Equilibria in the Hydration of Ethylene at Elevated Pressures and Temperatures

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Values of equilibrium composition for the hydration of ethylene to form ethanol have been calculated for a series of elevated pressures and temperatures by using equilibrium data available from previous low-pressure studies. To obtain satisfactory agreement between these values and those measured experimentally, it is essential (1) to take into account the formation of ethyl ether and (2) to use available vapor-liquid equilibrium data for the binary ethanol-water system at elevated temperatures, instead of the standard "mixture rules" often employed.

Thermochemical data and low-pressure equilibrium data for both the ethylene hydration and ether formation reactions are critically reviewed. Experimentally measured values for the equilibrium concentrations of ethanol and ether in the liquid phase at 221°C. and 273 atm., with dilute sulfuric acid used as catalyst in a lined rocking-bomb reactor, are presented.

This paper compares equilibrium compositions measured experimentally for the hydration of ethylene at elevated pressures and temperatures with those predicted from available thermodynamic data and presents a critical review of these data.

The hydration of ethylene to form ethanol, as well as the reverse reaction, has been the subject of numerous past investigations. Most of the equilibrium studies for the ethylene-water-ethanol system were carried out at relatively low pressures such that a vapor phase only was present. The investigation by Gilliland, Gunness, and Bowles (*16*) is the only published work pertaining specifically to equilibrium states for the hydration of ethylene at conditions under which both liquid and vapor phases were simultaneously present. A similar study of the hydration of propylene is reported by Majewski and Marek (*30*).

Dodge (*13*) has presented a comparison of predicted and measured equilibrium compositions for both the liquid and vapor phases for a specific set of conditions used by Gilliland, Gunness, and Bowles. At the time that the predicted values were calculated it was necessary to make a considerable number of simplifying assumptions. Later pertinent vapor-liquid equilibrium data at elevated temperatures for the binary ethanol-water system were obtained by Griswold, Haney, and Klein (*17*), and also recently in this laboratory by Barr-David (*6*). During the present work inconsistencies were found in the results given by Gilliland, Gunness, and Bowles, and it therefore appeared advisable both to recalculate the predicted values of composition and to remeasure equilibrium compositions experimentally.

PREDICTION OF EQUILIBRIUM COMPOSITIONS FROM THERMODYNAMIC DATA

In order to calculate values of equilibrium composition for a two-phase system it is essential to know what the fugacities of the various participating substances are and how the fugacities vary as functions of the composition of each phase. In this specific case values of K_f, the equilibrium constant defined in terms of fugacities, are known from equilibrium studies at low pressures and at various temperatures. This equilibrium constant is independent of pressure and composition. By determining (or assuming) how the fugacities of the various substances are affected by pressure and by the composition of each phase, it is possible to calculate the equilibrium compositions of the two phases for given conditions of pressure and temperature.

The difficulty lies in the fact that rigorous calculation of the fugacities of components of solutions requires partial volume data for one of the phases coupled with phase-equilibrium data, both of which are seldom available. As a consequence one is forced to make various assumptions which cannot usually be tested, and the accuracy of the calculated result is in doubt. It seemed desirable, nevertheless, to attempt a calculation of the equilibrium composition, since if it agreed reasonably well with the experimental data, the confidence in both would be strengthened. Another, and perhaps more important, purpose of the calculation was to show the great difference between equilibrium in the system ethylene-water-ethanol and that in the system ethylene-water-ethanol-ether. Many investigators have ignored the formation of ether, but the present calculations, confirmed by experimental data, show that this leads to very large errors.

The method of calculating the fugacities of these four substances was as follows. Fugacities of ethanol and water in binary vapor solutions at the vapor pressure were calculated from the equilibrium data of Griswold, Haney, and Klein (*17*)* by using the method proposed by Joffe (*25*). The appropriate generalized charts of Hougen and Watson (*21*) were used to obtain compressibility factors, enthalpy differences, and fugacity coefficients for the mixture (f_m/p). The limitations of such charts are apparent when applied to mixtures of substances as polar as ethanol and water, but under the circumstances no entirely reliable approach seems available.

The values of fugacity thus obtained must be corrected to the total pressure at which the hydration reaction is to be carried out by using the standard relation for the change of fugacity with pressure. Such calculations can generally be made more conveniently via calculations on the liquid phase rather than on the vapor phase, especially here, since the concentrations of ethylene and ethyl ether in the liquid phase can reasonably be assumed to be negligible. However, since volumetric data for the liquid solutions are unavailable, the following two assumptions are made: (1) for water, the partial molal volume is assumed equal to the true molal volume at the same temperature, and the change in volume with pressure is neglected; and (2) for ethanol, for which the assumptions to be made are less reliable, one starts with data (*35*) from which the partial molal volume in dilute aqueous solutions at 25°C. may be obtained and assumes that the fractional increase in the partial molal volume with temperature is the same as that shown by pure *water* over the same temperature range. This assumption very probably underestimates the value of the true increase of the partial molal volume and therefore may increase somewhat the final calculated values for ethanol concentration in the liquid phase. However the error

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*The results recently obtained for this system by Barr-David (*6*) were not available at the time the calculations given here were carried out. The agreement between the two sets of data is sufficiently close that no significant differences in the final results are obtained when one set or the other is used.

