LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

1

92
3-2-83

(2)

I-8132

ORNL/Sub/81-1012/1

Dr. 1222

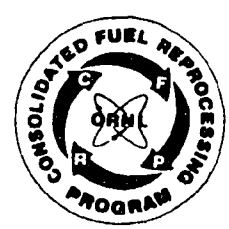
ornl

OAK RIDGE NATIONAL LABORATORY

UNION CARBIDE

A THERMODYNAMIC CONSISTENCY TEST PROCEDURE USING ORTHOGONAL COLLOCATION AND THE PENG-ROBINSON EQUATION OF STATE

Prepared by
Luther L. Hamm and V. Van Brunt
College of Engineering
University of South Carolina
Columbia, South Carolina 29208



OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

MASTER

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes — Printed Copy: A18, Microfiche: A01

ORNL/Sub/81-1012/1
Dist. Category UC-86

Consolidated Fuel Reprocessing Program

A THERMODYNAMIC CONSISTENCY TEST PROCEDURE USING ORTHOGONAL COLLOCATION AND THE PENG-ROBINSON EQUATION OF STATE

ORNL/Sub--81-1012/1
DE83 007160

Prepared by
Luther L. Hamm and V. Van Brunt
College of Engineering
University of South Carolina
Columbia, South Carolina 29208

August, 1982

NOTICE This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

Under subcontract DE-AS05-79SR1012
for
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY
Contract No. W-7405-eng-26

ACKNOWLEDGEMENT

This work was performed at the College of Engineering, University of South Carolina, for the U. S. Department of Energy under the supervision of Dr. Vincent Van Brunt on Grant No. EY-77-S-09-1012 (DE-AS05-79SR1012). The author wishes to express appreciation to the original program package developers, L. J. Christiansen and A. Fredenslund, for their prior work on the programs. Also the author would like to thank Dr. J. R. Merriman for the copy of the original programs and information he provided and to M. J. Stephenson for his guidance.

Several people contributed substantially to the completion of this report. The author would like to express appreciation to Dr. Thomas G. Stanford for his professional advice on thermodynamic topics and for the subroutines used for plotting the the diagrams. The author would like to express his appreciation to Dr. J. Begg for his professional advice on the use of the computer system at the University of South Carolina and to M. Jankowski of the Computer Center staff for his aid in producing the computer printouts of the modified programs.

The author would further like to thank Ms. Barbara Antaya for reviewing the report and providing constructive comments. Speical thanks goes to Dr. Vincent Van Brunt for both his professional guidance concerning the work and his efforts to increase incentive to perform. The author is especially grateful for the secretarial assistance of Kay McPherson.

Her patience with the author and in typing and editing of this manuscript is evident.

ABSTRACT

The Christiansen and Fredenslund programs for calculating vapor-liquid equilibria have been modified by replacing the Soave-Redlich-Kwong equation of state with the newly developed Peng-Robinson equation of state. This modification was shown to be a decided improvement for high pressure systems, especially in the critical and upper retrograde regions. Thermodynamic consistency tests were developed and used to evaluate and compare calculated values from both the modified and unmodified programs with reported experimental data for several vapor-liquid systems.

A THERMODYNAMIC CONSISTENCY TEST PROCEDURE USING ORTHOGONAL COLLOCATION AND THE PENG-ROBINSON EQUATION OF STATE

BY

LUTHER L. HAMM
AND
V. VAN BRUNT

SCOPE

Christiansen and Fredenslund have extended the differential consistency test developed by Van Ness et al. (1967) to high-pressure systems. In the extention of the development, they introduced a numerical method for solving differential equations, known as orthogonal collocation, to calculate the value of the excess Gibbs free energy at chosen values of liquid composition. From these values, the Christiansen and Fredenslund program package evaluates the equilibrium vapor mole fractions corresponding to each experimental liquid mole fraction, x_i.

Experimental data of the form pressure, temperature, and the composition of both phases enables one to test the data for thermodynamic consistency. Two forms of the Gibbs-Duhem equation can be used to test the data. The first form is the common isothermal, isobaric Gibbs-Duhem equation. This

equation is used in the commonly applied area tests; however, Van Ness et al. (1967)[6] have shown that this method is of limited value. The second form, which is the one used in this study, is known as the isothermal, nonisobaric differential Gibbs-Duhem equation. The major difference between the two forms is that the second form includes a term containing the slope of the P-X curve. The value of this term is small at low pressures and is often neglected, but at higher pressures this term cannot be neglected. Additionally, the isothermal, nonisobaric differential Gibbs-Duhem equation requires additional knowledge of the liquid molar volumes of both the pure components and mixtures.

In this report, the Christiansen and Fredenslund programs are modified with the Peng-Robinson equation of state. Comparison of the results obtained with the original and the modified sets of programs showed definitive superiority of the Peng-Robinson modification.

Development of a separate program for determining the interaction parameter used in the Peng-Robinson equation has been generated. The correlating parameters for the critical temperature, critical volume, and the characteristic constant for the i-j interaction must be taken from the literature. Procedures for the estimation of these parameters are under development.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

Advances in chemical engineering made during the 1950's through the development of the Benedict-Webb Rubin[1] and Redlich-Kwong[2] equations of state have broadened the base for performing fluid property calculations. Further advancement in the 1960's came from the advent of the generalized or mixed-model type correlation by Chueh and Prausnitz.[3]

At that particular time, the design engineer had available to him an analytical method which could use entirely computer calculations for calculating vapor-liquid equilibria. These methods relied mainly on the Soave-Redlich-Kwong two-constant equation of state to describe the behavior of the equilibrium vapor phase.

In 1976, the Peng-Robinson two-constant equation of state was made available[4]. The primary advantages of the Peng-Robinson equation to that of the Soave-Redlich-Kwong equation are its ability to describe more accurately the behavior of the equilibrium vapor phase in the critical region as well as in the upper retrograde region. One further feature of the Peng-Robinson equation is the reduction of the four omega constants required for a binary mixture in the Soave-Redlich-Kwong equation to a single interaction parameter.

In this report, the Christiansen and Fredenslund[5] programs which use the Soave-Redlich-Kwong equation of state have been modified by replacing the equation of state with the newly

developed Peng-Robinson equation of state. An additional computer output of graphs for the pressure and excess Gibbs free energy versus mole fractions are also included. In addition to the differential consistency analysis used, an integral consistency test is included to completely confirm the thermodynamic consistency.

II. THERMODYNAMIC ANALYSIS

Phase-rule restrictions limit the form of binary vapor-liquid equilibrium data that can be taken. Binary data cannot be taken with pressure and temperature constant. However, data of this type may still be tested for thermodynamic consistency using the common isothermal, isobaric Gibbs-Duhem equation provided the system in question is a low pressure system.

If the system to be investigated is at high pressures, a more general form of the Gibbs-Duhem equation is required. The nonisothermal, nonisobaric Gibbs-Duhem equation is discussed in detail by Van Ness (1959)[7]. Applied to liquid systems in equilibrium with their vapors, it takes the form

$$\ln \gamma_1 - \ln \gamma_2 = \left(\frac{dg}{dx_1}\right)_\sigma - \left[V\left(\frac{dP}{dx_1}\right)_\sigma - \sum_{i=1}^{2} x_i V_i^\circ \left(\frac{dP_i^\circ}{dx_i}\right)_\sigma\right]\frac{1}{RT} + \frac{H^E}{RT^2}\left(\frac{dT}{dx_1}\right)_\sigma, \quad (1)$$

where σ is the constraint of saturation and g is equal to G^E/RT. For a binary mixture, the following relationship is also valid:

$$g = x_1 \ln \gamma_1 + x_2 \ln \gamma_2. \quad (2)$$

When restricted to isothermal data, combination of equations 1 and 2 yields:

$$\ln \gamma_1 = g + x_2\left(\frac{dg}{dx_1}\right)_\sigma - \frac{x_2}{RT}\left[V\left(\frac{dP}{dx_1}\right)_\sigma - \sum_{i=1}^{2} x_i V_i^\circ \left(\frac{dP_i^\circ}{dx_1}\right)_\sigma\right] \quad (3)$$

and

$$\ln \gamma_2 = g - x_1\left(\frac{dg}{dx_1}\right)_\sigma + \frac{x_1}{RT}\left[V\left(\frac{dP}{dx_1}\right)_\sigma - \sum_{i=1}^{2} x_i V_i^\circ \left(\frac{dP_i}{dx_i}\right)_\sigma\right]. \qquad (4)$$

Since the terms $\left(\frac{dP}{dx_1}\right)_\sigma$ and $\left(\frac{dP_i^\circ}{dx_1}\right)_\sigma$ are approximately equal in most cases, both brackets of equations 3 and 4 are approximated as

$$V^E\left(\frac{dP}{dx_i}\right)_\sigma, \qquad (5)$$

where $V^E = V_{mix} - \sum_{i-1}^{2} x_i V_i^\circ$ when the standard states are the pure components at the temperature and pressure of the system (i.e. symmetric convention) or $V^E = \overline{V} - x_i \overline{V}_1^\infty - x_2 V_2$ when the standard states where component one is infinitely dilute in pure component two are both at the temperature and pressure of the system (unsymmetric convention). The reference fugacity of the non-condensable component is the Henry's constant at the system's pressure and temperature (Prausnitz, 1969)[8].

III. THE METHOD OF ORTHOGONAL COLLOCATION

The representation of excess thermodynamic functions by a particular set of orthogonal polynomials has been demonstrated to be advantageous in the treatment of data for binary systems by Van Ness (1967). The methods discussed by Klaus and Van Ness allow such data to be treated thoroughly, efficiently, and rigorously, with the added benefit of being well suited for numerical computation.

In the test for thermodynamic consistency, the differential nonisobaric Gibbs-Duhem equation is applied on a point to point basis. The choice of points to be analyzed is an optimum one; in this study the selected points on the abscissa of the pressure versus liquid mole fraction data are the zero roots to a Jacobi polynomial, specifically the Legendre polynomial.

The experimental pressure-liquid mole fraction data are fitted by Legendre polynomials. The Legendre polynomials used for fitting represent the deviation from Raoult's Law. Once the fitting of the data is complete, an analytical equation for the system's vapor pressure versus liquid-mole fraction can readily be computed.

In equations 3 and 4 the differential operator for g is determined by the orthogonal collocation method. The differential operator is approximated at each collocation point by the weighted sum of the function values of the discretization matrix A_{kl}, which is determined from the Legrendre polynomials. The

appropriate collocation approximation for the derivative is

$$\left(\frac{dg}{dx_1}\right)_\sigma \Big|_{x_k} = \sum_{1=0}^{N} A_{k1} g_1, \tag{6}$$

where x_k refers to the particular collocation point and N is the number of internal collocation points plus the two end points. In order to compute g at the data points, a Lagrangian four point interpolation is used. This enables computations to be made at any desired liquid mole fraction when the liquid activity is required to be known. The ability to know γ_i as a function of x_i is used in the development of a integral consistency test.

IV. THE THERMODYNAMIC CONSISTENCY TEST

Binary vapor-liquid equilibrium data in the form of $x_i(P)$ and $y_i(P)$ at constant temperature, variable pressure are analyzed. The derivatives of $[dP/dx_1]_\sigma$ and $[dg/dx_1]_\sigma$ are evaluated by use of the orthogonal collocation method already mentioned, while values for the volumes and fugacity coefficients are evaluated by the equation of state, or from the Lychman-Eckert-Chueh correlation. When the system of interest is a mixture with Freon-12 as the solvent, the equation of state for the solvent is the one developed by McHarness[10].

From the definition of liquid activity coefficients, γ_i,

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i^\circ} = \frac{y_i \phi_i P}{x_i f_i^\circ} , \tag{7}$$

where ϕ_i is the vapor phase fugacity coefficient of component i and is calculated by equation 31 and since the sum of the partial pressures must equal the system pressure (i.e. $\sum_{i=1}^{2} y_i P_i = P$) one obtains

$$P = \frac{x_1 \gamma_1 f_1^\circ}{\phi_1} + \frac{x_2 \gamma_2 f_2^\circ}{\phi_2} . \tag{8}$$

Substitution of equation 3 and 4 for γ_1 and γ_2 respectively into equation 8 generates an equation with g as the unknown.

The equation is a highly nonlinear differential equation which applies at one given liquid mole fraction, namely a single collocation point. However, the differential equation can be

reduced to an algebraic equation by using the appropriate collocation approximation (Equation 6). The result is shown in equation 9.

$$P = \frac{x_1}{\phi_1} f_1^\circ \exp[g + x_2 \sum_{i=0}^{N} A_{ki} g_i - \frac{x_2}{RT} V^E (\frac{dP}{dx_1})_\sigma]$$

$$+ \frac{x_2}{\phi_2} f_2^\circ \exp[g - x_1 \sum_{i=0}^{N} A_{ki} g_i + \frac{x_1}{RT} V^E (\frac{dP}{dx_1})_\sigma]. \qquad (9)$$

In using this collocation approximation, the approximation itself consists of a function using elements which contain the g's at all the collocation points. In other words, the N differential equations in g are now converted to N coupled algebraic equations in g, where N stands for the total number of collocation points plus the two end points. To solve these equations for the correct N number of g's, a Newton-Raphson iteration procedure is used.

The initial estimates of g for the symmetric convention are the following:

$$g = x_k(1 - x_k) \quad \text{for all } k, \qquad (10)$$

where x_k refers to each collocation point (i.e. the first order Redlich-Kister function).

The initial estimates for the unsymmetric convention are

$$g = 0 \quad \text{for all } k. \qquad (11)$$

Since the Legendre polynomials are all developed on an abscissa of range zero to one, the zero's of the polynomial for the unsymmetric case must have the following variable substitution introduced:

$$x'_k = x_k \cdot x_{1,\,max}, \tag{12}$$

where $x_{1,max}$ is the largest experiment liquid mole fraction introduced into the data. This effectively normalizes the mole fraction variable.

V. EQUATION OF STATE

The equation of state (Peng and Robinson, 1976[11]) used for work has the form

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} . \tag{13}$$

Equation 13 can be rewritten as

$$Z^3 + (B-1)Z^2 + (A-3B^2-2B)Z + (B^3+B^2-AB) = 0, \tag{14}$$

where

$$A = \frac{a(T)P}{R^2T^2}, \tag{15}$$

$$B = \frac{bP}{RT}, \tag{16}$$

and

$$Z = \frac{Pv}{RT}. \tag{17}$$

Equation 14 yields one real and two imaginary roots in the one-phase region or three real roots in the two-phase region. In the vapor-liquid two-phase region, the largest positive real root applies to the vapor's compressibility factor, while the smallest positive real root corresponds to the liquid's compressibility factor.

By imposing the restrictions of the classical derivatives at the critical point:

$$\left(\frac{\partial P_c}{\partial V_c}\right)_{T_c} = 0 \tag{18}$$

and

$$\left(\frac{\partial^2 P_c}{\partial V_c^2}\right)_{T_c} = 0 \tag{19}$$

to equation 13 one obtains:

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \tag{20}$$

and

$$b = 0.07780 \frac{RT_c}{P_c} . \tag{21}$$

At temperatures differing from the critical

$$a(T) = a(T_c) \cdot \alpha(T_r, \omega) \tag{22}$$

and

$$b(T) = b(T_c), \tag{23}$$

where the functional form of $\alpha(T_r, \omega)$ was determined by literature vapor pressure values such that the equilibrium condition

$$f^L = f^V, \tag{24}$$

and the thermodynamic relationship

$$\ln \frac{f}{P} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P}\right) dP, \tag{25}$$

when applied to equation 13 is satisfied along the pure vapor pressure curve. $\alpha(T_r,\omega)$ was linearized by the following equations:

$$\alpha(T_r,\omega)^{1/2} = 1 + k(1-T_r^{1/2}), \tag{26}$$

where

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2. \tag{27}$$

For mixtures, the recommended rules for use with equation 13 are:

$$b_m = \sum_i x_i b_i, \tag{28}$$

$$a_m = \sum_{ij} x_i x_j a_{ij}, \tag{29}$$

and

$$a_{ij} = (1-C_{ij})(a_i a_j)^{1/2}, \tag{30}$$

where x_i is the mole fraction corresponding to that phase and C_{ij} is the binary interaction parameter fitted from binary vapor-liquid equilibrium data.

The following expression for the fugacity coefficient of component k in a mixture can be derived from equations 25 and 13.

$$\ln \phi_k = \frac{b_k}{b}(Z-1) - \ln(Z-B) +$$

$$-\frac{A}{\sqrt{2}\,2B}\left(\frac{2\sum_i x_i a_{ik}}{a} - \frac{b_k}{b}\right) \ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right). \qquad (31)$$

The partial molar volume of component k in a mixture of N components is defined by the triple-product relation,

$$\bar{V}_k = \frac{-\left(\frac{\partial P}{\partial n_k}\right)_{T,V,n_i(i\neq k)}}{\left(\frac{\partial P}{\partial V}\right)_{T,n_i(\text{all } i)}} = f(x,T,v). \qquad (32)$$

Using equation 13, equation 32 provides $\bar{V}_k$ as a function of the composition, temperature and the saturated molar volume of the liquid mixture. By performing the indicated operations of equation 32 on equation 13 and applying the mixing rules, one obtains

$$\bar{V}_k = \frac{\frac{RT}{v-b}\left(1+\frac{b_k}{v-b}\right) - \frac{2}{v(v+b)+b(v-b)}\left(\sum x_i a_{ki} - \frac{ab_k(v-b)}{v(v+b)+b(v-b)}\right)}{\frac{RT}{(v-b)^2} - \frac{2a(v+b)}{[v(v+b)+b(v-b)]^2}}. \qquad (33)$$

These equations have been utilized to implement the Peng-Robinson equation of state in subroutines PRVOL, PRFUG, and PRRON.

VI. SATURATED MOLAR VOLUME OF A LIQUID MIXTURE

The saturated liquid phase molar volume is calculated with the Lyckman-Eckert-Chueh correlation:

$$\frac{\rho_{ci}}{\rho_{si}} = V_r^{(o)} + \omega V_r^{(1)} + \omega^2 V_r^{(2)}, \qquad (34)$$

where $V_r^{(j)}$'s are functions of the true reduced temperature of the mixture. The formulation and values of the coefficients in the equation for $V_r^{(j)}$ are tabulated by Prausnitz[12].

In order to calculate the mixture's reduced temperature, a pseudocritical temperature has been defined as

$$T_{cm} = \sum_i \sum_j \Phi_i \Phi_j T_{cij}, \qquad (35)$$

where Φ_i is a volume fraction defined by

$$\Phi_i = \frac{x_i V_{ci}}{\sum_j x_j V_{cj}}, \qquad (36)$$

and

$$T_{cij} = (1-K_{ij})(T_{ci}\, T_{cj})^{1/2}, \qquad (37)$$

where K_{ij} is a binary interaction parameter which is found from experimental data.

Two regions of interest exist, one where $T_{rm} \leq 0.93$ and the other where $1.0 > T_{rm} > 0.93$. When $T_{rm} \leq 0.93$, equation 34 is used with the following suggested rules for mixtures:

$$\frac{1}{\rho_{cm}} = V_{cm} = \sum_i x_i V_{ci} \tag{38}$$

and

$$\omega_m = \sum \Phi_i \omega_i. \tag{39}$$

For $T_{rm} > 0.93$, to assure that $T_{rm} = V_{rm} = 1.0$, corrected pseudo-critical temperatures and volumes are defined:

$$T'_{cm} = T_{cm} + (T_{cT} - T_{cm})\, D(T'_{rm}) \tag{40}$$

and

$$V'_{cm} = V_{cm} + (V_{cT} - V_{cm})\, D(T'_{rm}), \tag{41}$$

where T_{cT} and V_{cT} are the true mixture critical properties. $D(T'_{rm})$ is a deviation function with constraints forcing $T_{rm} = V_{rm} = 1.0$ at the critical point. $D(T'_{rm})$ is tabulated by Prausnitz and in order to calculate equation 40, the modified regula-falsi method is employed.

VII. THE REFERENCE FUGACITIES AND FUGACITY COEFFICIENTS

In these programs for low pressure systems where nonidealities are negligible, the reference fugacities are the vapor pressures of the pure components at the system's pressure and temperature. When the pressures are high enough for nonidealities to be significant, the reference fugacities for the symmetric convention are

$$f_i^\circ = p_i^{sat}\,\phi_i^{sat}\,\exp\left(\int_{p_i^{sat}}^{P_{sys}} \frac{V_i}{RT}\,dP\right), \qquad (42)$$

while for systems where one of the components is above its critical temperature, the solute's reference fugacity is

$$f_i^\circ = H_{(1,2)}^{P_2^{sat}}\,\exp\left(\int_{p_2^{sat}}^{P_{sys}} \frac{\overline{V}_i^{\infty}}{RT}\,dP\right). \qquad (43)$$

The exponential term is the Poynting correction factor and the solvent's reference fugacity is that of equation 42.

The unsymmetric convention of normalization is used when one component is a noncondensable, supercritical component. The advantage of its use is that it avoids the ambiguity which exists for standard-state fugacities for supercritical gases. It avoids this ambiguous reference-state by using the well-defined and experimentally accessible Henry's constant, $H_{1,2}^{P_2^{sat}}$. The Henry's constant is evaluated by extrapolating to $x_1 = 0$ on a plot of

ln f_1/x_1 versus x_1. The superscript P_2^{sat} is the saturation vapor pressure of the pure solvent and $\bar{V}^{\infty}$ is the liquid partial molar volume of the solute infinitely dilute in the solvent, mathematically stated as follows:

$$H^{P}_{(1,2)} = \lim_{x_1 \to 0} \frac{\hat{f}_1}{x_1} = \lim_{x_1 \to 0} \frac{\hat{\Phi}_1 y_1 P}{x_1} . \qquad (44)$$

The vapor phase fugacity coefficients for all pure components as well as the mixtures are calculated directly from equation 31 which was derived from the Peng-Robinson equation of state.

VIII. AREA TEST

With the integral isothermal, isobaric Gibbs-Duhem consistency test equation[13]

$$\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0, \tag{45}$$

and the analytic expressions for the γ_i's obtained by evaluating equation 9, an area test was developed. Equation 45 was proposed by Redlich and Kister[14] using the isothermal, isobaric Gibbs-Duhem equation and for isothermal data equation 45 is an extremely good approximation.

To approximate the integral of equation 45, the trapezoidal rule was applied to 2^{NMAX} equally spaced values of liquid mole fractions. The maximum value allotted to NMAX is 6. Romberg integration was employed to evaluate the integral. As stated earlier, the results obtained from the area test were inconclusive.

For systems where one component is noncondensable, equation 45 was rearranged by Newman[15] to

$$\int_Z^{XMAX} \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = \text{constant}, \tag{46}$$

where the lower limit of the integral is fixed as the smallest experimental liquid mole fraction; however, the lower limit was selected arbitrarily for convenience.[15]

IX. CALCULATION OF THE INTERACTION PARAMETER

When using equation 13 for the gas mixtures, the mixing rules of equation 28 through 30 apply. The same rules apply for vapor as well as liquids, with y replacing x in the mixing rules. Equation 30 contains the interaction parameter C_{ij}. This parameter represents the deviation of a_{ij} from the classical geometrical mean.

Noting that the equilibrium ratio is defined as

$$K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^L}{\hat{\phi}_i^V}, \tag{47}$$

where $\hat{\phi}_i^L$ and $\hat{\phi}_i^V$ are calculated by equation 31, the interaction coefficient C_{ij} can be found by trial and error at any given x-y datum point.[16]

To minimize the error in the value of C_{ij} for a particular system, each datum point was used in the trial and error method.

The procedure used to converge on the results is: a series of C_{ij}'s are assumed, and the K_i's from equation 47 are calculated. The accepted value for C_{ij} is the one which yields the minimum sum of absolute deviations in the experimental and calculated equilibrium ratios, namely

$$/\Delta K_i/ + /\Delta K_j/ = \text{minimum sum.} \tag{48}$$

X. PROGRAM DESCRIPTION

Program one: (PROGRAM 1)

PROGRAM 1 calculates vapor phase mole fractions for systems under low pressure. The activity coefficients used in the algorithm are normalized under the symmetric convention. Since the system's pressure is low, the standard reference state fugaciy used is the vapor pressure of each pure component.

Program two: (PROGRAM 2)

PROGRAM 2 calculates vapor phase mole fractions for systems under high pressures where both components are below their critical temperature. The activity coefficients are also normalized by the symmetric convention. At high pressures it is necessary to take non-idealities in the vapor phase into account. This is done by using for the standard reference state fugacity the liquid phase pure component fugacity for each component.

Program three: (PROGRAM 3)

PROGRAM 3 calculates vapor phase mole fractions for systems under high pressures where one component is a non-condensable. The asymmetric convention for normalization of activity coefficient is used. The standard reference state fugacity used for the noncondensable is Henry's constant, while for the solvent it's the pure component fugacity.

Program four: (PROGRAM 4)

PROGRAM 4 estimates the binary interaction parameter, C_{ij}, for the Peng-Robinson equation of state.

All four programs have some of the same subroutines in common. Table 1 is a list of the subroutines needed for each main program.

TABLE 1

LIST OF SUBROUTINES

PROGRAM 1	PROGRAM 2	PROGRAM 3	PROGRAM 4
MAIN SECTION			
INTRP	INTRP	INTRP	PLTRE
DFOPR	DFOPR	DFOPR	
JCOBI	JCOBI	JCOBI	
GAUSL	GAUSL	GAUSL	
POLEG	POLEG	POLEG	
SCALE	SCALE	SCALE	
PLOT	PLOT	PLOT	
IPOINT	IPOINT	IPOINT	
ROMB	ROMB	ROMB	
GIBBS	GIBSH	GIBSA	
LEFIT	LEFIT	ALFIT	
PCAL	PCAL	PCALA	
	DPX	DPXA	
	DPOLE	DPOLE	
	PLTRE	PLTRE	
	GNVOL	*MCVOL	
	MLMGN	GNVOL	
	ITERE	MLMGN	
		ITERE	
		INTDAL	
		INTP	
SUBSECTION ONE (The Peng-Robinson Equation of State)			
	PRVOL	PRVOL	PRFUG
	PRFUG	PRFUG	PRVOL
	PRRON	PRRON	
		PNRPV	
SUBSECTION TWO (The Soave-Redlich-Kwong Equation of State)			
	RKVOL	RKVOL	
	RKFUG	RKFUG	
	RKKON	RKKON	
		RDKPV	

Description of each individual subroutine can be found in Appendix A; in addition, computer printouts of the main programs and their subroutines written in Fortran IV for use on a IBM 370 are in Appendix A.

*When the system under investigation has Freon-12 (Dichlorodifluoromethane) as the solvent, subroutine GNVOL should be replaced with MCVOL in PROGRAM 3. Subroutine MCVOL contains the equation of state developed by McHarness for Freon 12.

XI. RESULTS

Two systems that were previously investigated using the Soave-Redlich-Kwong equation of state by Christiansen and Fredenslund[5] were chosen to demonstrate the performance of all the programs listed and the program superiority when the Peng-Robinson equation of state is used. The effects of varying the number of internal collocation points and the value of the Peng-Robinson interaction parameter, C_{ij}, are also shown. The actual computer printouts have also been included in Appendix B. From the ten different runs reviewed here, the evidence clearly indicates that the modified programs are indeed substantially superior to the original programs. Table 2 lists each different run made and indicates the values of the pertinent variables used.

Case Study # 1:

The carbon dixoide-ethane system at 10°C[17] was chosen to illustrate the superiority that the new modified programs have over the original programs. Even though several differing systems of this type were tested (CH_4-Ar, CO_2-C_3H_8), this particular system appears to show the typical improvement one should expect from the modified program, PROGRAM 2.

The system chosen is a high pressure system with both components under their respective critical temperatures; therefore, the use of the high pressure program, PROGRAM 2, was appropriate in this case. Both the Peng-Robinson and Soave-Redlich-Kwong equations of state were used in PROGRAM 2 for comparison. To

Table 2. A Listing of the Runs Made and Their Pertinent Values.

System	Run #	Number of Collocation Points	Degree of Legendre Polynomial	Interaction Parameter, C_{ij}	Equation of State	Program Used
CO_2-C_2H_6	(1)	3	2	*	*	PROGRAM 1
	(2)	3	2	*	S-R-K[1]	PROGRAM 2 (R-K)
	(3)	3	2	0.147	P-R[2]	PROGRAM 2 (P-R)
	(4)	3	2	0.000	P-R[2]	PROGRAM 2 (P-R)
CH_4-C_3H_8	(1)	2	1	-0.050	P-R[2]	PROGRAM 3 (P-R)
	(2)	2	1	0.010	P-R[2]	PROGRAM 3 (P-R)
	(3)	2	1	0.050	P-R[2]	PROGRAM 3 (P-R)
	(4)	2	1	*	S-R-K[1]	PROGRAM 3 (R-K)
	(5)	3	1	0.010	P-R[2]	PROGRAM 3 (P-R)
	(6)	4	1	0.010	P-R[2]	PROGRAM 3 (P-R)

* This category does not apply.

1 The Soave-Redlich-Kwong Equation of State employs four interaction paramters which were obtained from the literature (3).

2 The Peng-Robinson Equation of State employs one interaction parameter which was obtained by PROGRAM 4.

illustrate the need for taking into account nonidealities due to high pressures, the low pressure program, PROGRAM 1, was used for comparing results.

The values of the deviation between the observed and calculated vapor phase mole fractions for the four runs are tabulated in Table 3 and are plotted on Figure 1. Figure 1 clearly indicates that the high pressure effects on the system must be taken into account. Run # 3 and Run # 4 in Figure 1 also show the effect of varying the Peng-Robinson interaction parameter, C_{ij}. The value of the interaction parameter was computed by PROGRAM 4 for Run # 3, while in Run # 4 it was set equal to zero. This com-

Table 3. The Results of the Consistency Test for the CO_2-C_2H_6 System

Experimental Values		Calculated Values			
yexp	yexp	ycalc			
		Run # 1	Run # 2	Run # 3	Run # 4
0.0	0.0	0.0	0.0	0.0	0.0
0.061	0.033	0.0916	0.0648	0.0633	0.0730
0.198	0.128	0.2821	0.2055	0.1982	0.1578
0.315	0.234	0.4228	0.3228	0.3105	0.2006
0.384	0.311	0.4985	0.3962	0.3824	0.2628
0.480	0.421	0.5825	0.4920	0.4794	0.3878
0.578	0.542	0.6531	0.5896	0.5813	0.5575
0.666	0.655	0.7076	0.6759	0.6724	0.7012
0.711	0.711	0.7334	0.7180	0.7165	0.7564
0.727	0.730	0.7423	0.7324	0.7315	0.7726
0.815	0.833	0.7983	0.8136	0.8150	0.8418
0.852	0.873	0.8270	0.8488	0.8505	0.8771
0.908	0.928	0.8803	0.9042	0.9056	0.9119
0.947	0.961	0.9251	0.9437	0.9446	0.9416
1.0	1.0	1.0	1.0	1.0	1.0

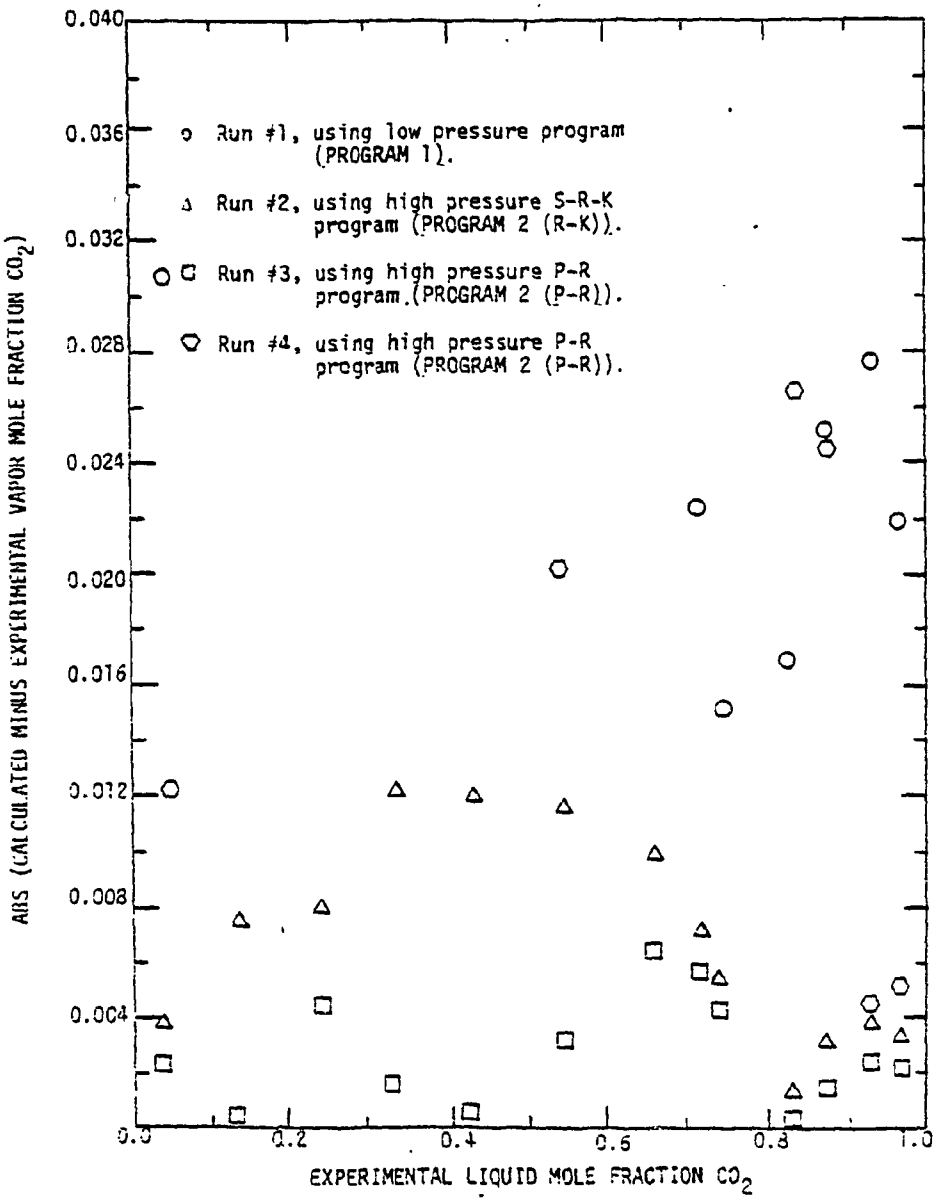


Figure 1. The effect of the equation of state. The CO_2-C_2H_6 system at 10°C, 3 collocation points, and a second degree Legendre polynomial (data from Fredenslund and Mollerup, 1974).

parison indicates the degree of improvement obtainable when the interaction parameter is adjusted to its optimum value by PROGRAM 4.

Further investigation of the outputs between Run # 3 and Run # 4 in Appendix B indicates that the criteria that the sum of deviations must be minimized is not sufficient. In order to conclude that the Peng-Robinson interaction parameter C_{ij}, is at its optimum value, the entire set of thermodynamic properties calculated should be reviewed. This can clearly be seen by viewing the excess Gibbs free energy diagrams of Run # 3 and Run # 4. Even though Run # 4 converged to a solution*, its diagram of excess Gibbs free energy predicts that two homogeneous azeotropes exist . No system of this kind has been physically observed; therefore, Run # 4 should be discarded on these grounds.

Even though PROGRAM 2 predicts a behavior which has not been physically observed, this prediction is easily explained by reviewing the significance of the Peng-Robinson interaction parameter C_{ij}. From equation 30 it is seen that C_{ij} is a parameter which indicates the amount of deviation from the geometrical mean that the unlike molecules present. By setting C_{ij} equal to zero in Run #4, this implies that each molecule will interact with every other molecule identically. Therefore, the excess Gibbs free energy should be zero throughout the entire range of liquid mole fractions. The diagram of excess

* The sum of deviations for Run # 4 were smaller than for Run #1, (see Table 4).

Gibbs free energy in Run # 4 shows this tendency to force the excess Gibbs free energy function to zero.

Figure 2 is an expanded view of Figure 1 which shows the superiority that exists when the Peng-Robinson equation of state, using its optimum value for the interaction paramter, C_{ij}, is used in PROGRAM 2. The four interaction paramters required by the Soave-Redlich-Kwong equation of state were taken from the literature[3].

An optimization of these four parameters was performed. Run # 2 represents the results with the four interaction parameters at a local optimum. The optimization was limited due to the extensive time requirements of iterating the program, PROGRAM 2 (R-K).

Although small deviations exist for both equations of state in Figure 2, an apparent trend at each experimental data point can be seen. The trend is a definite increase in the prediction of the vapor phase mole fractions with use of the modified program. In most cases in the literature, deviations of this nature are plotted with experimental vapor, not liquid, mole fractions. By choosing the liquid mole fractions as the abscissa, one is able to see a systematic error as one ranges from zero to one. This is more apparent when solubility data are being investigated. The systematic error in the deviations appear to be an oscillation about the zero axis as shown in Figure 2.

Table 4 shows one small drawback in the modified program. An extra iteration was required for finding the correct values

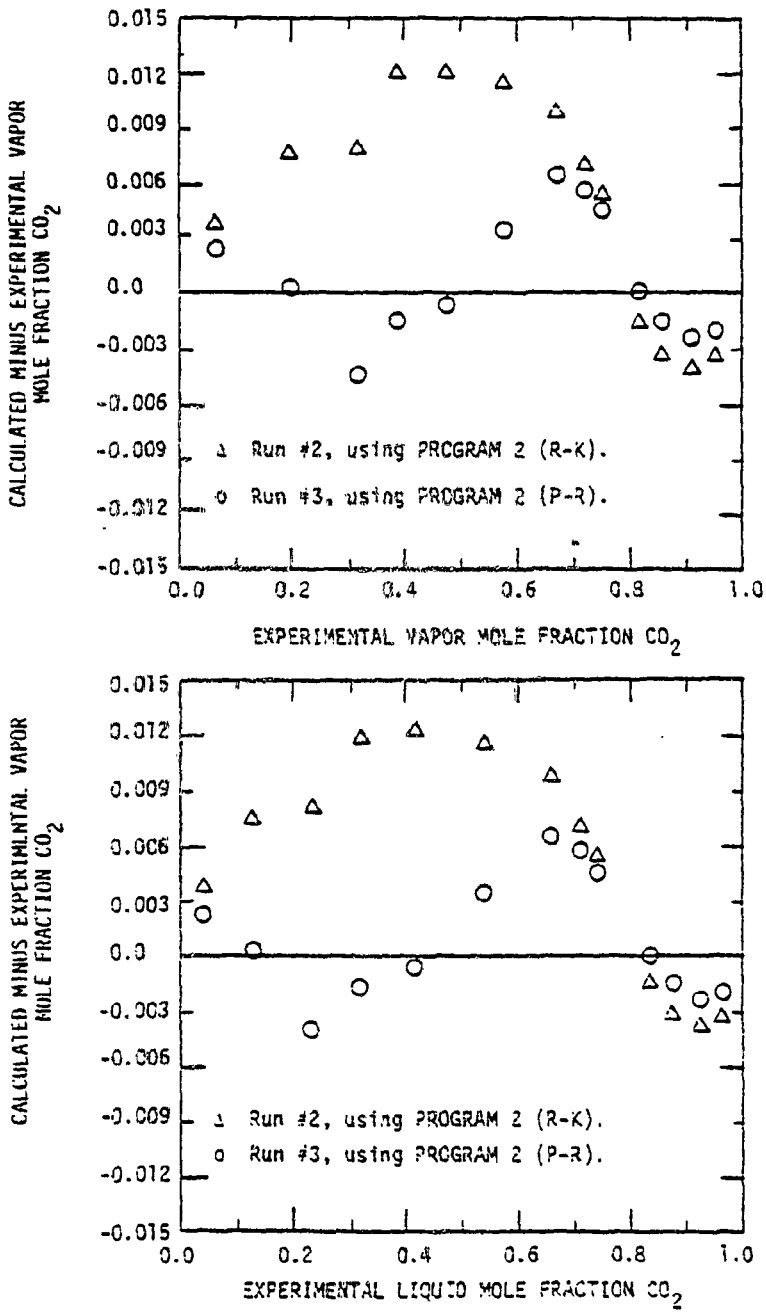


Figure 2. An expanded view of Figure 1 for the CO_2-C_2H_6 system at 10°C.

of the excess Gibbs free energy; however, this is insignificant compared to the improved vapor phase mole fraction prediction obtained.

Table 4. Results of the Consistency Test for the CO_2-C_2H_6 System.

Run #	Deviation* Sum	Total # of Iterations
(1)	0.0535097	4
(2)	0.0007760	14
(3)	0.0001447	15
(4)	0.0452195	16

* Deviation Sum = $\frac{1}{m}\sum_{i=1}^{m}|ycalc_i - yexp_i|^2$

where m = the number of data points (excluding pure components).

Case Study # 2:

The methane-propane binary system at -17°C[18] was chosen to illustrate the effects of varying the internal collocation points and the value of the Peng-Robinson interaction parameter. This system is one of several solubility systems tested that were studied by Christiansen and Fredenslund[5] (CO_2-C_3H_8, N_2-CH_4, CO_2-C_2H_6, CH_4-Ar). Solubility systems are high pressure systems where one component is noncondensable and the unsymmetric con-

vention for normalization of the activity coefficients is preferred. When the unsymmetric convention is used, the evaluation of the Henry's constant is required.

Since the system chosen is a solubility system, the use of the high pressure program, PROGRAM 3, was appropriate in this case. Both the Peng-Robinson and the Soave-Redlich-Kwong equations of state were used in PROGRAM 3 for comparison.

The values of the deviations between the observed and calculated vapor phase mole fractions for the six runs are tabulated in Table 5 and plotted in Figure 3 and Figure 4. Figure 3 shows the effect of the number of internal collocation points on the calculated vapor phase mole fractions. Figure 4 shows the effect of the interaction parameter on the calculated vapor phase mole fractions. In both figures the results from using the Soave-Redlich-Kwong equation of state have been included for comparison. Figure 5 is an expanded view of Figure 4 which clearly shows the superiority in the vapor phase mole fraction prediction when the Peng-Robinson equation of state is used. Also the systematic trend is quite apparent in Figure 5 when the abscissa is the liquid mole fraction The Henry's constant for each run is tabulated in Table 6.

The results reported here clearly indicate that the new modified programs are superior to the original programs. Further superiority resides in the fact that only one interaction parameter is required for the Peng-Robinson equation, while four are needed for the Soave-Redlich-Kwong equation. The availability

Table 5. The Results of the Consistency Test for the CH_4-C_3H_8 System

		ycalc					
yexp	xexp	Run # 1	Run # 2	Run # 3	Run # 4	Run # 5	Run # 6
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.560	0.034	0.6665	0.6682	0.6693	0.6739	0.6867	0.6893
0.767	0.089	0.8283	0.8310	0.8327	0.8351	0.8437	0.8428
0.832	0.142	0.8765	0.8798	0.8819	0.8330	0.8882	0.8866
0.861	0.197	0.9001	0.9040	0.9065	0.9073	0.9089	0.9073
0.880	0.249	0.9124	0.9169	0.9197	0.9202	0.9191	0.3729
0.888	0.303	0.9199	0.9250	0.9283	0.9285	0.9250	0.4571
0.890	0.357	0.9240	0.9300	0.9337	0.9337	0.9283	0.6706
0.892	0.410	0.9257	0.9328	0.9370	0.9368	0.9300	0.9289
0.891	0.464	0.9257	0.9341	0.9390	0.9385	0.9307	0.9296
0.889	0.518	0.9240	0.9343	0.9399	0.9391	0.9307	0.9295
0.882	0.572	0.9207	0.9334	0.9400	0.9388	0.9302	0.9288
0.869	0.636	0.9145	0.9312	0.9392	0.9376	0.9290	0.9276
0.845	0.718	0.9060	0.9293	0.9390	0.9370	0.9285	0.9270
0.800	0.800	0.9023	0.9306	0.9414	0.9392	0.9294	0.9279

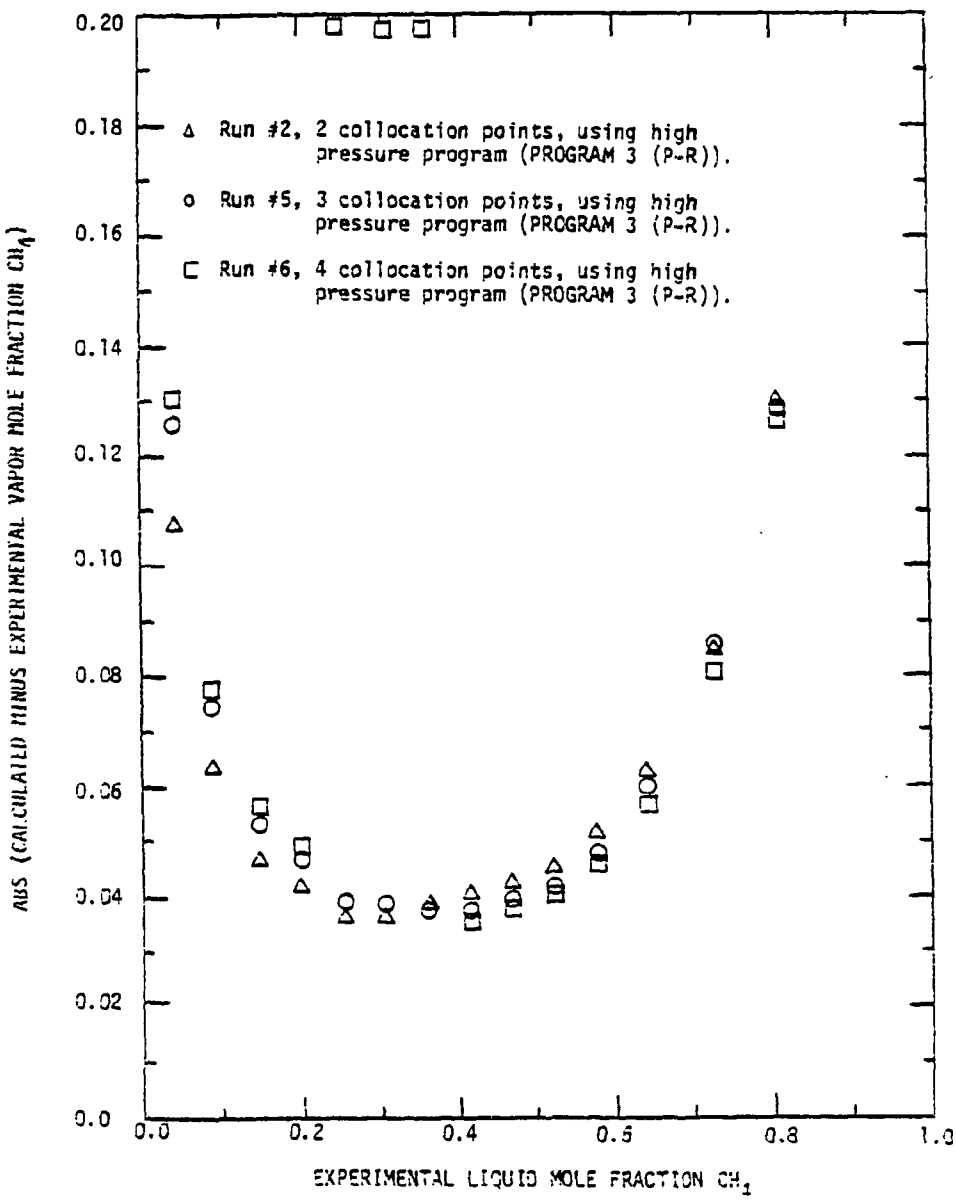


Figure 3. The effect of the number of internal collocation points. The CH_4-C_3H_8 system at -17°C, C_{ij} = 0.01, and a second degree Legendre polynomial.

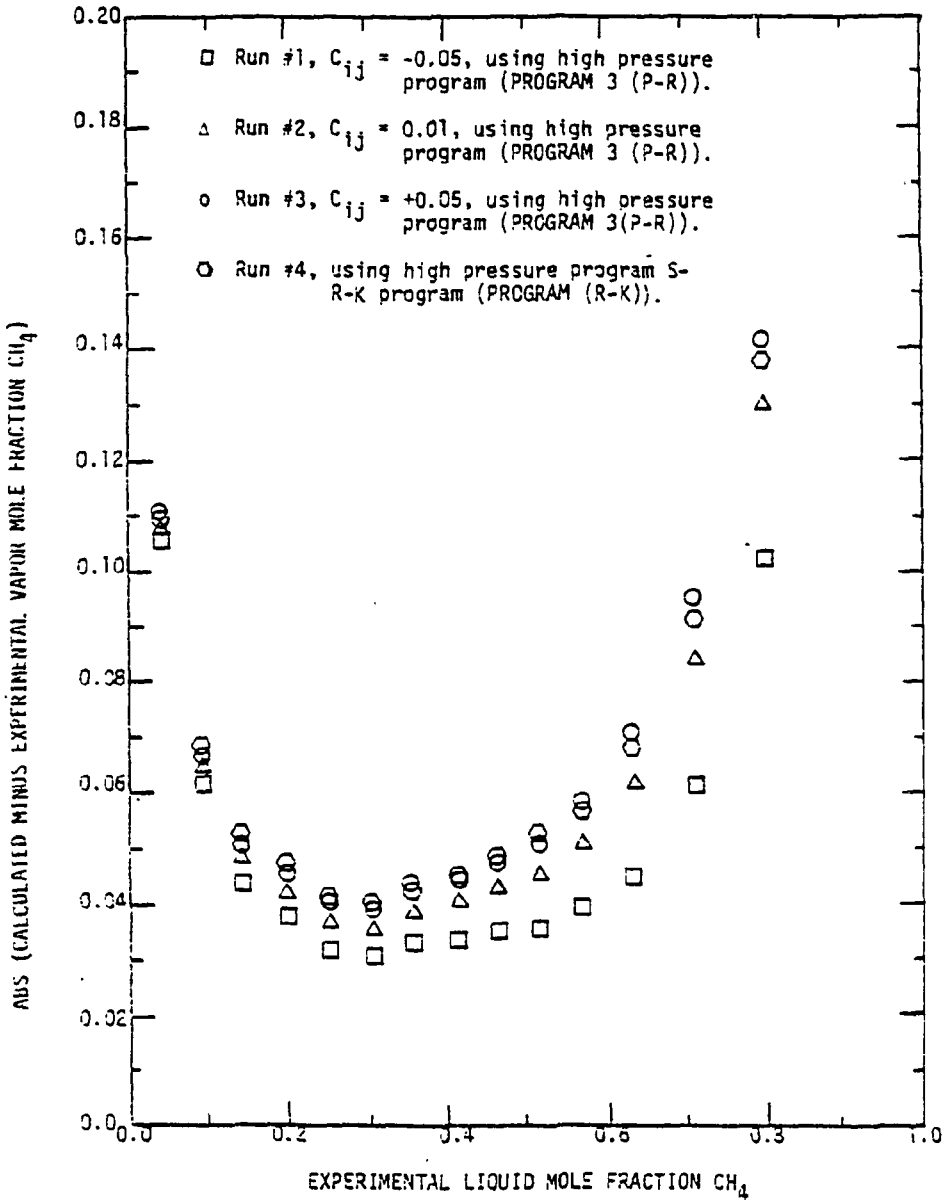


Figure 4. The effect of the interaction parameter, C_{ij}. The CH_4-C_3H_8 system at -17°C, 2 collocation points, and a second degree Legendre polynomial (data from Wichterle and Kobayashi, 1972).

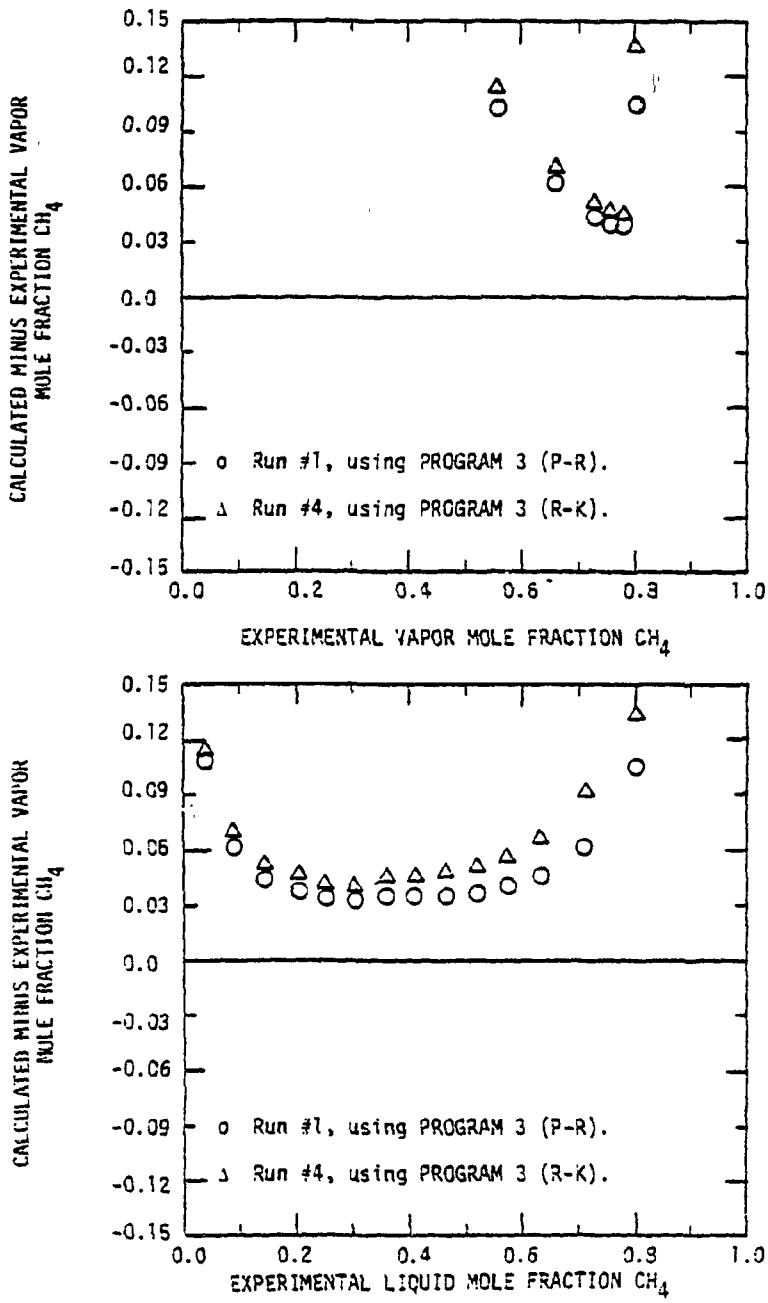


Figure 5. An expanded view of Figure 4 (Run #1 and 4) for the the CH_4-C_3H_8 system at -17°C.

