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Calculation of Multicomponent Liquid-Liquid Equilibrium with Renon's and Black's Activity Equations

The combination of optimization theory and thermodynamics was used to develop a fast, reliable computerized procedure for predicting or representing multicomponent liquid-liquid phase equilibrium. Both the Renon and Black activity coefficient equations were compared with experimental data using the procedure. Experimental data for three quarternary systems from the literature were examined. Prediction of ternary data from binary data is not very reliable, although ternary data can nearly always be represented by adjustment of the predicted binary constants. Quarternary data can be predicted from accurate ternary representations of similar species provided the additional compound is from the same family group. The Renon equation is recommended rather than the Black equation.

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SCOPE

In the design of extraction equipment, it is necessary to represent graphically or analytically experimental liquid-liquid phase equilibrium data so that the data can be interpolated or extrapolated. In the past, this has been done primarily with algebraic, graphical correlations which lent themselves readily to graphical design procedures. Twenty-six calculation methods have been reviewed by Guffey (1971). These procedures can be time consuming and involve approximations.

Previous procedures can be divided into those intended for the correlation of ternary and quaternary experimental data and those for prediction of quaternary from ternary or

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ternary from binary data. Some of the procedures fall into both categories. These categories can be further subdivided into algebraic and geometric correlations and solution of activity equations by numerical and other methods. Solution of activity equations by numerical or optimization procedures was the method used in this research. This calculation procedure has been used by several authors in order to compare activity coefficient equations in ternary systems. Boberg (1960) used the Redlich-Kister equation, Chen and Kyle (1963) used the Van Laar and Margules equations, and Renon and Prausnitz (1968a, 1968b) used their NRTL equation.

It was the purpose of this research to develop a computerized procedure for representing multicomponent liquid-liquid phase equilibrium using activity coefficient equations. It was hoped that multicomponent equilibrium could be predicted from binary data alone by using activity equations containing constants that required only binary data for evaluation. This predictive ability could be valuable in screening potential extraction solvents prior to experimental evaluation as well as eliminating the need for a large amount of experimental data.

CONCLUSIONS AND SIGNIFICANCE

The calculation of multicomponent liquid-liquid phase equilibrium by numerical solution of the equal activity equations can be performed in less than two seconds of computer time (IBM 360/65) in most cases so that repetitive calculations in a trial-and-error design routine are now economically feasible. Prediction of ternary data from binary data is not very reliable—particularly near the plait point, although ternary data can nearly always be represented by adjustment of the predicted binary constants. Quaternary data can be predicted from accurate ternary representations of similar chemical species provided the additional species is from the same family group. The presence of highly immiscible binaries such as benzene-water makes the quaternary prediction difficult.

The Renon equation is recommended for the calculation of liquid-liquid equilibrium rather than the Black equation. Uncertainties in the formulation of the Black equation and the much greater tendency to yield multiple solutions to the liquid-liquid equilibrium equations make the use of this equation difficult. The Renon equation is much simpler to program and is more clearly derived from theoretical considerations by Renon. The difference in accuracy of the Renon and Black equations where both can be applied was not established by this research but is not thought to be appreciable.

ACTIVITY COEFFICIENT EQUATIONS

Activity coefficient equations are algebraic expressions which attempt to relate the activity of a component in a solution to the composition of the solution. Renon and Prausnitz (1968a) have derived equations from fundamental considerations of molecular forces. Black (1958) has modified the Van Laar equation with an empirical term. The Van Laar derivation accounts for only the internal energy change of mixing while the Renon equation accounts for both the enthalpy and entropy change of mixing.

Black's equation for a two-component system is

$$\log \gamma_1 = \frac{a^2_{12}}{\left(\dfrac{a^2_{12}x_1}{a^2_{21}x_2} + 1\right)^2} + C_{12}\left[x_2^2 + 12\,x_1^2x_2^2 - 8\,x_1x_2^2\right] \qquad (1)$$

Renon's equation is

$$\tau_{12} = \frac{D_{12}}{RT} \qquad G_{12} = \exp(-\alpha_{12}\cdot\tau_{12}) \qquad (2)$$

$$\ln \gamma_1 = \frac{\tau_{21}G_{21}}{\left(\dfrac{x_1}{x_2} + G_{21}\right)^2} + \frac{\tau_{12}G_{12}}{\left(\dfrac{x_1}{x_2}G_{12} + 1\right)^2}$$

Black has included the term in his equation containing the third constant C_{12} for the apparent reason that at infinite dilution the C_{12} appears as a correction to the Van Laar constant.

$$\log \gamma_1{}^\circ = a^2_{12} + C_{12}$$

Both Renon (1968a) and Black (1959) have presented the multicomponent forms of their equations. Expression of Black's empirical addition is not simple and has been the subject of much conjecture. The form used in this research is given in the dissertation by Guffey (1971).

The activity coefficient equations above require three constants to represent a binary system. These three constants a_{12}, a_{21}, C_{12}; D_{12}, D_{21}, α_{12} can be evaluated from three data points for immiscible binaries—the two mutual solubilities of the two components and the infinite dilution activity coefficient of one of the components in the other $\gamma_1{}^\circ$. At equilibrium, the activity of each of the components must be the same in the two immiscible phases. This criterion and the limiting value of the activity coefficient equation form a system of three equations in three unknowns.

$$(x \text{ Phase}) \quad \begin{matrix} a_1 = a_1' \\ a_2 = a_2' \end{matrix} \quad (y \text{ Phase}) \qquad (3)$$

$$\log \gamma_1{}^\circ = \lim_{x_1 \to 0} (\log \gamma_1) \qquad (4)$$

Using the activity equation

$$x_1\gamma_1 = y_1\gamma_1' \qquad (3a)$$
$$x_2\gamma_2 = y_2\gamma_2'$$

$$\log \gamma_1{}^\circ = \frac{D_{21}}{RT} + \frac{D_{12}}{RT}\exp\left(-\alpha_{12}\frac{D_{12}}{RT}\right) \quad \text{(Renon)} \quad (4b)$$

$$\log \gamma_1{}^\circ = a^2_{12} + C_{12} \quad \text{(Black)} \quad (4a)$$

The Renon or Black equation is used in Equation (3a) to represent γ or γ', the activity coefficients for the respective phases. Black has reduced Equations (3a) to one equation and Equation (4a) can be substituted into this to give one equation in one unknown C_{12}. This equation can be solved by a root finding or one dimensional search procedure. Equations (3a) cannot be reduced as before when using the Renon equation for the activity coefficients. Substitution of Equation (4b) for D_{12} in Equations (3a) yields two equations in two unknowns. This system has been solved by reduction of the equation residuals to zero using an optimization procedure.

