Water-Quality Principles
QW1022–TEL

Lesson 3—Basics of Aqueous Chemistry

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U.S. Department of the Interior
U.S. Geological Survey

■ The Unique Properties of Water

Water is the only common pure compound on Earth that is a liquid and also possesses many unusual—even unique—properties. If it behaved like other chemical compounds of similar molecular weight and structure, life on Earth could not exist. The reason for most of water's extraordinary properties is hydrogen bonding. Although hydrogen bonds are much weaker than ionic or covalent bonds, they have a profound effect on the physical properties of water in both its liquid and solid states.

The Water Molecule and Hydrogen Bonding

A water molecule can form four hydrogen bonds (Figure 7.3). The oxygen atom in the molecule can bond to two hydrogen atoms in other molecules because it has two pairs of unshared electrons. Each hydrogen atom in a water molecule can bond to an oxygen atom in another molecule. These bonds are directional, which means that they can form only when the molecules are correctly oriented relative to each other.

In the liquid state, water molecules are in constant motion, and hydrogen bonds are continually being formed and broken. The arrangement of the molecules is random, and not all possible hydrogen bonds are formed. In solid water (*ice*), molecular motion is at a minimum, and molecules become oriented so that the maximum number of hydrogen bonds is formed. This results in an ordered, strong, extended, three-dimensional, open-lattice structure (Figure 7.4a). The size of the "holes" in the lattice is dictated by the bond angle in the water

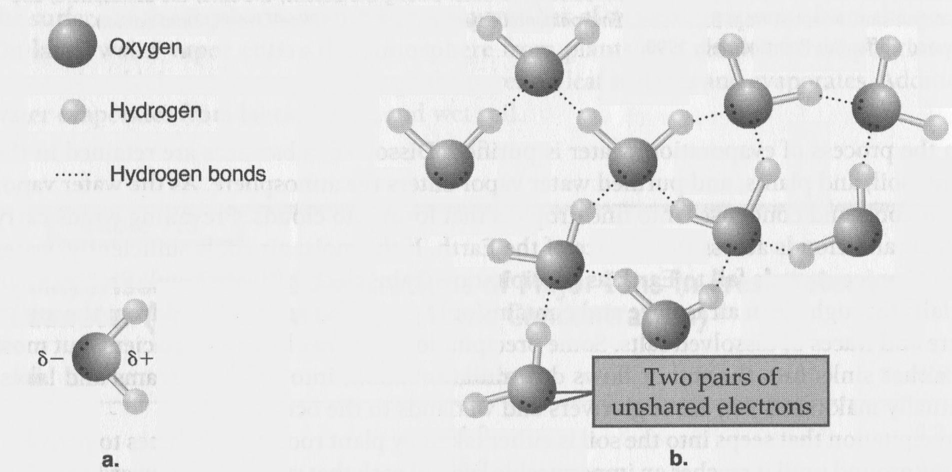

Figure 7.3 Hydrogen bonding in water: (a) Water is an angular polar molecule. Because oxygen is more electronegative that hydrogen, it has a partial negative charge (d–), and the two hydrogen atoms have partial positive charges (d+). (b) The slightly negatively charged oxygen atoms are attracted to the slightly positively charged hydrogen atoms, and hydrogen bonds form between adjacent water molecules. Each oxygen atom has two pairs of unshared electrons and can bond to two hydrogen atoms. Thus, each water molecule can form four hydrogen bonds.

