ON THE DEVIATION OF GASEOUS MIXTURES FROM DALTON'S LAW OF PARTIAL PRESSURES DUE TO CHEMICAL CAUSES.

III. HYDROGEN CHLORIDE AND METHYL ALCOHOL.

By **Jitaro SHIDEI.**

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Introduction. In the previous papers of this series⁽¹⁾ the action of hydrogen chloride on methyl ether and on water was described. It was shown that the volume contraction or pressure diminution which will take place when the two component gases are mixed was due to the addition reaction prevailing between them, and this reaction was ascribed to the ability of the oxygen atom which is contained in both methyl ether and water to act as quadrivalent.

Methyl alcohol is similar in its constitution to methyl ether and water and contains the oxygen atom above mentioned. The evidence that with

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(1) Previous papers of this series have appeared as follows:—
I, *Memoirs of Coll. Sci. Kyoto Imp. Univ.*, Series A, IX, No. 2, (1925), p. 98.
II, The Sexagint (being a collection of papers dedicated to Prof. Yukichi Osaka by his pupils in celebration of his 60th Birthday), (1927), p. 143.

hydrogen chloride it forms a similar addition compound was shown briefly in the second paper of this series. In methyl ether and water molecules, however, the similar radicals are attached to the oxygen atom, while in methyl alcohol the two are different from each other. Hence, though methyl alcohol is able to form the addition compound with hydrogen chloride, the kind of the reaction may be in its nature somewhat different from those with methyl ether and water.

Carter and Butler⁽¹⁾ proved the formation of methyl chloride from the mixtures of dry methyl alcohol and dry hydrogen chloride at 18°C., but no exact quantitative study of the reaction seems to have been published. The formation of methyl chloride may be illustrated by the addition reaction between the components and the subsequent decomposition of the resulting substance into methyl chloride and water, as may be shown by the expressions:—

$$CH_3OH + HCl = CH_3OH{\cdot}HCl$$
$$CH_3OH{\cdot}HCl = CH_3Cl + H_2O.$$

The formation of the halogen alkyl has also been considered by some investigators to take place in this way. Thus, from the results of the reactions between alcohols and halogen acids, Norris and Mulliken⁽²⁾ came to the conclusion: "It seems probable . . . the reaction between an alcohol and a halogen acid consists in the addition of the two compounds and the subsequent elimination of water. The ease with which the two separate steps occur determines whether reaction takes place or not under the condition used."

The object of the experiments herein described is to obtain some information as to the addition reaction between methyl alcohol and hydrogen chloride in the gaseous state under the influence of the second reaction, if that second reaction takes place.

Experimental Part.

Materials. *Methyl alcohol:*—Methyl alcohol of a high grade of Kahlbaum was employed. This was distilled first with lime and then with anhydrous copper sulphate three times respectively. The methyl alcohol thus dried was kept in a glass bottle, tightly sealed. Through all the experiments, this same material was used.

In the case of the measurements of its pressures it was sealed in a small tube of Pyrex glass in the same manner as was previously adopted in the case of the hydrochloric acid.

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(1) *J. Chem. Soc.*, **125** (1924) 963.

(2) *J. Am. Chem. Soc.*, **42** (1920), 2093.

Hydrogen chloride:—It was prepared by the usual method of adding conc. sulphuric acid to conc. hydrochloric acid. This was thoroughly dried in a way which will be described later.

The weights of the hydrogen chloride used in the pressure measurements could not be determined directly. Hence, they were found by calculation from its pressures as measured.

Apparatus and Experimental Procedure. For the measurements of the gaseous pressures, the apparatus which had previously been used in the case of the system $HCl—H_2O$ was here employed again. The general construction of the apparatus to conduct hydrogen chloride from its generator into the apparatus for the measurements of the pressures, Q, is shown in Fig. 1, which is not drawn to scale.

