Since the total rate of conversion in a fluidized reactor depends on the transfer rate and the reaction rate in the continuous phase, the rate-determining step evidently depends on the relative magnitude of these rate coefficients. Measurement of the transfer coefficient should enable design calculations and evaluation of the optimum conditions to be made from fixed-bed studies.

NOTATION

a = surface area of particles per unit volume, sq.ft/cu.ft.
A = a constant; area of the reactor, sq.ft.
B = a constant
C = concentration, moles/cu.ft.
C_p = specific heat of gas, B.t.u./(lb.) (°F.)
C_s = specific heat of solid, B.t.u./(lb.) (°F.)
D_p = particle diameter, ft.
D_T = reactor diameter, ft.
h = heat transfer coefficient, B.t.u./(hr.) (°F.) (sq.ft.)
k_d = transfer coefficient for consecutive model, min.$^{-1}$
k'_d = transfer coefficient for continuous model, min.$^{-1}$
k_c = first-order reaction-rate constant, min.$^{-1}$
L = height of bed, ft.
l, m = constants
ΔP_{mf} = pressure drop at minimum fluidization, in. of water
ΔP_{ke} = pressure drop above ΔP_{mf}, caused by kinetic energy losses, in. of water
N_{Re} = Reynolds number, $D_p u \rho_g/\mu$, dimensionless
Q = volume of bed, cu.ft.
T = temperature, °F.
u = linear gas velocity, ft./sec.
V = volumetric gas velocity, cu.ft./min.
w = mass rate of flow of gas, lb./hr.
z = length coordinate, ft.

Greek Letters

β = constant
ε = porosity
θ = time, min.
μ = viscosity, lb./(ft.) (sec.)
ρ = density, lb./cu.ft.

Subscripts

1 = inlet condition
2 = outlet condition
c = continuous phase
d = discontinuous phase
f = fluidization condition
g = gas
s = solid
v = incipient two-phase fluidization
mf = minimum fluidization
ke = kinetic energy

LITERATURE CITED

1. Damköhler, G., and G. Delcker, *Z. Elektrochem.*, 44, 193 (1938).
2. Johnstone, H. F., R. L. Pigford, and J. H. Chapin, *Trans. Am. Inst. Chem. Engrs.*, 37, 95 (1941).
3. Johnstone, H. F., J. D. Batchelor, and C. Y. Shen, *A.I.Ch.E. Journal*, 1, 318 (1955).
4. Lewis, W. K., E. R. Gilliland, and W. C. Bauer, *Ind. Eng. Chem.*, 41, 1104 (1949).
5. Schwab, G. M., and H. Schultes, *Z. physik. Chem.*, **B9**, 265 (1930).
6. Schwab, G. M., and G. Stager, *Z. physik. Chem.*, **B25**, 418 (1934).
7. Shen, C. Y., Ph.D. thesis, Univ. Illinois (1954); microfilm copies from University Microfilms, Inc., Ann Arbor, Michigan.
8. Toomey, R. D., and H. F. Johnstone, *Chem. Eng. Progr.*, 48, 220 (1952).
9. Wagner, C., *J. Chem. Phys.*, 18, 69 (1950).
10. Wamsley, W. W., and L. N. Johanson, *Chem. Eng. Progr.*, 50, 347 (1954).
11. Wright, N., *Ind. Eng. Chem., Anal. Ed.*, 13, 1 (1941).

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Prediction of Ternary Vapor-liquid Equilibria from Boiling-point Data

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A knowledge of ternary vapor-liquid equilibrium relations is indispensable to the design of columns for ternary rectification as well as azeotropic and extractive distillations. To determine these relations experimentally requires very involved analyses. It is, therefore, highly desirable to estimate ternary equilibrium relations without those analyses and, better still, without experimentation.

Attempts have been made to predict the ternary vapor-liquid equilibria on the theoretical basis of thermodynamic relations among activity coefficients of three components and by use of three binary equilibrium relations available for three combinations of components from Carlson and Colburn (*3*), Benedict, Johnson, Solomon, and Rubin (*1*), Colburn and Schoenborn (*4*), White (*20*), Wohl (*21*), Redlich and Kister (*16*), and Edwards, Hashmall, Gilmont, and Othmer (*6*). Some of these give good estimations for certain ternary systems but fail in other systems or are laborious to calculate accurately.

