

Thermodynamic Equilibrium in the Vapor Phase Esterification of Acetic Acid with Ethanol

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A study of vapor-phase equilibrium in the reaction system acetic acid-ethanol-ethyl acetate-water has been made including an evaluation of past investigations, a calculation of equilibrium constants from thermal data, and new experimental determinations utilizing gas chromatography in a novel method. It was found that the magnitude of the thermodynamic equilibrium constant and its true variation with temperature are appreciably different than previously indicated. This is due to the failure of earlier workers to adequately account for competing reactions, primarily the dehydration of ethanol to ethyl ether. Equilibrium constants were obtained at 100, 120.8, and 170°C. for the ethanol dehydration reaction. Equilibrium positions of the esterification reaction have been determined accurately at the same three temperatures, however the corresponding values of the thermodynamic equilibrium constant remain imperfectly specified because of uncertainty concerning the acetic acid association equilibrium.

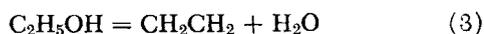
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has been studied experimentally by many investigators (1 to 16). Detailed critical evaluations of all of these investigations are given by Hawes (17). The major source of error in the previous studies was the neglect of the competing reaction



which has been shown (17, 18) to occur at conditions which promote Reaction (1). Similarly it has been shown (8, 17, 19) that a third reaction may also interfere under certain conditions.



ACETIC ACID ASSOCIATION

In an attempt to explain the anomalous equilibrium data of Herrman (15), Babcock and Johanson (20) investigated the vapor phase association among all of the components of Reaction (1). They concluded that "Calculations of the reaction equilibrium constant for the formation of ethyl acetate from ethyl alcohol and acetic acid may therefore safely be made, allowing only for the association of acetic acid with itself."

The most recent papers treating acetic acid association (21 to 25) agree that acetic acid can dimerize in the vapor phase, but they differ as to whether trimers also exist. Trial calculations in this work showed that trimerization, if it exists, need not be taken into account in calculation of thermodynamic equilibrium constants for Reaction (1), since the equilibrium constants for the reaction to form the trimer (21, 22) are quite small. Discrepancies also exist in regard to the temperature function and absolute values of the equilibrium constant for association to the dimer. To provide a valid comparison, Reaction (1) equilibrium constants of previous studies were recalculated from the equilibrium data given, using dimerization constants of Potter, Bender, and Ritter (21) and the method described in the Appendix. All results shown on Figure 1 are so revised except those (1 to 6, 13) having other defects which made revision pointless and those (8, 10) in which revision would not affect the numerical values.

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CALCULATION OF EQUILIBRIUM CONSTANTS FROM THERMAL DATA

Values of the equilibrium constant for any reaction may be predicted from thermochemical data by means of the equation:

$$\begin{aligned} R \ln K = & -\frac{\Delta H^\circ}{T} + \Delta S^\circ + \Delta \alpha \left[\frac{T_0}{T} - 1 + \ln \frac{T}{T_0} \right] \\ & + \frac{\Delta \beta}{2T} (T_0 - T)^2 + \frac{\Delta \gamma}{6T} [T^3 - 3TT_0^2 + 2T_0^3] \quad (4) \end{aligned}$$

The thermal data required for evaluation of equilibrium constants in this manner are the heats of formation and absolute entropies, at the standard state of the compounds, which take part in the reaction of interest, as well as their molar heat capacities, in the form $C_p = \alpha + \beta T + \gamma T^2$. Standard state conditions for the pure components, chosen for convenience, are the ideal gas state at 1 atm. and 25°C. In some cases, recently reported values of good reliability are available, while in others the available data are conflicting or out of date.

All of the necessary thermal data for ethanol and water have been tabulated by Cope and Dodge (19). Their values were arrived at after careful evaluation and correction where necessary, and will be employed herein.

The thermal data for acetic acid must be obtained on a monomeric basis, in keeping with the standard state condition of ideal gas. Child and Hay (24), and Weltner (25) provide these in tabulations of thermodynamic functions which have been calculated from statistical thermodynamics. However, the statistical treatment of Child and Hay was more sophisticated and had a more reliable experimental basis, and therefore is preferred. The heat of formation was selected accordingly. For absolute entropy, an average value calculated from three values (24 to 26) based solely on thermochemical experimentation is preferred to the statistical values. The heat capacity function selected was that of Child and Hay and has been shown (17) to coincide closely with that which may be estimated by the method of Dobratz (27), as modified (28).

