THE EQUILIBRIUM BETWEEN DIMETHYL ETHER, METHYL ALCOHOL AND WATER.

By N. G. Gajendragad, S. K. Kulkarni Jatkar and H. E. Watson.

In a previous communication (S. K. Kulkarni Jatkar and H. E. Watson, *J. Indian Inst. Sci.*, 1926, **9A**, 71) an account was given of experiments designed to determine the equilibrium constant in the reaction between ethyl ether, ethyl alcohol and water. These were subsequently extended to the corresponding reactions with methyl and *n*-propyl alcohols but the results, although complete 3 years ago, were not published as it was desired to supplement them by theoretical calculations involving the specific heats of the alcohols and ethers which were being measured in these laboratories. It has now been found that specific heat determinations of sufficient accuracy are likely to occupy a longer period than was anticipated and meanwhile the dehydration of methyl alcohol has assumed considerable importance in connection with the synthesis of this compound, so that it seems desirable to place the results on record without further delay.

The equilibrium between dimethyl ether, methyl alcohol and water has received little attention. McKee and Burke (*Ind. Eng. Chem.*, 1923, **15**, 686) in studying the preparation of methyl alcohol from methane deduced that at 300°, 80 per cent. of alcohol would be converted to the ether, a figure which was supported by calculations made by means of Nernst's equation using the available thermal data. Smith and Hawk (*J. Phys. Chem.*, 1928, **32**, 415) have shown that large quantities of methyl ether may be formed during the synthesis of methyl alcohol from carbon monoxide and hydrogen when dehydrating catalysts are used. Brown and Galloway (*Ind. Eng. Chem.*, 1929, **21**, 319; 1930, **22**, 175) give 54 per cent. as the proportion of alcohol converted into ether under actual working conditions.

Our experiments indicate that the amount of anhydrous alcohol converted to ether is 88.7 per cent. at 230° and 93.3 per cent. at 130°.

Experimental.

The dehydration of methyl alcohol is somewhat more difficult to investigate experimentally than that of ethyl alcohol owing to the ether being a gas. Preliminary experiments were made using the same apparatus as before and potassium alum as a catalyst. The reaction products were condensed in a tube cooled in liquid air and the gas evolved on warming collected over sodium silicate solution previously saturated with dimethyl ether as recommended by McKee and Burke (*loc. cit.*). Irregular results were obtained at first, the maximum conversion at 230° being 85 per cent. Further experiments indicated an appreciable reduction in the yield of ether at 220°, but between 225° and 240° the effect of temperature was not very marked. Using 99 per cent. alcohol and 100 g. of catalyst in a tube 2.5 cm. in diameter, the amount of unchanged alcohol recovered when the rate of flow was 40 c.c./hour, was nearly twice as much as when the rate was only 20 c.c./hour indicating that the catalyst was far less efficient than in the case of ethyl alcohol, 200 c.c. of which could be passed hourly in the same apparatus without appreciably diminishing the amount dehydrated.

The necessity of working with small quantities of methyl alcohol adds to the experimental difficulties not only on account of the analytical procedure but also because a small change in temperature of the catalyst may alter the quantity of water it contains and affect the composition of the reaction products. A new type of apparatus was therefore constructed in which the temperature of the catalyst could be maintained constant to less than 2° throughout a length of 60 cm. and the variation during an experiment was not more than 1°. This apparatus was oil-heated and is shown diagrammatically in Fig. I.

The copper tube C containing the catalyst was 110 cm. long and 1.3 cm. in diameter. It was placed inside a wider tube D leaving an annulus of 1.4 mm. into which a spiral copper wire E was inserted to form a baffle. The joints between the tubes were made oil-tight by means of stuffing boxes, and oil could be circulated through the system by a pump H connected to an external pipe system as shown, and driven by a motor J and reduction gearing I. Heat was supplied to the oil electrically by an insulated winding between the pump and the point G and loss of heat from the larger tubes was prevented by two independent auxiliary windings, the whole apparatus being thickly lagged. By suitably adjusting the heating currents, the thermocouples at F and G could be made to indicate substantially the same temperature. The actual temperature was measured by a thermometer at F, which was an open tube to allow the oil to expand.

