//)
      WRITE(3,546)
  546 FORMAT(2X,7HPAIR NO,3X,1HP,7X,1HI,7X,2HII,6X,3HIII,5X,1HD,7X,
     1 4HDMAX,4X,2HDX,6X,2HDP,6X,2HDT                                 //)
      DO 100 I=1,NOBS
      T=460.+TT(I)
      RT=10.73*T
      DZ=0.0
      DX=0.0
      DP=0.0
      DTEMP=0.0
      DTHI=0.0
      DPVOL=0.0
      TERMI=0.0
      TERMJ=0.0
      TERMK=0.0
   40 DO 110 J=1,NCOMP
      XAB=XX(I,J)+XX(I+1,J)
      TERMI=TERMI+XAB*ALOG(C(I+1,J)/C(I,J))
      TERMJ=TERMJ+XAB*ALOG(FP(I,J)/FP(I+1,J))
      TERMK=TERMK+XAB*(VP(I+1,J)-VP(I,J))
      DZ=DZ+(XAB*(1.0/YY(I,J)+1.0/YY(I+1,J)+1.0/XX(I,J)+1.0/XX(I+1,J))
     1    )*FX
      DX=DX+(XAB*(1.0/YY(I,J)+1.0/YY(I+1,J)+1.0/XX(I,J)+1.0/XX(I+1,J))+
     1 2.0* ABS(ALOG(C(I+1,J)/C(I,J))-ALOG(FP(I,J)/FP(I+1,J))
     2    -VP(I+1,J)+VP(I,J)))*EX
      DP=DP+XAB*(1./PP(I)+1./PP(I+1)+ABS(VORT(I+1,J))
     1    +ABS(VORT(I,J)))*EP
      DTEMP=DTEMP+XAB*( ABS(VP(I+1,J)/T)+ ABS(VP(I,J)/T))*ET
      DTHI=DTHI+XAB*2.0*ETHI
      DPVOL=DPVOL+XAB*( ABS(VP(I+1,J) -       VP(I,J)))*EV
C     DPVOL=DPVOL+XAB*( ABS(VP(I+1,J))+ ABS(VP(I,J)))*EV
  110 CONTINUE
      DTERMS=TERMI-TERMJ-TERMK
C     DMAX=DX+DP+DTEMP+DTHI+DPVOL
      DMAX=DX+DP+DTEMP
      I1=I+1
      P=(PP(I+1)+PP(I))/2.0
      WRITE(3,580)I,I1,P,TERMI,TERMJ,TERMK,DTERMS,DMAX,DX,DP,DTEMP,DTHI,
     1   DPVOL,DZ
C 580 FORMAT(I5,1H-,I2,2X,F8.1,11F8.4)
  580 FORMAT(I5,1H-,I2,2X,F8.1,8F8.4,24X,3F8.4)
      IF(I.GE.NOBS-1)GO TO 41
```

```
  100 CONTINUE
   41 GO TO (36,36,600),KK
  800 STOP
  500 FORMAT(20A4)
  510 FORMAT(1H ,6X,2I2,2F10.2,2F10.4)
  520 FORMAT(9F8.4,2A4)
  530 FORMAT(2F10.4,F10.3,5F10.4)
  532 FORMAT(1H1,20A4)
  550 FORMAT(8F10.4)
  560 FORMAT(1H0,F10.3,F12.3,F12.4,6X,2F10.4,F10.3,6F10.4)
  570 FORMAT(I5,F8.1,4F8.4,8F8.4)
  590 FORMAT(2I5)
      END
```

VI. 3 MODIFIED BARKER'S METHOD

VI. 3. 1 GENERAL INFORMATION

PURPOSE - Calculation of the vapor phase compositions by fitting the binary isothermal and liquid composition data of low pressure systems to Redlich-Kister's equation of one to five terms.

LANGUAGE - FORTRAN IV in E level

SUBROUTINE REQUIRED - SOLVEJ.

