nitrate and barium nitrate) have effects on the activity-coefficient product of silver bromate that differ by amounts (3 or 10% at 0.05 N) which indicate specific effects of the separate ions that are pronounced enough to deserve recognition as important secondary factors, though they do not invalidate the principle that the valence of the ions has the primary influence.

The added salts of different valence types have on an average, in conformity with the rule of Lewis and Randall[1] nearly equal activating effects when $\Sigma(c\,\nu^2)$ (summated for all kinds of ions in the solution) has the same value (c denoting the molality and ν the valence of any ion). Thus, without entering into the details of the treatment of the results, it may be mentioned that at $^1/_2\,\Sigma\,(c\,\nu^2) = 0.05\,M$ the average value of the ratio of the activity-coefficient products is 0.779 (limits 0.764 – 0.794) for the two uni-univalent salts; 0.766 (limits 0.741–0.804) for the four unibivalent salts; 0.794 for the two bi-bivalent salts; and 0.775 for the uni-trivalent salt.

PASADENA, CALIFORNIA

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

ESTERIFICATION EQUILIBRIA IN THE GASEOUS PHASE[1]

BY GRAHAM EDGAR AND WILLIAM H. SCHUYLER[2]

RECEIVED OCTOBER 27, 1923

Introduction

At the Rochester meeting of the American Chemical Society in April, 1921, a paper was presented by Reid and Mulliken containing the results of preliminary experiments upon the use of silica gel in catalyzing the reaction of gaseous acetic acid with gaseous ethyl alcohol to form ethyl acetate, at a temperature of 150°. The yields of ester formed from an equivalent mixture of the two gases were as high as 90% of that which would be formed by complete reaction. It is well known from the work of previous investigators[3,4,5] that in the liquid phase this reaction at any temperature reaches an equilibrium after esterification has proceeded to about 66% of completion. Professor Reid did not offer an explanation of the high yields of ester obtained in his experiments, but in the discussion following the presentation of the paper the opinion was expressed that the

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[1] Preliminary results reported at the Birmingham meeting of the American Chemical Society, April, 1922.

[2] DuPont Fellow in Chemistry.

[3] Berthelot and Péan de Saint-Gilles, *Ann. chim. phys.*, [3] **66**, 64 (1862); [3] **68**, 235 (1863); [5] **14**, 437 (1878).

[4] Menschutkin, *ibid.*, [5] **20**, 305 (1880).

[5] Tobin, *Dissertation*, Bryn Mawr College, **1920.**

data represented experimental evidence of the shift of an equilibrium by a contact catalyst. This explanation assumes that the equilibrium of the reaction in the gaseous phase is identical with that in the liquid phase, an assumption entirely unjustified from theoretical considerations, as a brief discussion will show.[6] Let us consider a two-phase (liquid-gaseous) system of this (or any other) reaction mixture, in which sufficient time has been allowed for the reaction to proceed to equilibrium in both phases.

If the liquid phase were a perfect solution in which each constituent obeyed Raoult's law, the composition of the gaseous phase and, hence, the value of the gaseous equilibrium constant would indeed be predictable from the composition of the liquid phase and the vapor pressures of the pure reacting substances, since we have $X_{A(\text{gas})} = X_{A(\text{liq.})} \times \frac{\text{vap. pres. of } A}{\text{total pressure}}$, but numerical identity between the equilibrium constants in the liquid and gaseous phase would be purely fortuitous. In any actual non-ideal solution the situation will be always much more complex, since no simple laws relate the composition of the vapor to that of the liquid. We can, therefore, say that in general the equilibrium constant of a reaction in the gaseous phase will not be identical with that in the liquid phase, and cannot even be simply predicted from it, but must be measured experimentally.

That in the particular reaction in question the gaseous equilibrium permits a higher esterification in the gaseous phase than in the liquid is indicated by a series of experiments carried out by Berthelot and Péan de Saint-Gilles,[3] which have apparently escaped attention or at least have not been properly interpreted. In these experiments equimolecular mixtures of acetic acid and alcohol were heated in sealed tubes of various capacities so that the vapor space in the tube varied in the different experiments. It was found that after the mixtures had been heated for a sufficient length of time, the yield of ester *increased with the amount of vapor space*, and only when the tubes were nearly filled with liquid did the mixtures result in 67% esterification. The obvious interpretation of these data is that the equilibrium mixture in the gaseous phase is higher in percentage of ester than that in the liquid phase. It is true that in an experiment in which *only* vapor was present a low yield of ester was obtained, but Berthelot correctly attributed this result to the slow rate of reaction in the gaseous phase as compared with that in the liquid.

