Chemical of the Week

WATER

Water covers about 70% of Earth's surface, makes up about 70% of your mass, and is essential for life. This photograph of planet Earth, taken by the Apollo 17 crew as they traveled toward the moon on December 7, 1972, shows an area of the planet from the Mediterranean Sea to Antarctica. Water is visible in this photograph as the Atlantic, Indian and Southern (or Antarctic) Oceans, the south polar icecap, and as heavy cloud cover in the southern hemisphere and scattered along the equator.

Water is the only substance that exists naturally on Earth in all three physical states of matter—gas, liquid, and solid—and it is always on the move among them. The Earth has oceans of liquid water and polar regions covered by solid water. Energy from the sun is absorbed by liquid water in oceans, lakes, and rivers and gains enough energy for some of it to evaporate and enter the atmosphere as an invisible gas, water vapor. As the water vapor rises in the atmosphere it cools and condenses into tiny liquid droplets that scatter light and become visible as clouds. Under the proper conditions, these droplets further combine and become heavy enough to precipitate (fall out) as drops of liquid or, or if the air is cold enough, flakes of solid, thus returning to the surface of the Earth to continue this cycle of water between its condensed and vapor phases. (Visit http://www.eoearth.org/article/Hydrologic_cycle for more information on the Hydrologic Cycle.)

Water in all three states makes a large contribution to the planet's climate. Water vapor is a greenhouse gas that traps energy radiated from the surface of the planet and helps to keep the planet warm enough to sustain the complex life that has evolved in this environment. Water vapor is responsible for more than half the Earth's greenhouse gas warming. On the other hand, clouds and ice fields on the surface reflect a good deal of the radiation from the sun, so this radiation does not reach the surface and warm it. The reflectivity of clouds and ice has a cooling effect on the planet. However, where the earth's surface has been heated by solar radiation, clouds help trap energy radiated from the heated surface and thus have a warming effect as well. Variations in the amount and form of water in the atmosphere have a complex relationship to our climate that is difficult to model and predict.