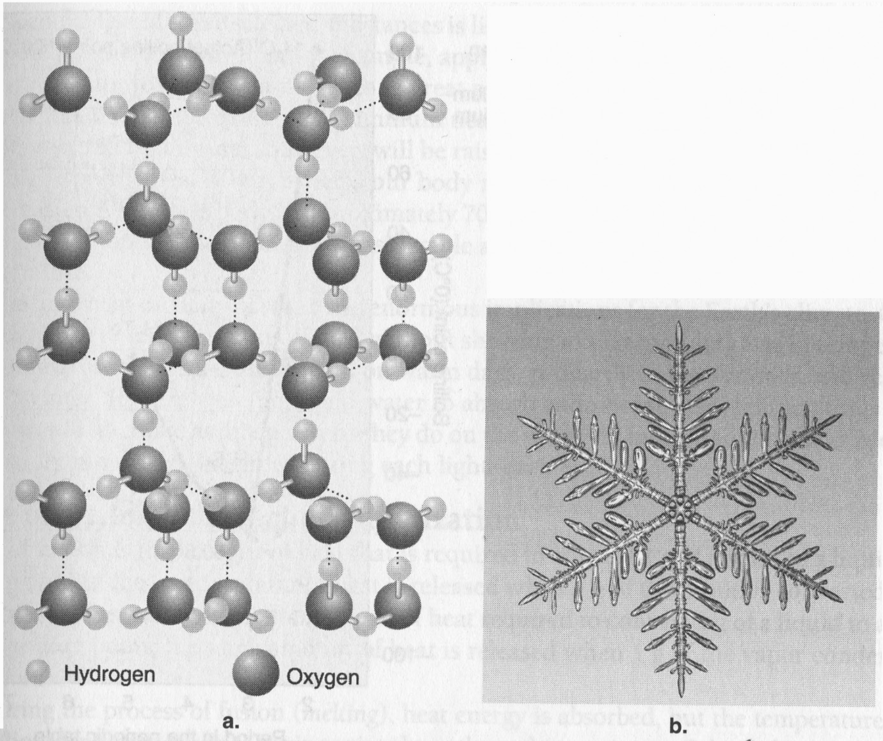

Figure 7.4 (a) In the well-ordered three dimensional structure of ice, each water molecule is hydrogen bonded to four other water molecules. (b) The ordered arrangement of water molecules in ice accounts for the intricate hexagonal shapes of snowflakes.

molecule, which determines how close adjacent molecules can be. As a result, adjacent water molecules in ice are not as close to each other as they can be in liquid water. Thus, ice is less dense than water and floats. The ordered arrangement of atoms in ice accounts for the symmetry of ice crystals in snowflakes (Figure 7.4b).

Boiling Point and Melting Point

Compared with hydrogen compounds of other elements in group VIA (16) of the periodic table (H_2S, H_2Se, and H_2Te), water (H_2O) has an unexpectedly high boiling point (Figure 7.5). Normally, boiling points in a series of compounds of elements in the same group increase regularly with increasing molecular weight; this occurs for H_2S, H_2Se, and H_2Te. The hydrogen bonding that water molecules engage in causes the unexpectedly high boiling point of H_2O; the molecules of other hydrogen compounds in group VIA elements do not hydrogen bond to any significant extent. When water is converted to vapor, additional energy in the form of heat is required to break the hydrogen bonds; consequently, water's boiling point is higher than would be expected. If water boiled at the predicted temperature of –80°C (–112°F), it would be a gas at the temperatures found on Earth, and life as we know it would not be possible.

Water also has an exceptionally high melting point because of the large quantity of heat energy required to break its hydrogen bonds. When ice melts, approximately 15% of its hydrogen bonds are broken. The three-dimensional lattice structure collapses, and water forms.

