

*THE STRUCTURE OF CHLORINE HYDRATE*

BY LINUS PAULING AND RICHARD E. MARSH

THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY,\* CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

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In 1811 Humphry Davy<sup>1</sup> showed that water is a component of the phase that had earlier been thought to be solidified chlorine, and twelve years later Michael Faraday<sup>2</sup> reported an analysis that corresponds to the formula  $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ . He surmised that his determination of the chlorine content was low, and later studies have indicated the composition to be close to  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ . Since Faraday's time similar crystalline hydrates of many gases with small molecular volume, including the noble gases and simple hydrocarbons, have been reported. The determination of the structure of ice and the development of an understanding of the nature of the hydrogen bond have strongly suggested that these substances are clathrate compounds, with a tetrahedral hydrogen-bonded framework of water molecules (with  $\text{O}-\text{H} \cdots \text{O} = 2.76 \text{ \AA}$ , as in ice) defining cavities large enough to contain the other molecules.

Only recently have serious steps been taken toward determining the structure of these hydrates. About ten years ago von Stackelberg and his collaborators<sup>3,4</sup> made x-ray studies of some of these compounds, including the hydrates of xenon, chlorine, bromine, sulfur dioxide, hydrogen sulfide, methyl bromide, methyl iodide, ethyl chloride and chloroform. They reported that most of the crystals have a cubic unit cell with  $a_0$  equal to about 12.0  $\text{\AA}$ . From single-crystal x-ray photographs of the hydrate of sulfur dioxide they decided on the space group  $O_h^3$ , and postulated a structure consisting of a framework of 48 oxygen atoms in a set of general positions  $x, y, z$  in the unit cell. With this structure each oxygen atom has neighboring oxygen atoms at a distance of about 2.4  $\text{\AA}$ , and the framework has eight cavities in which the gas molecules could lie. The ideal formula would thus be  $\text{M} \cdot 6\text{H}_2\text{O}$ . This structure is not acceptable because of the very short  $\text{O}-\text{H} \cdots \text{O}$  distance of 2.4  $\text{\AA}$ ; in addition, the hydrogen bonds lie at angles between  $60^\circ$  and  $145^\circ$ , which differ greatly from the expected tetrahedral angle.

Claussen<sup>5</sup> then proposed a structure based on a larger cubic unit cell, about 17  $\text{\AA}$  on edge, containing 136 water molecules. The oxygen atoms would be arranged to form 16 pentagonal dodecahedra and 8 hexakaidecahedra. This structure leads to the empirical formula  $\text{M} \cdot 5\frac{2}{3}\text{H}_2\text{O}$  for smaller molecules which occupy all of the polyhedra, and  $\text{M} \cdot 17\text{H}_2\text{O}$  for larger molecules which occupy only the hexakaidecahedra. The obvious advantage of such a structure is the presence of hydrogen bond angles of

about  $108^\circ$  in the dodecahedra and in the twelve pentagonal faces of the hexakaidecahedra; the other hydrogen bond angles, in the four hexagonal faces of the hexakaidecahedra, are about  $120^\circ$ . Von Stackelberg and Müller<sup>6</sup> have recently reported evidence for the existence of this structure derived from analysis of x-ray diffraction photographs of alkyl halide hydrates.

We have been studying the structures of intermetallic compounds that involve icosahedral and pentagonal dodecahedral arrangements of atoms, and in the course of this work a structure was found which seemed to be ideally suited to the hydrates of smaller gas molecules. This structure is based on the cubic group  $O_h^3$ , and has  $a_0$  equal to 11.88 Å for the O—H···O distance 2.76 Å, in close agreement with the first results reported by von Stackelberg. The unit cell contains 46 water molecules, with the oxygen atoms arranged so as to form two pentagonal dodecahedra and six tetrakaidecahedra; the empirical formula is hence  $M \cdot 7\frac{2}{3}/_3\text{H}_2\text{O}$  for molecules M occupying only the tetrakaidecahedra, and  $M \cdot 5\frac{3}{4}/_4\text{H}_2\text{O}$  for smaller molecules which occupy all of the polyhedra.<sup>7</sup> In order to test the predicted structure we have prepared and interpreted x-ray diffraction photographs of chlorine hydrate.

