DETERMINATION OF COMPOSITION-DEPENDENT LIQUID ACTIVITY COEFFICIENTS

BY USE OF THE VAN LAAR EQUATION

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PREFACE

A series of vapor-liquid "K" values were estimated using modified van Laar liquid activity coefficients. The calculations evaluate a method of calculating A and B constants in the van Laar equation to give composition-dependent liquid activity coefficients. It is hoped that the method investigated here will prove to be an asset in the estimation of more accurate vapor-liquid equilibrium values.

The counseling given by professor Wayne C. Edmister is greatly appreciated. The author wishes to express his appreciation to the Computing Center for making available machine time to aid in the calculations and to the Department of Chemical Engineering at Oklahoma State University.

Also, the author wishes to thank the N.G.A.A. for the research assistantship received during the spring semester of 1959.

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CHAPTER I

THE PROBLEM

Statement of the Problem

Vapor-liquid "K" values can be found from the following combination of fugacity and activity coefficients (26),

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

where: γ_i = The activity coefficient for component i in the liquid phase mixture,

        ν_i = The fugacity coefficient for pure liquid i ,

        ϕ_i = The fugacity coefficient for component i in the gas phase mixture.

In using Equation 1 for the solute, the problem is in evaluating the the activity coefficient and the liquid fugacity coefficient, i.e. γ and ν. The problem in applying this equation for the solvent is in evaluating the vapor fugacity coefficient, ϕ.

For the vapor phase, the deviations from ideal mixtures and perfect gases can be calculated using the Benedict, Webb, Rubin (B-W-R) equation of state (3) or the more recent Redlich-Kwong (R-K) equation of state (27). The B-W-R equation is a complex equation using eight constants, whereas, the R-K equation employs only two constants, which are found from the critical properties of the pure components. The Redlich-Kwong

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equation was programmed for use on the IBM 650 computer (8). Fugacity coefficient calculations made with this program on the computer were used in this work.

For the liquid phase it is convenient to separate the deviations from ideal mixtures and perfect gases and work with the activity coefficient for the component in the mixture and the fugacity coefficient for the pure component, i.e. γ and ν. This work is concerned with evaluating these values for ethane in ethane-heavy hydrocarbon binaries.

Liquid phase activity coefficients from the van Laar equation have been shown to represent the effect of composition on the vapor-liquid "K" values for hydrocarbon-gas binaries with sufficient accuracy for engineering purposes (26). Constants for the van Laar equations can be predicted from the system temperature and the physical properties of the solute and solvent. These properties are the solubility parameter, δ, of Hildebrand (11) and the molar volume, V.

For the solute, δ, ν and V cannot be calculated directly for all substances and conditions. The lighter components of a mixture are frequently in solution at a temperature and pressure where they could not exist as pure components. Values of δ, ν and V, in this hypothetical liquid state, were obtained by back-calculation from experimental vapor-liquid equilibrium data.

Scope of Study

The back-calculation method of determining δ, ν and V, mentioned above and discussed in more detail in a later chapter, required that each system analyzed have the same component in common at the same

temperature and pressure. The data available in the literature with the greatest number of such systems were the ethane-binaries at a pressure of 400 psia. The data reported in the literature were smoothed so that intermediate points could be obtained. These data appear in Appendix A.

This work deals, only, with binary mixtures, although extension to multicomponent systems can be done with little difficulty (2, 26).

Clarification of Terms

The "K" values for a component i are computed by the thermodynamic relation

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

where: y_i = The mole fraction of i in the gas phase mixture,

x_i = The mole fraction of i in the liquid phase mixture,

$\nu_i = \dfrac{\overline{f}_i^L}{P}$ = The fugacity coefficient for pure liquid i,

$\phi_i = \dfrac{f_i^V}{Py_i}$ = The fugacity coefficient for component i in the gas phase mixture,

$\gamma_i = \dfrac{\overline{f}_i^L}{f_i^o x_i}$ = The activity coefficient for component i in the liquid phase to be given by the Hildebrand-Scatchard equation and the van Laar equation for regular solutions.

Superscripts indicate the phase.

Bar above "f" identifies the fugacity as being that of component i in the indicated mixture.

Subscript "i" indicates that the term
applies to each component
in the mixture.

All fugacities in Equation 1 are at the system pressure and temp-
erature.

Regular Solutions: Broadly speaking, a regular solution is one in
which the nonideality is due entirely to the heat of mixing. Its
entropy of solution is equal to that of an ideal solution. Based upon
this definition, no solution is exactly regular. However, the
properties of solutions of nonpolar fluids, e.g. the hydrocarbons, are
approximated by the regular solution equations (11, 26).

Fugacity and Activity Coefficients: The fugacity coefficient is
defined as the ratio of the fugacity of the component in the vapor
mixture to its partial pressure:

$$\phi_i \ = \ \frac{\bar{f}_i^V}{Py_i} \ .$$

The activity coefficient is defined as the ratio of the fugacity
of the component in the liquid mixture to the product of the pure
component reference state fugacity and the mole fraction:

$$\gamma_i \ = \ \frac{\bar{f}_i^L}{f_i^o x_i} \ .$$

In other words, the activity coefficient is a correction, for non-
ideality, to the Lewis and Randall rule. The reference state in the
activity coefficient is at the system temperature and at any convenient
pressure: (a) system pressure, (b) vapor pressure or (c) atmospheric
pressure.

Although there is no theoretical reason why fugacity and activity

coefficients could not be used in each phase, the fugacity coefficient is used mostly for the vapor phase, whereas, the activity coefficient is evaluated mostly for the liquid phase (26). For this reason, the symbol y_i is used in the fugacity coefficient for the mole fraction of i and x_i is used in the activity coefficient.

CHAPTER II

REVIEW OF THE LITERATURE

Background

Much work has been done in developing equations and charts by
which vaporization equilibrium ratios, "K," can be estimated.
Frequently, the composition dependence of these "K" values is neglected.
That is, to assume Raoult's law for the liquid phase:

$$P y_i = P_i^\circ x_i = \overline{P}_i \qquad (2)$$

and Dalton's law for the vapor phase:

$$P = \overline{P}_i + \overline{P}_j + \cdots. \qquad (3)$$

where: P = Total pressure

P_i° = The vapor pressure of pure
component i.

$\overline{P}_i$ = The partial pressure of
component i.

The Lewis and Randall fugacity rule leads, likewise, to composition-
independent "K" values:

$$\overline{f}_i^{\,L} = x_i f_i^{\,L} \qquad (4)$$

$$\overline{f}_i^{\,V} = y_i f_i^{\,V} \qquad (5)$$

Lewis and Kay (21) as well as, Souder, Selheimer and Brown (33)

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derived "ideal K" value charts using these assumptions. The well known
MIT "K" charts (31) applied Equations 4 and 4' giving composition-
independent "ideal K" values.

Prausnitz, Edmister and Chao (26) point out that, while these "ideal
K" values are approximately applicable to systems composed of only one
class of hydrocarbons, i.e. the aliphatics, large deviations are en-
countered for systems composed of different classes of hydrocarbons,
e.g. those containing aromatics.

One of the criteria for equilibria is that the fugacity of i in the
liquid phase equal the fugacity of i in the vapor phase, i.e.

$$\overline{f}_i^V = \overline{f}_i^L \tag{5}$$

Combining Equations 1 and 5, the fugacities are introduced into the
equilibrium "K" value definition, giving

$$K_i = \frac{\overline{f}_i^L / x_i}{\overline{f}_i^V / y_i} \quad . \tag{6}$$

Multiplying and dividing the denominator by P (system pressure) gives

$$K_i = \frac{\overline{f}_i^L / x_i}{\overline{f}_i^V / Py_i} \frac{1}{P} \cdot \tag{7}$$

Equation 7 is the "K" value relation that Benedict, et al. used in
developing the Polyco or Kellogg "K" charts (18) for the Benedict,
Webb, Rubin equation of state (3). Equation 7 gives the "K" values as
functions of temperature, pressure and composition of both phases. The
Polyco charts are valuable at high pressures and temperatures for the
aliphatic systems.

Edmister and Ruby (7) went one step further and multiplied the numerator of Equation 7 by P_i^o / P_i^o (vapor pressure) giving

$$K_i = \frac{(\overline{f}_i^L / P_i^o x_i)}{(\overline{f}_i^V / P_i y_i)} \frac{P_i^o}{P} . \tag{8}$$

Applying Raoult's law for ideal solutions and perfect gases and using the definitions of ϕ (fugacity coefficients), Equation 8 becomes

$$K_i = \frac{\phi_i^L}{\overline{\phi}_i^V} K_{\text{Raoult}}$$

The ratio of the two fugacity coefficients is the correction for the deviation from Raoult's law. These fugacity coefficients are functions of temperature, pressure and composition of both phases.

Solomon (32) has proposed the application of a correction factor to the Benedict, Webb, Rubin "K" values for light hydrocarbons in other than aliphatic solvents. However. this method is purely empirical and could lead to appreciable deviations under some conditions.

The convergence pressure method of G. G. Brown and co-workers has been used by many authors and has led to the N.G.A.A. "K" charts (24). These "K" values apply only to the aliphatic mixtures and their use in aromatic-containing systems may lead to large deviations.

Carlson and Colburn (4) point out that vapor-liquid equilibria data are readily extended when they are calculated as activity coefficients. Of the several methods of calculating these activity coefficients, the equation of van Laar (19, 20) has been found to be capable of fitting most of the available data. The van Laar equation expresses the activity coefficients of both components of a binary mixture as functions of

liquid composition and empirical constants A and B. Van Laar developed his equation for a van der Waal's fluid and based the constants A and B upon the van der Waal constants. These van der Waal constants were assumed to be calculated for mixtures from the physical constants of the pure components. For a binary mixture, the van Laar equation becomes

$$\ln \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \tag{9}$$

$$\ln \gamma_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \tag{9'}$$

where:
$$A = \frac{b_1}{R}\left(\sqrt{\frac{a_1}{b_1}} - \sqrt{\frac{a_2}{b_2}}\right)^2 \tag{10}$$

$$B = \frac{b_2}{R}\left(\sqrt{\frac{a_1}{b_1}} - \sqrt{\frac{a_2}{b_2}}\right)^2 \tag{10'}$$

For the development of Equations 9 and 10, see Appendix B.

Lu and Lavergne (23) have developed a new graph paper for determining the van Laar constants without taking logarithms or square roots. Values of γ_1 and γ_2 are plotted directly and the values of A and B are obtained without further calculation. Eliminating x_1 and x_2 in the van Laar equations for binary mixtures gives

$$(\log \gamma_1)^{1/2} = A^{1/2} - (A/B)^{1/2} (\log \gamma_2)^{1/2}$$

This is an equation of a straight line with the intercept $A^{1/2}$ and the slope $(A/B)^{1/2}$. Thus, by plotting $(\log \gamma_1)^{1/2}$ vs $(\log \gamma_2)^{1/2}$ and extrapolating, values of A and B can be obtained.

This new graph paper can be constructed from the data in Table I by plotting values of γ_1, γ_2, A, and B against equivalent values in terms

TABLE I

PLOTTING DATA FOR VAN LAAR PAPER

Gamma Scales		Van Laar Constant Scales	
Linear Scales	γ_1 and γ_2 Scales	Linear Scales	A and B Scales
0	1.00	0	0
0.066	1.01	0.071	0.005
0.093	1.02	0.100	0.01
0.130	1.04	0.142	0.02
0.159	1.06	0.173	0.03
0.183	1.08	0.200	0.04
0.203	1.10	0.223	0.05
0.282	1.20	0.245	0.06
0.338	1.30	0.265	0.07
0.382	1.40	0.283	0.08
0.420	1.50	0.316	0.10
0.452	1.60	0.387	0.15
0.505	1.80	0.500	0.25
0.528	1.90	0.547	0.30
0.548	2.00	0.592	0.35
0.631	2.50	0.632	0.40
0.691	3.00	0.671	0.45
0.778	4.00	0.707	0.50
0.836	5.00	0.742	0.55
0.882	6.00	0.775	0.60
0.919	7.00	0.806	0.65
0.950	8.00	0.837	0.70
0.977	9.00	0.866	0.75
1.000	10.00	0.894	0.80
		0.922	0.85
		0.948	0.90
		0.975	0.95
		1.000	1.00
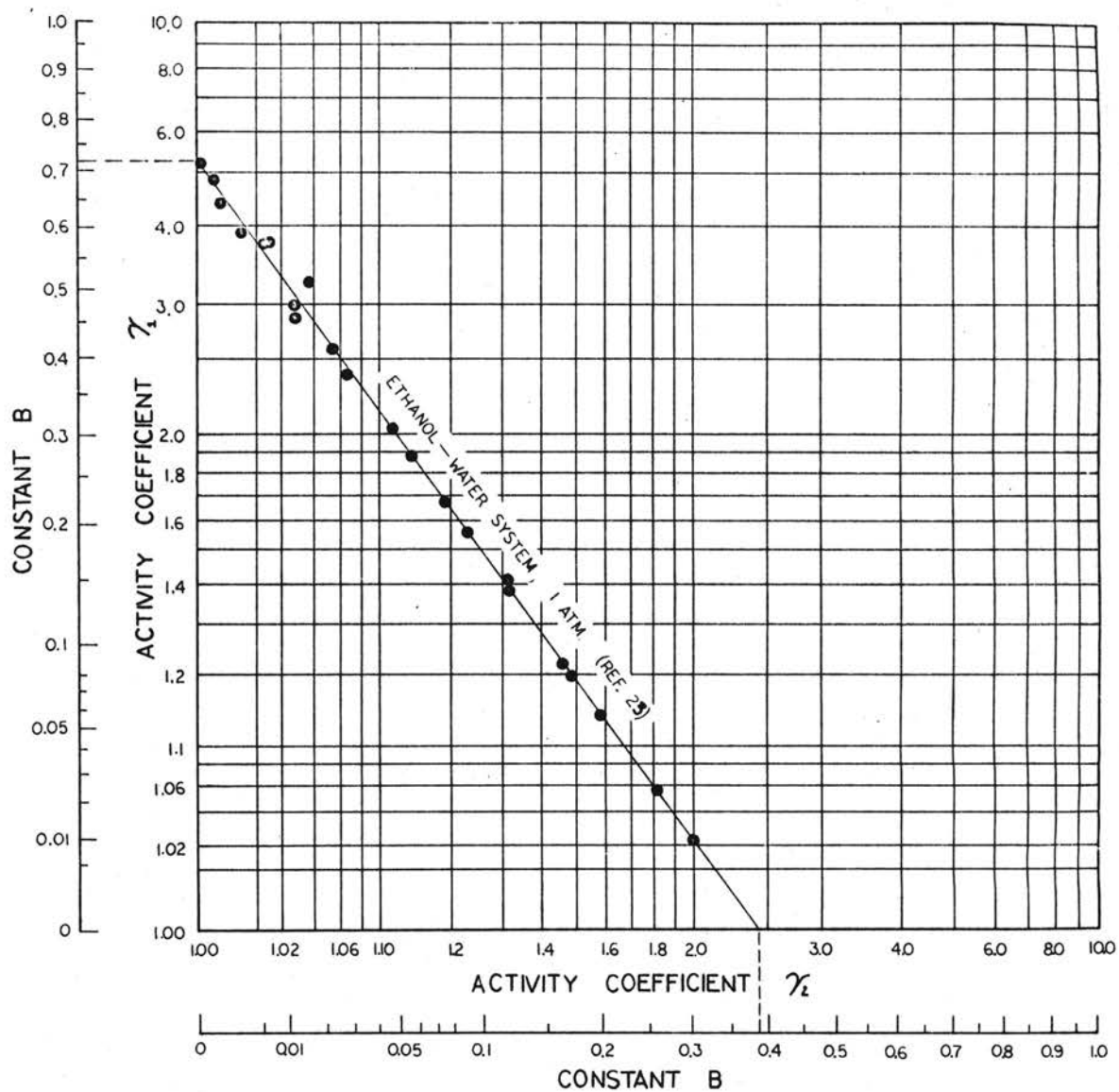
FIGURE 1

VAN LAAR GRAPH PAPER

REF. 23

of linear coordinates. The γ's are then plotted directly. Figure 1 is a plot of this graph paper. The experimental γ values plotted in Figure 1 are for an ethanol-water system (23).