Table 6. Calculation of Henry's Constant and Results of the Consistency Test for the CH_4-C_3H_8 System.

Run #	Henry's Constant, (atm)	Deviation* Sum	Total # of Iterations
(1)	112.55	0.0431585	16
(2)	113.02	0.0605322	17
(3)	113.02	0.0699474	17
(4)	115.65	0.0700868	16
(5)	120.46	0.0661260	17
(6)	124.16	0.5517500	greater than 100

* Deviation sum = $\frac{1}{m}\sum_{i=1}^{m}|ycalc_i - yexp_i|^2$

where m = the number of data points (excluding pure components).

of data to estimate these four parameters in some cases does not exist. The estimation of the Peng-Robinson interaction parameter can always be computed when data for a thermodynamic consistency test are present.

XII. DISCUSSION OF RESULTS

The two systems tested appear to be thermodynamically consistent. However, to assure that they are one must first compute the experimental uncertainties in the liquid and vapor phase mole fractions. Christiansen stated that the following empirical criterion must be met if the data is to be thermodynamically consistent[19]:

$$|ycalc_i - yexp_i| \leq \Delta x_i + \Delta y_i, \qquad (49)$$

where Δx_i and Δy_i are the experimental uncertainties in the data at each data point i.

The modifications done in this work on the original programs show that the Peng-Robinson equation of state has improved performance over the Soave-Redlich-Kwong equation of state in the critical and upper retrograde regions. The reduction of four interaction paramters to one when using the Peng-Robinson equation shows the strength of the equation of state for this application, since the procedure for optimizing the constants is further simplified. Further modifications can be made by extending the modified programs to multicomponent high-pressure systems and by placing specific equations of state for a desired system into subroutines PRVOL, PRRON and PRFUG.

NOMENCLATURE

Symbol	Description	Typical Units
Roman Form:		
A	Grouping of parameters used in the Peng-Robinson equation	unitless
ABS(X)	The absolute value of the expression x	unitless
a_{ij}	Parameter used in the Peng-Robinson equation	$(atm \cdot cc^2)/gmole^2$
A_{kl}	Elements of the discretization matrix	unitless
a_m,a(T)	Mixture parameter used in the Peng-Robinson equation	$(atm \cdot cc^2)/gmole^2$
B	Grouping of parameters used in the Peng-Robinson equation	unitless
b_i	Parameter used in the Peng-Robinson equation	cc/gmole
b_m	Mixture parameter used in the Peng-Robinson equation	cc/gmole
C_{ij}	Binary interaction parameter for the i-j interaction	unitless
f_i^o	Reference-state fugacity of component i	atm
$\hat{f}_i$	Partial fugacity of component i	atm
g	G^E/RT	joules/(atm·cc)
G^E	Excess Gibbs free energy	joules/gmole
H^E	Excess enthalpy	joules/gmole

NOMENCLATURE (Cont.)

Symbol	Description	Typical Units
$H_{(1,2)}$	Henry's constant for solute 1 in solvent 2	atm
k	Constant in Peng-Robinson equation for α	unitless
k_{ij}	Characteristic constant for the i-j interaction of the deviation from the geometrical mean	unitless
K_i	Equilibrium ratio	unitless
n_i	Moles of component i	gmole
NMAX	Maximum number of Romberg integration employed	unitless
P	Pressure of the system	atm
P_c	Critical pressure	atm
P_i	Partial pressure of component i	atm
P_i^o	Vapor pressure of pure component i	atm
P-R	The Peng-Robinson equation of state	____
R	The gas-constant	(atm• cc)/ (gmole• °K)
S-R-K	The Soave-Redlich-Kwong equation of state	_____
T	Temperature of the system	°K
T_{ci}	Critical temperature of component i	°K
T_{cij}	Critical temperature characteristic of the i-j interaction	°K

NOMENCLATURE (Contd.)

Symbol	Description	Typical Units
T_{cm}	Pseudocritical temperature of the mixture	°K
T_{cT}	True critical temperature of the mixture	°K
T_{rm}	Reduced mixture temperature	unitless
T'_{cm}	Corrected pseudocritical temperature of the mixture	°K
v	Specific molar volume	cc/gmole
V	Volume of the solution	cc
V^E	Excess molar volume of the solution	cc/gmole
$\overline{V}$	Partial molar volume	cc/gmole
V_{ci}	Critical molar volume of component i	cc/gmole
V_{cm}	Pseudocritical volume of the mixture	cc/gmole
V_{cT}	True critical volume of the mixture	cc/gmole
V_{mix}	Mixture molar volume	cc/gmole
V_{rm}	Reduced volume of the mixture	unitless
$\overline{V}_i^{\infty}$	Partial molar volume of species i at infinite dilution	cc/gmole
V'_{cm}	Corrected pseudocritical volume of mixture	cc/gmole
V_i°	Molar volume of pure component i	cc/gmole
$V_r^{(j)}$	Generalized reduced molar volume function	unitless

NOMENCLATURE (Cont.)

Symbol	Description	Typical Units
X_i, x_i	Liquid mole fraction of species i	unitless
x_k	Collocation point for a liquid mole fraction	unitless
x'_k	Normalized liquid mole fraction at a collocation point	unitless
xexp	Experimental liquid mole fraction	unitless
XMAX	Maximum experimental liquid mole fraction in solubility data	unitless
y_i	Vapor mole fraction of species i	unitless
ycalc	Calculated vapor mole fraction	unitless
yexp	Experimental vapor mole fraction	unitless
Z	The compressibility factor	unitless
Greek Form:		
α	Correlation used in Peng-Robinson equation	unitless
γ_i	Activity coefficient of species i	unitless
ρ_{ci}	Critical liquid density of component i	gmole/cc
ρ_{si}	Saturated liquid density of component i	gmole/cc
ω_i	Acentric factor	unitless
ω_m	Mixture's acentric factor	unitless
σ	Constraint of saturation	unitless

NOMENCLATURE (Contd.)

Symbol	Description	Typical Units
$\hat{\Phi}_i$	Vapor phase fugacity coefficient of component i	unitless
$\Delta(x)$	The difference between the calculated and experimental values of the property x.	units of property x
Φ_i	Volume fraction of species i	unitless

Subscripts:

c	Critical property
i,j,l	Indexing
k	A collocation point
max	The maximum value
m,mix	Mixture property
r	Reduced property
s,sat	Saturation
sys	System property
1,2	Solute 1 in solvent 2

Superscripts:

L	Liquid property
sat	Saturation
V	Vapor property
o	Pure component property
—	Partial molar property

REFERENCES

1. Benedict, M., Webb, G. B., and Rubin, L. C., Chem Engr. Prog., 47, 419 (1951).

2. Redlich, O., and Kwong, J. N. S., Chem. Rev., 44, 233 (1949).

3. Prausnitz, J. M., and Chueh, P. K., "Computer Calculations for High Pressure Vapor-Liquid Equilibria," Prentice-Hall, Englewood Cliffs, N. J. (1968).

4. Peng, D. Y., and Robinson, D. B., Ind. Engr. Chem. Fundam., 15, 59 (1976).

5. Christiansen, L. J., and Fredenslund, A., AIChE Journ., 21, 49 (1975).

6. Klaus, R. L., and Van Ness, H. C., "The Orthogonal Polynomial Representation of Thermodynamic Excess Functions," Chem. Engr. Prog. Symp. Ser., # 81, 88 (1967).

7. Van Ness, H. C., Chem. Engr. Sci., 10, 225 (1959).

8. Prausnitz, J. M., Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice-Hall, Englewood Cliffs, N. J. (1969).

9. Klaus, R. L. and Van Ness, H. C., "The Orthogonal Polynomial Representation of Thermodynamic Excess Functions," Chem. Engr. Prog. Symp. Ser., # 81, 101 (1967).

10. McHarness, R. C., Eiseman, B. J., and Martin, J. J., Refrigeration Engineering, 4, 32 (1955).

11. Peng, D. Y., and Robinson, D. B., Ind. Engr. Chem., Fundam., 15, 59 (1976).

12. Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., "The Properties of Gases and Liquids." McGraw-Hill, New York, N. Y. (1977).

13. Balziser, R. E., Samuels, M. R., and Eliassen, J. D., "Chemical Engineering Thermodynamics," Prentice-Hall, Englewood Cliffs, N. J. (1972).

14. Redlich, O., and Kister, A. T., Ind. Engr. Chem, 40, 345 (1948).

15. Newman, J. S., Integral Test for Consistency of Vapor-Liquid Equilibrium Data," Lawrence Berkeley Laboratory, University of California, No. LBL-3964, June 1975.

REFERENCES (Contd.)

16. Zulkevitch, D. and Joffe, J., AIChE Journ. 16, 112 (1970).

17. Fredenslund, A., and Mollerup, J., "Measurement and Prediction of Equilibrium Ratios for the Ethane-Carbon Dioxide System," Faraday Trans. I, 70, 1653 (1974).

18. Wichterle, I., and Kobayashi, R., "Vapor-Liquid Equilibrium of Methane-Ethane System at Low Temperatures and High Pressures," J. Chem. Eng. Data, 17, 9 (1972).

19. Christiansen, L. J., "Vapor-Liquid Equilibria in the Normal and Critical Regions," Ph. D., thesis, Inst. Kemite knik, Darmarks Tekniske Hojskole (in English) (1974).

APPENDICES

APPENDIX A

PROGRAM, SUBROUTINE, AND STATEMENT FUNCTION DESCRIPTIONS AND LISTINGS

PROGRAM DESCRIPTIONS AND COMPUTER PRINTOUTS

This section contains descriptions of the subroutines followed by a listing of the subroutines written in FORTRAN IV for an IBM 370 computer. For a quick reference, use Table 7 to locate a desired subroutine. All four main programs have also been listed at the very end of this appendix.

NOTE: PROGRAM 2 and PROGRAM 3 are available for either the Peng-Robinson or Soave-Redlich-Kwong equation of state. When choosing an equation of state, one must also use the correct main program which is indicated in the description of each main program.

TABLE 7. GLOSSARY OF NAMES FOR SUBROUTINES AND MAIN PROGRAMS

Descriptions and Printouts of

Main Programs (MAIN),

Subroutines (SUBR),

and Statement Functions (FUNCT)

SUBROUTINE ALFIT (X, Y, N,K)

Input Parameters:

Real X: The normalized value for the experimental mole fraction of component one in the liquid phase.

Real Y: The experimental pressure of the system at each given XEXP which corresponds to the normalized values, X.

Integer N: The dimension of vectors X and Y, (i.e. number of data points).

Integer K: The degree of the Legendre polynomial used for fitting the P-X data.

The Output Is:

By a common statement

COMMON/LEG/AA

Vector $\overline{AA}$: Dimension [K + 1] and contains the coefficients to the fitting function which represents the deviation from ideality, (i.e. Raoult's Law).

ALFIT fits P-X data to a curve using Legendre polynomials and calls for GAUSL, a Gaussian elimination method to solve $\overline{A} * \overline{X} = B$ where $\overline{X}$ is the vector $\overline{AA}$. In order to use the Legendre polynomials, which are for a range of zero to one, the liquid mole fractions of the solubility data must first be normalized to zero to one.

ALFIT employs the following algorithm:

A: Calculate S(I) at data points.

B: Formulate curve with S(I) as a weighting function.

C: Formulate matrix with unknown coefficients.

D: Invert matrix (solve for $\overline{AA}$) (call to GAUSL).

LIST OF EQUATIONS

Deviation Function: $S(i) = P_{sys} - P_i^{sat}(1 - x)$

Weighting Function: x

Fitting Function: $C(i) = \sum_{i=1}^{N} S(j) x P_i(x)$

where $P_i(x) = i^{th}$ degree Legendre polynomial.

```
      SUBROUTINE ALFIT(X,Y,N,K)
C
C     SUBROUTINE ALFIT FITS INDIVIDUAL POINTS ON A CURVE WHERE X IS
C     THE INDEPENDENT VARIABLE AND Y IS THE DEPENDENT VARIABLE USING
C     A FUNCTION CONTAINING LEGENDRE POLYNOMIALS AS THE FITTING FUNCTION.
C
      DOUBLE PRECISION X2,X3
      DOUBLE PRECISION PP
      DOUBLE PRECISION X1
      DOUBLE PRECISION DFLOAT
      DOUBLE PRECISION C(21),B(25,25),AA(21),PPP(51)
      DOUBLE PRECISION X(25),Y(25),S(25)
      DOUBLE PRECISION POLEG
      COMMON/LEG/AA
      KP1=K+1
      DO 1 I=1,KP1
    1 C(I)=0.
      DO 2 I=1,KP1
      DO 2 J=1,KP1
    2 B(I,J)=0.
      DO 3 I=1,N
    3 S(I)=Y(I)-Y(1)*(1.-X(I))
      DO 4 IB=1,KP1
      DO 4 J=1,N
      X3=X(J)
    4 C(IB)=C(IB)+S(J)*X(J)*POLEG(X3,IB)
      DO 5 NA=1,KP1
      DO 5 L=1,KP1
      DO 5 KA=1,N
      X2=X(KA)
    5 B(NA,L)=B(NA,L)+X(KA)*X(KA)*POLEG(X2,NA)*POLEG(X2,L)
      DO 6 I=1,KP1
      KP2=K+2
    6 B(I,KP2)=C(I)
      CALL GAUSL(25,25,KP1,1,B)
      DO 7 I=1,KP1
    7 AA(I)=B(I,KP2)
      RETURN
      END
```

SUBROUTINE DFOPR (ND, N, NO, NL, I, ID, FA, FB, FC, ROOT, VECT)

Input Parameters:

Interger DN,

NO, NL, N: As in JCOBI.

Interger ID: The degree of the deviative of weights needed.

Vector $\overline{FA}$, $\overline{FB}$,

$\overline{FC}$: Dimension [NT = N + NO + NL] and contains the 1st, 2nd, and 3rd derivatives of the polynomial at the zero roots, (i.e. collocation points).

The Output is:

Vector $\overline{VECT}$: Dimension [NT] and contains the computed interpolation weights for the given root.

DFOPR calculates interpolation weights in order to form a computational quadrature which enables the main program to approximate derivatives of a dependent variable at any given point, provided we have the root, FA, FB, and FC available, (e.g. evaluates the discretization matrix).

DFOPR employs the following algorithm:

A: If ID = 1, compute discretization matrix for $y^{(1)}$.
If ID = 2, compute discretization matrix for $y^{(2)}$.
If ID = 3, compute gaussian quadrature weights.

B: Place computed values in $\overline{VECT}$.

LIST OF EQUATIONS

In this program only ID = 1 is of concern. At a given root

x_i

$$VECT(j) = L_j^{(1)}(x_i) = 1/2\left(\frac{P_{n+1}^{(2)}(x_i)}{P_{n+1}^{(1)}(x_i)}\right.$$

where $x = x_i$. The vector of $L_i^{(1)}(x_i)$ values may now be used to approximate the first derivative of any dependent variable of x at the given root x_i.

$$\left(\frac{dy}{dx}\right)_{x=x_i} = \sum_{k=1}^{NI} L_k^{(1)}(x_i) \cdot y_k$$

```
      SUBROUTINE DFOPR(ND,N,NO,N1,I,ID,FA,FB,FC,ROOT,VECT)
C
C     SUBROUTINE DFOPR CALCULATES THE ELEMENTS OF THE DISCRETIZATION
C     MATRIX
C
      DOUBLE PRECISION FA(ND),FB(ND),FC(ND),ROOT(ND),VECT(ND),X,Y,AX,AY
      NT=N+NO+N1
      IF(ID.GE.3) GO TO 10
      DO 20 J=1,NT
      IF(J.NE. I) GO TO 21
      IF(ID.EQ.1)  VECT(I)=FB(I)/FA(I)/2.
      IF(ID.EQ.2)  VECT(I)=FC(I)/FA(I)/3.
      GO TO 20
   21 Y=ROOT(I)-ROOT(J)
      VECT(J)=FA(I)/FA(J)/Y
      IF(ID.EQ.2)  VECT(J)=VECT(J)*(FB(I)/FA(I)-2./Y)
   20 CONTINUE
      GO TO 50
   10 Y=0.
      IF(ID.EQ.4) GO TO 30
      DO 25 J=1,NT
      X=ROOT(J)
      AX=X*(1.-X)
      IF(NO.EQ.0)  AX=AX/X/X
      IF(N1.EQ.0)  AX=AX/(1.-X)/(1.-X)
      VECT(J)=AX/FA(J)/FA(J)
   25 Y=Y+VECT(J)
      GO TO 60
   30 DO 35 J=1,NT
      X=ROOT(J)
      IF(NO.EQ.0)  AX=1./X
      IF(N1.EQ.0)  AX=1./(1.-X)
      VECT(J)=AX/FA(J)/FA(J)
   35 Y=Y+VECT(J)
   60 DO 61 J=1,NT
   61 VECT(J)=VECT(J)/Y
   50 RETURN
      END
```

DOUBLE PRECISION FUNCTION DPOLE (X, K)

Input Parameters:

Real X: As in POLEG.

Integer K: As in POLEG.

The Output Is: The first derivative of the Legendre polynomials, specifically the K^{th} degree.

DPOLE is a statement function which contains the recursion formula for the first derivative of the Legendre polynomials.

LIST OF EQUATIONS

$$DPOLE = \frac{dP_k(x)}{dx}$$

```
      DOUBLE PRECISION FUNCTION DPOLE(X,K)
      DOUBLE PRECISION DAL(21),X
      DOUBLE PRECISION DFLOAT,POLEG
      DAL(1)=0.
      DAL(2)=2.
      DO 1 LG=3,K
      LGM1=LG-1
1     DAL(LG)=(DFLOAT(2*LGM1-1)*((2.*X-1.)*DAL(LG-1)+2.*POLEG(X,LGM1))
     1-DFLOAT(LGM1-1)*DAL(LG-2))/DFLOAT(LGM1)
      DPOLE=DAL(K)
      RETURN
      END
```

SUBROUTINE DPX (P2S, P1S, K, DDX, X)

Input Parameters:

Real P2S: Vapor pressure of pure component two.

Real P1S: Vapor pressure of pure component one.

Integer K: The degree of the Legendre polynomial used for fitting the P-X data.

Real X: Mole fraction of component one in liquid phase where derivative is desired.

The Output Is:

Real DDX: The derivative of pressure versus mole fraction at the given X input, (i.e. pressure gradient).

DPX generates the derivative of the P-X curve by using the recursion formula for the first derivative of the Legendre polynomial and evaluates it at the given X.

DPX employs the following algorithm.

A: Generate the deviation from Raoult's law by

Legendre polynomial and evaluates it at the given X.

DPX employs the following algorithm.

A: Generate the deviation from Raoult's law by Legendre polynomials and evaluate it at the given X.

B: Generate the derivative of Part A.

C: Compute pressure gradient.

LIST OF EQUATIONS

Pressure Deviation: $P_{dev} = x(1 - x)\ ALEG = x(1 - x) \sum_{i=1}^{K} AA(i)P_i(x)$

where ALEG is the deviation function and $x(1 - x)$ is the weight function.

Pressure System: (see subroutine PCAL).

$$P_{sys} = x(P_1^s - P_2^s) + P_2^s + x(1 - x)ALEG$$

$$\frac{dP_{sys}}{dx} = P_2^s + P_1^s + (1 - 2x)ALEG + x(1 - x)\frac{d(ALEG)}{dx}$$

where $\frac{d(ALEG)}{dx} = \sum_{i=1}^{K} AA(i)DPOLE(x,i)$, (see FUNCTION DPOLE).

```
      SUBROUTINE DPX(P2S,P1S,K,DDX,X)
      DOUBLE PRECISION P2S,P1S,AA(21),DDX,X
      DOUBLE PRECISION POLEG,DPOLE
      DOUBLE PRECISION DALEG,ALEG
      COMMON/LEG/AA
      DALEG=0.
      ALEG=0.
      DO 1 IL=1,K
    1 ALEG=ALEG+AA(IL)*POLEG(X,IL)
      DO 2 IK=1,K
    2 DALEG=DALEG+AA(IK)*DPOLE(X,IK)
      DDX=P1S-P2S+(1.-X)*ALEG-X*ALEG+(1.-X)*K*DALEG
      RETURN
      END
```

SUBROUTINE DPXA (P2S, K, DDX, X)

Input Parameters:

Real P2S: The vapor pressure of pure component two.

Integer K: The degree of the Legendre polynomial used for fitting the P-X data.

Real X: The normalized value for the mole fraction of component one in the liquid phase.

The Output Is:

Real DDX: The derivative of pressure versus mole fraction at the given X input, (i.e pressure gradient).

DPXA generates the derivative of the P-X curve by using the recursion formula for the first derivative of the Legendre polynomial and evaluates it at the given X. Since the Legendre polynomials range from zero to one, the liquid mole fraction must also be normalized.

DPXA employs the following algorithm:

A: Generate the deviation function from the Legendre polynomial.

B: Generate the derivative of Part A.

C: Compute the pressure gradient.

LIST OF EQUATIONS

Deviation Function: $ALEG = \sum_{i=1}^{K} AA(i)P_i(x)$

Weighting Function: x

Pressure of System (see subroutine PCALA):

$$P_{sys} = P_2^{sat}(1 - x) + x(ALEG)$$

Gradient:

$$\frac{dP_{sys}}{dx} = x\frac{d(ALEG)}{dx} + ALEG - P_2^{sat}$$

where $\frac{d(ALEG)}{dx} = \sum_{i=1}^{K} AA(i)DPOLE(x,i)$, (see Function DPOLE).

```
      SUBROUTINE DPIA(P2S,K,DDX,X)
      DOUBLE PRECISION P2S,P1S,AA(21),DDX,X
      DOUBLE PRECISION POLEG,DPOLE
      DOUBLE PRECISION DALEG,ALEG
      COMMON/LEG/AA
      DALEG=0.
      ALEG=0.
      DO 1 IL=1,K
    1 ALEG=ALEG+AA(IL)*POLEG(X,IL)
      DO 2 IK=1,K
    2 DALEG=DALEG+AA(IK)*DPOLE(X,IK)
      DDX=ALEG+X*DALEG-P2S
      RETURN
      END
```

SUBROUTINE GAUSL (NRA, NCA, N, NS, A)

Input Parameters:

Integer NRA: The number of rows to the matrix $\overline{\overline{A}}$ read into subroutine.

Integer NCA: The number of columns to the matrix $\overline{\overline{A}}$ read into subroutine.

Integer N: Dimension of square matrix to be solved.

Integer NS: The number of columns to shift over for result to be placed.

Matrix $\overline{\overline{A}}$: Dimension [N, N + 1] and contains the matrix $\overline{\overline{B}}$ [N, N], plus in the column N + 1 it also contains vector $\overline{C}$, (i.e. $\overline{\overline{B}} \cdot X = \overline{\overline{C}}$).

The Output Is:

Matrix $\overline{\overline{A}}$: In column N plus one the result to $\overline{\overline{B}} \cdot \overline{X} = \overline{C}$ for $\overline{X}$ is placed.

GAUSL solves $B \cdot \overline{X} = \overline{C}$ by Gaussian elimination with parapivoting. The matrix $\overline{\overline{A}}$ in solving is destroyed and the result is then placed in matrix $\overline{\overline{A}}$'s N plus first column for output.

GAUSL employs the following algorithm:

A: Find largest element (value) in given column.

B: Check to see if the element in A is the first nonzero diagonal position in matrix.

If - yes, go to D.

If - no, go to C.

C: Interchange rows, setting the element in A in first nonzero diagonal position.

D: Row reduce matrix (gaussian elimination).

E: Parapivot by column reducing matrix.

F: Return to A to select new element from next given column.

```
      SUBROUTINE GAUSL(NRA,NCA,N,NS,A)
      DOUBLE PRECISION X,A(NRA,NCA)
      DOUBLE PRECISION DABS
C
C     GAUSL SOLVES A*X=B. WHERE A IS N*N, BY GAUSSIAN ELIMINATION WITH
C     PARAPIVOTING. THE VECTOR B IS PLACED IN COLUMN N+1 OF A
C     A IS DESTROYED, AND THE SOLUTION IS PLACED IN COLUMN N+1
C
      N1=N+1
      NT=N+NS
      IF(N.EQ.1) GO TO 50
C
C     START ELIMINATION
C
      DO 10 I=2,N
      IP=I-1
      I1=IP
      X=DABS(A(I1,I1))
      DO 11 J=I,N
      IF(DABS(A(J,I1)).LT.X) GO TO 11
      X= DABS(A(J,I1))
      IP=J
 11   CONTINUE
      IF(IP.EQ.I1) GO TO 13
C
C     ROW INTERCHANGE
C
      DO 12 J=I1,NT
      X=A(I1,J)
      A(I1,J)=A(IP,J)
 12   A(IP,J)=X
 13   DO 10 J=I,N
      X=A(J,I1)/A(I1,I1)
      DO 10 K=I,NT
 10   A(J,K)=A(J,K)-X*A(I1,K)
C
C     ELIMINATION FINSHED, NOW BACKSUBSTITUTION
C
 50   DO 20 IP=1,N
      I=N1-IP
      DO 20 K=N1,NT
      A(I,K)=A(I,K)/A(I,I)
      IF(I.EQ.1) GO TO 20
      I1=I-1
      DO 25 J=1,I1
 25   A(J,K)=A(J,K)-A(I,K)*A(J,I)
 20   CONTINUE
      RETURN
      END
```

SUBROUTINE GIBBS (P1S, P2S)

Input Parameters:

Real P1S: Pure component one vapor pressure.

Real P2S: Pure component two vapor pressure.

By COMMON/DIV/A, P, G, ROD, NT, NPI, AA

Matrix $\overline{\overline{A}}$: Dimension [NT, NT] and contains the discretization weights in each row for each root (i.e. i^{th} row implies i^{th} root).

Vector $\overline{P}$: Dimension [NT] and contains system pressure at the given roots.

Vector $\overline{G}$: Dimension [NT] and contains the initial values of Gibbs excess free energy [G^E/RT].

VECTOR $\overline{ROD}$: Dimension [NT] and contains the zero roots to the Jacobi polynomial.

Integer NT: The number of internal collocation points plus the end points. (NT = N + NO + N1).

The Output Is: By COMMON/DIV/SA, G

Vector $\overline{SA}$: Dimension [NT] and contains the derivatives at G at each zero root, [i.e. $\frac{dg}{dx}|_{x=root}$].

Vector $\overline{G}$: Dimension [NT] and contains the values of G after determination of iteration procedure.

GIBBS uses a Newton-Raphson iteration procedure with initial estimates of Gibbs excess free energy at low pressures. The equations (1) and (2) are inserted in equation (3), a differential equation in G results. The derivatives are approximated by equation (4).

As a result of inserting equation (4) for the derivatives, the reduced differential equation is solved at the collocation points to N coupled linear equations. These equations are then solved by Gaussian elimination ($\bar{\bar{A}} \cdot \bar{X} = \bar{B}$).

Note: In Gibbs, the nonisothermal, nonisobaric Gibbs-Duhem equation has been simplified by taking into account the low pressure.

1) Close to the ideal state the volume excess is zero and this implies that $\frac{dP}{dx_1} = \sum_i \frac{dP_i}{dx_i}$. Thus, only the excess Gibbs free energy terms are included in the low pressure analysis.

2) The reference state is taken as the pure component vapor pressure.

GIBBS employs the following algorithm:

A: Calculate SA(I) by last approximation of G at the collocation points.

B: Compute the activity coefficients S1, S2 by using last approximation of G and SA at the collocation points.

C: Formulate next approximation of deviation term by the Newton-Raphson procedure.

D: Invert matrix (Gaussian elimination).

E: Compute new approximation to G at the collocation points.

F: Test for convergence of Del and new value of G.
If/S^2/ < 10^{-6}, go to return.
If/S^2/ > 10^{-6}, go to A.

LIST OF EQUATIONS

$$(1)\quad \ln\gamma_1 = g + x_2\left(\frac{dg}{dx_1}\right) = S1$$

$$(2)\quad \ln\gamma_2 = g - x_1\left(\frac{dg}{dx_1}\right) = S2$$

$$(3)\quad P - x_1\gamma_1 P_1^{sat} - x_2\gamma_2 P_2^{sat} = 0$$

$$(4)\quad \left(\frac{dg}{dx_1}\right)\Big|_{\substack{\text{saturation}\\ x_k}} = \sum_{i=1}^{NT} A_{ki}(g)_i$$

where $g = G = G^E/RT$ and $SA = \frac{dg}{dx_1}$.

The Newton-Raphson Procedure is as follows:

$$g_{k+1} = g_k - \frac{f(g_k)}{f'(g_k)}$$

minimize this term by letting it equal y_k.

The resulting set of equations are of the form:

$$f'(g_k)\cdot y_k = f(g_k)$$

$$\overline{\overline{A}}\cdot\overline{y} = \overline{B}$$

Inversion yields $\overline{y}$, which contains new approximation for $\overline{G}$.

```
      SUBROUTINE GIBBS(P1S,P2S)
C
C     SUBROUTINE GIBBS SOLVES THE COUPLED NON LINEAR COLLOCATION
C     EQUATIONS
C
      DOUBLE PRECISION A(25,25),SA(25),P(25),G(25),ROD(25)
      DOUBLE PRECISION B(25,25),S1(25),S2(25),P1S,P2S,SQ
      DOUBLE PRECISION DEXP
      DOUBLE PRECISION AA(21)
      COMMON/DIV/A,SA,P,G,ROD,NT,NP1,N
      COMMON/LEG/AA
  502 FORMAT(1HO,'MORE THAN 15 ITERATIONS')
  503 FORMAT(1HO,'ITERATION NR',I5)
      NWR=6
      ITER=0
   25 ITER=ITER+1
      IF(ITER-15) 27,27,26
   26 WRITE(NWR,502)
      GO TO 100
   27 DO 28 I=1,NT
   28 SA(I)=0.
      DO 30 I=1,NT
      DO 30 J=1,NT
      SA(I)=SA(I)+A(I,J)*G(J)
   30 CONTINUE
      DO 40 I=2,NP1
      S1(I)=ROD(I)*P1S*DEXP(G(I)+(1.-ROD(I))*SA(I))
      S2(I)=(1.-ROD(I))*P2S*DEXP(G(I)-ROD(I)*SA(I))
      IM1=I-1
      B(IM1,NP1)=P(I)-S1(I)-S2(I)
   40 CONTINUE
      DO 50 I=2,NP1
      IM1=I-1
      DO 50 J=2,NP1
      JM1=J-1
      IF(I-J) 45,48,45
   45 B(IM1,JM1)=-S1(I)*(1.-ROD(I))*A(I,J)+S2(I)*ROD(I)*A(I,J)
      GO TO 50
   48 B(IM1,IM1)=-S1(I)*(1.+(1.-ROD(I))*A(I,I))-S2(I)*(1.-ROD(I)*A(I,I))
   50 CONTINUE
      CALL GAUSL(25,25,N,1,B)
      SQ=0.
      DO 60 I=1,N
      IP1=I+1
      G(IP1)=G(IP1)-B(I,NP1)
      SQ=SQ+B(I,NP1)**2
   60 CONTINUE
      IF(SQ-1.D-12) 70,25,25
   70 WRITE(NWR,503) ITER
  100 CONTINUE
      RETURN
      END
```

SUBROUTINE GIBSA (FPP1, FPP2, STKOR, DELTA, ITER)

Input Parameters:

$\overline{\overline{A}}$, $\overline{P}$, $\overline{G}$, $\overline{ROD}$: As in GIBBS.

Real FPP1: This quantity is the solute's reference fugacity with the Poynting correction factor. (See equation 1A.)

Real FPP2: As in GIBSH. (See equation 2A.)

Real STKOR: Pertains to the volume excess multiplied by the pressure gradient. (See equation 3A.)

Real DELTA: The value of the maximum experimental liquid mole fraction given.

The Ouput Is:

Integer ITER: Gives number of iterations done before convergence occured.

Vector $\overline{SA}$, $\overline{G}$: As in GIBBS.

GIBSA uses the same iteration technique GIBBS does except both the higher pressure effects and the noncondensable component are taken into account, Ii.e. the unsymmetric convention).

1) The reference state is taken as FPP1 and FPP2.
2) The volume-excess terms in the Gibbs-Duhem equation are included in the calculations of the activity coefficients.

LIST OF EQUATIONS

$$\text{Equation (1A):} \quad FPP1 = \frac{H_{1,2}^{P^{sat}} \; EXP\{\frac{V^E \Delta P}{RT}\}}{\Phi_1}$$

Equation (2A): $FPP2 = \dfrac{f_2^{\circ}\ EXP\{\frac{V^E \Delta P}{RT}\}}{\phi_2}$

Equation (3A): $STKOR = \dfrac{V^E}{RT}(\dfrac{dP}{dx_1})_{saturation}$

Activity Coefficients:

1) $\ln \gamma_1 = g + x_2(\dfrac{dg}{dx_1} - \dfrac{V^E}{RT}(\dfrac{dP}{dx_1}))_{sat}$

2) $\ln \gamma_2 = g - x_1(\dfrac{dg}{dx_1} + \dfrac{V^E}{RT}(\dfrac{dP}{dx_1}))_{sat}$

3) $P_{sys} - x_1(FPP1)\gamma_1 - x_2(FPP2)\gamma_2 = 0$

```
      SUBROUTINE GIBSA(FPP1,FPP2,STKOR,DELTA,ITER)
C
C     SUBROUTINE GIBSA SOLVES THE COUPLED NON LINEAR COLLOCATION
C     EQUATIONS
C
      DOUBLE PRECISION A(25,25),SA(25),P(25),G(25),ROD(25)
      DOUBLE PRECISION B(25,25),S1(25),S2(25),FPP1(25),FPP2(25),STKOR
     1(25),DELTA,SQ
      DOUBLE PRECISION DEXP
      COMMON/DIV/A,SA,P,G,ROD,N,NT
      ITER=0
      NP1=N+1
 25   ITER=ITER+1
      IF(ITER-100) 27,27,100
 27   DO 28 I=1,NT
 28   SA(I)=0.
      DO 30 I=1,NT
      DO 30 J=1,NT
      SA(I)=SA(I)+A(I,J)*G(J)*2.*ROD(I)/DELTA**2.
 30   CONTINUE
      DO 35 I=1,NT
      IF(SA(I).GT.100.) GO TO 36
 35   CONTINUE
      GO TO 38
 36   ITER=101
      GO TO 100
 38   DO 40 I=2,NT
      S1(I)=ROD(I)*FPP1(I)*DEXP(G(I)+(1.-ROD(I))*(SA(I)-STKOR(I)))
      S2(I)=(1.-ROD(I))*FPP2(I)*DEXP(G(I)-ROD(I)*(SA(I)-STKOR(I)))
      IM1=I-1
      B(IM1,NT)=P(I)-S1(I)-S2(I)
 40   CONTINUE
      DO 50 I=2,NT
      IM1=I-1
      DO 50 J=2,NT
      JM1=J-1
      IF(I-J) 45,48,45
 45   B(IM1,JM1)=-S1(I)*(1.-ROD(I))*A(I,J)*2.*ROD(I)/DELTA**2.+S2(I)
     1*ROD(I)*A(I,J)*2.*ROD(I)/DELTA**2.
      GO TO 50
 48   B(IM1,IM1)=-S1(I)*(1.+(1.-ROD(I))*A(I,I)*2.*ROD(I)/DELTA**2.)-
     1S2(I)*(1.-ROD(I)*A(I,I)*2.*ROD(I)/DELTA**2.)
 50   CONTINUE
      CALL GAUSL(25,25,NP1,1,B)
      SQ=0.
      DO 60 I=1,NP1
      IP1=I+1
      G(IP1)=G(IP1)-B(I,NT)
      SQ=SQ+B(I,NT)**2
 60   CONTINUE
      IF(SQ-1.D-06) 100,25,25
 100  CONTINUE
      RETURN
      END
```

SUBROUTINE GIBSH (FPP1, FPP2, STKOR, ITER)

Input Parameters:

$\overline{\overline{A}}$, $\overline{P}$, $\overline{G}$, $\overline{ROD}$: As in GIBBS.

Real FPP1: This quantity is a corrected pressure (i.e. a reference state) for component one, (see equation 1A).

Real FPP2: Same as for FPP1 except for component two, (see equation 2A).

Real STKOR: Pertains to the volume excess multiplied by the pressure gradient, (see equation 3A).

The Output Is:

Integer ITER: Gives number of iterations done before convergence occured.

Vector SA,G: As in GIBBS.

GIBSH uses the same iteration technique GIBBS does except the higher pressure effects are taken into account.

1) The reference state is taken as FPP1 amd FPP2.
2) The volume-excess terms in Gibbs-Duhem equation are included in the calculation of the activity coefficients.

LIST OF EQUATIONS

$$(1A)\quad FPP1 = \frac{f_1^{\circ}\,EXP\left\{\frac{V^E_{\Delta}P}{RT}\right\}}{\Phi_1}$$

Poynting correction factor used.

$$(2A)\quad FPP2 = \frac{f_2^{\circ}\,EXP\left\{\frac{V^E P}{RT}\right\}}{\Phi_2}$$

$$(3A)\quad STKOR = \frac{V^E}{RT}\left(\frac{dP}{dx_1}\right)_{saturation}$$

Activity Coefficients:

1) $$\ln \gamma_1 = g + x_2\left(\frac{dg}{dx_1} - \frac{V^E}{RT}\left(\frac{dP}{dx_1}\right)\right)_{saturation}$$

2) $$\ln \gamma_2 = g - x_1\left(\frac{dg}{dx_1} + \frac{V^E}{RT}\left(\frac{dP}{dx_1}\right)\right)_{saturation}$$

3) $$P - x_1(FPP1)\gamma_1 - x_2(FPP2)\gamma_2 = 0$$

```
      SUBROUTINE GIBSH(FPP1,FPP2,STKOR,ITER)
C
C     SUBROUTINE GIBSH SOLVES THE COUPLED NON LINEAR COLLOCATION
C     EQUATIONS
C
      DOUBLE PRECISION FPP1(25),FPP2(25),STKOR(25),B(25,25),S1(25),
     1S2(25),SQ
      DOUBLE PRECISION A(25,25),SA(25),P(25),G(25),ROD(25)
      DOUBLE PRECISION AA(21)
      DOUBLE PRECISION DEXP
      COMMON/DIV/A,SA,P,G,ROD,N,NP1,NT
      COMMON/LEG/AA
      ITER=0
 25   ITER=ITER+1
      IF(ITER-100) 27,27,100
 27   DO 28 I=1,NT
 28   SA(I)=0.
      DO 30 I=1,NT
      DO 30 J=1,NT
      SA(I)=SA(I)+A(I,J)*G(J)
 30   CONTINUE
      DO 35 I=1,NT
      IF(SA(I).GT.100.) GO TO 36
 35   CONTINUE
      GO TO 38
 36   ITER=26
      GO TO 100
 38   DO 40 I=2,NP1
      ARG1=(G(I)+(1.-ROD(I))*(SA(I)-STKOR(I)))
      ARG2=(G(I)-ROD(I)*(SA(I)-STKOR(I)))
      IF(ARG1.GE.100..OR.ARG2.GE.100.) GO TO 36
      S1(I)=ROD(I)*FPP1(I)*DEXP(G(I)+(1.-ROD(I))*(SA(I)-STKOR(I)))
      S2(I)=(1.-ROD(I))*FPP2(I)*DEXP(G(I)-ROD(I)*(SA(I)-STKOR(I)))
      IM1=I-1
      B(IM1,NP1)=P(I)-S1(I)-S2(I)
 40   CONTINUE
      DO 50 I=2,NP1
      IM1=I-1
      DO 50 J=2,NP1
      JM1=J-1
      IF(I-J) 45,48,45
 45   B(IM1,JM1)=-S1(I)*(1.-ROD(I))*A(I,J)+S2(I)*ROD(I)*A(I,J)
      GO TO 50
 48   B(IM1,IM1)=-S1(I)*(1.+(1.-ROD(I))*A(I,I))-S2(I)*(1.-ROD(I)*A(I,I))
 50   CONTINUE
      CALL GAUSL(25,25,N,1,B)
      SQ=0.
      DO 60 I=1,N
      IP1=I+1
      G(IP1)=G(IP1)-B(I,NP1)
      SQ=SQ+B(I,NP1)**2
 60   CONTINUE
      IF(SQ-1.D-06) 100,25,25
 100  CONTINUE
      RETURN
      END
```

SUBROUTINE GNVOL (NKOMP, X, VC, ACEM,
TCT, T, TAU, ANY, TC, VMIX)

Input Parameters:

Integer

NKOMP: The number of components in the mixture.

Real X: The mole fractions of the NKOMP components in the liquid phase.

Vector VC: Dimension [NKOMP] and contains the pure components' critical volumes.

Vector ACEM: Dimension [NKOMP] and contains the pure components' acentric factor.

Matrix TCT: Dimension [NKOMP, NKOMP] and contains the pseudocritical constants (T_{cij}) which has no physical significance except to characterize bimolecular interactions between unlike molecules, i.e. critical temperature characteristic of the i-j interaction.

Real T: The temperature of the system.

Matrix TAU,

ANY: Dimension [NKOMP, NKOMP] and contains the binary interaction parameters.

Vector TC: Dimension [NKOMP] and contains the pure components' critical temperatures.

The Output Is:

Real VMIX: The saturalted liquid molar volume at the given composition.

GNVOL calculates the saturated molar volume at the given composition using the suggested mixing rules for liquid mixtures in The Properties of Gases and Liquids, 3rd edition.

GNVOL employs the following algorithm:

A: Calculate mixture properties by set of equations (I).

B: Test if $T_r \leq 0.93$, go to C.

if $T_r > 0.93$, go to D.

C: Calculate new mixture properties by set of equations (II).

D: Compute saturated molar volume with correct mixture properties.

LIST OF EQUATIONS

SET (I)

$$V_{cm} = \sum_i x_i V_{ci}$$

The Pseudocritical Parameters:

$$T_{cm} = \sum_i \sum_j \theta_i \theta_j T_{cij}$$

where $T_{cij} = TCT_{ij}$

$$\omega_m = \sum_i \theta_i \omega_i$$

$$\theta_i = FFI_i$$

$$\omega_i = ACEN_i$$

$$\theta_i = \frac{x_i V_{ci}}{\sum_{k=1}^{NKOMP} x_k V_{ck}}$$

$$T_{rm} = T/T_{cm}$$

SET (II)

The Corrected Pseudocritical Parameters:

$$T'_{cm} = T_{cm} + (T_{ct} - T_{cm}) \cdot DTR$$

$$V'_{cm} = V_{cm} + (V_{ct} - V_{cm}) \cdot DTR$$

where $T_{ct} = \sum_i \theta_i T_{ci} + \sum_i \sum_j \theta_i \theta_j T_{ij}$

$$V_{ct} = \sum_i \theta_i V_{ci} + \sum_i \sum_j \theta_i \theta_j V_{ij}$$

$$\theta_k = \frac{y_k V_{ck}^{2/3}}{\sum_i y_i V_{ci}^{2/3}}$$

$$V_m = V_{rm} \cdot V_{cm}$$

```
      SUBROUTINE GMVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,VMIX)
C
C     SUBROUTINE GMVOL CALCULATES THE MIXTURE PROPERTIES USED IN THE
C     CALCULATION OF THE SATURATED LIQUID MOLAR VOLUME.
C
      DIMENSION X(2),VC(2),ACEN(2),TCT(2,2),ANY(2,2),TAU(2,2),TC(2)
      DIMENSION FFI(5),TETA(5)
      VCM=0.
      ACENM=0.
      TCM=0.
      DO 14 I=1,NKOMP
      VCM=VCM+X(I)*VC(I)
   14 CONTINUE
      DO 15 I=1,NKOMP
      FFI(I)=X(I)*VC(I)/VCM
      ACENM=ACENM+FFI(I)*ACEN(I)
   15 CONTINUE
      DO 16 I=1,NKOMP
      DO 16 J=1,NKOMP
      TCM=TCM+FFI(I)*FFI(J)*TCT(I,J)
   16 CONTINUE
      TRMIX=T/TCM
      VCMM=VCM
      IF(TRMIX-0.93) 50,50,20
   20 VC23=0.
      DO 21 I=1,NKOMP
      VC23=VC23+X(I)*VC(I)**(2./3.)
   21 CONTINUE
      DO 22 I=1,NKOMP
      TETA(I)=X(I)*VC(I)**(2./3.)/VC23
   22 CONTINUE
      VMY=0.
      TTAU=0.
      VTC=0.
      TTC=0.
      DO 24 I=1,NKOMP
      DO 23 J=1,NKOMP
      VMY=VMY+TETA(I)*TETA(J)*ANY(I,J)
      TTAU=TTAU+TETA(I)*TETA(J)*TAU(I,J)
   23 CONTINUE
      VTC=VTC+TETA(I)*VC(I)
      TTC=TTC+TETA(I)*TC(I)
   24 CONTINUE
      VTC=VTC+VMY
      TTC=TTC+TTAU
      CALL ITERM2(T,TTC,TCM,TRMIX,DTM)
      VCMM=VCM+(VTC-VCM)*DTM
      TCM=T/TRMIX
   50 CALL MLMGM(TRMIX,ACENM,VRMIX)
      VMIX=VRMIX*VCMM
      RETURN
      END
```

SUBROUTINE INTDAL (X, ARG, VAL, Y, NDIM, EPS, IER)

Input Parameters:

Real X: The experimental liquid mole fraction where interpolation value is desired.

VECTOR ARG: Dimension [NDIM] and contains the ordered, by magnitude of distance, collocation points.

Vector VAL: Dimension [NDIM] and contains the corresponding values of g for the ordered collocation points in ARG.

Real EPS: Given numerical value for testing results obtained in program.

Integer IER: An error code.

IER = 0 implies no error (convergent),

IER = 1, 3 implies divergence and last iteration value used for result.

Integer NDIM: States maximum number of collocation points.

The Output Is:

Real Y: The interpolated value of y pertaining to the given X experimental point.

INTDAL computes the $y_i = f(x_i)$ value where x_i is the experimental liquid mole fraction by four point Lagrange interpolation. The algorithm consists of interpolation using an increasing number of interpolation points, (i.e. collocation points).

INTDAL employs the following algorithm:

A: Test whether or not in the range and dimension of the matrix.

B: Compute new approximation of y at the given x experimental value.

C: Test approximation of new and old.

If/ y new - y old/ < EPS, go to E.

If/ y new - y old/ > EPS, go to D.

D: Recompute approximation of y with increased number of collocation points. Go to C.

E: Test for divergence; STOP.

LIST OF EQUATIONS

Lagrange interpolation equation for y = f(x) where x_o is the given mole fraction where value is desired:

$$f_{k+1}(x)_{k+1} = \frac{f_k(x)_k \cdot (x-x_{k+1}) - f_{k+1}(x_{k+1}) \cdot (x-x_k)}{x_k - x_{k+1}}$$

f(x) is approximated by iterations of increasing number of collocation points included, $f_{k+1}(x_{k+1})$.

```
      SUBROUTINE INTDAL(X,ARG,VAL,Y,NDIM,EPS,IER)
      DIMENSION ARG(NDIM),VAL(NDIM)
      DOUBLE PRECISION ARG,VAL,X,Y,H
      DOUBLE PRECISION DABS
      DOUBLE PRECISION EPS
      IER=2
      DELT2=0.
      IF(NDIM-1) 9,7,1
1     DO 6 J=2,NDIM
      DELT1=DELT2
      IEND=J-1
      DO 2 I=1,IEND
      H=ARG(I)-ARG(J)
      IF(H) 2,13,2
2     VAL(J)=(VAL(I)*(X-ARG(J))-VAL(J)*(X-ARG(I)))/H
      DELT2=DABS(VAL(J)-VAL(IEND))
      IF(J-2) 6,6,3
3     IF(DELT2-EPS) 10,10,4
4     IF(J-8) 6,5,5
5     IF(DELT2-DELT1) 6,11,11
6     CONTINUE
7     J=NDIM
8     Y=VAL(J)
9     RETURN
10    IER=0
      GO TO 8
11    IER=1
12    J=IEND
      GO TO 8
13    IER=3
      GO TO 12
      END
```

SUBROUTINE INTP (X, Z, F, WORK, IROW, ICOL, ARG, VAL, NDIM)

Input Parameters:

Real X: The experimental liquid mole fraction where interpolation value is desired.

Real Z: Dimension [IROW] and contains the set of collocations points, (i.e. $x_i \Longrightarrow i = 1, IROW$).

Real F: Dimension [IROW] and contains the corresponding values of y at each collocation point, (i.e. $y_i = f(x_i)$).

Integer IROW: Denotes the number of elements given in a column vector, states size, (i.e. dimension).

Inter ICOL: States number of column vectors used in interpolation.

Integer NDIM: States maximum number of collocation points to be used in the interpolation algorithm.

The Output Is:

Real Vector

ARG: Dimension [IROW] and contains the values of the collocation points in increasing order of magnitude of distance from X experimental.

Real Vector

VAL: Dimension [IROW] and contains the values of y corresponding to the collocation points ordered in ARG.

INTP orders the collocation vectors according to distance from

the X experimental point and places the values in ARG_i and VAL_i.

INTP employs the following algorithm:

A: Test whether desired point is within the range.

If number of rows L.E., then quit.

If number of rows G.T., then use last value.

B: $Work_i = |\Delta X_i|$.

Find and set B = maximum value of $|\Delta X_i|$.

C: Find value II corresponding to the minimum distance value of X_i to the minimum distance value of X_i to the X experimental value.

D: Put values corresponding to the minimum into ART and VAL vectors.

E: Eliminate test for all previous values set in ARG and VAL vectors.

F: Return to B to test remaining collocation points.

```
      SUBROUTINE INTP(X,Z,F,WORK,IROW,ICOL,ARG,VAL,NDIM)
      DIMENSION Z(NDIM),F(NDIM),WORK(NDIM),ARG(NDIM),VAL(NDIM)
      DOUBLE PRECISION DABS
      DOUBLE PRECISION X,F,Z,WORK,ARG,VAL,B,DELTA
      IF(IROW) 11,11,1
1     N=NDIM
      IF(N-IROW) 3,3,2
2     N=IROW
3     B=0.D0
      DO 5 I=1,IROW
      DELTA=DABS(Z(I)-X)
      IF(DELTA-B) 5,5,4
4     B=DELTA
5     WORK(I)=DELTA
      B=B+1.D0
      DO 10 J=1,N
      DELTA=B
      DO 7 I=1,IROW
      IF(WORK(I)-DELTA) 6,7,7
6     II=I
      DELTA=WORK(I)
7     CONTINUE
      ARG(J)=Z(II)
      IF(ICOL-1) 8,9,8
8     VAL(2*J-1)=F(II)
      III=II+IROW
      VAL(2*J)=F(III)
      GO TO 10
9     VAL(J)=F(II)
10    WORK(II)=B
11    RETURN
      END
```

SUBROUTINE INTRP (ND, NT, X, ROD, FA, XINTP)

Input Parameters:

Integer ND,

NT: As in JCOBI.

Real X: The abscissa x where y(x) is desired.

Vector $\overline{ROD}$,

FA: Dimension [NT] and contains the zero roots of the Jacobi polynomial plus the first derivative of the Jacobi polynomial at the zero roots.

The Output Is:

Vector $\overline{XINTP}$: Dimension [NT] and contains the interpolation weights $L_i(x)$ used for the approximation of y(x).

INTRP finds the interpolation weights for a given x by a four point Lagrange interpolation and then places them in vector XINTP. This can be done for any $\ddot{x}$ value within the limits of the given root and FA.

INTRP employs the following alforithm:

A: Generate the polynomial $P_{NT}(\ddot{x}_A)$.

B: Evaluate the Lagrangian interpolation coefficients.

LIST OF EQUATIONS

Let x_A = x the abscissa point where y is desired.

x_i the zero roots of the Jacobi polynomial.

