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ACTIVITY COEFFICIENTS OF GASES IN BINARY MIXTURES

BY

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A THESIS
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ABSTRACT

Engleman, John G. - Activity Coefficients of Gases in
Binary Mixtures, Calculated by the Methods
of Joffe, of Edmister and Ruby, and of
Redlich et al. - Thesis, submitted to
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The theory and usefulness of vapor phase activity coefficients have been developed. The equations, charts and calculation procedures to be used for the three methods are included with a set of sample calculations in their most convenient form.

Activity coefficients for 236 experimental points have been calculated by the three methods for both components of four binary gaseous systems. These systems are Argon - Ethylene (36 points), Hydrogen - Nitrogen (32 points), Methane - Ethane (112 points) and Methane - n Butane (56 points). Wide ranges of pressure, temperature and mol fraction are included.

The % deviations of calculated from experimental activity coefficients have been determined. From these deviations and a time study, the general and specific utilities of the three methods have been estimated.

Results indicate that the method of Redlich et al is of greatest all-round utility. It is applicable to all substances and conditions tested herein, and its overall accuracy is superior to the other two methods.

The method of Edmister and Ruby takes only 1/3 the time but appears to be limited to the light hydrocarbons for which it was derived. Its accuracy is generally the equal of that obtainable by Redlich's method. The method of Joffe takes 20% longer than that of Redlich et al, and while also of all round utility, seldom approaches it or the method of Edmister and Ruby in accuracy.

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________________

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NEWARK, NEW JERSEY

JUNE, 1956

PREFACE

The methods of Joffe, Edmister and Ruby, and Redlich et al for predicting vapor activity coefficients for components of a gaseous mixture from pressure, temperature and composition data were applied to four systems for which experimental values were available in the literature.

ACKNOWLEDGEMENTS

I would hereby like to acknowledge and express my appreciation to -

Dr. Joseph Joffe, who suggested the topic and helped immeasurably through his timely assistance and advice.

Dr. Otto Redlich who furnished data from which time saving charts could be plotted.

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INTRODUCTION

The fugacities of components of gaseous mixtures are useful in studying chemical equilibria and phase composition. While this property may be determined experimentally for each component from mixture P-V-T-composition data, thermodynamic methods for prediction have great utility where experimental data are not available, or for extrapolation and interpolation.

A basic thermodynamic approach is the Lewis and Randall Rule for Fugacity, based on the law of additive volumes. It states that the fugacity of a component is equal to the product of the fugacity of the pure component at system temperature and pressure times its mol fraction. However, this rule loses accuracy as pressure increases, and more advanced methods are required.

Three such methods have been selected for evaluation in four binary gaseous systems for which experimental values of component fugacities have been determined (9, 17, 21, 23). Both the experimental and predicted results are presented in the form of activity coefficients rather than fugacities (Tables 13-45). The activity coefficient is defined as a component's fugacity divided by the system pressure and component mol fraction. (Eq. 1)

$$\phi_{n} = fn/Py_{n} \qquad \text{(Eq. 1)}$$

Before discussing the three methods of calculation tested in this paper, further background on the utility of fugacities and activity coefficients is in order. Component fugacities can be used to predict the

Thermodynamic equilibrium constant K_f for gaseous reactions as defined by the relationship

$$K_f = \frac{(f_3)\,(f_4)}{(f_1)\,(f_2)} \qquad \text{(Eq. 2)}$$

which is based on the typical reaction $1 + 2 = 3 + 4$. This was done by Joffe in his paper (15). Also, activity coefficients for each component in each of the coexisting phases can be used to predict K'-values (vaporization equilibrium constants) for each component in vapor-liquid systems. Existing correlations for predicting component K values (vaporization ratios) directly without the intermediate calculation of activity coefficients for each phase are valuable, but it is the feeling of the authors of (7) and (19) that the more basic approach described below is preferable.

It is felt that the value of thermodynamic analysis lies in extending easily obtained experimental values for binary mixtures near atmospheric pressure to multi-component systems at higher or reduced pressures. A vapor phase activity coefficient for each component and another activity coefficient for each component in the liquid phase would be the most useful forms of fundamental data, free from the limitations of the original experiment. The activity coefficient of the vapor would reflect only the properties of the vapor phase and would not depend on the liquid phase, and conversely. Each could be manipulated to give partial thermodynamic properties of the components in both phases, and could be combined to yield K'-values. (See Equation 5) Correlations of K-values, while valuable for predicting phase equilibria, have the disadvantage that they cannot yield activity coefficients for either phase and thus cannot predict partial thermodynamic properties. The vaporization ratio K for a component of a mixture is defined as the ratio of its mol fraction in the vapor phase to its mol fraction in the liquid phase.

$$K_n = y_n/x_n \qquad \text{(Eq. 3)}$$

Since the coexisting phases are in equilibrium when $f_l = f_v$, f_l and f_v

$$K_n = \frac{f_{nv}/\ x_n}{f_{nl}/y_n} \qquad \text{(Eq. 4)}$$

can be calculated from P-V-T- composition data on mixtures, using thermodynamic relationships and an equation of state. Values of y_n and x_n are obtained from vapor-liquid equilibrium data.

For correlation purposes a vaporization equilibrium constant K' is defined by Equation (5) for a given component (subscript n omitted).

$$K' = \left[\frac{f_l/P'\ x}{f_v/P_y}\right] \left[\frac{P'}{P}\right] \qquad \text{(Eq. 5)}$$

In Equation (5), f_l/P'_x is the activity coefficient of the component in the liquid phase and f_v/P_y is its activity coefficient in the vapor phase. P'/P is the Raoult's Law K-value, which is defined as the vapor pressure of a component at temperature T, divided by the total system pressure at that temperature. The denominator of each activity coefficient may be considered its standard reference state. For the liquid phase this will be the partial vapor pressure (Raoult's Law) and for the vapor the partial pressure (Dalton's Law). These choices of standard state are logical and convenient since the ratio of activity coefficients is then a correction term for the Raoult's Law K-value, P'/P.

Serious attempts have been made to achieve prediction of K'-values by first predicting an activity coefficient for each phase. Among other investigators, Edmister and Ruby (7) and Redlich et al (19) have presented methods for this evaluation. Their liquid phase calculations are not discussed since this paper is limited to an evaluation of gas phase activity coefficients. Nevertheless it should be kept in mind that the ultimate intention of (7) and (19) in their papers is to successfully predict K'. This paper is to determine the applicability of their vapor phase correlations to prediction of component activity coefficients in the four purely gaseous systems. A brief check of the vapor correlation on the two two-phase systems is undertaken only parenthetically. Multicomponent systems have been omitted from this paper due to its limited scope.

The four gaseous systems selected are listed below, with the designation used to indicate each in the balance of this paper.

A. Argon - Ethylene (9) -- System A - E
B. Hydrogen - Nitrogen (17) -- System H - N
C. Methane - Ethane (23) -- System M - E
D. Methane - n - Butane(21) -- System M - B

The three methods used for predicting activity coefficients are listed below, with the designation used to indicate each in the balance of this paper.

A. Method of Joffe (15) - Method 1
B. Method of Edmister and Ruby (7) - Method 2
C. Method of Redlich, Kister and Turnquist (19) - Method 3

The experimental values were determined by the authors of the reference articles in basically the same fashion for each of the four systems. The total or specific volume of gaseous mixture was measured and from this the partial volume of each component calculated. By graphical intergration of this or another partial property with respect to system pressure, the free energy, fugacity or activity coefficient of a component was determined. Free energy was converted to fugacity by the relationship.

$$\log f_n = F_n/2.303\ RT \qquad \text{(Eq. 6)}$$

Variations and combinations of the above procedures were used by the authors of the four sources of data, in each case utilizing experimental P - V - T - composition data. The volumetric data of Masson and Dolley (16) was converted to component free energies by Gibson and Sosnick (9) for system A - E. The volumetric data of Bartlett (2) were converted to fugacities by Merz and Whittaker (17) for system H - N. Sage and co-workers performed all experiments and calculations to report fugacities for systems M - E (23) and M - B (21).

Data were found in the literature for several systems experimentally determined in the two-phase or vapor-liquid regions. Smoothed P - V - T - composition values and activity coefficients for Ethane - Ethylene vapor-liquid equilibria were reported in (10) and vapor fugacities were calculated in the conventional manner from volumetric data of York (26) and of Barkelow et al (1). The other system was that of Methane and n-Butane in the two phase region (22), with the vapor fugacities established using some unpublished data. These two systems have been segregated from the four purely gaseous systems.

Only limited calculations on these systems have been made in the present study by the three methods, in view of the disappointing results, and will be found labeled System "(E - E)" v-1 for Ethane-Ethylene and System "(M - B)" v-1 for Methane - n Butane.

Methods 1, 2 and 3 have been applied to 255 points in the six systems. Joffe's Method 1 which is applicable only to gaseous mixtures, and the vapor correlation of (7) and (19), Methods 2 and 3 respectively, are briefly described below.

Method 1 involves determining a fugacity for the mixture based on generalized charts and Kay's molal pseudoreduced relationships for mixtures. The fugacity of a component is calculated by applying two correction terms to f_m in equation 8, found on page 10.
Each is based on the deviation of the component's critical constants from the pseudo-critical constants of the mixture, and on the magnitude of the mixture's compressibility factor and enthalpy correction due to pressure. Z_m and $\Delta H/T_{cm}$ are read from generalized charts at the pseudoreduced mixture properties, as is the value of f_m.

Method 2 has as its basis the fugacity values of Benedict et al (3) for twelve light hydrocarbons, at pressures of up to 3600 psi. These were given in (3) on some 276 charts. Edmister and Ruby (7) have reduced the number of charts to six, based on a generalized correlation giving vapor and liquid activity coefficients as functions of T_{rn}, P_{rn} and b_{rn} (reduced boiling point). The use of boiling point as a parameter may be considered as taking into account the effects of molecule size.

For mixtures other than the twelve light hydrocarbons, such as napthenes or aromatics, application of an unspecified correction for differences in molecular character is recommended (7). A special chart is provided for Methane vapor and another for Methane liquid. Only the three charts applicable to vapors are used in this paper.

Method 3 is taken from the paper of Redlich et al (19), in which may be found an excellent presentation concerning liquid activity coefficients. The present paper, however, treats only the vapor phase procedure, described next.

Instead of employing the Benedict equation of state which requires fairly extensive data on pure substances, and somewhat lengthy calculations, some accuracy was sacrificed to minimize calculations and data requirements by utilizing an approximate equation of state (20).

$$P = \frac{RT}{(v - b)} - \frac{a}{V(v + b)(T)^{0.5}} \qquad \text{(Eq. 7)}$$

Where experimental data exist for a specific case the authors (20) indicate that insertion of this data into Equation (7) will lead to improved accuracy for calculations based on this equation. A number of relationships and a subsequent calculation procedure have been developed from it, including a set of specialized generalized-type charts.

The calculation procedure involves use of generalized charts as by Method 1, special charts having been developed specifically for this application by Redlich et al. While the accuracy of Methods 1 and 3 is limited by the failure of the theory of corresponding states, this limit is closely approached by both methods. It is stated in (19) that Method

3 has several practical advantages over Method 1, which this paper will attempt to evaluate. They are:

A. Consistency is automatically insured by algebraic derivation from an equation of the Equation (7) type. Suitable correction terms may be introduced where experimental P-V-T- composition data are available.

B. Calculation of pseudoreduced quantities by linear combination is not entirely satisfactory, while the combination proposed by Joffe (15) leads to fairly complicated calculations.

(Note: This latter proposal was not used with Method 1 in this paper - linear combination was utilized).

C. With the usual generalized charts, including the chart for Z, an appreciable error in interpolation with respect to T_r is difficult to avoid because the functions are far from linear in T_r. They are however, roughly linear in A^2/B(Method 3 parameter), so that interpolation on the special charts entails a minimum loss of accuracy.

The equations and calculation procedures for Methods 1, 2, and 3 are described in detail later in this paper.

It should be noted in conclusion that several other methods of predicting vapor and liquid activity coefficients are available but not utilized in this paper.

De Priester (5) has improved the Kellogg correlation charts and reduced them in number to 24, 12 for vapors and 12 for liquids. Each pair applies to one of twelve light paraffin and olefin hydrocarbons through N-Heptane. For a particular hydrocarbon, as part of a mixture, its activity coefficient in each phase is obtained by locating a point on the proper charts for the system temperature, pressure and molal average atmospheric boiling point. This method is claimed to have a somewhat lower percentage error than the Kellogg charts. It was by-passed for this paper since its charts would not be strictly applicable to the A-E and H-N systems. Although Method (2) is also based on the same 12 hydrocarbons, it was thought that its more generalized nature would make it applicable to other substances as well.

Smith and Watson (24) have developed a method which is basically a graphical form of the method of Gamson and Watson (8). This latter method has as its basis a relationship similar to that of Method 1, but with an empirical correction factor to make it agree with data on light hydrocarbon systems. Bennett (4) tested the method of Watson and Smith (and several others), and logically recommends that it be used only to predict vapor-liquid equilibria for these hydrocarbons, which rules it out for use in the present paper.

EQUATIONS AND CALCULATION PROCEDURES

Method 1

Method 1 has as its basis Equation (8), derived by Joffe in his paper (15)

$$\log (f_n/y_n) = \log f_m + (T_{cm} - T_{cn})\left(\Delta H/T_{cm}\right) / _{2.303\ RT}$$

$$+ (P_{cm} - P_{cn})\ (Z_m - 1) / _{2.303\ P_{cm}} \qquad \text{(Eq. 8)}$$

To evaluate the various terms of Equation (8) it is first necessary to calculate the pseudoreduced properties of the gaseous mixture, using Kay's relations (Equations 9, 10, 11 and 12).

$$T_{cm} = \text{Summation } (T_{cn}\ y_n) \qquad \text{(Eq. 9)}$$

$$P_{cm} = \text{Summation } (P_{cn}\ y_n) \qquad \text{(Eq. 10)}$$

$$T_{rm} = T/T_{cm} \qquad \text{(Eq. 11)}$$

$$P_{rm} = P/P_{cm} \qquad \text{(Eq. 12)}$$

These pseudoreduced properties are used to evaluate V_m, Z_m and $\Delta H/T_{cm}$ from three generalized charts. Table 49 lists the references in which the various charts used in this paper may be found, and indicates the parameter ranges covered.

V_m is plotted as a function (T_{rm}, P_{rm})

Z_m is plotted as a function (T_{rm}, P_{rm})

$\Delta H/T_{cm}$ is plotted as a function (T_{rm}, P_{rm})

With these properties Equation (8) may be evaluated. V_m is converted to f_m by Equation (13).

$$f_m = V_m P \qquad \text{(Eq. 13)}$$

To obtain the precision possible for Method 1 it is necessary to read the values of V_m and $\Delta H/T_{cm}$ very carefully from the respective charts, and to use logarithms in calculating the temperature "correction term" (11). Note that the antilogarithm of the left side of Equation (8) must be divided by P to obtain the activity coefficient .

The evaluation of Equation (8) for each component will utilize the same values of V_m, Z_m and $\Delta H/T_{cm}$. The $(T_{cm}-T_{cn})$ and $(P_{cm}-P_{cn})$ terms, however, will differ in both sign and magnitude from one component to the other, and the values of $\log (f_n/y_n)$ can differ radically.

