CORRELATION OF EQUILIBRIUM DATA FOR METHANE BINARIES THROUGH USE OF SOLUBILITY PARAMETERS

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PREFACE

The variation of methane equilibrium behavior with chemical nature of solvents has not always been recognized. Indeed, the relatively ideal behavior of methane in the vapor phase is often accepted as a prima facie case for ideal behavior in general; whereas, in fact, substantial deviations exist in the liquid phase.

A satisfactory correlation for the prediction of methane phase behavior at various pressures and temperatures in all types of solvents does not exist. It has been the purpose of this work to test a correlation technique centered around the regular solution theory of Scatchard and Hildebrand for liquids. For the coexisting vapor phase, the Redlich-Kwong equation of state has been used as a correlating tool.

Utility of the method of correlation is demonstrated in certain regions, but a satisfactory prediction of vapor-liquid equilibrium near the critical point of mixtures is not obtained. Thus, a need for additional work in this area is indicated.

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CHAPTER I

INTRODUCTION

The Problem

In the past decade the petroleum industry has become much more diversified. Catalytic cracking and catalytic reforming processes are now commonplace. These processes, plus a host of others, have amplified the significance of nonaliphatic hydrocarbons. There is now a more pressing need for information on the equilibrium phase behavior of mixtures involving a variety of chemical species. None of the widely used K correlations (5, 11, 13, 21, 26, 37, 38, 61, 62) can be considered adequate.

Specifically, a correlation is needed which represents the complete spectrum of hydrocarbons and related compounds encountered in the petroleum industry. Further, the correlation should be one which can be readily adapted for use on a digital computer for maximum utilization. The general problem is wide in scope, but logically divided into two separate problems.

(1) The determination of chemical composition dependent K correlations for the individual hydrocarbons.

(2) The determination of a generalized K correlation applicable to all hydrocarbons.

A solution of the first problem must precede solution of the second problem. This study deals only with solution of the first problem for methane. Once the first problem has been solved for a large number of individual hydrocarbons, then it is anticipated that generalization would be possible with three-parameter methods such as used by Lydersen, Greenkorn, and Hougen (36) and Curl and Pitzer (10) for correlation of pure component properties.

The first problem has been approached by a method suggested by Edmister (14) in a paper presented at the 39th annual convention of the Natural Gasolene Association of America (N.G.A.A.) in Houston, Texas, April, 1960. Edmister proposed a correlation based on the following expression:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^L}{\gamma_i^V} K_i' \qquad \text{(I-1)}$$

where: $K_i' = \frac{f_i^L}{f_i^V}$ = the ideal K value for component "i" in the mixture.

$\gamma_i^L = \frac{\bar{f}_i^L}{f_i^L x_i}$ = the activity coefficient of component "i" in the liquid phase.

$\gamma_i^V = \frac{\bar{f}_i^V}{f_i^V y_i}$ = the activity coefficient of component "i" in the vapor phase.

Use of Equation I-1 involves the problem of finding methods for calculating the liquid activity coefficient, γ_i^L, and the vapor activity coefficient, γ_i^V, such that consistent values of the ideal equilibrium constant ($K_i' = f_i^L/f_i^V$) are obtained regardless of variations in chemical nature of the solvent. The ideal equilibrium constant is a ratio of the liquid phase standard state fugacity, f_i^L, and the vapor phase standard state fugacity, f_i^V. These standard states are defined to be the pure component fugacity at the temperature and pressure of the system in the corresponding state of aggregation. Thus, the value of K_i' for a particular solute should be a function of temperature and pressure only. This property is the criterion for an acceptible combination of methods for calculation of γ_i^L and γ_i^V.

Purpose and Scope of the Study

It has been the purpose of this study to explore the proposed correlation method by applying it to experimental vapor-liquid equilibrium data for methane in binary mixtures.

Successful application of Equation I-1 depends upon the comprehensiveness of the methods used for calculating vapor and liquid phase activity coefficients. The vapor phase activity coefficient, γ_i^V, must correct for departure from the Lewis and Randall rule (34) and perfect gas behavior. Analytical calculation of γ_i^V is possible through use of an equation of state. The Redlich-Kwong equation of state (50) has been used in this study. Calculations were performed using the IBM 650 digital computer with a program prepared by Erbar and Thompson (17).

The liquid phase activity coefficient, γ_i^L, corrects for non-ideal solution behavior due to differences in molecular size, volatility and chemical nature. Equations of the van Laar and Margules type are commonly used to predict γ_i^L. The van Laar type equation developed by Scatchard (60) in his quantitative treatment of the "regular" solution theory has been used in this study. With this treatment the van Laar constants are functions of system temperature and physical properties of the solute and solvent. These properties are solubility parameter, δ_i, and molar liquid volume, $\underline{V}_i^L$. Solubility parameter is the name used by Hildebrand (25) to define the important property,

$$\delta_i = \left[\frac{\Delta \underline{E}_i^V}{\underline{V}_i^L}\right]^{\frac{1}{2}} \tag{I-2}$$

where $\Delta \underline{E}_i^V$ is the energy required to vaporize one mole of liquid to a state of infinite volume and $\underline{V}_i^L$ is the molar liquid volume.

The indicated methods of calculating activity coefficients were used to determine ideal equilibrium constants, K_i', in seventeen experimental binary mixtures. Twelve of these binaries included methane as the solute (see Table I). Over three-hundred selected data points were considered. The calculated activity coefficients and ideal equilibrium constants are included in the tables of Appendix A.

Methane binaries were selected for study for three reasons:

(1) Methane binary data are plentiful, especially from the publications of Sage, Lacey and co-workers.

(2) Data were available for methane in a variety of solvents. Two aromatic and three naphthenic solvents are included.

(3) The widely different observed equilibrium constants for methane provide a stringent correlation test. This is illustrated in Table II where the observed K values at 150°F for the binaries of this study are recorded at 400 and 1000 psia.

Multicomponent mixtures have not been considered. It is accepted that for a correlation to be successful in general, it must first predict the behavior of binary mixtures.

This study is related to a similar study by Pigg (45) on ethane binaries. Pigg's work, which was sponsored by the N.G.A.A., involved a slightly different correlation technique. His conclusion that solubility parameter differences are essentially independent of temperature has been used in this study to simplify the correlation scheme.

TABLE I

BINARIES STUDIED

Binary Number	Solute	Solvent	Author	Reference
1.	Methane	Propane	Sage, Lacey and Schaafsma	(54)
2.	Methane	Propane	Reamer, Sage and Lacey	(48)
3.	Methane	Isobutane	Olds, Sage and Lacey	(40)
4.	Methane	n-Butane	Sage, Lacey and Hicks	(57)
5.	Methane	n-Pentane	Olds, Sage and Lacey	(41)
6.	Methane	n-Heptane	Reamer, Sage and Lacey	(49)
7.	Methane	Decane	Reamer, Olds, Sage and Lacey	(46)
8.	Methane	Benzene	Elbishlawi and Spencer	(16)
9.	Methane	Toluene	Elbishlawi and Spencer	(16)
10.	Propane	Isopentane	Vaughan and Collins	(64)
11.	Propane	n-Pentane	Sage and Lacey	(56)
12.	Propane	Benzene	Glanville, Sage and Lacey	(20)
13.	n-Butane	n-Heptane	Kay, W. B.	(30)
14.	n-Pentane	n-Heptane	Katz and Brown	(29)
15.	Methane	Cyclopentane	Clark, G. A.	(9)
16.	Methane	Cyclohexane	Clark, G. A.	(9)
17.	Methane	Methylcyclohexane	Clark, G. A.	(9)

TABLE II

OBSERVED METHANE K VALUES
(150°F)

Solvent	Reference	400 Psia	1000 Psia
Propane	(54)	6.18	1.89
Propane	(48)	4.76	1.60
Isobutane	(40)	6.24	2.40
n-Butane	(57)	7.17	2.81
n-Pentane	(41)	8.05	3.30
n-Heptane	(49)	8.61	3.75
Decane	(46)	8.68	3.95
Benzene	(16)	16.20	6.69
Toluene	(16)	14.33	5.75
Cyclopentane	(9)	11.61	4.66
Cyclohexane	(9)	12.98	5.21
Methylcyclohexane	(9)	11.42	4.60

CHAPTER II

METHOD OF CORRELATION

Basis Equation

The basic correlating expression of this study was introduced in Chapter I. Rearrangement of Equation I-1 to be explicit for the ideal equilibrium constant, K_i', gives a more useful form for the present discussion.

$$K_i' = \frac{f_i^L}{f_i^V} = \frac{y_i}{x_i} \frac{\dfrac{\bar{f}_i^V}{\bar{f}_i^V y_i}}{\dfrac{\bar{f}_i^L}{f_i^L x_i}} = \frac{y_i}{x_i} \frac{\gamma_i^V}{\gamma_i^L} \qquad \text{(II-1)}$$

The ideal equilibrium constant, K_i', is the quantity to be correlated. It is observed to be a function of y_i/x_i, γ_i^V and γ_i^L. Values of y_i/x_i are available from experimental data, but the quantities γ_i^V and γ_i^L are to be calculated. With successful methods of calculation for γ_i^V and γ_i^L, the ideal equilibrium constant, K_i', for a particular solute will be independent of solvent composition and dependent only on temperature and pressure.

Standard States

Activity coefficient calculations involve the concept of standard state fugacity. Thus, standard states will be discussed briefly.

An activity coefficient is by definition a ratio of the activity of a component in a given phase to the mole fraction of that component in the same phase. That is,

$$\gamma_i^V = \frac{a_i^V}{y_i} \qquad \text{(II-2)}$$

where vapor phase notation is used, but the discussion applies to the liquid phase as well. Further, activity is defined to be the ratio of fugacity to a standard state fugacity,

$$a_i^V = \frac{\bar{f}_i^V}{f_i^o} \qquad \text{(II-3)}$$

Before the activity coefficient can be calculated the standard state fugacity, f_i^o, must be defined. The most meaningful standard state fugacity is that of the pure component at the same temperature and pressure and corresponding physical state. With the standard state fugacity defined in this manner, the activity coefficient measures the effect of composition on the activity of the component relative to the pure state. This is in harmony with the ultimate goal of predicting all solution properties in terms of those of the pure components. Further, with this definition of standard state fugacity, f_i^o becomes equal to f_i^V or f_i^L, as the case may be. The activity coefficients of Equation II-1 are based on pure component standard state fugacities.

Two obvious complications arise when using the pure component as a reference for defining the standard state. First, a component in the gas phase may be present at a pressure exceeding its vapor pressure, thus the vapor state for the pure component is hypothetical, or, second, a component in the liquid phase may be present at a temperature exceeding its critical temperature, then the pure component liquid is hypothetical. These points have been well covered in recent papers by Edmister (14) and Prausnitz (44). As indicated by Edmister, the exact values of the standard state fugacities are not nearly so important as their consistency. In the separate treatments of liquid and vapor phase activity coefficients the methods used to obtain consistent standard state fugacities in each case, for both the real and hypothetical regions, will be discussed.

From the choice of standard states discussed in the preceding paragraphs, it is apparent that as $x_i \rightarrow 1$, $\gamma_i^L \rightarrow 1$. Likewise, as $y_i \rightarrow 1$, $\gamma_i^V \rightarrow 1$. Moreover, the approach of γ_i^L or γ_i^V to unity at any other concentrations would indicate ideal solution behavior and applicability of the Lewis and Randall rule.

Vapor Phase Activity Coefficient

The vapor phase activity coefficients, γ_i^V, used in Equation II-1 have been determined from the ratio of two fugacity coefficients calculated through use of the Redlich-Kwong (50) equation of state.

$$\gamma_i^V = \frac{\phi_i}{\phi_i^o} \tag{II-4}$$

where,

$$\phi_i = \frac{\bar{f}_i^V}{Py_i} \tag{II-5}$$

and,

$$\phi_i^o = \frac{f_i^V}{P} \tag{II-6}$$

Equation II-5 is an expression for the fugacity coefficient of component "i" in the vapor phase mixture; whereas, Equation II-6 is the fugacity coefficient of pure component "i" in the vapor state at the same temperature and pressure. The Redlich-Kwong equation of state was used to calculate these fugacity coefficients because it is believed to offer the best compromise between simplicity and rigor. A complete discussion of this equation, and the expressions for fugacity coefficients derived from it, is presented in Appendix C. A sample activity coefficient calculation is given in Appendix G. All of the vapor phase activity coefficients calculated in this study are included in the tables of Appendix A.

With this method of determining the vapor phase activity coefficient, the standard state fugacity is consistently defined by the Redlich-Kwong equation of state; that is, $\left|f_i^V\right|_{SS} = P \left|\phi_i^o\right|_{R-K.}$ No complications arise in the treatment of the methane solute, the primary concern of this report, since in all cases the system temperature is above the critical temperature of methane, hence a real pure component vapor state is assured. Difficulties are encountered in the calculation of standard state fugacities for the hypothetical solvent vapor. This does not impose a restriction on the specific study of this report, but it would affect a general study. The problem has been averted in a general study with a slightly different correlation technique used by Chao and Seader (8).

The vapor phase activity coefficients, calculated as described, are, of course, no better than the Redlich-Kwong equation of state representation of the mixture and pure component behavior. Use of this method requires only a knowledge of critical pressure and critical temperature for each component.

It is the function of the vapor phase activity coefficient to correct for departure from perfect gas and ideal solution behavior.

Liquid Phase Activity Coefficient

The method of determining the liquid phase activity coefficients, γ_i^L, is a key point in the correlation. The requirements on γ_i^L are far more stringent than on γ_i^V, for in the strictest sense, it should account for chemical dissimilarity between solute and solvent, as well as the differences in molecular size and volatility. Corrections for chemical dissimilarity are essential if the method is to be an improvement over some of the previous methods which are discussed in Chapter III.

A van Laar type (32) equation is used in this study to determine the γ_i^L values needed in Equation II-1. For a binary mixture, equations of the van Laar type may be expressed in the following form:

$$\ln \gamma_1^L = \left| \frac{A}{\frac{Ax_1}{Bx_2} + 1} \right|^2 \qquad \text{(II-7)}$$

$$\ln \gamma_2^L = \left| \frac{B}{\frac{Bx_2}{Ax_1} + 1} \right|^2 \qquad \text{(II-8)}$$

In van Laar's original development the A and B values in the foregoing equations were expressible in terms of constants in the van der Waals equation of state. Later van Laar and Lorenz (1925) improved the van der Waals theory and the A and B values then became functions of the van der Waals attraction term (a) and molar liquid volumes. Scatchard (60) in 1931, through his quantitative treatment of the "regular" solution theory, made it possible to obtain Equations II-7 and II-8 without any connection to the van der Waals equation. Scatchard's development is covered thoroughly in Appendix B.

Carlson and Colburn (7a) have discussed the utility of Equations II-7 and II-8 for the extention of data in systems of widely different chemical nature where the values of A and B are determined empirically. Scatchard's treatment is significant because it relates the values of A and B to physical properties of the solute and solvent. From Appendix B the derived expressions for A and B are:

$$A = \frac{V_1^L}{RT} (\delta_1 - \delta_2)^2 \qquad \text{(II-9)}$$

$$B = \frac{V_2^L}{RT} (\delta_1 - \delta_2)^2 \qquad \text{(II-10)}$$

The use of these expressions for A and B in conjunction with Equations II-7 and II-8 does not constitute a rigorous method for determination liquid phase activity coefficients. However, if a solution has the properties which Hildebrand (22) described as "regular", or more specifically those properties assumed in the Scatchard development, then the method is applicable. Scatchard's assumptions are repeated here for convenience. They are:

(1) Ideal entropy of mixing.

(2) No volume change on mixing.

(3) Orienting and chemical effects are absent.

(4) Pair additivity.

(5) Geometric mean for cohesive energy of unlike pairs.

Hydrocarbon mixtures often approach the requirements of a "regular" solution. Prausnitz, Edmister and Chao (43) were the first to introduce this concept as a hydrocarbon vapor-liquid equilibria correlation tool.

The standard state fugacities for γ_1^L and γ_2^L are those of the respective pure component liquids at the temperature and pressure of the mixture. This is not readily apparent without referring to Scatchard's development, though this would be suspected from the symmetry of the equations. Implicitly, consistent standard state fugacities are defined for both the real and hypothetical liquid regions by use of Watson's equation (65) for molar liquid volume.

$$\underline{V}_i^L = \underline{V}_1 \omega_1 (5.7 + 3.0\ T_{r_i}) \qquad \text{(II-11)}$$

The full significance of this equation is discussed in Appendix E. Equation II-11 has been used by Smith and Watson (62) in a correlation discussed in Chapter III. The fact that this equation does approximate actual liquid volumes is illustrated by a sample calculation in Appendix F.

Solubility parameters are needed to complete the calculation for A and B. These parameters are functions of temperature and essentially independent of pressure (25, 43). However, Pigg (45) has observed that temperature has only a small influence on the difference in solubility parameters. Thus, since the equations for A and B do involve a difference in solubility parameters, it is possible to use a constant set of values without introducing serious errors. The constant set of values used in this work is listed in Table III. These values are from Hildebrand and Scott (25) measured at 25°C, except for the values for methane and propane which were obtained by Prausnitz, Edmister and Chao (43). Ethane was not used in this study, but back-calculations made by Pigg indicate a value of 6.3 to be preferred. Further, Pigg found a value of 8.5 to be more suitable for cyclohexane in his correlation of ethane binaries.

Hildebrand's solubility parameter was introduced and defined in Chapter I. The potency of this parameter in accounting for the chemical nature of hydrocarbons is apparent from the calculated liquid phase activity coefficients for methane in the various hydrocarbon solvent types listed in the tables of Appendix A. From Table III, the paraffinic hydrocarbons are observed to have lower solubility parameters than the aromatics, with naphthenic hydrocarbon parameters intermediate to the two. In general, the solubility parameter increases with increasing molecular weight in a homologous series. This increase is more pronounced at lower molecular weights. Higher equilibrium constants are predicted for methane in aromatic solvents due to the wide differences in solubility parameter. This prediction is in agreement with fact.

The quantity $(\underline{V}_1 \omega_1)$ in the Watson equation is a constant for each substance as pointed out in Appendix E. The values listed in Table III are the same as reported by Hougen and Watson (27).

A sample liquid phase activity coefficient calculation is given in Appendix F.

Experimental data at selected temperatures and pressures from the binaries listed in Table I were processed by the methods of this chapter to obtain the ideal equilibrium constants listed in the tables of Appendix A.

In summary, there are two important features of the correlation method described in this chapter.

(1) The methods of calculation are analytical.

(2) A parameter is introduced to account for chemical dissimilarity.

The following assumptions were made in obtaining a wieldy correlation framework.

(1) Redlich-Kwong equation of state representation of pure component and mixture properties in the vapor phase.

(2) Scatchard's assumptions for "regular" solutions.

(3) Applicability of Watson's expression for molar liquid volume.

(4) Temperature independence of solubility parameter differences.

The influence of these assumptions on the correlation results is discussed in Chapter V.

TABLE III

CONSTANTS FOR VAPOR AND LIQUID ACTIVITY COEFFICIENT CALCULATIONS

	Watson Expansion Factor $\underline{V}_1 \omega_1$ (27)	Hildebrand Solubility Parameter δ (25)	T_c ° K	P_c (psia) (38)
CH_4	5.00	5.45 (43)	190.6	673.1
C_3H_8	9.70	6.00 (43)	370.0	617.4
iC_4H_{10}	11.69	6.25	408.0	529.1
nC_4H_{10}	11.62	6.70	426.1	550.7
iC_5H_{12}	14.08	6.75	461.0	483.0
nC_5H_{12}	14.07	7.05	470.0	489.5
nC_7H_{16}	18.96	7.45	540.0	396.9
$nC_{10}H_{22}$	26.28	7.75	619.5	320.0
Cyclopentane	11.22	8.10	512.0	654.7
Cyclohexane	14.07	8.20	554.0	561.4
Methylcyclohexane	16.51	7.85	572.0	504.4
Benzene	11.64	9.15	562.0	714.0
Toluene	14.15	8.90	594.0	611.0

Note: Units of expansion factor and solubility parameter are

$V_1 \omega_1$	cc/g-mol
δ	$(cal/ml)^{1/2}$

CHAPTER III

REVIEW OF THE LITERATURE

General Background

A brief review of activities during the past four decades on the development of hydrocarbon vapor-liquid equilibria correlations shows that many simplifications have been made in the rigorous thermodynamic relationship (12, 51):

$$\ln \frac{\overline{f}_i^{\,V}}{f_i^{\,V} y_i} = \frac{1}{RT}\int_0^P (\overline{V}_i^{\,V} - \underline{V}_i^{\,V})\,dP \qquad \text{(III-1)}$$

As written, Equation III-1 applies for the vapor phase, but it is equally rigorous for the liquid phase with proper substitution of liquid volumes and mole fraction. This equation makes use of fugacity, an important concept introduced by G. N. Lewis (34). Fugacity was defined by Lewis in terms of free energy:

$$f = e^{\frac{F-\phi(T)}{RT}} \qquad \text{(III-2a)}$$

Also, as a part of the definition is the requirement,

$$\lim_{P \to 0} \frac{f}{P} = 1 \qquad \text{(III-2b)}$$

Unfortunately, Equation III-1 cannot always be used in a straight forward manner. Often the partial volumes, $\overline{V}_i^{\,V}$, are not available. Further, the pure component molar volume, $\underline{V}_i^{\,V}$, may be hypothetical. To circumvent this difficulty, Lewis and Randall, approximately forty years ago, introduced the simplifying assumption of additive volumes, i.e., $\overline{V}_i^V - \underline{V}_i^V = 0$. At first glance this would seem to be a mild assumption; whereas, in fact, as will be seen later, the assumption is often drastic, especially for the liquid phase. With this simplification Equation III-1 reduces to the expression known as the Lewis and Randall rule:

$$\overline{f}_i^V = f_i^V y_i \qquad \text{(III-3)}$$

Between 1930 and 1940 the first great strides were made toward predicting hydrocarbon vapor-liquid equilibria. By use of the Lewis and Randall rule, the assumption of van der Waals' law of corresponding states and available compressibility data, generalized fugacity correlations were prepared. Two significant equilibrium constant treatments were an outgrowth of the generalized fugacity correlations: (1) The Michigan K's of G. G. Brown (7) and (2) The MIT K's of W. K. Lewis (35).

By definition, $K_i = y_i/x_i$, where y_i is the mole fraction of component "i" in the vapor phase and x_i is the mole fraction of component "i" in the liquid phase. In attempts to predict K values numerous expressions arise, depending upon assumptions used and choice of standard states. Some of the many possibilities are considered by Adler and Palazzo (2).

The Michigan and MIT K's were derived through cognizance of equal chemical potential between phases, assumption of the Lewis and Randall rule for both phases and neglect of pressure influence on liquid fugacity.

$$K_i \text{ (Michigan and MIT)} = \frac{f_{i(VP)}^L}{f_i^V} \qquad \text{(III-4)}$$

where,

$f_{i(VP)}^L$ = liquid fugacity under its vapor pressure and temperature of the mixture.

f_i^V = vapor fugacity at the total pressure and temperature of the mixture.

These correlations did not take into consideration composition of the system and chemical nature of the components. Such inadequacies in the Michigan and MIT K's were recognized early. Except for the inclusion of some experimental data, these correlations did little more than correct for non-ideal gas behavior of the vapor phase. However, these correlations have been used extensively, with success, especially for mixtures of the intermediate paraffin hydrocarbons in areas away from mixture critical point. This fortunate circumstance resulted from the near ideal solution behavior of paraffin hydrocarbons.

If further simplification is made by assuming both perfect gas and ideal solution behavior, then Equation III-1 becomes,

$$K_i(\text{Ideal}) = \frac{P_{VP}}{P_T} \qquad \text{(III-5)}$$

Equation III-5 is recognized to be the same result that would be obtained by combining Raoult's and Dalton's laws. Thus, background of fundamental expression used in predicting hydrocarbon equilibria is traced back to 1887 in the case of Raoult's law and 1805 for Dalton's law. Except to include Henry's law (1802), the general background is complete.

Previous Correlation Methods

There are certain prerequisites for a satisfactory vapor-liquid equilibria correlation method. In the preceding sections the Michigan and MIT correlations were found to lack some of these prerequisites. As early as 1938 Sage and Lacey (55) enumerated the five points to be considered in a precise K correlation:

(1) Pressure.
(2) Temperature.
(3) Critical state of system.
(4) Chemical nature of components.
(5) Composition of the system.

All of these factors are embodied in a rigorous thermodynamic expression for the equilibrium vaporization ratio,

$$K_i = \frac{y_i}{x_i} = \left| \frac{f_i^L}{f_i^V} \right| e^{-\frac{1}{RT}\int_0^P (\Delta \overline{V}_i - \Delta \underline{V}_i)\,dP} \qquad \text{(III-6)}$$

where $\Delta \overline{V}_i = (\overline{V}_i^V - \overline{V}_i^L)$ and $\Delta \underline{V}_i = (\underline{V}_i^V - \underline{V}_i^L)$. Equation III-6 is obtained by considering Equation III-1 for both phases. The equation in this form is of limited usefulness, however, since partial volumes are generally less available than the K values. In fact, K data are often reported without volumetric data on the phases. This is unfortunate since a check for thermodynamic consistency is thus precluded. Equation III-6 is important because it points out the significance of partial volume data. Typically, the equation involves the problem of specifying hypothetical volumes for the pure component in certain regions.