The present paper presents the results of an investigation carried out with the purpose of determining the condition of equilibrium in the gaseous state of the reaction between acetic acid and ethyl alcohol to form ethyl acetate and water.

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[6] This principle appears frequently in the literature, but in view of apparent failure to recognize it in this particular case, it seems well to introduce this brief discussion.

General Procedure

The direct determination of the composition of the gaseous equilibrium mixture presents certain difficulties. A dynamic method, such as passing the mixed gases over a catalyst at low rates of flow, involves the very question of a possible shift in the equilibrium by the catalyst. A static method, such as heating the constituents in a vessel so large that no condensation occurs involves the difficulty that the rate of reaction of the gases in the absence of a catalyst is extraordinarily slow, and also that the calculation of the equilibrium constant is complicated by the presence of some associated molecules of acetic acid, which cannot be determined unless the total pressure is known. It was therefore determined to calculate the equilibrium constant in the gaseous phase by analyzing the vapor in (thermal) equilibrium with the liquid equilibrium mixture. That the gaseous mixture in thermal equilibrium with the liquid equilibrium mixture must represent the equilibrium in the gaseous phase, regardless of whether or not *reaction* is actually possible at an appreciable rate among the gaseous components, is evident from thermodynamic considerations, for the liquid equilibrium mixture in a two-phase system must certainly be in equilibrium with the gaseous equilibrium mixture, given infinite time, and if it could be in equilibrium with two different gaseous mixtures, a perpetual motion would be at once possible. Therefore, the vapor in thermal equilibrium with the liquid equilibrium mixture at constant pressure must contain the four constituents in the proportions required by the equilibrium constant for the gaseous reaction.

The procedure was adopted of preparing a large quantity of liquid equilibrium mixture, distilling from it a sample of vapor so small as not to change appreciably the composition of the residue, and analyzing this distillate for acetic acid, alcohol, ethyl acetate and water.

While theoretically this process should afford a rather simple and reasonably accurate method of effecting the result, unexpected difficulties developed in the experimental work. The exact analysis of the distillate for four components proved to be of surprising difficulty, and the extremely small amount of one constituent (acetic acid) which was found always to be present magnified the analytical error when the equilibrium constant was calculated. Furthermore, other sources of error, difficult to eliminate, rendered the best results somewhat uncertain. Nevertheless, the data show conclusively that the equilibrium constant in the gaseous phase is of a quite different order from that in the liquid, and it is believed that the average values are not far from the truth.

It has been shown by Berthelot and Péan de Saint-Gilles[3] that the condition of equilibrium for the reaction in question in the liquid phase is represented by the equation

$$K = \frac{\text{Mols. ester} \times \text{mols. water}}{\text{Mols. acid} \times \text{mols. alcohol}} \tag{1}$$

and that the value of the constant is nearly 4.0 at any temperature. Quite recent work by Miss Tobin[5] indicates that the constant is more nearly 3.7, and that the temperature coefficient is negligible. The difference between these values is hardly outside the experimental error of the analyses, particularly in the earlier work. In the experiments here recorded the equilibrium mixtures were made from pure materials, in such proportions as are required by the value of 4.0 for the constant, but in some cases these mixtures were first heated for 720 hours at 80° in order to be sure that they were actually at the equilibrium condition.

A number of preliminary experiments were carried out as follows.

About 500 g. of a liquid equilibrium mixture was placed in a 1.5-liter flask of Pyrex glass connected with a reflux condenser and with a side condenser that could be opened into the flask by a large stopcock. The material was boiled gently for several hours, by means of a coil of fine platinum wire through which a current was passed, and then by opening the stopcock to the side condenser a sample of about 5 cc. was distilled and analyzed.

These preliminary experiments indicated that the method was feasible, and that the equilibrium constant for the gaseous phase is undoubtedly much higher than that in the liquid, but they also demonstrated that the analysis is extremely difficult, that the platinum heating coil slowly decomposes the reaction mixture, and that the materials used were not of sufficient purity. The final results were obtained with the apparatus and general technique described below.

Apparatus and General Technique

Apparatus.—The apparatus employed for the final experiments is shown in Fig. 1.

