search & discovery

Anomalous water: polywater or impurities?

A year ago last June the results of University of Maryland spectroscopist Ellis Lippincott and his coworkers at the National Bureau of Standards seemed to indicate that anomalous water, first studied in the Soviet Union, was a new compound of formula $(H_2O)_n$.[1,2] Since then "polywater" and Lippincott's assertions about it have been vigorously attacked with a variety of experimental, theoretical and linguistic techniques.

Are those groups that are working with dilute solutions of anomalous water studying the same substance as are those working with concentrated residues? Why do some groups get better yields with Pyrex capillaries and others with quartz? And why are good Raman spectra so difficult to obtain? What is needed is, as one experimentalist puts it, "exploration of the ways of making macroscopic amounts of anomalous water so as to allow convincing resolution of its nature by analysis." Then physical scientists will know whether polywater, which has been proposed as everything from a heat-transfer liquid for engines to a useful medium for performing chemical reactions, really exists.

An American Chemical Society symposium at Lehigh University, Bethlehem, Pa., last June gave both pro- and anti-polywater forces a chance to present their findings. Most participants agreed there is as yet no proof that the peculiar properties of the substance, which is generally produced in quantities no greater than a microgram, are not due to impurities. Although work is continuing at a rapid pace, as of the end of August most of the questions remained unanswered.

Lippincott himself admits that his results are not as clear as he first thought, and that some of his samples may have been impure. But he maintains that spectral analyses (infrared, Raman, mass, nuclear magnetic resonance, electronic) of his cleanest samples have shown no evidence of the silicon, chlorine, potassium, calcium and carbon impurities that others have found in their samples.

Extraordinary care, he stresses, must be taken in preparing anomalous water, and he presented the Raman spectrum

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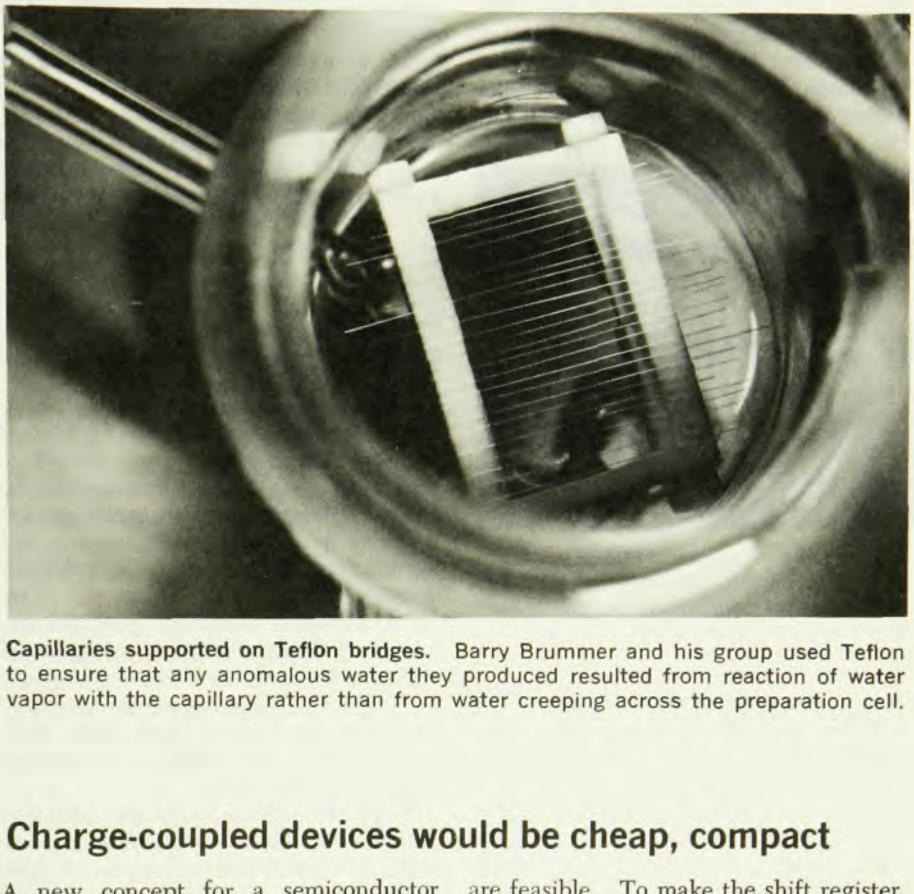


Capillaries supported on Teflon bridges. Barry Brummer and his group used Teflon to ensure that any anomalous water they produced resulted from reaction of water vapor with the capillary rather than from water creeping across the preparation cell.

