GENERALIZED PREDICTION METHODS OF VAPOR-LIQUID EQUILIBRIUM RATIO AND ENTHALPY FOR HYDROCARBON MIXTURES

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PREFACE

An improved K-value correlation together with an enthalpy prediction method was developed for hydrocarbon mixtures. The correlations can be applied easily with digital computers. In connection with the K-value and enthalpy correlations, a new equation of state and expressions for pure liquid fugacity coefficient and activity coefficient were also developed. The expressions may be used for other purposes than those studied in this investigation.

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CHAPTER I

INTRODUCTION

This study consists of theoretical investigations on the vapor-liquid equilibrium ratio and the enthalpy of hydrocarbon mixtures containing none or some of the non-hydrocarbon gases such as hydrogen, nitrogen, carbon dioxide and hydrogen sulfide.

The accurate prediction of these quantities is of paramount importance in quantitative treatment of a great many physical and chemical processes including distillation, absorption and extraction. The nature of equilibrium between phases may also be an important factor in many other problems such as mixed phase flow, condensing or boiling heat transfer, and chemical reactions involving coexisting phases.

Because of the great importance of phase equilibria in practical engineering problems, numerous experimental and theoretical studies have been conducted on that subject over the past several decades. Consequently a vast amount of experimental data has been accumulated and a number of useful correlation methods have been developed.

The vapor-liquid equilibrium ratio which is generally referred to as a K-value, depends on many variables such as temperature, pressure, composition, and the chemical nature of substances involved. The rigorous functional relationship of the K-value to these variables has not been established and may take another decade or longer for the complete development. However, for practical purposes, one can formulate an empirical or semi-theoretical relationship among those variables using the large accumulation of experimental data and related thermodynamics. The advanced computing techniques provide another factor to facilitate the development of a more sophisticated correlation. In fact, many such studies have been made in recent years. But they are still limited either by their range of applicability or their accuracy.

In addition, a companion enthalpy prediction method that is consistent with the K-value correlation would be not only of theoretical importance but also convenient for process design calculations. Therefore, this investigation was undertaken to develop a set of K-value and enthalpy correlations that are accurate and generalized for hydrocarbon mixtures.

The K-value can be expressed as a combination of vapor phase fugacity coefficient ϕ_i, pure liquid fugacity coefficient ν_i, and activity coefficient γ_i as follows.

$$K_i = \frac{\nu_i \gamma_i}{\phi_i} \tag{1-1}$$

An equation of state was developed to calculate the fugacity coefficients and enthalpies of the vapor phase. Two different expressions were derived for pure liquid fugacity coefficients, one for the real liquid state and the other for the hypothetical liquid state. A new expression for the activity coefficient was formulated by combining the modified Scatchard-Hildebrand equation with athermal terms and fitting the resulting expression to experimental K-values to obtain the numerical constants. The temperature derivatives of ν_i and γ_i expressions provide the tools for predicting liquid enthalpies.

These correlations can be used in designing separation or heat transfer equipment which process coexisting vapor and liquid phases.

In Chapters II and III the theory of phase equilibrium and previous investigations are discussed respectively. In subsequent chapters equations of state, fugacity coefficients, activity coefficients, and enthalpies are discussed and a set of new equations are developed for K-value and enthalpy correlations.

CHAPTER II

THEORY OF PHASE EQUILIBRIA

The Criteria of Phase Equilibrium

Phase equilibrium is a special form of equilibrium that exists between coexisting phases. "Equilibrium" implies a state in which there is no spontaneous change in a system. Such a condition can result only when all potentials that tend to promote change are absent or exactly balanced against similar opposing potentials.

In order for a system to be at equilibrium, every possible change that might take place to an infinitesimal extent must be reversible. This necessity immediately leads to the following thermodynamic criterion of equilibrium: "For any change that takes place, the total entropy change in any isolated system shall be zero at equilibrium".

Applying this criterion to vapor-liquid phase equilibria gives

$$T^V = T^L \tag{2-1}$$

$$P^V = P^L \tag{2-2}$$

$$\bar{\mu}_i^V = \bar{\mu}_i^L \quad (i = 1, 2, \ldots N) \tag{2-3}$$

Hence the phase equilibrium can be characterized by the equalities of pressure, temperature and the chemical potentials of each component in all phases. The derivation of these criteria is shown in Appendix A.

The chemical potential, however, is an awkward mathematical quantity for application to engineering problems. Thus, it is convenient to transform the quantity into fugacity as defined by Lewis (108).

$$d\bar{\mu}_i = d\bar{G}_i = RT\, d(\ln \hat{f}_i) \qquad @ \text{ constant } T \qquad (2\text{-}4)$$

where $\lim\limits_{P \to 0} \dfrac{\hat{f}_i}{Py_i} = 1$

From Equations 2-3 and 2-4, one can show that

$$\hat{f}_i^V = \hat{f}_i^L \qquad (2\text{-}5)$$

At present there is no rigorous method to evaluate both fugacities in Equation 2-5 which would result in the unique solution for the phase compositions. A perfect equation of state, if such an equation can be devised, would be the tool to handle this problem. Equation 2-5, however, provides the principal basis relating K-values with various thermodynamic functions that can be calculated from experimentally accessible quantities such as P-V-T and composition data.

K-Value Relationships With Thermodynamic Functions

The K-value of a component is defined as the ratio of the mole fraction of that component in the vapor phase to its mole fraction in the coexisting liquid phase.

Introduction of Equation 2-5 into the definition of K-value gives

$$K_i = \frac{y_i}{x_i} = \frac{(\hat{f}_i^L / x_i)}{(\hat{f}_i^V / y_i)} \qquad (2\text{-}6)$$

Converting the denominator into the familiar fugacity coefficient,

$\phi_i = \hat{f}_i^V / Py_i$, gives

$$K_i = \frac{(\hat{f}_i^L / x_i)}{\phi_i} \frac{1}{P} \tag{2-7}$$

This is the K-value relationship that Benedict et al. (18) used in developing the Polyco K-charts.

By introducing vapor pressure into the numerator of Equation 2-7 Edmister and Ruby (64) obtained the following equation which the authors used for the modification of Kellogg K-charts.

$$K_i = \frac{(\hat{f}_i^L / p_i^s \; x_i)}{\phi_i} \frac{p_i^s}{P} \tag{2-8}$$

The apparent liquid fugacity coefficients that appear in numerators of Equations 2-7 and 2-8 can not be easily predicted by thermodynamic methods. This limits the application of these correlations.

Ehrett, Weber and Hoffman (68) introduced two standard state fugacities into Equation 2-6 to obtain

$$K_i = \frac{(\hat{f}_i^L / f_i^{oL} x_i)}{(\hat{f}_i^V / f_i^{oV} y_i)} \frac{f_i^{oL}}{f_i^{oV}} \tag{2-9}$$

This equation has two distinct disadvantages, one being the awkwardness of predicting the vapor phase activity coefficient, the other being the hypothetical states associated with the standard state fugacities. The hypothetical states are encountered for both liquid and vapor mixtures.

Assuming that the liquid partial molal volume is equal to the molal volume of pure component, Black (21, 22) derived a more sophisticated expression for K-values.

$$K_i = \frac{(\hat{f}_i^L/f_i^L\, x_i)}{\bar{\theta}_i}\,\frac{p_i^s}{P} \qquad (2\text{-}10)$$

where $$\bar{\theta}_i = \frac{\phi_i}{(f_i^s/p_i^s)}\exp\left[-\frac{1}{RT}\int_{p^s}^{P}\bar{V}_i^L\,dP\right]$$

Equation 2-10 is not completely rigorous, however.

A similar but thermodynamically rigorous K-value relationship was proposed by Prausnitz, Edmister, and Chao (145).

$$K_i = \frac{\nu_i\gamma_i}{\phi_i} \qquad (2\text{-}11)$$

This equation has been most frequently used, since all the three quantities in the right-hand side of the equation are easily obtainable from either experimental data or appropriate correlation methods. This expression, however, has an inherent drawback, that it can not be applied to the supercritical components without the assumption of hypothetical states.

In an attempt to eliminate the hypothetical state problem, Prausnitz and his co-workers (144) chose the Henry's constant as the standard state fugacity for the supercritical components. Besides, the authors evaluated all the liquid thermodynamic properties at zero pressure and system temperature to make the properties independent of pressure. Thus, the pressure effect is solely reflected by the Poynting correction. Their proposed K-value relationship for condensable components is given by

$$K_i = \frac{\gamma_i^{(o)}}{\phi_i} \frac{f_i^{L(o)}}{P} \exp\left[\frac{1}{RT}\int_o^P \bar{V}_i^L \, dP\right]$$

The counterpart for non-condensable gases is

$$K_i = \frac{\gamma_i^{*(o)}}{\phi_i} \frac{H_i^{(o)}}{P} \exp\left[\frac{1}{RT}\int_o^P \bar{V}_i^L \, dP\right]$$

The superscript (o) indicates that the corresponding properties are evaluated at zero pressure, while the asterisk * implies that the activity coefficient is normalized by the unsymmetric convention.

Among the many thermodynamic functions related to K-value, the vapor phase fugacity coefficient, the liquid phase activity coefficient and the standard state fugacity merit special discussion and this discussion appears in the following chapters.

CHAPTER III

PREVIOUS INVESTIGATIONS

Since the fugacity concept was introduced into the phase equilibrium criteria, many K-value correlations have been developed based on this concept. Perhaps the first significant work of this kind may be the graphical correlation prepared at Massachusetts Institute of Technology in the early 1930's. Because of the complex nature of K-values, most of earlier correlations were prepared in chart form with various simplified assumptions, some of which were quite limiting and resulted in inadequate correlations. Independent from the fugacity concept, a different correlation which was based on convergence pressure concept was developed in the early 1950's and used as widely as the fugacity-based K-value correlation until the present.

Fugacity Based K-Value Correlations

The MIT K-Charts and Michigan K-Charts

MIT K-charts were prepared from the fugacity coefficient correlations developed by Lewis and Kay (109) and Newton (131) and some of the solubility data of light gases. The necessary input information for this correlation were the vapor pressure, the critical pressure and temperature of components involved, in addition to system pressure and temperature. Thus, this correlation did not account for the composition effects, nor adequately describe the influence of the chemical nature of the constituents. Such inadequacies were recognized early. The Michigan K-charts (33) were developed in a manner similar to MIT charts.

Polyco and DePriester K-Charts

Benedict et al. (18) prepared the Polyco K-charts using the fugacity values calculated from their equation of state. This correlation included the composition effects in a simplified manner. As the composition variable, the authors selected molal average boiling point of the phase in question. This was admitted to be a compromise between accuracy and practicality. With this simplification, several series of fugacity calculations were made for a number of selected hydrocarbon systems. In their calculations the authors assumed that the balance of the mixture other than the component of interest could be treated as a single hypothetical component. The resulting binary system fugacity coefficients were correlated as a function of temperature, pressure and the molal average boiling point of the phase in question.

The original Polyco K-charts were replotted and published by the M. W. Kellogg Co. in 1950. A few years later, DePriester (58) improved the Kellogg K-charts by (a) condensing the original 144 charts to 24 charts (b) facilitating the pressure interpolations and (c) providing better accuracy in some ranges.

Edmister-Ruby Correlation

Using the values of fugacity coefficients from the original Polyco K-charts and the vapor pressure data from A.P.I. Research Project 44 (5), Edmister and Ruby (64) developed separate correlations for vapor and liquid phase fugacity coefficients as functions of reduced temperature, reduced pressure, and boiling point ratio. The authors again introduced an intermediate parameter θ to make the fugacity coefficients as functions of reduced pressure and θ only, where θ is a separate function of reduced temperature and boiling point ratio. Thus, the authors were able to reduce the 276 original Polyco charts to six charts which can be directly used in calculating K-values via Equation 2-8. The necessary information for this correlation are the critical properties and vapor pressure of the component of interest and the normal boiling points of all components in the mixture.

Black-Derr-Papadopoulos Correlation

Black et al. (25) developed a comprehensive K-value correlation method by summarizing the material contained in a series of papers presented by Black (21, 22, 23, 24).

The Black-Derr-Papadopoulos correlation which uses Equation 2-10 as the key equation is not intended for generalization. Instead, it treats the problems case by case, thus making it possible to extend its application to various systems including polar component systems.

The authors recommended the use of the modified van der Waals equation (21) and the Redlich-Kwong equation of state for the calculation of vapor phase fugacity coefficients, with greater emphasis on the former equation. For the liquid activity coefficient the authors recommended a modified van Laar equation (22) which contains a set of adjustable constants that can be determined from experimental data. In addition, the method requires determining the liquid partial molal volume and the pure fugacity coefficient of supercritical components also from experimental data. Thus, this correlation can be applied to a system only when some experimental data for the same or similar system are available. However, the flexibility of this correlation is a valuable feature that assures a diversified utility of the correlation.

Prausnitz-Edmister-Chao Correlation

This correlation is worth special mention because of its great influence on the later development of similar correlations. Prausnitz, Edmister and Chao (145) proposed the well-known K-value relationship given by Equation 2-11. The authors calculated the vapor phase fugacity coefficient and the liquid phase activity coefficient via Redlich-Kwong equation (166) and Scatchard-Hildebrand equation (86), respectively. The pure liquid fugacity coefficients for real components were obtained from the correlations prepared by Lydersen, Greenkorn and Hougen (112), and those for hypothetical components were obtained by fitting Equation 2-11 to the solubility data of a gas in at least two solvents having different chemical nature. The values of ν_i and solubility parameter for supercritical components were simultaneously optimized by regression analyses. They used Watson's (200) expression for the hypothetical liquid volume necessary for Scatchard-Hildebrand equation. This correlation places more emphasis on the K-values of light components.

Chao-Seader Correlation

Chao-Seader correlation uses the same equations as were employed by Prausnitz, Edmister and Chao (145) except for the expression of pure liquid fugacity coefficient, for which Chao and Seader developed a generalized algebraic equation. The generalization as well as the inclusion of hydrogen and cyclic compounds is the prominent feature that makes the Chao-Seader correlation one of the most widely accepted K-value prediction methods in petroleum industry today.

Chao and Seader (41) obtained the solubility parameters of light components by regression analyses using the solubility data of the components in different solvents and calculated the hypothetical pure liquid fugacity coefficient via Equation 2-11. For the liquid fugacity coefficient of heavier components experimental equilibrium data were processed according to Equation 2-11. The ν_i values obtained in this manner together with the tabulated values of Curl and Pitzer (57) were used in formulating the expression of ν_i in terms of reduced temperature, reduced pressure and acentric factor. This correlation has been extended and modified by Grayson and Streed (77) and by Cavett (39).

Several similar correlations were attempted by different investigators, but from a generalization standpoint they were less successful than Chao-Seader method. For instance, Chang et al. (40) used Wilson's (205) modified Redlich-Kwong equation of state for the calculation of ϕ_i and employed Chao-Seader expressions for ν_i. The authors developed an activity coefficient model based on Miller-Gugenheim theory and the interchange energy concept given by Ashworth and Everett, but the expression was not generalized.

In a similar study, using the modified Redlich-Kwong equation of Barner et al. (12) instead of Wilson's, Avasthi and Kobayashi (8) further refined the activity coefficient model. However, the model still retained the interchange energy parameters which are characteristic of each binary pair and which must be determined from experimental equilibrium data.

Adler et al. (1) employed the Redlich-Kwong equation, the Benedict-

Webb-Rubin equation of state, and the Margules four suffix equation for the evaluations of ϕ_i, ν_i, and γ_i respectively. This correlation also requires a set of characteristic constants that must be determined from experimental data.

Prausnitz-Eckert-Orye-O'Connell Correlation

This correlation starts with Equation 2-12 which the authors formulated (144). Vapor phase fugacity coefficients are calculated from virial equation of state using two different second virial coefficient expressions, one for non-polar, the other for polar substances. The original Wilson equation and its simplified version are used for the activity coefficients of subcritical and supercritical components, respectively. For the reference fugacity, the zero pressure fugacity correlation of Lyckman et al. (110) is employed for condensable components and the Henry's constant is used for non-condensable gases. Accordingly, two differently normalized γ_i's are used, i.e., one is symmetrically normalized, the other is normalized by the unsymmetric convention. The merits and demerits of these are discussed in Chapter VII.

Since all the liquid phase properties are corrected to zero pressure values, only the liquid partial molal volume is expected to account for the pressure effects. As the authors admitted, the correlation of the partial molal volume is not accurate enough to handle the pressure effects adequately. This weakness together with the use of virial equation of state restricts this correlation to low pressure systems. Furthermore, this correlation can hardly be used for general purpose because of the Henry's constant which can not be easily generalized.

Chueh-Prausnitz Correlation

This correlation is basically the same as that of Prausnitz et al. (144) except for the equations chosen for the correlation. Chueh and Prausnitz presented a series of papers dealing with high pressure vapor-liquid equilibria (46, 47, 48, 49) and summarized the concept in a single monograph (143).

The authors chose the Redlich-Kwong equation of state for the calculations of vapor phase fugacity coefficient and of liquid partial molal volume. They redetermined the Redlich-Kwong equation of state constants for the individual components ignoring the critical point requirements. In addition, they introduced new mixing rules for the mixture applications. For the evaluation of activity coefficient Chueh and Prausnitz developed a dilated van Laar model which has proven particularly useful for supercritical components. However, the model contains a set of characteristic constants for each binary pair. These constants plus the Henry's constants prevent the correlation from being generalized. The authors studied the critical region in some detail and developed a supplemental correlation method for the particular region, but the practical application of the method appears to be tedious. Besides the authors assigned a different temperature limit to each different substance. Accordingly their correlation can be applied only to the common temperature range of all the components involved in the system of interest. Another weakness of this correlation is the calculation of the liquid partial molal volume from a simple equation of state using the constants determined from the volumetric data of saturated pure liquids.

Direct Use of Equation of State

Until recently, no intensive effort was made to calculate K-values directly from equations of state. This inactivity is mainly ascribed to the poor performance of available equations of state in dense phases, and to the imperfection of mixing rules which have a strong influence over the partial quantity that is calculated from an equation of state.

The equation of state method has, however, a distinct advantage in that it requires no assumptions whatsoever and exhibits a reliability in the critical region where most of the preceeding correlations fail to work.

The study of the utility of equations of state in K-value prediction is generally centered on (a) the modification of mixing rules, (b) the refinement of temperature functionality, and (c) the adjustment on the equation of state constants of pure component.

The simplest way of using equations of state for K-value prediction is to calculate the fugacities of both phases without any modifications or corrections as Schiller and Canjar (183) did. But this method in general does not yield a reliable result.

Stotler and Benedict (191) applied the Benedict-Webb-Rubin equation of state to the vapor-liquid equilibria of nitrogen-methane mixture by modifying the mixing rule on A_o. Although not clearly stated, the authors implicitly introduced the so called "binary interaction coefficient" into the mixing rule.

A similar study was made by Wilson (205) with the simpler Redlich-Kwong equation of state as modified by himself. But Wilson's approach shows a greater promise than that of Stotler and Benedict, because it uses a generalized equation of state. Recently, Zudkevitch et al. (217) also studied the application of R-K equation of state to the K-value predictions. The authors determined the equation constants using saturated liquid P-V-T data and saturation fugacity data. The use of binary interaction coefficients are not different from Wilson's method.

Other interesting studies in this field include the works by Wolfe (210) and by Starling (187). Wolfe applied Benedict-Webb-Rubin equation to the natural gas phase equilibria with no modifications. On the other hand, Starling used the same equation of state for the K-values of condensate reservoir fluids, determining the B-W-R equation constants of heavier components from the experimental equilibrium data so that the equation will reproduce the K-values with sufficient accuracy.

More recently, Kaufman (93) employed a generalized Benedict-Webb-Rubin equation (193) to predict the K-values of systems consisting of some olefins. The author readjusted the generalized constants specifically for the olefin homolog, and assigned a temperature function to C_o for each component to satisfy the fugacity identity of coexisting phases. But the latter procedure made the original purpose of using the generalized equation of state meaningless.

A more rigorous study was performed by Klekers (101) who used a different generalized B-W-R equation of state (65) for the K-values of multicomponent hydrocarbon systems. Klekers optimized the generalized B-W-R constants B_o and C_o from binary experimental data, and made C_o a function of temperature. The recommended mixing rule for the constant B_o is the linear square root model having a binary interaction coefficient.

Recently, Orye (138) presented a comprehensive study on the utility of B-W-R equation of state for the K-value prediction of hydrocarbon systems including some non-hydrocarbon gases. The technique used is not drastically different from previous studies by others (101, 205).

Convergence Pressure Based K-Value Correlations

The convergence pressure concept is based on an observed critical phenomenon of a binary mixture, i.e., the K-value of each component converges to unity at the critical pressure of the mixture having a critical temperature equal to the system temperature.

For binary system, when the system temperature is between the critical temperatures of both components, the convergence pressure has a unique relation to the phase compositions for a given mixture. Thus, the convergence pressure can be effectively used as a composition correlating parameter. However, the idea becomes totally invalid when it is applied to multicomponent mixtures. All the experimental and theoretical evidence prove the invalidity, that is, the convergence pressure of a multicomponent system has no one-to-one relation to the phase compositions, nor can it describe the chemical nature of components involved. This is evidenced by the fact that all the convergence pressure-based K-value correlations are generally limited to aliphatic hydrocarbons of which the chemical nature is similar. Due to the lack of theoretical background, the convergence pressure correlation for a multicomponent system should be entirely based on empiricism, which is a serious disadvantage of the K-value correlation based on this correlating parameter. A good review of the convergence pressure concept and its application to the K-value correlation is given by Edmister (62).

The use of convergence pressure for a K-value correlation was first proposed by Katz and Brown (92) in 1933. After this pioneering study, many investigators including Katz and Hachmuth (91), White and Brown

(202), and Hadden (78) worked along this line until the years 1949 through 1953 when several notable convergence pressure-based K-value correlations were presented by Rzasa et al. (175), Organick and Brown (137), Winn (208), and Hadden (79) successively. These correlations are particularly worth mentioning because they formed the bases for the well-known NGPSA K-charts and Hadden-Grayson nomographic correlation.

Using the critical data on binary and complex hydrocarbon mixtures, Rzasa et al. (175) devised a chart form correlation for estimating the convergence pressures of complex hydrocarbon systems. The correlating variables are the system temperature and the product of the molecular weight and the specific gravity of heptanes-plus fraction. Using this convergence pressure correlation, the authors also developed a K-value correlation for normal hydrocarbons ranging from methane through n-decane. The K-value correlation is a function of pressure, temperature, and convergence pressure for the individual components.

Organick and Brown (137) developed a correlation by which the convergence pressures of complex hydrocarbon systems can be predicted from system pressure, the molal average boiling point of vapor phase, and the weight average molecular weight of liquid phase. This correlation was prepared from the critical and equilibrium data of binary hydrocarbon mixtures containing methane as one of the components. However, it can be applied to any multicomponent mixtures with proper corrections. Since this convergence pressure correlation includes composition effects, a trial and error procedure is required to compute the phase compositions as well as the convergence pressure. The authors claimed that the correlation could be extended to systems containing small amounts of inert gases, and other non-paraffinic hydrocarbons.

Winn (208) developed a K-value correlation in nomographic form. This correlation uses Hadden's method (79) for the estimation of convergence pressures, and is applicable for temperatures from 40 to 800° F and pressures from 10 to 5,000 psia for the systems containing light hydrocarbons, narrow cut petroleum fractions, and certain non-hydrocarbons. This correlation is relatively compact and easy to use.

Hadden (79) demonstrated that the convergence pressure of ternaries or more complex systems is a function of the operating temperature and of the liquid-phase composition excluding the concentration of the lightest component. In addition, the author introduced the concept of quasi-convergence pressure for the vapor liquid equilibria at temperatures below the critical temperature of the lightest component and showed its validity for binary systems. This convergence pressure correlation is being used in many K-value correlations.

In parallel with the investigations discussed above, Lenoir and his co-workers (105, 106, 107, 127) developed a different K-value correlation based on the convergence pressure. The final correlation was prepared by Cajander, Hipkin and Lenoir (36) in nomographic form. The nomograms use an intermediate parameter K_{10} which is the K-value of the component in question at the system temperature and 10 psia and at 5,000 psia convergence pressure, thus making the K-value a function of the K_{10}, the system pressure, and the convergence pressure. The K_{10} values are given in a series of 12 graphs for 58 pure hydrocarbons and 10 petroleum fractions. The convergence pressures are calculated from the charts presented by Lenoir and White (105).

Based on the earlier work of Hadden (79) and Winn (208), Hadden and Grayson (80) developed a correlation which uses only two primary working charts to relate K-value with the component identity, temperature, pressure and convergence pressure. Ten other figures are provided for determining the convergence pressure. This correlation is applicable for temperatures from -260° F to 800° F and pressures up to 10,000 psia for the systems covered by Winn (208). The A.P.I. Technical Data Book (32) recommends this K-value correlation for desk use.

The most recent development in convergence pressure correlations is the NGPSA K-charts (129). This correlation is an improved version of earlier charts which were originally prepared by Fluor Corporation from the data compiled by G. G. Brown and Fluor. The new K-charts cover pressures from 10 to 10,000 psia and temperatures from -300° F to 500° F for 12 aliphatic hydrocarbons ranging from methane to n-decane as well as for nitrogen, carbon dioxide and hydrogen sulfide. Each of the 69 charts is a logarithmic graph of K-value versus pressure with a family of constant temperature curves at a given values of convergence pressure. The available convergence pressures in this correlation are 800, 1,000, 2,000, 4,000 and 10,000 psia. The new NGPSA K-charts, Hadden-Grayson correlation and the correlation of Cajander et al. are particularly useful for high pressure range where the fugacity-based correlations are inaccurate.

CHAPTER IV

EQUATION OF STATE

An equation of state not only provides a means of storing a large amount of P-V-T data, but also facilitates the derivations of various thermodynamic functions for many fluids. The importance of an accurate equation of state is reflected by the appearance of more than a hundred such equations in literature. In spite of the presence of such a large number of equations of state, none of them has been proven completely satisfactory.

Reviews on Previews Equations of State

The earliest equation of state may be the ideal gas law which results from Boyle's and Charles' laws.

$$PV = RT \tag{4-1}$$

This equation does not adequately describe the volumetric behavior of real gases except at infinite attenuation. Hence a great many attempts have been made in the past century to develop an equation of state for the real fluids.

Van der Waals equation was the first equation of state that was capable of expressing the continuity from gaseous to liquid states.

$$(P - a/V^2)\ (V - b) = RT \tag{4-2}$$

Though inaccurate, this equation deserves special mention because of its enormous contribution to the corresponding states principle and to the later development of similar equations of state.

The constant "a" is assumed to account for the attractive force between molecules and the constant "b", known as co-volume, is considered to reflect the volume of molecules. These two constants can be determined from the critical point requirements as shown by the author, i.e.,

$$\left[\frac{\partial P}{\partial V}\right]_T = \left[\frac{\partial^2 P}{\partial V^2}\right]_T = 0 \qquad \text{@ critical point} \qquad (4\text{-}3)$$

The equation of state constants requiring only two of the three critical properties for the complete definitions, are usually expressed by the critical pressure and critical temperature, since the properties are more reliable than the critical volume.

Several investigators including Clausius, Berthelot, Dieterici, Wohl, and Redlich and Kwong, improved the van der Waals equation of state mainly by modifying the pressure correction term a/V^2. Among the many modified versions, the Redlich-Kwong equation (166) is believed to be the most successful modification.

$$P = \frac{RT}{V - b} - \frac{a/T^{\frac{1}{2}}}{V(V + b)} \qquad (4\text{-}4)$$

This equation was formulated using the assumption that the constant "b" is 0.26 times of critical volume. Despite the doubtful soundness of this assumption, the resultant equation has been shown to be the best two constant equation of state. The evaluation of the Redlich-Kwong equation is shown in Table I along with those of other equations of state.

Wilson (205) modified the Redlich-Kwong equation of state by making the constant "a" a function of reduced temperature and of the constant "b". Wilson introduced a binary interaction coefficient into the mixing rule of "a" to improve mixture properties. Robinson and Jacoby (173) studied the temperature dependencies of the constants "a" and "b" and set both constants as linear functions of temperature, and reported a number of binary interaction coefficients to be used for the mixing rule of "a". A more rigorous modification was performed by Barner et al. (12), who modified the temperature dependency of R-K equation of state to improve its prediction of second virial coefficient below the critical temperature. Acentric factor was introduced to account for the component identities.

$$P = \frac{RT}{V - b} - \frac{(a/T^{\frac{1}{2}} + c/T^2)}{V(V + b)} \tag{4-5}$$

Earlier in 1927, Beattie and Bridgeman (14) proposed a five constant equation of state which had no resemblance to the van der Waals equation of state.

$$PV^2 = RT\left[V + B_o(1 - \frac{b}{V})\right](1 - \frac{c}{VT^3}) - A_o(1 - \frac{a}{V}) \tag{4-6}$$

This equation is perhaps the first satisfactory equation of state for the quantitative discription of the real gas behavior. Owing to its acceptable accuracy for the gaseous region, the Beattie-Bridgeman equation of state was the most widely used equation until the more sophisticated Benedict-Webb-Rubin equation of state appeared in 1940.

Benedict and his co-workers (16) developed an eight constant equation of state based on their empirical "work content" expression which was in part based on the Beattie-Bridgeman equation of state.

$$P = \frac{RT}{V} + (B_oRT - A_o - C_o/T^2)/V^2 + (bRT - a)/V^3$$

$$+ a\alpha/V^6 + \frac{c}{T^2V^2}(1 + \gamma/V^2)\ \exp(-\gamma/V^2) \qquad (4\text{-}7)$$

In a series of papers Benedict et al. (17, 18) presented various thermodynamic functions derived from the equation of state and also proposed the mixing rules and the technique to evaluate the constants. Although many later investigations have extended its utility to many substances other than those light hydrocarbons originally intended, this equation still finds limited applications. Moreover, this complex equation inherently suffers from the unavoidable trial and error solution for density.

Many efforts have been made to generalize the Benedict-Webb-Rubin equation of state. Relatively successful generalizations were accomplished by Su and Viswanath (193) and by Edmister et al. (65). Su and Viswanath used the critical temperature and pressure as the correlating parameters, but Edmister et al. used an additional parameter, the Pitzer's acentric factor, to improve the accuracy of the equation.

Another interesting work in this field is the work of Hirshfelder et al. (87). The authors developed a generalized set of equations of state based on the critical temperature, critical pressure, critical compressibility factor, and the Riedel's third parameter. Three reduced form equations were proposed, one for each of three regions of P-V-T diagram. These equations are fairly complicated.

Recently, Martin (114) proposed a more complicated, but reportedly more satisfactory equation of state by complementing his previous equation of state (115). Because of the limited information on the constants and the mixing rules, this equation has not attracted very great attention.

All the foregoing equations of state are empirical or at best semi-theoretical, but they are in closed form, which is of great advantage for practical application.

In contrast to those equations of state mentioned above, the virial equation of state has a theoretical meaning in the view of statistical mechanics, but has the form of an infinite power series of density, which is not convenient for practical usage.

$$P = RT(1/V + B/V^2 + C/V^3 + \ldots) \tag{4-8}$$

This equation, however, is worth reviewing, because all the foregoing equations bear a formal resemblance to it when expanded into infinite series, nevertheless the numerical values obtained for the coefficients will not correspond to the true virial coefficients.

The virial equations, originally suggested by Onnes (136) as early as 1901, can be derived by the methods of statistical mechanics, from which the virial coefficients take on physical significance as reflecting the molecular interactions of particular numbers of molecules.

Another infinite series equation of state is the orthogonal polynomial form proposed by Ping and Sage (140). This equation uses normalized independent variables (density and temperature) for the

Tchebichef and the Gram polynomials. The authors proposed two forms, namely, the Tchebichef-Gram form and the Tchebichef-Tchebichef form, depending on the polynomials used for the density and the temperature. This equation, however, was not widely accepted due to the peculiarity of such polynomials.

The evaluations of a certain number of well-known equations of state were given by Shah and Thodos (185) and by Martin (114).

Development of a New Equation of State

This new equation of state has been specifically designed for the vapor phase with three main objectives: (a) analytical solvability, (b) generality, (c) capability of representing fugacity coefficients and enthalpies with accuracy. None of the available equations of state possesses the three characteristics altogether. These three capabilities are highly desired in K-value correlation in which (a) the solution of an equation of state is involved in a loop of trial and error calculations (b) many different components require similar mathematical or thermodynamic treatments (c) accurate fugacity coefficients are needed over wide range of conditions.

Among various models tested, the following equation was chosen over the others.

$$P = \frac{RT}{(V - b)} - \frac{a}{V(V - b)} + \frac{c}{V(V - b)(V + b)} \qquad (4\text{-}9)$$

The most frequently used critical point requirements as given by Equation 4-3 were ignored in favor of the improved capability of representing the second virial coefficients, the vapor pressure, and the volumetric behavior around critical region. The accurate representation of enthalpy is closely related to the ability of describing the second virial coefficient as shown below. From the virial equation truncated after the second term one can show that

$$\frac{H^o - H}{RT} = \frac{T}{V}\left(\frac{dB}{dT} - \frac{B}{T}\right) \tag{4-10}$$

The accurate values of $\frac{dB}{dT}$ can hardly be obtained without having a well-behaving temperature function of second virial coefficient.

The three parameters a, b, and c in Equation 4-9 were converted to dimensionless forms by writing the equation in a reduced form.

$$P_r = \frac{T_r}{(V_r' - b')} - \frac{a'}{V_r'(V_r' - b')} + \frac{c'}{V_r'(V_r' - b')(V_r' + b')} \tag{4-11}$$

where $V_r' = VP_c/RT_c$

$$b' = bP_c/RT_c \tag{4-12}$$

$$a' = aP_c/R^2T_c^2 \tag{4-13}$$

$$c' = cP_c^2/R^3T_c^3 \tag{4-14}$$

In view of the temperature functionality of second virial coefficient, a' was assigned by the following temperature function.

$$a' = a_1' - a_2'T_r + a_3'/T_r + a_4'/T_r^5 \tag{4-15}$$

The temperature dependence of c' was arbitrarily determined to improve the overall representation of P-V-T data, especially the data around critical region.

$$c' = c_1'/T_r^{\frac{1}{2}} + c_2'/T_r^2 \tag{4-16}$$

The constant b' was assumed independent of temperature.

The constants a_1', a_2', a_3', a_4', b', c_1', and c_2' were determined by performing simultaneous curve fits to the P-V-T and fugacity data of Canjar and Manning (37) and to the second virial coefficient data of McGlashan and Potter (119). These constants were first obtained with the restriction of the critical point requirements. But the restriction was removed later because applying the critical point requirements results in a universal critical compressibility factor of 1/3 as shown in Appendix B. All the constants but b' were nearly linear with acentric factor. Therefore, by forcing every constant to be a linear function of acentric factor, the regression analysis was repeated to obtain the best set of constants.

Baer's non-linear regression program (10) was partly revised and used in this analysis. This program minimizes the sum of squares of normalized dependent variables.

$$SS = \sum\left[\frac{V_{calc}}{V_{expl}} - 1\right]^2 + W_1\sum\left[\frac{f_{calc}}{f_{expl}} - 1\right]^2 + W_2\sum\left[\frac{B_{calc}}{B_{expl}} - 1\right]^2 \qquad (4\text{-}17)$$

The weighing factors relavent to the fugacity and the second virial coefficient were given by 0.5 each, since the uncertainty incorporated with those data are generally larger than that of P-V-T data. The value of b' determined in this way was about 0.12. But the mixture applications of this equation indicated that b' should be smaller than 0.1 to avoid instability near the mixture critical points. Therefore, the regression analysis was repeated with b' restricted to the value less than 0.1. This restriction resulted in a slight loss of accuracy for pure components. Another restriction imposed on the determination of the constants was that each constant must be greater than zero for any value of ω between zero and unity so that no difficulties would be encountered when mixing rules are applied to these constants. The upper limit ω = 1.0 was arbitrarily set, but is sufficiently high to include most of the substances of interest. It is also suggested that zero value of ω be assigned to the substances whose ω is less than zero. The finally obtained constants are as follows.

$$b' = 0.0982 \tag{4-18}$$

$$a_1' = 0.25913 - 0.031314\ \omega \tag{4-19}$$

$$a_2' = 0.0249 + 0.15369\ \omega \tag{4-20}$$

$$a_3' = 0.2015 + 0.21642\ \omega \tag{4-21}$$

$$a_4' = 0.042\ \omega \tag{4-22}$$

$$c_1' = 0.059904\ (1 - \omega) \tag{4-23}$$

$$c_2' = 0.018126 + 0.091944\ \omega \tag{4-24}$$

Combining Equations 4-13 through 4-16 with Equations 4-18 through 4-24 yields the following expressions of the three parameters that are involved in Equation 4-9.

$$b = \frac{RT_c}{P_c}\ 0.0982 \tag{4-25}$$

$$a = a_1 - a_2T + a_3/T + a_4/T^5 \tag{4-26}$$

$$c = c_1/T^{\frac{1}{2}} + c_2/T^2 \tag{4-27}$$

where

$$a_1 = \frac{R^2T_c^{\ 2}}{P_c}\ (0.25913 - 0.031314\ \omega) \tag{4-28}$$

$$a_2 = \frac{R^2T_c}{P_c}\ (0.0249 + 0.15369\ \omega) \tag{4-29}$$

$$a_3 = \frac{R^2T_c^3}{P_c} (0.2015 + 0.21642\ \omega) \qquad (4\text{-}30)$$

$$a_4 = \frac{R^2T_c^7}{P_c} (0.042\ \omega) \qquad (4\text{-}31)$$

$$c_1 = \frac{R^3T_c^{3.5}}{P_c^2} 0.059904\ (1 - \omega) \qquad (4\text{-}32)$$

$$c_2 = \frac{R^3T_c^5}{P_c^2} (0.018126 + 0.091044\ \omega) \qquad (4\text{-}33)$$

Equation 4-9 and Equations 4-25 through 4-33 constitute the proposed equation of state for vapor phases. The derivations of various thermodynamic functions from this equation of state are given in Appendix C.

Mixing Rules

Due to the complexity caused by composition effects, an equation of state is customarily derived for pure substances and then applied to mixtures employing appropriate mixing rules. Such mixing rules are usually determined arbitrarily.

Gillespie (73), and Beattie and Ikehara (15) studied the mixing rules for equations of state mostly by analyzing the second virial coefficients of mixtures. The second virial coefficient for a gaseous mixture of N constituents is given exactly by

$$B = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i\ y_j\ B_{ij} \qquad (4\text{-}34)$$

If $B_{ij} = (B_i + B_j)/2$ Equation 4-34 is reduced to a linear mixing rule

$$B = \sum_{i=1}^{N} y_i \; B_i \tag{4-35}$$

If $B_{ij} = (B_i B_j)^{\frac{1}{2}}$, Equation 4-34 is simplified to a square root mixing rule

$$B = \left[\sum_{i=1}^{N} y_i \; B_i^{\frac{1}{2}}\right]^2 \tag{4-36}$$

Beattie and Ikehara suggested that the square root mixing rule be used for the constants such as "a" in Equation 4-9 if the linear mixing rule is used for "b".