For miscible binary systems, the three constants can be determined by a regression fit of constant temperature vapor-liquid data. Prausnitz et al. (1967) have recommended a procedure where the total solution vapor pressure is calculated with the activity coefficient equation and fitted to the experimental pressure data.

Black (1958) gives three graphical procedures for calculating the three constants for his equation from vapor-liquid data. Although his procedures can be computerized, they are still rather complicated and the more direct regression fit has been used in this work. Vapor-liquid and liquid-liquid binary constants are given in Tables 1 and 2 for both activity equations.

PHASE EQUILIBRIUM CALCULATION

The phase equilibrium calculation used here is based on the thermodynamic criterion of equilibrium that the activity of each of the n components is the same in all of the phases present. That is, for two phases

$$a_1 = a_1' \qquad (5)$$
$$a_2 = a_2'$$

where the $'$ indicates one phase and unprimed the other phase. Using the activity coefficient for a given component in the x or y phase,

$$\gamma_1 x_1 = \gamma_1' y_1 \qquad (6)$$
$$\gamma_2 x_2 = \gamma_2' y_2$$

where the γ_i is an exponential polynomial function of the mole fraction x's and γ_i' of the mole fraction y's. Renon's, Black's, or other activity equations can be used to represent the dependence of γ on x. This substitution yields a set of n nonlinear equations in x_i and y_i with a total of n unknown compositions. The number of unknown compositions is reduced to n-2 by using the stoichiometry relations. This is in accord with the phase rule which confirms that there are n-2 degrees of freedom for an n-component two phase system under constant temperature and pressure.

One method of solving Equation Set (5) is to formulate an optimization (minimization) problem using the sum of the squared residuals of each equation as an objective function.

$$R_i = (a_i - a_i') = 0 \qquad (7)$$

$$\text{OBJ FUNCTION} = \sum_i (R_i)^2 \qquad (8)$$

The optimization procedure varies the n unknown compositions until the objective function, Equation (8) has been forced to zero or as near as practical. The corresponding compositions represent the equilibrium phase compositions.

One complication in the solution of Equation (8) is the existence of the trivial solution where each phase has the same composition or $x_i = y_i$. This causes the objective function to be zero just as at the actual equilibrium composition. Previous investigators have relied on starting the search close enough to the desired solution so that the trivial solution is not found by the optimization routine. This can make the prediction of unknown equilibrium very difficult.

In this research, a constraint factor has been introduced into the objective function by modifying Equation (8) with a penalty function.

$$R_i = (a_i - a_i')/(x_i - y_i)^4 \qquad (9)$$

Near the trivial solution, the denominator goes to zero causing the objective function to grow very large. Of course, the numerator is going to zero at the same time so the denominator must approach zero faster. This is the reason for the fourth degree exponent. Too large an exponent can cause the objective function to decrease (where it would normally be relatively flat) due to x_i and y_i being far apart. This additional term erects a high barrier around the trivial solution without changing the location of the desired solution. Several types of penalty function have been used in this work although Equation (9) was the main one. Another more useful form may be

$$R_i = (a_i - a_i') \Bigg/ \left(\sum_{i=1}^{n} (x_i - y_i)^2 \right)^2 \qquad (10)$$

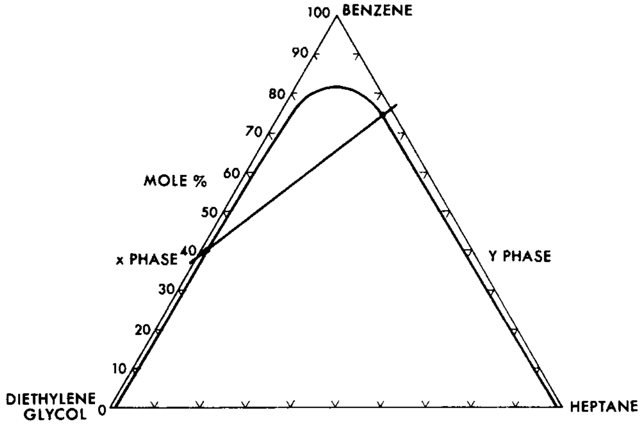

Fig. 1. Optimization surface profile paths diethylene glycol (1)—benzene (2)—heptane (3) 100°C. Black Equation.

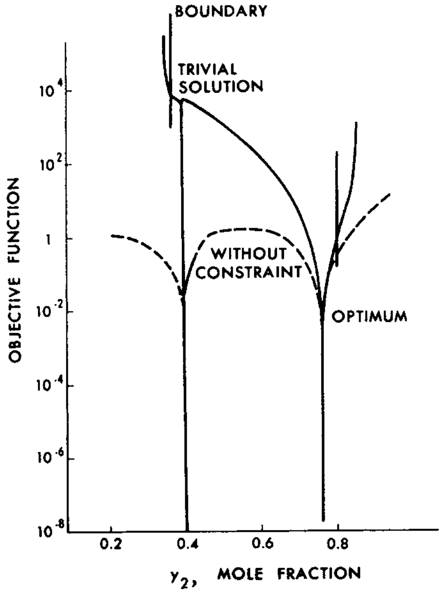

Fig. 2. Surface profile No. 1 corresponding to Figure 1. Effect of constraint.

In order to understand better the optimization problem, it was desirable to visualize the optimization surface. For a ternary system, there are three variable compositions and it was necessary to fix one of them and restrain the other two by moving along a line on the ternary diagram. As shown in Figure 1, the benzene-heptane-diethylene glycol system at 100°C. was used for this investigation. A tie line was determined with the optimization routine and Black's activity equation, yielding an objective function value of 1.2×10^{-8}. This tie line is represented by six mole fractions:

$$x_1 = 0.59644 \qquad y_1 = 0.02727$$
$$x_2 = 0.4 \text{ (Fixed)} \qquad y_2 = 0.7464$$
$$x_3 = 0.0056 \qquad y_3 = 0.22633$$

The x phase compositions were all fixed and the y compositions were varied along the tie line, although any straight line would serve the purpose. The objective function, Equation (8), was determined both with and without the constraint factor. These surface profiles are given in Figure 2 where the values of the objective function are plotted on a logarithmic scale versus the mole fraction of benzene in the y phase along the line. These and other profiles indicate that a narrow curved valley lies along the phase boundary with a very steep "hole" corresponding to the minimum.

