

Properties of Water Substance

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Introductory Remarks by Chairman

Occam (1300-1349) is usually credited with introducing into science the principle of necessary and sufficient assumptions—"Essentia non sunt multiplicanda praeter necessitatem." This has been called "Occam's Razor" with which to slash away unnecessary assumptions. In dealing with complex actual systems, it is often practically impossible to carry along in the theoretical treatment of the entire system even all the necessary and sufficient available knowledge on the components. Hence, a practical decision must be made on how much we can carry along and how much we can slash away. With respect to the behavior of water in soil, it seems that a number of contemporary soil physicists have slashed away too many of the real properties of the water substance. This situation manifests itself in lack of agreement between actual experimental findings and certain theoretical conclusions. The remedy, of course, is to go back and add to the basic assumptions more of the real properties of the water substance even if this makes the calculations more bulky. The paper by Rodebush and Buswell summarizes in a simple and concise manner present knowledge on the properties of the water substance. The time has come when this knowledge must be part and parcel of the equipment of every soil physicist and must be built into the foundations of his theoretical structures.

● WATER is the only liquid with which we are really familiar. There are many substances that exist in liquid form and it is noteworthy that water is in no sense a typical liquid. It is best described by discussing those properties which differentiate it from the general class of liquids.

Water is a polar liquid (Fig. 1). Other examples of polar liquids are hydrogen fluoride and hydrogen cyanide, which are indeed bizarre substances. Polar liquids are made up of small molecules containing hydrogen which is sufficiently mobile or active to serve as a link between molecules. The molecules linked together in this manner by hydrogen bonds orient in an electric field and exhibit the property of high dielectric constant.

Ambivalence of Hydrogen. The hydrogen atom is capable of forming but one primary valence bond. When this is formed between hydrogen and oxygen, the oxygen atom appears to accumulate an excess of electronic charges and the hydrogen with a deficiency of electrons appears to have a positive charge. The positively charged hydrogen is capable of attracting an oxygen atom from another molecule, forming the so-called hydrogen bond which is, compared to the primary valence bond, a weak bond. The hydrogen atom in this bond lies between the two oxygen atoms, but not at equal distances from the two. It is much closer to the oxygen atom to which it is attached by a primary valence bond and to which it may be considered to belong (Fig. 2).

The Association of Water. The association of water has been the subject of many misconceptions. For example, it has been supposed that liquid water consisted of dihydrol or trihydrol, that is groups of two or three molecules. Such a concept is

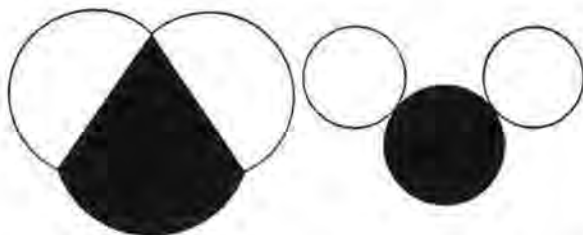


Figure 1. Molecule of water consists of one oxygen atom (black) and two hydrogen atoms (white). The distance between the center of the oxygen atoms and the center of each of the hydrogen atoms is 0.9 Angstrom unit (one Angstrom unit: 0.0000001 centimeter). The angle formed by the two hydrogen atoms is 105 degrees. These dimensions are fitted together in the drawing at left. In the more schematic drawing at right the size of the atoms has been reduced. This representation of the molecule is used in the following drawings.

absorption. A hydrogen bond shows a primary absorption at a wave length of about three microns. Liquid water shows this absorption even in the thinnest layer so that if the eyes were sensitive to the infrared region water would appear jet black. One may assume that the higher harmonics show absorption extending into the visible region, thus accounting for the familiar blue-green color characteristic of liquid water. It is not possible to determine the degree of association of liquid water by absorption experiments, but one may assume that water is highly associated, that is to say, there are practically no unassociated molecules present. The best clue to the structure of water is by a consideration of the structure of ice. The structure of ice is itself reasonably well understood although certain details are still in doubt.