For lack of knowledge in three body interaction, the mixing rules for the third virial coefficient have not been extensively studied. If C represents the third virial coefficient for a gaseous solution of N constituents, it is given by

$$C = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} y_i \; y_j \; y_k \; C_{ijk} \tag{4-37}$$

It is interesting to note that Equation 4-37 is reduced to the same form as Equation 4-34 if $C_{ijk} = \left[(C_i C_j)^{\frac{1}{2}} + (C_i C_k)^{\frac{1}{2}} + (C_j C_k)^{\frac{1}{2}}\right]/3$, and to the form of Equation 4-35 if $C_{ijk} = (C_i + C_j + C_k)/3$. Equation 4-37 is also simplified to the following expression when $C_{ijk} = (C_i C_j C_k)^{1/3}$ is assumed.

$$C = \left[\sum_{i=1}^{N} y_i \; C_i^{1/3}\right]^3 \tag{4-38}$$

Benedict et al. (17) used this mixing rule for some of the constants of their equation of state. After all, the mixing rules given by Equations 4-35, 4-36 and 4-38 are special forms of Equation 4-37.

Based on the suggestions of Beattie and Ikehara, and of Redlich and Kwong, and of Benedict et al., the following mixing rules are recommended when Equation 4-9 is used for the mixture property evaluations.

$$a_j = \left[\sum_{i=1}^{N} y_i \, a_{ji}^{\frac{1}{2}}\right]^2, \ (j = 1, 2, 3, 4) \qquad (4\text{-}39)$$

$$b = \sum_{i=1}^{N} y_i \, b_i \qquad (4\text{-}40)$$

$$c_j = \left[\sum_{i=1}^{N} y_i \, c_{ji}^{1/3}\right]^3, \ (j = 1, 2) \qquad (4\text{-}41)$$

These mixing rules, however, are not completely adequate for the evaluations of partial properties including the fugacity coefficients of a component in a mixture particularly when the component of interest is diluted. Thus, a modified set of mixing rules are recommended for the calculation of fugacity coefficients. The modifications are given in Chapter V.

Evaluations

The proposed equation of state has been evaluated and compared with four other equations of state in the capability of representing the densities and second virial coefficients. The evaluations for the fugacity coefficients and the isothermal enthalpy differences are given in Chapters V and IX.

Table I presents the average absolute percent deviations of the five equations of state in predicting the densities of 13 pure substances in the vapor phase. These evaluations were made against the tabulated data of Canjar and Manning (37). The compressibility factors

TABLE I

COMPARISON OF PURE COMPONENT DENSITIES FROM FIVE EQUATIONS OF STATE

		Conditions		Average Absolute % Deviations of Densities from Canjar and Manning Data (37)				
Substance	Number of Points	$T_{min.}$ °F	$P_{max.}$ PSIA	Redlich -Kwong (166)	Barner et al. (12)	Benedict et al. (16)	Edmister et al. (65)	Equation 4-9
Nitrogen	63	-320	5,000	0.955	0.915	--	0.904	0.739
Carbon Dioxide	68	- 65	3,000	0.848	0.783	0.772	0.772	0.805
Methane	115	-250	5,000	0.606	0.589	0.384	1.145	0.225
Acetylene	51	-113	1,400	2.341	1.650	--	1.449	1.278
Ethene	78	-155	3,500	1.102	0.814	0.422	0.666	0.562
Ethane	71	-128	3,500	0.933	0.435	0.394	0.386	0.298
Propene	86	- 54	3,500	1.475	1.003	0.420	0.672	0.501
Propane	81	- 43	3,500	1.378	0.537	0.327	0.415	0.263
i-Butene	54	32	1,000	1.144	0.837	0.481	0.481	0.448
i-Butane	81	11	3,500	2.250	1.438	0.276	1.011	0.741
n-Butane	75	40	3,500	1.585	0.676	0.434	0.401	0.411
n-Pentane	76	97	3,500	2.050	0.832	0.562	0.350	0.336
n-Hexane	55	160	600	2.987	1.635	1.550	1.510	1.059

of six hydrocarbon binary mixtures are compared in Table II (153, 156, 157, 158, 163, 179).

From Tables I and II, one can see that Equation 4-9 is more accurate than any other generalized equations of state and as accurate as the Benedict-Webb-Rubin equation of state. The accuracy of the proposed equation of state is further verified by the high performance of derived thermodynamic functions as will be shown in the following chapters.

In Table III the second virial coefficients calculated from six different expressions are compared with experimental values of McGlashan and Potter (119). The six expressions include the second virial coefficient expressions derived from Equation 4-9, Redlich-Kwong (166), Benedict et al. (16), and Martin (143) equations of state, and the expressions of McGlashan and Potter (119) and Curl and Pitzer (56).

The second virial coefficient expression derived from the proposed equation of state is

$$B = \frac{RT_c}{P_c}\Big[(0.1231 - 0.25913/T_r - 0.2015/T_r^2) + \omega\,(0.15269 + 0.031314/T_r - 0.2164/T_r^2 - 0.042/T_r^6)\Big] \tag{4-42}$$

The derivation of this equation is given in Appendix C.

The agreement of Equation 4-42 with experimental values is satisfactory in that it is derived from an equation of state. It is interesting to note that the values obtained from Equation 4-42 generally lie between the corresponding values of McGlashan and Potter, and Curl and Pitzer expressions.

TABLE II

COMPARISON OF Z VALUES FROM FOUR GENERALIZED EQUATIONS OF STATE WITH EXPERIMENTAL DATA FOR SIX HYDROCARBON BINARY MIXTURES

			Conditions		Average Absolute Percent Deviations			
System	Reference	Number of Points	$T_{min.}$ °F	$P_{max.}$ PSIA	Redlich-Kwong (166)	Barner et al. (12)	Edmister et al. (65)	Equation 4-9
Methane-Propane	163	21	40	1,300	2.287	3.404	2.096	1.869
Methane-n-Pentane	179	26	160	2,338	1.525	2.466	1.136	0.939
Methane-n-Decane	157	18	100	5,000	2.269	3.883	1.320	1.513
Ethane-n-Pentane	153	15	100	800	6.124	6.560	5.499	4.209
Ethane-n-Decane	156	16	160	1,500	2.061	5.151	3.629	2.166
Propane-n-Decane	158	16	160	600	1.183	2.086	1.681	1.307
Overall Average Absolute Percent Deviations of 112 Points :					2.431	3.747	2.364	1.871

TABLE III

COMPARISON OF SECOND VIRIAL COEFFICIENTS FROM SIX EQUATIONS WITH EXPERIMENTAL VALUES

			Percent Deviations of Second Virial Coefficients					
Substance	Temp. $^{\circ}K$	Experimental B $cm^3/g\text{-}mol$ (119)	Redlich -Kwong (166)	Martin (113)	Benedict et al. (16)	Equation 4-42	McGlashan -Potter (119)	Pitzer -Curl (142)
Propane	295.4	-399.0	-7.157	27.482	6.885	2.243	-0.912	2.537
	337.8	-299.0	-2.501	10.377	4.110	2.568	-0.515	2.520
	377.7	-229.0	3.457	0.255	4.527	5.177	2.470	4.514
	412.9	-182.0	9.585	-5.768	6.319	8.397	6.354	6.998
n-Butane	296.4	-720.0	-16.231	40.051	4.847	1.684	0.603	2.531
	337.8	-533.0	-9.688	24.885	3.814	2.349	0.574	3.177
	377.9	-410.0	-3.824	13.114	3.666	3.940	1.824	4.316
	413.4	-322.0	3.874	7.638	6.884	8.481	6.395	8.180
n-Pentane	298.2	-1194.0	-26.457	40.566	10.201	-0.036	0.339	1.154
	339.0	-863.0	-18.087	30.282	9.454	0.989	0.360	2.465
	378.9	-652.0	-10.610	20.943	8.922	3.266	1.717	4.570
	413.6	-517.0	-3.542	15.002	9.759	6.695	4.653	7.493
n-Hexane	313.5	-1676.0	-33.935	31.320	1.201	-3.573	-2.274	-2.056
	354.0	-1194.0	-24.400	26.429	3.092	-1.282	-1.160	0.620
	387.2	-913.0	-15.234	24.471	6.605	3.773	2.800	5.741
	413.1	-771.0	-10.362	19.804	6.589	5.423	3.745	7.150
n-Heptane	349.4	-1819.0	-28.807	32.496	-2.809	3.810	5.670	6.149
	368.5	-1560.0	-24.107	30.905	-1.530	5.000	6.218	7.550
	389.1	-1325.0	-18.551	29.877	0.487	7.455	7.926	10.143
	413.7	-1108.0	-12.366	27.829	2.337	10.248	9.847	12.899
Average Absolute Percent Deviations			14.139	22.975	5.202	4.319	3.318	5.138

CHAPTER V

VAPOR PHASE FUGACITY COEFFICIENT

The vapor phase fugacity coefficient is one of the three major thermodynamic functions that are used in the present K-value correlation.

The fugacity coefficient of a component is defined as the ratio of the fugacity of that component in actual vapor to the fugacity that would exist in ideal gas state, thus indicating the component's departure from ideal gas behavior.

$$\phi_i = \frac{\hat{f}_i^V}{Py_i} \tag{5-1}$$

The fugacity of a component in a phase is rigorously related to the volumetric properties of that phase. The functional relationship can be derived from basic thermodynamic laws. At constant composition and temperature

$$\left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,y} = \bar{V}_i \tag{5-2}$$

Combining Equation 5-2 with 2-4 gives

$$\left(\frac{\partial \ln \hat{f}_i}{\partial P}\right)_{T,y} = \frac{\bar{V}_i}{RT} \tag{5-3}$$

Integrating Equation 5-3 from zero pressure where $\hat{f}_i = Py_i$ to system pressure gives the following expression.

$$\ln \phi_i = \frac{1}{RT}\int_0^P (\bar{V}_i - \frac{RT}{P})\, dP \qquad (5\text{-}4)$$

For pure component "i" for which $y_i = 1.0$ and $\bar{V}_i = V_i$, Equation 5-4 becomes

$$\ln \frac{f_i}{P} = \frac{1}{RT}\int_0^P (V_i - \frac{RT}{P})\, dP \qquad (5\text{-}5)$$

Equation 5-4 is useful for evaluating the fugacity coefficient from the measurements of pressure and partial molal volume taken at constant composition and temperature. However, such experimental data are generally tedious and time consuming to obtain. Thus, one customarily uses an equation of state in representing the P-V-T composition data necessary for the calculation of the fugacity coefficient.

Since most equations of state are of the pressure-explicit form, it is more convenient to express Equation 5-4 in a volume integral form. Beattie (13) derived such an expression starting with the Helmholz free energy relationship to obtain

$$\ln \phi_i = \frac{1}{RT}\int_{V_t}^{\infty} \left[(\frac{\partial P}{\partial n_i})_{T,V_t,n_j} - \frac{RT}{V_t} \right] dV_t - \ln Z \qquad (5\text{-}6)$$

From this expression and any pressure-explicit equation of state, one can derive the fugacity coefficient as a function of pressure, temperature and composition. But the derived function generally does not yield accurate values of the thermodynamic property, mainly because of the arbitrariness of the mixing rules associated with the equation of state used. The empirical nature of the equation of state may be another source of error. Nevertheless, this is apparently the best method available at present.

The Benedict-Webb-Rubin equation of state and the Redlich-Kwong equation of state have been most widely used for this purpose. The virial equation of state truncated after the second term is also frequently used for low and moderate pressure ranges. In this investigation the equation of state derived in Chapter IV is used, because it has many advantages which are shown in the related chapter. The fugacity coefficient expression derived from Equation 4-9 is

$$\ln \phi_i = B_i(Z - 1) - \ln Z + \left(\frac{A_i - aB_i}{RT\ b} - 1\right) \ln\left(1 - \frac{b}{V}\right)$$

$$- \left(\frac{0.5C_i - cB_i}{RT\ b^2}\right) \ln\left(1 - \frac{b^2}{V^2}\right) \qquad (5\text{-}7)$$

where $B_i = b_i/b$ (5-8)

$$A_i = 2\left[(a_1\ a_{1i})^{\frac{1}{2}} - (a_2\ a_{2i})^{\frac{1}{2}}T + a_{3i}^{\frac{1}{2}}\left(\sum_{j=1}^{N} y_j\, \alpha_{ij}\ a_{3j}^{\frac{1}{2}}\right)/T\right.$$

$$\left. + a_{4i}^{\frac{1}{2}}\left(\sum_{j=1}^{N} y_j\, \beta_{ij}\ a_{4j}^{\frac{1}{2}}\right)/T^5 \right] \qquad (5\text{-}9)$$

$$C_i = 3\left[c_1(c_{1i}/c_1)^{1/3}/T^{\frac{1}{2}}\right.$$

$$\left. + c_{2i}^{1/3} \sum_{j=1}^{N} \sum_{k=1}^{N} y_j\ y_k\, \theta_{ijk}(c_{2j}\ c_{2k})^{1/3}/T^2\right] \qquad (5\text{-}10)$$

The derivation of these expressions is given in Appendix C and the interaction coefficients α_{ij}, β_{ij}, and θ_{ijk} are given by Equations 5-14 through 5-16.

The accurate evaluation of the fugacity coefficient expression is practically impossible, because the fugacity coefficient can not be measured experimentally. One way of evaluating such a thermodynamic property expression is to compare the fugacity coefficients calculated from the expression with the values obtained from the direct integration of experimental P-V-T data of pure components. Table IV shows such evaluation results of five different fugacity coefficient expressions, as referenced. The evaluations were made against the fugacity coefficient data compiled by Canjar and Manning (37).

The accurate prediction of pure component fugacity coefficient, however, is not necessarily the indication that the fugacity coefficient expression would also be satisfactory for the fugacity coefficient of a component in a mixture. This statement is especially true for the component that is diluted in the mixture. It is mainly due to the striking effect of the mixing rules on the calculated fugacity coefficients of minor components.

In Table V the component fugacity coefficients that are calculated from four different equations of state are given. The table shows that the calculated fugacity coefficients of light components are not sensitive to the expressions, nor to the mixing rules, whereas those of heavy components are highly dependent on both the expressions and the mixing rules. The effect of mixing rules on the heavy component fugacity coefficient is demonstrated in the last two columns of this table.

As is evident from Table V, care must be exercised in formulating the mixing rules to be used for the calculation of partial properties including the fugacity coefficient. In the past the great concern in mixing rules has been focused on the capability of representing the

TABLE IV

COMPARISON OF PURE COMPONENT FUGACITY COEFFICIENTS FROM FIVE EQUATIONS OF STATE

		Conditions		Average Absolute % Deviations of Fugacity Coefficients from Canjar and Manning Data (37)				
Substance	Number of Points	$T_{min.}$ °F	$P_{max.}$ PSIA	Redlich -Kwong (166)	Barner et al. (12)	Benedict et al. (16)	Edmister et al. (65)	Equation C-13
Saturated								
Methane	13	-250	527	0.616	0.575	0.189	2.637	0.393
Ethane	12	-100	632	1.189	0.347	0.421	2.796	0.287
Propane	13	- 20	525	1.112	0.229	0.915	1.262	0.284
n-Butane	12	40	437	1.476	0.376	0.469	0.430	0.553
n-Pentane	14	100	393	1.814	0.365	0.982	1.425	0.265
Overall Average Absolute Percent Deviations:				1.248	0.379	0.606	1.719	0.353
Superheated								
Methane	10	-200	3,000	0.920	0.829	0.744	1.816	0.191
Ethane	11	0	3,000	1.246	0.349	0.677	0.680	0.262
Propane	11	100	2,000	1.499	0.665	0.308	0.679	0.324
n-Butane	11	180	1,000	0.914	1.311	0.241	0.609	0.305
n-Pentane	10	240	700	1.179	0.934	0.563	1.268	0.600
Overall Average Absolute Percent Deviations:				1.164	0.776	0.512	1.063	0.335

TABLE V

COMPONENT FUGACITY COEFFICIENTS CALCULATED FROM FOUR EQUATIONS OF STATE

System	Temp. °F	Pressure PSIA	y of Light Component	Fugacity Coefficients of Light Components				
				Redlich -Kwong (166)	Benedict et al. (12)	Edmister et al. (65)	Equation 5-7 Mixing Rules	
							Original	Modified
H_2-Cyclohexane (26)	100	500	0.9921	1.021	--	1.023	1.027	1.027
		2,000	0.9969	1.087	--	1.103	1.113	1.113
		4,000	0.9973	1.186	--	1.231	1.242	1.242
	280	500	0.8582	1.030	--	1.036	1.038	1.038
		2,000	0.9503	1.075	--	1.091	1.099	1.098
		4,000	0.9651	1.150	--	1.189	1.198	1.197
Methane-n-Heptane (162)	160	1,000	0.9804	0.935	0.937	0.934	0.942	0.942
		2,000	0.9705	0.889	0.892	0.887	0.901	0.901
	340	200	0.5047	1.066	1.082	1.093	1.090	1.090
		1,000	0.8260	1.021	1.029	1.030	1.038	1.037
		2,000	0.8041	1.058	1.080	1.081	1.097	1.090
Ethane-n-Decane (74)	220	100	0.9817	0.975	--	0.976	0.976	0.976
		500	0.9934	0.878	--	0.882	0.883	0.883
		1,000	0.9919	0.767	--	0.777	0.776	0.776
	400	200	0.8362	0.985	--	0.992	0.992	0.993
		600	0.9118	0.940	--	0.950	0.952	0.952
		1,600	0.8389	0.897	--	0.944	0.950	0.965

TABLE V (Continued)

				Fugacity Coefficients of Heavy Components				
							Equation 5-7 Mixing Rules	
System	Temp. °F	Pressure PSIA	y of Heavy Component	Redlich -Kwong (166)	Benedict et al. (12)	Edmister et al. (65)	Original	Modified
H_2-Cyclohexane (26)	100	500	0.0079	0.960	--	0.984	0.971	0.915
		2,000	0.0031	0.950	--	1.090	1.011	0.820
		4,000	0.0027	1.042	--	1.370	1.157	0.813
	280	500	0.1418	0.860	--	0.846	0.847	0.832
		2,000	0.0497	0.893	--	0.941	0.914	0.846
		4,000	0.0349	1.003	--	1.164	1.066	0.931
Methane-n-Heptane (162)	160	1,000	0.0196	0.376	0.403	0.417	0.350	0.353
		2,000	0.0295	0.154	0.163	0.175	0.120	0.129
	340	200	0.4953	0.761	0.747	0.730	0.724	0.724
		1,000	0.1740	0.472	0.484	0.479	0.438	0.443
		2,000	0.1959	0.247	0.251	0.250	0.206	0.220
Ethane-n-Decane (74)	220	100	0.0183	0.826	--	0.816	0.795	0.814
		500	0.0066	0.376	--	0.370	0.319	0.360
		1,000	0.0081	0.121	--	0.118	0.082	0.105
	400	200	0.1638	0.764	--	0.754	0.725	0.736
		600	0.0882	0.500	--	0.518	0.456	0.481
		1,600	0.1611	0.129	--	0.116	0.081	0.082

mixture properties, not the partial properties. Consequently a good formulation of mixing rules must be preceded by an extensive study on the capability of mixing rules of predicting the partial properties as well as the mixture properties. This kind of study, however, requires a considerable amount of time and efforts. Thus, in this investigation attentions were paid solely to the mixture volume and the fugacity coefficient of heavy component. It should be noted that the pure liquid fugacity coefficient is a real state property and the activity coefficient is close to unity for the heavy component in a binary mixture. Therefore, only the fugacity coefficient can be arbitrarily adjusted, when Equation 2-11 is applied to the heavy component. This fact together with the high sensitivity of heavy component fugacity coefficient to mixing rules leads to the modification of the mixing rules.

The heavy component fugacity coefficients calculated via Equation 5-7 generally indicated that the quantities should be corrected at low temperatures and near the critical region to satisfy Equation 2-11. Therefore, the mixing rules for the constants a_3 and a_4 were modified for the correction of the fugacity coefficients at low temperatures, and the mixing rule for c_2 was modified for the adjustment of the property around the critical region. The modifications are as follows.

$$a_3 = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i \, y_j \alpha_{ij} (a_{3i} \, a_{3j})^{\frac{1}{2}} \tag{5-11}$$

$$a_4 = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i \, y_j \beta_{ij} (a_{4i} \, a_{4j})^{\frac{1}{2}} \tag{5-12}$$

$$c_2 = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} y_i \, y_j \, y_k \theta_{ijk} (c_{2i} \, c_{2j} \, c_{2k})^{1/3} \tag{5-13}$$

As these constants are associated with energy terms, the interaction coefficients were expressed in terms of critical temperatures as follows.

$$\alpha_{ij} = \left[\frac{2(T_{ci}\ T_{cj})^{\frac{1}{2}}}{T_{ci} + T_{cj}}\right]^{m_1} \tag{5-14}$$

$$\beta_{ij} = \left[\frac{2(T_{ci}\ T_{cj})^{\frac{1}{2}}}{T_{ci} + T_{cj}}\right]^{m_2} \tag{5-15}$$

$$\theta_{ijk} = \left[\frac{3(T_{ci}\ T_{cj}\ T_{ck})^{1/3}}{T_{ci} + T_{cj} + T_{ck}}\right]^{m_3} \tag{5-16}$$

The exponents m_1, m_2, m_3 were determined by regression analysis. The detailed description of this analysis is given in Chapter VIII, but the values of the constants are given in this chapter (Table VI).

TABLE VI

CONSTANTS FOR VAPOR PHASE INTERACTION COEFFICIENTS IN EQUATIONS 5-14, 5-15, AND 5-16

	m_1	m_2	m_3
Hydrogen Binaries	-1	-8	-3
Nitrogen Binaries	0	-5	-2
Methane Binaries	0	-5	-2
Others	2	7	5

CHAPTER VI

LIQUID FUGACITY COEFFICIENTS OF PURE COMPONENT

The fugacity of a pure liquid is frequently used in defining the activity coefficient expressing the departure from ideal solutions. But a satisfactory analytical correlation for this thermodynamic property has not been developed except for a few tabular correlations. The Chao-Seader (41) correlation is in equation form but this expression does not represent the actual values of the fugacity coefficient, especially at temperatures lower than $T_r = 0.8$, below which the correlation is good only for the corresponding Chao-Seader K-value correlation.

Since this chapter discusses the pure component properties only, the subscripts indicating the component identity are omitted throughout the chapter.

Lydersen et al.(112) calculated the fugacity coefficient from their generalized compressibility factor and tabulated the values as a function of T_r, P_r and Z_c over a range of $T_r = 0.5$ to 1 and $P_r = 0.01$ to 30.

Curl and Pitzer (56) constructed similar tabulations using ω as the third parameter over the conditions of $T_r = 0.8$ to 1.0 and $P_r = 0.1$ to 9. The authors presented the following expression for ν.

$$\log \nu = \log \nu^{0} + \omega \log \nu' \tag{6-1}$$

Recently Chao et al. (43) calculated ν values using low vapor pressure data (194) over the conditions of $T_r = 0.35$ to 0.75 and $P_r \leqslant 10$.

and presented two generalized tabular correlations, ω being the third parameter of one and Z_c the third parameter of the other.

Real Liquid Fugacity Coefficient of Pure Component

The objective of the work described in this section is to develop a generalized analytical equation for the fugacity coefficient of pure liquid hydrocarbons, as the correlation is to be used in a computer algorithm for the prediction of vapor-liquid K-values. The performance requirements of this equation are: (a) agreement with ν values calculated from P-V-T data over wide range of conditions and (b) satisfactory representation of the isothermal enthalpy differences obtained from the temperature derivatives of ln ν.

This fugacity coefficient equation is limited to "real" liquids and is not intended for "hypothetical" liquids, thus fixing $T_r = 1.0$ as the upper temperature limit. The lower temperature limit is set at $T_r = 0.4$ below which sufficiently accurate input data are not available. Also $T_r = 0.4$ seems to represent a satisfactory lower limit for a general purpose correlation, excluding cryogenic conditions.

Values of fugacities, for use in developing the desired empirical equation, were obtained from following thermodynamic relationship.

$$\ln f = \ln \nu^s + \ln p^s + \frac{1}{RT}\int_{p^s}^{P} V^L \, dP \qquad (6\text{-}2)$$

Since fugacities are identical for coexisting equilibrium vapor and liquid, the values of ν^s for the saturated vapor can be used as those of saturated liquid.

Values of ν^s, V^s and p^s for methane through n-pentane were taken from the tabulations of Canjar and Manning (37) for the temperature range of $T_r = 0.6$ to 1.0. As the tabulations contain no data at subatmospheric conditions, the vapor pressure and liquid volume data in the range of $T_r = 0.4$ to 0.6 were obtained from other sources (5, 11, 125, 189, 194). The ν^s values in this low temperature range were calculated from the equation of state derived in Chapter IV. The latter is justified by the fact that (a) the variation of ν^s is between 0.97 and 1.0, and (b) the equation of state has a satisfactory performance at this low vapor pressure condition.

In evaluating the Poynting effect, i.e., the last term in Equation 6-2, the Chueh and Prausnitz (49) correlation of liquid molal volume was used.

$$V^L = V^s \left[1 + 9\beta (P_r - P_r^s) \right]^{-1/9} \tag{6-3}$$

where

$$\beta = Z_c(1 - 0.89\, \omega^{\frac{1}{2}}) \exp(6.9547 - 76.2853\, T_r + 191.306\, T_r^2 - 203.5472\, T_r^3 + 82.7631\, T_r^4) \tag{6-4}$$

The frequently made assumption that V^L is independent of pressure is not satisfactory at temperatures above $T_r = 0.7$.

Integrating Equation 6-3 with respect to pressure between the vapor pressure and system pressure gives

$$\frac{1}{RT} \int_{P^s}^{P} V^L dP = \frac{P_c V^s}{8RT\beta} \left[\left\{ 1 + 9\beta (P_r - P_r^s) \right\}^{8/9} - 1 \right] \tag{6-5}$$

When the bracketed term is expanded into an infinite series, Equation 6-5 becomes

$$\frac{1}{RT}\int_{P^s}^{P} V^L dP = \frac{P_c V^s}{RT}(P_r - P_r^s) - \frac{P_c V^s \beta}{2RT}(P_r - P_r^s)^2 + \ldots \tag{6-6}$$

The first term of the right-hand side of Equation 6-6 is identical to the term that would result when the liquid volume is assumed incompressible. Since the effects of third and higher terms were negligible, the series was truncated after the second term and rearranged to give

$$\ln \frac{f}{P_c} = F_1 + F_2 P_r + F_3 P_r^2 \tag{6-7}$$

where

$$F_1 = \ln \nu^s + \ln P_r^s - \frac{p^s V^s}{RT}\left(1 + \frac{\beta}{2} P_r^s\right) \tag{6-8}$$

$$F_2 = \frac{P_c V^s}{RT}(1 + \beta P_r^s) \tag{6-9}$$

$$F_3 = -\frac{P_c V^s \beta}{2RT} \tag{6-10}$$

As ν^s, p^s, and V^s are all functions of temperature and independent of pressure, F_1, F_2, and F_3 are also functions of temperature only. More convenient temperature functions than Equations 6-8, 6-9, and 6-10 were desired. An empirical form for these functions can be deduced from a fugacity-enthalpy relationship. The isobaric temperature derivative of ln f is related to the isothermal enthalpy difference by

$$\left(\frac{\partial \ln f}{\partial T}\right)_P = (H^o - H)/RT^2 \tag{6-11}$$

Integrating Equation 6-11 at constant pressure, combining with $H = \int C_p dT$, and $C_p = b_1 + b_2 T + b_3 T^2$ and expressing the temperature in reduced form gives the following expression.

$$\ln \frac{f}{P_c} = B_1 + B_2/T_r + B_3 \ln T_r + B_4 T_r + B_5 T_r^2 \tag{6-12}$$

This form is more convenient than Equations 6-8, 6-9, and 6-10 for the temperature effects. It also has semi-theoretical justification, as shown above. Thus, an empirical equation of this form after being fitted to derived fugacities should also fit enthalpy difference values.

F_1 and F_2 were recasted by fitting Equation 6-12 to the values obtained from Equations 6-8 and 6-9, and F_3 was approximated by a single constant function of temperature.

The constants obtained in this manner were all nearly linear with the acentric factor. Therefore, all the constants were forced to be linear functions of ω and readjusted by fitting the resulting equation to the values of f/P_c obtained from Equations 6-2 and 6-5. In this fitting operation a T_r^6 term was added to improve the enthalpy prediction near the critical region. This prediction is made via Equation 6-11. The deviation function which is multiplied by ω was simplified to a more convenient form without loss of accuracy. The final equation is

$$\begin{aligned}\ln \nu = {} & A_1 + A_2/T_r + A_3 \ln T_r + A_4 T_r^2 + A_5 T_r^6 \\ & + (A_6/T_r + A_7 \ln T_r + A_8 T_r^6)\, P_r + A_9 T_r^3 P_r^2 - \ln P_r \\ & + \omega \left[(1 - T_r)(A_{10} + A_{11}/T_r) + A_{12} P_r/T_r + A_{13} T_r^3 P_r^2 \right]\end{aligned} \tag{6-13}$$

where

$A_1 = 6.32873$ $A_2 = -8.45167$

$A_3 = -6.90287$ $A_4 = 1.87895$

$A_5 = -0.33448$ $A_6 = -0.018706$

$A_7 = -0.286517$ $A_8 = 0.28940$

$A_9 = -0.002584$ $A_{10} = 8.70150$

$A_{11} = -11.201$ $A_{12} = -0.05044$

$A_{13} = 0.002255$

Evaluations

Values of ν from Equation 6-12 are compared with other values in Figures 1 through 5. Figures 1, 2, and 3 show the ν values of methane, n-pentane, and n-decane over the conditions of $T_r = 0.6$ to 1.0 and $P_r = 0.1$ to 10, while Figures 4 and 5 are for propane and n-decane at $T_r = 0.4$ and 0.5. On these Figures the solid curves are from Equation 6-12 and the dashed lines are from the Chao-Seader (41) equation. Other ν values shown on these plots are the values of Curl and Pitzer (56), Chao et al. (43) and also some values of ν that were calculated for propane at $T_r = 0.4$ and 0.5 via Equations 6-2 and 6-5, using the vapor pressure data of Tickner and Lossing (194) and the liquid volume data from A.P.I. Research Project 44 (5).

As can be seen on Figures 1, 2, and 3, the proposed equation agrees very well with the tabular values of Curl and Pitzer (56). Agreement between the proposed equation and the Chao et al. (43) correlation values is only fair at the lower temperatures despite the fact that the same experimental data were used in both studies. An average difference of about five percents was observed. In order to ascertain the possible sources of the difference, the fugacity coefficients of propane were calculated at $T_r = 0.4$ and 0.5 using the same method as was used by Chao et al. In Table VII these values are compared with the values obtained from the present calculation method, and also with the values predicted via the Chao et al. and the present correlations.

