A Generalized Method for Predicting Vapor-Liquid Equilibrium

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Vapor-liquid equilibrium distribution ratios for hydrocarbons can be computed by the new equations presented in this work with higher accuracy than is possible by previous generalized methods. In this proposed new method, the three coefficients of the combination $\nu_i\gamma_i/\phi_i$ are newly developed and generalized functions.

The vapor-phase fugacity coefficient ϕ_i was formulated via a new generalized equation of state, and the liquid-phase activity coefficient γ_i is predicted via a proposed new equation that contains three generalized binary interaction coefficients for each binary set in a mixture. These interaction coefficients were developed from experimental K value data. Two expressions are employed in predicting the liquid fugacity coefficient ν_i, one for the real liquid state and one for the hypothetical liquid state, the latter being developed empirically from experimental K value data also. These two ν_i equations are also generalized.

This new K value prediction method gave an average absolute deviation of 5.25% on a total of 3,504 data points on 19 hydrocarbons in binary and ternary mixtures, these data points being selected so that they cover the range of pure component $T_r = 0.5$ and up and pressures up to 0.9 of the true mixture critical pressure. Inclusion of nonhydrocarbon-hydrocarbon systems in the evaluation gave an overall absolute deviation of 6.33% for 4,290 K value data points on 23 components.

The phase distribution ratio, $K_i = y_i/x_i$, for the components of coexisting equilibrium vapor and liquid mixtures is a complex function of the conditions and compositions of the coexisting phases. Analytical prediction methods for the K value have been based on the equal-fugacity criterion of equilibria, that is, the fugacity of each component is the same in both vapor and liquid phases. Two approaches have been used in predicting equilibrium K values by this equal-fugacity criterion.

In one approach, an equation of state, describing PVT behavior, is used to compute the fugacities for the components of both phases. In the other approach, liquid-phase fugacities are found via an activity coefficient plus pure component reference state fugacity relationship and combined with equation of state vapor-phase fugacities to obtain the K values.

The works of Benedict et al. (*1*) and Starling (*13*) are examples of the first method, while the works of Chao and Seader (*2*) and of Prausnitz et al. (*9, 10*) are examples of the latter. The present work follows the second approach.

MATHEMATICAL MODEL

In terms of fugacity and activity coefficients, the equal-fugacity criterion of equilibria may be written as

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

The left-hand side terms in Equation (1) give the fugacity of component i in the vapor phase, while the right-hand side terms give the fugacity of component i in the liquid phase. Rearranging and defining y_i/x_i as K_i, one gets

$$K_i = \gamma_i \nu_i / \phi_i \tag{2}$$

Equation (2) was proposed in 1960 by Prausnitz, Edmister, and Chao (*10*) as a rigorous thermodynamic relationship for correlating and predicting K values of hydrocarbons. Chao and Seader (*2*) used Equation (2) as the basis for their generalized correlation. Equation (2) is the model for the present generalized K value prediction method.

In the present work, as in the previous Chao-Seader (*2*) work, analytical expressions were derived for the three right-hand terms of Equation (2). These semitheoretical expressions were based upon a vapor-phase equation of state and a large quantity of experimental vapor-liquid equilibria data, which were used to determine constants in the theoretical and empirical expressions derived for the liquid fugacity and activity coefficients. The vapor-phase fugacity coefficient ϕ_i is formulated via a new three-parameter equation of state (*6*), an improvement over the Redlich-Kwong (*12*) equation that was used by Chao and Seader (*2*).

VAPOR-PHASE FUGACITY COEFFICIENT

The vapor-phase fugacity coefficient ϕ_i is calculated via expressions that have been derived from a new three-parameter equation of state that has been proposed by these authors (*6*). Improved constant combination relationships were developed by applying this previously developed equation to experimental vapor-liquid equilibria data. Resulting expresssions are

$$Z = \frac{V}{V-b} - \frac{a}{RT(V-b)} + \frac{c}{RT(V-b)(V+b)} \tag{3}$$

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

$$c = c_1T^{-0.5} + c_2T^{-2} \tag{5}$$

$$b = \sum_i y_i\, b_i \tag{6}$$

$$b_i = 0.0982\, RT_{ci}/P_{ci}$$

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$$a_1 = \left[\sum_i y_i \, a_{1i}^{1/2} \right]^2 \tag{7}$$

