Molecular Structure of Deeply Super-cooled Water

RAU[1], working in Prof. Regener's laboratory, has succeeded in super-cooling liquid water to − 72° C., with a number of remarkable observations. In view of the relative inaccessibility of the publication at present, it will be well to summarize these before discussing them.

Rau's observations were made on droplets, up to a few millimetres in diameter, supported on highly polished surfaces of chromium or nickel. These metal plates were attached at one edge to a tube carrying cooling fluid, and were enclosed in a 5-litre closed chamber containing air saturated with water vapour, having provision for stirring, and all suspended in a low-temperature thermostat. The first series of experiments show that, in repeated freezing and melting of a given drop, crystallization commences repeatedly at a reproducible temperature, with a reproducible pattern of crystal growth from a single nucleus, but that after a while this nucleus loses its activity and on subsequent repetitions of melting and cooling, crystallization occurs, again reproducibly, at a lower temperature from a different nucleus : after a while, this nucleus becomes inactive in turn, and a further degree of supercooling becomes possible. On drying (partial evaporation of the drop uncovering some of the base surface), nuclei recover their activity. In short, the foreign bodies which, acting as crystallization nuclei, ordinarily prevent the supercooling of water to any great extent, can be rendered innocuous by the prolonged influence of liquid water in a saturated atmosphere, especially, it seems, with repeated freezing and thawing. Access of fresh air, bringing further foreign bodies, must of course be avoided.

Using this process for 'sterilization' of nuclei, Rau at length succeeded in cooling droplets condensed from the vapour down to − 72° C. At this temperature they invariably froze, with spontaneous formation of numerous nuclei throughout the drop. The resulting crystals are regular (usually octahedra, sometimes tetrahedra or cubes), and melt again to liquid at − 70° C. Below − 72° C., it is possible to demonstrate direct condensation of an ice fog (the same cubic modification, m.p. − 70° C.) in the air. The properties of the liquid are also of interest, as it appears that water largely loses its surface tension below the range − 50° to − 60° C. Droplets flatten below − 50° and commonly spread to a film by − 70° C. On warming, droplets separate again above − 60° and gradually resume their form. Less complete observations are reported on two other modifications of ice, of melting points − 40° C. (hexagonal plates) and − 55° C. (form not visible). By way of physico-chemical interpretation of these results, Rau makes no suggestions in detail except that the lowest-temperature form of ice (m.p. − 70° C.) may correspond to Bridgman's highest pressure form, ice VI.

The two strikingly unusual facts about this case are the pronounced reduction of surface tension, and the appearance of a crystal form of high symmetry as a low-temperature modification. The high surface tension of water at ordinary temperatures is undoubtedly attributable to hydrogen bonding between H_2O molecules (as indeed is the existence of water and ice as liquid and solid at temperatures at which H_2S is a gas). There can be no question of this bonding becoming weaker at low temperatures. The only possible explanation must be that 'extrovert' association, extending throughout the substance, gives place to 'introvert' association in which the hydrogen bonds are saturated in closed molecular groups, which behave virtually as complex molecules attracted to each other only by Van der Waals forces. The low melting point indicates that the complexes cannot have very high molecular weights ; and the regular crystal form and easy crystallization 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 extrovert association ; 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 hydrogen 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.

Each H_2O molecule can act as donor in two and acceptor in two hydrogen 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 best to satisfy all the requirements is the regular octahedron. It appears probable, therefore, that the complex molecule of water at temperatures below − 60° C. comprises six molecules of H_2O, with the oxygen atoms situated at the corners of a regular octahedron. The hydrogen bonds will be nearly straight if the H_2O molecules lie in the planes of equatorial squares, with hydrogen atoms slightly outside the edges of the octahedron. 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 through a maxi-
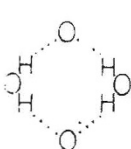
$(H_2O)_6$
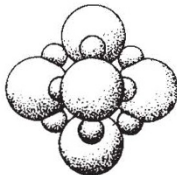
mum (perhaps in the neighbourhood of − 40°, though the nature of water between this temperature and − 20° is still largely unknown) and sink to relatively low values below − 60° C. However, it is part of the argument that the modification of ice melting at − 70° C. contains the same complex molecules, and as this modification can easily be obtained at least in powder form by sublimation below this temperature, diffraction analysis should suffice to confirm or deny the hypothesis.

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        Oct. 9.

[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 Travers[1] and Letort[2]. The structure suggested for it by Staudinger[3] was a chain :

$$ \cdots - \underset{\underset{CH_3}{|}}{CH} - O - \underset{\underset{CH_3}{|}}{CH} - O - \underset{\underset{CH_3}{|}}{CH} - O - \cdots $$
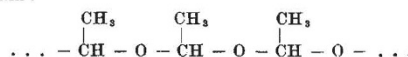
The formation of this polymer has been further investigated by Letort and Duval[4], but so far little positive evidence has been given for Staudinger's proposed structure.

In connexion with a study of the infra-red spectra of various acetaldehyde 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_3 group is presumably responsible for the strong band at 1375 cm.$^{-1}$, the − C − O − C linkages for a strong group of bands near 1100 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

$$ \cdots - \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}} - CH_2 - \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}} - CH_2 - \cdots $$
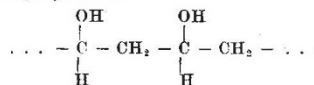
This can be ruled out at once on infra-red evidence, as there is no sign of the characteristic OH absorption near 3 mμ. Furthermore, the strong band at 1375 cm.$^{-1}$ would be very hard to interpret if the polyvinyl alcohol structure were correct. The disappearance of the CO group on polymerization is confirmed by the absence of characteristic carbonyl absorption near 5·8 mμ.

A full discussion of this spectrum will be published elsewhere as part of the larger investigation referred to above.

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    Dec. 19.

[1] Travers, M. W., Trans. Far. Soc., 32, 246 (1936).
[2] Letort, M., C.R. Acad. Sci., 202, 767 (1936).
[3] Staudinger, A., Trans. Far. Soc., 32, 249 (1936).
[4] Letort, M., and Duval, X., C.R. Acad. Sci., 216, 58 and 608 (1943).

Flow of Water Through Very Narrow Channels

IN connexion with the flow of air and water through very narrow channels discussed recently[1], certain experiments which were conducted in our laboratories may be of interest[2]. 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 corollary of (1) above.

These experiments are reported in greater detail in another paper[3], where experiments with water and aqueous solutions of various materials were also performed with a fine 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 conclusion that if in the sub-viscous regime surface as well as viscous and kinetic energies were involved, then the permeability of the system should be a function of a dimensionless group :