As shown in the table, the ν values from Equation 6-13 agree with

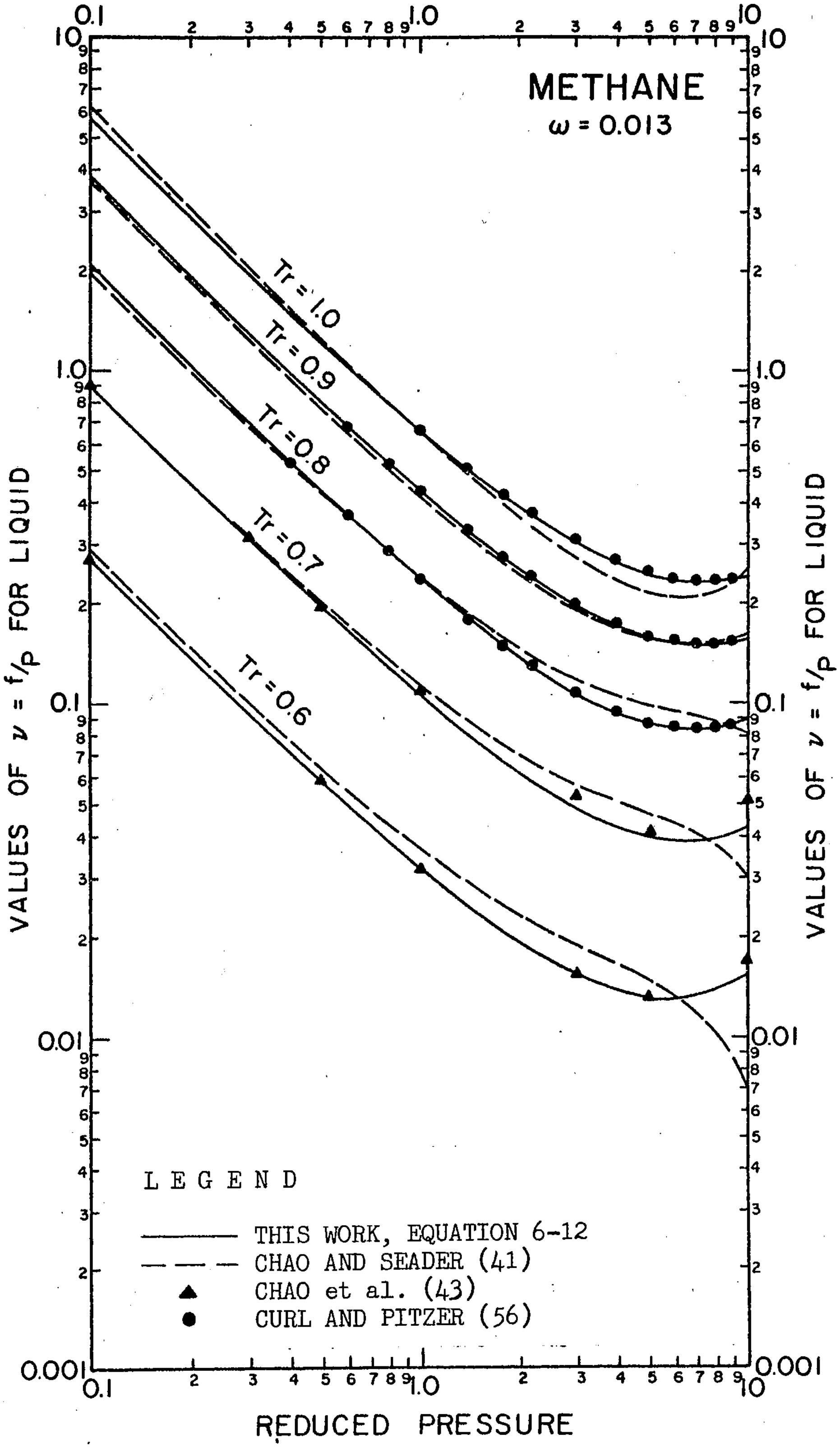

Figure 1. Comparison of ν Values for Methane

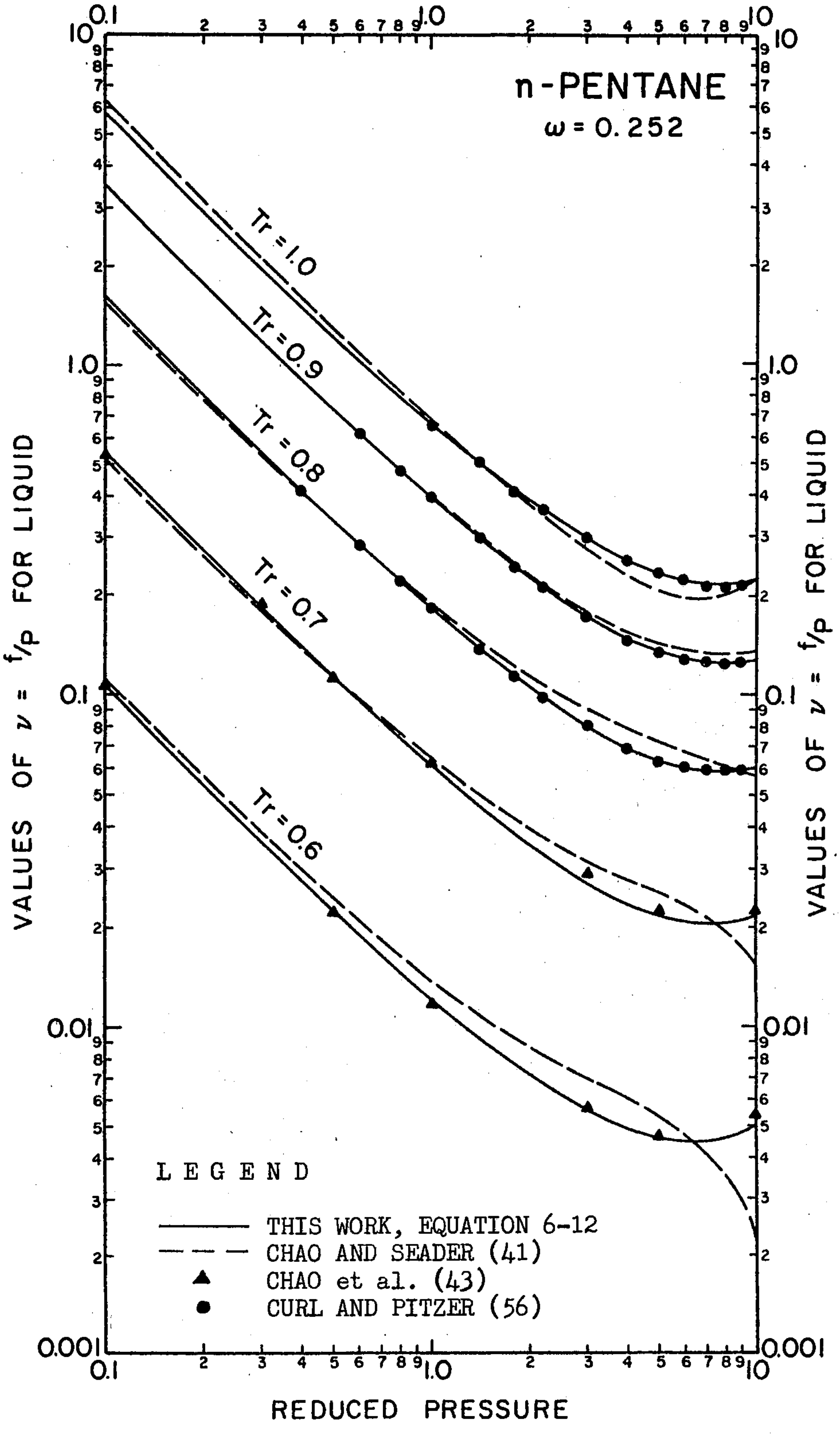

Figure 2. Comparison of ν Values for n-Pentane

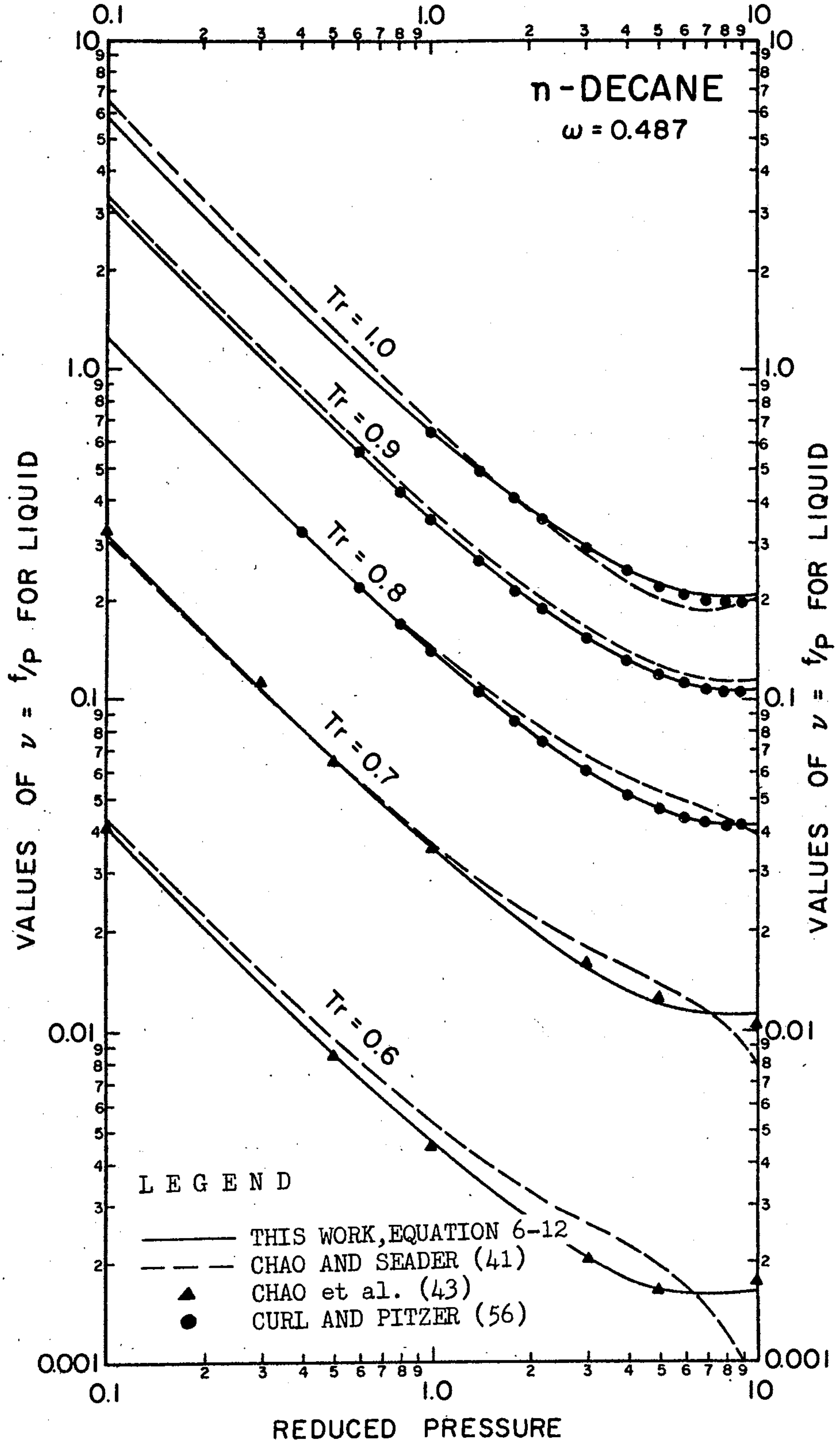

Figure 3. Comparison of ν Values for n-Decane

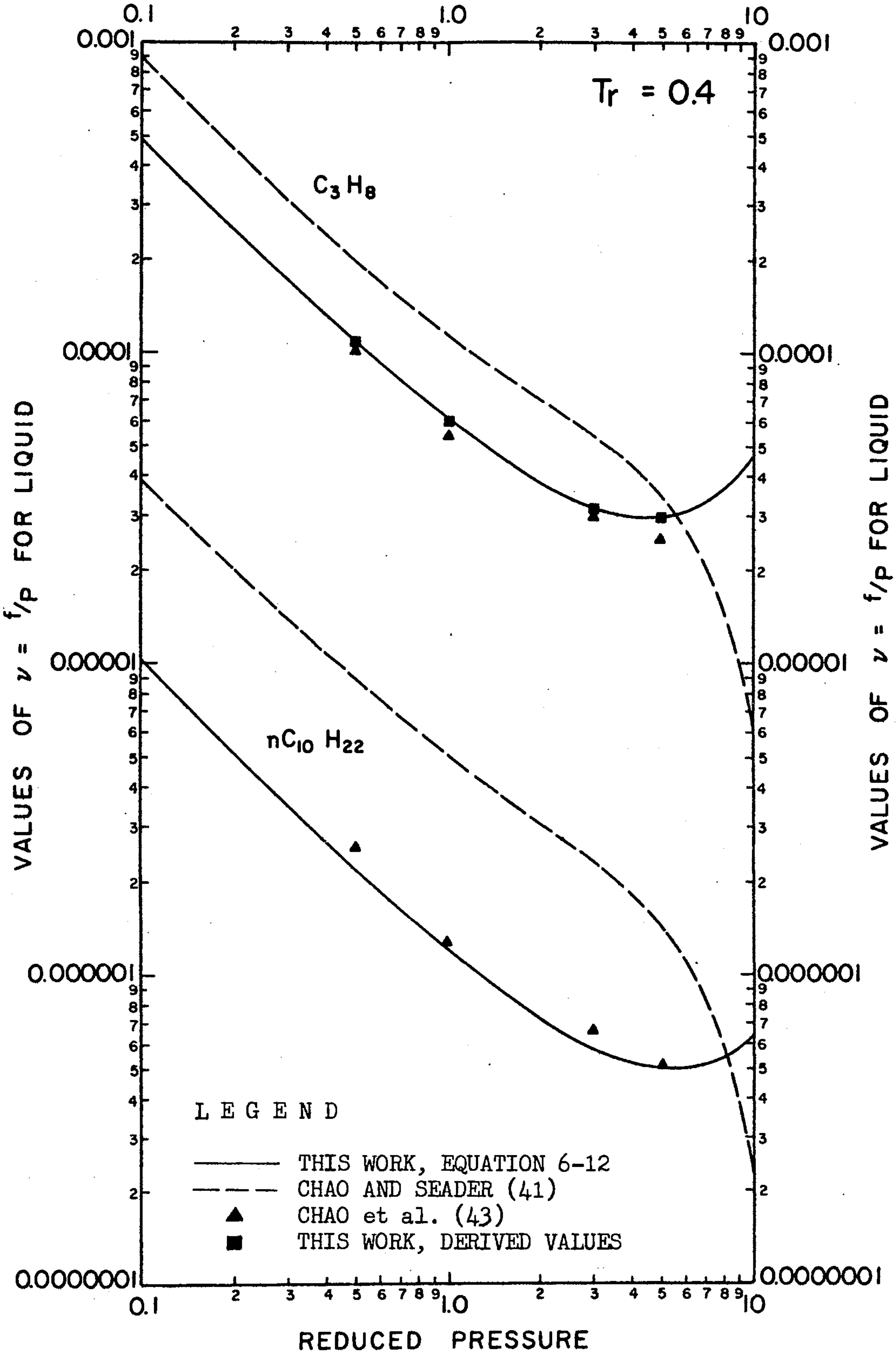

Figure 4. Comparison of ν Values at T_r = 0.4

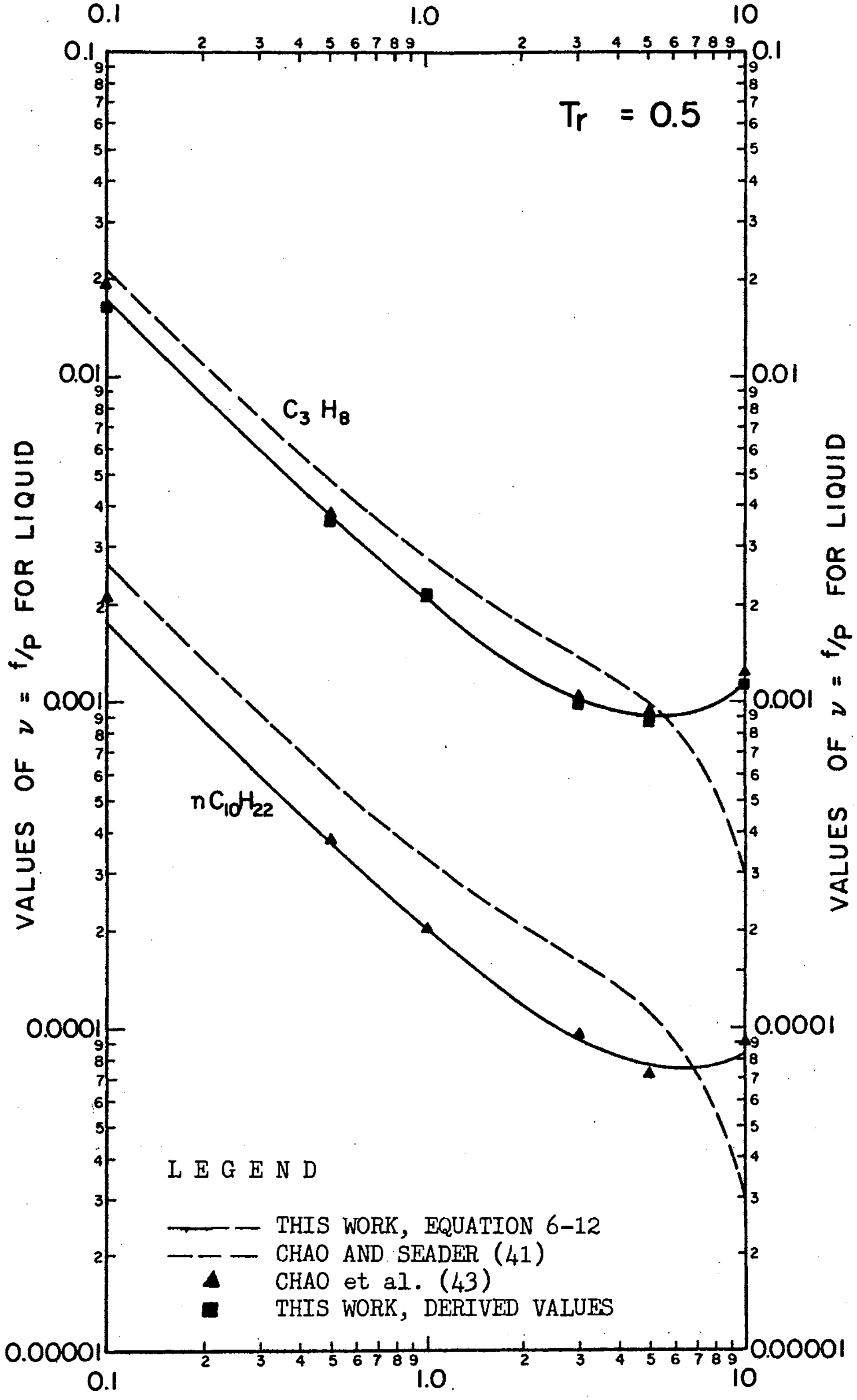

Figure 5. Comparison of ν Values at T_r = 0.5

TABLE VII

COMPARISON OF LIQUID FUGACITY COEFFICIENTS FOR PROPANE AT LOW TEMPERATURES

Conditions		ν Values			
		Chao et al. (43)		This Work	
T_r	P_r	Calculated	Predicted	Calculated	Predicted
0.4	0.5	0.109×10^{-3}	0.105×10^{-3}	0.109×10^{-3}	0.108×10^{-3}
	1.0	0.610×10^{-4}	0.540×10^{-4}	0.610×10^{-4}	0.607×10^{-4}
	3.0	0.320×10^{-4}	0.299×10^{-4}	0.319×10^{-4}	0.318×10^{-4}
	5.0	0.303×10^{-4}	0.254×10^{-4}	0.300×10^{-4}	0.300×10^{-4}
0.5	0.5	0.380×10^{-2}	0.381×10^{-2}	0.381×10^{-2}	0.378×10^{-2}
	1.0	0.209×10^{-2}	0.210×10^{-2}	0.210×10^{-2}	0.208×10^{-2}
	3.0	0.102×10^{-2}	0.106×10^{-2}	0.102×10^{-2}	0.102×10^{-2}
	5.0	0.901×10^{-3}	0.946×10^{-3}	0.895×10^{-3}	0.896×10^{-3}
	10.0	0.118×10^{-2}	0.125×10^{-2}	0.113×10^{-2}	0.115×10^{-2}

the values calculated from experimental vapor pressure data, whereas the Chao et al. correlation values do not agree. A similar comparison was made for n-pentane, for which the Chao et al. correlation agreed with the data-based ν values as well as did the present correlation.

The evaluation of isothermal enthalpy difference equation derived from Equation 6-13 is given in Chapter IX.

Hypothetical Liquid Fugacity Coefficient of Pure Component

This hypothetical property was devised to extend the K-value relationship of Equation 2-11 to the gaseous components dissolved in a liquid. The introduction of such a hypothetical property automatically requires that the reference state fugacity for the relevant activity coefficient should be also hypothetical, which contradicts the original idea of employing a "reference state". However, from a practical viewpoint, the use of a hypothetical reference state fugacity is as convenient as the use of a real state reference fugacity, providing the hypothetical property is properly determined.

Being devoid of any theoretical and physical meaning, the hypothetical liquid fugacity coefficient of pure component must be empirically determined using such a relationship as Equation 2-11 as was done in this investigation. But the hypothetical ν values of a component must be the same for given pressure and temperature regardless of the solvents in which the component is dissolved. Therefore, Equation 6-13, the ν expression that satisfies such a requirement for the real liquid was retained as the model for expressing ν of the hypothetical liquids with minor changes in the high power temperature terms. These changes were made to reduce the temperature sensitivity of the model at elevated temperatures. The numerical constants A_9 through A_{13} were kept unchanged.

$$\ln \nu = B_1 + B_2/T_r + B_3 \ln T_r + B_4 T_r^2 + B_5 T_r^3 + (B_6/T_r + B_7 \ln T_r + B_8 T_r^2) P_r + A_9 T_r P_r^2 - \ln P_r + \omega \left[(1 - T_r)(A_{10} + A_{11}/T_r) + A_{12} P_r/T_r + A_{13} T_r P_r^2\right] \tag{6-14}$$

This equation was fitted to the calculated ν values to determine the constants B_1 through B_8. The fitting procedure is described in detail in Chapter VIII. But the numerical values of the constants are given here (table VIII) for the sake of convenience. In the curve fitting operations, Equation 6-14 was forced to give the same values as does Equation 6-13 at $T_r = 1.0$, the junction point of the two ν expressions. The mathematical continuity of the two equations at the junction point was disregarded in favor of improved K-value predictions. This continuity, however, is important for the isothermal enthalpy difference that can be obtained by differentiating the ln ν expression with respect to temperature. As shown in Figure 6 the two ν expressions are fairly continuous at $T_r = 1.0$ for hydrocarbons.

TABLE VIII

CONSTANTS FOR FUGACITY COEFFICIENT OF HYPOTHETICAL LIQUID, EQUATION 6-14

	Hydrogen	Nitrogen	Carbon Dioxide	Hydrogen Sulfide	Methane	Ethene and Heavier Hydrocarbons
B_1	1.45610	9.82866	23.2166	14.5790	4.48018	7.83420
B_2	8.68977	-11.27670	-24.6427	-18.6046	-3.64274	-9.54010
B_3	0.60461	-3.65750	-25.5662	-22.7804	2.24320	-7.92000
B_4	-0.00375	0.18236	0.27361	3.77412	-1.40489	1.43018
B_5	0.0	0.0	1.10841	-0.17797	0.31421	-0.30278
B_6	0.09453	-0.13227	1.15963	-0.08928	-0.06910	0.22371
B_7	0.00491	0.0	7.81163	0.39462	0.95059	0.36252
B_8	0.0	-0.00715	-1.69703	0.01698	-0.12945	-0.05302

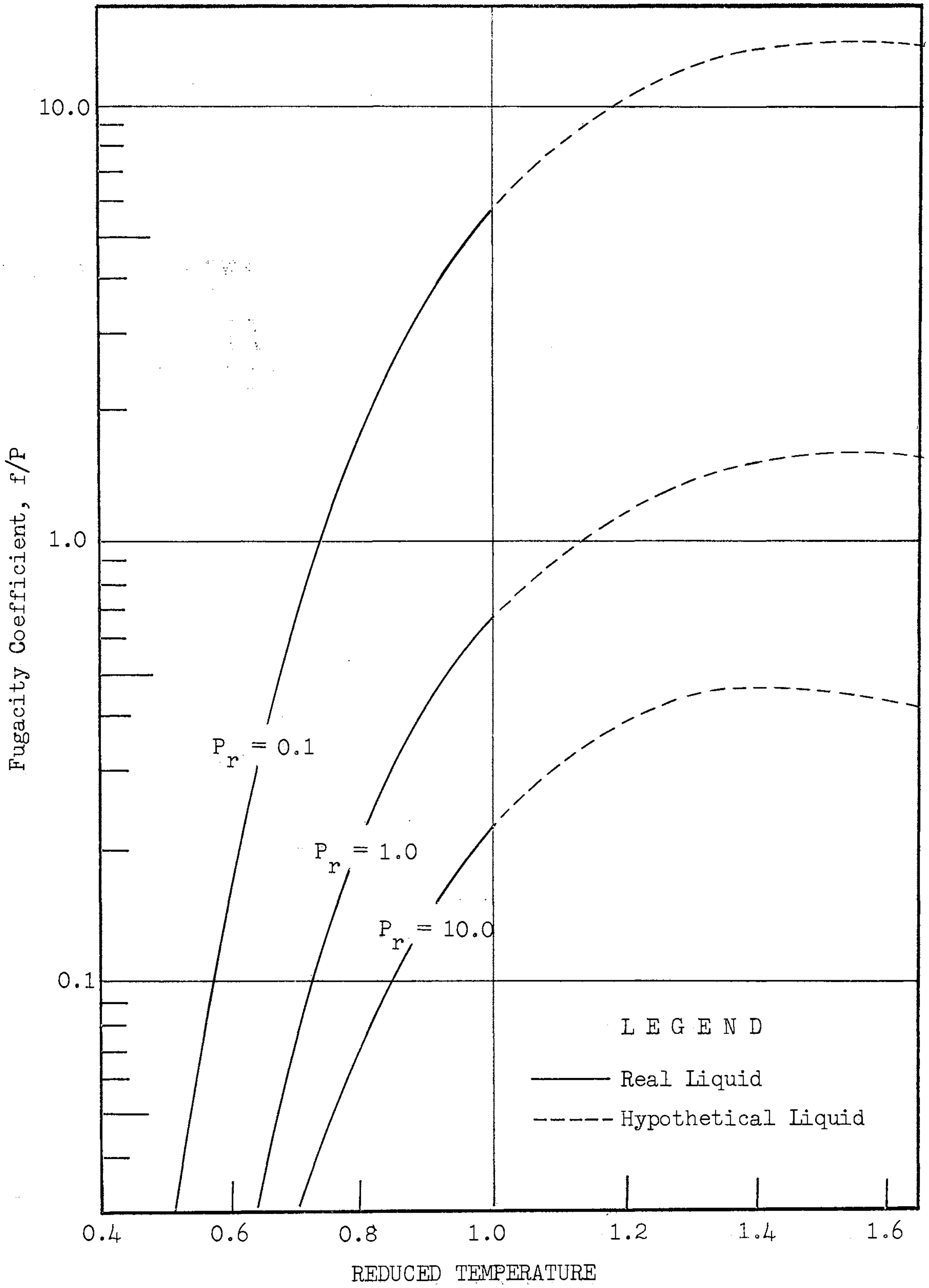

Figure 6. Fugacity Coefficients of Real and Hypothetical Liquid Propane in Pure State

CHAPTER VII

LIQUID PHASE ACTIVITY COEFFICIENTS

The activity coefficient was invented to relate the liquid fugacity of a component at some condition of pressure and composition to its liquid fugacity at some other "reference" condition where its numerical value can be accurately estimated. So the activity coefficient is not completely defined unless the standard state fugacity is clearly specified. Conventionally, the activity coefficient has been defined in such a way that it accounts for the departure of a real solution from ideal solution behavior, i.e., the departure from the Lewis-Randall rule. Symbolically,

$$\gamma_i = \frac{\hat{f}_i^L}{x_i f_i^L} \tag{7-1}$$

where f_i^L is the fugacity of pure component i at system temperature and pressure. Equation 7-1 is very convenient for the component that actually exists as a liquid at system pressure and temperature. However, the expression loses its physical meaning for a component that can not exist as a liquid at system conditions, since the standard state fugacity would be hypothetical at these conditions. This ambiguity necessitates the second definition of activity coefficient which describes the deviation from Henry's law, i.e.,

$$\gamma_i = \frac{\hat{f}_i^L}{x_i H_{ir}} \tag{7-2}$$

where H_{ir} is Henry's constant for component i in pure solvent r.

Equation 7-2 is not only meaningful but also convenient for the supercritical component in a pure solvent if the Henry's constant is available. However, for the solute dissolved in a mixed solvent, special care must be exercised in selecting the Henry's constant, since the constant depends on the nature of solvent as well as on temperature. This inconvenience plus the limited data on Henry's constants makes Equation 7-2 much less attractive than it appears to be.

The activity coefficient as defined by Equation 7-1 is said to be symmetrically normalized, because it approaches unity as x_i goes to unity for all real components. On the other hand, its counterpart as defined by Equation 7-2 is termed unsymmetrically normalized, since it approaches unity as x_i goes to zero for the supercritical component dissolved in pure solvents. The latter normalization can also be used for a noncondensable gas dissolved in a solvent mixture if the Henry's constant is properly selected. For this purpose Prausnitz et al. (144) proposed to define the reference fugacity of a supercritical component as the Henry's constant of that component in a pure reference solvent which is a constituent of the solvent mixture.

Notwithstanding the disadvantage of hypothetical state assumption, the activity coefficient as defined by Equation 7-1 has been used much more in practical engineering problems than has the unsymmetrical model, Equation 7-2, and it is also used in the present K-value correlation. Therefore, further discussion will be devoted only to Equation 7-1.

As is obvious from the derivation, Equations 5-4 and 5-5 are not restricted to any particular phase. Thus the equations can be equally applicable to liquid phase. Subtracting Equation 5-5 from Equation 5-4 and replacing y_i with x_i

$$\ln \gamma_i = \frac{1}{RT}\int_0^P (\bar{V}_i - V_i)\,dP \tag{7-3}$$

This equation shows the rigorous relationship of activity coefficient to the P-V-T composition data, but it is seldom used due to the lack of methods for accurately representing the volumetric data of dense phases. Therefore, the activity coefficient is customarily derived from its relationship with partial excess Gibbs free energy.

Integrating Equation 2-4 at constant temperature and composition from P^o to the system pressure P gives

$$\bar{G}_i - \bar{G}_i^o = RT \ln \frac{\hat{f}_i}{x_i P^o} \tag{7-4}$$

For pure component i, Equation 7-4 becomes

$$G_i - G_i^o = RT \ln \frac{f_i}{P^o} \tag{7-5}$$

Subtracting Equation 7-5 from 7-4 gives

$$(\bar{G}_i - G_i) - (\bar{G}_i^o - G_i^o) = RT \ln \gamma_i \tag{7-6}$$

Integrating Equation 2-4 at constant temperature and P^o from the pure component state to the state of composition x_i gives

$$\bar{G}_i^o - G_i^o = RT \ln x_i \tag{7-7}$$

Combining Equation 7-6 with Equation 7-7 gives

$$\bar{G}_i - G_i - RT \ln x_i = RT \ln \gamma_i \tag{7-8}$$

Applying Equation 7-5 to an ideal solution for which $\gamma_i = 1$, one obtains

$$(\bar{G}_i - G_i)^{id} = RT \ln x_i \tag{7-9}$$

Subtracting Equation 7-9 from 7-8 gives

$$(\bar{G}_i - G_i) - (\bar{G}_i - G_i)^{id} = \bar{G}_i^E = RT \ln \gamma_i \tag{7-10}$$

or

$$\ln \gamma_i = \frac{1}{RT}\left[\frac{\partial}{\partial n_i}(nG^E)\right]_{P,T,n_j} \tag{7-11}$$

Various activity coefficient expressions have been derived from Equation 7-11 using appropriate models for excess Gibbs free energy.

Activity Coefficient Models

A general model for excess Gibbs free energy was developed statistically by Wohl (209) in terms of composition x_i, and effective volume V_i' of individual components.

$$G^E/RT = \left[\sum_{i=1}^{N} x_i V_i'\right]\left[\sum_{i=1}^{N}\sum_{j=1}^{N} \Phi_i'\Phi_j' a_{ij} + \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N} \Phi_i'\Phi_j'\Phi_k' a_{ijk} + \ldots\right] \tag{7-12}$$

where

$$\Phi_i' = \frac{x_i V_i'}{\sum_{j=1}^{N} x_j V_j'}$$

From a three-suffix equation of the form of Equation 7-12 the commonly encountered van Laar, Porter, and Margules equations can be derived (88), even though the activity coefficient equations had already been derived before the G^E model was proposed.

Another open series model for G^E was proposed by Redlich and Kister (165). This model is a series of compositions at constant pressure and temperature. For a binary system,

$$G^E/RT = x_1x_2\left[B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \ldots\right] \tag{7-13}$$

$$\ln \gamma_1 = x_2^2\left[B - C(4x_2 - 3) + D(2x_2 - 1)(6x_2 - 5) + \ldots\right] \tag{7-14}$$

In order to apply Equation 7-13 or 7-14 to a liquid phase at equilibrium, Chao and Hougen (42) modified the model by eliminating the constant temperature restriction. Equation 7-14 is reduced to Porter's equations when $B \neq 0$, $C = D = \ldots = 0$, and to Margules' equations if $B \neq 0$, $C \neq 0$, but $D = \ldots = 0$. Van Ness (198) expressed the reciprocal of the left-hand side of Equation 7-13 as a power series of composition to obtain a van Laar type equation from the expression.

Flory (71) and Huggins (89) independently derived an expression for the entropy of mixing in an athermal solution using the concept of a quasicrystalline lattice as the model for a liquid. The negative of this expression multiplied by the absolute temperature T is identical to the excess Gibbs free energy for athermal solutions.

$$G^E/RT = -\frac{S^M}{R} = \sum_{i=1}^{N} x_i \ln \frac{\Phi_i}{x_i} \tag{7-15}$$

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} - \frac{\Phi_i}{x_i} + 1 \tag{7-16}$$

where $$\Phi_i = \frac{x_iV_i}{\sum_{j=1}^{N} x_jV_j}$$

In consideration of the nonrandomness in liquid mixtures, Wilson (206) proposed an expression for local composition.

$$\frac{x_{ij}}{x_{ii}} = \frac{x_j}{x_i} \exp\ (\lambda_{ji} - \lambda_{ii})/RT \qquad (\lambda_{ij} = \lambda_{ji}) \tag{7-17}$$

Expressing the volume fraction in terms of the local composition and substituting the local volume fraction for Φ_i in Equations 7-15 and 7-16, Wilson obtained the following equations.

$$G^E/RT = -\sum_{i=1}^{N} x_i \ln\left[\sum_{j=1}^{N} x_j \Lambda_{ij}\right] \tag{7-18}$$

$$\ln \gamma_i = 1 - \ln\left[\sum_{j=1}^{N} x_j \Lambda_{ij}\right] - \sum_{j=1}^{N} \xi_j \Lambda_{ji} \tag{7-19}$$

where

$$\xi_i = x_i/\left[\sum_{j=1}^{N} x_j \Lambda_{ij}\right]$$

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left[(\lambda_{ii} - \lambda_{ij})/RT\right]$$

Orye and Prausnitz (138) demonstrated that the Wilson equation is useful in representing equilibrium data for a wide variety of liquid mixtures.

Heil and Prausnitz (84) extended Wilson equation to nonathermal mixtures by adding heat effect terms to obtain

$$G^E/RT = -\sum_{i=1}^{N} x_i \ln\left[\sum_{j=1}^{N} x_j \Lambda_{ij}\right] + \sum_{i=1}^{N} \xi_i \sum_{j=1}^{N} x_j \Lambda_{ij} \tau_{ji} \tag{7-20}$$

$$\ln \gamma_i = 1 - \ln\left[\sum_{j=1}^{N} x_j \Lambda_{ji}\right] - \sum_{j=1}^{N} \xi_j \Lambda_{ji} + \frac{\xi_i}{x_i} \sum_{j=1}^{N} x_j \Lambda_{ij} \tau_{ji}$$

$$+ \sum_{j=1}^{N} \xi_j \Lambda_{ji} \left(\tau_{ij} - \frac{\xi_j}{x_j} \sum_{k=1}^{N} x_k \Lambda_{jk} \tau_{kj} \right) \tag{7-21}$$

where

$$\tau_{ji} = (\lambda_{ji} - \lambda_{ii})/RT$$

Based on Scott's two liquid theory and on a nonrandomness in liquid mixtures, Renon and Prausnitz (167) derived a different equation in terms of local compositions. This equation is essentially the same as the nonathermal part of the Heil-Prausnitz equation except that an additional parameter α_{ij} ($= \alpha_{ji}$) is introduced and $V_i = V_j$ is assumed.

$$G^E/RT = \sum_{i=1}^{N} \xi_i \sum_{j=1}^{N} x_j \, g_{ji} \, \tau_{ji} \tag{7-22}$$

$$\ln \gamma_i = \frac{\xi_i}{x_i} \sum_{j=1}^{N} x_j \, g_{ji} \, \tau_{ji} + \sum_{j=1}^{N} \xi_j \, g_{ij} \left[\tau_{ij} - \frac{\xi_j}{x_j} \sum_{k=1}^{N} x_k \, g_{kj} \, \tau_{kj}\right] \tag{7-23}$$

where $g_{ji} = \exp(- \alpha_{ji} \, \tau_{ji}/RT)$

The authors claimed that their NRTL (nonrandom, two-liquid) equation can be applied to strongly nonideal mixtures as well as to partially miscible liquids.

The equations of Wilson, Heil and Prausnitz, and Renon and Prausnitz all require determining two parameters per binary pair from experimental data. The NRTL equation requires another constant α_{ij} which is characteristic to each system under consideration.

Scatchard (181) and Hildebrand (85) independently proposed a regular solution model, which appears to be more suitable for hydrocarbon mixtures if appropriate modifications are made. The general form of Scatchard-Hildebrand equation is given by

$$G^E = E^E = \sum_{i=1}^{N} \sum_{j=1}^{N} \Phi_i \, A_{ij} \qquad (7\text{-}24)$$

$$\ln \gamma_i = \frac{V_i^L}{RT} \left[\sum_{j=1}^{N} \Phi_i \, A_{ij} - \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} \Phi_j \, \Phi_k \, A_{jk} \right] \qquad (7\text{-}25)$$

where A_{ij} is related to the cohesive energy density by

$$A_{ij} = C_{ii} + C_{jj} - 2C_{ij} \qquad (7\text{-}26)$$

Originally C_{ij} was assumed to be the geometric mean of C_{ii} and C_{jj}. In this case a simpler short-cut derivation of the activity coefficient is possible. The derivation is given in Appendix D.

As shown by Hildebrand and Scott (86) the geometric mean assumption is valid only if the ionization potentials and the collision diameters of the unlike molecules are equal. Hildebrand and Scott suggested using a correction factor to the geometric mean. Eckert and Prausnitz (61) proposed the following relationship to account for the deviation of C_{ij} from geometric mean of C_{ii} and C_{jj}.

$$C_{ij} = (1 - k_{ij})(C_{ii} \, C_{jj})^{\frac{1}{2}} \qquad (7\text{-}27)$$

Even with the correction to geometric mean, Equation 7-25 is not fully capable of describing the thermal and athermal parts of the activity coefficient altogether. In this regard, Weimer and Prausnitz (201), Chung and Zander (44), and recently Robinson and Chao (172) added the Flory-Huggins equation to Equation 7-25 to take the molecular size differences into account. From a theoretical view-point the addition of the two equations is not justified, for the equations are based on mutually exclusive assumptions. However, the combined form is generally more capable of representing wide variety of solutions, if the expression contains one or more adjustable parameters. Chang et al. (40) and Avasthi and Kobayashi (8) also proposed to express the activity coefficient as a sum of thermal and athermal contributions in a study of phase equilibria.

All of these facts imply that any activity coefficient model is applicable to any type of solution regardless of the assumptions made for the derivation, if the expression can satisfactorily describe the actual behavior of the solution.

Present Model for Activity Coefficient

By analogy to the models of Wohl and Margules, the excess Gibbs free energy has been formulated in this work as follows

$$G^E/RT = \frac{1}{2}\left[(\sum_{i=1}^{N} x_i V_i^L)(\sum_{j=1}^{N}\sum_{k=1}^{N} \Phi_j \Phi_k B_{jk}^*) + \sum_{j=1}^{N}\sum_{k=1}^{N} x_j x_k C_{jk}^* + \sum_{j=1}^{N}\sum_{k=1}^{N} \Phi_j \Phi_k D_{jk}^*\right] \qquad (7\text{-}28)$$

The first term on the right-hand side of the equation is identical to Wohl's two-suffix term and the second term is the same as Margules two-suffix term. The third term was added to make the model more flexible. This term is similar to the second term except for the replacement of mole fractions with volume fractions. Applying Equation 7-11 to Equation 7-28 results in

$$\ln \gamma_i = V_i^L \left[\sum_{j=1}^{N} \Phi_j B_{ij}^* - \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} \Phi_j \Phi_k B_{jk}^* \right]$$

$$+ \left[\sum_{j=1}^{N} x_j C_{ij}^* - \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} x_j x_k C_{jk}^* \right]$$

$$+ \left[\frac{\Phi_i}{x_i} \sum_{j=1}^{N} \Phi_j D_{ij}^* - \left(\frac{\Phi_i}{x_i} - \frac{1}{2}\right) \sum_{j=1}^{N} \sum_{k=1}^{N} \Phi_j \Phi_k D_{jk}^* \right] \tag{7-29}$$

The derivation is given in Appendix E.

The B_{ij}^* in the above equation was set equal to A_{ij}/RT to make the first bracketed term identical to Scatchard-Hildebrand equation which has been frequently used for hydrocarbon solutions. The A_{ij} is given by Equation 7-26. Combining Equation 7-26 with Equation 7-27 and replacing C_{ii} with the square of the solubility parameter δ_i gives

$$A_{ij} = (\delta_i - \delta_j)^2 + 2\, k_{ij}\, \delta_i\, \delta_j \tag{7-30}$$

or

$$B_{ij}^* = \left[(\delta_i - \delta_j)^2 + 2\, k_{ij}\, \delta_i\, \delta_j \right] / RT \tag{7-31}$$

For the generalization of Equation 7-31 the binary interaction coefficient k_{ij} was expressed in terms of solubility parameters.

$$k_{ij} = q \left[\frac{\delta_i + \delta_j}{2(\delta_i\, \delta_j)^{\frac{1}{2}}} - 1 \right] = \frac{q}{2(\delta_i\, \delta_j)^{\frac{1}{2}}} (\delta_i^{\frac{1}{2}} - \delta_j^{\frac{1}{2}})^2 \tag{7-32}$$

As k_{ij} is associated with the thermal part of activity coefficient, q was assumed to be a function of temperature. A linear temperature function was chosen over the other models tested.

$$q = q_1 + q_2 (T_{ri}\, T_{rj})^{\frac{1}{2}} \tag{7-33}$$

Combining Equations 7-30, 7-31, and 7-32 gives

$$B^*_{ij} = \frac{1}{RT}\left[(\delta_i - \delta_j)^2 + \left\{q_1 + q_2(T_{ri}\ T_{rj})^{\frac{1}{2}}\right\}(\delta_i\ \delta_j)^{\frac{1}{2}}\ (\delta_i^{\frac{1}{2}} - \delta_j^{\frac{1}{2}})^2\right] \tag{7-34}$$

Since the first bracketed term in Equation 7-29 was used to reflect the thermal effect, the other terms were made to represent the athermal effect on the activity coefficient. This was accomplished by defining C^*_{ij} and D^*_{ij} as follows.

$$C^*_{ij} = 4\ q_3\left[\frac{V_i^L + V_j^L}{2(V_i^L\ V_j^L)^{\frac{1}{2}}} - 1\right]^2 = q_3\left[\left(\frac{V_i^L}{V_j^L}\right)^{\frac{1}{4}} - \left(\frac{V_j^L}{V_i^L}\right)^{\frac{1}{4}}\right]^4 \tag{7-35}$$

Similarly

$$D^*_{ij} = q_4\left[\left(\frac{V_i^L}{V_j^L}\right)^{\frac{1}{4}} - \left(\frac{V_j^L}{V_i^L}\right)^{\frac{1}{4}}\right]^4 \tag{7-36}$$

In the formulation of Equations 7-35 and 7-36 it was tacitly assumed that the liquid molal volume could effectively represent the molecular size. Equations 7-29, and 7-33 through 7-35 constitute the proposed activity coefficient expression for the present K-value correlation. The constants q_1 through q_4 were determined by regression analysis which was carried out by using the K-values of various binary hydrocarbon systems. The regression procedures are given in Chapter VIII. Table IX contains five sets of such constants. The top priority is given to the constants for hydrogen, then to those for nitrogen and so on. For example, for the pair of hydrogen-benzene the constants for hydrogen should be used in preference to those for aromatics, and for the pair of propane-cyclohexane, the constants for cyclo-paraffins should be used. The characteristic constants used in this correlation are listed in Table X.