It consists of a 1.5-liter flask of Pyrex glass to the bottom of which a tube is sealed to admit the heating element, two side tubes being sealed in as shown to create a circulation of the boiling liquid. The heating element, a coil of Nichrome wire contained in a silica tube, is connected into the bottom tube by a rubber stopper. The flask is closed by a rubber stopper, through which pass two thermometers, one in the vapor and one in the liquid, a reflux condenser, and a side tube, connecting through a stopcock of 4mm. bore with a side condenser through which the sample for analysis may be collected. The whole flask is covered with magnesia to prevent any fractionating effect due to partial condensation of the distillate. The side condenser ends in an adapter reaching to the bottom of a narrow test-tube which is cooled with ice when the sample is taken, to prevent evaporation. In all final experiments ice water was circulated through the condensers. The whole system is connected with a vacuum pump, a manometer, and a 10-liter bottle (for capacity) so that experiments could be carried out at reduced pressures.

In carrying out a determination about 500 g. of the equilibrium mixture was placed in the flask, the stopcock leading to the side condenser was closed, and the mixture was boiled for some time (usually an hour or so) to bring the whole apparatus into thermal equilibrium. The stopcock leading to the side condenser was then opened, and about 2 g. of liquid was allowed to distil. This was analyzed as soon as possible, by the method outlined below. The ratio of distillate to residue is so small that the composition of the latter cannot be appreciably affected, and may be regarded as representing the equilibrium mixture throughout the process.

Materials.—The equilibrium mixtures were prepared by weighing out the requisite quantity of pure materials.

The ethyl acetate used in earlier experiments, though purchased as "absolute," showed a variable boiling point. Finally, a quantity of ester was obtained[7] which proved to be of perfectly constant boiling point, and contained 100% of ester by analysis. This was redistilled and employed in all final experiments.

Ethyl alcohol was prepared by dehydrating commercial 96% alcohol with lime in the usual manner. It was redistilled with all precautions to prevent absorption of water, and was kept over anhydrous copper sulfate.

The acetic acid used was a commercial sample of special grade, supposed to contain 99.9% acid. The composition was checked by analysis.

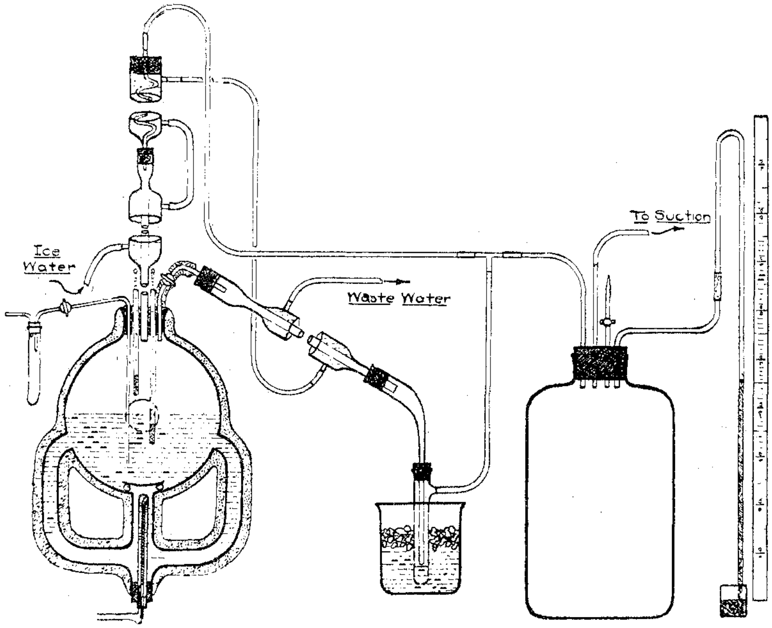

Fig. 1

The composition of the mixtures employed is given in Table I.

Analysis of Distillate.—The analysis of the distillate proved to be a problem of considerable difficulty. The preliminary method was as follows.

(1) Acetic acid was determined by diluting the sample with ice water, and titrating with 0.1 *N* barium hydroxide solution, using phenolphthalein as indicator. (2) Ethyl acetate was determined in a portion of the sample by hydrolyzing it with an excess of standard alkali and determining the excess by titration with standard acid. (3) Ethyl alcohol was determined in a second portion of the sample by adding an excess of sodium hydroxide solution, allowing the mixture to stand until the ester was hydrolyzed, neutralizing the excess of alkali, and then determining the total alcohol by making up to

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[7] From the U. S. Industrial Alcohol Company.

a definite volume, distilling a definite fraction, and determining the specific gravity of the distillate. This gives the sum of the alcohol present as such and that formed by hydrolysis of the ester, and from this the free alcohol can be calculated. (4) Water was determined by difference. Numerous attempts at a direct determination, based upon the reaction with calcium carbide failed to give concordant results upon known mixtures, and the method was abandoned.

