

Water

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Because of the large amount of water present on our planet, especially in liquid form, this substance has become centrally important for many aspects of science and technology. This importance is connected partly to the peculiar behavior of pure water, partly to its qualifications as a liquid solvent, and partly to its role as a fluid medium for support of life.

The most prominent peculiarities exhibited by pure water are the reduction in volume upon melting at 0°C (by 8.3%), followed by further shrinkage to a density maximum as the liquid is heated to 4°C. These attributes are also shared by D₂O (m.p. 3.8°C, density max. at 11.2°C) and by T₂O (m.p. 4.5°C, density max. at 13.4°C). Although rare, these observations are not unique with water; the elements Si, Ge, and Bi also shrink upon melting, while In₂Te₃ appears to have a liquid-phase density maximum.

Additional water anomalies are (a) large number of ice polymorphs (including those that form at high pressure); (b) tendency toward reduced viscosity when liquid water below 30°C is compressed; and (c) minimum in isothermal compressibility [$-(\partial \ln V / \partial p)_T$] for the liquid at 46°C.

Observable properties of water in pure form and as a solvent stem from the structure of the individual water molecules and from the way that intermolecular forces between those molecules cause aggregation into liquid and solid.

The isolated H₂O molecule is shaped like a wide-open V, with the oxygen nucleus at the central bend and hydrogen nuclei forming "arms" of length 0.96 Å. The HOH angle is 104.5°. These dimensions can vary slightly as the molecule vibrates and interacts with neighbors in a crystal or the liquid, but the overall shape remains.

The dominant effect in water molecule interactions is the formation of hydrogen bonds. When two water molecules form a hydrogen bond, one (the hydrogen donor) points one of its OH groups toward the back side of the oxygen atom of the second (the hydrogen acceptor). This arrangement is illustrated in Fig. 1. The oxygen-oxygen lengths of these bonds normally lie in the range 2.7–3.0 Å, so that the donated hydrogen resides only about one third of the way between oxygens, and so still "belongs" to the donor.

The maximum hydrogen bond strength is achieved when the molecules are arranged as shown in Fig. 1. This strength is about 4.2×10^{-13} ergs (6.0 kcal/mole of bonds), and exceeds thermal energy $k_B T$ by a factor of 10 at room temperature. The existence of these relatively strong hydrogen bonds between water molecules explains the relatively high melting and boiling temperatures for water, compared to other substances of comparable molecular weight (e.g., Ne, CH₄, NH₃, O₂, CO).

In a large aggregate of water molecules, optimum hydrogen bonding is achieved if each water molecule hydrogen-bonds to four others. Toward two of these four it donates its hydrogens, while it accepts hydrogens from the other two. This fourfold bonding is present in ordinary ice, causing formation of hydrogen bond hexagons. Without disturbing hydrogen bond strengths substantially, four-coordinated water networks can also form, which additionally incorporate squares, pentagons, and heptagons of hydrogen bonds.

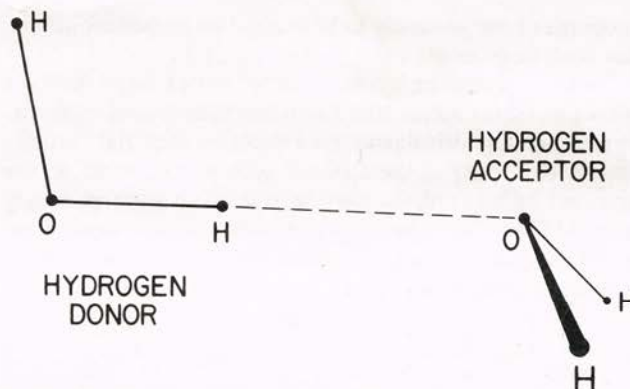


FIG. 1. Hydrogen bond (dashed line) linking two water molecules.

These patterns also exist in high-pressure ice polymorphs and in hydrate crystals.

Evidently the capacity for water molecules to form a diverse collection of three-dimensional networks of hydrogen bonds, while maintaining fourfold bonding at each molecule, has structural relevance for the liquid. Currently available evidence, both experimental and theoretical, indicates that liquid water consists of a structurally random network of hydrogen bonds uniformly filling the volume occupied by the liquid. That random network incorporates strained and broken hydrogen bonds, with greater frequency the higher the temperature. Furthermore, the network is labile, with bonds breaking in one place and reforming nearby, so that normal liquid flow and molecular diffusion are possible.

An isolated water molecule has dipole moment 1.86 debye (D), with hydrogens acting as though each bore one third of a protonic charge, and the oxygen as though it bore minus two thirds. Neighboring molecules in the liquid tend to have their dipoles somewhat aligned, so as to act in concert under the polarizing influence of an electrical field. The net result of this alignment, and of molecular polarizability, is a large static dielectric constant (88.0 at 0°C, but declining to 55.3 at 100°C).

The ease with which water dissolves many ionic crystals, such as the alkali halides, stems partly from its high static dielectric constant. However, it is also connected with the relatively small size of the water molecules, which permits them to approach ions closely, solvate them strongly, and thus overcome the largely electrostatic binding of the ionic crystals.

The solvating power of water for ions facilitates the dissociation of water molecules themselves into H⁺ and OH⁻ ions. In the liquid at room temperature, roughly one molecule in 55 million will have dissociated. The H⁺ and OH⁻ formed in this way can readily be incorporated into the liquid's random hydrogen bond network, and they tend to form shortened hydrogen bonds in their vicinity. Both H⁺ and OH⁻ have high apparent mobilities in water, due to the possibility of moving a succession of hydrogens along a chain of hydrogen bonds so as to cause a net transfer of ionic charge along that chain.

Nonionic substances with high solubility in water tend to have molecules with which water can hydrogen-bond. Usually this requires that molecules of those "hydrophilic" substances contain oxygen or nitrogen atoms.

Hydrocarbons (such as methane, hexane, acetylene, benzene) form an important group of "hydrophobic" molecular substances that are sparingly soluble in water. They cannot form hydrogen bonds with water strong enough to compete with those already present in that liquid itself. Consequently the random water network is obliged to restructure around the rare dissolved hydrocarbons so as to form a "cage" of hydrogen bonds of the required size. The corresponding geometric constraints on the water network cause entropies of solution for hydrocarbons in water to be negative.

Biologically important molecules (e.g. lipids, enzymes, RNA, hemes) often contain both hydrophilic and hydrophobic chemical groups. Consequently the biologically active conformations of these molecules, to the extent it is possible, place the hydrophilic groups on the outside to be in contact with water while the hydrophobic groups cluster within to avoid water contact. Since conformation is crucial to operation in most cases, it is obvious that specific solvation properties of water have profound effects in biology and doubtless have exerted a powerful influence on the course of chemical evolution from the first rudimentary "protolife" to present complex biochemistry.

See also HYDROGEN BOND; ICE.

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