TABLE IX

CONSTANTS FOR INTERACTION RELATIONS IN ACTIVITY COEFFICIENT EQUATION

Constant	Hydrogen	Nitrogen	Aromatics	Cycloparaffins	General
q_1	-2.4063	19.8416	-3.2294	-3.2294	-2.0000
q_2	-0.3291	-19.9182	3.2943	5.0836	8.6762
q_3	-0.9746	-4.0250	-3.4483	-3.4483	-4.0000
q_4	4.8054	20.6178	42.6910	42.6910	-1.3333

TABLE X

CHARACTERISTIC CONSTANTS FOR PURE COMPONENTS

Compound	Critical Temperature °R	Critical Pressure PSIA	Acentric Factor ω	Solubility Parameter δ $(cal./ml)^{\frac{1}{2}}$	Liquid Molal Volume V^L ml/g.-mole
<u>Paraffins</u>					
Methane	343.9	673.1	0.013	5.66	64.0
Ethane	550.0	709.8	0.105	6.03	75.0
Propane	666.0	617.4	0.152	6.40	88.0
i-Butane	734.7	529.1	0.192	6.73	105.5
n-Butane	765.3	550.7	0.201	6.73	101.4
i-Pentane	829.8	483.5	0.206	7.02	117.4
n-Pentane	845.6	489.5	0.252	7.02	116.1
neo-Pentane	780.8	464.0	0.195	7.02	123.3
n-Hexane	914.2	440.0	0.290	7.27	131.6
n-Heptane	972.3	396.8	0.352	7.43	147.5
n-Octane	1024.3	362.1	0.399	7.55	163.5
n-Nonane	1073.0	332.1	0.444	7.65	179.6
n-Decane	1114.7	304.2	0.487	7.72	196.0
n-Undecane	1153.7	282.2	0.501	7.79	212.2
n-Dodecane	1187.7	261.6	0.539	7.84	228.6
n-Tridecane	1220.7	249.8	0.582	7.89	244.9
n-Tetradecane	1250.7	235.1	0.617	7.92	261.3
n-Pentadecane	1277.7	220.0	0.649	7.96	277.8
n-Hexadecane	1303.0	206.0	0.675	7.99	294.1
n-Heptadecane	1328.0	191.1	0.687	8.03	310.4
<u>Olefins</u>					
Ethene	509.5	742.2	0.089	6.02	73.0
Propene	657.2	667.2	0.143	6.43	84.0
1-Butene	755.3	583.4	0.203	6.76	95.3
cis-2-Butene	784.0	602.5	0.273	6.76	91.2
trans-2-Butene	771.6	602.5	0.234	6.76	93.8
i-Butene	752.2	579.8	0.201	6.76	95.4
1,3-Butadiene	765.7	628.0	0.203	6.94	88.0
1-Pentene	853.0	586.4	0.218	7.05	110.4
1-Hexene	920.0	471.7	0.246	7.40	125.8
<u>Naphthenes</u>					
Cyclopentane	921.2	654.7	0.205	8.11	94.7
Methylcyclopentane	959.0	549.0	0.235	7.85	113.1
Cyclohexane	995.3	591.5	0.203	8.20	108.7
Methylcyclohexane	1030.2	504.4	0.242	7.83	128.3

TABLE X (Continued)

Compound	Critical Temperature °R	Critical Pressure PSIA	Acentric Factor ω	Solubility Parameter δ $(cal./ml)^{\frac{1}{2}}$	Liquid Molal Volume V^L ml/g.-mole
Aromatics					
Benzene	1012.7	714.2	0.215	9.16	89.4
Toluene	1069.2	590.0	0.252	8.92	106.8
o-Xylene	1138.0	529.9	0.298	8.99	121.2
m-Xylene	1114.6	510.0	0.316	8.82	123.5
p-Xylene	1112.8	500.0	0.307	8.77	124.0
Ethylbenzene	1115.8	539.9	0.317	8.79	123.1
Non-hydrocarbon Gases					
Hydrogen	59.8	188.1	0.0	3.25	31.0
Nitrogen	227.3	492.9	0.040	3.30	33.0
Carbon Dioxide	547.7	1070.0	0.225	5.98	62.3
Hydrogen Sulfide	672.5	1306.5	0.106	6.03	57.1

CHAPTER VIII

NEW K-VALUE CORRELATION

This chapter describes the techniques for obtaining the generalized binary interaction coefficients that appear in the expressions of activity and fugacity coefficients, and for determining the pure liquid fugacity coefficients of hypothetical liquids.

In order to avoid the possible confusion in distinguishing the interaction coefficients in the activity coefficient expression from those in the fugacity coefficient expression, the former coefficients will be called liquid-phase interaction coefficients, and the latter will be termed as vapor-phase interaction coefficients.

From a theoretical view-point, it is logical to calculate the activity coefficient of a heavy component in a binary system via Equation 2-11, because the equation is completely rigorous for such a component. But it is also commonly known that the activity coefficient is much more sensitive to the light component than to the heavy component, whereas the fugacity coefficient has much greater effect on the heavy component than on the light component. Due to the insensitivity of activity coefficient to the heavy components, the liquid-phase interaction coefficients determined solely from heavy component K-data may not describe the activity coefficients of light components adequately. Therefore, the liquid-phase interaction coefficients must be determined in such a way that the coefficients satisfy the activity coefficients of both light and heavy components equally. This requirement can be satisfied by fitting the activity coefficients of both components and the ν_i's of light components simultaneously. Prior to this least square fitting, the vapor-phase interaction coefficients should be properly determined, however.

Fortunately, the determination of the vapor-phase interaction coefficients is relatively easy because of the favorable characteristics of the relevant equation of state constants, i.e., constants a_3, a_4, and c_2 are all insignificant for the light components of which the ω values are small and the critical temperatures are low, but they are significant for the heavy components of which the ω values are large and the critical temperatures are high. These characteristics of the constants are exactly what is desired for the adjustment of fugacity coefficients. In other words, it is desirable to correct the fugacity coefficients of the heavy components at low temperatures and around the critical region without affecting those of the light components.

Correlation Procedures

Experimental equilibrium data were selected from available binary systems over a wide range of conditions. The systems as well as the range of conditions studied are given in Tables XI through XVI.

Equation 2-11 is the key equation used in this correlation. Rearranging the equation gives

$$\gamma_i = \frac{y_i \phi_i}{x_i \nu_i} \tag{8-1}$$

The experimental equilibrium K-data for the heavy components of paraffin and olefin binary systems excluding methane-binaries were first processed according to Equation 8-1 to compute the activity coefficients of the components. Since the heavy components in binary liquid mixtures always exist as liquids at system conditions, the real liquid ν_i expression derived in Chapter VI was used for the calculation of ν_i in Equation 8-1. The ϕ_i values were calculated via Equaion 5-7 by setting the constants m_1, m_2, and m_3 equal to zero for the first approximation. This is equivalent to using the mixing rules given by Equations 4-39 through 4-41.

Equation 7-28 along with Equations 7-33, 7-34, and 7-35 was then fitted to the calculated activity coefficients to obtain the numerical constants q_1 through q_4 appearing in the expressions. In this work the solubility parameters and the liquid molal volumes given by Chao and Seader were retained except for those values of ethylene, ethane, propylene, and propane, for which Chao and Seader determined the parameters arbitrarily. These hypothetical thermodynamic properties were redetermined in such a way that they would give the best possible fit of Equation 7-28 to the calculated activity coefficients.

Using Equation 7-28 together with the newly obtained values of q_1 through q_4, the ϕ_i's of heavy components were back-calculated via Equation 8-1. Then the constants m_1, m_2, and m_3 that appear in the vapor-phase interaction coefficient expressions were determined by fitting the fugacity coefficient equation to the calculated values of ϕ_i. Next the activity coefficients of both light and heavy components and the pure liquid fugacity coefficient of light components were simultaneously regressed to obtain improved values of q_1 through q_4 in the activity coefficient expression and B_1 through B_8 in the hypothetical ν_i equation. Using the newly obtained values of q_1 through q_4, the ϕ_i's of heavy components were again back-calculated to obtain improved values of constants m_1, m_2, and m_3 by least square fitting. This procedure was repeated until all the constants converge to unchanging values. In effect, only a few iterations were sufficient to obtain the convergence.

For the methane-binaries, a different set of constants were determined by using the same techniques as were used for ethylene and heavier hydrocarbon binaries except the part of activity coefficients. In regressing the methane-binary data the solubility parameter and the liquid molal volume of methane were optimized retaining the numerical values of q_1 through q_4 that had been obtained from the analysis of ethylene and heavier binary mixture data. The same procedure was followed for the binary mixtures containing carbon dioxide or hydrogen sulfide as one of the components.

The binaries of hydrogen, and of nitrogen were separately correlated in a similar manner as the aliphatic hydrocarbon systems. But in this instance the solubility parameters and the liquid molal volumes of the light gases were also optimized.

In view of the highly non-ideal behaviors of cyclo-paraffins and aromatic compounds in the liquid phase, the binaries of these compounds were also separately correlated. But the correlation procedure was relatively simple. In this case, only the constants q_1 through q_4 were optimized keeping all the other constants unchanged. All the numerical constants determined in this manner are given in Table VI, VIII, and IX.

In all regression analyses Baer's non-linear regression deck (10) was used with proper modifications whenever necessary. The computer programs are given in Appendix F.

Evaluations

The present K-value correlation was evaluated in two different ways, and compared with other K-value correlations.

The first evaluation method is to calculate the K-values via Equation 2-11 using experimental composition data over a wide variety of systems comprising a total of 4290 K-values. The NGPA (128) version of the Chao-Seader method was also evaluated and compared, because it is the only other correlation that is applicable to all the systems of interest. The average absolute percent deviations of calculated K-values from experimental values are shown in Tables XI through XIX. The maximum deviations are also included in the tables. The average absolute percent deviations of K-values for individual components are summarized in Table XX. Another comparison of these two prediction methods with observed data is shown on Figure 7 in which calculated K-values are plotted along with observed values for the 200° F multicomponent data of Yarborough and Vogel (210).

The second evaluation method is to predict the saturation pressure and vapor compositions with known values of bubble point temperature and liquid compositions. This method is evidently more convincing than the first method, but requires much longer computing time due to the lengthy trial and error calculations. Thus, it was applied only to a few selected systems to support the first evaluation method. The results of this evaluation are given in Tables XXI and XXIII. In this evaluation the Chueh and Prausnitz correlation (143) was also included. As can be seen from the tables, the three correlations are all sufficiently accurate for the light component K-values, but they are considerably different in the capability of predicting heavy component

TABLE XI

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA FOR BINARIES OF METHANE

				Conditions		Average Absolute % Deviations from Observed K-Values			
						Solute		Solvent	
Solute	Solvent	Reference	Number of Points	Temperature °F	Pressure PSIA	This Work	NGPA(128)	This Work	NGPA(128)
Methane	Ethane	27	20	-160 to 40	100 to 800	7.00	16.36	7.38	8.26
	Ethane	148	8	-100 to 50	200 to 600	3.28	15.48	7.77	9.66
	Propane	157	52	40 to 160	100 to 1300	7.09	21.22	3.71	5.40
	n-Butane	177	31	40 to 250	200 to 1835	9.19	13.06	3.36	4.73
	n-Pentane	178	27	100 to 280	100 to 2000	2.94	9.22	5.15	4.99
	n-Hexane	147	21	100 to 340	500 to 2500	2.70	6.33	6.23	9.81
	n-Hexane	186	29	167 to 302	147 to 1470	1.99	4.33	6.95	8.01
	n-Heptane	162	42	40 to 460	200 to 2750	6.10	5.78	5.31	10.12
	n-Octane	102	13	212 to 302	147 to 1029	3.23	7.49	9.06	16.25
	n-Decane	156	24	220 to 460	100 to 4000	6.67	5.35	9.32	19.90
	Cyclopentane	51	14	150	100 to 3000	4.28	7.83	1.90	6.76
	Cyclohexane	151	28	70 to 340	200 to 3000	5.40	12.90	9.16	13.31
	Toluene	69	4	150	100 to 3000	3.47	1.33	16.72	23.07
Overall Average Absolute Percent Deviations of 311 Data Points :						5.44	10.70	6.04	9.32
Maximum Percent Deviations :						-24.42	51.62	37.71	-96.78

TABLE XII

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA FOR BINARIES OF ETHENE AND ETHANE

				Conditions		Average Absolute % Deviations from Observed K-Values			
						Solute		Solvent	
Solute	Solvent	Reference	Number of Points	Temperature °F	Pressure PSIA	This Work	NGPA(128)	This Work	NGPA(128)
Ethene	Ethane	82	27	-100 to 0	36 to 371	5.50	7.97	3.01	6.00
	Propene	83	13	-22 to 59	50 to 450	5.29	5.82	2.50	6.26
	n-Heptane	96	30	50 to 450	100 to 1000	3.38	24.34	4.28	6.14
Ethane	Propene	120	16	10 to 160	100 to 700	4.48	5.27	3.80	7.39
	Propane	117	22	50 to 180	100 to 700	2.04	7.28	2.75	5.56
	n-Butane	123	12	150 to 250	500 to 800	2.72	7.62	2.69	7.35
	n-Butane	94	8	0 to 150	100 to 400	3.00	3.58	0.37	3.65
	n-Pentane	151	48	40 to 280	50 to 900	2.17	5.94	4.59	7.49
	n-Heptane	122	31	150 to 350	450 to 1150	2.16	7.44	3.11	4.75
	n-Decane	163	31	220 to 460	100 to 1600	2.86	22.74	6.28	13.03
	Cyclohexane	98	27	100 to 500	100 to 1300	8.12	8.95	7.11	6.70
	Benzene	99	17	122 to 482	300 to 1000	6.55	24.53	3.86	4.09
Overall Average Absolute Percent Deviations of 282 Data Points :						3.84	11.58	4.15	7.26
Maximum Percent Deviations :						-34.24	-116.50	-37.00	-39.21

TABLE XIII

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA FOR BINARIES OF MISCELLANEOUS HYDROCARBONS

			Number	Conditions		Average Absolute % Deviations From Observed K-Values			
		Refer-	of	Temperature	Pressure	Solute		Solvent	
Solute	Solvent	ence	Points	°F	PSIA	This Work	NGPA(128)	This Work	NGPA(128)
Propene	Propane	159	22	10 to 190	49 to 587	1.96	4.29	0.55	3.21
	Propane	81	9	83 to 160	158 to 424	1.70	3.48	0.81	3.22
	1-Butene	76	12	40 to 250	30 to 550	1.31	4.55	2.35	6.60
	i-Butane	74	14	108 to 256	200 to 600	3.34	5.42	5.15	4.43
Propane	i-Butene	180	11	119 to 198	200 to 500	6.40	5.28	2.80	4.52
	n-Butane	97	24	194 to 248	300 to 590	2.49	3.09	2.05	4.16
	i-Pentane	195	19	32 to 338	15 to 515	2.39	4.35	5.10	2.67
	n-Pentane	97	23	194 to 356	300 to 650	2.98	5.28	3.74	8.80
	n-Pentane	174	31	160 to 340	60 to 650	5.42	3.60	2.38	4.10
	n-Decane	155	26	280 to 460	50 to 1000	3.30	11.12	3.62	12.68
	Benzene	75	22	100 to 400	20 to 700	5.66	13.39	7.63	10.83
1-Butene	n-Butane	177	12	100 to 280	53 to 499	1.05	3.82	1.30	3.34
n-Butane	n-Hexane	45	21	195 to 412	147 to 426	1.61	4.60	3.57	7.09
	n-Heptane	124	10	200 to 400	65 to 480	2.10	4.79	3.68	5.22
	n-Heptane	95	14	200 to 440	100 to 400	1.40	5.49	2.28	34.16
	n-Decane	153	28	220 to 460	50 to 714	2.11	3.24	5.62	12.74
n-Pentane	n-Heptane	55	7	310 to 488	147 to 444	7.29	6.44	2.92	6.76
n-Hexane	Toluene	126	9	80 to 215	3 to 15	4.67	2.41	3.35	8.98
Overall Average Absolute Percent Deviations of 314 Data Points :						3.13	5.45	4.56	7.73
Maximum Percent Deviations :						-23.23	52.23	53.62	68.38

TABLE XIV

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA FOR HYDROGEN BINARIES

				Conditions		Average Absolute % Deviations From Observed K-Values			
						Solute		Solvent	
Solute	Solvent	Reference	Number of Points	Temperature °F	Pressure PSIA	This Work	NGPA(128)	This Work	NGPA(128)
Hydrogen	Ethene	204	22	-175 to 0	500 to 8000	8.29	19.45	7.74	18.59
	Ethane	204	20	-150 to 50	500 to 8000	9.35	15.55	2.11	13.77
	Propene	204	19	-100 to 75	500 to 8000	13.70	10.97	4.38	12.21
	Propane	204	18	-50 to 75	500 to 8000	8.42	6.20	3.95	14.72
	Propane	35	16	40 to 160	500 to 5000	9.29	8.58	3.01	5.35
	i-Butane	57	9	100 to 200	500 to 3000	5.66	5.12	14.04	17.61
	n-Butane	130	8	10 to 75	350 to 4000	5.30	5.81	7.14	9.73
	n-Butane	7	4	75 to 240	326 to 1376	10.57	13.41	9.37	11.12
	n-Hexane	132	22	40 to 340	500 to 4000	8.57	8.73	8.89	7.50
	n-Octane	52	17	392 to 500	180 to 1818	6.46	10.66	3.10	2.51
	Cyclohexane	195	12	150 to 250	500 to 9999	6.57	19.07	4.91	31.73
	Cyclohexane	20	30	100 to 280	500 to 6000	11.40	13.75	5.60	13.29
	Benzene	195	18	150 to 320	200 to 9999	9.18	16.09	3.81	20.00
	Benzene	52	22	320 to 500	304 to 2230	4.43	12.36	1.47	2.90
Overall Average Absolute Percent Deviations of 237 Data Points:						8.68	13.75	5.11	13.29
Maximum Percent Deviations:						43.60	70.65	-23.56	-98.05

TABLE XV

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA FOR NITROGEN BINARIES

				Conditions		Average Absolute % Deviations From Observed K-Values			
						Solute		Solvent	
Solute	Solvent	Reference	Number of Points	Temperature °F	Pressure PSIA	This Work	NGPA(128)	This Work	NGPA(128)
Nitrogen	Methane	31	3	-181 to -145	500	7.50	347.3	1.37	17.33
	Methane	50	29	-240 to -150	50 to 600	4.17	398.3	1.05	15.24
	Methane	26	5	-220 to -140	100 to 500	3.58	385.9	0.93	15.00
	Ethane	60	22	-200 to 40	100 to 950	6.83	109.6	7.48	40.67
	n-Butane	169	11	100 to 280	236 to 1800	16.11	45.2	3.69	27.40
	n-Hexane	147	16	100 to 340	150 to 2000	13.35	24.1	11.30	106.78
	n-Heptane	3	6	90 to 260	1020 to 2111	6.89	25.3	29.43	251.57
	n-Heptane	30	4	77 to 239	1483	8.25	29.8	42.16	148.75
	n-Decane	9	6	220 to 280	80 to 150	45.73	25.0	30.82	429.23
Overall Average Absolute Percent Deviations of 102 Data Points:						10.31	178.8	9.31	79.93
Maximum Percent Deviations:						-50.15	637.5	-57.15	881.31

TABLE XVI

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA FOR BINARIES OF HYDROGEN SULFIDE AND CARBON DIOXIDE

				Conditions		Average Absolute % Deviations From Observed K-Values			
						Solute		Solvent	
Solute	Solvent	Reference	Number of Points	Temperature °F	Pressure PSIA	This Work	NGPA(128)	This Work	NGPA(128)
H_2S	Propene	45	8	-22 to 59	44 to 235	9.20	8.81	6.10	8.18
	Propane	100	8	80 to 190	200 to 600	16.90	23.68	0.88	2.22
	Propane	74	6	124 to 197	400 to 600	12.32	17.89	3.43	2.19
	n-Butane	170	35	100 to 250	75 to 1100	4.76	6.06	4.36	6.30
	n-Pentane	161	16	40 to 340	20 to 1000	6.40	5.13	7.61	8.14
	n-Decane	164	8	280 to 340	200 to 1400	6.39	6.51	5.38	7.48
Average Absolute Percent Deviations of 81 Data Points for H_2S:						7.44	8.81	4.86	6.26
CO_2	Propene	83	22	-22 to 140	50 to 700	7.29	11.71	2.90	5.29
	Propane	4	5	-40 to 32	50 to 300	8.58	11.35	5.44	7.28
	Propane	160	58	40 to 160	100 to 900	6.11	8.85	5.32	6.69
	Propane	146	9	50 to 175	500 to 800	6.08	6.31	11.57	5.35
	n-Butane	146	7	50 to 250	600 to 800	4.83	15.79	5.07	5.86
	n-Butane	45	9	52 to 268	600 to 800	5.20	16.29	3.65	7.95
	n-Butane	134	44	100 to 280	60 to 1000	5.58	10.75	3.93	2.38
	n-Pentane	146	11	100 to 350	600 to 1000	23.82	29.10	13.08	15.75
	n-Decane	153	38	280 to 460	200 to 2500	6.39	15.96	8.18	18.05
Average Absolute Percent Deviations of 203 Data Points for CO_2:						7.11	12.59	5.91	7.88
Maximum Percent Deviations:						-45.39	66.39	41.54	-45.49

TABLE XVII

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA
FOR METHANE TERNARIES

Conditions		Observed K-Values			Percent Deviations From Observed K-Values					
					Component 1		Component 2		Component3	
Temp. °F	Press. PSIA	K_1	K_2	K_3	This Work	NGPA(128)	This Work	NGPA(128)	This Work	NGPA(128)
Methane(1)-Propane(2)-n-Butane(3), (168)										
100	1000	2.174	0.437	0.224	-1.86	14.48	-5.57	-5.23	-7.43	-7.30
100	1573	1.520	0.523	0.378	3.37	28.00	-3.97	-4.97	-15.87	-20.34
100	972	2.472	0.445	0.228	-3.26	12.97	-1.71	-2.71	-5.17	-7.28
100	1390	1.573	0.606	0.373	3.72	28.08	-10.61	-12.76	-6.54	-12.79
Average Absolute % Deviations of 23 Points:					4.43	18.38	6.32	7.26	8.43	11.19
Methane(1)-Propane(2)-n-Pentane(3), (38, 59)										
100	1000	2.806	0.403	0.084	-5.16	3.94	-3.42	-2.71	-1.87	0.59
100	1500	1.858	0.458	0.148	-3.14	14.13	-6.88	-5.57	-5.72	-11.09
220	1000	3.030	0.792	0.294	-1.49	10.06	2.04	-2.13	-1.91	-2.60
220	1500	1.858	0.792	0.411	3.81	20.53	-3.16	-10.63	-7.13	-11.00
Average Absolute % Deviations of 28 Points:					4.08	11.87	2.52	3.51	6.37	11.15
Methane(1)-Propane(2)-n-Decane(3), (203)										
100	1000	2.791	0.448	0.006	-7.76	3.26	-2.23	-3.16	-28.52	-44.90
100	3000	1.637	0.472	0.022	-12.75	1.82	5.41	6.15	1.20	-87.52
460	1000	2.729	1.515	0.308	0.29	10.65	-1.40	-28.74	-5.25	-10.45
460	2000	1.780	1.079	0.313	-21.92	-6.39	-0.96	-57.95	-14.41	-22.27
Average Absolute % Deviations of 40 Points:					8.98	6.71	4.41	19.74	15.15	34.71
Methane(1)-n-Butane(2)-n-Decane(3), (149, 158)										
160	2000	2.180	0.271	0.015	-6.03	-1.73	6.19	11.50	-21.22	-51.77
160	2500	1.372	0.514	0.139	-8.68	4.46	-5.26	-10.12	17.94	-94.60
Average Absolute % Deviations of 27 Points:					6.15	3.65	9.84	11.68	16.37	37.80
Overall Ave.Abs. % Deviations of 118 Points:					6.29	9.50	5.58	11.68	12.04	24.40

TABLE XVIII

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA
FOR ETHANE TERNARIES

Conditions		Observed K-Values			Percent Deviations From Observed K-Values					
					Component 1		Component 2		Component 3	
Temp. °F	Press. PSIA	K_1	K_2	K_3	This Work	NGPA(128)	This Work	NGPA(128)	This Work	NGPA(128)
Ethane(1)-n-Butane(2)-n-Pentane(3),(121)										
200	525	1.972	0.578	0.351	-5.26	3.98	0.54	-2.21	-4.44	-9.70
200	625	1.680	0.573	0.359	-3.65	3.55	-0.91	-3.97	-3.07	-9.22
200	848	1.189	0.771	0.617	0.91	4.85	-6.29	-13.36	-5.47	-19.58
250	658	1.765	0.761	0.514	-0.45	8.91	-2.17	-4.49	-2.97	-7.90
250	826	1.273	0.835	0.730	1.67	7.29	0.24	-4.89	-5.22	-15.15
250	742	1.456	0.780	0.639	1.16	9.56	0.47	-3.32	-7.82	-15.34
300	598	1.905	0.955	0.675	1.81	20.02	-0.54	-0.85	2.76	-1.80
300	632	1.750	0.941	0.700	3.64	20.42	-0.28	-1.05	0.55	-4.44
300	572	2.064	0.969	0.678	-0.26	18.44	-0.65	-0.70	1.31	-2.70
Average Absolute % Deviations of 75 Points:					3.58	9.23	2.58	4.10	3.44	7.52
Ethane(1)-n-Butane(2)-n-Heptane(3),(124)										
150	615	1.560	0.394	0.047	-3.21	-3.00	-8.69	-9.50	11.60	5.73
150	819	1.222	0.451	0.126	-2.41	-2.04	-4.39	-7.95	-0.71	-23.35
150	799	1.215	0.457	0.139	-2.87	-1.26	-0.04	-5.25	7.52	-22.04
200	1045	1.215	0.599	0.272	-1.72	-5.48	3.59	-1.85	8.01	-21.89
200	746	1.540	0.516	0.124	-0.83	0.69	0.28	-1.26	-1.90	-12.07
200	867	1.375	0.571	0.194	-3.67	-3.41	0.37	-2.69	5.81	-16.02
250	765	1.756	0.663	0.173	-0.47	0.68	0.66	-1.24	3.53	-2.84
250	1024	1.295	0.745	0.395	-1.36	-5.22	2.29	-3.29	6.57	-19.36
Average Absolute % Deviations of 54 Points:					2.59	4.27	2.79	3.05	5.04	11.06
Overall Ave.Abs. % Deviations of 129 Points:					3.17	7.15	2.67	3.66	4.11	9.00
Maximum Percent Deviations :					23.38	53.85	38.04	37.68	-12.03	-28.68

TABLE XIX

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA FOR NITROGEN TERNARIES

Conditions		Number of Points	Average Absolute % Deviations from Observed K-Values					
Temperature $^{\circ}$F	Pressure PSIA		Component 1		Component 2		Component 3	
			This Work	NGPA(128)	This Work	NGPA(128)	This Work	NGPA(128)
Nitrogen(1)-Methane(2)-Ethane(3), (54)								
-200 to 100	500 to 1000	5	10.58	160.68	17.06	15.36	8.08	13.27
Nitrogen(1)-Methane(2)-n-Butane(3), (170)								
100 to 280	500 to 2000	58	19.99	70.35	7.88	17.58	5.35	5.90
Nitrogen(1)-Methane(2)-n-Pentane(3), (28)								
77 to 185	522 to 1965	10	35.82	47.83	4.13	7.56	18.37	18.04
Nitrogen(1)-Methane(2)-n-Hexane(3), (29)								
77 to 185	532 to 2464	9	29.23	89.09	5.36	5.01	15.17	22.03
Nitrogen(1)-Methane(2)-n-Heptane(3), (30)								
77 to 185	532 to 2468	9	27.14	73.26	5.97	2.59	27.29	33.83
Nitrogen(1)-Ethane(2)-n-Butane(3), (103)								
100 to 280	500 to 2000	72	21.07	76.10	7.26	8.62	8.96	9.71
Overall Ave. Abs. % dev. of 163 Pts :			22.05	75.47	7.41	11.44	9.75	10.82
Maximum Percent Deviations :			82.18	228.90	-46.81	44.42	-77.24	-71.83

TABLE XX

COMPARISON OF CALCULATED K-VALUES WITH OBSERVED DATA FOR INDIVIDUAL COMPONENTS

Component	Number of Points	Average Absolute % Deviations From Observed K-Values This Work	 NGPA(128)
Methane	557	5.67	11.25
Ethene	92	4.12	15.54
Ethane	513	4.32	9.73
Propene	135	3.04	6.44
Propane	472	3.97	5.42
1-Butene	24	1.70	5.21
i-Butene	11	2.79	4.52
i-Butane	23	8.63	9.59
n-Butane	587	4.48	6.44
i-Pentane	19	5.10	2.67
n-Pentane	276	5.27	7.71
n-Hexane	127	7.58	21.11
n-Heptane	207	6.76	19.14
n-Octane	30	5.68	8.16
n-Decane	228	9.90	31.73
Cyclopentane	14	1.90	6.76
Cyclohexane	97	6.96	15.70
Benzene	79	4.23	9.26
Toluene	13	7.46	13.32
Hydrogen	237	8.64	13.75
Nitrogen	265	17.53	115.24
Carbon Dioxide	203	7.11	12.59
Hydrogen Sulfide	81	7.44	8.81
Overall	4290	6.33	17.75

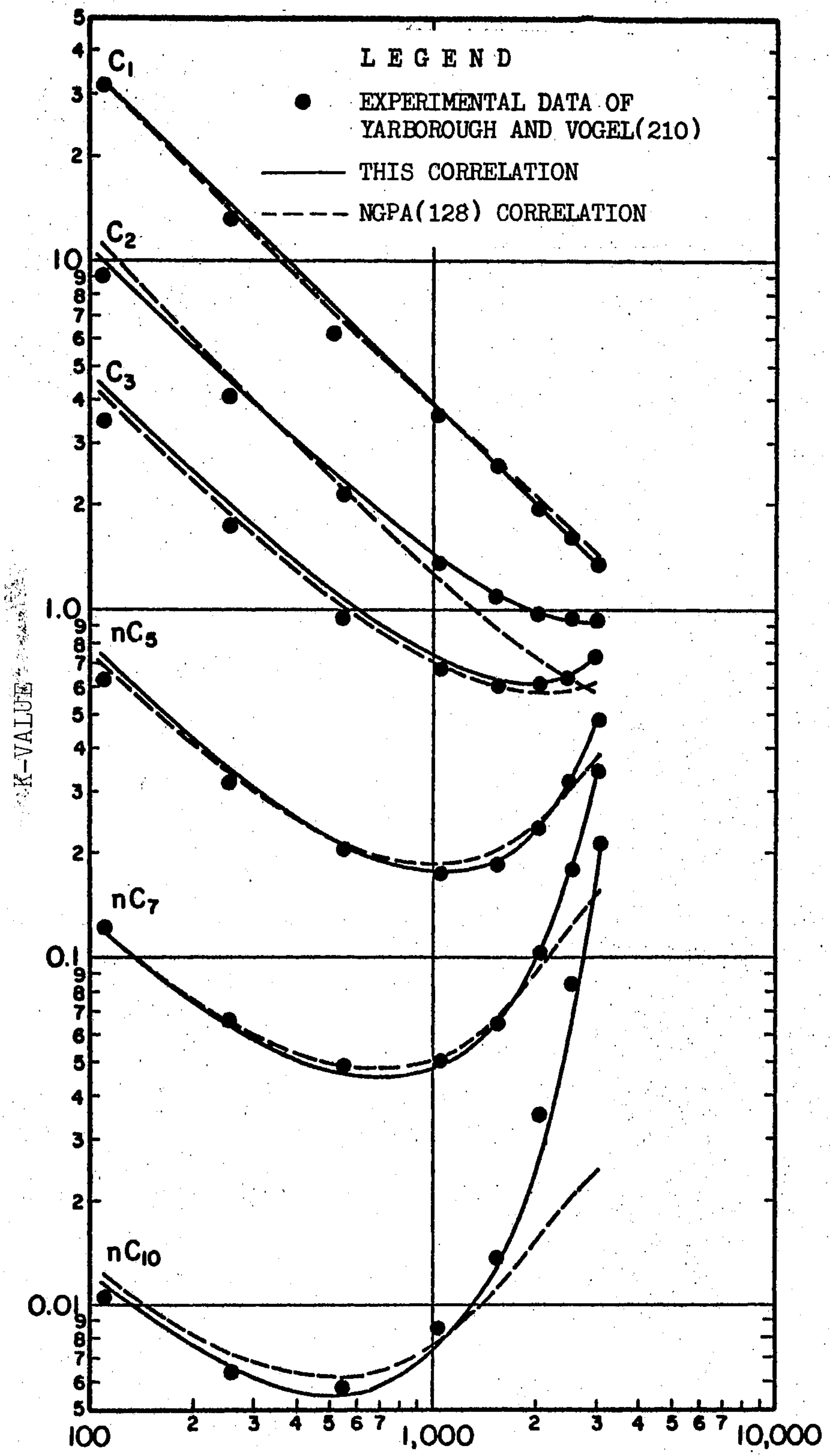

Figure 7. Comparison of K-Values for
a Multicomponent System
at 200° F

TABLE XXI

COMPARISON OF K-VALUES PREDICTED VIA THREE CORRELATIONS WITH EXPERIMENTAL DATA (122) ON ETHANE-n-HEPTANE SYSTEM

Conditions		% Deviations in Saturation Pressure			% Deviations in Ethane K-Values			% Deviations in n-Heptane K-Values		
Temp. °F	Press. PSIA	Prausnitz -Chueh (143)	Chao-Seader (41)	This Work	Prausnitz -Chueh (143)	Chao-Seader (41)	This Work	Prausnitz -Chueh (143)	Chao-Seader (41)	This Work
200	450	7.199	7.491	5.195	-0.420	-0.085	0.028	9.431	1.953	-0.592
	550	5.499	4.275	3.054	-0.512	-0.090	-0.022	12.294	2.286	0.630
	650	3.044	0.670	0.459	-0.589	0.002	-0.032	14.506	0.007	0.785
	750	1.160	-2.257	-1.359	-0.719	0.170	-0.044	17.731	-4.085	1.084
	850	-0.363	-4.794	-2.556	-0.828	0.552	0.037	19.363	-12.733	-0.837
	950	-0.927	-6.873	-2.789	-1.081	1.218	0.158	22.785	-25.590	-3.326
250	450	14.543	15.744	8.896	-0.360	0.413	0.551	3.622	-4.146	-5.536
	650	8.865	4.259	2.880	-1.229	0.003	0.064	14.687	-0.009	-0.767
	750	7.321	-0.004	1.176	-1.737	0.155	-0.062	21.421	-1.865	0.763
	850	6.073	-3.957	-0.282	-2.330	0.663	-0.021	28.252	-7.982	0.268
	950	5.384	-7.739	-1.599	-3.725	1.476	0.088	42.836	-16.922	-0.971
	1050	9.846	-10.976	-2.046	-10.717	2.593	-0.074	114.185	-27.573	0.799
300	450	12.538	19.449	7.791	-1.024	0.379	0.268	5.346	-2.009	-1.394
	550	10.227	12.608	5.444	-1.457	-0.103	0.088	8.500	0.545	-0.492
	650	8.017	6.368	3.237	-1.996	-0.206	-0.116	12.534	1.289	0.732
	750	8.124	2.076	3.195	-2.719	0.188	-0.232	17.740	-1.229	1.518
	850	8.147	-2.245	2.884	-3.638	1.342	-0.045	23.251	-8.578	0.297
Ave. Abs. % Dev.: (31 Points)		5.131	6.779	4.228	2.209	1.207	2.108	19.280	8.191	7.880*

* Two data points having the deviations larger than 150 % caused this large average value. The two data points are outside the recommended correlation limits, i. e., the pressures are higher than 0.85 of mixture critical pressures.

TABLE XXII

COMPARISON OF K-VALUES PREDICTED VIA THREE CORRELATIONS WITH EXPERIMENTAL DATA(97) ON PROPANE-n-PENTANE SYSTEM

Conditions		% Deviations in Saturation Pressure			% Deviations in Propane K-Values			% Deviations in n-Pentane K-Values		
Temp. °F	Press. PSIA	Prausnitz -Chueh (143)	Chao-Seader (41)	This Work	Prausnitz -Chueh (143)	Chao-Seader (41)	This Work	Prausnitz -Chueh (143)	Chao-Seader (41)	This Work
212	300	0.275	-3.085	-4.983	-1.054	-0.574	-2.503	3.626	2.008	8.614
	400	2.234	-0.804	-3.547	0.139	1.119	-0.158	-0.823	-6.569	0.934
	500	4.810	0.756	-2.119	-0.252	1.155	0.397	2.782	-12.648	-4.366
	600	--	1.759	-0.513	--	0.740	0.527	--	-22.289	-15.865
248	300	3.298	1.298	-1.653	4.160	4.826	1.013	-5.705	-6.611	-1.382
	400	1.143	-0.574	-4.200	0.550	2.016	-0.484	1.013	-4.804	1.158
	500	1.755	0.384	-3.212	-0.407	2.112	0.379	1.478	-7.626	-1.371
	600	--	2.652	0.259	--	2.907	1.438	--	-15.044	-7.470
	650	--	4.332	4.039	--	4.723	1.958	--	-26.583	-11.043
302	300	3.158	3.104	1.024	-0.178	19.120	9.256	0.047	-5.061	-2.441
	400	4.242	2.456	-0.908	6.004	8.356	2.533	-4.004	-5.566	-1.689
	500	4.062	1.727	-1.120	-0.389	7.820	3.442	0.403	-8.074	-3.559
	600	--	0.977	0.650	--	8.839	1.372	--	-12.044	-1.870
	650	--	7.230	14.172	--	15.543	5.496	--	-23.424	-8.289
Ave. Abs. % Dev.: (23 Points)		2.417	2.093	2.874	1.451	4.150	2.360	12.904	9.702	4.740

TABLE XXIII

COMPARISON OF K-VALUES PREDICTED VIA TWO CORRELATIONS WITH EXPERIMENTAL DATA (153) ON PROPANE-n-DECANE SYSTEM

Conditions		% Deviations in Saturation Pressure		% Deviations in Propane K-Values		% Deviations in n-Decane K-Values	
Temp. ^{o}F	Press. PSIA	Chao-Seader (41)	This Work	Chao-Seader (41)	This Work	Chao-Seader (41)	This Work
280	100	16.713	12.614	1.176	0.765	-18.475	-11.932
	200	11.878	9.269	0.548	0.368	-15.093	-10.176
	400	3.339	2.356	0.339	0.170	-13.968	-7.034
	800	-5.237	-1.625	2.046	0.710	-59.934	-20.797
340	100	17.489	6.919	3.555	1.389	-19.650	-7.652
	200	12.766	4.677	1.472	0.702	-15.388	-7.332
	400	3.256	0.580	0.757	0.473	-12.419	-7.770
	800	-9.545	-2.209	2.474	0.914	-40.065	-14.840
400	100	13.586	0.455	8.497	1.206	-16.833	-2.375
	200	12.247	0.401	2.939	0.534	-12.899	-2.332
	400	2.361	-0.577	1.116	0.544	-8.383	-4.088
	1000	-16.654	11.781	12.177	-5.504	-66.677	30.144
460	150	10.671	-2.682	11.226	0.907	-13.255	-1.067
	200	11.481	-1.621	6.356	0.368	-11.450	-0.648
	400	1.962	-1.927	1.843	0.631	-6.533	-2.234
	800	-15.789	0.788	7.132	1.905	-30.520	-8.140
Ave. Abs. % Dev.: (26 Points)		9.648	3.908	3.290	0.982	19.855	8.067

K-values and saturation pressures. The computer program for the calculation equilibrium pressure and vapor composition from liquid composition and temperature data is given in Appendix G.

Discussions

A. The Accuracy of Experimental Equilibrium Data. The use of accurate experimental data is one of the most important parts of the present K-value correlation, because the final determination of all the interaction coefficients is entirely based on the experimental equilibrium data. Therefore care must be exercised in selecting the best quality of experimental data. Unfortunately no perfect method is available to test the accuracy of such data. Even if such a method exists, it is practically impossible to apply the method to the vast amount of data that are to be used in the correlation. In this regard, some arbitrary criteria were set up for the selection of reliable experimental data. First, every data point that contains mole fractions less than 0.01 was removed. Literature survey indicated that the expected experimental error in composition data ranges from 0.0005 to 0.005 mole fraction. This amounts to five to 50 percent error for a composition data of 0.01 mole fraction.

Secondly, the data points that failed to exhibit "self-consistancy" were eliminated. The smoothness and appearance of the isothermal and isobaric K-curves were the criteria in this test. For example, the 190° F isothermal K-curve of n-pentane in a propane-n-pentane mixture (174) did not show the tendency of having a minimum value at high pressures, even near at the mixture critical point. Such a minimum value usually occurs in the pressure range from 0.8 to 0.95 of mixture critical pressure. Discarding these isothermal data points seems to be justified by more recent data of others (97).

