

The Properties of Seawater

Water is just not water. It is a vital substance, the earth's blood, something of rich and infinite variety.

—L. Watson, *The Water Planet*, 1988

PREVIEW

WATER IS EVERYWHERE. Its presence on our planet is crucial for the existence of life. “Biology,” said Berg, “is wet and dynamic.”

What exactly are the chemical and physical properties of water generally and seawater specifically? How variable are these properties over time and space? How do chemical elements enter the oceans, and—once there—how do they interact with other substances, both living and nonliving? A discussion of these questions forms the basis of this chapter. Here, we will examine the chemical and physical nature of seawater and lay the foundation for later discussions of ocean circulation and marine life. The concluding section of the chapter integrates these ideas into the global water cycle and examines the ocean as a complex and dynamic biogeochemical system.



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One of the most obvious properties of seawater is its salty taste. If you believe that its taste is due to dissolved salt, you are correct, and this is what makes the water of the oceans different from the water of lakes and rivers. Seawater is made up mainly of liquid water (about 96.5 percent by weight) in which chloride (Cl) and sodium (Na) are the dominant dissolved chemicals. The common table salt you use to flavor your food is composed of precisely the same elements. Before continuing our discussion about the chemistry of water, we must, however, become familiar with a few basic chemical and physical concepts. So let's begin.

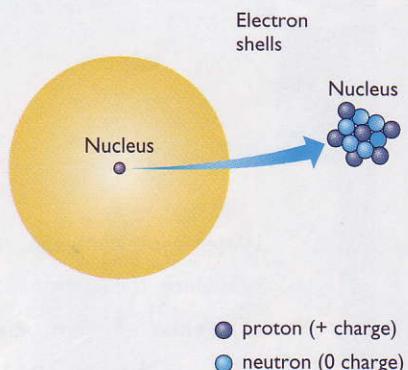
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Basic Chemical Notions

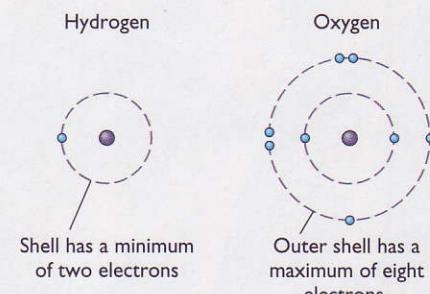
All matter is composed of “building blocks” termed **atoms**. An atom is the smallest unit of a substance that retains all of its chemical properties. For example, a single atom of hydrogen possesses all of the chemical characteristics of a large collection of hydrogen atoms. If you tried to divide a single hydrogen atom into simpler units, you could do so, but these bits of matter would no longer display the properties of a hydrogen atom. Atoms that are chemically bonded to one another comprise a **molecule**. Or, if you prefer, a molecule is a chemical substance that can be separated into distinct atoms. Sodium chloride (NaCl) is a molecule of salt that can be separated into a positively charged atom of Na and a negatively charged atom of Cl .

The internal structure of any atom consists of elementary particles that possess mass and electric charge. The center of an atom, the **nucleus**, is composed of two distinct kinds of particles that contain essentially all of its mass: **protons** with a positive electric charge and **neutrons** with no electrical charge (Figure 5-1a). Surrounding the nucleus are collections of orbiting **electrons** that have little mass and carry a negative electrical charge. The electron orbits are not randomly distributed around the nucleus, but are confined to discrete levels termed **electron shells**. All elements (except

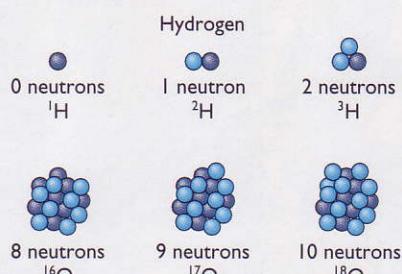
for one type of hydrogen that does not have neutrons) contain protons, neutrons, and electrons, and differ from one another because of the number and structural arrangement of these fundamental subatomic particles. A stable atom of an element is electrically neutral, indicating that the positive charges from the protons are balanced by the negative charges from the electrons.



(a) ATOM



(b) ELECTRON SHELLS



(c) ISOTOPES

FIGURE 5-1

Atomic structure. (a) A simplified version of an atom depicts a nucleus of protons and neutrons, surrounded by shells of orbiting electrons. (b) A depiction of electrons within the shells of hydrogen (one electron) and oxygen (eight electrons) atoms. (c) The isotopes of an element have a variable number of neutrons. Hydrogen isotopes have zero, one, or two neutrons; oxygen isotopes have eight, nine, or ten neutrons.

Basic Physical Notions

A

nother important notion that we must consider in order to understand the behavior of water is the physical concept of **heat**, the property that one measures with a thermometer and that results from the physical vibrations of atoms and molecules. These physical vibrations represent energy of motion, called **kinetic energy**. The more heat in a material, the greater the agitation of its atoms and molecules.

Let's consider a specific example. A block of ice consists of an orderly, rigid arrangement of water molecules (**Figure 5-2a**) that are held firmly in place by strong electrical bonds between the molecules. Although an ice cube appears inert to the naked eye, it is not inert on an atomic scale. Its molecules are vibrating back and forth even though they are locked together into a crystalline framework. If we add heat to the ice cube, the molecules vibrate faster and move farther back and forth in the crystal. Above 0°C, the melting temperature of ice, the back-and-forth motions of the molecules are so vigorous that they exceed the strength of the electrical bonds holding the molecules in place in the crystal. At that temperature, the crystal's structure disintegrates (melts), and the solid ice becomes liquid water (**Figure 5-2b**). Liquids are loose aggregates of molecules that are in contact, but are free to move relative to one another, unlike the fixed molecules in a solid. As

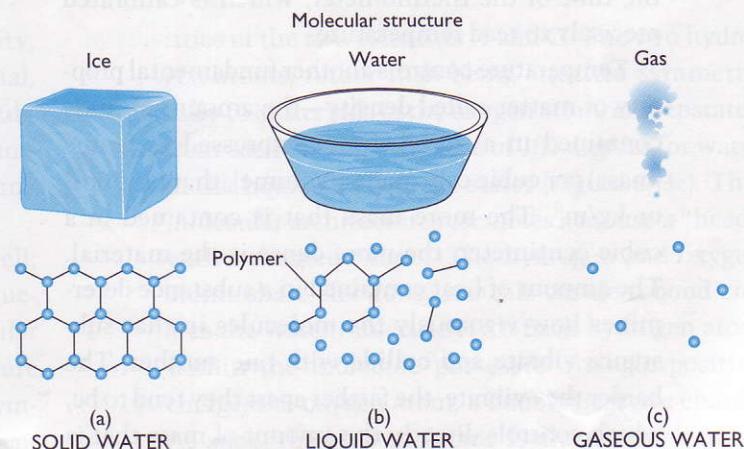
Let's clarify this by being specific. Hydrogen (**Figure 5-1b**) possesses one proton in its nucleus; the positive charge from its single proton is neutralized by the negative charge from its one orbiting electron. Oxygen, on the other hand, contains eight protons in its nucleus, balanced electrically by eight orbiting electrons. So hydrogen atoms consist of a single proton and a single electron, and oxygen atoms of eight protons and eight electrons. If electrons are either added or removed from any single atom, the atom is no longer electrically balanced. Atoms with more electrons than protons have a net negative charge. Atoms with more protons than electrons have a net positive charge. An atom with either a positive or a negative charge is called an **ion**. For example, when NaCl dissolves in water, it separates into the ions Na^+ and Cl^- . The charge of an ion is the single most important reason for its ability to bond with other elements.

The story does not end there though. Although the number of protons is fixed for any element, the quantity of neutrons in its nucleus can vary. Because the neutron carries no electrical charge but has mass, variations in the number of neutrons change the weight of the element, but not its basic chemistry. Atoms of the same element that differ in weight due to variable numbers of neutrons are called **isotopes**. Hydrogen has three isotopes. Each isotope contains a single proton, but either zero, one, or two neutrons (**Figure 5-1c**). Oxygen similarly has three isotopes containing either eight, nine, or ten neutrons in a nucleus (see Figure 5-1c). The most abundant hydrogen isotope has zero neutrons and the most abundant oxygen isotope has eight.

FIGURE 5-2

States of matter. Water occurs in three states, which depend on temperature and pressure.

(a) Solid water (ice) consists of ordered molecules that are tightly bonded to one another. (b) Liquid water consists of molecules that move relative to one another. Polymers are bits of crystalline structure that can exist in liquid water near its melting temperature. (c) Gaseous water (gas) is made up of independently moving molecules.



more heat is added to the liquid water, its temperature rises as its molecules vibrate more energetically. Some of these molecules contain so much kinetic energy that they escape from the liquid surface and become a gas (**Figure 5–2c**); this process is called **evaporation**. At 100°C, the boiling temperature of water, all of the molecules are highly energized and, hence, are **vaporized** (converted into **gas**). Free gas molecules move independently of one another between collisions, and are the least ordered of the three states of matter because of their very high kinetic energy.

The kinetic theory of heat has important implications for measuring temperature and for understanding the density of materials, whether they be solids, liquids, or gases. Imagine a thermometer, which is nothing more than a narrow glass tube filled with mercury. If we wish to determine the temperature of a water sample, we stick the thermometer in the liquid. What happens? The mercury in the tube rises and eventually stops. It is then an easy matter to read the temperature of the water off the thermometer's scale. But what exactly does the rise of mercury in the tube represent in a physical sense? Well, it's quite simple, provided you grasp the kinetic theory of heat. Recall that the water molecules are vibrating at a rate that depends on the water's temperature. When the thermometer is placed in the liquid, water molecules strike the tube; these collisions add energy to the molecules of the tube, so they vibrate faster. This in turn transfers kinetic energy to the atoms of mercury. The atoms of mercury begin to vibrate vigorously and collide with one another harder and harder, forcing them on the average farther apart than they were before the addition of kinetic energy from the water. Therefore, the mercury expands and rises in the tube of the thermometer, which is calibrated precisely to read temperature.

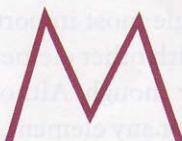
Temperature controls another fundamental property of matter called **density**—the amount of mass contained in a unit volume, expressed as grams (mass) per cubic centimeter (volume), that is, g/cm^3 or kg/m^3 . The more mass that is contained in a cubic centimeter, the more dense is the material. The amount of heat contained in a substance determines how vigorously the molecules in that substance vibrate and collide with one another. The harder they vibrate, the farther apart they tend to be, which controls directly the amount of mass that is

contained in a unit volume. This means that 10°C water is denser than 15°C water, and that warm air is less dense than cold air is at the same pressure.

Now that we have a solid conceptual understanding of the structure of atoms, of the kinetic theory of heat, and of temperature and density under our caps, we can examine the chemical and physical properties of water in general, and seawater in particular. Let's start by inspecting the common molecule on the Earth that we refer to simply as **water**.

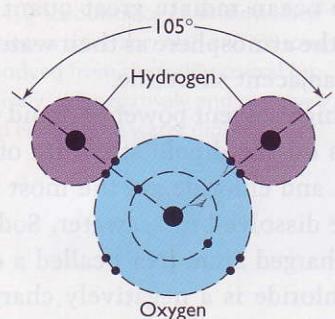
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The Water Molecule

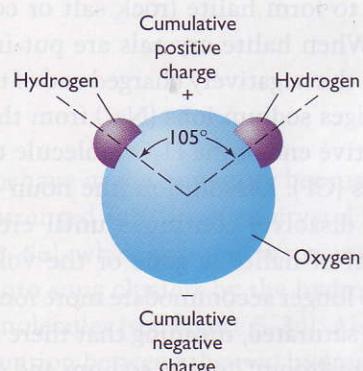


Most people know that the chemical formula for water is H_2O . This formula means that water consists of two atoms of hydrogen (H) that are chemically bonded to one atom of oxygen (O) (**Figure 5–3a**). However, despite its simple chemical composition, water is a complex substance with truly remarkable physical properties. For example, the melting and boiling temperatures of water are much higher than expected when compared to chemically related hydrogen compounds (**Figure 5–3b**). This is fortunate; otherwise, water would be able to exist only as a gas at the temperatures that prevail at the Earth's surface. Consequently, the oceans could not have formed, and life could not have developed. In fact, H_2O is the only substance that can coexist naturally as a gas, a liquid, and a solid on the Earth's surface. Therefore, it is not surprising to discover how fundamental it is to all forms of life.

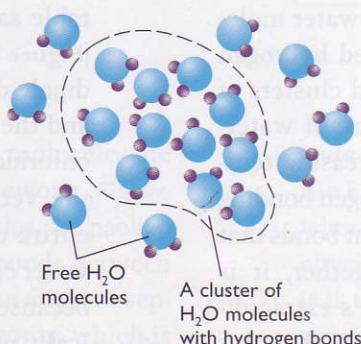
Water also has an unusually high heat capacity and tremendous solvent power. **Heat capacity** is defined as the quantity of heat required to raise the temperature of 1 gram of a substance by 1°C. More energy is required to raise the temperature of a substance with high heat capacity than one with low heat capacity. In other words, adding the same amount of heat will raise the temperature of a substance with a low heat capacity to a greater degree than one with a high heat capacity. The high heat capacity of water explains why so much energy is required to heat water.



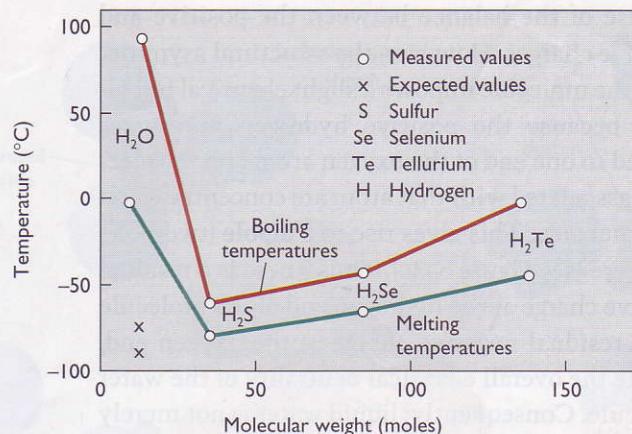
(a) H_2O MOLECULE



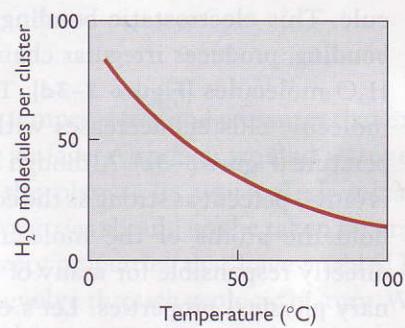
(c) DIPOLE STRUCTURE



(d) CLUSTERS OF WATER



(b) MELTING AND BOILING TEMPERATURES OF WATER



(e) SIZE OF WATER CLUSTERS

FIGURE 5-3

The water molecule. (a) The chemical bonding of two hydrogen atoms and one oxygen atom produces a water (H_2O) molecule. (b) The observed (o) melting and boiling temperatures of water are much higher than theory (x) indicates. [Adapted from R. A. Home, *Marine Chemistry: The Structure of Water and the Chemistry of the Hydrosphere* (New York: John Wiley, Interscience, 1969).] (c) The two small hydrogen atoms are separated from each other at their points of attachment to the large oxygen atom by an angle of 105 degrees, so that the molecule resembles the familiar caricature of a mouse's head. This structure creates a dipolar molecule with a residual positive charge at one end and a residual negative charge at the other end. (d) A cluster of H_2O molecules with hydrogen bonds is contrasted here with free H_2O molecules. (e) The size of the clusters decreases with increasing temperature.

In addition to its unusually high heat capacity, the capability of liquid water to dissolve material, its **solvent power**, is unsurpassed by any other substance. In fact, chemists refer to water as the "universal solvent," meaning that virtually anything can be dissolved to some extent in liquid water.

Water possesses other unusual properties as well, but the case for this substance's chemical uniqueness should be clear. To account for water's singular properties we must examine the physical structure of the water molecule, H_2O . The molecule's asymmetrical shape is as important as the chemical iden-

tities of the two elements H and O. The two hydrogen atoms, rather than being attached symmetrically to either side of the oxygen atom, are separated from each other by an angle of 105 degrees for water in the liquid and gaseous states (Figure 5-3c). This molecular architecture resembles a mouse's "head" with hydrogen "ears." The hydrogen and oxygen atoms share electrons, and this **covalent bond** creates the water molecule H_2O . Each hydrogen atom within the molecule possesses a single positive charge; the oxygen atom, a double negative charge. As such, the H_2O molecule is electrically neutral

because of the balance between the positive and negative charges. However, the structural asymmetry of the molecule imposes a slight electrical imbalance, because the positive hydrogen atoms are bonded to one end of the oxygen atom and the electrons associated with that atom are concentrated on the other side. This gives rise to a **dipole** (two-pole) structure (see Figure 5–3c). Thus, there is a residual positive charge at the hydrogen end of the molecule and a residual negative charge at the oxygen end, despite the overall electrical neutrality of the water molecule. Consequently, liquid water is not merely a collection of freely moving molecules. Rather, its dipole structure causes the negative end of the molecule to be attracted to and become electrically bonded to the positive end of a nearby water molecule. This electrostatic bonding, called **hydrogen bonding**, produces irregular chains and clusters of H₂O molecules (Figure 5–3d). The size of water-molecule clusters decreases with increasing temperature (Figure 5–3e). Although hydrogen bonding is only 4 percent as strong as the covalent bonds that hold the atoms of the molecule together, it is directly responsible for many of water's extraordinary physical properties. Let's examine how this comes about.

The higher than expected melting and boiling temperatures of water (see Figure 5–3b) depend directly on the dipole structure of the H₂O molecule. More energy is required than expected to vaporize liquid water and to melt ice, because hydrogen bonds that link H₂O-molecule to H₂O-molecule must first be broken before the solid can melt and the liquid can vaporize. This is also the reason for water's high heat capacity. When heat is added to water, only a fraction of this energy is actually used to increase the vibrations of the molecules, which would be detected as a rise of temperature. Much of the added heat is used to break hydrogen bonds that link the H₂O molecules into irregular clusters. Hence, as water is heated, its temperature rises slowly relative to the amount of energy used. Conversely, when cooled, water releases more heat than expected from the decrease in its temperature.