<u>Method 2</u>

Three special charts developed by Edmister and Ruby (7) are required for Method 2. These, plus three charts used in calculating activity coefficients for liquids, may be obtained for $1.35 and in 8½" x 11" size from:

A. D. I. Auxiliary Publications
Photoduplication Service
Library of Congress
Washington, D. C.

Figures (1) (2) and (3) of Reference 7 apply to vapors and were used in this paper. Figures (4) (5) and (6) of Reference 7 would be used for liquids. The parameters for both phases are the same and defined by Equations (14) (15) and (16).

$$T_{rn} = T/T_{cn} \qquad \text{(Eq. 14)}$$

$$P_{rn} = P/P_{cn} \qquad \text{(Eq. 15)}$$

$$b_{rn} = b_m/b_n = \frac{\text{mol. ave, atmos. B. P. of mixt.}}{\text{atmos. B. P. of comp. "n"}} \qquad \text{(Eq. 16)}$$

An intermediate parameter Θ_n is used to relate the two charts to evaluate ϕ_n for either phase. Aside from the calculations by Equations (14) (15) and (16), Method 2 is completely a matter of locating one point on each of two charts. A description of Figures (1), (2) and (3) is found below. The parameter ranges covered on these charts are listed in Table 50.

Figure (1) has b_{rn} as its ordinate and T_{rn} as abscissa (see Fig. 1, this paper). Θ_n^V is read by interpolation between lines of constant Θ_n^V. It is ued for vapors of light paraffins and olefins other than Methane, and it is hoped, for other substances judged to possess thermodynamic properties quite different from those of Methane.

Figure (2) differs from Figure (1) only in the shape and distribution of the lines of constant Θ_n^V. It is used exclusively for Methane vapors and, it is hoped, for other non-paraffin, non-olefins judged to have thermodynamic properties similar to Methane's. This latter type of substance is exemplified in this paper by Argon.

Figure (3) (see Fig. 3, this paper) has P_{rn} as abscissa and has lines of Θ_n^V in the manner of Figures (1) and (2). ϕ_n is read directly as the ordinate, using a value of Θ_n^V obtained from either Figure (1) or (2).

This procedure of calculating T_{rn}, P_{rn} and B_{rn}, reading Θ_n^V from Figure (1) or (2), and reading ϕ_n from Figure (3), is carried out for each component.

Method 3

Method 3 has as its basis generalized-type relationships and parameters derived by Redlich et al (19) from Equation (7).

$$P = \frac{RT}{(v - b_o)} - \frac{a}{V(v + b_o)\,(T)^{0.5}} \qquad \text{(Eq. 7)}$$

The constants a and b of Equation (7) are defined as follows for a pure gas:

$$a = 0.4278\ R^2\ (T_c)^{2.5}/P_c \qquad \text{(Eq. 17)}$$

$$b_o = 0.0867\ R\ T_c/P_c \qquad \text{(Eq. 18)}$$

Further definitions for a pure gas:

$$A^2 = a/R^2T^{2.5} \qquad \text{(Eq. 19)}$$

$$B = b/RT \qquad \text{(Eq. 20)}$$

$$Z = PV/RT \qquad \text{(Eq. 21)}$$

For a gaseous mixture, the derived parameters are defined as:

$$A_n = 0.6541\ T_{cn}^{1.25}/\ T^{1.25}\ P_{cn}^{0.5} \qquad \text{(Eq. 22)}$$

$$B_n = 0.0867\ T_{cn}/\ T\ P_{cn} \qquad \text{(Eq. 23)}$$

$$A = \text{Summation}\ (A_n\ y_n) \qquad \text{(Eq. 24)}$$

$$B = \text{Summation}\ (B_n\ y_n) \qquad \text{(Eq. 25)}$$

Using the results of Equations (24) and (25) the quantities A^2/B and BP are calculated. These are used to evaluate three secondary parameters, either by calculation from Equations (26), (27) and (28) or from three charts appearing in (19) as Figures (15), (16) and (17) (see Figures 4, 5 and 6, this paper). The three secondary parameters and their defining equations are:

$$\log \bar{\phi} = 0.4343\ (Z_m - 1) - \log\ (Z_m - BP) - A^2/B\ \log\ (1 + BP/Z_m) \qquad \text{(Eq. 26)}$$

$$u = 2\ A^2/B\ \log\ (1 + BP/Z_m) \qquad \text{(Eq. 27)}$$

$$w = 0.4343\ (Z_m - 1) + A^2/B\ \log\ (1 + BP/Z_m) \qquad \text{(Eq. 28)}$$

These three secondary parameters and values from Equations (22), (23), (24) and (25) are now inserted into Equation (29) which yields the desired vapor activity coefficient.

$$\log \phi_n = \log \bar{\phi} - u\,(A_n/A - 1) + w\,(B_n/B - 1) \qquad \text{(Eq. 29)}$$

In Equation (29) it is interesting to note that only the quantities A_n and B_n are properties of component "n", all other quantities (save the constant 1) being mixture properties.

If fairly extensive calculations are to be carried out using Method 3 it is recommended that the charts be used for evaluating $\log \bar{\phi}$, u and w, as a time-saving measure. Unfortunately, Figures (14), (15) and (16) of (9) are not available commercially at present. However, they may be plotted from data which will be supplied on request by Dr. O. Redlich, whose current address is:

704 Keeler Avenue
Berkeley 8, California

From Figures (4), (5) and (6) of this paper it can be seen that BP is the abscissa and A^2/B is plotted as a parameter for each of the three charts, with the secondary parameters as the ordinates. If these charts are not plotted and used it will be necessary to determine Z_m to evaluate Equations (26), (27) and (28). This may be done as for Method 1, or preferably by plotting Z_m as ordinates with BP as abscissa and A^2/B parameters. Data for this chart are included in Dr. Redlich's transmittal, and take the general form shown in Figure (7) of this paper.

RESULTS (GENERAL)

Activity coefficients for 236 experimental points have been calculated by three methods for both components of four binary gaseous systems. These calculated values are found along with the experimental values in Tables 13 through 43.

The % deviations of calculated from experimental values have been determined and are presented in Tables 1 through 12. These deviations are grouped by pressure, and the trends of the deviations indicated (% positive). From these % deviations and a time study, the general and specific merits of the three methods have been estimated, and are discussed under "General Conclusions" and "Specific Results", respectively. Also, the value of certain corrections and alternate procedures has been tested for Methods 1 and 3 on a limited scale, and results are presented under "Refinements".

Calculated and experimental data for 19 points selected from two vapor - liquid systems are presented to indicate the unfortunately large deviations occurring (Tables 44 and 45). These data are discussed at the end of the section entitled "Specific Results".

CONCLUSIONS (GENERAL)

These are based on the % deviation reported in Tables 1 through 12 and on a time evaluation performed on the M-B calculations, reported under "Specific Results".

Method 3 is in all cases the most accurate, and has no practical limits on severity of reduced conditions. (See tables 48 and 51). It may be used with all types of gases tested. It requires roughly triple the time of Method 2, 5/6 the time of Method 1.

Method 2 provides an accurate, rapid calculation for light hydrocarbons, but it appears doubtful that it can or should be used with other gaseous substances or for severe reduced conditions. It is slightly less accurate than Method 3 for Methane in Systems M-E and M-B and for Butane above 100 atm. Its limits on reduced conditions are found in Table 50.

Method 1 is the most time-consuming, and due to doubtful accuracy and unavoidable poor precision in reading generalized charts for $\Delta H/T_c$ and V at severe or even moderate conditions, is the least accurate. It may be used for any gaseous substances under any practical reduced conditions (Table 49), but is less accurate than Method 3 in all cases, although taking 20% longer.

As can be seen from Table 49, a number of generalized charts are necessary to apply Method 1 to various systems. Selection is based on matching parameter ranges of the system and charts, and on experience as to which chart will lead to a minimum of error.

The relative utilities of the three methods logically seem to be functions of their chronological appearance and their theoretical and empirical aspects.

Method 1 appeared in 1948 with its contribution being the special thermodynamic relationship derived by Joffe. To evaluate this equation (Eq. 8) it is necessary to use values read from three generalized charts, each having been in existence for some years and primarily intended for other more basic applications. For moderate and severe reduced conditions their admitted poor precision is included in the evaluation of Equation 8, in not one but three places, namely Z, V, and $\Delta H/T_c$, and sizeable errors may be expected.

Method 2 was published in 1955 and is based on extensive correlations of experimental data for twelve light hydrocarbons. IBM facilities were used for tabulations and calculations needed to condense over one hundred specific vapor charts to the three general ones used in the present paper. Boiling point was added to temperature and pressure as a third reduced property to serve as parameters.

Method 3 appeared in 1952. The inherent shortcomings of generalized correlations were critically examined by the authors, and their complex set of equations, parameters and charts developed from extensive literature experimental data. These developments were designed to minimize generalized shortcomings, and include making linear interpolation possible over all ranges.

To summarize, Method 1 is an early attempt to use existing generalized charts by means of a special thermodynamic relationship. Method 2 is the result of a most recent condensation of experimental data for twelve light hydrocarbons. Method 3 is a recent combination of a new concept of generalized correlations based on experimental data for a variety of substances.

It appears that the advantages claimed for Method 3 in the "Introduction" have been verified. Further, the value of each method for calculating gaseous activity coefficients appears to be proportional to the complexity and scope of the original work done by the respective authors.

RESULTS (SPECIFIC)

A. Time Required for Each Method

To establish these data a record was kept of the hours required to calculate activity coefficients of 56 points for the M-B system, starting with P, T and y data. Since this system was the last to be calculated and had a large number of points, time per point benefited from both experience and from economies of mass production. For calculations by those not as familiar with the procedures it is believed that while the relative times of each method would remain essentially the same, the actual time per point would increase.

Method 1.	$9\frac{1}{2}$ hours	10.2 min./point	3.45 times longer than Method 2
2.	2 3/4 hours	3.0 min./point	1.0
3.	8 hours	8.6 min./point	2.9 times longer than Method 2

B. Severity of Reduced Conditions for Each System

By reference to Tables 46 through 51 it is possible to determine the approach to chart limits of reduced conditions and derived parameters for each system by each method. Mild conditions may be normally expected to lead to small errors, while systems near chart limits (severe conditions) will usually involve higher errors by calculation. Generalizations as to parameter severity encountered in each system are found below.

1. A - E. For Methods 1 and 3 only some values of $\Delta H/T_{cm}$ could be considered severe. Results should be good. Method 2 shows mild conditions, but use of the Methane Chart for Argon is an experiment of unpredictable accuracy.

2. H - N. Very severe conditions for Method 1 with the exception of $\Delta H/T_{cm}$. Method 2 not applicable - T_r, P_r and b_r all off charts. Method 3 has high B.P. values, but other parameters are low. Low errors may be anticipated for Method 3.

3. M - E. Moderate to severe V_m and $\Delta H/T_{cm}$ values for Method 1. Up to moderate parameter values for Method 2. Fairly severe log $\bar{\phi}$ and u values over limited range for Method 3. Overall high accuracy may be expected from Methods 2 and 3.

4. M - B. Slightly more severe V_m and $\Delta H/T_{cm}$ values than M - E for Method 1. MOderate to severe Method 2 parameter values. Method 3 parameters approximate most severe M - E parameters. Methods 2 and 3 should be only slightly less accurate than for M - E.

C. Results by System

Several generalizations concerning the effects of mol fraction and pressure on % deviation can be made.

1. The lower a component's mol fraction the greater will be its deviation from an activity coefficient of 1.0.
2. The higher the system pressure (and in some cases the lower its temperature) the greater will be the deviation from $\phi = 1.0$.
3. The greater ϕ's deviation from 1.0 the greater will be the % of deviation of calculated from experimental values. This effect is reduced when ϕ is greater than 1.0 but will be greatly exaggerated by % deviation for values of ϕ approaching 0.0, since % deviation is calculated by dividing the error by the experimental value.

If, for example, the experimental value of ϕ is 0.1, and by calculation is 0.11 (an error of 0.01), % deviation = $+$ 10%. This effect, primarily due to high Methane mol fractions, is responsible for the excessive % deviation reported for Butane in System M - B.

Several generalizations may also be made regarding Method 1.

When the % deviations of one component are opposite in sign to those of the other it may be assumed that the correction terms are too large or too small. Since the pressure correction term is seldom appreciable the $\Delta H/T_{cm}$ value read from the chart is probably at fault.

When the % deviations of both components have the same sign, the probable cause is the value of V_m read from a chart.

A slight error in reading V_m and $\Delta H/T_{cm}$ chart values can lead to an appreciable error in ϕ. This factor and the failure of the theory of corresponding states can lead to large errors under severe conditions.

The slight improvement in % deviation for System A - E over Joffe's values (15) are probably due to use of the most recent $\Delta H/T_{cm}$ chart from (6).

Where two or more of the methods give % deviations of the same sign it may be assumed that all include the same generalized error or that experimental results may be at fault.

The Results by System

1. System A - E. % deviations by all methods are very low. This

is due to fairly low pressures and a symmetrical mol fraction pattern of 0.2, 0.4, 0.6, 0.8. The use of Fig. 2 (Methane Vapors) in Method 2 to determine Θ^V for Argon gives much better results than the use of Fig. 1, but is still a poor approximation. The error for Ethylene by Method 2, however, is lowest, indicating that a hydrocarbon component may possibly be calculated accurately in the presence of a non-hydrocarbon by Method 2. Deviations by Methods 1 and 2 are generally positive, and are generally negative by Method 3.

2. System H - N. Experimental values of ϕ ranging up to 2.3 and 2.1 for the two components represent very severe tests for the calculation methods. Excessively high pressures are encountered. A symmetrical mol fraction pattern of 0.2, 0.4, 0.6, 0.8 minimizes the % deviation effects described at the beginning of this section.

Method 1 is relatively hopeless until the pseudocritical constants of Newton (18) are used as described later under "Refinements". Excellent results for all pressures below 800 atmospheres are obtained by the Newton refinement, especially for Hydrogen. However, even these values are in much greater error than those obtained by Method 3, which gives surprising accuracy up to and including 1000 atmospheres. It is interesting that the use of Newton's pseudocritical constants for Method 3 actually decreased its accuracy, most markedly in the case of Hydrogen. Since Newton's refinement involves revising Hydrogen's critical properties it is not surprising that this component surfered or gained the most through its use.

Deviations by Method 1 are generally positive and by Method 3 generally negative. Method 2 cannot be tested on System H - N since all chart parameters are widely exceeded due to the very low critical constants and boiling points of Hydrogen and Nitrogen.

3. System M - E, -- 112 points

A fairly symmetrical pattern of Methane mol fractions of 0.32, 0.56, 0.74 and 0.88 and rather high pressures (4 of 7 over 100 atmos) give rise to large % deviations. ϕ for Ethane dips as low as 0.2 at 0.32 mol fraction Methane.

Method 1 gives % deviations for Methane which are much higher, and % deviations for Ethane which are only slightly higher, than those calculated by Methods 2 and 3. % deviations are positive for Methane and negative for Ethane by all methods, with the exception of $y_m = 0.882$, where % deviations for Ethane also become positive. Method 2 is optimum for calculating M - E System activity coefficients.

4. System M - B -- 56 points

Due to the nature of the system, single phase gaseous data must be taken at high Methane mol fractions, which averages 0.81 for points calculated. This factor and fairly high pressures yield Butane activity coefficients as low as 0.06. % deviations for Butane are therefore extremely high while Methane gives very low ones. Another contributing factor to this situation may be the wide difference in the critical properties and boiling points of Methane and Butane.

