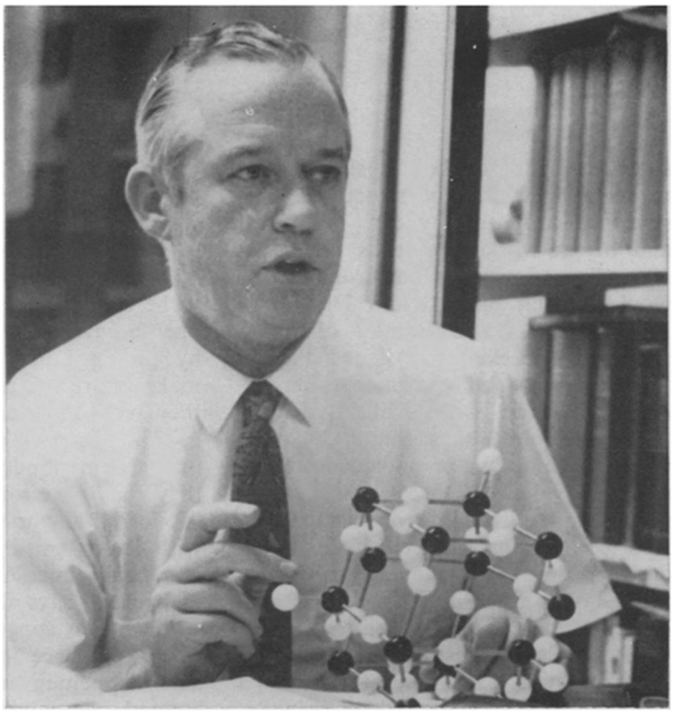
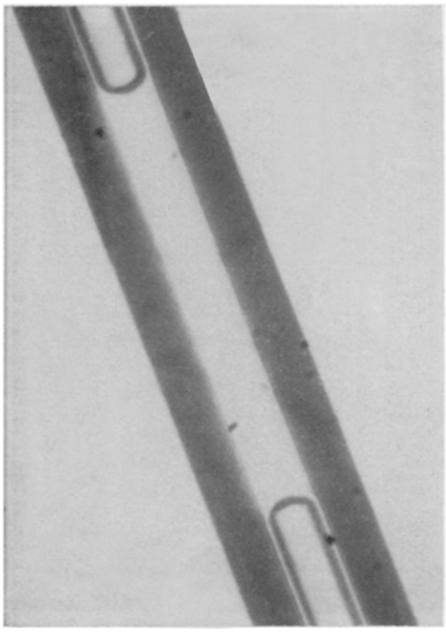


Frank Ross
*Donohue: A rhombic dodecahedron from 14 molecules.*



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*Polywater in 10-micron capillary.*

CHEMISTRY

# Analyzing anomalous water

## A form of water as thick as sludge still finds some chemists skeptical; others are excited

by Dietrick E. Thomsen

A few years ago Dr. B. V. Deryagin of the Institute of Surface Chemistry of the Soviet Academy of Sciences discovered what he thought was an unusual form of water. It seemed to have a molecular weight about four times that of water; it was 15 times as viscous and about 40 percent denser than water (SN: 12/21/68, p. 615).

**Yet the** substance had condensed from water vapor in glass capillary tubes that Dr. Deryagin had been using to study the chemistry of liquids spread on solid surfaces. He called it anomalous water and surmised that something in the glass, silicon perhaps, acted as a catalyst and caused unusual forces to appear that bound water molecules together in some kind of larger structure.

The notion that water could appear in any form but the common one was so contrary to everything chemists had believed that Dr. Deryagin's report stirred some very emotional reactions. While some chemists set out to study the anomalous substance and see whether they could elucidate its structure, others refused to believe in its existence.

"Scientists are supposed to be skeptical in the first place and openminded in the second," says Dr. Lewis Friedman of Brookhaven National Laboratory. But a balance between the two attitudes proved difficult in the face of something so weird as anomalous water. There were, and are, believers and nonbelievers, and they talk of converting rather than convincing each other.

