NOTATION

A = a conversion factor, 5.2 x 10^{13}, ev./g. rep.
C = phenol concentration, μ moles/liter
CR = difference in liquid phase conversion from paired radiation and blank runs, (moles converted by radiation/mole feed) x 100, %
D = total radiation dose received, krep.
$G(X)$ = G value for compound X, number of molecules of X converted per 100 ev. absorbed
L = distance along beam port center line measured from the end nearest the nuclear reactor core, in.
MW = molecular weight, in this case n-heptane, 100.2 g./g.-mole
Na = Avogadro's number, 6.02 x 10^{23} molecules/g.-mole
P = nuclear reactor power level, kw.
V = irradiation vessel volume, in this work 5.3 liters
C_KH_{2K+2} = any one of the series of hydrocarbons designated by letting $K = 1, 2, \ldots$
C_KH_{2K+1} = radical corresponding to the above hydrocarbon
F = flow rate for liquid or gas passing through the irradiation vessel evaluated at the vessel temperature and pressure, liters/hr.

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A General Correlation of Vapor-Liquid Equilibria in Hydrocarbon Mixtures

K. C. CHAO and J. D. SEADER
California Research Corporation, Richmond, California

A general correlation of vapor-liquid equilibria in hydrocarbon mixtures is developed. The vaporization equilibrium ratio (K-value) is calculated through a combination of three factors

$$K = \frac{(\nu^0\gamma)}{(\phi)}$$

The quantity ν^0 is a pure liquid component property and is correlated within the framework of Pitzer's modified form of the principle of corresponding states. The quantity γ is calculated from Hildebrand's equation, with regular liquid solutions assumed. The necessary parameters in this equation are specially determined for the very light components. The vapor state quantity ϕ is calculated from Redlich and Kwong's equation of state. The correlation is in the form of a compact set of equations which are especially suitable for application with an electronic digital computer.

The correlation applies to hydrocarbons of various molecular types, including paraffins, olefins, aromatics, and naphthenes. Hydrogen in hydrocarbon mixtures is likewise correlated. The correlation has been tested with a systematic compilation of literature data on mixtures of these components. The over-all average deviation from 2,696 data points is 8.7%.

Previous investigators have used two different approaches in developing correlations of vapor-liquid equilibria in hydrocarbon mixtures: through an equation of state such as the Benedict-Webb-Rubin equation (*2*) to describe the PVT behavior, and through a convergence pressure correlation such as that presented in the National Gasoline Association of America Equilibrium Ratio Data Book (*15*). Both methods are in wide use. Neither of these methods in their present form however satisfies the need for generality. Thus their application is restricted to mixtures containing paraffins and/or olefins. Aromatics and naphthenes are excluded. The same is true of hydrocarbon mixtures containing inert gases such as hydrogen. In view of the growing industrial importance of mixtures containing paraffins, olefins, aromatics, naphthenes, and/or inert gases a more general correlation has been developed to apply to all components in these mixtures.

DESCRIPTION OF CORRELATION

The vaporization equilibrium ratio K_i of component i in a mixture is computed from a combination of three

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J. D. Seader is with Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California.

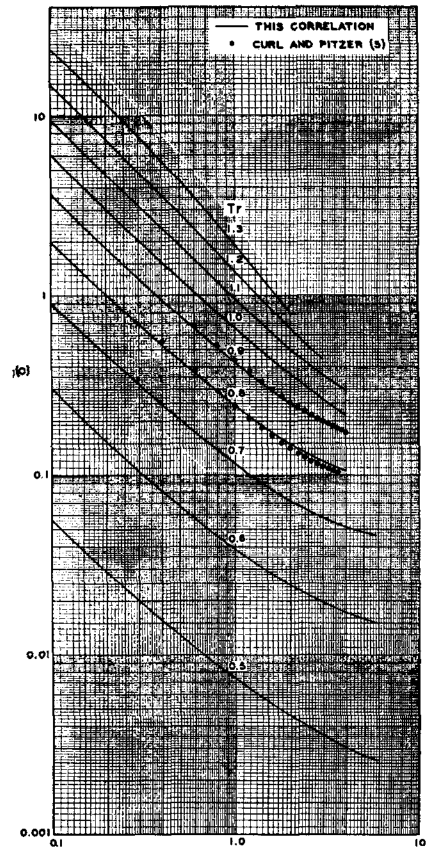

Fig. 1. Liquid fugacity coefficient of simple fluids.

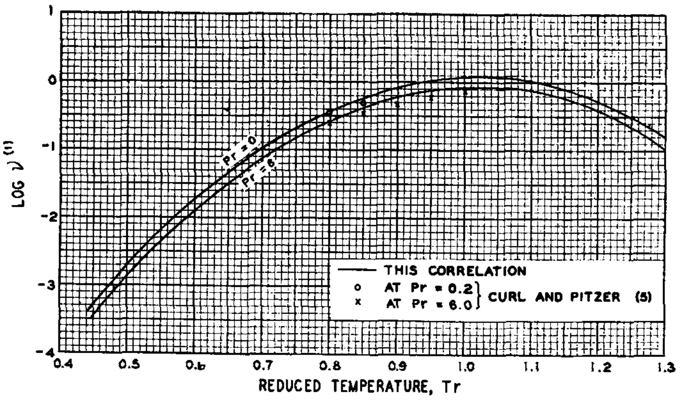

Fig. 2. Liquid fugacity coefficient correction factor.

rigorously defined thermodynamic quantities:

$$K_i \equiv \frac{y_i}{x_i} \equiv \nu^0_i \frac{\gamma_i}{\phi_i} \qquad (1)$$

Several other combinations are possible. However Equation (1) was chosen to make the maximum use of the methods that were already available in the literature for evaluating the appropriate terms.