Methods 1 and 2 give results for Methane which are comparable and contain a greater error than those of Method 3. Method 1 gives a consistently higher error for Butane. Method 2 keeps pace with Method 3 for Butane except for pressures over 125 atm, particularly at temperatures below 100° C.

% deviations for Butane are positive for all methods. Methane % deviations are generally positive also.

D. $(E - E)_{vL}$ and $(M - B)_{vL}$ System Results

Calculated and experimental ϕ values are presented in Tables 44 and 45. % deviations have not been calculated. The data on System $(E - E)_{vL}$ indicate that Methods 1, 2 and 3 check each other very closely but do not check the experimental values for either component. From Table 46 it can be seen that reduced properties are all below 1.0, definitely a contributing factor to the large discrepancy.

For System $(M - B)_{vL}$ Methods 1 and 2 check each other fairly well, but except for either extreme of pressure, do not check experimental values. Calculations have not been performed by Method 3. Values for Methane are not greatly out of line but show a continuous trend below experimental. Values for Butane, on the other hand, are consistently much higher than experimental values.

These discouraging results, while very, very limited in scope, raise a question as to the value of Methods 2 and 3 for calculating K' values from an activity coefficient calculated for each phase.

REFINEMENTS

A. Method 1

1. In applying relationships based on generalized correlations to Hydrogen and Helium, better agreement (18) with experimental values is obtained by using modified reduced conditions calculated from the equations: $T_r = T/(T_c + 8)$ and $P_r = P/(P_c + 8)$

where $T = {}^{\circ}K$ and $P = \text{atmos.}$

In the work reported herein, System H - N has been evaluated by Methods 1 and 3, first by using the exact values for Hydrogen, $P_c = 12.8$ and $T_c = 33.3$, and next by taking the proposed pseudocritical values of $P_c = 12.8 + 8 = 20.8$, and $T_c = 33.3 + 8 = 41.3$. Results by the latter method are listed in Tables 3 and 17 through 24 under "H - N pseudo". As noted earlier, this revision helped Method 1 accuracy but decreased it for Method 3.

2. York and Weber (27) have proposed a correction factor to be applied to the $\Delta H/T_{cm}$ pressure correction read from generalized charts. It is limited to a range of T_r of from 1.0 to 1.6, and is determined from the relationship $\delta = (T_c/370)^n$, where n is a function of T_r. In this paper a modification by Hougen and Watson (12) has been adopted, with their values of n shown in Table 53 as applied to their relationship $\delta = (T_c/470)^n$. To test its effect on results calculated by Method 1 it has been applied to 56 points in System M - E for y_m - 0.319, and 0.555, where T_{rm} lies between 1.0 and 1.6.

Table 54 presents δ correction factors for System M - E. Tables 55 through 62 give a detailed listing of activity coefficients calculated with and without the ϕ correction. Table 63 summarizes % deviations with and without the correction. It can be seen that use of the correction factor improves accuracy 25% for Methane and 35% for Ethane.

It thus appears that if Method 1 must be used rather than Methods 2 or 3, the expenditure of time in calculating the correction is probably justified by the increased accuracy.

B. Method 3

As indicated in the "Equations and Calculation Procedure" section, the use of Figs. 4, 5 and 6 may be omitted for evaluating log $\bar{\Phi}$, u and w, and these quantities calculated from Equations (26), (27) and (28).

These equations have been used to test activity coefficients evaluated using the charts. 21 points in System A - E and 20 points in System H - N evaluated by each procedure show that use of the equations gives a net improvement in accuracy of 0.2 % deviation units. This is a negligible increase for the time expended, and charts are greatly to be preferred whenever a sufficiently large number of calculations will be made to justify plotting them.

APPENDIX

SAMPLE CALCULATIONS

A point has been selected at random from the M-E system to illustrate in detail use of the equations and charts required by Methods 1, 2 and 3.

The data found in the literature (23) :

T = 130° F	wt fraction Methane = 0.2
P = 2750 psia	f/yP - Methane = 0.958
	- Ethane = 0.372

Wt. fraction is converted to mol fraction - 0.319

Changing units for T and P,

T becomes 327.6 degrees Kelvin

P becomes 187.22 atmospheres

With only these three defining properties it is possible to calculate the activity coefficient of each component by the three methods. A vertical tabular form of calculation proved efficient for evaluating the various quantities involved. The symbols evaluated are listed below at the far left in the exact vertical order used throughout the calculations. The table, chart or formula used for evaluation is shown to the right of the symbol, followed by numerical substitutions where indicated. The numerical value of the symbol is found at the extreme right.

Before work can begin on this tabulation, (14) or another suitable source is consulted for component critical properties and boiling point. For this system -

	T_{cn} (°K)	P_{cn} (atm)	b (°K)
Methane	190.7	45.8	111.8
Ethane	305.3	48.8	184.9

Methane will be referred to as component 1 in subscripts, Ethane as 2.

THE TABULATION

Method 1

General

T_{cm}	Summation$(T_{cn}y_n)$	(190.7) (0.319) + (305.3) (0.681)	268.7 °K
P_{cm}	Summation$(P_{cn}yn)$	(45.8) (0.319) + (48.8) (0.681)	47.84 atm.
P	System Property		187.22 atm.
T	System property		327.6 °K
T_{rm}	T/T_{cm}	327.6/268.7	1.219
P_{rm}	P/P_{cm}	187.22/47.84	3.916
$P_{cm} - P_{c1}$		47.84 - 45.8	2.04 atm.
Z_m	Gen. Compress Chart	(25) P. 108 Fig. 3	0.624
$Z_m - 1$		0.624 - 1.000	−0.376
$(P_{cm}-P_{c1})/2.303\ P_{cm}$		2.04/(2.303) (47.84)	0.01854
$T_{cm} - T_{c1}$		268.7 - 190.7	78.0°K
$(T_{cm} - T_{c1})/2.303\ RT$		78/(2.303) (1.987) (327.6)	0.0580
$\Delta H/T_{cm}$	Generalized Chart	(6) P. 140 Fig. 48	5.75
V_m	Generalized Chart	(13) Fig. 142	0.493
f_m	$V_m\ P$	0.493 x 187.22	92.31 atm.
$\log f_m$	(11), or any log tables		1.96525

Temp. corrn	$\left[(T_{cm} - T_{c1})/2.303\ RT\right]\left[\Delta H/T_{cm}\right]$	(.0580) (5.75)	0.33365
Sum of two previous lines		1.96525 + 0.33365	2.29890
Press. corrn	$\left[(P_{cm} - P_{c1})/2.303\ P_{cm}\right]\ (Z_m - 1)$	(0.01854) (- 0.376)	-0.00698
log (f_1/y_1)	Sum of two previous lines	2.29890 - 0.00698	2.29192
f_1/y_1		Antilog (2.29192)	195.85
ϕ_1	f_1/y_1P	195.85/187.22	1.047
$P_{cm} - P_{c2}$		47.84 - 48.8	-0.96 atm
$T_{cm} - T_{c2}$		268.7 - 305.3	- 36.6°K
$T_{cm} - T_{c2}/2.303\ RT$		(-736.6/(2.303) (1.987) (327.6)	-0.0272
$P_{cm} - P_{c2}/2.303\ P_{cm}$		(-)0.96/(2.303) (47.84)	-0.00872
log f_m	Repeat from eleven lines above		-1.96525
Temp. Corrn	$\left[(T_{cm} - T_{c2})/2.303\ RT\right](\Delta H/T_{cm})$	(- 0.0272) (5.75)	-0.15640
Sum of two previous lines		1.96525 - 0.15640	1.80885
Press. corrn.	$\left[(P_{cm} - P_{c2})/2.303\ P_{cm}\right](Z_m-1)$	(- 0.00872) (-0.376)	0.00328
log (f_2/y_2)	Sum of two previous lines	1.80885 + 0.00328	1.81213
f_2/y_2		Antilog (1.81213)	64.88
ϕ_2	f_2/y_2P	64.88/187.22	0.346

Method 2

b_m	Summation $(b_n y_n)$	(11.8) (0.319) $+$ (184.9) (0.681)	161.6°K
b_{r1}	b_m/b_1	161.6/111.8	1.446
T_{r1}	T/T_{c1}	327.6/190.7	1.719
θ_1^V	Fig. 2		2.475
P_{r1}	P/P_{c1}	187.22/45.8	4.092
ϕ_1	Fig. 3		1.058
b_{r2}	b_m/b_2	161.6/184.9	0.874
T_{r2}	T/T_{c2}	327.6/305.3	1.073
θ_2^V	Fig. 1		1.083
P_{r2}	P/P_{c2}	187.22/48.8	3.841
ϕ_2	Fig. 3		0.370

Method 3

T_{c1}/T		190.7/327.6	0.5817
$1/P_{c1}$		1/45.8	0.02184
B_1	$0.0867\ T_{c1}/TP_{c1}$	(0.0867) (0.5817) (0.02184)	0.001102

$(T_{c1}/T)^{1.25}$		$(0.5817)^{1.25}$	0.5078
$(1/P_{c1})^{0.5}$		$(0.02184)^{0.5}$	0.1478
A_1	$(0.6541)\,(T_{c1})^{1.25}/T^{1.25}P_{c1}^{0.5}$	(0.6541) (0.5078) (0.1478)	0.04914
T_{c2}/T		305.3/327.6	0.9319
$1/P_{c2}$		1/48.8	0.02049
B_2	$(0.0867)\,T_{c2}/TP_{c2}$	(0.0867) (0.9319) (0.02049)	0.001656
$(T_{c2}/T)^{1.25}$		$(0.9319)^{1.25}$	0.9157
$(1/P_{c2})$		$(0.02049)^{0.5}$	0.1432
A_2	$(0.6541)\,(T_{c2})^{1.25}/T^{1.25}P_{c2}^{0.5}$	(0.6541) (0.9157) (0.1432)	0.08574
B	Summation (B_n)	(0.001102) (0.319$\not{-}$ (0.001656) (0.681)	0.001479
A	Summation (A_n)	(0.04914) (0.319) $\not{-}$ (0.08574) (0.681)	0.07416
A^2/B		$(0.07416)^2/$ 0.001479	3.719
B P		(0.001479) (187.22)	0.277
$(A_1/A) - 1$		(0.04914/0.7416) - 1.00	-0.336
u	Fig. 5		1.143
$(B_1/B) - 1$		(0.001102/0.001479) - 1.00	- 0.255
w	Fig. 6		0.430
log $\bar{\phi}$	Fig. 4		-0.30670

B_1 corrn.	$w\left[(B_1/B) - 1.00\right]$	(0.430) (- 0.255)	-0.10975
Sum of two previous lines		- (0.30670 + 0.10975)	-0.41645
A_1 corrn.	$- u\left[(A_1/A) - 1.0\right]$	- (1.143) (-)(0.336)	0.38400
log ϕ_1		- (41645) + 0.38400	-0.03245
ϕ_1		antilog. (0.96755 - 1.0)	0.928
$(A_2/A) - 1.0$		(0.08574/0.07416) - 1.0	0.158
$(B_2/B) - 1.0$		(0.001656/0.001479)-1.0	0.120
log $\bar{\phi}$	Fig. 4	see 8 lines above	-0.30670
A_2 corrn.	$- u\left[(A_2/A) - 1.0\right]$	- (1.143) (0.158)	-0.18080
Sums of 2 previous lines		- (0.30670 + 0.18080)	-0.48750
B_2 corrn.	$w\left[(B_2/B) - 1.0\right]$	(0.430) (0.120)	0.05160
log ϕ_2	Sum of 2 previous lines	- (0.48750) + 0.05160	-0.43590
ϕ_2		antilog (0.56410 - 1.0)	0.367
			0.367
% Deviation	$\left[\frac{\text{Calc. - Exper.}}{\text{Exper.}}\right]$ For ϕ_2 by Method 3	$\frac{0.367 - 0.372}{0.372}$	- 1.35%

FIGURE 1

Θ^V vs. T_r and b_r for Hydrocarbon Vapors
Method 2. Appears as Figure 1 in (7)

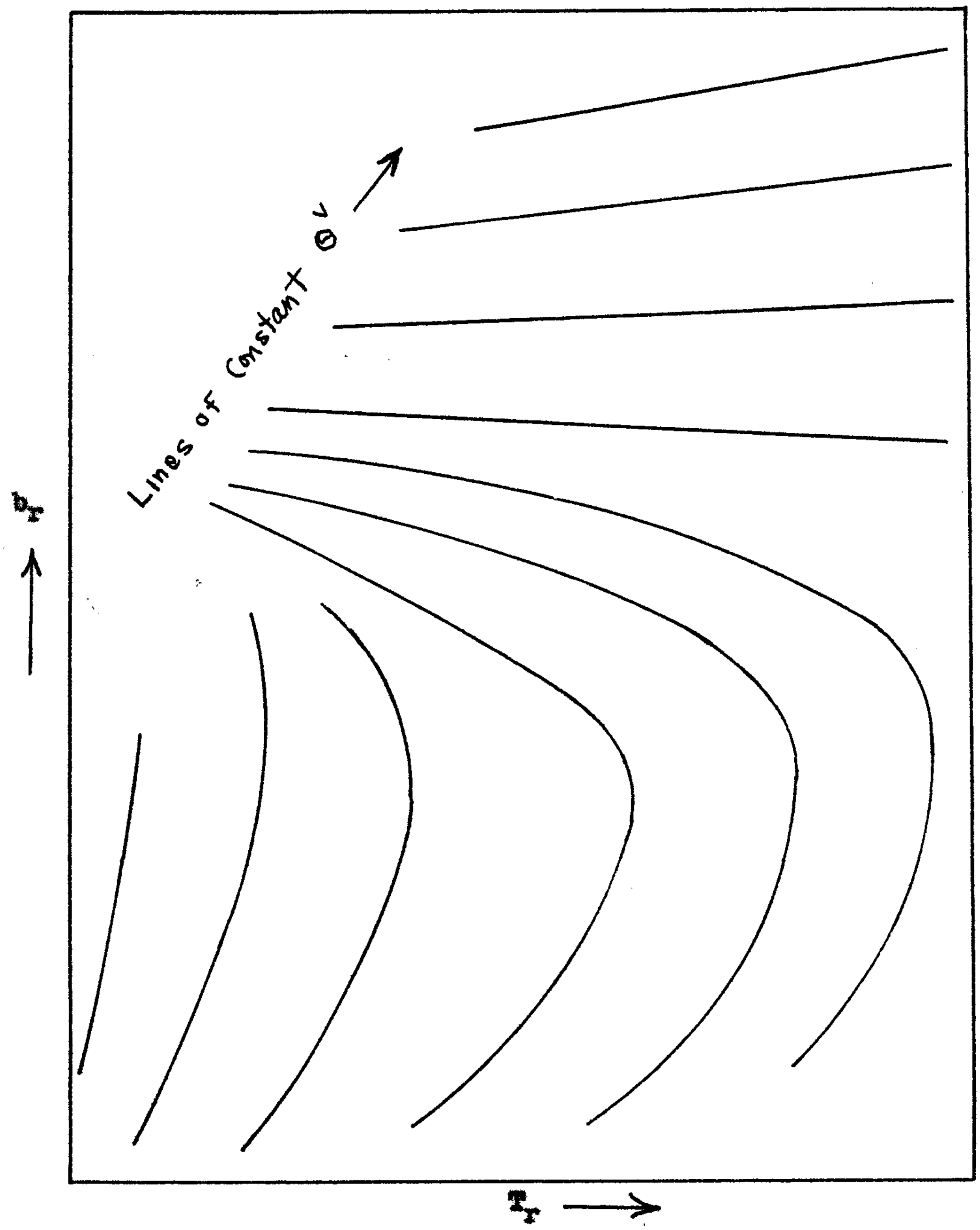

FIGURE 2

Θ^V vs. T_r and b_r for Methane Vapors
Method 2. Appears as Figure 2 in (7)