A comparison of Equation III-6 with Equation I-1 will show that they are equivalent. Moreover, the framework of any rigorous correlating method must resolve to Equation III-6. Consideration of some of the previous correlation methods will illustrate this point. For example, Edmister and Ruby (13) used the following expression to prepare a generalized correlation of the Benedict-Webb-Rubin (B-W-R) equation of state (5) results for light hydrocarbons:

$$K_i = \frac{f_i^L / P_i^o x_i}{\bar{f}\ V / P y_i} \, \frac{P_i^o}{P} \qquad \text{(III-7)}$$

where,

$$K_{Raoult's} = \frac{P_i^o}{P} = \frac{\text{vapor pressure}}{\text{system pressure}}$$

In the Edmister-Ruby correlation the boiling point ratio (B_{r_i}) was used as a third parameter to account for composition effects. The standard parameters of reduced temperature and pressure were also used. The boiling point ratio or reduced boiling point was defined as,

$$B_{r_i} = \frac{B}{B_i} = \frac{\text{M.A.B.P. of vapor or liquid-phase mixture, } {}^oR}{\text{Atmospheric boiling point of i th component, } {}^oR}$$

The Kellogg (PTC) K charts (37) which Edmister and Ruby recorrelated were originally developed around the following relationship by Benedict et al.

$$K_i = \frac{\bar{f}_i^L/x_i}{\bar{f}_i^V/Py_i} \frac{1}{P} \qquad \text{(III-8)}$$

Gamson and Watson (18) introduced a correlation structure which is very similar to the one used in this study. Their form is,

$$K_i = K_i' \frac{\gamma_i \bar{\phi}_i^L}{\bar{\phi}_i^V} \qquad \text{(III-9)}$$

where $\bar{\phi}_i^V$ is equivalent to γ_i^V used in this study, and the combined term $\gamma_i \bar{\phi}_i^L$ would be the same as γ_i^L for the correlation method described in Chapter II. Equation III-9 was used by Smith and Watson (62) to prepare a K correlation for what they termed ideal systems. That is, they in effect defined $\gamma_i = 1$ for paraffin hydrocarbon systems. No chemical dissimilarity was considered in $\bar{\phi}_i^L$ which was correlated by them to account only for difference in molecular size and volatility. Through use of the pseudo-critical concept they prepared empirical charts for $\bar{\phi}_i^L$ and $\bar{\phi}_i^V$. This method was also discussed in a publication by Smith and Smith (61). Several shortcomings have prevented wide acceptance of the method. First, the method is tedious to use, second, components of intermediate volatility are not well represented in complex mixtures and, third, the γ_i values have not been developed. However, the method does represent the behavior of methane very well since a number of methane binaries were used in developing the empirical activity coefficients.

A more recent correlation form is the one used by Prausnitz, Edmister and Chao (43).

$$K_i = \frac{\nu_i^L \gamma_i^L}{\phi_i^V} \qquad \text{(III-10)}$$

where: $\gamma_i^L = \dfrac{\bar{f}_i^L}{f_i^L x_i}$ = liquid phase activity coefficient for component "i"

$\phi_i^V = \dfrac{\bar{f}_i^V}{P y_i}$ = vapor phase fugacity coefficient for component "i"

$\nu_i^L = \dfrac{f_i^L}{P}$ = liquid phase fugacity coefficient for pure component "i"

Chao and Seader (8) have used Equation III-10 in an extensive correlation study which included over twenty-five hundred data points. Their results were encouraging. In Chapter V their results for methane are compared with those obtained in this report. Pigg (45) in an even more recent study used Equation III-10 to correlate ethane binary data. Average predicted K values were reported to deviate only 6 percent from experimental values, compared to 26 percent when using the N.G.A.A. (38) convergence pressure method.

There are several other points of interest about Equation III-6. If additive volumes are assumed for both phases, then it reduces to $K_i = f_i^L/f_i^V$. This is identically the Michigan and MIT composition independent K. Further, it will be observed that the integral in the exponent is an energy term, thus there is a striking resemblance of Equation III-6 to the Boltzmann distribution law. This probably is not to be too unexpected since equilibrium constants are expressed in terms of partition functions in statistical thermodynamics. Equation III-6 makes it clear why the exponential form $K = ce^{b/T}$, used by some investigators, as mentioned by Reid and Sherwood (51), has had a degree of success in correlations.

Equations III-7 through III-10 are rigorous correlation forms, thus any failure of these methods to predict actual K values must arise from assumptions and simplifications used in obtaining the various structural components. In the methods discussed thus far, the components have been found by,

(1) equations of state

(2) empirical methods

(3) the solubility parameter technique

In the Kellogg K charts both the vapor and liquid components, $\bar{f}_i^V/Py_i$ and $\bar{f}_i^L/x_i$, were determined by the Benedict-Webb-Rubin equation of state. The Smith and Watson correlation employed essentially empirical methods to obtain $\bar{\phi}_i^V$ and $\bar{\phi}_i^L$. In the Prausnitz-Edmister-Chao expression, Equation III-10, the vapor phase fugacity coefficient is calculated through use of the Redlich-Kwong (50) equation of state (see Appendix C); whereas, the liquid phase activity coefficient, γ_i^L, is predicted from the following equation of Hildebrand and Scott (25) based on "regular" solution behavior:

$$\ln \gamma_i = \frac{\underline{V}_i^L(\delta_i - \bar{\delta})^2}{RT} \tag{III-11}$$

where,

$$\bar{\delta} = \frac{\sum_i x_i \underline{V}_i^L \delta_i}{\sum_i x_i \underline{V}_i^L}$$

Hydrocarbons tend to manifest a behavior in solution corresponding to what Hildebrand (22) termed as "regular". Scatchard (60) is responsible for the first quantitative development of the "regular" solution theory. His development for a binary solution is included in Appendix B. Equation III-11 introduces the important property, solubility parameter, δ , which was defined in Chapter I. From this parameter the method obtains its name.

Once ϕ_i^V and γ_i^L of Equation III-10 have been determined by the described methods, then, δ_i^L, can be correlated with the aid of experimental K values. Chao and Seader used δ_i^L values determined in this manner to obtained a generalized correlation within the framework of Pitzer's (10) modification of the corresponding state principle.

Though solubility parameters, of themselves, are not new, certainly their use in hydrocarbon vapor-liquid equilibria correlation represents a fresh approach to the problem. Except for empirical correction of the Kellogg K charts for "aromaticity" by Solomon (63), none of the foregoing methods but that of Prausnitz, Edmister and Chao can profess to account for chemical dissimilarity.

Up to this point the "convergence pressure" technique of correlation, first introduced by Katz and Brown (29), has not been discussed. The empirical nature of the method does not permit it to be readily associated with some of the more rigorous correlation frameworks to which attention has been directed in the preceding paragraphs. This should not detract from the significance of the method, however, since probably the most widely used K values are those published by N.G.A.A. (38) which are based on the convergence pressure method. The Braun correlation (26) is another of this type.

In words, convergence pressure is defined (for hydrocarbon systems at temperatures above the critical temperature of the lightest component where liquid and vapor phases can coexist) as that pressure, for a specific composition and temperature, at which the K values for all components converge to unity, simultaneously. For binary systems convergence pressure is a unique function of temperature. In multicomponent systems, Hadden (21a) has shown convergence pressure to be a function of temperature and liquid phase composition. These functional relationships have not been expressible in analytical form. This, plus lack of a parameter to account for chemical dissimilarity, imposes limitations on the method. The N.G.A.A. has recognized these weaknesses, as they continue to support work for development of an improved correlation.

Anomalous Behavior of Methane

Since the first attempts to correlate hydrocarbon equilibrium data, methane has proven to be an anomaly. Methane was poorly represented by the original K charts prepared from fugacities (7, 35). Subsequent correlations have included special treatment for methane, even where only paraffin solvents are involved. For example, Hadden (21) provided two graphs of corrections for methane equilibrium ratios determined from his nomograph. Likewise, Edmister and Ruby (13) found it necessary to include separate plots for methane in their generalized temperature-composition function. This was true for both the liquid and vapor phase. Arnold (4) in his work correlated methane equilibria at high pressure in terms of convergence composition, but was forced to exclude butane and lighter solvents to make a single correlation suffice. The special treatment which has been mentioned is necessary, but independent of chemical composition effects.

Sage and Lacey (55) in 1938 made one of the earliest attempts to account for the influence of chemical nature of the solvent on methane equilibrium constants. They were only mildly successful in using an empirical correlating parameter which they called viscosity-gravity factor (A).

$$A = \frac{G - 0.10752 \text{ Log } (S-38)}{1-0.10 \text{ Log } (S-38)} \qquad \text{(III-12)}$$

The viscosity-gravity factor was used in the following equation in conjunction with a K versus P plot of A = 0.82 as reference.

$$K_A = K_{0.82}\left[1 + 1.87(A-0.82) + 13(A-0.82)^2\right] \qquad \text{(III-13)}$$

A number of investigators have considered the Watson or U.O.P. characterization factor ($\overline{K}$) as a means of correlating the influence of solvent chemical composition.

$$\overline{K} = \sqrt[3]{T_B/G} \qquad \text{(III-14)}$$

Clark (9) obtained a fair, but limited, correlation with this parameter when studying his experimental results on naphthenic solvents. Later, Elbishlawi and Spencer (16) extended the data for such a correlation by obtaining experimental equilibrium constants on the methane-benzene and methane-toluene systems at 150°F. In this last study, an empirical expression was found relating Henry's law constant (C) for methane and the characterization factor ($\overline{K}$) for the solvent at a given pressure. The reported expression is:

$$\text{Log } C = 0.0953\,\overline{K} - 4.732 \qquad \text{(III-15)}$$

The authors upon assuming Dalton's law as well as Henry's law obtained

$$K = \frac{y}{x} = \frac{1}{CP} \qquad \text{(III-16)}$$

By elimination of (C) between Equations III-15 and III-16 they determined an expression for the equilibrium constant of methane at 150°F in terms of the $\bar{K}$ factor for the solvent.

$$\text{Log } K = (4.732 - 0.0953\bar{K}) - \log P \tag{III-17}$$

This expression has limited value. First, it does not hold at high pressure. Second, the paraffin hydrocarbons solvents tend to have like characterization factors while the methane equilibrium constant varies substantially.

Solomon (63) also used the characterization factor to determine "aromaticity" corrections for the Kellogg K charts (37). He found a correction factor

$$\alpha = \frac{K_{\text{OBS.}}}{K_{\text{MWK}}} \tag{III-18}$$

could be correlated with the characterization factor ($\bar{K}$).

Availability of Data for Methane

Comparatively, methane binary data are plentiful. Sage, Lacey and co-workers, with the support of API Project 37, have contributed heavily. Nevertheless, there are some significant voids to be filled. For example, additional data are needed at a number of temperature levels on the equilibrium constant of methane in aromatic and naphthenic solvents. At present data are available only at the 150°F level (9, 16), a fact which has limited the extent of this analysis. Further, the fragmentary data do not include volumetric properties of the phases essential for test of thermodynamic consistency. (See Appendix D)

To the author's knowledge, Table I, with the exception of the methane-isopentane binary of Amick, Johnson and Dodge (3), includes all of the methane binary data in the literature not possessing one of the following limitations:

(1) Small amounts of a third component present

(2) Temperatures lower than those selected for study

(3) Solubility data only reported

(4) Data presented in a form prohibiting accurate analysis

The data of Boomer and Johnson (6) for n-hexane and n-heptane are examples of the first limitation. In this case nitrogen was present as a diluent. Ruhemann's (52) data for the methane-ethane binary fall into the second category. Numerous pieces of literature possessed the third limitation. The data of Savyina and Velikovskii (59) for methane binaries of 2,2,3-trimethylbutane and n-nonane could not be used because of poor chart readability.

In general, the equilibrium data have been accepted to be thermodynamically consistent as reported. However, special cases of possible inconsistency have been studied. Sage and Lacey (55) mentioned the lack of high precision in the methane-propane data reported by Sage, Lacey and Schaafsma (54). Later, Reamer, Sage and Lacey (48) reported the results of new determinations for the methane-propane system. Adler et al.(1) obtained an excellent consistency check on the last set of data for the 100°F case.

Savyina and Velikovskii commented on the inaccuracy of the data of Elbishlawi and Spencer (16) for the methane binaries of benzene and toluene at high pressure. Presumably they reached this conclusion from data of their own, since volumetric data are not reported by Elbishlawi and Spencer to permit a consistency check.

CHAPTER IV

METHOD OF PROCESSING THE DATA

P-T-x-y data were compiled from the experimental results reported for the seventeen binary mixtures listed in Table I.

Specific pressures and temperatures were selected for common points of comparison. The selections were made with consideration of the prevalent practice for reporting experimental data in the binaries subject to study. This was done to minimize the amount of graphical interpolation. The conventions of Sage, Lacey and co-workers would appear to be the logical choice, since their work is the most abundant for methane binaries. For temperature, their practice has been to start at 100°F and proceed in successive thirty-degree increments up to temperatures approaching the critical temperature of the heavier component. However, due to the fact that the important naphthenic and aromatic data of Clark (9) and Elbishlawi and Spencer (16), respectively, were reported only at 150°F, it was necessary to include this temperature among those specified for comparison. Thus, the final choice for temperatures in this study has been to start at 100°F and proceed in fifty-degree increments up to the highest temperature reported in the experiment results. In those cases where the experimental data were not available at the selected temperatures, large-scale T-x and T-y plots, with pressure parameters, were prepared to permit accurate interpolation.

The selection of pressure points for comparison presented less of a problem since most investigators have reported results on the same pressure basis. However, in some cases interpolation has been required. The pressures used in this study are those shown in Table IV.

With P-T-x-y data systematically compiled as described in the preceding paragraphs for each binary, then only a knowledge of physical properties for each component is required to permit all of the calculations of the correlation method described in Chapter II. The physical properties used in this study are listed in Table III.

Vapor phase activity coefficients were determined as a ratio of two fugacity coefficients. The mixture and pure component fugacity coefficients were calculated on an IBM 650 digital computer with a program prepared by Erbar and Thompson (17). The calculation method makes use of the Redlich-Kwong equation of state which is discussed in Appendix C. Punched card input data to the computer included the following information.

(1) Composition of the vapor mixture
(2) Pure component critical pressures and temperatures
(3) The gas constant
(4) System temperature and pressure
(5) Number of components
(6) Problem number

A sample vapor phase activity coefficient calculation is presented in Appendix G.

Liquid phase activity coefficients calculations were also done on the computer using a program prepared by Robinson. The equations for the calculation were presented in Chapter II. Punched card input data to the computer included the following information:

(1) Problem number

(2) System pressure

(3) Number of temperatures

(4) Component expansion factors

(5) Component solubility parameters

(6) Component critical temperatures

(7) Composition of the liquid phase

A sample liquid phase activity coefficient calculation is presented in Appendix F.

The results of calculations for over three-hundred data points are summarized in the tables of Appendix A.

CHAPTER V

DISCUSSION OF RESULTS

It is the purpose of this chapter to study the effectiveness of the correlation method outlined in Chapter II when applied to the methane binaries listed in Table I. All calculation results and experimental data are summarized in the tables of Appendix A. Attention will rest heavily on the methane binary data at 150°F, since only at this temperature is information available on aromatic and naphthenic solvents.

Experimental K values for methane at 150°F, in the twelve solvents considered, are shown in Figure 1. This figure clearly illustrates the dependence of K upon the nature of the solvent. It is seen that not only does the K value for methane vary widely with the chemical nature of the solvent, but it also varies appreciably with molecular weight of solvents in the same homologous series. For example, the K value for methane at 1000 psia in benzene is higher than in propane by a factor 3.9, and in decane the K value is higher by a factor 2.3. These observations indicate the need for a powerful correlation method.

Figure 2 shows the degree of success attained with the correlation method of this study in resolving the widely different K values of Figure 1 into a single correlation line. The ideal K values in Figure 2 were calculated from the basic correlating equation (Equation II-1) of Chapter II. Each data point in Figure 2 has been resolved from its counterpart in Figure 1. The results in Figure 2 are encouraging at first glance. But, certain systematic departures from the correlation require attention. This is most apparent for the K value of methane in propane at 800 and 1000 psia.

The general problem is more readily seen in the comparison of Figure 3 with Figure 4. Here, as in the preceding figures, experimental K values and ideal K values, respectively, are plotted for comparison, but at the 250°F temperature level. Fewer data are available at this temperature, but the point is clearly shown that "fanning out" of the ideal K value occurs as mixture critical regions are approached. This problem is obviously one independent of solvent chemical nature, since all of the solvents in Figure 3 and 4 are paraffin hydrocarbons. Moreover, the problem is an old one which, to date, has probably been best handled through the "artistry" of convergence pressure methods. A number of subsequent paragraphs will be devoted to possible solutions of this problem within the framework of the present correlation method.

Attention is now directed toward the boundary conditions which will permit use of the best line of correlation in Figure 2 with a reasonable predicted deviation. The requirement that the vapor phase activity coefficient of methane not deviate more than two (2) percent from unity, as predicted through use of the Redlich-Kwong equation of state, has been found to be a suitable restriction. All of the data of Figure 2 surviving the restriction are listed in Table V. With these data an average absolute deviation of 6.65% is predicted. Further, it has been found that a purely empirical correction, in which the liquid phase activity coefficient is raised to the 0.875 power, reduces the deviation to 5.58%. These results are shown in Table VI. If in addition to the foregoing restriction, ($\gamma^V_{methane} < 1.02$), naphthenic solvents are also excluded, then the ideal K values in Table VII remain. The average standard deviation of the ideal K with these two restrictions is 4.2%. Figure 5 has been prepared by plotting the ideal K values of Table II. When adjusted ideal K values are determined from those of Table VII by applying the 0.875 power correction to the methane liquid phase activity coefficient, the average standard deviation is reduced to 2.1% as shown in Table VIII.

The restriction, ($\gamma^V_{methane} < 1.02$), excludes the three lightest solvents, propane, isobutane and n-butane from the correlation. It is of interest to compare the restrictions considered in this study with those specified by Chao and Seader (8) for their generalized correlation which is also of the solubility parameter type. For hydrocarbons in general (excluding methane), they recommended that the method not be used outside the reduced temperature range of 0.5 to 1.3 (based on the pure component), or at pressures exceeding 2000 psia or 0.8 of the critical pressure of the system. Specifically for hydrogen and methane, they allowed a range of pressures up to 8000 psia, but restricted temperature to 0.93 in pseudo-reduced temperature of the equilibrium liquid mixture, and not to exceed 500°F. The last restriction when considered for this study is equivalent to exclusion of all propane data and most isobutane and normal butane data at high pressure. Thus, it is seen that the restrictions of the two methods are comparable.

In predicting K values for methane, Chao and Seader encountered the largest deviations with naphthenic solvents: about 15 percent, compared to less than 5 percent for methane in other solvents. These results, plus those of this study, point to possible inconsistency in the experiment data (9). These data have been reviewed to see if a thermodynamic consistency check could be made. Unfortunately, the necessary volumetric data on the phases are not available. Similarly, it was not possible to check the aromatic solvent data of Elbishlawi and Spencer (16) which had been questioned at high pressure by Savyina and Velikovskii (59). Consistency calculations are included in Appendix H for the methane-n-pentane binary (41) and the methane-decane (46) binary. A detailed discussion of the calculation method is included in Appendix D.

An observation made by Pigg (45) is related to the problem encountered with naphthenic solvents. Pigg in his ethane binary study found a solubility parameter of 8.5 for cyclohexane to give better results than the value of 8.2 reported by Hildebrand and Scott (25). Though the value of 8.2 has been used in this study, spot checks confirm that the value determined by Pigg would also give better results for the ideal K value of methane in cyclohexane. For example, at 800 psia and 150°F, the ideal K value of methane in cyclohexane is 3.88 using a solubility parameter of 8.2, and 3.45 with a solubility parameter of 8.5 compared to an ideal K value of 3.25 from the best line of correlation in Figure 2. These results tend to remove doubts about the experimental data for methane in naphthenic solvents (since the ethane data were from a different source) and suggest the possibility of revising all the solubility parameters for naphthenes. As a follow-up on this point three back-calculations have been made on each of the three naphthenic solvent binaries to determine the solubility parameters which would satisfy the correlation line of Figure 5. The following very encouraging results were obtained.

Pressure (psia)		Back-Calculated Solubility Parameters		
		Cyclopentane	Cyclohexane	Methycyclohexane
100		8.46	8.66	8.37
800		8.46	8.63	8.33
2000		8.41	8.58	8.20
	Approximate Average	8.45	8.60	8.30

These results tend to verify the correlation line in Figure 5 and suggest new solubility parameters to be used, at least, in methane binaries. By using these new parameters, it appears that the naphthenic data could be included in Table VII with an even lower average deviation obtained. Then by applying the 0.875 power correction to the liquid phase activity coefficient, it is very probable that all of the data, excluding that where $\gamma^{V}_{\text{methane}} > 1.02$, could be represented by a single line of correlation with a deviation of 2 percent or less.

The balance of this discussion will be devoted to an exploration of reasons for the restriction, ($\gamma^{V}_{\text{methane}} < 1.02$). From the obvious importance of volumes in the K expression (Equation III-6), the logical point to start would appear to be in the volume terms. Clearly the Watson equation for liquid volume used in this study is empirical and could only represent an incompressible liquid since no provisions are made for the influence of pressure. This, of course, was a compromise accepted in setting up the correlation framework with the hope that it would be justified by the final results. An even simpler approach was used in the work of Chao and Seader, where no influence of temperature was considered, and a constant set of volumes was used throughout. In Table IX the two volume methods are compared. Ideal K value differences for methane in propane and methane in toluene were calculated by the method of this study, using the respective volumes of the following tabulation.

Component	Molar Liquid Volume (cc/g mole) Watson Equation (150°F)	Chao and Seader (Constants)
Methane	55.1	52.0
Propane	82.0	84.0
Toluene	105.0	106.8

The solvents propane and toluene were selected because, in the case of the former, a wide departure occurred in Figure 2; whereas, ideals K values for methane in the latter were in good agreement with the best line of correlation. At all pressures in Table IX the Chao and Seader volumes tend to hinder correlation. The large differences in ideal K values for methane at 800 and 1000 psia are apparent for both volume methods.

Further comparisons with the Chao and Seader correlation method are made in Figures 6 through 8. In Figure 6, the calculated K values for methane in propane by the Chao and Seader method are beyond their recommended range, but the results are included for comparison. It is observed that by using an accentric factor of $\omega = 0.013$ for methane, the method more closely approximates the actual K value of methane in propane. This however, was not the case for the K value of methane in toluene as shown in Figure 7. Chao and Seader recommended the use of an accentric factor of $\omega = 0$ for methane in their correlation. The reason is obvious from Figure 7. As expected, the calculated K values more closely approximate the actual values as the solvents become progressively heavier. The data for Figures 6 and 7 are shown in Tables X and XI, respectively.

When the assumption is made that all the correction for the ideal K of methane in propane at high pressure should occur in the liquid phase activity coefficient, and specifically in the volume term, it is seen that an activity coefficient of less than unity is required, which in turn requires that the molar liquid volume of methane be negative. This is absurd for actual molar volume and unlikely for partial molar volume with any conceivable extrapolation of the partial volume diagram of Sage and Lacey (58). In the reduced partial volume plot for gases in liquid solutions at infinite dilution prepare by Prausnitz (42), negative volumes are not indicated. In fact, Prausnitz's plot, which has reduced temperature as the abscissa and solubility parameter as a parameter, predicts higher partial volumes for methane in the solvents with the lowest solubility parameter. This is the reverse of the correction needed. Hildebrand and Gjaldbaek (24) have reported partial molar volumes for dissolved methane at 25°C and atmospheric pressure in widely different solvents which are in remarkably good agreement with the Watson volume as shown in the following summary:

Solvent	Methane Partial Volume cc/g mole
C_7F_{16}	68.4
C_6H_{14}	60.0
$C\ Cl_4$	52.4
C_6H_6	52.0
$C\ S_2$	56.1
Watson Volume	51.9

Further, it has been observed that the compressibility of dissolved gases is approximately the same as for normal liquids (33). All of these facts point to negative volumes being explainable only from an empirical point of view. An alteration of the Watson equation (which has been successful in predicting both partial liquid volumes and actual liquid volumes•••• see Appendix F) to provide negative volumes in certain regions is difficult to conceive, and seems unjustified.

If the liquid volume is accepted to be positive and it is still required that correction be made in the liquid activity coefficient, then this can only be done by altering the form of the Scatchard-Hildebrand equation, since the solubility parameter difference term is squared and, hence, always positive. Failure of the Scatchard-Hildebrand equation to predict negative deviations comes from the assumption of the geometric mean for cohesive energy density between unlike molecules. If this assumption is not made a third parameter is introduced which would conceivable account for negative deviations. Though a third parameter would undoubtedly introduce additional flexibility for correlation, it still remains that negative deviations for solutions of this type would be difficult to explain.

