Correlation and Prediction of Vapor-Liquid Equilibria with the Redlich-Kwong Equation of State

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A modified Redlich-Kwong equation has been applied to the calculation of phase equilibria in multicomponent systems. The two parameters of the Redlich-Kwong equation are treated as temperature functions. They are obtained for each pure component from experimental vapor pressures and liquid densities with the help of a generalized fugacity coefficient correlation for saturated vapors. The need to submit coefficients for pure components is thus eliminated. At least one experimental vapor-liquid equilibrium point is required to establish an interaction constant for each binary system. Applications have been made to binary and multicomponent systems containing hydrocarbons, hydrogen, carbon dioxide, and hydrogen sulfide.

The interpretation and prediction of phase equilibrium data at high pressures are everyday necessities in the design of separation processes. The present study has been devoted to finding the most effective way for handling mixtures at high pressures that would also apply to the vicinity of the vapor-liquid critical locus. A description of the problems encountered and prediction of data in the critical region are given in a separate paper (*38*). The aim of the present work has been to develop a method applicable to pure compounds as well as to narrow-cut petroleum fractions and hydrogen, a method dependent on minimum information on individual components, and a method capable of application to two-phase azeotropes and critical points.

EQUATIONS OF STATE IN PHASE EQUILIBRIA CALCULATIONS

The basic relationship for defining phase equilibria is the equality of the fugacity (f^V and f^L) of each component i when distributed between two phases in equilibrium:

$$f_i^V = f_i^L \tag{1}$$

The fugacities are often replaced with fugacity coefficients which are related to them through pressure and composition:

$$f_i^L = \phi_i^V y_i P \tag{2}$$

and

$$f_i^L = \phi_i^L x_i P \tag{3}$$

In practical design, the equilibrium ratio K_i is used, which may be related to the fugacity coefficients through the equations

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \tag{4}$$

The fugacity coefficients in Equation (4) can be derived from equations of state which apply to both phases. This fundamental approach has been used in the past with the B-W-R equation (*2*). While the B-W-R equation, with mixture constants computed by means of combining rules, has been reasonably successful in predicting K constants in paraffin and olefin systems, extension to other systems or to the critical region would necessitate the introduction of special interaction constants, which, in view of the complexity of the B-W-R equation, is a formidable undertaking. The problem is further compounded by the fact that there is no unique set of B-W-R constants which will best represent the vapor pressure and the P-V-T behavior in both gas and liquid phases of a pure substance (*20*).

The only other equation of state which has been widely applied to mixtures at high pressures is the Redlich-Kwong equation. The R-K equation, while admittedly less accurate than the B-W-R equation when applied to pure substances (*1*), is attractive for mixtures because of the simple manner in which binary interaction constants can be introduced into it (*14*). In the process of introducing interaction constants into the R-K equation for mixtures, Wilson (*35, 36*) and Chueh and Prausnitz (*6, 7, 8*) modified the original R-K equation. This approach appeared sufficiently promising to be followed up and developed in the present study.

THE R-K EQUATION OF A PURE COMPOUND

The Redlich-Kwong equation is

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2} V(V + b)} \tag{5}$$

In order to obtain better volumetric properties along the saturation line, Chueh and Prausnitz have proposed that the R-K constants for a pure compound i be computed from the expressions

$$a_i = \frac{\Omega_{ai} R^2 T_{ci}^{2.5}}{P_{ci}} \tag{6}$$

$$b_i = \frac{\Omega_{bi} R T_{ci}}{P_{ci}} \tag{7}$$

One pair of constants, ${}_g\Omega_a$ and ${}_g\Omega_b$, has been evaluated

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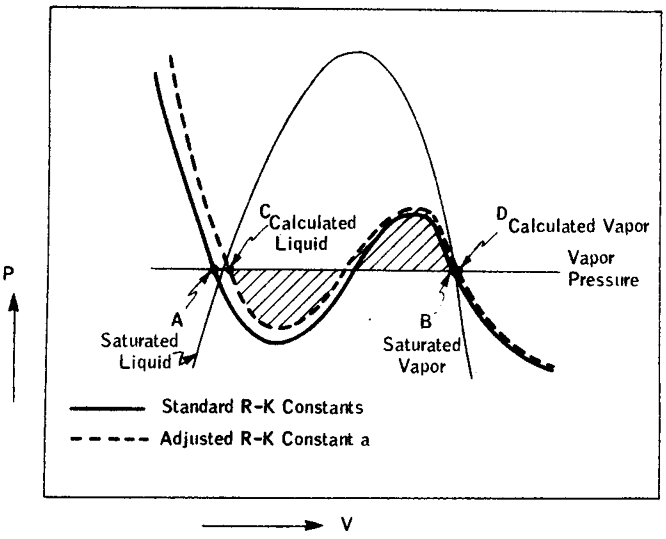

Fig. 1. Schematic of procedure for finding R-K constant *a* by equalizing vapor and liquid fugacities.

by them from volumetric data of the saturated vapor; the other pair ${}_l\Omega_a$ and ${}_l\Omega_b$, has been obtained from saturated liquid data (*6, 7*).

