

On the Reaction between Gaseous Methyl Ether and Hydrogen Chloride.

By

Jitaro Shidei.

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ABSTRACT.

The results obtained by M. Friedel in the reaction between gaseous HCl and $(\text{CH}_3)_2\text{O}$ are not in harmony with the theory, for he found that the formation of the reaction product, $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$, was at the minimum when the reactants, HCl and $(\text{CH}_3)_2\text{O}$, were mixed in equal volumes, while the law of mass-action required that it should be at the maximum. The author carried out experiments to examine this matter theoretically and experimentally.

Pure anhydrous HCl and $(\text{CH}_3)_2\text{O}$ were mixed in different proportions with regard to volume, and the volume contractions which took place after the mixing were observed. On the assumption that the reaction would take place according to the equation, $(\text{CH}_3)_2\text{O}\cdot\text{HCl} \rightleftharpoons (\text{CH}_3)_2\text{O} + \text{HCl}$, the equilibrium constants in terms of partial pressures at 1°, 5°, 9° and 19° C. were found as follows:

$$K = 1.4906 \text{ at } 1^\circ \text{C. and } 0.9959 \text{ atm.}$$

$$K = 1.7224 \text{ at } 5^\circ \text{C. and } 0.9959 \text{ atm.}$$

$$K = 2.0837 \text{ at } 9^\circ \text{C. and } 0.9956 \text{ atm.}$$

$$K = 3.1744 \text{ at } 19^\circ \text{C. and } 0.9955 \text{ atm.}$$

The author found that through all the experiments the equilibrium partial pressures of $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$ were at the maximum when the two reactants were mixed in equal volumes and diminished with an excess of one of them; the maximum partial pressures experimentally determined of the reaction product, $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$, and the corresponding values of $(\text{CH}_3)_2\text{O}$ were in good agreement with the theoretical values.

The temperature effect on the equilibrium constant was determined in the temperature intervals given above. In the present case, the heat of reaction at constant pressure was proved to be independent of temperature at least in the range of the experiments, and therefore, the van't Hoff equation was expressed, in its integral form, by

$$K = \frac{0.4343}{RT} Q + C.$$

The calculated amount of the heat of reaction Q and the integration constant C were as follows:

$$Q = -6725 \text{ cal. } C = 5.5373.$$

The agreement between the theoretical and experimental values of the equilibrium constants was very satisfactory

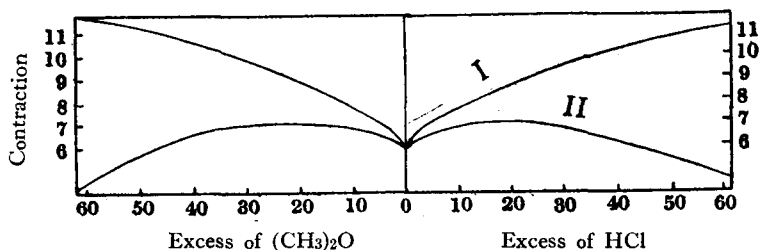
Introduction.

As early as 1878, M. Friedel¹ obtained a liquid compound boiling at -3° to -1° C. by allowing pure anhydrous hydrogen chloride and methyl ether to react with each other in a tube strongly cooled. Its composition could not be determined exactly owing to its being dissociated, even in the liquid state, into the components; but it was considered as a molecular compound of the two reactants.

From the freezing-point curve of the liquid mixture of pure anhydrous hydrogen chloride and methyl ether, G. Baumé² proved the existence of the two molecular compounds corresponding to the compositions $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$ and $(\text{CH}_3)_2\text{O}\cdot 4\text{HCl}$ the melting points of which were -97.1° C. and -102.8° C. respectively. O. Maass and D. McIntosh³ also carried out the same investigation as Baumé, and determined clearly the existence of the two compounds above mentioned, the melting points of which were, however, -96° C. and -102° C. respectively.

The reaction between gaseous methyl ether and hydrogen chloride was first investigated by M. Friedel⁴ and the reaction product was considered to be methyl ether hydrochloride of the composition $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$. He discussed the conditions for the maximum dissociation of the hydrochloride in the neighbourhood of 20° C. The pure and anhydrous hydrogen chloride and methyl ether were mixed in different proportions with respect to volume and the volume contractions which were effected from the molecular combination of the two were observed. The accompanying diagram (Fig. 1) is one which was found by him and shows graphically the results of his investigation.

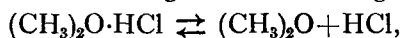
Fig. 1.



- 1 Bull. soc. Chim., 24, 160, (1875).
- 2 J. Chim. Phys., 9, 245, (1911).
- 3 J. Amer. Chem. Soc., 34, 1283, (1912).
- 4 Bull. soc. Chim., 24, 241, (1875).

The "excess" in the figure means the percentage ratio of the volume excess of one of the two reactants initially taken, to the total volume. The "contraction" was, however, used in two different meanings. In one case, it was used to designate the percentage ratio of the volume contraction which took place after mixing the two gases to twice the initial volume of the one which was employed in a smaller amount, and in the other, it was used to designate that of the volume contraction to the total volume of the two gases initially taken. Thus, in the accompanying diagram, Curve I was plotted in the former meaning, and Curve II in the latter. From the results obtained, Friedel concluded that the two gases would give the minimum yield of the methyl ether hydrochloride when they were mixed in equal volumes and that excess of any one of them would increase the yield. He explained these facts by assuming the excess molecules to oppose the dissociation of the hydrochloride.

Ostwald¹ discussed thoroughly, however, the results of Friedel's investigation from the stand point of the law of mass-action. If the dissociation takes place according to the following equation—



the equilibrium should be determined by the relation—

$$\frac{p_1 p_2}{q} = K \dots\dots\dots(1)$$

where q , p_1 and p_2 show the equilibrium partial pressures of methyl ether hydrochloride, methyl ether and hydrogen chloride respectively, and K the dissociation constant in terms of partial pressures. If P be the total pressure exerted by the system, then

$$P = p_1 + p_2 + q \dots\dots\dots(2)$$

Eliminating P_2 from equation (1) and (2), we obtain the relation—

$$q = \frac{p_1(P-p_1)}{K+p_1} \dots\dots\dots(3)$$

From equation (3) it is evident that the partial pressure of methyl ether hydrochloride, q , will be at the maximum for a certain value of p_1 , provided that the total pressure is kept constant. To find the maximum value of q we must differentiate equation (3) with respect to p_1 and put

$$\frac{dq}{dp_1} = 0.$$

¹ Ostwald : *Chemie*, 2 Aufl., II. 2. p.489.

Since

$$\frac{dq}{dp_1} = \frac{P - q - 2p_1}{p_1 + K} = \frac{p_2 - p_1}{p_1 + K},$$

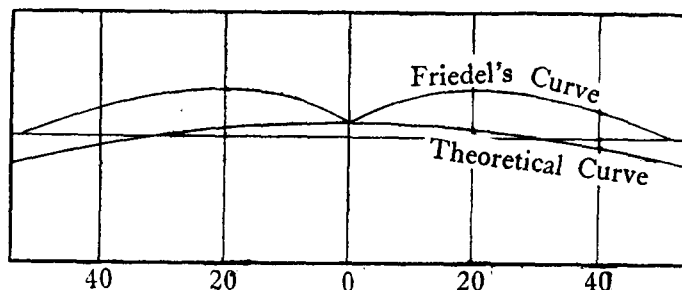
it follows that, for the maximum value of q ,

$$p_1 = p_2$$

must be satisfied. Therefore, as Ostwald discussed, the formation of methyl ether hydrochloride must be most favoured when its components are mixed in equal volumes.