Pure water is colorless, odorless, and tasteless and so common that you probably never think about how unique it is and how essential to life. Most plants and animals contain more than 60% water by volume. Without water, life would not have evolved on Earth, and it is the presence of water on Mars and some moons of Jupiter and Saturn that causes us to speculate about past or present life there as well.
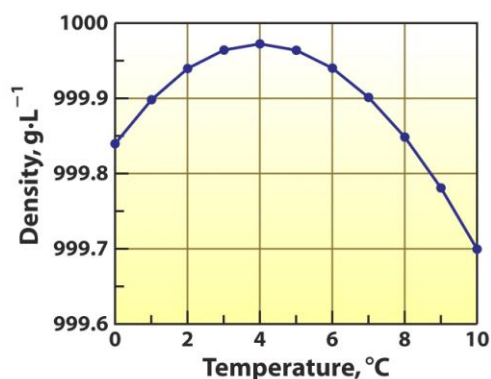
Water has a number of unique chemical and physical properties that make it essential for life. One such property is familiar to everyone: solid water floats on liquid water. Almost all liquids contract when they get colder and reach a maximum density when they solidify. Water is different. As water cools, it contracts until it reaches 4°C, then it expands until it freezes at 0°C. Ice is less dense than water which allows ice cubes to float in a soft drink, icebergs to float in the ocean, and ponds and lakes to freeze from the top down so that aquatic plants and animals can survive in the unfrozen liquid below.
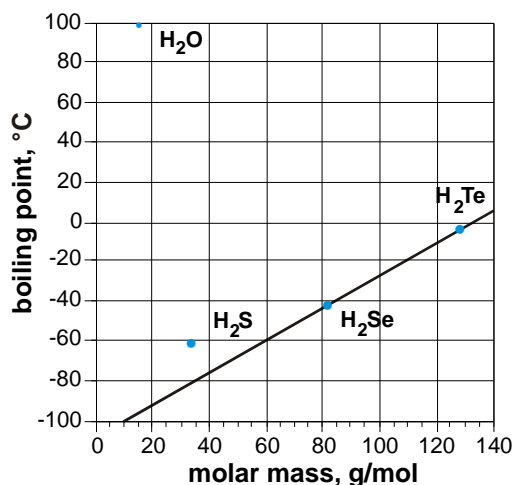
Water molecules have a simple structure: two hydrogen atoms bonded to one oxygen atom – H_2O. This simple structure is responsible for water's unique properties. The bond between each hydrogen atom and the oxygen atom results from a pair of electrons shared between the two atoms. In water, the electrons in the shared pair are not shared equally between the hydrogen and oxygen atoms. The oxygen atom has a greater affinity for electrons than does the hydrogen atom, and the electrons in the O–H bond are more attracted to oxygen. Because electrons have a negative charge, the unequal sharing in the O–H bond results in oxygen acquiring a partial negative charge (δ−) and hydrogen a partial positive charge (δ+). The H–O–H bond angle in water is 104.5°, which means that the molecule has a bent shape. This bent geometry and the accumulation of electrons on the oxygen side of the molecule cause the water molecule to have a negative charge on one side, the oxygen side, and a positive charge on the other side, the hydrogen side. Molecules with negative regions and positive regions are called polar molecules. Water molecules are polar molecules.
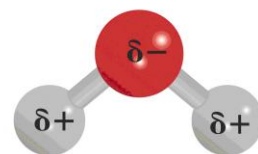
Polar molecules are attracted to each other. The attraction results from the negative region of one molecule, the oxygen atom, being drawn to the positive region of another molecule, the hydrogen atom. Opposites attract! The attractions between water molecules are particularly strong. Oxygen atoms have a very great affinity for electrons, and so the hydrogen atoms bonded to an oxygen atom acquire a significant positive charge. These hydrogen atoms are very tiny, so the positive charge is quite concentrated. This concentrated positive charge enhances the attraction of the hydrogen atoms in one molecule for the oxygen atom in another molecule. These attractions are represented by the green lines (highlighted by arrows) in the figure. This attraction is so strong that it has been given a particular name: hydrogen bonding. The energy associated with hydrogen bonds in water is about 20 kJ·mol^{-1}, which is about 1/10 the strength of a typical shared-electron bond within a molecule.
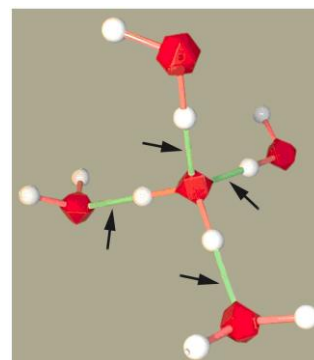
Hydrogen bonding between water molecules gives water its unique properties. For example, hydrogen bonding is responsible for the lower density of ice, solid water, than of liquid water. Any one water molecule can form four hydrogen bonds with four neighboring molecules. Extension of this hydrogen bonding in three dimensions produces interconnected cages of water molecules in ice, with empty space inside the cages. When the solid melts, many of the hydrogen bonds are broken and the structure collapses, so liquid water is denser than the solid. Hydrogen bonding is also responsible for the six-fold symmetry of snowflakes (http://www.its.caltech.edu/~atomic/snowcrystals/), for im-

portant interactions with biological molecules in living organisms, and for the unusually high boiling point, melting point, surface tension, and specific heat of water. Hydrogen bonding and the polarity of water also explain its solvent properties.

Water has a remarkably high boiling point for a substance with such small molecules. In order for a substance to boil, the molecules of the liquid must have enough energy to overcome the forces of attraction between them. Generally, boiling points of related compounds increase with molar mass. When the boiling points of the hydrogen compounds (hydrides) of Group VI elements, H_2O, H_2S, H_2Se, and H_2Te are plotted versus molar mass, water is far out of line with the heavier compounds. If water followed the trend for the two heaviest hydrides, its boiling point would be about −90 °C. The boiling point of water is 100 °C, which is 190 °C above the extrapolated value. It requires a high temperature to give water molecules enough kinetic energy to overcome the extensive hydrogen-bonded network among them. For similar reasons, water also has a higher melting point than would be expected for its low molar mass. The H_2S molecule is only slightly polar, but enough to make its boiling point a bit higher than predicted by the extrapolation from the non-polar heaviest hydrides.

