

(Thus, Equation 3 need no longer hold.) Third, Equation 4 reduces to a linear isotherm, when either the anionic fraction alone or the cationic fraction alone is held constant. Because of this property, V^q is referred to here as the quasi-additive molar volume and δ^q is referred to as the deviation from quasi-additivity.

In Equation 4, each molar volume of a pure substance is weighted by the product of the corresponding cationic and anionic fractions and this product equals the Temkin expression for the concentration of the pure substance in the mixture (3, 7). Thus, $(N_K N_{Cl})$ equals the Temkin concentration for KCl in the melt.

Deviations from quasi-additivity, δ^q , for the (Li,K)-(Cl,NO₃) system were computed and found to be less than 0.5% for all compositions, except one—namely, $N_K = 0.41$ and $N_{Cl} = 0.50$ —for which δ^q was about 0.9%. The uncertainty in the ternary density data was considered to be about 0.2% and the uncertainty in δ^q to be 0.4 to 0.6%, depending on the chloride content. The 0.9% deviation was out of line with the deviations for neighboring compositions and did not seem to represent a trend.

By comparison, when these same data for the (Li,K)-(Cl,NO₃) system are tested for strict ternary additivity, it is found that to within the uncertainty of the deviations (0.4 to 0.6%) at least one V_i^A will represent the data for a given mixture about as well as V^q , but at least one other V_i^A will give a decidedly poorer representation. Furthermore, different concentration ranges are best represented by different V_i^A .

The quasi-additivity isotherms of pseudobinaries are represented by parabolas, one of which is

$$V^q = V_{LiNO_3}^0 + N_{Cl}(V_{KNO_3}^0 + V_{LiCl}^0 - 2V_{LiNO_3}^0) + N_{Cl}^2(V_{KCl}^0 + V_{LiNO_3}^0 - V_{KNO_3}^0 - V_{LiCl}^0)$$

for $N_K - N_{Cl} = 0$ (the LiNO₃ - KCl pseudobinary).

These parabolas, of course, intersect at the common composition ($N_{Cl} = 1/2$) and, when Equation 3 holds, reduce to the formalism of binary additivity.

The molar-volume isotherms of the (Na,K)-(Cl,I) pseudobinaries were tested for quasi-additivity at 700° C. using the data of Bloom and coworkers. The molar volumes along the KCl-NaI pseudobinary may be represented fairly well by a parabolic function which differs from the quasi-additivity function by a maximum of $+(0.6 \pm 0.2)\%$. The molar volumes along the KI-NaCl pseudobinary show positive deviations from quasi-additivity which average 0.6%, but which do not follow any simple function of concentration.

ACKNOWLEDGMENT

Special thanks are due to W.M. Ewing who assisted in some of the density determinations and to H.T. Murrin of the Mechanical Department who contributed much to the design of the apparatus.

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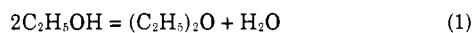
RECEIVED for review September 15, 1960. Accepted January 16, 1961. The Oak Ridge National Laboratory is operated for the U.S. Atomic Energy Commission by the Union Carbide Corp.

Thermodynamic Equilibrium in the Ethyl Alcohol-Ethyl Ether-Water System

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THE VAPOR PHASE DEHYDRATION of ethyl alcohol, catalyzed by Dowex 50 hydrogen as ion exchange resin to give ethyl ether and water, has been studied.



The work deals specifically with the equilibrium relationships in this system. The existence of the reaction, while not unknown, has often been ignored by past investigators whose primary concern was with some competing reaction of ethyl alcohol. In studying the vapor phase esterification of acetic acid with ethyl alcohol, Herrman (6) found that the equilibrium constant for this reaction appeared to vary with the total pressure. This suggests the presence of a side reaction, possibly ether formation. Klem (9), repeating Herrman's experiments, found the same effect. He prepared, by distillation, an acid-free sample of the reaction product for analysis by the authors. The analysis showed a considerable concentration of ether. In several studies of this

esterification (2, 7, 13, 14), the side reaction to ethyl ether was not considered. The authors, in a preliminary investigation of the reaction of isobutylene and ethyl alcohol to give *tert*-butyl ethyl ether, also found large amounts of diethyl ether in the product. Cope and Dodge (5) studied the hydration of ethylene with emphasis upon the formation of ethyl ether as well as ethyl alcohol. Their work specifically shows that one cannot neglect the possibility of ether formation. Hence, information on the dehydration of ethyl alcohol to ethyl ether would appear to be of value in a number of reactions involving ethyl alcohol.

