

The jagged underwater edge of a pinnacled iceberg broke the hull of the “unsinkable” White Star liner RMS *Titanic* on the night of 14 April 1912; 1,517 people lost their lives. The iceberg had reached the Atlantic shipping lanes after separating from its glacier, being swept down the west coast of Greenland, and then moving south toward the Gulf Stream and North Atlantic Current.

6.1

## CHAPTER AT A GLANCE

### The Water Molecule

#### Water and Heat

Heat Capacity

Water Temperature and Density

Freezing Water

Evaporating Water

#### Global Thermostatic Effects

#### The Density Structure of the Ocean

The Pycnocline

The Thermocline

The Halocline

#### Refraction, Light, and Sound

Light in the Ocean

Sound in the Ocean

The Sofar Layer

Sonar

### The Dissolving Power of Water

#### Seawater

Salinity: Dissolved Solids and Water Together

The Source of the Ocean's Salts

The Principle of Constant Proportions

Determining Salinity

Chemical Equilibrium and Residence Times

Mixing Time

#### Dissolved Gases

Nitrogen

Oxygen

Carbon Dioxide (CO<sub>2</sub>)

#### Acid-Base Balance

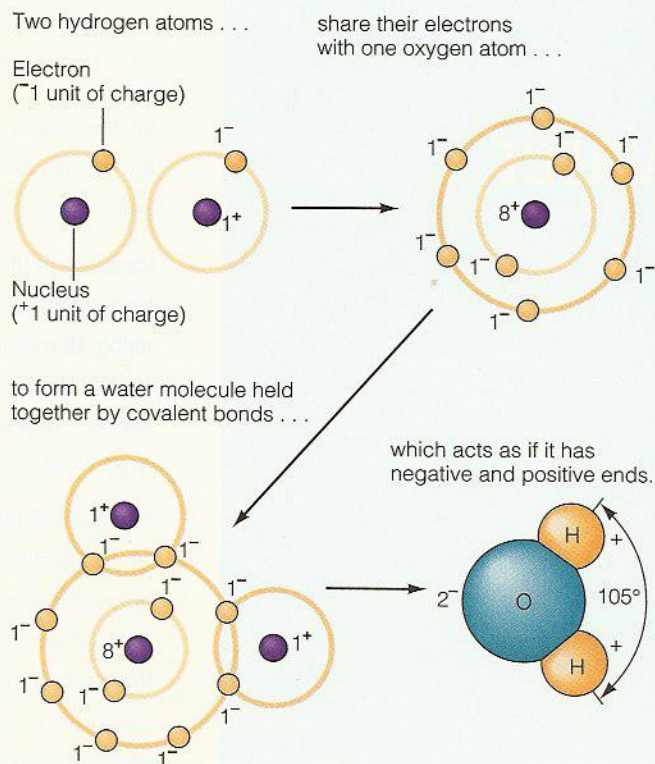
# The Water Molecule

6.2

As you may recall from Chapter 2, most of Earth's surface waters are thought to have escaped from the crust and mantle through the process of outgassing. Outgassing of substances other than water, and water's ability to dissolve crustal material, have added salts and other solids and gases to the ocean. In this chapter we will investigate the structure of pure water and discuss some of water's physical and chemical properties and the implications of these properties for the ocean and Earth as a whole.

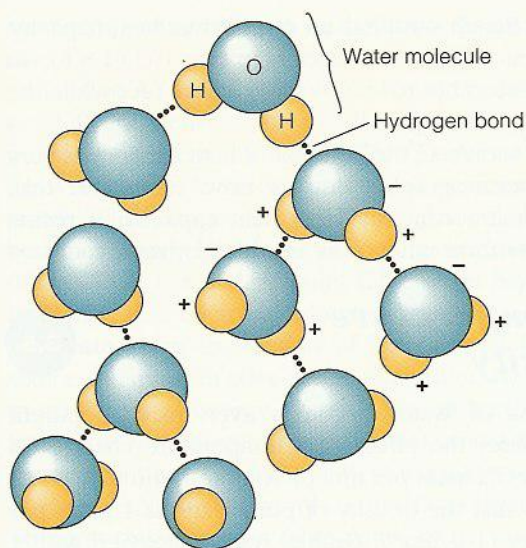
Water is a molecule. A **molecule** is a group of atoms held together by chemical bonds. **Chemical bonds**, the energy relationships between atoms that hold them together, are formed when **electrons**—tiny negatively charged particles found toward the outside of an atom—are shared between atoms or moved from one atom to another. A water molecule forms when electrons are shared between two hydrogen atoms and one oxygen atom. The bonds formed by shared pairs of electrons are known as **covalent bonds**. Covalent bonds hold together many familiar molecules, including CO<sub>2</sub>, CH<sub>4</sub> (methane gas), and O<sub>2</sub> (atmospheric oxygen). Because of the way a water molecule's oxygen electrons are distributed, the overall geometry of the molecule is a bent or angular shape. The angle formed by the two hydrogen atoms and the central oxygen atom is about 105°. The formation of a water molecule is depicted in **Figure 6.1**.

The angular shape of the water molecule makes it electrically asymmetrical, or **polar**. Each water molecule can be thought of as having a positive (+) end and a negative (−)



**Figure 6.1** The formation of a water molecule.





**Figure 6.2** Hydrogen bonds in liquid water. The attractions between adjacent polar water molecules form a webwork of hydrogen bonds. These bonds are responsible for cohesion and adhesion, the properties of water that cause surface tension and wetting. Hydrogen bonds between water molecules also make it difficult for individual molecules to escape from the surface.

end. This is because **protons**—positively charged particles at the center of the hydrogen atoms—are left partially exposed when the negatively charged electrons bond more closely to oxygen. The polar water molecule acts something like a magnet; its positive end attracts particles that have a negative charge, and its negative end attracts particles that have a positive charge. When water comes in contact with compounds whose elements are held together by the attraction of opposite electrical charges (most salts, for example), the polar water molecule will separate that compound's component elements from each other. This explains why water can easily dissolve so many other compounds.

The polar nature of water also permits it to attract other water molecules. When a hydrogen atom (the positive end) in one water molecule is attracted to the oxygen atom (the negative end) of an adjacent water molecule, a **hydrogen bond** forms. The water molecules are bonded together by electrostatic forces. The resulting loosely held webwork of water molecules is shown in **Figure 6.2**. Hydrogen bonds greatly influence the properties of water by allowing individual water molecules to stick to each other, a property called **cohesion**. Cohesion gives water an unusually high surface tension, which results in a surface “skin” capable of supporting needles, razor blades, and even walking insects.

Water is a polar chemical compound composed of two hydrogen atoms and one oxygen atom. Many of water's remarkable properties result from the large number and relatively great strength of hydrogen bonds between water molecules.

**Adhesion**, the tendency of water to stick to other materials, enables water to adhere to solids—that is, to make them wet. Cohesion and adhesion are the causes of capillary action, the tendency of water to spread through a towel when one corner is dipped in water.

## Water and Heat

6.3

Heat and temperature are not the same thing. **Heat** is energy produced by the random vibration of atoms or molecules. On the average, water molecules in hot water vibrate more rapidly than water molecules in cold water. Heat is a measure of *how many* molecules are vibrating and *how rapidly* they are vibrating. Temperature records only *how rapidly* the molecules of a substance are vibrating. **Temperature** is an object's response to an input (or removal) of heat. The amount of heat required to bring a substance to a certain temperature varies with the nature of that substance.

