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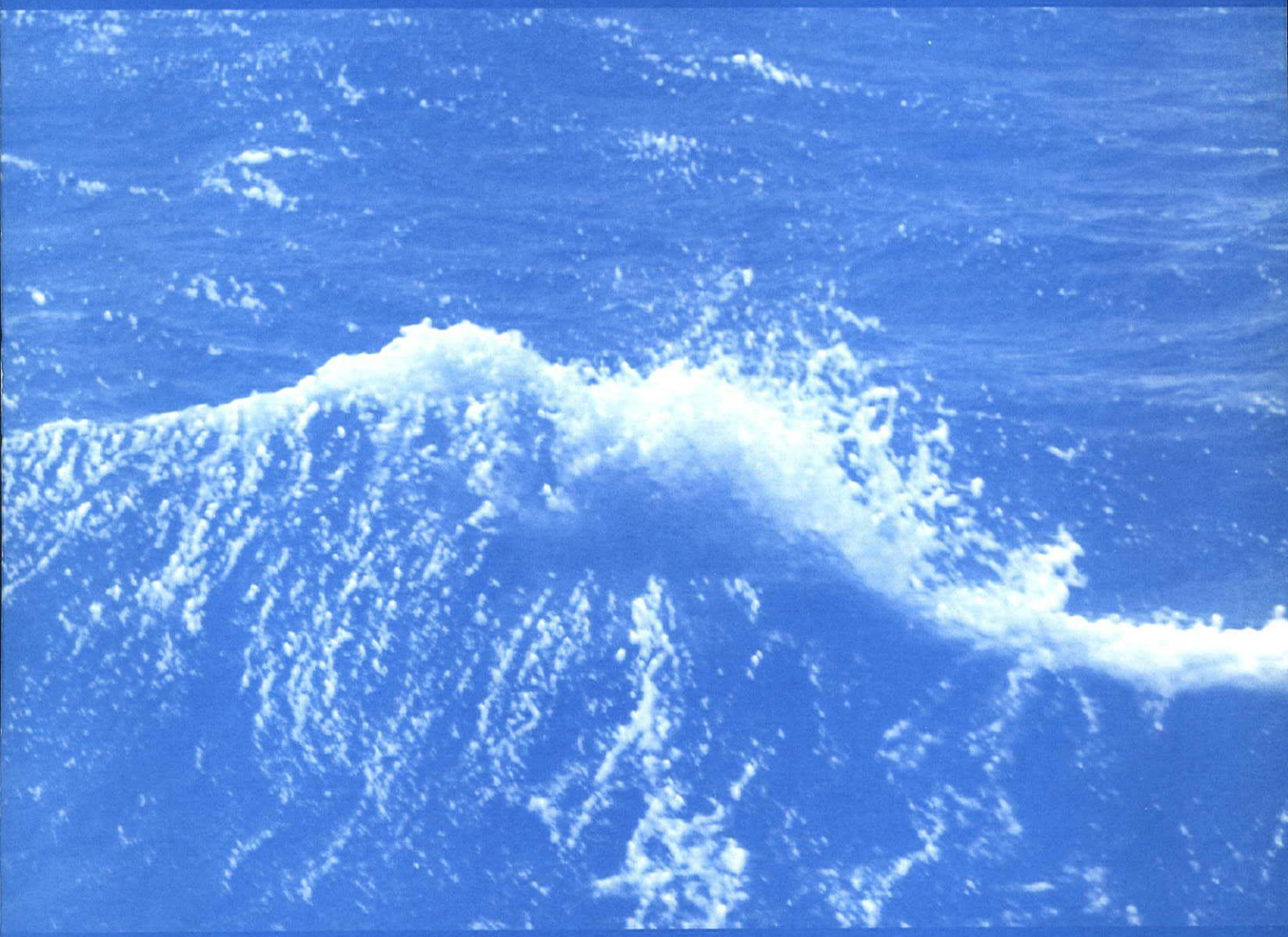

SCIENTIFIC SERIES NO. 18

INLAND WATERS DIRECTORATE,
WATER QUALITY BRANCH,
OTTAWA, CANADA, 1972.

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Introduction

In the early nineteen-sixties Dr. B.V. Deryagin of the U.S.S.R. observed that water vapor, when condensed in microscopic capillaries of freshly-drawn glass, produced a liquid which showed properties much different from those exhibited by water in bulk quantities. These properties included a high but ill-defined viscosity and density, a low, ill-defined freezing temperature, and phase separation at low temperatures. Because Deryagin could detect no impurities in his product and because he believed that the diameter of his capillaries was sufficiently large to neglect surface effects, it was proposed that a new phase of pure water – anomalous water – had been isolated.

Because of the potential importance of such a discovery, (anomalous water could be used to explain many things from biological processes in cold climates to percolation of groundwater), scientists around the world undertook to produce and describe anomalous water.

In the Water Science Laboratory it was decided that a program to produce larger quantities of this compound with an analysis of its composition and properties would best serve to prove or disprove its existence. Furthermore, with bulk quantities it would be possible to determine those regions in the water phase diagram in which it would be stable and to study the effects of such a compound as it would occur in the environment. Investigation of the nature of anomalous water was approached with an open mind. Experiment results, however, strongly indicate that anomalous water is primarily a solution of silicic acid and that its unique properties are attributable to the incorporated silicate.

This report takes the form of a bibliographical review which is followed by an account of the work (both theoretical and experimental) undertaken by this group into the subject of anomalous water. Briefly, this work includes molecular orbital calculations, experiments with glass capillaries, porous Vycor glass diffusion experiments and analyses of the products of these experiments. The review attempts to be comprehensive to the end of 1970, but later articles are included for completeness wherever possible.

Bibliographical Review

POPULAR AND REVIEW ARTICLES

There have been many articles published on the subject of the anomalous water of Deryagin and his co-workers, ranging from popular articles on the history of its production to detailed experimental descriptions and calculations to test the validity of the many proposed structures.

An example of the distorted reporting which has frequently accompanied this subject was the brief article in *Time* (1969). More serious scientific publications have also been guilty of publishing science-fiction stories; these include Donahoe's letter to *Nature* (1969) in which he reported fears that anomalous water might catalyse a transformation to Venus-like conditions on earth! Replies to Donahoe's letter were made in subsequent issues (Bernal *et al.*, 1969; Everett, Haynes and McElroy, 1969; Anderson, 1969).

Many other popular accounts of polywater have appeared in print, some of which are quite interesting in that they provide background information on polywater workers and early references to polywater-like material. An article in *Chemical and Engineering News* (1969) referred to Sheehan's 1939 work. He felt that repeated distillations of water in a platinum still would produce long-chain and cyclic polymers capable of being spun into fabrics ("aquaprene" and "hydrophane"). Edelstein (1969) recalled the early controversy on "Conversion of Water into Earth" by Van Helmont and described the pamphlet "A Curious Research into the Element of Water" by Ambrose and John Godfrey written in 1747. Lavoisier later (1770) proved that the brothers had obtained a solution of glass, not a true conversion of water to "earth". History may be repeating itself.

Perhaps the most readable of the popular review articles appeared in the *Saturday Review* (1969). This article reported Patrick's observation that a portion of water was unusually difficult to evaporate from silica gel. Included was Shereshefsky's study of the abnormally low vapour pressure of water in small capillaries (1928), the early Russian work of Chmutov, and Fedyakin's first report of "offspring water" in sealed capillaries (1961). Fedyakin's collaboration with Deryagin has accounted for most of the Soviet research into anomalous water. An explanation of the sudden interest of Western scientists in polywater enhanced the article.

A more scientific review article was written by Falk (1970). He both summarized recent research and indicated where contradictions occurred. In particular, he was unimpressed with Lippincott's infrared spectra of anomalous water and offered alternative explanations of bands at 1110, 1595 and 1400 cm^{-1}.

An excellent article summarizing existing technical information prior to 1970, was written by Thomsen (1970). More recently a review of structural proposals has appeared by Kamb (1971), who concluded his article by stating that it is important to examine the theoretical explanations of the properties of anomalous water for consistency with structural principles and with available evidence on the forces of interaction between water molecules. Unfortunately, from this point of view many of the proposed structures are unsatisfactory.

SOVIET WORK

Many papers on anomalous water have been written and presented at meetings by the corresponding member of the Academy of Sciences of the USSR, B.V. Deryagin. Throughout the controversy on polywater, this worker has adhered firmly to the opinion that a modified form of water exists. He first supported the work of Fedyakin in 1962 and was coauthor with Fedyakin of a paper later that year. Fedyakin (1962) carried out experiments to elucidate the behaviour of liquids in sealed capillaries. He described in his paper the condensation of films of liquid on the capillary wall; these films thickened and then formed "daughter" columns of liquid differing from the original liquid in bulk, in volume, expansion and vapour pressure. He suggested that the condensed liquid retained some of the characteristics it possessed as a film. After Fedyakin's closed capillary experiments, he and Deryagin (1962) produced anomalous liquids in open capillaries at greater than 93% relative humidity. They recorded that water and acetone condensates had unusually high viscosities, but found that normal viscosities were attained after passing the liquids several times back and forth through a section of a capillary. Higher viscosity returned after the liquids had been standing for 24 hours. They commented that a different saturation vapour pressure was indicated by the formation of "daughter" columns as described by Fedyakin (1962), and maintained their belief in an anomalous form of water. In later experiments by Anisimova, Deryagin and co-workers (1967), inorganic solutions were used as

sources of water vapour, since it was claimed an increased yield of anomalous condensate resulted when the vapour pressure of the source was lowered. A partial vacuum of 1-2mm Hg was also used as an experimental condition. The thermal expansion was observed and contrasted with that of saturated salt solutions and distilled water. More recently Deryagin and different coauthors have given further details of apparatus they have used (1969). They have also recorded the point of maximum density as occurring at a temperature below 0°C and the densities of some samples as being 1.35 gm/cm^3. There is reference to distillation of anomalous water, two-phase behaviour (β-phase suspended in an α-phase), and a hysteresis loop in the thermal expansion and contraction through the range $-55°$ to 0°C.