$$a_{1i} = (0.25913 - 0.031314\,\omega_i)\, R^2T^2{}_{ci}/P_{ci}$$

$$a_2 = \left[\sum_i y_i \, a_{2i}^{1/2} \right]^2 \tag{8}$$

$$a_{2i} = (0.0249 + 0.15369\,\omega_i)\, R^2T_{ci}/P_c$$

$$a_3 = \sum_i \sum_j y_i \, y_j \, \alpha_{ij} \sqrt{a_{3i}\, a_{3j}} \tag{9}$$

$$a_{3i} = (0.2015 + 0.21642\,\omega_i)\, R^2T^3{}_{ci}/P_{ci}$$

$$a_4 = \sum_i \sum_j y_i \, y_j \, \beta_{ij} \sqrt{a_{4i}\, a_{4j}} \tag{10}$$

$$a_{4i} = (0.042\,\omega_i)\, R^2T^7{}_{ci}/P_{ci}$$

$$c_1 = \left[\sum_i y_i \, c_{1i}^{1/3} \right]^3 \tag{11}$$

$$c_{1i} = 0.059904(1 - \omega_i)\, R^3T^{3.5}{}_{ci}/P_{ci}^2$$

$$c_2 = \sum_i \sum_j \sum_k y_i \, y_j \, y_k \, \theta_{ijk} \, (c_{2i}\, c_{2j}\, c_{2k})^{1/3} \tag{12}$$

$$c_{2i} = (0.018126 + 0.091944\,\omega_i)\, R^3T^5{}_{ci}/P_{ci}^2$$

The binary interaction coefficients $\alpha_{ij} = \alpha_{ji}$ and $\beta_{ij} = \beta_{ji}$. Also $\alpha_{ii} = 1.0$ and $\beta_{ii} = 1.0$. If $\alpha_{ij} = 1.0$ and $\beta_{ij} = 1.0$, Equations (9) and (10) reduce to the originally proposed (6) constant combination relationships.

The ternary interaction coefficient $\theta_{ijk} = \theta_{ikj} = \theta_{jki} = \theta_{kij} = \theta_{kji}$. Also $\theta_{iii} = 1.0$, etc. If $\theta_{ijk} = 1.0$, Equation (12) reduces to the originally proposed (6) constant combination.

All the interaction coefficients were determined by regression analysis using experimental equilibrium data with the proposed mathematical model for the equal-fugacity criterion of equilibrium. The procedure used to determine these interaction coefficients will be described later. Satisfactory generalizations for these interaction coefficients were found to be functions of the critical temperatures, as follows, for hydrocarbon mixtures:

$$\alpha_{ij} = \left(\frac{2\sqrt{T_{ci}\, T_{cj}}}{T_{ci} + T_{cj}} \right)^{m_1} \tag{13}$$

$$\beta_{ij} = \left(\frac{2\sqrt{T_{ci}\, T_{cj}}}{T_{ci} + T_{cj}} \right)^{m_2} \tag{14}$$

$$\theta_{ijk} = \left(\frac{3\sqrt[3]{T_{ci}\, T_{cj}\, T_{ck}}}{T_{ci} + T_{cj} + T_{ck}} \right)^{m_3} \tag{15}$$

The ratios inside the brackets on the right-hand sides of Equations (13), (14), and (15) are the ratios of the geometric to arithmetic means of the critical temperatures. The exponents m_1, m_2, and m_3 are found as part of the regression procedures used in deriving the liquid-phase expressions.

In terms of the above equation of state and constants, the vapor-phase fugacity coefficient expression is

$$\ln \phi_i = \left(\frac{A_i' - aB_i'}{RTb} - 1 \right) \ln \left(1 - \frac{b}{V} \right) - \left(\frac{0.5C_i' - cB_i'}{RTb^2} \right) \ln \left(1 - \frac{b^2}{V^2} \right) + B_i'\,(Z - 1) - \ln Z \tag{16}$$

where

$$B_i' = b_i/b$$

$$A_i' = 2 \left[(a_1\, a_{1i})^{1/2} - (a_2\, a_{2i})^{1/2}\, T + a_{3i}^{1/2} \left[\sum_j^n y_j\, \alpha_{ij}\, a_{3j}^{1/2} \right] \Big/ T + a_{4i}^{1/2} \left[\sum_j^n y_j\, \beta_{ij}\, a_{4j}^{1/2} \right] \Big/ T^5 \right] \tag{17}$$

$$C_i' = 3 \left[c_1^{2/3}\, c_{1i}^{1/3}/T^{0.5} + c_{2i}^{1/3} \left\{ \sum_j^n \sum_k^n y_j\, y_k\, \theta_{ijk}\, (c_{2j}\, c_{2k})^{1/3} \right\} \Big/ T^2 \right] \tag{18}$$

The solution of Equation (16) for $\ln \phi_i$ requires a prior solution of Equation (3) for the compressibility factor, which can be obtained by a direct analytical solution.