Another equation of this type is the Hildebrand-Scatchard equation which expresses the activity coefficient as a function of liquid composition, temperature and solubility parameters (11). It is not necessary to assume a van der Waal fluid when using this equation. For a regular solution containing n components, the Hildebrand-Scatchard equation is

$$\ln \gamma_i = \frac{V_i (\delta_i - \bar{\delta})^2}{RT} \tag{11}$$

where: V_i = The liquid molal volume of pure i

δ_i = The solubility parameter of pure i

$\bar{\delta}$ = The volume average solubility parameter of the liquid solution $= \displaystyle\sum_{j=i}^{n} \Psi_i \delta_i$.

Ψ_i = The volume fraction of i $= \dfrac{x_i V_i}{\displaystyle\sum_{j=i}^{n} x_i V_i}$

For a binary system, Equation 11 becomes

$$\ln \gamma_1 = \frac{V_1 (\delta_1 - \delta_2)^2 \Psi_2^2}{RT} \tag{12}$$

$$\ln \gamma_2 = \frac{V_2 (\delta_1 - \delta_2)^2 \Psi_1^2}{RT} \tag{12'}$$

The derivation of Equation 11 and Equations 13 and 13' appear in

Appendix C.

The solubility parameter is the square root of an energy density
(11). For a liquid it is defined as

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} \qquad (13)$$

where: ΔE = The energy required to vaporize
the liquid to infinite volume.

Equation 13 indicates that the solubility parameter decreases with
temperature, but is practically independent of pressure at a given
temperature. Omitting pressure as a parameter greatly simplifies the
use of Equations 11, 12 and 12' (26).

Prausnitz, Edmister and Chao (P-E-C), in their recent work presented
at the Atlantic City A.I.Ch.E. meeting (26), applied the Hildebrand-
Scatchard equation to hydrocarbon-gas systems and evaluated the solubili-
ty parameters and the liquid phase fugacity coefficients for light gases
in liquid solution. P-E-C point out that, "In general, solubility
parameter values of the aromatic hydrocarbons are higher than those of
the napthenes; the latter are in turn higher than those of the paraffins.
Among the normal paraffins, the solubility parameter increases rapidly
with molecular weight starting from methane but tends to level off for
compounds heavier than n-pentane. Thus, the difference in solubility
parameters between a light paraffin and a heavy paraffin is less than
that between the same light paraffin and an aromatic hydrocarbon. This
explains the high "K" values of the light paraffins in aromatics."
Figure 2 is a plot of the solubility data from Prausnitz, Edmister and
Chao (26) (see page 20).

Summary of the Literature

Despite the wide utilization of distillation and similar contacting apparatus and the need for reliable data on vapor-liquid equilibria to design such apparatus, relatively little attention has been paid to the important problem of evaluating and extending such data to nonideal solutions. Most of the work done to date applies to the aliphatic systems alone.

Prausnitz, Edmister and Chao (26) calculated vapor-liquid equilibria for light hydrocarbons using solubility parameters with fairly good success. Composition corrected "K" values, inculding this method, are not convenient to apply in most practical problems. However, simplification was obtained by taking the solubility parameter and the liquid molal volume to be independent of pressure. Prausnitz, Edmister and Chao justified this simplification up to pressures of 1000 psia (26).

This work goes one step further in simplifying the application of the van Laar and the Hildebrand-Scatchard equations. The solubility parameter, for reasons discussed in Chapter III, was assumed to be insensitive to temperature as well as pressure.

CHAPTER III

DESCRIPTION OF EVALUATION PROCEDURE

Selection of the Subject

Of the many methods for estimating vapor-liquid "K" values mentioned in the previous chapter, the method employed by Prausnitz, Edmister and Chao (26) offers the most promising solution for light hydrocarbons in various solvents. The work of Prausnitz, Edmister and Chao used the Hildebrand-Scatchard equation (Equation 11) to evaluate the liquid activity coefficients and the Redlich-Kwong equation (Equation 3-D) to evaluate the vapor fugacity coefficient. Their results showed the following:

(1) The calculation of light hydrocarbon vapor-liquid equilibria by use of solubility parameters appears to give correctly, the the liquid phase composition effects.

(2) Composition-corrected "K" values are not convenient to apply in practical problems and this method is no exception.

(3) Simplification was obtained by taking the solubility parameter and the liquid molal volume to be pressure-insensitive. No trend in deviation was detected with pressure in the comparison with experimental data.

(4) The results indicate that the solubility parameter is a useful tool for the correlation and prediction of hydrocarbon vapor-liquid equilibria.

Based on these conclusions, the method of determining composition-dependent liquid activity coefficients outlined by Prausnitz, Edmister and Chao (26) was used in this work with the following simplification:

The solubility parameter was assumed to be insensitive to both temperature and pressure.

Materials

The experimental data of W. B. Kay, et. al. were used in the evaluation of vapor-liquid "K" values for ethane-hydrocarbon binaries (13, 14, 15, 16, 17). These data were smoothed to obtain intermediate points. See Appendix A for the tabulation of these data.

The IBM 650 computer was used to aid in the calculation of the vapor fugacity coefficients (8) and, also, for the trial-and-error calculations, described later in this chapter, for determining liquid fugacity coefficients, solubility parameters and liquid molal volumes for the light component.

Treatment of the Data

Rearranging the terms in the Hildebrand-Scatchard equation (Equation 12) leads to

$$\ln \gamma_1 = \frac{\frac{V_1}{RT}(\delta_1 - \delta_2)^2}{\left(1 + \frac{x_1 V_1}{x_2 V_2}\right)^2}.$$

Likewise, for component 2

$$\ln \gamma_2 = \frac{\frac{V_2}{RT}(\delta_1 - \delta_2)^2}{\left(1 + \frac{x_2 V_2}{x_1 V_1}\right)^2}.$$

By combining the constants and the molar volumes and rearranging,
the Hildebrand-Scatchard equation can be written in the form identical
to the van Laar equations for binaries, but with A and B defined
differently:

$$\ln \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \tag{14}$$

$$\ln \gamma_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \tag{14'}$$

where:

$$A = \frac{V_1(\gamma_1 - \gamma_2)^2}{RT} \tag{15}$$

$$B = \frac{V_2(\gamma_1 - \gamma_2)^2}{RT} \tag{15'}$$

For a system containing one component above its critical temperature,
Equation 11 is treated as a semi-empirical relation with adjustable
parameters suitable for all liquid-phase hydrocarbon solutions, including
those containing both liquid and gaseous components (26).

The partial molal volume of the dissolved gas is used in place of
the liquid molal volume for a solution containing a gaseous solute.
This partial molal volume, $\overline{V}$, can be estimated with fair accuracy from
Watson's expansion factor (9, 26),

$$\overline{V} = (V_1 \omega_1)(5.7 - 3.0\, T_1/T_c). \tag{16}$$

where: V_1 = The liquid molal volume at a low
temperature T_1

ω_1 = The Watson's expansion factor at
T_1

$$T_c = \text{The critical temperature of the dissolved gas}$$

The product $(V_1 \omega_1)$ is a constant for each component. Values of this liquid volume characteristic constant have been evaluated and tabulated (9, 26). Typical values are listed in Table II.

Equation 16 was used to calculate one of the hypothetical pure component properties for light gases in liquid solution, namely, $\overline{V}$. The remaining two, δ and ν, were determined by applying Equations 1, 14 and 15 to experimental vapor-liquid data. Prausnitz, Edmister and Chao have shown that ν is a function of temperature and pressure, and that the solubility parameter is insensitive to pressure over a moderate pressure range. From Equations 15 and 15', it can be seen that the solubility parameters always appear as the difference squared, $(\delta_1 - \delta_2)^2$, in the evaluation of the van Laar constants. In view of this and the fact that the δ vs T lines for the derived δ values in Figure 2 are essentially parallel, single characteristic values of δ were used in this work for each hydrocarbon.

The determination of ν and δ, then, consisted of fitting Equation 1 to the solubility data of a gas in at least two solvents at the same temperature and pressure. These calculations were of the trial-and-error type, using solubility data in two chemically different solvents to obtain sensitivity.

The following procedure was used in the calculations:

(1) To start the calculations, solubility parameter values for the solvents (δ_2) were fixed--values from Hildebrand and Scott (11) at 25°C were used, except for Cyclohexane. The value of δ for cyclohexane was adjusted to 8.5.

TABLE II

PHYSICAL PROPERTIES OF SEVERAL

ORGANIC COMPONENTS

Component	Normal Boiling Point	Critical Properties*		Watson's Characteristic Constants (9)	Solubility Parameters* δ
		Temp.	Press.		
	°R	°R	psia	V_{ω_1}	(cal/cc)
Ethane	332.2	549.8	708.3	7.77	6.30
n-Butane	490.8	765.3	550.7	11.62	6.70
n-Heptane	668.9	972.3	396.9	18.96	7.45
Benzene	636.2	1013.0	714.0	11.64	9.15
Cyclohexane	637.3	998.0	561.4	14.07	8.50

* API 44 Tables, except Benzene and Cyclohexane which are from NGSMA (23)

* From Reference (26), except Ethane which is from back calculation (26)