For ethyl acetate, the standard heat of formation was calculated as shown in Table 1.

This new calculation is considered to possess less error than the value of -103.4 kcal./mole of Vvedensky, et al. (32). Their value was based on experimentally determined equilibrium constants for the gas phase dehydration of ethanol to ethyl acetate and on heat capacities

in disagreement with those preferred herein. Vvedensky, et al., provided the only value available for the absolute entropy of ethyl acetate. Their value was revised, as indicated in Table 2, for use in this work. The estimation method used herein to evaluate heat capacity of ethyl acetate yields a function which is intermediate between experimental data of two separate references (33, 34).

After utilizing the thermal data of Table 2 in Equation (4), the following equation is obtained for the variation of Reaction (1) gas phase thermodynamic equilibrium constant with temperature

$$\ln K_1 = -20.05 + 2716/T + 2.979 \ln T - 3.533 \times 10^{-3}T + 0.52 \times 10^{-6}T^2 \quad (5)$$

The values of equilibrium constant predicted by this function are shown as a semilogarithmic function of reciprocal temperature in Figure 1 and Figure 3. Comparison of this function with the equilibrium constants from the previous work and with those determined in the experimental portion of this work shows some disagreement; this is probably attributable to errors in some of the thermal data employed in the above calculation. The absolute entropies of acetic acid monomer and ethyl acetate are thought to be the values most likely to possess error, and the displacement of the calculated function below the experimental one indicates that the acetic acid entropy in

TABLE 1. CALCULATION OF STANDARD HEAT OF FORMATION OF ETHYL ACETATE AT 25°C. FROM CALORIMETRIC DATA

process ^a	ΔH , cal.
$4C(s) + 4O_2(g.) \rightarrow 4CO_2(g.)$	-376,208†
$4H_2(g.) + 2O_2(g.) \rightarrow 4H_2O(l)$	-273,268†
$4CO_2(g.) + 4H_2O(l) \rightarrow EtOAc(l) + 5O_2(g.)$	535,100†
$EtOAc(l) \rightarrow EtOAc(g.)$	8,697§
$4C(s) + O_2(g.) + 4H_2(g.) \rightarrow EtOAc(g.)$	-105,680

^a All processes are at 25°C.

† (29).

‡ (30).

§ (31).

TABLE 2. THERMAL DATA FOR ACETIC ACID, ETHANOL, ETHYL ACETATE, AND WATER
Ideal gas state at 1 atm. and 25°C

Substance	Heat of formation kcal./mole	Absolute entropy e.u.
Acetic acid (monomer)	-103.1 ^a	68.6†
Ethanol	-56.18‡	67.58‡
Ethyl acetate	-105.68§	86.95¶
Water	-57.798‡	45.106‡

Heat capacity equations ideal gas state

Substance	α	$\beta \times 10^3$	$\gamma \times 10^6$	Temperature Range °K.
Acetic acid (monomer)#	3.041	54.11	-26.59	300-700
Ethanol†	4.3	40.25	-7.5	300-600
Ethyl acetate**	5.408	80.54	-30.54	300-500
Water‡	7.85	-0.217	2.656	300-700

^a (24).

† Averaged from three values (24, 25, 26).

‡ (19).

§ See Table 1.

¶ (32) corrected to vapor pressure data of (35).

Fitted to tabulated data of (24) by method of least squares.
** Estimated by method of (27) as revised by (28), using Einstein functions of (27).