LIQUID-PHASE FUGACITY COEFFICIENT

As indicated above, the fugacity of a mixture component in a pure liquid state is the reference state for the activity coefficient in our proposed new method for predicting K values. This pure liquid state will be a real state at temperatures below the critical temperature and pressure. At higher temperature and at pressures below the vapor pressures, a pure liquid state will be a hypothetical one. The system temperature of a coexisting equilibrium vapor/liquid mixture will be below the critical for the less volatile solvent components but may be above the critical for the more volatile solute components. Some components might be the solvent in one mixture and the solute in another.

Analytical expressions have been derived empirically for the fugacity coefficients of real and hypothetical liquid states. The real state f/P equation, which was based upon PVT and enthalpy data and presented previously (7), is a generalized equation for pure hydrocarbon liquids. For convenient reference and comparison of this real liquid state, fugacity coefficient equation is included, as follows:

$$\ln \nu = A_1 + A_2/T_r + A_3 \ln T_r + A_4\, T_r^2 + A_5\, T_r^6 + (A_6/T_r + A_7 \ln T_r + A_8\, T_r^2)\, P_r + A_9\, T_r^3\, P_r^2 - \ln P_r + \omega[(1 - T_r)(A_{10} + A_{11}/T_r) + A_{12}\, P_r/T_r + A_{13}\, T_r^3\, P_r^2] \tag{19}$$

where

$$\begin{array}{llll} A_1 = & 6.32873 & A_8 = & 0.18940 \\ A_2 = & -8.45167 & A_9 = & -\ 0.002584 \\ A_3 = & -6.90287 & A_{10} = & 8.7015 \\ A_4 = & 1.87895 & A_{11} = & -11.201 \\ A_5 = & -0.33448 & A_{12} = & -\ 0.05044 \\ A_6 = & -0.018706 & A_{13} = & 0.002255 \\ A_7 = & -0.286517 & \omega = & \text{acentric factor} \end{array}$$

Equation (19) can be used for hydrocarbons (excluding methane) at T_r values between 0.4 and 1.0 and at pressures up to $P_r = 10$, including pressures below the vapor pressure. Equation (19) should not be used at $T_r > 1.0$ values. For hydrocarbons at $T_r > 1.0$, methane, and nonhydrocarbon gases, another equation is recommended for calculating ν values.

A similar equation, which uses five of the same constants plus eight new constants, has been derived for the hypothetical liquids (that is, for liquid-phase components having T_{r_i} values greater than unity). This expression was derived from experimental K values in a data processing procedure that included the derivation of the liquid-phase activity coefficient. An outline of the procedure will be given later. The resulting expression for the fugacity coefficient of hypothetical liquid, that is, $T_r > 1.0$, is

$$\begin{aligned}\ln \nu = {} & B_1 + B_2/T_r + B_3 \ln T_r + B_4\, T_r^2 + B_5\, T_r^3 \\ & + (B_6/T_r + B_7 \ln T_r + B_8\, T_r^2) P_r + A_9\, T_r\, P_r^2 - \ln P_r \\ & + \omega[(1 - T_r)(A_{10} + A_{11}/T_r) + A_{12}\, P_r/T_r + A_{13}\, T_r\, P_r^2]\end{aligned} \tag{20}$$

Six sets of the constants B_1 through B_8 are given in Table 1, one set each for five components and a sixth for ethene-plus. The constants A_9 through A_{13} are the same as those used in Equation (19). From the above it is evident that Equation (20) is only partially generalized.

Equations (19) and (20) give exactly the same results at $T_r = 1.0$ for all values of P_r. There is a slight mathematical discontinuity between the equations at $T_r = 1.0$ but this was ignored in favor of improved accuracy in the prediction of K values.

In Figure 1 values of f/P from Equations (19) and (20) are plotted against T_r for lines of constant P_r for propane. As indicated in the legend, Equation (19) was used for temperatures up to $T_r = 1.0$ and Equation (20) was used for $T_r > 1.0$. These two curves join at $T_r = 1.0$, where the juncture is smooth. The Chao-Seader (*2*) equation for ν is also shown in Figure 1. As can be seen, there are large differences between the ν values predicted by the two equations at $T_r > 1.0$.

Since the hypothetical liquid fugacity coefficient is a derived property that depends upon the *x-y* data, the vapor fugacity coefficient ϕ_i and the liquid activity coefficient γ_i and since these ϕ_i and γ_i are calculated from different equations in this work and that of Chao and Seader, it is not surprising that the ν values from the two sources do differ so much.

Values of the acentric factor, for use with Equations (19) and (20) and also in evaluating the constants for Equation (16), were taken from a previous compilation (*4*) and are given in Table 2 for 35 hydrocarbons and four nonhydrocarbons.

