Application of the Wohl Equation to Ternary Liquid-Vapor Equilibria

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The use of the Wohl equation for activity coefficients is tested successfully for the most nonideal ternary systems for which experimental data could be found. The three-suffix form possessing seven constants is found to be successful in many cases. Owing to the high degree of nonideality resulting from one or more components being polar, however, the four-suffix form employing up to ten constants was required for ten of the twenty-five ternaries studied. Regardless of the form chosen, all the constants but one, C^*, are derived from phase equilibrium data on the constituent binaries.

The ternary constant C^* was found to be approximately zero. In only two instances did its value not fall in the region of —1.0 to +1.0. With the use of the binary constants and C^*, predictions of vapor compositions were made for each experimental ternary liquid composition, temperature, and pressure. The results so obtained yielded average absolute errors in predicted vapor mole fractions, without respect to sign, as follows: for ten systems, less than 0.01; for seventeen systems, less than 0.02; and for twenty-four systems, less than 0.03. For an additional three sets the error was still less than 0.05. Results were analyzed statistically for twenty-two of the systems determining mean values of the vapor mole fraction deviations and the confidence limits of the means.

The mass testing of the Wohl equation reported here far exceeds the sum of all work previously published in the literature. It appears that this equation provides a very good way of expressing liquid nonideality for a wide range of components.

This paper reports on the first part of a large-scale program underway at The M. W. Kellogg Company for representing the phase equilibria of any system whatever by a single approach. This program will include ideal and nonideal liquids in the presence of an ideal or nonideal vapor. Components may be polar or nonpolar, hydrocarbons, or nonhydrocarbons. Eventually it is hoped to include enthalpy as well as phase equilibrium in our single approach.

Initial work, reported herein, dealt with systems whose liquid phases were as nonideal as could be found in the literature. One or more of the components in each mixture was polar. Only ternary data were included. Pressures were atmospheric or below; the vapor phases were considered ideal.

Many equations have been proposed for describing the effect of liquid composition on phase equilibria at constant temperature and pressure. The Margules form of the Wohl equation was selected here. It permits a simple framework for expanding results on three-component systems to multicomponent ones. It is an empirical expression and we do not attach undue importance to its significance in terms of molecular interactions. Nevertheless, its constants are not meaningless and empirical; on the contrary, they are derived from thermodynamic relationships. Most of these constants can be obtained from equilibrium data for the three constituent binaries making up each ternary, in contrast to the constants of some equations, which are obtainable only from curve-fitting procedures applied to the multicomponent data. Frequently the use of these binary constants alone is sufficient to predict the multicomponent data. The three-suffix form was chosen for initial applications. When it was found to be unsatisfactory for some highly nonideal solutions a four-suffix equation was successfully applied.

It is the purpose of this paper to report the results of the rather extensive studies of both of these forms of this equation and to list the constants for a few systems not previously available in the literature.

BINARY FORM OF THE BASIC EQUATION

The Margules equations for components 1 and 2 of a binary system are well known in the form publicized by Carlson and Colburn (*5*). They are, respectively

$$\begin{aligned}\log \gamma_1 &= x_2^2\,[A_{12} + 2(A_{21} - A_{12})x_1] \\ \log \gamma_2 &= x_1^2\,[A_{21} + 2(A_{12} - A_{21})x_2]\end{aligned} \qquad (1)$$

These are for the three-suffix cases as required to furnish the constants appearing in the corresponding equation given below for ternary systems. The analogous four-suffix expressions for a binary system, which are not as well known, make use of an additional binary constant D. They are

$$\begin{aligned}\log \gamma_1 &= x_2^2\,[A_{12} + 2(A_{21} - A_{12} - D_{12})x_1 + 3D_{12}x_1^2] \\ &\qquad (2) \\ \log \gamma_2 &= x_1^2\,[A_{21} + 2(A_{12} - A_{21} - D_{12})x_2 + 3D_{12}x_2^2]\end{aligned}$$

BASIC EQUATION USED FOR TERNARY MIXTURES

The Margules form of the Wohl equation describes the influence of the liquid composition on the activity coefficient of the component in question. The expression shown below is from Wohl's 1953 modification (*59*) of his 1946 paper (*60*). It utilizes the ternary constant C^* rather than C. This has the advantage that the value of C^* is independent of which component is assumed to be 1, 2, and 3. It is as follows in the four-suffix form:

$$\begin{aligned}\log \gamma_1 - x_2^2\,&[A_{12} + 2x_1\,(A_{21} - A_{12} - D_{12}) + 3x_1^2D_{12}] + \\ &x_3^2\,[A_{13} + 2x_1\,(A_{31} - A_{13} - D_{13}) + 3x_1^2D_{13}] + \\ &x_2x_3\,[1/2\,(A_{21} + A_{12} + A_{31} + \\ &\qquad\qquad A_{13} - A_{23} - A_{32}) + \\ &x_1\,(A_{21} - A_{12} + A_{31} - A_{13}) + \\ &\qquad\qquad (x_2 - x_3)\,(A_{23} - A_{32}) + \\ &3x_2x_3D_{23} - (1 - 2x_1)\,C^*]\end{aligned} \qquad (3)$$

Evidently exchanging subscripts 2 and 3 does not alter the equation. The three-suffix form may be obtained simply by setting $D = 0$.