Ostwald showed this relation graphically for comparison with Friedel's results which have been illustrated above. This is shown in Fig. 2.

Fig. 2.



The theoretical curve in the figure was plotted by means of equation (3), putting $P=1$ (atmosphere) and $K=4$ which nearly agrees with that found by Friedel when equal volumes of the gases were mixed. He attributed the contradiction of Friedel's results to the theory to experimental error, for the formation of the hydrochloride was in a small amount at the temperatures of the experiments, and suggested that if the experiments were carried out at lower temperatures, at which the combination is expected to take place in larger amount, the results would support the theory.

The comparison of the two curves will, however, not be reasonable, for they are not of the same system of co-ordinates. Moreover, Friedel's results are all found under different conditions of equilibrium, varying from 18.6°C . to 22.6°C . in temperature and 552.2 (mm) to 763.5 in total pressure; and although there are some data of a series of experiments conducted under the same conditions, they are too small in number to give a graphical representation.

The present experiments were carried out to repeat those of Friedel more exactly and to discuss this gaseous equilibrium from the theoretical standpoint.

Description of Apparatus.

Two burettes of the capacities of 55 c.c. and 45 c.c. respectively, both of which were graduated into 0.1 c.c., were provided. The former was used for observing the reaction between methyl ether and hydrogen chloride, and the latter for measuring the volumes of the two gases which were to be brought into the reaction. Their upper ends were drawn out narrow and closed by well-ground double Greiner-Friedrich stop-cocks, the construction of which is shown in Fig. 3.

The tubes a, b, c and d of the stop-cocks were all capillary ones. The two burettes were connected by a capillary tube, both ends of which were tightly joined by means of pieces of rubber tubing to the tubes, b and c, respectively. The tube, d, was provided as an outlet for the gases, and the tube, a, as a passage for the reacting gases to the measuring burette. The latter tube was connected with the tube, f, of another double stop-cock, F (Fig. 4), in the same way as employed for connecting the burettes. The tubes, e and g, of the double stop-cock, F, were connected with a wash-bottle, the use of which will be described later, and with the gas generators respectively.

To the lower narrowed ends of the burettes were attached short rubber tubes, each provided with a simple stop-cock. These stop-cocks were connected by means of short rubber tubes with the two upper branches of a glass Y-tube, whose stem was connected with a levelling tube, G (Fig. 4), by means of a long patent rubber tube.

The burettes were accurately calibrated to 0.01 c.c. by weighing the mercury which they delivered.

The mercury used for measuring the gas volume was first washed with dilute nitric acid and then distilled in the air.

The thermostat for use at temperatures below that of the room, was prepared by means of the method designed by J. L. R. Morgan¹. The bath was made of a vessel which was provided with double walls in two opposite sides and with transparent walls in the other opposite sides. To cool the bath, the space between the double walls of the vessel was filled with water or ice-water in cases of experiments at lower temperatures.

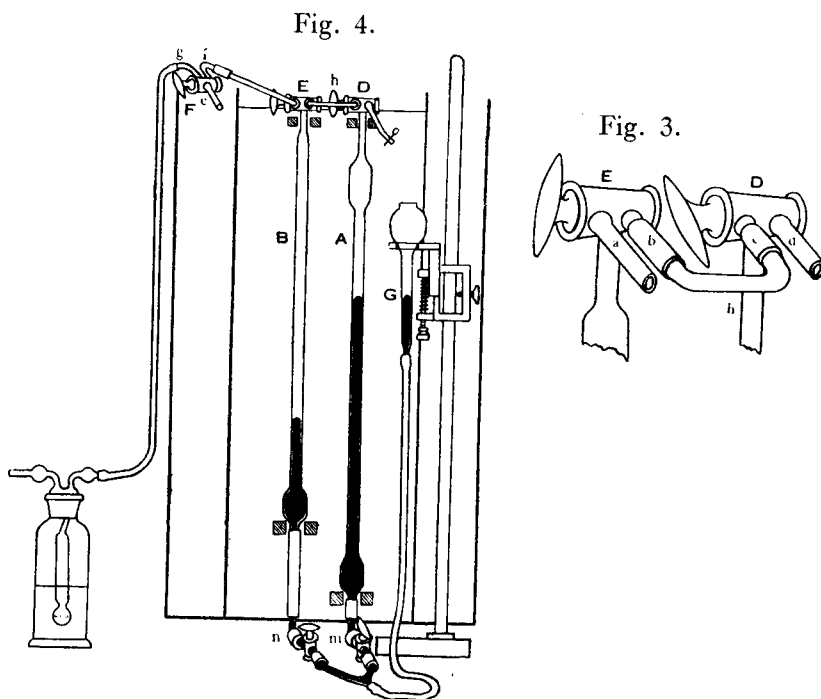
The thermo-regulator employed was the ordinary one as used for an electrically heated thermostat. Its electrical circuit contained a small

¹ J. Amer. Chem. Soc., **33**, 344, (1911); Zs. Phys. Chem., **78**, 123, (1912).

relay which was so arranged that the circuit of 12 V (D. C.) could be either made or broken in a large telegraph sounder. This was so placed as to act on a rod, which pressed tightly on a piece of rubber tubing, through which cold water could be automatically delivered to the thermostat. By such a regulator, the temperatures between 19° and 5°C . could be maintained constant with an accuracy of two-hundredths of a degree.

For the temperature so low as 1°C ., however, such regulation was not convenient because of the demand for a large amount of cold water below 0°C .. In such a case, nearly the same constancy in temperature as the above was attained by adding suitable amounts of powdered ice and water alternately to the bath.

The final construction of the measuring apparatus is shown, in some detail, diagrammatically in Fig. 4, in which the thermo-regulator and the cooling apparatus are omitted.



The two burettes were kept both parallel and vertical.

The levelling tube was held in a clamp, of which the fine adjustment of the vertical position was made in the same way as employed

for fine raising or lowering of a telescope in a kathetometer, and it was supported on an iron stand outside the thermostat.

The stop-cocks at the tops of the burettes were kept just outside the thermostat to prevent their dipping into the bath and were cooled by being covered with wet cotton cloth partly dipped into the bath.

Preparation of Materials.

Methyl ether was prepared by the action of concentrated sulphuric acid (Merck : Pure) on methyl alcohol (Merck : Extra Pure) in the ordinary way. The gas produced was first washed by water, cooled by ice and finally dried, as completely as possible, by passing it through drying tubes containing caustic potash and then through a long series of U-tubes containing calcium chloride.

Before the gas was admitted to the measuring burette it was passed through concentrated sulphuric acid contained in the wash-bottle (Fig. 4) until its bubblings in the acid were so slackened that only one or two very small bubbles per two minutes were evolved, the gas being almost completely absorbed in the acid. At this stage, the gas was considered to be almost free from air; and if any other gases were present, they were so only in traces.