Cope (4) has considered the thermal data necessary to predict the equilibrium constant for Reaction 1 as a function of temperature, and has made corrections to improve existing data where possible. He lists his best estimates (5), with an outline of the corrections made, the reliability, and the shortcomings. The temperature dependence of the equilibrium constant as calculated from these thermal data is shown as the broken line in Figure 1.

Cope and Dodge also critically discuss the experimentally determined values of the equilibrium constant, which are

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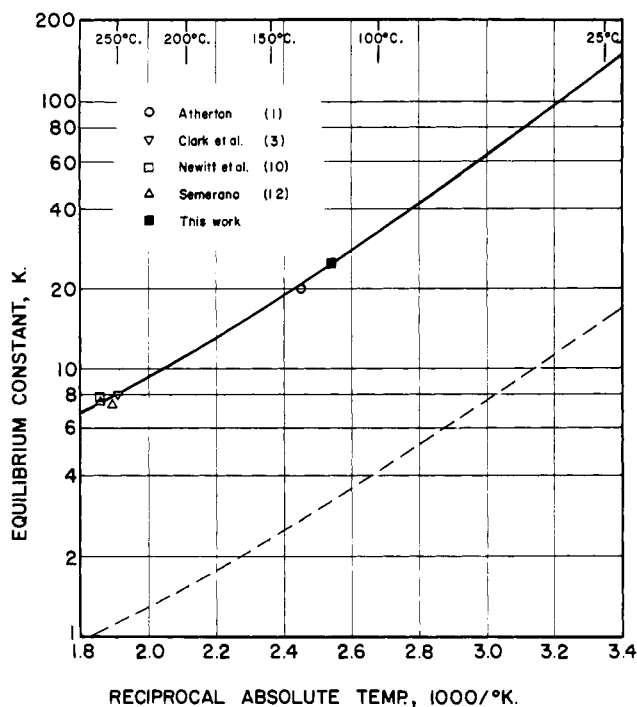
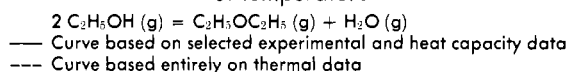


Figure 1. Thermodynamic equilibrium constant as a function of temperature



generally inconsistent. They concluded that the values of Semerano (12), Newitt and Semerano (10), Clark, Graham, and Winter (3), and Atherton (1) were the most reliable. On the basis of the value of 20. from Atherton's work at 135° C., an average best value of 8.0 at 250° C. from the results of the other authors, and the heat capacity data, Cope and Dodge estimated the standard enthalpy and entropy changes of reaction at 25° C. These values per gram mole of ether formed were -4220 cal. and -4.63 cal. per ° K., respectively. The corresponding values obtained from thermal data were $\Delta H^\circ = -4060$ and $\Delta S^\circ = -8.20$. It is evident that the major source of the discrepancy between these selected experimental results and the thermal data curve lies in the standard entropy of reaction. Cope and Dodge conclude that "since the entropy data for ethanol and water appear to be reliable, the major source of error must lie in the value for the absolute entropy of ether, although possible errors in the equilibrium data, in the specific heat of ether vapor, and in the heat of combustion of ether could account for a portion of the discrepancy."

The disagreement among measured values of the equilibrium constant, and between those apparently most reliable and the equilibrium constants based upon thermal data, was striking. In addition, the reliability of the unpublished measurement of Atherton was not readily subject to review. In order that later kinetics work might be carried out with confidence, the authors believed it necessary to supplement the data available at 250° C. as discussed above with additional equilibrium data at a lower temperature.

The present study was carried out in the vapor phase in a continuous flow reactor containing Dowex 50 cation exchange resin in the acid form. Feed mixtures of known composition, near the equilibrium composition, were passed, by gravity feed, to a control valve, through a rotameter, and into a vaporizing coil before passing upflow through the reactor. The reactor and coil were kept in an oil bath thermostat. The hot products were passed in the vapor state to a sampling chamber before passing on to a condenser. The sampling chamber consisted of a heated T,

one leg of which was fitted with a silicone rubber disk. A 10- μ l. syringe was inserted through the disk and the plunger drawn. The hot vapors condensed within the relatively cool syringe, giving a measurable liquid sample. This method avoided the problems involved in sampling an immiscible system and difficulties of condensing all of the ethyl ether without freezing the water.