PREVIOUS WORK REPORTED FOR TERNARY SYSTEMS

The three-suffix Margules equation was employed by Jordan, Gerster, Colburn, and Wohl (*24*) to represent their experimental data for the following systems: isobutane–1-butene–water, isobutane–1-butene–furfural, isobutane–water–furfural, 1-butene–water–furfural. They also similarly studied the quaternary system isobutane–1-butene–water–furfural.

Severns, Sesonske, Perry, and Pigford (*43*) applied the three-suffix equation in the C^* form to the systems acetone–methanol–methyl acetate and acetone–methanol–chloroform. For acetone–methanol–carbon tetrachloride, they found it necessary to use the four-suffix equation. Experimental data studied were their own.

Kenny (*23*) successfully applied the three-suffix equation, in the only known instance involving liquid-liquid data, for the system isooctane–furfural–benzene.

Subba Rao and Venkata Rao (*48*) pointed out that they were highly successful in working with the three-suffix Margules-Wohl equation.

Hollo, Ember, Lengyel, and Weig (*18*) applied Wohl's equations to four ternary systems each having only two or three experimental points. With so few points, the authors feel that a serious study of their systems is not warranted when a general correlation is the aim.

Griswold and Wong (*15*) made use of the three-suffix equation in their study of their experimental work on the system acetone–methanol–water.

SYSTEMS STUDIED IN THIS WORK

A complete list of all the systems tested in the present work may be found in Table 2. Also shown there is a record as to whether a given system was tested with the three-suffix, four-suffix, or both forms of the equation.

PROCEDURE FOLLOWED IN STUDYING THE DATA

Before going into the details of the procedure followed in this investigation, a brief summary of the approach taken to the problem will be given.

A seven-constant equation was selected which was expected thermodynamically to represent the liquid phase compositional effects on the phase equilibrium of ternary systems. Six of these constants were immediately derived from the binary equilibrium data. With a series of arbitrarily selected values for the seventh (ternary) constant, this equation was used to calculate the vapor phase compositions based on experimental liquid compositions published in the literature. The predictions were compared with the published values of the vapor compositions. An analysis of these results determined: (1) the best value for the seventh constant and (2) which systems required the use of a more complicated thermodynamic expression. For the latter systems a ten-constant equation was applied. Nine of the ten constants were obtained directly from the binary data and the best value of the tenth (ternary) constant was derived in the manner described for the simpler form of the equation. After testing only a few systems it became evident that the value of the ternary constant was in the neighborhood of zero. Values tested were then restricted to the range of +1.5 to −1.5.

At the start of the study of the application of the Wohl equation to the correlation of multicomponent nonideal liquid-vapor equilibrium data, certain assumptions were made and a restricted area was selected.

The assumptions were: (1) that Wohl's C^* equation rather than the one based on C should be tried; (2) that the data chosen from the literature were sufficiently thermodynamically consistent to be used; (3) that a three-suffix equation, that is, one with seven constants, for a ternary system, would be sufficient at the outset; and (4) that the Margules type of expression was more suitable for this problem than a Van Laar type, owing to the special restrictions placed on the binary constants in the latter. The area for initial study was confined to the following: (1) three-component systems; (2) low pressures where the vapor phase could be assumed ideal in every way; and (3) essentially nonhydrocarbon systems, although one of the components might be a hydrocarbon.

CALCULATIONS

Once a set of ternary data was selected for testing, phase equilibrium data for each constituent binary were located and the binary constants were obtained as discussed in a later section. Sufficient data were processed to permit plots of these constants to be constructed as a function of reciprocal absolute temperature over the range of the ternary data, as shown in Figure 4.

For each experimental ternary point liquid mole fractions and constants at the temperature in question were inserted in Equation (3). For seven arbitrary values of C^*, generally between ±1.5, activity coefficients were then calculated for each of the three components. Because calculations were carried out by a computer, as many as fifty experimental points were handled for a single system. By allowing for the seven different values of C^* which were tried, this was equivalent to storing data on three hundred and fifty points.

After computing $\log \gamma_i$ for each of the three components as a function of the six A_{ij}'s and the three x_i's, equilibrium constants K_i's were computed from

$$K_i = \gamma_i p^\circ_i / \pi$$

These K's were converted to relative volatilities, α's, by letting

$$\alpha_1 = \frac{K_1}{K_3}$$

$$\alpha_2 = \frac{K_2}{K_3}$$

$$\alpha_3 = 1.0$$

Then three normalized y's, which totaled exactly 1.0, were obtained from the equation

$$(y_i) \text{ pred.} = \frac{\alpha_i x_i}{\sum_1 \alpha_i x_i}$$

Finally, deviations were calculated for each experimental point for each component on the basis:

$$\Delta y = y_{\text{pred.}} - y_{\text{obs.}}$$

For each component the average of these deviations over a specific set of data was calculated. By doing this for each of the seven trial values of C^*, a plot similar to Figure 1 was developed. By observing the minimum point of the parabola the optimum C^* is apparent.

