CHAPTER 2

WATER'S UNIQUE PROPERTIES

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Case-in-Point

On the evening of 1 August 1986, Lake Nyos in Cameroon, Central Africa, literally exploded, killing 1700 residents of nearby villages. Although Lake Nyos occupies a volcanic crater, the explosion was no volcanic eruption. The cause of the disaster at Lake Nyos has been likened to what happens when the cap is removed from a bottle of carbonated beverage after it has been shaken vigorously.

Lake Nyos is about 2 km (1.3 mi) long, 1.2 km (0.8 mi) wide, and 185 m (610 ft) deep. A chamber of hot molten material (*magma*) some 80 km (50 mi) beneath the lake releases carbon dioxide (CO_2) some of which seeps upward into the lake bottom waters. Carbon dioxide dissolves in lake water much as it does when beverages are carbonated. The maximum amount of CO_2 that can dissolve in water increases with rising pressure (and falling temperature). Water at the bottom of Lake Nyos is under tremendous pressure produced by the weight of the overlying water. Every 10 m (33 ft) of water exerts a pressure equivalent to the average air pressure at sea level. At the bottom of Lake Nyos, the pressure was more than 18 times the usual air pressure at sea level. Under these conditions, the bottom waters of Lake Nyos could absorb a tremendous amount of dissolved CO_2 (perhaps 5 times the maximum per unit volume in a typical carbonated beverage).

Culminating a steady long-term input of CO_2, sometime prior to August 1986 the bottom waters of Lake Nyos became saturated with carbon dioxide—they could hold no more. A short-term jolt, perhaps a landslide or minor earthquake, caused a drop in pressure and triggered a catastrophic release of CO_2 from the saturated lake waters, producing a fountain of foaming water that rose nearly 90 m (300 ft) into the air above the lake surface. A cloud of freshly released CO_2, denser than air, spread along the ground and into low-lying villages surrounding the lake. Carbon dioxide concentration was well above the threshold for human toxicity and most victims died from asphyxiation.

Driving Question:

How do water's unique properties influence the functioning of the Earth system?

Water, an abundant and important component of the Earth system, is the central focus of this book. Although water is a very common substance, it has some very uncommon properties compared to substances of similar molecular size (or chemical composition). Water's unusually high freezing and boiling temperatures, coupled with the usual variations in temperature near Earth's surface, mean that water coexists on Earth in all three phases, as solid (ice), liquid, and gas (water vapor). Furthermore, water frequently changes phase and during these transitions, unusually large amounts of heat energy are either absorbed from the environment or released to the environment. The uniqueness of these and other properties of water (i.e., high specific heat) is derived from its molecular structure and the influence of hydrogen bonding.

In this chapter we examine water's unique properties, the fundamental reasons for those properties, and some of the implications for the functioning of the Earth system. We return to water's unique properties in subsequent chapters as we examine the flow of water and energy in the global water cycle.

Phases of Water

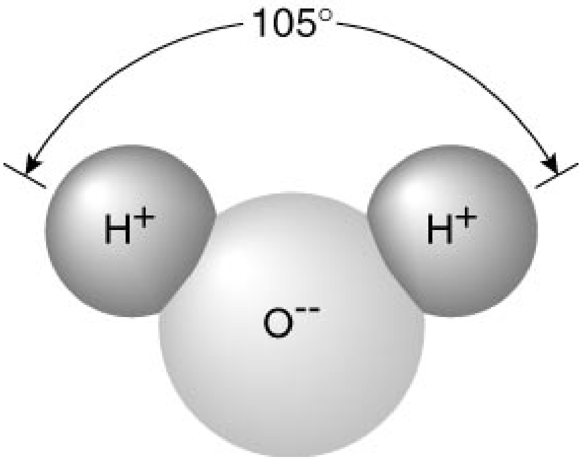


FIGURE 2.1
The water molecule is comprised of two hydrogen atoms and one oxygen atom.

The water molecule (H_2O) consists of two hydrogen (H) atoms bonded to an oxygen (O) atom (Figure 2.1). This chemical bonding is relatively strong so that the water molecule resists decomposition. In the atmosphere, for example, only very intense solar radiation at high altitudes can break a water molecule into its constituent atoms. Water is the only component of the Earth system that occurs naturally in all three phases, as solid (ice or snow), liquid, and gas (water vapor). The type and amount of molecular activity distinguish the phases of water. When water changes phase, its level of molecular activity either increases or decreases depending on the type of phase change.

In the solid phase, ice is crystalline and water molecules vibrate about fixed locations within a crystal lattice (Figure 2.2). (A *crystal lattice* is a 3-dimensional framework consisting of a repeated pattern of atoms or molecules.) For this reason an ice cube or any other piece of ice retains its shape. The ordered arrangement of water molecules in the crystal lattice is responsible for the hexagonal (six-sided) structure of ice crystals. Also, the open structure of the ice lattice explains why the density of ice is about 90% of the density of liquid water so that ice floats in water.

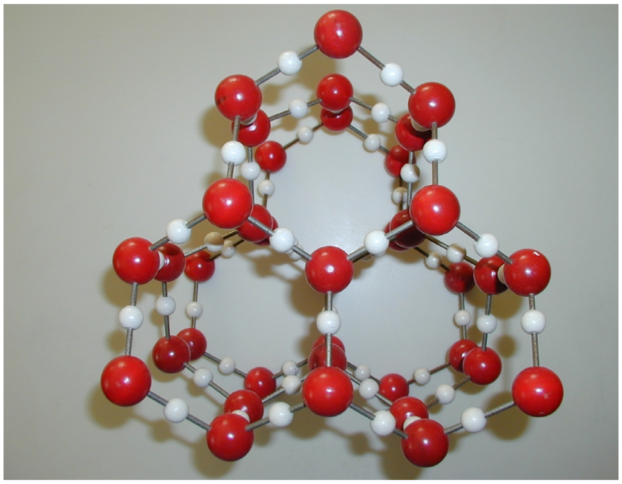


FIGURE 2.2

Crystal lattice of ice.

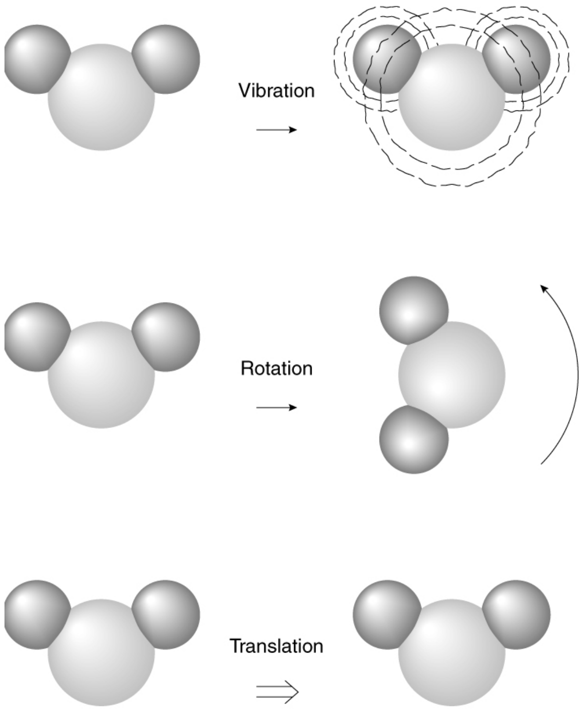


FIGURE 2.3
Vibrational, rotational, and translational motion of the water molecule.

Research published in the mid-1990s confirmed earlier speculation that an ice crystal is not uniformly rigid, and this finding may explain why ice is slippery. Apparently the outermost layer of water molecules in an ice crystal is much more mobile (molecules vibrate faster) than the inner molecules. While still bonded to the crystal lattice as a solid, the outermost molecules are more disordered and behave more like a liquid. This outermost layer of molecules can be thought of as a surface film that reduces the frictional resistance of ice making it slippery. It is widely but *erroneously* believed that objects such as ice skates readily glide across an ice surface because of pressure-induced melting; that is, pressure exerted on the ice suppresses the melting point of ice and a thin film of water forms on which an object slides. The surface becomes slippery because liquid water offers less frictional resistance than ice. Actual measurements demonstrate that the magnitude of the applied pressure is insufficient to lower the melting point enough to account for the slipperiness of an ice surface (unless the ice is already at a temperature very close to melting).

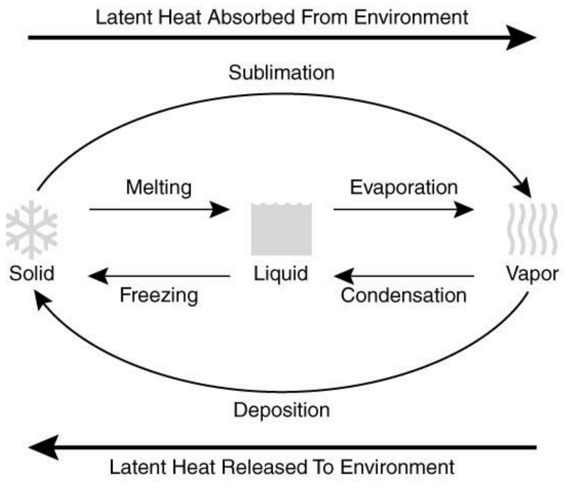


FIGURE 2.4
Heat is either absorbed from or released to the environment when water changes phase.

Water molecules exhibit much greater activity in the liquid phase than in the solid phase. In the liquid phase, water molecules exhibit vibrational, rotational, and translational motions as illustrated in Figure 2.3. This greater freedom of movement explains why liquid water takes the shape of its container. In the vapor phase, water molecules have maximum freedom of movement and disperse randomly into an empty space or gaseous environment by translation. Water vapor introduced into a room quickly spreads throughout the room's entire volume.