Ice Water Structure. The only properties which differ markedly for ice and water are density and viscosity and closely related properties. The infrared absorption, the dielectric constant, and the degree of association change in a continuous manner through the melting point. Even the heat of fusion is much smaller than might be expected.

Water is one of the few substances which shows a greater density as a liquid than as a solid, and it is perhaps the only substance

now known to be erroneous. Water is a liquid with structure such that the molecules are linked together by hydrogen bonds so that they are not free to rotate as, for example, are benzene molecules in liquid benzene. From this point of view, therefore, the whole mass of liquid water constitutes the molecule. The molecular weight depends on the size of the containing vessel.

The method par excellence for the detection of hydrogen bonds is infrared

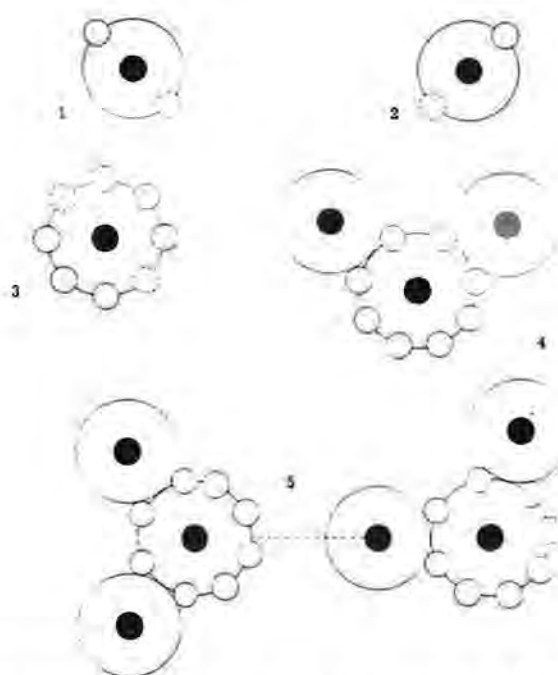


Figure 2. Electrons and protons of the water molecule account for most of its physical and chemical properties. The hydrogen atom (1 and 2 in this highly schematic picture) consists of one positively charged proton and one negatively charged electron. The oxygen atom (3) has eight electrons, six of which are arranged in an outer shell. Because the shell of hydrogen has room for one more electron (broken circle), and the outer shell of oxygen has room for two more electrons, the atoms have an affinity for each other. In the water molecule (4) the electrons of the hydrogen atoms are shared by the oxygen atom. Because the positively charged proton of the hydrogen atom now sticks out from the water molecule, it has an attraction for the negatively charged electrons of a neighboring water molecule (5). This relatively weak force (broken line) is called a hydrogen bond.