ACTIVITY COEFFICIENT IN LIQUID SOLUTION

In previous work by Prausnitz et al. (*10*) and by Chao and Seader (*2*), liquid solutions of hydrocarbons were assumed to be regular (that is, positive excess enthalpy and zero excess entropy) as formulated by Hildebrand and Scott (*5*). In this work we propose the following expression for the excess Gibbs free energy of a mixture:

$$\begin{aligned}\frac{G^E}{RT} = \frac{1}{2}\Bigg[& \left\{ \sum_i^n x_i\, V_i^L \right\} \left\{ \sum_j^n \sum_k^n \Phi_j\, \Phi_k\, B_{jk}^* \right\} \\ & + \sum_j^n \sum_k^n x_j\, x_k\, C_{jk}^* + \sum_j^n \sum_k^n \Phi_j\, \Phi_k\, D_{jk}^* \Bigg]\end{aligned} \tag{21}$$

The first term in the brackets on the right-hand side is identical to Wohl's (*14*) two-suffix term. The second term is the same as the first terms of Redlich-Kister (*11*). The third term, which is similar to the second term except for the use of liquid volume fractions Φ_j and Φ_k instead of mole fractions x_j and x_k, was arbitrarily added to make the proposed model more flexible. A theoretical justification of this empirical model is not possible. For the systems covered in this work, this model fitted the derived activity coefficients (that is, calculated from *x-y* data plus the equations for ϕ_i and ν_i) as well and more simply than the theoretical models tried.

From Equation (21) and the relationship $RT \ln \gamma_i = \overline{G_i}^E$, the following expression is found for the activity coefficient:

$$\begin{aligned}\ln \gamma_i = V_i^L & \left[\sum_j^n \Phi_j\, B_{ij}^* - \frac{1}{2} \sum_j^n \sum_k^n \Phi_j\, \Phi_k\, B_{jk}^* \right] \\ & + \left[\sum_j^n x_j\, C_{ij}^* - \frac{1}{2} \sum_j^n \sum_k^n x_j\, x_k\, C_{jk}^* \right] \\ & + \left[\frac{\Phi_i}{x_i} \sum_j^n \Phi_j\, D_{ij}^* - \left(\frac{\Phi_i}{x_i} - \frac{1}{2} \right) \sum_j^n \sum_k^n \Phi_j\, \Phi_k\, D_{jk}^* \right]\end{aligned} \tag{22}$$

Equation (22) gives the activity coefficient for component i as a function of three binary-pair parameters B_{ij}^*, C_{ij}^*, and D_{ij}^* as well as the liquid mole fraction, liquid volume fraction, and the liquid molar volume of pure i.

Binary-pair parameter B_{ij}^* was set equal to the term A_{ij}/RT that appears in the regular solution theory relationships (*5*) and is a function of solubility parameter, making

$$B_{ij}^* = \frac{1}{RT}\,[(\delta_i - \delta_j)^2 + 2 l_{ij}\, \delta_i\, \delta_j] \tag{23}$$

Interaction coefficient l_{ij} may be evaluated for each binary pair where there are sufficient data, as was proposed by Eckert and Prausnitz (*3*). A more general method for predicting l_{ij} is required for process design applications. The following generalizations are proposed to give l_{ij} as a

TABLE 1. CONSTANTS IN EQUATION (20): FUGACITY COEFFICIENT OF HYPOTHETICAL LIQUID STATE

	Hydrogen	Nitrogen	Carbon dioxide	Hydrogen sulfide	Methane	Ethene and higher hydrocarbons
B_1	1.45610	9.82866	23.2166	14.5790	4.48018	7.83420
B_2	8.68977	−11.2767	−24.6427	−18.6046	−3.64274	−9.54010
B_3	0.60461	−3.65750	−25.5662	−22.7804	2.24320	−7.92000
B_4	−0.00375	0.18236	0.27361	3.77412	−1.40489	1.43018
B_5	0.0	0.0	1.10841	−0.17797	0.31421	−0.30278
B_6	0.09453	−0.13227	1.15963	−0.08928	−0.06910	0.22371
B_7	0.00491	0.0	7.81163	0.39462	0.95059	0.36252
B_8	0.0	−0.00715	−1.69703	0.01698	−0.12945	−0.05302