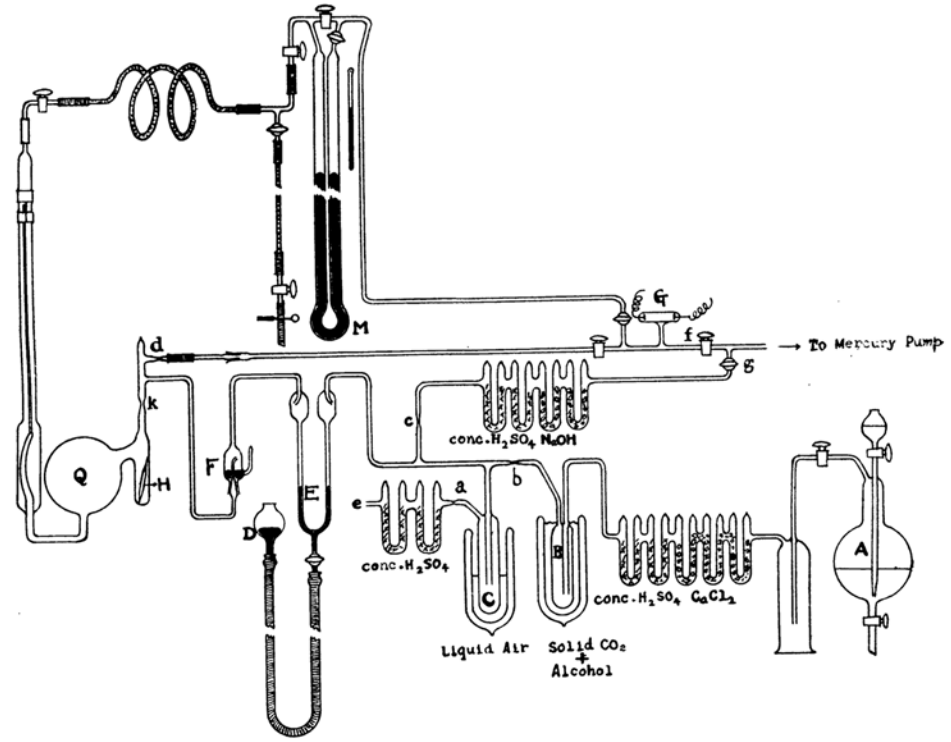

Fig. 1.

The gas generator and the conducting tubes were all made of ordinary glass. The conducting tubes were connected to the measuring apparatus, which was made of Pyrex glass, by the ground joint, F. The wax for sealing the joint was prevented from direct contact with the gas by being covered with a layer of pure dry mercury. The U-tube, E, with pure dry mercury was employed to cut off the direct communication of the measuring apparatus with the reservoir of the hydrogen chloride. Therefore, the passage of the gas from its generator to the measuring apparatus was constructed entirely of glass, so that the gas could never come in contact with any materials but glass and mercury.

Hydrogen chloride from its generator, A, was dried by being passed through $CaCl_2$ and conc. H_2SO_4 tubes successively and then through the cooling tube, B, which was immersed in a mixture of solid carbon dioxide and alcohol in a Dewar flask. The gas thus dried was at first driven out through the exit, e, until the air in the generator was nearly swept out with the gas, when the conducting tube was sealed off at the constriction, a. The cooling tube, C, which served as the reservoir of the hydrogen chloride, was then immersed in liquid air. When a suitable quantity of the gas was solidified in the tube, the tube was sealed off at b.

The exhaustion of the measuring apparatus and the reservoir of the hydrogen chloride was at first alternately carried out by means of a mercury pump, the cocks f and g being opened alternately, not to allow the gas to enter the measuring apparatus. In order to remove the foreign gases which may have been occluded in the solid hydrogen chloride, the reservoir when fairly well exhausted was for a while detached from the liquid air. Meanwhile the pumping was continued, the cock, g, alone being now opened. After this operation the reservoir was again immersed in the liquid air and the pumping was continued until a vacuum was reached, the degree of which was such that the Geissler tube, G, was covered with fluorescence, when the conducting tube was sealed off at c. Before sealing off the tube, d, the measuring apparatus and the reservoir were once more subjected to the pumping, being now allowed to communicate with each other by lowering the level bulb, D, suitably. Finally, the hydrogen chloride was allowed to evaporate and the required amount of it was introduced into the measuring apparatus by suitably adjusting its cooling. The apparatus was sealed off at k.

In the case of measuring the pressures of the mixtures, before the mixing of the two materials, the pressures of the hydrogen chloride alone were measured at 50°C., higher temperatures being avoided lest the sample tube of the methyl alcohol, H, should be broken by thermal expansion of the material.

The methods of measuring the pressures and also of mixing the two materials were the same as employed in the case of the study of the system $HCl—H_2O$.

Results of the Experiments. For the purpose of carrying out the theoretical calculation of the partial pressures of each component gas, which will be given later, the pressures of the single gases were first measured. The results of the experiments with the gaseous methyl alcohol are summarized in Table 1. The amounts of methyl alcohol used ranged from 0.15508 to 0.5565 gr. The volume of the reaction vessel was about 240 c.c., but it varied somewhat in every experiment. Therefore, the amounts of the sample used were converted to the weight per litre. These are given in column 1. The pressures of the hydrogen chloride observed are given in column 2 of Table 2. The results of the experiments with the mixtures are contained in Table 3.