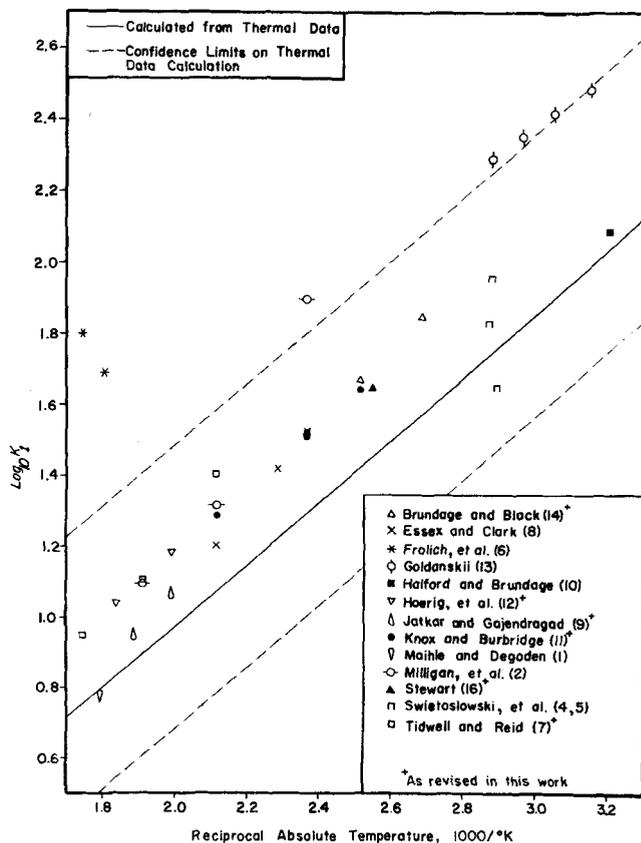


Fig. 1. Esterification equilibrium constants from previous work and from thermal data.

Table 2 may be too high, or the ethyl acetate entropy too low, or both. The difference in slopes between the two functions, seen best on Figure 3, suggests that some error may also be present in the standard heats of formation employed.

Confidence limits of the function from thermal data may be proposed by considering the probable error in the most questionable thermodynamic quantities used. For the standard state entropy of acetic acid monomer, the highest and lowest values used in computing the average value shown in Table 2 may be assumed to constitute the limits of the range of probable error. A 1% uncertainty is assumed in the third law liquid phase entropy value (36) on which the standard state entropy of ethyl acetate is based. These lead to the overall confidence limits, shown as broken lines in Figure 1, for the variation of the Reaction (1) thermodynamic equilibrium constant with temperature. The results of this research as well as most of the data from past work lie within the region bounded by the limits.

A considerable magnification of error is characteristic of calculations of equilibrium constants from thermal data; this is due to the standard enthalpy and entropy changes of reaction that are small in relation to many of the thermal data employed to obtain them, and the fact that the equilibrium constant is equated to these changes logarithmically. In view of this the discrepancy between the calculated and experimental results is not surprising.

EXPERIMENTAL

Materials

All chemicals were used as received and corrections for the major impurities were included in the calculations. Fisher certified reagent grade ethyl acetate containing approximately 0.01% water and ethyl ether containing approximately 0.01% each water and ethanol were used. Fisher reagent grade

acetic acid was used, with a water content of about 0.2% as determined by the Karl Fisher method. U.S.P. 200 proof absolute ethanol was employed. Analysis by gas chromatography showed no significant impurities in this ethanol. The water was laboratory distilled and deionized by passage through an ion exchange column. Experimental feed mixtures were prepared by weight. Components were successively added to a weighing bottle in reverse order of volatility, in order to minimize losses due to evaporation. Weights of each component added were measured to within 0.005 g. Feed compositions were dictated by the known or expected equilibrium compositions for Reactions (1) and (2) (see later) and by solubility considerations.

Two catalysts were employed. Dowex 50 cation exchange resin was partially air dried and mixed with about twice its volume of nonporous glass beads before using. The resin was of 20 to 50 mesh size. Davison 40 to 50 mesh silica gel was used as received.

The columns used in analysis by gas chromatography were fabricated from $\frac{1}{4}$ in. copper tubing and packed with approximately 15 wt. % polyethylene glycol (Carbowax 1500) supported on 40 to 60 mesh Teflon 6.