**The far-out** nature of the subject has made people reluctant to risk their reputations by signing their names to papers. Although interest and actual work are both widespread, there have been only about half a dozen papers published on it. News has traveled mostly by word of mouth, and, says Dr. Friedman, "the history of this subject has been vaguely presented."

Some of the vagueness and some of the reason for disbelief is attributable to the smallness of the samples of anomalous water available and the difficulty of obtaining them. If large and easily reproducible amounts were available, many chemists would be more ready to credit the properties claimed for anomalous water. But the tubes in which it is usually made yield a few millionths of a gram each.

The technique is to put a bundle of such tubes into a chamber filled with water vapor and manipulate the vapor pressure so as to make the anomalous water condense. But, says Dr. Sherman Rabideau of Los Alamos Scientific Laboratory, "you put in 1,000 capillaries and go through the procedure. When you take them out, not all are filled; most are empty." No one knows, he says, why one tube should work while another of the same glass does not.

NBS
*Stromberg, Grant: a hexagon model.*

Efforts to produce larger amounts of anomalous water by avoiding the use of capillaries are underway in a number of laboratories. Trays of glass or quartz particles or glass or quartz wool are being used with some success. Samples as large as a few thousandths of a gram are now being reported, and





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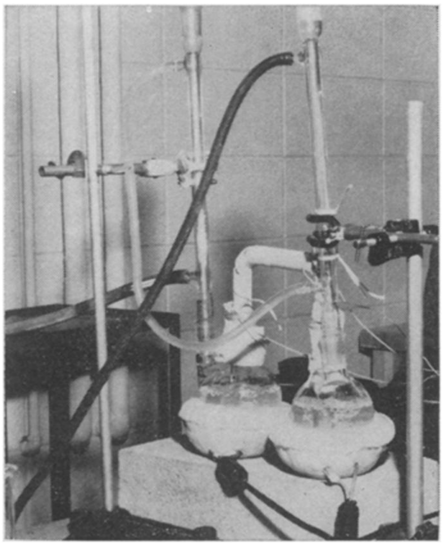

Ace Hoffman Studios

*Flasks and tubes to make polywater.*

one such experimenter, Dr. Bela Babuss of the Lowell Technological Institute in Lowell, Mass., says he hopes to produce gram amounts in the next year. At the moment the total of anomalous water in existence is probably not more than a few tenths of a gram.

When they have obtained samples, experimenters have been trying to find out what elements are present and how they are arranged. The geometry of the arrangement indicates the nature of the forces that hold the atoms together. Present experimental judgments call the anomalous substance anything from a new kind of polymer made of water to a corrosion product.

Studies of the infrared spectra of anomalous water led a team from the University of Maryland and the National Bureau of Standards, Drs. Ellis R. Lippincott, Robert R. Stromberg, Warren H. Grant and Gerald L. Cessac, to conclude that the substance is a polymer made by stringing water molecules together into a macromolecule (SN: 6/12, p. 23).

Hydrogen and oxygen molecules, they say, string themselves into hexagons, and the hexagons are then joined together in long chains. Because of this polymer structure they call the substance polywater.

Further support for this idea is now claimed by Drs. Thomas F. Page Jr., and Robert J. Jakobsen of Battelle Memorial Institute in Columbus, Ohio, and Dr. Lippincott. They did new infrared tests and used nuclear magnetic resonance, an independent way of determining structure. Both kinds of tests support the earlier suggestion, says Dr. Page, but "do not unequivocally prove it."

Meanwhile two theorists suggest that the nature of the forces involved, the so-called hydrogen bonds, should lead to somewhat different structures. The structure proposed by Dr. Lippincott and his co-workers extends chains in two dimensions; its macromolecules would be flat plates. Both Drs. Jerry Donohue of the University of Pennsylvania and Leland C. Allen of Princeton University feel that a three-dimensional structure is more likely.