*Experimental Methods and Results.*—A length of 6-mm. Pyrex tubing was drawn to a capillary at one end and connected to a tank of commercial chlorine. After thorough flushing, the capillary was sealed off and the end was immersed in a dry-ice-acetone bath. When some chlorine had condensed in the capillary a drop of water was admitted into the large end of the glass tube, which was then sealed off. Alternate warming and cooling of the capillary permitted thorough mixing of the water and chlorine. Small pale-yellow crystals soon formed in the capillary, and remained as the temperature was brought up to  $0^\circ\text{C}$ . A small amount of liquid chlorine also remained, showing the chlorine to be in excess and indicating a pressure of about 4 atmospheres.

The Pyrex tube was suspended, with capillary down, in a small-holed rubber stopper which, in turn, was fastened to a goniometer head by a length of stout copper wire. The solid material within the capillary was photographed in a cold room ( $4^\circ\text{C}$ .) using copper x-radiation, a camera with radius 5 cm., and oscillation range  $30^\circ$ . The effective camera radius was established by superimposing a powder spectrum of NaCl during an exposure of the sample; the lattice constant for NaCl at  $4^\circ\text{C}$ . was taken to be 5.634 Å.

The diffraction pattern of the sample of chlorine hydrate consisted of powder lines on which were superimposed a large number of more intense single-crystal reflections; for some planes only the latter were visible. The intensities of the lines were estimated by comparison with a previously calibrated powder photograph, and were averaged for several films pre-

pared from different parts of the capillary (and which, accordingly, varied as to the intensities of the single-crystal reflections). Despite this precaution, it was expected that the intensity estimations would be subject to considerably larger errors than would a properly ground powder sample. The averaged intensities were corrected for Lorentz and polarization factors and were adjusted by an empirical scale factor to give values of  $G_{\text{obs}}^2$ .

All of the observed reflections could be indexed on the basis of a cubic unit cell with  $a_0 = 11.82$  Å; the estimated probable error is 0.01 Å. The only systematic absences were  $hhl$  with  $l$  odd; this is characteristic of the space group  $O_h^3-Pm\bar{3}n$ , which also was reported by von Stackelberg from his single-crystal work on sulfur dioxide hydrate. For 46 H<sub>2</sub>O and 6 Cl<sub>2</sub> in the unit cell the calculated density is 1.26; densities reported by various observers range from 1.23 to 1.29.

In order for all of the O—H···O distances within the unit cell to be the same the oxygen atoms must lie in the following positions:

$$\begin{aligned} 6 \text{ O}_I & \text{ in } 6(c) \frac{1}{4} 0 \frac{1}{2} \dots; \\ 16 \text{ O}_{II} & \text{ in } 16(i) xxx, \dots, x = 0.183; \\ 24 \text{ O}_{III} & \text{ in } 24(k) 0yz, \dots, y = 0.310, z = 0.116. \end{aligned}$$

For comparison with  $G_{\text{obs}}^2$  values, calculated values were determined as follows:  $G_{\text{calc}}^2 = \sum_i m_i F_i^2$  where  $F_i$  is the structure factor and  $m_i$  the multiplicity of each set of planes  $i$  contained in the powder line. For preliminary calculations only the contributions of the oxygen atoms were included in the structure factor; nevertheless, there was rough agreement with the observed  $G^2$  values.

