A STUDY ON PHASE BEHAVIOUR OF SELECTED CARBON DIOXIDE - ALKANE SYSTEMS AND EQUATIONS OF STATE

by

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A B S T R A C T

Vapor-liquid equilibria data were experimentally investigated by means of a forced recirculation type apparatus for three carbon dioxide-hydrocarbon systems at the following isothermal conditions:

ethane-carbon dioxide	-60°, -20°, 20°, 60°F
propane-carbon dioxide	-20°, 20°F
propane-ethane-carbon dioxide	-20°, 20°F

A total of 109 data points were obtained.

The predicted values by means of the Redlich-Kwong equation of state with a modified procedure were compared favourably with the experimental results. The overall average deviation in P is 1.98% and in y is 0.0085 mole fraction. The results indicated that the ternary data can be predicted from pure component properties and binary interaction constants for the constituent binaries. The overall average deviation between the experimental and calculated P is less than 3% and in y is less than 0.0140 mole fraction.

The parameters Ω_a and Ω_b of the Redlich-Kwong equation were generalized. First of all, they were correlated in terms of T_r up to $T_r = 1.0$ for thirteen pure components; argon, nitrogen, benzene, ethylene, propylene and C_1 - C_8 for the available reliable saturation conditions. The coefficients of these correlations were further generalized in terms of ω. The generalized correlations have been used to compute the Ω_a and Ω_b values for seven arbitrarily selected components other than those included in the generalized correlation with an overall average deviation of 0.55% and 0.87% respectively. The applicability of the values computed from the generalized correlation was further demonstrated by the prediction of vapor-liquid equilibrium data for seven binary systems on thirty six isothermal conditions. It was also applied to the

ternary system propane-ethane-carbon dioxide at the two isothermal conditions. The overall average deviation in y for a total of 306 data points is 0.0074 mole fraction compared to 0.0066 mole fraction when the parameters were calculated from the saturation properties.

A further modification for the procedure previously proposed by Elshayal and Lu for predicting VLE using the three-parameter Clausius equation of state was attempted. The parameters Ω_a and Ω_b were treated as temperature-dependent while Ω_c was assigned a positive value determined from the original equation. The new proposed method was evaluated and compared with the Redlich-Kwong equation with the modified procedure for the purpose of vapor-liquid equilibrium calculations. The comparison covered 186 data points on fourteen isothermal conditions. The results obtained are comparable but not necessarily superior to the Redlich-Kwong equation. The overall average absolute deviation in P is 1.34% and in y is 0.0096 mole fraction for the Clausius equation compared to 1.40% and 0.0106 mole fraction for the Redlich-Kwong equation. These differences are within the experimental errors.

Dedicated:

To My Father!
For he gave me skill, stamina and
the knowledge of my past.

To My Mother!
For she gave me the love for life
and taught me to respect it.

"My Heart Soars"
by Chief Dan George

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NOMENCLATURE

a_i, b_i, c_i, d_i	coefficients in Equations (4.59) (4.62)
A, B, C, a, b, c	adjustable parameters or constants
a_{ij}, b_{ij}, c_{ij}, d_{ij}	coefficients in Equations (4.64) to (4.67)
a_{ij}	cross coefficient in Equation (4.39)
E	measuring error
f	fugacity
G	Gibbs' free energy
H,h	dummy variable of the equation of state (Equations (4.34), (4.72), (4.73))
H	enthalpy
i,j	pure numbers
K	equilibrium ratio, y/x
k_{ij}	interaction parameter as defined by $T_{c_{ij}} = (T_{c_i} T_{c_j})^{0.5}(1 - k_{ij})$
n	number of moles
N	number of components
P	pressure
R	universal gas constant
S	entropy
T	temperature
V	molal volume
x	liquid phase mole fraction
y	vapor-phase mole fraction
Z	compressibility factor

GREEK LETTERS

γ	activity coefficient
Δ	deviation
δ	absolute value of a relative deviation defined by Equation (4.63)
μ	chemical potential
ϕ	fugacity coefficient
ω	Pitzer's acentric factors
Ω_a, Ω_b, Ω_c	parameters of equations of state
$\Omega_{calc.}$	evaluated from the saturation properties
$\Omega_{comp.}$	computed from correlation equations

SUPERSCRIPTS

E	excess property
*	ideal state
°	standard state
s	saturated property
-	partial molar quantities
^	property in solution
calc.	calculated
exp.	experimental

SUBSCRIPTS

c	critical property
i, j or 1, 2	component identification
ij	i-j pair
ℓ	liquid phase
v	vapor phase
r	reduced property
T	total property

CHAPTER 1

I N T R O D U C T I O N

Phase equilibrium studies for carbon dioxide-hydrocarbon mixtures are useful in the understanding of the phase behaviour of these mixtures, in the design of efficient distillation towers for the processing of natural and refinery gases and in the secondary recovery techniques concerning reservoir fluids. The importance of the carbon dioxide-hydrocarbon systems results primarily from the fact that most natural gases contain sufficient carbon dioxide to warrant concern in a processing plant, where solidified carbon dioxide can dangerously plug the low temperature processing equipment. In addition to this operating problem, carbon-dioxide has the undesirable effect of reducing the heating value of natural gas in direct proportion to its concentration. It was reported [130] that gas mixtures of carbon dioxide with light hydrocarbons exhibit unusual PVT behviour.

Hsi and Lu[54] have presented a method for predicting vapor-liquid equilibria which was successfully applied to four binary and two ternary systems containing carbon dioxide, including methane-carbon dioxide, propane-carbon dioxide and n-butane-carbon dioxide. It was not possible to establish the validity of the prediction to the binary system ethane-carbon dioxide due to the unavailability of experimental data. For this reason, experimental measurement of vapor-liquid equilibria for this binary system was investigated in this work. During the course of this study, equilibrium data of Kurata and Swift [64] for this binary system became available on three mixtures at four temperatures. Poor agreement was obtained when these experimental values were compared with the calculated values obtained from the prediction method[54]. It was not certain whether the discrepancy obtained was due to the quality of the data or the validity of the calculation method. Therefore, vapor-liquid equilibria data were determined at the same four isothermal conditions (-60°, -20°, 20°

and 60°F) as those reported by Kurata and Swift[64] but with more data points collected.

Although the binary system propane-carbon dioxide has been reported in the literature[1,77,86,90], the equilibrium data are not available over the complete concentration range at temperatures below -4.4°F. To extend the range of lower temperatures and to smooth the correlation between the existing data, the isothermal vapor-liquid equilibria were experimentally determined at -20°F and 20°F over the complete concentration range. As a complement to the experimental data for systems containing propane, ethane and carbon dioxide, the ternary system propane-ethane-carbon dioxide was measured at -20° and 20°F. The experimental data for the preceding systems were collected using a forced recirculation apparatus.

A complete set of experimental binary and ternary data of this kind enables one to test many correlation and prediction methods and with the expectation that one of the methods can be used to establish the necessary information for the gas industry from the minimum required data. To estimate thermodynamic properties adequately, one must have access either to accurate data or to a suitable analytical expression. Such an expression could be based on an equation of state. One of the equations of state frequently used in chemical engineering is that proposed by Redlich and Kwong in 1949[91]. It is remarkably simple and employed in all property estimation[75]. It is generally accepted that the two parameters are temperature dependent and may be evaluated at the temperature of interest from the pure component vapor pressure and liquid density at saturation. The applicability of the equation is sometimes limited due to the unavailability of PVT data of the substance at saturation. A further limitation is the lack of a suitable generalized correlation of the parameters for vapor-liquid equilibria calculations.

Consequently one of the objectives of this study is to develop a generalized correlation for the temperature

dependent parameters of the Redlich-Kwong equation for the purpose of calculating liquid compressibility and vapor-liquid equilibria data.

Elshayal and Lu[33,34] have also presented a method for predicting vapor-liquid equilibria using the three-parameter Clausius equation of state with a modified procedure. The three parameters were treated temperature dependent to satisfy the three conditions at equilibrium. They were evaluated from three saturated properties of pure components, namely: vapor pressures, saturated liquid densities and saturated vapor densities. On further evaluation for the purpose of the calculation of thermodynamic properties, it yielded poor predictions of enthalpy departure while predicting accurate densities which might suggest that the temperature dependence of the Holmholz free energy as a generating function for the thermodynamic properties is inadequate[23,49,103]. Another limitation of this method is that the reliability of the saturated vapor densities is questionable and these uncertainties are reflected in the numerical value of the parameters.

Consequently, another phase of this work centers on investigating the proper variations of the parameters with temperature in order to by-pass the use of the unreliable saturated vapor-volumes for the establishment of these parameters. The proposed method was evaluated and compared with the modified procedure of the Redlich-Kwong equation of state and with the previous modified procedure of the Clausius equation of state[33,34].

CHAPTER 2

LITERATURE SURVEY

2.1 Vapor-liquid equilibria data:

The vapor-liquid equilibria of many different hydrocarbon-carbon dioxide systems have been investigated experimentally. A complete literature survey up to October 1959 was prepared by Flynn[37]. The bibliography of vapor-liquid equilibria, prepared by Ruhemann and Harmens[46], covers the period up to 1966. Special attention was drawn by the authors to the extensive bibliography published in Russian in 1963 by Malkov et al.[70]. In addition, the survey made by Kogan et al.[61] in Russian and published in 1966 entitled, "Vapor-liquid Equilibrium" provides useful references. Moreover, in the book by Hala et al.[43], a review is given which covers the period up to 1965. Recently, Wichterle et al.[118] presented 4800 references on systems whose vapor-liquid equilibrium had been measured and reported from 1900 through December 1972. Oellrich, Plöcker and Knapp[78] have also reviewed all the journals published since 1900 up to the end of 1972. Their review consists of a reference list in alphabetical order and tables with detailed information. Vapor-liquid equilibria data for 933 binary systems were presented in "Computer aided data book of vapor-liquid equilibria" by Hirata and Nagahama[48]. Wilson's equation and the Redlich-Kwong equation with a modified procedure were used to correlate the data. Of course, the systems more frequently studied have been the binary and the ternary systems. Unfortunately, there were few data existing for the ethane-carbon dioxide system. Kuenen[62,63] did, however report the azeotropic composition at -50°C and +20°C. Khazanova et al.[60] very briefly reported the vapor-liquid equilibrium compositions for several isotherms between +10°

and 20°C. The data shown are not experimental points but rather interpolated values. The measurements do not appear to be very accurate[38]. The stated uncertainty in the pressure is ±0.5 atm. For this reason, the work was undertaken for the purpose of obtaining a set of vapor-liquid equilibrium data for this system to use it for testing the validity of the prediction method by Hsi and Lu[54]. During the course of this work, experimental vapor-liquid equilibrium data became available in the literature[64] on three mixtures for the ethane-carbon dioxide system at four temperatures. However, poor agreement was obtained when these experimental values were compared with the calculated values obtained from the prediction method[54]. It was not certain whether the discrepancy obtained is due to the quality of the data or the validity of the calculation method. Consequently, vapor-liquid equilibrium data of the ethane-carbon dioxide system were needed. By the end of this work, the data became available elsewhere in the literature[35,41,77,93].

Vapor-liquid equilibrium data for the binary system propane-carbon dioxide have been reported in literature[1,77,86,90] but they are not available over the complete concentration range below -4.4°F. To extend the range and smooth the correlation between the existing data, experimental determinations of the isothermal vapor-liquid equilibrium in this system are needed.

The data on the ternary system propane-ethane carbon dioxide were not available. Therefore, experimental determinations of vapor-liquid equilibria of this mixture were determined at two isothermal conditions as those of the constituent binaries; ethane-carbon dioxide and propane-carbon dioxide.

The importance of the carbon dioxide-hydrocarbon systems results mainly from the low-temperature processing of natural gas. In this work, only those publications pertinent to the present study are briefly reviewed and quoted accordingly.

2.2 Experimental techniques:

The techniques and apparatus used to obtain vapor-liquid equilibrium data were reviewed in some detail by Hipkin[47], Robinson and Gilliland[92], Hala et al.[43] and Wilson[124a]. The merits and limitations of these techniques were also discussed[113]. These methods can be classified into the following:

(a) Static and Total Pressure Method[28]

In these methods, the liquid mixture is placed into a constant volume cell, either agitated or allowed to sit for a long time to reach equilibrium. In the static method, samples of the vapor and liquid phases are withdrawn and analyzed while in the total pressure method, only the liquid phase is analyzed. The main failure in the case of static method is that the mass of the material in the vapor phase at low pressure is quite small. The equilibrium can be greatly disturbed due to the withdrawal of the material which causes a pressure drop. This failure is reduced if the bomb is used for measurement at high pressure where the gas phase is more dense.

The disturbance due to sampling can be reduced by the use of a variable volume cell[36,39]. The pressure disturbance due to sampling is reduced by maintaining the equilibrium pressure as the sample is withdrawn by compressing the mixture with a piston. The piston may be a mechanical device or a slug of mercury. The use of a mercury piston causes some concern when used at high temperatures due to the toxicity of mercury vapor.

(b) Dew and Bubble-Point Method:[11,24,59,98]

In this method, a mixture of known composition

is introduced into a variable volume cell. The temperature is maintained constant and the pressure varied until a bubble in the liquid or a drop in the vapor inside the cell is observed in the window cell. The procedure is repeated at several temperatures for each constant composition mixture to determine the dew-point and bubble-point loop. The vapor-liquid equilibrium condition can be determined through the intersection of the dew-point curve of one composition with the bubble-point curve of another composition.

Another way to establish the dew and bubble points is to plot the pressure isotherm and obtain the points from discontinuities in the curve. Although the sampling technique is eliminated, the main disadvantages with this method are that the dew-point and bubble-point are not always well defined. However, this method is applicable to binary systems only because the fixing of temperature and pressure is not sufficient to define a multi-component system.

(c) Flow Method:[30,97,104]

In this method, gas is bubbled slowly through a series of cells containing the liquid. If the bubbling rate is low enough, phase equilibrium should be established between the phases. However a pressure gradient is necessary to drive the gas and hence, an exact equilibrium can not be established. There is also the danger of entrainment.

(d) Distillation Tower Method: [117]

It uses the same principle of a simple distillation operation. A distillation tower can be built for large scale operations. A modification of the tower or taking the tray efficiency into account

can improve the quality of the data. The method is poor as far as accuracy is concerned. However, it provides a rapid and practical way to speed up the accumulation of data.

(e) Forced Recirculation Method: [49,55]

A common method for obtaining vapor-liquid equilibrium data is by repeatedly circulating the vapor through the liquid phase until no further change in the composition of either takes place. The vapor is allowed to bubble through the liquid, thus ensuring good contact. As in the dynamic flow method, the flow is produced by small pressure gradient. Thus, there is a small concentration gradient in the cell from the top to the bottom. However, this effect is small in most cases[92]. Circulation of the vapor phase is achieved by means of a mercury pump[91] or an electro-magnetic pump[2,16]. The method has been widely adopted [10,95,105].

The weakest part in obtaining the equilibrium data is the analysis of the samples for composition. A small sample must be taken in such a manner as to disturb the system as little as possible. The composition of the phases are normally analysed by means of a gas chromatography. That is particularly true if relatively non-volatile components are present. While the error introduced due to the chromatograph can be analysed, the upset of equilibrium due to sampling produces a set of unacceptable data.

In this investigation, the forced recirculation method using an electro-magnetic pump in conjunction with a volume regulator was adopted. A long coil ensured that the temperature of the vapor passing through it was brought down to the bath temperature before being returned to the cell. A

detailed discussion is given elsewhere[16] and also a brief description is given in the next chapter.

2.3 Equations of State:

In view of the large number of equations of state which have been proposed in the literature, it is natural to search for the motivations. Martin[71] suggested that "there are two rather obvious reasons for the wide-spread activities in this field over an extended period of time. The first is the fact that the problem of developing an equation of state is mathematically fascinating and particularly tantalizing because it seems so simple, at least at the start. The second reason concerns the exceptional power and utility of an equation of state. When combined with appropriate thermodynamic relations, a well behaved equation may predict with high precision isothermal changes in heat capacities, enthalpy departure from ideal gas behaviour, partial molal volume, fugacity, vapor pressure, latent heat of vaporization and vapor-liquid equilibria in mixtures".

Extensive reviews have been written by many prominent workers, for instance, Shah and Thodos[102], Stewart and Timmerhaus[106], Martin[71] and Tsonopoulos and Prausnitz[111] to compare the relative merits and limitations of the most common equations of state. An interpretative review was presented by Vera and Prausnitz[93] to show the inter-relation between various commonly used equations of state. A state of affairs in thermodynamics has also been reported by Winnik[126]. Despite this prolific outpouring on the subject, some facts are either misunderstood or not fully appreciated and these justify further research in the field.

The degree of complexity of equations of state as indicated by the number of constants, has been deliberately increased to better represent the PVT behaviour of substances over wide ranges of temperature and pressure. In this respect,

the equation of state proposed by Martin and Hou[72] requires nine constants to predict the PVT behaviour of a substance. Similarily, the Benedict-Webb-Rubin equations require eight constants[6], while the Beattie-Bridgeman equation[5] has five constants to predict the PVT behaviour of substances for which the constants are calculated.

These equations have received considerable attention over recommended ranges of temperature and pressure[111]. Although these equations are logically developed from the well known thermodynamic principles, their application is frequently limited by the inaccessibility of the constants for the PVT conditions of interest. Establishing these constants is frequently a lengthy operation, requiring a curve fitting and a trial-and-error procedure. What appears to be the limitation is the fact that some PVT data of the substance must be available in order to begin establishing these constants.

Good accuracy is claimed by using these equations. The less complex equations of state, having two or three parameters, have been overlooked largely because of their lack of sophistication. This is consistent with the common notion that an equation of state with more constants should produce results that are more consistent with the experimental PVT behaviour of the substance. However, the two-parameter Redlich-Kwong equation proved to be superior over all the equations examined by Shah and Thodos[102].

2.3.1 Temperature Dependence of the Parameters of Equations of State

The parameters of the original equations of state were considered to be independent of temperature and were evaluated by two different general methods. The first method was often used in connection with the simpler equation of state, i.e., van der Waals type equation. The first and second derivative of pressure with respect to volume at the critical point were set equal to zero, plus the equation itself at the critical point was used. Another approach to the evaluation of the parameters yields a specified kind of minimum deviation from the available experimental data by means of the method of

least squares[49]. Benedict and co-workers were primarily interested in applying their equation to hydrocarbon mixtures for the calculation of K-values and enthalpies; mixing rules for eight constants were proposed[7] in 1942. To obtain eight meaningful constants, extensive experimental data are required and even if such data are at hand, the eight constants obtained from data reduction are probably not unique[111]. Several sets of constants are not an important matter as long as the attention is restricted to the properties of pure components but it becomes extremely important when pure component constants are used to predict mixture properties[49,50]. Constants for twelve pure hydrocarbons were given by Benedict, Webb and Rubin in 1951[8]. BWR constants have been obtained for nitrogen[66,107], hydrogen[66,76], carbon dioxide[42,66], hydrogen sulphide[80], argon[128] and carbon monoxide[101].

When fitting liquid saturation pressures, the important constant in the BWR equation is C_o. It was shown in 1951[8] that C_o must be adjusted when the saturation pressure is less than 1 atm., and in 1953[107] Stotler and Benedict showed that for calculations at low temperature, it is necessary to allow C_o to vary with temperature.

This modification has won wide acceptance[66,80,129]. Barner and Schreiner[4] have pointed out the need for this modification for accurate calculation of enthalpies.

On the other hand, many variations of van der Waals equation have been proposed but by far the most successful one is that of Redlich and Kwong in 1949[91] which combines simplicity with reasonable accuracy. Since it has only two constants, its primary use is not for representing extensive experimental data, but for estimating volumetric and derived properties for non-polar (or slightly polar) fluids and their mixtures from minimum experimental information such as critical temperature and pressure of the pure components[111]. The superiority of the Redlich-Kwong equation over the van der Waals equation and its early variations (Bertheholt, Dietirici) has been amply demonstrated by Shah and Thodos[45]. A good

compilation of the modification of this equation of state is available elsewhere[46,51].

To better represent the PVT relation calculated by the Redlich-Kwong equation of state, Wilson[121] proposed that the parameter a of the equation be temperature dependent according to the following relation

$$a_{ii}/R\,T_{ci}^{1.5} = 4.934\left[1 + k_i\left(\frac{1}{T_{Ri}} - 1\right)\right] T_{Ri}^{1.5} b_i \qquad (2.1)$$

$$a_{ij} = \theta_{ij}\, a_{ii} + (1 - \theta_{ij})\, a_{jj} \qquad (2.2)$$

Where T_{Ri} is the reduced temperature of i, k_i is a constant characteristic of i, θ_{ij} is a binary constant which must be determined from some experimental data for the binary and a_{ij} is a measure of the strength of attraction between a molecule i and a molecule j. If i and j are the same chemical species, the a_{ij} is clearly the Redlich-Kwong a for that substance.

Wilson has also applied his modification of the Redlich-Kwong equation of state to the calculation of enthalpies[122]. In this paper he introduced the acentric factor by letting

$$k_i = 1.57 + 1.62\,\omega_i \qquad (2.2a)$$

The agreement is good for gaseous mixtures.

Subsequently, Wilson[123] presented another relation which combines Equations (2.1) and (2.2) and further improved the calculation of mixture properties. A simplified form of this modification has been used by Chang, Chappllear and Kobayashi[15]. As pointed out by the authors, a further modification for the equation of state would be the inclusion of the effect of the intermolecular forces acting between unlike molecules on the mixing rules, which relate the constants of a mixture to those of pure component.

Robinson and Jacoby[94] assumed that both constants a and b are linear functions of temperature. They also found that prediction of properties for multi-component mixtures was much improved when Equation (2.2) was used instead of the geometric mean for a_{ij}. Their modification was applied to only restricted ranges of temperature and pressure.

Barner, Pigford and Schreiner[9] used the original Redlich-Kwong mixing rules, but they made the constant a temperature dependent, in order to improve the prediction of the second virial coefficient below the critical temperature, Thus,

$$\frac{a}{T^{\frac{1}{2}}} = \frac{\alpha}{T^{\frac{1}{2}}} + \frac{\gamma}{T^{\frac{3}{2}}} \qquad (2.3)$$

α and γ could be related to critical temperature, critical pressure and acentric factor. This modification produces a considerable improvement in predicting the enthalpies of non-polar condensable vapors[9].

The modification of Barner, Pigford and Schreiner as well as those of Wilson and Robinson and Jacoby, give a critical isotherm which is the same as that of the original Redlich-Kwong equation, as they introduced temperature dependence for one or both of the adjustable parameters.

Gray, Rent and Zudkevitch[40] combined Barner's modification with the deviation function approach, in which a function of temperature, pressure and acentric factor is added to the compressibility factor from the original equation to fit the compressibility and enthalpy data for vapor mixtures of light hydrocarbons and related non-polar substances. Although the fit near the critical point is improved, the modification has a limited range of applicability.

Chueh and Prausnitz[21] proposed that for the gas phase calculation, the constants Ω_a and Ω_b be adjusted to the properties of the saturated vapor; for liquid phase properties, these constants should be adjusted to liquid density

data. In both cases, Ω_a and Ω_b are considered to be temperature-independent. The purpose of this adjustment is to facilitate the calculation of the fugacity coefficient in saturated vapor mixture, partial molar volumes in liquid mixtures and critical properties of mixtures. However, this method is restricted to the prediction of partial molal volume at saturation pressure and at a temperature not lower than a reduced pseudocritical temperature of 0.56[20].

Zudkevitch and Joffe[57,129] have followed the approach of Wilson[121,122] and extended it to the quantity Ω_b. They evaluated Ω_a and Ω_b of the Redlich-Kwong equation separately for the saturated vapor phase and the saturated liquid phase. In the establishment of the values of Ω_a and Ω_b, the generalized fugacity coefficient values at saturation of Lyckman, Eckert and Prausnitz[69] were employed. The reduced fugacity coefficients at saturation were given by the following expression:

$$\log \phi^S = (\log \phi^S)^{(0)} + \omega(\log \phi^S)^{(1)}$$

where $(\log \phi^S)^{(0)}$ and $(\log \phi^S)^{(1)}$ are functions of the reduced temperature and are presented in a tabular form. The values of Ω_a and Ω_b evaluated from the saturated liquid properties were utilized for both phases due to the fact that for most compounds, the values of Ω_a and Ω_b calculated from the vapor phase ascend rapidly as T_R decreases[129]. In several cases, the vapor values take an erratic course and become negative after passing through a maximum. The parameters of pure component were combined to give that of mixture in the form of the following relation:

$$a_{ij} = (1 - C_{ij})\ (a_{ii}\ a_{jj})^{0.5}$$

where C_{ij} represents the deviation of a_{ij} from classical geometric mean assumption. The establishment of C_{ij} was found from the experimental data. It should be noted that

the temperature-dependent parameters Ω_a and Ω_b obtained with their method would not satisfy the fundamental condition $\phi_{iv} = \phi_{il}$. This drawback is also observed in the method of Wilson [121,122].

Joffe, Schroeder and Zudkevitch recognized the above mentioned pitfalls; subsequently, they proposed an alternate procedure for establishing the pure component Ω_a and Ω_b parameters as a temperature function[56]. The procedure is essentially similar to the method proposed by Chang and Lu in the calculation of vapor-liquid equilibrium[67], partial molal volumes[17] and enthalpies of mixing[19] of liquid mixtures. Lyckman's correlated values of ϕ_ℓ[69] were avoided by forcing the equalization of the fugacity coefficient in the saturated vapor and saturated liquid. Therefore, the following relation was derived[56].

$$\Omega_a = \Omega_b \left[\frac{\ln[(V_v - b)/(V_\ell - b)] - P(V_v - V_\ell)/RT}{(T_c/T)^3 \ln[(V_\ell + b)/V_\ell(V_v + b)]} \right] \quad (2.4)$$

Equation (2.4) was solved simultaneously with the Redlich-Kwong equation of state at each temperature below the critical point to yield Ω_a and Ω_b. The solution involves a trial-and-error procedure. This Equation (2.4) becomes indeterminate at the critical point. It is therefore necessary to use the previous method[129] to establish Ω_a and Ω_b at the critical point. The application of this procedure was preferred for the heat of mixing calculations.

The Redlich-Kwong equation of state has been successfully applied by Chang et al. for the prediction of thermodynamic properties[17,19,67] by considering both Ω_a and Ω_b temperature-dependent. They were obtained through a rigorous thermodynamic approach and the fundamental condition of equilibrium state, i.e., $\phi_{il} = \phi_{iv}$, was satisfied. The method has been extended by Hsi and Lu to evaluate Ω_a and Ω_b in the supercritical region.[52,53]

Chaudron, Asselineau and Renon[13] developed a new modification of the Redlich-Kwong equation of state for predicting volumetric properties. The parameters Ω_a and Ω_b were treated as a function of the reduced temperature. They were obtained from 7,600 volumetric data points of pure substances, in vapor and liquid phase in the whole range of temperature and pressure and not only at saturation. Their emphasis was placed on the application to volumetric properties of the liquid and vapor phases. The equal fugacity criterion for vapor-liquid equilibrium studies can not be satisfied by means of their calculation. The variations of Ω_a and Ω_b with temperature were represented by using the following analytical forms:

$$\Omega_a = \sum_i C_{a,i} / T_r^i \qquad i = 0,1,2 \qquad (2.5)$$

$$\Omega_b = \sum_j C_{b,j} \cdot T_r^j \qquad j = 0,1,2 \qquad (2.6)$$

The best values of $C_{a,i}$ and $C_{b,j}$ for a given substance are obtained using a computer program which minimizes the relative deviation between experimental and computed values of volume for all available data. The method was extended to mixtures[14] by using a new set of mixing rules. The rules were selected by analyzing a large set of molar volume data of mixture. It was applied to polar and non-polar substances, including supercritical gases. DeMateo and Kurata[26] have followed the approach of Zudkevitch and Joffe to evaluate the parameters Ω_a and Ω_b to correlate and predict the solubilities of solid hydrocarbon in liquid methane. For methane, the vapor pressure, fugacity coefficient and molar volume were taken from Canjar and Manning[12]. Since the solute in solid-liquid equilibrium is a subcooled liquid, this kind of experimental data can not be found. For this reason, extrapolations of the available generalized correlation have been done. The fugacity coefficients were estimated

by calculating the fugacity of the saturated vapor from the virial equation of state truncated after the second virial, with the second virial estimated according to the Pitzer and Curl[84] correlation. The values of Ω_a and Ω_b as calculated were fitted to a fifth degree polynomial in reduced temperature.

Soave[100] has also proposed a modification for the Redlich-Kwong equation by introducing the acentric factor ω as a third parameter. The parameter b in the original equation was assumed to be constant and determined from the critical data while a was treated as a function of reduced temperature and acentric factor. A generalized correlation for the parameter a was derived. This empirical function was adjusted such that the modified Redlich-Kwong equation gives a good representation of vapor pressure for light hydrocarbons with the application of the orignal generalized mixing rules. Acceptable results were obtained for mixtures of non-polar fluids such as hydrocarbons, nitrogen, carbon monoxide with the exclusion of carbon dioxide and hydrogen sulphide.

Recently Harmens[46] mentioned that for the pure substances embodied in his programme for the calculation of multi-component thermodynamic data at cryogenic temperatures, the two omega functions were fitted to known physical properties. Three ranges were distinguished: temperatures below $T_r = 0.96$, between $T_r = 0.96$ and 1.0 and above $T_r = 1.0$. Closely below the critical temperature, this simultaneous fitting fails because no values of omegas can produce a realistic Z_c, but for all substances, it was possible to derive valid omegas up to at least $T_r = 0.96$.

Generalized correlations have been established for the temperature dependence of the parameters a and b of helium and hydrogen in the Redlich-Kwong equation in the supercritical region[115].

Therefore, the need for individual and generalized correlation for calculating the parameters Ω_a and Ω_b of the Redlich-Kwong equation of state for the pure components

in the subcritical region was demonstrated. The computation of these parameters using the minimum information of the pure components properties can facilitate the application of the Redlich-Kwong equation for vapor-liquid equilibria and can be fitted as an integral part in Harmens' programme for the evaluation of thermodynamic properties.

Beret and Prausnitz[9] proposed a three-parameter equation of state applicable to small, spherical (argon-like) molecules and also to large structurally complex molecules including polymers. The equation has some fundamental advantages when compared with the Soave equation which fails to give meaningful results for PVT data of pure components at low temperatures or high pressures. The term (V-b) becomes negative[9]. This limitation, also present in the original van der Waals equation, was recognized by van der Waal and his co-workers. They showed that Soave's equation fails even at normal temperatures for complex liquids ($\omega > 0.2$). The ability of the Soave equation[100] to predict reasonable vapor pressures at low temperatures follows from a fortunate cancellation of errors: upon equating the chemical potential of liquid to that of vapor, Soave's equation calculates an erroneous saturated liquid volume, but this erroneous result often gives nearly correct vapor pressure[103].

The original Redlich-Kwong equation has only two parameters, and is used only with one binary interaction coefficient, for mixtures of the equation and its derived functions cannot, of course, be expected to hold for all possible substances, let alone for all possible mixtures. The approach of Zudkevitch and Joffe, Chang et al. extended by Hsi and Lu[19,20] relies greatly on the capability of the equation to represent the fluid properties despite the fact that the fundamental condition at equilibrium $\phi_{iv} = \phi_{i\ell}$ is satisfied, the condition of minimum deviation between experimental and calculated Z_v, is sacrificed. This is expected since Redlich-Kwong has only two adjustable parameters while we have three conditions to be satisfied at equilibrium.

Namely:

$$Z_v^{exp} = Z_v^{calc.} \tag{2.7}$$

$$Z_\ell^{exp} = Z_\ell^{calc.} \tag{2.8}$$

and the fundamental condition $\phi_{iV} = \phi_{i\ell}$ (2.9)

So, we must have an equation with at least three adjustable parameters to satisfy this condition at equilibrium.

Elshayal and Lu[33,34] successfully employed the Clausius equation of state with a modified procedure to calculate the fugacity coefficient, liquid phase activity coefficient and PVT data. In the original equation, Clausius[22,82] supplemented the van der Waals equation by the introduction of a third constant. Clausius postulated the existence of clusters of two or more molecules that are temporarily formed by collision at lower temperatures and which break-up very readily at higher temperatures. In such clusters, the forces are much greater than if the molecules were separated in the gas and hence the van der Waals term a/V^2 is too small to account for this force at lower temperatures. Further, Clausius considered correction on the cohesive pressure term, i.e., he replaced the term $\frac{a}{V^2}$ by the quantity $\frac{a}{T(V + c)^2}$. This correction is equivalent to treating the parameter a of the van der Waals equation of state as temperature dependent and shifting the calculated critical isotherm.

The technique was not fully appreciated at that time, possibly because Clausius offered a kinetic explanation that was only partially justified rather than a mathematical explanation based on the transformation of the independent variable. In the modified procedure of Elshayal and Lu[33,34] the parameters Ω_a, Ω_b and Ω_c of the equation were treated as temperature dependent and were obtained through a rigorous thermodynamic approach, therefore, the three conditions

for equilibrium state were satisfied. The applicability of treating Ω_a , Ω_b and Ω_c as temperature dependent parameters for vapor-liquid equilibrium calculations had been demonstrated[33,34]. When a further extension of the work to calculate the thermodynamic properties was carried out, the results indicated that it is more suited for calculating volume of mixing rather than heat of mixing[44]. The difficulty encountered may be due to the fact that the quality of the saturated vapor volume, V_v, values reported in the literature is not certain. The uncertainty is reflected in the numerical values of the parameters and in the trend which the parameters might have in certain regions, especially in the vicinity of the triple point and near the critical point. Consequently, it was rather difficult to establish a reliable value for the derivatives of Ω_a , Ω_b and Ω_c with respect to temperature which can lead to a large error in the calculated heat of mixing[44].

This can also be ascribed, in a way, to the fact that the Clausius equation lacks the accuracy in expressing the influence of temperature. All the above mentioned arguments also point to the desirability of by-passing the use of saturated vapor volume altogether, by minimizing the amount of information required to establish these parameters still within the objective of modifying the temperature effect described by the original Clausius equation of state. Furthermore, it seems to be sufficiently promising to follow the same approach of treating the parameters of the Clausius equation as temperature dependent to improve its predictive ability of thermodynamic properties but meanwhile, simplifying the minimum required reliable information to determine the adjustable parameters of the equation. What appears to be limiting at the moment, is the availablity of reliable saturated vapor volume data, beside the fact that at present, no generally satisfactory equation of state exists that has a good predictive ability over a wide range of temperature and pressure for both pure components and mixtures. Until such an

equation appears, the incentive remains to modify the currently occurring equations to their ultimate simplicity and/or versus refinement and accuracy.

CHAPTER 3

EXPERIMENTAL INVESTIGATION OF PHASE BEHAVIOUR OF SYSTEMS CONTAINING CARBON DIOXIDE, PROPANE AND ETHANE

In recent years, there has been an increasing interest in the phase equilibrium studies of systems, particularly those containing one of the non-hydrocarbon components frequently found in petroleum or natural gas reservoirs. Therefore, the present investigation was undertaken to provide new vapor-liquid equilibria data for systems for which:

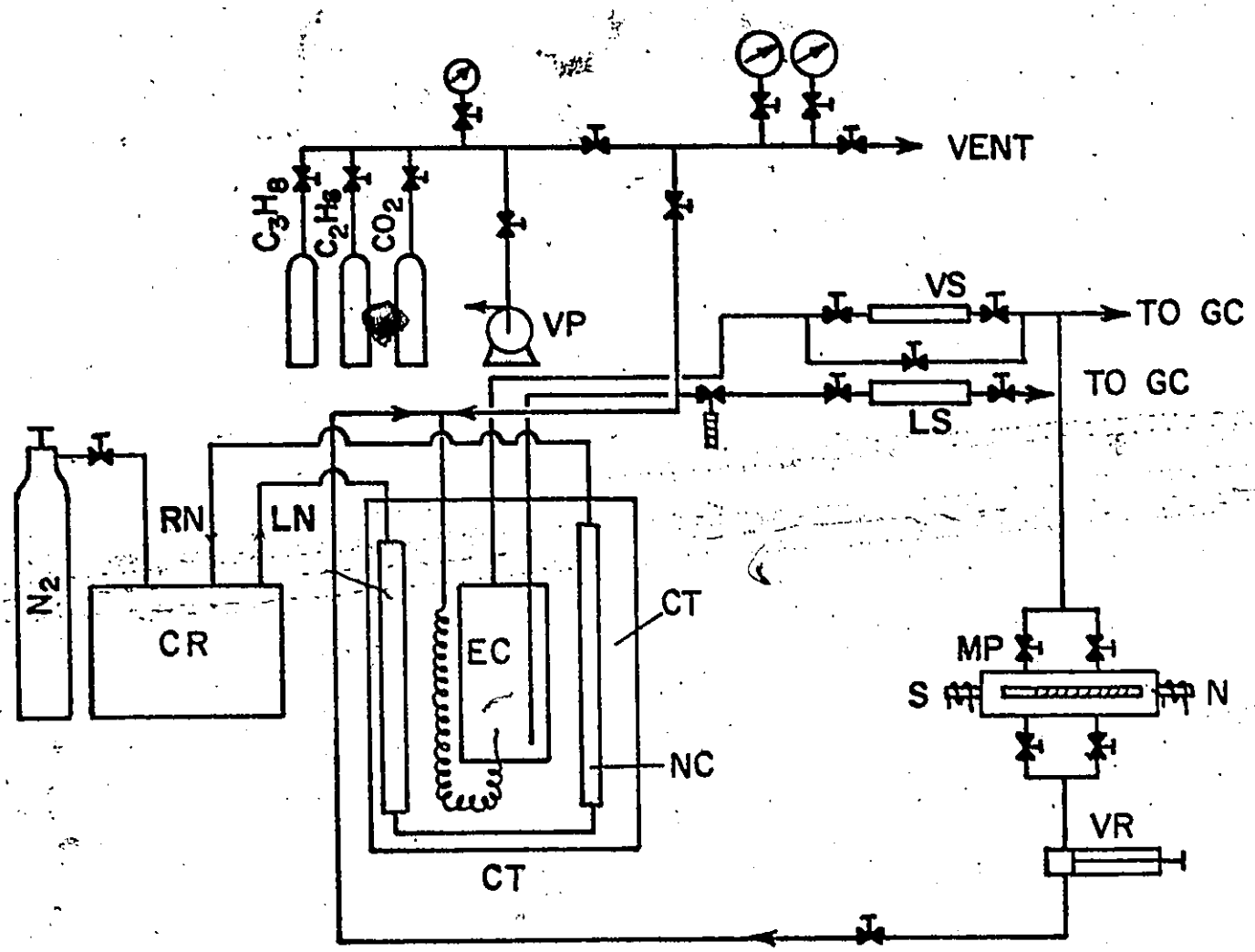
(1) there is a reason to believe that the available data in the literature are not of sufficient accuracy for use in the design of an efficient separation technique, or for the testing of the validity of a method based on an equation of state to predict thermodynamic properties,

(2) there are no available data in the literature.

Vapor-liquid equilibria were measured for carbon dioxide-ethane systems at the same isothermal conditions (-60°, -20°, 20° and 60°F) as those reported in the literature[64]. The binary system propane-carbon dioxide has been measured at -20° and 20°F. In addition, the ternary system propane-ethane-carbon dioxide was also measured at -20° and 20°F. The details of the equilibrium cell and its supporting equipment, the analytical equipment and the materials used in this study will be discussed in this chapter.

3.1 Apparatus:

The forced-recirculation type apparatus used was essentially the same as that used by previous researchers[18,52] with minor changes and only a brief description is given here. A schematic diagram is shown in Figure (3.1). The apparatus can be divided into six functional sections:



CT	CRYOSTAT	MP	MAGNETIC PUMP
EC	EQUILIBRIUM CELL	NC	NITROGEN VAPORIZATION COIL
CR	PHILIPS CRYOGENIC SYSTEM		
LS	LIQUID SAMPLING BULB	VP	VACUUM PUMP
		VR	VOLUME REGULATOR
		VS	VAPOR SAMPLING BULB
		LN	LIQUID NITROGEN
		RN	RETURN NITROGEN

FIG. 3.1 A Schematic Flow Diagram of the Apparatus

Feed charging system, equilibrium cell, recirculation loop, sampling, cryostat and its temperature control and temperature and pressure measuring devices.

Feed Charging System:

Pure gases were fed directly into the cell from the supply cylinders which were equipped with individual pressure regulators and valves.

The Equilibrium Cell:

A 100 ml. Jerguson transparent gauge with a stainless steel body was used for the cell. Teflon gaskets were used between the glass windows and the metal body.

Inlet and outlet holes were drilled in the bottom and the top of the guage respectively. All fittings were made of stainless steel and were tested to withstand the experimental conditions. The details of the equilibrium cell are shown in Figure (3.2)

The Recirculation Loop:

An electro-magnetic pump was used to remove vapor from the top of the cell and recirculate it through the liquid phase by forcing it into the bottom of the cell. The recirculation rate can be adjusted by varying the speed of the pump. The electrical circuit of the electro-magnetic pump is shown in Appendix B. The volume regulator served as a part of the recirculation loop and used in the regulation of pressure during the liquid sampling period.

Sampling System:

The vapor was trapped in a sampling bulb connected along the recirculation loop. The liquid samples were taken through capillary tubes 1/16" in diameter. A needle valve was inserted in the line between the equilibrium cell and the sampling bulb to minimize the sample size. A bubbler was used to count the number of bubbles per minute.

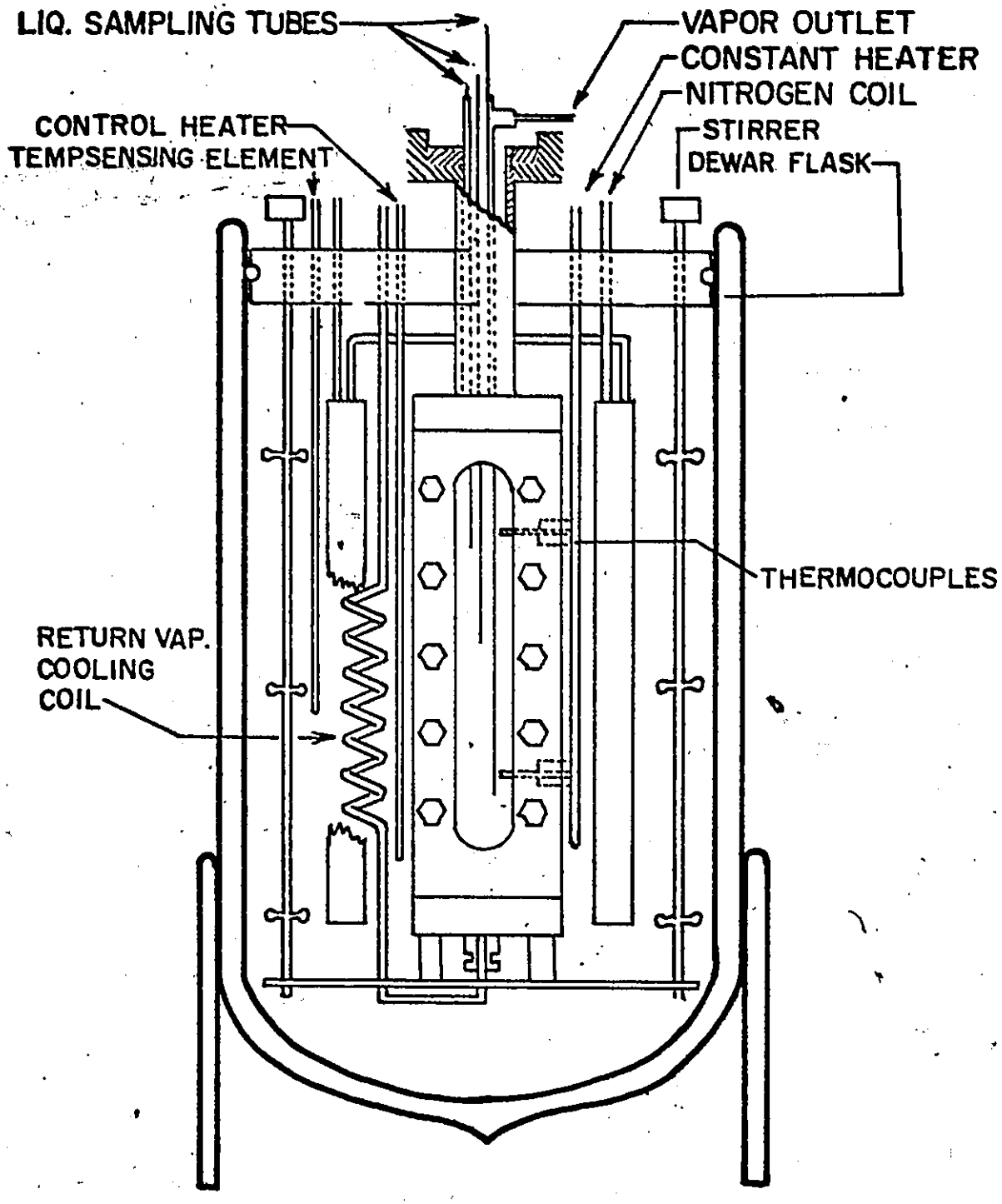


FIG. 3.2 The Equilibrium Cell and the Cryostat

The Cryostat and its Temperature Control System:

A Dewer flask of 18 litre capacity was used as the cryostat. It is silvered except for two vertical strips about 1" wide. The cryostat was equipped with two variable speed stirrers, refrigeration coil, and a heating element connected to a proportional-type Bayley temperature controller, model 250, which was used to control the bath temperature.

The cooling system employed in this investigation involved minor changes to that previously used in this laboratory. At -20° and -60°F, isopentane was used as the bath liquid in the cryostat. The temperature of the cryostat was regulated by controlling the evaporation rate of liquid nitrogen in the refrigeration coil and controlled to ±0.01K. The nitrogen was liquefied using a cryogenic system, Phillips PPG.102. For the other two temperatures (20°F and 60°F) a Nestlab cooling unit was used with methyl alcohol as the bath liquid.

Temperature and Pressure Measuring Devices:

Two thermocouples wells of capillary steel tubing were inserted about an inch from the top and the bottom of the equilibrium cell. The system temperatures were measured by means of a Leeds and Northrup K-5 Potentiometer; the thermocouples were calibrated against the vapor pressure of ethane[12,35].

The pressure of the system was measured by means of two tested Heise gauges. The ranges of these gauges are 0 to 200 and 0 to 2000 Psia, with 0.2 and 2 Psia per division respectively.

3.2 Materials:

Research grade gases were used without further purification. The sources of the materials used and their specifications were as follows:

Research Grade Gas	Specified Min. Purities	Supplier
Propane	99.9 mole%	Phillips Petroleum
Ethane	99.9 mole%	Phillips Petroleum
Carbon Dioxide	99.995 mole%	Matheson of Canada

3.3 Experimental procedure:

A four-step procedure was followed to collect the required vapor-liquid equilibrium data. They were: charging the components of the mixtures under investigation, equilibration, sampling and analysis.

3.3.1 Charging the Components of the Mixture:

At room temperature, the system was evacuated, purged with the less volatile component, evacuated and maintained under vacuum overnight. The equilibrium cell was immersed in the Dewer flask which was filled with the bath fluid. The windows of the equilibrium cell were centred with respect to the vertical unsilvered strips of the Dewer flask. A source of illumination was used to ensure clear visibility of the cell. The Phillips Cryogenic System was started. A sufficient quantity of nitrogen gas was fed at 10 Psig. A by-pass for the liquid nitrogen was necessary for a better temperature control by means of the appropriate valves. The bath stirrers were turned on and the system temperature was checked until its value was within a few degrees of the desired one, then, the temperature controller was turned on. For the binary system, the mixtures studied were synthesized and liquefied within the equilibrium cell with the heavier component charged first, followed with carbon dioxide until the liquid level had risen to about half of the equilibrium cell height. When the desired temperature was reached as indicated by the controller and by the thermocouple measurements, the electro-magnetic pump was activated and kept on until the equilibrium was attained.

3.3.2 Equilibriation:

When thermal equilibrium was reached in the cell, the circulation of the vapor within the circulation loop was continued for at least three hours at the desired temperature.

After this period, the electro-magnetic pump was shut down and the pressure and the temperature of the system were recorded.

3.3.3 Sampling and Analysis:

The vapor was trapped as soon as the pump was stopped. Liquid samples were withdrawn from the cell, after the liquid phase was allowed to settle for an hour, sampling of the liquid phase was carried out by manipulating the needle valve which allowed the slow vaporization of the liquid phase through the sampling tube. The system pressure was maintained constant by adjusting the volume regulator. A schematic diagram of the sampling system is shown in Figure (3.3).

Analyses of the samples were carried out by a Fisher-Hamilton gas partitioner, Model 29 in conjunction with a Perkin-Elmer recorder (Coleman 165). For the system ethane-carbon dioxide, silica gel (40-60 mesh) was used as the column's (4 ft.) packing material. The flow rate of helium was maintained at 80 ml. per minute at 30 Psig. A retention time of 10 minutes was required for separating the two components. The peaks were well spaced, completely separated and sharp in the sequence of carbon dioxide and ethane.

Samples of prepared mixtures of known gas compositions were used for the calibration of the chromatograph. The result of the calibration was plotted as composition ratios versus peak height ratios.

For the systems containing propane, Pora Pak Q (80-100) mesh was used as the column's (1 ft.) packing material and a retention time of 22 minutes was required to separate the propane-ethane-carbon dioxide mixtures. The Fisher-Hamilton gas partitioner is limited to operation at room temperatures. In addition, the propane peaks have the tendency to tail and the result of the calibration of the chromatograph was plotted as composition ratios versus area

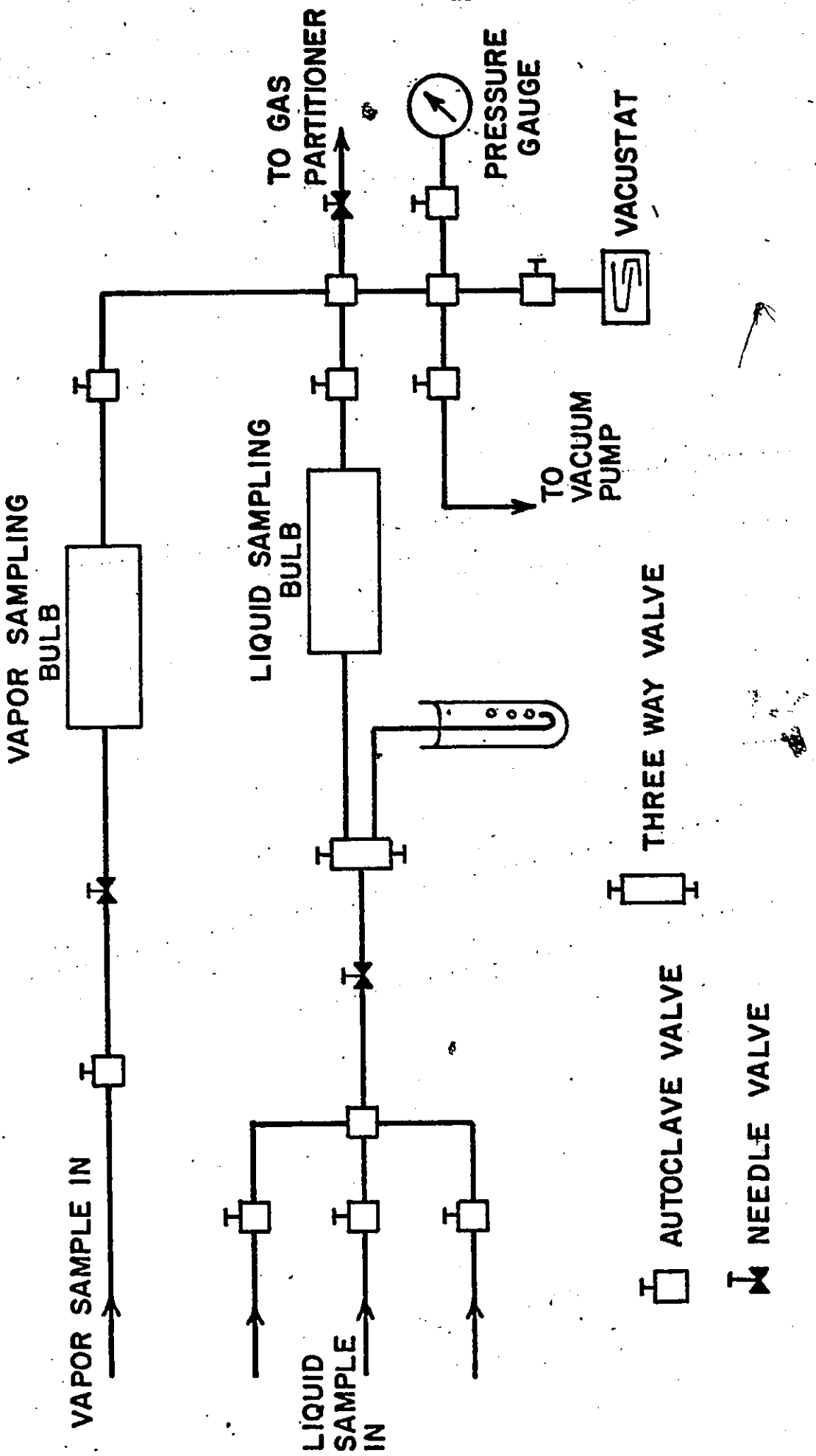


FIG. 3.3 Schematic Diagram of the Sampling System

ratios. Samples of prepared mixtures of known compositions of carbon dioxide-propane and carbon dioxide-ethane were used for the calibration. A saving of about 50% in the analysis time was achieved by simultaneous analysis of two samples, the second sample was injected after the elution of carbon dioxide and ethane of the first sample.

To overcome the difficulties of the required long retention time, accuracy and precision of the area determination, the Fisher-Hamilton gas partitioner was replaced by the Hewlett Packard Research Chromatograph series 5700 A using a thermal conductivity detector in conjunction with a Westronics recorder, Model 5700 A. The output signal was fed to a Hewlett Packard integrator, Model 3373. A Pora Pak Q Column (6 ft.) was used. The flow rate of helium was maintained at 30 ml. per minute at 40 Psig. The detector temperature was kept at 423 K and the oven temperature at 368 K. A retention time of 5 minutes was required to separate the propane-carbon dioxide mixtures. At least three analyses were made for each of the samples collected and an average was taken. The same analysis scheme was used for the mixture of propane-ethane-carbon dioxide.

After the first experimental point has been determined, the more volatile component was then fed to the system by bubbling it through the liquid, recirculation was resumed and another point was determined by following the same procedure described before. This allowed a wide composition range to be covered.

3.4 Experimental Results:

Equilibrium P-T-x-y measurements were made for the following systems at the conditions specified:

System	T°F	Pressure, Psia
ethane-carbon dioxide	60	637.5 - 827.0
	20	331.5 - 486.0
	-20	212.0 - 263.0
	-60	101.6 - 127.6
propane-carbon dioxide	20	117.0 - 379.0
	-20	73.6 - 197.0
propane-ethane-carbon dioxide	20	184.0 - 433.0
	-20	87.5 - 238.0

The data are shown in Tables (3.1), (3.2) and (3.3).

3.5 Error analysis:

The use of an error analysis in conjunction with the local area consistency test in judging the consistency of the vapor-liquid equilibria data within the given experimental error is valuable.

In this investigation of vapor-liquid equilibria, the possible sources of error arise in the fundamental measurements for γ - values from pressure, temperature and composition.

Pressure error: The accuracy of the Heise gauges is 0.1% of full scale. For pressures up to 200 Psia, the error is 0.2 Psia; for the higher pressures, the 2000 Psia gauge was used to give an error of 2 Psi. At the lowest experimental pressure (75 Psia), the relative error is 0.27% while at the highest experimental pressure (823 Psia) the relative error is about 0.25%.

Temperature error: The temperature of the cryrostat was controllable to 0.01 K and the temperatures measured were probably accurate to about ±0.1 K.

Concentration error: The reproducibility of the analysis was good to 0.002 mole fraction. The total concentration error is estimated from 0.002 to 0.003 mole fraction at the lowest concentration. Generally, this error was minimized by repeated analyses and by using average values in the calculation. Usually the peak height or area ratios for the different samples of the same mixture agreed within 1%. If there are discrepancies due to a bad injection technique, results have to be discarded. Peak areas determined by weighing the chart paper were of a relative accuracy of 2%.

The probability that all error contributes in the same direction is small; statistically, the errors should tend to cancel since the probability of negative and positive error is equal.

3.6 Consistency of the experimental data:

The consistency of the experimental data of the binary systems was tested by means of the method proposed by Chang and Lu[18]. The measurement errors in the calculation were set as follows:

$$E(P) = \pm 1.0 \text{ Psia}$$
$$E(T) = \pm 0.1 \text{ K}$$
$$E(X) = \pm 0.0005,\ 0.001,\ 0.002$$

The result of that consistency test[18,112] although developed in an approximate form, indicates the total error caused by both random and systematic error. In the calculation, the fugacity and the partial molal volumes were obtained from the Redlich-Kwong equation of state by means of the modified procedure[19]. The evaluation of these quantities using the Redlich-Kwong equation is shown in Chapter 4. Also, a brief description of the method is given in Appendix C.