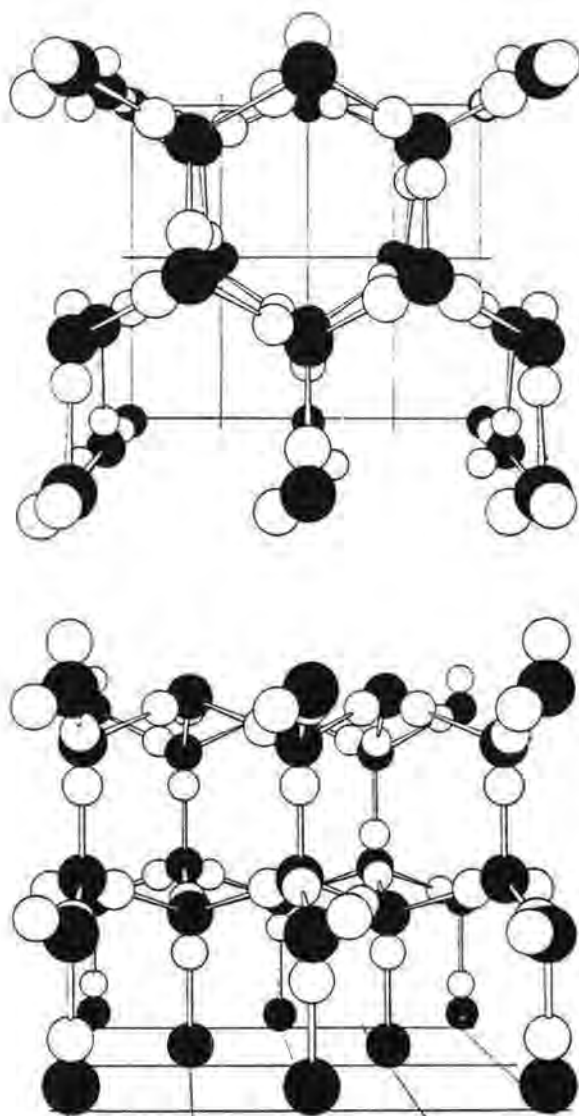


Figure 3. Ice consists of water molecules in this arrangement. The top drawing shows a model of ice seen from one direction. The bottom drawing shows the same model seen as if the reader had turned the top drawing forward on a horizontal axis in the plane of the page. Some hydrogens have been omitted from the molecules which touch the grid. Each hydrogen in each molecule is joined to an oxygen in a neighboring molecule by a hydrogen bond (rods). In actuality the molecules of ice are packed more closely together; here they have been pulled apart to show the structure. In a similar model of liquid water the molecules would be much more loosely organized, farther apart and joined by more hydrogen bonds.

that exhibits a maximum density a few degrees above the freezing point. In order to understand this behavior it is necessary to consider the crystal structure of ice (Fig. 3). Ice forms hexagonal crystals but it is rarely seen in perfect forms of greater than microscopic size. The hexagonal symmetry is exhibited by snow flakes which occur in an infinite variety of forms (Fig. 4). The normal form of the snow flake would be a flat hexagonal plate, and the skeletal forms are due to the fact that the crystal grows in an atmosphere which is really very dry so that water vapor is present in small amounts. The crystal growth is greatest at the extremities of the crystal axis leading to the star-like forms.

It is the internal arrangement of the molecules in the crystal which is the primary concern. By means of X-rays, the position of the oxygen atoms in the crystals can be determined and the positions of the accompanying hydrogen atoms can be inferred. Ice might be expected to crystalize in the regular or cubic system, but the tetrahedral angle required involves a strain of the bond angles of the water molecule which is in some way relieved in the hexagonal crystal. The two hydrogens in the vapor phase water molecule are at an angle of about 105 deg. Each water molecule is surrounded by four nearest neighbors, the group forming a tetrahedron with one molecule at the center and the other four molecules at the apices of the tetrahedron. X-ray determinations show that the distance between oxygen atoms is 2.76 deg Angstrom units. Since the distance between the oxygen atom and the hydrogen atom is about 0.9 deg Angstroms, it follows that the hydrogen atoms lie on a line jointing the oxygen atoms but one not halfway between. Each hydrogen atom belongs, therefore, to one oxygen atom (forming a water molecule) and is joined to another oxygen atom by the relatively weak hydrogen bond. Each water molecule is, therefore, joined to its neighbor by four hydrogen bonds. If the number of hydrogen bonds per molecule were counted there are only two instead of four since each hydrogen bond is shared between two molecules. If ice is vaporized the work of separating

all the molecules from each other must be done and, assuming that this work is entirely used up in separating the hydrogen bonds, 12,000 calories is the heat of vaporization of one mole (18 grams) of water. Then the energy of one mole of hydrogen bonds would be 6,000 calories.