The third criterion was rather subjective; for instance, in cases where two sets of data were available on the same system and they did not agree within a few percent, one set of data was arbitrarily selected based on the analytical techniques used and on the claim of the experimenters. For example, the data of Reamer and Sage (151) were chosen over the data of Clark (51) for methane-cyclohexane system, and the data of Roberts and Mcketta (169) were selected over the data of Akers et al. (2) for nitrogen-n-butane system. When more than two sets of data were available, the set or sets that were in poor agreement with the other sets were discarded. The propylene-propane system is such an example.

B. Generalized Correlation Versus Specific Correlation. All the available K-value correlations may be classified into two categories, one comprising the correlations that require only pure component properties, and the other including the correlations that require not only the pure component properties but also the specific interaction coefficients as the input information. The Chao-Seader and the present correlations are in the former category, which is frequently called "generalized correlations". The Robinson-Chao (172) and the Chueh-Prausnitz (143) correlations fall in the latter category, which may be called "specific correlations".

This classification is more or less arbitrary and consequently ambiguous. For example, even though both the Robinson-Chao, and the Chueh-Prausnitz correlations require specific interaction coefficient(s), the former uses a generalized expression for ν_i, while the latter uses specific ν_i expression for individual components. However, the above classification is convenient for the present discussion.

In general the merits of generalized correlation constitute the demerits of specific correlation and vice versa. As a result of generalization, the generalized correlation usually suffers from the accuracy which the specific correlation enjoys. On the other hand, the "specific" correlation can be applied only to those systems for which the specific constants are known, whereas the "generalized" correlation can be applied to any system for which the necessary pure component properties are available. But both the accuracy and the applicability to wide variety of substances are required for process designs. One of the ways to satisfy both of the requirements may be the combination of the two correlations by providing the generalized correlation with specific interaction coefficients whenever available. The present correlation is especially suitable to this purpose. A few examples are illustrated below.

The first case studied is the determination of the specific binary interaction coefficients involved in the activity coefficient expression. This modification gives satisfactory results for the systems of which the constituents are not drastically different. The next case investigated is the determination of the specific interaction coefficients appearing in both activity coefficient and fugacity coefficient expressions. This method substantially improves the K-value prediction for the systems of which the constituents exhibit significant differences in physical properties and in sizes.

Three binary systems of methane-n-butane, ethane-n-heptane, and hydrogen-cyclohexane were selected for the first case study. Introduction of two specific interaction coefficients into the activity coefficient expression resulted in a remarkable reduction in the maximum deviations. For example, the maximum deviation of methane-n-butane system was reduced from 19.3% to 10.3%, while that of ethane-heptane system was reduced from 12% to 8%. The overall accuracy was also improved from 6.2% to 4% for the methane-butane binary. But a slight improvement was gained for the ethane-heptane system for which the generalized correlation was already sufficiently accurate. Figure 8 shows the results of hydrogen-cyclohexane system. Only one isotherm is shown to avoid overcrowding. However, similar behavior was observed for other isotherms.

As the second case study, the binary systems of methane-n-decane, methane-cyclohexane, and nitrogen-n-hexane were selected because the generalized correlation is not satisfactory for these mixtures. The results are shown in Figure 9 through 11 along with the results from the NGPA version of Chao-Seader correlation. The specific interaction coefficients are given in the figures. The K-values used in Figures 8 through 11 were calculated via Equation 2-11 using experimental composition data.

The procedure to determine the specific interaction coefficients is the same as the one used for generalized correlation. But all the hypothetical ν_i expressions were kept unchanged in this regression analysis.

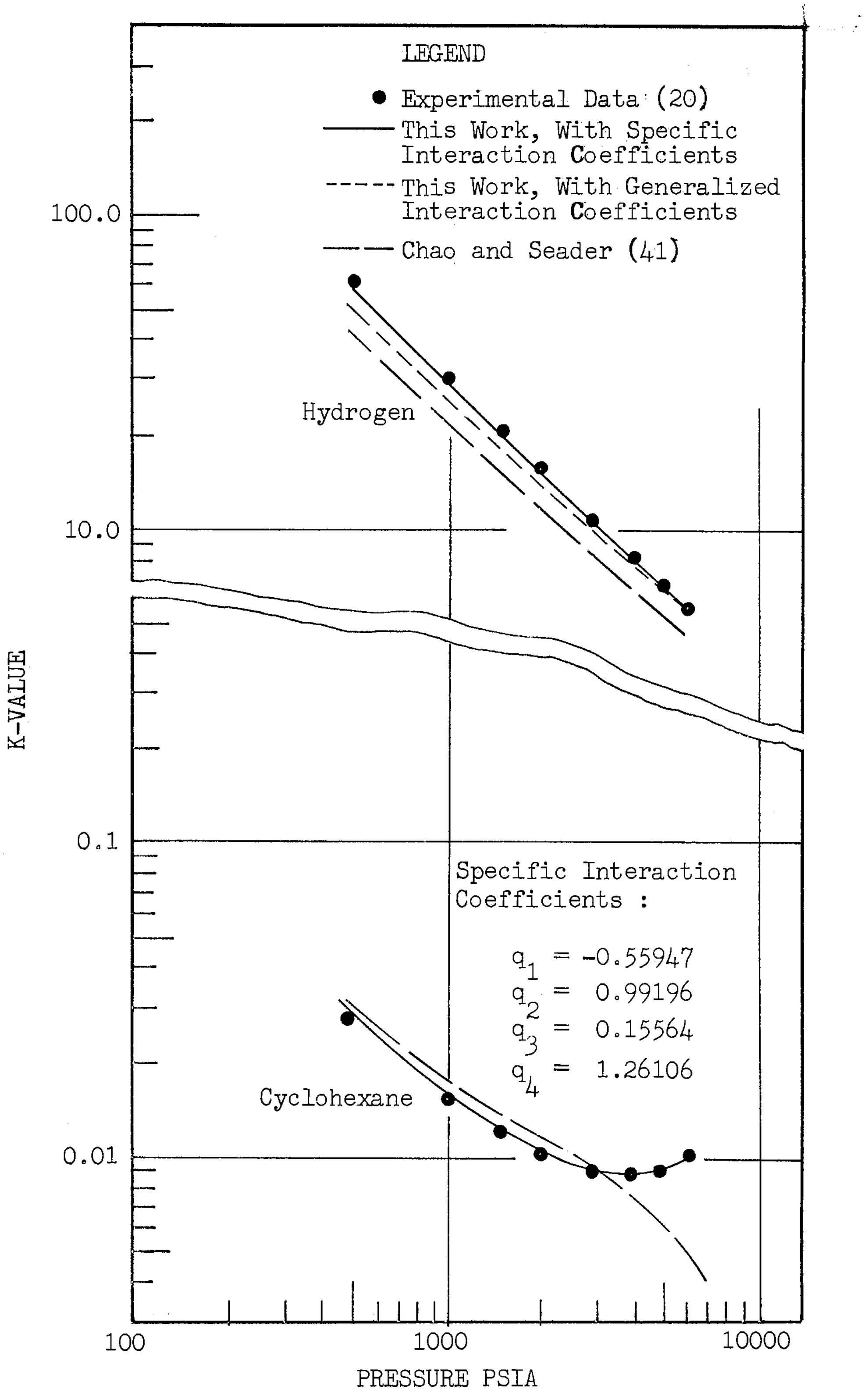

Figure 8. Comparison of K-Values for Hydrogen-Cyclohexane Binary at 160° F

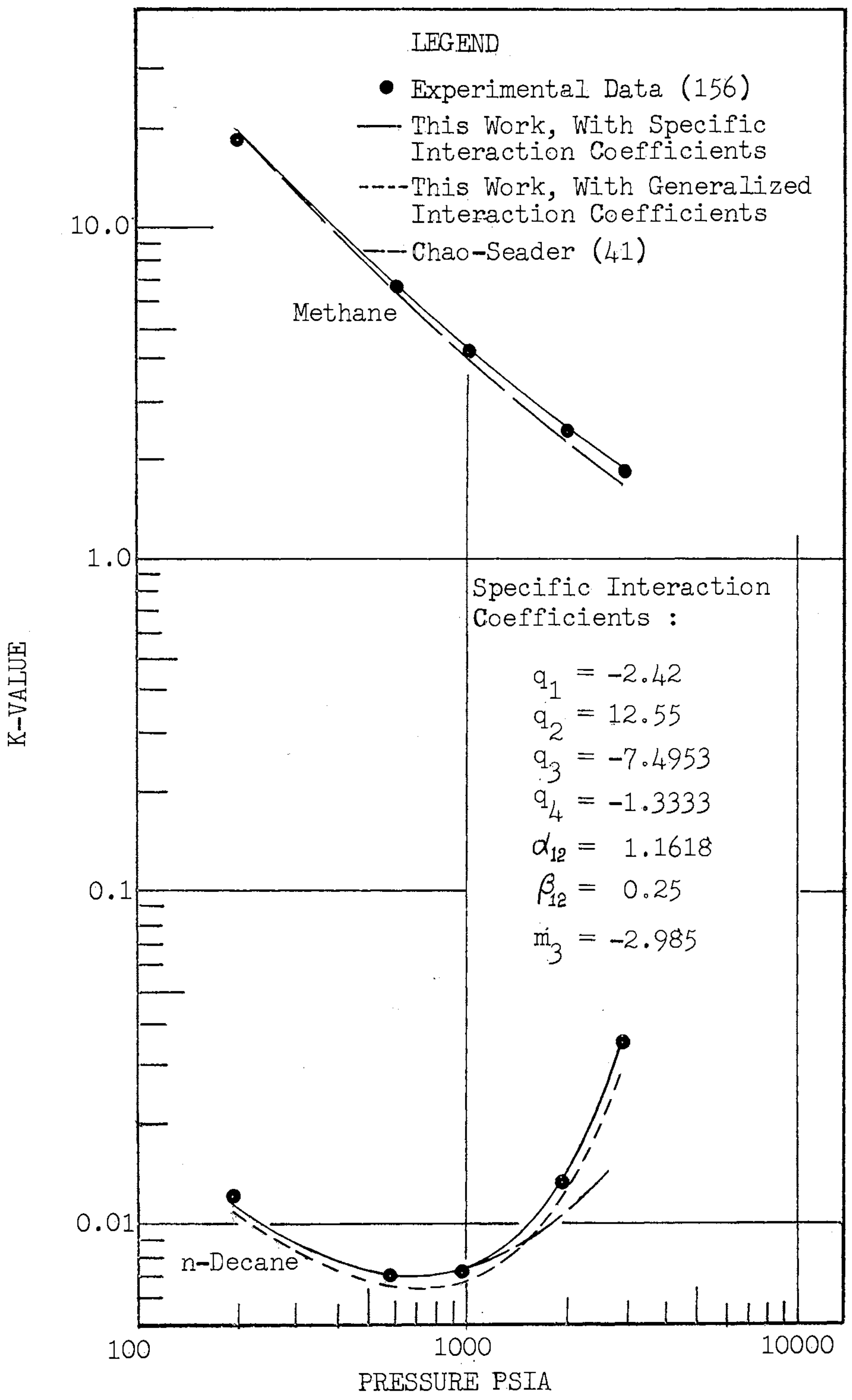

Figure 9. Comparison of K-Values for Methane-n-Decane Binary at 220° F

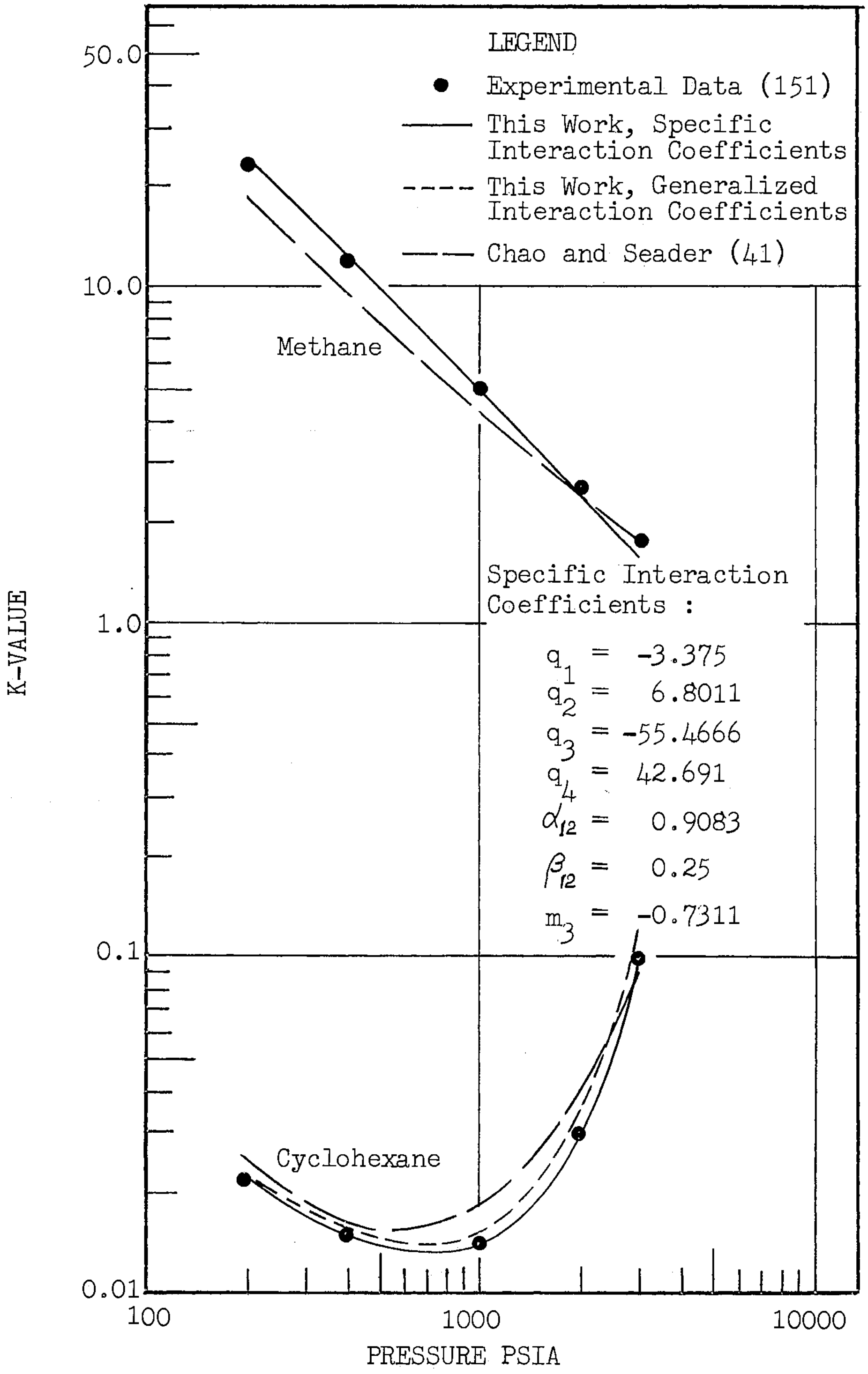

Figure 10. Comparison of K-Values for Methane-Cyclohexane Binary at 100° F

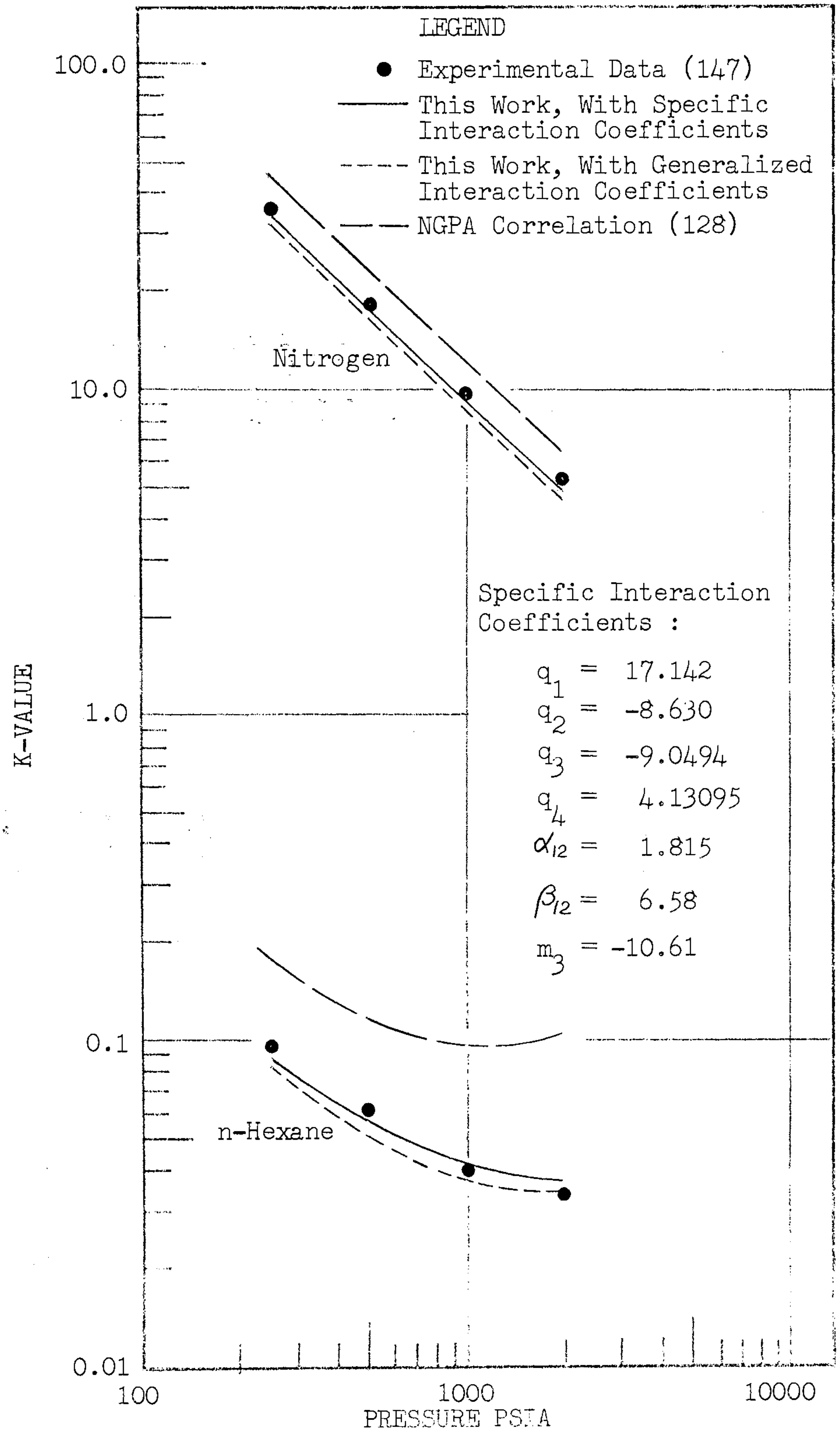

Figure 11. Comparison of K-Values for Nitrogen-n-Hexane Binary at 160° F

CHAPTER IX

ISOTHERMAL ENTHALPY DIFFERENCES FOR VAPORS AND LIQUIDS

A knowledge of enthalpies is necessary for accurate designs of thermal processes. In spite of their great demand in both quantity and quality, reliable experimental data on this property are not abundant. This is especially true for mixtures. The number of mixtures which have been investigated is infinitesimal relative to the number of systems of interest. Therefore, the development of a reliable enthalpy prediction method is essential. In effect a number of such enthalpy prediction methods have been developed. However, none of them are completely satisfactory.

Methods of Prediction

Basically, two approaches are possible for the calculation of enthalpies, one being from statistical mechanics, the other being from macroscopic thermodynamic data. Although the former approach is theoretically sound, it is still of no practical use except for a few gases having simple molecules. Thus, the methods based on macroscopic thermodynamic data are exclusively reviewed in this section.

Most of the predictive methods in common use require a knowledge of ideal gas state enthalpy, since the prediction methods give the departure from the ideal gas state enthalpy at the same temperature. A.P.I. Research Project 44 (5) tabulates the values of many hydrocarbons including some simple gases. A.P.I. Technical Data Book (196) stores the data in equation form which is more compact and convenient for computer use.

For the sake of reviewing convenience, all available methods are arbitrarily classified into three categories:

(a) methods based on P-V-T data or on equation of state.

(b) methods based on corresponding states principle.

(c) enthalpies from fugacity relationships.

Methods Based on P-V-T Data or on Equations of State

Enthalpy has a rigorous relationship with volumetric data of pure components or of mixtures. At constant temperature

$$H - H^{o} = \int_{o}^{P} \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P} \right] dP \qquad (9\text{-}1)$$

From Equation 9-1 it is obvious that enthalpy can be calculated if pertinent P-V-T data and ideal gas state enthalpies are available. However, accurate values of the temperature derivatives of volume are not easily obtainable by either graphical or numerical methods. In general some method of curve fitting is applied, which leads to the use of equation of state. Since most equations of state are of a pressure-explicit form, it is convenient to transform Equation 9-1 into a volume integral form.

$$H - H^{o} = \int_{\infty}^{V} \left[T\left(\frac{\partial P}{\partial T}\right) - P \right] dV + PV - RT \qquad (9\text{-}2)$$

The Benedict-Webb-Rubin equation of state is most frequently used for this purpose.

The mixture enthalpies calculated from an equation state are more sensitive to the mixing rules and to temperature than the volumetric data are. This fact implies that the equation of state constants determined from P-V-T data are not necessarily good for enthalpy calculations. From this viewpoint, Starling (188) applied a multiproperty analysis to determine the constants for the Benedict-Webb-Rubin equation or a modification of it. Unfortunately, the accurate thermodynamic data from which the equation of state constants can be determined are not always available for many substances of interest. In such cases generalized equations of state may be used. The Redlich-Kwong(166), the Hirshfelder-Buehler-McGee-Sutton (87), or the Martin-Hou (115) equations of state can be used for this purpose. Wilson (207) improved the temperature dependence of the Redlich-Kwong equation for the calculation of enthalpies. But the generalized equations of state are already based on the principle of corresponding states in one way or the other.

Methods Based on Corresponding States Principles

The principle of corresponding states provides the way of generalizing the expressions of many thermodynamic properties. Good reviews on this principle are given by Stiel (191) and by Leland and Chappelear (104).

The earlier two parameter principle was first utilized in describing P-V-T behavior of gases, but immediately extended to enthalpy correlations. Among the earliest correlations of this type are those of Cope et al. (53) and of Edmister (63).

Later Lydersen et al. (112) introduced the critical compressibility factor into the principle, thus initiating a three parameter corresponding states theorem. At about same time Pitzer et al. (141) devised another third parameter which is termed as acentric factor to describe the deviation from simple fluids.

The enthalpy correlation of Lydersen et al. has the form

$$\frac{H^o - H}{T_c} = \left[\frac{H^o - H}{T_c}\right]_{Z_c=0.27} + D(Z_c - 0.27) \qquad (9\text{-}3)$$

where the bracketed term and D are presented as generalized functions in tabular form by the authors. The applicable range of conditions are $P_r \leqslant 30$ and $0.5 \leqslant T_r \leqslant 15$. Yen and Alexander (214) revised these functions in equation and graphical form and extended the upper temperature limit to $T_r = 30$. A recent modification by Yen (213) applies for $P_r \leqslant 100$ and $0.4 \leqslant T_r \leqslant 60$. Stevens and Thodos (190) fitted the saturation data of Lydersen et al. to analytical equation and applied to mixtures using pseudocritical properties.

The correlation of Curl and Pitzer (56) is given by

$$\frac{H^o - H}{RT_c} = \left[\frac{H^o - H}{RT_c}\right]^{(0)} + \omega\left[\frac{H^o - H}{RT_c}\right]^{(1)} \qquad (9\text{-}4)$$

The first bracketed term represents the enthalpy difference of simple fluids, and the second term reflects the deviation from simple fluid condition. Both terms are tabulated as generalized functions of reduced pressure and temperature. The tables cover the range of pressures up to $P_r = 9$, and temperatures from $T_r = 0.8$ to 4. Yarborough (109) modified this correlation by using high pressure enthalpy data together with P-V-T data.

A similar correlation using two reference substances was proposed by Yesavage (215).

$$\frac{H^o - H}{RT_c} = \left[\frac{H^o - H}{RT_c}\right]_1 W_1 + \left[\frac{H^o - H}{RT_c}\right]_2 W_2 \tag{9-5}$$

where $W_1 = 1 - W_2$

This correlation is suitable when the values of two reference substances are available.

Enthalpies From Fugacities

The isothermal partial enthalpy difference of component i is related to its fugacity as follows.

$$\frac{\Delta \bar{H}_i}{RT} = - T\left[\frac{\partial \ln \hat{f}_i}{\partial T}\right]_{P,x} \tag{9-6}$$

For pure component i

$$\frac{\Delta H_i}{RT} = - T\left[\frac{\partial \ln f_i}{\partial T}\right]_P \tag{9-7}$$

When an equation of state is used, Equation 9-7 results in an identical expression to that derived from Equation 9-2.

Edmister, Thompson, and Yarborough (67) employed Equation 9-6 together with the Redlich-Kwong equation of state for the calculation of partial enthalpy of a component in a mixture. In general partial enthalpy is very sensitive to mixing rules used, while mixture enthalpy is much less sensitive.

Another utility of Equation 9-6 or 9-7 was demonstrated by Erbar et al. (70). The authors separated Equation 9-6 in such a way that the saturated liquid enthalpy can be calculated from a K-value correlation involving ν_i and γ_i.

$$\left[\frac{\partial \ln \hat{f}_i}{\partial T}\right]_{P,x} = \left[\frac{\partial \ln \nu_i}{\partial T}\right]_P + \left[\frac{\partial \ln \gamma_i}{\partial T}\right]_{P,x} \qquad (9\text{-}8)$$

Multiplying Equation 9-8 by $-RT^2$ gives the partial molal enthalpy of component i in a mixture. The accuracy of enthalpy values calculated from Equation 9-8 entirely depends on the exactness of the temperature dependence of ν_i and γ_i.

Present Correlation

In this work the equations derived for the K-value correlation are also intended to be used for the prediction of enthalpies. This correlation method not only assures the internal consistency of both correlations but also facilitates the calculations of process designs.

The most probable way to achieve this goal is to use an equation of state for vapor phase enthalpy, and to estimate liquid phase enthalpy from the temperature derivatives of pure liquid fugacity coefficient and activity coefficient.

Vapor Phase Enthalpy

Encouragingly enough, the soundness of equation of state approach for the prediction of vapor phase enthalpies is strongly supported by many previous evaluation studies on enthalpy prediction methods. American Petroleum Institute (196), Sehgal et al. (184), Yesavage et al. (216), and Yesavage (215) conducted the most extensive comparison studies of such methods. The comparison results show that equations of state, especially the Benedict-Webb-Rubin equation is, in general, one of the best means to estimate the vapor phase enthalpies. This fact led to the development of a new equation of state that is capable of predicting both enthalpy and fugacity coefficient with accuracy. The detailed derivation of the new equation of state is shown in Chapter IV. The isothermal enthalpy difference expression derived from the equation of state is given by

$$\frac{H - H^{o}}{RT} = Z - 1 + \frac{1}{bRT}(a_1 + 2a_3/T + 6a_4/T^5) \ln (1 - \frac{b}{V})$$

$$- \frac{1}{2b^2RT}(1.5c_1/T^{\frac{1}{2}} + 3c_2/T^2) \ln (1 - \frac{b^2}{V^2}) \qquad (9\text{-}9)$$

The derivation of this enthalpy equation is given in Appendix C, while its evaluation is shown in Tables XXIV and XXV. As shown in the tables, Equation 9-9 is as capable as the Benedict-Webb-Rubin equation of representing enthalpy data of pure components and mixtures.

Liquid Phase Enthalpy

The liquid enthalpies are calculated using the relationships of Equations 9-6 and 9-8. The first term on the right-hand side of Equation 9-8 is evaluated from Equation 7-13 for real liquids and from Equation 7-14 for hypothetical liquids. For pure component i in a real liquid state

$$\frac{\Delta H}{RT} = A_2/T_r - A_3 - 2A_4T_r^2 - 6A_5T_r^6 + (A_6/T_r - A_7 - 2A_8T_r^2)P_r$$

$$- 3A_9T_r^3 P_r^2 + \omega(A_{10}T_r + A_{11}/T_r + A_{12}P_r/T_r - 3A_{13}T_r^3 P_r^2) \qquad (9\text{-}10)$$

For pure component i in a hypothetical liquid state

$$\frac{\Delta H}{RT} = B_2/T_r - B_3 - 2B_4T_r^2 - 4B_5T_r^4 + (B_6/T_r - B_7 - 2B_8T_r^2)P_r -$$

$$A_9T_rP_r^2 + \omega(A_{10}T_r + A_{11}/T_r + A_{12}P_r/T_r - A_{13}T_rP_r^2) \tag{9-11}$$

The evaluation of Equation 9-10 is given in Table XXVI along with the results of some other correlations by Stevens and Thodos (190), by Yen and Alexander (213, 214), and by Erbar et al. (70).

The partial excess enthalpy term is derived from the activity coefficient expression, Equation 7-28.

$$\frac{\bar{H}_i^E}{RT} = -T\left[\frac{\partial \ln \gamma_i}{\partial T}\right]_{P,x} = -TV_i^L\left[\sum_{j=1}^{N} \Phi_j \frac{dB_{ij}^*}{dT} - \frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N} \Phi_j \Phi_k \frac{dB_{ij}^*}{dT}\right] \tag{9-12}$$

where $$\frac{dB_{ij}^*}{dT} = \frac{1}{RT}\left[(\delta_i - \delta_j)^2 + q_1(\delta_i \delta_j)^{\frac{1}{2}} (\delta_i^{\frac{1}{2}} - \delta_j^{\frac{1}{2}})^2\right] \tag{9-13}$$

Combining Equations 9-10 through 8-14 gives the following isothermal enthalpy difference for a liquid mixture.

$$\frac{\Delta H^L}{RT} = \sum_{i=1}^{N} x_i\left[\frac{\Delta H_i}{RT} + \frac{\bar{H}_i^E}{RT}\right] \tag{9-14}$$

Equation 9-14 was tested against the experimental data of Mather (116) and Yesavage (215). The results are given in Table XXVII with the results of a similar correlation by Erbar et al. (70). The enthalpy expression of Erbar et al. is not exactly the same relationship as Equation 9-8, because the authors modified the expression after making differentiations. Even with the modification this expression is not as satisfactory as the equation in this work. When applying Equation 9-11 to methane, the constants for general hydrocarbons are recommended for use.

TABLE XXIV

COMPARISON OF ISOTHERMAL ENTHALPY DIFFERENCES OF PURE COMPONENTS IN THE VAPOR PHASE VIA FIVE EQUATIONS OF STATE

		Conditions		Average Absolute Deviations of Isothermal Enthalpy Differences From Canjar and Manning Data (37), Btu/lb				
Substance	Number of Points	$T_{min.}$ ^{o}F	$P_{max.}$ PSIA	Redlich -Kwong (166)	Barner et al. (12)	Benedict et al. (16)	Edmister et al. (65)	Equation 9-9
Saturated								
Methane	13	-250	527	2.499	2.309	0.188	1.858	1.795
Ethane	12	-100	632	4.632	1.054	0.073	0.718	1.312
Propane	13	-20	525	4.013	0.421	1.420	0.586	0.556
n-Butane	12	40	437	5.634	1.691	1.827	1.669	2.289
n-Pentane	14	100	393	1.915	2.930	3.655	2.600	1.813
Overall Average Absolute Deviations, Btu/lb				3.666	1.710	1.595	1.513	1.549
Superheated								
Methane	10	-200	3,000	1.252	1.299	0.221	1.262	0.717
Ethane	11	0	3,000	1.792	1.458	0.809	0.519	0.984
Propane	11	100	2,000	1.720	1.215	0.930	0.468	0.581
n-Butane	11	180	1,000	2.912	2.103	1.699	1.782	1.510
n-Pentane	10	240	700	1.628	1.982	3.372	2.222	1.747
Overall Average Absolute Deviations, Btu/lb				2.046	1.520	1.411	1.259	1.145

TABLE XXV

COMPARISON OF MIXTURE ISOTHERMAL ENTHALPY DIFFERENCES IN THE VAPOR PHASE FROM FIVE EQUATIONS OF STATE WITH EXPERIMENTAL DATA

		Conditions		Average Absolute Deviations of Isothermal Enthalpy Differences From Experimental Data, Btu/lb				
Mol Fraction of Methane	Number of Points	Temperature °F	Pressure PSIA	Redlich -Kwong (166)	Barner et al. (12)	Benedict et al. (16)	Edmister et al. (65)	Equation 9-9
Nitrogen-Methane (116), Saturated								
0.434	7	-225 to -152	100 to 700	1.243	1.056	0.680	1.519	1.101
Nitrogen-Methane (116), Superheated								
0.434	19	-150 to 200	500 to 1500	0.385	0.440	1.027	1.301	0.861
Methane-Propane (116,215), Saturated								
0.000	14	-44 to 204	15 to 600	5.735	0.791	1.425	2.362	0.962
0.234	8	36 to 178	100 to 800	5.907	1.562	1.109	2.113	1.435
0.494	10	50 to 114	200 to 1300	6.058	2.853	0.758	3.115	1.480
0.720	10	-25 to 64	100 to 1300	4.858	4.159	1.265	2.990	1.466
0.883	11	-63 to 4	100 to 1100	3.389	3.689	1.337	2.845	1.716
0.948	7	-92 to -42	100 to 900	1.202	1.421	2.229	1.368	0.372
Methane-Propane (116,215), Superheated								
0.000	12	300 to 500	500 to 2000	2.959	2.695	0.737	0.359	1.454
0.234	12	200 to 300	500 to 2000	5.069	1.703	0.720	1.686	1.839
0.494	16	150 to 300	500 to 2000	4.551	3.761	1.134	2.814	0.871
0.720	16	100 to 300	500 to 2000	2.495	3.223	0.434	1.649	0.470
0.883	16	50 to 300	500 to 2000	1.287	2.361	0.383	1.268	0.186
0.948	17	50 to 300	200 to 2000	0.691	1.067	0.510	0.809	0.741
Overall Average Abs. Deviations of 175 Points, Btu/lb :				3.085	2.174	0.840	1.813	1.009

TABLE XXVI

COMPARISON OF PURE COMPONENT ISOTHERMAL ENTHALPY DIFFERENCES IN THE LIQUID PHASE FROM FOUR PREDICTION METHODS

			Conditions		Ave. Abs. Deviations of Isothermal Enthalpy Differences From Literature Data, Btu/lb			
Substance	Reference	Number of Points	Temperature °F	Pressure PSIA	Stevens -Thodos (190)	Yen-Alexander (213,214)	Erbar et al. (70)	Equation 9-10
Saturated								
Methane	37	6	-240 to -130	32 to 527	6.721	7.475	3.906	2.342
Methane	90	10	-200 to -120	115 to 631	9.486	9.975	2.637	3.512
Ethane	37	12	-100 to 80	32 to 633	2.085	7.967	4.759	1.460
Propane	37	12	-20 to 190	25 to 555	3.381	3.282	3.475	0.751
Propane	215	13	-44 to 201	15 to 588	3.475	3.426	5.990	1.885
n-Butane	37	12	40 to 280	18 to 437	3.279	8.431	3.588	2.170
i-Butane	37	14	0 to 260	12 to 461	6.275	14.328	3.678	2.046
n-Pentane	37	13	100 to 360	16 to 392	3.812	10.753	4.972	1.940
n-Pentane	34	15	100 to 380	16 to 465	5.319	12.220	5.076	1.979
Overall Average Absolute Deviations of 107 Data Points, in Btu/lb:					5.318	10.517	4.464	2.155
Subcooled								
Methane	90	29	-260 to -120	100 to 2000	--	--	6.156	1.641
Propane	215	52	-120 to 180	100 to 2000	--	--	2.953	1.656
n-Pentane	37	27	100 to 360	500 to 2000	--	--	2.868	2.229
n-Pentane	34	28	100 to 340	500 to 2000	--	--	2.193	1.415
Overall Average Absolute Deviations of 136 Data Points, in Btu/lb:							3.918	1.820

TABLE XXVII

COMPARISON OF MIXTURE ISOTHERMAL ENTHALPY DIFFERENCES IN THE LIQUID PHASE FROM TWO PREDICTION METHODS WITH EXPERIMENTAL DATA

Mol Fraction of Methane	Number of Points	Conditions		Average Absolute Deviations of Isothermal Enthalpy Differences From Experimental Data, Btu/lb	
		Temperature °F	Pressure PSIA	Erbar et al.(70)	Equations 9-10 Through 9-14
Methane-Propane, saturated (116, 215)					
0.000	13	-44 to 201	15 to 588	6.051	1.882
0.234	8	-144 to 102	100 to 800	4.241	1.732
0.494	10	-180 to 51	100 to 1200	5.762	3.902
0.720	13	-202 to -4	100 to 1300	8.675	3.683
0.883	11	-209 to -49	100 to 1100	10.861	6.235
0.948	9	-208 to -84	100 to 900	11.240	7.617
Overall Average Absolute Deviations of 64 Data Points, in Btu/lb:				7.869	4.099
Methane-Propane, subcooled (116, 215)					
0.000	29	-120 to 180	100 to 2000	2.500	1.783
0.234	19	-250 to 100	500 to 2000	12.251	4.305
0.494	15	-250 to 0	500 to 2000	11.071	4.116
0.720	20	-250 to 0	500 to 2000	8.744	3.269
0.883	17	-250 to -50	500 to 2000	7.072	2.457
0.948	15	-250 to -100	500 to 2000	6.651	2.786
Overall Average Absolute Deviations of 115 Data Points, in Btu/lb:				7.532	2.993

CHAPTER X

CONCLUSIONS AND RECOMMENDATIONS

Based on the investigations conducted in this work the following are concluded and recommended.

Conclusions

(1) The proposed equation of state and the thermodynamic expressions derived from the equation are sufficiently accurate in representing the vapor phase P-V-T data and other thermodynamic properties of pure components and mixtures.

(2) The equation of state mixing rules given by Equations 4-39 through 4-41 are satisfactory for the calculations of mixture properties, but they are not as satisfactory for the partial properties including the fugacity coefficient of a component in a mixture.

(3) The modified mixing rules containing a set of interaction coefficients substantially improve the prediction of heavy component fugacity coefficients, subsequently increasing the accuracy of K-value prediction for the components.

(4) The newly obtained pure liquid fugacity coefficient expression shows a high performance in the temperature range of $T_r = 0.55$ to 1.0. It can be also applied at lower temperatures down to $T_r = 0.4$ with slightly reduced accuracy.

(5) The temperature derivatives of $\ln \nu_i$ is found to be an excellent

tool for predicting the isothermal enthalpy difference of pure liquids.

(6) The mixture liquid enthalpies can be predicted via Equation 8-6 satisfactorily.

(7) The proposed activity coefficient model is flexible enough to describe the nonideality of many liquid mixtures.

(8) The present K-value correlation may not hold beyond the range of conditions specified below.

a. For hydrocarbons

Temperature: down to 0.55 reduced temperature.

Pressure: up to 0.85 of the critical pressure of the system.

b. For light gases

Temperature: down to -200° F.

Pressure: up to 10,000 lb./sq. in. abs.

Concentration: up to about 20 mole percent of gases in the liquid.