In obtaining the average absolute deviations, the Δy's were averaged without respect to sign. All three components were included even though the Δy for the third component was fixed by those of the first two. This avoided the problem of deciding which component should be disregarded for those systems where one component is so scarcely volatile that y, and hence Δy, must be very small. This graphical procedure of determining the optimum C^* is only one of many possible ones, but it appears to be the simplest.

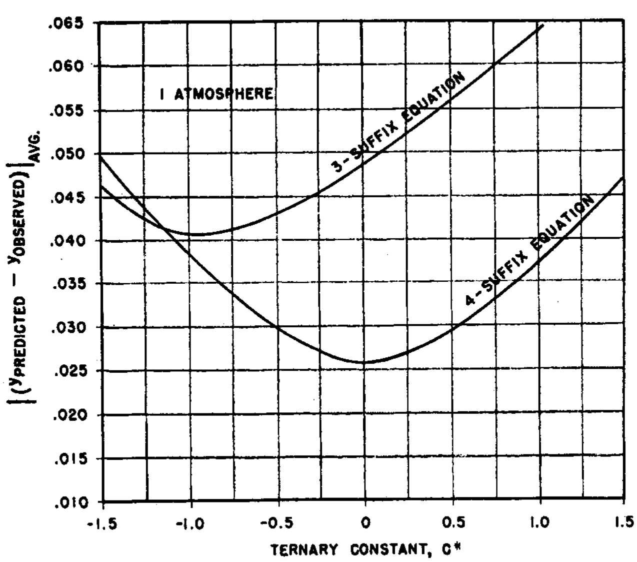

Fig. 1. Influence of C* on vapor phase predictions; isooctane-toluene-furfural system.

If the minimum average deviation as read from the plot for the three-suffix equation application was ~0.025 mole fraction or less, the quality of fit of the data was deemed satisfactory. If not, then the four-suffix form of the Margules-Wohl equation, Equation (3), was applied and the entire procedure as described for the three-suffix form was repeated. A new Δy vs. C^* curve was obtained as shown in Figure 1.

A plot having this same form was constructed for each of the twenty-five systems studied. Because of space considerations only one is shown, but data obtained from all twenty-five are given in Table 2.

A second program was employed to study the results statistically in the predictions of the vapor compositions as described in the section on "Results." In contrast to the first program, which was designed for application to one system at a time, the statistical program processed the results from all the various systems as a unit.

DETERMINATION OF THE BINARY CONSTANTS

For the three-suffix equation binary constants A_{ij} and A_{ji} were frequently available in the literature; quite often they were reported with the experimental data. Otherwise they were computed from plots of $(\log \gamma_i)/x_j^2$ as a function of x_i. The value of A_{ij} is simply the intercept at $x_i = 0$.

In the case of the four-suffix equation the extra binary constant D must be computed. The techniques suggested by Gearhart (*11*) were used in arriving at these coefficients because they qualitatively indicate the degree of thermodynamic consistency of the data. However, conventional least-squares procedures can be utilized. Four-suffix constants are so sparsely reported in the literature that all such coefficients used were our own. Figure 2 illustrates one simple graphical procedure for obtaining the constants.

The magnitude of these constants permitted us to judge the degree of nonideality of the ternary system. Every effort was made to select highly nonideal ternary systems for the study.

RESULTS

Before covering the results of this investigation in detail, our findings may be summarized as follows:

1. The three- or four-suffix form of the Margules-Wohl equation has been successfully applied to twenty-five ternary systems. Six binary constants were found to be sufficient to represent fifteen of these systems; that is, only the three-suffix form was necessary. Nine binary constants were required for the remainder in making use of the four-suffix form.
2. One ternary constant was used for each system but in all cases the optimum value was close to zero. The average value for all the systems studied was 0.22.
3. Vapor compositions were predicted by using the binary and ternary constants and were compared to experimental values. A statistical study was made of the resulting deviations in the compositions including the mean error of vapor composition and the standard deviation of the mean error. Confidence limits for the predictions were obtained. The mean errors of the predicted vapor mole fraction were compared with values that might be expected as a result of experimental errors.
4. An analysis of the influence of temperature on the A_{ij} constants in the Wohl equation indicated that the relationship sometimes recommended is quite successful; namely, $(A \times T)$ is a constant. This relationship can be derived from the work of White (*57*) and Yu and Coull (*61*).

Comparison of Predicted with Observed Vapor Compositions

Given a set of constants to insert in the Margules form of the Wohl equation, a design engineer will want to know how close to observed vapor compositions his computer compositions will come for given liquid compositions. This was exhaustively studied with respect to: (a) the absolute deviation of predicted y's from observed y's, where y is the componential vapor mole fraction, and (b) the percent absolute deviation in predicted y's as a function of the amount of the component present in the liquid.