The unusually high heat capacity of water prevents extreme variations in the temperature of the oceans and explains why the climates of coasts and islands experience less extreme temperature variations than those of land located far from the ocean or large lakes. During the summer, large

bodies of water absorb solar heat, helping keep air temperatures cool. During the winter, large lakes and the ocean radiate great quantities of stored heat to the atmosphere as their water cools, warming the adjacent shoreline.

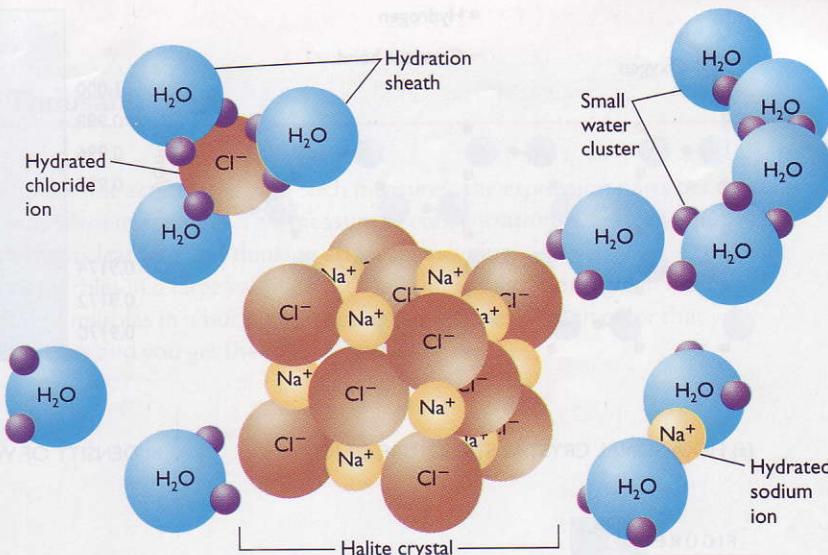
The high solvent power of liquid water likewise depends on the dipole structure of its molecule. Sodium and chloride are the most common salts that are dissolved in seawater. Sodium is a positively charged atom (Na⁺) called a **cation**. In contrast, chloride is a negatively charged atom (Cl⁻) called an **anion**. When these two ions come into contact, they are attracted to each other because of their opposing charges, and can be held together by **ionic bonds** to form halite (rock salt or common table salt). When halite crystals are put in water (Figure 5–4), the negatively charged end of the H₂O dipole dislodges sodium ions (Na⁺) from the solid, and the positive end of the H₂O molecule tears off chloride ions (Cl⁻). Dissolution (the noun form of the verb to dissolve) continues until either the entire crystal of halite is gone or the volume of water can no longer accommodate more ions of salt because it is **saturated**, meaning that there is physically no more "room" for the sodium and chloride in the water. (By way of an analogy, think about what happens when you keep adding spoonful after spoonful of sugar to your cup of coffee.) In solution, the sodium and chloride ions are surrounded by water molecules (see Figure 5–4). This keeps the cations separated from the anions, a process known as **hydration**. In other words, water acts as a solvent by preventing the chemical recombination of Na⁺ and Cl⁻ to form the solid halite.

The density of water is yet another unusual property of this familiar substance. Ice floats on water! All other solids sink in their own liquids. It's hard to imagine a solid bar of steel floating in a vat of molten steel. Once again, water behaves in a peculiar way. Why is this so?

At the freezing point, solids crystallize from liquids because the thermal vibrations of molecules are low enough so that chemical bonding can occur and a crystal forms. The loose assortment of molecules in the liquid is reconstructed into a rigid solid. Because the molecules in the solid vibrate less than do the molecules in the liquid, they are more tightly packed and denser in the solid than in the liquid state. Therefore, solids, because of their higher density, sink in their own liquids. Water does not

FIGURE 5-4

Halite (rock salt). The dipole structure of the H_2O accounts for its unsurpassed properties as a solvent. Na^+ and Cl^- ions are dislodged from the halite crystal by, respectively, the negatively and positively charged ends of the water dipole.



behave in the same way because ice molecules are arranged into an open crystal framework (Figure 5-5a), whereas liquid water molecules are packed into snug clusters by the hydrogen bonds between molecules (see Figure 5-3d). Also, the angle of separation between the two hydrogen atoms, which is 105 degrees in liquid and gaseous water, expands to 109.5 degrees in ice. This makes ice about 8 percent less dense than water. The H_2O molecules in ice are ordered into a porous **hexagon** (a six-sided structure) by the hydrogen bonds between oppositely charged ends of neighboring molecules (Figure 5-5a). When ice is warmed to 0°C , it begins to melt as thermal vibrations of the molecules cause the crystalline structure to break apart. Because of hydrogen bonds, the freed H_2O molecules in the liquid become more closely packed together than they were in the solid, resulting in an increase of density (more mass per unit volume). Water does not, however, reach its maximum density until it is warmed to 3.98°C (Figure 5-5b), because loose aggregates of molecules that resemble the open crystalline structure of ice (see Figure 5-2b), termed **polymers**, persist in water cooler than that critical temperature. Above 3.98°C , the density of water decreases with increasing temperature, as expected. Below 3.98°C , however, the density of water *decreases* as temperature *decreases* until it freezes into ice.

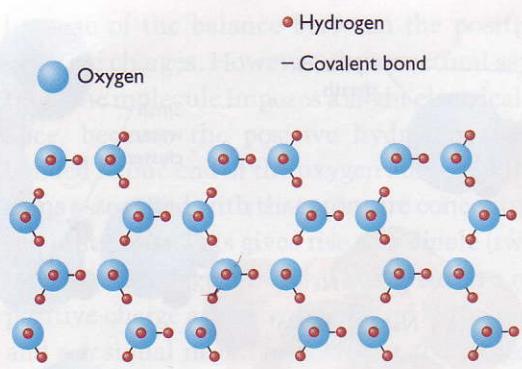
What we have learned so far about seawater is that it consists dominantly of H_2O , a chemical substance that can occur in a solid, liquid, and gaseous

state at the temperatures and pressures that exist at the Earth's surface. Although we find water everywhere on the planet, its unusual chemical and physical properties should not be taken for granted; it is these very properties that have enabled life to appear and evolve through geologic history. We can now proceed to examine seawater's other chemical ingredients.

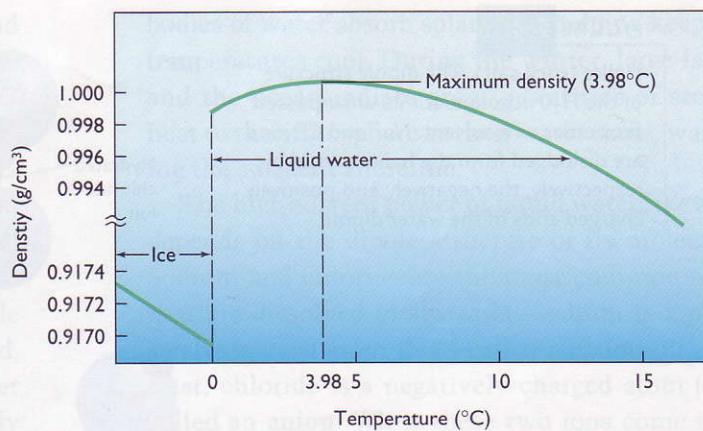
THE SOLUTES OF SEAWATER

Chemical analyses of samples from all over the world show that seawater consists of a small quantity of salt dissolved in water. The salt occurs as charged particles, cations and anions, that are dispersed among the molecules of liquid water. Seawater is a chemical solution. The dissolving agent, the liquid water, is the **solvent** and the dissolved substances, the salt ions, are the **solute**. Seawater also contains minor to trace amounts of dissolved metals, nutrients, gases, and organic compounds of seemingly infinite variety.

Before examining the chemistry of seawater solutions, we need to determine the amount of material that is dissolved in seawater, so that we can compare samples taken from different parts of an ocean or, for that matter, from different oceans. We can taste seawater samples and say qualitatively that this sample tastes "saltier" than this other one. But this is a rather subjective technique, and a scientist



(a) HEXAGONAL CRYSTAL STRUCTURE OF ICE



(b) DENSITY OF WATER

FIGURE 5-5

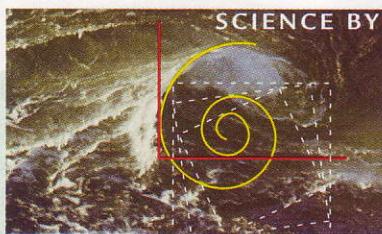
Properties of water. (a) The open network of the hexagonal structure of ice crystals is shown here. (b) Because of the open crystal structure of solid water, ice is less dense than liquid water. Water attains its maximum density at a temperature of 3.98°C ; polymers exist in liquid water colder than this temperature.

needs to know exactly and precisely how salty a parcel of water is. Oceanographers specify the concentration of a solute in seawater in units called **parts per thousand**, represented by either the abbreviation ppt or, as preferred by marine scientists, the symbol ‰. Although oceanographers also express salinity as a dimensionless unit in terms of PSS78—Practical Salinity Scale 1978—we will use ppt. Average or “normal” seawater has a salinity of about 35‰. This means that the dissolved salt occurs in a concentration of 35 parts per thousand (ppt). That is, the salt comprises 3.5 percent (divide 35 by 1,000, and convert it to a percentage by multiplying it by 100) of the sample, the rest (96.5 percent or 965 parts per thousand) being H_2O molecules. (Notice that $965 + 35 = 1,000$.) This signifies that a volume of seawater weighing 1,000 grams (or 1 kilogram) with a salinity of 35‰ contains 35 grams of solute. Obviously, a 100 gram sample of seawater with a salinity of 35‰ contains 3.5 grams of dissolved salts.

As you know, because of its high solvent power (ability to dissolve), many types of chemicals are dissolved in ocean water and most are found in minute quantities. All these solutes can be grouped into five broad categories: major constituents, nutrients, gases, trace elements, and organic compounds. A review of the general characteristics of each group follows:

MAJOR CONSTITUENTS

In terms of quantity, the primary solutes in seawater are cations and anions. By weight, chloride (Cl^-) and sodium (Na^+) together comprise more than 85.65 percent (Table 5-1) of all the dissolved substances in seawater. When these two ions bond chemically into a solid, they form halite and give seawater its most distinctive property—its saltiness. Surprisingly, the six most abundant ions—chloride (Cl^-), sodium (Na^+), sulfate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+)—make up over 99 percent of all of seawater’s solutes. The addition of five more solutes to the list—bicarbonate (HCO_3^-), bromide (Br^-), boric acid (H_3BO_3), strontium (Sr^{2+}), and fluoride (F^-)—elevates the quantity of dissolved ingredients in seawater to 99.99 percent (see Table 5-1). This means, of course, that everything else dissolved in seawater occurs in trace amounts and collectively comprises only 0.01 percent! But what appears to be insignificant cannot be ignored, because, even in tiny quantities many of these chemicals are absolutely critical for life in the ocean. Because the concentrations of these **major constituents** in seawater vary little over time at most localities, they are described as **conservative ions** of the ocean.



SCIENCE BY NUMBERS

Parts per Thousand

For those who are not acquainted with such measures, the expression parts per thousand (ppt) may seem mysterious. This measure of concentration is, actually, quite simple to understand, provided you spend a few moments learning and thinking about its meaning.

Let's begin by measuring the concentration of red marbles in a large vat filled with red, blue, yellow, and green marbles. A direct way to do this is to take a random collection of marbles in a bucket and count the marbles of each color that you sample. You do this until you have counted 1,000 marbles and you get the following results:

red marbles	112
blue marbles	464
green marbles	416
yellow marbles	8
Total	1,000 marbles

A convenient way to report these results is in parts per thousand. In other words, the red marbles appear in a concentration of 112 parts per thousand (ppt), meaning that, out of one thousand marbles, 112 are colored red. The concentrations of the others are: blue marbles 464 ppt, green marbles 416 ppt, and yellow marbles 8 ppt. It is that simple.

The conversion of ppt into a percentage is as straightforward. You simply divide the concentration of each colored marble by 1,000 and multiply the result by 100 to get the percentage value. Let's do this for the red and yellow marbles in our example.

$$\text{Red marbles: } (464/1,000)(100)\% = (464/10^3)(10^2)\% = 4 \times 10^{(2-3)}\% \\ = 464 \times 10^{-1}\% = 46.4\%$$

$$\text{Yellow marbles: } (8/1,000)(100)\% = (8/10^3)(10^2)\% = 8 \times 10^{(2-3)}\% \\ = 8 \times 10^{-1}\% = 0.8\%$$

This means that 464 ppt is equivalent to 46.4% and 8 ppt to 0.8%. A salinity of 35‰ (ppt) means that the salt by weight comprises 3.5% of the seawater sample. This, in turn, implies that 97.5% of the weight is made up of water molecules in the sample. Can you provide the calculations to bear this out?

TABLE 5-1

Major solutes in seawater

Salt Ion	Ions in Seawater* (%*)	Ions by Weight (%)	Cumulative (%)
Chloride (Cl^-)	18.980	55.04	55.04
Sodium (Na^+)	10.556	30.61	85.65
Sulfate (SO_4^{2-})	2.649	7.68	93.33
Magnesium (Mg^{2+})	1.272	3.69	97.02
Calcium (Ca^{2+})	0.400	1.16	98.18
Potassium (K^+)	0.380	1.10	99.28
Bicarbonate (HCO_3^-)	0.140	0.41	99.69
Bromide (Br^-)	0.065	0.19	99.88
Boric acid (H_3BO_3)	0.026	0.07	99.95
Strontium (Sr^{2+})	0.013	0.04	99.99
Fluoride (F^-)	0.001	0.00	99.99
Total	34.482	99.99	99.99

*The gram weight of ions per 1 kg of seawater, or g/kg.

Source: Adapted from H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, *The Oceans* (Englewood Cliffs, N.J.: Prentice-Hall, 1942).

NUTRIENTS

Nutrients are essential for plant growth, as anybody who has fertilized a lawn or garden knows. All plants, including those that live in the ocean, convert nutrients into food (organic compounds such as sugar) by photosynthesis. Nutrients in seawater are compounds that consist primarily of nitrogen (N), phosphorous (P), and silicon (Si). Representative concentrations of these nutrients in the ocean are listed in **Table 5–2**; note that the concentrations are specified in **parts per million (ppm)**. Most plants cannot use elemental nitrogen and phosphorus and so satisfy their nutrient needs by absorbing phosphate (PO_4^{3-}) and nitrate (NO_3^-). Silicon is used by important groups of microscopic plants (diatoms) and animals (radiolaria) to precipitate silica (SiO_2) shells around their fragile cells. Because of biological uptake and release, the concentrations of nutrients in seawater, as on land, vary from place to place and over time at any one place. Hence, oceanographers refer to these substances as **non-conservative ions** of seawater, signifying that levels of these substances are not constant in water, but vary over time and from place to place.

GASES

Listed in order of decreasing abundance (**Table 5–3**), gases in seawater include nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), hydrogen (H_2), and the noble gases argon (Ar), neon (Ne), and helium (He). Nitrogen and the three noble gases are **inert** (unreactive) and rarely involved directly in plant photosynthesis. In contrast, levels of dissolved O_2 and CO_2 are greatly influenced by photosynthesis and respiration of organisms. Therefore, they vary greatly in space and time depending on the activities of plants and animals and are regarded as nonconservative.

TABLE 5–2

Near-surface nutrient concentrations in seawater

Nutrient Element	Concentration (ppm)*
Phosphorus (P)	0.07
Nitrogen (N)	0.5
Silicon (Si)	3

*ppm = parts per million

TRACE ELEMENTS

Trace elements are all chemical ingredients that occur in minute (trace) quantities in the oceans. Most trace elements, such as manganese (Mn), lead (Pb), mercury (Hg), gold (Au), iodine (I), and iron (Fe), occur in concentrations of less than 1 ppm (part per million) (**Table 5–4**). Many occur in quantities of less than 1 **part per billion (ppb)** and even at 1 **part per trillion**. These low concentrations make certain trace elements difficult and sometimes even impossible to detect in seawater. However, despite their extremely low concentrations, trace elements can be critically important for marine organisms, either by helping to promote life or by retarding or killing life (**toxicity**).

ORGANIC COMPOUNDS

Organic compounds are large, complex molecules produced by organisms. They include substances such as lipids (fats), proteins, carbohydrates, hormones, and vitamins. Typically, they occur in low concentrations and are produced by **metabolic** (physical and chemical processes in the cell of an organism that produce living matter) and decay processes of organisms. For example, vitamin complexes are vital for promoting the growth of bacteria, plants, and animals, as shown by the control that thiamine and vitamin B_{12} have on the growth rate, size, and number of microscopic plants grown in laboratory experiments.

Now that we have a general understanding of the chemical makeup of seawater—a solution of mainly water with some salts, and tiny quantities of nutrients, gases, trace elements, and organic compounds—we can proceed to examine the nature of salinity and its effect on the properties of water, as well as the factors that control the saltiness of the ocean. In other words, why are the oceans salty, why are there variations in the salinity of the oceans, both on its surface and within its depths, and how does dissolved salt affect the physical properties of water? Answers to such questions are easy to grasp, provided that you understand the concepts just introduced. Also, the boxed feature, “Chemical Techniques,” reviews a few of the methods that chemists employ to measure the properties of seawater while at sea and in the laboratory.

TABLE 5-3

Quantities of gas in air and seawater

Gas	In Dry Air (%)	In Surface Ocean Water (%)	Water-Air Ratio
Nitrogen (N_2)	78.03	47.5	0.6
Oxygen (O_2)	20.99	36.0	1.7
Carbon dioxide (CO_2)	0.03	15.1	503.3
Argon (Ar), hydrogen (H_2), neon (Ne), and helium (He)	0.95	1.4	1.5

5-4



Salinity

A simple way to determine salinity is to evaporate water from a container of seawater and then compare the weight of the solid residue left behind in the bottom of the container—the salts—to the weight of the original sample of seawater. Unfortunately, the method is neither precise nor accurate, because salt crystals hold on to variable amounts of H_2O molecules, and that affects the weight of the salt residue. In order to compare accurately salinity data gathered from many parts of the ocean and measured in many different laboratories and ships, chemists have adopted a standardized and what seems to the non-chemists to be a rather cumbersome definition of **salinity**: the total mass expressed in grams of all the substances dissolved in 1 kilogram of seawater, when all the carbonate has been converted to oxide, all the bromine and iodine have been replaced by chlorine, and all organic compounds have been oxidized at a temperature of 480°C . Because we are not chemical oceanographers, we can simplify the definition of salinity as follows to suit our more general purpose: the total weight in grams of dissolved salts in 1 kilogram of seawater expressed as ‰ (parts per thousand).