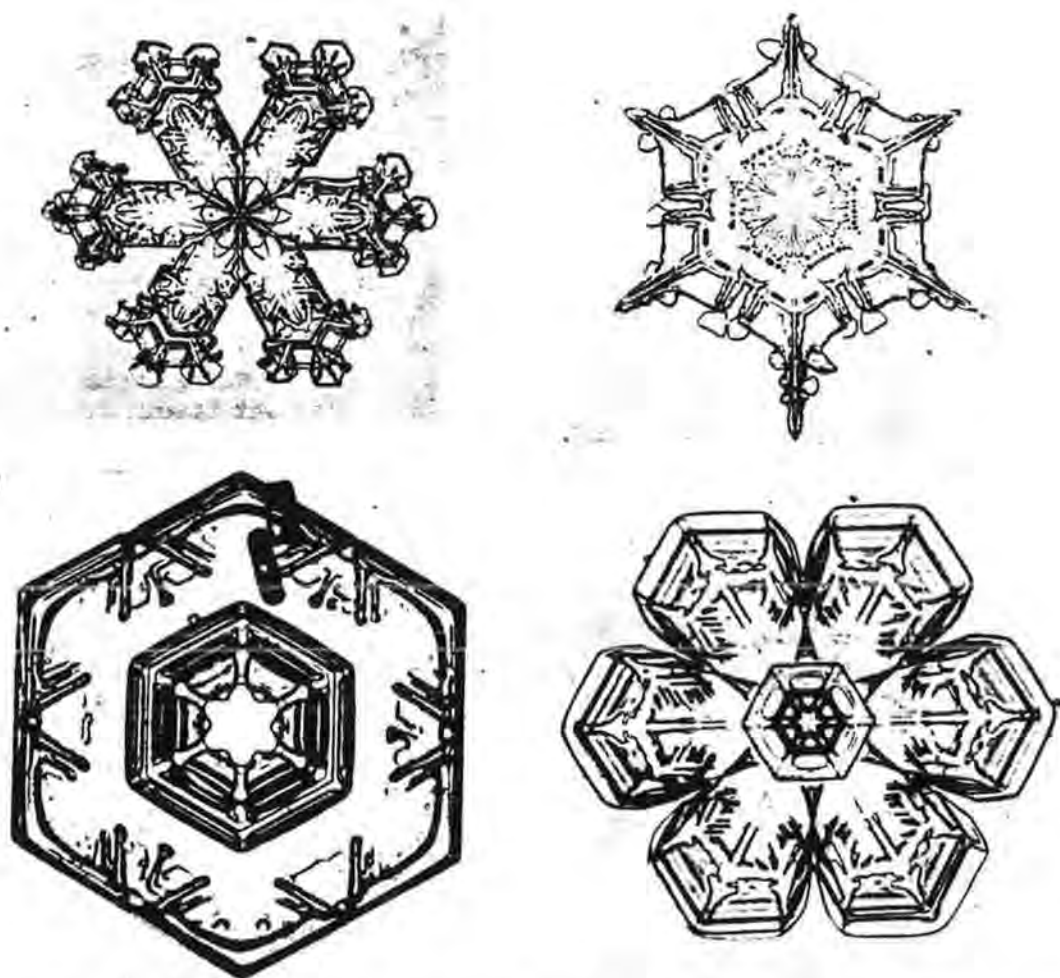


Figure 4. Snow crystals are enlarged in these photomicrographs by Vincent J. Schaefer of the Munitalp Foundation in Schenectady, N.Y. The hexagonal symmetry of the crystals is due to their molecular structure.

The exact arrangement of the water molecules in the ice crystal is not known with certainty, but it is known that the water molecules are arranged in hexagonal rings which form a network or lattice. Since each molecule is surrounded by only four others, the packing is not very close and ice is a relatively not very dense crystal.