L_i the i^{th} degree of a Lagrange interpolation polynomial.

(I) denotes first derivative.

$$XINTP(i) = L_i(x_A) = \frac{P_{NT}(x_A)}{(x_A - x_i)P_{NT}^{(1)}(x_i)}$$

Once values of y at the roots are known (y_i), the value of y at any point within the domain may then be computed by:

$$y(x_A) = \sum_{i=1}^{NT} XINTP(i) \cdot y(i)$$

```
      SUBROUTINE INTRP(ND,N,X,ROD,FA,XINTP)
C
C     SUBROUTINE INTRP DETERMINES THE WEIGHTS XINTP USED IN THE
C     LAGRANGIAN INTERPOLATION
C
      DOUBLE PRECISION X,Y,POL,ROD(ND),FA(ND),XINTP(ND)
      POL=1.
      DO 5 I=1,N
      Y=X-ROD(I)
      XINTP(I)=0.
      IF (Y.EQ.0.) XINTP(I)=1.
 5    POL=POL*Y
      IF (POL.EQ.0.) GO TO 10
      DO 7 I=1,N
 7    XINTP(I)=POL/FA(I)/(X-ROD(I))
 10   RETURN
      END
```

SUBROUTINE IPOINT (J, NUMPT, ARRAYP,
SSCALE, BSCALE, POINT, SYMBOL)

Input Parameters:

Vector
SSCALE: An array containing the minimum value from the prominent ordinate scale reading of each data set.

Vector
BSCALE: An array containing the maximum value from the prominant ordinate scale readings of each data set.

Vector
ARRAYP: An array containing the ordinate values for the given data set to be plotted.

Integer J: A number which indicates the desired data set to be plotted.

Vector NUMPT: An array containing the number of data points in each data set.

Vector
SYMBOL: An array containing the symbols designated for all data sets.

The Output is:

Vector POINT: An array containing the given symbol for the data set of interest and the symbol is located in the appropriate position in the 101 character long array.

IPOINT computes the right location for the symbol in its 101 character long array, POINT. It then places the designated symbol for the given data set into that position and returns to PLOT for plotting.

```
      SUBROUTINE IPOINT(J,NUMPT,ARRAYP,SSCALE,BSCALE,POINT,SYMBOL)
      DIMENSION NUMPT(10),ARRAYP(10),SSCALE(10),BSCALE(10)
      INTEGER O,POINT(101),SYMBOL(10),BLANK
      DATA L/'L'/,O/'O'/,BLANK/' '/
      DO 1 K=1,101
      POINT(K)=BLANK
    1 CONTINUE
      DO 6 I=1,10
      IF (J.GT.NUMPT(I)) GO TO 6
      YAXIS=IFIX(100.0*(ARRAYP(I)-SSCALE(I))/(BSCALE(I)-SSCALE(I))+0.5)
      YAXIS=YAXIS+1
      IF (YAXIS-101) 3,3,2
    2 POINT(101)=O
      GO TO 6
    3 IF (YAXIS-1) 4,5,5
    4 POINT(1)=L
      GO TO 6
    5 POINT(YAXIS)=SYMBOL(I)
    6 CONTINUE
      RETURN
      END
```

SUBROUTINE ITERE (T, TCT, TCM, TRMIX, DTR)

Input Parameters:

Real T: The temperature of the system.

Real TCT: The true mixture critical temperature.

Real TCM: The pseudocritical temperature of the mixture.

The Output Is:

Real TRMIX: The reduced temperature for the mixture.

Real DTR: A deviation function expressed in terms of the reduced temperature TRMIX.

ITERE used an iterative procedure in the computing of TRMIX by using the equations (4-10.7) and (4-10.9) from The Properties of Gases and Liquids, 3rd edition. Also, if failure to converge to a value results, a printout is obtained with the best approximation of TRMIX used.

ITERE employs the following algorithm:

A: Initial approximation to TRMIX.

B: Set iteration counter.

C: Compute value of DTR.

D: Test TRMIX old with new approximation.

If TRMIX (old) - (new) $\leq 10^{-8}$, go to E.

If TRMIX (old) - (new) $> 10^{-8}$, go to B.

E: Compute DTR with new approximation and return.

LIST OF EQUATIONS

(4-10.7) $T'_{cm} = T_{cm} + (T_{cT} - T_{cm}) \cdot DTR$

$$(4\text{-}10.9)\quad DTR = f(T'_{rm}) = EXP\ \{T'_{rm} - 1)(2901.010) - 5738.92\ T_{rm} + 2849.85\ T'^{2}_{rm} + \frac{104147}{1.01 - T'_{tm}}\}$$

```
      SUBROUTINE ITERR(T,TCT,TCM,TRMIX,DTR)
C
C     SUBROUTINE ITERR FINDS THE MIXTURE REDUCED TEMPERATURE USING
C     REGULAFALS
C
      DOUBLE PRECISION TR1,TR2,TR3,TRTRU,TRM,TRD,DTRD,F1,F2,F3
      DOUBLE PRECISION DABS,DEXP
  200 FORMAT(1H0,'  ITERR FAILS TO CONVERGE IN 50 ITERATIONS')
      NWR=6
      TR1=0.9
      TR2=1.0
      TRTRU=T/TCT
      TRM=T/TCM
      TRM=TRM/TRTRU-1.
      F1=(TRM/TR1-1.)-TRM*DEXP(-6.019D 00)
      F2=TRM-1.-TRM
      ITER=0
    5 ITER=ITER+1
      IF(ITER-50) 6,6,49
    6 TR3=TR2-F2*(TR2-TR1)/(F2-F1)
      DTRD=DEXP((TR3-1.D 00)*(2.90101D 03-5.73892D 03*TR3+2.84985D 03
     1*TR3**2+1.74127D 00/(1.01D 00-TR3)))
      F3=(TRM/TR3-1.)-TRM*DTRD
      IF(DABS(TR3-TR2).LT.1.D-08) GO TO 50
      IF(DABS(TR3-TR1).LT.1.D-08) GO TO 50
      IF(F2*F3) 25,50,23
   23 TR2=TR3
      F2=F3
      GO TO 5
   25 TR1=TR3
      F1=F3
      GO TO 5
   49 WRITE(NWR,200)
   50 CONTINUE
      TRMIX=TR3
      DTR=DTRD
      RETURN
      END
```

SUBROUTINE JCOBI (ND, N, NO, N1, AL, BE, FA, FB, FC, ROOT)

Input Parameters:

Integer ND: The dimension of vectors FA, FB, FC, and ROOT.

Integer N: The number of interior interpolation points.

Integer NO,

N1: Tells whether the end points are included.

If NO, N1 = 0, endpoints excluded.

If NO, N1 = 1, endpoints included.

Real AL, BE: The values of α and B which denotes the particular Jacobi polynomial used.

The Output Is:

Vector Root: Dimension [NT] and contains the zero roots to the given Jacobi polynomial.

Vector FA,

FB, FC: Dimension [NT] and contains the first, second and third derivatives at the zero roots of the given Jacobi polynomial.

JCOBI first calculates the coefficient for the recursion formula. Then the zeros of the polynomial are found by a Newton method with root suppression. Finally, the deriviatves of the Jacobi polynomial are evaluated at the zeros.

JCOBI employs the following algorithm:

A: Evaluation of coefficients in recursion formulas.

B: Store coefficients in FA and FB.

C: Determination of roots by Newton method with

```
      SUBROUTINE ITERE(T,TCT,TCM,TRMIX,DTR)
C
C     SUBROUTINE ITERE FINDS THE MIXTURE REDUCED TEMPERATURE USING
C     REGULAFALS
C
      DOUBLE PRECISION TR1,TR2,TR3,TRTRU,TRM,TRD,DTRD,F1,F2,F3
      DOUBLE PRECISION DABS,DEXP
  200 FORMAT(1HO,'  ITERE FAILS TO CONVERGE IN 50 ITERATIONS')
      NWR=6
      TR1=0.9
      TR2=1.0
      TRTRU=T/TCT
      TRM=T/TCM
      TRM=TRM/TRTRU-1.
      F1=(TRM/TR1-1.)-TRM*DEXP(-6.019D 00)
      F2=TRM-1.-TRM
      ITER=0
    5 ITER=ITER+1
      IF(ITER-50) 6,6,49
    6 TR3=TR2-F2*(TR2-TR1)/(F2-F1)
      DTRD=DEXP((TR3-1.D 00)*(2.90101D 03-5.73892D 03*TR3+2.84995D 03
     1*TR3**2+1.74127D 00/(1.01D 00-TR3)))
      F3=(TRM/TR3-1.)-TRM*DTRD
      IF(DABS(TR3-TR2).LT.1.D-08) GO TO 50
      IF(DABS(TR3-TR1).LT.1.D-08) GO TO 50
      IF(F2*F3) 25,50,23
   23 TR2=TR3
      F2=F3
      GO TO 5
   25 TR1=TR3
      F1=F3
      GO TO 5
   49 WRITE(NWR,200)
   50 CONTINUE
      TRMIX=TR3
      DTR=DTRD
      RETURN
      END
```

SUBROUTINE JCOBI (ND, N, NO, N1, AL, BE, FA, FB, FC, ROOT)

Input Parameters:

Integer ND: The dimension of vectors FA, FB, FC, and ROOT.

Integer N: The number of interior interpolation points.

Integer NO,

N1: Tells whether the end points are included.

If NO, N1 = 0, endpoints excluded.

If NO, N1 = 1, endpoints included.

Real AL, BE: The values of α and B which denotes the particular Jacobi polynomial used.

The Output Is:

Vector Root: Dimension [NT] and contains the zero roots to the given Jacobi polynomial.

Vector FA,

FB, FC: Dimension [NT] and contains the first, second and third derivatives at the zero roots of the given Jacobi polynomial.

JCOBI first calculates the coefficient for the recursion formula. Then the zeros of the polynomial are found by a Newton method with root suppression. Finally, the deriviatves of the Jacobi polynomial are evaluated at the zeros.

JCOBI employs the following algorithm:

A: Evaluation of coefficients in recursion formulas.

B: Store coefficients in FA and FB.

C: Determination of roots by Newton method with

suppression of previously determined roots.

D: Add interpolation points at end points.

E: Evaluate the derivatives of polynomial and store in FA, FB, and FC.

LIST OF EQUATIONS

The Coefficients of Recursion Formula:

$$g_1 = \frac{B + 1}{\alpha + B + 2},\ g_N = 1/2\left[1 - \frac{\alpha^2 - B^2}{(2N + \alpha + B + 1)^2 - 1}\right]$$

$$h_1 = 0,\ h_N = \frac{(N - 1)(N + \alpha - 1)(N + B - 1)(N + \alpha + B - 1)}{(2N + \alpha + B - 1)(2N + \alpha + B - 2)^2(2N + \alpha + B - 3)}$$

Root Determination:

$$P_j = [x_K^{(i)} - g_j]P_{j-1} - h_j P_{j-2}$$

$$P_j^{(1)} = [x_K^{(i)} - g_j]P_j^{(1)} - 1 - h_j P_{j-2}^{(1)} + P_{j-1}$$

$$\delta(x) = \frac{P_N/P_N^{(1)}}{1 - (P_N/P_N^{(1)})\sum_{i=1}^{K} \frac{1}{(x - x_i)}}$$

where $P_0 = 1$

$$P_0^{(1)} = 0$$

$$P_{-1} = P_1^{(1)}$$

Newton Iteration:

$$x_{K+1}^{(i)} = x_{K+1}^{(i-1)} - \delta[x_{K+1}^{(i-1)}]$$

where $x_{K+1}^{(0)} = x_K + \varepsilon$ and ε is a fixed value, e.g. 10^{-4}.

Derivatives:

$$P_j^{(1)}(x_i) = (x_i - x_j)P_{(j-1)}(x_i)$$

$$P_j^{(2)}(x_i) = (x_i - x_j)P_{j-1}^{(2)}(x_i) + 2P_{j-1}(x_i)$$

$$P_j^{(3)}(x_i) = (x_i - x_j)P_{j-1}^{(3)}(x_i) + 3P_{j-1}^{(2)}(x_i)$$

Starting with $P_1^{(1)}(x_i) = 1$, $P_1^{(2)}(x_i) = P_1^{(3)}(x_i) = 0$

$_K$ are the zero root approximations.

δ_K is the interval in which zero x_k is located.

(1), (2), (3) are indexes of the node telling what degree derivative is taken.

i, j are subscripts which denote the particular independent variable used in interpolation routine.

```
      SUBROUTINE JCOBI(ND,N,NO,N1,AL,BE,FA,FB,FC,ROOT)
C
C     SUBROUTINE JCOBI CALCULATES THE ROOTS OF THE JCOBI POLYNOMIAL
C
      DOUBLE PRECISION AL,BE,FA(ND),FB(ND),FC(ND),ROOT(ND),X,Y,Z,R,AB,
     1AC,AD,AP,XD,XN,XP,XD1,XN1
      DOUBLE PRECISION DABS
      AB=AL+BE
      AD=BE-AL
      AP=BE*AL
      FA(1)=(AD/(AB+2.)+1)/2.
      FB(1)=0.
      DO 10 I=2,N
      K=2*I-2
      Z=AB+K
      FA(I)=(AB/Z*AD/(Z+2.)+1.)/2.
      K=I-1
      IF(I.NE.2) GO TO 11
      FB(I)=(AB+AP+K)/Z/Z/(Z+1.)
      GO TO 10
 11   Z=Z*Z
      Y=K*(AB+K)
      Y=Y*(AP+Y)
      FB(I)=Y/Z/(Z-1.)
 10   CONTINUE
      X=0.
      DO 20 I=1,N
 26   XD=0.
      XD1=0.
      XN=1.
      XN1=0.
      DO 30 J=1,N
      XP=(FA(J)-X)*XN-FB(J)*XD
      XP1=(FA(J)-X)*XN1-FB(J)*XD1-XN
      XD=XN
      XD1=XN1
      XN=XP
 30   XN1=XP1
      Y=1.
      Z=XN/XN1
      IF(I.EQ.1) GO TO 21
      DO 23 J=2,I
 23   Y=Y-Z/(X-ROOT(J-1))
 21   Z=Z/Y
      X=X-Z
      IF(DABS(Z).GT.1D-9) GO TO 26
      ROOT(I)=X
      X=X+0.0005
 20   CONTINUE
      NT=NO+N1+N
      IF(NO.NE.1) GO TO 35
      DO 41 I=1,N
 41   ROOT(N+2-I)=ROOT(N+1-I)
      ROOT(1)=0.
 35   IF(N1.EQ.1) ROOT(NT)=1.
      DO 40 I=1,NT
      X=ROOT(I)
      FA(I)=1.
      FB(I)=0.
      FC(I)=0.
      DO 40 J=1,NT
      IF(J.EQ.I) GO TO 40
      Y=X-ROOT(J)
      FC(I)=Y*FC(I)+3.*FB(I)
      FB(I)=Y*FB(I)+2.*FA(I)
      FA(I)=Y*FA(I)
 40   CONTINUE
      RETURN
      END
```

SUBROUTINE LEFIT (X, Y, N, K)

Input Parameters:

Real X: The experimental mole fraction of component one in the liquid phase.

Reay Y: The experimental pressure of system at a given XEXP.

Integer N: The dimension of vectors X and Y, (i.e. number of data points).

Integer K: The degree of the Legendre polynomial used for fitting the P-X data.

The Output Is:

By a common statement

COMMON/LEG/AA

Vector $\overline{AA}$: Dimension [K + 1] and contains the coefficients to the fitting function which represents the deviation from ideality, (i.e. Raoult's Law).

LEFIT fits P-X data to a curve using Legendre polynomials and calls for GAUSL, a Gaussian elimination mehtod, to solve $\overline{\overline{A}} * X = B$ where $\overline{X}$ is the vector $\overline{AA}$. At $0.02 = \Delta X$ discrete intervals the pressure of the system is evaluated by the fitting function.

LEFIT employs the following algorithm:

A: Calculate S(I) (deviation of Raoult's Law) at data points.

B: Formulate curve (deviation of Raoult's Law) with S(I) as a weighting function.

C: Formulate matrix with unknown coefficients.

D: Invert matrix (solve for $\overline{AA}$) (call to GAUSL).

E: Compute system pressure at 0.02 discrete jumps.

LIST OF EQUATIONS

Deviation Function:

$$S(i) = P_{sys} - P_1^{sat} - (1 - x) - P_2^{sat}x$$

Weighting Function:

$$x(1 - x)$$

Fitting Function:

$$C(I) = \sum_{i=1}^{N} S(j)x(1 - x)P_i(x)$$

where $P_i(x) = i^{th}$ degree Legendre polynomial.

```
      SUBROUTINE LEFIT(X,Y,N,K)
C
C     SUBROUTINE LEFIT FITS INDIVIDUAL POINTS ON A CURVE WHERE X IS THE
C     INDEPENDENT VARIABLE AND Y IS THE DEPENDENT VARIABLE USING A FUN-
C     CTION CONTAINING LEGENDRE POLYNOMIALS AS THE FITTING FUNCTION.
C
      DOUBLE PRECISION X2,X3
      DOUBLE PRECISION PP
      DOUBLE PRECISION X1
      DOUBLE PRECISION DFLOAT
      DOUBLE PRECISION C(21),B(25,25),AA(21),PPP(51)
      DOUBLE PRECISION X(25),Y(25),S(25)
      DOUBLE PRECISION POLEG
      DIMENSION NUMPT(10),PTITLE(29),YSCALE(10,11),ISCALE(300),
     1          ARRAY(10,300)
      COMMON/LEG/AA
      COMMON PTITLE
  500 FORMAT(10(8F10.4,/))
  501 FORMAT(1HO,'INTERPOLATED PRESSURE-VALUES FOR X IN THE INTERVAL
     1BETWEEN 0.0 AND 1.0 . VALUES FOR DISCRETE JUMPS OF 0.02 IN X',/,
     2' A LEGENDRE POLYNOMIAL OF DEGREE ',I2,' IS USED AS FITTING FUNCTI
     3ON')
      NWR=6
      KP1=K+1
      DO 1 I=1,KP1
    1 C(I)=0.
      DO 2 I=1,KP1
      DO 2  J=1,KP1
    2 B(I,J)=0.
      DO 3 I=1,N
    3 S(I)=Y(I)-Y(1)*(1.-X(I))-Y(N)*X(I)
      DO 4 IB=1,KP1
      DO 4 J=1,N
      X3=X(J)
    4 C(IB)=C(IB)+S(J)*X(J)*(1.-X(J))*POLEG(X3,IB)
      DO 5 MA=1,KP1
      DO 5 L=1,KP1
      DO 5 KA=1,N
      X2=X(KA)
    5 B(MA,L)=B(MA,L)+X(KA)**2.*(1.-X(KA))**2.*POLEG(X2,MA)*POLEG(X2,L)
      DO 6 I=1,KP1
      KP2=K+2
    6 B(I,KP2)=C(I)
      CALL GAUSL(25,25,KP1,1,B)
      DO 7 I=1,KP1
    7 AA(I)=B(I,KP2)
      DO 8 IA=1,51
      X1=2.D-02*DFLOAT(IA-1)
      CALL PCAL(Y(1),Y(N),X1,PP,KP1)
    8 PPP(IA)=PP
      DO 99 I=1,51
   99 ARRAY(1,I)=PPP(I)
      WRITE(NWR,501) K
      WRITE(NWR,500)  (PPP(I),I=1,51)
      CALL SCALE(ISCALE,YSCALE,X,Y,N,ARRAY,NUMPT,2)
      CALL PLOT(ARRAY,NUMPT,PTITLE,YSCALE,ISCALE,1)
      RETURN
      END
```

SUBROUTINE MCVOL

This subroutine will be supplied on request. It provides the specific volume of the liquid phase utilizing the information contained in Reference 10.

SUBROUTINE MLMGN (TR, ACEN, VR)

Input Parameters:

Real TR: The reduced temperature of the mixture, (i.e. TRMIX).

Real ACEN: The acentric factor for each pure component.

The Output Is:

Real VR: The reduced liquid mixture molar volume.

MLMGN uses the correlations of Lyckman, Eckert, Chueh and Prausnitz for calculating the liquid density of the mixture. The coefficients for the (virial) reduced volume equation, page 64 in The Properties of Gases and Liquids, 3rd edition, are given in the table along with the equation (3-15.21) for $V_r^{(j)}$ and (3-15.20) for VRMIX.

LIST OF EQUATIONS

$$V_r^{(j)} = a_j + b_j T_r + c_j T_r^2 + d_j T_r^3 + \frac{e_j}{T_r} + f_i \cdot \ln(1-T_r)$$

$$V_r = \frac{\rho_c}{\rho_s} = V_r^{(o)} + \omega V_r^{(1)} + \omega^2 \cdot V_r^{(2)}$$

$V_r^{(j)}$ = A generalized reduced molar volume function for saturated liquid.

```
      SUBROUTINE MLMGN(TR,ACEN,VR)
C
C     SUBROUTINE MLMGN CALCULATES THE REDUCED LIQUID MIXTURE MOLAR
C     VOLUME USING THE LYCKMANN ECKERT CHUEH CORRELATION
C
      DIMENSION TRR(3),VRR(3),V(3)
      DIMENSION A(3),B(3),C(3),D(3),E(3),F(3)
      DATA A,B,C,D,E,F/0.11917,0.98465,-0.55314,0.009513,-1.60378,
     1-0.15793,0.21091,1.82684,-1.01601,-0.06922,-0.61432,0.34095
     20,.07480,-0.34546,0.46795,-0.084476,0.087037,-0.239938/
      TRR(3)=TR
      IF(TR-0.995) 209,209,211
  209 I=3
      GO TO 210
  211 TRR(1)=0.995
      TRR(2)=1.0
      I=1
  210 VRR(I)=0.
      DO 213 J=1,3
      V(J)=A(J)+B(J)*TRR(I)+C(J)*TRR(I)**2+D(J)*TRR(I)**3+E(J)/
     1TRR(I)+F(J)*ALOG(1.-TRR(I))
  213 CONTINUE
      VRR(I)=V(1)+V(2)*ACEN+V(3)*ACEN**2
      IF(2-I) 216,215,214
  214 VRR(2)=1.
  215 VRR(3)=VRR(1)+(VRR(1)-VRR(2))/(TRR(1)-TRR(2))*(TRR(3)-TRR(1))
  216 VR=VRR(3)
      RETURN
      END
```

SUBROUTINE PCAL (P2S, P1S, X, PP, K)

Input Parameters:

Real P1S,

P2S: The pure components' vapor pressures.

Real X: The mole fraction of component one in liquid phase in which the pressure of system is desired.

Integer K: The degree of the Legendre polynomial used for fitting curve.

The Output Is:

Real PP: The pressure of the system at the given mole fraction X.

PCAL evaluates the pressure of the system at a given composition by use of Raoult's Law added to the computed deviations. The deviation function is computed by the coefficients of $\overline{AA}$ and the appropriate Legendre polynmials.

PCAL employs the following algorithm:

A: Generates deviation function by Legendre polynomial & $\overline{AA}$ coefficients.

B: Computes pressure by addition of Raoult's Law and deviation function.

LIST OF EQUATIONS

Deviation Function:

$$ALEG = \sum_{i=1}^{K} AA(i)P_i(x)$$

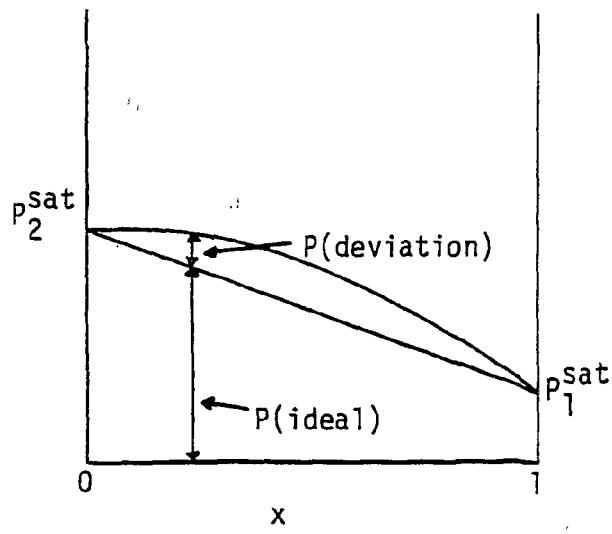
Raoult's Law:

$$P_{RL} = x(P_1^{sat} - P_2^{sat}) + P_2^{sat}$$

System Pressure:

$$P_{sys} = PP = P_{RL} + x(1 - x)ALEG$$

where $x(1 - x)$ is the chosen weight function.



$$P = P(ideal) + P(deviation)$$

$$= P_1^{sat}x + P_2^{sat}(1-x) + ALEG \cdot x(1-x)$$

```
      SUBROUTINE PCAL(P2S,P1S,X,PP,K)
C
C     SUBROUTINE PCAL CALCULATES THE PRESSURE OF A BINARY MIXTURE
C     WHERE COMPONENT 1 HAS THE MOLE FRACTION X.
C
      DOUBLE PRECISION POLEG
      DOUBLE PRECISION AA(21),PP,ALEG,X
      DOUBLE PRECISION P1S,P2S
      COMMON/LEG/AA
      ALEG=0.
      DO 1 IL=1,K
    1 ALEG=ALEG+AA(IL)*POLEG(X,IL)
      PP=P2S*(1.-X)+P1S*X+(1.-X)*X*ALEG
      RETURN
      END
```

SUBROUTINE PCALA (P2S, X, PP, K)

Input Parameters:

Real P2S: The pure component two's vapor pressure.

Real X: The normalized value for the mole fraction of component one in the liquid phase.

Integer K: The degree of the Legendre polynomial used for fitting the curve.

The Output Is:

Real PP: The pressure of the system at the given mole fraction X.

PCALA evaluates the pressure of the system at a given composition by use of the computed deviation function. The deviation function is computed by the coefficients of $\overline{AA}$ and the appropriate Legendre polynomials. Since the Legendre polynomials range from zero to one, the mole fractions used must also be normalized.

PCALA employs the following algorithm:

A: Generates deviation function by Legendre polynomials and $\overline{AA}$ coefficients.

B: Computes pressure from fitting function at the desired normlalized mole fraction.

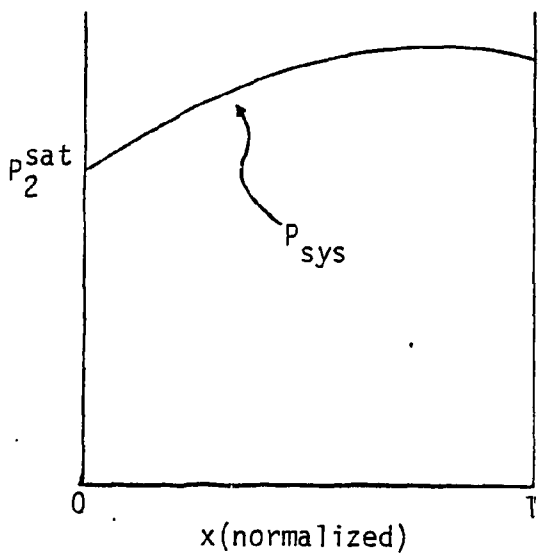
LIST OF EQUAITONS

Deviation Function:

$$ALEG = \sum_{i=1}^{K} AA(i)(x)$$

$$P_{sys} = P_2^{sat}(1 - x) + x(ALEG)$$

where x is the chosen weighting function.



```
      SUBROUTINE PCALA(P2S,X,PP,K)
C
C     SUBROUTINE PCALA CALCULATES THE PRESSURE OF A BINARY MIXTURE
C     WHERE COMPONENT 1 HAS THE MOLE FRACTION X.
C
      DOUBLE PRECISION POLEG
      DOUBLE PRECISION AA(21),PP,ALEG,X
      DOUBLE PRECISION P1S,P2S
      COMMON/LEG/AA
      ALEG=0.
      DO 1 IL=1,K
    1 ALEG=ALEG+AA(IL)*POLEG(X,IL)
      PP=P2S*(1.-X)+X*ALEG
      RETURN
      END
```

SUBROUTINE PLOT (ARRAY, NUMPT, YTITLE, YSCALE, XSCALE, XMARK)

Input Parameters:

MATRIX ARRAY: A matrix containing ordinate values for up to ten data sets which are to be plotted.

Vector NUMPT: An array containing the number of data points in each data set.

Vector YTITLE: An array containing the title for the plot (up to 116 characters).

MATRIX YSCALE: A matrix containing the prominant ordinate markings for the plot.

Real XMARK: The number of divisions between prominate abcissa markings.

PLOT will plot up to ten sets of data consisting of 300 data points each on a single graph. It plots the prominent ordinate markings for each data set and plots the prominant abcissa markings for the graph. Each particular data set is assigned a letter in order to distinguish it from the others. The ordinate values are also identified by the same assigned letter.

```
      SUBROUTINE PLOT(ARRAY,NUMPT,YTITLE,YSCALE,XSCALE,XMARK)
      INTEGER SYMBOL(10),POINT(101),XMARK
      DIMENSION ARRAY(10,300),NUMPT(10),YTITLE(29),YSCALE(10,11),
     1          SSCALE(10),BSCALE(10),ARRAYP(10),XSCALE(300)
      DATA SYMBOL/'A','B','C','D','E','F','G','H','I','J'/
      NR=5
      NW=6
      WRITE (NW,500) YTITLE
  500 FORMAT ('1'///1X,29A4///)
      DO 1 I=1,10
      IF (NUMPT(I).LE.0) GO TO 1
      WRITE (NW,510) SYMBOL(I),(YSCALE(I,J),J=1,11),SYMBOL(I)
  510 FORMAT (5X,A1,1X,11F10.2,1X,A1)
    1 CONTINUE
      WRITE (NW,520)
  520 FORMAT (5X,11(9X,'I')/13X,103('X'))
      NSAVE=NUMPT(1)
      DO 2 I=1,10
      IF (NUMPT(I).GT.NSAVE) NSAVE=NUMPT(I)
      SSCALE(I)=YSCALE(I,1)
      BSCALE(I)=YSCALE(I,11)
    2 CONTINUE
      MARK=XMARK-1
      DO 4 J=1,NSAVE
      DO 3 I=1,10
      ARRAYP(I)=ARRAY(I,J)
    3 CONTINUE
      CALL IPOINT(J,NUMPT,ARRAYP,SSCALE,BSCALE,POINT,SYMBOL)
      WRITE (NW,530) POINT
  530 FORMAT (13X,'X',101A1,'X')
      MARK=MARK+1
      IF (MARK.LT.XMARK) GO TO 4
      MARK=0
      WRITE (NW,540) XSCALE(J/XMARK+1)
  540 FORMAT ('+',F9.2,1X,'--',103X,'--')
    4 CONTINUE
      WRITE (NW,550)
  550 FORMAT (13X,103('X')/5X,11(9X,'I'))
      WRITE (NW,560)
  560 FORMAT ('1')
      RETURN
      END
```

SUBROUTINE PLTRE (XCOF, COF, M, ROOTR, ROOTI, IER)

Input Parameters:

Vector XCOF: Dimension [m+1] and contains the m plus one coefficients to the (virial) equation of state.

Vector COF: The working vector of dimension [m+1]

Integer M: The order of the polynomial to be solved for roots.

The Output Is:

Vector ROOTR: Dimension [m] and contains the real roots to the polynomial.

Vector ROOTI: Dimension [m] and contains the corresponding imaginary roots to the polynomial.

Integer IER: Error code where

IER = 0 no error,

IER = 1 m less than one,

IER = 2 m greater than 36,

IER = 3 unable to determine root with 500 iterations on 5 staring values,

IER = 4 high order coefficient is zero.

PLTRE computes the real and complex roots of a real polynomial of degree 'm'. The subroutine uses a Newton-Raphson iterative technique for computing a new approximation and then tests the result in the original polynomial.

PLTRE employs the following algorithm:

A: Zero initial value of counter.

B: Increment initial values and counter.

C: Set X and Y to current value.

D: Evaluate the polynomial and the derivatives.

E: Step up counter value.

F: Check number of iterations taken,

If .GT. 500, return.

If .LE. 500, go to C.

G: Place roots in vectors ROOTR and ROOTI.

LIST OF EQUATIONS

Given Polynomial:

$$f(z) = \sum_{n=0}^{n} a_n Z^n$$

let $Z = X - iY \xrightarrow{\text{implies}} Z^n = (X + iY)^n$

Initial Values:

$$X_o = 1, Y_o = 0 \text{ where } n = o$$

Recursion Formulas:

$$X_n = X \cdot X_{n-1} - Y \cdot Y_{n-1}$$

$$Y_n = X - Y_{n-1} + Y - X_{n-1}$$

$$U = a_o + \sum_{n=1}^{N} a_n X_n \qquad V = \sum_{n=1}^{N} a_n Y_n$$

$$\frac{\partial U}{\partial X} = \sum_{n=1}^{N} n \cdot x_{n-1} \cdot a_n \qquad \frac{\partial V}{\partial Y} = - \sum_{n=1}^{N} n \; Y_{n-1} a_n$$

Newton-Raphson Method:

$$\Delta X = \frac{(V\frac{\partial U}{\partial Y} - U\frac{\partial u}{\partial X})}{DET}, \quad \Delta Y = \frac{-(U\frac{\partial U}{\partial Y} + V\frac{\partial U}{\partial X})}{DET}$$

where $DET = (\frac{\partial U}{\partial X})^2 + (\frac{\partial U}{\partial Y})^2$

Next Iteration:

$$X' = X + \Delta X$$

$$Y' = Y + \Delta Y$$

```
      SUBROUTINE PLTRR(XCOF,COF,N,ROOTR,ROOTI,ITER)
C
C     SUBROUTINE PLTRR CALCULATES THE ROOTS OF A N'TH DEGREE POLYNOMIAL
C     THE SUBROUTINE IS A STANDARD IBM SSP ROUTINE
C
      DOUBLE PRECISION XO,YO,X,Y,XPR,YPR,UX,UY,V,VT,XT,U,XT2,YT2,SUMSQ,
     1DX,DY,TEMP,ALPHA
      DOUBLE PRECISION XCOF(4),COF(4),ROOTR(3),ROOTI(3)
      DOUBLE PRECISION DABS
      IFIT=0
      N=N
      ITER=0
      IF(XCOF(N+1)) 10,25,10
   10 IF(N) 15,15,32
C     SET ERROR CODE TO 1
   15 ITER=1
   20 RETURN
C     SET ERROR CODE TO 4
   25 ITER=4
      GO TO 20
C     SET ERROR CODE TO 2
   30 ITER=2
      GO TO 20
   32 IF(N-36) 35,35,30
   35 NX=N
      NIX=N+1
      N2=1
      NJ1=N+1
      DO 40 L=1,NJ1
      NT=NJ1-L+1
   40 COF(NT)=XCOF(L)
C     SET INITIAL VALUES
   45 XO=0.00500101
      YO=0.01000101
C     ZERO INITIAL VALUE COUNTER
      IN=0
   50 X=XO
C     INCREMENT INITIAL VALUES AND COUNTER
      XO=-10.0*YO
      YO=-10.0*X
C     SET X AND Y TO CURRENT VALUE
      X=XO
      Y=YO
      IN=IN+1
      GO TO 59
   55 IFIT=1
      XPR=X
      YPR=Y
C     EVALUATE POLYNOMIAL AND DERIVATIVES
   59 ICT=0
   60 UX=0.0
      UY=0.0
      V=0.0
      VT=0.0
      XT=1.0
      U=COF(N+1)
      IF(U) 65,130,65
   65 DO 70 I=1,N
      L=N-I+1
      TEMP=COF(L)
      XT2=X*XT-Y*YT
      YT2=X*YT+Y*XT
      U=U+TEMP*XT2
      V=V+TEMP*YT2
      FI=I
      UX=UX+FI*XT*TEMP
      UY=UY-FI*YT*TEMP
      XT=XT2
   70 YT=YT2
      SUMSQ=UX*UX+UY*UY
      IF(SUMSQ) 75,110,75
```

```
 75   DX=(V*DY-U*DX)/SUMSQ
      X=X+DX
      DY=-(U*DY+V*DX)/SUMSQ
      Y=Y+DY
 78   IF(DABS(DY)+DABS(DX)-1.0D-05) 100,80,80
C     STEP ITERRATION COUNTER
 80   ICT=ICT+1
      IF(ICT-500) 60,85,85
 85   IF(IFIT) 100,90,100
 90   IF(IN-5) 50,95,95
C     SET ERROR CODE TO 3
 95   ITER=3
      GO TO 20
 100  DO 105 L=1,NXX
      NT=NJ1-L+1
      TEMP=ICOF(NT)
      ICOF(NT)=COF(L)
 105  COF(L)=TEMP
      ITEMP=N
      N=NX
      NX=ITEMP
      IF(IFIT) 120,55,120
 110  IF(IFIT) 115,50,115
 115  X=XPR
      Y=YPR
 120  IFIT=0
 122  IF(DABS(Y)-1.0D-04*DABS(X)) 135,125,125
 125  ALPHA=X+X
      SUMSQ=X*X+Y*Y
      N=N-2
      GO TO 140
 130  X=0.0
      NX=NX-1
      NXX=NXX-1
 135  Y=0.0
      SUMSQ=0.0
      ALPHA=X
      N=N-1
 140  COF(2)=COF(2)+ALPHA*COF(1)
      IF(N.EQ.0) GO TO 155
 145  DO 150 L=2,N
 150  COF(L+1)=COF(L+1)+ALPHA*COF(L)-SUMSQ*COF(L-1)
 155  ROOTI(N2)=Y
      ROOTR(N2)=X
      N2=N2+1
      IF(SUMSQ) 160,165,160
 160  Y=-Y
      SUMSQ=0.0
      GO TO 155
 165  IF(N) 20,20,45
      END
```

SUBROUTINE PNRPV (NKOMP, X, AL, BL, R, T, V, VPART)

Input Parameters:

Integer

NKOMP: The number of components in the mixture.

Vector X: Mole fractions in liquid phase for the NKOMP components.

Real AL, BL: The mixture parameters for the liquid phase (no physical significance) which pertain to the constants A & B in the Peng-Robinson equation of state.

Real R: The universal gas constant.

Real T: The temperature of the system.

Real V: The liquid molar volume of the mixture.

The Output Is:

Vector

VPART: The partial molar volume of each component in the mixture.

PNPRV calculates the partial molar volume of each component in the mixture, given the mixture constants and the molar volume of the mixture.

LIST OF EQUATIONS

The Mixture Constants for the Peng-Robinson Equation:

$$AMIX = \sum_{i=1}^{NKOMP} \sum_{j=1}^{NKOMP} x_i x_j AL_{ij}$$

$$BMIX = \sum_{i=1}^{NKOMP} x_i BL_i \qquad (1)$$

Peng Robinson Equation:

$$P = \frac{RT}{\underline{V}-BMIX} - \frac{AMIX}{\underline{V}(\underline{V} + BMIX) + BMIX\ (\underline{V}-BMIX)}$$

where $\underline{V} = \frac{V}{n}$ (specific volume)

The Thermodynamic Partial Molar Volume Using the Triple Product:

$$\bar{v}_k = \left(\frac{\partial V}{\partial n_k}\right)_{P,\ T,\ n_i(i\neq k)} = \frac{-\left(\frac{\partial P}{\partial n_k}\right)_{T,\ V,\ n_i(i\neq k)}}{\left(\frac{\partial P}{\partial V}\right)_{T,\ n_i(\text{all } i)}} \qquad (2)$$

Doing the suggested operations of equation (2) on Equation (1) yields:

$$\bar{v}_i = \frac{S1-S2\cdot S3}{S4-S5}$$

where

$$S1 = \frac{RT(1 + BL_i/(\underline{V} - BMIX))}{\underline{V} - BMIX}$$

$$FACT = \underline{V}(\underline{V} + BMIX) + BMIX(\underline{V} - BMIX)$$

$$S2 = 2/FACT$$

$$S3 = \left(\sum_j x_j A_{ij}\right) - \frac{AMIX(BL_i)(\underline{V} - BMIX)}{FACT}$$

$$S4 = \frac{RT}{(\underline{V} - BMIX)^2}$$

$$S5 = \frac{2AMIX\ (\underline{V} - BMIX)}{FACT^2}$$

```
      SUBROUTINE PNRPV(NKOMP,X,AL,BL,R,T,V,VPART)
C
C     SUBROUTINE PNRPV CALCULATES THE PARTIAL MOLAR VOLUME USING
C     THE PENG-ROBINSON EQUATION OF STATE.
C
      DIMENSION AL(2,2),BL(2),VPART(2),SUM(2),X(2)
      AMIX=0.
      BMIX=0.
      DO 10 I=1,NKOMP
      BMIX=BMIX+X(I)*BL(I)
      DO 10 J=1,NKOMP
      AMIX=AMIX+X(I)*X(J)*AL(I,J)
   10 CONTINUE
      DO 20 I=1,NKOMP
      SUM(I)=0.
      DO 20 J=1,NKOMP
      SUM(I)=SUM(I)+X(J)*AL(J,I)
   20 CONTINUE
      DO 50 I=1,NKOMP
      FACT=V*(V+BMIX)+BMIX*(V-BMIX)
      S1=R*T*(1.+BL(I)/(V-BMIX))/(V-BMIX)
      S2=2./FACT
      S3=SUM(I)-(AMIX*BL(I)*(V-BMIX)/FACT)
      S4=R*T/((V-BMIX)**2)
      S5=2.0*AMIX*(V+BMIX)/(FACT**2)
      VPART(I)=(S1-S2*S3)/(S4-S5)
      WRITE(6,*)BL(I),SUM(I)
   50 CONTINUE
      RETURN
      END
```

DOUBLE PRECISION FUNCTION POLEG (X, K)

Input Parameters:

Real X: Mole fraction of component one in liquid phase where value stands for either experimental or internal collocation point.

Integer K: The degree of the Legendre polynomial used for fitting the P-X curve.

The Output Is: The Legendre polynomials, specifically the K^{th} degree.

POLEG is a statement function which contains the recursion formula for the Legendre polynomials.

LIST OF EQUATIONS

$$POLEG = P_k(x)$$

NOTE: POLEG evaluates the Legendre polynomial over the domain [0,1] rather than over the domain [-1, +1] thus

$$P_1(x) = 1$$

$$P_2(x) = 2x - 1$$

and as a result of this variable transformation the recursion formula is changed.

Recursion Formula:

$$P_m(x) = \frac{(2m - 3)(2x - 1)}{m - 1} P_{m-1}(x) - \frac{(m - 2)}{(m - 1)} P_{m-2}(x)$$

Legendre Polynomials are Orthogonal in [-1, + 1]

$$P_0(x) = 1$$

$$P_1(x) = x$$

$$P_2(x) = 1/2(3x^2 - 1)$$

$$P_3(x) = 1/2(5x^3-3x)$$

....

$$P_n(x) = \frac{2n - 1}{n} xP_{n-1}(x) - \frac{(n - 1)}{n}P_{n-2}(x)$$

We need to evaluate these polynomials in the Domain [0,1] thus a transformation is called for.

Let $Z = 1/2(x + 1)$

thus $x = -1, 0, +1$

$Z = 0, 1/2, +1$

or ... expressing x in terms of Z, $x = 2Z - 1$ and

$$P_0(Z) = 1$$

$$P_1(Z) = 2Z - 1$$

$$P_2(Z) = 1/2(3(2Z - 1)^2 - 1)$$

....

$$P_n(Z) = \frac{(2n - 1)}{n} (2Z - 1)P_{n-1}(Z) - \frac{(n - 1)}{n} P_{n-2}(Z)$$

Renumbering (starting with $m = n + 1$ because FORTRAN doesn't use zero subscripts,

$$P_m(Z) = \frac{(2m - 3)(2Z - 1)}{m - 1} P_{m-1}(Z) - \frac{(m - 2)}{(m - 1)}P_{m-2}(Z)$$

```
      DOUBLE PRECISION FUNCTION POLEG(X,K)
C
C     FUNCTION POLEG CONTAINS THE RECURSION [illegible] OF THE LEGENDRE
C     POLYNOMIAL.
C
      DOUBLE PRECISION AL(21)
      DOUBLE PRECISION X
      DOUBLE PRECISION DFLOAT
      AL(1)=1.
      AL(2)=2.*X-1.
      DO 1 LG=3,K
      LGM1=LG-1
    1 AL(LG)=(DFLOAT(2*LGM1-1)*(2.*X-1.)*AL(LG-1)-DFLOAT(LGM1-1)*AL
     1(LG-2))/DFLOAT(LGM1)
      POLEG=AL(K)
      RETURN
      END
```

SUBROUTINE PRFUG (Y, P, T, V, R, FUGCE, AP, BP, NKOMP)

Input Parameters:

Vector $\overline{Y}$: Mole fractions in gas phase for the NKOMP components.

Integer NKOMP: The number of components in the mixture.

Real P, T: The pressure and temperature of the system.

Real V: The molar volume of mixture in the gas phase.

Real R: The universal gas constant.

Real AP, BP: The mixture parameters for the gas phase (no physical significance) which pertain to the constants A & B in the Peng-Robinson equation of state.

The Output Is:

Vector FUGCE: Dimension [NKOMP] and contains the fugacity coefficients for each component in the mixture.

PRFUG calculates the fugacity coefficients for each component by using the Peng-Robinson equation of state, given the mixture constants and molar volume of the mixture.

LIST OF EQUATIONS

The Mixture Constants for Peng Robinson Equation:

$$A = \sum_{i=1}^{NKOMP} \sum_{i=1}^{NKOMP} y_i y_j AP_{ij}$$

$$B = \sum_{i=1}^{NKOMP} y_i BP_{ij}$$

The Fugacity Coefficients:

Let $Z = \frac{PV}{RT}$

$$A^* = \frac{AP}{R^2T^2}$$

$$B^* = \frac{BP}{RT}$$

$$S1 = \ln(Z - B^*)$$

$$S2 = \frac{A^*}{2(2^{\cdot 5})B^*}$$

$$S3 = \ln\left(\frac{Z + 2.414B^*}{Z - 0.414B^*}\right)$$

$$S4 = \frac{Z - 1}{B}$$

$$AK_i = \sum_{j=1}^{NKOMP} y_j AP_{ij}$$

$$Filn = \ln\hat{\phi}_i = BP_i \cdot S4 - S1 - S2 \cdot S3 \left(\frac{2.0AK_i}{A} - \frac{BP_i}{B}\right)$$

$$FUGCE\ (i) = EXP(FILN) = \hat{\phi}(i)$$

```
      SUBROUTINE PRFUG(Y,P,T,V,R,FUGCE,AP,BP,NKOMP)
C     SUBROUTINE PRFUG CALCULATES THE FUGACITY COEFFICIENTS
C     USING THE PENG-ROBINSON EQUATION OF STATE.
      DIMENSION AK(5)
      DIMENSION FUGCE(2),Y(2),AP(2,2),BP(2)
      A=0.0
      B=0.0
      DO 10 I=1,NKOMP
      DO 8 J=1,NKOMP
    8 A=A+Y(I)*Y(J)*AP(I,J)
      B=B+Y(I)*BP(I)
   10 CONTINUE
      AO=(A*P)/((R**2)*(T**2))
      BO=(B*P)/(R*T)
      Z=P*V/(R*T)
      S1=ALOG(Z-BO)
      S2=AO/(2.0*(2.0**0.5)*BO)
      S3=ALOG((Z+2.414*BO)/(Z-0.414*BO))
      S4=(Z-1.)/B
      DO 20 I=1,NKOMP
      AK(I)=0.0
   20 CONTINUE
      DO 30 I=1,NKOMP
      DO 25 J=1,NKOMP
   25 AK(I)=AK(I)+Y(J)*AP(J,I)
      FILN=BP(I)*S4-S1-S2*((2.0*AK(I)/A)-(BP(I)/B))*S3
      FUGCE(I)=EXP(FILN)
   30 CONTINUE
      RETURN
      END
```

SUBROUTINE PRRON (NKOMP, R, AP, BP, TCT,
TC, ANY, TAU, ACEN, VC, PC, T, LJC)

Input Parameters:

Integer

NKOMP: The number of components in the mixture.

Real R: The universal gas constant.

Real TC, PC,

VC: The pure component's critical temperature, pressure and volume.

Real DEL: Dimension [NKOMP] and is the i-j interaction parameter used for the Peng-Robinson equation of state.

Real ANY, TAU

FAK: The binary interaction paramters.

Real ACEN: The acentric factor for each component.

Real ZC: The critical compressibility factor for each component.

The Output is:

Real TCT: The pseudocritical constant which has no physical significance except to characterize bimolecular interactions betwen unlike molecules.

Real AP, BP: The mixture parameter constants for the Peng-Robinson equation of state.

PRRON reads in the i-j interaction parameter calculated by PROGRAM 4 and computes the mixture parameters to be used in the Peng-Robinson equation of state. This subroutine uses the 'mixing

rules' suggested by Peng and Robinson.

PRRON employs the following algorithm:

A: Read in all pure component parameters.

B: Read in the i-j interaction parameter, DEL.

C: Compute TCT, AP, and BP.

LIST OF EQUATIONS

Reduced Temperature:

$$T_{ri} = \frac{T}{T_{ci}}$$

The Pseudoparameter:

$$TCT = T_{cij} = (T_{ci}\ T_{cj})^{1/2}(1 - FAK_{ij})$$

The Mixture Constants for the Peng-Robinson Equation of State:

$$AKK = 0.3744 + 1.54226 \cdot \omega - 0.26992\omega^2$$

$$ALF = (1 + AKK\ (1 - TR^{0.5}))^2$$

$$AC = \frac{.45724\ R^2T_{ci}^2}{P_{ci}}$$

$$A_i = AC \cdot ALF$$

$$AP = (1 - DEL_{ij}) \cdot A_i^{.5} \cdot A_j^{.5} \text{ where } DEL_{ij} = C_{ij}$$

$$BP = \frac{0.778\ RT_c}{P_c}$$

```
      SUBROUTINE PRSON(NKOMP,R,AP,BP,TCT,TC,ANY,TAU,ACEN,VC,PC,
     1                 T,LJC)
C     SUBROUTINE PRSON READS THE PURE COMPONENTS PARAMETERS AND
C     CALCULATES THE MIXTURE PARAMETERS USED IN THE PENG-ROBINSON
C     EQUATION AND LYCKMANN-ECKERT-CHUEH CORRELATION.
      DIMENSION ZC(5),PAK(5,5),DEL(5,5),AP(2,2),BP(2),TC(2),
     1          A(5),TCT(2,2),ANY(2,2),TAU(2,2),ACEN(2),VC(2),PC(2)
  100 FORMAT(5E12.5)
  101 FORMAT(1H0,'PC-VC-TC-ZC-ACEN',4X,5E12.5)
  104 FORMAT(5F10.5)
  105 FORMAT(1H0,'PAK-ANY-TAU-DEL')
  106 FORMAT(1H0,5F10.5)
      NRD=5
      NWR=6
      READ(NRD,100) (PC(I),VC(I),TC(I),ZC(I),ACEN(I),I=1,NKOMP)
      WRITE(NWR,101) (PC(I),VC(I),TC(I),ZC(I),ACEN(I),I=1,NKOMP)
      NKOM1=NKOMP-1
      WRITE(NWR,105)
      DO 4 I=1,NKOM1
      IP1=I+1
      READ(NRD,104) (PAK(I,J),J=IP1,NKOMP)
      READ(NRD,104) (ANY(I,J),J=IP1,NKOMP)
      READ(NRD,104) (TAU(I,J),J=IP1,NKOMP)
      READ(NRD,104) (DEL(I,J),J=IP1,NKOMP)
      WRITE(NWR,106) (PAK(I,J),J=IP1,NKOMP)
      WRITE(NWR,106) (ANY(I,J),J=IP1,NKOMP)
      WRITE(NWR,106) (TAU(I,J),J=IP1,NKOMP)
      WRITE(NWR,106) (DEL(I,J),J=IP1,NKOMP)
    4 CONTINUE
      DO 6 I=1,NKOMP
      PAK(I,I)=0.0
      ANY(I,I)=0.0
      DEL(I,I)=0.0
      TAU(I,I)=0.0
      DO 6 J=1,NKOMP
      PAK(J,I)=PAK(I,J)
      ANY(J,I)=ANY(I,J)
      DEL(J,I)=DEL(I,J)
      TAU(J,I)=TAU(I,J)
    6 CONTINUE
      DO 15 I=1,NKOMP
      DO 15 J=1,NKOMP
      TCT(I,J)=SQRT(TC(I)*TC(J))*(1.-PAK(I,J))
   15 CONTINUE
      DO 30 I=1,NKOMP
      TR=T/TC(I)
      AKK=0.3744+1.54226*ACEN(I)-(ACEN(I)**2)*0.26992
      ALP=(1.+AKK*(1.-(TR**0.5)))**2
      AC=0.45724*((R**2)*(TC(I)**2))/PC(I)
      A(I)=AC*ALP
      BP(I)=0.07780*R*TC(I)/PC(I)
   30 CONTINUE
      DO 40 I=1,NKOMP
      DO 40 J=1,NKOMP
      AP(I,J)=(1.-DEL(I,J))*(A(I)**0.5)*(A(J)**0.5)
   40 CONTINUE
      RETURN
      END
```

SUBROUTINE PRVOL (NKOMP, V, Z, X, Y, P, T, AP, BP, R, ITYP)

Input Parameters:

Integer

NKOMP: Number of components in mixture.