An example will help. Which has a higher temperature: a candle flame or a bathtub of hot water? The flame. Which contains more heat? The tub. The molecules in the flame vibrate very rapidly, but there are relatively few of them. The molecules of water in the tub vibrate more slowly, but there are a great many of them, so the total amount of heat energy in the tub is greater.

Temperature is measured in **degrees**. One degree Celsius ( $^{\circ}\text{C}$ ) = 1.8 degrees Fahrenheit ( $^{\circ}\text{F}$ ). Though we are more familiar with the older Fahrenheit scale, Celsius degrees are more useful in science because they are based on two of pure water's most significant properties: its freezing point ( $0^{\circ}\text{C}$ ) and its boiling point ( $100^{\circ}\text{C}$ ).

Heat and temperature are not the same thing. *Heat* is a measure of how many molecules of a substance are vibrating and how rapidly they are vibrating. *Temperature* records only how rapidly the molecules of a substance are vibrating.

## Heat Capacity

6.4

**Heat capacity** is a measure of the heat required to raise the temperature of 1 gram (0.035 ounce) of a substance by  $1^{\circ}\text{C}$  ( $1.8^{\circ}\text{F}$ ). Different substances have different heat capacities. *Not all substances respond to identical inputs of heat by rising in temperature the same number of degrees (Table 6.1).* Heat capacity is measured in calories per gram. A **calorie** is the amount of heat required to raise the temperature of 1 gram (0.035 ounce) of pure water by  $1^{\circ}\text{C}$ .<sup>1</sup>

The heat capacity of water is among the highest of all known substances, so water can absorb (or release) large

<sup>1</sup> A nutritional Calorie, the unit we see on food labels, equals 1,000 of these calories. A gram is about ten drops of seawater.



Table 6.1 Heat Capacity of Common Substances

Substance	Heat Capacity <sup>a</sup> in calories/gram/°C
Silver	0.06
Granite	0.20
Aluminum	0.22
Alcohol (ethyl)	0.30
Gasoline	0.50
Acetone	0.51
<b>Pure water</b>	<b>1.00</b>
Ammonia (liquid)	1.13

<sup>a</sup>Heat capacity is a measure of the heat required to raise the temperature of 1 gram (0.035 ounce) of a substance by 1°C (1.8°F). Different substances have different heat capacities. Not all substances respond to identical inputs of heat by rising in temperature the same number of degrees. Notice how little heat is required to raise the temperature of 1 gram of silver 1 degree.

Because of the great strength and large number of the hydrogen bonds between water molecules, water can gain or lose large amounts of heat with very little change in temperature. This thermal inertia moderates temperatures worldwide. Of all common substances, only liquid ammonia has a higher heat capacity than liquid water.

amounts of heat while changing relatively little in temperature. Anyone who waits by a stove for water to boil knows a lot about water's heat capacity! Compared with water, ethyl alcohol has a much lower heat capacity. If both liquids absorb heat from identical stove burners at the same rate, pure ethyl alcohol, the active ingredient in alcoholic beverages, will rise in temperature about twice as fast as an equal

mass of water. Beach sand has an even lower heat capacity. Sand requires as little as 0.2 calorie to rise 1°C (1.8°F), so beaches can get too hot to stand on with bare feet while the water remains pleasantly cool.

As we will soon see, the concept of heat capacity is very important in oceanography. But for now, remember this: Water has an extraordinarily high heat capacity; it resists changing *temperature* when *heat* is added or removed.

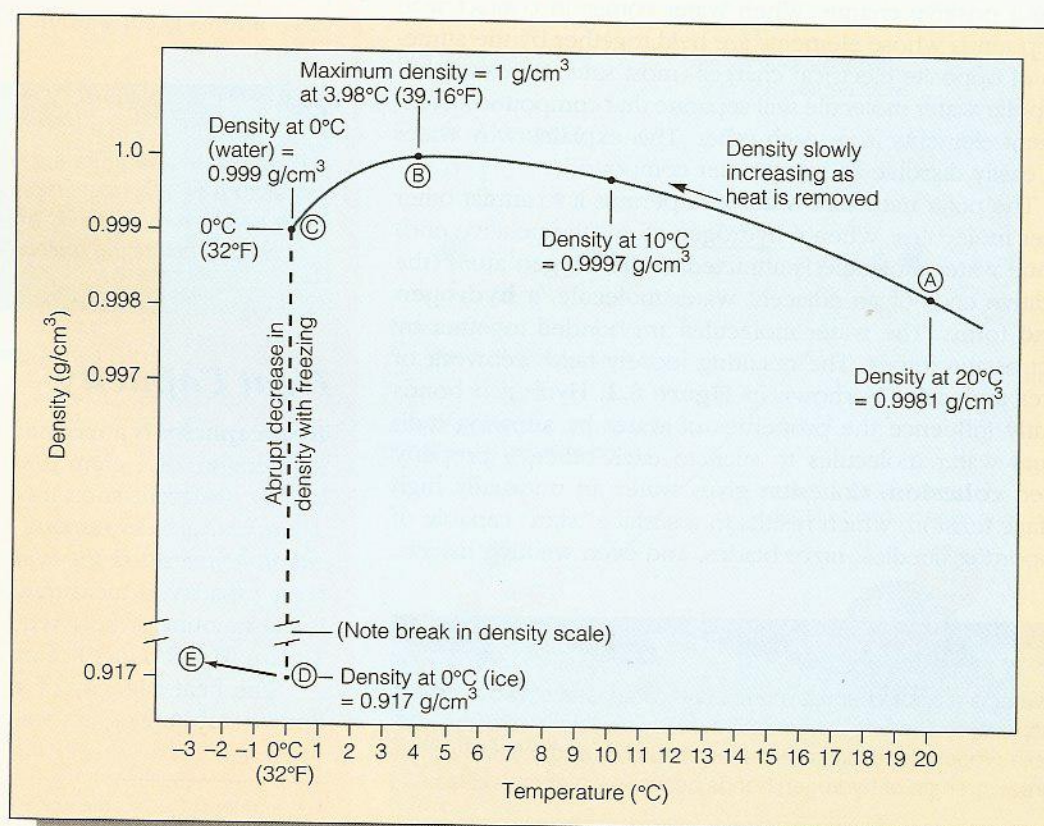
## Water Temperature and Density

6.5

The uniqueness of water becomes even more apparent when we consider the effect of a temperature change on water's **density** (its mass per unit of volume). You may recall from Chapter 3 that the density of pure water is 1 gram per cubic centimeter (1 g/cm<sup>3</sup>). Granite rock is heavier, with a density of about 2.7 g/cm<sup>3</sup>, and air is lighter, with a density of about 0.0012 g/cm<sup>3</sup>. Most substances become denser (weigh more per unit of volume) as they get colder. Pure water generally becomes denser as heat is removed and its temperature falls, but water's density behaves unexpectedly as the temperature approaches the freezing point.

A **density curve** shows the relationship between the temperature or salinity of a substance and its density. Most substances become progressively denser as they cool; their temperature–density relationships are linear (that is, appear as a straight line on graphs). But **Figure 6.3** shows the unusual temperature–density relationship of pure water. Imagine heat being removed from some water in a freezer. Initially, the water is at

**Figure 6.3** The relationship of density and temperature for pure water. Note that points **C** and **D** both represent 0°C (32°F) but different densities and different states of water. Ice floats because the density of ice is lower than the density of liquid water.





room temperature, point **A** on the graph. As expected, the density of water increases as its temperature drops along the line from point **A** toward point **B**. As the temperature approaches point **B**, the density increase slows, reaching a maximum at point **B** of  $1 \text{ g/cm}^3$  at  $3.98^\circ\text{C}$  ( $39.16^\circ\text{F}$ ). As cooling continues, the water begins to set up a more rigid framework of hydrogen bonds, which causes the liquid to expand slightly. Water thus becomes slightly less dense as cooling continues, until point **C** ( $0^\circ\text{C}$ ,  $32^\circ\text{F}$ ) is reached. At point **C** the water begins to freeze—to change state by crystallizing into ice.