SOLUBILITY PARAMETER – TEMPERATURE CURVES

SOURCE: REFERENCE 27
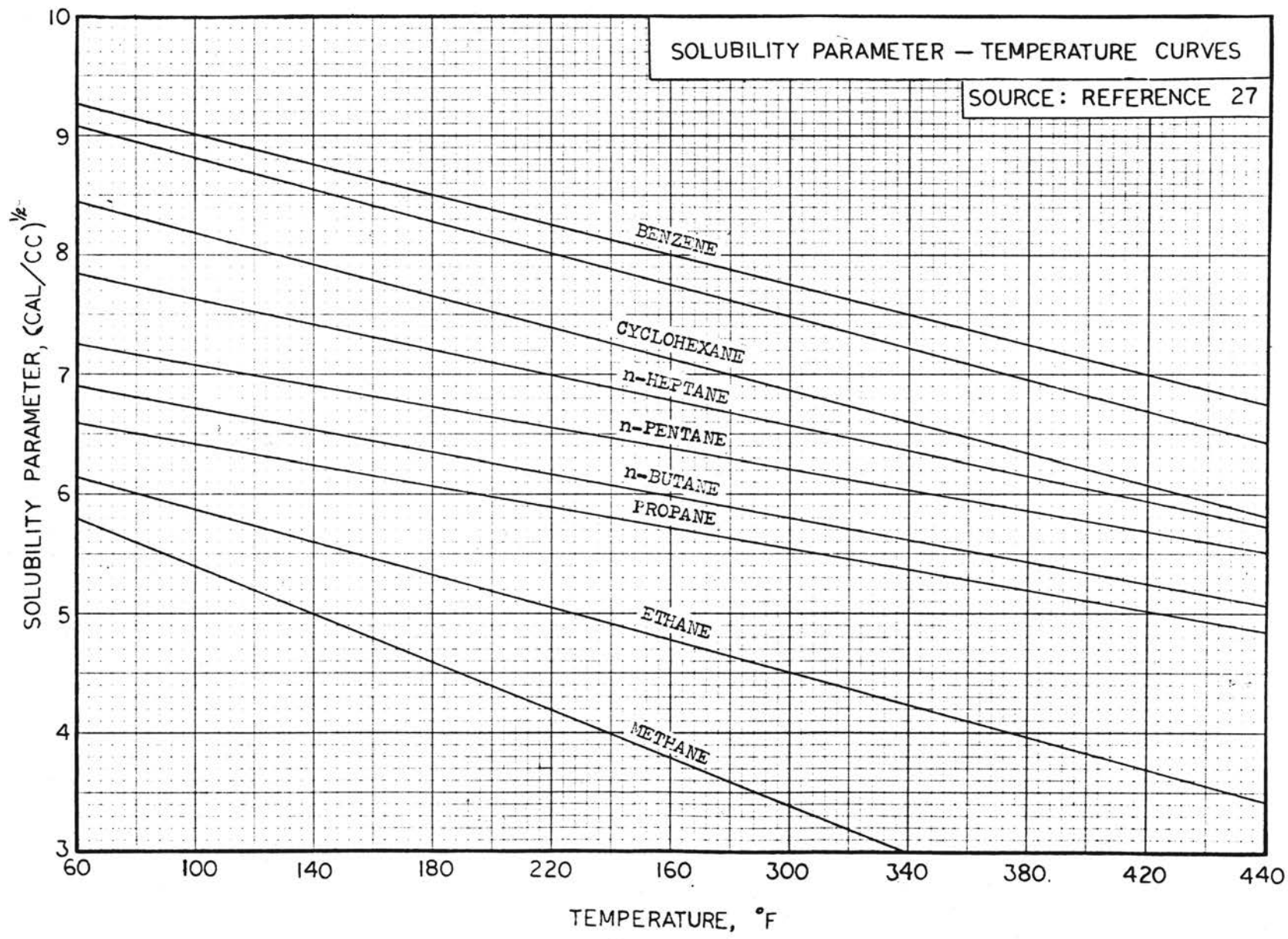
TEMPERATURE, °F

FIGURE 2

20
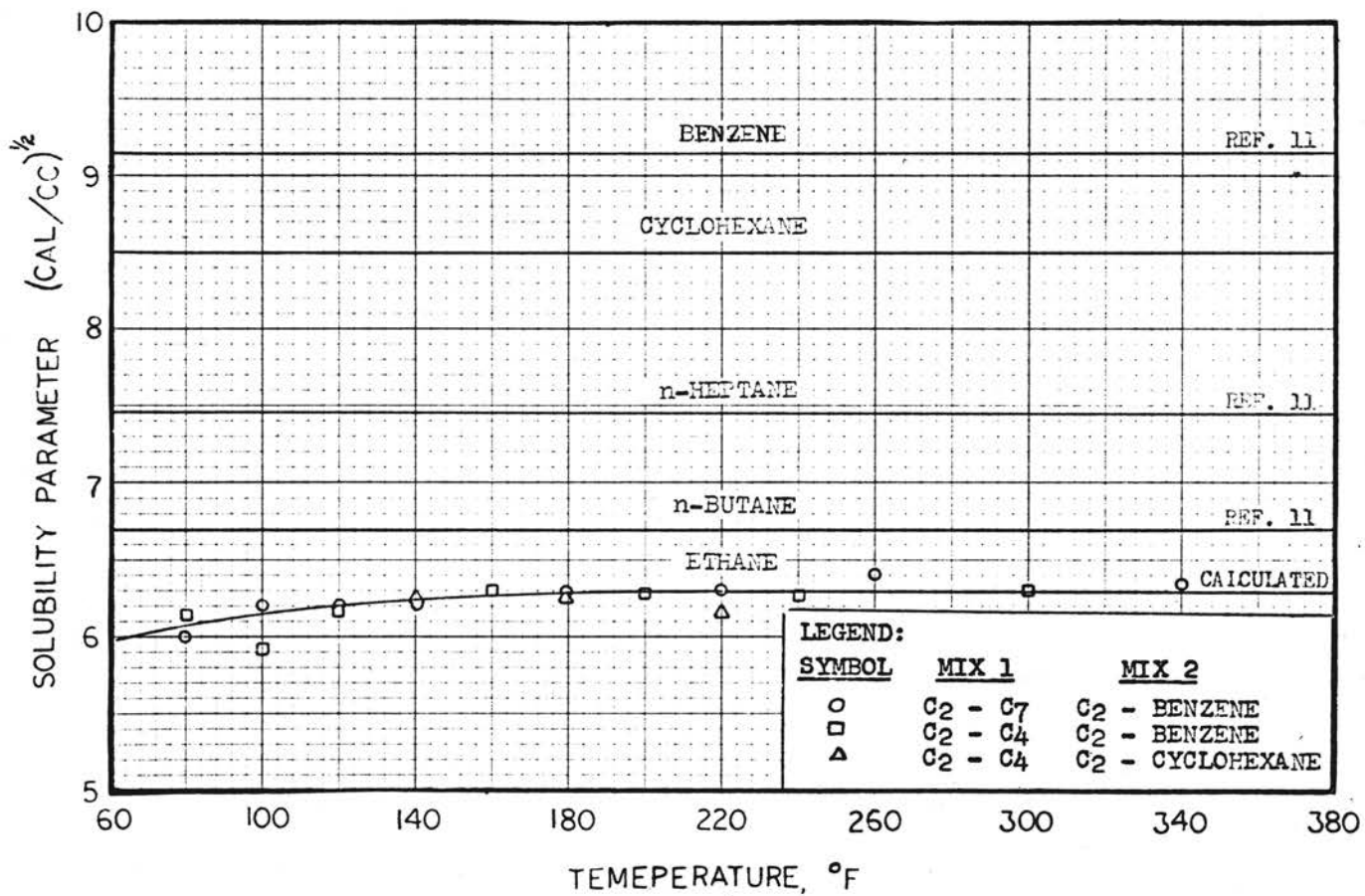
FIGURE 3

SOLUBILITY PARAMETER — TEMPERATURE CURVES
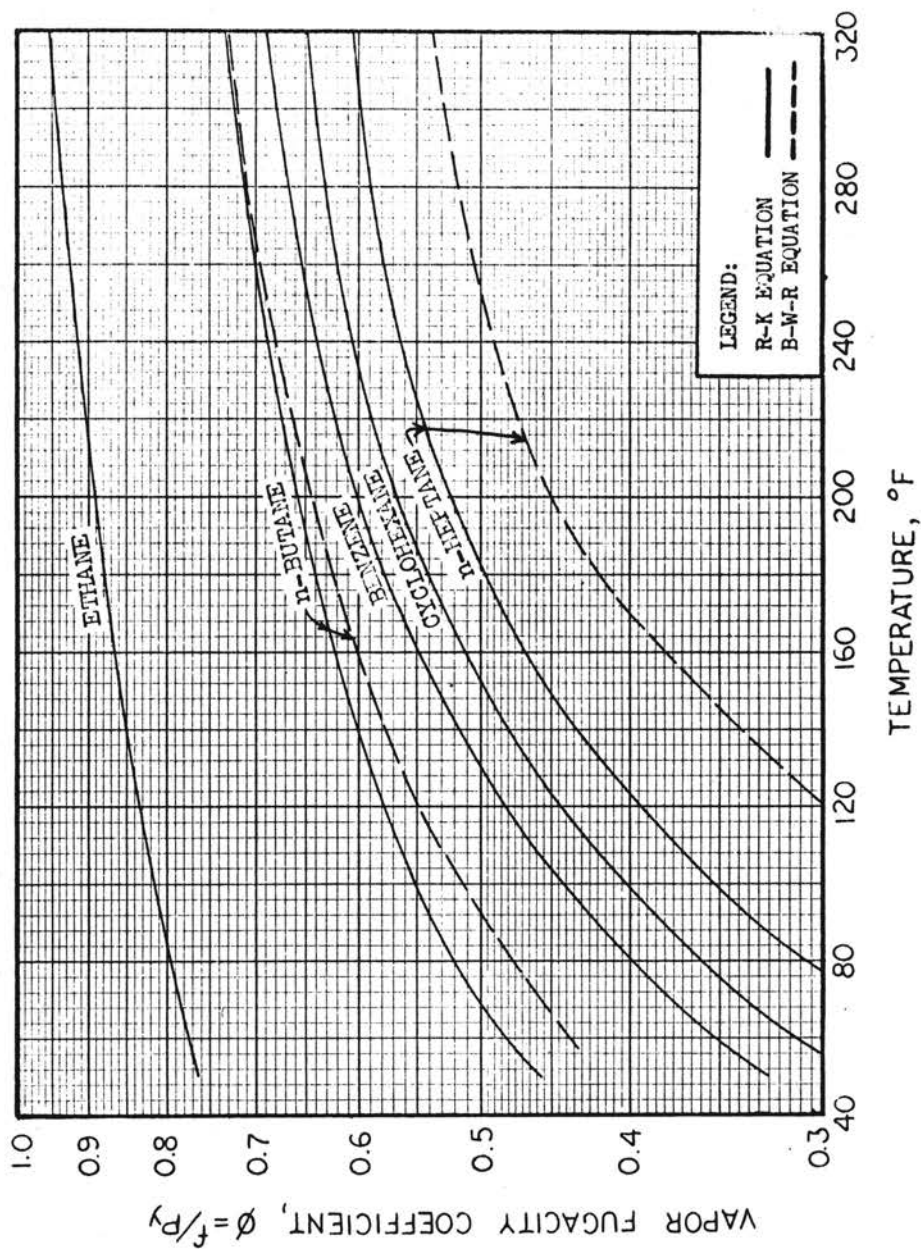
VAPOR FUGACITY COEFFICIENT — TEMPERATURE CURVES
PRESSURE = 400 PSIA
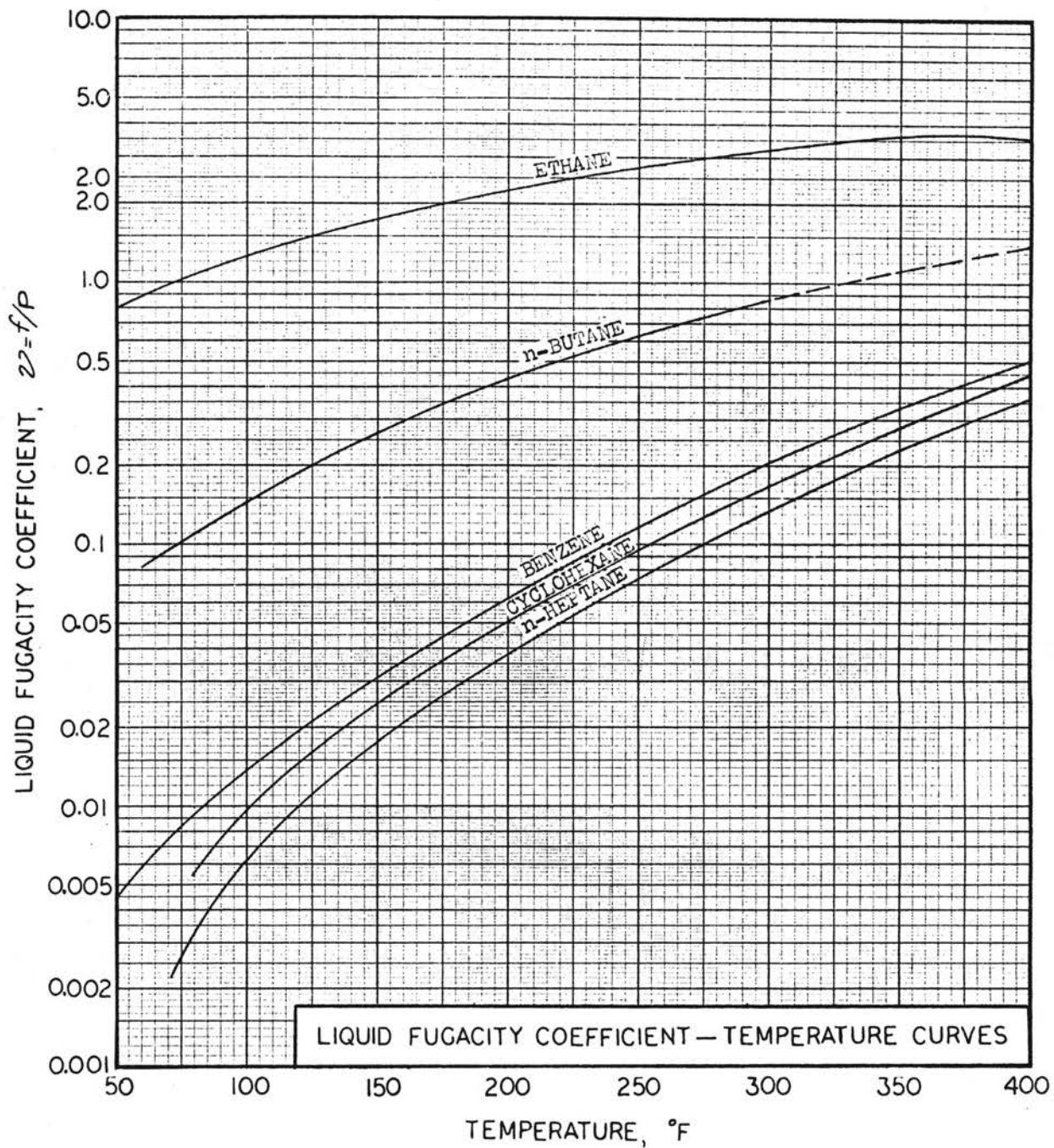
FIGURE 4

FIGURE 5

(2) The solubility parameter value for the solute (δ_1) was assumed.

(3) Equations 14 and 15 were used to evaluate the liquid activity coefficients, γ_1 and γ_2, for each of two systems. Each system contained a common solute (component 1) and chemically different solvents (component 2).

(4) Equation 1 was solved for the liquid fugacity coefficient, ν, for the common component in each system. The difference between these two ν values ($\nu - \nu'$) was called $\Delta \nu$.

(5) New assumptions for δ_1 were made until $\Delta \nu$ became zero. When $\Delta \nu_1$ became zero, the δ values and ν values were recorded.

(6) The Redlich-Kwong equation of state (Equation 3-D) was used to evaluate the vapor fugacity coefficient ϕ, (Appendix D).

(7) Equation 1 was solved for "K" values and compared with the experimental data.

The calculations in Step 6 were carried out on the IBM 650 computer (8). The results obtained from this program are shown in Figure 3. Also, the trial-and-error calculations were programmed for use on the computer. The values of δ and ν obtained by the back-calculations are shown in Figures 4 and 5 respectively. Appendix E contains a detailed, sample calculation for the ethane-n-heptane and ethane-benzene systems at 140°F and 400 psia.

RESULTS

A series of vapor-liquid "K" values were calculated using the van Laar activity coefficients with the A and B constants being determined by the Hildebrand-Scatchard equations for binary mixtures. The data presented in the following pages were obtained.

The following information is presented in tabular form:

(1) The calculated activity coefficients along with the molal volumes and the van Laar constants used.

(2) The calculated vapor-liquid equilibrium "K" values along with the liquid fugacity coefficients and the vapor fugacity coefficients.

(3) A comparison of the experimental and the calculated values of "K". The calculated "K" values listed are those of N.G.A.A. and Hildebrand and Scatchard.

The "K" value comparisons are, also, plotted in Figures 6 thru 10 for the purpose of discussion.