Hydrogen chloride was prepared by dropping concentrated sulphuric acid into concentrated hydrochloric acid (Merck : Pure). It was dried first by passing through a long series of U-tubes containing calcium chloride and then through concentrated sulphuric acid¹. Its purity was ascertained in a similar manner to the above by passing it through water.

Experimental Procedure.

Mercury was first drawn into the burette, B (Fig. 4), until it filled the latter, and also into the connecting tube of the two double stop-cocks so as to occupy entirely the bore of the outer stop-cock, F,

¹ With a short series of U-tubes of calcium chloride and one bottle of concentrated sulphuric acid, the hydrogen chloride coming out from them seemed to act upon the mercury in the burettes, the surface of which became dimmed soon after it had been in contact with the gas. When, however, two bottles of sulphuric acid and six U-tubes of calcium chloride were used, it was proved that the gas did not act appreciably upon the mercury, for the latter left in contact with the gas still preserved a bright surface for at least a day and night, and moreover, as will be shown later, the volume of the gas did not change appreciably in the course of that time.

which was a passage from the gas generator. The other burette, A, was evacuated by means of a pump which was connected by means of a rubber tube with the tube, d (Fig. 3), to expel air in the connecting tube, h, of the two burettes. Then, the mercury in the burette, B, was drawn into the burette, A, through the connecting tube until it filled completely the latter and the bores of the stop-cocks, through which it was passed, when the stop-cock, D, was closed.

The burette, A, was then filled up with mercury, being meanwhile connected, by means of rubber tubing joined to the tube d, with a wash-bottle containing concentrated sulphuric acid to prevent wet air from coming into it. After this, the other bore of the double stop-cock, F, was opened to allow methyl ether coming through the drying apparatus from its generator to pass into the wash-bottle containing the reagent for testing the purity of it. After its purity had been ascertained, the double stop-cocks E and F were turned to draw the gas into the measuring burette, the levelling tube being lowered to a suitable position. The gas was then drawn out of the burette through its former passage by raising the levelling tube, and it was expelled from the whole apparatus through the wash-bottle. This was repeated several times to expel air occluded in the joining parts outside the burette. Finally, a suitable volume of the gas was drawn into the burette and kept at a given constant temperature for over an hour.

To determine the volume of the gas, the position of the meniscus of the mercury in the burette was read by a kathetometer, the surface of the mercury being meanwhile lightened by diffused light from an incandescent filament.

It was then transferred completely to the reaction burette through the connecting tube by raising the levelling tube.

The determination of the volume of hydrogen chloride and also its transference into the reaction burette, or the mixing of the two gases in this case, were carried out entirely in the same way as the above; in this case, however, care was particularly taken not to allow the gas to remain in the connecting tube of the two burettes and the bores of the stop-cocks through which the gas was passed.

The volume of the gas which was now subjected to the reaction was then observed from time to time, the pressure being regulated to a given constant value.

When the experiments were finished the gas was drawn out of the burette through the tube, d, care being taken not to allow moisture in the air to come into the burette. Dry air was then drawn into the

burettes and mercury was allowed to flow out of them. To remove the gas which might have been absorbed by the mercury, the latter was washed first with water and then with a dilute solution of mercurous nitrate acidified with nitric acid in the usual manner. Finally it was dried on a sand bath. As to the measuring apparatus, for the same reason, dry air was passed through it for several hours.

The adjustment of the gaseous pressure to a desired one was carried out by raising or lowering the levelling tube to such a height that the pressure which was to be exerted by the level difference of the mercury in the burette and the levelling tube became equal to the difference between the barometric pressure and the desired pressure, the mercury level in the levelling tube being raised or lowered from that in the burette according as the barometric pressure was lower or higher than the desired pressure.

In order to maintain the temperature of the mercury in the levelling tube which stood outside the thermostat as uniform as possible, the bores of the simple stop-cocks m and n (Fig. 4) through which mercury at different temperatures in the burettes and the levelling tube was to pass were made so fine as to allow the mercury to flow through them very slowly; consequently for the temperature of the mercury column in the levelling tube, only that of its upper layer was read.

Preliminary Test for Accuracy of Experiments.

The identity of the volumes shown by the two burettes was first examined. To do this, the volume of dry-air was determined by means of the measuring burette. This was transferred into the reaction burette and the volume was again determined. The following data were found at 19° C..

Volume determined by means of the measuring burette=43.97 c.c.

Volume determined by means of the reaction burette=43.98 c.c.

From this experiment, the volumes shown by the two burettes were judged to be identical.

To ascertain whether or not the gases would act upon the India rubber wax used for sealing the double stop-cocks and the mercury in the burettes, the following experiments were carried out. The volume of each gas was first determined, and after being kept for a night in the burette at the room temperature, its volume was again determined with the following results :

Volume of $(\text{CH}_3)_2\text{O}$ first determined at $9^\circ \text{C.} = 17.58 \text{ c.c.}$

Volume of $(\text{CH}_3)_2\text{O}$ determined after a night at $9^\circ \text{C.} = 17.57 \text{ c.c.}$

Volume of HCl first determined at $9^\circ \text{C.} = 19.73 \text{ c.c.}$

Volume of HCl determined after a night at $9^\circ \text{C.} = 19.71 \text{ c.c.}$

For further confirmation, the gases determined above were transferred into the reaction burette, and after an hour the volumes were again determined. The results were as follows :

Volume of $(\text{CH}_3)_2\text{O}$ at $9^\circ \text{C.} = 17.57 \text{ c.c.}$

Volume of HCl at $9^\circ \text{C.} = 19.73 \text{ c.c.}$

As to hydrogen chloride, the confirmation was further carried out in the following way. After the gas had been kept in the burette for several hours, water was introduced into the burette to allow it to absorb the gas. The gas was almost entirely absorbed in the water, leaving only a small bubble which might have been present before the experiment.

From these preliminary observations, the gaseous reaction in question may be concluded not to receive any remarkable influence from the foreign matters used in the apparatus.

Results of Experiments.

The experiments¹ were carried out at $1^\circ, 5^\circ, 9^\circ$ and 19°C^2 . respectively, the total pressure being kept nearly at one atmosphere through all of them. The reaction proceeded mostly at the instant when the gases were mixed, and slowly afterwards. Equilibrium was completely reached after two or three hours at all the temperatures mentioned above.

The experimental results are shown in Tables I—IV. The corrections of the gaseous pressures observed were carried out as follows :—

Let P' = the barometric pressure in cm of mercury at the temperature t' .

P = the pressure of the gas in question in cm of mercury at 0°C.

t' = the temperature shown by a thermometer attached to the barometer.

t'' = the temperature of mercury in the levelling tube.

t = the temperature of the mercury in the burettes.

H = the height of mercury level, in cm, in the burettes from the bottom of the thermostat.

¹ The experiments below 0°C. were abandoned for the reason that the reaction product would condense at -3° to -1°C. as previously mentioned.

² This temperature was the mean of those, at which Friedel carried out his experiments, and it was selected for the purpose of comparing his results with ours.

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h = the difference in two levels of mercury, in cm, in the burettes and the levelling tube ; it was expressed by the minus sign when the former was higher than the latter and by the plus sign when reversed.