Calculation of the ternary phase equilibrium in some cases yielded more than one equilibrium composition that satisfied the equal activity criterion of Equations (5). The problem arose from the highly immiscible, water-containing binaries and seemed to be more common when using the Black equation to represent the activities.

Binary Gibbs free energy of mixing plots are shown in Figures 3 and 4 for two of the more commonly used binaries in this research, butanol-water and benzene-water. Normally phase separation occurs only if a common tangent can be drawn to two points on the free energy curve as shown in Figure 3. Experimental vapor-liquid data for the butanol-water binary indicate that the third parameter $\gamma_1°$ used to calculate the immiscible binary Black and Renon constants is about 50 to 70. In calculating ternary data, it was desirable to use a higher $\gamma_1°$ in order to represent the ternary data better. It can be seen in Figure 3 that for $\gamma_1°$ above 60 to 80 for the Black equation and above 100 for Renon that other tangents can be drawn to the free energy curve. These secondary solutions are also obtained when calculating the binary miscibility from solution of the binary activity equations. The problem is even more acute for the benzene-water binary shown in Figure 4. Three secondary phase compositions were found for this binary at $\gamma_1° = 2{,}475$ when using the Black equation. None was found with the Renon equation at this value. These solutions occur when there is no minimum tangent to the curve but, on the contrary, at maximum points in the free energy curve. The abnormal tangents occur inside of the normal miscibility gap of the two liquids where the presence of two phases makes the free energy equation invalid. In this region, solution of the activity equations is not thermodynamically meaningful. The multiple solutions were a definite problem in calculating highly immiscible phase equilibria. Values of $\gamma_1°$

TABLE 1. BINARY ACTIVITY COEFFICIENT EQUATION CONSTANTS USED IN CALCULATING MULTICOMPONENT SYSTEMS WITH BLACK'S EQUATION

Binary (1)-(2)	T, °C	a^2_{12}	a^2_{21}	C_{12}	Data author
Acetone-benzene	45	0.2030	0.1792	0.045	Brown (1957)
Aniline-benzene	25	0.4457	0.3422	0.0118	Pannetier (1966)
Acetone-ethanol	32	0.3418	0.3531	0.0148	Gordon (1946)
	40	0.2934	0.3279	0.0054	Gordon (1946)
	48	0.2728	0.3088	0.0056	Gordon (1946)
	25	0.37	0.35	0.017*	
Aniline-methanol	20	0.2415	0.2825	0.0573	Weissenberger (1926)
	25	0.8415	0.1825	0.0573*	
Acetone-methanol	100 mm	0.2148	0.3461	−0.001	Chu (1950)
	760 mm	0.2803	0.2431	−0.0132	Chu (1950)
Acetone-water	25	0.8300	0.7549	0.0169	Beare (1930)
	25	0.788	0.491	0.144	Solomko (1962)
Butanol-ethanol,	760 mm	0.0275	0.056	0.0564	Hellwig (1953)
81° to 96°C	25	1.0	0.867	0.9945*	
Butanol-acetone	25	1.951	1.254	0.981	Solomko (1962)
Benzene-ethanol	45	0.5826	0.9627	0.0683	Brown (1954)
Benzene-butanol	25	0.5293	0.8173	0.1096	Allen (1939)
Benzene-methanol	10	1.054	0.8136	−0.1527	Schmidt (1926)
	20	0.9983	0.7415	−0.1992	Schmidt (1926)
	30	0.9338	0.6905	−0.1468	Schmidt (1926)
	25	1.1863	0.7595	0.499*	
Butanol-methanol	25	1.6	1.065	0.17*	
Butanol-water	25	1.746	1.4056	0.8254	Jones (1929), Butler et al. (1933)
	30	1.5778	0.6663	0.1295	Randall (1940)
Ethanol-methanol	10	−0.0172	−0.4385	−0.0276	Schmidt (1926)
	20	−0.0469	−0.0158	−0.0596	Schmidt (1926)
	30	0.0036	−0.0458	0.0111	Schmidt (1926)
	40	−2.11	−0.003	−0.0258	Schmidt (1926)
	25	−0.02	−0.02	−0.02*	
Ethanol-water	25	0.7153	0.4072	−0.0939	Dodson (1925)
	25	0.6923	0.3232	−0.0959*	
Methanol-water	25	0.2521	0.181	−0.0987	Butler et al. (1933)
	25	0.2021	0.131	−0.0987*	
Water-benzene	25	2.0569	2.8351	0.5505	Seidell (1952)

* Values actually used obtained from ternary data.

had to be chosen that gave no secondary solutions, usually at some sacrifice in accuracy of representing the experimental data, particularly with the Black equation.

No secondary points occurred in the multicomponent system that could not be traced to the immiscible binary. That is, the presence of other components did not induce secondary points.

OPTIMIZATION PROCEDURES

Six different optimization procedures were tested in solving the set of nonlinear activity equations given above. Hooke and Jeeves' (1961) Pattern search as programmed by Moore et al. (1968) is a very simple but effective multivariable, discrete search technique. Rosenbrock's (1960) procedure is similar to Pattern search but aligns the coordinate system with the principal axis of any valley present. Powell's (1965) Non-Derivative method uses a quadratic fit along a line to locate the minimum of the objective function. Davidon's (1959) method uses a quadratic approximation to the optimization surface to define a direction in which to search for the optimum. A one-dimensional quadratic fit is used to determine the minimum along the direction line. Powell's (1968) equation-solving routine and Law's (1969) Diagonal Discrimination are the most sophisticated used in this research. They involve a combination of two optimization procedures—one that performs better away from the optimum and one that is better near the optimum. Both use the residual from each equation as well as the sum of squared residuals in reaching the optimum. These two programs require the greatest storage but, as will be seen, Powell's equation-solving routine gives significantly better convergence to the final answer than all of the others.

