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Sonic Cavitation in Water

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Abstract

Nearly four years of experiments in treating water to retard the onset of cavitation resulting from high-intensity acoustic waves is described. Sound intensity 23 times that at which cavitation occurs in pure (deionized) water can be applied to specially treated water without causing cavitation. The three effective methods examined are unusual in that the water is "strengthened" by additives that (1) remove nuclei by deoxygenation, (2) increase molecular bonding by hydrogenation, or (3) augment cohesion by introducing a natural polymer. An appended survey of the literature documents the complexity of water and serves as an excuse for omitting a hypothesis to explain the increased resistance to cavitation that results from the treatments.

Problem Status

This is a final report on one phase of the problem.

Problem Authorization

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Preface

This report summarizes the studies and experiments of Mr. Darner during a period of several years before his retirement. It is written primarily for the sonar engineer who still seeks a practical means of suppressing cavitation other than by applying high hydrostatic pressure. This being still an unsolved naval problem, Mr. Darner was asked to document his work so that others could continue his investigations.

SONIC CAVITATION IN WATER

Introduction

Before beginning the search for a way to increase the cohesiveness and adhesiveness of water, it was thought advisable first to obtain some knowledge of the structure of that liquid, the assumption being that the study would be simple and straightforward. Because of the normal, intimate, everyday acquaintance with the various forms of this abundant combination of hydrogen and oxygen, the complexities that arose were not anticipated. For this report, it would be unnecessary--nay, futile--to try to summarize all the vagaries of water or to discuss every hypothesis advanced to explain them; however, here are a few quotations about the structure of water.

Dr. R. A. Horne has said [1] that "Liquid water is easily the most complex and ill-understood substance known to man." In 1966, Professor Walter Drost-Hansen [2] portrayed water as the "... most abundant and at the same time most atypical liquid on the face of the earth. It...has challenged theoreticians for decades." Ten months later, Margaret Glos wrote [3], "Deciphering the structure of liquid water with its many anomalous properties is one of the most puzzling problems facing the chemist today." After having studied the molecular structure of water for more than 20 years, Buswell and Rodebush wrote [4], "Because it is so familiar, we are apt to overlook the fact that water is an altogether peculiar substance. Its properties and behavior are quite unlike those of any other liquid."

It seems that were it not for the fact that water is irregular, it would exist on this earth only as a gas, and the world probably would be as desolate as the moon.

These comments will suffice to emphasize that water is indeed a peculiar substance. A more complete discussion of this subject has been relegated to Appendix A so that we can get on immediately to the principal matter of this report--the suppression of sonic cavitation in water.

Sonic Cavitation

A Little History

Because of the striking similarity of the consequences then and now, sonic cavitation may well be introduced with some historical events:

More than 200 years ago, Leonhard Euler (1707-1783) considered the hydraulic-energy relations between pressure and speed. He anticipated the serious difficulties that later generations were to encounter when their propellers and hydraulic turbines would operate in areas of vapor-filled bubbles--the phenomenon that now is called cavitation. The speeds attained during that period probably were too low to cause trouble, but Euler understood clearly that a reduced pressure in the perfect liquid he had assumed for study would result in near-zero resistance and loss of thrust. He was thinking of bubbles only in relation to performance loss; damage to metal was not considered until this century.

About 1907, when the Lusitania and the Mauretania were powered with steam turbines generating 70,000 horsepower, two difficulties appeared: First, a marked increase in propeller shaft speed did not result in a commensurate increase in thrust; and second, the metal of the Mauretania's four propellers was eaten away to a depth of 3 to 4 inches on her maiden voyage! If no remedy were found, the propellers would have to be replaced every two months at a cost of $70,000! After studying the problem, Lord Rayleigh reported that the erosion was due to cavities that formed in the low-pressure areas and collapsed on the propeller surface with a pressure amounting to several thousand atmospheres. According to his calculations, a perfectly spherical bubble collapsing in an incompressible fluid would produce infinite peak pressure. In fact, pressure as high as 30,000 atm has been reported in a number of experiments.

The Modern Viewpoint

Similar problems occur in high-power sonar echo-ranging. First, during cavitation, the ranging distance is reduced by the generation of harmonics and noise, the mismatch of projector impedance, gaseous water, and other factors. That is, efficiency declines rapidly as acoustic intensity increases. Second, there is rapid mechanical destruction of the transducer, whose replacement may cost as much as the Mauretania's four propellers.

The problems presented by sonic cavitation in water probably are little better understood than the medium itself. Myriad papers appear in the literature, bearing inconsistent hypotheses both on the causes and the effects of cavitation. R. J. Bobber has produced a comprehensive appraisal [5] of published research on the subject, with an annotated bibliography; the abstract of this long-needed condensation reads, in part: "... research findings of several authors are discussed and compared in the light of the existing theories. It is concluded that none of the theories satisfactorily account for all the experimental results and that additional research on the following aspects of sonic cavitation would be profitable: the nature of cavitation nuclei; the theory of bubble dynamics within the range of parameters (bubble radii, ambient pressure, gas saturation pressure, *etc.*) that accompany sonic cavitation; the effects of surface tension, gas saturation pressure, frequency, physical boundaries, transducer geometry, transducer materials, and transducer and dome liquids in determining the acoustic pressure at which sonic cavitation begins. ..."

Pure Water

As used in the remainder of this report, "pure water" connotes the lay definition; distilled water would be called "pure." Pure water--completely free of suspended particles--is a rarity, however, and would be found only in a specialized chemical laboratory. Instances have been cited in which the water remained "contaminated with motes" after having been redistilled as many as 20 times in a quartz receptable ([6], page 318). Neutral water (pH = 7) is equally scarce; normally, it is weak carbonic acid (pH = 5.8 to 6.0) if there has been any brief contact with the atmosphere, which introduces carbon dioxide gas ($H_2O + CO_2 \rightarrow H_2CO_3$). A manufacturer of fused-quartz distillation apparatus cites the characteristic pH value of normal distilled water as 5.5, *versus* 6.2 for double-distilled water. Concerning the dissolving by water of carbon dioxide from the atmosphere, Johnson [7] has stated that "... even in an unstirred liquid contained in an open beaker, the process is substantially complete in about ten minutes."

Laboratory Methods of Inhibiting Cavitation

Retarding the onset of cavitation is more readily accomplished in laboratory experiments involving small volumes of water than with the large volumes encountered in modern ships' domes or transducer test tanks. Many laboratory investigations have been made using only a few gallons of water; the French [8] probably hold the miniaturization record with 35 cm^3!

Water resists cavitation under a comparatively low hydrostatic pressure, or for an indefinite time after the application and release of high pressure. "Low" pressure is considered to be 3 or 4 atm; high pressure, in the neighborhood of 1000 atm and upward. Eliminating micron-size particulate matter by a filter or a still or both is somewhat effective in retarding the onset of cavitation, because occluded gas molecules that can nucleate are removed. Degassing the water with vacuum equipment is highly effective in "strengthening" it, especially at audio frequencies. The degassing process usually cannot be carried out in a test tank, however, because of the external crushing force of the atmosphere. When the internal pressure in a vessel is reduced only from 760 to 500 mm Hg, the implosive force on each square foot of the outer surface is more than 700 pounds.

Deoxygenation

Exit: Oxygen

It seemed that there should be some way to obtain sufficient degassing by chemical means and thus circumvent the destructive force. Simply by removing the oxygen, which constitutes one third of all the absorbed gases, the partial pressure of the remainder could be reduced to 500 mm Hg. The simplest method of removing the oxygen seemed to be to allow steel to

rust. Only a few hours after the idea had occurred, an experiment was started whose completion was expected in a few days. That was 4 years ago!

The first experiment was both hasty and crude. For several weeks, the author had been investigating various methods for detecting the onset of cavitation, so all the necessary apparatus was on hand and the absolute sound intensities that would produce cavitation had been determined. The test tank was a 30-gal aquarium 36 in. long, 12 in. wide, and 16 in. deep. The sound source was centered at one end of the tank with its face brilliantly illuminated from the opposite end by the collimated beam of a 1000-W projection lamp. The light beam provided the means for visually detecting cavitation at the face of the sound source and at the two antinodal regions. Another indicator of cavitation was a small probe hydrophone connected to an oscilloscope. The acoustic projector was driven at its resonance (slightly below 4 kHz) by a 200-W power amplifier. The level of electrical power into the projector was monitored continuously and was correlated to the acoustic intensity at the antinodal points determined by the complex standing-wave system.