Another paper in the same year by Deryagin *et al.* (1969) evaluated the molecular weight of anomalous water by a cryoscopic technique. The β-phase seen below ~ -4°C is now considered to be solid.

In a long paper with Churaev (1968), Deryagin described firstly an experiment which subjected a thin layer of water between quartz plates to an oscillating frequency. Changes in viscosity supposedly due to greater structuring were retained for several days. The remainder of the report dealt with modified water prepared in glass capillaries. High viscosity, density increase, and high and low temperature behaviour were all cited. It is important to remember that all the stated properties were derived from measurements on quantities of about 10^{-5} to 10^{-6} grams. The current techniques are not adequate for handling and analyzing such quantities.

At first, Deryagin and co-workers were concerned with several liquids (1965). Experiments with quartz and glass capillaries (radius $\sim 1\mu$) in which the growth of condensed columns were observed, were conducted for various ratios of air pressure to liquid vapour pressure. It was concluded that a liquid phase of lower energy formed in the cases of water, acetone, methanol and acetic acid. No molecular or thermodynamic explanation was offered to account for the fact that if the anomalous phase is lower in energy, it has not nucleated ordinary water throughout nature.

Acetone cannot produce structures similar to those proposed for anomalous water since it is a non-hydrogen bonded substance. It is possible, in this case, that in the capillaries, surface reactions give rise to new compounds. For example, diacetone alcohol (4 hydroxy - 4 methyl - 2 pentanone) has been observed in acetone dried by 4Å molecular sieves (Adams, 1967). This compound would cause the lowered vapour pressure observed in the capillary-condensed acetone. In all the liquids examined, the presence of impurities or new compounds formed on the glass surface was not ruled out since no analytical investigations were attempted (Deryagin, Talaev and Fedyakin, 1965).

In a paper entitled "Formation of droplets of anomalous water on a flat quartz surface" (1968), Deryagin, Zorin and Churaev described droplets of less than 100μ formed by exposure of such surfaces to supersaturated water vapour followed by a long period of exposure to undersaturation. Fedyakin *et al.* (1965) examined the conductivity, evaporation and condensation of anomalous water and various salt solutions. Although the paper was fairly conclusive with regard to the low concentration of charged particles causing anomalous effects, it did not consider non-ionic species at all. A gel-like substance was observed, but the effect of such high viscosity on conductivity, evaporation and condensation was not discussed.

A discussion of the dependence of the aqueous vapour pressure on the concentration of the anomalous component in anomalous water was published in 1970 by Deryagin *et al.* They appeared to be so convinced of the existence of polywater that they did not identify a "granular structure" as anything other than "amorphous globules of completely modified water". They distilled water vapour onto and from "anomalous" water and observed changes in column length. These results were quite similar to the observation (by isopiestic measurements on a micro scale) of simple absorption of water molecules by a hygroscopic solution.

In a report given in 1970 to the 44th National Colloid Symposium in the United States, Deryagin sought to convince an increasingly skeptical body about the nature of anomalous water. Much of the report was a review of the earlier Russian work. Some explanations were rather dubious as, for example, his discounting the absence of high molecular weight fragments in mass spectroscopic analysis by assuming that all molecules degrade to monomers. Such a result is not consistent with the incomplete fragmentation invariably encountered during analysis of other polymers. Deryagin concluded by replying to criticisms of the impurities in his samples. He claimed that earlier organic contamination has now been excluded and that casual inorganic contaminants could not account for all the observed physical properties.

In a very recent review article (1970) Deryagin still maintained that "superdense water" was a polymerized form of water. Quartz, he pointed out, is soluble to only 0.02% in water, while anomalous water can be distilled with retention of properties.

WESTERN PROPONENTS

Certain Soviet scientists are not the only proponents of anomalous water. Perhaps the most frequently quoted among Western scientists who have taken this approach is E.R. Lippincott, who has been involved in the presentation of several papers on the subject. Among these scientists, Bellamy, Osborn, Lippincott and Bandy (1969) found that anomalous water retained its character on distillation and hence they considered contamination unlikely. It might be pointed out that some compounds of silicon and boron are capable of distillation. Lippincott and others (1969) reported the unique infrared and Raman spectra and coined

the term polywater from their interpretation of these spectra as indicating a high polymer of ordinary monomeric water molecules. A later report (1969) in *New Scientist* summarized the work reported in these two papers. Another *Science* article (Page, Jakobsen and Lippincott, 1970) referred to a proton magnetic resonance spectrum obtained on a micro sample of polywater in water; findings in this article were in agreement with Petsko's observation (1970) of a 300 Hz downfield shift. Lippincott's involvement with structures proposed for polywater will be discussed in Chapter 3.

SKEPTICS OF POLYWATER

Thus far we have considered mainly supporters of the existence of polywater or anomalous water. However, there have always been dissenters and these are becoming more numerous. In general, they believe the anomalous properties to be related to the presence of other materials in the water — most commonly products leached from the glass material essential to the formation of anomalous water.

Recently, many independent groups have detected significant amounts of cations in their anomalous water preparations. Kurtin and co-workers (1970), on the basis of dielectric constant measurements, suggested that anomalous water is a hydrosol of finely-divided particulate matter suspended in ordinary water. Goring and others (1970) have suggested that a component of silicone grease migrates spontaneously over glass and they point out that silicone grease is an ubiquitous component of ground glass apparatus.

Recent high-quality experimental studies using advanced analytical methods have shown that anomalous water samples prepared by non-Soviet workers are highly contaminated by cations or precipitated solid bodies. Rousseau and Porto (1970) found high concentrations (20%-60% sodium) of cations in anomalous water prepared in quartz capillaries. Rabideau and Florin (1970) found that a significant weight fraction of anomalous water residues consisted of sodium, boron and oxygen. Everett, Haynes and McElroy (1970) reported that the colligative properties of anomalous water were consistent with those of a silica gel.

The observation of solid bodies of various shapes, including both rough and smooth edges were made by Morariu, Mills and Woolf (1970) in anomalous water columns formed in Pyrex capillaries. These bodies were similar to those observed in anomalous water prepared in this laboratory, which contained 10 - 30% silicon (Adams *et al.*, 1971) (see experimental section). Further, Bascom, Brooks and Worthington (1970) found silicon and sodium in anomalous water condensates.

Cherkin (1969) also proposed that anomalous water was a silica dispersion, silicate being alkali-leached from structurally-anomalous locations on the glass surface. Hildebrand (1970) stated that if silica catalyzes polywater formation, it is difficult to understand why there is any ordinary water left on earth, since water and silica have been in contact for millions of years!

Studies by the new technique of electron spectroscopy for chemical analysis (ESCA) proved that there were many impurities and little water in the samples analysed (Davis, Rousseau and Board, 1971; *Chem. and Eng. News* 48, 1970). Similarities have been pointed out in the infrared spectra of polywater and human perspiration (Rousseau, 1971).

Luck and Ditter (1970) questioned the infrared spectroscopic results obtained by Lippincott *et al.* (1969). They found that the 1600 cm^{-1} region of the water spectrum was enhanced relative to the 3000 - 3500 cm^{-1} region when the spectra of water were recorded in capillaries instead of standard cuvettes. They suggested that Lippincott's spectra could be caused by a silica gel.

HIGH PRESSURE AND SURFACE EFFECTS

Several investigators have considered the high pressure effects present in the tiny curved capillary and the probable enhancement of the normal solubility of glass in water under these conditions.

Some experimentalists have attempted to produce polywater in bulk by high pressure experiments. In 1968 Bendeliani exposed water and quartz powder to pressures from 10 to 60 kbar without producing modifications in the water, although thermodynamic considerations would lead one to expect such changes. A later unsuccessful attempt was made by Wentorf (1970).

D'Ardenne (1970) proposed that polywater is formed as a result of high pressure in the coolant systems of nuclear reactors thus explaining an increased pH and 0.5% increase in reactivity; however, this report is very speculative.

O'Brien (1970) carried out experiments to show increased surface tension in small capillaries and thus, the greatly enhanced dissolving power of condensed water in such capillaries (*Chem. and Eng. News* 49, 1971). Critical comments on his work (Leinfelder, 1970) are refuted by him in a later paper (1970).

It is perhaps pertinent here to mention other studies of surface reactions which, though not directly concerned with polywater, may well have a bearing on its production in small capillaries or in the minute pores of porous glass. These references will be very relevent to the experimental section of this report.

