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A STUDY OF THE SYSTEM HYDROGEN CHLORIDE AND WATER.

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Introduction.

Our knowledge of the properties of the system hydrogen chloride and water has been limited to that of mixtures in which no liquid or solid phase exists, whose composition is more than about 50 per cent. hydrogen chloride. The vapor pressure of solutions of higher concentration exceeds atmospheric pressure and consequently ordinary methods used in investigating solubility, freezing points, density and other properties can not be applied.

The properties of hydrochloric acid solutions whose vapor pressure is one atmosphere or less have been quite fully studied. Numerous density determinations have been made; the most concentrated solution of which the density is known contains 44.35 per cent. hydrogen chloride.[1] The vapor pressures, boiling points and other properties have been determined up to about the same percentage. Pickering found the freezing points of solutions of concentrations ranging from 0 to 48.8 per cent. hydrogen chloride. His freezing point curve, which is copied as part of the one at the end of this paper, shows the existence of two solid hydrates, namely the dihydrate, containing 50.31 per cent. hydrogen chloride, and melting at —17.7°; and the trihydrate, containing 40.33 per cent. hydrogen chloride, and melting at —24.4°. The former had been prepared and isolated by Pierre and Puchot[2] in 1876, while the latter was discovered and analyzed by Pickering. A monohydrate of hydrogen bromide, $HBr.H_2O$ is known, and the original purpose of this investigation was to determine whether the solid monohydrate, $HCl.H_2O$ can be obtained.

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[1] Pickering, *Ber.*, **26**, 277-289 (1893).

[2] *C. r.*, **82**, 45.

The existence of the monohydrate in solution was assumed by Thomsen[1] on theoretical grounds, namely; the isomorphism of some chlorides containing water of crystallization with other salts when the former contain one more molecule of water for each chlorine atom than the latter; deductions from the density and specific heat of aqueous solutions of hydrochloric acid; and the heat of dilution of the acid, which by analogy with that of other acids gives figures more in accordance with the formula $HCl.H_2O$ for the dissolved substance than with HCl. These reasons of Thomsen's, however, are purely hypothetical as they deal with the theory of hydrates in solution. From the last of the facts mentioned Berthelot[2] argues rather for the existence of a hydrate $HCl.8H_2O$ than for that of the monohydrate, and theoretical views of the existence of other hydrates are held by other investigators; but these have no bearing on the question of the existence of the solid monohydrate or of other solid hydrates.

Since solutions having a composition in the neighborhood of that of the monohydrate have a vapor pressure much greater than one atmosphere, all work dealing with them must be carried on under pressure. In the present investigation this was accomplished by enclosing the materials in sealed tubes, in the method about to be described. It was expected that under proper conditions of temperature and concentration the monohydrate would crystallize out. Preliminary experiments gave almost unquestionable evidence that the monohydrate was obtained, but it was found advisable, in some respects necessary, to investigate some of the other properties of the system.

Apparatus and General Procedure.

Apparatus and General Procedure.—The hydrogen chloride used in the experiments was prepared from concentrated sulphuric acid and lump ammonium chloride. In the first experiments it was passed through sulphuric acid and then over glass wool, but in the later work it was further dried by phosphorus pentoxide. The gas was then condensed in thick-walled glass tubes and sealed. The tubes used in most determinations were 15 to 18 cm. long, about 10 mm. in diameter, and having walls about 0.6 mm. in thickness. Each tube was first sealed and rounded at one end, and dried in an air bath at 140°–180°, air dried with sulphuric acid being forced into the tubes. When pure hydrogen chloride was to be introduced, the tube was constricted near the open end and weighed, then connected with the generating apparatus as shown in Fig. 1. This procedure in filling the tube was found to give the best results of a number of methods. The acid generated in the Kipp A bubbles through sulphuric acid in the wash bottle B, is passed over pumice stone impregnated with sulphuric acid in the tower C, and over alternate layers of pumice stone

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[1] Thermochemischen Untersuchungen, Vol. 2, p. 430 (1882).

[2] *C. r.*, **76**, 41 (1873).

and phosphorus pentoxide in the tower D, in the top of which is a little glass wool. The vessels F and O contain mercury and constitute a reservoir for the gas in order to measure it approximately, O being low enough so that F would be nearly full of the gas under the pressure from the acid in A. The stopcock E allows the gas to flow through the straight tube or connects F with either side. The experimental tube is connected on at P and the vacuum jacketed tube H is adjusted to the position of the tube. The stopcock G connects the tube with the portion back to E, or with the suction pump, or the pump with the air through the calcium chloride tube J. The tower L contains calcium chloride to prevent water vapor from diffusing back into the apparatus. The side tube K with its stopcock N is necessary in order to exhaust the apparatus back of G. All connections were made as tight as possible, and all joints were connected with thick-walled pure gum tubing bound with wire.