Thus since the quantity ν^0 is a pure component property, it may be correlated within the framework of the principle of corresponding states. The activity coefficient γ is usually expressed in terms of either the van Laar type or the Margules type of equations. Hildebrand's equation, which belongs to the van Laar type, is used here. As for ϕ the relatively simple Redlich and Kwong equation of state has been found to yield satisfactory results over a wide range of conditions.

Liquid Fugacity Coefficient of Pure Component

This quantity is a well-defined thermodynamic property under conditions where the component actually exists as a liquid. As such it may be calculated from generalized correlations in terms of reduced temperature and reduced pressure. Two such correlations are worth special mention: Lydersen, Greenkorn, and Hougen (*14*), and Curl and Pitzer (*5*). Both employ a third parameter (to characterize the component) for improved accuracy. It has been demonstrated that a simple correlation exists between the third parameters of the two correlations (*21*).

At conditions where the component does not exist as a pure liquid, the quantity ν^0 becomes hypothetical and the above correlations cannot be used. Such conditions may occur in mixtures; they arise when the system pressure is lower than the vapor pressure of the component or when the temperature is above the critical temperature of the component. The correlation of the liquid fugacity coefficient has been extended to such conditions, as well as to conditions of low reduced temperature. The extension was achieved through calculation from experimental vapor-liquid equilibrium data. The development of this extension is described in a later section.

The extension of the liquid fugacity coefficient has been correlated within the framework of Pitzer's modified form of the principle of corresponding states. This form was chosen for easier formulation in algebraic expressions. Accordingly ν^0 is given by

$$\log \nu^0 = \log \nu^{(0)} + \omega \log^{(1)} \qquad (2)$$

The first term on the right-hand side gives the fugacity coefficient of simple fluids characterized by a zero value of the acentric factor. The second term is in the nature of a correction, accounting for departure of properties of real fluids from those of the simple fluids.

The two quantities $\nu^{(0)}$ and $\nu^{(1)}$ are dependent only on reduced temperature and reduced pressure. They have been fitted with approximating functions. The quantity $\nu^{(0)}$ is given by

$$\begin{aligned}\log \nu^{(0)} = {} & A_0 + A_1/T_r + A_2T_r \\ & + A_3T_r^2 + A_4T_r^3 \quad (3) \\ & + (A_5 + A_6T_r + A_7T_r^2)\,P_r \\ & + (A_8 + A_9T_r)P_r^2 - \log P_r\end{aligned}$$

The quantity $\nu^{(1)}$ is given by

$$\begin{aligned}\log \nu^{(1)} = {} & -4.23893 \\ & + 8.65808\,T_r - 1.22060/T_r \quad (4) \\ & - 3.15224\,T_r^3 - 0.025 \\ & (P_r - 0.6)\end{aligned}$$

The coefficients in Equation (3) are given in Table 1.

For methane and hydrogen the usual temperature of interest is far above their critical points, corresponding to exceptionally high values of reduced temperature. Under these conditions Equation (3) with the special coefficients given in Table 1 can be applied. The value of ω for these two components is then taken as zero.

In general three constants must be known for each component in order to determine its liquid fugacity coefficient ν^0. These are the critical temperature, critical pressure, and acentric factor ω. Values of ω for components usually encountered are given in Table 2.

Activity Coefficient in a Liquid Solution

Liquid solutions of hydrocarbons are considered to be regular solutions in this correlation. The regular solutions are characterized by their excess entropy being equal to zero. Any nonideal behavior is due entirely to the heat of solution. The following equation proposed by Hildebrand (7) is used in this work:

TABLE 1. COEFFICIENTS IN EQUATION (3)

	Simple fluid	Methane	Hydrogen
A_0	5.75748	2.43840	1.96718
A_1	—3.01761	—2.24550	1.02972
A_2	—4.98500	—0.34084	—0.054009
A_3	2.02299	0.00212	0.0005288
A_4	0	—0.00223	0
A_5	0.08427	0.10486	0.008585
A_6	0.26667	—0.03691	0
A_7	—0.31138	0	0
A_8	—0.02655	0	0
A_9	0.02883	0	0

TABLE 2. CONSTANTS FOR PURE COMPONENTS

	Modified ω	δ, (cal./ml.)$^{1/2}$	V, ml./g.-mole
Hydrogen		3.25	31
Paraffins			
Methane		5.68	52
Ethane	0.1064	6.05	68
Propane	0.1538	6.40	84
i-Butane	0.1825	6.73	105.5
n-Butane	0.1953	6.73	101.4
i-Pentane	0.2104	7.02	117.4
n-Pentane	0.2387	7.02	116.1
neo-Pentane	(0.195)	7.02	123.3
n-Hexane	0.2927	7.27	131.6
n-Heptane	0.3403	7.430	147.5
n-Octane	0.3992	7.551	163.5
n-Nonane	0.4439	7.65	179.6
n-Decane	0.4869	7.72	196.0
n-Undecane	0.5210	7.79	212.2
n-Dodecane	0.5610	7.84	228.6
n-Tridecane	0.6002	7.89	244.9
n-Tetradecane	0.6399	7.92	261.3
n-Pentadecane	0.6743	7.96	277.8
n-Hexadecane	0.7078	7.99	294.1
n-Heptadecane	0.7327	8.03	310.4
Olefins			
Ethylene	0.0949	6.08	61
Propylene	0.1451	6.43	79
1-Butene	0.2085	6.76	95.3
cis-2-Butene	0.2575	6.76	91.2
trans-2-Butene	0.2230	6.76	93.8
i-Butene	0.1975	6.76	95.4
1, 3-Butadiene	0.2028	6.94	88.0
1-Pentene	0.2198	7.05	110.4
cis-2-Pentene	(0.206)	7.05	107.8
trans-2-Pentene	(0.209)	7.05	109.0
2-Methyl-1-Butene	(0.200)	7.05	108.7
3-Methyl-1-Butene	(0.149)	7.05	112.8
2-Methyl-2-Butene	(0.212)	7.05	106.7
1-Hexene	0.2463	(7.40)	125.8
Naphthenes			
Cyclopentane	0.2051	8.11	94.7
Methylcyclopentane	0.2346	7.85	113.1
Cyclohexane	0.2032	8.20	108.7
Methylcyclohexane	0.2421	7.83	128.3
Aromatics			
Benzene	0.2130	9.16	89.4
Toluene	0.2591	8.92	106.8
o-Xylene	0.2904	8.99	121.2
m-Xylene	0.3045	8.82	123.5
p-Xylene	0.2969	8.77	124.0
Ethylbenzene	0.2936	8.79	123.1