Alcohol was admitted from the burette and capillary dropper A to the copper spiral B in which it was volatilised and superheated. Before coming into contact with the catalyst it was passed through a layer of pumice 20 cm. long, there being a similar packing of this material at the outlet end of the tube so that the catalyst itself was entirely within the region of uniform temperature. McKee and Burke's method of measuring the gas over sodium silicate solution was found unreliable and consequently the reaction products were passed into the vessel K cooled in a freezing mixture and the uncondensed gas after traversing the weighed calcium chloride tube L was absorbed in concentrated sulphuric acid in the vessel M.

Analysis of the Reaction Products.

Preliminary experiments showed that calcium chloride absorbed both water and methyl alcohol vapours but not dimethyl ether. At the conclusion of each experiment the tube K was warmed to about 60° to drive the dissolved gas into the absorption bulb M. Nearly all this gas was liberated below 0° so that the quantity of methyl alcohol and water vapour carried with it was small and the increase in weight of the calcium chloride tube L was rarely more than 1 per cent. of the total distillate. It was not necessary, therefore, to determine accurately the relative amounts of the two substances. No data are available for the composition of the vapour of water-methyl alcohol mixtures at low temperatures and hence it was assumed that the partial pressure of each constituent was a linear function of the molecular percentage in the liquid. The ratio of the quantities of the two substances in the vapour phase when so calculated does not vary greatly with temperature and hence 0° was assumed as an average.