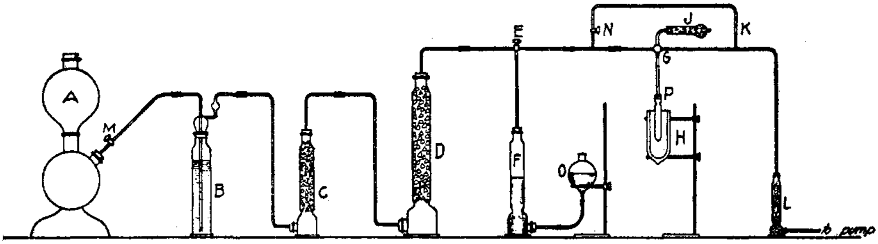

Fig. 1

To fill the tube, after being connected at P the stopcock G was turned so as to connect it to the pump, while stopcock E allowed the gas to flow from the generator into the reservoir. The tube H was then adjusted so as to immerse the experimental tube in liquid air, and E and G turned so as to allow the gas to flow from the reservoir into the tube and condense there. This took place quite rapidly when the gas was nearly free from air. The reservoir was connected alternately with the generator and tube until a sufficient amount of hydrogen chloride had condensed therein. When the presence of a quantity of air retarded the condensation the tube was again connected with the pump for a moment. At the beginning of each day's work, and whenever it seemed that air had leaked into the apparatus, stopcock N was opened, E left straight and the pump turned on, exhausting the apparatus back to the stopcock M.

When sufficient hydrogen chloride had been obtained in the tube it was again connected with the pump, sealed at the constriction, put in a safe place to warm up to room temperature and weighed, together with the piece sealed off.

When a solution of hydrogen chloride was desired instead of the pure material, the tube was weighed, the desired amount of water introduced, the tube constricted, weighed again and connected to the apparatus as before. In this case, in order to avoid so far as possible evaporation of the water on exhaustion, stopcock G was first adjusted so as to shut the tube off from all other connections, and the tube immersed in the liquid air until the water was all frozen and cooled far below the freezing point. Then the air was exhausted and the rest of the process carried out as in the case of the pure hydrogen chloride.

It was originally intended to prepare in this way solutions containing 50 to 100 per cent. hydrogen chloride, and to determine whether a maximum freezing point could be obtained at the composition of the monohydrate or any other hydrate. It was however, found that in solutions containing over about 66.9 per cent. hydrogen chloride, which corresponds to the composition of the monohydrate, two liquid layers are formed. The lighter layer, judging by comparisons of different tubes, consisted of nearly pure hydrogen chloride. At about —15° crystals are formed in solutions of this composition, while in less concentrated solutions crystallization takes place at a lower temperature and less completely. Only rough determinations could be made, however, on account of the slow rate of freezing of the solutions in tubes of this size. In order to obtain the exact composition of these solutions a correction was necessary on account of the vapor present. No record was found of any determination of the density of liquid or of gaseous hydrogen chloride at this temperature, though Ansdell[1] gives the density of the liquid and the ratio of that of the liquid to that of the vapor, for temperatures ranging from 0° to 51.3°, the latter figure being the critical point, according to his determination.

This investigation, then, includes: first, the determination of the density of pure liquid and of gaseous hydrogen chloride; second, the mutual solubility relations of the two liquid phases; third, the determination of the density of solutions unsaturated with respect to the hydrogen chloride phase and of the accompanying vapor; fourth, the freezing-point curve from 50 per cent. to the composition at which the two liquid phases appear; and, fifth, the isolation and analysis of the monohydrate. No pressure measurements wese made.

Density of Hydrogen Chloride.—The method of determining the density of hydrogen chloride was one of the methods used by Young, with some variations.[2] Various amounts of the substance were introduced as described above into tubes of approximately the same size, giving widely different proportions of the liquid and vapor. Then when any two of the tubes were compared, since the total weight of the contents is known and the volume of each phase in each tube can be obtained, the density of each phase can be calculated.

In the first series of experiments the temperatures used were 30°, 25°, 10°, 0°

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[1] *Chem. News*, **41**, 75 (1880).

[2] *J. Chem. Soc.*, **59**, 37, 126, 929 (1891). *Proc. Phys. Soc.*, **13**, 617 (1895). Young's Stoichiometry, 162 (1908).

and —15°. Those above 0° were obtained by use of an electrically heated and regulated thermostat bath, the lowering to give 10° when the room temperature was higher being produced by the frequent addition of ice. At 0° an ice bath was used. At all temperatures below 0° the bath consisted of a large vacuum jacketed tube containing alcohol, stirred by a motor and cooled by liquid air, small amounts of which were added from time to time, into a double-walled test tube immersed in the alcohol. It was possible by this arrangement to keep the temperature within one-tenth degree of that desired, when proper care was used.

On account of the high pressure no graduations or permanent marks could be made on the tubes. In the first set of experiments at temperatures of 0° and above, a graduated tube large enough to fit over the experimental tube was held in a vertical position by a clamp while both tubes rested on a horizontal surface, and the position of the meniscus on the graduated tube was read through a leveled telescope. As this method was impracticable with the apparatus used at the lower temperatures, a constriction was made in a graduated tube, which held the experimental tube in place, the tube clamped vertically and read as before. When all the observations on the tube were completed it was immersed in liquid air and the tip broken off. The hydrogen chloride was then allowed to warm and escape. After being washed and dried the tubes were calibrated by weighing with mercury, care being taken that each hydrogen chloride reading should come between two adjacent mercury readings. In correcting the volume for the difference in shape of the meniscuses, the form of that of the mercury was assumed to be a portion of a sphere, and that of the hydrogen chloride a semi-ellipsoid. Observation shows that the surfaces are very nearly of these forms, and the error due to deviation from them is certainly much smaller than the error in reading.

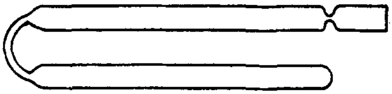
Fig. 2.