Chapter 5 in "Physical and Chemical Aspects of Absorbents and Catalysts" by Okkerse refers to the basic

reactions involving the condensation of silicic acid in colloidal particles. A paper by Garbutt and Gesser (1970) describes the catalytic effect of heat-treated porous Vycor glass, including the chemistry of the surface molecules as indicated by electron spin resonance techniques. Another book which is of use in considering glass surface interactions and the properties of colloidal silicates is "The Colloid Chemistry of Silica and Silicates" by R.K. Iler (1955). A different approach is that of Drost-Hansen (1969) who emphasizes that water could take up new structures at considerable molecular distance from the surface of glass. He does not discuss surface leaching.

OTHER EXPERIMENTAL TECHNIQUES

An assortment of techniques has been used to investigate and produce polywater, some of which will be described here.

Willis *et al.* (1969), repeated Deryagin's preparations and obtained similar columns which they examined by mass spectrometric, infrared and NMR techniques, reporting only results consistent with normal water. Peel and Martin (1969) prepared samples which remained liquid to $-50^{\circ}C$. They were unable to obtain larger quantities of anomalous water by evaporation from sintered glass discs or silica powder. Everett *et al.* (1971) made a careful study of the possibility of impurities in their samples and noted some solid glass-like residues. They pointed out that the disordered structure of the quartz surface contributed to ready leaching. Mass spectroscopic evidence supporting the silica leaching theory was put forward by DePaz *et al.* (1970) in a very convincing paper.

An interference microscope was used to measure the refractive indices of polywater columns by Castellion *et al.* (1970). The inference was drawn that polywater condenses initially with an ordered structure. Shaw (1970) referred to 1941 experiments by Eversole and Lahr in which a thin layer of water was distilled between two quartz surfaces and the thickness determined by consideration of the Newton rings. The liquid has a refractive index within the range suggested for polywater solutions.

A new form of polywater was proposed by Middlehurst and Fisher (1970). In their experiments water was condensed between two copper fluoride flats but the properties and infrared spectrum differed slightly from those normally reported for polywater. Angell and Sare (1970) suggested that vitreous water might be polywater.

In a very detailed study, Prirogine and Thomaes (1969) observed the growth of droplets of polywater at the expense of water, or vice versa, in order to determine their relative vapour pressures at different temperatures.

Differential thermal analysis was used to examine polywater by David (1970). He reported a lower freezing point for samples than could be obtained with supercooled distilled water.

Several researchers have linked the water in biological tissues to polywater by claiming a higher degree of ordering than could otherwise be expected (*New Scientist* 42, 1969). These include Cope (1969) who worked with muscle and brain tissues, and Hazlewood (1969) who performed further NMR studies on muscle cells. Other forms of ordered water have also been ascribed to polywater. Thus, Low and White (1970) noted similarities in the properties and I.R. spectra to those of clay-absorbed water. Glass and Graf (1970) studied water associated with proteins and found a high degree of ordering. They used a technique of γ-ray directional correlations. Leiga, Vance and Ward (1970) made an unsuccessful attempt to produce polywater in a gas discharge.

SPECIAL PUBLICATIONS AND MEETINGS

In addition to the publications quoted in this report, there have been many other papers presented at meetings and as internal research reports. A brief mention will be made of some of these.

A session of the 44th National Colloid Symposium held at Lehigh University in 1970 was devoted to anomalous water (1971). Deryagin gave the introductory lecture and many other well-known workers in the field gave talks at the session. A report (Zhirbilis, 1969) of a question session with B.V. Deryagin and other Soviet scientists and co-workers was given. It was apparent that Deryagin's water II had met with much skepticism in the Soviet Union.

Among the internal reports which have been obtained by this group are a series by Brummer *et al.* of Tyco Laboratories. These reports indicate that a very careful study was made of the conditions under which maximum yields of polywater were obtained, proving, for example, that temperature fluctuations are important. The latest communication was a preprint of a paper submitted to *Science* (Brummer *et al.*) entitled "A high-yield method for the preparation of anomalous water"; the method involved the use of flame-tapered glass tubes.

STRUCTURAL PAPERS

While many scientists debate the existence of polywater, others attempt to determine its structure. Kamb (1971), has critically reviewed several structural models.

The first proposal from Bellamy *et al.* (1969) was based on the evidence of their unique Raman and little-supported infrared spectrum. They deduced that there are few terminal O-H bonds, and that the majority of the hydrogen atoms are symmetrically placed between adjacent oxygens, which are separated by 2.30 Å. Of the several

structures proposed in this paper, the planar six-membered oxygen ring shown in Figure 1 was the most popular. There is little evidence for this structure, although a later paper by Bates *et al.* (1970) applied lattice dynamics to such a model with some success.

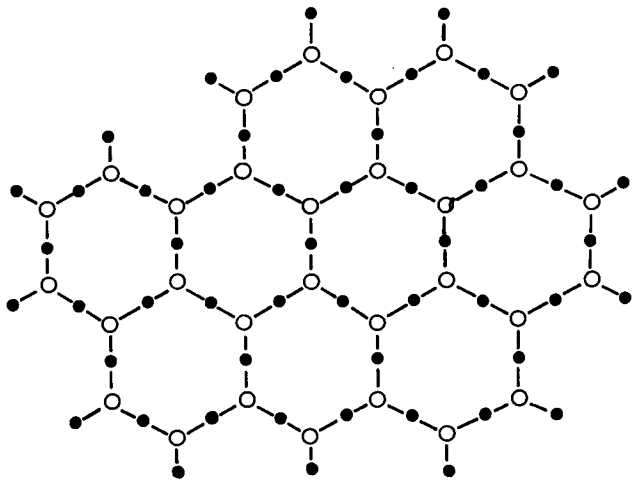

Figure 1. Planar structure of connected hexagonal rings.

Erlander (1969), in the first of two papers proposes an ice-II type cluster. The paper is very speculative and is mainly based on flickering clusters in conjunction with their aggregates. The later paper (Erlander, 1970) compares the infrared and Raman spectra of ice-II with polywater to support his contention. This interpretation is questioned by others including Allen and Kollman (1970), and some suggest that Lippincott's oxygen-oxygen distance of 2.30 Å is too short (Donahue, 1969; Chua, 1970). Donahue further proposed a hydrogen-bonded rhombic dodecahedral cluster of (H_2O) on the basis of density considerations (Anisimova *et al.*, 1967).

A tetrahedral cluster using "banana bonds" and an oxygen-oxygen distance of 2.76 Å has been proposed but not substantiated experimentally (Bolander, Kassner and Zung, 1969). Another proposed structure is a chain with each oxygen generally bonded to four hydrogen molecules as well as to two other oxygens, each pair of hydrogens being in alternating planes separated by 90° (O'Konski, 1970). There are no known compounds that support this hypothesis.

Linnett (1970) postulated that by allowing for increased electron correlation, a wave function can be derived that makes it possible to envisage a pseudo-wurtzite structure employing symmetrical hydrogen-bonds. He claimed that such a structure accounts for the spectroscopic properties, density and viscosity of polywater. Ageno's proposed star-like structure (1969) is consistent with some of the reported properties of polywater.

Using three types of *ab initio* MO calculations on Lippincott's polywater model (Fig. 1), Sabin *et al.* (1970) obtained conflicting results. The most sophisticated technique employed predicted that this model was unstable.

Allen and Kollman (1970) used the semi-empirical CNDO-2 (Pople, Santry and Segal, 1965) to show that a structure based on planer rings joined by symmetrical hydrogen bonds (Fig. 2) is stable and consistent with the physical properties of polywater. Their conclusions appear faulty because the different bond lengths assigned to external O-H bonds (which impart extra stability to the model) would become almost insignificant if a large number of rings are joined together. Later the authors suggested that the internal energy of a cyclic symmetrically hydrogen-bonded hexamer comes very close to that of liquid water. But to obtain a hydrogen bond energy of 8 kcal/mole for such a structure would require an oxygen-oxygen distance of ~2.5-2.6 Å, which is very different from that determined for water and ice (2.86 Å and 2.76 Å respectively) (Eisenberg and Kauzman, 1969). In addition, Allen and Kollman point out that the CNDO technique should not be used for charge-separated species, but they use it on precisely such species.

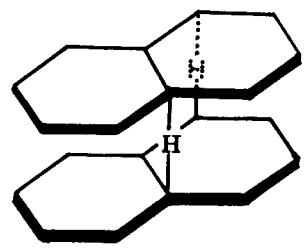

Figure 2. Structure composed of planar rings joined by symmetrical hydrogen bonds.

Goel, Murthy and Rao (1970) did not specify their water monomer reference unit in considering the stabilization energies of those structures proposed by Bellamy *et al.* (1969) and also structures based on planar branched polymeric chains and hexagonal rings. A consideration of six- and four-membered rings was given by Azman, Koller and Hadzi (1970).

Using an INDO technique (Pople, Beveridge and Dobosh, 1967), Pedersen (1969) estimated bond orders of proposed cyclic and linear models of polywater. Such calculations show the six-membered ring to be stable and the four-membered ring to be unstable. Messmer (1970) added parameters to the CNDO-2 method but the results obtained are of doubtful importance as the parameters were not calibrated. Other structural papers are Morokuma, 1969; Minton, 1970; Ageno, 1969; Allen, 1970.