Water readily changes phase, contributing to the dynamic nature of the Earth system. When water changes phase heat is either absorbed from the environment or released to the environment (Figure 2.4). Melting, evaporation, and sublimation are phase changes that absorb heat. Phase changes that release heat to the surroundings are freezing, condensation, and deposition. Before examining these phase changes in detail, we need to review the distinction between heat and temperature.

TEMPERATURE AND HEAT

From everyday experience, we know that temperature and heat are closely related concepts. Heating a pan of soup on the stove raises the temperature of the soup and dropping an ice cube into a warm beverage lowers the temperature of the beverage.

Although sometimes used interchangeably, temperature and heat are distinctly different concepts.

All matter is composed of atoms or molecules that are in continual vibrational, rotational, and/or translational motion. The energy represented by this motion is referred to as kinetic molecular energy or just *kinetic energy*, the energy of motion. In any substance, atoms or molecules actually move about with a range of kinetic energy. **Temperature** is directly proportional to the *average* kinetic energy of atoms or molecules composing a substance. At the same temperature, one liter of water has the same average kinetic molecular energy as five liters of water.

Internal energy encompasses all the energy in a substance, that is, the kinetic energy of atoms and molecules plus the potential energy arising from forces between atoms or molecules. If two objects are at different temperatures (different average kinetic molecular energies) and are brought into contact, energy will be transferred between the two objects; we call this energy in transfer, **heat**. Heat transferred from an object reduces the internal energy of that object whereas heat absorbed by an object increases its internal energy. Heat transferred to or from water brings about a change in temperature or phase.

Differences in temperature rather than differences in internal energy govern the direction of heat transfer. Heat energy is always transferred from a warmer object to a colder object. Heat is not necessarily transferred from an object having greater internal energy to an object with less internal energy. Consider a hot marble (at 40 ^{o}C) that is dropped into 5 liters of cold water (at 5 ^{o}C). The water has much more internal energy than the marble, but heat is transferred from the warmer marble to the cooler water.

The following illustration makes clearer the distinction between heat and temperature. A cup of water at 60 ^{o}C (140 ^{o}F) is much hotter than a bathtub of water at 30 ^{o}C (86 ^{o}F). That is, the average kinetic molecular energy of water molecules is greater at 60 ^{o}C than at 30 ^{o}C. Although lower in temperature, the greater volume of water in the bathtub means that it contains more total kinetic molecular energy than does the cup of water. If in both cases the water is warmer than its environment, energy (i.e., heat) is transferred from water to its surroundings. Much more heat energy must be removed from the bathtub water than from the cup of water for both to cool to the same temperature. Hence, the cup of hot water will cool down to room temperature much faster than the water in the bathtub.

Through the years, scientists have devised various scales that express the temperature of an object by a number representing the degree of warmth. Temperature scales were originally derived using the freezing and boiling points of water as fixed points of reference. Eighteenth century scientists who developed temperature scales used water for this purpose because it was readily available and inexpensive. In this book we use the Celsius temperature scale primarily with the Fahrenheit equivalent in parentheses. The Celsius scale, devised by the Swedish astronomer Anders Celsius in 1742, has the numerical convenience of a 100-degree increment between the melting point of ice (0 ^{o}C) and the boiling point of fresh water at average sea level air pressure (100 ^{o}C). The United States is one of only a few nations still using the Fahrenheit temperature scale, introduced by the German physicist Gabriel Fahrenheit in 1714. The Fahrenheit temperature scale features a 180-degree increment between the melting point of ice (32 ^{o}F) and the boiling point of fresh water at average sea level air pressure (212 ^{o}F).

On the Kelvin scale, temperature is the number of kelvins above *absolute zero* (a theoretical point where all molecular motion ceases and no radiation is emitted). Absolute zero corresponds to –273.15 ^{o}C and –459.67 ^{o}F). Nothing can be colder than absolute zero, so the Kelvin scale has no negative temperatures. Formulas for converting among the Celsius, Fahrenheit, and Kelvin temperature scales are given in Table 2.1.

A convenient unit of heat energy is the *calorie*, defined as the amount of heat needed to raise the temperature of 1 gram of water 1 Celsius degree (technically, from 14.5 ^{o}C to 15.5 ^{o}C). (The calorie used to measure the energy content of food is actually 1000 heat calories or 1 kilocalorie.) Although the preferred unit of energy in any form, including heat, is the *joule (J)*, we generally use the *calorie* (cal) in this book

TABLE 2.1
Temperature conversion formulas

$^{o}F = 9/5\ ^{o}C + 32\ ^{o}$
$^{o}C = 5/9\ (^{o}F - 32\ ^{o})$
$K = 5/9\ (^{o}F + 459.67)$
$K = ^{o}C + 273.15$

because of its numerical convenience. Furthermore, thermal characteristics of water were used to define the calorie. For conversion purposes, one calorie equals 4.1868 J and one joule equals 0.239 cal.

FREEZING AND MELTING

Fresh water cooled to 0 °C (32 °F) and subjected to additional loss of heat energy normally will freeze. A mixture of fresh water and ice has an equilibrium temperature of 0 °C (32 °F). Adding heat to the mixture (warming) causes ice to melt, whereas removing heat (cooling) causes water to freeze. For that reason, 0 °C is called the freezing point of fresh water. As discussed in Chapter 5, cloud droplets can cool well below the usual freezing point while remaining liquid. Such cloud droplets are composed of *supercooled water*. Supercooled water droplets are common components of certain types of clouds and fog. Additionally, substances dissolved in water suppress the equilibrium temperature of a mixture of ice and water to temperatures below the freezing point of fresh water.

The freezing point of seawater varies with **salinity**, a measure of the mass (grams) of dissolved salts in a kilogram of seawater. The original unit of salinity was *parts per thousand (‰)*. At first, salinity was determined by evaporating seawater and weighing the residual, and in later years by chemical analysis (i.e., titration). Today, salinity is based on measurements of electrical conductivity of seawater and the standard unit of salinity is the *practical salinity unit (psu)*. Numerically, one psu is essentially equivalent to 1.0 part per thousand. Seawater's freezing point at a salinity of 30 psu is –1.627 °C and –2.196 °C at a salinity of 40 psu. For seawater of average salinity (35 psu), the freezing point is –1.9 °C.

When water freezes, **latent heat** is released to the environment and for ice to melt an equivalent amount of latent heat is absorbed from the environment (Figure 2.4). The term *latent* means hidden—a reference to the fact that this heat energy is used only to change the phase of water and not the temperature of the water. If heat is added to a mixture of ice and water at 0 °C (32 °F), the ice-water mixture remains at constant temperature until all the ice melts. All available heat is used to bring about phase change. Whether freezing or melting is taking place, the latent heat involved is commonly called **latent heat of fusion**.

Growers sometimes take advantage of the latent heat released when water freezes to protect their crops from potential frost-damage during cold weather. Growers spray their plants with a fine water mist when the environmental temperature drops to 0 °C and lower. Mist freezes on the surface of leaves, fruits, and vegetables. Someone might question how a coating of ice could possibly help plants survive subfreezing air temperatures. As long as ice is actually forming, plant surfaces will remain at 0 °C because the latent heat released during water's phase change from liquid to solid helps keep the temperature of the plants from dropping below 0 °C. Stabilization of the temperature at or near 0 °C often prevents crop damage because the actively growing tissues of most crop species are not injured unless their internal temperature drops to between –5 °C and -1 °C (23 °F and 30 °F). Nonetheless, this freeze-prevention strategy requires careful monitoring. As long as sprinkling and freezing continue, the temperature of the ice remains at about 0 °C. If sprinkling were discontinued before the air temperature climbs to melting temperatures, then heat is conducted from the plant to the ice and leaf temperatures fall to potentially lethal levels. Also, care must be taken that the ice burden does not become so great that plants are damaged by excessive weight of the ice. For this reason, the sprinkling method is best suited to protecting low-growing crops such as cucumbers, strawberries, and cranberries, although sprinkling is also used in citrus groves.

VAPORIZATION AND CONDENSATION

At the interface between liquid water and air (e.g., lake or sea surface), water molecules continually change phase: some crossing the interface from water to air and others from air to water. If more water molecules enter the atmosphere as vapor than return as liquid, a net loss occurs in liquid water mass. This process is known as **evaporation**. Evaporation explains the drying of soil and disappearance of puddles following a rain shower. On the other hand, if more water molecules return to the water surface as a liquid than escape as vapor, net gain of liquid water mass results. This process is called **condensation**. Water vapor condenses on the cold surface of an aluminum beverage can on a humid summer day. Heat is absorbed from the environment during evaporation and released to the environment during condensation (Figure 2.4). Heat absorbed or released during these phase changes is known as the **latent heat of vaporization** (or condensation).

All of us have experienced evaporative cooling. We are chilled upon stepping out of a shower or swimming pool. Water droplets evaporate from the skin surface and absorb heat, lowering the skin's temperature. The human body uses evaporative cooling to guard against an unhealthy rise in the temperature of vital organs (e.g., heart, lungs) during hot and humid weather (Chapter 4). We perspire and the evaporation of tiny beads of sweat cools the skin. On a global scale, evaporative cooling is the most important process whereby heat at Earth's surface is transferred to the atmosphere (Chapter 10). When water evaporates at Earth's surface, water vapor moves into the atmosphere where it subsequently may condense into clouds. Heat that was absorbed in the evaporation of water at the surface is later released to the atmosphere during condensation. This heat transfer mechanism is very important in powering storms, especially tropical storms and hurricanes.

Whereas melting or freezing in an ice/water mixture occurs at a specific temperature (0 ^{o}C for fresh water), evaporation of water can occur at any temperature. The latent heat of fusion is 80 calories (335 J) per gram at 0 ^{o}C (lower for supercooled water). The latent heat of vaporization varies with temperature from 597 calories (2500 J) per gram at 0 ^{o}C (32 ^{o}F) to 540 calories (2260 J) per gram at 100 ^{o}C (212 ^{o}F).