In order to obtain the total volume of the tubes they were inverted in the bath at one of the temperatures, and the position of the meniscus read as before. From this was found the reading corresponding to the same position on the experimental tube when erect. Interpolating as before, and correcting for the difference in the meniscuses, the volume of the vapor was obtained and added to the volume of the liquid.

Now we have the following relations:

$$a_1x + b_1y = c_1$$

$$a_2x + b_2y = c_2$$

where x is the density of the liquid, y that of the vapor, a_1 and a_2 the respective volumes of the liquid, b_1 and b_2 those of the vapor, and c_1 and c_2 the weights. These equations can then be solved for x and y. The modified equations actually used in order to shorten the labor of a number of calculations can easily be derived from the above or from those given by Young.[1]

Seven tubes were used, and each compared with each of the others. The twenty-one results were then averaged, each being weighted by multiplying by a quantity shown algebraically to reduce the probable errors as they appear in the results to those of the original observations. The extreme values at 10° were 0.0720 and 0.0770 for the vapor and 0.8828 and 0.8941 for the liquid. Average, 0.0742 and 0.8848. The results for most of the other temperatures show the same general correspondence. Those for —15° differ more widely, the vapor density giving 0.0132 and 0.0608 as its extreme values and the liquid, 0.9252 and 1.0168.

The averaged results are:

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[1] *Loc. cit.*

Temperature.	Liquid density. Gram per cc.	Vapor density. Gram per cc.
30°	0.7791	0.1314
25°	0.8106	0.1128
20°	0.8351	0.0992
10°	0.8848	0.0742
0°	0.9246	0.0561
—15°	0.9756	0.0378

A second series was made with temperatures varying from +51° to —50°. The hydrogen chloride in the former series was not dried with phosphorus pentoxide and was found to contain a small amount of water; in the second series it was dried thoroughly and gave little or no indication of water when cooled nearly to the freezing point of hydrogen chloride. (How this is indicated will be shown in connection with the other experiments). The constricted graduated tube, into which holes had been blown to permit better circulation, was used in all cases for the sake of uniformity, and the position of the top of the experimental tube was always read as a check on the meniscus reading. This sometimes varied 0.3 mm. on account of irregularities in the bottom of the tube or in the constriction of the graduated tube and in some cases on account of the slightly slanting position of the tube when it did not fit tightly in the graduated tube. All readings were reduced to conform to the average position of the top. Before opening the tube a mark was made on it so that the reading of the top after it was open could be compared with that before opening. The total volume was found in the same way, but also by weighing the tube full of mercury, reading the position of its surface and extrapolating to find the volume before the tip had been broken off. The extent of this extrapolation was usually less than 0.005 cc., and this method may be regarded as more accurate than the other, except in cases where the tip had been broken too far down to make it a success.

Gauss'[1] method of averaging the results was used in this case, being much simpler. A few of the results of the first trial recalculated according to this method do not differ materially from those obtained by the other method.

A table of the calculations made at 20° follows:

	a.	*b.*	*c.*	*aa.*	*ab.*	*ac.*	*bb.*	*bc.*
H18	1.945	0.201	1.6492	3.783	0.391	3.207	0.040	0.331
H 9	1.752	0.734	1.5468	3.070	1.286	2.710	0.539	1.135
H16	2.090	0.801	1.8271	4.368	1.674	3.819	0.642	1.463
H 5	1.804	1.017	1.6167	3.255	1.835	2.916	1.034	1.644
H12	0.674	1.445	0.7076	0.454	0.974	0.477	2.088	1.023
H 4	0.690	2.479	0.8212	0.476	1.711	0.567	6.146	2.036
H11	0.346	2.180	0.5008	0.120	0.754	0.173	4.753	1.092
H 3	0.248	2.142	0.4154	0.061	0.531	0.103	4.588	0.890
H10	1.479	0.848	1.3206	2.187	1.254	1.953	0.719	1.120
H 7	1.877	1.403	1.7147	3.523	2.633	3.218	1.967	2.406
				21.207	13.043	19.144	22.516	13.140

a = volume of liquid in cc.
b = volume of vapor in cc.
c = total weight of HCl in grams.

The final equations are:

$$\Sigma aax + \Sigma aby = \Sigma ac$$
$$\Sigma abx + \Sigma bby = \Sigma bc$$

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[1] Mellor's Higher Mathematics for Students of Chemistry and Physics, p. 548.

Σaa, etc. being the sums of the respective columns.

Solving these equations, then, from the above values,

$$x = 0.8393 \text{ gm./cc.} \qquad y = 0.0974 \text{ gm./cc.}$$

Results at all temperatures used:

Temperature.	Liquid. Gram per cc.	Vapor. Gram per cc.
51°	0.572	0.278
50°	0.597	0.247
5°	0.658	0.215
40°	0.707	0.181
35°	0.749	0.152
30°	0.783	0.130
20°	0.839	0.0974
0°	0.929	0.0539
—15°	0.984	0.0543
—30°	1.032	0.0238
—50°	1.090	0.0125

Only three tubes showed both phases at 51° and 50°, and one of these contained a very small quantity of liquid. This gave results widely differing from the others, as did some others at lower temperatures under similar circumstances. The figures given in brackets are found by using only the other two tubes.

Tubes H5 and H9 show small deviations at all temperatures, as do H18 and H6 in the opposite directions. This appears to be an error outside the experimental error, but it is impossible to determine which pair is wrong. Excluding either of these pairs from the results changes the density of the liquid by about 0.0015 to 0.002 and that of the vapor about 0.0005 to 0.001.