Charge-coupled devices would be cheap, compact

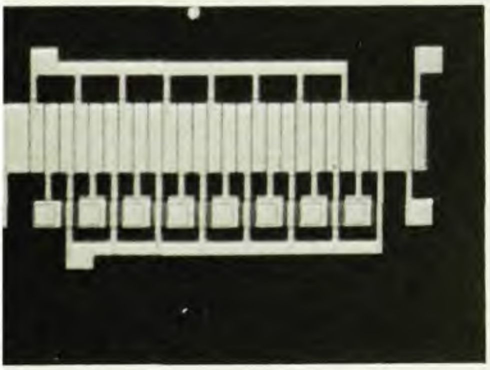
A new concept for a semiconductor device—charge coupling—shows promise for use as a shift register, delay line, memory and optical pick-up device. Because the devices transfer charge without the use of leads connecting discrete elements, they are inherently simpler than integrated circuits, and would, presumably be cheaper to make and more compact for some applications. The concept, proposed by Willard S. Boyle and George E. Smith of Bell Labs, essentially consists of storing charge carriers in potential wells created at the surface of a semiconductor and moving the charge across the surface by moving the potential minima. The easiest way to produce the minima is to apply fields across a thin oxide formed on the surface of the semiconductor.

In the 1 August issue of *Applied Physics Letters* Michael Tompsett, Gilbert Amelio and Smith report that they have produced an 8-bit shift register and shown that some other applications are feasible. To make the shift register the experimenters put 26 closely spaced MOS (metal oxide semiconductor) capacitors in a row on an n-type silicon substrate and put a p-n junction at either end. Information is shifted in successive steps from one capacitor to the next. One needs three capacitors to store one bit.

A dc biasing potential is applied to the metal electrode of each MOS capacitor, which forms a uniform depletion region at the semiconductor–insulator interface. Then one applies an even more negative voltage (storage voltage) to every third electrode, thus forming a potential well there. Now minority carriers representing information can be put in these potential wells at the semiconductor-insulator interface. To transfer the charge to an adjacent electrode, a still more negative voltage is applied to the adjacent electrode. After the transfer, the voltage on the first capacitor is restored to the original bias, and the voltage on the second to the storage value. The process can then be repeated. Once the charge has been transferred to the desired location, it can be detected by putting it into an external circuit.

The minority carriers can come from three sources: from bulk or surface generation–recombination centers within the depletion region, from hole–electron pairs produced by incident radiation or from the first p-n junction.

Because the device transfers charge (information) from one place to another, it serves as a shift register. Although the first model holds eight bits, the experimenters hope to put strings of the registers together, each about 100 bits long; Smith says that as many such registers as desired (conceivably millions) could be tied together. After 100 bits are shifted, though, one has to regenerate the signal, because it is attenuated as the transfer occurs.



8-bit shift register. Device stores charge carriers in potential wells created at surface of semiconductor and moves them by moving potential minima.

The charge-coupled device can serve as an imaging device by allowing the light image to strike the substrate, creating electron–hole pairs. The holes will then diffuse to the electrode side where they can be stored in the potential wells created by the electrodes. When enough energy has been stored, the information can be read out using the shift-register technique.

Charge-coupled devices can be made with the same technology already used for integrated circuits. However, Smith told us, to make the device work the electrodes must be close enough—about 0.1 mil—to allow the occurrence of charge coupling from one electrode to the next. Present manufacturing tolerances between metallization are about 0.3 mil.