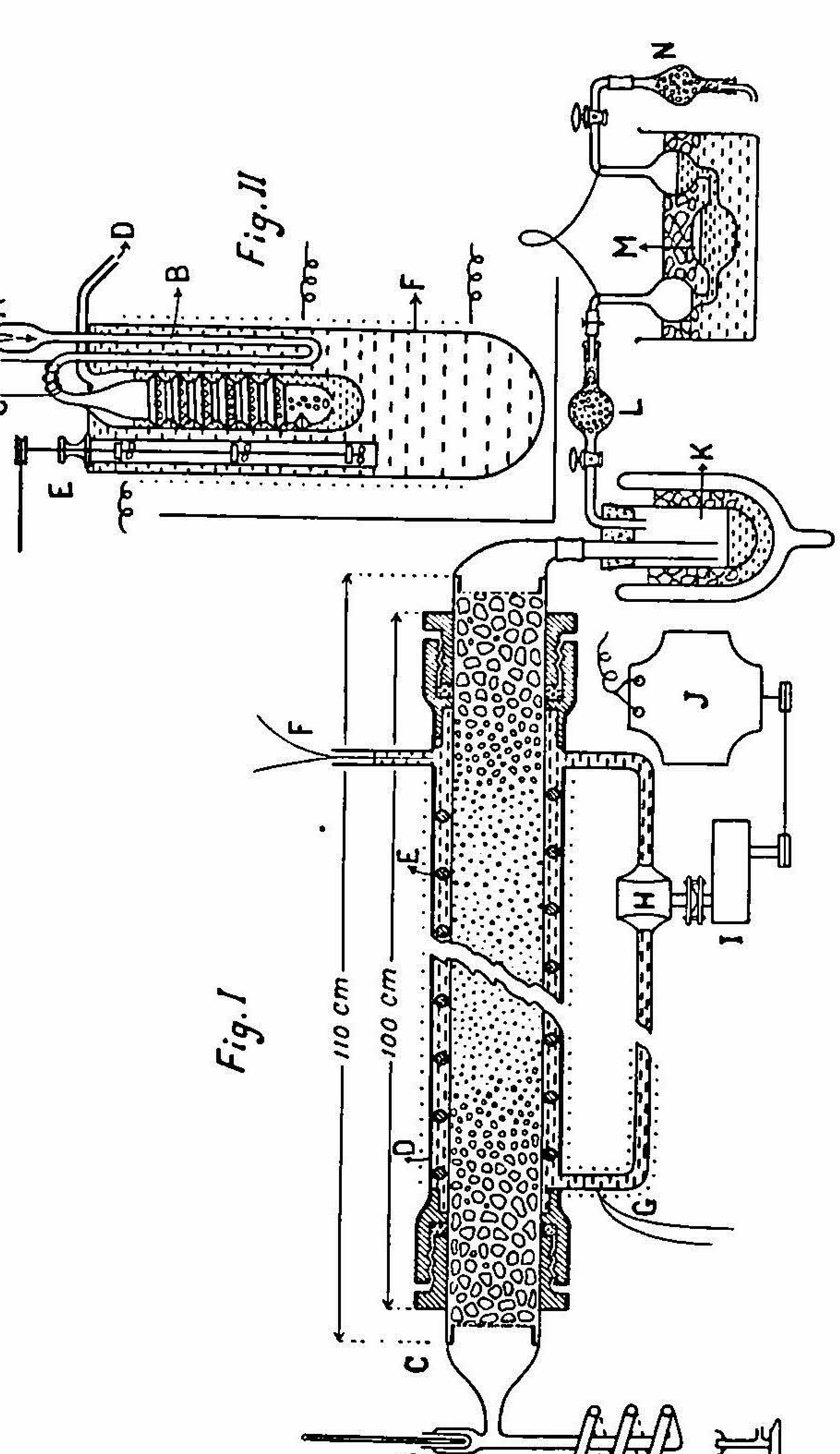

Fig. I

Fig. II

The following is a typical experiment to illustrate the method of calculation :—

Expt. 190. Increase in weight of tube K	.. ..	2.57 g.
,, ,, tube L	.. ..	0.05 g.
,, ,, bulb M	.. ..	5.49 g.
Total	.. ..	8.11 g.

Density of liquid in K at 15° :—0.9486.
Percentage of methyl alcohol :—33.2 by weight, or 21.8 mols. per cent.
Vapour pressures at 0° :—methyl alcohol 29.6, water 4.6 mm.
Vapour pressure of alcohol in mixture :—6.5 mm. ; of water 3.7 mm.
Weight of alcohol in L :—0.04 g. ; weight of water, 0.01 g.
Total : ether, 5.49 ; alcohol, 0.90 ; water, 1.72 g.
or 0.119 0.028 0.095 mols.
Hence *K*, the equilibrium constant$=119\times95\div28^2=14.4$.

The term 'percentage conversion' which affords a better physical conception of the extent of the reaction than the equilibrium constant *K*, is, strictly speaking, only applicable to the case of anhydrous alcohol, whereas *K* can always be calculated whatever the composition of the initial mixture. When anhydrous alcohol is used, every value of *K* corresponds with a definite conversion ; for instance, in the example just given *K* would have the value 14.4 if 88.5 per cent. of anhydrous alcohol were decomposed on passing through the catalyst. It is convenient when using dilute alcohol or mixtures to retain the term 'percentage conversion' bearing in mind that it does not refer to the actual liquids employed but to the conversion of anhydrous alcohol which would yield the same value of *K*. This has been done in the following tables.

Results.

With the new apparatus just described results were more regular than previously, but, at first, by no means satisfactory. In 20 experiments with 99 per cent. alcohol at 230°, conversions from 66 to 84 per cent. were obtained under identical conditions and when the rate of flow was reduced, even lower values were obtained. With fresh catalyst higher mean values were found, but irregularities were still apparent as may be seen from some typical results shown in table I. All rates are expressed in c.c. per hour and the experiments are numbered in the order in which they were performed.

TABLE I.

Formation of Methyl Ether from Methyl Alcohol.