TABLE III

CALCULATED LIQUID PHASE ACTIVITY COEFFICIENTS

FOR ETHANE-n-BUTANE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = ETHANE

Temp.	Liquid mf.	Molar Volumes		van Laar Constants		Activity Coefficients	
°F	x_1	V_1	V_2	A	B	$\ln \gamma_1$	$\ln \gamma_2$
271	0	75.29	99.53	6.061	8.012	0.01493	0
240	0.086	73.90	98.08	5.949	7.895	0.01334	0.00010
220	0.144	73.06	97.18	5.881	7.823	0.01227	0.00028
200	0.200	72.23	96.27	5.815	7.750	0.01125	0.00052
180	0.265	71.35	95.38	5.744	7.678	0.01002	0.00097
160	0.320	70.50	94.46	5.675	7.604	0.00902	0.00149
140	0.404	69.66	93.55	5.608	7.531	0.00743	0.00254
120	0.489	68.82	92.62	5.540	7.456	0.00587	0.00399
100	0.590	67.97	91.73	5.472	7.384	0.00411	0.00632
80	0.709	67.14	90.79	5.405	7.309	0.00229	0.01008
60	0.853	66.30	89.89	5.337	7.236	0.00101	0.01645
42.5	1.000	65.59	89.14	5.280	7.176	0	0.02572

TABLE IV

CALCULATED LIQUID PHASE ACTIVITY COEFFICIENTS

FOR ETHANE-n-HEPTANE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = ETHANE

Temp.	Liquid mf.	Molar Volumes		van Laar Constants		Activity Coefficients	
°F	x_1	V_1	V_2	A	B	$\ln \gamma_1$	$\ln \gamma_2$
512	0	85.50	161.16	56.900	107.252	0.10538	0
440	0.096	83.38	160.65	54.824	106.913	0.09863	0.00057
400	0.134	80.66	158.31	53.679	105.355	0.09657	0.00118
360	0.166	78.96	155.96	52.548	103.791	0.09514	0.00191
320	0.203	77.27	153.64	51.423	102.247	0.09326	0.00304
280	0.245	75.61	151.31	50.318	100.697	0.09077	0.00485
240	0.291	73.90	148.97	49.180	99.140	0.08731	0.00730
200	0.315	72.23	146.62	48.069	97.576	0.08722	0.00908
180	0.382	71.35	145.44	47.483	96.790	0.07869	0.01475
160	0.426	70.50	144.28	46.918	96.018	0.07339	0.01975
140	0.476	69.66	143.09	46.359	95.226	0.06690	0.02696
120	0.535	68.82	141.96	45.800	94.474	0.05860	0.03915
100	0.613	67.97	140.80	45.234	93.702	0.04671	0.05657
80	0.713	67.14	130.61	44.682	92.910	0.03062	0.09181
60	0.850	66.30	138.43	44.123	92.125	0.01141	0.17052
41	1.000	65.52	137.37	43.604	91.420	0	0.32867

TABLE V

CALCULATED LIQUID PHASE ACTIVITY COEFFICIENTS

FOR ETHANE-BENZENE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = ETHANE

Temp.	Liquid mf.	Molar Volumes		van Laar Constants		Activity Coefficients	
°F	x_1	V_1	V_2	A	B	$\ln \gamma_1$	$\ln \gamma_2$
464	0	83.47	98.20	341.175	401.383	0.66526	0
440	0.026	82.38	97.37	336.720	397.990	0.64401	0.00039
400	0.057	80.66	95.99	329.690	392.350	0.62534	0.00192
360	0.071	78.96	94.62	322.741	386.750	0.62613	0.00306
320	0.087	77.27	93.21	315.833	380.987	0.62641	0.00471
280	0.132	75.61	91.85	309.048	375.428	0.59404	0.01431
240	0.178	73.90	90.46	302.059	369.746	0.56100	0.02151
200	0.213	72.23	89.08	295.233	364.106	0.54179	0.03215
180	0.238	71.35	88.41	291.636	361.367	0.52340	0.04211
160	0.268	70.50	87.71	288.162	358.506	0.49975	0.05379
140	0.310	69.66	87.02	284.728	355.686	0.46222	0.07698
120	0.363	68.82	86.34	281.295	352.906	0.41298	0.10701
100	0.450	67.98	85.64	277.821	350.045	0.32835	0.17453
80	0.586	67.14	84.95	274.428	347.225	0.20387	0.32166
60	0.825	66.30	84.26	270.995	344.404	0.05479	0.68548
45	1.000	65.71	83.77	268.583	342.401	0	1.22133

TABLE VI

CALCULATED LIQUID PHASE ACTIVITY COEFFICIENTS

FOR ETHANE-CYCLOHEXANE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = ETHANE

Temp.	Liquid mf.	Molar Volumes		van Laar Constants		Activity Coefficients	
°F	x_1	V_1	V_2	A	B	$\ln \gamma_1$	$\ln \gamma_2$
485	0	84.36	120.17	205.467	292.686	0.39148	0
440	0.037	82.38	118.27	200.645	288.058	0.38081	0.00041
400	0.070	80.66	116.58	196.455	283.942	0.37167	0.00146
360	0.105	78.96	114.61	192.315	279.144	0.36161	0.00342
320	0.140	77.27	113.21	188.734	275.734	0.35196	0.00637
280	0.180	75.61	111.48	184.156	271.521	0.33951	0.01109
240	0.225	73.90	109.82	179.991	267.478	0.32406	0.01837
200	0.279	72.23	108.10	175.923	263.288	0.30304	0.03029
180	0.313	71.35	107.24	173.780	261.194	0.28991	0.03885
160	0.352	70.50	106.41	171.710	259.172	0.26972	0.05268
140	0.396	69.66	105.58	169.664	257.151	0.24185	0.07043
120	0.445	68.82	104.73	167.618	255.080	0.22326	0.09418
100	0.507	67.97	103.89	165.548	253.034	0.19022	0.13125
80	0.614	67.14	103.30	163.526	251.597	0.12580	0.21083
60	0.795	66.30	102.19	161.480	248.894	0.04523	0.44203
41.5	1.000	65.55	100.02	159.654	243.609	0	0.87488

TABLE VII

CALCULATED LIQUID PHASE ACTIVITY COEFFICIENTS

FOR n-BUTANE-n-HEPTANE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = n-BUTANE

Temp.	Liquid mf.	Molar Volumes		van Laar Constants		Activity Coefficients	
°F	x_1	V_1	V_2	A	B	$\ln \gamma_1$	$\ln \gamma_2$
512	0.001	110.51	161.16	30.180	44.013	0.05882	0
440	0.254	107.23	160.65	29.285	43.874	0.03889	0.00301
400	0.391	105.42	158.31	28.790	43.234	0.02959	0.00812
360	0.545	103.57	155.96	28.285	42.593	0.01926	0.01838
340	0.634	102.66	154.91	28.009	42.306	0.01369	0.02721
320	0.725	101.76	153.64	27.791	41.959	0.00852	0.03922
300	0.824	100.83	152.49	27.542	41.645	0.00389	0.05638
271	1.000	97.20	150.85	26.545	41.197	0	0.10148

TABLE VIII

CALCULATED VAPOR-LIQUID EQUALIBRIUM VALUES

FOR ETHANE-n-BUTANE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = ETHANE

Temp.	Liquid Fugacity Coefficients		Vapor Fugacity Coefficients		Liquid Activity Coefficients		K Values	
°F	ν_1	ν_2	ϕ_1	ϕ_2	γ_1	γ_2	K_1	K_2
240	2.6800	0.5889	0.9945	0.6910	1.0134	1.0001	2.731	0.852
220	2.4682	0.5094	0.5968	0.6773	1.0124	1.0003	2.611	0.752
200	2.2612	0.4250	0.9293	0.6580	1.0113	1.0005	2.460	0.646
180	2.0603	0.3575	0.9047	0.6448	1.0101	1.0010	2.300	0.555
160	1.8390	0.2884	0.8846	0.6232	1.0091	1.0015	2.092	0.464
140	1.6434	0.2353	0.8644	0.6064	1.0075	1.0025	1.915	0.389
120	1.4510	0.1847	0.8453	0.5798	1.0059	1.0040	1.727	0.320
100	1.2617	0.1419	0.8251	0.5557	1.0041	1.0063	1.535	0.257
80	1.0791	0.1091	0.8037	0.5194	1.0023	1.0101	1.346	0.212
60	0.9104	0.0814	0.7795	0.4830	1.0010	0.0166	1.169	0.171

TABLE IX

CALCULATED VAPOR-LIQUID EQUILIBRIUM VALUES

FOR ETHANE-n-HEPTANE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = ETHANE

Temp.	Liquid Fugacity Coefficients		Vapor Fugacity Coefficients		Liquid Activity Coefficients		K Values	
°F	ν_1	ν_2	ϕ_1	ϕ_2	γ_1	γ_2	K_1	K_2
440	4.3900	0.4636	1.1362	0.6203	1.1111	1.0000	4.265	0.748
400	4.0500	0.3550	1.0427	0.6155	1.1014	1.0012	4.278	0.578
360	3.7830	0.2474	0.9849	0.6148	1.0998	1.0019	4.224	0.401
320	3.4658	0.1743	0.9559	0.6077	1.0978	1.0030	3.980	0.288
280	3.0900	0.1127	0.9329	0.5925	1.0950	1.0049	3.627	0.191
240	2.6788	0.0696	0.9134	0.5642	1.0912	1.0073	3.200	0.124
200	2.2612	0.0396	0.8931	0.5234	1.0911	1.0091	2.762	0.076
180	2.0203	0.0286	0.8818	0.4979	1.0819	1.0149	2.528	0.058
160	1.8390	0.0200	0.8695	0.4687	1.0762	1.0200	2.274	0.044
140	1.6434	0.0137	0.8558	0.4352	1.0692	1.0273	1.946	0.032
120	1.4510	0.0098	0.8404	0.3968	1.0604	1.0399	1.831	0.026
100	1.2617	0.0060	0.8229	0.3556	1.0478	1.0582	1.606	0.018
80	1.0791	0.0029	0.8027	0.3104	1.0311	1.0962	1.474	0.010
60	0.9104	0.0013	0.7793	0.2584	1.0115	1.1859	1.182	0.006

TABLE X

CALCULATED VAPOR-LIQUID EQUILIBRIUM VALUES

FOR ETHANE-BENZENE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = ETHANE

Temp.	Liquid Fugacity Coefficients		Vapor Fugacity Coefficients		Liquid Activity Coefficients		K Values	
°F	ν_1	ν_2	ϕ_1	ϕ_2	γ_1	γ_2	K_1	K_2
440	4.3900	0.6386	1.0764	0.7407	1.9041	1.0004	7.916	0.862
400	4.0500	0.4889	1.0201	0.7216	1.8689	1.0019	7.420	0.679
360	3.7838	0.3620	0.9829	0.7057	1.8704	1.0031	7.201	0.514
320	3.4658	0.2545	0.9554	0.6896	1.8709	1.0047	6.787	0.371
280	3.0900	0.1698	0.9338	0.6691	1.8113	1.0144	5.994	0.258
240	2.6788	0.1042	0.9139	0.6422	1.7524	1.0217	5.137	0.166
200	2.2612	0.0624	0.8936	0.6034	1.7191	1.0327	4.178	0.107
180	2.0603	0.0481	0.8823	0.5791	1.6878	1.0430	3.941	0.087
160	1.8390	0.0371	0.8700	0.5512	1.6483	1.0553	3.484	0.071
140	1.6434	0.0279	0.8562	0.5201	1.5876	1.0800	3.047	0.058
120	1.4510	0.0203	0.8408	0.4833	1.5113	1.1130	2.608	0.047
100	1.2617	0.0135	0.8230	0.4469	1.3887	1.1907	1.990	0.030
80	1.0791	0.0088	0.8028	0.4029	1.2261	1.3794	1.648	0.030
60	0.9104	0.0047	0.7793	0.3550	1.0563	1.9847	1.234	0.026

TABLE XI

CALCULATED VAPOR-LIQUID EQUILIBRIUM VALUES

FOR ETHANE-CYCLOHEXANE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = ETHANE

Temp.	Liquid Fugacity Coefficients		Vapor Fugacity Coefficients		Liquid Activity Coefficients		K Values	
°F	ν_1	ν_2	ϕ_1	ϕ_2	γ_1	γ_2	K_1	K_2
440	4.3900	0.5300	1.1075	0.6909	1.4635	1.0004	5.479	0.767
400	4.0500	0.5300	1.0417	0.6724	1.4502	1.0015	5.638	0.596
360	3.7830	0.4000	0.9949	0.6587	1.4356	1.0034	5.459	0.449
320	3.4658	0.2950	0.9605	0.6468	1.4218	1.0064	5.130	0.319
280	3.0900	0.1350	0.9345	0.6329	1.4043	1.0112	4.644	0.216
240	2.6788	0.0883	0.9139	0.6076	1.3827	1.0185	4.053	0.148
200	2.2612	0.0506	0.8933	0.5693	1.3540	1.0308	3.427	0.092
180	2.0603	0.0388	0.8821	0.5439	1.3363	1.0396	3.121	0.074
160	1.8390	0.0296	0.8698	0.5150	1.3096	1.0541	2.769	0.061
140	1.6434	0.0216	0.8560	0.4827	1.2816	1.0730	2.490	0.048
120	1.4510	0.0152	0.8406	0.4464	1.2502	1.0988	2.158	0.037
100	1.2617	0.0096	0.8280	0.4064	1.2095	1.1402	1.854	0.027
80	1.0791	0.0053	0.8028	0.3619	1.1454	1.2347	1.540	0.018
60	0.9104	0.0011	0.7793	0.3131	1.0463	1.5559	1.223	0.005

TABLE XII

CALCULATED VAPOR-LIQUID EQUILIBRIUM CONSTANTS

FOR n-BUTANE-n-HEPTANE SYSTEM

PRESSURE = 400 PSIA   COMPONENT 1 = n-BUTANE

Temp.	Liquid Fugacity Coefficients		Vapor Fugacity Coefficients		Liquid Activity Coefficients		K Values	
°F	ν_1	ν_2	ϕ_1	ϕ_2	γ_1	γ_2	K_1	K_2
440	1.3000	0.4636	0.810	0.590	1.0397	1.0030	1.669	0.639
400	1.1500	0.3550	0.760	0.560	1.0300	1.0082	1.559	0.639
360	1.0200	0.2474	0.740	0.549	1.0194	1.0186	1.405	0.467
340	0.9500	0.2089	0.730	0.530	1.0138	1.0276	1.319	0.405
320	0.8800	0.1743	0.720	0.520	1.0086	1.0400	1.233	0.349
300	0.8200	0.1427	0.715	0.510	1.0039	1.0580	1.151	0.296
271	0.7100	0.1040	0.700	0.508	1.0000	1.1068	1.014	0.227

TABLE XIII

COMPARISON OF EXPERIMENTAL AND CALCULATED K VALUES

FOR ETHANE-n-BUTANE SYSTEM

PRESSURE = 400 PSIA

		ETHANE						n-BUTANE			
Temp	Exp.	H and S		N.G.A.A.		Exp.	H and S		N.G.A.A.		
			%		%			%		%
°F	K	K	Error	K	Error	K	K	Error	K	Error
240	2.570	2.731	6.28	2.55	7.88	0.852	0.852	0	0.89	3.17
220	2.472	2.611	5.62	2.40	-2.92	6.752	0.752	0	0.78	3.72
200	2.415	2.461	1.89	2.32	-3.94	0.646	0.646	0	0.68	5.26
180	2.234	2.300	2.96	2.20	-1.52	0.555	0.555	0	0.58	4.50
160	2.141	2.098	-2.01	2.05	-4.17	0.463	0.464	0.22	0.50	8.00
140	1.901	1.915	-0.74	1.95	2.58	0.389	0.389	0.	0.44	13.10
120	1.710	1.727	1.00	1.80	5.26	0.321	0.320	-0.31	0.39	21.50
100	1.515	1.535	1.32	1.60	5.61	0.258	0.257	-0.39	0.34	31.80
80	1.322	1.346	1.81	1.38	3.63	0.216	0.212	-1.85	0.28	29.30
Average % Error			2.01		1.39			-0.26		13.37

TABLE **XIV**

COMPARISON OF EXPERIMENTAL AND CALCULATED K VALUES

FOR ETHANE-n-HEPTANE SYSTEM

PRESSURE = 400 PSIA

		ETHANE						n-HEPTANE		
Temp	Exp.	H and S		N.G.A.A.		Exp.	H and S		N.G.A.A.	
			%		%			%		%
°F	K	K	Error	K	Error	K	K	Error	K	Error
440	3.375	4.265	26.40	3.45	2.22	0.748	0.748	0	0.760	1.61
400	3.731	4.278	14.70	3.80	1.85	0.577	0.578	0.17	0.580	0.52
360	4.012	4.224	5.30	3.70	-7.78	0.401	0.401	0	0.420	2.49
320	3.798	3.980	4.80	3.50	-7.85	0.287	0.288	0.35	0.310	4.52
280	3.494	3.627	3.80	3.25	-7.00	0.191	0.191	0	0.210	9.95
240	3.134	3.200	2.10	2.90	-7.48	0.124	0.124	0	0.130	4.84
200	2.738	2.762	0.87	2.65	-3.21	0.076	0.076	0	0.083	9.21
180	2.542	2.528	0.16	2.45	-2.93	0.058	0.058	0	0.065	12.06
160	2.289	2.274	-0.66	2.20	-3.01	0.044	0.044	0	0.051	15.91
140	2.065	1.964	-5.76	2.05	-0.73	0.032	0.032	0	0.040	25.00
120	1.847	1.831	-0.87	1.80	-2.54	0.026	0.026	0	0.040	53.80
100	1.620	1.606	-0.86	1.60	-1.24	0.018	0.018	0	0.032	77.70
80	1.398	1.474	5.47	1.40	0.14	0.010	0.010	0	0.023	130.00
Average % Error			4.26		-3.04			0.04		26.14