Real X, Y: The mole fractions of each component in liquid and gas phase.

Real P, T: The pressure and temperature of the system.

Real AP, BP: The mixture parameters used in the Peng-Robinson equation of state.

Real R: The universal gas constant.

Integer

ITYP: A command variable.

If ITYP = 1, evaluate liquid molar volume.

If ITYP = -1, evaluate vapor molar volume.

The Output Is:

Real Z: The compressibility factor for the given mixture.

Real V: The molar volume (liquid or vapor) for the given mixture.

PRVOL generates the mixture constants for the Peng-Robinson equation of state using the mixture parameters read into the subroutine. Once the mixture constants are placed into the virial equation form of the Peng-Robinson equation, this cubic equation, in terms of Z, is solved for the roots by a standard IBM SSP SUBROUTINE. The roots are then tested in order to find the correct

one. The volume is then computed using the root (Z) in PV = ZRT.

PRVOL employs the following algorithm:

A: Compute mixture constants A and B.

B: Evaluate the leading coefficients to the virial equation.

C: Solve for the roots of virial equation.

D: Test roots for the correct value.

E: Compute molar volume with given root (Z).

LIST OF EQUATIONS

For Vapor Phase Volume:

$$A = \sum_{i=1}^{NKOMP} \sum_{J=1}^{NKOMP} y_i \cdot y_J \cdot AP_{iJ}$$

$$B = \sum_{i=1}^{NKOMP} y_i \cdot BP_{iJ}$$

For Liquid Phase Volume:

$$A = \sum_{i=1}^{NKOMP} \sum_{J=1}^{NKOMP} x_i x_J \cdot AP_{ij}$$

$$B = \sum_{i=1}^{NKOMP} x_i BP_{iJ}$$

(Virial) Peng-Robinson Equation of State:

$$Z^3 - (1 - K)Z^2 + (Q - 3K^2 - 2K)Z - (QK - K^2 - K^3) = 0$$

where $Q = \frac{AP}{R^2T^2}$ and $K = \frac{BP}{RT}$

Molar Volume:

$$V = \frac{ZRT}{P}$$

```
      SUBROUTINE PRVOL(NKOMP,V,Z,X,Y,P,T,AP,BP,B,ITYP)
C     SUBROUTINE PRVOL SOLVES THE PENG-ROBINSON EQUATION AND
C     CALCULATES THE MOLAR VOLUME.
C     IF ITYP .EQ.  1 THEN THE LIQUID PHASE MOLAR VOLUME IS CALCULATED
C     IF ITYP .EQ. -1 THEN THE VAPOR PHASE MOLAR VOLUME IS CALCULATED
      DOUBLE PRECISION COF(4),ROOTR(3),ROOTI(3),ROD(3),C(4)
      DOUBLE PRECISION DABS
      DIMENSION X(2),Y(2),AP(2,2),BP(2)
      A=0.0
      B=0.0
      IF(ITYP) 300,300,200
  200 DO 210 I=1,NKOMP
      DO 205 J=1,NKOMP
  205 A=A+X(I)*X(J)*AP(I,J)
      B=B+X(I)*BP(I)
  210 CONTINUE
      GO TO 2
  300 DO 310 I=1,NKOMP
      DO 305 J=1,NKOMP
  305 A=A+Y(I)*Y(J)*AP(I,J)
      B=B+Y(I)*BP(I)
  310 CONTINUE
    2 Q=(A*P)/((R**2)*(T**2))
      ZO=(B*P)/(R*T)
      C(1)=-(Q*ZO-ZO**2-ZO**3.0)
      C(2)=Q-3.*ZO**2-2.*ZO
      C(3)=-(1.-ZO)
      C(4)=1.0
      CALL PLTRT(C,COF,3,ROOTR,ROOTI,ITER)
      NR=0
      DO 5 K=1,3
      IF(DABS(ROOTI(K)/ROOTR(K))-1.D-04) 3,3,5
    3 IF(ROOTR(K)) 5,5,4
    4 NR=NR+1
      ROD(NR)=ROOTR(K)
    5 CONTINUE
      IF(ITYP) 10,10,50
   10 AMAX=ROD(1)
      IF(NR-1) 25,25,20
   20 DO 23 I=2,NR
      IF(AMAX-ROD(I)) 22,22,23
   22 AMAX=ROD(I)
   23 CONTINUE
   25 Z=AMAX
      GO TO 100
   50 AMIN=ROD(1)
      IF(NR-1) 75,75,60
   60 DO 70 J=2,NR
      IF(AMIN-ROD(J)) 70,70,65
   65 AMIN=ROD(J)
   70 CONTINUE
   75 Z=AMIN
  100 V=Z*R*T/P
      RETURN
      END
```

SUBROUTINE RDKPV (NKOMP, X, AL, BL, R, T, V, VPART)

Input Parameters:

Integer

NKOMP: The number of components in the mixture.

Vector X: Mole fractions in liquid phase for the NKOMP components.

Real AL, BL: The mixture parameters for the liquid phase (no physical significance) which pertain to the constants A & B in the Redlich-Kwong equation of state.

Real R: The universal gas constant.

Real T: The temperature of the system.

Real V: The liquid molar volume of the mixture.

The Output Is:

Vector

VPART: The partial molar volume of each component in the mixture.

RDKPV calculates the partial molar volume of each component in the mixture given the mixture constants and the molar volume of the mixture.

LIST OF EQUATIONS

The Mixture Constants for the Redlich-Kwong Equation:

$$AMIX = \sum_{i=1}^{NKOMP} \sum_{j=1}^{NKOMP} x_i x_j AL_{ij}$$

$$BMIX = \sum_{i=1}^{NKOMP} x_i BL_i$$

Redlich-Kwong Equation of State:

$$P = \frac{RT}{\underline{V} - B} - \frac{A}{T^{.5}\underline{V}(\underline{V} + B)} \qquad (1)$$

where $\underline{V} = \frac{V}{n}$ (specific volume)

and B = BMIX, A = AMIX

The Thermodynamic Partial Molar Volume using the Triple Product:

$$\overline{v}_k = \left(\frac{\partial V}{\partial n_k}\right)_{P,\ T,\ n_i (i \neq k)} =$$

$$\frac{-\left(\frac{\partial P}{\partial n_k}\right)_{T,\ V,\ n_i (i \neq k)}}{\left(\frac{\partial P}{\partial V}\right)_{T,\ n_i\ (\text{all } i)}} \qquad (2)$$

Doing the suggested operation of Equation (2) on Equation (1) yields:

$$\overline{v}_i = \frac{(ST - S2/S3)}{(S4 - S5/S6)}$$

where

$$S1 = \frac{RT(1 + BL_i/(\underline{V} - B))}{\underline{V} - B}$$

$$S2 = 2 \sum_{j}^{NKOMP} x_j A_{ij} - \frac{A(BL_i)}{\underline{V} + B}$$

$$S3 = \underline{V}(\underline{V} + B)T^{.5}$$

$$S4 = \frac{RT}{(\underline{V} - B)^2}$$

$$S5 = \frac{A(2V + B)}{T^{.5}}$$

$$S6 = \underline{V}^2(\underline{V} + B)^2$$

```
      SUBROUTINE RDKPV(NKOMP,X,AL,BL,R,T,V,VPART)
C
C     SUBROUTINE RDKPV CALCULATES THE PARTIAL MOLAR VOLUME USING THE
C     REDLICH-KWONG EQUATION OF STATE.
C
      DIMENSION AL(2,2),BL(2),VPART(2),SUM(2),X(2)
      AMIX=0.
      BMIX=0.
      DO 10 I=1,NKOMP
      BMIX=BMIX+X(I)*BL(I)
      DO 10 J=1,NKOMP
      AMIX=AMIX+X(I)*X(J)*AL(I,J)
 10   CONTINUE
      DO 20 I=1,NKOMP
      SUM(I)=0.
      DO 20 J=1,NKOMP
      SUM(I)=SUM(I)+2.*X(J)*AL(J,I)
 20   CONTINUE
      DO 50 I=1,NKOMP
      S1=R*T*(1.+BL(I)/(V-BMIX))/(V-BMIX)
      S2=SUM(I)-AMIX*BL(I)/(V+BMIX)
      S3=V*(V+BMIX)*SQRT(T)
      S4=R*T/(V-BMIX)**2
      S5=AMIX*(2.*V+BMIX)/SQRT(T)
      S6=V**2*(V+BMIX)**2
      VPART(I)=(S1-S2/S3)/(S4-S5/S6)
 50   CONTINUE
      RETURN
      END
```

SUBROUTINE RKFUG (Y, P, T, V, R, FUGCE, AG, BG, NKOMP)

Input Parameters:

Vector $\overline{Y}$: Mole fractions in gas phase for the NKOMP components.

Integer NKOMP: The number of components in the mixture.

Real P, T: The pressure and temperature of the system.

Real V: The molar volume of mixture in the gas phase.

Real R: The universal gas constant.

Real AG, BG: The mixture parameters for the gas phase (no physical significance) which pertain to the constants A & B in the Redlich-Kwong equation of state.

The Output Is:

Vector FUGCE: Dimension [NKOMP] and contains the fugacity coefficients for each component in the mixture.

RKFUG calculates the fugacity coefficients for each component by using the Redlich-Kwong equation of state, given the mixture constants and molar volume of mixture.

LIST OF EQUATIONS

The Mixture Constants for Redlich-Kwong Equation:

$$A = \sum_{i=1}^{NKOMP} \sum_{J=1}^{NKOMP} y_i \cdot y_J \cdot AG_{ij}$$

$$B = \sum_{i=1}^{NKOMP} y_i \cdot BG_i$$

$$AK_i = \sum_{J=1}^{NKOMP} y_J AG_{ij}$$

where i=1, NKOMP

The Fugacity Coefficients:

$$S1 = \ln\left(\frac{V}{V-B}\right)$$

$$S2 = \ln\left(\frac{V + B}{V}\right)$$

$$S3 = BRT^{1.5}$$

$$S4 = \frac{A}{S3 \cdot B} \cdot \frac{S2 - B}{V + B}$$

$$S5 = \ln\left(\frac{PV}{RT}\right)$$

$$FILN = \ln\hat{\phi}_i = S1 + \frac{B_i}{V - B} +$$

$$- \frac{2AK_i}{S3 \cdot S2} + S4 \cdot B_i - S5$$

$$FUGCE(i) = EXP(FILN) = \hat{\phi}(i)$$

```
      SUBROUTINE RKFUG(T,P,T,V,R,FUGCE,AG,BG,NKOMP)
C
C     SUBROUTINE RKFUG CALCULATES THE FUGACITY COEFFICIENTS USING THE
C     REDLICH-KWONG EQUATION OF STATE
C
      DIMENSION AK(5)
      DIMENSION FUGCE(2),Y(2),AG(2,2),BG(2)
      A=0.
      B=0.
      DO 10 I=1,NKOMP
      DO 8 J=1,NKOMP
    8 A=A+Y(I)*Y(J)*AG(I,J)
      B=B+Y(I)*BG(I)
   10 CONTINUE
      S1=ALOG(V/(V-B))
      S2=ALOG((V+B)/V)
      S3=R*T**1.5*B
      S4=A/(S3*B)*(S2-B/(V+B))
      S5=ALOG(P*V/(R*T))
      DO 20 I=1,NKOMP
      AK(I)=0.
   20 CONTINUE
      DO 30 I=1,NKOMP
      DO 25 J=1,NKOMP
   25 AK(I)=AK(I)+Y(J)*AG(J,I)
      FILN=S1+BG(I)/(V-B)-2.*AK(I)/S3*S2+S4*BG(I)-S5
      FUGCE(I)=EXP(FILN)
   30 CONTINUE
      RETURN
      END
```

SUBROUTINE RKKON (NKOMP, R, AL, AG, BL, BG,
TCT, TC, ANY, TAU, ACEN, VC, PC, T, LJC)

Input Parameters:

Integer

NKOMP: Number of components in mixture.

Real R: The universal gas constant.

Real OMAL,
OMAG, OMBAL,
OMBG: The pure component liquid and gas phase constants for the Redlich-Kwong equation of state.

Real TC, PC,
VC: The pure component's critical temperature, pressure, and volume.

Real ANY,
TAU, FAK: The binary interaction parameters.

Real ACEN: The acentric factor for each component.

Real ZC: The critical compressibility factor for each component.

Real T: The temperature of the system.

Ineger LJC: A counter.

The Output Is:

Real TCT: The pseudocritical constant which has no physical significance except to characterize bimolecular interactions between unlike molecules.

Real AL, AG, BL,

BG: The mixture parameter constants for the Redlich-Kwong equation of state.

RKKON reads in the pure component parameters and calculates the mixture parameters to be used in the Redlich-Kwong equation of state. This subroutine uses the 'mixing rules' suggested by Prausnitz.

RKKON employs the following algorithm:

A: Read in all pure component parameters.

B: Compute reduced temperature $\{T_r\}$.

C: If/ $T_r < 0.93$/ go to E.

If/ $T_r \geq 0.93$/ go to D.

D: Reevaluate pure component parameters.

E: Compute T_{cij}, P_{cij}, V_{cij} where $i \neq J$.

F: Compute mixtue parameters where $i \neq J$.

G: Compute mixtue parameters where $i = J$.

LIST OF EQUATIONS

Reduced Temperature:

$$T_r = \frac{T}{T_{ci}}$$

The Pseudoparameters:

$$TCT = T_{cij} = (T_{ci}\ T_{cj})^{1/2}\ (1 - FAK_{ij})$$

$$VCV = V_{cij} = 1/8(V_{ci}^{1/3} + V_{cj}^{1/3})^3$$

$$ZCZ = Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2}$$

$$PCP = P_{cij} = \frac{Z_{cij} \cdot RT_{cij}}{V_{cij}}$$

The Mixture Constants for Redlich-Kwong Equation of State:

where $i \neq J$

K=L and G

$$AK = A_{ij} = \frac{\Omega^{k}_{A} \cdot T^{2.5}_{cij}}{P_{cij}}$$

where i=j

$$AK = A_{ii} = \frac{\Omega^{k}_{A} \cdot R^{2} T^{2.5}_{ci}}{P_{ci}}$$

$$BK = \frac{\Omega^{k}_{B} \cdot RT_{ci}}{P_{ci}}$$

```
      SUBROUTINE RKKON(NKOMP,R,AL,AG,BL,BG,TCT,TC,ANY,TAU,ACEN,VC,PC,
     1T,LJC)
C
C     SUBROUTINE RKKON READS THE PURE COMPONENTS PARAMETERS AND CALCULA-
C     TES THE MIXTURE PARAMETERS USED IN THE REDLICH KWONG EQUATION.
C
      DIMENSION ZC(5),OMAL(5),OMBL(5),OMAG(5),OMBG(5),FAK(5,5)
      DIMENSION AL(2,2),AG(2,2),BL(2),BG(2),TC(2),TCT(2,2),ANY(2,2),
     1TAU(2,2),ACEN(2),VC(2),PC(2)
  100 FORMAT(5E12.5)
  101 FORMAT(1HO,'PC-VC-TC-ZC-ACEN',4X,5E12.5)
  102 FORMAT(1HO,'OMAL-OMBL-OMAG-OMBG ',4X,4E12.5)
  103 FORMAT(4E12.5)
  104 FORMAT(5F10.5)
  105 FORMAT(1HO,'FAK-ANY-TAU')
  106 FORMAT(1HO,5F10.5)
      NRD=5
      NWR=6
      IF(LJC.NE.1) GO TO 8
      READ(NRD,100) (PC(I),VC(I),TC(I),ZC(I),ACEN(I),I=1,NKOMP)
      READ(NRD,103) (OMAL(I),OMBL(I),OMAG(I),OMBG(I),I=1,NKOMP)
      WRITE(NWR,101) (PC(I),VC(I),TC(I),ZC(I),ACEN(I),I=1,NKOMP)
      WRITE(NWR,102) (OMAL(I),OMBL(I),OMAG(I),OMBG(I),I=1,NKOMP)
      NKOM1=NKOMP-1
      WRITE(NWR,105)
      DO 4 I=1,NKOM1
      IP1=I+1
      READ(NRD,104) (FAK(I,J),J=IP1,NKOMP)
      READ(NRD,104) (ANY(I,J),J=IP1,NKOMP)
      READ(NRD,104) (TAU(I,J),J=IP1,NKOMP)
      WRITE(NWR,106) (FAK(I,J),J=IP1,NKOMP)
      WRITE(NWR,106) (ANY(I,J),J=IP1,NKOMP)
      WRITE(NWR,106) (TAU(I,J),J=IP1,NKOMP)
    4 CONTINUE
      DO 6 I=1,NKOMP
      FAK(I,I)=0.0
      ANY(I,I)=0.0
      TAU(I,I)=0.0
      DO 6 J=I,NKOMP
      FAK(J,I)=FAK(I,J)
      ANY(J,I)=ANY(I,J)
      TAU(J,I)=TAU(I,J)
    6 CONTINUE
    8 DO 13 I=1,NKOMP
      TR=T/TC(I)
      IF(TR-0.93) 13,13,10
   10 OMB=(OMBG(I)+OMBL(I))/2.
      B=OMB*R*TC(I)/PC(I)
      OMA=PC(I)*VC(I)*(VC(I)+B)/(R*TC(I))**2*(R*TC(I)/(VC(I)-B)-PC(I))
      IF(TR-1.) 11,12,12
   11 DTR=EXP((TR-1.)*(2901.01-5738.92*TR+2869.85*TR**2+1.7*127/(1.01-
     1TR)))
      OMAL(I)=OMAL(I)+(OMA-OMAL(I))*DTR
      OMBL(I)=OMBL(I)+(OMB-OMBL(I))*DTR
      OMAG(I)=OMAG(I)+(OMA-OMAG(I))*DTR
      OMBG(I)=OMBG(I)+(OMB-OMBG(I))*DTR
      GO TO 13
   12 OMAL(I)=OMA
      OMBL(I)=OMB
      OMAG(I)=OMA
      OMBG(I)=OMB
   13 CONTINUE
      DO 15 I=1,NKOMP
      DO 15 J=1,NKOMP
      TCT(I,J)=SQRT(TC(I)*TC(J))*(1.-FAK(I,J))
      IF(I-J) 14,15,15
   14 VCV=((VC(I)**0.3333333+VC(J)**0.333333)**3)/8.0
      ZCZ=(ZC(I)+ZC(J))/2.0
      PCP=(ZCZ*R*TCT(I,J))/VCV
      AL(I,J)=((OMAL(I)+OMAL(J))/2.)*R**2*TCT(I,J)**2.5/PCP
      AL(J,I)=AL(I,J)
```

```
      AG(I,J)=((OMAG(I)+OMAG(J))/2.)*R**2*TCT(I,J)**2.5/PCP
      AG(J,I)=AG(I,J)
15    CONTINUE
      DO 20 I=1,NKOMP
      AL(I,I)=(OMAL(I)*R**2*TC(I)**2.5)/PC(I)
      AG(I,I)=(OMAG(I)*R**2*TC(I)**2.5)/PC(I)
      BL(I)=(OMBL(I)*R*TC(I))/PC(I)
      BG(I)=(OMBG(I)*R*TC(I))/PC(I)
20    CONTINUE
      RETURN
      END
```

SUBROUTINE RKVOL (NKOMP, V, Z, X, Y,
P, T, AL, AG, BL, BG, R, ITYP)

Input Parameters:

Integer

NKOMP: Number of components in mixture.

Real X, Y: The mole fractions of each component in the liquid and gas phase.

Real P, T: The pressure and temperature of the system.

Real Al, AG,

BL, BG: The mixture parameters used in the Redlich-Kwong equation of state.

Real R: The universal gas constant.

Integer ITYP: A command variable.
If ITYP = 1, evaluate liquid molar volume.
If ITYP = -1, evaluate vapor molar volume.

The Output Is:

Real Z: The compressibility factor for the given mixture.

Real V: The molar volume (liquid or vapor) for the given mixture.

RKVOL generates the mixture constants for the Redlich-Kwong equation of state using the mixture parameters read into the subroutine. Once the mixture constants are placed into the virial equation form of the Redlich-Kwong equation, this cubic equation, in terms of Z, is solved for the roots by a standard IBM SSP SUBROUTINE. The roots are then tested in order to find

the correct one. The volume is then computed using the root (Z) in PV = ZRT.

RKVOL employs the following algorithm:

A: Compute mixture constants A and B.

B: Evaluate the leading coefficients to the virial equation.

C: Solve for the roots of virial equation.

D: Test roots for the correct value.

E: Compute molar volume with given root (Z).

LIST OF EQUATIONS

For Vapor Phase Volume:

$$A = \sum_{i=1}^{NKOMP} \sum_{J=1}^{NKOMP} y_i \cdot y_J \cdot AG_{ij}$$

$$B = \sum_{i=1}^{NKOMP} y_i \cdot BG_i$$

For Liquid Phase Volume:

$$A = \sum_{i=1}^{NKOMP} \sum_{J=1}^{NKOMP} x_i x_J \cdot AL_{iJ}$$

$$B = \sum_{i=1}^{NKOMP} x_i BL_i$$

(Virial) Redlich-Kwong Equation of State:

$$Z^3 - Z^2 + (Q - 1 - K) \cdot K \cdot Z - Q \cdot K^2 = 0$$

where $Q = \dfrac{A}{BRT^{1.5}}$

and $K = \dfrac{PB}{RT}$

Molar Volume:

$$V = \frac{ZRT}{P}$$

(Virial) Redlich-Kwong Equation of State from Program:

$$Z^3 - Z^2 + \left(\frac{A}{BRT^{1.5}} - 1 - \frac{PB}{RT}\right)\frac{PB}{RT}Z - \frac{A}{BRT^{1.5}}\left(\frac{PB}{RT}\right)^2 = 0$$

$$Z^3 - Z^2 + \left(\frac{AP}{R^2T^{2.5}} - \frac{PB}{RT} - \frac{P^2B^2}{R^2T^2}\right)Z - \frac{AP^2B}{R^3T^{3.5}} = 0$$

let $A^* = \frac{AP}{R^2T^{2.5}}$ and $B^* = \frac{BP}{RT}$

Then $Z^3 - Z^2 + (A^* - B^* - B^{*2})Z - A^*B^* = 0$

This is equation (3 - 5.6) page 38 Properties of Gases and Liquids; Reid, Prausnitz, and Sherwood; Third Edition McGraw Hill.

The original Redlich-Kwong Equation:

$$P = \frac{RT}{V-B} - \frac{A}{T^{.5}V(V+B)}$$

$$P = \frac{RT^{1.5}(V^2 - VB) - AV + AB}{T^{.5}V(V^2 - B^2)}$$

$$PT^{.5}V^3 - PT^{.5}B^2V = RT^{1.5}V^2 + BRT^{1.5}V - AV + AB$$

$$PT^{.5}V^3 - RT^{1.5}V^2 + (A - PT^{.5}B^2 - BRT^{1.5})V - AB = 0$$

Now let $PV = ZRT \Rightarrow V^N = \left(\frac{ZRT}{P}\right)^N$

where N = 1, 2, 3

$$PT^{.5}\left(\frac{ZRT}{P}\right)^3 - RT^{1.5}\left(\frac{ZRT}{P}\right)^2$$

$$+ (A - PT^{.5}B^2 - BRT^{1.5})\frac{ZRT}{P} - AB = 0$$

$$\frac{R^3T^{3.5}}{P^2}Z^3 - \frac{R^3T^{3.5}}{P^2}Z^2$$

$$+ \left(\frac{ART}{P} - B^2RT^{1.5} - \frac{BR^2T^{2.5}}{P}\right)Z - AB = 0$$

$$Z^3 - Z^2 + \left(\frac{AP}{R^2T^{2.5}} - \frac{BP}{RT} - \frac{B^2P^2}{R^2T^2}\right)Z - \frac{ABP^2}{R^3T^{3.5}} = 0$$

let $A^* = \frac{AP}{R^2T^{2.5}}$ and $B^* = \frac{BP}{RT}$

$$\therefore Z^3 - Z^2 + (A^* - B^* - B^{*2})Z - A^*B^* = 0$$

This is the same equation derived at by equation in the program.

```
      SUBROUTINE RKVOL(NKOMP,V,Z,X,Y,P,T,AL,AG,BL,BG,R,ITYP)
C
C     SUBROUTINE RKVOL SOLVES THE REDLICH-KWONG EQUATION AND CALCULATES
C     THE MOLAR VOLUME.
C     IF ITYP .EQ. 1 THEN THE LIQUID PHASE MOLAR VOLUME IS CALCULATED
C     IF ITYP .EQ. -1 THEN THE VAPOR PHASE MOLAR VOLUME IS CALCULATED
C
      DOUBLE PRECISION COF(4),ROOTR(3),ROOTI(3),ROD(3),C(4)
      DOUBLE PRECISION  DABS
      DIMENSION X(2),Y(2),AL(2,2),AG(2,2),BL(2),BG(2)
      A=0.
      B=0.
      IF(ITYP) 300,300,200
  200 DO 210 I=1,NKOMP
      DO 205 J=1,NKOMP
  205 A=A+X(I)*X(J)*AL(I,J)
      B=B+X(I)*BL(I)
  210 CONTINUE
      GO TO 2
  300 DO 310 I=1,NKOMP
      DO 305 J=1,NKOMP
  305 A=A+Y(I)*Y(J)*AG(I,J)
      B=B+Y(I)*BG(I)
  310 CONTINUE
  2   Q=A/(B*R*T**1.5)
      ZO=P*B/(R*T)
      C(1)=-Q*ZO**2
      C(2)=(Q-1.-ZO)*ZO
      C(3)=-1.
      C(4)=1.
      CALL PLTRE(C,COF,3,ROOTR,ROOTI,IER)
      NR=0
      DO 5 K=1,3
      IF(DABS(ROOTI(K)/ROOTR(K))-1.D-04) 3,3,5
  3   IF(ROOTR(K)) 5,5,4
  4   NR=NR+1
      ROD(NR)=ROOTR(K)
  5   CONTINUE
      IF(ITYP) 10,10,50
  10  AMAX=ROD(1)
      IF(NR-1) 25,25,20
  20  DO 23 I=2,NR
      IF(AMAX-ROD(I)) 22,22,23
  22  AMAX=ROD(I)
  23  CONTINUE
  25  Z=AMAX
      GO TO 100
  50  AMIN=ROD(1)
      IF(NR-1) 75,75,60
  60  DO 70 J=2,NR
      IF(AMIN-ROD(J)) 70,70,65
  65  AMIN=ROD(J)
  70  CONTINUE
  75  Z=AMIN
 100  V=Z*R*T/P
      RETURN
      END
```

SUBROUTINE ROMB (NMAX, C, B, T, JMAX, NRC)

Input Parameters:

Integer NMAX: Viewed as the number of times the initial integration interval [C, B] is to be halved to produce subintervals of length h, (i.e. $h = (B - C)/2^{NMAX}$).

Real B, C: The upper and lower limits of integration, respectively.

Integer JMAX: Viewed as the number of times the initial pair of adjacent elements in the sequence T_0, T_1, ... T_{NMAX} are extrapolated to converge to the true integral value.

Integer NRC: The size of the matrix of elements in the Romberg sequences.

The Output Is:

Matrix $\overline{\overline{T}}$: Dimension [NRC, NRC] and contains the Romberg tableau for the given integral.

ROMB calculates the initial values by repeated halving of the subintervals used in the estimation of the given integral using the composite trapezoidal rule. Provided that f(x) has a continuous and bounded second derivative on the interval (C,B), the sequence of elements generated by the general recursion relation will converge to the true integral value of $\int_C^B f(x)dx$. The Richardson extrapolation technique is then applied to each

pair of adjacent elements in the sequence to produce another sequence of estimates. The entire results are then placed in matrix $\bar{\bar{T}}$.

ROMB employs the following algorithm:

A: Compute initial estimates.

B: Repeat part A by repeated halving.

C: Calculate entire sequence of elements by recursion formula.

D: Compute each value of f(x) by a four point Lagrangian interpolation method.

E: Complete the matrix $\bar{\bar{T}}$ by the Richardson extrapolation technique.

LIST OF EQUATIONS

The Integral:

$$\int_C^B f(x)dx$$

The Composite Trapezoidal Rule:

$$\int_C^B f(x)dx = \frac{B - C}{n}\left[\frac{1}{2}f(c) + \frac{1}{2}f(B) + \sum_{i=1}^{n-1} f(c + \frac{(B - C)}{n}i)\right]$$

where n is the number of applications, B and C, the integration limits.

The General Recursion Relation:

$$T_{n,1} = \frac{1}{2}\{T_{n-1,1} + \frac{(B - C)}{2^{N-1}} \sum_{i=1}^{2^N-1} f(c + \frac{(B - C)}{2^n}i)\}$$

where n = 1, NMAX, NMAX = N.

The Richardson Extrapolation Technique:

$$T_{n,j} = \frac{4^{j-1} T_{n+1,\, j-1} - T_{n,\, j-1}}{4^{j-1} - 1}$$

where j=1, JMAX.

```
      SUBROUTINE ROMB(NMAX,C,B,T,JMAX,NRC)
      DOUBLE PRECISION XINT(25),SA(25),G(25),GGINT(256),SSINT(256)
      DOUBLE PRECISION FA(25),ROD(25),RATO(256),C,B,T(NRC,NRC)
      DOUBLE PRECISION XX,LGAM1,LGAM2,FR,CC(25,25),P(25)
      COMMON/DIV/CC,SA,P,G,ROD,N,NP1,NT
      COMMON/BEG/FA
      T(1,1)=(C+B)/2.0
      DO 2 NN=1,NMAX
      T(NN+1,1)=0.0
      FR=1/2.0**NN
      IMAX=2**NN-1
      XX=0.0
      DO 989 I=1,IMAX
      XX=XX+FR
      CALL INTRP(25,NT,XX,ROD,FA,XINT)
      SSINT(I)=0.0
      GGINT(I)=0.0
      DO 95 J=1,NT
      GGINT(I)=GGINT(I)+XINT(J)*G(J)
      SSINT(I)=SSINT(I)+XINT(J)*SA(J)
 95   CONTINUE
      LGAM1=GGINT(I)+(1.-XX)*SSINT(I)
      LGAM2=GGINT(I)-XX*SSINT(I)
989   RATO(I)=LGAM1-LGAM2
      DO 1 K=1,IMAX,2
 1    T(NN+1,1)=T(NN+1,1)+RATO(K)
 2    T(NN+1,1)=T(NN,1)/2.0+T(NN+1,1)/2.0**NN
      DO 3 J=2,JMAX
      NXMJP2=NMAX-J+2
      FORMJ1=4.0**(J-1)
      DO 3 NN=1,NXMJP2
 3    T(NN,J)=(FORMJ1*T(NN+1,J-1)-T(NN,J-1))/(FORMJ1-1.0)
      RETURN
      END
```

```
      SUBROUTINE BOMB(NMAX,C,B,T,JMAX,NRC,XC,II)
      DOUBLE PRECISION SA(25),ROD(25),P(25),G(25),A(25,25),
     1                 WORK(25),STORL,RATO(256),GIN,SAIN,T(NRC,NRC),
     2                 XEXP(25),LGAM1,LGAM2,ARG(25),VAL(25),XL(2),
     3                 PL(25),DPDXX(25),DELTA,GINN,SAINN,XC,H,FR,XX,
     4                 X2,PX,DDX
      DIMENSION VC(2),TCT(2,2),ACEN(2),TAU(2,2),ANY(2,2),TC(2),
     1          VPURE(2)
      COMMON/DIV/A,SA,P,G,ROD,NT,NP1,N
      COMMON/BEG/WORK,ARG,VAL,PSAT2,KP1,VPURE,ACEN,TCT,VC,TT,
     1          TAU,ANY
      COMMON/BEG1/DELTA,XEXP
      H=XEXP(II)-XC
      T(1,1)=(C+B)*H/2.0
      DO 2 NN=1,NMAX
      T(NN+1,1)=0.0
      FR=H/2.0**NN
      IMAX=2**NN-1
      XX=XC
      CALL INTRP(XX,ROD,G,WORK,NT,1,ARG,VAL,NT)
      CALL INTDAL(XX,ARG,VAL,GIN,NT,1.D-06,IER)
      GINN=GIN
      CALL INTRP(XX,ROD,SA,WORK,NT,1,ARG,VAL,NT)
      CALL INTDAL(XX,ARG,VAL,SAIN,NT,1.D-06,IER)
      SAINN=SAIN
      X2=XX/DELTA
      CALL PCALA(PSAT2,X2,PX,KP1)
      CALL DPXA(PSAT2,KP1,DDX,X2)
      PL(I)=PX
      DPDXX(I)=DDX
      XL(1)=XX
      XL(2)=1.-XL(1)
      CALL GNVOL(2,XL,VC,ACEN,TCT,TT,TAU,ANY,TC,V)
      VMIXL=V
      VEL=VMIXL-XL(1)*VPURE(1)-XL(2)*VPURE(2)
      STKORL=VEL*DPDXX(I)/(R*TT)
      LGAM1=GINN+(1.0-XX)*(SAINN-STKORL)
      LGAM2=GINN-XX*(SAINN-STKORL)
  989 RATO(I)=LGAM1-LGAM2
      DO 1 K=1,IMAX,2
    1 T(NN+1,1)=T(NN+1,1)*RATO(K)
    2 T(NN+1,1)=T(NN,1)/2.0+T(NN+1,1)/2.0**NN
      DO 3 J=2,JMAX
      NXNJP2=NMAX-J+2
      FORMJ1=4.0**(J-1)
      DO 3 NN=1,NXNJP2
    3 T(NN,J)=(FORMJ1*T(NN+1,J-1)-T(NN,J-1))/(FORMJ1-1.0)
      RETURN
      END
```

SUBROUTINE SCALE (XSCALE, YSCALE, X, Y, N, ARRAY, NUMPT, NZ)

Input Parameters:

Vector X, Y:	Arrays containing the pairs of data points for the abcissa and ordinate, respectively.
Integer N:	The number of pairs of data points to be plotted.
Integer NZ:	A number which designates where in ARRAY the results are placed.

The Output Is:

Vector XSCALE:	An array containing the prominant abcissa markings for the plot.
MATRIX YSCALE:	A matrix containing the prominant ordinate markings for the plot.
MATRIX ARRAY:	A matrix containing the array of ordinate values in the NZ column.
Vector NUMPT:	An array containing the number of data points in each data set.

SCALE generates the ordinate and abcissca scales used for plotting the pairs of data points. SCALE can only handle one set of data points per calling; therefore, multiple curves on a single graph will require a call statement for SCALE for each desired curve plot on the single graph.

```
      SUBROUTINE SCALE(XSCALE,YSCALE,X,Y,N,ARRAY,NUMPT,NZ)
      DOUBLE PRECISION X(25),Y(25)
      DIMENSION XSCALE(300),YSCALE(10,11),NUMPT(10),ARRAY(10,300)
      XSCALE(1)=0.0
      YMIN=Y(N)
      YMAX=Y(1)
      DO 9 I=1,N
      IF(YMIN-Y(I)) 9,9,11
11    YMIN=Y(I)
9     CONTINUE
      DO 19 I=1,N
      IF(YMAX-Y(I)) 17,19,19
17    YMAX=Y(I)
19    CONTINUE
      YMIN=YMIN-(YMIN*0.05)
      YMAX=YMAX+(YMAX*0.05)
      SPA=(YMAX-YMIN)/10.0
      DO 2 J=1,2
      YSCALE(J,1)=YMIN
      DO 2 I=2,11
      IM1=I-1
2     YSCALE(J,I)=YSCALE(J,IM1)+SPA
      DO 3 I=2,51
      IM1=I-1
3     XSCALE(I)=XSCALE(IM1)+0.02
      DO 4 I=1,10
4     NUMPT(I)=0
      NUMPT(1)=50
      NUMPT(NZ)=50
      DO 6 I=1,51
6     ARRAY(NZ,I)=0.0
      DO 5 I=1,N
      B=X(I)+0.01
      A=B*51.0
      J=A
5     ARRAY(NZ,J)=Y(I)
      RETURN
      END
```

PROGRAM 1

(low pressure systems)
(symmetric convention)

PROGRAM 1 requires the following sections of subroutines (see Table 1):

1) MAIN SECTION

```
C     PROGRAM CTLG1 CALCULATES VAPOR PHASE MOLEFRACTIONS FOR SYSTEMS
C     UNDER LOW PRESSURE USING THE CONVENTION FOR NORMALIZATION OF
C     ACTIVITY COEFFICIENTS
C
      DOUBLE PRECISION A(25,25),SA(25),P(25),G(25),ROD(25)
      DOUBLE PRECISION PP,GE(25)
      DOUBLE PRECISION XEXP(25),PEXP(25)
      DOUBLE PRECISION FA(25),FB(25),FC(25),Y1(25),XINT(25),Y1C(25),
     1Y2C(25),YEXP(25),P1S,P2S,ALFA,BETA,X1,PX,X,GAM1,GAM2,SUMY,PINT,
     2YINT1,YINT2,DY,SQ,WA1(25),WA2(25),WA3(25),WA4(25),DELY,DELYA,
     3DELYS
      DOUBLE PRECISION AA(21)
      DOUBLE PRECISION DEXP,DABS,DSQRT,DFLOAT
      DOUBLE PRECISION PCA(25),DP,SSQ,DELP,DELPS,DELPA
      DOUBLE PRECISION GINT(25),SAINT(25)
      DOUBLE PRECISION TL(25)
      DOUBLE PRECISION GAMC1(25),GAMC2(25),Y1CC(25),Y2CC(25),SUMYC
      DOUBLE PRECISION DDELP,HAT(20,20),C,B
      DIMENSION TEXT(12)
      DIMENSION NUMNT(10),PTITLE(29),YGCALE(10,11),XGCALE(300),
     1          AARAY(10,300),GTITLE(29)
      COMMON/DIV/A,SA,P,G,ROD,NT,NP1,N
      COMMON/BEG/FA
      COMMON/LEG/AA
      COMMON PTITLE
      DATA ALFA,BETA/0.D 00,0.D 00/
      DATA N0,N1/1,1/
  501 FORMAT(1H1,'CONSISTENCY TEST USING ORTHOGONAL COLLOCATION - NUMBER
     1 OF INTERNAL POINTS',I5,/)
  502 FORMAT(1H0,'COLLOCATION POINTS',/,1X,10F10.6)
  504 FORMAT(1H0,'       X',11X,'P',9X,'GE/RT',8X,'GOOT',7X,'GAMMA1',6X,
     1'GAMMA2',8X,'Y1',10X,'Y2',7X,'SUM COR',3X,'GE J/MOLE')
  532 FORMAT(1H1,'CONSISTENCY TEST BY REPEATED HALVING OF TRAPEZOIDAL
     1RULE WITH ROMBERG INTEGRATION, AREA=',E15.6)
  505 FORMAT(10F12.6)
  506 FORMAT(1H0,'NUMBER OF BINARY DATAPOINTS  ',I2//1X,'SATURATION
     1VAPOR PRESSURE OF COMPONENT 1 AND 2 ',2F12.4,'  ATM. ',//1X,'
     2TEMPERATURE',F12.4,' DEG. K.')
  507 FORMAT(1X,12F10.4)
  508 FORMAT(I2)
  509 FORMAT(1H0,'       X',8X,'P',10X,'Y1',7X,'Y1EXP',6X,'DY',8X,'Y2',
     18X,'SUMY',4X,'PCAL',8X,'DP')
  510 FORMAT(1H0,'  SUM OF SQUARES OF DELTA Y ',F16.10,//1X,' VARIATION
     1 OF DELTA Y ',F10.4,'   ARITHMETIC MEAN OF DELTA Y ',F10.4,//1X,'
     2  CALCULATED EXCLUDING GIVEN END POINTS')
  511 FORMAT(F8.3,2F8.4,F8.3,8F6.4)
  512 FORMAT(1H0,'THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION
     1PROCEDURE HAS ALFA = ',F10.4,'AND BETA = ',F10.4)
  513 FORMAT(4I2)
  556 FORMAT(29A4)
  514 FORMAT(1H0,'     XEXP      YEXP       PEXP')
  515 FORMAT(1H0,'CALCULATED VALUES OF Y1')
  516 FORMAT(1H0,'SOLUTION AT THE DATAPOINTS')
  517 FORMAT(3I1)
  518 FORMAT(1H1,'EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR
     1THE BINARY SYSTEM   ',12A4,/,120(1H*))
  519 FORMAT(12A4)
  520 FORMAT(2I2)
  521 FORMAT(1H0,'  SUM OF SQUARES OF DELTA P ',F16.10,//1X,' VARIATION
     1 OF DELTA P ',F10.4,'   ARITHMETIC MEAN OF DELTA P ',F10.4,//1X,
     2' ARITHMETIC MEAN OF DELTA P/P ',F14.6,//1X,' CALCULATED EXCLUDING
     3 GIVEN END DATAPOINTS')
  522 FORMAT(3F10.5)
  523 FORMAT(1H0,'SOLUTION AT THE COLLOCATION POINTS')
      NRD=5
      NWR=6
  600 READ(NRD,513) NJOB,NKOMP,NSTP1,NSTP2
      IF(NJOB.EQ.0) STOP
      READ(NRD,519) TEXT
      READ(NRD,556) PTITLE
      READ(NRD,556) GTITLE
```

```
      DO 500 LJC=1,NJOB
      READ(NRD,520) K,NMAX
      READ(NRD,508)  NBPTS
      READ(NRD,517)  N11,N2,N3
      DO 5 I=1,NBPTS
      READ(NRD,511)  PEXP(I),DU,DUM,TL(I),XEXP(I),DUMM,DUMMY,DM,YEXP(I),
     1DBU,DBMU,DMBUY
      T=TL(I)
 5    CONTINUE
C     N11  )
C     N2   ) IDENTIFICATION PARAMETERS. SEE TABLE BELOW
C     N3)
C       P                V                      T
C
C     N11               N2                     N3
C
C    1 ATM             CC/MOL                   K
C    2 BAR            GRM/CC                    P
C    3 PSIA           CUFT/LB.MOL               C
C    4 INCH.HG         LB/CUFT                  R
C    5 CM.HG           CUFT/LB
C    6 MM.HG             Z
C
      DO 9783 I=1,NBPTS
      GO TO (9992,9993,9994,9995,9996,99996),N11
 9993 PEXP(I)=PEXP(I)/1.01325
      GO TO 9992
 9994 PEXP(I)=PEXP(I)/14.696
      GO TO 9992
 9995 PEXP(I)=PEXP(I)*0.0334211
      GO TO 9992
 9996 PEXP(I)=PEXP(I)/76.
      GOTO 9992
99996 PEXP(I)=PEXP(I)/760.
 9992 GO TO (9997,9998,9999,99990),N3
 9998 T=(TL(I)+459.67)/1.8
      GO TO 9997
 9999 T=TL(I)+273.15
      GO TO 9997
99990 T=TL(I)/1.8
 9997 CONTINUE
 9783 CONTINUE
      KP1=K+1
      P1S=PEXP(NBPTS)
      P2S=PEXP(1)
      WRITE(NWR,518)TEXT
      WRITE(NWR,512)  ALFA,BETA
      WRITE(NWR,506)  NBPTS,P1S,P2S,T
      CALL LEFIT(XEXP,PEXP,NBPTS,K)
      WRITE(NWR,514)
      DO 8 I=1,NBPTS
      WRITE(NWR,522)XEXP(I),YEXP(I),PEXP(I)
 8    CONTINUE
      DO 400 N=NSTP1,NSTP2
C
C     GENERATION OF COLLOCATION CONSTANTS
C
      WRITE(NWR,501)  N
      NT=N+N0+N1
      CALL JCOBI(25,N,N0,N1,ALFA,BETA,FA,FB,FC,ROD)
      WRITE(NWR,502)  (ROD(I),I=1,NT)
      NP1=N+1
      DO 10 I=1,NT
      X1=ROD(I)
      CALL PCAL(P2S,P1S,X1,PP,KP1)
      P(I)=PP
      CALL DFOPR(25,N,N0,N1,I,1,FA,FB,FC,ROD,V1)
      DO 10 J=1,NT
      A(I,J)=V1(J)
 10   CONTINUE
C
```

```
C     INTIAL VALUES OF G
C
      G(1)=0.
      G(NT)=0.
      DO 20 I=2,NP1
      G(I)=ROD(I)*(1.-ROD(I))
 20   CONTINUE
      CALL GIBBS(P1S,P2S)
      WRITE(NWR,523)
      WRITE(NWR,504)
      DO 81 I=1,NT
      X=ROD(I)
      GAMC1(I)=DEXP(G(I)+(1.-X)*SA(I))
      GAMC2(I)=DEXP(G(I)-X*SA(I))
      Y1CC(I)=GAMC1(I)*X*P1S/P(I)
      Y2CC(I)=GAMC2(I)*(1.-X)*P2S/P(I)
      SUMYC=Y1CC(I)+Y2CC(I)
      Y1CC(I)=Y1CC(I)/SUMYC
      Y2CC(I)=Y2CC(I)/SUMYC
      GE(I)=G(I)*T*8.3144
      WRITE(NWR,505)X,P(I),G(I),SA(I),GAMC1(I),GAMC2(I),Y1CC(I),Y2CC(I)
     1,SUMYC,GE(I)
 81   CONTINUE
      C=DLOG(GAMC1(1)/GAMC2(1))
      B=DLOG(GAMC1(NT)/GAMC2(NT))
      WRITE(NWR,516)
      WRITE(NWR,504)
C
C     LAGRANGIAN INTERPOLATION
C
      DO 80 I=1,NBPTS
      X=XEXP(I)
      CALL INTRP(25,NT,X,ROD,FA,XINT)
      SAINT(I)=0.
      GINT(I)=0.
      DO 25 J=1,NT
      GINT(I)=GINT(I)+XINT(J)*G(J)
      SAINT(I)=SAINT(I)+SA(J)*XINT(J)
 25   CONTINUE
      GAM1=DEXP(GINT(I)+(1.-X)*SAINT(I))
      GAM2=DEXP(GINT(I)-X*SAINT(I))
      Y1C(I)=GAM1*X*P1S/PEXP(I)
      Y2C(I)=GAM2*(1.-X)*P2S/PEXP(I)
      SUMY=Y1C(I)+Y2C(I)
      Y1C(I)=Y1C(I)/SUMY
      Y2C(I)=Y2C(I)/SUMY
      GE(I)=GINT(I)*T*8.3144
      WRITE(NWR,505)X,PEXP(I),GINT(I),SAINT(I),GAM1,GAM2,Y1C(I),Y2C(I),
     1SUMY,GE(I)
 80   CONTINUE
      CALL SCALE(XGCALE,YGCALE,XEXP,GE,NBPTS,AARAY,NUMNT,1)
      CALL PLOT(AARAY,NUMNT,GTITLE,YGCALE,XGCALE,1)
      CALL ROMB(NMAX,C,B,MAT,NMAX,20)
      WRITE(NWR,532) MAT(1,NMAX)
      WRITE(NWR,515)
      WRITE(NWR,509)
      SQ=0.
      DELY=0.
      SSQ=0.
      DELP=0.
      DDELP=0.
      DO 100 I=1,NBPTS
      X=XEXP(I)
      PINT=PEXP(I)
      CALL PCAL(P2S,P1S,X,PP,KP1)
      PCA(I)=PP
      DP=PCA(I)-PEXP(I)
      SUMY=Y1C(I)+Y2C(I)
      DY=Y1C(I)-YEXP(I)
      WRITE(NWR,507)X,PINT,Y1C(I),YEXP(I),DY,Y2C(I),SUMY,PCA(I),DP
      SQ=SQ+DY*DY
```

```
      DELY=DELY+DABS(DY)
      SSQ=SSQ+DP*DP
      DELP=DELP+DABS(DP)
      DDELP=DDELP+DABS(DP)/PEXP(I)
  100 CONTINUE
      DELYS=DSQRT(SQ/(DFLOAT(NBPTS-3)))
      DELYA=DELY/(DFLOAT(NBPTS-2))
      DELPS=DSQRT(SSQ/(DFLOAT(NBPTS-3)))
      DELPA=DELP/(DFLOAT(NBPTS-2))
      DDELP=DDELP/(DFLOAT(N-2))
      WRITE(NWB,510) SQ,DELYS,DELYA
      WRITE(NWB,521)SSQ,DELPS,DELPA,DDELP
  400 CONTINUE
  500 CONTINUE
      GO TO 600
      END
```

PROGRAM 2 (P-R)

(high pressure systems)
(symmetric convention)
(Peng-Robinson Equation of State)

PROGRAM 2 (P-R) requires the following sections of subroutines (see Table 1):