The average absolute difference in $y_{\text{pred.}}$ and $y_{\text{obs.}}$, taken without respect to sign, has been summarized below for twenty-seven sets of data comprising the twenty-five systems studied:

For ten systems
$|y_{\text{pred.}} - y_{\text{obs.}}|$ is less than 0.01

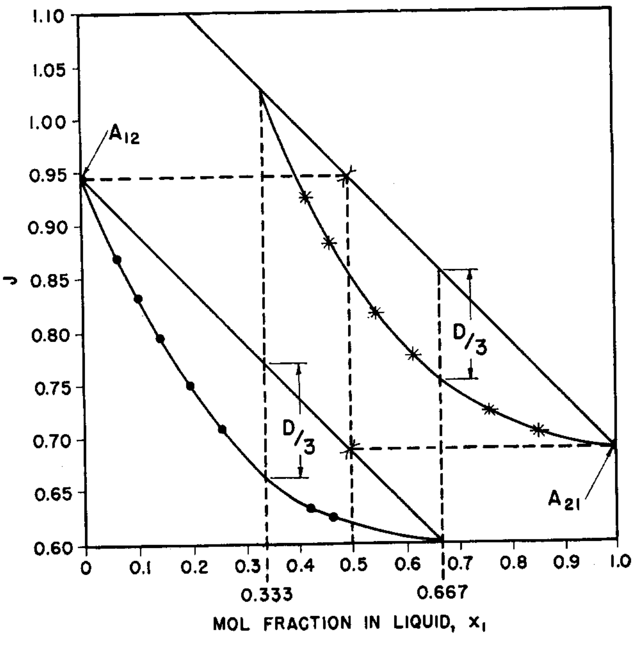

Fig. 2. Graphical procedure for obtaining four-suffix Margules binary constants.

For seventeen systems
$|y_{\text{pred.}} - y_{\text{obs.}}|$ is less than 0.02
For twenty-four systems
$|y_{\text{pred.}} - y_{\text{obs.}}|$ is less than 0.03
For three additional sets the difference is less than 0.05.

A comparison of basis (b) was needed as a supplement to the first one, to prove out those instances where, for example, the absolute difference in y's might deceptively appear to be excellent, such as 0.01, even though that component could never have been present in the vapor in an amount greater than 0.005. As an example, results obtained for the system ethanol–benzene–heptane illustrate our conclusion that large percentage deviations between predicted and observed vapor mole fractions occurred mainly when the experimental liquid or vapor compositions were small and were therefore expected to have large percentage errors owing to analysis. The percentage deviation of the predicted vapor mole fraction from the corresponding experimental value can be represented by $E_1 = 100\,|y_{\text{pred.}} - y_{\text{obs.}}|/y_{\text{obs.}}$; the estimated percentage deviation owing to an assumed experimental error in either liquid or vapor mole fraction can be represented by $E_2 = 100 \times 0.005\,(x^{-1} + y^{-1})$. Although the first error E_1 tended to be larger when x or y was small, it seldom exceeded E_2 in typical systems. Details of such a comparison may be seen in Table 1.*

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* Tabular material has been deposited as document 8775 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

TABLE 2. ANALYSIS OF TERNARY VAPOR-LIQUID EQUILIBRIUM DATA

System	Reference	Suffix	Best value of C^*	Mean of absolute deviation in y for all components: For best C^*	For $C^* = 0.25$	For $C^* = 0$	Mean arithmetic deviation in y for individual components	95% Confidence limits in mean arithmetic deviations
Acetone	*8*	3	0.40	0.0070	0.0077	0.0125	0.0154	±0.0125
Benzene							—0.0152	±0.0100
Chlorobenzene							0.0005	±0.0050
Acetone	*43*	3	0.325	0.0105	0.0106	0.0124	—0.0110	±0.0176
Chloroform							0.0109	±0.0077
Methanol							0.0001	±0.0120
Acetone	*22*	3	—0.075	0.0096	0.0123	0.0097	—0.0022	±0.0117
Chloroform							0.0085	±0.0100
Methyl isobutyl ketone							—0.0063	±0.0039
Acetone	*43*	3	—0.075	0.0244	0.0265	0.0245		
Methanol								
Carbon tetrachloride								
Acetone	*43*	4	0.0375	0.0237		0.0239	—0.0048	±0.0318
Methanol							0.0024	±0.0464
Carbon tetrachloride							0.0022	±0.0258
Acetone	*15*	3	0.525	0.0178	0.0203	0.035		
Methanol								
Water								
Acetone	*15*	4	0.50	0.0173		0.0228	0.00402	±0.0109
Methanol							0.0116	±0.0115
Water							—0.0185	±0.0090
Acetone	*43*	3	0.175	0.008	0.0081	0.011	—0.0091	±0.0116
Methyl acetate							0.0011	±0.0078
Methanol							0.0078	±0.0145
Benzene	*52*	3	0.975	0.0578	0.058	0.0598		
Cyclohexane								
Furfural								
Benzene	*52*	4	—0.10	0.0243		0.0244	—0.0364	±0.0173
Cyclohexane							0.0158	±0.0262
Furfural							0.0124	±0.0063
Benzene	*52*	4	—0.80	0.0220		0.031	0.0072	±0.0258
Cyclohexane							—0.0215	±0.0284
Methyl Cellosolve							0.0144	±0.0244
Cyclohexane	*28*	3	0	0.0040	0.0084	0.0040	0.0087	±0.0060
Heptane							—0.0019	±0.0037
Toluene							—0.0043	±0.0015
Diethyl ether	*27*	4	1.225	0.0373		0.0483	0.0404	±0.0291
Ethanol							—0.0749	±0.0304
Water							0.0345	±0.0188
Ethanol } 760 mm.	*55*	3	0.325	0.0214	0.0215	0.023		
Benzene								
Heptane								