TABLE 3.1

EXPERIMENTAL RESULTS FOR THE BINARY SYSTEM
ETHANE(1) - CARBON DIOXIDE(2)

Temp. °F	EXPERIMENTAL		
	x_1	y_1	P, Psi
60	0.7845	0.7571	637.5
	0.6874	0.6425	705.0
	0.4880	0.4295	809.0
	0.4376	0.3609	823.5
	0.2609	0.2659	827.0
	0.1499	0.1635	812.0
	0.1617	0.1645	813.0
20	0.9285	0.8784	331.5
	0.8956	0.8026	355.5
	0.8702	0.7864	361.5
	0.8103	0.7019	392.0
	0.7487	0.6500	409.0
	0.6406	0.5815	433.5
	0.5096	0.4527	471.0
	0.4714	0.4167	476.5
	0.4069	0.3589	486.0
	0.3929	0.2950	483.5
	0.1055	0.1369	463.5
	0.0825	0.0839	448.0
-20	0.0892	0.1585	240.0
	0.0981	0.1685	248.0
	0.1676	0.2310	253.5
	0.3312	0.3309	263.0
	0.4521	0.3989	261.5
	0.4541	0.4051	261.0
	0.5749	0.4689	257.0
	0.6631	0.5394	240.5
	0.8256	0.7124	216.0
-60	0.8703	0.6624	101.6
	0.7622	0.5881	115.2
	0.6203	0.5000	123.4
	0.4672	0.4317	127.2
	0.4673	0.4520	127.2
	0.4023	0.4015	127.6
	0.3726	0.3880	127.6
	0.3661	0.3805	127.6
	0.3307	0.3623	126.4
	0.2975	0.3552	126.2
	0.2253	0.3080	124.0
	0.1197	0.2344	117.8

TABLE 3.2

EXPERIMENTAL RESULTS FOR THE BINARY SYSTEM

PROPANE (1) - CARBON DIOXIDE (2)

Temp.°F	EXPERIMENTAL		
	x_1	y_1	P,Psia
20	0.9114	0.4793	117.0
	0.8380	0.3601	155.0
	0.8202	0.3293	168.5
	0.7485	0.2747	197.5
	0.6536	0.2118	241.0
	0.6004	0.1921	262.0
	0.5572	0.1682	294.0
	0.4734	0.1477	314.5
	0.3530	0.1249	351.0
	0.2250	0.0843	371.0
	0.1811	0.0735	379.0
-20	0.8866	0.3411	73.0
	0.8547	0.2867	85.0
	0.7755	0.2180	109.0
	0.7505	0.2055	114.0
	0.6771	0.1705	133.5
	0.5774	0.1420	154.3
	0.4671	0.1172	168.0
	0.3328	0.0933	184.5
	0.2536	0.0804	190.5
	0.1933	0.0684	197.0

3.7 Discussion:

Ethane-Carbon Dioxide System

The vapor-liquid equilibrium data obtained at four isothermal conditions (-60°, -20°, 20° and 60°F) are given in Table (3.1). The data are similar in appearance with those recently reported in the literature. The experimentally determined data points cover the whole concentration range and there exists an azeotropic composition as previously reported. It should be mentioned, however, that at 60°F, the cell was first cooled to a lower temperature to facilitate the charging of additional carbon dioxide to the mixture of the preceding run. This procedure was necessary because carbon dioxide cylinders were supplied with a maximum cylinder pressure of 830 Psia, while the total pressure of the mixture might reach up to 827 Psia. It was found that the experimental data are consistent within the bounds indicated by ±0.002 mole fraction.

Propane-Carbon Dioxide System

The vapor-liquid equilibrium data obtained at the two isothermal conditions (-20° and 20°F) are given in Table (3.2). The data are similar in appearance to those reported by previous authors[1,77,86,90]. There exists a reversal in the curvature in the P-y curve for each isotherm in the region of the rich carbon dioxide content. This behaviour is typical for systems made up of carbon dioxide and paraffin hydrocarbons at temperatures up to and slightly above the critical temperature of the hydrocarbon. This phenomenon is more evident as the temperature decreases as shown in Figure (4.6). The mixtures studied were synthesized and liquefied within the equilibrium cell with the propane being charged first, followed by carbon dioxide. A significant decrease in volume was observed during this procedure, especially in the vicinity of 170 Psia at 20°F. This behaviour was not observed for the system ethane-carbon dioxide which was experimentally determined

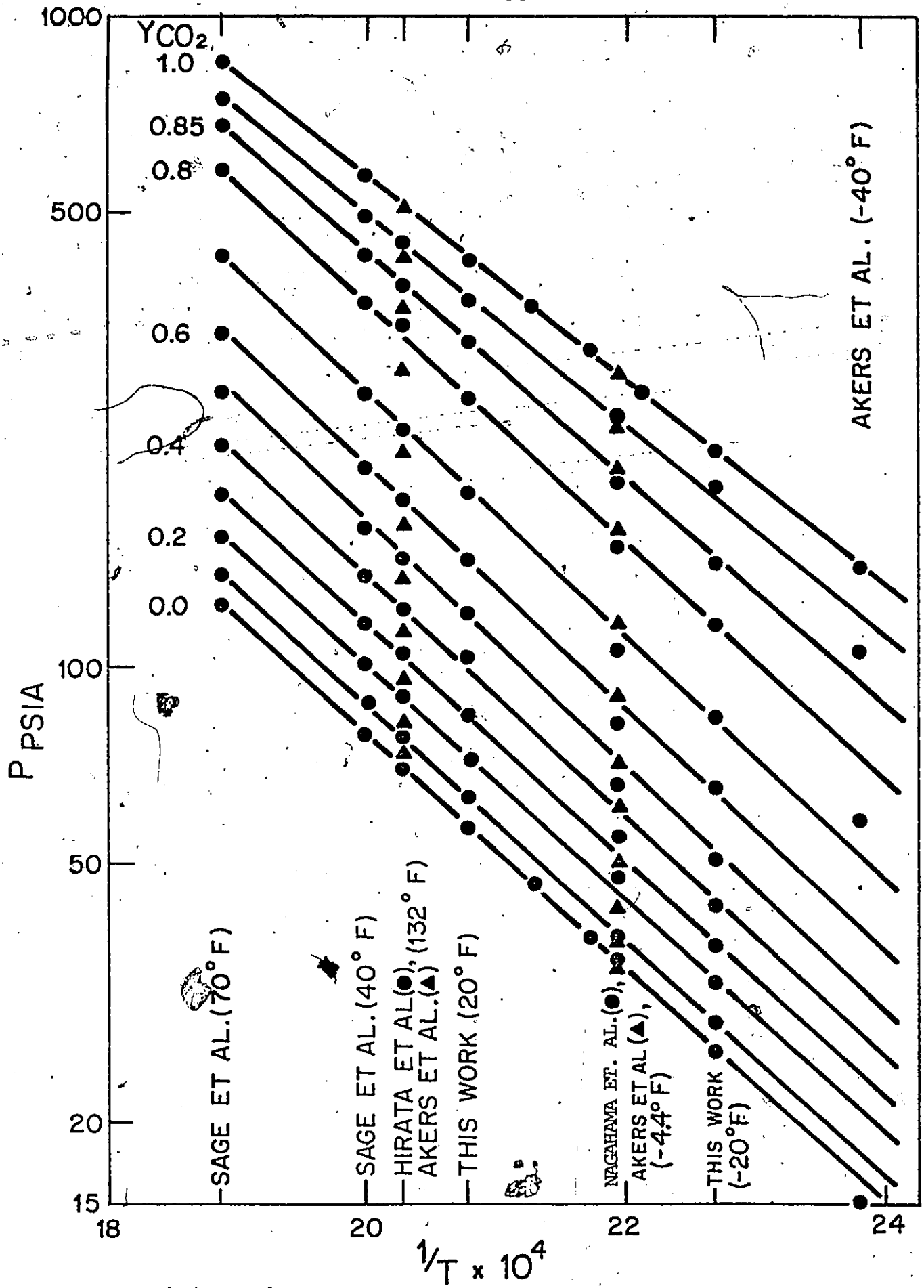


FIG. 3.4 Plot of the Logarithm of the Experimental Total Pressure versus 1/T at Constant Vapor Phase Composition y

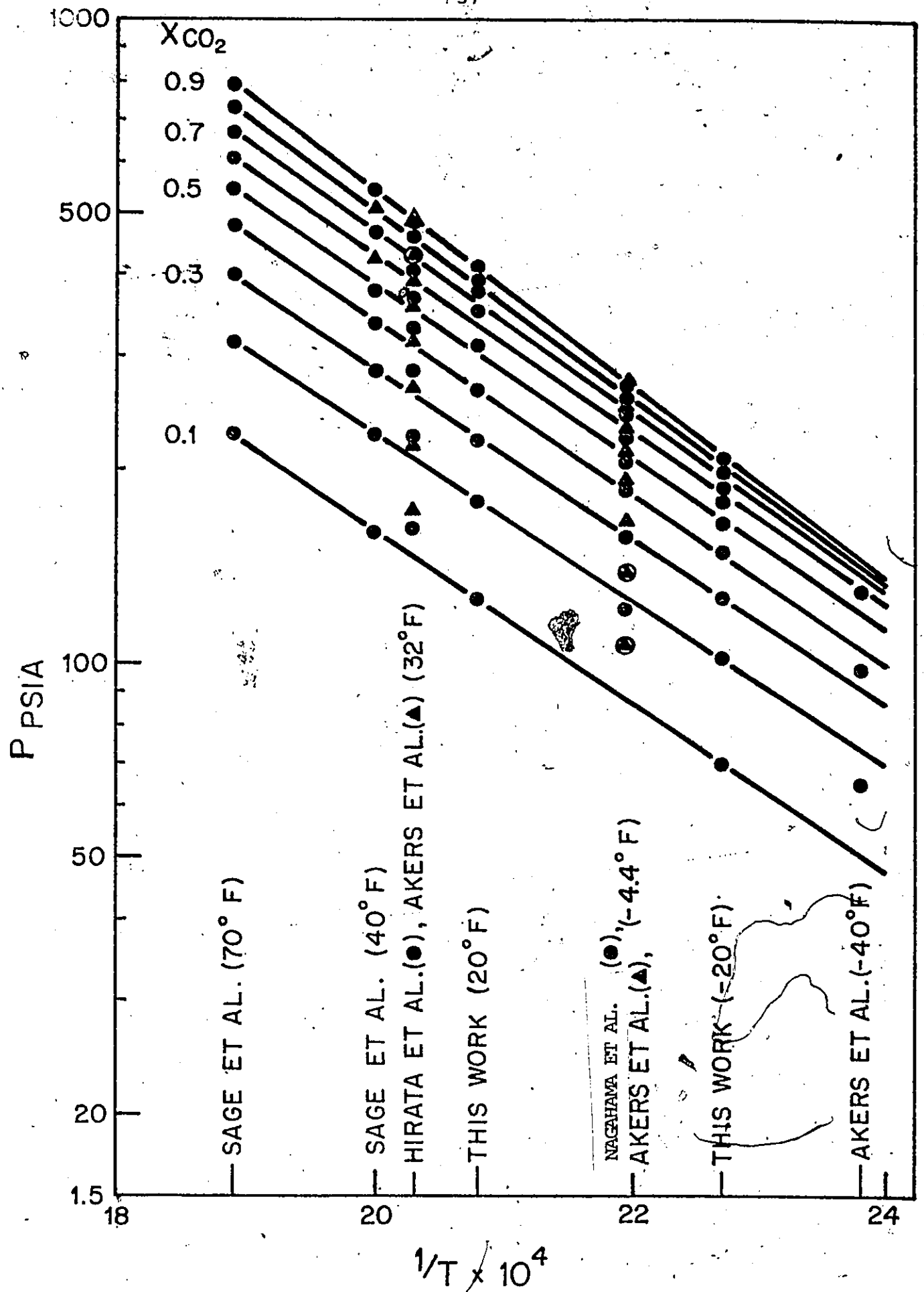


FIG. 3.5 Plot of the Logarithm of the Experimental Total Pressure versus 1/T at Constant Liquid Phase Composition x

previously[45]. This behaviour may be attributed to the difference of the chemical nature of these components despite their having the same molecular weight.

A comparison was made between the experimentally measured vapor-liquid equilibrium data at the two isothermal conditions (-20° and 20°F) with those reported in the literature[1,77,86,90]. Two plots were constructed from the smoothed P-x-y plot; one for constant liquid compositions, the other for constant vapor compositions as shown in Figures (3.3) and (3.4). Good agreement was obtained between the data presented in this investigation and those of Sage et al.[90,99]. It appears that the data reported by Nagahama et al.[77] and Akres et al.[1] do not follow the trend as shown in the graphs in the lower pressure range. The pressure measurement error in this work ranges from 0.25% in the lower region to 0.5% in the higher region while in the data reported by Nagahama et al., the accuracy of their pressure readings is 0.2% of the full scale (0-100 atm) of the Bourdon-tube gauge which gave an error of about 8% in the lower range compared to 0.6% for the highest reading.

In applying the consistency test,[18] it was found that the experimental data are consistent within the bounds indicated by ±0.0005 mole fraction with the exception of one experimental point (P = 351.0 Psia, x = 0.3530). With this point included, the data are consistent within the bound indicated by ±0.002 mole fraction.

Propane-Ethane-Carbon Dioxide System

The experimental data are tabulated in Table (3.3) at two isothermal conditions (-20° and 20°F). The mixtures were synthesized in the equilibrium cell with propane always introduced first followed by carbon dioxide or ethane. The collection of data was arranged in such a way that a binary mixture of propane-ethane or propane-carbon dioxide was synthesized followed by the successive introduction of the third component. During the charging procedure, it was observed

that over the concentration region investigated, the system pressure would not be greatly increased by increasing the concentration of carbon dioxide. The addition of carbon dioxide caused significant decrease in volume, especially at lower ethane concentration similar to that observed for the system propane-carbon dioxide.

Due to the limitation placed on the employed consistency test[18], namely that the experimental points should not be widely spaced, the consistency of the ternary data cannot be overemphasized.

TABLE 3.3

EXPERIMENTAL RESULTS FOR THE TERNARY SYSTEM
PROPANE (1) - ETHANE (2) - CARBON DIOXIDE (3)

Temp.°F	x_1	x_2	P_{psia}	y_1	y_2
20	0.4749	0.4876	184.0	0.1686	0.6908
	0.3549	0.6157	213.0	0.1193	0.7846
	0.6438	0.1477	219.0	0.2166	0.1910
	0.2686	0.7081	233.0	0.0863	0.8442
	0.4201	0.4276	236.0	0.1424	0.4717
	0.2147	0.7670	246.5	0.0685	0.8791
	0.1708	0.8124	252.0	0.0561	0.8994
	0.5515	0.1469	270.0	0.1724	0.1443
	0.3360	0.4469	285.0	0.1150	0.4480
	0.2088	0.6729	289.0	0.0601	0.6784
	0.1631	0.7541	291.0	0.0485	0.7601
	0.2262	0.6374	292.0	0.0674	0.6368
	0.3040	0.4425	309.5	0.1088	0.4174
	0.3289	0.2811	333.0	0.0935	0.2663
	0.4346	0.1005	336.0	0.1189	0.0906
	0.1549	0.6191	342.5	0.0417	0.5562
	0.3461	0.1197	343.0	0.1282	0.1291
	0.4036	0.0876	354.0	0.1048	0.0907
	0.3196	0.1311	361.0	0.0922	0.1086
	0.3036	0.0968	367.0	0.0930	0.0969
	0.3022	0.1852	370.5	0.0835	0.1749
	0.2183	0.3016	380.5	0.0699	0.2899
	0.2001	0.1818	383.5	0.0601	0.1869
	0.1211	0.0502	387.0	0.0613	0.0468
	0.1863	0.1573	391.0	0.0604	0.1644
	0.1591	0.1352	396.0	0.0578	0.1492
	0.1129	0.0339	396.0	0.0519	0.0402
	0.1765	0.1148	497.0	0.0535	0.1306
	0.1060	0.3986	421.5	0.0260	0.3380
	0.0741	0.2931	433.0	0.0238	0.2864
-20	0.7136	0.1929	87.5	0.2315	0.2932
	0.5512	0.3688	103.0	0.1603	0.4957
	0.6380	0.1825	110.5	0.1723	0.2339
	0.6024	0.1695	125.5	0.1431	0.2020
	0.5384	0.1681	141.0	0.1191	0.1791
	0.2275	0.6716	150.5	0.0449	0.6670
	0.2167	0.1711	211.0	0.0537	0.1941
	0.3656	0.2635	172.5	0.0645	0.2454
	0.4578	0.1208	166.5	0.0999	0.1290
	0.3915	0.1060	186.0	0.0855	0.1131
	0.2366	0.0678	199.5	0.0604	0.0861
	0.1563	0.6007	201.5	0.0197	0.5204
	0.0686	0.6502	215.0	0.0142	0.5235
	0.1786	0.3894	217.0	0.0363	0.3530
	0.1371	0.4958	220.5	0.0254	0.4285
	0.1685	0.3702	221.0	0.0338	0.3406
	0.1020	0.2488	232.0	0.0232	0.2615
	0.0685	0.4403	238.0	0.0108	0.3868

CHAPTER 4

APPLICATION OF EQUATIONS OF STATE FOR PREDICTION AND CORRELATION OF THERMODYNAMIC PROPERTIES

In an effort to describe analytically the equilibrium relation; equation of state, among volume, temperature, pressure and composition of substance whether it be quite pure or in a uniform mixture, much ingenuity has been used in its development.

Equations of state seem as a new Helen of Troy, who says of herself in Geothe's Faust (2nd part, 3rd Act), "Admired much and much reviled"[91a]. Admiration, indeed, goes so far that we are expected to pull answers out of our sleeves even without first having put in some experimental data. It is also due to the exceptional power and utility of an equation of state in representation, smoothing, interpolation of PVT data, and calculation of derived thermodynamic properties of pure components. Furthermore, a suitable equation of state, when combined with appropriate thermodynamic relationships and mixing rules, may predict vapor-liquid equilibria and excess thermodynamic properties. In spite of that, reviling has not been lacking because there is no single equation of state which can achieve even one of the above mentioned goals over a wide range of conditions with complete satisfaction.

Two approaches to the development of an equation of state may be followed[71]. One is a theoretical approach based on kinetic theory or statistical mechanics involving intermolecular force, exemplified by the van der Waals equation, ...etc. The other approach is empirical or at best only semi-theoretical, e.g., as in the Redlich-Kwong, Clausius, Berthelot equations, etc.

However, in search for an equation of state, one must make three decisions at the beginning. The first concerns the amount and the kind of data that will be required

to obtain the parameters of the equation, the second concerns the range of density to be covered, and the third concerns the precision with which the PVT data are to be represented. There is a common notion in the literature that an equation with more parameters can precisely describe the behaviour of the substance over a wide range of temperature but what appears to be the limitation is the availability of the necessary experimental data to establish these parameters and the range to be covered is that for which the experimental data are available.

On the other hand, the literature has indicated a popularity in adopting two-parameter equations of state which requires a minimum number of the experimental data to determine its parameters. One of the methods often applied to evaluate the parameters of such an equation is to use the critical properties and apply the two conditions at critical points, namely:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \qquad (4.1) \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \qquad (4.2)$$

Due to the fact that there are three equations, the original equation together with the two equations (4.1 and 4.2) and two parameters, the parameters of such an equation can be expressed in different combinations based on the selection of any two of the independent variables (P_c, V_c, T_c). It has been demonstrated by Martin[34] that expressing the parameters in the van der Waals equation using P_c and T_c is the most suitable combination for representation of the general appearance of the critical isothermal except for a horizontal displacement in volume as shown in Figures (4.1 and 4.2). Thus, a linear transformation in the volume coordinate is indicated as a good possibility particularly because it has no effect on the two pressure-volume derivatives. This is accomplished by merely adding a constant to the volume term in the equation of state for the calculated critical

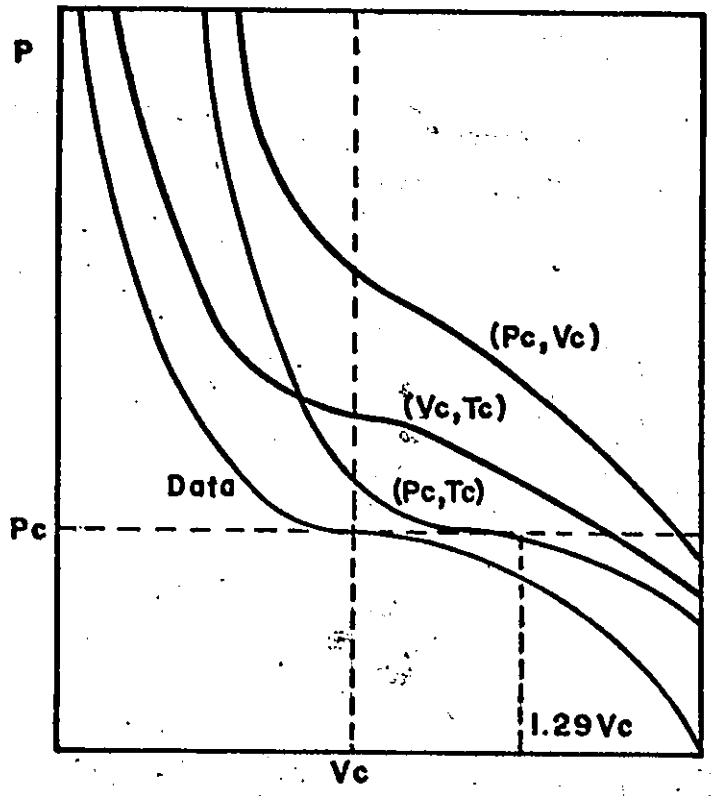


Figure 4.1 Pressure-volume plot using two constant equations

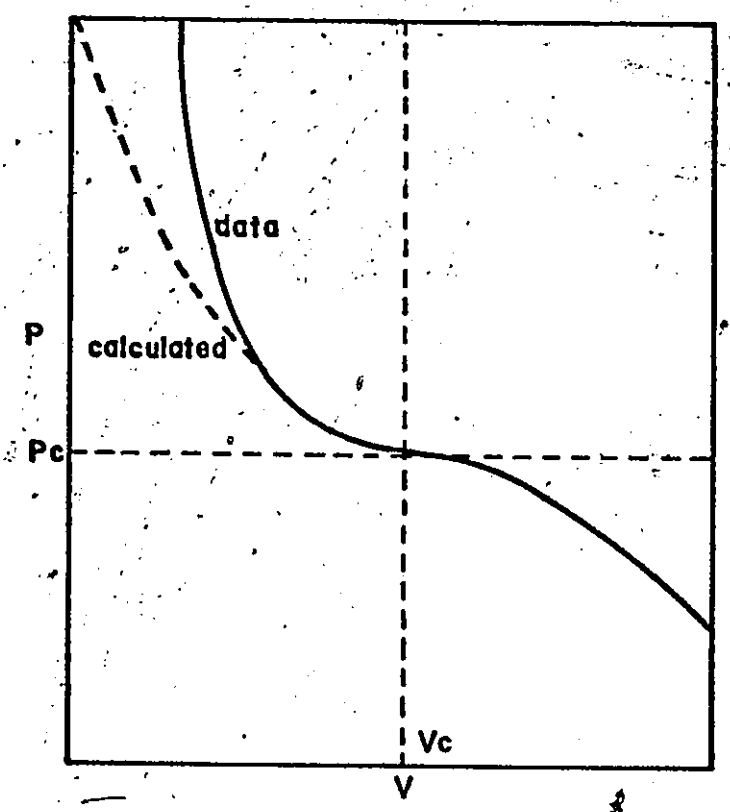


Figure 4.2 Pressure-volume plot using three constant equations

point to fall precisely on the true critical one as shown in Figure (4.2). However, when this is done, the transformation has been carried too far to the left. Further refinement to this adjustment depends upon where it is desired best to fit the data. This is shown in Figure (4.2).

The calculated parameters in the above mentioned manner, although they were evaluated from the critical properties which represents the most sensitive region they do not necessarily fit at any other conditions. This puts a severe strain on the equation of state leading to a value of Z_c which is too large. Subsequently, it has been proposed that the parameters of an equation of state may be treated as temperature dependent[19,20,33,52,59].

In order to apply an equation of state to the representation of vapor-liquid equilibrium of pure component, the equation must satisfy the three conditions given by Equations (2.7) to (2.9). The most important condition for vapor-liquid equilibrium is the equality of the fugacity in both phases.

Therefore, an equation must have at least three adjustable parameters to satisfy these conditions at equilibrium. It should be mentioned, however, that this approach has the limitation that one of these conditions has to be sacrificed when it is applied to a two-parameter equation. Mixing rules for combining the pure component parameters are required for extending these equations to mixture.

One of the equations of state frequently used in chemical engineering is that proposed by Redlich-Kwong in 1949 (RK equation). It is remarkably simple and is employed in all property estimation systems[75]. It has been the subject of much research in order to improve its predictive ability for both pure components and mixtures.

It is now generally accepted that the two parameters of the Redlich-Kwong equation, Ω_a and Ω_b are not universal constants. They vary from substance to substance and are temperature dependent.

On the other hand, there are few three-constant equations of state available in the literature[102], none of them is capable of describing the behaviour of pure substance especially in the liquid region. In many ways, the equation of Clausius embodies a certain definite advantage over the other three-parameter equation of state which is attributed largely to the introduction of the quantity $(V + c)$.

As a matter of fact, the Clausius equation of state has appeared promising because it does reproduce perfectly the qualitative behaviour of substances and further improvement could be attained by assuming temperature-dependent parameters.

It is intended to study both the Redlich-Kwong and the Clausius equations for the purpose of the prediction of vapor-liquid equilibria data. The Redlich-Kwong equation of state with the modified procedure developed by Chang and Lu[17,67] and extended by Hsi and Lu[52,52] was adopted. The evaluation of Ω_a and Ω_b as temperature-dependent at the subcritical and critical conditions using the saturation properties available in the literature will be discussed in this chapter.

To facilitate the calculation procedure using the Redlich-Kwong equation in the absence of the saturation properties, a generalized correlation for the two parameters Ω_a and Ω_b will be developed.

A further modification for the method previously proposed by Elshayal and Lu[33] for predicting vapor-liquid equilibria using the Clausius equation of state with a modified procedure will be demonstrated.

This work arises from the assumption that an improvement in reproducing the saturation conditions of pure substances also leads to an improvement for mixtures. Good agreement between the experimental and the calculated saturation properties is, of course, not a sufficient condition for a good representation for mixture but is a necessary one.

4.1 Thermodynamic consideration:

The criterion for equilibrium between two phases ℓ and v at a given temperature and pressure is that for any component i present

$$\mu_{i\ell} = \mu_{iv} \tag{4.3}$$

However, for practical purposes, it is necessary to relate the chemical potential of the equilibrated phases in terms of a certain auxiliary function as fugacity[27,87].

The fugacity of any component i of a solution $\hat{f}_i$, is defined by the equation[27,87]

$$\begin{cases} \mu_i = \mu_i^\circ + RT \ln \hat{f}_i \\ \\ \dfrac{\hat{f}_i}{y_i P} \to 1 \quad \text{as} \quad P \to 0 \end{cases} \tag{4.4}$$

where μ_i° is a function of temperature only and has precisely the same value as for the pure component i at the same temperature and unit fugacity.

For vapor-liquid equilibrium substitution of Equation (4.4) into Equation (4.3) gives,

$$\hat{f}_{iv} = \hat{f}_{i\ell} \tag{4.5}$$

To predict phase equilibria data using an equation of state with a modified procedure, an expression for the fugacity of the pure component is needed to evaluate the adjustable parameters of the equation at the temperature of interest.

4.1.1 Fugacity of substance i :

The chemical potential of a pure substance i, is related to the temperature and pressure by the differential form[87]

$$d\mu_i = -S_i\,dT + V_i dp \tag{4.6}$$

where S_i is the molar entropy and V_i is the molar volume. Therefore, for any single component fluid,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = V_i \tag{4.7}$$

Hence, $\partial \mu_i = [V_i\,dP]_T$

Equation (4.4) can be rewritten for pure components as follows:

$$\begin{cases} \mu_i = \mu_i^\circ + RT\,\ell nf \\ \frac{f}{P} \to 1 \qquad P \to 0 \end{cases} \tag{4.4a}$$

Subsequently, $[d\mu_i = RT\,d\,\ell nf]_T$

where the subscript denotes constancy of temperature and thus,

$$[RT\,d\ell nf = VdP]_T \tag{4.8}$$

Subtracting $RT\,d\,\ell nP$ from both sides of this equation, taking the constancy of temperature to be understood, henceforth,

$$d\,\ell n\,f/P = \left(\frac{V}{RT} - \frac{1}{P}\right)dP \tag{4.9}$$

integrating

$$\ell n\,(f/P) = \int_0^P \left(\frac{V}{RT} - \frac{1}{P}\right) dP \tag{4.10}$$

where (f/P) is defined as the fugacity coefficient, ϕ_i, of the pure component, i.

An equation for the calculation of the fugacity of component i of a mole fraction y_i in a mixture, $\hat{f}_i$, may be derived as above, where,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i;n_j} = \overline{V}_i \tag{4.11}$$

and under the same conditions from (4.4), one obtains

$$RT \ln \frac{\hat{f}_i}{y_i P} = \int_o^P [\bar{V}_i - \frac{RT}{P}] dP \qquad (4.12)$$

where $\bar{V}_i$ is the partial molar volume defined as

$$\bar{V}_i = (\frac{\partial V_T}{\partial n_i})_{T,P,n_j} \qquad (4.13)$$

Since most of the equations of state are explicit in P, the fugacity coefficient can be expressed as follows:

$$RT \ln \frac{\hat{f}_i}{y_i P} = \int_V^\infty [(\frac{\partial P}{\partial n_i})_{T,V_T,n_j} - \frac{RT}{V}] dV - RT \ln Z \qquad (4.14)$$

where Z is the compressibility of the mixture and the quantity $\hat{f}_i/y_i P$ as the fugacity coefficient.

4.1.2 Prediction of Vapor-Liquid Equilibria Data:

For vapor-liquid equilibria of N-Component system, the following equation must be satisfied

$$\hat{f}_{iv} = \hat{f}_{i\ell} \qquad i = 1,2,... \quad \text{same as (4.5)}$$

in which

$$\hat{f}_{iv} = \hat{\phi}_{iv} y_i P \qquad (4.15)$$

$$\hat{f}_{i\ell} = \phi_{i\ell} x_i P \qquad (4.16)$$

where $\hat{\phi}_{i\ell}$ and $\hat{\phi}_{iv}$ are the fugacity coefficients of component i in the mixture and can be evaluated using an equation of state by means of Equation (4.12) or (4.14) together with the mixing rules as will be explained in detail in the forthcoming section.

If the temperature and (N-1) independent liquid-phase mole fractions are specified, the total pressure P and (N-1) independent vapor-phase mole fractions could be

calculated with the aid of Equation (4.5). The simultaneous equations may be solved by a trial-and-error procedure. This is the so-called bubble-point calculation. Arbitrary values of P and $\hat{\phi}_{iv}$ are assumed for the first iteration. From the given x's and T, $\hat{\phi}_{i\ell}$ is calculated by means of equations (4.12) or (4.14), using the liquid properties and an equation of state. Vapor phase compositions are calculated by:

$$y_i = (\hat{\phi}_{i\ell}/\hat{\phi}_{iv})\, x_i \qquad (4.17)$$

and the total pressure is calculated by:

$$P = \sum_{i=1}^{N} \hat{f}_{i\ell}/\hat{\phi}_{iv} \qquad (4.18)$$

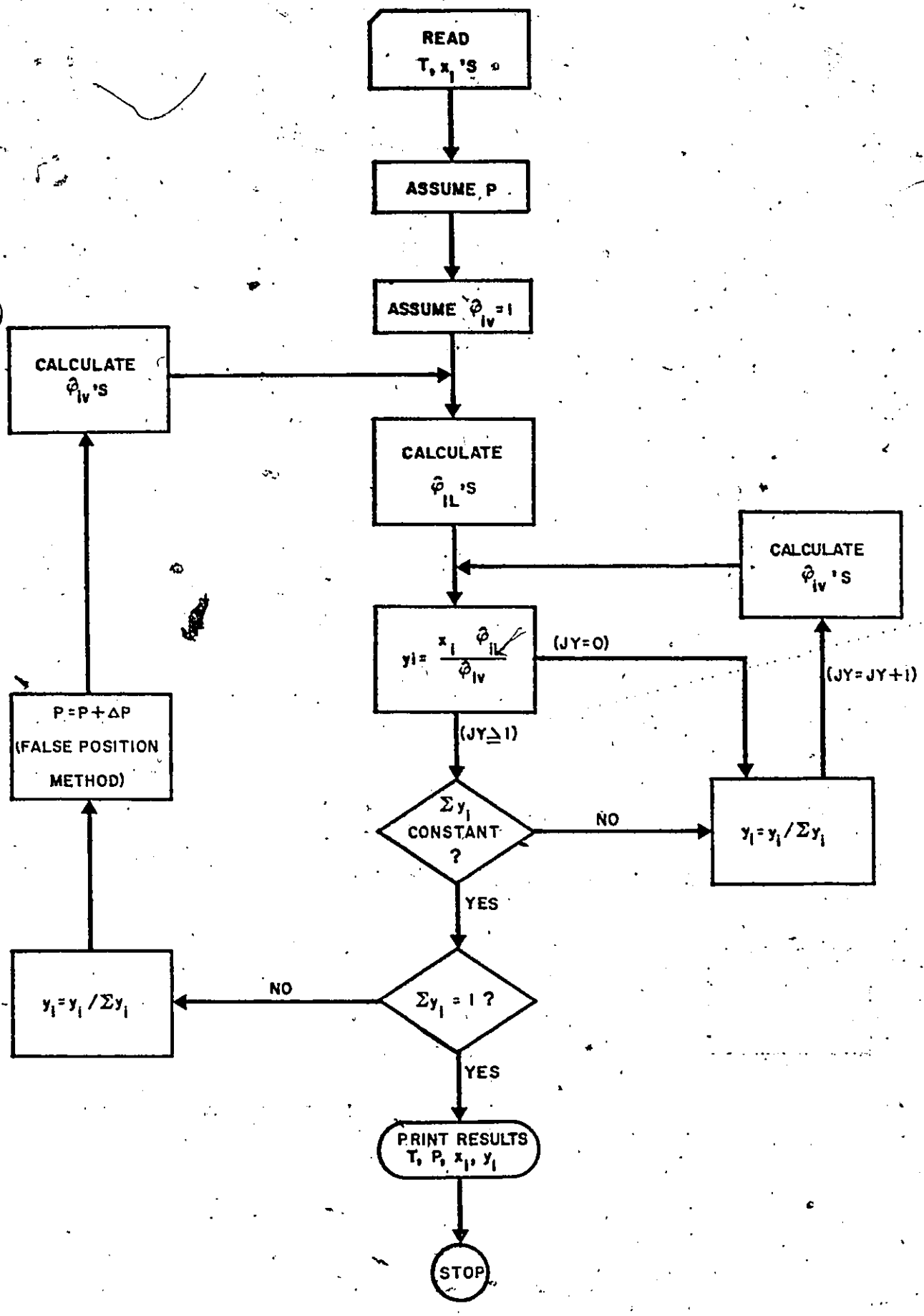
which is then compared with the previously assumed value. If it is different, $\hat{\phi}_{iv}$'s are recalculated by Equation (4.12) or (4.14) using an equation of state with the newly obtained value of pressure and the normalized vapor-phase composition. Then the $\hat{\phi}_{i\ell}$'s are recalculated with the new value of P, using the liquid properties. When the pressure is no longer changed within a specified tolerance ($|\Delta P/P| = 0.0001$) the relation

$$\sum_{i=1}^{N} y_i = 1.0 \qquad (4.19)$$

is finally tested until a specified tolerance of 0.0001 is met. Usually this is satisfied when the pressure has attained an unchanged value. A schematic diagram of the iteration is shown in Figure (4.3). A computer program to perform the calculation is given in Appendix E.

4.1.3 Liquid Phase Activity Coefficients:

Another useful and alternate technique to represent the non ideality of the liquid phase is by defining an ideal solution and by describing deviations from the ideal behaviour



4.3 Block Diagram of Bubble Point Program

in terms of the familiar activity coefficients. The fugacity of component i in a liquid solution is most conveniently related to the mole fraction x_i by an equation of the form

$$\hat{f}_{i\ell} = \gamma_i x_i f^{\circ}_{i\ell} \tag{4.20}$$

where $\hat{f}^{\circ}_{i\ell}$ is the fugacity of component i at the same arbitrary condition known as the standard state. At any composition, the activity coefficient depends on the choice of the standard state and the numerical value of γ_i has no significance unless the numerical value of $f^{\circ}_{i\ell}$ is also specified.

Since the choice of the standard state is arbitrary, it is convenient to choose $f^{\circ}_{i\ell}$ such that γ_i assumes values close to unity and when γ_i is exactly equal to unity, the solution is said to be ideal[87]. However, because the intimate relation between the activity coefficient and the standard-state fugacity, the definition of solution ideality ($\gamma_i = 1$) is not complete unless the choice of standard state is clearly indicated.

In the liquid phase, the usual practice is to have the temperature of the system, a fixed composition and specified pressure as the independent variables which determine the standard state of a component. A convenient choice of the standard state is the pure liquid at the system temperature and a reference pressure, P°. If P° is chosen to be higher than all the saturation pressures encountered, then a hypothetical liquid state can be avoided. In defining the activity coefficients, there are two commonly used conventions:

$$\gamma_i \to 1 \qquad \text{as} \quad x_i \to 1 \tag{4.21}$$

where the normalization holds for all the components and this is called the symmetric convention for normalization. The other convention is

$$\begin{cases} \gamma_i \to 1 & \text{as} \quad x_i \to 1 \quad \text{(solvent)} \\ \gamma_2^* \to 1 & \text{as} \quad x_2 \to 0 \quad \text{(solute)} \end{cases} \tag{4.22}$$

Since solute and solvent are not normalized in the same way, Equation (4.22) gives the unsymmetric convention or normalization.

The symmetric normalization of the activity coefficients is easily extended to solutions containing more than two components and will be adopted in this work. The choice of P° as the reference pressure gives the γ_i values as constant pressure activity coefficients. At isothermal conditions, one obtains the constant temperature-constant pressure activity coefficients which are only composition dependent.

The activity coefficient can be defined as

$$\mu_i = \mu_i^* + RT \ln \gamma_i x_i \qquad (4.23)$$

where μ_i^* is to be taken as a function of temperature and pressure. The definition is completed by one of the conventions given by Equation (4.21) or (4.22).

Therefore, the pressure dependence of the activity coefficient, if the standard state is taken at a fixed value, is given by the exact thermodynamic relation

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\overline{V}_i}{RT} \qquad (4.24)$$

Partial differentiation of Equation (4.4) with respect to pressure gives the pressure dependence of the fugacity

$$\left(\frac{\partial \ln \hat{f}_i}{\partial P}\right)_{T,x} = \frac{1}{RT}\left(\frac{\partial \mu_i}{\partial P}\right)_{T,x} = \frac{\overline{V}_i}{RT} \qquad (4.25)$$

Integrating (4.26) from the system pressure P to the reference pressure P° gives:

$$\hat{f}_{i\ell}(P^\circ,T,x) = \hat{f}_{i\ell}(P,T,x) \exp \int_P^{P^\circ} \frac{\overline{V}_i}{RT}\, dP \qquad (4.26)$$

Combining Equations (4.20) and (4.26) gives:

$$\gamma_i(P^\circ,T,x) = \frac{\hat{f}_{i\ell}(P,T,x)}{x_i f^\circ_{i\ell}(P^\circ,T)} \exp \int_P^{P^\circ} \frac{\overline{V}_i}{RT}\, dp \qquad (4.27)$$

The fugacity and the partial molar volume can be evaluated using an equation of state, e.g., the Redlich-Kwong equation or the Clausius equation. The mixing rules are identical to those used by Chueh and Prausnitz[87] and Lu and Co-workers[19,33]. The expressions for the mixing rules will be presented in sections (4.2) and (4.4). Values of the binary interaction constant were obtained in such a manner that the sum of the absolute difference between the experimental and the calculated system pressure, P, is minimum. Equation (4.28) can be written as

$$\gamma(P^\circ,T,x) = \frac{\hat{\phi}_{iv}(P,T,y) \cdot Py_i}{x_i f^\circ_{i\ell}(P^\circ,T)} \exp \int_P^{P^\circ} \frac{\bar{V}_{i\ell}}{RT} dP \qquad (4.28)$$

The quantity $\hat{\phi}_{iv}$ was evaluated using the experimental vapor composition, y and the total pressure. The γ values obtained in this manner were used to obtain the excess Gibbs free energy by means of the following expression

$$G^E = RT \Sigma x_i \ln \gamma_i \qquad (4.29)$$

The γ and G^E values were also calculated using the predicted P and y values for the isotherms under study. A comparison of the G^E values obtained would clearly reflect the quality of the experimental data. A computer program is given in Appendix E.

4.1.4 Evaluation of the Partial Molal Volume in a Mixture:

An expression for the evaluation of the partial molar volume for component i in a mixture is necessary to account for the pressure effect on the fugacity which becomes significant at high pressure conditions. It can be computed by the following relation:

$$\bar{V}_i = - \frac{(\partial P/\partial n_i)_{P,V_T,n_j(i\neq j)}}{(\partial P/\partial V)_{T,n_j(\text{all } j)}} \qquad (4.30)$$

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

4.2 Redlich-Kwong Equation of State:

The working equation originally proposed by Redlich and Kwong[91] is of the following form:

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}\,V(V+b)} \tag{4.31}$$

where

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c} \tag{4.32}$$

$$b = \Omega_b \frac{RT_c}{P_c} \tag{4.33}$$

or, it may be written in the form;

$$Z = \frac{1}{1-h} - \frac{A^2}{B}\left(\frac{h}{1+h}\right) \tag{4.34}$$

where

$$h = \frac{b}{V} = \frac{BP}{Z} \tag{4.35}$$

$$A^2 = a/R^2T^{2.5} = \Omega_a\, T_c^{2.5}/P_cT^{2.5} \tag{4.36}$$

$$B = b/RT = \Omega_b\, T_c/P_cT \tag{4.37}$$

When the Redlich-Kwong equation of state is applied to the mixture, the following mixing rules are used:

$$a = \sum_i \sum_j x_i\, x_j\, a_{ij} \tag{4.38}$$

$$b = \sum_i x_i b_i \tag{4.39}$$

where

$$a_{ij} = \Omega_{a_{ij}}\, R^2 T_{c_{ij}}^{2.5}/P_{c_{ij}} \tag{4.40}$$

These parameters reduce to those of the pure components if $i = j$ in Equations (4.38) to (4.40). Equations (4.38), (4.39) and (4.40) follow the proposal of Redlich and Kwong[91].

In addition,

$$T_{c_{ij}} = (T_{c_i} T_{c_j})^{0.5}(1 - k_{ij}) \quad (4.41)$$

$$\Omega_{a_{ij}} = 0.5(\Omega_{a_{ii}} + \Omega_{a_{jj}}) \quad (4.42)$$

$$P_{c_{ij}} = Z_{c_{ij}} R T_{c_{ij}} / V_{c_{ij}} \quad (4.43)$$

$$V_{c_{ij}} = \frac{1}{8}(V_{c_i}^{\frac{1}{3}} + V_{c_j}^{\frac{1}{3}})^3 \quad (4.44)$$

$$Z_{c_{ij}} = 0.291 - 0.08\,\omega_{ij} \quad (4.45)$$

$$\omega_{ij} = 0.5(\omega_i + \omega_j) \quad (4.46)$$

It should be noted that the quantity k_{ij} in Equation (4.41) is the binary interaction constant, which is a constant characteristic of the interaction of two dissimilar molecules, as a reasonable approximation of k_{ij} is assumed to be independent of temperature, density and composition[20]. Equations (4.41) to (4.43) follow the proposal of Chueh and Prausnitz[20] and Equations (4.45) and (4.46) that of Pitzer and his co-workers[84,85]. Equation (4.44) is the well-known Lorentz relationship.

4.2.1 Evaluation of the Temperature-Dependent Parameters Ω_a and Ω_b of the Redlich-Kwong Equation

The two temperature-dependent parameters of the Redlich-Kwong equation may be evaluated from any two pure component properties at saturation at a given temperature. For vapor-liquid equilibrium calculations, the condition

of equal fugacity in the liquid and vapor phases, is a necessity. Our experience indicates that vapor pressure and saturated liquid volume are the two desirable properties for the evaluation. This modified procedure was used by Chang and Lu[17,19,67] and by Joffe et al.[56].

In their method[17,19,67] the basic fundamental condition at equilibrium was satisfied, i.e.,

$$f_{i\ell} = f_{iv} \qquad \text{same as (4.5)}$$

or

$$\phi_{i\ell} = \phi_{iv} \qquad (4.47)$$

where $\phi_{i\ell}$ and ϕ_{iv} are the fugacity coefficients of component i, in the liquid and vapor phases respectively and can be expressed using the Redlich-Kwong equation as follows:

$$\ln \phi_\ell = Z_\ell - 1 - \ln Z_\ell - \ln(1-h_\ell) - \frac{(A^2/B)}{\ln(1+h_\ell)} \qquad (4.48)$$

$$\ln \phi_v = Z_v - 1 - \ln Z_v - \ln(1-h_v) - \frac{(A^2/B)}{\ln(1+h_v)} \qquad (4.49)$$

Combining Equations (4.47), (4.49) and the Redlich-Kwong equation, (Equations (4.34) to (4.37)), one obtains,

$$\ln Z_\ell \phi_v + 1 - Z_\ell + \ln(1-h_\ell) + \frac{[1 - Z_\ell(1-h_\ell)](1+h_\ell)}{h_\ell(1-h_\ell)} + \ln(1 + h_\ell) = 0 \qquad (4.50)$$

An iteration loop of the computation is set up to evaluate Ω_a and Ω_b, employing Equation (4.50) as the working equation.

The calculation procedure may be briefly outlined as follows:

1) Assume initial values for Ω_a and Ω_b and calculate A^2 and B.

2) For a given value of Z_ℓ, and assumed value of ϕ_v, calculate h_ℓ by means of Equation (4.50).
3) Calculate B from Equation (4.35) and A^2 from Equation (4.34).
4) Substitute the new values of A^2 and B into Equations (4.34) and (4.35) and solve simultaneously for another set of roots of Z_v and h_v.
5) Calculate ϕ_{iv} from Equation (4.49) using the new set for h_v and Z_v.
6) Obtain a new value for h_ℓ from Equation (4.50) and compare it with that obtained in Step 2. If they disagree, repeat the calculation starting from Step 2. An iteration loop is thus built until the change of h_ℓ value is less than the specified tolerance. The tolerance used in this investigation is 0.00005. A computer program for performing the calculation is given in Appendix E.

In this work, the values of Ω_a and Ω_b were evaluated using the above mentioned procedure at the experimental conditions (-60°, -20°, 20° and 60°F) using the saturated molar liquid volumes and vapor pressures available in the literature for ethane[12,29], propane[12,25,29] and carbon dioxide[29,99]. The calculated values are listed in Table (A.1). Values of Ω_a and Ω_b for ethane, propane and carbon dioxide at conditions other than the experimental ones are also given in Table (A.1).

Furthermore, values of Ω_a and Ω_b were evaluated for thirteen pure components, including ethane and propane, in the temperature region where reliable saturated properties are available. The critical properties of all the hydrocarbons were taken from the API Technical Data Book[109], with the exception of T_c and P_c for methane which were taken from the values reported by Prydz and Goodwin[89]. For argon, the critical data given by Michels et al.[75] were employed

while for nitrogen, the critical data were taken from Din[29]. The source of the saturation data used for the evaluation of the parameters are listed in Table (A.2). Although the same procedure was used for evaluating these two paramaters at $T = T_c$ and $T < T_c$ conditions, critical volume and critical pressure were treated as the saturated liquid volume and vapor pressure at the critical point.

Values of the parameters obtained, together with the temperature range investigated are reported in Table (A.3). The computer program to carry these calculations is given in Appendix E.

4.2.2 Application of the Redlich-Kwong Equation to Phase Equilibrium Calculations:

The Redlich-Kwong equation can be used in the evaluation of the fugacity coefficients in a mixture and partial molar volume which are the supporting properties for phase-equilibrium calculation as outlined in Sections (4.1.1) to (4.1.4). In the application, the two parameters Ω_a and Ω_b were considered temperature dependent. Upon substituting Equation (4.34) and the mixing rules, Equations (4.38) to (4.46), into Equation (4.14), the fugacity coefficients of component i in a multi-component mixture for both phases may be expressed as follows:

$$\ell n\ \hat{\phi}_{iv} = (Z_v - 1)\ \frac{B_i}{B} - \ell n[Z_v(1 - h_v)] - (\frac{A^2}{B}) - (\frac{2\ \Sigma_j\ y_i\ A_{ij}^2}{A^2} - \frac{B_i}{B})\ \ell n(1 + h_v) \tag{4.51}$$

$$\ell n\ \hat{\phi}_{i\ell} = (Z_\ell - 1)\ \frac{B_i}{B} - \ell n\ (Z_\ell)\ (1 - h_\ell) - (\frac{A^2}{B})\ (\frac{2\ \Sigma_j\ x_j\ A^2_{ij}}{A^2} - \frac{B_i}{B})\ \ell n(1 + h_\ell) \tag{4.52}$$

The compressibility factor Z is one of three roots of Equation (4.34) rearranged in the following form:

$$f(Z) = Z^3 - Z^2 + BP\left(\frac{A^2}{B} - 1 - BP\right)Z - \frac{A^2}{B}(BP)^2 = 0 \tag{4.53}$$

The smallest root is taken as the compressibility factor of the saturated liquid, Z_ℓ, and the largest root is taken as that of the saturated vapor, Z_v. If the Redlich-Kwong equation of state is used with its mixing rules (Equations (4.38) to (4.46)), Equation (4.30) becomes

$$\bar{V}_i = \frac{\frac{RT}{V-b}\left(1 + \frac{b_i}{V-b}\right) - \frac{2\left(\left(\sum_j x_j a_{ij}\right) - a b_i/(V+b)\right)}{T^{0.5}V(V+b)}}{\frac{RT}{(V-b)^2} - \frac{a}{T^{0.5}}\frac{2V+b}{V^2(V+b)^2}} \tag{4.54}$$

Rearrangement of the mixing rules in terms of total number of moles rather than molar basis is needed where

$$a = \sum_i \sum_j x_i x_j a_{ij} = \frac{1}{n^2}\sum_i \sum_j n_i n_j a_{ij} \tag{4.55}$$

$$b = \sum_i x_i b_i = \frac{1}{n}\sum_i n_i b_i \tag{4.56}$$

$$\frac{\partial n^2 a}{\partial n_i} = 2\sum_j n_j a_{ij} \tag{4.57}$$

and

$$\frac{\partial nb}{\partial n_i} = b_i \tag{4.58}$$

where n is the total number of moles.

4.2.3 Results and Discussion:

Prediction of Vapor-Liquid Equilibrium

As discussed in Section (4.1.2), the Redlich-Kwong equation of state with the modified procedure was used to

evaluate the system pressure and the equilibrium vapor composition with the system temperature and liquid composition specified. The saturated properties; liquid molar volumes and vapor pressures, reported in the literature for ethane[12,29] propane[12,25,29] and carbon dioxide[29,99] were employed for evaluating the temperature dependent parameters Ω_a and Ω_b. The calculated values of the parameters are listed in Table (A.1). The predicted P and y values are listed in Tables (A.4), (A.5) and (A.9) and are compared with the experimental data together with the values reported by Kurata and Swift[64]. The overall average deviation for the total of 109, experimentally determined data points in this investigation, in P is 1.98% and y is 0.0085 mole fraction.

Furthermore, the vapor-liquid equilibrium data for the system ethane-carbon dioxide[38,41,93], which were made available by the end of this phase of the investigation, were also used for the purpose of comparison.

In the calculation procedure, the mixing rules are identical to those reported in earlier sections. Values of the binary interaction constant, assumed to be independent of temperature, pressure and composition of the solution, were determined in such a manner that the sum of the absolute difference between the calculated and experimental P was minimum. The calculated k_{ij} values are comparable to that reported by Chueh and Prausnitz[21]. Although the k_{ij} values are frequently considered to be independent of temperature, density and composition, there is evidence that k_{ij} is not a true constant, but varies with temperature[11,44]. The values obtained in this investigation, as listed in Tables (4.1), (4.2) and (4.3) substantiate that k_{ij} does vary with temperature in spite of the fact that the values of Ω_a and Ω_b were determined individually at the temperature concerned.

A conclusion concerning the variation of k_{ij} with temperature can not be established at this stage. These changes in the values of k_{ij} with temperature may be attributed to the uncertainty of the data or to the inadequacy

of the equation of state. In addition, k_{ij} was obtained for the system propane-carbon dioxide by minimizing the difference between the experimental and the calculated values of the vapor-phase composition y. The values obtained based on the selection of either P or y are different. There is no assurance that either values will predict a better result than the other[58]. A minimum of one experimental data point on the binary vapor-liquid equilibrium data is needed for the evaluation of the value of k_{ij} to be subsequently used in vapor-liquid equilibria calculations. Because most of the isothermal vapor-liquid equilibrium data are reported as P-x, the evaluation of k_{ij} through the minimization of P is preferred.

It has been our experience that a better agreement between the experimental and calculated results are obtained when the temperature dependent parameters Ω_a and Ω_b are evaluated using the saturation properties which are reported together with the vapor-liquid equilibrium data. In this case, the vapor pressure of the pure components can be predicted precisely and accurately.