1) MAIN SECTION

2) SUBSECTION ONE.

```
C      PROGRAM CTLG2 CALCULATES VAPOR PHASE MOLEFRACTIONS FOR SYSTEMS
C      UNDER HIGH PRESSURE USING THE SYMMETRIC CONVENTION FOR NORMALI-
C      SATION OF ACTIVITY COEFFICIENTS
C
       DOUBLE PRECISION FA(25),FB(25),FC(25),Y1(25),Y1C(25),Y2C(25)
      1XINT(25),GAM1(25),GAM2(25),SUMYC(25),FPP1(25),FPP2(25),FI1(25),
      2FI2(25),YANC(25),FP1(25),FP2(25),DPDX(25),VMIX(25),VE(25),STKOR(25
      3)
       DOUBLE PRECISION A(25,25),SA(25),P(25),G(25),BOD(25),GE(25)
       DOUBLE PRECISION XEXP(25),YEXP(25),PEXP(25),DELX(25),WA1(25),
      1WA2(25),WA3(25),WA4(25)
       DOUBLE PRECISION PCA(25),DP,SSQ,DELP,DELPS,DELPA
       DOUBLE PRECISION ALFA,BETA,X1,PK,DDX,SQ,XB,PINT,YINT1,YINT2,SUMY,
      1DY,DELY,DELYS,DELYA
       DOUBLE PRECISION AA(21),PP
       DOUBLE PRECISION PS(2),MAT(20,20),C,B
       DOUBLE PRECISION DEXP,DABS,DSQRT,DFLOAT
       DOUBLE PRECISION FPP1L(25),FPP2L(25),FI1L(25),FI2L(25),FP1L(25),
      1FP2L(25),VMIXL(25),VEL(25),STKORL(25),PL(25),GINT(25),SAINT(25),
      2GAM1L(25),GAM2L(25),Y1CL(25),Y2CL(25),SUMYCL(25),DPDXL(25)
       DOUBLE PRECISION TL(25)
       DOUBLE PRECISION DDELP
       DIMENSION AP(2,2),BP(2),Y(2),X(2),FUGCE(2),FUGS(2),
      1VOL(2)
       DIMENSION TCT(2,2),TC(2),ANY(2,2),TAU(2,2),ACEN(2),VC(2),PC(2)
       DIMENSION TEXT(12)
       DIMENSION IL(2),YL(2)
       DIMENSION NUMBT(10),PTITLE(29),XGCALE(10,11),XGCAL2(30)),
      1          AARAY(10,300),GTITLE(29)
       COMMON/DIV/A,SA,P,G,BOD,N,NP1,NT
       COMMON/LEG/AA
       COMMON/BEG/FA
       COMMON PTITLE
       DATA R/82.0567/
       DATA ALFA,BETA/0.D 00,0.D 00/
       DATA N0,N1/1,1/
  501  FORMAT(1H1,'CONSISTENCY TESTS USING ORTHOGONAL COLLOCATION  -
      1 NUMBER OF INTERNAL POINTS',I5)
  502  FORMAT(1HO,'COLLOCATION POINTS',/,1X,10F10.6)
  504  FORMAT(1HO,'       X',9X,'P',7X,'GE/RT',6X,'GOOT',5X,'GAMMA1',4X,
      1'GAMMA2',6X,'Y1',8X,'Y2',5X,'SUM COR',2X,'GE J/MOLE')
  505  FORMAT(1HO,'NUMBER OF BINARY POINTS',I5,5X,'AT THE ISOTHERM',
      1F10.3,5X,'TEMPERATURE IN DEG K')
  506  FORMAT(1HO,'T',F10.4,4X,'PS',2F10.4,4X,'VOL',2F10.4,4X,//,1X,
      1'FISAT',2F10.4,4X,'FREESAT',2F10.4,/)
  507  FORMAT(1X,11F10.4,F10.4)
  508  FORMAT(I2)
  556  FORMAT(29A4)
  509  FORMAT(1HO,'       X',8X,'P',10X,'Y1',7X,'Y1EXP',6X,'DY',8X,'Y2',
      17X,'SUMY',6X,'PCAL',7X,'DP')
  510  FORMAT(1HO,' SUM OF SQUARES OF DELTA Y  ',F16.7,//,'  VARIANCE OF
      1DELTA Y  ',F10.4,'     ARITHMETIC MEAN OF DELTA Y  ',F10.4,//,'
      2CALCULATED EXCLUDING GIVEN END POINTS')
  511  FORMAT(5I2)
  512  FORMAT(F8.3,2F8.4,F8.3,8F6.4)
  513  FORMAT(1HO,'ITERATION NUMBER GREATER THAN 100')
  514  FORMAT(1HO,1X,'NUMBER OF ITERATIONS IN G',I5)
  515  FORMAT(1HO,' THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION
      1PROCEDURE IS OF THE TYPE ALFA = ',F10.4,'   BETA =  ',F10.4,//)
  516  FORMAT(1HO,'       X       FUGCE1     FUGCE2     VMIX        VE
      1DPDX       CORR TO GOOT')
  517  FORMAT(1HO,'     XEXP       YEXP      PEXP')
  518  FORMAT(1HO,'SOLUTION AT THE DATAPOINTS')
  519  FORMAT(1HO,'CALCULATED VALUES OF Y1  ')
  520  FORMAT(3I1)
  521  FORMAT(12A4)
  522  FORMAT(1H1,'EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR
      1THE BINARY SYSTEM   ',12A4,/120(1H*))
  523  FORMAT(2I2)
  524  FORMAT(1HO,' SUM OF SQUARES OF DELTA P  ',F16.7,//,'  VARIANCE OF
      1DELTA P   ',F10.4,'     ARITHMETIC MEAN OF DELTA P  ',F10.4,//,
```

```
     2' ARITHMETIC MEAN OF DELTA P/P  ',F14.6,//1X,' CALCULATED EXCLUDIN
     3G GIVEN END POINTS')
 525  FORMAT(3F10.5)
 530  FORMAT(1HO,'SOLUTION AT THE COLLOCATION POINTS')
 532  FORMAT(1H1,'CONSISTENCY TEST BY REPEATED HALVING OF TRAPEZOIDAL
     1RULE WITH ROMBERG INTEGRATION, AREA= ',E15.6)
C
C      LOGICAL UNIT NUMBERS
C
       NRD=5
       NWR=6
 600   READ(NRD,511) NJOB,NKOMP,NSTP1,NSTP2
       IF(NJOB.EQ.0)  STOP
       READ(NRD,521)  TEXT
       READ(NRD,556) PTITLE
       READ(NRD,556) GTITLE
       DO 500 LJC=1,NJOB
       READ(NRD,523)  K,NMAX
       READ(NRD,508)  NBPTS
       READ(NRD,520)  N11,N2,N3
       WRITE(NWR,522)  TEXT
       WRITE(NWR,515) ALPA,BETA
       DO 5 I=1,NBPTS
       READ(NRD,512)  PEXP(I),DU,DUM,TL(I), XEXP(I),DUMM,DUMMY,DM,YEXP(I)
     1,DMU,DMMU,DMMUY
       T=TL(I)
 5     CONTINUE
       CALL PRROM(NKOMP,R,AP,BP,TCT,TC,ANY,TAU,ACEN,VC,PC,T,LJC)
C
C      N11     )
C      N2      ) IDENTIFICATION PARAMETERS, SEE TABLE BELOW
C      N3      )
C        P                V                  T
C       N11              N2                 N3
C
C  1    ATM           CC/MOL                  K
C  2    BAR           GRM/CC                  F
C  3    PSIA          CUFT/LB.MOL             C
C  4   INCH.HG        LB/CUFT                 R
C  5   CM.HG          CUFT/LB
C  6   MM.HG             Z
C
       DO 9783 I=1,NBPTS
       GO TO (9992,9993,9994,9995,9996,99996),N11
 9993  PEXP(I)=PEXP(I)/1.01325
       GO TO 9992
 9994  PEXP(I)=PEXP(I)/14.696
       GO TO 9992
 9995  PEXP(I)=PEXP(I)*0.0334211
       GO TO 9992
 9996  PEXP(I)=PEXP(I)/76.
       GO TO 9992
99996  PEXP(I)=PEXP(I)/760.
 9992  GO TO (9997,9998,9999,99990),N3
 9998  T=(TL(I)+459.67)/1.8
       GO TO 9997
 9999  T=TL(I)+273.15
       GO TO 9997
99990  T=TL(I)/1.8
 9997  CONTINUE
 9783  CONTINUE
       KP1=K+1
       PS(1)=PEXP(NBPTS)
       PS(2)=PEXP(1)
       WRITE(NWR,505) NBPTS,T
       CALL LEFIT(XEXP,PEXP,NBPTS,K)
       WRITE(NWR,517)
       DO 8 I=1,NBPTS
       WRITE(NWR,525)XEXP(I),YEXP(I),PEXP(I)
 8     CONTINUE
C
```

```
C     CALCULATION OF PURE COMPONENT PROPERTIES
C
      DO 10 I=1,NKOMP
      J=1+NKOMP-I
      PSAT=PS(I)
      Y(I)=1.0
      Y(J)=0.
      CALL PRVOL(NKOMP,V,Z,X,Y,PSAT,T,AP,BP,R,-1)
      CALL PRFUG(Y,PSAT,T,V,R,FUGCE,AP,BP,NKOMP)
      Y(I)=0.
      FUGS(I)=FUGCE(I)*PS(I)
   10 CONTINUE
      X(1)=1.0
      X(2)=0.0
      CALL GNVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      VOL(1)=V
      X(1)=0.0
      X(2)=1.0
      CALL GNVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      VOL(2)=V
   11 CONTINUE
      DO 400 N=NSTP1,NSTP2
C
C     GENERATION OF COLLOCATION CONSTANTS
C
      WRITE(NWR,501) N
      NT=N+N0+N1
      CALL JCOBI(25,N,N0,N1,ALPA,BETA,FA,FB,FC,ROD)
      WRITE(NWR,502) (ROD(I),I=1,NT)
      DO 14 I=1,NT
      CALL DFOPR(25,N,N0,N1,I,1,FA,FB,FC,ROD,V1)
      DO 14 J=1,NT
      A(I,J)=V1(J)
   14 CONTINUE
      NP1=N+1
      FI1(NT)=FUGS(1)/PS(1)
      FI2(1)=FUGS(2)/PS(2)
      WRITE(NWR,506) T,PS(1),PS(2),VOL(1),VOL(2),FI1(NT),FI2(1),
     1FUGS(1),FUGS(2)
C
C     THERMODYNAMIC PROPERTIES AT THE COLLOCATION POINTS
C
      DO 22 I=1,NT
      X1=ROD(I)
      CALL PCAL(PS(2),PS(1),X1,PP,KP1)
      CALL DPX(PS(2),PS(1),KP1,DDX,X1)
      P(I)=PP
      DPDX(I)=DDX
      X(1)=X1
      X(2)=1.-X(1)
      CALL GNVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      VMIX(I)=V
      VE(I)=VMIX(I)-X(1)*VOL(1)-X(2)*VOL(2)
      STKOR(I)=VE(I)*DPDX(I)/(R*T)
      FP1(I)=FUGS(1)*DEXP(VOL(1)/(R*T)*(P(I)-PS(1)))
      FP2(I)=FUGS(2)*DEXP(VOL(2)/(R*T)*(P(I)-PS(2)))
      YANC(I)=0.5
   22 CONTINUE
C
C     THERMODYNAMIC PROPERTIES AT THE DATA POINTS
C
      DO 227 I=1,NDPTS
      X1=XEXP(I)
      CALL PCAL(PS(2),PS(1),X1,PP,KP1)
      CALL DPX(PS(2),PS(1),KP1,DDX,X1)
      PL(I)=PP
      DPDXL(I)=DDX
      XL(1)=X1
      XL(2)=1.-XL(1)
      CALL GNVOL(NKOMP,XL,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      VMIXL(I)=V
```

```
      VEL(I)=VMIXL(I)-XL(1)*VOL(1)-XL(2)*VOL(2)
      STKORL(I)=VEL(I)*DPDXL(I)/(R*T)
      FP1L(I)=FUGS(1)*DEXP(VOL(1)/(R*T)*(PL(I)-PS(1)))
      FP2L(I)=FUGS(2)*DEXP(VOL(2)/(R*T)*(PL(I)-PS(2)))
  227 CONTINUE
C
C     INITIAL VALUES OF G AND FI
C
      DO 26 I=1,NT
      G(I)=ROD(I)*(1.-ROD(I))
      FI1(I)=1.
      FI2(I)=1.
   26 CONTINUE
      DO 261 I=1,NBPTS
      FI1L(I)=1.0
      FI2L(I)=1.0
  261 CONTINUE
C
C     START ITERATION
C
      NI=0
   28 DO 30 I=1,NT
      FPP1(I)=FP1(I)/FI1(I)
      FPP2(I)=FP2(I)/FI2(I)
   30 CONTINUE
      DO 301 I=1,NBPTS
      FPP1L(I)=FP1L(I)/FI1L(I)
      FPP2L(I)=FP2L(I)/FI2L(I)
  301 CONTINUE
      CALL GIBSH(FPP1,FPP2,STKOR,ITER)
      NI=NI+1
      IF(NI.GT.20) GO TO 400
      IF(ITER-100) 33,32,32
   32 WRITE(NWR,513)
      GO TO 400
   33 WRITE(NWR,514) ITER
      DO 50 I=1,NT
      GAM1(I)=DEXP(G(I)+(1.-ROD(I))*(SA(I)-STKOR(I)))
      GAM2(I)=DEXP(G(I)-ROD(I)*(SA(I)-STKOR(I)))
      Y1C(I)=GAM1(I)*ROD(I)*FPP1(I)/P(I)
      Y2C(I)=GAM2(I)*(1.-ROD(I))*FPP2(I)/P(I)
      SUMYC(I)=Y1C(I)+Y2C(I)
   50 CONTINUE
      C=DLOG(GAM1(1)/GAM2(1))
      B=DLOG(GAM1(NT)/GAM2(NT))
C
C     LAGRANGE INTERPOLATION
C
      DO 411 I=1,NBPTS
      GINT(I)=0.
      SAINT(I)=0.
      XB=XEXP(I)
      CALL INTRP(25,NT,XB,ROD,FA,XINT)
      DO 412 J=1,NT
      GINT(I)=GINT(I)+XINT(J)*G(J)
      SAINT(I)=SAINT(I)+XINT(J)*SA(J)
  412 CONTINUE
      GAM1L(I)=DEXP(GINT(I)+(1.-XB)*(SAINT(I)-STKORL(I)))
      GAM2L(I)=DEXP(GINT(I)-XB*(SAINT(I)-STKORL(I)))
      Y1CL(I)=GAM1L(I)*XEXP(I)*FPP1L(I)/PL(I)
      Y2CL(I)=GAM2L(I)*(1.-XEXP(I))*FPP2L(I)/PL(I)
      SUMYCL(I)=Y1CL(I)+Y2CL(I)
      Y1CL(I)=Y1CL(I)/SUMYCL(I)
      Y2CL(I)=Y2CL(I)/SUMYCL(I)
      YL(1)=Y1CL(I)
      YL(2)=Y2CL(I)
      PR=PL(I)
      CALL PRVOL(NKOMP,V,Z,XL,YL,PR,T,AP,BP,R,-1)
      CALL PRFUG(YL,PR,T,V,R,FUGCE,AP,BP,NKOMP)
      FI1L(I)=FUGCE(1)
      FI2L(I)=FUGCE(2)
```

```
 411  CONTINUE
C
C     TEST FOR VARIATION IN Y1CAL
C
      DO 60 I=1,NT
      IF(DABS(Y1C(I)-YANC(I))-1.D-05) 60,65,65
 60   CONTINUE
      GO TO 80
C
C     NEW VALUES OF FUGACITY COEFFICIENTS
C
 65   DO 68 I=1,NT
      YANC(I)=Y1C(I)
      Y(1)=Y1C(I)
      Y(2)=Y2C(I)
      PR=P(I)
      CALL PRVOL(NKOMP,V,Z,X,Y,PR,T,AP,BP,R,-1)
      CALL PRFUG(Y,PR,T,V,R,FUGCE,AP,BP,NKOMP)
      FI1(I)=FUGCE(1)
      FI2(I)=FUGCE(2)
 68   CONTINUE
      GO TO 28
 80   CONTINUE
      WRITE(NWR,530)
      WRITE(NWR,504)
      DO 4117 I=1,NT
      GE(I)=G(I)*T*8.3144
      WRITE(NWR,507)ROD(I),P(I),G(I),SA(I),GAM1(I),GAM2(I),Y1C(I),
     1Y2C(I),SUMYC(I),GE(I)
4117  CONTINUE
      WRITE(NWR,516)
      DO 4116 I=1,NT
      WRITE(NWR,507)ROD(I),FI1(I),FI2(I),VMIX(I),VE(I),DPDX(I),STKOR(I)
4116  CONTINUE
      WRITE(NWR,518)
      WRITE(NWR,504)
      DO 85 I=1,NBPTS
      GE(I)=GINT(I)*T*8.3144
      WRITE(NWR,507)XEXP(I),PL(I),GINT(I),SAINT(I),GAM1L(I),GAM2L(I),
     1Y1CL(I),Y2CL(I),SUMYCL(I),GE(I)
 85   CONTINUE
      CALL SCALE(XGCALE,YGCALE,XEXP,GE,NBPTS,AABAY,NUMNT,1)
      CALL PLOT(AABAY,NUMNT,GTITLE,YGCALE,XGCALE,1)
      CALL BOMB(NMAX,C,B,MAT,NMAX,20)
      WRITE(NWR,532) MAT(1,NMAX)
      WRITE(NWR,516)
      DO 86 I=1,NBPTS
      WRITE(NWR,507)XEXP(I),FI1L(I),FI2L(I),VMIXL(I),VEL(I),DPDXL(I),
     1STKORL(I)
 86   CONTINUE
      WRITE(NWR,519)
      WRITE(NWR,504)
      SQ=0.
      SSQ=0.
      DELY=0.
      DELP=0.
      DO 100 I=1,NBPTS
      XX=XEXP(I)
      CALL PCA(PH(2),PH(1),XX,PP,NP1)
      PCA(I)=PP
      YY=PCA(I)-YEXP(I)
      PP=PEXP(I)
      SUMY=Y1CL(I)+Y2CL(I)
      DY=Y1CL(I)-YEXP(I)
      WRITE(NWR,507)XX,PINT,Y1CL(I),YEXP(I),DY,Y2CL(I),SUMY,PCA(I),DP
      SQ=SQ+DY**2
      DELY=DELY+DABS(DY)
      SSQ=SSQ+DP*DP
      DELP=DELP+DABS(DP)
      DDELP=DDELP+DABS(DP)/PEXP(I)
```

```
100   CONTINUE
      DELYS=DSQRT(SQ/(DFLOAT(NBPTS-3)))
      DELYA=DELY/(DFLOAT(NBPTS-2))
      DELPS=DSQRT(SSQ/(DFLOAT(NBPTS-3)))
      DELPA=DELP/(DFLOAT(NBPTS-2))
      DDELP=DDELP/(FLOAT(N-2))
      WRITE(NWR,510) SQ,DELYS,DELYA
      WRITE(NWR,524) SSQ,DELPS,DELPA,DDELP
400   CONTINUE
500   CONTINUE
      GO TO 600
      END
```

PROGRAM 2 (R-K)

(high Pressure systems)
(symmetric convention)
(Soave-Redlich-Kwong Equation of State)

PROGRAM 2 (R-K) requires the following sections of subroutines (see Table 1):

1) MAIN SECTION,

2) SUBSECTION TWO.

```
C      PROGRAM CTLG2 CALCULATES VAPOR PHASE MOLEFRACTIONS FOR SYSTEMS
C      UNDER HIGH PRESSURE USING THE SYMMETRIC CONVENTION FOR NORMALI-
C      SATION OF ACTIVITY COEFFICIENTS
C
       DOUBLE PRECISION FA(25),FB(25),FC(25),V1(25),Y1C(25),Y2C(25),
      1XINT(25),GAM1(25),GAM2(25),SUMYC(25),FPP1(25),FPP2(25),FI1(25),
      2FI2(25),YANC(25),FP1(25),FP2(25),DPDX(25),VMIX(25),VE(25),STKOR(25
      3)
       DOUBLE PRECISION A(25,25),SA(25),P(25),G(25),ROD(25),GE(25)
       DOUBLE PRECISION XEXP(25),YEXP(25),PEXP(25),DELX(25),WA1(25),
      1WA2(25),WA3(25),WA4(25)
       DOUBLE PRECISION PCA(25),DP,SSQ,DELP,DELPS,DELPA
       DOUBLE PRECISION ALFA,BETA,X1,PX,DDX,SQ,XR,PINT,YINT1,YINT2,SUMY,
      1DY,DELY,DELYS,DELYA
       DOUBLE PRECISION AA(21),PP
       DOUBLE PRECISION PS(2),MAT(20,20),C,B
       DOUBLE PRECISION DEXP,DABS,DSQRT,DFLOAT
       DOUBLE PRECISION FPP1L(25),FPP2L(25),FI1L(25),FI2L(25),FP1L(25),
      1FP2L(25),VMIXL(25),VEL(25),STKORL(25),PL(25),GINT(25),SAINT(25),
      2GAM1L(25),GAM2L(25),Y1CL(25),Y2CL(25),SUMYCL(25),DPDXL(25)
       DOUBLE PRECISION TL(25)
       DOUBLE PRECISION DDELP
       DIMENSION AL(2,2),BL(2),AG(2,2),BG(2),Y(2),X(2),FUGCE(2),FUGS(2),
      1VOL(2)
       DIMENSION TCT(2,2),TC(2),ANY(2,2),TAU(2,2),ACEN(2),VC(2),PC(2)
       DIMENSION TEXT(12)
       DIMENSION XL(2),YL(2)
       DIMENSION NUMMT(10),PTITLE(29),YGCALE(10,11),XGCALE(300),
      1          AARAY(10,300),GTITLE(29)
       COMMON/DIV/A,SA,P,G,ROD,N,NP1,NT
       COMMON/LEG/AA
       COMMON/BEG/FA
       COMMON PTITLE
       DATA R/82.0567/
       DATA ALFA,BETA/0.D 00,0.D 00/
       DATA NO,N1/1,1/
  501  FORMAT(1H1,'CONSISTENCY TESTS USING ORTHOGONAL COLLOCATION  -
      1 NUMBER OF INTERNAL POINTS',I5)
  502  FORMAT(1HO,'COLLOCATION POINTS',/,1X,10F10.6)
  504  FORMAT(1HO,'       X',9X,'P',7X,'GE/RT',6X,'GOOT',5X,'GAMMA1',4X,
      1'GAMMA2',6X,'Y1',8X,'Y2',5X,'SUM COR',2X,'GE J/MOLE')
  505  FORMAT(1HO,'NUMBER OF BINARY POINTS',I5,5X,'AT THE ISOTHERM',
      1F10.2,5X,'TEMPERATURE IN DEG K')
  506  FORMAT(1HO,'T',F10.4,4X,'PS',2F10.4,4X,'VOL',2F10.4,4X,//,1X,
      1'FISAT',2F10.4,4X,'FREESAT',2F10.4,/)
  507  FORMAT(1X,11F10.4,F10.4)
  508  FORMAT(I2)
  556  FORMAT(29A4)
  509  FORMAT(1HO,'       X',8X,'P',10X,'Y1',7X,'Y1EXP',6X,'DY',8X,'Y2',
      17X,'SUMY',6X,'PCAL',7X,'DP')
  510  FORMAT(1H0,' SUM OF SQUARES OF DELTA Y  ',F16.7,//,'  VARIANCE OF
      1DELTA Y  ',F10.4,'     ARITHMETIC MEAN OF DELTA Y  ',F10.4,//,'
      2CALCULATED EXCLUDING GIVEN END POINTS')
  511  FORMAT(5I2)
  512  FORMAT(F8.3,2F8.4,F8.3,8F6.4)
  513  FORMAT(1HO,'ITERATION NUMBER GREATER THAN 100')
  514  FORMAT(1HO,1X,'NUMBER OF ITERATIONS IN G',I5)
  515  FORMAT(1HO,' THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION
      1PROCEDURE IS OF THE TYPE ALFA = ',F10.4,'   BETA =  ',F10.4,//)
  516  FORMAT(1HO,'       X        FUGCE1     FUGCE2     VMIX        VE
      1DPDX       CORR TO GOOT')
  517  FORMAT(1HO,'    XEXP       YEXP      PEXP')
  518  FORMAT(1HO,'SOLUTION AT THE DATAPOINTS')
  519  FORMAT(1HO,'CALCULATED VALUES OF Y1  ')
  520  FORMAT(3I1)
  521  FORMAT(12A4)
  522  FORMAT(1H1,'EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR
      1THE BINARY SYSTEM   ',12A4,/120(1H*))
  523  FORMAT(2I2)
  524  FORMAT(1HO,' SUM OF SQUARES OF DELTA P  ',F16.7,//,'  VARIANCE OF
      1DELTA P   ',F10.4,'     ARITHMETIC MEAN OF DELTA P  ',F10.4,//,
```

```
     2' ARITHMETIC MEAN OF DELTA P/P  ',F14.6,//1X,' CALCULATED EXCLUDIN
     3G GIVEN END POINTS')
  525  FORMAT(3F10.5)
  530  FORMAT(1H0,'SOLUTION AT THE COLLOCATION POINTS')
  532  FORMAT(1H1,'CONSISTENCY TEST BY REPEATED HALVING OF TRAPEZOIDAL
     1RULE WITH ROMBERG INTEGRATION, AREA= ',E15.6)
C
C      LOGICAL UNIT NUMBERS
C
       NRD=5
       NWR=6
  600  READ(NRD,511)NJOB,NKOMP,NSTP1,NSTP2
       IF(NJOB.EQ.0)  STOP
       READ(NRD,521)  TEXT
       READ(NRD,556)PTITLE
       READ(NRD,556)GTITLE
       DO 500 LJC=1,NJOB
       READ(NRD,523)  K,NMAX
       READ(NRD,508)  NBPTS
       READ(NRD,520)  N11,N2,N3
       WRITE(NWR,522)  TEXT
       WRITE(NWR,515)  ALPA,BETA
       DO 5 I=1,NBPTS
       READ(NRD,512)  PEXP(I),DO,DUM,TL(I),  XEXP(I),DUMM,DUMMY,DM,YEXP(I)
     1,DMU,DMMU,DMMUY
       T=TL(I)
  5    CONTINUE
       CALL REKON(NKOMP,R,AL,AG,BL,BG,TCT,TC,ANY,TAU,ACEN,VC,PC,T,LJC)
C
C      N11    )
C      N2     ) IDENTIFICATION PARAMETERS, SEE TABLE BELOW
C      N3     )
C        P               V                    T
C       N11             N2                   N3
C
C   1   ATM          CC/MOL                   K
C   2   BAR          GRM/CC                   P
C   3   PSIA         CUFT/LB.MOL              C
C   4  INCH.HG       LB/CUFT                  R
C   5  CM.HG         CUFT/LB
C   6  MM.HG            Z
C
       DO 9783 I=1,NBPTS
       GO TO (9992,9993,9994,9995,9996,99996),N11
  9993 PEXP(I)=PEXP(I)/1.01325
       GO TO 9992
  9994 PEXP(I)=PEXP(I)/14.696
       GO TO 9992
  9995 PEXP(I)=PEXP(I)*0.0334211
       GO TO 9992
  9996 PEXP(I)=PEXP(I)/76.
       GO TO 9992
 99996 PEXP(I)=PEXP(I)/760.
  9992 GO TO (9997,9998,9999,99990),N3
  9998 T=(TL(I)+459.67)/1.8
       GO TO 9997
  9999 T=TL(I)+273.15
       GO TO 9997
 99990 T=TL(I)/1.8
  9997 CONTINUE
  9783 CONTINUE
       KP1=K+1
       PS(1)=PEXP(NBPTS)
       PS(2)=PEXP(1)
       WRITE(NWR,505)  NBPTS,T
       CALL LEFIT(XEXP,PEXP,NBPTS,K)
       WRITE(NWR,517)
       DO 8 I=1,NBPTS
       WRITE(NWR,525)XEXP(I),YEXP(I),PEXP(I)
  8    CONTINUE
```

```
C
C       CALCULATION OF PURE COMPONENT PROPERTIES
C
        DO 10 I=1,NKOMP
        J=1+NKOMP-I
        PSAT=PS(I)
        Y(I)=1.0
        Y(J)=0.
        CALL BKVOL(NKOMP,V,Z,X,Y,PSAT,T,AL,AG,BL,BG,R,-1)
        CALL BKFUG(Y,PSAT,T,V,B,FUGCE,AG,BG,NKOMP)
        Y(I)=0.
        FUGS(I)=FUGCE(I)*PS(I)
        X(I)=1.
        X(J)=0.
        CALL GNVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
        VOL(I)=V
        X(I)=0.
 10     CONTINUE
        DO 400 N=NSTP1,NSTP2
C
C       GENERATION OF COLLOCATION CONSTANTS
C
        WRITE(NWR,501) N
        NT=N+NO+N1
        CALL JCOBI(25,N,NO,N1,ALPA,BETA,FA,FB,FC,ROD)
        WRITE(NWR,502) (ROD(I),I=1,NT)
        DO 14 I=1,NT
        CALL DFOPR(25,N,NO,N1,I,1,FA,FB,FC,ROD,V1)
        DO 14 J=1,NT
        A(I,J)=V1(J)
 14     CONTINUE
        NP1=N+1
        FI1(NT)=FUGS(1)/PS(1)
        FI2(1)=FUGS(2)/PS(2)
        WRITE(NWR,506) T,PS(1),PS(2),VOL(1),VOL(2),FI1(NT),FI2(1),
       1FUGS(1),FUGS(2)
C
C       THERMODYNAMIC PROPERTIES AT THE COLLOCATION POINTS
C
        DO 22 I=1,NT
        X1=ROD(I)
        CALL PCAL(PS(2),PS(1),X1,PP,KP1)
        CALL DPX(PS(2),PS(1),KP1,DDX,X1)
        P(I)=PP
        DPDX(I)=DDX
        X(1)=X1
        X(2)=1.-X(1)
        CALL GNVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
        VMIX(I)=V
        VE(I)=VMIX(I)-X(1)*VOL(1)-X(2)*VOL(2)
        STKOR(I)=VE(I)*DPDX(I)/(R*T)
        FP1(I)=FUGS(1)*DEXP(VOL(1)/(R*T)*(P(I)-PS(1)))
        FP2(I)=FUGS(2)*DEXP(VOL(2)/(R*T)*(P(I)-PS(2)))
        YANC(I)=0.5
 22     CONTINUE
C
C       THERODYNAMIC PROPERTIES AT THE DATA POINTS
C
        DO 227 I=1,NBPTS
        X1=XEXP(I)
        CALL PCAL(PS(2),PS(1),X1,PP,KP1)
        CALL DPX(PS(2),PS(1),KP1,DDX,X1)
        PL(I)=PP
        DPDXL(I)=DDX
        XL(1)=X1
        XL(2)=1.-XL(1)
        CALL GNVOL(NKOMP,XL,VC,ACEN,TCT,T,TAU,ANY,TC,V)
        VMIXL(I)=V
        VEL(I)=VMIXL(I)-XL(1)*VOL(1)-XL(2)*VOL(2)
        STKORL(I)=VEL(I)*DPDXL(I)/(R*T)
        FP1L(I)=FUGS(1)*DEXP(VOL(1)/(R*T)*(PL(I)-PS(1)))
        FP2L(I)=FUGS(2)*DEXP(VOL(2)/(R*T)*(PL(I)-PS(2)))
```

```
 227  CONTINUE
C
C     INITIAL VALUES OF G AND FI
C
      DO 26 I=1,NT
      G(I)=ROD(I)*(1.-ROD(I))
      FI1(I)=1.
      FI2(I)=1.
 26   CONTINUE
      DO 261 I=1,NBPTS
      FI1L(I)=1.0
      FI2L(I)=1.0
 261  CONTINUE
C
C     START ITERATION
C
      NY=0
 28   DO 30 I=1,NT
      FPP1(I)=FP1(I)/FI1(I)
      FPP2(I)=FP2(I)/FI2(I)
 30   CONTINUE
      DO 301 I=1,NBPTS
      FPP1L(I)=FP1L(I)/FI1L(I)
      FPP2L(I)=FP2L(I)/FI2L(I)
 301  CONTINUE
      CALL GIBSH(FPP1,FPP2,STKOR,ITER)
      NY=NY+1
      IF(NY.GT.20) GO TO 400
      IF(ITER-100) 33,32,32
 32   WRITE(NWR,513)
      GO TO 400
 33   WRITE(NWR,514) ITER
      DO 50 I=1,NT
      GAM1(I)=DEXP(G(I)*(1.-ROD(I))*(SA(I)-STKOR(I)))
      GAM2(I)=DEXP(G(I)-ROD(I)*(SA(I)-STKOR(I)))
      Y1C(I)=GAM1(I)*ROD(I)*FPP1(I)/P(I)
      Y2C(I)=GAM2(I)*(1.-ROD(I))*FPP2(I)/P(I)
      SUMYC(I)=Y1C(I)+Y2C(I)
 50   CONTINUE
      C=DLOG(GAM1(1)/GAM2(1))
      B=DLOG(GAM1(NT)/GAM2(NT))
C
C     LAGRANGE INTERPOLATION
C
      DO 411 I=1,NBPTS
      GINT(I)=0.
      SAINT(I)=0.
      XR=XEXP(I)
      CALL INTRP(25,NT,XR,ROD,PA,XINT)
      DO 412 J=1,NT
      GINT(I)=GINT(I)+XINT(J)*G(J)
      SAINT(I)=SAINT(I)+XINT(J)*SA(J)
 412  CONTINUE
      GAM1L(I)=DEXP(GINT(I)*(1.-XR)*(SAINT(I)-STKORL(I)))
      GAM2L(I)=DEXP(GINT(I)-XR*(SAINT(I)-STKORL(I)))
      Y1CL(I)=GAM1L(I)*XEXP(I)*FPP1L(I)/PL(I)
      Y2CL(I)=GAM2L(I)*(1.-XEXP(I))*FPP2L(I)/PL(I)
      SUMYCL(I)=Y1CL(I)+Y2CL(I)
      Y1CL(I)=Y1CL(I)/SUMYCL(I)
      Y2CL(I)=Y2CL(I)/SUMYCL(I)
      YL(1)=Y1CL(I)
      YL(2)=Y2CL(I)
      PR=PL(I)
      CALL BKVOL(NKOMP,V,Z,XL,YL,PR,T,AL,AG,BL,BG,R,-1)
      CALL BKFUG(YL,PR,T,V,R,FUGCE,AG,BG,NKOMP)
      FI1L(I)=FUGCE(1)
      FI2L(I)=FUGCE(2)
 411  CONTINUE
C
C     TEST FOR VARIATION IN Y1CAL
C
```

```
      DO 60 I=1,NT
      IF(DABS(Y1C(I)-YANC(I))-1.D-05) 60,65,65
 60   CONTINUE
      GO TO 80
C
C     NEW VALUES OF FUGACITY COEFFICIENTS
C
 65   DO 68 I=1,NT
      YANC(I)=Y1C(I)
      Y(1)=Y1C(I)
      Y(2)=Y2C(I)
      PR=P(I)
      CALL RKVOL(NKOMP,V,Z,X,Y,PR,T,AL,AG,BL,BG,R,-1)
      CALL RKFUG(Y,PR,T,V,R,FUGCE,AG,BG,NKOMP)
      FI1(I)=FUGCE(1)
      FI2(I)=FUGCE(2)
 68   CONTINUE
      GO TO 28
 80   CONTINUE
      WRITE(NWR,530)
      WRITE(NWR,504)
      DO 4117 I=1,NT
      GE(I)=G(I)*T*8.3144
      WRITE(NWR,507)ROD(I),P(I),G(I),SA(I),GAM1(I),GAM2(I),Y1C(I),
     1Y2C(I),SUMYC(I),GE(I)
 4117 CONTINUE
      WRITE(NWR,516)
      DO 4116 I=1,NT
      WRITE(NWR,507)ROD(I),FI1(I),FI2(I),VMIX(I),VE(I),DPDX(I),STKOR(I)
 4116 CONTINUE
      WRITE(NWR,518)
      WRITE(NWR,504)
      DO 85 I=1,NBPTS
      GE(I)=GINT(I)*T*8.3144
      WRITE(NWR,507)XEXP(I),PL(I),GINT(I),SAINT(I),GAM1L(I),GAM2L(I),
     1Y1CL(I),Y2CL(I),SUMYCL(I),GE(I)
 85   CONTINUE
      CALL SCALE(XGCALE,YGCALE,XEXP,GE,NBPTS,AARAY,NUMMT,1)
      CALL PLOT(AARAY,NUMMT,GTITLE,YGCALE,XGCALE,1)
      CALL ROMB(NMAX,C,B,MAT,NMAX,20)
      WRITE(NWR,532) MAT(1,NMAX)
      WRITE(NWR,516)
      DO 86 I=1,NBPTS
      WRITE(NWR,507)XEXP(I),FI1L(I),FI2L(I),VMIXL(I),VEL(I),DPDXL(I),
     1STKORL(I)
 86   CONTINUE
      WRITE(NWR,519)
      WRITE(NWR,509)
      SQ=0.
      DELY=0.
      SSQ=0.
      DELP=0.
      DDELP=0.
      DO 100 I=1,NBPTS
      XR=XEXP(I)
      CALL PCAL(PS(2),PS(1),XR,PP,KP1)
      PCA(I)=PP
      DP=PCA(I)-PEXP(I)
      PINT=PEXP(I)
      SUMY=Y1CL(I)+Y2CL(I)
      DY=Y1CL(I)-YEXP(I)
      WRITE(NWR,507)XR,PINT,Y1CL(I),YEXP(I),DY,Y2CL(I),SUMY,PCA(I),DP
      SQ=SQ+DY**2
      DELY=DELY+DABS(DY)
      SSQ=SSQ+DP*DP
      DELP=DELP+DABS(DP)
      DDELP=DDELP+DABS(DP)/PEXP(I)
 100  CONTINUE
      DELYS=DSQRT(SQ/(DFLOAT(NBPTS-3)))
      DELYA=DELY/(DFLOAT(NBPTS-2))
      DELPS=DSQRT(SSQ/(DFLOAT(NBPTS-3)))
```

```
      DELPA=DELP/(DFLOAT(NBPTS-2))
      DDELP=DDELP/(FLOAT(N-2))
      WRITE(NWR,510) SQ,DELTS,DELTA
      WRITE(NWR,524) SSQ,DELPS,DELPA,DDELP
400   CONTINUE
500   CONTINUE
      GO TO 600
      END
```

PROGRAM 3 (P-R)

(high pressure systems)
(asymmetric convention)
(Peng-Robinson Equation of State)

PROGRAM 3 (P-R) requires the following sections of subroutines (see Table 1):

1) MAIN SECTION

2) SUBSECTION ONE.

```
C
C      PROGRAM CTLG3 CALCULATES VAPOR PHASE MOLEFRACTIONS FOR BINARY
C      SYSTEMS UNDER HIGH PRESSURE USING THE ASYMMETRIC CONVENTION FOR
C      NORMALIZATION OF ACTIVITY COEFFICIENTS.
C
       DOUBLE PRECISION A(25,25),SA(25),P(25),G(25),ROD(25)
       DOUBLE PRECISION FA(25),FB(25),FC(25),V1(25),XINT(25),Y1C(25),
      1Y2C(25),FD(25),GAM1(25),GAM2(25),SUMYC(25),RDOT(25),FPP1(25),
      2FPP2(25),FI1(25),FI2(25),YANC(25),FP1(25),FP2(25),DPDX(25),
      3VMIX(25),VE(25),STKOR(25),FE(25),FF(25),XEXP(25),YEXP(25),
      4PEXP(25),DELX(25),WA1(25),WA2(25),WA3(25),WA4(25)
       DOUBLE PRECISION ALFA,BETA,XI,PI,D,DELTA,X1,PX,DDX,HENRY,XR,SQ,
      1DELY,DELYA,DY,YINT1,YINT2,DELYS
       DOUBLE PRECISION XDOT(25),X2,X4
       DOUBLE PRECISION AA(21),PP
       DOUBLE PRECISION PCA(25),DP,SSQ,DELP,DELPA,DELPS
       DOUBLE PRECISION DABS,DEXP,DFLOAT,DSQRT
       DOUBLE PRECISION TL(25)
       DOUBLE PRECISION PL(25),DPDXL(25),VMIXL(25),VEL(25),STKORL(25),
      1FP1L(25),FP2L(25),FI1L(25),FI2L(25),GAM1L(25),GAM2L(25),Y1CL(25),
      2Y2CL(25),SUMYCL(25)
       DOUBLE PRECISION GINT(25),SAINT(25)
       DOUBLE PRECISION FPP1L(25),FPP2L(25)
       DOUBLE PRECISION SROOT(25)
       DOUBLE PRECISION WORK(25),GIN,SAIN
       DOUBLE PRECISION MAT(20,20),C,B(25),UNSY,XC
       DOUBLE PRECISION ARG(25),VAL(25)
       DOUBLE PRECISION WILL(50),WILLRY
       DOUBLE PRECISION DDELP
       DIMENSION TEXT(12),ZC(5)
       DIMENSION XL(2),YL(2)
       DIMENSION VPURE(2),VPART(2),TCT(2,2),TC(2),ANY(2,2),TAU(2,2),
      1ACEN(2),VC(2),PC(2),AP(2,2),BP(2),Y(2),X(2),FUGCE
      2(2),FUGS(2),VOL(2)
       COMMON/DIV/A,SA,P,G,ROD,N,NT
       COMMON/SEG/ZC
       COMMON/BEG/WORK,ARG,VAL,PSAT2,KP1,VPURE,ACEN,TCT,VC,T,TAU,
      1       ANY
       COMMON/LEG/AA
       COMMON/BEG1/DELTA,XEXP
       DATA ALFA,BETA/0.D 00,0.D 00/
       DATA R/82.0567/
       DATA N0,N1/1,1/
  501  FORMAT(1H1,'CONSISTENCY TEST USING ORTHOGONAL COLLOCATION  -
      1NUMBER OF INTERNAL POINTS',I5)
  502  FORMAT(1H0,'COLLOCATION POINTS'/,1X,10F10.6)
  504  FORMAT(1H0,'      X',10X,'P',7X,'GE/RT',5X,'GOOT',6X,'GAMMA1',4X,
      1'GAMMA2',5X,'Y1',8X,'Y2',6X,'SUM CORR',4X,'GE J/MOLE')
  505  FORMAT(1H0,'NUMBER OF BINARY POINTS',I5,5X,'AT THE ISOTHERM',F10
      1.2,5X,'TEMPERATURE IN DEG K')
  506  FORMAT(1H0,'T',F10.4,4X,'PS',F10.4,4X,'VOL',2F10.4,4X,//,1X,
      1'FISAT',2F10.4,4X,'FRESAT',2F10.4)
  507  FORMAT(1X,11F10.4,F14.4)
  508  FORMAT(I2)
  509  FORMAT(1H0,'     X',8X,'P',10X,'Y1',7X,'Y1EXP',5X,'DY',8X,'Y2',
      18X,'SUMY',6X,'PCAL',7X,'DP')
  510  FORMAT(1H0,' SUM OF SQUARES OF DELTA Y  ',F16.7,//,'  VARIANCE OF
      1DELTA Y  ',F10.4,'   ARITHMETIC MEAN OF DELTA Y  ',F10.4,//,'
      1CALCULATED EXCLUDING GIVEN END POINTS')
  511  FORMAT(5I2)
  512  FORMAT(F8.3,2F8.4,F8.3,8F6.4)
  513  FORMAT(1H0,'ITERATION NUMBER GREATER THAN 100')
  514  FORMAT(1H0,1X,'NUMBER OF ITERATIONS IN G',I5)
  515  FORMAT(1H0,' THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION
      1PROCEDURE IS OF THE TYPE ALPA  = ',F10.4,'   BETA  = ',F10.4,//)
  516  FORMAT(1H0,'HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION',
      1F10.4)
  517  FORMAT(1H0,'     XEXP       YEXP       PEXP')
  518  FORMAT(1H0,'SOLUTION AT THE DATA POINTS')
  519  FORMAT(1H0,'CALCULATED VALUES OF Y1')
  520  FORMAT(3I1)
```

```
  521  FORMAT(1H0,'     X       FUGCF1       FUGCF2     VMIX      VE
     1DFDX      CORR TO GOOT')
  522  FORMAT(I2)
  523  FORMAT(12A4)
  524  FORMAT(1H1,'EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR
     1THE BINARY SYSTEM    ',12A4,/,120(1H*))
  525  FORMAT(1H0,' SUM OF SQUARES OF DELTA P  ',F16.7,//,'  VARIANCE
     1OF DELTA P  ',F10.4,'      ARITHMETIC MEAN OF DELTA P  ',F10.4,
     2//,' ARITHMETIC MEAN OF DELTA P/P  ',F14.6,//1X,' CALCULATED
     3EXCLUDING GIVEN END POINTS')
  526  FORMAT(3F10.5)
  527  FORMAT(1H0,'SOLUTION AT THE COLLOCATION POINTS')
  532  FORMAT(1H1,'CONSISTENCY TEST BY REPEATED HALVING OF TRAPZOIDAL
     1RULE WITH ROMBERG INTEGRATION')
  533  FORMAT(1H1,15X,'CONSTANT=  ',E15.6)
C
C      LOGICAL UNIT NUMBERS
C
       NRD=5
       NWR=6
  600  READ(NRD,511)NJOB,NKOMP,NSTP1,NSTP2
       IF(NJOB.EQ.0) STOP
       READ(NRD,523) TEXT
       DO 500 LJC=1,NJOB
       READ(NRD,522)K
       READ(NRD,508) NBPTS
       READ(NRD,520)N11,N2,N3
       WRITE(NWR,524) TEXT
       WRITE(NWR,515) ALPA,BETA
       DO 5 I=1,NBPTS
       READ(NRD,512)PEXP(I),DU,DUM,TL(I),XEXP(I),DUMM,DUMMY,DM,YEXP(I),
     1DMU,DMMU,DMMUY
       T=TL(I)
  5    CONTINUE
       CALL PHROM(NKOMP,R,AP,BP,TCT,TC,ANY,TAU,ACEN,VC,PC,T,LJC)
       WRITE(6,*)AP,BP
C
C      N11    )
C      N2     ) IDENTIFICATION PARAMETERS, SEE TABLE BELOW
C      N3     )
C        P                V                    T
C       N11              N2                   N3
C
C   1   ATM            CC/MOL                  K
C   2   BAR            GRM/CC                  P
C   3   PISA          CUFT/LB.MOL              C
C   4 INCH.HG          LB/CUFT                 R
C   5  CM.HG           CUFT/LB
C   6  MM.HG              Z
C
       DO 9783 I=1,NBPTS
       GO TO (9992,9993,9994,9995,9996,99996),N11
  9993 PEXP(I)=PEXP(I)/1.01325
       GO TO 9992
  9994 PEXP(I)=PEXP(I)/14.696
       GO TO 9992
  9995 PEXP(I)=PEXP(I)*0.0334211
       GO TO 9992
  9996 PEXP(I)=PEXP(I)/76.0
       GO TO 9992
 99996 PEXP(I)=PEXP(I)/760.
  9992 GO TO (9997,9998,9999,99990),N3
  9998 T=(TL(I)+459.67)/1.8
       GO TO 9997
  9999 T=TL(I)+273.15
       GO TO 9997
 99990 T=TL(I)/1.8
  9997 CONTINUE
  9783 CONTINUE
C
C      NORMISATION FACTOR
```

```
C
      DELTA=XEXP(NBPTS)
      KP1=K+1
      WRITE(NWR,505) NBPTS,T
      DO 250 I=1,NBPTS
  250 XDOT(I)=XEXP(I)/DELTA
      CALL ALFIT(XDOT,PEXP,NBPTS,K)
      WRITE(NWR,517)
      DO 8 I=1,NBPTS
      WRITE(NWR,526) XEXP(I),YEXP(I),PEXP(I)
    8 CONTINUE
      PSAT2=PEXP(1)
C
C     CALCULATION OF PURE COMPONENT PROPERTIES AND INITIAL GUESS OF
C     HENRYS CONSTANT
C
      X(1)=0.
      X(2)=1.
      Y(1)=0.
      Y(2)=1.
      CALL GMVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      VOL(2)=V
      CALL PRVOL(NKOMP,V,Z,X,Y,PSAT2,T,AP,BP,R,-1)
      CALL PRFUG(Y,PSAT2,T,V,R,FUGCE,AP,BP,NKOMP)
      FUGS(2)=FUGCE(2)*PSAT2
      X(1)=0.05
      X(2)=1.-X(1)
      XI=X(1)
      CALL PCALA(PSAT2,XI,PI,KP1)
      PIE=PI
      CALL PRVOL(NKOMP,VL,Z,X,Y,PIE,T,AP,BP,R,1)
      CALL PMRPV(NKOMP,X,AP,BP,R,T,VL,VPART)
      WRITE(6,*)VL,VPART
      Y(2)=X(2)*FUGS(2)/PI
      Y(1)=1.-Y(2)
      CALL PRVOL(NKOMP,VG,Z,X,Y,PIE,T,AP,BP,R,-1)
      CALL PRFUG(Y,PIE,T,VG,R,FUGCE,AP,BP,NKOMP)
      FUGS(1)=(PI-X(2)*FUGS(2)/FUGCE(2)*DEXP(VOL(2)*(PI-PSAT2)/(R*T)))*
     1FUGCE(1)/XI*DEXP(-VPART(1)*(PI-PSAT2)/(R*T))
      FI2(1)=FUGS(2)/PSAT2
      FPP1(1)=0.
      FPP2(1)=PSAT2
      X(1)=0.
      X(2)=1.-X(1)
      CALL GMVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      CALL PMRPV(NKOMP,X,AP,BP,R,T,V,VPART)
      WRITE(6,*)V,VPART
      VPURE(1)=VPART(1)
      VPURE(2)=V
      WRITE(NWR,506) T,PSAT2,VPURE(1),VPURE(2),FUGCE(1),FI2(1),FUGS(1),
     1FUGS(2)
      DO 400 N=NSTP1,NSTP2
C
C     GENERATION OF COLLOCATION CONSTANTS
C
      WRITE(NWR,501) N
      NT=N+N0+N1
      CALL JCOBI(25,N,N0,N1,ALFA,BETA,FA,FB,FC,ROOT)
      WRITE(NWR,502) (ROOT(I),I=1,NT)
      DO 12 I=1,NT
      CALL DFOPR(25,N,N0,N1,I,1,FA,FB,FC,ROOT,V1)
      DO 12 J=1,NT
      A(I,J)=V1(J)
   12 CONTINUE
      DO 19 I=1,NT
      ROD(I)=DELTA*ROOT(I)**.5
   19 CONTINUE
C
C     THERMODYNAMIC PROPERTIES AT THE COLLOCATION POINTS
C
      DO 22 I=1,NT
```

```
4001 CONTINUE
     DO 40 I=1,NT
     GAM1(I)=DEXP(G(I)+(1.-ROD(I))*(SA(I)-STKOR(I)))
     GAM2(I)=DEXP(G(I)-ROD(I)*(SA(I)-STKOR(I)))
     Y1C(I)=GAM1(I)*ROD(I)*FPP1(I)/P(I)
     Y2C(I)=GAM2(I)*(1.-ROD(I))*FPP2(I)/P(I)
     SUMYC(I)=Y1C(I)+Y2C(I)
40   CONTINUE
C
C    LAGRANGE INTERPOLATION
C
     DO 411 I=1,NBPTS
     XR=XEXP(I)
     CALL INTP(XR,ROD,G,WORK,NT,1,ARG,VAL,NT)
     CALL INTDAL(XR,ARG,VAL,GIN,NT,1.D-06,IER)
     GINT(I)=GIN
411  CONTINUE
     DO 412 I=1,NBPTS
     XR=XEXP(I)
     CALL INTP(XR,ROD,SA,WORK,NT,1,ARG,VAL,NT)
     CALL INTDAL(XR,ARG,VAL,SAIN,NT,1.D-06,IER)
     SAINT(I)=SAIN
412  CONTINUE
     DO 401 I=1,NBPTS
     GAM1L(I)=DEXP(GINT(I)+(1.0-XEXP(I))*(SAINT(I)-STKORL(I)))
     GAM2L(I)=DEXP(GINT(I)-XEXP(I)*(SAINT(I)-STKORL(I)))
     Y1CL(I)=GAM1L(I)*XEXP(I)*FPP1L(I)/PL(I)
     Y2CL(I)=GAM2L(I)*(1.-XEXP(I))*FPP2L(I)/PL(I)
     SUMYCL(I)=Y1CL(I)+Y2CL(I)
     Y1CL(I)=Y1CL(I)/SUMYCL(I)
     Y2CL(I)=Y2CL(I)/SUMYCL(I)
     B(I)=DLOG(GAM1L(I)/GAM2L(I))
401  CONTINUE
     C=DLOG(GAM1L(2)/GAM2L(2))
C
C    TEST FOR VARIATION IN Y1CAL
C
     DO 60 I=1,NT
     IF(DABS(Y1C(I)-YANC(I))-5.D-05) 60,65,65
60   CONTINUE
     GO TO 80
C
C    NEW VALUES OF THE FUGACITY COEFFICIENTS
C
65   DO 68 I=1,NT
     YANC(I)=Y1C(I)
     Y(1)=Y1C(I)
     Y(2)=Y2C(I)
     PR=P(I)
     CALL PRVOL(NKOMP,V,Z,X,Y,PR,T,AP,BP,R,-1)
     CALL PRFUG(Y,PR,T,V,R,FUGCE,AP,BP,NKOMP)
     FI1(I)=FUGCE(1)
     FI2(I)=FUGCE(2)
68   CONTINUE
     DO 6815 I=1,NBPTS
     XL(1)=XEXP(I)
     XL(2)=1.-XL(1)
     YL(1)=Y1CL(I)
     YL(2)=Y2CL(I)
     PR=PL(I)
     CALL PRVOL(NKOMP,V,Z,XL,YL,PR,T,AP,BP,R,-1)
     CALL PRFUG(YL,PR,T,V,R,FUGCE,AP,BP,NKOMP)
     FI1L(I)=FUGCE(1)
     FI2L(I)=FUGCE(2)
6815 CONTINUE
C
C    CALCULATION OF HENRYS CONSTANT
C
     DO 70 I=2,NT
     FD(I)=Y1C(I)*FI1(I)*P(I)/ROD(I)
70   CONTINUE
```

```
      NHENR=NHENR+1
      IF(NHENR-2) 28,28,72
   72 CALL JCOBI(25,N,0,0,ALFA,BETA,FE,FB,FC,FF)
      HENRY=0.
      XR=0.
      CALL INTRP(25,N,XR,FF,FE,XINT)
      DO 74 I=1,N
      J=I+1
      HENRY=HENRY+XINT(I)*FD(J)
   74 CONTINUE
      WILL(NY)=HENRY
      IF(NY.LT.7) GO TO 873
      HENRY=(WILL(NY)+WILL(NY-1)+WILL(NY-2)+WILL(NY-3)+WILL(NY-4))/5.
      WILLRY=0.001*HENRY
      IF(DABS(HENRY-WILL(NY)).LE.WILLRY) GO TO 80
  873 FUGS(1)=HENRY
      DO 75 I=1,NT
      FP1(I)=FUGS(1)*DEXP(VPART(1)/(R*T)*(P(I)-PSAT2))
   75 CONTINUE
      WRITE(NWR,516) HENRY
      IF(NY.GT.50) GO TO 80
      DO 681 I=1,NBPTS
      FP1L(I)=FUGS(1)*DEXP(VPART(1)/(R*T)*(PL(I)-PSAT2))
  681 CONTINUE
      GO TO 28
   80 CONTINUE
C
C     PRINTS THE RESULTS
C
      WRITE(NWR,527)
      WRITE(NWR,504)
      DO 8557 I=1,NT
      GE=G(I)*T*8.3144
      WRITE(NWR,507)ROD(I),P(I),G(I),SA(I),GAM1(I),GAM2(I),Y1C(I),
     1Y2C(I),SUMYC(I),GE
 8557 CONTINUE
      WRITE(NWR,521)
      DO 8667 I=1,NT
      WRITE(NWR,507)ROD(I),FI1(I),FI2(I),VMIX(I),VE(I),DPDX(I),
     1STKOR(I)
 8667 CONTINUE
      WRITE(NWR,518)
      WRITE(NWR,504)
      DO 85 I=1,NBPTS
      GE=GINT(I)*T*8.3144
      WRITE(NWR,507)XEXP(I),PL(I),GINT(I),SAINT(I),GAM1L(I),GAM2L(I),
     1Y1CL(I),Y2CL(I),SUMYCL(I),GE
   85 CONTINUE
      WRITE(NWR,521)
      DO 86 I=1,NBPTS
      WRITE(NWR,507)XEXP(I),FI1L(I),FI2L(I),VMIXL(I),VEL(I),DPDXL(I),
     1STKORL(I)
   86 CONTINUE
      WRITE(NWR,532)
      IC=IEXP(2)
      DO 57 I=3,NBPTS
      UNSY=B(I)
      CALL ROMB(6,C,UNSY,MAT,6,20,IC,I)
      WRITE(NWR,533) MAT(1,6)
   57 CONTINUE
      WRITE(NWR,519)
      WRITE(NWR,509)
      SQ=0.
      DELY=0.
      SSQ=0.
      DELP=0.
      DDELP=0.
      DO 100 I=1,NBPTS
      IR=IEXP(I)/DELTA
      I8=IEXP(I)/DELTA
      CALL PCALA(PSAT2,I8,PP,KP1)
```

```
      PCA(I)=PP
      DP=PCA(I)-PEXP(I)
      SUMY=Y1CL(I)+Y2CL(I)
      DY=Y1CL(I)-YEXP(I)
      WRITE(NWR,507)XEXP(I),PEXP(I),Y1CL(I),YEXP(I),DY,Y2CL(I),SUMY,
     1PCA(I),DP
      SQ=SQ+DY**2
      DELY=DELY+DABS(DY)
      SSQ=SSQ+DP*DP
      DELP=DELP+DABS(DP)
      DDELP=DDELP+DABS(DP)/PEXP(I)
100   CONTINUE
      DELYS=DSQRT(SQ/(DFLOAT(NBPTS-2)))
      DELYA=DELY/(DFLOAT(NBPTS-1))
      DELPS=DSQRT(SSQ/(DFLOAT(NBPTS-2)))
      DELPA=DELP/(DFLOAT(NBPTS-1))
      DDELP=DDELP/(FLOAT(N-2))
      WRITE(NWR,510) SQ,DELYS,DELYA
      WRITE(NWR,525) SSQ,DELPS,DELPA,DDELP
400   CONTINUE
500   CONTINUE
      GO TO 600
      END
```