A 1-lb package of steel wool was halved, rolled into two 3-in.-diam cylinders, and placed in the aquarium at each side of the projector. Wooden boards 1 in. thick were floated on the surface to prevent re-entry of oxygen into the water from the atmosphere. At this time, the water was nearly saturated (98-100%) with oxygen. On the following day, the oxygen content was 70% of saturation; on the second day, it had dropped to 35%. The first readings were recorded in the laboratory notebook with the remarks that "the power had to be increased about 4 times," and "be suspicious of the data because they are too good"!

On the third day, the visibility was so obscured by rust particles that the tank had to be emptied, washed, and refilled with distilled (deionized) water, and the boards again floated on the surface. While this fresh water was reaching thermal and gaseous equilibrium, the foreign literature pertinent to this particular experiment was searched. Britain and France supplied encouraging data; Iyengar and Richardson [9], experimenting at King's College, published a curve showing the relation between cavitation threshold and air content. Although the work had been done at a frequency 100 times that of this project, it did indicate that a five-fold power increase might be expected for water that had been degassed to 70% of saturation. The French scientists Degrois and Badilian at the Laboratory for Physiological Acoustics showed [10] that water saturated only with nitrogen gas produced no *erosion* of a 1-mil-thick aluminum sheet exposed to cavitation for 3 hours, whereas very strong erosion (greater than that with air saturation) was observed when the water was saturated with oxygen. Not so encouraging, however, are recent indications in the literature that deoxygenation actually can increase the *corrosion* rate of high-purity aluminum.

Improving Experimental Technique

More care was exercised in the second experiment; the pads of steel wool were enclosed in water-filled plastic (sandwich) bags to prevent the contamination of the water that had occurred in the first experiment. The mechanism by which these polymeric bags are permeable to gases is discussed by Lebovits [11]. The bags retarded somewhat the rate of withdrawal of oxygen; nevertheless, it was sufficiently rapid. On the eighth day, when the oxygen content of the water was 4% of saturation, a little more than twice the normal power could be applied before cavitation occurred. The calculated gas content (67%) was in disagreement with that measured with the Van Slyke apparatus (80%). At that time, this discrepancy was very puzzling, because both the oxygen meter and the Van Slyke apparatus seemed blameless.

Further strengthening of the water was not expected, because the results agreed closely with data published by both Galloway [12] and Barger [13], which showed that power could be doubled at 2/3 saturation. Nevertheless, it was decided to continue, hopefully to determine the reason for greater power increase in the initial crude test. The cohesiveness of the water increased almost daily until, on the 18th day, it withstood 8 times the initial power without cavitation (Fig. 1, top curve). This increase was perplexing, because changes in the oxygen and the total gas content were so slight that they could have been within experimental accuracy. The oxygen meter indicated 2%, the Van Slyke apparatus indicated 83%, and there seemed to be no reason for the strength of the water to have increased.

To be certain that the water was becoming more resistant to cavitation, data were not recorded unless the power could be applied continuously for 30 min. This was considered to be an exceptionally severe test on a considerable volume of water, because of the circulation created by thermal currents from heat produced by the acoustic projector and the collimated beam of light.

The second test terminated abruptly when the high sound intensity cracked the tank; the vibrational amplitude of the glass walls opposite either of the two antinodes was large enough to produce a loud clatter when the walls were touched with any metallic object.

Cavitation of "Rested" Water

The encouraging results of these first two tests still were eyed askance. The major uncertainty lay in the cavitation level of a sample of untreated water after it had remained undisturbed for a considerable time. Some investigators had reported great increase in the "strength" of water after it had "aged" for a number of days. Consequently, for the third test, the tank was filled with distilled water and was tested three times a week over a period of 22 days. Without fail, cavitation did not occur with 3 W electrical power input, but repeatedly occurred at 3.5 W (Fig. 1, lower curve). Many measurements of the sound pressure level at

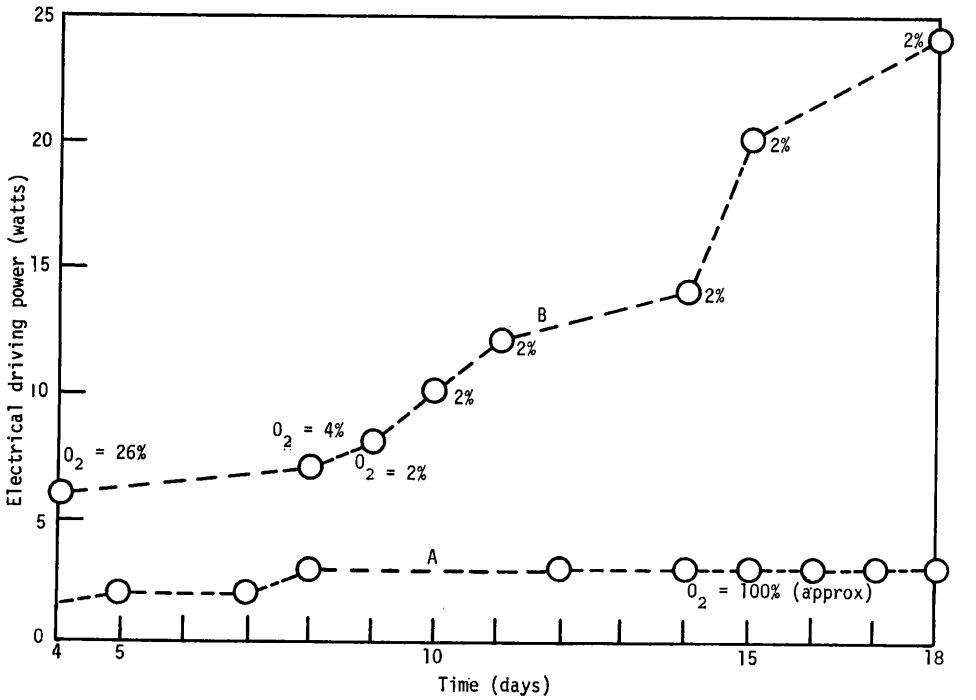

Fig. 1. Comparison of power that can be applied to "normal" and to deoxygenated water without inducing cavitation. Curve A: "normal" water; for 3-W input to projector, the acoustic intensity at the antinodes is 0.3 W/cm^2. Curve B shows the perplexing increase in driving power that was possible in deoxygenated water.

both antinodes proved that the 3-W input produced 1 atm peak sound pressure, within the usual accuracy of acoustical measurement (probably ±1 dB). That is, the ratio of electrical driving power to acoustical intensity was 10 to 1: 3 W in, for 0.3 W/cm^2 out.

Progress with Deoxygenation

After it had been established that this water did not become more resistant to cavitation by "resting," the deoxygenation process was repeated; that is, the bagged steel wool pads were inserted, and the water surface was covered. The following results were noted: without causing cavitation, the electrical power could be increased by factors of 2 on the second day, 7 on the thirteenth day, and 10 on the seventeenth day. Of course, these levels always had to be exceeded during the daily tests to determine the level at which cavitation did occur. The breakdown of the water at one of the antinodes was evidenced by the appearance of a sparkling bubble. To regain its former strength after cavitation, untreated water reportedly requires a resting period varying from 2 to 24 hours. This deoxygenated water, on the other hand, could be healed in seconds simply by reducing the power to only 4 times that for ordinary cavitation level. For example, after withstanding 10X power for

30 min, the water would break down after only a few minutes at 11X power. Then, when power was reduced to only 4X, the bubble would go into an erratic dance and suddenly disappear, leaving the water with its original strength and permitting immediate reapplication of 11X power for another few minutes.