Ethane-Carbon Dioxide

Good agreement was obtained between the calculated and experimental values at the three lower temperatures, -60°, -20° and 20°F, experimentally investigated in this work. The predicted P and y values are listed in Table (A.4) and are compared with the experimental data together with the values reported by Kurata and Swift[64] in Figure (4.4). A summary of the comparison is given in Table (4.1). The calculated P and y values at 60°F are also compared with those of Robinson and Kalra[93] in Table (A.6). The average absolute deviation between the calculated and experimental P values is 1% at the three lower temperatures (-60°, -20° and 20°F). At 60°F, it is 2%. These differences are better than that between the experimental and the calculated values

TABLE 4.1

COMPARISON OF THE CALCULATED AND EXPERIMENTAL TOTAL PRESSURE AND VAPOR COMPOSITION VALUES FOR THE SYSTEM ETHANE (1) - CARBON DIOXIDE (2)

T°F	Pressure, Psia		k_{ij}*		% Absolute Deviation in P				Absolute Deviation in y_1				No. of Points	
					Experimental		Literature [64]		Experimental		Literature [64]			
	Experimental	Literature [64]	Exp.	Lit. [64]	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.	Exp.	Lit. [64]
60	637.5-827.0	662.2-814.0	0.098	0.087	2.01	3.4	2.39	3.7	0.0229	0.0533	0.008	0.0167	7	3
20	331.5-486.0	400.8-477.3	0.102	0.106	0.80	2.73	2.71	5.4	0.0272	0.0627	0.0330	0.0725	12	3
-20	212.0-263.0	229.0-258.5	0.101	0.101	0.92	2.24	2.4	6.2	0.0153	0.0447	0.0297	0.0638	9	3
-60	101.6-127.6	113.7-123.9	0.108	0.104	0.54	1.74	4.24	11.0	0.0213	0.0454	0.0499	0.1193	12	3

* Determined from vapor-liquid equilibrium data by minimizing the difference between the calculated and experimental P values. This quantity is involved in the mixing rules[21] and is defined by $k_{ij} = 1 - [T_{c_{ij}} / (T_{c_i} T_{c_j})^{0.5}]$

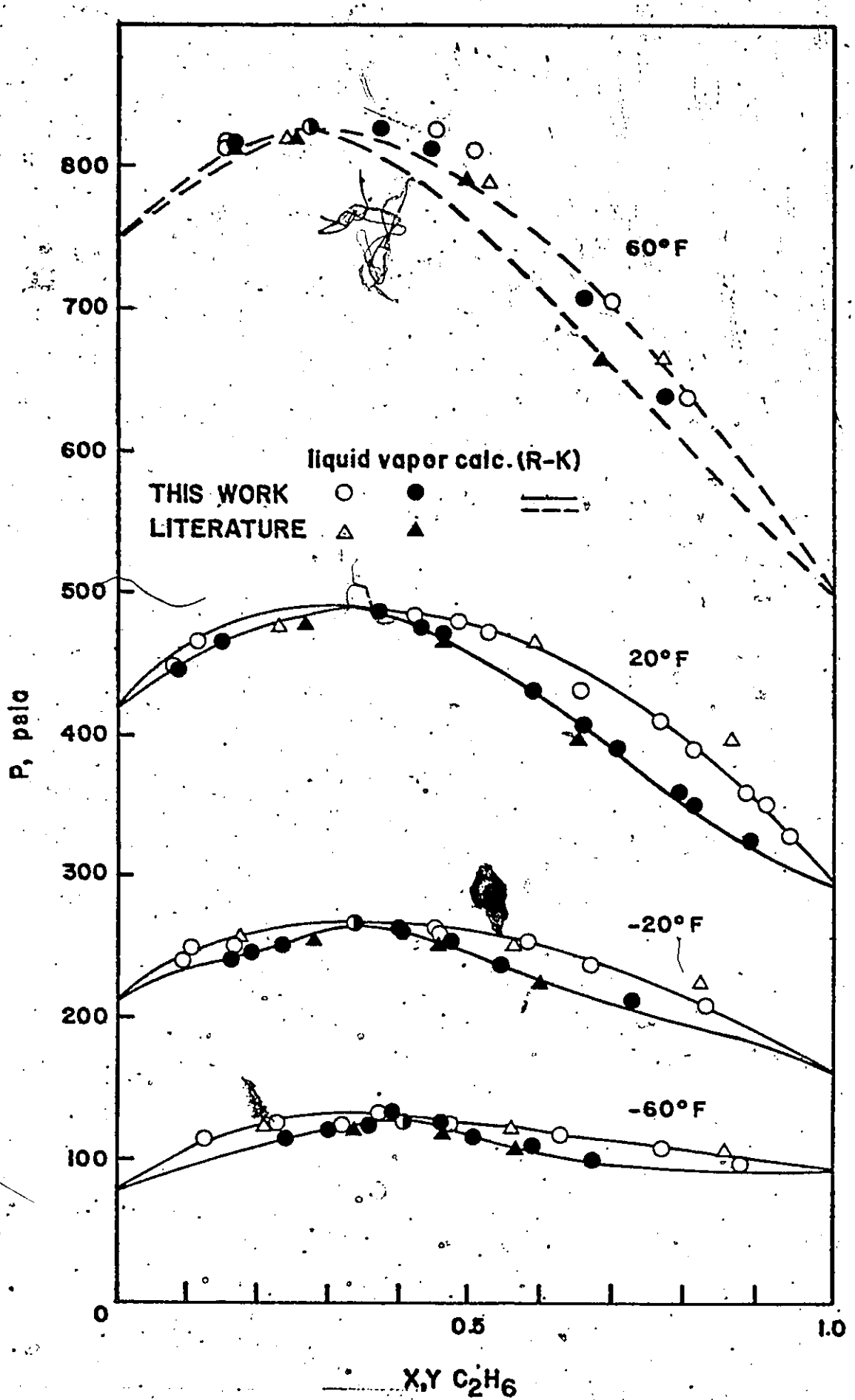


FIG. 4.4 Comparison of the Calculated, Experimental and Literature P-x-y Values for the Binary System Ethane-Carbon Dioxide

by Kurata and Swift[64] (2.4 to 4.2%) or that by Robinson and Kalra[93] where the average absolute deviation in P is 3.2% as shown in Tables (4.1) and (4.2). The average absolute deviation in y values is around 0.023 mole fraction, which is higher than the error bound indicated by the consistency test. The average absolute deviations between the calculated y values and those of Kurata and Swift[64] as shown in Table (4.1) are higher at the lower three temperatures. At 60°F, the average absolute deviations between the calculated and the experimental y values of Kurata and Swift, Robinson and Kalra and those collected in this work are 0.008, 0.006 and 0.0229 mole fraction respectively.

The large difference obtained between the calculated and experimental values for the isotherm at 60°F might be due to the fact that this temperature is rather close to the critical temperatures of ethane and carbon dioxide. It has been reported[54] that in the critical region, the predicted values deviate from the experimental results. For this reason, the calculated values are presented by dotted lines for this isotherm.

The data on the system ethane-carbon dioxide reported by Fredenslund and Mollerup[38] and Gugnoni et al.[41] at isothermal conditions other than those investigated in this work were used for the purpose of comparison. The predicted P and y values are listed in Tables (A.7) and (A.8) and are compared with the experimental data in Figures (4.5 to 4.6). A summary of the comparison is given in Table (4.2). The average absolute deviation between the calculated and experimental P values of Fredenslund and Mollerup[38] for five isothermal conditions (-50°, -30°, -10°, 10° and 20°C) is less than 1%. The average absolute deviation between the calculated and experimental y values is 0.0088 mole fraction. Furthermore, the average absolute deviation between the calculated and experimental P values of Gugnoni et al.[41] for four isothermal conditions (-25°, 0°, 25° and 50°F) is 0.70%. At 50°F the average absolute deviation between the experimental

TABLE 4.2

SUMMARY OF THE EXPERIMENTAL AND THE CALCULATED TOTAL PRESSURE AND VAPOR COMPOSITION VALUES FOR THE SYSTEM ETHANE (1) - CARBON DIOXIDE (2) BY MEANS OF THE REDLICH-KWONG EQUATION

Temp.K	Pressure atm.	k_{ij}	Ref.	% Absolute Deviation in P		Average Absolute Deviation in y	No. of data Points
				Max.	Average		
383.15(50°F)	29.72 - 48.84	0.099	41	1.73	0.65		12
269.25(25°F)	21.37 - 31.05	0.097	41	1.27	0.46		13
255.35(0°F)	14.83 - 20.72	0.098	41	3.33	0.82		15
241.55(-25°F)	9.96 - 13.23	0.097	41	2.16	0.91		9
293.15(20°C)	31.37 - 56.44	0.103	38	1.12	0.36	0.0118	8
283.15(10°C)	29.70 - 44.34	0.101	38	0.81	0.35	0.0082	13
263.15(-10°C)	18.35 - 26.07	0.099	38	3.37	0.74	0.0096	11
243.15(-30°C)	10.50 - 14.09	0.098	38	1.53	0.72	0.0068	12
223.15(-50°C)	5.45 - 6.72	0.099	38	2.56	1.01	0.0089	11
288.71(60°F)	516-833.5 Psia	0.088	93	4.75	3.18	0.0066	8

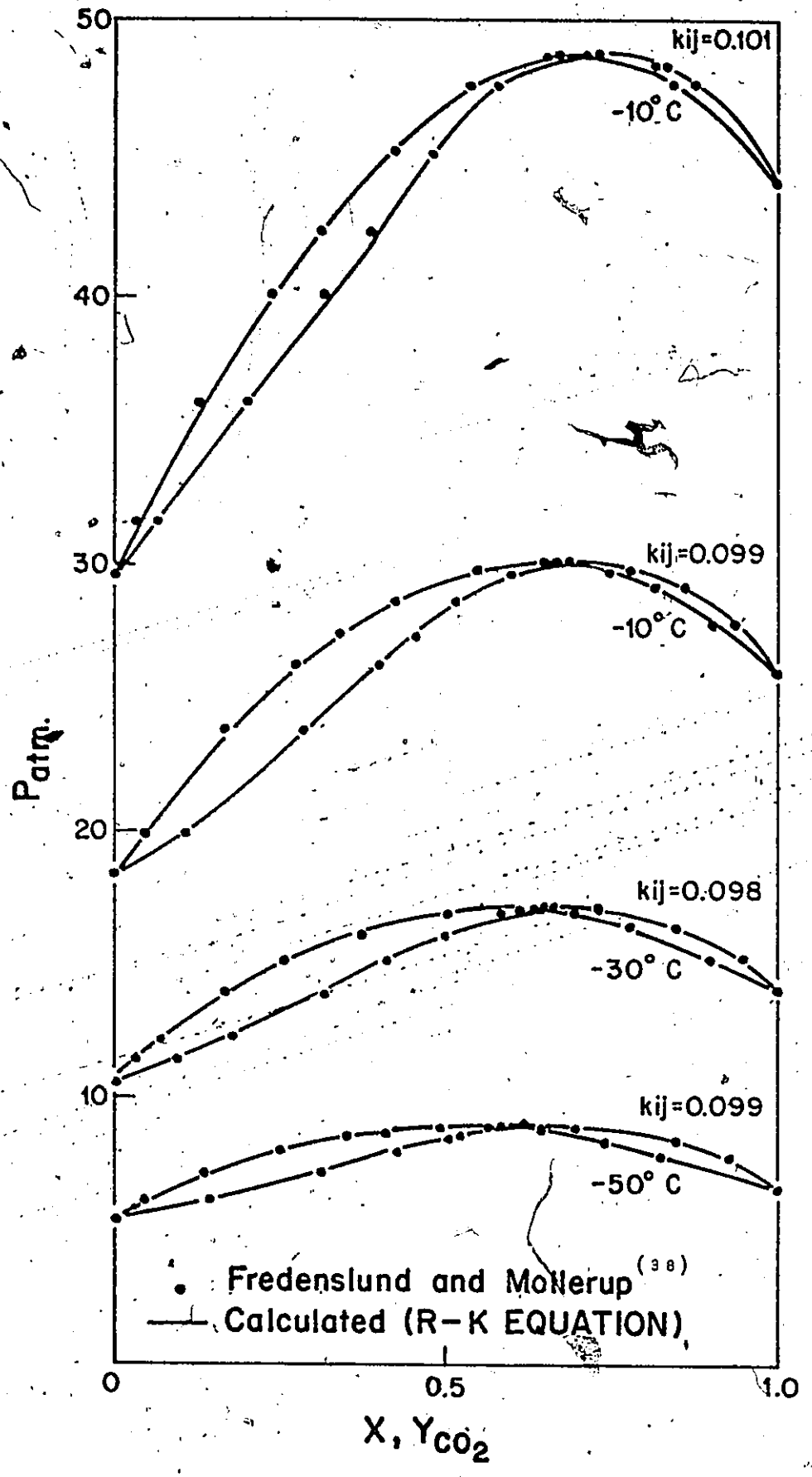


FIG. 4.5 Comparison of the Calculated and Experimental P-x-y Values for the Binary System Carbon Dioxide-Ethane

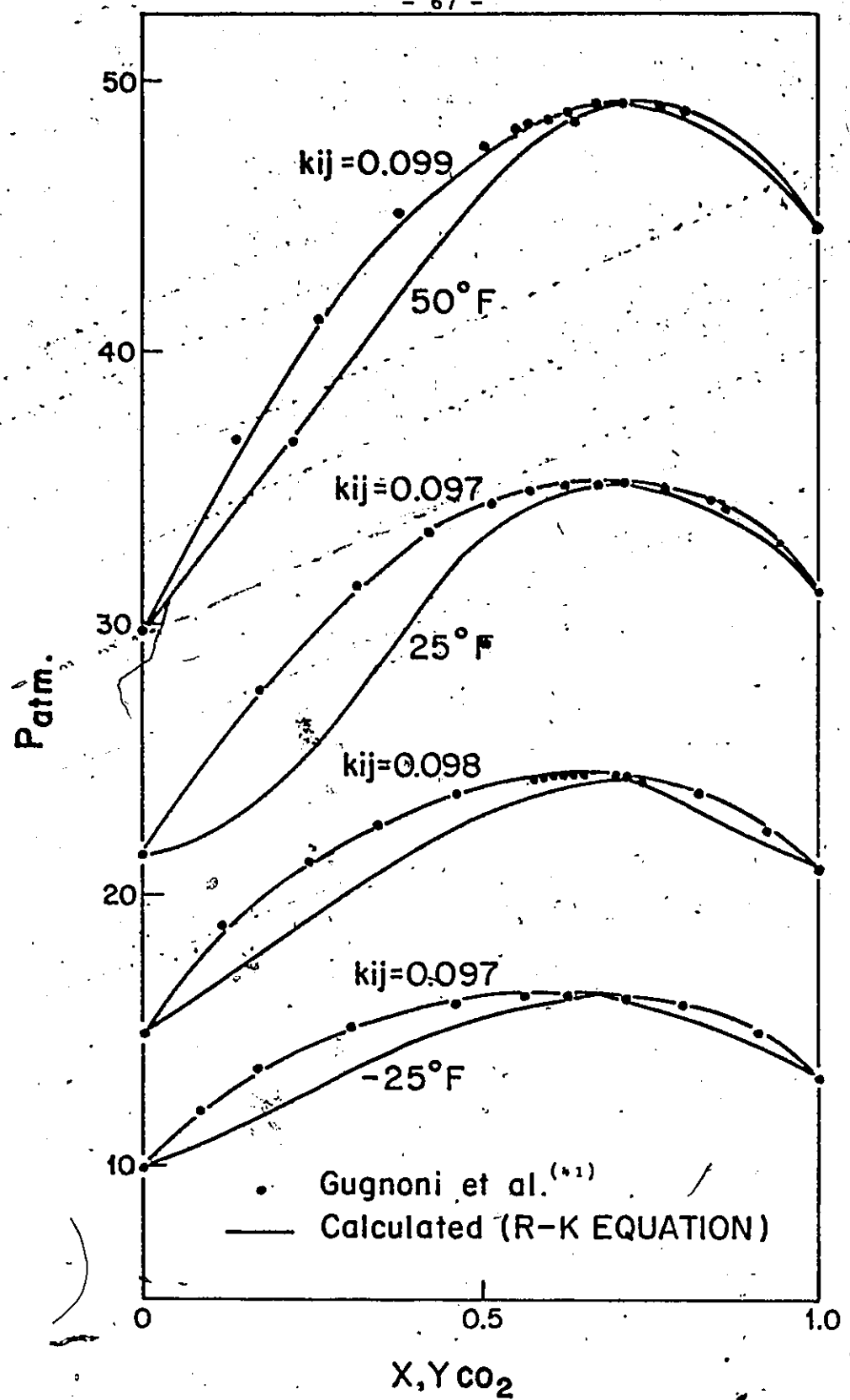


FIG. 4.6 Comparison of the Calculated and the Experimental P-x-y Values for the Binary System Carbon Dioxide-Ethane

and the calculated P value is 1.20% which is higher compared to the other three isothermal conditions and could be traced to the individual deviation of the point (x_{CO_2} = 0.2281). When this point was excluded, the average absolute deviation in P is nearly halved ($|\Delta P/P|\%$ = 0.65).

It should be mentioned that difficulties were encountered in the bubble-point calculations at the higher temperatures. A reasonable convergent solution could not be obtained with an assumed initial value for P and k_{ij}. In such an instance, the numerical solution, the initial guesses for the pressure and the value of k_{ij} have to be thoroughly checked.

Propane-Carbon Dioxide

The established values of Ω_a and Ω_b of Table (A.1) at -20° and 20°F were used in the calculation. The predicted P and y values are listed in Table (A.5) and compared with the experimental data in Figure (4.7). Values of the binary interaction constants k_{ij} determined from the minimization of the quantity $\Sigma|P^{calc.} - P^{exp.}|$ are comparable to those reported by Chueh and Prausnitz [21]. In addition, k_{ij} was obtained by minimizing the quantity $\Sigma|y^{calc.} - y^{exp.}|$. An average value of k_{ij}, calculated by averaging the two values obtained from the minimization of $\Sigma|\Delta P|$ at each individual temperature, was used to recalculate the total pressure and the vapor-phase compositions. The calculated results, as summarized in Table (4.3), indicate that the use of an average value for k_{ij} did not introduce a large deviation compared to the optimum value for k_{ij}.

The average absolute deviation between the predicted and the experimental P values is about 2.5%. The average absolute deviation between the predicted and experimental y values is about 0.007 mole fraction. Moreover the average value of k_{ij} was used in the modified procedure of the Redlich-Kwong equation of state to predict P-y at the conditions reported by Sage et al. (40° and 70°F). A summary of the

TABLE 4.3

COMPARISON OF THE CALCULATED AND EXPERIMENTAL TOTAL PRESSURE AND COMPOSITION VALUES FOR THE SYSTEM PROPANE (1) - CARBON DIOXIDE (2)

°F	Pressure, Psia	k_{ij}	% Absolute Deviation in P		Average Absolute Deviation in P	Absolute Deviation in y		No. of Points
			Max.	Avg.		Max.	Avg.	
70 (a)	125.0-860.9	0.094*	2.90	1.25	4.8	0.0129	0.0088	15
		0.100**	2.17	1.27	6.9	0.0164	0.0086	15
40 (a)	79 -566.5	0.094*	4.74	1.84	4.2	0.0201	0.0102	10
		0.100**	3.28	1.74	5.2	0.0164	0.0088	10
20 (b)	117.0-397.0	0.102*	4.01	2.02	5.0	0.0148	0.0069	11
		0.100**	4.76	2.10	5.1	0.0181	0.0065	11
		0.096***	6.24	2.47	5.7	0.0248	0.0062	11
-20 (b)	73.0-197.0	0.099*	4.59	2.26	3.0	0.0102	0.0062	10
		0.100**	4.02	2.20	3.1	0.0106	0.0060	10
		0.103***	4.51	2.51	3.9	0.0116	0.0058	10

*Determined from VLE data by the minimization of the quantity $\Sigma|P^{exp.} - P^{calc.}|$

**Determined from VLE data by averaging the two values of k_{ij} at -20° and 20°F.

***Determined from VLE data by the minimization of the quantity $\Sigma|y^{exp.} - y^{calc.}|$

(a) Sage and Lacey (1955)
(b) This work

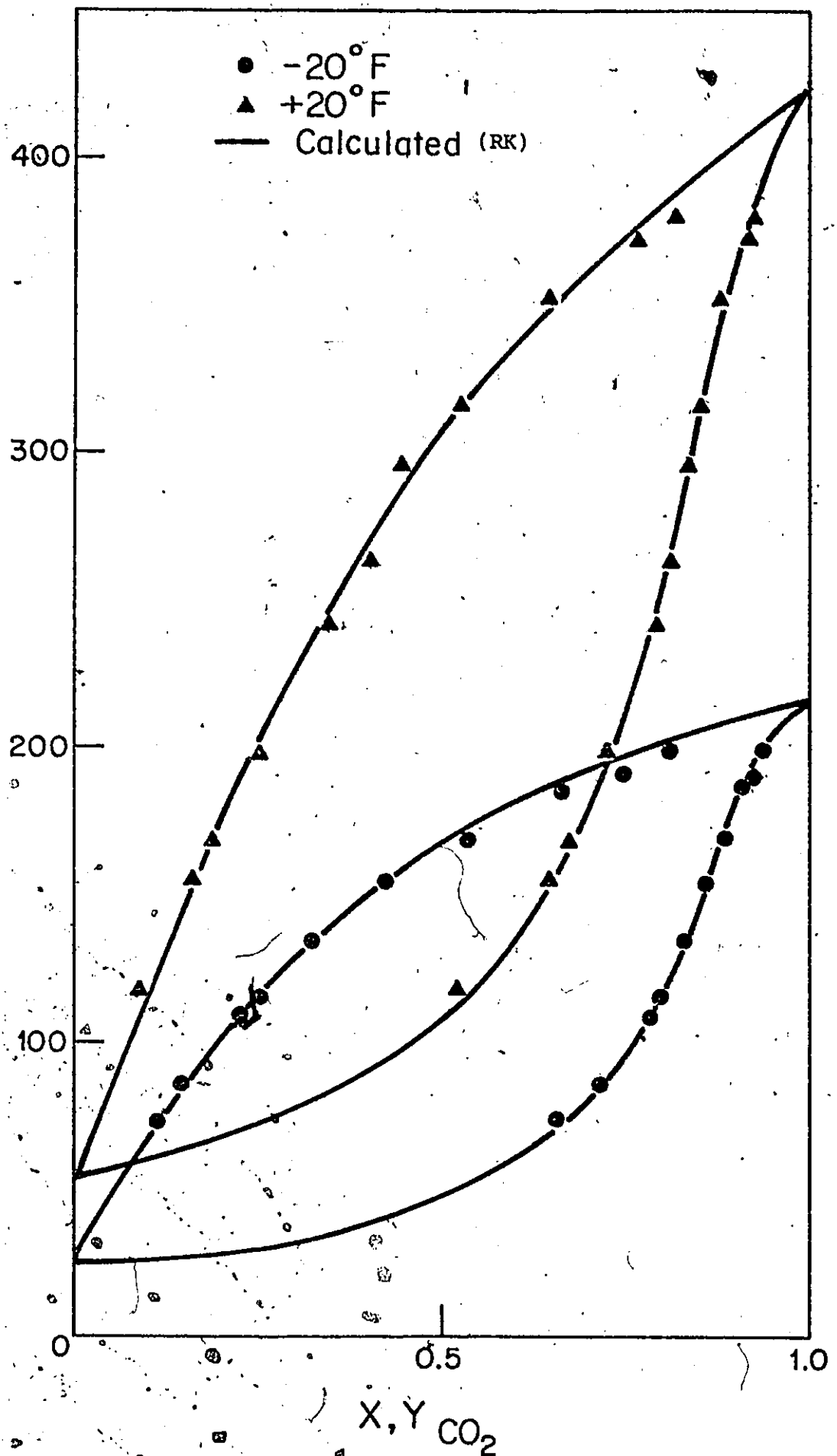


FIG. 4.7 Comparison of the Calculated and Experimental P-x-y Values for the Binary System Propane-Carbon Dioxide

comparison is also listed in Table (4.3). The average absolute deviation in P is less than 1.25% and in y is less than 0.0088 and 0.0102 mole fraction at 70° and 40°F respectively. To ensure that the vapor pressure of the pure components can be predicted precisely and accurately, the saturated properties reported by Sage et al.[99] were used for the evaluation of the parameters Ω_a and Ω_b at 40° and 70°F.

Ternary System

Propane-Ethane-Carbon Dioxide:

The values of Ω_a and Ω_b listed in Table (A.1) were used. In the calculation procedure, the calculated k_{ij} values obtained from the binary systems ethane-carbon dioxide and propane-carbon dioxide by minimizing the sum of the absolute differences between the calculated and experimental P values were employed in the calculation. For the system propane-ethane, an average value of k_{ij} (-0.025) was obtained from the vapor-liquid equilibria data reported by Djordjevich and Budenholzer[29a] between 0° and -200°F. The predicted P and y values are listed in Table (A.9) and compared with the experimental data. As the geometric mean represents the upper limit for $T_{c_{ij}}$, it is expected that values of k_{ij} be positive. Should k_{12} be taken as zero, as reported by Chueh and Prausnitz[87]. The calculated results are in fact not affected significantly as shown in the following summary:

T°F	Pressure psia	k_{12}	k_{23}	k_{13}	$\left\|\frac{\Delta P}{P}\right\|_{Avg}$ %	$\|\Delta y\|_{Avg}$	No. of data points
20	184-433	-0.025	0.102	0.102	2.76	0.0116	30
		0.00	0.102	0.102	2.68	0.0066	
-20	87.5-238	-0.025	0.101	0.099	2.61	0.0140	18
		0.00	0.101	0.099	2.92	0.0079	

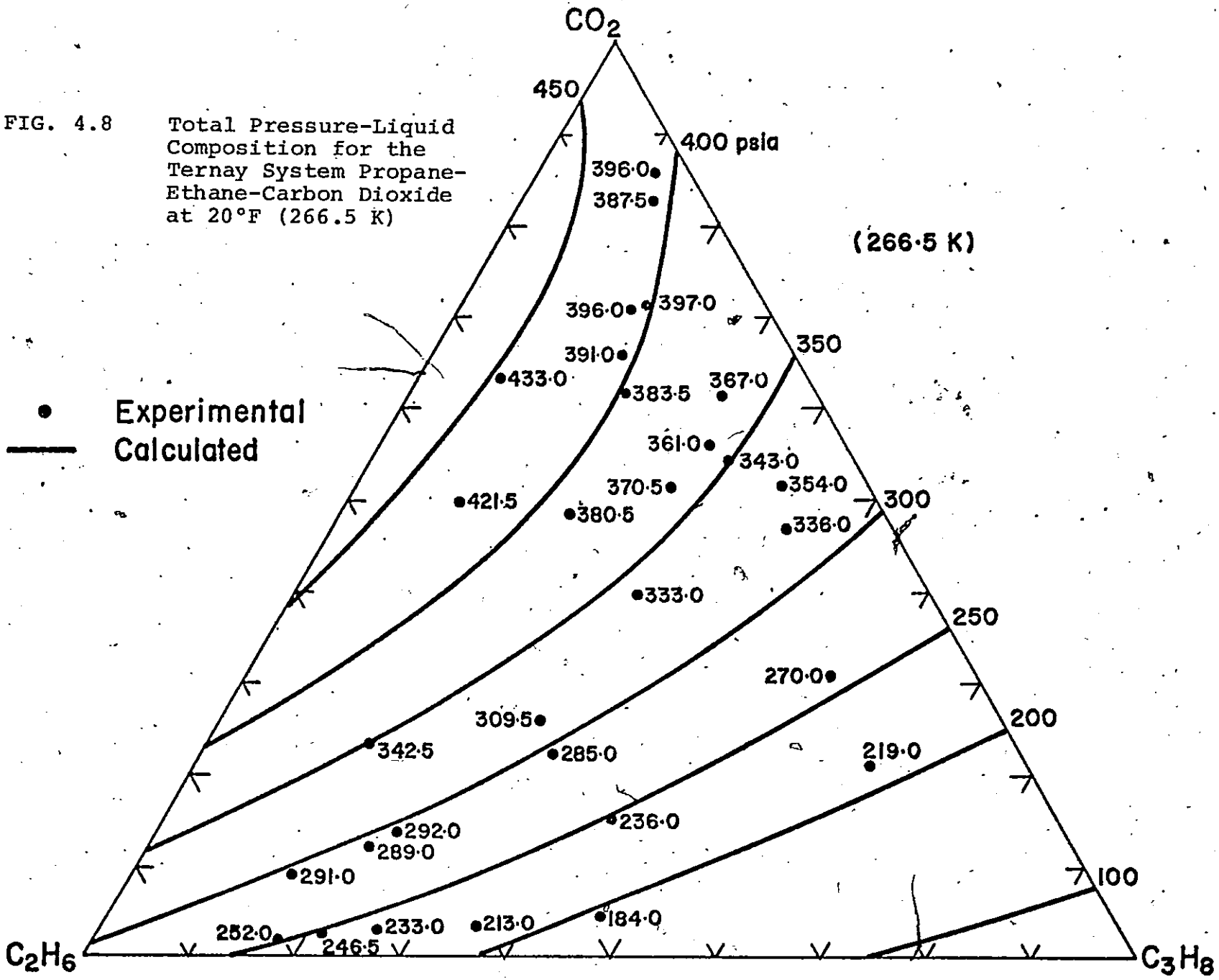


FIG. 4.8 Total Pressure-Liquid Composition for the Ternay System Propane-Ethane-Carbon Dioxide at 20°F (266.5 K)

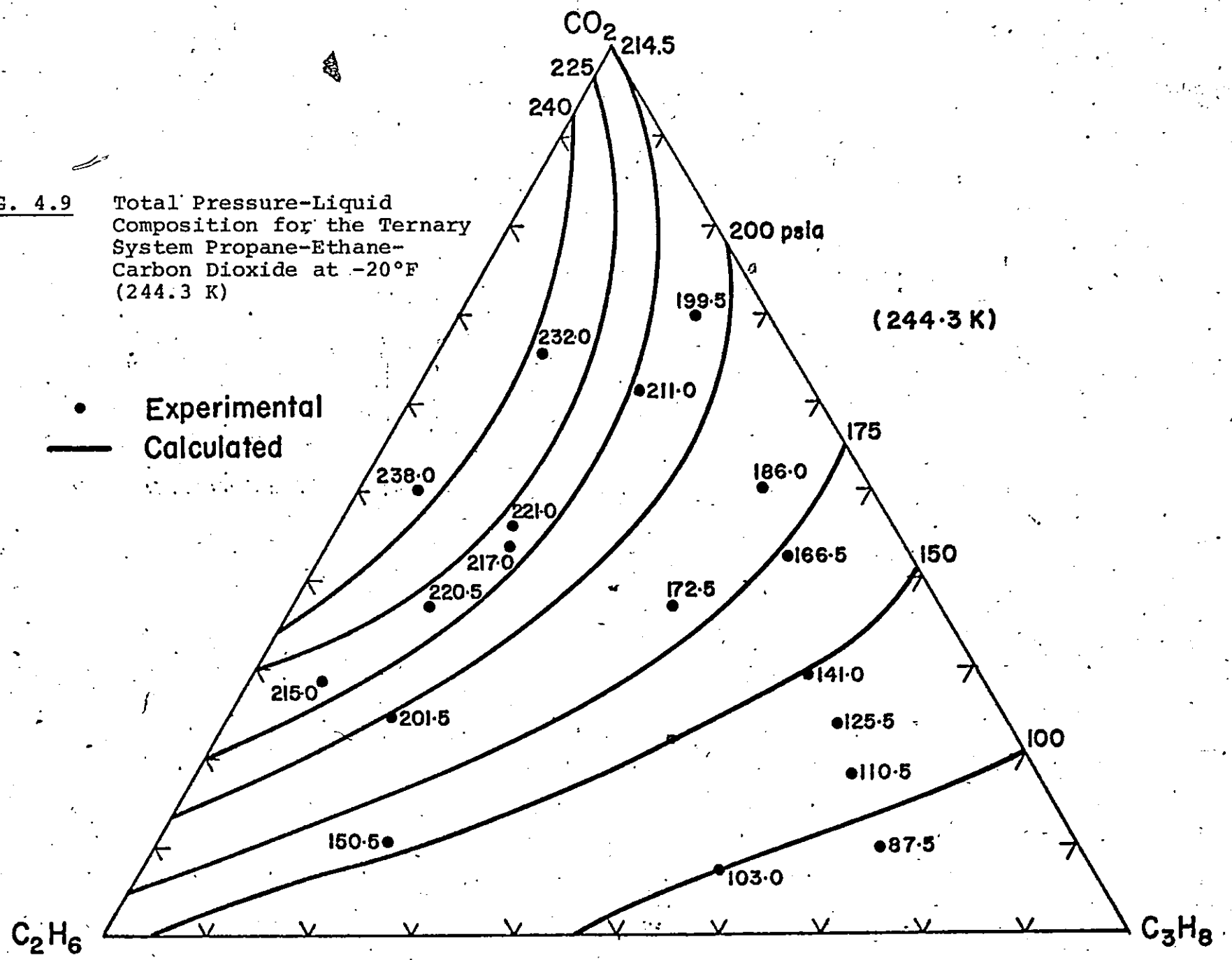


FIG. 4.9 Total Pressure-Liquid Composition for the Ternary System Propane-Ethane-Carbon Dioxide at -20°F (244.3 K)

Constant Pressure Lines:

Calculated total pressure-liquid composition lines for this ternary system are presented at constant pressure conditions. At each isothermal condition, liquid compositions were selected so that the whole ternary composition range was covered. The calculated values of pressure were first plotted against carbon dioxide liquid mole fraction with ethane to propane ratio as the parameter. By means of a graphical interpolation procedure, liquid compositions were established at constant pressure conditions. The results thus obtained are shown in Figures (4.8) and (4.9). It was established earlier in this discussion that the average absolute deviation between the calculated and experimental P values is less than 3%. Hence, it is expected that these constant pressure lines inherited this deviation.

Evaluation of Liquid Phase Activity Coefficients:

The γ values were calculated from the experimental data using Equation (4.28).

In this study, P°, the reference pressure was arbitrarily taken to be 900 Psia, which is above the highest saturation pressure encountered in this work. This was done to avoid the problem of finding the fugacity of physically unattainable state, i.e., hypothetical liquid state. The fugacity and the partial molal volume values were evaluated using the Redlich-Kwong equation by means of the modified procedure. Mixing rules are identical to those previously employed[19,54,67]. Values of k_{ij} were obtained from the minimization of the quantity $\Sigma|P^{calc.} - P^{exp.}|$. The γ values were then used to obtain the Gibbs free energy using Equation (4.29).

The calculated γ and G^E values, obtained in this manner, for the binary systems ethane-carbon dioxide, propane-carbon dioxide and the ternary system propane-ethane-carbon dioxide are listed in Tables (A.10) to (A.12). The γ and G^E values were again calculated using the predicted P and y values

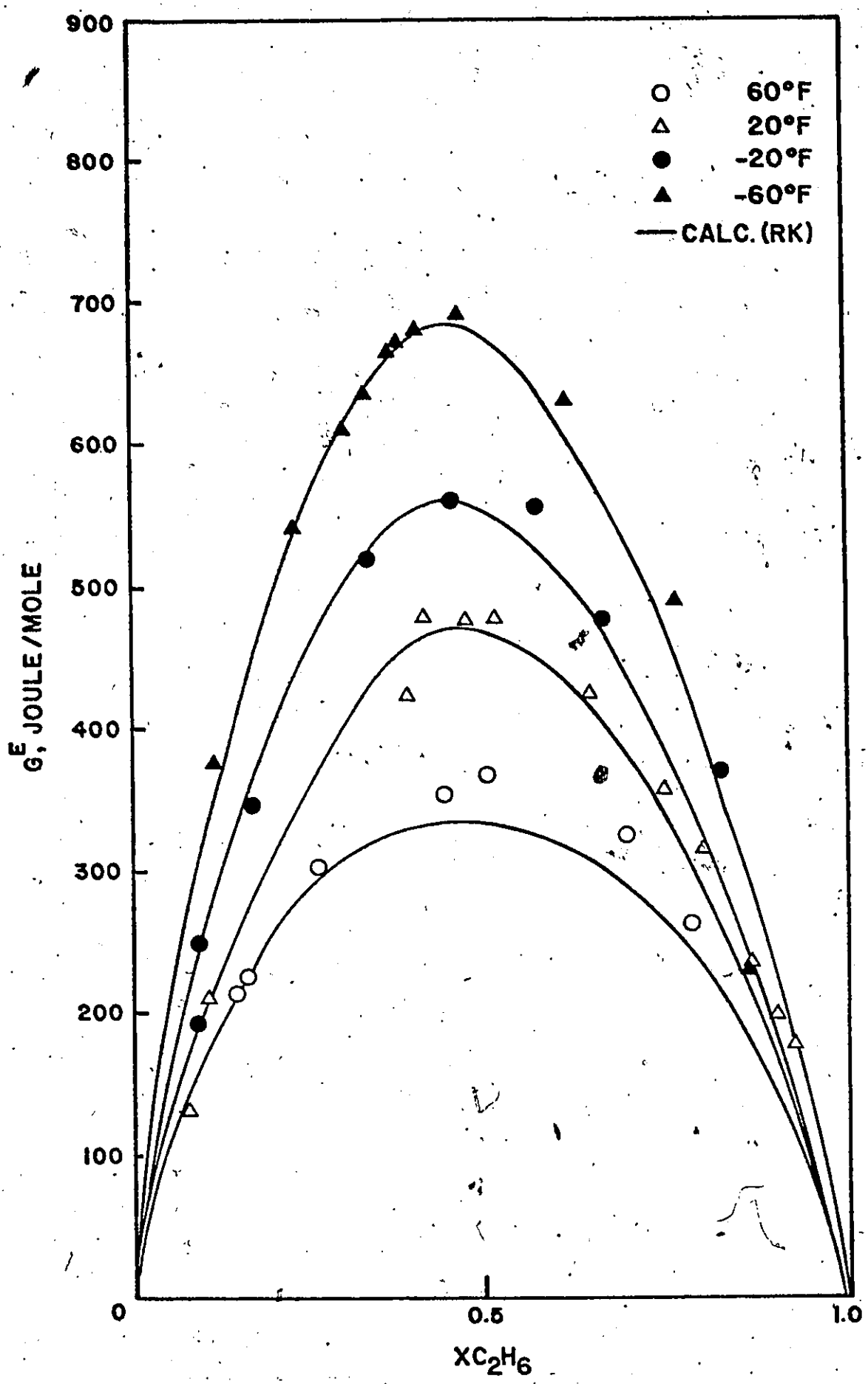


FIG. 4.10 Comparison of the Calculated and Experimental Excess Gibbs Free Energy of Mixing Values for the Binary System Ethane-Carbon Dioxide

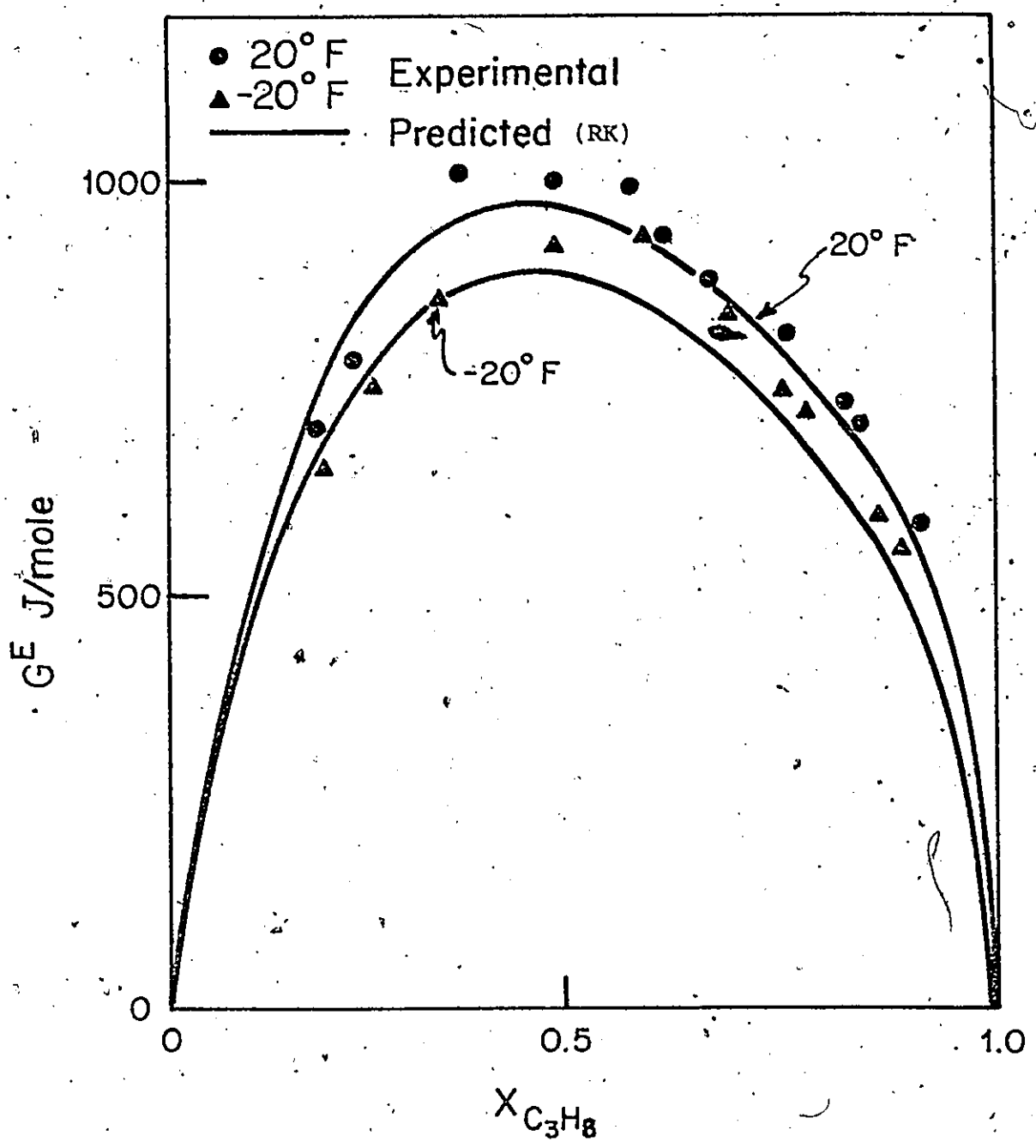


FIG. 4.11 Comparison of the Calculated and the Experimental Excess Gibbs Free Energy of Mixing Values for the Binary System Propane-Carbon Dioxide

for the above mentioned isotherms. The values obtained are also listed in Tables (A.10) to (A.12). A comparison is shown in Figures (4.10) and (4.11) for the two binary systems.

The calculated values are satisfying the isothermal, isobaric Gibbs-Duhem equation and the final results in terms of G^E can clearly reflect the quality of the experimental data. For the system, ethane-carbon dioxide, the agreement between the calculated G^E values in the two different manners is better at the lower temperatures. For the system, propane-carbon dioxide, and the ternary system, propane-ethane carbon dioxide, the agreement between the calculated γ and G^E values from the experimental and predicted values at the two isothermal conditions investigated are fairly good.

However, as it was pointed out by Lu and Polak[68], the agreement in the values of the excess Gibbs free energy G^E between different investigators for the same system is better if G^E values have been calculated from T-P-x data rather than T-P-x-y data. The discrepancy may reflect a difference in y values up to 0.02 in mole fraction due to the less accurate vapor-phase composition measurement obtained from recirculation still. Hence, this calculation can serve as an indication of the quality of data.

4.3 Generalization and Correlation of Ω_a and Ω_b

It appears that there is no generalized correlation available for the temperature dependence of the two parameters Ω_a and Ω_b of the Redlich-Kwong equation of state with the equal fugacity criterion considered in their evaluation for the purpose of calculating vapor-liquid equilibrium data. The need of a correlation, especially a generalized one, for the two

parameters can not be over-emphasized. In the absence of such a correlation, values of the two parameters would have to be determined from the saturation properties whenever a temperature is specified. Furthermore, the required saturation properties for the evaluation may not be available at the specified temperature conditions.

The values of the parameters obtained in Section (4.2.1) were first of all correlated in terms of T_r for all the pure components investigated individually in the following two ranges of temperature:

$$0.85 \leq T_r \leq 1.0$$

$$T_{r(min)} \leq T_r \leq 0.85$$

The subscript (min) represents the lowest temperature investigated as reported in Table (A.13). In the temperature range $T_r = 0.85$ to 1.0, the two parameters were fitted by means of Equations (4.59) and (4.60).

$$\Omega_a = a_0 + a_1 (1 - T_r) + a_2 (1 - T_r)^{\frac{1}{3}} + a_3 (1 - T_r)^{\frac{2}{3}} \qquad (4.59)$$

$$\Omega_b = c_0 + c_1 (1 - T_r) + c_2 (1 - T_r)^{\frac{1}{3}} + c_3 (1 - T_r)^{\frac{2}{3}} \qquad (4.60)$$

In the lower temperature range ($T_{r(min)} \leq T_r \leq 0.85$), the two parameters were fitted by a different temperature function as shown in Equations (4.61) and (4.62).

$$\Omega_a = \sum_{i=0}^{2} b_i T_r^i \qquad (4.61)$$

$$\Omega_b = \sum_{i=0}^{2} d_i T_r^i \qquad (4.62)$$

The coefficients a_i, b_i, c_i and d_i were determined using the method of least-squares and are given in Table

(A.13) for the thirteen pure components investigated. The values of Ω_a and Ω_b from Equations (4.59) to (4.62), ($\Omega_{comp.}$), are compared with those obtained from the saturated properties ($\Omega_{calc.}$) in terms of δ as defined by the following expression:

$$\delta = \left| \frac{\Omega_{calc.} - \Omega_{comp.}}{\Omega_{calc.}} \right| \cdot 100\% \qquad (4.63)$$

Both the maximum and the average deviations for the thirteen compounds are reported in Table (A.14). The overall deviations are summarized as follows:

Temperature range	δ in Ω_a		δ in Ω_b	
	Max.	Avg.	Max.	Avg.
$T_{r(min)} \leq T_r \leq 0.85$	0.1491	0.0605	0.1054	0.0388
$0.85 \leq T_r \leq 1.0$	0.1187	0.0504	0.1482	0.0630

Furthermore, the coefficients a_i, b_i, c_i and d_i were generalized in terms of Pitzer's acentric factor ω, by the following expressions:

$$a_i = \sum_{j=0}^{2} a_{ij} \omega^j \qquad i = 0,1,2,3 \qquad (4.64)$$

$$b_i = \sum_{j=0}^{2} b_{ij} \omega^j \qquad i = 0,1,2 \qquad (4.65)$$

$$c_i = \sum_{j=0}^{2} c_{ij} \omega^j \qquad i = 0,1,2,3 \qquad (4.66)$$

$$d_i = \sum_{j=0}^{2} d_{ij} \omega^j \qquad i = 0,1,2 \qquad (4.67)$$

For the hydrocarbons, the revised values of ω reported by Passut and Danner[83] were used in the correlation. The ω values of argon and nitrogen were taken from Prausnitz[87]. The ω values of the thirteen pure components investigated cover a range of ω of 0 to 0.3942. The coefficients a_{ij}, b_{ij}, c_{ij}, and d_{ij} were evaluated using the least-squares method and are reported in Table (A.13). Similarly, the computed values of Ω_a and Ω_b from the generalized equations are compared with the calculated values of Ω_a and Ω_b obtained from the saturation properties in terms of δ as expressed by Equation (4.63). The results of the comparison are given in Table (A.15). The overall deviations are summarized as follows:

Temperature range	δ in Ω_a		δ in Ω_b	
	Max.	Avg.	Max.	Avg.
$T_{r(min)} \leq T_r \leq 0.85$	0.7000	0.4525	0.7480	0.5715
$0.85 \leq T_r \leq 1.0$	0.7746	0.3204	1.2733	0.5500

The temperature-dependence characteristics of Ω_a and Ω_b are depicted in Figure (4.12) for propane using the proposed Equations (4.59) to (4.62) and (4.64) to (4.67).

It should be mentioned that other combinations of the fitting equations were investigated. For example, the polynomial equations, as expressed in Equations (4.61) to (4.62) were used for representing Ω_a and Ω_b in two ranges of temperature (e.g., $T_{r(min)} \leq T_r \leq 0.85$, $0.80 \leq T_r \leq 1.00$) with the coefficients subsequently represented by the generalized equations, (Equations (4.64) to (4.67)). It was found that the representation is unfortunately restricted to $T_r \leq 0.97$. Much larger δ values were obtained at higher T_r values. Another drawback of this combination is that the parameters at the critical point cannot be accurately predicted. If the upper temperature range was taken to be $T_r = 0.80$

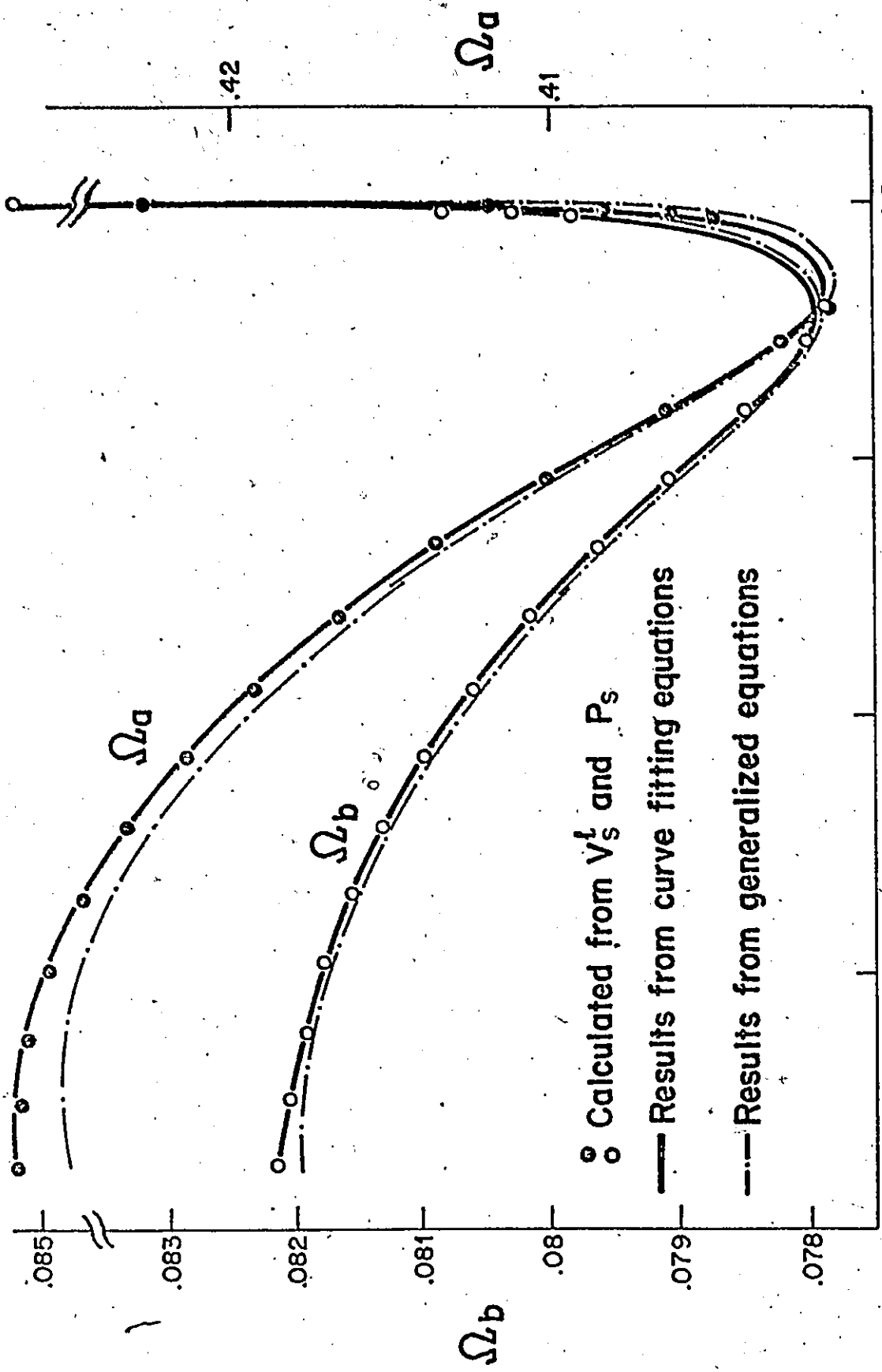


FIG. 4.12 Temperature Dependence Characteristics of Ω_a and Ω_b of Propane

to 0.97 the δ values in Ω_a and Ω_b are 0.3002 and 0.4982 respectively. These deviations are somewhat lower than those obtained by the proposed equations.

Another approach investigated was to use one function such as that shown in Equations (4.59) and (4.60) to represent the two parameters over the whole temperature range ($T_{r(min)} \leq T_r \leq 1.0$) with the coefficients subsequently generalized by means of Equations (4.64) and (4.66). The δ values in Ω_a and Ω_b obtained by this approach are 0.5182 and 0.5954 respectively. Although these values are not significantly different from those obtained from the proposed combination, the deviations are mainly contributed from those obtained at lower temperatures. This is the reason why Equations (4.61) and (4.62) are preferable for the lower temperature range ($T_{r(min)} \leq T_r \leq 0.85$).

The computer program for the evaluation of the coefficients using the method of the least-squares is given in Appendix E.

4.3.1 Applicability of the Generalized Correlation:

Accuracy of the Pure Components Parameters Ω_a and Ω_b from T_r and ω :

For testing the applicability of the generalized correlation, seven components other than those included in the generalization were selected. These components are either of different chemical nature (carbon dioxide, hydrogen sulphide, carbon tetrachloride, cyclohexane and oxygen) or having ω values greater than those covered in the generalization (n-nonane and n-decane). The values of the parameters Ω_a and Ω_b computed from the generalized correlation at arbitrarily selected temperatures are compared with those obtained from saturation properties and shown in Table (A.16) in terms of

δ . The overall average δ values are 0.55% and 0.87% respectively for Ω_a and Ω_b. With the exception of one point (n-decane at $T_r = 0.503$), the maximum deviations are less than 1% and 2% for Ω_a and Ω_b respectively.

Saturated Molar Liquid Volume:

In order to evaluate the effect of the deviation in Ω_a and Ω_b values caused by the generalization on the prediction of saturated molal volume of liquids, n-hexane was selected for the testing purpose. The calculated V_ℓ^s values obtained at different temperatures with different deviations in Ω_a and Ω_b values are compared in Table (A.17) with the literature values in terms of δ by an expression similar to Equation (4.63). The results indicated that the δ in V_ℓ^s of n-hexane is 0.5% when the relative errors in both Ω_a and Ω_b are +0.5%, while for the relative error of -0.5% and +0.5% in Ω_a and Ω_b respectively δ is 0.69% at 32°F. These levels of errors are similar to those obtained from the generalized correlation for Ω_a and Ω_b (Equations (4.59) to (4.62) and (4.63) to (4.67)).

Calculation of Vapor-Liquid Equilibrium

The applicability of the generalized correlation to vapor-liquid equilibrium calculation is of the utmost importance as far as this investigation is concerned. For this reason, isothermal vapor-liquid equilibria have been predicted for the systems experimentally investigated in this work. The vapor-liquid equilibrium for the system ethane-carbon dioxide at 60°F by Robinson and Kalra[93] was also used for the purpose of comparison. Furthermore, the isothermal vapor-liquid equilibria have been predicted for five arbitrarily selected binary systems containing methane, ethane, propane, butane, carbon monoxide and carbon dioxide at 26 isothermal conditions. The generalized correlation permits the computation of Ω_a and Ω_b with only the knowledge of ω and T_c of the pure

components concerned. In the prediction of vapor-liquid equilibria data, the same mixing rules given by Equations (4.38) to (4.46) were employed. Values of the binary interaction constants k_{ij}, which is involved in the mixing rule, were taken from the literature. The calculation results for the three systems measured experimentally in these investigations are given in Tables (A.4), (A.5) and (A.9). The calculated P and y values were comparable to those obtained with the parameters Ω_a and Ω_b evaluated from the saturation properties as shown in the following summary:

R-K Parameters evaluated from	$\lvert\Delta P/P\rvert$ % Avg.		$\lvert\Delta y\rvert$ Avg.		No. of Points	
	Binary	Ternary	Binary	Ternary	Binary	Ternary
Saturated properties	1.36	2.77	0.0167	0.0071	61	48
Generalized equations	1.96	2.97	0.0176	0.0108	61	48

The overall average absolute deviation in y for the total of 197 data points, other than these measured experimentally in this work, is 0.0034 mole fraction. The same average absolute deviation was obtained when the parameters Ω_a and Ω_b were calculated from the saturation properties. The calculation results are summarized in Table (4.5).

For the carbon dioxide-hydrocarbon systems given in Table (4.4), the overall absolute average deviation of the vapor composition y is 0.0176 mole fraction and that of P is 1.96%. In particular, the magnitude of the deviation in the calculated vapor composition is, y , as small as the results obtained by means of the Redlich-Kwong equation with the modified procedure[54].

TABLE 4.4

SUMMARY OF THE CALCULATED VAPOR-LIQUID EQUILIBRIA DATA

FOR THE SYSTEMS INVESTIGATED EXPERIMENTALLY IN THIS WORK

T°F	R-K Parameters Evaluated from Saturated Properties			R-K Parameters Computed from Generalized Equations			k_{ij}		
	$\lvert\Delta P\rvert_{Psia}$	$\lvert\Delta P/P\rvert_{Avg}$ %	$\lvert\Delta y\rvert_{Avg}$	$\lvert\Delta P\rvert$	$\lvert\Delta P/P\rvert_{Avg}$ %	$\lvert\Delta y\rvert_{Avg}$			
			ETHANE-CARBON DIOXIDE						
60	11.38	2.01	0.0229	9.56	1.25	0.0232	0.098		
20	3.38	0.80	0.0272	2.98	0.71	0.0270	0.102		
-20	2.24	0.92	0.0153	2.69	1.06	0.0184	0.101		
-60	0.71	0.54	0.0213	3.77	2.96	0.0233	0.108		
			PROPANE-CARBON DIOXIDE						
20	5.0	2.02	0.0069	4.91	2.24	0.0061	0.102		
-20	3.01	2.26	0.0062	3.25	3.24	0.0077	0.099		
			PROPANE-ETHANE-CARBON DIOXIDE				k_{12}	k_{13}	k_{23}
20	9.13	2.68	0.0066	9.26	2.75	0.0101	0.0	0.102	0.102
-20	4.98	2.92	0.0079	5.66	3.22	0.0120	0.0	0.101	0.099

TABLE 4.5

SUMMARY OF THE CALCULATED VAPOR-LIQUID EQUILIBRIA DATA FOR SYSTEMS OTHER THAN THOSE INVESTIGATED EXPERIMENTALLY IN THIS WORK

	R-K parameters evaluated from saturated properties			R-K parameters computed from generalized equations			
T K	$\lvert\Delta P\rvert_{psia}$	$\lvert\Delta y\rvert_{Avg.}$	k_{12}	$\lvert\Delta P\rvert_{psia}$	$\lvert\Delta y\rvert_{Avg.}$	k_{12}*	Ref.
			METHANE - NITROGEN				
95.00	0.13	0.0021	0.024	0.50	0.0037	0.025	81
100.00	0.28	0.0032	0.024	0.39	0.0036	0.025	81
105.00	0.31	0.0040	0.024	0.84	0.0039	0.025	81
110.00	0.58	0.0046	0.024	0.89	0.0041	0.025	81
113.71	0.91	0.0065	0.028	2.00	0.0045	0.025	108
115.00	0.68	0.0049	0.026	1.85	0.0041	0.025	81
120.00	1.09	0.0065	0.027	2.76	0.0049	0.025	81
122.04	1.38	0.0066	0.023	3.70	0.0063	0.025	124
			METHANE - ETHANE				
130.37	0.25	0.0004	0.011	0.59	0.0005	0.005	120
144.26	0.24	0.0009	0.009	1.24	0.0018	0.005	120
158.15	1.13	0.0031	0.005	2.61	0.0048	0.005	120
172.04	1.12	0.0030	0.006	2.56	0.0041	0.005	120
186.11	1.95	0.0045	0.006	4.16	0.0033	0.005	120
189.65	1.97	0.0048	-0.001	6.17	0.0044	0.005	120
			METHANE - PROPANE				
130.37	0.44	0.0000	0.018	3.91	0.0000	0.020	119
144.26	1.18	0.0000	0.024	2.82	0.0001	0.020	119
158.15	1.07	0.0002	0.028	2.05	0.0003	0.020	119
172.04	1.54	0.0007	0.025	4.02	0.0010	0.020	119
187.54	3.47	0.0014	0.019	6.02	0.0017	0.020	119
			METHANE - N-BUTANE				
144.26	0.44	0.0000	0.029	7.18	0.0000	0.027	32
155.38	1.67	0.0000	0.032	9.12	0.0001	0.027	32
166.50	2.58	0.0001	0.030	11.47	0.0001	0.027	32
177.62	3.96	0.0002	0.030	9.87	0.0002	0.027	32
189.06	9.49	0.0004	0.022	5.85	0.0006	0.027	32

(continued)

TABLE 4.5

(continued)

SUMMARY OF THE CALCULATED VAPOR-LIQUID EQUILIBRIA DATA FOR SYSTEMS OTHER THAN THOSE INVESTIGATED EXPERIMENTALLY IN THIS WORK

	R-K parameters evaluated from saturated properties			R-K parameters computed from generalized equations			
T K	$\lvert\Delta P\rvert_{psia}$	$\lvert\Delta y\rvert_{Avg.}$	k_{12}	$\lvert\Delta P\rvert_{psia}$	$\lvert\Delta y\rvert_{Avg.}$	k_{12}*	Ref.
			METHANE - CARBON MONOXIDE				
122.04	2.95	0.0200	0.029	3.02	0.0192	0.028	110
130.37	3.73	0.0150	0.027	3.55	0.0108	0.028	110
			ETHANE - CARBON DIOXIDE				
288.71	26.60	0.0066	0.088	21.39	0.0090	0.088	93
Overall average deviation		0.0034			0.0034		

* Values of the binary interaction constant were taken from Kato et al. (1975) and k_{12} for Ethane-Carbon Dioxide were obtained from VLE by the minimization of $\Sigma|P^{calc.} - P^{exp.}|$ using the Redlich-Kwong equation[17].