SUBLIMATION AND DEPOSITION

At the interface between ice and air (e.g., the surface of a snow cover), water molecules are also continually changing phase: directly from ice to vapor and from vapor to ice. If more water molecules enter the atmosphere as vapor than make the transition to ice, a net loss of ice mass occurs. **Sublimation** is the process whereby ice or snow becomes vapor without first becoming a liquid. Sublimation explains the gradual disappearance of a snow cover even though the air temperature remains well below freezing. On the other hand, if more atmospheric water molecules transition to ice than move from ice to vapor, a net gain of ice mass results. **Deposition** is the process whereby water vapor becomes ice without first becoming a liquid. During a cold winter night, the formation of frost on automobile windows is an example of deposition.

Heat is absorbed from the environment during sublimation and heat is released to the environment during deposition (Figure 2.4). Latent heat involved in sublimation or deposition must equal the total amount of heat absorbed or released during the combined solid-liquid plus liquid-vapor phase changes. Sublimation requires the latent heats of fusion plus vaporization, known as the **latent heat of sublimation**. Deposition releases to the environment an equivalent amount of latent heat, that is, the **latent heat of deposition**. The magnitude of the latent heats of sublimation and deposition are remarkably uniform, varying only from 677 calories (2835 J) per gram at 0 ^{o}C to 678 calories (2839 J) per gram at –30 ^{o}C.

Why is Water so Unique?

Compared to other naturally occurring substances, water's thermal properties are unique. For one, water's freezing and boiling points are exceptionally high. Based only on water's molecular weight and the freezing and boiling temperatures of chemically related substances, fresh water should freeze at about –90 ^{o}C (-130 ^{o}F) and boil at about –68 ^{o}C (-90 ^{o}F). Actually, fresh water's freezing point is 0 ^{o}C (32 ^{o}F) and its boiling point is 100 ^{o}C (212 ^{o}F) at average sea level pressure. The unusually high values of water's freezing and boiling temperatures permit water to occur naturally in all three phases in the Earth system (Figure 2.5). Furthermore, an unusually great quantity of heat energy is involved when water changes phase, and a relatively large amount of heat is needed to change the temperature of water. All of these unique thermal properties of water have important implications for the functioning of the Earth system.

Why does water exhibit these unusual thermal properties? Ultimately, the answer lies in the structure of the water molecule. Within the water molecule, bonding between hydrogen and oxygen atoms involves sharing of two electrons, one from each hydrogen atom and another from the oxygen atom. (An *electron* is a negatively charged subatomic particle.) The oxygen atom has a stronger attraction for the shared electrons than do the hydrogen atoms so that the oxygen acquires a small negative charge and the hydrogen is left with a small positive charge. The 105-degree angle formed by the arrangement of the hydrogen-oxygen-hydrogen atoms produces a charge separation in the water molecule

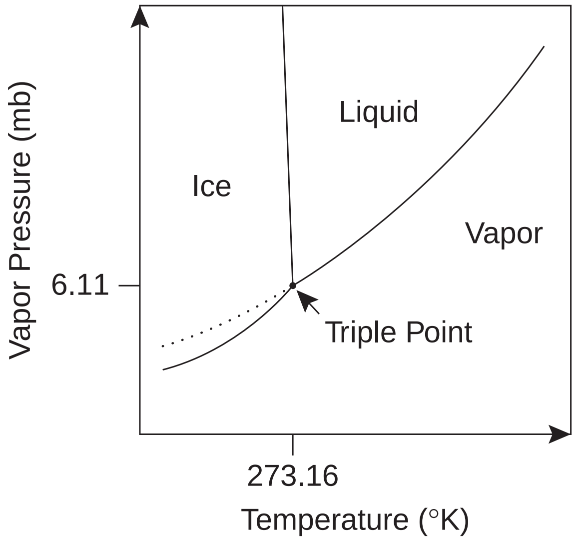


FIGURE 2.5
Phase diagram of water. At the triple point, water exists simultaneously as a solid, liquid, and vapor.

(Figure 2.1). Molecules having a separation of positive and negative charges are described as *dipolar*.

Opposite electrical charges attract so that, like tiny magnets, neighboring dipolar water molecules link together. The positively charged (hydrogen) pole of one water molecule attracts the negatively charged (oxygen) pole of another water molecule; this special attractive force is known as **hydrogen bonding**. Hydrogen bonding is roughly 10 to 50 times weaker than the bonds between the hydrogen and oxygen atoms in individual water molecules. Each water molecule can form hydrogen bonds in three directions because the molecule has three potential sites for hydrogen bonding.

Hydrogen bonding inhibits changes in the internal energy of individual water molecules. As heat is transferred to or from water, the accompanying change in internal energy is unusually small. Recall from earlier in this chapter that temperature is proportional to average kinetic molecular energy, part of the internal energy of a substance. Addition or removal of heat from a volume of water is accompanied by relatively little change in water temperature; that is, the *specific heat* of water is relatively high (discussed below). In addition, greater amounts of heat, and unusually high temperatures are required for water to reach its melting and boiling points. Hydrogen bonding also means that exceptionally large amounts of heat energy are needed to change the phase of water.

In a general sense, for any substance to change phase from solid to liquid or liquid to gas, heat energy must be supplied to break intermolecular forces of attraction. *Van der Waals force* is the relatively weak electrostatic attraction between the atomic nuclei of one molecule and the electrons of another molecule. Van der Waals forces are stronger in the solid and liquid phases (when molecules are closest together). In the case of water, a change in phase from solid (ice or snow) to liquid or from liquid to vapor, requires an addition of heat energy in amounts sufficient to overcome not only van der Waals forces but also the much stronger hydrogen bonds. For this reason, water has unusually great latent heat requirements.

For water to change from solid (ice or snow) to liquid, heat energy must be supplied to break some of the hydrogen bonds that maintain water in the crystalline (solid) phase (Figure 2.2). This heat is the *latent heat of fusion*, discussed above. Not all hydrogen bonds are broken as water changes from solid to liquid; that is, numerous small clusters of bonded water molecules persist into the liquid phase. Considerably greater amounts of heat are required for water to vaporize (by either evaporating or boiling) because essentially all hydrogen bonds must be broken. For this reason, the magnitude of water’s *latent heat of vaporization* is more than seven times the magnitude of water’s latent heat of fusion. When phase changes are reversed, that is when water vapor changes to liquid (or solid) or liquid changes to ice, unusually large quantities of latent heat are released to the environment.

In summary, in the solid and liquid phases, dipolar water molecules are linked by hydrogen bonds. Hydrogen bonding inhibits changes in the internal energy of water so that water requires or releases unusually great quantities of heat when changing phase. Hydrogen bonding also means that greater additions or losses of heat accompany a change in water temperature as compared to other substances.

Water’s Specific Heat

The temperature change associated with an input (or output) of a specified quantity of heat varies from one substance to another. The amount of heat that will raise the temperature of 1 gram of a substance by 1 Celsius degree is defined as the **specific heat** of that substance. Joseph Black, a Scottish chemist, first proposed the

TABLE 2.2
Specific Heats of Some Familiar Substances

Substance	*Specific Heat (cal per g per Celsius degree)*
Water	1.000
Ice (at 0 ^{o}C)	0.478
Wood	0.420
Aluminum	0.214
Brick	0.200
Granite	0.192
Sand	0.188
Dry air[a]	0.171
Copper	0.093
Silver	0.056
Gold	0.031

[a] At constant volume

concept of specific heat in 1760. The specific heat of all substances is measured relative to that of liquid water, which is defined as 1 calorie per gram per Celsius degree (at 15 ^{o}C). The specific heat of ice is 0.5 calorie per gram per Celsius degree (near 0 ^{o}C). The specific heats of some other familiar substances are listed in Table 2.2. The variation in specific heat from one substance to another implies that different materials have different capacities for storing internal energy.

Upon absorbing the same amount of heat energy, a substance with a high specific heat experiences a smaller increase in temperature (warms less) than a substance having a low specific heat. Because of hydrogen bonding, water has an unusually high specific heat, in fact the highest specific heat of any naturally occurring common substance. From Table 2.2, water's specific heat is about 5 times that of dry sand. One calorie of heat will raise the temperature of one gram of water by 1 Celsius degree whereas one calorie of heat will raise the temperature of one gram of dry sand by 5 Celsius degrees. This contrast in specific heat helps explain why at the beach in summer the sand feels considerably hotter to bare feet than the water. This also largely explains why wet sand feels cooler than dry sand.

Water's unusually high specific and latent heats are illustrated by a simple experiment conducted at sea level (Figure 2.6). A one-gram ice cube initially at –20 ^{o}C (-4 ^{o}F) is heated to 0 ^{o}C (32 ^{o}F). Every 1-Celsius degree (2-Fahrenheit degree) rise in temperature of the ice cube requires an addition of 0.5 calorie of heat energy (*specific heat of ice*). A total of 10 calories of heat (20 C^{o} × 0.5 cal/C^{o}) are required to warm the one-gram ice cube to 0 ^{o}C (32 ^{o}C). Once it reaches 0 ^{o}C (32 ^{o}F), the temperature of the water substance remains constant while 80 calories of heat (*latent heat of fusion*) are added to completely melt the 1-gram ice cube. Liquid water is then heated to 100 ^{o}C (212 ^{o}F). Every 1-Celsius degree (2-Fahrenheit degree) rise in temperature of the 1 gram of liquid water requires an addition of 1.0 calorie of heat energy (*specific heat of water*). Assuming that none of the water evaporates, a total of 100 calories of heat (100 C^{o} × 1.0 cal/C^{o}) are required to warm the one-gram of liquid water to 100 ^{o}C (212 ^{o}F). At 100 ^{o}C, the water vaporizes requiring an input of 540 calories of heat (*latent heat of vaporization*).