$$\ln \gamma_i = \frac{V_i(\delta_i - \overline{\delta})^2}{RT} \tag{5}$$

Equation (5) requires two constants for each component. These are the solubility parameter δ_i and liquid molar volume V_i. The quantity $\overline{\delta}$ designates an average value of the solubility parameter for the solution

$$\overline{\delta} = \frac{\Sigma_i x_i V_i \delta_i}{\Sigma_i x_i V_i} \tag{6}$$

The δ_i and V_i of the usually encountered components are given in Table 2. A number of these values were specially determined to fit experimental vapor-liquid equilibrium data. The development of these values is described in a later section.

Fugacity Coefficient in a Vapor Mixture

The relatively simple Redlich and Kwong equation of state (*20*) is employed for the calculation of the fugacity coefficient in vapor mixtures.

This equation requires two constants for each component. These are directly related to the critical temperature and pressure. The equation is

$$\left\{ \begin{aligned} z &= \frac{1}{1-h} - \frac{A^2}{B}\,\frac{h}{1+h} \\ h &= \frac{BP}{z} \end{aligned} \right. \tag{7}$$

The fugacity coefficient is derived in terms of the compressibility factor following standard procedures:

$$\ln \phi_i = (z-1)\frac{B_i}{B} - \ln(z - BP) - \frac{A^2}{B}\left[2\frac{A_i}{A} - \frac{B_i}{B}\right]\ln\left(1 + \frac{BP}{z}\right)$$

Any two-constant equation of state cannot be expected to yield great accuracy. This one is no exception. Nevertheless the fugacity coefficient calculated from this equation has been found in general to be in good agreement (to within a few per cent) with that from the Benedict-Webb-Rubin equation at conditions specified in the next section. This is due to the fact that the equation is used here only to calculate vapor-phase properties.

The fugacity coefficient calculated from this equation tends to be less reliable as pressure is increased to approach the critical pressure of the mixture. This accounts for the diverging trend of the curves for the heavy components in Figures 3, 4, 5, and 6 and to a large extent limits the validity of the correlation to the conditions specified in the next section.

Restrictions

This correlation has been tested against an extensive compilation of literature experimental data. Results of the test show that the correlation might not hold beyond the range of conditions specified below. Within the specified range the average accuracy of data fitting is given in Tables 5 and 6.*

a. For hydrocarbons (except methane)

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* Tabular material has been deposited as document 6884 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

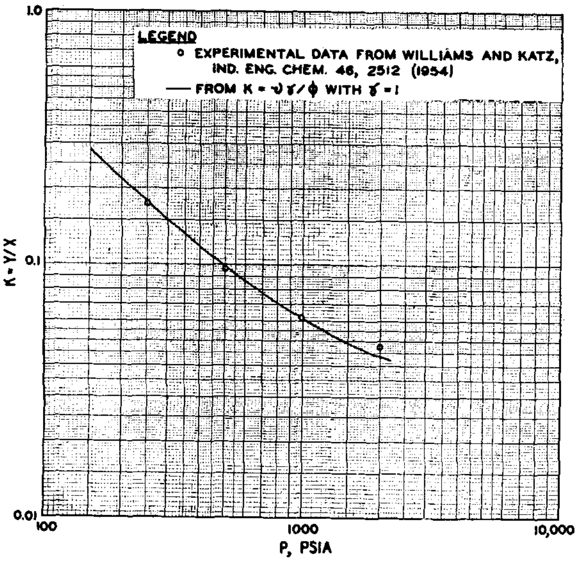

Fig. 3. K-value of propane in hydrogen-propane at 0°F.

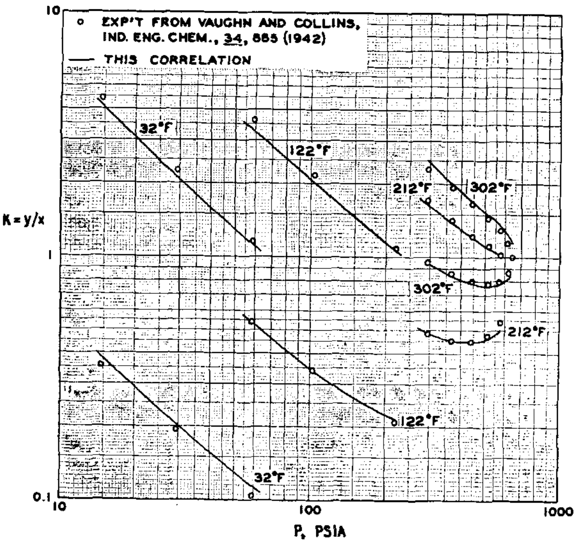

Fig. 4. Propane-isopentane.