For a one-component system, the fugacity coefficient ϕ is obtained from the Redlich-Kwong equation as

$$\ln\phi = \ln RT/P\ (V - b) + PV/RT - 1 - (a/RT^{3/2}b)\ \ln(V + b)/V \quad (8)$$

To be thermodynamically consistent, Equation (8) must yield the same value of ϕ at the vapor pressure of the pure component, whether the liquid or the vapor volume is substituted from Equation (5) into Equation (8). Utilization of Equations (5), (6), and (7) with the constants established by Chueh and Prausnitz has been tested, and sample results calculated for saturated methane are given in Tables 1 and 2.[*] It is seen that different coefficients, established from volumetric data on the saturated phases, when substituted into Equation (8) do not yield equal fugacities, the requirement of Equation (1).

Wilson (*35, 36*) has proposed to apply the Redlich-Kwong equation simultaneously to the coexisting vapor and liquid phases with one set of constants in the manner of the B-W-R equation (*2*). He has proposed to utilize the Redlich-Kwong constant $\Omega_b = 0.0867$ at all temperatures and make the *a* constant temperature dependent, established by equalizing fugacities along the vapor-pressure curve. Wilson's procedure is illustrated with a sketch in Figure 1. The dashed-line curve represents the R-K equation with constant *a* adjusted so as to give equal areas enclosed between the curve and the horizontal vapor-pressure line. Equality of the two shaded areas corresponds to the condition that the fugacities of vapor and liquid are equal. The abscissas of points A and B represent volumes calculated from standard values of the constants; those of points C and D represent volumes calculated after adjustment of constant *a*. Neither calculated set of volumes necessarily coincides with experimental volumes, represented on Figure 1 by the intersections of the saturation curve (thin line) with the vapor-pressure line.

In a later development, a temperature function was suggested by Wilson for the R-K constant *a* as follows (*4, 36*):

$$a = 4.934RT^{3/2}b\left[1 + (1.45 + 1.62\omega)\left(\frac{1}{T_r} - 1\right)\right]\left(\frac{1}{T_r}\right)^{0.12} \quad (9)$$

Application of Wilson's method and Equation (9) to saturated methane is illustrated in Tables 1 and 2.[*]

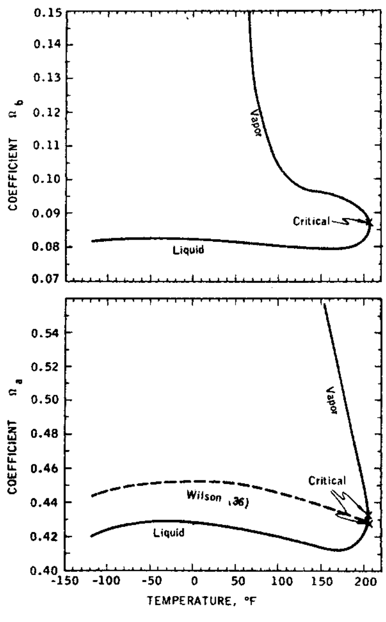

Fig. 2. Saturated propane, Ω coefficients for the R-K equation.

NEW APPROACH TO UTILIZATION OF R-K EQUATION

In developing a new approach, the authors have made the following basic assumptions: the R-K equation may be applied to both the vapor and liquid phases, both coefficients Ω_a and Ω_b vary with temperature, Equation (8) must yield the same fugacity whether applied to the saturated vapor or liquid phase, and fugacity coefficients calculated with Equation (8) must be in reasonable agreement with values obtained independently from the generalized correlation of Lyckman, Eckert, and Prausnitz (*17*):

$$\log\phi^s = (\log\phi^s)^{(0)} + \omega(\log\phi^s)^{(1)} \quad (10)$$

where $(\log\phi^s)^{(0)}$ and $(\log\phi^s)^{(1)}$ are functions of reduced temperature, tabulated by Lyckman, Eckert, and Prausnitz. This correlation has been checked against experimental values and found to be valid over the tabulated temperature range from $T_r = 0.56$ to $T_r = 0.99$, with the exception of the critical point itself. It is recommended that the fugacity, at the critical point, be taken as

$$\log\phi_{ci} = 0.1754 - 0.0361\ \omega_i \quad (11)$$

Below $T_r = 0.56$, the vapor pressure is so low that the approximation $\phi^s = Z^v$ may be used.

Our object was to adjust the coefficients of the R-K equation so that it would yield reasonable fugacities for each phase while satisfying Equation (1). This can be done for each phase, independent of the other phase, by simultaneous solution of Equations (5), (8), and (10). The establishment of the Ω coefficients does not require

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[*] Tables 1, 2, 4, and 6 have been deposited as document 00657 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $1.00 for microfiche or $3.00 for photocopies.

[*] See footnote on column 1.

