Journal of Inclusion Phenomena **4** (1986), 235–240. © 1986 *National Research Council of Canada.*

Structure of Oxygen Clathrate Hydrate by Neutron Powder Diffraction★

J. S. TSE★★, Y. P. HANDA, and C. I. RATCLIFFE
Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9

and

B. M. POWELL
Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada K0J 1J0

(Received: 8 November 1985; in final form: 2 May 1986)

Abstract. Oxygen hydrate was prepared by reacting oxygen with deuteriated ice at high pressure. Its structure was examined with powder neutron diffraction. It was found to crystallize in the cubic space group $Fd\bar{3}m$ with $a = 17.070(1)$ Å. The formation of the type II structure rather than type I can be attributed to the larger Langmuir constant of sorption for the oxygen molecules in the 12-hedral cages. The encaged oxygen molecules are orientationally disordered. A comparison of the oxygen thermal parameters in both cages suggests the existence of local potential minima in the 16-hedral cages.

Key words: Hydrate, oxygen, structure, neutron, diffraction.

1. Introduction

It was shown in the mid-1950's by von Stackelberg that water clathrates can crystallize in two distinct crystallographic structures [1]. Both structures have cubic unit cells. The first structure (Type I) belongs to space group $Pm\bar{3}n$ [2,3]. It is built up from a network of hydrogen-bonded water molecules forming 2 pentagonal dodecahedra (12-hedra) and 6 tetrakaidecahedra (14-hedra) per unit cell [4,5]. The second structure (Type II) has a larger unit cell and belongs to space group $Fd\bar{3}m$ [6]. It contains 16 pentagonal dodecahedra and 8 hexakaidecahedra (16-hedra) per unit cell [7].

It has generally been thought [8] that molecules with van der Waals diameter up to about 5.8 Å, which can fit into the 14-hedra, form structure I hydrates whereas larger molecules, which can fit into the 16-hedra, form structure II. However, Holder and Manganiello argued [9], on the grounds of maximal intermolecular interaction, that clathrate hydrates of *very small* guests should be more stable in the structure II form than in the structure I form. This prediction was recently substantiated when neutron and X-ray diffraction studies showed that both argon and krypton hydrates exist in the structure II form [12].

This situation can be explained in terms of the solid solution thermodynamic theory [10, 11]. The theory suggests that structure I hydrates are formed only when the size of the guest is less than 5.8 Å but sufficiently large such that occupation of the 14-hedra is favoured over the 12-hedra. If the size of the guest is very small and the latter requirement no longer holds, structure II with its more numerous 12-hedra has greater stability than structure I.

★ Published as NRCC 25940.

★★ Author for correspondence.

In a previous structural study [12], it was established that both argon and krypton form structure II hydrates and methane forms a structure I hydrate. These observations have an important consequence. Since the effective van der Waals diameter of methane is only about 0.5 Å larger than krypton, the structural difference of their hydrates indicates a delicate interplay between stability of the crystal types and the size of the guests. Oxygen has a molecular size intermediate between krypton and methane and its hydrate requires higher pressure for stability. A knowledge of the structure is pertinent to further the understanding of the relative stability of the two types of hydrates.

The preparation of oxygen hydrate was first reported in 1960 by van Cleeff and Diepen [13] though the possibility of its existence had been suggested by von Stackelberg [14] and Platteeuw and van der Waals [15]. In 1897, Villard [16] formed a solid compound by pressurizing an aqueous solution of iodine with oxygen to 330 bar at 281 K and may have prepared the oxygen hydrate itself for the first time. The natural occurrence of air hydrate (a mixed hydrate of oxygen and nitrogen) in deep Antarctic ice was proposed by Miller [17] and later confirmed by Shoji and Langway [18] and Nakahara *et al.* [19]. The occurrence of air hydrate in the earth's upper atmosphere has also been proposed [20]. The swimbladder of some deep-sea fish is also expected to contain oxygen hydrate [21].

2. Experimental Techniques

2.1. PREPARATION OF O_2 HYDRATE

D_2O was obtained from MSD Isotopes, Montreal and contained 99.8 atom % deuterium. Oxygen was obtained from Air Products and Chemicals Inc. and had a specified purity of 99.9%. Hydrate was prepared by grinding ice in the presence of oxygen in a Parr reaction vessel at 243 K for three days. At the completion of the reaction, the oxygen pressure in the vessel was 138 bar, almost three times as high as the dissociation pressure of about 48 bar at 243 K extrapolated from the work of van Cleeff and Diepen [22]. A large excess of oxygen was used to ensure complete enclathration. At the end of the reaction, the vessel was cooled to liquid nitrogen temperature and the hydrate recovered at 1 bar and stored in liquid nitrogen.