The regularity of the divergence with molecular weight in Figure 4 suggests the influence of differences in molecular size on randomness of mixing. Hildebrand and Scott (25) have shown that for athermal mixing the partial molar entropy of mixing is given by the following expression if free volumes are assumed to be proportional to molar volumes.

$$\Delta \overline{S}_i = -R \left[\ln \phi_i + \phi_j \left[1 - \frac{\underline{V}_i}{\underline{V}_j} \right] \right]$$

This expression reduces to, $\Delta \overline{S}_i = -R \ln x_i$, when the solute and solvent have equal molar volumes, thus corresponding to the entropy term used in the Scatchard development. It is therefore indicated that methane behavior in propane should be more nearly ideal than in some of the heavier solvents with greater molar volumes. However, as pointed out by Hildebrand

and Scott, the departure from ideal entropy of mixing is usually small, except when dealing with very large molecules such as those in polymers.

There is another explanation for the liquid activity coefficient being in error which perhaps overshadows any of those previously discussed; that is, the mixing process is not at constant volume. Obviously, since methane is above its critical temperature it must be present in the gaseous state prior to mixing, thus a large volume change must occur when the methane is dissolved into the liquid state. However, it is difficult to reconcile this explanation with the fact that the mixtures involving the heavier solvents have greater percentages of methane present in the liquid phase at higher pressure and yet are apparently well behaved.

Even though the Scatchard-Hildebrand equation is not strictly applicable to gas-liquid solutions without modification, as pointed out by Prausnitz (42), its tremendous utility as a semi-theoretical correlation method has been demonstrated in this study and in others (43, 8, 45).

In the preceding paragraphs an attempt has been made to find an explanation for the deviations in Figure 2 in terms of the liquid phase activity coefficient. That the deviation does exist in the liquid phase activity coefficient is a belief held by Chao and Seader (8). In the opinion of the author, the question is still open, for certainly the demands on an equation of state are severe when attempting to predict vapor phase fugacity coefficients near the critical point of mixtures. A study of the tables in Appendix A for the points of departure will show that the vapor phase fugacity coefficients for the mixture are increasing in each case, as is necessary to make the proper correction, but perhaps the increase is short of the amount required. This is a point which should be subjected to future study.

TABLE IV

OBSERVED K VALUES FOR METHANE IN SOLVENTS AT 150°F

(Data points are deleted where methane vapor activity coefficient deviates more than 2 percent from unity by Redlich-Kwong equation)

Pressure (psia)	n-Pentane	n-Heptane	Decane	Cyclopentane	Cyclohexane	Methyl-cyclohexane	Benzene	Toluene	Average	Maximum Absolute Deviation %	Average Absolute Deviation %
100	28.57	-	31.76	45.48	50.93	44.09	63.80	57.24	45.95	38.80	21.10
200	-	16.64	-	23.15	25.87	22.52	31.90	28.88	24.83	32.98	14.35
400	8.05	8.61	8.68	11.61	12.98	11.42	16.20	14.33	11.48	41.10	18.90
600	-	5.91	-	7.78	8.66	7.63	10.80	9.52	8.38	29.45	15.15
800	3.98	4.56	-	5.84	6.53	5.75	8.30	7.17	6.02	37.80	18.75
1000	3.29	3.75	3.95	4.66	5.21	4.60	6.69	5.75	4.74	41.10	16.80
1500	-	2.67	-	3.11	3.51	3.08	4.67	3.90	3.49	33.80	19.23
2000	-	-	-	2.32	2.65	2.35	3.48	3.02	2.76	26.10	13.78
2500	-	-	-	-	2.14	1.94	-	2.49	2.19	13.69	9.13
3000	-	-	1.77	-	1.78	1.80	2.39	2.16	1.98	20.70	11.90
3500	-	-	-	-	-	1.46	-	1.92	1.69	13.60	13.60
4000	-	-	-	-	-	-	1.82	1.74	1.78	22.50	22.50

TABLE V

CALCULATED IDEAL K VALUES FOR METHANE IN SOLVENTS AT 150°F

(Data points are deleted where methane vapor activity coefficient deviates more than 2 percent from unity by Redlich-Kwong equation)

Pressure (psia)	n-Pentane	n-Heptane	Decane	Cyclopentane	Cyclohexane	Methyl-cyclohexane	Benzene	Toluene	Average	Maximum Absolute Deviation %	Average Absolute Deviation %
100	23.69	-	20.75	26.07	27.77	27.76	21.31	21.97	24.18	14.86	10.67
200	-	12.18	-	13.56	14.26	14.31	10.86	11.29	12.74	14.75	10.20
400	6.73	6.39	5.80	6.94	7.34	7.40	5.76	5.81	6.52	13.50	9.32
600	-	4.45	-	4.80	5.02	5.04	4.02	4.00	4.55	11.82	8.78
800	3.43	3.49	-	3.71	3.88	3.87	3.20	3.13	3.53	11.32	7.06
1000	2.87	2.91	2.75	3.05	3.19	3.16	2.68	2.60	2.90	10.33	6.08
1500	-	2.15	-	2.20	2.29	2.23	2.07	1.93	2.15	10.22	4.41
2000	-	-	-	1.77	1.84	1.79	1.69	1.62	1.74	6.90	4.02
2500	-	-	-	-	1.59	1.55	-	1.45	1.53	5.23	3.48
3000	-	-	1.40	-	1.41	1.47	1.38	1.35	1.40	5.00	2.14
3500	-	-	-	-	-	1.28	-	1.28	1.28	0.00	0.00
4000	-	-	-	-	-	-	1.24	1.23	1.235	0.41	0.41

Total Weighted Average Absolute Deviation 6.65%

TABLE VI

ADJUSTED IDEAL K* VALUES FOR METHANE IN SOLVENTS AT 150°F

(Data points are deleted where methane vapor activity coefficient deviates more than 2 percent from unity by Redlich-Kwong equation)

Pressure (psia)	n-Pentane	n-Heptane	Decane	Cyclopentane	Cyclohexane	Methyl-cyclohexane	Benzene	Toluene	Average	Maximum Absolute Deviation %	Average Absolute Deviation %
100	24.25	-	21.90	28.03	29.90	29.40	24.44	24.65	26.08	16.05	9.95
200	-	12.65	-	14.50	15.35	15.15	12.43	12.70	13.80	11.22	9.05
400	6.89	6.64	6.11	7.39	7.88	7.82	6.55	6.50	6.97	13.05	7.78
600	-	4.61	-	5.11	5.37	5.31	4.56	4.46	4.92	9.34	7.30
800	3.50	3.61	-	3.92	4.14	4.07	3.60	3.47	3.76	10.10	6.48
1000	2.93	3.02	2.88	3.22	3.40	3.31	3.00	2.87	3.08	10.39	5.65
1500	-	2.21	-	2.30	2.41	2.32	2.30	2.11	2.28	7.46	3.29
2000	-	-	-	1.85	1.92	1.85	1.845	1.755	1.84	4.35	2.06
2500	-	-	-	-	1.65	1.59	-	1.56	1.60	3.13	2.06
3000	-	-	1.445	-	1.45	1.505	1.480	1.430	1.46	3.08	1.64
3500	-	-	-	-	-	1.30	-	1.370	1.335	2.62	2.62
4000	-	-	-	-	-	-	1.305	1.280	1.292	0.93	0.93

Total Weighted Average Absolute Deviation 5.58%

* $K_1^*(\text{Ideal}) = K_1(\text{Observed}) \dfrac{\gamma_1^V}{\left[\gamma_1^L\right]^{0.875}}$

TABLE VII

COMPARISON OF IDEAL K VALUES FOR METHANE AT 150°F*

Pressure (psia)	n-Pentane	n-Heptane	Decane	Benzene	Toluene	Average	Maximum Absolute Deviation %	Average Absolute Deviation %
100	23.69	-	20.75	21.31	21.97	21.93	8.0	4.1
200	-	12.18	-	10.86	11.29	11.44	6.5	4.3
400	6.73	6.39	5.80	5.76	5.81	6.10	10.3	6.1
600	-	4.45	-	4.02	4.00	4.16	7.0	5.7
800	3.43	3.49	-	3.20	3.13	3.31	5.4	4.5
1000	2.87	2.91	2.75	2.68	2.60	2.76	5.8	4.4
1500	-	2.15	-	2.07	1.93	2.05	5.8	3.9
2000	-	-	-	1.69	1.62	1.66	2.1	1.9
3000	-	-	1.40	1.38	1.35	1.38	2.2	1.2
4000	-	-	-	1.24	1.23	1.235	0.6	0.6

Total Weighted Average Absolute Deviation 4.2%

* (1) Naphthenic solvents excluded

(2) All data points are deleted where methane vapor activity coefficient deviates more than 2 percent from unity by Redlich-Kwong equation

TABLE VIII

COMPARISON OF ADJUSTED IDEAL K* VALUES FOR METHANE AT 150°F**

Pressure (psia)	n-Pentane	n-Heptane	Decane	Benzene	Toluene	Average	Maximum Absolute Deviation %	Average Absolute Deviation %
100	24.25	-	21.90	24.44	24.65	23.81	6.8	4.0
200	-	12.65	-	12.43	12.70	12.59	1.3	0.9
400	6.89	6.64	6.11	6.55	6.50	6.54	6.6	2.8
600	-	4.61	-	4.56	4.46	4.54	1.8	1.3
800	3.50	3.61	-	3.60	3.47	3.55	2.8	2.0
1000	2.93	3.02	2.88	3.00	2.87	2.94	2.7	1.9
1500	-	2.21	-	2.30	2.11	2.21	4.5	2.9
2000	-	-	-	1.85	1.75	1.80	2.5	2.5
3000	-	-	1.45	1.48	1.43	1.45	1.9	1.3
4000	-	-	-	1.30	1.28	1.29	1.0	1.0

Total Weighted Average Absolute Deviation 2.1%

* $K_1^*(\text{Ideal}) = K_1(\text{Observed}) \dfrac{\gamma_1^{V}}{\left[\gamma_1^{L}\right]^{0.875}}$

** (1) Naphthenic solvents are excluded

(2) All data points are deleted where methane vapor activity coefficient deviates more than 2 percent from unity by Redlich-Kwong equation

TABLE IX

EFFECT OF LIQUID VOLUME ON IDEAL K DIFFERENCES FOR METHANE
(150°F)

Watson Volume Method

Pressure (psia)	K' (in Toluene)	K' (in Propane)	$\Delta K'$	$\frac{\Delta K'}{K'}$ (in Toluene)
400	5.809	5.568	0.241	0.0415
600	4.004	3.837	0.167	0.0417
800	3.131	2.488	0.643	0.2060
1000	2.604	1.965	0.639	0.2456

Chao and Seader Volume Method

Pressure (psia)	K' (in Toluene)	K' (in Propane)	$\Delta K'$	$\frac{\Delta K'}{K'}$ (in Toluene)
400	6.075	5.575	0.500	0.0823
600	4.160	3.840	0.320	0.0769
800	3.240	2.490	0.750	0.2320
1000	2.690	1.966	0.724	0.2690

TABLE X

COMPARISON OF PREDICTED AND EXPERIMENTAL K VALUES FOR METHANE IN PROPANE (150°F)

Pressure (psia)	K Experimental (48)	Calculated K Values		
		This Study	Chao-Seader (ω=0)	Chao-Seader (ω=0.013)
400	4.762	5.31	5.71	4.61
600	3.330	3.65	4.09	3.30
800	1.794	2.34	2.64	2.12
1000	1.596	2.19	2.48	2.00

Note: These data are plotted in Figure 7

TABLE XI

COMPARISON OF PREDICTED AND EXPERIMENTAL K VALUES FOR METHANE IN TOLUENE (150°F)

		Calculated K Values		
Pressure (psia)	K Experimental (16)	This Study	Chao-Seader (ω =0)	Chao-Seader (ω =0.013)
100	57.24	58.60	59.10	46.90
400	14.33	15.30	14.05	11.32
600	9.52	9.99	9.63	7.76
800	7.17	7.45	7.29	5.86
1000	5.75	5.96	6.12	4.76
2000	3.02	3.16	3.10	2.16
4000	1.74	1.70	1.72	1.38

Note: These data are plotted in Figure 8

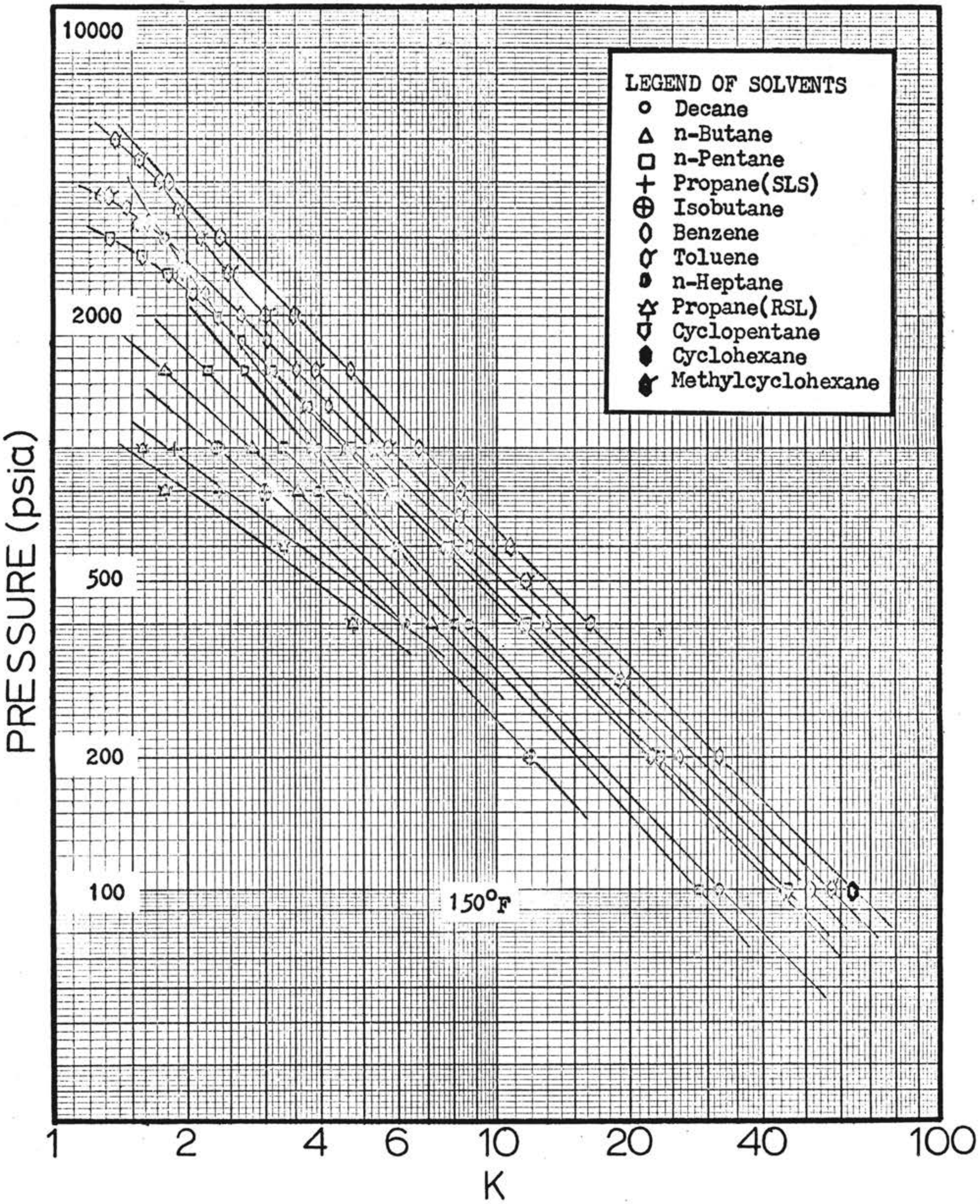


FIGURE 1
Experimental K Values for Methane

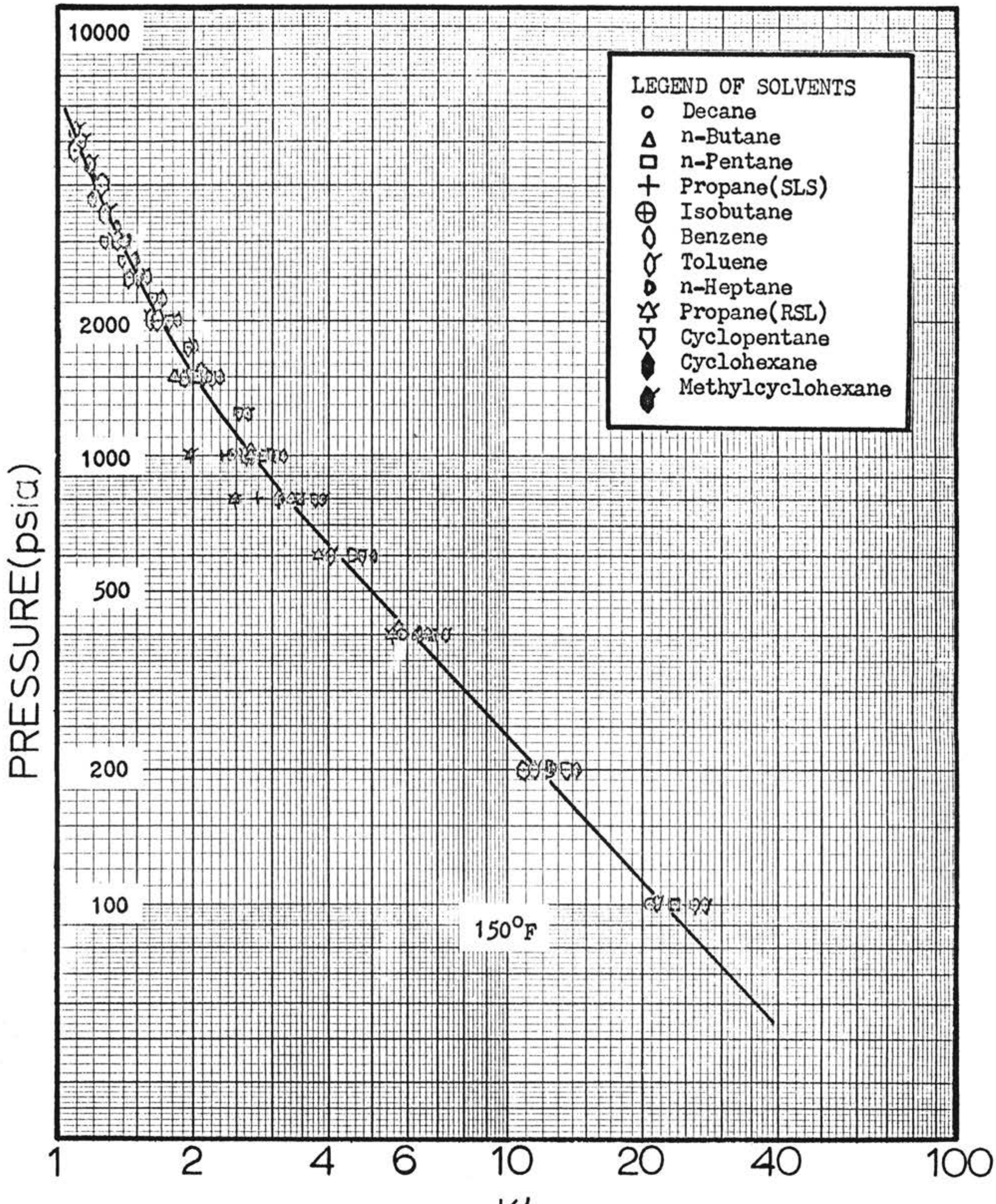


FIGURE 2
Ideal K Values for Methane

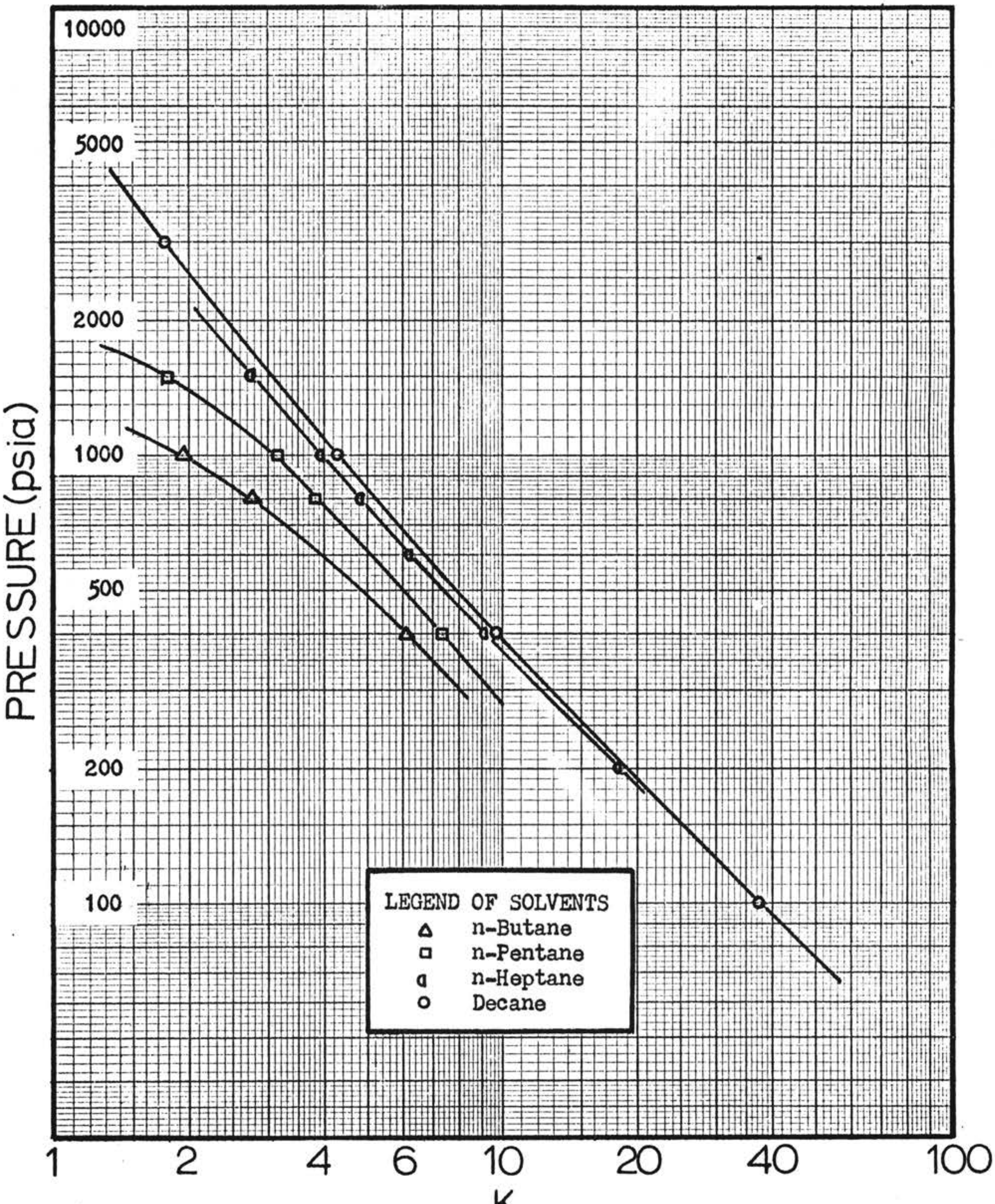
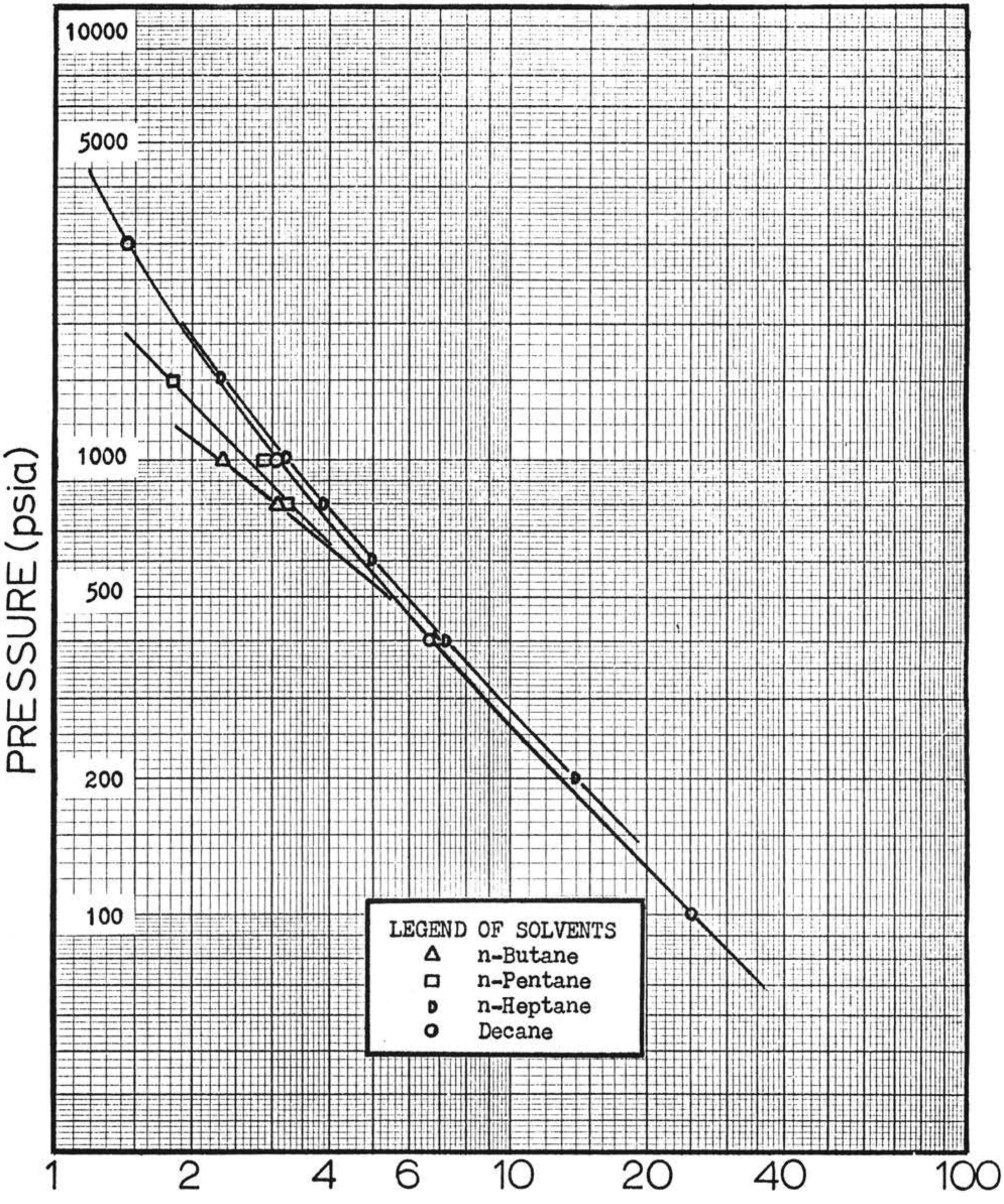