TABLE 3. SATURATED PROPANE (*10*): EFFECT OF TEMPERATURE ON REDLICH-KWONG Ω COEFFICIENTS

T, °F.	T_R	${}_l\Omega_a$	${}_l\Omega_b$	${}_g\Omega_a$	${}_g\Omega_b$	Ω_a, Wilson (*36*)
−118.6	0.512	0.4205	0.08192	—	—	0.4444
− 69.9	0.585	0.4272	0.08234	—	—	0.4498
− 43.7	0.625	0.4283	0.08233	—	—	0.4512
− 13.2	0.670	0.4284	0.08217	—	—	0.4518
7.1	0.701	0.4274	0.08189	—	—	0.4516
22.8	0.724	0.4267	0.08173	—	—	0.4511
35.7	0.744	0.4258	0.08155	—	—	0.4505
46.9	0.761	0.4250	0.08139	—	—	0.4498
56.7	0.775	0.4241	0.08122	—	—	0.4491
65.6	0.789	0.4235	0.08110	0.9430	0.1500	0.4484
73.6	0.801	0.4226	0.08094	0.8677	0.1240	0.4477
81.1	0.812	0.4219	0.08081	0.8273	0.1182	0.4470
111.7	0.858	0.4187	0.08028	0.6871	0.1001	0.4435
135.6	0.894	0.4159	0.07977	0.6095	0.09666	0.4402
155.4	0.924	0.4136	0.07938	0.5561	0.09584	0.4371
172.5	0.949	0.4132	0.07948	0.5141	0.09442	0.4340
187.6	0.972	4.4151	0.08037	0.4780	0.09201	0.4314
201.2	0.992	0.4208	0.08257	0.4482	0.09013	0.4288
206.3	1.0	0.4328	0.08764	0.4378	0.08764	0.4278

hard-to-find data, since densities at saturation and vapor pressures are either available for many compounds or can be correlated. The following procedure was followed for each pure compound:

1. Select a trial value of ${}_l\Omega_b$, and from the known temperature, vapor pressure, liquid density, and critical constants find the corresponding values of a and ${}_l\Omega_a$ with Equations (5) and (6).
2. Utilize the values of a and b and calculate the fugacity coefficient ϕ_i^L with Equation (8). Compare with the value of ϕ_i^s that was obtained with Equation (10).
3. If $\phi_i^L \neq \phi_i^s$, repeat the two steps with a new selected value of ${}_l\Omega_b$ until a solution is obtained.
4. The same three steps are followed for the saturated vapor phase. In this case, ${}_g\Omega_b$ is assumed and vapor density is used; the value of ϕ_i^s is the same.

A computer program was written, and the procedure outlined above was tried on several hydrocarbons. It was noted that for most compounds the values of ${}_l\Omega_a$ and ${}_l\Omega_b$ do not vary much with temperature, while their counterparts in the vapor phase ascend rapidly as T_r decreases, as illustrated in Tables 1, 2,* and 3 and in Figure 2. In several cases, the vapor-phase values take an erratic course and become negative after passing through a maximum. Thus, it appears that the R-K equation applies better to saturated liquids than to saturated vapors (*11*).

SIMPLIFICATION; FUGACITIES IN BOTH PHASES FROM LIQUID CONSTANTS ONLY

As has been demonstrated in past publications (*2, 35, 37*), prediction of mixtures' phase behavior by utilizing equations of state is simpler if only one set of constants for each component is utilized. Furthermore, the application can be extended to the critical region where the two separate sets of coefficients may not agree with stability requirements. It was decided to utilize the values of ${}_l\Omega_a$ and ${}_l\Omega_b$ for both phases. Thus, knowingly, the accurate prediction of the vapor-phase properties along the vapor pressure of the pure compound was somewhat compromised.

Following a series of test runs on seven light paraffins, it was concluded that the average maximum error in the fugacity coefficient of the pure saturated vapor is about +2.5%. Also included in the study were tests of the magnitude of the error that may be introduced if Wilson's coefficients [derived by Equation (9)] are used for both phases. The comparison of calculated properties of saturated methane is given in Tables 1 and 2.* Although Chueh and Prausnitz (*6*) did not recommend their constants for calculating liquid fugacities, use of their coefficients was also included in the comparison. The review of the results illustrated graphically on Figure 3 shows that the error introduced by utilizing the authors' liquid Ω coefficients for the vapor phase does not seriously upset the prediction of ϕ_i^V, and the ratio ϕ_i^L/ϕ_i^V for a pure compound stays very close to unity, validating the assumption.

Since the variation of both the saturated liquid density and its fugacity with temperature complies with the theorem of the corresponding states (*17, 21*), the prediction of Ω_a and Ω_b for every compound in a mixture becomes even simpler. For compounds at temperatures above their criticals, coefficients established at the critical point should be used. The suggested numerical value of the fugacity coefficient at the critical point is given by Equation (11).