Evaluating Sea Water

This method of inhibiting the onset of cavitation appeared to be practical for use in ships' sonar domes, except that some domes contain salt water, whose characteristics were not known. Consequently, eight 5-gal jugs were filled with clean sea water about 10 miles off Cape Kennedy by the skipper of a shrimping boat, and were transported back to the laboratory. Evaluating this water provided a challenge for many days. After six of the jugs had been emptied into the aquarium, the oxygen content and total gas content of the water were found to be far too low to establish the initial power level for the onset of cavitation. It was expected that this level would be the same as for fresh water, but there was a dearth of information on the subject, and to obtain reliable data, the liquid must contain gases to within about 2% of saturation. To aerate the sea water and obtain gaseous equilibrium with the atmosphere, the output of the charcoal-glasswool aquarium filter was elevated and allowed to splash onto the water surface for a few days. At the end of this period, the oxygen meter showed that the oxygen content had risen to 100%; the Van Slyke apparatus showed that the total gas content had risen to only about 85% of saturation.

After the water had rested for a few days, the oxygen content decreased about 20%; the total gas content fell off only slightly. After some contemplation, an explanation arose for this seemingly peculiar action: First, it had been assumed that a like amount of gas would saturate both sea and fresh water. Sea water becomes saturated, however, with only 85% of the amount required to saturate fresh water. Second, it is normal for the oxygen meter to indicate 100% while the total air content is 15% lower than for fresh water. The polarographic oxygen-measuring probe is sensitive to gas *pressure*, whereas the Van Slyke apparatus indicates gas *volume*, computed from a pressure-differential reading and determined by referring to a graph applicable only to fresh water. Third, what had been thought to be dust particles in the water were identified finally as a swarm of plankton that, although microscopic in size, could be numbered in the millions and could reduce the oxygen supply by respiration. Unfortunately, the problem posed by the plankton never was solved; they could not be removed by continued operation of the aquarium filter, and eliminating them by poisoning was rejected because it would have introduced another unknown into the already complex problem.

Consequently, the first cavitation measurements on sea water had to be made with the oxygen content 5% below saturation; the power applied just before the onset of cavitation had to be accepted as 50% higher than the value established for fresh water. At the end of the third week of deoxygenating the sea water as previously described, the oxygen saturation

was 10% and the electrical power applied to the acoustic projector could be increased to eight times the value that initially would have caused cavitation in the untreated water. A nine-fold increase was recorded after the experiment had been set aside for 4 months.

Hydrogenation

Enter: Hydrogen

The equivalence of the results between fresh and salt water tended to indicate further that the increased resistance to cavitation was far too great to be attributed only to the absence of one-third of the gas. Fortunately, the reason for this anomalous increase was discovered many experiments later. It had been observed that a small gas bubble would appear at the top of the water-filled plastic bag containing the steel wool. It had been assumed that this was air that finally had freed itself from the tightly bound steel-wool roll to form a bubble. When the bubble continued to appear after every precaution had been taken to be certain that the steel wool was wetted and devoid of occluded air, the suspicion arose that the gas was not simply air, but a byproduct of the deoxygenation process. This proved to be true; tests indicated that the bubble was hydrogen.

It seemed inconceivable that this small volume of hydrogen gas could influence the tensile strength of water; the unrealistic idea that the hydrogen bond might be augmented was immediately discarded when a rough estimate showed that only a single molecule of H_2 would be available for each million molecules of H_2O; and it was heretical even to imagine that the addition of a gas to water could do anything but weaken it further. There had to be an explanation, however, for the increasing resistance of this treated water to cavitation after the oxygen had been depleted. Again, the aquarium was filled with distilled water, which was permitted to age until tests showed that cavitation was not present until a 3-W input was exceeded. Then, hydrogen was introduced slowly in what might be termed "molecular" form. For this experiment, an individual test for the onset of cavitation was reduced from 30 to 15 min to save time.

At the end of 10 days, the electrical driving power could be increased to more than 6 times that used before the introduction of the hydrogen. By combining the two processes, deoxygenation and additional hydrogenation, 23 times the power that would have caused cavitation in untreated water could be applied. For a few minutes at a time, the water would withstand an increase of 36X normal power! This exceeded the power handling capacity of the acoustic projector, and it failed!

The cohesiveness of this "strong" water was compared with that of ordinary water by counting the drops from a medicine dropper necessary to make 1 cc. It required 20 drops of ordinary water, but 40 drops of the treated water to fill 1 cc. A coworker verified this count by repeating the measurements without knowing the previous answers; he

recorded 20 and 39 drops, respectively. These results were contrary to what had been expected.

The Hydrogen Generator

The hydrogen generator used to add the hydrogen to the water in "molecular" form deserves description. The outer case of an alkaline-type "D" cell is removed to expose the poles that this case serves to reverse in making the cell interchangeable with the ordinary carbon-zinc cell. Then, the cell is dropped into a 1-in.-diam by 8-in.-long gum-rubber bag into which steel particles have been placed to a depth of ¼ in. These steel particles also are added between the battery case and the rubber container, which then is filled with water and either knotted or tied off at its opening about 4 in. above the cell. The electrolysis of the water releases oxygen from the large area of the case, which is positive. This readily combines chemically with the surrounding steel particles to form Fe_xO_y, or rust. Hydrogen is generated at the negative (center) electrode, and is absorbed by the water in the bag. The gum rubber container is extremely permeable to hydrogen [11] and readily allows the gas molecules to pass through into the water in the tank. The generating rate, determined by the ionization of the liquid, can be controlled from very slow in pure water to quite rapid in water to which a few drops of vinegar or other weak acid have been added.

An Improved Deoxygenation Method

In the later and final tests, a modification of the deoxygenation process was considered to be a vast improvement. Small steel punchouts of 1/8-in. diam, a byproduct of the steel-strap-making industry, were substituted for the steel wool with equal or greater effectiveness. They required less volume than the steel wool to maintain the same steel/water ratio, and the bubbles of hydrogen that had occurred in the plastic bags were never evident. Although the pellets are very active chemically in forming rust, they probably would last for many years when used in a covered or enclosed vessel; once the water has been depleted of O_2, the steel pellets become inactive. The reduced volume and attendant decrease in the diffusive area of the containers was more than compensated for by substituting natural rubber for the plastic bags. The permeance of natural rubber to oxygen is 750 times as great as that of Mylar (polyethylene terephthalate) and 4000 times as great as that of Saran (polyvinylidene chloride). This rubber, in the economical and readily available form of "penny balloons," proved to be a very satisfactory bagging material; the small diameter of the balloons (1.5 cm) was an optimal size for conveniently inserting them into a sonar dome.

Polymers

Related Fields

The results of these tests provided the material for an oral paper on the "Increase of Cavitation Threshold by Water Treatment," delivered at the 25th U. S. Navy Symposium on Underwater Acoustics in Orlando, Florida, on 7-9 November 1967. During this meeting, Dr. J. W. Hoyt of the Naval Undersea Research and Development Laboratory, Pasadena, California, mentioned his work on the reduction of drag resistance coefficient in water, and suggested that the USRD might be interested in some of its aspects. He mentioned some anomalies that had remained unexplained until this last decade: Occasionally, the trials of supposedly identical ships tested some months apart had yielded rather wide variations in the power required to produce a given speed--much more than reasonably could have been explained by deviation from shipyard tolerance. On a smaller scale, the resistance of ship models, as measured in towing tanks, sometimes seemed to vary without any explanation other than that of a "change in resistance quality of the water." At times, some towing tanks underwent resistance "storms," during which the apparent friction decreased greatly, sometimes for months.

Polysaccharides

The recent discovery that dilute high-molecular-weight polymer solutions have unusually low turbulent-flow friction coefficients has provided the key to progress in understanding these anomalies. It appears that many marine organisms can exude into the sea (or into a towing tank) high-polymer substances that are effective in changing the resistance of immersed bodies to turbulent friction. Moreover, they can cause a hemispheric-nosed cylinder to show less tendency to cavitate in a blowdown tunnel.

Among these organisms are algae, about which *Encyclopedia Brittanica* says: "Algae are invaluable in the economy of nature. In all but a few isolated cases they contain chlorophyll and are thus of great importance as primary producers of the food that ultimately sustains all aquatic animal life." It seemed not unreasonable to Dr. Hoyt that these algae might play some role in changing the inception of acoustic cavitation. When he offered to culture sufficient *Porphyridium Aerugineum* for tests in the 30-gal aquarium, the thought of embarking on further cavitation experiments became very appealing. This simple, fresh-water alga with the long name exudes a high-molecular-weight polysaccharide (10^5 to 10^6 atomic-weight units) into the water; why it does this is not known. It has been suggested that the exudation may aid in developing resistance to bacteria or may offer some disagreeable aspect to predators.