The oxygen atoms placed in the above positions form, in each unit cell, a framework consisting of two pentagonal dodecahedra, centered at (000) and  $\left(\frac{111}{222}\right)$ , and six tetrakaidecahedra, centered at  $\left(\frac{11}{42}0\right)$ ,  $\left(\frac{31}{42}0\right)$ ,  $\left(\frac{1}{2}0\frac{1}{4}\right)$ ,  $\left(\frac{1}{2}0\frac{3}{4}\right)$ ,  $\left(0\frac{11}{42}\right)$ , and  $\left(0\frac{31}{42}\right)$ . It soon became apparent that the agreement between calculated and observed values of  $G^2$  was markedly improved if the chlorine molecules were placed within the six tetrakaidecahedra only, leaving the dodecahedra empty. These tetrakaidecahedra have two nearly regular hexagonal faces at opposite ends, separated by twelve nearly regular pentagons, as shown in figure 1. A cross-section taken parallel to the hexagonal faces is nearly circular, and the equatorial diameter is considerably larger than the polar diameter (between hexagons). The figure thus is a close approximation to an oblate spheroid. If the twelve chlorine atoms are to lie in fixed positions within the tetrakaidecahedra conforming to the crystal symmetry, a pair must lie along the short polar

axis. This arrangement is sterically unfavorable, and calculations based on it gave rather poor intensity agreement. Since the tetrakaidecahedra containing the chlorine molecules so nearly approximate spheroids, it was

TABLE 1  
CALCULATED AND OBSERVED  $G^2$  VALUES FOR CHLORINE HYDRATE

$hkl$	(I) UNIFORM SHELL	(II) EQUAT. CIRCLE	$mF_{calc}^2$ (III) WEIGHTED SHELL	(IV) V. STACKEL- BERG	$G_{obs}^2$
110	555	488	527	34	207
200	10	18	0	722	<48
210	865	986	916	278	636
211	8	4	1	221	<74
220	412	809	562	3204	582
310	981	602	808	23	694
222	4390	4283	4390	1656	2732
320	4195	3120	3741	2307	3394
321	6416	6037	6304	723	9216
400	970	1083	972	207	679
410	1579	4494	2528	60	1817
{ 330	522	844	653	83	1074
{ 411	274	1142	525	292	
420	94	389	167	2679	139
421	246	16	117	3	323
332	429	666	509	357	318
422	4	528	107	1144	141
430	346	0	110	2323	206
{ 431	37	299	128	1354	229
{ 510	330	80	194	128	
{ 432	1129	1260	1109	701	2411
{ 520	180	5	42	2949	
521	161	493	272	46	196
440	0	4	0	631	<183
{ 433	2401	2599	2578	1144	10080
{ 530	5040	3863	4437	1234	
531	2611	2611	2611	10	1374
{ 442	484	955	730	1080	1020
{ 600	1568	274	957	234	
610	1152	2	459	750	304
{ 532	5685	4264	5069	10	5236
{ 611	392	2035	764	99	
620	960	2964	1562	359	1320
{ 540	620	1008	890	5317	1654
{ 621	296	3192	973	1290	
541	49	85	37	491	<378
622	166	95	164	689	<400

decided to treat the chlorine molecules as freely rotating about their centers or else as being statistically distributed over a large number of orientations within the polyhedra. In either case, a sufficiently close

approximation to the electron density is given by considering the centers of the chlorine atoms to lie on spherical shells concentric with the tetrakaidecahedra; the diameter of these shells is the Cl—Cl bonded distance, taken as 1.98 Å. Since the tetrakaidecahedra are oblate, it would be expected that the chlorine atoms would be concentrated toward the equator. Calculations of structure factors were made on the basis of three different configurations for the chlorine atoms within each tetrakaidecahedron: (I) a spherical shell of uniform density; (II) the limiting case in which all of the chlorine atoms were assumed to lie on the equator; that is, on a circle parallel to and midway between the hexagonal faces; (III) a spherical shell with density weighted according to the function  $\cos^2 \alpha$ , where  $\alpha$  is the angle of latitude. For arrangement I the calculated structure factor for the center of the sphere, including the form factor for two chlorine atoms, was multiplied by the factor  $\frac{\sin P}{P}$ , where  $P = \frac{2\pi r}{d_{hkl}}$ ,  $d_{hkl}$  is the spacing of the diffracting plane, and  $r$  ( $= 0.99$  Å) is the radius of the sphere. For the circle in arrangement II the factor is  $J_0(P \sin \psi)$ , where  $J_0$  is the zero-order Bessel coefficient and  $\psi$  is the angle between the axis of the circle and the normal to the diffracting plane  $hkl$ . Arrangement III was approximated by summing up the appropriately weighted contributions of circles with radius  $r \cos \alpha$ , taken at each  $15^\circ$  of latitude; the calculated structure factor for the center of each circle was multiplied by the correction factor  $J_0(P \cos \alpha \sin \psi)$ . As a check that  $15^\circ$  was a sufficiently small interval, another calculation was made in which the latitudinal circles were weighted so as to give an approximation to a uniform spherical shell; the results were essentially identical with those of arrangement I throughout the observed range of diffraction angle.