It will be noted that the entire process involves several "difference" methods, and while theoretically correct and actually feasible, the total experimental error is apt to be considerable.

The method finally adopted was as follows. The sample (about 2 cc.) was drawn into a special pycnometer of about 2cc. capacity, and its density at 20° carefully determined. It was then divided into two portions, these being run rapidly into small weighing bottles. After being weighed these bottles were dropped into flasks containing ice water, and were titrated for acetic acid with standard barium hydroxide solution. An excess of 0.5 *M* sodium hydroxide solution was then added, the flasks were stoppered, and after 24 hours' standing the ester was estimated by titration of the excess alkali. The density and ester data were then referred to a large scale chart compiled by the U. S. Industrial Alcohol Company and kindly furnished to us by them, in which the density was plotted as ordinate, the percentage of water as abscissa and a series of iso-ester-concentration curves drawn, for the *three-component system*, alcohol-ester-water. Our own experiments upon known mixtures had proved that the values for water read from this chart gave values equal to the sum of the water and acetic acid, where the latter was present to less than 0.5%, as was true in all of our determinations. The alcohol was then determined by difference. Analyses made by the method upon known mixtures demonstrated that it is quite accurate for the mixtures concerned, although of course it could not be applied to the analysis of mixtures much higher in acetic acid content. Incidentally, one of the greatest sources of error is the loss of ethyl acetate by evaporation in handling. It was found that when a sample was taken by means of a pipet in the usual way, an error of several per cent. might be caused in the ester determination. By following the technique indicated above, and working as rapidly as possible when not operating in closed vessels, fairly concordant results upon known mixtures could be obtained.

The temperatures given are the mean temperatures of liquid and vapor which differed by only about 0.2°.

The pressures are taken as 1.0 atmosphere except when operating at reduced pressure, as the data are not appreciably affected by minor fluctuations.

Experimental Data

Three liquid equilibrium mixtures of widely differing composition were selected for the investigation. These had the following compositions, expressed in percentages by weight, and in moles. Each mixture corresponds to an equilibrium constant of 4.0.[8]

TABLE I

COMPOSITION OF LIQUID MIXTURES

Mixture	Acetic Acid		Alcohol		Ethyl Acetate		Water	
	%	Moles	%	Moles	%	Moles	%	Moles
1	18.90	$^1/_3$	14.36	$^1/_3$	55.38	$^2/_3$	11.34	$^2/_3$
2	12.63	$^1/_3$	9.66	$^1/_3$	73.94	$^4/_3$	3.74	$^1/_3$
3	22.00	$^1/_3$	16.90	$^1/_3$	21.50	$^2/_9$	39.60	2.0

Table II gives the analyses of the distillates from these mixtures, as determined by the procedure outlined above. It should be noted that in some cases the determination of the density was made on the entire sample, which was then divided for the determination of ester and acid. The alcohol and water were then calculated from the mean value of the ester, so that in these experiments identical values appear for the alcohol and water. These pairs of duplicates are obvious in the table.

TABLE II

COMPOSITION OF DISTILLATES, IN PERCENTAGES

Expt.	Liquid mixture	Acetic acid	Alcohol	Ethyl acetate	Water	Temp. °C.	Pressure Atm.
1	1	0.218	9.97	83.40	6.63	74.2	1.0
2	1	.213	9.97	83.14	6.53	74.2	1.0
3	1	.224	9.87	83.27	6.73	74.2	1.0
4	2	.230	9.93	81.50	7.73	72.6	1.0
5	2	.228	12.10	81.49	6.32	72.6	1.0
6	2	.230	12.10	18.21	6.17	72.6	1.0
7	2	.073	9.23	84.02	6.68	72.6	1.0
8	3	.199	12.38	79.11	8.10	77.6	1.0
9	3	.202	12.38	79.53	8.10	77.6	1.0
10	3	.233	11.70	79.53	7.86	77.6	1.0
11	3	.291	9.77	84.33	5.81	77.6	1.0
12	3	.290	9.77	84.04	5.81	77.6	1.0
13	1	.126	9.38	84.73	5.97	53.3	0.546
14	1	.134	9.38	84.73	5.97	53.3	.546
15	1	.136	9.23	84.32	6.12	53.3	.546
16	1	.134	9.23	84.72	6.12	53.3	.546
17	2	.156	10.30	84.20	5.35	52.2	.487
18	2	.156	12.11	84.27	3.46	52.2	.487
19	2	.155	12.20	84.10	3.54	52.2	.487
20	2	.052	9.98	82.87	7.09	52.2	.487
21	3	.208	12.07	79.58	8.00	56.3	.585
22	3	.370	10.05	83.94	6.05	56.3	.585
23	3	.332	10.05	84.15	6.05	56.3	.585
24	3	.450	12.23	79.77	7.55	56.3	.585