Water's relatively great capacity to store internal energy is the reason water is a highly effective cooling agent. Coal-fired and nuclear electric power plants routinely pipe water from lakes and rivers through the facility to absorb and carry off waste heat. Heated water is discharged into the source waterway or evaporated from cooling towers or storage lagoons.

Water's exceptional capacity to store heat also has important implications for weather and climate. A large body of water (such as the ocean or Great Lakes) can significantly influence the climate of downwind localities. The most persistent influence is on air temperature. Compared to an adjacent landmass, a body of water does not warm as much during the day (or in summer) and does not cool as much at night (or in winter). In other words, a body of water exhibits a greater resistance to temperature change, called **thermal inertia**, than does a landmass. Whereas the difference in specific heat between land and water is the major reason for this contrast in thermal inertia, differences in heat transport also contribute. Sunlight penetrates water to some depth and is absorbed (converted to heat) through a significant volume of water. But sunlight cannot penetrate the opaque land surface and is absorbed only at the surface. Furthermore, circulation of ocean and lake-waters transports heat through great volumes of water, whereas heat is conducted only very slowly into soil. The input (or output) of equal amounts of heat energy causes a land surface to warm (or cool) more than the equivalent surface area of a body of water.

Air temperature is regulated to a considerable extent by the temperature of the surface over which air

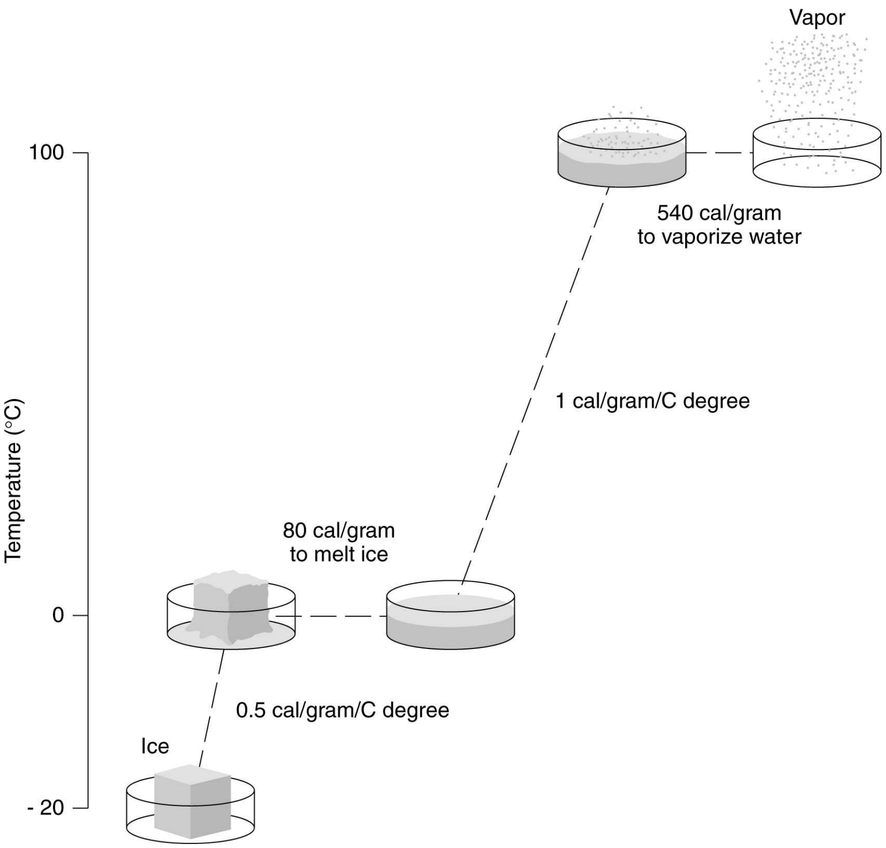


FIGURE 2.6
Heating a 1-gram ice cube causes the ice to change phase.

resides or travels. Air over a large body of water tends to take on similar temperature characteristics as the surface water. Winds blow from sea to land and from land to sea. Places immediately downwind of the ocean experience much less contrast between average winter and summer temperatures and the climate is described as *maritime*. Places at the same latitude but well inland experience a much greater temperature contrast between winter and summer and the climate is described as *continental*.

Consider an example of the contrast between continental and maritime climates. The latitude of Stevens Point, WI (44.5 degrees N) is about the same as that of Newport, OR (44.6 degrees N) so that the seasonal variation in the amount of solar radiation striking Earth's atmosphere (due to astronomical factors) is about the same at both places. Stevens Point is situated far from the moderating influence of the ocean and its climate is continental. Stevens Point's average summer (June, July, August) temperature is 19.9 ^{o}C (67.9 ^{o}F) and its average winter (December, January, February) temperature is -8.2 ^{o}C (17.2 ^{o}F), giving an average summer-to-winter seasonal temperature contrast of 28.1 Celsius degrees (50.7 Fahrenheit degrees). Newport, on the other hand, is located on the Oregon coast, immediately downwind of the Pacific Ocean; its climate is maritime. The average summer temperature at Newport is 13.6 ^{o}C (56.5 ^{o}F) and the average winter temperature is 7.0 ^{o}C (44.6 ^{o}F), giving an average seasonal temperature contrast of only 6.6 Celsius degrees (11.9 Fahrenheit degrees).

The moderating influence of the ocean is also evident in the contrast in climate between Western Europe and Eastern North America. At mid-latitudes, prevailing winds blow from west to east so that the maritime influence of the North Atlantic Ocean is much more apparent in Western Europe than Eastern North America. In the same latitude belt, winters are considerably milder in Western Europe than in Eastern North America. Consider, for example, the contrast in average January temperatures for Montreal, Quebec (45.5 degrees N) versus London, England (51.5 degrees

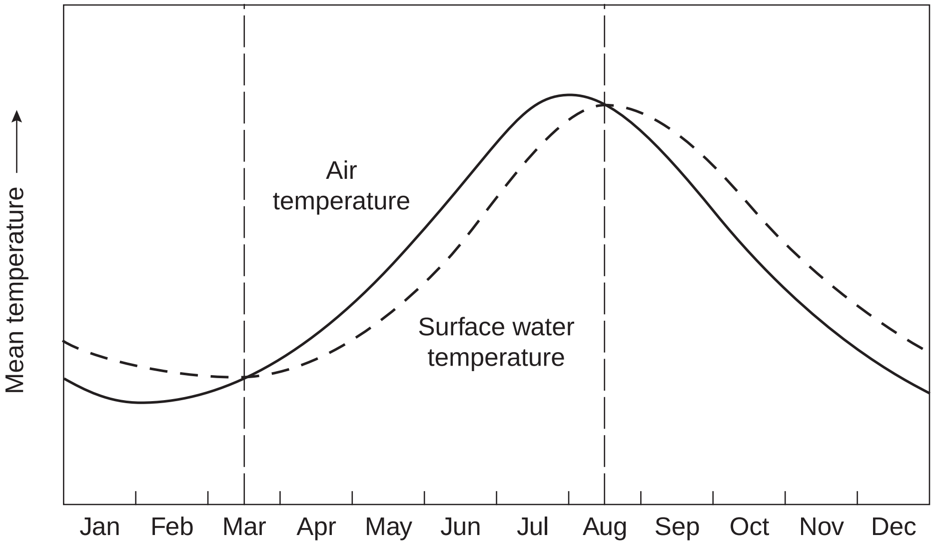


FIGURE 2.7
A schematic drawing of the mean monthly temperature variations of Lake Michigan surface waters and adjacent land areas.

N). In January, the average daily high temperature is -6.1 ^{o}C (21 ^{o}F) at Montreal and 6.7 ^{o}C (44 ^{o}F) in London. The January average daily low temperature is -14.4 ^{o}C (6 ^{o}F) at Montreal and 1.7 ^{o}C (35 ^{o}F) in London. Although London is considerably further north than Montreal, its January temperatures are significantly milder.

The greater thermal inertia of water bodies compared to landmasses is responsible for two distinctive seasonal regimes on the Great Lakes (Figure 2.7). These regimes are based on the average temperature difference between water and land. Lake Michigan’s average surface temperatures are lower than the average air temperature over adjacent land surfaces from about mid-March into early or mid-August, with the greatest temperature contrast usually between mid-May and early June. The relatively cool lake surface chills the overlying warmer air inhibiting the development of convective weather systems such as thunderstorms. Fog forms over the lake when warm humid air streams over the cold water surface and cool onshore lake-breezes often develop during the daytime along the coast.

Lake Michigan’s average surface temperatures are higher than the average surface temperatures of adjacent land areas from about late August into middle or late March. The greatest temperature contrast usually occurs from late November into early December. The relatively warm lake surface heats and supplies water vapor to the overlying cooler air spurring cloud development. At times very cold air streams across the relatively warm lake water surface triggering substantial lake-effect snowfall on the downwind shores.

Water as a Solvent

Pure water is unknown in the Earth system, that is, water free of all dissolved and suspended materials does not occur naturally. This is because water is an excellent solvent (sometimes referred to as the *universal solvent*). The dipolar nature of the water molecule favors the solution of both ionic and non-ionic substances. Many inorganic materials (primarily salts) are bonded ionically, whereas many organic chemicals have non-ionic (covalent) bonds. River water, groundwater, and ocean water dissolve some of the bedrock or sediment (both organic and inorganic) that water contacts. Some Earth materials dissolve in water more readily than other Earth materials. Formation of huge subsurface caverns is dramatic evidence of the ability of groundwater to dissolve limestone ($CaCO_3$).

