

# Water—General Principles

*Fish say, they have their stream and pond;  
 But is there anything Beyond! . . .  
 One may not doubt that, somehow, good  
 Shall come of Water and of Mud;  
 And, sure, the reverent eye must see  
 A Purpose in Liquidity.*

Rupert Brooke

## 14.1 UNIQUE PHYSICAL AND CHEMICAL PROPERTIES

Water is such a common, seemingly simple substance that we tend to forget the fact that its physical and chemical properties often lie at the extremes of the ranges established by the many substances chemists have synthesized. But in most cases it is just these unique properties which make water especially suitable or "fit" for the support of life as we know it. As we examine a number of its characteristics, it should become apparent why water plays so many and such important roles in the functioning of the biosphere.

Density — 4°C

It is a well-known fact that the density of water, unlike that of most other liquids, reaches a maximum at 277 K and normal ice floats on the surface rather than sinking to the bottom of the liquid phase. The unusually low density of ice and of liquid water just above the melting point is attributed to the rather open structure necessary if both hydrogens and both oxygen lone pairs of each water molecule are to be involved in the formation of

linear hydrogen bonds.<sup>1</sup> A number of important ecological and environmental consequences may be attributed to the expansion of water as it freezes. One—the initiation of rock weathering by ice formation in small cracks and fissures—has already been discussed (Section 12.1).

If water behaved as most liquids, lakes would freeze solid in regions of the world where temperatures drop below 273 K for extended periods. Fish and other aquatic organisms would have had to adapt to being frozen for much of their lives. Instead, a layer of water at 277 K collects at the bottom of most lakes in winter while only the surface layer freezes (Figure 14.1). In summer the opposite situation applies—a layer of water warmed by solar radiation (epilimnion) collects at the surface above colder, denser liquid at the bottom (hypolimnion). The boundary between the epilimnion and hypolimnion is known as the thermocline. In spring and fall, as the surface layer warms and cools, a point is reached at which the entire lake is nearly uniform in temperature so that vertical mixing (turnover) can occur. This distributes dioxygen and nutrients throughout the water.

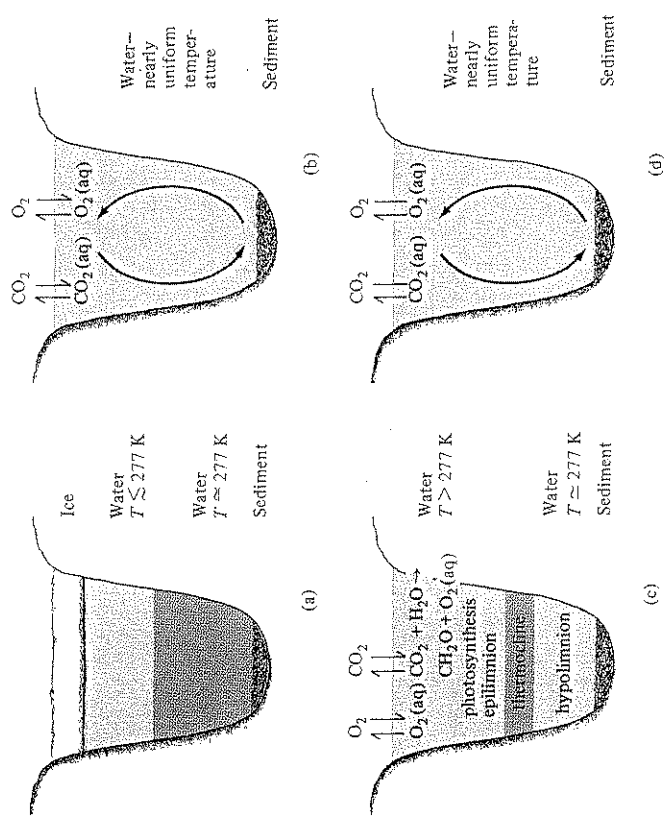


Figure 14.1 Thermal stratification of a lake through four seasons: (a) winter, (b) spring (turnover), (c) summer, and (d) fall (turnover).