A shift register made with insulated gate field-effect transistors (IGFET) would occupy several times the space of a charge-coupled shift register. Although charge-coupled devices would be compact and easy to fabricate, these advantages may be offset (to a still uncertain extent) by complexities of generation, regeneration and sensing.—GBL

X-ray data suggest existence of 3-K blackbody radiation

More evidence that the cosmic three-degree blackbody radiation does not have a hump in its spectrum at about 1 mm has been reported by E. T. Byram, T. A. Chubb and Herbert Friedman of the Naval Research Laboratory [*Science* **169**, 366 (1970)]. Measurements by James Houck, Kandiah Shivanandan and Martin Harwit (and subsequently by Dirk Muehlner and Rainer Weiss) had indicated a flux 50 times higher than expected from a 3-K blackbody spectrum (PHYSICS TODAY, July 1970, page 56).

In a rocket-borne x-ray survey of Centaurus A the NRL group found a flux consistent with 3 K. Although measurements were made at energies from 1 to 10 KeV, the experimenters infer that they are looking at inverse Compton scattering of cosmic-ray electrons in the galaxy from the infrared photons; as a result the photon energy is raised into the x-ray region.

Harwit told PHYSICS TODAY that the NRL conclusion is based on a very specific model of Centaurus A. "Specifically," he said, "the assumed magnetic field intensities could differ by more than an order of magnitude from the assumed values; this affects the conclusion drastically."

Chubb told us that although NRL did assume a specific model, it is a reasonable one because it is based on an electron–proton ratio equal to that observed in cosmic rays on earth and on an equipartition in energy between the particles and magnetic field in Centaurus A. —GBL

Polywater

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(Raman spectra show the symmetric vibrational modes that may not be excited by infrared radiation) of one sample to prove his point. The spectrum had no free OH-stretch band, an omission that supports a polymer structure, and did have what seemed to be a hydrogen band at 1700 to 1800 cm^{-1}. This band, although consistent with the expected hydrogen bonding, is identical with a sodium-nitrate frequency; nitrate had been introduced when the preparation tube was washed with nitric acid, and a crystal of $NaNO_3$ subsequently appeared in the water.

Water II. Boris Deryagin (Karpov Institute of Physical Chemistry, Moscow) has, according to Lippincott, produced samples of anomalous water that are "a lot cleaner than anything we have produced in this country." Deryagin, one of the original champions of "polywater"[3] (which he calls "water II") still believes in its existence and proposes a molecular weight of about 180. He claims that those groups who have found impurities have simply been careless in their preparation.

A significant part of Deryagin's evidence is his distillation data. One end of a sample-containing capillary was heated to 250–300°C while the other end was chilled; the distillate had the same anomalous properties as the original sample. His group also distilled water II across a 700–800°C thermal barrier, and here the distillate had properties indistinguishable from those of "water I" (normal water).

To most of the assembled group, these data were hard to refute. But Alan E. Florin (Los Alamos Scientific Laboratory), who with Sherman Rabideau has also been trying to prepare impurity-free anomalous water, pointed out that boron, a constituent of borosilicate glasses, is volatile in steam. If boron were originally present in the anomalous water, it could be carried along during the 250–300° distillation.

He is generally suspicious, Rabideau later told PHYSICS TODAY, of the distillation data. In a small (10–50 micron) capillary, he claims, the liquid is more likely to "go flying down from one end to the other like a little shotgun slug" or to be transferred along the walls than it is to distill properly. Deryagin had tried to minimize this possibility by widening some of the capillaries before distillation; this attempt, says Rabideau, probably does not prevent film transport along the walls.

Impurities found. Rabideau and Florin have prepared[4] anomalous water in quartz capillaries by two fairly standard methods. They examined weighed residues (the nonvolatile part of the sample, which is believed to be concentrated "polywater") with electron microprobe and neutron-activation techniques, and did boron isotope-dilution studies; they found an average of 6% boron and 5% sodium. They reproduced some of the anomalous-water properties (increased refractive index, long tapered meniscus and a flat cooling curve) with aqueous sodium borate. "We have been unable to make any polywater that did not show the relatively high impurities in the concentrated material. I think the burden of proof now really rests with those who say they have something unusual." His work, Rabideau says, will continue only if and when they get samples from other laboratories.