$d_t, d_{t'}, d_{t''}$ and d_0 = the densities of mercury at t, t', t'' and 0° C. respectively.

The gaseous pressure required, in cm of mercury at 0° C., will then be calculated by the equation--

$$P'd_{t'} + (H+h)d_{t''} = Pd_0 + Hd_t,$$

therefore,

$$P = \frac{P'd_{t'} - \{H(d_t - d_{t''}) - hd_{t''}\}}{d_0}.$$

Since the gaseous pressures, under which the volumes of methyl ether, hydrogen chloride and their mixture at the equilibrium were determined, were each somewhat different, the volumes of the former two gases were reduced to those which they would have at the pressure under which the equilibrium was observed. The symbol V_2 in the tables shows the values obtained by such calculations, V_1 showing the original values. The symbols a, b and c denote methyl ether, hydrogen chloride and their mixture respectively.

TABLE I.

Results of observations at 1° C.

No.	Subst.	V_1	V_2	P'	H	h	t'	t''	P
1	a	16.15	16.14	76.97	42.38	-0.99	18.0	16.0	75.61
	b	16.46	16.47	76.33	42.14	-0.27	18.0	16.0	75.70
	c	28.95	28.95	76.39	37.07	-0.39	16.5	14.0	75.68
2	a	19.23	19.22	76.07	39.93	-0.09	17.0	14.0	75.66
	b	22.27	22.26	76.24	37.58	-0.25	17.3	15.0	75.65
	c	36.98	36.98	76.38	29.76	-0.38	17.0	14.0	75.70
3	a	15.94	15.92	76.17	42.54	-0.19	20.0	17.0	75.58
	b	22.26	22.25	76.34	37.58	-0.36	19.2	16.0	75.62
	c	34.14	34.14	76.32	32.35	-0.31	17.5	15.0	75.69
4	a	16.88	16.87	76.20	41.74	-0.18	19.5	17.0	75.63
	b	30.28	30.28	76.35	31.28	-0.33	19.5	17.0	75.66
	c	42.28	42.28	76.48	24.97	-0.49	19.0	16.0	75.65
5	a	16.28	16.27	76.19	42.28	-0.17	16.0	14.0	75.70
	b	36.26	36.22	75.42	26.58	+0.57	16.5	14.0	75.70
	c	47.61	47.61	75.39	20.19	+0.63	15.0	13.0	75.77

TABLE I (continued).
Results of observations at 1° C.

No.	Subst.	V ₁	V ₂	P'	H	h	t'	t''	P
6	a	19.88	19.88	75.78	39.40	+0.22	20.0	17.0	75.62
	b	22.97	22.97	74.66	37.03	+1.35	19.5	17.0	75.62
	c	37.89	37.89	74.72	28.90	+1.26	19.8	17.5	75.63
7	a	21.16	21.14	75.23	38.42	+0.77	19.5	16.0	75.63
	b	18.58	18.56	75.70	40.44	+0.31	18.5	16.0	75.64
	c	35.26	35.26	75.88	31.33	+0.13	17.2	15.0	75.69
8	a	22.85	22.85	76.21	37.12	-0.21	16.2	14.0	75.69
	b	18.15	18.15	75.73	40.77	+0.27	17.2	15.0	75.67
	c	36.39	36.39	75.86	30.43	+0.13	16.6	14.0	75.69
9	a	26.48	26.49	76.57	34.24	-0.57	19.7	17.2	75.70
	b	16.52	16.51	76.47	42.09	-0.47	18.3	15.0	75.64
	c	38.34	38.34	76.42	28.50	-0.42	18.0	15.0	75.68
10	a	34.22	34.24	75.57	28.19	+0.44	16.0	13.0	75.73
	b	15.98	15.97	76.47	42.51	-0.47	19.5	17.0	75.61
	c	45.06	45.06	76.65	22.50	-0.65	18.5	16.0	75.69
11	a	24.81	24.78	76.84	35.56	-0.85	19.0	16.0	75.63
	b	24.75	24.74	76.80	35.63	-0.80	17.3	14.0	75.68
	c	43.89	43.89	76.76	23.54	-0.75	16.5	14.0	75.72
12	a	26.20	26.19	76.29	34.46	-0.29	16.5	14.0	75.69
	b	24.29	24.27	76.11	35.99	-0.11	17.5	15.0	75.67
	c	44.81	44.81	76.27	22.71	-0.26	16.0	14.0	75.74
13	a	25.66	25.65	76.64	34.90	-0.64	14.0	12.0	75.74
	b	25.18	25.17	76.67	35.29	-0.68	15.5	13.0	75.70
	c	45.13	45.13	76.63	22.44	-0.64	14.5	12.0	75.75
14	a	25.01	25.00	75.97	35.42	+0.03	18.0	16.0	75.65
	b	26.99	26.98	75.78	33.84	+0.22	19.7	17.0	75.63
	c	46.27	46.27	75.72	21.39	+0.28	19.4	17.0	75.67
15	a	24.68	24.67	75.97	35.68	+0.03	15.6	13.7	75.72
	b	29.76	29.72	76.35	31.67	-0.35	18.3	17.0	75.66
	c	48.35	48.35	76.35	19.57	-0.34	15.5	14.0	75.75

TABLE II.
Results of observations at 5° C.

No.	Subst.	V ₁	V ₂	P'	H	h	t'	t''	P
1	a	14.64	14.64	76.10	43.58	-0.10	18.0	17.0	75.66
	b	14.95	14.95	76.04	43.30	-0.04	18.0	17.0	75.66
	c	26.54	26.54	76.13	39.24	-0.13	18.0	17.0	75.66
2	a	13.96	13.98	75.84	44.12	+0.16	19.0	18.0	75.73
	b	13.94	13.94	76.05	44.12	-0.06	19.0	18.0	75.63
	c	25.06	25.06	76.07	40.58	-0.07	19.0	18.0	75.64

TABLE II (continued)
Results of observations at 5° C.