**State** is an expression of the internal form of a substance. Changes in state are accompanied by either an input or an output of energy. Water exists on Earth in three physical states: liquid, gas (water vapor), and solid (ice). If the freezer continues to remove heat from the water at point **C** in Figure 6.3, the water will change from liquid to solid state. Through this transition from water to ice—from point **C** to point **D**—the density of the water *decreases* abruptly. Ice is therefore lighter than an equal volume of water. Ice increases in density as it gets colder than  $0^\circ\text{C}$ . No matter how cold it gets, however, ice never reaches the density of liquid water. Being less dense than water, ice “freezes over” as a floating layer instead of “freezing under” like the solid forms of virtually all other liquids.

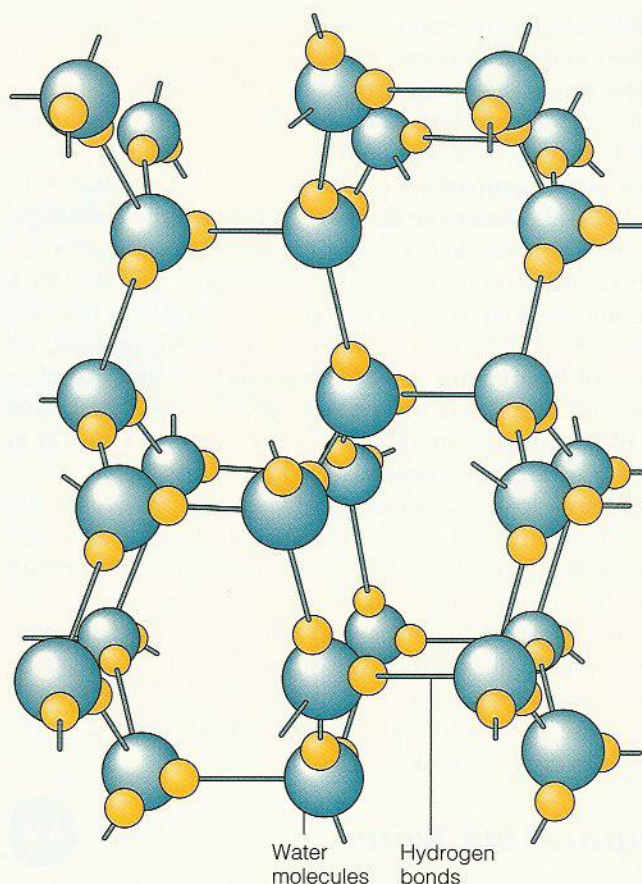
As we’ll see in a moment, the implications of water’s high heat capacity and the ability of ice to float are vital in maintaining Earth’s moderate surface temperature. First, we look at the transition from point **C** to point **D** in Figure 6.3.

## Freezing Water

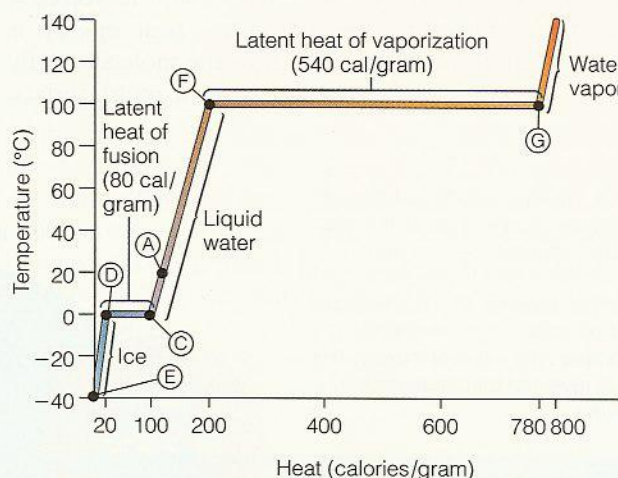
6.6

During the transition from liquid to solid state at the freezing point, the bond angle between the oxygen and hydrogen atoms in water expands from about  $105^\circ$  to slightly more than  $109^\circ$ . This change allows the hydrogen bonds in ice to form a crystal lattice (Figure 6.4). The space taken by 27 water molecules in the liquid state would be occupied by only 24 water molecules in the solid lattice, however; so water has to expand about 9% as the crystal forms. Because the molecules are packed less efficiently, ice is less dense than liquid water—and so it floats. A cubic centimeter of ice at  $0^\circ\text{C}$  ( $32^\circ\text{F}$ ) has a mass of only 0.917 gram, but a cubic centimeter of liquid water at  $0^\circ\text{C}$  has a mass of 0.999 gram.

The transition from liquid water to ice crystal (point **C** to point **D** in Figure 6.3) requires continued removal of heat energy; the change in state does not occur instantly throughout the mass when the cooling water reaches  $0^\circ\text{C}$  ( $32^\circ\text{F}$ ). Again, consider water in a freezer. **Figure 6.5**, a plot of heat removal versus temperature, illustrates the water’s progress to ice. As in Figure 6.3, point **A** represents  $20^\circ\text{C}$  ( $68^\circ\text{F}$ ) water just placed in the freezer. The removal of heat does not stop when the water reaches point **C**, *but the decline in temperature stops*. Even though heat continues to be removed, the water will not get colder until all of it has changed state from liquid (water) to solid (ice). Heat may therefore be removed from water when it is changing state (that is, when it is freezing) without the water dropping in temperature. Indeed, the continued removal of heat is what makes the change in state



**Figure 6.4** The lattice structure of an ice crystal, showing its hexagonal arrangement at the molecular level. The space taken by 24 water molecules in the solid lattice could be occupied by 27 water molecules in liquid state, so water expands about 9% as the crystal forms. Because molecules of liquid water are packed less efficiently, ice is less dense than liquid water and will float.



**Figure 6.5** A graph of temperature versus heat as water freezes, melts, and vaporizes. The horizontal line between points **C** and **D** represents the latent heat of fusion, when heat is being added or removed but the temperature is not changing. The horizontal line between points **G** and **F** represents the latent heat of vaporization, when heat is being added or removed but the temperature is not changing. (Note that points **A–E** on this graph are the same as those in Figure 6.3.)





possible. Heat is released as bonds form to make ice, and that heat must be removed to allow more ice to form.

The removal of heat from point **A** to point **C** in Figures 6.3 and 6.5 produces a *measurable* lowering of temperature detectable by a thermometer. Removing just 1 calorie of heat from a gram of liquid water causes its temperature to drop 1°C. This detectable decrease in heat is called **sensible heat** loss. But the loss of heat as water freezes between points **C** and **D** is not measurable (that is, not sensible) by a thermometer. Removing a calorie of heat from freezing water at 0°C (32°F) won't change its temperature at all; 80 calories of heat energy must be removed per gram of pure water at 0°C (32°F) to form ice. This heat is called the **latent heat of fusion**. The straight line between points **C** and **D** in Figure 6.5 represents water's latent heat of fusion.

No more ice crystals can form when all the water in the freezer has turned to ice. If the removal of heat continues, the ice will get colder and will soon reach the temperature inside the freezer, point **E** in Figures 6.3 and 6.5.

