relatively difficult, as with hydrogen chloride, then the more stable product, IV, is formed from minor proportions of the less stable[4] but more reactive radical, III. (3) When radicals like II and III contain several halogen atoms,[5] their stabilities and reactivities are altered. (4) Free radical-chain additions of hydrogen chloride to 1-alkenes cannot give high proportions of primary chlorides because of rearrangements such as reaction 1. (5) Reported proportions of primary chlorides in such additions[3] (12% with propylene, 24% with *t*-butylethylene, 30% with allyl chloride) may be, or approach, equilibrium mixtures of monohalides and the highest proportions of primary halides theoretically attainable by addition of hydrogen chloride. (6) The structure of the allyl chloride-hydrogen chloride telomerization product[3] is now uncertain because of possible rearrangement. (7) In view of chain-branching due to hydrogen shifts in the free radical polymerization of ethylene, the telomerization of ethylene with hydrogen chloride cannot give exclusively primary chloride, although the proportion of this may be higher than in 1:1 addition. (7) Rearrangement of alkyl bromides need not always involve complete elimination and readdition of hydrogen bromide.[2]

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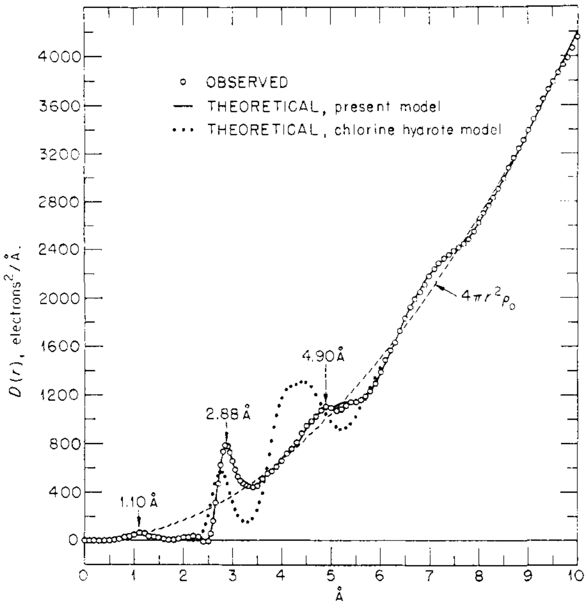
## THE STRUCTURE OF WATER AT ROOM TEMPERATURE

*Sir:*

Many reports on theoretical and experimental studies of the structure of water, although differing in basic conclusions, have made considerable contribution to an understanding of its properties. We present a preliminary report on an X-ray diffraction study undertaken in an attempt to consolidate results and remove conflicts from past studies.

The X-ray diffractometer used has been described briefly in previous publications.[1] MoK$\alpha$ radiation was monochromatized after scattering from the free surface of the sample. As the diffraction pattern showed interference throughout the observable range of the instrument (to $s_{\max} = (4\pi/\lambda) \sin \theta_{\max} = 16$, $\theta$ being half the scattering angle), the data are appreciably more extensive than the earlier ones.[2-11]

The radial distribution curve (Fig. 1) shows a well-resolved peak at 2.9 Å., followed by a minimum at 3.4 Å. and a broad region of scattering density rising to a barely resolved maximum at 4.9 Å. Thus, the nearest neighbors of a water molecule occur at an average distance about 5.5% greater than in ice, and others occur in considerable numbers in the intermediate region between the first and second neighbor distances of ice (2.75 and 4.50 Å., respectively). A distinct maximum at $r$ = 1.1 Å. is attributed to the closest O–H distance in $H_2O$. Any suitable model must clearly provide such a radial distribution while conforming to the proper density.



Radial Distribution, $H_2O$, 25°C.

**Figure 1.**

We have constructed a model, based on the normal ice structure as a point of departure, which fulfills both of these requirements; it proved capable of refinement by a least-squares procedure to give a remarkably close fit to the observed diffraction pattern.

The model consists of an ice-like framework in which each oxygen atom is tetrahedrally surrounded by other oxygen atoms, forming layers of puckered six-membered rings. Two adjacent layers, related by mirror symmetry, form polyhedral cavities with 12 vertices, point symmetry $\bar{6}m2$. The model is accommodated to the required density and distance spectrum by permitting some of the cavities to be occupied by "interstitial" water molecules and by permitting expansion of the framework from that occurring in ice. For simplicity, the model retains the hexagonal symmetry of the ice-like framework and restricts the position of the "interstitial" molecule to the triad axis; however, anisotropic expansion of the framework is permitted.