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[8] While the experimental values for the equilibrium constant have usually been determined at higher temperatures than those employed in this investigation, there seems little doubt that the value of 4.0 is quite close to the truth. No changes could be observed in the composition of the mixtures on heating them for extended lengths of time at 80°.

Treatment of Data

General.—If the theory of the method is borne out, each of the three widely differing liquid equilibrium mixtures should give a distillate containing the four constituents in such proportions as to give identical equilibrium constants for the vapor phase (except for possible variations caused by temperature). Examination of the data in Table II shows certain rather surprising facts, in regard to the composition of the mixtures. The acetic acid is extremely low in all cases, and the ester very high, varying only from 79 to 84%, while the liquid mixtures varied from 21 to 74%. The alcohol and water vary irregularly. On the whole, considering the wide difference in composition of the liquid mixtures, the distillates show a surprisingly constant composition.

Calculation of the Gaseous Equilibrium Constant.—The calculation of the equilibrium constants in the gaseous phase from the data in Table II presents certain difficulties. Acetic acid vapor is known to be considerably polymerized and, therefore, the number of single acid molecules must be determined in each case before the equilibrium constant can be calculated. The exceedingly small quantities of total acetic acid present in the distillates make the numerical value of the constant vary greatly with the value selected for the concentration of single molecules. Nevertheless, it seemed advisable to attempt the calculation. Data on this subject given in the literature show great variations and many of them are measured at such high temperatures as to render doubtful the extrapolation to the temperatures employed in this investigation. The results of Drucker and Ullman[9] are apparently the most reliable for our purposes as they permit extrapolation over a shorter range. They give for the equilibrium constant for the reaction

$$(CH_3COOH)_2 = 2CH_3COOH \tag{2}$$

the following values,

$$K_p = \frac{P_{2CH_3COOH}}{P_{(CH_3COOH)_2}} \tag{3}$$

$K_p = 0.0483$ at $t = 80.2°$; 0.11768 at $t = 95.5°$; 0.2858 at $t = 110°$.

Calculating the heat of dissociation from these values and employing the van't Hoff equation, we obtain for the temperatures appearing in Table II the following values for K_p.

TABLE III

VALUES FOR K_p

t°C	77.6	74.2	72.6	56.3	53.3	52.2
K_p	0.0376	0.0295	0.0263	0.0785	0.0624	0.00575

The method of calculation is as follows: the percentages given in Table II are converted into moles, the acetic acid being calculated as double

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[9] Drucker and Ullmann, *Z. physik. Chem.*, **74**, 567 (1910).

moles. These data are given in Table IV, Col. 3. If "a" is the total number of (double) moles of acid, and x the fraction dissociated, we have for the partial pressure of the single molecules $P_{CH_3COOH} = \frac{2ax}{b} \times P$ where P is the pressure and b the total moles (of all constituents). Similarly for the double molecules, $P_{(CH_3COOH_2)} = \left(\frac{a-ax}{b}\right) \times P$, when from Equation 4 and the numerical values for K_p previously calculated, we may obtain values for X, and for the total number of single moles of acid present in each mixture. These data appear in Table IV, Cols. 4 and 5. It is a little difficult to estimate their accuracy, particularly at the lower temperatures.