Though the existence of polywater had not been proposed at that time, some early papers referred to anomalous effect of water in capillaries and silica gel (Shereshefsky, 1928; Patrick and Cohan, 1936; Deryagin, 1962.) Some further references are Chojnacki, 1970; Kiszthelyi, 1970; Iwaskai, 1970; Krauss, 1970; Deryagin, Churaev and Rabinovi, 1970; Ito, 1970; Karlsson, 1970; Fedchuk, 1970; Bertoluzza and Bonino, 1970; Christian and Berka, 1971. These are either related to the topic indirectly, not available for translation at this time or have appeared very recently in print.

Experimental Section

STRUCTURAL WORK

Two models were selected to be treated by the CNDO-2 technique (Pople, Santry and Segal, 1965). In both instances the O-H distances were identical for the particular model and for the monomeric unit used as reference for energy calculations. If all the O-H bonds were not identical in a particular model, further explanations would be needed when additional polymerization occurs.

The first model investigated was Lippincott's six-sided ring (Bellamy *et al.*, 1969) with oxygens set 2.3Å apart, with all angles 120° and all O-H distances 1.15Å. It was found that the hydrogen bond energy for the dimer was 2.38 kcal. However, when the six-membered ring system was considered, a stabilization energy of 156.89 kcal was realized.

The second system was a pentameric model developed by us as a possible structure (see Fig. 2). This consisted of a five-membered ring with symmetrical hydrogen bonds, having all O-H distances set at 1.25Å and all angles tetrahedral. For the dimer, a hydrogen bond energy of 18.79 kcal was found. The pentamer has a stabilization energy of 123.48 kcal. From such considerations it appears that both structures are very stable and both are capable of contributing to the structure of polywater. But, before accepting these two structures as probable contributing models of polywater, several facts should be considered.

Although the six-unit cyclic structure might have enormous stabilization energy, the total energy of the system is less than that of a cyclic structure composed of six ordinary water monomers, as occurs in ice-II. Utilizing O-O distances 2.86Å and O-H bond lengths of 1.02Å with tetrahedral angles about the oxygens, an energy of -119.393 A.U. is calculated for a six-water-membered, ice-like structure. This figure should be compared to -119.282 A.U. obtained for Lippincott's structure. The ordinary water structure is thus more stable by 69.9 kcal than polywater. But this is misleading because the O-H distance in the ice-like structure was set at the best energy distance. This is also the case with the five-membered ring structure. The total energy (-99.123 A.U.) is proportionally less than either of the six-membered rings considered. This too results from fixing the bond distances. As the O-H bond distance falls away from the ideal value 1.02Å, the theoretical energy of the monomer increases appreciably. For example, in moving from an O-H length of 1.02Å to 1.15Å, the energy of a tetrahedrally-bonded water molecule having an internal angle of 109.46° increases 30 kcal/mole, or is 30 kcal/mole less stable.

It can thus be seen that the CNDO-2 technique is internally adjusted to give best energies at predetermined bond angles and distances. For water, this is an angle of 104.5° and an O-H distance of 1.02Å. Thus, the limitations of the routine should be carefully considered when it is used – this has not always been done in the structural studies of polywater.

Another factor frequently overlooked in MO calculations is the possible catalytic effect of the silica surface since anomalous water has not been prepared in the absence of such a surface. Water molecules approaching the silica surface could be deformed and in this state react with other water molecules to eventually produce an anomalous substance. If the product is polywater, it could be a metastable form of water having an extremely high activation energy barrier which could only be overcome in the presence of the deforming agent. Therefore, it is the deformed water monomer of higher aggregate in the presence of the surface that constitutes the ground state and that should be considered when ascertaining the stabilization energy of the system.

Many possible structures of polywater can be imagined; but MO calculations on the subject will continue to be inconclusive and misleading until the existence of polywater is proven, and more is known about it and the structure of any intermediate products during its formation.

ATTEMPTED PREPARATION OF POLYWATER

Capillary Experiments

Work undertaken by this group pertained initially to the production of anomalous water in glass capillaries. Also attention was given to a method involving a process of diffusion through porous Vycor glass for the production of larger quantities of polywater.

Capillaries were usually freshly drawn of Pyrex or quartz glass. Prior to drawing out the capillaries, the glass tubes were cleaned successively with chromic acid, distilled water, hydrochloric acid, ethanol and acetone. A thorough rinsing and soaking in distilled water and drying with either nitrogen gas or in a warm oven completed the cleaning

procedure. The inside diameters of the capillaries were found to range from 5-50μ from photographs taken under high-magnification and observations made with a scanning electron microscope.

Various designs of apparatus were used, but in most cases they resembled those described by Deryagin (Anisimova *et al.*, 1967; Deryagin *et al.*, 1969). Capillaries were exposed to water vapour for periods ranging from a few days to several weeks. Conditions of lowered water vapour pressure were obtained in many cases by raising the temperature of the region surrounding the capillaries 1-2°C by means of a heating tape. KH_2PO_4 and $KHSO_4$ solutions were used to decrease the vapour pressure. Water used in the experiments was varied in an attempt to change the percentage yield. Tap water, distilled and triply-distilled water were all used in different experiments. A vacuum of ~ 1-2mm Hg was obtained by using a vacuum-pump in most cases. An aspirator was used in some of the early experiments. In a given experiment, a maximum 15% of the capillaries contained condensate. Smaller capillaries more often contained drops or columns of liquid. A higher yield was obtained in quartz than in Pyrex. A high yield was obtained where a coil of copper wire was wrapped around the capillary chamber and a current of 2 amps passed through the coil. This could, however, have been due to increased temperature fluctuations as noted by Brummer. Heating effects in the coil raised the temperature 10 - 18°C and these were counterbalanced by heating the remainder of the apparatus with heating tapes.

Separate experiments were set up in which capillaries from the centre of the extended region of freshly-drawn Pyrex tubes were grouped together, then those from the adjacent region and so on, making six groups in all. 11% of the tubes in the central group contained condensate, whereas yields of 0-4% were obtained in all other cases.

Two series of experiments were set up to observe Fedyakin's "daughter" columns (1962). In the first series, relatively wide capillaries were used (about 100μ, while in the second the capillaries were narrower (5-30μ). In both cases, the capillaries had columns of water or dilute solutions introduced into them by capillarity, and were sealed. A higher yield (50% as opposed to 20%) was obtained with the finer capillaries. The condensate in the case of the larger capillaries behaved like water, whereas anomalous behaviour was observed in the narrower capillaries.

Testing the contents of capillaries for anomalous behaviour was attempted by two methods. At first, a determination of the boiling point was attempted by sealing one end of the capillaries and heating them in a glycerine bath. This technique proved unreliable and a special refrigerated stage for a microscope was constructed. A coolant (dry ice-acetone mixture) was passed through an aluminum block in a dry-nitrogen atmosphere, and capillaries could be observed in the range +10 to -40°C; temperature was measured with a thermocouple placed close to the capillaries.

After observing the condensates of capillaries from many of the experiments, it was concluded that the condensate in many cases exhibited anomalous behaviour, as cited in the literature. The evidence may be summarized as follows:

1. At low temperatures, the condensate appeared to remain liquid, even at about -40°C. A normal liquid surface meniscus was retained, and as the temperature was altered the column appeared to move smoothly. Water introduced by capillarity into similar capillaries exhibited an irregular broken appearance even at the ice-air interface.

2. In the temperature range -25 to +5°C (varying somewhat in different specimens), globules within the liquid column could be observed. As the temperature varied, the globules changed in relative number and size. Whether they were solid or due to two liquid phases was difficult to decide. Two-phase behaviour has been noted by many observers (Deryagin *et al.*, 1969; Bellamy *et al.*, 1969; DePaz, Pozzo and Vallauri, 1970).

Anomalous water droplets have been produced on flat surfaces of quartz and other materials by successive cycles of condensation and evaporation. This procedure was successfully applied to the production of anomalous water in capillaries. By reversing the slight temperature gradient between the capillary chamber and water source, the capillaries were exposed for a short time to saturated water vapour which condensed in them. This was followed by a longer period (days or weeks) of exposure to lower vapour pressure. Frequently, the condensed columns of liquid would almost completely evaporate but would leave a ring or band of tiny droplets, and in some cases these would readily absorb more water vapour to form a column of liquid again (when exposed to a higher level of saturation of water vapour).

In connection with experiments on capillaries, various concentrations of NaOH or NaCl solutions were introduced into capillaries and observed at low temperatures. NaCl solutions did not exhibit any anomalous behaviour, merely a depression of freezing point. With NaOH solutions, a phenomenon was seen similar to that of the two-phase behaviour of the anomalous water, but the appearance was more clearly that of solid particles suspended in liquid. The shape of these particles was somewhat irregular, whereas in the case of anomalous water the particles appeared to be spherical or elliptical (Fig. 3).