When ice melts to liquid water the hydrogen bonds are stretched and the molecules move farther apart. X-ray studies show that the distance between oxygens is now increased to about 2.9 deg Angstroms on the average. The effect of this stretching would be to decrease the density and to produce a large absorption of energy which would disappear at the heat of fusion were it not for a compensating effect. This is a crowding together of additional molecules. The regular structure disappears and instead of each molecule being surrounded by four neighbors in a regular arrangement, the number of nearest neighbors is increased to five or more on the average in an arrangement that is constantly shifting. This crowding together of the molecules means a closer packing and an increase in density. The number of hydrogen bonds is also increased so that the heat of fusion is less than might be expected. This chaotic disorder in which water molecules exist in the liquid state is difficult to picture since it is continually shifting, but it may be described as an average state rather than as a series of instantaneous states. The water molecules retain their identity. That is, two hydrogen atoms are bound to each oxygen atom and remain so for long periods of time. The electrons are more closely associated with the oxygen atom and the hydrogen atoms are separated

somewhat further from the oxygen atom than in an isolated water molecule and appear more as isolated positive charges. The water molecule becomes more flexible in that the angle between the two hydrogen atoms no longer remains fixed at or near a right angle, but becomes variable. Each oxygen atom, in addition to the two hydrogen atoms which are firmly attached by primary valence bonds, now attracts by electrical forces not two additional hydrogen atoms as in ice, but three or more hydrogen atoms. Thus, an oxygen atom is surrounded by five or six hydrogens and a hydrogen atom is surrounded by as many as three oxygens. This may have a closely packed, closely knit structure which is flexible with continuously shifting hydrogens displacing one another and the whole body of liquid has the property that if a hydrogen is displaced anywhere the displacement is propagated in chain or zipper fashion throughout the liquid. This has consequences which affect the viscosity, dielectric constant, and electrical conductivity.

Viscosity. In an ordinary unassociated liquid such as benzene, the molecules slide past each other when the liquid flows, encountering a certain amount of resistance resulting from the fact that they have to move around each other. In liquid water the molecules are attached by hydrogen bonds and one at least must be broken before any flow can occur. This means that the motion is rolling rather than sliding. Since the hydrogens of one molecule are now bonded on the average to the oxygens of two other molecules, it is not necessary to break both of these bonds at once, but rather one at a time so that the viscosity of liquid water is much less than might be expected from the fact that the molecules are bonded together. The greater viscosity of ice is due to the fact that each hydrogen is firmly bonded to a single oxygen atom from another molecule and this bond must be completely broken before any movement can occur. The temperature coefficient of viscosity indicates that the energy required to break the bond between water molecules is about 3,600 calories per mole. This is much smaller than that required for a normal hydrogen bond and supports the theory of the partial or multiple hydrogen bond where each hydrogen is bonded to two or more oxygens of adjacent water molecules. It is only necessary to break one of these partial bonds at a time in order to permit movement of molecules past each other.

Heat Capacity. The assumption of an increased ionic character for the atoms in liquid water receives additional support from a consideration of the heat capacity of liquid water. The heat capacity shows a remarkable discontinuous change at the melting point. The heat capacity of ice corresponds to that to be expected for an organic molecule. The oxygen atom should contribute four calories per mole, and the two hydrogen 2.3 calories each, and this is about what is observed. For liquid water the heat capacity is 18 calories per mole, which is high and remarkably constant from the melting point to the boiling point. It has been commonly assumed that the abnormally high heat capacity is due to the dissociation of hydrogen bonds, but this explanation appears inadequate. Hydrogen bonds are not being dissociated and if they are it would scarcely account for a constant value over a range of 100 degrees. A striking fact is that the heat capacity corresponds to the Dulong and Petit value of 6.0 calories per atom. This is the value to be expected when the frequencies of vibration of the atom, which occur at the rate of three per atom corresponding to the three degrees of freedom, are low enough to be excited at the temperature prevailing. The significance of this is that the atoms must be more loosely bound than in ice where the structure is rigid. Part of this freedom of motion may arise from the bending of the water molecule from the normal configuration of approximately 105 deg angle. It is possible to accumulate energy in the hydrogen bonds without dissociation.

Liquid Structure. The infrared absorption of liquid water indicates a high degree of association. The high dielectric constant is additional evidence for this conclusion, but the strongest evidence is perhaps obtained from energy consideration. Even at the boiling point the heat of vaporization is abnormally high. This means that the boiling point is actually lower than it would otherwise be if it were not for the large increase in entropy resulting from the dissociation that takes place when the liquid vaporizes. On the other hand, the low heat of fusion indicates hydrogen bonding in the liquid to a degree almost as great as that in ice. This causes the melting point to be higher than might otherwise be the case.