Latent heat of fusion is also a factor during thawing. When ice melts, it *absorbs* large quantities of heat (the same 80 calories per gram), but it does not change in temperature until all the ice has turned to liquid. This is why ice is so effective in cooling drinks.

## Evaporating Water

6.7

Let's reverse the process now and warm the ice. Imagine the water resting at -40°C (-40°F), point **E** at the lower left of Figure 6.5. Add heat, and the ice warms toward point **D**. It begins to melt. The horizontal line between point **D** and point **C** represents the latent heat of fusion: Heat is absorbed but temperature does not change as the ice melts. All liquid now at point **C**, the water warms past our original point **A** and arrives at point **F**. It begins to boil—it *vaporizes*.

When water vaporizes (or evaporates), individual water molecules diffuse into the air. Since each water molecule is hydrogen-bonded to adjacent molecules, heat energy is required to break those bonds and allow the molecule to fly away from the surface. Evaporation cools a moist surface

because departing molecules of water vapor carry this energy away with them. (This is how perspiring cools us when we're hot. The heat energy required to evaporate water from our skin is taken away from our bodies, cooling us.)

Hydrogen bonds are quite strong, and the amount of energy required to break them—known as the **latent heat of vaporization**—is very high. The long horizontal line between points **F** and **G** represents the latent heat of vaporization. Even though more heat is applied, the water cannot get warmer until all of it has vaporized. At 540 calories per gram at 20°C (68°F), water has the highest latent heat of vaporization of any known substance. As before, the term *latent* applies to heat input that does not cause a temperature change but does produce a change of state—in this case, from liquid to gas.

About 1 meter (3.3 feet) of water evaporates each year from the surface of the ocean, a volume of water equivalent to 334,000 cubic kilometers (80,000 cubic miles). The great quantities of solar energy that cause this evaporation are carried from the ocean by the escaping water vapor. When a gram of water vapor condenses back into liquid water, the same 540 calories is again available to do work. As we will see, winds, storms, ocean currents, and wind waves are all powered by that heat.

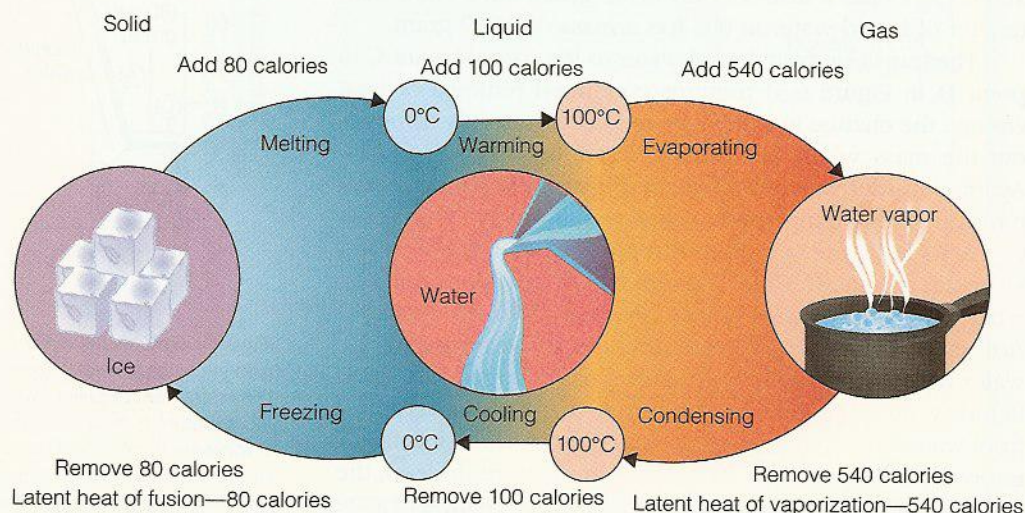
Why the big difference between water's latent heat of *fusion* (80 calories per gram) and its latent heat of *vaporization* (540 calories per gram)? Only a small percentage of hydrogen bonds are broken when ice melts, but *all* must be broken during evaporation. Breaking these bonds requires additional energy in proportion to their number. **Figure 6.6** summarizes this information.

## Global Thermostatic Effects

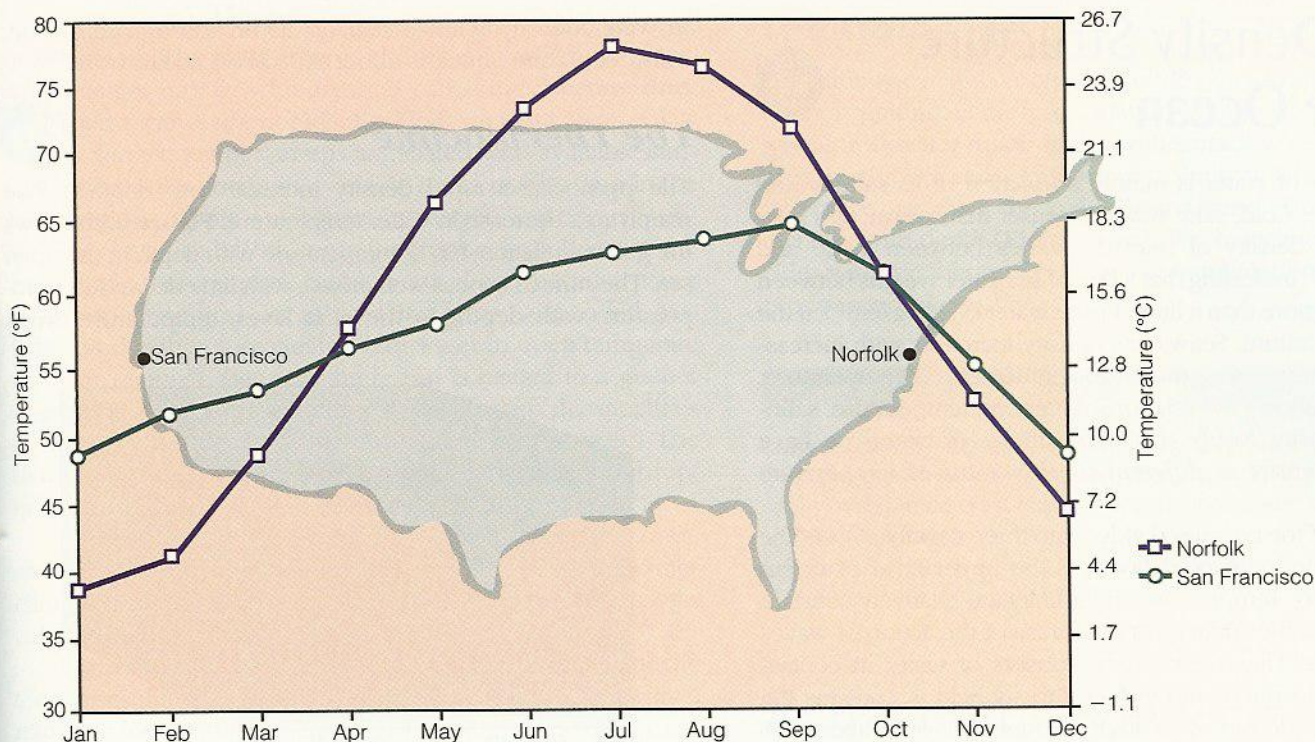
6.8

The **thermostatic properties** of water are those properties that act to moderate changes in temperature. Water temperature rises as sunlight is absorbed and changed to heat, but

**Figure 6.6** We must add 80 calories of heat energy to change 1 gram of ice to liquid water. After the ice is melted, about 1 calorie of heat is needed to raise each gram of water by 1°C. But 540 calories must be added to each gram of water to vaporize it—to boil it away. The process is reversed for condensation and freezing.