System		Reference	Suffix	Best value of C^*	Mean of absolute deviation in y for all components			Mean arithmetic deviation in y for individual components	95% Confidence limits in mean arithmetic deviations
					For best C^*	For C^* = 0.25	For C^* = 0		
Ethanol		*55*	4	0.325	0.0143		0.016	—0.0075	±0.0085
Benzene	760 mm.							0.0079	±0.0067
Heptane								—0.0003	±0.0041
Ethanol		*29*	4	0.175	0.0125	0.0126	0.013	0.0049	±0.0085
Benzene	400 mm.							—0.0041	±0.0067
Heptane								—0.0003	±0.0041
Ethanol		*14*	3	1.075	0.0444	0.050	0.0537		
Ethyl acetate									
Water									
Ethanol		*14*	4	1.050	0.0395		0.0489	—0.0587	±0.0222
Ethyl acetate								0.0058	±0.0571
Water								0.0474	±0.0495
Heptane		*17*	3	0.125	0.0290	0.0291	0.0291	0.0042	±0.0097
Methyl cyclohexane								—0.0211	±0.0093
Furfural								0.0143	±0.0084
Heptane		*17*	3	0.0	0.0175	0.0190	0.0175	—0.0184	±0.0060
Toluene								—0.0070	±0.0112
Furfural								0.0254	±0.0056
Isobutane		*12*	3	—0.075	0.0094	0.0110	0.0095	0.0093	±0.0036
1-Butene								—0.0067	±0.0079
Furfural								—0.0026	±0.0071
Isobutane		*24*	3	—1.0	0.0066	0.0119	0.0100	—0.0133	±0.0040
Water								0.0149	±0.0039
Furfural								—0.0015	±0.0009
Isooctane		*52*	3	—1.0	0.0405	0.0520	0.0486		
Toluene									
Furfural									
Isooctane		*52*	4	0.0	0.0256		0.0256	—0.0127	±0.0083
Toluene								—0.0240	±0.0100
Furfural								0.0367	±0.0070
Isooctane		*6*	3	—0.25	0.0083	0.0133	0.0096	0.0049	±0.0138
Toluene								—0.0014	±0.0130
Phenol								—0.0035	±0.0037
Methanol		*40*	3	1.75	0.0223	0.0443	0.0499		
Carbon tetrachloride	95°F.								
Benzene									
Methanol		*40*	4	0.80	0.0105		0.0213	0.0105	±0.0391
Carbon tetrachloride	95°F.							0.0031	±0.0197
Benzene								—0.0136	±0.0218
Methanol		*40*	3	1.475	0.0165	0.0256	0.0387		
Carbon tetrachloride	131°F.								
Benzene									
Methanol		*40*	4	0.75	0.0125		0.0226	0.0078	±0.0292
Carbon tetrachloride	131°F.							0.0066	±0.0128
Benzene								—0.0144	±0.0207
Methanol		*2*	3	0.875	0.0160	0.0191	0.0220		
Heptane									
Toluene									
Methanol		*2*	4	0.50	0.0110		0.0139	—0.0061	±0.0185
Heptane								0.0081	±0.0136
Toluene								—0.0012	±0.0080
Methyl cyclohexane		*17*	3	—0.175	0.0213	0.0240	0.0218	—0.0284	±0.0104
Toluene								—0.0016	±0.0090
Furfural								0.0299	±0.0102
Methyl ethyl ketone		*47*	3	0.125	0.0056	0.0060	0.0063	0.0015	±0.0080
Heptane								0.0028	±0.0077
Toluene								—0.0043	±0.0048

Returning to consideration of the results obtained when computed on basis (a), mean values and standard deviations of the means were computed for these differences in the predicted and observed mole fractions. Confidence intervals at the 95% level were determined for use in making estimates of the expected value of the amount of a component in the vapor; that is, $y_{\text{exp.}} = y_{\text{calc.}}$ + mean value of the difference in y ± confidence interval of the mean difference.