2.2. NEUTRON DIFFRACTION

Elastic neutron diffraction measurements on O_2 deutero-hydrate were made on the C5 spectrometer operated in a two-axis mode at the NRU reactor, Chalk River. A powdered hydrate sample was pressed at close to liquid nitrogen temperature into an aluminium sample holder. The holder was then loaded into a cryostat maintained at liquid helium temperature. The monochromator was Si(111) and the neutron wavelength was 2.2238 Å. A sapphire filter was placed in the incident beam to reduce the background. Restricted by the geometry of the sample holder, the accessible scattering angle range was limited to 70°. The data were analyzed with the Rietveld technique [23, 24]. In this method, the Debye–Scherrer peaks are fitted with Gaussian functions. Structural parameters, such as atom positions, temperature factors and cage occupancy of the guests, are treated as the variables in the least-squares minimization. A total of 26 Debye–Scherrer peaks were used in the structural refinement.

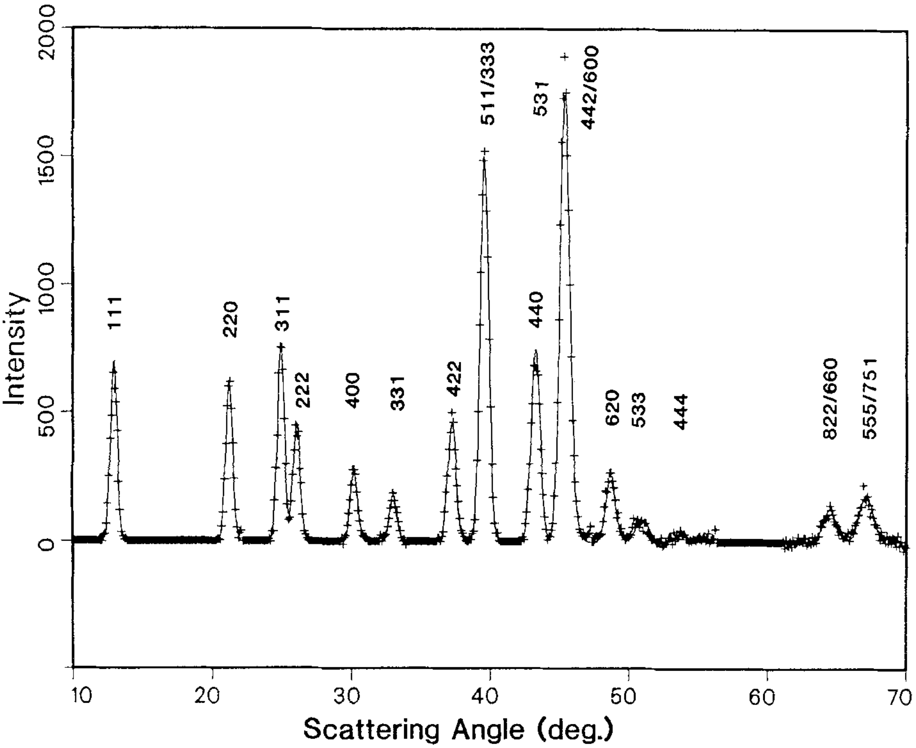

Fig. 1. The neutron powder diffraction pattern for oxygen deuterio-hydrate.

3. Structural Refinement

The neutron diffraction pattern of the D_2O/O_2 hydrate at 5.7 K is shown in Figure 1. All the observed peaks can be indexed on the space group $Fd\bar{3}m$ except for three weak peaks between 58 and 60° which arise from the presence of a small quantity of hexagonal ice. These peaks have been suppressed in the analysis. Refinement of the unit cell lattice parameters converged rapidly to 17.070(1) Å. The initial structure factors were calculated from the published positional parameters for the hydrogen sulphide-tetrahydrofuran hydrate [7]. The thermal parameters B were set to 0.6 Å^2 for the water oxygen atoms and 1.6 Å^2 for the deuterium atoms. This choice of thermal parameters is suggested by previous neutron studies of D_2O ices under similar conditions [25]. The encaged oxygen molecule was treated as two overlapping oxygen atoms in the refinement. Its position was fixed at the center of the respective 12-hedral (16c) and 16-hedral (8*b*) cages. It is expected that the oxygen molecules are orientationally disordered. To account for this distribution, their thermal parameters were set to 5.0 Å^2. One cycle of least-squares refinement on the scale factor led to an agreement index R of 26.2. Successive refinements of the occupancy and thermal parameter of the enclathrated oxygen lowered R to 13.2. Refinement of the water oxygen positions alone did not lead to any significant improvement. All the positional parameters were then allowed to vary. However, the refinement converged to an unrealistic occupancy for the oxygen in the large cages. Therefore, the occupancy of the oxygen in the large cages was constraint to 1.0. Several cycles of full matrix isotropic refinement were performed until the shifts in the variables were less than 0.3 σ. The final cycle involved 18 variables and converged to a R factor of 6.9. The