Apparatus

In all experimentation the apparatus consisted of a tubular flow reactor preceded by a feed supply and delivery system, and followed by a sampling and analysis system. Portions of the apparatus to be contacted with acetic acid solutions were of glass or 316 stainless steel. From a constant head feed tank, liquid feed mixtures passed by gravity flow through a rotameter and a flow control valve to a vaporizing coil and thence to the reactor. The vaporizing coil and reactor were immersed in a stirred, electrically heated oil bath whose temperature could be controlled to within 0.1°C. The reactor was oriented vertically within the bath, with feed entering at the base. Temperature within the reactor was measured with a thermocouple positioned axially inside it and was shown to be the same as the bath temperature. The thermocouple had been calibrated against a secondary standard. Accuracy of temperature measurement was estimated to be 0.1°C. The product vapor exited to the top of the reactor and passed through a jacketed and insulated product line to a gas sampling valve. Air heated by passage through a coil of tubing within the oil bath was directed through the jacket about the product line, enabling a vapor phase product to be maintained. Samples of product vapor were introduced into a Perkin-Elmer Model 154L Vapor Fractometer by means of a Perkin-Elmer gas sampling valve, part number 154-0068. The carrier gas used was helium.

Procedure

Thermodynamic equilibrium constants for Reaction (1) were determined by an adaptation of the method previously reported (37). In each run, liquid feed mixtures of ethanol, ethyl ether, water, acetic acid, and ethyl acetate were blended such that the composition of the first three components corresponded to an equilibrium composition of Reaction (2) at the temperature of the run. In order to do this, knowledge of the Reaction (2) equilibrium constants at the temperatures of the Reaction (1) determinations was required. Determinations of thermodynamic equilibrium constants for Reaction (2) were made by using the method previously described (37), except that the gas sampling valve was employed in place of sampling with a syringe. This was regarded as an improvement, providing greater reproducibility in sample size.

With Reaction (2) at equilibrium, amounts of acetic acid and ethyl acetate in the feed to the esterification runs were adjusted so that the Reaction (1) equilibrium constant corresponding to the feed composition would be close to the expected true equilibrium constant. Approach to equilibrium was observed from trend of change of product composition with flow rate. Since Reaction (2) would be at equilibrium initially, any change observed must be initiated by Reaction (1) alone, and thus error owing to the competing reaction could be entirely avoided. The absence of Reaction (3) was a requirement in these determinations, and this could be assured by observation of product chromatograms for evidence

of ethylene.

The height ratio of the ether peak to the ethyl acetate peak on the product chromatograms was measured and taken to be qualitatively indicative of the corresponding mole ratio. The trend of variation of this height ratio with flow rate indicated whether the true equilibrium constant was larger or smaller than the feed constant for Reaction (1). If, for example, the height ratio increased as the flow rate decreased, it was concluded that acetic acid and ethanol were being formed at the expense of ethyl acetate and water. The depletion of water and formation of ethanol imbalances the Reaction (2) equilibrium, resulting in the formation of ether. Therefore the feed composition was deduced to be on the ester-water side of the Reaction (1) equilibrium. After a series of runs at a single temperature, using feed mixture equilibrium constants on both sides of equilibrium, a true equilibrium position at that temperature could be accurately deduced. All feed equilibrium constants were calculated as described in the Appendix.

APPLICATION OF THE EXPERIMENTAL METHOD

Determinations of vapor-phase equilibrium constants for Reaction (2) were attempted at 100, 120.8, and 140°C. using 45 g. of Dowex 50 cation exchange resin as catalyst, and at 170°C. using 100 g. of silica gel. Preliminary experimentation using pure ethanol feed demonstrated that Reaction (2) occurred appreciably at these conditions. At 100°C. changes in product composition with flow rate were smallest because of a slow rate of reaction. In the earlier study (37), trends in height ratio at 102°C. could not be clearly distinguished. In this study, however, the trends were distinguishable. The improvement was thought to be a result of the improved sampling technique, which minimized height ratio variations resulting from variations in sample size. At 120.8°C., the temperature used previously (37), the equilibrium constant 24.7 ± 0.1 determined in the earlier paper was confirmed. At 140°C., small ethylene peaks appeared on the product chromatograms. An attempt to evaluate the Reaction (2) equilibrium constant by disregarding the ethylene indicated that the constant would clearly be too low. It was concluded that the extent of ethylene formation over Dowex 50 resin is too great at 140°C. to permit effective use of the method. At 170°C. the trends in height ratio were small but clearly discernible.