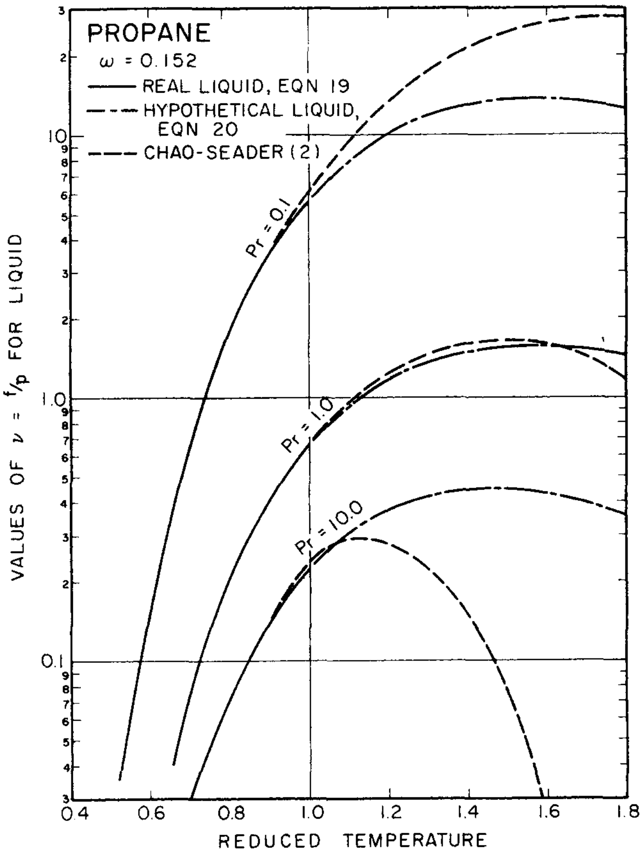

Fig. 1. Fugacity coefficients of propane as function of T_r and P_r from three equations.

function of solubility parameters and reduced temperatures:

$$l_{ij} = [q_1 + q_2(T_{ri}\,T_{rj})^{1/2}]\left[\frac{(\delta_i^{1/2} - \delta_j^{1/2})^2}{(\delta_i\delta_j)^{1/2}}\right] \quad (24)$$

Since the first right-hand term of Equation (22) represents thermal effects, the remaining right-hand side terms were made to reflect size differences. The interaction constants for these terms were expressed as the following functions of pure liquid molal volumes, which are measures of molecule sizes:

$$C_{ij}^* = q_3\left[\left(\frac{V_i^L}{V_j^L}\right)^{1/4} - \left(\frac{V_j^L}{V_i^L}\right)^{1/4}\right]^4 \quad (25)$$

$$D_{ij}^* = q_4\left[\left(\frac{V_i^L}{V_j^L}\right)^{1/4} - \left(\frac{V_j^L}{V_i^L}\right)^{1/4}\right]^4 \quad (26)$$

Values of the constants q_1, q_2, q_3, and q_4 were determined by a regression analysis, using experimental K values for binary mixtures and calculated fugacity coefficients for various binary mixtures.

CORRELATION PROCEDURE

A mathematical model for predicting vapor-liquid K values was presented in the foregoing. Portions of the equations and many of the constants of this model were derived by processing experimental x-y data for binary mixtures of hydrocarbons and associated gases. Experimental data covering a wide range of conditions were selected from available binary data, eliminating points having pressures higher than 0.9 of the true critical pressure of the mixture. Most of the experimental data used are in the pure component T_r range of 0.5 to 2.0 except for the lighter gases (nitrogen and hydrogen). Data points having concentrations less than 1 mole % were excluded because of large composition uncertainties that are usually found in such data.

The objectives of the data processing were (1) an expression for the fugacity coefficient of the hypothetical liquid phase [that is, Equation (20)]; (2) liquid-phase interaction relationship constants (that is, q_1 through q_4) for predicting activity coefficients; and (3) vapor-phase interaction relationships [that is, Equations (13), (14), and (15)] for predicting the vapor fugacity coefficients.

Table 2. Characterizing Constants for Pure Components

	Acentric factor ω	Solubility parameter δ, (cal./ml.)$^{1/2}$	Liquid molal volume V^L, ml./g.-mole
Paraffins:			
Methane	0.013	5.66	64
Ethane	0.105	6.03	75
Propane	0.152	6.40	88
i-Butane	0.192	6.73	105.5
n-Butane	0.201	6.73	101.4
i-Pentane	0.206	7.02	117.4
n-Pentane	0.252	7.02	116.1
neo-Pentane	0.195	7.02	123.3
n-Hexane	0.290	7.27	131.6
n-Heptane	0.352	7.43	147.5
n-Octane	0.399	7.55	163.5
n-Nonane	0.444	7.65	179.6
n-Decane	0.487	7.72	196.0
n-Undecane	0.501	7.79	212.2
n-Dodecane	0.539	7.84	228.6
n-Tridecane	0.582	7.89	244.9
n-Tetradecane	0.617	7.92	261.3
n-Pentadecane	0.649	7.96	277.8
n-Hexadecane	0.675	7.99	294.1
n-Heptadecane	0.687	8.03	310.4
Olefins:			
Ethylene	0.089	6.02	73
Propylene	0.143	6.43	84
1-Butene	0.203	6.76	95.3
cis-2-Butene	0.273	6.76	91.2
trans-2-Butene	0.234	6.76	93.8
i-Butene	0.201	6.76	95.4
1,3-Butadiene	0.203	6.94	88.0
1-Pentene	0.218	7.05	110.4
1-Hexene	0.246	7.40	125.8
Naphthenes:			
Cyclopentane	0.205	8.11	94.7
Methylcyclopentane	0.235	7.85	113.1
Cyclohexane	0.203	8.20	108.7
Methylcyclohexane	0.242	7.83	128.3
Aromatics:			
Benzene	0.215	9.16	89.4
Toluene	0.252	8.92	106.8
o-Xylene	0.298	8.99	121.2
m-Xylene	0.316	8.82	123.5
p-Xylene	0.307	8.77	124.0
Ethylbenzene	0.317	8.79	123.1
Other gases:			
H_2	0.0	3.25	31.0
N_2	0.035	3.30	33.0
CO_2	0.225	5.98	62.3
H_2S	0.106	6.03	57.1