Reduced temperature: 0.5 to 1.3 based on the pure component critical temperature.

Pressure: up to about 2,000 lb./sq. in. abs. but not to exceed about 0.8 of the critical pressure of the system.

b. For light gases—hydrogen and methane

Temperature: from −100°F. to about 0.93 in pseudoreduced temperature of the equilibrium liquid mixture but not to exceed 500°F. The pseudoreduced temperature is based on the molal average of the critical temperatures of the components.

Pressure: up to about 8,000 lb./sq. in. abs.

Concentration: up to about 20 mole % of other dissolved gases in the liquid.

RELATIVE SIGNIFICANCE OF ν°_i, γ_i, AND ϕ_i

It is useful in applying the correlation to understand the relative significance of the three factors ν^0, γ, and ϕ under various conditions.

The pure liquid fugacity coefficient ν^0 is primarily responsible for reflecting the effects of component identity, temperature, and pressure. It takes the place of the familiar ideal *K*-value. Indeed it is identical to the true *K*-value when the vapor mixture is an ideal gas and the liquid solution is also ideal.

The fugacity coefficient in the vapor mixture ϕ is always close to unity at sufficiently low pressures. As pressure is increased, it decreases markedly for the heavy components; however for the light gases it usually changes only slightly.

The activity coefficient in the liquid solution approaches unity for the component present in high concentration in the liquid phase. It takes the place of the aromaticity correction factor in common use for the light components (*24*).

The *K*-value of propane in the system hydrogen-propane is typical of that of the heavy components. Since the liquid solution consists almost entirely of propane, its activity coefficient is close to unity. Thus *K* is approximately equal to ν^0/ϕ. The resulting calculated *K*-values are compared with experimental data in Figure 3.

The effect of the activity coefficient on the *K*-value of the light components is exemplified in the case of methane. Table 3 shows calculated vs. experimental *K*-values for methane in various binary mixtures at one temperature and pressure. The large variation of the *K*-value arises mainly from the variation of the activity coefficient.

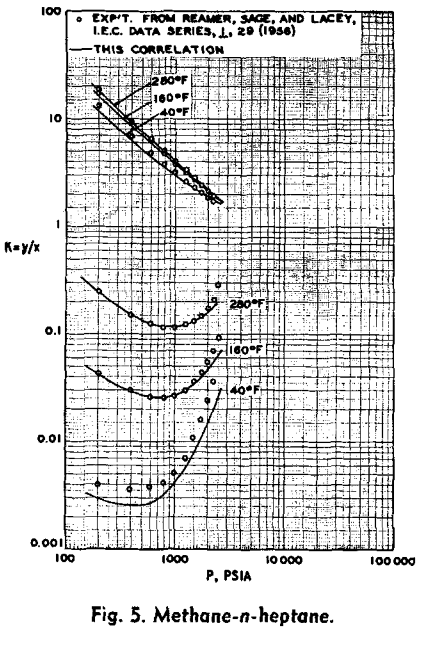

Fig. 5. Methane-*n*-heptane.

Correlated and experimental *K*-values for both components in the binary mixture propane-isopentane are compared in Figure 4. Figures 5, 6, and 7 show the systems methane-*n*-heptane, hydrogen-*n*-hexane, and hydrogen-benzene, respectively.

The reduced accuracy of the correlation at low reduced temperature is demonstrated in Figure 5 for *n*-heptane at 40°F. ($T_r = 0.52$). The relatively large deviation for hydrogen at high temperatures is demonstrated in Figures 6 and 7. The highest temperature in both charts corresponds to a reduced temperature above 0.93 for the solvents and therefore also above this value for the pseudoreduced temperature of the equilibrium liquid mixture.

DEVELOPMENT OF CORRELATION

Empirical Development of Hildebrand's Equation

The required constants in Hildebrand's equation are defined in terms of pure component properties. The solubility parameter is defined as the square root of an energy density:

$$\delta = \left(\frac{\Delta E_v}{V} \right)^{1/2} \qquad (9)$$

Prausnitz, Edmister, and Chao demonstrated the applicability of Hildebrand's equation to hydrocarbon solutions (*17*). The solubility parameter and molal volume were considered to be functions of temperature. It was found in the course of this work that no appreciable loss of accuracy was introduced by treating these two quantities as characteristic constants of a component. Furthermore this simplification assures that the excess free energy be independent of temperature as required by the vanishing of excess entropy in a regular solution.

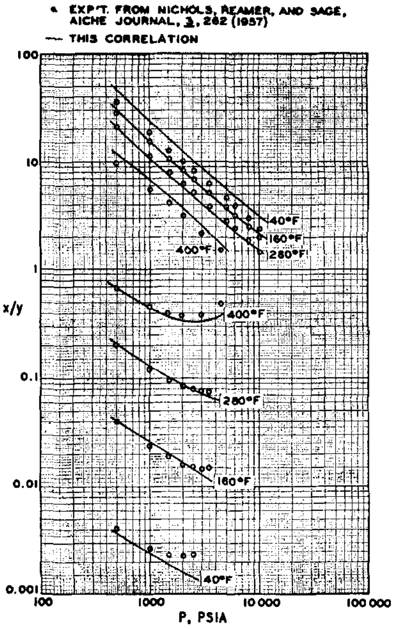

Fig. 6. Hydrogen-*n*-hexane.