Consider what happens when a pinch of common household table salt (sodium chloride, NaCl) is added to water. In salt’s crystalline form, ionic bonds hold the positively charged sodium ions (Na^+) and the negatively charged chloride (Cl^-) ions together (Figure 2.8A). (An *ion* is an electrically charged atom or

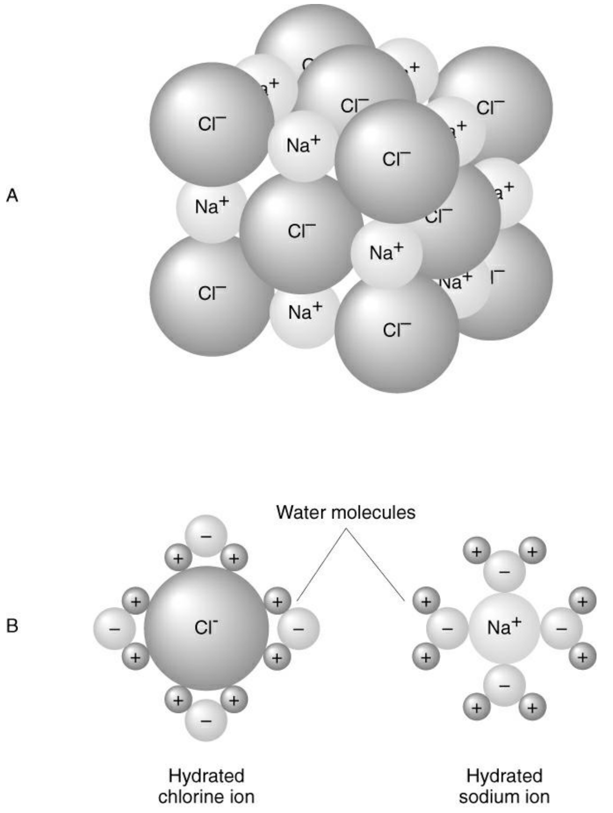


FIGURE 2.8
Dissociation of sodium chloride (table salt) in water.

molecule.) Once in the water, however, the hydrogen-bonded complexes of water molecules greatly reduce the force of attraction between oppositely charged sodium and chloride ions. That is, the strength of ionic bonding between sodium and chloride diminishes so that the compound readily dissociates into sodium and chloride ions (Figure 2.8B). Sodium ions are attracted to the negatively charged pole of the water molecule and chloride ions are attracted to the positively charged pole of the water molecule. That is, salt dissolves in water.

We are well aware from personal experience that solids (such as salt and sugar) dissolve in water. What may be less obvious is that gases also dissolve in water. An example is carbon dioxide (CO_2) dissolved under pressure in a carbonated beverage. When we open a can of cola, for example, tiny bubbles of carbon dioxide escape, giving the drink its fizz. Some of the dissolved CO_2 becomes carbonic acid (H_2CO_3), a weak acid that is responsible for the beverage's tart taste. The most abundant gases dissolved in surface seawater are nitrogen (N_2), oxygen (O_2), and carbon dioxide (CO_2). Gases (and particles) that dissolve in rain can impact the quality of precipitation. Carbonic acid formed by carbon dioxide dissolved in water is important in the chemical disintegration of bedrock (*chemical weathering*). Also, oxygen dissolved in water is essential for the survival of aerobic aquatic life.

ACID DEPOSITION

Rain and snow are normally slightly acidic because they dissolve some atmospheric carbon dioxide, producing weak carbonic acid. Where air is polluted with oxides of sulfur or oxides of nitrogen, however, these gases interact with moisture in the atmosphere to produce tiny droplets of sulfuric acid (H_2SO_4) and nitric acid (HNO_3). These acid droplets dissolve in precipitation, increasing its acidity. Precipitation that falls through such contaminated air may become 200 times more acid than normal. Even in the absence of precipitation, sulfuric acid droplets convert to tiny acid (sulfate) particles that reduce visibility and may cause health problems in humans when inhaled. Acid particles eventually settle to Earth's surface as *dry deposition*. The combination of acid precipitation and dry deposition is known as **acid deposition**.

The **pH scale** encompasses the range of acidity and alkalinity, where pH is a measure of the hydrogen ion (H^+) concentration (Figure 2.9). By definition, pure water has a pH of 7, which is considered neutral; a pH above 7 is increasingly alkaline while a pH below 7 is increasingly acidic. Rain falling through an unpolluted atmosphere dissolves carbon dioxide and has an average pH of 5.6. On this basis, a pH of 5.6 is taken as the threshold for acid precipitation; that is, rain or snow having a pH less than 5.6 is described as **acid rain** (or snow). Small amounts of naturally occurring acids (other than that produced by atmospheric CO_2) lower the normal pH of precipitation closer to 5.0, arguing for a revision of the current criterion for acid rain and snow. The pH scale is logarithmic; that is, each unit increment on the scale corresponds to a tenfold change in acidity or alkalinity. A drop in pH from 5.6 to 3.6, for example, represents a one hundred fold (10×10) increase in acidity.

Gene E. Likens was one of the first scientists to sound the alarm regarding the potential impact of acid rain on the functioning of aquatic ecosystems. Likens and his colleagues reported an increase in the acidity of

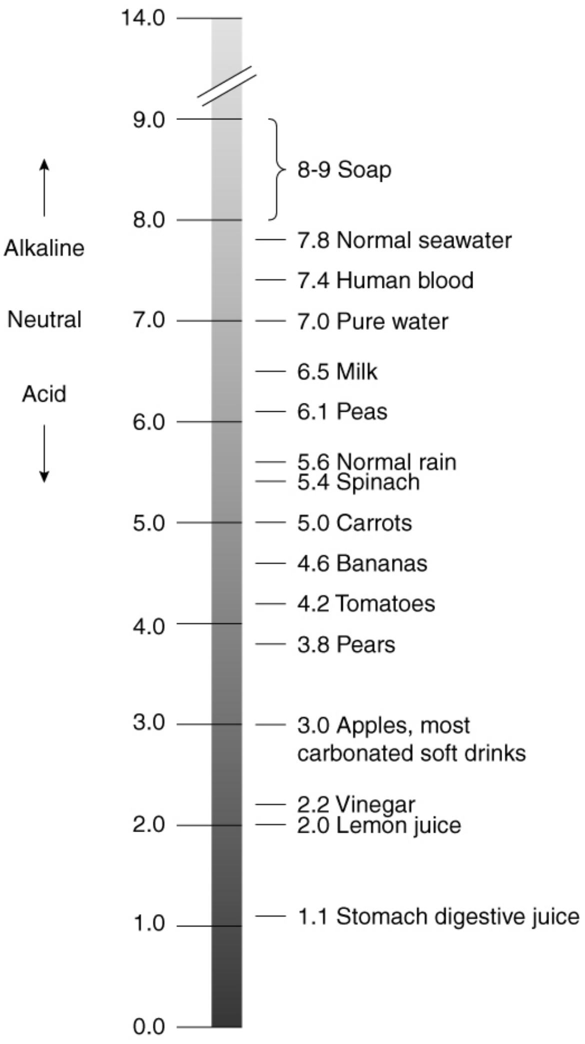


FIGURE 2.9
Scale of acidity and alkalinity (pH scale).

rainfall over portions of the United States between 1955 and 1973. Measurements made by the National Atmospheric Deposition Program in the United States and the Canadian Network for Sampling Precipitation later confirmed and updated Liken's findings. In general, the mean annual pH of precipitation is greater than 5 west of the Mississippi River and less than 5 east of the Mississippi. Rain and snow tend to be most acidic in northeastern United States and adjacent portions of Canada, where average annual pH since 1963 ranges between 4.05 and 4.3, with individual storms having produced rainfall with pH values as low as 2 to 3. In this region, sulfuric acid is suspected to be responsible for 55% to 75% of excess acidity.

Most acid deposition is derived from gases emitted as byproducts of fuel combustion for electric power, industry, and motor vehicles. Coal burning for electric power generation is the principal source of sulfur oxides, whereas high-temperature industrial processes and internal combustion engines (in motor vehicles) produce nitrogen oxides.

Where soils are thin and the bedrock is non-carbonate (does not contain carbonate ions), acid rain and snowmelt are not neutralized and may adversely impact waterways. (*Neutralization* is a chemical reaction between acid and alkaline substances to produce a salt and water, with the pH of the solution approaching 7.) For this reason, acid deposition is potentially a much greater problem where the bedrock consists of granite than where the bedrock is limestone or dolostone. Acid deposition lowers the pH of lakes and streams, disrupting the reproductive cycles of fish. Furthermore, acid rains leach metals (such as aluminum) from the soil, washing them into lakes and streams where they may harm fish, microorganisms, and aquatic plants. Lowered pH is responsible for the decline and even elimination of fish populations in some lakes and streams in Norway, Sweden, eastern Canada, and the northeastern United States.

DISSOLVED OXYGEN

Aquatic organisms, like terrestrial organisms, require oxygen for cellular respiration. Recall from Chapter 1 that *cellular respiration* is the process whereby organisms break down food and release energy in a usable form. Essential for survival of aquatic animals (e.g., fish, shellfish) is **dissolved oxygen (DO)**, oxygen that is dissolved in water. (Note that dissolved oxygen is not the O in the H_2O.) Dissolved oxygen levels in surface waters (i.e., rivers, lakes, ocean) vary considerably depending on water's capacity to dissolve oxygen, factors governing the rate of transfer of oxygen between the atmosphere and the water body, and the supply of organic matter in the water body.