PROGRAM 4

(Peng-Robinson interaction parameter)

PROGRAM 4 requires the following sections of subroutines (see Table 1):

1) MAIN SECTION,

2) SUBSECTION TWO.

```
C
C     PROGRAM CTLG3 CALCULATES VAPOR PHASE MOLEFRACTIONS FOR BINARY
C     SYSTEMS UNDER HIGH PRESSURE USING THE ASYMMETRIC CONVENTION FOR
C     NORMALIZATION OF ACTIVITY COEFFICIENTS.
C
      DOUBLE PRECISION A(25,25),SA(25),P(25),G(25),ROD(25)
      DOUBLE PRECISION FA(25),FB(25),FC(25),Y1(25),XINT(25),Y1C(25),
     1Y2C(25),FD(25),GAM1(25),GAM2(25),SUMYC(25),ROOT(25),FPP1(25),
     2FPP2(25),FI1(25),FI2(25),YANC(25),FP1(25),FP2(25),DPDX(25),
     3VMIX(25),VE(25),STKOR(25),FE(25),FF(25),XEXP(25),YEXP(25),
     4PEXP(25),DELX(25),WA1(25),WA2(25),WA3(25),WA4(25)
      DOUBLE PRECISION ALFA,BETA,XI,PI,D,DELTA,X1,PX,DDX,HENRY,XB,SQ,
     1DELY,DELYA,DY,YINT1,YINT2,DELIS
      DOUBLE PRECISION XDOT(25),Y2,X4
      DOUBLE PRECISION AA(21),PP
      DOUBLE PRECISION PCA(25),DP,SSQ,DELP,DELPA,DELPS
      DOUBLE PRECISION DABS,DEXP,DFLOAT,DSQRT
      DOUBLE PRECISION TL(25)
      DOUBLE PRECISION PL(25),DPDXL(25),VMIXL(25),VEL(25),STKORL(25),
     1FP1L(25),FP2L(25),FI1L(25),FI2L(25),GAM1L(25),GAM2L(25),Y1CL(25),
     2Y2CL(25),SUMYCL(25)
      DOUBLE PRECISION GINT(25),SAINT(25)
      DOUBLE PRECISION FPP1L(25),FPP2L(25)
      DOUBLE PRECISION SROOT(25)
      DOUBLE PRECISION WORK(25),GIN,SAIN
      DOUBLE PRECISION ARG(25),VAL(25)
      DOUBLE PRECISION WILL(50),WILLBY
      DOUBLE PRECISION DDELP
      DIMENSION TEXT(12)
      DIMENSION IL(2),IL(2)
      DIMENSION VPURE(2),VPART(2),TCT(2,2),TC(2),ANY(2,2),TAU(2,2),
     1ACEN(2),VC(2),PC(2),AL(2,2),BL(2),AG(2,2),BG(2),Y(2),X(2),FUGCE
     2(2),FUGS(2),VOL(2)
      COMMON/DIV/A,SA,P,G,ROD,N,NT
      COMMON/LEG/AA
      DATA ALFA,BETA/0.D 00,0.D 00/
      DATA R/82.0567/
      DATA N0,N1/1,1/
  501 FORMAT(1H1,'CONSISTENCY TEST USING ORTHOGONAL COLLOCATION  -
     1NUMBER OF INTERNAL POINTS',I5)
  502 FORMAT(1HO,'COLLOCATION POINTS'/,1X,10F10.6)
  504 FORMAT(1HO,'      X',10X,'P',7X,'GE/RT',5X,'GOOT',6X,'GAMMA1',4X,
     1'GAMMA2',5X,'Y1',8X,'Y2',6X,'SUM CORR',4X,'GE J/MOLE')
  505 FORMAT(1HO,'NUMBER OF BINARY POINTS',I5,5X,'AT THE ISOTHERM',F10
     1.2,5X,'TEMPERATURE IN DEG K')
  506 FORMAT(1HO,'T',F10.4,4X,'PS',F10.4,4X,'VOL',2F10.4,4X,//,1X,
     1'PISAT',2F10.4,4X,'FREESAT',2F10.4)
  507 FORMAT(1X,11F10.4,F14.4)
  508 FORMAT(I2)
  509 FORMAT(1HO,'      X',9X,'P',10X,'Y1',7X,'Y1EXP',5X,'DY',8X,'Y2',
     18X,'SUM',6X,'PCAL',7X,'DP')
  510 FORMAT(1HO,' SUM OF SQUARES OF DELTA Y  ',F16.7,//,'  VARIANCE OF
     1DELTA Y  ',F10.4,'   ARITHMETIC MEAN OF DELTA Y  ',F10.4,//,'
     1CALCULATED EXCLUDING GIVEN END POINTS')
  511 FORMAT(5I2)
  512 FORMAT(F8.3,2F8.4,F8.3,8F6.4)
  513 FORMAT(1HO,'ITERATION NUMBER GREATER THAN 100')
  514 FORMAT(1HO,1X,'NUMBER OF ITERATIONS IN G',I5)
  515 FORMAT(1HO,' THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION
     1PROCEDURE IS OF THE TYPE ALFA  = ',F10.4,'   BETA  = ',F10.4,//)
  516 FORMAT(1HO,'HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION',
     1F10.4)
  517 FORMAT(1HO,'    XEXP      YEXP      PEXP')
  518 FORMAT(1HO,'SOLUTION AT THE DATA POINTS')
  519 FORMAT(1HO,'CALCULATED VALUES OF Y1')
  520 FORMAT(3I1)
  521 FORMAT(1HO,'    X      FUGCF1      FUGCF2     VMIX      VE
     1DPDX      CORR TO GOOT')
  522 FORMAT(I2)
  523 FORMAT(12A4)
  524 FORMAT(1H1,'EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR
```

```
     1THE BINARY SYSTEM   ',12A4,/,120(1H*))
  525  FORMAT(1H0,' SUM OF SQUARES OF DELTA P  ',F16.7,//,'  VARIANCE
     1OF DELTA P  ',F10.4,'     ARITHMETIC MEAN OF DELTA P  ',F10.4,
     2//,' ARITHMETIC MEAN OF DELTA P/P  ',F14.6,//1X,' CALCULATED
     3EXCLUDING GIVEN END POINTS')
  526  FORMAT(3F10.5)
  527  FORMAT(1H0,'SOLUTION AT THE COLLOCATION POINTS')
C
C      LOGICAL UNIT NUMBERS
C
       NRD=5
       NWR=6
  600  READ(NRD,511)NJOB,NKOMP,NSTP1,NSTP2
       IF(NJOB.EQ.0) STOP
       READ(NRD,523) TEXT
       DO 500 LJC=1,NJOB
       READ(NRD,522)K
       READ(NRD,508) NBPTS
       READ(NRD,520)N11,N2,N3
       WRITE(NWR,524) TEXT
       WRITE(NWR,515) ALFA,BETA
       DO 5 I=1,NBPTS
       READ(NRD,512)PEXP(I),DU,DUM,TL(I),XEXP(I),DUMM,DUMMY,DM,YEXP(I),
     1DMU,DMMU,DMMUY
       T=TL(I)
  5    CONTINUE
       CALL REKON(NKOMP,R,AL,AG,BL,BG,TCT,TC,ANY,TAU,ACEN,VC,PC,P,LJC)
C
C      N11     )
C      N2      ) IDENTIFICATION PARAMETERS, SEE TABLE BELOW
C      N3      )
C        P                 T                  T
C       N11               N2                 N3
C
C  1    ATM             CC/MOL               R
C  2    BAR             GRM/CC               P
C  3    PISA           CUFT/LB.MOL           C
C  4 INCH.HG            LB/CUFT              R
C  5  CM.HG             CUFT/LB
C  6  MM.HG               Z
C
       DO 9783 I=1,NBPTS
       GO TO (9992,9993,9994,9995,9996,99996),N11
  9993 PEXP(I)=PEXP(I)/1.01325
       GO TO 9992
  9994 PEXP(I)=PEXP(I)/14.696
       GO TO 9992
  9995 PEXP(I)=PEXP(I)*0.0338211
       GO TO 9992
  9996 PEXP(I)=PEXP(I)/76.0
       GO TO 9992
 99996 PEXP(I)=PEXP(I)/760.
  9992 GO TO (9997,9998,9999,99990),N3
  9998 T=(TL(I)+459.67)/1.8
       GO TO 9997
  9999 T=TL(I)+273.15
       GO TO 9997
 99990 T=TL(I)/1.8
  9997 CONTINUE
  9783 CONTINUE
C
C      NORMISATION FACTOR
C
       DELTA=XEXP(NBPTS)
       KP1=K+1
       WRITE(NWR,505) NBPTS,T
       DO 250 I=1,NBPTS
  250  XDOT(I)=XEXP(I)/DELTA
       CALL ALFIT(XDOT,PEXP,NBPTS,K)
       WRITE(NWR,517)
       DO 8 I=1,NBPTS
```

```
      WRITE(NWR,526) XEXP(I),YEXP(I),PEXP(I)
    8 CONTINUE
      PSAT2=PEXP(1)
C
C     CALCULATION OF PURE COMPONENT PROPERTIES AND INITIAL GUESS OF
C     HENRYS CONSTANT
C
      X(1)=0.
      X(2)=1.
      Y(1)=0.
      Y(2)=1.
      CALL GMVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      VOL(2)=V
      CALL RKVOL(NKOMP,V,Z,X,Y,PSAT2,T,AL,AG,BL,BG,R,-1)
      CALL RKFUG(Y,PSAT2,T,V,R,FUGCE,AG,BG,NKOMP)
      FUGS(2)=FUGCE(2)*PSAT2
      X(1)=0.05
      X(2)=1.-X(1)
      XI=X(1)
      CALL PCALA(PSAT2,XI,PI,KP1)
      PIE=PI
      CALL RKVOL(NKOMP,VL,Z,X,Y,PIE,T,AL,AG,BL,BG,R,1)
      CALL RDKPV(NKOMP,X,AL,BL,R,T,VL,VPART)
      Y(2)=X(2)*FUGS(2)/PI
      Y(1)=1.-Y(2)
      CALL RKVOL(NKOMP,VG,Z,X,Y,PIE,T,AL,AG,BL,BG,R,-1)
      CALL RKFUG(Y,PIE,T,VG,R,FUGCE,AG,BG,NKOMP)
      FUGS(1)=(PI-X(2)*FUGS(2)/FUGCE(2)*DEXP(VOL(2)*(PI-PSAT2)/(R*T)))*
     1FUGCE(1)/XI*DEXP(-VPART(1)*(PI-PSAT2)/(R*T))
      FI2(1)=FUGS(2)/PSAT2
      FPP1(1)=0.
      FPP2(1)=PSAT2
      X(1)=0.
      X(2)=1.-X(1)
      CALL GMVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      CALL RDKPV(NKOMP,X,AL,BL,R,T,V,VPART)
      VPURE(1)=VPART(1)
      VPURE(2)=V
      WRITE(NWR,506) T,PSAT2,VPURE(1),VPURE(2),FUGCE(1),FI2(1),FUGS(1),
     1FUGS(2)
      DO 400 N=NSTP1,NSTP2
C
C     GENERATION OF COLLOCATION CONSTANTS
C
      WRITE(NWR,501) N
      NT=N+NO+N1
      CALL JCOBI(25,N,NO,N1,ALPA,BETA,PA,PB,PC,ROOT)
      WRITE(NWR,502) (ROOT(I),I=1,NT)
      DO 12 I=1,NT
      CALL DPOPR(25,N,NO,N1,I,1,PA,PB,PC,ROOT,V1)
      DO 12 J=1,NT
      A(I,J)=V1(J)
   12 CONTINUE
      DO 19 I=1,NT
      ROD(I)=DELTA*ROOT(I)**.5
   19 CONTINUE
C
C     THERMODYNAMIC PROPERTIES AT THE COLLOCATION POINTS
C
      DO 22 I=1,NT
      X1=ROD(I)
      X2=ROOT(I)**.5
      CALL PCALA(PSAT2,X2,PI,KP1)
      CALL DPXA(PSAT2,KP1,DDX,X2)
      P(I)=PX
      DPDX(I)=DDX
      X(1)=X1
      X(2)=1.-X(1)
      CALL GMVOL(NKOMP,X,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      VMIX(I)=V
      VE(I)=VMIX(I)-X(1)*VPURE(1)-X(2)*VPURE(2)
```

```
      STKOR(I)=VE(I)*DPDX(I)/(R*T)
      FP1(I)=FUGS(1)*DEXP(VPART(1)/(R*T)*(P(I)-PSAT2))
      FP2(I)=FUGS(2)*DEXP(VOL(2)/(R*T)*(P(I)-PSAT2))
      IANC(I)=0.5
   22 CONTINUE
C
C     THERMODYNAMIC PROPERTIES AT THE DATA POINTS
C
      DO 227 I=1,NBPTS
      X1=XEXP(I)
      X2=XEXP(I)/DELTA
      CALL PCALA(PSAT2,X2,PX,KP1)
      CALL DPXA(PSAT2,KP1,DDX,X2)
      PL(I)=PX
      DPDXL(I)=DDX
      XL(1)=X1
      XL(2)=1.-XL(1)
      CALL GEVOL(NKOMP,XL,VC,ACEN,TCT,T,TAU,ANY,TC,V)
      VMIXL(I)=V
      VEL(I)=VMIXL(I)-XL(1)*VPURE(1)-XL(2)*VPURE(2)
      STKORL(I)=VEL(I)*DPDXL(I)/(R*T)
      FP1L(I)=FUGS(1)*DEXP(VPART(1)/(R*T)*(PL(I)-PSAT2))
      FP2L(I)=FUGS(2)*DEXP(VOL(2)/(R*T)*(PL(I)-PSAT2))
  227 CONTINUE
C
C     INITIAL VALUES OF GE/RT AND FI
C
      DO 26 I=1,NT
      G(I)=0.
      FI1(I)=1.
      FI2(I)=1.
   26 CONTINUE
      NHERR=0
      NY=0
      FPP2L(1)=PSAT2
      DO 261 I=1,NBPTS
      FI1L(I)=1.
      FI2L(I)=1.
  261 CONTINUE
C
C     START ITERATION
C
   28 DO 30 I=2,NT
      FPP1(I)=FP1(I)/FI1(I)
      FPP2(I)=FP2(I)/FI2(I)
   30 CONTINUE
      DO 301 I=2,NBPTS
      FPP1L(I)=FP1L(I)/FI1L(I)
      FPP2L(I)=FP2L(I)/FI2L(I)
  301 CONTINUE
      NY=NY+1
      CALL GIBSA(FPP1,FPP2,STKOR,DELTA,ITER)
      IF(ITER-100) 33,32,32
   32 WRITE(NWR,513)
      DO 3377 I=1,NT
      SA(I)=0.1
      G(I)=0.01
 3377 CONTINUE
      GO TO 4001
   33 WRITE(NWR,514) ITER
 4001 CONTINUE
      DO 40 I=1,NT
      GAM1(I)=DEXP(G(I)*(1.-ROD(I))*(SA(I)-STKOR(I)))
      GAM2(I)=DEXP(G(I)-ROD(I)*(SA(I)-STKOR(I)))
      Y1C(I)=GAM1(I)*ROD(I)*FPP1(I)/P(I)
      Y2C(I)=GAM2(I)*(1.-ROD(I))*FPP2(I)/P(I)
      SUMYC(I)=Y1C(I)+Y2C(I)
   40 CONTINUE
C
C     LAGRANGE INTERPOLATION
C
```

```
      DO 411 I=1,NBPTS
      XR=XEXP(I)
      CALL INTP(XR,ROD,G,WORK,NT,1,ARG,VAL,NT)
      CALL INTDAL(XR,ARG,VAL,GIN,NT,1.D-06,IER)
      GINT(I)=GIN
  411 CONTINUE
      DO 412 I=1,NBPTS
      XR=XEXP(I)
      CALL INTP(XR,ROD,SA,WORK,NT,1,ARG,VAL,NT)
      CALL INTDAL(XR,ARG,VAL,SAIN,NT,1.D-06,IER)
      SAINT(I)=SAIN
  412 CONTINUE
      DO 401 I=1,NBPTS
      GAM1L(I)=DEXP(GINT(I)+(1.0-XEXP(I))*(SAINT(I)-STKORL(I)))
      GAM2L(I)=DEXP(GINT(I)-XEXP(I)*(SAINT(I)-STKORL(I)))
      Y1CL(I)=GAM1L(I)*XEXP(I)*PPP1L(I)/PL(I)
      Y2CL(I)=GAM2L(I)*(1.-XEXP(I))*PPP2L(I)/PL(I)
      SUMYCL(I)=Y1CL(I)+Y2CL(I)
      Y1CL(I)=Y1CL(I)/SUMYCL(I)
      Y2CL(I)=Y2CL(I)/SUMYCL(I)
  401 CONTINUE
C
C     TEST FOR VARIATION IN Y1CAL
C
      DO 60 I=1,NT
      IF(DABS(Y1C(I)-YANC(I))-5.D-05) 60,65,65
   60 CONTINUE
      GO TO 80
C
C     NEW VALUES OF THE FUGACITY COEFFICIENTS
C
   65 DO 68 I=1,NT
      YANC(I)=Y1C(I)
      Y(1)=Y1C(I)
      Y(2)=Y2C(I)
      PR=P(I)
      CALL RKVOL(NKONP,V,Z,X,Y,PR,T,AL,AG,BL,BG,R,-1)
      CALL RKFUG(Y,PR,T,V,R,FUGCE,AG,BG,NKONP)
      FI1(I)=FUGCE(1)
      FI2(I)=FUGCE(2)
   68 CONTINUE
      DO 6815 I=1,NBPTS
      XL(1)=XEXP(I)
      XL(2)=1.-XL(1)
      YL(1)=Y1CL(I)
      YL(2)=Y2CL(I)
      PR=PL(I)
      CALL RKVOL(NKONP,V,Z,XL,YL,PR,T,AL,AG,BL,BG,R,-1)
      CALL RKFUG(YL,PR,T,V,R,FUGCE,AG,BG,NKONP)
      FI1L(I)=FUGCE(1)
      FI2L(I)=FUGCE(2)
 6815 CONTINUE
C
C     CALCULATION OF HENERYS CONSTANT
C
      DO 70 I=2,NT
      FD(I)=Y1C(I)*FI1(I)*P(I)/ROD(I)
   70 CONTINUE
      NHENR=NHENR+1
      IF(NHENR-2) 28,28,72
   72 CALL JCOBI(25,N,0,0,ALPA,BETA,PR,PB,PC,PP)
      HENRY=0.
      XR=0.
      CALL INTRP(25,N,XR,PP,PB,XINT)
      DO 74 I=1,N
      J=I+1
      HENRY=HENRY+XINT(I)*FD(J)
   74 CONTINUE
      WILL(NT)=HENRY
      IF(NT.LT.7) GO TO 873
      HENRY=(WILL(NT)+WILL(NT-1)+WILL(NT-2)+WILL(NT-3)+WILL(NT-4))/5.
```

```
      WILLEY=0.001*HENRY
      IF(DABS(HENRY-WILL(NY)).LE.WILLEY) GO TO 80
  873 FUGS(1)=HENRY
      DO 75 I=1,NT
      PP1(I)=FUGS(1)*DEXP(VPART(1)/(R*T)*(P(I)-PSAT2))
   75 CONTINUE
      WRITE(NWR,516) HENRY
      IF(NY.GT.50) GO TO 80
      DO 681 I=1,NBPTS
      PP1L(I)=FUGS(1)*DEXP(VPART(1)/(R*T)*(PL(I)-PSAT2))
  681 CONTINUE
      GO TO 28
   80 CONTINUE
C
C     PRINTS THE RESULTS
C
      WRITE(NWR,527)
      WRITE(NWR,504)
      DO 8557 I=1,NT
      GE=G(I)*T*8.3144
      WRITE(NWR,507)ROD(I),P(I),G(I),SA(I),GAM1(I),GAM2(I),Y1C(I),
     1Y2C(I),SUMYC(I),GE
 8557 CONTINUE
      WRITE(NWR,521)
      DO 8667 I=1,NT
      WRITE(NWR,507)ROD(I),PI1(I),PI2(I),VMIX(I),VE(I),DPDX(I),
     1STKON(I)
 8667 CONTINUE
      WRITE(NWR,518)
      WRITE(NWR,504)
      DO 85 I=1,NBPTS
      GE=GINT(I)*T*8.3144
      WRITE(NWR,507)XEXP(I),PL(I),GINT(I),SAINT(I),GAM1L(I),GAM2L(I),
     1Y1CL(I),Y2CL(I),SUMYCL(I),GE
   85 CONTINUE
      WRITE(NWR,521)
      DO 86 I=1,NBPTS
      WRITE(NWR,507)XEXP(I),PI1L(I),PI2L(I),VMIXL(I),VEL(I),DPDXL(I),
     1STKORL(I)
   86 CONTINUE
      WRITE(NWR,519)
      WRITE(NWR,509)
      SQ=0.
      DELY=0.
      SSQ=0.
      DELP=0.
      DDELP=0.
      DO 100 I=1,NBPTS
      XR=XEXP(I)/DELTA
      X4=XEXP(I)/DELTA
      CALL PCALA(PSAT2,XR,PP,KP1)
      PCA(I)=PP
      DP=PCA(I)-PEXP(I)
      SUMY=Y1CL(I)+Y2CL(I)
      DY=Y1CL(I)-YEXP(I)
      WRITE(NWR,507)XEXP(I),PEXP(I),Y1CL(I),YEXP(I),DY,Y2CL(I),SUMY,
     1PCA(I),DP
      SQ=SQ+DY**2
      DELY=DELY+DABS(DY)
      SSQ=SSQ+DP*DP
      DELP=DELP+DABS(DP)
      DDELP=DDELP+DABS(DP)/PEXP(I)
  100 CONTINUE
      DELYS=DSQRT(SQ/(DFLOAT(NBPTS-2)))
      DELYA=DELY/(DFLOAT(NBPTS-1))
      DELPS=DSQRT(SSQ/(DFLOAT(NBPTS-2)))
      DELPA=DELP/(DFLOAT(NBPTS-1))
      DDELP=DDELP/(FLOAT(N-2))
      WRITE(NWR,510) SQ,DELYS,DELYA
      WRITE(NWR,525) SSQ,DELPS,DELPA,DDELP
  400 CONTINUE
```

```
500   CONTINUE
      GO TO 600
      END
```

PROGRAM 3 (R-K)

(high pressure systems)
(asymmetric convention)
(Soave-Redlich-Kwong Equation of State)

PROGRAM 3 (R-K) requires the following sections of subroutines (see Table 1):

1) MAIN SECTION,

2) SUBSECTION TWO.

```
C
C     PROGRAM4 ESTIMATES THE BINARY INTERACTION PARAMETER FOR THE
C     PENG-ROBINSON EQUATION OF STATE.
C
      DIMENSION XEXP(25),YEXP(25),PEXP(25),FUGCEL(2),FUGCEV(2),
     1          AP(2,2),BP(2),DEL(1000),TC(2),PC(2),ACEN(2),A(2),
     2          SUM(25),TEXT(12),C(2,2),TL(25),X(2),Y(2),CC(25),
     3           SUMMM(25)
      DATA R/82.0567/
  512 FORMAT(4F10.4)
  521 FORMAT(12A4)
  655 FORMAT(2E12.5)
  644 FORMAT(1H1,'  C(I,J)      DEVIATION')
  508 FORMAT(2I2)
  666 FORMAT(1H1,3X,'X(1)',5X,'Y(1)',6X,'KEXP1',5X,'KEXP2',5X,
     1       'KCAL1',5X,'KCAL2',5X,'SUM')
  522 FORMAT(1H1,'EXPERIMENTAL RESULTS AND CALCULATIOND CONSTANTS
     1FOR THE BINARY SISTEM  ',12A4,/120(1H*))
  100 FORMAT(3E12.5)
  101 FORMAT(1HO,'PC-TC-ACEN',4X,3E12.5)
  601 FORMAT(1HO,'THE INTERACTION PARAMETER VALUE USED IN THE
     1FOLLOWING TEST, C(I,J)= ',E10.3)
  602 FORMAT(7E10.3)
  603 FORMAT(1H1,'THE SUM OF DEVIATIONS FOR ALL DATA POINTS ARE,
     1 SUM= ',E10.3)
      NRD=5
      NWR =6
      READ(NRD,521) TEXT
      READ(NRD,508) NBPTS,NKOMP
      WRITE(NWR,522) TEXT
      DO 5 I=1,NBPTS
      READ(NRD,512) PEXP(I),TL(I),XEXP(I),YEXP(I)
      T=TL(I)
    5 CONTINUE
      READ(NRD,100) (PC(I),TC(I),ACEN(I),I=1,NKOMP)
      WRITE(NWR,101) (PC(I),TC(I),ACEN(I),I=1,NKOMP)
      DEL(1)=0.0
      DO 1 I=2,100
      DEL(I)=DEL(I-1)+0.001
    1 CONTINUE
      DO 200 K=1,100
      C(1,2)= 0.100+DEL(K)
      DO 6 I=1,NKOMP
      C(I,I)=0.0
      DO 6 J=1,NKOMP
      C(J,I)=C(I,J)
    6 CONTINUE
      DO 30 I=1,NKOMP
      TR=T/TC(I)
      AKK=0.3744+1.54226*ACEN(I)-0.26992*(ACEN(I)**2)
      ALP=(1.+AKK*(1.-(TR**0.5)))**2
      AC=0.45724*((R**2)*(TC(I)**2))/PC(I)
      A(I)=AC*ALP
      BP(I)=0.07780*R*TC(I)/PC(I)
   30 CONTINUE
      DO 40 I=1,NKOMP
      DO 40 J=1,NKOMP
      AP(I,J)=(1.-C(I,J))*(A(I)**0.5)*(A(J)**0.5)
   40 CONTINUE
      WRITE(NWR,601) C(1,2)
      WRITE(NWR,666)
      DO 99 L=1,NBPTS
      X(1)=XEXP(L)
      X(2)=1.-X(1)
      Y(1)=YEXP(L)
      Y(2)=1.-Y(1)
      P=PEXP(L)
C
C     CALCULATION OF THE LIQUID MOLAR VOLUME AND FUGACITY
C     COEFFICIENT.
C
```

```
      CALL PRVOL(NKOMP,VL,Z,X,Y,P,T,AP,BP,R,1)
      CALL PRFUG(X,P,T,VL,R,FUGCEL,AP,BP,NKOMP)
C
C     CALCULATION OF THE VAPOUR MOLAR VOLUME AND FUGACITY
C     COEFFICIENT.
C
      CALL PRVOL(NKOMP,VV,Z,X,Y,P,T,AP,BP,R,-1)
      CALL PRFUG(Y,P,T,VV,R,FUGCEV,AP,BP,NKOMP)
C
C     CALCULATION OF MINIMUM SUM OF ABSOLUTE DEVIATIONS OF
C     EQUILIBRIUM RATIOS.
C
      REXP1=Y(1)/X(1)
      REXP2=Y(2)/X(2)
      RCAL1=FUGCEL(1)/FUGCEV(1)
      RCAL2=FUGCEL(2)/FUGCEV(2)
      DRCAL1=ABS(RCAL1-REXP1)
      DRCAL2=ABS(RCAL2-REXP2)
      SUM(L)=DRCAL1+DRCAL2
      SUMM=SUM(L)
C
C     PRINTS RESULTS
C
      WRITE(NWR,602)X(1),Y(1),REXP1,REXP2,RCAL1,RCAL2,SUMM
   99 CONTINUE
      SUMM=0.0
      DO 9 I=1,NBPTS
      SUMM=SUMM+SUM(I)
    9 CONTINUE
      WRITE(NWR,603) SUMM
      SUMMM(K)=SUMM
      CC(K)=C(1,2)
  200 CONTINUE
      WRITE(NWR,644)
      DO 25 I=1,100
      WRITE(NWR,655) CC(I),SUMMM(I)
   25 CONTINUE
      STOP
      END
```

APPENDIX B

SAMPLE INPUT AND OUTPUT

Results of Run # 1 for the

CO_2-C_2H_6 System at 10°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 3 3
CARBON DIOXIDE(1)-ETHANE(2)
INTERPOLATED AND EXPERIMENTAL PRESSURE-VALUES(ATM) VS. MOLE FRACTIONS
GIBBS EXCESS FREE ENERGY(J/MOLE) VS. MOLE FRACTIONS
 2 6
15
111
 29.700                          0.0                    0.0
 31.610                          0.033                  0.061
 36.700                          0.128                  0.198
 40.15                           0.234                  0.315
 42.52                           0.311                  0.384
 45.57                           0.421                  0.480
 47.88                           0.542                  0.578
 49.10                           0.655                  0.666
 49.31                           0.711                  0.711
 49.29                           0.730                  0.727
 48.60                           0.833                  0.815
 48.99                           0.873                  0.852
 46.79                           0.928                  0.908
 45.78                           0.961                  0.947
 44.34                 283.150   1.0                     1.0
 0 0 0 0
```

The formated output is as follows:

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

THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION PROCEDURE HAS ALFA = 0. AND BETA = 0.

NUMBER OF BINARY DATAPOINTS 15

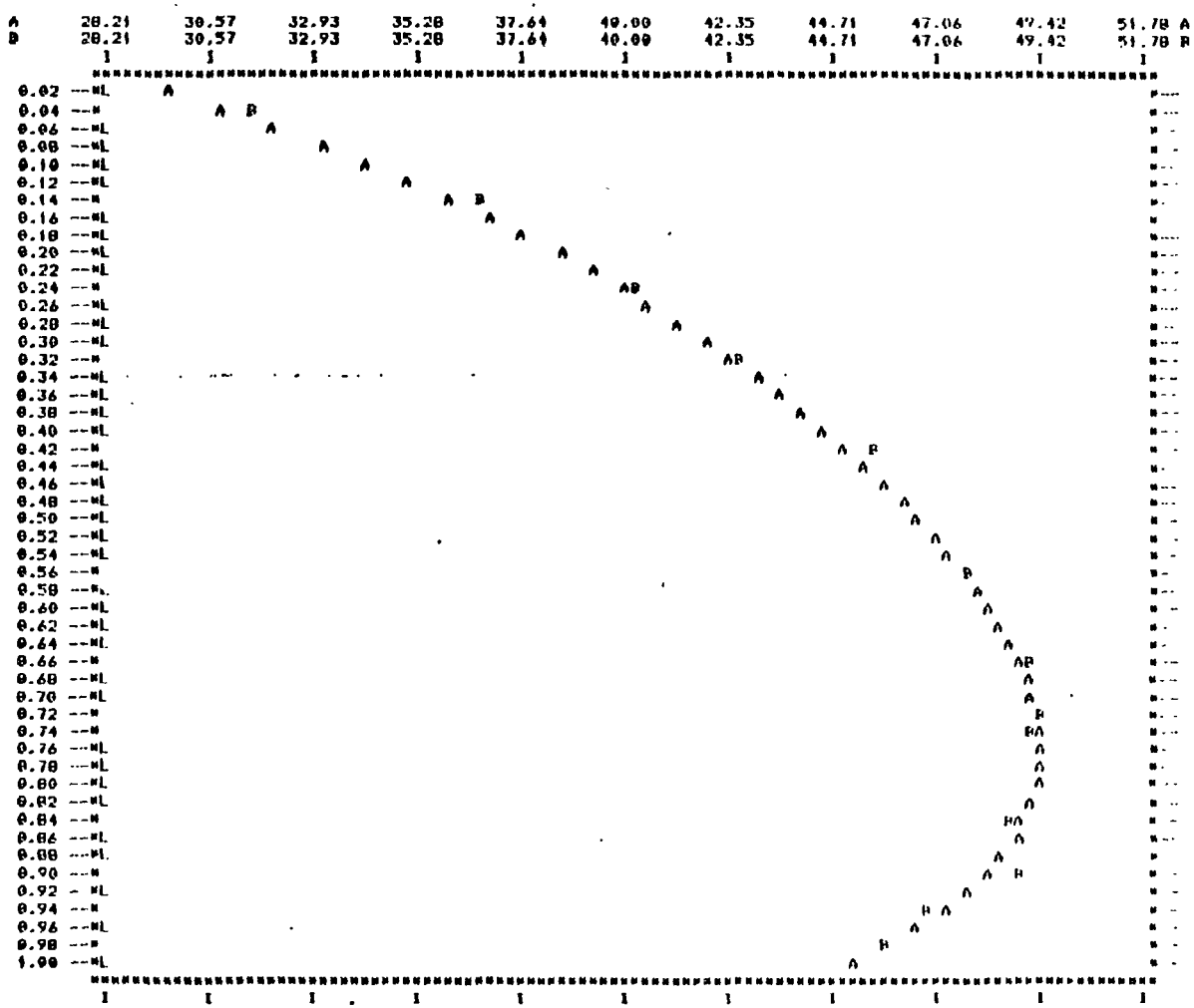
SATURATION VAPOR PRESSURE OF COMPONENT 1 AND 2 44.3400 29.7000 ATM.

TEMPERATURE 283.1499 DEG. K.

INTERPOLATED PRESSURE-VALUES FOR X IN THE INTERVAL BETWEEN 0.0 AND 1.0 . VALUES FOR DISCRETE JUMPS OF 0.02 IN X
A LEGENDRE POLYNOMIAL OF DEGREE 2 IS USED AS FITTING FUNCTION

29.7000	30.9091	32.0500	33.1269	34.1444	35.1062	36.0165	36.8786
37.6961	38.4721	39.2096	39.9113	40.5797	41.2173	41.8260	42.4077
42.9642	43.4968	44.0068	44.4951	44.9627	45.4100	45.8374	46.2450
46.6329	47.0006	47.3476	47.6733	47.9767	48.2566	48.5116	48.7402
48.9405	49.1105	49.2480	49.3504	49.4151	49.4392	49.4195	49.3528
49.2354	49.0637	48.8336	48.5408	48.1811	47.7497	47.2417	46.6522
45.9758	45.2069	44.3400					

INTERPOLATED AND EXPERIMENTAL PRESSURE-VALUES(ATM) VS. MOLE FRACTIONS



XEXP	YEXP	PEXP
0.	0.	29.70000
0.03300	0.06100	31.61000
0.12800	0.19800	36.70000
0.23400	0.31500	40.15000
0.31100	0.38400	42.52000
0.42100	0.48000	45.57000
0.54200	0.57800	47.88000
0.65500	0.66600	49.10000
0.71100	0.71100	49.31000
0.73000	0.72700	49.29000
0.83300	0.81500	48.60000
0.87300	0.85200	48.99000
0.92800	0.90800	46.79000
0.96100	0.94700	45.78000
1.00000	1.00000	44.34000

CONSISTENCY TEST USING ORTHOGONAL COLLOCATION - NUMBER OF INTERNAL POINTS 3

COLLOCATION POINTS

0. 0.112702 0.500000 0.887298 1.000000

ITERATION NR 4

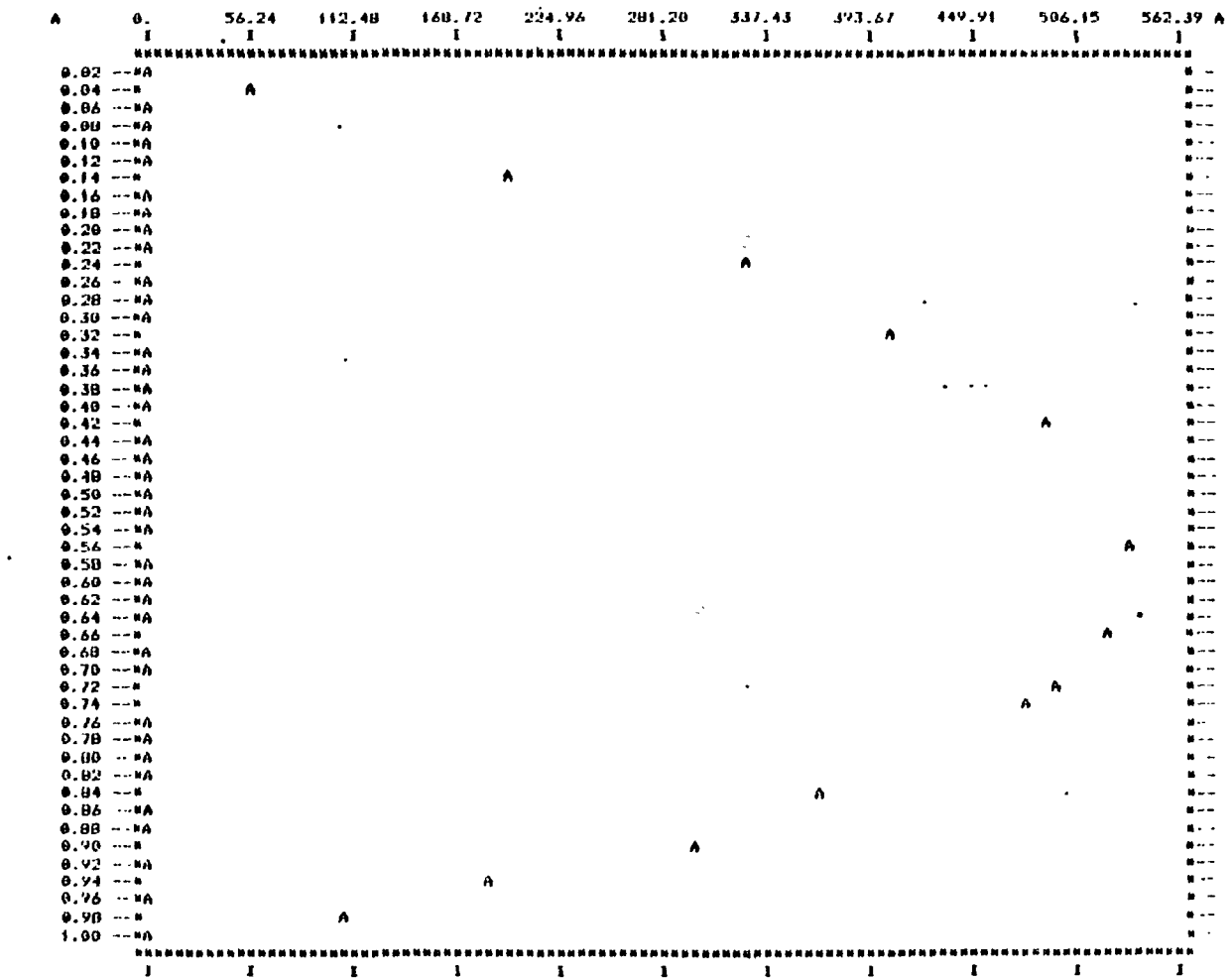
SOLUTION AT THE COLLOCATION POINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM COR	GE J/MOLE
0.	29.700000	0.	0.719253	2.052900	1.000000	0.	1.000000	1.000000	0.
0.112702	35.690064	0.074218	0.599444	1.833274	1.006682	0.256608	0.743312	1.000000	174.725167
0.500000	47.000552	0.223343	0.133801	1.336753	1.169243	0.630542	0.369458	1.000000	525.798506
0.887298	48.032193	0.115674	-0.813525	1.024279	2.310616	0.838979	0.161021	1.000000	272.323367
1.000000	44.340000	0.	-1.254457	1.000000	3.505934	1.000000	0.	1.000000	0.

SOLUTION AT THE DATAPOINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM COR	GE J/MOLE
0.	29.700000	0.	0.719253	2.052900	1.000000	0.	1.000000	1.000000	0.
0.033000	31.610000	0.023135	0.683067	1.981118	1.000594	0.091631	0.908369	1.000815	54.464717
0.128000	36.700000	0.083268	0.583725	1.808100	1.008588	0.282054	0.717946	0.991355	196.031345
0.234000	40.150000	0.139356	0.473886	1.652604	1.028876	0.422813	0.577187	1.010058	328.074809
0.311000	42.520000	0.172618	0.388902	1.553595	1.053027	0.498549	0.501451	1.010632	406.380925
0.421000	45.570000	0.208030	0.250900	1.423759	1.107827	0.582482	0.417518	1.001274	489.747995
0.542000	47.880000	0.227511	0.063667	1.292619	1.212886	0.653125	0.346875	0.993379	535.610276
0.655000	49.100000	0.222656	-0.158309	1.182983	1.385898	0.707552	0.292448	0.988954	524.180916
0.711000	49.310000	0.210194	-0.289286	1.134952	1.515678	0.733353	0.266647	0.989452	494.844509
0.730000	49.290000	0.204245	-0.337283	1.119832	1.569035	0.742323	0.257677	0.990648	480.837227
0.833000	48.600000	0.154039	-0.632200	1.050495	1.976765	0.798200	0.201720	1.000099	364.524779
0.873000	48.990000	0.126950	-0.763924	1.030304	2.211908	0.827007	0.172993	0.984447	298.869177
0.928000	46.790000	0.079574	-0.962295	1.010342	2.644768	0.880251	0.119749	1.009374	187.334031
0.961000	45.780000	0.045708	-1.091462	1.003146	2.987998	0.925096	0.074904	1.009301	107.607303
1.000000	44.340000	0.	-1.254457	1.000000	3.505934	1.000000	0.	1.000000	0.

GIBBS EXCESS FREE ENERGY(J/MOLE) VS. MOLE FRACTIONS



CONSISTENCY TEST BY REPEATED HALVING OF TRAPEZOIDAL RULE WITH ROMBERG INTEGRATION, AREA= 0.5680140 16

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	PCAL	DP
0.	29.7000	0.	0.	0.	1.0000	1.0000	29.7000	0.
0.0330	31.6100	0.0916	0.0610	0.0306	0.9084	1.0000	31.6582	0.0482
0.1280	36.7000	0.2821	0.1980	0.0841	0.7179	1.0000	36.3669	-0.3331
0.2340	40.1500	0.4228	0.3150	0.1078	0.5772	1.0000	40.3825	0.2325
0.3110	42.5200	0.4985	0.3840	0.1145	0.5015	1.0000	42.7168	0.1968
0.4210	45.5700	0.5825	0.4800	0.1025	0.4175	1.0000	45.4318	-0.1382
0.5420	47.8800	0.6531	0.5780	0.0751	0.3469	1.0000	47.7047	-0.1753
0.6550	49.1000	0.7076	0.6660	0.0416	0.2924	1.0000	49.0710	-0.0290
0.7110	49.3100	0.7334	0.7110	0.0224	0.2666	1.0000	49.3908	0.0808
0.7300	49.2900	0.7423	0.7270	0.0153	0.2577	1.0000	49.4324	0.1424
0.8330	48.6000	0.7983	0.8150	-0.0167	0.2017	1.0000	48.9210	0.3210
0.8730	48.9900	0.8270	0.8520	-0.0250	0.1730	1.0000	48.3149	-0.6751
0.9280	46.7900	0.8803	0.9080	-0.0277	0.1197	1.0000	47.0160	0.2260
0.9610	45.7800	0.9251	0.9470	-0.0219	0.0749	1.0000	45.9396	0.1596
1.0000	44.3400	1.0000	1.0000	0.	0.	1.0000	44.3400	0.

SUM OF SQUARES OF DELTA Y 0.0535097231

VARIATION OF DELTA Y 0.0668 ARITHMETIC MEAN OF DELTA Y 0.0527

CALCULATED EXCLUDING GIVEN END POINTS

SUM OF SQUARES OF DELTA P 3.9189254508

VARIATION OF DELTA P 0.2767 ARITHMETIC MEAN OF DELTA P 0.2122

ARITHMETIC MEAN OF DELTA P/P 0.061535

CALCULATED EXCLUDING GIVEN END DATAPOINTS

STOP

TIME 1.5 SECS

Results of Run # 2 for the

CO_2-C_2H_6 System at 10°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 3 3
CARBON DIOXIDE(1)-ETHANE(2)
INTERPOLATED AND EXPERIMENTAL PRESSURE-VALUES(ATM) VS. MOLE FRACTIONS
GIBBS EXCESS FREE ENERGY(J/MOLE) VS. MOLE FRACTIONS
 2 6
15
111
 29.700                          0.0                          0.0
 31.610                          0.033                        0.061
 36.700                          0.128                        0.198
 40.15                           0.234                        0.315
 42.52                           0.311                        0.384
 45.57                           0.421                        0.480
 47.88                           0.542                        0.578
 49.10                           0.655                        0.666
 49.31                           0.711                        0.711
 49.29                           0.730                        0.727
 48.60                           0.833                        0.815
 48.99                           0.873                        0.852
 46.79                           0.928                        0.908
 45.78                           0.961                        0.947
 44.34                 283.150   1.0                           1.0
 72.907       94.182    304.167      0.274       0.225
 48.196      141.584    305.444       0.285      0.105
 0.4184       0.0794    0.4470       0.0911
 0.4347       0.0827    0.4340       0.0880
 0.130
-40.292
-27.768
 0 0 0 0
```

The formated output is as follows:

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

THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION PROCEDURE IS OF THE TYPE ALFA = 0. BETA = 0.

PC-VC-TC-ZC-ACEN 0.72907E+02 0.94182E+02 0.30417E+03 0.27400E+00 0.22500E+00

PC-VC-TC-ZC-ACEN 0.48196E+02 0.14158E+03 0.30544E+03 0.28500E+00 0.10500E+00

OMAL-OMBL-OMAG-OMBG 0.41840E+00 0.79400E-01 0.44700E+00 0.91100E-01

OMAL-OMBL-OMAG-OMBG 0.43470E+00 0.82700E-01 0.43400E+00 0.88000E-01

FAK-NY-TAU

0.13000

-40.29201

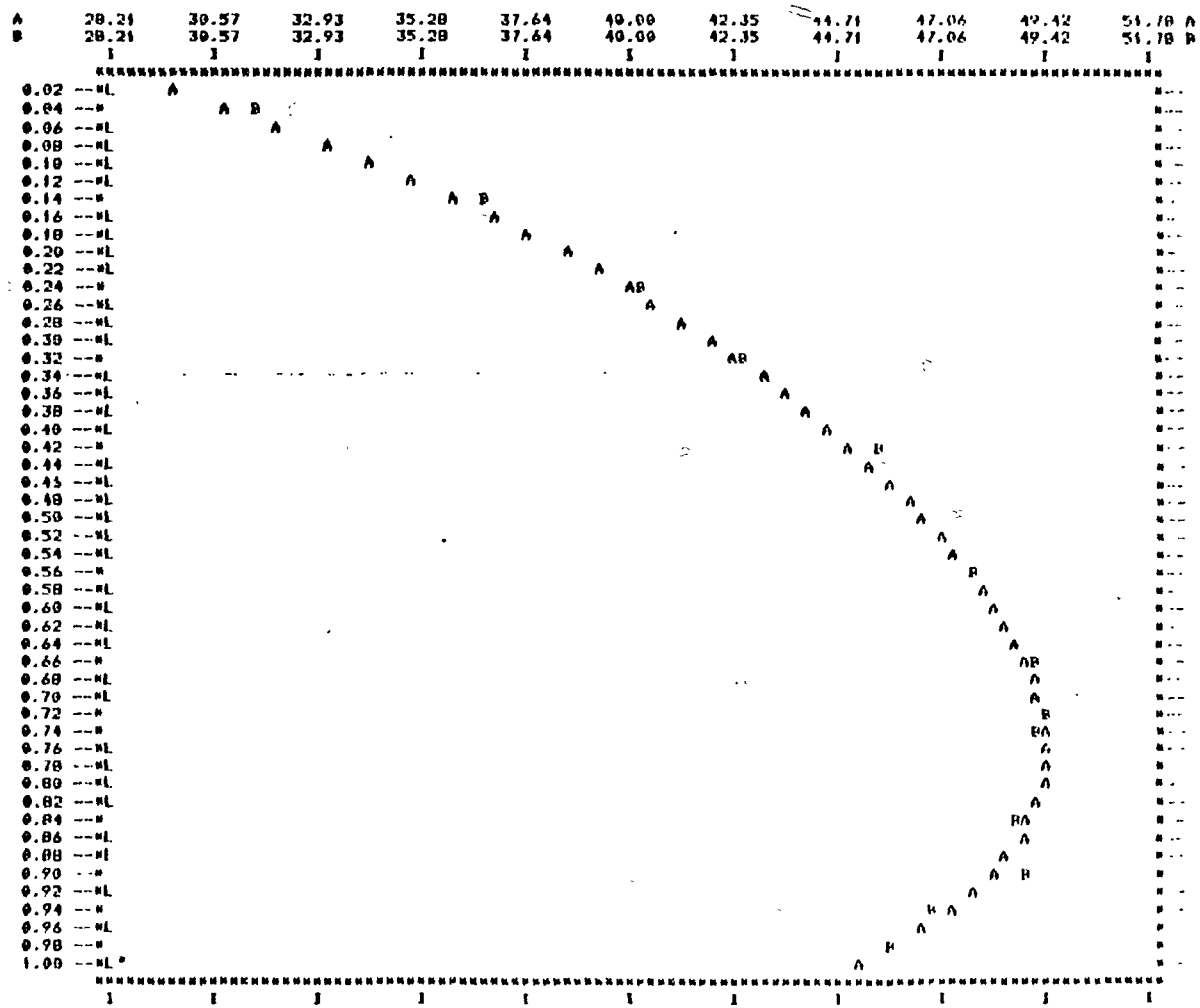
-27.76801

NUMBER OF BINARY POINTS 15 AT THE ISOTHERM 283.15 TEMPERATURE IN DEG K

INTERPOLATED PRESSURE-VALUES FOR X IN THE INTERVAL BETWEEN 0.0 AND 1.0 . VALUES FOR DISCRETE JUMPS OF 0.02 IN X
A LEGENDRE POLYNOMIAL OF DEGREE 2 IS USED AS FITTING FUNCTION

29.7000	30.9091	32.0500	33.1269	34.1444	35.1062	36.0165	36.8786
37.6961	38.4721	39.2096	39.9113	40.5797	41.2173	41.8260	42.4077
42.9642	43.4968	44.0068	44.4951	44.9627	45.4100	45.8374	46.2450
46.6329	47.0006	47.3476	47.6733	47.9767	48.2566	48.5116	48.7402
48.9405	49.1105	49.2480	49.3504	49.4151	49.4392	49.4195	49.3528
49.2354	49.0637	48.8336	48.5408	48.1811	47.7497	47.2417	46.6522
45.9758	45.2069	44.3400					

INTERPOLATED AND EXPERIMENTAL PRESSURE-VALUES(ATM) VS. MOLE FRACTIONS



XEXP	YEXP	PEXP
0.	0.	29.70000
0.03300	0.06100	31.61000
0.12800	0.19800	36.70000
0.23400	0.31500	40.15000
0.31100	0.38400	42.52000
0.42100	0.48000	45.57000
0.54200	0.57800	47.88000
0.65500	0.66600	49.10000
0.71100	0.71100	49.31000
0.73000	0.72700	49.29000
0.83300	0.81500	48.60000
0.87500	0.85200	48.99000
0.92800	0.90800	46.79000
0.96100	0.94700	45.78000
1.00000	1.00000	44.34000

CONSISTENCY TESTS USING ORTHOGONAL COLLOCATION - NUMBER OF INTERNAL POINTS 3

COLLOCATION POINTS
0. 0.112702 0.500000 0.887298 1.000000

I 283.1499 PS 44.3400 29.7000 VOL 51.5144 51.9454

FISAT 0.7398 0.7400 FREESAT 32.8043 21.9769

NUMBER OF ITERATIONS IN G 4

NUMBER OF ITERATIONS IN G 4

NUMBER OF ITERATIONS IN G 2

NUMBER OF ITERATIONS IN G 1

NUMBER OF ITERATIONS IN G 1

NUMBER OF ITERATIONS IN G 1

NUMBER OF ITERATIONS IN G 1

SOLUTION AT THE COLLOCATION POINTS

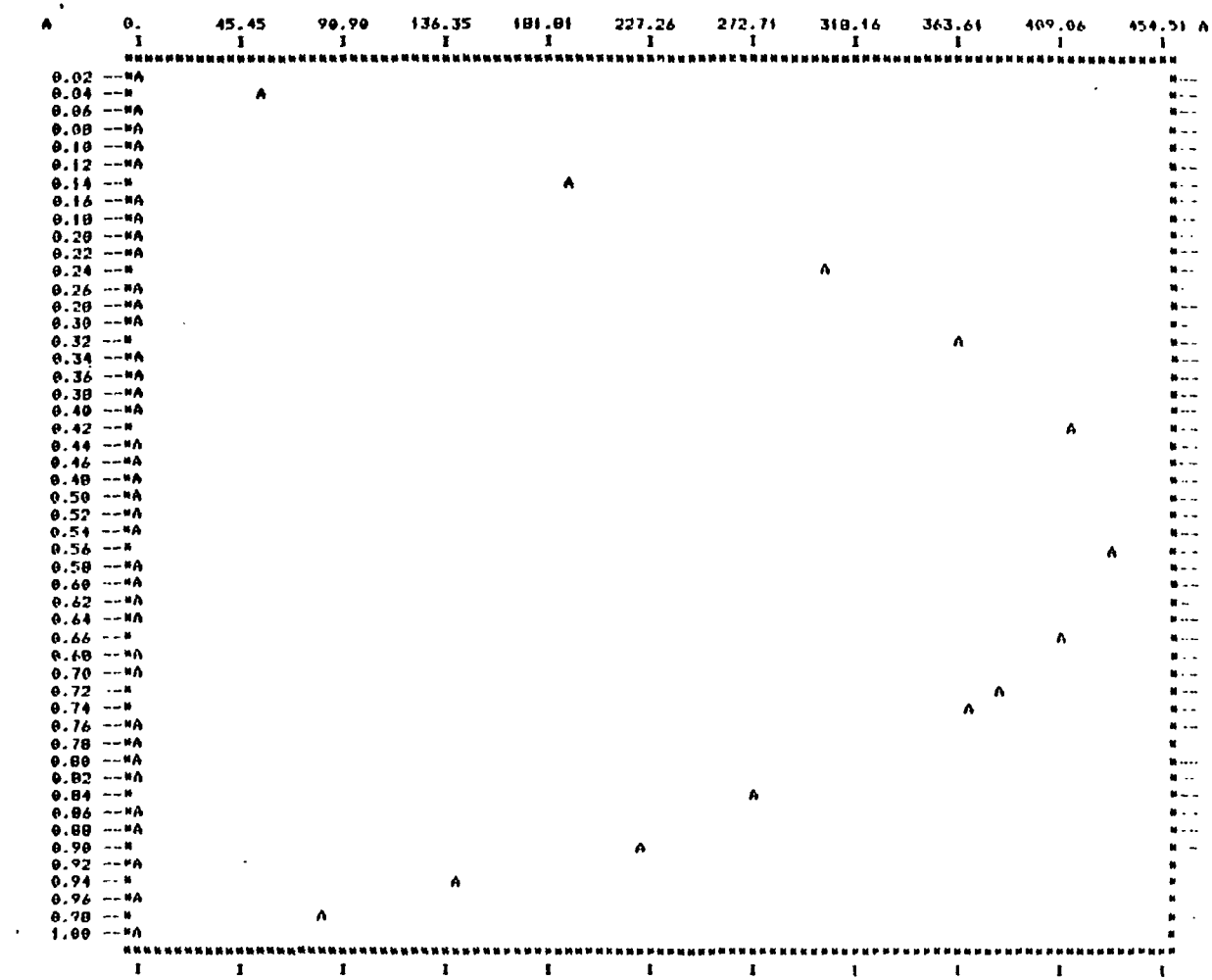
X	P	GE/RT	GOOT	GAMMA1	GAMMA2	Y1	Y2	SUM COR	GE J/MOLE
0.	29.7000	0.	0.7622	2.1430	1.0000	0.	1.0000	1.0000	0.
0.1127	35.6901	0.0736	0.5515	1.6778	1.0173	0.1860	0.8140	1.0000	173.2095
0.5000	47.0006	0.1832	0.0421	1.2148	1.1875	0.5565	0.4435	1.0000	431.3075
0.8873	48.0322	0.0866	-0.6190	1.0178	1.8771	0.8622	0.1378	1.0000	203.9515
1.0000	44.3400	0.	-0.9308	1.0000	2.5365	1.0000	0.	1.0000	0.