Dr. Donohue says that instead of flat hexagons, water molecules form themselves into three dimensional shapes called rhombic dodecahedrons. Fourteen water molecules make a dodecahedron, and the dodecahedrons then build themselves together into cubical superclusters.

Dr. Allen retains the hexagons, in his hypothesis, and builds them into a three-dimensional lattice like graphite. Indeed, he says, drawing structural analogies to two forms of carbon, "ice is to diamond as anomalous water is to graphite."

**On the other side** of the question are those who say anomalous water is not water at all but a corrosion product. Analyzing the substance with electron probes, says Willard D. Bascom of the Naval Research Laboratory, "one can detect silicon and sodium." The presence of these elements leads Bascom and his co-workers at NRL to believe that the anomalous substance is not water but a substance called colloidal silica sol, which is formed from corrosion of the glass surface by the water vapor.

The proponents of polywater stand firm, however. "We have no indication of silicon," says Dr. Page. "We have no indication of sodium of any consequence."

Another who finds evidence of impurities is Dr. Dennis Rousseau of Bell Telephone Laboratories. In his sample he found sodium, potassium, chlorine, carbon and oxygen. But he doubts that the substance is silica sol because too little silicon showed up in his analysis. He describes himself as on the unbelieving side, "but I don't think all the evidence is in," he says.

Dr. Rabideau takes a somewhat more positive view. "I believe there is no question that the material that is unlike ordinary water exists," he says. "The question is: Is it possible to describe this material as resulting from a polymeric form of ordinary water or could it be impurities?" That electron probes find some silicon "does not prove that silicon is responsible for what we see," he says. On the other hand, his own analysis of the material in a mass spectrometer came up with nitrogen, oxygen and carbon dioxide from air in the tube and only ordinary water besides. This would tend to indicate that either the macromolecules don't exist or that they are too fragile to stand much handling.

If whatever is in the tubes turns out to be an unusual form of water, it will open a new field for structural chemists by proving that hydrogen bonds can make more kinds of structures than they were believed capable of. Hydrogen bonds play a prominent part in many compounds besides water, and they may do similar tricks with them. "A lot of alcohols and acids, anything with an oxygen-hydrogen group on it, is a good candidate for polymerization in cycles," says Dr. Allen.

Dr. Allen suggests that there is already evidence of something of the sort happening in another hydrogen-bonded compound, hydrogen fluoride. Drs. Jay Janzen and L.S. Bartell of the University of Michigan find that six hydrogen fluoride molecules sometimes join together to form a hexagon. Drs. Janzen and Bartell make no claim of a relationship to anomalous water, but Dr. Allen thinks there is an analogy. The hydrogen fluoride, as it happens, will not build up any larger structures, but other compounds may, he says, and they may have useful properties.

**Anomalous water** itself, says Dr. Allen, may find its greatest use as an intermediary in making "new compounds you couldn't get before." It is too soon to say what they might be.

The existence of anomalous water, if it is proved, may stimulate research on certain biological and geological questions, says Dr. Allen. The cells of a plant contain a lot of water, he points out, but plants don't freeze in weather that freezes ponds. One of the properties reported for anomalous water is a lower freezing point than water, or perhaps no freezing at all, so it might be responsible.

Likewise, there is much water locked into various geological features, and some of this seems to have strange properties. This too could be an unusual molecular form. The point is, says Dr. Allen, that even if the anomalous form of water chemists now think they have found is not responsible for particular effects, its proven existence would open up the possibility of others.

Some people have suggested a possible disastrous geological effect: that polywater could grow at the expense of ordinary water and a little of it dropped into a harbor could turn the oceans to sludge. But Dr. Lippincott says experimentally this just doesn't happen, and Dr. Allen says his theoretical calculation convinces him it never will. ◻