No.	Subst.	V ₁	V ₂	P'	H	h	t'	t''	P
3	a	14.29	14.29	76.49	43.85	-0.50	20.0	19.0	75.60
	b	18.14	18.14	75.91	40.78	+0.10	20.0	19.0	75.63
	c	29.19	29.19	75.96	36.85	+0.03	20.0	19.0	75.63
4	a	13.89	13.88	75.49	44.17	+0.51	20.5	19.0	75.62
	b	30.91	30.90	75.62	30.80	+0.38	20.0	19.0	75.65
	c	41.11	41.11	75.71	26.04	+0.29	18.0	17.0	75.69
5	a	14.20	14.20	75.83	43.92	+0.17	19.0	18.0	75.64
	b	14.38	14.37	75.96	43.79	+0.03	19.0	18.0	75.63
	c	25.42	25.42	76.00	40.25	0.00	19.0	18.0	75.65
6	a	14.32	14.30	76.52	43.83	-0.50	20.0	19.0	75.64
	b	18.12	18.12	76.23	40.80	-0.23	18.0	17.0	75.66
	c	29.12	29.12	76.37	36.91	-0.37	17.0	16.0	75.70
7	a	15.26	15.25	76.60	43.08	-0.60	14.0	13.0	75.75
	b	31.79	31.70	76.11	30.09	-0.11	15.0	14.0	75.74
	c	42.99	42.99	76.09	24.33	-0.09	13.0	12.0	75.79
8	a	13.34	13.31	75.88	44.60	+0.12	15.0	14.0	75.72
	b	24.43	24.42	76.26	35.88	-0.26	17.0	16.0	75.70
	c	34.30	34.30	76.45	32.21	-0.46	14.0	13.0	75.75
9	a	21.31	21.30	75.69	38.31	+0.31	19.2	18.1	75.65
	b	16.24	16.24	75.28	42.31	+0.73	19.1	18.4	75.66
	c	33.80	33.80	75.50	32.65	+0.50	17.5	16.0	75.69
10	a	21.69	21.68	75.77	38.02	+0.23	16.5	15.5	75.70
	b	18.21	18.21	75.80	40.72	+0.20	16.0	14.5	75.71
	c	35.94	35.94	75.88	30.71	+0.12	15.5	14.0	75.74
11	a	21.55	21.54	75.98	38.13	+0.02	15.5	14.5	75.72
	b	19.15	19.14	76.47	39.98	-0.48	16.0	15.0	75.70
	c	36.67	36.67	76.34	30.04	-0.33	16.5	15.0	75.73
12	a	21.84	21.85	75.90	37.91	+0.10	17.0	15.7	75.70
	b	20.75	20.75	76.12	38.73	-0.12	19.0	17.5	75.65
	c	38.25	38.25	76.04	28.59	-0.05	19.5	17.5	75.66
13	a	29.94	29.93	75.74	31.54	+0.27	18.0	16.3	75.70
	b	18.52	18.51	75.86	40.47	+0.15	17.7	16.7	75.68
	c	43.96	43.96	75.82	23.47	+0.19	18.5	17.0	75.72
14	a	37.83	37.84	75.07	25.34	+0.92	17.5	16.0	75.70
	b	11.54	11.54	75.47	45.91	+0.53	19.0	18.0	75.62
	c	45.57	45.57	75.46	22.03	+0.53	19.5	18.5	75.69
15	a	20.64	20.64	76.01	38.82	+0.01	21.3	19.5	75.63
	b	23.03	23.03	75.95	36.98	+0.06	22.5	20.0	75.60
	c	39.11	39.11	75.89	27.81	+0.10	21.9	20.0	75.61

TABLE III.
Results of observations at 9° C.

No.	Subst.	V ₁	V ₂	P'	H	h	t'	t''	P
1	a	22.23	22.23	75.45	37.58	+0.55	21.0	19.5	75.64
	b	20.25	20.25	75.51	39.13	+0.51	21.2	20.0	75.65
	c	38.70	38.70	75.50	28.19	+0.50	20.9	19.5	75.66
2	a	26.20	26.19	75.22	34.46	+0.77	21.0	20.0	75.63
	b	20.30	20.29	75.55	39.09	+0.44	21.5	20.0	75.61
	c	42.56	42.56	75.63	24.72	+0.37	21.1	19.6	75.66
3	a	30.73	30.73	75.41	30.95	+0.60	21.2	19.6	75.66
	b	16.16	16.15	75.78	42.37	+0.23	20.8	19.5	75.64
	c	42.89	42.89	75.69	24.42	+0.31	21.4	20.0	75.65
4	a	22.72	22.70	75.66	37.23	+0.33	19.6	18.1	75.66
	b	24.97	24.95	75.95	35.46	+0.05	19.2	18.0	75.68
	c	43.43	43.43	76.02	23.95	0.00	18.3	16.7	75.74
5	a	19.46	19.46	75.53	39.74	+0.47	19.8	18.4	75.66
	b	24.15	24.14	75.77	36.10	+0.22	22.0	20.5	75.62
	c	39.80	39.80	75.79	27.20	+0.22	21.5	20.0	75.66
6	a	15.54	15.52	75.85	42.85	+0.15	22.9	21.5	75.59
	b	30.33	30.32	75.65	31.25	+0.35	21.0	20.0	75.65
	c	42.43	42.43	75.57	24.84	+0.43	20.5	19.0	75.68
7	a	20.55	20.56	75.18	38.89	+0.82	21.4	20.0	75.63
	b	19.96	19.96	75.35	39.35	+0.61	22.5	21.5	75.56
	c	36.87	40.50	75.28	29.85	+0.72	25.0	23.8	75.58

TABLE IV.
Results of observations at 19° C.

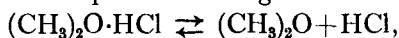
No.	Subst.	V ₁	V ₂	P'	H	h	t'	t''	P
1	a	21.25	21.23	75.60	38.36	+0.39	25.7	25.0	75.60
	b	21.17	21.19	75.11	33.42	+0.99	22.7	22.0	75.77
	c	39.53	39.53	75.04	27.44	+0.96	22.3	21.7	75.68
2	a	20.99	20.98	75.59	38.55	+0.41	25.8	25.2	75.61
	b	22.06	22.06	75.73	37.74	+0.27	24.2	23.3	75.64
	c	40.27	40.27	75.67	26.76	+0.32	23.6	22.6	75.65
3	a	20.62	20.61	74.39	38.84	+1.61	23.1	22.1	75.64
	b	22.40	22.41	75.02	37.41	+0.98	21.5	21.0	75.70
	c	40.22	40.22	75.04	26.81	+0.98	23.0	22.5	75.69
4	a	21.27	21.28	75.72	38.34	+0.28	23.2	22.7	75.65
	b	25.39	25.38	75.62	35.12	+0.38	26.5	25.5	75.61
	c	43.81	43.81	75.69	23.61	+0.31	25.8	25.0	75.62
5	a	16.47	16.47	75.40	42.12	+0.61	22.8	22.0	75.68
	b	30.14	30.14	75.40	31.39	+0.60	22.9	22.7	75.67
	c	43.98	43.98	75.43	23.46	+0.57	22.3	21.8	75.68

TABLE IV (continued)
Results of observations at 19° C.

No.	Subst.	V ₁	V ₂	P'	H	h	t'	t''	P
6	a	20.32	20.32	75.01	39.07	+1.00	25.0	24.0	75.63
	b	19.47	19.47	74.98	39.73	+1.03	24.3	23.5	75.65
	c	37.19	37.19	75.22	29.56	+0.78	23.9	23.3	75.65
7	a	22.51	22.51	75.37	37.39	+0.62	23.3	22.6	75.64
	b	20.13	20.13	75.31	39.22	+0.69	23.7	23.0	75.65
	c	40.00	40.00	75.35	27.01	+0.64	23.5	22.9	75.65
8	a	27.13	27.12	75.62	33.74	+0.38	24.4	23.5	75.64
	b	20.76	20.75	75.57	38.73	+0.44	24.5	23.7	75.65
	c	44.93	44.93	75.61	22.60	+0.41	24.2	23.2	75.67
9	a	31.39	31.40	74.81	30.42	+1.19	23.2	22.3	75.66
	b	15.75	15.75	75.17	42.68	+0.84	23.9	23.8	75.64
	c	44.52	44.52	75.15	22.98	+0.85	24.2	23.9	75.65
10	a	24.52	24.52	74.82	35.81	+1.20	23.8	23.4	75.66
	b	24.22	24.23	75.03	36.05	+0.99	24.6	24.0	75.65
	c	45.62	45.62	75.26	21.99	+0.73	23.5	22.8	75.65
11	a	20.72	20.71	75.57	38.76	+0.42	25.2	24.6	75.60
	b	27.82	27.81	75.56	33.19	+0.43	26.3	25.5	75.60
	c	45.54	45.54	75.65	22.06	+0.36	25.2	24.4	75.64

Calculation of the Results.

