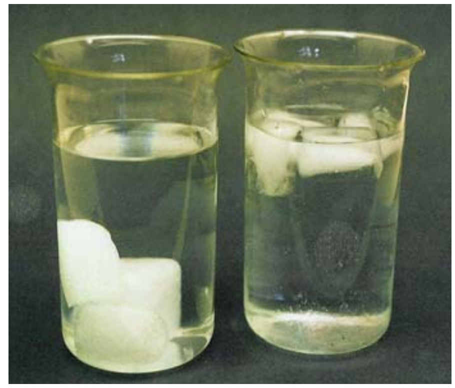
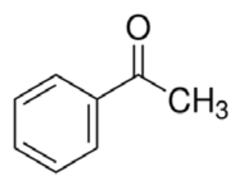
Chapter 4 Water and hydrogen bonding



Discovery consists of seeing what everybody has seen, and thinking what nobody has thought. 1937 Nobel physiology prize winner and vitamin C discoverer, Albert Szent-Gyorgyi.

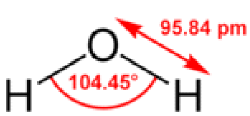
The beakers to the right each contains a single substance. Which one contains water? Based on hundreds or even thousands of previous experiences, you probably correctly identified the beaker on the far right as the container with the water. You undoubtedly noticed that the solid in the beaker on the right floats in its own liquid as contrasted to the beaker on the left where the solid sinks in its own liquid. But wait! Very early on in this book, the high importance of being complete with observations was stressed. And yet, how many of you ever questioned the observation that ice floats in liquid water? Think about it. As a liquid cools down and approaches its freezing temperature, should the volume of a given mass of water contract or expand. The conclusion you should now be reaching is that the liquid should contract and then contract some more upon freezing resulting in a solid that should sink. The observation that ice floats in water should have been noticed as an unexpected observation and should have caused each of us to reflect on this observation and ask why ice floats. Very few people demonstrate this level of observational ability partially because we do not question enough and also because water and ice probably represents the only single substance solid liquid system we ever observe. As a result, it is accepted as the norm and the question goes unasked and not answered. Some of you might be thinking of a candle and its wax or solder and its melted form but both are generally mixtures as contrasted with the water and it was probably not possible to tell if the liquid would float or sink in its liquid if and when you saw these two phase systems anyway.

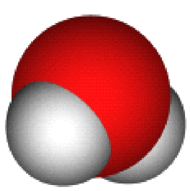


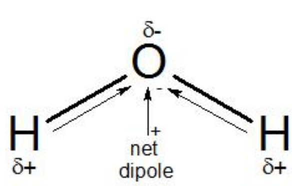
Acetophenone

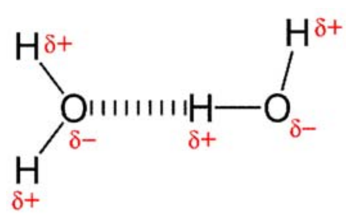
It turns out that if you ever do observe the liquid and solid of almost any substance other than water such as in the beaker on the left, the solid does sink as we would expect. In other words, water behaves anomalously and is an exception to the general rule. The beaker on the left contains liquid and solid acetophenone. Acetophenone has a melting point a little below room temperature. By placing a beaker of acetophenone in an ice bath for a short time and inducing freezing, solid forms that sinks rather than floats in its liquid. As we shall find out, for living systems, it is very important that water has this exceptional behavior.

The question we should ask now is why does ice float in liquid water? To try to answer this rather complex question, we need to return to the bonding discussion introduced at the end of the last chapter. The H-O bond is polar covalent with the electron density of the shared bonding electrons