INPUT AND OUTPUT COMMANDS:

Input - READ (1, FORMAT's statement number)
Print - WRITE (3, FORMAT's statement number)
Card output - WRITE (2, FORMAT's statement number)

Printing Control:

Single space - blank in the first column
Double space - 0 in the first column
Starting a new page - 1 in the first column

VI. 3. 2 INPUT and OUTPUT

OUTPUT:

Card 1	It contains the initial estimation of adjustable parameters in F - FORMAT, 10 column per field.
Card 2	The title of the problem can be entered into the card from columns 1 to 8
Card 3	It contains the control variables in I - FORMAT.

Column	
1 - 5	N, number of observations
6 - 10	NZ, the minimum number of terms in the Redlich-Kister equation desired
11 - 15	MAX, the maximum number of terms in the Redlich-Kister equation desired

Cards 4 and 5 : They bear the critical properties, one card for each component in F-FORMAT.

Column	
1 - 10	P_c, critical pressure
11 - 20	V_c, critical volume
21 - 30	T_c, critical temperature
31 - 40	R, the gas constant of which the unit used should be consistent with the critical properties entered.
41 - 50	ω , acentric factor

Card 6 : It bears the properties of the pure components in F-FORMAT.

Column	
1 - 10	P_1^s
11 - 20	P_2^s
21 - 30	v_{1L}