Water as a Solvent for Electrolytes. The picture of water as a largely associated structure of high dielectric constant accounts very well for the extraordinary ability to act as a solvent for electrolytes. Ice has no space in its lattice to permit ions to dissolve but the water molecules can arrange themselves in such a way as to largely neutralize the forces between ions, the hydrogen surrounding the anion and the oxygens the cation. The only discordant note in this picture is the extremely small electrical conductivity of pure water itself. This means that the water molecule has very little tendency to dissociate into free ions. The two hydrogens and the oxygen remain attached to each other.

The hydrogen bonded water molecule in the medium of high dielectric constant exists in essentially ionic form. But the oxygen ion is doubly charged and of small radius so that the Coulomb's law attraction is still large. Comparison with a molecule such as hydrogen chloride will make this clear. The chlorine ion is singly charged and of large radius so that the Coulomb's law attraction is small. Hence hydrogen chloride is largely dissociated into ions and behaves in water solution as a strong acid. The dissociation of the water molecule, while measurable, is small indeed.

Water is, therefore, to be thought of as a highly associated liquid with a semi-ionic structure. The molecular weight is indefinitely large, the molecule depending upon the total mass present. Because of its ionic nature and high dielectric constant, it is a solvent for electrolytes par excellence. When ions dissolve because of the powerful electrostatic forces which surround them, the structure of the liquid is broken down and undergoes modification. There is another class of substances for which the solubility is small which actually has the effect of augmenting the structure of water. These are nonpolar molecules which will be discussed below. There is a class of substances which are intermediate in their behavior in that the molecule includes both ions and nonpolar parts. An important example of these are protein molecules and the reaction between water and protein molecules plays an important role in living organisms. Proteins may be likened to plastics and water may be regarded as a plasticizer for proteins.

Solutions of Nonpolar Molecules. While water is primarily to be regarded as a solvent for electrolytes, more about water itself is learned from solutions of nonpolar molecules. A nonpolar molecule is a molecule that contains no potential ions and is not, therefore, surrounded by any strong electrical fields. Nonpolar molecules do not, therefore, attract other molecules strongly, either polar or nonpolar. The solubility of nonpolar molecules in water is, therefore, expected to be slight and this is the case. The interest in these solutions arises from the existence of solid hydrates which separate at temperatures well above the freezing point when the partial pressure of the gas above the solution is sufficiently high. These hydrates came to attention in a dramatic fashion when natural gas lines became clogged with a solid precipitate at temperatures as high as 20 C. Methane is, of course, a nonpolar molecule, but even more striking is the existence of hydrates with the inert gases such as argon and xenon. The noble gases form no compounds and fantastic explanations have been offered for the supposed attraction. Actually, it is clear that the reason for these compounds is the lack of attraction between the water and gas molecules. The water molecules form a cage around the gas molecules. Since this cage is only one layer thick, the strain which prevents ice forming a cubic crystal does not build up as it would in a continuous lattice. When the gas molecules in solution reach a certain concentration, these cages unite to form a cubic lattice. The resulting lattice is more stable than ice and has a higher melting point. It is not, of course, stable if the gas escapes from solution (Fig. 5).

The fundamental picture here is that the water molecules form a cage around the gas molecule with the oxygen atom turned inward and hydrogen bonds on the outer surface of the cage. The simplest of these structures is a pentagonal dodecahedron which contains 20 water molecules but larger cages are also formed. The heat and entropy of formation are comparable to that for ice. If the inert gas molecules were replaced by water molecules the attractive forces of the hydrogens would break the structure from within, causing it to collapse, and the situation would revert to the chaotic condition of liquid water. There are two lattices known for the gas hydrates

and the lattice constants are given in Table 1. It will be noted that the ratio of the number of molecules of water to gas is fractional, or odd. Furthermore, it appears that the holes in the lattice may not all be filled, giving rise to further variation.