Attempts to examine polywater contained in capillaries by Raman and infrared spectroscopy, and X-ray diffraction techniques were unsuccessful; fluorescence interfered with obtaining a Raman spectrum, as previously reported. On removing the material from the capillaries by centrifuging several hundred at a time, a liquid containing a few solid bodies, whitish and needle-shaped in some cases, was extracted. This mixture is, of course, open to the criticism that the solid particles are pieces of glass broken from the

capillaries by the action of the centrifuge. However, later work suggests that it may have been an early observation of solid material dissolved in the anomalous water since precautions were taken to prevent capillary glass from contaminating the centrifuged liquid. Infrared spectra of this liquid showed only normal water peaks. When a drop of this liquid was allowed to dry on an AgCl plate a faint residue was observed. Attempts to produce an infrared spectrum yielded only the background AgCl spectrum.

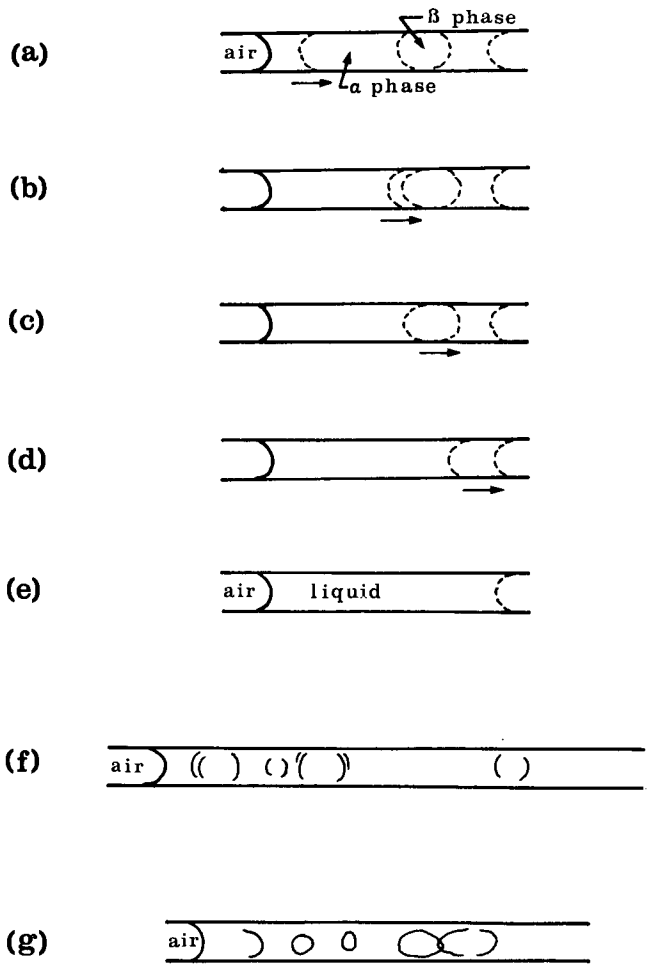

Figure 3. Two-phase behaviour observed in capillaries at low temperatures: (a) to (e), changes in anomalous water during warming from ~ -30°C to -6°C; (f) the same capillary recooled to ~ -25°C; (g) the appearance of a 1.5M NaOH solution between -30°C and -10°C.

Diffusion Experiments

The second phase of the work was then undertaken. It was decided to attempt to produce larger quantities of anomalous water by using porous Vycor glass (Corning Glass, Special Products Code No. 7930, 96% silica, 4% borate, average pore size 40Å and surface area 100 $m^2 g^{-1}$) as a diffusion media, and allowing unsaturated water vapour to pass through it. The apparatus is shown in Fig. 4.

A scrupulous procedure of cleaning was adopted both for the porous Vycor cell itself and for the quartz and Pyrex glass of the remainder of the apparatus. The ends of a porous Vycor tube were fused to regular Vycor glass by exposing them to a temperature of 1200°C in a muffle furnace. The Vycor tube was then heated to 85°C in a solution of 5NHCl in a quartz container for 15 hours, rinsed, and heated repeatedly in distilled water baths until a neutral pH was recorded for three consecutive baths. Rapid drying of porous Vycor would cause it to crack so a slow procedure of drying in a gentle stream of nitrogen was used. Finally, the Vycor was placed in an oven for 8 hours and the temperature slowly raised to about 565°C, while oxygen was passed continuously through the oven. This temperature was high enough to oxidize any organic impurities which may have been sorbed by the glass, but too low to cause fusion of the glass with resultant loss of porosity. Yellowish discolorations of the glass were removed, indicating that the desired oxidation had taken place. The Vycor was now ready to be fused into the assembled apparatus.

Other precautions included the use of Teflon valves throughout the apparatus to avoid any grease contamination, and the use of a liquid-nitrogen trap to prevent oil from the vacuum pump from entering the apparatus. Also the thorough cleaning of the quartz and Pyrex glass used in the apparatus was carried out by detergent washing, soaking in chromic acid, hot hydrochloric acid and repeated distilled water baths and rinses.

In accordance with published conditions for production of anomalous water, the water vapour pressure was lowered. This was achieved by cooling the water source to about 0°C by means of a surrounding ice-water bath. Condensate production was too slow when a temperature of -67°C (dry-ice-acetone bath) was used at the water source. To provide energy to aid the reaction, the Vycor cell was illuminated by light sources; the outer wall of this cell was made of quartz glass to allow transmission of ultraviolet frequencies to the Vycor surface. The different light sources were:

1) 254 mμ Gelman ultraviolet lamp

2) 350 mμ Gelman ultraviolet lamp

3) 55 watt 2 v. quartz halide lamp

4) Rayonet photochemical reactor (16 x 75 watt ultraviolet lamps), and

5) 1000 watt quartz-iodide lamp (T.V. spotlight lent by C.B.C., Ottawa) which was used during the production of most samples and appeared to cause the samples to be more concentrated in the anomalous component.

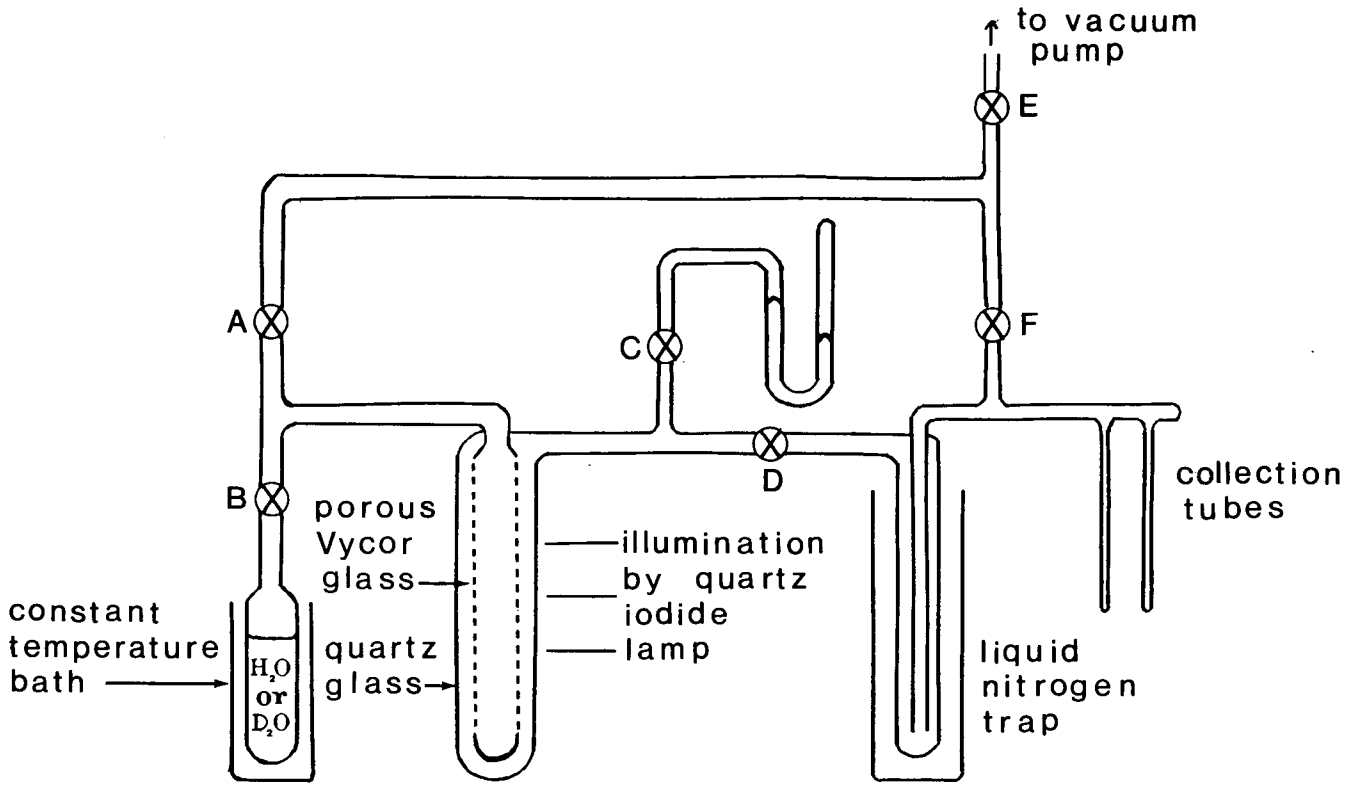

Figure 4. Diffusion apparatus incorporating porous Vycor glass.