Prior to the experimental runs to determine esterification equilibrium constants, preliminary experiments showed that Reaction (2) occurred to a significant degree as a side reaction to Reaction (1) at 100 and 120.8°C. over Dowex 50 resin and at 170°C. over silica gel. This demonstrated that precautions are indeed necessary to properly account for the competing etherification in vapor phase equilibrium studies of Reaction (1). Esterification equilibrium constants were determined at 100 and 120.8°C., where 20 g. of Dowex 50 resin were employed as catalyst, and at 170°C., where 100 g. of silica gel were used.

RESULTS AND DISCUSSION

The experimental results of this research are shown in Table 3.

ETHERIFICATION EQUILIBRIUM

In Figure 2 the vapor phase equilibrium constants of Reaction (2) determined experimentally in this research are shown, together with two constants from past studies (38 to 41). The latter have been selected (19, 37) as providing the most reliable values among all previ-

TABLE 3. EXPERIMENTAL EQUILIBRIUM CONSTANTS AND COMPOSITION

Temp., °C.	Equilibrium constants			Equilibrium compositions in esterification determinations† (mole fractions)				
	K_2	K_1^*	K_1^\dagger	HOAc	EtOH	H ₂ O	Et ₂ O	EtOAc
100.0	33.4 ± 0.1	60.3 ± 0.3	65.1 ± 0.3	0.04256	0.04302	0.20047	0.30836	0.40558
120.8	24.7 ± 0.1	49.4 ± 0.3	51.0 ± 0.3	0.04752	0.04769	0.22200	0.25304	0.42975
170.0	15.0 ± 0.2	32.1 ± 0.1	32.1 ± 0.1	0.05983	0.05994	0.27095	0.19889	0.41039

* Calculated by using acetic acid association equilibrium constants from (21).

† Calculated by using acetic acid association constants from (23).

‡ These equilibrium compositions are based on a total pressure of 730 mm. mercury, which was approximately the average pressure of the experimental runs.

ous determinations of the etherification equilibrium constant. Of the earlier equilibrium constants, Kabel and Johanson (37) considered the average value (38 to 40) of 8.0 at 250°C., first proposed by Cope and Dodge (19), to be most reliable, while pointing out that Atherton's (41) value of 20 at 135°C. was of unknown reliability. After the determinations of the present work, the average value at 250°C. and the three points determined or confirmed herein were deemed most reliable. As these appeared to lie approximately in a straight line in the usual log K vs. reciprocal temperature plot, a linear function was fitted to them by the method of least squares, resulting in the equation

$$\log_{10} K_2 = 800/T - 0.628 \quad (6)$$

This temperature function is shown as the solid line in Figure 2. The broken line is an earlier function proposed by Kabel and Johanson (37) using their point at 120.8°C., the average value at 250°C., and data for heat capacity change of reaction (19).

From Equation (6) the thermodynamic quantities $\Delta H^\circ = -3,660$ cal./mole and $\Delta S^\circ = -2.87$ e.u. are obtained. In contrast to these, Kabel found $\Delta H^\circ = -4,350$ cal./mole and $\Delta S^\circ = -4.85$ e.u. The thermal data prediction of Cope and Dodge, revised according to an im-

proved value of ethyl ether heat of formation recently communicated (42), gives $\Delta H^\circ = -4,230$ cal./mole and $\Delta S^\circ = -8.20$ e.u. The discrepancies between the thermodynamic quantities from Equation (6) and the earlier values are attributable mainly to small differences in slope and curvature of the temperature functions of log K_2 . The straight line function of Equation (6) implies no heat capacity change upon reaction, in disagreement with the thermal data heat capacities developed by Cope and Dodge (19). Nevertheless a straight line function appears to fit the four preferred experimental equilibrium constants satisfactorily, and an attempt to fit a more complex function to them does not seem warranted. No clear explanation is apparent for the differences in slope and curvature, but it may be that some error still exists among the thermal data in spite of earlier indications (42). It is also possible that significant error is present in the average value 8.0 at 250°C., since some ethylene formation was encountered in the equilibrium studies (38 to 40) from which this average was taken. If the competing Reaction (3) were significant in those studies, one could expect that the true equilibrium constant for Reaction (2) would be greater than 8.0 at 250°C. In this case a curve fitted through the three points of this research and passing above the point of 250°C. might be indicated as the best description of the temperature function of log K_2 . The three points of this research when taken alone would be best fitted by a function which would agree more closely in curvature with the thermal data result.