There are two cubic lattices, one with a spacing of 12.0 deg Angstroms and one with 17.0 deg Angstroms. The smaller one contains 46 molecules and the larger one 136 molecules. The smaller lattice contains holes of 12 to 14 sides respectively, while the larger lattice contains holes of 12 to 16 sides. These holes are of different sizes and make it possible to explain the bewildering array of hydrates. It was formerly supposed that chloroform formed a hydrate with 16 molecules of water, but it now appears by counting the number of holes in the lattice that the correct number is 17. Furthermore, the different sized holes can be filled only with different size molecules and not all holes need be filled. Thus, fractional numbers of waters of crystallization and variability in these numbers are accounted for. Certain hydrates involve two different substances in a definite ratio, each substance filling a particular sized hole. Such a case is $\text{CHCl}_3 \cdot 2\text{H}_2\text{S} \cdot 17 \text{H}_2\text{O}$.

Before a crystalline hydrate can be formed the molecular clusters must exist in solution. These complexes which exist in solution are not observed by direct means but are of great significance. In the case of ions reliance must be entirely on inference since the solid hydrate cannot form because the powerful electrostatic forces between ions prevent the water molecules from entering the crystal in the same ratio that exists in the hydrate in the solution.

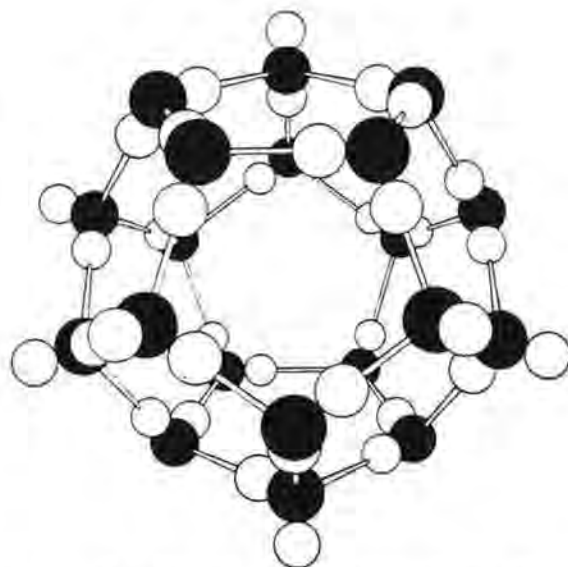


Figure 5. Hydrate is formed when a foreign molecule in water is electrically neutral and just the right size for the water molecules to collect around it in crystalline cage. This cage can then grow to a much larger crystal. It is part of a repeating unit of 136 molecules.

TABLE 1
PHYSICAL DATA ON THE TWO CUBIC HYDRATE LATTICES

	Diamond Type	Body-centered Type
Cell constant (approx.)	17 deg A	12 deg A
Number of H_2O molecules in cell	136	46
Number of dodecahedra (small holes)	16	2
Number of 14-hedra (medium holes)	none	6
Number of 16-hedra (large holes)	8	none
Hypothetical hydrative numbers		
(a) Filling all holes	$136/24=5-2/3$	$46/8=5-3/4$
(b) Filling only larger holes	$136/8=17$	$46/6=7-2/3$

Ionic Hydration and Mobility. The mobility for ions of like charge should vary inversely as the square of the effective diameter. If the mobility of the ions is considered a most peculiar behavior is observed in that the smallest ions appear to have the lowest mobility. A little consideration, however, shows the mobility depends upon the degree of hydration, i.e., the number of water molecules which are attached. The effective diameter of an ion is the diameter of the shell of attached water molecules.

While this is perhaps not always a definite number, certain positive conclusions can be drawn. Only the small cations are strongly hydrated.