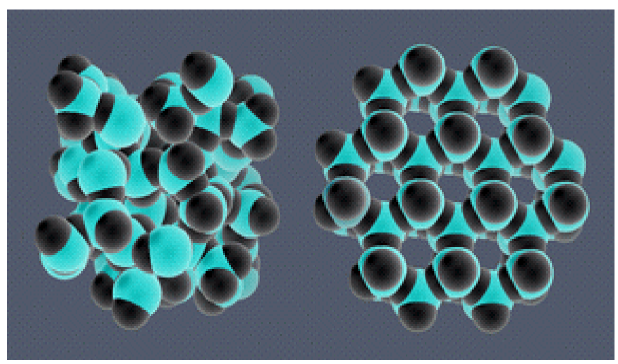




much higher in the vicinity of the oxygen than near the hydrogen. This results in a partial negative charge on the oxygen and a partial positive charge on each hydrogen. In the image above, the resulting bond dipoles are indicated with the head of the arrow representing the negative end of the dipole. Adding the two dipoles results in partial cancellation of the dipoles but still a remaining net dipole for the molecule as indicated in the figure. Water is therefore a very polar molecule. Since positive and negative charges attract each other, water molecules are intermolecularly attracted to each other via a special attraction appropriately called a hydrogen bond. The polarity of a bond between hydrogen and its bonding partner is only large enough to form a hydrogen bond when the hydrogen is bonded to F, O or N. While hydrogen bonds to other elements such as chlorine are polar, the bonds are not polar enough to create these exceptionally strong intermolecular bonds that are roughly 10% as strong as intramolecular bonds. This might not sound very strong but typically intermolecular attractions are considerably weaker than this.

When hydrogen is bonded to F, O or N and only when it is bonded to one of these elements, it can form hydrogen bonds to any and only the elements F, O or N. For water, each molecule hydrogen bonds to its neighbors throughout the system. This, first of all, results in the observation that water has a much higher boiling point that similar molecules that lack hydrogen bonds. When a liquid is converted into a gas by heating, the energy input must overcome the attractive forces in the liquid in order to separate the molecules. For water, substantial energy is required to overcome the hydrogen bonding with a resultant high boiling point. The boiling points of methane (CH_4), water (H_2O) and dihydrogen sulfide (H_2S) are -164ºC, 100ºC and -60ºC respectively. Thus the boiling point of water is about 200ºC higher than it would be in the absence of hydrogen bonding.

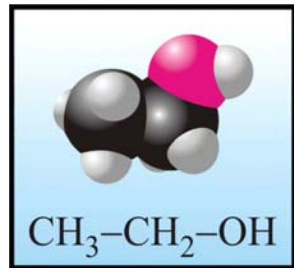
The situation for the liquid and solid states of water is very unusual. Both states have hydrogen bonds throughout. However, in the solid state, the hydrogen bonding results in a 3d structure that has holes between the molecules. In the liquid, the molecules are basically touching each other on all sides. The formation of the holes upon freezing causes the molecules to be farther apart and gives ice a lower density than water. This phenomenon is extremely rare and as noted, for almost all other substances, the solid sinks in its liquid as intuitively expected. For better molecular models representing water in the solid and liquid states, please visit:



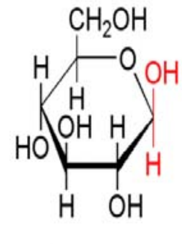
http://www.nyu.edu/pages/mathmol/textbook/info_water.html

Besides affecting the density and boiling point of water, hydrogen bonding is very important in determining its solvent properties. For a substance to dissolve in water, energy considerations must be favorable or water and the substance will not mix. If you pour sand into water, the sand does not dissolve as this would be energetically unfavorable. When you are about to pour some kinds of dressings on your salad, vigorous shaking followed by quick pouring is required or the water and oil phases will separate. Oil and water do not mix as there are no beneficial attractive forces between water and oil that would counteract the loss of the attractive forces that exist in water and in oil. One of the primary problems is that for oil molecules to dissolve in water, they would have to fit in between some waters and cause the loss of the very beneficial hydrogen bonds without producing new attractions. On the other hand, substances like ethanol and glucose are very soluble in water as both have H-O bonds and form their own strong hydrogen bonds to water.