CORRELATION AND REDUCTION OF BINARY VAPOR-LIQUID EQUILIBRIUM DATA WITH C_{ij} COEFFICIENTS

In applying Equation (6) to gas mixtures, the following rules have been used in the current work, following the suggestion of Chueh and Prausnitz (*7*):

$$b_m = \sum_{i=1}^{n} y_i b_i \tag{12}$$

$$a_m = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j a_{ij} \tag{13}$$

The same rules apply to the liquid phase, with x replacing y in the equations (*6*).

In the present work, the interaction parameter a_{ij} was calculated from the following equation:

$$a_{ij} = (1 - C_{ij}) \sqrt{a_i a_j} \tag{14}$$

and

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* See footnote on p. 113.

* See footnote on column 1.

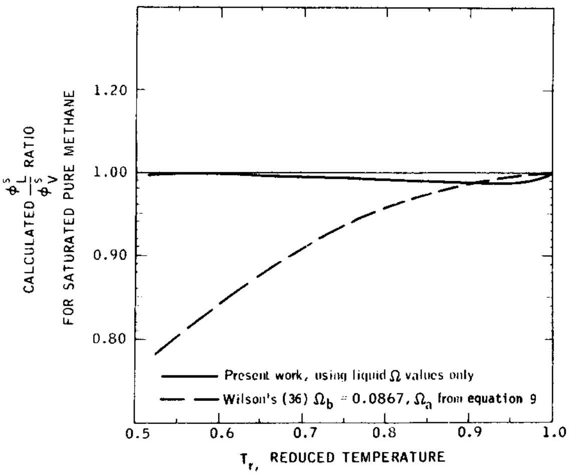

Fig. 3. Test of validity of the various coefficients of the R-K equation for calculating fugacity coefficient ratios for pure methane.

$$a_{ii} = a_i \tag{15}$$

The parameter C_{ij} represents the deviation of a_{ij} from the classical geometric mean assumption. The establishment of the C_{ij} parameter from experimental data is discussed in a later part of this presentation.

In order to calculate the fugacity coefficient of a component at a given temperature and pressure, the volume of the mixture, vapor or liquid, is first found by trial from Equation (5). The fugacity coefficient for a component K in a multicomponent vapor mixture is then calculated from the following equation (*17*):

$$\ln\phi_k^v = \ln\frac{V}{V-b} + \frac{b_k}{V-b} + \ln\frac{RT}{PV} - \frac{2\sum_{i=1}^{n} y_i a_{ik}}{RT^{3/2}b}\ln\frac{V+b}{V} + \frac{ab_k}{RT^{3/2}b^2}\left[\ln\frac{V+b}{V} - \frac{b}{V+b}\right] \tag{16}$$

For a binary vapor mixture, the above equation reduces to

$$\ln\phi_1^v = \ln\frac{V}{V-b} + \frac{b_1}{V-b} + \ln\frac{RT}{PV} - \frac{2(y_1a_1 + y_2a_{12})}{RT^{3/2}b}\ln\frac{V+b}{V} + \frac{ab_1}{RT^{3/2}b^2}\left[\ln\frac{V+b}{V} - \frac{b}{V+b}\right] \tag{17}$$

and a similar equation for $\ln\phi_2$, obtained by interchanging subscripts 1 and 2, remembering that $a_{12} = a_{21}$. The fugacity coefficients of the components in the liquid phase are also calculated with Equations (16) and (17) with ϕ_i^L, x_i and all the R-K a and b values for the liquid replacing their corresponding terms.

The interaction coefficient C_{ij} in Equation (14) may be found by trial-and-error solution of Equations (5) and (17), if an $x-y$ datum point is known for the binary mixture at given conditions. The same value of C_{ij} is used for both phases. There may be several approaches to establish a value for C_{ij}.

The procedure adopted by the authors is: a series of values of C_{ij} is assumed, and the equilibrium ratios K_i and K_j are calculated. The accepted value of C_{ij} is the one that yields the minimum sum of absolute deviations, that is, $|\Delta K_i| + |\Delta K_j| =$ minimum. An example of the application of the procedure for establishing the best value of C_{ij} for an experimental equilibrium point in the methane-ethane system is illustrated in Figure 4.

Although, as has been pointed out by Wilson (*35*), the interaction coefficient may be determined from only one measurement, it is recommended that at least four sets of $x-y$ points be used to account for possible scatter in the experimental data. It was found that, indeed, the coefficient C_{ij} is practically a constant for every binary system through quite a wide range of conditions. A summary of points used in establishing the coefficient C_{ij} of each binary system analyzed in the current study is presented in Table 8.

APPLICATIONS TO SYSTEMS CONTAINING HYDROGEN

Because of quantum effects, gases such as hydrogen and helium do not follow the simple law of corresponding states and, therefore, do not fit generalized correlations such as Pitzer's tables or the standard Redlich-Kwong equation. Newton (*19*) was the first to suggest that hydrogen and helium could be brought into line with other gases by replacing their true critical constants with effective critical constants. Newton's procedure considerably improves P-V-T correlations for hydrogen and helium at above room temperature but gives poor results at lower temperatures. It appears that the effective critical constants vary with temperature. Gunn, Chueh, and Prausnitz have proposed expressions for the effective critical constants of hydrogen, helium, and other quantum gases (*5, 12*).