**Figure 6.7** San Francisco, California, and Norfolk, Virginia, are on nearly the same line of latitude. Wind tends to flow from west to east at this latitude. Compared to Norfolk, San Francisco is warmer in the winter and cooler in the summer, in part because air in San Francisco has moved over the ocean while air in Norfolk has approached over land. Water doesn't warm as much as land in the summer, nor cool as much in winter—a demonstration of thermal inertia.

as we've seen, water has a very high heat capacity, so its temperature will not rise very much even if a large quantity of heat is added. This tendency of a substance to resist a change in temperature with the gain or loss of heat energy is called **thermal inertia**. To investigate the impact of water's thermostatic properties on conditions at Earth's surface, we need to look at the planet's overall heat balance.

Only about 1 part in 2.2 billion of the sun's radiant energy is intercepted by Earth, but that amount averages 7 million calories per square meter per day at the top of the atmosphere or, for Earth as a whole, an impressive 17 trillion kilowatts (23 trillion horsepower)! About half of this light reaches the surface, where it is converted to heat and then transferred into the atmosphere by conduction, radiation, and evaporation. The atmosphere, like the land and ocean, eventually radiates this heat back into space in the form of long-wave (infrared) radiation. As in your personal financial budget, income must eventually equal outgo. Over long periods of time the total *incoming* heat (plus that from earthly sources) equals the total *outgoing* heat, so Earth is in **thermal equilibrium**; it is growing neither significantly warmer nor colder.<sup>2</sup> Heat input comes mainly from the sun; heat outflow can occur only as heat radiates into the cold of space.

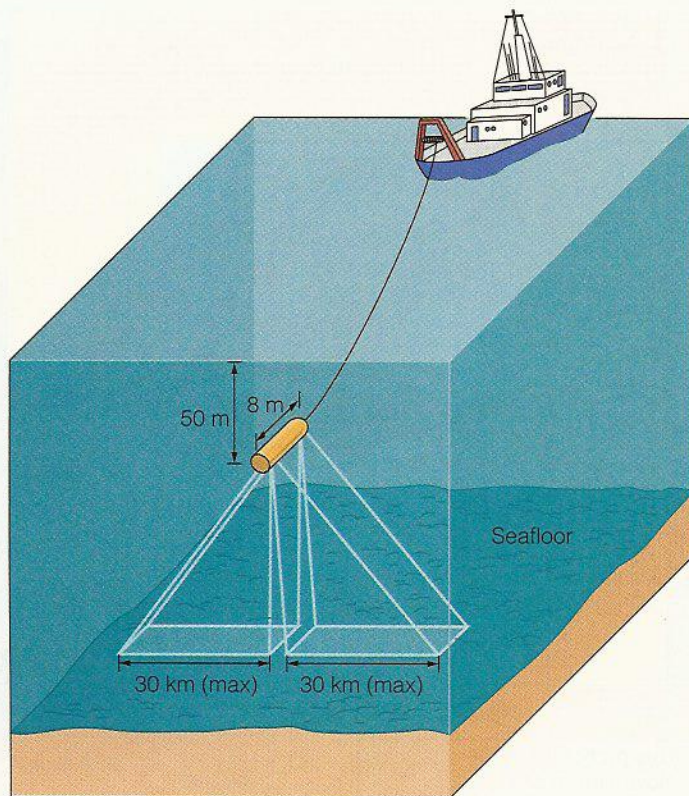
<sup>2</sup> Changes in heat balance do occur over short periods of geological time. Increasing amounts of carbon dioxide and methane in Earth's atmosphere may be contributing to an increase in surface temperature called the *greenhouse effect*. More on this subject may be found in Chapter 15.

Liquid water's thermal characteristics prevent broad swings of temperature during day and night and, through a longer span, during winter and summer (**Figure 6.7**). Heat is stored in the ocean during the day and released at night. A much greater amount of heat is stored through the summer and given off during the winter. If our ocean were made of alcohol—or almost any other liquid—summer temperatures would be much hotter and winters bitterly cold. Sea ice in the polar regions also contributes to thermal inertia. Because water expands and floats when it freezes, ice can absorb the morning warmth of the sun, melt, and then refreeze at night, giving back to the atmosphere the heat it stored through the daylight hours. The *heat content* of the water changes through the day; its *temperature* does not.

And why doesn't the ocean freeze solid near the poles or boil away at the equator? Because heat is carried from equatorial regions to polar regions by seawater currents and atmospheric water vapor. Again, whether in liquid or vapor form, water's ability to carry heat without a dramatic rise in temperature acts to moderate surface temperatures worldwide.

Without water's unique thermal properties, temperatures on Earth's surface would change dramatically with only minor changes in atmospheric transparency or solar output. Water acts as a "global thermostat."



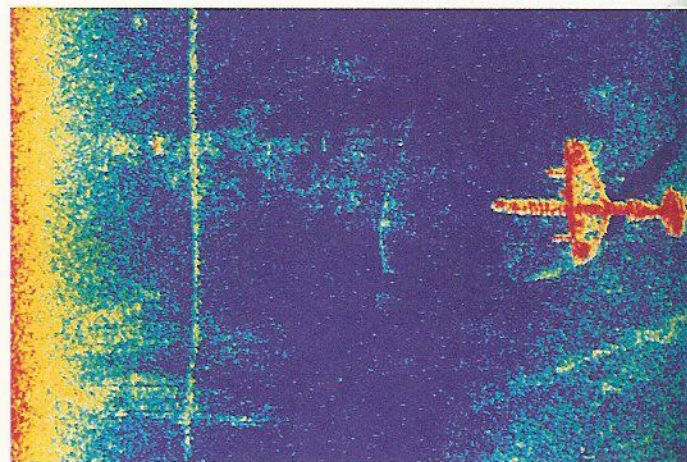


a

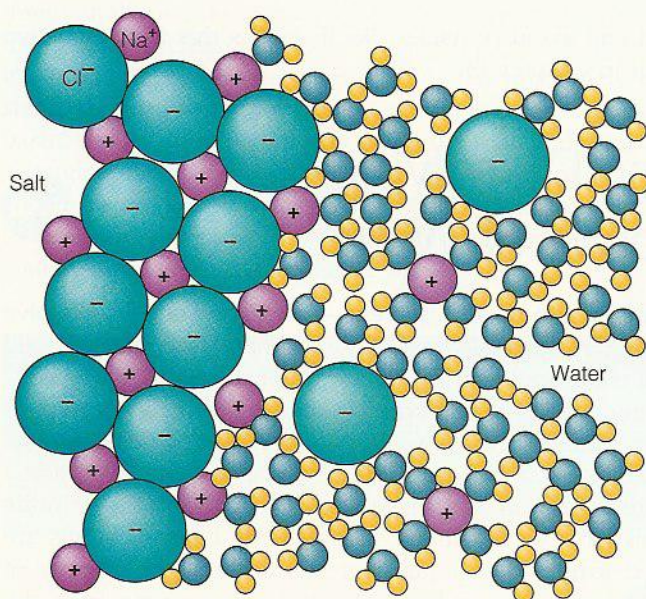
**Figure 6.16** Side-scan sonar. (a) Side-scan sonar in action. Sound pulses leave the submerged towed array (b), bounce off the bottom, and return to the device. One of the two slits through which sound pulses depart and return is visible on its side. Computers process the impulses into images: (c) A side-scan sonar record showing a downed World War II-era PB4Y-2 Privateer at a depth of 50 meters (165 feet). The artificial colors enhance target detail and clarity.



b



c



**Figure 6.17** Salt in solution. When a salt such as NaCl is put in water, the positively charged hydrogen end of the polar water molecule is attracted to the negatively charged  $\text{Cl}^-$  ion, and the negatively charged oxygen end is attracted to the positively charged  $\text{Na}^+$  ion. The ions are surrounded by water molecules that are attracted to them and become solute ions in the solvent (right side of figure).