In order to compare the six optimization procedures, two tie lines in the benzene-heptane-diethylene glycol system at 100°C. were calculated with each optimization routine. Two different starting points for each tie line were used to calculate the phase equilibrium composition. The starting and final composition for these ternary points differed by as much as 0.18 mole fraction. Two 5-component tie lines were also calculated with the starting and final compositions much closer. A comparison of the average execution times on the IBM 360/65 computer and the number of objective function evaluations is given in Table 3. Powell's (1968) equation-solving routine was by far the quickest and most reliable in terms of convergence. Convergence was faster with Renon's activity equation than Black's. The phase equilibrium program using Renon's equation requires 42,400 bytes of computer storage.

MULTICOMPONENT CALCULATED PHASE EQUILIBRIA

Three quaternary systems were found in the literature for which constituent ternary and binary data were available. The binary vapor-liquid and liquid-liquid data were used to evaluate the activity coefficient constants for Renon's and Black's activity equations. These binary con-

TABLE 2. BINARY ACTIVITY COEFFICIENT EQUATION CONSTANTS USED IN CALCULATING MULTICOMPONENT SYSTEMS WITH RENON'S EQUATION

Binary (1)-(2)	T, °C	$(g_{21} - g_{11})$	$(g_{12} - g_{22})$	α_{12}	Data author
Acetone-benzene	45	−69.4	390	0.3	Brown (1957)
Aniline-benzene	25	166	476	0.543	Pannetier (1966)
Acetone-ethanol	32	273	24.7	0.3	Gordon (1946)
	40	357	121.4	0.3	Gordon (1946)
	48	342	122.5	0.371	Gordon (1946)
	25	210	325	0.3*	
Aniline-methanol	20	467	−59.9	0.3	Weissenberger (1926)
	25	−1,458	2,453	0.424*	
Acetone-methanol	100 mm	300	99.2	0.8091	Chu (1950)
	760 mm	−45.4	471	0.2199	Chu (1950)
Aniline-water	20	1,682	2,383	0.2694	Speakman (1935)
	25	732	2,484	0.3356*	
Acetone-water	25	452	769	0.2138	Beare (1930)
Butanol-acetone	25	1,347	−547	0.188	Solomko (1962)
Butanol-ethanol,	760 mm	451	−325	0.3	Hellwig (1953)
81°-96°C	25	491	−225	0.05*	
Benzene-ethanol	45	1,244	486	0.5086	Brown (1954)
Benzene-butanol	25	1,085	463	0.6363	Allen (1939)
Benzene-methanol	10	−785	2,171	0.0445	Schmidt (1926)
	20	−1,264	2,669	0.0384	Schmidt (1926)
	25	−1,430	2,800	0.0372	Schmidt (1926)
	30	−1,628	3,065	0.0352	Schmidt (1926)
	25	−1,342	2,325	0.0239*	
Butanol-methanol	25	−126	381	0.4*	
Butanol-water	25	776	2,163	0.44	Jones (1929), Butler et al. (1933)
	30	518	2,163	0.393	Randall (1940)
Ethanol-methanol	10	−992	1,340	0.1595	Schmidt (1926)
	20	−274	265	0.2694	Schmidt (1926)
	30	−102	115	0.2183	Schmidt (1926)
	40	−176	172	0.2725	Schmidt (1926)
	25	−173	219	0.225*	
Ethanol-water	25	−621	1,579	0.1043	Dodson (1925)
Methanol-water	25	134	138.5	0.0286	Butler et al. (1933)
	25	−898	332	0.3369*	
Water-benzene	25	3,645	2,640	0.223	Seidell (1952)

* Values actually used obtained from ternary data.

stants were then used to calculate the immiscible ternaries, varying the γ_i^0 for the immiscible binaries to give the best fit to the ternaries. The values that could be used for γ_i^0 were severely restricted for the Black equation due to the desire to avoid secondary solutions. Usually the calculated fit was improved by varying some of the binary constants for the immiscible binaries. In order to do this, a regression fit of the calculated to the experimental tie lines was used. The Pattern search of Moore et al. (1968) was used to vary the constants and change the fit while Powell's (1968) equation-solving routine was used to calculate the ternary tie lines for comparison with the experimental. Boberg (1960) has attempted such a calculation using the Redlich-Kister activity coefficient equations but was forced to use approximate linearization of the activity equations because of poor convergence of his ternary calculation. The improved convergence of the ternary calculation used here has permitted the immiscible ternaries to be represented quite accurately using a regression fit, particularly with the Renon equation. All of the calculations were carried out with both the Renon and Black equations.

The constituent ternaries for the three quaternaries are shown in Figures 5 and 6. Figure 6 contains two quater-

Table 3. Comparison of Optimization Procedures

Optimization procedure and activity equation	Number of variables or components	Execution time, sec	Objective function evaluations*
Powell 1968			
Renon	3	0.5	23
	5	1.5	17
Black	3	0.9	34
	5	2.1	22
Law's Diag. Dis.			
Renon	3	2.3	87
	5	4.0	46
Davidon			
Renon	3	3.1	343
	5	88.2	5,800**
Powell Non-Deriv.			
Renon	3	2.5	249
	5	14.2	500**
Rosenbrock			
Renon	3	7.5	817
	5	28.5	1,042**
Pattern			
Renon	3	11.3	921
	5	39.9	1,500**

* Function evaluations equivalent to summing the squared residuals of three or five equations.