The graphical results of the second series are shown in Fig. 3. Comparison of these results with those obtained by Ansdell shows the former to be uniformly higher. The difference is greater than the deviations due to the two tubes just mentioned, which are in turn larger than the average experimental error for this series, and the densities found in the two trials agree much better with each other than they do with Ansdell's results. In criticism of those of Ansdell, it may be said that he did not weigh the material at any time but took a fixed volume of the gas and condensed it, making the accuracy of the whole experiment depend on the accuracy of the knowledge of the density of the gas under the conditions under which he worked.

Mutual Solubility of the Liquid Phases.—One of the most remarkable facts brought out in the study of this system is the extremely small solubility of water in hydrogen chloride. A tube containing less than a drop of water and more than a gram of hydrogen chloride showed some of the water phase undissolved. This solubility, moreover, increases but slightly with the temperature. The solubility of the hydrogen chloride phase in the other, which will be designated the water phase, decreases slightly with rising temperature; so it is evident that no critical solution temperature exists below the critical temperature of hydrogen chloride, and the two phases must be dealt with separately.

Very small quantities of water were introduced into the tubes, which were then filled with hydrogen chloride as in the density determinations. The tubes were kept for at least an hour at the required temperature and shaken frequently, then the presence or absence of the aqueous phase noted. Below about —15° the second phase consists of a solid crystalline substance.

The tubes in the first series had been filled without having the hydrogen chloride thoroughly dry, and gave somewhat inconsistent results, which probably are due more or less to this fact. As a comparison the tubes used in the first series of density determinations were cooled, and all deposited a few fine crystals at from —24° to —32°, supposedly of the monohydrate, showing the presence of water. For this reason two tubes of this series were used in the density determinations already described, giving practically as pure hydrogen chloride as did the other series. A second series was made, in which the hydrogen chloride was dried with phosphorus pentoxide. Results:

First Series.

	Wt. water. Grams.	Total wt. Grams.	Per cent. water corrected.	Saturation temp.
C 3	0.0732	2.711	2.80	Above 25°
C 4	0.0253	4.901	0.56	" 25°
C14	0.0132	3.771	0.36	" 25°
C13	0.0080	2.644	0.33	" 25°
C 6	0.0042	2.07	0.21	21°
C22	0.0081	4.15	0.20	Above 25°
C18	0.0073	4.29	0.18	15°
C19	0.0031	2.84	0.12	Between 0.1° and 1.3°
C26	0.00405	3.75	0.11	" 4.3° and 20°
C 7	0.0018	3.12	0.06	" —4.7° and —15°
C 9	0.0008	2.20	0.04	" —24° and —31°
C10	0.0009	3.38	0.03	" —24° and —31°
C16	0.0006	4.21	0.014	" —24° and —31°

The percentage of water is corrected for the quantity of hydrogen chloride present as vapor, which must be subtracted from the total weight.

Second Series.

No.	Wt. Water. Gram.	Total wt. Grams.	Per cent. water. corrected.	Saturation Temp.
J1	0.0001	1.31	0.008	Below —50°
J2	0.0002	1.20	0.017	" —50°
J4	0.0003	1.45	0.021	Above + 45°
J6	0.0006	1.16	0.052	" + 47°
J7	0.0010	1.32	0.077	Between 0° and —15°
J8	0.0014	1.24	0.11	Above 45°
J9	0.00175	1.32	0.13	" 45°

Others having higher compositions were heterogeneous at 45°, beyond which it appeared unsafe to warm the tubes.

These were subject to a small absolute, but still relatively large error on account of the difficulty of weighing out exactly such small quantities of water, and the possibility or gaining or losing water while filling with the hydrogen chloride. Another difficulty was that before drying the tubes were washed with distilled water, but where a film or drop of it had stood and dried a slight deposit was often left. This is insoluble in the hydrogen chloride, but when very small amounts of the water phase were present the latter appeared on the place occupied by the deposit, dissolving it. In some cases it was difficult to determine whether the substance on the walls of the tubes was the water phase or the solid deposit. This also introduces another component into the system which may change the saturation temperature materially. Tubes C7 in the first series, and J7 in the second do not display this phenomenon, but the second phase appears in them as a turbidity, becoming more pronounced as the temperature is lowered, but the temperature at which it appears can only be located within several degrees. In spite of the causes for error just mentioned, the experiments show that the solubility of water in hydrogen chloride is 0.2 per cent. or less at 20° and less than 0.1 per cent. at 0°.

For the work with the water phase, mixtures were prepared of such a concentration as to give both phases, the aqueous in the larger quantity. Readings were made of the positions of both meniscuses and the tubes opened and calibrated as before. The weights of the hydrogen chloride phase and of the vapor are found by multiplying the density found for pure hydrogen chloride by their respective volumes and subtracted from the weight of the whole, and other simple calculations give the density and the percentage composition of the water phase. This involves the assumption, which is not quite true, that no water is present in the liquid hydrogen chloride phase or in the vapor. This would cause an error in the third decimal place in the density and in the last figure given in the composition. The greatest source of error, apart from that in reading, in these experiments and all others with the aqueous phase is that small drops of it stick to the sides and top of the tube. Another cause for inaccuracy at the lower temperatures is that the tubes could not be shaken without taking them out of