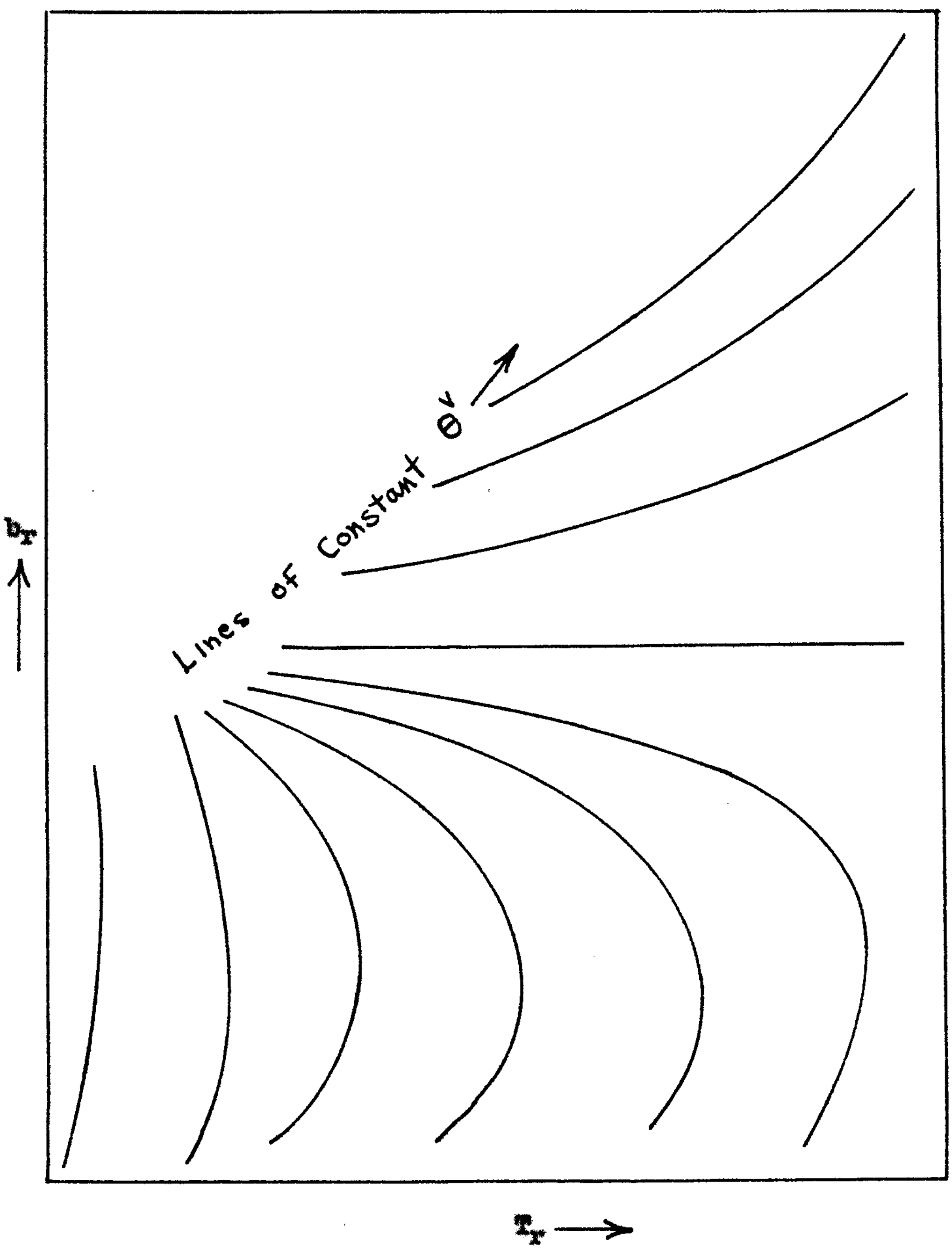

FIGURE 3

ϕ vs. P_r and Θ^V for Hydrocarbon and Methane Vapor
Method 2. Appears as Figure 3 in (7)

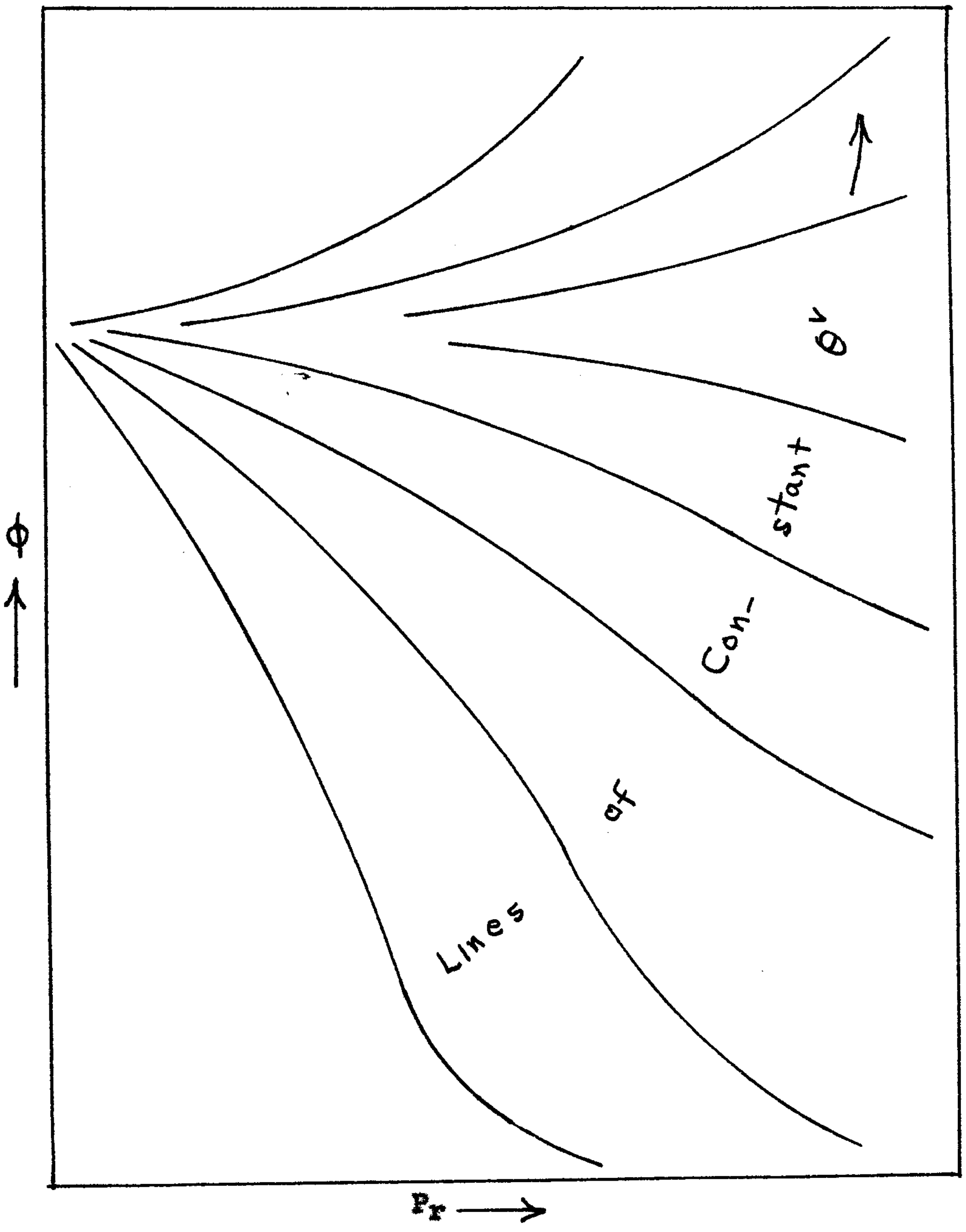

FIGURE 4

Log $\bar{\phi}$ vs. BP and A^2/B
Method 3. Appears as Fig. 15 in (19)

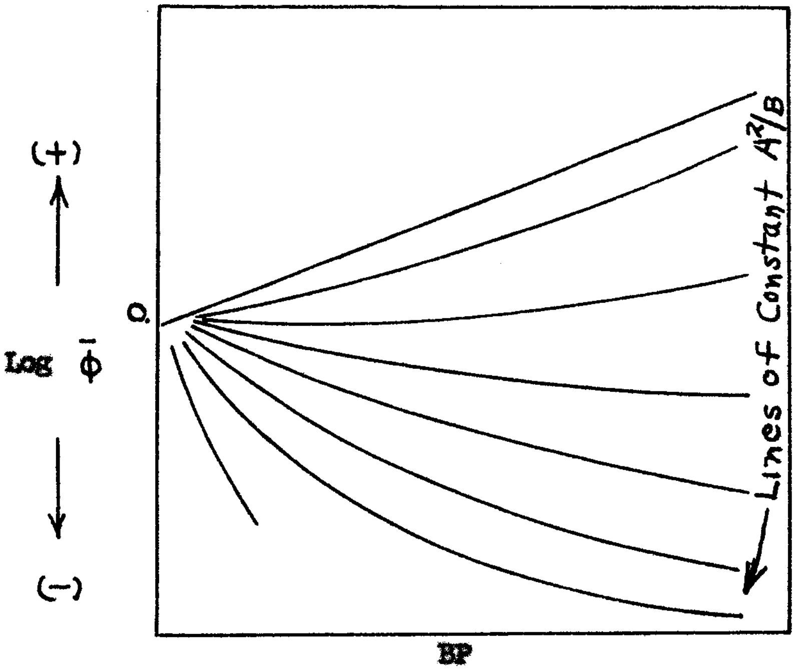

FIGURE 5
u vs. BP and A^2/B
Method 3. Appears as Fig. 16 in (19)

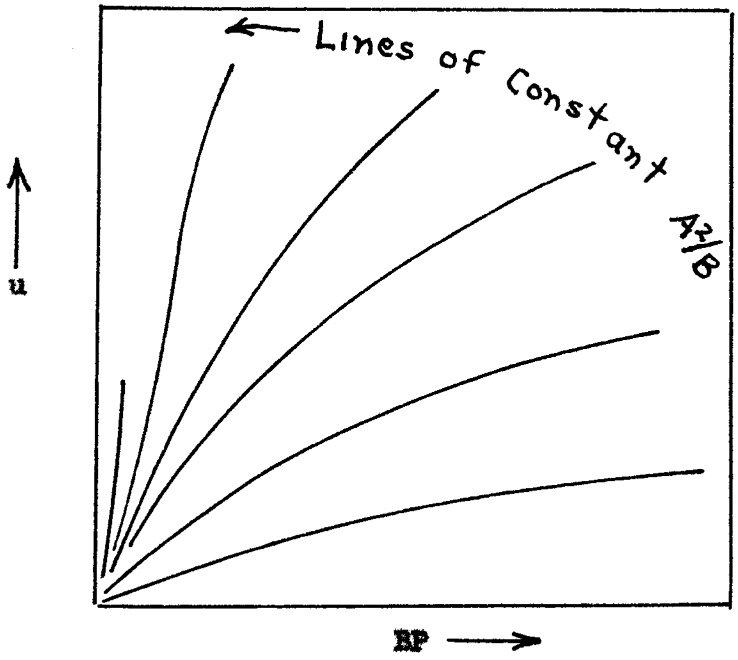

FIGURE 6
w vs. BP and A^2/B
Method 3. Appears as Fig. 17 in (19)

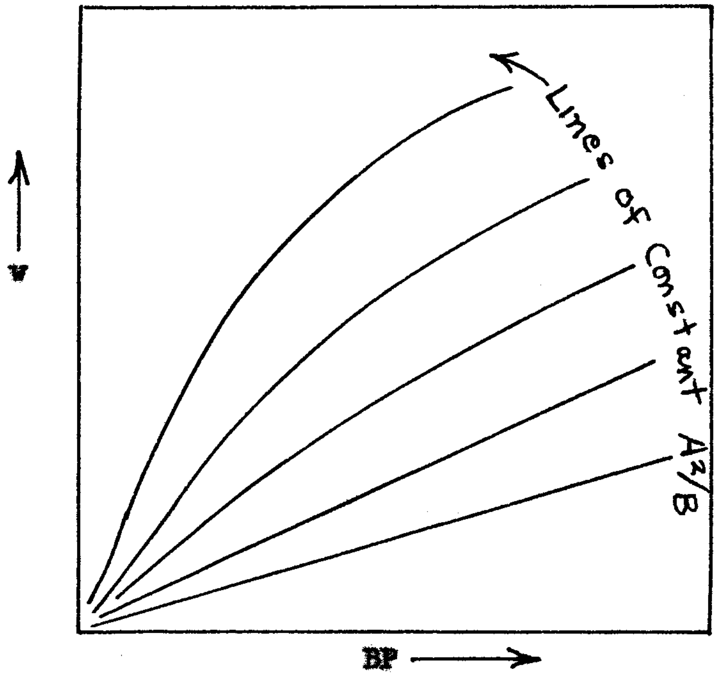

FIGURE 7
Z vs. BP and A^2/B
Method 3. Plotted from data of Redlich

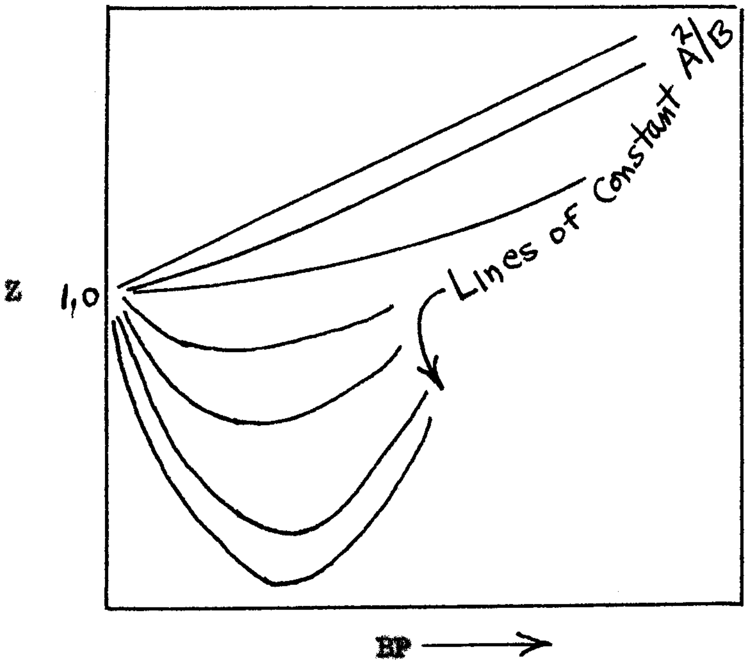

TABLE 1

Deviation of Calculated Activity Coefficients From Experimental Argon - Ethylene Mixtures at 25° C

(4 mixtures - mol fraction Argon = 0.2, 0.4, 0.6, 0.8)