Water has the second highest surface tension of all common liquids; only mercury is higher. The intermolecular forces between liquid molecules are responsible for surface tension. Molecules in the bulk of the liquid are surrounded by other molecules and feel no net force of attraction. However, molecules at the surface of a liquid are pulled inward by the molecules on the inside of the liquid, which keeps them firmly attached to the liquid. The molecules on the surface are also attracted to each other. The forces between them cause them to behave something like a stretched elastic film that squeezes the liquid into the shape with the smallest possible surface area. The shape with the smallest surface-to-volume ratio is a sphere, so surface tension causes drops of water into as close to a spherical shape as possible.
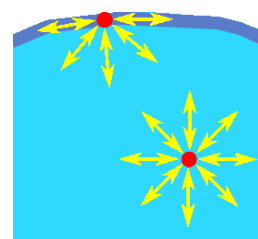
Water molecules (red) experience intermolecular forces (yellow).

Surface tension makes it more difficult to move an object through the surface of a liquid than to move an object when it is completely submerged. Surface tension is typically expressed in dynes·cm^{-1}, the force in dynes required to break a film of length 1 cm. At 20 °C, the surface tension of water is 72.8 dynes·cm^{-1}. For comparison, the surface tension of mercury and ethanol are 465 and 22.3 dynes·cm^{-1}, respectively. Surface tension allows water striders, insects that hunt prey on the surface of still water, to skate across the top of a pond. Likewise, you can suspend a metal paperclip or needle on the surface of water due to the high surface tension of water, even though the metal is seven to eight times denser than water.

Water has an unusually high specific heat. It takes more energy to raise the temperature of one gram of water by 1°C than any other liquid. Temperature is an expression of the amount of kinetic energy in the molecules of a substance; increasing temperature corresponds to increasing kinetic energy. Again, hydrogen bonds are responsible for the high specific heat of water. As water is heated, much of the added energy goes to breaking apart hydrogen bonds. The energy used in breaking hydrogen bonds is not available to increase the kinetic energy of the water molecules, so the temperature of water does not rise as much as would a liquid with lower intermolecular forces. Therefore, water must absorb more heat energy to raise its temperature. Water can absorb large amounts of heat energy before it begins to get hot. Similarly, as water cools, it releases a great deal of heat. The high specific heat of water is responsible for the ocean's ability to act as a thermal reservoir that moderates

swings in the Earth's temperature from day to night and from winter to summer, and this makes the planet suitable for its diverse inhabitants.

Many substances dissolve in water, but others are quite insoluble—water and many of the Earth's rocks and minerals have coexisted for billions of years and the rocks are still here. The properties of solvents are often summed up in the phrase, "like dissolves like," with the implication that "like does not dissolve unlike." In these generalizations, the property that is like or unlike is molecular polarity. A solvent with polar molecules like water tends to dissolve other substances having polar molecules, as well as substances that form ions when dissolved. This is the case because the charges or partial charges of the solvent molecules and solute molecules attract one another. The molecules of the solvent surround molecules or ions of the solute, an arrangement called solvation. This solvation holds the solute in solution. On the other hand, substances with nonpolar molecules, such as hydrocarbons, fats, and oils, are not appreciably soluble in water. However, they are relatively soluble in solvents that have nonpolar molecules, solvents like those used for dry cleaning clothing..

Why are nonpolar molecules generally insoluble in water and why are some ionic compounds, the minerals in rocks, for example, also so insoluble. The answers can be put in terms of favorable and unfavorable arrangements of molecules and ions in the solvent-solute system and are essentially the same in each case. In a system that consists of two or more different kinds of molecules (or molecules and ions) mixing them together so they are dispersed among one another is always a favorable arrangement. Thus, dissolution, mixing one substance into another, is always favorable. (This qualitative idea can be quantified by introducing the concept of entropy. Favorable arrangements have higher entropy than unfavorable arrangements and systems always change toward higher entropy.) The qualitative idea of favorable and unfavorable arrangements is sufficient to understand solubility.