FIGURE 3
Experimental K Values
Methane 250°F



Ideal K Values
Methane 250°F
FIGURE 4

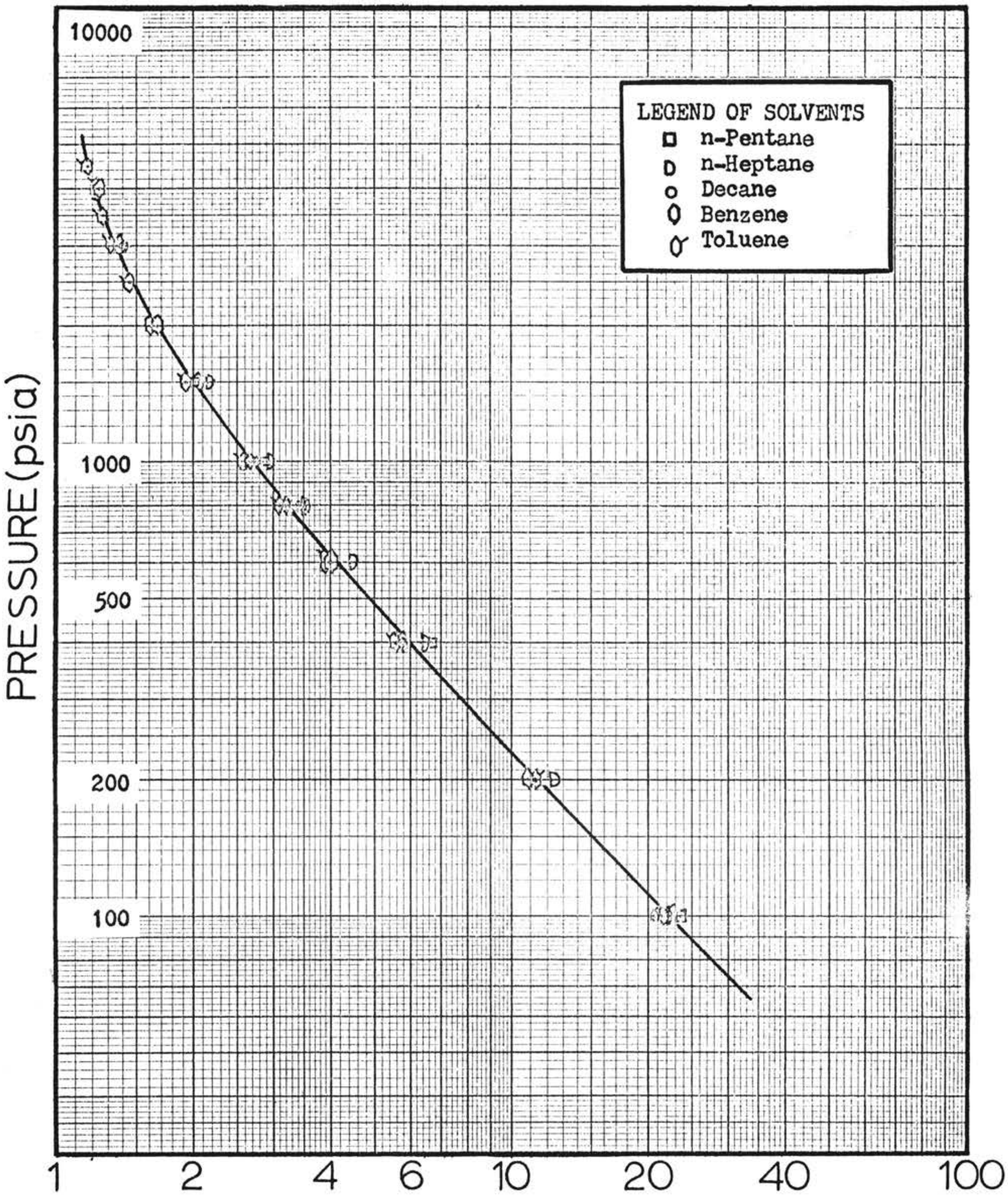


FIGURE 5
Limited Ideal K Values
Methane 150°F

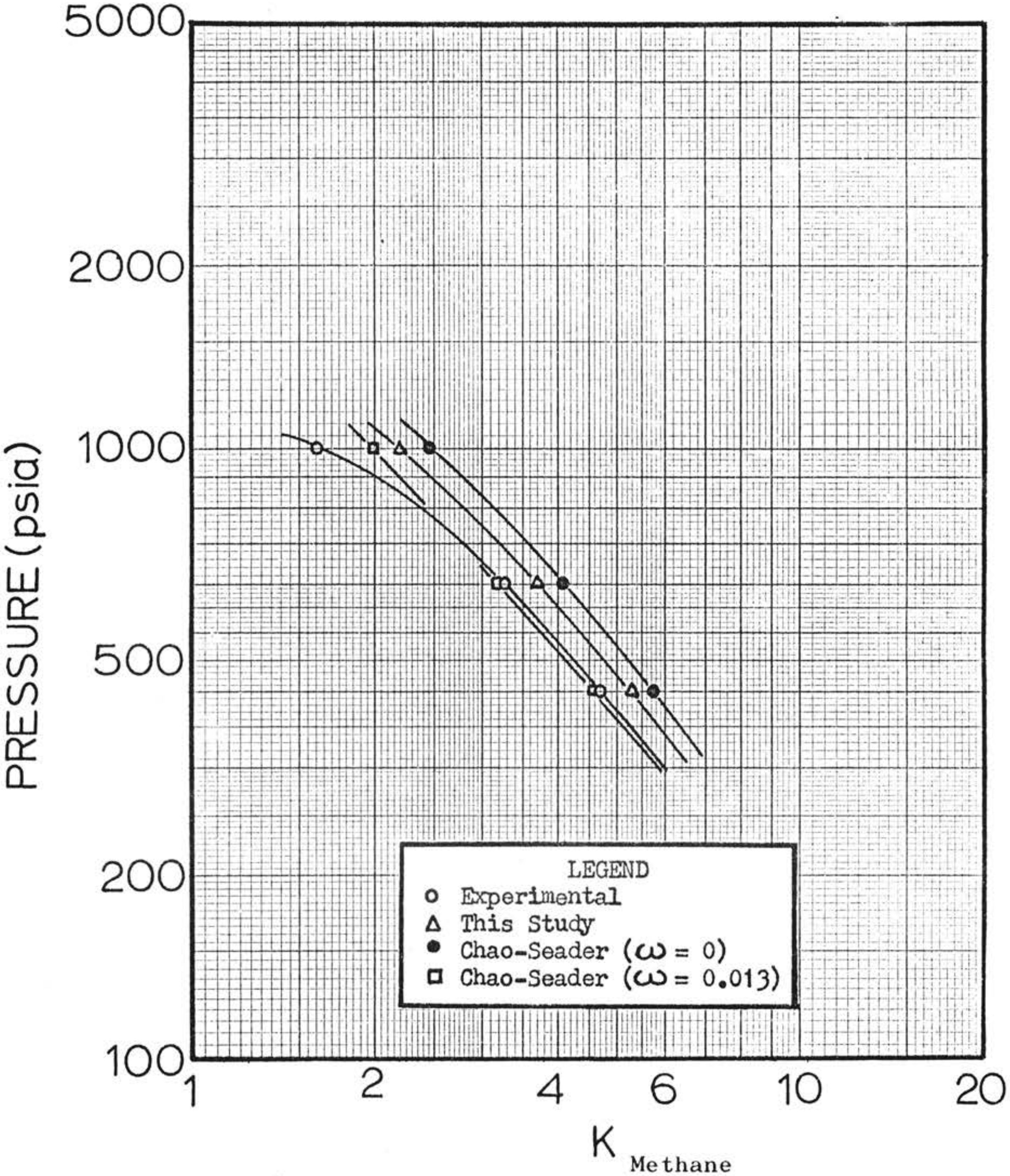


FIGURE 6

K-Pressure Diagram

Methane-Propane

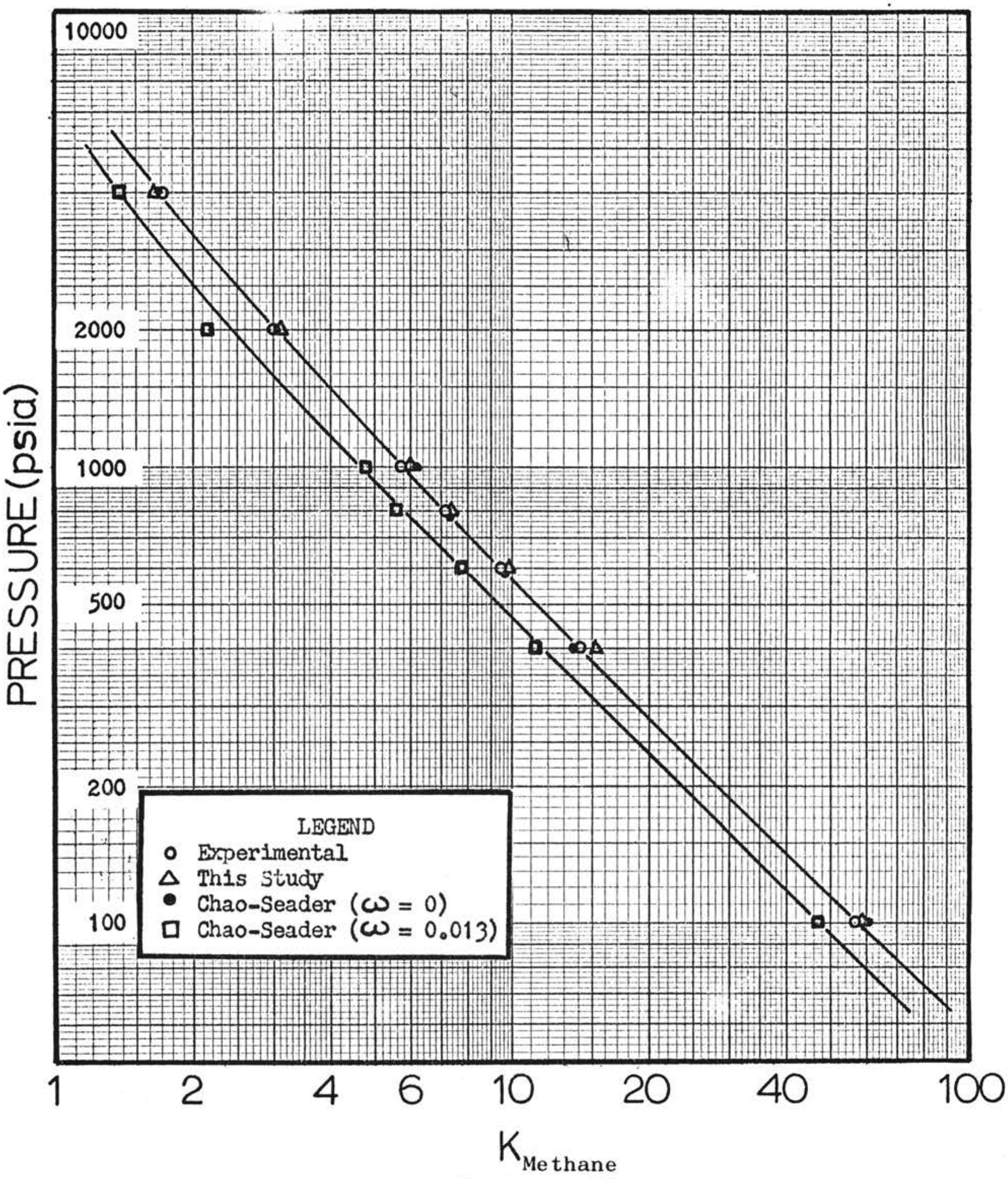


FIGURE 7

K-Pressure Diagram
Methane-Toluene

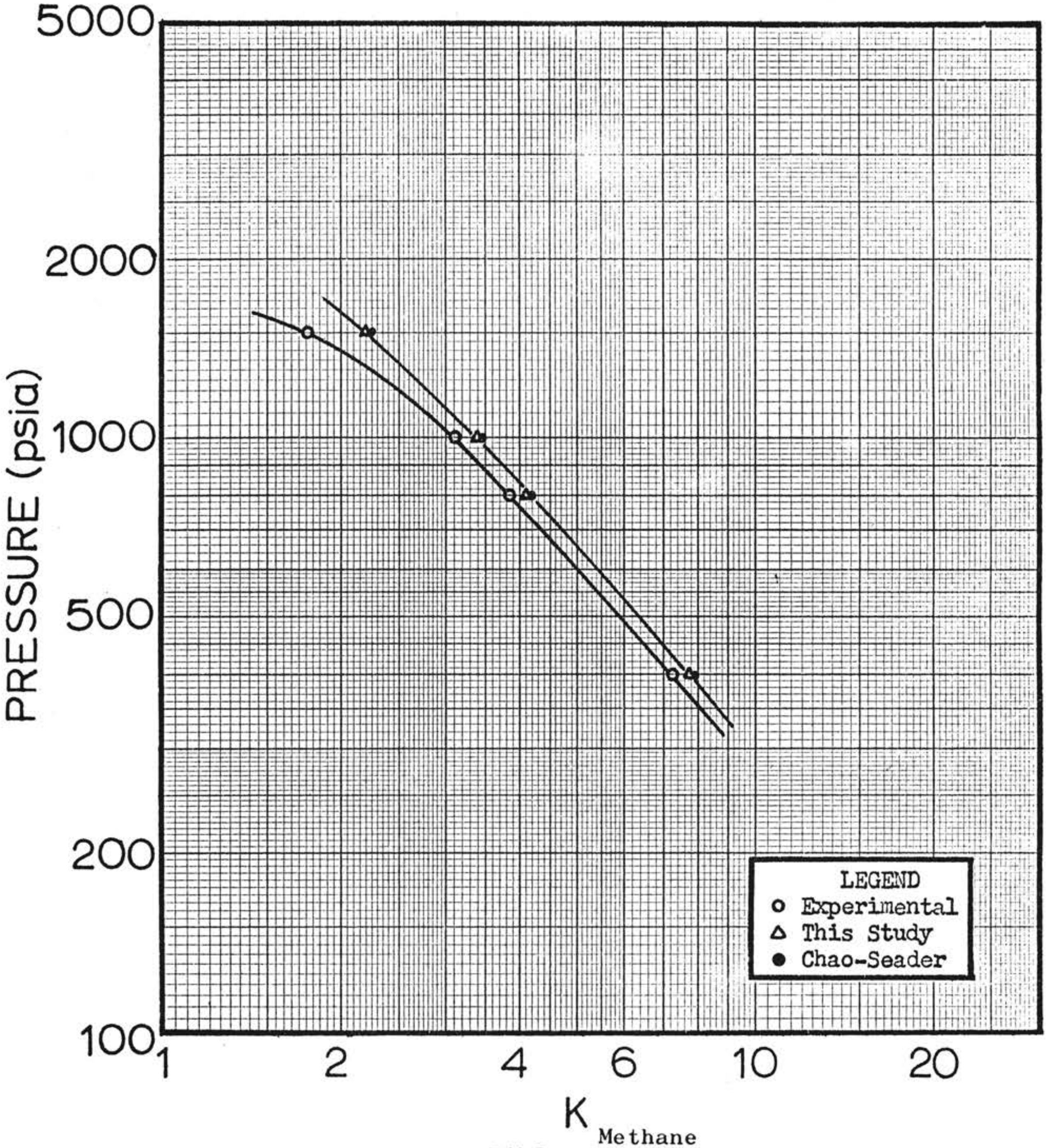


FIGURE 8

K-Pressure Diagram
Methane-n-Pentane

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this study has been to explore a proposed vapor-liquid equilibria correlation method by applying it to experimental binary mixtures of methane. The method makes use of the Redlich-Kwong equation of state to predict vapor phase activity coefficients and a van Laar type equation to predict liquid phase activity coefficients.

There are two important features of the correlation method. First, the method is analytical. Second, provisions are made to account for chemical dissimilarity. The latter is accomplished through use of the equations of the Scatchard-Hildebrand "regular" solution treatment for liquids. These equations include the important property defined as solubility parameter.

Attention was focused on the methane data at 150°F where the greatest variety of solvents were available.

Ideal K values for methane, calculated with the described correlation technique, were found to correlate well for most of the data considered. Two modifications to the method greatly enhance the correlation:

(1) Liquid phase activity coefficients can be empirically adjusted by applying an 0.875 power correction.

(2) Solubility parameters for the naphthenic solvents can

be increased to the following values:

Cyclopentane	8.45
Cyclohexane	8.60
Methylcyclohexane	8.30

Neither of these modifications alter the analytical nature of the method. The modified correlation method gives excellent results in all regions except where the vapor phase activity coefficient for methane deviates more than two (2) percent from unity.

The cause of the deviations which occur when $\gamma^{V}_{\text{methane}} > 1.02$ has not been found in this study. However, most evidence tends to exonerate the liquid phase activity coefficient.

The Watson liquid volume expression was found to give slightly better correlation results than the constant volume method of Chao and Seader. Results of this study tend to verify that the Watson equation is adequate for the correlation method.

Three areas of future study are recommended.

(1) The equation of state method of predicting fugacity coefficients of vapor phase mixtures in regions near the critical should be studied. This appears to be a key point in extending the range of the correlation method.

(2) If the problem is not solved by item (1), then it is suggested that a modified Scatchard-Hildebrand equation be used in which the geometric mean of cohesive energy density of unlike molecules is not assumed. This would introduce another parameter in addition to the two solubility parameters already used.

(3) Experimental data are needed on the equilibrium phase behavior of methane in aromatic and naphthenic solvents at a number of higher temperature levels. The fact that these data were available only at the 150°F level has limited the scope of this study.

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APPENDIX A

TABLES OF EXPERIMENTAL EQUILIBRIUM DATA AND CALCULATED ACTIVITY COEFFICIENTS

APPENDIX A

LIST OF TABLES

CALCULATED ACTIVITY COEFFICIENTS AND IDEAL K VALUES

TABLE A-1

METHANE - PROPANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Sage, Lacey and Schaafsma
IEC Vol. 26, 214, (1934)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						Propane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
200	50	0.033	0.518	1.026	0.997	0.971	1.027	15.697	15.708	1.000	0.800	*	-	0.498	-
	100	0.008	0.121	1.026	1.059	0.979	1.082	15.125	15.946	1.000	0.823	0.822	1.002	0.886	0.888
400	50	0.121	0.662	1.023	0.972	0.943	1.031	5.471	5.512	1.000	0.651	*	-	0.385	-
	100	0.080	0.433	1.023	1.030	0.959	1.075	5.413	5.684	1.000	0.687	0.455	1.508	0.616	0.929
	150	0.017	0.105	1.025	*	0.970	-	6.176	-	1.000	*	0.719	-	0.910	-
800	50	0.274	0.787	1.018	0.890	*	-	2.872	-	1.002	0.557	*	-	0.293	-
	100	0.238	0.601	1.018	*	*	-	2.525	-	1.001	*	*	-	0.524	-
	150	0.170	0.405	1.019	1.127	0.943	1.195	2.382	2.794	1.001	0.522	*	-	0.717	-
	200	0.083	0.142	1.021	1.546	0.959	1.612	1.711	2.701	1.000	0.557	*	-	0.936	-
1000	50	0.365	0.791	1.015	0.902	0.865	1.042	2.167	2.226	1.003	0.350	*	-	0.329	-
	100	0.326	0.633	1.015	1.002	0.903	1.117	1.942	2.138	1.002	0.397	*	-	0.545	-
	150	0.235	0.445	1.017	1.153	0.930	1.239	1.894	2.307	1.001	0.439	*	-	0.725	-

* Computer did not calculate

TABLE A-2

METHANE - PROPANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Reamer, Sage and Lacey
IEC Vol. 42, 534, (1950)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						Propane Solvent					
PSIA	^{o}F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
200	50	0.049	0.527	1.026	0.996	0.971	1.016	10.755	10.757	1.000	0.801	0.766	1.045	0.497	0.520
	100	0.005	0.052	1.026	1.077	0.979	1.100	10.400	11.151	1.000	0.822	0.822	1.000	0.953	0.953
400	50	0.138	0.716	1.023	0.962	0.943	1.021	5.188	5.179	1.000	0.666	*	-	0.329	-
	100	0.084	0.446	1.023	1.026	0.959	1.070	5.310	5.553	1.000	0.689	0.455	1.513	0.605	0.915
	150	0.021	0.100	1.024	1.162	0.970	1.198	4.762	5.568	1.000	0.723	0.719	1.[illegible]5	0.919	0.924
600	50	0.223	0.773	1.020	0.936	0.916	1.022	3.466	3.476	1.001	0.550	*	-	0.292	-
	100	0.163	0.571	1.021	1.004	0.939	1.069	3.503	3.669	1.001	0.583	*	-	0.513	-
	150	0.094	0.313	1.022	1.126	0.956	1.178	3.330	3.837	1.000	0.614	*	-	0.758	-
800	50	0.310	0.772	1.016	0.922	0.890	1.036	2.490	2.538	1.002	0.435	*	-	0.330	-
	100	0.242	0.632	1.018	0.989	0.921	1.074	2.612	2.755	1.001	0.493	*	-	0.485	-
	150	0.175	0.314	1.019	1.332	0.943	1.413	1.794	2.488	1.001	0.477	*	-	0.832	-
1000	50	0.402	0.782	1.013	0.906	0.865	1.047	1.945	2.010	1.004	0.344	*	-	0.365	-
	100	0.327	0.664	1.015	0.979	0.903	1.084	2.031	2.168	1.002	0.415	*	-	0.499	-
	150	0.275	0.439	1.016	1.163	0.930	1.251	1.596	1.965	1.002	0.436	*	-	0.774	-
1200	50	0.507	0.792	1.010	0.890	0.842	1.056	1.562	1.634	1.007	0.274	*	-	0.422	-
	100	0.423	0.678	1.012	0.974	0.887	1.099	1.603	1.741	1.004	0.347	*	-	0.558	-

* Computer did not calculate

TABLE A-3

METHANE - ISOBUTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Olds, Sage and Lacey
IEC Vol. 34, 1008, (1942)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						Isobutane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
200	100	0.049	0.589	1.053	1.007	0.979	1.028	12.020	11.738	1.000	0.786	0.719	1.092	0.432	0.472
	150	0.019	0.227	1.053	1.078	0.985	1.095	11.947	12.429	1.000	0.793	0.784	1.011	0.788	0.797
400	100	0.120	0.760	1.048	0.978	0.959	1.020	6.333	6.163	1.001	0.659	*	-	0.273	-
	150	0.086	0.537	1.048	1.036	0.970	1.068	6.244	6.363	1.000	0.664	*	-	0.507	-
	200	0.049	0.271	1.049	1.146	0.978	1.172	5.531	6.179	1.000	0.679	*	-	0.767	-
800	100	0.270	0.830	1.038	0.942	0.921	1.023	3.074	3.029	1.003	0.458	*	-	0.233	-
	150	0.228	0.694	1.039	1.003	0.943	1.064	3.044	3.117	1.002	0.483	*	-	0.396	-
	200	0.187	0.489	1.040	1.136	0.957	1.185	2.615	2.979	1.001	0.485	*	-	0.629	-
1000	100	0.352	0.843	1.033	0.926	0.903	1.026	2.395	2.379	1.005	0.381	*	-	0.242	-
	150	0.305	0.713	1.034	0.999	0.930	1.074	2.338	2.429	1.004	0.407	*	-	0.413	-
	200	0.270	0.490	1.035	1.208	0.950	1.272	1.815	2.230	1.003	0.389	*	-	0.699	-

