which are not small compared to the dissipative scale of the turbulence.

NOTATION

a = apparent origin of jet measured from orifice
$\overline{C}$ = mean concentration at a point (relative to ambient fluid)
d = orifice diameter
l = transport mixing length
N = dimensionless number
$\overline{q}$ = mean dynamic pressure at a point
r = radial distance from jet axis
r_o = $(\equiv 1/2d)$
r_1 = value of r for which $\overline{q} = 1/2\ \overline{q}_{\max}$
r_2 = value of r for which $\overline{U} = 1/2\ \overline{U}_{\max}$
r_3 = value of r for which $\overline{C} = 1/2\ \overline{C}_{\max}$
$\overline{U}$ = axial component of mean velocity at a point
x = axial distance from orifice
ξ_1 = $(x + a)/d$
ξ_2 = $r/(x + a)$
ϵ = turbulent diffusion coefficient

Subscripts

c = material
m = momentum
max = maximum value at a cross-section
o = at the orifice
Pr = Prandtl number
Re = Reynolds number
Sc = Schmidt number
turb = turbulent

LITERATURE CITED

1. Corrsin, S., and M. S. Uberoi, *Natl. Advisory Comm. Aeronaut. Tech. Rept. 998* (1950).
2. Hinze, J. O., and B. G. van der Hegge Zijnen, *Appl. Sci. Research,* **1A**, 435 (1949).
3. Ruden, P., *Naturwissenschaften,* **21**, 375 (1933).
4. Reichardt, H., *Forsch. Gebiete Ingenieurw.*, 414 (1951).
5. Keagy, W. R., and A. E. Weller, *Proc. Heat Trans. Fluid Mech. Inst.*, p. 89, Berkeley, California (1949).
6. Forstall, W., Jr., and A. H. Shapiro, *J. Appl. Mech.*, **17**, 399 (1950).
7. Corrsin, S., and A. L. Kistler, *Nat'l. Advisory Comm. Aeronaut. Tech. Note 3133* (1954).
8. Townsend, A. A., "The Structure of Turbulent Flow," Cambridge University Press, New York (1956).
9. Forstall, W., Jr., and E. W. Gaylord, *J. Appl. Mech.*, **22**, 161 (1955).
10. Prausnitz, J. M., and R. H. Wilhelm, *Rev. Sci. Instr.*, **27**, 941 (1956).
11. Cairns, E. J., Ph.D. dissertation, Univ. of Calif., Berkeley, California (1959).
12. Manning, F. S., Ph.D. dissertation, Princeton Univ., Princeton, New Jersey (1959).
13. Hinze, J. O., "Turbulence," McGraw-Hill, New York (1959).
14. Rosensweig, R. E., H. C. Hottel, and G. C. Williams, *Chem. Eng. Sci.*, **15**, 111 (1961).
15. Corrsin, S., and M. S. Uberoi, *Nat'l. Advisory Comm. Aeronaut. Tech. Rept. 1040* (1951).
16. Hottel, H. C., "Fourth Symposium on Combustion," pp. 97-113, Williams and Wilkins, Baltimore, Maryland (1953).
17. Cleeves, V., and L. M. K. Boelter, *Chem. Eng. Progr.*, **43**, 123 (1947).
18. Forstall, W., Jr., Sc.D. dissertation, Mass. Inst. of Technol., Boston, Massachusetts (1949).

Manuscript received May 21, 1962; revision received September 24, 1962; paper accepted October 30, 1962.

The Prediction of Vapor-Liquid Equilibria Using a Theory of Liquid Mixtures

ROBERT F. SWEENEY and ARTHUR ROSE
Applied Science Laboratories, Incorporated, State College, Pennsylvania

Much investigation in the field of thermodynamics of liquid solutions has been undertaken in connection with vapor-liquid equilibrium phenomena. The nature of such investigations has been determined by the objective. One objective is to determine whether the experimental data, specifically the measured relationship between liquid and vapor compositions, temperature in an isobaric system or pressure in an isothermal system, and vapor pressures of the pure substances, are thermodynamically consistent. The objective is accomplished by determining whether or not the variables follow the Gibbs-Duhem relationship, and the degree to which they do is a measure of the reliability of the experimental data. Such investigations are referred to as correlations.