Thus, when one follows the assumption of regular solutions, it is permissible to evaluate the properties V and δ of all the components at a fixed standard reference temperature; the selection of this temperature is not important. As a matter of practical convenience the standard reference temperature was chosen to be 25°C. The extensive tabulation of density and heat of vaporization of a large number of hydrocarbons at this temperature in API Project 44 were then immediately available for the calculation of V and δ. Values in Table 2 for the usual hydrocarbons were derived in this manner.

This approach cannot be applied to the determination of these constants for the light gases, such as hydrogen, and a number of light hydrocarbons, such as methane, ethane, and ethylene. For these substances the reference temperature of 25°C. is either above the critical temperature or very close to it.

The constants for the light components were treated as empirical parameters determined from the best fitting of experimental data. A similar empirical treatment of these constants was adopted by Cook (*4*). The approach used here differs mainly in that V is taken as the partial molal volume; only δ was determined from data fitting. Cook also considered the Flory and Huggins expression for excess entropy, whereas in this work an ideal solution entropy was assumed for the regular solutions.

Table 3. *K*-Value of Methane in Various Solvents at 150°F. and 800 Lb./Sq. In. Abs.

Solvent	*K*-value Experimental	New correlation	% dev.
n-Butane	3.53 (*23*)	3.69	4.5
n-Pentane	4.00 (*22*)	3.98	—0.5
n-Heptane	4.59 (*19*)	4.41	—3.9
n-Decane	4.79 (*18*)	4.87	0.9
Benzene	8.30 (*6*)	8.15	—1.8
Toluene	7.20 (*6*)	7.23	0.3
Cyclopentane	5.85 (*3*)	5.25	—10.3
Cyclohexane	6.53 (*3*)	5.49	—15.8
Methylcyclohexane	5.75 (*3*)	4.91	—14.6

For methane, ethane, and ethylene the partial volumes were taken from Hildebrand and Scott's compilation (*7*). The value for hydrogen was taken from Lachowicz, et al. (*13*). The slight variation of partial volume with solvent, composition, and pressure was disregarded in view of the lack of data; instead a representative value was used.

The solubility parameter for the light components was then determined so as to best represent their *K*-values in hydrocarbon mixtures of widely different types and under a wide range of conditions of temperature and pressure. The procedure was as follows:

Rearranging Equation (1) one gets

$$\nu^0_i \equiv K_i \frac{\phi_i}{\gamma_i} \qquad (1a)$$

Take the logarithm of Equation (1*a*) and combine with Equation (5):

$$\ln \nu^0_{ijk} = \ln \phi_{ijk} + \ln K_{ijk} - \frac{V_i v^2_{jk} (\delta_i - \delta_j)^2}{RT_k} \qquad (10)$$

Here the activity-coefficient expression has been reduced to a form more suitable for binary mixtures.

δ_i denotes the solubility parameter of the light component (solute) that is being determined. δ_j stands for the value for the solvent that has been calculated according to the defining Equation (9). All the quantities in Equation (10) may be calculated from experimental vapor-liquid equilibrium data, except ν^0_{ijk} and δ_i.

A large number of experimental determinations of *K*-values were used. Since ν^0_{ijk} depends only on temperature and pressure, all the ν^0_i's at the same condition k should be equal if the theoretical relations are exactly true and the experimental measurements perfectly precise. The value of δ_i was so chosen that this was realized as much as possible. Mathematically this may be considered as a problem of least squares. This means that the following quantity is minimized:

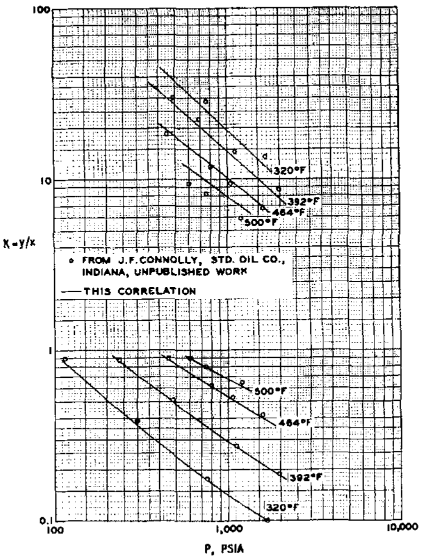

Fig. 7. Hydrogen-benzene.

$$S = \sum_k \sum_j (\ln \nu^0_{ijk} - \overline{\nu^0_{ik}})^2 \qquad (11)$$

where

$$\overline{\nu^0_{ik}} = \frac{1}{n_k} \sum_j \ln \nu^0_{ijk}$$

The use of logarithms in this minimizing operation was justified on the ground that the best over-all relative accuracy instead of absolute accuracy of *K*-values was desired.

Substitute Equation (10) into (11) and determine the value of δ_i corresponding to the minimum value of S by setting $\partial S/\partial \delta_i = 0$:

$$\frac{\partial S}{\partial \delta_i} = -4 \sum_k \sum_j \left[\frac{V_i v^2_{jk} (\delta_i - \delta_j)}{RT_k} - \frac{1}{n_k} \sum_j \left\{ \frac{V_i v^2_{jk} (\delta_i - \delta_j)}{RT_k} \right\} \right]$$

$$\left[\ln \phi_{ijk} + \ln K_{ijk} - \frac{V_i v^2_{jk} (\delta_i - \delta_j)^2}{RT_k} - \frac{1}{n_k} \sum_j \left\{ \ln \phi_{ijk} + \ln K_{ijk} - \frac{V_i v^2_{jk} (\delta_i - \delta_j)^2}{RT_k} \right\} \right] = 0 \qquad (12)$$

This is an equation in δ_i. Each time this equation is solved, one obtains the solubility parameter that best characterizes the solubility behavior of a particular light component under all conditions investigated.