Expt. No.	Rate	Conversion	Expt. No.	Rate	Conversion	Expt. No.	Rate	Conversion
52	26	77	63	15	44	81	8	74*
53	12	83	64	10	62	82	8	75*
54	24	79	65	4	64	83	15	66*
55	33	70	61	3.5	69	84	9	68*
56	18	78	67	3	74	85	8.5	67*
57	14	78	71	11	42	90	5.5	76
58	8	83	72	11	48	91	6	73

* 220°

The first group of experiments (52-58) was made with 98 per cent. alcohol at 230°, and experiments 90, 91 with similar conditions indicate a decrease in activity of the catalyst. The second group (63-72) shows the effect of using 85 per cent. alcohol ; the rate of conversion is very low and the last two experiments after 4 runs with 96 per cent. alcohol give even smaller values. Experiments 81-85 were made at 220° and the difference is not very marked.

It thus appeared that there was a tendency for the catalyst to become inactive and this was confirmed by occasionally passing ethyl alcohol, which reacts much more easily than methyl alcohol and comparing the results at different times. It also seemed likely that irregular and low values were due to channelling of the catalyst owing to the vibration of the circulating pump ; the whole apparatus was consequently tilted at an angle of 45° and this gave greatly improved results. Table II shows a series of values with a fresh batch of catalyst using 98.7 per cent. alcohol at 230° in the order in which they were determined.

TABLE II.

Rate	9.6	9.6	9.6	3.2	3.2	9.6	12.8	19.2	9.6
Conversion ..	86.8	88.5	89.0	88.2	87.5	87.0	86.3	76.0	85.1

In these experiments 6 to 12 grams of distillate were collected for analysis and to ensure equilibrium, alcohol was passed over the heated catalyst for at least half an hour before the absorption tubes were attached. When the last experiment was made, the catalyst had been used for about 30 hours and the somewhat lower result may have been due to slight deterioration.

As these results appeared sufficiently concordant, a further series of experiments was made to determine more accurately the most favourable temperature for the reaction, preliminary experiments having indicated 225-230°. Table III shows the results in the order in which they were obtained, each value being the mean of two agreeing within 1 per cent. using 98 per cent. alcohol at the rate of 10 c.c. an hour.

TABLE III.

Temperature	Conversion	Temperature	Conversion
160	0	230	79.9
170	9.8	240	83.3
180	23.3	250	85.5
190	35.5	230	73.0
200	50.5	210	52.0
210	62.9	250	84.0
220	69.5		

There was very little reaction below 170° but above this temperature a steady rise was found in the conversion, that is to say, in the reaction velocity. At the higher temperatures, equilibrium was approached and consequently the change in the conversion for equal increments of temperature became less, but it was evident that the greatest velocity reached was at 250°, the highest temperature tried. This was not however a practicable working temperature owing to its causing a loss in activity of the catalyst as shown by the fact that the conversions at 230° and 210° after heating were decidedly less than before. 230° was therefore adopted as the most suitable temperature in subsequent experiments, the rate of conversion being sufficiently rapid and the deterioration of the catalyst not excessive.

The Reverse Reaction.

In order to obtain more definite information regarding the equilibrium point it was desirable to approach it from both directions. Previous experience with ethyl alcohol indicated that the reverse reaction would probably take place very slowly and this was found to be the case, reliable results being difficult to obtain.

Methyl ether was generated from its solution in sulphuric acid by adding water at a regulated rate, washed with very dilute alkali and passed through a humidifier consisting of a copper tube packed with moistened Lessing rings maintained at about 86°. Spray was removed, the gases passed into the apparatus and the product analysed as before.

The first experiments were irregular and indicated the formation of only 1 to 6 per cent. of methyl alcohol. A fresh batch of catalyst was prepared with which more satisfactory results were obtained. These are shown in table IV. The rate recorded is the number of grams of reaction products collected per hour and the temperature 230°.

TABLE IV.