	Ave. % Deviation, Argon			Ave. % Deviation, Ethylene		
Method	1	2	3	1	2	3
Deviat. (+)	95%	58%	17%	100%	83%	75%
Pres. Atmos.						
10	0.35	0.42	0.35	1.73	1.37	1.23
20	0.69	0.87	0.72	3.01	1.43	2.11
30	0.84	1.94	0.96	2.96	1.12	2.01
40	1.20	2.81	0.74	3.48	0.80	2.00
50	1.23	3.64	1.06	3.36	0.62	1.35
60	1.15	4.49	0.95	3.18	0.58	1.24
80	1.16	5.15	1.29	2.96	1.72	0.82
100	1.15	*3.73	1.91	2.68	2.98	2.10
125	1.02	*4.84	3.01	1.54	3.92	3.38
Ave. for all 36 Points	0.98	3.10	1.22	2.77	1.62	1.81

* Not including 0.2 Argon mol fraction

TABLE 2

Deviation of Calculated Activity Coefficients From Experimental
Using True Critical Constants of Hydrogen
Hydrogen - Nitrogen Mixtures at 0 degrees C
(4 mixtures - mol fraction Hydrogen = 0.2, 0.4, 0.6, 0.8)

	Ave. % Deviation, Hydrogen			Ave. % Deviation, Nitrogen		
Method	1	2	3	1	2	3
Deviat. (+)	88%	-	56%	94%	-	13%
Pres. Atmos.						
50	1.10		1.76	2.29		0.46
100	0.45		1.82	3.94		0.76
200	4.76	Charts	1.09	2.96	Charts	1.50
300	9.88	Do Not	1.36	3.36	Do Not	2.71
400	14.1	Include	1.44	7.25	Include	3.64
600	26.1	This	1.81	10.15	This	5.12
800	38.4	Range	2.99	19.5	Range	7.19
1000	55.7		4.29	16.7		9.19
Ave. for all 32 Points	18.81		2.07	8.27		3.82

TABLE 3

Deviation of Calculated Activity Coefficients From Experimental
Using Pseudocritical Constants of Hydrogen
Hydrogen - Nitrogen Mixtures at 0 degrees C
(4 mixtures - mol fraction Hydrogen = 0.2, 0.4, 0.6, 0.8)

	Ave. % Deviation, Hydrogen			Ave. % Deviation, Nitrogen		
Method	1	2	3	1	2	3
Deviat (↓)	91%	-	0%	75%	-	9%
Pres. Atmos.						
50	0.68		2.84	0.67		0.46
100	1.65	Charts	4.03	1.90	Charts	0.92
200	2.29	Do Not	5.65	0.94	Do Not	2.63
300	1.54	Include	7.38	1.42	Include	3.83
400	2.05	This	9.05	4.07	This	5.17
600	2.10	Range	12.06	6.57	Range	7.68
800	12.74		15.51	17.74		9.77
1000	20.60		19.25	20.90		12.68
Ave. 32 Points	5.46		9.47	6.78		5.39

TABLE 4

Deviation of Calculated Activity Coefficients From Experimental Methane - Ethane Mixtures - Summary for 21, 54.5, 88., 121.3 degrees C (4 mixtures - mol fraction Methane = 0.319, 0.555, 0.738, 0.882)

	Ave. % Deviation, Methane			Ave. % Deviation, Ethane		
Method	1	2	3	1	2	3
Deviat. (+)	95%	84%	93%	29%	31%	37%
Pres. Atmos.						
17.02	1.70	1.02	0.55	1.05	1.51	1.00
51.06	4.03	2.19	1.32	3.23	2.33	2.30
85.10	5.78	2.49	2.14	4.91	3.60	3.75
119.14	7.47	2.69	2.81	5.91	4.57	4.91
153.18	9.27	3.91	3.56	6.66	5.13	5.16
187.22	10.52	4.69	4.30	7.51	5.33	5.98
221.26	11.91	5.99	4.64	8.43	6.34	6.35
Ave. 112 Points	7.24	3.28	2.76	5.39	4.12	4.21

TABLE 5
Deviation of Calculated Activity Coefficients From Experimental Methane - Ethane Mixtures at 21 degrees C
(4 mixtures - mol fraction Methane = 0.319, 0.555, 0.738, 0.882)

	Ave. % Deviation, Methane			Ave. % Deviation, Ethane		
Method	1	2	3	1	2	3
Deviat. (+)	79%	80%	84%	32%	39%	57%
Pres. Atmos.						
17.02	1.14	0.62	0.97	1.01	1.43	0.92
51.06	1.66	1.71	0.81	3.30	2.02	1.48
85.10	4.03	1.63	1.85	5.29	4.11	3.74
119.14	3.79	1.79	2.93	6.25	6.18	6.10
153.18	4.72	2.76	3.54	5.67	6.02	6.91
187.22	6.95	3.96	6.16	5.71	5.46	8.32
221.26	8.43	5.10	7.38	6.96	7.34	8.95
Ave. 28 Points	4.39	2.51	3.38	4.88	4.65	5.20

TABLE 6
Deviations of Calculated Activity Coefficients From Experimental Methane - Ethane Mixtures at 54.5 degrees C
(4 mixture - mol fraction Methane = 0.319, 0.555, 0.738, 0.882)

	Ave. % Deviation, Methane			Ave. % Deviation, Ethane		
Method	1	2	3	1	2	3
Deviat. (‡)	100%	79%	93%	25%	32%	36%
Pres. Atmos.						
17.02	1.97	1.28	0.49	1.27	1.87	1.14
51.06	4.35	2.61	1.38	3.38	2.58	2.91
85.10	4.75	2.32	1.96	5.02	3.31	3.39
119.14	7.02	2.01	2.62	5.60	3.28	4.33
153.18	8.99	4.43	3.83	6.71	3.71	3.50
187.22	8.73	4.60	3.54	7.08	4.02	4.26
221.26	10.05	6.50	3.13	8.12	5.26	5.03
Ave. 28 Points	6.55	3.39	2.42	5.31	3.43	3.51

Deviation of Calculated Activity Coefficients From Experimental
Methane - Ethane Mixtures at 88 degrees C
(4 mixtures - mol fraction Methane = 0.319, 0.555, 0.738, 0.882)

TABLE 7

	Ave. % Deviation, Methane			Ave. % Deviation, Ethane		
Method	1	2	3	1	2	3
Deviat. (‡)	100%	86%	95%	32%	28%	28%
Pres. Atmos.						
17.02	1.85	1.15	0.33	0.93	1.84	1.02
51.06	4.85	2.29	1.39	2.98	2.53	2.47
85.10	6.68	2.85	2.24	4.72	3.60	4.04
119.14	9.21	3.19	2.66	5.69	4.13	4.84
153.18	11.71	4.22	3.42	6.87	5.15	5.02
187.22	12.91	5.41	3.71	8.17	5.48	5.40
221.26	14.55	6.57	4.07	9.13	6.08	5.04
Ave. 28 Points	8.84	3.67	2.55	5.50	4.12	3.98

Deviation of Calculated Activity Coefficients From Experimental
Methane - Ethane Mixtures at 121.3 degrees C
(4 mixtures - mol fraction Methane = 0.319, 0.555, 0.738, 0.882)

TABLE 8

	Ave. % Deviation, Methane			Ave. % Deviation, Ethane		
Method	1	2	3	1	2	3
Deviat. (‡)	100%	89%	100%	25%	25%	28%
Pres. Atmos.						
17.02	1.83	1.04	0.41	0.98	0.90	0.90
51.06	5.26	2.15	1.68	3.24	2.29	2.33
85.10	7.67	3.14	2.50	4.59	3.37	3.81
119.14	9.85	3.76	3.04	6.08	4.69	4.38
153.18	11.64	4.22	3.44	7.38	5.62	5.20
187.22	13.47	4.79	3.78	9.08	6.36	5.92
221.26	14.62	5.80	3.96	9.49	6.66	6.37
Ave. 28 Points	9.19	3.56	2.69	5.83	4.26	4.13

TABLE 9

Deviation of Calculated Activity Coefficients From Experimental
Methane - n Butane Mixtures - Summary for 21.1, 54.5, 88. and 121.3 deg. C
(No. of Mixtures as Indicated - Average mol fraction Methane = 0.81)

		Ave. % Deviation, Methane			Ave. % Deviation, n Butane		
Method		1	2	3	1	2	3
Deviat.	(#)	91%	45%	55%	100%	100%	100%
Pres. Atmos.							
6.81	(8)	1.07	0.85	1.08	6.28	4.65	5.60
13.62	(5)	1.48	1.27	0.92	12.36	7.93	10.20
20.43	(3)	0.91	0.84	0.45	15.67	7.43	11.36
27.23	(6)	1.05	1.02	0.59	28.39	18.52	21.26
34.05	(5)	1.92	1.73	1.03	28.25	20.42	23.91
54.46	(2)	1.14	1.36	1.12	41.00	20.43	24.95
68.10	(6)	3.11	3.27	1.79	50.34	28.36	34.93
102.15	(5)	1.94	1.12	1.26	59.43	29.41	33.28
136.2	(7)	3.42	4.90	0.62	71.48	51.06	42.20
170.25	(1)	5.00	4.30	2.84	50.5	30.7	29.5
204.3	(8)	3.32	6.27	0.77	85.55	69.6	49.6
Ave. for Points	56	2.14	2.62	1.00	42.65	28.8	27.3

TABLE 10

Deviations of Calculated Activity Coefficients From Experimental Methane - n Butane Mixtures at 21.1 and 54.5 degrees C
(no. of mixtures as indicated - average mol fraction Methane = 0.87)

		Ave. % Deviation, Methane			Ave. % Deviation n Butane		
Method		1	2	3	1	2	3
Deviat. (±)		79%	16%	34%	100%	100%	100%
Pres. Atmos.							
6.81	(4)	0.78	0.51	1.72	7.39	5.23	6.80
13.62	(1)	0.47	0.21	0.34	20.05	10.31	8.30
20.43	(2)	0.47	0.46	0.18	16.49	6.81	11.42
27.23	(4)	0.83	0.60	0.44	30.27	20.83	23.13
34.05	(0)						
54.46	(1)	0.31	0.75	0.18	49.1	24.1	28.5
68.10	(1)	1.26	0.74	0.02	59.85	36.1	39.2
102.15	(2)	1.22	1.39	0.52	60.23	32.37	35.15
136.2	(2)	1.28	2.75	0.36	86.58	53.2	41.4
204.3	(2)	1.64	4.60	0.64	110.6	93.	54.
Ave. for Points	(19)	0.93	1.29	0.66	43.5	28.7	25.3

TABLE 11

Deviations of Calculated Activity Coefficients From Experimental Methane - n Butane Mixtures at 88 degrees C

(no. of mixtures as indicated - average mol fraction Methane = 0.82)

		Ave. % Deviation, Methane			Ave. % Deviation, n Butane		
Method		1	2	3	1	2	3
Deviat (‡)		100%	53%	69%	100%	100%	100%
Pres. Atmos.							
6.81	(3)	1.76	1.55	0.45	4.98	3.68	3.96
13.62	(2)	1.51	1.19	1.22	12.31	9.04	13.67
20.43	(0)						
27.23	(2)	1.49	1.84	0.87	24.62	13.90	17.52
34.05	(3)	1.29	0.44	0.67	32.08	23.12	26.81
54.46	(0)						
68.10	(2)	2.15	0.44	0.92	59.1	38.6	41.35
102.15	(2)	2.10	0.22	1.30	65.3	32.5	37.35
136.2	(2)	1.87	1.39	0.72	85.3	75.5	54.45
204.3	(3)	1.24	3.13	1.02	92.6	83.2	56.97
Ave. for Points	(19)	1.58	1.34	0.87	46.5	35.2	31.2

TABLE 12
Deviations of Calculated Activity Coefficients From Experimental
Methane - n Butane Mixtures at 121.3 degrees C
(No. of mixtures as indicated - average mol fraction Methane = 0.74)

		Ave. % Deviation, Methane			Ave. % Deviation, n Butane		
Method		1	2	3	1	2	3
Deviat (+)		95%	67%	67%	100%	100%	100%
Pres. Atmos.							
6.81	(1)	0.15	0.14	0.40	5.70	5.26	5.70
13.62	(2)	1.95	1.87	0.91	8.56	5.64	7.69
20.43	(1)	1.78	1.59	0.98	14.02	8.67	11.25
27.23	(0)						
34.05	(2)	2.85	3.66	1.57	22.5	16.37	19.61
54.46	(1)	1.96	1.97	2.06	32.9	16.75	21.4
68.10	(3)	4.37	5.99	2.95	41.33	18.95	29.23
102.15	(1)	3.06	2.37	2.66	46.1	17.32	23.4
136.2	(3)	5.88	8.67	0.73	52.2	33.33	34.9
204.3	(3)	6.51	10.60	0.60	61.8	40.4	39.2
170.25	(1)	5.00	4.30	2.84	50.5	30.7	29.5
Ave. for Points	(18)	3.99	5.40	1.49	37.7	22.3	25.4

TABLE 13

Activity Coefficients (ϕ_n) - Experimental (9) and calculated by 3 methods
Argon - Ethylene mixtures at 25° C and Argon mol fraction 0.2

	Argon				Ethylene			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
10	1.007	1.016	1.018	1.005	0.932	0.941	0.941	0.949
20	1.018	1.037	1.047	1.023	0.876	0.892	0.885	0.896
30	1.034	1.051	1.087	1.047	0.823	0.835	0.829	0.841
40	1.058	1.078	1.135	1.061	0.772	0.788	0.778	0.790
50	1.090	1.110	1.190	1.088	0.725	0.734	0.729	0.739
60	1.128	1.153	1.25	1.116	0.677	0.692	0.685	0.689
80	1.228	1.240	1.365	1.206	0.587	0.589	0.605	0.595
100	1.354	1.377	1.40	1.292	0.508	0.515	0.533	0.519
125	1.444	1.452	1.40	1.311	0.437	0.439	0.460	0.453

TABLE 14

Activity Coefficients (ϕ_n) - Experimental (9) and calculated by 3 methods
Argon - Ethylene Mixtures at 25° C and Argon mol fraction 0.4

	Argon				Ethylene			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
10	1.006	1.009	1.010	0.999	0.933	0.950	0.945	0.948
20	1.011	1.003	1.024	1.004	0.877	0.908	0.888	0.901
30	1.016	1.024	1.035	1.003	0.830	0.857	0.837	0.845
40	1.021	1.032	1.053	1.012	0.785	0.811	0.788	0.800
50	1.030	1.045	1.074	1.027	0.741	0.769	0.745	0.748
60	1.038	1.050	1.095	1.021	0.700	0.722	0.702	0.703
80	1.062	1.080	1.137	1.047	0.622	0.644	0.621	0.618
100	1.089	1.114	1.177	1.081	0.554	0.565	0.553	0.538
125	1.120	1.140	1.227	1.117	0.485	0.488	0.484	0.466

TABLE 15

Activity Coefficients (ϕ_m) - Experimental (9) and Calculated by 3 methods
Argon - Ethylene mixtures at 25° C and Argon mol fraction 0.6

	Argon				Ethylene			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
10	0.999	1.000	0.998	1.001	0.934	0.955	0.949	0.940
20	1.002	1.002	0.998	0.995	0.885	0.912	0.898	0.893
30	1.001	1.000	0.999	0.993	0.840	0.868	0.851	0.858
40	1.000	1.006	0.995	0.987	0.800	0.833	0.807	0.817
50	1.000	1.008	0.992	0.988	0.761	0.796	0.768	0.774
60	1.000	1.006	0.990	0.977	0.725	0.754	0.727	0.743
80	1.002	1.010	0.988	0.987	0.658	0.687	0.653	0.659
100	1.005	1.008	0.987	0.988	0.599	0.622	0.587	0.593
125	1.008	1.012	0.982	0.990	0.537	0.552	0.517	0.523