31 - 40	v_{2L}
41 - 50	β_{11} or blank
51 - 60	β_{22} or blank
61 - 70	T

Cards 7 to (N + 6) : They bear the experimental data, one point per card in F-FORMAT.

Column	
1 - 10	x_1
11 - 20	P

OUTPUT : see flow diagram

VI.3.3 FLOW DIAGRAM : (see figure VI.3)

Figure VI.3 Flow Diagram of the Program "Modified Barker's Method"

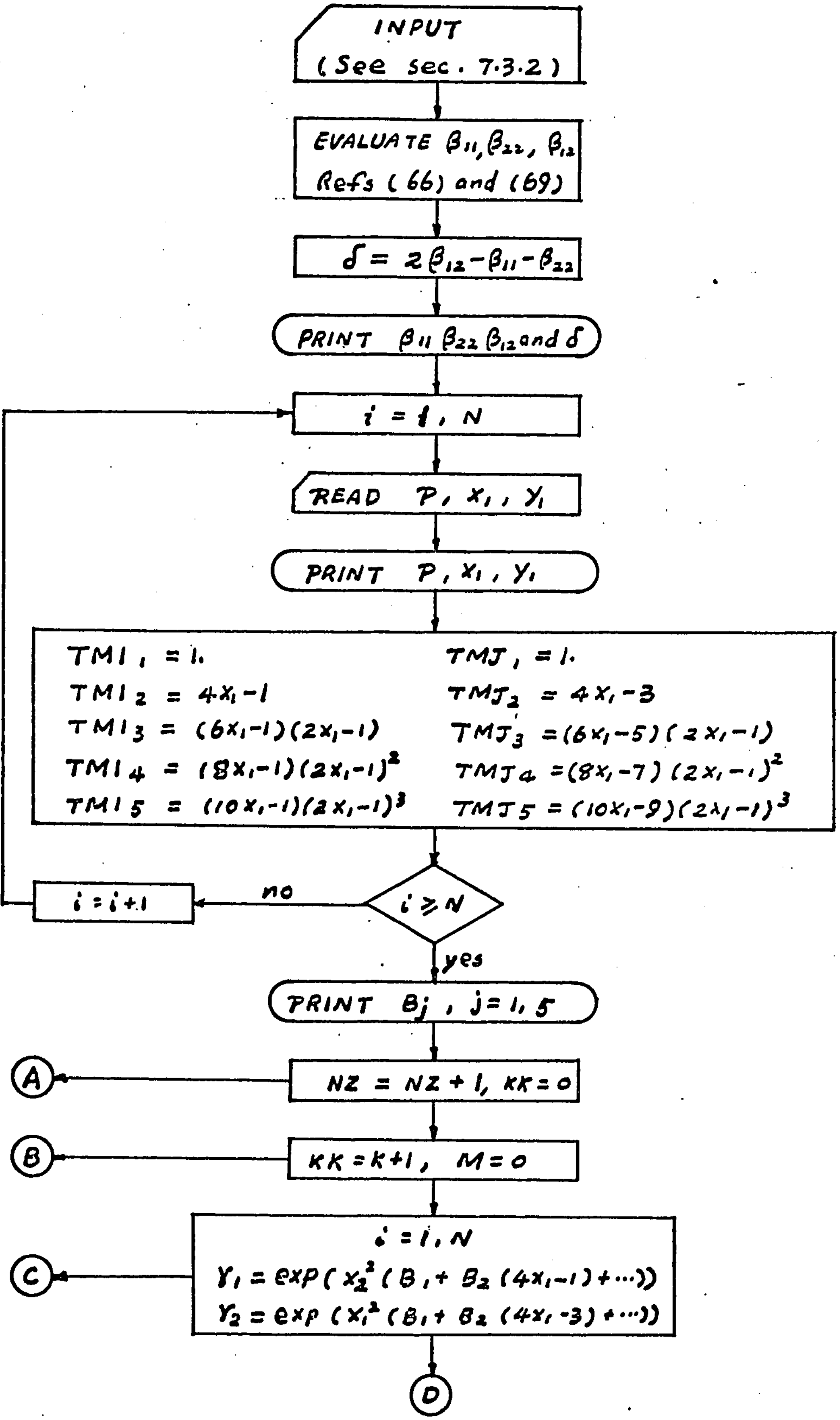


Figure VI. 3 (continued)

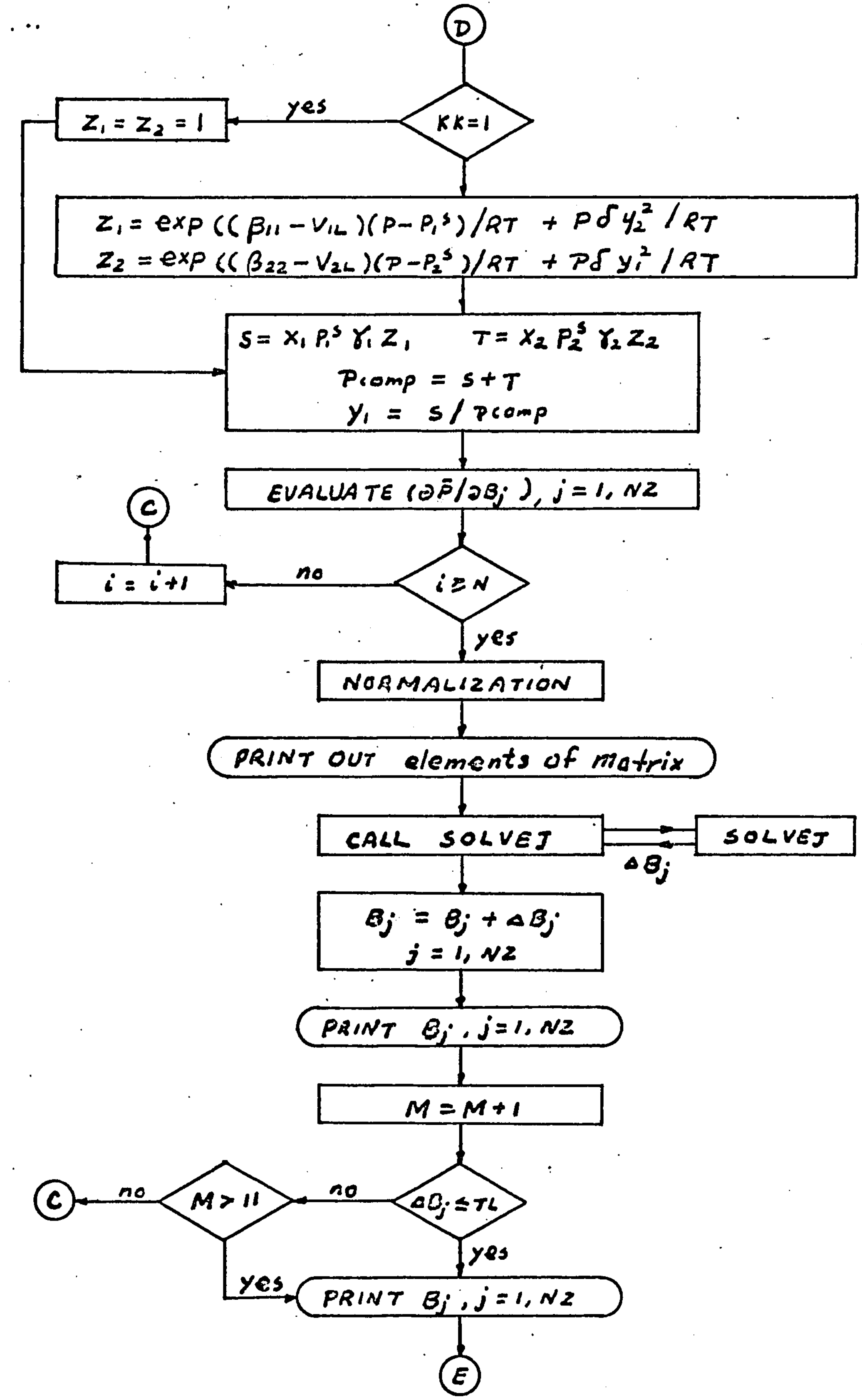
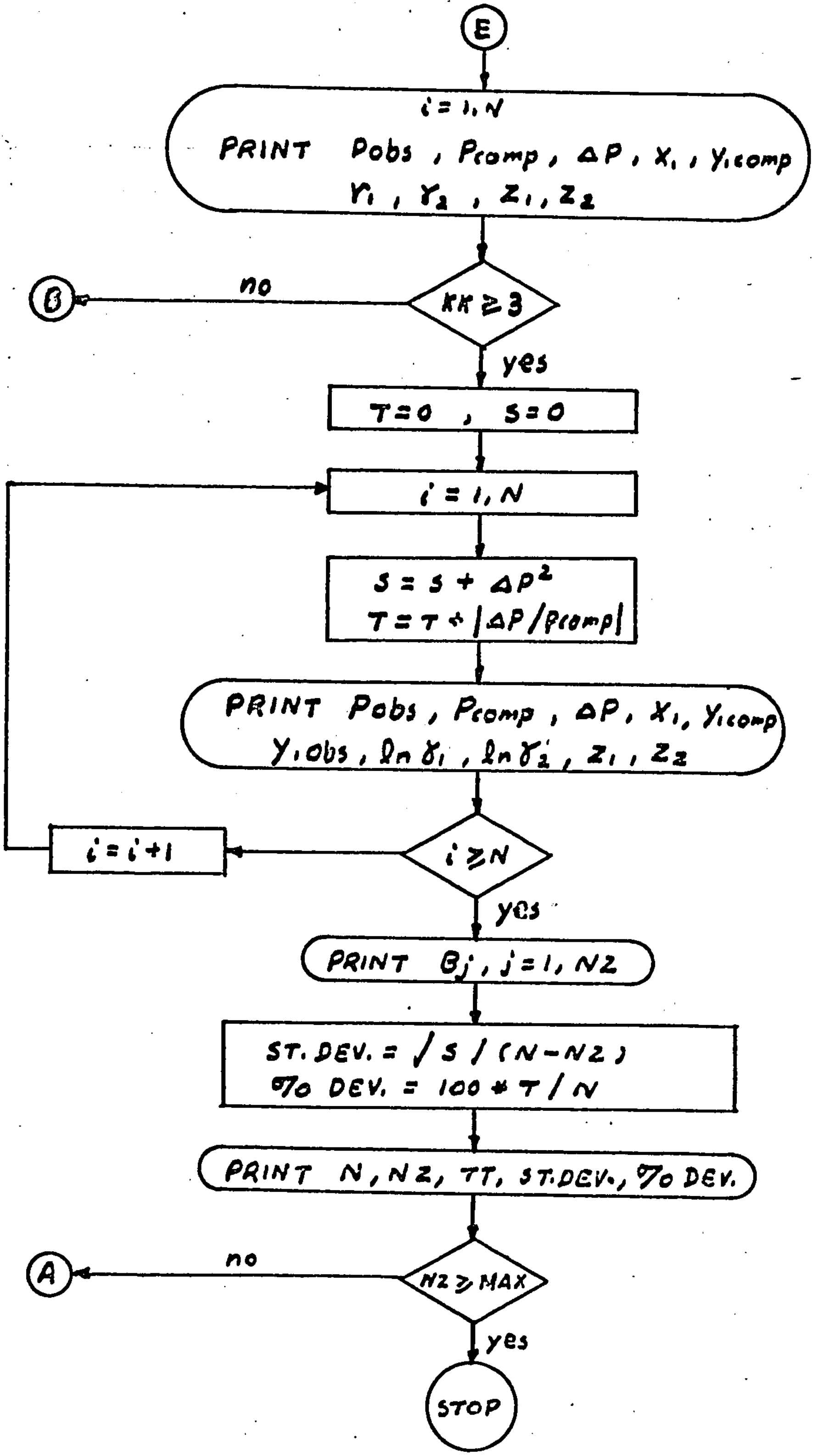


Figure VI. 3(continued)



VI. 3. 4 COMPUTER PROGRAM

```
C     S.D.CHANG(CHEM.ENG.)
      DIMENSION Q(50),X(50),GI(50),GJ(50),TMI(50,5),TMJ(50,5),
     1   V(50,6),PM(5),Z(6,6)
      DIMENSION ZI(50),ZII(50),YY(50),PT(50),Y(50)
      DIMENSION TITLE(40)
      DO 6 I=1,5
    6 PM(I)=0.0
      READ(1,101)(PM(I),I=1,5)
      TL=0.00001
      FACT=1.0E0
    1 READ(1,1000)(TITLE(I),I=1,40)
 1000 FORMAT(40A2)
      WRITE(3,2000)(TITLE(I),I=1,40)
 2000 FORMAT(/1H1,40A2//)
      READ(1,100)N,NZ,MAX
      IF(N)20,21,20
   20 READ(1,101)PCI,VCI,TCI,R,WI
      READ(1,101)PCII,VCII,TCII,R,WII
      READ(1,101)PI,PII, VLI,VLII,BJ,BII,TT
      K=1
  200 GO TO(201,202,203,208),K
  201 TR=TT/TCI
      U=WI
      GO TO 204
  202 TR=TT/TCII
      U=WII
      GO TO 204