If the reaction takes place according to the following equation—



the volume, in the equilibrium value, of methyl ether hydrochloride formed must be represented by the contraction of the total volume, namely by the difference between the sum of the volumes of the two gases which were initially taken and that which the mixed gas took at the equilibrium. The volumes of the methyl ether and the hydrogen chloride uncombined, in the equilibrium values, are then to be obtained by subtracting the volume contraction from their initial volumes.

The partial pressures of the three gases, in the equilibrium values, were each calculated in unit of atmosphere by the following equation :

$$p = \frac{v \cdot P}{V \cdot 76},$$

where p shows the partial pressure, v , the volume of the gas in question, in the equilibrium values, V , the total volume of the mixed gas at the equilibrium and P , the pressure, in cm, under which the equilibrium was reached.

The equilibrium constant at any temperature will then be calcu-

lated by substituting these values of the partial pressures of every gas in the following equation which has already been illustrated,

$$K = \frac{p_{(\text{CH}_3)_2\text{O}} \times p_{\text{HCl}}}{p_{(\text{CH}_3)_2\text{O} \cdot \text{HCl}}}$$

where p_{HCl} , $p_{(\text{CH}_3)_2\text{O}}$ and $p_{(\text{CH}_3)_2\text{O} \cdot \text{HCl}}$ express the partial pressures of hydrogen chloride, methyl ether and methyl ether hydrochloride respectively. The results of the calculations are summarised with the total pressure P in Tables V to VIII.

TABLE V.

Partial pressures of $(\text{CH}_3)_2\text{O}$, HCl and $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$ and equilibrium constant of the system at 1° C.

No.	P in atm.	$p_{(\text{CH}_3)_2\text{O}}$ in atm.	p_{HCl} in atm.	$p_{(\text{CH}_3)_2\text{O} \cdot \text{HCl}}$ in atm.	K
1	0.99580	0.42929	0.44061	0.12590	1.5024
2	0.99608	0.39646	0.47834	0.12120	1.5647
3	0.99593	0.34717	0.53199	0.11766	1.5696
4	0.99540	0.28252	0.59824	0.11466	1.4741
5	0.99698	0.23831	0.65630	0.10240	1.5273
6	0.99513	0.39183	0.47298	0.13026	1.4228
7	0.99593	0.47171	0.39912	0.12513	1.5046
8	0.99593	0.49920	0.37057	0.12617	1.4662
9	0.99580	0.56700	0.30778	0.12104	1.4418
10	0.99593	0.64292	0.23913	0.11382	1.3508
11	0.99633	0.43473	0.43359	0.12803	1.4722
12	0.99660	0.45659	0.41411	0.12588	1.5021
13	0.99672	0.44082	0.43022	0.12566	1.5092
14	0.99566	0.41510	0.45771	0.12287	1.5463
15	0.99672	0.38405	0.48815	0.12451	1.5057

Mean 1.4906

TABLE VI.

Partial pressures of $(\text{CH}_3)_2\text{O}$, HCl and $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$ and equilibrium constant of the system at 5° C.

No.	P in atm.	$p_{(\text{CH}_3)_2\text{O}}$ in atm.	p_{HCl} in atm.	$p_{(\text{CH}_3)_2\text{O} \cdot \text{HCl}}$ in atm.	K
1	0.99555	0.43476	0.44639	0.11441	1.6963
2	0.99528	0.44163	0.44004	0.11358	1.7109
3	0.99513	0.37669	0.50793	0.11045	1.7323
4	0.99593	0.24735	0.65969	0.08891	1.8352
5	0.99540	0.43269	0.43915	0.12335	1.5412
6	0.99608	0.37658	0.50689	0.11258	1.6955
7	0.99724	0.26190	0.64349	0.09186	1.8346
8	0.99672	0.28709	0.60992	0.09967	1.7569
9	0.99593	0.51741	0.36831	0.11020	1.7297
10	0.99660	0.49161	0.39540	0.10953	1.7748
11	0.99646	0.47637	0.41115	0.10897	1.8392
12	0.99555	0.45548	0.42685	0.11322	1.7172
13	0.99633	0.57677	0.31796	0.10153	1.8063
14	0.99593	0.74367	0.16893	0.08326	1.5088
15	0.99488	0.40903	0.46982	0.11599	1.6567

Mean 1.7224

TABLE VII.

Partial pressures of $(\text{CH}_3)_2\text{O}$, HCl and $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$ and equilibrium constant of the system at 9°C .

No.	P in atm.	$P_{(\text{CH}_3)_2\text{O}}$ in atm.	P_{HCl} in atm.	$P_{(\text{CH}_3)_2\text{O}\cdot\text{HCl}}$ in atm.	K
1	0.99560	0.47462	0.42369	0.09724	2.0680
2	0.99560	0.52093	0.38292	0.09170	2.1754
3	0.99550	0.62062	0.28223	0.09261	1.8914
4	0.99660	0.42210	0.47568	0.09683	2.0735
5	0.99560	0.39173	0.50880	0.09506	2.0968
6	0.99580	0.28420	0.63154	0.08003	2.2428
7	0.99450	0.45608	0.43990	0.09845	2.0380

Mean 2.0837

TABLE VIII.

Partial pressures of $(\text{CH}_3)_2\text{O}$, HCl and $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$ and equilibrium constant of the system at 19°C .

No.	P in atm.	$P_{(\text{CH}_3)_2\text{O}}$ in atm.	P_{HCl} in atm.	$P_{(\text{CH}_3)_2\text{O}\cdot\text{HCl}}$ in atm.	K
1	0.99580	0.46200	0.46099	0.07280	2.9255
2	0.99540	0.45009	0.47678	0.06871	3.1231
3	0.99593	0.44103	0.48560	0.06908	3.0999
4	0.99500	0.41855	0.51166	0.06472	3.3088
5	0.99580	0.31338	0.62291	0.05955	3.2780
6	0.99540	0.47429	0.45154	0.06959	3.0774
7	0.99540	0.49444	0.43522	0.06569	3.2757
8	0.99566	0.53581	0.39466	0.06514	3.2459
9	0.99540	0.64323	0.29333	0.05880	3.2088
10	0.99540	0.46669	0.46037	0.06829	3.1461
11	0.99528	0.38750	0.54268	0.06513	3.2288