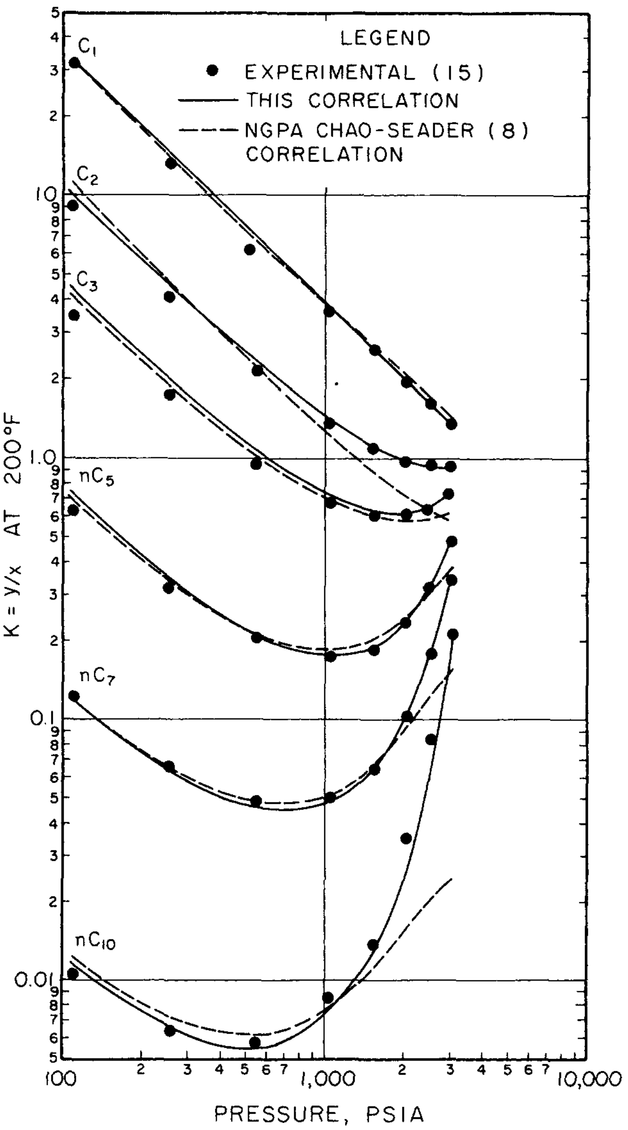

Fig. 2. Comparison of calculation with observed K values for components of natural gas-gasoline.

At the beginning of this data processing, the forms of the above equations were not known. The forms and constant values were found by iterative procedures in the data processing, which was done on the IBM 360/65 in the following steps:

Step 1: Values of the activity coefficient γ_i were calculated for the solvent component of binary hydrocarbon mixtures using experimental y/x data and Equation (2), from which

$$\gamma_i = \phi_i y_i / \nu_i x_i \qquad (27)$$

For this calculation, the vapor-phase interaction coefficients, that is, Equations (13), (14), and (15), were set equal to unity.

Step 2: Equation (22) was fitted to the values of γ_i, calculated in Step 1 for the solvent components, obtaining tentative values of the constants q_1 through q_4.

Step 3: Using the values of q_1 through q_4 from Step 2, we applied Equation (22) to compute the liquid activity coefficients of the solute, or lighter component of the binary hydrocarbon system.

Step 4: First-pass values of the hypothetical pure liquid fugacity coefficients were calculated for the solutes by using the x-y data and Equation (2), from which

$$\nu_i = \phi_i y_i / \gamma_i x_i \qquad (28)$$

Equations (13), (14), and (15) were again set equal to unity in this step. Values of α_{ij}, β_{ij}, and θ_{ijk} are insensitive to ϕ_i of the solute. These calculations were made for each solute in several solvents, according to the availability of experimental y/x data. A requirement of this model is that the values of these ν_i for a given solute be independent of the solvent and the composition of the binary mixtures from which the γ_i values were derived. In other words, ν_i is a pure component property for the hypothetical as well as real liquid states.