The other objective is to predict the vapor-liquid equilibria from a limited amount of experimental data. The more modest attempts have been aimed at predicting the most essential data, vapor composition as a function of liquid composition, from other more easily obtained experimental data. An example is the calculation of these data from experimental determinations of vapor pressures of pure components, and the boiling temperatures of mixtures at constant pressure.

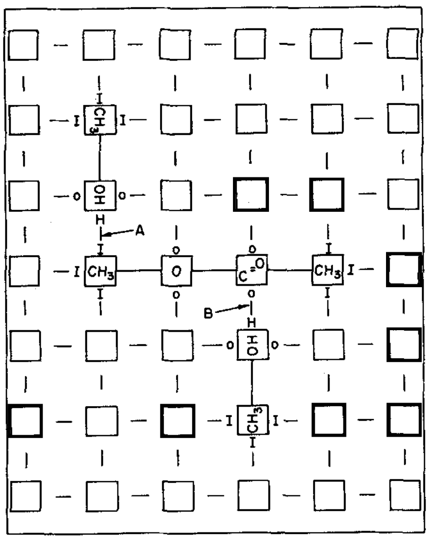


Fig. 1. Interaction between molecules on a lattice.

The more ambitious attempts at prediction involve calculation of complete equilibria from the properties of the pure substances and a measure, independent of experimental vapor-liquid equilibrium determinations, of their behavior in mixtures. The simple example of such a method is a common Raoult's-law prediction in which the vapor pressures are used and it is assumed that the behavior upon mixing is ideal. Where this assumption cannot be made, the prediction, essentially a matter of determining the liquid nonidealities, becomes much more difficult.

Pierotti, Deal, and Derr (*5*) published an excellent empirical method for predicting vapor-liquid equilibria, in which an extremely large number of systems were treated. Even though it is empirical, it is a prediction, not a correlation for testing thermodynamic consistency. Based upon the number and arrangement of carbon atoms in organic molecules and the empirical constants determined for various types of binary systems, the liquid-activity coefficients at infinite dilution, γ°, are calculated. Once the γ° for each of the components in a system are known, the activity coefficients over the entire composition range can be estimated with the help of one of the integrated forms of the Gibbs-Duhem equation.

The method described herein is a prediction method. It is different from Pierotti's method in that it is based on more detailed theoretical considerations of how the molecules behave in mixtures; that is, it is an application of a theory of solutions.

One of the approaches to the theory of solutions is the quasi-crystalline model, which is based essentially on a high degree of order such as in crystals but with some degree of disorder which represents the fluidity of the liquid state. The method has met with considerable success in the theory of polymer solutions (*4*).

Barker (*1*) used the quasi-crystalline approach in predicting excess free energy (and excess chemical potentials), entropy, and heats of mixing for solutions of strongly associated substances, such as alcohols, in relatively nonpolar solvents such as chloroform and benzene. Although the prediction of entropy and heat of mixing was not completely successful, the prediction of excess chemical potential μ^E was quite reliable. The quantity needed for equilibria prediction is γ, which is obtained directly from the excess chemical potential. The method involves quite a bit of tedious calculation, but the advent of high-speed computers since Barker published his work removes this objection to the method. Thus, the method of Barker was chosen for use in the investigation reported herein.

The present work was done using various alcohol-ester binary systems. Barker investigated one system, ethanol-chloroform, which could be treated in the same manner as the alcohol-ester systems. Alcohol is a hydrogen-bonded substance. Neither esters nor chloroform are hydrogen bonded in the pure state, but both can form hydrogen bonds with alcohol, the ester contributing a donor to the bond and the chloroform contributing an active hydrogen. However, whereas Barker attributed very little energy to the hydrogen bond between alcohol and chloroform, the present work attributed a relatively large energy to the alcohol-ester hydrogen bond.

As finally worked out for the predictions made herein, the only data required (other than properties of the pure components) are the energy values for the alcohol-alcohol hydrogen bond and the alcohol-ester hydrogen bond. These quantities have been obtained by choosing the values which cause the calculated data to be the same as experimental data. The method in its present form is thus empirically applied. It is possible, however, that the proper energy values could be measured by means independent of actual equilibrium determinations, for example by spectrometric means. Vapor-liquid equilibria could then be calculated from only fundamental data independent of any equilibrium measurements.

THEORY

The theoretical relations which form the basis for the predictions described here are expressed by a series of mathematical relations first derived by Barker (*1*). The mathematical equations are themselves based on a physical model describing the relative positions and interactions of the individual molecules in a mixture.