Table 1. Calculated Values of Equilibrium Composition for the Hydration of Ethylene

Pressure, atm.	Ethanol concentration in liquid phase Weight %	Mole %	Concentrations in vapor phase Mole % Ethanol	Water	Ethylene	Ether
A. Formation of Ethyl Ether Assumed						
Temperature = 200°C.						
100	10.2	4.3	11.1	23.6	18.7	46.6
200	12.8	5.5	14.2	19.5	13.2	54.1
300	14.1	6.1	16.6	19.2	10.8	53.4
Temperature = 250°C.						
100	8.0	3.3	10.5	49.5	24.9	15.1
200	12.3	5.2	14.6	36.7	21.8	26.9
300	14.6	6.4	15.8	35.2	19.3	29.7
B. Formation of Ethyl Ether Neglected						
Temperature = 200°C.						
100	42.0	22.	27.0	20.2	52.8	
200	62.1	39.	38.1	15.1	46.8	
300	67.5	45.	45.5	13.9	40.6	
Temperature = 250°C.						
100	12.4	5.3	15.1	48.2	36.7	
200	26.0	12.1	25.0	34.7	40.3	
300	36.0	18.0	29.0	33.3	37.7	

is probably not large, especially in view of the fact that these corrections being calculated are fairly small in magnitude. The use of the molal volume of pure *ethanol* as a means of estimating the partial molal volume in dilute solution would result in an overestimate of the true correction to the fugacity, especially at temperatures above the critical temperature of ethanol (243°C.), in all probability.

The fugacities and mole fractions of all four substances in the vapor phase are assumed to be related by the ideal-solution law (Lewis and Randall rule). At temperatures below the critical temperature of ethanol this requires extrapolation into a region where ethanol cannot actually exist as a gas, but the chart of Hougen and Watson shows lines to guide the extrapolation. The same is true in the case of water. It is unfortunate that recourse to the Lewis and Randall rule must be made in all four instances, but there appears to be no alternative more satisfactory than the use of this or of some similar rule. The severe limitations of the Lewis and Randall rule at elevated pressures have long been recognized.

The calculation of the equilibrium concentrations proceeds by the following steps. (1) For the temperature in question select the appropriate value of K_f (as given in a later section) for each of the two simultaneous reactions:

$$C_2H_4 + H_2O = C_2H_5OH \quad (1)$$

$$2C_2H_5OH = C_2H_5OC_2H_5 + H_2O \quad (2)$$

The standard state chosen for each substance is the gas at a fugacity of 1 atm. (2) Assume an ethanol concentration in the liquid phase. (This fixes the composition, since water is the only other component.) (3) Obtain the fugacities of ethanol and water at the desired temperature and total pressure from log graphs of fugacity vs. liquid-phase composition, based on the calculations previously described. (4) Obtain the vapor-phase concentrations of ethanol and water from their respective fugacities via the Lewis and Randall rule. (5) Assume an ethylene concentration in the vapor phase and calculate its fugacity. (6) Obtain the concentration of ethyl ether from the relation $\sum y_i = 1$, and from this calculate the fugacity. The calculated fugacities must satisfy the two equilibrium constants, and trial values of ethanol concentration in the liquid phase and ethylene concentration in the vapor phase are taken until they are satisfied.

The results of the calculations are given in Table 1A. If the formation of ethyl ether according to reaction (2) is not taken into account, the results are as given in Table 1B. A comparison of these two sets of figures shows that formation of ether causes significant reductions in the concentrations of ethanol and ethylene at equilibrium but has little influence on the concentration of water in the vapor phase.

When the formation of ether is taken into account, the following observations are significant.

1. The change in the concentration of ethanol in the liquid phase as a function of temperature is small, and the concentration may even rise with increasing temperature at higher pressures. This behavior may seem surprising in view of

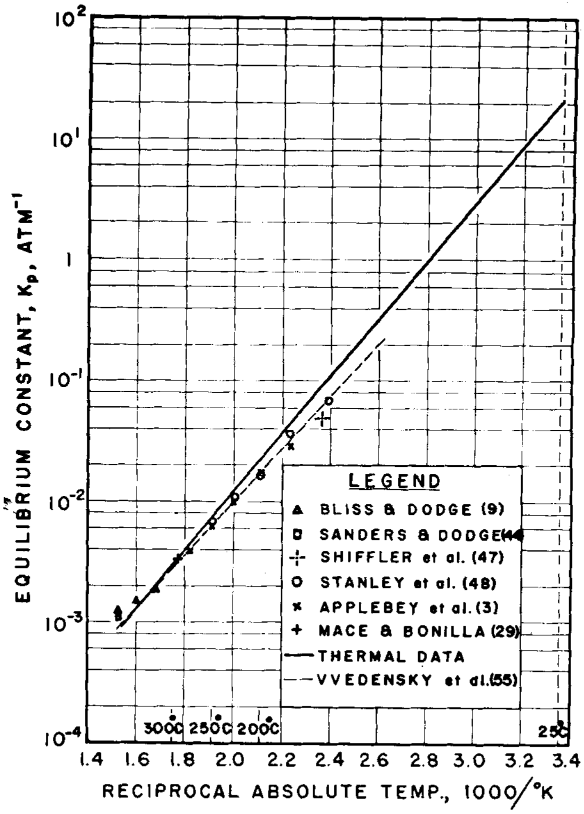

Fig. 1. Logarithm of equilibrium constant vs. reciprocal absolute temperature $C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$.