A modified version of the method of Gunn, Chueh, and Prausnitz was used in the present work with mixtures containing hydrogen. The mixture was treated as if it were a mixture of classical gases, except that effective critical constants were used instead of the true critical constants for hydrogen, along with a value of zero for the acentric factor ω of hydrogen. At any given temperature the R-K parameters a and b of hydrogen were established by substituting the effective critical constants into Equations (5) and (8) and by solving these equations simultaneously for a and b. The left side of Equation (8) was evaluated from the earlier established value of the fugacity coefficient at the critical point, with the acentric factor ω set equal to zero in Equation (11). An example of this procedure, illustrated with the hydrogen-ethane system in Table 5, is discussed below.

PREDICTIONS OF VAPOR-LIQUID EQUILIBRIUM K RATIOS IN BINARY AND MULTICOMPONENT SYSTEMS

The method proposed as the conclusion of the present study utilizes only the Redlich-Kwong equation for predicting vapor/liquid K ratios in multicomponent systems. In essence, the method utilizes temperature dependent R-K coefficients a_i and b_i (directly related to ${}_l\Omega_{ai}$ and ${}_l\Omega_{bi}$) and binary interaction coefficients C_{ij}.

For every component, Ω_{ai} and Ω_{bi} are calculated from vapor pressures, liquid densities, and fugacities at saturation. Since these three properties can be predicted, the method is also applicable to petroleum fractions, and to some extent to nonhydrocarbons. The binary interaction parameters C_{ij} must be obtained by analyzing experimental data.

The method relies on the following assumptions:

1. The individual compounds obey the theorem of corresponding states.

TABLE 5. COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS FOR THE SYSTEM METHANE-BUTANE-DECANE (*24*)

Temp., °F.	Pressure, lb./sq.in.abs.	Component	Liq. phase mole fract.	Vap. phase mole fract.	K Exp.	K Calc.	% deviation
280°	1,000	C_1	0.203	0.774	3.813	3.764	−1.280
		C_4	0.346	0.212	0.613	0.613	1.342
		C_{10}	0.451	0.0146	0.032	0.032	−3.084
280°	2,000	C_1	0.402	0.748	1.861	1.821	−2.116
		C_4	0.370	0.224	0.605	0.620	2.481
		C_{10}	0.228	0.0278	0.122	0.111	−8.631
280°	3,000	C_1	0.575	0.839	1.459	1.488	−0.756
		C_4	0.179	0.113	0.631	0.656	3.891
		C_{10}	0.246	0.0475	0.193	0.182	−5.922
160°	1,000	C_1	0.253	0.803	3.174	3.086	−2.777
		C_4	0.661	0.196	0.297	0.294	−0.841
		C_{10}	0.086	0.0011	0.013	0.009	−33.539
160°	2,000	C_1	0.459	0.851	1.854	1.817	−1.977
		C_4	0.390	0.143	0.367	0.372	1.568
		C_{10}	0.151	0.0059	0.039	0.033	−16.160
160°	3,000	C_1	0.663	0.804	1.213	1.217	0.323
		C_4	0.229	0.161	0.703	0.703	0.044
		C_{10}	0.108	0.0356	0.330	0.305	−7.360

$C_{12} = 0.024$, $C_{13} = 0.00$, $C_{23} = 0.025$.

2. The effect of temperature and pressure on the binary interaction parameters C_{ij} is negligible.

3. The phase envelopes and the critical locus surface are continuous within the range of interest.

4. Since knowledge of the compositions of the phases is a prerequisite for using equations of state, these are to be supplied, guessed, or calculated by a flash routine, prior to phase equilibrium calculations, as is done when utilizing the B-W-R method.

The schematic step-by-step procedure is as follows:

1. The coefficients Ω_{ai} and Ω_{bi} are calculated for each compound from their vapor pressure P_i, liquid density d_L, and Lyckman's fugacity coefficient at saturation ϕ_1^s. Values of a_i and b_i are calculated from Equations (5) and (8) for all components.

2. Binary interaction coefficients C_{ij} are submitted for all possible binary permutations. These must be evaluated by a separate program for analyzing experimental data.

3. Equations (12) and (13) are then used to predict all four R-K coefficients for the mixtures $_la_m$, $_lb_m$, $_ga_m$, and $_gb_m$.