ESTERIFICATION EQUILIBRIUM

The experimental esterification equilibrium constants calculated using acetic acid association data from two sources (21, 23) are shown in Table 3 and Figure 3. The results of the calculations using the data of Potter, Bender, and Ritter (21) are preferred. However the results of calculations from Taylor's (23) association data are presented to provide a measure of the effect of uncertainty as to the degree of acetic acid association on the magnitude and temperature dependence of the esterification equilibrium constant. The two sources of association data employed lead to appreciably different constants at low temperatures where the association effect becomes large. Thus uncertainty will necessarily be present in the experimental values of the esterification thermodynamic equilibrium constant until such time as the disagreement among the association constants has been resolved.

Equilibrium compositions that were deduced from the esterification runs are also shown in Table 3. In this tabulation the mole fractions for acetic acid are based on its formula weight of 60.052. By using these compositions one may calculate equilibrium constants for Reaction (1) with association data other than those utilized herein.

Straight line functions could be fitted well within experimental error to the logarithms of the experimental Reaction (1) constants of this research as functions of

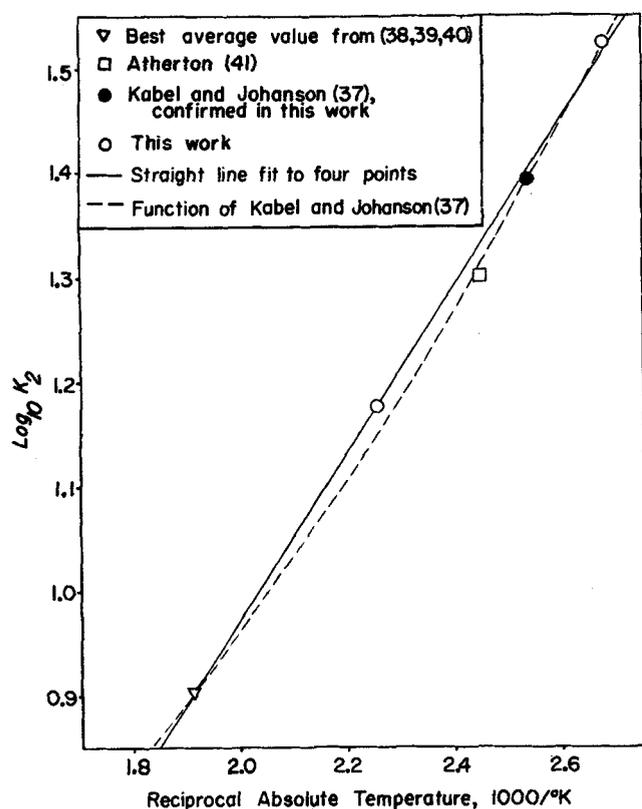


Fig. 2. Etherification thermodynamic equilibrium constant. $2 \text{ C}_2\text{H}_5\text{OH (g.)} = \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \text{ (g.)} + \text{H}_2\text{O (g.)}$