Oxygen (O_2), the second most abundant atmospheric gas, enters an aquatic system through the air-water interface and via photosynthesis by aquatic plants. The maximum amount of oxygen that can dissolve in water (saturation concentration) depends on temperature. Oxygen and most other gases are more soluble in cold water than warm water. As shown in Figure 2.10, at saturation the amount of dissolved oxygen

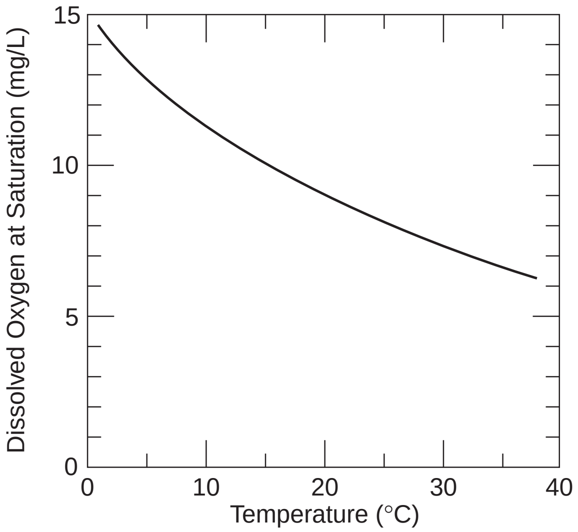


FIGURE 2.10
Variation in the saturation concentration of dissolved oxygen with water temperature.

declines from about 15 milligrams per liter at 0 °C (32 °F) to less than 7 milligrams per liter at 35 °C (95 °F). All other factors being equal, we would expect less dissolved oxygen in water bodies in summer than in the cooler seasons. On the other hand, in cold-climate regions, winter ice cover on lakes is a barrier to oxygen transfer and results in lower dissolved oxygen levels.

Turbulence in waterfalls, river rapids, and dam spillways as well as waves on the surface of open bodies of water enhance oxygen transfer from air to water (unless the water is already saturated with oxygen). The cross-sectional profile of a waterway also affects oxygen transfer. A wide, shallow stretch of a river presents a larger surface area for oxygen uptake than does a narrow, deep segment. Furthermore, the amount of oxygen produced per unit area by photosynthesis depends on the density of aquatic plants. (Recall from Chapter 1 that *photosynthesis* is the process whereby green plants use sunlight, water and carbon dioxide to manufacture their food and generate oxygen as a byproduct.)

Dissolved oxygen is removed from water primarily through cellular respiration by decomposer organisms. *Decomposers* are microorganisms, primarily bacteria and fungi, that consume the remains of dead plants and animals as a food source. Fish, shellfish, and zooplankton remove smaller amounts of dissolved oxygen through cellular respiration. Warm water enhances decomposer activity, increasing the rate at which they remove dissolved oxygen through cellular respiration.

The amount of organic waste available to decomposers also affects the level of dissolved oxygen in aquatic systems. In most natural waterways, the supply of organic waste is relatively small and the concentration of dissolved oxygen usually remains relatively constant at more than 5 milligrams per liter, the minimum level considered essential for survival of the most sensitive fish, such as trout. When saturated with oxygen, natural waters typically contain between 10 and 14 milligrams of dissolved oxygen per liter. Industrial and municipal wastewater, however, usually contain relatively high concentrations of organic waste and when dumped into a waterway may cause serious depletion of dissolved oxygen. Abundant organic waste spurs the growth of decomposer populations, which consume large quantities of dissolved oxygen. Many aquatic organisms, including the more desirable species of fish, cannot tolerate the resulting low levels of dissolved oxygen.

The amount of dissolved oxygen that decomposers require to break down organic waste in a given volume of water is known as **biochemical oxygen demand (BOD)**. A major source of BOD is human waste. Sewage entering a treatment plant typically has a BOD level of about 100 to 200 milligrams per liter. That water is likely to contain only a few milligrams of dissolved oxygen per liter so that microbial decomposition of sewage quickly depletes the water's supply of dissolved oxygen. Decomposition of the daily waste produced by one person requires all the dissolved oxygen in about 9000 liters (2200 gal) of water. Water used for processing organic materials such as paper, vegetables, and meat also acquires substantial levels of BOD. Some concentrated industrial wastewater has BOD levels that exceed by one thousand times the BOD levels in sewage water. Another source of high-level BOD waste is runoff from livestock feedlots. Runoff from farmland where animal waste is spread on fields is also BOD-rich.

At mid latitudes, discharge of organic waste has its greatest negative impact on aquatic life during warm summer months. At that time of year stream flow is often relatively low so that organic waste is less diluted. Also, as pointed out earlier, oxygen is less soluble in warm water and decomposers have higher metabolic rates (and greater oxygen demand) at higher water temperatures.

What is the impact of changing dissolved oxygen levels on aquatic life? Consider an example. Suppose a discharge pipe delivers substantial amounts of organic waste to a river. Upstream from the pipe, the river water is oxygen-rich and supports a variety of fish, shellfish, and other organisms. Fishing is fine. Immediately downstream from the pipe, bacteria (decomposers) begin to consume the organic waste. Bacterial populations grow rapidly in direct proportion to the concentration of organic matter, and soon they are removing dissolved oxygen at a faster pace than it is naturally replenished (from the atmosphere and via photosynthesis). Dissolved oxygen levels may decline to levels that can support only species of rough fish (e.g., carp, gar, and catfish), which tolerate relatively low dissolved oxygen levels. Fishing is less than desirable. As the organic waste flows downstream, however, decomposers consume more of the waste and as the amount of organic waste declines, BOD levels also decrease. Oxygen transfer from the atmosphere plus photosynthesis slowly reduces the dissolved oxygen deficit. Eventually the rate of oxygen replacement exceeds the rate of removal and dissolved oxygen gradually returns to what it was upstream of the discharge pipe. With restoration of oxygen-rich aquatic conditions, a diverse and desirable community of fish thrives.

Aquatic systems are resilient and gradually recover from inputs of organic waste. On occasion, however, a single BOD discharge is so great that decomposer populations increase to the point that they remove all the dissolved oxygen from the water. Such a drastic shift from an *aerobic environment* (with oxygen) to an *anaerobic environment* (without oxygen) triggers major changes in species composition. Aerobic decomposers (microorganisms that require oxygen) are replaced by anaerobic decomposers (those that cannot tolerate oxygen). Furthermore, the byproducts of aerobic and anaerobic decay are distinctly different. Decay products of aerobic decomposers are mainly carbon dioxide (CO_2), water, nitrate (NO_3^-), and sulfate (SO_4^{2-}), which are not usually harmful. On the other hand, some of the decay products produced by anaerobic decomposers are potentially dangerous to humans and other species. Products of anaerobic decay include methane (CH_4) which is potentially explosive when mixed with oxygen, hydrogen sulfide (H_2S), which is recognized by its rotten-egg odor, and ammonia (NH_3). Surface waters that develop anaerobic conditions become a putrid, turbid, decaying mess, in stark contrast to the inviting oxygen-rich waters teaming with aquatic life.

Water Density and Temperature

Density is defined as mass per unit volume, usually expressed as grams per cubic centimeter. Objects placed in water that are less dense than water will float to the surface and materials that are denser than water will sink. Fresh water density varies primarily with temperature whereas seawater density varies chiefly with temperature and salinity. Water is essentially incompressible so that pressure arising from the weight of water does not significantly impact its density.

FRESH WATER

Most substances contract when cooled and expand when heated; that is, their density increases with falling temperature and decreases with rising temperature. As the average kinetic molecular energy of a substance decreases (i.e., as the temperature falls), the same number of molecules occupy a progressively smaller volume. However, for fresh water, the situation is not quite that simple (Figure 2.11). As the temperature of fresh water falls steadily from say 25 °C (77 °F), the water contracts and its density increases. Fresh water density reaches a maximum at about 4 °C (39.2 °F) and, with additional cooling (below 4 °C), the water expands (its density decreases).

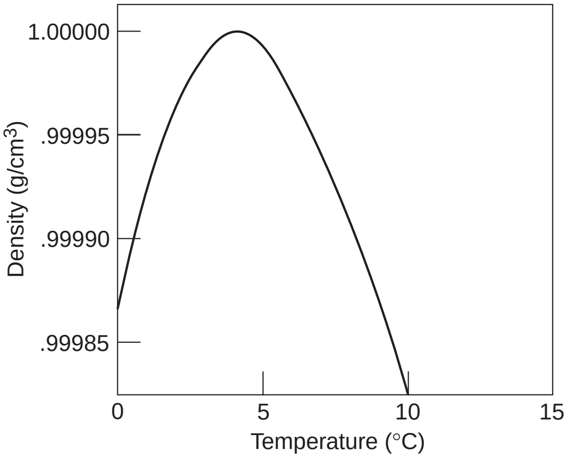


FIGURE 2.11
Variation in the density of fresh water with temperature.

An increasing number of ice-like molecular clusters that continually form and break-up in the liquid is responsible for the anomalous behavior of fresh water density at temperatures below 4 °C. These clusters occupy more volume than the unorganized water molecules in the liquid. Recall that ice crystals are open hexagonal (six-sided) structures with widely spaced water molecules (Figure 2.2). As the water temperature falls from 4 °C, the decrease in water density caused by the presence of ice-like molecular clusters more than offsets the increase in water density that accompanies a reduction in kinetic molecular activity.

Whereas most liquids contract when they solidify, ice expands so that the density of ice is about 90% of liquid water. (This expansion has some interesting consequences as anyone who has had frozen water pipes can attest.) As water freezes, its molecules chemically bond into an open hexagonal crystalline structure and its density drops dramatically. The unique temperature-density behavior of fresh water explains why less dense ice floats in more dense water and lakes freeze from the top down rather than the bottom up. If ice were denser than liquid water, ice that forms at the air-water interface would sink and in winter lakes in cold climates would freeze solid from the bottom up, destroying all aquatic life.