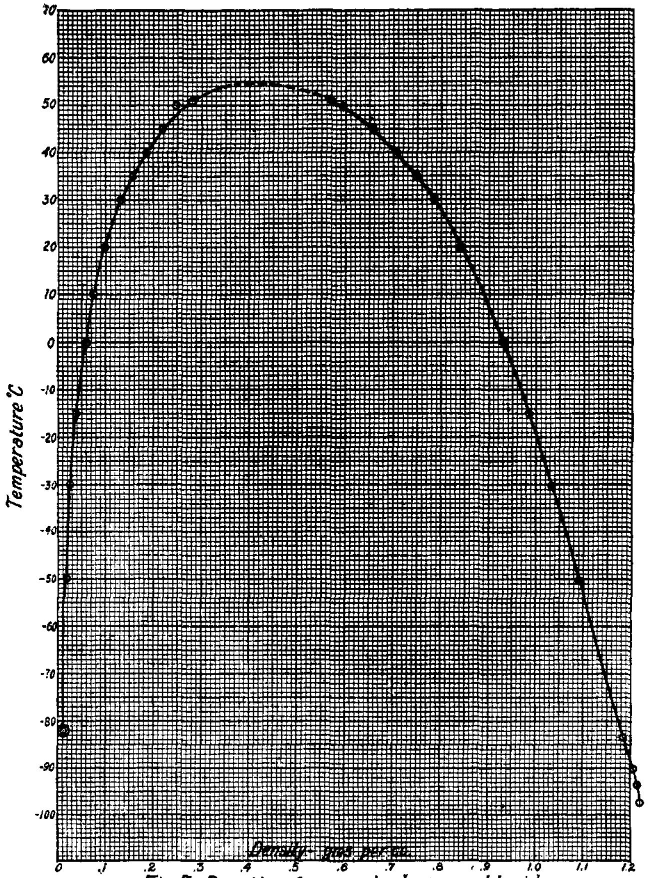

Fig. 3 Density of pure hydrogen chloride

the bath, consequently raising their temperature and decreasing the solubility of hydrogen chloride in the aqueous phase.

Formulas used and results are:

$$\text{Percentage water} = \frac{a - cf - dg}{a + b - cf - dg}$$

$$\text{Density of water phase} = \frac{a + b - cf - dg}{c}$$

where a = weight of water
b = weight of hydrogen chloride
c = volume of hydrogen chloride phase
d = volume of vapor
c = volume of aqueous phase
f = density of liquid hydrogen chloride
g = density of vapor.

Five tubes were read, calculated and averaged.

COMPOSITION OF THE TUBES.

Tube No.	Wt. HCl.	Wt. water.	Total per cent. HCl.
E1	1.2998	0.6718	66.0
E2	1.3329	0.6828	68.5
E3	1.3541	0.5067	71.2
G7	2.4396	1.0968	69.0
G9	4.1626	1.5272	73.3

E1 contained only one liquid phase below 15°, while G7 and G9 were not warmed above 20° as it was feared they would not be safe at high temperatures.

The averaged results are:

Temp. ° C.	Per cent. HCl.	Density.	Temp. ° C.	Per cent. HCl.	Density.
50	61.65	1.219	10	65.18	1.240
45	61.76	1.212	5	65.48	1.245
40	62.27	1.218	0	65.85	1.247
35	62.90	1.227	−5	66.44	1.255
30	63.21	1.229	−10	66.71	1.260
20	64.19	1.228	−50	67.29	1.269
15	64.70	1.231	−20	67.65	1.279

Graphical results are given in the curve, Fig. 6.

Density of the Unsaturated Solution and its Vapor.—It was desired to know the density of solutions ranging from 45 per cent. to the maximum hydrogen chloride content with the density of the accompanying vapor. The task here is more complex as the composition of any particular solution is unknown on account of the hydrogen chloride which is present as vapor. It is evident that as there are three unknown quantities they can be evaluated only by a series of approximations. The concentration of the water, however, in each solution can be readily found, since the weight of the water and the volume of the solution are known. If two tubes were taken in which the water in the liquid had the same concentration, the vapor density and the liquid density could be found as were those of the pure hydrogen chloride; but it was impossible to foretell the concentration of any solution while preparing it, and difficult even to bring the contents of the tube exactly to any desired total composition; therefore two series of tubes were filled, in one of which each tube contained about four-fifths its volume of the liquid, and in the other, about one-fifth. Nineteen tubes were prepared for the first series and twelve for the second. The meniscus was read at the desired temperatures, the tubes opened and volumes calculated as in the other experiments. The approximate density of the solutions in the tubes of the first series was obtained by dividing the total weight of the contents by the volume of the liquid, and the results plotted against the concentration of the water in the solution. By referring the concentration of the water in the second series to this curve the approximate density was obtained, and this quantity multiplied by the volume of the liquid gives its approximate weight. Subtracting this from the total weight and dividing by the volume of the vapor, gives the first approximation to the vapor density. This was then plotted against concentration of the water. By referring the concentration of the water in the first series to this curve, multiplying the density so obtained by the volume of the vapor, and subtracting the weight of the vapor thus found from the weight of the contents we have a second approximation to the weight of the liquid in the tubes in the first series. Using this value instead of the total weight the whole process was repeated. By a third series of calculations, using the vapor density obtained in the second, the density of the liquid and of the vapor at 35° were found to agree closely with the values found by the second approximation; and as the correction at that temperature is greater than at any lower temperature, the results of the second ap-