In table 1 there are listed the values of  $G^2$  calculated on the basis of these three arrangements, together with the observed values; it is seen that arrangement III—the spherical shell of non-uniform density—gives the best agreement, especially for the reflections 430, 610, and  $540 + 621$ . Indeed, the agreement with the observed values is quite satisfactory in view of the relatively large uncertainty in observed intensities. Contributions of the hydrogen atoms were not included in the calculations, and no temperature factor was applied. The reliability factor  $R^2 = \frac{\sum |G_{\text{obs.}}^2 - G_{\text{calc.}}^2|}{\sum G_{\text{obs.}}^2}$  has a value of 0.32, which corresponds to a value of 0.16 if  $F$  values were used.

In column IV there are listed the  $G^2$  values calculated from the parameters proposed by von Stackelberg. As an approximation to the configuration of the chlorine molecules spherical shells of uniform density were placed at the centers of the eight cavities formed by the oxygen atoms. It is seen that the calculated values are not compatible with

the observed ones, and it seems extremely unlikely that any change in the positions of the chlorine atoms would make the agreement between calculated and observed intensities satisfactory.

*Discussion of the Structure.*—Figures 1 and 2 show two different representations of the framework of oxygen atoms. The structure may be derived, as shown in figure 2, by placing dodecahedra at the corners and body center of the unit cube and adding six additional atoms per unit cell (three of these are indicated by circles) to form the tetrakaidecahedra. Each dodecahedron shares its faces with twelve surrounding tetrakaidecahedra, and each tetrakaidecahedron shares its two hexagonal faces and eight pentagonal faces with neighboring tetrakaidecahedra, the remaining four pentagonal faces being shared with dodecahedra. With the oxygen parameters given above, which result in O—H···O distances of 2.75 Å

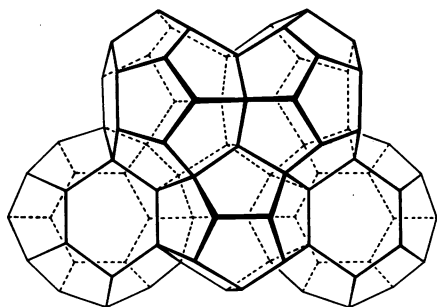


FIGURE 1

Dodecahedron of oxygen atoms surrounded by four out of a total of twelve tetrakaidecahedra.

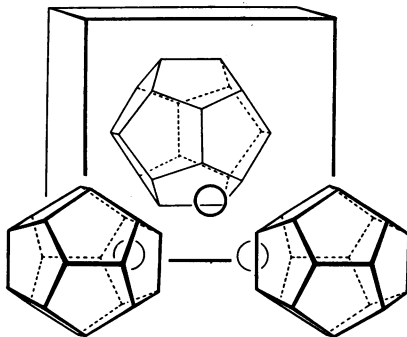


FIGURE 2

Dodecahedra of oxygen atoms at two corners and body center of unit cell, with three additional oxygen atoms (circles) needed to complete the structure.

throughout, the pentagons deviate slightly from planarity, while the hexagons are planar but not equi-angular. The O-O-O angles on the pentagonal faces range from  $106.1^\circ$  to  $114.8^\circ$ , while each hexagon has two angles of  $109.6^\circ$  and four of  $125.2^\circ$ .