<sup>1</sup> W. L. Masterton and E. J. Slowinski, "Chemical Principles," pp. 292-295, Saunders, Philadelphia, Pennsylvania, 1973; any general chemistry text will have a similar discussion.

In summer the hypolimnion serves an important function since certain fish and other organisms prefer the lower temperatures it provides. However, except for spring and fall turnovers, there is no mechanism by which  $O_2$  dissolved in surface waters from air or produced by photosynthesis can reach the lower strata of a lake. If too much organic matter (which must be decomposed by oxidation) falls into the hypolimnion it may become anaerobic (dioxigen deficient) and species which live there may be unable to survive. One of the dangers of thermal pollution (Section 5.2) of a deep lake is that warm water discharged to the epilimnion will postpone (or even prevent) fall turnover, leaving the hypolimnion anaerobic.

### Surface Tension

The water molecule's ability to form large numbers of strong hydrogen bonds is related to another unusual physical property, its large surface tension. Because water molecules strongly attract one another and have lesser attraction for other types of molecules, it is difficult to break through the surface of liquid water. As a result of this property, many insects are able to walk on the surfaces of lakes and streams. More importantly, large surface tension is related to the rise of a liquid in a tube of small diameter, a property known as *capillarity*. The movement of water in plant vessels of small diameter and the retention of water in small interstices between soil particles are facilitated by its large surface tension.

### Polarity

Because of its bent structure and the sizable difference in electronegativity between hydrogen and oxygen, the water molecule is extremely polar. When ionic substances dissolve in water each ion is immediately surrounded (hydrated) by from four to eight dipolar water molecules. The resultant ion-dipole attractions stabilize the ions in solution. Since dipolar water molecules align with an electric field, water also has one of the highest *dielectric constants* of known substances. The complete statement of Coulomb's law:

$$F = q_1 q_2 / D r_{12}^2 \quad (14.1)$$

where  $F$  is the force between two charges  $q_1$ ,  $q_2$  separated by a distance  $r_{12}$  in a medium of dielectric constant  $D$ , shows that for the same pair of particles at the same distance the force decreases with increasing  $D$ . Thus, ions dissolved in water are less likely to approach closely enough to pack into a regular crystal lattice. Its polarity and high dielectric constant make water an excellent solvent for many of the ionic compounds which constitute the earth's crust. Thus, it is ideal as a medium for transporting inorganic nutrients within living organisms.

### Thermal Properties

When compared with those of other common liquids, the thermal properties of water are also unusual. Its large *heat capacity* of 75.5 J/mol K allows a given quantity of heat to be stored with minimal temperature change, and its large *thermal conductivity* allows for rapid transfer of heat to or from adjacent substances. Because a large number of hydrogen bonds must be broken upon melting or vaporizing water, its *heats of fusion* (6.00 kJ/mol) and *vaporization* (44.1 kJ/mol) are unusually large.

Organisms (such as *Homo sapiens*) that require a narrow range of temperature for their internal environments have used these properties to produce excellent thermoregulation systems. Heat produced by metabolic chemical reactions is transferred to water in the bloodstream and thereby distributed throughout the body. Should the temperature begin to rise, perspiration is allowed to vaporize and energy is transferred to the surroundings. The body temperatures of most warm-blooded animals lie in the range of 308–311 K, where the heat capacity of water passes through a minimum. Thus, attempts to increase or decrease this temperature meet with a small amount of negative feedback since slightly more than twice as much heat is required for a two-degree change than for a one-degree change.

The temperature of the entire biosphere is also moderated by the storage of solar energy in water or its phase changes. Temperatures near large bodies of water usually do not fall much below its freezing point because of the heat of fusion given off, and solar energy trapped in one geographic region may be transferred to another by means of atmospheric water vapor or warm ocean currents such as the Gulf Stream. Hence, winter temperatures in European coastal cities as much as 1500 km closer to the North Pole are comparable to those in Philadelphia or New York. Of the common liquids only water, by virtue of its unusual thermal properties, could accomplish this sort of climate modification.