

Summary

1. The rate of adsorption at 25° of arsenious acid by hydrous aluminum oxide is quite rapid, 50% or more of the adsorption taking place within the first few minutes. An apparent equilibrium was reached in about 24 hours but at the end of 232 hours further adsorption had taken place. Several causes have been suggested to account for this slow continued adsorption.

2. Concentration functions at 25°, and for 24- and 72-hour adsorption periods gave results which may be expressed by the simple adsorption-isotherm equation. In the case of a 232-hour run the ideal isotherm is not followed.

3. Adsorption at 25° by hydrous aluminum oxide precipitated at 0° is about 2.5 times greater than that formed at 100° and about 5.5 times greater than that precipitated at 100°, and boiled under a reflux condenser for 24 hours. Causes of this difference in adsorptive power have been suggested and the mechanism of the adsorption process has been discussed.

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[CONTRIBUTION FROM THE COBB-CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

THE POSITION OF EQUILIBRIUM IN THE ALCOHOL-ETHER REACTION AT 130° AND 275°

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From the kinetic measurements of the catalytic dehydration of pure ethyl alcohol¹ at 275° and 300°, it was shown that the total percentage conversion of alcohol reaches a constant value which is unchanged as the time of run is increased. This, we concluded, was due to the fact that the reaction, $2C_2H_5OH \rightleftharpoons (C_2H_5)_2O + H_2O$, approaches a state of equilibrium at about 60-70% conversion. Accordingly, two series of measurements were made with the hope that this equilibrium point might be determined quantitatively, the first using alumina at 275° and the second using a mixture of concd. sulfuric acid and alcohol at 130° as the catalytic agent.

As a preliminary step, we definitely established the reversibility of the reaction by carrying out a run in which 154.5 cc. of ether and 24.2 cc. of water were introduced from separate burets. This mixture was passed over the alumina catalyst at 275°. The product was then fractionated and the following results were obtained. About 132.4 cc. distilled between 35° and 70°, 6.1 cc. between 70° and 78°, 4.2 cc. at 78°, and 9.5 cc. between 78° and 85°. The portion that distilled at 78° was undoubtedly mainly alcohol. A similar run was carried out later in the course of the

¹ THIS JOURNAL, 46, 390 (1924).

investigation and the 78–85° portion of the distillate was subjected to a qualitative test. This was treated by repeatedly dipping a red-hot copper wire into it and then pouring a 2cc. portion with the addition of one drop of a 5% solution of resorcinol down the side of a test-tube containing 5 cc. of concd. sulfuric acid. A distinct, green ring appeared which indicated the presence of acetaldehyde and hence ethyl alcohol.

Apparatus and Procedure

With alumina as the catalyst, the general set-up of the apparatus was identical with that employed in the kinetic measurements.

When using the mixture of sulfuric acid and alcohol as the catalytic agent, the arrangement was somewhat altered, the catalyst chamber being replaced in the tube furnace by a bubbler containing the liquid catalyst. This bubbler was made of Pyrex glass tubing 2 cm. in diameter and 12 cm. in length. Two pieces of glass tubing, having an internal diameter of about 5 mm., were sealed to the bulb as shown in Fig. 1. By this means, the incoming vapor was bubbled through the liquid catalyst before passing out of the reaction chamber.

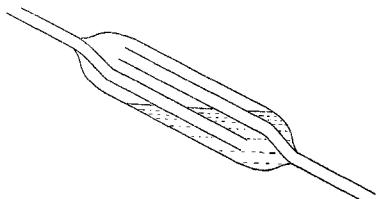


Fig. 1.—Bubbler.

In order to ensure complete condensation of the vapor, ice water was circulated in the condenser during all runs. The receiving flask was also immersed in an ice-bath. Since all of our measurements were made at temperatures at which the amount of ethylene formed was negligible, the gasometer served only as a means of occasional inspection.