* Computer did not calculate

TABLE A-4

METHANE - NORMAL BUTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Sage, Lacey and Hicks
IEC Vol. 32, 1085, (1940)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						n-Butane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	100	0.018	0.455	1.140	1.015	0.989	1.026	25.562	23.002	1.000	0.871	0.852	1.022	0.555	0.567
400	100	0.118	0.831	1.122	0.969	0.959	1.011	7.042	6.341	1.001	0.669	*	-	0.192	-
	150	0.092	0.660	1.121	1.006	0.970	1.037	7.174	6.636	1.001	0.678	*	-	0.374	-
	200	0.061	0.432	1.121	1.072	0.978	1.096	7.082	6.925	1.000	0.685	0.468	1.464	0.605	0.885
	250	0.023	0.141	1.122	1.224	0.984	1.243	6.130	6.791	1.000	0.704	0.694	1.015	0.879	0.892
800	100	0.247	0.881	1.099	0.931	0.921	1.012	3.567	3.283	1.006	0.469	*	-	0.158	-
	150	0.217	0.773	1.099	0.976	0.943	1.035	3.562	3.355	1.004	0.499	*	-	0.290	-
	200	0.183	0.617	1.101	1.047	0.959	1.092	3.372	3.345	1.003	0.511	*	-	0.469	-
	250	0.148	0.410	1.102	1.198	0.971	1.234	2.770	3.103	1.002	0.515	*	-	0.692	-
1000	100	0.320	0.883	1.086	0.917	0.903	1.015	2.759	2.578	1.011	0.387	*	-	0.172	-
	150	0.278	0.782	1.089	0.970	0.930	1.043	2.813	2.694	1.007	0.422	*	-	0.302	-
	200	0.242	0.638	1.091	1.053	0.950	1.109	2.636	2.679	1.005	0.436	*	-	0.478	-
	250	0.222	0.433	1.090	1.254	0.964	1.301	1.950	2.327	1.004	0.431	*	-	0.729	-
1500	100	0.478	0.872	1.059	0.890	0.864	1.030	1.824	1.774	1.028	0.232	*	-	0.245	-
	150	0.428	0.766	1.064	0.977	0.902	1.083	1.790	1.823	1.021	0.262	*	-	0.409	-
	200	0.425	0.595	1.061	1.159	0.930	1.246	1.400	1.644	1.020	0.262	*	-	0.704	-

* Computer did not calculate

TABLE A-5

METHANE - NORMAL PENTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Olds, Sage and Lacey
IEC Vol. 34, 1108, (1942)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						n-Pentane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	100	0.029	0.820	1.238	0.994	0.989	1.004	28.276	22.948	1.000	0.875	0.781	1.120	0.185	0.208
	150	0.021	0.600	1.229	1.010	0.992	1.018	28.571	23.693	1.000	0.869	0.828	1.050	0.409	0.429
	200	0.008	0.279	1.222	1.047	0.994	1.053	34.875	30.057	1.000	0.870	0.862	1.009	0.727	0.734
400	100	0.120	0.934	1.213	0.961	0.958	1.003	7.783	6.435	1.002	0.648	*	-	0.075	-
	150	0.108	0.869	1.205	0.978	0.970	1.008	8.046	6.731	1.001	0.678	*	-	0.147	-
	200	0.095	0.743	1.199	1.004	0.978	1.066	7.821	6.953	1.001	0.680	*	-	0.284	-
	250	0.076	0.560	1.196	1.055	0.984	1.072	7.368	6.602	1.001	0.673	*	-	0.476	-
	300	0.051	0.325	1.195	1.161	0.989	1.174	6.373	6.258	1.000	0.672	*	-	0.711	-
	350	0.016	0.028	1.197	1.536	0.993	1.547	1.750	2.262	1.000	0.690	0.690	1.000	0.988	0.988
800	100	0.249	0.947	1.176	0.924	0.921	1.004	3.803	3.245	1.009	0.429	*	-	0.071	-
	150	0.227	0.904	1.173	0.951	0.943	1.009	3.982	3.426	1.007	0.486	*	-	0.124	-
	200	0.206	0.829	1.171	0.982	0.959	1.024	4.024	3.521	1.005	0.513	*	-	0.215	-
	250	0.186	0.712	1.169	1.030	0.971	1.061	3.828	3.477	1.004	0.517	*	-	0.354	-
	300	0.165	0.533	1.167	1.141	0.980	1.164	3.230	3.222	1.003	0.500	*	-	0.559	-
	350	0.146	0.309	1.166	1.456	0.987	1.475	2.116	2.677	1.002	0.480	*	-	0.809	-
1000	100	0.303	0.948	1.161	0.907	*	-	3.129	-	1.014	0.348	*	-	0.075	-
	150	0.275	0.906	1.160	0.941	0.930	1.011	3.295	2.873	1.011	0.408	*	-	0.130	-
	200	0.252	0.838	1.159	0.976	0.950	1.028	3.325	2.950	1.009	0.442	*	-	0.217	-
	250	0.232	0.729	1.157	1.031	0.964	1.069	3.142	2.904	1.007	0.449	*	-	0.353	-
	300	0.216	0.566	1.155	1.151	0.975	1.180	2.620	2.677	1.006	0.434	*	-	0.554	-
	350	0.204	0.270	1.152	1.855	0.984	1.885	1.324	2.165	1.005	0.372	*	-	0.917	-
1500	100	0.432	0.944	1.124	0.871	0.864	1.008	2.185	1.961	1.034	0.206	*	-	0.095	-
	150	0.404	0.902	1.124	0.919	0.902	1.019	2.233	2.024	1.027	0.264	*	-	0.160	-
	200	0.390	0.829	1.122	0.975	0.930	1.048	2.126	1.986	1.024	0.294	*	-	0.274	-
	250	0.395	0.707	1.115	1.075	0.951	1.131	1.790	1.815	1.024	0.292	*	-	0.473	-
	300	0.428	0.519	1.102	1.328	0.966	1.375	1.213	1.512	1.029	0.270	*	-	0.817	-

* Computer did not calculate

TABLE A-6

METHANE - NORMAL HEPTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Reamer, Sage and Lacey
IEC Chem. Eng. Data Series Vol. 1, 29, (1956)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						n-Heptane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
200	100	0.064	0.987	1.385	0.979	0.979	1.000	15.415	11.129	1.001	0.771	*	-	0.014	-
	150	0.058	0.965	1.367	0.985	0.985	1.001	16.637	12.177	1.000	0.803	*	-	0.037	-
	200	0.051	0.920	1.353	0.991	0.989	1.002	18.039	13.364	1.000	0.816	*	-	0.084	-
	250	0.045	0.836	1.340	1.000	0.992	1.008	18.577	13.976	1.000	0.812	*	-	0.172	-
	300	0.038	0.676	1.330	1.023	0.994	1.029	17.789	13.762	1.000	0.790	*	-	0.337	-
	350	0.029	0.463	1.332	1.071	0.996	1.075	16.228	13.191	1.000	0.774	0.710	1.090	0.553	0.603
	400	0.013	0.206	1.317	1.163	0.998	1.166	15.606	13.809	1.000	0.772	0.759	1.017	0.805	0.818
400	100	0.124	0.991	1.362	0.959	0.959	1.000	7.987	5.865	1.002	0.600	*	-	0.011	-
	150	0.114	0.977	1.347	0.970	0.970	1.000	8.607	6.395	1.002	0.660	*	-	0.026	-
	200	0.105	0.946	1.334	0.980	0.978	1.002	9.052	6.800	1.002	0.692	*	-	0.060	-
	250	0.097	0.902	1.323	0.990	0.984	1.006	9.341	7.105	1.001	0.709	*	-	0.109	-
	300	0.090	0.825	1.313	1.005	0.989	1.016	9.166	7.097	1.001	0.706	*	-	0.192	-
	350	0.081	0.693	1.305	1.038	0.993	1.046	8.549	6.852	1.001	0.683	*	-	0.335	-
	400	0.067	0.522	1.300	1.102	0.995	1.107	7.795	6.636	1.001	0.662	*	-	0.512	-
	450	0.053	0.311	1.297	1.239	0.998	1.242	5.914	5.664	1.000	0.648	*	-	0.728	-
	500	0.036	0.057	1.294	1.744	0.999	1.745	1.583	2.135	1.000	0.651	0.636	1.025	0.978	1.002
600	100	0.181	0.991	1.339	0.939	0.939	1.000	5.476	4.089	1.005	0.466	*	-	0.011	-
	150	0.166	0.981	1.327	0.956	0.956	1.001	5.907	4.454	1.004	0.543	*	-	0.023	-
	200	0.154	0.958	1.316	0.970	0.968	1.002	6.221	4.736	1.004	0.592	*	-	0.050	-
	250	0.144	0.919	1.306	0.983	0.977	1.006	6.382	4.916	1.003	0.618	*	-	0.095	-
	300	0.137	0.855	1.297	1.001	0.984	1.017	6.264	4.911	1.003	0.620	*	-	0.168	-
	350	0.130	0.752	1.289	1.034	0.989	1.045	5.807	4.705	1.002	0.602	*	-	0.285	-
	400	0.120	0.621	1.283	1.091	0.994	1.098	5.175	4.428	1.002	0.582	*	-	0.431	-
	450	0.120	0.456	1.275	1.205	0.997	1.209	3.800	3.602	1.002	0.562	*	-	0.618	-
	500	0.123	0.263	1.267	1.470	0.999	1.471	2.143	2.487	1.002	0.549	*	-	0.840	-
800	100	0.234	0.991	1.318	0.921	0.921	1.000	4.235	3.215	1.010	0.362	*	-	0.012	-
	150	0.215	0.981	1.308	0.943	0.943	1.001	4.560	3.490	1.008	0.445	*	-	0.025	-
	200	0.200	0.963	1.299	0.961	0.959	1.002	4.813	3.713	1.006	0.508	*	-	0.047	-
	250	0.190	0.932	1.290	0.976	0.971	1.006	4.916	3.833	1.006	0.545	*	-	0.085	-
	300	0.182	0.875	1.281	0.996	0.980	1.017	4.821	3.825	1.005	0.553	*	-	0.153	-
	350	0.177	0.787	1.273	1.029	0.987	1.043	4.446	3.643	1.005	0.539	*	-	0.259	-
	400	0.174	0.670	1.266	1.088	0.992	1.097	3.851	3.338	1.004	0.517	*	-	0.400	-
	450	0.188	0.504	1.253	1.228	0.996	1.233	2.681	2.637	1.005	0.483	*	-	0.611	-
	500	0.215	0.294	1.237	1.638	0.999	1.639	1.367	1.811	1.007	0.448	*	-	0.899	-

Continued

TABLE A-6 (Continued)

METHANE - NORMAL HEPTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Reamer, Sage and Lacey
IEC Chem. Eng. Data Series Vol. 1, 29, (1956)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						n-Heptane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
1000	100	0.284	0.991	1.296	0.903	0.903	1.000	3.487	2.690	1.016	0.283	*	-	0.013	-
	150	0.262	0.981	1.289	0.931	0.930	1.001	3.750	2.911	1.012	0.367	*	-	0.026	-
	200	0.245	0.965	1.282	0.952	0.950	1.002	3.939	3.080	1.010	0.437	*	-	0.046	-
	250	0.235	0.939	1.273	0.970	0.964	1.006	4.002	3.162	1.009	0.483	*	-	0.080	-
	300	0.227	0.885	1.265	0.993	0.975	1.018	3.896	3.134	1.008	0.492	*	-	0.149	-
	350	0.225	0.808	1.256	1.026	0.984	1.043	3.591	2.981	1.008	0.485	*	-	0.248	-
	400	0.229	0.693	1.247	1.093	0.990	1.104	3.026	2.679	1.008	0.458	*	-	0.398	-
	450	0.263	0.516	1.228	1.278	0.996	1.284	1.966	2.055	1.011	0.410	*	-	0.656	-
1500	100	0.396	0.988	1.247	0.864	0.864	1.001	2.493	2.001	1.036	0.154	*	-	0.020	-
	150	0.367	0.981	1.245	0.903	0.902	1.001	2.672	2.149	1.029	0.234	*	-	0.031	-
	200	0.347	0.965	1.241	0.933	0.930	1.003	2.781	2.248	1.024	0.303	*	-	0.054	-
	250	0.335	0.939	1.235	0.959	0.950	1.009	2.806	2.291	1.021	0.352	*	-	0.092	-
	300	0.330	0.889	1.227	0.989	0.966	1.024	2.694	2.247	1.020	0.368	*	-	0.166	-
	350	0.334	0.820	1.217	1.032	0.978	1.054	2.455	2.127	1.021	0.368	*	-	0.270	-
	400	0.373	0.694	1.196	1.137	0.988	1.150	1.863	1.792	1.027	0.330	*	-	0.488	-

* Computer did not calculate

TABLE A-7

METHANE - DECANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Reamer, Olds, Sage and Lacey
IEC Vol. 34, 1526, (1942)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						Decane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	100	0.034	0.999	1.560	0.989	0.989	1.000	29.041	18.618	1.000	0.848	*	-	0.0010	-
	150	0.031	0.994	1.530	0.992	0.992	1.000	31.757	20.753	1.000	0.877	*	-	0.0062	-
	200	0.028	0.985	1.507	0.994	0.994	1.000	35.182	23.353	1.000	0.897	*	-	0.015	-
	250	0.026	0.966	1.486	0.996	0.996	1.000	37.734	25.407	1.000	0.907	*	-	0.035	-
	300	0.024	0.919	1.468	0.999	0.997	1.002	39.941	26.576	1.000	0.905	*	-	0.083	-
	350	0.021	0.822	1.452	1.005	0.998	1.007	39.143	27.135	1.000	0.889	0.737	1.206	0.182	0.219
	400	0.018	0.666	1.440	1.020	0.999	1.021	37.207	26.394	1.000	0.867	0.780	1.113	0.340	0.378
	450	0.012	0.422	1.429	1.059	0.999	1.060	34.590	25.652	1.000	0.846	0.813	1.040	0.585	0.609
400	100	0.125	0.999	1.521	0.959	0.959	1.000	7.989	5.253	1.002	0.519	*	-	0.0007	-
	150	0.115	0.998	1.496	0.970	0.960	1.000	8.680	5.802	1.002	0.604	*	-	0.0020	-
	200	0.107	0.995	1.476	0.978	0.978	1.000	9.296	6.300	1.002	0.670	*	-	0.0059	-
	250	0.101	0.981	1.457	0.985	0.984	1.000	9.717	6.671	1.001	0.708	*	-	0.021	-
	300	0.096	0.971	1.441	0.990	0.989	1.001	10.125	7.032	1.001	0.745	*	-	0.032	-
	350	0.093	0.942	1.427	0.995	0.993	1.003	10.140	7.088	1.001	0.753	*	-	0.064	-
	400	0.093	0.894	1.414	1.004	0.995	1.008	9.665	6.893	1.001	0.744	*	-	0.117	-
	450	0.094	0.813	1.401	1.020	0.998	1.023	8.665	6.341	1.001	0.716	*	-	0.206	-
1000	100	0.268	0.999	1.452	0.903	0.903	1.000	3.729	2.567	1.014	0.199	*	-	0.0010	-
	150	0.253	0.998	1.434	0.930	0.930	1.000	3.949	2.754	1.012	0.295	*	-	0.0024	-
	200	0.238	0.996	1.419	0.950	0.950	1.000	4.184	2.948	1.010	0.385	*	-	0.0055	-
	250	0.229	0.991	1.404	0.965	0.964	1.000	4.327	3.082	1.009	0.463	*	-	0.012	-
	300	0.223	0.983	1.390	0.976	0.975	1.001	4.408	3.173	1.008	0.526	*	-	0.022	-
	350	0.221	0.963	1.377	0.987	0.984	1.003	4.357	3.174	1.008	0.555	*	-	0.048	-
	400	0.226	0.936	1.363	0.997	0.990	1.007	4.141	3.061	1.008	0.570	*	-	0.083	-
	450	0.235	0.890	1.348	1.014	0.996	1.018	3.787	2.861	1.009	0.557	*	-	0.144	-
3000	100	0.583	0.995	1.264	0.785	0.784	1.000	1.707	1.351	1.136	0.020	0.0017	12.210	0.013	0.142
	150	0.561	0.992	1.262	0.845	0.845	1.001	1.768	1.402	1.115	0.051	*	-	0.018	-
	200	0.548	0.987	1.256	0.892	0.890	1.001	1.803	1.437	1.102	0.096	*	-	0.029	-
	250	0.544	0.976	1.245	0.929	0.925	1.004	1.794	1.446	1.097	0.143	0.0186	7.684	0.053	0.369
	300	0.551	0.963	1.230	0.959	0.952	1.007	1.748	1.431	1.099	0.191	*	-	0.082	-
	350	0.564	0.940	1.213	0.988	0.973	1.015	1.667	1.395	1.105	0.224	*	-	0.138	-
	400	0.592	0.903	1.190	1.023	0.989	1.034	1.525	1.325	1.122	0.237	*	-	0.238	-

* Computer did not calculate

TABLE A-8

METHANE - BENZENE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Elbishlawi and Spencer
IEC Vol. 43, 1811, (1951)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						Benzene Solvent					
PSIA	F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	150	0.014	0.925	3.000	0.993	0.992	1.001	63.80	21.314	1.000	0.908	0.803	1.131	0.076	0.086
200	150	0.030	0.957	2.940	0.985	0.985	1.000	31.90	10.855	1.001	0.837	*	-	0.045	-
400	150	0.060	0.977	2.810	0.970	0.970	1.000	16.20	5.762	1.003	0.714	*	-	0.024	-
600	150	0.090	0.980	2.685	0.956	0.956	1.000	10.80	4.021	1.006	0.606	*	-	0.022	-
800	150	0.118	0.980	2.588	0.943	0.943	1.000	8.30	3.201	1.011	0.513	*	-	0.023	-
1000	150	0.146	0.977	2.495	0.931	0.930	1.001	6.69	2.682	1.017	0.432	*	-	0.027	-
1500	150	0.213	0.974	2.259	0.903	0.902	1.002	4.67	2.073	1.038	0.286	*	-	0.033	-
2000	150	0.278	0.969	2.070	0.881	0.878	1.003	3.48	1.685	1.070	0.193	*	-	0.043	-
3000	150	0.400	0.956	1.746	0.851	0.845	1.008	2.39	1.381	1.166	0.097	*	-	0.073	-
4000	150	0.514	0.935	1.496	0.842	0.828	1.018	1.82	1.241	1.329	0.057	0.010	5.675	0.134	0.572
4800	150	0.695	0.775	1.208	0.963	0.824	1.169	1.12	1.088	1.858	0.020	0.010	1.986	0.737	0.787

* Computer did not calculate

TABLE A-9

METHANE - TOLUENE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Elbishlawi and Spencer
IEC Vol. 43, 1811, (1951)

Pressure	Temp.	Methane Mole Fraction		Methane Solute						Toluene Solvent					
PSIA	^{o}F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	150	0.017	0.973	2.605	0.992	0.992	1.000	57.235	21.972	1.000	0.905	0.731	1.237	0.027	0.034
200	150	0.034	0.982	2.560	0.985	0.985	1.000	28.882	11.285	1.001	0.823	*	-	0.019	-
400	150	0.069	0.989	2.468	0.970	0.970	1.000	14.333	5.809	1.003	0.684	*	-	0.012	-
600	150	0.104	0.990	2.377	0.956	0.956	1.000	9.519	4.004	1.006	0.568	*	-	0.011	-
800	150	0.138	0.990	2.292	0.943	0.943	1.000	7.174	3.131	1.011	0.472	*	-	0.012	-
1000	150	0.172	0.989	2.209	0.930	0.930	1.000	5.750	2.604	1.018	0.391	*	-	0.013	-
1500	150	0.253	0.987	2.019	0.902	0.902	1.000	3.901	1.934	1.043	0.249	*	-	0.017	-
2000	150	0.325	0.985	1.860	0.879	0.878	1.001	3.015	1.622	1.079	0.164	*	-	0.030	-
2500	150	0.393	0.980	1.720	0.861	0.859	1.002	2.494	1.452	1.127	0.111	*	-	0.033	-
3000	150	0.452	0.976	1.607	0.847	0.845	1.003	2.159	1.348	1.185	0.080	0.0058	13.734	0.044	0.508
3500	150	0.505	0.971	1.511	0.838	0.834	1.005	1.923	1.278	1.254	0.061	0.0058	10.449	0.059	0.488
4000	150	0.554	0.962	1.428	0.834	0.828	1.008	1.736	1.225	1.336	0.046	0.0059	7.915	0.085	0.505
4500	150	0.604	0.945	1.350	0.837	0.824	1.016	1.564	1.177	1.444	0.035	*	-	0.139	-
5000	150	0.664	0.919	1.264	0.850	0.824	1.032	1.384	1.130	1.619	0.026	*	-	0.241	-
5300	150	0.729	0.870	1.182	0.884	0.825	1.072	1.193	1.083	1.890	0.180	*	-	0.480	-

* Computer did not calculate

TABLE A-10

PROPANE - ISOPENTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Vaughan and Collins
IEC Vol. 32, 885, (1942)

Pressure	Temp.	Propane Mole Fraction		Propane Solute						Isopentane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	100	0.453	0.921	1.029	0.911	0.911	1.000	2.033	1.977	1.014	0.817	0.789	1.036	0.144	0.148
	150	0.212	0.577	1.049	0.934	0.930	1.005	2.722	2.608	1.003	0.843	0.834	1.011	0.537	0.541
	200	0.020	0.118	1.065	0.961	0.944	1.018	5.900	5.640	1.000	0.867	0.867	1.000	0.900	0.900
200	150	0.577	0.862	1.017	0.861	0.860	1.001	1.494	1.471	1.024	0.711	*	-	0.326	-
	200	0.263	0.604	1.042	0.896	0.889	1.009	2.297	2.224	1.004	0.751	0.729	1.029	0.537	0.551
	250	0.085	0.196	1.056	0.939	0.910	1.032	2.306	2.254	1.000	0.785	0.783	1.002	0.879	0.881
400	200	0.703	0.877	1.009	0.782	0.780	1.003	1.248	1.241	1.036	0.546	*	-	0.414	-
	250	0.411	0.648	1.027	0.838	0.823	1.019	1.577	1.563	1.010	0.603	*	-	0.598	-
	300	0.181	0.328	1.045	0.908	0.856	1.062	1.812	1.842	1.002	0.649	0.559	1.160	0.821	0.951
600	250	0.662	0.800	1.012	0.756	0.738	1.025	1.208	1.224	1.030	0.416	*	-	0.592	-
	300	0.443	0.540	1.024	0.871	0.787	1.106	1.219	1.317	1.011	0.469	*	-	0.826	-

* Computer did not calculate

TABLE A-11

PROPANE - NORMAL PENTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Sage and Lacey
IEC Vol. 32, 992, (1940)

Pressure	Temp.	Propane Mole Fraction		Propane Solute						n-Pentane Solvent					
PSIA	^{o}F	x	y	Gamma Liquid	ϕ_1	ϕ_1^{o}	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2^{o}	Gamma Vapor	K Observed	K Ideal
100	150	0.232	0.749	1.094	0.931	0.930	1.002	3.228	2.957	1.006	0.843	0.827	1.016	0.327	0.330
	200	0.063	0.256	1.123	0.957	0.944	1.014	4.063	3.671	1.000	0.863	0.861	1.002	0.794	0.795
200	150	0.571	0.902	1.035	0.861	0.860	1.001	1.580	1.528	1.046	0.706	*	-	0.228	-
	200	0.294	0.658	1.077	0.895	0.889	1.007	2.238	2.093	1.010	0.746	0.717	1.041	0.484	0.499
	250	0.112	0.321	1.107	0.932	0.910	1.024	2.866	2.652	1.001	0.779	1.127	0.691	0.765	0.528
400	200	0.715	0.904	1.016	0.781	0.780	1.002	1.264	1.247	1.075	0.539	*	-	0.337	-
	250	0.437	0.687	1.050	0.836	0.823	1.016	1.572	1.521	1.022	0.594	*	-	0.556	-
	300	0.222	0.417	1.082	0.896	0.856	1.047	1.878	1.818	1.005	0.642	0.519	1.235	0.749	0.921
	350	0.051	0.111	1.109	0.971	0.881	1.103	2.176	2.164	1.000	0.691	0.689	1.003	0.937	0.939
600	250	0.715	0.820	1.015	0.753	0.738	1.021	1.147	1.154	1.072	0.407	*	-	0.632	-
	300	0.477	0.598	1.042	0.843	0.843	1.070	1.254	1.288	1.026	0.472	*	-	0.769	-

* Computer did not calculate

TABLE A-12

PROPANE - BENZENE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Glanville, Sage and Lacey
IEC Vol. 42, 508, (1950)