Scheibel and Friedland (*17*) proposed an empirical method which gives good agreement with many observed data; however, it is lacking in theoretical background and requires different procedures of calculation for different types of ternary systems concerned.

Othmer, Ricciardi and Thaker (*15*) derived a fundamental thermodynamic equation for ternary systems and used it for checking the vapor-liquid equilibrium data available for a ternary system.

PREDICTION FROM TEMPERATURE-COMPOSITION DATA

A method is here presented for estimating vapor compositions at constant-pressure equilibrium from boiling-point data of ternary systems. This method requires the boiling-point–composition data of the system, but the experimental procedures for determining boiling points of definite ternary liquid mixtures are generally much simpler than those required for determining entire vapor compositions of the system.

The method offered for ternary systems is a natural extension of the method for binary systems developed by the author (*8*) and Othmer, Ricciardi, and Thaker (*15*). It is based on the linear property of the equilibrium relations when

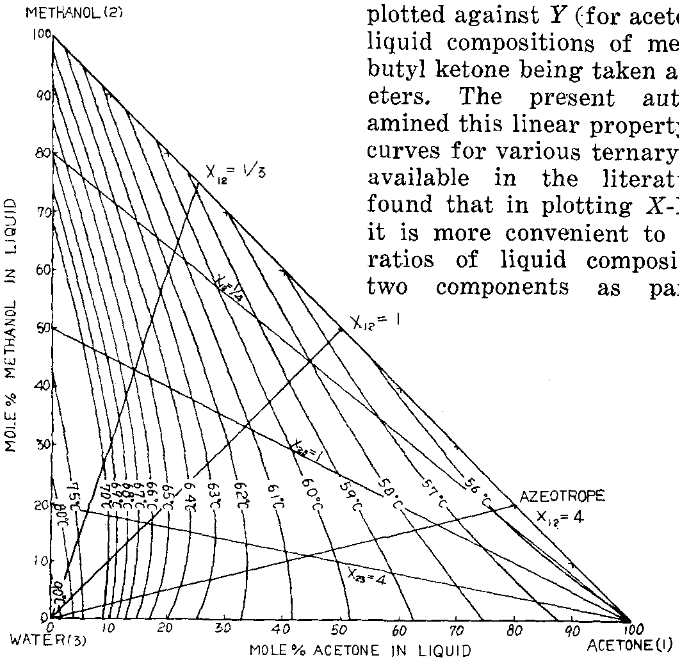

Fig. 1. Triangular diagram of ternary boiling point for the system acetone (1)–methanol (2)–water (3).

they are represented by X-Y curves, $X = x/(1-x)$ vs. $Y = y/(1-y)$, on logarithmic paper.

Othmer et al.(*15*) suggested that ternary systems, such as acetone–chloroform–methyl isobutyl ketone, can also be represented as straight lines on logarithmic paper when X (for acetone, for example) is plotted against Y (for acetone), the liquid compositions of methyl isobutyl ketone being taken as parameters. The present author examined this linear property of X-Y curves for various ternary systems available in the literature and found that in plotting X-Y curves it is more convenient to take the ratios of liquid compositions of two components as parameters rather than the liquid compositions of one component. This manner of indicating parameters for the ternary equilibria was introduced by Colburn and Schoenborn(*4*) in the relation of activity coefficients and liquid compositions. They used as parameters the relative compositions of secondary components instead of the ratios of them, but both are essentially the same.

PREDICTION OF TERNARY SYSTEMS

The calculation procedures of the present method for ternary systems are similar to those for binary systems except for some modifications due to the nature of the ternary system. The entire ternary equilibrium relation may be estimated and determined by the steps given below.

1. Plot available ternary-boiling-point data on a triangular diagram and draw smoothed lines for the constant value of the boiling point, as shown in Figure 1. The system of acetone-methanol-water examined by Uchida, Ogawa, and Hirata(*19*) is used as an example.

2. Plot the boiling point against the liquid composition of any component (preferably the lowest or highest boiling component) along a line on the ternary diagram at a constant ratio of mole fractions of the other two components. Thus the values of the boiling point are plotted against x_1 (in this example, mole fraction of acetone) for a constant value of X_{23}, as in Figure 2, where X_{23} is equal to 1, 4, and ¼. These values of X_{23} indicate in Figure 1 a series of straight lines passing through the corner of component 1 (acetone).