Mean deviations and confidence limits are listed in Table 2 for many of the systems studied; nearly all the four-suffix cases are shown. These results, presented in the last two columns of Table 2, have been obtained for those computer runs where C^* had been set equal to 0.0. As the optimum C^* value was not always zero for many of these systems, as noted in column 4, results shown are conservative. By presenting mean deviations and confidence limits on the basis selected here, one is able to assess the likely error for a similar system when no ternary data are available and predictions must be made on the basis of binary information alone. (Note that the results given in the last two columns of Table 2 have been computed by taking into consideration the sign of $y_{\text{pred.}} - y_{\text{obs.}}$, in contrast to the manner in which this difference was applied elsewhere in this work.)

In the section on "Calculations" the development of a chart for each of the twenty-five systems, having the form of Figure 1, was described. The improvement in the prediction of the vapor compositions through the use of the four-suffix over the three-suffix equation is clearly seen in Figure 1.

Table 2 summarizes the results obtained from the series of charts. Listed in this table are: the best C^* value as obtained by reading the curve at the minimum average absolute deviation, calculated as previously described; the corresponding deviation for the best C^*; the deviation for $C^* = 0$; and the deviation for $C^* = 0.25$. If both forms of the equation were applied, both sets of results are reported in the table.

The average C^* for the twenty-five systems based on the three-suffix equation for all but two of these (for which only the four-suffix had been applied) was found to be 0.22. This was conservatively rounded off to 0.25 and the corresponding deviations were read from the aforementioned series of plots and noted in Table 2. Similarly the deviations for a C^* of 0.0 were recorded.

Table 2 helps us answer these two questions: If one is interested in a ternary system for which no data for even a similar system are available, what is the best value of C^* to assume and what is the likely error in the predicted vapor composition? For the same case, what error is likely if C^* is simply assumed to be 0.25?

The average of absolute deviations in the predictions of the vapor compositions based on the three-suffix equation for the twenty-three cases where it was applied was:

for the best C^*: 0.020 mole fraction
for $C^* = 0.25$: 0.024 mole fraction
for $C^* = 0.0$: 0.025 mole fraction

Evidently from these results the most likely expected value of C^* for any system is very near zero. This implies that the term in the series expansion of the excess free energy owing to clusters of three molecules, all different, is not exceptionally important. In fact the expected population of such clusters seems to be about equal to the average of the populations expected for triple clusters from the binary data.

Variation of A_{ij} Constants with Temperature

Phase equilibrium calculations in process design through the use of the procedures employed here are only practical if the constants in the Wohl equation can be varied with temperature in a straightforward manner. Whether carried out by computer, which in most cases they will be, or by hand calculation, the temperature influence can be incorporated by interpolation from a table of constants supplied, or by use of an analytical expression. From a study of the mass of data on this subject accumulated here in the intensive testing of the Wohl equation, a real appraisal for first time can be made for the oft repeated rule of thumb that the product of the A_{ij} constant and the absolute temperature is a constant; that is

$$A_{ij} = cT^{-1}$$

Results are summarized in Table 3 and Figures 3 and 4. Figure 4 shows impressively that this rule of thumb is a very good one for most systems. When more complete data are not available, it is recommended that this relationship be used for the temperature modifications of these constant.

DISCUSSION

Satisfactory as the results reported here are, a further improvement could undoubtedly have been obtained if:

1. Thermodynamic consistency tests had been applied to the data prior to their being selected for this study. Data of questionable quality accordingly would have been eliminated.

2. The most accurate binary constants that would be possible to compute had been utilized instead of simply taking those readily accessible from the literature when they were available. As the work stands, all the random experimental errors of the experiment and the errors owing to failure of the binary equations to fit the binary

