

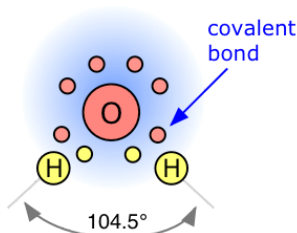
12.8: Water - An Extraordinary Substance

Learning Objectives

- Identify three special properties of water that make it unusual for a molecule of its size, and explain how these result from hydrogen bonding.
- Explain what is meant by hydrogen bonding and the molecular structural features that bring it about.
- Describe the "structure", such as it is, of liquid water.
- Sketch out structural examples of hydrogen bonding in three small molecules other than H_2O .
- Describe the roles of hydrogen bonding in proteins and in DNA.

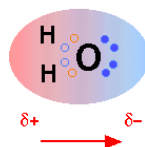
Most students of chemistry quickly learn to relate the structure of a molecule to its general properties. Thus we generally expect small molecules to form gases or liquids, and large ones to exist as solids under ordinary conditions. And then we come to H_2O , and are shocked to find that many of the predictions are way off, and that water (and by implication, life itself) should not even exist on our planet! In this section we will learn why this tiny combination of three nuclei and ten electrons possesses special properties that make it unique among the more than 15 million chemical species we presently know.

In water, each hydrogen nucleus is covalently bound to the central oxygen atom by a pair of electrons that are shared between them. In H_2O , only two of the six outer-shell electrons of oxygen are used for this purpose, leaving four electrons which are organized into two non-bonding pairs. The four electron pairs surrounding the oxygen tend to arrange themselves as far from each other as possible in order to minimize repulsions between these clouds of negative charge. This would ordinarily result in a tetrahedral geometry in which the angle between electron pairs (and therefore the H-O-H *bond angle*) is 109.5° . However, because the two non-bonding pairs remain closer to the oxygen atom, these exert a stronger repulsion against the two covalent bonding pairs, effectively pushing the two hydrogen atoms closer together. The result is a distorted tetrahedral arrangement in which the H—O—H angle is 104.5° .

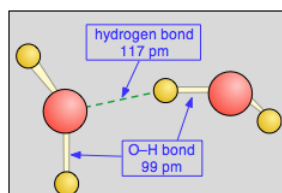


Water's large dipole moment leads to hydrogen bonding

The H_2O molecule is electrically neutral, but the positive and negative charges are not distributed uniformly. This is illustrated by the gradation in color in the schematic diagram here. The electronic (negative) charge is concentrated at the oxygen end of the molecule, owing partly to the nonbonding electrons (solid blue circles), and to oxygen's high nuclear charge which exerts stronger attractions on the electrons. This charge displacement constitutes an *electric dipole*, represented by the arrow at the bottom; you can think of this dipole as the electrical "image" of a water molecule.

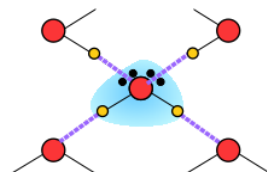


Opposite charges attract, so it is not surprising that the negative end of one water molecule will tend to orient itself so as to be close to the positive end of another molecule that happens to be nearby. The strength of this *dipole-dipole attraction* is less than that of a normal chemical bond, and so it is completely overwhelmed by ordinary thermal motions in the gas phase. However, when the H_2O molecules are crowded together in the liquid, these attractive forces exert a very noticeable effect, which we call (somewhat misleadingly) *hydrogen bonding*. And at temperatures low enough to turn off the disruptive effects of thermal motions, water freezes into ice in which the hydrogen bonds form a rigid and stable network.



Notice that the hydrogen bond (shown by the dashed green line) is somewhat longer than the covalent O—H bond. It is also *much weaker*, about 23 kJ mol^{-1} compared to the O—H covalent bond strength of 492 kJ mol^{-1} .

Water has long been known to exhibit many physical properties that distinguish it from other small molecules of comparable mass. Although chemists refer to these as the "anomalous" properties of water, they are by no means mysterious; all are entirely predictable consequences of the way the size and nuclear charge of the oxygen atom conspire to distort the electronic charge clouds of the atoms of other elements when these are chemically bonded to the oxygen.