TABLE 1.—Methyl alcohol.

A. Temperature: 70°C.

Weight (per litre) gr.	Pressure mm.
0.23129	154.54
0.26690	177.35
0.29574	197.15
0.35129	233.85
0.45679	302.74
0.48005	319.42
0.64458	426.40

B. Temperature: 90°C.

Weight (per litre) gr.	Pressure mm.
0.23124	163.87
0.26685	187.45
0.29568	208.86
0.35122	248.00
0.45670	321.42
0.47995	339.07
0.64445	453.90

C. Temperature: 110°C.

Weight (per litre) gr.	Pressure mm.
0.23119	172.67
0.26679	198.08
0.29562	220.56
0.35115	261.95
0.45661	339.84
0.47986	358.16
0.64432	480.01

D. Temperature: 130°C.

Weight (per litre) gr.	Pressure mm.
0.23115	181.41
0.26674	208.54
0.29557	231.82
0.35108	276.64
0.45652	357.97
0.47976	377.99
0.64420	506.29

TABLE 2.—Hydrogen chloride.

A. m (calc.) = 0.0024904;
Volume of the reaction vessel(1)
at 25°C. = 241.466 c.c.

Temp. °C.	Pressure obs. mm.	Pressure calc. mm.
50	207.57	207.57
70	220.47	220.41
90	233.20	233.23
110	246.00	246.06
130	259.10	258.87

B. m (calc.) = 0.0032072;
Volume of the reaction vessel
at 25°C. = 240.847 c.c.

Temp. °C.	Pressure obs. mm.	Pressure calc. mm.
50	267.99	267.99
70	284.47	284.51
90	300.95	301.07
110	317.59	317.63
130	333.97	334.18

C. m (calc.) = 0.0040254;
Volume of the reaction vessel
at 25°C. = 240.145 c.c.

Temp. °C.	Pressure obs. mm.	Pressure calc. mm.
50	337.14	337.14
70	358.10	358.01
90	378.82	378.88
110	399.77	399.73
130	421.29	420.57

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(1) The change of the volume of the reaction vessel with temperature was calculated from the linear expansion coefficient 0.0000031 of Pyrex glass.

TABLE 3.

Experiment 1.

Weight of CH_3OH taken = 0.06256 gr. (= 0.0019527 mol);
Pressure of HCl at 50°C. = 193.50 mm.;
Mol of HCl calculated = 0.0023201;
Volume of reaction vessel (less vol. of glass tube)
at 25°C. = 241.411 c.c.(1) [−0.078].

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.25903	172.80	205.39	378.2	375.9	2.3
90	0.25897	183.15	217.35	400.5	398.8	1.7
110	0.25892	193.20	229.29	422.5	421.2	1.3

Experiment 2.

Weight of CH_3OH taken = 0.05477 gr. (= 0.0017096 mol);
Pressure of HCl at 50°C. = 331.64 mm.;
Mol of HCl calculated = 0.0039725;
Volume of reaction vessel (less vol. of glass tube)
at 25°C. = 240.995 c.c. [−0.068].

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.22716	151.90	352.07	504.0	500.49	3.5
90	0.22712	160.85	372.59	533.4	530.70	2.7
110	0.22707	169.70	393.04	562.7	560.75	2.0
130	0.22703	178.10	414.20	592.3	590.80	1.5

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(1) The volumes of the reaction vessel at 25°C. given in this table are distinguished from those in Table 2 in showing the volume of the vessel minus the volume of the glass of the sample tube. For the calculation of the mols of hydrogen chloride from its data at 50°C. the volume of the methyl alcohol sealed in the tubes, which is given in the brackets, was again subtracted from that of the vessel just mentioned at 50°C.

TABLE 3. (continued).

Experiment 3.

Weight of CH_3OH taken = 0.07178 gr. (= 0.0022405 mol);
Pressure of HCl at 50°C. = 207.31 mm.;
Mol of HCl calculated = 0.0024710;
Volume of reaction vessel (less vol. of glass tube)
at 25°C. = 239.979 c.c. [−0.090].

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.29898	198.90	220.55	419.5	416.6	2.9
90	0.29892	211.20	232.85	444.1	441.8	2.3
110	0.29886	222.90	245.65	468.6	467.0	1.6
130	0.29380	234.34	258.85	493.2	492.0	1.2

Experiment 4.