Table I. Structural parameters for oxygen hydrate at 5.7 K[a,b]

Atom	Site	x	y	z	Occupancy	B (Å^2)
O	8*a*	0.875	0.875	0.875	1.0	0.6
O	32*e*	0.784(6)	0.784(6)	0.784(6)	1.0	0.6
O	96*g*	0.815(5)	0.815(5)	0.635(14)	1.0	0.6
D	32*e*	0.801(6)	0.801(6)	0.801(6)	0.5	1.6
D	32*e*	0.844(2)	0.844(2)	0.844(2)	0.5	1.6
D	96*g*	0.796(5)	0.796(5)	0.723(5)	0.5	1.6
D	96*g*	0.810(7)	0.810(7)	0.663(9)	0.5	1.6
D	96*g*	0.864(5)	0.864(4)	0.632(3)	0.5	1.6
D	192*i*	0.843(10)	0.986(8)	0.149(12)	0.5	1.6
O′	16*c*	0.000	0.000	0.000	0.80(3)	2.8(2.8)
O″	8*b*	0.375	0.375	0.375	1.0	6.8(4.0)

[a] The origin is at centre ($\bar{3}m$).
[b] Estimated standard deviation given in parenthesis.

resulting structural parameters are listed in Table I. Owing to the limited range of diffraction data and the problem with disordering of the oxygen molecules, the standard deviations associated with the variables are fairly high. The difficulty inherent in the refinement of proton and deuterium disordered solids also adds to the uncertainty in the oxygen positions [26]. An accurate treatment requires precise diffraction data extending to higher scattering angles (smaller d spacing) and a more elaborate model to describe the disordered deuterium atoms and the enclathrated oxygen molecules. As a check on the unusually large thermal parameter for oxygen in the large cage, we have repeated the refinement employing a conventional least-square program using the intensities extracted from the neutron diffraction profile and treating the oxygen molecule as a freely rotating group [7]. The effective scattering length for the oxygen molecule is approximated by $b = b_0 \sin\phi/\phi$ where $\phi = 4\pi r \sin\theta/\lambda$ with r equal to 0.6 Å [30]. This treatment did not alter the previous results to any extent. The thermal parameter derived for the oxygen resides in the large cage remains much larger than that in the small cage.

4. Discussion

The main features of the hydrogen-bonded water network in the O_2 hydrate are the same as those in the tetrahydrofuran—H_2S hydrate [7]. There are only slight differences in the bond lengths and bond angles. The O···D—O bond distances range from 2.7(2) to 2.8(3) Å. A similar distribution of the hydrogen-bond distances was also observed in the tetrahydrofuran hydrate [7]. Except for the oxygen atom situated at symmetry position (8a), the O—O—O angles show a slight distortion from ideal tetrahedral values. The angles of the type O···D—O—D···O vary between 107(5) and 120(9). However, considering the limited accuracy of our data, it is difficult to assess whether the opening of the O—O—O angle in O_2 hydrate is of real significance.

One of the factors which determines the stability of a hydrate is the degree of occupancy of the cavities [10, 11]. Structure II is more stable when the guest is small and the Langmuir constants of adsorption (a measure of the strength of encagement interaction) are similar for both the small and the large cages. The free diameters are about 5.0 and 6.6 Å for the small and large cages in structure II hydrates, respectively. The molecular diameter of an oxygen molecule is small enough (4.2 Å [8,27]) for it to fit comfortably in both types of cages. Employing van der Waals' solid solution theory with a reasonable choice of oxygen–water interaction potential [10], we estimate that the Langmuir constants for sorption at 273 K are 846 and 350 MPa^{-1} for the small and large cages respectively. From the experiment, we derived an 80% occupancy of the small cages but full occupancy of the large cages. It is interesting that the occupancy of the 12-hedral cages is slightly less than the 16-hedral cages even though occupation of the small cages has a higher encagement energy. Moreover, in O_2 hydrate the number of small cages occupied per water molecule of 0.09 ($16 \times 0.8/136$) is still much higher than that in the structure I hydrate ($2/46 = 0.04$) even if all the small cages are filled. This extra stability favours the formation of the type II structure.