The position of equilibrium in the reaction was found by passing through the apparatus various mixtures of alcohol, ether and water of known composition and determining the increase or decrease in the quantity of ether resulting therefrom. By plotting the "shift" in this quantity against the composition of the original mixture, the composition corresponding to zero "shift" and hence to equilibrium may be obtained by interpolation. In all mixtures, the ether and water were present in equimolecular proportion, the total quantity of mixture used always being chemically equivalent to 50.0 g. of pure alcohol. These mixtures were made up by volume, taking as the densities at 25° of alcohol 0.788, ether 0.709 and water 1.000.

Before each run the furnace was brought to the desired temperature and a volume of mixture equal to one-tenth of that to be used in the regular run was passed through the apparatus at the standard rate. After this preliminary run the receiver was connected with the apparatus and the calculated mixture was introduced into the buret and allowed to flow through. The rate of flow was controlled by counting the number of drops from the buret tip per minute. At the conclusion of each run the amount of ether produced was determined by "salting out."

Ether Determination.—Numerous difficulties were experienced in finding a satisfactory method of analysis of the products of the reaction.

The method finally adopted was essentially the same as that employed in the kinetic measurements: namely, the separation of the ether by addition of saturated salt solution and direct determination of the ether volume. A saturated sodium chloride solution, which was approximately four times the volume of the reacting mixture, was poured into the receiving flask at the beginning of each run. As this flask was immersed in an ice-bath, both the salt solution and the product of the reaction were kept cooled and loss of ether was thus prevented. When a run was completed, the entire solution was shaken and poured into a 250cc. flask to the neck of which a 50cc. buret was sealed (Fig. 2). The volume of the ether layer was read directly from the buret. As this method involves loss of ether by vaporization and by incomplete separation, corrections must be made to obtain results of the desired accuracy. In order to measure this loss, the volume of the ether recoverable by this method from mixtures of known composition was determined. This volume was plotted against the true volume of ether so that by means of this chart (Fig. 3) the true volume of ether in the mixture could be determined from the observed volume. Both the saturated salt solution and the reagents were left in a refrigerator for some time before using so as to make the results of these experiments directly comparable with those of the product from the furnace which were to be determined.

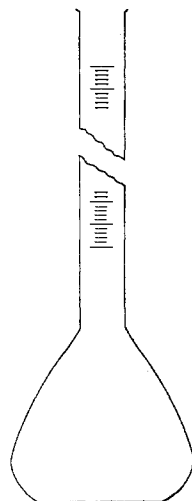


Fig. 2.—Measuring apparatus.

Preparation of Reagents

Catalysts.—The measurements at 275° recorded in the following pages were made with a sample of alumina furnished by the Fixed Nitrogen Research Laboratory. Its behavior was satisfactory throughout the investigation. Tests for ethylene were made at frequent intervals during each run, and in no case was any appreciable quantity of it being formed. This sample of alumina was considerably less active than that used in the previous work.

The use of alumina as catalyst is limited on the one hand by its inactivity at temperatures much below 225° , and on the other by its initiation of the ethylene reaction at 300° and above. In order to obtain a value of the equilibrium constant at a temperature well removed from 275° , concd. sulfuric acid at 130° has been employed. The true catalytic action of this material is well substantiated. In fact, it is understood that the most modern commercial practise in England is to use the sulfuric acid process in continuous operation.

In using a liquid catalyst for an equilibrium determination, it is essential

that it does not change in composition or amount during a run. In order to make certain that the sulfuric acid catalyst fulfils this requirement, we have passed four separate portions of 30.0 cc. each of alcohol through the apparatus containing in the bubbler 20 cc. of a 50% (by volume) mixture of concd. sulfuric acid and alcohol.² The weights of these samples before and after passage were compared and found to agree within a few tenths of a gram. This was considered to be satisfactory evidence that the