TABLE IV

DATA ON EQUILIBRIA

Expt.	Liquid mixture	Total acetic acid as double moles $\times 10^3$	Fraction dissociated	Single moles acetic acid $\times 10^3$	Moles alcohol	Moles ethyl acetate	Moles water	Total moles per 100 g.	Temp. °C.	Pressure tm.	Equilibrium constant
1	1	1.82	0.876	3.18	0.217	0.947	0.363	1.528	74.2	1.0	499
2	1	1.92	.870	3.35	.217	.944	.363	1.525	74.2	1.0	473
3	1	1.87	.871	3.18	.214	.946	.374	1.536	74.2	1.0	519
4	2	1.92	.860	3.30	.216	.926	.429	1.572	72.6	1.0	559
5	2	1.90	.860	3.26	.263	.922	.351	1.538	72.6	1.0	377
6	2	1.92	.860	3.30	.263	.925	.343	1.532	72.6	1.0	370
7	2	0.61[a]	...	..	.200	.954	.371	1.526	72.6	1.0	...
8	3	1.66	.910	3.02	.269	.899	.450	1.619	77.6	1.0	499
9	3	1.68	.910	3.06	.269	.903	.445	1.623	77.6	1.0	494
10	3	1.94	.906	3.51	.254	.903	.436	1.595	77.6	1.0	441
11	3	2.42	.870	4.22	.212	.958	.323	1.495	77.6	1.0	345
12	3	2.42	.870	4.20	.212	.954	.323	1.491	77.6	1.0	347
13	1	1.05	.839	1.76	.204	.962	.331	1.498	53.3	0.56	888
14	1	1.12	.837	1.90	.204	.958	.331	1.494	53.3	.55	822
15	1	1.13	.837	1.95	.200	.962	.340	1.503	53.3	.55	830
16	1	1.12	.837	1.90	.200	.962	.340	1.503	53.3	.55	835
17	2	1.30	.816	2.12	.224	.956	.297	1.478	52.2	.49	598
18	2	1.29	.812	2.05	.201	.957	.192	1.351	52.2	.49	447
19	2	1.30	.812	2.11	.265	.951	.197	1.413	52.2	.49	344
20	2	0.44[a]	...	..	.217	.941	.397	1.552	52.2	.49	..
21	3	1.73	.778	2.70	.262	.904	.444	1.612	56.3	.58	573
22	3	3.08	.712	4.39	.218	.953	.336	1.610	56.3	.58	335
23	3	2.77	.729	4.35	.218	.956	.336	1.613	56.3	.58	330
24	3	3.45	.700	5.25	.265	.906	.419	1.594	56.3	.58	273

[a] Omitted as being almost certainly in error.

The values for the gaseous equilibrium constant are then at once calculable, following Equation 1. These data appear in Table IV, Col. 12.

Discussion of Data

General.—The nature of the distillates in Tables II and IV increases greatly the difficulties of the analysis, and at the same time magnifies the experimental error in the calculation of the equilibrium constants. A discussion of the chief sources of possible error and the direction of their influence may be given here.

The acetic acid is the most simply determined constituent, but its amount is so extremely small that some uncertainty attends even its values. Moreover, there is always the possibility that during the condensation of the vapor and before the analysis, very slight hydrolysis of the ester may take place, and such action would cause the acetic acid values to be too large. In fact the use of ice water in the condenser was found to diminish slightly acetic acid percentages from those obtained in preliminary experiments. It is impossible to state that this effect has been entirely eliminated, but if it is present the calculated values of the equilibrium constants are *smaller* than the true ones.

Another possible effect, acting in the opposite direction, would be a partial reflux condensation of acetic acid in the connection to the side condenser. In the apparatus there is good thermal insulation here, but the acetic acid concentration is so small that any effect would cause variation in the constant.

Exact determinations of the ester are difficult because of the danger of loss from volatilization. Error here affects the equilibrium constant very little directly, but as the alcohol and water are both estimated from tables involving the percentage of ester a serious error may be introduced in both of these constituents.

The exact determination of the density of the very small sample of very volatile material is not altogether simple, and an error here affects the alcohol and water percentages greatly. In fact, certain unexplained fluctuations in the alcohol-water ratio of experiments in the tables which are otherwise fair duplicates, can almost certainly be attributed to some error in the density determination. (Compare Expts. 17, 18, and 19 in which the agreement of acid and ester is all that could be desired, yet the constant varies greatly.)

Altogether it is obvious that the numerical values of the constant are affected by uncertainties in the value of three of the factors from which they are calculated, acetic acid, alcohol and water, and it would be expected that there would be considerable discrepancy between the values. The data in Table IV bear this out, and it remains to consider what conclusions may be drawn from them.