The product was analyzed by gas chromatography. The product sample collected from the reaction system was immediately injected onto the column, using Carbowax 400 on Chromosorb for packing. The instrument was calibrated with accurately proportioned liquid mixtures of alcohol-water, alcohol-ether, and alcohol-ether-water. The mole ratios of alcohol to water and alcohol to ether for the known mixtures were plotted against, and therefore can be represented by, the corresponding peak height ratios from the chromatograms.

The usual method of obtaining the equilibrium composition in a flow system was employed. Feed mixtures were blended to molar compositions in the neighborhood of the equilibrium value, on the order of 91% ether, 5% water, and 4% ethyl alcohol. A plot of resulting product composition vs. flow rate should then allow extrapolation to the presumed equilibrium value of composition at zero flow rate. This procedure was carried out with mixtures containing both more alcohol and less alcohol (more ether and water) than would be present at equilibrium. Approaching equilibrium from both sides should guard against failure to reach true equilibrium.

The traditional method of basing the equilibrium constant directly upon the analysis of the reactor product resulted in an undesirable loss of absolute accuracy, because of a variety of sampling and analysis problems (8). This method bracketed the equilibrium constant between the limits of 21.6 and 25.6, but gave no indication as to where between the limits the true value of the constant lay.

Since reproducibility or precision in a given run sequence remained high, approach to equilibrium was observed entirely from the trend of change of product composition with flow rate, without regard to the actual product composition found. The authors are not aware that this technique has been reported previously. It is believed to be a sensitive and convenient method of determining equilibrium. Depending upon precision, rather than absolute accuracy of analysis, it does not necessitate tedious calibration in the analysis method or the flowmetering system. Aside from the routine blending of feed mixtures to a known composition, it is a qualitative approach which may yield quantitative information to any desired degree of accuracy.

For feed mixtures very close to the expected equilibrium composition, an "equilibrium constant" in accordance with the feed analysis was calculated. Then by observing the trend of height ratio of alcohol to ether with flow rate, one could observe whether the true equilibrium constant was larger or smaller than the feed "constant." For example, if the height ratio increases as flow rate decreases, alcohol is being formed at the expense of ether and water, and hence the feed composition must have been on the ether-water side of equilibrium. Thus, by making up a series of feed mixtures on the alcohol-rich and the ether-water-rich sides of equilibrium, it was possible to "zero in" upon the true value of the constant at the given temperature.

This equilibrium study is believed to be free of the complications to which Cope and Dodge attribute errors in previous studies. If there are competing reactions, the products thereof will probably be revealed by chromatographic analysis. Tests showed specifically that ethylene, if formed in the reaction, would have appeared in the analysis, as ethylene intentionally added to the feed was always found in the product. Temperature measurements by a thermometer in the oil bath were supplemented in some cases by measurements with a thermocouple in the catalyst

bed. Comparison of these results for the conditions of this study indicated the oil bath temperature to be within $\pm 0.1^\circ \text{C}$. of the true mean reaction temperature. The oil bath temperature at which this study was carried out was found to be 120.8°C . as corrected by means of a thermometer calibrated by the National Bureau of Standards.

It is difficult to operate at a temperature much lower than 120.8°C ., even with this relatively active catalyst, because of the reduced rate of reaction. Reaction kinetics considerations and experiments indicated that trends in height ratio with flow rate could not be clearly distinguished at 102°C .

Of the ten runs made with varying feed composition, six were judged to be sufficiently reliable for use in the determination of the equilibrium constant. The other four supported the final result within the limits of their reliability. At each flow rate, for each composition, ten samples were analyzed and the results averaged. This lessened the effect of fluctuations in sampling and analysis variables. The following table indicates the feed composition "equilibrium constant" and whether the value of the true equilibrium constant was indicated by the trends of composition change with flow rate to be greater than, equal to, or less than the feed "contant."