TABLE XV

COMPARISON OF EXPERIMENTAL AND CALCULATED K VALUES

FOR ETHANE-BENZENE SYSTEM

PRESSURE = 400 PSIA

		ETHANE						BENZENE			
Temp	Exp.	H and S		N.G.A.A.		Exp.	H and S		N.G.A.A.	
			%		%			%		%
°F	K	K	Error	K	Error	K	K	Error	K	Error
440	6.154	7.916	28.70			0.862	0.862	0		
400	6.136	7.420	17.50			0.679	0.679	0		
360	6.092	7.201	18.20			0.515	0.514	-0.19		
320	5.744	6.787	18.20			0.372	0.371	-0.27		
280	5.313	5.994	11.88			0.257	0.258	0.39		
240	4.854	5.134	5.78			0.166	0.166	0		
200	4.300	4.178	-5.16			0.107	0.107	0		
180	3.924	3.941	0.43			0.087	0.087	0		
160	3.537	3.484	-1.78			0.071	0.071	0		
140	3.097	3.047	-1.62			0.058	0.058	0		
120	2.672	2.608	-2.31			0.047	0.047	0		
100	2.178	1.990	-8.63			0.036	0.036	0		
80	1.684	1.648	-2.14			0.031	0.030	-3.22		
Average % Error			6.08					-0.25		

TABLE XVI

COMPARISON OF EXPERIMENTAL AND CALCULATED K VALUES

FOR ETHANE-CYCLOHEXANE SYSTEM

PRESSURE = 400 PSIA

		ETHANE						CYCLOHEXANE			
Temp	Exp.	H and S		N.G.A.A.		Exp.		H and S		N.G.A.A.	
			%		%				%		%
°F	K	K	Error	K	Error	K		K	Error	K	Error
440	6.135	5.479	-12.30			0.803		0.767	-4.47		
400	5.643	5.638	-0.09			0.650		0.596	-8.31		
360	5.257	5.459	3.84			0.501		0.449	-10.30		
320	4.943	5.130	3.79			0.358		0.319	-10.89		
280	4.489	4.644	3.45			0.234		0.216	-7.69		
240	3.933	4.053	3.05			0.148		0.148	0		
200	3.348	3.427	2.36			0.092		0.092	0		
180	3.032	3.121	2.81			0.074		0.074	0		
160	2.730	2.769	1.43			0.060		0.061	1.67		
140	2.452	2.490	1.55			0.048		0.048	0		
120	2.200	2.158	-1.91			0.038		0.037	-2.63		
100	1.945	1.854	-4.68			0.028		0.027	-3.57		
80	1.616	1.540	-3.46			0.021		0.018	-14.28		
Average % Error			-0.01						-4.65		

TABLE XVII

COMPARISON OF EXPERIMENTAL AND CALCULATED K VALUES

FOR n-BUTANE-n-HEPTANE SYSTEM

PRESSURE = 400 PSIA

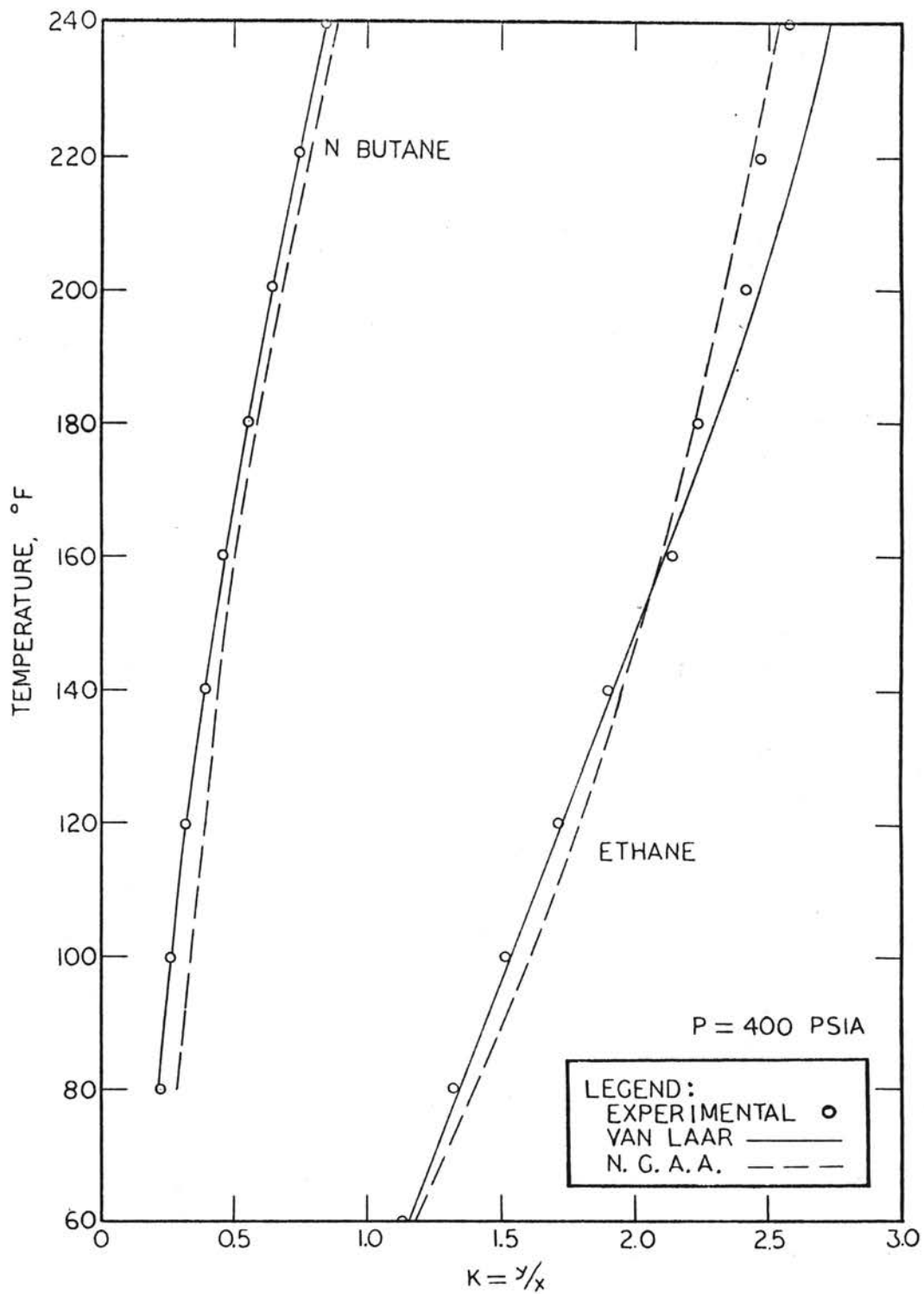|		n-BUTANE					n-HEPTANE			
Temp.	Exp.	H and S		N.G.A.A.		Exp.	H and S		N.G.A.A.	
°F	K	K	% Error	K	% Error	K	K	% Error	K	% Error
440	1.634	1.669	2.14	1.90	16.28	0.784	0.788	0.51	0.760	-3.06
400	1.565	1.559	-0.38	1.65	5.43	0.637	0.639	0.31	0.640	0.47
360	1.411	1.405	-0.43	1.45	2.76	0.508	0.467	-8.06	0.530	4.33
340	1.317	1.319	0.15	1.35	2.51	0.451	0.405	-10.18	0.470	4.21
320	1.230	1.233	0.24	1.28	4.07	0.393	0.349	-11.18	0.410	4.33
300	1.140	1.151	0.96	1.20	5.26	0.915	0.296		0.350	
Average % Error			0.45		6.05			-4.77		1.71

FIGURE 6

K-TEMPERATURE DIAGRAM
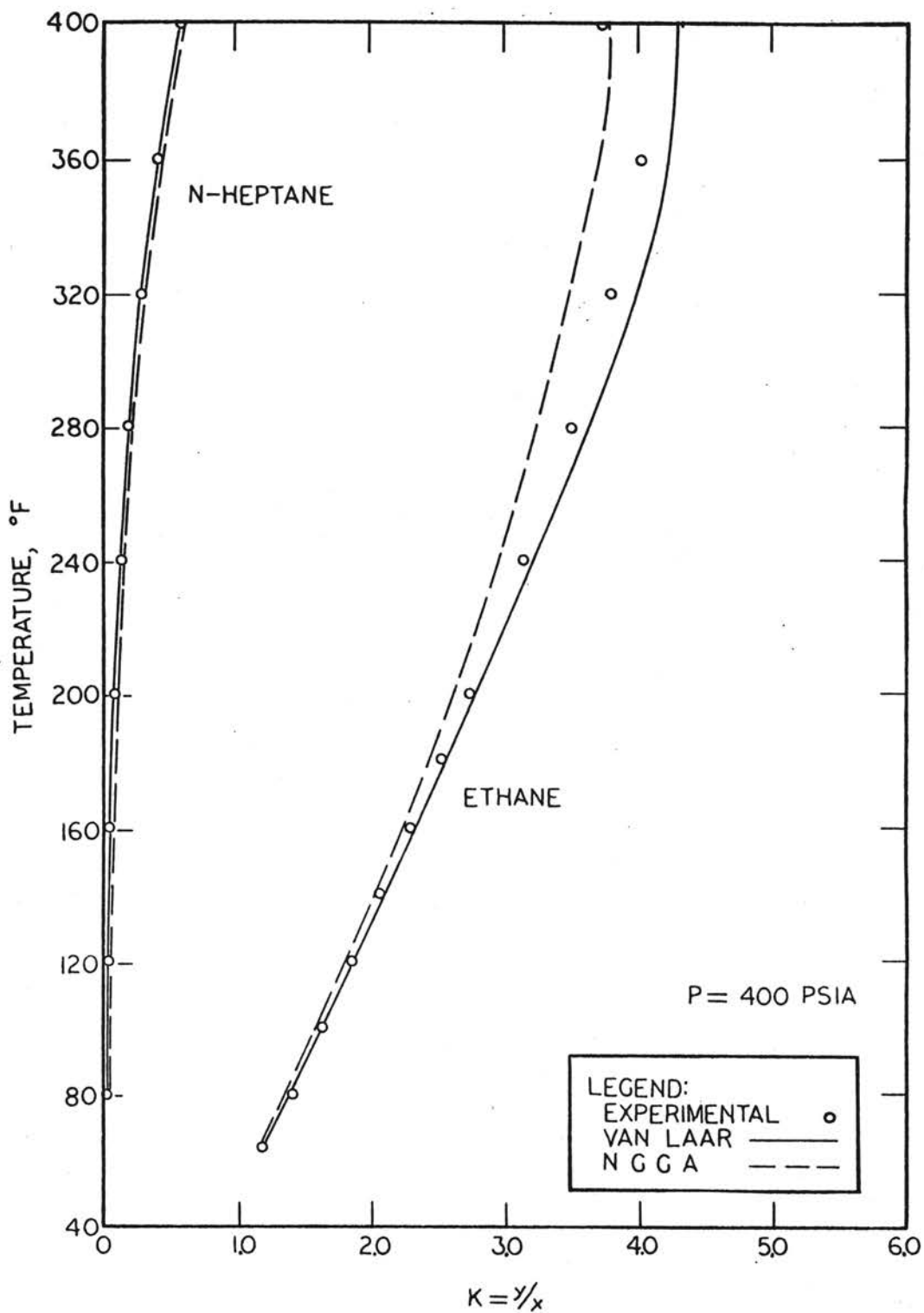
ETHANE—N-BUTANE BINARY

FIGURE 7

K — TEMPERATURE DIAGRAM
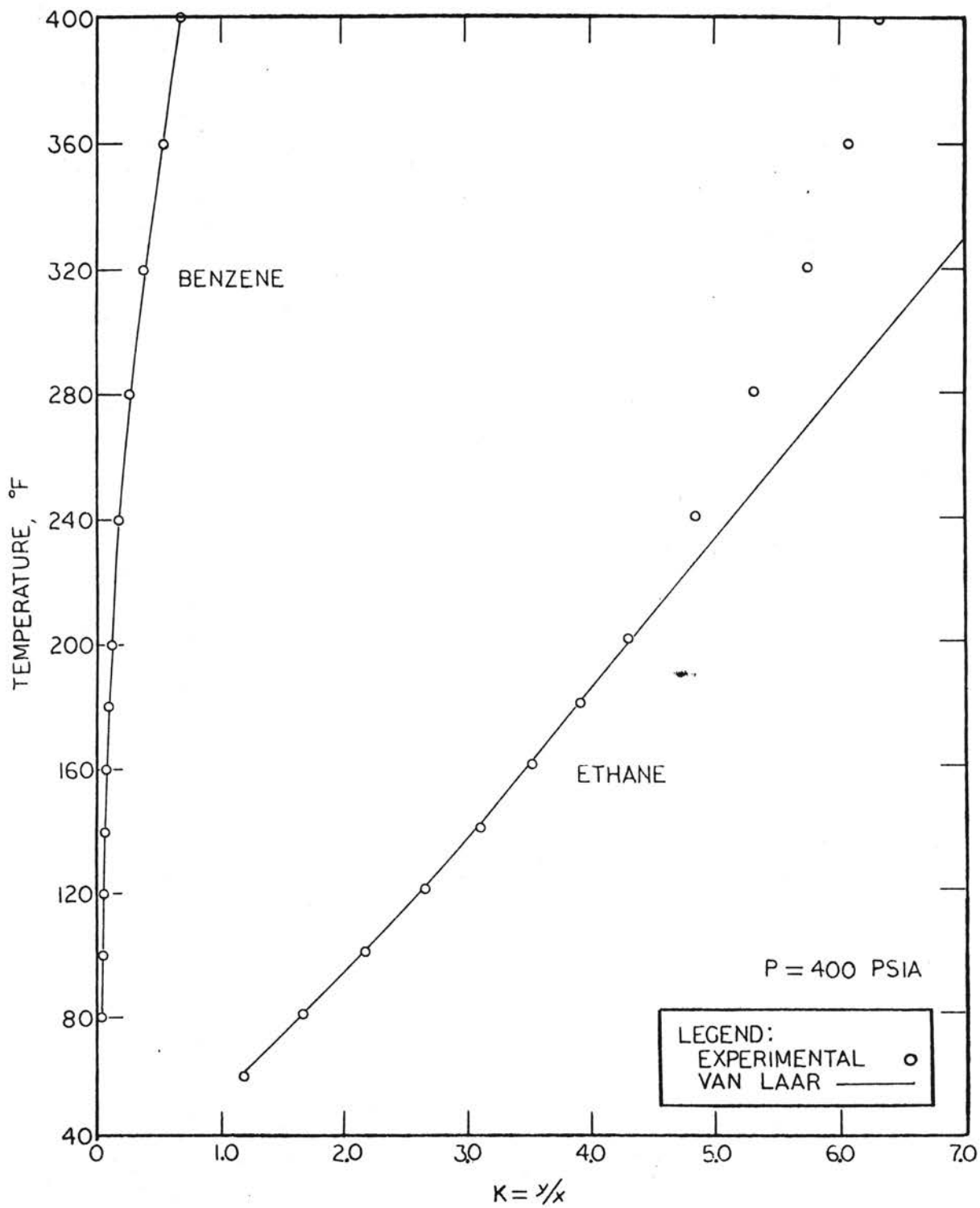
ETHANE — N — HEPTANE BINARY