the quite highly exothermic nature of reaction (1) but is caused by the endothermic nature (with respect to ethanol formation) of reaction (2) and the manner in which phase-equilibrium relationships change with temperature.

2. At constant temperature an increase in pressure raises the concentration of ethanol in the liquid phase; the rate of increase with pressure in general falls off with increasing pressure.

3. The concentration of ether drops fairly rapidly with rising temperature.

4. It is interesting that the $K = y/x$ value (column 4/column 3, Table 1A) for ethanol does not change greatly with temperature or with pressure, whereas it drops rather rapidly with rise in temperature (and hence in pressure) for dilute solutions of ethanol of fixed liquid-phase composition in the binary ethanol-water system.

In the preceding discussion it was necessary to know values of the equilibrium constants for reactions (1) and (2) as functions of temperature. Generally these values may be obtained by direct studies of equilibrium composition, usually made at low pressures, or they may be *predicted* from auxiliary data by means of thermodynamics. In the following section both methods of approach are considered by use of data already available in the literature.

RESULTS OF *PREVIOUS DIRECT LOW-PRESSURE* MEASUREMENTS OF EQUILIBRIUM CONSTANTS; CALCULATION OF EQUILIBRIUM CONSTANTS FROM THERMAL DATA

Ethylene Hydration Reaction

The results of a number of investigators who determined equilibrium compositions directly for the vapor-phase hydration of ethylene by using a variety of catalysts are given in Figure 1, which is a semilogarithmic graph of the equilibrium constant K_p (based on partial pressures) against the reciprocal of absolute temperature. For most of these investigations K_p can be assumed equal to K_f, since the pressure was sufficiently low. The results of Sanders and Dodge (44) and of Mace and Bonilla (29)[*] have also been included for the sake of completeness, even though both these studies were made at pressures of about 70 atm. The solid line on the graph represents values of equilibrium constant calculated from thermal data by using standard procedures. Thermal data are summarized in Table 2.

A recent article by Barrow (7) has done a great deal to resolve the discrepancies which previously existed between experimental thermal data for ethanol and the values calculated by means of statistical mechanics. The primary cause of these discrepancies was the underestimation of the important effects of hydrogen bonding on the thermal properties of ethanol. A successful quantitative treatment of hydrogen-bonding phenomena, first achieved by Weltner and Pitzer (56) for methanol, has been extended to ethanol by Barrow and to water by McCullough et al. (31).

This new approach gives a correction of 60 cal./mole[†] for converting the value obtained by Rossini (39) for the heat of formation of ethanol to the ideal-gas state at 1 atm. The value of 5 cal./mole given by Aston (4) is typical of previous estimates of the magnitude of this correction.

The experimental equilibrium results in Figure 1 are perhaps, but may not necessarily be, in agreement with those calculated purely from thermal data when allowance for the uncertainty of each is made. Should the data not be in agreement, no specific cause of any discrepancy is apparent at this time. For practical applications the data are satisfactory at all temperatures. Probably the best representation of the purely experimental results is that proposed a number of years ago by Vvedensky and Feldman (55), as indicated by the dashed line in Figure 1; the values of equilibrium constant used for the calculations described in the previous section are based on this relationship.

Ether Formation Reaction

No thermal data for ethyl ether are listed in reference *43*, but data are given in other standard listings (23, 35). Closer inspection reveals that the heats of combustion (or heats of formation) given were derived from the data of either Thomsen (52) or Stohmann (49) or perhaps from an average of the two. Both of these series of measurements were made long before the advent of precise modern thermochemical techniques, and so the data must be evaluated very carefully and subjected to several corrections to bring them to the same bases and standard conditions as are now used in thermochemical work. Space limitations prevent elaboration of the various individual corrections made. (For details see reference *12*.) The value finally obtained for the heat of formation of ether is judged to be accurate to within ±1.0 kcal./mole.