An extensive collection of literature experimental data was compiled for the determination of the solubility parameter of hydrogen, methane, and ethane according to this procedure. The solvents and the range of conditions used are summarized in Table 4 for each component.

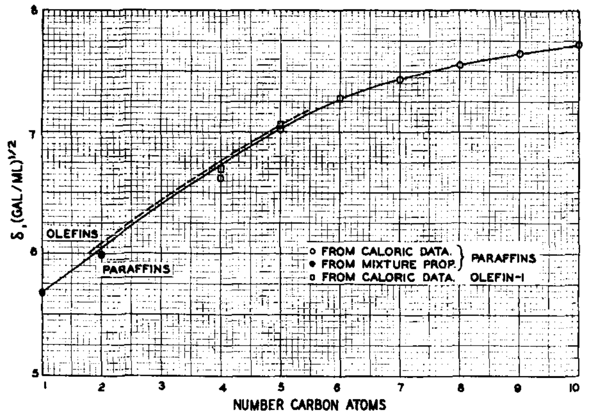

Fig. 8. Solubility parameter of *n*-paraffins and olefins.

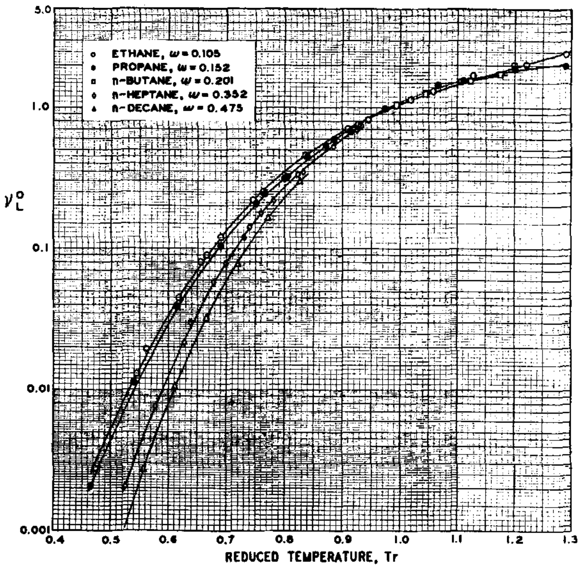

Fig. 10. Liquid fugacity coefficient at $P_r = 0.6$.

The solubility parameter thus determined for ethane was slightly adjusted to fit into a smooth curve for the normal paraffins. This curve was then used to determine the value for propane as shown in Figure 8. The liquid molal volumes were smoothed in the same manner as shown in Figure 9.

Lack of data on ethylene in solvents of various types made it impossible to determine its solubility parameter with this procedure. The values for the light olefins were obtained by extrapolation, following the trend of the paraffins as shown in Figure 10. These values are, therefore, subject to some uncertainty.

It is believed that the accuracy of Hildebrand's equation is not sufficient to differentiate between the behavior of homologous isomers in solution. The solubility parameters of isomeric paraffins were therefore assigned values equal to those of the normal paraffins and the isomeric olefins those of the 1-olefins.

Extension of Generalized Correlation of ν^0

Literature data on vapor-liquid equilibria in hydrocarbon mixtures were processed to determine values of ν^0 according to Equation (1*a*).

The obtained values are consistent with generalized correlations, such as that prepared by Curl and Pitzer, at conditions where the generalized correlation applies.

Extensive data were available on the normal paraffins including ethane, propane, *n*-butane, *n*-heptane, and *n*-decane. These components span a considerable range of values in acentric factor. Values of ν^0 determined for these components were used to extend Curl and Pitzer's correlation of ν^0.

Figure 10 shows the variation of ν^0 with reduced temperature and ω at a reduced pressure of 0.6. A cross plot of Figure 10 was used to determine values of the two functions $\nu^{(0)}$ and $\nu^{(1)}$ according to Equation (2).

The fitting of values of $\nu^{(1)}$ with an approximating function was simplified by the observation that $\nu^{(1)}$ is only weakly dependent on pressure. Curl and Pitzer's tabulated values of log $\nu^{(1)}$ were fitted to within ± 0.02 up to 5.0 in reduced pressure and to within ± 0.05 up to 9.0 in reduced pressure with a linear pressure coefficient taken to be temperature independent; that is

$$\log \nu^{(1)} = \log \nu\, P_r = 0.6^{(1)} - 0.025\,(P_r - 0.6) \quad (13)$$

The same pressure-dependent term was then applied to temperatures bepond Pitzer's tabulated values.

Values of $\nu^{(1)}$ at a reduced pressure of 0.6 were correlated with the temperature function in Equation (4). Pitzer's tabulated values at reduced temperature from 0.8 to 1.0 were included in the correlation. A combination of this temperature function with the pressure term given in Equation (13) yields the complete expression in Equation (4).

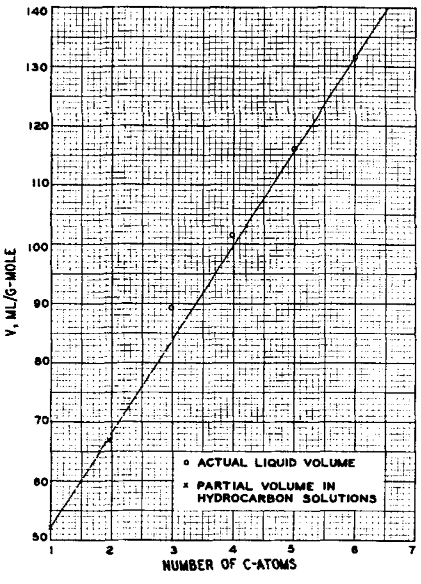

Fig. 9. Liquid molal volume of *n*-paraffins at the reference temperature of 25°C.