TABLE 16

Activity Coefficients (ϕ_m) - Experimental (9) and calculated by 3 methods
Argon - Ethylene mixtures at 25° C and Argon mol fraction 0.8

	Argon				Ethylene			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
10	0.997	0.994	0.996	0.994	0.938	0.958	0.955	0.946
20	0.993	0.998	0.991	0.983	0.895	0.927	0.913	0.920
30	0.987	0.995	0.987	0.982	0.859	0.890	0.869	0.875
40	0.981	0.993	0.980	0.976	0.825	0.859	0.831	0.837
50	0.978	0.989	0.974	0.975	0.794	0.824	0.795	0.800
60	0.972	0.981	0.967	0.967	0.764	0.789	0.762	0.762
80	0.965	0.977	0.957	0.960	0.710	0.734	0.690	0.702
100	0.958	0.973	0.946	0.952	0.660	0.685	0.629	0.645
125	0.949	0.962	0.934	0.942	0.609	0.622	0.568	0.588

TABLE 17

Activity Coefficients (ϕ_n)-Experimental (17) and calculated by 3 methods
Hydrogen-Nitrogen mixtures at 0°C and Hydrogen mol fraction 0.2
Hydrogen ,using both normal and pseudocritical constants of Hydrogen

	Normal				Pseudocritical		
P(atm)	Meth.1	2	3	Exper.	Meth.1	2	3
50	1.087		1.063	1.074	1.069		1.047
100	1.159	Be-	1.123	1.137	1.145	Be-	1.098
200	1.341	yond	1.266	1.258	1.308	yond	1.191
300	1.574	scope	1.395	1.375	1.386	scope	1.268
400	1.658	of	1.521	1.493	1.537	of	1.346
600	2.213	charts	1.790	1.739	1.804	charts	1.510
800	2.705		2.091	2.015	2.265		1.649
1000	3.757		2.486	2.325	2.781		1.732

TABLE 18

Activity Coefficients (ϕ_n)-Experimental (17) and calculated by 3 methods
Hydrogen-Nitrogen mixtures ay 0°C and Hydrogen mol fraction 0.2
Nitrogen,using both normal and pseudocritical constants of Hydrogen

	Normal				Pseudocritical		
P(atm)	Meth.1	2	3	Exper.	Meth.1	2	3
50	0.985	0.978	0.978	0.979	0.989		0.974
100	0.977	0.960	0.966	0.969	0.979	Be-	0.956
200	0.972	0.939	0.968	0.977	0.971	yond	0.947
300	0.992	0.920	1.000	1.011	1.009	scope	0.968
400	1.082	Be- yond	1.050	1.073	1.081	of	1.017
600	1.285	scope of	1.208	1.250	1.285	charts	1.165
800	1.614	charts	1.429	1.508	1.612		1.364
1000	2.012		1.710	1.858	2.012		1.550

TABLE 19

Activity Coefficients (ϕ_n)-Experimental(17) and calculated by 3 methods Hydrogen-Nitrogen mixtures at 0°C and Hydrogen mol fraction 0.4 Hydrogen, using both normal and pseudocritical constants f Hydrogen

	Normal				Pseudocritical		
P(atm)	Meth.1	2	3	Exper.	Meth.1	2	3
50	1.061		1.050	1.066m	1.071		1.041
100	1.119	Be-	1.097	1.113	1.137	Be-	1.079
200	1.263	yond	1.209	1.208	1.255	yond	1.159
300	1.418	scope	1.320	1.307	1.312	scope	1.243
400	1.608	of	1.445	1.412	1.430	of	1.321
600	1.955	charts	1.696	1.638	1.638	charts	1.482
800	21480		1.994	1.895	21087		1.665
1000	3.499		2.267	2.185	2.457		1.867

TABLE 20

Activity Coefficients (ϕ_n)-Experimental (17) and calculated by 3 methods Hydrogen-Nitrogen mixtures at 0°C and Hydrogen mol fraction 0.4 Nitrogen, using normal and pseudocritical constants of Hydrogen

	Normal				Pseudocritical		
P(atm)	Meth.1	2	3	Exper.	Meth.1	2	3
50	1.041	0.984	0.980	0.981	0.995		0.982
100	1.010	0.968	0.964	0.976	0.988	Be-	0.976
200	1.009	0.953	0.966	0.990	1.001	yond	0.956
300	1.069	0.940	0.993	1.031	1.066	scope	1.006
400	1.186	Be- yond	1.042	1.093	1.132	of	1.056
600	1.429	scope of	1.189	1.278	1.377	charts	1.209
800	1.757	charts	1.411	1.546	1.785		1.431
1000	21133		1.641	1.902	2.233		1.744

TABLE 21

Activity Coefficients (ϕ_n)-Experigental (17) and calculated by 3 methods
Hydrogen-Nitrogen mixtures ay 0 C and Hydrogen mol fraction o.6
Hydrogen,using both normal and pseudocritical constants of Hydrogen

	Normal				Pseudocritical		
P(atm)	Meth.1	2	3	Exper.	Meth.1	2	3
50	1.041		1.042	1.063	1.075		1.032
100	1.104	Be-	1.083	1.105	1.143	Be-	1.057
200	1.248	yond	1.175	1.193	1.235	yond	1.117
300	1.519	scope	1.273	1.285	1.336	scope	1.180
400	1.666	of	1.387	1.384	1.429	of	1.249
600	2.195	charts	1.608	1.605	1.676	charts	1.404
800	2.740		1.885	1.855	2.004		1.562
1000	3.170		2.228	2.141	2.445		1.746

TABLE 22

Activity Coefficients (ϕ_n)- Experimental (17) and calculated by 3 methods
Hydrogen-Nitrogen mixtures at 0°C and Hydrogen mol fraction 0.6
Nitrogen,using both normal and pseudocritical constants of Hydrogen

	Normal				Pseudocritical		
P(atm)	Meth.1	2	3	Exper.	Meth.1	2	3
50	1.038	0.991	0.990	0.986	0.985		0.983
100	1.069	0.983	0.984	0.989	0.965	Be-	0.979
200	1.093	0.989	0.990	1.013	1.002	yond	0.985
300	1.115	0.998	1.020	1.061	1.080	scope	1.009
400	1.278	Be- yond	1.078	1.121	1.181	of	1.059
600	1.520	scope of	1.249	1.325	1.429	charts	1.197
800	1.968	charts	1.460	1.600	1.896		1.416
1000	2.324		1.786	1.969	2.347		1.711

TABLE 23

Activity Coefficients (ϕ_n)- Experimental(17) and calculated by 3 methods Hydrogen-Nitrogen mixtures at $0^{\circ}C$ and Hydrogen mol fraction 0.8 Hydrogen, using both normal and pseudocritical constants of Hydrogen

	Normal				Pseudocritical		
P(atm)	Meth.1	2	3	Exper.	Meth.1	2	3
50	1.053		1.033	1.060	1.053		1.023
100	1.100	Be-	1.073	1.101	1.098	Be-	1.044
200	1.237	yond	1.154	1.179	1.182	yond	1.099
300	1.359	scope	1.241	1.266	1.279	scope	1.158
400	1.509	of	1.340	1.358	1.348	of	1.220
600	1.900	charts	1.559	1.568	1.565	charts	1.364
800	2.542		1.832	1.808	1.898		1.521
1000	3.362		2.137	2.086	2.231		1.700

TABLE 24

Activity Coefficients (ϕ_n)-Experimental(17) and calculated by 3 methods Hydrogen-Nitrogen mixtures at $0^{\circ}C$ and Hydrogen mol fraction 0.8 Nitrogen, using both normal and pseudocritical constants of Hydrogen

	Normal				Pseudocritical		
P(atm)	Meth.1	2	3	Exper.	Meth.1	2	3
50	1.023	1.003	0.998	0.987	0.988		0.996
100	1.023	1.009	1.003	0.993	0.962	Be-	1.008
200	1.041	1.037	1.027	1.031	1.022	yond	1.018
300	1.179	1.078	1.067	1.091	1.088	scope	1.050
400	1.326	Be- yond	1.135	1.170	1.258	of	1.103
600	1.620	scope of	1.322	1.383	1.490	charts	1.261
800	2.117	charts	1.571	1.672	2.176		1.494
1000	2.631		1.924	2.052	2.847		1.791

TABLE 25

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 21.1° C and Methane mol fraction 0.319

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	1.000	0.996	1.006	0.985	0.887	0.873	0.865	0.877
51.06	1.000	0.981	1.009	1.003	0.635	0.595	0.630	0.636
85.10	1.000	1.108	1.017	1.016	0.418	0.386	0.460	0.436
119.14	1.000	1.046	1.025	1.024	0.301	0.286	0.344	0.322
153.18	1.000	0.963	1.036	0.963	0.248	0.241	0.274	0.277
187.22	1.000	0.911	1.046	0.882	0.222	0.218	0.233	0.252
221.26	1.000	0.879	1.058	0.857	0.208	0.204	0.204	0.234

TABLE 26

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 21.1° C and Methane mol fraction 0.555

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.965	0.985	0.982	0.984	0.894	0.887	0.876	0.902
51.06	0.918	0.931	0.947	0.936	0.681	0.652	0.652	0.666
85.10	0.891	0.902	0.911	0.922	0.500	0.479	0.493	0.477
119.14	0.860	0.892	0.872	0.891	0.379	0.365	0.374	0.362
153.18	0.816	0.850	0.837	0.850	0.311	0.304	0.303	0.306
187.22	0.773	0.818	0.809	0.811	0.275	0.269	0.263	0.271
221.26	0.736	0.791	0.792	0.783	0.252	0.249	0.232	0.250

TABLE 27

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane Mixtures at 21.1° C and Methane mol fraction 0.738

	Methane				Ethane			
P(atm	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.966	0.978	0.967	0.970	0.893	0.895	0.883	0.890
51.06	0.906	0.923	0.926	0.914	0.696	0.697	0.676	0.698
85.10	0.853	0.879	0.873	0.870	0.537	0.536	0.522	0.530
119.14	0.805	0.844	0.825	0.844	0.422	0.417	0.408	0.403
153.18	0.757	0.820	0.783	0.798	0.348	0.346	0.339	0.345
187.22	0.722	0.793	0.754	0.767	0.302	0.302	0.302	0.306
221.26	0.695	0.764	0.730	0.743	0.274	0.278	0.268	0.280

TABLE 28

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane Mixtures at 21.1° C and Methane mol fraction 0.882

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.968	0.976	0.968	0.968	0.887	0.902	0.889	0.900
51.06	0.909	0.896	0.914	0.910	0.693	0.710	0.694	0.716
85.10	0.857	0.866	0.855	0.860	0.535	0.584	0.547	0.561
119.14	0.811	0.827	0.805	0.818	0.417	0.480	0.441	0.455
153.18	0.773	0.796	0.762	0.780	0.336	0.393	0.364	0.381
187.22	0.741	0.765	0.725	0.753	0.285	0.338	0.321	0.333
221.26	0.718	0.748	0.704	0.732	0.251	0.310	0.295	0.303

TABLE 29

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 54.4° C and Methane mol fraction 0.319

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.978	1.011	1.007	0.987	0.921	0.910	0.901	0.909
51.06	0.967	1.016	1.012	0.988	0.753	0.724	0.732	0.734
85.10	0.988	1.042	1.024	1.016	0.598	0.561	0.586	0.582
119.14	1.017	1.105	1.035	1.041	0.484	0.458	0.487	0.469
153.18	0.944	1.068	1.047	0.997	0.413	0.384	0.418	0.411
187.22	0.958	1.047	1.058	0.928	0.372	0.346	0.370	0.367
221.26	0.924	1.022	1.075	0.928	0.346	0.322	0.342	0.348

TABLE 30

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 54.4° C and Methane mol fraction 0.555

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.976	0.995	0.989	0.980	0.927	0.911	0.894	0.913
51.06	0.938	0.971	0.964	0.954	0.779	0.745	0.752	0.759
85.10	0.910	0.961	0.939	0.929	0.643	0.607	0.619	0.623
119.14	0.887	0.970	0.917	0.924	0.533	0.499	0.516	0.513
153.18	0.863	0.973	0.895	0.905	0.457	0.425	0.444	0.445
187.22	0.838	0.952	0.873	0.881	0.409	0.382	0.399	0.402
221.26	0.814	0.941	0.854	0.860	0.379	0.352	0.370	0.374

TABLE 31

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 54.4° C and Methane Mol fraction 0.738

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.975	0.990	0.980	0.980	0.927	0.920	0.918	0.920
51.06	0.930	0.952	0.948	0.944	0.789	0.768	0.768	0.771
85.10	0.892	0.938	0.911	0.913	0.667	0.652	0.642	0.647
119.14	0.859	0.910	0.871	0.888	0.565	0.551	0.542	0.552
153.18	0.832	0.901	0.837	0.863	0.488	0.466	0.474	0.484
187.22	0.808	0.887	0.809	0.847	0.434	0.417	0.424	0.435
221.26	0.789	0.884	0.792	0.831	0.397	0.378	0.396	0.402

TABLE 32

Activity Coefficients(ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 54.4° C and Methane mol fraction 0.882

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.978	0.988	0.981	0.977	0.915	0.928	0.922	0.924
51.06	0.937	0.960	0.927	0.938	0.764	0.794	0.785	0.797
85.10	0.901	0.926	0.898	0.906	0.640	0.678	0.664	0.671
119.14	0.870	0.906	0.857	0.875	0.540	0.584	0.568	0.584
153.18	0.844	0.862	0.823	0.852	0.465	0.503	0.502	0.511
187.22	0.823	0.841	0.793	0.832	0.409	0.453	0.453	0.465
221.26	0.807	0.831	0.772	0.816	0.367	0.416	0.423	0.430

TABLE 33

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 88.0° C and Methane mol fraction 0.319

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.985	1.013	1.008	0.990	0.942	0.931	0.929	0.932
51.06	0.971	1.037	1.015	0.987	0.821	0.799	0.806	0.805
85.10	0.975	1.063	1.027	0.997	0.708	0.671	0.695	0.690
119.14	0.981	1.13	1.041	1.004	0.616	0.580	0.605	0.599
153.18	0.975	1.187	1.057	1.008	0.549	0.522	0.535	0.537
187.22	0.961	1.182	1.070	0.990	0.503	0.472	0.490	0.494
221.26	0.944	1.195	1.085	0.973	0.472	0.439	0.459	0.464

TABLE 34

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 88.0° C and Methane mol fraction 0.555

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.981	1.001	0.992	0.988	0.931	0.937	0.935	0.937
51.06	0.952	0.990	0.972	0.969	0.842	0.807	0.819	0.819
85.10	0.928	1.002	0.955	0.958	0.744	0.709	0.712	0.711
119.14	0.908	1.005	0.941	0.946	0.660	0.619	0.623	0.632
153.18	0.891	1.010	0.930	0.940	0.594	0.541	0.558	0.567
187.22	0.876	1.020	0.920	0.930	0.545	0.490	0.512	0.521
221.26	0.861	1.022	0.913	0.919	0.511	0.451	0.481	0.490

TABLE 35

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 88.0° C and Methane mol fraction 0.738

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.981	0.996	0.990	0.981	0.947	0.937	0.937	0.941
51.06	0.947	0.996	0.966	0.964	0.846	0.832	0.828	0.832
85.10	0.919	0.976	0.942	0.944	0.754	0.724	0.727	0.737
119.14	0.895	0.960	0.918	0.924	0.674	0.641	0.645	0.662
153.18	0.876	0.945	0.897	0.912	0.609	0.562	0.580	0.600
187.22	0.861	0.934	0.877	0.901	0.559	0.515	0.533	0.553
221.26	0.848	0.929	0.859	0.894	0.522	0.482	0.501	0.521

