

are somewhat larger than the effective radius of the water molecule (1.40 Å) and some distortion of the local structure would accompany substitution. Each substitution would tend to inject up to 2 D defects into the lattice. Such a mechanism of defect formation would account for the unexpected breadth of the dispersion loci and for its large temperature dependence (last section), as well as for the differences between the activation energies and entropies of the two hydrates. It is consistent with the volumes of activation.

It is instructive to compare the effect of impurities, including air, on the relaxation of ice I. For "slightly impure" ice, $\log \tau$ vs. $1/T$ plots show curvature toward decreasing slopes at low temperatures in both dielectric (11) and spin-lattice (28, 29) relaxation time measurements. In the dielectric case, additional absorption appears at relatively high frequencies to broaden the dispersion loci. Impurities clearly act as sources of orientational defects, the effect of which is not purely local since the whole relaxation spectrum is shifted to higher frequencies. At low enough temperatures defects so originating outnumber those arising intrinsically in ice and the activation energy and entropy become appreciably smaller.

Since argon and nitrogen hydrates have nearly the same relaxation times as ice I at 0 °C, about the same fraction of normal bonds is converted to defects, i.e. about 3×10^{-7} . The impurity-induced defects must be more numerous than the intrinsic defects or the activation energy would be temperature dependent.

This semiquantitative discussion has neglected the differences between the different "ice" structures and between the D and L defects, and is by no means complete. It does, however, serve to explain in a general way the dielectric behavior.

The lattice impurity mechanism suggested for argon and nitrogen hydrates would not be expected to determine the rate of defect formation in the hydrates of much larger molecules which would substitute with more difficulty. Relaxation in SF₆ hydrate is considered in the following paper (25).

Acknowledgments

We are indebted to R. E. Hawkins for help in the construction of the cell and to A. Lavergne for installation and maintenance of the high-pressure equipment.

1. R. P. AUTY and R. H. COLE. *J. Chem. Phys.* **20**, 1309 (1952).
2. R. K. CHAN, D. W. DAVIDSON, and E. WHALLEY. *J. Chem. Phys.* **43**, 2376 (1965).
3. G. J. WILSON, R. K. CHAN, D. W. DAVIDSON, and E. WHALLEY. *J. Chem. Phys.* **43**, 2384 (1965).
4. E. WHALLEY, D. W. DAVIDSON, and J. B. R. HEATH. *J. Chem. Phys.* **45**, 3976 (1966).
5. G. A. JEFFREY and R. K. MCMULLAN. *In Progress in inorganic chemistry*. Vol. 8. Edited by F. A. Cotton. Interscience Publishers, New York, 1967.
6. D. W. DAVIDSON, M. M. DAVIES, and K. WILLIAMS. *J. Chem. Phys.* **40**, 3449 (1964).
7. G. J. WILSON and D. W. DAVIDSON. *Can. J. Chem.* **41**, 264 (1963).
8. D. W. DAVIDSON and G. J. WILSON. *Can. J. Chem.* **41**, 1424 (1963).
9. R. E. HAWKINS and D. W. DAVIDSON. *J. Phys. Chem.* **70**, 1889 (1966).
10. A. VENKATESWARAN, J. R. EASTERFIELD, and D. W. DAVIDSON. *Can. J. Chem.* **45**, 884 (1967).
11. D. W. DAVIDSON. Unpublished work.
12. R. K. MCMULLAN and G. A. JEFFREY. *J. Chem. Phys.* **42**, 2725 (1965).
13. D. R. MARSHALL, S. SAITO, and R. KOBAYASHI. *A.I.Ch.E. J.* **10**, 202, 723 (1964).
14. A. VAN CLEEFF and G. A. M. DIEPEN. *Rec. Trav. Chim.* **79**, 582 (1960); **84**, 1085 (1965).
15. A. D. POTTS and D. W. DAVIDSON. *J. Phys. Chem.* **69**, 996 (1965).
16. W. SCHROEDER. *Ahren's Sammlung Chemischer und Chemisch-technischer Vortrage*, **29**, 1 (1926).
17. K. S. COLE and R. H. COLE. *J. Chem. Phys.* **9**, 341 (1941).
18. A. MICHELS, C. A. TEN SELDAM, and S. D. J. OVERDIJK. *Physica*, **17**, 781 (1951).
19. A. MICHELS, A. JASPERS, and P. SANDERS. *Physica*, **1**, 627 (1934).
20. C. J. F. BÖTTCHER. *Theory of electric polarization*. Elsevier Publishing Co., New York, 1952, p. 318.
21. J. E. BERTIE and E. WHALLEY. *J. Chem. Phys.* **46**, 1271 (1967).
22. L. D. CALVERT. Private communication.
23. M. VON STACKELBERG and W. JAHNS. *Z. Elektrochem.* **58**, 162 (1954).
24. D. F. SARGENT and L. D. CALVERT. *J. Phys. Chem.* **70**, 2689 (1966).
25. Y. A. MAJID, S. K. GARG, and D. W. DAVIDSON. *Can. J. Chem.* This issue.
26. N. BJERRUM. *Kgl. Danske Videnskab. Selskab Mat. Fys. Medd.* **27**, 3 (1951).
27. H. GRÄNICHNER. *Physik Kondensierten Materie*, **1**, 1 (1963).
28. K. KUME. *J. Phys. Soc. Japan*, **15**, 1493 (1960).
29. D. E. BARNAAL. Ph.D. Dissertation, University of Minnesota, Minneapolis, Minnesota, 1965. University Microfilms 65-7867, Ann Arbor, Mich.