The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 12.8.6. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O—H covalent bonds and two O···H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

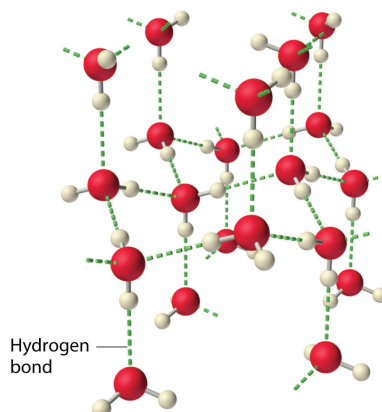


Figure 12.8.6: The Hydrogen-Bonded Structure of Ice.

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.

Boiling Point

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 12.8.5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of -130°C for water! Imagine the implications for life on Earth if water boiled at -130°C rather than 100°C .

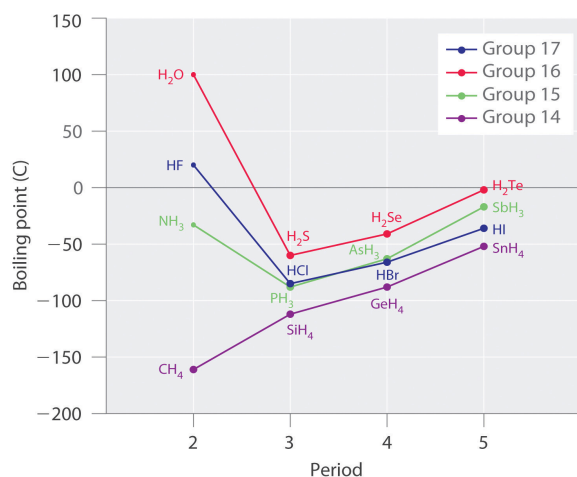
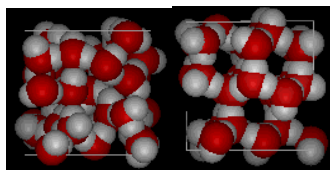


Figure 12.8.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3 , and H_2O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles.

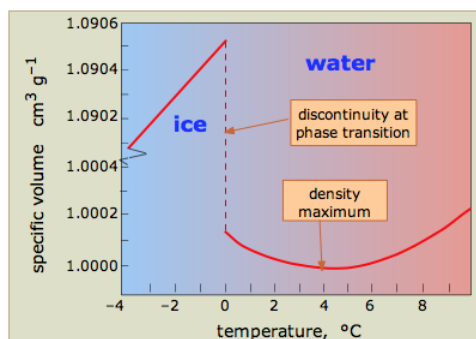
Ice Floats on Water

The most energetically favorable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to four neighboring molecules. Owing to the thermal motions described above, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of an arrangement in the ice crystal. This arrangement requires that the molecules be somewhat farther apart than would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.



Here are three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of hydrogen bonding in a uniform, extended crystal lattice. The more crowded and jumbled arrangement in liquid water can be sustained only by the greater amount of thermal energy available above the freezing point.

When ice melts, the more vigorous thermal motion disrupts much of the hydrogen-bonded structure, allowing the molecules to pack more closely. Water is thus one of the very few substances whose solid form has a lower density than the liquid at the freezing point. Localized clusters of hydrogen bonds still remain, however; these are continually breaking and reforming as the thermal motions jiggle and shove the individual molecules. As the temperature of the water is raised above freezing, the extent and lifetimes of these clusters diminish, so the density of the water increases.



At higher temperatures, another effect, common to all substances, begins to dominate: as the temperature increases, so does the amplitude of thermal motions. This more vigorous jostling causes the average distance between the molecules to increase, reducing the density of the liquid; this is ordinary thermal expansion. Because the two competing effects (hydrogen bonding at low temperatures and thermal expansion at higher temperatures) both lead to a decrease in density, it follows that there must be some temperature at which the density of water passes through a maximum. This temperature is 4 $^{\circ}\text{C}$; this is the temperature of the water you will find at the bottom of an ice-covered lake in which this most dense of all water has displaced the colder water and pushed it nearer to the surface.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Contributors

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