FIGURE 8

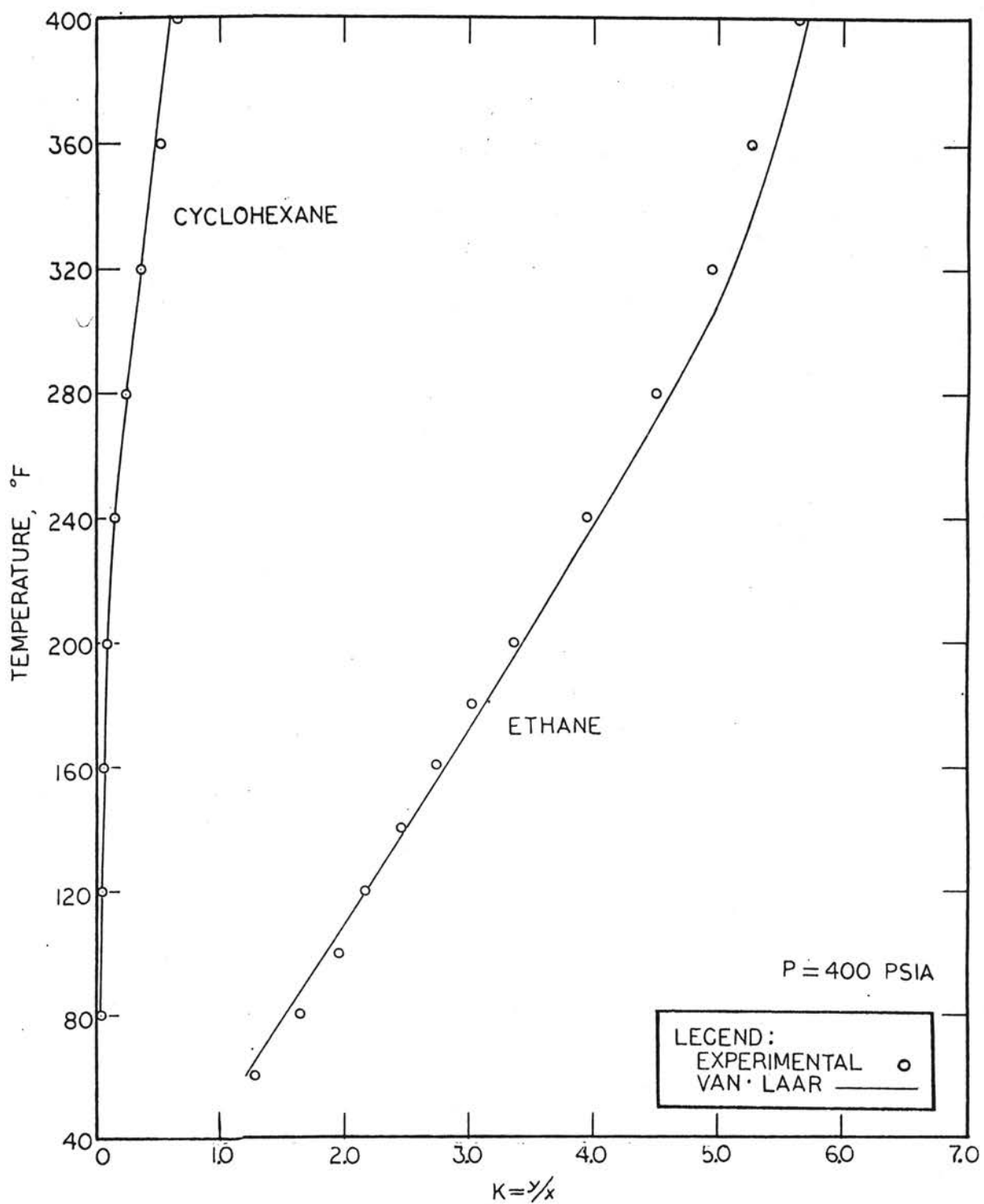K – TEMPERATURE DIAGRAM
ETHANE – BENZENE BINARY

FIGURE 9

K—TEMPERATURE DIAGRAM
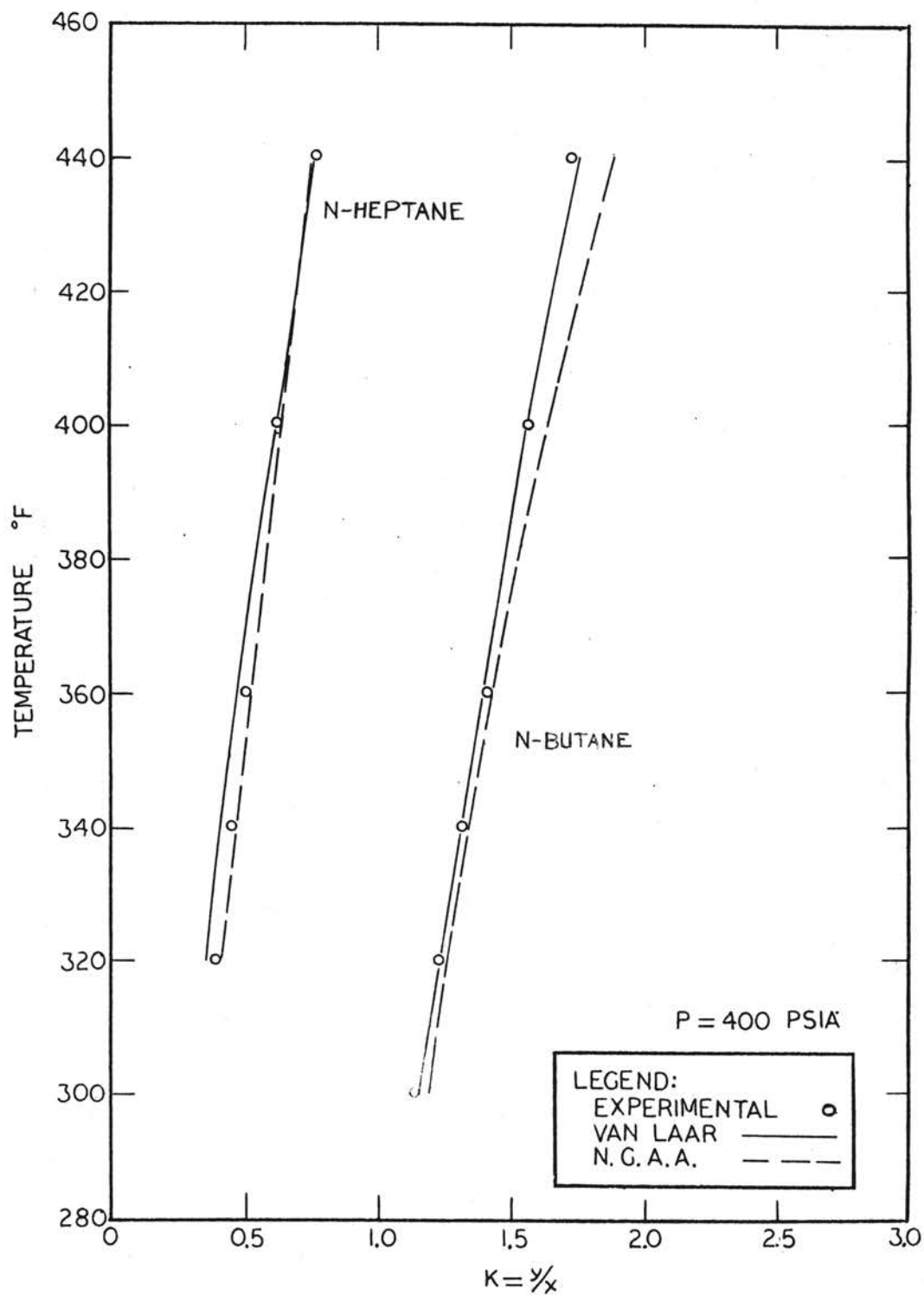
ETHANE—CYCLOHEXANE BINARY

FIGURE 10

K—TEMPERATURE DIAGRAM
N–BUTANE—N–HEPTANE BINARY

CHAPTER V

DISCUSSION OF RESULTS

Composition-dependent liquid activity coefficients were calculated using only physical properties of each component. The Hildebrand-Scatchard equation was used to evaluate A and B constants for the van Laar equation. Experimental data was necessary to test the method. Due to the limited available experimental data and for simplicity, the calculations were confined to binary mixtures. However, this is not a restriction to the method. Over moderate temperature ranges, the Hildebrand-Scatchard equation can be used satisfactorily to include the effect of composition in estimating vapor-liquid "K" values.

Figure 3 shows the solubility parameter values for the heavier components as straight lines of constant δ. These values of δ, with the exception of cyclohexane, were obtained from Hildebrand and Scott (11). For cyclohexane, the Hildebrand-Scott δ value of 8.2 gave the following results when the trial-and-error calculations were made with the ethane-n-butane system (mix 1) and the ethane-cyclohexane system (mix 2):

1. The ethane δ values were seven per cent lower than those calculated from the data of the other systems.

2. The K values calculated for the light component (ethane) in each mixture were low at higher temperatures, compared with the experimental data.

3. The K values calculated for the heavy components were low at
    lower temperatures in each mixture.

Since the δ (ethane) values determined in all other calculations
were approximately 6.3 above 140°F, the δ value for ethane was fixed
at 6.3 and the trial-and-error calculations were repeated assuming values
of δ for cyclohexane. The result of these calculations was a δ value
of 8.5 for cyclohexane. Figure 9 shows very good agreement between the
experimental K values and the values calculated using this adjusted δ
value.

To simplify the calculation of the liquid activity coefficients,
the δ value for ethane was assumed to be constant at the average value
of 6.3. This simplification appears to be justified in the comparison
of the calculated and the experimental K values (Figures 6 thru 10).

Figure 4 shows the vapor fugacity coefficients obtained by the
Redlich-Kwong equation of state and by the Benedict-Webb-Rubin equation
of state. The broken lines represent the Benedict-Webb-Rubin values (5).
The Redlich-Kwong ϕ values were determined on the IBM-650 computer using
equation 3-D (8). The Benedict-Webb-Rubin ϕ values for ethane, n-butane
and n-heptane were evaluated using the Kellogg charts presented by
DePriester (5). The evaluation of the vapor fugacity coefficients from
these charts required only a matter of 15 to 20 minutes. However, these
charts do not inclued components other than the paraffins. Since this
work was interested in extending the methods of calculating liquid
activity coefficients to systems containing aromatics and napthenes, the
Kellogg charts were not used.

Figure 4 shows a deviation between the Redlich-Kwong ϕ values and the
Benedict-Webb-Rubin ϕ values for the heavy components. A series of

calculations showed that, if the values of ϕ for the heavy components were in error to the same extent (i.e. both 10 per cent high or 30 per cent low, etc.), the effect on the values of δ and $\mathcal{V}$ was nil. The difference between the Redlich-Kwong ϕ values and the Benedict-Webb-Rubin ϕ values for n-butane and n-heptane were found to differ in approximately the same magnitude, therefore, the solubility parameters and liquid fugacity coefficients were not affected. The Redlich-Kwong ϕ values were used to evaluate "K" values for the ethane binaries. This vapor effect warrants further study.

The van Laar activity coefficients obtained by the use of the Hildebrand-Scatchard A and B values are tabulated in Tables III thre VIII. These values represent smoothed curves when plotted vs mole fraction of ethane (x_1) and do not contain maximum or minimum points within the limits of $x_1 = 0$ to $x_1 = 1$. It is interesting to note from Equations 14 and 14' that

$$(\ln \gamma_1)_{x_1=0} = A$$
$$(\ln \gamma_1)_{x_2=0} = 0$$
$$(\ln \gamma_2)_{x_1=0} = 0$$
$$(\ln \gamma_2)_{x_2=0} = B$$

Other generalities about deviations from ideal solutions are:

1. Temperature has a small effect on the liquid activity coefficient as shown by Equations 14 and 15. An indirect effect of temperature on A and B is thru the molar volume V in Equations 15 and 15'. This latter effect and the direct effect of temperature in the denominator of Equations 15 and 15' just about cancel each other.

2. The effect of pressure on γ (liquid) is less clear as it does not appear in Equations 14 and 15. The effect on molar volume is an indirect effect on γ, which would decrease with increasing pressure. Since the effect of pressure on liquid volume is very small over moderate pressure ranges, it may be assumed negligible.

The "K" values presented in Tables VIII thru XII were calculated as follows:

Fitting the van Laar equation to the ethane-benzene system at 180°F:

Calculation	Ethane	Benzene	Remarks:
x	0.238	0.762	Reference 15
Tc, °R	549.8	1013.0	API-44 Tables
Tr	1.164	0.631	
Vω	7.77	11.64	Reference 9
$\bar{V}_1$	71.35	88.41	Equation 16
A	291.6		Equation 15
B	361.4		Equation 15'
γ_1 / γ_2	0.542	0.032	Equations 14 and 14'
ϕ	0.882	0.579	Equation 3-D
ν	2.060	0.048	Back Calculation
K, calc.	3.941	0.087	Equation 1
E, exp.	3.924	0.087	Reference 15

These calcuculations show that, once δ, ν, and ϕ have been determined, the calculation of "K" is straight forward.

Tables XIII thru XVII show that the "K" values obtained using the composition dependent liquid activity coefficients (A and B being defined by solubility parameters and molar volumes) agree with the experimental

values. The average per cent error over the given temperature ranges were within 6 per cent for this method and within 26 percent for the N.G.A.A. values. Figures 6 thru 10 show that the greatest error for the Hildebrand-Scatchard values for ethane occured at temperatures approaching the critical. This error may well be a result of an error in the estimation of of $\bar{V}_1$ (molar volume) at these elevated temperatures. However, averaging over the entire temperature range, this method shows great promise.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this study was to evaluate composition-dependent liquid activity coefficients from which reliable vapor-liquid "K" values can be estimated. The method utilizes the Hildebrand-Scatchard equation to evaluate A and B constants for the van Laar liquid activity coefficient equation. For this work, the solubility parameters were regarded as empirical constants, independent of both temperature and pressure.