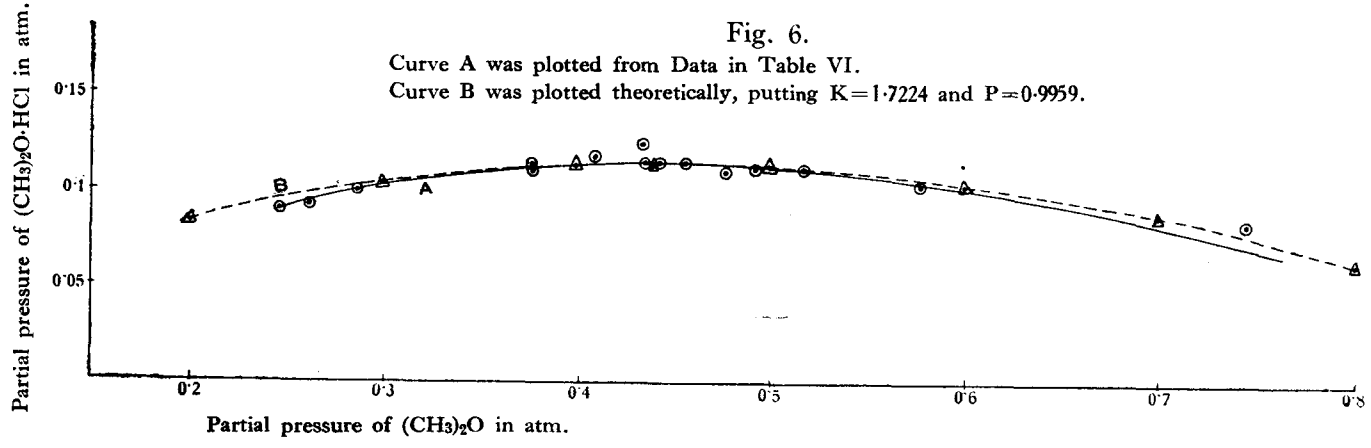
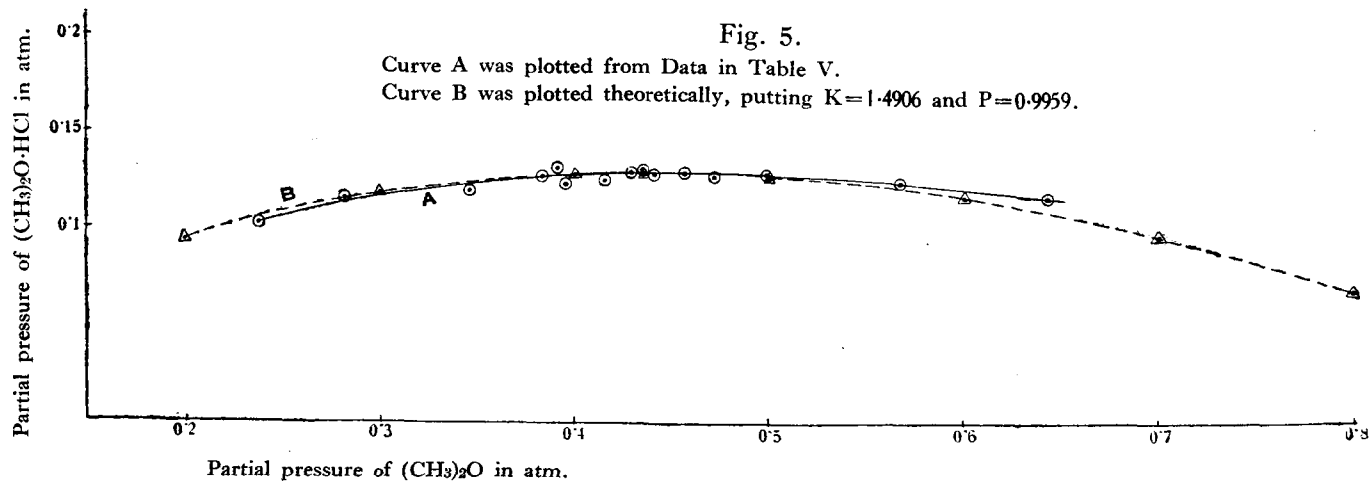
Mean 3.1744

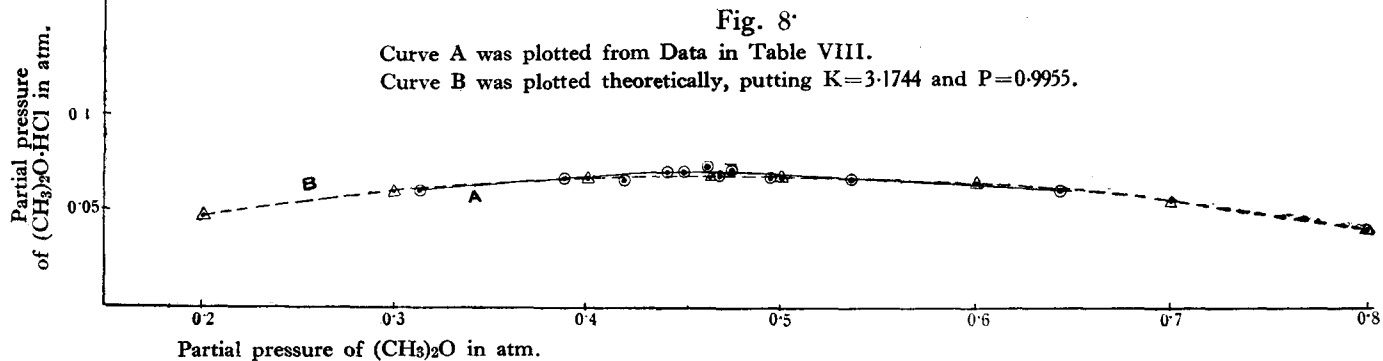
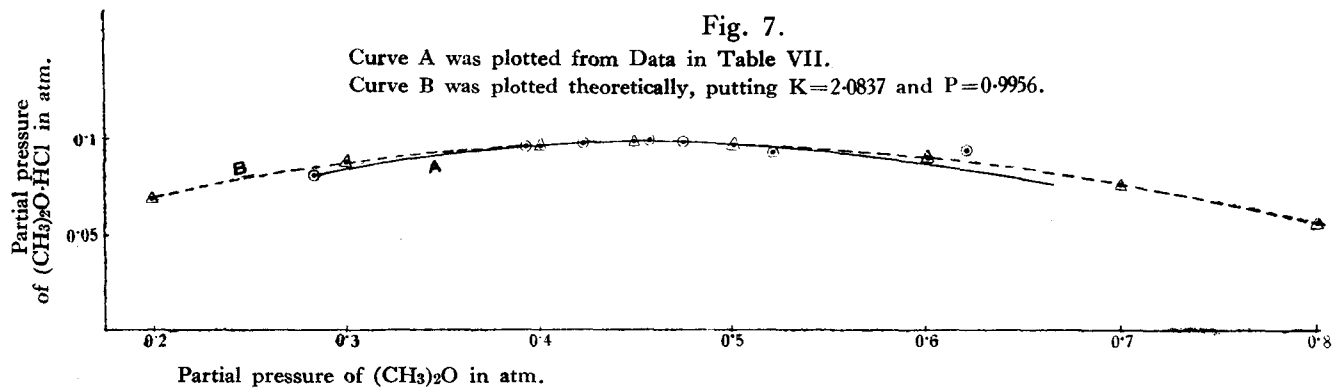
The values of the equilibrium constant K thus obtained are nearly constant in each series of the experiments. There are however a few which deviate considerably from the mean value of them. This can be attributed to experimental error.