PRINCIPLE OF CONSTANT PROPORTION

Salinity determinations from the world's oceans have revealed an important, unexpected finding. Although salinity varies quite a bit because of dif-

TABLE 5-4

Examples of trace elements in seawater

Trace Element	Concentration (ppb)*
Lithium (Li)	170
Iodine (I)	60
Molybdenum (Mo)	10
Zinc (Zn)	10
Iron (Fe)	10
Aluminum (Al)	10
Copper (Cu)	3
Manganese (Mn)	2
Cobalt (Co)	0.1
Lead (Pb)	0.03
Mercury (Hg)	0.03
Gold (Au)	0.004

* ppb = parts per billion

ferences in the total amount of dissolved salts, the relative proportions of the major constituents are constant. In other words, the ratio of any two major constituents dissolved in seawater, such as Na^+/K^+ or $\text{Cl}^-/\text{SO}_4^{2-}$, is a fixed value, whether the salinity is 25, 30, 35‰, or whatever. To put it in more familiar terms, let's imagine that the ratio of females to males in a population is $1/4$ (1 female for every 4 males) and that this ratio never changes regardless of population size. This means that the total number of people in the population can vary, but the *relative proportion* of females to males does not change. In other words, the ratio of females to males is constant and is independent of population size. Just so, the ratio of any two major salt constituents in ocean water is constant and is independent of salinity.

This important discovery, made during the *Challenger* expedition (see Figure 1–10 in Chapter 1), is termed the **principle of constant proportion** or **constant composition**, and was a major breakthrough in



Chemical Techniques

In trying to characterize and explain the chemical properties of seawater, marine chemists find it critically important to collect sufficient and appropriate seawater samples, prevent their chemical contamination, determine sampling depths, and use accurate and precise analytical procedures.

SAMPLE COLLECTION

Seawater samples for chemical analysis are collected in metallic or plastic cylindrical bottles. The metallic bottles have interior liners composed of inert plastic to prevent contamination of the sample by metal ions. One such sampling device, the Niskin bottle, has valves on both ends that are opened and attached to a cable (Figure B5-1). Typically, several open bottles are attached at predetermined positions on the cable. After the bottles are lowered, a weight, known as a *messenger*, is fastened to the cable and released. When the messenger strikes the first water bottle, it causes it to close tightly, trapping a sample of seawater. A messenger attached to a clamp beneath the first bottle is then released, dropping and triggering the next bottle below. The procedure is repeated until all the bottles on the cable have been closed. Depending on the nature of the study, chemists usually collect seawater volumes of between 1 and 3 liters (~1.06 and 3.17 quarts) with these bottle samplers.

A more elaborate sample-bottle configuration is known as the *rosette cluster*. It consists of a rigid frame that holds a number of collection bottles upright, arranged in a circular pattern (Figure B5-2). The bottles can be set to open and close automatically, or a technician can trigger any of the bottles electronically from a shipboard console.

FIGURE B5-1

Niskin bottles. Open Niskin bottles are attached to a cable and lowered to water depths where seawater samples are to be obtained for chemical analysis. A metal messenger “trips” each bottle on the cable individually, causing it to fill with water and close securely.

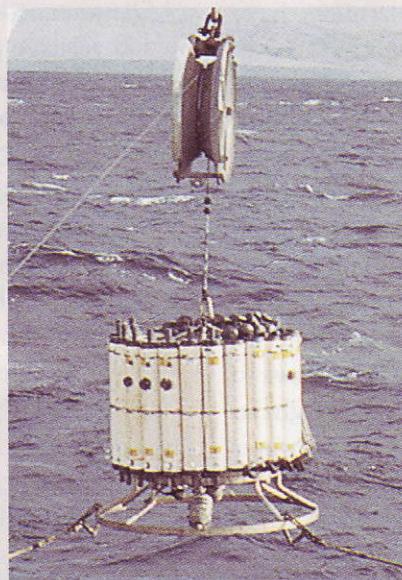


FIGURE B5-2

A rosette cluster. Water collecting bottles are arranged around a rigid, circular frame in a rosette pattern. Technicians are able to close the bottles individually as the array is lowered or raised through the water column.

SAMPLING DEPTHS

Chemists must establish the exact sampling depth for each bottle. Otherwise, the analytical work, no matter how accurate, is of limited use in determining the exact chemical structure of the water column. A common technique is to measure the length of the cable between the ocean surface and the depth at which the bottle was triggered by the messenger. However, the cable rarely hangs straight down,

because of the drift of the ship relative to the bottles on the cable. Depth corrections are applied by measuring the angle of the cable and by noting the difference between the temperature readings on the pressure-protected and unprotected thermometers mounted on the sampling bottles. (Temperature discrepancies are indicators of water pressure, which is a function of water depth.) When near-bottom water samples are collected, it is customary to

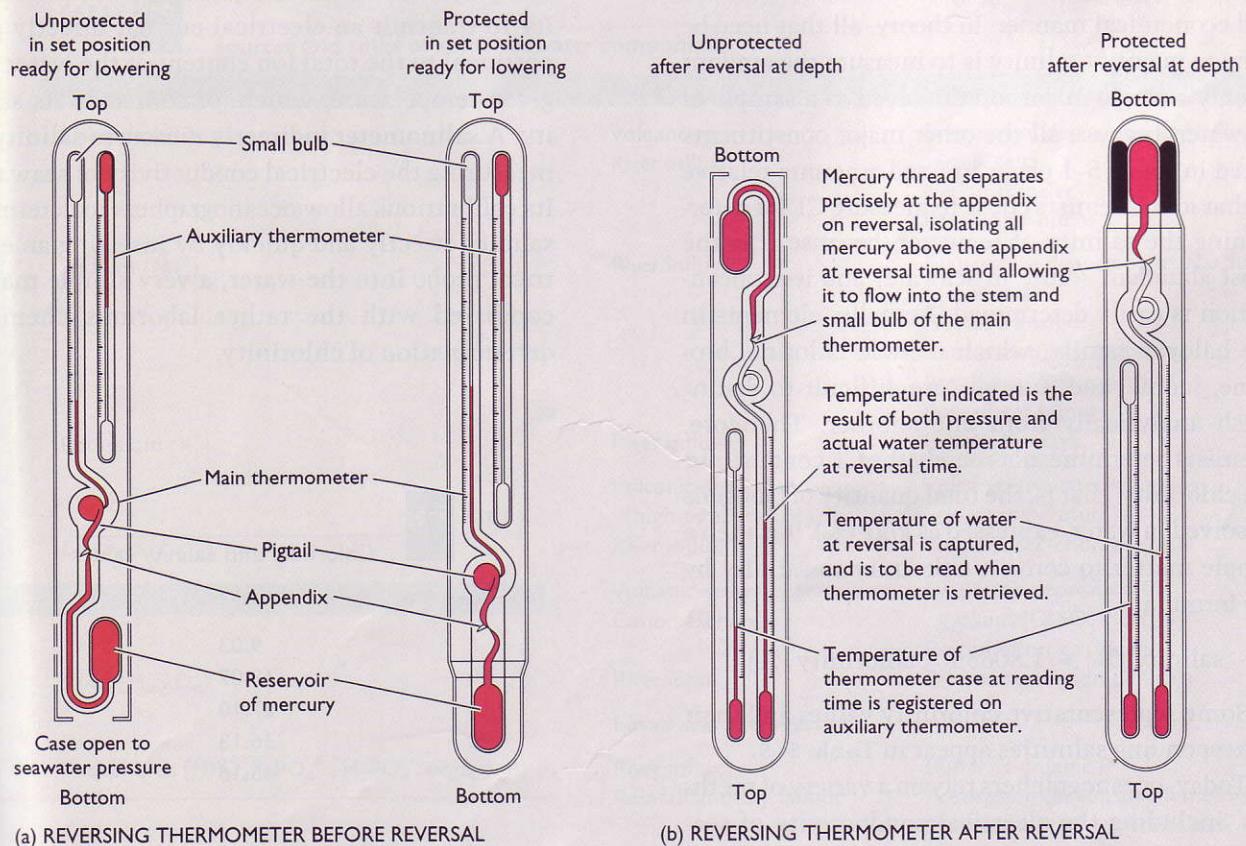
attach a *pinger* (a pulsing sound source) to the free end of the cable. Sound signals reflected off the sea floor and transmitted to the ship are used to determine the distance between the pinger and the bottom to within a meter or so.

ANALYTICAL PROCEDURES

Analytical procedures reveal temperature and salinity of water. Reversing thermometers, which are fastened

FIGURE B5-3

Reversing thermometers. Attached to each sampling bottle are thermometers that become reversed when the bottle is “tripped” by the messenger. The reversal breaks the column of mercury, preserving the temperature of the water at the sampling site. Protected and unprotected thermometers are shown, each with an auxiliary thermometer. (a) Thermometers are shown as they are lowered on a cable. (b) Thermometers are shown in the reverse position. [Adapted from A. C. Duxbury and A. Duxbury, *The World's Oceans* (Reading, Mass.; Addison-Wesley, 1984).]



to water-sampling bottles, are used to measure the temperature of water *in situ*. When the messenger strikes the bottle, either the bottle flips over or the thermometers themselves turn upside down. The inversion causes the mercury in the thermometer stem to separate from a large reservoir (Figure B5–3). This isolated volume of mercury then can be related to the *in situ* temperature of the water at the sampling depth by means of the auxiliary thermometer, even though both thermometers pass through water that varies in temperature as they are hauled back up to the surface. Better precision (up to 0.0001°C) is obtained

by using temperature-sensitive materials, such as quartz crystals, which vibrate at frequencies that depend on temperature. These signals are transmitted electronically to the ship. This allows the temperature of the water to be monitored continuously as the instrument is lowered.

Because the composition of seawater is constant, chemists traditionally have determined water *salinity* by chemical titration—the process of standardizing silver nitrate against a normal seawater sample of known chemical composition. The electrical conductivity of seawater, which is proportional to the total concentration of dissolved

ions, is now used routinely to determine salinity rapidly. The salinometer compares the electrical conductivity of an unknown sample with that of a known, standard sample of seawater, and converts the difference into a salinity value after correcting for temperature effects. An important instrument called the CTD (conductivity, temperature, depth) consists of a salinometer, an electronic thermometer, and a pressure sensor. As it is lowered through the water column, the CTD transmits electronic signals to the ship, where they are stored in a shipboard computer for analysis later.

determining salinity of seawater in a rapid, accurate, and economical manner. In theory, all that need be done to quantify salinity is to measure the amount of only a single major ion dissolved in a sample of seawater, because all the other major constituents listed in Table 5–1 occur in fixed amounts relative to that ion. Chemists chose to measure Cl^- for determining the salinity of seawater, because it is the most abundant solute in seawater and its concentration is easily determined. Actually, elements in the halogen family, which include chlorine, bromine, iodine, and fluorine, are difficult to distinguish analytically from one another. Therefore, chemists determine, not merely the Cl^- content, but the **chlorinity**, that is, the total quantity of halogens dissolved in water, expressed as g/kg (%). It is then a simple matter to convert chlorinity to salinity by the formula

$$\text{salinity (\%)} = 1.80655 \times \text{chlorinity (\%)}.$$

Some representative chlorinity values and their corresponding salinities appear in Table 5–5.

Today, oceanographers rely on a variety of methods, including the electrical conductivity of seawater, to make routine determinations of salinity.

The electrical conductivity of a solution is its ability to transmit an electrical current directly proportional to the total ion content of the water at a given temperature, which, of course, is its salinity. A **salinometer** indirectly measures salinity by measuring the electrical conductivity of seawater. Its calibrations allow oceanographers to determine salinity directly and quickly by inserting an electrical probe into the water, a very simple matter compared with the rather laborious chemical determination of chlorinity.

TABLE 5–5

Chlorinity and salinity values

Chlorinity (%)	Salinity (‰)
5	9.03
10	18.07
15	27.10
20	36.13
25	45.16

FACTORS THAT REGULATE THE SALINITY OF SEAWATER

There is a lot of dissolved salt in the ocean. An important question is, what supplied all this material to the sea? The answer is straightforward (**Table 5–6**). Rivers disgorge huge volumes of freshwater into the ocean every year. Chemical analyses of water samples from rivers all over the world indicate that they contain a variety of dissolved substances in concentrations of ppm (**Table 5–7**). Rivers have a dissolved load of chemicals because of the chemical weathering of rocks on the land. These rocks are made up of an assemblage of minerals composed predominantly of the elements silicon, aluminum, and oxygen. Acidic water breaks down these rocks into their component elements. When carbon dioxide (CO_2) is dissolved in water, it reacts with H_2O molecules to produce H_2CO_3 , a weak acid called **carbonic acid**. In turn this acid separates into hydrogen (H^+) and **bicarbonate**

(HCO_3^-) ions. The specific chemical reactions are reversible, are quite simple and are represented by



Notice that the reaction yields free ions of H^+ , which because of their small size and high chemical reactivity, replace cations such as Na^+ and K^+ that are bound to minerals in rocks. The amount of H^+ is a measure of the acidity of the water. This process—the bathing of rocks in acidic water—slowly weathers minerals, releasing ions, which go into solution and become part of a river's dissolved chemical load (Table 5–7).

Let's firm up our understanding of weathering by examining the chemical breakdown of an actual mineral, **orthoclase** (KAlSi_3O_8), the common potassium-bearing feldspar of granite. The chemical reaction is

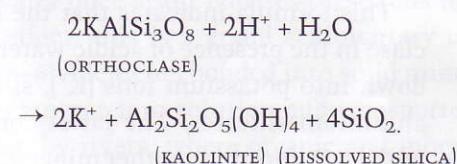


TABLE 5–6

Sources and sinks of some seawater components

Chemical Component	Sources	Sinks
Chloride (Cl^-)	Volcanoes River influx	Evaporative deposition as NaCl (rock salt) Net air transfer Pore-water burial
Sodium (Na^+)	River influx	Evaporative deposition as NaCl (rock salt) Net air transfer Cation exchange with clays Basalt-seawater reactions Pore-water burial
Potassium (K^+)	River influx	Uptake by clays
Calcium (Ca^{2+})	Volcanic-seawater reactions (high temperature) River influx	Volcanic-seawater reactions (low temperature) Biogenic secretion of shells
Silica (H_4SiO_4)	River influx Basalt-seawater reactions	Evaporitic deposition of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) Precipitation as calcite Biogenic secretion of shells
Phosphorus (HPO_4^{2-} , PO_4^{3-} , H_2PO_4^- , organic P)	River influx Rainfall and dry fallout	Burial as organic P Adsorption on volcanic ferric oxides Formation of phosphorite rock

Source: Adapted from E. K. Berner and R. A. Berner, *The Global Water Cycle* (Englewood Cliffs, N.J.: Prentice-Hall, 1987).

TABLE 5-7

Dissolved substances in river water

Substance	Concentration (ppm)	Concentration (%)
Bicarbonate/carbonate ($\text{HCO}_3^-/\text{CO}_3^{2-}$)	58.8	48.7
Calcium (Ca^{2+})	15.0	12.4
Silica (SiO_2)	13.1	10.8
Sulfate (SO_4^{2-})	1.2	9.3
Chloride (Cl^-)	7.8	6.5
Sodium (Na^+)	6.3	5.2
Magnesium (Mg^{2+})	4.1	3.4
Potassium (K^+)	2.3	1.9
Nitrate (NO_3^-)	1.0	0.8
Iron aluminum oxide $[(\text{Fe}, \text{Al})_2\text{O}_3]$	0.9	0.8
Remainder	0.3	0.3

Source: D. A. Livingstone, Chemical composition of rivers and lakes, U.S. Geological Survey, Professional Paper 440-G (U.S. Government Printing Office, 1963).

This formula indicates that the mineral orthoclase in the presence of acidic water (H^+) is broken down into potassium ions (K^+), silica (SiO_2), and aluminum silicates. The latter compound bonds with H_2O , forming another mineral, the clay **kaolinite**. Rivers transport these materials to the ocean in two distinct states: as a **dissolved load** (K^+ and SiO_2) and as a **suspended load** (particles of kaolinite). The dissolved K^+ and SiO_2 contribute to the salinity of seawater; the clay accumulates as sediment on the ocean floor (see Figure 4–16a in Chapter 4). So what was a solid mineral in rocks on land becomes, by the processes of chemical weathering and transport, dissolved salts in the ocean and mud on the sea bottom.

How much mass is actually added to the ocean by the river influx of dissolved matter? The first response by most people is that the amount could not be much, because the concentration of solutes in rivers is low (that's why freshwater doesn't taste salty), and it's dissolved, so you can't see it (how can anything that can't be seen amount to much?). It turns out that the annual river input of material in solution to the oceans is somewhere between 2.5×10^{15} and 4×10^{15} grams. True, 10^{15} (10 multiplied by itself fifteen times) seems to be quite a big number. But how big is it, really? This rate of influx, 10^{15} grams per year, is about equivalent to the mass of mud supplied each year to the oceans by the rivers of North America, South America, Africa, and Europe combined! Although dissolved material is invisible to the naked eye, it represents

a major annual input of mass to the oceans, all of it derived by the chemical weathering of rocks on land. In addition to the supply from rivers, the Earth is degassing. This means that volcanoes on the crests of spreading ocean ridges and in the volcanic arcs of subduction zones spew out large quantities of cations (including Ca^{2+} and K^+) and anions (including SO_4^{2-} and Cl^-) into the water column, although the exact amount of this input has yet to be determined reliably.

The fossil record and sedimentary rocks themselves indicate that oceans have existed on the Earth for at least as long as 3.4 billion years. Geochemical data indicate that the salinity of the oceans has changed little over the past 1.5 billion years. This constant ocean salinity despite the tremendous annual supply of dissolved chemicals to the oceans by rivers can only mean that on average a similar quantity of salt must be removed from the oceans each year. Otherwise, the salinity of the world's oceans would have increased over geologic time. This balance between inputs and outputs of salt to the ocean is called a **steady-state equilibrium**.