The absolute entropy of ethyl ether was obtained by Parks and Huffman (33a) in a study of the specific heat over the range of temperature from about 90° to 300°K. By means of a method which they had devised from studies on a number of compounds down to about 20°K. they extrapolated the curve of specific heat vs. temperature for ether from 90°K. to absolute zero and were then able to calculate the absolute entropy at 25°C. by standard methods. The standard entropy change for reaction (2) as obtained from thermal data is questionable, as it appears to be primarily responsible for the lack of agreement of the more reliable experimental values of equilibrium constant for this reaction with those predicted by thermal methods. 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. Since the low-temperature specific-heat measurements of Parks and Huffman for various organic compounds are generally regarded as being reliable, the main source of possible error in their value for the absolute entropy lies in the extrapolation of the specific-heat data from 90°K. to absolute zero. The general reliability of the extrapolation method has already been questioned by Pitzer (36). A thorough study of equilibrium in reaction (2), together with studies of the heat of combustion of ether at 25°C. and of the heat capacity from near 0° to about 600°K., would be most desirable.

TABLE 2. THERMAL DATA FOR ETHYLENE, WATER, ETHANOL, AND ETHER

Ideal Gas State at 1 Atm. and 298.2°K. (25°C.)

Substance	Heat of formation, kcal./mole	Absolute entropy, cal./(mole) (°K.)
Ethylene	+12.366[a]	52.45[b]
Water	−57.798[b]	45.106[b]
Ethanol	−56.18[c]	67.58[d]
Ethyl ether	−58.62[e]	81.85[f]
Water (liq)	−68.3174[b]	
Carbon dioxide (g)	−94.0518[b]	

Specific Heat Equations[g]
Ideal Gas State

$$C_p^0 = \alpha + \beta T + \gamma T^2, \text{ cal./(mole)(°K.)}$$

Substance	α	$\beta \times 10^3$	$\gamma \times 10^6$	Temperature range, °K.
Ethylene[h]	1.52	33.6	−12.75	300–700
Water[b]	7.85	−0.217	2.656	300–700
Ethanol[i]	4.3	40.25	−7.5	300–600
Ethyl ether[i]	6.8	80.5	−25.0	300–600

[a] Derived from a value of 32.59 kcal./mole for the standard heat of hydrogenation of ethylene, based mainly of the precise heat-of-reaction measurements of (27), as corrected by Rossini (40) and supported by equilibrium data summarized in (51). This value is lower by 0.14 kcal./mole than that given in (43), which is a weighted average of the data of (27) and (41). The necessary auxiliary value for the standard heat of formation of ethane is taken from (43). *The correction to the ideal-gas state given by Aston* (4) has been applied.

[b] (43).

[c] (39) and (7), corrected (see text).

[d] (7).

[e] (49) and (52), corrected to 25°C. and to modern values of the calorie (38) and of the molecular weight of ether; weighings corrected to vacuum. The data in (49) for liquid ether were rejected as being too low. The relatively large negative corrections generally made by Kharasch (26) to the results of Thomsen (52) were not felt to be applicable in this specific case.

[f] (33) corrected to the ideal-gas state at 1 atm. by using data from (45) and the modified Berthelot equation (4).

[g] Fitted to tabulated or graphed data given in the specific references cited.

[h] (42).

[i] (15).

When one attempts to calculate values of equilibrium constant for reaction (2) from thermal data, the situation is somewhat different from that already used for reaction (1), since in the present instance the values

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[*] Mace and Bonilla converted their value of K_p measured at high pressure to a K_f value by assuming ideal-solution behavior and using a generalized activity-coefficient chart. [redacted]

[†] The existence of a numerical error in the value of 250 cal./mole calculated by Barrow for this correction by means of an equation of state has been confirmed by him in a private communication. Also, the correction to the reported heat of combustion at 25°C. should strictly be calculated at 32.5°C., the temperature of ethanol vapor just before combustion in the experiments of Rossini.

for both the heat of reaction and (especially) for the entropy change of reaction at 25°C. are open to question. Studies giving direct experimental determinations of equilibrium composition have been numerous, but unfortunately many of the results conflict, as shown in Figure 2, which is a semilogarithmic graph of equilibrium constant against the reciprocal of absolute temperature. Care must be taken in judging which sets of data are likely to be the most reliable. The chief causes of error in some studies appear to have been interference by competing reactions, inaccuracy of measurement of temperature, and/or failure to reach true equilibrium (usually by deactivation of catalyst).

The most reliable determinations appear to have been those of Semerano (*46*), Newitt and Semerano (*32*), Clark, Graham, and Winter (*11*) (all at about 250°C.), and a hitherto unpublished one of Atherton (*5*) at 135°C. A recent study by Valentin (*53*) over a fairly considerable range of temperature appears to be far out of line with other results and would indicate that reaction (2) is strongly endothermic, which is highly improbable according to the thermal data of Table 2. The error in Valentin's work may be ascribed to deactivation of the catalyst, and it is thought runs involving synthesis of ethanol from ethylene and water would have shown at once that equilibrium conditions were not being reached merely by decomposition of ethanol.