Expt. No.	Mols. $Me_2O : H_2O$	Rate	K	Conv.	Expt. No.	Initial mixture	Rate	K	Conv.
185	41 : 59	8	15.7	88.8	187	99% MeOH	7.8	15.1	88.6
186	60 : 40	4	16.4	89.0	188	”	7.8	15.2	88.6
189	48 : 52	7	17.4	89.3	193	”	7.8	14.9	88.5
190	55 : 45	6	14.4	88.5	194	”	7.8	13.9	88.2
191	60 : 40	4.5	19.8	89.9	195	”	4.0	16.0	88.9
192	65 : 35	2	20.0	90.0					

The experiments were conducted in the order in which they are numbered and it will be noted that although the values of K obtained for the direct reaction experiments 193 and 194 are slightly lower than in 187 and 188, the difference when expressed as percentage conversion is very small and within the limit of experimental error so that any loss in activity of the catalyst was slight. The reverse reaction experiments 185, 186 and 189 gave, as might be expected, slightly higher values for K indicating that equilibrium was not quite reached, but they suffice to restrict the true point of equilibrium within very narrow limits. The high values in experiments 191, 192 and 195 and the low one in 190 are no doubt due to experimental error, considerable difficulty being experienced in keeping conditions steady during the two to four hours necessary to accumulate sufficient material for analysis in the experiments at very low rates.

A few attempts were made to obtain the value of K using a mixture of methyl alcohol and water in the ratio 65 mols. of alcohol to 35 mols. of water, but the reaction was so slow that equilibrium could not be attained. With rates of flow of 9.5 and 8.0 g. per hour, the values were 5.1 and 8.2 corresponding with conversions of 81.9 and 85.1 per cent. respectively. When the rate was diminished to 2.5 g. per hour, K rose only to 11.6, or 87.2 per cent. conversion. This reduction in reaction velocity is analogous to that previously observed with ethyl alcohol.

The mean result of all these experiments is that at 230° the equilibrium point for anhydrous methyl alcohol is reached when 88.7 per cent. has decomposed, the corresponding value of *K* being 15.4.

The Reaction at 130°.

The figures given in table III, make it evident that there would be little chance of determining the equilibrium point of the reaction at temperatures much removed from 230° if an alum catalyst were used. A few attempts at 200° confirmed this supposition, values of 3.6 and 225 being obtained for *K* in the direct and reverse reactions respectively.

As it was desirable to study the reaction at two temperatures at least, it was decided to experiment with sulphuric acid as catalyst, either alone, or mixed with aluminium sulphate as recommended by Senderens (*Compt. rend.*, 1910, **151**, 392). The reaction vessel used is shown in Fig. II and consisted of a Friedrich's spiral wash bottle 4 cm. in diameter completely immersed in an electrically heated oil thermostat with a powerful stirrer. The temperature was hand-controlled and usually did not vary by more than 0.5° during an experiment. The reaction mixture was admitted at A at a controlled rate and was volatilised and superheated to the bath temperature in the tubes B and C. The products issued at D and were examined in the same way as before.

A disadvantage of sulphuric acid catalysts was their low activity which made it necessary to employ 100 g. in order to collect the reaction products at the rate of about 10 c.c. an hour. Analysis showed that the catalyst when equilibrium had been established was not sulphuric acid or a hydrate, but a mixture with the approximate composition $H_2SO_4.4H_2O$, 0.25MeOH at 128° and $H_2SO_4.2.6H_2O$, 0.20MeOH at 140° and thus if the temperature varied or the gas was passed too rapidly for equilibrium to be attained, the catalyst might change its composition, giving out or absorbing methyl alcohol and water. It was not convenient to collect more than about 15 c.c. of reaction products, only one-tenth of which or less was methyl alcohol and consequently it was very easy for large errors to be introduced.

In order to compensate the effects produced by these changes the emerging mixture was analysed completely when possible and was assumed to be in equilibrium. For slow rates this was probably true to a first approximation, the substances introduced reacting not only as they would with a solid catalyst but also combining with what may be regarded as the surplus products of the catalyst at the moment. It follows that the mixture issuing from the catalyst need not necessarily correspond in amount or in composition with the reactants introduced. The weight of alcohol and water evolved on raising the temperature of the catalyst 0.5° was approximately 1 g. but the difference between the weight introduced and that obtained frequently exceeded this amount in spite of an apparent constancy in temperature. The reason for this was not apparent, but when considering the results, those experiments for which the discrepancy was large were given less weight. Calculations of the equilibrium constant made with the assumption that the change in weight was due to absorption or evolution of water and a small proportion of methyl alcohol by the catalyst gave more concordant values for *K* in many cases but the composition of the distillate so calculated did not agree with the analytical values.