Five months after the Symposium, nine gallons of the alga *Porphyridium Aerugineum* were received. They were mixed with sufficient pure water to fill a standby 30-gal aquarium, and irradiated with four 36-in.-long GRO-LUX fluorescent lamps, which emit light primarily in the lower part

of the spectrum and provide considerable red light to promote photosynthesis of chlorophyll. When it was learned later that 3 months had been required to culture only 9 gallons, the practicality of large-scale production appeared to be remote, even though the algae secretion should inhibit cavitation!

Polyox

With the shipment of algae from California was some poly(ethylene oxide) that, too, had promoted reduction in the drag coefficient. This polymer is the chemical compound that gained attention by siphoning itself out of a beaker; its sliminess for laboratory experiments is unparalleled. To allow the algae more growing time, the "Polyox" was tested first. The powder was added to the aquarium full of fresh water in increments of 10 ppm by weight each day. Between the 8th and the 10th days, the cavitation resistance of the water peaked at an encouraging power increase of 8X normal. Because 100 ppm was the maximum used in the water-tunnel experiments, testing with a higher concentration was not contemplated; however, the utility of this solution (or suspension) seemed to justify continuing the tests to determine the long-time stability of the material, although a white fuzzy growth had begun to appear on the sound projector and the tank walls. During the following month, a flocculent precipitate continued to form on the bottom of the tank, despite intermittent operation of a glass-wool filter. By the end of the month, all the Polyox must have been out of suspension, because the onset of cavitation then occurred at the same level of power as before the polymer had been added. The action of the high-power underwater sound on the Polyox suspension appeared to be similar to the flocculation and precipitation of smoke particles with high-intensity sound radiation in air.

Algae and Cavitation

Following this dead-end experiment with Polyox, the biopolymer-water solution was transferred from the culture aquarium to the test aquarium. After some days of stabilizing to get the gas concentration at 98% of saturation, it was found that 10X normal power could be used without causing cavitation.

Now that the polysaccharide had been shown to be useful in solution, the thought occurred that it might be possible to extract it in crystalline form and reconstitute it by adding water--like instant coffee, or tea! This would be a very practical method for storing and transporting such a water strengthener, and would provide the substance in a convenient form to use as an additive to the water in ships' domes or in acoustic test tanks.

Instant Inhibitor

The water was evaporated by boiling until the residue reached the consistency of light syrup, at which time "boiling" would cease, and further evaporation would occur in explosive bursts. This transition seemed

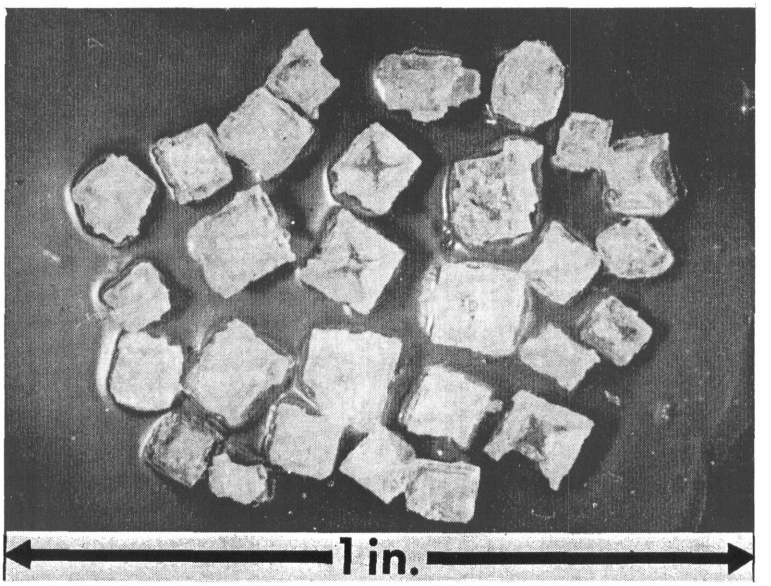

Fig. 2. Crystals from excretion of the alga *Porphyridium Aerugineum.*

to happen suddenly, and required constant vigil to prevent loss of the entire product. At reduced heat, the syrup finally would crystallize into white cubes (Fig. 2) that proved to be very deliquescent--had they been otherwise, the experiment would have terminated abruptly. After the solvent had been evaporated, the crystallized solute remaining averaged 2.5 g/liter of water--that is, 2.5 g/Kg, or 2500 ppm by weight. When these crystals were added to a tank of pure water, the cavitation resistance of the solution was found to be identical to that of the mixture before it had undergone dehydration; the ability to withstand 10X power without cavitation had not been affected. Adding 30% more solute did nothing to augment the resistance to cavitation.

An Inexhaustible Source

Here, then, was the ideal additive to inhibit cavitation--readily condensed, conveniently stored, and easily transported. The only obstacle was to culture sufficient algae to produce polysaccharide for some millions of gallons of water. When the idea that these crystals might be synthesized easily was broached to members of the Chemistry Division of NRL, the consensus was that analyzing the polymer might take as long as a year; even then, producing this giant molecular structure synthetically might be impossible.

Algae by the Acre

An alternative to this seeming impasse occurred in storybook manner: More than half a century ago, Dr. R. H. Conwell told of Ali Hafed, an old Persian, who sold his farm and traveled to distant lands in search of diamonds. As the story goes (and the author stated that it is historically true), the new owner of Ali's farm bought the land that later

became the famous Golconda diamond mine and so possessed, in fact, "Acres of Diamonds." This story came to mind when a bountiful quantity of the algal exudation was discovered in the "back yard" of the laboratory. After months had been spent culturing and then transporting a small amount of the secretion more than 3000 miles, a better variety of alga was found in Lake Gem Mary, just 300 feet from the test aquarium.

The water in this lake had never been noted for its ability to withstand extraordinary acoustic intensity without cavitation; in fact, the presence of plankton, nekton, minnows, and methane gas bubbles ascending from the mucky bottom should have made the water acoustically "weak," and the effect of these natural causes should have been compounded by the periodic bubbling of air through pipes on the bottom to stir the water and prevent temperature gradients. The lake was rich, however, in green algal growth, which suggested that the desirable polysaccharide secretion might be present.

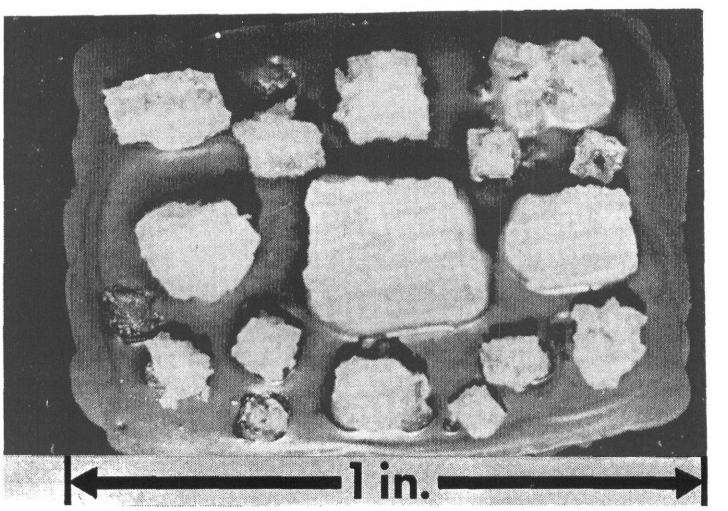

Fig. 3. Crystals from algae in lake water at NRL-USRD laboratory.