  203 TCIII=(TCI*TCII)**.5
      WIII=(WI+WII)/2.0
      PCIII=4.00*TCIII*(PCI*VCI/TCI+PCII*VCII/TCII)/
     1   (VCI**(1./3.)+VCII**(1./3.))**3
      TR=TT/TCIII
      U=WIII
  204 BIII=(0.144500-0.3300/TR-0.1385/TR**2-0.0121/TR**3)+
     1   U*(0.073+0.4600/TR-0.500/TR**2-0.097/TR**3-0.007300/TR**8)
      GO TO (205,206,207,208),K
  205 BJ=R*TCI*BIII/PCI
      K=K+1
      GO TO 200
  206 BII=R*TCII*BIII/PCII
      K=K+1
      GO TO 200
  207 BIII=R*TCIII*BIII/PCIII
```

```
      K=K+1
      GO TO 200
  208 DIII=2.00*BIII-BJ-BII
      WRITE(3,102)BJ,BII,BIII,DIII
C
      ZOI=(BJ-VLI)/R/TT
      ZOII=(BII-VLII)/R/TT
      DO 298 I=1,N
      READ(1,101)G(I),X(I),Y(I)
      WRITE(3,102)G(I),X(I),Y(I)
       XX=2.0*X(I)-1.0
      TMI(I,1)=1.0E0
      TMI(I,2)=4.0*X(I)-1.0
      TMI(I,3)=(6.0*X(I)-1.0)*XX
      TMI(I,4)=(8.0*X(I)-1.0)*XX**2
      TMI(I,5)=(10.0*X(I)-1.0)*XX**3
      TMJ(I,1)=1.0E0
      TMJ(I,2)=TMI(I,2)-2.0
      TMJ(I,3)=TMI(I,3)-4.0*XX
      TMJ(I,4)=TMI(I,4)-6.0*XX**2
      TMJ(I,5)=TMI(I,5)-8.0*XX**3
  298 CONTINUE
      WRITE(3,102)TL,(PM(I),I=1,5)
  297 NZ=NZ+1
      NZ1=NZ+1
      KK=0
  299 KK=KK+1
      M=0
  300 DO 410 I=1,N
      GI(I)=0.0
      GJ(I)=0.0
      DO 320 J=1,NZ