A striking observation in Figure 2 is that some boiling-point curves

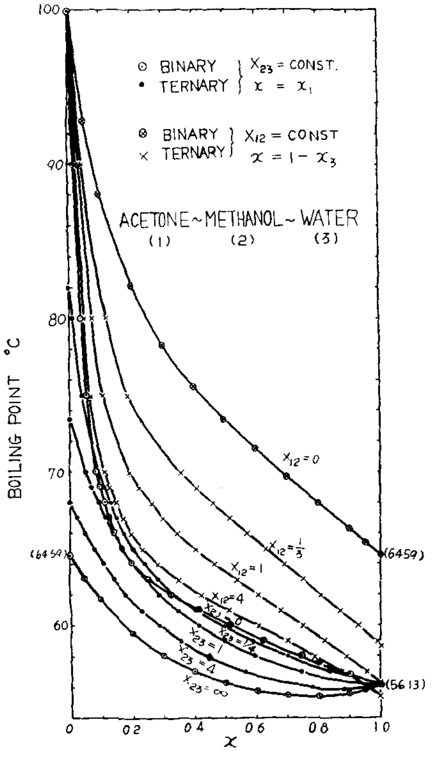

Fig. 2. Plot of boiling point, °C., vs. mole fraction in liquid x for the system acetone (1)–methanol (2)–water (3).

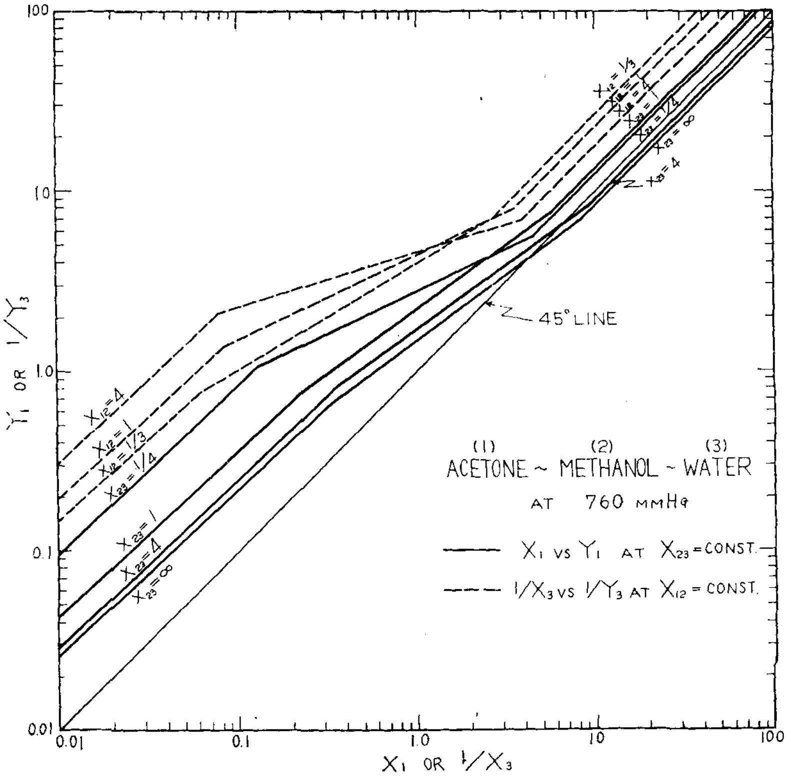

Fig. 3. Ternary X-Y curves calculated for the system acetone (1)–methanol (2)–water (3).

cross the limiting curves for binary systems. In such cases it is obvious that a linear interpolation would be greatly in error.

3. Calculate and determine X_1-Y_1 curves as shown in Figure 3 by using the boiling-point curves of Figure 2 for $X_{23} = 1$, 4, ¼, etc., and by following the same steps developed for binary systems [*cf.* Othmer et al. (*15*) or Hirata(*8* and *10*)]. In these calculations, however, it is usually difficult to find or estimate the latent heat of vaporization of ternary solutions, λ_x, which appears in the term $f(T)$; that is,

$$f(T) = \frac{\lambda_x}{RT^2}\left(\frac{dT}{dx}\right)_P$$

The author proposes here the following approximation for ternary systems:

$$(T) = \frac{(\lambda_x/RT)}{T}\left(\frac{dT}{dx_1}\right)_P = \text{approx.}\frac{(\lambda_1/RT_1)X_1+(\lambda_{23}/RT_{23})(1-x_1)}{T}\left(\frac{dT}{dx_1}\right)_P \tag{1}$$

where λ_{23}/RT_{23} is the value of λ_x/RT for the binary mixture of component 2 and component 3 at the definite value of X_{23} and may be estimated from binary data.