Evaporating 10 liters of the lake water yielded only 2.5 grams of crystals of assorted size and shape, Fig. 3. The lack of uniformity could have meant that the exudation was from a number of species. Obtaining this small amount of solute (250 ppm by weight) was not encouraging, because it was only 10% of that obtained from the cultured algae. Conversely, the presence of a number of species of alga could increase the odds for a successful experiment, because it had been found that 50 of 65 species produce a solution that reduces friction, and also that the friction-reducing effectiveness of some secretions decays with time, while that of others retains its potency for long periods. Success or failure could not be predicated on the quantity, size, or shape of the crystals,

because statistics on the potential of the many species were wholly inadequate.

The test aquarium was filled with lake water, which then was allowed to stand for a few days to reach thermal and gaseous equilibrium. Tests on the 5th day showed that the power into the sound source could be increased to 7X that of normal water before cavitation began. The measurement without cavitation was continuous for the 15-min duration that had been decided on as a standard interval. A week later, the power could be increased to 9X and there it remained, cavitation occurring whenever the power was increased to 10X. It was surprising that this conglomeration of algal species should produce results that nearly equalled the "pure-bred" culture, especially with only 10% of the solute.

Because further strengthening could not be observed, the water from the tank was evaporated until only the crystals remained. This residue then was added in increments of 25 ppm to distilled water in the tank to determine how much the effectiveness would be decreased by reducing the concentration. When half of the solute had been added, 2.7X the normal power could be applied; when all of the crystals had been added, the power could be increased to 7X normal, slightly lower than the initial result.

During these tests, a superabundance of lake-water plankton of undetermined origin turned the water cloudy. These plankton were far more worrisome than the sea-water ones had been; their gas content and mobility were much greater. Further, it was observed that not all the plankton produced enough gas to initiate the cavitation event; maybe only one in thousands. With the multimillions of them present, however, acoustic tests were destroyed repeatedly. They could not be eliminated by glasswool-charcoal filtering, weak poisoning, or deoxygenating the water. Consequently, the water again was evaporated and the crystals stored for two weeks to allow the aquarium and the acoustic projector to dry thoroughly. All surfaces were washed repeatedly with a volatile glass cleaner.

Again, the tank was filled with distilled water and allowed to remain undisturbed for two full weeks. Tests at the end of the first week and again after two weeks showed that 3-W power input created no cavitation, whereas, at higher power, cavitation occurred; results were identical to those tabulated for similar conditions all during the previous 2-year period. At 8:30 on the morning of the 15th day, the crystals were dissolved in a 2-liter beaker of distilled water. To minimize disturbance, the beaker was gently lowered into the tank and slowly inverted. This provided a crude method of determining the diffusion rate of the concentrated biopolymer. By 10:30, the power could be increased to 6 W; at 1:00, 9 W was applied three consecutive times. Cavitation occurred each time after approximately 12 min--just 3 min short of the time interval established as standard. By 2:30, the water withstood 9 W for the full 15 min, and an hour later, 12 W could be applied. Two days later, power could be increased to 27 W, which was that applied to the original lake water. Violent cavitation occurred at the projector face with 30 W.

Just seven days after the crystals had been dissolved, the unbelievable happened again; the tank water became saturated with plankton. Sufficient evidence seemed to have been gathered, however, to demonstrate the usefulness of this biopolymer, and there was a further desire to determine if plankton obtain their sustenance from the exuded polysaccharide. The power that could be applied to the water without causing cavitation diminished gradually in succeeding months. After 9 months, the water would withstand only 4X normal power, but this small increase could not be attributed solely to the residual polymer because of the subnormal oxygen content. The oxygen meter showed that this gas was 22% below saturation, probably because of the respiration of the live plankton/nekton and the decay of the defunct ones. Many of the nekton had grown large enough to be observed readily at five feet from the lighted aquarium. This growth, together with a considerable decrease in the crystalline content per liter of solution, led to the conclusion that the aquatic life indeed had obtained its nourishment from the polysaccharide.

Conclusion

The need for further tests is evident; preferably, they should be conducted with a standard sonar dome. The deoxygenation of water by any method probably would permit a doubling of power without cavitation. However, the rusting of steel not only removes the O_2, but also releases a small quantity of H_2 that augments the cohesiveness of the water to the extent that 10X the usual power can be applied.

A further strengthening of the water by generating additional hydrogen gas seems unnecessary, because it is probable that the high electrical driving power is not available, the projector is not designed for the greatly increased power, and uncontrollable cavitation outside the dome will occur.

Deoxygenation (and partial "hydrogenation") is most inexpensive; the raw materials to treat a cubic foot of water cost less than 1¢. (The rubber containers cost ½¢ and 4 ounces of steel punchouts cost ¼¢.)

The dissolving of biopolymer crystals in the dome water provides the capability for increasing the acoustic power by a factor of 9X and seemingly has the advantage of a longer period of service. Also, it would be simple to replenish the polymer if deterioration should occur. The initial treatment would require approximately 7 grams of crystals per cubic foot of water. It might be possible to obtain the polymer, either in crystalline form or as a highly concentrated solution, from local processors who have a seasonal business producing citrus concentrate. The cost should be reasonable, because the polymer could be produced during their slack season. If the cost can be made low enough for the material to be considered expendable, it might have an additional advantage: Conceivably, it could be ejected into the water outside and ahead of a sonar dome to suppress cavitation in that region as well as within the dome.

The experiments that have been described represent barely one bubble in the cavitation cloud. For the experimenter, the best of nearly 18,000 species of algae are yet to be selected. Numerous hypotheses remain to be (and probably will be) propounded by theorists. And for the chemist, there is the problem of analyzing and synthesizing the polymer.

If this report stimulates interest in further research, its purpose will have been accomplished. A Russian scientist has remarked: "If you fully understand what you are doing, you are not engaged in the field of science."

Appendix A

REVIEW OF THE PHYSICS AND CHEMISTRY OF WATER

The Black Sheep

Look at the sixth main group of elements in the periodic table of any elementary chemistry textbook ([14], for example) and observe that the hydrides of this group (excepting polonium) constitute a homologous series that strikingly indicates the abnormality of water. This series is plotted in Fig. 4 in decreasing order of molecular weight, acidity, boiling point, freezing point, and center-to-center atomic distance. The angle formed by the two hydrogen atoms of each hydride increases in the series. The telluride, selenide, and sulfide of hydrogen are colorless gases; all have unpleasant odors and are very poisonous.

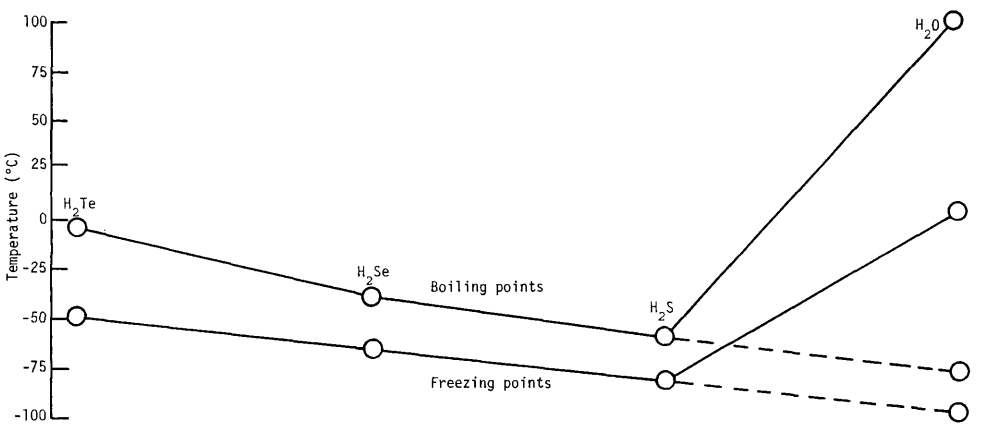

Fig. 4. Actual and extrapolated boiling and freezing points of water.

If water were not so unusual, it should be possible to extrapolate the line connecting the boiling points of these three substances and that joining their freezing points to determine, roughly, the boiling and freezing points of water. When this is done, however, it appears that water should boil at a temperature below that of any naturally existing earthly substance, and really should be present only as a gas! In fact, the actual boiling-point temperature on the Kelvin scale is nearly twice the extrapolated value. This seeming violation of the natural order is caused by hydrogen bonding, to be discussed later.