In a representation of the physical model, each of the molecules immediately adjacent to one another in a mixture are considered to occupy a definite number of sites on a well-defined lattice. Each site so occupied is identified with a particular atom or group of atoms in a molecule. Each site is considered to have a certain coordination number which refers to the number of possible directions or surfaces of contact of the atoms at a given site with other atoms of either the same molecule or a different molecule. A pictorial representation of the model is given in Figure 1.

The lattice must of course be three dimensional to represent the liquid state, and the mathematical derivations are based on three dimensions. However, a tetragonal lattice, such as was used, cannot be represented clearly in a drawing, and so a two-dimensional picture has been used for the illustrations in the same way that structural formulas for organic molecules are drawn. Each surface labelled I represents a hydrocarbon type of contact point, each O represents an oxygen surface contact point, and the H represents an active hydrogen contact point.

This example arrangement of three molecules results in an I-I contact (A) and a hydrogen bond (B). Each different arrangement of course leads to corresponding force interactions depending on the kinds of contact surfaces that become adjacent. There are many different ways of arranging a given number of two different kinds of molecules on this lattice and various total-association energies will arise with different arrangements. There will be a particular probability of obtaining each possible energy. Conventional statistical thermodynamics then leads to calculation of the excess chemical potential μ^E for each component.

It would be surprising if a rigorous lattice picture resulted in a successful theory of solution, since it is obvious that such extreme order does not exist in a liquid. This, however, is allowed for by setting up the rigorous order only for a given site on the lattice and its nearest-neighbor sites (those sites coordinated directly to a given site). In this way, there is a short-range order, but long-range disorder is allowed.

Barker's expressions (with slightly different nomenclature) for excess chemical potential for a binary are

$$\overset{E}{\mu_A} = RT \Big[\Sigma_\mu \overset{A}{Q_\mu} \ln \big(\overset{A}{X_\mu} / x_A \overset{A1}{X_\mu}\big) +$$

TABLE 1. EXPERIMENTAL AND PREDICTED DATA N-HEXANOL-N-HEXYL ACETATE ATMOSPHERIC PRESSURE

Mol. fraction n-hexanol in liquid	Experimental mol. fraction n-hexanol in vapor	Predicted mol. fraction n-hexanol in vapor	Temperature °C.	Pressure mm. Hg.	Vapor pressures of n-hexyl acetate Temperature °C.	Vapor pressure of n-hexyl acetate mm. Hg.
0.168	0.269	0.270	166.1_5	733.8	147.9_2	396.7
0.261	0.360	0.372	164.4_1	736.3	155.0_8	490.4
0.575	0.635	0.641	159.7_5	734.2	160.3_4	570.6
0.819	0.848	0.846	157.4_3	734.2	169.7_3	735.7
0.825	0.858	0.854	157.2_9	733.8		

$$r_A \left(\frac{1}{2} z - 1\right) \ln\left(\frac{r_A x_A + r_B x_B}{r_A}\right)\Bigg] \qquad (1)$$

$$\mu_B^{E} = RT\Bigg[\, \Sigma_\upsilon\, Q_\upsilon^{B} \ln \left(X_\upsilon^{B} / x_B X_\upsilon^{B1}\right) +$$

$$r_B \left(\frac{1}{2} z - 1\right) \ln\left(\frac{r_A x_A + r_B x_B}{r_B}\right)\Bigg] \qquad (2)$$

The values X^A and X^B in Equations (1) and (2) are determined from Equations such as (3) and (4) below (there is one equation for each type of contact on each component),

and X_μ^{A1} and X_υ^{B1} are the values at $x_A = 1$ and $x_B = 1$.

$$X_\mu^{A}\ [\Sigma_\mu\, \eta_{\mu\mu}^{AA}\, X_\mu^{A} +$$

$$\Sigma_\upsilon\, \eta_{\mu\upsilon}^{AB}\, X_\upsilon^{B}\ ] = \frac{Q_\mu^{A}\, x_A}{2} \qquad (3)$$

$$X_\upsilon^{B}\ [\Sigma_\mu\, \eta_{\mu\upsilon}^{AB}\, X_\mu^{A} +$$

$$\Sigma_\upsilon\, \eta_{\upsilon\upsilon}^{BB}\, X_\upsilon^{B}\ ] = \frac{Q_\upsilon^{B}\, x_B}{2} \qquad (4)$$