In autumn, lakes begin cooling at the air-water interface when the temperature of the overlying air falls below that of lake surface. Lake-surface water cools and contracts, reaching maximum density at 4 °C, and sinks to the bottom. This process of surface cooling and sinking is repeated until the entire lake has a uniform temperature of 4 °C (and uniform density). With further cooling of surface waters, water density decreases and at 0 °C an ice cover begins to form. Once ice forms, it contracts (becomes denser) as its temperature falls. But no matter how cold it is, ice remains less dense than liquid water.

As described in this chapter's Essay, the temperature-density relationship of fresh water also plays an important role in the spring and fall turnover of mid-latitude lakes. Lake turnover is necessary for replenishment of dissolved oxygen in lake waters.

SEAWATER

At constant temperature, the density of seawater increases with increasing salinity because the atomic mass of dissolved salts is greater than that of water molecules. Hence, less dense fresh water floats on more dense seawater. The salinity of seawater also affects the temperature of maximum density and the freezing temperature for the same reason: adding dissolved materials such as salt apparently interferes with the formation of ice-like clusters. As shown in Figure 2.12, the temperature of maximum density decreases linearly

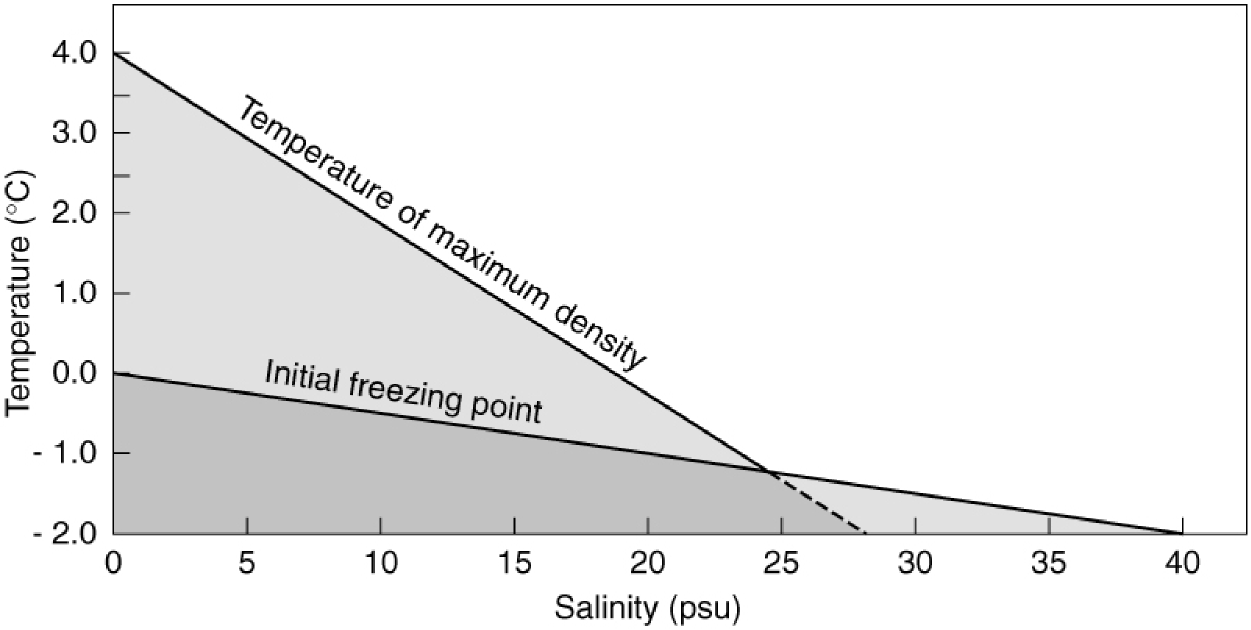


FIGURE 2.12
Variation in water's temperature of maximum density versus salinity (in psu).

with increasing salinity. At any salinity less than 24.7 psu, the maximum density of water occurs at a temperature above the freezing point (which also decreases linearly with increasing salinity). At a salinity of 24.7 psu, the temperature of maximum density is the same as the freezing temperature (–1.33 ^{o}C). At any salinity greater than 24.7 psu, the maximum-density temperature is lower than water's freezing point. The density of seawater of average salinity (35 psu) varies inversely with temperature; that is seawater density always increases with falling temperature and decreases with rising temperature.

Freezing of seawater affects the salinity of surrounding water. During the freezing process, dissolved substances are largely excluded from the crystalline structure of growing ice, and are concentrated in the surrounding surface water, lowering its freezing point and increasing its density. Even small amounts of seawater that is trapped between crystals in the developing ice mass eventually migrate downward (toward higher temperature) to the sea. Sea ice therefore freshens with time.

As we will see in Chapter 8, differences in the density of seawater, caused mainly by variations in temperature and salinity, are very important controls of the vertical circulation of ocean water. Denser seawater sinks and less dense seawater rises.

Water's Surface Tension

Water can fill a container to a level that is slightly higher than the rim, forming a convex surface (Figure 2.13). Individual raindrops hold together as they strike the soil surface making them more effective weathering agents. An insect known as a water strider literally walks on water. And a soap bubble forms a nearly perfect sphere. All these phenomena are the consequence of water's strong surface tension.

Surface tension, the attraction between molecules at or near the surface of a liquid that acts to reduce the surface area, is another property of water arising from hydrogen bonding. The density of water molecules in the air above the water surface is relatively low so that water molecules in the surface layer are more strongly attracted (by hydrogen bonding) to each other and to the layer of molecules immediately below. In fact, among liquids water is second only to mercury in the strength of its surface tension.

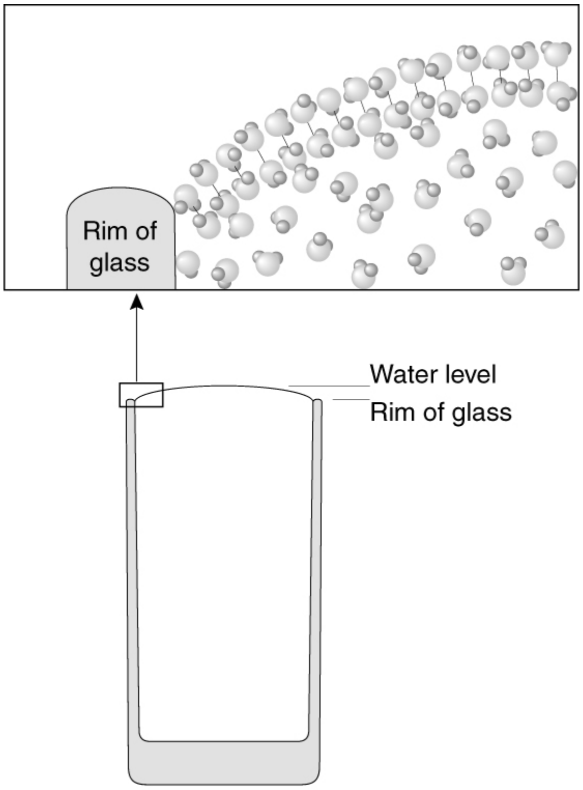


FIGURE 2.13
Surface tension allows water to fill a container slightly higher than its rim.

Water adheres to the surface of many different materials including glass, soil, and rock. Consider, for example, water partially filling a narrow glass tube. Water climbs up the sides of the glass tube until the forces of adhesion to the tube balance the weight of the water in the tube. The water forms a concave surface because the adhesive forces at the water-glass interface are stronger than the attractive forces among molecules at the center of the tube. This phenomenon is called *capillarity*. Capillary behavior is common in soil, sediment or rock where groundwater rises above the water table through tiny openings and fissures (Chapter 6).

Conclusions

Water is a common ingredient of the Earth system with very unusual properties. Most of these properties arise from the structure of the water molecule and hydrogen bonding. Water's capacity to absorb large quantities of heat has important implications for climate, contributing to the moderating influence of the ocean and large lakes on the average temperature of downwind localities. Water is referred to as the *universal solvent* because it readily dissolves inorganic and organic solids so that chemically pure water does not occur in nature. Water also dissolves gases; in fact, dissolved oxygen is essential for the survival of most aquatic organisms. The density of water varies with temperature and the amount of dissolved materials (salinity). The maximum density of fresh water occurs at about 4 Celsius degrees above its freezing point so that freshwater lakes freeze from the top down. Another unique property of water is its unusually strong surface tension—an additional consequence of hydrogen bonding.

In subsequent chapters, we will revisit the unusual properties of water as we examine the role of water in the functioning of the Earth system. We begin our study of water in the Earth system by investigating the global water cycle in the next chapter.

Basic Understandings

- Water is the only common constituent of the Earth system that occurs naturally in all three phases, as solid (ice or snow), liquid, and vapor at or near Earth's surface. These three phases are distinguished by level of kinetic-molecular activity.
- Water continually changes phase. Melting, evaporation, and sublimation absorb heat from the environment whereas freezing, condensation, and deposition release heat to the environment.
- Temperature is directly proportional to the average kinetic energy of the atoms or molecules composing a substance. Heat is the name given to the energy transferred from a warmer object to a colder object.
- The freezing point of fresh water is 0 ^{o}C. Dissolved salts suppress the freezing point of seawater by about 1.5 to 2 Celsius degrees depending on salinity. Latent heat in the amount of 80 calories (335 J) per gram is released to the environment when water freezes at 0 ^{o}C and the same amount is absorbed from the environment when ice melts. This is called the latent heat of fusion.
- Heat absorbed during evaporation or released during condensation is known as the latent heat of vaporization (or condensation). Evaporation can occur at any temperature that water exists as a liquid and requires an input of 597 calories (2500 J) per gram at 0 ^{o}C to 540 calories (2260 J) per gram at 100 ^{o}C. The latent heat of vaporization is greater than the latent heat of fusion because all hydrogen bonds must be broken in the phase change from liquid to vapor.
- Water's unique thermal properties stem from its molecular structure. The water molecule is dipolar; that is, its oxygen atom acquires a small negative charge and its hydrogen atoms have a small positive charge. Opposite charges attract so water molecules link together with the positively charged hydrogen of one water molecule attracting the negatively charged oxygen of a neighboring water molecule. This attraction between neighboring water molecules is known as hydrogen bonding.
- Hydrogen bonding inhibits changes in the internal energy of water molecules and thereby explains water's unusually high freezing and boiling points, latent heats of fusion and vaporization, and specific heat. Hydrogen bonding is also responsible for water's excellent dissolving properties.
- Water's unusually high specific heat has important implications for weather and climate. Compared to an adjacent landmass, a water body does not warm as much in summer or during the day and does not cool as much in winter or at night. The moderating influence of the ocean on air temperature is felt in the maritime climates of downwind localities. In places having a maritime climate winters are milder and summers are cooler than at places in the same latitude belt having a continental climate.
- Water is an excellent solvent, dissolving both solids and gases. Salts readily dissociate into ions when they enter water. Some gases and solids that dissolve in rain or snow may turn precipitation excessively acidic.
- Oxygen dissolved in surface waters is essential for aquatic life. Oxygen enters water directly from the atmosphere and as a byproduct of photosynthesis. Turbulence of the water, the surface area of a waterway, temperature, and density of photosynthetic organisms govern the input of

dissolved oxygen. Dissolved oxygen is removed from water via cellular respiration. An excessive load of organic waste can seriously deplete the supply of dissolved oxygen and stress or even eliminate aquatic life.