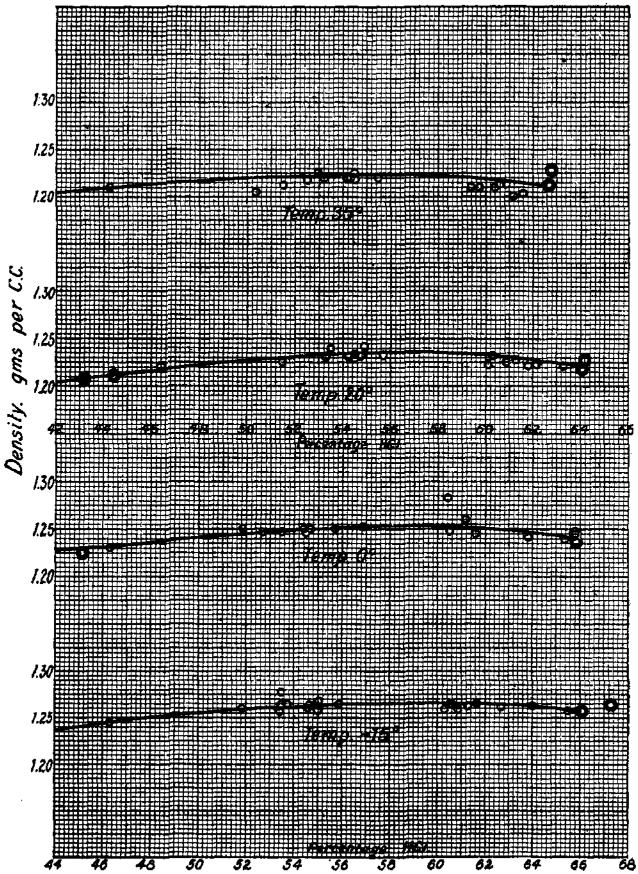

Fig. 4. Density of HCl solutions.

proximation were taken as correct. The percentage of water in each solution was then found by dividing the concentration of water by the density of the solution. Great exactness can not be claimed for this as a method for obtaining the density of the vapor, still it is sufficiently accurate for the purpose for which it was intended, namely the correction of the composition of the solution in the freezing-point curve.

The results obtained for the density of the liquid are shown in the curves, Fig. 4. The points on the left in some of the curves are from previous determinations;[1] those on the right are from my experiments on the saturated solution of liquid hydrogen chloride. The results for the vapor density are given in the curves, Fig. 5. The points on the extreme left of the curves for 0° and —15° are obtained by calculating the vapor density of solutions whose vapor pressure is one atmosphere, and whose composition is that given, according to Roscoe and Dittmar[2] or to extrapolation from their table. These points on the curves for 20° and 35° lie outside the space given. The points on the right are the values obtained for the density of the vapor in equilibrium with pure liquid hydrogen chloride.

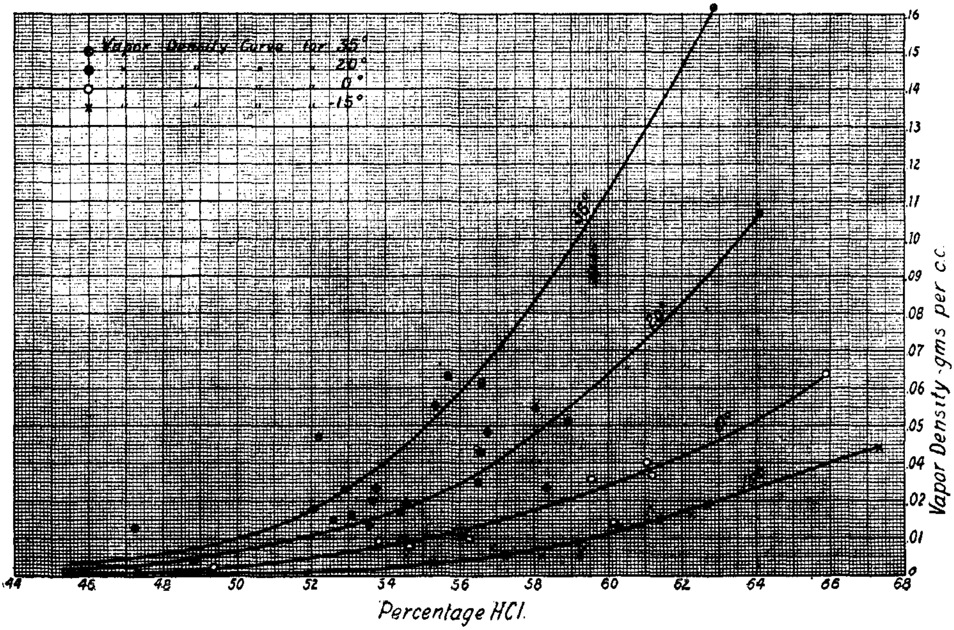

Fig.5 Vapor Density of HCl solutions

Freezing-point Determinations.—The method used for the freezing-point determinations was similar to that ordinarily used for finding melting points except that the tube must be comparatively thick-walled and must contain enough of the solution so that its composition can be known with some exactness. Tubes about 10 cm. long and 2 mm. in diameter were partly filled with solutions of various content, in the same manner as the large tubes. In finding the freezing points the tube was suspended in the alcohol bath previously described, the temperature of which was in the vicinity of the expected freezing point. After being in the bath a few minutes and shaken

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[1] Deicke, *Pogg. Ann.*, **119**, 156; Jahresber, 1863, 91; Pickering, *Ann.*, **112**, 327.