Equations (1) and (2) applied to the generalized model are
alcohol:

$$\mu_A^{E} = RT\ [\ln \left(X_H^{A} / x_A X_H^{A1}\right) +$$

$$2 \ln \left(X_O^{A} / x_A X_O^{A1}\right) + (1 + 2n)$$

$$\ln \left(X_I^{A} / x_A X_I^{A1}\right) + (n + 1) \ln$$

$$\left(\frac{(n + 1)\, x_A + (n' + 1)\, x_B}{(n + 1)}\right)\Bigg] \qquad (5)$$

ester:

$$\mu_B^{E} = RT\Bigg[\, 2 \ln \left(X_O^{B} / x_B X_O^{B1}\right) +$$

$$2 \ln \left(X_{O'}^{B} / x_B X_{O'}^{B1}\right) + 2n' \ln$$

$$\left(X_I^{B} / x_B X_I^{B1}\right) + (n' + 1) \ln$$

$$\left(\frac{(n + 1)\, x_A + (n' + 1)\, x_B}{(n' + 1)}\right)\Bigg] \qquad (6)$$

The application of Equations (3) and (4) to the generalized model yields six simultaneous equations for solving the quantities X for ester-alcohol interactions.

In formulating such expressions, the order in which the various types of surface are considered may result in reversing the order of subscripts and superscripts. Such reversal, if on both subscripts and superscripts, does not change the meaning of the symbol. For example, the following identity is true:

$$\eta_{IH}^{BA} \equiv \eta_{HI}^{AB}$$

It must also be noted that η values such as η_{HH}^{AA} and η_{OO}^{AA} which represent interaction of identical surfaces must be identically one since the net energy of forming such a bond is zero.

APPLICATION TO ALCOHOL-ESTER SYSTEMS

It has been noted that the necessary association energies for the prediction method were obtained by choosing values such that the predicted data were the same as the experimental data for three systems. The first system was methanol-methyl acetate. All the values required in the generalized equations (except the energy values) are given below.

Methanol	Methyl acetate
$r_A = (n{+}1) = 2$	$r_B = (n'{+}1) = 4$
$Q_H^{A} = 1$	$Q_O^{B} = 2$
$Q_O^{A} = 2$	$Q_{O'}^{B} = 2$
$Q_I^{A} = (2n{+}1) = 3$	$Q_I^{B} = (2n') = 6$

The methanol molecule was considered to occupy two sites on a lattice of coordination number 4, allowing one active hydrogen contact point, two oxygen donor points, and three hydrocarbon type of points. The methyl acetate occupies four sites on the same lattice, allowing two oxygen donor points for each of the two oxygen atoms, and six hydrocarbon type of points.

Similar values for ethanol-ethyl acetate and butanol-butyl acetate are presented below.

Ethanol	Ethyl acetate
$r_A = 3$	$r_B = 5$
$Q_H^{A} = 1$	$Q_O^{B} = 2$
$Q_O^{A} = 2$	$Q_{O'}^{B} = 2$
$Q_I^{A} = 5$	$Q_I^{B} = 8$
n-Butanol	**n-Butyl acetate**
$r_A = 5$	$r_B = 7$
$Q_H^{A} = 1$	$Q_O^{B} = 2$
$Q_O^{A} = 2$	$Q_{O'}^{B} = 2$
$Q_I^{A} = 9$	$Q_I^{B} = 12$

The possible types of interactions are the same for all the systems, and are simply all the combinations of types of contact points. There are the three different hydrogen bonds and the six other contacts between different kinds of sites on unlike molecules. The latter interactions had some energy attributed to them in early trials, but the successful case required zero energy. In addition, thre are the trivial bond between identical sites and negligible interactions between unlike sites on like molecules.

This is the information used to represent the picture of the liquid state. The energies of the various bonds were then determined by the trial-and-error procedure. The successful trial used an energy for the hydrogen bond between alcohol molecules (H^A—O^A) of − 5,300 cal./mol. and an energy for both of the alcohol-ester hydrogen bonds (H^A—O^B and H^A—O'^B) of − 4,300 cal./mol. All other combina-

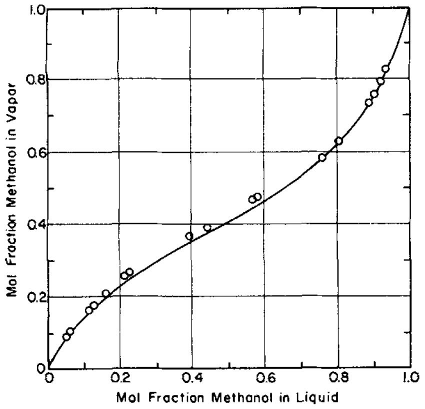


Fig. 2. Vapor-liquid equilibria of methanol-methyl acetate at 760 mm. of mercury. Solid line is predicted. Points are experimental (2).