The hydration of the cations is explained as due to a cage of water molecules formed in a manner similar to the gas hydrates. The cation which is positively charged attracts the oxygens of two water molecules quite strongly. If the cation is small enough (smaller than the potassium ion) so that the volume of the ion plus two water molecules is comparable to the volume of a methane molecule, then a cage of water molecules forms around this group as nucleus. The attraction of the ion for the oxygen atoms polarizes the central water molecules and increases the hydrogen bonding tendency so that a second layer of water molecules is attached in a symmetrical rigid shell. The number of molecules bound may be very large.

If the cation is too large, the shell cannot form. Anions may attach one or more water molecules by hydrogen bonding, but the hydrogen bond does not propagate through adjacent water molecules and the shell does not form.

This theory works admirably until the case of the hydrogen and hydroxyl ions which have the highest mobilities of any ions and many times that of most ions is considered. Hence it is concluded that these ions exist in a cage of water molecules but that they manage in some way to escape from the cage of water molecules, leaving the cage behind. Actually, of course, they continually form a new cage as they travel. The mechanism for this is not hard to picture. It involves what is called proton transfer.

The hydrogen ion or proton is attached at any instant to one of the oxygens but it oscillates between the two oxygen atoms many times per second. Under the influence of an electric field the proton, therefore, jumps from one molecule to the next. When this has occurred its task is done and the hydrogen on the farther side of the water molecule takes up its part in the race like a relay runner and jumps to the next water molecule. Thus a succession of protons, each doing its bit, carry the current. This makes for a rapid motion since each proton moves only a short step. It is, however, different from the original theory proposed by Grotthius who supposed that a whole series of protons moved in step in a continuous motion.

The mechanism of the conduction of hydroxyl ions is explained similarly by proton transfer. The formula for the hydroxyl is: $\text{HOH} \longrightarrow \text{OH}^-$. The proton jumps toward the right which is in effect the motion of the hydroxyl ion toward the left.

Bound Water. It is clear from the preceding discussion that liquid water undergoes a change in structure in the presence of molecules or at the surface or interface of a solid phase. This may be the result either of hydrogen bonding with active groups or if no active groups are present a considerable structure may be built out of water molecules themselves. In the case of protein molecules, both effects probably occur. It is evident that this is a subject that requires further exploration.

There is plenty of evidence for this formation of hydrates. Most of the phenomena of this sort have been ascribed to "bound" water. "Bound" water is essentially a term covering ignorance but there can be no doubt that water tends to solidify or crystallize in the presence of foreign molecules.

The solidification of water by gel formation is a familiar phenomenon which occurs at ambient temperatures. The key to the swelling of proteins and the imbibing of water by large molecules is undoubtedly to be found in hydrate formation as a result of one or the other of the above mentioned processes. The jelly fish is said to be more than 95 percent water.

The most commonly observed phenomenon of solidification is the formation of ice at temperatures below zero centigrade. Ice occupies a larger volume than liquid water so that if freezing occurs in an enclosed space the walls will rupture unless they are capable of resisting enormous pressures. The damage to living cells from freezing is ordinarily explained as due to this effect, but the evidence indicates that it is a much more complicated affair. The simple analogy of the anti-freeze in an automobile radiator cannot be applied to the sap of a frost-resistant plant. The mechanical effect of freezing does, of course, play an important role in the action of frost on the soils in the northern and central United States. The productivity of these soils is greatly increased by the loosening action of winter freezing. This process, which amounts to a natural cultivation of the soils, becomes harmful, of course, in the case of road

materials. The disruptive action of freezing water extends to even the hardest material, such as granite, over geological periods.

One of the most important products of this geological weathering action is the group of complex materials known as the clays. These substances exhibit a bewildering variety of colloid behavior in which water behaves as a plasticizer. This plasticizing action involves the hydrogen bonding of water to the oxygen of the silica or alumina groups. Silica gel is, of course, pure silica plus water. This bonding of the water molecules is a more or less reversible process except when high temperatures are reached, in which case the molecules become so closely bonded that the water molecules cannot intrude. The analogy is very close between the burning of ceramic material and the denaturation of proteins by dehydration.

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