4.4 Clausius Equation of State:

The equation originally proposed by Clausius[22,82] is of the following form:

$$P = \frac{RT}{V-b} - \frac{a}{T(V+c)^2} \tag{4.68}$$

where

$$a = \frac{27}{64}\frac{R^2T_c^3}{P_c} = \frac{\Omega_a R^2T_c^3}{P_c} \tag{4.69}$$

$$b = \frac{1}{4} V_c \left(4 - \frac{RT_c}{P_cV_c}\right) = \Omega_b V_c (4-s) \tag{4.70}$$

$$c = \frac{1}{8} V_c \left(\frac{3RT_c}{P_cV_c} - 8\right) = \Omega_c V_c (3s-8) \tag{4.71}$$

$$s = \frac{1}{Z_c}$$

Equation (4.68) could be rearranged as follows:

$$Z = \frac{1}{1-h} - \left(\frac{A^2}{C}\right)\left(\frac{H}{(1+H)^2}\right) \tag{4.72}$$

or

$$Z = \frac{1}{1-h} - \left(\frac{A^2}{B}\right)\left(\frac{h}{(1+H)^2}\right) \tag{4.73}$$

where

$$h = \frac{b}{V} = \frac{BP}{Z} \tag{4.74}$$

$$H = \frac{c}{V} = \frac{CP}{Z} \tag{4.75}$$

$$A^2 = \frac{a}{R^2T^3} \tag{4.75a}$$

$$B = \frac{b}{RT} \tag{4.76}$$

$$C = \frac{c}{RT} \tag{4.77}$$

The values of Ω_a, Ω_b and Ω_c were obtained originally from (4.68) by setting the first and second partial

derivatives of pressure with respect to volume equal to zero at the critical point (as given by Equation (4.1) and (4.2)). When the Clausius equation of state is applied to a mixture, the following mixing rules were used[33]

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{4.78}$$

$$b = \sum_i x_i b_i \tag{4.79}$$

$$c = \sum_i x_i c_i \tag{4.80}$$

where

$$a_{ij} = \Omega_{a_{ij}} R^2 T_{c_{ij}}{}^3 / P_{c_{ij}} \tag{4.81}$$

The quantities $\Omega_{a_{ij}}$, $T_{c_{ij}}$, $P_{c_{ij}}$, $V_{c_{ij}}$, $Z_{c_{ij}}$ and ω_{ij} involved in the mixing rules are defined with expressions identical to those given by Equations (4.41) to (4.48).

To follow up with the work of Elshayal and Lu[33] it was believed that the inadequacy of such an equation for calculation of heat of mixing may be due to the sensitivity of the equation where the heat of mixing, as shown by the expression in Appendix D, is a result of subtracting two large quantities, so any small error can lead to a large error in the heat of mixing. The main sources of error could be the inadequacy of the mixing rules for the mixture properties and erroneous derivatives of the parameters.

In addition, in the Berthelot equation[102], $(P + \frac{a}{TV^2})(V-b) = RT$, the introduction of the temperature in the cohesive pressure term offers no advantage over the van der Waals equation of state, while the Clausius equation has a certain improvement due to the introduction of the constant C. In applying the modified procedure of Elshayal and Lu[33] negative values for Ω_c were obtained[44] which means that a linear transformation of the volume coordinates to the right rather than to the left. This may be due to the quality

of the saturated vapor volume values available in the literature. The uncertainty was also reflected in the numerical values of the parameters obtained. Also, an erratic trend in the calculated results was observed by Zudkevitch and Joffe[129] whenever the condition of $Z_v^{calc.} = Z_v^{exp.}$ together with the equality of fugacity in both phases were satisfied using the Redlich-Kwong with the modified procedure[128]. This may be attributed to the inaccuracy of saturated vapor volume data. Therefore, it was always recommended to satisfy the condition of the equality of the calculated liquid volume at saturation with the experimental one plus the condition of equal fugacity in both liquid and vapor phases[11,93,129].

This work arose from all the above mentioned difficulties aiming at investigating the proper variation of the parameters of the Clausius equation of state, minimizing the required reliable information to establish these parameters and by-passing the unreliable saturated vapor volume data so as to modify this three-parameter equation, where the parameter c is responsible for the linear transformation of the volume coordinate, which can be suitably applied to calculate the the thermodynamic properties.

Consequently, the parameter Ω_c was assigned a constant value given by the original equation ($\Omega_c = 0.125$) and treating the other two parameters Ω_a and Ω_b as temperature dependent. The data required to calculate these two adjustable parameters Ω_a and Ω_b are the vapor pressures and the saturated liquid densities. The Clausius equation of state with this modified procedure was applied satisfactorily for the calculations of volumes and heats of mixing[44]. The new proposed method will be further investigated for the purpose of vapor-liquid equilibrium calculations.

4.4.1 Evaluation of the Parameters Ω_a, Ω_b and Ω_c

The primary information required for the evaluation is the saturated liquid densities and vapor pressures of the pure

components. The value of Ω_c is 0.125 as given by equation (4.71).

At equilibrium

$$\phi_{iv} = \phi_{il} \qquad \text{as given by} \quad (4.47)$$

on re-writing the Clausius equation as in the forms given by Equation (4.72) to (4.77). The quantities ϕ_{il} and ϕ_{iv} for pure component, i, were obtained from the following equations:

$$\ln \phi_{il} = \frac{h_l}{1-h_l} - \ln Z_l - \ln(1-h_l) - \left(\frac{A^2}{B}\right) h_l \left[\frac{2 + h_l}{(1 + H_l)^2}\right] \qquad (4.82)$$

$$\ln \phi_{iv} = \frac{h_v}{1-h_v} - \ln Z_v - \ln(1-h_v) - \left(\frac{A^2}{B}\right) h_v \left[\frac{2 + H_v}{(1 + H_v)^2}\right] \qquad (4.82a)$$

Combining Equation (4.82), (4.47) and the Clausius equation of state (Equations (4.73) to (4.77)), one obtains:

$$\ln \phi_{iv} Z_l = \left(\frac{h_l}{1-h_l}\right) + \ln(1-h_l) + \left[\frac{1}{(1-h_l)} - Z_l\right] (2+H_l) \qquad (4.83)$$

These quantities were used to evaluate Ω_a and Ω_b. The calculation procedure contains one iteration loop and is outlined as follows:

1. Assume initial values of Ω_a, Ω_b (e.g., the values at the critical points, 0.422 and 0.250 respectively which are given by Equations (4.69) to (4.71).

2. For a given value of Z_l (experimental) and assumed values of ϕ_{iv}, calculate h_l by means of Equation (4.83).

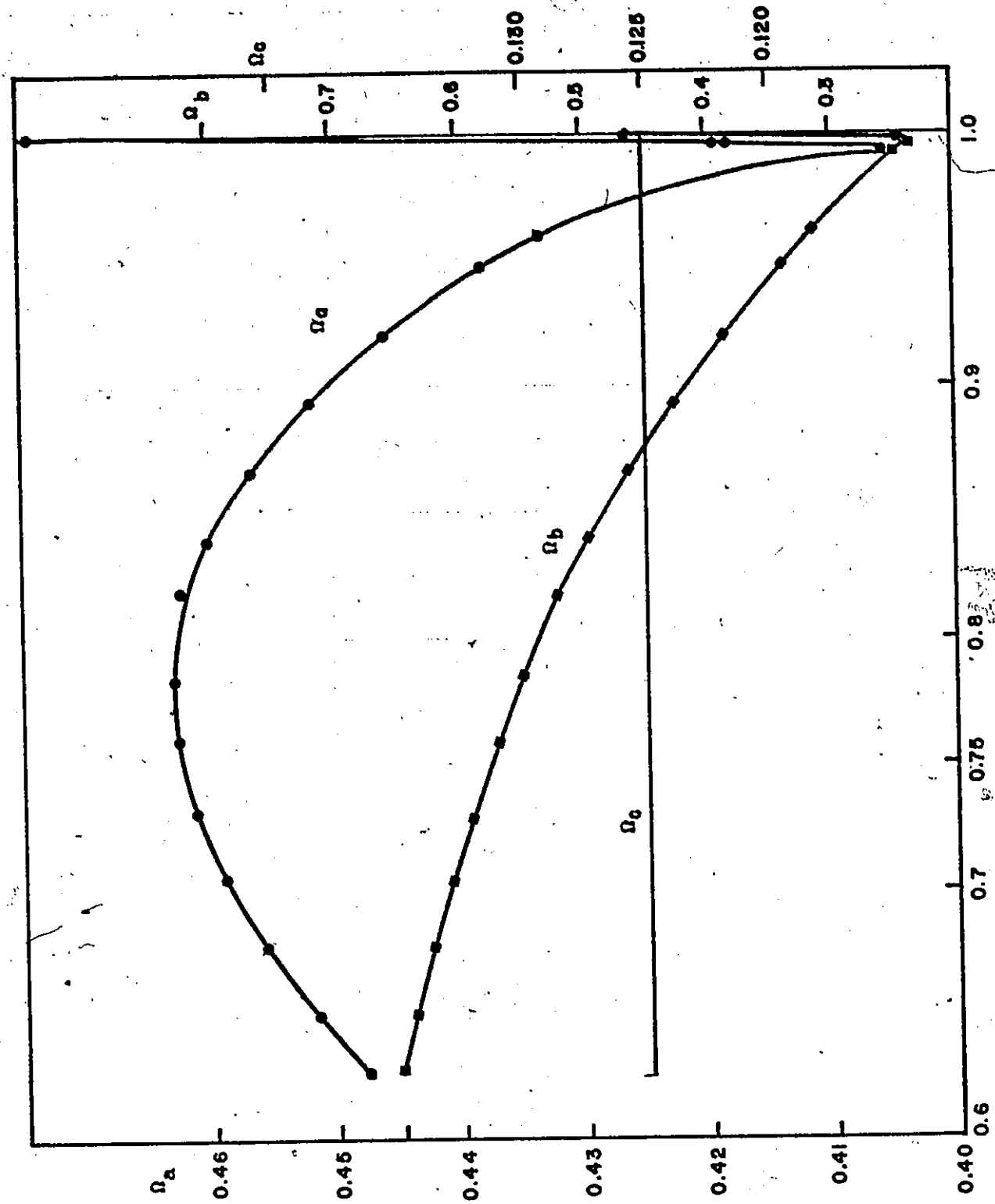


FIG. 4.13 Temperature Dependence Characteristics of Ω_a, Ω_b and Ω_c of Propane

3. Calculate B from Equation (4.74) and A^2 from (4.73).

4. Substitute the new values of A^2 and B into Equation (4.73) and (4.74) and solve simultaneously for another set of roots Z_v and h_v.

5. Calculate ϕ_{iv} from Equation (4.82) using the new set of Z_v and h_v.

6. Obtain new values for h_ℓ from Equation (4.83) and compare it with that from Step 2. If they disagree, repeat the calculation starting from Step 2. An iteration loop is thus built until the change in the h_ℓ value is less than the specified tolerance. The tolerance used in this investigation is 0.00005.

The computer program is given in Appendix E.

4.4.2 Application of the Clausius Equation of State to Phase Equilibrium Calculations

Using the Clausius equation of state and following the same procedure given in Section (4.1.1), the fugacity coefficients of component i in a multi-component mixture may be expressed as follows:

$$\ln \hat{\phi}_i = \ln\left(\frac{V}{V-b}\right) - \frac{b_i}{V-b} - \frac{2\sum_j x_i a_{ij}}{RT^2(V+c)^2} + \frac{ac_i}{RT^2(V+c)^2} - \ln Z \tag{4.84}$$

or

$$\ln \hat{\phi}_i = \ln\left(\frac{1}{1-h}\right) - \ln Z + \frac{b_i}{b}\left(\frac{h}{1-h}\right) - \left(\frac{A^2}{C}\right)\left(\frac{H}{1+H}\right)$$

$$\left[\frac{2\sum_j x_i a_{ij}}{a} - \left(\frac{H}{1+H}\right)(c_i/c)\right] \tag{4.85}$$

In deriving the equation, the mixing rules given by Equations (4.78) to (4.81) and Equations (4.41) to (4.46) together with the following two expressions

$$c = \sum_i x_i c_i = \frac{1}{n} \sum_i n_i c_i \tag{4.86}$$

$$c_i = \left(\frac{\partial nc}{\partial n_i}\right)_{n_j} \tag{4.87}$$

are required to extend the pure components parameters to mixture.

In addition, when the Clausius equation of state was employed to evaluate the partial molal volume following the same procedure shown in Section (4.1.4), the following expression was obtained.

$$\bar{V}_i = \frac{\frac{RT}{V-b}\left(1+\frac{b_i}{V-b}\right) - 2\,\frac{\sum_j x_j a_{ij} - ac_i/(V+c)}{T(V+c)^2}}{\frac{RT}{(V-b)^2} - \frac{2a}{T(V+c)^3}} \tag{4.88}$$

where V is the liquid molar volume of the mixture. These supporting properties $\hat{\phi}_i$ and $\bar{V}_i$ are needed for the calculation of vapor-liquid equilibrium using the same procedure as outlined in Section (4.1.2). The specified tolerance in P used in the work is $|\Delta P/P| = 0.0001$. The specified tolerance in y is $|\Delta y| = 0.0001$. A computer program to perform the calculation is given in Appendix E.

4.4.3 Results and Discussion

The Clausius equation of state with the proposed modified procedure was used for the determination of the system pressure, P, and the equilibrium vapor composition, y, with the system temperature and liquid composition, x, specified. The saturation properties; liquid molar volumes and vapor pressures, available in the literature for propane[12,25] ethane[12,29] and carbon dioxide[29,29] were employed in

evaluating the temperature-dependent parameters Ω_a and Ω_b. The value of Ω_c was chosen to be 0.125. The same procedure was used to evaluate Ω_a and Ω_b, at the critical point. The critical volume and critical pressure were treated as the saturated volume and vapor pressure of the component. The temperature-dependent characteristics of Ω_a and Ω_b are depicted for propane in Figure (4.13). The calculated values of the parameters are listed in Table (A.1.1). Isothermal vapor-liquid equilibria have been predicted for the two binary and the ternary systems experimentally determined in this investigation. The predicted P and y values are also listed in Tables (A.4), (A.5) and (A.9). The overall average absolute deviation for the total of 102 data points selected from the experimentally determined data points, in P is 1.89% and in y is 0.0117 mole fraction compared to 1.98% and 0.0118 mole fraction when the Redlich-Kwong equation with the modified procedure was employed. Furthermore, the vapor-liquid equilibrium data for the system ethane-carbon dioxide at eight isothermal conditions were also used for the purpose of comparison.

A summary of the calculation results using the Redlich-Kwong equation and the Clausius equation both with the modified procedures is given in Tables (4.6) and (4.7). The comparison covered 186 data points, including the experimentally determined ones, on fourteen isothermal conditions. The overall average absolute deviation in P is 1.34% and in y is 0.0096 mole fraction for the Clausius equation compared to 1.40% and 0.0106 mole fraction for the Redlich-Kwong equation. In the application of the mixing rules, Equations (4.78) to (4.81) and (4.41) to (4.46) which are identical to those reported by Chueh and Prausnitz and were used in Section (4.2.2), the binary interaction constants k_{ij}, are required.

They were determined in the same manner as described with the Redlich-Kwong. The calculated k_{ij} values as listed in Tables (4.6) and (4.7) appear to follow the same pattern as that in the Redlich-Kwong equation.

In addition, it was rather difficult to obtain a convergent solution for the system pressures and vapor phase mole fractions with the assumed initial values for the pressure and the binary interaction constant at the higher temperatures.

ETHANE-CARBON DIOXIDE

The established values of Ω_a, Ω_b and Ω_c of Table (A.1.1) at the isothermal conditions were used in the calculation. The predicted P and y values are listed in Table (A.4) and compared with the experimental data in Figure (4.14). A summary of the comparison is given in Table (4.6). The results, as presented, are better than those obtained using the Redlich-Kwong equation. The overall average absolute deviation between the experimental and the calculated P values is 0.64% and in y is 0.0094 mole fraction compared to 0.74% and 0.0218 mole fraction respectively when the Redlich-Kwong equation was used. Furthermore, the data on this system reported by Fredenslund and Mollerup[38] and Gugnoni et al.[41] were used for the purpose of comparison. The predicted P and y values are also listed in Tables (A.7) and (A.8) and also compared with the experimental data in Figures (4.15) and (4.16). The average absolute deviation between the experimental and the calculated P values is 0.66%. The average absolute deviation in y for the reported data by Fredenslund and Mollerup[38] is 0.0051 mole fraction compared to 0.0083 mole fraction when the Redlich-Kwong equation was used for the prediction.

It should be borne in mind, however, that these differences between the deviations obtained using the two equations are within the experimental error. Due to the fact that a meaningful convergent solution is difficult to obtain at temperatures near the critical point of the constituent pure components, the comparison was not done using the isotherms at 50°F[41] and 60°F[93].

TABLE 4.6

SUMMARY OF THE CALCULATED RESULTS FOR VLE FOR THE SYSTEMS MEASURED IN THIS WORK USING EQUATIONS* OF STATE WITH MODIFIED PROCEDURES

ETHANE - CARBON DIOXIDE

Temp. °F	k_{ij}	$\lvert\Delta p/p\rvert_{Avg.}$ %	$\lvert\Delta y\rvert_{Avg.}$	No. of Data Points
-60	0.092	0.35	0.0183	12
	0.108	0.54	0.0213	
-20	0.086	0.89	0.0076	9
	0.101	0.92	0.0153	
20	0.090	0.74	0.0213	12
	0.102	0.80	0.0272	

PROPANE - CARBON DIOXIDE

-20	0.086	2.64	0.0067	10
	0.099	2.26	0.0062	
20	0.093	2.06	0.0122	11
	0.102	2.02	0.0069	

PROPANE - ETHANE - CARBON DIOXIDE

	k_{12}	k_{13}	k_{23}			
20	0.0	0.090	0.093	2.52	0.0090	30
	0.0	0.102	0.102	2.68	0.0066	
-20	0.0	0.086	0.086	2.59	0.0100	18
	0.0	0.101	0.099	2.92	0.0079	

	$\lvert\Delta p/p\rvert$ % Avg		$\lvert\Delta y\rvert$ Avg		No. of Points	
	Binary	Ternary	Binary	Ternary	B	T
Clausius	1.30	2.55	0.0138	0.0094	54	48
RK	1.28	2.77	0.0159	0.0071	54	48

* The first line for each isotherm is the calculation results using the Clausius equation with the modified procedure, while the second line is the calculation results using the Redlich-Kwong equation with the modified procedure.

TABLE 4.7

SUMMARY OF THE CALCULATED RESULTS FOR VAPOR-LIQUID EQUILIBRIUM USING EQUATIONS* OF STATE WITH MODIFIED PROCEDURES

ETHANE - CARBON DIOXIDE

Temp.K	k_{ij}	$\lvert\Delta p/p\rvert_{Avg.}$%	$\lvert\Delta y\rvert_{Avg.}$	No. of Data Points	Ref.
241.45 (-25°F)	0.084 0.097	0.77 0.91		9	41
255.35 (0°F)	0.085 0.098	0.77 0.82		15	41
269.25 (25°F)	0.088 0.097	0.47 0.46		13	38
223.15	0.085 0.099	0.80 1.01	0.0067 0.0089	11	38
243.15	0.084 0.098	0.70 0.72	0.0047 0.0068	12	38
263.15	0.087 0.099	0.66 0.74	0.0039 0.0096	11	38
283.15	0.083 0.101	0.56 0.35	0.0052 0.0082	13	38

* The first line for each one of the isotherms is the calculation results using the Clausius equation with the modified procedure, while the second line is the calculation results using the Redlich-Kwong equation with the modified procedure.

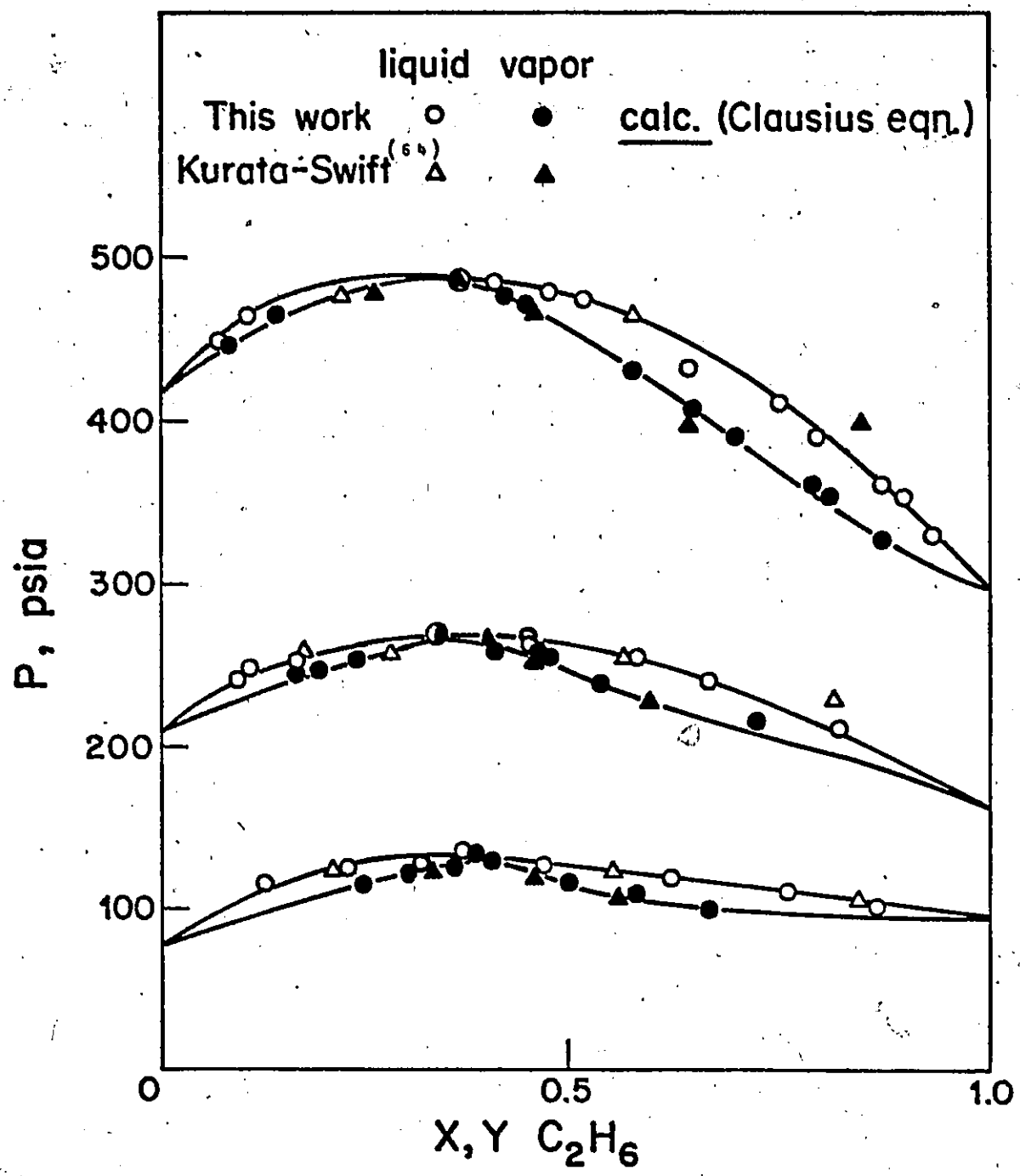


FIG. 4.14 Comparison of the Calculated and Experimental P-x-y Values for the Binary System Ethane-Carbon Dioxide

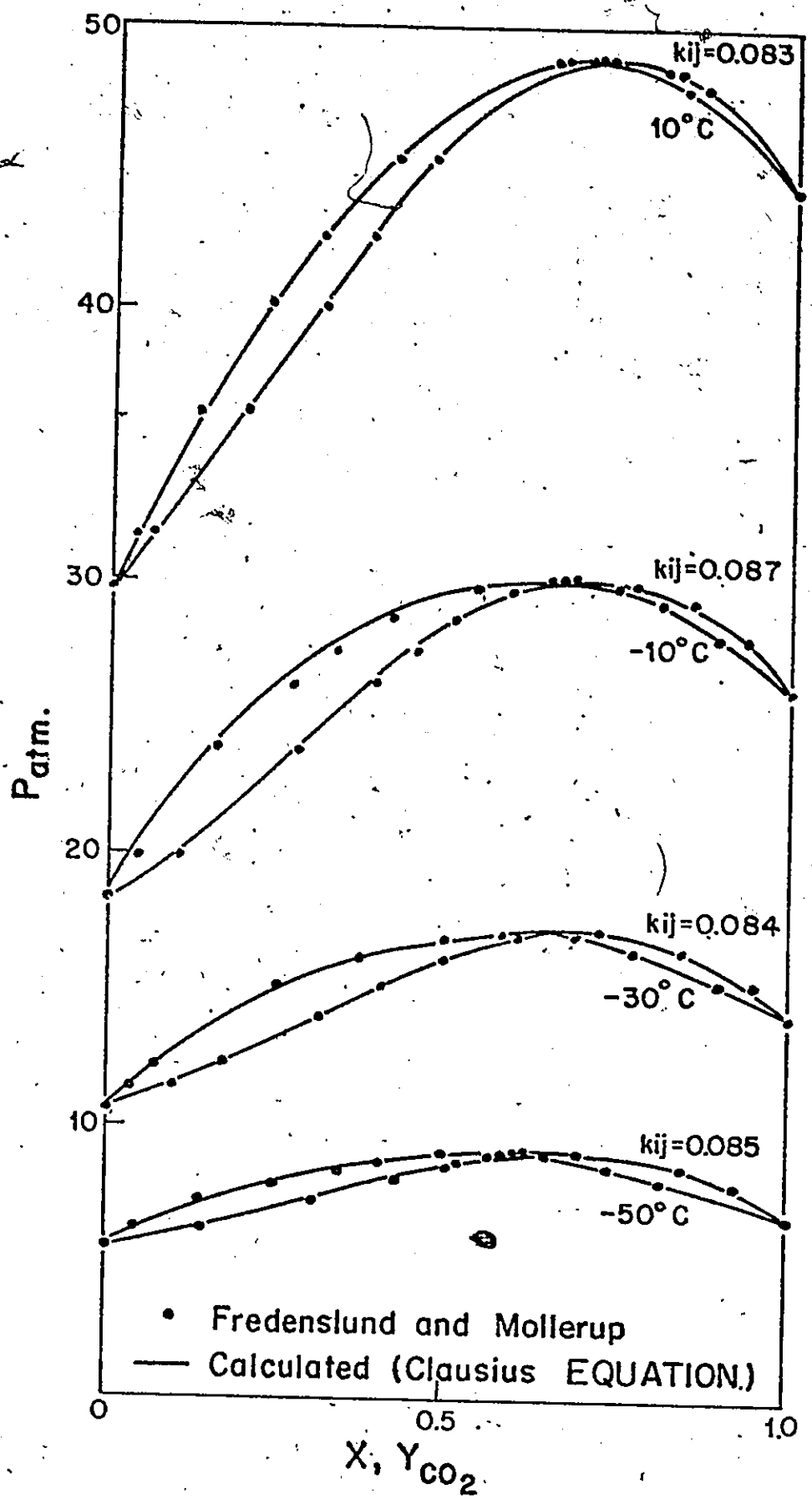


FIG. 4.15 Comparison of the Calculated and Experimental P-x-y Values for the Binary System Carbon Dioxide - Ethane

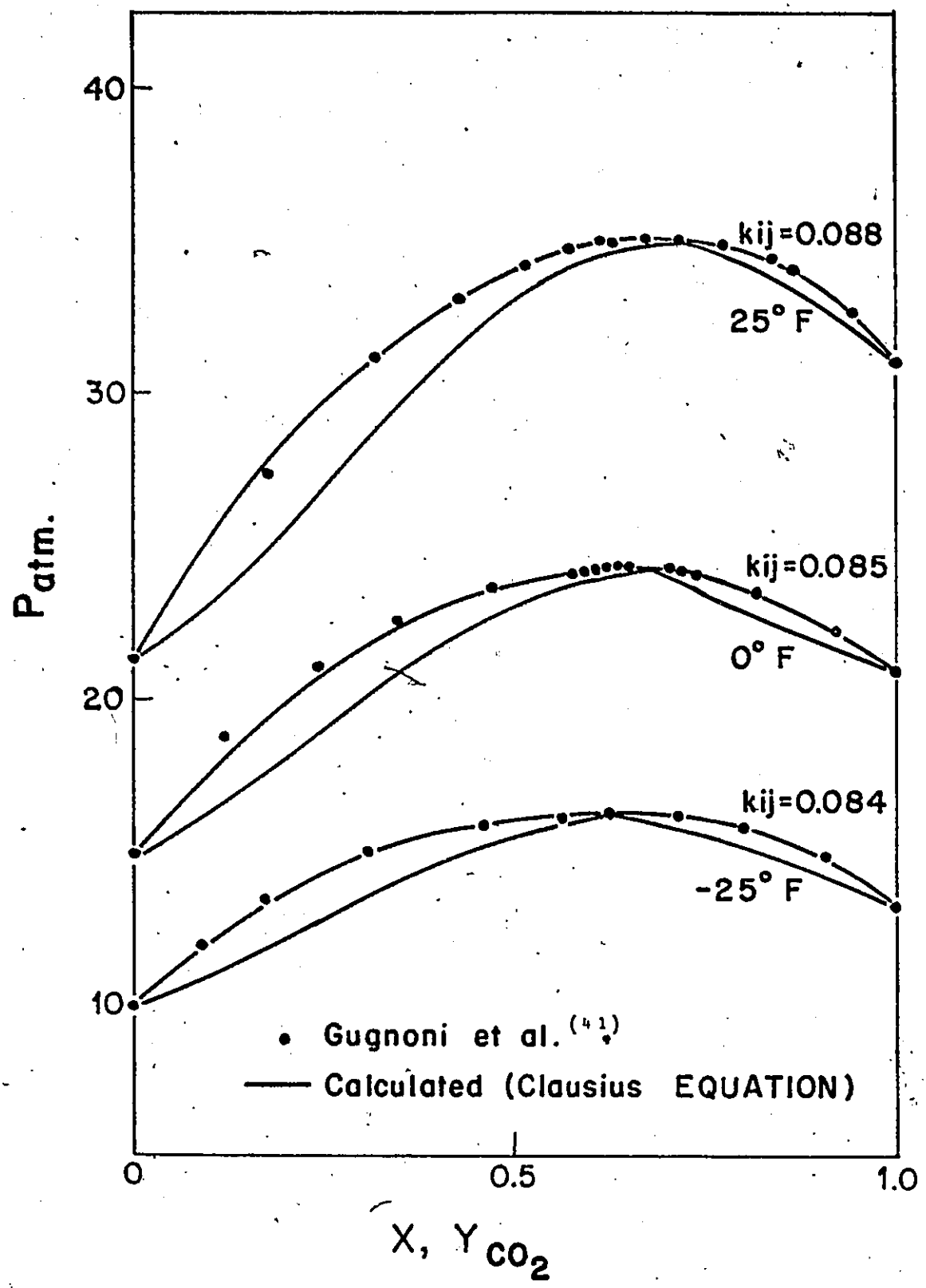


FIG. 4.16 Comparison of the Calculated and the Experimental P-x-y Values for the Binary System Carbon Dioxide-Ethane

PROPANE-CARBON DIOXIDE

A good agreement was obtained between the calculated and experimental values of phase equilibrium for the system propane-carbon dioxide at -20° and 20°F. The predicted P and y values are also listed in Table (A.5) and compared with the experimental data in Figure (4.17). A summary of the comparison is given also in Table (4.5). The results are comparable to those obtained using the Redlich-Kwong equation with the modified procedure[54]. The overall average absolute deviation between the calculated and experimental P values is 2.34% and in y is 0.0096 mole fraction compared to 2.45% and 0.0066 mole fraction when the Redlich-Kwong equation was used.

PROPANE-ETHANE-CARBON DIOXIDE

The predicted P and y values are also listed in Table (A.9) and are compared with the experimental data. In the calculation procedure, the values of the binary interaction constant k_{ij} for the systems ethane-carbon dioxide and propane-carbon dioxide obtained by the minimization of the quantity $\Sigma|P^{calc.} - P^{exp.}|$ were employed in the calculation. The value of k_{12} representing the interaction between propane and ethane were taken to be zero. A summary of the calculation results is given in Table (A.9). The results are comparable to those obtained using the Redlich-Kwong equation with the modified procedure. The average absolute deviation between the calculated and experimental P values is 2.55% and in y is 0.0094 mole fraction compared to 2.77% and 0.0071 mole fraction for the Redlich-Kwong equation with the modified procedure[54] as shown in Table (4.6).

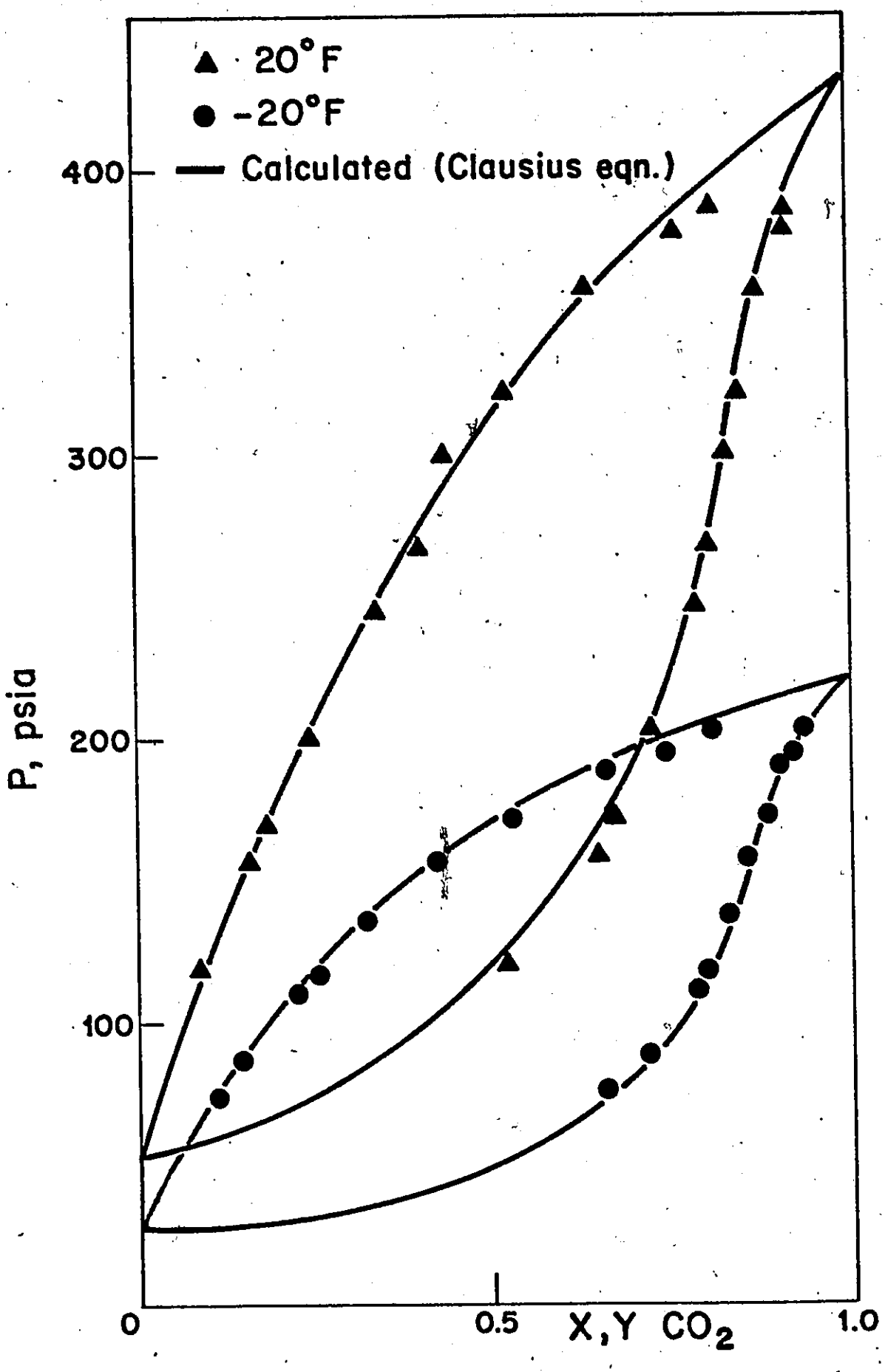


FIG. 4.17 Comparison of the Calculated and the Experimental P-x-y Values for the Binary System Propane-Carbon Dioxide

4.5 GENERAL DISCUSSION ON THE USE OF THE EQUATIONS OF STATE WITH MODIFIED PROCEDURES

The two simple equations of states, the Redlich-Kwong and the Clausius equations were adopted for the calculation of thermodynamic properties with modified procedures. For pure components calculations, a small loss of accuracy is offset by the ease of implementation, speed of calculation and that the required information to establish the parameters of the equation is minimal. The two equations are attractive for mixture calculations because of the ease of the introduction of the binary interaction constants.

Although, as stated before, there are three conditions to satisfy at equilibrium and an equation of state should have at least three parameters, the two-parameter Redlich-Kwong equation satisfying only two conditions has been widely used for the prediction of thermodynamic properties. One of the problems of satisfying the three conditions at equilibrium is the uncertainty of the saturated vapor volume. Hence, the Clausius equation of state was used with only two-parameters temperature dependent.

The amount of the required information to establish the temperature-dependent parameters is the same, i.e., the pure components vapor pressures and molar liquid volume at saturation.

Basically, this approach in treating the parameters of the Clausius equation was adopted to avoid the negative values for the parameters Ω_c which, otherwise, would be obtained if unreliable values of the saturated vapor volume was employed in the evaluation.

The reliability of the saturated vapor volume is not of great concern in vapor-liquid equilibria for the purpose of the determination of the three parameters of the Clausius equation since it was applied successfully by Elshayal

TABLE 4.8

COMPARISON OF THE EXPERIMENTAL AND CALCULATED COMPRESSIBILITY FACTORS OF PURE HEPTANE USING DIFFERENT EQUATIONS OF STATE

T K	P_{bars}	Z_{exp}	$Z_{calc.}$		$\lvert\Delta Z/Z\rvert$ x 100%	
			Clausius Equation	Redlich-Kwong Equation	Clausius Equation	Redlich-Kwong Equation
303.16	50	0.29213	0.28697	0.29178	1.77	0.12
	100	0.58032	0.56067	0.57904	3.39	0.22
	200	1.14650	1.08159	1.14296	5.67	0.31
	300	1.70116	1.57920	1.69612	7.17	0.30
	500	2.78260	2.53287	2.78000	8.97	0.09
	1000	5.36767	4.79992	5.41436	10.5	0.87
	2000	10.21710	9.15812	10.54256	10.37	3.18
	3000	14.79750	13.43800	15.59678	9.19	5.40
	5000	23.45430	21.92816	25.62304	6.51	9.25
323.16	50	0.28070	0.27343	0.27900	2.59	0.60
	100	0.55700	0.53159	0.55288	4.56	0.74
	200	1.09844	1.01868	1.08865	7.26	0.89
	300	1.62305	1.48080	1.61262	8.76	0.65
	500	2.65642	2.36172	2.63657	11.09	0.75
	1000	5.10780	4.44472	5.11772	12.98	0.19
	2000	9.69216	8.45071	9.93710	12.98	2.53
	3000	14.01255	12.34778	14.58215	11.88	4.06
	5000	22.16677	20.10572	24.09182	9.30	8.68
373.16	50	0.25996	0.24773	0.25866	4.70	0.50
	100	0.51366	0.47310	0.50914	7.90	0.88
	200	1.00654	0.88646	0.99319	11.93	1.33
	300	1.48440	1.27056	1.46179	14.41	1.52
	500	2.40700	1.99157	2.36997	17.26	1.54
	1000	4.58614	3.67100	4.55220	19.95	0.74
	2000	8.62856	6.85660	8.76854	20.54	1.62
	3000	12.42070	9.96760	12.90880	19.75	3.93
	5000	19.55180	16.12629	21.11479	17.52	7.99
423.16	50	0.24868	0.22769	0.24592	8.44	1.11
	100	0.48734	0.42193	0.47865	13.43	1.78
	200	0.94011	0.76448	0.92063	18.68	2.12
	300	1.38351	1.07443	1.34319	22.34	2.91
	500	2.22371	1.64509	2.15488	26.02	3.10
	1000	4.18946	2.94870	4.08924	29.62	2.39
	2000	7.80662	5.38731	7.80942	31.00	0.04
	3000	11.18376	7.75540	11.45178	30.65	2.40
	5000	17.51210	12.43027	18.66873	29.02	6.60
473.16	50	0.24746	0.20960	0.24173	15.29	2.32
	100	0.47635	0.36798	0.46042	22.75	3.34
	200	0.90641	0.63288	0.86598	30.18	4.46
	300	1.31393	0.86409	1.24831	34.24	4.99
	500	2.08726	1.27787	1.97627	38.78	5.32
	1000	3.88068	2.19365	3.69800	43.47	4.71
	2000	7.15634	3.86386	6.99160	46.02	2.30
	3000	10.20212	5.46622	10.21537	46.42	0.13
	5000	15.89450	8.61189	16.59320	45.82	4.40

and Lu[33] but it has an adverse affect on the evaluation of the derivatives of Ω_a, Ω_b and Ω_c with temperature. This leads to erroneous results for the heat of mixing calculations.

As far as vapor-liquid equilibrium is concerned, the two equations with the modified procedures produced satisfactory and comparable results. It is rather surprising that the Clausius equation of state, while admittedly less accurate for PVT calculations, yielded better results than the Redlich-Kwong equation with the modified procedure for the system ethane-carbon dioxide.

In addition, the Clausius equation still has a third parameter responsible for the linear shift of the volume coordinate as indicated by Martin[71].

A comparison of the two equations with the modified procedures for the purpose of calculating compressibilities of pure liquid heptane is shown in Table (4.8). These results indicate the superiority of the Redlich-Kwong equation with the proposed modified procedure over the Clausius equation with only two parameters temperature dependent.

Presuming that both equations can be applied to calculate the compressibility factors of saturated liquids, as shown in Table (4.8), a shift of the isotherm has been carried too far to the left using the Clausius equation compared to the Redlich-Kwong equation both with the modified procedures. In other words, a further modification to the Clausius equation would be by adjusting the cohesive pressure term $\frac{a}{T(V+c)^2}$.

The k_{ij} values obtained in this work using the two equations substantiate the dependence of k_{ij} with temperature. However, no definite trend was observed in both equations which makes it rather difficult to establish k_{ij} as a function of temperature.

However, the validity of the method of Hsi and Lu[26] has been confirmed for the system ethane-carbon dioxide. It has been shown that the experimental results obtained in Chapter III are somewhat better than those reported by

Kurata and Swift[64] at the same temperatures.

Finally, the generalized correlation for Ω_a and Ω_b of the Redlich-Kwong equation introduced a different method for the evaluation of these parameters from T_r and ω in the absence of the experimental saturation properties. These generalized correlations were used in this work for the prediction of vapor-liquid equilibrium for systems containing carbon dioxide which were not included in the generalization.

CHAPTER 5

SUMMARY AND CONCLUSIONS

The experimental results as presented in this work provided more data points for the binary system ethane-carbon dioxide at four isothermal conditions (-60°, -20°, 20°, 60°F). Good agreement is obtained between the calculated and experimental values at the three lower temperatures, -60°, -20° and 20°F using the Redlich-Kwong equation. In the application of the Redlich-Kwong equation, the proposed modified procedure previously proposed by Chang and Lu[17] has been adopted throughout this work. It appears that the experimental results obtained at these temperatures are somewhat better than those reported by Kurata and Swift[64] at the same temperature.

Experimental vapor-liquid equilibria data of the system propane-carbon dioxide at two isothermal conditions of -20° and 20°F extended the range of the available data over the whole concentration range below -4.4°F. It was found also that isothermal data at -20° and 20°F follow a trend with the high temperature data in the literature[99].

The experimentally determined vapor-liquid equilibria for the system propane-ethane-carbon dioxide at -20° and 20°F provided a new set of data to the literature. A forced recirculation type equipment was employed and a total of 109 data points were collected.

The prediction by means of the Redlich-Kwong Equation of state yielded results that compared favourably with the experimental data. The equation was also used to predict vapor - liquid equilibria for the binary system ethane-carbon dioxide and propane-carbon dioxide at isothermal conditions other than those investigated in this work.

In the prediction of the binary data, only pure component parameters, binary interaction constants and mixing rules are needed. The calculated results were satisfactory

and showed that the use of an average k_{ij}, over the range investigated, did not introduce a large deviation compared to the optimum values of k_{ij} determined by the minimization of the quantity

$$\Sigma \left| P^{calc.} - P^{exp.} \right|$$

For the ternary system, propane-ethane-carbon dioxide, only the binary data are required and the binary interaction constants for mixtures of ethane and propane can be taken to be zero without affecting the calculated results.

In addition, a generalized correlation was established for the temperature dependence of the parameters Ω_a and Ω_b of the Redlich-Kwong equation of state in terms of T_r and the acentric factor ω in the subcritical region. The expressions are simple, adequate and lend themselves easily to computer evaluation. They can be used, for example, in Harmen's[46] programme for the evaluation of liquid compressibility and vapor-liquid equilibria. The acentric factors cover a range up to 0.4902. They produce favourable results over the range of study and satisfy the critical point.

The Clausius equation of state with the proposed modified procedure was used for the calculation of the vapor-liquid equilibria in the binary and ternary systems. The results obtained were comparable to those obtained from the Redlich-Kwong equation. The comparison included 186 data points for systems ethane-carbon dioxide, propane-carbon dioxide, and propane-ethane-carbon dioxide at 14 isothermal conditions. The most important conclusion is that an equation of state can reproduce precisely the saturation properties but this does not necessitate an equally good prediction of the enthalpy of mixing[103]. Moreover, the fact that the Redlich-Kwong equation produces more accurate pure component PVT data than the Clausius equation does not necessary ensure that the former will represent vapor-liquid equilibrium data better than the latter. Both equations satisfy the equal fugacity between the liquid and vapor phases as well as the experimental V_ℓ.

Our experience indicates that in order to improve the quality of the prediction methods by means of an equation of state, the parameters should be evaluated, whenever possible, using the saturation properties which are reported, together with the vapor-liquid equilibrium data. Improvement may also be directed towards finding the proper variations of k_{ij} with temperatures which may be expressed in terms of the pure molecular properties rather than from the experimental data.

In addition, attention should be directed towards the analytical method for the calculation of the total pressure to ensure the convergence of the solution. The extension of the adjustable parameter of the pure components to mixture via the available mixing rules should be investigated thoroughly to see if there is any inter-relationship between the equation of state as represented by $f(P,V,T) = 0$ and the mixing rules.