From the value of 20 for the equilibrium constant as furnished by Atherton at 135°C. and an average best value of 8.0 selected from the results mentioned previously for the neighborhood of 250°C., together with the specific heat relationships given in Table 2, it is possible to calculate values of both the standard enthalpy and entropy changes of reaction at 25°C. The values so obtained are −4,220 cal./mole of ether and −4.63 cal./°K./mole of ether, respectively; the curve marked I in Figure 2 is based on these values. The values obtained purely from the thermal data given in Table 2 are −4,060 and −8.20 and give the curve marked II in Figure 2. The agreement of the two values for the enthalpy change of reaction is very good and lies well within the possible errors involved; there appears to be little reason to doubt that reaction (2) is exothermic. The values for the entropy change of reaction are not in agreement; as indicated previously, this is ascribed primarily to a possible discrepancy in the available value for the absolute entropy of ether, which appears to be too low. The values of equilibrium constant used for the calculations described in the first section are based on the relationship given by curve I.

DISCUSSION OF PREVIOUS EQUILIBRIUM STUDIES AT ELEVATED PRESSURES

The experimental data presented in the aforementioned paper of Gilliland, Gunness, and Bowles were taken from the dissertation of Gunness (*18*). From the results for the composition of the vapor phase it was possible to calculate changes of standard free energy of reaction by using the Lewis and Randall rule and generalized activity-coefficient charts. When these values were plotted against absolute temperature, they described a straight line in good agreement with previous low-pressure equilibrium measurements. The authors have repeated the calculations of changes of standard free energy and believe that significant errors were made in the original calculations at both the lowest and highest of the four temperatures involved; the corrected values of free-energy change vary erratically with temperature. It is difficult to determine how much the divergence of the corrected values from the results of other workers at low pressure can be ascribed to inaccuracies in the compositional data or to the limitations of the assumptions made in calculating the standard free-energy changes from data obtained at these high-pressure conditions. However the relatively erratic behavior of the $K = y/x$ values for the various species in the system as functions of temperature and pressure suggests that the data are not wholly accurate.

In view of the authors' experimental observations, due account of ether formation was not taken in the experiments performed by Gunness, who reported a considerable concentration of ether in the vapor phase at 218°C. but zero concentration at both lower and higher temperatures. In the paper by Gilliland, Gunness, and Bowles the statement is made that at temperatures below 220°C. ether formation was very noticeable, but no indication of the presence of ether is given in the tabulation presented for the composition of the vapor phase at the lowest temperature, 176°C. The following probably represents the two main reasons why ether formation was not adequately considered: slow rate of formation of ether at 176°C. and inadequate means of separation of the highly volatile ether in the analytical train. Fortunately however the formation of ether should not have caused the measured concentrations of ethanol in the liquid phase to be much different from those which actually existed. Nevertheless some uncertainty does exist as to whether a state of over-all equilibrium was closely approached in all cases.

The importance of formation of ethers in olefin hydration reactions is clearly shown in the experimental results of Majewski and Marek (*30*) and also in the unpublished work of Winer (*57*) and of Holden and Stackpole (*20*) on the hydration of propylene at elevated pressures and temperatures. Ethyl ether was found to be present by Antonio (*2*) in a study of the continuous hydration of ethylene at elevated pressures and temperatures with sulfuric and phosphoric acids as catalysts and also by Reynoso (*37*), Van Alphen (*54*), and Erlenmeyer and Tscheppe (*14*) in simple sealed-tube experiments, sulfuric acid being used as catalyst in each case. For nearly all conditions employed by Antonio the mole fraction of ethylene converted to ether was greater than that converted to ethanol.

The general difficulty of preventing entirely the formation of ether in the acid-catalyzed hydration of ethylene would be predicted on the basis of kinetic studies* of other olefin hydration reactions and of etherification reactions of alcohols. Thus it is probable that a common species, specifically the conjugate acid of ethanol, $C_2H_5OH_2^+$, is involved in both the hydration of ethylene and the etherification of ethanol. The pi-electron complex $C_2H_5^+$, which is a precursor to the foregoing intermediate (or transition) state in the hydration of ethylene, is probably also important in the sequence of steps leading to the polymerization of ethylene.

EXPERIMENTAL

The hydration of ethylene was studied at a constant absolute pressure of 273 atm. by using first dilute phosphoric acid as catalyst at a temperature of 296°C. and later dilute sulfuric acid as catalyst at 221° and 248°C. The hydration was carried out in a rocking-bomb reactor by a modified batch technique. A tantalum liner was used in the bomb for the runs with sulfuric acid; copper liners were used for the runs with phosphoric acid, since the tantalum liner was not available when these runs were made. Both liners were of the removable type.

Pressure in the reactor was maintained within ± 7 atm. of the desired value by admitting ethylene to the bomb from a high-pressure storage tank whenever necessary. A precise Bourdon-tube gauge, with a scale having a range from 0 to 6,000 lb./sq. in. and divided into 20 lb./sq. in. intervals, was used to measure the pressure.

A calibrated chromel-alumel thermocouple located in a bayonet which extended well into the interior of the reactor was used to measure the temperature of the bomb to within ± 3°C.

Concentrations of ethanol and ether in liquid-phase samples taken during the runs were measured, and the concentration of acid in each sample was also determined. Attempts to analyze vapor-phase samples quantitatively were unsuccessful, primarily because no satisfactory method of separating ethylene and ether could be found which would be both accurate and reasonably rapid for samples as obtained in these experiments.

