

153. *Chlorine Hydrate.*

By S. ANWAR-ULLAH.

CHLORINE hydrate was discovered in 1811 by Davy (*Phil. Trans.*, **101**, 155) and analysed in 1823 by Faraday (*Quart. J. Sci.*, **15**, 71), who proposed the constitution $\text{Cl}_2, 10\text{H}_2\text{O}$. It has since been examined many times, and other formulæ suggested. Maumené (*Bull. Soc. chim.*, 1883, **39**, 397) concluded that under different conditions $\text{Cl}_2, 12\text{H}_2\text{O}$, $\text{Cl}_2, 7\text{H}_2\text{O}$, and $\text{Cl}_2, 4\text{H}_2\text{O}$ could all exist. Roozeboom (*Z. physikal. Chem.*, 1888, **2**, 452) decided in favour of $\text{Cl}_2, 8\text{H}_2\text{O}$, and Bouzat and Azinières (*Compt. rend.*, 1923, **177**, 1444) obtained results pointing to $\text{Cl}_2, 6\text{H}_2\text{O}$, the value supported by analogy with

other hydrates and by the theories put forward by De Fourcraud (*Compt. rend.*, 1901, 133, 1304; 1902, 134, 88). The uncertainty of the formula of this hydrate was realised during the examination of the hydrate deposited from the solution of mixtures of bromine and chlorine (see following paper), and several attempts were made to determine the constitution. The results obtained by two different methods, involving different conditions and different manipulation, agreed satisfactorily and entirely support the formula $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$.

The difficulty of drying and handling a hydrate of a material so volatile as chlorine is obvious, and Faraday, who made a direct analysis of the crystals, was driven to base his conclusions on the highest percentage of chlorine found during his series of experiments, rather than on the mean; even then, he realised that his estimate might be too low. It is probably owing to the same difficulty that such inconsistent values have since been reported; and the experiments described below were designed to evade it as far as possible.

EXPERIMENTAL.

Method I.—An attempt was made to determine the composition by measuring the volume of chlorine absorbed by a known weight of water in forming the solid hydrate at 0° , at which temperature the dissociation pressure is well below 760 cm. The water was weighed in a thin glass bulb, which was afterwards broken in a chamber filled with dry chlorine. This chamber was attached to a gas burette, modified for use with chlorine, but the apparatus is not described in further detail, as the method failed completely owing to the slow rate of absorption of the gas. A thin crust of the hydrate was formed on the surface of the water and seemed to be almost impervious to the gas.

Method II.—The hydrate is in equilibrium with a chlorine pressure of 1 atm. at about 0° , and it can be stabilised up to much higher temperatures by increasing the chlorine pressure. If, therefore, water and excess of liquid chlorine are introduced together in a tube which is subsequently sealed, the hydrate is formed at laboratory temperatures, without fear of dissociation. The tube may then be cooled at 0° , and opened, the excess of chlorine being allowed to escape, and the hydrate remaining unchanged. The contents of the tube may then be analysed for water and chlorine.

This is the method which was used by Bouzat and Azinières, and it gives concordant results if appropriate precautions are taken. The vessels (Fig. 1) were made of stout glass, to withstand about 10 atm. pressure. Water (about 5 g., insufficient to reach the bottom of tube *A*) was introduced through that tube and weighed. The apparatus was then cooled in solid carbon dioxide, and about 25 c.c.

of liquid chlorine (prepared by the permanganate method, and dried over phosphoric oxide) were condensed in it. The tubes *A* and *B* were sealed off, and the apparatus allowed to warm. A thick crust of the hydrate was always formed at the junction of the chlorine and the aqueous layer, and delayed the combination of the remaining water almost indefinitely (see above). It was necessary, therefore, to heat the tube to 30° , at which temperature the hydrate dissociated within the sealed tube into two liquid layers. The tube was then shaken well while cooling, so that the hydrate was

FIG. 1.

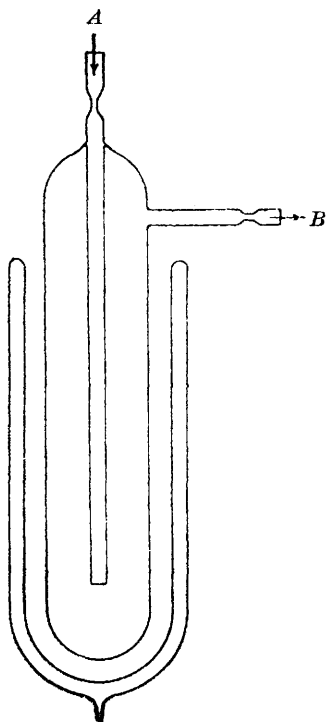
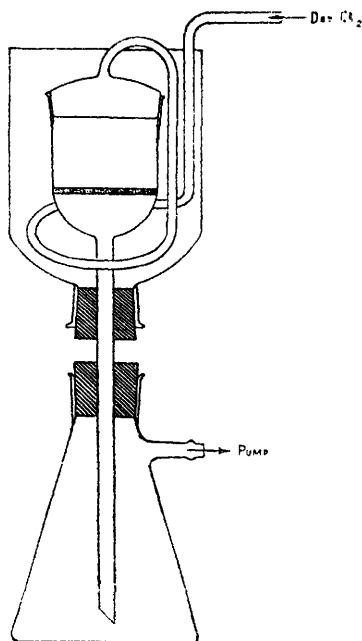


FIG. 2.



deposited as a sludge and not as a continuous layer. After various periods (several hours), the tubes were cooled to 0° , and the tip of *B* broken. The excess of chlorine rapidly distilled away, and when the evolution of gas was complete, the tubes were re-sealed and re-weighed, this giving the weight of chlorine that had combined with water, a correction being applied for the gaseous chlorine present in the tube. The tubes were finally reopened and an independent estimate of the chlorine was obtained by boiling it off into potassium iodide solution. The results of the first few trials on this procedure

were disappointing, giving 7—10 mols. of water per mol. of chlorine. It was soon realised that the inconsistencies were due to the slowness of the reaction, frozen globules of water evidently being retained within the solid hydrate. Table I shows that this hypothesis was correct: only after the chlorine and water have been in contact for many days can consistent results be assured.