** Stopped prior to convergence.

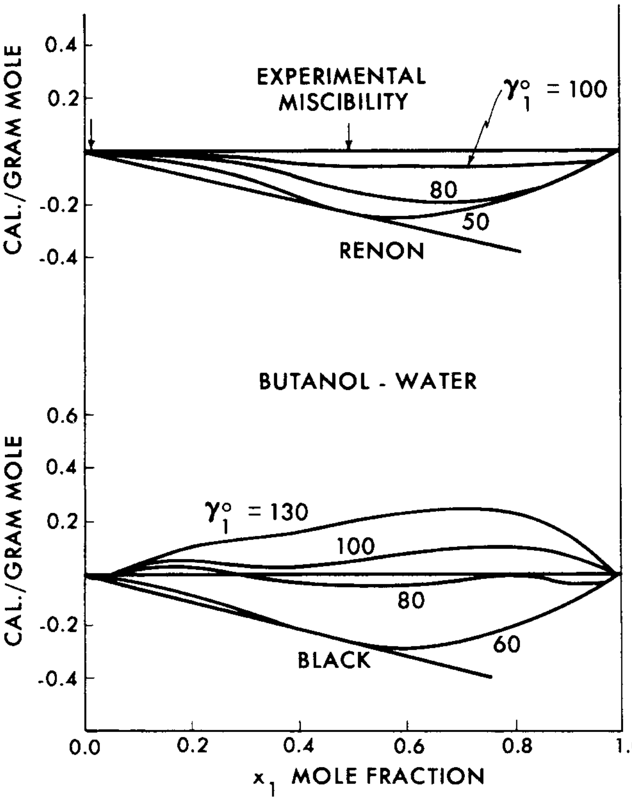

Fig. 3. Calculated molar Gibbs free energy of mixing versus mole fraction butanol at different infinite dilution activity coefficients for the butanol (1)—water (2) binary at 25°C.

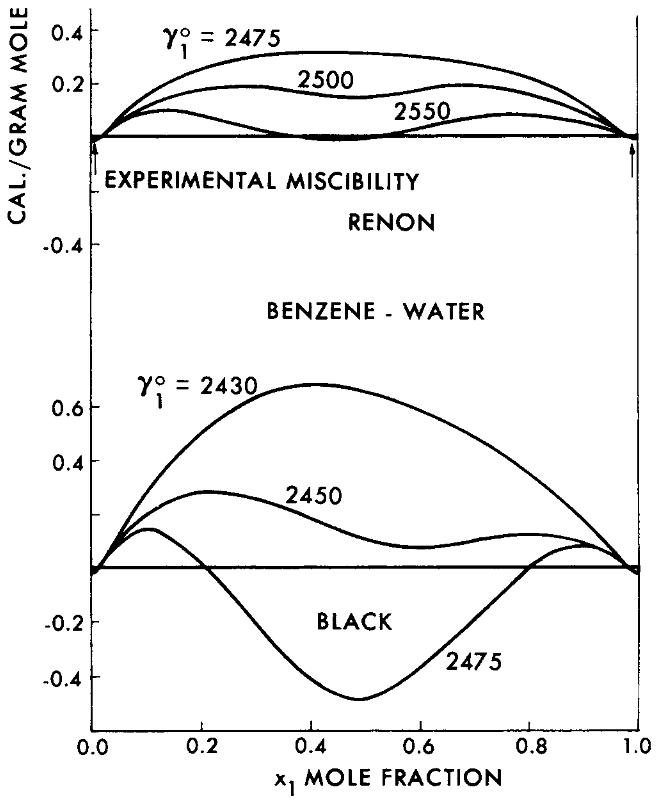

Fig. 4. Calculated molar Gibbs free energy of mixing versus mole fraction benzene at different infinite dilution activity coefficients for the benzene (1)—water (2) binary at 25°C.

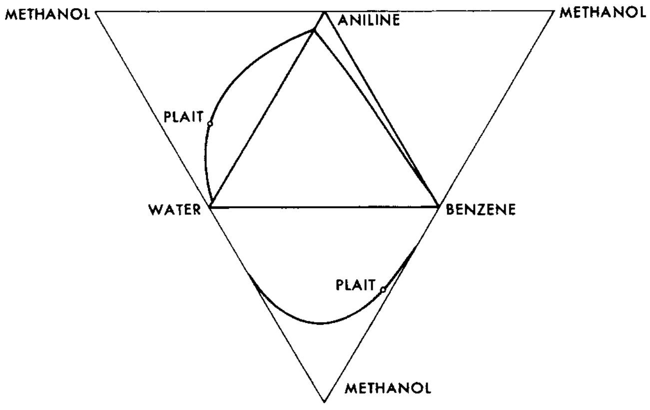

Fig. 5. Ternaries for water-methanol-aniline-benzene quaternary tetrahedron, unfolded and viewed from above. Mole fraction.

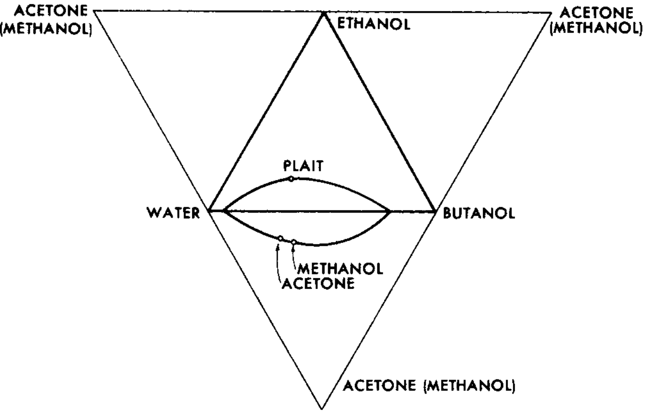

Fig. 6. Ternaries for the water-ethanol-butanol-acetone quaternary tetrahedron, unfolded and viewed from above. Mole fraction.

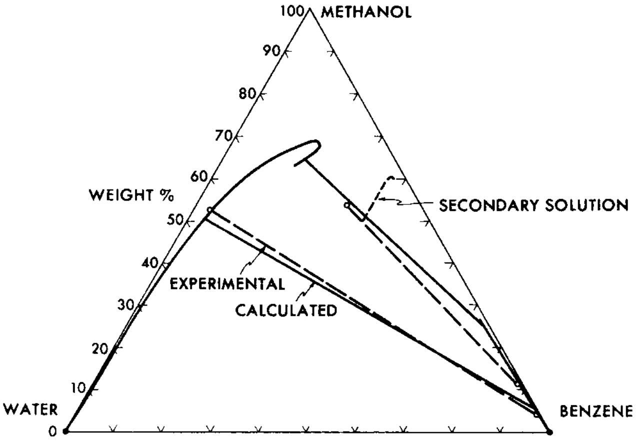

Fig. 7. Phase equilibria for the water-methanol-benzene ternary at 25°C. using Black's activity equation.

naries differing by only the fourth component—acetone and methanol. The constituent ternaries are quite similar for these systems. The tetrahedron normally used to represent the quaternary has been folded open and viewed from above. Only the ternary boundaries are shown and the quaternary surface connecting these lines must be imagined.