Some of the preliminary results are shown in table V. The equilibrium constant and hence the percentage conversion has been calculated by assuming that the amount of water in the distillate was equivalent to the dimethyl ether obtained, the balance being alcohol. The values are in consequence by no means accurate. In a few cases (indicated by a star) the liquid distillate was analysed. Some of the results refer to two or more experiments with similar rates of flow, the products of which were mixed before examination.

TABLE V.

99.5 per cent. Methyl Alcohol with Sulphuric Acid and 5 per cent. Aluminium Sulphate.

No.	Temp.	Rate g./hr.	MeOH added g.	Total distillate g.	Me_2O	Conversion per cent.
11	125	18	41.5	45.85	25.7	83.0*
12	125	13	26.95	27.95	17.25	86.7
13	125	9	18.7	18.3	11.6	88.1*
14	125	8	7.8	8.33	5.36	90.1
18	125	14	21.1	19.77	12.70	88.9
19	125	14	20.2	19.88	11.83	83.3
20	125	8	15.7	13.80	9.16	93.1
21	126	7	18.7	20.24	13.73	89.6*
22/3	127	9	17.9	16.84	10.64	88.5*
24/5	128	5.5	18.3	18.25	11.75	89.1*
26/7	128	17	18.5	19.43	10.46	75.8

After conducting some experiments on the reverse reaction additional determinations were made at a slightly higher temperature and the reaction-products examined in every case. These results are shown in table VI.

TABLE VI.

99.5 per cent. Methyl Alcohol, Sulphuric Acid.

No.	Temp.	Rate g./hr.	MeOH added g.	Total distillate g.	Me_2O	H_2O	MeOH	Conversion per cent.
41/3	129	12.5	24.9	22.97	15.56	5.13	2.28	89.6
44/5	128	17	17.2	16.00	9.91	3.95	2.14	86.7
46/7	129	4.5	17.0	16.01	10.85	3.88	1.28	92.2
48	129	8	12.1	10.73	7.08	2.65	1.00	90.7
49	128*	4.5	11.6	13.23	6.38	5.67	1.20	92.1
50	140	3.5	17.3	16.90	11.10	4.46	1.34	92.3
51/2	130	12	25.1	26.14	16.35	6.77	3.02	88.6
54/5	130	7	25.8	24.56	15.89	6.35	2.32	90.6
62/3	130	7.5	16.5	18.44	11.87	4.66	1.91	89.6
64	130	12.5	14.5	13.76	8.74	3.54	1.48	89.3
65	130	4.5	18.3	17.63	12.08	4.11	1.44	91.9
66	130	5.5	12.4	12.49	8.25	3.17	1.07	91.6

* Irregular.

Newly made catalysts required a considerable time to attain equilibrium. The one used for expts. 41-49 consisted of 75 g. concentrated sulphuric acid and 5 g. aluminium sulphate to which was added 62 g. methyl alcohol, the whole being heated until no more gas was evolved. When these experiments were completed, a fresh catalyst was prepared in a similar manner and heated to 150°. On passing methyl alcohol, the product separated into 2 layers owing to the formation of methyl sulphate. At 140° the side reaction was less, but traces of methyl sulphate were found and after a few experiments the catalyst appeared to decrease in activity. Expt. 50 was made at this temperature but subsequent determinations were restricted to 130°.

Expts. 51-59 were made with the same type of catalyst but after No. 59 which was made by passing methyl ether and water to investigate the reverse reaction, low results were obtained on again passing methyl alcohol. A new catalyst was then made consisting of 62 g. sulphuric acid and 38 g. water through which methyl alcohol vapour was passed for several hours. This gave satisfactory results and was used for the remaining experiments. The values for the conversion have been plotted against the rate of flow in Fig. III, and it will be seen that even at the slowest rates measured, equilibrium is not attained.