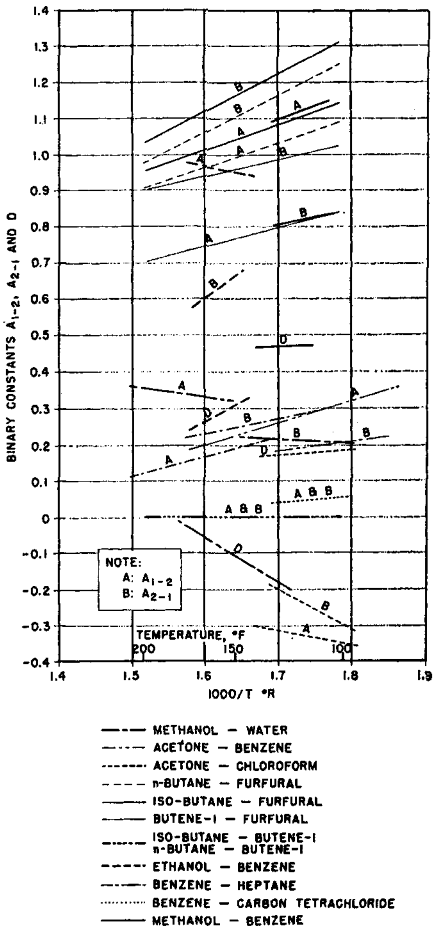
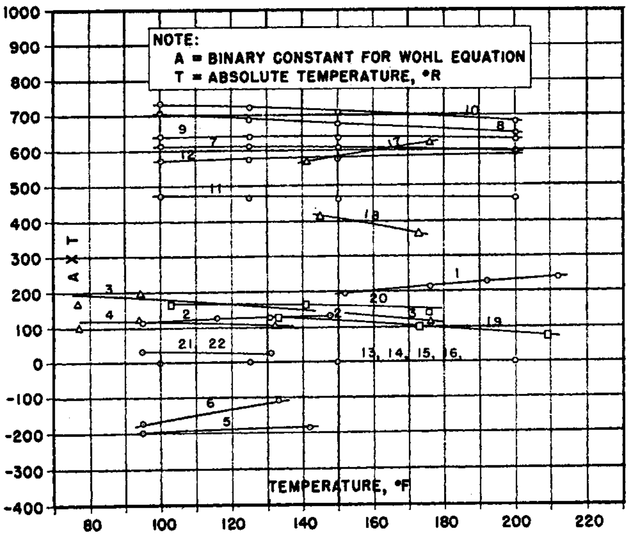


Fig. 3. Effect of temperature on binary constants A_{12}, A_{21}, and D.

TABLE 3. PHASE EQUILIBRIA IN NONIDEAL SYSTEMS

Effect of temperature on binary system constants

System	Temp., °F.	Press., lb./sq. in. abs.	A_{1-2}	A_{2-1}	D	$(T, °R.)$ (A_{1-2})	$(T, °R.)$ (A_{2-1})	$T_{avg.} \times D$
n-Butane-furfural (*12*)	100		1.096	1.257	—	614	704	—
	125		1.045	1.171	—	612	685	—
	150		0.998	1.108	—	609	676	—
	200		0.908	0.975	—	599	644	—
Isobutane-furfural (*12*)	100		1.142	1.310	—	640	733	—
	125		1.090	1.231	—	638	720	—
	150		1.042	1.160	—	636	708	—
	200		0.955	1.030	—	630	680	—
Butene-1-furfural (*12*)	100		0.842	1.029	—	471	576	—
	125		0.800	0.986	—	468	577	—
	150		0.763	0.951	—	465	580	—
	200		0.700	0.900	—	467	594	—
Acetone-benzene (*26, 31*)	77		0.36	0.228	—	193	122	—
	94		0.32	0.188	—	177	104	—
	176-134	14.7	0.185	0.185	—	118	108	—
Acetone-chloroform (*29, 39*)	95		−0.354	−0.312	0.186	−196	−173	103
	142-134	14.7	−0.30	−0.185	0.165	−181	−108	98.5
Methanol-water (*32, 53*)	152-95	3.9	0.32	0.206	−0.20	196	114	−117
	176-116	6.8	0.335	0.211	−0.12	213	122	−73
	192-131	9.7	0.350	0.215	−0.07	228	127	−43.5
	212-148	14.7	0.360	0.22	−0.01	242	134	−6.4
Ethanol-water (*27, 62, 63*)	77		0.67	0.42	—	360	225	—
	212		0.729	0.40	—	490	269	—
	273-226	41.7	0.724	0.375	—	530	257	—
	356-300	140	0.65	0.40	—	530	304	—
Ethanol-heptane (*21*)	133-114	3.5	1.10	1.30	0.803	652	848	468
	173-145	7.7	1.40	1.04	0.891	886	921	552
	208-172	14.5	1.41	1.17	1.192	942	740	774
Benzene-heptane (*28, 29, 44*)	133-103	3.5	0.2162	0.3022	—	129	170	—
	173-141	7.7	0.1644	0.2676	—	104	161	—
	209-176	14.7	0.10	0.219	—	67	139	—
	209-176	14.7	0.113	0.232	—	76	147	—
Ethanol-benzene (*29, 64*)	141-145	7.7	0.945	0.688	0.327	568	416	197
	176-173	14.7	0.975	0.572	0.24	621	362	152
Methanol-carbon tetrachloride (*40, 42, 43*)	95		1.70	0.880	1.19	994	488	660
	122		1.132	0.891	0.483	660	520	223
	131		1.70	0.880	1.19	1,000	520	704
Methanol-benzene (*25, 40*)	104		1.14	0.830	0.465	643	468	262
	131		1.08	0.798	0.460	639	471	272
Benzene-carbon tetrachloride (*42*)	95		0.06	0.06	—	33.3	33.3	—
	131		0.04	0.04	—	23.6	23.6	—
Butene-1-water (*12*)	100		3.58	2.53	—	2,000	1,420	—
	150		3.52	2.08	—	2,150	1,270	—
	200		3.46	1.69	—	2,280	1,110	—
Furfural-water (*12*)	100		2.114	1.072	—	1,180	600	—
	150		1.945	0.909	—	1,190	554	—
	200		1.748	0.780	—	1,150	515	—
Isobutane-water (*12*)	100		4.35	3.5	—	2,440	1,960	—
	150		4.04	2.78	—	2,460	1,700	—
	200		3.78	1.22	—	2,500	806	—