The binary constants used for each quaternary are given in Table 1 for Black's equation and in Table 2 for Renon's equation. The additional constants required for the five- and six-component systems are also given. In some cases, the constants actually used differed from the values calculated from binary vapor/liquid data. These constants were obtained by adjusting the vapor/liquid (V/L) constants to give a better fit to the experimental ternary data using the ternary regression program as discussed previously.

Figure 7 illustrates the problem of multiple solutions to the activity equations for a highly immiscible ternary system when using Black's activity equation. The dotted line representing the methanol-rich phase satisfied the optimization criteria the same as the solid line. Another problem here was the hook at the top of the diagram. This may have been caused by the presence of another secondary solution. Several attempts were made to overcome these problems without success, and calculation of this system with Black's equation was not successful. These problems were not encountered using Renon's equation, and the calculation of the quaternary containing this ternary was completed.

The water-methanol-aniline-benzene quaternary is shown in Figure 8 at different methanol contents. The quaternary surface has been projected directly into the bottom plane of the tetrahedron—as though it were the shadow from an overhead light. The water-rich phase is barely visible in the lower left corner. It was extremely difficult to obtain convergence to the equation solution for this quaternary at methanol contents greater than 18%. The objective function could not be reduced below 10^{-2} in most cases indicating that no solution to the activity equations existed. The desired value was usually 10^{-6} to 10^{-8}. Figure 9 shows the selectivity of benzene relative to aniline as very irregular curves. There is no experimental data for comparison to Figure 9, but it is unlikely that it is so irregular. A comparison of the data in Figure 8 to experimental data is presented later. Apparently, both of the activity equations fail in attempting to represent a system so diverse as this. The highly immiscible benzene-water binary is certainly the problem here.

The ternary system shown in Figure 10 forms the basis for the other multicomponent systems studied. The best fit that could be obtained by adjusting the Black constants to fit the data gave too large an immiscible region. The adjustment of the constants was restricted by the need to avoid secondary solutions due to the water-butanol binary. The Renon equation fit quite well and is not

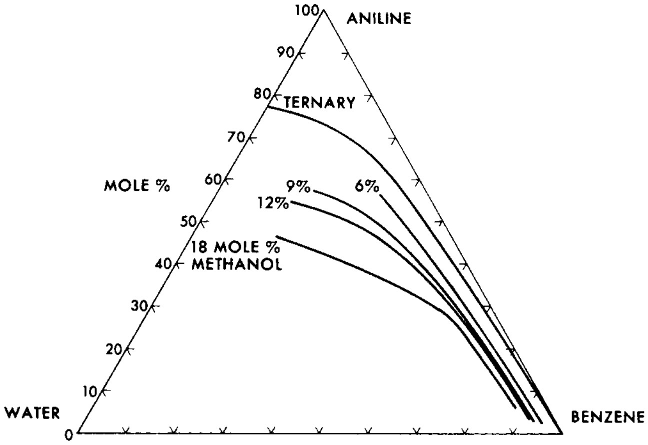

Fig. 8. Phase equilibria for the water-methanol-aniline-benzene quaternary at 25°C. using Renon's activity equation.

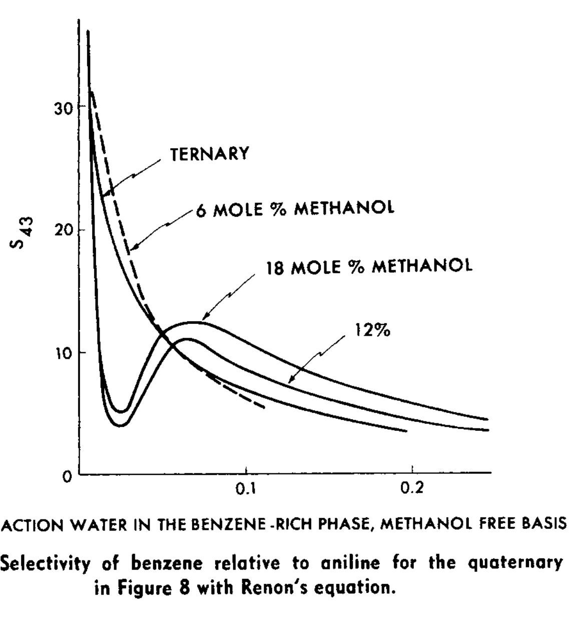

Fig. 9. Selectivity of benzene relative to aniline for the quaternary in Figure 8 with Renon's equation.

shown. The predicted vapor-liquid fit was very far from the experimental data as indicated by the dashed curve.

In Figure 11, one of the other immiscible ternary systems making up the quaternaries studied is shown. The Renon equation fit the ternary data quite well and only the Black equation representation is given. Again, the constants could not be adjusted to improve the fit of the Black equation to the experimental data because of limitations imposed by the potential presence of secondary solutions. The result was the same as in Figure 10—the calculated phase envelope was larger than the experimental using the Black equation.

In Figure 12, the calculated quaternary surface is shown projected into the water-ethanol-butanol ternary at different acetone compositions using Renon's equation. With the Black equation, the figure is quite similar except for a larger immiscible region due to the larger constituent, ternary, immiscible regions presented previously. The calculated selectivity is given in Figure 13.

The calculated quaternary phase equilibria for the third quaternary is given in Figure 14, again projected onto the ternary base. The Black equation gave a similar, but somewhat larger, immiscible region and is not shown. The selectivity plot in Figure 15 shows very little change in selectivity with methanol addition.

In order to demonstrate the capability of the calculation procedure, three 5-component and one 6-component systems were calculated, based on binary activity data. No experimental data were available for comparison but the multicomponent effects seemed logical based on the available ternary and quaternary data. The six-component system is shown in quaternary form in Figures 16 and 17. Three of the components were grouped into one pseudocomponent for presentation purposes only.