(9) The present generalized K-value correlation is more accurate than the Chao-Seader correlation, and applicable to a wider variety of mixtures than are the correlations of Chueh and Prausnitz, and of Robinson and Chao. A further improvement can be obtained in the prediction of K-values by using specific rather than generalized interaction coefficients.

Recommendations

(1) An extensive study on mixing rules is necessary for an improved prediction of K-values. This study should be made in parallel with a modification of Equation 4-9.

(2) An improved temperature dependence of activity coefficient may be obtained from heat of mixing data. This approach assures more accurate predictions of liquid enthalpies via Equation 9-14.

(3) More accurate experimental data on cyclo-paraffin and aromatic compound mixtures are required. Remarkable disagreements are observed for these mixtures. This is also true for nitrogen systems. Therefore, it is recommended that accurate experimental determinations be repeated for these systems to discriminate between right and wrong data.

(4) Specific binary interaction coefficients should be determined for each binary system for which accurate experimental equilibrium data are available. These specific interaction coefficients would result in more accurate K-value predictions.

(5) The need for a separate K-value correlation for low temperature systems is suggested. In this case, the ν_i expressions for both real and hypothetical liquids should be redetermined. At the same time, the mixing rules for vapor phase fugacity coefficient should be also changed.

(6) An improved K-value correlation may be obtained by modifying Equation 4-9 or by developing a new equation of state, so that the vapor and liquid fugacities can be calculated directly. The necessary constants should be determined from experimental P-V-T data of both pure components and mixtures by applying a certain predetermined set of mixing rules.

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NOMENCLATURE

a, b - parameters in the van der Waals and the Redlich-Kwong equations of state

a, b, c - parameters in Benedict-Webb-Rubin equation of state and in Equation 4-9

a_1, a_2, a_3, a_4 - parameters in Equation 4-9

c_1, c_2 - parameters in Equation 4-9

A_i, B_i, C_i - parameter functions for Equation 5-7

A_1 through A_{13} - constants in Equation 7-13

A_{ij} - parameter in the Scatchard-Hildebrand equation

A_o, B_o, C_o - constants in Benedict-Webb-Rubin and in the Beattie-Bridgeman equations of state

B - second virial coefficient

B, C, D - constants in the Redlich-Kister equation

B^*, C^*, D^* - binary interaction coefficients in Equation 7-29

B_1 through B_8 - constants in Equation 7-14

C - third virial coefficient

- cohesive energy density

E - molal internal energy

f - fugacity

$\hat{f}$ - component fugacity in a mixture

g - parameter in Renon-Prausnitz equation

G - molal Gibbs free energy

$\bar{G}$ - partial molal Gibbs free energy

H - molal enthalpy

$\bar{H}$ - partial molal enthalpy

k - binary interaction coefficient in the modified Scatchard-Hildebrand equation

K - vapor-liquid equilibrium ratio

m_1, m_2, m_3 - constants for the generalized interaction coefficients in Equations 5-14, 5-15, and 5-16

M - number of phases

n - number of moles

N - total number of components

p - vapor pressure

P - system pressure

q_1, q_2, q_3, q_4 - constants for the generalized interaction coefficients in Equation 7-29

R - gas constant

S - molal entropy

SS - sum of square

T - absolute temperature

V - molal volume

$\bar{V}$ - partial molal volume

W_1, W_2 - parameters in Yesavage enthalpy equation

x - liquid composition

y - vapor composition

Z - compressibility factor

Greek Symbols

α - parameter in Heil-Prausnitz equation

α, γ - constants in Benedict-Webb-Rubin equation of state

α, β, θ - interaction coefficients in Equations 5-11, 5-12, and 5-13

β - liquid compressibility

γ - activity coefficient

δ - solubility parameter

Δ - difference in property

$\lambda, \Lambda, \xi, \tau$ - parameters in the Wilson, Heil-Prausnitz, and Renon-Prausnitz equations

$\bar{\mu}$ - chemical potential of a component in a mixture

ν - pure liquid fugacity coefficient

ϕ - vapor phase fugacity coefficient

Φ - volume fraction

$\sum$ - summation

ω - acentric factor

Subscripts

c - critical point property

calc - calculated

expl - experimental

i, j, k - components

ij, jk - interaction relationship

m - mixture

r - reduced condition

t - total

Superscripts

E - excess property

id - ideal solution

L - liquid phase

M - mixing property

s - saturation condition

V - vapor phase

o - reference state

- zero pressure state

APPENDIX A

DERIVATION OF PHASE EQUILIBRIUM CRITERIA

Applying the entropy criterion of equilibrium to a closed system involving M phases and N components gives

$$\left[\sum_{k=1}^{M} dS^{(k)}\right]_{E,V,n} = 0 \tag{A-1}$$

Expressing it in more explicit mathematical form

$$\sum_{k=1}^{M} dS^{(k)} = 0 \quad \text{or} \quad dS^{(m)} = -\sum_{\substack{k=1\\k\neq m}}^{M} dS^{(k)} \tag{A-2}$$

$$\sum_{k=1}^{M} dE^{(k)} = 0 \quad \text{or} \quad dE^{(m)} = -\sum_{\substack{k=1\\k\neq m}}^{M} dE^{(k)} \tag{A-3}$$

$$\sum_{k=1}^{M} dV^{(k)} = 0 \quad \text{or} \quad dV^{(m)} = -\sum_{\substack{k=1\\k\neq m}}^{M} dV^{(k)} \tag{A-4}$$

$$\sum_{k=1}^{M} dn_i^{(k)} = 0 \quad \text{or} \quad dn^{(m)} = -\sum_{\substack{k=1\\k\neq m}}^{M} dn_i^{(k)} \quad (i = 1, \ldots, N) \tag{A-5}$$

where m denotes an arbitrary phase. From the definition of internal energy

$$dE = TdS - PdV + \sum_{i=1}^{N} \bar{\mu}_i \, dn_i \tag{A-6}$$

Applying Equation A-6 to every phase and combining the expression for phase m with Equations A-2 through A-5 and summing up gives

$$\sum_{k=1}^{M} dE^{(k)} = \sum_{k=1}^{M} (T^{(k)} - T^{(m)})dS^{(k)} - \sum_{k=1}^{M} (P^{(k)} - P^{(m)})dV^{(k)}$$

$$+ \sum_{i=1}^{N} \sum_{k=1}^{M} (\bar{\mu}_i^{(k)} - \bar{\mu}_i^{(m)})dn_i^{(k)} = 0 \qquad \text{(A-7)}$$

All the $dS^{(k)}$, $dV^{(k)}$, and $dn_i^{(k)}$ $(i = 1, \ldots, N)$ are independent, since the dependent terms of a phase (phase m) have been eliminated. Thus, from the theorem of linear independency all the term in Equation A-7 must be identically zero in order for the equation to be generally valid, i.e.

$$T^{(k)} - T^{(m)} = 0 \ (k = 1, \ldots, M) \quad \text{or} \quad T^{(1)} = T^{(2)} = \ldots T^{(M)} \qquad \text{(A-8)}$$

Similarly

$$P^{(1)} = P^{(2)} = \ldots P^{(M)} \qquad \text{(A-9)}$$

$$\bar{\mu}_i^{(1)} = \bar{\mu}_i^{(2)} = \ldots \bar{\mu}_i^{(M)} \ (i = 1, \ldots, N) \qquad \text{(A-10)}$$

For vapor-liquid phase equilibrium

$$T^V = T^L \qquad \text{(A-11)}$$

$$P^V = P^L \qquad \text{(A-12)}$$

$$\bar{\mu}_i^V = \bar{\mu}_i^L \ (i = 1, 2, \ldots, N) \qquad \text{(A-13)}$$

APPENDIX B

CRITICAL POINT REQUIREMENTS FOR PROPOSED EQUATION OF STATE

Rewriting Equation 4-9 in more convenient form for differentiation gives

$$P = \frac{1}{V - b}\left[RT - \frac{1}{V}\left(a - \frac{c}{V + b}\right)\right] \qquad \text{(B-1)}$$

Differentiating Equation B-1 with respect to volume at constant temperature gives

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{V - b}\left[\frac{1}{V^2}\left(a - \frac{c}{V + b}\right) - \frac{c}{V(V + b)^2} - P\right] \qquad \text{(B-2)}$$

The second derivative is

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{1}{V - b}\left[-\frac{2}{V^3}\left(a - \frac{c}{V + b}\right) + \frac{2c}{V^2(V + b)^2}\right.$$

$$\left. + \frac{2c}{V(V + b)^3} - 2\left(\frac{\partial P}{\partial V}\right)_T\right] \qquad \text{(B-3)}$$

At critical point

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \qquad \text{(B-4)}$$

Applying Equation B-4 to Equations B-2 and B-3 gives

$$\frac{1}{V_c^2}\left(a - \frac{c}{V_c + b}\right) + \frac{c}{V_c(V_c + b)^2} - P_c = 0 \qquad \text{(B-5)}$$

$$\frac{1}{V_c^2}\left(a - \frac{c}{V_c + b}\right) + \frac{c}{V_c(V_c + b)^2} + \frac{c}{(V_c + b)^3} = 0 \qquad \text{(B-6)}$$

Combining Equations B-5 and B-6 gives

$$c = P_c(V_c + b)^3 \tag{B-7}$$

Combining Equations B-5 and B-7 gives

$$a = P_cV_c(2V_c + b) + P_c(V_c + b)^2 \tag{B-8}$$

Writing Equation B-1 for critical point and combining with Equations B-7 and B-8 results in

$$\frac{P_cV_c}{RT_c} = Z_c = \frac{1}{3} \tag{B-9}$$

Defining $b' = P_cb/RT_c$, $a' = P_ca/(RT_c)^2$, and $c' = P_cc/(RT_c)^3$, and using $Z_c = 1/3$ permits to rewrite Equations B-7 and B-8 as follows.

$$c' = (b' + 1/3)^3 \tag{B-10}$$

$$a' = (b'^2 + b' + 1/3) \tag{B-11}$$

The constant b' can take on any values without violating the equalities given by Equation B-4.

APPENDIX C

THERMODYNAMIC FUNCTIONS DERIVED FROM PROPOSED EQUATION OF STATE

(1) Second Virial Coefficient Expression

Rewriting the proposed equation of state, Equation 4-9, in terms of Z gives

$$Z = \frac{V}{V - b} - \frac{a}{RT(V - b)} + \frac{c}{RT(V - b)(V + b)} \tag{C-1}$$

Expanding Equation C-1 into infinite series gives

$$Z = 1 + (b - \frac{a}{RT})/V + (b^2 - \frac{ab - c}{RT})/V^2 + \ldots \tag{C-2}$$

Thus, the second virial coefficient is

$$B = b - \frac{a}{RT}$$

From Equations 4-25, 4-26, 4-28 through 4-31, one obtains

$$B = \frac{RT_c}{P_c}\left[(0.1231 - 0.25913/T_r - 0.2015/T_r^2) + \omega\,(0.15269 + 0.031314/T_r - 0.2164/T_r^2 - 0.042/T_r^6)\right] \tag{C-3}$$

(2) Isothermal Enthalpy Difference

Starting with Equations 9-2 and 4-9

$$H - H^{o} = \int_{\infty}^{V} \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV + PV - RT \qquad (9\text{-}2)$$

$$P = \frac{RT}{(V - b)} - \frac{a}{V(V - b)} + \frac{c}{V(V - b)(V + b)} \qquad (4\text{-}9)$$

where $a = a_1 - a_2 T + a_3/T + a_4/T^5$

$c = c_1/T^{0.5} + c_2/T^2$

Differentiating Equation 4-9 with respect to temperature at constant volume gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{(V - b)} + \frac{a_2 + a_3/T^2 + 5a_4/T^6}{V(V - b)} - \frac{0.5c_1/T^{1.5} + 2c_2/T^3}{V(V - b)(V + b)} \qquad (C\text{-}4)$$

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{a_1 + 2a_3/T + 6a_4/T^5}{V(V - b)} - \frac{1.5c_1/T^{0.5} + 3c_2/T^2}{V(V - b)(V + b)} \qquad (C\text{-}5)$$

Combining Equations C-4 and C-5 with Equation 9-2 gives

$$H - H^{o} = \Delta H$$

$$= PV - RT + \frac{1}{b}(a_1 + 2a_3/T + 6a_4/T^5) \ln\left(1 - \frac{b}{V}\right) - \frac{1}{2b^2}(1.5c_1/T^{0.5} + 3c_2/T^2) \ln\left[1 - \left(\frac{b}{V}\right)^2\right] \qquad (C\text{-}6)$$

(3) Fugacity Coefficient

Starting with Equations 5-6 and 4-9

$$\ln \phi_i = \frac{1}{RT}\int_{\infty}^{V_t}\left[\frac{RT}{V_t} - \left(\frac{\partial P}{\partial n_i}\right)_{T,V_t,n_j}\right]dV_t - \ln Z \qquad (5\text{-}6)$$

where $V_t = nV =$ total volume

$n_j = n_1, n_2, \ldots n_{i-1}, n_{i+1}, \ldots n_N$

$$P = \frac{nRT}{(V_t - nb)} - \frac{(n^2 a)}{V_t(V_t - nb)} + \frac{(n^3 c)}{V_t(V_t - nb)(V_t + nb)} \qquad (C\text{-}7)$$

Combining Equation C-7 with Equations 4-39 through 4-41 and 5-11 through 5-13 and differentiating P with respect to n_i at constant T, V_t, and n_j gives

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,V_t,n_j} = \frac{RT}{(V_t - nb)} + \frac{nRTb_i}{(V_t - nb)^2} - \frac{n^2 ab_i}{V_t(V_t - nb)^2}$$

$$- \frac{nA_i}{V_t(V_t - nb)} + \frac{2n^4 cbb_i}{V_t^2(V - nb)^2(V + nb)^2}$$

$$+ \frac{n^2 C_i}{V_t(V_t - nb)(V_t + nb)} \qquad (C\text{-}8)$$

where

$$A_i = 2\left[(a_1\ a_{1i})^{\frac{1}{2}} - (a_2\ a_{2i})^{\frac{1}{2}}T + a_{3i}^{\frac{1}{2}}\left(\sum_{j=1}^{N} y_j\ \alpha_{ji}\ a_{3j}^{\frac{1}{2}}\right)/T\right.$$

$$\left. + a_{4i}^{\frac{1}{2}}\left(\sum_{j=1}^{N} y_j\ \beta_{ji}\ a_{4j}^{\frac{1}{2}}\right)/T^5\right] \qquad (C\text{-}9)$$

$$C_i = 3\left[c_1^{2/3}\ c_{1i}^{1/3}\ /T^{\frac{1}{2}} + \right.$$

$$c_{2i}^{1/3} \sum_{j=1}^{N} \sum_{k=1}^{N} y_j\, y_k\, \theta_{ijk}(c_{2j}\, c_{2k})^{1/3} / T^2 \Big] \tag{C-10}$$

Combining Equations 5-6 and C-8 and integrating gives

$$\ln \phi_i = \frac{1}{RT}\Bigg[RT \ln \left(\frac{V_t}{V_t - nb}\right) + \frac{nRTb_i}{(V_t - nb)} + \frac{A_i}{b} \ln \left(\frac{V_t - nb}{V_t}\right)$$

$$+ n^2 a\, b_i \left\{ - \frac{1}{nb(V_t - nb)} - \frac{1}{n^2 b^2} \ln \left(\frac{V_t - nb}{V_t}\right) \right\}$$

$$- 2\, n\, cbb_i \left\{ \frac{1}{2n^2 b^2 (V_t^2 - n^2 b^2)} - \frac{1}{2n^4 b^4} \ln \left(\frac{V_t^2 - n^2 b^2}{V_t^2}\right) \right\}$$

$$- \frac{C_i}{2b^2} \ln \left(\frac{V_t^2 - n^2 b^2}{V_t^2}\right) \Bigg]_{\infty}^{V_t} - \ln Z \tag{C-11}$$

Rearranging and simplifying gives

$$\ln \phi_i = B_i (Z - 1) - \ln Z + \left(\frac{A_i - a\, B_i}{RTb} - 1\right) \ln \left(1 - \frac{b}{V}\right)$$

$$- \left(\frac{0.5 C_i - c\, B_i}{RTb^2}\right) \ln \left(1 - \frac{b^2}{V^2}\right) \tag{C-12}$$

where $B_i = b_i / b$

For pure component for which $A = 2a$, $C = 3c$, $B = 1$, and $\alpha = \beta = \theta = 1$

$$\ln \left(\frac{f_i}{P}\right) = Z - 1 - \ln Z + \left(\frac{a}{RTb} - 1\right) \ln \left(1 - \frac{b}{V}\right)$$

$$- \frac{c}{2RTb^2} \ln \left(1 - \frac{b^2}{V^2}\right) \tag{C-13}$$

(4) Partial Volume

Differentiating Equation C-7 with respect to n_i with P, T, and n_j

constant using the mixing rules given by Equations 4-39 through 4-41 gives

$$\left(\frac{\partial P}{\partial n_i}\right)_{P,T,n_j} = \frac{RT}{(V_t - nb)} - \frac{n\,RT}{(V_t - nb)^2}(\bar{V}_i - b_i) - \frac{n\,A_i}{V_t(V_t - nb)}$$

$$+ \frac{n^2\,a}{V_t^2\,(V_t - nb)^2}\Big[(V_t - nb)\bar{V}_i + V_t(\bar{V}_i - b_i)\Big]$$

$$+ \frac{n^2\,C_i}{V_t(V_t - nb)(V_t + nb)}$$

$$- \frac{n^3\,c}{V_t^2\,(V_t - nb)^2(V_t + nb)^2}\Big[(V_t^2 - n^2b^2)\bar{V}_i$$

$$+ V_t(2V_t\bar{V}_i - 2nbb_i)\Big] = 0 \qquad \text{(C-14)}$$

where $\bar{V}_i = \left(\frac{\partial V_t}{\partial n_i}\right)_{P,T,n_j}$, and A_i and C_i are given by Equations C-9 and C-10.

Collecting terms multiplied by $\bar{V}_i$, using $nV = V_t$ and Equation 4-9, and rearranging gives

$$\bar{V}_i = \frac{\left(P - \frac{c}{V(V + b)^2}\right)b_i + RT - \frac{A_i}{V} + \frac{C_i}{V(V + b)}}{P - \frac{a}{V^2} + \frac{c(2V + b)}{V^2(V + b)^2}} \qquad \text{(C-15)}$$

(5) Partial Enthalpy

By definition

$$\Delta\bar{H}_i = \frac{\partial}{\partial n_i}(n\Delta H)_{P,T,n_j} = \Delta H + n\frac{\partial}{\partial n_i}(\Delta H)_{P,T,n_j} \qquad \text{(C-16)}$$

where $\triangle H$ is given by Equation C-6.

If the mixing rules given by Equations 4-39 through 4-41 are used,

$$n\left(\frac{\partial \triangle H}{\partial n_i}\right)_{P,T,n_j} = P(\bar{V}_i - V) - \frac{b + b_i}{b^2}(a_1 + 2a_3/T + 6a_4/T^5) \ln \left(1 - \frac{b}{V}\right)$$

$$+ \frac{2}{b}\left[(a_1 \; a_{1i})^{\frac{1}{2}} + 2(a_3 \; a_{3i})^{\frac{1}{2}}/T + 6(a_4 \; a_{4i})^{\frac{1}{2}}/T^5\right] \ln \left(1 - \frac{b}{V}\right)$$

$$+ \frac{1}{b}(a_1 + 2a_3/T + 6a_4/T^5)\left(\frac{\bar{V}_i}{V} b - b_i\right)/(V - b)$$

$$+ \frac{b + 2b_i}{2b^3}(1.5c_1/T^{\frac{1}{2}} + 3c_2/T^2) \ln \left[1 - \left(\frac{b}{V}\right)^2\right]$$

$$- \frac{3}{2b^2}\left[1.5c \left(\frac{c_{1i}}{c_1}\right)^{1/3}/T^{\frac{1}{2}} + 3c \left(\frac{c_{2i}}{c_2}\right)^{1/3}/T^2\right] \ln \left[1 - \left(\frac{b}{V}\right)^2\right]$$

$$- \frac{1}{b}(1.5c_1/T^{\frac{1}{2}} + 3c_2/T^2)\left(\frac{\bar{V}_i}{V} b - b_i\right)/(V^2 - b^2) \qquad \text{(C-17)}$$

Rearranging Equation C-17 and combining it with Equation C-16 gives

$$\triangle \bar{H}_i = \triangle H + \frac{1}{b} \ln \left(1 - \frac{b}{V}\right) \left[2a_1\left(\frac{a_{1i}}{a_1}\right)^{\frac{1}{2}} + 4a_3\left(\frac{a_{3i}}{a_3}\right)^{\frac{1}{2}}/T\right.$$

$$\left. + 12a_4\left(\frac{a_{4i}}{a_4}\right)^{\frac{1}{2}}/T^5 - \left(1 + \frac{b_i}{b}\right)(a_1 + 2a_3/T + 6a_4/T^5)\right]$$

$$+ \frac{1}{2b^2} \ln \left(1 - \frac{b^2}{V^2}\right) \left[4.5 \; c_1\left(\frac{c_{1i}}{c_1}\right)^{1/3}/T^{\frac{1}{2}} + 9c_2\left(\frac{c_{2i}}{c_2}\right)^{1/3}/T^2\right.$$

$$\left. - \left(1 + \frac{2b_i}{b}\right)(1.5 \; c_1/T^{\frac{1}{2}} + 3c_2/T^2)\right]$$

$$- \frac{1}{(V - b)}\left(\frac{\bar{V}_i}{V} - \frac{b_i}{b}\right)\left[a_1 + 2a_3/T + 6a_4/T^5\right.$$

$$\left. - \frac{1}{(V + b)}(1.5 \; c_1/T^{\frac{1}{2}} + 3c_2/T^2)\right] + P(\bar{V}_i - V) \qquad \text{(C-18)}$$

APPENDIX D

SCATCHARD-HILDEBRAND EQUATION

From the definition of cohesive energy density

$$-E_i = C_i V_i^L \tag{D-1}$$

$$-E_m = \frac{1}{V_m^L}\left[\sum_{j=1}^{N} \sum_{k=1}^{N} C_{jk}\, x_j\, x_k\, V_j^L\, V_k^L\right] \tag{D-2}$$

Assuming $C_{jk} = (C_j\, C_k)^{\frac{1}{2}}$ gives

$$-E_m = V_m^L\left[\sum_{j=1}^{N} C_j^{\frac{1}{2}}\, \Phi_j\right]^2 \tag{D-3}$$

The internal energy of mixing is

$$E^M = E_m - \sum_{j=1}^{N} x_j\, E_j = \sum_{j=1}^{N} x_j\, C_j\, V_j^L - V_m^L\left[\sum_{j=1}^{N} C_j^{\frac{1}{2}} \Phi_j\right]^2 \tag{D-4}$$

For regular solution

$$E^M = G^E \tag{D-5}$$

Applying Equation 7-11 to Equations D-4 and D-5 results in

$$\ln \gamma_i = \frac{1}{RT}\, \frac{\partial}{\partial n_i}(nG^E)_{P,T,n_j}$$

$$= \frac{1}{RT}\left[C_i V_i^L - V_i^L\left\{\sum_{j=1}^{N} C_j\, \Phi_j\right\}^2 - \right.$$

$$2\left\{\sum_{j=1}^{N} n_j \; V_j^L\right\}\left\{\sum_{j=1}^{N} C_j^{\frac{1}{2}}\Phi_j \quad \frac{C_i^{\frac{1}{2}}\; V_i^L}{\sum_{j=1}^{N} n_j V_j^L} - \sum_{j=1}^{N} C_j^{\frac{1}{2}} \frac{n_j \; V_j^L \; V_i^L}{\left(\sum_{k=1}^{N} n_j \; V_j^L\right)^2}\right\}\Bigg]$$

$$= \frac{V_i^L}{RT}\left[C_i - 2C_i^{\frac{1}{2}}\left\{\sum_{j=1}^{N} C_j^{\frac{1}{2}}\Phi_j\right\} + \left\{\sum_{j=1}^{N} C_j^{\frac{1}{2}}\Phi_j\right\}^2\right]$$

$$= \frac{V_i^L}{RT}\left[\delta_i - \sum_{j=1}^{N}\delta_j \; \Phi_j\right]^2 \qquad \text{(D-6)}$$

APPENDIX E

ACTIVITY COEFFICIENT EXPRESSION

Expressiong Equation 5-33 as total excess Gibbs free energy gives

$$nG^E/RT = \frac{1}{2}\left[\left\{\sum_{j=1}^{N}\sum_{k=1}^{N} n_j\ V_j^L\ n_k\ V_k^L\ B_{jk}^{*}\right\}\Big/\left\{\sum_{j=1}^{N} n_j\ V_j^L\right\}\right.$$

$$+\ \frac{1}{n}\sum_{j=1}^{N}\sum_{k=1}^{N} n_j\ n_k\ C_{jk}^{*}$$

$$\left.+\ \frac{n}{\left\{\sum_{j=1}^{N} n_j\ V_j^L\right\}^2}\sum_{j=1}^{N}\sum_{k=1}^{N} n_j\ V_j^L\ n_k\ V_k^L\ D_{jk}^{*}\right] \qquad \text{(E-1)}$$

$$\frac{\partial}{\partial n_i}(nG^E/RT)_{P,T,n_j} = \frac{1}{2}\left[V_i^L\left\{\sum_{j=1}^{N} n_j\ V_j^L\ B_{ij}^{*} + \sum_{k=1}^{N} n_k\ V_k^L\ B_{ik}^{*}\right\}\Big/\left\{\sum_{j=1}^{N} n_j\ V_j^L\right\}\right.$$

$$-\ \frac{V_i^L}{\left\{\sum_{j=1}^{N} n_j\ V_j^L\right\}^2}\left\{\sum_{j=1}^{N}\sum_{k=1}^{N} n_j\ V_j^L\ n_k\ V_k^L\ B_{jk}^{*}\right\}$$

$$+\ \frac{1}{n}\left\{\sum_{j=1}^{N} n_j\ C_{ij}^{*} + \sum_{k=1}^{N} n_k\ C_{ik}^{*}\right\} - \frac{1}{n^2}\left\{\sum_{j=1}^{N}\sum_{k=1}^{N} n_j\ n_k\ C_{jk}^{*}\right\}$$

$$+\ \frac{1}{\left\{\sum_{j=1}^{N} n_j\ V_j^L\right\}^2}\left\{\sum_{j=1}^{N}\sum_{k=1}^{N} n_j\ V_j^L\ n_k\ V_k^L\ D_{jk}^{*}\right\} +$$

$$\frac{n}{\left\{\sum_{j=1}^{N} n_j V_j^L\right\}^2}\left\{V_i^L \sum_{j=1}^{N} n_j V_j^L D_{ij}^{*} + V_i^L \sum_{k=1}^{N} n_k V_k^L D_{ik}^{*}\right\}$$

$$- \frac{2nV_i^L}{\left\{\sum_{j=1}^{N} n_j V_j^L\right\}^3}\left\{\sum_{j=1}^{N}\sum_{k=1}^{N} n_j V_j^L n_k V_k^L D_{jk}^{*}\right\}\Bigg]$$

$$= V_i^L\left[\sum_{j=1}^{N} \Phi_j B_{ij}^{*} - \frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N} \Phi_j \Phi_k B_{jk}^{*}\right]$$

$$+ \left[\frac{\Phi_i}{x_i}\sum_{j=1}^{N} \Phi_j D_{ij}^{*} - \left\{\frac{\Phi_i}{x_i} - \frac{1}{2}\right\}\left\{\sum_{j=1}^{N}\sum_{k=1}^{N} \Phi_j \Phi_k D_{jk}^{*}\right\}\right]$$

$$+ \left[\sum_{j=1}^{N} x_j C_{ij}^{*} - \frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N} x_j x_k C_{jk}^{*}\right] \qquad \text{(E-2)}$$

APPENDIX F

COMPUTER PROGRAMS USED FOR DEVELOPING THE PRESENT K-VALUE CORRELATION

(1) Main Program for Heavy Component Activity Coefficients

```
      DIMENSION AX3(7),AX4(7),CX2(7),BIC(7,7),TIC(7,7,7),SQA3(7,7),
     1SQA4(7,7),CUBC(7,7,7)
C     EMBEDDING PRCGRAM FOR GAUSS
       DIMENSION B(24), Z(12,400), MM(12),DEL(7) ,TITLE(20),ACT(7),VL(7)
      DIMENSICN CC(64),PC(7),TC(7),ZC(7),WM(7),W(7),TB(7),CA(7),SK(7),
     1GL(7),SB(7),A1(7),A2(7),A3(7),C1(7),C2(7),XE(7),YE(7),TR(7),A4(7),
     2YOX(7),F(7),ZS(7),FOP(7),AFOP(7),BX(7),AX(7),CX(7),PHI(7),APHI(7)
     3,SVL(7),PS(7),PR(7),SFOP(7),QFC(7),QACT(7)
      COMMON NUM,B,Z,LLM
       COMMON /COMA/ MM
       COMMON /COMB/ JJ
    1 FORMAT(2CA4)
    2 FORMAT (12I6)
    3 FORMAT(8F10.4)
    4 FORMAT(13F10.3)
    6 FORMAT(I2,F8.2)
    9 FORMAT(40X,4F10.3)
   10 FORMAT(20A4,T69,4I3)
   11 READ (5,2) (MM(J),J=1,12)
      NSET=MM(2)
      JJ=MM(3)
      READ(5, 3) (B(J),J=1,24)
      LML = 1
      LLM= 0
      L = 1
      NUN=1
   21 CONTINUE
      READ(5,1)(TITLE(I),I=1,20)
      WRITE(6,1) (TITLE(I),I=1,20)
      NC=2
      DO 12 I=1,NC
      READ(5,3) PC(I),TC(I),ZC(I),WM(I),W(I),TB(I),VL(I),DEL(I)
      RTC = 10.7315*TC(I)
      CP = RTC/PC(I)
      CPP = CP*RTC
      SB(I) = CP*0.0982
      A1(I) = CPP*(0.25913-0.031314*W(I))
      A2(I) = CPP*(0.0249+0.15369*W(I))/TC(I)
      A3(I) = CPP*(0.2015+0.21642*W(I))*TC(I)
      A4(I) = CPP*0.042*W(I)*TC(I)**5
      C1(I) = CP*CPP* C.C59904*(1.0-W(I))*SQRT(TC(I))
      C2(I) = CP*CPP*(0.018126+0.091944*W(I))*TC(I)*TC(I)
   12 CONTINUE
   19 DO 23 N=NUN,400
```

```
      READ(5,9) TEMP,P,XE(1),YE(1)
      IF(P.LE.0.0) GO TO 24
      XE(2) = 1.0-XE(1)
      YE(2) = 1.0-YE(1)
      T = TEMP+459.7
      RT = 10.7315*T
      BS = 0.0
      AS1 = 0.0
      AS2 = 0.0
      AS3 = 0.0
      AS4 = 0.0
      CS1 = 0.0
      CS2 = 0.0
      DO 17 I=1,NC
      F(I) = YE(I)
      AX3(I) = 0.0
      AX4(I) = 0.0
      CX2(I) = 0.0
   17 CONTINUE
      KA = 2
      KB = 7
      KC = 5
      DO 14 I=1,NC
      YOX(I) = YE(I)/XE(I)
      BS = BS+F(I)*SB(I)
      AS1 = AS1+F(I)*SQRT(A1(I))
      AS2 = AS2+F(I)*SQRT(A2(I))
      CS1 = CS1+F(I)*C1(I)**.33333333
      DO 14 M=1,NC
      SQA3(I,M) = SQRT(A3(I)*A3(M))
      SQA4(I,M) = SQRT(A4(I)*A4(M))
      BIC(I,M) = 2.0*SQRT(TC(I)*TC(M))/(TC(I)+TC(M))
      AS3 = AS3+F(I)*F(M)*BIC(I,M)**KA*SQA3(I,M)
      AS4 = AS4+F(I)*F(M)*BIC(I,M)**KB*SQA4(I,M)
      AX3(I) = AX3(I)+F(M)*BIC(I,M)**KA*SQA3(I,M)
      AX4(I) = AX4(I)+F(M)*BIC(I,M)**KB*SQA4(I,M)
      DO 14 K=1,NC
      CUBC(I,M,K) = (C2(I)*C2(M)*C2(K))**.3333333333
      TIC(I,M,K)=3.*(TC(I)*TC(M)*TC(K))**.3333333333/(TC(I)+TC(M)+TC(K))
      CS2 = CS2+F(I)*F(M)*F(K)*TIC(I,M,K)**KC*CUBC(I,M,K)
      CX2(I) = CX2(I)+F(M)*F(K)*TIC(I,M,K)**KC*CUBC(I,M,K)
   14 CONTINUE
      I = 2
      TR(I) = T/TC(I)
      PR(I) = P/PC(I)
      TR2 = TR(I)*TR(I)
      TR3 = TR2*TR(I)
      TPR = TR3*PR(I)*PR(I)
      F1 = 6.32873-8.45167/TR(I)-6.90287*ALOG(TR(I))+1.87895*TR2-.334478
     1*TR3*TR3-(.018706/TR(I)-0.18940*TR2+0.28652*ALOG(TR(I)))*PR(I)
     2-0.0025839*TPR-ALOG(PR(I))
      F2 = (1.0-TR(I))*(8.7015 -11.201 /TR(I))-0.05044 /TR(I)*PR(I)+
     10.002255*TPR
      AFOP(I) = F1+F2*W(I)
      FUP(I) = EXP(AFOP(I))
      AS1 = AS1*AS1
      AS2 = AS2*AS2
      CS1 = CS1**3
      AS = AS1-AS2*T+AS3/T+AS4/T**5
```

```
      CS = CS1/SQRT(T)+CS2/(T*T)
      CALL RKEQN(AS,BS,CS,RT,P,V,L)
      ZZ = P*V/RT
      BOV = BS/V
      BX(I) = SB(I)/BS
      AX(I) = SQRT(AS1*A1(I))-SQRT(AS2*A2(I))*T+AX3(I)/T+AX4(I)/T**5
      CX(I) = CS1*(C1(I)/CS1)**.3333333/SQRT(T)+CX2(I)/(T*T)
      APHI(I) = ((2.*AX(I)/BS-RT-AS*BX(I)/BS)*ALOG(1.-BOV)+(CS*BX(I)-
     11.5*CX(I))/(BS*BS)*ALOG(1.-BOV*BOV))/RT+BX(I)*(ZZ-1.)-ALOG(ZZ)
      PHI(I)=EXP(APHI(I))
      ACT(I) = YOX(I)*PHI(I)/FOP(I)
      Z(1,N) = VL(1)
      Z(2,N) = DEL(1)
      Z(3,N) = XE(1)
      Z(4,N) = 1.0
      Z(5,N) = ACT(2)
      Z(6,N) = VL(2)
      Z(7,N) = DEL(2)
      Z(8,N) = XE(2)
      Z(9,N) = T
      Z(10,N) = TC(1)
      Z(11,N) = P
      Z(12,N) = TC(2)
   22 NUM = N
   23 CONTINUE
   24 CONTINUE
      NUN = NUM+1
      IF(TEMP.LE.-1000.0) GO TO 25
      GO TO 21
   25 CONTINUE
      MM(1) = NUM
      GO TO 16
   15 CONTINUE
      READ(5,2) (MM(J),J=1,12)
      NSET = MM(2)
      JJ = MM(3)
      MM(1) = NUM
      READ(5,3) (B(J),J=1,8)
   16 CONTINUE
   81 CONTINUE
      CALL GAUSS
      LLM  =LLM+1
      IF(LLM.LT.LML) GO TO 15
      IF (MM(8)-2) 30,20,30
   20 MM(8)=1
   30 MM(11)=MM(11)-1
      MM(8) = 1
      IF (MM(11)) 11,11,21
      END
       SUBROUTINE YCOMP
       DIMENSION B(24),Z(12,400),CY(400),WAC(400)
      COMMON NUM,B,Z,LLM
       COMMON /COMC/ CY
      DO 1 N=1,NUM
      R1 = Z(6,N)*Z(8,N)/(Z(1,N)*Z(3,N))+1.0
      R2 = R1/(R1-1.0)
      DELZ = Z(7,N)-Z(2,N)
      SQD2 = SQRT(Z(2,N))
      SQD7 = SQRT(Z(7,N))
```

```
      BACD = 10.5
      BZX =-1.25+BACD*Z(9,N)/SQRT(Z(10,N)*Z(12,N))
      BCD = BZX *SQD2*SQD7*(SQD2-SQD7)**2+DELZ*DELZ
      BCE =  B(2)
      VM = Z(1,N)*Z(3,N)+Z(6,N)*Z(8,N)
      SQVR = SQRT(Z(1,N)/Z(6,N))
      BIC = (SQVR-1.0/SQVR)**2
      TFUN = B(1)
      BCY = BCE*BIC*Z(1,N)*Z(6,N)/(VM*VM)*Z(3,N)*(1.+Z(8,N)-2.0/R2)
      BCX = TFUN*Z(3,N)*Z(3,N)*BIC+BCY
      VL2 = BCD*Z(6,N)/(1.10389*Z(9,N) *R1*R1)+BCX
      CY(N) = EXP(VL2)/Z(5,N)
    1 CONTINUE
      RETURN
      END
      SUBROUTINE ANSWER(N,YC,RTIO,Z)
      DIMENSION Z(12,400)
      YC = YC*Z(5,N)
      WRITE(6,9) N,Z(9,N),Z(11,N),Z(2,N),Z(7,N),Z(3,N),Z(8,N),Z(12,N),
     1Z(5,N),YC,RTIO,Z(10,N)
    9 FORMAT(I5,9F10.4,7X,2F10.4)
      RETURN
      END
```