Step 5: The ν_i values calculated in Step 4 were fitted for Equation (20) to obtain eight new empirical constants, B_1 through B_8. Five of the previously obtained constants for the real state ν_i expression, that is, Equation (19), are used in Equation (20). For CH_4, H_2, N_2, CO_2, and H_2S, these eight constants were determined separately. The final values of these constants are given in Table 1.

Step 6: Values of the vapor-phase interaction coefficients α_{ij}, β_{ij}, and θ_{ijk}, which are required in Equations (9), (10), and (12) to improve the overall accuracy of the heavy component K value predictions, were found by a similar regression analysis. The coefficients α_{ij}, β_{ij}, and θ_{ijk} are fairly sensitive to ϕ_i of solvents.

Step 7: Using the values of α_{ij}, β_{ij}, and θ_{ijk} obtained in the previous step, we repeated the above six steps of this procedure, obtaining new values of the constants as re-

Table 3. Summary of Comparisons of K-Value Prediction Methods with Experimental Data

Components	Number of points	Av. abs. dev. % This work	Av. abs. dev. % Chao-Seader NGPA(57)
Methane	557	5.67	11.25
Ethene	92	4.12	15.54
Ethane	513	4.32	9.73
Propene	135	3.04	6.44
Propane	472	3.97	5.42
Isobutene	11	2.79	4.52
Butene-1	24	1.70	5.21
Isobutane	23	8.63	9.59
n-Butane	587	4.48	6.44
Isopentane	19	5.10	2.67
n-Pentane	276	5.27	7.71
n-Hexane	127	7.58	21.11
n-Heptane	207	6.76	19.14
n-Octane	30	5.68	8.46
n-Decane	228	9.90	31.73
Cyclopentane	14	1.90	6.76
Cyclohexane	97	6.96	15.70
Benzene	79	4.23	9.26
Toluene	13	7.46	13.32
Hydrogen	237	8.64	13.75
Nitrogen	265	17.53	115.24
Carbon dioxide	203	7.11	12.59
Hydrogen sulfide	81	7.44	8.81
Overall	4290	6.33	17.75

Table 4. Exponents of Equations (13), (14), and (15) for Vapor-Phase Interactions

	Hydrogen	Nitrogen and methane	General
m_1	−1	0	2
m_2	−8	−5	7
m_3	−3	−2	5

TABLE 5. CONSTANTS FOR INTERACTION RELATIONS IN ACTIVITY COEFFICIENT EQUATION

Constant	Equation	Hydrogen	Nitrogen	Aromatics	Cycloparaffins	General
q_1	(24)	−2.4063	19.8416	−3.2294	−3.2294	−2.0000
q_2	(24)	−0.3291	−19.9182	3.2943	5.0836	8.6762
q_3	(25)	−0.9746	−4.0250	−3.4483	−3.4483	−4.0000
q_4	(26)	4.8054	20.6178	42.6910	42.6910	−1.3333

quired to optimize the prediction of K values, until no further improvement was obtained. The exponents in Equations (13), (14), and (15) were made even integers for convenience.

During the above iterative calculations, the solubility parameters and liquid molal volumes were obtained empirically for the lighter solutes, such as methane, ethylene, ethane, and the nonhydrocarbon gases. Values of V^L and δ for methane, ethylene, and ethane were adjusted so that their values could be plotted against carbon atom number with the values for the heavier hydrocarbons and smooth curves obtained. The δ's and V^L's for other components are taken from Chao-Seader tabulation (*2*). These values are assumed independent of temperature in this work, as was done by Chao and Seader (*2*). Values of δ and V^L are given in Table 2 for 35 hydrocarbons and four nonhydrocarbons.

EVALUATION OF CORRELATION

In the derivation of the above equations, selected points from the experimental data for hydrocarbon and nonhydrocarbon binaries were used. The data input to the regressions programs was limited to less than 400 sets of binary y/x values for each regression analysis in order to shorten the time required for convergence. Many more data points were included in the comparisons of calculated with experimental K values, however. Comparisons were made of K values predicted by the proposed method and the NGPA version (*8*) of the Chao-Seader correlation (*2*).

An overall summary of calculated K values is given in Table 3, in which the averages of all of the deviations for each component are given along with the number of points included for each component. As can be seen, a total of 4,290 K values for 23 substances gave an overall absolute average deviation of 6.33% for the proposed correlation versus 17.75% for the NGPA version (*8*) of the Chao-Seader correlation (*2*). Comparisons of the K value predictions for different binaries and ternaries and at different conditions are given in the Appendix.*

Another comparison of these two prediction methods with observed data is shown in Figure 2, in which calculated K values are plotted with observed values for the 200°F. multicomponent data of Yarborough and Vogel (*15*). It will be noted that the results of this work agree with the observed values for the heavy components better than does the NGPA method (*8*).