ANALYTICAL

Prior to the development of quantitative analytical procedures a careful qualitative analysis was carried out to determine what substances were present in reacted mixtures of ethylene, water, and catalyst. The only substances present in significant concentration were ethylene, water, ethanol, ethyl ether, acetaldehyde, polymers of ethylene, and acid (catalyst). In particular, C_4 derivatives, which conceivably could have arisen by dimerization of ethylene and subsequent reaction of the dimer, were found to be absent. In the runs made in copper liners small concentrations of copper ion were present in the liquid samples. The tantalum liner appeared to be inert under the conditions used. When phosphoric acid was used as catalyst, the presence of organic

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*See, for example, a number of papers by R. W. Taft, Jr., and coworkers during the past several years in *J. Am. Chem. Soc.* and reference *10*.

phosphate esters could not be detected; in the runs with sulfuric acid as catalyst the absence of organic sulfate esters was not certain, but if such substances were present, their concentrations must have been small. Small concentrations of sulfur dioxide were formed in the runs made at 221°C., but considerable decomposition of the acid occurred at 248°C.

For the quantitative determination of the combined amounts of ethanol and ether in aqueous solutions, the method proposed by Szeberényi (*50*) was used with slight modifications. In this method both substances are oxidized to acetic acid with an excess of a concentrated solution of potassium dichromate in sulfuric acid, and the excess dichromate is titrated iodimetrically. It was discovered that dilution of the reagent with an appropriate amount of distilled water would give a reagent capable of oxidizing ethanol quantitatively to acetic acid while leaving the ether essentially unattacked. By making analyses with both concentrations of reagent it was possible to determine concentrations of ether by difference. Generally the rather broad range of applicability of chromic acid reagents for the determination of organic substances in dilute aqueous solution was impressive. The analytical procedures were calibrated by using dilute aqueous solutions of ethanol of known concentration available commercially and also by using the saturated water-rich layer of the two-phase ether-water system. Precise data for the solubility of ether in water as a function of temperature in the neighborhood of 25°C. are available from a number of investigators; in this study the data of Hill (*19*) were selected as being the most reliable. The ether-water mixture was maintained in a water bath at 25.2 ± 0.1°C. prior to use.

The concentrations of phosphoric and sulfuric acid in samples from the hydration runs were measured by titration with a standard solution of sodium hydroxide. Phosphoric acid was titrated to the second equivalence point by using slight modifications of the method proposed by Kolthoff (*28*); sulfuric acid was titrated to a pale rose color of phenolphthalein indicator.

Concentrations of acetaldehyde in the liquid phase were determined by precipitation of the aldehyde with 2,4-dinitrophenylhydrazine reagent, according to the gravimetric method of Iddles and Jackson (*22*). In all cases the concentration of acetaldehyde was negligible.

The quantity of ethylene polymer formed during a run was determined by fractional distillation of the liquid mixture recovered from the reactor after it had cooled to room temperature at the end of the run. For the runs made at 221°C. the amount of polymer recovered was negligible.

Analytical reagent-grade chemicals were used throughout the work.

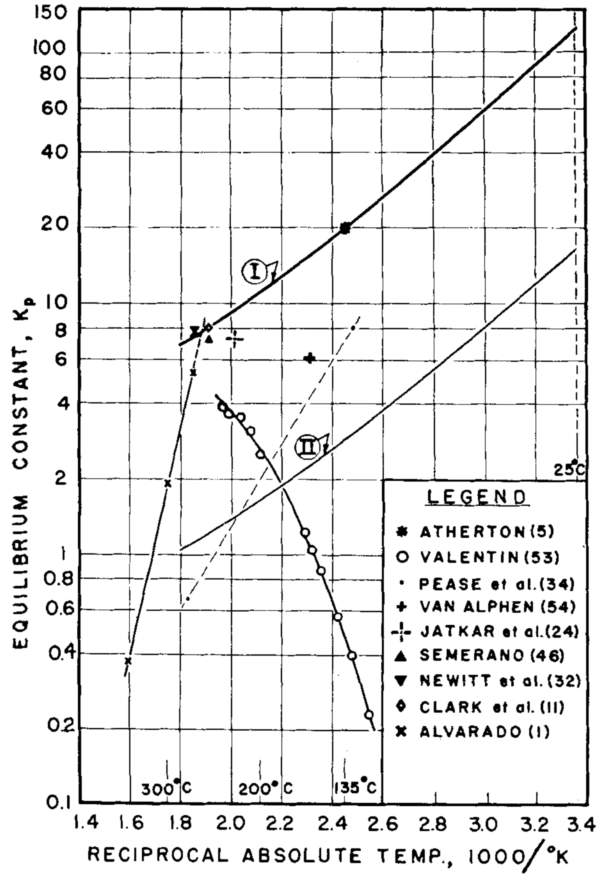

Fig. 2. Logarithm of equilibrium constant vs. reciprocal absolute temperature $2\ C_2H_5OH(g) = C_2H_5OC_2H_5(g) + H_2O(g)$.