Oceanographers refer to inputs of material as **sources** and their outputs as **sinks**. We've already identified several of the principal sources of the salt ions to the ocean. Let's now examine the principal sinks of dissolved salt in the ocean (see Table 5–6). The removal of salt occurs by both inorganic and organic processes. Evaporation is an excellent example of an inorganic process and, as discussed

in the boxed feature, "Desalination," is a technique for producing drinkable water from seawater. In arid climates, evaporation rates are high. Evaporation removes water from the ocean, but not the dissolved salt ions. This indicates that, with time, the concentration of salt will rise by the evaporation of water molecules, creating a **brine**, or a very salty solution. The Dead Sea and the Great Salt Lake, both in arid settings, are fine examples of this very process. As more and more water molecules are evaporated from the water, the solution eventually becomes saturated, which means that the solution is holding as much material in a dissolved state as it can for the temperature and pressure conditions of the water. The removal of more water creates a **supersaturated** solution (a solution containing a quantity of dissolved ions that exceeds the theoretical saturation value). This leads to the precipitation of **evaporite** minerals from seawater, notably halite (NaCl) and gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$). Precipitation of evaporite minerals from seawater represents a sink, because dissolved salt ions are being removed from the ocean to form sedimentary deposits on the seafloor.

Wind also blows onshore a large amount of sea spray, which on evaporation, forms a coating of salt on land—as anybody who wears glasses and lives by the seashore can attest. In addition, freshly extruded basalt lavas on the ocean floor are quite reactive and extract dissolved ions, such as Mg^{2+} and SO_4^{2-} , from the seawater that comes in contact with the hot lava. Finally, **adsorption** (the "sticking" of ions to a surface) of cations like K^+ and Mg^{2+} by certain clay minerals in the ocean and the formation of authigenic minerals, such as ferromanganese nodules (see Chapter 4), remove a large, unknown quantity of ions from the sea. All of these represent chemical sinks for ions dissolved in seawater.

Organisms help maintain the steady-state equilibrium of the ocean's salinity as well. We already know that diatoms have silica shells and forams carbonate shells that are precipitated from the uptake of Si^{4+} and Ca^{2+} , respectively, from seawater. Once these organisms die, their hard parts may settle to the sea bottom to form deep-sea oozes (see Figure 4–16a in Chapter 4). Also, many species of animals extract certain chemical substances that are dissolved in seawater. Some of these chemicals are concentrated in fecal pellets that sink to the ocean floor and become incorporated in sediment.

Let's synthesize all that we have learned about steady-state equilibrium, sources and sinks of salt ions, and geologic cycles. The salt ions dissolved in ocean water are derived largely from the weathering and erosion of rocks on land. Because the average chemical composition of seawater has remained remarkably stable (in a steady state) over geologic time, the inputs of salt must be balanced by the outputs. The river-supplied ions remain in ocean water for a long time, but eventually are extracted by inorganic and organic processes and become part of the ocean's sedimentary record. These sediments, as they are buried, become cemented into sedimentary rocks and eventually are subducted along the colliding boundaries of lithospheric plates. Some of these sedimentary units are melted and intruded as igneous rocks, others are crumpled and raised into large mountain belts, where chemical attack by acidic water once again releases these ions to the sea. In effect, this is a grand sedimentary cycle (Figure 5–6). Elements bonded into solid minerals in rocks are put into solution and transported to the ocean by rivers, where organic and inorganic processes cause them to be precipitated into solids (such as halite, and silica and carbonate shells) and reincorporated into sedimentary rocks that become uplifted by tectonic processes and weathered once again, repeating this grand cycle.

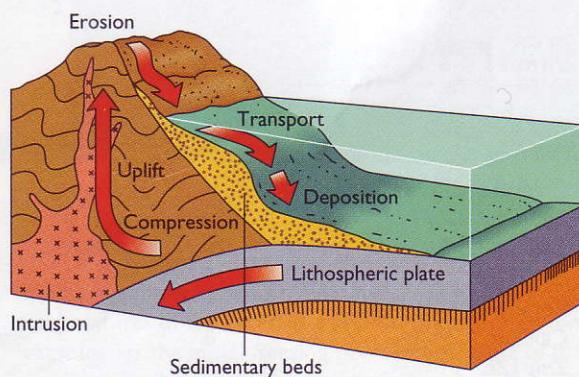


FIGURE 5–6

Sedimentary cycle. Over geologic time, mountains are leveled by rivers. The weathering products are dispersed into the ocean and collect on the sea bottom, forming sedimentary beds. Eventually, these accumulations of sediment are deformed and uplifted into mountain ranges by plate tectonics. Then a new cycle of river erosion begins.

If rivers are the primary source of salt ions to the oceans, why aren't the ionic compositions of freshwater and seawater similar? They clearly are not, as a comparison of Tables 5–1 and 5–7 shows. Shouldn't they be, if one is supplying material directly to the other? The difference in the relative composition of solutes in seawater and river water is a result of the **residence time** of ions in the ocean, which is simply the average length of time that an ion remains in solution there. It ranges between 2.6×10^8 years for sodium and 1.5×10^2 years for aluminum (Table 5–8). This is no different from saying that your "residence time" in your bedroom, asleep in bed, is eight hours a day. Note that the two most abundant components of seawater (Na^+ and Cl^-) have long residence times, on the order of hundreds of million years. Their persistence in a dissolved state in ocean water reflects their low geochemical and biochemical reactivity; in other words, they are essentially inert. (To carry our analogy one step further, an inert, listless person would tend to spend more time in bed and have a longer residence time in the bedroom than would an active, alert person.) By contrast, many of the principal ions in river water are characterized by short residence times in the oceans because they are much more reactive or are important for biological cycles. For example, many marine organisms require dissolved Ca^{2+} to secrete their carbonate (CaCO_3) shells. These calcium ions are in constant

demand by the marine biota, so calcium has a relatively low residence time of 8×10^6 years.

Long residence times also help to explain the principle of constant proportions. Water is stirred and mixed by ocean currents, much as stirring a pot of soup with a spoon creates eddies and swirls (turbulence) that mix the ingredients. Studies of currents indicate that mixing rates in the oceans are on the order of a thousand (10^3) years or less. This rate is much lower than are the residence times of the major ions of seawater, which range from millions (10^6) to hundreds of millions (10^8) of years (see Table 5–8). Thus, rapid mixing and very long residence times of salt ions in seawater assure that these substances are distributed uniformly throughout the oceans. A more familiar way to think about this is to imagine yourself making a cake. Slowly adding dye along the edge of a bowl (this is equivalent to a river supplying ions at the edge of an ocean basin) to a cake batter that is being rapidly stirred by an electric beater (this is equivalent to mixing by ocean currents) quickly distributes the dye molecules evenly throughout the batter, so that its color (this is equivalent to the ocean's salinity) is uniform (Figure 5–7).

EFFECTS OF SALINITY ON THE PROPERTIES OF WATER

In the previous sections, we learned a great deal about the structure of the water molecule and the salinity of the ocean. A few other important properties of water are reviewed in the boxed feature, "Other Physical Properties of Water." Now we are ready to examine the effect dissolved ions have on the physical properties of water. As you might guess, the addition of salt modifies some of the properties of water in a number of significant ways. Most of these changes come about because the ions are hydrated (see Figure 5–4), which modifies the chemical behavior of the H_2O molecules in the solution. Let me explain by examining some specific water properties as they are affected by solutes.

FREEZING POINT

Pure freshwater freezes at 0°C . The addition of salt to the water lowers its freezing point. For example,

TABLE 5-8

Residence in ocean waters

Substance	Residence Time ($\times 10^6$ yr)
Chloride (Cl^-)	∞
Sodium (Na^+)	260
Lithium (Li^+)	20
Strontium (Sr^{2+})	19
Potassium (K^+)	11
Calcium (Ca^{2+})	8
Zinc (Zn^{2+})	0.18
Barium (Ba^{2+})	0.084
Cobalt (Co^{2+})	0.018
Chromium (Cr)	0.00035
Aluminum (Al)	0.00015

Source: Adapted from C.K. Wentworth, A scale of grade and class terms for clastic sediments, *Journal of Geology* 30, (1922): 377–92.

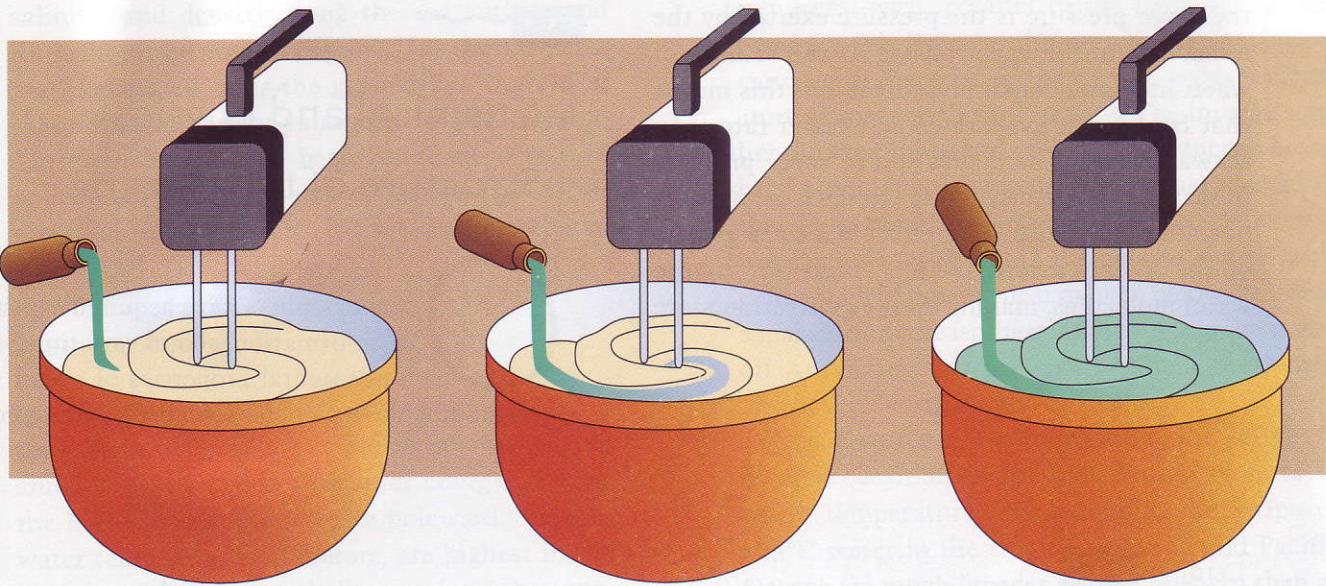


FIGURE 5-7

Rapid mixing spreads dye evenly throughout the cake batter.

seawater with a salinity of 35‰ freezes at a temperature of -1.91°C (Figure 5-8). The reason that the freezing temperature of seawater is depressed relative to that of freshwater is quite simple. The hydrated salt ions “hold on” to individual H_2O molecules, interfering with their rearrangement into an ordered ice crystal.

DENSITY

Because solutes have a greater atomic mass than do H_2O molecules, the density of water increases with salinity. This means that freshwater floats on salt water. For salinities $>24.7\%$ (see Figure 5-8), the temperature of maximum density (3.98°C for freshwater; see Figure 5-5b) is below the freezing point (0°C).

VAPOR PRESSURE

The vapor pressure on a liquid surface is the pressure exerted by its own vapor. When a liquid such as water is placed in a closed container, some of the molecules will vaporize, decreasing the amount of liquid. Once equilibrium is reached,

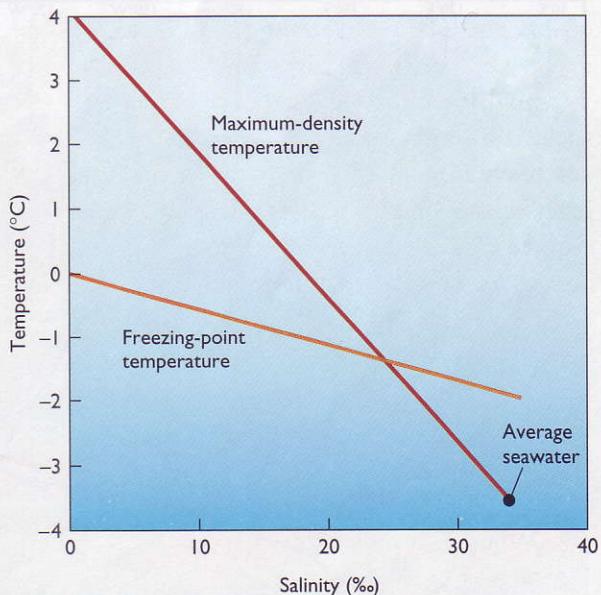


FIGURE 5-8

Effects of salinity on the maximum-density and freezing-point temperatures of seawater. The addition of dissolved ions to water lowers the initial freezing point temperature of the solution because the hydrated ions interfere with the rearrangement of the H_2O molecules into an ordered ice structure. Also, an increase in salinity depresses the maximum-density temperature of seawater. Consequently, the temperature of maximum-density of average seawater is well below its freezing point. This means that seawater of average salinity will freeze before it will sink.

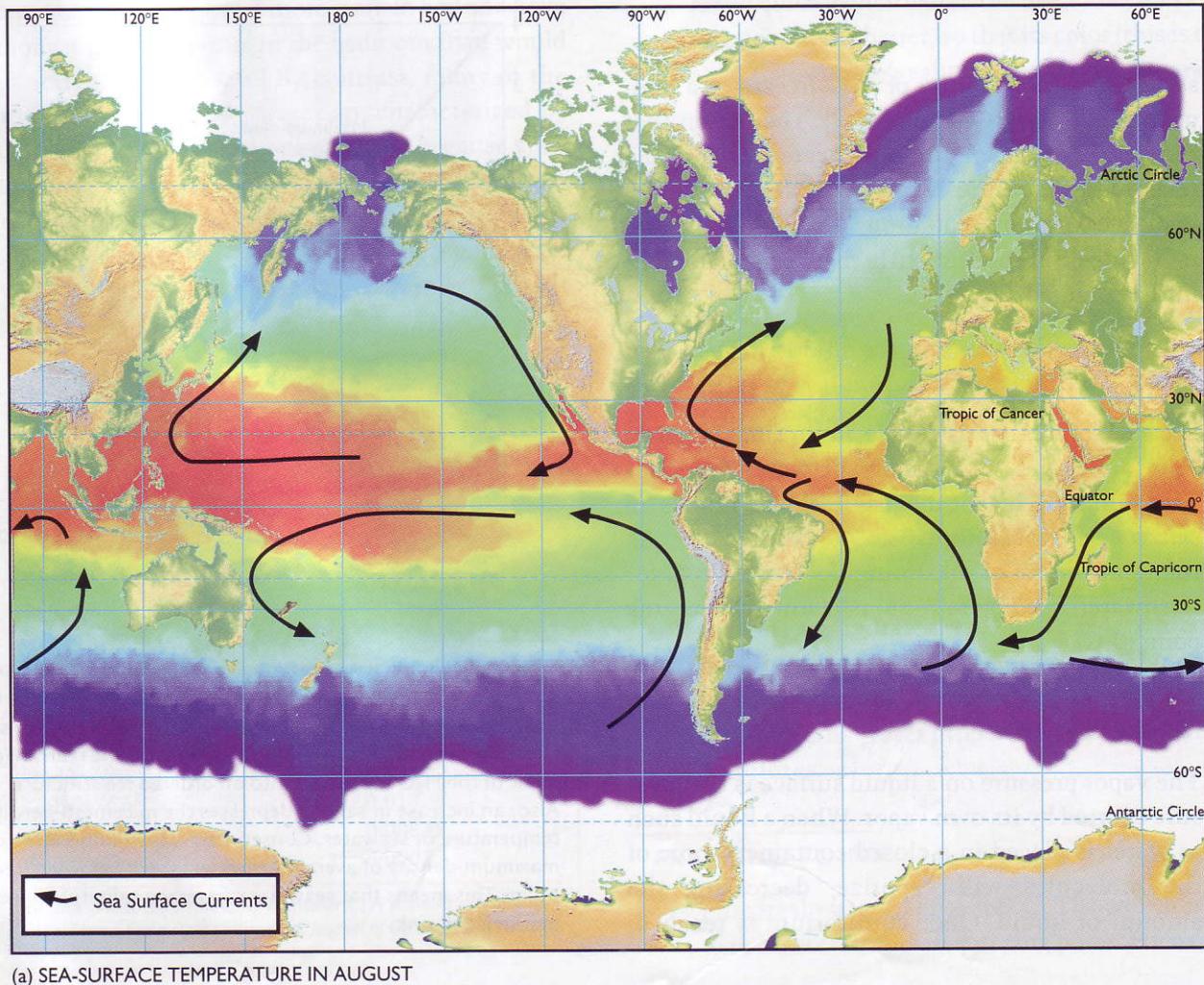
the vapor pressure is the pressure exerted by the molecules in the vapor phase. As the salinity of water increases, vapor pressure drops; this means that freshwater evaporates at a faster rate than seawater does. The depression of vapor pressure in seawater is directly related to the total number of solute molecules. This effect is a consequence of the hydrated ions, which "hold on" to the water molecules, making their vaporization more difficult.

Chemical and Physical Structure of the Oceans

Oceanographers have acquired a great deal of information about variations in the fundamental properties of ocean water, including the regional distribution of temperature,

FIGURE 5-9

Sea-surface temperatures. Because water is heated by the sun, and solar radiation decreases with distance from the equator, sea-surface temperatures vary directly with latitude. Large-scale ocean circulation transports warm water poleward at the western edges of the ocean basins and cold water equatorward at their eastern peripheries. (a) Global sea-surface temperature (SST) is shown for August. (b) Global SST is shown for February. [Adapted from H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, *The Oceans* (Englewood Cliffs, N.J.: Prentice-Hall, 1942).]