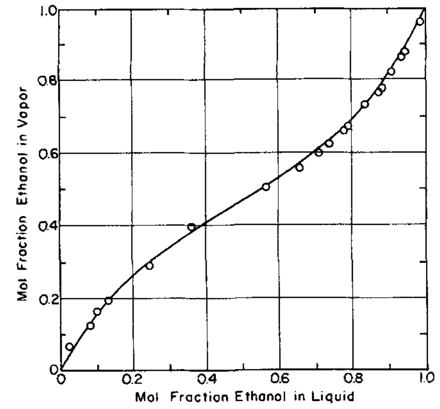


Fig. 3. Vapor-liquid equilibria of ethanol-ethyl acetate at 760 mm. of mercury. Solid line is predicted. Points are experimental. (3).

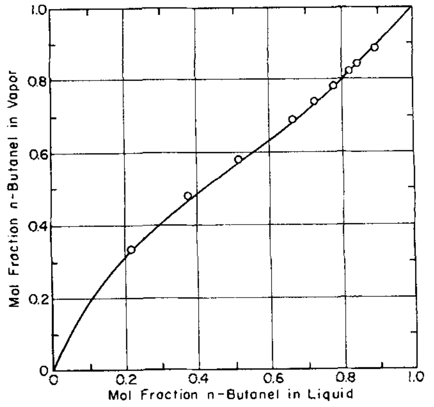


Fig. 4. Vapor-liquid equilibria of n-butanol-n-butyl acetate at 760 mm. of mercury. Solid line is predicted. Points are experimental (7).

tions (that is, I—I, O—O, H—H, I—O) needed to be made equal to zero in the successful trials.

Using these energies in Barker's equations, the excess chemical potentials divided by RT, μ_A^E/RT, and μ_B^E/RT, were calculated for each binary system at various liquid compositions. The activity coefficients, γ_A and γ_B, were then calculated. The temperatures and vapor compositions were calculated from the activity coefficients and vapor-pressure data.

The composition equilibria are given in Figures 2, 3, and 4. Experimental data are also given for comparison. The discrepancies between predicted and experimental are within expected experimental error for all three binary systems.

The predicted activity coefficients are within 10% of those calculated from experimental data, except at extremes of the composition range where experimental errors may be very large. Experimental error of 4 or 5% in the composition ratio and another 2 or 3% in the pressure ratio is not unusual. These errors could total to an overall experimental error of 8%.

TEST OF PREDICTION METHOD ON n-HEXANOL-n-HEXYL ACETATE SYSTEM, AND n-HEXANOL-METHYL CAPROATE SYSTEM

In order to test the prediction method further, experimental data were obtained for a higher molecular weight homologous binary, the n-hexanol-n-hexyl acetate system. The data are given in Table 1. The data were determined in a self-lagging Cottrell tube type of still according to the method given by Rose, Papahronis, and Williams (6). The predicted vapor compositions are also listed. The prediction was made using the same energies that were used in the other three binaries. The discrepancies are about the same as for the first three systems and are in fact within the experimental errors that might be expected.

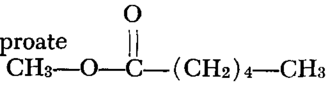
It seemed of interest to attempt extrapolation of the prediction method to a somewhat different kind of system. The system chosen was n-hexanol-methyl caproate. It was necessary to determine the experimental data, which are given in Table 2. Predicted vapor compositions are also listed.

TABLE 2. EXPERIMENTAL AND PREDICTED DATA N-HEXANOL-METHYL CAPROATE 50 MM. HG.

