THE CRYSTAL STRUCTURE OF ICE.

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SYNOPSIS.

Crystal Structure of Ice as Determined from X-ray Pattern.—A small sample of ice composed of minute crystals, gave by Hull's method a pattern of 12 clearly defined lines whose positions indicate that the lattice of an ice crystal corresponds to a hexagonal close-packed arrangement of molecules, consisting of two sets of interpenetrating triangular prisms with sides 4.52 A and height 7.32 A. Since for close-packed spheres the axial ratio should be 1.633 instead of 1.62, the ice molecules act like spheres which have become flattened by 0.8 per cent. in the direction of the hexagonal axis. This lattice is practically the same as that found for magnesium, but the differences in relative intensity between the lines of the two X-ray patterns suggest that ice molecules and magnesium atoms must differ considerably in shape.

Molecular Formula for Ice.—From the density of ice and the dimensions of the lattice it follows that the formula for an ice molecule is $(H_2O)_2$ or H_4O_2.

X-RAY photographs of ice were made in the same manner as the crystal powder photographs described by A. W. Hull.[1] A small quantity of distilled water was inclosed in a thin-walled capillary tube of lime glass. The tube was then plunged quickly into liquid air, freezing the water with such rapidity that only very minute crystals were formed. The tube was then kept at liquid air temperature in a specially constructed Dewar flask. The sample was rotated continuously during the 10-hour exposure to the X-rays from the molybdenum target of a water-cooled Coolidge tube which was running at 32,000 volts, 25 milliamperes direct current. The photographic film was bent in a semicircular arc of radius 19.8 cm. The tube of ice was placed in the axis of this arc. A good photograph was obtained which contained 12 lines, the data from which are recorded in the table.

The first column gives the angular deviation of each line, the second gives the intensities, which were only roughly estimated, and the third gives the intensities of the corresponding magnesium lines as estimated by Dr. Hull.[2] The fourth column gives the observed plane spacings, while the fifth gives the theoretical plane spacings which would correspond to a close packed hexagonal lattice, consisting of two sets of interpenetrating triangular prisms, the sides of whose bases are each

[1] PHYS. REV., 9, 85, Jan., 1917.

[2] Pro. Nat. Acad. Sci., Vol. 3, pp. 470–473, July, 1917.

4.52 Angstroms and whose height is 7.32 Ångstroms. The observed and theoretical spacings agree within the limit of experimental error.

Angular Deviation of Line 2θ (Degrees).	Intensity of Line (Estimated).	Intensity of Magnesium Line for Comparison.	Spacing of Planes in Ångstroms.		Indices of Form.	No. of Coöperating Planes.
			Obs.	Cal.		
10.44	1	4.7	3.92	3.915	$10\bar{1}0$	3
11.16	10	—	3.67	3.671	0001	1
11.88	2	10.0	3.44	3.453	$10\bar{1}1$	6
15.30	1.5	3.3	2.68	2.675	$10\bar{1}2$	6
18.12	1	4.7	2.26	2.260	$11\bar{2}0$	3
19.86	5	4.0	2.065	2.065	$10\bar{1}3$	6
21.38	1	4.0	1.92	1.925	$11\bar{2}2$	6
27.16	1.5	1.0	1.516	1.528	$20\bar{2}3$	6
30.20	2	1.3	1.368	1.372	$10\bar{1}5$	6
			1.368	1.372	$12\bar{3}2$	12
31.76	.25	0.2	1.30	1.305	$10\bar{1}0$	3
33.08	.25	1.0	1.25	1.268	$12\bar{3}3$	12
35.54	.5	0.3	1.167	1.165	$20\bar{2}5$	6

The above values give an axial ratio of 1.62 in good agreement with the crystallographer's value of 1.617.[1] An hexagonal lattice of close packed spheres has an axial ratio of 1.633. The data from the photograph seem to indicate that 1.62 is a more probable value than 1.633 for the structure of ice. This ratio and the dimensions of the elementary prism were determined by means of a set of graphs, made by Dr. Hull and Dr. Davey, which is to be published shortly.

Estimating ρ the density of ice at liquid air temperature as $\rho = .944$, the number N of molecules of H_2O per cubic centimeter may be calculated.

$$N = \frac{\rho(6.023) \times 10^{23}}{18} = 3.154 \times 10^{22}.$$

The volume V of the elementary prism may also be found, knowing that a the base and h the height of the prism are 4.52 Å. and 7.32 Å. respectively.

$$V = \frac{\sqrt{3}a^2h}{4} = 0.6478 \times 10^{-22} \text{ c.c.}$$

The number n of H_2O molecules per unit prism is then equal to the product VN.

$$n = VN = 2.04.$$

Ice belongs then very nearly to one of the two alternate arrangements which inelastic uniform spheres may assume if packed as closely as

[1] Gmelin Kraut, Handbuch der Anorganischen Chemie, Heidelberg, Vol. I, 1, p. 107 (1907).

possible. This is the same form that magnesium atoms take. If the molecules of ice and the atoms of magnesium were identical in arrangement and form, not only would the plane spacings be proportional but also the intensities of the lines would be similar. From columns 2 and 3 of the table it may be seen that the intensities are not proportional. With increased knowledge of crystal structure these data may furnish information regarding the shape of the molecule of water. With the hexagonal close packed type of lattice each prism contains on the average one molecule. The result calculated above indicates that in ice crystals the molecules of water are of the form $(H_2O)_2$ or H_4O_2.

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