For every value of ν^0 obtained through processing of experimental data a corresponding value of $\nu^{(0)}$ was then calculated by using Equation (2), the necessary value of $\nu^{(1)}$ being given by Equation (4) at the specified T_r and P_r. The values of $\nu^{(0)}$ thus obtained were then correlated with the function given by Equation (3).

A Gaussian procedure (*26*) was employed to determine the best numerical values of the coefficients in Equation (3). The procedure depends on the usual least-squares criterion. Convergence was accelerated through parabolic fitting of the error sums and the iterative values of the coefficients.

The computation made use of Curl and Pitzer's tabulated values of $\nu^{(0)}$ at T_r from 0.8 to 0.95. Values of $\nu^{(0)}$ obtained from experimental data processing were used at temperatures above and below this range. A total of fifty-seven smoothed points for ethane, forty-six for propane, twenty-nine for *n*-heptane, and twenty-seven for *n*-decane were included for this purpose.

Agreement of the resulting equations for $\nu^{(0)}$ and $\nu^{(1)}$ with the respective tabulated values of Curl and Pitzer is shown in Figures 1 and 2.

Development of the correlation for methane and hydrogen was relatively simple. Experimental data were processed according to Equation (1*a*) to yield values of ν^0. These were then correlated with the function given by Equation (3). with the same Gaussian procedure to determine the coefficients.

Best Values of ω

The acentric factor gives a measure of the deviation of the behavior of usual substances from that of an idealized simple fluid. It is a characteristic

Table 4. Range of Source Data for Determination of Solubility Parameter

Component	Solvent	Temp, °F.	P, lb./sq. in. abs.	Source
Hydrogen	*n*-Heptane	−13 to 95	14.7	4
	n-Octane	−13 to 95	14.7	4
	Isooctane	−13 to 95	14.7	4
	Toluene	−13 to 95	14.7	4
	Benzene	77 to 95	14.7	4
	Ethane	−85 to 32	711 to 1,422	25
	Propane	−85 to 77	711 to 1,422	25
	n-Butane	−85 to 77	711 to 1,422	1
	n-Hexane	77 to 392	711 to 1,422	16
	n-Heptane	77	711 to 1,422	13
	n-Octane	77	711 to 1,422	13
	Benzene	77 to 392	711 to 1,422	8
	Toluene	77 to 392	711 to 1,422	8
	Cyclohexane	77 to 257	711 to 1,422	8
Methane	*n*-Pentane	150	100 to 2,000	22
	n-Heptane	150	200 to 2,000	19
	n-Decane	150	100 to 2,000	18
	Cyclopentane	150	100 to 2,000	3
	Cyclohexane	150	100 to 2,000	3
	Methylcyclohexane	150	100 to 2,000	3
	Benzene	150	100 to 2,000	6
	Toluene	150	100 to 2,000	6
Ethane	*n*-Butane	100 to 200	100 to 800	10
	n-Heptane	50 to 350	100 to 1,000	9
	Cyclohexane	50 to 350	100 to 1,000	11
	Benzene	100 to 350	400 to 1,000	12

constant for each component. According to Pitzer it is defined as

$$\omega = -\,(1.000 + \log P_r{}^{\circ})_{T_r = 0.7} \quad (14)$$

with $P_r{}^{\circ}$ the reduced vapor pressure. This permits a simple calculation of its numerical value.

The acentric factors given in Table 2 were however not derived from the original definition. Instead they were determined as a parameter for the best fitting of the vapor-pressure curve by the K-value correlation developed here. The differences between these table values and the values following from the original definition are usually slight. Nevertheless it should be stressed that the values in Table 2 are intended only for use in the correlation presented here.

The values in Table 2 were obtained by treating vapor-pressure data according to Equation (1). Since K and γ are both equal to 1, it follows that

$$\nu^{0} = \phi \quad (15)$$

Upon taking the logarithm of both sides and substituting with Equation (2), one obtains

$$\log \nu^{(0)} + \omega \log \nu^{(1)} = \log \phi \quad (16)$$

Departure from equality is then minimized to give

$$\omega = \frac{\sum_k \log \nu_k{}^{(1)} \left[\log \phi_k - \log \nu_k{}^{(0)}\right]}{\sum_k \left[\log \nu_k{}^{(1)}\right]^2} \quad (17)$$

where k denotes data number.

The acentric factors determined in this manner give an improvement of about 1% in accuracy in the fitting of vapor-pressure data. The average deviation after the fitting is 4.1% for the thirty-seven hydrocarbons tested.

TEST OF CORRELATION

The K-value correlation presented here has been tested against a systematic compilation of experimental K-value data from the literature. Mixtures of various types covering a wide range of conditions were included. Some variation in the agreement of the correlation with data was noticed depending on the conditions, the nature of the mixture, and the source of data.

It is impractical to report here the complete results of the comparisons. Average values for systems of different nature will be discussed. Where marked variation of fitting with conditions occurred, it will be pointed out.