- The maximum density of fresh water occurs at a temperature of about 4 ^oC and water density decreases with further cooling. Ice, being less dense than water, floats and lakes freeze from the top down. The freezing point of seawater lowers with increasing salinity, and the temperature of water's maximum density also drops with increasing salinity.
- Hydrogen bonding also accounts for water's exceptionally strong surface tension. Surface tension explains why water can fill a vessel to slightly above its rim and the capillary movement of water.

ESSAY: Lake Turnover

The unusual way water density varies with temperature plays an important role in the autumn and spring turnover of freshwater lakes in temperate latitudes. Lake turnover is important for organisms living in lakes because this process replenishes the dissolved oxygen supply of those water bodies. Bright summer sun penetrates a lake to shallow depths, warming the surface layer of water. Meanwhile, the dark deep water does not benefit from solar heating and remains cold, with an average temperature perhaps as low as 4 ^{o}C. This stable stratification (layering) of warmer, less dense surface water and colder, denser water at depth persists through most of the summer, with little mixing between the two layers. The upper layer of the stratified lake is known as the *epilimnion* and the lower layer is known as the *hypolimnion*, with the transition zone between the two layers called the *thermocline*. The thermocline features a rapid drop in temperature with depth.

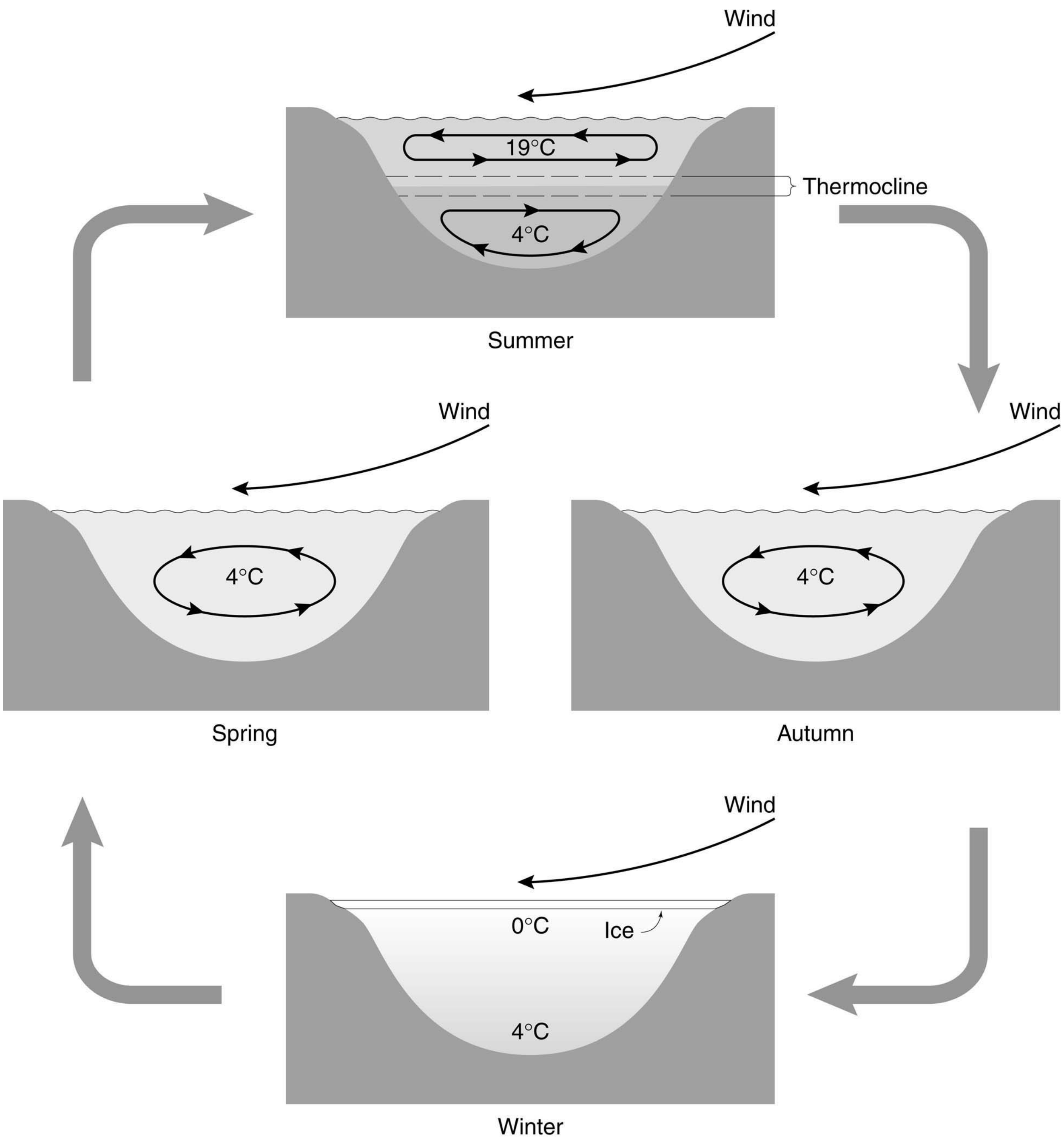
In a stratified lake, oxygen that is supplied by the atmosphere and photosynthesis replenishes the dissolved oxygen supply of only the epilimnion. In the hypolimnion, cellular respiration by decomposers and other organisms remove dissolved oxygen. Without transfer of oxygen from the epilimnion, dissolved oxygen levels in the hypolimnion steadily diminish. If lake stratification were to persist, the dissolved oxygen concentration could decline to a level that would severely stress cold-water fish species (e.g., trout, whitefish) living in the hypolimnion. Fortunately, these fish and other inhabitants of the hypolimnion usually do not die because the lake stratification eventually breaks down and the dissolved oxygen content of the hypolimnion is replenished.

As summer gives way to autumn, the sun is lower in the sky, daylight becomes shorter, and air temperatures drop. Heat is lost from the warm surface waters to the overlying cool air and space. Eventually the temperature of the epilimnion cools to that of the hypolimnion, the thermocline disappears, and the lake has a uniform temperature and density from top to bottom. Winds blowing across the lake transport surface water from the upwind shore toward the downwind shore. Oxygen-depleted water wells up from below on the upwind shore and oxygen-rich surface water sinks at the downwind shore (see Figure). *Fall turnover* of lake-waters brings oxygen-depleted water from the lake bottom to the surface where it is exposed to the atmosphere and replenished in dissolved oxygen.

Cooling during late autumn and early winter eventually drops the surface water temperature to 4 ^{o}C and lower. The lake begins to stratify with the coldest and least dense water at the surface. With continued cooling, the surface water temperature drops to 0 ^{o}C and a skim of ice forms on the lake surface. In the Northern U.S. and Canada, lakes are ice-covered for at least part of the winter and the ice may thicken to tens of centimeters depending on winter air temperatures. Lake-water temperature typically varies from 0 ^{o}C just under the ice to 4 ^{o}C at the lake bottom. Ice forms a barrier that prevents exchange of oxygen between the lake-water and atmosphere, and biological processes within the lake (e.g., cellular respiration) cause a gradual decline in dissolved oxygen levels. By the time the ice finally melts in spring, the lake waters may be seriously depleted of dissolved oxygen.

With the arrival of spring, days get warmer and surface waters warm. Eventually, the temperature of the surface water reaches 4 ^{o}C and once again the temperature and density of the lake become uniform from top to bottom. Just as in autumn, strong winds trigger turnover of lake waters and the mixing that accompanies *spring turnover* brings oxygen-depleted water to the surface where oxygen is replenished directly from the atmosphere and via photosynthesis. As spring gives way to summer, lake stratification is reestablished.

In mid latitudes, fall and spring turnovers are essential for re-supplying the dissolved oxygen content of lake-bottom waters and permit the survival of cold-water species. Lake turnovers also play an important role in recycling nutrients, especially nitrogen and phosphorus compounds, from bottom sediments to the overlying water, where they become available to aquatic plants, especially algae. However, in tropical climates surface water temperatures may never drop as low as 4 ^{o}C and the seasonal variation in air temperature is minimal so that lake-turnover is a rare event. This is one of the reasons why such a tremendous amount of carbon dioxide was able to build up in the bottom waters of Lake Nyos, as described in this chapter's Case-in-Point.



ESSAY FIGURE
Turnover of mid latitude lakes in spring and fall replenishes the supply of dissolved oxygen in bottom waters.