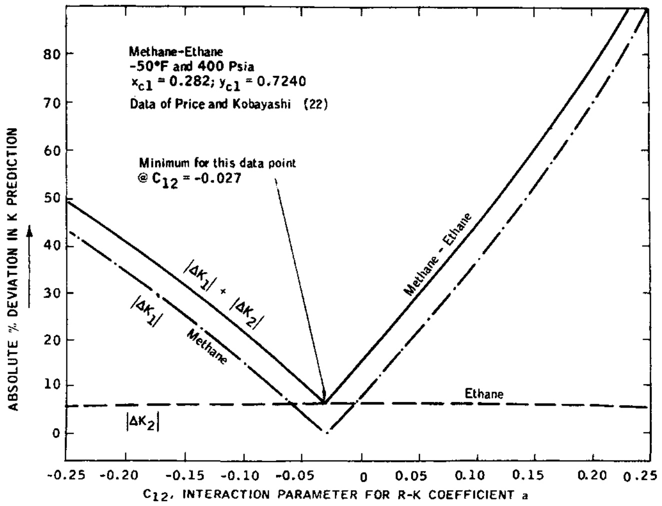

Fig. 4. Example: establishing an interaction parameter C_{12} for a given data point.

4. Equation (5) is used twice to calculate the volumes of the vapor and liquid mixtures, supposed at equilibrium. A trial-and-error procedure for establishing V_L and V_g with the R-K equation is followed.

5. For each component, Equation (16) is used twice: for calculating ϕ_i^L from V_L, $_la_m$, $_lb_m$, a_i, and b_i, and for calculating ϕ_i^V from V_g, $_ga_m$, $_gb_m$, a_i, and b_i.

6. The equilibrium ratio for every component is calculated from Equation (4).

The above procedure is easy to follow if all the *x*-*y* data are available. In actual engineering work, the compositions are arrived at via flash routine. If a flash routine supplies the assumed values of *x* and *y*, additional steps are necessary.

COMPARISON WITH EXPERIMENTAL DATA

An extensive comparison was carried out for the results from the proposed method, utilizing only R-K coefficients established for the indivdual compounds from their saturated liquids at system temperature as the valid Ω_a and Ω_b for both phases. Experimental *x*-*y* data from binary systems were used for establishing the values of the interaction parameters. Several data points, ranging from a single *x*-*y*-*t*-*P* point to as many as ten, were utilized for establishing the parameter C_{ij} in each binary. The comparison covered 183 experimental data points on seventeen different binaries and two ternary systems. Altogether, 391 *K* values were compared.

The overall results are very encouraging. An average deviation of ±3.69% was observed. Furthermore, the results indicate that the method is especially good for very high pressures, especially near the true critical locus (*38*).

Examples of the application of the method to six different systems are given in Tables 4,* 5, 6,* and 7 and Figures 5 and 6. The summary and the statistics for the examples are given in Table 8. These examples, though not representing the best agreement with experimental data, were chosen to illustrate the versatility of the method. The simple methane-ethane system, the methane-decane sys-

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* See footnote on p. 113.

Table 7. Comparison of Calculated and Experimental K Values In the System Propane (1)—Carbon Dioxide (2) $C_{12} = 0.147$: Data by Reamer, Sage, and Lacey (*28*)

T, °F.	P, lb./sq.in.abs.	x_1	K_1 Exp.	K_1 Calc.	% deviation	K_2 Exp.	K_2 Calc.	% deviation
40	200	0.8398	0.4720	0.4640	−1.637	3.768	3.873	+2.804
	450	0.3286	0.3993	0.3952	−1.022	1.294	1.310	+1.256
100	300	0.9074	0.7151	0.7106	−6.326	3.792	3.866	+1.975
	700	0.5260	0.5673	0.5571	−1.802	1.481	1.489	+0.544
160	500	0.9274	0.8807	0.8584	−2.54	2.523	2.552	+1.122
	800	0.7334	0.8276	0.8208	−0.83	1.474	1.443	−2.08

tem, representing applicability to systems with large differences in boiling points, and the methane-butane-decane ternary suggest wide applicability within a range of conditions in paraffinic systems. Mixtures containing nonhydrocarbons are represented by the ethane-hydrogen sulfide, propane-carbon dioxide, and hydrogen-ethane binaries.

The prediction of K values in the methane-ethane system was tested against the data of Price and Kobayashi (*22*). The results are listed in Table 4.* The average deviation of ±4.01% is very satisfying, in view of the fact that the validity of some data points has been questioned. The small bias observed in the deviations was not traced for explanation. However, the large discrepancies in predicting some specific values could be traced to disputable data points. As indicated, some scatter and uncertainties could be shown to exist for K values reported on this system by different sources (*3*, *22*, *23*).

Close to excellent agreement between calculated and experimental values was observed for the system methane-decane. The data were taken from Reamer, Olds, and Sage (*25*). Only six points were analyzed for establishing the interaction parameter C_{ij}. The comparison for this system is made in Figure 5. The solid curves are drawn through the experimental data, while the triangles represent the calculated values. Although not apparent, the agreement is especially good when the true critical points are approached. This aspect of the prediction method is discussed by the authors in another publication (*38*).