(2) Main Program for Hypothetical Liquid Fugacity Coefficients of Light Components in Ethene and Heavier Hydrocarbon Systems

```
      DIMENSION AX3(7),AX4(7),CX2(7),BIC(7,7),TIC(7,7,7),SQA3(7,7),
     1SQA4(7,7),CUBC(7,7,7)
       DIMENSION B(24), Z(12,400), MM(12),DEL(7) ,TITLE(20),ACT(7),VL(7)
      DIMENSION CC(64),PC(7),TC(7),ZC(7),WM(7),W(7),TB(7),CA(7),SK(7),
     1RA(7),SB(7),A1(7),A2(7),A3(7),C1(7),C2(7),XE(7),YE(7),TR(7),A4(7),
     2YOX(7),F(7),ZS(7),FOP(7),AFOP(7),BX(7),AX(7),CX(7),PHI(7),APHI(7)
     3,SVL(7),PS(7),PR(7),SFOP(7),QFC(7),QACT(7),ZX(4,400)
      COMMON NUM,B,Z
       COMMON /COMA/ MM
       COMMON /COMB/ JJ
      COMMON /BIL/LLM,ZX
    1 FORMAT(20A4)
    2 FORMAT (12I6)
    3 FORMAT(8F10.4)
    4 FORMAT(13F10.3)
    6 FORMAT(I2,F8.2)
    9 FORMAT(40X,4F10.3)
   10 FORMAT(20A4,T65,4I3)
   11 READ (5,2) (MM(J),J=1,12)
      NSET=MM(2)
      JJ=MM(3)
      READ(5, 3) (B(J),J=1,24)
      LML = 2
      LLM= 0
      L = 1
      NUN=1
   21 CONTINUE
      READ(5,1)(TITLE(I),I=1,20)
      WRITE(6,1) (TITLE(I),I=1,20)
      NC=2
      DO 12 I=1,NC
      READ(5,3) DMM
      READ(5,3) PC(I),TC(I),ZC(I),WM(I),W(I),TB(I),VL(I),DEL(I)
      RTC = 10.7315*TC(I)
      CP = RTC/PC(I)
      CPP = CP*RTC
      SB(I) = CP*0.0982
      A1(I) = CPP*(0.25913-0.031314*W(I))
      A2(I) = CPP*(0.0249+0.15369*W(I))/TC(I)
      A3(I) = CPP*(0.2015+0.21642*W(I))*TC(I)
      A4(I) = CPP*0.042*W(I)*TC(I)**5
      C1(I) = CP*CPP* 0.059904*(1.0-W(I))*SQRT(TC(I))
      C2(I) = CP*CPP*(0.018126+0.091944*W(I))*TC(I)*TC(I)
   12 CONTINUE
   19 DO 23 N=NUN,400
      READ(5,9) TEMP,P,XE(1),YE(1)
      IF(P.LE.0.0) GO TO 24
      XE(2) = 1.0-XE(1)
      YE(2) = 1.0-YE(1)
      T = TEMP+459.7
      RT = 10.7315*T
      BS = 0.0
      AS1 = 0.0
      AS2 = 0.0
```

```
      AS3 = 0.0
      AS4 = 0.0
      CS1 = 0.0
      CS2 = 0.0
      VLM = 0.0
      DO 17 I=1,NC
      AX3(I) = 0.0
      AX4(I) = 0.0
      CX2(I) = 0.0
      F(I) = YE(I)
      VLM = VLM + XE(I)*VL(I)
   17 CONTINUE
      KA = 2
      KB = 7
      KC = 5
      DO 14 I=1,NC
      YOX(I) = YE(I)/XE(I)
      TR(I) = T/TC(I)
      PR(I) = P/PC(I)
      BS = BS+F(I)*SB(I)
      AS1 = AS1+F(I)*SQRT(A1(I))
      AS2 = AS2+F(I)*SQRT(A2(I))
      CS1 = CS1+F(I)*C1(I)**.33333333
      FVL(I) = XE(I)*VL(I)/VLM
      DO 14 M=1,NC
      SQA3(I,M) = SQRT(A3(I)*A3(M))
      SQA4(I,M) = SQRT(A4(I)*A4(M))
      BIC(I,M) = 2.0*SQRT(TC(I)*TC(M))/(TC(I)+TC(M))
      AS3 = AS3+F(I)*F(M)*BIC(I,M)**KA*SQA3(I,M)
      AS4 = AS4+F(I)*F(M)*BIC(I,M)**KB*SQA4(I,M)
      AX3(I) = AX3(I)+F(M)*BIC(I,M)**KA*SQA3(I,M)
      AX4(I) = AX4(I)+F(M)*BIC(I,M)**KB*SQA4(I,M)
      DO 14 K=1,NC
      CUBC(I,M,K) = (C2(I)*C2(M)*C2(K))**.3333333333
      TIC(I,M,K)=3.*(TC(I)*TC(M)*TC(K))**.3333333333/(TC(I)+TC(M)+TC(K))
      CS2 = CS2+F(I)*F(M)*F(K)*TIC(I,M,K)**KC*CUBC(I,M,K)
      CX2(I) = CX2(I)+F(M)*F(K)*TIC(I,M,K)**KC*CUBC(I,M,K)
   14 CONTINUE
      SQD1 = SQRT(DEL(1))
      SQD2 = SQRT(DEL(2))
      AINT1=(-1.25+10.5    *SQRT(TR(1)*TR(2)))*SQD1*SQD2*(SQD1-SQD2)**2
     1+(DEL(1)-DEL(2))**2
      SQVR = SQRT(VL(2)/VL(1))
      VRATIO = (SQVR-1.0/SQVR)**2
      AINT2 = -0.1*VRATIO
      AINT3 =-.38*VRATIO
      I = 1
      K = 2
      ACT(I) = EXP(VL(I)*AINT1*FVL(K)*FVL(K)/(1.1039*T)+AINT2*XE(K)*
     1(1.0+XE(I)-2.0*FVL(I))*VL(I)*VL(K)/(VLM*VLM)+AINT3*XE(K)*XE(K))
      AS1 = AS1*AS1
      AS2 = AS2*AS2
      CS1 = CS1**3
      AS = AS1-AS2*T+AS3/T+AS4/T**5
      CS = CS1/SQRT(T)+CS2/(T*T)
      CALL RKEQN(AS,BS,CS,RT,P,V,L)
      BX(I) = SB(I)/BS
      ZZ = P*V/RT
      BOV = BS/V
```

```
      AX(I) = SQRT(AS1*A1(I))-SQRT(AS2*A2(I))*T+AX3(I)/T+AX4(I)/T**5
      CX(I) = CS1*(C1(I)/CS1)**.3333333/SQRT(T)+CX2(I)/(T*T)
      APHI(I) = ((2.*AX(I)/BS-RT-AS*BX(I)/BS)*ALOG(1.-BOV)+(CS*BX(I)-
     11.5*CX(I))/(BS*BS)*ALOG(1.-BOV*BOV))/RT+BX(I)*(ZZ-1.)-ALOG(ZZ)
      PHI(I)=EXP(APHI(I))
      FOP(I) = YOX(I)*PHI(I)/ACT(I)
      Z(1,N) = TR(1)
      Z(2,N) = PR(1)
      Z(3,N) =  W(1)
      Z(4,N) = 1.0
      Z(5,N) = FUP(1)
      Z(7,N) = TEMP
      Z(8,N) = P
      Z(9,N) = XE(1)
      Z(10,N) = YE(1)
   22 NUM = N
   23 CONTINUE
   24 CONTINUE
      NUN = NUM+1
      IF(TEMP.LE.-1000.0) GO TO 25
      GO TO 21
   25 CONTINUE
      MM(1) = NUM
   15 CONTINUE
      CALL GAUSS
      LLM  =LLM+1
      IF(LLM.LT.LML) GO TO 15
      IF (MM(8)-2) 30,20,30
   20 MM(8)=1
   30 MM(11)=MM(11)-1
      MM(8) = 1
      IF (MM(11)) 11,11,21
      END
       SUBROUTINE YCOMP
       DIMENSION B(24),Z(12,400),CY(400)
      COMMON NUM,B,Z,LLM
       COMMON /COMC/ CY
    5 FORMAT(I6,8F10.5)
      DO 1 N=1,NUM
      Z1 = Z(1,N)
      Z2 = Z1*Z1
      Z3 = Z2*Z1
      Z12 = Z1*Z(2,N)*Z(2,N)
      BBCC = 7.92
      F1 = B(1)-B(2)/Z1-BBCC*ALOG(Z1)+B(4)*Z2-(B(1)-B(2)+B(4)+0.57847)
     1*Z3-(B(5)/Z1+B(3)*ALOG(Z1)-(0.17069+B(5))*Z2)*Z(2,N)-.002584*
     2Z12-ALOG(Z(2,N))
      F2 = (1.0-Z1)*(8.7015-11.201/Z1)-0.05044/Z1*Z(2,N)+.002255*Z12
      CY(N) = EXP(F1+F2*Z(3,N))/Z(5,N)
    1 CONTINUE
      RETURN
      END
```

(3) Main Program for Activity Coefficients and Hypothetical Liquid Fugacity Coefficients of Methane, CO_2, H_2S, H_2, and N_2

```
C     EMBEDDING PROGRAM FOR GAUSS
      DIMENSION AX3(7),AX4(7),CX2(7),BIC(7,7),TIC(7,7,7),SQA3(7,7),
     1SQA4(7,7),CUBC(7,7,7)
       DIMENSION B(24), Z(12,400), MM(12),DEL(7) ,TITLE(20),ACT(7),VL(7)
      DIMENSION CC(64),PC(7),TC(7),ZC(7),WM(7),W(7),TB(7),CA(7),SK(7),
     1GL(7),SB(7),A1(7),A2(7),A3(7),C1(7),C2(7),XE(7),YE(7),TR(7),A4(7),
     2YOX(7),F(7),ZS(7),FOP(7),AFOP(7),BX(7),AX(7),CX(7),PHI(7),APHI(7)
     3,SVL(7),PS(7),PR(7),SFOP(7),QFC(7),QACT(7),FVL(7)
      COMMON NUM,B,Z,LLM
       COMMON /COMA/ MM
       COMMON /COMB/ JJ
    1 FORMAT(20A4)
    2 FORMAT (12I6)
    3 FORMAT(8F10.4)
    4 FORMAT(13F10.3)
    6 FORMAT(I2,F8.2)
    9 FORMAT(40X,4F10.3)
   10 FORMAT(20A4,T69,4I3)
   11 READ (5,2) (MM(J),J=1,12)
      NSET=MM(2)
      JJ=MM(3)
      READ(5, 3) (B(J),J=1,24)
      LML = 2
      LML = 1
      LLM= 0
      L = 1
      NUN=1
   21 CONTINUE
      READ(5,1)  (TITLE(I),I=1,20)
      WRITE(6,1) (TITLE(I),I=1,20)
      NC=2
      DO 12 I=1,NC
      READ(5,3) PC(I),TC(I),ZC(I),WM(I),W(I),TB(I),VL(I),DEL(I)
      RTC = 10.7315*TC(I)
      CP = RTC/PC(I)
      CPP = CP*RTC
      SB(I) = CP*0.0982
      A1(I) = CPP*(0.25913-0.031314*W(I))
      A2(I) = CPP*(0.0249+0.15369*W(I))/TC(I)
      A3(I) = CPP*(0.2015+0.21642*W(I))*TC(I)
      A4(I) = CPP*0.042*W(I)*TC(I)**5
      C1(I) = CP*CPP* 0.059904*(1.0-W(I))*SQRT(TC(I))
      C2(I) = CP*CPP*(0.018126+0.091944*W(I))*TC(I)*TC(I)
   12 CONTINUE
   19 DO 23 N=NUN,400
      READ(5,9) TEMP,P,XE(1),YE(1)
      XE(2) = 1.0-XE(1)
      YE(2) = 1.0-YE(1)
      IF(P.LE.0.0) GO TO 24
      T = TEMP+459.7
      RT = 10.7315*T
      BS = 0.0
      AS1 = 0.0
      AS2 = 0.0
```

```
   AS3 = 0.0
   AS4 = 0.0
   CS1 = 0.0
   CS2 = 0.0
   TCL = 0.0
   DO 18 I=1,NC
   AX3(I) = 0.0
   AX4(I) = 0.0
   CX2(I) = 0.0
   F(I) = YE(I)
   TR(I) = T/TC(I)
   PR(I) = P/PC(I)
   TCL = TCL+XE(I)*TC(I)
18 CONTINUE
   KA = 0
   KB = -5
   KC = -2
   DO 14 I=1,NC
   YOX(I) = YE(I)/XE(I)
   BS = BS+F(I)*SB(I)
   AS1 = AS1+F(I)*SQRT(A1(I))
   AS2 = AS2+F(I)*SQRT(A2(I))
   CS1 = CS1+F(I)*C1(I)**.33333333
   DO 14 M=1,NC
   SQA3(I,M) = SQRT(A3(I)*A3(M))
   SQA4(I,M) = SQRT(A4(I)*A4(M))
   BIC(I,M) = 2.0*SQRT(TC(I)*TC(M))/(TC(I)+TC(M))
   AS3 = AS3+F(I)*F(M)*BIC(I,M)**KA*SQA3(I,M)
   AS4 = AS4+F(I)*F(M)*BIC(I,M)**KB*SQA4(I,M)
   AX3(I) = AX3(I)+F(M)*BIC(I,M)**KA*SQA3(I,M)
   AX4(I) = AX4(I)+F(M)*BIC(I,M)**KB*SQA4(I,M)
   DO 14 K=1,NC
   CUBC(I,M,K) = (C2(I)*C2(M)*C2(K))**.3333333333
   TIC(I,M,K)=3.*(TC(I)*TC(M)*TC(K))**.3333333333/(TC(I)+TC(M)+TC(K))
   CS2 = CS2+F(I)*F(M)*F(K)*TIC(I,M,K)**KC*CUBC(I,M,K)
   CX2(I) = CX2(I)+F(M)*F(K)*TIC(I,M,K)**KC*CUBC(I,M,K)
14 CONTINUE
   DO 16 I=1,NC
   IF(TR(I).GT.1.0) GO TO 33
   TR2 = TR(I)*TR(I)
   TR3 = TR2*TR(I)
   TPR = TR3*PR(I)*PR(I)
   F1 = 6.32873-8.45167/TR(I)-6.90287*ALOG(TR(I))+1.87895*TR2-
  10.33448*TR(I)**6-(0.018706/TR(I)-0.1894*TR2 +0.28652*ALOG(TR(I)))*
  2PR(I)-0.0025839*TPR-ALOG(PR(I))
   F2 = (1.-TR(I))*(8.7015-11.201/TR(I))-0.05044/TR(I)*PR(I)+
  10.002255*TPR
   GO TO 32
33 TR2 = TR(I)*TR(I)
   TPR = TR(I)*PR(I)*PR(I)
   F1 = 7.854 -9.9813/TR(I)-8.92*ALOG(TR(I))+2.1568*TR2-0.60796*TR2
  1*TR(I)+(0.19839/TR(I)+0.22483*ALOG(TR(I))-0.0277*TR2)*PR(I)
  2-0.002584*TPR-ALOG(PR(I))
   F2 = (1.-TR(I))*(8.7015-11.201/TR(I))-C.05044/TR(I)*PR(I)+
  10.002255*TPR
32 CONTINUE
   AFOP(I) = F1+F2*W(I)
   FOP(I) = EXP(AFOP(I))
16 CONTINUE
```

```
      AS1 = AS1*AS1
      AS2 = AS2*AS2
      CS1 = CS1**3
      AS = AS1-AS2*T+AS3/T+AS4/T**5
      CS = CS1/SQRT(T)+CS2/(T*T)
      CALL RKEQN(AS,BS,CS,RT,P,V,L)
      DO 17 I=1,NC
      ZZ = P*V/RT
      BOV = BS/V
      BX(I) = SB(I)/BS
      AX(I) = SQRT(AS1*A1(I))-SQRT(AS2*A2(I))*T+AX3(I)/T+AX4(I)/T**5
      CX(I) = CS1*(C1(I)/CS1)**.3333333/SQRT(T)+CX2(I)/(T*T)
      APHI(I) = ((2.*AX(I)/BS-RT-AS*BX(I)/BS)*ALOG(1.-BOV)+(CS*BX(I)-
     11.5*CX(I))/(BS*BS)*ALOG(1.-BOV*BOV))/RT+BX(I)*(ZZ-1.)-ALOG(ZZ)
      PHI(I)=EXP(APHI(I))
      ACT(I) = YOX(I)*PHI(I)
   17 CONTINUE
      Z(1,N) = VL(1)
      Z(2,N) = TR(1)
      Z(3,N) = XE(1)
      Z(4,N) = 1.0
      Z(5,N) = ACT(1)
      Z(6,N) = VL(2)
      Z(7,N) = DEL(2)
      Z(8,N) = XE(2)
      Z(9,N) = T
      Z(10,N) = ACT(2)
      Z(11,N) = PR(1)
      Z(12,N) = TR(2)
      ZX(1,N) = W(1)
      ZX(2,N) = FOP(2)
      ZX(3,N) = T/TCL
   22 NUM = N
   23 CONTINUE
   24 CONTINUE
      NUN = NUM+1
      IF(TEMP.LE.-1000.0) GO TO 25
      GO TO 21
   25 CONTINUE
      MM(1) = NUM
      DO 31 N=1,NUM
      NMM = N+NUM
      Z(1,NMM) = Z(6,N)
      Z(2,NMM) = Z(12,N)
      Z(3,NMM) = Z(8,N)
      Z(4,NMM) = Z(4,N)
      Z(5,NMM) = Z(10,N)
      Z(6,NMM) = Z(1,N)
      Z(7,NMM) = Z(7,N)
      Z(8,NMM) = Z(3,N)
      Z(9,NMM) = Z(9,N)
      Z(10,NMM) = ZX(3,N)
      Z(11,NMM) = Z(11,N)
      Z(12,NMM) = Z(2,N)
      ZX(2,NMM) = ZX(2,N)
   31 CONTINUE
      NUM = 2*NUM
      MM(1) = NUM
   15 CONTINUE
```

```
   CALL GAUSS
   LLM  =LLM+1
   IF(LLM.LT.LML) GO TO 15
   IF (MM(8)-2) 30,20,30
20 MM(8)=1
30 MM(11)=MM(11)-1
   MM(8) = 1
   IF (MM(11)) 11,11,21
   END
    SUBROUTINE YCCMP
    DIMENSION B(24),Z(12,400),CY(400),ZX(4,400)
   COMMON NUM,B,Z
    COMMON /COMC/ CY
   COMMON /BIL/LLM,ZX
 4 FORMAT(I5,10F12.6)
   DO 1 N=1,NUM
   IF(N.LE.(NUM/2)) GO TO 14
   Z(6,N) = 64.0
   IF(LLM.EQ.1) Z(6,N) = 62.0
   GO TO 15
14 Z(1,N) = 64.0
   IF(LLM.EQ.1) Z(1,N) = 62.0
15 CONTINUE
   R1 = Z(6,N)*Z(8,N)/(Z(1,N)*Z(3,N))+1.0
   R2 = R1/(R1-1.0)
   IF(B(9).LT.5.58) B(9) = 5.58
   IF(B(9).GT.5.65) B(9) = 5.65
   BH = B(9)
   DELZ = Z(7,N)-BH
   SQD2 = SQRT(BH)
   SQD7 = SQRT(Z(7,N))
   BZX = -1.25+10.5   *SQRT(Z(2,N)*Z(12,N))
   BCD = BZX*SQD2*SQD7*(SQD2-SQD7)**2+DELZ*DELZ
   VM = Z(1,N)*Z(3,N)+Z(6,N)*Z(8,N)
   SQVR = SQRT(Z(6,N)/Z(1,N))
   BIC = (SQVR-1.0/SQVR)**2
   BCX = -BIC*Z(8,N)*( 0.10  *Z(1,N)*Z(6,N)/(VM*VM)*(1.+Z(3,N)-2./R1)
  1+.38*Z(8,N))
   ACT = EXP(BCD*Z(1,N)/(1.10389*Z(9,N)*R2*R2)+BCX)
   IF(N.LE.(NUM/2))GO TO 11
   ANU = ZX(2,N)
   GO TO 12
11 CONTINUE
   Z1 = Z(2,N)
   Z2 = Z1*Z1
   Z3 = Z2*Z1
   Z12 = Z1*Z(11,N)*Z(11,N)
   Z12 = 0.0
   F1 = B(1)+B(2)/Z1+B(3)*ALOG(Z1)+B(4)*Z2+B(5)*Z3+(B(6)/Z1+B(7)*
  1ALOG(Z1)+B(8)*Z2)*Z(11,N)-0.002584*Z12-ALOG(Z(11,N))
   F2 = (1.0-Z1)*(8.7015-11.201/Z1)-0.05044/Z1*Z(11,N)+.002255*Z12
   ANU= EXP(F1+F2*ZX(1,N))
12 CONTINUE
   CY(N) = ACT*ANU/Z(5,N)
 1 CONTINUE
   RETURN
   END
```

(4) Main Program for Activity Coefficients of Cyclic Compounds

```
      DIMENSION AX3(7),AX4(7),CX2(7),BIC(7,7),TIC(7,7,7),SQA3(7,7),
     1SQA4(7,7),CUBC(7,7,7)
       DIMENSION B(24), Z(12,400), MM(12),DEL(7) ,TITLE(20),ACT(7),VL(7)
      DIMENSION CC(64),PC(7),TC(7),ZC(7),WM(7),W(7),TB(7),CA(7),SK(7),
     1GL(7),SB(7),A1(7),A2(7),A3(7),C1(7),C2(7),XE(7),YE(7),TR(7),A4(7),
     2YOX(7),F(7),ZS(7),FOP(7),AFOP(7),BX(7),AX(7),CX(7),PHI(7),APHI(7)
     3,SVL(7),PS(7),PR(7),SFOP(7),QFC(7),QACT(7),ZV(5,400),IDN(7)
      COMMON NUM,B,Z
       COMMON /COMA/ MM
       COMMON /COMB/ JJ
      COMMON/BIL/LLM,ZV
    1 FORMAT(20A4)
    2 FORMAT (12I6)
    3 FORMAT(7F10.4,F8.3,I2)
    4 FORMAT(13F10.3)
    6 FORMAT(I2,F8.2)
    8 FORMAT(8F10.3)
    9 FORMAT(40X,4F10.3)
   10 FORMAT(20A4,T69,4I3)
   11 READ (5,2) (MM(J),J=1,12)
      NSET=MM(2)
      JJ=MM(3)
      READ(5, 8) (B(J),J=1,24)
      READ(5,8) (CC(M),M=1,56)
      LML = 1
      LLM= 0
      L = 1
      NUN=1
   21 CONTINUE
      READ(5,1)  (TITLE(J),J=1,20)
      WRITE(6,1) (TITLE(J),J=1,20)
      READ(5,6) NC
      DO 12 I=1,NC
      READ(5,3) SVL(I),CA(I)
      READ(5,3) PC(I),TC(I),ZC(I),WM(I),W(I),TB(I),VL(I),DEL(I),IDN(I)
      RTC = 10.7315*TC(I)
      CP = RTC/PC(I)
      CPP = CP*RTC
      SB(I) = CP*0.0982
      A1(I) = CPP*(0.25913-0.031314*W(I))
      A2(I) = CPP*(0.0249+0.15369*W(I))/TC(I)
      A3(I) = CPP*(0.2015+0.21642*W(I))*TC(I)
      A4(I) = CPP*0.042*W(I)*TC(I)**5
      C1(I) = CP*CPP* 0.059904*(1.0-W(I))*SQRT(TC(I))
      C2(I) = CP*CPP*(0.018126+0.091944*W(I))*TC(I)*TC(I)
   12 CONTINUE
   19 DO 23 N=NUN,400
      READ(5,9) TEMP,P,XE(1),YE(1)
      IF(P.LE.0.0) GO TO 24
      XE(2) = 1.0-XE(1)
      YE(2) = 1.0-YE(1)
      T = TEMP+459.7
      RT = 10.7315*T
      BS = 0.0
```

```
      AS1 = 0.0
      AS2 = 0.0
      AS3 = 0.0
      AS4 = 0.0
      CS1 = 0.0
      CS2 = 0.0
      DO 18 I=1,NC
      YOX(I) = YE(I)/XE(I)
      AX3(I) = 0.0
      AX4(I) = 0.0
      CX2(I) = 0.0
      F(I) = YE(I)
      TR(I) = T/TC(I)
      PR(I) = P/PC(I)
   18 CONTINUE
      DO 14 I=1,NC
      BS = BS+F(I)*SB(I)
      AS1 = AS1+F(I)*SQRT(A1(I))
      AS2 = AS2+F(I)*SQRT(A2(I))
      CS1 = CS1+F(I)*C1(I)**.33333333
      DO 14 M=1,NC
      IF(IDN(I).EQ.2.OR.ICN(M).EQ.2) GO TO 42
      IF(IDN(I).EQ.3.OR.IDN(M).EQ.3) GO TO 38
      IF(IDN(I).EQ.1.OR.ICN(M).EQ.1) GO TO 38
      KA = 2
      KB = 7
      GO TO 39
   38 CONTINUE
      KA = 0
      KB = -5
      GO TO 39
   42 CONTINUE
      KA = -1
      KB = -8
   39 CONTINUE
      SQA3(I,M) = SQRT(A3(I)*A3(M))
      SQA4(I,M) = SQRT(A4(I)*A4(M))
      BIC(I,M) = 2.0*SQRT(TC(I)*TC(M))/(TC(I)+TC(M))
      AS3 = AS3+F(I)*F(M)*BIC(I,M)**KA*SQA3(I,M)
      AS4 = AS4+F(I)*F(M)*BIC(I,M)**KB*SQA4(I,M)
      AX3(I) = AX3(I)+F(M)*BIC(I,M)**KA*SQA3(I,M)
      AX4(I) = AX4(I)+F(M)*BIC(I,M)**KB*SQA4(I,M)
      DO 14 K=1,NC
      KC = 5
      IF(IDN(I).EQ.1.OR.IDN(M).EQ.1.OR.IDN(K).EQ.1) KC = -2
      IF(IDN(I).EQ.2.OR.IDN(M).EQ.2.OR.IDN(K).EQ.2) KC = -3
      CUBC(I,M,K) = (C2(I)*C2(M)*C2(K))**.3333333333
      TIC(I,M,K)=3.*(TC(I)*TC(M)*TC(K))**.3333333333/(TC(I)+TC(M)+TC(K))
      CS2 = CS2+F(I)*F(M)*F(K)*TIC(I,M,K)**KC*CUBC(I,M,K)
      CX2(I) = CX2(I)+F(M)*F(K)*TIC(I,M,K)**KC*CUBC(I,M,K)
   14 CONTINUE
      DO 16 I=1,NC
      IF(IDN(I).GE.1.AND.IDN(I).LT.4) GO TO 26
      IF(TR(I).GT.1.0) GO TO 26
      TR2 = TR(I)*TR(I)
      TR3 = TR2*TR(I)
      TPR = TR3*PR(I)*PR(I)
      F1 = 6.32873-8.45167/TR(I)-6.90287*ALOG(TR(I))+1.87895*TR2-
     10.33448*TR(I)**6-(0.018706/TR(I)-0.1894*TR2 +0.28652*ALOG(TR(I)))*
```

```
     2PR(I)-0.0025839*TPR-ALOG(PR(I))
      F2 = (1.-TR(I))*(8.7015-11.201/TR(I))-0.05044/TR(I)*PR(I)+
     10.002255*TPR
      GO TO 27
   26 M = 9
      IF(IDN(I).EQ.1) M = 17
      IF(IDN(I).EQ.2) M = 25
      IF(IDN(I).EQ.3) M = 33
      IF(IDN(I).EQ.4) M = 41
      IF(IDN(I).EQ.5) M = 49
      TR2 = TR(I)*TR(I)
      TR3 = TR2*TR(I)
      TPRT = TR(I)*PR(I)*PR(I)
      IF(IDN(I).GE.1.AND.IDN(I).LT.4) TPRT = 0.0
      F1 = CC(M)+CC(M+1)/TR(I)+CC(M+2)*ALOG(TR(I))+CC(M+3)*TR2+CC(M+4)*
     1TR3+(CC(M+5)/TR(I)+CC(M+6)*ALOG(TR(I))+CC(M+7)*TR2)*PR(I)-.002584
     2*TPRT-ALOG(PR(I))
      F2 = (1.-TR(I))*(8.7015-11.201/TR(I))-0.05044/TR(I)*PR(I)+
     10.002255*TPRT
   27 AFOP(I) = F1+F2*W(I)
      FOP(I) = EXP(AFOP(I))
   16 CONTINUE
      AS1 = AS1*AS1
      AS2 = AS2*AS2
      CS1 = CS1**3
      AS = AS1-AS2*T+AS3/T+AS4/T**5
      CS = CS1/SQRT(T)+CS2/(T*T)
      CALL RKEQN(AS,BS,CS,RT,P,V,L)
      DO 17 I=1,NC
      ZZ = P*V/RT
      BOV = BS/V
      BX(I) = SB(I)/BS
      AX(I) = SQRT(AS1*A1(I))-SQRT(AS2*A2(I))*T+AX3(I)/T+AX4(I)/T**5
      CX(I) = CS1*(C1(I)/CS1)**.3333333/SQRT(T)+CX2(I)/(T*T)
      APHI(I) = ((2.*AX(I)/BS-RT-AS*BX(I)/BS)*ALOG(1.-BOV)+(CS*BX(I)-
     11.5*CX(I))/(BS*BS)*ALOG(1.-BOV*BOV))/RT+BX(I)*(ZZ-1.)-ALOG(ZZ)
      PHI(I)=EXP(APHI(I))
      ACT(I) = YOX(I)*PHI(I)/FOP(I)
   17 CONTINUE
      Z(1,N) = VL(1)
      Z(2,N) = DEL(1)
      Z(3,N) = XE(1)
      Z(4,N) = 1.0
      Z(5,N) = ACT(1)
      Z(6,N) = VL(2)
      Z(7,N) = TR(1)
      Z(8,N) = XE(2)
      Z(9,N) = T
      Z(10,N) = DEL(2)
      Z(11,N) = P
      Z(12,N) = TR(2)
      ZV(1,N) = ACT(2)
   22 NUM = N
   23 CONTINUE
   24 CONTINUE
      NUN = NUM+1
      IF(TEMP.LE.-1000.0) GO TO 25
      GO TO 21
   25 CONTINUE
```

```
      MM(1) = NUM
      NUN = NUM
      DO 31 N=1,NUN
      NMM = N+NUM
      Z(1,NMM) = Z(6,N)
      Z(2,NMM) = Z(10,N)
      Z(3,NMM) = Z(8,N)
      Z(4,NMM) = Z(4,N)
      Z(5,NMM) = ZV(1,N)
      Z(6,NMM) = Z(1,N)
      Z(7,NMM) = Z(12,N)
      Z(8,NMM) = Z(3,N)
      Z(9,NMM) = Z(9,N)
      Z(10,NMM) = Z(2,N)
      Z(11,NMM) = Z(11,N)
      Z(12,NMM) = Z(7,N)
   31 CONTINUE
      NUM = NUM+NUN
      MM(1) = NUM
   15 CONTINUE
      CALL GAUSS
      LLM  =LLM+1
      IF(LLM.LT.LML) GO TO 15
      IF (MM(8)-2) 30,20,30
   20 MM(8)=1
   30 MM(11)=MM(11)-1
      MM(8) = 1
      IF (MM(11)) 11,11,21
      END
       SUBROUTINE YCOMP
       DIMENSION B(24),Z(12,400),CY(400),ZV(5,400)
      COMMON NUM,B,Z
      COMMON/BIL/LLM,ZV
       COMMON /COMC/ CY
    4 FORMAT(I5,11F10.3)
      DO 1 N=1,NUM
      SQD7 = SQRT(Z(10,N))
      SQD2 = SQRT(Z(2,N))
      DELZ=Z(10,N)-Z(2,N)
      BZX = B(1)+    B(2)    *SQRT(Z(7,N)*Z(12,N))
      BCD = BZX*SQD2*SQD7*(SQD2-SQD7)**2+DELZ*DELZ
      R1 = Z(6,N)*Z(8,N)/(Z(1,N)*Z(3,N))+1.0
      R2 = R1/(R1-1.0)
      VM = Z(1,N)*Z(3,N)+Z(6,N)*Z(8,N)
      VR = Z(6,N)/Z(1,N)
      BIC = (1.0-SQRT(VR))**4/VR
      BCX =  BIC*Z(8,N)*(-1.3333*Z(1,N)*Z(6,N)/(VM*VM)*(1.0+Z(3,N)-2./R1
     1)-B(3)*Z(8,N))
      ACT = EXP(BCD*Z(1,N)/(1.10389*Z(9,N)*R2*R2)+BCX)
      CY(N) = ACT/Z(5,N)
    1 CONTINUE
      RETURN
      END
```