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A P P E N D I X A

TABLES OF CALCULATION

RESULTS FOR CHAPTER 4

TABLE A.1

VALUES OF Ω_a and Ω_b OF THE REDLICH-KWONG EQUATION

Component	TK	Ω_a	Ω_b	Reference
Ethane	293.15	0.39331	0.07600	38
	288.70(60°F)	0.39799	0.07701	12,29
	283.15	0.39957	0.07732	38
	283.15(50°F)	0.40688	0.07934	41
	269.25(25°F)	0.40824	0.07942	41
	266.48(20°F)	0.40517	0.07865	12,29
	263.15	0.40651	0.07893	38
	255.35(0°F)	0.41764	0.08168	41
	244.26(-20°F)	0.41275	0.08044	12,29
	243.15	0.41243	0.08047	38
	241.45(-25°F)	0.41939	0.08223	41
	223.15	0.41597	0.08164	38
	222.04(-60°F)	0.41600	0.08160	12,29
Propane	294.26(70°F)	0.41947	0.08055	99
	277.59(40°F)	0.42230	0.08111	99
	266.48(20°F)	0.42522	0.08164	12,25
	244.26(-20°F)	0.42671	0.08201	12,25
Carbon Dioxide	294.26(70°F)	0.39778	0.07702	99
	293.15	0.40111	0.07744	38
	288.70(60°F)	0.40180	0.07727	29
	283.15(50°F)	0.40527	0.07763	41
	277.59(40°F)	0.40754	0.07779	99
	269.25(25°F)	0.41145	0.07830	41
	266.48(20°F)	0.41363	0.07862	29
	263.15	0.41616	0.07896	38
	255.35(0°F)	0.41966	0.07928	41
	244.26(-20°F)	0.42349	0.07973	29
	243.15	0.42469	0.07987	38
	241.45(-25°F)	0.42627	0.08003	41
	223.15	0.43159	0.08042	38
	222.04(-60°F)	0.43176	0.08063	29
Heptane	303.15	0.446456	0.075946	127
	323.15	0.445634	0.076201	127
	373.15	0.438349	0.076424	127
	423.15	0.426966	0.076165	127
	473.15	0.411183	0.075206	127

TABLE A.1.1

VALUES OF Ω_a and Ω_b OF THE CLAUSIUS EQUATION OF STATE*

COMPONENT	TK	Ω_a	Ω_b
ETHANE	283.15	0.43587	0.32518
	269.25	0.44415	0.36965
	266.48	0.44114	0.36832
	263.15	0.44134	0.37713
	255.35	0.44747	0.41357
	244.26	0.44223	0.42373
	243.15	0.44148	0.42558
	241.45	0.44536	0.44211
	233.15	0.43712	0.46492
	224.04	0.43687	0.46628
PROPANE	231.10	0.44734	0.64779
	240.00	0.45159	0.63586
	244.26	0.45344	0.63005
	250.00	0.45564	0.62127
	260.00	0.45878	0.60502
	266.48	0.46034	0.59369
	270.00	0.46094	0.58681
	280.00	0.46217	0.56653
	290.00	0.46235	0.54379
	300.00	0.46146	0.51831
	310.00	0.45948	0.48985
	320.00	0.45630	0.45802
	330.00	0.45168	0.42209
	340.00	0.44558	0.38160
	350.00	0.43780	0.33597
	360.00	0.43328	0.31128
	368.00	0.40539	0.19263
	368.50	0.41837	0.23766
	369.00	0.41921	0.24003
	369.82	0.47457	0.45174
CARBON DIOXIDE	283.15	0.44648	0.37764
	269.25	0.46339	0.46172
	266.48	0.46482	0.47457
	263.15	0.46704	0.48996
	255.35	0.47036	0.52057
	244.26	0.47325	0.55969
	243.15	0.47434	0.56485
	241.45	0.47579	0.57204
	233.15	0.47742	0.62330
	222.04	0.48066	0.62965
HEPTANE	473.15	0.48932	0.95958
	423.15	0.51408	1.28266
	373.15	0.52431	1.49387
	323.15	0.52068	1.63218
	303.15	0.51433	1.67656

* $\Omega_c = 0.125$

TABLE A.2

LITERATURE SOURCES OF THE SATURATION PROPERTIES USED IN THE DEVELOPMENT OF THE GENERALIZED CORRELATION

Component	V^{ℓ}	P
Argon	29,75	29,75
Methane	39	89
Nitrogen	125	125
Ethylene	12	12
Ethane	35	35
Propane	25	25
Propylene	35	35
n-Butane	35	35
Benzene	35	35
n-Pentane	35	35
n-Hexane	35	35
n-Heptane	127	127
n-Octane	127	127
n-Nonane	99	99
n-Decane	99	99

TABLE A.3

(REDLICH-KWONG EQUATION)

VALUES OF Ω_a AND Ω_b CALCULATED FROM THE SATURATED PROPERTIES

T_r	Ω_a	Ω_b
	ARGON	
0.55535	0.40304	0.08776
0.57862	0.40652	0.08784
0.62594	0.41047	0.08734
0.65756	0.41162	0.08675
0.70244	0.41367	0.08617
0.73565	0.41525	0.08583
0.79643	0.41732	0.08505
0.80306	0.41699	0.08489
0.80969	0.41661	0.08472
0.81632	0.41617	0.08453
0.82295	0.41576	0.08436
0.82958	0.41530	0.08417
0.83621	0.41486	0.08398
0.84283	0.41448	0.08381
0.84946	0.41400	0.08362
0.85609	0.41353	0.08343
0.86272	0.41301	0.08323
0.86935	0.41249	0.08302
0.87598	0.41206	0.08285
0.88261	0.41160	0.08266
0.88923	0.41114	0.08247
0.89586	0.41067	0.08228
0.90249	0.41023	0.08210
0.90912	0.40971	0.08190
0.91575	0.40935	0.08174
0.92238	0.40890	0.08155
0.92901	0.40851	0.08138
0.93564	0.40822	0.08124
0.94889	0.40790	0.08103
0.95552	0.40779	0.08094
0.96215	0.40777	0.08087
0.96878	0.40785	0.08083
0.97541	0.40841	0.08093
0.98204	0.40957	0.08121
0.98866	0.41105	0.08157
0.99529	0.41563	0.08286
0.99861	0.42056	0.08428
1.00000	0.42557	0.08577

T_r	Ω_a	Ω_b
	METHANE	
0.49861	0.39263	0.08653
0.52485	0.39671	0.08646
0.55109	0.40028	0.08636
0.57734	0.40337	0.08622
0.58222	0.40390	0.08619
0.59681	0.40537	0.08610
0.60358	0.40600	0.08605
0.62982	0.40818	0.08583
0.64053	0.40895	0.08573
0.68425	0.41136	0.08525
0.75715	0.41293	0.08416
0.81551	0.41212	0.08302
0.83005	0.41165	0.08270
0.87388	0.40963	0.08165
0.90295	0.40787	0.08092
0.93224	0.40595	0.08021
0.97680	0.40473	0.07978
0.98431	0.40558	0.08005
0.99228	0.40798	0.08079
0.99538	0.40999	0.08140
1.00000	0.42376	0.08552

T_r	Ω_a	Ω_b
	NITROGEN	
0.50040	0.41025	0.08732
0.52211	0.41365	0.08747
0.54208	0.41641	0.08759
0.56981	0.41795	0.08728
0.58994	0.41910	0.08712
0.61292	0.42040	0.08698
0.66403	0.42210	0.08653
0.69762	0.42251	0.08614
0.74556	0.42218	0.08545
0.78130	0.42202	0.08501
0.82274	0.42002	0.08419
0.87615	0.41646	0.08278
0.91759	0.41208	0.08147
1.00000	0.42477	0.08583

(continued)

TABLE A.3
(continued - 2)

VALUES OF Ω_a AND Ω_b CALCULATED FROM THE SATURATED PROPERTIES

T_r	Ω_a	Ω_b
ETHYLENE		
0.60012	0.41514	0.08339
0.60929	0.41485	0.08325
0.62896	0.41643	0.08328
0.64864	0.41788	0.08325
0.66831	0.41802	0.08319
0.68799	0.41730	0.08300
0.70766	0.41613	0.08272
0.72734	0.41543	0.08245
0.74701	0.41648	0.08229
0.76669	0.41634	0.08200
0.78636	0.41660	0.08173
0.84539	0.41400	0.08093
0.86507	0.41287	0.08056
0.88474	0.41018	0.08001
0.90442	0.40782	0.07950
0.92409	0.40561	0.07907
0.94377	0.40298	0.07859
0.96344	0.40077	0.07820
1.00000	0.42211	0.08503

T_r	Ω_a	Ω_b
PROPANE		
0.62491	0.42683	0.08214
0.64896	0.42674	0.08205
0.67600	0.42645	0.08192
0.70304	0.42581	0.08176
0.73008	0.42473	0.08155
0.75713	0.42331	0.08128
0.78417	0.42146	0.08095
0.81121	0.41919	0.08056
0.83825	0.41655	0.08011
0.86529	0.41356	0.07962
0.89233	0.41013	0.07906
0.91937	0.40644	0.07848
0.94641	0.40281	0.07798
0.95993	0.40134	0.07786
0.99508	0.40494	0.07981
0.99643	0.40630	0.08025
0.99778	0.40836	0.08089
0.99913	0.41190	0.08197
1.00000	0.42282	0.08524

T_r	Ω_a	Ω_b
ETHANE		
0.65484	0.41883	0.08301
0.68758	0.41922	0.08276
0.72032	0.41902	0.08246
0.75306	0.41824	0.08208
0.78580	0.41708	0.08168
0.81854	0.41531	0.08119
0.85129	0.41298	0.08063
0.88403	0.41010	0.07998
0.91677	0.40669	0.07928
0.94951	0.40322	0.07866
0.95606	0.40264	0.07858
0.96916	0.40181	0.07853
0.97571	0.40177	0.07861
0.99208	0.40534	0.07993
0.99535	0.40756	0.08065
0.99699	0.41018	0.08145
0.99862	0.41373	0.08253
1.00000	0.42350	0.08544

T_r	Ω_a	Ω_b
PROPYLENE		
0.61808	0.42451	0.08212
0.62395	0.42490	0.08219
0.63919	0.42531	0.08218
0.65442	0.42541	0.08215
0.66965	0.42538	0.08209
0.68488	0.42544	0.08206
0.70011	0.42551	0.08203
0.71534	0.42514	0.08192
0.73057	0.42444	0.08179
0.74580	0.42389	0.08165
0.76103	0.42315	0.08151
0.77626	0.42221	0.08134
0.79149	0.42107	0.08113
0.80672	0.41967	0.08087
0.82195	0.41811	0.08059
0.85241	0.41464	0.07994
0.86765	0.41308	0.07968
0.88288	0.41109	0.07931
0.89811	0.41019	0.07926
0.91334	0.40919	0.07919
0.92857	0.40797	0.07910
0.94380	0.40631	0.07890
0.95903	0.40358	0.07843
1.00000	0.42184	0.08495

(continued)

TABLE A.3
(continued - 3)

VALUES OF Ω_a AND Ω_b CALCULATED FROM THE SATURATED PROPERTIES

T_r	Ω_a	Ω_b
n - BUTANE		
0.64126	0.43245	0.08100
0.65289	0.43262	0.08102
0.66596	0.43201	0.08098
0.67902	0.43168	0.08094
0.69209	0.43113	0.08088
0.70516	0.43043	0.08080
0.71822	0.42957	0.08070
0.73129	0.42913	0.08062
0.74436	0.42757	0.08048
0.75742	0.42636	0.08033
0.77049	0.42504	0.08017
0.78355	0.42371	0.08001
0.79662	0.42205	0.07978
0.80969	0.42006	0.07947
0.82275	0.41805	0.07916
0.84889	0.41507	0.07881
0.86195	0.41381	0.07870
0.87502	0.41200	0.07846
0.88809	0.41007	0.07816
0.90115	0.40795	0.07786
0.91422	0.40569	0.07756
0.92729	0.40438	0.07751
0.94035	0.40309	0.07749
0.99262	0.40694	0.08033
1.00000	0.42149	0.08484

T_r	Ω_a	Ω_b
BENZENE		
0.55309	0.42750	0.07915
0.56298	0.42784	0.07922
0.57286	0.42796	0.07926
0.58274	0.42816	0.07930
0.59262	0.42820	0.07935
0.60251	0.42820	0.07938
0.61239	0.42840	0.07941
0.62227	0.42841	0.07942
0.62838	0.42810	0.07941
0.63215	0.42815	0.07940
0.64204	0.42797	0.07943
0.65192	0.42766	0.07944
0.66180	0.42775	0.07945
0.67168	0.42776	0.07944
0.68157	0.42756	0.07946
0.69145	0.42729	0.07944
0.70133	0.42679	0.07938
0.71121	0.42640	0.07936
0.72110	0.42542	0.07929
0.73098	0.42445	0.07919
0.74086	0.42396	0.07918
0.75074	0.42353	0.07915
0.76063	0.42341	0.07912
0.77051	0.42213	0.07900
0.78039	0.42130	0.07892
0.79027	0.42077	0.07887
0.80016	0.41978	0.07876
0.81004	0.41865	0.07865
0.81992	0.41729	0.07849
0.82980	0.41630	0.07837
0.83969	0.41558	0.07829
0.84957	0.41450	0.07814
0.85945	0.41314	0.07801
0.86933	0.41153	0.07785
0.87922	0.41021	0.07768
0.88910	0.40897	0.07755
0.89898	0.40742	0.07738
0.90886	0.40603	0.07724
0.91875	0.40462	0.07711
0.92863	0.40258	0.07685
0.93851	0.40105	0.07674
0.94839	0.39962	0.07666
0.95828	0.39791	0.07651
1.00000	0.42101	0.08470

(continued)

TABLE A.3
(continued - 4)

VALUES OF Ω_a AND Ω_b CALCULATED FROM THE SATURATED PROPERTIES

T_r	Ω_a	Ω_b	T_r	Ω_a	Ω_b
n - PENTANE			n - HEXANE		
0.65841	0.43547	0.07933	0.53830	0.44070	0.07719
0.66204	0.43562	0.07940	0.54706	0.44082	0.07726
0.67387	0.43544	0.07946	0.55801	0.44112	0.07738
0.68570	0.43506	0.07951	0.56896	0.44081	0.07739
0.69753	0.43473	0.07957	0.57991	0.44069	0.07745
0.70936	0.43390	0.07954	0.59086	0.44055	0.07751
0.72119	0.43289	0.07947	0.60180	0.44042	0.07759
0.73302	0.43194	0.07943	0.61275	0.44013	0.07764
0.74485	0.43076	0.07935	0.62370	0.43953	0.07764
0.75667	0.42969	0.07929	0.63465	0.43907	0.07767
0.76850	0.42821	0.07916	0.64560	0.43845	0.07768
0.78033	0.42675	0.07902	0.65655	0.43821	0.07778
0.79216	0.42542	0.07892	0.66750	0.43779	0.07785
0.80399	0.42377	0.07875	0.67844	0.43587	0.07761
0.81582	0.42200	0.07856	0.68939	0.43496	0.07760
0.82765	0.42048	0.07844	0.70034	0.43403	0.07758
0.83948	0.41874	0.07827	0.71129	0.43265	0.07750
0.85131	0.41669	0.07802	0.72224	0.43159	0.07746
0.86314	0.41432	0.07772	0.73319	0.43071	0.07744
0.87497	0.41210	0.07744	0.76603	0.42726	0.07729
0.88680	0.41010	0.07723	0.77698	0.42549	0.07714
0.89862	0.40789	0.07697	0.78793	0.42432	0.07707
0.91045	0.40557	0.07670	0.79888	0.42314	0.07701
0.92228	0.40323	0.07643	0.80983	0.42106	0.07685
0.93411	0.40140	0.07628	0.82077	0.41941	0.07671
0.94594	0.40005	0.07630	0.83172	0.41770	0.07657
0.95777	0.39831	0.07622	0.84267	0.41580	0.07641
1.00000	0.41887	0.08406	0.85362	0.41376	0.07622
			0.86457	0.41210	0.07607
			0.87552	0.41005	0.07589
			0.88646	0.40834	0.07572
			0.89741	0.40611	0.07548
			0.90836	0.40429	0.07535
			0.93026	0.40152	0.07537
			0.94121	0.39870	0.07509
			1.00000	0.41937	0.08421

(continued)

TABLE A.3
(continued - 5)

VALUES OF Ω_a AND Ω_b CALCULATED FROM THE SATURATED PROPERTIES

T_r	Ω_a	Ω_b	T_r	Ω_a	Ω_b
n - HEPTANE			n - OCTANE		
0.50559	0.44760	0.07572	0.48020	0.45256	0.07389
0.52410	0.44837	0.07593	0.49778	0.45401	0.07416
0.54261	0.44806	0.07610	0.56810	0.45363	0.07492
0.56112	0.44797	0.07626	0.58568	0.45257	0.07506
0.57963	0.44779	0.07640	0.60326	0.45124	0.07517
0.59814	0.44712	0.07651	0.62084	0.44950	0.07527
0.61665	0.44631	0.07661	0.67358	0.44446	0.07549
0.63516	0.44502	0.07668	0.69116	0.44269	0.07553
0.65367	0.44350	0.07673	0.70874	0.44008	0.07555
0.67218	0.44172	0.07674	0.72632	0.43801	0.07556
0.69069	0.43982	0.07674	0.74390	0.43558	0.07552
0.70902	0.43838	0.07674	0.76148	0.43258	0.07545
0.72771	0.43607	0.07670	0.77906	0.42972	0.07536
0.74621	0.43389	0.07666	0.79664	0.42713	0.07529
0.76472	0.43094	0.07657	0.81422	0.42439	0.07519
0.78323	0.42835	0.07647	0.83180	0.42113	0.07507
0.80174	0.42512	0.07631	0.84938	0.41751	0.07488
0.82025	0.42222	0.07616	0.86696	0.41386	0.07469
0.83876	0.41916	0.07596	0.88454	0.41045	0.07457
0.85727	0.41614	0.07576	0.90212	0.40605	0.07438
0.87578	0.41254	0.07551	0.91970	0.40208	0.07419
0.89429	0.40878	0.07526	0.93728	0.39790	0.07397
0.91280	0.40504	0.07503	1.00000	0.41791	0.08378
0.93131	0.40147	0.07487			
0.94982	0.39734	0.07473			
1.00000	0.41911	0.08414			

TABLE A.4

EXPERIMENTAL AND CALCULATED RESULTS FOR THE BINARY SYSTEM
ETHANE (1) - CARBON DIOXIDE (2)

Temp. °F	EXPERIMENTAL x_1	EXPERIMENTAL y_1	EXPERIMENTAL P,psia	CALCULATED(RK) P,psia	CALCULATED(RK) y_1	Calculated With Ω_a and Ω_b Computed From The Generalized Eqn. P,psia	Calculated With Ω_a and Ω_b Computed From The Generalized Eqn. y_1	CALCULATED (Clausius Eqn.) P,psia	CALCULATED (Clausius Eqn.) Y_1
60	0.7845	0.7571	637.5	644.7	0.7037	646.6	0.7066		
	0.6874	0.6425	705.0	698.4	0.6090	701.0	0.6118		
	0.4880	0.4295	809.0	781.2	0.4408	784.9	0.4427		
	0.4376	0.3609	823.5	795.8	0.4005	799.4	0.4021		
	0.2609	0.2659	827.0	819.9	0.2601	822.6	0.2616		
	0.1499	0.1635	812.0	809.7	0.1672	810.7	0.1695		
	0.1617	0.1645	813.0	812.0	0.1776	813.0	0.1799		
20	0.9285	0.8784	331.5	333.7	0.8537	334.1	0.8556	330.3	0.8600
	0.8956	0.8026	355.5	350.3	0.7996	350.6	0.8018	347.2	0.8083
	0.8702	0.7864	361.5	362.3	0.7623	362.5	0.7646	359.3	0.7726
	0.8013	0.7019	392.0	391.8	0.6752	392.0	0.6774	389.3	0.6889
	0.7487	0.6500	409.0	411.3	0.6196	411.5	0.6217	409.3	0.6350
	0.6406	0.5815	433.5	444.0	0.5247	444.2	0.5262	442.9	0.5412
	0.5096	0.4527	471.0	471.1	0.4311	471.3	0.4324	471.1	0.4450
	0.4714	0.4167	476.5	476.6	0.4065	476.7	0.4077	476.8	0.4188
	0.4069	0.3589	486.0	483.4	0.3663	483.4	0.3677	483.8	0.3756
	0.3929	0.2950	483.5	484.5	0.3577	484.3	0.3593	484.9	0.3662
	0.1055	0.1369	463.5	466.8	0.1525	464.4	0.1579	462.9	0.1492
	0.0825	0.0839	448.0	460.2	0.1273	457.3	0.1325	455.7	0.1238
-20	0.0892	0.1585	240.0	245.5	0.1683	245.5	0.1803	243.8	0.1603
	0.0981	0.1685	248.0	247.3	0.1788	247.5	0.1908	245.6	0.1709
	0.1676	0.2310	253.5	256.9	0.2421	257.9	0.2531	255.5	0.2366
	0.3312	o.3309	263.0	263.6	0.3339	265.4	0.3401	263.2	0.3366
	0.4521	0.3989	261.5	261.2	0.3910	263.4	0.3947	260.8	0.3988
	0.4541	0.4051	261.0	261.1	0.3920	263.3	0.3956	260.7	0.3998
	0.5749	0.4689	257.0	253.1	0.4563	255.6	0.4585	252.6	0.4676
	0.6631	0.5394	240.5	243.1	0.5141	245.6	0.5158	245.5	0.5266
	0.8256	0.7124	216.0	212.9	0.6677	215.3	0.6689	212.3	0.6787
-60	0.8703	0.6624	101.6	101.6	0.6893	103.6	0.6862	101.8	0.6946
	0.7622	0.5881	115.2	114.5	0.5646	117.1	0.5606	114.6	0.5725
	0.6203	0.5000	123.4	123.7	0.4714	126.7	0.4672	123.7	0.4803
	0.4672	0.4317	127.2	127.4	0.4126	130.8	0.4095	127.3	0.4198
	0.4637	0.4520	127.2	127.4	0.4116	130.8	0.4085	127.3	0.4197
	0.4023	0.4015	127.6	127.8	0.3942	131.1	0.3922	127.6	0.3997
	0.3726	0.3880	127.6	127.8	0.3863	131.1	0.3849	127.6	0.3909
	0.3661	0.3805	127.6	127.7	0.3847	131.1	0.3834	127.6	0.3890
	0.3307	0.3623	126.4	127.2	0.3754	130.9	0.3750	127.3	0.3783
	0.2975	0.3552	126.2	127.2	0.3664	130.7	0.3670	126.9	0.3678
	0.2253	0.3080	124.0	125.8	0.3431	129.4	0.3464	125.2	0.3405
	0.1197	0.2344	117.8	119.8	0.2798	123.5	0.2884	118.6	0.2701

TABLE A.5

EXPERIMENTAL AND CALCULATED RESULTS FOR THE BINARY SYSTEM

PROPANE (1) - CARBON DIOXIDE (2)

Temp. °F	EXPERIMENTAL			CALCULATED (RK)		Calculated With Ω_a and Ω_b Computed From the Generalized Eqn.		CALCULATED (Clausius Eqn.)	
	x_1	y_1	P,psia	P,psia	y_1	P,psia	y_1	P,psia	y_1
20	0.9114	0.4793	117.0	112.3	0.4941	110.4	0.5054	111.9	0.0577
	0.8380	0.3601	155.0	155.2	0.3509	151.7	0.3602	154.8	0.3662
	0.8202	0.3293	168.5	165.1	0.3281	161.3	0.3369	164.7	0.3436
	0.7485	0.2747	197.5	202.5	0.2605	197.6	0.2672	202.3	0.2766
	0.6536	0.2118	241.0	246.6	0.2048	240.6	0.2093	246.6	0.2214
	0.6004	0.1921	262.0	268.5	0.1825	262.2	0.1861	268.7	0.1994
	0.5572	0.1682	294.0	285.0	0.1674	278.5	0.1703	285.3	0.1844
	0.4734	0.1477	314.5	313.6	0.1431	307.0	0.1448	314.1	0.1601
	0.3530	0.1249	351.0	348.1	0.1148	341.7	0.1152	348.8	0.1310
	0.2250	0.0843	371.0	378.7	0.0867	372.2	0.0863	379.6	0.1008
	0.1811	0.0735	388.1	379.0	0.0761	381.7	0.0755	389.0	0.0890
-20	0.8866	0.3411	73.0	69.9	0.3497	68.0	0.3626	69.4	0.3599
	0.8547	0.2867	85.0	81.1	0.2969	78.7	0.3084	80.6	0.3070
	0.7755	0.2180	109.0	106.4	0.2172	103.1	0.2255	106.0	0.2269
	0.7505	0.2055	114.0	113.6	0.2005	110.1	0.2080	113.2	0.2101
	0.6771	0.1705	133.5	132.9	0.1639	128.8	0.1696	132.7	0.1732
	0.5774	0.1420	154.3	154.4	0.1318	150.0	0.1356	154.5	0.1407
	0.4671	0.1172	168.0	172.8	0.1082	168.3	0.1105	173.2	0.1166
	0.3328	0.0933	184.5	189.0	0.0873	184.7	0.0883	189.7	0.9493
	0.2536	0.0804	190.5	196.3	0.0764	192.2	0.0767	197.2	0.0834
	0.1933	0.0684	197.0	201.3	0.0673	197.2	0.0673	202.3	0.0738

TABLE A.6

EXPERIMENTAL AND CALCULATED RESULTS FOR CARBON DIOXIDE (1) - ETHANE (2) at 60°F by ROBINSON AND KALRA[93]

EXPERIMENTAL			CALCULATED(RK) (k_{ij} = 0.088)		Calculated with Ω_a and Ω_b Computed with The Generalized Eqn.	
x_{CO_2}	y_{CO_2}	P_{psia}	P	y_1	P	y_1
0.0167	0.0334	516.0	505.0	0.0289	507.7	0.0285
0.0999	0.1515	584.5	563.0	0.1543	565.0	0.1525
0.2398	0.3023	678.5	646.2	0.3178	648.7	0.3152
0.4688	0.4908	779.0	748.3	0.5250	752.0	0.5229
0.6575	0.6606	827.5	795.6	0.6779	799.1	0.6763
0.7574	0.7547	833.5	803.5	0.7584	805.7	0.7566
0.8295	0.8182	822.0	800.0	0.8191	801.0	0.8167
0.9157	0.8996	791.5	783.3	0.9000	782.0	0.8975

TABLE A.7

EXPERIMENTAL AND CALCULATED RESULTS FOR THE BINARY SYSTEM CARBON DIOXIDE (1) - ETHANE (2) by FREDENSLUND AND MOLLERUP[38]

Temp.°K	EXPERIMENTAL x_1	EXPERIMENTAL y_1	EXPERIMENTAL P_{atm}	CALCULATED (RK) P	CALCULATED (RK) y_1	CALCULATED (CLAUSIUS EQN.) P	CALCULATED (CLAUSIUS EQN.) y_1
223.15				$k_{ij} = 0.099$		$k_{ij} = 0.087$	
	0.043	0.141	6.16	6.06	0.127	6.07	0.126
	0.136	0.314	7.27	7.11	0.306	7.13	0.302
	0.245	0.423	8.03	7.95	0.430	7.98	0.423
	0.349	0.505	8.52	8.46	0.506	8.48	0.498
	0.402	0.521	8.64	8.63	0.536	8.65	0.527
	0.493	0.569	8.83	8.81	0.576	8.83	0.569
	0.589	0.607	8.90	8.89	0.611	8.90	0.607
	0.619	0.619	8.91	8.90	0.621	8.91	0.616
	0.691	0.647	8.85	8.88	0.645	8.88	0.643
	0.847	0.738	8.44	8.55	0.719	8.50	0.724
	0.926	0.822	7.86	7.98	0.804	7.92	0.812
243.15				$k_{ij} = 0.098$		$k_{ij} = 0.084$	
	0.033	0.096	11.41	11.28	0.086	11.26	0.084
	0.071	0.177	12.28	12.09	0.168	12.08	0.163
	0.166	0.316	13.96	13.80	0.318	13.80	0.309
	0.253	0.410	15.13	15.00	0.413	15.00	0.402
	0.376	0.500	16.17	16.17	0.510	16.18	0.499
	0.504	0.573	16.85	16.87	0.585	16.89	0.576
	0.576	0.610	17.07	17.08	0.621	17.10	0.614
	0.636	0.645	17.15	17.16	0.650	17.17	0.645
	0.656	0.656	17.15	17.17	0.659	17.17	0.656
	0.723	0.691	17.07	17.12	0.692	17.12	0.692
	0.844	0.776	16.52	16.65	0.768	16.59	0.772
	0.948	0.894	15.26	15.39	0.886	15.31	0.892

continued

TABLE A.7
(continued)

EXPERIMENTAL AND CALCULATED RESULTS FOR THE BINARY SYSTEM CARBON DIOXIDE (1) - ETHANE (2) by FREDENSLUND AND MOLLERUP[38].

	EXPERIMENTAL			CALCULATED (RK)		CALCULATED (CLAUSIUS EQN.)	
Temp.°K	x_1	y_1	P_{atm}	P	y_1	P	y_1
263.15				$k_{ij} = 0.099$		$k_{ij} = 0.087$	
	0.045	0.104	19.92	19.94	0.098	19.78	0.094
	0.165	0.286	23.80	23.53	0.287	23.44	0.276
	0.273	0.397	26.26	26.02	0.404	25.97	0.390
	0.339	0.453	27.44	27.23	0.462	27.21	0.446
	0.425	0.514	28.58	28.47	0.526	28.50	0.512
	0.548	0.596	29.69	29.64	0.606	29.72	0.596
	0.654	0.666	30.11	30.11	0.670	30.18	0.665
	0.690	0.690	30.07	30.15	0.692	30.20	0.688
	0.773	0.745	29.89	29.99	0.745	29.97	0.745
	0.858	0.816	29.22	29.34	0.810	29.22	0.813
	0.937	0.900	27.87	28.01	0.895	27.79	0.898
283.15				$k_{ij} = 0.101$		$k_{ij} = 0.083$	
	0.033	0.061	31.61	31.38	0.062	31.30	0.056
	0.128	0.198	36.07	35.78	0.207	35.50	0.188
	0.234	0.315	40.15	39.94	0.330	39.55	0.304
	0.311	0.384	42.52	42.51	0.404	45.08	0.375
	0.421	0.480	45.57	45.52	0.497	45.15	0.468
	0.542	0.578	47.88	47.91	0.590	47.70	0.570
	0.655	0.666	49.10	49.15	0.674	49.10	0.666*
	0.711	0.711	49.31	49.39	0.715	49.36	0.713
	0.730	0.727	49.29	*49.39	0.730	49.37	0.729
	0.833	0.815	48.60	48.82	0.811	48.73	0.818
	0.873	0.852	47.99	48.25	0.847	48.13	0.854
	0.928	0.908	46.79	47.02	0.903	46.92	0.910
	0.961	0.947	45.78	45.97	0.943	45.90	0.948

(continued)

TABLE A.7
(continued)

EXPERIMENTAL AND CALCULATED RESULTS FOR THE BINARY SYSTEM CARBON DIOXIDE (1) - ETHANE (2) by FREDENSLUND AND MOLLERUP[36]

	EXPERIMENTAL			CALCULATED (RK)		CALCULATED* (CLAUSIUS EQN.)
Temp.°K	x_1	y_1	P	P	y_1	
293.15				$k_{ij} = 0.103$		
	0.037	0.058	39.50	39.36	0.062	
	0.119	0.159	43.88	43.85	0.177	
	0.216	0.263	48.63	48.55	0.286	
	0.313	0.341	52.03	52.61	0.379	
	0.774	0.771	62.22	61.96	0.769	
	0.822	0.812	61.52	61.58	0.810	
	0.889	0.876	60.19	60.43	0.872	
	0.961	0.952	58.07	58.22	0.945	

* A convergent solution was not obtained with the initial guesses for P and k_{ij}.

TABLE A.8

EXPERIMENTAL AND CALCULATED RESULTS FOR THE BINARY SYSTEM CARBON DIOXIDE (1) - ETHANE (2) by GUGNONI et al.[41]

	EXPERIMENTAL		CALCULATED(RK)		CALCULATED (CLAUSIUS EQN.)	
Temp.°F	x_1	P	P	y_1	P	y_1
-25(-31.7°C)			k_{ij} = 0.097		k_{ij} = 0.084	
	0.0832	11.89	11.70	0.1915	11.71	0.1869
	0.1711	13.45	13.16	0.3250	13.19	0.3170
	0.3047	14.98	14.74	0.4587	14.78	0.4483
	0.4594	15.89	15.80	0.5612	15.84	0.5516
	0.5604	16.17	16.14	0.6130	16.18	0.6056
	0.6330	16.24	16.24	0.6471	16.28	0.6420
	0.7145	16.15	16.21	0.6856	16.23	0.6839
	0.7996	15.89	15.99	0.7323	15.97	0.7346
	0.9098	14.96	15.13	0.8268	15.05	0.8335
0(-17.8°C)			k_{ij} = 0.098		k_{ij} = 0.085	
	0.1209	18.81	18.18	0.2375	18.13	0.2288
	0.2436	21.17	20.75	0.3875	20.71	0.3746
	0.3478	22.64	22.34	0.4791	22.32	0.4653
	0.4651	23.72	23.56	0.5603	23.56	0.5483
	0.5785	24.27	24.23	0.6268	24.25	0.6185
	0.5927	24.34	24.29	0.6346	24.30	0.6270
	0.6064	24.31	24.33	0.6421	24.34	0.6351
	0.6237	24.37	24.37	0.6516	24.39	0.6453
	0.6384	24.37	24.40	0.6597	24.41	0.6540
	0.6554	24.37	24.43	0.6690	24.43	0.6641
	0.7053	24.37	24.44	0.6966	24.43	0.6942
	0.7091	24.31	24.44	0.6988	24.42	0.6966
	0.7368	24.22	24.39	0.7147	24.37	0.7138
	0.8235	23.76	24.01	0.7714	23.92	0.7747
	0.9272	22.40	22.73	0.8715	22.58	0.8773

(continued)

TABLE A.8
(continued)

EXPERIMENTAL AND CALCULATED RESULTS FOR THE BINARY SYSTEM CARBON DIOXIDE (1) - ETHANE (2) by GUGNONI et al.[41]

Temp.°F	EXPERIMENTAL		CALCULATED (RK)		CALCULATED (CLAUSIUS EQN.)	
	x_1	P	P	y_1	P	y_1
25 (-3.9°C)			k_{ij} = 0.097		k_{ij} = 0.088	
	0.1656	27.51	27.16	0.2765	26.97	0.2662
	0.3188	31.35	31.05	0.4353	30.98	0.4195
	0.4229	33.20	32.45	0.5188	32.95	0.5028
	0.5125	34.27	34.13	0.5821	34.19	0.5682
	0.5762	34.75	34.72	0.6242	34.79	0.6129
	0.6211	35.02	35.00	0.6532	35.08	0.6440
	0.6284	35.05	35.04	0.6579	35.11	0.6490
	0.6713	35.18	35.19	0.6855	35.24	0.6787
	0.7183	35.19	35.24	0.7161	*35.24	0.7118
	0.7692	34.99	35.14	0.7508	35.06	0.7486
	0.8407	34.50	34.66	0.8052	34.45	0.8054
	0.8611	34.23	34.43	0.8228	34.17	0.8235
	0.9366	32.84	33.09	0.9020	32.65	0.9035
50 (10°C)			k_{ij} = 0.099		(*)	
	0.1398	36.73	36.15	0.2189		
	0.2281	36.69	39.57	0.3203		
	0.2598	41.25	40.68	0.3525		
	0.3813	45.15	44.37	0.4625		
	0.5092	47.58	47.24	0.5647		
	0.5539	48.23	47.99	0.5987		
	0.5736	48.46	48.25	0.6131		
	0.6062	48.60	48.65	0.6381		
	0.6249	48.87	48.84	0.6519		
	0.6749	49.23	49.21	0.6890		
	0.7119	49.24	49.34	0.7166		
	0.7712	49.00	49.27	0.7617		
	0.8012	48.84	49.10	0.7853		

* A convergent solution was not obtained using the initial guesses for P and k_{ij}.

TABLE A.9

EXPERIMENTAL AND CALCULATED RESULTS FOR THE TERNARY SYSTEM

PROPANE (1) - ETHANE (2) - CARBON DIOXIDE (3)

	EXPERIMENTAL					CALCULATED			Calculated with Ω_a and Ω_b Computed from the Generalized Eqn.			CALCULATED (Clausius Eqn.)		
Temp. °F	x_1	x_2	P_{psia}	y_1	y_2	P_{psia}	y_1	y_2	P_{psia}	y_1	y_2	P_{psia}	y_1	y_2
20	0.4749	0.4876	184.0	0.1686	0.6908	175.4	0.1740	0.6748	189.2	0.1778	0.6894	182.8	0.1902	0.6764
	0.3549	0.6157	213.0	0.1193	0.7846	202.3	0.1140	0.7820	214.6	0.1234	0.7836	207.8	0.0928	0.1325
	0.6438	0.1477	219.0	0.2166	0.1910	210.1	0.2166	0.1633	215.4	0.2176	0.1908	212.7	0.2326	0.1811
(k_{12}= -0.025	0.2686	0.7081	233.0	0.0863	0.8442	223.3	0.0786	0.8464	233.4	0.0895	0.8424	226.6	0.0962	0.8360
	0.4201	0.4276	236.0	0.1424	0.4717	242.9	0.1240	0.4580	252.2	0.1308	0.4841	246.6	0.1426	0.4741
k_{23}= 0.102	0.2147	0.7670	246.5	0.0685	0.8791	236.4	0.0594	0.8849	244.8	0.0700	0.8787	238.2	0.0753	0.8739
	0.1708	0.8124	252.0	0.0561	0.8994	248.9	0.0450	0.9065	255.7	0.0547	0.9002	249.4	0.0588	0.8967
k_{13}= 0.102)	0.5515	0.1469	270.0	0.1724	0.1443	259.0	0.1651	0.1424	263.1	0.1677	0.1647	260.8	0.1827	0.1569
	0.3360	0.4469	285.0	0.1150	0.4480	290.5	0.0893	0.4290	297.4	0.0969	0.4511	292.0	0.1077	0.4446
	0.2088	0.6729	289.0	0.0601	0.6784	289.1	0.0524	0.6676	295.1	0.0614	0.6754	289.2	0.0676	0.6731
	0.1631	0.7541	291.0	0.0485	0.7601	286.4	0.0401	0.7588	291.7	0.1631	0.7541	285.9	0.0532	0.7601
	0.2262	0.6374	292.0	0.0674	0.6368	291.8	0.0570	0.6261	298.0	0.0660	0.6364	292.1	0.0728	0.6336
	0.3040	0.4425	309.5	0.1088	0.4174	311.7	0.0784	0.4087	317.6	0.0858	0.4292	312.4	0.0962	0.4241
	0.3289	0.2811	333.0	0.0935	0.2663	337.5	0.0874	0.2488	341.8	0.0926	0.2691	338.0	0.1055	0.2630
	0.4346	0.1005	336.0	0.1189	0.0960	318.4	0.1250	0.0901	320.2	0.1276	0.1033	319.3	0.1430	0.0981
	0.1549	0.6191	342.5	0.0417	0.5562	349.3	0.0362	0.5485	352.8	0.0429	0.5580	347.7	0.0487	0.5603
	0.3461	0.1197	343.0	0.1282	0.1291	349.2	0.1005	0.1077	351.0	0.1033	0.1206	349.9	0.1181	0.1152
	0.4036	0.0876	354.0	0.1048	0.0907	331.0	0.1176	0.0786	332.2	0.1200	0.0899	331.8	0.1353	0.0852
	0.3169	0.1311	361.0	0.0922	0.1086	358.9	0.0924	0.1185	360.8	0.0954	0.1315	359.5	0.1098	0.1259
	0.3036	0.0968	367.0	0.0930	0.0969	364.2	0.0923	0.0896	365.1	0.0947	0.0999	364.9	0.1092	0.0948
	0.3022	0.1852	370.5	0.0835	0.1749	361.2	0.0849	0.1649	363.9	0.3022	0.1852	361.7	0.1024	0.1745
	0.2183	0.3016	380.5	0.0699	0.2899	385.6	0.0579	0.2634	388.9	0.0626	0.2782	385.2	0.0737	0.2747
	0.2001	0.1818	383.5	0.0601	0.1869	399.5	0.0602	0.1697	401.6	0.0633	0.1816	399.9	0.0753	0.1759
	0.1211	0.0502	387.0	0.0613	0.0468	412.7	0.0518	0.0613	410.9	0.0534	0.6631	413.0	0.0628	0.0610
	0.1863	0.1573	391.0	0.0604	0.1644	404.1	0.0586	0.1515	405.7	0.0614	0.1622	404.6	0.0732	0.1562
	0.1591	0.1352	396.0	0.0578	0.1492	412.3	0.0535	0.1369	413.3	0.0559	0.1463	412.8	0.0669	0.1399

(continued)

TABLE A.9
(continued)

EXPERIMENTAL AND CALCULATED RESULTS FOR THE BINARY SYSTEM

PROPANE (1) - ETHANE (2) - CARBON DIOXIDE (3)

	EXPERIMENTAL					CALCULATED			Calculated with Ω_a and Ω_b Computed from the Generalized Eqn.			CALCULATED (Clausius Eqn.)		
Temp. °F	x_1	x_2	P_{psia}	y_1	y_2	P_{psia}	y_1	y_2	P_{psia}	y_1	y_2	P_{psia}	y_1	y_2
20	0.1129	0.0339	396.0	0.0519	0.0402	411.3	0.0513	0.0435	408.7	0.0529	0.0473	411.4	0.0619	0.0431
	0.1765	0.1148	397.0	0.0535	0.1306	405.0	0.0599	0.1166	405.8	0.0622	0.1257	405.7	0.0738	0.1194
	0.1060	0.3986	421.5	0.0260	0.3380	428.1	0.0273	0.3440	430.6	0.0309	0.3524	427.1	0.0376	0.3549
	0.0741	0.2931	433.0	0.0238	0.2864	450.8	0.0220	0.2748	452.7	0.0242	0.2819	450.7	0.0301	0.2807
-20	0.7136	0.1929	87.5	0.2315	0.2932	82.6	0.2413	0.2791	88.0	0.2350	0.3299	85.9	0.2449	0.3174
	0.5512	0.3688	103.0	0.1603	0.4957	98.8	0.1559	0.4873	106.5	0.1562	0.5292	103.5	0.1645	0.5182
	0.6380	0.1825	110.5	0.1723	0.2339	113.4	0.1667	0.2035	117.5	0.1672	0.2437	115.6	0.1756	0.2338
	0.6024	0.1695	125.5	0.1431	0.2020	127.8	0.1446	0.1727	131.2	0.1463	0.2076	129.5	0.1543	0.1989
(k_{12}= -0.025	0.5384	0.1681	141.0	0.1191	0.1791	146.9	0.1182	0.1571	149.7	0.1208	0.1874	148.3	0.1285	0.1794
	0.2275	0.6716	150.5	0.0449	0.6670	154.4	0.0407	0.6697	158.9	0.0488	0.6824	155.8	0.0519	0.6811
k_{23}= 0.101	0.2167	0.1711	211.0	0.0537	0.1941	213.8	0.0479	0.1639	215.1	0.0509	0.1811	214.4	0.0566	0.1727
	0.3656	0.2635	172.5	0.0645	0.2454	181.6	0.0702	0.2281	184.4	0.0745	0.2561	182.4	0.0811	0.2489
k_{13}= 0.099)	0.4578	0.1208	166.5	0.0999	0.1290	171.1	0.0965	0.1064	172.5	0.0991	0.1269	171.9	0.1065	0.1205
	0.3915	0.1060	186.0	0.0855	0.1131	184.1	0.0839	0.0945	185.1	0.0865	0.1114	184.9	0.0935	0.1053
	0.2366	0.0678	199.5	0.0604	0.0861	205.2	0.0619	0.0731	205.0	0.0642	0.0836	206.1	0.0699	0.0769
	0.1563	0.6007	201.5	0.0197	0.5204	200.0	0.0241	0.5032	202.4	0.0294	0.5174	199.5	0.0322	0.5993
	0.0686	0.6502	215.0	0.0142	0.5235	222.1	0.0097	0.5189	224.0	0.0125	0.5264	221.2	0.0139	0.4537
	0.1786	0.3894	217.0	0.0363	0.3530	218.7	0.0305	0.3253	220.8	0.0348	0.3431	218.4	0.0389	0.3406
	0.1371	0.4958	220.5	0.0254	0.4285	221.0	0.0215	0.4036	223.0	0.0257	0.4177	220.3	0.0287	0.4189
	0.1685	0.3702	221.0	0.0388	0.3406	222.3	0.0293	0.3124	224.3	0.0333	0.3294	221.9	0.0374	0.3265
	0.1020	0.2488	232.0	0.0232	0.2615	237.6	0.0222	0.2471	239.0	0.0247	0.2605	273.5	0.0282	0.2528
	0.0685	0.4403	238.0	0.0108	0.3868	249.4	0.0072	0.3806	251.0	0.0087	0.3877	248.9	0.0101	0.3903

TABLE A.10

ACTIVITY COEFFICIENTS AND GIBBS FREE ENERGY OF MIXING FOR THE BINARY SYSTEM ETHANE (1) - CARBON DIOXIDE (2)

		EXPERIMENTAL		CALCULATED		G^E J/mole	
Temp. °F	x_1	γ_1	γ_2	γ_1	γ_2	Experimental	Calculated
60	0.1617	1.4261	1.0438	1.5318	1.0277	224.2	220.5
	0.1499	1.5292	1.0299	1.5597	1.0239	213.0	208.2
	0.2609	1.0595	1.0595	1.3489	1.0612	303.9	292.9
	0.4376	1.0744	1.2313	1.1677	1.1369	356.3	336.0
	0.4880	1.1178	1.2166	1.1354	1.1644	371.4	335.9
	0.6874	1.1107	1.2234	1.0569	1.3110	294.6	371.4
	0.7845	1.1036	1.1644	1.0388	1.4063	264.4	248.0
20	0.0825	1.4957	1.0411	2.2868	1.0132	155.4	177.8
	0.1055	1.9235	1.0310	2.1450	1.0183	213.5	214.4
	0.3929	1.0939	1.2913	1.3118	1.1853	422.1	465.0
	0.4069	1.2717	1.2138	1.2921	1.1959	471.4	466.2
	0.4714	1.2475	1.2325	1.2191	1.2528	475.8	470.9
	0.5096	1.2382	1.2434	1.1836	1.2890	478.0	466.2
	0.6406	1.1907	1.2496	1.6978	1.4347	425.3	419.9
	0.7487	1.0959	1.4497	1.0515	1.5751	358.8	336.3
	0.8013	1.0755	1.5255	1.0365	1.6534	315.2	285.1
	0.8702	1.0535	1.5921	1.0240	1.7676	234.2	209.6
	0.8956	1.0335	1.8098	1.0195	1.8106	202.6	175.7
	0.9285	1.0422	1.5560	1.0184	1.8748	155.1	137.1
-20	0.0892	2.6188	1.0096	2.8273	1.0172	192.1	219.9
	0.0981	2.5901	1.0345	2.7389	1.0196	251.8	236.2
	0.1676	2.0935	1.0571	2.2128	1.0540	345.4	359.3
	0.3312	1.5340	1.1854	1.5500	1.1826	518.9	522.6
	0.4521	1.3359	1.3019	1.3094	1.3170	559.5	554.0
	0.4541	1.3480	1.2918	1.3064	1.3195	559.3	554.0
	0.5749	1.2093	1.4733	1.1651	1.4870	556.4	521.0
	0.6631	1.1440	1.5392	1.1012	1.6392	476.2	466.5
	0.8256	1.1115	1.7297	1.0321	1.9643	371.4	292.1
-60	0.1197	2.9360	1.0866	3.5787	1.0389	375.1	343.8
	0.2253	2.1463	1.1702	2.4143	1.1268	542.5	537.4
	0.2975	1.8939	1.2236	1.9651	1.2115	612.6	620.0
	0.3307	1.7382	1.2726	1.8091	1.2543	635.5	642.0
	0.3661	1.6589	1.3176	1.6778	1.3098	665.0	665.7
	0.3726	1.6611	1.3156	1.6566	1.3209	666.9	669.6
	0.4023	1.5898	1.3517	1.5639	1.3696	677.0	679.3
	0.4637	1.5425	1.3798	1.4098	1.4810	689.8	682.9
	0.4672	1.4638	1.4390	1.4027	1.4882	686.8	683.0
	0.6203	1.2381	1.7398	1.1715	1.8408	632.9	609.0
	0.7622	1.1139	2.1680	1.0648	2.2760	491.5	449.4
	0.8703	0.9857	2.9242	1.0249	2.6953	233.7	277.0

TABLE A.11

ACTIVITY COEFFICIENTS AND GIBBS FREE ENERGY OF MIXING

FOR THE BINARY SYSTEM PROPANE (1) - CARBON DIOXIDE (2)

		EXPERIMENTAL		CALCULATED		G^E J/mole	
Temp.°F	x_1	γ_1	γ_2	γ_1	γ_2	Experimental	Predicted
20	0.9114	1.2143	2.6298	1.2084	2.4582	582.0	558.8
	0.8380	1.2473	2.2748	1.2180	2.3089	705.4	666.6
	0.8202	1.2440	2.3105	1.2205	2.2706	730.5	688.9
	0.7485	1.2826	2.0453	1.2417	2.1317	811.5	780.9
	0.6536	1.3082	1.8934	1.2865	1.9489	879.1	877.1
	0.6004	1.3687	1.7902	1.3245	1.8496	933.2	918.5
	0.5572	1.3919	1.8095	1.3604	1.7631	990.2	936.4
	0.4734	1.5213	1.6154	1.4742	1.6197	999.8	969.9
	0.3530	1.9215	1.4153	1.7661	1.4211	1008.9	948.8
	0.2250	2.3870	1.2256	2.4736	1.2427	783.1	824.8
	0.1811	2.7907	1.1722	2.9141	1.1915	700.2	747.2
-20	0.8866	1.1963	2.6926	1.1792	2.5499	550.9	512.4
	0.8547	1.1924	2.6160	1.1843	2.4666	589.3	560.1
	0.7755	1.2360	2.3178	1.2065	2.2685	717.0	669.2
	0.7505	1.2175	2.2098	1.3106	2.0283	740.0	701.8
	0.6771	1.3106	2.0283	1.2565	2.0357	835.8	786.2
	0.5774	1.4450	1.7927	1.3447	1.8157	932.8	859.3
	0.4671	1.6070	1.5388	1.5165	1.5938	916.6	899.6
	0.3328	2.0275	1.3211	1.9328	1.3581	855.1	860.2
	0.2536	2.4726	1.2045	2.4003	1.2419	748.4	779.4
	0.1933	2.9771	1.1442	2.9765	1.1672	649.1	681.5

TABLE A.12

ACTIVITY COEFFICIENTS AND GIBBS FREE ENERGIES OF MIXING

FOR THE TERNARY SYSTEM PROPANE (1) - ETHANE (2) CARBON DIOXIDE (3)

Temp.°F	x_1	x_2	EXPERIMENTAL γ_1	EXPERIMENTAL γ_2	EXPERIMENTAL γ_3	CALCULATED γ_1	CALCULATED γ_2	CALCULATED γ_3	G^E J/mole Experimental	G^E J/mole Calculated
20	0.4794	0.4876	1.0937	1.1812	2.7757	1.0921	1.1072	2.8470	359.0	289.6
(k_{12}= -0.025	0.3549	0.6157	1.0991	1.2161	2.8565	1.0170	1.1607	2.9385	409.6	286.8
	0.6438	0.1477	1.2332	1.2260	2.2561	1.2026	1.0132	2.2700	741.7	646.3
k_{13}= 0.102	0.2686	0.7081	1.0659	1.2360	2.9094	0.9471	1.1967	3.0105	425.6	306.4
	0.4201	0.4276	1.2276	1.1378	2.2800	1.0939	1.1329	2.5267	591.3	514.5
k_{23}= 0.102)	0.2147	0.7670	1.0560	1.2500	3.0022	0.8949	1.2164	3.0611	449.7	325.5
	0.1708	0.8124	1.0651	1.2396	2.8997	0.8479	1.2332	3.1039	450.1	357.1
	0.5515	0.1469	1.3133	1.1216	2.1251	1.2273	1.0698	2.0709	874.2	758.7
	0.3360	0.4469	1.3434	1.2131	2.1263	1.0646	1.1819	2.3659	774.0	626.4
	0.2088	0.6729	1.0349	1.2421	2.5436	0.9058	1.2237	2.7167	583.9	517.2
	0.1631	0.7541	1.0258	1.2517	2.7684	0.8448	1.2349	2.8593	571.1	484.4
	0.2262	0.6374	1.0505	1.2389	2.5031	0.9321	1.2219	0.2651	604.5	543.0
	0.3040	0.4425	1.4470	1.2198	2.0960	1.0588	1.2061	2.2695	859.4	682.6
	0.3289	0.2811	1.2683	1.3200	1.8344	1.2017	1.2491	1.9200	870.5	835.9
	0.4346	0.1005	1.3272	1.3385	1.8150	1.3559	1.2047	1.7343	951.6	901.9
	0.1549	0.6191	0.9979	1.2684	2.2812	0.8773	1.2702	2.3914	738.5	719.8
	0.3461	0.1197	1.8029	1.5814	1.5010	1.4502	1.3487	1.6180	1054.4	934.0
	0.4036	0.0876	1.3081	1.5298	1.7449	1.4160	1.2595	1.6492	950.4	920.0
	0.3169	0.1311	1.4783	1.2858	1.6081	1.4735	1.3954	1.5809	928.6	929.3
	0.3036	0.0968	1.6110	1.6016	1.4917	1.5967	1.4741	1.4965	953.2	933.6
	0.3022	0.1852	1.3636	1.4713	1.6680	1.3739	1.3634	1.6517	947.3	909.9
	0.2183	0.3016	1.6434	1.5319	1.6120	1.2352	1.4134	1.7210	977.2	911.0
	0.2001	0.1818	1.5600	1.7732	1.3829	1.5946	1.6611	1.4602	872.0	929.9
	0.1211	0.0502	3.5917	1.9396	1.1240	3.1121	2.6581	1.1760	631.4	711.0

(continued)

TABLE A.12
(continued)

ACTIVITY COEFFICIENTS AND GIBBS FREE ENERGIES OF MIXING

FOR THE TERNARY SYSTEM PROPANE (1) - ETHANE (2) CARBON DIOXIDE (3)

Temp.°F	x_1	x_2	EXPERIMENTAL γ_1	γ_2	γ_3	CALCULATED γ_1	γ_2	γ_3	G^E J/mole Experimental	Calculated
	0.1863	0.1573	1.7649	1.8746	1.3344	1.7428	1.7718	1.3948	873.2	912.7
	0.1591	0.1352	2.1036	2.0853	1.2516	1.9892	1.9741	1.3180	833.3	878.0
	0.1129	0.0339	3.4413	2.5529	1.1216	3.4514	2.8371	1.1522	596.6	656.0
	0.1765	0.1148	1.7838	2.1385	1.2831	2.0138	1.9373	1.3156	811.2	872.7
	0.1060	0.3986	1.0423	1.5003	1.6627	1.0970	1.5402	1.6654	926.1	963.2
	0.0741	0.2931	1.5787	1.9541	1.3242	1.4799	1.9195	1.3914	900.9	951.0
-20	0.7136	0.1929	1.1639	1.0212	2.8423	1.1554	0.9218	2.7132	426.6	367.0
	0.5512	0.3688	1.1731	1.0584	2.8546	1.1041	1.0021	2.8428	391.6	282.3
(k_{12}= -0.025	0.6380	0.1825	1.1782	1.0711	2.2727	1.1677	0.9548	2.4669	537.3	513.0
k_{13}= 0.101	0.6024	0.1695	1.1507	1.1202	2.1980	1.1820	0.9742	2.3286	575.7	587.2
k_{23}= 0.099)	0.5384	0.1681	1.1763	1.1189	2.0127	1.2074	1.0182	2.1566	632.9	670.4
	0.2275	0.6716	0.9874	1.1171	2.7783	0.9118	1.1463	2.8601	354.7	358.9
	0.2167	0.1711	1.8468	1.8265	1.3548	1.6727	1.5650	1.4340	857.0	830.3
	0.3656	0.2635	1.0735	1.1886	1.8534	1.2125	1.1544	1.9725	610.0	731.7
	0.4578	0.1208	1.3335	1.3170	1.7366	1.3186	1.1136	1.8382	807.6	804.7
	0.3915	0.1060	1.4663	1.4710	1.6320	1.4335	1.2200	1.6572	887.4	844.7
	0.2336	0.0678	1.9988	2.0097	1.2552	2.0922	1.7475	1.3034	747.2	803.1
	0.1563	0.6007	0.7513	1.2526	2.2818	0.9146	1.2047	2.3283	591.2	616.0
	0.0686	0.6502	1.2074	1.2371	2.0790	0.8403	1.2587	2.1797	725.3	724.6
	0.1786	0.3894	1.3649	1.4296	1.6925	1.1697	1.3420	1.8103	857.2	810.3
	0.1371	0.4958	1.1915	1.3668	1.8502	1.0160	1.2933	1.9484	822.3	760.8
	0.1685	0.3702	1.3751	1.4838	1.6311	1.2038	1.3713	1.7219	864.1	810.1
	0.1020	0.2488	1.7996	1.9024	1.2889	1.7553	1.8346	1.3427	781.4	811.8
	0.0685	0.4403	1.5651	1.5127	1.4918	1.1452	1.5435	1.5752	827.3	875.8

TABLE A.13

VALUES OF COEFFICIENTS FROM EQUATIONS (4.59 - 4.62)
AND (4.64 - 4.67) DETERMINED BY LEAST-SQUARES METHOD

Component	ω	a_0	a_1	a_2	a_3	b_0	b_1	b_2
ARGON	.0	0.43050847	0.11665583	-0.10999946	0.08830323	0.25961721	0.40208006	-0.25819763
METHANE	.0072	0.42382532	0.02691722	-0.11197112	0.15443376	0.23915571	0.45931979	-0.30318139
NITROGEN	.0400	0.42477338	-1.34808950	-0.40747377	1.45596590	0.29126589	0.36945645	-0.25915534
ETHYLENE	.0856	0.42210929	-0.18885579	-0.18049869	0.41318894	0.34406275	0.20792589	-0.14819453
ETHANE	.0908	0.42400640	0.12294196	-0.12047286	0.12606536	0.30222886	0.33788769	-0.24402109
PROPANE	.1454	0.42299465	0.05276018	-0.14266127	0.21666270	0.31851814	0.33788427	-0.26353364
PROPYLENE	.1477	0.42183207	-0.34365098	-0.18345442	0.50138547	0.27216744	0.45519515	-0.33757827
N-BUTANE	.1928	0.42149785	0.35832305	-0.07565617	-0.06636675	0.29004230	0.45609479	-0.36449222
BENZENE	.2100	0.42101009	-0.35831820	-0.23373155	0.60621499	0.33178720	0.31417268	-0.25545976
N-PENTANE	.2510	0.41886845	0.09019055	-0.14777929	0.22349830	0.27550871	0.51002512	-0.40477487
N-HEXANE	.2957	0.41936437	-0.10854373	-0.19142998	0.40041157	0.35334601	0.32002029	-0.29191426
N-HEPTANE	.3506	0.41911367	-0.24673535	-0.23343743	0.56458532	0.36113856	0.32857740	-0.30986680
N-OCTANE	.3942	0.41791410	-0.34989054	-0.27149607	0.69530262	0.37889108	0.30054547	-0.30104005

	$T_{r_{min.}}$	c_0	c_1	c_2	c_3	d_0	d_1	d_2
ARGON	.555	0.08725108	0.03695091	-0.03333784	0.03073563	0.08337414	0.02226552	-0.02564472
METHANE	.498	0.08553866	0.02789869	-0.03204719	0.03472820	0.07913984	0.03052690	-0.03159514
NITROGEN	.500	0.08582632	-0.61091693	-0.16938938	0.63210227	0.08075903	0.02777774	-0.02869842
ETHYLENE	.600	0.08502854	-0.05192614	-0.05093685	0.10885643	0.07418960	0.03358657	-0.03040850
ETHANE	.654	0.08558042	0.03894500	-0.03446969	0.02754644	0.07546995	0.02960534	-0.02763319
PROPANE	.624	0.08528425	0.00757169	-0.04137974	0.05558074	0.06932972	0.04271199	-0.03558690
PROPYLENE	.618	0.08494582	-0.08609311	-0.05057639	0.12283132	0.06234304	0.06170222	-0.04800880
N-BUTANE	.641	0.08484495	0.10286707	-0.01981869	-0.03753787	0.05819075	0.07074648	-0.05483369
BENZENE	.553	0.08470032	-0.08358340	-0.06011521	0.13429129	0.06534117	0.04331831	-0.03322676
N-PENTANE	.658	0.08406250	0.00306417	-0.04330415	0.05862516	0.04751686	0.09151685	-0.06546539
N-HEXANE	.538	0.08421014	-0.01432214	-0.04899557	0.07182131	0.06230470	0.04693287	-0.03580114
N-HEPTANE	.505	0.08413559	-0.06502115	-0.06066771	0.11939901	0.06149217	0.04461033	-0.03258488
N-OCTANE	.480	0.08377900	-0.14036081	-0.07738044	0.18837684	0.05969904	0.04473506	-0.03158729

(continued)

T A B L E A.13

(continued)

VALUES OF COEFFICIENTS FROM EQUATIONS (4.59 - 4.62)

AND (4.64 - 4.67) DETERMINED BY LEAST-SQUARES METHOD

$a_{00} = 0.42693395$	$a_{01} = -0.04052565$	$a_{02} = 0.04784060$
$a_{10} = -0.30832269$	$a_{11} = 2.30697800$	$a_{12} = -5.73271910$
$a_{20} = -0.19114806$	$a_{21} = 0.41568655$	$a_{22} = -1.48055420$
$a_{30} = 0.47833642$	$a_{31} = -1.84504300$	$a_{32} = 5.68333250$
$b_{00} = 0.27047169$	$b_{01} = 0.17543951$	$b_{02} = 0.19940365$
$b_{10} = 0.37561136$	$b_{11} = 0.13735650$	$b_{12} = -0.67950561$
$b_{20} = -0.24335111$	$b_{21} = -0.39910050$	$b_{22} = 0.53413329$
$c_{00} = 0.08635863$	$c_{01} = -0.01104743$	$c_{02} = 0.01219090$
$c_{10} = -0.13797069$	$c_{11} = 1.08314740$	$c_{12} = -2.51864620$
$c_{20} = -0.06899741$	$c_{21} = 0.23526222$	$c_{22} = -0.60612746$
$c_{30} = 0.19217689$	$c_{31} = -1.06506430$	$c_{32} = 2.46211940$
$d_{00} = 0.08448929$	$d_{01} = -0.17053425$	$d_{02} = 0.27681320$
$d_{10} = 0.01861857$	$d_{11} = 0.33391897$	$d_{12} = -0.68448992$
$d_{20} = -0.02338694$	$d_{21} = -0.19347031$	$d_{22} = 0.43969793$

TABLE A.14

COMPARISON OF Ω_a AND Ω_b VALUES OBTAINED FROM THE SATURATED PROPERTIES WITH THOSE COMPUTED FROM THE CORRELATION EQUATIONS (4.59 - 4.62)

	δ in Ω_a				δ in Ω_b			
	A*	B*	A*	B*	A*	B*	A*	B*
Component	Maximum		Average		Maximum		Average	
ARGON	0.2556	0.2986	0.0700	0.1445	0.3810	0.2467	0.1036	0.1342
METHANE	0.0994	0.0467	0.0620	0.0203	0.1258	0.0249	0.0771	0.0112
NITROGEN	0.0	0.2466	0.0	0.0906	0.0	0.2392	0.0	0.0689
ETHYLENE	0.0468	0.3522	0.0222	0.1510	0.0447	0.1583	0.0281	0.0743
ETHANE	0.3355	0.0126	0.1607	0.0058	0.4661	0.0128	0.2172	0.0060
PROPANE	0.1175	0.0172	0.0651	0.0078	0.1486	0.0250	0.0806	0.0138
PROPYLENE	0.1854	0.0545	0.0867	0.0233	0.2635	0.0530	0.1257	0.0249
N-BUTANE	0.0843	0.1237	0.0396	0.0374	0.0988	0.1498	0.0453	0.0353
BENZENE	0.0580	0.1156	0.0253	0.0462	0.0668	0.0730	0.0241	0.0256
N-PENTANE	0.0720	0.0930	0.0283	0.0408	0.0884	0.0928	0.0385	0.0371
N-HEXANE	0.1691	0.2032	0.0515	0.0580	0.2028	0.2210	0.0645	0.0445
N-HEPTANE	0.0538	0.1012	0.0185	0.0479	0.0309	0.0346	0.0105	0.0117
N-OCTANE	0.0659	0.2728	0.0250	0.1133	0.0086	0.0397	0.0033	0.0168
OVERALL AVG.	0.1187	0.1491	0.0504	0.0605	0.1482	0.1054	0.0630	0.0388

* A: $0.85 \leq T_r \leq 1.0$

B: $T_{rmin} \leq T_r \leq 0.85$

$$\delta = \left| \frac{\Omega_{calc.} - \Omega_{comp.}}{\Omega_{calc.}} \right| \cdot 100\%$$

TABLE A.15

COMPARISON OF Ω_a AND Ω_b VALUES OBTAINED FROM THE SATURATED PROPERTIES WITH THOSE COMPUTED FROM THE GENERALIZED EQUATIONS (4.59 - 4.62) AND (4.64 - 4.67)

Component	δ in Ω_a				δ in Ω_b			
	A* Maximum	B* Maximum	A* Average	B* Average	A* Maximum	B* Maximum	A* Average	B* Average
ARGON	2.2444	0.4924	0.5649	0.1919	4.0649	0.6668	1.2450	0.3854
METHANE	0.7655	1.4444	0.5279	0.8851	2.2251	1.2241	1.2458	1.0579
NITROGEN	1.0475	2.0544	0.7126	1.5295	1.3434	1.9209	0.8781	1.6029
ETHYLENE	0.5250	1.1802	0.2959	0.6973	0.5568	0.8889	0.4974	0.7512
ETHANE	1.0324	0.4250	0.3511	0.3965	1.9078	0.7834	0.6425	0.7416
PROPANE	0.5742	0.3950	0.2368	0.2275	0.8760	0.1877	0.3610	0.0743
PROPYLENE	0.7900	0.1887	0.3521	0.1170	1.2000	0.4719	0.6033	0.3858
N-BUTANE	1.5426	0.6809	0.2366	0.4036	2.2848	0.5553	0.3762	0.3487
BENZENE	0.4615	0.8306	0.2312	0.6072	0.4942	0.8400	0.2759	0.6779
N-PENTANE	0.2388	0.5152	0.1119	0.4200	0.5250	0.7881	0.2276	0.6836
N-HEXANE	0.4655	0.4077	0.2953	0.1841	0.6835	0.5050	0.5145	0.2737
N-HEPTANE	0.2781	0.1797	0.1938	0.0917	0.2493	0.5718	0.2111	0.2860
N-OCTANE	0.1146	0.3053	0.0554	0.1314	0.1422	0.3200	0.0717	0.1609
OVERALL AVG.	0.7746	0.7000	0.3204	0.4525	1.2733	0.7480	0.5500	0.5715

* A: $0.85 \leq T_r \leq 1.0$

B: $T_{rmin} \leq T_r \leq 0.85$

$$\delta = \left| \frac{\Omega_{calc.} - \Omega_{comp.}}{\Omega_{calc.}} \right| \cdot 100\%$$

TABLE A.16

COMPARISON OF THE COMPUTED VALUES OF Ω_a AND Ω_b FROM THE GENERALIZED EQUATIONS (4-7) and (9-12) WITH THOSE OBTAINED FROM SATURATION PROPERTIES FOR COMPOUNDS NOT INCLUDED IN THE GENERALIZATION.[a]

Component	T_r	Ω_a	δ	Ω_b	δ
OXYGEN[116]	0.492	0.399395	0.61	0.086895	0.26
	0.453	0.405495	0.32	0.086746	0.15
HYDROGEN SULFIDE[52]	0.743	0.420820	0.12	0.082598	0.05
	0.832	0.415890	0.05	0.081239	0.55
CARBON TETRACHLORIDE[52]	0.536	0.428565	0.13	0.079706	0.75
CYCLO-HEXANE[52]	0.527	0.429701	0.86	0.079203	1.44
	0.539	0.430327	0.83	0.079344	1.36
	0.561	0.431174	0.78	0.079553	1.24
	0.566	0.431340	0.81	0.079598	1.27
	0.621	0.432024	0.74	0.079910	1.14
CARBON DIOXIDE[52]	0.913	0.405831	0.46	0.077043	1.02
N-NONANE	0.523	0.459692	0.13	0.073867	0.74
	0.607	0.455198	0.07	0.074406	0.33
	0.719	0.442273	0.22	0.074626	0.36
	0.747	0.437803	0.32	0.074592	0.57
	0.831	0.421421	0.43	0.074277	0.24
N-DECANE	0.503	0.466449	2.72	0.073199	2.92
	0.577	0.463759	0.90	0.073441	1.74
	0.611	0.459258	0.27	0.073611	0.79
	0.665	0.452949	0.15	0.073707	0.59
	0.719	0.444829	0.61	0.073730	0.76
		OVERALL AVERAGE:	0.55		0.87

a Values of the parameters obtained from saturated properties were taken from Hsi (1971).