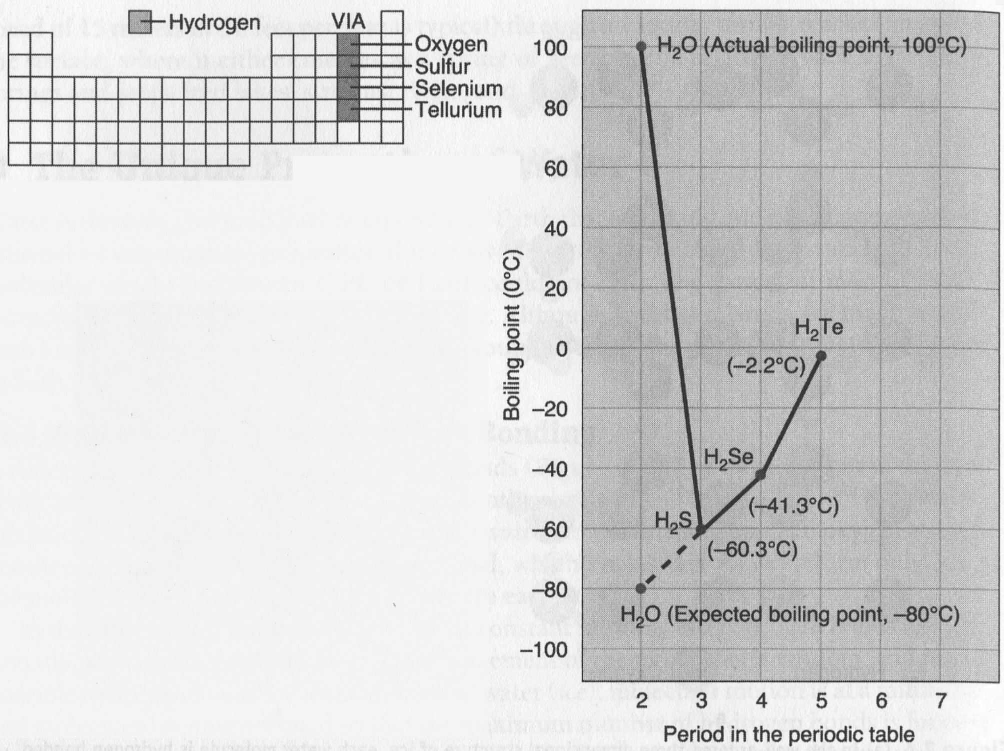

Figure 7.5 With the exception of oxygen, the boiling points of the hydrogen compounds of the Group VIA elements increase regularly going down the group. The unexpectedly high boiling point of water is due to hydrogen bonding, which occurs in H_2O but not to any extent in H_2S, H_2Se, and H_2Te.

Heat Capacity

Heat capacity is the quantity of heat that is required to raise the temperature of a given mass of substance by 1°C. It takes 1 calorie of heat to raise the temperature of 1 g of liquid water by 1°C. Water has the highest heat capacity of any common liquid or solid. From the definition of heat capacity, it follows that the higher the heat capacity of a substance, the less its temperature will rise when it absorbs a given amount of heat, and conversely, the less its temperature will fall when the same amount of heat is released from it.

The heat capacity (C) of a substance can be expressed as the ratio $q/\Delta T$, where q is the total heat flow into or out of an object, and ΔT is the temperature change produced. The heat flow equals the heat capacity times the temperature change:

$$q = (C)(\Delta T)$$

The heat capacity for 1 g of a substance is called the **specific heat**. The units of specific heat are Joules/gram C° (J/gC°). If we know the mass of the substance in grams, we can use the specific heat to determine the quantity of heat transferred when the temperature changes in ΔT.

$$q = (\text{grams of substance})(\text{specific heat})(\Delta T)$$

The specific heat of some selected substances is listed in Table 7.4. Water has one of the highest specific heats known. It is, for example, approximately five times as great as that of aluminum and approximately nine times as great as iron. That means that 4.184 J of heat will increase the temperature of 1 g of aluminum nearly 5°C and 1 g of iron more than 9°C. The temperature of 1 g of water, however, will be raised only one degree by this amount of heat. The high specific heat of water helps our body maintain the constant temperature of 37°C much easier. A human's body is approximately 70% water, and because of its high heat capacity, the body can release or absorb considerable amounts of energy with little effect on body temperature.

The high heat capacity of water has enormous implications for the Earth's climate. Oceans can absorb very large amounts of heat without showing a corresponding rise in temperature. The oceans absorb heat from the sun on warm days, primarily in the summer, and release it in the winter. If there were no liquid water to absorb and release heat, temperatures on the Earth would fluctuate as drastically as they do on the waterless moon and the planet Mercury, varying by hundreds of degrees during each light–dark cycle.

Heat of Fusion and Heat of Vaporization

Heat of fusion is the amount of heat that is required to convert 1 g of a solid to a liquid at its melting point; the same amount of heat is released when 1 g of the liquid is converted to the solid. **Heat of vaporization** is the amount of heat required to convert 1 g of a liquid to a vapor at its boiling point; the same amount of heat is released when 1 g of the vapor condenses to its liquid.

During the process of fusion (*melting*), heat energy is absorbed, but the temperature of the solid/liquid mixture does not begin to rise above the melting point until the melting is complete. During the reverse process of freezing, heat energy is released to the surroundings; the temperature does not begin to fall until freezing is complete. Similarly, there is no change in the temperature of a substance during vaporization and condensation until each process is complete. The changes in energy and temperature that occur when water transforms successively from a solid to a liquid and to a gas and then back again are shown diagrammatically in Figure 7.6.

Table 7.4

Specific Heat of Pure Substances

Substance	Specific Heat (J/gC°)
H_2O (l)	4.184
H_2O (s)	2.03
Al (s)	0.89
C	0.71
Fe	0.45
$CaCO_3$ (s)	0.85

l = liquid; s = solid.