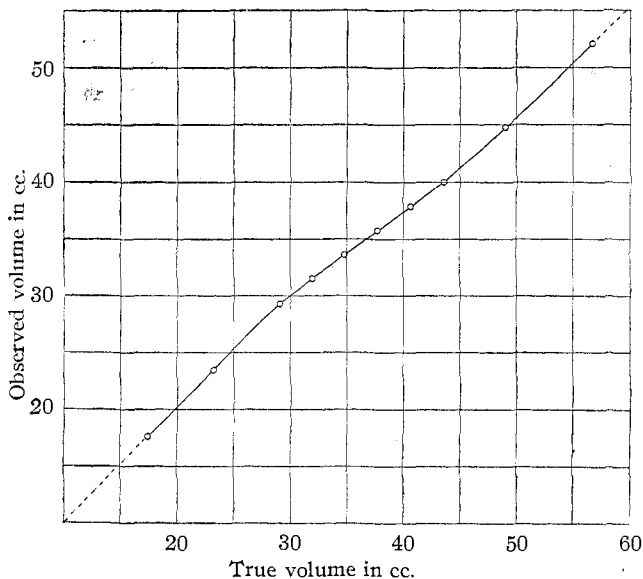


Fig. 3.—Correction chart for ether determination. True volume measured at 23° (average room temperature). Observed volume measured at 10°.

mixture was functioning as a true catalyst. In all, something like 700 cc. of various mixtures of alcohol, ether and water were passed through the one sample of 20 cc. of catalyst.

Ether and Alcohol.—The ether and alcohol used were purified as described in our previous paper. Their densities were accurately determined at 25° and calculations were made from them.

Results and Discussion

Alcohol-Ether-Water Equilibrium at 275°.—The first series of measurements was made to determine the equilibrium constant, K , for the reaction, $2\text{C}_2\text{H}_5\text{OH} \rightleftharpoons (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O}$, at 275° in the presence of alumina. The results are shown in Fig. 4.

From the plot it was found that the mixture corresponding to zero shift contained 38.0 mole % of alcohol. It therefore contained also 31.0 mole %

² These conditions were worked out by Mr. P. R. Burch in this Laboratory.

each of ether and water. This gives for the equilibrium constant $K_{275^\circ} = \frac{31.0 \times 31.0}{(38.0)^2} = 0.66$.

We might state the results of these experiments in another way by saying that the maximum possible conversion of alcohol into ether in the vapor phase at 275° is $100.0 - 38.0 = 62.0\%$.

A point of interest was observed when experiments with a mixture composed of 18.07 cc. of alcohol, 40.60 cc. of ether and 7.00 cc. of water were performed at the rates of 1.5, 3 and 6 hours, respectively. The shifts found varied only within 0.2 cc. At a glance, this seems inexplicable from the equilibrium standpoint. As this mixture lies quite a distance from the equilibrium ratio, we should naturally expect the shift to increase with decreasing rates. Yet, this was not found to be the case. On the other hand, we must remember from our kinetic studies that water dimin-

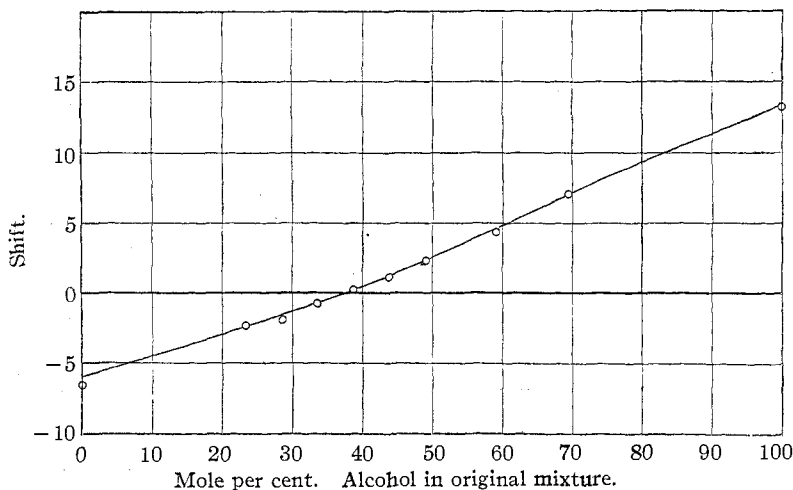


Fig. 4.—Curve of "Shift" against composition. Temperature, 275° .

ishes somewhat the efficiency of the catalyst for alcohol dehydration. Since the amount of water in the mixture is well over 30.0 mole %, it is reasonable that the shift in this case should be very slow.