TABLE I.

Time of storage.	W. of hydrate, g.	W. of water taken, g.	Ratio Cl:H ₂ O.	Time of storage.	W. of hydrate, g.	W. of water taken, g.	Ratio Cl:H ₂ O.
1½ Hrs.	5.994	4.39	1 : 9.6	5 Days	7.9607	4.8008	1 : 6.35
Week-end	6.6964	1.1438	1 : 6.8	5 „	7.3234	4.7943	1 : 7.55
3 Hrs.	7.1100	4.8125	1 : 8.2	24 Hrs.	2.9843	1.8106	1 : 6.08
2 Days	7.3086	4.6996	1 : 7.05	4½ Months	7.3570	4.9382	1 : 6.12
10 Min.	6.9359	4.7958	1 : 8.8	4½ „	9.5301	5.8270	1 : 6.30
1 Week	7.9400	4.9260	1 : 6.442	9 „	7.9388	4.8228	1 : 6.10
24 Hrs.	8.0153	4.7958	1 : 5.898	9 „	8.0744	4.8624	1 : 5.97

It is evident that when sufficient time is allowed for completion of the reaction, this method of estimation gives a molecular ratio Cl₂:H₂O of 1 : 6. The mean of the four values from tubes which have stood for 4½—9 months is 6.12. The mean of Bouzat and Azinières' results by a similar procedure was 6.45, the maximum being 6.75, and the minimum 6.32. These higher values may well have been due to incomplete reaction, for their tubes were apparently not stored for any length of time.

A few tubes were kept for about 2 days at — 34°. The analyses agreed with a hexahydrate, showing that the compound is still stable at this temperature.

Method III.—The foregoing method would seem to establish the formation of the hexahydrate under the conditions imposed, *i.e.*, excess of chlorine under pressure. The higher values given in the literature are so numerous as to make it possible that a different hydrate would be found by examining the crystals formed from aqueous solutions of chlorine, as these were invariably the material on which the earlier determinations were based, and further experiments were made to test the point. It was found that such crystals can be dried satisfactorily at 0°, in a current of chlorine, and that consistent analyses can be obtained in this way. The apparatus employed is shown in Fig. 2. A sintered-glass disc, of 2 cm. diameter, was sealed into a glass tube, the top of which was connected by a cap and a ground joint to a supply of chlorine. Suction from a water-pump was applied to the lower end of the tube, and the whole arrangement was cooled in an ice-bath.

A crop of hydrate crystals, prepared by passing chlorine into water at 0°, was transferred to the filter tube, the cap replaced, and the

crystals sucked dry in an atmosphere of chlorine. Variation in the time of drying had no influence on the results. The crystals when dry were removed with a cool glass spatula, and dropped into a weighed vessel containing dilute aqueous ammonia or potassium iodide. The total weight of the hydrate, and the chlorine content were thence obtained. Table II shows that, under these conditions also, the hexahydrate is formed.

TABLE II.

W. of hydrate, g.	W. of chlorine, g.	Mol. ratio $\text{Cl}_2 : \text{H}_2\text{O}$.	W. of hydrate, g.	W. of chlorine, g.	Mol. ratio $\text{Cl}_2 : \text{H}_2\text{O}$.
0.5406	0.2061	1 : 6.15	0.7202	0.2802	1 : 6.15
0.3187	0.1264	1 : 6.01	0.7196	0.2851	1 : 6.02
0.3247	0.1242	1 : 6.45	0.4425	0.1760	1 : 5.9
0.2628	0.1020	1 : 6.25	0.3790	0.1509	1 : 6.0

Method IIIa.—Finally, a few determinations were made by a slight modification of this procedure. The hydrate was prepared in a dilute solution of copper sulphate of known concentration instead of in water, and the crystals were collected as before, but were only imperfectly dried. The analysis was carried out as before, but the copper sulphate retained by the wet crystals was afterwards estimated colorimetrically by the ferrocyanide method; calculation then gave the amount of uncombined water adhering to the crystals. This modification yielded less consistent results, but sufficed to indicate that the drying procedure is free from serious error. The molecular ratios found were $\text{Cl}_2 : \text{H}_2\text{O} = 1 : 6.15, 1 : 6.4, \text{ and } 1 : 5.6$.

Summary.

The chlorine hydrate formed under different conditions of temperature, pressure, and relative concentration of the constituents, within the range of the present experiments, has always the composition $\text{Cl}_2, 6\text{H}_2\text{O}$. The higher values previously recorded are probably to be ascribed either to incomplete reaction between water and chlorine, or to imperfect drying of the hydrate before analysis.

THE SIR WILLIAM RAMSAY LABORATORY OF PHYSICAL
AND INORGANIC CHEMISTRY, UNIVERSITY COLLEGE,

LONDON.

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