The trap was maintained at liquid-nitrogen temperatures to freeze out any water or polywater. The temperature of the diffusion cell varied with the heating effect of the various light sources. In the case of the quartz-iodide spotlight, a temperature of about 100°C was maintained. Higher temperatures were prevented by blowing air over the diffusion cell. A manometer could be opened to the vacuum by means of a Teflon valve but was usually kept closed to prevent contamination by mercury vapour. Pressures were maintained at about 0.3 mm Hg, which is well within the range described by other experimenters for polywater production (Anisimova *et al.*, 1967; Bascom, Brooks and Worthington III, 1970).

After operating the apparatus for periods of several hours, the liquid-nitrogen trap was removed and stopcocks closed to isolate that portion of the apparatus. Gentle heat was then applied to the cold trap whilst the liquid-nitrogen flask was placed over one of the small collecting tubes. The tube was sealed under vacuum when all the sample had been distilled into it.

When a more concentrated sample was required, evacuation by means of the vacuum pump was used, but in some cases samples were lost by sudden "bumping" of the tube contents. Thus, a second method was adopted whereby the sample was frozen by immersing the tube in liquid nitrogen. The tube was then broken and was sealed in a larger tube containing anhydrous calcium sulphate (Drierite). After several days the liquid was reduced to about one sixth of its former volume and this was arbitrarily taken as being sufficiently concentrated.

Some other experiments are worthy of mention. Attempts to produce polywater by passing water vapour over glass wool and quartz wool were made, but yielded water which behaved normally. When samples of glass wool

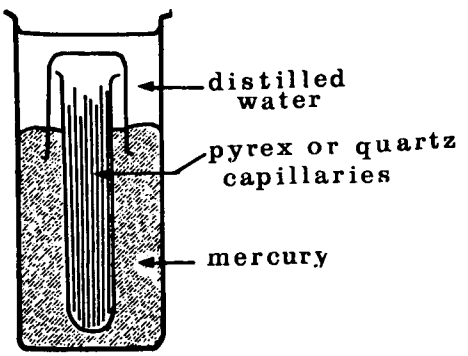

Figure 5. Cell containing capillaries for high pressure experiment.

were exposed to pressures of 3 kbar, a small increase in the refractive index of the water was noted; this was presumably due to increased solubility of glass at high pressures — a condition found in very small pores, for example in porous Vycor glass or fine-bore capillaries. An attempt to prepare anomalous water in fine Pyrex or quartz capillaries by pressurizing them was apparently unsuccessful. The capillaries were removed after enclosing them (as shown in Fig. 5) and pressurizing to 3 kbar for several hours. The water from these capillaries was ejected onto an AgCl minicell but the infrared spectrum contained only bands expected of normal water.

D_2O was used in the diffusion cell apparatus to yield a product which appeared to have similar physical properties to the H_2O product. Some comparative tests by mass-spectrometry of D_2O- and H_2O-produced samples are discussed in the following section.

Results of Diffusion Experiments

The pH of unconcentrated samples as determined by an Alkacid full-range pH kit varied, but was as low as 4.0 in some instances. The liquid was usually clear, although sometimes a little cloudy, on first being distilled into the small tubes. On concentration, solid material was frequently seen to appear in the liquid. This material was clear or whitish, of various shapes and often in the form of platelets. One sample was completely evaporated and the solid residue accounted for 0.08% of the weight. The material would not redissolve in pure distilled water after 2 hours with repeated shakings.

A small conductivity cell with inner diameter of 0.08 cm (Fig. 6) was constructed and calibrated using 1M KCl solution. An unconcentrated specimen was introduced and the conductivity determined to be

$$K_{sp} = 0.80\ \Omega^{-1}\ cm^{-1}\ (\pm 3\%)$$

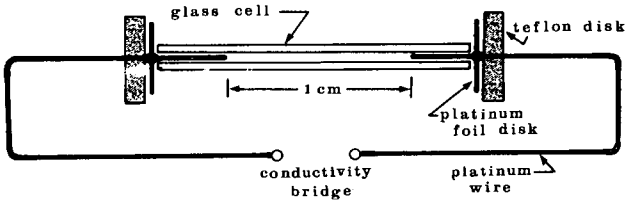

Figure 6. Apparatus for conductivity measurements.

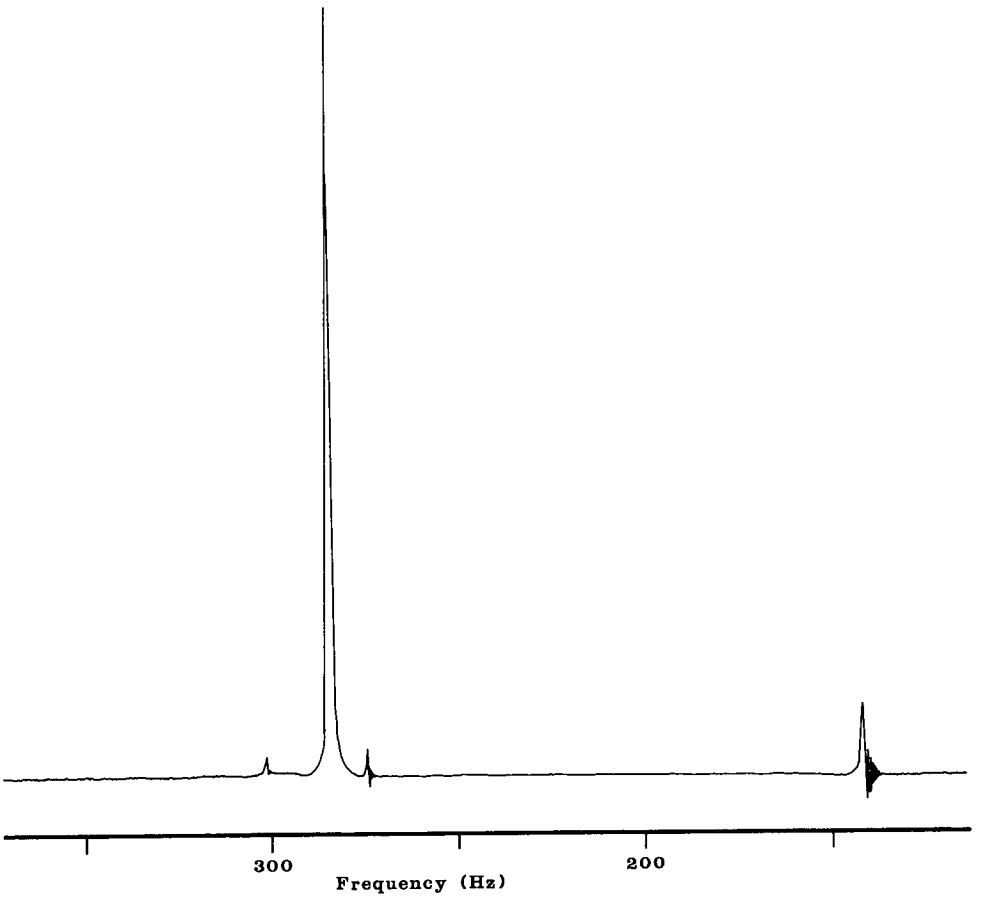

Figure 7. Nuclear magnetic resonance spectrum of anomalous water.