Non-polar molecules like oils are generally not very soluble in water. Consider what happens when you open a can or bottle of carbonated soda. While carbon dioxide does have polar covalent bonds, unlike water's bent structure, CO_2 is linear. This results in a complete cancellation of the bond dipoles leaving the molecule without a net dipole. Thus, carbon dioxide is non-polar and forms only extremely weak attractions to water. As a consequence, CO_2 has a very low solubility in water and bubbles out of water as soon as the pressure that forced the carbon dioxide into solution is released.



Ethanol

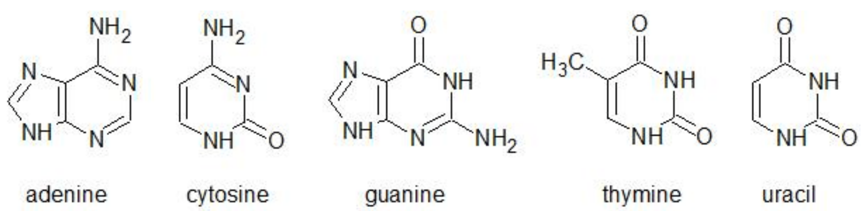


β-glucose

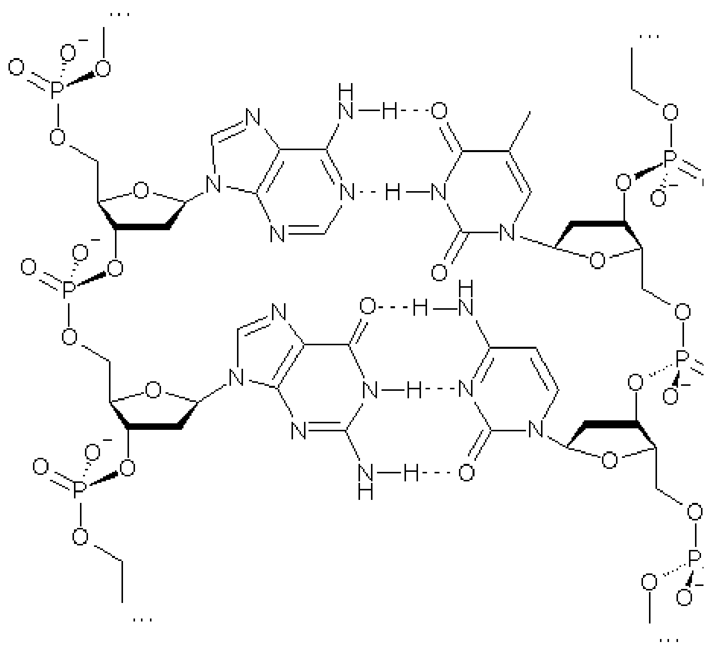
Carbon dioxide

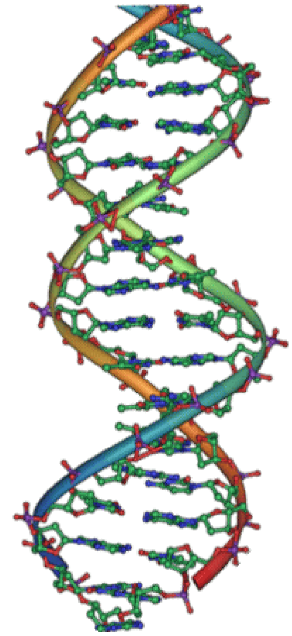
Ionic compounds such as table salt (sodium chloride, NaCl) have a more complex behavior in water. Many but not all dissociate into their positive and negative ions (e.g., Na^+ and Cl^-). These highly localize charged particles are strongly attracted to the waters with the sodium ions finding themselves surrounded by the partially negatively charged oxygens of water. The partially positively charged hydrogens of water surround the chlorides. The resulting attractive forces for many ionic compounds results in substantial solubility. However, a number of ionic compounds such as silver chloride, calcium carbonate and barium sulfate are energetically better off in the crystalline state than dissolved in water and have very low solubilities in water. Even those that dissolve generally have solubility limits. Salt can be dissolved in water until the solution is saturated at about 26% by mass salt. While ocean water might seem salty, it has less than 3% salt dissolve in it.