      GI(I)=GI(I)+PM(J)*TMI(I,J)
  320  GJ(I)=GJ(I)+PM(J)*TMJ(I,J)
      GI(I)= EXP((1.0-X(I))*(1.0-X(I))*GI(I))
      GJ(I)= EXP(X(I)*X(I)*GJ(I))
C
      IF(KK-1)301,302,301
  302 ZI(I)=1.00
      ZII(I)=1.00
      GO TO 303
  301 ZI(I)=     (ZOI*(PT(I)-PI)
     1    +PT(I)*DIII*(1.00-YY(I))*(1.00-YY(I))/R/TT)
```

```
      ZII(I)=      (ZOII*(PT(I)-PII)
     1    +PT(I)*DIII*(YY(I)*YY(I))/R/TT)
      IF(ZI(I))304,305,306
  304 ZI(I)=1.00/ EXP(-ZI(I))
      GO TO 307
  305 ZI(I)=1.00
      GO TO 307
  306 ZI(I)= EXP(ZI(I))
  307 IF(ZII(I))309,310,311
  309 ZII(I)=1.00/ EXP(-ZII(I))
      GO TO 312
  310 ZII(I)=1.00
      GO TO 312
  311 ZII(I)= EXP(ZII(I))
  312 CONTINUE
      ZI(I)=1.00/ZI(I)
      ZII(I)=1.00/ZII(I)
  303 S=X(I)*PI*GI(I)*ZI(I)
      T=(1.0-X(I))*PII*GJ(I)*ZII(I)
      PT(I)=S+T
      YY(I)=S/PT(I)
      DO 400 J=1,NZ
      V(I,J)=S*(1.0-X(I))*(1.0-X(I))*TMI(I,J)
     1    +T*X(I)*X(I)*TMJ(I,J)
  400 CONTINUE
      V(I,NZ1)=(Q(I)-PT(I))*FACT
  410 CONTINUE
  500 DO 508 I=1,NZ1
      DO 508 J=1,NZ1
      SUM=0.0
      DO 509 K=1,N
  509 SUM=SUM+V(K,I)*V(K,J)
      Z(I,J)=SUM
      Z(J,I)=Z(I,J)
  508 CONTINUE
      DO 510 I=1,NZ
  510  WRITE(3,102)(Z(I,J),J=1,NZ1)
      CALL SOLVEJ(NZ,Z,INDIC)
C
      DO 600 I=1,NZ