Weight of CH_3OH taken = 0.07147 gr. (= 0.0022309 mol);
Pressure of HCl at 50°C. = 113.33 mm.;
Mol of HCl calculated = 0.0013508;
Volume of reaction vessel (less vol. of glass tube)
at 25°C. = 240.096 c.c. [−0.089].

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.29754	198.1	120.29	318.4	316.8	1.6
90	0.29748	210.2	127.26	337.5	336.3	1.2
110	0.29742	221.9	134.22	356.1	355.2	0.9
130	0.29736	233.3	141.39	374.7	374.0	0.7

Experiment 5.

Weight of CH_3OH taken = 0.12032 gr. (= 0.0037557 mol);
Pressure of HCl at 50°C. = 362.81 mm.;
Mol of HCl calculated = 0.0043397;
Volume of reaction vessel (less vol. of glass tube)
at 25°C. = 240.698 c.c. [−0.150].

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
90	0.49955	351.7	407.49	759.20	753.29	5.9
110	0.49946	371.9	429.92	801.80	797.40	4.4
130	0.49936	391.9	452.90	844.80	841.60	3.2

TABLE 3. (continued).

Experiment 6.

Weight of CH_3OH taken=0.14140 gr. (=0.0044137 mol);
Pressure of HCl at 50°C.=227.50 mm.;
Mol of HCl calculated=0.0027141;
Volume of reaction vessel (less vol. of glass tube)
at 25°C.=240.260 c.c. [−0.177].

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
90	0.58815	414.0	255.44	669.4	664.40	5.0
110	0.58803	438.1	269.49	707.6	703.60	4.0
130	0.58791	461.9	283.92	745.8	742.47	3.3

Experiment 7.

Weight of CH_3OH taken=0.10400 gr. (=0.0032463 mol);
Pressure of HCl at 50°C.=214.86 mm.;
Mol of HCl calculated=0.0025546;
Volume of reaction vessel (less vol. of glass tube)
at 25°C.=239.408 c.c. [−0.130].

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
90	0.43412	305.5	241.29	546.8	543.8	3.0
110	0.43404	323.0	254.80	577.8	575.5	2.3
130	0.43395	340.2	268.20	608.4	606.6	1.8

Experiment 8.

Weight of CH_3OH taken=0.08413 gr. (=0.0026260 mol);
Pressure of HCl at 50°C.=316.41 mm.;
Mol of HCl calculated=0.0037793;
Volume of reaction vessel (less vol. of glass tube)
at 25°C.=240.369 c.c. [−0.105].

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.34985	232.4	335.84	568.2	563.3	4.9
90	0.34978	246.9	355.41	602.3	598.4	3.9
110	0.34971	260.6	374.97	635.6	632.7	2.9
130	0.34964	274.1	395.00	669.1	666.9	2.2

TABLE 3. (continued).

Experiment 9.

Weight of CH_3OH taken $= 0.09465$ gr. ($= 0.0029544$ mol);
Pressure of HCl at 50°C. $= 156.80$ mm.;
Mol of HCl calculated $= 0.0018737$;
Volume of reaction vessel (less vol. of glass tube) at 25°C. $= 240.676$ c.c. $[-0.118]$.

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.39309	260.5	166.40	426.9	424.10	2.8
90	0.39301	276.9	176.00	452.9	450.70	2.2
110	0.39293	292.6	185.76	478.4	476.79	1.6
130	0.39286	308.2	195.70	503.9	502.67	1.2

Experiment 10.

Weight of CH_3OH taken $= 0.07716$ gr. ($= 0.0024085$ mol);
Pressure of HCl at 50°C. $= 199.57$ mm.;
Mol of HCl calculated $= 0.0023767$;
Volume of reaction vessel (less vol. of glass tube) at 25°C. $= 239.777$ c.c. $[-0.096]$.

Temp. °C.	Weight of CH_3OH (per litre) gr.	p_{CH_3OH} mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.32165	214.0	211.80	425.8	422.9	2.9
90	0.32159	227.1	224.16	451.3	449.1	2.2
110	0.32153	239.7	236.48	476.2	474.6	1.6
130	0.32146	252.2	249.20	501.4	500.2	1.2

Theoretical Part.