Denis Rousseau (Bell Telephone Laboratories) has also found a variety of impurities in anomalous water. Rousseau, a spectroscopist, believes that anomalous water is most likely a mixed aqueous salt solution, with carboxylic-acid salts the main determinant of the infrared spectrum and the freezing point. Rousseau has recently found that human sweat, whose major organic constituent (sodium lactate) is a carboxylic-acid salt, has an infrared spectrum qualitatively similar to that of "polywater." He is now confident that the spectroscopic properties of anomalous water do not result from a polymer of water.

One of Rousseau's key experiments was the preparation of anomalous water from D_2O. If the 1600 cm^{-1} and 1400 cm^{-1} infrared absorption lines of anomalous water are due to a hydrogen vibration in "polywater," then there should be a frequency shift for poly D_2O because of the change in mass. He found no such shift (see figure). Although he feels that his D_2O results are proof that the 1600 cm^{-1} line is due to impurities, others are not so certain. They question whether or not he was looking at the spectrum of anomalous D_2O; if incomplete exchange occurred, he might have been looking at anomalous H_2O instead. None of the other groups have as yet done D_2O studies that they consider sufficiently reliable to report.

Robert E. Davis (Purdue University) and R. L. Board (Hewlett-Packard Company) have done ESCA ("Electron Spectroscopy for Chemical Analysis")[5] studies of anomalous water in collaboration with Rousseau. ESCA, a fairly new way of mapping electron levels in atoms and molecules through x-ray induced electron emission, yields information about the shift in binding energies of the electrons in a particular chemical environment relative to the binding energy in the isolated atoms. Davis found, as one conference participant put it, "most of the periodic table" in his samples; he believes he has identified sodium, nitrate, potassium, carbon, chloride, borate, sulfate and silicate.

Factors analyzed. At Tyco Laboratories Inc, Waltham, Mass., a group led by Barry Brummer has contracts from the Advanced Research Projects Agency and the Office of Saline Water to find ways of producing "polywater" in large quantities. Although the group has not reached this goal, they have identified two of the factors that appear to control yields—the state of the capillary surface and the instability of the water-vapor pressure during preparation. Brummer's group (Frank Cocks, Gerald Entine and Juanita Bradspies) compared the yields from capillaries treated to ensure that they were fully hydrated (the drawing process dehydrates the glass surface) with the yields in as-drawn capillaries; they found that the hydrated capillaries give higher yields. Particularly good results came from those capillaries that had been treated with substituted silicon hydrides to form a surface containing only "vicinal" hydroxyl groups—any hydroxyl group present is close enough to another hydroxyl group to interact with it. The samples were shown by thermal-expansion and freezing behavior to be essentially the same as those of Deryagin.

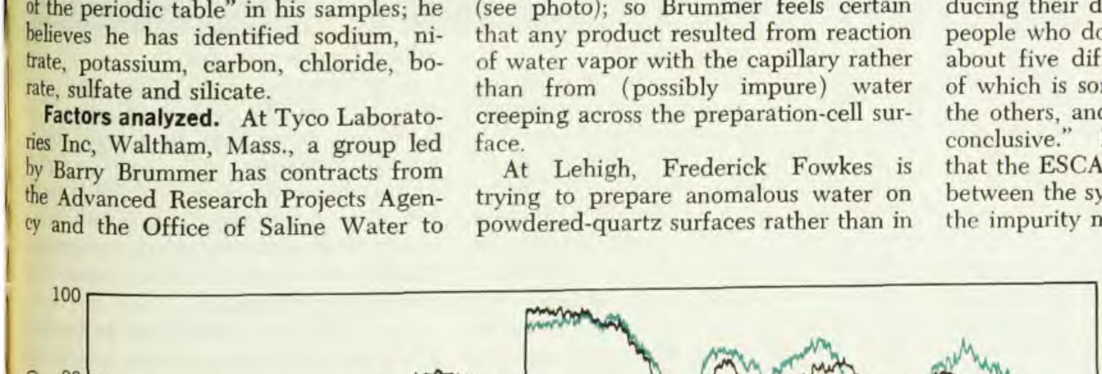
Only Deryagin, according to Brummer, describes anomalous-water production procedures in detail. Deryagin claims that the substance is formed only in an unstable environment. This observation led Brummer's group to carry out anomalous-water preparations during which the ambient temperature was deliberately varied over a 0.50-C-deg range. These fluctuations, which ranged from 15-minute to two-hour periods during a week-long experiment, subjected the capillaries to alternating undersaturated and supersaturated atmospheres.