Results at Atmospheric Pressure.—The manipulation of the experiments at atmospheric pressure is a little simpler than that at reduced pressure, and the data are in better agreement. Twelve separate experiments on three different equilibrium mixtures of widely different composition gave values of K varying between the extreme ranges of 347 and 559 (the value 559, Expt. 4, is almost certainly affected by an error in the density determination), and an average value of 450, at a mean temperature of 75°. Since the value in the liquid phase is 4.0 the data certainly seem to show that in the gaseous phase the equilibrium is largely displaced in the direction of ester formation.

Results at Diminished Pressure.—The experiments at reduced pressure were undertaken with the purpose of obtaining data on the temperature coefficient of the equilibrium constant, and the heat of reaction (see below).

The results are very far from satisfactory, for reasons which are not altogether clear.

The data from Liquid Mixtures 2 and 3 are irregular, showing no definite indication of a temperature coefficient. The data from Mixture 1 show a consistent set of very high values, which lead to a temperature coefficient undoubtedly too great. The results can hardly be taken as having definite significance with regard to the temperature coefficient, but they indicate an equilibrium constant at lower temperatures of the same order as that at the higher.

The Heat of Reaction.—The heat of reaction in the liquid phase is apparently very close to zero.[3,4,5] The heat of reaction in the gaseous phase should then be calculable from the heats of vaporization of the constituents and the heats of mixing. The net heat of vaporization is about —2000 cal., from the data in Landolt-Börnstein "Tabellen," while no data seem available on the net heat of mixing. This would indicate for the heat of reaction in the gaseous phase a value of —2000 cal. plus the net heat of mixing. Apparently, the latter is likely to be positive, which would indicate a small value for the heat of reaction in the vapor phase, and a correspondingly small temperature coefficient.

Conclusions

The difficulties in the analytical method, and the particular composition of the mixtures in question, have made the experimental data presented herein much less satisfactory than could be desired; nevertheless, they seem to warrant certain conclusions of interest.

1. The equilibrium in the gaseous phase of a reaction is in general different from that in the liquid phase, and in the particular reaction studied is widely different.
2. The method outlined for the indirect determination of gaseous equilibrium is apparently sound in theory and experimentally feasible.
3. From the results obtained it may be calculated that at 150°, under the conditions employed by Reid and Mulliken, the equilibrium corre-

sponds to about 95% esterification. Their yields were always below this value and cannot, therefore, be taken as indicating a shift in an equilibrium by a contact catalyst.

Summary

1. The equilibrium between acetic acid, alcohol, ethyl acetate and water, in the gaseous phase, has been measured by an indirect method.

2. The data indicate a value of the equilibrium constant very much greater than that in the liquid phase. This is in accord with the experiments of Reid on ester formation in the vapor phase with the use of a catalyst.

3. Theoretical considerations are discussed.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 37]

THE FREE ENERGY OF AQUEOUS SULFURIC ACID

BY DAVID F. SMITH[1] AND JOSEPH E. MAYER

RECEIVED OCTOBER 30, 1923

Previous Work and Outline of this Investigation

Though aqueous sulfuric acid is one of the most important acids, its free energy and its oxidizing power are very imperfectly known. In concentrated solution, especially when hot, sulfuric acid is strongly oxidizing while in dilute solution it oxidizes scarcely any of even the most strongly reducing substances.

The researches which may be used for calculating the free energy of aqueous sulfuric acid have recently been briefly discussed by Lewis and Randall.[2] The equilibria studied, however, were such that it is necessary to approximate the fugacities of the gases and the activities of the liquids involved, and to recalculate the results to standard temperature, which involves the use of uncertain heat data and a rather large extrapolation. Lewis and Randall[2] nevertheless give —176,500 calories as a "provisional value" for the free energy of $1H_2SO_4$ at 25° at hypothetical 1 molal.

The determinations here presented are based upon measurements of the equilibrium in aqueous solution at 80° of the reaction, $H_2SO_4 + 6HI = 3I_2 + 4H_2O + S_{rh}$. Equilibrium was attained with sulfuric acid at 5–7 *M*, hydriodic acid at 0.4–1.0 *M*, and iodine at 0.04–0.3 *M*. The concentrations of hydrogen iodide and iodine were kept as small as possible in comparison to that of the sulfuric acid, so that their presence would not largely change its activity. The reaction proceeds from either side

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[1] National Research Fellow in Chemistry.

[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., **1923**, pp. 552–555.