Curve I: based on selected experimental and specific-heat data.
Curve II: based entirely on thermal data.

RESULTS AND DISCUSSION

Equilibrium was not attained in any of the runs with phosphoric acid as catalyst. The failure to reach equilibrium is attributed both to the slow rates of approach to an equilibrium state for reactions (1) and (2), even at the relatively high temperature of 296°C., and to disturbing effects caused by polymerization of ethylene. As criteria of equilibrium both the attainment of a constant pressure in the reactor and the attainment of the same (final) liquid-phase concentration of ethanol (and also of ether) in separate runs made with different concentrations of ethylene, water, ethanol, and/or ether in the original charge were selected.*

Equilibrium appeared to be quite closely approached however in runs of about 18 hr. made at 221°C. and 273 atm. absolute pressure with sulfuric acid as catalyst. The equilibrium concentration of ethanol in the liquid phase was judged to be 111 ± 5 g./liter of withdrawn sample; the equilibrium concentration of ether, known with less precision, was estimated to be 20 ± 7 g./liter. The acid concentrations of near-equilibrium liquid-phase samples varied from 1.4 to 2.1 molar in different runs, primarily because of variations in the ratio of acid to water in the mixtures charged to the reactor.

Expressed in terms of mole percentage the measured equilibrium concentration of ethanol is 4.6. By interpolation in Table 1A the calculated value of concentration for the same conditions is 6.0 mole %. These two values are in quite good agreement, especially in view of the following considerations.

1. As indicated previously, the calculated value of concentration is expected to be somewhat high because of the assumption made concerning the behavior of the partial molal volume of ethanol as a function of temperature. Unfortunately it is difficult to estimate the limits of uncertainty of the calculated compositions because of the several assumptions made in obtaining them.

2. If the formation of ether were neglected, as appears to have been almost universally the case in the past, the calculated value of equilibrium concentration would be considerably greater than 6.0, thereby giving a marked divergence between the calculated and experimental results. For example the concentration obtained by interpolation in Table 1B is roughly 30 mole %, nearly an order of magnitude higher than the measured value.

3. In addition to the necessity of taking into account the formation of ether, the use of available vapor-liquid equilibrium

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*In such a case as that involved here, in which two simultaneous equilibria occur, the traditional concept of approaching equilibrium from both sides must necessarily be expanded to a more "generalized" form.

data for the binary ethanol-water system at elevated temperatures appears to be essential to obtain values of about the correct magnitude for equilibrium concentrations of ethanol in the liquid phase for the hydration of ethylene. When the phase-equilibrium relationships for ethanol are predicted solely on the basis of vapor-pressure data and of fugacity data obtained from generalized charts, together with the assumption of ideal-solution or ideal-gas behavior or of the applicability of other equivalent "mixture rules," the predicted equilibrium concentration of ethanol is almost invariably too high. Space limitations prevent the presentation of detailed examples to substantiate this conclusion, which is based on considerable experience with various methods of calculating equilibrium compositions for this system. Unfortunately vapor-liquid equilibrium data at elevated pressures and temperatures are in general not available for most binary systems, and so the number of high-pressure, high-temperature reactions for which this general method of approach can presently be used is very limited. Most of the necessary basic data are available (*6*, *47*, *48*) to permit application of the method to the hydration of propylene at elevated pressures and temperatures, for comparison with the *experimental* results of Majewski and Marek (*30*). However equilibrium constants for the dehydration of isopropanol to isopropyl ether at various temperatures can at present be derived only from thermal data which are quite uncertain. For isopropyl ether the available value (*33b*) of the absolute entropy is questionable, and the heat of formation can only be estimated from data on other compounds, since no direct measurements of the heat of combustion appear to have been reported.

4. Further support for the method of calculation presented here is obtained when the calculated values of equilibrium composition are compared with the experimental results of Gunness for the liquid phase. Although it is important to keep in mind that both of these sets of values are subject to some uncertainties, the agreement between them is close enough to indicate that the calculated values are at least of the correct magnitude; they are probably correct within a factor of about two. Thus for the wide ranges of temperature and pressure used by Gunness the observed range of ethanol concentrations was 1.4 to 8.4 mole %; the range of the calculated values for the same conditions is about 3.0 to 6.0 mole %. The observed change in concentration with pressure at constant temperature (254°C.) is somewhat greater than the calculated one but is in the same direction. The trend of concentration as a function of temperature is predicted less well; the calculated results indicate a slow decrease of concentration with rising temperature at a constant pressure of 200 atm., whereas a maximum was found experimentally over the same temperature range at about this pressure.

The experimental value of equilibrium composition reported here is lower by perhaps 40 % than the value which would be predicted on the basis of Gunness's data. Although there is some uncertainty in extrapolating Gunness's results to the conditions of these experiments, most of this difference is best explained by the fact that these runs were of considerably longer duration than those of Gunness. This may have permitted a closer approach to true equilibrium with respect to both the ethylene hydration and (especially) the ether formation reactions, with a consequent reduction in the final measured ethanol concentration. It is significant in this regard that nearly all Gunness's runs were made with an initial ethanol concentration greater than the final equilibrium value and that in no run was any ether charged to the reactor.