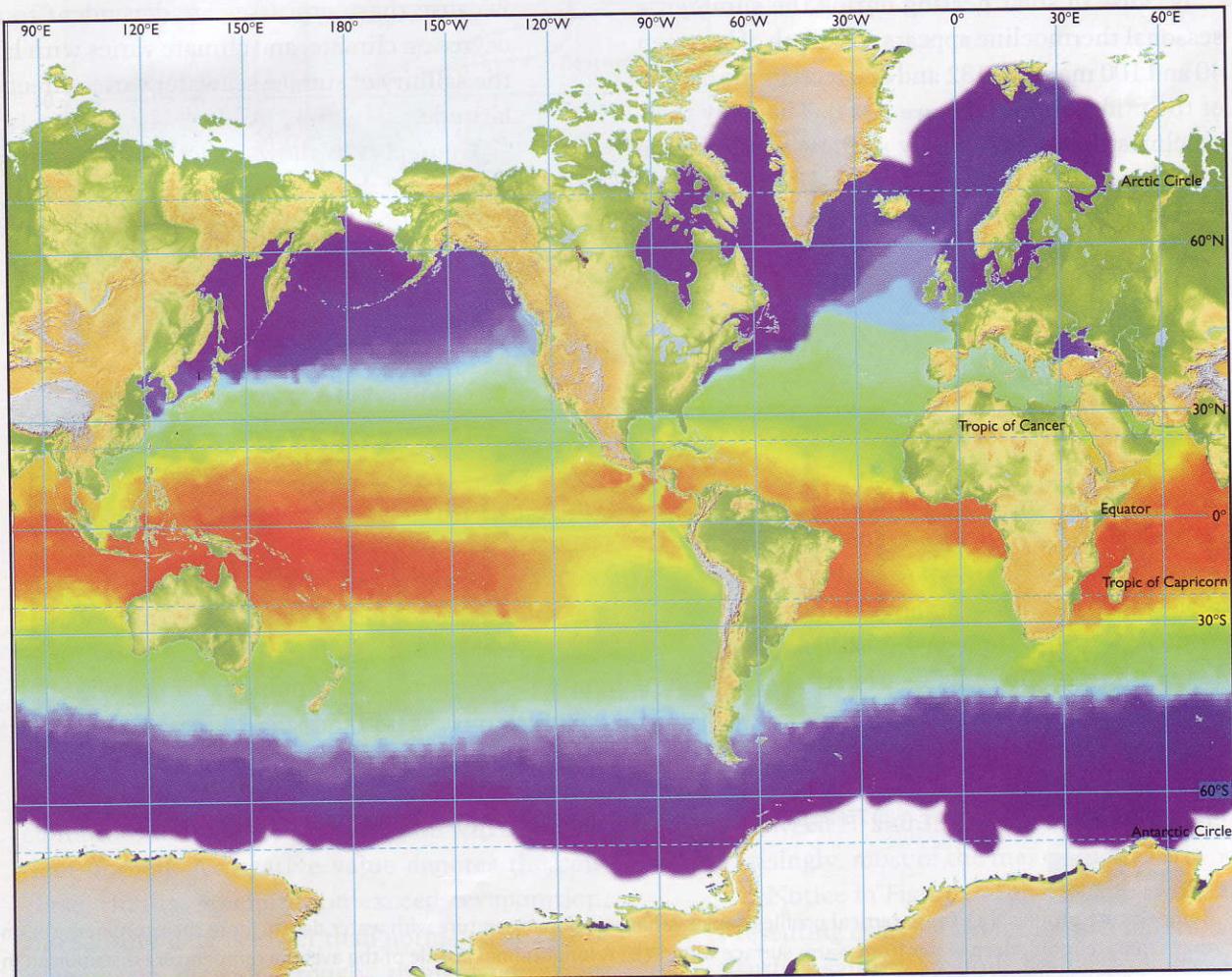
salinity, and density along the sea surface and throughout the ocean's depths. This section summarizes and explains the general distribution of these three important parameters of ocean water. This will provide the background necessary to understand variations in the ocean's content of gases, the important topic of the following section.

TEMPERATURE

Latitude (Appendix IV) exerts a strong control on the surface temperature of the ocean, because the amount of **insolation** (the solar energy striking the Earth's surface) decreases poleward. Surface-water temperatures, therefore, are highest in the tropics and decrease with distance from the equator. **Isotherms**, imaginary contour lines that connect points of equal water temperature, generally

trend east-west, parallel to the lines of latitude (**Figure 5-9**). Because the amount of insolation varies with the seasons, the surface-water temperature changes with time as well. The intense sunlight in the tropics and subtropics produces a broad band of water with a temperature higher than 25°C that shifts north or south depending on the season (see Figure 5-9). Water in the polar oceans is very cold, much of it being near or even below 0°C. Seasonal shifts of the isotherms are minor in the ocean off Antarctica, but are significant in the North Pacific and North Atlantic Oceans.

Ocean currents that flow around the periphery of each ocean affect the distribution of surface-water temperature. For example, the strips of >25°C water in the tropical Atlantic and Pacific Oceans are much broader at their western than at their eastern margins. This distortion is produced by currents that move warm water poleward along



(b) SEA-SURFACE TEMPERATURE IN FEBRUARY

the western side of oceans and cold water equatorward along their eastern sides (see Figure 5–9).

Investigations of water temperature with water depth reveal that the oceans in the middle and lower latitudes have a layered thermal structure (Figure 5–10). A layer of warm water, several hundred to a thousand meters thick, floats over colder, denser water that fills up the rest of the basin. The two water masses are separated from each other by a band of water that has a sharp temperature gradient (meaning that temperature changes rapidly with depth); it is called the **thermocline** (see Figure 5–10). The thermocline is a permanent hydrographic feature of temperate and tropical oceans, and ranges in water depth between 200 and 1,000 meters (~660 to 3300 feet). Surprisingly, in terms of volume, the most typical water of the tropics is not the warm, thin surface-water layer so familiar to sailors and tourists, but the deeper water below the thermocline, where temperatures are near freezing even at the equator!

Because of solar heating during the summer, a seasonal thermocline appears at a depth of between 40 and 100 meters (~132 and 330 feet) in the oceans of the mid-latitudes (Figure 5–11). The daily thermoclines that occur at very shallow water depths (<12 meters; ~39 feet) are diurnal. Unlike the surface water, where temperature changes with the

hour, the day, and the season, water below the permanent thermocline maintains a low, stable temperature over time, averaging <4°C for most of the ocean (see Figure 5–10).

SALINITY

The salinity of the ocean's surface water, although more complicated in detail than the pattern of the sea-surface temperature, also shows a clear latitudinal dependence (Figure 5–12a). The highest salinity values occur between 20 and 30 degrees north and south latitude and decrease toward the equator and the poles. Salinity variations are caused by the addition or removal of H₂O molecules from seawater. Processes that remove H₂O molecules from seawater include evaporation and the formation of ice. Precipitation (rain, snow, sleet), river runoff, and ice melting add H₂O molecules, diluting the salinity of seawater and reducing its density. Because these processes are dependent to a large degree on climate, and climate varies with latitude, the salinity of surface seawater varies directly with latitude.

Figure 5–12b shows exactly how ocean salinity changes with latitude. Maximum salinity values occur in the subtropics and minimum values near

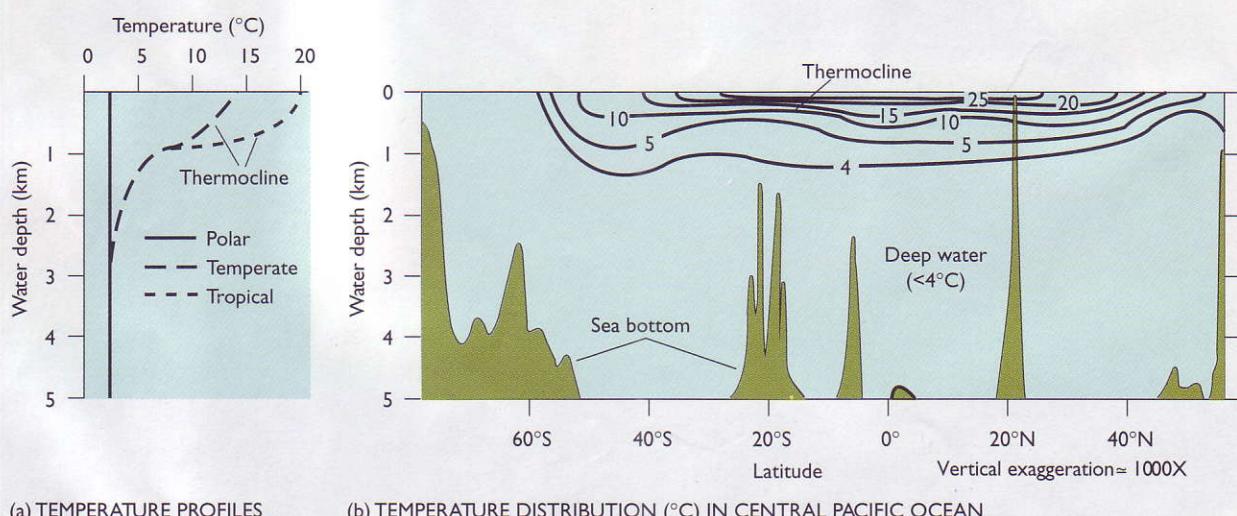
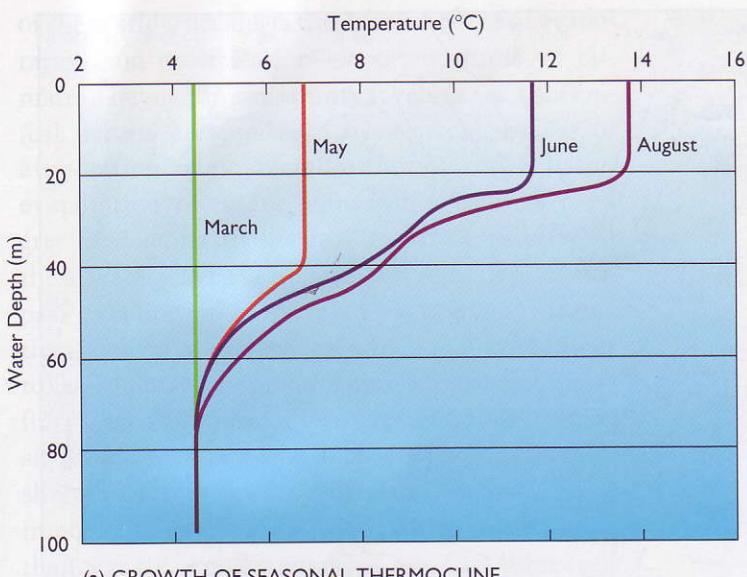
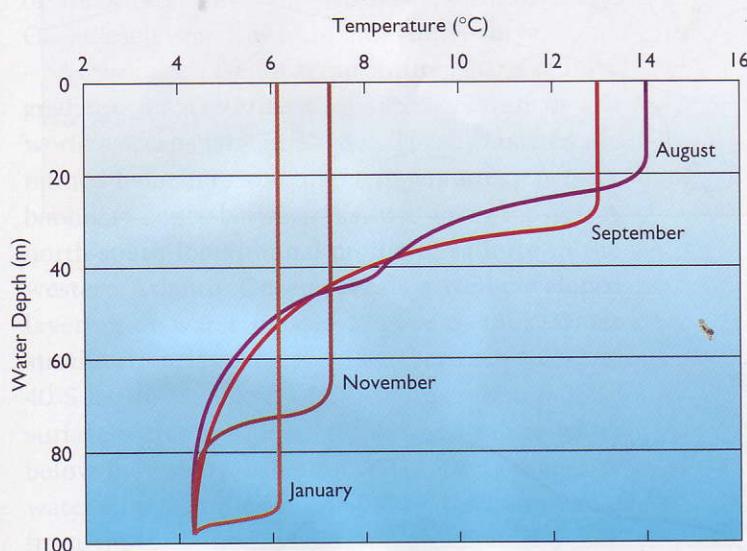


FIGURE 5-10

Temperature profiles. (a) These vertical profiles depict variations of temperature with water depth. Note the prominent thermocline that separates cold, deep water from warm surface water. (b) A longitudinal profile of the average temperature distribution in the Pacific Ocean indicates that the bulk of all ocean water is colder than 4° Celsius. [Adapted from J. L. Reid, Jr., *Intermediate Waters of the Pacific Ocean* (Baltimore: Johns Hopkins Press, 1965).]



(a) GROWTH OF SEASONAL THERMOCLINE



(b) DECAY OF SEASONAL THERMOCLINE

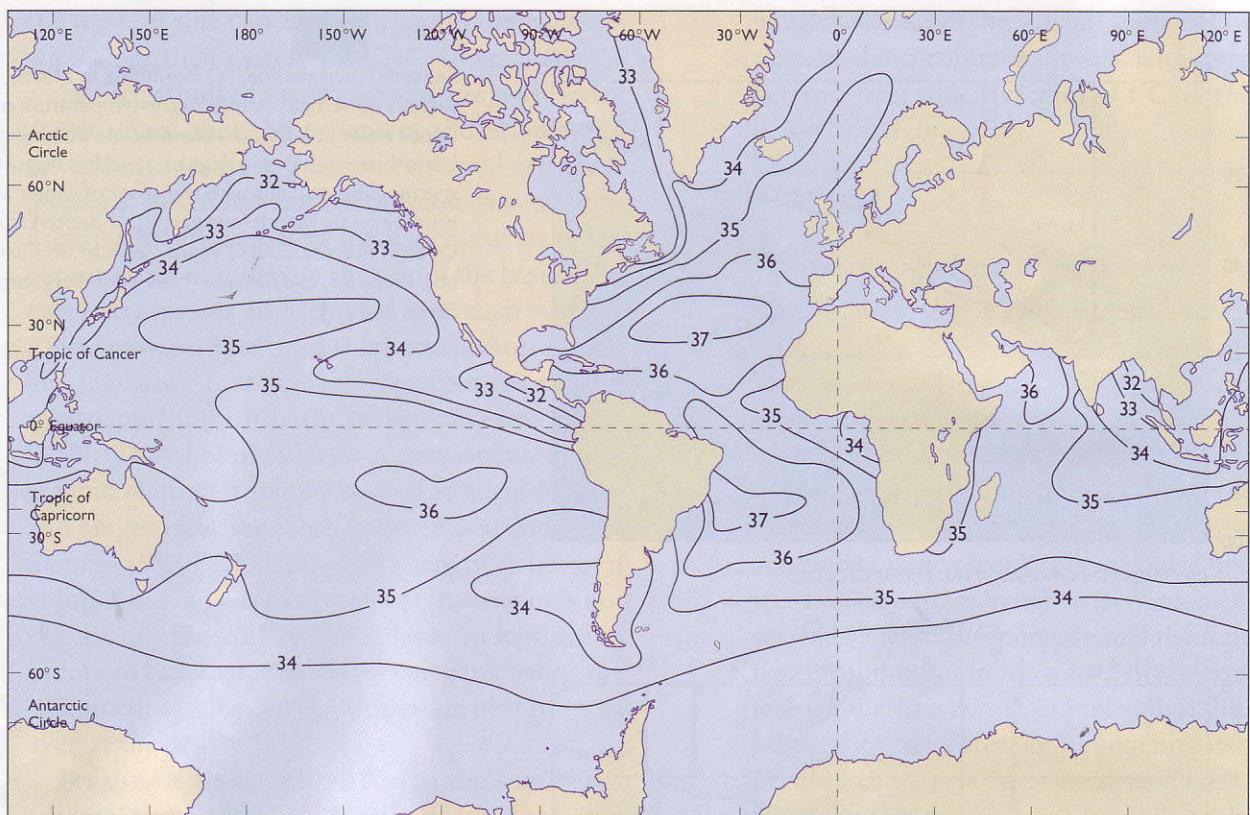
FIGURE 5-11

Seasonal thermocline. (a) Beginning in March, when there is no vertical change in the temperature of the upper water column, the thermocline develops; it is most pronounced in August. (b) After August, the thermocline weakens with the onset of winter and disappears by March (see part a). [Adapted from Open University Course Team, *Seawater: Its Composition, Properties, and Behavior* (New York: Pergamon Press, 1989).]

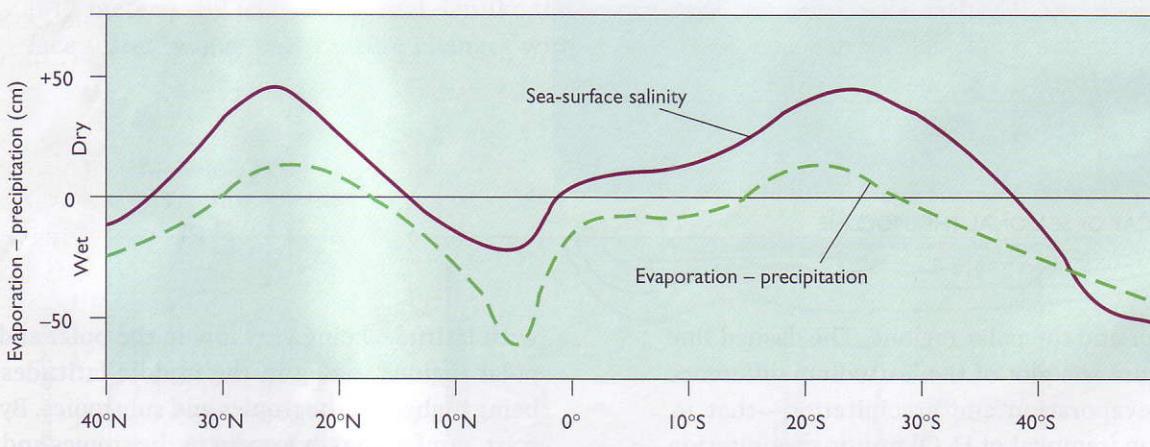
the equator and the polar regions. The dashed line in this figure is a plot of the latitudinal difference between evaporation and precipitation—that is, evaporation (removal of H_2O) minus precipitation (addition of H_2O). To calculate this value for any latitude, the total amount of evaporation for one year is subtracted from the total precipitation for that same year. If the result of the calculation is a positive value, then evaporation has exceeded precipitation, and salinity in this region will be higher than normal. A negative value denotes the converse, that is, precipitation exceeds evaporation, and salinity here is lower than normal. The rate of evaporation depends strongly, thought not exclusively, on temperature and, hence, varies directly

with latitude, being very low in the polar and subpolar regions, rising in the middle latitudes, and being highest in the tropics and subtropics. By contrast, rainfall maxima occur in the tropics and temperate latitudes, and minima in the subtropics and high latitudes. Therefore, during the course of a year, there is a net excess of precipitation over evaporation in the tropics and temperate latitudes, and an excess of evaporation over precipitation between 20 and 35 degrees latitude, where, not surprisingly, most of the major land deserts occur.