X	FUGCE1	FUGCE2	VMIX	VE	DPDX	CORR TO GOOT
0.	0.9942	0.7400	51.9454	0.	62.2426	0.
0.1127	0.9169	0.6920	78.2404	26.3436	45.1682	0.0512
0.5000	0.7663	0.6507	76.9980	25.2690	17.8740	0.0194
0.8873	0.7212	0.7320	59.1942	7.6312	-21.0627	-0.0069
1.0000	0.7398	0.8031	51.5144	0.	-45.8988	0.

SOLUTION AT THE DATAPOINTS

X	P	GE/RT	GOOT	GAMMA1	GAMMA2	Y1	Y2	SUM COR	GE J/MOLE
0.	29.7000	0.	0.7622	2.1430	1.0000	0.	1.0000	1.0000	0.
0.0330	31.6582	0.0240	0.6954	1.8867	1.0032	0.0648	0.9352	1.0004	56.5894
0.1280	36.3669	0.0818	0.5264	1.6454	1.0209	0.2055	0.7945	0.9999	192.6192
0.2540	40.3025	0.1291	0.3700	1.4675	1.0527	0.3228	0.6772	0.9995	303.8911
0.3110	42.7168	0.1537	0.2704	1.3746	1.0827	0.3962	0.6038	0.9998	361.8014
0.4210	45.4318	0.1761	0.1377	1.2733	1.1371	0.4920	0.5080	1.0001	414.5262
0.5420	47.7047	0.1839	-0.0109	1.1869	1.2198	0.5896	0.4104	0.9998	432.8707
0.6550	49.0710	0.1748	-0.1607	1.1199	1.3354	0.6759	0.3241	0.9989	409.5717
0.7110	49.3908	0.1620	-0.2587	1.0904	1.4159	0.7180	0.2820	0.9985	381.4987
0.7300	49.4324	0.1568	-0.2915	1.0810	1.4402	0.7324	0.2676	0.9985	369.1962
0.8330	48.9210	0.1168	-0.4934	1.0360	1.6871	0.8136	0.1864	0.9990	274.8969
0.8730	48.3149	0.0952	-0.5845	1.0221	1.8213	0.8488	0.1512	0.9997	224.2837
0.9280	47.0160	0.0594	-0.7251	1.0078	2.0641	0.9042	0.0958	1.0008	139.7251
0.9610	45.9396	0.0340	-0.8144	1.0024	2.2538	0.9437	0.0563	1.0011	80.0437
1.0000	44.3400	0.	-0.9308	1.0000	2.5365	1.0000	0.	1.0000	0.

GIBBS EXCESS FREE ENERGY(J/MOLE) VS. MOLE FRACTIONS



CONSISTENCY TEST BY REPEATED HALVING OF TRAPEZOIDAL RULE WITH ROMBERG INTEGRATION, AREA= 0.[illegible]D 1A

X	FUGCE1	FUGCE2	VMIX	VE	DPDX	CURR TO GOOT
0.	0.9942	0.7400	51.9454	0.	62.2426	0.
0.0330	0.9680	0.7229	78.1300	26.1989	56.5388	0.0630
0.1280	0.9084	0.6874	78.2603	26.3701	43.3328	0.0492
0.2340	0.8570	0.6640	78.3553	26.5108	33.1004	0.0378
0.3110	0.8258	0.6546	78.3403	26.5290	27.7586	0.0317
0.4210	0.7884	0.6493	77.9410	26.1771	21.8157	0.0246
0.5420	0.7560	0.6531	76.1482	24.4364	15.6238	0.0164
0.6550	0.7339	0.6656	72.4531	20.7901	8.1088	0.0073
0.7110	0.7263	0.6757	69.8545	18.2156	3.1432	0.0025
0.7300	0.7243	0.6799	68.8637	17.2329	1.2108	0.0009
0.8330	0.7192	0.7097	62.7372	11.1509	-11.9539	-0.0057
0.8730	0.7203	0.7255	60.1391	8.5700	-18.5083	-0.0068
0.9280	0.7254	0.7529	56.4664	4.9210	-29.0458	-0.0062
0.9610	0.7307	0.7734	54.2136	2.6825	-36.3155	-0.0042
1.0000	0.7398	0.8031	51.5144	0.	-45.8988	0.

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	PCAL	DP
0.	29.7000	0.	0.	0.	1.0000	1.0000	29.7000	0.
0.0330	31.6100	0.0648	0.0610	0.0038	0.9352	1.0000	31.6582	0.0482
0.1280	36.7000	0.2055	0.1980	0.0075	0.7945	1.0000	36.3669	-0.3331
0.2340	40.1500	0.3228	0.3150	0.0078	0.6772	1.0000	40.3825	0.2325
0.3110	42.5200	0.3962	0.3840	0.0122	0.6038	1.0000	42.7168	0.1968
0.4210	45.5700	0.4920	0.4800	0.0120	0.5080	1.0000	45.4518	-0.1382
0.5420	47.8800	0.5896	0.5780	0.0116	0.4104	1.0000	47.7047	-0.1753
0.6550	49.1000	0.6759	0.6660	0.0099	0.3241	1.0000	49.0710	-0.0290
0.7110	49.3100	0.7180	0.7110	0.0070	0.2820	1.0000	49.3908	0.0808
0.7300	49.2900	0.7324	0.7270	0.0054	0.2676	1.0000	49.4324	0.1424
0.8330	48.6000	0.8136	0.8150	-0.0014	0.1864	1.0000	48.9210	0.3210
0.8730	48.9900	0.8488	0.8520	-0.0032	0.1512	1.0000	48.3149	-0.6751
0.9280	46.7900	0.9042	0.9080	-0.0038	0.0958	1.0000	47.0160	0.2260
0.9610	45.7800	0.9437	0.9470	-0.0033	0.0563	1.0000	45.9396	0.1596
1.0000	44.3400	1.0000	1.0000	0.	0.	1.0000	44.3400	0.

SUM OF SQUARES OF DELTA Y 0.0007760

VARIANCE OF DELTA Y 0.0080 ARITHMETIC MEAN OF DELTA Y 0.0068

CALCULATED EXCLUDING GIVEN END POINTS

SUM OF SQUARES OF DELTA P 0.9189255

VARIANCE OF DELTA P 0.2767 ARITHMETIC MEAN OF DELTA P 0.2122

ARITHMETIC MEAN OF DELTA P/P 0.061535

CALCULATED EXCLUDING GIVEN END POINTS
STOP
TIME 3.0 SECS

Results of Run # 3 for the

CO_2-C_2H_6 System at 10°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 3 3
CARBON DIOXIDE(1)-ETHANE(2)
INTERPOLATED AND EXPERIMENTAL PRESSURE-VALUES(ATM) VS. MOLE FRACTIONS
GIBBS EXCESS FREE ENERGY(J/MOLE) VS. MOLE FRACTIONS
 2 6
15
111
 29.700                          0.0                          0.0
 31.610                          0.033                        0.061
 36.700                          0.128                        0.198
 40.15                           0.234                        0.315
 42.52                           0.311                        0.384
 45.57                           0.421                        0.480
 47.88                           0.542                        0.578
 49.10                           0.655                        0.666
 49.31                           0.711                        0.711
 49.29                           0.730                        0.727
 48.60                           0.833                        0.815
 48.99                           0.873                        0.852
 46.79                           0.928                        0.908
 45.78                           0.961                        0.947
 44.34                 283.150    1.0                          1.0
 72.907       94.182     304.167      0.274       0.225
 48.196      141.584     305.444       0.285      0.105
 0.130
-40.232
-27.768
 0.1470
 0 0 0 0
```

The formated output is as follows:

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

THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION PROCEDURE IS OF THE TYPE ALFA = 0. BETA = 0.

PC-VC-TC-ZC-ACEN 0.72907E+02 0.94182E+02 0.30417E+03 0.27400E+00 0.22500E+00

PC-VC-TC-ZC-ACEN 0.48196E+02 0.14158E+03 0.30544E+03 0.28500E+00 0.10500E+00

FAK-NY-TAU-DEL

0.13000

-40.29201

-27.76801

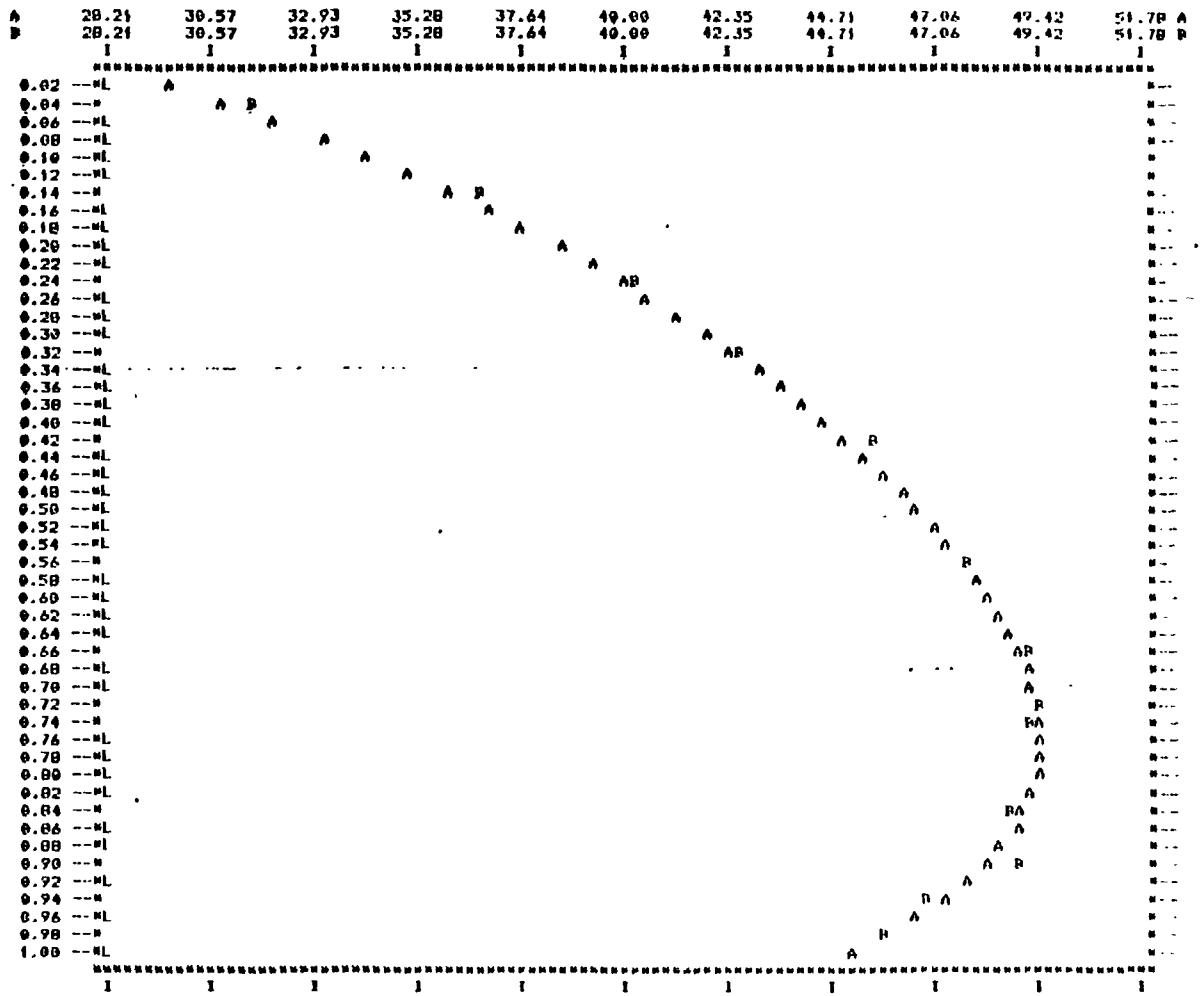
0.14700

NUMBER OF BINARY POINTS 15 AT THE ISOTHERM 283.15 TEMPERATURE IN DEG K

INTERPOLATED PRESSURE-VALUES FOR X IN THE INTERVAL BETWEEN 0.0 AND 1.0 . VALUES FOR DISCRETE JUMPS OF 0.02 IN X
A LEGENDRE POLYNOMIAL OF DEGREE 2 IS USED AS FITTING FUNCTION

29.7000	30.9091	32.0500	33.1269	34.1444	35.1062	36.0165	36.8786
37.6961	38.4721	39.2096	39.9113	40.5797	41.2173	41.8260	42.4077
42.9642	43.4968	44.0068	44.4951	44.9627	45.4100	45.8374	46.2450
46.6329	47.0006	47.3476	47.6733	47.9767	48.2566	48.5116	48.7402
48.9405	49.1105	49.2480	49.3504	49.4151	49.4392	49.4195	49.3528
49.2354	49.0637	48.8336	48.5408	48.1811	47.7497	47.2417	46.6522
45.9758	45.2069	44.3400					

INTERPOLATED AND EXPERIMENTAL PRESSURE-VALUES(ATM) VS. MOLE FRACTIONS



```
      XLAP          YLAP          PLAP
    0.            0.          29.70000
    0.05300       0.06100     31.61000
    0.12800       0.19800     36.70000
    0.23400       0.31500     40.15000
    0.31100       0.38400     42.52000
    0.42100       0.48000     45.57000
    0.54200       0.57800     47.88000
    0.65500       0.66600     49.10000
    0.71100       0.71100     49.31000
    0.73000       0.72700     49.29000
    0.83300       0.81500     48.60000
    0.87300       0.85200     48.99000
    0.92800       0.90800     46.79000
    0.96100       0.94700     45.78000
    1.00000       1.00000     44.34000
CONSISTENCY TESTS USING ORTHOGONAL COLLOCATION -      NUMBER OF INTERNAL POINTS    3

COLLOCATION POINTS
  0.          0.112702  0.500000  0.887298  1.000000

T  285.1499     PS    44.3400    29.7000     VOL    51.5144    51.9454

FISAT     0.7256     0.7229     FREESAT    32.1733    21.4697


 NUMBER OF ITERATIONS IN G     5

 NUMBER OF ITERATIONS IN G     4

 NUMBER OF ITERATIONS IN G     2

 NUMBER OF ITERATIONS IN G     1

 NUMBER OF ITERATIONS IN G     1

 NUMBER OF ITERATIONS IN G     1

 NUMBER OF ITERATIONS IN G     1
```

SOLUTION AT THE COLLOCATION POINTS

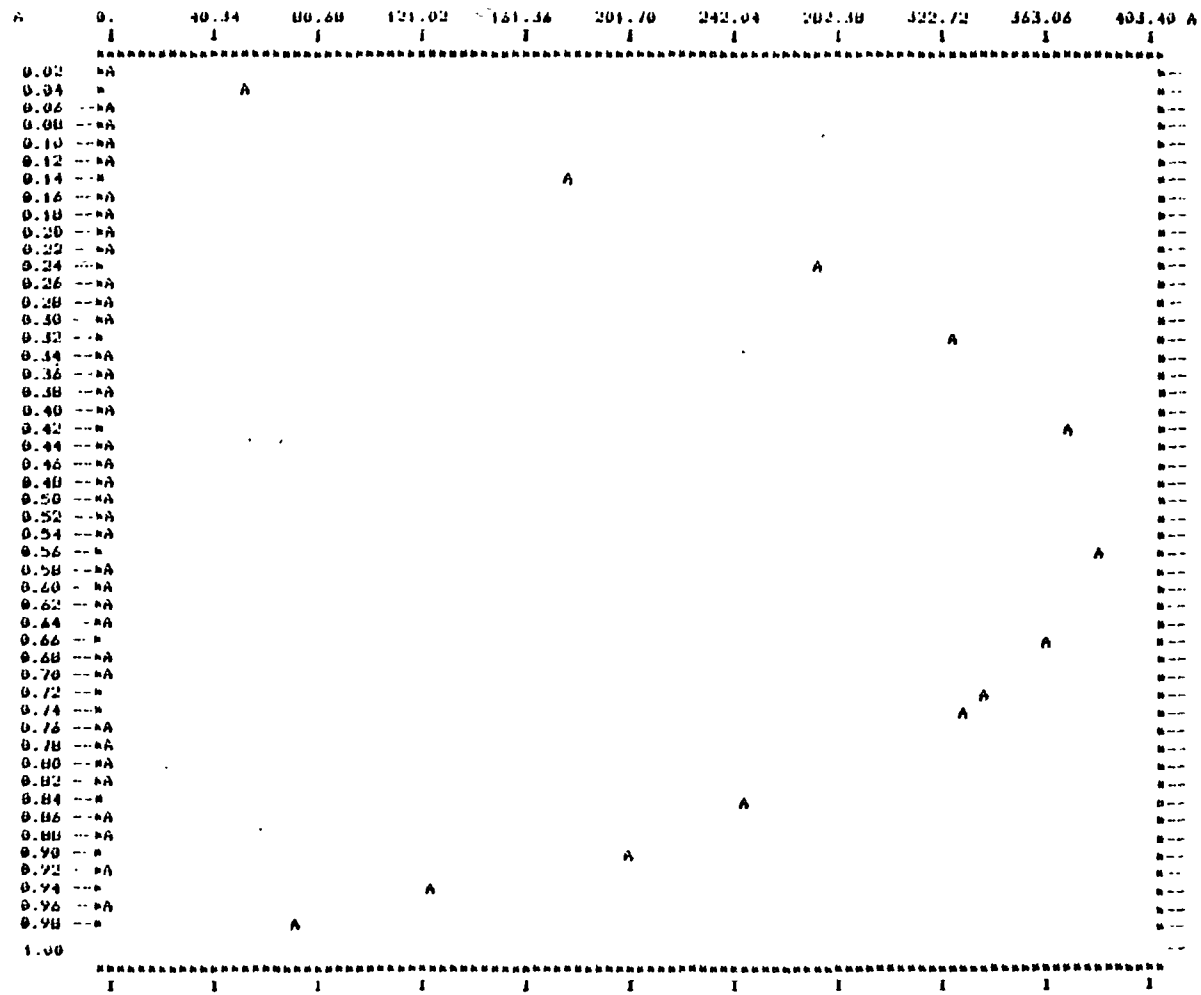
X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM COR	GE J/MOLE
0.	29.7000	0.	0.7182	2.0507	1.0000	0.	1.0000	1.0000	0.
0.1127	35.6981	0.0680	0.4984	1.5916	1.0177	0.1796	0.8204	1.0000	160.0206
0.5000	47.0006	0.1627	0.0331	1.1040	1.1687	0.5465	0.4535	1.0000	383.0925
0.8873	48.0322	0.0782	-0.5513	1.0170	1.7529	0.8639	0.1361	1.0000	184.1525
1.0000	44.3400	0.	-0.8505	1.0000	2.3409	1.0000	0.	1.0000	0.

X	FUGCE1	FUGCE2	VMIX	VE	DPDX	CORR TO GDOT
0.	0.9480	0.7229	51.9454	0.	62.2426	0.
0.1127	0.8834	0.6710	70.2404	28.5436	45.1682	0.0512
0.5000	0.7464	0.6118	76.9988	25.2690	17.8740	0.0194
0.8873	0.7054	0.6761	59.1942	7.6312	-21.0627	-0.0069
1.0000	0.7256	0.7370	51.5144	0.	-45.8988	0.

SOLUTION AT THE DATAPOINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM COR	GE J/MOLE
0.	29.7000	0.	0.7182	2.0507	1.0000	0.	1.0000	1.0000	0.
0.0330	31.6582	0.0225	0.6473	1.7902	1.0033	0.0633	0.9367	1.0007	53.0022
0.1280	36.3669	0.0754	0.4730	1.5605	1.0214	0.1982	0.8018	0.9998	177.5113
0.2340	40.3025	0.1171	0.3205	1.3961	1.0523	0.3105	0.6895	0.9991	275.7516
0.3110	42.7168	0.1382	0.2289	1.3153	1.0799	0.3824	0.6176	0.9992	325.3563
0.4210	45.4318	0.1569	0.1134	1.2317	1.1270	0.4794	0.5206	0.9998	369.4414
0.5420	47.7047	0.1632	-0.0112	1.1624	1.1950	0.5813	0.4187	1.0000	384.1878
0.6550	49.0710	0.1546	-0.1448	1.1076	1.2895	0.6724	0.3276	0.9996	364.0118
0.7110	49.3908	0.1444	-0.2230	1.0824	1.3562	0.7165	0.2835	0.9993	339.8730
0.7300	49.4524	0.1399	-0.2519	1.0742	1.3832	0.7315	0.2685	0.9992	329.2557
0.8330	48.9210	0.1049	-0.4344	1.0339	1.5872	0.8150	0.1850	0.9993	246.9861
0.8730	48.3149	0.0859	-0.5190	1.0210	1.7040	0.8505	0.1495	0.9998	202.1633
0.9280	47.0160	0.0538	-0.6500	1.0075	1.9100	0.9056	0.0944	1.0006	126.6769
0.9610	45.9596	0.0309	-0.7376	1.0023	2.0870	0.9446	0.0554	1.0008	72.8237
1.0000	44.3400	0.	-0.8505	1.0000	2.3409	1.0000	0.	1.0000	0.

GIBBS EXCESS FREE ENERGY(J/MOLE) VS. MOLE FRACTIONS



CONSISTENCY TEST BY REPEATED HALVING OF TRAPEZOIDAL RULE WITH ROMBERG INTEGRATION, AREA= -0.7184800D-16

X	FUGCE1	FUGCE2	VMIX	VE	DPDX	CORR TO GODT
0.	0.9480	0.7229	51.9454	0.	62.2426	0.
0.0330	0.9262	0.7050	78.1300	26.1909	56.5388	0.0650
0.1280	0.8763	0.6657	78.2603	26.3701	43.3328	0.0492
0.2340	0.8317	0.6371	78.3553	26.5108	33.1004	0.0378
0.3110	0.8034	0.6259	78.3403	26.5290	27.7506	0.0317
0.4210	0.7680	0.6137	77.9410	26.1771	21.8157	0.0246
0.5420	0.7364	0.6125	76.1482	24.4364	15.6230	0.0164
0.6550	0.7151	0.6287	72.4531	20.7901	8.1088	0.0073
0.7110	0.7080	0.6385	69.8545	18.2156	3.1432	0.0025
0.7300	0.7062	0.6319	68.8537	17.2329	1.2108	0.0009
0.8330	0.7025	0.6569	62.7372	11.1509	-11.9539	-0.0057
0.8730	0.7043	0.6706	60.1391	8.5700	-18.5003	-0.0068
0.9280	0.7102	0.6941	56.4664	4.9210	-29.0458	-0.0062
0.9610	0.7161	0.7117	54.2136	2.6825	-36.3155	-0.0042
1.0000	0.7256	0.7370	51.5144	0.	-45.8988	0.

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	PCAL	DP
0.	29.7000	0.	0.	0.	1.0000	1.0000	29.7000	0.
0.0330	31.6100	0.0633	0.0610	0.0023	0.9367	1.0000	31.6502	0.0402
0.1280	36.7000	0.1982	0.1980	0.0002	0.8018	1.0000	36.3669	-0.3331
0.2340	40.1500	0.3105	0.3150	-0.0045	0.6895	1.0000	40.3825	0.2325
0.3110	42.5200	0.3824	0.3840	-0.0016	0.6176	1.0000	42.7160	0.1960
0.4210	45.5700	0.4794	0.4800	-0.0006	0.5206	1.0000	45.4318	-0.1382
0.5420	47.8800	0.5813	0.5780	0.0033	0.4187	1.0000	47.7047	-0.1753
0.6550	49.1000	0.6724	0.6660	0.0064	0.3276	1.0000	49.0710	-0.0290
0.7110	49.3100	0.7165	0.7110	0.0055	0.2835	1.0000	49.3908	0.0808
0.7300	49.2900	0.7315	0.7270	0.0045	0.2685	1.0000	49.4324	0.1424
0.8330	48.6000	0.8150	0.8150	0.0000	0.1850	1.0000	48.9210	0.3210
0.8730	48.9900	0.8505	0.8520	-0.0015	0.1495	1.0000	48.3149	-0.6751
0.9280	46.7900	0.9056	0.9080	-0.0024	0.0944	1.0000	47.0160	0.2260
0.9610	45.7000	0.9446	0.9470	-0.0024	0.0554	1.0000	45.9396	0.1596
1.0000	44.3400	1.0000	1.0000	0.	0.	1.0000	44.3400	0.

SUM OF SQUARES OF DELTA Y 0.0001447

VARIANCE OF DELTA Y 0.0035 ARITHMETIC MEAN OF DELTA Y 0.0027

CALCULATED EXCLUDING GIVEN END POINTS

SUM OF SQUARES OF DELTA P 0.9189255

VARIANCE OF DELTA P 0.2767 ARITHMETIC MEAN OF DELTA P 0.2122

ARITHMETIC MEAN OF DELTA P/P 0.061535

CALCULATED EXCLUDING GIVEN END POINTS
STOP
TIME 3.0 SECS

Results of Run # 4 for the

CO_2-C_2H_6 Systems at 10°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 3 3
CARBON DIOXIDE(1)-ETHANE(2)
INTERPOLATED AND EXPERIMENTAL PRESSURE-VALUES(ATM) VS. MOLE FRACTIONS
GIBBS EXCESS FREE ENERGY(J/MOLE) VS. MOLE FRACTIONS
 2 6
15
111
 29.700                          0.0                          0.0
 31.610                          0.033                        0.061
 36.700                          0.128                        0.198
 40.15                           0.234                        0.315
 42.52                           0.311                        0.384
 45.57                           0.421                        0.480
 47.88                           0.542                        0.578
 49.10                           0.655                        0.666
 49.31                           0.711                        0.711
 49.29                           0.730                        0.727
 48.60                           0.833                        0.815
 48.99                           0.873                        0.852
 46.79                           0.928                        0.908
 45.78                           0.961                        0.947
 44.34                  283.150  1.0                           1.0
 72.907       94.182     304.167      0.274       0.225
 48.196      141.584     305.444       0.285      0.105
0.130
-40.292
-27.768
0.0000
0 0 0 0
```

The formated output is as follows:

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

****

THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION PROCEDURE IS OF THE TYPE ALFA = 0. BETA = 0.

PC-VC-TC-ZC-ACEN 0.72907E+02 0.94182E+02 0.30417E+03 0.27400E+00 0.22500E+00

PC-VC-TC-ZC-ACEN 0.48196E+02 0.14158E+03 0.30544E+03 0.28500E+00 0.10500E+00

FAK-NY-TAU-DEL

0.13000

-40.29201

-27.76801

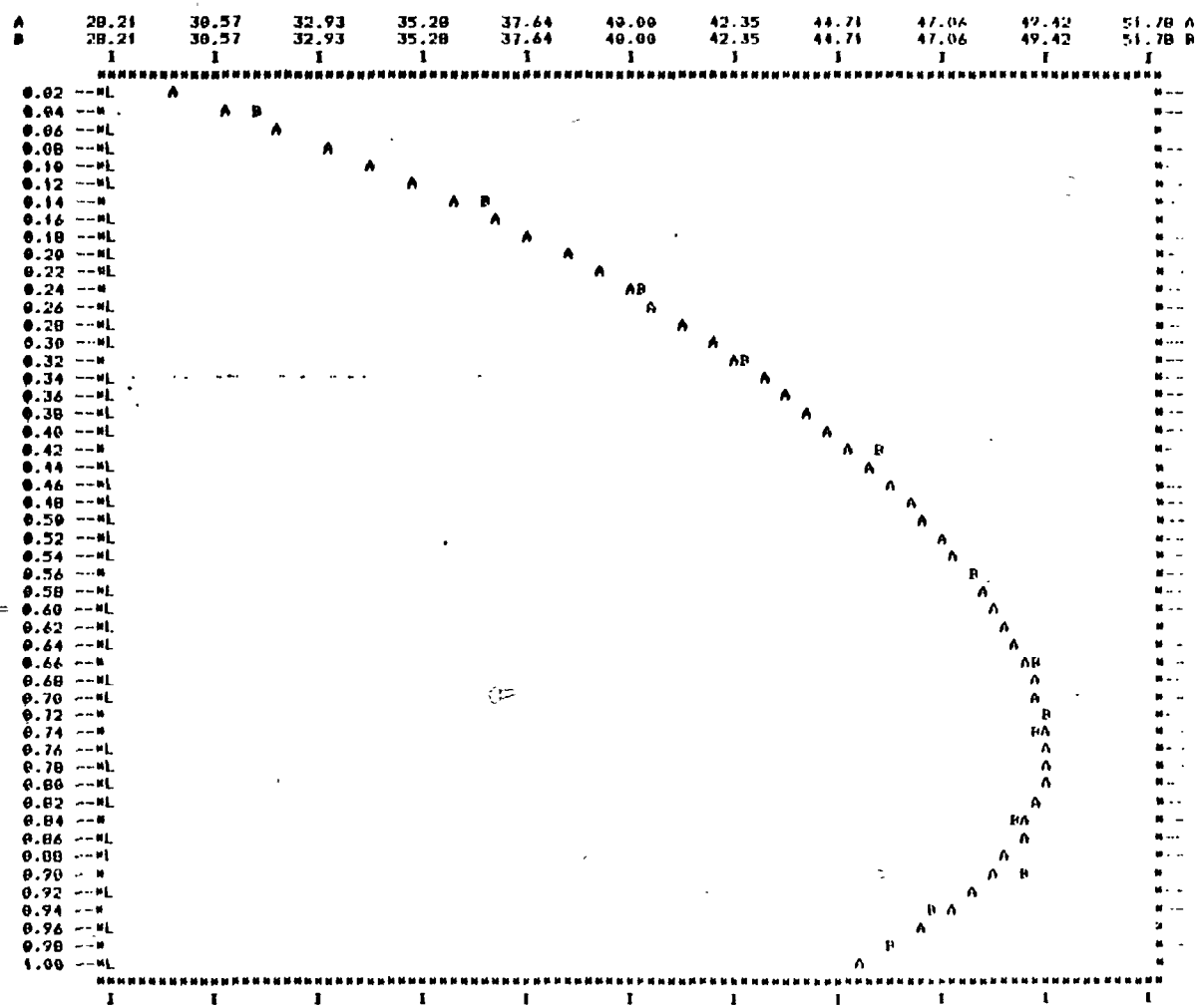
0.

NUMBER OF BINARY POINTS 15 AT THE ISOTHERM 283.15 TEMPERATURE IN DEG K

INTERPOLATED PRESSURE-VALUES FOR X IN THE INTERVAL BETWEEN 0.0 AND 1.0 , VALUES FOR DISCRETE JUMPS OF 0.02 IN X
A LEGENDRE POLYNOMIAL OF DEGREE 2 IS USED AS FITTING FUNCTION

29.7000	30.9091	32.0500	33.1269	34.1434	35.1062	36.0165	36.8786
37.6961	38.4721	39.2096	39.9113	40.5797	41.2173	41.8260	42.4077
42.9642	43.4968	44.0068	44.4951	44.9627	45.4100	45.8374	46.2450
46.6329	47.0006	47.3476	47.6733	47.9767	48.2566	48.5116	48.7402
48.9405	49.1105	49.2480	49.3504	49.4151	49.4392	49.4195	49.3528
49.2354	49.0637	48.8336	48.5408	48.1811	47.7497	47.2417	46.6522
45.9758	45.2069	44.3400					

INTERPOLATED AND EXPERIMENTAL PRESSURE-VALUES(ATM) VS. MOLE FRACTIONS



```
      XEXP        YEXP        PEXP
    0.          0.          29.70000
    0.03300     0.06100     31.61000
    0.12800     0.19800     36.70000
    0.25400     0.31500     40.15000
    0.31100     0.38400     42.52000
    0.42100     0.48000     45.57000
    0.54200     0.57000     47.88000
    0.65500     0.66600     49.10000
    0.71100     0.71100     49.31000
    0.75000     0.72700     49.29000
    0.83600     0.81500     48.60000
    0.87500     0.85200     48.99000
    0.92800     0.90000     46.79000
    0.96100     0.94700     45.78000
    1.00000     1.00000     44.34000
CONSISTENCY TESTS USING ORTHOGONAL COLLOCATION  -      NUMBER OF INTERNAL POINTS    3

COLLOCATION POINTS
    0.          0.112702  0.500000  0.887298  1.000000

1  203.1499    PS    44.3400    29.7000    VOL    51.5144    51.9454

FISAT     0.7256     0.7229     FREESAT    32.1733    21.4697


 NUMBER OF ITERATIONS IN G    5

 NUMBER OF ITERATIONS IN G    5

 NUMBER OF ITERATIONS IN G    3

 NUMBER OF ITERATIONS IN G    1

 NUMBER OF ITERATIONS IN G    1

 NUMBER OF ITERATIONS IN G    1
```

SOLUTION AT THE COLLOCATION POINTS

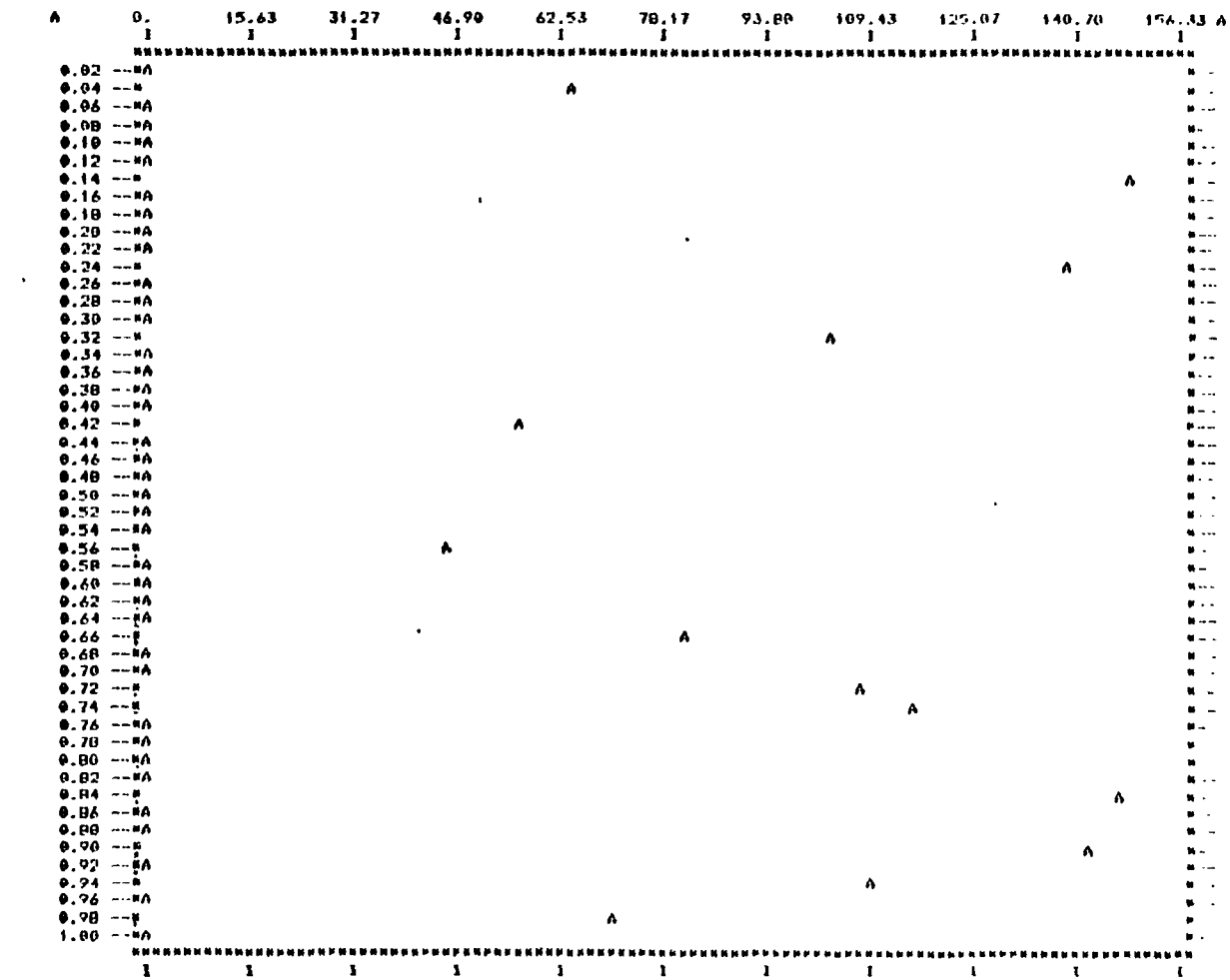
X	P	GE/RT	GOUT	GAMMA1	GAMMA2	Y1	Y2	SUM COR	GE J/MOLE
0.	29.7000	0.	0.9591	2.6093	1.0000	0.	1.0000	1.0000	0.
0.1127	35.6901	0.0600	0.1979	1.2103	1.0452	0.1491	0.8509	1.0000	143.0244
0.5000	47.0006	0.0183	-0.0079	1.0047	1.0325	0.4976	0.5024	1.0000	43.1628
0.8873	48.0322	0.0583	-0.1852	1.0389	1.2418	0.8054	0.1946	1.0000	137.2620
1.0000	44.3400	0.	-0.9275	1.0000	2.5201	1.0000	0.	1.0000	0.

X	FUGCE1	FUGCE2	VMIX	VE	DPDX	CORR TO GOUT
0.	0.8382	0.7229	51.9454	0.	62.2426	0.
0.1127	0.8089	0.6645	78.2404	26.3436	45.1682	0.0512
0.5000	0.6951	0.4880	76.9988	25.2690	17.8740	0.0194
0.8873	0.7031	0.5688	59.1942	7.6312	-21.0627	-0.0069
1.0000	0.7256	0.6141	51.5144	0.	-45.8988	0.

SOLUTION AT THE DATAPOINTS

X	P	GE/RT	GOUT	GAMMA1	GAMMA2	Y1	Y2	SUM COR	GE J/MOLE
0.	29.7000	0.	0.9591	2.6093	1.0000	0.	1.0000	1.0000	0.
0.0330	31.6582	0.0270	0.6864	1.8759	1.0065	0.0730	0.9270	1.0152	65.6209
0.1280	36.3669	0.0632	0.1291	1.1421	1.0544	0.1578	0.8422	0.9957	140.8901
0.2340	40.3825	0.0588	-0.1630	0.9094	1.1116	0.2006	0.7994	1.0473	138.3878
0.3110	42.7168	0.0436	-0.2117	0.8833	1.1267	0.2628	0.7372	1.0523	102.7110
0.4210	45.4318	0.0238	-0.1263	0.9384	1.0912	0.3878	0.6122	1.0076	55.9801
0.5420	47.7047	0.0194	0.0581	1.0393	0.9968	0.5575	0.4425	1.0019	45.6698
0.6550	49.0710	0.0344	0.1895	1.1021	0.9185	0.7012	0.2988	1.0250	80.8835
0.7110	49.3908	0.0455	0.2017	1.1086	0.9083	0.7564	0.2436	1.0370	107.1912
0.7300	49.4374	0.0493	0.1942	1.1060	0.9123	0.7726	0.2274	1.0410	116.0704
0.8330	48.9210	0.0624	0.0172	1.0608	1.0425	0.8418	0.1582	1.0539	146.9384
0.8730	48.3149	0.0605	-0.1228	1.0468	1.1755	0.8771	0.1229	0.9977	142.4202
0.9280	47.0160	0.0466	-0.3999	1.0184	1.5098	0.9419	0.0881	1.0059	109.6739
0.9610	45.9396	0.0299	-0.6169	1.0060	1.8567	0.9616	0.0584	1.0083	70.4343
1.0000	44.3400	0.	-0.9275	1.0000	2.5201	1.0000	0.	1.0000	0.

GIBBS EXCESS FREE ENERGY(J/MOLE) VS. MOLE FRACTIONS



CONSISTENCY TEST BY REPEATED HALVING OF TRAPEZOIDAL RULE WITH RIMBERG INTEGRATION, AREA= 0.4122750 17

X	FUGCE1	FUGCE2	VMIX	VL	DPDX	FUNK TO GUUI
0.	0.8382	0.7229	51.9454	0.	62.2426	0.
0.0530	0.8260	0.7044	78.1300	26.1989	56.5388	0.0638
0.1280	0.8006	0.6570	70.2803	26.3701	43.3328	0.0492
0.2340	0.7998	0.5538	78.3553	26.5100	33.1004	0.0378
0.3110	0.7598	0.5279	78.3405	26.5290	27.7505	0.0317
0.4210	0.7178	0.5014	77.9410	26.1771	21.8157	0.0246
0.5420	0.6852	0.4825	76.1482	24.4364	15.6238	0.0164
0.6550	0.6664	0.4734	72.4531	20.7901	8.1088	0.0073
0.7110	0.6620	0.4721	69.8545	18.2156	3.1432	0.0025
0.7300	0.6613	0.4722	68.8637	17.2329	1.2108	0.0009
0.8330	0.6667	0.4705	62.7372	11.1509	-11.9539	-0.0057
0.8730	0.7015	0.5642	60.1391	8.5700	-18.5003	-0.0068
0.9280	0.7092	0.5826	56.4664	4.9210	-29.0458	-0.0062
0.9610	0.7157	0.5955	54.2136	2.6825	-36.3155	-0.0042
1.0000	0.7256	0.6141	51.5144	0.	-45.8908	0.

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	PCAL	DP
0.	29.7000	0.	0.	0.	1.0000	1.0000	29.7000	0.
0.0530	31.6100	0.0730	0.0610	0.0120	0.9270	1.0000	31.6582	0.0482
0.1280	36.7000	0.1578	0.1980	-0.0402	0.8422	1.0000	36.3669	-0.3331
0.2340	40.1500	0.2006	0.3150	-0.1144	0.7994	1.0000	40.3825	0.2325
0.3110	42.5200	0.2628	0.3840	-0.1212	0.7372	1.0000	42.7168	0.1968
0.4210	45.5700	0.3878	0.4800	-0.0922	0.6122	1.0000	45.4318	-0.1382
0.5420	47.8800	0.5575	0.5780	-0.0205	0.4425	1.0000	47.7047	-0.1753
0.6550	49.1000	0.7012	0.6660	0.0352	0.2988	1.0000	49.0710	-0.0290
0.7110	49.3100	0.7564	0.7110	0.0454	0.2436	1.0000	49.3908	0.0808
0.7300	49.2900	0.7726	0.7270	0.0456	0.2274	1.0000	49.4324	0.1424
0.8330	48.6000	0.8418	0.8150	0.0268	0.1582	1.0000	48.9210	0.3210
0.8730	48.9900	0.8771	0.8520	0.0251	0.1229	1.0000	48.3149	-0.6751
0.9280	46.7900	0.9119	0.9080	0.0039	0.0881	1.0000	47.0160	0.2260
0.9610	45.7800	0.9416	0.9470	-0.0054	0.0584	1.0000	45.9396	0.1596
1.0000	44.3400	1.0000	1.0000	0.	0.	1.0000	44.3400	0.

SUM OF SQUARES OF DELTA Y 0.0452195

VARIANCE OF DELTA Y 0.0614 ARITHMETIC MEAN OF DELTA Y 0.0452

CALCULATED EXCLUDING GIVEN END POINTS

SUM OF SQUARES OF DELTA P 0.9189255

VARIANCE OF DELTA P 0.2767 ARITHMETIC MEAN OF DELTA P 0.2122

ARITHMETIC MEAN OF DELTA P/P 0.081535

CALCULATED EXCLUDING GIVEN END POINTS
STOP
TIME 3.0 SECS

Results of Run # 1 for the

CH_4-C_3H_8 System at -17°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 2 2
METHANE(1)-PROPANE(2)
 1
15
111
 1.8                              0.0                              0.0
 6.8                              0.034                            0.56
 13.6                             0.089                            0.767
 20.4                             0.142                            0.832
 27.2                             0.197                            0.861
 34.0                             0.249                            0.880
 40.8                             0.303                            0.888
 47.6                             0.357                            0.890
 54.4                             0.41                             0.892
 61.2                             0.464                            0.891
 68.0                             0.518                            0.889
 74.9                             0.572                            0.882
 81.7                    256.40   0.636                            0.869
 88.5                    256.40   0.718                            0.845
 93.9                    256.40   0.80                             0.80
 45.4          99.0      190.6          0.288       0.008
 41.9          203.0     369.8          0.281       0.152
 0.00618
-110.3206
 79.0164
-0.05
 0 0 0 0
```

The formated output is as follows:

```
EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR    THE BINARY SYSTEM   METHANE(1)-PROPANE(2)
**********************************************************************************************************

 THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION    PROCEDURE IS OF THE TYPE ALFA =     0.       BETA =     0.


PC-VC-TC-ZC-ACEN      0.45400E+02 0.99000E+02 0.19060E+03 0.28000E+00 0.80000E-02

PC-VC-TC-ZC-ACEN      0.41900E+02 0.20300E+03 0.36980E+03 0.28100E+00 0.15200E+00

FAK-NY-TAU-DEL

   0.00618

-110.32060

  79.01640

  -0.05000

NUMBER OF BINARY POINTS   15     AT THE ISOTHERM    256.40     TEMPERATURE IN DEG K

    XEXP       YEXP       PEXP
  0.         0.         1.80000
  0.03400    0.56000    6.80000
  0.08900    0.76700   13.60000
  0.14200    0.83200   20.40000
  0.19700    0.86100   27.20000
  0.24900    0.88000   34.00000
  0.30300    0.88800   40.80000
  0.35700    0.89000   47.60000
  0.41000    0.89200   54.40000
  0.46400    0.89100   61.20000
  0.51800    0.88700   68.00000
  0.57200    0.88200   74.90000
  0.63600    0.86900   81.70000
  0.71800    0.84500   88.50000
  0.80000    0.80000   93.90000

T  256.3999    PS    1.8000    VOL   79.6212   81.5029

FISAT    0.9769    0.9555    FREESAT  104.3365    1.7200
CONSISTENCY TEST USING ORTHOGONAL COLLOCATION  -      NUMBER OF INTERNAL POINTS    2

COLLOCATION POINTS
  0.         0.211325  0.788675  1.000000

 NUMBER OF ITERATIONS IN G    4

 NUMBER OF ITERATIONS IN G    4
```

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 112.6140

NUMBER OF ITERATIONS IN G 3

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 112.5308

NUMBER OF ITERATIONS IN G 1

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 112.4911

NUMBER OF ITERATIONS IN G 1

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 112.5517

NUMBER OF ITERATIONS IN G 1

SOLUTION AT THE COLLOCATION POINTS

X	P	GE/RT	GOOI	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.3678	49.6207	-0.0544	-0.3442	0.7782	1.0617	0.9249	0.0755	1.0004	-115.9619
0.7105	87.4697	-0.2915	-1.1474	0.5391	1.6637	0.9069	0.0933	1.0001	-621.4653
0.8000	96.2919	-0.4086	-1.4745	0.4955	2.1507	0.9024	0.0977	1.0001	-870.9880

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GOOI
0.	1.0093	0.9555	81.5029	0.	112.1372	0.
0.3678	0.8412	0.3706	73.4460	-7.3648	95.9141	-0.0336
0.7105	0.7519	0.1411	74.8246	-5.3413	80.7967	-0.0205
0.8000	0.7347	0.1127	78.2168	-1.7807	76.8467	-0.0065

SOLUTION AT THE DATA POINTS

X	P	GE/RT	GOOI	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.0340	6.5340	-0.0027	-0.0194	0.9829	0.9979	0.6665	0.3335	0.8944	-5.6503
0.0890	14.0569	-0.0068	-0.0543	0.9546	0.9970	0.8283	0.1717	0.9013	-14.5862
0.1420	21.1484	-0.0114	-0.0932	0.9256	0.9995	0.8765	0.1235	0.9236	-24.3820
0.1970	28.3438	-0.0176	-0.1403	0.8934	1.0058	0.9001	0.0999	0.9476	-37.4765
0.2490	34.9933	-0.0254	-0.1923	0.8606	1.0161	0.9124	0.0876	0.9680	-54.1582
0.3030	41.7407	-0.0364	-0.2552	0.8243	1.0324	0.9199	0.0801	0.9854	-77.5227
0.3570	48.3274	-0.0510	-0.3283	0.7860	1.0559	0.9240	0.0760	0.9983	-108.6777
0.4100	54.6357	-0.0696	-0.4112	0.7471	1.0883	0.9257	0.0743	1.0066	-148.4313
0.4640	60.9037	-0.0938	-0.5083	0.7069	1.1336	0.9257	0.0743	1.0106	-199.9142
0.5180	67.0109	-0.1239	-0.6194	0.6667	1.1955	0.9240	0.0760	1.0109	-264.1243
0.5720	72.9574	-0.1608	-0.7456	0.6276	1.2802	0.9207	0.0793	1.0084	-342.7175
0.6360	79.7968	-0.2143	-0.9166	0.5833	1.4236	0.9145	0.0855	1.0031	-456.7668
0.7180	88.2298	-0.3003	-1.1728	0.5350	1.6947	0.9060	0.0940	0.9999	-640.2236
0.8000	96.2919	-0.4086	-1.4745	0.4955	2.1507	0.9023	0.0977	1.0001	-870.9880

CONSISTENCY TEST BY REPEATED HALVING OF TRAPZOIDAL RULE WITH ROMBERG INTEGRATION

CONSTANT= 0.112612D-11
CONSTANT= 0.382519D-11
CONSTANT= 0.934151D-11
CONSTANT= 0.185001D-10
CONSTANT= 0.341084D-10
CONSTANT= 0.954794D-10
CONSTANT= 0.150644D-09
CONSTANT= 0.230371D-09
CONSTANT= 0.343502D-09
CONSTANT= 0.538061D-09
CONSTANT= 0.898596D-09
CONSTANT= 0.145673D-08

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	P'AL	DP
0.	1.8000	0.	0.	0.	1.0000	1.0000	1.8000	-0.0000
0.0340	6.8000	0.6665	0.5600	0.1065	0.3335	1.0000	6.5340	-0.2660
0.0890	13.6000	0.8283	0.7670	0.0613	0.1717	1.0000	14.0569	0.4569
0.1420	20.4000	0.8765	0.8320	0.0445	0.1235	1.0000	21.1484	0.7484
0.1970	27.2000	0.9001	0.8610	0.0391	0.0999	1.0000	28.3438	1.1438
0.2490	34.0000	0.9124	0.8800	0.0324	0.0876	1.0000	34.9933	0.9933
0.3030	40.8000	0.9199	0.8880	0.0319	0.0801	1.0000	41.7407	0.9407
0.3570	47.6000	0.9240	0.8900	0.0340	0.0760	1.0000	48.3274	0.7274
0.4100	54.4000	0.9257	0.8920	0.0337	0.0743	1.0000	54.6357	0.2357
0.4640	61.2000	0.9257	0.8910	0.0347	0.0743	1.0000	60.9037	-0.2963
0.5180	68.0000	0.9240	0.8890	0.0350	0.0760	1.0000	67.0109	-0.9891
0.5720	74.9000	0.9207	0.8820	0.0387	0.0793	1.0000	72.9574	-1.9426
0.6360	81.7000	0.9145	0.8690	0.0455	0.0855	1.0000	79.7968	-1.9032
0.7180	88.5000	0.9060	0.8450	0.0610	0.0940	1.0000	88.2298	-0.2702
0.8000	93.9000	0.9023	0.8000	0.1023	0.0977	1.0000	96.2919	2.3919

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO BUBT
0.	1.0093	0.9555	81.5029	0.	112.1372	0.
0.0340	0.9832	0.8665	80.6193	-0.8197	110.6373	-0.0043
0.0890	0.9544	0.7531	79.2315	-2.1039	108.2111	-0.0100
0.1420	0.9298	0.6592	77.9509	-3.2848	105.8731	-0.0165
0.1970	0.9060	0.5739	76.6921	-4.4401	103.4469	-0.0210
0.2490	0.8848	0.5031	75.5819	-5.4524	101.1530	-0.0262
0.3030	0.8642	0.4384	74.5306	-6.4021	98.7709	-0.0301
0.3570	0.8448	0.3813	73.6105	-7.2206	96.3888	-0.0331
0.4100	0.8271	0.3319	72.8741	-7.8573	94.0508	-0.0351
0.4640	0.8103	0.2874	72.3549	-8.2749	91.6607	-0.0361
0.5180	0.7948	0.2479	72.1714	-8.3567	89.2866	-0.0355
0.5720	0.7808	0.2128	72.5131	-7.9135	86.9045	-0.0327
0.6360	0.7663	0.1761	74.1978	-6.1083	84.0813	-0.0244
0.7180	0.7505	0.1381	74.9800	-5.1718	80.4640	-0.0198
0.8000	0.7347	0.1127	78.2168	-1.7807	76.8467	-0.0065

```
 SUM OF SQUARES OF DELTA Y          0.0431585

 VARIANCE OF DELTA Y      0.0576   ARITHMETIC MEAN OF DELTA Y      0.0500

    CALCULATED EXCLUDING GIVEN END POINTS

 SUM OF SQUARES OF DELTA P        18.8602577

 VARIANCE    OF DELTA P      1.2045     ARITHMETIC MEAN OF DELTA P      0.9504

ARITHMETIC MEAN OF DELTA P/P         0.320483

 CALCULATED      EXCLUDING GIVEN END POINTS
STOP
TIME 2.9 SECS
```

Results of Run # 2 for the

CH_4-C_3H_8 System at -17°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 2 2
METHANE(1)-PROPANE(2)
 1
15
111
 1.8                              0.0                              0.0
 6.8                              0.034                            0.56
 13.6                             0.089                            0.767
 20.4                             0.142                            0.832
 27.2                             0.197                            0.861
 34.0                             0.249                            0.880
 40.8                             0.303                            0.888
 47.6                             0.357                            0.890
 54.4                             0.41                             0.892
 61.2                             0.464                            0.891
 68.0                             0.518                            0.889
 74.9                             0.572                            0.882
 81.7                      256.40 0.636                            0.869
 88.5                      256.40 0.718                            0.845
 93.9                      256.40 0.80                             0.80
 45.4          99.0        190.6        0.288        0.008
 41.9          203.0       369.8        0.281        0.152
 0.00618
-110.3206
 79.0164
 0.01
 0 0 0 0
```

The formated output is as follows:

EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR THE BINARY SYSTEM METHANE(1) PROPANE(2)

THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION PROCEDURE IS OF THE TYPE ALFA = 0. BETA = 0.