In all the experiments referred to above, the molecular proportions of ether and water were 1 : 1. To test the correctness of the value arrived at for the equilibrium constant, an equilibrium mixture was made up containing ether and water in molecular proportions of 2 : 1. This mixture consisted of 17.05 cc. (0.292 mole) of alcohol, 35.07 cc. (0.336 mole) of ether and 3.02 cc. (0.168 mole) of water. This gives for the equilibrium constant, $K_{275^\circ} = \frac{0.336 \times 0.168}{(0.292)^2} = 0.66$, as before. The recovered ether amounted to 33.2 cc. Blank runs with identical mixtures gave 33.0 and

33.1 cc. Hence, within the experimental error there was no shift, and this is an equilibrium mixture.

Alcohol-Ether-Water Equilibrium at 130°.—In order to be able to calculate the heat of reaction, the equilibrium constant, K , for any temperature and the free-energy change of the reaction and of the formation of ether, the determination of the equilibrium at one other temperature is necessary. As mentioned before, the reaction catalyzed by alumina is very slow at low temperatures. On the other hand, ethylene begins to form in large quantities above 275°. Under these circumstances we employed a mixture of alcohol and sulfuric acid as the catalyst, which would promote the reaction at a comparatively low temperature. Preliminary results showed that 130° was the most favorable temperature

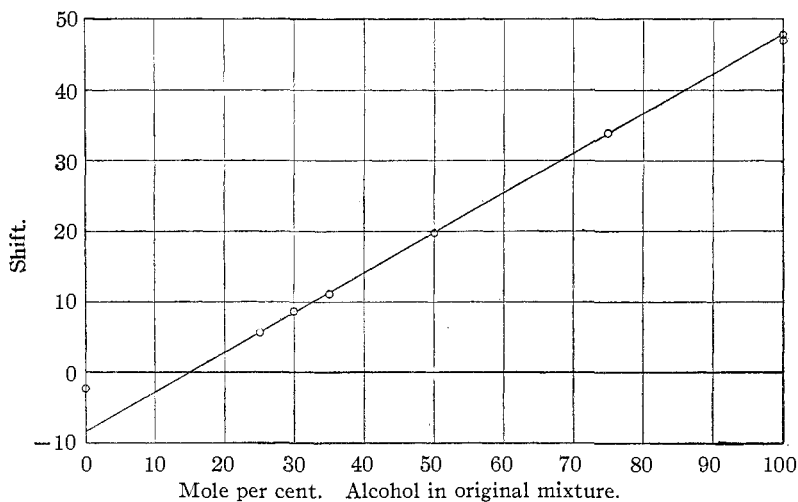


Fig. 5.—Curve of "Shift" against composition. Temperature, 130°.

at which to work. The results of these measurements are shown in Fig. 5. Since the reaction is quite rapid at this temperature, an approximate time of 3.5 hours was found to be sufficient for each run.

In carrying out the experiments at 130° a new difficulty was met in the fact that the equilibrium mixture of alcohol, ether and water separates into layers. Hence, it was not practicable to use mixtures in the neighborhood of equilibrium. Fortunately, however, the reaction was so rapid in the presence of the liquid catalyst that all of the mixtures originally high in alcohol came to the same point within experimental error—that is, the curve of shifts against mole % alcohol was a straight line. Taking the common end-point of the different runs as corresponding to equilibrium, we find from the graph that the equilibrium mixture contains 15.0 mole % of alcohol and hence 42.5 mole % each of ether and water. This gives