In the determination of the calculated values of equilibrium composition the presence of catalyst in the liquid phase has been neglected. The experimental value of equilibrium composition has not been converted to a catalyst-free basis, however, since the assumption that the catalyst behaves merely as an inert diluent seems questionable.

The relatively small solubility of ether in liquid-phase samples was found, as would be expected, to depend strongly on the ethanol concentration and rose as the ethanol concentration increased. Presumably the same was true for ethylene, but its (small) solubility was not measured. It is unfortunate that most rules used for thermodynamic calculation, including Lewis and Randall's rule, make no allowance for these specific solubility effects, which are often pronounced at high pressures. The apparently small solubilities of ether and ethylene provide some justification for assuming the concentrations of these substances negligible in the previous equilibrium calculations.

The formation of sulfur-containing decomposition products caused the authors to terminate the run made at 248°C. rather quickly. Perhaps the use of a lower concentration of catalyst would have prevented substantial decomposition. Nevertheless the trend of early analyses did not exclude the possibility that the equilibrium concentration of ethanol may be higher at this temperature than it is at 221°C., at a pressure of 273 atm. If so, this behavior would be in agreement with the results of Gunness at temperatures of 218° and 254°C. and a pressure of 197 atm. but would differ from that observed by Majewski and Marek for the hydration of propylene. Unfortunately it was necessary to terminate the experimental program shortly after this run had been made.

On the basis of some rough measurements of vapor-phase composition, as well as from the results of other investigators, it is thought that the calculated concentrations of ether in equilibrium mixtures are in general probably higher than the true values and that the predicted proportions of the other substances, especially ethylene, are correspondingly low. Whether this comes about through errors in the values of equilibrium constant selected for the ether formation reaction and/or from assumptions made in the calculations which may not be valid for high-pressure conditions cannot be determined. In spite of the formation of substantial concentrations of ether in these experiments, it is reasonably certain that only a single liquid phase was present under reaction conditions.

Mention should be made of calculated values of equilibrium composition published not long ago by Bennett (*8*), who applied the method of Joffe on a trial-and-error basis to the ternary gaseous system ethylene-ethanol-water and combined this with the vapor-liquid equilibrium data of Griswold, Haney, and Klein to predict liquid-phase compositions of ethanol for the hydration of ethylene. Although the details of the calculations are not given, the numerical result obtained by Bennett for ethanol concentration is much too high, even in view of the fact that formation of ether has been neglected. At relatively high values of pseudoreduced pressure, such as are involved here, the method of Joffe may properly be applied only in the region in which the pseudoreduced temperature is equal to or greater than 1. In this specific calculation a set of vapor-phase concentrations which would permit this requirement and the existing equilibrium and compositional restrictions to be satisfied simultaneously could not be found.

SUMMARY

Values of equilibrium constant calculated for the hydration of ethylene to form ethanol over a range of temperature appear to be in good agreement with those determined experimentally by other investigators in studies made at low pressures and elevated temperatures. For the dehydration of ethanol to ethyl ether there is wide variation in the experimental values of equilibrium constant measured by different investigators, and the thermal data also are subject to greater uncertainty. However by the selection of what appear to be the most reliable experimental equilibrium results it is possible to obtain satisfactory agreement with the standard heat of reaction obtained from thermal data. For the standard entropy change of reaction the agreement is poor, primarily because of a probable error in the value available for the entropy of ethyl ether.

In an extension of the low-pressure equilibrium results to the prediction of equilibrium compositions for the hydration of ethylene at elevated pressures, it is necessary to allow for the formation of ethyl ether and to make use of available vapor-liquid equilibrium data for the binary system ethanol-water at elevated temperatures. Failure to take these two factors into account generally results in an overestimation of the equilibrium concentration of ethanol; when both are properly allowed for, the agreement between the calculated and measured concentrations in the liquid phase appears to be good. Previous studies of this system have neglected to take the formation of ether into account.

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NOTATION

α, β, γ = empirical constants in equation expressing molar specific heat as a function of absolute temperature

C_p = molar specific heat of a gas, cal./(mole)(°K.)

f_m = fugacity of a gas mixture, defined by the equation $\ln f_m = (1/RT) \int_0^p V_m\, dp$ (T constant), where V_m is the molal volume of the mixture

K_f = equilibrium constant of a chemical reaction based on the fugacities of the participating substances

K_p = equilibrium constant of a chemical reaction based on the partial pressures of the participating substances

P = (total) pressure, atm.

R = gas constant, consistent units

T = absolute temperature, °K. = °C. + 273.2

y = mole fraction in vapor phase, dimensionless

Subscripts

m = mixture (solution)

i = individual component of a mixture

Superscript

0 = standard state (ideal gas at a pressure of 1 atm.)

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