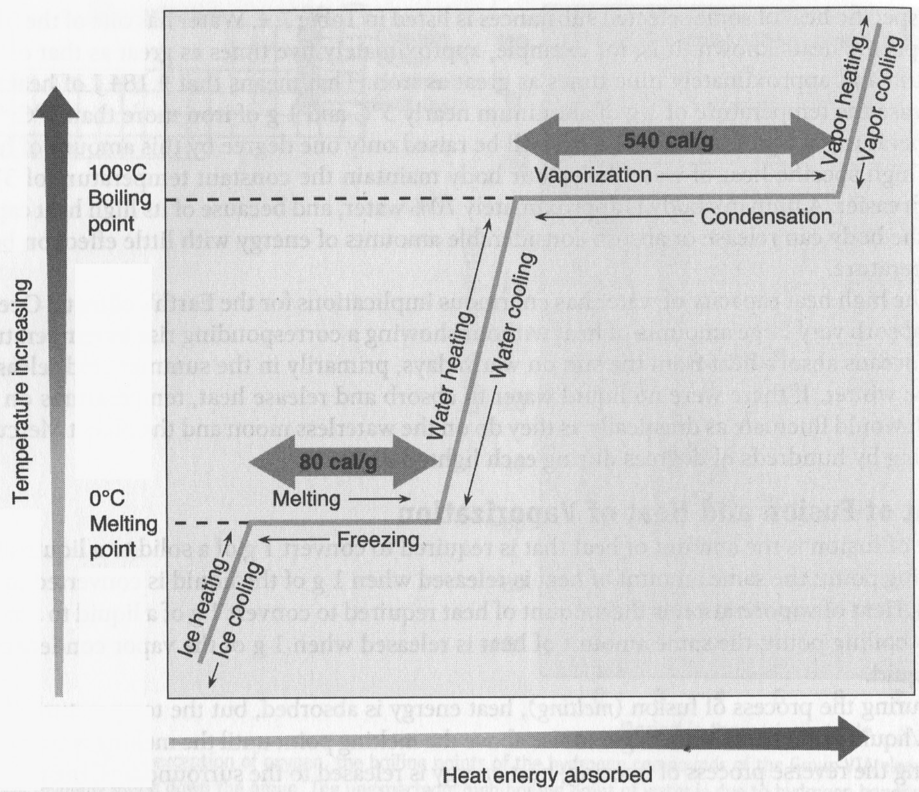

Figure 7.6 Changes in state as water is heated and cooled. There is no change in temperature as water melts, vaporizes, condenses, or freezes until the process has been completed. During melting and vaporization of water 80 and 540 cal/g, respectively, are absorbed; during condensation and freezing, 540 and 80 cal/g, respectively, are released.

Because heat of fusion and heat of vaporization are related to heat capacity, it is not surprising that their values are higher for water than for practically any other substance. Again, the explanation is hydrogen bonding: For ice to melt and water to vaporize, hydrogen bonds must be broken, and breaking them requires a considerable input of energy in the form of heat.

The fact that a relatively large amount of heat is required to evaporate a small volume of water has important consequences. It means that evaporation of a small amount of water (*perspiration*) from the skin can cool the human body efficiently. Extensive water loss from the body, which could upset the internal fluid balance, is thus kept at a minimum.

Anyone who has accidentally put his or her hand in the steam coming from a kettle of boiling water knows how painful the resulting burn can be. As the steam condenses, it releases heat, damaging the skin and causing pain. In contrast, a burn from water at the same temperature (100°C or 212°F) is far less severe.

Water's high heat of vaporization affects Earth's climate. In the summer, water evaporates from the surfaces of oceans and lakes. The heat energy needed for evaporation is drawn from the surroundings, and in consequence, nearby land masses are cooled. On a hot day, land close to a large body of water is always cooler than land farther away from the water. At night, when moist air cools, water vapor condenses, and heat is released; the temperature of the surroundings is raised. In this way, temperature variations between day and night are minimized. A similar modifying effect occurs in winter. When water freezes, heat energy is released, and the surroundings are warmed.

Temperature–Density Relationship

Density is defined as mass per unit volume. We often say that one substance is heavier or lighter than another. What we actually mean is that the two substances have different densities: A particular volume of one substance weighs more or less than the same volume of the other substance.

The density of most liquids increases with decreasing temperature and reaches a maximum at the freezing point, but the density of water does not. When water is cooled, its density reaches a maximum at 4°C—four degrees above the freezing point—and then decreases until the freezing point is reached at 0°C (32°F). The fortunate consequence of this property is that ice floats on the surface of water. This behavior is so familiar that we tend to forget that it is not typical of most liquids. For example, if a piece of solid paraffin is put into a container of liquid paraffin, it sinks to the bottom of the container because it is denser than the liquid (Figure 7.7).