By contrast, oil doesn't dissolve in water even if the two are thoroughly shaken together. When oil is dispersed in water, it forms a mixture because molecules of oil are non-polar. This means that oil has no positive or negative charges to attract the polar water molecule. In a way this is fortunate: Living tissues would readily dissolve in water if the oils within their membranes didn't blunt water's powerful attack.

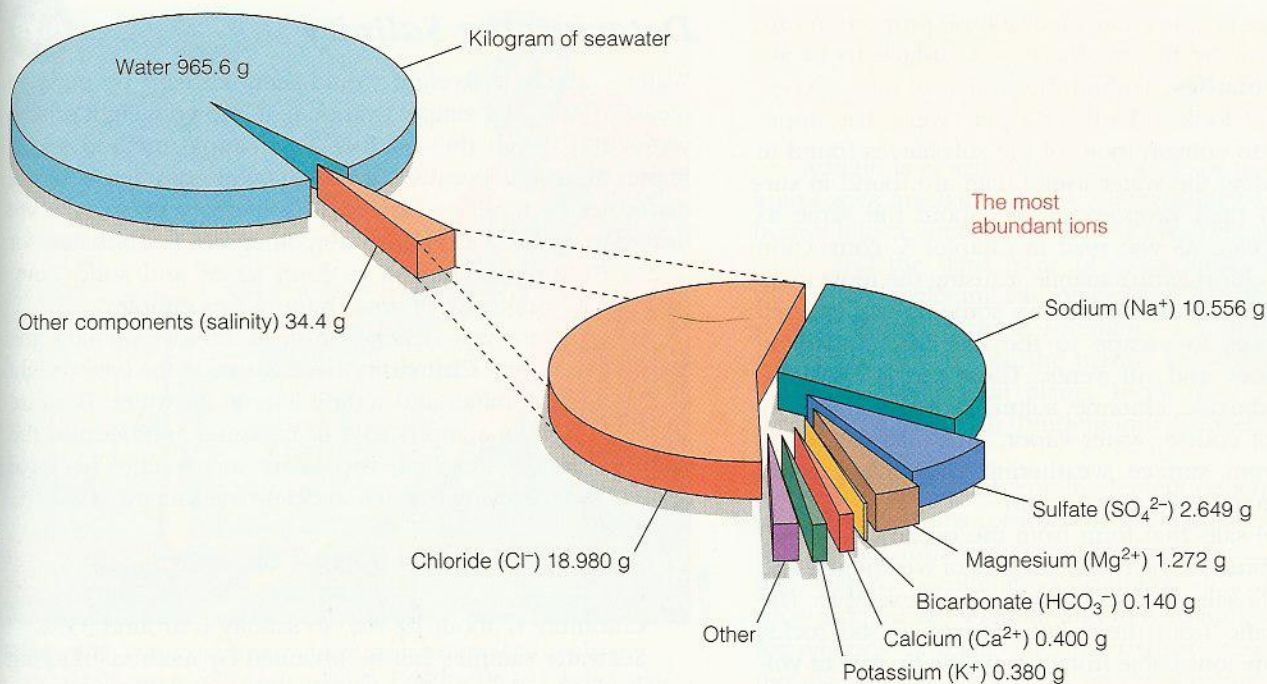
The polar nature of the water molecule produces some unexpected chemical properties. One of the most important is water's remarkable ability to dissolve more substances than any other natural solvent.

## Seawater

6.19

The total quantity (or concentration) of dissolved inorganic solids in water is its **salinity**. The ocean's salinity varies from about 3.3% to 3.7% by weight, depending on such factors as evaporation, precipitation, and freshwater runoff from the





**Figure 6.18** A representation of the most abundant components of a kilogram of seawater at 35‰ salinity. Note that the specific ions are represented in grams per kilogram, equivalent to parts per thousand (‰).

continents, but the average salinity is usually given as 3.5‰. The world ocean contains some 5,000 trillion kilograms (5.5 trillion tons) of salt. If the ocean's water evaporated completely, leaving its salts behind, the dried residue could cover the entire planet with an even layer 45 meters (150 feet) thick! Most of the dissolved solids in seawater are salts that have been separated into ions. Chloride and sodium are the most abundant of these.

## Salinity: Dissolved Solids and Water Together

6.20

About 3.5‰ of seawater consists of dissolved substances. Boiling away 100 kilograms of seawater theoretically produces a residue that weighs 3.5 kilograms. Variations of 0.1‰ are significant, and oceanographers prefer to use parts-per-thousand notation (‰) rather than percent (%; parts per hundred) in discussing these materials.<sup>3</sup> The seven ions shown in the pie on the right in **Figure 6.18** make up more than 99% of this residual material. When seawater evaporates, its ionic components combine in many different ways to form table salt (NaCl), epsom salts (MgSO<sub>4</sub>), and other mineral salts.

Seawater also contains minor constituents. The ocean is sort of an "Earth tea": Every element present in the crust and atmosphere is also present in the ocean, though sometimes in extremely small amounts. Only 14 elements have concentrations in seawater greater than one part per million (ppm).

<sup>3</sup> Note that 3.5‰ = 35‰. If you began with 1,000 kilograms of seawater, you would expect 35 kilograms of residue.

Elements present in amounts less than 0.001‰ (1 ppm) are known as **trace elements**.

The most abundant ions dissolved in seawater are chloride, sodium, and sulfate.

## The Source of the Ocean's Salts

6.21

Remembering the effectiveness of water as a solvent, you might think that the ocean's saltiness has resulted from the ability of rain, groundwater, or crashing surf to dissolve crustal rock. Much of the sea's dissolved material originated in that way, but is crustal rock the source of all the ocean's solutes? An easy way to find out would be to investigate the composition of salts in river water and compare these figures to those of the ocean as a whole. If crustal rock is the only source, then the salts in the ocean should be like those in concentrated river water. But they are not. River water is usually a dilute solution of calcium and bicarbonate ions, while the principal ions in seawater are chloride and sodium. The magnesium content of seawater would also be higher if seawater were simply concentrated river water. The proportions of salts in isolated salty inland lakes, such as Utah's Great Salt Lake or the Dead Sea, are indeed much different from the proportions of salts in the ocean. So, weathering and erosion of crustal rocks cannot be the sole sources of sea salts.



The components of ocean water whose proportions are *not* accounted for by the weathering of surface rocks are called **excess volatiles**. To find the source of these excess volatiles we must look to Earth's deeper layers. The upper mantle appears to contain more of the substances found in seawater (including the water itself) than are found in surface rocks, and their proportions are about the same as found in the ocean. As you read in Chapter 3, convection currents slowly churn Earth's mantle, causing the movement of tectonic plates. This activity allows some deeply trapped volatile substances to escape to the exterior, outgassing through volcanoes and rift vents. These excess volatiles include carbon dioxide, chlorine, sulfur, hydrogen, fluorine, nitrogen, and, of course, water vapor. This material, along with residue from surface weathering, accounts for the chemical constituents of today's ocean.