The extrapolation to zero rate is rather wide and consequently experiments were made upon the reverse reaction. Water was added from the burette and a steady stream of dimethyl ether generated by dropping water into a solution of the gas in sulphuric acid, admitted through a side tube. The rate was measured approximately by counting the bubbles. The results are given in table VII which shows the initial and final weights of the different constituents. The initial weights of dimethyl ether were obtained by calculation and are not accurate.

TABLE VII.

Reverse Reaction and Miscellaneous Mixtures.

			Initial			Final			
No.	Temp.	Rate g./hr.	Me_2O	H_2O	MeOH	Me_2O	H_2O	MeOH	Conversion
59	130	8.5	10.0	63.0	0	9.25	7.04	1.06	94.0
67	130	11	11.8	6.9	0	11.10	6.46	1.07	94.6
68	130	9	16.6	7.3	0	15.58	8.47	1.50	94.5
69	130	5	13.1	0	0	12.48	4.30	0.89	94.8
56	130	16	11.0	5.6	1.9	11.44	4.79	1.20	93.2
57	130	13	10.2	4.6	1.5	10.53	4.60	1.04	93.7
58	130	8	10.9	4.65	1.55	11.16	5.22	1.23	93.3
70	130	9	11.7	3.25	1.75	12.11	4.23	1.16	93.2
71	130	16	9.1	4.55	2.45	10.07	4.33	1.10	93.1

In expt. 69 no water was added and it will be seen that the results are not greatly affected, the catalyst temporarily supplying the necessary water.

Expts. 56-58 were made by passing dimethyl ether and a 25 per cent. aqueous solution of methyl alcohol, the mixture approximating to the equilibrium mixture. This causes a minimum amount of alteration in the composition of the catalyst at the point of entry and results in a longer periods of effective contact. Expts. 70 and 71 were of a similar nature but with a 35 per cent. solution of alcohol.

