Molecular Structure of Deeply Super-cooled Water

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have very ingin indicate that they are uniform (though groups of two different sizes might be a possibility), compact, and fairly highly symmetrical. This conclusion forces us to depart from one hitherto acceptable conclusion about hydrogen bonds. It has hitherto appeared that, if the oxygen atom be regarded as situated at the centre of a regular tetrahedron, two corners of which are occupied by covalently attached atoms (of hydrogen, in the case of water), it will act as acceptor of hydrogen bonds in the neighbourhood of the other two corners. But tetrahedrally distributed bonds lead inevitably to extrover associa-tion; for if any imaginary flat or convex boundary surface passes through the oxygen atom, at least one bond is directed outwards. For introvert association there must be at least some molecules accepting bydrogen bonds on the same hemisphere of the oxygen atom as its own hydrogen atoms, if all available hydrogen atoms are to take part in hydrogen bonds. Bach Ho0 molecule can act as donor in two and acceptor in two hydro-gen bonds: hence in seeking possible structures of the low-temperature complex molecule of water, we must consider groups of points each of which has four equidistant nearest neighbours. Such groups are the corners of the coronary polyhedra (having two opposite faces in the form of regular polygons, joined edge to corner by equilateral triangles). Of these the simplest and that which appears probable, therefore, that the complex molecule of water at temperatures below - 60° C, comprises six molecules of H₂O, with the oxygen atoms situated at the corners of a regular octahedron. The hydrogen bonds will be easily straight if the H₂O molecules lie in the planes of equatorial squares, with hydrogen atoms slightly outside the edges of the octa-hedron. Accompanying figures indicate the binding in such a plane, and show a ball-model representation of the structure. A prediction from this theory which might be tested is that the dielectric constant of supercooled water should pass thr



$$(H_2 O)_6$$

mum (perhaps in the neighbourhood of -40° , though the nature of water between this temperature and -20° is still largely unknown) and sink to relatively low values below -60° C. However, it is part of the argument that the modification of ice melting at -70° C. con-tains the same complex molecules, and as this modification can easily be obtained at least in powder form by sublimation below this tem-perature, diffraction analysis should suffice to confirm or deny the hypothesis.

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¹ Rau, W., Schrift. Deut. Akad. Luftfahrtforsch., 8 (ii), 65 (1944).

Infra-Red Spectrum and Molecular Structure of the Low-Temperature Polymer of Acetaldehyde

THE low temperature polymer of acetaldehyde was first described by Travers¹ and Letort². The structure suggested for it by Staudinger³ was a chain :

$$\begin{array}{ccc} \mathbf{CH}_{\mathtt{s}} & \mathbf{CH}_{\mathtt{s}} & \mathbf{CH}_{\mathtt{s}} \\ -\mathbf{CH} & -\mathbf{O} & -\mathbf{CH} &$$

 $\dots - CH - 0 - CH - 0 - CH - 0 - ...$ The formation of this polymer has been further investigated by Letort and Duval*, but so far little positive evidence has been given for Staudinger's proposed structure. In connexion with a study of the infra-red spectra of various acet-aldehyde polymers, this low-temperature polymer has been prepared by Travers's method and its infra-red spectrum examined between 2 and 15 mµ. Although the complete spectrum cannot be interpreted, the main features provide strong confirmatory evidence for the Staudinger structure. Thus the CH, group is presumably responsible for the strong band at 1375 cm.⁻¹, while the isolated CH group may be connected with the band at 1340 cm.⁻¹. There are also general resemblances between this spectrum and those of the simpler ring polymers, namely, paraldehyde and metaldehyde, containing the same repeating units. The only other likely structure would be one based on the enol form of acetaldehyde, such as OH OH OH

$$\dots - \begin{array}{c} OH \\ C \\ H \\ H \end{array} = \begin{array}{c} OH \\ C \\ - CH_2 \\ - C \\ H \\ H \end{array} = \begin{array}{c} OH \\ C \\ - CH_2 \\ -$$

This can be ruled out at once on infra-red evidence, as there is no sign of the characteristic OH absorption near $3 \text{ m}\mu$. Furthermore, the strong baud at 1375 cm.^{-1} would be very hard to interpret if the polyvinyl alcohol structure were correct. The disappearance of the CO group on polymerization is confirmed by the absence of character-istic carbonyl absorption near $5\cdot8 \text{ m}\mu$. A full discussion of this spectrum will be published elsewhere as part of the larger investigation referred to above. G. B. B. M. SUTHERLAND.

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² Letort, M., C.R. Acad. Sci., 202, 767 (1936).
³ Staudinger, A., Trans. Far. Soc., 32, 249 (1936).
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Flow of Water Through Very Narrow Channels

IN connexion with the flow of air and water through very narrow

In connexion with the flow of air and water through very narrow channels discussed recently', certain experiments which were con-ducted in our laboratories may be of interest³. In these experiments dry air was passed through highly impervious limestone and sandstone cylindrical specimens, and the necessary measurements of pressure, rates, temperatures, etc., taken. It was found that flow of air under such conditions exhibited certain anomalies which led us to believe that there is a sub-viscous regime of flow. The anomalies are, briefly: (1) The rate of flow (corrected for viscosity) is not linear with pressure, but at low rates follows a curve. (2) When the rate is increased, a straight line is obtained for the curve of rate of flow v. pressure, but this straight line does not pass through the origin upon extrapolating backward. (3) The permeability of a sample calculated from the flow of air was not constant but varied in a complex manner with the rate of flow. This is, of course, a cor-ollary of (1) above. These experiments with water and a queous solutions of various materials were also performed with a flne Jena glass filter. Again anomalies led us to postulate a sub-viscous regime. Whereas the flow with water and solutions showed linear relationship between rate and pressure—that is, constant permeability for the sample—the permeability obtained from different liquids was significantly different. Thus, we postulated that surface phenomena in narrow channels become magnified and affect the flow characteristics of the systems. On this basis, we applied dimensional analysis and derived the con-clusion that if in the sub-viscous regime surface as well as viscous and kinctic energies were involved, then the permeability of the system should be a function of a dimensionless group :