PC-VC-TC-ZC-ACEN 0.45400E+02 0.99000E+02 0.19060E+03 0.28800E+00 0.80000E-02

PC-VC-TC-ZC-ACEN 0.41900E+02 0.20300E+03 0.36980E+03 0.28100E+00 0.15200E+00

FAR-NY-IAU-DEL

0.00610

-110.32060

79.01640

0.01000

NUMBER OF BINARY POINTS 15 AT THE ISOTHERM 256.40 TEMPERATURE IN DEG K

XEXP	YEXP	PEXP
0.	0.	1.80000
0.03400	0.56000	6.80000
0.08900	0.76700	13.60000
0.14200	0.83200	20.40000
0.19700	0.86100	27.20000
0.24900	0.88000	34.00000
0.30500	0.88800	40.80000
0.35700	0.89000	47.60000
0.41000	0.89200	54.40000
0.46400	0.89100	61.20000
0.51800	0.88900	68.00000
0.57200	0.88200	74.90000
0.63600	0.86900	81.70000
0.71800	0.84500	88.50000
0.80000	0.80080	93.90000

I 256.3999 PS 1.8000 VOL 83.5936 81.5029

FISAT 0.9774 0.9555 FREESAT 104.5793 1.7200

CONSISTENCY TEST USING ORTHOGONAL COLLOCATION - NUMBER OF INTERNAL POINTS 2

COLLOCATION POINTS

0. 0.211325 0.788675 1.000000

NUMBER OF ITERATIONS IN G 4

NUMBER OF ITERATIONS IN G 4

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 113.1255

NUMBER OF ITERATIONS IN G 3

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 113.0136

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 113.0158

NUMBER OF ITERATIONS IN G 1

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 113.0219

NUMBER OF ITERATIONS IN G 1

SOLUTION AT THE COLLOCATION POINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.3678	49.6207	-0.0572	-0.3583	0.7723	1.0615	0.9308	0.0693	1.0000	-122.0302
0.7105	87.4697	-0.2985	-1.1539	0.5361	1.6471	0.9294	0.0706	1.0000	-636.3591
0.8000	96.2919	-0.4158	-1.4738	0.4932	2.1144	0.9306	0.0694	1.0000	-806.3599

X	FUGCF1	FUGCF2	VMIX	VE	DF/DX	CORR TO GDOT
0.	1.0119	0.9555	81.5029	0.	112.1372	0.
0.3678	0.8405	0.4041	73.4460	-8.0257	95.9141	-0.0402
0.7105	0.7442	0.1850	74.0246	-8.1636	80.7967	-0.0314
0.8000	0.7243	0.1570	78.2168	-4.9586	76.8467	-0.0181

SOLUTION AT THE DATA POINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.0340	6.5340	-0.0026	-0.0212	0.9820	0.9980	0.6682	0.3318	0.9950	-5.4854
0.0890	14.0569	-0.0068	-0.0589	0.9522	0.9973	0.8310	0.1690	0.9917	-14.5705
0.1420	21.1484	-0.0117	-0.1003	0.9221	0.9998	0.8798	0.1202	0.9236	-24.9361
0.1970	28.3438	-0.0183	-0.1497	0.8808	1.0062	0.9040	0.0960	0.9474	-38.7883
0.2490	34.9953	-0.0267	-0.2035	0.8553	1.0164	0.9169	0.0831	0.9676	-56.0541
0.3030	41.7407	-0.0383	-0.2680	0.8186	1.0326	0.9250	0.0750	0.9850	-81.6647
0.3570	48.3274	-0.0537	-0.3422	0.7802	1.0559	0.9300	0.0700	0.9980	-114.4161
0.4100	54.6357	-0.0731	-0.4258	0.7414	1.0877	0.9328	0.0672	1.0064	-155.0139
0.4640	60.9037	-0.0980	-0.5230	0.7014	1.1322	0.9341	0.0659	1.0106	-208.9807
0.5180	67.0109	-0.1289	-0.6335	0.6617	1.1929	0.9343	0.0657	1.0112	-274.8127
0.5720	72.9574	-0.1665	-0.7586	0.6230	1.2756	0.9334	0.0666	1.0087	-354.8953
0.6360	79.7968	-0.2207	-0.9273	0.5795	1.4150	0.9312	0.0688	1.0033	-470.4495
0.7180	88.2298	-0.3073	-1.1788	0.5320	1.6769	0.9293	0.0707	0.9998	-655.2031
0.8000	96.2919	-0.4158	-1.4738	0.4932	2.1144	0.9306	0.0694	1.0000	-806.3599

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GOUT
0.	1.0119	0.9555	81.5029	0.	112.1372	0.
0.0340	0.9841	0.8705	80.6193	-0.9547	110.6373	-0.0050
0.0890	0.9547	0.7651	79.2315	-2.4574	108.2111	-0.0126
0.1420	0.9299	0.6775	77.9509	-3.8482	105.8731	-0.0194
0.1970	0.9059	0.5975	76.6921	5.2226	103.4469	-0.0257
0.2490	0.8847	0.5305	75.5819	-6.4415	101.1530	-0.0310
0.3030	0.8639	0.4689	74.5306	-7.6058	98.7709	-0.0357
0.3570	0.8443	0.4143	73.6105	-8.6388	96.3008	-0.0396
0.4100	0.8263	0.3667	72.8741	-9.4860	94.0508	-0.0424
0.4640	0.8098	0.3238	72.3549	-10.1181	91.6687	-0.0441
0.5180	0.7929	0.2858	72.1714	-10.4144	89.2866	-0.0442
0.5720	0.7780	0.2522	72.5131	-10.1857	86.9045	-0.0421
0.6360	0.7617	0.2176	74.1970	-8.6348	84.0813	-0.0345
0.7180	0.7425	0.1822	74.9800	-8.0240	80.4648	-0.0307
0.8000	0.7243	0.1570	78.2168	-4.9586	76.8467	-0.0181

CONSISTENCY TEST BY REPEATED HALVING OF TRAPZOIDAL RULE WITH ROMBERG INTEGRATION

CONSTANT= 0.127060D-11
CONSTANT= 0.425136D-11
CONSTANT= 0.102210D-10
CONSTANT= 0.199571D-10
CONSTANT= 0.362921D-10
CONSTANT= 0.617417D-10
CONSTANT= 0.991893D-10
CONSTANT= 0.154878D-09
CONSTANT= 0.234639D-09
CONSTANT= 0.346942D-09
CONSTANT= 0.538690D-09
CONSTANT= 0.890960D-09
CONSTANT= 0.143251D-08

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	PCAL	DP
0.	1.8000	0.	0.	0.	1.0000	1.0000	1.8000	-0.0000
0.0340	6.8000	0.6682	0.5600	0.1082	0.3318	1.0000	6.5340	-0.2660
0.0890	13.6000	0.8310	0.7670	0.0640	0.1690	1.0000	14.0569	0.4569
0.1420	20.4000	0.8798	0.8320	0.0478	0.1202	1.0000	21.1484	0.7484
0.1970	27.2000	0.9040	0.8610	0.0430	0.0960	1.0000	28.3438	1.1438
0.2490	34.0000	0.9169	0.8800	0.0369	0.0831	1.0000	34.9933	0.9933
0.3030	40.8000	0.9250	0.8880	0.0370	0.0750	1.0000	41.7407	0.9407
0.3570	47.6000	0.9300	0.8900	0.0400	0.0700	1.0000	48.3274	0.7274
0.4100	54.4000	0.9328	0.8920	0.0408	0.0672	1.0000	54.6357	0.2357
0.4640	61.2000	0.9341	0.8910	0.0431	0.0659	1.0000	60.9037	-0.2963
0.5180	68.0000	0.9343	0.8890	0.0453	0.0657	1.0000	67.0109	-0.9891
0.5720	74.9000	0.9334	0.8820	0.0514	0.0666	1.0000	72.9574	-1.9426
0.6360	81.7000	0.9312	0.8690	0.0622	0.0688	1.0000	79.7968	-1.9032
0.7180	88.5000	0.9293	0.8450	0.0843	0.0707	1.0000	88.2298	-0.2702
0.8000	93.9000	0.9306	0.8000	0.1306	0.0694	1.0000	96.2919	2.3919

```
 SUM OF SQUARES OF DELTA Y          0.0605322

 VARIANCE OF DELTA Y      0.0682   ARITHMETIC MEAN OF DELTA Y      0.0596

    CALCULATED EXCLUDING GIVEN END POINTS

 SUM OF SQUARES OF DELTA P         18.8602577

 VARIANCE    OF DELTA P      1.2045     ARITHMETIC MEAN OF DELTA P      0.9504

ARITHMETIC MEAN OF DELTA P/P         0.320483

 CALCULATED      EXCLUDING GIVEN END POINTS
STOP
TIME 2.9 SECS
```

Results of Run # 3 for the

CH_4-C_3H_8 System at -17°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 2 2
METHANE(1)-PROPANE(2)
 1
15
111
 1.8                              0.0                              0.0
 6.8                              0.034                            0.56
 13.6                             0.089                            0.767
 20.4                             0.142                            0.832
 27.2                             0.197                            0.861
 34.0                             0.249                            0.880
 40.8                             0.303                            0.888
 47.6                             0.357                            0.890
 54.4                             0.41                             0.892
 61.2                             0.464                            0.891
 68.0                             0.518                            0.889
 74.9                             0.572                            0.882
 81.7                    256.40   0.636                            0.869
 88.5                    256.40   0.718                            0.845
 93.9                    256.40   0.80                             0.80
 45.4          99.0      190.6            0.288          0.008
 41.9          203.0     369.8            0.281          0.152
 0.00618
-110.3206
 79.0164
 0.05
 0 0 0 0
```

The formated output is as follows:

EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR THE BINARY SYSTEM METHANE(1)-PROPANE(2)

THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION PROCEDURE IS OF THE TYPE ALFA = 0. BETA = 0.

PC-VC-TC-ZC-ACEN 0.45400E+02 0.99000E+02 0.19060E+03 0.28800E+00 0.00000E-02

PC-VC-TC-ZC-ACEN 0.41900E+02 0.20300E+03 0.36980E+03 0.28100E+00 0.15200E+00

FAK-NY-TAU-DEL

0.00618

-110.32060

79.01640

0.05000

NUMBER OF BINARY POINTS 15 AT THE ISOTHERM 256.40 TEMPERATURE IN DEG K

XEXP	YEXP	PEXP
0.	0.	1.00000
0.03400	0.56000	6.80000
0.08900	0.76700	13.60000
0.14200	0.83200	20.40000
0.19700	0.86100	27.20000
0.24900	0.88000	34.00000
0.30300	0.88800	40.80000
0.35700	0.89000	47.60000
0.41000	0.89200	54.40000
0.46400	0.89100	61.20000
0.51800	0.88900	68.00000
0.57200	0.88200	74.70000
0.63600	0.86900	81.70000
0.71800	0.84500	88.50000
0.80000	0.80000	93.90000

T 256.3999 PS 1.0000 VOL 86.2419 81.5029

FISAT 0.9777 0.9555 FREESAT 104.7392 1.7200

CONSISTENCY TEST USING ORTHOGONAL COLLOCATION - NUMBER OF INTERNAL POINTS 2

COLLOCATION POINTS

0. 0.211325 0.788675 1.000000

NUMBER OF ITERATIONS IN G 4

NUMBER OF ITERATIONS IN G 4

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 113.4470

NUMBER OF ITERATIONS IN G 3

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 113.3264

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 113.3218

NUMBER OF ITERATIONS IN G 1

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 113.3187

NUMBER OF ITERATIONS IN G 1

SOLUTION AT THE COLLOCATION POINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.3678	49.6207	-0.0592	-0.3676	0.7685	1.0614	0.9345	0.0655	1.0000	-126.1085
0.7105	87.4697	-0.3038	-1.1635	0.5328	1.6411	0.9390	0.0610	1.0000	-647.7395
0.8000	96.2919	-0.4219	-1.4830	0.4900	2.1039	0.9414	0.0586	1.0000	-899.5103

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GDOT
0.	1.0137	0.9555	81.5029	0.	112.1372	0.
0.3678	0.8402	0.4275	73.4460	-9.7997	95.9141	-0.0447
0.7105	0.7421	0.2133	74.8246	-10.0451	80.7967	-0.0386
0.8000	0.7218	0.1849	78.2168	-7.0773	76.8467	-0.0258

SOLUTION AT THE DATA POINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.0340	6.5340	-0.0026	-0.0226	0.9810	0.9980	0.6693	0.3307	0.8250	-5.5271
0.0890	14.0569	-0.0070	-0.0624	0.9501	0.9974	0.8327	0.1673	0.9014	-14.8548
0.1420	21.1484	-0.0120	-0.1055	0.9192	0.9999	0.8819	0.1181	0.9231	-25.6409
0.1970	28.3438	-0.0189	-0.1563	0.8854	1.0063	0.9065	0.0935	0.9468	-40.3016
0.2490	34.9933	-0.0276	-0.2112	0.8516	1.0166	0.9197	0.0803	0.9671	-58.0840
0.3030	41.7407	-0.0397	-0.2765	0.8147	1.0327	0.9283	0.0717	0.9847	-84.5633
0.3570	48.3274	-0.0555	-0.3514	0.7763	1.0558	0.9337	0.0663	0.9979	-118.2893
0.4100	54.6357	-0.0754	-0.4355	0.7375	1.0874	0.9370	0.0630	1.0065	-160.7264
0.4640	60.9037	-0.1009	-0.5329	0.6977	1.1314	0.9390	0.0610	1.0109	-215.0154
0.5180	67.0109	-0.1323	-0.6436	0.6581	1.1915	0.9399	0.0601	1.0115	-282.0125
0.5720	72.9574	-0.1704	-0.7687	0.6196	1.2733	0.9400	0.0600	1.0091	-363.2815
0.6360	79.7968	-0.2253	-0.9372	0.5761	1.4114	0.9392	0.0608	1.0035	-480.2310
0.7180	88.2298	-0.3128	-1.1884	0.5208	1.6707	0.9390	0.0610	0.9997	666.7395
0.8000	96.2919	-0.4219	-1.4830	0.4900	2.1039	0.9414	0.0586	1.0000	899.5103

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GODT
0.	1.0137	0.9555	81.5029	0.	112.1372	0.
0.0340	0.9846	0.8731	80.6193	-1.0448	110.6373	-0.0055
0.0890	0.9550	0.7731	79.2315	-2.6931	108.2111	-0.0139
0.1420	0.9300	0.6899	77.9509	-4.2250	105.8731	-0.0213
0.1970	0.9059	0.6136	76.6921	-5.7444	103.4469	-0.0282
0.2490	0.8846	0.5495	75.5019	-7.1010	101.1530	-0.0341
0.3030	0.8637	0.4901	74.5306	-8.4082	98.7709	-0.0395
0.3570	0.8440	0.4373	73.6105	-9.5842	96.3888	-0.0439
0.4100	0.8258	0.3911	72.8741	-10.5710	94.0508	-0.0473
0.4640	0.8084	0.3493	72.3549	-11.3469	91.6687	-0.0494
0.5180	0.7921	0.3122	72.1714	-11.7862	89.2866	-0.0500
0.5720	0.7769	0.2793	72.5131	-11.7005	86.9045	-0.0483
0.6360	0.7601	0.2454	74.1978	-10.3191	84.0813	-0.0417
0.7180	0.7403	0.2105	74.9800	-9.9254	80.4640	0.0500
0.8000	0.7218	0.1849	78.2168	-7.0773	76.8467	-0.0258

CONSISTENCY TEST BY REPEATED HALVING OF TRAPZOIDAL RULE WITH ROMBERG INTEGRATION

CONSTANT= 0.139669D-11
CONSTANT= 0.459796D-11
CONSTANT= 0.108902D-10
CONSTANT= 0.210072D-10
CONSTANT= 0.377985D-10
CONSTANT= 0.637426D-10
CONSTANT= 0.101683D-09
CONSTANT= 0.157846D-09
CONSTANT= 0.238014D-09
CONSTANT= 0.350615D-09
CONSTANT= 0.542522D-09
CONSTANT= 0.894536D-09
CONSTANT= 0.143531D-08

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	PCAL	DP
0.	1.8000	0.	0.	0.	1.0000	1.0000	1.8000	0.0000
0.0340	6.8000	0.6693	0.5600	0.1093	0.3307	1.0000	6.5340	-0.2660
0.0890	13.6000	0.8327	0.7670	0.0657	0.1673	1.0000	14.0569	0.4569
0.1420	20.4000	0.8819	0.8320	0.0499	0.1181	1.0000	21.1484	0.7484
0.1970	27.2000	0.9065	0.8610	0.0455	0.0935	1.0000	28.3438	1.1438
0.2490	34.0000	0.9197	0.8800	0.0397	0.0803	1.0000	34.9933	0.9933
0.3030	40.8000	0.9283	0.8880	0.0403	0.0717	1.0000	41.7407	0.9407
0.3570	47.6000	0.9337	0.8900	0.0437	0.0663	1.0000	48.3274	0.7274
0.4100	54.4000	0.9370	0.8920	0.0450	0.0630	1.0000	54.6457	0.2357
0.4640	61.2000	0.9390	0.8910	0.0480	0.0610	1.0000	60.9037	-0.2963
0.5180	68.0000	0.9399	0.8890	0.0509	0.0601	1.0000	67.0109	-0.9891
0.5720	74.9000	0.9400	0.8820	0.0580	0.0600	1.0000	72.9574	-1.9426
0.6360	81.7000	0.9392	0.8690	0.0702	0.0608	1.0000	79.7968	-1.9032
0.7180	88.5000	0.9390	0.8450	0.0940	0.0610	1.0000	88.2298	-0.2702
0.8000	93.9000	0.9414	0.8000	0.1414	0.0586	1.0000	96.2919	2.3919

```
 SUM OF SQUARES OF DELTA Y          0.0699474

 VARIANCE OF DELTA Y      0.0734   ARITHMETIC MEAN OF DELTA Y      0.0644

    CALCULATED EXCLUDING GIVEN END POINTS

 SUM OF SQUARES OF DELTA P         18.0602577

 VARIANCE    OF DELTA P      1.2045     ARITHMETIC MEAN OF DELTA P      0.9504

ARITHMETIC MEAN OF DELTA P/P        0.320483

 CALCULATED      EXCLUDING GIVEN END POINTS
STOP
TIME 2.9 SECS
```

Results of Run # 4 for the

CH_4-C_3H_8 System at -17°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 2 2
METHANE(1)-PROPANE(2)
 1
15
111
 1.8                              0.0                              0.0
 6.8                              0.034                            0.56
 13.6                             0.089                            0.767
 20.4                             0.142                            0.832
 27.2                             0.197                            0.861
 34.0                             0.249                            0.880
 40.8                             0.303                            0.888
 47.6                             0.357                            0.890
 54.4                             0.41                             0.892
 61.2                             0.464                            0.891
 68.0                             0.518                            0.889
 74.9                             0.572                            0.882
 81.7                      256.40 0.636                            0.869
 88.5                      256.40 0.718                            0.845
 93.9                      256.40 0.80                             0.80
 45.4          99.0        190.6        0.288        0.008
 41.9          203.0       369.8        0.281        0.008
 0.4546        0.0872      0.4278       0.0867
 0.4138        0.0802      0.4380       0.0889
 0.01113
 -110.3206
 79.0164
 0 0 0 0
```

The formated output is as follows:

```
EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR     THE BINARY SYSTEM    METHANE(1)-PROPANE(2)
**********************************************************************************************************************

 THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION    PROCEDURE IS OF THE TYPE ALFA  =      0.       BETA  =      0.


PC-VC-TC-ZC-ACEN      0.45400E+02 0.99000E+02 0.19060E+03 0.28800E+00 0.80000E-02

PC-VC-TC-ZC-ACEN      0.41900E+02 0.20300E+03 0.36980E+03 0.28100E+00 0.80000E-02

OMAL-OMBL-OMAG-OMBG       0.45460E+00 0.87200E-01 0.42780E+00 0.86700E-01

OMAL-OMBL-OMAG-OMBG       0.41380E+00 0.80200E-01 0.43800E+00 0.88900E-01

FAK-NY-TAU

   0.01113

-110.32060

  79.01640

NUMBER OF BINARY POINTS   15      AT THE ISOTHERM     256.40      TEMPERATURE IN DEG K

     XEXP       YEXP       PEXP
  0.          0.          1.80000
  0.03400     0.56000     6.80000
  0.08900     0.76700    13.60000
  0.14200     0.83200    20.40000
  0.19700     0.86100    27.20000
  0.24900     0.88000    34.00000
  0.30300     0.88800    40.80000
  0.35700     0.89000    47.60000
  0.41000     0.89200    54.40000
  0.46400     0.89100    61.20000
  0.51800     0.88900    68.00000
  0.57200     0.88200    74.90000
  0.63600     0.86900    81.70000
  0.71800     0.84500    88.50000
  0.80000     0.80000    93.70000

T  256.3999     PS     1.8000     VOL    80.6475    83.5078

FISAT     0.9811     0.9586     FREESAT  105.0540     1.7255
CONSISTENCY TEST USING ORTHOGONAL COLLOCATION  -       NUMBER OF INTERNAL POINTS     2

COLLOCATION POINTS
  0.          0.211325  0.788675  1.000000

 NUMBER OF ITERATIONS IN G     4
```

NUMBER OF ITERATIONS IN G 3

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 115.7748

NUMBER OF ITERATIONS IN G 3

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 115.6550

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 115.6515

NUMBER OF ITERATIONS IN G 1

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 115.6502

NUMBER OF ITERATIONS IN G 1

SOLUTION AT THE COLLOCATION POINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.3678	49.6207	-0.0549	-0.3410	0.7811	1.0585	0.9344	0.0656	1.0000	-116.9726
0.7105	87.4697	-0.2825	-1.0858	0.5542	1.6043	0.9370	0.0630	1.0000	-602.1941
0.8000	96.2919	-0.3929	-1.3885	0.5122	2.0380	0.9392	0.0608	1.0000	-837.5371

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GDOT
0.	1.0118	0.9586	83.5078	0.	112.1372	0.
0.3678	0.8607	0.4292	74.3160	-8.1398	95.9141	-0.0371
0.7105	0.7716	0.2043	75.5323	-5.9434	80.7967	-0.0228
0.8000	0.7527	0.1747	79.1824	-2.0371	76.8467	-0.0074

SOLUTION AT THE DATA POINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.0340	6.5340	-0.0025	-0.0216	0.9814	0.9981	0.6739	0.3261	0.9044	-5.3677
0.0890	14.0569	-0.0067	-0.0590	0.9517	0.9975	0.8351	0.1649	0.9096	-14.2514
0.1420	21.1484	-0.0114	-0.0991	0.9224	1.0001	0.8833	0.1167	0.9292	-24.3267
0.1970	28.3433	-0.0178	-0.1461	0.8907	1.0063	0.9073	0.0927	0.9508	-37.8785
0.2490	34.9933	-0.0258	-0.1967	0.8592	1.0161	0.9202	0.0798	0.9695	-54.9935
0.3030	41.7407	-0.0369	-0.2569	0.8246	1.0314	0.9285	0.0715	0.9857	-78.6440
0.3570	48.3274	-0.0515	-0.3260	0.7885	1.0532	0.9337	0.0663	0.9980	-109.7522
0.4100	54.6357	-0.0699	-0.4038	0.7519	1.0830	0.9368	0.0632	1.0061	-148.9739
0.4640	60.9037	-0.0935	-0.4943	0.7139	1.1246	0.9385	0.0615	1.0103	-199.2540
0.5180	67.0109	-0.1226	-0.5974	0.6759	1.1812	0.9391	0.0609	1.0109	-261.4275
0.5720	72.9574	-0.1581	-0.7143	0.6387	1.2584	0.9388	0.0612	1.0085	-336.9824
0.6360	79.7968	-0.2092	-0.8725	0.5964	1.3889	0.9376	0.0624	1.0031	-445.9023
0.7180	88.2298	-0.2908	-1.1093	0.5502	1.6321	0.9370	0.0630	0.9997	-619.9385
0.8000	96.2919	-0.3929	-1.3885	0.5122	2.0300	0.9392	0.0608	1.0000	-837.5371

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GOUT
0.	1.0110	0.9586	83.5078	0.	112.1372	0.
0.0340	0.9868	0.8797	82.5042	-0.9063	110.6373	-0.0048
0.0890	0.9614	0.7807	80.9270	-2.3262	108.2111	-0.0120
0.1420	0.9398	0.6973	79.4698	-3.6318	105.8731	-0.0183
0.1970	0.9189	0.6202	78.0355	-4.9088	103.4469	-0.0241
0.2490	0.9001	0.5548	76.7680	-6.0276	101.1530	-0.0290
0.3030	0.8816	0.4939	75.5643	-7.0768	98.7709	-0.0332
0.3570	0.8641	0.4393	74.5060	-7.9807	96.3888	-0.0366
0.4100	0.8478	0.3913	73.6516	-8.6835	94.0508	-0.0388
0.4640	0.8321	0.3476	73.0362	-9.1444	91.6687	-0.0398
0.5180	0.8173	0.3086	72.7908	-9.2354	89.2866	-0.0392
0.5720	0.8034	0.2739	73.1230	-8.7487	86.9045	-0.0361
0.6360	0.7882	0.2381	74.9281	-6.7605	84.0813	-0.0270
0.7180	0.7700	0.2013	75.7134	-5.7406	80.4640	-0.0220
0.8000	0.7527	0.1747	79.1824	-2.0371	76.8467	-0.0074

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	PLAI	DP
0.	1.0000	0.	0.	0.	1.0000	1.0000	1.0000	-0.0000
0.0340	6.8000	0.6739	0.5600	0.1139	0.3261	1.0000	6.5340	-0.2660
0.0890	13.6000	0.8351	0.7670	0.0681	0.1649	1.0000	14.0569	0.4569
0.1420	20.4000	0.8833	0.8320	0.0513	0.1167	1.0000	21.1484	0.7484
0.1970	27.2000	0.9073	0.8610	0.0463	0.0927	1.0000	28.3438	1.1438
0.2490	34.0000	0.9202	0.8800	0.0402	0.0798	1.0000	34.9933	0.9933
0.3030	40.8000	0.9285	0.8880	0.0405	0.0715	1.0000	41.7407	0.9407
0.3570	47.6000	0.9337	0.8900	0.0437	0.0663	1.0000	48.3274	0.7274
0.4100	54.4000	0.9368	0.8920	0.0448	0.0632	1.0000	54.6357	0.2357
0.4640	61.2000	0.9385	0.8910	0.0475	0.0615	1.0000	60.9037	-0.2963
0.5180	68.0000	0.9391	0.8890	0.0501	0.0609	1.0000	67.0109	-0.9891
0.5720	74.9000	0.9388	0.8820	0.0568	0.0612	1.0000	72.9574	-1.9426
0.6360	81.7000	0.9376	0.8690	0.0686	0.0624	1.0000	79.7968	-1.9032
0.7180	88.5000	0.9370	0.8450	0.0920	0.0630	1.0000	88.2298	-0.2702
0.8000	93.9000	0.9392	0.8000	0.1392	0.0608	1.0000	96.2919	2.3919

SUM OF SQUARES OF DELTA Y 0.0700868

VARIANCE OF DELTA Y 0.0734 ARITHMETIC MEAN OF DELTA Y 0.0645

CALCULATED EXCLUDING GIVEN END POINTS

SUM OF SQUARES OF DELTA P 18.8602587

VARIANCE OF DELTA P 1.2045 ARITHMETIC MEAN OF DELTA P 0.9504

ARITHMETIC MEAN OF DELTA P/P 0.320483

CALCULATED EXCLUDING GIVEN END POINTS

STOP

TIME 2.5 SECS

Results of Run # 5 for the

CH_4-C_3H_8 System at -17°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 3 3
METHANE(1)-PROPANE(2)
 1
15
111
 1.8                              0.0                              0.0
 6.8                              0.034                            0.56
 13.6                             0.089                            0.767
 20.4                             0.142                            0.832
 27.2                             0.197                            0.861
 34.0                             0.249                            0.880
 40.8                             0.303                            0.888
 47.6                             0.357                            0.890
 54.4                             0.41                             0.892
 61.2                             0.464                            0.891
 68.0                             0.518                            0.889
 74.9                             0.572                            0.882
 81.7                    256.40   0.636                            0.869
 88.5                    256.40   0.718                            0.845
 93.9                    256.40   0.80                             0.80
 45.4          99.0      190.6          0.288       0.008
 41.9          203.0     369.8          0.281       0.152
 0.00618
-110.3206
 79.0164
 0.01
 0 0 0 0
```

The formated output is as follows:

EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR THE BINARY SYSTEM METHANE(1)-PROPANE(2)

****

THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION PROCEDURE IS OF THE TYPE ALFA = 0. BETA = 0.

PC-VC-TC-ZC-ACEN 0.45400E+02 0.99000E+02 0.19060E+03 0.28800E+00 0.80000E-02

PC-VC-TC-ZC-ACEN 0.41900E+02 0.20300E+03 0.36980E+03 0.28100E+00 0.15200E+00

FAK-NY-TAU-DEL

0.00618

-110.32060

79.01640

0.01000

NUMBER OF BINARY POINTS 15 AT THE ISOTHERM 256.40 TEMPERATURE IN DEG K

XEXP	YEXP	PEXP
0.	0.	1.80000
0.03400	0.56000	6.80000
0.08900	0.76700	13.60000
0.14200	0.83200	20.40000
0.19700	0.86100	27.20000
0.24900	0.88000	34.00000
0.30300	0.88800	40.80000
0.35700	0.89000	47.60000
0.41000	0.89200	54.40000
0.46400	0.89100	61.20000
0.51800	0.88900	68.00000
0.57200	0.88200	74.90000
0.63600	0.86900	81.70000
0.71800	0.84500	88.50000
0.80000	0.80000	93.90000

T 256.3999 PS 1.8000 VOL 83.5936 81.5029

FISAT 0.9774 0.9555 FREESAT 104.5793 1.7200

CONSISTENCY TEST USING ORTHOGONAL COLLOCATION - NUMBER OF INTERNAL POINTS 3

COLLOCATION POINTS

0. 0.112702 0.500000 0.887298 1.000000

NUMBER OF ITERATIONS IN G 4

NUMBER OF ITERATIONS IN B 4

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 120.6768

NUMBER OF ITERATIONS IN G 3

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 120.4842

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 120.4700

NUMBER OF ITERATIONS IN G 1

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 120.4558

NUMBER OF ITERATIONS IN G 1

SOLUTION AT THE COLLOCATION POINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.2686	37.4570	-0.0327	-0.2727	0.8120	1.0323	0.9216	0.0783	0.9999	-69.4993
0.5657	72.2703	-0.1920	-0.8475	0.5818	1.3013	0.9303	0.0697	1.0000	402.3806
0.7536	91.7727	-0.3973	-1.3717	0.4823	1.8537	0.9284	0.0716	1.0000	-847.0510
0.8000	96.2919	-0.4650	-1.5508	0.4623	2.1406	0.9294	0.0706	1.0000	-991.3816

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GDOT
0.	1.0119	0.9555	81.5029	0.	112.1372	0.
0.2686	0.8769	0.5080	75.1077	-6.8766	100.2898	-0.0328
0.5657	0.7802	0.2535	72.4361	-10.2494	87.1831	-0.0425
0.7536	0.7347	0.1694	76.2819	-6.7964	78.8940	-0.0255
0.8000	0.7246	0.1562	78.2168	-4.9586	76.8467	-0.0181

SOLUTION AT THE DATA POINTS

X	P	GE/RT	GDOT	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.8000	0.	0.	1.0000	1.0000	0.	1.0000	1.0000	0.
0.0340	6.5340	0.0002	-0.0031	1.0021	1.0002	0.6067	0.3133	0.9480	0.5087
0.0890	14.0569	-0.0019	-0.0339	0.9790	1.0000	0.8437	0.1563	0.9739	-4.0014
0.1420	21.1484	-0.0070	-0.0870	0.9370	1.0026	0.8882	0.1118	0.9915	-14.8068
0.1970	28.3438	-0.0157	-0.1599	0.8839	1.0108	0.9089	0.0911	0.9991	-33.4451
0.2490	34.9933	-0.0274	-0.2403	0.8314	1.0251	0.9191	0.0809	1.0002	-58.3472
0.3030	41.7407	-0.0434	-0.3319	0.7789	1.0475	0.9250	0.0750	0.9989	-92.4669
0.3570	48.3274	-0.0637	-0.4291	0.7304	1.0782	0.9283	0.0717	0.9974	-135.8246
0.4100	54.6357	-0.0883	-0.5284	0.6872	1.1173	0.9300	0.0700	0.9969	-180.7843
0.4640	60.9037	-0.1186	-0.6336	0.6475	1.1676	0.9307	0.0693	0.9976	-232.0859
0.5180	67.0109	-0.1548	-0.7439	0.6114	1.2308	0.9307	0.0693	0.9989	-329.9360
0.5720	72.9574	-0.1974	-0.8617	0.5780	1.3119	0.9302	0.0698	1.0000	-420.7576
0.6360	79.7968	-0.2572	-1.0163	0.5409	1.4438	0.9290	0.0710	0.9999	-548.2763
0.7180	88.2298	-0.3504	-1.2514	0.4992	1.6923	0.9285	0.0715	1.0006	-747.0249
0.8000	96.2919	-0.4650	-1.5508	0.4623	2.1406	0.9294	0.0706	1.0000	-991.3816

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GOUT
0.	1.0119	0.9555	81.5029	0.	112.1372	0.
0.0340	0.9832	0.8720	80.6193	-0.9547	110.6373	-0.0050
0.0890	0.9541	0.7677	79.2315	-2.4574	108.2111	-0.0126
0.1420	0.9294	0.6801	77.9509	-3.8489	105.8731	-0.0194
0.1970	0.9056	0.5995	76.6921	-5.2226	103.4469	-0.0257
0.2490	0.8845	0.5316	75.5819	-6.4415	101.1530	-0.0310
0.3030	0.8639	0.4689	74.5306	-7.6058	98.7709	-0.0357
0.3570	0.8445	0.4132	73.6105	-8.6388	96.3808	-0.0396
0.4100	0.8266	0.3648	72.8741	-9.4860	94.0508	-0.0424
0.4640	0.8095	0.3213	72.3549	-10.1181	91.6807	-0.0441
0.5180	0.7935	0.2832	72.1714	-10.4144	89.2866	-0.0442
0.5720	0.7705	0.2498	72.5131	-10.1857	86.9045	-0.0421
0.6360	0.7621	0.2160	74.1978	-8.6548	84.0813	-0.0345
0.7180	0.7427	0.1816	74.9800	-8.0240	80.4640	-0.0307

CONSISTENCY TEST BY REPEATED HALVING OF TRAPZOIDAL RULE WITH ROMBERG INTEGRATION

CONSTANT= 0.302474D-12
CONSTANT= 0.309231D-11
CONSTANT= 0.121691D-10
CONSTANT= 0.296268D-10
CONSTANT= 0.593199D-10
CONSTANT= 0.102564D-09
CONSTANT= 0.159706D-09
CONSTANT= 0.234969D-09
CONSTANT= 0.331006D-09
CONSTANT= 0.454219D-09
CONSTANT= 0.651697D-09
CONSTANT= 0.100749D-08
CONSTANT= 0.158815D-08

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	PCAL	DP
0.	1.8000	0.	0.	0.	1.0000	1.0000	1.8000	-0.0000
0.0340	6.8000	0.6867	0.5600	0.1267	0.3133	1.0000	6.5340	-0.2660
0.0890	13.6000	0.8437	0.7670	0.0767	0.1563	1.0000	14.0569	0.4569
0.1420	20.4000	0.8882	0.8320	0.0562	0.1118	1.0000	21.1484	0.7484
0.1970	27.2000	0.9089	0.8610	0.0479	0.0911	1.0000	28.3438	1.1438
0.2490	34.0000	0.9191	0.8800	0.0391	0.0809	1.0000	34.9933	0.9933
0.3030	40.8000	0.9250	0.8880	0.0370	0.0750	1.0000	41.7407	0.9407
0.3570	47.6000	0.9283	0.8900	0.0383	0.0717	1.0000	48.3274	0.7274
0.4100	54.4000	0.9300	0.8920	0.0380	0.0700	1.0000	54.6357	0.2357
0.4640	61.2000	0.9307	0.8910	0.0397	0.0693	1.0000	60.9037	-0.2963
0.5180	68.0000	0.9307	0.8890	0.0417	0.0693	1.0000	67.0109	-0.9891
0.5720	74.9000	0.9302	0.8820	0.0482	0.0698	1.0000	72.9574	-1.9426
0.6360	81.7000	0.9290	0.8690	0.0600	0.0710	1.0000	79.7968	-1.9032
0.7180	88.5000	0.9285	0.8450	0.0835	0.0715	1.0000	88.2298	-0.2702
0.8000	93.9000	0.9294	0.8000	0.1294	0.0706	1.0000	96.2919	2.3919

```
 SUM OF SQUARES OF DELTA Y          0.0661260

 VARIANCE OF DELTA Y      0.0713   ARITHMETIC MEAN OF DELTA Y      0.0616

    CALCULATED EXCLUDING GIVEN END POINTS

 SUM OF SQUARES OF DELTA P         18.8602577

 VARIANCE    OF DELTA P      1.2045     ARITHMETIC MEAN OF DELTA P      0.9504

ARITHMETIC MEAN OF DELTA P/P         0.160241

 CALCULATED      EXCLUDING GIVEN END POINTS
STOP
TIME 3.1 SECS
```

Results of Run # 6 for the

CH_4-C_3H_8 System at -17°C.

See Table 1 for the Values of the

Pertinent Variables Used.

The formated input is as follows:

```
 1 2 4 4
METHANE(1)-PROPANE(2)
 1
15
111
 1.8                              0.0                              0.0
 6.8                              0.034                            0.56
 13.6                             0.089                            0.767
 20.4                             0.142                            0.832
 27.2                             0.197                            0.861
 34.0                             0.249                            0.880
 40.8                             0.303                            0.888
 47.6                             0.357                            0.890
 54.4                             0.41                             0.892
 61.2                             0.464                            0.891
 68.0                             0.518                            0.889
 74.9                             0.572                            0.882
 81.7                    256.40   0.636                            0.869
 88.5                    256.40   0.718                            0.845
 93.9                    256.40   0.80                             0.80
 45.4          99.0      190.6          0.288          0.008
 41.9          203.0     369.8          0.281          0.152
 0.00618
 -110.3206
 79.0164
 0.01
 0 0 0 0
```

The formated output is as follows:

EXPERIMENTAL RESULTS AND CALCULATED QUANTITIES FOR THE BINARY SYSTEM METHANE(1) PROPANE(2)
****

THE POLYNOMIAL USED IN THE ORTHOGONAL COLLOCATION PROCEDURE IS OF THE TYPE ALFA = 0. BETA = 0.

PC-VC-TC-ZC-ACEN 0.45400E+02 0.99000E+02 0.19060E+03 0.28800E+00 0.80000E-02

PC-VC-TC-ZC-ACEN 0.41900E+02 0.20300E+03 0.36980E+03 0.28100E+00 0.15200E+00

FAK-NY-TAU-DEL

0.00618

-110.32060

79.01640

0.01000

NUMBER OF BINARY POINTS 15 AT THE ISOTHERM 256.40 TEMPERATURE IN DEG K

XEXP	YEXP	PEXP
0.	0.	1.80000
0.03400	0.56000	6.80000
0.08700	0.76700	13.60000
0.14200	0.83200	20.40000
0.19700	0.86100	27.20000
0.24900	0.88000	34.00000
0.30300	0.88800	40.80000
0.35700	0.89000	47.60000
0.41000	0.89200	54.40000
0.46400	0.89100	61.20000
0.51800	0.88900	68.00000
0.57200	0.88200	74.90000
0.63600	0.86900	81.70000
0.71800	0.84500	88.50000
0.80000	0.80000	93.90000

T 256.3999 PS 1.8000 VDL 83.5936 81.5029

FISAT 0.9774 0.9555 FREESAT 104.5793 1.7200

CONSISTENCY TEST USING ORTHOGONAL COLLOCATION - NUMBER OF INTERNAL POINTS 4

COLLOCATION POINTS

0. 0.069432 0.330009 0.669991 0.930568 1.000000

NUMBER OF ITERATIONS IN G 10

ITERATION NUMBER GREATER THAN 100

ITERATION NUMBER GREATER THAN 100

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 125.3382

NUMBER OF ITERATIONS IN G 27

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 127.3888

NUMBER OF ITERATIONS IN G 5

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 124.9436

NUMBER OF ITERATIONS IN G 7

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 123.9927

NUMBER OF ITERATIONS IN G 4

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 125.5156

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 125.2429

NUMBER OF ITERATIONS IN G 2

HENRY LAW CONSTANT BY LAGRANGIAN EXTRAPOLATION 124.1647

NUMBER OF ITERATIONS IN G 2

SOLUTION AT THE COLLOCATION POINTS

X	P	GE/RT	GOOI	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.0000	0.0100	0.	1.0101	1.0101	0.	1.0101	1.0101	21.3181
0.2108	30.1229	-0.0122	-0.2283	0.8429	1.0306	0.9107	0.0894	1.0000	-26.0585
0.4596	60.3957	-0.1285	-0.6697	0.6322	1.1818	0.9295	0.0705	1.0000	-256.8225
0.6548	81.7654	-0.2927	-1.1128	0.5144	1.5116	0.9272	0.0728	1.0000	-623.9194
0.7717	93.5541	-0.4433	-1.4865	0.4595	1.9877	0.9262	0.0739	1.0000	-944.9622
0.8000	96.2919	-0.4869	-1.5997	0.4479	2.1780	0.9266	0.0734	1.0000	-1037.9207

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GOOI
0.	1.0126	0.9555	81.5029	0.	112.1372	0.
0.2108	0.9000	0.5000	76.3893	-5.5544	102.8382	-0.0271
0.4596	0.8110	0.3239	72.3066	-10.0771	91.8641	-0.0440
0.6548	0.7578	0.2060	74.0589	-8.0130	83.2509	-0.0349
0.7717	0.7314	0.1621	77.2143	-5.9020	78.0939	-0.0219
0.8000	0.7253	0.1542	78.2168	-4.9586	76.8467	-0.0181

SOLUTION AT THE DATA POINTS

X	P	GE/RT	GOUT	GAMMA1	GAMMA2	Y1	Y2	SUM CORR	GE J/MOLE
0.	1.0000	0.0100	0.	1.0101	1.0101	0.	1.0000	1.0101	21.3181
0.0340	6.5340	0.0080	-0.0216	0.9920	1.0086	0.6893	0.3107	0.9638	16.9828
0.0890	14.0569	0.0045	-0.0707	0.9528	1.0097	0.8428	0.1572	0.9779	9.5454
0.1420	21.1484	-0.0007	-0.1321	0.9072	1.0154	0.8866	0.1134	0.9911	-1.4947
0.1970	28.3438	-0.0094	-0.2077	0.8559	1.0268	0.9073	0.0927	0.9989	-20.0118
0.2490	34.9933	-0.0216	-0.2880	0.8068	1.0433	0.9229	0.0771	0.9846	-46.1010
0.3030	41.7407	-0.0391	-0.3784	0.7573	1.0669	0.9429	0.0571	0.9259	-83.3816
0.3570	48.3274	-0.0619	-0.4745	0.7107	1.0979	0.9706	0.0294	0.8398	-131.9060
0.4100	54.6357	-0.0896	-0.5733	0.6685	1.1366	0.9289	0.0711	1.0006	-190.9833
0.4640	60.9037	-0.1235	-0.6785	0.6291	1.1864	0.9296	0.0704	1.0000	-263.2114
0.5180	67.0109	-0.1632	-0.7893	0.5931	1.2495	0.9295	0.0705	0.9999	-347.9788
0.5720	72.9574	-0.2092	-0.9078	0.5601	1.3312	0.9288	0.0712	1.0000	-445.0748
0.6360	79.7968	-0.2722	-1.0630	0.5238	1.4651	0.9276	0.0724	0.9993	-580.2664
0.7180	88.2296	-0.3686	-1.2986	0.4838	1.7189	0.9270	0.0730	1.0006	-785.8569
0.8000	96.2919	-0.4869	-1.5997	0.4479	2.1780	0.9279	0.0721	1.0000	-1037.9207

X	FUGCF1	FUGCF2	VMIX	VE	DPDX	CORR TO GOUT
0.	1.0119	0.9555	81.5029	0.	112.1372	0.
0.0340	0.9831	0.8722	80.6193	-0.9547	110.6373	0.0050
0.	1.0119	0.9555	81.5029	0.	112.1372	0.
0.0340	0.9831	0.8722	80.6193	-0.9547	110.6373	-0.0050
0.0890	0.9541	0.7675	79.2315	-2.4574	108.2111	-0.0126
0.1420	0.9295	0.6796	77.9509	-3.8489	105.8731	-0.0194
0.1970	0.9057	0.5988	76.6921	-5.2226	103.4469	-0.0257
0.2490	2.7163	0.0867	75.5819	-6.4415	101.1530	-0.0310
0.3030	2.1582	0.0785	74.5306	-7.6058	98.7709	-0.0357
0.3570	1.3582	0.1143	73.6105	-8.6308	96.3888	-0.0396
0.4100	0.8267	0.3641	72.8741	-9.4860	94.0508	-0.0424
0.4640	0.8096	0.3205	72.3549	-10.1181	91.6687	-0.0441
0.5180	0.7937	0.2823	72.1714	-10.4144	89.2866	-0.0442
0.5720	0.7788	0.2488	72.5131	-10.1857	86.9045	-0.0421
0.6360	0.7624	0.2149	74.1978	-8.6348	84.0013	-0.0345
0.7180	0.7430	0.1805	74.9800	-8.0240	80.4640	-0.0307
0.8000	0.7250	0.1551	78.2168	-4.9586	76.8467	-0.0181

CONSISTENCY TEST BY REPEATED HALVING OF TRAPZOIDAL RULE WITH ROMBERG INTEGRATION

CONSTANT= 0.209162D-11
CONSTANT= 0.840364D-11
CONSTANT= 0.222156D-10
CONSTANT= 0.444873D-10
CONSTANT= 0.792339D-10
CONSTANT= 0.127675D-09
CONSTANT= 0.190337D-09
CONSTANT= 0.271936D-09
CONSTANT= 0.375201D-09
CONSTANT= 0.506576D-09
CONSTANT= 0.715008D-09
CONSTANT= 0.108665D-08
CONSTANT= 0.169106D-08

CALCULATED VALUES OF Y1

X	P	Y1	Y1EXP	DY	Y2	SUMY	PCAL	DP
0.	1.8000	0.	0.	0.	1.0000	1.0000	1.8000	-0.0000
0.0340	6.8000	0.6893	0.5600	0.1293	0.3107	1.0000	6.5340	-0.2660
0.0890	13.6000	0.8428	0.7670	0.0758	0.1572	1.0000	14.0569	0.4569
0.1420	20.4000	0.8866	0.8320	0.0546	0.1134	1.0000	21.1484	0.7484
0.1970	27.2000	0.9073	0.8610	0.0463	0.0927	1.0000	28.3438	1.1438
0.2490	34.0000	0.3729	0.8800	-0.5071	0.6271	1.0000	34.9933	0.9933
0.3030	40.8000	0.4571	0.8880	-0.4309	0.5429	1.0000	41.7407	0.9407
0:3570	47.6000	0.6706	0.8900	-0.2194	0.3294	1.0000	48.3274	0.7274
0.4100	54.4000	0.9289	0.8920	0.0369	0.0711	1.0000	54.6357	0.2357
0.4640	61.2000	0.9296	0.8910	0.0386	0.0704	1.0000	60.9037	-0.2963
0.5180	68.0000	0.9295	0.8890	0.0405	0.0705	1.0000	67.0109	-0.9891
0.5720	74.9000	0.9288	0.8820	0.0468	0.0712	1.0000	72.9574	-1.9426
0.6360	81.7000	0.9276	0.8690	0.0586	0.0724	1.0000	79.7968	-1.9032
0.7180	88.5000	0.9270	0.8450	0.0820	0.0730	1.0000	88.2298	-0.2702
0.8000	93.9000	0.9279	0.8000	0.1279	0.0721	1.0000	96.2919	2.3919

SUM OF SQUARES OF DELTA Y 0.5517500

VARIANCE OF DELTA Y 0.2060 ARITHMETIC MEAN OF DELTA Y 0.1353

CALCULATED EXCLUDING GIVEN END POINTS

SUM OF SQUARES OF DELTA P 10.8602577

VARIANCE OF DELTA P 1.2045 ARITHMETIC MEAN OF DELTA P 0.9504

ARITHMETIC MEAN OF DELTA P/P 0.106028

CALCULATED EXCLUDING GIVEN END POINTS

STOP

TIME 4.7 SECS