Notice in Figure 5-12b that the two curves representing evaporation minus precipitation and sea-surface salinity are quite similar in shape. This suggests that the major control on the surface salinity



(a) SEA-SURFACE SALINITY (‰) IN AUGUST



(b) LATITUDINAL VARIATIONS IN SALINITY AND "DRYNESS"

FIGURE 5-12

Salinity variations. (a) The surface salinity of the world's ocean in parts per thousand (‰) during August shows a regular pattern that depends on latitude, with maximum amounts in the center of each ocean and minimal amounts at the equator and polar regions. [Adapted from H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, *The Oceans* (Englewood Cliffs, N.J.:Prentice-Hall, 1942).] (b) A comparison of evaporation and precipitation rates accounts for the maximum salinity levels in the subtropics and the minimum salinity levels near the equator and the polar regions. This profile is a global average.

of the world's oceans is the relative effect of evaporation and precipitation—in other words, of climate. The maximum salinity levels in the subtropical oceans are produced by a strong excess of evaporation over precipitation. At the equator, evaporation rates are high, but rainfall is even greater, leading to the lower surface salinity in these waters. In the midlatitudes, rainfall rates surpass evaporation rates to an even greater degree than they do in the tropics, which reduces salinity to less than 34‰. Surface salinity in the polar seas fluctuates as ice forms and melts with the changing seasons. The water of the coasts and continental shelves is diluted by the freshwater of rivers. A case in point is the Amazon River, which injects more than 5×10^{12} cubic meters ($\sim 1.8 \times 10^{14}$ cubic feet) of freshwater into the western South Atlantic Ocean each year, lowering the salinity there.

As was the case for temperature, sharp salinity gradients characterize the water column of the world's oceans (Figure 5–13a). These gradients are termed **haloclines** and, like temperature, represent boundary zones between distinct water masses. A north-south longitudinal profile of salinity in the western Atlantic Ocean reveals a well-developed layering of water masses (Figure 5–13b). **Water stratification** (layering) is evident between 40°N and 40°S latitudes, where a lens of high-salinity (35‰) surface water is separated from less saline water below by a sharp halocline. Also, two tongues of water with salinities of <34.74‰ extend northward from the Antarctic region: one at about a 1,000-meter (~3,300-feet) depth, the other along the deep-sea bottom. These tongues indicate that their water originated at the sea surface in the south polar seas and are separated from each other by a water mass that flowed southward out of the North Atlantic Ocean (see Figure 5–13b). What is truly remarkable about this North Atlantic water below a depth of 2 kilometers (~1.2 miles) is its uniform salinity of ~34.9‰. This condition reflects the fact that once water sinks, it is no longer in contact with the atmosphere, where precipitation and evaporation alter the salinity. Hence, the salinity of deep water remains relatively stable (unchanging) over time, although very slow mixing processes not well understood do eventually change the salinity of water masses.

DENSITY

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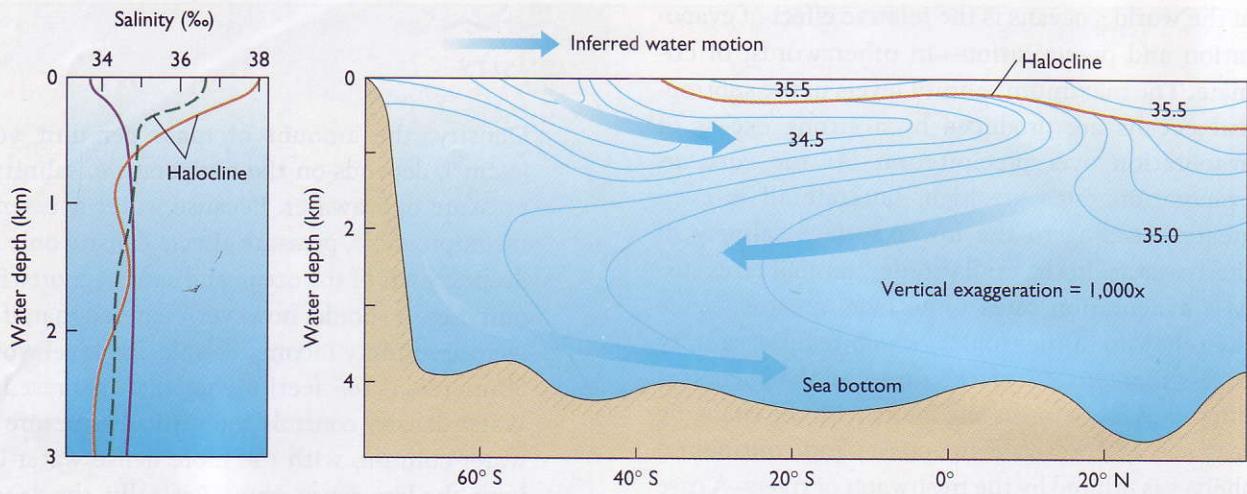
Density, the amount of mass per unit volume ( $\text{g/cm}^3$ ), depends on the temperature, salinity, and pressure of seawater. Because water is essentially incompressible, pressure affects density only in the deepest parts of the ocean and can be ignored for our purposes. It should, however, be noted that, if water were absolutely incompressible, sea level would be 50 meters (~165 feet) higher than it presently is! Water density controls the vertical structure of the water column, with the more dense water underlying the less dense water. Basically, the density of water is increased by dropping its temperature and raising its salinity. This means that cold, saline water is more dense than warm freshwater is. The conversion of temperature and salinity data to water density can be done simply by consulting either tables or graphs (Figure 5–14a).

It is possible to have high-salinity water overlie low-salinity water, provided that the temperature of the surface water is much higher than the temperature of the deep water. Thus warm water with high salinity levels can overlie cold water with low salinity—a water-mass arrangement that is common in the ocean of the low and middle latitudes (see Figure 5–13a), where high evaporation rates increase the salt content of surface water relative to subsurface water.

If vertical gradients of water temperature (thermoclines) and salinity (haloclines) exist in the ocean, then it stands to reason that density will show a similar gradient, because it depends directly on variations of temperature and salinity. A sharp density gradient with depth is called a **pycnocline** (Figure 5–14b). Density stratification of the ocean imposes a three-layered structure on the water column: a surface layer, a pycnocline layer, and a deep layer (Figure 5–14c).

## SURFACE LAYER

This topmost layer, the **surface layer**, is thin, averaging about 100 meters (~330 feet) in thickness, and represents about 2 percent of the ocean's volume. Being at the surface, it is the least dense water of the water column, largely because of its warm



**FIGURE 5-13**

**Salinity profiles.** (a) Vertical profiles of salinity show that sea-surface water may be more or less saline than the water below it. Note the prominent haloclines. (b) Isohalines (lines connecting points of equal salinity) in a longitudinal profile of the western Atlantic Ocean reveal distinct water-mass stratification and a prominent halocline. Below a 2-kilometer depth, the water has a remarkably uniform salinity, ranging between 34.7 and 34.9 ‰. [Adapted from D. Tolmazin, *Elements of Dynamic Oceanography* (Winchester, Mass.: Allen and Unwin, 1985).]

temperatures. Because it is in contact with the atmosphere, its water is affected by weather and climate, which cause diurnal, seasonal, and annual fluctuations of salinity and water temperature. Light penetrates to the bottom of this zone, allowing plant photosynthesis to occur wherever nutrient levels are adequate. In the polar regions, cooling of the surface water produces dense water that sinks. This sinking process prevents the formation of a pycnocline in the oceans of the high latitudes.

#### PYCNOCLINE LAYER

The boundary zone between the surface-water and deep-water layers is the **pycnocline layer**, where a sharp density gradient exists. It is not really a distinct water mass, but a transition zone where the surface-water layer grades into the deep-water layer. Water in this transition zone amounts to about 18 percent of the ocean's volume. In the low latitudes, the pycnocline corresponds to the permanent thermocline, which is created by the strong and persistent heating of the water by the tropical sun. In the midlatitudes, the pycnocline weakens and coincides with the halocline, which is produced by the abundant rainfall that dilutes the salinity of the water in the surface layer (see Figure 5-12b).

#### DEEP LAYER

About 80% of the total volume of the oceans belong to the **deep layer**. The bulk of this deep water originates in the high latitudes, where it is cooled while in contact with the frigid polar atmosphere. This cold (<4°C) polar water sinks to the ocean bottom because of its high density, and flows slowly equatorward, supplying the depths of the ocean with water that was once near the ocean's surface. Chapter 6 provides a thorough review of the origin and flow patterns of these deep-water masses.

We can now discuss the nature and distribution of gases dissolved in the ocean. As you will see, gas concentrations depend a great deal on the density structure of the water column.

5-6

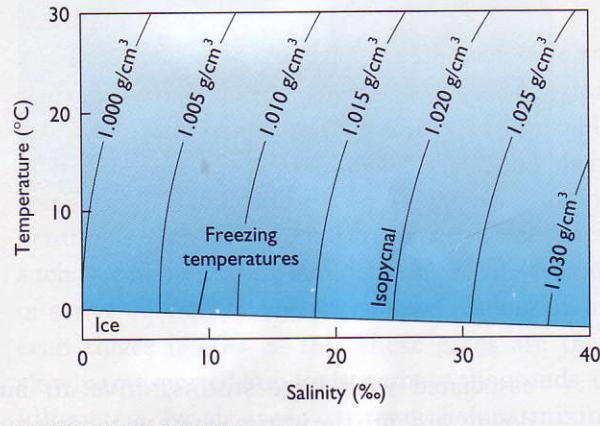


#### Gases in Seawater

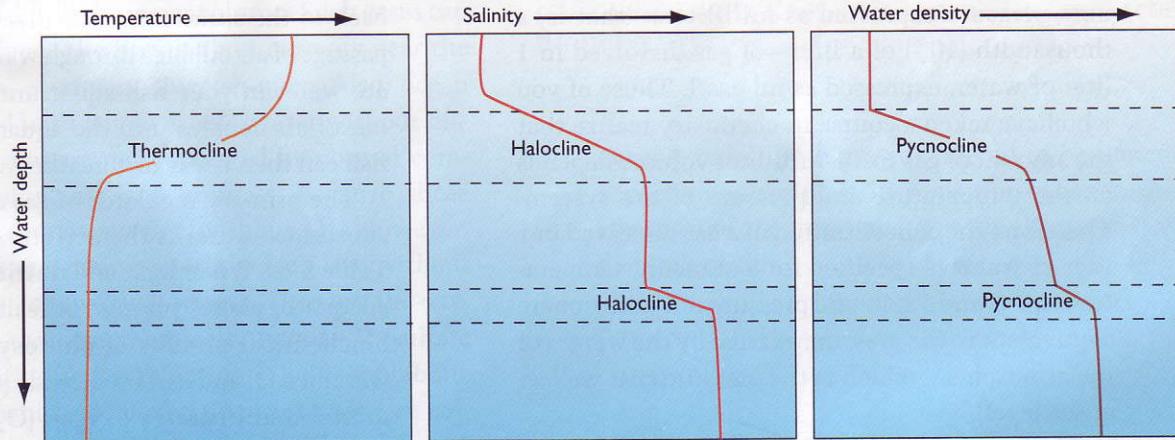
To understand better the levels and distribution of gases in seawater, we need a thorough grasp of certain chemical concepts. The first is **saturation value**, which refers to the amount of gas at

equilibrium that can be dissolved by a volume of water at a specific salinity, temperature, and pressure. The higher the saturation value is for a gas, the greater is its **solubility**, which is the property of being dissolved and going into solution. The solubility of gases increases with a drop in either water temperature or salinity, and a rise in pressure (**Figure 5-15a**). This means that cold, brackish (slightly salty) water can dissolve more gas than can warm,

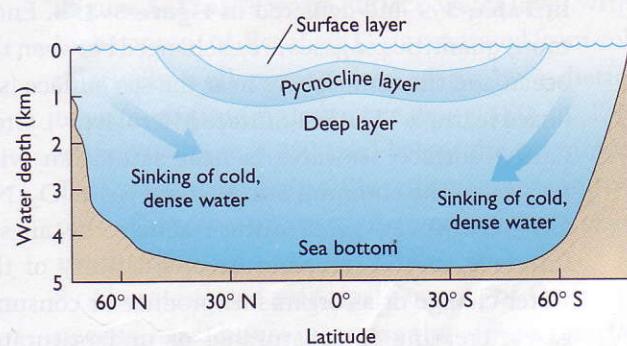
saline (salty) water at the same pressure. If a parcel of water is saturated with a gas, a change of water temperature or salinity will cause the quantity of gas to be below or above the water's new saturation value, conditions called **undersaturation** and **supersaturation**, respectively. Water that is undersaturated can dissolve more gas, whereas water that is supersaturated can release gas from solution (bubbles may form under the right conditions).



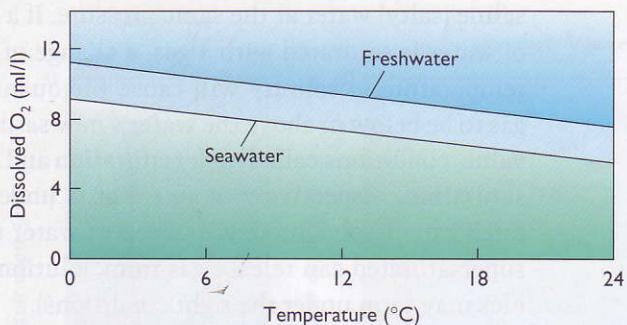
(a) SEAWATER DENSITY



(b) THERMOCLINE, HALOCLINE, AND PYCNOCLINE



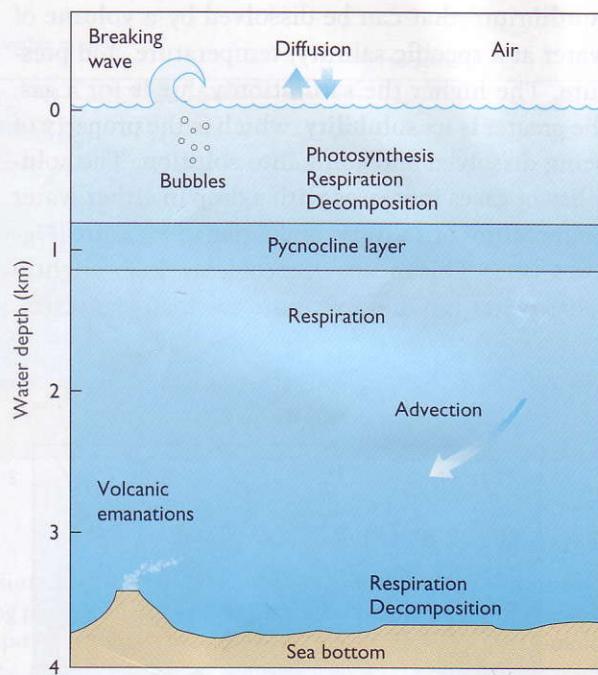
(c) DENSITY STRUCTURE OF THE OCEANS



(a) SOLUBILITY OF OXYGEN

FIGURE 5-15

Gases in seawater. (a) The solubility of oxygen decreases as water temperature and salinity rise. (b) Dissolved gases in the oceans are derived from both external and internal sources and organic and inorganic processes.



(b) SOURCES AND SINKS OF GASES

At this point, it is necessary to specify the types of units that chemists use to characterize the quantity of dissolved gases in water. We will use a volume measure expressed as milliliters—that is, a thousandth ( $10^{-3}$ ) of a liter—of gas dissolved in 1 liter of water, expressed as ml gas/l. Those of you who have taken a course in chemistry realize that the amount of gas in a 1-milliliter volume depends on the temperature and pressure of the system. Therefore, the concentration of a gas dissolved in 1 liter of water is specified for a standard temperature of 0°C and a standard pressure of 1 atmosphere (equivalent to the pressure exerted by the weight of the atmosphere, which is the pressure that we feel at sea level).

The processes that produce, consume, and regulate gas concentrations in the ocean are summarized in **Table 5–9** and depicted in **Figure 5–15b**. Enormous quantities of gases are exchanged between the ocean and the atmosphere near the sea surface (see boxed feature, “The Sea-Surface Microlayer”). Ordinarily, surface seawater is near saturation with respect to the common atmospheric gases ( $O_2$ ,  $N_2$ ,  $CO_2$ ). However, gases diffuse across the air-sea interface, as the temperature and salinity of the water change or as organisms produce or consume gases, creating supersaturated or undersaturated conditions. Also, breaking waves, particularly those

associated with large storms, drive air bubbles downward into the water, where water pressure dissolves some of the bubbles before they can ascend back to the surface. In fact, this very process—the passage of air bubbles through water—is used to aerate water in your fish aquarium. Oxygen diffuses out of air bubbles into the aquarium water where fish can then use it to “breathe.”

The primary regulator of gas concentrations in subsurface water is the activity of organisms (see Table 5–9). When light and nutrient conditions are adequate, plants photosynthesize. This complex biochemical process of **photosynthesis** converts water ( $H_2O$ ) and carbon dioxide ( $CO_2$ ) into organic matter and liberates oxygen ( $O_2$ ) as a product of the reactions. Thus, plants simultaneously reduce the dissolved content of  $CO_2$  and augment the levels of dissolved  $O_2$  as they conduct photosynthesis in the upper, sunlit part of the water column during daylight hours. In contrast, **respiration**, the chemical breakdown of food in cells for the release of energy, is conducted by both plants and animals in surface water, and by animals at all depths of the ocean. This results in the uptake of  $O_2$  and the release of  $CO_2$  as organisms oxidize food for nutritional purposes. As you sit reading this passage, you are respiring, “burning” food in the presence of oxygen, which releases the energy that your

body requires to live. Consequently, these life-sustaining processes—photosynthesis and respiration—have a profound impact on the concentrations of dissolved CO<sub>2</sub> and O<sub>2</sub> in the oceans, an important topic that we will cover in subsequent chapters on biological oceanography. Last, dead organic matter and excrement are decomposed by microbes, chiefly bacteria. Enzymes that are secreted by microbes chemically “attack” organic matter and break it down into simpler chemical compounds by the process of **oxidation**, a chemical reaction that consumes O<sub>2</sub> and produces CO<sub>2</sub> and other gases.