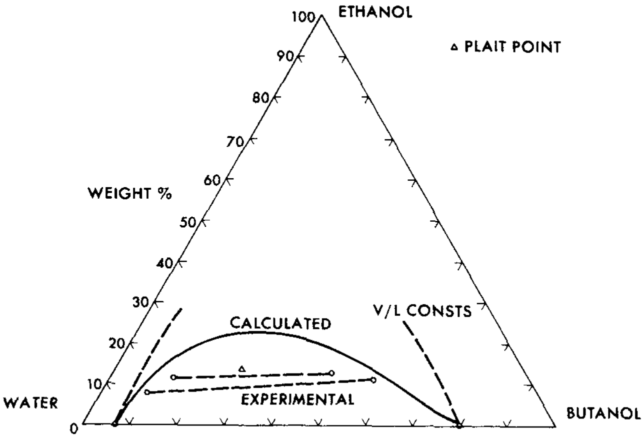

Fig. 10. Phase equilibria for the water-ethanol-butanol ternary at 25°C. using Black's activity equation.

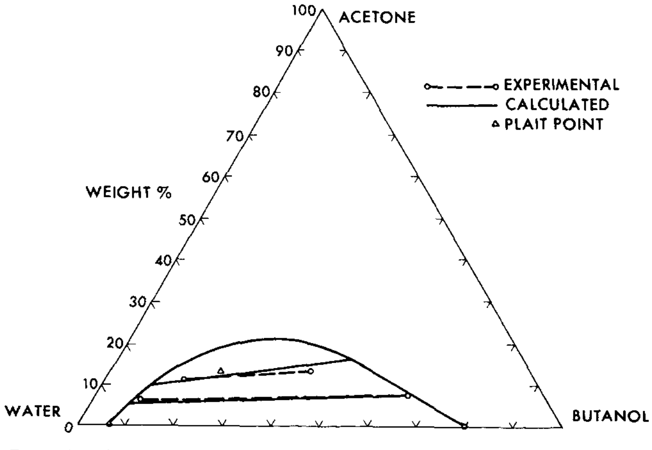

Fig. 11. Phase equilibria for the water-acetone-butanol ternary at 25°C. using Black's activity equation and Solomko's data.

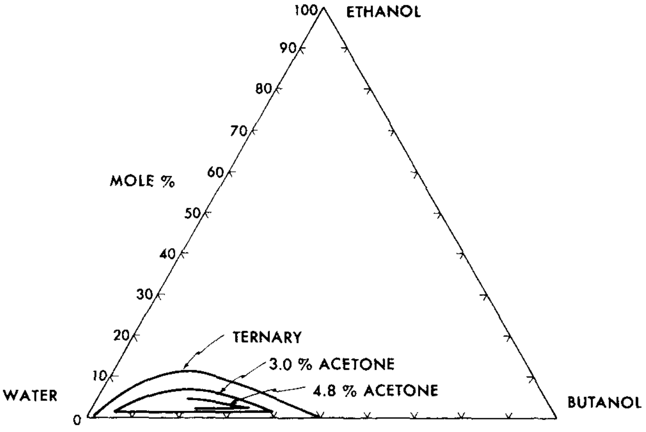

Fig. 12. Calculated phase equilibria for the water-ethanol-butanol-acetone quaternary at 25°C. using Renon's activity equation.

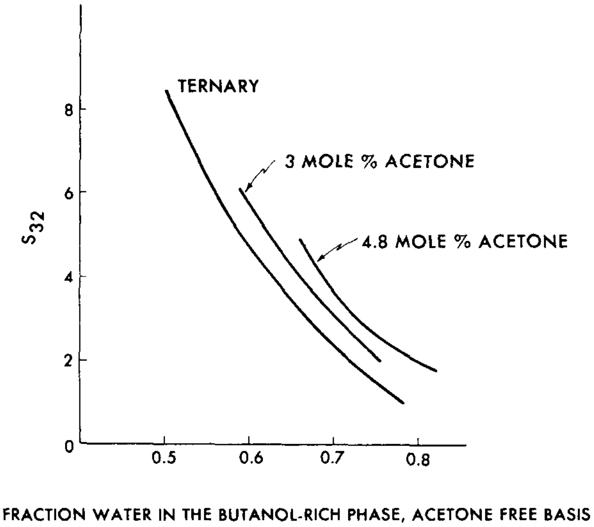

Fig. 13. Selectivity of butanol relative to ethanol corresponding to quaternary in Figure 12 with Renon's equation.

EXPERIMENTAL COMPARISON

No direct comparison has been given above between the calculated and experimental quaternary equilibria. This was due to the quaternary data being obtained by the different authors in a way that could not be easily presented on the quaternary figures. The experimental data were mostly taken at scattered compositions rather than at a fixed level of one component. Therefore, to form this comparison, a number of representative experimental points were calculated with the phase equilibrium calculation.

In two of the quaternaries, no tie lines were given, only the equilibrium surface location. In these two cases, only one of the four compositions in one phase could be compared—two were arbitrarily fixed by the phase rule and one by stoichiometry. In the second quaternary, tie line phase equilibrium data were available and the compositions of both phases were compared to the experimental data. Two of the compositions were fixed at the experimental values by the phase rule and two were determined by stoichiometry—leaving only four for comparison with the experimental data. Selection of two of the compositions arbitrarily at the experimental values throws all of the error into the other compositions. A more judicious selection of the two fixed compositions (presumably by trial and error) could probably reduce the Root-Mean-Square errors given in Table 4 by up to 20%.

The first quaternary in Table 4 was the most nonideal and contained the highly immiscible benzene-water binary. In light of the peculiar behavior of the system in Figures 8 and 9 above, the largest root mean square error in the calculation was not surprising. The Black equation was not used due to the occurrence of multiple solutions to the activity equation. In the second quaternary, the experimental data show that the size of the immiscible region increases markedly as acetone is added, with ethanol compositions as high as 22 mole percent. The low values of the acetone-ethanol binary constants obtained from vapor/liquid data (Tables 1 and 2) do not indicate such an interaction. The experimental data also show that at high ethanol content the relative acetone content of the two phases reverses and the water phase has the higher

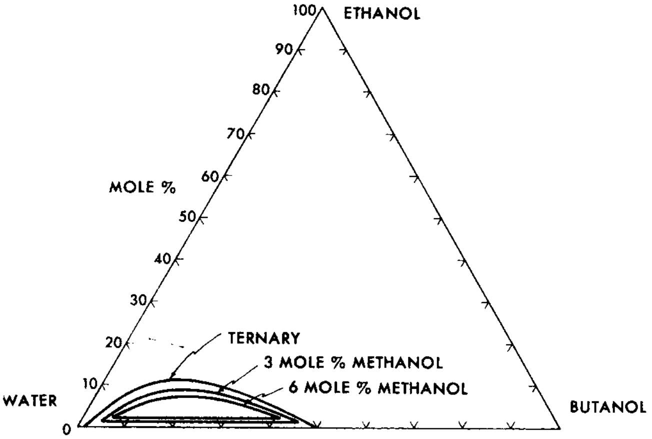

Fig. 14. Calculated phase equilibria for the Water-ethanol-butanol-methanol quaternary at 25°C. using Renon's activity equation.