Many Kinds of Water

Seven-decimal values of the density of water were published in the temperature range 0 to 40°C [6] more than a half century ago. Then, before isotopes had been discovered, this degree of precision was challenged by Lamb and Lee [15], who reported that the densities of various

samples of distilled water--which had been expected to be identical--varied by as much as 8 parts in 10^7.

Heavy Water - Deuterium Oxide

About a third of a century ago, Harold Urey discovered that the purest water obtainable contained minute portions of a substance that he called "heavy water" because, though it apparently had the same chemical formula as ordinary water, its molecular weight was 20. The extra weight was caused by strange new water molecules whose hydrogen atoms had twice the atomic weight of ordinary hydrogen; each of their nuclei contained a neutron in addition to the single proton that is the nucleus of ordinary hydrogen. The properties of the new hydrogen were sufficiently different from those of ordinary hydrogen to justify giving it a name of its own: deuterium. Its oxide, "heavy water," has the formula D_2O and is physiologically inert; seeds watered with D_2O will never sprout and animals with only D_2O to drink will die of thirst. It is variously reported to be present in water in the ratio 150-200 ppm; its presence increases the density of water by 150-200 parts in 10^7. The amount of D_2O in natural water appears to be the same, whether the water comes from an alpine glacier, the ocean bottom, or from willow or mahogany woods. The largest use of heavy water is as a moderator in nuclear reactors, but it is widely used also in theoretical research, especially organic and biological chemistry. When a compound containing active hydrogen is treated with D_2O, deuterium replaces the hydrogen, and the resulting compound possesses new chemical properties resulting from the lesser activity of the deuterium. [4]

Tritium

After the discovery of deuterium came that of tritium, which is hydrogen of mass 3, having two neutrons in addition to the proton. The inland waters of the earth contain only about one-third ounce of tritium but, because of its radioactivity and the modern techniques of analysis, it is possible to measure accurately the amount of this radioactive hydrogen in a single gallon of river water. The content is given in tritium atoms per 10^{18} hydrogen atoms. The quantity in rain can vary considerably from time to time: measurements in Chicago showed an increase from 37 ± 3 to 66 ± 1 in a single day--followed four months later by the minimum, 1.2 ± 0.2. According to Libby [16], the production of tritium in the air might be brought about by at least two independent reactions: (1) Cosmic rays produce many neutrons in the atmosphere; when a fast neutron hits a nitrogen atom, it parts the atom into a carbon-12 and a tritium atom. (2) Tritium appears as a fragment of an atomic disintegration; very-high-energy cosmic rays sometimes hit an atom so hard that they produce a "star" of fragments flying in all directions, with tritium nuclei among this debris.

The dating of agricultural and vintage products by their tritium content is based on the decline in the tritium content of their water after they have been harvested and have lost contact with rain and snow. Because

of the relatively rapid decay of tritium, the dating span is limited to about 30 years.

Isotope Combinations

The three hydrogen isotopes mentioned can combine with each of the isotopes of oxygen--atomic weights 16 (ordinary oxygen), 17, and 18--in the ratio 2/1. Also, because each isotope ionizes in the same way, any sample of pure water must be said to be, in strict accuracy, a mixture of no less than 18 different molecular compounds (upper 3 rows, Fig. 5) and 15 different kinds of ions (bottom 3 rows). Thus, water consists of 33 different substances in all, but most of them are present only in minute quantities [17]. Careful determinations have shown that a ton of pure water contains only about 0.1 mg of H^+ ions and 1.7 mg of OH^- ions, which causes its electrical conductivity to be very low.

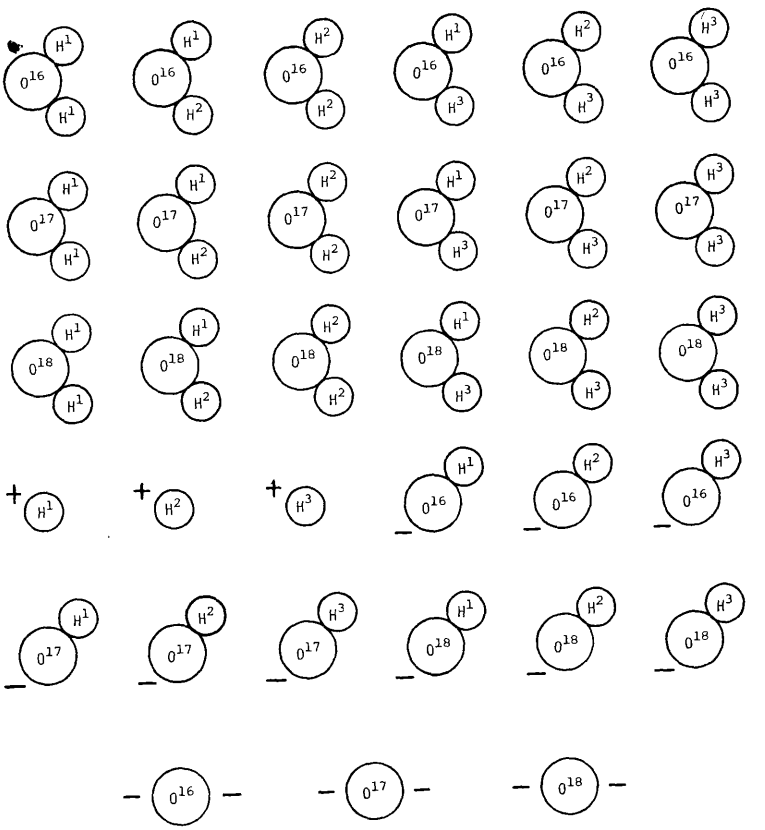

Fig. 5. The 33 different substances that compose pure water. The upper three rows depict the 18 isotopes; the 15 kinds of ions are shown below. (Adapted from [9]).

Temperature-Related Anomalies of Water

Thermal "Kinks"

Water reaches its maximal density at 3.98°C, but its minimal compressibility occurs at a much higher temperature. A curve by Alexander Wood [18] shows the maximal bulk modulus, or minimal compressibility, at 60°C. Dorsey ([6], page 243) tabulates the minimum at 40 to 50°C (approximately 45°C) and mentions Bridgman's "more recent" data giving 30°C. It is a striking coincidence that these particular temperatures 30, 45, and 60°C that had been observed by different investigators 40 to 70 years ago have been noticed recently by a single investigator in plots of viscosity *versus* temperature.

In the course of probing into the generation of electrical charges in thunderstorms, Drost-Hansen [2] discovered thermal anomalies, or "kinks" in the physical properties of water and of aqueous solutions at 15, 30, 45, and 60°C, each kink extending over a temperature range of 1 or 2°. These kinks are more or less abrupt changes of slope in the plots of various physical parameters as functions of temperature; they represent additional anomalies in the already anomalous behavior of water. As an example, evidence was found for kinks in the data for viscosity of aqueous solutions, index of refraction, ultrasonic absorption coefficient, thermal conductivity, transverse proton relaxation times, and specific heat.

The authenticity of this discovery was attacked strongly by T. F. Young of the Argonne National Laboratory. After going over many of Drost-Hansen's results, he said: "... nearly all the claims [for discontinuities]--if not all--are grossly false ...," and went on to criticize the fact that no checks had been carried out to make sure that the results were free from experimental error. [3]

Superheating and Supercooling

Even more confusing is the remarkable fact that, although the density of water decreases as it is heated from 4 to 100°C, the extent of molecular crowding increases, which is just the opposite of what happens to most other liquids [2]. Any theory about the structure of water must try to explain this phenomenon; some current theories built on statistical mechanics and statistical thermodynamics have achieved partial success.

Professor Drost-Hansen remarks [2] that "... pure water never freezes at 0°C; it always must be supercooled." Dorsey ([6], pages 638-643) cites numerous experiments in which water remained liquid at -20°C; in one instance, -40°C was reached. The supercooling of water is a phenomenon readily observed in the north, where it is not unusual for rain to fall during subfreezing temperature and turn to ice only on impact. A melting point below -40°C is documented briefly by Hueter and Bolt [19] with the additional observation that "If a clean liquid, one that has been freed from impurities and dissolved gas, is slowly heated above its normal

boiling point the phenomenon of superheating occurs. Under this condition the external temperature can be raised considerably above the normal boiling point without the phase transition taking place. If a liquid in this state is disturbed, *e.g.*, by mechanical shock or an added impurity, it will turn explosively into vapor."