The average radius of the tetrakaidecahedra at the equator is 4.46 Å, while the average distance from the center to the six vertices of the hexagonal faces is 4.03 Å; the average radius of the dodecahedra is 3.85 Å. Using a single-bond radius for chlorine of 0.99 Å and van der Waals radii for chlorine and oxygen of 1.80 and 1.40 Å, respectively, we would expect a minimum radius of 4.19 Å for accommodation of a chlorine molecule. Even if the presence of hydrogen-chlorine contacts would decrease somewhat the effective van der Waals radius of chlorine, it is doubtful that the over-all minimum radius could drop to 3.85 Å; hence one would predict

that the dodecahedra are too small to accommodate the chlorine molecules. Moreover, the tetrakaidecahedra are barely long enough to hold the chlorine molecules along the polar axis; the  $\cos^2 \alpha$  weighting of the density of the spherical shells representing the centers of the chlorine atoms thus appears to be justified.

On the basis of this structure for chlorine hydrate, the empirical formula is  $6\text{Cl}_2 \cdot 46\text{H}_2\text{O}$ , or  $\text{Cl}_2 \cdot 7\frac{2}{3}\text{H}_2\text{O}$ . This is in fair agreement with the generally accepted formula  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ , for which Harris<sup>7</sup> has recently provided further support. For molecules slightly smaller than chlorine, which could occupy the dodecahedra also, the predicted formula is  $M \cdot 5\frac{3}{4}\text{H}_2\text{O}$ .

\* Contribution No. 1652.

<sup>1</sup> Davy, H., *Phil. Trans. Roy. Soc.*, **101**, 155 (1811).

<sup>2</sup> Faraday, M., *Quart. J. Sci.*, **15**, 71 (1823).

<sup>3</sup> *Fiat Review of German Science*, Vol. 26, Part IV.

<sup>4</sup> v. Stackelberg, M., Gotzen, O., Pietuchovsky, J., Witscher, O., Fruhbuss, H., and Meinhold, W., *Fortschr. Mineral.*, **26**, 122 (1947); cf. *Chem. Abs.*, **44**, 9846 (1950).

<sup>5</sup> Claussen, W. F., *J. Chem. Phys.*, **19**, 259, 662 (1951).

<sup>6</sup> v. Stackelberg, M., and Müller, H. R., *Ibid.*, **19**, 1319 (1951).

<sup>7</sup> In June, 1951, a brief description of the present structure was communicated by letter to Prof. W. H. Rodebush and Dr. W. F. Claussen. The structure was then independently constructed by Dr. Claussen, who has published a note on it (*J. Chem. Phys.*, **19**, 1425 (1951)). Dr. Claussen has kindly informed us that the structure has also been discovered by H. R. Müller and M. v. Stackelberg,

<sup>8</sup> Harris, I., *Nature*, **151**, 309 (1943).

## ON THE HOMOMORPHISM THEOREM FOR SEMIRINGS

BY SAMUEL BOURNE

DEPARTMENT OF MATHEMATICS, THE UNIVERSITY OF CONNECTICUT,  
STORRS, CONNECTICUT

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In a recent paper,<sup>1</sup> we have given a statement of the homomorphism theorem for semirings,<sup>2</sup> which is in part incorrect. We have noted this in these PROCEEDINGS, **37**, 461 (1951). At present, it is our purpose to give and prove a corrected statement of this theorem.

*Definition.* A semiring  $S$  is said to be semi-isomorphic to the semiring  $S'$ , if  $S$  is homomorphic to  $S'$  and the kernel of this homomorphism is  $(0)$ .

*THEOREM.* If the semiring  $S$  is homomorphic to the semiring  $S'$ , then the difference semiring  $S - I$  is semi-isomorphic to  $S'$ , where  $I$  is the ideal of elements mapped onto  $0'$ .