Table 5. Comparison of Correlation with Data and with BWR Equation

Component	No. Points	Avg. Abs. % Dev. New Correlation	Avg. Abs. % Dev. BWR
Paraffins			
Methane	204	8.9	5.2
Ethane	221	9.2	10.2
Propane	247	6.8	7.5
i-Butane	49	5.4	4.8
n-Butane	142	7.1	7.2
i-Pentane	39	3.4	3.8
n-Pentane	101	9.6	8.8
n-Hexane	32	8.3	5.3
n-Heptane	118	8.3	11.3
Olefins			
Ethylene	102	10.8	11.0
Propylene	72	5.3	3.4
i-Butylene	18	3.8	3.8
Total	1,345	7.9	7.7

By far the majority of data in the literature is on binary mixtures at elevated pressures. In compiling such data for the comparison, some selection was made. Four points were taken along each isothermal curve at nearly equal intervals in the logarithm of pressure, starting from about the lowest pressure up to the highest but not exceeding 0.8 in the critical pressure of the mixture. The same procedure was repeated for each isotherm reported. The points so chosen adequately defined the K-value curves.

There is also a considerable quantity of experimental literature data on binary mixtures at atmospheric pressure or below. They served the valuable purpose of establishing the activity coefficients in liquid mixtures of hydrocarbons of various molecular types. Three points were selected for test from each system at a fixed pressure. Two of these points were at about 0.1 mole fraction on either component; the third point was at, or close to, the equimolal concentration. The three points adequately define the activity coefficient as a function of composition.

No selective screening was done for data on multicomponent mixtures, since available data usually were not even sufficient to define completely the behavior of the system at the range of conditions investigated.

Data points lying beyond the restrictions specified for the correlation, as discussed in the first section of this report, are excluded from the following discussions.

Mixtures of Light Paraffins and/or Olefins

Mixtures of this type have been the center of interest in studies of vapor-liquid equilibria in hydrocarbon mixtures. Both experimental data and correlations abound. In addition to comparing the correlation presented here with experimental data, a comparison has been made with results of calculations with the Benedict-Webb-Rubin (BWR) equation of state in the belief that this equation is the most accurate of the available correlations in the literature. This comparison is given in Table 5. It is limited to mixtures composed entirely of the twelve light paraffins and olefins to which the series of papers by Benedict, et al. (2) were devoted. These include paraffins from methane to *n*-heptane and olefins from ethylene to isobutylene. More than 1,000 experimental points were used.

In general both correlations give the most accurate results for components of medium molecular weight in the given range. The accuracies of the two correlations are comparable.

The restriction on the correlation for methane not to exceed 0.93 in pseudoreduced temperature of the liquid mixture leads to the exclusion of a large number of data on methane in very light hydrocarbons, such as ethane and propane. Apparently the equation used for the liquid activity coefficient is not adequate under these conditions.

Other Systems

Comparison of the correlation with all experimental data compiled from the literature is summarized in Table 6.*

The correlation fits data on hydrogen to an average accuracy of about 10%. Notable exceptions are hydrogen mixtures with ethylene at subzero temperature, giving rise to an average deviation of about 30%. This error may very likely be reduced substantially by properly adjusting the solubility parameter for ethylene. For hydrogen in aromatic solvents, above average deviation was observed in toluene at subzero temperature.

Agreement of the correlation with data on methane is generally within an accuracy of 10%. Methane in naphenic solvents however gives higher deviations.

Behavior of the hydrocarbons in their mixtures with hydrogen at elevated pressure is in general well correlated for the light hydrocarbons, including hexane and benzene. Decane shows large deviations at elevated pressures. The correlation could not be tested on naphthene-hydrogen mixtures at elevated pressure because of a complete lack of experimental data.

The correlation fits data on aromatic mixtures well at elevated pressures, the only apparent exception being m-xylene in its mixture with benzene. For aromatics in mixture with paraffins at elevated pressures, close fitting is obtained in some cases, such as benzene in ethane, but relatively large deviations occur in some other cases, such as benzene in methane and toluene in methane, propane, and *n*-hexane.

Available data on naphthene mixtures are mostly at atmospheric pressure or below. Such data were correlated usually within 5%. Data on the naphthenes at elevated pressure are available in their mixtures with light paraffins. The correlation agrees with those data usually to within 10%.

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NOTATION

A = $\sum_i y_i A_i$

A_i = $\left(0.4278 \frac{T_{ci}^{2.5}}{P_{ci} T^{2.5}}\right)^{0.5}$

B = $\sum_i y_i B_i$

B_i = $0.0867 \frac{T_{ci}}{P_{ci} T}$

ΔE_V = energy of vaporization

f = fugacity

f_L^0 = fugacity of pure liquid component at system conditions

h = a density term in Redlich and Kwong equation

K = y/x = vaporization equilibrium ratio

n_k = number of solvents used for the same light component in question at the *k*th condition of temperature and pressure

P = pressure

P_c = critical pressure

T = absolute temperature

T_c = critical temperature

T_r = reduced temperature

V = liquid molal volume

v_i = $\frac{x_i V_i}{\sum_j x_j V_j}$ = volume fraction of component *i* in liquid solution

x = mole fraction in liquid solution

y = mole fraction in vapor mixture

z = compressibility factor

Greek Letters

γ_i = $\frac{f_i}{x_i f_{iL}^0}$ = activity coefficient of component *i* in liquid solution

δ = solubility parameter

ϕ_i = $\frac{f_i}{y_i P}$ = fugacity coefficient of component *i* in vapor mixture

ν^0_i = f_{iL}^0/P = fugacity coefficient of pure liquid component *i* at system conditions

$\nu^{(0)}$ = fugacity coefficient of simple fluid in liquid state

$\nu^{(1)}$ = fugacity coefficient correction factor

ω = acentric factor

Subscripts

j = solvent

k = condition of temperature and pressure

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* See footnote on page 600.