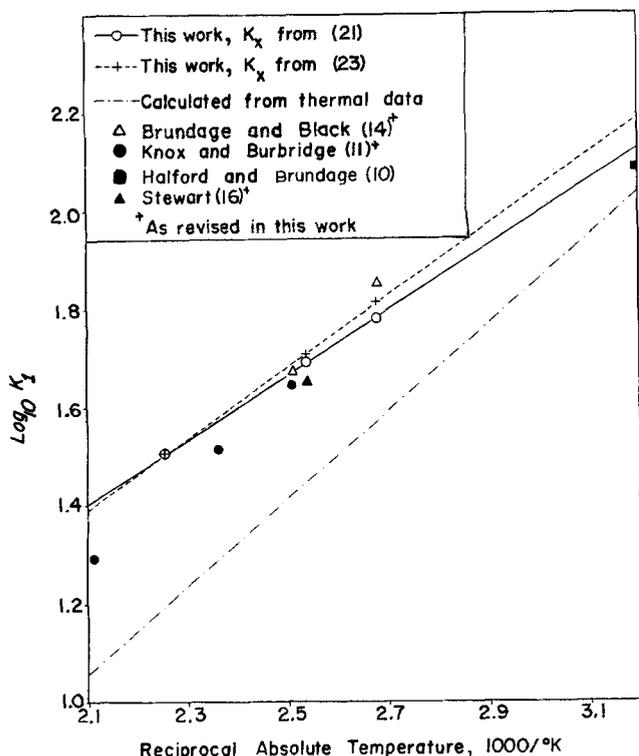


Fig. 3. Esterification thermodynamic equilibrium constant $\text{CH}_3\text{COOH (g.)} + \text{C}_2\text{H}_5\text{OH (g.)} = \text{CH}_3\text{COOC}_2\text{H}_5 \text{ (g.)} + \text{H}_2\text{O (g.)}$

reciprocal absolute temperature. The equations for these lines, determined by the method of least squares, are

$$\log_{10} K_1 = 649/T + 0.042 \quad (7)$$

$$\log_{10} K_1 = 724/T - 0.127 \quad (8)$$

Equation (7) describes the constants calculated using dimerization constants from Equation (9) taken from the work of Potter, Bender, and Ritter (21):

$$\ln K_x = (3000/T) - 10.149 \quad (9)$$

Equation (8) gives the constants calculated using dimerization constants from Taylor (23). The thermodynamic quantities $\Delta H^\circ = -2,970$ cal./mole and $\Delta S^\circ = 0.19$ e.u. are obtained from Equation (7) and $\Delta H^\circ = -3,310$ cal./mole and $\Delta S^\circ = -0.58$ e.u. from Equation (8). These are to be compared to $\Delta H^\circ = -4,200$ cal./mole and $\Delta S^\circ = -4.1$ e.u. which may be obtained from the thermal data in Table 2. The poor agreement is thought to be due to erroneous thermal data, as discussed earlier.

A comparison of the experimental results of the present work with those of earlier workers is of interest. This comparison is best made on Figure 3. In all previous studies except that of Stewart (16), analyses were performed by titration of acid or saponified ester. This procedure affords no indication of the presence of products of competing reactions. The equilibrium constant from the work of Stewart (16) is in greater disagreement with those of this work than one would expect, since his experimental method was similar to that employed herein. Although his sampling and analysis techniques were less sensitive and reliable than those of this work, they should have been adequate. The method of Halford and Brundage (10) also excluded the possibility of error due to side reactions. Allowing for the extrapolation involved, good agreement is obtained between this work and their datum at 40°C. Since the specificities of the catalysts used by Knox and Burbridge (11), and Brundage and Black (14) are not known it is possible, but not likely, that their

studies were free of side reactions. Since side reactions are known to occur at the conditions of all of the other studies, not having other defects more severe, the data of only these four studies (10, 11, 14, 16) are shown on Figure 3. Excellent agreement with the present results is shown by the constant of Brundage and Black (14) at 125°C., however their constant at 100°C. is above those of this research.

It can be seen from Figure 1 that the constants of Knox and Burbridge (11) are representative of the consensus of the earlier data. A comparison of the results of Knox and Burbridge with those of this study on Figure 3 shows that the reciprocal temperature function of $\log_{10} K_1$, when extrapolated to higher temperatures, lies above the line of variation indicated by the previous data and possesses a smaller slope.

Of the equilibrium constants determined at temperatures of 150°C. and above, it appears probable that the majority were obtained in the presence of one or more side reactions and are therefore in error to some extent. The occurrence of Reaction (2) or Reaction (3), unobserved in the experimental determinations, can be expected to have depleted the ethanol in the reaction products to a lower concentration than was surmised by the investigators from the results of their titrations and to have correspondingly increased the water concentration. Thus the constants reported are likely to be smaller than the true thermodynamic constants at corresponding temperatures. Furthermore, experiments in the present work have confirmed that the extent of reactions competing with Reaction (1) increases with increasing temperature over specific catalysts. The relative magnitude of error owing to side reactions will then be greater at higher temperatures. One may conclude that the true variation of the thermodynamic equilibrium constant above 150°C. should consist of a straight or slightly curved line lying above the apparent straight line roughly indicated by the data in Figure 1 (or the data of Knox and Burbridge in Figure 3) and possessing a smaller slope. One is limited to this qualitative explanation of the behavior observed in this work relative to the previous work, because quantitative correction of the previously reported constants cannot be made without kinetic data concerning the simultaneous reaction system. It is unlikely that Reactions (2) and (3) approached equilibrium in any of the studies cited. Thus the temperature dependence and the absolute magnitudes of the esterification thermodynamic equilibrium constant found in this work are credible.