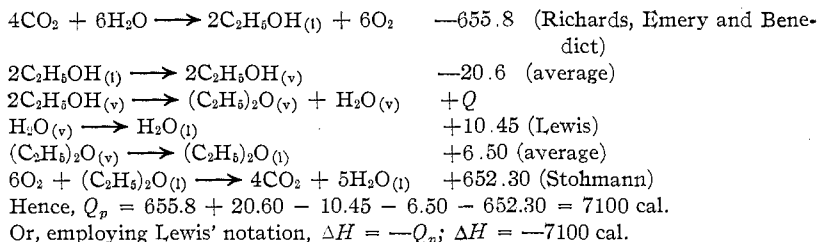
for the equilibrium constant, $K_{130^\circ} = \frac{42.5 \times 42.5}{(15.0)^2} = 8.0$. The maximum conversion of alcohol to ether in the vapor phase at 130° is, therefore, 85.0% as against 62.0% at 275° .

A summary of the measurements at the two temperatures is found in Table I.

TABLE I

Temp. °C.	RESULTS OF EQUILIBRIUM MEASUREMENTS			Equilibrium			K
	Equilibrium Mixtures in g.			Mixtures in mole %			
	Alc.	Ether	Water	Alc.	Ether	Water	
275	19.10	24.86	6.04	38.0	31.0	31.0	0.66 ± 0.01
130	7.60	34.11	8.29	15.0	42.5	42.5	8.0 ± 0.2

Heat of Reaction from Thermal Data.—The existing thermal data applicable to the reaction are rather unsatisfactory. We have taken averages of what are believed to be the best data on heats of combustion. The heats of vaporization have been obtained by drawing the best curve through the datum points and interpolating for 20° . The results³ are as follows:



The value of ΔH calculated from our two equilibrium determinations by means of the van't Hoff equation (assuming ΔH independent of temperature) is -7560 cal. This agrees with the value determined thermochemically (-7100 cal.) within the limit of error of the latter. We shall use the first of these values for ΔH . The corresponding value for the integration constant, I , of the free energy equation⁴ is 14.61. We have, therefore, for the reaction, $\Delta F = -7560 + 14.61T$.

Standard Free Energy of the Reaction and of the Formation of Ether from its Elements

The equation above gives for the standard free energy of the reaction in question at 25° : $\Delta F_{298} = -7560 + 4350 = -3210 \text{ cal.}$ Now, we may combine this value with the known standard free energies of water and alcohol to obtain that of ether. Gibson, Parks and Latimer⁵ have cal-

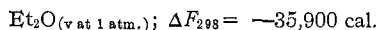
³ Landolt-Börnstein, "Tabellen," Julius Springer, Berlin, 1912, p. 909.

⁴ $\Delta F = -RT \ln K = \Delta H + IT$.

⁵ Gibson, Parks and Latimer, THIS JOURNAL, 42, 1542 (1920).

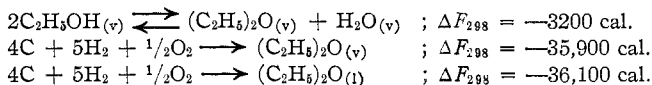
culated the free energy of formation of liquid ethyl alcohol at 25° to be $\Delta F_{298} = -45,100$ cal. The vapor pressure of ethyl alcohol at 25° is 59.0 mm. of mercury. The free-energy change in passing from liquid ethyl alcohol to its vapor at 25° and one atmosphere is given by $C_2H_5OH_{(l)} \rightleftharpoons C_2H_5OH_{(v \text{ at } 1 \text{ atm.})}$; $\Delta F_{298} = -RT \ln \frac{59.0}{760} = 1515$ cal. Hence, the standard free energy of ethyl alcohol vapor at 25° and one atmosphere is $\Delta F_{298} = -45,100 + 1515 = -43,585$ cal. The standard free energy of water vapor at 25° and one atmosphere is $\Delta F_{298} = -54,507$ cal.⁶

Combining these data with the free energy of the reaction, we obtain



The free-energy change in passing from ether vapor at 25° and 1 atmosphere to liquid ether is given by $\Delta F = -RT \ln \frac{760}{537.0} = -206$ cal. (The vapor pressure of ether at 25° is 537.0 mm. of mercury.) Hence, the standard free energy of liquid ether at 25° is $\Delta F_{298} = -36,100$ cal.