TABLE A.17

THE RELATIVE DEVIATION OF V_ℓ^s AT SPECIFIED RELATIVE DEVIATIONS OF Ω_a AND Ω_b FOR n-HEXANE AT DIFFERENT TEMPERATURES

$(\Omega/\Omega_{calc.})$		δ in V_ℓ^s				
Ω_a	Ω_b	32°F	60°F	140°F	190°F	250°F
1.015	1.015	1.50	2.11	1.50	1.35	0.87
1.005	1.005	0.50	1.11	0.49	0.35	0.12
1.005	0.995	0.69	0.13	0.83	1.07	1.77
1.000	1.000	0.00	0.00	0.00	0.00	0.00
0.995	1.005	0.69	1.30	0.83	0.97	0.57
0.995	0.995	0.50	0.10	0.51	0.65	1.11
0.985	0.985	1.50	0.91	1.51	1.64	2.10

T A B L E A.18

EXPERIMENTAL AND CALCULATED RESULTS
OF THE BINARY SYSTEM
METHANE (1) - NITROGEN (2)

	EXPERIMENTAL			Calculated (Ω_a and Ω_b computed from the Generalized Equation)	
Temp.K	P_{psia}	x_1	y_1	P_{psia}	y_1
95.00[81]	32.7	0.2679	0.9216	33.0	0.9276
	39.7	0.3562	0.9374	39.4	0.9430
	43.8	0.4249	0.9460	43.7	0.9512
	49.8	0.5271	0.9573	49.4	0.9606
	52.9	0.5889	0.9618	52.6	0.9653
	61.6	0.7495	0.9756	60.7	0.9770
	66.4	0.8271	0.9823	65.0	0.9830
100.00[81]	28.8	0.1329	0.8336	28.3	0.8368
	42.9	0.2397	0.8907	42.8	0.8984
	52.5	0.3301	0.9168	52.8	0.9222
	57.8	0.3831	0.9277	57.9	0.9318
	63.8	0.4463	0.9372	63.5	0.9406
	68.2	0.5069	0.9448	68.4	0.9478
	73.0	0.5638	0.9508	72.8	0.9536
	81.2	0.6671	0.9618	80.6	0.9634
	93.6	0.8133	0.9764	92.2	0.9773
105.00[81]	52.9	0.2101	0.8533	53.0	0.8598
	65.4	0.2869	0.8855	65.4	0.8910
	82.2	0.4108	0.9149	82.3	0.9202
	91.3	0.4836	0.9275	91.0	0.9318
	105.0	0.6012	0.9440	104.0	0.9470
	122.1	0.7548	0.9626	120.9	0.9647
	142.2	0.8990	0.9829	139.0	0.9834
110.00[81]	69.8	0.2093	0.8237	69.6	0.8294
	85.8	0.2856	0.8615	85.8	0.8668
	108.1	0.4061	0.8950	108.0	0.9014
	121.3	0.4843	0.9113	120.8	0.9168
	123.0	0.5008	0.9147	123.4	0.9197
	139.3	0.6056	0.9319	139.3	0.9359
	153.5	0.6948	0.9456	152.8	0.9484
	171.1	0.7956	0.9612	168.8	0.9628
	191.1	0.8978	0.9790	187.2	0.9794

(continued)

TABLE A.18
(continued)

EXPERIMENTAL AND CALCULATED RESULTS
OF THE BINARY SYSTEM
METHANE (1) - NITROGEN (2)

	EXPERIMENTAL			Calculated (Ω_a and Ω_b computed from the Generalized Equation)	
Temp.K	P_{psia}	x_1	y_1	P_{psia}	y_1
113.71[108]	250.0	0.0442	0.0126	245.9	0.0112
	222.5	0.1420	0.0355	221.1	0.0318
	199.5	0.2509	0.0557	197.7	0.0507
	200.2	0.2505	0.0550	197.8	0.0506
	149.5	0.5016	0.1010	149.8	0.0926
	100.0	0.7391	0.1710	97.8	0.1632
	75.0	0.8329	0.2340	72.5	0.2289
	50.0	0.9106	0.3509	48.6	0.3503
115.00[81]	85.3	0.1891	0.7782	83.9	0.7821
	112.0	0.2868	0.8363	111.0	0.8418
	138.9	0.3989	0.8739	138.2	0.8800
	161.4	0.5027	0.8983	160.7	0.9038
	177.2	0.5789	0.9129	176.4	0.9180
	205.5	0.7110	0.9377	203.4	0.9403
	227.0	0.8043	0.9538	223.8	0.9564
	253.4	0.9040	0.9750	248.7	0.9759
120.0[81]	72.3	0.0977	0.6122	70.6	0.6100
	109.5	0.1938	0.7458	107.7	0.7507
	144.8	0.2990	0.8125	143.6	0.8198
	175.5	0.3978	0.8512	173.8	0.8576
	202.2	0.4954	0.8773	201.3	0.8840
	230.9	0.5938	0.9000	227.5	0.9052
	261.5	0.7055	0.9225	257.5	0.9271
	288.3	0.7877	0.9414	281.0	0.9435
122.04[124]	398.0	0.0120	0.0054	389.2	0.0048
	380.0	0.0486	0.0215	371.3	0.0180
	354.0	0.1038	0.0411	347.6	0.0347
	311.0	0.2163	0.0692	306.9	0.0620
	300.3	0.2476	0.0775	296.7	0.0687
	284.8	0.2907	0.0891	283.3	0.0777
	200.0	0.5717	0.1589	199.3	0.1425
	99.8	0.8589	0.3345	96.4	0.3270
	75.0	0.9140	0.4412	72.6	0.4391
	50.0	0.9649	0.6534	49.2	0.6528
	40.5	0.9835	0.8037	40.3	0.7986

T A B L E A.19

EXPERIMENTAL[120] AND CALCULATED RESULTS OF THE BINARY SYSTEM METHANE (1) - ETHANE (2)

	EXPERIMENTAL			Calculated (Ω_a and Ω_b computed from the Generalized Equation)	
Temp.K	P	x_1	y_1	P	y_1
130.37	28.0	0.4319	0.9948	28.2	0.9958
	35.0	0.5989	0.9965	36.1	0.9973
	43.3	0.7788	0.9984	43.9	0.9986
	48.6	0.8935	0.9992	49.1	0.9993
144.26	27.3	0.1965	0.9716	28.5	0.9751
	37.0	0.2702	0.9796	37.9	0.9823
	43.0	0.3241	0.9834	44.4	0.9855
	56.0	0.4385	0.9880	57.4	0.9899
	66.0	0.5314	0.9910	67.1	0.9922
	81.0	0.6882	0.9943	82.5	0.9950
	98.0	0.8581	0.9973	99.1	0.9976
158.15	25.8	0.1090	0.8990	29.3	0.9123
	28.8	0.1230	0.9089	32.6	0.9217
	40.0	0.1640	0.9354	42.2	0.9407
	50.0	0.2186	0.9485	54.7	0.9555
	70.0	0.2953	0.9645	71.7	0.9675
	100.0	0.4382	0.9767	101.5	0.9794
	140.0	0.6528	0.9864	142.7	0.9886
	170.0	0.8107	0.9922	172.5	0.9933
	181.0	0.8650	0.9942	183.4	0.9950
	199.0	0.9407	0.9974	200.1	0.9976
172.04	30.8	0.0685	0.7681	32.6	0.7840
	45.5	0.1087	0.8469	47.4	0.8530
	81.0	0.2050	0.9161	82.2	0.9179
	120.0	0.3164	0.9434	121.4	0.9468
	180.0	0.5042	0.9656	184.7	0.9688
	247.5	0.7082	0.9788	251.2	0.9818
	299.0	0.8609	0.9878	303.8	0.9900
	324.0	0.9175	0.9921	326.0	0.9934
	339.5	0.9513	0.9953	340.8	0.9958

(continued)

TABLE A.19
(continued)

EXPERIMENTAL[120] AND CALCULATED RESULTS OF THE BINARY SYSTEM METHANE (1) - ETHANE (2)

	EXPERIMENTAL			Calculated (Ω_a and Ω_b computed from the Generalized Equation)	
Temp.K	P	x_1	y_1	P	y_1
186.11	36.7	0.0417	0.5585	37.6	0.5698
	61.5	0.0897	0.7358	62.3	0.7415
	104.0	0.1707	0.8471	103.9	0.8469
	180.0	0.3100	0.9116	175.0	0.9116
	275.0	0.5019	0.9435	272.4	0.9476
	400.0	0.7486	0.9674	399.9	0.9714
	482.0	0.8844	0.9792	479.1	0.9833
	524.0	0.9395	0.9866	517.7	0.9895
	550.0	0.9684	0.9919	541.4	0.9937
	562.0	0.9802	0.9949	552.2	0.9957
	568.0	0.9877	0.9973	559.4	0.9972
189.65	35.8	0.0320	0.4600	37.3	0.4774
	60.0	0.0752	0.6741	61.4	0.6832
	95.5	0.1380	0.7964	96.4	0.7995
	140.0	0.2138	0.8626	138.7	0.8620
	200.0	0.3202	0.9026	197.8	0.9053
	300.0	0.4975	0.9369	296.1	0.9403
	400.0	0.6816	0.9550	399.3	0.9607
	500.0	0.8403	0.9706	495.6	0.9753
	562.0	0.9214	0.9803	554.3	0.9844
	600.0	0.9580	0.9876	586.2	0.9900
	615.0	0.9729	0.9908	601.2	0.9928
	625.0	0.9819	0.9934	610.9	0.9948
	634.0	0.9893	0.9963	619.6	0.9967

TABLE A.20

EXPERIMENTAL[119] AND CALCULATED RESULTS OF THE BINARY SYSTEM METHANE (1) - PROPANE (2)

	EXPERIMENTAL			Calculated (Ω_a and Ω_b Computed from the Generalized Equation)	
Temp.K	P_{psia}	x_1	y_1	P_{psia}	y_1
130.37	27.0	0.3924	0.99992	32.3	0.99998
	34.0	0.5007	0.99994	37.8	0.99999
	42.0	0.6982	1.00000	44.6	1.00000
144.26	31.0	0.2109	0.99940	37.4	0.99963
	48.0	0.3005	0.99959	50.8	0.99973
	74.0	0.5258	0.99959	77.4	0.99988
	91.0	0.7200	0.99976	92.9	0.99920
	98.0	0.8306	0.99990	100.3	0.99997
	108.0	0.9287	1.00000	107.8	0.99991
158.15	25.0	0.0873	0.9958	26.7	0.9967
	51.5	0.1791	0.9979	53.3	0.9983
	100.0	0.3510	0.9989	98.2	0.9991
	138.5	0.5450	0.9992	139.5	0.9994
	176.0	0.8000	0.9996	179.3	0.9997
	187.0	0.8738	0.9996	189.9	0.9997
	194.0	0.9135	0.9997	196.3	0.9998
	201.5	0.9497	0.9998	203.1	0.9999
172.04	30.8	0.0692	0.9862	31.6	0.9885
	52.6	0.1196	0.9915	54.0	0.9932
	100.0	0.2270	0.9950	100.6	0.9962
	200.0	0.4909	0.9973	203.8	0.9981
	260.0	0.6907	0.9979	267.0	0.9987
	300.0	0.8423	0.9984	307.8	0.9990
	320.0	0.9032	0.9988	325.2	0.9993
	342.0	0.9650	0.9992	347.4	0.9916
187.54	41.0	0.0629	0.9656	40.7	0.9680
	100.0	0.1506	0.9894	95.7	0.9858
	200.0	0.3042	0.9907	191.3	0.9923
	300.0	0.4769	0.9929	295.0	0.9945
	400.0	0.6728	0.9937	402.7	0.9958
	490.0	0.8450	0.9947	488.0	0.9966
	540.0	0.9230	0.9958	529.8	0.9973
	565.0	0.9623	0.9967	556.7	0.9980
	586.0	0.9810	0.9980	573.4	0.9987

T A B L E A.21

EXPERIMENTAL[32] AND CALCULATED RESULTS FOR THE BINARY SYSTEM METHANE (1) - BUTANE (2)

	EXPERIMENTAL			Calculated (Ω_a and Ω_b computed with the Generalized Eqn.)	
Temp.K	P	x_1	y_1	P	y_1
144.26	25.2	0.1492	1.0000	31.9	1.0000
	49.9	0.3006	1.0000	59.5	1.0000
	99.9	0.8173	1.0000	105.1	1.0000
155.38	20.1	0.0802	0.9998	25.8	0.9999
	50.1	0.1925	0.9999	60.0	1.0000
	100.1	0.3860	0.9999	111.3	1.0000
	150.1	0.6678	0.9999	159.7	1.0000
166.50	50.0	0.1370	0.9997	60.1	0.9999
	100.0	0.2640	0.9998	113.1	0.9999
	150.0	0.3930	0.9998	162.4	1.0000
	200.0	0.5451	0.9999	211.1	1.0000
	250.0	0.7910	0.9999	260.7	1.0000
177.62	50.0	0.0980	0.9990	56.5	0.9994
	100.0	0.1879	0.9994	108.1	0.9997
	149.8	0.2804	0.9995	160.3	0.9997
	199.9	0.3716	0.9996	210.0	0.9998
	299.9	0.5812	0.9997	310.8	0.9998
	350.0	0.7288	0.9997	363.0	0.9998
	400.0	0.9370	0.9997	411.7	0.9999
	420.0	0.9793	0.9998	427.7	1.0000
	420.0	0.9841	0.9998	430.3	1.0000
189.06	101.1	0.1526	0.9983	110.7	0.9989
	201.0	0.2860	0.9990	208.7	0.9993
	300.3	0.4150	0.9991	302.1	0.9995
	400.0	0.5521	0.9990	395.8	0.9994
	501.0	0.7511	0.9987	506.5	0.9994
	550.0	0.9009	0.9986	561.6	0.9994
	600.0	0.9808	0.9987	599.6	0.9995

TABLE A.22

EXPERIMENTAL[110] AND CALCULATED RESULTS OF THE BINARY SYSTEM METHANE (1) - CARBON MONOXIDE (2)

	EXPERIMENTAL			Calculated (Ω_a and Ω_b computed from the Generalized Equation)	
Temp.K	P_{psia}	x_1	y_1	P_{psia}	y_1
122.04	200.0	0.4090	0.0591	194.1	0.1132
	100.0	0.7900	0.3150	99.8	0.2962
130.37	300.0	0.3840	0.1170	289.3	0.1349
	200.0	0.6410	0.2425	201.6	0.2383
	110.0	0.8780	0.4925	109.6	0.4846
	100.0	0.9040	0.5570	98.4	0.5440

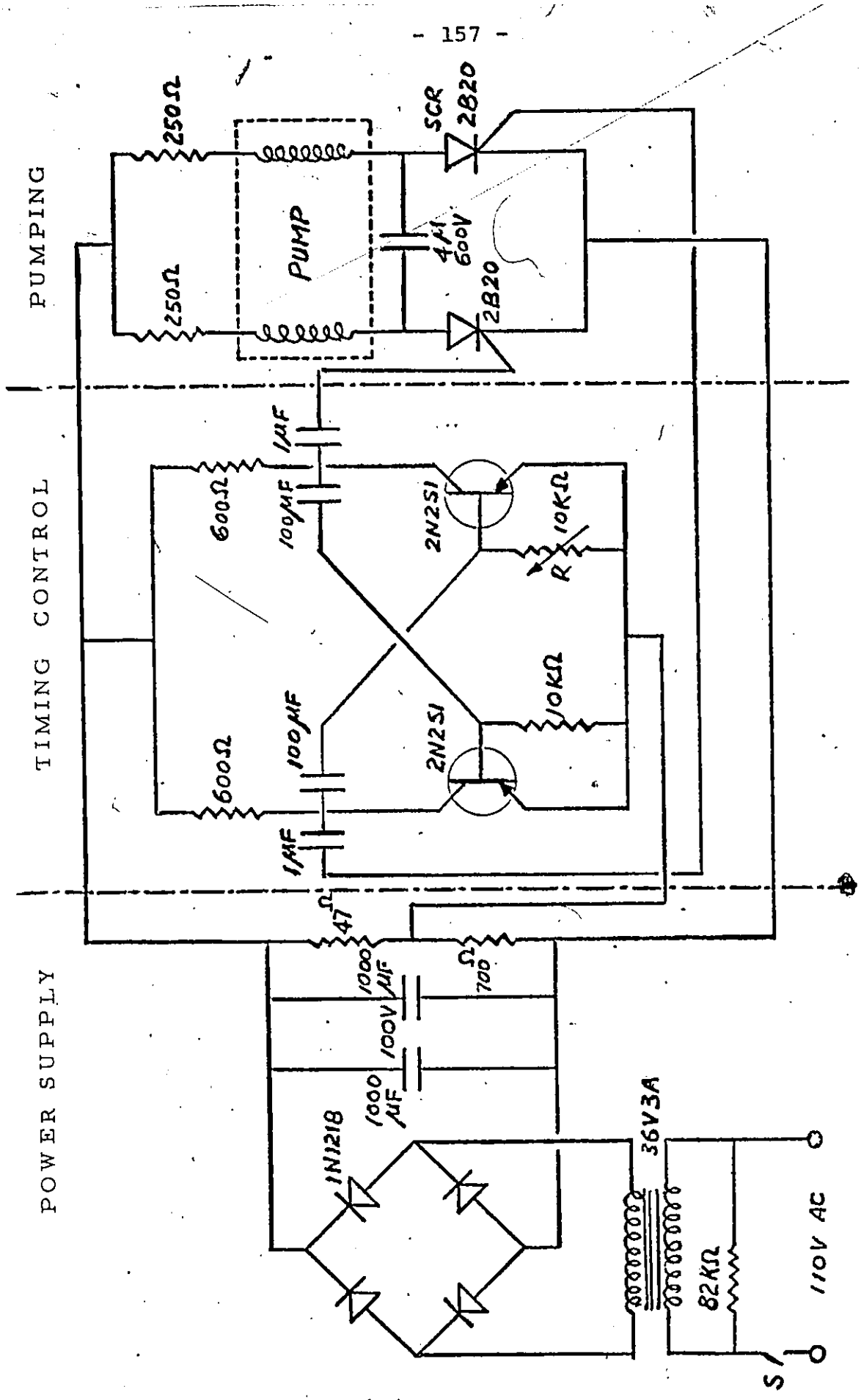
A P P E N D I X B

The Electrical Circuit of the Electromagnetic Pump

The circuit consists of three sections:

(1) the power supply section
(2) the timing control section
(3) the pumping section

The major part of the circuit is similar to that of a Flip-Flop circuit which produces a square wave-output. The action of the pump is within the range of 1.5 milli-second to 1 second per cycle and can be adjusted through a variable resistance.



Electrical Circuit of Electromagnetic Pump

A P P E N D I X C

The General Consistency Test of Chang and Lu[18]

Consistency Test:

For isothermal data, the method proposed by Chang and Lu[18] was employed. A brief description of the method is presented below.

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

$$\sum_{i=1}^{n} x_i \, d \ln \gamma_i = 0 \qquad (A.1)$$

Integrating from point a to its adjacent point b by the trapezoidal rule gives

$$\sum_{i=1}^{n} (x_{ia} + x_{ib}) (\ln \gamma_{ib} - \ln \gamma_{ia}) = 0 \qquad (A.2)$$

The assumption involved here is that all the $\ln \gamma$ vs. x curves can be approximated by segments of straight lines connecting the points. This approach is identical to that employed by Li and Lu[65] and by McDermott and Ellis[73]. At equilibrium

$$\hat{f}_{i\ell} = \hat{f}_{iv}$$

and in the vapor phase

$$\hat{f}_{iv} = y_i \hat{\phi}_i P$$

Hence,

$$\gamma_i(P^\circ,T,x) = \frac{y_i \hat{\phi}_i P}{x_i f^\circ_{i\ell}} \exp \int_{P}^{P^\circ} \frac{\bar{V}_i}{RT} dP \qquad (A.3)$$

Substituting Equation (A.3) into Equation (A.2)

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

$$+ \sum_{i=1}^{n} (x_{ib} + x_{ia}) \int_{P_a}^{P_b} \frac{\bar{V}_{i\ell}}{RT} dP \qquad (A.4)$$

in which $K_i = y_i/x_i$. The left-hand side of Equation (A.4) contains only the experimental equilibrium data while the right-hand side contains the quantities which can be evaluated from the Redlich-Kwong equation of state as modified above. In order to make a test conclusive, maximum experimental error bounds must be estabished. For isothermal data, the overall deviation resulting from experimental errors of the pair tested may be obtained by rearranging Equation (A.4) as follows:

$$\Delta = \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left[\ln \frac{K_{ib}}{K_{ia}} - \ln \frac{\hat{\phi}_{ia} P_a}{\hat{\phi}_{ib} P_b} - \int_{P_a}^{P_b} \frac{\bar{V}_{i\ell}}{RT} dP\right] \qquad (A.5)$$

Differentiating Equation (A.5) and replacing dP, dT and dx by the measuring errors, E(P), E(T) and E(x) respectively, the maximum experimental error bounds are established as follows

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

$$\left. + 2 \left| \left(\ln \frac{K_{ib}}{K_{ia}} - \ln \frac{\hat{\phi}_{ia} P_a}{\hat{\phi}_{ib} P_b} - \int_{P_a}^{P_b} \frac{\bar{V}_{i\ell}\, dP}{RT}\right) \right| \right] E(x)$$

$$+ \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left(\frac{1}{P_a} + \frac{1}{P_b} + \left| \frac{\partial}{\partial P} \int_{P_a}^{P_b} \frac{\bar{V}_{i\ell}\, dP}{RT} \right| \right) E(P)$$

$$+ \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left| \left(\frac{\partial}{\partial T} \int_{P_a}^{P_b} \frac{\bar{V}_{i\ell}\, dP}{RT}\right) \right| E(T) \qquad (A.6)$$

where

E(x) = error in composition x or y measurement

E(P) = error in pressure measurement

E(T) = error in temperature measurement

Experimental data which are widely separated are arranged along any arbitrary path, and tested in pairs by means of Equation (A.5) and (A.6). Each experimental point appears twice in the test, with the exceptions of the first and the last points of the chosen path. An experimental point is considered inconsistent if Δ is greater than $|D|_{max}$. In doing so, a point-by-point evaluation of the data is achieved.

A P P E N D I X D

Evaluation of Volumes and Heats of Mixing by means of the Clausius Equation of State

Calculation of Volume of Mixing:

The volume of mixing of liquid mixtures can be calculated using the expression:

$$\Delta V = \Sigma x_i (\bar{V}_i - V_i) \qquad (D.1)$$

where $\bar{V}_i$ is the partial molar volume and can be expressed using an equation of state as shown in Sections (4.2.2) and (4.4.2).

Calculation of Heat of Mixing:

Heat of mixing is defined by:

$$\Delta H = \sum_i x_i (H_i^* - H_i) - (H^* - H) \qquad (D.2)$$

where $(H^* - H)_T$ is the enthalpy departure from ideal gas behaviour and could be obtained from the thermodynamic relation at a constant temperature

$$(H^* - H)_T = RT - PV + \int_{\infty}^{V} \left[P - T(\partial P/\partial T)_V \right] dV \qquad (D.2)$$

Using the Clausius equation of state (4.68), Equations (4.69) to (4.77) and the mixing rules previously mentioned, one can obtain:

$$\left(\frac{H_i^* - H_i}{RT} \right) = 1 - Z + \left(\frac{A^2}{B} \right) \left[\left[\frac{2h}{1+H} \right] + \left(\frac{V_c}{RB} \right) \left[\frac{h}{1+H} \right]^2 (3s-8) \right] \frac{d\Omega_c}{DT}$$

$$+ \left(\frac{V_c}{RB} \right) \left(\frac{h}{1-h} \right) (4-s) \frac{d\Omega_b}{dT} - \left(\frac{H}{1+H} \right) \left(\frac{s^2 V_c^2 P_c T_c}{C R^2 T^2} \right) \frac{d\Omega_a}{dT} \qquad (D.3)$$

and

$$\left(\frac{H^* - H}{RT}\right) = 1 - Z + \left(\frac{A^2}{B}\right)\left[\left(\frac{2h}{1+H}\right) + \left(\frac{1}{RB}\right)\left(\frac{h}{1+H}\right)^2 \Sigma x_i \frac{dC_i}{dT}\right]$$

$$+ \left(\frac{1}{RB}\right)\left(\frac{h}{1-H}\right)\left(\Sigma x_i \frac{db_i}{dT}\right) - \left(\frac{H}{1+H}\right)\left(\frac{\sum_i \sum_j x_i x_j \frac{da_{ij}}{dT}}{C R^2 T^2}\right) \qquad (D.4)$$

where

$$\frac{da_{ij}}{dT} = a_{ij}\left[\frac{\frac{d(1-k_{ij})}{dT}}{1-k_{ij}} + \frac{\frac{d\Omega_a}{dT} + \frac{d\Omega_{aj}}{dT}}{\Omega_{ai} + \Omega_{aj}}\right] \qquad (D.5)$$

$$\frac{db_i}{dT} = V_c\,(4 - s)\,\frac{d\Omega_{bi}}{dT} \qquad (D.6)$$

$$\frac{dC_i}{dT} = V_c\,(3s - 8)\,\frac{d\Omega_{ci}}{dT} \qquad (D.7)$$

k_{ij} was assumed to be independent of temperature, composition and pressure of the solution, so Equation (D.5) reduces to:

$$\frac{da_{ij}}{dT} = a_{ij}\left[\frac{\frac{d\Omega_{ai}}{dT} + \frac{d\Omega_{aj}}{dT}}{\Omega_{ai} + \Omega_{aj}}\right] \qquad (D.8)$$

A P P E N D I X E

COMPUTER PROGRAMS

- Evaluation of the adjustable parameters of the Redlich-Kwong Equation
- Comparison of the compressibility factors of vapor and liquid using the Redlich-Kwong equation
- Solving a cubic equation (SUBROUTINE CUBEQN)
- Prediction of P-x-y curve
- Evaluation of supporting properties for RK (SUBROUTINE SUPT)
- Evaluation of the activity coefficients and Gibbs Free energy of mixing from both liquid and vapor properties of the mixtures
- Correlation of Ω_a and Ω_b [$\Omega = \Omega(1 - T_r)$]
- Correlation of Ω_a and Ω_b [$\Omega = \Omega(T_r)$]
- k_{12} estimation for binary system (collective version)
- Testing the thermodynamic consistency
- Evaluation of Ω_a, Ω_b and Ω_c of the Clausius equation
- Predict P-x-y curve using the Clausius equation

```
C     ******************************************************************
CCCCCC
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C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION TITLE(20),X(8)
      DIMENSION TT(50),PP(50),VV(50),VVL(50)
    1 READ(1,300)(TITLE(I),I=1,15)
  300 FORMAT(20A4)
      WRITE(3,400)(TITLE(I),I=1,15)
      WRITE(2,400)(TITLE(I),I=1,15)
  400 FORMAT(1H1,10X,51HEVALUATION OF ADJUSTABLE PARAMETERS OF R-K EQN F
     1OR ,15A4///)
      I = 1
      R = 82.0567
      TOL = 0.5D-05
      READ(1,100)PC,VC,TC,W,AMWT
      IF(PC.LE.0.0D0) GO TO 800
  100 FORMAT(8F10.0)
C     THE NEXT TWO CARDS ARE THE INITIAL VALUES OF WA,WB FOR ITERATION
      WA = 0.4278D0
      WB = 0.0867D0
   20 READ(1,100) PP(I),VV(I),TT(I),VVL(I)
      P = PP(I)
      T = TT(I)
      V = VV(I)
      V=R*T/P
      VL = VVL(I)
      IF(P.LT.0.0) GO TO 1
      PR=P/PC
      TR=T/TC
      BATA = (DLOG10(PR)-DLOG10(TR)*8.0D0/3.0D0-0.1832D0*(PR/TR/TR-
     2 1.0D0))/((1.0D0-TR)/TR+DLOG10(TR)*1.8D0)
      ALFA = (VC/VL-1.0D0-(1.0D0-TR)**(1./3.))/((1.0D0-TR)+(1.0D0-TR)
     2**(1./3.))
C     WRITE(3,100)ALFA,BATA
      RT=R*T
      CALL PFK(BATA,TR,PR)
      P=PR*PC
      VL = VC/(1.0D0+ALFA*(1.0D0-TR)+(1.0D0+ALFA)*(1.0D0-TR)**(1./3.))
      ZL=P*VL/R/T
      ZV=P*V/R/T
      A2=WA*TC**2.5/PC/T**2.5
      B=WB*TC/PC/T
      H=B*P/ZL
      E=B*P/ZV
      CALL FUG(W,PR,TR,THI)
      THI = DEXP(2.30259D0*THI)
C     WRITE(3,100)T,P,VL,V,THI
      ZLL=ZL
      ZVV=ZV
      THIL=THI
      THIV=THI
      HOLD=H
      IJK=0
   39 IJK=IJK+1
      IF(IJK.GE.30) GO TO 49
      J=0
   40 CONTINUE
      IH=0
   41 IF(H.LT.1.0D0) GO TO 42
      H = H - 0.05D0
      IH=IH+1
      IF(IH.LT.20) GO TO 41
   43 H = 0.98D0
   42 J=J+1
      RH = (1.0D0-ZL*(1.0D0-H))*(1.0D0+H)*DLOG(1.0D0+H)/H/(1.0D0-H)
      FFH = DLOG(ZL*THIV)+1.D0-ZL+DLOG(1.0D0-H)+RH
      DFFH = -1.0D0/(1.0D0-H)+RH*(ZL/(1.0D0-ZL*(1.0D0-H))
     2 +(-1.0D0+2.0D0*H+H*H)/H/(1.0D0-H*H)+1.0D0/(1.0D0+H)/DLOG(1.0D0+H
```

```
     3 ))
       TEST=FFH/DFFH
       H=H-TEST
       IF(J.GT.40)GO TO 45
       IF(DABS(TEST/H).GT.TOL) GO TO 40
    45 B=H*ZL/P
       A2 = B*(1.0D0/(1.0D0-H)-ZL)*(1.0+H)/H
       IJ=0
    47 IF(E.GT.0.0D0) GO TO 46
       E = E + 0.01D0
       IH=IH+1
       IF(IH.LT.20)GO TO 47
       E = 0.02D0
    46 IJ=IJ+1
       IH=0
       FE = -B*P/E+1.0D0/(1.0D0-E)-(A2/B)*E/(1.0D0+E)
       DFE = B*P/E**2+1.0D0/(1.0D0-E)**2-(A2/B)/(1.0D0+E)**2
       TEST=FE/DFE
       E=E-TEST
       IF(IJ.GT.40)GO TO 48
       IF(DABS(TEST/E).GT.TOL) GO TO 47
    48 ZVV=B*P/E
       THIV = ZVV-1.0D0-DLOG(ZVV*(1.0D0-E))-(A2/B)*DLOG(1.0D0+E)
       THIV = DEXP(THIV)
C      WRITE(3,501) J,IJ,IJK
  501  FORMAT(3I5)
       IF(DABS(H-HOLB)/H.LE.TOL*10.0D0) GO TO 49
C      WRITE(3,200)P,T,ZV,ZVV,VL,VLL,THIV,THIL,WA,WB,THI,H,E
       HOLD=H
       GO TO 39
    49 ZLL=B*P/H
       VLL=R*T*ZLL/P
       THIL = ZLL -1.0D0-DLOG(ZLL-B*P)-(A2/B)*DLOG(1.0D0+B*P/ZLL)
       THIL = 1.0D0/DEXP(-THIL)
       WB=B*PC*T/TC
       WA=A2*PC*T**2.5/TC**2.5
  500  FORMAT(I5,3F10.4,5F10.6)
       DTHI=THI-THIV
       DZV=ZV-ZVV
C   51 WRITE(3,200) P,T,ZV,WA,WB
       WRITE(3,200) I,P,T,TR,WA,WB,DZV,VL,VLL
       WRITE(2,5000) T,TR,WA,WB
 5000  FORMAT(4(F10.7))
       WRITE(3,2000)
 2000  FORMAT('----------------------------------------------------------
      &----------------------------------------------------------')
  200  FORMAT(//I3,8(3X,D13.8))
C 200  FORMAT(//I3,6(5X,D14.8))
 1000  FORMAT(3D15.8)
       I = I + 1
       GO TO 20
  800  STOP
       END
       SUBROUTINE FUG(W,PR,TR,THI)
C      GENERALIZED CORRELATION OF FUGACITY COEFFICIENT OF PURE
C      COMPONENTS AT SATURATION.
       IMPLICIT REAL*8(A-H,O-Z)
    10 IF(TR.GT.0.56D0) GO TO 20
       THI=(PR/2.303)*((.1445-(.330+(.1385+(.0121)/TR)/TR)/TR)/TR
      1+W*(.073+(.460-(.5+(.097+.0073/TR**5)/TR)/TR)/TR)/TR)
       RETURN
    20 IF(TR.GT.0.70D0) GO TO 30
       THI=(-.53746+(.58798-(.18226-.009499/TR)/TR)/TR)
      1+W*(.11821-(.006542+(.045992-.0116504/TR)/TR)/TR)
       RETURN
    30 IF(TR.GT.0.84D0) GO TO 40
       THI=(-.65625+(.47890+(.13943-.12167/TR)/TR)/TR)
      1+W*(-.47886+(.53604+(.08951-.14448/TR)/TR)/TR)
       RETURN
    40 THI=(-0.87471+(0.73459-(0.11130-(0.27772-0.20204/TR)/TR)/TR)/TR)
      1+W*(-1.15987+(1.25872-(.13670-(.35086-.34700/TR)/TR)/TR)/TR)
       RETURN
       END
       SUBROUTINE PFK(BATA,TR,PR)
       IMPLICIT REAL*8(A-H,O-Z)
       ITER=0
```

```
      TOL=0.00001D0
      PRC=-0.1832D0
   30 PR=BATA*(1.-TR)/TR+(1.8*BATA+8./3.)*DLOG10(TR)+PRC
      PRC=0.1832D0*(DEXP(PR*2.30259D0)/TR/TR-1.0D0)
      ITER=ITER+1
      IF(ITER.GT.20) GO TO 32
      IF(ITER.EQ.1) GO TO 31
      IF(DABS((PR-PROLD)/PR).LT.TOL) GO TO 32
   31 PROLD=PR
      GO TO 30
   32 PR = DEXP(PR*2.30259D0)
      RETURN
      END
```

****
****
****

```
C     ******************************************************************
C
C     COMPARISON OF COMPRESSIBLITY FACTORS OF VAPOR AND LIQUID
C     USING THE REDLICH-KWONG EQUATION OF STATE
C
C     ******************************************************************
C
C     THE SAME PROGRAM CAN BE USED FOR ANY CUBIC EQUATION AS CLAUSIUS
C     THE COEFFICIENTS OF THE EQUATION HAST/ BE CHANGED
C
C     M = 1 FOR VAPOR PHASE
C     M = 2 FOR LIQUID PHASE
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION TITLE(80)
      DIMENSION PP(50),VV(50),TT(50)
      DIMENSION VL(50),VAP(50),DVL(50),DVAP(50),DV(50)
      DIMENSION A(4),Z(3)
    1 READ (1,10) (TITLE(I),I=1,80)
      WRITE(3,20) (TITLE(I),I=1,80)
   10 FORMAT(80A1)
   20 FORMAT(1H1,80A1)
      READ(1,30) M,N
      DO 3 I=1,N
    3 DV(I) = 0.0
      DZ = 0.0
      IF(N.EQ.0) GO TO 400
   30 FORMAT(2I5)
      READ(1,40) PC,TC,VC,W,WA,WB,R
      WRITE(3,41) PC,VC,TC,W,WA,WB,R
   40 FORMAT(8F10.0)
   41 FORMAT(///5X,8(F10.5))
      DO 51 I=1,N
      READ(1,50) PP(I),VV(I),TT(I)
   51 WRITE(3,52) PP(I),VV(I),TT(I)
   50 FORMAT(3F10.0)
   52 FORMAT(///20X,3(F10.5,10X))
      A2=WA*R*R*(TC**2.5)/PC
      B=WB*R*TC/PC
      DO100 I=1, N
      RT = R*TT(I)
      P=PP(I)
      T=TT(I)
      A(1)=1.0
      A(2)=-RT/P
      A(3)=-(B*B +RT*B/P-A2/P/T**.5)
      A(4)=-(A2*B/P/T**.5)
      CALL CUBEQN(INDEX,A,Z)
      WRITE(3,300) Z(1),Z(2),Z(3)
  300 FORMAT(10X,3D15.8)
      IF(INDEX.EQ.1)GOTO9001
      IF(M.EQ.1) GO TO 60
      IF(M.EQ.2) GO TO 70
   60 VAP(I) =DMAX1(Z(1),Z(2),Z(3))
      DVAP(I) = VV(I) - VAP(I)
      WRITE(3,80) PP(I),TT(I),VV(I),VAP(I),DVAP(I)
   80 FORMAT(5X,'P= ',F10.5,2X,'T= ',F10.5,2X,'V= ',F10.5,2X,'VCAL= ',
     2 F10.5,2X,'DEV= ',D15.8)
      DV(I) = DV(I) + DABS(DVAP(I))
      ZV = (PP(I)*VV(I))/RT
      ZVCAL = (PP(I)*VAP(I))/RT
      DZV = ZV - ZVCAL
      WRITE(3,90) ZV,ZVCAL,DZV
   90 FORMAT(5X,'Z= ',D15.8,2X,'ZCAL= ',D15.8,2X,'DZ= ',D15.8)
      DZ = DZ + DABS(DZV)
      GO TO 101
   70 VL(I) = DMIN1(Z(1),Z(2),Z(3))
      DVL(I) =VV(I) - VL(I)
      WRITE(3,80) PP(I),TT(I),VV(I),VL(I),DVL(I)
      DV(I)= DV(I) + DABS(DVL(I))
      ZL = (PP(I)*VV(I))/RT
      ZLCAL = (PP(I)*VL(I))/RT
      DZL = ZL - ZLCAL
      WRITE(3,90) ZL,ZLCAL,DZL
```

```
      DZ = DZ + DABS(DZL)
      GO TO 101
 9001 VAP(I)=Z(2)
      DVAP(I)=VV(I)-VAP(I)
      WRITE(3,80) PP(I),TT(I),VV(I),VAP(I),DVAP(I)
      DV(I) = DV(I) + DABS(DVAP(I))
      ZV = (PP(I)*VV(I))/RT
      ZVCAL = (PP(I)*VAP(I))/RT
      DZV = ZV - ZVCAL
      WRITE(3,90) ZV,ZVCAL,DZV
      DZ = DZ + DABS(DZV)
      GO TO 101
  101 CONTINUE
  100 CONTINUE
      DDV=0.0
      DO433 K=1,N
  433 DDV=DDV+DV(K)
      DDV  =DDV/N
      DZ = DZ / N
      WRITE(3,200) DDV   ,DZ
  200 FORMAT(////25X,'AV. DEV. IN MOL. VOLUME = ',2X,D15.8///
     2 25X ,'AV, DEV, IN COMPRESSIBILITY = ',2X,D15.8)
      GO TO 1
  400 RETURN
      END
```

****
****
****

```
C     ******************************************************************
C
      SUBROUTINE CUBEQN(INDEX,LI,LJ)
C     ******************************************************************
C    SOLVING EQN F(Z)=A(1)*Z**3+A(2)*Z**2+A(3)*Z+A(4)=0
C    BY SHINN-DER CHANG ( DEPT OF CHEM ENG , UNIV OF OTTAWA )
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*4 LI(4),LJ(3)
      DIMENSION A(4),Z(3)
      DO 15 I=1,4
   15 A(I)=LI(I)
      DO 25 I=1,3
   25 Z(I)=LJ(I)
      P=(A(3)-A(2)**2/A(1)/3.0D0)/A(1)
      Q=2.0D0*(A(2)/3.0D0/A(1))**3-A(3)*A(2)/3.0D0/A(1)**2+A(4)/A(1)
      DE=(P/3.0D0)**3+(Q/2.0D0)**2
      T=A(2)/3.0D0/A(1)
      IF(DE.GE.0.0D0) GO TO 5
      THI=DARCOS(-(Q/2.0D0)/DSQRT(-(P/3.0D0)**3))
      R=2.0D0*DSQRT(-P/3.0D0)*DCOS(THI/3.0D0)
      GO TO 8
    5 S=(-(Q/2.0D0)+DSQRT(DE))
      U=(-Q/2.0D0-DSQRT(DE))
      IF(S) 6,7,6
    6 S=S/DABS(S)*(S*S)**(1.0D0/6.0D0)
    7 IF(U) 9,11,9
    9 U=U/DABS(U)*(U*U)**(1.0D0/6.0D0)
   11 R=S+U
    8 DISC=R*R-4.0D0*(P+R*R)
      IF(DISC)40,10,30
   10 INDEX=0
      Z(1)=R-T
      Z(2)=-R/2.0D0-T
      Z(3)=Z(2)
      GO TO 26
   30 INDEX=-1
      Z(1)=R-T
      Z(2)=-R/2.0D0+DSQRT(DISC)/2.0D0-T
      Z(3)=-R/2.0D0-DSQRT(DISC)/2.0D0-T
      GO TO 26
   40 INDEX=1
      Z(1)=R-T
      DB=DSQRT(DABS(DISC))/2.0D0
      DA=-R/2.0D0-T
      Z(2)=Z(1)
      Z(3)=Z(1)
C     WRITE(3,100)DA,DB
  100 FORMAT( /'THERE ARE TWO CONJUGATE ROOTS , REAL PART= ',E15.6
     1 /27X,'IMAG. PART= ',E15.6/)
   26 DO 27 I=1,3
   27 LJ(I)=Z(I)
      RETURN
      END
```

```
*****************************************
**********************
```

```
C     ******************************************************************
C
C     PREDICT P-X-Y CURVE
C     MODIFIED REDLICH-KWONG EQUATION OF STATE IS USED
C     FOR MULTICOMPONENT  SYSTEMS CALCULATION
C     FROM THE PURE COMPONENT PROPERTIES
C     ONE OF THE COMPONENTS IS AT ITS HYPERCRITICAL STATE
C     WRITTEN BY CHU HSI ,CHEMICAL ENGINEERING DEPARTMENT, UNIV. OF OTTA
C     SUBROUTINES SUPT,EQNRK, CUBEQN ARE SUPPLIED BY S.D.CHANG
C     FALSI-POSITION METHOD IS EMPLOYED
C     MAY 28,1971
C
C     ******************************************************************
      DIMENSION PHI(5),X(5), F( 5),GAMMA(5),FREFER(5),PVOL(5),Y(5),
     1 PC(5),VC(5),TC(5),W(5),C1RKV(5),C2RKV(5),C1RKL(5),C2RKL(5),
     2 AMOLWT(5),COMPA(5),COMPB(5),CORRV(5,5),CORRL(5,5),GAMALN(5),
     3 A(4),Z(3),TITLE(20),D(5),PCO(5),VCO(5),TCO(5),PHIV(5),FREF(5),
     4 PS(5),PP(80),XX(80,5),YY(80,5),YCAL(5),PPVOL(5),DC1DT(5),DC2DT(5)
     5,YD(5),RATIO(5),VVL(80),ZZL(80),ZZV(80),YI(5),G(5),YO(5),YPD(5)
      COMMON  /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM,ZZZL,ZZZV
     1    /SECOND/ Z,A,MTYPE
  800 READ(1,5)(TITLE(I),I=1,19)
    6 FORMAT(1H1,19A4)
    5 FORMAT(    19A4)
      WRITE(3,6)(TITLE(I),I=1,19)
      READ(1,500)NCOMP,NQNTUM,IJK,R
      IF(NCOMP.LE.0) GO TO 900
      WRITE(3,505)
      DO 210 I=1,NCOMP
      READ(1,510)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),
     1                                 COMPA(I),COMPB(I)
      C1RKV(I)=C1RKL(I)
      C2RKV(I)=C2RKL(I)
  210 WRITE(3,515)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),
     1                                 COMPA(I),COMPB(I)
      CORRL(NCOMP,NCOMP)=0.0
      NCOMP1=NCOMP-1
      WRITE(3,519)
  519 FORMAT(/10X,12HINPUT DATA :///4X,1HP,8X,2HX1,8X,2HX2,9X,1HT,7X,3HRA
     11,7X,3HRB1,7X,3HRA2,7X,3HRB2//)
      DO 9 I=1,NCOMP1
      I1=I+1
      DO 9 J=I1,NCOMP
    9 READ(1,520)CORRL(I,J)
      READ(1,520)  TTT,PSI,(YI(J),J=1,NCOMP)
C     THE LOOP HAS TO BE THOROUGHLY CHECKED FOR THE SELECTION OF
      THE INITIAL VALUES OF PRESSURE
      PSI=PSI/14.697
      PSII=PSI
C     PSI=PSI/760.
      I=0
   10 I=I+1
C     YPD=PERCENTAGE DEVIATION IN Y
      SX=0.0
      SY=0.0
C     READ(1,520)TTT,PP(I),(XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
C     READ( 1,520)  PP(I),(XX(I,J),J=1,NCOMP1),(YY(I,J),J=1,NCOMP1)
C    1 ,VVL(I)
     1  ,ZZL(I),ZZV(I)
      DO 15 J=1,NCOMP1
      SY=SY+YY(I,J)
   15 SX=SX+  XX(I,J)
      XX(I,NCOMP)=1.0-SX
      YY(I,NCOMP)=1.0-SY
      IF(R.LT.11.0)  GO TO 16
C     PP(I)=PP(I)/760.
      PP(I)=PP(I)/14.697
   16 WRITE(3,520)  PP(I),(XX(I,J),J=1,NCOMP ),(YY(I,J),J=1,NCOMP )
C    1 ,VVL(I)
      IF(PP(I).GE.0) GO TO 10
   20 NOBS=I-1
      READ(1,525)IJK,KIJ,CINI,CFIN
  525 FORMAT(2I5,2F10.4)
   30 KIJ=KIJ+1
      IF(KIJ.GE.2)  GO TO 800
```

```
      WRITE(3,525)IJK,KIJ,CINI,CFIN
      K=0
C     THE NEXT TWO CARDS CAN BE INTERCHANGED IF A SEARCH FOR K12 NEEDED
      KK=0
      KK=20
  280 CONTINUE
      WRITE(3,6)(TITLE(I),I=1,19)
      KK=KK+1
      WRITE(3,516)
      DO 220 I=1,NCOMP1
      CORRL(I,I)=0.0
      I1=I+1
      DO 220 J=I1,NCOMP
      IF(KK.GE.20) GO TO 214
      CORRL(I,J)=CINI+(KK-1)*(CFIN-CINI)/10.
      PSI=PSII
  214 WRITE(3,530)I,J,CORRL(I,J)
      CORRL(J,I)=CORRL(I,J)
  220 CONTINUE
      K=0
      SDP=0.0
      SDV=0.0
      SSYD=0.0
      IF(NONTUM.GE.1) GO TO 223
      DO 221 I=1,NCOMP
      PC(I)=PCO(I)
      VC(I)=VCO(I)
  221 TC(I)=TCO(I)
  120 T=TTT
      RT=R*T
      WRITE(3,535)
  535 FORMAT(/10X,9HCOMPONENT,1X,1HX,7X,1HY,7X,2HYY,7X,2HYD,4X,4HV(P),6X
     1  ,5HV(PO),5X,4HPHIL,6X,4HPHIV,6X,4HSUMY,6X,4HITER,4X,3HNIY/)
  223 CONTINUE
      NIP=0
      MIP=0
      P=PSI
      K=K+1
      ZZZV=ZZV(K)
      ZZZL=ZZL(K)
      DO 39 J=1,NCOMP
   39 PHIV(J)=1.0
   54 CONTINUE
      DO 40 J=1,NCOMP
   40 X(J)=XX(K,J)
   42 CALL SUPT(VL,PHI,PPVOL,C1RKL,C2RKL,CORRL,X,1,KIJ)
      JY=0
   63 IF(JY.GT.20) GO TO 61
      SUMY=0.
      DO 50 J=1,NCOMP
      Y(J)=PHI(J)*X(J)/PHIV(J)
   50 SUMY=SUMY+Y(J)
      IF(JY)60,45,60
   60 IF(ABS((SUMYO-SUMY)/SUMY).LE.0.0005) GO TO 61
   45 SUMYO=SUMY
      JY=JY+1
      DO 62 J=1,NCOMP
   62 Y(J)=Y(J)/SUMY
      CALLSUPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
      GO TO 63
   61 CONTINUE
      DY=SUMY-1.0
      IF(ABS(DY).LE.0.0001) GO TO 110
      IF(NIP.GT.100) GO TO 105
      IF(MIP.GT.20) GO TO 105
      IF(MIP)52,52,56
   52 IF(NIP.LE.0) GO TO 51
      IF((DY*DDY).LT.0.0) GO TO 55
   51 NIP=NIP+1
      IF(NIP-1)91,91,92
   91 POLD=P
      DDY=DY
      P=P+0.01
      GO TO 70
   92 SLOPE=(P-POLD)/(DY-DDY)
      DELP=SLOPE*DY
```

```
      IF(ABS(DELP)-1.0)79,79,78
   78 DELP=SIGN(1.0,DELP)
   79 POLD=P
      DDY=DY
      P=P-DELP
      GO TO 70
   56 IF((DY*DDY).LT.0.0)GO TO 55
      IF((DY*DYO).LT.0.0)  GO TO 57
   55 IF(ABS((P-POLD)/P).LE.0.0001) GO TO 105
      PN=(DY*POLD-DDY*P)/(DY-DDY)
      GO TO 58
   57 IF(ABS((P-PO)/P).LE.0.0001) GO TO 105
      PN=(DY*PO-DYO*P)/(DY-DYO)
      GO TO 59
   58 PO=POLD
      DYO=DDY
   59 POLD=P
      DDY=DY
      P=PN
      MIP=MIP+1
   70 DO 53 J=1,NCOMP
   53 Y(J)=Y(J)/SUMY
      CALL SUPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
      GO TO 54
  105 IF(ABS(DY).LE.0.005) GO TO 110
   96 WRITE(3,601)
C     WHEN ATM. UNIT ARE USED THE NEXT TWO CARDS ARE COMMENTED AND 11/ G
C     THE NEXT CARD
  110 P=P*14.697
      PP(K)=PP(K)*14.697
C 110 DP=P-PP(K)
      DP=P-PP(K)
      SDP=SDP+ABS(DP)
      PDPP=ABS(DP)/PP(K)
      WRITE(3,600) T,P,PP(K),DP,PDPP
C     COMMENT FOR ATMOS UNIT
      PP(K)=PP(K)/14.697
  600 FORMAT(3X,3HT= ,F8.2,5H  P= ,F10.4,7HPP(K)= ,E10.4,4HDP= ,F10.4,
     C5HPDPP=,F10.4)
      SYD=0.0
      DO 111 J=1,NCOMP
      YD(J)=Y(J)-YY(K,J)
C     YPD(J)=YD(J)/YY(K,J)
  111 SYD=SYD+ABS(YD(J))
      SSYD=SSYD+SYD
      DO 311 J=1,NCOMP
  311 WRITE(3,610)YPD(J),
     C              COMPA(J),COMPB(J),X(J),Y(J),YY(K,J),YD(J),PPVOL(J),
     1PVOL(J),PHI(J),PHIV(J),SUMY,NIP,MIP
      DV=VL-VVL(K)
      SDV=SDV+ABS(DV)
      WRITE(3,901)VL,VVL(K),DV
  901 FORMAT(15X,4HVL= ,F10.4,5HVVL= ,F10.4,4HDV= ,F10.4)
  610 FORMAT(F10.4,2A3,4E12.4,4F10.4,F8.4,2I5)
  601 FORMAT(1H0,87HFAILED TO CONVERGE, RESULTS BELOW ARE NOT RELIABLE I
     1F SUMY IS MUCH DIFFERENT FROM UNITY)
      PSI=P
C     COMMENT THE NEXT CARD IF ATMOS. IS USED
      PSI=PSI/14.697
      IF(K-NOBS) 223, 850,850
  850 CONTINUE
      WRITE(3,620)SDP,SSYD,SDV
  620 FORMAT(/10X,'ACCUM. SUM OF DEV. IN P IS ',E12.4,'ACCUM. SUM OF
     1DEV. IN Y IS ',E12.4,'SDV IS ',E12.4/)
      IF(KK-11)280,30,30
  900 STOP
  500 FORMAT (3I5,F10.4)
  505 FORMAT(1H0,4X,2HPC,10X,2HVC,6X,2HTC,10X,1HW,7X,5HC1RKL,5X,5HC2RKL,
     15X,5HMOLWT,4X,9HCOMPONENT//)
  515 FORMAT(1H ,6E12.5,3X,2A4)
  516 FORMAT(1H0 / 1H ,16X,3HKIJ                    / )
  510 FORMAT(4F8.4,2F8.4,24X,2A4)
  520 FORMAT(14F10.4)
  530 FORMAT(1H ,6X,2I2,F10.4,2F10.4)
      END
C
```

```
C
CC      ***********************************************************************
        SUBROUTINE SUPT(VL,PHI, PVOL ,C1RKL,C2RKL,CORRL,X,LV,KIJ)
C       ***********************************************************************
CCCC    EVALUTION OF SUPPORTING PROPERTIES,THE FUGACITY AND THE
        PARTIAL MOLAL VOLUME OF FLUID MIXTURES.
C       SHINN-DER CHANG, DEPT.OF CHEM.ENG., UNIV. OF OTTAWA.
        DIMENSION TC(5),PC(5),VCO(5),W(5),AMOLWT(5)   ,ARKL(5,5),BRKL(5),
       1  WIJ(5,5),TCOIJ(5,5),TCIJ(5,5),A(4),Z(3),C1RKL(5),C2RKL(5),
       1  PVOL(5),PHI(5),CORRL(5,5),X(5),A2I(5),BI(5),AIRKL(5)
        DIMENSION ZZ(3)
        COMMON  /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM,ZZZL,ZZZV
       1   /SECOND/ Z,A,MTYPE
C       LV=0, FOR VAPOR PHASE.
CCCC    LV=1, FOR LIQUID PHASE.
        KIJ=1, TCIJ=SQRT(TCI*TCJ)*(1.-KIJ)
CCCC    KIJ=2, AIJ=SQRT(AI*AJ)*(1.-KIJ)
C       KIJ=3, AIJ=(AI*KIJ+(1.-KIJ)*AJ)/2.
        RT=R*T
   91   DO 100 I=1,NCOMP
        ARKL(I,I)=C1RKL(I)* R*R     *(TC(I)**2.5)/PC(I)
        BRKL(I)=C2RKL(I)* R    *TC(I)/PC(I)
  100   CONTINUE
        I=1
  197   I1=I+1
        DO1100 J=I1,NCOMP
        IF(KIJ.GT.1)  GO TO 97
        TCIJ( I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
        TCIJ( J,I)=TCIJ( I,J)
        WIJ(I,J)=(W(I)+W(J))*0.5
        ZCOIJ=0.291-0.08*WIJ(I,J)
   94   VCOIJ=(VCO(I)**(1./3.)+VCO(J)**(1./3.))**3/8.0
   96   PCOIJ=ZCOIJ* R    *TCIJ( I,J)/VCOIJ
        PCIJ=PCOIJ
   95   ARKL(I,J)=(C1RKL(I)+C1RKL(J))*0.5* R   **2*TCIJ(I,J)**2.5/PCIJ
        GO TO 98
   97   IF(KIJ.GT.2)  GO TO 99
        ARKL(I,J)=(ARKL(I,I)*ARKL(J,J))**0.5*(1.0-CORRL(I,J))
        GO TO 98
   99   ARKL(I,J)=(ARKL(I,I)*CORRL(I,J)+(1.-CORRL(I,J))*ARKL(J,J))
   98   ARKL(J,I)=ARKL(I,J)
 1100   CONTINUE
        I=I+1
        IF(I.NE.NCOMP)GOTO 197
        AMRKL=0.0
        BMRKL=0.0
        DO 120 I=1,NCOMP
        A2I(I)=ARKL(I,I)/RT**2/T**0.5
        BI(I)=BRKL(I)/RT
        BMRKL=BMRKL+X(I)*BRKL(I)
        AIRKL(I)=0.0
        DO 120 J=1,NCOMP
        AIRKL(I)=AIRKL(I)+X(J)*ARKL(I,J)
  120   AMRKL=AMRKL+X(I)*X(J)*ARKL(I,J)
        A2=AMRKL/RT**2/T**0.5
        B=BMRKL/RT
C       WRITE(3,711)BMRKL,      B,R,T,P
  711   FORMAT(3X,5E12.5)
        A(1)=1.0
        A(2)=-1.0
        A(3)=B*P*(A2/B-1.0-B*P)
        A(4)=-(A2/B)*(B*P)**2
        CALL CUBEQN(MTYPE,A,Z)
        IF(MTYPE)115, 140, 140
  115   IF(LV.EQ.0)  GO TO 145
C       ZL=AMIN1(Z(1),Z(2),Z(3))
        ZL=AMIN1(Z(1),Z(2),Z(3))
C       JJ=0
CC      DO 146 I=1,3
CC      ZZ(I)=9999.
CC      JJ=JJ+1
CC      IF(Z(I).LT.0.0)  GO TO 146
CC      ZZ(JJ)=Z(I)
C 146   CONTINUE
C       ZL=AMIN1(ZZ(1),ZZ(2),ZZ(3))
```

```
      GO TO 150
  145 ZL=AMAX1(Z(1),Z(2),Z(3))
      GO TO 150
  140 ZL=Z(1)
C     IF(ZL.GT.0.0) GO TO 126
C     ZL=ZZZL
C 126 IF(ZL.LE.1000.) GO TO 123
C     ZL=ZZZV
  123 CONTINUE
  150 H=B*P/ZL
      IF(1.0-H) 127,127,128
  127 IF(LV.EQ.0) GO TO 124
      H=0.98
      GO TO 128
  124 H=0.02
  128 IF(1.0+H) 129,129,131
  129 IF(LV.EQ.0) GO TO 132
      H=0.98
      GO TO 131
  132 H=0.02
  131 CONTINUE
      VL=RT*B/H
C     WRITE(3,710)LV,ZL,VL,B,H,MTYPE
  710 FORMAT(3X,'LV= ',I3,2X,'ZL= ',E12.5,2X,'VL= ',E12.5,2X
     1,'B= ',E12.5,2X,'H= ',E12.5,2X,'MTYPE= ',I3)
C     CALL EQNRK(A2,B,P,H,ZL,LV)
      IF(LV.EQ.0) GO TO 135
      QD=(T**0.5)*VL*(VL+BMRKL)
      QH=(AMRKL/(T**0.5))*((2.*VL+BMRKL)/(VL**2*(VL+BMRKL)**2))
      QK=RT/((VL-BMRKL)**2  )
  135 DO 130 I=1,NCOMP
C     WRITE(3,591)ZL,H
      PHILN =(ZL-1.0)*BI(I)/B-ALOG(ZL)-ALOG(1.0-H)
     1   -(A2/B)*(2.0*AIRKL(I)/AMRKL  -BI(I)/B)*ALOG(1.0+H)
      PHI(I)= EXP(PHILN )
C     WRITE(3,592)PHI(I),LV
  592 FORMAT(/3X,E12.5,2X,I3)
      IF(LV.EQ.0) GO TO 130
      QE1=0.0
      DO 125 J=1,NCOMP
  125 QE1=QE1+X(J)*ARKL(I,J)
      QE=2.0*QE1-AMRKL*BRKL(I)/(VL+BMRKL)
      QG=(RT/(VL-BMRKL))*(1.0+BRKL(I)/(VL-BMRKL))
      FVOL(I)=((QE/QD)-QG)/(QH-QK)
  130 CONTINUE
  300 RETURN
      END
```