(5) Common Subprograms for All the Foregoing Main Programs

```
      SUBROUTINE GAUSS                                                  GAUS0030
      DIMENSION A(20,21),B(24),BMIN(20),BSTT(20),  C(20,1),X(20,1),     GAUS0040
    X Z(12,400),DEL(20),E(20),MM(12),RCRD(100),  CY(400),FP(20,400)     GAUS0050
      COMMON NUM,B,Z
      COMMON /COMA/ MM                                                  GAUS0061
      COMMON /COMB/ JJ                                                  GAUS0062
      COMMON /COMC/ CY                                                  GAUS0063
      COMMON /COMD/ FP                                                  GAUS0064
      COMMON /COME/ A,C,M                                               GAUS0065
     EQUIVALENCE (A,X)                                                  GAUS0070
C      SECTION 0.    IDENTIFICATION OF CCNTROL VARIABLES                GAUS0100
C      B(1)-B(20)    PARAMETERS TO BE DETERMINED                        GAUS0120
C      B(21) = TOLERANCE                                                GAUS0130
C      B(22) = CONTRCL FOR DIFFERENT YCOMPS                             GAUS0140
C     B(23) = SCALE FACTOR FOR B(J) VECTOR.  USUALLY UNITY.             GAUS0150
C     MM(1) = NUMBER OF DATA POINTS                                     GAUS0170
C     MM(2) = INDEX OF DEPENDENT VARIABLE                               GAUS0180
C     MM(3) = NUMBER OF PARAMETERS                                      GAUS0190
C     MM(4) = LIMIT ON NUMBER OF ITERATIONS                             GAUS0200
C     MM(5) IS USED BY THE EMBEDDING PROGRAM, WHEN NEGATIVE IT SKIPS    GAUS0210
C     READING OF THE Z(J,K)                                             GAUS0220
C     MM(6) = -1  GIVES INTERMEDIATE RESULTS AT EACH ITERATION          GAUS0240
C     MM(6) =  0  GIVES NO INTERMEDIATE RESULTS                         GAUS0250
C     MM(6) =  1  GIVES INTERMEDIATE RESULTS AT FIRST ITERATION ONLY    GAUS0260
C      MM(7) = 1  GIVES STRAIGHT GAUSS                                  GAUS0280
C      MM(7) = 0  GIVES PARABOLIC GAUSS (RECOMMENDED)                   GAUS0290
C     MM(8) = -1  UPON RETURN MEANS OVERFLOW OR SINGULARITY OF MATRIX   GAUS0310
C     MM(8) = -2  UPON RETURN MEANS THAT ITERATION LIMIT IS EXCEEDED    GAUS0320
C     MM(8) =  1  GIVES THE BACK SOLUTION AT THE OUTSET OF THE PROGRAM GAUS0330
C     MM(8) = 2 SIGNALS THAT CONVERGENCE HAS OCCURRED                   GAUS0340
C     MM(9) = 1  RECORDS INPUT DATA ON TAPE 6                           GAUS0360
C     MM(9) = 0  BYPASSES THIS RECORDING                                GAUS0370
C     MM(10) = -1  RECORDS THE MATRICES AT EACH ITERATION               GAUS0390
C     MM(10) =  0  BYPASSES RECORDING OF MATRICES                       GAUS0400
C     MM(10) =  1  RECORDS THE MATRICES AT FIRST ITERATION ONLY         GAUS0410
C     MM(11)) = NUMBER OF PROBLEMS TO BE FED THE EMBEDDING PROGRAM      GAUS0430
C     MM(12) WHEN NEGATIVE NULLIFIES ALL PROGRAM                        GAUS0440
C     IT IS SUGGESTED THAT B(20) BE USED TO GIVE THE FUNCTION CHOICE    GAUS0470
C     IN YCOMP, WHEN THERE ARE MULTIPLE FUNCTIONS TO BE TESTED.         GAUS0480
     NUM=MM(1)                                                          GAUS0490
      NSET =   MM(2)                                                    GAUS0500
      JJ =     MM(3)                                                    GAUS0510
     LIMT=MM(4)
      NULL = MM(12)                                                     GAUS0530
      MM(12) = MM(12) + 1                                               GAUS0540
     IDNT=MM(12)                                                        GAUS0550
     TZRO=1.                                                            GAUS0570
     SCL1=0.2                                                           GAUS0580
     SCL2=1.5                                                           GAUS0590
     SCL3=1.                                                            GAUS0600
      TOL1 = B(21)                                                      GAUS0610
     XNRM=0.0                                                           GAUS0620
     NSPN=0
     MRKP=0                                                             GAUS0640
```

```
      KKPA=-1                                                           GAUS0650
      NDN=0                                                             GAUS0660
        NN = 0                                                          GAUS0670
      NNRA=0                                                            GAUS0680
      NPA=1                                                             GAUS0690
      NTZO=-1                                                           GAUS0700
      SMSQ=0.0                                                          GAUS0710
       T = 0.0                                                          GAUS0720
       X3 = 3.0                                                         GAUS0730
      X1 =0.0
      Y1 = 0.0
       X2 = 2.0                                                         GAUS0740
       Y2 = 2.0                                                         GAUS0750
       Y3 = 3.0                                                         GAUS0760
       IF (LIMT-100) 2,47,47                                            GAUS0780
    2  IF (TOL1) 420,420,1                                              GAUS0790
    1  DO 4 J=1,JJ                                                      GAUS0810
       BMIN(J) = B(J)                                                   GAUS0820
      BSTT(J)=B(J)                                                      GAUS0830
      XNRM=XNRM+B(J)**2                                                 GAUS0840
       DEL(J) = 0.05*ABS (B(J))                                         GAUS0850
       IF (DEL(J)) 4,3,4                                                GAUS0860
    3  DEL(J) = 0.05                                                    GAUS0870
    4  CONTINUE                                                         GAUS0880
       WRITE (6,5)                                                      GAUS0900
    5  FORMAT (51H1   GAUSSIAN PARAMETER SUBROUTINE       Z(12,300)  ) GAUS0910
       WRITE (6,412)            (MM(L), L=1,12)                         GAUS0930
       WRITE (6,108)            (B(J), J = 1,24)                        GAUS0940
       IF (MM(9)) 400,6,400                                             GAUS0960
    6  IF (MM(8) - 1) 7,80,7                                            GAUS0980
    7  IF (B(23)) 8,8,430                                               GAUS1000
    8 JPRA=-1                                                           GAUS1010
      MPA=-1                                                            GAUS1020
       T = 0.0                                                          GAUS1030
       MM(8) = 2                                                        GAUS1040
       WRITE(6,59)                                                      GAUS1050
       DO 9  J=1,JJ                                                     GAUS1060
    9 BSTT(J)=B(J)                                                      GAUS1070
   10 SQLA=SMSQ                                                         GAUS1090
      SMSQ=0.0                                                          GAUS1100
      NTZO=NTZO+1                                                       GAUS1110
       NN = NN+1                                                        GAUS1120
       IF (NN - LIMT) 12,12,11                                          GAUS1130
   11  MM(8) = -2                                                       GAUS1150
       GO TO 80                                                         GAUS1160
   12  CALL YCOMP                                                       GAUS1180
       DO 17 N= 1,NUM                                                   GAUS1181
       YC = CY(N)                                                       GAUS1190
       DELY = Z(NSET,N) - YC                                            GAUS1200
      SMSQ=SMSQ+DELY**2                                                 GAUS1210
       IF (NULL) 17,13,13                                               GAUS1220
   13  IF (MM(6)) 14,17,14                                              GAUS1230
   14  IF (N-1)  16,15,16                                               GAUS1240
   15  WRITE (6,410)                                                    GAUS1250
   16  WRITE (6,18)             N,YC,Z(NSET,N),DELY                     GAUS1260
      MRKP=1                                                            GAUS1270
   17  CONTINUE                                                         GAUS1280
      RCRD(NN)=SMSQ                                                     GAUS1290
   18  FORMAT (I6,4E18.7)                                               GAUS1300
```

```
    GO TO 440                                                           GAUS1310
19  IF (NN - 1) 20,22,30                                                GAUS1330
20 IF(SMSQ-SQMI) 21,21,27                                               GAUS1360
21 NDN=1                                                                GAUS1370
22 SQMI=SMSQ                                                            GAUS1380
    DO 24  J=1,JJ                                                       GAUS1390
24  BMIN(J) = B(J)                                                      GAUS1400
25 IF(MPA) 301,200,38                                                   GAUS1410
27 IF(NDN) 28,28,29                                                     GAUS1430
28 NDN=-1                                                               GAUS1440
29 IF(MPA) 301,200,36                                                   GAUS1450
30  IF (MM(6)) 32,32,31                                                 GAUS1470
31  MM(6) = 0                                                           GAUS1480
32  IF (MM(10)) 20,20,33                                                GAUS1490
33  MM(10) = 0                                                          GAUS1500
    GO TO 20                                                            GAUS1510
36 TZRO=TZRO*SCL1                                                       GAUS1530
   NTZO=-1                                                              GAUS1540
38  DO 39  J=1,JJ                                                       GAUS1560
     B(J) = BMIN(J)                                                     GAUS1570
39 BSTT(J)=BMIN(J)                                                      GAUS1580
    Y1 = SQMI                                                           GAUS1600
    X1 = 0.0                                                            GAUS1610
   JPRA=-1                                                              GAUS1620
   MPA=-1                                                               GAUS1630
    GO TO 301                                                           GAUS1640
40  SUM2 = SUM1                                                         GAUS1660
    SUM1 = SMSQ                                                         GAUS1670
   NNRA=0                                                               GAUS1680
    IF (SUM1 - SUM2) 19,45,19                                           GAUS1690
45 TZRO=SCL1*TZRO                                                       GAUS1710
   NDN=0                                                                GAUS1720
    T = 0.0                                                             GAUS1730
    GO TO 8                                                             GAUS1740
47 LIMT=99                                                              GAUS1760
    GO TO 2                                                             GAUS1770
49  T = -0.5*((X1*X1-X2*X2)*(Y1-Y3)-(X1*X1-X3*X3)*(Y1-Y2))/             GAUS1800
  X      ((X1-X3)*(Y1-Y2)-(X1-X2)*(Y1-Y3))                              GAUS1810
   MPA=1                                                                GAUS1830
   JPRA=-1                                                              GAUS1840
   NNRA=-1                                                              GAUS1850
   NDN=0                                                                GAUS1860
    GO TO 366                                                           GAUS1870
53  WRITE (6,54)                                                        GAUS1890
54  FORMAT (24H0 OVER-UNDERFLOW            //)                          GAUS1900
    MM(8) = -1                                                          GAUS1910
    MM(10) = -1                                                         GAUS1920
    GO TO 301                                                           GAUS1930
56  WRITE (6,57)                                                        GAUS1960
57  FORMAT (24H0 MATRIX IS SINGULAR        //)                          GAUS1970
    MM(8) = -1                                                          GAUS1980
    MM(10) = -1                                                         GAUS1990
    GO TO 301                                                           GAUS2000
59  FORMAT (114H0CYCLE     SUM OF SQUARES        ***********************GAUS2020
  X**************** PARAMETERS ********************************//)  GAUS2030
58  FORMAT (I6, F18.5, 5E18.6/(E42.6,4E18.6))                           GAUS2040
60  DO 66  J=1,JJ                                                       GAUS2090
   BTST=B(J)-BSTT(J)-DEL(J)                                             GAUS2100
   IF(BTST) 63,63,62                                                    GAUS2110
```

```
  62  B(J) = BSTT(J)+DEL(J)                                             GAUS2120
  63  CONTINUE                                                          GAUS2130
     BTST=B(J)-BSTT(J)+DEL(J)                                           GAUS2140
     IF(BTST) 65,65,66                                                  GAUS2150
  65  B(J) = BSTT(J)-DEL(J)                                             GAUS2160
  66  CONTINUE                                                          GAUS2170
     MPA=-1                                                             GAUS2190
  67  DO 69  J=1,JJ                                                     GAUS2200
  69 BSTT(J)=B(J)                                                       GAUS2210
      GO TO 10                                                          GAUS2220
  80  IF (NULL) 1000,82,82                                              GAUS2260
  82  AV = 0.0                                                          GAUS2270
      AV1 = 0.0                                                         GAUS2280
      AV2 = 0.0                                                         GAUS2290
      YMAX = 0.0                                                        GAUS2300
      ZMAX = 0.0                                                        GAUS2310
     ZZMX=0.0                                                           GAUS2320
      DO 81  J=1,JJ                                                     GAUS2330
  81  B(J) = BMIN(J)                                                    GAUS2340
      N = 1                                                             GAUS2350
      DO 90  J=1,JJ                                                     GAUS2360
  90  WRITE (6,91)             J,B(J)                                   GAUS2370
  91  FORMAT (4H   B I2, E14.5)                                         GAUS2380
      WRITE (6,100)                                                     GAUS2390
  92  WRITE (6,93)                                                      GAUS2410
  93  FORMAT (82HONUMBER           Y OBSERVED      Y CALCULATED         GAUS2420
    X  DELTA Y      PCT DEVIATION ///)                                  GAUS2430
  94  CALL YCOMP                                                        GAUS2450
  98  YC = CY(N)                                                        GAUS2451
      DELY = YC - Z(NSET,N)                                             GAUS2460
     RTIO=100.*(DELY/Z(NSET,N))                                         GAU0 4 0
     ABRT=ABS(RTIO)                                                     GAUS2480
      AV = AV + DELY                                                    GAUS2490
      AV1 = AV1 + RTIO                                                  GAUS2500
      AV2 = AV2 + ABRT                                                  GAUS2510
     CALL ANSWER(N,YC,RTIO,Z)
     ABVA=ABS(DELY)                                                     GAUS2540
      IF (YMAX - ABVA) 96,96,97                                         GAUS2550
  96  YMAX = ABVA                                                       GAUS2560
     YYMX=DELY                                                          GAUS2570
      MARK = N                                                          GAUS2580
  97 IF(ZMAX-ABRT) 971,971,972                                          GAUS2590
 971  ZMAX = ABRT                                                       GAUS2600
     ZZMX=RTIO                                                          GAUS2610
     MRK1=N                                                             GAUS2620
 972  N = N+1                                                           GAUS2630
     IF(N-NUM) 98,98,99                                                 GAUS2640
  99  D = NUM                                                           GAUS2660
      AV = AV/D                                                         GAUS2670
      AV1 = AV1/D                                                       GAUS2680
      AV2 = AV2/D                                                       GAUS2690
     RMSQ=SQRT(SMSQ/D)                                                  GAUS2700
      WRITE (6,100)                                                     GAUS2710
 100  FORMAT(118HO******************************************************GAUS2720
    X*****************************************************************//GAUS2730
    X/)                                                                 GAUS2740
      WRITE (6,101)           AV,AV1,AV2                                GAUS2750
 101  FORMAT (30HO  AVERAGE DEVIATION           E14.5,                  GAUS2760
    X        20H      AVERAGE PCT DEV           E14.5,                  GAUS2770
```

```
   X         20H     AVE ABS PCT DEV          E14.5)                  GAUS2780
     WRITE (6,103)  YYMX,MARK                                         GAUS2790
103  FORMAT (30H0  MAXIMUM DEVIATION          E14.5,I6)               GAUS2800
     WRITE (6,104)            ZMAX,MRK1                               GAUS2810
104  FORMAT (30H0  MAXIMUM   PCT DEV          E14.5,I6)               GAUS2820
     WRITE (6,105)          RMSQ                                      GAUS2830
105  FORMAT (30H0  ROOT MEAN SQUARE DEVIATION E14.5)                  GAUS2840
107  FORMAT ( 21H0        AT ITERATION I3,  24H, THE SUM OF SQUARES IS GAUS2860
   X    E16.7/ 22H0 FOR PARAMETER VALUES /1H0//(6E20.7))              GAUS2870
108  FORMAT (5F20.5)                                                  GAUS2880
109  FORMAT (//)                                                      GAUS2890
110  FORMAT (I20, F20.8)                                              GAUS2900
     WRITE (6,5)                                                      GAUS2910
     IF (MM(8) + 2) 114,111,114                                       GAUS2920
111  WRITE (6,112)                                                    GAUS2930
112  FORMAT (30H0 EXCEEDED ITERATION LIMIT       //)                  GAUS2940
     GO TO 999                                                        GAUS2950
114  IF (MM(8) - 1) 999,8,999                                         GAUS2970
200 IF(NDN) 201,201,202                                               GAUS2990
201  T = T*SCL1                                                       GAUS3000
     GO TO 203                                                        GAUS3010
202  T = T*SCL2                                                       GAUS3020
203 MPA=0                                                             GAUS3030
    JPRA=JPRA+1                                                       GAUS3040
     GO TO 366                                                        GAUS3050
301 MPA=0                                                             GAUS3070
    NDN=0                                                             GAUS3080
     DO 305  M=1,JJ                                                   GAUS3090
     C(M,1) = 0.0                                                     GAUS3100
302  DO 305 N=1,JJ                                                   GAUS3110
305  A(M,N) = 0.0                                                     GAUS3120
     CALL DERIV                                                       GAUS3170
     CALL YCOMP                                                       GAUS3160
     DO 313 N = 1,NUM                                                 GAUS3210
     DO 313 K = 1,JJ                                                  GAUS3220
     C(K,1) = C(K,1) + FP(K,N) * (Z(NSET,N) - CY(N))                  GAUS3230
     DO 313 J = K,JJ                                                  GAUS3240
313  A(K,J) = A(K,J) + FP(K,N) * FP(J,N)                              GAUS3250
    IF(NTZO) 318,318,317                                              GAUS3300
317 TZRO=1.0                                                          GAUS3310
318 T=TZRO                                                            GAUS3320
     DO 316  I=2,JJ                                                   GAUS3340
     II=I-1                                                           GAUS3350
     DO 316 J=1,II                                                    GAUS3360
316  A(I,J) = A(J,I)                                                  GAUS3370
     IF (MM(10)) 319,331,319                                          GAUS3390
319  WRITE (6,320)           NN                                       GAUS3410
320  FORMAT (19H0 MATRIX, ITERATION I3)                               GAUS3420
    MMPA=0                                                            GAUS3430
322  DO 323  I=1,JJ                                                   GAUS3440
323  WRITE (6,324)           (A(I,J), J=1,JJ)                         GAUS3450
324  FORMAT (9E13.5)                                                  GAUS3460
     DO 328  I=1,JJ                                                   GAUS3480
328  WRITE (6,324)           C(I,1)                                   GAUS3490
    IF(MMPA) 350,331,350                                              GAUS3500
331  DO 340  I=1,JJ                                                   GAUS3520
    DNM=ABS(A(I,1))                                                   GAUS3530
     DO 336  J=2,JJ                                                   GAUS3540
    IF(DNM-ABS(A(I,J))) 335,336,336                                   GAUS3550
```

```
335 DNM=ABS(A(I,J))                                                     GAUS3560
336  CONTINUE                                                           GAUS3570
     DO 338  K=1,JJ                                                     GAUS3580
338 A(I,K)=A(I,K)/DNM*SCL3                                              GAUS3590
340 C(I,1)=C(I,1)/DNM*SCL3                                              GAUS3600
    MMPA=1                                                              GAUS3620
     IF (MM(10)) 322,350,322                                            GAUS3630
350  DD = 1.0                                                           GAUS3650
     IF (MM(8)) 999,354,354                                             GAUS3660
354  CALL SOLV                                                          GAUS3670
     GO TO (351,53,56), M                                               GAUS3680
351  IF (MM(6)) 352,363,352                                             GAUS3690
352  WRITE (6,353)            (X(J,1), J=1,JJ)                          GAUS3700
353  FORMAT (13H0 DELTA B(J) /(9E13.5))                                 GAUS3710
363 YNRM=0.0                                                            GAUS3730
     DO 364  J=1,JJ                                                     GAUS3740
364 YNRM=YNRM+X(J,1)**2                                                 GAUS3750
    IF(YNRM-XNRM) 366,366,365                                           GAUS3770
365 T=0.5*SQRT(XNRM)/SQRT(YNRM)                                         GAUS3780
     X1 = T                                                             GAUS3790
366   DO 367  J=1,JJ                                                    GAUS3800
367 B(J)=BSTT(J)+T*X(J,1)                                               GAUS3810
371  DO 376  J=1,JJ                                                     GAUS3820
     IF (B(J)) 372,374,372                                              GAUS3830
372  XX = ABS ((B(J) - BSTT(J))/B(J))                                   GAUS3840
     GO TO 375                                                          GAUS3850
374  XX = ABS (B(J) - BSTT(J))                                          GAUS3860
375  IF (XX-TOL1)  376,376,378                                          GAUS3870
376  CONTINUE                                                           GAUS3880
     MM(8) = 2                                                          GAUS3890
     GO TO 80                                                           GAUS3900
378  IF (MM(7)) 60,379,60                                               GAUS3920
379 IF(NDN) 10,10,380                                                   GAUS3940
380 IF(JPRA) 10,10,49                                                   GAUS3960
400  IF (NULL) 6,401,401                                                GAUS3980
401  WRITE (6,100)                                                      GAUS3990
     IF (MM(5)) 406,403,403                                             GAUS3991
403  WRITE (6,402)                                                      GAUS4000
402  FORMAT (15H   OBSERVATIONS//)                                      GAUS4010
     DO 404  N=1,NUM                                                    GAUS4030
404  WRITE (6,405)           N, (Z(J,N), J=1,12)                        GAUS4040
405  FORMAT (I4,8E14.5/(E18.5,7E14.5))                                  GAUS4050
406  WRITE (6,5)             IDNT                                       GAUS4060
     GO TO 6                                                            GAUS4070
410  FORMAT ( 60H0 DATA       Y COMP             Y OBS             DIFFEGAUS4080
   XRENCE                                )                              GAUS4090
411  FORMAT (I6,F20.7)                                                  GAUS4100
412  FORMAT (12I6)                                                      GAUS4110
420  TOL1 = 0.0001                                                      GAUS4130
     GO TO 1                                                            GAUS4140
430  IF (B(23) - 1.0) 431,8,8                                           GAUS4160
431 TZRO=B(23)                                                          GAUS4170
     WRITE (6,433)              TZRO                                    GAUS4180
433  FORMAT ( 30H0 VECTOR SCALE FACTOR = B(23),    E12.4//)             GAUS4190
     GO TO 8                                                            GAUS4200
440  IF (NULL) 446,441,441                                              GAUS4220
441 NSPN=NSPN+1                                                         GAUS4230
442 IF(MRKP) 444,443,444                                                GAUS4240
443 IF(NSPN-15) 445,444,444                                             GAUS4250
```

```
  444 NSPN=0                                                            GAUS4260
      WRITE (6,59)                                                      GAUS4270
  445 WRITE (6,58) NN,SMSQ,(B(J),J=1,JJ)                                GAUS4280
  446 X3 = X2                                                           GAUS4290
      X2 = X1                                                           GAUS4300
      X1 = T                                                            GAUS4310
      Y3 = Y2                                                           GAUS4320
      Y2 = Y1                                                           GAUS4330
     Y1=SMSQ                                                            GAUS4340
     IF(NNRA) 40,19,40                                                  GAUS4350
  999 WRITE (6,991)                                                     GAUS4360
      DO 990  J=1,NN                                                    GAUS4370
  990 WRITE (6,405) J,RCRD(J)                                           GAUS4380
  991 FORMAT ( 28H0  RECORD OF SUM OF SQUARES       //  )               GAUS4390
  993 FORMAT (24H0 MINIMIZING PARAMETERS     //)                        GAUS4400
      WRITE (6,993)                                                     GAUS4410
      WRITE (6,108)               (BMIN(J), J=1,JJ)                     GAUS4420
 1000 RETURN                                                            GAUS4450
      END                                                               GAUS4460


      SUBROUTINE SOLV                                                   SOLV0010
      DIMENSION A(20,21), C(20,1),           LOC(20), CK(20)            SOLV0020
      COMMON /COMB/ JJ                                                  SOLV0030
      COMMON /COME/ A,C,M                                               SOLV0040
      M = 1                                                             SOLV0050
      NP = JJ+ 1                                                        SOLV0060
      DO 11 I = 1,JJ                                                    SOLV0070
      CK(I) = 0.                                                        SOLV0080
   11 A(I,NP) = C(I,1)                                                  SOLV0090
      DO 50 I = 1,JJ                                                    SOLV0100
      IP = I + 1                                                        SOLV0110
C     FIND MAX ELEMENT IN I'TH COLUMN.                                  SOLV0120
      AMAX = 0.                                                         SOLV0130
      DO 2 K = 1,JJ                                                     SOLV0140
      IF (AMAX - ABS(A(K,I))) 3,2,2                                     SOLV0150
C     IS NEW MAX IN ROW PREVIOUSLY USED AS PIVOT                        SOLV0160
    3 IF (CK(K)) 4,4,2                                                  SOLV0170
    4 LOC(I) = K                                                        SOLV0180
      AMAX = ABS(A(K,I))                                                SOLV0190
    2 CONTINUE                                                          SOLV0200
      IF (ABS(AMAX).LE.1.E-12)GO TO 99                                  SOLV0210
C     MAX ELEMENT IN I'TH COLUMN IS A(L,I)                              SOLV0220
    5 L = LOC(I)                                                        SOLV0230
      CK(L) = 1.                                                        SOLV0240
C     PERFORM ELIMINATION.  L IS PIVOT ROW, A(L,I) IS PIVOT ELEMENT.    SOLV0250
      DO 50 J = 1,JJ                                                    SOLV0260
      IF (L-J) 6,50,6                                                   SOLV0261
    6 F = -A(J,I) / A(L,I)                                              SOLV0262
      DO 40 K = IP,NP                                                   SOLV0270
   40 A(J,K) = A(J,K) + F * A(L,K)                                      SOLV0280
   50 CONTINUE                                                          SOLV0290
      DO 200 I = 1,JJ                                                   SOLV0300
      L = LOC(I)                                                        SOLV0310
  200 A(I,1) = A(L,NP) / A(L,I)                                         SOLV0320
      RETURN                                                            SOLV0330
   99 M = 3                                                             SOLV0340
      RETURN                                                            SOLV0350
      END                                                               SOLV0360
```

```
      SUBROUTINE DERIV                                                  DERIV010
      DIMENSION B(24),Z(12,400),CY(400),FP(20,400),H(20),Y(400)         DERIV020
      COMMON NUM,B,Z                                                    DERIV030
      COMMON /COMB/ JJ                                                  DERIV040
      COMMON /COMC/ CY                                                  DERIV050
      COMMON /COMD/ FP                                                  DERIV060
      IF (B(22)) 20,1,20                                                DERIV070
    1 B(22) = 1.                                                        DERIV080
      DO 7 J = 1,JJ                                                     DERIV090
      TEST = ABS(B(J))                                                  DERIV100
      IF (TEST - 0.001) 5,6,6                                           DERIV110
    5 H(J) = 0.001                                                      DERIV120
      GO TO 7                                                           DERIV130
    6 H(J) = 0.0001 * TEST                                              DERIV140
    7 CONTINUE                                                          DERIV150
   20 DO 22 J = 1,JJ                                                    DERIV160
      TEMP = B(J)                                                       DERIV170
      B(J) = TEMP + H(J)                                                DERIV180
      CALL YCOMP                                                        DERIV190
      DO 21 N = 1,NUM                                                   DERIV200
   21 Y(N) = CY(N)                                                      DERIV210
      B(J) = TEMP - H(J)                                                DERIV220
      CALL YCOMP                                                        DERIV230
      B(J) = TEMP                                                       DERIV240
      DO 22 N = 1,NUM                                                   DERIV250
   22 FP(J,N) = (Y(N) - CY(N))/(2. * H(J))                              DERIV260
      RETURN                                                            DERIV270
      END                                                               DERIV280
```

```
      SUBROUTINE RKEQN(A,B,C,RT,P,V,L)
      C1 = -RT/P
      C2 = (A-B*RT)/P-B*B
      AB = A*B
      IF(C.EQ.0.0) AB=-AB
      C3 = (AB-C)/P
      GG = (C2-C1*C1/3.0)/3.0
      FF = (2.0*C1**3/27.0-C1*C2/3.0+C3)/2.0
      TEST = FF*FF+GG**3
      IF(TEST) 11,12,13
   11 PHI = -SIGN((ARCOS(SQRT(-FF*FF/GG**3))/3.0),FF)
      Q = 2.0*SQRT(-GG)
      V1 = Q*COS(PHI)
      V2 = Q*COS(PHI+2.0944)
      V3 = Q*COS(PHI+4.18879)
      IF(L.EQ.2) GO TO 14
      V = AMAX1(V1,V2,V3)
      GO TO 15
   14 V = AMIN1(V1,V2,V3)
      GO TO 15
   12 V = 0.0
      GO TO 15
   13 AA = SQRT(TEST)-FF
      BB = -AA-2.0*FF
      CAA = SIGN((ABS(AA)**.3333333),AA)
      CBB = SIGN((ABS(BB)**.3333333),BB)
      V = CAA+CBB
```

```
    15 V = V-C1/3.0
       ZZ=V**3+C1*V*V+C2*V+C3
       RETURN
       END
//
```

APPENDIX G

COMPUTER PROGRAM FOR BUBBLE POINT PRESSURE CALCULATION

(1) Main Program

```
   DIMENSION XE(10),YE(10),SUMY(31),YSUM(31),PY(31),DEVK(10),YOX(10),
  1EXK(10),SUMK(10),AVGK(10)
   COMMON/ALL/ NC,ICN(10), WM(10),X(10),Y(10),T,P,RT,FOP(10),ACT(10),
  1PHI(10),TC(10),PC(10),W(10)
   COMMON/NHU/ B(64)
 1 FORMAT(I5,10F10.4)
 3 FORMAT(8F10.4)
 4 FORMAT(F10.1,3X,2F10.1,F10.3,3X,3F10.3,3X,3F10.3,5X,I2,F8.4)
 5 FORMAT(/, 3X,'AVERAGE OF ',I3, ' DATA POINTS =',2X,F10.3,23X,
  1F10.3,23X,F10.3)
 6 FORMAT(1H1)
 7 FORMAT(40X,4F10.3)
 8 FORMAT(8E14.4)
 9 FORMAT(5X,'TEMP',14X,'PRESSURE PSIA',20X,'K OF COMPONENT 1',
  116X,'K OF COMPONENT 2'/
  27X,'F',10X,'EXPTL',5X,'CALC',6X,'% DEV',8X,'EXPTL',5X,'CALC',6X,
  3'% DEV', 8X,'EXPTL',5X,'CALC',6X,'% DEV',//)
   READ(5,3) (B(I),I=1,56)
   TEMP = 1.0
24 CONTINUE
   IF(TEMP.LT.-1111.0) GO TO 22
   SUMP = 0.0
   SUM1 = 0.0
   SUM2 = 0.0
   CALL CONST
   WRITE(6,9)
   DO 25 I=1,NC
   SUMK(I) = 0.0
25 CONTINUE
   DO 20 N=1,400
   READ(5,7) TEMP,PE,XE(1),YE(1)
   IF(TEMP.LT.-999.0) GO TO 21
   T = TEMP+459.7
   RT = 10.7315*T
   XE(2) = 1.0-XE(1)
   YE(2) = 1.0-YE(1)
   DO 11 I=1,NC
   X(I) = XE(I)
   EXK(I) = YE(I)/XE(I)
11 PHI(I) = 1.0
C  CALCULATION OF ACTIVITY COEFFICIENT
   CALL ACTCOF
   P = 100.0
   PY(1) = P
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      YSUM(1) = 1.0
      DO 18 M=1,30
      DO 13 J=1,31
   13 SUMY(J) = 0.0
C    CALCULATION OF LIQUIC PHASE FUGACITY COEFFICIENT OF PURE COMPONENT
      CALL NHULIQ
      DO 14 J=2,30
      DO 15 I=1,NC
      Y(I) = X(I)*FOP(I)*ACT(I)/PHI(I)
   15 SUMY(J) = SUMY(J)+Y(I)
      IF(ABS(SUMY(J)-SUMY(J-1)).LE.0.5E-4) GO TO 17
      DO 16 I=1,NC
      Y(I) = Y(I)/SUMY(J)
   16 CONTINUE
C    CALCULATION OF VAPOR PHASE FUGACITY COEFFICIENT
      CALL FUGVAP
   14 CONTINUE
   17 YSUM(M) = SUMY(J)
      IF(M.GT.3) GO TO 33
      PY(M+1) = PY(M)*YSUM(M)
      GO TO 29
   33 PY(M+1) = PY(M)-(PY(M)-PY(M-1))*(YSUM(M)-1.)/(YSUM(M)-YSUM(M-1))
   29 P = PY(M+1)
      IF(ABS(PY(M+1)-PY(M))/PY(M+1)-1.0E-4) 19,19,18
   18 CONTINUE
   19 CONTINUE
      DEVP = (P-PE)/PE*100.0
      DO 23 I=1,NC
      YOX(I) = Y(I)/X(I)
      DEVK(I) = (YOX(I)/EXK(I)-1.0)*100.0
   23 CONTINUE
      WRITE(6,4) TEMP,PE,P,DEVP,(EXK(I),YOX(I),DEVK(I),I=1,NC),M,YSUM(M)
      SUMP = SUMP+ABS(DEVP)
      DO 26 I=1,NC
      SUMK(I) = SUMK(I)+ABS(DEVK(I))
   26 CONTINUE
   20 CONTINUE
   21 CONTINUE
      N = N-1
      XN = N
      AVGP = SUMP/XN
      DO 27 I=1,NC
      AVGK(I) = SUMK(I)/XN
   27 CONTINUE
      WRITE(6,5)   N,AVGP,(AVGK(I),I=1,NC)
      GO TO 24
   22 CONTINUE
      STOP
      END
```

(2) Subprogram for Input Data

```
      SUBROUTINE CONST
      DIMENSION TITLE(20),BIA(10,10),BIB(10,10)
      COMMON/ALL/ NC,IDN(10), WM(10),X(10),Y(10),T,P,RT,FOP(10),ACT(10),
     1PHI(10),TC(10),PC(10),W(10)
      COMMON/GAM/BA1,BA2,VL(10),DEL(10),BINB(10,10),BINC(10,10)
      COMMON/FUG/ SB(10),A1(10),A2(10),A3(10),A4(10),C1(10),C2(10)
     1,BIC(10,10),BID(10,10),TIC(10,10,10)
    1 FORMAT(20A4)
    2 FORMAT(7F10.4,F8.3,I2)
    5 FORMAT(5I2)
    6 FORMAT(1H1)
    7 FORMAT(5X,20A4,///)
      WRITE(6,6)
      READ(5,1) (TITLE(I),I=1,20)
      WRITE(6,7) (TITLE(I),I=1,20)
      READ(5,5) NC
      DO 11 I=1,NC
      READ(5,2) PC(I),TC(I),DUMMY,WM(I),W(I),DUMMY,VL(I),DEL(I),IDN(I)
      RTC = 10.7315*TC(I)
      CP = RTC/PC(I)
      CPP = CP*RTC
      SB(I) = CP*0.0982
      A1(I) = CPP*(0.25913-0.031314*W(I))
      A2(I) = CPP*(0.0249+0.15369*W(I))/TC(I)
      A3(I) = CPP*(0.2015+0.21642*W(I))*TC(I)
      A4(I) = CPP*0.042*W(I)*TC(I)**5
      C1(I) = CP*CPP* 0.059904*(1.0-W(I))*SQRT(TC(I))
      C2(I) = CP*CPP*(0.018126+0.091944*W(I))*TC(I)*TC(I)
   11 CONTINUE
      DO 16 I=1,NC
      DO 16 M=1,NC
      VR = VL(I)/VL(M)
      VRDIF = (1.0-SQRT(VR))**4/VR
      IF(IDN(I).EQ.2.OR.IDN(M).EQ.2) GO TO 12
      IF(IDN(I).EQ.3.OR.IDN(M).EQ.3) GO TO 13
      IF(IDN(I).GT.10.OR.IDN(M).GT.10) GO TO 14
      BA1 = -2.0
      BA2 = 8.6762
      BB1 = -1.3333
      BB2 = -4.0
      GO TO 15
   12 CONTINUE
      BA1 = 2.40633
      BA2 = -0.32908
      BB1 = 4.80537
      BB2 = -0.97461
      GO TO 15
   13 CONTINUE
      BA1 = 19.8416
      BA2 = -19.9182
      BB1 = 20.6178
      BB2 = -4.025
      GO TO 15
```

```
14 CONTINUE
   BA1 = -3.22944
   BA2 = 5.0836
   IF(IDN(I).GT.13.OR.IDN(J).GT.13) BA2 = 3.29426
   BB1 = 42.691
   BB2 = -3.44826
15 CONTINUE
   BINB(I,M)=BB1*VRDIF
   BINC(I,M) = BB2*VRDIF
   BINB(M,I) = BINB(I,M)
   BINC(M,I) = BINC(I,M)
   IF(IDN(I).EQ.2.OR.IDN(M).EQ.2) GO TO 17
   IF(IDN(I).EQ.3.OR.IDN(M).EQ.3) GO TO 18
   IF(IDN(I).EQ.1.OR.IDN(M).EQ.1) GO TO 18
   KA = 2
   KB = 7
   GO TO 19
17 CONTINUE
   KA = -1
   KB = -8
   GO TO 19
18 CONTINUE
   KA = 0
   KB = -5
19 CONTINUE
   BIBI      = 2.0*SQRT(TC(I)*TC(M))/(TC(I)+TC(M))
   BIA(I,M) = BIBI**KA
   BIB(I,M) = BIBI**KB
   BIC(I,M) = BIA(I,M)*SQRT(A3(I)*A3(M))
   BID(I,M) = BIB(I,M)*SQRT(A4(I)*A4(M))
   DO 16 K=1,NC
   KC = 5
   IF(IDN(I).EQ.1.OR.IDN(M).EQ.1.OR.IDN(K).EQ.1) KC = -2
   IF(IDN(I).EQ.3.OR.IDN(M).EQ.3.OR.IDN(K).EQ.3) KC = -2
   IF(IDN(I).EQ.2.OR.IDN(M).EQ.2.OR.IDN(K).EQ.2) KC = -3
   TICI =(3.*(TC(I)*TC(M)*TC(K))**.33333333/(TC(I)+TC(M)+TC(K)))**KC
   TIC(I,M,K) = TICI*(C2(I)*C2(M)*C2(K))**.33333333
16 CONTINUE
   RETURN
   END
```

(3) Subprogram for Pure Liquid Fugacity Coefficient Calculation

```
      SUBROUTINE NHULIQ
      DIMENSICN TR(10),PR(10)
      COMMON/ALL/ NC,IDN(10), WM(10),X(10),Y(10),T,P,RT,FOP(10),ACT(10),
     1PHI(10),TC(10),PC(10),W(10)
      COMMON/NHU/ B(64)
      DO 11 I=1,NC
      TR(I) = T/TC(I)
      PR(I) = P/PC(I)
      TR2 = TR(I)*TR(I)
      TR3 = TR2*TR(I)
      TR6 = TR3*TR3
      PSQ = PR(I)*PR(I)
      TPR = TR3*PSQ
      IF(TR(I).GT.1.0) GO TO 12
      IF(IDN(I).GE.3.AND.IDN(I).LE.5) GO TO 12
      M = 1
      F1 = B(M)+B(M+1)/TR(I)+B(M+2)*ALOG(TR(I))+B(M+3)*TR2+B(M+4)*TR6
     1+(B(M+5)/TR(I)+B(M+6)*ALOG(TR(I))+B(M+7)*TR2)*PR(I)-0.002584*TPR
     2-ALOG(PR(I))
      F2 = (1.-TR(I))*(8.7015-11.201/TR(I))-0.05044/TR(I)*PR(I)+
     10.002255*TPR
      GO TO 13
   12 CONTINUE
      TR6 = TR3
      TPR = TR(I)*PSQ
      M = 9
      IF(IDN(I).EQ.1) M=17
      IF(IDN(I).EQ.2) M=25
      IF(IDN(I).EQ.3) M=33
      IF(IDN(I).EQ.4) M=41
      IF(IDN(I).EQ.5) M=49
      IF(IDN(I).GE.1.AND.IDN(I).LT.4) TPR = 0.0
      F1 = B(M)+B(M+1)/TR(I)+B(M+2)*ALOG(TR(I))+B(M+3)*TR2+B(M+4)*TR6
     1+(B(M+5)/TR(I)+B(M+6)*ALOG(TR(I))+B(M+7)*TR2)*PR(I)-0.002584*TPR
     2-ALOG(PR(I))
      F2 = (1.-TR(I))*(8.7015-11.201/TR(I))-0.05044/TR(I)*PR(I)+
     10.002255*TPR
   13 CONTINUE
      FOP(I) = EXP(F1+W(I)*F2)
   11 CONTINUE
      RETURN
      END
```

(4) Subprogram for Liquid Phase Activity Coefficient Calculation

```
      SUBROUTINE ACTCOF
      DIMENSION VOLF(10),TR(10),TRM1(10),TRM2(10),TRM3(10),BINA(10,10)
      COMMON/ALL/ NC,IDN(10), WM(10),X(10),Y(10),T,P,RT,FOP(10),ACT(10),
     1PHI(10),TC(10),PC(10),W(10)
      COMMON/GAM/BA1,BA2,VL(10),DEL(10),BINB(10,10),BINC(10,10)
      VM = 0.0
      DO 18 I=1,NC
   18 TR(I) = T/TC(I)
      DO 11 I=1,NC
      TRM1(I) = 0.0
      TRM2(I) = 0.0
      TRM3(I) = 0.0
      VM = VM+X(I)*VL(I)
      DO 11 M=1,NC
      DDEL = DEL(I)-DEL(M)
      SQDI = SQRT(DEL(I))
      SQDJ = SQRT(DEL(M))
      BINA(I,M)=DDEL*DDEL+(BA1+BA2*SQRT(TR(I)*TR(M)))*SQDI*SQDJ*
     1(SQDI-SQDJ)**2
      BINA(M,I) = BINA(I,M)
   11 CONTINUE
      TRMM1 = 0.0
      TRMM2 = 0.0
      TRMM3 = 0.0
      DO 16 J=1,NC
      VOLF(J) = VL(J)*X(J)/VM
      DO 16 I=1,NC
      TRM1(I) = TRM1(I) + BINA(I,J)*VOLF(J)
      TRM2(I) = TRM2(I) + BINB(I,J)*VOLF(J)
      TRM3(I) = TRM3(I) + BINC(I,J)*X(J)
   16 CONTINUE
      DO 19 J=1,NC
      DO 19 M=J,NC
      TRMM1= TRMM1+BINA(J,M)*VOLF(J)*VOLF(M)
      TRMM2= TRMM2+BINB(J,M)*VOLF(J)*VOLF(M)
      TRMM3 = TRMM3+BINC(J,M)*X(J)*X(M)
   19 CONTINUE
      DO 17 I=1,NC
      VLVM = VL(I)/VM
      ACT(I)=EXP(VL(I)/(T*1.10389)*(TRM1(I)-TRMM1)+VLVM*TRM2(I)-(2.*VLVM
     1-1.0)*TRMM2+TRM3(I)-TRMM3)
   17 CONTINUE
      RETURN
      END
```

(5) Subprogram for Vapor Phase Fugacity Coefficient Calculation

```
      SUBROUTINE FUGVAP
      DIMENSION AX3(10),AX4(10),CX2(10),AX(10),BX(10),CX(10),F(10)
      COMMON/ALL/ NC,IDN(10), WM(10),X(10),Y(10),T,P,RT,FOP(10),ACT(10),
     1PHI(10),TC(10),PC(10),W(10)
      COMMON/FUG/ SB(10),A1(10),A2(10),A3(10),A4(10),C1(10),C2(10)
     1,BIC(10,10),BID(10,10),TIC(10,10,10)
      BS = 0.0
      AS1 = 0.0
      AS2 = 0.0
      AS3 = 0.0
      AS4 = 0.0
      CS1 = 0.0
      CS2 = 0.0
      DO 13 I=1,NC
      F(I) = Y(I)
      AX3(I) = 0.0
      AX4(I) = 0.0
      CX2(I) = 0.0
   13 CONTINUE
      DO 11 I=1,NC
      BS = BS+F(I)*SB(I)
      AS1 = AS1+F(I)*SQRT(A1(I))
      AS2 = AS2+F(I)*SQRT(A2(I))
      CS1 = CS1+F(I)*C1(I)**.33333333
      DO 11 M=1,NC
      AS3 = AS3+F(I)*F(M)*BIC(I,M)
      AS4 = AS4+F(I)*F(M)*BID(I,M)
      AX3(I) = AX3(I)+F(M)*BIC(I,M)
      AX4(I) = AX4(I)+F(M)*BID(I,M)
      DO 11 K=1,NC
      CS2 = CS2+F(I)*F(M)*F(K)*TIC(I,M,K)
      CX2(I) = CX2(I)+F(M)*F(K)*TIC(I,M,K)
   11 CONTINUE
      AS1 = AS1*AS1
      AS2 = AS2*AS2
      CS1 = CS1**3
      AS = AS1-AS2*T+AS3/T+AS4/T**5
      CS = CS1/SQRT(T)+CS2/(T*T)
C   CALCULATION OF VAPOR PHASE MOLAL VOLUME
      CALL CUBEQN(AS,BS,CS,RT,P,V)
      DO 16 I=1,NC
      BX(I) = SB(I)/BS
      ZZ = P*V/RT
      BOV = BS/V
      AX(I) = SQRT(AS1*A1(I))-SQRT(AS2*A2(I))*T+AX3(I)/T+AX4(I)/T**5
      CX(I) = CS1*(C1(I)/CS1)**.3333333/SQRT(T)+CX2(I)/(T*T)
      PHI(I) =EXP(((2.*AX(I)/BS-RT-AS*BX(I)/BS)*ALOG(1.-BOV)+(CS*BX(I)-
     11.5*CX(I))/(BS*BS)*ALOG(1.-BOV*BOV))/RT+BX(I)*(ZZ-1.)-ALOG(ZZ))
   16 CONTINUE
      RETURN
      END
```

(6) Subprogram for Molal Volume Calculation

```
      SUBROUTINE CUBEQN(A,B,C,RT,P,V)
      C1 = -RT/P
      C2 = (A-B*RT)/P-B*B
      AB = A*B
      IF(C.EQ.0.0) AB=-AB
      C3 = (AB-C)/P
      GG = (C2-C1*C1/3.0)/3.0
      FF = (2.0*C1**3/27.0-C1*C2/3.0+C3)/2.0
      TEST = FF*FF+GG**3
      IF(TEST) 11,12,13
   11 PHI = -SIGN((ARCOS(SQRT(-FF*FF/GG**3))/3.0),FF)
      Q = 2.0*SQRT(-GG)
      V1 = Q*COS(PHI)
      V2 = Q*COS(PHI+2.0944)
      V3 = Q*COS(PHI+4.18879)
      V = AMAX1(V1,V2,V3)
      GO TO 15
   12 V = 0.0
      GO TO 15
   13 AA = SQRT(TEST)-FF
      BB = -AA-2.0*FF
      CAA = SIGN((ABS(AA)**.3333333),AA)
      CBB = SIGN((ABS(BB)**.3333333),BB)
      V = CAA+CBB
   15 V = V-C1/3.0
      RETURN
      END
//GO.SYSIN DD *
```

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