We have, therefore,



Actual Production of Ether and Alcohol from Each Other.—In order to demonstrate still more completely the reversibility of the alcohol-ether reaction, runs with somewhat larger quantities of alcohol on the one hand and ether and water in equimolecular proportion on the other have been carried out at the two temperatures, the product being subsequently fractionated using the very efficient Clarke and Rahrs fractionating column.⁷ The volumes of the separate fractions were determined and mole per cents. calculated. The results of these runs are summarized in Table II.

TABLE II
YIELDS OF ETHER AND WATER AND ALCOHOL FROM ONE ANOTHER

Catalyst	Temp. °C.	Moles introduced			Moles recovered			Mole % in distillate of		
		Alc.	Ether	Water	Alc.	Ether	Water	Alc.	Ether	Water
H ₂ SO ₄	130	3.10	0.80	1.05	1.15	26.5	35.0	38.5
		To be expected at equilibrium ^a						15.0	42.5	42.5
		..	1.45	1.30	0.15	1.30	1.25	5.5	48.0	46.6
Al ₂ O ₃	275	2.60	1.80	0.30	0.35	73.5	12.5	14.5
		To be expected at equilibrium ^a						38.0	31.0	31.0
		..	1.25	1.05	0.20	1.15	0.95	8.5	50.0	41.5

^a When ether and water are present in equimolecular proportions.

It appears from Table II that at 130°, the recovered liquid contained 26.5 mole % of alcohol when starting from the alcohol side and 5.5 mole %

⁶ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 607.

⁷ Clarke and Rahrs, *Ind. Eng. Chem.*, 15, 349 (1923).

of alcohol when starting from the ether side. The equilibrium value of 15.0 mole % of alcohol lies between the two as it should. At 275°, the recovered liquid contained 73.5 mole % of alcohol when starting from the alcohol side and 8.5 mole % when starting from the ether side, these values being on either side of the equilibrium value of 38.0 mole % as they should be.

So far as the writers are aware, these experiments constitute the first preparation of alcohol from ether and water on a laboratory scale.

Summary

The position of equilibrium in the reaction, $2\text{C}_2\text{H}_5\text{OH}_{(v)} \rightleftharpoons (\text{C}_2\text{H}_5)_2\text{O}_{(v)} + \text{H}_2\text{O}_{(v)}$ has been determined at 275°, using alumina as catalyst, and at 130°, using a sulfuric acid-alcohol mixture as catalyst. The values of the equilibrium constants are 0.66 and 8.0, respectively. These correspond to maximum possible conversions of alcohol to ether of 62.0% at 275° and 85.0% at 130°.

The free-energy change in the reaction and the free energy of formation of ether vapor at 25° have been calculated and found to be, respectively, —3210 cal. and —35,900 cal.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE RELATION BETWEEN THE TEMPERATURE COEFFICIENT AND THE MECHANISM OF A CHEMICAL REACTION

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A great number of reactions between dissolved substances are characterized by the fact that they proceed at a slow, measurable rate; in the field of inorganic chemistry, reactions between dissolved substances usually proceed at a rate too fast to be measured, although occasionally we find a slow reaction such as the catalytic decomposition of hydrogen peroxide by the iodide ion; on the other hand, in the field of organic chemistry, reactions between dissolved substances usually proceed at a measurable rate. A striking characteristic of these slow reactions is that in nearly all cases they are catalytic; indeed, the few exceptions to this may prove ultimately to be catalytic, so that the study of reaction velocity may be said to be a study of catalysis.

By assuming that reaction rate is proportional to the concentrations of reactants, a satisfactory formulation of experimental results has been obtained in practically all of the hundreds of reactions studied; when, how-