Yields, although erratic, did increase with increasing fluctuations. "We found, in common with university students, that the more you agitate, the more change you get," says Brummer. Preparations were carried out with the capillaries mounted on Teflon bridges (see photo); so Brummer feels certain that any product resulted from reaction of water vapor with the capillary rather than from (possibly impure) water creeping across the preparation-cell surface.

At Lehigh, Frederick Fowkes is trying to prepare anomalous water on powdered-quartz surfaces rather than in capillaries. Fowkes also wants to study the effect of using hydrogen fluoride to leach sodium from the glass; Robert Stromberg, an NBS polymer chemist who has been one of Lippincott's collaborators, has found that he can not produce anomalous water in pure fused quartz, which is free of (among other substances) sodium. Fowkes also plans to try the D_2O studies, as does Brummer.

Theoretical models. Experimental results have, of course, led theorists to analyze polywater. Leland Allen and Peter Kollman (Princeton University) developed[6] a quantum-mechanical model soon after they heard of the Lippincott group's results. Using the semi-empirical CNDO (complete neglect of differential overlap) method, they found the most stable structure to be sheets of water hexamers arranged in a graphite-like structure. Jerry Donohue (University of Pennsylvania) proposed[7] a cluster of 14 water molecules located at the vertices of a rhombic dodecahedron as the most likely structure. Theorists are playing a role somewhat atypical in chemical physics; they have been willing to work out models as the experimental data come in, rather than waiting until all results are safely tabulated.

Kollman and Allen have had reason to change their minds[8] about their original model. As their calculations have become more extensive and accurate, they feel that their results, coupled with Deryagin's new information on the molecular weight of water II, indicate that the symmetric bonding they originally proposed is energetically unlikely. "It turns out," Allen recently told us, "that the problem is truly unresolved. Those people who did experiments that seemed to indicate the presence of 'polywater' are having a hard time reproducing their data. On the other hand, people who don't believe it have found about five different explanations, each of which is somewhat inconsistent with the others, and none of which is really conclusive." He feels, for example, that the ESCA data do not discriminate between the symmetric-bond model and the impurity model.



Poly-D_2O (color) and poly-H_2O. These infrared spectra, taken by Denis Rousseau, show no frequency shift in the 1600-cm^{-1} hydrogen-stretch band.

The tone of anomalous-water discussions has become negative; many of the experimentalists who were enthusiastic about studying anomalous water have lost interest. In a letter to the editor of *Science* titled " 'Polywater' Is Hard to Swallow," Joel Hildebrand, a former president of ACS, says he is "skeptical about the contents of a container whose label bears a novel name but no clear description of the contents."[9] Continued careful experimental work, and particularly exchange of samples among the various laboratories, will eventually provide a more complete label. —MSR

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AGS's second decade: more precise experiments

The 30-GeV Alternating Gradient Synchrotron at Brookhaven National Laboratory will remain the best place to study many kinds of particle reactions (such as those that test time reversal) even after the much higher energy Batavia accelerator comes into operation. This view was offered by Jack Sandweiss at a summer study held at Brookhaven to explore the future role of the AGS. Sandweiss mentioned that the AGS will continue to be this country's best K-meson factory for K-meson energies in the region less than 10 GeV. Although the 500-GeV machine due to turn on a year from now at Batavia will produce K-meson beams at much higher energies, the CP-violating decays (first observed with K mesons produced by the AGS) are most easily studied with the lower energy K's available at Brookhaven.

As part of the summer study organized by David Berley and Timothy Toohig, a panel discussion examined future patterns of high-energy physics research. The discussion, moderated by Berley (head of the experimental division of the AGS) took place in the newly dedicated Hartland Snyder Seminar Room. In 1952 Snyder, along with Stanley Livingston and Ernest Courant, invented the strong-focusing principle, which had been discovered earlier (1949) by Nicholas Christofilos, then in Athens, Greece. The principle made possible the AGS and subsequent alternating gradient machines including the Batavia machine.