The initial agreement being promising, the model was subjected to systematic refinement by iterative non-linear least squares, in which the reduced intensity function was fitted to values derived from the measurements. The observational equations contained terms for all discrete distances in the model less than 10 Å. and a term for the scattering from a continuous medium beyond this distance. The usual "temperature factor"

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was included with each term to represent the effect of the variation of each distance. Three distances were treated as independent variables: the two near-neighbor O–O framework distances parallel and roughly perpendicular to the triad axis and the shortest distance from the interstitial oxygen atom to the framework. All other distances in the model (out to 10 Å.) were properly related to the foregoing. These three adjustable parameters, together with associated "temperature" coefficients, were sufficient to yield a good fit to all but the low-angle region of the intensity function; ultimately this region was also fitted well through the introduction of additional "temperature" coefficients associated with longer distances and adjustment of the distance characteristic of the start of the continuum. The calculations were performed on an IBM 7090 computer with a general least-squares program prepared by Busing and Levy,[12] suitably modified for the problem. The "occupancy" of cavities by interstitial molecules was constrained to that required for proper density.

Figure 1 compares observed and calculated radial distribution functions. Significant features of the refined model are the following: (a) each framework oxygen atom has one framework neighbor at 2.77 Å. and three framework neighbors at 2.94 Å. (b) Each interstitial oxygen atom has three framework neighbors at each of the distances 2.94, 3.30, 3.40 and 3.92 Å. (c) The ratio of framework molecules to interstitial molecules is 4.0, corresponding to filling 50% of the framework "cavities."

The present model is, in a sense, a clathrate, since it consists of a framework and a guest, the interstitial molecule. The qualitative distinction between framework and interstitial molecules is supported by a distinctly larger "temperature" coefficient associated with distances involving interstitials. This model, however, is not the clathrate model suggested by Pauling,[13] which is built of pentagonal dodecahedra and is based on the crystal structure of chlorine hydrate; its calculated radial distribution function, shown in Fig. 1, indicates the model to be inconsistent with our observations.

The observed radial distribution of Fig. 1 is in substantial agreement with that recently presented by Brady and Romanow,[4] and that reported earlier by Morgan and Warren,[3] except for greater resolution and detail present in the current results; these arise from the greater range of scattering angle in which interference was observed. The disagreement with the results of van Panthaleon van Eck and co-workers,[6] as pointed out by Brady, is thus confirmed.

Full details of this study will be reported elsewhere.

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[14] This paper is based upon work performed at Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the Atomic Energy Commission.

## THE STRENGTHS OF HYDROGEN BONDS FORMED BY PROTIUM AND DEUTERIUM

*Sir:*

The deuterium isotope effect in hydrogen bonding has been measured for the system fluoroform, tetrahydrofuran and cyclohexane. In this system only one type of hydrogen bond interaction is present, the hydrogen bond is linear, and no interference arises from dimers and polymers. The fluorine chemical shifts of fluoroform and fluoroform-*d* reflect their hydrogen bonding propensities.

Previous investigations[1–10] of the isotope effect in hydrogen-bonding have involved complicating factors including competing equilibria and the formation of large aggregates, and are reviewed elsewhere.[11]

Fluoroform was obtained from trifluoromethyl iodide and potassium hydroxide in acetone.[12] Fluoroform-*d* was prepared from potassium deuteroxide, trifluoromethyl iodide, and a solution of ethyl alcohol and ethyl alcohol-*d*. Fluorine n.m.r. indicated a mixture of 52% fluoroform-*d* and 48% fluoroform.

Fluorine n.m.r. spectra were observed at 56.45 Mc./sec. using 5 mm. o.d. sample tubes containing 14 cm. of solution and 2 cm. of dead space and thermostated to within ±0.3°. All chemical shifts, measured by the side-band technique with a standard deviation of approximately 0.003 p.p.m., were up-field from the reference, hexafluoro-2,2,3,3-tetrachlorobutane.

In Table I are presented the chemical shifts of fluoroform in solutions containing cyclohexane, 0.0096 mole fraction (m.f.) fluoroform, 0.0104 m.f. fluoroform-*d*, 0.049 m.f. hexafluoro-2,2,3,3-tetrachlorobutane, and various mole fractions of tetrahydrofuran. The decrease of the chemical shift of the reference with increasing temperature due to different populations of rotational isomers did not affect the results since the relative shifts at each temperature were employed.

The observed chemical shift, $\delta_{\text{obsd.}}$, can be represented by the equation[13,14]

$$\delta_{\text{obsd.}} = (C/A)(\Delta) + \delta_{\text{free}}$$

where $C/A$ is the ratio of moles of complex to initial moles of fluoroform, $\Delta$ is the "hydrogen bond shift" ($\delta_{\text{complex}} - \delta_{\text{free}}$) of the fluorine resonance and

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