Water's Memory

In certain instances, water seems to have a memory and to react according to its past history. An experiment was reported [20] in which water from freshly melted ice froze more quickly than that from freshly condensed steam, under the same conditions and starting from the same temperature! A similar instance is recorded by Deryagin [21]: "... it was shown that water obtained by the melting of ice retains some of the properties of ice for many hours. It is as if water remembers its past. The memory is comparatively short--on the order of twenty-four hours up to several days--and the changes are insignificant."

Pressure-Related Anomalies of Water

Others [22] have reported that water can be heated at atmospheric pressure to temperatures above 200°C without bursting into vapor, after it has been subjected to high hydrostatic pressure (1000 atm). When high-frequency sound waves at very high power were passed through this water, no cavitation occurred.

L. H. Bernd, of the General Electric Company, reported [23] that water from the surface (6-in. depth) of a lake cavitated at 0.23 W/cm^2, whereas the same water from 6-ft depth cavitated at 0.94 W/cm^2. Both samples were tested under the same head of water (just below the surface) at 18 kHz.

While the viscosity of water was being considered for adoption as a standard by the International Organization for Standardization, measurements made at Brown University [24] demonstrated that it was not affected by the dissolution of air in the water and, moreover, remained unaffected by cycles of hydrostatic pressure to 5000 psi. Surprisingly, after pressurization, the viscosity of water bears no relation to its resistance to change of state at elevated temperature, or to cavitation with increased acoustic intensity.

The change in viscosity of water with pressure again illustrates its extraordinary behavior. At low temperature, the viscosity of pure water *decreases* with increasing hydrostatic pressure up to 10 000 psi. The viscosity of other fluids *increases* with increasing hydrostatic pressure!

Structure of Water

With the idiosyncrasies of water documented, it is only normal for scientists to seek the causes. It is with trepidation, however, that the theories of the molecular structure of ordinary water are broached. There is no particular theory that is universally accepted, and the dissidents range all the way from those adhering to structural theories of their own to a small but vocal minority that seems to deny that liquid water has any structure at all.

The Hydrogen Bond

Fortunately, there is at least a general acceptance of the structure of the H_2O molecule and some common basis in the various theories. A brief review of the hydrogen atom and the first isotope of oxygen (16) will introduce the concept of the bonding of water molecules by molecular forces.

It has been calculated that 93% of all atoms in the universe are hydrogen, and that this element makes up 76% of the universal mass [17]. This plentiful atom is composed of a positively charged proton and a negatively charged electron revolving in the K (first) shell, which requires an additional electron for stability. A molecule of hydrogen (H_2) is stable because the two hydrogen atoms can share a pair of electrons. The oxygen atom has eight electrons, six of which are arranged in the outer L (second) shell, which leaves room for two more electrons. In the water molecule, these two vacancies are occupied by the two hydrogen electrons to establish a covalent bond. The covalent bond, often called by the cumbersome expression "electron-pair bond," or "shared electron-pair bond," is merely a pair of electrons held jointly by two atoms. Instead of joining along the diameter of the oxygen atom, the two shared atoms are at one side, which causes the water molecule to have a dipole moment.

This has been shown in Fig. 5, where it is seen that the large circle representing the shell of the oxygen atom has a negative charge to the left because of the exposed electrons. The two small circles, each with an electron in the large shell, can be thought of as the positively charged protons of the hydrogen atoms. Because these positively charged protons protrude from the water molecule, there is an attraction for the negatively charged electrons of a neighboring water molecule. This is a simplified picture of the hydrogen bond (electrostatic attraction) that causes molecules of water to cling together with such tenacity and makes the values of its dielectric constant and its boiling and freezing points abnormally high. This force, purportedly, ranges from four to fourteen times that of the van der Waals force bond. The comparatively weak van der Waals attraction exists between all molecules because the mutual attraction between one molecule's nucleus and another's electrons is slightly greater than the mutual repulsion of their electrons and their nucleii.

Exceptions to Hydrogen Bonding

Many, but not all, of the hydrides display the hydrogen bonding; for example, the methane molecule consists of a central carbon atom joined by a single covalent bond to each of four hydrogen atoms lying at the corners of a regular tetrahedron around the carbon atom. The hydrogen electrons occupy the four vacancies in the carbon's L shell. The carbon atom is completely surrounded by the four bare hydrogen protons; consequently, it lacks the dipole moment of the water molecule. Methane molecules cannot form hydrogen bonds between each other or with water molecules to any appreciable extent; methane, therefore, is almost insoluble in water and boils at -160°C.

The hydrogen bond (sometimes called the hydrogen bridge) is described in considerable detail by Pauling [25]. The concept of "resonance" to enhance even further the bonding of water molecules is essentially quantum-mechanical; the concept requires recognition, although it is much too complicated for this report.

Hydrols and Hydrates

Most of the scientific hierarchy are disposed to regard the abnormalities of water as arising from an association of molecules. One proposal suggests the names hydrol (H_2O), dihydrol $(H_2O)_2$, and trihydrol $(H_2O)_3$ for the vapor, the liquid, and the solid forms, respectively, with the theory that water is a mixture of all three. Densities of 1.09 and 0.88 g/cm^3 are attributed to dihydrol and trihydrol, respectively ([6], page 168). In 1892, just three years before he discovered X-rays, W. C. Roentgen suggested that water was a saturated solution of ice in a liquid composed of simpler molecules. Since then, there has been considerable acceptance of the idea without any agreement as to the sizes of the molecular groups; it has been suggested that water is a mixture of H_2O and $(H_2O)_n$, the subscript n running the numerical gamut from a high of 23 in 1911 to a recently suggested high of 10 000. For the layman, ordinary water could be defined as a mixture of ice, liquid, and steam. One author [25] expressed the opinion that water is a hydrate (a compound formed by the union of water with some other substance) of itself.

The Frank-Wen Theory

The individual theories that have been advanced are so numerous that even mention of most of the theoreticians must be omitted; Dorsey noted fifty references [6] thirty years ago. In personal correspondence, Dr. Horne [26] remarked, "Generally speaking, I think the Frank-Wen theory in broadest outline is correct, yet I also suspect that, in detail, as developed by Némethy and Scheraga [27], it is over-simplification." In another exchange, he wrote, "A word of caution--recently the Frank-Wen theory has come under some heavy criticism, but I still have faith in its qualitative correctness." The criticism appears in references 28, 29, and 30. The abstract of reference 27 begins: "The thermodynamic parameters of liquid water are derived by means of a statistical thermodynamic

treatment, based on the 'flickering cluster' model proposed by Frank and Wen. Various models proposed for the structure of liquid water are reviewed, and the advantages of the Frank-Wen model are pointed out. The hydrogen-bonded ice-like clusters of H_2O molecules in equilibrium with non-hydrogen-bonded liquid are described quantitatively in terms of the molecular species participating in different numbers of hydrogen bonds in the clusters. ..." Three years after this had been published, Vand and Senior [29] called attention to the fact that the results disagreed with the experiments performed by other investigators, and suggested an explanation for the discrepancy.

Professors Frank and Wen (also, Frank and Quist) at the University of Pittsburgh have introduced into their theory the concept of the collapse and reformation (flickering) of the quasi-crystalline cage structures at the terrific rate 10^{11} times per second. The frequency with which the molecules themselves vibrate around their equilibrium positions in the clusters is much higher--10^{13} to 10^{14} times per second. Thus, the molecules may oscillate hundreds or thousands of times around their equilibrium positions in a clathrate (lattice-like or zigzag construction) cage before the cage falls apart; but the constituent molecules quickly reform to create new clusters.

Two-State Theory of Water

An abstract of a publication by Davis and Litovitz [31] states, in part: "A new model of the structure of water is proposed. This model is based on the existence in water of puckered hexagonal rings similar to those in ice. In water, these rings are assumed to coexist in two structures: an open-packed icelike structure optimum for forming hydrogen bonds between rings, and a close-packed structure in which the molecules occupy a nearly complete body-centered cubic structure. ... The structure of water is estimated to be approximately 60% icelike at 0°C and 30% icelike at 100°C. ..."