4. Transform X_1-Y_1 curves into x_1-y_1 curves, as shown in Figure 4. Plot the values of vapor composition y_1 on a ternary diagram and draw lines for the constant value of y_1. (*See* Figure 5.)

5. Calculate and determine X_2-Y_2 curves or X_3-Y_3 curves for another set of lines, X_{13} = constant or X_{12} = constant, by the procedure explained above. Draw lines for the constant value of y_2 or y_3.

6. The constant y_1 lines first obtained, together with the constant y_2 or y_3 lines determined, define the whole vapor-liquid equilibria of the ternary system, as in Figure 5, for the system acetone-methanol-water.

The result calculated by these procedures is compared with the observed data of Othmer, Friedland, and Scheibel(*14*) in Figure 5 and shows fairly good agreement. The method was applied to other systems available, such as acetone–chloroform–methyl isobutyl ketone (*11*), methyl ethyl ketone heptane–toluene(*18*), ethyl acetate–ethanol–water(*7*), carbon tetrachloride–ethanol–benzene(*2*), ethanol-benzene-water(*31*), and isooctane-toluene-phenol(*5*). Comparisons between calculated and observed data show good agreement for the first three systems, but for the latter three systems, mainly owing to the incompleteness of boiling-point data, good agreements are local.

MATHEMATICAL PREDICTION OF VAPOR COMPOSITIONS

As indicated in steps 5 and 6, two sets of X-Y curves must be calculated to determine all the ternary equilibria by the method presented above. If, therefore, only X_1-Y_1 curves are determined, only y_1 and $y_2 + y_3$ have been found, y_2 and y_3 separately are not yet known. In such a case the following mathematical method may be used instead of calculating another set of X_2-Y_2 or X_3-Y_3, though it requires much more laborious calculations. This mathematical method is useful especially when boiling points are measured only along lines such as X_{23} = constant on a triangular diagram.

For ternary systems the fundamental thermodynamic equation may be expressed as follows(*15*), if x_1 is chosen as the independent variable:

$$\frac{x_1}{y_1}\frac{dy_1}{dx_1}+\frac{x_2}{y_2}\frac{dy_2}{dx_1}+\frac{x_3}{y_3}\frac{dy_3}{dx_1}=f(T) \tag{2}$$

For a constant value of X_{23} this relation becomes

$$\frac{d}{dx_1}\left(\ln y_2^{X_{23}} y_3\right) = (X_{23}+1)\left(\frac{f(T)}{1-x_1} - \frac{x_1}{1-x_1}\frac{d\ln y_1}{dx_1}\right) \tag{3}$$

Equation (3) is thermodynamically rigorous and represents the relation between vapor and liquid compositions for a constant value of

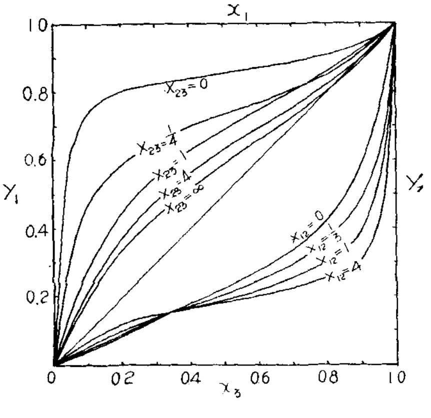

Fig. 4. Ternary x-y curves calculated for the system acetone (1)–methanol (2)–water (3).