Gases other than oxygen and carbon dioxide are also released and taken up by physical and biological processes. For example, the decay of unstable radioactive elements contained in the minerals of deep-sea muds produces a variety of gases, including helium (He), radon (Rn), and argon (Ar). Some gases, such as carbon dioxide and helium, are spewed out of active submarine volcanoes on spreading mid-ocean ridges (**Figure 5–16**). These gases are then slowly transported hundreds, perhaps thousands, of kilometers by deep-sea currents before mixing dilutes them to such a degree that they are no longer distinguishable in the water column. Such gases can be used to trace the flow path of currents near the sea bottom, even very sluggish ones. Also, ocean basins filled with **anoxic** water (water without dissolved oxygen) are not populated by normal communities of plants and animals, because these organisms cannot survive without O<sub>2</sub>. However, specialized **anaerobic** bacteria, which live without free oxygen, inhabit such waters. They use the oxygen atoms that are chemically bonded to sulfate ions (SO<sub>4</sub><sup>2-</sup>) for conducting their metabolic processes, which yields the toxic gas hydrogen sulfide (H<sub>2</sub>S) as a reaction by-product. Although anaerobic conditions rarely develop in the well-mixed, and hence well-ventilated, water of the open ocean, they do occur in some restricted basins where circulation is sluggish and the supply of oxygen is limited. For example, water trapped in the small basins that are part of the continental shelf of southern California commonly is anoxic because of sluggish bottom currents and poor mixing.

In order to firm up our understanding of the gas chemistry of the oceans, we will consider in the next two sections the sources, sinks, and distribution of O<sub>2</sub> and CO<sub>2</sub>—two gases vital for the

TABLE 5-9

Summary of factors that regulate the concentration of gases in water

| Factors                         | Effects                                                                                                                                                                                    |
|---------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Wave and current turbulence     | Increases the exchange of seawater gases with the atmosphere.                                                                                                                              |
| Difference in gas concentration | Diffuses gases across the air-sea interface from high to low areas of concentration until chemical equilibrium is attained.                                                                |
| Temperature                     | A drop in water temperature increases the solubility of gases.                                                                                                                             |
| Salinity                        | A rise in salinity decreases the solubility of gases.                                                                                                                                      |
| Pressure                        | A rise in pressure increases the solubility of gases.                                                                                                                                      |
| Photosynthesis                  | Increases concentration of O <sub>2</sub> ; decreases concentration of CO <sub>2</sub> .                                                                                                   |
| Respiration                     | Increases concentration of CO <sub>2</sub> ; decreases concentration of O <sub>2</sub> .                                                                                                   |
| Decomposition                   | Increases concentration of CO <sub>2</sub> ; decreases concentration of O <sub>2</sub> .                                                                                                   |
| pH                              | Controls the relative concentrations of the various species of CO <sub>2</sub> in water (H <sub>2</sub> CO <sub>3</sub> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> ). |

Source: Adapted from H. S. Parker, *Exploring the Oceans* (Englewood Cliffs, N.J.: Prentice-Hall, 1985).

ocean's biota. Both are considered to be nonconservative substances in seawater because their concentrations vary greatly over short time and distance scales.

## OXYGEN

The vertical distribution of O<sub>2</sub> in the ocean of the low and middle latitudes shows a distinct pattern (**Figure 5–17a**). A warm surface-water layer with a high content of dissolved O<sub>2</sub> is separated from cold, relatively well-aerated deep water by a distinct oxygen-minimum layer at about 150 to 1,500 meters (~495 to 4,950 feet) below the sea surface. This vertical oxygen profile reflects inputs and outputs of gases by a variety of processes. Let's examine them.

There are two principal sources of O<sub>2</sub> for the oceans—gas diffusion across the air-sea interface and plant photosynthesis. Both of these processes

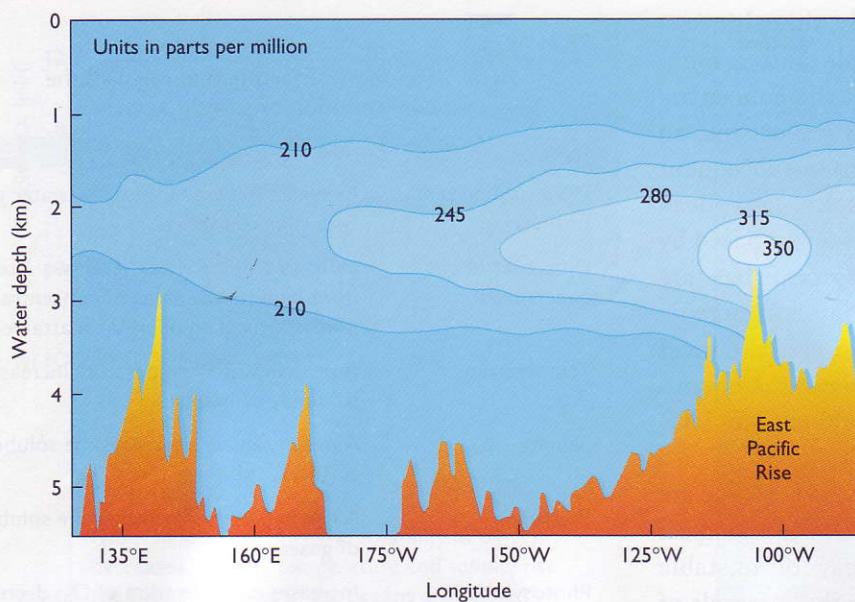


FIGURE 5-16

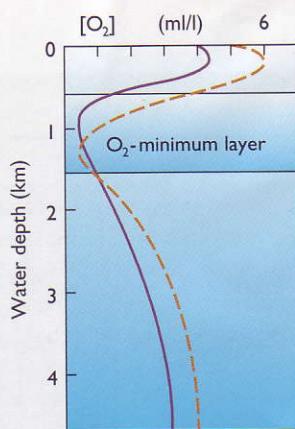
Helium-3. A large plume of water enriched in helium-3 extends westward from the East Pacific Rise, tracing the flow of water at mid-depth in the Pacific Ocean. Volcanic emissions are clearly the source of this gas, which originated deep in the Earth's mantle. [Adapted from W. J. Jenkins, Tracers in oceanography, *Oceanus* 35, no. 1 (1992): 47–56.]

are limited to the uppermost levels of the water column, and account for the high concentrations of dissolved O<sub>2</sub>, typically in excess of 5 milliliters per liter, in the surface-water layer. The O<sub>2</sub>-minimum zone coincides with the pycnocline layer; this implies a connection between the two. Apparently, the sharp density gradient in this intermediate water layer slows down the settling rate of organic detritus falling from above, so that dead organic matter tends to accumulate and form a rich food source in the pycnocline. (This is somewhat similar to cars that are on a large highway entering a city area. Far from the city, cars are widely spaced and moving rapidly. Once in the city limits, however, the average speed of the vehicles slows down and they bunch up, sometimes bumper to bumper.) Organisms of all kinds are drawn to the pycnocline layer because of the ample food supply, and, as they respire, they deplete the O<sub>2</sub> content of the water. Also, bacteria there decompose the abundant dead organic matter, which further reduces the dissolved O<sub>2</sub>. The sharp pycnocline indicates that the water column is stable and that vertical mixing of water is minimal at these intermediate water depths. Thus, the high demand for dissolved O<sub>2</sub> by animals and bacteria that are feeding on the dead and living organic matter, combined with a relatively slow rate of water mixing and, hence, of O<sub>2</sub> replenishment, produces the O<sub>2</sub>-minimum layer with O<sub>2</sub> concentrations of <2 milliliters per liter (see Figure 5-17a).

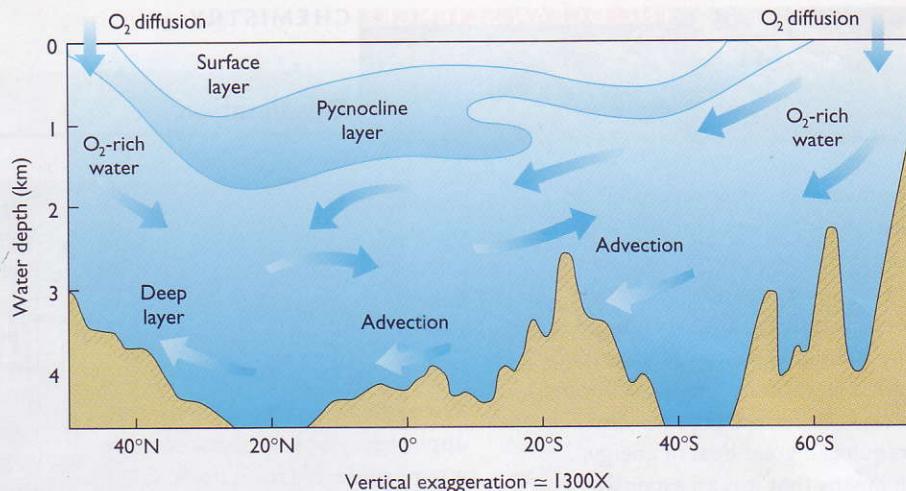
Below the pycnocline, water is sparsely populated because food is scarce. The biological demand for dissolved O<sub>2</sub> is low here, and O<sub>2</sub> concentrations rise with depth to between 3 and 5 milliliters per liter. Because oxygen production is restricted to surface water, the dissolved O<sub>2</sub> found in this deep layer must have been derived from shallow depths. Temperature and salinity data (see Figure 5-13b) indicate that deep water in all the ocean basins is derived from the polar regions. In the high latitudes, surface water is cooled, which raises its gas-saturation values. These cold, O<sub>2</sub>-rich water masses sink because of their high densities. They flow equatorward, ventilating the depths of all the ocean basins (Figure 5-17b). Although this **advection** process (the horizontal movement of a fluid, as distinguished from **convection**, the vertical flow of a fluid) is slow, it occurs at a rate that satisfactorily meets the respiration requirements of the scanty populations of deep-sea fauna.



Carbon dioxide (CO<sub>2</sub>) is a gas that is actively involved in photosynthesis and respiration. Plants cannot produce food and survive in its absence. Animals release CO<sub>2</sub> as they break down food for energy by the chemical process of respiration. Also, CO<sub>2</sub> regulates the acidity of seawater. Let's examine this latter chemical property of seawater.



(a) VERTICAL O<sub>2</sub> PROFILES IN THE ATLANTIC OCEAN



(b) O<sub>2</sub>-ADVECTION PATTERN IN THE ATLANTIC OCEAN

FIGURE 5-17

Dissolved oxygen. (a) Vertical profiles of dissolved oxygen reveal a distinct pattern consisting of well-ventilated surface and deep waters that are separated by an O<sub>2</sub>-minimum zone in the pycnocline layer. Apparently, the accumulation of dead organic matter in the pycnocline layer produces a high demand for O<sub>2</sub> because of respiration and decomposition. (b) The deep water of the ocean is aerated by the advection of cold, dense, O<sub>2</sub>-rich polar water.

The degree to which water provides a suitable habitat for marine biota is determined, in part, by the concentration of dissolved hydrogen ions (H<sup>+</sup>), a measure termed the **pH** of water. In pure water (water containing nothing but H<sub>2</sub>O molecules) at 25°C, a very tiny fraction of the H<sub>2</sub>O molecules, about 10<sup>-7</sup>, or one in 10 million (10<sup>7</sup>), spontaneously dissociates (breaks apart) into a hydroxyl (OH<sup>-</sup>) and a hydrogen (H<sup>+</sup>) ion. The free hydrogen ions are what control the acidity of water. The formal definition of pH is

$$\text{pH} = -\log_{10}(\text{H}^+).$$

At first glance, this formula looks quite difficult to grasp, but it need not be. Remember that the pH of water is, to a first approximation, merely a measure of the concentration of the H<sup>+</sup> ion. The parentheses in the preceding equation can be equated to the concentration of H<sup>+</sup>, although technically they refer to the chemical activity of this ion, which is an indirect function of its concentration level. Now, if we go back to our example of pure water, measurements indicate that 10<sup>-7</sup> H<sub>2</sub>O molecules (one in 10 million) are separated into their ionic components. If we substitute 10<sup>-7</sup>, the concentration of H<sup>+</sup>, into the formula and solve for its nega-

tive log, we get a pH value of 7 (Figure 5-18). The log to the base ten of 10<sup>-7</sup> is the exponent -7; hence, the negative log of 10<sup>-7</sup> is -(-7) or 7. Water with a pH of 7 is, by definition, a **neutral solution** consisting of equal parts (10<sup>-7</sup>) of OH<sup>-</sup> and H<sup>+</sup> (see Figure 5-18). Raising the amount of H<sup>+</sup> to 10<sup>-6</sup>—remember that 10<sup>-7</sup>, one H<sup>+</sup> ion in 10 million of the H<sub>2</sub>O molecules, is a much smaller value than 10<sup>-6</sup>, which is one H<sup>+</sup> ion in a million H<sub>2</sub>O molecules—lowers the pH to 6, a solution that is no longer neutral but **acidic** (see Figure 5-18). The log to the base 10 of 10<sup>-6</sup> is the exponent -6; hence, the negative log of 10<sup>-6</sup> is -(-6) or 6. Low concentrations of H<sup>+</sup> that impart a higher pH than the neutral level of 7 create a **basic** solution, in which the amount of OH<sup>-</sup> surpasses the amount of H<sup>+</sup> (see Figure 5-18).

It's important that you understand the preceding discussion. Let's review what we've learned so far about pH. A neutral solution has a pH of 7, which means that the H<sup>+</sup> concentration is 10<sup>-7</sup>. A basic solution has a pH value that is greater than 7 (remember that this means low concentrations of H<sup>+</sup>) and an acidic solution has a pH value that is lower than 7 (high H<sup>+</sup> concentrations). So the pH scale, to a first approximation, is nothing more than a measure of the content of H<sup>+</sup> in the water.



## Desalination

**F**reshwater is a precious commodity that is essential for all living organisms. Its distribution on the Earth is variable. In arid regions, the amount of freshwater is very limited, making **desalination**, the production of drinkable water from seawater, very important. Unfortunately, desalination requires a great deal of energy, which means that it is an expensive process.

If seawater consists overwhelmingly of water (about 96.5 percent on the average), why is it so expensive to purify it into drinkable freshwater? The answer is related to the dipole structure of H<sub>2</sub>O molecules, which results in tightly bonded clusters that must be disrupted for desalination to occur.

Desalination relies on five general techniques:

1. *Distillation*. The evaporation of seawater produces water vapor, which is then cooled to form a liquid-water condensate.

2. *Freezing*. As seawater begins to freeze, the H<sub>2</sub>O molecules arrange themselves into a crystal structure, leaving behind the salt ions in a highly concentrated brine. The pure ice must then be separated from the brine.
3. *Reverse osmosis*. Seawater, under an applied pressure, is forced through a semipermeable membrane. Only the H<sub>2</sub>O molecules are able to pass through the membrane, which separates them from the salt ions.
4. *Electrodialysis*. Electrically charged, semipermeable membranes draw salt ions out of the seawater solution, leaving behind freshwater. This technique is most effective for brackish (low-salinity) water.
5. *Salt absorption*. Chemically active resins or charcoals are used to draw off the dissolved salt ions from seawater, producing freshwater.

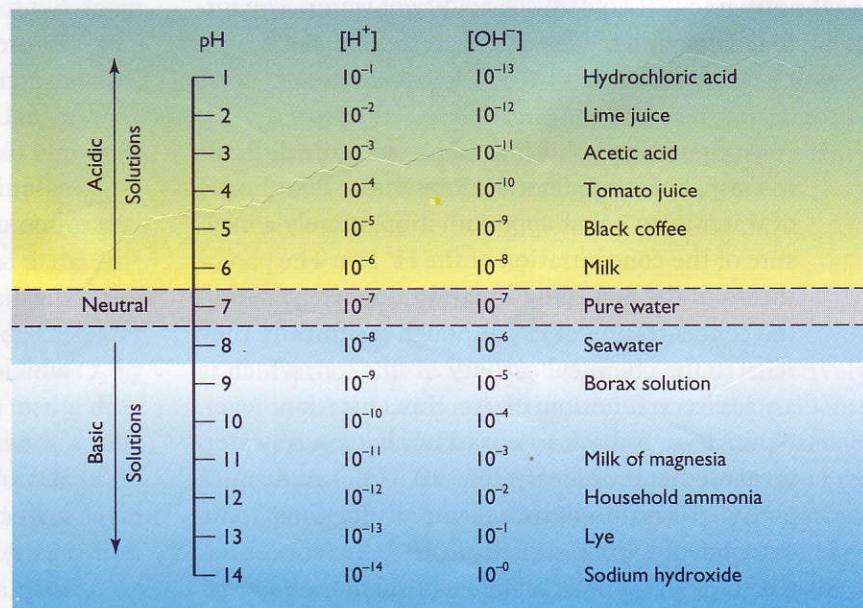
All of these techniques are currently in use somewhere in the world (**Figure B5-4**).

**B5-4**). Perhaps the simplest, least expensive, and most widely employed one is distillation. In Kuwait, Saudi Arabia, Israel, Greece, Pakistan, Australia, India, and Chile, as well as in the United States in Texas, southern California, and the Florida Keys, freshwater is obtained by distillation. A large saltwater pond is covered with plastic, glass, or even canvas. Solar radiation heats the enclosed volume of saltwater. Evaporation produces water vapor, which rises, cools, and condenses on the covering fabric of the structure (**Figure B5-5**). This condensed water then trickles down the underside of the sloping roof, and is collected in large receptacles. In Kuwait, the heat of the sun combined with waste heat generated by petroleum-fired power plants greatly increases evaporation and the production rate of freshwater at little additional cost.

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FIGURE 5-18

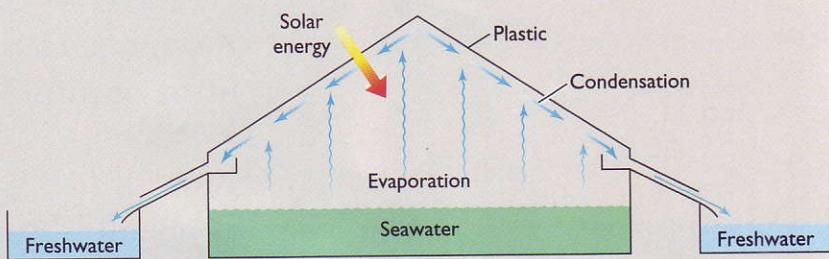
The pH scale. The concentration of H<sup>+</sup> in water is specified by pH. A pH of 7 denotes that the H<sup>+</sup> concentration is 10<sup>-7</sup>, or one part in 10 million. Solutions with low pH values (high concentrations of H<sup>+</sup>) are acidic. Solutions with high pH values (low concentrations of H<sup>+</sup>) are basic.