Calculation of the Pressures of the Single Gases. *Methyl alcohol*:— The pressures of the gaseous methyl alcohol given in Table 1 are shown plotted against weight in Fig. 2. It will be seen that though the values of the pressures observed differ somewhat from those of Ramsay and Steele(1) they change regularly with the weights taken and give a series of straight

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(1) *Z. physik. Chem.*, **44** (1903), 348.

lines which nearly pass through the origin of the co-ordinates. No irregularities in the pressure change are found through the whole series. Hence, the partial pressures which the methyl alcohol would exert if it behaved independently of the other component in the gaseous mixtures may be found graphically with sufficient accuracy by means of the curves in Fig. 2. The partial pressures p_{CH_3OH} shown in Table 3 are those which were found in this way, the weights per litre being employed, to which the weights of the substance actually taken were converted.

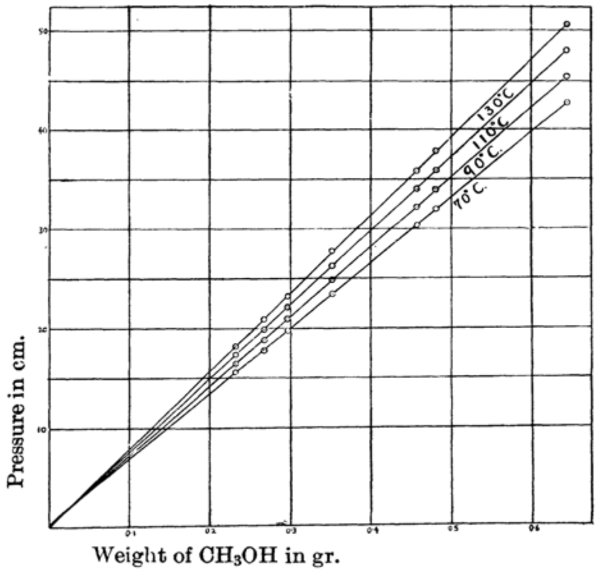

Fig. 2.

Hydrogen chloride :—In the second paper of this series the pressures of hydrogen chloride were calculated by means of van der Waals' equation :—

$$\left(p+\frac{a}{v^2}\right)(v-b) = RT, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

changes of a and b with temperature being allowed for by van Laar's equations for their temperature coefficients :—

$$\left.\begin{aligned} a_T &= a_c e^{\alpha\left(\frac{1}{RT}-\frac{1}{RT_c}\right)} \\ b_T &= b_c e^{\alpha\left(\frac{1}{RT}-\frac{1}{RT_c}\right)} \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

As was shown previously, if p is measured in atmospheres and v in the volume which the quantity of gas concerned would occupy in the normal state, then the value of R is equal to 1/273.09.

The calculated values of a and b of hydrogen chloride at 323.09° and 343.09°K. respectively are as follows :—

$$a_{323.09} = 7444 \times 10^{-6}; \qquad b_{323.09} = 1826 \times 10^{-6};$$
$$a_{343.09} = 7021 \times 10^{-6}; \qquad b_{343.09} = 1722 \times 10^{-6}.$$

The values above 343.09°K. are given in the second paper.

For m mols of the gas, Equation (1) may be written in the following form :—

$$\left(p + \frac{a}{\dfrac{v^2}{(22412\,m)^2}}\right)\left(\frac{v}{22412\,m} - b\right) = RT,$$

or

$$\left(p + \frac{a}{v'^2}\right)(v' - b) = RT, \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1a)$$

where $v' = v/22412\,m$.

Solving Equation (1a) for v', we obtain

$$\begin{aligned} v' &= \frac{v}{22412\,m} \\ &= \Bigg[\frac{1}{27}\left(b + \frac{RT}{p}\right)^3 + \frac{a}{6p}\left(2b - \frac{RT}{p}\right) + \Bigg\{\frac{1}{4}\Bigg[\frac{2}{27}\left(b + \frac{RT}{p}\right)^3 \\ &\quad + \frac{a}{3p}\left(2b - \frac{RT}{p}\right)\Bigg]^2 + \frac{1}{27}\left[\frac{a}{p} - \frac{1}{3}\left(b + \frac{RT}{p}\right)^2\right]^3\Bigg\}^{\frac{1}{2}}\Bigg]^{\frac{1}{3}} + \Bigg[\frac{1}{27}\left(b + \frac{RT}{p}\right)^3 \\ &\quad + \frac{a}{6p}\left(2b - \frac{RT}{p}\right) - \Bigg\{\frac{1}{4}\Bigg[\frac{2}{27}\left(b + \frac{RT}{p}\right)^3 + \frac{a}{3p}\left(2b - \frac{RT}{p}\right)\Bigg]^2 \\ &\quad + \frac{1}{27}\left[\frac{a}{p} - \frac{1}{3}\left(b + \frac{RT}{p}\right)^2\right]^3\Bigg\}^{\frac{1}{2}}\Bigg]^{\frac{1}{3}} + \frac{1}{3}\left(b + \frac{RT}{p}\right), \end{aligned}$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(3)$$

for the real root. Then, substituting the experimental values in Equation (3), mols of hydrogen chloride can be calculated. For the purpose of the calculation, the experimental data at 50°C. given in Table 2 were employed. The results of the calculation are shown in the same table. The last column of the table contains the pressures of the hydrogen chloride at the temperatures given in column 1 calculated by means of Equation (1) employing each value of m above obtained.