1, 2 METHANOL – WATER
3, 4 ACETONE – BENZENE
5, 6 ACETONE – CHLOROFORM
7, 8 n-BUTANE – FURFURAL
9, 10 ISO-BUTANE – FURFURAL
11, 12 BUTENE-1 – FURFURAL
13, 14 ISO-BUTANE – BUTENE-1
15, 16 n-BUTANE – BUTENE-1
17, 18 ETHANOL – BENZENE
19, 20 BENZENE – HEPTANE
21, 22 BENZENE – CARBON TETRACHLORIDE

Fig. 4. Effect of temperature on product of absolute temperature and binary constant ($A \times T$).

data are reflected in the final values of $|\Delta y|$ listed above. The true values of $|\Delta y|$, owing solely to the failure of the ternary composition terms, are undoubtedly smaller.

In the early phase of this work only the simpler three-suffix, six- to seven-constant, equation was considered. Evaluation of its success depended solely on a plot like Figure 1. If the $|y_{\text{pred.}} - y_{\text{obs.}}|$avg. values found thereon were less than approximately 0.025, the equation was considered satisfactory. When later the four-suffix form was applied to systems which had failed this test, no attempt was made to attain further improvement in the other systems.

Because the Wohl equation is not the only one which has been presented in the literature for describing nonideal liquids, it might be well to review its advantages.

1. Its constants have a thermodynamic significance; for example, the A_{ij}'s are related to the intercepts on the conventional activity coefficient diagram.

2. The constants for a constituent binary of several multicomponent systems do not change from mixture to mixture.

3. The thermodynamic basis of the equation results in its possessing fewer constants for a given number of composition variables than if it were developed empirically from statistical concepts. This can be seen by examining the four-suffix binary Equation (2); instead of the expected five constants, generally associated with an equation of the fifth degree in mole fraction, it has only three.

CONCLUSIONS

No matter how nonideal is the liquid phase, the Margules form of the Wohl equation has been found to represent the phase equilibria of ternary systems in all twenty-five cases investigated. Although frequently aided by the use of a single ternary constant C^*, satisfactory results can be obtained by assuming that C^* equals 0.25 if it is not known independently; thus, three-component systems can be represented by constants obtained only from information on the constituent binaries.

The procedures applied here are not only compatible with the growing use of the computer, but the use of such machines in this work is highly desirable.

NOTATION

A = binary system constant for the Wohl equation
A_{ij}, A_{ji} = end values of the logarithms of activity coefficients in the binary system $i - j$
C = ternary system constant for the earlier form of the Wohl equation
C^* = ternary system constant for the revised form of the Wohl equation
D = binary system constant for the four-suffix Wohl equation
K = liquid-vapor equilibrium constant, y/x
J = $\log \gamma/(1-x)^2$
p^o = vapor pressure
T = absolute temperature
t = temperature
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Δy = difference in the predicted and observed vapor mole fraction, $y_{\text{pred.}} - y_{\text{obs.}}$

Greek Letters

α = relative volatility, K_1/K_2
γ = activity coefficient referred to the pure component standard state
π = total pressure of the system

Subscripts

1, 2, 3 . . . . = component in the mixture
i, j = component in the mixture

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Skin Friction of Power Law Fluids in Turbulent Flow over a Flat Plate

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An analysis is presented for skin friction of power law fluids in turbulent flow over a flat plate. A momentum balance is combined with a logarithmic velocity profile and the resulting equation is integrated. Skin friction is shown to be a function of non-Newtonian Reynolds number and power law shear rate exponent. Closed form solutions for viscous drag are obtained for some values of shear rate exponent, but in general a numerical integration is necessary.

The equations and curves presented are valid for any power law fluid. Computations may be carried out once the fluid viscosity and shear rate exponent are known. As an example, the results are applied to a power law fluid consisting of Carbopol in water. It is shown how viscous drag is affected by changes in the polymer concentration.

Industrial processes involving non-Newtonian fluids have become increasingly important during the past decades. In the design of these processes pumping power and pressure drop may need to be determined as a function of flow rate (*1* to *6*). This need has stimulated interest in the study of laminar and turbulent flows of non-Newtonian fluids. Results of these studies (*7* to *9*) indicate that the pressure drop of non-Newtonian fluids cannot always be predicted satisfactorily from experimental correlations obtained for Newtonian fluids. In other words, the behavior of non-Newtonian fluids should be described by theories and experimental correlations developed specifically for these fluids (*8, 9*).

Flows in pipes and along flat plates are two flow situations of practical interest. Laminar and turbulent pipe flows, and laminar flow along a flat plate (*10* to *15*) have