The advantages of this method for estimating liquid activity coefficients are:

1. The van Laar constants, A and B, can be estimated from physical properties.

2. The effect of temperature on A and B is included.

3. The effect of concentration on activity coefficients is included.

The main disadvantage is that lighter components of a mixture are frequently in a solution at a temperature and pressure where they could not exist as liquids in the pure state. It is, therefore, necessary to regard this as a hypothetical liquid state for these components. This requires extrapolation or back calculation from experimental equilibrium data to obtain values of $\overline{V}$ and δ. However, the simplification imposed by this work (that is, that the solubility parameter is constant with temperature and pressure) greatly simplifies the calculations.

The results indicate good possibilities in estimating composition-

dependent "K" values using solubility parameters to evaluate the van Laar constants.

Recommendations for future investigations are:

1. As more and more experimental vapor-liquid equilibrium data becomes available, similar calculations should be made to test the reliability of the method over a greater range of systems, temperatures and pressures.

2. The extension of this method to other than binary mixtures may be possible with more experimental data.

3. Computer application of the above procedure would greatly enhance the study.

4. The assumption of liquid molal volume, as well as solubility parameter, to be insensitive to temperature and pressure would be still a further simplification to this method of calculating liquid activity coefficients.

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APPENDIX A

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM

DATA USED IN EVALUATION

TABLE XVIII

EXPERIMENTAL DATA FOR ETHANE-n-BUTANE BINARY (13)

Pressure = 400 PSIA

| Temp. | Mole Fraction Ethane | | Equilibrium Constants | |
°F	Liquid x_1	Vapor y_1	Ethane K_1	Butane K_2
240	0.086	0.221	2.570	0.852
220	0.144	0.356	2.472	0.752
200	0.200	0.483	2.415	0.646
180	0.265	0.592	2.234	0.555
160	0.320	0.685	2.141	0.463
140	0.404	0.768	1.901	0.389
120	0.489	0.836	1.710	0.321
100	0.590	0.894	1.515	0.258
80	0.709	0.937	1.322	0.216
60	0.853	0.937	1.141	0.184

TABLE XIX

EXPERIMENTAL DATA FOR ETHANE-n-HEPTANE BINARY (14)

PRESSURE = 400 PSIA

Temp. °F	Mole Fraction Ethane		Equilibruim Constants	
	Liquid x_1	Vapor y_1	Ethane K_1	Heptane K_2
440	0.096	0.324	3.375	0.748
420	0.115	0.413	3.591	0.663
400	0.134	0.500	3.731	0.577
380	0.150	0.590	3.933	0.482
360	0.166	0.666	4.012	0.400
340	0.184	0.722	3.924	0.341
320	0.203	0.771	3.798	0.287
300	0.223	0.815	3.655	0.238
280	0.245	0.856	3.494	0.191
260	0.267	0.897	3.360	0.140
220	0.317	0.933	2.943	0.098
200	0.347	0.950	2.738	0.077
180	0.382	0.964	2.524	0.058
160	0.426	0.975	2.289	0.044
140	0.476	0.983	2.065	0.032
120	0.535	0.988	1.847	0.026
100	0.613	0.993	1.620	0.018
80	0.713	0.997	1.398	0.010
60	0.850	0.998	1.174	0.013

TABLE XX

EXPERIMENTAL DATA FOR ETHANE-BENZENE BINARY (15)

PRESSURE = 400 PSIA

Temp. °F	Mole Fraction Ethane Liquid x_1	Vapor y_1	Equilibrium Constants Ethane K_1	Benzene K_2
440	0.026	0.160	6.154	0.862
420	0.042	0.264	6.286	0.768
400	0.057	0.360	6.316	0.679
380	0.071	0.450	6.338	0.592
360	0.087	0.530	6.092	0.515
340	0.102	0.605	5.931	0.440
320	0.117	0.672	5.744	0.372
300	0.132	0.729	5.523	0.312
280	0.147	0.781	5.313	0.257
260	0.163	0.826	5.068	0.208
240	0.178	0.864	4.854	0.166
220	0.194	0.895	4.613	0.130
200	0.213	0.916	4.300	0.107
180	0.238	0.934	3.924	0.087
160	0.268	0.948	3.537	0.071
140	0.310	0.960	3.097	0.058
120	0.363	0.970	2.672	0.047
100	0.450	0.980	2.179	0.036
80	0.586	0.987	1.864	0.031
60	0.825	0.995	1.206	0.029

TABLE XXI

EXPERIMENTAL DATA FOR ETHANE-CYCLOHEXANE BINARY (16)

PRESSURE = 400 PSIA

Temp. °F	Mole fraction Ethane		Equilibrium Constants	
	Liquid x_1	Vapor y_1	Ethane K_1	Cyclohexane K_2
440	0.037	0.227	6.135	0.803
420	0.053	0.314	5.924	0.724
400	0.070	0.395	5.643	0.650
380	0.086	0.475	5.523	0.574
360	0.105	0.552	5.257	0.501
340	0.121	0.624	5.157	0.428
320	0.140	0.692	4.943	0.358
300	0.160	0.754	4.712	0.293
280	0.180	0.808	4.489	0.234
260	0.202	0.852	4.218	0.186
240	0.225	0.885	3.933	0.148
220	0.250	0.914	3.656	0.115
200	0.279	0.934	3.348	0.092
180	0.313	0.949	3.032	0.074
160	0.352	0.961	2.730	0.060
140	0.396	0.971	2.452	0.048
120	0.445	0.979	2.200	0.038
100	0.507	0.986	1.945	0.028
80	0.614	0.992	1.616	0.021
60	0.795	0.998	1.255	0.010

TABLE XXII

EXPERIMENTAL DATA FOR n-BUTANE-n-HEPTANE BINARY (17)

PRESSURE = 400 PSIA

Temp. $^\circ F$	Mole Fraction Butane		Equilibrium Constants	
	Liquid x_1	Vapor y_1	Butane K_1	Heptane K_2
440	0.254	0.415	1.634	0.784
400	0.391	0.612	1.565	0.637
360	0.545	0.769	1.411	0.508
340	0.634	0.835	1.317	0.451
320	0.725	0.892	1.230	0.393
300	0.824	0.939	1.140	0.346

APPENDIX B

DEVELOPMENT OF VAN LAAR EQUATION

APPENDIX B

DEVELOPMENT OF VAN LAAR EQUATION

The development of the van Laar equation was based upon the mixing of pure liquids at constant temperature (19, 20).

For an isothermal process,

$$\Delta \bar{F} = \Delta \bar{H} - T\Delta \bar{S} \qquad (1\text{-}B)$$

and

$$\partial \Delta \bar{F} = RT\, \partial \ln f \qquad (2\text{-}B)$$

where: $\Delta \bar{F}$ = The partial molal change in free energy

$\Delta \bar{H}$ = The partial molal change in enthalpy

$\Delta \bar{S}$ = The partial molal change in entropy

f = Fugacity

For an ideal mixture the following are true:

1. $(\Delta V_{mixing})_T = 0$

2. $(\Delta H)_P = 0$

3. The Lewis and Randall fugacity rule applies:

$$\bar{f} = xf$$

4. Raoult's law applies:

$$\bar{P} = Py = P^\circ x$$

5. The change in partial molal free energy is

$$\Delta \bar{F} = -T\Delta S = +RT\ln x$$

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For an actual system, it is necessary to introduce a correction factor to the Lewis and Randall rule and to Raoult's law:

$$\gamma_i \bar{f}_i = x_i f_i \qquad (5\text{-B})$$

$$\gamma_i \bar{P}_i = x_i P_i^\circ \qquad (6\text{-B})$$

The term γ, introduced as the deviation factor, is, under conditions to be defined immediately, equivalent to the thermodynamic property, activity coefficient. Lewis and Randall (22) define activity, a, as the ratio between the fugacity of the component in a mixture and its fugacity as a pure liquid:

$$a_i = \frac{\bar{f}_i}{f_i^\circ}$$

where: a_i = The activity of i

f_i° = The fugacity of pure liquid i

$\bar{f}_i$ = The partial fugacity of i

The activity coefficient is defined as the activity divided by its mole fraction:

$$\gamma_i = \frac{a_i}{x_i} = \frac{\bar{f}_i}{f_i^\circ x_i} \qquad (7\text{-B})$$

When the vapors are perfect gases,

$$\gamma_i = \frac{\bar{P}_i}{P_i^\circ x_i} \qquad (8\text{-B})$$

It is now possible to define actual and ideal partial molal free energy changes as

$$\Delta \bar{F}_A = RT \ln \bar{f}_A \qquad (9\text{-B})$$

$$\Delta \bar{F}_I = RT \ln \bar{f}_I \qquad (10\text{-}B)$$

Defining excess partial molal free energy change as

$$\Delta \bar{F}_E = \Delta \bar{F}_A - \Delta \bar{F}_I = \Delta \bar{H}_E - T\Delta \bar{S}_E \qquad (11\text{-}B)$$

where: $\Delta \bar{F}_A$ = The actual partial molal change in free energy,

$\Delta \bar{F}_I$ = The ideal partial molal change in free energy,

$\Delta \bar{F}_E$ = The excess partial molal change in free energy,

$\Delta \bar{H}_E$ = The excess partial molal change in enthalpy = ΔH_A,

$\Delta \bar{S}_E$ = The excess partial molal change in entropy = $T\Delta S_A$ - $RT \ln x$.

Combining Equations 9-B, 10-B and 11-B,

$$\Delta \bar{F}_E = RT \ln \gamma \qquad (12\text{-}B)$$

Van Laar made the following assumptions in the derivation of his equation:

1. $\Delta \bar{S}_E = 0$; i.e., $\Delta \bar{S}_A = \Delta \bar{S}_I$.

2. $\Delta V_{mixing} = 0$.

3. The van der Waal equation applies to each of the components and to the mixture, both as liquids and as vapors.

4. The van der Waal constants of the mixture can be calculated from the constants of the pure components.

From these assumptions, equation 11-B becomes

$$\Delta \bar{F}_E = RT \ln \gamma = \Delta \bar{H}_E = \Delta \bar{E}_E$$

or

$$\ln \gamma = \frac{\Delta E}{RT} \qquad (13\text{-}B)$$

A van der Waal's fluid is defined as one that satisfies

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{14-B}$$

where: a and b = the van der Waal constants

It can be shown that for such a fluid,

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^2} \quad .$$

From the thermodynamic relation

$$A = E - TS$$

$$dA = dE - TdS - SdT \tag{15-B}$$

and from the first and second laws of thermodynamics

$$\triangle E = Q - W$$

$$dE = dQ - PdV \tag{16-B}$$

and

$$dQ = TdS \tag{17-B}$$

Then

$$dE = TdS - PdV \tag{18-B}$$

Equating 15-B, 16-B and 18-B gives

$$dA = -PdV - SdT \tag{19-B}$$

Applying Green's theorem, if

$$dz = Mdx + Ndy$$

then

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial M}{\partial y}\right)_x \quad ,$$

the following relation is obtained;

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T . \qquad (20\text{-}B)$$

Dividing Equation 18-B through by dV at constant temperature gives,

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \qquad (21\text{-}B)$$

From Equations 20-B and 21-B,

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P . \qquad (22\text{-}B)$$

Taking the $(\partial P/\partial T)_V$ in the van der Waal equation gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b} .$$

Thus,

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{R}{V - b}\right) - P = \frac{a}{V^2} \qquad (23\text{-}B)$$

Rearranging and integrating form a vapor at zero pressure to the liquid state

$$\int_{V = \infty}^{V = V_L} \partial E = \int_{V = \infty}^{V = V_L} a \frac{\partial V}{V^2}$$

gives

$$E_L - E_\infty = \frac{a}{\infty} - \frac{a}{V_L} = \frac{a}{V_L} \qquad (24\text{-}B)$$

Van Laar substituted the van der Waal's constant, b, for the liquid molal volume in Equation 24-B. And, for a mixture, van Laar used the constant values developed by Berthelot, et. al.(12):

$$a_{mix} = (x_1 \sqrt{a_1} + x_2 \sqrt{a_2} + \ldots)^2 \qquad (25\text{-}B)$$

$$b_{mix} = (x_1 b_1 + x_2 b_2 + \ldots) \qquad (26\text{-}B)$$

where: a_{mix} and b_{mix} are the van der Waal constants for mixtures

a_1, a_2, b_1, b_2 are the van der Waal constants for pure components

For a binary, the internal energy of mixing pure components (at constant temperature) per mole of mixture is

$$\Delta E_L = \Delta E_{LM} - x_1 E_{L_1} + x_2 E_{L_2} \qquad (27\text{-}B)$$

where: ΔE_L = The internal energy in mixing per mole of mixture

ΔE_{LM} = The molal internal energy of the liquid mixture

E_{L_1} and E_{L_2} = The molal internal energies of the pure components (1 and 2) as liquids before mixing

Using Equations 24-B and 27-B and b = V gives

$$\Delta E_L = \left(-\frac{a_{mix}}{b_{mix}} + E_{mix\,\infty} \right) - x_1 \left(-\frac{a_1}{b_1} + E_{1\,\infty} \right) - x_2 \left(-\frac{a_2}{b_2} + E_{2\,\infty} \right)$$

$$= -\frac{a_{mix}}{b_{mix}} + x_1 \frac{a_1}{b_1} + x_2 \frac{a_2}{b_2} + (E_{mix\,\infty} - x_1 E_{1\infty} - x_2 E_{2\infty}). \qquad (28\text{-}B)$$

The last term in Equation 28-B is the internal energy of mixing of vapors at zero pressure and is equal to zero. Substituting Equations 25-B and 26-B into 28-B gives

$$\Delta E_L = \frac{x_1 b_1 x_2 b_2}{x_1 b_1 + x_2 b_2} \left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2 \qquad (29\text{-}B)$$

Thus, the partial molal change in internal energy is

$$\frac{\partial(\triangle E)_L}{x_1} = (\triangle \bar{E}_1)_L = b_1\left(\frac{x_2 b_2}{x_1 b_1 + x_2 b_2}\right)^2 \left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2, \quad (30\text{-}B)$$

and on the basis of van Laar's assumptions, equation 13-B becomes

$$\ln \gamma_1 = \frac{(\triangle E_1)_L}{RT} = \frac{\frac{b_1}{RT}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2}{\left(1 + \frac{b_1 x_1}{b_2 x_2}\right)^2} \quad (31\text{-}B)$$

Combining the constants,

$$\ln \gamma_1 = \frac{B'/T}{\left(1 + A'\frac{x_1}{x_2}\right)^2} \quad (32\text{-}B)$$

$$\ln \gamma_2 = \frac{A'B'/T}{\left(A' + \frac{x_2}{x_1}\right)^2}$$

where: $A' = b_1/b_2$

$B' = \frac{b_1}{R}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2$

Letting $B' = A$ and $A' = A/B$, These equations can be written in another form:

$$\ln \gamma_1 = \frac{A/T}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \quad (34\text{-}B)$$

$$\ln \gamma_2 = \frac{A^2/BT}{\left(\frac{A}{B} + \frac{x_2}{x_1}\right)^2} \quad (35\text{-}B')$$

Dividing the numerator and the denominator of 35-B' by A^2/B^2 gives

$$\ln \gamma_2 = \frac{B/T}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \quad (35\text{-}B)$$

where: $\quad A = \dfrac{b_1}{R}\left(\dfrac{\sqrt{a_1}}{b_1} - \dfrac{\sqrt{a_2}}{b_2}\right)^2$

$\quad\quad\quad\quad B = \dfrac{b_2}{R}\left(\dfrac{\sqrt{a_1}}{b_1} - \dfrac{\sqrt{a_2}}{b_2}\right)^2$

APPENDIX C

DEVELOPMENT OF HILDEBRAND-SCATCHARD EQUATION

APPENDIX C

DEVELOPMENT OF THE HILDEBRAND-SCATCHARD EQUATION
FOR BINARY MIXTURES

The Hildebrand-Scatchard equation for liquid activity coefficients can be obtained from the energy of mixing (11). For an ideal solution (Raoult's law applies), the heat of mixing is zero and the partial free energy of mixing is

$$\Delta \overline{F}_1^\circ \; = \; RT \ln \frac{\overline{P}_1}{P_1^\circ} \; = \; RT \ln x_1 : \qquad (1\text{-}C)$$

where: x_1 = The mole fraction of component i in the liquid mixture,

$\overline{P}_1$ = The partial pressure of component i,

P_1° = The vapor pressure of pure component i.