TABLE 36

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 88.0° C and Methane mol fraction 0.882

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.984	0.994	0.987	0.983	0.933	0.942	0.943	0.943
51.06	0.956	0.989	0.961	0.959	0.813	0.847	0.841	0.842
85.10	0.931	0.964	0.933	0.938	0.712	0.747	0.745	0.761
119.14	0.911	0.943	0.906	0.919	0.629	0.667	0.666	0.696
153.18	0.896	0.928	0.881	0.902	0.563	0.604	0.604	0.630
187.22	0.883	0.915	0.855	0.890	0.511	0.555	0.555	0.584
221.26	0.873	0.905	0.838	0.882	0.470	0.518	0.525	0.537

TABLE 37

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 121.3° C and Methane mol fraction 0.319

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.988	1.019	1.009	0.996	0.956	0.949	0.949	0.950
51.06	0.975	1.033	1.020	0.998	0.867	0.833	0.858	0.852
85.10	0.974	1.079	1.034	1.005	0.783	0.752	0.770	0.765
119.14	0.978	1.129	1.052	1.008	0.712	0.674	0.695	0.693
153.18	0.981	1.181	1.068	1.016	0.655	0.609	0.635	0.639
187.22	0.981	1.218	1.081	1.014	0.613	0.563	0.591	0.595
221.26	0.977	1.237	1.100	1.010	0.582	0.531	0.558	0.567

TABLE 38

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 121.3° C and Methane mol fraction 0.555

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.985	1.008	0.997	0.991	0.962	0.949	0.951	0.953
51.06	0.961	1.022	0.984	0.982	0.886	0.853	0.861	0.861
85.10	0.942	1.031	0.974	0.975	0.814	0.771	0.779	0.782
119.14	0.926	1.038	0.966	0.968	0.752	0.692	0.709	0.717
153.18	0.915	1.038	0.959	0.963	0.700	0.630	0.649	0.663
187.22	0.905	1.042	0.953	0.960	0.659	0.575	0.603	0.622
221.26	0.898	1.043	0.947	0.956	0.628	0.547	0.575	0.592

TABLE 39

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 121.3° C and Methane mol fraction 0.738

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.985	0.998	0.991	0.987	0.961	0.949	0.954	0.954
51.06	0.959	1.013	0.976	0.993	0.886	0.868	0.873	0.889
85.10	0.938	0.998	0.961	0.963	0.816	0.779	0.793	0.798
119.14	0.921	0.991	0.948	0.954	0.755	0.707	0.727	0.737
153.18	0.907	0.985	0.935	0.944	0.705	0.647	0.671	0.689
187.22	0.897	0.985	0.925	0.939	0.665	0.601	0.627	0.647
221.26	0.890	0.988	0.918	0.934	0.633	0.572	0.596	0.617

TABLE 40

Activity Coefficients (ϕ_n) - Experimental (23) and calculated by 3 methods
Methane - Ethane mixtures at 121.3° C and Methane mol fraction 0.882

	Methane				Ethane			
P(atm)	Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
17.02	0.989	0.996	0.992	0.990	0.945	0.951	0.955	0.958
51.06	0.969	1.002	0.973	0.973	0.848	0.876	0.877	0.885
85.10	0.952	0.990	0.957	0.958	0.766	0.801	0.802	0.818
119.14	0.939	0.981	0.941	0.948	0.699	0.731	0.740	0.760
153.18	0.928	0.966	0.927	0.936	0.644	0.671	0.684	0.713
187.22	0.921	0.965	0.916	0.929	0.599	0.634	0.645	0.673
221.26	0.916	0.959	0.906	0.925	0.563	0.600	0.609	0.645

TABLE 41

Activity Coefficients (ϕ_n)- Experimental (21) and calculated by 3 methods Methane-nButane mixtures at 21 and 54.6°C, Methane mol fract. as indicated

T= 21°C

P(atm)	y_M	Methane				Ethane			
		Exper.	Meth. 1	2	3	Exper.	Meth.1	2	3
6.81	0.707	0.997	0.995	0.997	0.995	0.810	0.884	0.861	0.878
20.43	0.845	0.972	0.974	0.962	0.971	0.675	0.746	0.685	0.706
6.81	0.894	0.990	0.989	0.987	1.007	0.835	0.914	0.903	0.923
27.23	0.894	0.964	0.959	0.951	0.954	0.497	0.698	0.637	0.647
1362	0.970	0.976	0.981	0.974	0.973	0.759	0.874	0.837	0.822
27.23	0.970	0.952	0.963	0.949	0.950	0.587	0.741	0.682	0.705
54.46	0.970	0.908	0.911	0.901	0.906	0.367	0.547	0.455	0.471
102.15	0.970	0.838	0.849	0.822	0.835	0.180	0.274	0.243	0.253
136.2	0/970	0.798	0.809	0.776	0.796	0.118	0.226	0.181	0.161
204.3	0.970	0.739	0.751	0.706	0.739	0.063	0.140	0.123	0.099
				T= 54.4°C					
6.81	0.475	1.001	1.025	1.013	1.039	0.852	0.891	0.871	0.873
6.81	0.707	0.995	0.999	1.002	1.005	0.857	0.914	0.893	0.907
20.43	0.707	0.993	1.003	1.005	0.995	0.672	0.768	0.703	0.741
27.23	0.845	0.976	0.981	0.971	0.974	0.582	0.731	0.701	0.720
102.15	0.845	0.914	0.925	0.907	0.921	0.209	0.352	0.270	0.271
27.23	0.935	0.969	0.981	0.968	0.967	0.628	0.803	0.746	0.744
68.10	0.945	0.926	0.938	0.919	0.926	0.353	0.565	0.481	0.492
136.2	0.935	0.863	0.873	0.840	0.869	0.180	0.329	0.276	0.263
204.3	0.935	0.821	0.834	0.784	0.832	0.115	0.232	0.221	0.175

TABLE 42

Activity Coefficients (ϕ_n) -Experimental (21) and calculated by 3 methods Methane-nButane mixtures at 88°C, Methane mol fraction as indicated

P(atm)	y_M	Methane				Ethane			
		Experm	Meth. 1	2	3	Exper.	Meth. 1	2	3
6.81	0.287	0.997	1.044	1.039	1.006	0.886	0.905	0.893	0.911
13.62	0.609	0.995	1.017	1.018	1.010	0.789	0.866	0.835	0.846
27.23	0.609	1.002	1.021	1.034	1.018	0.621	0.735	0.682	0.716
6.81	0.783	0.994	0.999	0.995	0.992	0.890	0.945	0.931	0.916
34.05	0.783	0.978	0.995	0.985	0.986	0.580	0.746	0.693	0.713
102.15	0.783	0.959	0.980	0.968	0.979	0.261	0.433	0.338	0.357
27.23	0.845	0.981	0.991	0.985	0.982	0.650	0.818	0.767	0.778
68.10	0.845	0.955	0.973	0.959	0.967	0.400	0.608	0.521	0.534
136.2	0.845	0.923	0.940	0.921	0.935	0.230	0.385	0.319	0.314
204.3	0.845	0.902	0.919	0.885	0.915	0.158	0.279	0.267	0.226
6.81	0.894	0.995	0.995	0.998	0.993	0.894	0.954	0.955	0.949
34.05	0.894	0.975	0.984	0.978	0.981	0.603	0.794	0.744	0.762
102.15	0.894	0.931	0.955	0.938	0.935	0.315	0.520	0.427	0.438
204.3	0.894	0.886	0.889	0.863	0.899	0.180	0.312	0.303	0.255
13.62	0.970	0.989	0.997	0.989	0.981	0.809	0.929	0.908	0.972
34.05	0.970	0.974	0.986	0.971	0.980	0.609	0.826	0.785	0.795
68.10	0.970	0.950	0.973	0.946	0.944	0.415	0.690	0.610	0.619
136.2	0.970	0.911	0.929	0.888	0.910	0.243	0.493	0.415	0.418
204.3	0.970	0.885	0.899	0.840	0.884	0.168	0.384	0.357	0.313

TABLE 43

Activity Coefficients (ϕ_n)-Exreimental (21) and calculated by 3 methods
Methane-nButene mixtures at 121.2°C,Methane mol fraction as indicated

P(atm)	y_M	Methane				Ethane			
		Exper.	Meth. 1	2	3	Exper.	Meth. 1	2	3
13.62	0.475	0.997	1.029	1.034	1.013	0.828	0.878	0.855	0.874
34.05	0.475	1.033	1.076	1.107	1.065	0.613	0.710	0.6622	0.691
68.10	0.475	1.111	1.189	1.305	1.195	0.366	0.481	0.435	0.445
136.2	0.475	1.231	1.375	*	1.222	0.190	0.268	0.232	0.256
204.3	0.475	1.160	1.322	*	1.164	0.149	0.218	0.177	0.207
20.43	0.707	0.990	1.008	1.006	1.000	0.762	0.869	0.828	0.848
54.46	0.707	0.992	1.011	1.011	1.012	0.516	0.685	0.602	0.636
102.15	0.707	0.999	1.029	1.022	1.025	0.339	0.496	0.398	0.419
170.25	0.707	0.998	1.048	1.041	0.970	0.224	0.337	0.292	0.290
13.62	0.845	0.993	1.001	0.993	0.990	0.837	0.930	0.904	0.919
68.10	0.845	0.989	0.999	0.979	0.978	0.493	0.699	0.606	0.622
136.2	0.845	0.950	0.979	0.950	0.963	0.330	0.500	0.412	0.418
204.3	0.845	0.936	0.964	0.933	0.951	0.244	0.399	0.352	0.322
6.81	0.935	0.996	0.995	0.993	0.995	0.913	0.965	0.961	0.974
34.05	0.935	0.983	0.998	0.981	0.982	0.662	0.856	0.820	0.838
68.10	0.935	0.968	0.996	0.967	0.965	0.493	0.744	0.677	0.690
136.2	0.935	0.941	0.968	0.945	0.942	0.344	0.566	0.480	0.490
204.3	0.935	0.936	0.950	0.912	0.927	0.265	0.469	0.420	0.392

* Above range of Figure 3

TABLE 44

Activity Coefficients (ϕ_n)-Experimental (10) and calculated by 3 methods
Ethane-Ethylene (v-L) at -17.8°C,Ethane mol fraction as indicated

P(atm)	y_E	Ethane Exper.	Meth. 1	2	3	Ethylene Exper.	Meth. 1	2	3
16.17	0.848	0.939	0.797	0.783	0.814	5.61	0.865	0.859	*
18.58	0.601	1.272	0.765	0.755	0.809	2.085	0.834	0.832	*
20.81	0.402	1.830	0.735	0.730	0.798	1.360	0.810	0.807	*
23.04	0.229	3.084	0.708	0.700	0.787	1.024	0.787	0.782	*
25.24	0.074	9.17	0.682	0.680	0.778	0.830	0.764	0.760	*

*Ethylene not calculated by Method 3--values will approximate those of Methods 1 and 2

TABLE 45

Activity Coefficients (ϕ_n)-Experimental (22) and calculated by 3 methods
Methane-nButane (vL) at 21°C,Methane mol fraction as indicated
* Not calculated by Method 3

P(atm)	y_M	Methane Exper.	Meth. 1	2	3	nButane Exper.	Meth. 1	2	3
2.72	0.212	1.015	1.056	1.030	*	0.923	0.898	0.918	*
4.08	0.425	1.080	1.028	1.012	*	0.830	0.898	0.882	*
5.45	0.520	1.122	1.022	1.011	*	0.731	0.884	0.853	*
6.08	0.575	1.144	1.016	1.010	*	0.649	0.863	0.828	*
10.90	0.643	1.178	1.007	1.010	*	0.492	0.804	0.745	*
13.61	0.676	1.185	1.006	1.009	*	0.396	0.772	0.697	*
20.42	0.707	1.189	1.000	1.000	*	0.278	0.687	0.590	*
34.03	0.734	1.167	0.981	0.986	*	0.169	0.523	0.440	*
54.48	0.745	1.132	0.950	0.968	*	0.103	0.338	0.245	*
81.61	0.746	1.070	0.969	0.953	*	0.068	0.172	0.120	*
129.25	0.687	1.030	1.003	1.097	*	0.047	0.062	0.034	*
109.0	0.736	1.037	0.978	0.950	*	0.056	0.100	0.060	*
131.0	0.652	1.080	1.080	1.155	*	0.043	0.050	0.028	*
119.1	0.719	1.012	0.981	0.986	*	0.052	0.082	0.043	*

TABLE 46

Parameter Ranges - Method 1

System	Points	y_1	P_{rm}	T_{rm}	V_m	$\Delta H/T_{cm}$	Z_m
A-E	36	0.2--0.8	0.2--2.6	1.16--1.68	0.56--0.99	0.2--5.5	0.5--0.99
H-N	32	0.2--0.8	1.7--59.	2.5--5.3	1.01--3.2	0.2(-)1.11	0.98--2.14
H-N (pseudo)	32	0.2--0.8	1.6--43.	2.5--4.7	1.01--2.41	0.2(-)0.92	1.0--2.1
M-E	28	0.319	0.36--4.63	1.09--1.47	0.33-0.97	0.4--7.60	0.63--0.96
M-E	28	0.555	0.36--4.69	1.22--1.63	0.47--0.98	0.3--6.00	0.68--0.98
M-E	28	0.738	0.36--4.76	1.33--1.79	0.59--0.99	0.3--5.20	0.74--0.98
M-E	28	0.882	0.37--4.79	1.44--1.93	0.68--0.99	0.2--4.60	0.81--0.99
M-B	56	0.28--0.97	0.16--4.51	1.01--1.92	0.51--0.99	0.1--5.80	0.61--0.99
$(E\text{-}F)_{vL}$	5	0.08--0.85	0.33-0.50	0.85--0.90	0.76--0.81	1.6--2.30	0.68--0.78
$(M\text{-}B)_{vL}$	14	0.21--0.75	0.07--3.07	0.78--1.18	0.37--0.95	0.3--7.40	0.46--0.96

TABLE 47

Parameter Ranges - Method 2

System	Points	y_1	P_r	T_r	B_r	θ^V
A - E	36	0.2--0.8	0.2--2.6	1.05--1.97	0.6--1.75	1.06--2.90
H - N	32	0.2--0.8	1.5--80	2.16--8.20	0.42--3.10	2.19-- ?
H - N (pseudo)	32	0.2--0.8	1.5--80	2.16--8.20	0.42--3.10	2.19-- ?
M - E	28	0.319	0.35--4.84	0.96--2.07	0.87--1.45	0.97--2.50
M - E	28	0.555	0.35--4.84	0.96--2.07	0.78--1.29	1.00--2.20
M - E	28	0.738	0.35--4.84	0.97--2.07	0.71--1.17	1.02--2.11
M - E	28	0.882	0.35--4.84	0.97--2.07	0.65--1.08	1.04--2.08
M - B	56	0.28--0.97	0.15--5.60	0.69--2.07	0.43--2.03	0.79--3.22
(E - E)$_{vL}$	5	0.08--0.85	0.33-0.52	0.84--0.90	0.92--0.98	0.84
(M - B)$_{vL}$	14	0.21--0.75	0.06--3.65	0.69--1.54	0.56--2.24	0.70--3.65