Pressure	Temp.	Propane Mole Fraction		Propane Solute						Benzene Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	100	0.436	0.971	1.542	0.911	0.911	1.000	2.227	1.445	1.273	0.799	0.753	1.062	0.051	0.042
	150	0.213	0.914	2.157	0.930	0.930	1.000	4.299	1.993	1.054	0.836	0.806	1.037	0.110	0.108
	200	0.120	0.773	2.461	0.945	0.944	1.002	6.438	2.620	1.016	0.861	0.844	1.020	0.259	0.260
	250	0.054	0.533	2.678	0.960	0.955	1.005	9.953	3.737	1.003	0.879	0.872	1.008	0.494	0.496
	300	0.009	0.171	2.798	0.977	0.963	1.014	19.000	6.887	1.000	0.895	0.894	1.001	0.837	0.837
200	150	0.548	0.963	1.303	0.860	0.860	1.000	1.759	1.350	1.439	0.687	*	-	0.082	-
	200	0.307	0.883	1.769	0.889	0.889	1.001	2.876	1.627	1.111	0.738	*	-	0.169	-
	250	0.182	0.757	2.107	0.913	0.910	1.003	4.159	1.981	1.037	0.775	0.739	1.048	0.297	0.300
	300	0.105	0.565	2.334	0.935	0.926	1.009	5.407	2.338	1.011	0.803	0.787	1.020	0.486	0.490
	350	0.043	0.283	2.523	0.960	0.939	1.021	6.659	2.695	1.002	0.826	0.822	1.004	0.749	0.751
400	200	0.726	0.966	1.098	0.780	0.780	1.000	1.331	1.212	1.859	0.512	*	-	0.124	-
	250	0.463	0.879	1.392	0.825	0.823	1.003	1.897	1.367	1.263	0.583	*	-	0.226	-
	300	0.293	0.753	1.711	0.863	0.856	1.009	2.570	1.515	1.092	0.635	*	-	0.349	-
	350	0.193	0.603	1.946	0.897	0.881	1.018	3.130	1.638	1.037	0.678	0.390	1.739	0.492	0.826
	400	0.116	0.382	2.149	0.935	0.901	1.038	3.289	1.588	1.013	0.712	*	-	0.699	-
	450	0.042	0.134	2.375	0.980	0.918	1.068	3.217	1.447	1.002	0.746	0.744	1.003	0.904	0.905
600	250	0.748	0.925	1.078	0.740	0.738	1.004	1.237	1.152	1.871	0.398	*	-	0.297	-
	300	0.515	0.818	1.294	0.797	0.787	1.012	1.588	1.242	1.320	0.475	*	-	0.375	-
	350	0.354	0.688	1.541	0.846	0.825	1.026	1.946	1.296	1.132	0.535	*	-	0.483	-
	400	0.238	0.536	1.773	0.894	0.855	1.045	2.249	1.326	1.056	0.586	*	-	0.609	-
	450	0.142	0.359	2.010	0.945	0.879	1.075	2.537	1.357	1.019	0.630	0.507	1.244	0.747	0.912
	500	0.056	0.155	2.258	1.008	*	-	2.793	-	1.003	0.673	0.636	1.058	0.895	0.944
800	350	0.528	0.722	1.263	0.815	0.772	1.056	1.367	1.143	1.325	0.382	*	-	0.589	-
	400	0.383	0.584	1.461	0.884	0.811	1.090	1.523	1.136	1.152	0.448	*	-	0.675	-
	450	0.265	0.429	1.674	0.961	0.842	1.164	1.619	1.126	1.067	0.504	*	-	0.777	-

* Computer did not calculate

TABLE A-13

NORMAL BUTANE - NORMAL HEPTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: W. B. Kay
IEC Vol. 33, 590, (1941)

Pressure	Temp.	n-Butane Mole Fraction		n-Butane Solute						n-Heptane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	150	0.912	0.997	1.001	0.883	0.883	1.000	1.093	1.092	1.095	0.749	*	-	0.034	-
	200	0.522	0.920	1.026	0.907	0.906	1.000	1.762	1.719	1.020	0.790	0.744	1.061	0.167	0.174
	250	0.293	0.763	1.045	0.926	0.924	1.002	2.604	2.499	1.005	0.818	0.794	1.031	0.335	0.344
	300	0.140	0.490	1.057	0.946	0.937	1.010	3.500	3.344	1.001	0.838	0.830	1.010	0.593	0.599
	350	0.018	0.077	1.065	0.974	0.948	1.028	4.400	4.245	1.000	0.858	0.858	1.000	0.939	0.940
200	250	0.650	0.922	1.014	0.849	0.849	1.001	1.418	1.399	1.033	0.666	*	-	0.223	-
	300	0.404	0.778	1.033	0.880	0.876	1.004	1.926	1.873	1.010	0.706	*	-	0.372	-
	350	0.232	0.550	1.046	0.911	0.897	1.016	2.371	2.302	1.003	0.736	0.710	1.037	0.586	0.606
	400	0.83	0.235	1.057	0.951	0.914	1.041	2.831	2.789	1.000	0.764	0.760	1.005	0.834	0.839
300	250	0.923	0.984	1.001	0.774	0.774	1.000	1.066	1.065	1.088	0.523	*	-	0.208	-
	300	0.635	0.882	1.015	0.817	0.815	1.003	1.389	1.372	1.030	0.585	*	-	0.323	-
	350	0.418	0.718	1.030	0.856	0.847	1.011	1.718	1.686	1.010	0.629	*	-	0.485	-
	400	0.246	0.477	1.043	0.902	0.872	1.035	1.939	1.924	1.003	0.662	0.516	1.284	0.694	0.888
	450	0.086	0.184	1.055	0.966	0.892	1.083	2.140	2.197	1.000	0.670	0.691	1.009	0.893	0.901
400	300	0.825	0.938	1.004	0.755	0.754	1.001	1.137	1.134	1.060	0.468	*	-	0.354	-
	350	0.587	0.803	1.017	0.805	0.797	1.010	1.368	1.358	1.023	0.527	*	-	0.477	-
	400	0.390	0.611	1.031	0.858	0.831	1.033	1.567	1.569	1.008	0.569	*	-	0.638	-
	450	0.223	0.362	1.043	0.931	0.857	1.085	1.623	1.689	1.002	0.605	*	-	0.821	-
	500	0.053	0.078	1.056	1.079	0.879	1.227	1.472	1.710	1.000	0.648	0.636	1.017	0.974	0.990
500	350	0.732	0.853	1.008	0.757	0.748	1.012	1.165	1.169	1.041	0.422	*	-	0.549	-
	400	0.526	0.681	1.021	0.822	0.790	1.040	1.295	1.318	1.017	0.474	*	-	0.673	-
	450	0.354	0.450	1.033	0.924	0.824	1.122	1.271	1.381	1.007	0.507	*	-	0.851	-

* Computer did not calculate

TABLE A-14

NORMAL PENTANE - NORMAL HEPTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: Katz and Brown
IEC Vol. 25, 1375, (1933)

Pressure	Temp.	n-Pentane Mole Fraction		n-Pentane Solute						n-Heptane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1^{c}	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2^{o}	Gamma Vapor	K Observed	K Ideal
100	250	0.700	0.890	1.003	0.887	0.887	1.000	1.271	1.268	1.013	0.809	*	-	0.367	-
	300	0.310	0.610	1.012	0.909	0.907	1.003	1.968	1.948	1.002	0.836	*	-	0.565	-
200	300	0.880	0.951	1.001	0.815	0.815	1.000	1.081	1.080	1.021	0.691	*	-	0.408	-
	350	0.450	0.672	1.008	0.849	0.846	1.004	1.493	1.488	1.004	0.729	*	-	0.596	-
	400	0.140	0.285	1.017	0.886	0.870	1.017	2.036	2.038	1.000	0.762	*	-	0.831	-
400	400	0.715	0.790	1.002	0.750	0.744	1.008	1.105	1.111	1.012	0.546	*	-	0.737	-
	450	0.405	0.480	1.009	0.813	0.785	1.036	1.185	1.218	1.003	0.596	*	-	0.874	-

* Computer did not calculate

TABLE A-15

METHANE - CYCLOPENTANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: G. A. Clark
M.S. Thesis, University of Texas, June, 1949

Pressure	Temp.	Methane Mole Fraction		Methane Solute						Cyclopentane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	150	0.017	0.755	1.755	0.998	0.992	1.006	45.48	26.07	1.000	0.894	0.837	1.068	0.249	0.266
200	150	0.038	0.868	1.729	0.988	0.985	1.013	23.15	13.56	1.001	0.828	*	-	0.137	-
400	150	0.079	0.917	1.677	0.973	0.970	1.003	11.61	6.94	1.002	0.708	*	-	0.090	-
600	150	0.120	0.934	1.627	0.959	0.956	1.003	7.78	4.80	1.006	0.607	*	-	0.075	-
800	150	0.161	0.942	1.578	0.945	0.943	1.002	5.84	3.71	1.011	0.520	*	-	0.069	-
1000	150	0.202	0.944	1.531	0.933	0.930	1.003	4.66	3.05	1.018	0.444	*	-	0.070	-
1250	150	0.253	0.944	1.475	0.920	0.915	1.005	3.73	2.54	1.029	0.364	*	-	0.076	-
1500	150	0.302	0.941	1.423	0.908	0.902	1.007	3.11	2.20	1.043	0.298	*	-	0.085	-
1750	150	0.352	0.936	1.373	0.897	0.889	1.009	2.66	1.95	1.062	0.242	*	-	0.099	-
2000	150	0.400	0.928	1.327	0.890	0.878	1.014	2.32	1.77	1.084	0.196	*	-	0.120	-
2250	150	0.451	0.919	1.280	0.884	0.868	1.018	2.04	1.62	1.113	0.159	*	-	0.148	-
2500	150	0.501	0.904	1.238	0.883	0.859	1.028	1.80	1.49	1.147	0.126	*	-	0.193	-
2750	150	0.555	0.880	1.195	0.891	0.851	1.047	1.59	1.39	1.194	0.096	*	-	0.270	-
3000	150	0.631	0.838	1.140	0.918	0.845	1.086	1.33	1.27	1.278	0.069	*	-	0.438	-

* Computer did not calculate

TABLE A-16

METHANE - CYCLOHEXANE BINARY

Calculated Activity Coefficients and Ideal K Values

x-y Data Source: G. A. Clark
M.S. Thesis, University of Texas, June, 1949

Pressure	Temp.	Methane Mole Fraction		Methane Solute						Cyclohexane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	150	0.018	0.927	1.836	0.993	0.992	1.001	50.930	27.77	1.000	0.899	0.761	1.181	0.074	0.087
200	150	0.037	0.965	1.814	0.985	0.985	1.000	25.870	14.26	1.000	0.826	*	-	0.037	-
400	150	0.075	0.976	1.769	0.970	0.970	1.000	12.980	7.34	1.002	0.691	*	-	0.026	-
600	150	0.113	0.978	1.724	0.956	0.956	1.000	8.655	5.02	1.005	0.577	*	-	0.025	-
800	150	0.150	0.980	1.681	0.943	0.943	1.000	6.526	3.88	1.008	0.484	*	-	0.024	-
1000	150	0.188	0.979	1.638	0.931	0.930	1.001	5.212	3.19	1.014	0.405	*	-	0.026	-
1250	150	0.234	0.979	1.586	0.916	0.915	1.001	4.192	2.65	1.023	0.326	*	-	0.028	-
1500	150	0.279	0.978	1.536	0.903	0.902	1.001	3.512	2.29	1.034	0.264	*	-	0.031	-
1750	150	0.323	0.976	1.488	0.891	0.889	1.002	3.020	2.03	1.048	0.214	*	-	0.036	-
2000	150	0.367	0.973	1.441	0.880	0.878	1.002	2.649	1.84	1.066	0.175	*	-	0.042	-
2250	150	0.410	0.970	1.397	0.871	0.868	1.003	2.366	1.70	1.088	0.144	*	-	0.051	-
2500	150	0.452	0.966	1.354	0.863	0.859	1.005	2.137	1.59	1.113	0.119	*	-	0.062	-
2750	150	0.493	0.960	1.314	0.857	0.851	1.007	1.949	1.49	1.144	0.098	*	-	0.079	-
3000	150	0.535	0.951	1.274	0.851	0.845	1.007	1.778	1.41	1.182	0.086	0.012	7.167	0.105	0.637
3250	150	0.576	0.939	1.237	0.853	0.839	1.024	1.631	1.35	1.227	0.065	0.011	5.909	0.145	0.698
3500	150	0.620	0.918	1.197	0.860	0.834	1.031	1.482	1.28	1.285	0.050	0.011	4.545	0.215	0.760
3750	150	0.680	0.871	1.150	0.889	0.831	1.070	1.282	1.19	1.389	0.034	0.012	2.833	0.402	0.820

* Computer did not calculate

TABLE A-17

METHANE - METHYLCYCLOHEXANE BINARY

Calculated Activity Coefficient and Ideal K Values

x-y Data Source: G. A. Clark
M.S. Thesis, University of Texas, June, 1949

Pressure	Temp.	Methane Mole Fraction		Methane Solute						Methylcyclohexane Solvent					
PSIA	°F	x	y	Gamma Liquid	ϕ_1	ϕ_1°	Gamma Vapor	K Observed	K Ideal	Gamma Liquid	ϕ_2	ϕ_2°	Gamma Vapor	K Observed	K Ideal
100	150	0.022	0.948	1.588	0.992	0.992	1.000	44.090	27.764	1.000	0.928	0.860	1.079	0.053	0.057
200	150	0.043	0.968	1.574	0.985	0.985	1.000	22.520	14.307	1.000	0.866	*	-	0.033	-
400	150	0.086	0.980	1.544	0.970	0.970	1.000	11.420	7.396	1.002	0.754	*	-	0.022	-
600	150	0.129	0.983	1.514	0.956	0.956	1.000	7.628	5.038	1.004	0.657	*	-	0.020	-
800	150	0.171	0.983	1.485	0.943	0.943	1.000	5.749	3.871	1.008	0.571	*	-	0.021	-
1000	150	0.214	0.982	1.455	0.930	0.930	1.000	4.600	3.161	1.013	0.496	*	-	0.023	-
1250	150	0.266	0.982	1.418	0.916	0.915	1.001	3.694	2.607	1.021	0.417	*	-	0.025	-
1500	150	0.318	0.980	1.381	0.902	0.902	1.000	3.081	2.231	1.032	0.351	*	-	0.030	-
1750	150	0.367	0.977	1.347	0.890	0.889	1.001	2.662	1.978	1.046	0.295	*	-	0.036	-
2000	150	0.414	0.974	1.313	0.879	0.878	1.001	2.353	1.794	1.063	0.249	*	-	0.044	-
2250	150	0.457	0.970	1.283	0.870	0.868	1.002	2.124	1.659	1.082	0.211	*	-	0.055	-
2500	150	0.496	0.965	1.256	0.862	0.859	1.003	1.944	1.552	1.104	0.178	*	-	0.070	-
2750	150	0.534	0.959	1.229	0.855	0.851	1.005	1.797	1.469	1.129	0.151	*	-	0.088	-
3000	150	0.570	0.952	1.205	0.851	0.844	1.008	1.671	1.398	1.157	0.128	*	-	0.112	-
3250	150	0.603	0.942	1.182	0.848	0.839	1.011	1.563	1.337	1.188	0.108	*	-	0.146	-
3500	150	0.636	0.928	1.160	0.849	0.834	1.018	1.459	1.280	1.225	0.089	*	-	0.196	-
3750	150	0.680	0.904	1.132	0.857	0.831	1.031	1.330	1.211	1.285	0.069	*	-	0.300	-

* Computer did not calculate

APPENDIX B

DEVELOPMENT OF MODIFIED VAN LAAR EQUATION THROUGH SCATCHARD-HILDEBRAND REGULAR SOLUTION TREATMENT

APPENDIX B

DEVELOPMENT OF MODIFIED VAN LAAR EQUATION THROUGH SCATCHARD-HILDEBRAND REGULAR SOLUTION TREATMENT

Hildebrand (22) is responsible for the terminology, "regular solution". The name was first used to describe the solubility behavior of iodine as a solute in various solvents. Hildebrand observed that when the logarithm of solute concentration was plotted versus the reciprocal of absolute temperature, approximately straight lines resulted until the melting point of the solute was approached. Further, he observed that the solubility lines for different solvents were essentially parallel. The spread between lines was found to be a function of "internal pressure" difference. Later the term "solubility parameter" was used (25).

The class of solutions which behaved as described in the preceding paragraph were far from ideal as measured by deviation from Raoult's law, but because of their consistent behavior, they were termed "regular".

The exact definition of "regular solutions" has varied some since the original conception. However, the following properties are generally accepted for defining such solutions and have been used to develop quantitative treatments (23, 60).

(1) Entropy of mixing is ideal.

(2) Volume change on mixing is zero.

(3) Orienting and chemical effects are absent.

(4) Pair additivity.

Scatchard (60) is given credit for the first quantitative development of the regular solution theory. Hildebrand and Wood (18) are responsible for a similar treatment. Both works were based on statistical treatment of the intermolecular potential in solutions. The development which follows is essentially that of Scatchard. Only the binary mixture is considered.

Total cohesive energy of one mole of mixture is given by equation B-1.

$$-\underline{E}_m = \left[C_{11}\phi_1^{\,2} + 2C_{12}\phi_1\phi_2 + C_{22}\phi_2^{\,2}\right](\underline{V}_1x_1 + \underline{V}_2x_2) \qquad \text{(B-1)}$$

By definition, the internal energy change on mixing is given by Equation B-2.

$$\Delta\,\underline{E}_m = \underline{E}_m - \left[x_1\left[\underline{E}_m\right]_{(x_1=1)} + x_2\left[\underline{E}_m\right]_{(x_2=1)}\right] \qquad \text{(B-2)}$$

A combination of the pure component energies, $-\underline{E}_1 = C_{11}\underline{V}_1$ and $-\underline{E}_2 = C_{22}\underline{V}_2$, with the value of $\underline{E}_m$ from Equation B-1, converts Equation B-2 to the following:

$$\Delta\,\underline{E}_m = (x_1\underline{V}_1 + x_2\underline{V}_2)(C_{11} + C_{22} - 2C_{12})\phi_1\phi_2 \qquad \text{(B-3)}$$

It is at this point that a simplification is made which has a significant bearing on what can be expected in the final result. Scatchard assumed that the cohesive energy behaved as gravitational energy between point masses or as the electrostatic energy between point charges, that is

$$C_{12} = \sqrt{C_{11}C_{22}} \qquad \text{(B-4)}$$

Equation B-4 is the same as proposed by Berthelot. A conclusive justification for use of the geometric average is not available. However, it is certainly better than the arithmetic average which would force $\Delta \underline{E}_m$ to be zero.

The simplified equation obtained by substituting Equation B-4 into Equation B-3 is,

$$\Delta \underline{E}_m = (x_1\underline{V}_1 + x_2\underline{V}_2)(\sqrt{C_{11}} - \sqrt{C_{22}})^2\phi_1\phi_2 \tag{B-5}$$

It is worthwhile to note at this point that negative deviations cannot be predicted by Equation B-5. This results from the Berthelot assumption. In some instances this may hinder the usefulness of the development. Note that had $\Delta \underline{E}_m$ been left in the form of Equation B-3, negative deviations could result.

By noting that $-\underline{E}_1$ and $-\underline{E}_2$ are energies of the liquids measured with respect to a reference of infinite molecular separation, they they can be replaced by equivalent expressions $\Delta \underline{E}_1{}^V$ and $\Delta \underline{E}_2{}^V$ representing energy of vaporization to a state of infinite volumes. Thus, the cohesive energy densities become,

$$C_{11} = \frac{\Delta \underline{E}_1{}^V}{\underline{V}_1{}^L}, \quad C_{22} = \frac{\Delta \underline{E}_2{}^V}{\underline{V}_2{}^L} \tag{B-6}$$

These values are included in Equation B-5 to obtain,

$$\Delta \underline{E}_m = (x_1\underline{V}_1 + x_2\underline{V}_2)\left[\left[\frac{\Delta \underline{E}_1{}^V}{\underline{V}_1{}^L}\right]^{\frac{1}{2}} - \left[\frac{\Delta \underline{E}_2{}^V}{\underline{V}_2{}^L}\right]^{\frac{1}{2}}\right]^2 \phi_1\phi_2 \tag{B-7}$$

Hildebrand gave the one-half power of cohesive energy density term the name "solubility parameter" and identified it as delta (δ). Further, since $\Delta \underline{V}_m$ is postulated to be zero, and mixing is assumed to be done at constant pressure, then $\Delta \underline{H}_m$ and $\Delta \underline{E}_m$ become equivalent. By making these substitutions, and converting to a total mole basis, then Equation

B-7 becomes,

$$\Delta H_m = (n_1\underline{V}_1 + n_2\underline{V}_2)\left[\delta_1 - \delta_2\right]^2\phi_1\phi_2 \tag{B-8}$$

Taking the partial derivative of ΔH_m with respect to n_1,

$$\Delta \overline{H}_1^{\,m} = \left[\frac{\partial \Delta H_m}{\partial n_1}\right]_{n_2,T,P} = \underline{V}_1\phi_2^{\,2}(\delta_1 - \delta_2)^2 \tag{B-9}$$

From the definition of free energy and the fact that temperature is constant,

$$\Delta \overline{F}_1^{\,m} = \Delta \overline{H}_1^{\,m} - T\Delta \overline{S}_1^{\,m} \tag{B-10}$$

Further, from the definition of fugacity and activity, another expression for $\Delta \overline{F}_1^{\,m}$ is obtained.

$$\begin{aligned} \mu_1 &= \overline{F}_1 = RT \ln \overline{f}_1 + \phi(T) \\ \mu_1^{\circ} &= F_1^{\circ} = RT \ln f_1^{\circ} + \phi(T) \\ a_1 &= \frac{\overline{f}_1}{f_1^{\circ}} \end{aligned}$$

Therefore, since the pure liquid is used as the reference state,

$$\Delta \overline{F}_1^{\,m} = (\overline{F}_1 - F_1^{\circ}) = RT \ln a_1 \tag{B-11}$$

As a part the theory,

$$\Delta \overline{S}_1^{\,m} = -R \ln x_1 \tag{B-12}$$

The activity coefficient is

$$\gamma_1 = \frac{a_1}{x_1} \tag{B-13}$$

by definition.

Thus, Equation B-10 becomes,

$$RT \ln \gamma_1 = \underline{V}_1\phi_2^{\,2}(\delta_1 - \delta_2)^2 \tag{B-14}$$

By further manipulation,

$$\ln \gamma_1 = \frac{\underline{V}_1}{RT}\,\frac{(\delta_1 - \delta_2)^2 (x_2\underline{V}_2)^2}{(x_1\underline{V}_1 + x_2\underline{V}_2)^2} \tag{B-15}$$

or

$$\ln \gamma_1 = \frac{A}{\left[\frac{x_1\underline{V}_1}{x_2\underline{V}_2} + 1\right]^2} \tag{B-16}$$

Where (A) is defined in Equation B-17.

$$A = \frac{\underline{V}_1}{RT}(\delta_1 - \delta_2)^2 \tag{B-17}$$

An equation similar to B-16 can be derived for the second component. Then the quantity (B) is defined as,

$$B = \frac{\underline{V}_2}{RT}(\delta_1 - \delta_2)^2 \tag{B-18}$$

From the ratio of the two previous equations, it is seen that,

$$\frac{A}{B} = \frac{\underline{V}_1}{\underline{V}_2} \tag{B-19}$$

Now Equation B-16 is written in the final form.

$$\ln \gamma_1 = \frac{A}{\left[\frac{Ax_1}{Bx_2} + 1\right]^2} \tag{B-20}$$

Equation B-20 is recognized as a form of the van Laar equation. It is significant that this equation was derived without any connection to the van der Waals' equation of state which was used by van Laar in his work.

The corresponding equation for the second component is,

$$\ln \gamma_2 = \frac{B}{\left[\frac{Bx_2}{Ax_1} + 1\right]^2} \tag{B-21}$$

APPENDIX C

DEVELOPMENT OF REDLICH-KWONG EQUATION FOR VAPOR FUGACITY COEFFICIENTS

APPENDIX C

DEVELOPMENT OF REDLICH-KWONG EQUATION FOR VAPOR FUGACITY COEFFICIENTS

The Redlich-Kwong (50) equation of state was introduced in 1949. It is a two-constant equation recommended for pure gases and mixtures of gases above the critical temperature for any pressure. The equation is expressed explicitly in pressure as

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

A good fit of high pressure data is obtained with this equation since Redlich and Kwong designed into it the requirement that

$$b = 0.26V_c \qquad \text{(C-2)}$$

which corresponds to the limiting volume of practically all gases at high pressure as observed by Kuenen.

In the application of Equation C-1, a number of auxiliary equations are introduced.

$$Z = \frac{1}{(1-h)} - \frac{A^2}{B}\frac{h}{(1+h)} \qquad \text{(C-3)}$$

$$Z = \frac{PV}{RT} \qquad \text{(C-4)}$$

$$A^2 = \frac{a}{R^2T^{2.5}} = \frac{0.4278T_c^{2.5}}{P_c\ T} \qquad \text{(C-5)}$$

$$B = \frac{b}{RT} = 0.0867\frac{T_c}{P_cT} \qquad \text{(C-6)}$$

$$h = \frac{BP}{Z} = \frac{b}{V} \qquad \text{(C-7)}$$

It will be observed that only critical temperature and pressure data are required in applying the equation.

Any equation of state can be utilized to develop thermodynamic properties. In particular, the fugacity coefficient can be calculated through the fundamental definition of fugacity, expressed in the form

$$\ln \phi^{o} = \int_0^P (Z-1)\frac{dP}{P} \qquad \text{(C-8)}$$

At this point only the pure component fugacity coefficient is considered. With the proper values of Z, Equation C-8 can be integrated. The Redlich-Kwong equation cannot be expressed explicitly in Z, but rather a cubic equation evolves.

$$Z^3 - Z^2 + (A^2P - B^2P^2 - BP)Z - BA^2P^2 = 0 \qquad \text{(C-9)}$$

By applying Cardan's method for solving cubic equations, an expression for Z is obtained. On substituting into Equation C-8 and performing the integration, Equation C-10 results.

$$\ln \phi^{o} = (Z-1) - \ln(Z-BP) - (A^2/B)\ \ln\left(1-\frac{BP}{Z}\right) \qquad \text{(C-10)}$$

Use of this equation for calculating pure component fugacity coefficient is illustrated in Appendix G.