However, Drs. Narten and Levy of the Chemistry Division, Oak Ridge National Laboratory, believe that most proposed models of liquid water are either incompatible with observed X-ray scattering or insufficiently defined for adequate testing. They conclude [32] that: "Any realistic model of liquid water must accommodate (or at least avoid conflict with) the significant features which can be deduced directly from the available diffraction data. In particular, the idea that water molecules form clusters sufficiently different in size, shape, density, and structure from other such aggregates, or from 'unstructured' water, to warrant the distinction seems to be extremely difficult to reconcile with data from small-angle X-ray scattering."

In addition to Raman spectroscopy, nuclear magnetic resonance spectroscopy, X-ray diffraction, and other methods, a neutron-scattering technique leads [3] to the conclusion that a model that sees liquid water as a multistate substance composed of ice-like and steam-like structures

or as "bound" and "free" H_2O molecules within an ice-like, tetrahedral lattice may be the correct one.

Sea Water

Naturally, adding an electrolyte to water multiplies the complexities many fold; sea water is a particularly complex electrolytic solution. Goldberg [33] has listed 92 elements that can be identified in sea water in some amount. Unfortunately, there can be no general formula, because the ocean is not uniform; few compositions of minerals, gases, or organic matter can be called universal. The content of some of the elements, like iron and silicon, can vary by a thousand times from one area to another.

The phosphorus content of deep water in the North Pacific is more than twice that found in the North Atlantic. The sea water in the Caribbean and that on the other side of Central America in the Pacific differ--differ even in their salinity. The formula for artificial sea water is most complex, and requires that no less than twenty-one chemical compounds be dissolved in particular sequence. Also, in elasmobranch biology (studies and experiments in behavior, physiology, pharmacology, biochemistry, and metabolism of sharks, rays, etc.), the laboratory sea water must be tailored to the particular natural environment of the specimen [34]. One wonders what part measurement errors play in the reported variation of the chemical parameters of sea water, especially after reading [35] that "One of the rare elements in the earth's crust, indium, has until recently been reported as present in sea water in concentrations approaching 20 parts per billion. However, David Robertson of Battelle Northwest, who has turned refined neutron activation techniques to the search for various elements in sea water, finds that indium cannot be present in amounts greater than 20 millionths of a part per billion."

Sea water is approximately a half-mole solution of the two ions sodium (Na^+) and chlorine (Cl^-), thus making it a concentration that is a vexation to physical chemists. It is too concentrated to be treated by the theories developed for dilute solutions, without the addition of suspect terms, and it is too dilute to be of interest to those concerned with the solute-solute and solute-solvent interactions encountered in concentrated solutions. This particular concentration, together with numerous other factors, makes the physical chemistry of sea water very much an unexplored field. [1]

Ice

The late P. W. Bridgman gained renown for his work with water at high pressure and for the discovery of six new forms of ice, none of which float in water. He reported [36] considerable difficulty in freezing water into ice V because it tended to persist indefinitely as a liquid in a supercooled condition. To make state V appear, ice of state VI had to be produced first. After ice V had been kept in the neighborhood of its

melting point for several days, however, it was found that the instant the temperature was reduced below its melting point, the liquid froze to ice V immediately.

There are indications that water in its solid state is by no means a quiescent system; ice seethes with activity. According to L. K. Runnels [37] every molecule in a crystal of ice just below the melting point normally rotates 10^5 times per second. He reports that, several years ago, two Swiss chemists discovered another kind of movement in ice by tagging some of the molecules with deuterium to form HDO. Other molecules were identified by using the third isotope, oxygen-18, which indicated that the tagged atoms jumped about in the crystal primarily as members of intact molecules, not as separated hydrogen or hydroxide ions. Calculations from various experimental data, including measurements of the "relaxation" of nuclear magnetic resonance, led to the conclusion that, in ice, at a temperature just below the melting point, the average molecule jumps out of its lattice position about once every one-millionth of a second and travels about eight molecules away before regaining a normal lattice site. Thus, the process takes place some ten times as fast as the in-place rotation previously mentioned.

Polywater

While the forgoing material was being prepared, a new form of water was "discovered" in Russia and seems to be of considerable interest in this country. It is reported [38] that a Waltham, Massachusetts electrochemical research organization has been awarded contracts from the U. S. Office of Saline Water and the Advanced Research Projects Agency of the Department of Defense totalling $125,000 to stimulate production of this newly named polywater. Also are reported, through the interest of the American Society for Testing and Materials/Dow Chemical Company SIRCH program, the results of a computer search of 100,000 infrared spectra, in which no structures similar to that of polywater were found. Chemists at the National Bureau of Standards and the University of Maryland have shown considerable interest and have collaborated [39] to state bluntly that "Its properties are not those of water, and it should not be considered to be or even called water any more than the properties of the polymer polyethylene can be directly correlated to the properties of the gas ethylene." Their technical discussion terminates with 18 excellent references.

The most elucidative treatise [40] contains a historical background of the various experiments leading to the discovery that this "water" is genuinely unique. It is reported [41] that the properties of the polymer are very different from those of normal water; the spectrochemical analysis (laser probe and copper spark) shows no impurities and the microprobe tests no significant content of silicon and only traces of sodium. The same characteristics mentioned in the other references are enumerated: low vapor pressure, high density (1.4 g/cm^3), stability to 700°C, and

solidification at -40°C to a glassy form with much lower expansion coefficient than that of ordinary water when it forms ice.

A brief description [42] of the experimental hardware used by the Russian scientist B. V. Deryagin indicates that the apparatus consists of a chamber with an isothermal vacuum jacket. The lower wall of the chamber bears a well that can be filled with water and maintained at a temperature lower than that of the jacket. In this way, vapor pressure is held constant at a level below the saturation vapor pressure. When an empty quartz tube 1 to 2 microns in diameter is placed in the chamber, condensation ultimately will take place inside the tube and the properties of the condensate will be markedly different from those of ordinary water. Deryagin attributes these differences to wall effect. It is well known that the dipole moment of the water molecule causes the two hydrogen atoms to be aligned toward a glass or quartz surface because of the oxygen content of the surface and the positive charge of the hydrogen proton. The direction of alignment is exactly the opposite at an air-water interface, where the surface layer is so oriented that the oxygen atoms point up and the hydrogen atoms down, with most of the H-atoms forming hydrogen bonds to the O-atoms of the water molecules in the next lower layer, *etc.*, to a considerable depth. A microdroplet of water also has a much lowered vapor pressure.

The present concerted effort to produce polywater in quantity can be likened to the quantity production of the isotope Cf-252, of which the current U. S. supply 18 years after its discovery is less than 0.0005 g. The production of any appreciable quantity of polywater by "banks" of capillaries of such minute diameter would require 470,000 miles of tubing to produce 1 gallon of liquid.

Doubt exists in this author's mind as to the novelty of this "Water That Won't Freeze [40]." Dorsey ([6], page 639) claimed no difficulty at all in repeatedly supercooling water to -21°C in a half-filled glass bulb whose volume was slightly more than a cubic inch. He reported that another experimenter had found that the supercooling of water seems to be favored by certain conditions such as its presence in small drops on hydrophobic surfaces, as a thin layer between glass plates that are clamped together, and *in narrow capillary tubes*! This latter finding appeared in print in 1858!

If the foregoing excerpts leave the reader in a quandary, then the purpose of this discussion has been achieved. Professor Drost-Hansen sees very dim hope for a complete understanding of the structure of water within the next few decades.

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13. ABSTRACT

Nearly four years of experiments in treating water to retard the onset of cavitation resulting from high-intensity acoustic waves is described. Sound intensity 23 times that at which cavitation occurs in pure (deionized) water can be applied to specially treated water without causing cavitation. The three effective methods examined are unusual in that the water is "strengthened" by additives that (1) remove nuclei by deoxygenation, (2) increase molecular bonding by hydrogenation, or (3) augment cohesion by introducing a natural polymer. An appended survey of the literature documents the complexity of water and serves as an excuse for omitting a hypothesis to explain the increased resistance to cavitation that results from the treatments.

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