TABLE 48

Parameter Ranges - Method 3

System	Points	y_1	B P	A^2/B	log Φ	u	w
A-E	36	0.2--0.8	0.011--0.185	2.3--4.0	(-)0.01--(-)0.26	0.03--1.06	0.01-0.33
H-N	32	0.2--0.8	0.045--1.12	0.41--1.22	(-)0.01-- 0.32	0.02--0.49	0.02--0.63
H-N (pseudo)	32	0.2--0.8	0.037--1.08	0.54--1.28	(-)0.01-- 0.254	0.02--0.50	0.02--0.64
M-E	28	0.319	0.02--0.36	2.81--4.36	(-)0.016-(-)0.452	0.05--1.64	0.01--0.67
M-E	28	0.555	0.019--0.32	2.42--3.73	(-)0.011-(-)0.32	0.04--1.23	0.01--0.48
M-E	28	0.738	0.017--0.31	2.11--3.25	(-)0.01--(-)0.24	0.03--0.95	0.01--0.38
M-E	28	0.882	0.016--0.29	1.89--2.88	(-)0.01--(-)0.18	0.03--0.77	0.01--0.30
M-B	56	0.28--0.97	0.01--0.361	1.90--5.00	(-)0.01--(-)0.33	0.03--1.25	0.01--0.52
$(E\text{-}E)_{vL}$	5	0.08--0.85	0.041--0.05	5.8--6.30	(-)0.09--(-)0.11	0.25--0.34	0.22--0.37
$(M\text{-}B)_{vL}$	14	0.21--0.75	0.008--0.26	3.72--8.00	NOT CALCULATED		

TABLE 49

Generalized Charts used for Method 1 with Systems Calculated in this Paper

Generalized Mixture Property	Reference Number	Page and Fig. No.	Range of Pseudoreduced Property P_{rm}	T_{rm}	Systems for which used (X) A-E	H-N	M-E	M-B	$(E-E)_{vL}$	$(M-B)_{vL}$
Z_m	25	P.108-Fig. 3	0-5.0	0.8-2.0	X	X	X	X		X
	25	P.109 -Fig. 4	0-50.0	1.6-15.0		X				
	13	Fig. 103-Low Pr.	0-0.4	0.5-1.2	X				X	X
	13	Fig. 103-High Pr.	0.1-30.0	0.7-15.0		X				
V_m	25	P.198-Fig.1	0-3.0	0.75-2.2	X					
	25	P.199-Fig.2	0-20.0	1.0-3.5		X				
	25	P.199-Fig.3	0-70.0	3.5-35.0		X				
	13	Fig. 142-Low Pr.	0-0.5	0.5-1.6			X			
	13	Fig. 142-High Pr.	0.2-40.	0.5-10.0		X	X	X	X	X
$\Delta H/T_{cm}$	6	P.140-Fig.48	0.01-10.0	0.6-4.0	X		X	X	X	X
$\Delta H/T$	25	P.219-Fig.4	0.1-40.	0.7-6.0		X				

TABLE 50

Parameter Ranges - Charts for Method 2

Fig. No.	Parameter	Range
1	T_{rn}	0.4 - 2.4
	b_{rn}	0.3 - 2.1
	e^{v}_{n}	0.5 - 4.0
2	T_{rn}	0.4 - 2.4
	b_{rn}	0.3 - 3.3
	e^{v}_{n}	0.5 - 4.8
3	P_{rn}	0.0 -10.0
	e^{v}_{n}	0.5 - 4.8
		0.0 - 1.4

TABLE 51

Parameter Ranges - Charts for Method 3

Parameter	Range
HP	0.0 - 9.0
A^2/B	0.0 -11.0
Z_m	0.03 - 9.53
log Φ	0.598-3.9
u	0.0 - 2.75
w	0.004 - 4.27

TABLE 52

Critical Constants and Boiling Points of Components of all Systems

Substance	T_{cn} (°C)	P_{cn} (atmos.)	b_n(boil. pt. at 1 atmos, °C)
Argon	- 122.	48.	- 185.7
N-Butane	153.	36.	0.6
Ethane	32.1	48.8	- 88.3
Ethylene	9.7	50.9	- 103.8
Hydrogen	- 239.9	12.8	- 252.7
Methane	- 82.5	45.8	- 161.4
Nitrogen	- 147.1	33.5	- 195.8

TABLE 53

York & Weber (27) Correction Factor ϕ Data $\phi = (T_c/470)^n$

T_r	1.0	1.05	1.10	1.20	1.3	1.4	1.5	1.6
n	0.37	0.28	0.25	0.20	0.18	0.16	0.15	0.14

TABLE 54

York & Weber Correction Factor ϕ for System M-E, y_m - 0.319, 0.555

T, °K	294.3	327.6	361.1	394.4

y_M - 0.319 T_{cm}, °K = 268.7

T_r	1.091	1.219	1.342	1.468
n	0.255	0.196	0.172	0.153
ϕ	0.867	0.896	0.9085	0.918

y_M = 0.555 T_{cm}, °K = 241.7

T_r	1.220	1.355	1.493	1.632
n	0.196	0.169	0.151	0.137
ϕ	0.878	0.894	0.905	0.913

TABLE 55

Effect of York & Weber ϕ Correction Factor to $\Delta H/T_{cm}$ on Method 1 Activity Coefficients for System M - E

$T - 21^\circ$ C, $y_M = 0.319$, $\phi = 0.867$

P (atm)	17.02	51.06	85.10	119.14	153.18	187.22	221.26
$\Delta H/T_{cm}$	0.71	2.65	5.58	6.80	7.23	7.43	7.57
Methane - M							
Exper.	1.000	1.000	1.000	1.000	1.000	1.000	1.000
without corr.	0.996	0.981	1.108	1.046	0.963	0.911	0.879
with corr.	0.984	0.935	1.002	0.927	0.848	0.799	0.769
Ethane - E							
Exper.	0.887	0.635	0.418	0.301	0.248	0.222	0.208
without corr.	0.873	0.595	0.386	0.286	0.241	0.218	0.204
with corr.	0.879	0.609	0.403	0.302	0.256	0.232	0.217

TABLE 56

Effect of York & Weber ϕ Correction Factor to $\Delta H/T_{cm}$

vs. Method 1 Activity Coefficients for System M - E

$T = 54.4^{\circ}$ C, $y_M = 0.319$, $\phi = 0.896$

P(atm)	17.02	51.06	85.10	119.14	153.18	187.22	221.26
$\Delta H/T_{cm}$	0.56	1.80	3.27	4.62	5.35	5.75	6.0

Methane - M

Exper.	0.978	0.967	0.988	1.017	0.944	0.958	0.924
Without corr.	1.011	1.016	1.042	1.105	1.068	1.047	1.022
With corr.	1.002	0.991	0.995	1.035	0.993	0.965	0.939

Ethane - E

Exper.	0.921	0.753	0.598	0.484	0.413	0.372	0.346
Without corr.	0.910	0.724	0.561	0.458	0.384	0.346	0.322
With corr.	0.914	0.732	0.572	0.471	0.398	0.360	0.335

TABLE 57

Effect of Yark and Weber ϕ Correction Factor to $\Delta H/T_{cm}$ on Method 1 Activity Coefficients for System M - E

$T = 88^\circ$ C, $y_M = 0.319$, $\phi = 0.9085$

P(atm)	17.02	51.06	85.10	119.14	153.18	187.22	221.26
$\Delta H/T_{cm}$	0.45	1.38	2.42	3.5	4.35	4.78	5.17
				Methane - M			
Exper.	0.985	0.971	0.975	0.981	0.975	0.961	0.944
Without corr.	1.013	1.037	1.063	1.130	1.187	1.182	1.195
With corr.	1.008	1.019	1.032	1.081	1.125	1.116	1.119
				Ethane - E			
Exper.	0.942	0.821	0.708	0.616	0.549	0.503	0.472
Without corr.	0.931	0.799	0.671	0.580	0.522	0.472	0.439
With corr.	0.942	0.805	0.681	0.591	0.529	0.485	0.452

TABLE 58

Effect of York and Weber ϕ Correction Factor to $\Delta H/T_{cm}$ on Method 1 Activity Coefficients for System M - E

T = 121.2° C, y_M = 0.319, ϕ = 0.918

P(atm)	17.02	51.06	85.10	119.14	153.18	187.22	221.26
$\Delta H/T_{cm}$	0.38	1.14	1.90	2.70	3.45	4.00	4.37
			Methane - M				
Exper.	0.988	0.975	0.974	0.978	0.981	0.981	0.977
Without corr.	1.019	1.033	1.079	1.129	1.181	1.218	1.237
With corr.	1.015	1.021	1.048	1.095	1.138	1.165	1.178
			Ethane - E				
Exper.	0.956	0.867	0.783	0.712	0.655	0.613	0.582
Without Corr.	0.949	0.833	0.752	0.674	0.609	0.563	0.531
With corr.	0.951	0.837	0.759	0.684	0.620	0.574	0.544

TABLE 59

Effect of York and Weber ϕ Correction Factor to $\Delta H/T_{cm}$ on Method 1 Activity Coefficients for System M- E

$T = 21^\circ$ C, $y_M = 0.555$, $\phi = 0.878$

P(atm)	17.02	51.06	85.10	119.14	153.18	187.22	221.26
$\Delta H/T_{cm}$	0.56	1.81	3.35	4.70	5.38	5.79	6.00
			Methane - M				
Exper.	0.965	0.918	0.891	0.860	0.816	0.773	0.736
Without corr.	0.985	0.931	0.902	0.892	0.850	0.818	0.791
With corr.	0.980	0.914	0.871	0.844	0.803	0.774	0.743
			Ethane - E				
Exper.	0.894	0.681	0.500	0.379	0.311	0.275	0.252
Without corr.	0.887	0.652	0.479	0.365	0.304	0.269	0.249
With corr.	0.894	0.676	0.501	0.388	0.327	0.290	0.270

TABLE 60

Effect of York and Weber ϕ Correction Factor to $\Delta H/T_{cm}$ on Method 1 Activity Coefficients for System M-E

$T = 54.4^\circ$ C, $y_M = 0.555$, $\phi = 0.894$

P(atm)	17.02	51.06	85.10	119.14	153.18	187.22	221.26
$\Delta H/T_{cm}$	0.46	1.40	2.41	3.49	4.32	4.78	5.10
				Methane - M			
Exper.	0.976	0.938	0.910	0.887	0.863	0.838	0.814
Without corr.	0.995	0.971	0.961	0.970	0.973	0.953	0.941
With corr.	0.990	0.959	0.938	0.939	0.935	0.916	0.898
				Ethane - E			
Exper.	0.927	0.779	0.643	0.533	0.457	0.409	0.379
Without corr.	0.911	0.745	0.607	0.499	0.425	0.382	0.352
With corr.	0.916	0.757	0.624	0.518	0.447	0.404	0.373

TABLE 61

Effect of York and Weber σ Correction Factor to $\Delta H/T_{cm}$ on Method 1 Activity Coefficients for System M-E

$T = 88^\circ$ C, $y_M = 0.555$, $\sigma = 0.905$

P(atm)	17.02	51.06	85.10	119.14	153.18	187.22	221.26
$\Delta H/T_{cm}$	0.36	1.08	1.82	2.53	3.25	3.80	4.22
				Methane - M			
Exper.	0.981	0.952	0.928	0.908	0.891	0.876	0.861
Without corr.	1.001	0.990	1.002	1.005	1.010	1.020	1.022
With corr.	1.000	0.981	0.988	0.984	0.982	0.988	0.988
				Ethane - E			
Exper.	0.931	0.842	0.744	0.660	0.594	0.545	0.511
Without corr.	0.937	0.807	0.709	0.619	0.541	0.490	0.451
With corr.	0.939	0.815	0.722	0.635	0.559	0.509	0.472

TABLE 62

Effect of York and Weber σ Correction Factor to $\Delta H/T_{cm}$ on Method 1 Activity Coefficients for System M-E

$T = 121.^{\circ}$ C, $y_M = 0.555$, $\sigma = 0.913$

P(atm)	17.02	51.06	85.10	119.14	153.18	187.22	221.26
$\Delta H/T_{cm}$	0.31	0.95	1.52	2.11	2.61	3.03	3.34
			Methane - M				
Exper.	0.986	0.961	0.942	0.926	0.915	0.905	0.898
Without corr.	1.008	1.022	1.031	1.038	1.038	1.042	1.043
With corr.	1.005	1.014	1.019	1.021	1.016	1.018	1.018
			Ethane - E				
Exper.	0.962	0.886	0.814	0.752	0.700	0.659	0.628
Without corr.	0.949	0.853	0.771	0.692	0.630	0.575	0.547
With corr.	0.953	0.860	0.781	0.706	0.647	0.597	0.571

TABLE 63

% Deviation of Calculated from Experimental Activity Coefficients - Method 1 - M-E - with and without York & Weber ϕ corr. to $\Delta H/T_{cm}$

T = 21, 54.5, 88, 121.2° C y_M = 0.319, 0.555

	Methane		Ethane	
P(atm)	with	without	with	without
17.02	1.94	2.25	0.65	1.12
51.06	3.74	4.40	2.78	3.93
85.10	4.29	7.58	3.15	5.35
119.14	7.19	9.97	3.28	5.75
153.18	10.37	12.80	4.54	6.26
187.22	11.31	14.57	4.24	6.75
221.26	12.91	16.36	5.47	7.18
Avg. for all (56) points	7.40	9.72	3.39	5.18
	24% improvement in accuracy		35% improvement in accuracy	

LIST OF SYMBOLS USED

Notes: 1. Subscript or superscript "L" refers to property of liquid and "v" to vapor where distinction is necessary. Capitalized subscripts other than "L" refer to a component. Subscript "n" refers to component "n".

2. With no distinction reference is made to vapor.

a - constant in Method 3 equation of state (Eq. 7).

A - system primary parameter in Method 3 - Summation $(y_n A_n)$

A_n- component primary parameter im Method 3

b_o- constant in Method 3 equation of state (Eq. 7)

B - system primary parameter in Method 3 - Summation $(y_n B_n)$

B_n- component primary parameter in Method 3

b_m- molal average atmospheric boiling point of mixture

b_n- component atmospheric boiling point

b_{rm}- pseudocritical boiling point of system

$\bar{\phi}$ - system secondary parameter in Method 3

ϕ_{γ} component activity coefficient (vapor)

ϕ - York and Weber correction factor for $\Delta H/T_c$

f_m- fugacity of mixture at system T, P and y

f_n- fugacity of component at system T, P and y

F - free energy

$\Delta H/T_c$- enthalpy correction for pressure

K_f- thermodynamic equilibrium constant for gaseous reaction

K_n- component vaporization ratio

$K^v{}_n$- component vaporization equilibrium constant

LIST OF SYMBOLS USED (Cont'd.)

ϕ_n^v - component parameter in Method 2

P - system pressure

P'_n - vapor pressure of component

P_{cn} - critical pressure of component

P_{cm} - pseudo critical pressure of mixture

P_{rm} - pseudo reduced pressure of mixture

P_{rn} - reduced pressure of component

R - universal gas constant

T - system temperature

T_{cm} - pseudo critical temperature of mixture

T_{rm} - pseudo reduced temperature of mixture

T_{rn} - reduced temperature of component

x_n - mol fraction of component in liquid

u - secondary parameter of Method 3

w - secondary parameter of Method 3

V_m - fugacity coefficient of mixture

y_n - mol fraction of component in vapor

Z_m - compressibility factor of mixture

T_{cn}- component critical temperature

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