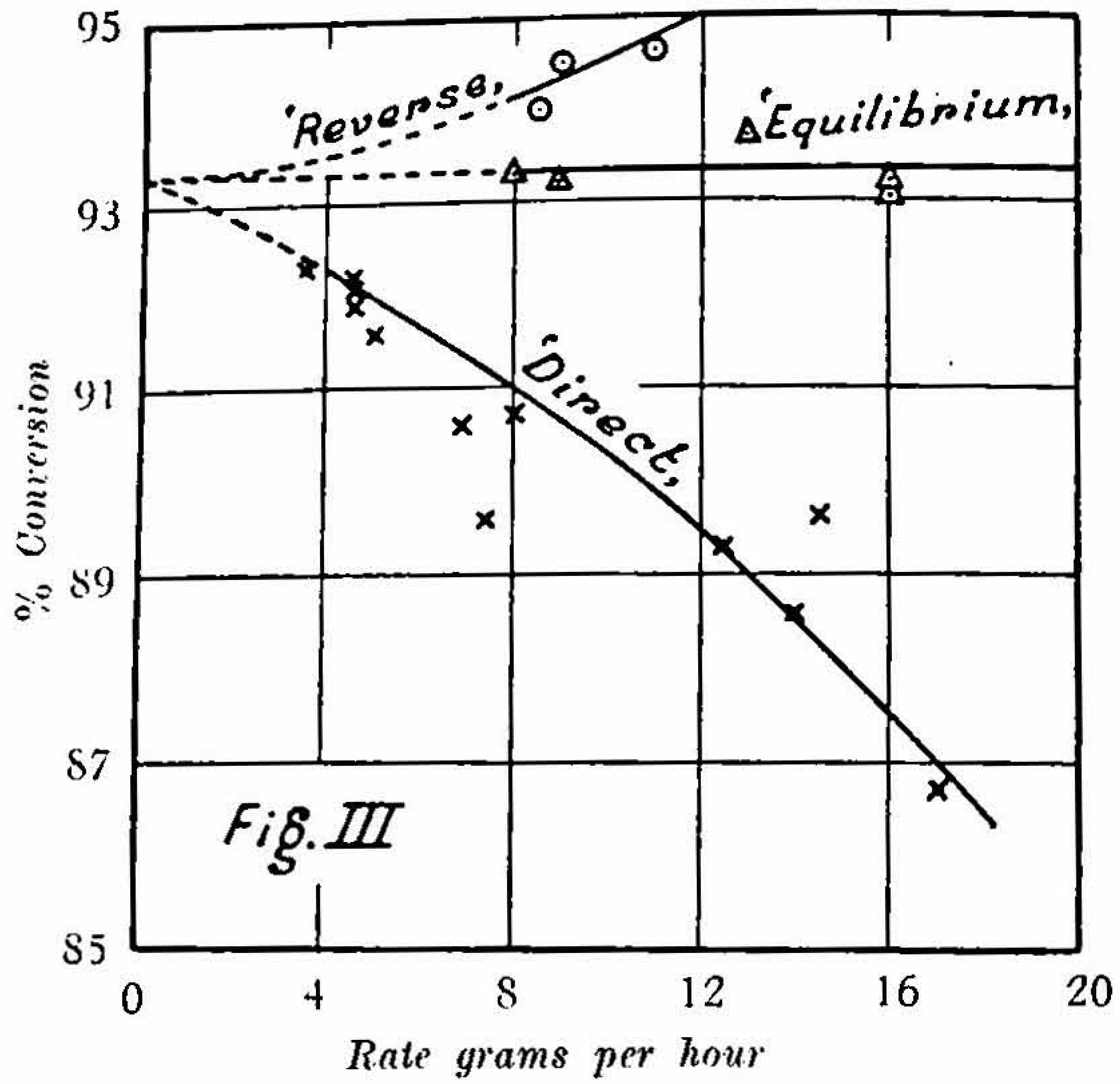

Fig. III

Extrapolation of the results in table VI shown in Fig. III indicates a value for the conversion at zero rate between 93 and 94 per cent. and the reverse reaction shows that the figure is certainly less than 94.5. In view of the slow rate of this reaction the mean value is probably at least 1 per cent. too high. The figure 93.3 would agree well with the results of these determinations and is in accordance with the results for the " equilibrium mixture ". It may therefore be taken as the most probable value. The corresponding value of the equilibrium constant is 48.5, but since the values of K for 93 and 94 per cent. conversions are 44.1 and 61.5 respectively, it is evident that this constant is not known with any great degree of accuracy.

If the above result be taken in conjunction with the value $K_1=15.4$ at 230°, the heat of reaction calculated according to the equation

$$Q=4.58 \log K_2/K_1 \,.\, T_1T_2/(T_1-T_2)$$

is 4.62 Cals.

Taking Thomsen's data for the heats of combustion of methyl alcohol (182.2 Cals.) and dimethyl ether (349.4 Cals.) and 10.6 Cals. as the molecular latent heat of vaporisation of water at 18° the heat of reaction is 4.4 Cals. in fair agreement with the value calculated above.

Summary.

1. The equilibrium between dimethyl ether, methyl alcohol and water has been investigated by a continuous flow method using an alum catalyst at 230° and sulphuric acid at 130° the equilibrium point being approached from both directions.

2. The value of the equilibrium constant was found to be 15.4 at 230° and 48.5 at 130° corresponding respectively with the conversion of 88.7 per cent. and 93.3 per cent. of anhydrous alcohol into ether and water.

3. The heat of reaction calculated from the equilibrium constants agrees as closely as can be expected with the value from thermal data.

4. With the alum catalyst the reaction is much less rapid than in the case of ethyl alcohol. The velocity increases with rise in temperature up to about 250° but at this temperature the catalyst loses its activity.

5. Sulphuric acid catalysts cannot be used at temperatures above 130° even with addition of aluminium sulphate owing to the formation of dimethyl sulphate.

[Accepted, 2-8-32.]

Department of General Chemistry,
Indian Institute of Science,
Bangalore.

1569-32 Printed at The Bangalore Press, Mysore Road, Bangalore City.