Another interesting observation is the large difference in the thermal parameters for oxygen enclathrated in the 12-hedral and the 16-hedral cages. The thermal parameter plays several roles in the refinement process. First, it allows for the thermal vibration of the oxygen. At the experimental temperature of 5.7 K, this motion is expected to be very small. Second, it compensates for the random orientation of the oxygen molecules. It also partially compensates for the error introduced in neglecting the actual molecular shape (i.e., when the oxygen molecule is represented by two overlapping oxygen atoms). The thermal parameter of an atom is related to its root-mean-square displacement (u) by $B = 8\pi^2u^2$ [28]. The average B value for the small cage is 2.8(2.8) Å^2. This can be converted into a vibration amplitude of 0.2(1) Å. Since the equilibrium bond length of an isolated oxygen molecule is 1.20 Å [29], the small root-mean-square amplitude reflects the lack of motion of the oxygen, and indirectly suggests that the center of mass of the oxygen molecules, on the average, are located at the center of the 12-hedral cages. In contrast, the root-mean-square amplitude in the 16-hedral cages is much smaller. The large amplitude motion (0.9(3) Å) suggests that the oxygen molecules are free to wander within the clathrate cages. The average position of the center of mass may not be situated at the center of the large cage even though the crystal symmetries require the statistical distribution should be symmetrical. It is likely that maximal interaction between the oxygen and the surrounding water molecules may displace the oxygen from the center.

References

1. M. von Stackelberg and H. R. Müller: *Z. Elektrochem.* **58**, 25 (1954).
2. M. von Stackelberg: *Naturwiss.* **36**, 327, 359 (1949).
3. M. von Stackelberg: *Naturwiss.* **39**, 20 (1952).
4. R. K. McMullan and G. A. Jeffery: *J. Chem. Phys.* **42**, 2725 (1965).
5. F. Hollander and G. A. Jeffery: *J. Chem. Phys.* **66**, 4699 (1977).
6. M. von Stackelberg and H. R. Müller: *Naturwiss.* **38**, 456 (1951).
7. T. C. W. Mak and R. K. McMullan: *J. Chem. Phys.* **42**, 2732 (1965).
8. D. W. Davidson: *Water – A Comprehensive Treatise*, (Ed. F. Franks), Plenum Press, New York (1973).
9. G. D. Holder and D. J. Manganiello: *Chem. Eng. Sci.* **37**, 9 (1982).
10. J. H. van der Waals and J. C. Platteeuw: *Adv. Chem. Phys.* **2**, 1 (1959).
11. D. W. Davidson, S. K. Garg, S. R. Gough, Y. P. Handa, C. I. Ratcliffe, J. S. Tse, and J. A. Ripmeester: *J. Incl. Phenom.* **2**, 231 (1984).
12. D. W. Davidson, Y. P. Handa, C. I. Ratcliffe, J. S. Tse, and B. M. Powell: *Nature* **311**, 142 (1984).
13. A. van Cleeff and G. A. M. Diepen: *Recl. Trav. Chim. Pays-Bas* **79**, 582 (1960).
14. M. von Stackelberg: *Z. Elektrochem.* **58**, 104 (1954).
15. J. H. van der Waals and J. C. Plateeuw: *Mol. Phys.* **1**, 91 (1958).
16. P. Villard: *Ann. Chim.* **11**, 289 (1897).
17. S. L. Miller: *Science* **165**, 489 (1969).
18. H. Shoji and C. Langway: *Nature* **298**, 548 (1982).

19. J. Nakahara, Y. Shigesato, A. Higashi, and C. C. Langway Jr.: *Proc. IXth Int. Conf. Raman Spectroscopy*, p. 624, Tokyo (1984).
20. S. L. Miller: *Proc. Nat. Acad. Sci. (U.S.)* **47**, 1798 (1961).
21. E. A. Hemmingsen: *Deep Sea Res.* **22**, 145 (1975).
22. A. van Cleeff and G. A. M. Diepen: *Recl. Trav. Chim. Pays-Bas* **84**, 1085 (1965).
23. H. M. Rietveld: *J. Appl. Crystallogr.* **2**, 65 (1969).
24. A. W. Hewat: *J. Phys.* **C6**, 2559 (1973).
25. W. F. Kuhs, J. L. Finney, C. Vettier, and D. V. Bliss: *J. Chem. Phys.* **81**, 3612 (1984).
26. J. D. Jorgensen and T. G. Worlton: *J. Chem. Phys.* **83**, 329 (1984).
27. J. E. Huheey: *Inorganic Chemistry*, 2nd edn., p. 232, Harper and Row, New York (1977).
28. G. H. Stout and L. H. Jensen: *X-ray Structure Determination*, MacMillan, Toronto (1968).
29. K. P. Huber and G. Herzberg: *Molecular Spectra and Molecular Structure*, Vol. 4, Van Nostrand–Reinhold, New York (1979).
30. R. W. James: *The Optical Principles of the Diffraction of X-rays*, G. Bell, London (1962).