[2] Jahresber, 1859, 102.

several times the tube was taken out and the end dipped into liquid air until the solution began to crystallize. Then it was warmed in the room until only a small group of crystals remained, and again submerged in the alcohol bath, and the temperature kept constant for several minutes. If the crystals grew noticeably and showed sharp edges the temperature was raised slightly and the crystals watched again; in case they diminished and appeared rounded the temperature was lowered until a temperature was reached at which a growth of the crystals could be barely detected in five minutes, and this temperature taken as the freezing point. It was corrected by determining the freezing point of water in the same way. Usually only one determination was made, but several which were repeated agreed to within two or three-tenths of a degree. One error is especially likely to occur; super-cooling takes place to a considerable extent, consequently the composition of the solution in the portions where the crystals have melted approaches the composition of the solid and the freezing point is raised. On account of the capillarity in so small a tube it was impossible to shake it sufficiently to mix it thoroughly without warming it enough to melt the solid. This accounts in part for the irregularity of the curve. A table giving the corrected composition of the solutions with their freezing points follows:

No.	Per cent. HCl.	Freezing point.	No.	Per cent. HCl.	Freezing point.
F 7	45.9	—21.2	F28	59.1	—20.7
F17	48.6	—18.4	F 8	59.7	—19.8
F11	49.3	—17.8	F10	59.8	—19.5
F 6	49.4	—17.8	F 4	61.1	—18.4
F 5	51.0	—17.6	F 3	61.9	—17.6
F23	52.85	—18.7	F15	62.4	—17.4
F19	54.1	—19.4	F22	62.4	—17.4
F14	55.7	—20.8	F27	63.8	—16.5
F20	56.5	—21.3	F13	65.3	—15.4
F21	57.3	—23.2	F32	66.9	—15.3
F25	57.8	—22.7	F24	66.80	—15.35
F29	58.2	—21.5	F31	66.84	—15.5

These results are plotted in the appropriate part of the curve, Fig. 6. Maximum values are shown at near 50.3 per cent. and 66.9 per cent., the composition of the dihydrate and monohydrate respectively. A eutectic point is found at —23.5°, the solution having about 57 per cent. hydrogen chloride. The crystals separating out from solutions having a higher hydrogen chloride content than this are markedly different from those from the lower solutions. Those of the monohydrate closely resemble those of ammonium chloride in their manner of crystallization.

Analysis of the Monohydrate.—Tubes were made of the shape shown in Fig. 2 (page 855), of about the dimensions of those used in most of the previous experiments, and water and hydrogen chloride introduced as before. The tube was cooled below the freezing point of the monohydrate, which was allowed to crystallize. The liquid remaining in one limb was drained off into the other by inclining the tube, after which the crystals were allowed to melt slightly and the process repeated. Then the whole was immersed in liquid air and sealed apart at the bend. The part containing the isolated crystals, after being warmed to room temperature was weighed, cooled with liquid air again, opened, and as it warmed the hydrogen chloride was allowed to escape into a known volume of a standard sodium hydroxide solution and the amount of hydrogen chloride determined by titration. Calculations were then made as shown in the following example:

Tube D 6.

Weight of hydrogen chloride by titration	1.692 g.
Volume of vapor, from reading and calibration	2.035 cc.
Weight of vapor . . . . 2.035 × 0.0343 =	0.0696 g.
Total weight of contents	2.5002 g.

$$\text{Percentage HCl} = 100 \times \frac{1.692 - 0.070}{2.500 - 0.070} = 66.75$$

The results obtained for percentage hydrogen chloride were 67.3, 63.7, 66.75, 58.0, 60.9, 66.1 and 66.5. Four of these are seen to be near the value for the monohydrate. This method is subject to error on account of the difficulty, when cooling the contents of the U-tube in liquid air, in getting the substance in the two limbs cooled equally so as to prevent distillation of most of the vapor present into one limb and consequent decomposition of the crystals. Also, the liquid is not easily drained off the crystals and would affect the result materially in case its composition is much different from that of the crystals, as was the case in at least two of the tubes which give results too low to appear to be the monohydrate. Though these results are not entirely satisfactory, further attempts were abandoned as the percentage of tubes surviving all the operations without explosion or accident is very small, and as no way was found of obviating the difficulty just given.