Run No.	True K Related to K_{feed}
3	$K < 26.02$
6	$K > 22.57$
7	$K = 24.85$
8	$K < 24.87$
9	$K > 23.64$
10	$K > 24.41$

The data for runs 8 and 10 were believed to be of the highest precision, and these are also the compositions closest to equilibrium. Feed mixtures farther removed from equilibrium did not require as high precision to distinguish trends in change. Results using feed 7 were less precise than results using feed 8 and thus no trend could be definitely assured. The data for runs 8 and 10 are:

Run 8				
Flowmeter reading	3.8	4.4 ⁻	4.95	5.5
Height ratio	0.0862	0.0861	0.0857	0.0851
Run 10				
Flowmeter reading	4.3	4.6 ⁺	5.0 ⁺	5.4 ⁺
Height ratio	0.0837	0.0837	0.0842	0.0851

The opposite directions of change of peak height ratio with flowmeter reading for runs 8 and 10 establish that the equilibrium constant lies between 24.41 and 24.87. The range of height ratios in run 8 is less than in run 10, although run 8 was carried out over a greater range of flow rates. This would place the true value of the constant closer to 24.87 than to 24.41. Run 7 seems to support this analysis.

The true value of the thermodynamic equilibrium constant at 120.8°C . for this reaction is therefore estimated to be 24.7 ± 0.1 . Since this reaction involves no change in the total number of moles and is carried out at a low pressure, the equilibrium constants based upon concentrations, mole fractions, fugacities, activities, and partial pressures all have the same numerical value. This value of the equilibrium constant at 120.8°C ., together with the average value of 8.0 at 250°C ., can be utilized with known heat capacity data (5) in the form $a + bT + cT^2$ to evaluate the temperature dependence of the equilibrium constant:

$$R \ln K = -\frac{\Delta H^\circ}{T} + \Delta S^\circ + \Delta a \left[\frac{T_0}{T} - 1 + \ln \frac{T}{T_0} \right] + \frac{\Delta b}{2} \left[\frac{(T - T_0)^2}{T} \right] + \frac{\Delta c}{6} \left[T^2 - 3T_0^2 + \frac{2T_0^3}{T} \right] \quad (2)$$

where values of the constants are $\Delta H^\circ = -4350$ cal. per g. mole, $\Delta S^\circ = -4.85$ cal. per g. mole $^\circ \text{K}$., $\Delta a = 6.1$, $\Delta b =$

-0.2×10^{-3} , $\Delta c = -7.3 \times 10^{-6}$, and $T_0 = 298.2^\circ \text{K}$. This equation is represented as the solid line in Figure 1.

The new value of the equilibrium constant presented here is in good agreement with, and is believed to add considerable strength to, the estimate of the equilibrium curve proposed by Cope and Dodge. The value of K calculated from Equation 2 at 135°C . is also in excellent agreement with the datum of Atherton. The increased confidence in the experimental curve of Figure 1 warrants a brief discussion of Cope and Dodge's conclusion quoted above. The contribution of the heat capacity terms in Equation 2 to the value of K is sufficiently small that errors in these items could not explain the discrepancy between the curves in Figure 1. Furthermore, at 25°C ., where the heat capacity terms have no effect, the curves remain widely separated. If the experimental equilibrium data are correct, this can be due only to errors in the values of ΔH° and ΔS° . If the standard heats of formation of ethyl alcohol and water at 25°C . as reported by Cope and Dodge are taken to be correct, the standard heat of formation of ethyl ether vapor is calculated from ΔH° to be $-58,910$ cal. per mole. This agrees with the value of $-58,620$ cal. per mole, as corrected by Cope and Dodge from published data, well within their estimated outside limits of error of ± 1000 cal. per mole. If it is assumed that all thermodynamic data considered here, with the exception of the entropy of the ether vapor, are reliable, the absolute entropy of ethyl ether vapor at 25°C . may be calculated to be 85.2 cal. per mole $^\circ \text{K}$. This is believed to be more reliable than the value of 81.85 , calculated by Cope and Dodge from the value for liquid ether reported by Parks, Kelley, and Huffman in 1929 (11). Arguments supporting each of these values are outlined by Kabel (8).

SUMMARY

The thermodynamic equilibrium constant has been determined to be 24.7 ± 0.1 for the vapor phase dehydration of ethyl alcohol to ethyl ether at 120.8°C . This additional value should considerably increase confidence in the experimentally determined curve of equilibrium constant as a function of temperature in preference to that curve determined entirely from thermal data. These results and previous reported discussions, particularly those of Cope and Dodge, suggest that the major error in the thermal data resides in the value for the entropy of ethyl ether.

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RECEIVED for review September 2, 1960. Accepted May 15, 1961.