From Table 2, it will be seen that up to 110°C., the theoretical and experimental values of the pressures are in good agreement within 0.1 mm. Hence, up to 110°C., Equation (1) will be available with sufficient accuracy within 0.1 mm. for the calculation of the partial pressures which the hydrogen chloride would exert if it behaved independently of the other component in the mixtures. At 130°C., a discrepancy of 0.2 to 0.7 mm. may be found, so that in this case the corrections due to the discrepancy must be applied to the theoretical values.

The partial pressures of the hydrogen chloride in the mixtures thus calculated are given under p_{HCl} in Table 3. In this table, the mols of the hydrogen chloride were calculated from the experimental data at 50°C. given in the same table.

Discussion of the Results. A comparison of the values of the total pressures calculated by Dalton's law with those observed shows evidently the occurrence of pressure diminution by the mixing of the two gases. The last column of Table 3 contains the pressure diminutions.

To elucidate the cause of the diminution from the chemical standpoint, at least the following two reactions must be taken into consideration :—

$$CH_3OH + HCl \rightleftarrows CH_3OH{\cdot}HCl \cdots\cdots\cdots\cdots [I]$$

$$CH_3OH{\cdot}HCl \rightleftarrows CH_3Cl + H_2O \cdots\cdots\cdots\cdots [II]$$

Reaction [I], as considered by Norris and Mulliken, is the primary reaction of the ester formation of halogen acid. The addition compound thus formed will then be decomposed into methyl chloride and water ultimately. On the other hand, it may be possible that methyl chloride undergoes hydrolytic decomposition, however trivial in amount, although it is generally believed that such decomposition, if it takes place at all, must be accomplished with great difficulty. In this case, however, it is probable that the methyl chloride and water will also primarily make the addition reaction and will again produce $CH_3OH{\cdot}HCl$. Therefore, the second reaction of the ester formation will be expressed by the balanced action as above shown.

If K_1 and K_2 be the equilibrium constants of reactions [I] and [II] at constant volume respectively, then, as usual, they are given by the expressions—

$$K_1 = \frac{c_{CH_3OH}\ c_{HCl}}{c_{CH_3OH{\cdot}HCl}} \cdots\cdots\cdots\cdots (4)$$

$$K_2 = \frac{c_{CH_3OH{\cdot}HCl}}{c_{CH_3Cl}\ c_{H_2O}}, \cdots\cdots\cdots\cdots (5)$$

in which c with the suffixes are concentration terms at equilibrium.

Let m_1 and m_2 be the mols of methyl alcohol and hydrogen chloride initially taken respectively; α the fraction of the methyl alcohol transformed at equilibrium; γ the dissociation degree of the addition compound at equilibrium; v the volume of the reaction vessel measured in c.c. Then the equilibrium constants can be represented by the expressions—

$$K_1 = \frac{(m_1 - m_1\alpha)(m_2 - m_1\alpha)}{v\, m_1\alpha\,(1-\gamma)} = \frac{(1-\alpha)(m_2 - m_1\alpha)}{v\,\alpha\,(1-\gamma)}, \quad \cdots\cdots(4a)$$

$$K_2 = \frac{v\, m_1\alpha\,(1-\gamma)}{m_1^2\alpha^2\gamma^2} = \frac{v\,(1-\gamma)}{m_1\,\alpha\,\gamma^2}. \quad \cdots\cdots(5a)$$

If P is the total pressure of the system at equilibrium in which the existence of the two reactions is assumed, and if P' is that which the mixture would exert if the component gases behaved independently of each other, then

$$\frac{P}{P'} = \frac{m_1(1-\alpha) + m_2 - m_1\alpha + m_1\alpha\,(1-\gamma) + 2\, m_1\alpha\,\gamma}{m_1 + m_2}$$

or

$$= \frac{m_1 + m_2 - m_1\alpha\,(1-\gamma)}{m_1 + m_2},$$

wherefore

$$\alpha = \frac{(m_1 + m_2)(1 - P/P')}{m_1(1-\gamma)}. \quad \cdots\cdots(6)$$

Substituting α thus found in Equation (4a), there is obtained

$$K_1 = \frac{(m'P/P' - m_2 - m_1\gamma)(m'P/P' - m_1 - m_2\gamma)}{v\, m'\,(1 - P/P')(1-\gamma)^2}, \quad \cdots\cdots(7)$$

where $m' = m_1 + m_2$.