  600 PM(I)=PM(I)+Z(I,NZ1)
      WRITE(3,102)(Z(I,NZ1),I=1,NZ)
      M=M+1
```

```
      DO 612 I=1,NZ
      IF( ABS(Z(I,NZ1))-TL)612,612,616
  616 IF(M-11)622,622,632
  622 GO TO 300
  612 CONTINUE
  632 WRITE(3,104)M,(PM(I),I=1,NZ)
C
      DO 633 I=1,N
      V(I,NZ1)=V(I,NZ1)/FACT
  633 WRITE(3,102)Q(I),PT(I),V(I,NZ1),X(I),YY(I),GI(I),GJ(I),ZI(I),
     1   ZII(I)
      IF(KK-3)299,700,700
C     EVALUATION
  700 WRITE(3,105)
      WRITE(3,2000)(TITLE(I),I=1,40)
      WRITE(3,906)
      WRITE(2,906)
  906 FORMAT(1H ,2X,4HPOBS,4X,5HPCOMP,3X,2HDP,6X,1HX,7X,1HY,7X,4HYOBS,4X
     1,6HGAMMA1,2X,6HGAMMA2,2X,2HZI,6X,3HZII////)
      S=0.0
      T=0.0
      DO 750 I=1,N
      GI(I)=ALOG(GI(I))
      GJ(I)=ALOG(GJ(I))
      S=S+V(I,NZ1)*V(I,NZ1)
      T=T+ ABS(V(I,NZ1)/PT(I))
      WRITE(3,902)Q(I),PT(I),V(I,NZ1),X(I),YY(I), Y(I),GI(I),GJ(I),
     1    ZI(I),ZII(I)
      WRITE(2,902)Q(I),PT(I),V(I,NZ1),X(I),YY(I), Y(I),GI(I),GJ(I),
     1    ZI(I),ZII(I)
  902 FORMAT(1H ,3F8.2,2F8.3,3F8.4,2F7.3)
  750 CONTINUE
      WRITE(3,105)
      WRITE(3,922)(PM(I),I=1,NZ)
      WRITE(2,922)(PM(I),I=1,NZ)
  922 FORMAT(1H ,2HB=,F10.5,3X,2HC=,F10.5,3X,2HD=,F10.5,3X,2HE=,F10.5,3X
     1,2HF=,F10.5 )
      S=(S/(N-NZ))**0.5
      T=T/N*100.