****
****
****

```
C     ******************************************************************
CCCCCCC
      EVALUATION OF THE ACTIVITY COEFFICIENTS FROM BOTH LIQUID AND
      VAPOR PROPERTIS OF THE MIXTURES
      REDLICH -KWONG EQUATION OF STATE WITH AMODIFIED PROCEDUREWAS USED

      HSI THESIS ,UNIVERSITY OF OTTAWA 1970
      THE UNITS IS GIVEN IN ATM.,CC,DEGREE K
C
C     ******************************************************************
      DIMENSION PHI(5),X(5), F( 5),GAMMA(5),FREFER(5),PVOL(5),Y(5),
     1 PC(5),VC(5),TC(5),W(5),C1RKV(5),C2RKV(5),C1RKL(5),C2RKL(5),
     2 AMOLWT(5),COMPA(5),COMPB(5),CORRV(5,5),CORRL(5,5),GAMALN(5),
     3 A(4),Z(3),TITLE(20),D(5),PCO(5),VCO(5),TCO(5),PHIV(5),FREF(5),
     4 PS(5),PP(80),XX(80,5),YY(80,5),YCAL(5),PPVOL(5),DC1DT(5),DC2DT(5)
     5,YD(5),PPP(80), VVL(80),ZZL(80),ZZV(80),YI(5),G(5),YO(5),PCOR(5)
      COMMON  /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM,ZZZL,ZZZV
     1    /SECOND/ Z,A,MTYPE
  800 READ(1,5)(TITLE(I),I=1,19)
    6 FORMAT(1H1,19A4)
    5 FORMAT(     19A4)
      WRITE(3,6)(TITLE(I),I=1,19)
      READ(1,500)NCOMP,NQNTUM,IJK,R
      IF(NCOMP.LE.0) GO TO 900
      WRITE(3,505)
      DO 210 I=1,NCOMP
      READ(1,510)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),
     1DC1DT(I),DC2DT(I),                  COMPA(I),COMPB(I)
      C1RKV(I)=C1RKL(I)
      C2RKV(I)=C2RKL(I)
  210 WRITE(3,515)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),
     1DC1DT(I),DC2DT(I),                  COMPA(I),COMPB(I)
      CORRL(NCOMP,NCOMP)=0.0
      NCOMP1=NCOMP-1
      WRITE(3,519)
  519 FORMAT(/10X,12HINPUT DATA :///4X,1HP,8X,2HX1,8X,2HX2,9X,1HT,7X,3HRA
     11,7X,3HRB1,7X,3HRA2,7X,3HRB2//)
      DO 9 I=1,NCOMP1
      I1=I+1
      DO 9 J=I1,NCOMP
    9 READ(1,520)CORRL(I,J)
      I=0
   10 I=I+1
      SX=0.0
      SY=0.0
C     READ(1,520)TTT,PP(I),(XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
      READ( 1,520)  PP(I),(XX(I,J),J=1,NCOMP1),(YY(I,J),J=1,NCOMP1)
     C,PPP(I)
C     PP(I)=PP(I)/760.
      PP(I)=PP(I)/14.697
      PPP(I)=PPP(I)/14.697
      DO 15 J=1,NCOMP1
      SY=SY+YY(I,J)
   15 SX=SX+ XX(I,J)
      XX(I,NCOMP)=1.0-SX
      YY(I,NCOMP)=1.0-SY
      IF(R.LT.11.0)  GO TO 16
   16 WRITE(3,520)  PP(I),(XX(I,J),J=1,NCOMP ),(YY(I,J),J=1,NCOMP )
     1,PPP(I)
C    1  ,VVL(I)
      IF(PP(I).GE.0) GO TO 10
   20 NOBS=I-1
      READ(1,520)TTT,PS0,(PS(I),I=1,NCOMP)
      IF(R.LT.11.0)GO TO21
C     PS0=PS0/14.697
   21 WRITE(3,520)TTT,PS0,(PS(I),I=1,NCOMP)
      READ(1,525)IJK,KIJ,CINI,CFIN
  525 FORMAT(2I5,2F10.4)
   30 KIJ=KIJ+1
      IF(KIJ.GE.2) GO TO 800
      WRITE(3,525)IJK,KIJ,CINI,CFIN
      K=0
C     THE COMING TWO CARDS HAS TO BE PLACED AFTER EACH OTHER  AS
C     KK=0  FIRST IF  THE BINARY INTERACTION CONSTANT WAS CALCULATED
```

```
C       BEFORE  OR BY ANY OTHER CORRELATION
C       KK=20 FIRST IF THE INTERACTION CONSTANT TO BE CALCULATED BY
C       MINIMISATICN OF ERROR
        KK=0
        KK=20
  280   CONTINUE
        WRITE(3,6)(TITLE(I),I=1,19)
        KK=KK+1
        WRITE(3,516)
        DO 220 I=1,NCOMP1
        CORRL(I,I)=0.0
        I1=I+1
        DO 220 J=I1,NCOMP
        IF(KK.GE.20) GO TO 214
        CORRL(I,J)=CINI+(KK-1)*(CFIN-CINI)/10.
  214   WRITE(3,530)I,J,CORRL(I,J)
        CORRL(J,I)=CORRL(I,J)
  220   CONTINUE
        K=0
        SSDY=0.0
  219   CONTINUE
        IF(NONTUM.GE.1) GO TO 223
        DO 221 I=1,NCOMP
        PC(I)=PCO(I)
        VC(I)=VCO(I)
  221   TC(I)=TCO(I)
  120   T=TTT
        RT=R*T
        DO226   I=1,NCOMP
        DO224   J=1,NCOMP
        X(J)=0.0
  224   CONTINUE
        X(I)=1.0
        P=PSO
        CALL SUPT(VL,PHI,PVOL,C1RKL,C2RKL,CORRL,X,1,KIJ)
        FREFER(I)=PHI(I)*X(I)*PSO
  226   D(I)=PVOL(I)
        WRITE(3,521)T,PSO,(FREFER(I),I=1,NCOMP),(D(I),I=1,NCOMP)
  521   FORMAT(//5X,2F10.2,9E11.4//)
        WRITE(3,535)
  535   FORMAT(/26X,9HCOMPONENT,1X,1HX,7X,4HYCAL,4X,4HYOBS,4X,6HGAMALN,
       12X,5HGAMA,5X,5HV(PO),5X,4HPHIL,6X,4HPHIV,6X,5HPHILL/)
  223   CONTINUE
        K=K+1
        DO234 J=1,NCOMP
        Y(J)=YY(K,J)
  234   X(J)=XX(K,J)
        P=PSO
        CALL SUPT(VL,PHI,PPVOL,C1RKL,C2RKL,CORRL,X,1,KIJ)
  233   PPVOL(J)=PVOL(J)
  236   P=PP(K)
        CALL SUPT(VL,PHI,PPVOL,C1RKL,C2RKL,CORRL,X,1,KIJ)
        DO 237 J=1,NCOMP
  237   PCOR(J)=(PPVOL(J)+PVOL(J))*(PSO-P)/2.0/RT
        CALL SUPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
        WRITE(3,789)PP(K),(Y(J),J=1,NCOMP),(PHIV(J),J=1,NCOMP),(PCOR(J),
      1 J=1,NCOMP)
  789   FORMAT(10X,7F10.4)
        RATIO=PHIV(1)*Y(1)  /PHI(1)/X(1)
        RATO =PHIV(2)*Y(2)/PHI(2)/X(2)
  266   WRITE(3,600)T,P,RATIO,RATO
        DO 235 J=1,NCOMP
        GAMALN(J)=ALOG(PHIV(J)*P*Y(J)/(FREFER(J)*X(J)))+PCOR(J)
C       GAMALN(J)=ALOG(PHIV(J)*P*Y(J)/(FREFER(J)*X(J)))
        PHIV(J)=1.0
  235   GAMMA(J)=EXP(GAMALN(J))
        GEM=0.0
        DO 777 J=1,NCOMP
  777   GEM=    (GEM+X(J)*GAMALN(J))
        GEM=GEM*RT
        GEM=GEM*.10133
        WRITE(3,317)GEM
  317   FORMAT(//30X,'GEM=',F15.4)
        ITER=0
  240   ITER=ITER+1
        SDY=0.0
```

```
      IF(ITER-60)242,242,260
  242 DO245 J=1,NCOMP
      YCAL(J)=PHI(J)/PHIV(J)*X(J)
      SDY=SDY+YCAL(J)
  245 CONTINUE
      DO246  J=1,NCOMP
      IF(ITER.LE.1)GOTO 250
  246 YCAL(J)=YCAL(J)/SDY
      DO 247  J=1,NCOMP
      IF(ABS(YCAL(J)-Y(J)) .GT.0.00001) GO TO 250
  247 CONTINUE
      GO TO 260
  250 DO255  J=1,NCOMP
  255 Y(J)=YCAL(J)
C     THIS CARD TO CALCULATE GAMMA AT P  CALCULATED
      P=PPP(K)
      CALL SUPT(VL,PHIV,PVOL,C1RKL,C2RKL,CORRL,Y,0,KIJ)
      GO TO240
  260 SDY=0.0
      DO 265  J=1,NCOMP
  265 SDY=SDY+ABS(YCAL(J)-YY(K,J))
      SSDY=SSDY+SDY
      IF(R.LT.11.)GO TO 266
C     P=P*14.697
  540 FORMAT(8F10.4)
      DO 300 J=1,NCOMP
  300 WRITE(3,610)COMPA(J),COMPB(J),X(J),YCAL(J),YY(K,J),GAMALN(J),
     1  GAMMA(J),PVOL(J),PPVOL(J),PHI(J),PHIV(J), ITER
C
CCCC
C     THIS SET OF CARDS TO CALCULATE GAMMA,GEM FROM  CALCULATED   Y
      DO 885 J=1,NCOMP
      GAMALN(J)=ALOG(PHIV(J)*P*Y(J)/(FREFER(J)*X(J)))+PCOR(J)
C     GAMALN(J)=ALOG(PHIV(J)*P*Y(J)/(FREFER(J)*X(J)))
  885 GAMMA(J)=EXP(GAMALN(J))
      GEM=0.0
      DO 877 J=1,NCOMP
  877 GEM=    (GEM+X(J)*GAMALN(J))
      GEM=GEM*RT
      GEM=GEM*.10133
      WRITE(3,317)GEM
      DO 398 J=1,NCOMP
  398 WRITE(3,610)COMPA(J),COMPB(J),X(J),YCAL(J),YY(K,J),GAMALN(J),
     1  GAMMA(J),PVOL(J),PPVOL(J),PHI(J),PHIV(J), ITER
C
C
  600 FORMAT(3X,3HT= ,F8.2,5H   P=  ,F10.4,9H  RATIO=,F8.4,7H  RATO=,
     1 F8.4)
  610 FORMAT(27X,2A4,5F8.4,4F10.4,I5)
  270 IF(K-NOBS) 223, 850,850
  850 CONTINUE
      WRITE(3,620)SSDY
  620 FORMAT(/ 10X, 'ACCUM.SUM OF DEV. IN Y IS', E12.4/)
      IF(KK-11)280,30,30
  900 STOP
  500 FORMAT (3I5,F10.4)
  505 FORMAT(1H0,4X,2HPC,10X,2HVC,6X,2HTC,10X,1HW,7X,5HC1RKL,5X,5HC2RKL,
     15X,5HMOLWT,4X,9HCOMPONENT//)
  510 FORMAT(4F8.4  ,2F8.4,2E12.5,2A4)
  515 FORMAT(1H ,8E12.5,3X,2A4)
  516 FORMAT(1H , /1H ,16X,3HKIJ                    / )
  520 FORMAT(14F10.4)
  530 FORMAT(1H ,6X,2I2,F10.4,2F10.4)
  562 FORMAT(45X,2A4,3F10.4)
      END
                    ********************************
                         **********************
                              ***********
```

```
C     ******************************************************************
CCC   CORRELATICN OF WA,WB IN TERMS OF (1-TR)
CCC   LEAST SQUARES METHOD IS USED
C     ******************************************************************
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(40,40),B(40,40),X(100),Y(100,1),C(40,40),YC(100),
     1DY(100),YCAL(100),YORIG(100,1),DY0(100),XX(100),TITLE(20)
      DIMENSION EDY(100)
        DIMENSION WW(100)
    1 READ (1, 101) W, XK
          L = 1
      M = 2
       WRITE (3, 307) W
  307 FORMAT (1H0, '  W=', D16.10)
      READ(1, 102) (TITLE(I), I = 1, 19)
  102 FORMAT(19A4)
      WRITE(3, 306) (TITLE(I), I = 1, 19)
  306 FORMAT(1H0, 19A4)
       IF (XK .LT. .0) READ(1, 101) TC
       I = 1
  101 FORMAT(4D20.14)
   20  READ (1, 101) X(I), (Y(I,J), J = 1, L)
        IF ( XK .LT. .0) X(I) = X(I)/TC
       IF( X(I) .LT. .0) GO TO 21
      WW(I) = 1.
       WRITE (3, 300) X(I), (Y(I,J), J = 1, L)    ,WW(I)
  300 FORMAT (1H0, 3D20.14)
        I = I + 1
         GO TO 20
   21 N = I - 1
      DO 30 I = 1, N
   30 C(I, 1) = 1.0
      MP1 = M+1
      DO 35 J =2, MP1
      DO 35 I = 1, N
   35 C(I,J) = C(I, J-1)*X(I)
      DO 40 I = 1, MP1
      DO 40 J = 1, MP1
      A(I,J) =0.
      DO 40 K =1, N
   40 A(I,J) = A(I,J) + C(K,I)*C(K,J) *WW(K)
      DO 45 J = 1, L
      DO 45 I =1, MP1
      B(I,J) = 0.
       DO 45 K = 1, N
   45 B(I,J) = B(I,J) + C(K,I)*Y(K,J) *WW(K)
      CALL CHAP8(A, MP1, B, L, DET)
      WRITE(3, 111)
  111 FORMAT (1H0, '-------------------------------------------')
      WRITE (3, 301) N
  301 FORMAT(1H ,' THE NUMBER OF GIVEN DATA POINTS=', I3)
       WRITE (3, 302) M
  302 FORMAT(1H ,' THE DEGREE OF POLYNOMIAL=',I3)
      DO 50 J = 1, L
      DO 50 I = 1, MP1
      II = I - 1
   50 WRITE (3, 303) II, B(I,J)
  303 FORMAT(1H0, I3,'   DEGREE COEFFICIENT= ', D20.14)
 1919 FORMAT (4D20.8)
      SEDY = 0.
       SDY = 0.0
         XMEDY = 0.
       DO 70 J = 1, N
       YC(J) = 0.
      DO 60 IL = 1, L
      DO 60 I = 1, MP1
      II = I - 1
       IF (X(J) .LE. 0.0) GO TO 80
      YC(J) = YC(J) + B(I, IL)*X(J)**II
   60 CONTINUE
      DY(J) = YC(J) - Y(J,IL)
       EDY(J) = (DY(J)/Y(J,IL))*100.
         IF ( XMEDY .LT. DABS(EDY(J))) XMEDY = DABS(EDY(J))
      SEDY = SEDY + DABS(EDY(J))
      SDY = SDY + DABS(DY(J))
```

```
 70 WRITE (3, 304) J, YC(J), J, DY(J) , J, EDY(J)
304 FORMAT(1HO,' YC(',I2,')=',D20.14,'  DY(',I2,')=',D20.14,
   1'  EDY(',I2,')=',D20.14,'%')
    EDYAV = SEDY/N
      SDYAV = SDY/N
    WRITE (3,305) SDY, EDYAV,SDYAV
305 FORMAT(1HO,' SUM OF DY=',D20.14,' AVE. D.Y.=',D20.14,'%,  AVE. D.
   1Y.=',D20.14)
      WRITE ( 3, 308) XMEDY
308   FORMAT (1HO,' MAX. DEVIATION = ', D20.14)
      GO TO 1
 80 YC(J) = B(I, IL)
  GO TO 60
  3 RETURN
    END
C
C   ****************************************************************
C THIS SUBROUTINE IS FOR MATRIX INVERSION AND SIMULT. LINEAR EQS.
C   ****************************************************************
    SUBROUTINE CHAP8 (A,N,B,M,DET)
    IMPLICIT REAL*8(A-H,O-Z)
    DIMENSION A(40,40),B(40,40),IPVOT(40),INDEX(40,2),PIVOT(40)
    COMMON IPVOT, INDEX, PIVOT
    EQUIVALENCE (IROW, JROW), (ICOL, JCOL)
C   FOLLOWING 3 STATEMENTS FOR INITIALIZATION
 57 DET = 1.
    DO 17 J = 1, N
 17 IPVOT(J) = 0
    DO 135 I = 1, N
C   FOLLOWING 12 STATEMENTS FOR SEARCH FOR PIVOT ELEMENT
    T = 0.
    DO 9 J = 1, N
    IF (IPVOT(J) - 1) 13, 9, 13
 13 DO 23 K = 1, N
      IF (IPVOT(K) -1) 43, 23, 81
 43 IF(DABS(T) - DABS(A(J,K))) 83, 23, 23
 83 IROW = J
    ICOL = K
    T = A(J, K)
 23 CONTINUE
  9 CONTINUE
    IPVOT(ICOL) = IPVOT(ICOL) + 1
C   FOLLOWING 15 STATEMENT TO PUT PIVOT ELEMENT ON DIAGONAL
    IF (IROW - ICOL) 73, 109, 73
 73 DET = - DET
    DO 12 L = 1, N
    T = A(IROW, L)
    A(IROW, L) = A(ICOL, L)
 12 A(ICOL, L) = T
    IF(M) 109, 109, 33
 33 DO 2 L = 1, M
    B(IROW, L) = B(ICOL, L)
    T = B(IROW, L)
  2 B(ICOL, L) = T
109 INDEX(I,1) = IROW
    INDEX(I,2) = ICOL
    PIVOT(I) = A(ICOL, ICOL)
    DET = DET*PIVOT(I)
C    FOLLOWING 6 STATEMENTS TO DIVIDE PIVOT ROW BY PIVOT ELEMENT
    A(ICOL, ICOL) = 1.
    DO 205 L = 1, N
205 A(ICOL, L) = A(ICOL, L)/PIVOT(I)
    IF (M) 347, 347, 66
 66 DO 52 L = 1, M
 52 B(ICOL, L) = B(ICOL, L)/PIVOT(I)
C   FOLLOWING 10 STATEMENTS TO REDUCE NON-PIVOT ROWS
347 DO 135 LI = 1, N
    IF(LI - ICOL) 21, 135, 21
 21 T = A(LI, ICOL)
    A(LI, ICOL) = 0.
    DO 89 L = 1, N
 89 A(LI, L) = A(LI, L) - A(ICOL, L) *T
    IF (M) 135, 135, 18
 18 DO 68 L = 1, M
 68 B(LI, L) = B(LI, L) - B(ICOL, L) *T
135 CONTINUE
```

```
C      FOLLOWING 11 STATEMENTS TO INTERCHANG5&3oLUMNS
  222  DO 3 I = 1, N
       L = N - I + 1
       IF (INDEX(L, 1) - INDEX(L, 2)) 19, 3, 19
   19  JROW = INDEX(L, 1)
       JCOL = INDEX(L,2)
       DO 549 K = 1, N
       T = A(K, JROW)
       A(K, JROW) = A(K, JCOL)
       A(K, JCOL) = T
  549  CONTINUE
    3  CONTINUE
   81  RETURN
       END
C                  ********************************************
                          **********************
                                ***********
```

```
C     ******************************************************************
CCCCCC
      CORRELATION OF THE REDLICH-KWONG EQUATION PARAMETERS
      THIS PROGRAM IS USED IN THE GENERALIZATION
      LEAST-SQUARES METHOD IS EMPLOYED
      THIS PROGRAM WAS USED FOR APOLYNOMIAL FITTING IN TR OR W
C     ******************************************************************
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(80,4),Y(80),COEFF(4),
     PTR(80),W(80),WA(80),WB(80)
      DIMENSION TITLE(80)
      COMMON / FIRST / OMEGA
 1000 READ (1, 100) OMEGA, XK
        IF ( OMEGA .LT. .0) GO TO 2
      READ(1,20) (TITLE(I),I=1,80)
   20 FORMAT(80A1)
      WRITE(3,60) (TITLE(I),I=1,80)
   60 FORMAT(1H1,80A1)
         WRITE (3, 301) OMEGA
  301 FORMAT(1H0,'  W=',D20.8)
      N = 3
      IF (XK .LE. -1.) READ (1, 100) TC
      I = 1
    8 READ (1, 100) TR(I), WA(I)
  100 FORMAT(2D20.14)
        IF (XK .LE. -1.) TR(I) = TR(I)/TC
      IF (TR(I) .LE. 0.) GO TO 7
       IF ( TR(I) .LE. .85) GO TO 8
       I = I + 1
         GO TO 8
    7 NDATA = I - 1
      A0 = 1.00
      WRITE(3,50) N,NDATA
      DO  9 I = 1 , NDATA
    9 WRITE(3,200) TR(I),WA(I),WB(I)
  200 FORMAT(5X,'TR= ',F10.7,10X,'WA= ',F10.7,10X,'WB= ',F10.7,/)
   50 FORMAT(2I5)
      DO 1 I=1,NDATA
      X(I,1) =  1. - TR(I)
      X(I,2) =   (1. -TR(I))**(1./3.)
      X(I,3) =   (1. -TR(I))**(2./3.0)
      Y(I) = WA(I)
    1 CONTINUE
      DO 300 J=1,N
  300 COEFF(J) = 0.0
      CALL REGM(X,Y,N,NDATA,COEFF,A0,TR,WA)
      WRITE(3,801)
  801 FORMAT('-----------------------------------------------------------
     &-----------------------------------------')
       GO TO 1000
    2 RETURN
       END
C     ******************************************************************
      SUBROUTINE REGM(X,Y,N,NDATA,COEFF,A0,TR,W)
C
C     ******************************************************************
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(80,4),Y(80),COEFF(4),
     &TR(80),W(80)
      DIMENSION A(11,12),B(11,12),YCALC(80)
      DIMENSION XPLOT(80,2),YPLOT(80,2),NPNTS(2)
C
CCCCC THE FOLLOWING DIMENSIONS SHOULD AGREE WITH THE CALLING PROGRAM
      DIMENSION X(250,10),Y(250),COEFF(11)
C
C     CHECK INPUT DATA
      COMMON / FIRST / OMEGA
          XMER =0.0
      WRITE(3,2070) N,NDATA
      IF(N-10)2002,2002,2003
 2002 IF(NDATA-250) 2009,2009,2010
 2009 DATA=NDATA
      NN=N+1
      NNN=N+2
```

```
C
C       DETERMINATION OF REGRESSION MATRIX B(I,J)
        DO 2001 I=1,NN
        DO 2001 J=1,NNN
        A(I,J)=0.0
 2001   B(I,J)=0.0
        DO 2007 KDATA=1,NDATA
        A(1,1)=1.0
        DO 2004 J=2,NN
        KK=J-1
 2004   A(1,J)=X(KDATA,KK)
        A(1,NNN)=Y(KDATA)
        DO 2005 I=2,NN
        LL=I-1
        DO 2005 J=1,NNN
 2005   A(I,J)=A(1,J)*X(KDATA,LL)
        DO 2006 I=1,NN
        DO 2006 J=1,NNN
 2006   B(I,J)=B(I,J) + A(I,J)
 2007   CONTINUE
C
C       MODIFICATION FOR A KNOWN A(0) TERM / PART 1
C       DO 2060 I=2,NN
C2060   B(I,NNN)=B(I,NNN)-A0*B(I,1)
C       NN=N
C       NNN=N+1
C       DO 2068 I=1,NN
C       DO 2068 J=1,NNN
C2068   B(I,J)=B(I+1,J+1)
C
C       DETERMINATION OF THE REGRESSION COEFFICIENTS USING THE MATRIX
C       INVERSION METHOD.
        DO 2013 K=1,NN
        J=NNN
        L=K+1
 2051   IF(J-K) 2036,2025,2025
 2025   IF(B(K,K)) 2015,2017,2015
C       CORRECTION FOR ZERO DIAGONAL TERM
 2017   IF(NN-L) 2052,2047,2047
 2047   DO 2018 J=1,NNN
 2018   B(K,J)=B(K,J) + B(L,J)
        L=L+1
        GO TO 2051
C       END OF CORRECTION CALCULATION
 2015   B(K,J)=B(K,J)/B(K,K)
        J=J-1
        GO TO 2051
 2036   DO 2013 I=1,NN
        IF(I-K) 2066,2013,2066
 2066   J=NNN
 2041   IF(J-K) 2013,2099,2099
 2099   B(I,J)=B(I,J) - B(I,K)*B(K,J)
        J=J-1
        GO TO 2041
 2013   CONTINUE
C
CC      MODIFICATION FOR A KNOWN A(0) TERM / PART 2
CC      NN=N+1
CC      NNN=N+2
C       DO 2067 I=2,NN
C2067   B(I,NNN)=B(I-1,NN)
C       B(1,NNN)=A0
CC
C       WRITE COEFFICIENTS AND STORE THEM IN COEFF
        WRITE(3,2053)
        DO 2011 I=1,NN
        MM=I-1
        COEFF(I)=B(I,NNN)
 2011   WRITE(3,2077) MM,B(I,NNN)
C
C       CALCULATION OF DATA BASED ON REGRESSION COEFFICIENTS
        WRITE(3,2091)
        DO 2064 MMM=1,NDATA
        YCALC(MMM)=B(1,NNN)
        DO 2064 I=2,NN
        IJK=I-1
```

```
 2064 YCALC(MMM)=YCALC(MMM)  + B(I,NNN)*X(MMM,IJK)
      SUMYE=0.0
      SUMYC=0.0
      DSQ=0.0
      SUM = 0.0
      DO 2069 I=1,NDATA
      SUMYE=SUMYE + Y(I)*Y(I)
      SUMYC=SUMYC + YCALC(I)*YCALC(I)
      DELTAY=Y(I)-YCALC(I)
      DSQ=DSQ+DELTAY*DELTAY
C     ERROR=DELTAY/YCALC(I)*100.0
       ERROR = DELTAY/Y(I)*100.0
      PERERR=DABS(ERROR)
          IF (XMER .LT. PERERR)  XMER = PERERR
C     PERERR=ABS(ERROR)
      SUM= SUM+PERERR
 2069 WRITE(3,2080) I, TR(I),(X(I,J),J=1,N),Y(I),YCALC(I),ERROR
C2069 WRITE(3,2080) I,T(I),D(I),(X(I,J),J=1,N),Y(I),YCALC(I),ERROR
      WRITE(3,2071)
      SY=(SUMYE-SUMYC)/DATA
      SIGMA=SUMYE/DATA
      PERAVE=SUM/NDATA
          WRITE (2, 1920) XMER, PERAVE
 1920 FORMAT(2F6.4)
      R=1.0-SY/SIGMA
C     R=SQRT(ABS(R))
      R = DSQRT(DABS(R))
      WRITE(3,2096) PERAVE
      WRITE(3,2021) DSQ
      WRITE(3,2082) SY
      WRITE(3,2083) SIGMA
      WRITE(3,2084) R
      DO 2098 I=1,NDATA
      XPLOT(I,1)=Y(I)
      XPLOT(I,2)=Y(I)
      YPLOT(I,1)=YCALC(I)
 2098 YPLOT(I,2)=XPLOT(I,2)
      NPNTS(1)=NDATA
      NPNTS(2)=NDATA
      WRITE(3,2097)
      RETURN
 2003 WRITE(3,2008)
      RETURN
 2010 WRITE(3,2012)
      RETURN
 2052 WRITE(3,2081)
      RETURN
C
C     FORMAT STATEMENTS
 2008 FORMAT(' N IS GREATER THAN 5',/)
 2012 FORMAT(' NDATA IS GREATER THAN 250',/)
 2021 FORMAT(1X,/,' ERROR CRITERON --- SUM OF SQUARES OF DELTAY IS',
     1D14.7,/)
C    1E14.7,/)
 2053 FORMAT(' THE REGRESSION COEFFICIENTS ARE',/)
 2070 FORMAT(' REGRESSION EQUATION IS OF DEGREE',I2,' AND IS BASED ON',
     1I4,' DATA POINTS',/)
 2071 FORMAT(1X,///,' ERROR CRITERION',/)
 2077 FORMAT(32X,'A(',I2,') IS ',D22.16)
C2077 FORMAT(32X,'A(',I2,') IS ',D14.7,/)
C2077 FORMAT(32X,'A(',I2,') IS ',E14.7,/)
 2080 FORMAT(1X,I2,5X,8F14.5)
 2081 FORMAT(' EVALUATION IMPOSSIBLE DUE TO ZERO DIAGONAL TERMS',/)
C2082 FORMAT(' MEAN SQUARE DEVIATION IS',E14.7,/)
 2082 FORMAT(' MEAN SQUARE DEVIATION IS',D14.7,/)
C2083 FORMAT(' VARIANCE IS',E14.7,/)
 2083 FORMAT(' VARIANCE IS',D14.7,/)
 2084 FORMAT(' REGRESSION INDEX OF CORRELATION IS    R=',F9.5,/)
 2091 FORMAT(' DATA COMPARISON FOLLOWS AS (X(NDATA,I),I=1,N),Y(NDATA)',
     1',YCALC(NDATA),ERROR(PERCENT)',/)
 2097 FORMAT(30X,' PLOT OF YCALC(I) VERSUS YEXPT(I)',/)
 2096 FORMAT(' THE PERCENT AVE. ERROR = ',F14.5,/)
      END
C                    ********************************
                        ************************
                            ************
```

```
C     ******************************************************************
CCC
CCC     THIS PROGRAM IS USED TO FIND THE VALUE OF K12 FOR BINARY SYSTEM
CCC     SUCH THAT THE DEVIATION OF PRESSURE, PCALC. - PEXP., IS MINIMUM
CC    OR SUCH THAT THE  SUM OF PCALC. - PEXP.,  IS MINIMUM BY  INTERCHANGIN
CCC     THE CARDS IN STATEMENTS 3002, 5000, 3003, THE FOLLOWING CARD, 3004
CCC     THE  FOLLOWING CARD, AND THE FIFTH CARD FOLLOWING THE STATEMENT 50
CCC     THIS PROGRAM IS A COLLECTIVE VERSION OF THE PREVIOS ONES WRITTENBY
CCC     WHO-KEE CHUNG, DEPT. OF CHEMICAL ENGINEERING, U. OF O.
CCC     FEB. 5, 1975
CCC     SUBROUTINES PYINIT, PCALC, YVCALC, SUPT, CUBEQN AND EQNRK ARE REQU
C     ******************************************************************
      DIMENSION TITLE (20) ,PCII(5),VCII(5),TCII(5),W(5),WAII(5), WBII(5
     1),COMPA(5), COMPB(5), COMPC(5), FREFER(5), PHI(5), PHIV(5),
     2 PHIJ(5), PHIK(5), P1(5), PTVOL(5), PPVOL(5), VVV(5), CORRL(5,5),
     3 X(5), Y(5),          VC(5), TC(5),                EXG(5), EXGF(5),
     4 YY(5), VVL(5), DY(5), PVOL(5), GAMMB(5), GAMMA(5), AMOLWT(5)
     5 , PC(5), XX(50,5), YY(50,5), PP(50), EXG1(5), COMPD(5)
          DIMENSION A0(20),A1(20),A2(20),A3(20),B(20),TR(5),S(5)
      DIMENSION EDYAV(5),DYAV(5),EDY(5)
      COMMON /FIRST/ TC, PC, VCII, W, AMOLWT, T, P, R, NCOMP, NQNTUM
     1   /SECOND/ Z, A, NTYPE
     2 / THIRD/ PCII, TCII, WAII, WBII, PSI, PP, XX, YY, IJK, KIJ, NOI,
     3 ITER,K, CORRL, EXGT, PPVOL, PHI, PHIV, VV, VVL1, DV, P1, PPP, Y
     4  / FOURTH / SDP, EP, DP, SSDY, SDY, SDV,          PHIK, GAMMA, EXG,
     5 X, SUMY, GAMMB, PG, RT, PF, FREFER, YX, DY, EXG1
     6 / FIFTH / DPAV,EDYAV,EDY, EDP, EDPAV, DYAV
     7/ SIXTH / PN
           READ (1, 112) M
  112      FORMAT(2I5)
           M4 = 2*(M+1) + 2*(M+2)
           M1 = M + 2
           DO 1213 I = 1, M4
           READ(1, 113) A0(I), A1(I), A2(I), A3(I)
 1213 WRITE(3, 3113) A0(I), A1(I), A2(I), A3(I)
 3113    FORMAT(1H0,4D20.8)
    1 READ (1,100)  (TITLE (I), I = 1, 19)
  100 FORMAT (19A4)
      WRITE (3,200)  (TITLE (I), I = 1, 19)
  200 FORMAT (1H1, 19A4)
      READ (1,101) NCOMP, NQNTUM, IJK, R
  101 FORMAT (3I5, F10.4)
      IF ( NCOMP .LE. 0) GO TO 1
C     NCOMP MUST BE GREATER THAN ZERO
C     NCOMP: NO. OF COMPONENTS IN THE MIXTURE
C     R: GAS CONSTANT
C     IJK: CONTROL VARIABLE
C     WRITE HEADINGS
      WRITE (3, 203)
  203 FORMAT (1H0, 'INPUT DATA:'//)
      WRITE ( 3, 201)
  201 FORMAT (1H0,6X, 'PCII', 8X, 'VCII', 8X, 'TCII', 8X, 'W', 11X, 'WAI
     1I', 8X, 'WBII', 4X, 'COMPONENT', 3X, 'AMOLWT'//)
      DO 2 I = 1, NCOMP
      READ (1, 102) PCII(I), VCII(I), TCII(I), W(I), WAII(I), WBII(I),
     1COMPA(I), COMPB(I), COMPC(I),COMPD(I)
  102 FORMAT (4F8.4,F8.5,F9.6,4A4)
    2 WRITE (3,202) PCII(I), VCII(I), TCII(I), W(I), WAII(I), WBII(I),
     1COMPA(I), COMPB(I), COMPC(I),COMPD(I)
  202 FORMAT (1H , 6F12.6, 3X, 4A4)
      READ (1, 102) T, PSI
      WRITE (3, 204) T, PSI
  204 FORMAT (1H0, 'T=', F10.4, 3X, 'PSI=', F10.4)
      READ (1, 104) IJK, KIJ, CINI, CFIN
  104 FORMAT (2I5, 2F10.4)
C     PP IS EXPERIMENTAL VALUE OF PRESSURE
      NCOMP1 = NCOMP - 1
      NOI = 1
   32 READ (1, 105) PP(NOI),(XX(NOI,J),J=1,NCOMP1),(YY(NOI,J),J=1,NCOMP1
     1)
C 105 FORMAT(6F10.0)
  105 FORMAT(F14.8,F10.9,F14.13)
C 105 FORMAT(F14.8,F10.9,F14.13)
C     IF NQNTUM IS DIFFERENT FROM ZERO, XX IS K VALUE, X = Y/K
```

```
      IF ( NQNTUM .NE. 0) XX(NOI,1) = YY(NOI,1)/XX(NOI,1)
      SX = 0.0
      SY = 0.0
      IF (PP(NOI)) 33, 34, 34
   34 DO 4 J = 1, NCOMP1
      SY = SY + YY(NOI, J)
    4 SX = SX + XX(NOI, J)
      XX(NOI, NCOMP) = 1.0 - SX
      YY(NOI, NCOMP) = 1.0 -SY
      WRITE (3, 205) NOI, PP(NOI), (XX(NOI,J),J=1,NCOMP),(YY(NOI,J),
     1 J = 1, NCOMP)
  205 FORMAT (1H , 3X,I4,3X,'PP=',F10.4,3X,'XX(1)=',F10.4,3X,'XX(2)=',
     1 F10.4, 3X, 'YY(1)=',F10.4,3X,'YY(2)=',F10.4)
      NOI = NOI + 1
      GO TO 32
   33 NOI = NOI - 1
  400 READ (1, 151) BK4
  151 FORMAT(5F10.4)
      DO 1218 I = 1, NCOMP
 1218 TR(I) = T/TCII(I)
      WRITE (3, 1245) (TR(I), I = 1, NCOMP)
 1245 FORMAT(1H0,'TR(1)=',F6.4,' TR(2)=',F6.4,' TR(3)=',F6.4)
 1216      READ(1, 113) W(1),W(2),W(3),XK
  113      FORMAT(4D20.8)
      DO 1220 JJJ = 1, NCOMP
      IF (TR(JJJ) .LT. .85) GO TO 1212
      II = 1
      IFF = M1
      DO 1214 IN= II, IFF
      I = IN - II + 1
      B(I) = A0(IN) + A1(IN)*W(JJJ) + A2(IN)*W(JJJ)*W(JJJ) + A3(IN)*
     1W(JJJ)*W(JJJ)*W(JJJ)
      JN = M + 2 + IN
      J = M + 2 + I
 1214      B(J) = A0(JN) + A1(JN)*W(JJJ) + A2(JN)*W(JJJ)*W(JJJ) + A3
     1(JN)*W(JJJ)*W(JJJ)*W(JJJ)
      IF (TR(JJJ) .GE. 1.0) WAII(JJJ) = B(1)
      IF (TR(JJJ) .GE. 1.0) WBII(JJJ) = B(5)
      IF (TR(JJJ) .GE. 1.0)  GO TO 1220
      WAII(JJJ) = B(1) + B(2)*(1.-TR(JJJ)) + B(3)*(1.-TR(JJJ))**(1./
     13.) + B(4)*(1.-TR(JJJ))**(2./3.)
      WBII(JJJ) = B(5)+B(6)*(1.-TR(JJJ))+B(7)*(1.-TR(JJJ))**(1./3.)+B(8)
     1*(1.-TR(JJJ))**(2./3.)
      GO TO 1220
 1212 II = 2*(M+2) + 1
      IFF = 2*(M+2) + (M+1)
      WAII(JJJ) =0.0
      WBII(JJJ) =0.0
      DO 1222 IN = II, IFF
      I = IN - II + 1
      B(I) = A0(IN) +A1(IN)*W(JJJ)+A2(IN)*W(JJJ)*W(JJJ)
      JN = M + 1 + IN
      J = M + 1 + I
 1222 B(J) = A0(JN)+A1(JN)*W(JJJ) + A2(JN)*W(JJJ)*W(JJJ)
      M2 = M + 1
      DO 1215 I = 1, M2
      JJ = I -1
      J = M + 1 + I
      WAII(JJJ) = WAII(JJJ) + B(I)*TR(JJJ)**JJ
 1215 WBII(JJJ) = WBII(JJJ) + B(J)*TR(JJJ)**JJ
 1220      CONTINUE
      WRITE(3,3132) (WAII(I),I=1,NCOMP),(WBII(I),I=1,NCOMP),(S(I),I=1,NCO
     1MP)
 3132 FORMAT(1H0,9F12.8)
   99 KIJ = KIJ + 1
      IF (KIJ .GE. 2) GO TO 1
  401 WRITE (3, 207) IJK, KIJ, CINI, CFIN
  207 FORMAT (1H0, 3X, 'IJK=', I5, 3X, 'KIJ=', I5, 3X, 'CINI=', F10.4,
     1 3X, 'CFIN=', F10.4 //)
C     GOLDEN SECTION SEARCH TECHNIQUE FOR FINDING THE VALUE K12 SUCH
C     THAT SDP IS MINIMUM
      TOL = .00005
      TOL = .0001
      I1 = 0
      I2 = 0
      I3 = 0
```

```
      I4 = 0
      BK4 = CFIN
      BK1 = CINI
      NOS = 1
      IF (I1 .EQ. 1) GO  TO 4002
      PPP = PSI
      CALL PYINIT (BK1)
      DO 510 K = 1, NOI
      CALL PCALC
  510 CONTINUE
      PSI = PPP
      DP1 = SDP
      DY1 = SSDY
      I1 = 1
 4002 IF (I2 .EQ. 1) GO TO 3002
      BK2 = BK1 + (3.0 - SQRT(5.0))/2.0*(BK4-BK1)
      PPP = PSI
      CALL PYINIT (BK2)
      DO 501  K = 1, NOI
      CALL PCALC
  501 CONTINUE
      PSI = PPP
      DP2 = SDP
      DY2 = SSDY
      I2 = 1
C3002 IF (ABS(DP2 - DP1).LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7001
C3002 IF (ABS(DY2 - DY1).LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7001
 3002 IF (ABS(DP2 - DP1).LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7001
C5000 IF (DP2 .GT. DP1) GO TO 4001
 5000 IF (DP2 .GT. DP1) GO TO 4001
 4000 IF (I3 .EQ. 1) GO TO 3003
      BK3 = BK4 - (3.0 - SQRT(5.0))/2.0 * (BK4 - BK1)
      PPP = PSI
      CALL PYINIT (BK3)
      DO 503  K = 1, NOI
      CALL PCALC
  503 CONTINUE
      PSI = PPP
      DP3 = SDP
      DY3 = SSDY
      I3 = 1
C3003 IF (ABS(DP3 - DP2).LE. TOL .OR. ABS(BK3-BK2) .LE. TOL) GO TO 7002
C3003 IF (ABS(DY3 - DY2).LE. TOL .OR. ABS(BK3-BK2) .LE. TOL) GO TO 7002
 3003 IF (ABS(DP3 - DP2).LE. TOL .OR. ABS(BK3-BK2) .LE. TOL) GO TO 7002
C     IF (DP3 .GT. DP2) GO TO 4003
      IF (DP3 .GT. DP2) GO TO 4003
      IF (I4 .EQ. 1) GO TO 3004
      PPP = PSI
      CALL PYINIT ( BK4 )
      DO 504  K = 1, NOI
      CALL PCALC
  504 CONTINUE
      PSI = PPP
      DP4 = SDP
      DY4 = SSDY
      I4 = 1
C3004 IF (ABS(DP4 - DP3).LE. TOL .OR. ABS(BK4-BK3) .LE. TOL) GO TO 7003
C3004 IF (ABS(DY4 - DY3).LE. TOL .OR. ABS(BK4-BK3) .LE. TOL) GO TO 7003
 3004 IF (ABS(DP4 - DP3).LE. TOL .OR. ABS(BK4-BK3) .LE. TOL) GO TO 7003
C     IF (DP3 .GT. DP4) GO TO 4004
      IF (DP3 .GT. DP4) GO TO 4004
      BK1 = BK2
      DP1 = DP2
      DY1 = DY2
      BK2 = BK3
      DP2 = DP3
      DY2 = DY3
      I3 = 0
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 4000
 4001 BK4 = BK2
      DP4 = DP2
      DY4 = DY2
      I4 = 1
      I2 = 0
```

```
      I3 = 0
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 4002
 4003 BK4 = BK3
      DP4 = DP3
      DY4 = DY3
      BK3 = BK2
      DP3 = DP2
      DY3 = DY2
      I4 = 1
      I2 = 0
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 4002
 4004 BK1 = BK3
      DP1 = DP3
      DY1 = DY3
      I2 = 0
      I3 = 0
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 4002
 7001 BK4 = BK2
      DP4 = DP2
      DY4 = DY2
      I4 = 1
      I3 = 0
 5001 BK2 = BK1 + (3.0 - SQRT(5.0))/2.0 * (BK4 - BK1)
      PPP = PSI
      CALL PYINIT (BK2)
      DO 502  K = 1, NOI
      CALL PCALC
  502 CONTINUE
      PSI = PPP
      DP2 = SDP
      DY2 = SSDY
      I2 = 1
C     IF (ABS(DP2 - DP1) .LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7000
C     IF (ABS(DY2 - DY1) .LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7000
      IF (ABS(DP2 - DP1) .LE. TOL .OR. ABS(BK2-BK1) .LE. TOL) GO TO 7000
      IF (NOS .GE. 30) GO TO 8000
      NOS = NOS + 1
      GO TO 5000
 7002 BK1 = BK2
      DP1 = DP2
      DY1 = DY2
      I1 = 1
      BK4 = BK3
      DP4 = DP3
      DY4 = DY3
      I4 = 1
      I3 = 0
      GO TO 5001
 7003 BK1 = BK3
      DP1 = DP3
      DY1 = DY3
      I1 = 1
      I3 = 0
      GO TO 5001
 8000 WRITE (3, 2004) BK1,BK2,BK3,BK4,DP1,DP2,DP3,DP4,DY1,DY2,DY3,DY4
 2004 FORMAT(1H0,'K12 DID NOT CONVERGE,  THE FOLLOWING RESULT IS NOT OPT
     1IMUM '/8(2X,E13.7)/4(2X,E13.7))
 7000 WRITE ( 3, 2005) BK4, DP4, DY4, NOS
 2005 FORMAT (1H0,' THE VALUE OF K12 IS ', F10.8, '     THE CORRESPONDING
     1 D.P. IS ',E14.8/' AND THE CORRESPONDING D.Y. IS ',E14.8, ' NO. OF
     2 ITERATIONS = ', I4)
      CALL PYINIT(BK4)
           WRITE(3, 301) ((CORRL(I,J), I =1, NCOMP),J=1, NCOMP)
  301 FORMAT (1H0, 9(3X,F10.5))
      WRITE (3, 209)
  209 FORMAT (1H0,  'RESULT:')
      EDYAV(3)=0.0
      DYAV(3) = 0.0
      EDPAV = 0.0
      DPAV = 0.0
```

```
      EDYAV(1) = 0.0
      EDYAV(2) = 0.0
      DYAV(1) = 0.0
      DYAV(2)=0.0
       SDP=0.0
       SSDY=0.0
       SDV=0.0
      DO 500 K = 1, NOI
      CALL PCALC
      WRITE (3, 210) VV, P
  210 FORMAT(1H0, 3X, 'VV=', F14.4, 3X, 'P=', F10.4)
      IF ( YY(K, 1) .LE. 0.0) GO TO 500
      DO 40 I = 1, NCOMP
   40 WRITE (3, 226) I, PHIV(I), I, Y(I)
  226 FORMAT (1H , 3X, 'PHIV(', I2, ')=', F10.4, 3X, 'Y(',I2,')=',F10.4)
      DO 41 I = 1, NCOMP
   41 WRITE (3, 211) I, PHIK(I), I, P1(I)
  211 FORMAT (1H , 3X, 'PHIK(', I2, ')=', F10.4, 3X, 'P1(', I2,')=',F10.4)
      WRITE (3, 213) T, P, K, PP(K), DP, EP
  213 FORMAT (3X, 'T=', F10.4, 3X, 'P=', F10.4,3X,'PP(',I3,')=',F10.4,3X
     1 'DP=', F10.4, 20X,'EP=',F10.4,'%')
      CALL YXCALC
      WRITE (3, 305) (X(I),I=1,3), (Y(I),I=1,3), (EDY(I),I=1,3),DP,EDP
  305 FORMAT(1H ,'  X(1)=',F10.8,'  X(2)=',F10.8,'  X(3)=',F10.8,'  Y(1)
     1=',F10.8,'  Y(2)=',F10.8,'  Y(3)=',F10.8/'  EDY(1)=',E12.6,'%  EDY
     2(2)=',E12.6,'%  EDY(3)=',E12.6,'%  DP=',E12.6,'  EDP=',E12.6,'%')
        WRITE (3, 307) DY(1), DY(2), DY(3)
  307 FORMAT(1H ,'  DY(1)=',E12.6,'  DY(2)=', E12.6,'  DY(3)=',E12.6)
      DO 26 J = 1, NCOMP
   26 WRITE (3,214) COMPA(J), COMPB(J), COMPC(J), COMPD(J),PG,J,X(J),J,
     1 GAMMB(J)
  214 FORMAT (10X, 4A4, 3X, 'P=', F10.4, 3X, 'X(', I2, ')=', F10.4, 3X,
     1 'GAMMB(', I2, ')=', F10.4)
      WRITE ( 3, 215) ( EXG1(I), I = 1, NCOMP)
  215 FORMAT ( 10X, 'LN @      EXG(I)=', 3F10.4)
      WRITE (3, 216) EXGT
  216 FORMAT (10X, 'EXGT=', F10.4)
      DO 29 J = 1, NCOMP
   29 WRITE (3, 217) COMPA(J), COMPB(J),COMPC(J),COMPD(J),P,J,YX(J),J,
     1 GAMMA(J)
  217 FORMAT (10X, 4A4, 3X, 'P=', F10.4, 3X, 'YX(', I2, ')=', F10.4,3X,
     1 'GAMMA(', I2, ')=', F10.4)
      WRITE (3, 215) ( EXG(I), I = 1, NCOMP)
      DO 31 J = 1, NCOMP
   31 WRITE(3,218) COMPA(J),COMPB(J),COMPC(J),COMPD(J),J,X(J),J,Y(J),K,
     1J,YY(K
     2,J),J,DY(J),J,PPVOL(J),J,PHI(J),J,PHIV(J),SUMY,ITER
  218 FORMAT (1H0, 3X, 4A4, 3X, 'X(', I2, ')=', F10.6, 3X, 'Y(', I2,
     1')=',F10.8,3X,'YY(',I4,I2,')=',F10.8,3X,'DY(',I2,')=',
     2 E12.4/ 21X, 'PPVOL(', I2, ')=', F10.4,3X, 'PHI(', I2, ')=',
     3 F10.4, 3X, 'PHIV(',I2, ')=', F10.4, 3X, 'SUMY=', F10.4, 3X,
     4 'ITER=', I4)
      WRITE (3, 219) VV, VVL1, DV
  219 FORMAT (15X, 'VV=', F10.4, 3X, 'VVL1=', F10.4, 3X, 'DV=', E12.4)
  500 CONTINUE
       WRITE(3, 306) DPAV, EDPAV,(DYAV(J), J=1,3),(EDYAV(J),J=1,3)
  306 FORMAT(1H0,'  DPAV=',E12.6,'EDPAV=',E12.6,'%  DYAV(1)=',E12.6,'  D
     1YAV(2)=',E12.6,'  DYAV(3)=',E12.6/'  EDYAV(1)=',E12.6,'%  EYDAV(2)
     2=',E12.6,'%  EDYAV(3)=',E12.6,'%')
          SDP = SDP/NOI
          SSDY = SSDY/NOI /NCOMP
      WRITE ( 3, 300) BK4, SDP, SSDY, SDV
  300 FORMAT (1H0,3X,'K12=',E14.8,3X,'SDP=',E14.8,3X,'SSDY=',E14.8,3X,
     1 'SDV=',E14.8)
      PSI = PPP
      GO TO 99
        END
C
C     ******************************************************************
      SUBROUTINE PYINIT ( BK )
C
C     ******************************************************************
C     PREDICT P-X-Y CURVE
C     MODIFIED REDLICH-KWONG EQUATION OF STATE IS USED FOR MULTI-
C     COMPONENT SYSTEMS CALCULATION FROM THE PURE COMPONENT PROPERTIES
C     ONE OF THE COMPONENTS IS AT ITS HYPERCRITICAL STATE
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C     ******************************************************************
CC    DECEMBER 10, 1974
C     WHO KEE CHUNG, DEPT. OF CHEMICAL ENGINEERING, U. OF O.
      DIMENSION TITLE (20) ,PCII(5) ,VCII(5) ,TCII(5) ,W(5) ,WAII(5) , WBII(5
     1) ,COMPA(5) , COMPB(5) , COMPC(5) , FREFER(5) , PHI(5) , PHIV(5) ,
     2 PHIJ(5) , PHIK(5) , P1(5) , PTVOL(5) , PPVOL(5) , VVV(5) , CORRL(5,5) ,
     3 X(5) , Y(5) , VC(5) , TC(5) , EXG(5) , EXGF(5) ,
     4 YX(5) , VVL(5) , DY(5) , PVOL(5) , GAMMB(5) , GAMMA(5) , AMOLWT(5)
     5 , PC(5) , XX(50, 5) , YY(50,5) , PP(50) , EXG1(5) , COMPD(5)
      COMMON /FIRST/ TC, PC, VCII, W, AMOLWT, T, P, R, NCOMP, NQNTUM
     1 /SECOND/ Z, A, MTYPE
     2 / THIRD/ PCII, TCII, WAII, WBII, PSI, PP, XX, YY, IJK, KIJ, NOI,
     3 ITER,K, CCRRL, EXGT, PPVOL, PHI, PHIV, VV, VVL1, DV, P1, PPP, Y
     4 / FOURTH / SDP, EP, DP, SSDY, SDY, SDV, PHIK, GAMMA, EXG,
     5 X, SUMY, GAMMB, PG , RT , PF , FREFER, YX , DY , EXG1
      SDP = 0.0
      SDV = 0.0
      SSDY = 0.0
C     PF = REFERENCE PRESSURE OF 1000 LB OR 1000./14.697 ATMOSPHERE
CC    SINCE ONE ATMOSPHERE = 14.697 LB
      PF = 1000/14.697
      PPP = PSI
      PSI = PSI/14.697
          DO 3 I = 1, NCOMP
    3 CORRL(I,I) = 0.0
      CORRL(1, 2) = BK
      CORRL(2,1) = CORRL(1,2)
C     SET UP THE NECESSARY INFORMATION FOR THE SUPPORT SUBROUTINE
      RETURN
      END
C     ******************************************************************
C     SUBROUTINE PCALC
C     ******************************************************************
      DIMENSION TITLE (20) ,PCII(5) ,VCII(5) ,TCII(5) ,W(5) ,WAII(5) , WBII(5
     1) ,COMPA(5) , COMPB(5) , COMPC(5) , FREFER(5) , PHI(5) , PHIV(5) ,
     2 PHIJ(5) , PHIK(5) , P1(5) , PTVOL(5) , PPVOL(5) , VVV(5) , CORRL(5,5) ,
     3 X(5) , Y(5) , VC(5) , TC(5) , EXG(5) , EXGF(5) ,
     4 YX(5) , VVL(5) , DY(5) , PVOL(5) , GAMMB(5) , GAMMA(5) , AMOLWT(5)
     5 , PC(5) , XX(50, 5) , YY(50,5) , PP(50) , EXG1(5) , COMPD(5)
      DIMENSION EDYAV(5) ,DYAV(5) , EDY(5)
      COMMON /FIRST/ TC, PC, VCII, W, AMOLWT, T, P, R, NCOMP, NQNTUM
     1 /SECOND/ Z, A, MTYPE
     2 / THIRD/ PCII, TCII, WAII, WBII, PSI, PP, XX, YY, IJK, KIJ, NOI,
     3 ITER,K, CORRL, EXGT, PPVOL, PHI, PHIV, VV, VVL1, DV, P1, PPP, Y
     4 / FOURTH / SDP, EP, DP, SSDY, SDY, SDV, PHIK, GAMMA, EXG,
     5 X, SUMY, GAMMB, PG , RT , PF , FREFER, YX , DY , EXG1
     6 / FIFTH / DPAV,EDYAV,EDY, EDP, EDPAV, DYAV
     7 / SIXTH / PN
      ITER = 0
      DO 8 I = 1, NCOMP
      PC(I) = PCII(I)
       VC(I) = VCII(I)
    8 TC(I) = TCII(I)
      RT = R * T
      P = PF
C     USE TO CALCULATE THE MOLAL VOLUMN VL, FUGACITY COEFFICIENT PHI,
CC    PARTIAL MOLAL VOLUMN PPVOL AND FUGACITY FREFER OF LIQUID PHASE
C     FOR PURE COMPONENT AT REFERENCE PRESSURE
   35 DO 9 I = 1, NCOMP
      DO 10 J = 1, NCOMP
   10 X(J) = 0.0
      X(I) = 1.0
      CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
    9 FREFER(I) = PHI(I) * P
C     ****************************
CCC   USE TO CALCULATE VAPORMOLE FRACTIONS Y(I) FOR MIXTURE ASSUMING
C     CORRESPONDING FUGACITY COEFFICIENTS PHIV(I) ARE 1. ( INITIAL GUESS
      P = PP(K)/14.697
       DO 7 J = 1, NCOMP
       PHIV(J) = 1.0
    7 X(J) = XX(K,J)
      SUMY = 0.0
      CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
      DO 37 I = 1, NCOMP
      Y(I) = PHI(I) * X(I)/PHIV(I)
   37 SUMY = SUMY + Y(I)
```

```
C     ***************************
      DO 11 I = 1, NCOMP
   11 Y(I) = Y(I) / SUMY
      SUMY1 = SUMY
      CALL SUPT (VV, PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
C     SET UP THE LOOP TO FIND Y(I) SUCH THAT SUMY IS EQUAL TO SUMY1
C     ,THE SUMY OBTAINED IN IMMEDIATE PRECEDING CALCULATION, I. E. TEST
C     FOR STABILITY BY CHANGING Y(I) AND TEST FOR SUMY = 1.0
   25 CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
   17 SUMY = 0.0
      DO 12 J = 1, NCOMP
      Y(J) = PHI(J) * X(J) / PHIV(J)
   12 SUMY = SUMY + Y(J)
      DO 13 I = 1, NCOMP
   13 Y(I) = Y(I)/SUMY
      IF ( ABS(SUMY1 - SUMY) - 1.0E-4) 14, 14, 15
C     FIND A NEW VALUE OF Y(I) AND SUMY USING Y(I) IF SUMY1 IS DIFFERENT
C     FROM SUMY
   15 IF (ITER - 50) 16, 21, 21
   16 ITER = ITER + 1
      SUMY1 = SUMY
      CALL SUPT(VV,PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
      CALL SUPT(VV,PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
      GO TO 17
C     Y(I) IS STABLE. NOW WE HAVE TO TEST FOR SUMY = 1. BY CHANGING P
C     CHANGE P
   14 SUMP =0.0
      DO 18 I = 1, NCOMP
      PHIJ(I) = PHI(I) * X(I)
      PHIK(I) = PHIV(I) * Y(I)
      P1(I) = P * Y(I)
      P1(I) = PHIJ(I) * P1(I)/PHIK(I)
   18 SUMP = SUMP + P1(I)
      P = SUMP
C      ***********************************
      CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
      CALL SUPT (VV, PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
      SUMY = 0.0
      DO 20 I = 1, NCOMP
      Y(I) = PHI(I) * X(I)/PHIV(I)
   20 SUMY = SUMY + Y(I)
      IF ( ABS (SUMY - 1.0) - 1.0E-4) 21, 21, 22
   22 IF (ITER - 50) 23, 21, 21
   23 DO 24 I = 1, NCOMP
   24 Y(I) = Y(I)/SUMY
      ITER = ITER + 1
      SUMY1 = SUMY
      CALL SUPT(VV, PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
      GO TO 25
C     GATHER STATISTICS AND PRINT OUT RESULTS
   21 P = P * 14.697
      DP = P - PP( K)
      EDP = (DP/PP(K))*100.
      SDP = SDP + ABS(DP)
      DPAV = (DPAV*(K-1) + ABS(DP))/K
      EDPAV = (EDPAV*(K-1) + ABS(EDP))/K
      EP = (DP/PP(K))*100.
      RETURN
      END
C     ***************************************************************
      SUBROUTINE YVCALC
C     ***************************************************************
      DIMENSION TITLE (20) ,PCII(5) ,VCII(5) ,TCII(5) ,W(5) ,WAII(5), WBII(5
     1) ,COMPA(5), COMPB(5), COMPC(5), PREPER(5), PHI(5), PHIV(5),
     2 PHIJ(5), PHIK(5), P1(5), PTVOL(5), PPVOL(5), VVV(5), CORRL(5,5),
     3 X(5), Y(5), VC(5), TC(5), EXG(5), EXGP(5),
     4 YX(5), VVL(5), DY(5), PVOL(5), GAMMB(5), GAMMA(5), AMOLWT(5)
     5 , PC(5), XX(50, 5), YY(50,5) ,PP(50), EXG1(5), COMPD(5)
      DIMENSION EDYAV(5) ,DYAV(5) ,EDY(5)
      COMMON /FIRST/ TC, PC, VCII, W, AMOLWT, T, P, R, NCOMP, NONTUM
     1 /SECOND/ Z, A, MTYPE
     2 / THIRD/ PCII, TCII, WAII, WBII, PSI, PP, XX, YY, IJK, KIJ, NOI,
     3 ITER,K, CORRL, EXGT, PPVOL, PHI, PHIV, VV, VVL1, DV, P1, PPP, Y
     4 / FOURTH / SDP, EP, DP, SSDY, SDY, SDV, PHIK, GAMMA, EXG,
     5 X, SUMY, GAMMB, PG , RT , PF , PREPER, YX , DY , EXG1
     6 / FIFTH / DPAV,EDYAV,EDY, EDP, EDPAV, DYAV
```

```
      P = P/14.697
      PP(K) = PP(K)/14.697
      PG = P
      CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
      CALL SUPT(VV, PHIV, PVOL, WAII, WBII, CORRL, Y, 0, KIJ)
      P = PF
      CALL SUPT (VL, PHI, PTVOL, WAII, WBII, CORRL, X, 1, KIJ)
      P = PG
      DO 26 J = 1, NCOMP
      VVV(J) = (PTVOL(J) + PPVOL(J)) * (PF - P)/2./RT
      FREFER(J) = FREFER(J) * X(J)
      GAMMB(J) = ALOG(PHIV(J) * P * Y(J)/FREFER(J)) + VVV(J)
   26 GAMMB(J) = EXP(GAMMB(J))
      SEXGF = 0.0
      DO 27 I = 1, NCOMP
      EXG1(I) = ALOG(GAMMB(I))
      EXGF(I) = X(I) * EXG1(I)
   27 SEXGF = SEXGF + EXGF(I)
      EXGT = 8.31 * T * SEXGF
      DO 28 J = 1, NCOMP
   28 YX(J) = YY(K,J)
      P = PP(K)
      CALL SUPT (VL, PHI, PPVOL, WAII, WBII, CORRL, X, 1, KIJ)
      CALL SUPT (VV, PHIV, PVOL, WAII, WBII, CORRL, YX, 0, KIJ)
      DO 29 J = 1, NCOMP
      VVL(J) = (PTVOL(J) + PPVOL(J)) * (PF - P)/2./RT
      GAMMA(J) = ALOG(PHIV(J) * P * YX(J)/FREFER(J)) + VVL(J)
   29 GAMMA(J) = EXP(GAMMA(J))
      SEXGT = 0.0
      DO 30 I = 1, NCOMP
      DO 30 I = 1, NCOMP
      EXG(I) = ALOG(GAMMA(I))
      EXGF(I) = X(I) * EXG(I)
   30 SEXGT = SEXGT + EXGF(I)
C      GATHER ANOTHER STATISTICS
      DO 31 J = 1, NCOMP
      SDY = 0.0
      DY(J) = Y(J) - YY(K,J)
      SDY = SDY + ABS(DY(J))
      EDY(J) = (DY(J)/YY(K,J))*100.
      EDYAV(J) = (EDYAV(J)*(K-1) + ABS(EDY(J)))/K
      DYAV(J) = (DYAV(J)*(K-1) + ABS(DY(J)))/K
   31 SSDY = SSDY + SDY
      VVL1 = 0.0
      DO 39 I = 1, NCOMP
   39 VVL1 = VVL1 + VVL(I)
      DV = VV - VVL1
      DV = VV - VVL1
      SDV = SDV + ABS(DV)
      PSI = P
      PP(K) = PP(K) * 14.697
      RETURN
      END
C     ******************************************************************
      SUBROUTINE CUBEQN
C     SOLVES CUBIC EQUATION OF REDLICH-KWONG EQUATION
CC    FOR COMPRESSIBILITY FACTORS
C     ******************************************************************
      DIMENSION A(4),Z(3),B(3)
      COMMON /SECOND/ Z,A,MTYPE
    1 CONTINUE
      B(1)=A(2)/A(1)
      B1OV3=B(1)/3.0
      B(2)=A(3)/A(1)
      B(3)=A(4)/A(1)
      ALF=B(2)-B(1)*B1OV3
      BET=2.0*B1OV3**3  -B(2)*B1OV3+B(3)
      BETOV2=BET/2.0
      ALFOV3=ALF/3.0
      CUAOV3=ALFOV3**3
      SQBOV2=BETOV2**2
      DEL=SQBOV2+CUAOV3
      IF(DEL)40,20,30
   20 MTYPE=0.0
      GAM=SQRT(-ALFOV3)
      IF(BET)22,22,21
```

```
   21 Z(1)=-2.0*GAM-B1OV3
      Z(2)=GAM-B1OV3
      Z(3)=Z(2)
      GO TO 50
   22 Z(1)=2.0*GAM-B1OV3
      Z(2)=-GAM-B1OV3
      Z(3)=Z(2)
      GO TO 50
   30 MTYPE=1
      EPS=SQRT(DEL)
      TAM=-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
C     ***********************************************************************
      SUBROUTINE SUPT(VL,PHI, PVOL ,C1RKL,C2RKL,CORRL,X,LV,KIJ)
C
C     ***********************************************************************
C     EVALUTION OF SUPPORTING PROPERTIES,THE FUGACITY AND THE
C     PARTIAL MOLAL VOLUME OF FLUID MIXTURES.
C     SHINN-DER CHANG, DEPT.OF CHEM.ENG., UNIV. OF OTTAWA.
      DIMENSION TC(5),PC(5),VCO(5),W(5),AMOLWT(5)   ,ARKL(5,5),BRKL(5),
     1  WIJ(5,5),TCOIJ(5,5),TCIJ(5,5),A(4),Z(3),C1RKL(5),C2RKL(5),
     1  PVOL(5),PHI(5),CORRL(5,5),X(5),A2I(5),BI(5),AIRKL(5)
      DIMENSION ZZ(3)
      DIMENSION TC1(5), VC1(5), PC1(5), TC11(5,5),VC11(5,5),WAII(5),WBII
     1(5),PCII(5), TCII(5)
      COMMON   /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM
     1   /SECOND/ Z,A,MTYPE
     2 / THIRD / PCII, TCII, WAII, WBII
C     LV=0, FOR VAPOR PHASE.
C     LV=1, FOR LIQUID PHASE.
C     KIJ=1, TCIJ=SQRT(TCI*TCJ)*(1.-KIJ)
C     KIJ=2, AIJ=SQRT(AI*AJ)*(1.-KIJ)
C     KIJ=3, AIJ=(AI*KIJ+(1.-KIJ)*AJ)/2.
      RT=R*T
      WA0 = 0.42748
      WB0 = 0.08664
   91 DO 100 I=1,NCOMP
      ARKL(I,I)=C1RKL(I)* R*R     *(TC(I)**2.5)/PC(I)
      BRKL(I)=C2RKL(I)* R    *TC(I)/PC(I)
      IF(I.EQ.NCOMP) GO TO 100
      I1=I+1
      DO 100 J=I1,NCOMP
      IF(KIJ.GT.1)  GO TO 97
      TCIJ( I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
      TCIJ( J,I)=TCIJ( I,J)
      WIJ(I,J)=(W(I)+W(J))*0.5
      ZCOIJ=0.291-0.08*WIJ(I,J)
   94 VCOIJ=(VCO(I)**(1./3.)+VCO(J)**(1./3.))**3/8.0
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```
   96 PCOIJ=ZCOIJ* R    *TCIJ( I,J)/VCOIJ
      PCIJ=PCOIJ
   95 ARKL(I,J)=(C1RKL(I)+C1RKL(J))*0.5* R    **2*TCIJ(I,J)**2.5/PCIJ
      GO TO 98
   97 IF(KIJ.GT.2) GO TO 99
      ARKL(I,J)=(ARKL(I,I)*ARKL(J,J))**0.5*(1.0-CORRL(I,J))
      GO TO 98
   99 IF (KIJ .GT. 3) GO TO 998
      ARKL(I,J) = (ARKL(I,I)*CORRL(I,J)+(1.-CORRL(I,J))*ARKL(J,J))
      GO TO 98
  998 DO 1 II = 1, NCOMP
      TC1(II) = (WAII(II)/WA0*WB0/WBII(II))**(2./3.)*TCII(II)
    1 PC1(II) = (WAII(II)/WA0)**(2./3.)*(WB0/WBII(II))**(5./3.)*PCII(II)
      VC1(I) = (1./3.)*R*TC1(I)/PC1(I)
      VC1(J) = (1./3.)*R*TC1(J)/PC1(J)
      TC11(I,J)= (1.-CORRL(I,J))*(TC1(I)*TC1(J))**0.5
      IF (KIJ .GT. 4) GO TO 999
      VC11(I,J)= (1./2.)*(VC1(I)+VC1(J))
  997 ARKL(I,J) = WA0*R*R*TC11(I,J)**2.5/((1./3.)*R*TC11(I,J)/VC11(I,J))
      GO TO 98
  999 VC11(I,J)= (1./8.)*(VC1(I)**(1./3.)+VC1(J)**(1./3.))**3.0
      GO TO 997
   98 ARKL(J,I)=ARKL(I,J)
  100 CONTINUE
      AMRKL=0.0
      BMRKL=0.0
      DO 120 I=1,NCOMP
      A2I(I)=ARKL(I,I)/RT**2/T**0.5
      BI(I)=BRKL(I)/RT
      BI(I)=BRKL(I)/RT
      BMRKL=BMRKL+X(I)*BRKL(I)
      AIRKL(I)=0.0
      DO 120 J=1,NCOMP
      AIRKL(I)=AIRKL(I)+X(J)*ARKL(I,J)
  120 AMRKL=AMRKL+X(I)*X(J)*ARKL(I,J)
      A2=AMRKL/RT**2/T**0.5
      B=BMRKL/RT
      A(1)=1.0
      A(2)=-1.0
      A(3)=B*P*(A2/B-1.0-B*P)
      A(4)=-(A2/B)*(B*P)**2
      CALL CUBEQN
      IF(MTYPE)115,140,140
  115 IF(LV.EQ.0) GO TO 145
C     ZL=AMIN1(Z(1),Z(2),Z(3))
      ZL=AMIN1(Z(1),Z(2),Z(3))
C     JJ=0
C     DO 146 I=1,3
C     ZZ(I)=9999.
C     JJ=JJ+1
C     IF(Z(I).LT.0.0) GO TO 146
C     ZZ(JJ)=Z(I)
C 146 CONTINUE
C     ZL=AMIN1(ZZ(1),ZZ(2),ZZ(3))
      GO TO 150
  145 ZL=AMAX1(Z(1),Z(2),Z(3))
      GO TO 150
  140 ZL=Z(1)
  150 H=B*P/ZL
C     WRITE (3,591) H,ZL,B,Z(1),Z(2),Z(3),LV
C 591 FORMAT(5X,6E12.4,I2)
      CALL EQNRK(A2,B,P,H,ZL,LV)
      VL=RT*B/H
  123 CONTINUE
      IF(LV.EQ.0) GO TO 135
      QD=(T**0.5)*VL*(VL+BMRKL)
      QH=(AMRKL/(T**0.5))*((2.*VL+BMRKL)/(VL**2*(VL+BMRKL)**2))
      QK=RT/((VL-BMRKL)**2   )
  135 DO 130 I=1,NCOMP
C     WRITE(3,591)ZL,H
      PHILN =(ZL-1.0)*BI(I)/B-ALOG(ZL)-ALOG(1.0-H)
     1   -(A2/B)*(2.0*AIRKL(I)/AMRKL  -BI(I)/B)*ALOG(1.0+H)
      PHI(I)= EXP(PHILN )
      IF(LV.EQ.0) GO TO 130
      QE1=0.0
      DO 125 J=1,NCOMP
```

```
  125 QE1=QE1+X(J)*ARKL(I,J)
      QE=2.0*QE1-AMRKL*BRKL(I)/(VL+BMRKL)
      QG=(RT/(VL-BMRKL))*(1.0+BRKL(I)/(VL-BMRKL))
      PVOL(I)=((QE/QD)-QG)/(QH-QK)
  130 CONTINUE
  300 RETURN
      END
C     ******************************************************************
C     SUBROUTINE EQNRK(A2,B,P,E,Z,LV)
C     ******************************************************************
      TOL=1.0E-6
      IH=0
      IJ=0
   45 IF(LV.LT.1) GO TO 47
      IF(E.LT.1.0) GO TO 46
      E=E-0.02
      IH=IH+1
      IF(IH.LT.20) GO TO 45
      E=0.98
      GO TO 46
   47 IF(E.GT.0.0) GO TO 46
      E=E+0.01
      IH=IH+1
      IF(IH.LT.20)GO TO 47
      E=0.02
   46 IJ=IJ+1
      FE=-B*P /E+1./(1.0-E)-(A2/B)*E/(1.+E)
      DFE=B*P /E**2 +1./(1.-E)**2-(A2/B)/(1.+E)**2
C     WRITE(3,592)E,FE,DFE,LV
C 592 FORMAT(20X,3E12.4,5X,I2)
C     IF(ABS(DFE).LT.1.0E-20) DFE=DFE/ABS(DFE)*1.0E-20
      TEST=FE/DFE
      E=E-TEST
      IF(IJ.GT.60)GO TO 48
      IF( ABS(TEST/E).GT.TOL) GO TO 45
   48 Z  =B*P/E
      RETURN
      END
                  ************************************
                       ***************************
                            ************
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C     ******************************************************************
C
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     MODIFIED VERSION SEPT.3,1968 BY CHANG
C     CHANG,S.-D. AND BENJAMIN C.-Y. LU,JULY 2,1968
C
C     ******************************************************************
      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
      EEX=EX
      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
C     THIS READ STATEMENT TO BE USED FOR TERNARY SYSTEM OF C2-"3-CO2
C     READ(1,550)TT(I),PP(I),(XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
      READ(1,550)TT(I),      (XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
     1,PP(I)
      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))
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      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-PSO)*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+EEX
   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
      IF(I.GE.NOBS)GO TO 100
      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*(VORT(I+1,J)+VORT(I,J))*(PP(I+1)-PP(I))/2.0
C     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   )*EX
      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   -(VORT(I+1,J)+VORT(I,J))*(PP(I+1)-PP(I))/2.0))*EX
C    2   -VP(I+1,J)+VP(I,J)))*EX
      DP=DP+XAB*(1./PP(I)+1./PP(I+1)+ABS((VORT(I+1,J)+VORT(I,J))/2.))*EP
C     DP=DP+XAB*(1./PP(I)+1./PP(I+1)+ABS(VORT(I+1,J))
C    1   +ABS(VORT(I,J)))*EP
C     DTEMP=DTEMP+XAB*(ABS(VP(I+1,J)/T)+ABS(VP(I,J)/T))*ET
      DTEMP=DTEMP+XAB*ABS((VORT(I+1,J)+VORT(I,J))*(PP(I+1)-PP(I))/2./T)
      DTHI=DTHI+XAB*2.0*ETHI
      DPVOL=DPVOL+XAB*(ABS(VP(I+1,J)-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)
  100 CONTINUE
      IF(KK.LT.12)GO TO 36
      GO TO 600
  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
C     ******************************************************************
C
      SUBROUTINE VOLPAR
C
C     ******************************************************************
C     CALCULATE PARTIAL MOLAR VOLUMES IN A MULTICOMPONENT LIQUID MIXTURE
C     ******************************************************************
      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
      TRM1=0.9
      TRM0=1.0
      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
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```
      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*0.2082
      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)
      VR0F=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=(VR0F+WMIX*VR1F+WMIX**2*VR2F)*(1.0+(TRMIX-0.9925)*2.4)
      GO TO 90
   85 VRMIX=VR0F+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
C     ******************************************************************
C
      SUBROUTINE PHIMIX (CUBEQN)
C     ******************************************************************
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),
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     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,CORRP,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
```