But simple mixing is not all that goes on in forming a solution. As described above, when solutes dissolve, they are solvated and the effect of solvation on the arrangement of solvent molecules has to be accounted for. In a pure solvent like water, the molecules attract one another and form transient hydrogen bonds, but are still relatively free to tumble about and move around in the liquid, When ionic compounds dissolve, water molecules solvate them and become more tied up in the solvent shell around the ions. This is an unfavorable arrangement, because the solvent-shell molecules are less free to move about in the solution and mix with the others. Similarly, nonpolar molecules in water are surrounded by water molecules in something like the ice structure, which, once again, ties them up and is an unfavorable arrangement for the solvent.

Thus, dissolution is a competition between a favorable arrangement, mixing of solute and solvent, and an unfavorable arrangement, solvation that ties up solvent molecules. For nonpolar solutes, the unfavorable factor almost always outweighs the favorable and they are not soluble in water, that is, oil and water do not mix. For ionic solutes, salts of singly-charged cations and anions, NaCl, NH_4NO_3, CsI, and so on, are almost all soluble. (The notable exceptions are the silver halides.) In these cases, the favorable mixing factor outweighs the unfavorable solvent arrangement factor, because the charges on the ions are small and molecules in the solvent shell are held rather loosely. Salts of multiply-charged cations and anions, $BaSO_4$, $CaCO_3$, $Co_3(PO_4)_2$, and so on, are almost all insoluble. The unfavorable solvent arrangement factor predominates in these cases, because the more highly charged ions hold the molecules in the solvent shell more tightly.

The acid-base chemical properties of water contribute to the dissolution of solutes that also have acid-base properties. In pure water, about two molecules in every billion react to form a hydroxide ion, $OH^-(aq)$, and a hydronium ion, $H_3O^+(aq)$:

$$H_2O \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O^+ \quad + \quad OH^-$$
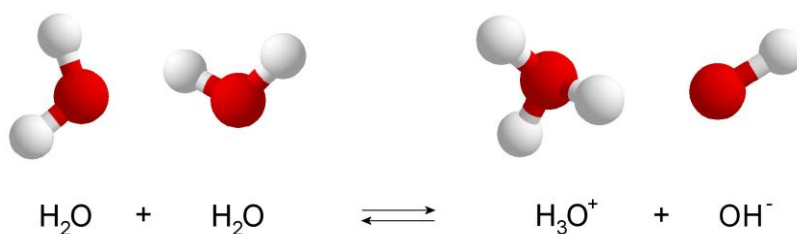
In this reaction, a hydrogen ion is released from a bonding pair of electrons in one molecule and transferred to a non-bonding pair of electrons in the other molecules. Releasing a hydrogen ion in this way is characteristic behavior for an acid, and accepting a hydrogen ion is characteristic behavior of a base. This reaction is reversible, and the hydroxide ion can accept a hydrogen ion from a hydronium ion. In the reverse direction, the hydroxide ion is the base, and the hydronium ion is the acid. In pure water, the number and concentration of hydronium ions is the same as that of the hydroxide ions. This equality means that there is no net acidity or basicity in pure water. Pure water is neutral in the acid-base sense.

Water molecules can act as acids with other molecules, too. For example, they can transfer a hydrogen ion to a nonbonding electron pair on a solute molecule like ammonia, $NH_3(aq)$, to form an ammonium ion, $NH_4^+(aq)$, and a hydroxide ion.

$$NH_3 \quad + \quad H_2O \quad \rightleftharpoons \quad NH_4^+ \quad + \quad OH^-$$
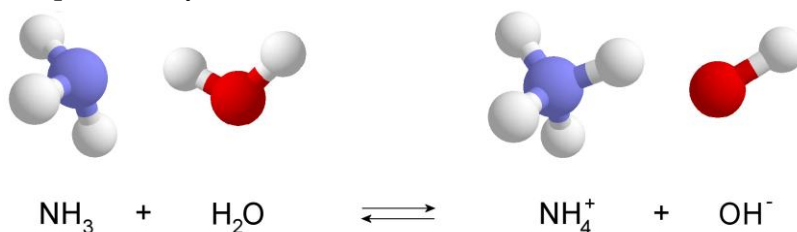
This reaction produces an excess of hydroxide ions over hydronium ions in the solution of ammonia in water. Therefore, this solution is basic. Ammonia is called a base, because it can accept a hydrogen ion from water to form a basic aqueous solution. Water molecules can also act as bases, accepting a hydrogen ion from a solute molecule like acetic acid, $HOOCCH_3(aq)$, to form a hydronium ion and an acetate ion, $OOCCH_3^-(aq)$.