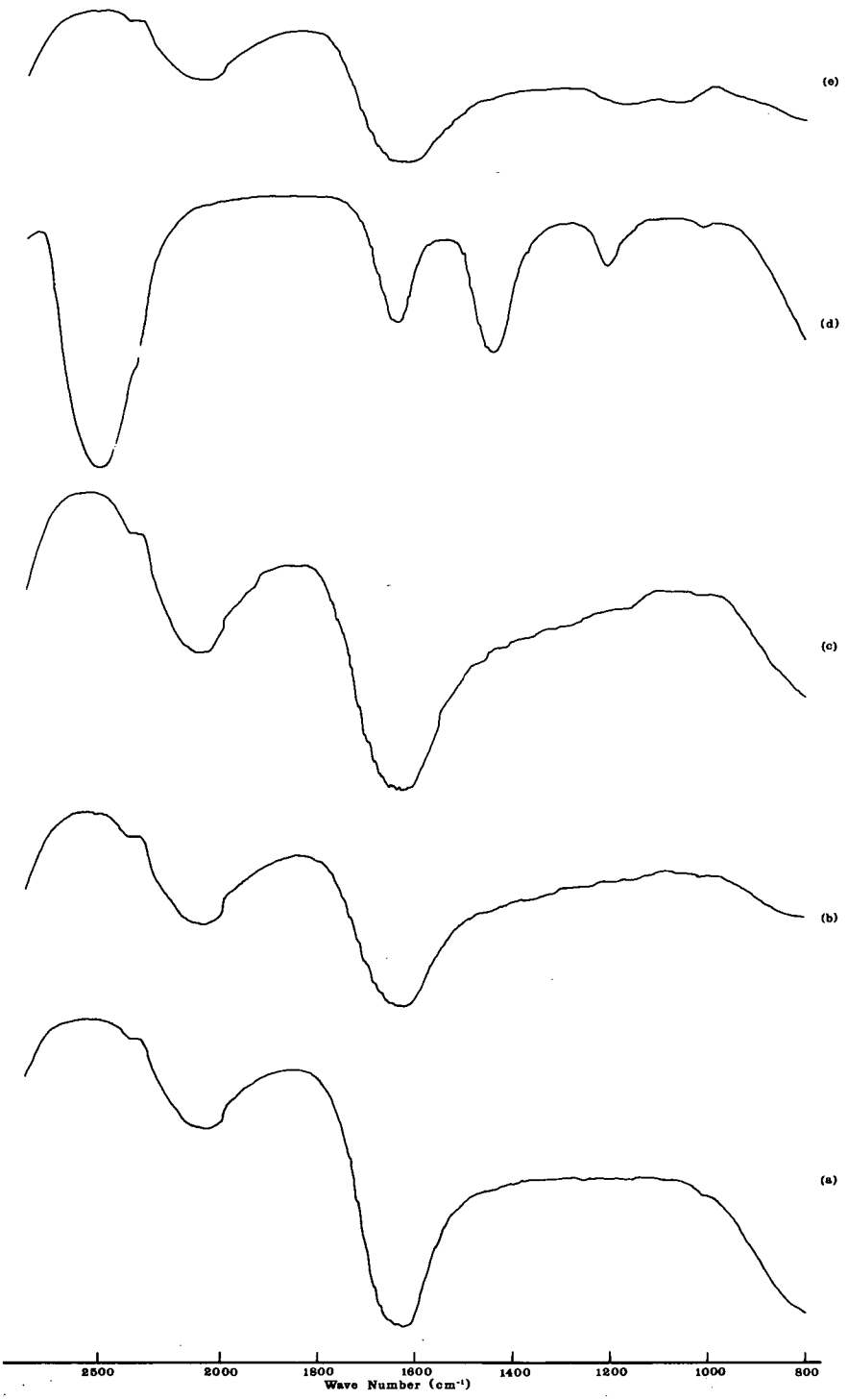

Figure 8. Infrared spectra: (a) water; (b) anomalous water; (c) anomalous water residue; (d) poly - D_2O; (e) silica sol.

It was observed that the platinum darkened and a few small bubbles appeared, possibly indicating that electrolysis was taking place. Such a high conductance might be partially attributable to a gel or micelle type of material. An ionic solution would have to be of a very high concentration to yield this result. The acidic pH suggests that proton conductivity is largely responsible for the high K_{sp}.

Two atomic emission spectra were determined to evaluate the quantity of sodium in the condensate. The first test used a sample produced in an initial diffusion apparatus in which the porous Vycor had been attached by means of shrinkable Teflon sleeves (and cleaning procedures had not been as thorough). As a result of the irradiation, the Teflon appeared to disintegrate, so the condensate may have been contaminated by the products of this reaction. Flame-emission analysis indicated 0.26% sodium; however, an unconcentrated sample of pH 4 produced in the final version of the apparatus was shown from atomic absorption spectrophotometry to contain 0.003% Na.

Electron microprobe analysis was carried out on some of the solid material obtained from the solutions. The results were:

Silicon 5-10%

Sodium 1-5%

Aluminum trace ($\ll$1%)

Calcium trace.

The Ca might be attributable to slight contamination from the Drierite used to concentrate the samples. It should be noted that a 1-5% Na content in the solid is consistent with the atomic absorption results and the dry weight of solid present in the liquid samples.

Previous NMR results are conflicting and a broad, low band 300 Hz downfield from the normal water peak has been attributed by various workers to polywater or the capillaries containing it (Page, Jakobsen and Lippincott, 1970; Petsko, 1970; Rabideau and Florin, 1970; Morariu, Mills and Woolf, 1970). NMR spectra of our unconcentrated liquid samples showed a small sharp peak shifted upfield about 150 Hz (Fig. 7). The downfield, broad peak was not visible, and this may support the contention that the capillary glass used by other workers gives rise to this peak. Furthermore, the sample to glass ratio was higher in the current work than in previous works.

Several attempts were made to obtain X-ray diffraction patterns which have been reported by Petsko and Massey at the Anomalous Water Symposium, 1971. Samples of anomalous water produced in capillaries and by the diffusion process were used, as were the solid bodies precipitated from the concentrated material. In no case could a diffraction pattern be seen. This suggests that the solid material is not crystalline but has a vitreous structure.

Infrared spectra (run on a Perkin Elmer 427 Spectrophotometer) of liquid samples showed only bands characteristic of normal water. Moreover, in one instance when the sample was evaporated on an AgCl plate until it was nearly dry, the resulting spectrum contained in addition to normal water peaks, very weak bands at 1410, 1360 and 1150 cm^{-1} (Fig. 5). On complete drying, a white residue remained on the plate. For comparison purposes, a silica sol was prepared by adding excess dilute HCl to sodium silicate and dialysing to remove excess acid. This spectrum bore a close resemblance to the anomalous water spectrum. Reduction of O-H absorption (as compared to normal water) was similar for both synthetic and anomalous water solutions, and small peaks were visible at 1050 and 1150 cm^{-1} (Fig. 8). Silicate solutions at several concentrations, sodium tetraborate solutions and other salt solutions were also used to obtain infrared spectra for comparison

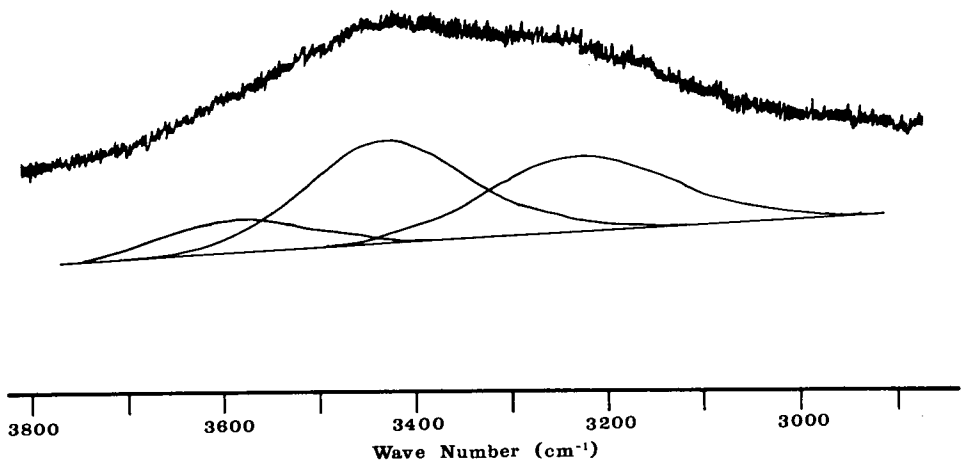

Figure 9. Raman spectrum of anomalous water.

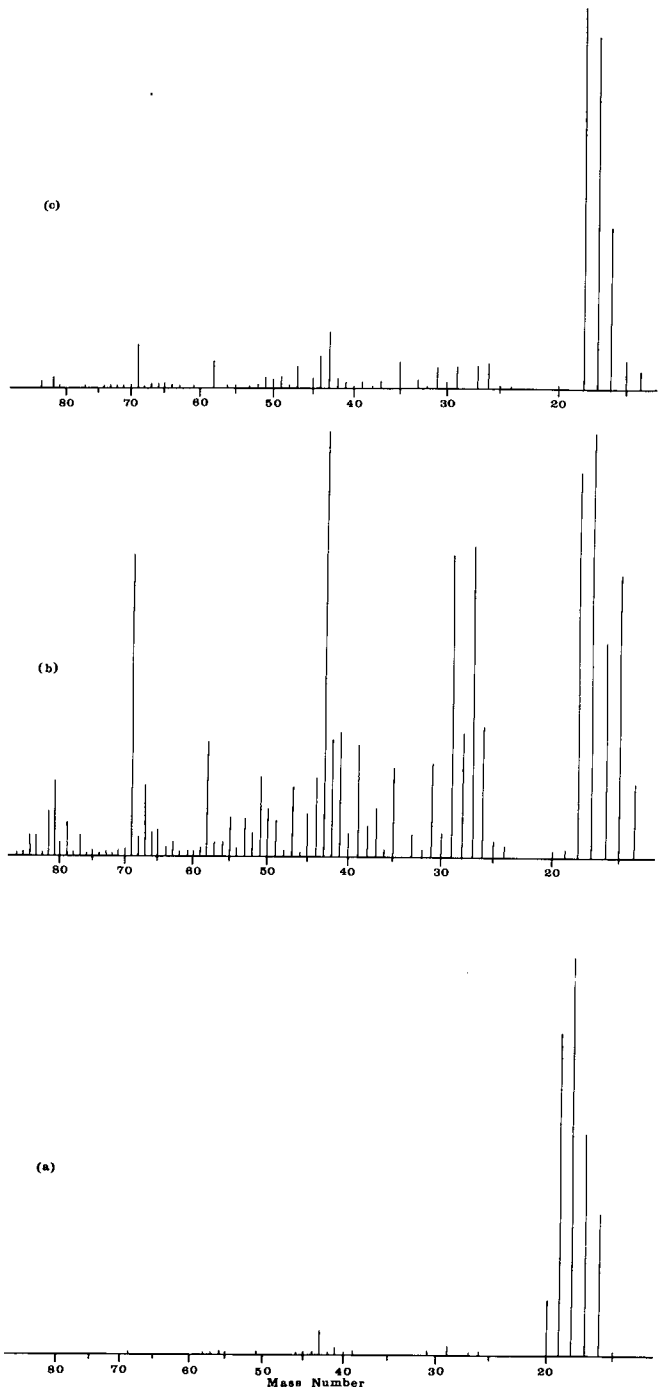

Figure 10. Mass spectra: (a) poly - D_2O; (b) anomalous water; (c) water.

purposes. The spectrum of silica sol showed the closest resemblance. Spectra were also obtained of samples of poly-D_2O. The result appeared similar to a mixture of H_2O and D_2O and it was concluded that some H_2O molecules had been retained by the Vycor and released into the D_2O condensate. Several spectra were obtained of various proportions of H_2O and D_2O and were compared with the poly-D_2O spectra. Small peaks at 1010 cm^{-1} and 2850 cm^{-1} in the poly-D_2O were absent in the H_2O-D_2O mixtures.