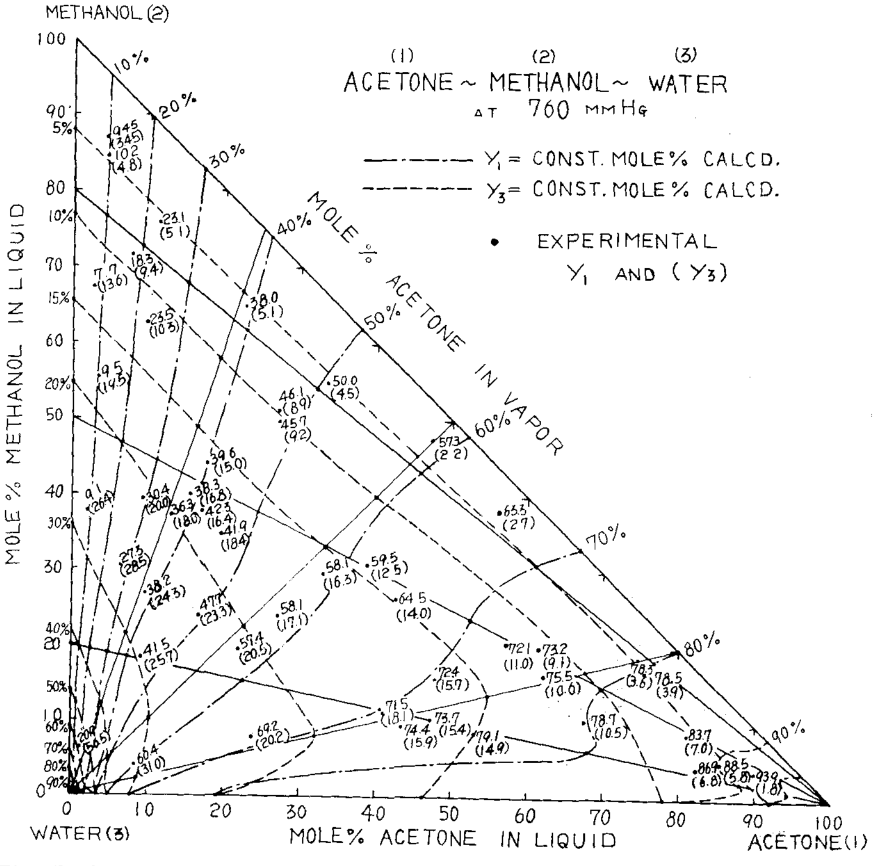

Fig. 5. Comparison between calculated and observed vapor-liquid–equilibrium data for the system acetone (1)–methanol (2)–water (3).

TABLE 1.—CALCULATIONS FOR THE SYSTEM ACETONE (1)—METHANOL (2)—WATER (3). ($X_{23} = \frac{1}{4}$)

x_1	y_1	t, °C.	$y_2^{X_{23}}y_3$	y_2	y_3
0.05	0.286	74.0	0.266	0.38	0.334
.1	.412	69.8	.216	.30	.288
.2	.545	65.1	.170	.205	.250
.4	.667	61.1	.121	.13	.203
.6	.750	58.9	.077	.095	.155
.8	.857	57.2	.034	.06	.083

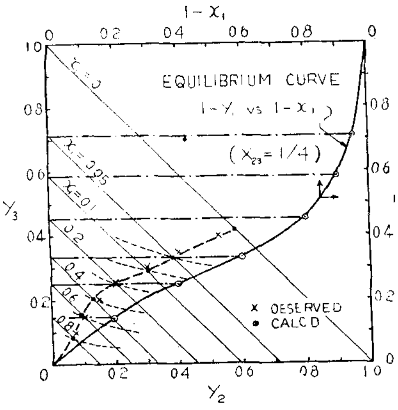

Fig. 6. Determination of ternary vapor compositions for the system acetone (1)–methanol (2)–water (3).

X_{23}. Integrating and rearranging result in the following relation:

$$\log y_2^{X_{23}} y_3 = \left(\log y_2^{X_{23}} y_3\right)_{x_1=0} + \frac{(X_{23}+1)}{2.303}(S_1 - S_2) \qquad (4)$$

where

$$S_1 = \int_o^{x_1} \frac{f(T)}{1-x_1}\,dx_1 \qquad (5)$$

and

$$S_2 = \int_o^{x_1} \frac{x_1}{1-x_1}\,\frac{d\ln y_1}{dx_1}\,dx_1 = \int_o^{y} \frac{x_1}{1-x_1}\,\frac{dy_1}{y_1} \qquad (6)$$

If Equation (1) is substituted in Equation (5), the integration may be simplified as follows:

$$S_1 = \text{approx.}\,\frac{\lambda_1}{RT_1}\int_{T_{23}}^{T}\frac{x_1}{1-x_1}\,\frac{dT}{T} - \frac{\lambda_{23}}{RT_{23}}\ln\frac{T}{T_{23}} \qquad (7)$$

By use of the aforementioned method of estimating the relation y_1 vs. x_1, the relation T vs. x_1 being known for a constant value of X_{23}, the integrations of S_1 and S_2 are carried out numerically and the term $y_2^{x_{23}}y_3$ may be determined as a function of x_1, say $F(x_1)$. This function, together with the equation $y_2 + y_3 = 1\text{-}y_1$, determines the vapor compositions y_2 and y_3 for the definite value of x_1. Therefore the intercepts of these lines determine y_2 and y_3 at the same time.