Discussion of the Results.

Since the equilibrium constants were obtained, the question as to the dissociation of methyl ether hydrochloride should now be solved naturally. This has already been discussed in the introduction of the paper.

To confirm this consideration, the experimental results obtained were plotted in the curves in the following figures, the partial pressures of methyl ether hydrochloride at the equilibrium being taken as the ordinate and that of methyl ether as the abscissa.





In these figures, the curves A are plotted from the data obtained experimentally, and the B ones, from equation (3), where for K and the total pressure P the mean values obtained in each series of the experiments were employed. The partial pressures of methyl ether corresponding to the maximum ones of the hydrochloride can be calculated by means of equation (3), putting $p_1=p_2$. Thus, it is shown by the equation—

$$p_{(\text{CH}_3)_2\text{O}} = p_{\text{HCl}} = \sqrt{K^2 + PK} - K.$$

Then, for the maximum partial pressure of the hydrochloride, it follows that—

$$p_{(\text{CH}_3)_2\text{O} \cdot \text{HCl}} = P - 2p_{(\text{CH}_3)_2\text{O}}.$$

The results of the calculation are tabulated below with the experimental ones, which are found graphically from the curves in the figures shown above.

TABLE IX.

The maximum partial pressures of $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$ and the corresponding partial pressures of $(\text{CH}_3)_2\text{O}$.

Temp.	K	P	$p_{(\text{CH}_3)_2\text{O}}$		$p_{(\text{CH}_3)_2\text{O} \cdot \text{HCl}}$	
			Calc.	Obs.	Calc.	Obs.
1°	1.4906	0.9959	0.4346	0.434-	0.1267	0.127-
5°	1.7224	0.9959	0.4414	0.438-	0.1131	0.113-
9°	2.0837	0.9956	0.4494	0.450-	0.0969	0.097-
19°	3.1744	0.9955	0.4639	0.460-	0.0677	0.069-

The agreement of the two results are satisfactory.

Hence, from these results it is proved that when gaseous methyl ether and hydrogen chloride are mixed in equal volumes, the dissociation of the resulting substance, namely methyl ether hydrochloride, is at the minimum; and it increases gradually with the increase of the excess of one of the components. The constancy of the equilibrium constant found and the agreement, as will be seen clearly from Fig. 5, 6, 7 and 8, between the experimental and theoretical values of the partial pressures of methyl ether and methyl ether hydrochloride show that the volume contraction is not due to the molecular attraction between hydrogen chloride and methyl ether.

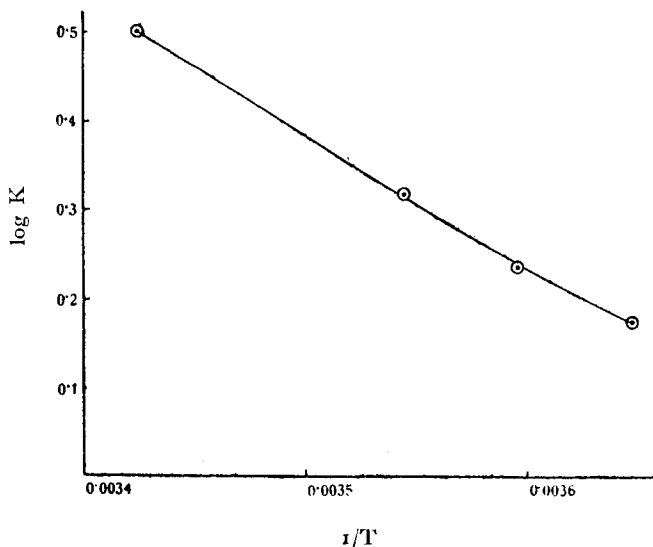
Thermodynamic Consideration of the Results.

It is evident from the experimental results that the higher the temperature, the higher are the equilibrium constant, and therefore, the dissociation degree of methyl ether hydrochloride. The dissociation of the hydrochloride must therefore be considered to be accompanied with the absorption of heat. The effect of temperature on the dissociation constant is given by the van't Hoff equation—

$$\frac{d \ln K}{dT} = \frac{-Q}{RT^2}, \dots\dots\dots(4)$$

where K is the dissociation constant in terms of partial pressures, T is the absolute temperature, R is the gas constant and Q is the total heat evolved when the reaction occurs at constant pressure. If Q is expressed in calories, R=1.985. To integrate this expression it is first necessary to know how the heat of formation of the hydrochloride from its components varies with temperature. Unfortunately, at present this and the thermal properties of methyl ether and the hydrochloride are not known. When, however, the change of *log* K with 1/T is plotted graphically by means of the data obtained in the present experiments, it is approximately represented by a straight line as will be

Fig. 9.



seen in Fig. 9. The heat of reaction in the present case is therefore independent of the temperature at least in the range of the present experiments. Then equation (4) is, in its integral form,

$$\ln K = \frac{Q}{RT} + C', \dots\dots\dots(5)$$

where C' is the integration constant; or changing from natural to common logarithms, we have

$$\log K = \frac{0.4343Q}{RT} + C, \dots\dots\dots(6)$$

where C is another constant.

Substituting the observed values of K and T in the four series of the experiments in equation (6) we obtained the four observation equations. The most probable values for Q and C were then calculated by means of the method of the least square. The values thus obtained are

$$Q = -6725 \text{ cal. and } C = 5.5373.$$

We have then finally,

$$\log K = -\frac{1471.4}{T} + 5.5373, \dots\dots\dots(7)$$

This simple equation permits the calculation of the dissociation constant of methyl ether hydrochloride at any temperature in the range above mentioned. In order to show the agreement of the experimental values of K with the theory these are again tabulated as follows side by side with the values calculated from equation (7).

TABLE X.
Dissociation constants.

Temperature (absol.)	Dissociation constant	
	K° obs.	K calc.
274°	1.4906	1.4701
278°	1.7224	1.7563
282°	2.0837	2.0877
292°	3.1744	3.1504

Summary¹.

1. The experimental results of M. Friedel on the reaction between gaseous $(\text{CH}_3)_2\text{O}$ and HCl and the discussion by W. Ostwald on them from the standpoint of the Mass Law are described.
2. The experiments involve measurements on the volume contractions which will take place after the mixing of gaseous $(\text{CH}_3)_2\text{O}$ and HCl .
3. The equilibrium values for the reaction, $(\text{CH}_3)_2\text{O}\cdot\text{HCl} \rightleftharpoons (\text{CH}_3)_2\text{O} + \text{HCl}$, have been determined at the temperatures 1° , 5° , 9° and 19°C . and under the constant pressure of nearly an atmosphere.
4. The experimental results have shown that the equilibrium partial pressure of $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$ is at the maximum when the two reactants are mixed in equal volumes.
5. The temperature effect on the equilibrium constant has been calculated in the temperature range of the experiments.

The author wishes to express his thanks to Prof. Y. Osaka for suggesting this work and for his kind advice.

¹ After the author's completing the series of experiments recorded in this paper in July, 1923, there appeared a paper on a similar subject by O. Maass and D. M. Morrison in *J. Amer. Chem. Soc.*, 45, 1675—1682, (1923). Their results did not come, therefore, to consideration in the present work.