Since very few solutions are ideal, it is necessary to develop an equation for $\Delta \overline{F}^\circ$ for a nonideal system. This work deals with "regular solutions" which are nonideal to the extent that there is a heat of mixing, but, the entropy of mixing is the same as for ideal solutions. Thus, for a regular solution,

$$\Delta \overline{V}^M \; = \; 0.$$

and from the thermodynamic relation,

$$\Delta \overline{F}_1 \; = \; \Delta \overline{H}_1 \; - \; T \Delta \overline{S}_1 \, , \qquad (2\text{-}C)$$

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the entropy of mixing is given by

$$T\Delta \bar{S}_1 = -\Delta \bar{F}_1 = -RT\ln x_1 \qquad (3\text{-}C)$$

Substituting Equation 3-C in to Equation 2-C gives

$$\Delta \bar{F}_1 = \Delta \bar{H}_1 + RT\ln x_1 \qquad (4\text{-}C)$$

It is now necessary to obtain an expression for $\Delta \bar{H}_1$. Scatchard derived a relationship for the energy of mixing as a function of "cohesive energy" densities of the components (30). This development was regarded by Scatchard himself as "a method of freeing the van Laar treatment from the inadequacies of the van der Waals equation."(11). His basic assumptions were:

(1) The mutual energy of two molecules is dependent upon the distance between them and their relative orientation; independent of the nature of the other molecules between and around them; and of the temperature. This assumption is essentially that of the additivity of the energies of molecular pairs. This is not exactly true for dispersion forces, but, it has proved very successful as the basis for nearly all theories of liquids and solutions (11).

(2) The distribution of the molecules in position and in orientation is random, i.e., independent of temperature and nature of the other molecules. This assumption is the characteristic feature of the theory of "regular solutions." It ignores the ordering effect of molecular shapes and differences in intermolecular potentials and, therefore, is, at least, only a good approximation.

(3) At constant pressure the change in volume on mixing is zero.

These assumptions permit writing the cohesive energy of a mole of liquid mixture (essentially its potential energy E, but opposite in sign) as

$$-\Delta E_m = \frac{c_{11}V_1^2 x_1^2 + 2c_{12}V_1 x_1 V_2 x_2 + c_{22}V_2^2 x_2^2}{V_1 x_1 + V_2 x_2} . \qquad (5\text{-}C)$$

For pure components $-E_1 = c_{11}V_1$, etc. and $c_{11} = -E_1/V_1$ or the "cohesive density." Transforming to volume fractions, Ψ_1 and Ψ_2,

$$-\Delta E_m = (x_1 V_1 + x_2 V_2)(c_{11}\Psi_1^2 + 2c_{12}\Psi_1\Psi_2 + c_{22}\Psi_2^2) \qquad (6\text{-}C)$$

From this, Scatchard obtained for the free energy of mixing

$$\begin{aligned}
\Delta_E^M &= \Delta E_m - E_1 x_1 - E_2 x_2 \\
&= (x_1 V_1 + x_2 V_2)(c_{11} + 2c_{12} + c_{22})(\Psi_1 \Psi_2) \\
&= (x_1 V_1 + x_2 V_2)A_{12}\Psi_1\Psi_2 \qquad (7\text{-}C)
\end{aligned}$$

$$\text{where:} \quad A_{12} = c_{11} + 2c_{12} - c_{22} \qquad (8\text{-}C)$$

Scatchard further assumed that

$$c_{12} = \sqrt{c_{11}c_{22}} . \qquad (9\text{-}C)$$

Equation 8-C can then be written

$$A_{12} = (\sqrt{c_{11}} - \sqrt{c_{22}})^2 . \qquad (10\text{-}C)$$

For liquids at ordinary temperatures, the vapor is nearly ideal, so, -E can be identified with ΔE^V, the energy of vaporization. The Scatchard equation (Equation 7-C) may be written as

$$\Delta E^M = x_1 V_1 + x_2 V_2 \left[\left(\frac{\Delta E_1}{V_1}\right)^{0.5} - \left(\frac{\Delta E_2}{V_2}\right)^{0.5} \right] \Psi_1 \Psi_2 \qquad (11\text{-}C)$$

The term $\left(\Delta E_1 / V_1\right)^{0.5}$ is designated by Hildebrand and Scott at the parameter, δ_1 (11). The partial molal heat of mixing for component 1 is then

$$\Delta \bar{H}_1^M = \Delta \bar{E}_1^M = V_1 \Psi_2^2 (\delta_1 - \delta_2)^2 . \qquad (12\text{-}C)$$

Combining equations 4-C and 12-C, gives the following expressions for partial free energy of mixing for regular solutions:

$$\Delta \bar{F}_1 = RT \ln x_1 + V_1 (\delta_1 - \delta_2)^2 \Psi_2^2 \qquad (13\text{-}C)$$

$$\Delta \bar{F}_2 = RT \ln x_2 + V_2 (\delta_1 - \delta_2)^2 \Psi_1^2 \qquad (14\text{-}C)$$

The last term in Equations 13-C and 14-C will always be positive since the solubility parameter difference is squared.

From the definition of fugacity and the choice of the reference state, the following equations are obtained for the activity coefficient:

$$\ln \gamma_1 = \ln \frac{\bar{f}_1}{f_1^\circ x_1} = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \Psi_2^2 \qquad (15\text{-}C)$$

$$\ln \gamma_2 = \ln \frac{\bar{f}_2}{f_2^\circ x_2} = \frac{V_2}{RT} (\delta_1 - \delta_2)^2 \Psi_1^2 \qquad (16\text{-}C)$$

where:

$$\Psi_1 = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2}$$

$$\Psi_2 = \frac{x_2 V_2}{x_1 V_1 + x_2 V_2}$$

Equation 15-C leads directly to

$$\ln \gamma_1 = \frac{B'/T}{\left(1 + A'\frac{x_1}{x_2}\right)^2} \qquad (17\text{-}C)$$

where: $A' = V_1/V_2$

$\qquad B' = \dfrac{V_1}{R}(\delta_1 - \delta_2)^2$

Another form of this equation defines $A = B'$ and $A/B = A'$, or

$$A = \frac{V_1}{R}(\delta_1 - \delta_2)^2 \tag{18-C}$$

$$B = \frac{V_2}{R}(\delta_1 - \delta_2)^2 \tag{19-C}$$

then

$$\ln \gamma_1 = \frac{A/T}{\left(1 + \dfrac{Ax_1}{Bx_2}\right)^2} \tag{20-C}$$

Similarly, Equation 16-C leads directly to

$$\ln \gamma_2 = \frac{B/T}{\left(1 + \dfrac{Bx_2}{Ax_1}\right)^2} \tag{21-C}$$

Note: Equations 20-C and 21-C are identical with the van Laar Equations 34-B and 35-B for binary mixtures. Only A and B are defined differently.

APPENDIX D

DISCUSSION OF REDLICH-KWONG EQUATION

FOR EVALUATING VAPOR FUGACITY

COEFFICIENTS

APPENDIX D

DISCUSSION OF REDLICH-KWONG EQUATION

FOR EVALUATING VAPOR FUGACITY

COEFFICIENTS

The Redlich-Kwong equation of state seems to be the best compromise
between rigor and practicability available for calculating the vapor
phase fugacity coefficient (8,25,26). This equation uses only two
constants for each component of the vapor mixture, with each constant
being calculated from the critical constants of the pure components.
However, even in its simplified form, the use of the Redlich-Kwong
equation is time-consuming and sufficiently complex that errors may be
made in the computations. For this reason, the equation has been
programmed for use on the IBM 650 computer to calculate thermodynamic
properties of a gas mixture (8).

The Redlich-Kwong equation of state defines pressure and comp-
ressibility factor as functions of temperature and volume with two
constants:

$$P = \frac{RT}{V - b} - \frac{a}{T^{0.5} V(V - b)} \quad . \tag{1-D}$$

$$Z = \frac{RT}{V - b} - \frac{a}{RT^{1.5}(V - b)} \quad . \tag{2-D}$$

And the fugacity coefficient of a component in a vapor mixture is given

by equation (3-D), which is based upon equations (1-D) and (2-D):

$$\ln \phi_i = (Z - b)\frac{B_i}{B} - \ln (Z - b) -$$

$$\frac{A^2}{B}\left[2\frac{A_i}{A} - \frac{B_i}{B}\right]\ln\left(1 + \frac{BP}{Z}\right) \qquad (3\text{-}D)$$

where: $\phi_i = \dfrac{\bar{f}^V}{Py_i}$ = Fugacity coefficient of i in the vapor mixture

$A_i^2 = a_i/R^2T^{2.5}$

$a_i^2 = 0.4278\ R^2T_{ci}^{2.5}/P_{ci}$

$A = y_iA_i$

$B_i = b_i/RT$

$b_i = 0.0867\ RT_{ci}/P_{ci}$

$B = y_iB_i$

P = Pressure

T = Temperature

$Z = \dfrac{1}{1 - h} - \dfrac{(A^2/B)h}{1 - h}$

$h = \dfrac{BP}{Z} = \dfrac{b}{V}$

$\bar{f}_i^V$ = Fugacity of component i in the gas mixture

y_i = Mole fraction of component i in the gas mixture

Equation (3-D) was the equation used on the computer. The values of ϕ_i, obtained with this program, are shown in Figure 4.

APPENDIX E

SAMPLE CALCULATIONS

APPENDIX E

SAMPLE CALCULATIONS

The form of the van Laar equation used to calculate the liquid activity coefficient was

$$\ln \gamma_1 = \frac{A/T}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \tag{14}$$

$$\ln \gamma_2 = \frac{B/T}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \tag{14'}$$

where:

$$A = \frac{V_1(\delta_1 + \delta_2)^2}{R} \tag{15}$$

$$B = \frac{V_2(\delta_1 - \delta_2)^2}{R} \tag{15'}$$

$$V_i = (V\omega)_i(5.7 - 3T/T_c) \tag{16}$$

The thermodynamic relation (Equation 1) was rewritten to give

$$\nu_i = \frac{K_i \phi_i}{\gamma_i}$$

The set of calculations presented in Table XXIII is the final trial for the ethane-n-heptane (System 1) and the ethane-benzene (System 2) systems at 400 psia and 140°F.

TABLE XXIII

SAMPLE CALCULATION FOR DETERMINATION OF SOLUBILITY PARAMETERS

AND LIQUID FUGACITY COEFFICIENTS

TEMPERATURE = 140°F   PRESSURE = 400 PSIA

	Symbol	Ethane	n-Heptane	Ethane	Benzene	Remarks
Critical Temperature	T_c	305.95	540.72	305.95	562.78	°K, API-44 Tables
Liquid Mole Fraction	x	0.476	0.524	0.310	0.690	Reference 14 and 15
Vapor Mole Fraction	y	0.983	0.017	0.960	0.040	Reference 14 and 15
Watson Characteristic Constant	$V\omega$	7.77	18.96	7.77	11.64	Reference 9
Vapor Fugacity Coefficient	ϕ	0.8558	0.4352	0.8562	0.5201	Reference 8
Solubility Parameter	δ	6.251*	7.45	6.251*	9.15	Reference 26
Experimental "K" Value	K	2.065	0.032	3.097	0.058	K = y/x
Partial Molal Volume	V	69.714	143.16	69.714	87.031	Equation 16
van Laar Constant	A	50.3850		294.6106		Equation 15
van Laar Constant	B	103.4995		367.9693		Equation 15'
Liquid Activity Coefficient	γ	1.0754	1.0296	1.6134	1.0804	Equations 14 and 14'
Liquid Fugacity Coefficient	ν	1.64341	0.0137	1.64344	0.0279	Equation 1
$\nu - \nu'$	$\Delta\nu$		-0.00003			

* Assumed value for trial-and-error calculation

NOMENCLATURE

NOMENCLATURE

A, B,   =   van Laar constants or Redlich-Kwong constants

a, b,   =   van der Waal's constants or Redlich-Kwong constants

a   =   activity $f/f°$

E   =   energy

F   =   free energy

f   =   fugacity

H   =   enthalpy

K   =   vapor-liquid equilibrium constant

N   =   mole fraction

P   =   total pressure

$P°$ =   vapor pressure

P_r =   reduced pressure

P_c =   critical pressure

Q   =   heat

R   =   gas law constant

S   =   entropy

S^M =   entropy of mixing

T   =   temperature

T_r =   reduced temperature

T_c =   critical temperature

V   =   molar volume or volume

V^f =   free volume

$(V\omega)$ =   Watson's expansion factor

W   = work + VdP

x   = liquid mole fraction

y   = vapor mole fraction

z, Z = compressibility factor

Greek Symbols:

$\triangle$ = represents a change, $(\Delta\mu = \mu_2 - \mu_1)$

δ = solubility parameter, (cal/cc)

γ = activity coefficient

μ = chemical potential (E, H, F)

ν = liquid fugacity coefficient

ϕ = vapor fugacity coefficient

ψ = liquid volume fraction = $\dfrac{x_1V_1}{x_1V_1 + x_2V_2}$, etc.

Subscripts:

i   = component "i"

j   = component "j"

1, 2 = components 1 and 2

L   = liquid state

V   = vapor state

Superscripts:

°   = reference state

L   = liquid state

V   = vapor state

$-$ = a bar over a letter represents the partial property of the
component in a mixture.

VITA

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