Mol. fraction n-hexanol in liquid	Experimental mol. fraction n-hexanol in vapor	Predicted mol. fraction n-hexanol in vapor	Temperature °C.	Pressure mm. Hg.
0.211	0.148	0.137	75.7_5	52.1_1
0.225	0.159	0.146	75.9_8	52.2_5
0.430	0.270	0.261	77.3_8	51.2_4
0.430	0.270	0.261	77.5_1	51.6_4
0.835	0.597	0.652	83.3_8	50.8_0

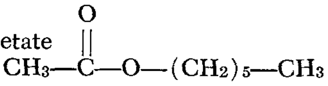
This binary resembles the alcohol-acetate systems in that it consists of an alcohol and an ester. However, it can be easily ascertained from comparing the structural formulas of the esters that the orientation of the functional groups is different:

methyl caproate



$$CH_3{-}O{-}\overset{\overset{\textstyle O}{\|}}{C}{-}(CH_2)_4{-}CH_3$$

n-hexyl acetate



$$CH_3{-}\overset{\overset{\textstyle O}{\|}}{C}{-}O{-}(CH_2)_5{-}CH_3$$

There is no way of expressing this difference in the proposed model except by changing the association energy values. This may be responsible for the relatively poor results for this system, compared to the others studied. Although the prediction describes the general behavior of the experimental data, there are definitely significant differences. The prediction would probably serve a purpose in a preliminary investigation of distillation separation of the components, but would not serve as foundation for design of an industrial column.

CONCLUSIONS

The prediction of vapor-liquid equilibrium nonidealities was very successful within the homologous series used, but only partially successful when applied to a different type of alcohol-ester mixture. The prediction method is believed to be a possible basis for a practical semitheoretical prediction method of broader scope and application.

Although the method is theoretical, its use depends on energy values which must be obtained by fitting the model to actual vapor-liquid equilibrium data for some mixtures of the kinds that are to be predicted.

Further investigation of the use of this model in vapor-liquid equilibrium prediction would logically proceed along one or both of two different avenues. First, the method can be applied to other solutions and energy values determined for use in the various types of binary systems (that is, alcohol-acid, ester-acid, ether-alcohol, etc.). The result will be a prediction method which in use will be similar to the method of Pierotti, et al., described in the introduction. The proposed method will differ in that it will have a broader theoretical basis.

The second logical avenue for further investigation is the measurement of association energies by a method independent of equilibrium measurements. In this way a prediction method completely independent of equilibrium determinations can be devised. It appears that the most fruitful area of investigation would be the spectrometric measurement of hydrogen-bond energies. These energies are known to appear as absorption bands in the infrared spectrum.

NOTATION

n = number of carbon atoms in an alcohol molecule
n' = number of carbon atoms in an ester molecule
r_A = number of sites on lattice occupied by alcohol molecule
r_B = number of sites on lattice occupied by ester molecule
Q_μ^A and Q_v^B = total number of contact points of types μ on alcohol molecules and types v on B molecules
R = gas constant
T = absolute temperature
x_A = mol. fraction alcohol in liquid
x_B = mol. fraction ester in liquid
z = coordination number ($z = 4$ was used)
γ = activity coefficient
$\eta_{\mu\mu}^{AA} = e^{-[U_{\mu\mu}^{AA}/RT]}$
$\eta_{\mu v}^{AB} = e^{-[U_{\mu v}^{AB}/RT]}$
$\eta_{vv}^{BB} = e^{-[U_{vv}^{BB}/RT]}$
$U_{\mu\mu}^{AA}, U_{\mu v}^{AB}, U_{vv}^{BB}$ = net energies associated with formation of the various interactions indicated by the subscripts
μ^E = excess chemical potential

LITERATURE CITED

1. Barker, J. A., *J. Chem. Phys.*, **20**, 1526-32 (1952).
2. Bushmakin, I. N., and I. N. Kis, *Zh. Prikl. Khim.*, **30**, 200 (1957).
3. Furnas, C. C., and W. B. Leighton, *Ind. Eng. Chem.*, **29**, 709 (1937).
4. Miller, A. R., "Theory of High Polymer Solutions," Oxford University Press, New York (1948).
5. Pierotti, G. J., C. H. Deal, and E. L. Derr, *Ind. Eng. Chem.*, **51**, 95-102 (1959).
6. Rose, Arthur, B. T. Papahronis, and E. T. Williams, *Ind. Eng. Chem.*, 3, 216-219 (1958).
7. Sheinker, Yu N., and E. M. Peresleni, *Zh. Fiz. Khim.*, **26**, 1103-9 (1952).

Manuscript received September 12, 1961; revision received November 9, 1962; paper accepted November 12, 1962. Paper presented at A.I.Ch.E. New York meeting.