For gaseous mixtures the volume coefficients are expressed as the following linear combinations.

$$b = \sum_i y_i b_i \qquad B = \sum_i y_i B_i \qquad \text{(C-11)}$$

The attraction coefficient for mixtures as predicted by molecular theory involves mole fractions to the second degree.

$$a = a_1 y_1{}^2 + a_2 y_2{}^2 + \cdots\cdots 2a_{12} y_1 y_2 + \cdots\cdots \qquad \text{(C-12)}$$

Cross-products are expressed as

$$a_{12} = \sqrt{a_1 a_2} \text{ etc} \tag{C-13}$$

and the total attraction coefficient is

$$A = \sum_i y_i A_i \tag{C-14}$$

Fugacity coefficient for a component in the mixture is by definition

$$\phi_i = \frac{\bar{f}_i}{y_i P} \tag{C-15}$$

An equation similar to C-8 yields the value of fugacity coefficient for the component in the mixture; that is,

$$\ln \phi_i = \int_0^P (\bar{Z}_i - 1)\frac{dP}{P} \tag{C-16}$$

Redlich and Kwong performed the integration which will not be repeated here. The equation resulting from the integration is

$$\text{Log } \phi_i = 0.4343 \, (Z-1) \frac{B_i}{B} - \text{Log } (Z-BP) - \frac{A^2}{B}\left[\frac{2A_i}{A} - \frac{B_r}{B}\right] \text{Log}(1-\frac{BP}{Z}) \tag{C-17}$$

Use of the equation is illustrate in Appendix G. All calculations were performed using the IBM 650 digital computer with a program prepared by Erbar and Thompson (17).

APPENDIX D

DEVELOPMENT OF METHOD FOR TEST OF THERMODYNAMIC CONSISTENCY

APPENDIX D

DEVELOPMENT OF METHOD FOR TEST OF THERMODYNAMIC CONSISTENCY

The commonly used Gibbs-Duhem expression

$$x_1 \left[\frac{\partial \ln \gamma_1}{\partial x_1} \right]_{T,P} = x_2 \left[\frac{\partial \ln \gamma_2}{\partial x_2} \right]_{T,P} \qquad \text{(D-1)}$$

is not satisfactory for use in tests of thermodynamic consistency for binary mixtures at high pressure. Equation D-1 is so frequently used in testing the consistency of data obtained at atmospheric pressure that the restrictions of negligible liquid volume in comparison with the vapor phase tends to be overlooked when considering the case of constant temperature and variable pressure.

Ibl and Dodge (28) have developed the rigorous relationships for binaries. Their development considered both the case of constant temperature and variable pressure and the reverse. Lachowicz, Newitt and Weale (33) considered the former case in the development of expressions for slightly soluble gases in relatively non-volatile solvents. Nord (39) has discussed the latter case.

The intent of this study has not been to check the thermodynamic consistency of all data used. However, a study of the correlation results has indicated the need to explore certain pieces of data. Only the case of constant temperature and variable pressure is needed. Thus, the development which follows is for that case (28).

When Equation D-1 is considered in light of the phase rule,

$$V = C + 2 - P \tag{D-2}$$

it is apparent that equilibrium cannot exist with both temperature and pressure fixed. To make the system variant, one restriction must be removed (i.e., pressure in this development).

From Euler's theorem for homogeneous functions.

$$f(\lambda x, \lambda y, \lambda z) = \lambda^n f(x,y,z) \tag{D-3}$$

where λ is an arbitrary constant and n is the degree of homogeneity. Further, by partial differentiation with respect to λ.

$$x\frac{\partial f}{\partial(\lambda x)} + y\frac{\partial f}{\partial(\lambda y)} + z\frac{\partial f}{\partial(\lambda y)} = n\lambda^{n-1} f \tag{D-4}$$

Since λ is completely arbitrary, it may be assumed to be unity without loss of generality. Thus,

$$x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = nf \tag{D-5}$$

Consider specifically the extensive property free energy, which is of first degree with respect to the amount of the constituents, then apply Equation D-5 for a binary of variable molar quantities n_1 and n_2, to obtain,

$$n_1\frac{\partial F}{\partial n_1} + n_2\frac{\partial F}{\partial n_2} = F \tag{D-6}$$

The intensive properties $\frac{\partial F}{\partial n_1}$ and $\frac{\partial F}{\partial n_2}$ are recognized as chemical potentials μ_1 and μ_2, respectively, by definition. Thus,

$$F = n_1\mu_1 + n_2\mu_2 \tag{D-7}$$

Differentiate Equation D-7 to obtain,

$$dF = n_1 d\mu_1 + n_2 d\mu_2 + \mu_1 dn_1 + \mu_2 dn_2 \qquad \text{(D-8)}$$

Further, free energy for any phase can be expressed as

$$F = F(T, P, n_1, n_2) \qquad \text{(D-9)}$$

Thus,

$$dF = \left|\frac{\partial F}{\partial T}\right|_{P,n_1,n_2} dT + \left|\frac{\partial F}{\partial P}\right|_{T,n_1,n_2} dP + \left|\frac{\partial F}{\partial n_1}\right|_{T,P,n_2} dn_1 + \left|\frac{\partial F}{\partial n_2}\right|_{T,P,n_1} dn_2 \qquad \text{(D-10)}$$

Equivalently,

$$dF = vdP - SdT + \mu_1 dn_1 + \mu_2 dn_2 \qquad \text{(D-11)}$$

By subtracting Equation D-8 from Equation D-11, the most general form of the Gibbs equation results.

$$VdP - SdT = n_1 d\mu_1 + n_2 d\mu_2 \qquad \text{(D-12)}$$

Equation D-12 is manipulated by considering the constant temperature case for the liquid phase, dividing by total moles $(n_1 + n_2)$ and substituting $d\mu_i = RTd \ln \bar{f}_i$.

Thus,

$$x_1 \, d\ln \bar{f}_1 + x_2 \, d \ln \bar{f}_2 = \frac{V_m{}^L}{RT} \, dP \qquad \text{(D-13)}$$

Equation D-13 is then put into a form used by Adler et al. (1) for convenience in checking thermodynamic consistency. It is at this point that a compromise is made in thermodynamic rigor. The Lewis and Randall rule is assumed for the vapor phase. This of course imposes a limitation on the method near the critical region.

The following expressions are used in converting Equation D-13.

$$\ln \frac{\bar{f}_i}{Py_i} = \int_0^P \left[\frac{\bar{V}_i{}^g}{RT} - \frac{1}{P} \right] dP \qquad \text{(D-14)}$$

Therefore,

$$d\ln\bar{f}_i = d\ln(Py_i) + \left[\frac{P\bar{V}_i^g}{RT} - 1\right] d\ln P \qquad \text{(D-15)}$$

By definition,

$$Z_i^g = \frac{P\bar{V}_i^g}{RT} \qquad \text{(D-16)}$$

Since the Lewis and Randall rule implies additive volumes, then $\bar{V}_1^g = \underline{V}_1^g$. The value of $\bar{V}_2^g$ can be calculated from the expression, $\underline{V}_m^g = y_1\bar{V}_1^g + y_2\bar{V}_2^g$; that is,

$$\bar{V}_2^g = \frac{\underline{V}_m^g - y_1\bar{V}_1^g}{y_2} \cong \frac{\underline{V}_m^g - y_1\underline{V}_1^g}{y_2} \qquad \text{(D-17)}$$

By substitution of Equations D-15, D-16 and D-17 into equation D-13 along with y_i/K_i for x_i, one form of Adler's equation is developed.

$$x_1 d\ln K_1 + x_2 d\ln K_2 = \left[Z^L + Z_1^g y_1\left[\frac{1}{K_2} - \frac{1}{K_1}\right] - \frac{Z^g}{K_2}\right] d\ln P \qquad \text{(D-18)}$$

In Adler's development it was implied that Equation D-18 represented only the restricted case in which the Lewis and Randall rule held for the vapor phase. Actually Equation D-18 is a rigorous equation if the partial volume of component (1) is used to calculate Z_1^g. This is apparent upon substitution of $y_i = K_i x_i$ and $Z^g = x_1 Z_1^g + x_2 Z_2^g$ into Equation D-13 subsequent to the use of Equation D-15 and D-16.

Equation D-18, when integrated between the proper limits, provides a check of thermodynamic consistency.

For the range of data considered in this study, methane is always above its critical temperature, thus the integration can only proceed to the critical composition.

$$\int_{K_1(x_1=0)}^{K_1(x_1=x_c)} x_1 \, d \ln K_1 + \int_{K_2(x_2=1)}^{K_2(x_2=1-x_c)} x_2 \, d \ln K_2$$

$$= \int_{P=0}^{P=P_c} \left[Z^L + Z_1{}^g y_1 \left(\frac{1}{K_2} - \frac{1}{K_1} \right) - \frac{Z^g}{K_2} \right] d \ln P \qquad \text{(D-19)}$$

Prausnitz (44) presented a similar equation to D-19 in terms of activity coefficients.

$$\int_0^{x_1 = x_c} \ln \frac{\gamma_1}{\gamma_2} \, dx_1 + \int_{P(x_1=0)}^{P_c} \frac{\Delta V}{RT} \, dP = x_1{}^c \ln \gamma_1{}^c + x_2{}^c \ln \gamma_2{}^c \qquad \text{(D-20)}$$

where

$$\Delta V = \underline{V}_m{}^L - x_1 \underline{V}_1{}^L - x_2 \underline{V}_2{}^L$$

Equation D-19 is found to be more easily applied. A sample calculation is given in Appendix H.

Adler et al. applied Equation D-19 to check the methane-propane binary data of Reamer, Sage and Lacey (48). This is one of the binaries studied in this report. They obtained an excellent check of consistency at 100°F for the pressure range from propane vapor pressure to critical pressure of the mixture. Similar checks have been made in this report in Appendix H for methane-n-pentane and methane-decane (46, 58) at 160°F for the full pressure range.

A fair consistency check was obtained for pentane and a poor check for decane. The results probably do not prove that the data are inconsistent. Rather, the assumption of additive vapor volumes is likely to breakdown at the higher critical pressures which exist with the progressively heavier solvents. For the two binaries considered, Sage and Lacey have reported partial volumes but they are not available for the range of data tested, otherwise a rigorous consistency check would have been possible.

A check of the data of Elbishlawi and Spencer (16) was desired since Savyina and Velikovskii (59) questioned the accuracy at high pressure. Unfortunately, volume data are not available in the Elbishlawi and Spencer work which would permit such a check. Further, the critical pressures are high for the methane-benzene and methane-toluene binaries, thus the method of Adler is probably not applicable.

Clark's data (9) are suspect, since in this study and that of Chao and Seader (8) the greatest deviations occur when attempting to compare the predicted methane equilibrium constant with the actual in the naphthenic solvents. As in the case of the Elbishlawi and Spencer aromatic data, no volume data are available to permit a consistency check.

APPENDIX E

BACKGROUND OF WATSON'S VOLUME EXPRESSION

APPENDIX E

BACKGROUND OF WATSON'S VOLUME EXPRESSION

In the process of evaluating the liquid phase activity coefficients by the equations developed in Appendix B it is necessary to know the molar liquid volumes of the pure components. Complications arise, however, when a component in the liquid phase is above its critical temperature, since pure component liquid cannot exist. This is the case for methane for the range of data considered in this study.

This problem is not new. Gamson and Watson (19) in 1944 introduced the following empirical equation to represent the hypothetical molar liquid volume.

$$\underline{V}^L = \underline{V}_1 \omega_1 \ (5.7 + 3.0\ T_r) \qquad \text{(E-1)}$$

The quantity $(\underline{V}_1 \omega_1)$ is the product of a molar liquid volume $(\underline{V}_1)$ of the component at some measureable state and the expansion factor (ω_1) at the same state. This product is a constant for each substance; therefore, Equation E-1 represents the volume for a hypothetical incompressible liquid, since no provisions are made for the influence of pressure.

The terminology "expansion factor" (ω) is logically applied to a term which includes the reciprocal of compressibility factor. The significance of the term (ω) and the product $(\underline{V}\,\omega)$ will be obvious from the defining equation of (ω) presented by Watson (65). In developing a generalization for liquid properties, Watson started by applying the gaseous phase equation ($PV = ZRT$) to the liquid phase as well to obtain,

$$\rho = \frac{PM}{ZRT} = \left(\frac{P_r}{ZRT_r}\right)\frac{PcM}{T_c} = \omega\frac{PcM}{T_c} \qquad \text{(E-2)}$$

Thus, by definition

$$\omega = \frac{P_r}{ZRT_r} \qquad \text{(E-3)}$$

Further,

$$\frac{\omega}{\rho} = \underline{V}\,\omega = \frac{T_c}{P_cM} \qquad \text{(E-4)}$$

As indicated, the product ($\underline{V}\omega$) is a constant for each substance which can be calculated from the critical temperature and pressure and molecular weight. The values of ($\underline{V}\omega$) used in this study are listed in Table III.

Watson did not find (ω) to be a completely satisfactory generalizing function in terms of P_r and T_r. However, he did demonstrate significant utility for the following expression,

$$\underline{V} = \underline{V}_1\frac{\omega_1}{\omega} \qquad \text{(E-5)}$$

when used in conjunction with an (ω) correlation in terms of P_r and T_r for one specific material. Isopentane was used by Watson to prepare the first expansion factor plot (65). Equation E-5 is used to determine the unknown molar volume ($\underline{V}$) of any substance at specified temperature and pressure when some measured value ($\underline{V}_1$) is available at a convenient pressure and temperature. Both (ω) values are read from the expansion factor plot at the corresponding reduced temperatures and pressures.

An expansion factor correlation of the type mentioned has been presented by Hougen and Watson (27). Recently, Ritter, Lenoir and Schweppe (53) have published a purportedly improved correlation of omega.

By comparing Equation E-1 with E-5, it is seen that the simplified empirical expression for omega is

$$\frac{1}{\omega} = (5.7 + 3.0\ T_r) \qquad \text{(E-6)}$$

The constant (5.7) is in effect the common multiplier for $\underline{V}_1\omega_1$ which yields the extrapolated molar liquid volume at absolute zero temperature. The constant (3.0) establishes the fixed volumetric coefficient of expansion which holds at absolute zero and all other temperatures.

At low reduced temperatures Equation E-1 gives molar volumes for liquids closely approximating the actual values. As the critical point is approached, the calculated volumes are less than actual volumes. In general, saturated liquids tend to have larger volumes than predicted by Equation E-1.

A more complicated expression than Equation E-1 for hypothetical liquid volume does not appear justified. In fact, the equation has been used in this work to predict actual pure liquid volumes in regions where more rigorous volumes could be obtained from three parameter generalized correlations such as that of Lydersen, Greenkorn and Hougen (36). However, the generalized correlations cannot be readily expressed in analytical form to permit calculation on a digital computer. This compromise does not appear to introduce serious errors in the calculated liquid activity coefficients as will be illustrated by example in Appendix F.

The hypothetical liquid volumes could be expressed independent of pressure simply as those corresponding to saturation temperature. Ehrett, Weber and Hoffman (15) used this method is some of their correlation work with apparent success. Chao and Seader (8) used a fixed set of pure liquid volumes for both the hypothetical and real liquid regions at all temperatures and pressures.

APPENDIX F

SAMPLE LIQUID PHASE ACTIVITY COEFFICIENT CALCULATION

APPENDIX F

SAMPLE LIQUID PHASE ACTIVITY COEFFICIENT CALCULATION

The equations for calculation of liquid phase activity coefficients were developed in Appendix B.

Binary: Methane-Benzene (16)
Table A-8 Appendix A

Temperature: 150°F

Pressure: 4800 Psia

Data:

	x	$V_1\omega_1$	δ	T_c °K
Methane	0.695	5.00	5.45	190.6
Benzene	0.305	11.64	9.15	562

Step 1 Calculation of Reduced Temperatures

$$T_r \text{ (Methane)} = \frac{339}{190.6} = 1.78$$

$$T_r \text{ (Benzene)} = \frac{339}{562} = 0.603$$

Step 2 Calculation of Watson Molar Liquid Volumes

$$\underline{V}^L \text{ (Methane)} = \underline{V}_1\,\omega_1\left[(5.7 + 3.0\ T_r)\right]$$

$$= (5.00)\ \left[5.7 + 3.0(1.78)\right]$$

$$= \underline{55.2}\ \text{cc/g mole}$$

$$\underline{V}^L \text{ (Benzene)} = (11.64)\left[5.7 + 3.0(0.603)\right]$$

$$= \underline{87.5}\ \text{cc/g mole}$$

Step 3 Calculation of A and B Coefficients

From Equations B-17 and B-18 of Appendix B,

$$A = \frac{V_1}{RT} \left(\delta_1 - \delta_2 \right)^2$$

$$B = \frac{V_2}{RT} \left(\delta_1 - \delta_2 \right)^2$$

$$A = \frac{(55.2)\,(5.45 - 9.15)^2}{(1.987)(339)} = \underline{1.120}$$

$$B = \frac{(87.5)\,(5.45 - 9.15)^2}{(1.987)(339)} = \underline{1.780}$$

It will be observed that the units on terms in the A and B expressions are consistent with rendering these coefficients dimensionless.

Step 4 Calculation of γ_1 and γ_2

Reference is made to Equations B-20 and B-21 of Appendix B.

$$\ln \gamma_1 = \frac{A}{\left| \frac{Ax_1}{Bx_2} + 1 \right|^2}$$

$$= \frac{(1.12)}{\left| \frac{(1.12)(0.695)}{(1.78)\ 0.305} + 1 \right|^2}$$

$$= 0.189$$

γ_1 = $\underline{1.208}$ (Corresponds to same value obtained on Computer)

$$\ln \gamma_2 = \frac{B}{\left| \frac{Bx_2}{Ax_1} + 1 \right|^2}$$

$$= \frac{(1.78)}{\left| \frac{(1.78)(0.305)}{(1.12)(0.695)} + 1 \right|^2}$$

$$= 0.619$$

$$\gamma_2 = \underline{1.858}$$ (Corresponds to same value obtained on computer)

These calculations have been made by hand to illustrate the method. All such calculations were performed on the IBM 650 digital computer in the course of this work. Calculation of the coexisting vapor phase activity coefficients is demonstrated in Appendix G which follows.

In Appendix E it was indicated that the Watson equation could be used to predict real liquid volumes which would not alter greatly the calculated liquid activity coefficient. This is illustrated by an example.

In the foregoing calculation, the temperature and pressure are such that Benzene could exist as a real liquid. The Watson equation predicted a liquid volume of 87.5 cc/g mole. With the same conditions, a pure component liquid volume of 91.6 cc/g mole is predicted from Table VI of the Lydersen, Greenkorn and Hougen three-parameter correlation. The calculated activity coefficients with the more rigorous volume are compared with those previously calculated.

	L.G.H. Volume	Watson Volume	% Difference
γ_1	1.221	1.208	1.08
γ_2	1.860	1.858	nil

Clearly in this case a more complicated expression for liquid volume would not be justified.

APPENDIX G

SAMPLE VAPOR PHASE ACTIVITY COEFFICIENT CALCULATION

APPENDIX G

SAMPLE VAPOR PHASE ACTIVITY COEFFICIENT CALCULATION

This sample calculation illustrates the complexity of the vapor phase activity coefficient calculation utilizing the Redlich-Kwong equation of state. It is evident that use of the digital computer for these calculations resulted in less expenditure of time and, no doubt, better quality results.

Binary: Methane-Benzene (16)
Table A-8 Appendix A

Temperature: 150°F

Pressure: 4800 Psia

Data:

	y	Tc°K	Pc Atm
Methane	0.775	190.6	45.8
Benzene	0.225	562.0	48.7

Redlich-Kwong Equation of State (50):

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

The expression for fugacity coefficient is:

$$\text{Log } \phi_i^V = 0.4343(Z-1)\frac{Bi}{B} - \log(Z-BP) - \frac{A^2}{B}\left(\frac{2Ai}{A} - \frac{Bi}{B}\right)\text{Log}(1+\frac{BP}{Z}) \qquad \text{(G-2)}$$

The compressibility factor is not explicit, but is expressed in the following cubic equation.

$$Z^3 - Z^2 + (A^2P - B^2P^2 - BP)Z - BA^2P^2 = 0 \qquad (G-3)$$

Step 1 Calculation of A_1 and B_1

$$A_1{}^2 = 0.4278 \frac{T_{1C}{}^{2.5}}{P_{1C}\ T^{2.5}} \qquad (G-4)$$

$$= \frac{(0.4278)(190.6)^{2.5}}{(45.8)\ (339)^{2.5}} = 0.002095$$

$$A_1 = \sqrt{0.002095} = \underline{0.0457}$$

$$A_2{}^2 = \frac{0.4278 T_{2C}{}^{2.5}}{P_{2C} T^{2.5}}$$

$$A_2{}^2 = \frac{(0.4278)(562)^{2.5}}{(48.7)(339)^{2.5}} = 0.0312$$

$$A_2 = \sqrt{0.0312} = \underline{0.1765}$$

Step 2 Calculation of B_1 and B_2

$$B_1 = 0.0867 \frac{T_{1C}}{P_{1C}\ T} \qquad (G-5)$$

$$= \frac{(0.0867)(190.6)}{(45.8)(339} = 0.00106$$

$$B_2 = 0.0867 \frac{T_{2C}}{P_{2C}}\ T$$

$$= \frac{(0.0867)(562)}{(48.7)\ (339)} = \underline{0.00295}$$

Step 3 Calculation of A

$$A = y_1A_1 + (1-y_1)A_2$$

$$A = (0.775)(0.0457) + (0.225)(0.1765)$$

$$A = \underline{0.0751}$$

Step 4 Calculation of B

$$B = y_1B_1 + (1-y_1)\ B_2$$

$$B = (0.775)(0.00106) + (0.225)(0.00295)$$

$$B = \underline{0.001487}$$

Step 5 Calculation of Z (trial and error)

$$Z^3 - Z^2 + (A^2P-B^2P^2 - BP)Z - BA^2P^2 = 0$$

$$\text{Assume } Z = 0.88 \quad \text{(last trial)}$$

$$- 0.002 \cong 0$$

Step 6 Calculation of ϕ

This is done by utilizing Equation G-2

$$\text{Log } \phi_1 = 0.4343(0.88 - 1.0)\frac{(0.00106)}{(0.001487)}$$

$$- \log \left[0.88 - (0.001487)(327)\right]$$

$$- \frac{(0.0751)^2}{0.001487} \left[\frac{(2)(0.0457)}{0.0751} - \frac{0.00106}{0.001487}\right] \text{Log} \left[1 + \frac{(0.001487)(327)}{0.88}\right]$$

$$\text{Log } \phi_1 = -0.0102$$

$$\phi_1 = \underline{0.974} \quad \text{(Compare to 0.963 from computer)}$$

A similar calculation is now made for methane in the pure vapor state.

Calculation of $\phi_1{}^o$:

$$\ln \phi_1{}^o = Z_o - 1 - \ln(Z_o-B_oP) - \frac{A_o{}^2}{B_o} \ln(1-\frac{B_oP}{Z_o}) \qquad \text{(G-6)}$$

$$A_o{}^2 = 0.4278\ Tc^{2.5}/P_cT^{2.5} \qquad \text{(G-7)}$$

$$Z_o{}^3 - Z_o{}^2 + (A_o{}^2P - B_o{}^2P^2 - B_oP)Z_o - B_oA_o{}^2P^2 = 0 \qquad \text{(G-8)}$$

$A_o = \underline{0.0457}$ (From previous calculation)

$B_o = \underline{0.00106}$ (From previous calculation)

Substituting values in Equation G-8 gives

$$Z_o^3 - Z_o^2 + 0.359Z_o - 0.237 = 0$$

Assume $Z_o = 0.9$ (Last trial)

$$+ 0.003 \cong 0$$

With the value of Z_o determined, then ϕ_1^o is calculated from Equation G-6.

$$\ln \phi_1^o = (0.9 - 1) - \ln\left[0.9 - (0.00106)(327)\right] - \frac{(0.0457)^2}{0.00106} \ln\left[1 + \frac{(0.00106)(327)}{0.9}\right]$$

$$\ln \phi_1^o = -0.148$$

$$\phi_1^o = \underline{0.862}$$ (Compared to 0.824 from computer result)

$$\gamma_1^V = \frac{\phi_1}{\phi_1^o} = \frac{0.974}{0.862} = \underline{1.13}$$

APPENDIX H

SAMPLE THERMODYNAMIC CONSISTENCY CALCULATION

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APPENDIX H

SAMPLE THERMODYNAMIC CONSISTENCY CALCULATION

The consistency test involves evaluation of the three integrals in the following equation which was developed in Appendix D.

$$\int_{K_1(x_1=0)}^{K_1(x_1=x_c)} x_1 \, d \ln K_1 + \int_{K_2(x_2=1)}^{K_2(x_2=1-x_c)} x_2 \, d \ln K_2 \qquad \text{(H-1)}$$

$$= \int_{P(x_1=0)}^{P=P_c} \left[Z^L + Z_1{}^g y_1 \left(\frac{1}{K_2} - \frac{1}{K_1} \right) - \frac{Z^g}{K_2} \right] d\ln P$$

The data are considered to be consistent when the sum of the two left hand integrals is approximately equal to that of the right hand integral.