For very small magnitudes of γ, Equation (7) is reduced to that which was obtained in the case of the system HCl—H_2O and it will approximately regulate the equilibrium in the absence of the second reaction. The values of K_1' given in Table 4 are those which were calculated by Equation (7) in which γ was put at zero. Column 2 and 3 of the table contain the mols of the methyl alcohol and the hydrogen chloride initially taken respectively, column 5 contains the ratios of the larger value to the smaller one in m_1 and m_2 and column 6 the substances which were taken in excess of the other component.

TABLE 4.

Exp. No.	m_1 $\times 10^7$	m_2 $\times 10^7$	m' $\times 10^7$	Ratio	Subst. in excess	K'_1 (70°C.) $\times 10^6$	K'_1 (90°C.) $\times 10^6$	K'_1 (110°C.) $\times 10^6$	K'_1 (130°C.) $\times 10^6$
10	24085	23767	47851	1.01	CH_3OH	712	1003	1466	2063
3	22405	24710	47115	1.10	HCl	689	985	1413	1991
5	37557	43397	80954	1.16	HCl	—	1038	1489	2172
1	19527	23201	42728	1.19	HCl	704	1016	1408	—
7	32463	25546	58008	1.27	CH_3OH	—	1063	1475	1992
8	26260	37793	64053	1.44	HCl	721	968	1385	1932
9	29544	18737	48281	1.58	CH_3OH	706	960	1398	1936
6	44137	27141	71278	1.63	CH_3OH	—	906	1207	1550(1)
4	22309	13508	35817	1.65	CH_3OH	682	970	1371	1859
2	17096	39725	56821	2.32	HCl	688	956	1407	1931
Mean						700	995	1424	1985
Deviation (%)						1.71	3.08	2.49	3.53

The deviation of each value of K_1' from its mean value is small. But, there may be pointed out some peculiarities in the deviation. Thus, within experimental error the values of K_1' appear to increase, on the one hand, with the approaching of the values of m_1 and m_2 to each other so far as the total mols are constant, and on the other, with the increase of the total mols. The deviation must certainly be caused by neglecting the terms containing γ. The values of γ change with the proportions in which the two gases are mixed, and it will easily be shown that in case of a given total of mols of the two gases initially taken γ attains a maximum value when $m_1 = m_2$(2).

In order to test the effect of the terms containing γ upon the values of K_1 several values of γ were tried. The results of the calculation show that the deviation of each value of K_1 from its mean value becomes smaller with the increase of the maximum values of γ and then seems to become again greater. Table 5 gives the results of only three cases in which the maximum values assigned to γ are 0.7, 0.8 and 0.9 at 90°C. respectively. Each value of γ used in the calculation is put in brackets below the respective figure for K_1.

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(1) The results of Exp. 6 are not in harmony with the others. Hence they are omitted from the calculation of the mean values of K_1'.

(2) Combining Equation (4a) with (5a), there is obtained

$$K_1 = \frac{[K_2 m_1 \gamma^2 - v(1-\gamma)]\,[K_2 m_2 \gamma^2 - v(1-\gamma)]}{K_2 v^2 \gamma^2 (1-\gamma)^2}. \quad \cdots\cdots\cdots\cdots(8)$$

Providing $m' = m_1 + m_2 =$ const., $\frac{d\gamma}{dm_1}$ and $\frac{d^2\gamma}{dm_1^2}$ will be deduced from Equation (8). Then it can be proved that $\frac{d\gamma}{dm_1}$ vanishes when $m_1 = m'/2$ and that for this value of m_1, $\frac{d^2\gamma}{dm_1^2}$ is negative.

TABLE 5.