Since the reported phase equilibria data on the system butane-decane (*25*) do not readily translate into K values, the prediction of K values for the methane-butane-decane ternary required the estimation of the proper value of C_{23}. By studying data on several binaries containing hydrocarbons (*16*, *27*, *32*), the authors estimated the interaction parameter for this binary, given in Table 9. Sample results from the comparison of predicted values with experimental data taken from Reamer, Fiskin, and Sage (*24*) are given in Table 5. It was noted that some of the smoothed data tabulated for this system in section XXII of Sage and Lacey's monograph (*31*) represent extrapolations that could not be reproduced. The seemingly larger than expected deviations observed in the prediction of the butane and the decane K values may result from the assumed value of $C_{23} = 0.025$ that was used. As in the former cases, the predictions prove the validity of the method for high-pressure systems. Sample results of K values predictions in a seven-component system are given in another publication (*38*).

Good results were obtained in predicting the behavior of the hydrogen-ethane binary. These are given in Table 6. The negative interaction parameter established for this system is representative of the many observed for hydrogen-hydrocarbons systems. Since recent publications (*9*, *13*) dispute the validity of some of the data of Williams and Katz (*34*), the discrepancy in predicting the one data point at −200°F. and 8,000 lb./sq.in.abs. may not be considered a serious error.

Mixtures of carbon dioxide and hydrocarbons have been noted for their irregular behavior (*14*). Therefore, the good reproducibility obtained for the data of Reamer, Sage, and Lacey (*28*) on the carbon dioxide-propane binary listed in Table 7 deserves special attention. Several uncertainties about the method have been clarified with the prediction of the K values of the system ethane-hydrogen sulfide shown in Figure 6. The interaction parameter, established from only one data point, was good enough for predicting all the K values plotted. Although the so-called *experimental* values were obtained by interpolation of Kay and Brice data on dew and bubble points (*15*), both the azeotrope at 300 lb./sq.in.abs. and the true critical point at 800 lb./sq.in.abs. were reproduced. Better prediction of the azeotrope at 300 lb./sq.in.abs. was not tried in view of some uncertainties regarding the temperatures reported by Kay and Brice (*15*).

CONCLUSIONS

It has been demonstrated that the utilization of the Redlich-Kwong equation of state for describing the properties of pure compounds along their vapor-pressure curves requires temperature dependent coefficients a and b. Although when we consider the view that the packing of molecules is different in vapors and liquids, an assumption that at a given temperature a single equation of state, that is, one set of coefficients, can describe both phases was

Table 8. Summary of Data for Determination of Binary Interaction Coefficients

System	No. of binary points analyzed	Temp °F.	Pressures, lb./sq.in.abs.	Reference
Methane-ethane	3	−50	200, 600, 800	*22*
	2	−100	200, 600	
	2	−150	100, 200	
	1	−200	100	
Methane-butane	2	70	800, 1,750	*32*
	2	220	800, 1,200	
Methane-decane	2	160	1,500, 4,000	*25*
	2	220	1,500, 4,000	
	2	340	1,000, 3,000	
Propane,carbon dioxide	1	40	450	*28*
	1	100	700	
	1	160	800	
Ethane-hydrogen sulfide	1	102	800	*15*
Ethane-hydrogen	1	−125	4,000	*34*
	1	00	4,000	
	1	+50	400	

Table 9. Interaction Coefficients C_{ij} for the Sample Calculations and Comparisons Statistics

System	Reference	Establishing C_{ij}: No. of binary points analyzed	Establishing C_{ij}: Recommended C_{ij}	No. of K values tested	Prediction % deviation in K: Average ±	Prediction % deviation in K: Maximum
Methane-ethane	*22*	8	0.009	32	4.01	−27.61*
Methane-butane		4	0.024	18	2.05	4.86
Methane-decane	*25*	6	0.000	70	3.17	4.80
Butane-decane†	*26*	—	0.025	—	—	—
Propane-carbon dioxide	*28*	3	0.147	12	2.04	−6.33
Ethane-hydrogen sulfide	*15*	1	0.0980	35	2.79	13.36
Ethane-hydrogen	*34*	3	−0.286	16	5.11	35.28**
Methane-butane-decane	*24*	—		33	6.10	−39.59

* Questionable, see Table 5, the next largest deviation observed −15.86%.

† No vapor/liquid K ratios data, C_{ij} estimated.

** Questionable, see Table 7, the next largest observed was −4.38%.

validated as a good approximation. Furthermore, it has been demonstrated that a simultaneous solution of two relationships, one for density and one for fugacity, is necessary for establishing the two coefficients of the R-K equation for use in phase equilibria calculations. Thus, our procedure for establishing the coefficients a and b at the temperature of interest is different from procedures recommended heretofore (*6, 7, 35, 36*).

The present work demonstrated that the Redlich-Kwong equation with a single set of coefficients, established at the temperature of interest from vapor pressure, saturated liquid density, and generalized fugacity at saturation (*17*), is also capable of predicting acceptable (within 2.5%) saturated vapor-phase fugacities of individual compounds and K ratios in binary and multicomponent systems. Moreover, the utilization of a single set of coefficients enables predictions in the vicinity of the true critical point of a mixture.