Hydrogen bonding is not confined to systems with water. In fact hydrogen bonding has many extremely important roles in nature including the key to the to the inherited characteristics of all animals. The code of life is contained in four nitrogen bases that are present in the DNA molecule.



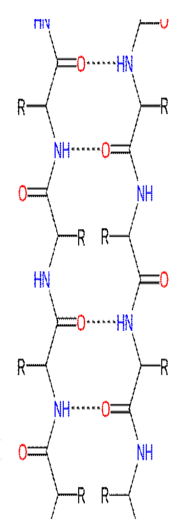
The first four molecules adenine (A), cytosine (C), guanine(G), and thymine (T) form the internal core of DNA and hold the double helix together with hydrogen bonds. RNA contains the first three but instead of thymine, contains uracil. Note that all of the bases have nitrogens bonded to hydrogens and four of the five have oxygens. The hydrogens bonded to nitrogen are capable of hydrogen bonding to the nitrogens and oxygens on other nitrogen bases.



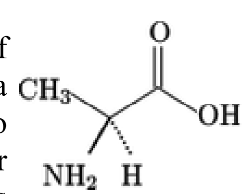


The image to the left above shows a very small segment of a DNA chain. The dashes indicate hydrogen bonds. The top base pair shows adenine paired with thymine and the bottom shows guanine paired with cytosine. These are the only pairings possible among the 16 possible combinations. There are two primary reasons for the exclusion of the other pairs. Two of the bases have one ring (pyrimidines) and the other two have two rings (purines). To maintain the right distance between the two segments of the double helix, a purine must be bonded to a pyrmidine. If two purines were to be bonded together, a bulge would result in the double helix. Two pyrimidines would pull the two strands too close together. Adenine bonds to thymine and cytosine bonds to guanine because these combinations form the strongest hydrogen bonds. The switched options are not as energetically favorable.

The genetic code is expressed in three letter segments made from the four possible letters. 64 possible three letter sequences of A, G, T and C exist (4x4x4). When DNA replicates, part of the double helix unwinds and a new strand is synthesized for each of the freed strands. The matching bases are fed in and joined to the newly forming companion strand. This replication results in two DNA polymers with base sequences identical to the original. It is extremely rare for an error to occur but the consequences of an error can be severe including deformity or cancer. Parts of the double helix also unwind so that the base template can be appropriately matched as RNA is formed. RNA is then used as the template for the synthesis of proteins. There are 20 amino acids used to make proteins and 64 possible codes. Many of the many acids have more than one code.



The structure of alanine is given to the right. Hundreds of amino acids must link together in the correct sequence to form a protein. The sequence of nitrogen bases determines which amino acids are linked and their order. Proteins must form a particular shape to be able to perform their functions. Parts of the proteins



might form helical shapes and others the pleated sheets as shown in the figure above. Both the helical forms and as illustrated the pleated sheets have structures that are determined by hydrogen bonding.

Water quality. Dangerous contaminants in water include bacteria that can cause diseases, heavy metals such as arsenic that can cause physiological damage, toxins such as pesticides and potential carcinogens such as nitrite. Various methods are used by municipalities to lower the concentration of the contaminants below the allowed limits. In many parts of the world such as Central and South America, water purification is not sufficient to provide safe drinking water. However, in the United States, Canada and most of Europe, there are rigid standards for the purity of tap water. Bottled water is not always subject to the same high standards as tap water and is often (except for convenience such as when driving) just a waste of money and resources. Bottled water companies often just take tap water, filter it and add it to the bottle. Filtering does not significantly change the purity of the water. While some plastic bottles are recycled, way too many end up in landfills or polluting other parts of our environment.

Some contaminants are the result of environmental pollution but others are from natural sources. Well water is often very high in nitrates and sometimes heavy metals such as arsenic. Pesticides are overused and run off into our rivers and lakes and also slowly make their way down into aquifers. A good way to complete this section is for you to search for a report on your local water quality. For Modesto, CA please visit and read the report at:

http://www.modestogov.com/uppd/reports/water/regs/modesto.pdf