A Raman spectrum proved difficult to obtain because the level of fluorescence was very high. In one case, the spectrum was capable of curve resolution (Fig. 9). Peaks were centered at 3430, 3225, and 3585 cm^{-1} (in order of strength) which compared with bands attributed to anomalous water (Bellamy *et al.*, 1969; Lippincott *et al.*, 1969). It is worthy of note that these authors assigned the peak at ~3400 cm^{1} to exact locations of 3400 cm^{-1} and 3420Å. Water bands in this region vary depending on salt contamination or temperature changes (Walrafen, 1967). The very strong band centred at about 620 cm^{-1} which Bellamy *et al.*, (1969) assign to anomalous water could not be detected in our samples. This band has been ascribed to the quartz capillary by Rousseau and Porto (1970).

An attempt was made to detect such elements as silicon in the anomalous water samples by neutron-activation analysis. The only element detected was a minute trace of copper. Since the sample had to be sealed in a polythene tube with hot metal forceps, this was probably the source of this trace element. Radioactive silicon isotopes have short half-lives, but transportation difficulties between reactor and counter made the detection of Si marginal.

Mass spectroscopic analysis was undertaken on samples of anomalous water produced from H_2O and D_2O by the diffusion technique, and also on a sample produced by diffusing D_2O through the Vycor glass. Pure distilled water was analysed for purposes of comparison.

The anomalous-H_2O sample gave a more complex spectrum (Fig. 10) than did the other two samples. Peaks which appear at mass-numbers 27, 29, 43 and 69 in anomalous H_2O are absent or very weak in spectra of anomalous-D_2O and normal water. These peaks are assumed to be due to unidentified contaminants. Other peaks at 78, 39 and 26 in spectra of anomalous-H_2O suggest singly-, doubly- and triply-charged H_2SiO_3 respectively. It would appear from its spectrum that a comparable poly-D_2O has not been produced; there is a lack of fragmentation (no peaks above ~58). Peaks at 19 and 20 in the D_2O spectrum are due to DHO^+ and D_2O^+.

Conclusions and Recommendations

The experimental work done by this group has not only reproduced Deryagin's anomalous water in capillaries, but has produced it in sufficient quantity to allow greater precision than previously possible in the determination of its properties and the analysis of its components. Following these investigations, it is concluded that siliceous material is leached from glass in pores of small diameter under the influence of the high pressure effects of surface forces. A silica sol is formed from which solid silicates may be precipitated by concentration. Such a silica sol can be distilled (Heitmann, 1964).

In view of the fact that silica sols are produced under similar conditions it is reasonable to compare the properties of anomalous water to those reported for silica sols (Stericker, 1924).

Composition: – Anomalous water contains ~0.1% solid material in which the ratio of silicon to sodium is about 3 to 1;

– Stabilized silica sols contain ~0.1% solid material in which the ratio of silicon to sodium is about 2 to 1.

Viscosity: – Anomalous water has a relatively high, but inexact, viscosity about 15 times that of normal water;

– Silica sols have relatively high viscosities which vary markedly according to the ratio of silicon to sodium in the sol.

Conductivity: – When an electrical potential was applied across electrodes in anomalous water a very high conductivity was observed, as well as gas evolution and darkening of the electrodes;

– A silica sol is a better conductor than a solution of any other salt at equivalent concentration. When a potential is applied across electrodes in a silica sol there is brisk evolution of a gas and a covering of the electrodes with a vitreous layer.

Dehydration: – Anomalous water produces platelets and eventually a powdered or granular residue;

– Silica sols produce platelets during dehydration and may be dried to a silica gel which has a granular appearance.

Rehydration: – A column of anomalous water in a capillary with normal water was seen to increase its volume at the expense of the normal water;

– Silica sols and gels absorb water and increase their volume in so doing.

The comparison indicates that anomalous water is probably a silica sol containing ~0.1% solid material. In view of the fact that other researchers were able to produce only microgram quantities it follows that in order to identify their product as a silica sol they would have had to detect 10^{-10} grams of silicon in their product. Such a measurement is exceedingly difficult.

The authors of this report conclude that the so-called anomalous water is a silica sol. Unless a sufficiently large quantity of a second phase of liquid water having its own region of existence is prepared and shown to contain no impurities, further attempts to study such a compound should cease.

Furthermore, the authors recommend that:

(i) Techniques be developed for the accurate chemical analysis of microgram samples (for example ESCA). The absence of such techniques has been to a large extent responsible for the long duration of the efforts expended on anomalous water studies by many groups throughout the world.

(ii) The role of surface forces on the properties of liquids permeating microscopic pores in solids is an area where further investigation is required. These would be relevant to many applied problems in hydrology e.g. dissolution studies of minerals into groundwater, the stability of the different soil types under load when the water table is changed.

(iii) Interdisciplinary groups of scientists actively conducting fundamental studies into the properties of materials affecting the environment, should be encouraged. This project, in which a new technique was developed, has contributed to the resolution of a controversy. An interdisciplinary approach has made this possible.

Some Recent Papers

Most of the articles that have appeared in the last few months (up to November 1971) have been critical of the chemical integrity of polywater. Although Allen (1971) and Donahue (1971) have criticized Kamb's rejection of their proposed structures, Allen and Kollman (1971) very recently retracted their structural model on the grounds that (i) a new measurement by Deryagin indicated a molecular weight of ~180, a value that is inconsistent with their original model, (ii) the failure of Lippincott and co-workers (1971) to produce their Raman spectra, and (iii) *ab initio* calculations on cyclic symmetrically-bonded water molecules show that this type of bond possesses a much higher energy than the normal asymmetric type.

Pethica, Thompson and Pike, (1971) concluded from interpretations of Raman, infrared and mass spectrometric data, that anomalous water is not polywater, and suggested that infrared absorption observed by Lippincott and co-workers at 1105 cm^{-1}, 1015 cm^{-1} and 780 cm^{-1} are close in energy to bands expected of hydrogen carbonate ion. Significantly, Lippincott has noted very recently the formation of sodium bicarbonate when glass-wool is extracted with water and with methanol (Advanced Research Projects Agency Order No. 1463). The paper by Pethica and co-workers was criticized by Deryagin and Churaev, who feel that the distillation experiments unambiguously demonstrate that molecules of water II exist in the vapour phase. However, according to Mansfield (1971) most of the physical properties of anomalous water are quite typical of ordinary salt solutions.

O'Brien (1971) has suggested that the anomalous liquid behaviour may be viewed as a result of an increase in surface tension in isolated capillaries. Christian and Berka (1971) showed that even non-hydrogen-bonded liquids form anomalous residues after exposure of silica surfaces to their vapours. Lippincott points out that this seems to be outside all plausible structural interpretations of polymeric liquids.

Review articles on anomalous water have been published by Rossotti (1971), Hasted (1971), Peschel and Adlfinger (1971), and Smutek (1971); they contain references up to the end of 1970. Hasted (1971) pointed out that (i) the entropy of structures proposed by Allen and Kollman are very low compared to tetrabedral structures and (ii) similar NMR shifts to those ascribed to anomalous water have been observed for electrolyte solutions and empty capillaries. Rossotti (1971) drew attention to the fact that the case for symmetrical H-bonding rested on the assignment of the 1595 cm^{-1} infrared band, which Everett and co-workers later re-assigned to O-H stretch displaced from 3400 cm^{-1}.

Some of the papers presented at Lehigh are particularly interesting. Rousseau (1971) did not observe the predicted isotope frequency shift for D_2O-polywater, and concluded that the reported infrared features do not originate from H_2O units. This, in conjunction with a wide variety of analyses indicating significant contamination, led him to believe that polywater does not exist. Fowkes *et al.* (1971) exposed silica powders to water vapour, cyclic condensation and evaporation which led to a viscous high-boiling liquid that dried to a glass having an infrared spectrum like that of polywater. On the other hand, Page and Jakobsen (1971) did not detect significant concentrations of Si, B or Al in their polywater preparations using "cleaned" capillaries, and concluded that for the most reasonable interpretation of the 1600 cm^{-1} infrared band, a form of water stable to ~400°C be present.

Barnes and co-workers (1971) have proposed that the properties of anomalous water are due to organic impurities from apparatus occlusions and sample handling; and possibly due to some Si from vacuum-pump oil but not from glass leaching. Hoekstra and co-workers (1971) found that samples exhibiting the anomalous thermal behaviour reported by other investigators showed normal water dielectric behaviour; samples that did not freeze at -60°C had a dielectric constant and dielectric loss less than those of normal water, which may indicate increased polymerization.

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