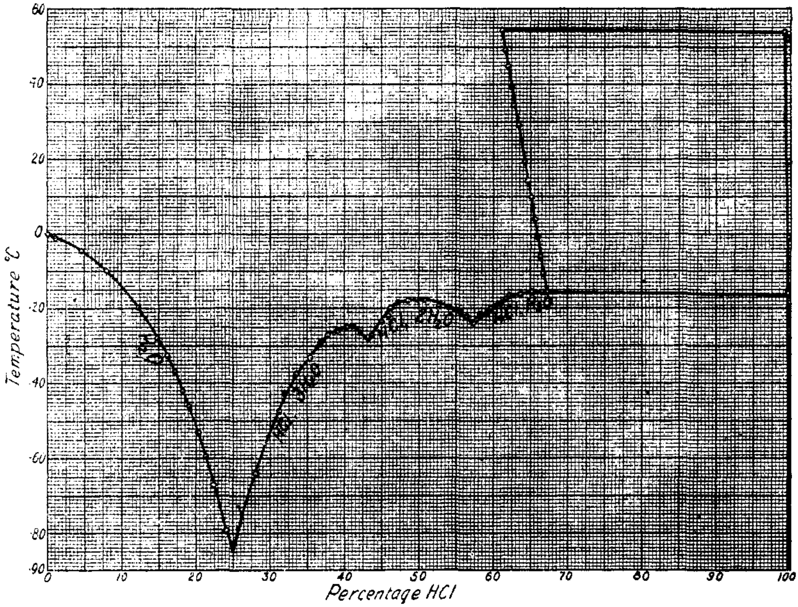

Fig 6. Concentration-Temperature Curve for HCl, H_2O

Other Observations and Remarks.—The tubes in all except the very earliest experiments and those for the analysis were exhausted of air to a pressure of 20 to 30 mm. mercury before being sealed, but some air was present as shown by forming a cushion at the bottom or other places in the tube, in which the hydrogen chloride did not condense. All weights were corrected for the total calculated weight of the air, this correction amounting to about 7 mg. in the largest tube. Considerably more air than corresponds to a pressure of 30 mm. may have been left in the tube on account of the low temperature and the possibility of adsorption by the particles of solid hydrogen chloride; yet it does not appear that this error is enough to affect the results seriously.

When some tubes containing hydrogen chloride and some containing the solution were cooled to the temperature of liquid air a pink coloration was obtained. On warming the coloration disappeared below the melting point of hydrogen chloride. This color always appears to about the same extent in the same tube, and not at all in many whole series. When the color is very pronounced it is seen to be in patches as if the monohydrate or solid hydrogen chloride crystallizing out leaves a substance in greater concentration which gives the pink color. The tubes which show the color are in no other way preceptibly different from the others.

In connection with the density of the liquid phases a rough determination was made of the density of the monohydrate, by permitting one of the solutions used in the other experiments, having a composition nearly that of the monohydrate, to freeze nearly completely, reading the position of the top of the mass of the solid, calculating its volume and correcting for the vapor present. The density so obtained is 1.48 grams per cc.

Conclusion.

The composition-temperature curve (Fig. 6) for the system hydrogen chloride and water has been completed for all conditions in which the liquid and a solid, or two liquid phases, appear.

The curve from 0 to 50 per cent. hydrogen chloride is copied from Pickering's paper previously mentioned and is given for the sake of completeness. The extension of this curve shows the presence of another eutectic point at 57 per cent. hydrogen chloride and —23.5°, where we have the system monohydrate-dihydrate-solution-vapor, and beyond this point a maximum freezing point is found at about 66.9 per cent. and —15.35°. Very near this point two liquid phases are formed, the new phase containing more than 99.9 per cent. hydrogen chloride. This gives a quadruple point for the system monohydrate-solution-solution-vapor. The solubility of the hydrogen chloride phase in the water phase decreases with rising temperature, while the opposite is true of the solubility of the latter in the former. This relation continues up to 54.5°, the critical point of the hydrogen chloride phase.

The portion of the curve showing the equilibrium between the monohydrate and the liquid hydrogen chloride phase was not worked on, on account of the difficulty of measuring so small quantities of water. A break would appear at the junction of the solubility curves of the aqueous phase and of the monohydrate. Unless there is a retrograde solubility relation, which is not probable, as none of the crystals dissolve at a lower temperature after being formed at a higher, the curve would have the form as shown, lying very near the 100 per cent. hydrogen chloride composition line. A eutectic point would appear, very close to the freezing point of the pure chloride.

Analysis though made under difficulties and subject to some error tends to confirm the existence of the monohydrate. It is a white crystalline substance, having a density of 1.48, freezing at —15.35°, and resembling ammonium chloride in general character. It is very soluble in water but very slightly in hydrogen chloride. Since it is in equilibrium with the hydrogen chloride phase, or very nearly so, at its melting point, its vapor pressure at that temperature must be nearly equal to that of the liquid, which is in turn practically equal to that of the pure hydrogen chloride. This according to Faraday is 17.3 atmospheres.

The density of solutions and of their vapor have been determined up to the saturation point at the temperatures —15°, 0°, 20° and 35°.

The density of liquid and of gaseous hydrogen chloride have been determined at temperatures from +51° to —50°.

In conclusion, I wish to acknowledge my obligations to Dr. H. P. Cady for his kindly interest and valuable suggestions during this work.

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THE SOLID HYDRATES OF AMMONIA.

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In connection with the work on the system hydrogen chloride and water it was noticed that there are several similar systems on which little work has been done in the matter of freezing points and the search for solid compounds. One of these is the system ammonia and water. It is familiar to all that the monohydrate of ammonia, or ammonium hydroxide, has been regarded as a compound by practically all chemists for many years from the resemblance of the properties of a solution of ammonia to those of hydroxides, but it never has been obtained as a solid.

The method for investigating ammonia was very much simpler than that necessary in the case of hydrogen chloride, as liquid ammonia and water are miscible in all proportions, and solutions in all concentrations can be prepared whose vapor pressure is less than one atmosphere. Weighed quantities of water and of ammonia were introduced into a large test tube containing a stirring rod and toluene thermometer. When it was necessary to keep this below room temperature when weighing, the tube was inserted through a cork into a vacuum jacketed tube previously cooled with liquid air, and the whole weighed. To find the freezing point the tube was immersed in a bath as described in the paper on hydrochloric acid, except that gasoline has been found more satisfactory as a bath liquid at the temperatures used. The bath was cooled and freezing points found in the ordinary way.

The following measurements of percentage composition and freezing points have been made.

These results are given graphically in the accompanying curve, which