      WRITE(3,907)N,NZ,TT,S,T
      WRITE(2,907)N,NZ,TT,S,T
  907 FORMAT(21H NO.OF OBSERVATIONS =,I10/
     1 18H NO.OF CONSTANTS =,I10/
```

```
     2 22H SYSTEM TEMPERATURE AT,F10.2,5HDEG K/
     3 26H ST.DEV. OF CORRELATICN IS,F10.2,6HMM.HG./
     4 27H AV.% DEV OF CORRELATION IS,F10.2/    )
      WRITE(3,2000)(TITLE(I),I=1,40)
      IF(NZ-MAX)297,760,760
  100 FORMAT(3I5)
  101 FORMAT (8F10.0)
  102 FORMAT(1H ,9E14.6)
  104 FORMAT(//I5,5E15.7/)
  105 FORMAT(////)
  760 GO TO 1
   21 RETURN
      END
```

```
      SUBROUTINE SOLVEJ(NA,A,INDIC)
      DIMENSION A(6,6)
      NA1=NA+1
      DO 205 I=1,NA
      IF(A(I,I))200,206,200
  200 P=1./A(I,I)
      DO 201 J=I,NA1
  201 A(I,J)=P*A(I,J)
      DO 202 K=1,NA
      IF (I-K) 203,202,203
  203 Q=A(K,I)
      DO 204 J=I,NA1
  204 A(K,J)=A(K,J)-Q*A(I,J)
  202 CONTINUE
  205 CONTINUE
      INDIC=0
      RETURN
  206 IF(NA-1) 300,304,300
  300 I1 = I+1
      DO 303 L=I1,NA
      IF(A(L,I)) 301,303,301
  301 DO 302 J=I,NA1
      HOLD=A(I,J)
      A(I,J)=A(L,J)
  302 A(L,J)=HOLD
      GO TO 200
  303 CONTINUE
      INDIC=1
  304 WRITE(3,207)I
  207 FORMAT(//25H DIAGONAL ELEMENT IN EQN ,I4,40H IS ZERO TRANSPOSE EQN
     1 WITH PREVIOUS ONE//)
      RETURN
      END
```