It is a basic assumption of this method that a single binary interaction constant is sufficient to describe the interaction of two components and that binary interaction constants suffice to describe all interactions in multicomponent systems. Furthermore, it has been assumed that the binary interaction constant is independent of system temperature, pressure, and composition and may be established from even a single binary equilibrium point. These simplifying assumptions are a convenient way to treat multicomponent systems. As demonstrated in this work, the method based on these assumptions yields satisfactory results. The average deviation of ±3.7%, observed in predicting 390 K values, is a good validation.

It has been shown in this work and in previous publications (*2, 33, 36*) that equations of state are especially useful in predicting vapor/liquid equilibrium data for mixtures that contain compounds above their critical point. It follows, therefore, that an equation with two coefficients, generated from two pieces of information, density and generalized fugacity, would be preferred over any equation that utilizes many parameters. The more parameters to the equation, the more complicated is the assignment of interaction coefficients. It should be borne in mind, however, that the best results are obtained when conditions under which the interaction parameter are used approxi-

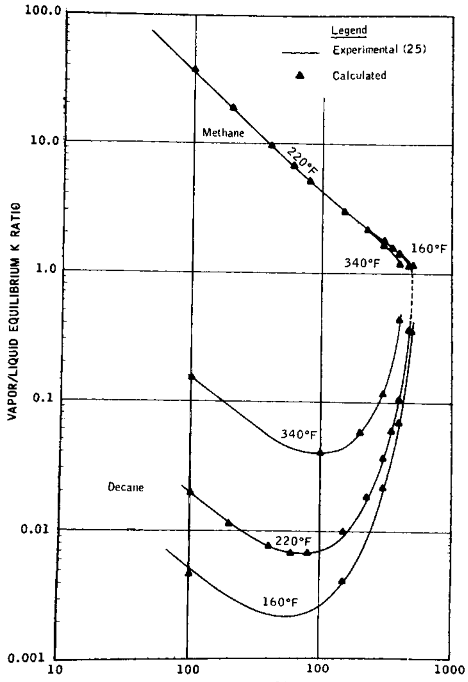

Fig. 5. Comparison of predicted and experimental K values in the system methane-decane.

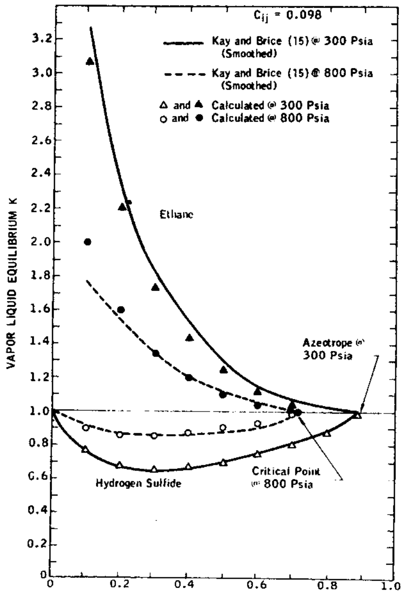

Fig. 6. Comparison of K values in the system ethane-hydrogen sulfide.

mate those of the data used in their determination. Thus, if large changes in temperature and pressure are envisaged, it may be necessary to establish the interaction parameters as temperature or pressure functions rather than pure constants. In the current work it was found sufficient to use one interaction parameter for each binary. It is quite likely that even better results can be obtained with two interactions parameter, one for R-K constant a and the other for the constant b. This approach has been discussed in an earlier paper (*14*).

In the present work it was observed that in hydrocarbon systems the mixing interaction parameters C_{ij} are somewhat smaller at relatively high pressures than those obtained at low pressures (below 100 lb./sq.in.abs. data). This could qualitatively explain some of the discrepancies between predicted and experimental K values.

The agreement between predicted K values and those obtained experimentally in the vicinity of the true critical point of mixtures suggests that the method proposed herein is especially applicable to multicomponent mixtures within that region. A comprehensive discussion and examples confirming the above statement are given in another publication by the authors (*38*). Although not shown in the examples, equally good results have been obtained in predicting K values by using Maxwell-Bonnell's and Riedel's correlations for predicting vapor pressures and liquid densities (*18*, *29*, *30*) instead of experimental data for establishing the R-K a and b constants.

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NOTATION

a, b = constants in Redlich-Kwong equation, Equation (6)
C_{12}, k_{12} = interaction constants for pair of components 1 and 2
K = y/x = vapor-liquid equilibrium ratio
n = number of components in mixture
P = pressure
P^0 = vapor pressure
R = gas constant
T = absolute temperature
V = molar volume
Z = compressibility factor
f = fugacity
x = mole fraction in liquid phase
y = mole fraction in vapor phase
ϕ = fugacity coefficient
ω = acentric factor
Ω = R-K coefficient following Chueh and Prausnitz

Subscripts

i, j, 1, or 2 = component i, j, 1, or 2
k = any component
ij or 12 = binary pair of components i and j or 1 and 2
c = critical state
r = reduced property
g = vapor or gas phase
l = liquid phase
m = mixture property

Superscripts

s = saturated state
L = liquid state
V = vapor state

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