$$H_2O \quad + \quad HOOCCH_3 \quad \rightleftharpoons \quad H_3O^+ \quad + \quad {}^-OOCCH_3$$
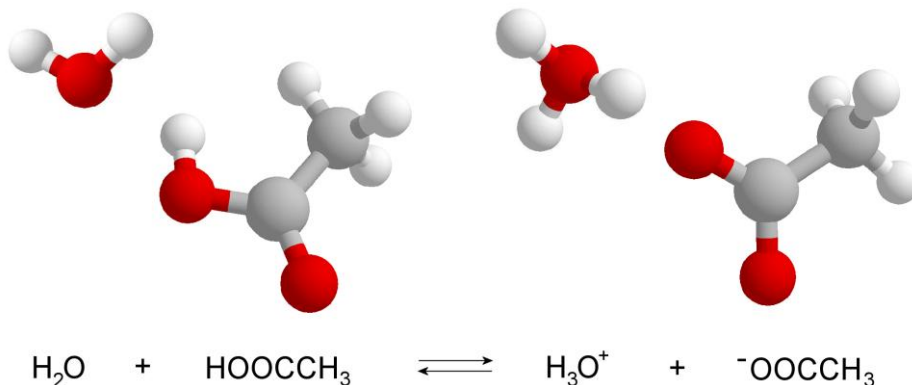
This solution has a higher concentration of hydronium ions than pure water; it is acidic. Acetic acid is called an acid, because it can transfer a hydrogen ion to water to form an acidic aqueous solution.

Carbon dioxide, $O=C=O$, is an acidic solute that plays a particularly important role in the Earth's oceans. The electrons in the carbon-oxygen bonds are attracted more to the oxygen atom giving the oxygen atoms a partial negative charge and the carbon atom a partial positive charge. Because carbon dioxide is a linear molecule these bond dipoles cancel one another, so the molecule has no permanent

dipole moment and is usually said to be nonpolar. However, when dissolved in water, the partial positive charge on the CO_2 carbon and the partial negative charge on the water H_2O oxygen attract one another. Similarly, of course, the partial negative charges on the CO_2 oxygens and the partial positive charge on the water H_2O hydrogens attract one another. One result is that carbon dioxide is about 40 times more soluble in water than the truly nonpolar atmospheric gases, nitrogen, N_2, and oxygen, O_2.

Another result is that some of the dissolved carbon dioxide reacts with water to form carbonic acid, $(HO)_2CO$*(aq)*, which can donate a proton to water to form a hydronium ion and the hydrogen carbonate (bicarbonate) ion, $HOCO_2^-$*(aq)*. Carbon dioxide from the Earth's atmosphere dissolves in the oceans and there is equilibrium between the dissolved and atmospheric gas. The concentration of dissolved carbon dioxide depends on the concentration of carbon dioxide in the atmosphere. Over the past half century, due to our burning of large amounts of fossil fuels, the concentration of carbon dioxide in the atmosphere has increased from about 310 parts per million (ppm, by volume) to about 390 ppm.

Over the past half century, due to our burning of large amounts of fossil fuels, the concentration of carbon dioxide in the atmosphere has increased from about 310 parts per million (ppm, by volume) to about 390 ppm. The consequence of increased atmospheric carbon dioxide is an increase in the amount of carbon dioxide dissolved in the oceans. This has caused their acidity to increase and endanger several forms of life, including corals and some microscopic organisms that are at the base of the oceanic food chain. These organisms depend upon the appropriate acid-base properties of seawater to build exoskeletons made of calcium carbonate (familiar to us as chalk, limestone, and marble, formed over millions of years from the exoskeletons of organisms like these and other shells). Calcium carbonate is quite insoluble in slightly basic seawater, but as the sea has become less basic (more acidic), calcium carbonate is more soluble. This is because carbonate ions can react with hydronium ion to form the hydrogen carbonate ion and displace the calcium carbonate solubility equilibrium toward the dissolved side.