All of the K value calculations described above and summarized in Table 3 were made with the interaction coefficients obtained by using the exponents in Table 4 and the constants in Table 5. In both tables several sets of values are given. The values labeled general are used for all components except for those indicated by specific component or component type heading. The priority order in Tables 4 and 5 is from left to right. For example, if in Equation (24) the ij binary consisted of an aromatic and a cycloparaffin, the q_1 and q_2 parameters from Table 5 would be found in the aromatic column.

CONCLUSIONS

The new generalized K value prediction method presented here agrees with experimental y_i/x_i values appreciably better than does the NGPA (*8*) or the Chao-Seader (*2*) method, the only other generalized method. Agreement with observed vapor-liquid equilibria data is good enough to make this new method an acceptable design tool for equilibrium stage separation calculations. The proposed K value correlation is not recommended beyond the range of conditions specified below:

For hydrocarbons: temperature, from 0.5 reduced temperature of individual component to 500°F.; pressure, up to 0.9 of true critical pressure of the mixtures.

For light gases: Temperature, down to −200°F.; pressure, up to 10,000 lb./sq.in.; concentration, up to 20 mole % of gases in the liquid.

NOTATION

A_1 through A_{13} = constants in Equations (19) and (20) for fugacity coefficient of liquids
A'_i = parameter function in equation of state [see Equation (17)]
a = parameter in equation of state
B_1 through B_8 = constants in Equation (20) for fugacity coefficient of hypothetical liquid (see Table 1)
B'_i = parameter function in equation of state [see Equation (16)]
B^*_{ij} = parameter in equation for activity coefficient [see Equations (22) and (23)]
b = parameter in equation of state
C'_i = parameter function in equation of state [see Equation (18)]
C^*_{ij} = parameter in equation for activity coefficient [see Equations (22) and (25)]
c = parameter in equation of state
D^*_{ij} = parameter in equation for activity coefficient [see Equations (22) and (26)]
G^E = excess Gibbs free energy
$\overline{G}^E_i$ = partial excess Gibbs free energy of i
K_i = y_i/x_i = vapor-liquid equilibrium constant
l_{ij} = binary interaction coefficient [see Equations (23) and (24)]
P = pressure
P_r = reduced pressure
q_1, q_2, q_3, q_4 = constants in activity coefficient expressions
R = gas constant
T = temperature
T_{ci} = critical temperature of component i

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* Appendix has been deposited as document No. 01615 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 909 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $5.40 for photocopies.

T_r = reduced temperature
V = molal volume

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Flow of Viscoelastic Fluids Through a Rectangular Duct

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A study is carried out on the flow of polymer melts in a rectangular duct. As the theoretical study a three-constant Oldroyd model is used to derive expressions which correlate the rheological properties of materials with the distributions of wall shear rates and wall normal stresses in the rectangular duct. As the experimenal study, a die of rectangular cross section having an aspect ratio of 6 is designed, and then melt extrusion experiments are performed with high density polyethylene. In the experiments wall normal stresses are measured along two adjacent walls of the rectangular duct as a funcion of the axial position. The measurements permit one to obtain the normal stress differences at the duct exit, and then to calculate the distributions of shear rates at two adjacent walls of the rectangular duct, by use of the theoretically derived expressions. Also measured is the extrudate swell, showing trat more pronounced extrudate swell occurs at the long side of the rectangular duct than at the short side. This behavior of extrudate swell correlates with the exit pressure measurements at two adjacent walls of the rectangular duct.

Fully developed flow through a circular tube belongs to the class of viscometric flow, and the extensive theoretical and experimental treatments of such flow problems have well been made for both Newtonian and non-Newtonian viscoelastic fluids. On the other hand, flow through a rectangular duct having a finite aspect ratio may be classified as nonviscometric flow in general, and its theoretical treatment is not as simple as that of viscometric flow. It is particularly difficult for non-Newtonian viscoelastic fluids. As a result, very little work has been done on the problems involved in nonviscometric flow of viscoelastic fluids, from a theoretical as well as experimental point of view.

Some attempts have been made in the past to describe steady rectilinear flow of power law fluids through a rectangular duct (*1* to *4*). Since the power law fluid cannot describe the elastic properties of polymer melts, solution of the equations of motion with the power law model does not explain the elastic behavior of a real viscoelastic fluid, for instance, the die swell phenomenon at the exit of a rectangular duct. Therefore attempts at solving the equations of motion with a more realistic viscoelastic model appear to be desirable. Several years ago Rivlin (*5*) and Langlois and Rivlin (*6*) discussed the slow flow of a viscoelastic fluid along a straight, noncircular tube, using the general constitutive equation advanced by Rivlin and Ericksen (*7*), and showed that rectilinear flow is pos-