The unusual behavior of ice is the result of the open-lattice structure of hydrogen-bonded molecules that forms when water freezes (see Figure 7.4). As noted earlier, molecules of water are farther apart in ice than in liquid water. As a result, when water starts to freeze, the number of molecules per unit volume (and thus the mass per unit volume or the density) decreases.

Because of the density of water, lakes develop a seasonal pattern. During the summer, lakes develop a three-layer profile. As can be seen in Figure 7.8, the **epilimnion layer** is near the surface. The **metalimnion layer** is the middle layer, and the **hypolimnion layer** is the bottom

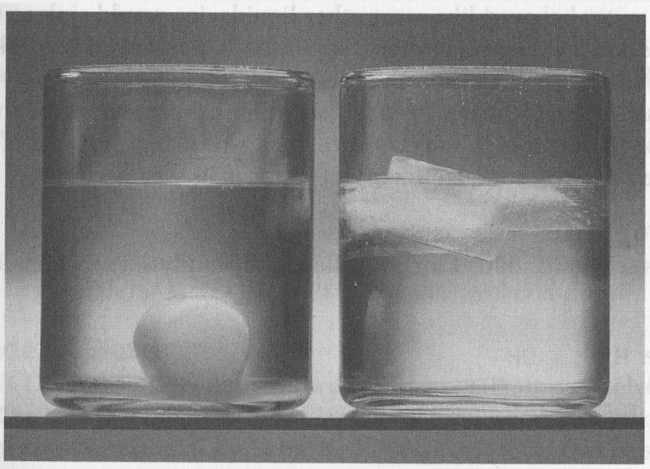

Figure 7.7 Left: A solid piece of paraffin sinks in liquid paraffin. Right: Ice cubes float in water. This behavior of water is exceptional; most chemical compounds behave like paraffin.

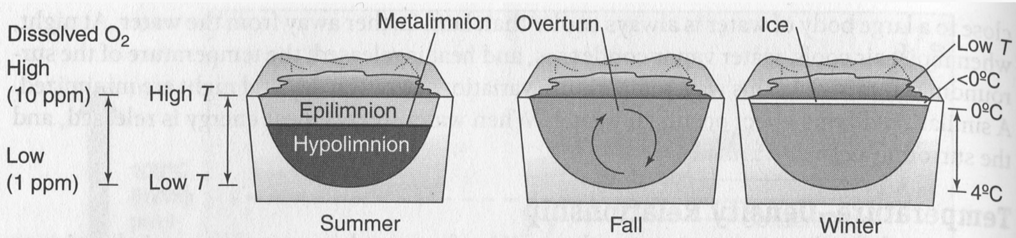

Figure 7.8 Changes in the temperature of air over a lake causes the layers of the lake to mix in a process that is called overturn.

layer. Photosynthesis takes place in the epilimnion as solar radiation penetrates, stimulating algae to produce oxygen. The hypolimnion is relatively dark but is rich in nutrients. Decomposition of organic matter on the bottom consumes oxygen and depletes the dissolved oxygen in the hypolimnion. When the warm season ends and cooling occurs, surface water (epilimnion) becomes denser than the hypolimnion, causing the surface water to sink, carrying with it dissolved oxygen. The deep water (hypolimnion) rises. This mixing process is called **overturn**, and it causes an increase in the chemical and microbiological activity of the lake. Water in the epilimnion, which has a large quantity of dissolved oxygen (10 ppm), drops oxygen to the creatures living deep in the lake. Conversely, water in the hypolimnion, in which the oxygen has been depleted, rises to the epilimnion where it can come in contact with atmospheric oxygen gas at the surface and start to replenish the dissolved oxygen.

The fact that ice is less dense than water has important consequences for aquatic life. When the air temperature falls below freezing in winter, water at the surface of lakes and ponds begins to freeze, and a layer of ice forms and floats on the water below it. The ice covering the surface acts as an insulating layer, reducing heat loss from the water under it. As a result, most lakes and large ponds in temperate climates never freeze to a depth of more than a few feet, and fish and other aquatic organisms are able to survive the winter in the water under the ice. If water behaved like most other liquids, ice would sink to the bottom as it formed, and lakes and ponds would freeze from the bottom up. Even deep lakes would freeze solid in winter, and aquatic life would be killed.

Water's unusual behavior when freezing has other consequences for the environment. When water trapped in cracks in rocks freezes, it expands, and the force of expansion is so powerful that the rock may split, an important factor in its weathering.