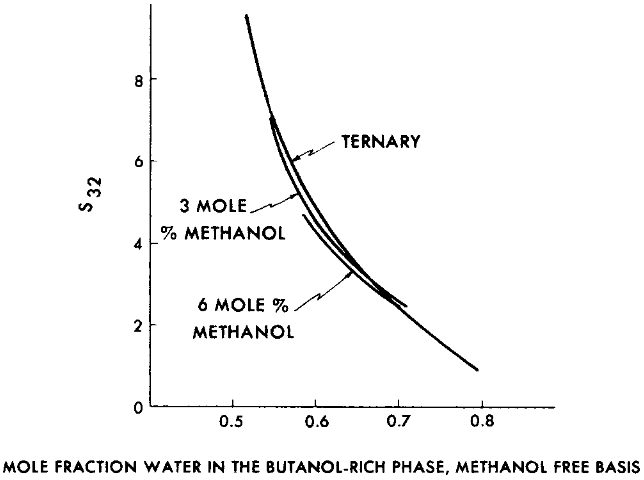

Fig. 15. Selectivity of butanol relative to ethanol corresponding to Figure 14 with Renon's equation.

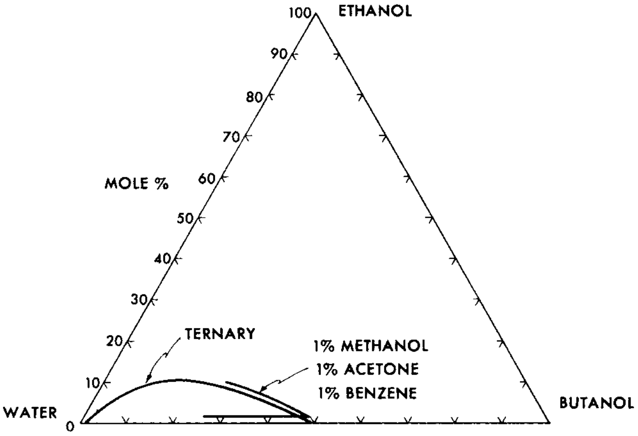

Fig. 16. Calculated phase equilibria for water-ethanol-butanol-methanol-acetone-benzene six-component system at 25°C. using Renon's equation.

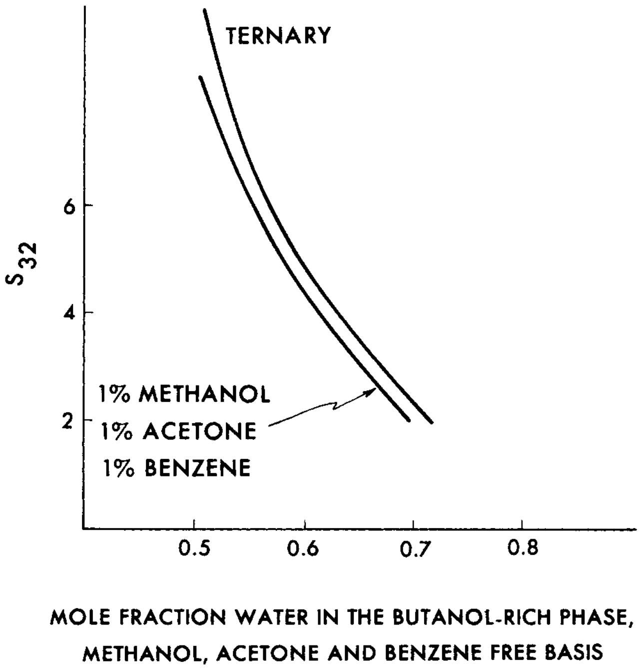

Fig. 17. Selectivity of butanol relative to ethanol for system in Figure 16 with Renon's equation.

TABLE 4. ROOT MEAN SQUARE DEVIATIONS BETWEEN EXPERIMENTAL AND CALCULATED QUATERNARY PHASE EQUILIBRIA

Quaternary	Number of points	Number compositions	Root mean sq deviation, mole fraction Renon	Black	Exp'l. data source
Water-methanol-aniline-benzene	5	5	0.049	—	Francis (1954) Leikola (1940)
Water-ethanol-butanol-acetone	5	20	0.034	0.023	Solomko (1962) Jones (1929)
Water-ethanol-butanol-methanol	4	4	0.0145	0.012	Frolov (1968) Mueller (1931)

acetone composition. This was not predicted with the quaternary calculation (Figures 12 and 13). The Black equation gives a better representation of the quaternary data than Renon's due to compensating errors. As pointed out above, the immiscible region calculated with the Black equation for the ternaries was too large. This error causes the calculated quaternary immiscible region to be large and gives a higher ethanol content than the Renon equation. This coincides with the increased region of immiscibility of the experimental data due to the strong acetone-ethanol interaction but for a different reason. A similar reasoning applied to the third quaternary although the errors are much smaller here and primarily due to inaccuracies in fitting the ternary systems.

ACKNOWLEDGMENT

Work was supported by Phillips Petroleum Company and NDEA fellowships.

NOTATION

a_i = activity of component i
a^2_{ij} = Black's constant for ij binary
C_{ij} = Black's constant for ij binary
C_i = arbitrary constant
D_{ij} = Renon's constant $(g_{ji} - g_{ii})$ for ij binary, cal/g.-mole
g_{ij} = interaction energy
n = number of components
R = gas constant
R_i = equation i residual
R_{ij} = Black's ratio, a^2_{ij}/a^2_{ji}
S_{ij} = selectivity of component i relative to component j
T = temp., °C. or °K.
x_i, y_i = phase composition
α_{ij} = Renon's constant for ij binary
γ_1^0 = infinite dilution activity coefficient of component 1 in 2
γ_i = activity coefficient of component i

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Manuscript received November 5, 1971; revision received April 11, 1972; paper accepted April 12, 1972.