Some of the salts that form from the ocean's dissolved materials are hybrids of the two processes of weathering and outgassing. Table salt, sodium chloride, is an example. The sodium ions come from the weathering of crustal rocks, while the chlorine ions come from the mantle by way of volcanic vents and outgassing from mid-ocean rifts. As for the lower-than-expected quantity of magnesium ions in the ocean, recent research at a spreading center east of the Galápagos Islands suggests that mid-ocean rifts may play a role in reducing the magnesium content and increasing the calcium content of seawater. The water that circulates through new ocean floor at these sites is apparently stripped of magnesium and a few other elements. The magnesium seems to be incorporated into mineral deposits, but calcium is added as hot water dissolves adjacent rocks.

The quantity of dissolved inorganic solids in water is its salinity. The proportion of ions in seawater is not the same as the proportion in concentrated river water, which indicates that ongoing geological and chemical processes affect the ocean's salinity.

## The Principle of Constant Proportions

6.22

In 1865 the chemist Georg Forchhammer noted that although the total *amount* of dissolved solids (salinity) might vary between samples, the *ratio* of major salts was constant in samples of seawater from many locations. In other words, the percentage of various salts in seawater is the same in samples from many places regardless of how salty the water is. This constant ratio is known as **Forchhammer's principle**, or the **principle of constant proportions**. Forchhammer was also the first to observe that seawater contains fewer silica and calcium ions than concentrated river water, and the first to realize that removal of these compounds by marine animals and plants to form shells and other hard parts might account for part of the difference.

## Determining Salinity

Water's salinity by weight would seem an easy property to measure. Why not simply evaporate a known weight of seawater and weigh the residue? This simple method yields imprecise results because some salts will not release all the molecules of water associated with them. If these salts are heated to drive off the water, then other salts (carbonates, for example) will decompose to form gases and solid compounds not originally present in the water sample.

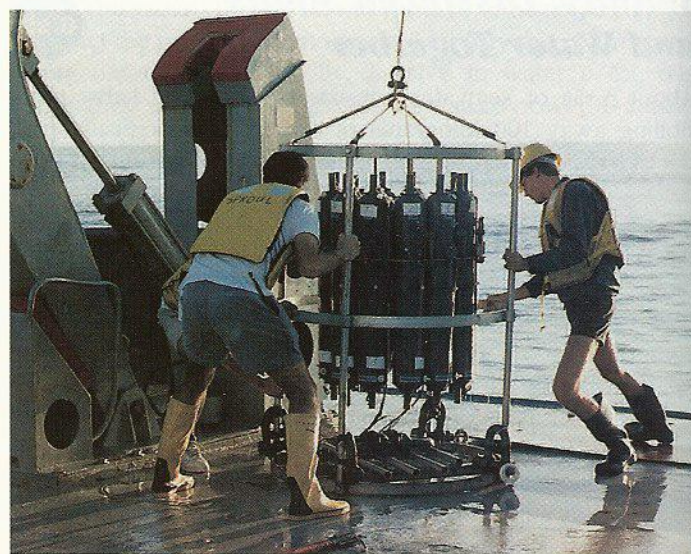
Modern analysis depends instead on determining the sample's chlorinity. **Chlorinity** is a measure of the total weight of chlorine, bromine, and iodine ions in seawater. Because chlorinity is comparatively easy to measure, and because the ratio of chlorinity to salinity is constant, marine chemists have devised the following formula to determine salinity:

$$\text{Salinity in } \text{‰} = 1.80655 \times \text{Chlorinity in } \text{‰}$$

Chlorinity is about 19.4‰, so salinity is around 35‰.

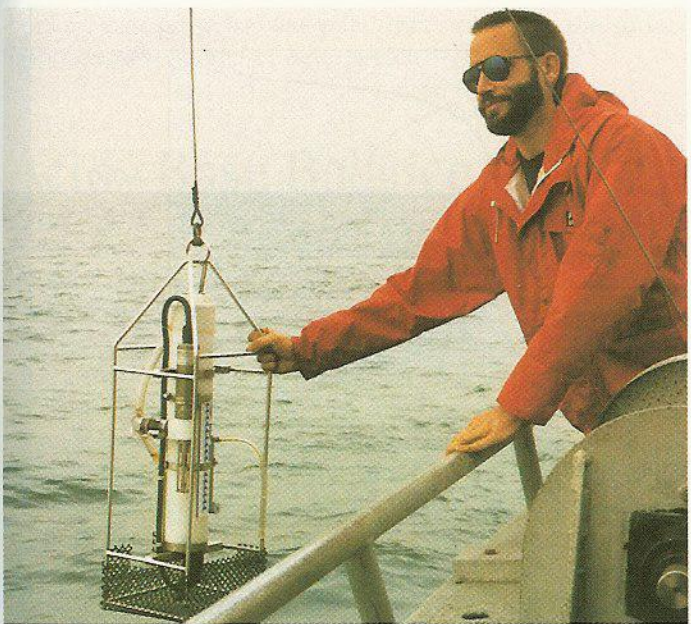
Seawater samples can be obtained by methods ranging from tossing a clean bucket over the side of the ship to sophisticated tube-and-pump systems. Typically water samples are collected using a group of sampling bottles (as in **Figure 6.19**). The bottles are lowered from a ship and triggered to close at specific depths by an electronic signal. Later the bottles are hauled to the surface and their contents analyzed.

Until recently, marine chemists used a delicate chemical procedure involving a silver nitrate solution to measure the chlorinity of seawater. Conversion to salinity was made by a set of mathematical tables. The procedure was calibrated against a standard sample of seawater of precisely known chlorinity. Today's marine scientists use an electronic device called a **salinometer** that measures the electrical conductivity of seawater (**Figure 6.20**). Conductivity varies with the



**Figure 6.19** A "rosette" of sampling bottles. Each of these 10-liter Niskin bottles may be mechanically sealed by a signal from the research ship when the array reaches predetermined depths. The bottles are hauled to the surface and their contents analyzed.





David Breiter

**Figure 6.20** This portable salinometer reads temperature, pH, and dissolved oxygen as well as conductivity. Designed to be lowered over the side of a research vessel at the end of a line, the self-powered device contains a small pump that passes water over sensors. This model takes two readings every second and operates down to about 200 meters (660 feet). Data may be retrieved by a cable connected to the research vessel or stored in the salinometer's memory to be retrieved when it is brought back aboard ship. A microprocessor contained within the white tube converts conductivity to salinity and, when connected to a portable computer, displays the results of all readings as graphs.

concentration and mobility of ions present and with the water temperature. Circuits in the salinometer adjust for water temperature, convert conductivity to salinity, and then display salinity. Salinometers are also calibrated against a sample of known conductivity and salinity. The best salinometers can determine salinity to an accuracy of 0.001%. Some salinometers are designed for remote sensing—the electronics stay aboard ship while the sensor coil is lowered over the side.

## Chemical Equilibrium and Residence Times

6.24

If outgassing and the chemical weathering of rock are continuing processes, shouldn't the ocean become progressively saltier with age? Landlocked seas and some lakes usually become saltier as they grow older, but the ocean does not. The ocean appears to be in **chemical equilibrium**; that is, the proportion *and amounts* of dissolved salts per unit volume of ocean are nearly constant. Evidently, whatever goes in must come out somewhere else.

Geologists in the 1950s developed the concept of a "steady state ocean." The idea suggests that ions are added to the ocean at the same rate as they are being removed. This theory helps explain why the ocean is not growing saltier. The idea led to the concept of **residence time**—the average length of time an element spends in the ocean. Residence time for a particular element may be calculated by this equation:

$$\text{Residence time} = \frac{\text{Amount of element in the ocean}}{\text{Rate at which the element is added to (or removed from) the ocean}}$$

Additions of salts from the mantle or from the weathering of rock are balanced by subtractions of minerals being bound into sediments. Dissolved salts precipitate out of the water and the hard parts of living organisms containing silicon and calcium carbonate drift slowly down to the seabed. Some of these sediments are removed from the ocean and drawn into the mantle at subduction zones by the cycling of crustal plates. Input from runoff and outgassing equals outfall (binding into sediments) for each dissolved component.