1. Maximum value of $\gamma = 0.72$ at 90°C.

Exp. No.	K_1 (70°C.) $\times 10^6$	K_1 (90°C.) $\times 10^6$	K_1 (110°C.) $\times 10^6$	K_1 (130°C.) $\times 10^6$
10	667 (0.70)	953 (0.72)	1407 (0.75)	1993 (0.78)
3	644 (0.70)	932 (0.72)	1355 (0.75)	1925 (0.78)
5	—	963 (0.70)	1405 (0.72)	2073 (0.75)
1	668 (0.68)	976 (0.70)	1366 (0.72)	—
7	—	1013 (0.68)	1419 (0.70)	1928 (0.73)
8	673 (0.65)	916 (0.67)	1324 (0.70)	1861 (0.73)
9	670 (0.65)	920 (0.67)	1352 (0.70)	1885 (0.72)
4	662 (0.60)	946 (0.62)	1347 (0.65)	1834 (0.67)
2	654 (0.60)	918 (0.62)	1365 (0.64)	1885 (0.67)
Mean	**663**	**949**	**1371**	**1923**
Deviation (%)	1.19	2.60	1.90	2.95

2. Maximum value of $\gamma = 0.8$ at 90°C.

Exp. No.	K_1 (70°C.) $\times 10^6$	K_1 (90°C.) $\times 10^6$	K_1 (110°C.) $\times 10^6$	K_1 (130°C.) $\times 10^6$
10	644 (0.78)	925 (0.80)	1377 (0.82)	1952 (0.85)
3	622 (0.78)	904 (0.80)	1326 (0.82)	1882 (0.85)
5	—	911 (0.80)	1342 (0.82)	1987 (0.85)
1	650 (0.76)	955 (0.78)	1339 (0.80)	—
7	—	980 (0.78)	1380 (0.80)	1877 (0.83)
8	640 (0.76)	877 (0.78)	1281 (0.80)	1812 (0.82)
9	648 (0.75)	895 (0.77)	1324 (0.79)	1851 (0.81)
4	643 (0.73)	927 (0.75)	1322 (0.77)	1800 (0.80)
2	635 (0.70)	902 (0.70)	1347 (0.72)	1863 (0.75)
Mean	**640**	**920**	**1338**	**1878**
Deviation (%)	1.07	2.63	1.61	2.49

TABLE 5. (continued).

3. Maximum value of $\gamma = 0.9$ at 90°C.

Exp. No.	K_1 (70°C.) $\times 10^6$	K_1 (90°C.) $\times 10^6$	K_1 (110°C.) $\times 10^6$	K_1 (130°C.) $\times 10^6$
10	575 (0.88)	833 (0.90)	1247 (0.92)	1703 (0.95)
3	554 (0.88)	808 (0.90)	1198 (0.92)	1638 (0.95)
5	—	763 (0.90)	1132 (0.92)	1752 (0.93)
1	601 (0.86)	892 (0.88)	1255 (0.90)	—
7	—	921 (0.86)	1304 (0.88)	1782 (0.90)
8	580 (0.85)	800 (0.87)	1179 (0.89)	1701 (0.90)
9	606 (0.84)	842 (0.86)	1255 (0.88)	1760 (0.90)
4	612 (0.83)	888 (0.85)	1273 (0.87)	1741 (0.89)
2	608 (0.78)	864 (0.80)	1302 (0.82)	1811 (0.84)
Mean	591	846	1238	1736
Deviation (%)	3.07	4.79	3.71	2.39

From the table it will be seen that the deviation at all the temperatures studied is minimum when the maximum value assigned to γ is 0.8 or so at 90°C. If this value of γ be taken as its most probable value, then the values of α will be found to be between about 0.03 to 0.08 at 90°C. in the range of the experiments given above. But the pressure diminution observed here is very small and the influence of the terms given above upon the values of K_1 is not remarkable unless the γ values should be very large as above shown. Then, whether these values of α be really the true values or not must be ascertained by direct experiment. It is hoped, therefore, to obtain further experimental data on this point.

Summary.

1. The gaseous pressures of methyl alcohol of several amounts have been measured at temperatures ranging from 70° to 130°C. It is shown that the pressures measured when plotted against the weights contained in a litre, to which the weights actually taken were converted, give a series of excellent straight lines which nearly pass through the origin of the co-ordinates.

2. The pressures of gaseous hydrogen chloride have been measured over the temperature range, 50° to 130°C. These are shown to be in good

agreement with those which are calculated by van der Waals' equation, changes of his constants with temperature being allowed for by van Laar's equations.

3. Measurements have been carried out of the deviation from Dalton's law at temperatures between 70° and 130°C. in mixtures of several proportions of hydrogen chloride and methyl alcohol. The deviation is discussed from the assumption of the existence of the two reactions :—

$$CH_3OH + HCl \rightleftarrows CH_3OH \cdot HCl$$
$$CH_3OH \cdot HCl \rightleftarrows CH_3Cl + H_2O.$$

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Chemical Institute, Faculty of Science,
Kyoto Imperial University.