CONCLUSIONS

1. A method has been developed for determining the reaction equilibrium position of any reaction system in which a homogeneous liquid phase of equilibrium composition can be obtained. Excellent accuracy is possible because it depends only upon accuracy in formulation of the feed mixtures and in precision of analyses. Accuracy of analysis is not required.

2. New equilibrium constants at 100 and 170°C. have been obtained experimentally for the dehydration of ethanol to ethyl ether.

3. Equation (7), in conjunction with Equation (9) and the method described in the Appendix, is believed to be the most reliable basis presently available for predicting the equilibrium position of the esterification reaction of acetic acid and ethanol.

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NOTATION

- C_p = heat capacity, cal./mole °K.
 K = thermodynamic equilibrium constant for any reaction
 K_1 = thermodynamic equilibrium constant for Reaction (1), dimensionless
 K_2 = thermodynamic equilibrium constant for Reaction (2), dimensionless
 K_x = thermodynamic equilibrium constant for the dimerization of acetic acid = P_2/P_1^2 , (mm. Mercury)⁻¹
 $n_1, n_2, n_3, n_4, n_5, n_6$ = number of moles of acetic acid monomer, dimer, ethanol, ethyl acetate, water, and additional compounds, respectively, present in an equilibrium mixture
 P_1, P_2 = partial pressure of acetic acid monomer and dimer, respectively, mm. Mercury
 R = gas constant = 1.987 cal./mole °K.
 T = temperature, °K.
 T_0 = standard state temperature = 298.2°K.
 w = number of formula weights of acetic acid (mol. wt. = 60.052) present in the equilibrium mixture
 y_1, y_3, y_4, y_5 = mole fraction of acetic acid monomer, ethanol, ethyl acetate, and water, respectively, present in the equilibrium mixture, dimensionless

Greek Letters

- α, β, γ = coefficients in equation for heat capacity of each component, $C_p = \alpha + \beta T + \gamma T^2$
 $\Delta\alpha, \Delta\beta, \Delta\gamma$ = changes of heat capacity coefficients with chemical reaction
 ΔH = enthalpy change for a process, cal./mole
 ΔH° = standard heat of reaction, cal./mole
 ΔS° = standard entropy of reaction, cal./mole °K.
 π = total pressure of system, mm. Mercury

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APPENDIX

The equilibrium constants calculated in this work are defined in terms of Equation (1), that is on the basis of reaction involving only the monomeric form of acetic acid. The reaction mixture is taken to be an ideal gas comprising the dimer of acetic acid and monomers of acetic acid and all other compounds. Thus the thermodynamic equilibrium constant is

$$K_1 = \frac{y_4 y_5}{y_1 y_3} \quad (1A)$$

By synthesis or analysis of an equilibrium mixture, w , n_3 , n_4 , n_5 , and n_6 are known. The number of moles of monomer and dimer can be obtained from the following equations

$$n_1 = - \frac{n_3 + n_4 + n_5 + n_6}{4\pi K_x + 1} + \sqrt{\left(\frac{n_3 + n_4 + n_5 + n_6}{4\pi K_x + 1}\right)^2 + \frac{2w}{4\pi K_x + 1} \left(\frac{w}{2} + n_3 + n_4 + n_5 + n_6\right)} \quad (2A)$$

$$n_2 = (w - n_1)/2 \quad (3A)$$

Equation (2A) was originally derived by Essex and Clark (8) for the case of one atmosphere pressure and a four component system. It has been generalized for use in this work. From knowledge of the number of moles of each species, the mole fractions of all species can be obtained and the equilibrium constant determined.

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