An illustrative example is given in Table 1 and Figure 6 for the system acetone (1) -methanol (2) -water (3). The agreement with the observed data(*14*) is fairly good.

CONCLUSION

The method of predicting vapor-liquid equilibrium relations from boiling-point data for binary systems can be used with slight modifications for ternary systems, for which it is particularly useful, as only the boiling-point–composition data are needed to determine the entire vapor-liquid equilibrium relation.

The method may be used also to check the available ternary equilibrium data.

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NOTATION

$f(T)$ = function defined in Equations (1) and (2)
R = gas constant
T = absolute boiling point of ternary solution
T_1 = absolute boiling point of component 1
T_{23} = absolute boiling point of binary mixture of components 2 and 3, ratio of their compositions being X_{23}
x = mole fraction of component in liquid
x_i = mole fraction of component i in liquid
$X = x/(1—x)$
$X_i = x_i/(1—x_i)$
$X_{ij} = x_i/x_j$, ratio of compositions of components i and j
y = mole fraction of component in vapor
y_i = mole fraction of component i in vapor
$Y = y/(1—y)$
$Y_i = y_i/(1—y_i)$
λ_x = molal latent heat of vaporization of solution
λ_1 = molal latent heat of vaporization of component 1
λ_{23} = molal latent heat of vaporization of binary mixture of components 2 and 3, ratio of their composition being X_{23}
Subscripts 1, 2, and 3 refer to components 1, 2, and 3 respectively

LITERATURE CITED

1. Benedict, M., C. A. Johnson, E. Solomon, and L. C. Rubin, *Trans. Am. Inst. Chem. Engrs.*, **41**, 371 (1945).
2. Campbell, A. N., and W. J. Dulnage, *J. Am. Chem. Soc.*, **70**, 1723 (1948).
3. Carlson, H. C., and A. P. Colburn, *Ind. Eng. Chem.*, **34**, 581 (1942).
4. Colburn, A. P., and E. M. Schoenborn, *Trans. Am. Inst. Chem. Engrs.*, **41**, 421 (1945).
5. Drickamer, H. G., G. G. Brown, and R. R. White, *loc. cit.*, **41**, 555 (1945).
6. Edwards, B. S., F. Hashmall, R. Gilmont, and D. F. Othmer, *Ind. Eng. Chem.*, **46**, 194 (1954).
7. Griswold, J., P. L. Chu, and W. O. Winsauer, *loc. cit.*, **41**, 2352 (1949).
8. Hirata, M., *Chem. Eng.* (*Japan*), **13**, 152 (1949); **14**, 65 (1950).
9. *Ibid.*, **15**, 72 (1951); **18**, 14 (1954).
10. ———, *Japan Sci. Rev.*, **2**, 265 (1952).
11. Karr, A. E., E. G. Scheibel, W. M. Bowes, and D. F. Othmer, *Ind. Eng. Chem.*, **43**, 961 (1951).
12. Nagasako, N., and M. Hirata, *Chem. Eng.* (*Japan*), **16**, 83 (1952).
13. Norman, W. S., *Trans. Inst. Chem. Engrs.* (*London*), **25**, 66 (1945).
14. Othmer, D. F., D. Friedland, and E. G. Scheibel, cited in Ju Chin Chu, "Distillation Equilibrium Data."
15. Othmer, D. F., L. G. Ricciardi, and H. S. Thaker, *Ind. Eng. Chem.*, **45**, 1815 (1953).
16. Redlich, O., and A. T. Kister, *loc. cit.* **40**, 341, 345 (1948).
17. Scheibel, E. G., and D. Friedland, *loc. cit.*, **39**, 1329 (1947).
18. Steinhauser, H. H., and R. R. White, *loc. cit.*, **41**, 2912 (1949).
19. Uchida, S., S. Ogawa, and M. Hirata, *Chem. Eng.* (*Japan*), **17**, 193 (1953).
20. White, R. R., *Trans. Am. Inst. Chem. Engrs.*, **41**, 539 (1945).
21. Wohl, K., *loc. cit.*, **42**, 215 (1946).