The residence time of an element depends on its chemical activity. Atoms (or ions) of some elements, such as aluminum and iron, remain in seawater for a relatively short time before becoming incorporated in sediments; others, such as chloride, sodium, and magnesium, remain in water for millions of years. The approximate residence times for the major constituents of seawater vary greatly. Iron has a residence time of about 200 years, but calcium stays in the ocean for about a million years, and the abundant chloride ion has a residence time of about 100 million years. Because of evaporation and precipitation, ocean water itself has a residence time of about 4,100 years.

Though most solids and gases are soluble in water, the ocean is in chemical equilibrium, and neither the proportion nor the amount of most dissolved substances changes significantly through time.

## Mixing Time

6.25

If constituent minerals are added to ocean water at rates that are less than the ocean's mixing time, they will become evenly distributed throughout the ocean. Because of the vigorous activity of currents, the **mixing time** of the ocean is thought to be on the order of 1,600 years, so the ocean has been mixed hundreds of thousands of times during its long history. The relatively long residence times of seawater's major constituents assure thorough mixing, which is the basis of Forchhammer's principle of constant proportions.

## Dissolved Gases

6.26

Gases in the air dissolve readily in seawater at the ocean's surface. Plants and animals living in the ocean require these dissolved gases to survive. No marine animal has the ability to break down water molecules to obtain oxygen directly, and no marine plant can manufacture enough carbon



dioxide to support its own metabolism. In order of their relative abundance, the major gases found in seawater are nitrogen, oxygen, and carbon dioxide. Because of differences in their solubility in water and air, the proportions of dissolved gases in the ocean are very different from the proportions of the same gases in the atmosphere.

Unlike solids, gases dissolve most readily in *cold* water. A cubic meter of chilly polar water usually contains a greater volume of dissolved gases than a cubic meter of warm tropical water.

## Nitrogen

6.27

About 48% of the dissolved gas in seawater is nitrogen. (In contrast, the atmosphere is slightly more than 78% nitrogen by volume.) The upper layers of ocean water are usually saturated with nitrogen; that is, additional nitrogen will not dissolve. Living organisms require nitrogen to build proteins and other important biochemicals, but they cannot use the free nitrogen in the atmosphere and ocean directly. It must first be “fixed” into usable chemical forms by specialized organisms. Though some species of bottom-dwelling bacteria can manufacture usable nitrates from the nitrogen dissolved in seawater, most of the nitrogen compounds needed by living organisms must be recycled among the organisms themselves.

## Oxygen

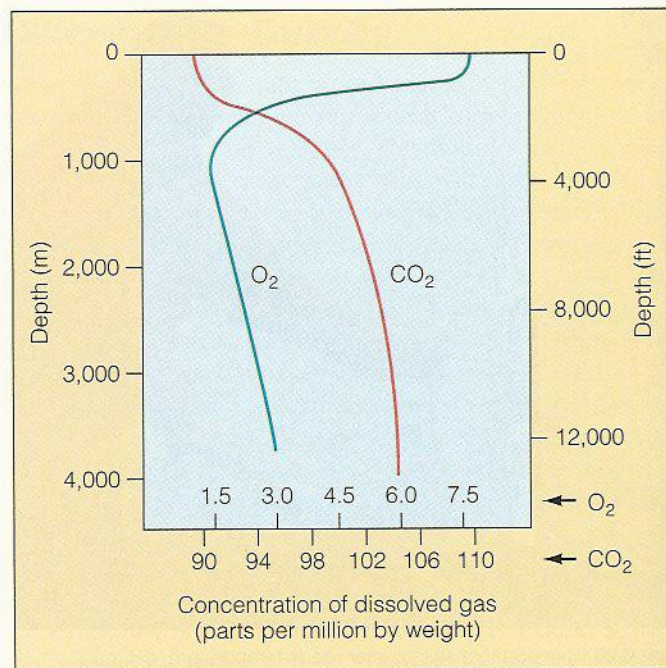
6.28

About 36% of the gas dissolved in the ocean is oxygen, but there is about a hundred times more gaseous oxygen in Earth’s atmosphere than is dissolved in the whole ocean. An average of 6 milligrams of oxygen is dissolved in each liter of seawater (that is, 6 parts per million parts of oxygen per liter of seawater, by weight). Yet this small amount of oxygen is a vital resource for animals that extract oxygen with gills. The sources of the ocean’s dissolved oxygen are the photosynthetic activity of plants and plantlike organisms, and the diffusion of oxygen from the atmosphere (as seen in **Figure 6.21**).

## Carbon Dioxide (CO<sub>2</sub>)

6.29

The amount of carbon dioxide in the atmosphere is very small (0.03%) because CO<sub>2</sub> is in great demand by photosynthesizers as a source of carbon for growth. Carbon dioxide is very soluble in water, though; the proportion of dissolved CO<sub>2</sub> in water is about 15% of all dissolved gases. Because CO<sub>2</sub> combines chemically with water to form a weak acid (H<sub>2</sub>CO<sub>3</sub>, carbonic acid), water can hold perhaps a thousand times more carbon dioxide than either nitrogen or oxygen at saturation. Carbon dioxide is quickly used by marine plants, so dissolved quantities of CO<sub>2</sub> are almost always much less than this theoretical maximum. Even so, at the present time there is about 60 times as much CO<sub>2</sub> dissolved in the ocean as in the atmosphere. Much more CO<sub>2</sub> moves from atmosphere to ocean than from ocean to atmosphere, in part because some dissolved CO<sub>2</sub> forms carbonate ions, which are locked into sediments, minerals, and the shells and skeletons of living organisms.



**Figure 6.21** How concentrations of oxygen and carbon dioxide vary with depth. Oxygen is abundant near the surface because of the photosynthetic activity of marine plants. The oxygen concentration decreases below the sunlit layer because of the respiration of marine animals and bacteria, and because of the oxygen consumed by the decay of tiny dead organisms slowly sinking through the area. In contrast, plants use carbon dioxide during photosynthesis, so surface levels of CO<sub>2</sub> are low. Because photosynthesis cannot take place in the dark, CO<sub>2</sub> given off by animals and bacteria tends to build up at depths below the sunlit layer. Levels of CO<sub>2</sub> also increase with depth because its solubility increases as pressure increases and temperature decreases.

Figure 6.21 illustrates how carbon dioxide and oxygen concentrations vary with depth. Carbon dioxide concentrations increase with increasing depth, but oxygen concentrations usually decrease through the middle depths and then rise again toward the bottom. High concentrations of oxygen at the surface are usually by-products of photosynthesis in the ocean’s brightly lit upper layer. Since plants and plantlike organisms require carbon dioxide for metabolism, surface CO<sub>2</sub> concentrations tend to be low. A decrease in oxygen below the sunlit upper layer is usually due to the respiration of bacteria and marine animals, which leads to higher concentrations of carbon dioxide. Oxygen levels are slightly higher in deeper water because fewer animals are present to take up the oxygen that reaches these depths and

Gases dissolve in water in proportions that vary with their physical properties. Nitrogen is the most abundant dissolved gas in seawater; oxygen is the second most abundant. Carbon dioxide is the most soluble gas, and one of many substances that affect the ocean’s pH balance.