Conversion. Now, after ten years, the AGS is scheduled to shut down the latter half of next year for several months to be converted to higher intensity. When it starts up again it will be producing 30-GeV protons at an intensity of 10^{13} protons/sec or a factor of ten improvement over present intensity. Sandweiss, chairman of an AEC advisory subpanel studying future patterns of high-energy research, opened the discussion by requesting ideas on what administrative and technical problems in high-energy physics will be like.

Two other panel members, Rodney Cool (who was then associate director for high-energy physics) and Maurice Goldhaber (laboratory director), pointed out that the role of the AGS in its second decade of life will be that of an instrument for precision experiments, in contrast to the exploratory era of the first ten years. To carry out precision experiments, Cool foresees that the experimental groups will have to be even larger than they have been in the past and must be allowed to keep their setups in place on the accelerator floor for longer periods of time.

CP violation. Likely to be high in priority on the list of precision experiments are those involving the CP-violating weak interactions. For instance a whole class of CP-violating interactions is found in the leptonic decay of the K^0 meson ($K^0 \rightarrow \pi^\pm + \mu^\mp$ or $e^\mp + \nu$). Particle physicists would also like to study the form factors of these reactions and investigate them for both the $\Delta Q/\Delta S$ conserving and violating interactions. A particularly interesting manifestation of CP violation has been observed for the two reactions $K_L{}^0 \rightarrow \pi^+ + \mu^- + \nu$ and $K_L{}^0 \rightarrow \pi^- + \mu^+ + \nu$. The violation shows up as a difference in the decay rates for the two reactions. A more precise measurement of this asymmetry is sorely needed.

Another area in which the AGS has pioneered and which would now benefit from a series of precision experiments is that of the asymptotic behavior of interactions among hadrons. Theory holds that the characteristics of these interactions should approach asymptotic values at higher energies. Energies available at the AGS (10–30 GeV) are believed to be high enough to begin to study this effect. Such experiments are best carried out at the AGS, Berley argues, before they are attempted at Batavia.

Detailed investigations of mass spectra from hadron interactions, differential cross sections, and reactions involving the production of many particles such as $\pi^+ + p \rightarrow p + \pi^+ + \pi^+ + \pi^-$ or $K^- + p \rightarrow p + K^- + \pi^+ + \pi^-$ would be valuable for checking out the predictions of particle theorists.

Procedures. Two other members of the panel, Ronald Rau (then chairman of the BNL physics department) and Larry Rosenson (chairman of the BNL users organization), were concerned with how experimental facilities and operating procedures should change to accomodate the new kinds of experiments best and take most advantage of the new intensity. Both felt numbers of semipermanent secondary particle beams ("particle spigots") should be set up with each one being shared by a number of groups. At the same time, ways must be found to allow more groups to function on the floor simultaneously. Although now traditionally each group custom-builds its own collection of analysis and detection hardware, in the future the largest of these hardware components might be supplied by the laboratory to be shared in common by various groups.

For example several groups have developed large wire-spark-chamber systems that function as multiparticle magnetic spectrometers. They are connected to an on-line computer, can analyze complex multiparticle interactions with great precision and can handle certain events at rates many orders of magnitude higher than is possible with a bubble chamber.

Cryotecnics. Fred Mills, the new chairman of the BNL Accelerator Department, noted that, in general, high-energy physicists will have available low-temperature superconducting technology to reduce the size and cost of detection and beam-handling equipment. Smaller size in itself leads to lower cost and greater efficiency.

Both Mills and Goldhaber looked forward to a new higher-energy accelerator for BNL. A multithousand-GeV synchrotron having a cryogenic magnet ring a mile in diameter and an experimental area several miles long would just fit the present BNL site. Mills suggests that alternatively an intersecting storage ring may be the next step to higher energy. Such a plan would be permanently stymied, however, if BNL is forced to bow to current pressure from the government to sell the North Tract, which accounts for 30% of the total site. —HLD □