$$CO_3^{2-} \quad + \quad H_3O^+ \quad \rightleftharpoons \quad HCO_3^- \quad + \quad H_2O$$
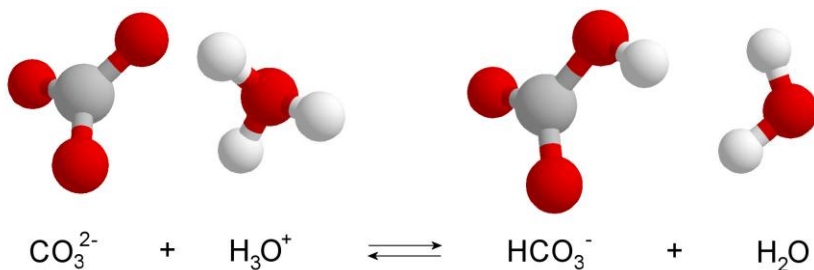
Many organisms are unable to cope with the increased solubility, are unable to form the necessary structures to maintain their integrity, and die, thus decreasing the amount of food available to higher trophic levels in the ocean ecosystem.

Other acidic solutes, oxides of sulfur and nitrogen, also formed in the combustion of fossil fuels, are quite soluble in water, are incorporated into condensed water vapor in the atmosphere, and fall to the ground as acid rain (and other forms of precipitation). Acid rain falls mainly in areas downwind from power plants that burn large quantities of coal, oil, and gas. Lakes in these areas become more acidic and toxic to many organisms and vegetation on land is also adversely affected. Limnology, the study of lakes and the factors that affect them (UW-Madison has a major limnology program, see http://limnology.wisc.edu/), has demonstrated the adverse affects of sulfur and nitrogen oxides from burning fossil fuels. Legislation requiring removal of oxides of sulfur and nitrogen from effluent gases has had beneficial effects. Visit http://www.epa.gov/acidrain/ to find out more and see what changes have taken place.

With water covering more than two-thirds of the Earth's surface, it is hard to imagine that it is a scarce resource. The problem is that less than 1% of the water on the planet is readily available for drinking or for most agriculture. Most of the water on Earth, 97%, is salt water stored in the oceans; only 3% is freshwater. Of all of the freshwater on Earth, 68% is locked up in the icecaps of Antarctica and Greenland, 30% is in the ground, and only 0.3% is contained in surface waters such as lakes and rivers. (About 22% of all surface water is in the Great Lakes.) Over one billion people lack access to safe drinking water worldwide.

Solutions to the water scarcity problem include collection and storage of precipitation and desalinization of seawater. Since precipitation is dispersed over large areas, the cost to build the infrastructure for collection and storage is very high. Desalinization of seawater (or other undrinkable water) by either vaporization-condensation processes or reverse osmosis is centralized, so the initial capital investment is less. The energy requirements for desalinization are high, but lower for reverse osmosis, which has been growing as the favored method. Desalinized water, at about 0.5 cents per gallon is three to five times more expensive than municipal water from freshwater sources. For comparison, bottled water from the supermarket (often no more than tap water in a plastic bottle) costs 2 to 5 dollars per gallon, or 400 to 1000 times as much as desalinized water. Bottled water is about a $10 billion industry in the United States. Can you think of other possible uses for these dollars? For more detailed information on this scarce resource, drinkable water, visit http://water.usgs.gov/, http://www.epa.gov/ow/, and http://www.sciam.com/article.cfm?id=facing-the-freshwater-crisis.

The economics of drinkable water scarcity pale in comparison to its effects on human resources. Diseases caused by unsafe drinking water and inadequate sanitation are a serious public health concern, causing 80% of illnesses in developing countries and killing 2 to 5 million people, mainly young children, every year. To read more about this problem and explore solutions visit http://www.drinking-water.org/flash/splash.html.

There is much more about the properties of water and aqueous solutions at: http://www.btinternet.com/~martin.chaplin/index.html.

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