****
****

```
C*************************************************************************
CCC                                                                      *
CCC     EVALUATION OF THE ADJUSTABLE PARAMETRS OF THE CLAUSIUS  EQUATION *
CCC     OF STATE                                                         *
CCC                                                                      *
C*************************************************************************
CCC
CCC     SUBROUTINE FUG IS REQUIRED.
CCC
CCC     EQUALITY OF ZV IS SACRIFIED
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION TITLE(20),X(8)
      DIMENSION TT(50)
    1 READ(1,300) (TITLE(I),I=1,15)
  300 FORMAT(20A4)
      WRITE(3,400) (TITLE(I),I=1,15)
C     WRITE(2,402)  (TITLE(I),I=1,15)
  400 FORMAT(1H1,10X,' EVALUATION OF ADJUSTABLE PARAMETERS OF CLAUSIUS
     2 EQUATION FOR',15A4///)
  402 FORMAT(         ' EVALUATION OF ADJUSTABLE PARAMETERS OF CLAUSIUS
     2 EQUATION FOR',15A4///)
      EL = 1.0D0
      LL = 1
C     WC = 0.125D0
      NOBS=3
   10 READ(1,100)PC,VC,TC,W,R,TOL
      IF(PC.LE.0.0D0)  GO TO 800
  100 FORMAT(8F10.4)
      SDTHI=0.0D0
      SDZV=0.0D0
   20 READ(1,1111)  P,V,T,VL
C  20 READ(1,100)P,V,T,VL
      PR=P/PC
      TR=T/TC
      BATA =  (DLOG10(PR)-DLOG10(TR)*8.0D0/3.0D0-0.1832D0*(PR/TR/TR-
     2 1.0D0))/((1.0D0-TR)/TR+DLOG10(TR)*1.8D0)
      READ(1,1111)  P,V,T,VL
 1111 FORMAT(4F10.0)
C     READ(1,100)P,V,T,VL
      TR=T/TC
      ALFA =  (VC/VL-1.0D0-(1.0D0-TR)**(1./3.))/((1.0D0-TR)+(1.0D0-TR)
     2**(1./3.))
      READ(1,100)  (TT(I),I=1,NOBS)
C     DELWC: CHANGE IN WC ADOPTED IF FURTHER ITERATION IS NEEDED
      READ(1,1111)  WC ,DELWC
      WRITE(3,100)ALFA,BATA
  999 CONTINUE
      DO 80 I=1,NOBS
      T=TT(I)
      RT=R*T
      TR=T/TC
      CALL PFK(BATA,TR,PR)
      P=PR*PC
      VL =  VC/(1.0D0+ALFA*(1.0D0-TR)+(1.0D0+ALFA)*(1.0D0-TR)**(1./3.))
C     V=R*T/P
      ZL=P*VL/R/T
      ZV=P*V/R/T
      SSS =(R*TC)/(PC*VC)
      EL2 =  EL  + 2.0D0
C     THE NEXT TWO CARDS ARE THE INITIAL VALUES FOR  THE PARAMETERS
C     THEY HAVE TO BE CHOSEN ,SOME TIMES, WITH CARE
      WA=.422
      WB=.250
      A2 =  (WA*SSS**2*VC**2*TC**EL*PC)/
     2 (R**2*T**EL2)
C     A2 =  (WA*SSS**2*VC**2*TC*PC) /(R**2*T**3)
      B =  ((WB*VC)/(R*T))*(4.0D0 - SSS)
      CCC =  (WC*VC*(3.0D0*SSS - 8.0D0))  /  (R*T)
C     CCC = VC*((3.0D0*SSS/8.0D0)  - 1.0D0) /(R*T)
C     WRITE(3,1001)  ZL,ZV,SSS,A2,B,CCC
 1001 FORMAT('ZL',F10.5,'ZV',F10.5,4E15.8)
      H=B*P/ZL
      E=B*P/ZV
      HHL = CCC*P/ZL
```

```
      EEV = CCC * P/ZV
C     WRITE(3,1002)H,E,HHL,EEV
 1002 FORMAT(1H ,'H',4E15.8)
      CALL FUG(W,PR,TR,THI)
      THI = DEXP(2.30259D0*THI)
C     THI CAN BE ASSUMED EQUAL 1.00 TO START ITERATION
C     WRITE(3,100)T,P,VL,V,THI
      ZLL=ZL
      ZVV=ZV
      THIL=THI
      THIV=THI
      HOLD=H
      IJK=0
   39 IJK=IJK+1
      IF(IJK.GE.30) GO TO 49
      J=0
   40 CONTINUE
      IH=0
   41 IF(H.LT.1.0D0) GO TO 42
      H = H - 0.05D0
      IH=IH+1
      IF(IH.LT.20) GO TO 41
   43 H = 0.98D0
C     H VALUES MAY BE ADJUSTED TO ENSURE CONVERGENCE
   42 J=J+1
      FFH = DLOG(THIV*ZL) + DLOG(1.0D0 - H) -
     1 H/(1.0D0-H) + (HHL + 2.0D0) *
     2  ((1.0D0/(1.0D0-H)) - ZL)
      DFFH = (HHL+1.0D0)/(1.0D0-H)**2 -(1.0D0/(1.0D0-H))
      TEST=FFH/DFFH
C     WRITE(3,1003) FFH,DFFH,TEST
 1003 FORMAT(1H ,'FFH',3E15.8)
      H=H-TEST
      IF(J.GT.40)GO TO 45
      IF(DABS(TEST/H).GT.TOL) GO TO 40
   45 B=H*ZL/P
      A2 = B*((1.0D0/(1.0D0-H)) - ZL)*(1.0D0+HHL)**2/H
C     WRITE(3,1004) B,A2
 1004 FORMAT(1H ,'B',E15.8,10X,'A2',E15.8)
      IJ=0
   47 IF(E.GT.0.0D0) GO TO 46
      E = E + 0.01D0
      IH=IH+1
      IF(IH.LT.20)GO TO 47
      E = 0.02D0
C     E VALUES CAN BE ADJUSTED TO ENSURE CONVERGENCE
   46 IJ=IJ+1
      IH=0
      FE = -B*P/E+1./(1.-E)-(A2/B)*E/(1.+EEV)**2
      DFE = B*P/E**2 + 1./(1.-E)**2 - (A2/B)/(1.+EEV)**2
      TEST=FE/DFE
C     WRITE(3,1005) FE,DFE,TEST
 1005 FORMAT(1H ,5X,'FE',3E15.8)
      E=E-TEST
      IF(IJ.GT.40)GO TO 48
      IF(DABS(TEST/E).GT.TOL) GO TO 47
   48 ZVV=B*P/E
      THIV = E/(1.0D0-E) - DLOG(ZVV) - DLOG(1.0D0-E) -
     2 (A2/B)*((2.0D0+EEV)/((1.0D0+EEV)**2)) *E
C     WRITE(3,1006)THIV
 1006 FORMAT(1H , 30X,'THIV',E15.8)
      THIV = DEXP(THIV)
      WRITE(3,501) J,IJ,IJK
  501 FORMAT(3I5)
      IF(DABS(H-HOLD)/H.LE.TOL*10.0D0) GO TO 49
C     WRITE(3,200)P,T,ZV,ZVV,VL,VLL,THIV,THIL,WA,WB,THI,H,E
      HOLD=H
      GO TO 39
   49 ZLL=B*P/H
      VLL=R*T*ZLL/P
      THIL = H/(1.0D0-H) - DLOG(ZLL) - DLOG(1.0D0-H) -
     2 (A2/B)*H*((2.0D0+HHL)/((1.0D0+HHL)**2))
 1007 FORMAT(1H , 50X,'THIL',E15.8)
      THIL = 1.0D0/DEXP(-THIL)
      WB = (B*R*T/VC)*(1.0D0/(4.0D0-SSS))
      WA = (A2*R**2*T**EL2) /(SSS**2*VC**2*TC**EL*PC)
```

```
C       WA = A2*R**2*T**3 / (SSS*VC)**2*TC*PC
C       WRITE(3,1008) WB,WA
 1008   FORMAT(1H ,20X,'WB',E15.8,5X,'WA',E15.8)
  500   FORMAT(I5,3F10.4,5F10.6)
        DTHI=THI-THIV
        DZV=ZV-ZVV
        SDTHI = SDTHI + DABS(DTHI)
        SDZV = SDZV + DABS(DZV)
C   51  WRITE(3,200) P,T,ZV,WA,WB
    51  WRITE(3,200)P,T,ZV,ZVV,VL,VLL,THIV,THIL,WA,WB,THI,H,E
C 200   FORMAT(1H ,5X,5(D15.8,5X))
  200   FORMAT(1H ,D11.4,F8.2,6F9.5,2F10.6,2F8.4,D11.4)
C       WRITE(2,1000) EL
C       WRITE(2,1000) T,WA,WB
 1000   FORMAT(3D15.8)
   80   CONTINUE
        ADTHI=SDTHI/NOBS
        ADZV=SDZV/NOBS
        WRITE(3,311) ADTHI,ADZV
        WRITE(3,3111) WC
 9999   GO TO 1
C       THE NEXT ITERATION LOOP CAN BE ACTIVATED IF WC IS TAKEN AS
C       TEMERATURE DEPENDANT
C       WRITE(3,3111) EL
C       TOLZV = 0.0000D0
C       TOLZV = 0.001D0
C       TOLZV = 0.005D0
C       IF(ADZV.LE.TOLZV) GO TO 9999
C       WC = WC - 0.01
C       WC = WC - 0.0001
C       WC = WC - DELWC
C       IF(WC.LT.0.0D0) GO TO 9999
C       IF(LL.EQ.20) GO TO 9999
C       LL = LL + 1
C       EL = EL - 0.250D0
C       IF(EL.EQ.0.0D0) GO TO 9999
C       SDTHI=0.0D0
C       SDZV=0.0D0
C       GO TO 999
 3111   FORMAT(///25X,' WC = ',5X,D15.8)
C3111   FORMAT(///25X,'TEMP. EXPN=',2X,F10.5)
  311   FORMAT(//20X,'AV. DEV. IN FUGACITY = ',D15.8
     1  ,'AV. DEV. IN ZV = ',D15.8/)
  800   STOP
        END
C       ***************************************************************
        SUBROUTINE PFK(BATA,TR,PR)
C       ***************************************************************
        IMPLICIT REAL*8(A-H,O-Z)
        ITER=0
        TOL=0.00001D0
        PRC=-0.1832D0
   30   PR=BATA*(1.-TR)/TR+(1.8*BATA+8./3.)*DLOG10(TR)+PRC
        PRC=0.1832D0*(DEXP(PR*2.30259D0)/TR/TR-1.0D0)
        ITER=ITER+1
        IF(ITER.GT.20) GO TO 32
        IF(ITER.EQ.1) GO TO 31
        IF(DABS((PR-PROLD)/PR).LT.TOL) GO TO 32
   31   PROLD=PR
        GO TO 30
   32   PR = DEXP(PR*2.30259D0)
        RETURN
        END
```

****
****
****

```
C     ******************************************************************
C
C     PREDICT P-X-Y CURVE
C     CLAUSIUS EQUATION OF STATE IS USED
C     ATMOSPHERIC UNITS ARE USED
C
C     ******************************************************************
C
C     THIS PROGRAN IS A MODIFIED VERSION OF ELSHAYAL
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION PHI(5),X(5),F(5),GAMMA(5),FREFER(5),PVOL(5),Y(5),
     1PC(5),VC(5),TC(5),W(5),C1RKV(5),C2RKV(5),C3RKV(5),
     A C1RKL(5),C2RKL(5),C3RKL(5),
     2 AMOLWT(5),COMPA(5),COMPB(5),CORRV(5,5),CORRL(5,5),GAMALN(5),
     3 A(4),Z(3),TITLE(20),D(5),PCO(5),VCO(5),TCO(5),PHIV(5),FREF(5),
     4 PS(5),PP(80),XX(80,5),YY(80,5),YCAL(5),PPVOL(5),DC1DT(5),DC2DT(5)
     5,YD(5),RATIO(5),VVL(80),YPD(5)
      COMMON /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM
     1    /SECOND/ Z,A,MTYPE
  800 READ(1,5)(TITLE(I),I=1,19)
    6 FORMAT(1H1,19A4)
    5 FORMAT(    19A4)
      WRITE(3,6)(TITLE(I),I=1,19)
      READ(1,500)NCOMP,NQNTUM,IJK,R
      IF(NCOMP.LE.0) GO TO 900
      WRITE(3,505)
      DO 210 I=1,NCOMP
      READ(1,510)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),C3RKL(I),
     1                                 COMPA(I),COMPB(I)
C     1C3RKV(I),                       COMPA(I),COMPB(I)
      C1RKV(I)=C1RKL(I)
      C2RKV(I)=C2RKL(I)
C       THE CARD WAS COMMENTED IN THR ORIGINAL PROG.
      C3RKV(I)  = C3RKL(I)
C     C3RKV(I)  = C3RKL(I)
  210 WRITE(3,515)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),C3RKL(I),
     &C3RKV(I),COMPA(I),COMPB(I)
C     1                                 COMPA(I),COMPB(I)
      CORRL(NCOMP,NCOMP)=0.0
      NCOMP1=NCOMP-1
      WRITE(3,519)
  519 FORMAT(/10X,12HINPUT DATA :///4X,1HP,8X,2HX1,8X,2HX2,9X,1HT,7X,3HRA
     1,7X,3HRB1,7X,3HRA2,7X,3HRB2//)
      DO 9 I=1,NCOMP1
      I1=I+1
      DO 9 J=I1,NCOMP
    9 READ(1,520)CORRL(I,J)
      READ(1,520)  TTT,PSI
      PSI=PSI/14.697
      PSII=PSI
      I=0
   10 I=I+1
      SX=0.0
      SY=0.0
C INPUT FOR MULTI COMPONENT SYSTEMS
C
C
      READ(1,666)     PP(I),(XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
C
C INPUT FOR BINARY SYSTEMS
C
C
      READ( 1,666) PP(I),(XX(I,J),J=1,NCOMP1),(YY(I,J),J=1,NCOMP1)
C
C     READ( 1,520) PP(I),(XX(I,J),J=1,NCOMP1),(YY(I,J),J=1,NCOMP1)
      PP(I)=PP(I)/14.697
  666 FORMAT(8F10.0)
C     1  ,VVL(I)
      DO 15 J=1,NCOMP1
      SY=SY+YY(I,J)
   15 SX=SX+ XX(I,J)
      XX(I,NCOMP)=1.0-SX
```

```
      YY(I,NCOMP)=1.0-SY
      IF(R.LT.11.0) GO TO 16
   16 WRITE(3,520) PP(I),(XX(I,J),J=1,NCOMP ),(YY(I,J),J=1,NCOMP )
     1 ,VVL(I)
C     IF(PP(I).GE.0) GO TO 10
   20 NOBS=I-1
      READ(1,525)IJK,KIJ,CINI,CFIN
  525 FORMAT(2I5,2F10.4)
   30 KIJ=KIJ+1
      IF(KIJ.GE.2) GO TO 800
      WRITE(3,525)IJK,KIJ,CINI,CFIN
      K=0
      KK=0
      KK=20
  280 CONTINUE
      WRITE(3,6)(TITLE(I),I=1,19)
      KK=KK+1
      WRITE(3,516)
      DO 220 I=1,NCOMP1
      CORRL(I,I)=0.0
      I1=I+1
      DO 220 J=I1,NCOMP
      IF(KK.GE.20) GO TO 214
      CORRL(I,J)=CINI+(KK-1)*(CFIN-CINI)/10.
      PSI=PSII
  214 WRITE(3,530)I,J,CORRL(I,J)
      CORRL(J,I)=CORRL(I,J)
  220 CONTINUE
      K=0
      SDP=0.0
      SDV=0.0
      SSYD=0.0
      IF(NONTUM.GE.1) GO TO 223
      DO 221 I=1,NCOMP
      PC(I)=PCO(I)
      VC(I)=VCO(I)
  221 TC(I)=TCO(I)
  120 T=TTT
      RT=R*T
      WRITE(3,535)
  535 FORMAT(/10X,9HCOMPONENT,1X,1HX,7X,1HY,7X,2HYY,7X,2HYD,4X,4HV(P),6X
     1 ,5HV(PO),5X,4HPHIL,6X,4HPHIV,6X,4HSUMY,6X,4HITER,4X,3HNIY/)
  223 CONTINUE
      P=PSI
      NIP=0
      MIP=0
      K=K+1
C     P=PP(K)
      DO 39 J=1,NCOMP
   39 PHIV(J)=1.0
   54 CONTINUE
      DO 40 J=1,NCOMP
   40 X(J)=XX(K,J)
   42 CALL SUPT(VL,PHI,PPVOL,C1RKL,C2RKL,C3RKL,CORRL,X,1,KIJ)
      JY=0
   63 IF(JY.GT.20) GO TO 61
      SUMY=0.
      DO 50 J=1,NCOMP
      Y(J)=PHI(J)*X(J)/PHIV(J)
   50 SUMY=SUMY+Y(J)
      IF(JY)60,45,60
   60 IF(ABS((SUMYO-SUMY)/SUMY).LE.0.0005) GO TO 61
   45 SUMYO=SUMY
      JY=JY+1
      DO 62 J=1,NCOMP
   62 Y(J)=Y(J)/SUMY
      CALL SUPT(VL,PHIV,PVOL,C1RKL,C2RKL,C3RKV,CORRL,Y,0,KIJ)
      GO TO 63
   61 CONTINUE
      DY=SUMY-1.0
      IF(ABS(DY).LE.0.0001) GO TO 110
      IF(NIP.GT.100) GO TO 105
      IF(MIP.GT.20) GO TO 105
      IF(MIP)52,52,56
   52 IF(NIP.LE.0) GO TO 51
      IF((DY*DDY).LT.0.0) GO TO 55
```

```
   51 NIP=NIP+1
      IF(NIP-1)91,91,92
   91 POLD=P
      DDY=DY
      P=P+.01
      GO TO 70
   92 SLOPE=(P-POLD)/(DY-DDY)
      DELP=SLOPE*DY
      IF(ABS(DELP)-1.0)79,79,78
   78 DELP=SIGN(1.0,DELP)
   79 POLD=P
      DDY=DY
      P=P-DELP
      GO TO 70
   56 IF((DY*DDY).LT.0.0) GO TO 55
      IF((DY*DYO).LT.0.0)  GO TO 57
   55 IF(ABS((P-POLD)/P).LE. 0.00001)GOTO105
      PN=(DY*POLD-DDY*P)/(DY-DDY)
      GO TO 58
   57 IF(ABS((P-PO  )/P).LE. 0.00001)GOTO105
      PN=(DY*PO-DYO*P)/(DY-DYO)
      GO TO 59
   58 PO=POLD
      DYO=DDY
   59 POLD=P
      DDY=DY
      P=PN
      MIP=MIP+1
   70 DO 53 J=1,NCOMP
   53 Y(J)=Y(J)/SUMY
      CALL SUPT(VL,PHIV,PVOL,C1RKL,C2RKL,C3RKV,CORRL,Y,0,KIJ)
      GO TO 54
  105 IF(ABS(DY).LE.0.005) GO TO 110
   96 WRITE(3,601)
C     WHEN ATM. UNIT ARE USED THE NEXT TWO CARDS ARE COMMENTED AND 11/ G
C     THE NEXT CARD
C 110 P=P*14.697
C     PP(K)=PP(K)*14.697
C 110 DP=P-PP(K)
  110 DP=P-PP(K)
      SDP=SDP+ABS(DP)
      PDPP=ABS(DP)/PP(K)
      WRITE(3,600) T,P,PP(K),DP,PDPP
C     COMMENT FOR ATMOS UNIT
C     PP(K)=PP(K)/14.697
  600 FORMAT(3X,3HT=  ,F8.2,5H  P= ,F10.4,7HPP(K)= ,F10.4,4HDP= ,F10.4,
     C5HPDPP=,F10.4)
      SYD=0.0
      DO 111 J=1,NCOMP
      YD(J)=Y(J)-YY(K,J)
C     YPD(J)=YD(J)/YY(K,J)
  111 SYD=SYD+ABS(YD(J))
      SSYD=SSYD+SYD
      DO 311 J=1,NCOMP
  311 WRITE(3,610)YPD(J),
     C                COMPA(J),COMPB(J),X(J),Y(J),YY(K,J),YD(J),PPVOL(J),
     1PVOL(J),PHI(J),PHIV(J),SUMY,NIP,MIP
      DV=VL-VVL(K)
      SDV=SDV+ABS(DV)
      WRITE(3,901)VL,VVL(K),DV
  901 FORMAT(15X,4HVL=  ,F10.4,5HVVL=  ,F10.4,4HDV= ,F10.4)
  610 FORMAT(F10.4,2A3,4E12.4,4F10.4,F8.4,2I5)
  601 FORMAT(1H0,87HFAILED TO CONVERGE, RESULTS BELOW ARE NOT RELIABLE I
     1F SUMY IS MUCH DIFFERENT FROM UNITY)
C     P=PSI
      PSI=P
C     COMMENT THE NEXT CARD IF ATMOS. IS USED
C     PSI=PSI/14.697
      IF(K-NOBS) 223, 850,850
  850 CONTINUE
      WRITE(3,620)SDP,SSYD,SDV
  620 FORMAT(/10X,'ACCUM. SUM OF DEV. IN P IS ',E12.4,'ACCUM. SUM OF
     1DEV. IN Y IS ',E12.4,'SDV IS ',E12.4/)
      IF(KK-11)280,30,30
  900 STOP
  500 FORMAT (3I5,F10.4)
```

```
  505 FORMAT(1H0,4X,2HPC,10X,2HVC,6X,2HTC,10X,1HW,7X,5HC1RKL,5X,5HC2RKL,
     15X,5HMOLWT,4X,9HCOMPONENT//)
 510  FORMAT(4F8.4,4F8.4,2A4)
 515  FORMAT(1H ,8D12.5,3X,2A4)
C 515 FORMAT(1H ,6E12.5,3X,2A4)
C 510 FORMAT(4F8.4,2F8.4,24X,2A4)
  516 FORMAT(1H  /1H ,16X,3HKIJ                              / )
  520 FORMAT(14F10.4)
  530 FORMAT(1H ,6X,2I2,F10.4,2F10.4)
      END
C     ******************************************************************
C
      SUBROUTINE SUPT(VL,PHI, PVOL ,C1RKL,C2RKL,C3RKL,CORRL,X,LV,KIJ)
C     EVALUTION OF SUPPORTING PROPERTIES,THE FUGACITY AND THE
C     PARTIAL MOLAL VOLUME OF FLUID MIXTURES.
C     USING THE CLAUSIUS EQUATION OF STATE
C     ******************************************************************
C     IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION TC(5),PC(5),VCO(5),W(5),AMOLWT(5)   ,ARKL(5,5),BRKL(5),
     A CRKL(5),
     1  WIJ(5,5),TCOIJ(5,5),TCIJ(5,5),A(4),Z(3),C1RKL(5),C2RKL(5),
     BC3RKL(5),
     1  PVOL(5),PHI(5),CORRL(5,5),X(5),A2I(5),BI(5),AIRKL(5),
     CCI(5)
      DIMENSION ZZ(3)
      COMMON  /FIRST/ TC,PC,VCO,W,AMOLWT,T,P,R,NCOMP,NQNTUM
     1   /SECOND/ Z,A,MTYPE
C     LV=0, FOR VAPOR PHASE.
C     LV=1, FOR LIQUID PHASE.
C     KIJ=1, TCIJ=SQRT(TCI*TCJ)*(1.-KIJ)
C     KIJ=2, AIJ=SQRT(AI*AJ)*(1.-KIJ)
C     KIJ=3, AIJ=(AI*KIJ+(1.-KIJ)*AJ)/2.
      RT=R*T
   91 DO 100 I=1,NCOMP
      ZC = (PC(I)*VCO(I))/(R*TC(I))
      ARKL(I,I) = C1RKL(I)*(VCO(I)**2)*PC(I)*TC(I)/(ZC**2)
      BRKL(I) = C2RKL(I)*        (4.0 - (1.0/ZC))*VCO(I)
      CRKL(I) = C3RKL(I)*        ((3./ZC)-8.)*VCO(I)
      IF(I.EQ.NCOMP) GO TO 100
      I1=I+1
      DO 100 J=I1,NCOMP
      IF(KIJ.GT.1)  GO TO 97
      TCIJ(I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
      TCIJ(J,I)=TCIJ(I,J)
      WIJ(I,J)=(W(I)+W(J))*0.5
      ZCOIJ=0.291-0.08*WIJ(I,J)
   94 VCOIJ=(VCO(I)**(1./3.)+VCO(J)**(1./3.))**3/8.0
   96 PCOIJ=ZCOIJ* R    *TCIJ(I,J)/VCOIJ
      PCIJ=PCOIJ
   95 ARKL(I,J)=(C1RKL(I)+C1RKL(J))*0.5*
     2(VCOIJ)**2*PCOIJ*TCIJ(I,J)/((ZCOIJ)**2)
      GO TO 98
   97 IF(KIJ.GT.2)  GO TO 99
      ARKL(I,J)=(ARKL(I,I)*ARKL(J,J))**0.5*(1.0-CORRL(I,J))
      GO TO 98
   99 ARKL(I,J)=(ARKL(I,I)*CORRL(I,J)+(1.-CORRL(I,J))*ARKL(J,J))
   98 ARKL(J,I)=ARKL(I,J)
  100 CONTINUE
      AMRKL=0.0
      BMRKL=0.0
      CMRKL = 0.0
      DO 120 I=1,NCOMP
      A2I(I) = ARKL(I,I)/((R**2)*(T**3))
      BI(I)=BRKL(I)/RT
      CI(I) = CRKL(I)/RT
      BMRKL=BMRKL+X(I)*BRKL(I)
      CMRKL = CMRKL + X(I)*CRKL(I)
      AIRKL(I)=0.0
      DO 120 J=1,NCOMP
      AIRKL(I)=AIRKL(I)+X(J)*ARKL(I,J)
  120 AMRKL=AMRKL+X(I)*X(J)*ARKL(I,J)
      A2 = AMRKL/((R**2)*(T**3))
      B=BMRKL/RT
      C = CMRKL/RT
      A(1)=1.0
      A(2) = (C*P*2.0) - (B*P) - 1.0
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C     2 + ((A2/B)*B*P)
      A(3)=((C*P)**2)-(2.0*C*B*(P**2))-(2.0*C*P) +A2*P
C     A(4) = (-B*(C**2)*(P**3)) - ((C**2)*(P**2)) - ((A2/B)*(B**2)*(P**2
C     2))
      A(4)=(-B*((C*P)**2)*P)-((C*P)**2)-(A2*B*(P**2))
      CALL CUBECN (MTYPE,A,Z)
      IF(MTYPE)115,140,140
  115 IF(LV.EQ.0) GO TO 145
C     ZL=AMIN1(Z(1),Z(2),Z(3))
      ZL=AMIN1(Z(1),Z(2),Z(3))
C     ZL = DMIN1(Z(1),Z(2),Z(3))
CC    JJ=0
CC    DO 146 I=1,3
CC    ZZ(I)=9999.
CC    JJ=JJ+1
CC    IF(Z(I).LT.0.0) GO TO 146
CC    ZZ(JJ)=Z(I)
CC146 CONTINUE
C     ZL=AMIN1(ZZ(1),ZZ(2),ZZ(3))
      GO TO 150
C 145 ZL = DMAX1(Z(1),Z(2),Z(3))
  145 ZL = AMAX1(Z(1),Z(2),Z(3))
      GO TO 150
  140 ZL=Z(1)
  150 H=B*P/ZL
      HH = C*P/ZL
C     WRITE(3,591) H,HH,P,A2,B,ZL,LV
  591 FORMAT(5X,6D12.4,I2)
C     THE NEXT CARD IS COMMENTED TO SEE THE EFFECT ON THE LIMITS VALUE
C     CALL EQNRK(A2,B,P,H,HH,ZL,LV)
      VL=RT*B/H
  123 CONTINUE
      IF(LV.EQ.0) GO TO 135
      QD = T*(VL+CMRKL)**2
      QH = (2.0*AMRKL)/(T*(VL+CMRKL)**3)
      QK = RT/((VL-BMRKL)**2)
  135 DO 130 I=1,NCOMP
C     WRITE(3,591)ZL,H
C     PHILN = DLOG(1.0/(1.0-H)) - DLOG(ZL) +
      PHILN = ALOG(1.0/(1.0-H)) - ALOG(ZL) +
     2 (H/(1.0-H))*(BRKL(I)/BMRKL)-(A2/C)*(HH/(1.0+HH))*
     3((2.0*AIRKL(I)/AMRKL)-((HH/(1.0+HH))*(CRKL(I)/CMRKL)))
C    3((2.0*AIRKL(I)/AMRKL)-((HH/(1.0+HH))*(1.00000/CMRKL)))
CC   3((2.0*AIRKL(I)/AMRKL)-((HH/(1.0+HH))*(CRKL(I)/CMRKL)))
C     PHI(I)=DEXP(PHILN)
      PHI(I)= EXP(PHILN)
      IF(LV.EQ.0) GO TO 130
      QE1 = 0.0
      DO 125 J=1, NCOMP
  125 QE1 = QE1+ X(J)*ARKL(I,J)
      QE = 2.0* (QE1 - ((AMRKL*CRKL(I))/(VL+CMRKL)))
      QG = (RT/(VL-BMRKL)) * (1.0 + (BRKL(I)/(VL-BMRKL)))
      PVOL(I) = ((QE/QD) - QG) / (QH-QK)
  130 CONTINUE
  300 RETURN
      END
      SUBROUTINE EQNRK(A2,B,P,E,EE,Z,LV)
      IMPLICIT REAL*8(A-H,O-Z)
      TOL=1.0D-6
      IH=0
      IJ=0
   45 IF(LV.LT.1) GO TO 47
      IF(E.LT.1.0) GO TO 46
      E=E-0.02
      IH=IH+1
      IF(IH.LT.20) GO TO 45
      E=0.98
      GO TO 46
   47 IF(E.GT.0.0) GO TO 46
      E=E+0.01
      IH=IH+1
      IF(IH.LT.20)GO TO 47
      E=0.02
   46 IJ=IJ+1
      FE=-B*P /E+1./(1.0-E)-(A2/B)*E/(1.+EE)**2
      DFE=B*P /E**2 +1./(1.-E)**2-(A2/B)/(1.+EE)**2
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C       WRITE(3,592)E,FE,DFE,LV
C 592   FORMAT(20X,3E12.4,5X,I2)
C       IF(ABS(DFE).LT.1.0E-20) DFE=DFE/ABS(DFE)*1.0E-20
        TEST=FE/DFE
        E=E-TEST.
        IF(IJ.GT.60)GO TO 48
        IF(DABS(TEST/E).GT.TOL) GO TO 45
   48   Z   =B*P/E
        RETURN
        END
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