Table H-1 for the methane-n-pentane binary illustrates how the data are handled in preparation for graphical integration. All data in the table originates with the experimentally determined values of x, y, $\underline{V}_m{}^g$ and $\underline{V}_m{}^L$, except for $Z_1{}^g$ for methane which is taken from the tables of Lydersen, Greenkorn and Hougen (36). $Z_1{}^g$ could have been determined equally well from the data of Curl and Pitzer (10). The tie-in with a pure component property such as $Z_1{}^g$ comes from the assumption of Lewis and Randall rule for the vapor phase. Thus, the validity of the consistency test is also dependent upon the reliability of the pure component compressibility data or generalized correlation.

It is absolutely essential for actual volume data to be available on the two phases in equilibrium before a consistency test with any significance can be made.

Graphical integration of the first integral in Equation H-1 (designated A_1) for the methane-n-pentane binary is shown in Figure H-1. Likewise, the second integral (A_2) is determined in Figure H-2. The value of the integral on the right hand side (A_3) of Equation H-1 is found in Figure H-3. The integral values are:

$$\left.\begin{aligned} A_1 &= -0.8327 \\ A_2 &= -1.0194 \end{aligned}\right] = -1.8521$$

$$A_3 = -1.9492$$

Thus,

$$A_1 + A_2 \cong A_3$$

and a fair check for consistency is obtained.

Data for the methane-decane binary are shown in Table H-2. The graphical integrations are not included, but the values of A_1 and A_2 were determined to be -1.0005 and -3.738, respectively. A_3 was not determined since it is obviously positive, indicating a large deviation. The significance of this case is discussed in Appendix D.

TABLE H-1

CHECK FOR THERMODYNAMIC CONSISTENCY

METHANE - n-PENTANE (References 41 and 58)
(160°F)

P(psia)	x_1	y_1	K_1	K_2	ln K_1	ln K_2	$\underline{V}_M^L$	$Z^L = \frac{\underline{V}_M^L P}{RT}$	$\underline{V}_M^g$	$Z^g = \frac{\underline{V}_M^g P}{RT}$	Z_1^g(*)	$Z_1^g y_1$	$\frac{1}{K_2} - \frac{1}{K_1}$	$(Z_1^g y_1) x \left[\frac{1}{K_2} - \frac{1}{K_1}\right]$	$\frac{Z^g}{K_2}$	Z''	ln P
42.48	0.0000	0.0000	-	1.000	-	0.000	2.029	0.0129	142.3	0.907	0.996	0.000	1.000	0.000	0.907	-0.8941	3.75
60	0.00537	0.2805	52.25	0.724	3.96	-0.3224	2.023	0.01824	101.4	0.9135	0.994	0.2784	1.362	0.3800	1.261	-0.863	4.095
80	0.0115	0.4505	39.20	0.556	3.67	-0.5860	2.016	0.02420	76.5	0.919	0.993	0.4470	1.775	0.793	1.650	-0.863	4.38
100	0.0176	0.5524	31.38	0.456	3.445	-0.7850	2.010	0.0302	61.5	0.924	0.992	0.5480	2.163	1.188	2.024	-0.806	4.61
150	0.0329	0.6894	20.94	0.322	3.040	-1.132	1.995	0.0450	41.4	0.9325	0.991	0.6820	3.056	2.080	2.898	-0.773	5.01
200	0.04801	0.7568	15.76	0.256	2.760	-1.361	1.980	0.0594	31.1	0.9330	0.991	0.7500	3.841	2.880	3.644	-0.705	5.30
400	0.1070	0.8485	7.93	0.170	2.070	-1.770	1.923	0.1156	15.40	0.9240	0.982	0.8320	5.754	4.790	5.435	-0.529	5.99
600	0.1655	0.8785	5.31	0.146	1.670	-1.921	1.868	0.1681	10.10	0.9050	0.978	0.8590	6.651	5.710	6.200	-0.322	6.40
800	0.2212	0.8900	4.03	0.1415	1.392	-1.955	1.818	0.2182	7.40	0.8890	0.963	0.8565	6.822	5.845	6.280	-0.217	6.59
1000	0.2743	0.8937	3.25	0.1465	1.180	-1.918	1.773	0.2663	5.78	0.8680	0.955	0.8530	6.522	5.560	5.925	-0.099	6.91
1250	0.3381	0.8929	2.64	0.1619	0.971	-1.820	1.724	0.3240	4.48	0.8410	0.943	0.8415	5.800	4.870	5.200	-0.006	7.14
1500	0.4002	0.8875	2.205	0.1876	0.791	-1.673	1.685	0.3796	3.62	0.8175	0.929	0.8240	4.886	4.025	4.360	+0.045	7.32
1750	0.4671	0.8772	1.879	0.2304	0.630	-1.465	1.654	0.4350	2.992	0.7850	0.916	0.8030	3.807	3.060	3.400	+0.095	7.465
2000	0.5460	0.8558	1.569	0.3177	0.451	-1.147	1.644	0.4940	2.505	0.7520	0.909	0.7775	2.517	1.954	2.368	+0.080	7.60
2250	0.6654	0.8142	1.222	0.5550	0.2004	-0.589	1.723	0.5820	2.074	0.7010	0.908	0.7390	0.985	0.728	1.263	+0.047	7.815
2338 (Critical)	0.7665	0.7665	1.000	1.000	0.000	0.000	1.874	0.6560	1.874	0.6580	0.908	0.6960	0.000	0.000	0.658	0.000	7.900

* From Lydersen, Greenkorn and Hougen (36)

$$Z'' = Z^L + Z_1^g y_1 \left[\frac{1}{K_2} - \frac{1}{K_1}\right] - \frac{Z^g}{K_2}$$

TABLE H-2

CHECK FOR THERMODYNAMIC CONSISTENCY

METHANE - DECANE (References 46 and 58)
(160°F)

P(psia)	x_1	y_1	K_1	K_2	ln K_1	ln K_2	$\underline{V}_M{}^L$	$Z^L = \frac{\underline{V}_M{}^L P}{RT}$	$\underline{V}_M{}^g$	$Z^g = \frac{\underline{V}_M{}^g P}{RT}$	$Z_1{}^g$(*)	$Z_1{}^g y_1$	$\frac{1}{K_2} - \frac{1}{K_1}$	$(Z_1{}^g y_1) \times \left[\frac{1}{K_2} - \frac{1}{K_1}\right]$	$\frac{Z^g}{K_2}$	Z"	ln P
20	0.0061	0.9792	160.5	0.0021	5.08	-3.86	3.29	0.0099	-	1.000	1.000	0.9792	47.6	51.25	476.0	-0.01	3.0
100	0.0307	0.9950	32.4	0.0052	3.48	-5.25	3.23	0.0478	-	0.992	0.992	0.987	192.5	190.0	191.0	-0.95	4.61
400	0.1138	0.9980	8.78	0.0023	2.17	-6.07	3.02	0.1785	-	0.982	0.982	0.980	435.0	426.0	426.5	-0.82	5.99
600	0.1629	0.9982	6.13	0.00215	1.815	-6.14	2.903	0.2580	-	0.978	0.978	0.976	465.0	454.0	455.0	-0.74	6.40
800	0.2079	0.9982	4.81	0.00227	1.57	-6.09	2.793	0.3300	-	0.963	0.963	0.961	440.0	423.0	424.0	-0.67	6.59
1000	0.2496	0.9980	4.00	0.00266	1.388	-5.93	2.692	0.3980	6.21	0.932	0.955	0.953	376.0	358.0	350.0	+8.40	6.91
1500	0.3429	0.9974	2.91	0.00396	1.070	-5.52	2.465	0.5470	4.04	0.903	0.929	0.926	252.0	233.5	228.0	+6.05	7.32
2000	0.4234	0.9963	2.36	0.00641	0.859	-5.04	2.270	0.6720	2.98	0.895	0.909	0.905	155.5	141.0	139.5	+2.172	7.60
2500	0.4943	0.9945	2.02	0.0109	0.703	-4.51	2.101	0.7770	2.37	0.890	0.908	0.902	91.4	82.5	81.6	+1.68	7.83
3000	0.5593	0.9915	1.78	0.0193	0.576	-3.89	1.948	0.8640	1.963	0.884	0.918	0.910	51.34	46.70	45.8	+1.76	8.00
3500	0.6202	0.9863	1.59	0.0286	0.464	-3.55	1.812	0.9400	1.716	0.902	0.941	0.929	34.37	31.85	31.55	+1.24	8.16
4000	0.6796	0.9779	1.44	0.067	0.365	-2.70	1.684	0.9970	1.531	0.920	0.960	0.938	14.22	13.35	13.72	+0.627	8.30
4500	0.7441	0.9647	1.30	0.138	0.262	-1.98	1.551	1.0300	1.406	0.949	0.991	0.955	6.47	6.18	6.87	+0.34	8.41
5000	0.8240	0.9364	1.14	0.362	0.131	-1.015	1.406	1.0400	1.319	0.989	1.025	0.960	1.88	1.80	2.73	+0.11	8.52
5180 (Critical)	0.8912	0.8912	1.00	1.000	0.000	0.000	1.322	1.0150	1.322	1.030	1.038	0.925	0.00	0.00	1.03	-0.015	8.55

* From Lydersen, Greenkorn and Hougen (36)

$$Z'' = Z^L + Z_1{}^g y_1 \left[\frac{1}{K_2} - \frac{1}{K_1}\right] - \frac{Z^g}{K_2}$$

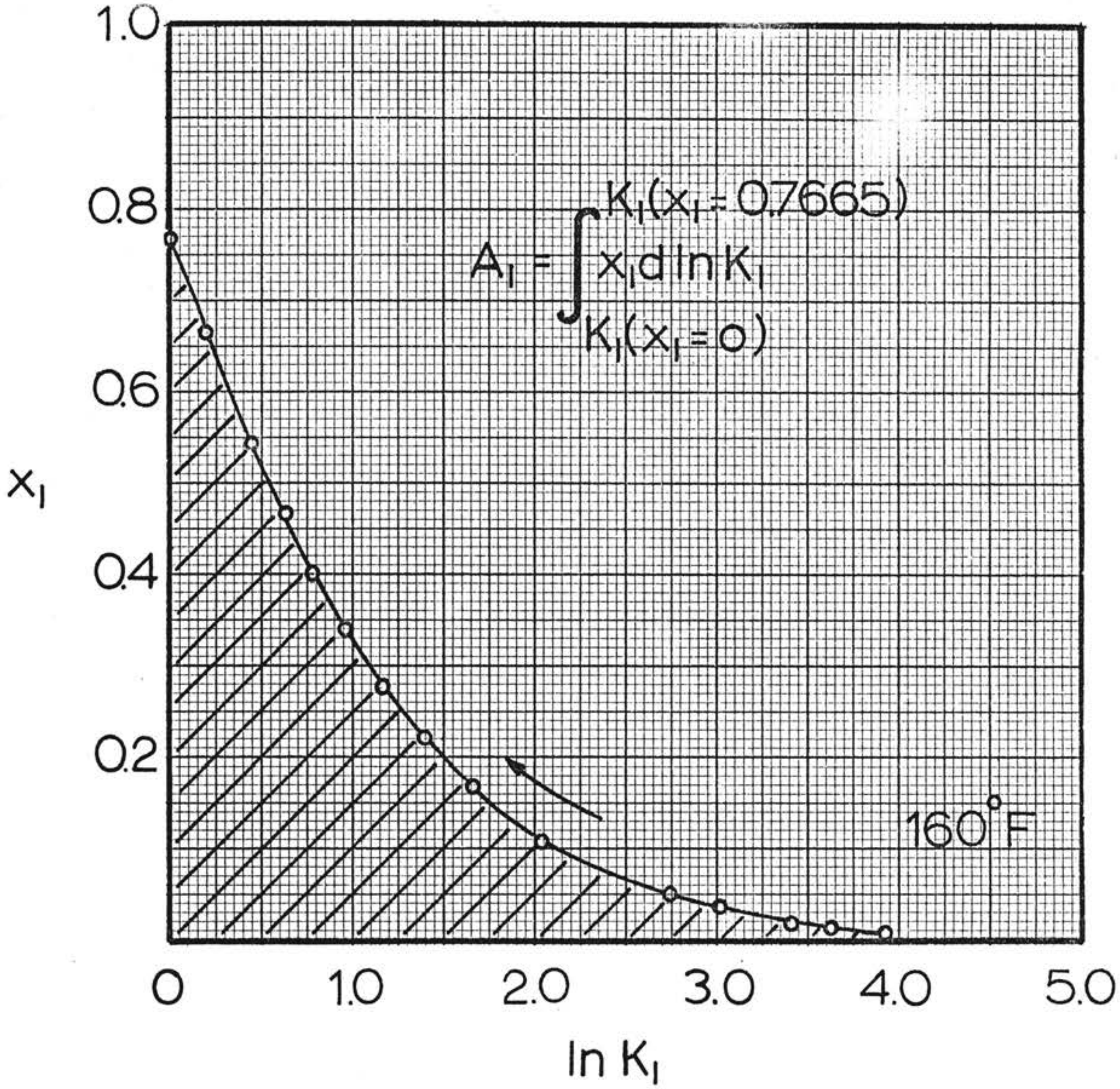

FIGURE H-1

Graphical Integration for A_1

Methane - n-Pentane

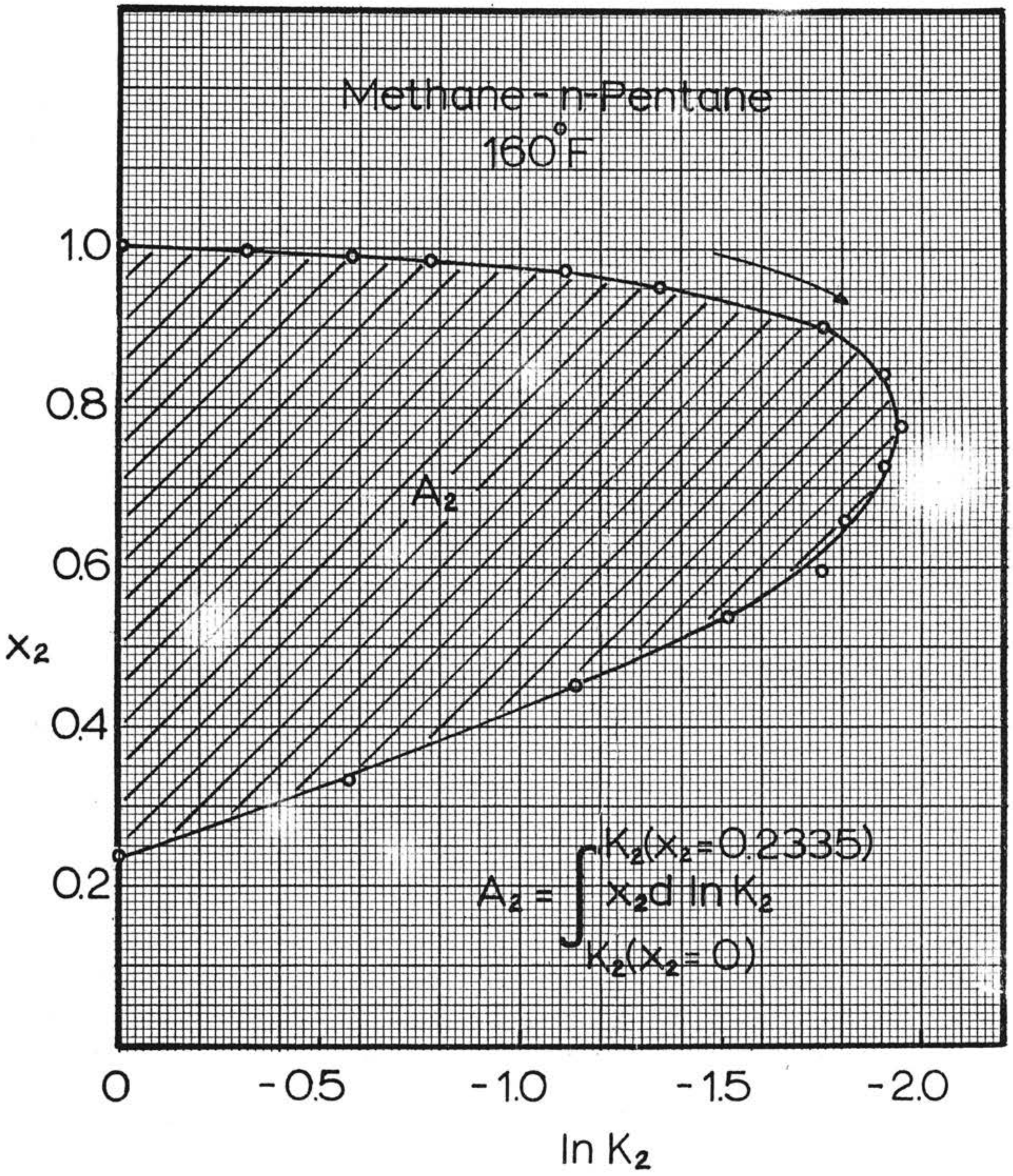

FIGURE H-2

Graphical Integration for A_2

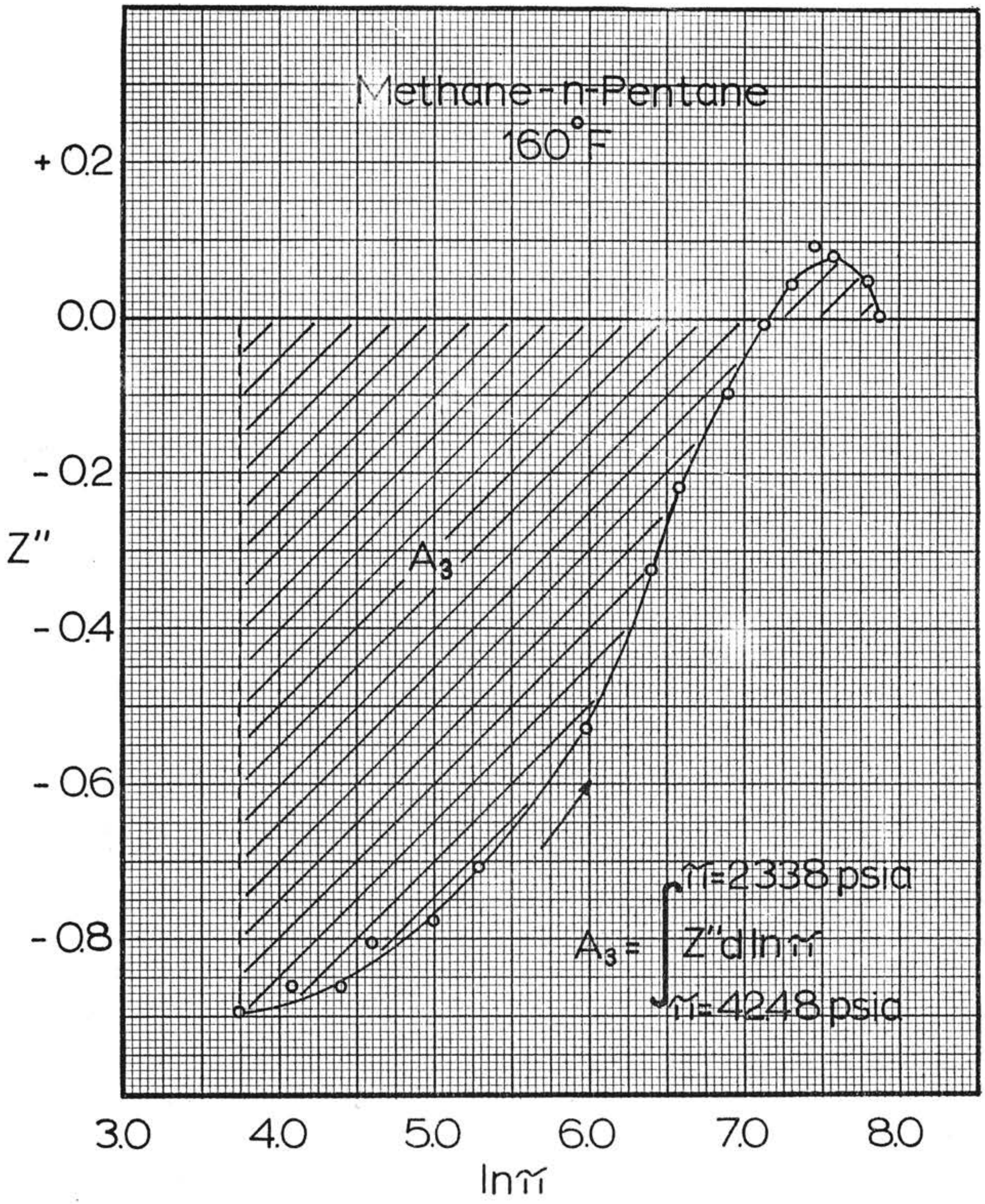

FIGURE H-3

Graphical Integration for A_3

NOMENCLATURE

NOMENCLATURE

A = $\frac{V_1{}^L}{RT}(\delta_1 - \delta_2)^2$ modified van Laar coefficient

= $\sum_i y_i A_i$ Redlich-Kwong total attraction coefficient

= Sage and Lacey (Viscosity-gravity factor)

= area

a = $\bar{f}/f^o$ activity by definition

= Redlich-Kwong molecular attraction coefficient

B = $\frac{V_2{}^L}{RT}(\delta_1 - \delta_2)^2$ modified van Laar coefficient

= $\sum_i y_i B_i$ Redlich-Kwong volume coefficient

b = Redlich-Kwong molecular volume coefficient

C_{ii} = $-\underline{E}_i/\underline{V}_i$ Scatchard's cohesive energy density

C = number of components in phase rule

= Henry's law constant

E = internal energy

F = Gibbs free energy

f = $e^{\frac{F-\phi(T)}{RT}}$ fugacity defined by Lewis

G = Specific gravity @ 60°/60°F

H = E + PV(enthalpy)

h = b/V for Redlich-Kwong equation

K_i = y_i/x_i vapor-liquid equilibrium ratio

K_i' = $K_i \dfrac{\gamma_i^V}{\gamma_i^L}$ ideal equilibrium ratio

$\bar{K}$ = $\sqrt[3]{T_B / G}$ U.O.P. or Watson characterization factor

M = molecular weight

n = number of moles

P = total system pressure

= number of phases in phase rule

P_c = critical pressure

P_r = P/P_c reduced pressure

R = universal gas constant

= Rankine temperature

S = viscosity (SUS @ 100°F)

= entropy

T = temperature

T_c = critical temperature

T_r = T/T_c reduced temperature

V = volume

= variants in phase rule

$\bar{V}$ = partial molar volume

$\underline{V}$ = pure component molar volume

x = liquid phase mole fraction

y = vapor phase mole fraction

Z = $\dfrac{PV}{RT}$ compressibility factor

Greek Symbols

Δ = difference e.g., $\Delta E = (E_2 - E_1)$

$\delta_i = \left[\dfrac{\Delta \underline{E}_i^{V}}{\underline{V}_i^{L}} \right]^{\frac{1}{2}}$ Hildebrand's solubility parameter

$\gamma = \frac{a}{x}$ or $\frac{a}{y}$ activity coefficient

λ = arbitrary parameter in Euler's equation

$\mu_i = \left(\dfrac{\partial F}{\partial n_i} \right)_{T,P,n_j}$ etc., chemical potential

$\nu = f/_p$ pure component fugacity coefficient

$\phi = \bar{f}/_{Px}$ or $\bar{f}/_{Py}$ fugacity coefficient

= function of some variable, e.g., $\phi(T)$

$\phi_j = \dfrac{x_j \underline{V}_j}{\sum_i x_i \underline{V}_i}$ liquid volume fraction

$\rho = \frac{PM}{RT}$ density

$\omega = \dfrac{P_r}{ZRT_r}$ Watson's liquid expansion factor

$= -\text{Log}\, \frac{Ps}{Pc} - 1.000$ Pitzer's accentric factor,

$\left(P_s = \text{vapor pressure at } T_r = 0.700 \right)$

Σ = summation

Subscripts

1 = component 1 or initial state

2 = component 2 or final state

B = normal atmospheric boiling point

c = critical state

i = i th component

j = j th component

m = mixture property

s = saturation

Superscripts

o = pure component, reference state or degree

g = gaseous state

L = liquid state

m = mixture

T = total

V = vapor state

Miscellaneous

Superbar = partial molar property

Subbar = pure component molar property

VITA

Omer Allen Pipkin

Candidate for the Degree

Master of Science

Thesis: CORRELATION OF EQUILIBRIUM DATA FOR METHANE BINARIES THROUGH USE OF SOLUBILITY PARAMETERS

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Personal Data: Born at Blanco, Oklahoma, August 30, 1927, the son of Omer H. and Aleene Pipkin. Married to Marjorie M. Cooper, Bartlesville, Oklahoma, in August, 1951. Two sons, Allen Cooper and Omer Thomas.

Education: Attended elementary schools at Blanco and Tannehill, Oklahoma; attended high school at Crowder and Haileyville, Oklahoma; graduated from Haileyville High School in 1943; received the Bachelor of Science degree in Chemical Engineering from the University of Oklahoma in June, 1950; completed requirements for the Master of Science degree in May, 1961.

Professional Experience: From high school graduation until enlistment in United States Navy in 1945, worked as retail sales clerk; served as Seaman 2/C in United States Navy until enrolment at the University of Oklahoma in 1946; have been engaged in work for the petroleum refining industry since graduation from the University of Oklahoma in 1950; held various positions as process engineer, operating foreman, project engineer and department superintendent; supervised operations in crude oil distillation, thermal cracking, catalytic cracking, catalytic reforming and steam generation.