**FIGURE B5-4**

**Reverse osmosis.** At the desalination facility on Culebra Island, Puerto Rico, the seawater is forced through a series of membranes in each white tube. By the time the seawater is forced through the last tube and reaches the tank in the back, it is fresh enough to drink

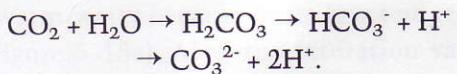


**FIGURE B5-5**

**Distillation of seawater.** A widely used technique for desalination (taking salt out of seawater) involves the evaporation of seawater from a pool, the condensation of freshwater on a covering fabric, and its collection in a storage vat.

Because the  $\text{H}^+$  ion is so reactive with other compounds, acid water (water with a pH of less than 7 and, hence, a relatively high concentration of  $\text{H}^+$ ) is a powerful weathering agent, able to weather rocks chemically. Also, plants and animals living in the ocean are affected by the content of  $\text{H}^+$  in the water they inhabit, because many metabolic activities are regulated by the seawater's pH. The question remaining to be answered is, what exactly determines the amount of  $\text{H}^+$  in the ocean?

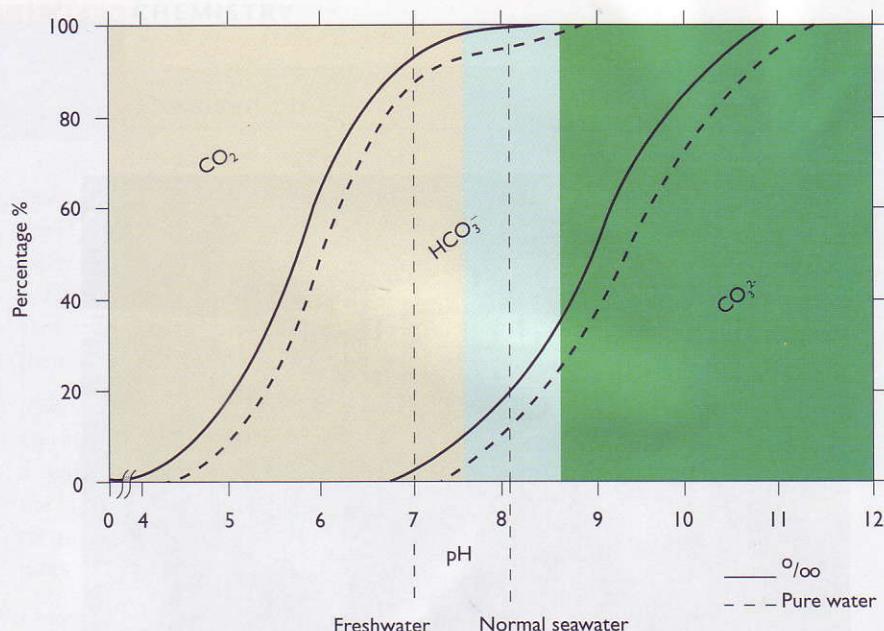
The pH of water is directly linked to the  $\text{CO}_2$  system. When  $\text{CO}_2$  is added to water, most of it is rapidly converted into carbonic acid ( $\text{H}_2\text{CO}_3$ ) as it bonds with water molecules (hydration). This acid then rapidly dissociates into bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) ions, which yields  $\text{H}^+$  ions, making the water acidic. The specifics of the chemical reaction are



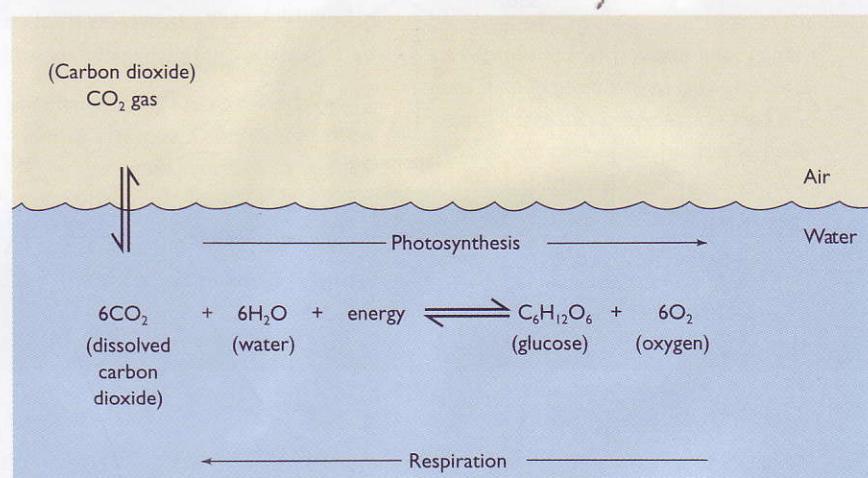
This formula summarizes each step of the reaction when  $\text{CO}_2$  is dissolved in water. Notice that the free ions of  $\text{H}^+$  lower the pH of the water. Therefore, we conclude that the addition of dissolved  $\text{CO}_2$  tends to lower the pH of water. At equilibrium, the proportion of each of the carbon compounds ( $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) depends on the pH of the water. At the pH of normal seawater (7.8 to 8.2), about 80 percent of the carbon compounds occur as  $\text{HCO}_3^-$  (Figure 5–19a). A change in the amount of any of these carbon substances disrupts the balance of the  $\text{CO}_2$  system, and reactions occur to reestablish equilibrium. For example, the removal of  $\text{CO}_2$  from water by plant photosynthesis (Figure 5–19b) or by solar heating, which reduces its saturation value and causes bubbles to form,

FIGURE 5-19

Carbon species and the CO<sub>2</sub> system in the oceans. (a) Carbon dissolved in water occurs in the form of carbon dioxide (CO<sub>2</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), and carbonate (CO<sub>3</sub><sup>2-</sup>). At equilibrium, the relative proportion of these carbon species depends on the pH of the water. Basic solutions are dominated by CO<sub>3</sub><sup>2-</sup>; acidic solutions, by CO<sub>2</sub>. At the pH of normal seawater, HCO<sub>3</sub><sup>-</sup> makes up about 80% of the carbon species. (b) The CO<sub>2</sub> system is also involved in biological processes, notably photosynthesis, which removes dissolved CO<sub>2</sub> from the water, and respiration, which liberates CO<sub>2</sub> into the water. Hence, the CO<sub>2</sub>-carbonate cycle influences and is influenced by both chemical and life processes. (c) Carbon dioxide diffuses from the atmosphere into the oceans, where it complexes with water to form weak carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and hydrogen (H<sup>+</sup>) ions. Some of the bicarbonate ions dissociate into carbonate (CO<sub>3</sub><sup>2-</sup>) ions, which may complex with calcium (Ca<sup>2+</sup>) to form calcium carbonate (CaCO<sub>3</sub>). (d) The pH of seawater (7.8) is buffered by the CO<sub>3</sub><sup>2-</sup> carbonate cycle. If the pH rises, H<sub>2</sub>CO<sub>3</sub> dissociates and yields H<sup>+</sup>, reversing the trend. If the pH drops, H<sup>+</sup> complexes with HCO<sub>3</sub><sup>-</sup>, causing the pH to rise again.



(a) DISTRIBUTION OF CARBON SPECIES IN WATER

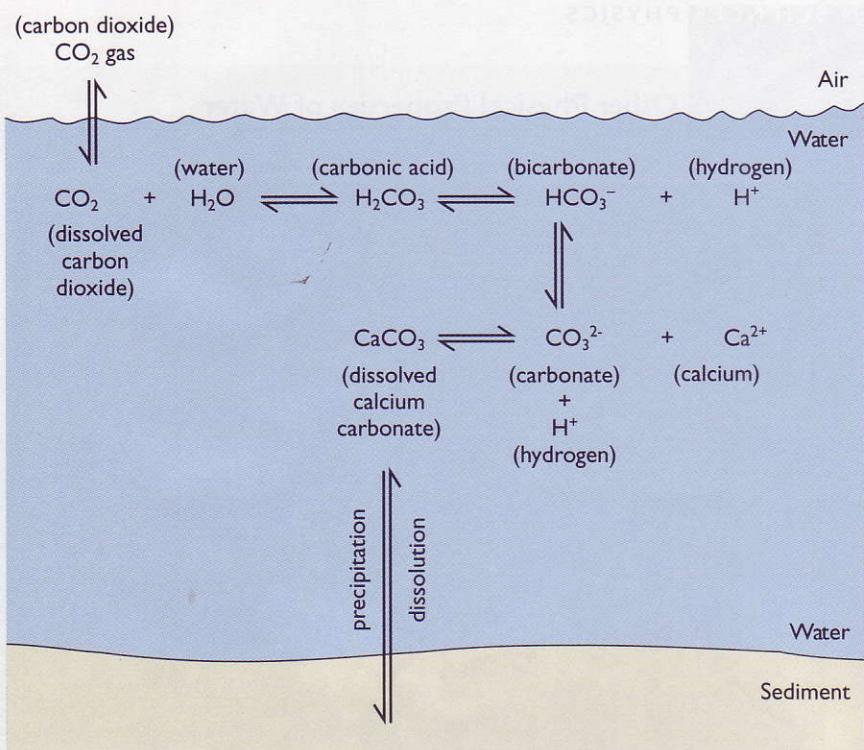


(b) PHOTOSYNTHESIS AND RESPIRATION.

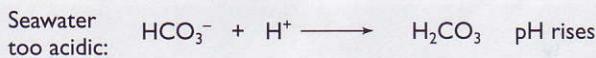
initiates a series of chemical responses that shift the reactions specified in the formula to the left. This results in the production of CO<sub>2</sub>. Respiration, in contrast, releases CO<sub>2</sub> into the water (see Figure 5-19b). This process causes the reactions in the formula to move to the right, which increases the concentrations of the other chemical species at the expense of CO<sub>2</sub>.

Organisms are sensitive to pH, quite a few extremely so. Fortunately, the many rapid chemical reactions within the CO<sub>2</sub> system (Figure 5-18) prevent large fluctuations in the pH levels of the

world's oceans. Seawater is essentially a stable solution with a pH that rarely ranges below 7.5 or above 8.5. This condition is described as **buffered**, meaning that the mixture of compounds and the nature of the reactions are such that the pH of the solution is hardly affected despite an input or output of H<sup>+</sup>. Let me explain. Increasing the level of H<sup>+</sup>, which should lower the pH (make the water more acidic), causes the reactions (see Figure 5-19c) to shift to the left; as a consequence, H<sup>+</sup> is removed as it complexes with HCO<sub>3</sub><sup>-</sup> to form H<sub>2</sub>CO<sub>3</sub>, buffering the solution (keeping the pH near its original value).



(c) THE CO<sub>2</sub> SYSTEM



(d) CARBONATE BUFFER

**Figure 5–19d.** Conversely, reducing the level of H<sup>+</sup> (making the solution more basic by raising the pH) reverses the reactions. There is a rapid release of H<sup>+</sup> into solution, as H<sub>2</sub>CO<sub>3</sub> dissociates to HCO<sub>3</sub><sup>-</sup> and releases H<sup>+</sup> (see Figure 5–19d). The end result is that the pH is stable despite changes in the relative amounts of the carbon species in the CO<sub>2</sub> system; the system is basically self-regulating or buffered.

With this background, we can now explain the dissolution of CaCO<sub>3</sub> shells in cold, deep water, but not in warm, shallow water, and the ocean's carbonate compensation depth (CCD) (see Figure 4–17 in Chapter 4). Recall that the pH level of water is inversely proportional to the concentration of dissolved CO<sub>2</sub>. This means that the higher the CO<sub>2</sub> content of the water is, the lower the pH (or, if you prefer, the greater the content of H<sup>+</sup>). Cold water has a higher gas-saturation value than

does warm water because of its low temperature (see Figure 5–15a). Also, the saturation value of gases in water increases with increasing pressure and therefore water depth. This means simply that the cold, dense water that fills the ocean depths contains high levels of dissolved gases like CO<sub>2</sub> (see Figure 5–17b). Its high CO<sub>2</sub> concentration lowers the pH, making the water acidic and dissolving CaCO<sub>3</sub> shells that sink to the deep-sea floor. Shallow water, on the other hand, is relatively warm and has a lower concentration of CO<sub>2</sub> at saturation than does the deep, cold water. This raises the water's pH level, which releases carbonate ions (CO<sub>3</sub><sup>2-</sup>) that chemically bond to the abundant calcium ions (Ca<sup>2+</sup>) and precipitate CaCO<sub>3</sub>. Therefore, as discussed in Chapter 4, carbonate oozes tend to accumulate in relatively shallow water of the deep sea above the CCD,

## Other Physical Properties of Water

In the body of the chapter, we discussed the unusual nature of water as a chemical compound. Its unique and remarkable properties are extensive. Here we examine a few more of these properties, including the formation of sea ice and the transmission of light and sound in water.

#### ■ FORMATION OF SEA ICE

When water is chilled below its freezing temperature, it solidifies and crystals of ice form and grow. The very same process happens to seawater, except that seawater freezes at a lower temperature than freshwater does (see Figure 5–8). Once ice crystals begin to form, they impart a dull, cloudy appearance to the water as they grow into needles and platelets several centimeters long. When these solids become abundant in the water, a slush forms. The dissolved ions of salt are not, however, incorporated into the structure of the crystals, that is, the ice. Their exclusion from the solid ice raises the salinity of the remaining water and, as a consequence, depresses its freezing temperature. As more and more sea ice forms, some seawater becomes trapped in the thickening ice mass; the quantity depends on the rate of ice formation. Slow freezing rates increase the chances that trapped brines will escape out of the ice. Aging of the sea ice also leads to the slow drainage of the trapped brine, so that, in time, the mass of ice consists mostly of freshwater and is drinkable.

Once a continuous sheet of sea ice is formed, wind and waves break the cover into pieces, creating **pancake ice** (Figure B5–6a). These pieces of ice drift about and unite into rather flexible masses. Some of them collide and buckle, raising hummocks called **pressure ridges** (Figure B5–6b). Ice masses thicken with time, as seawater



(a) PANCAKE ICE



(b) PRESSURE RIDGES

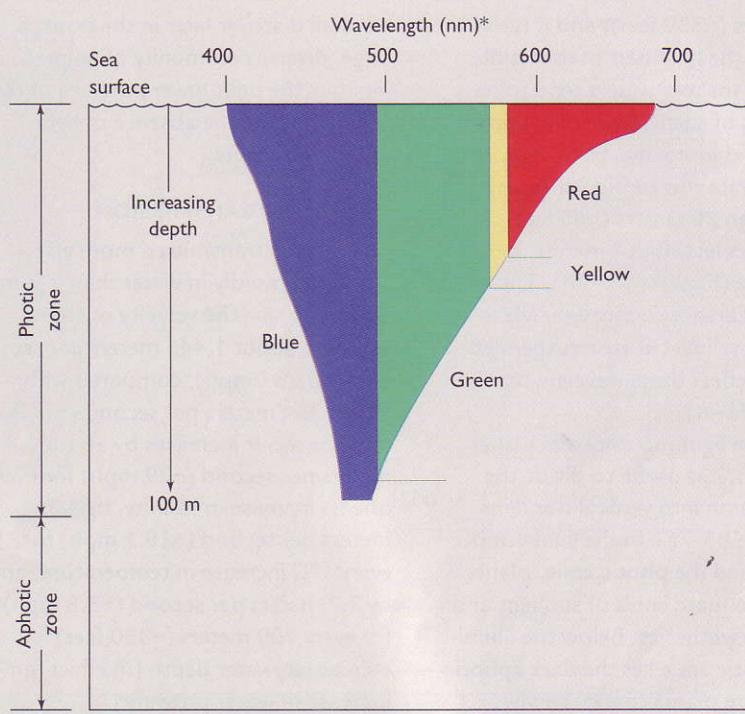
#### FIGURE B5–6

Sea ice. (a) Wind and waves can break newly formed sea ice into irregular masses, or pancake ice. (b) The drift and collision of ice masses raise large pressure ridges.

freezes to their bottom and snow freezes to their surface. In the polar latitudes, an ice mass about 2 meters (~6.5 feet) thick typically will form during the winter. A continuous ice cover may be broken into small and large **floes**, which keep separating and freezing together again in response to wind, waves, and currents. Floes should not be confused with **bergs**, which are large, very thick masses of floating ice that became detached from a glacier near a shoreline and are swept out to sea.

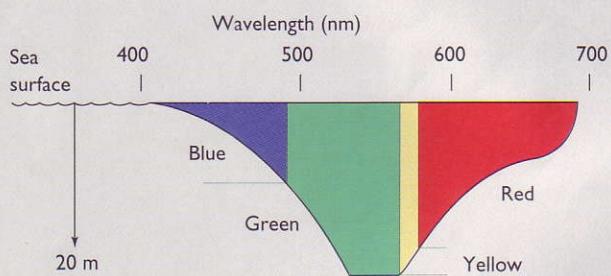
#### ■ LIGHT TRANSMISSION

Life—with a few exceptions—depends directly or indirectly on energy from sunlight. As do land plants, marine plants use green chlorophyll and a few other pigments to capture the visible light from the sun. As solar radiation strikes the ocean, a large fraction of it is reflected from the sea surface back into the atmosphere. The amount of reflected light depends on the height of the sun above the horizon and the smoothness of the water surface. What isn't reflected enters the water and is absorbed by water molecules. About 65 percent of the visible light is absorbed within 1 meter (~3.3 feet) of the sea surface in shelf and open-ocean water. This absorbed energy manifests itself as heat, elevating the temperature of the surface water. The longer wavelengths of visible light, the reds and yellows, are absorbed by water more readily than are the shorter wavelengths, the greens and blues (Figure B5-7a). This property of water—the selective absorption of certain wavelengths of light—combined with the scattering of the visible light accounts for the blue color of the open ocean. In very clear water, not even 1 percent of the light that enters the ocean reaches a water depth of



\* nm = nanometer (one billionth of a meter)

(a) LIGHT ABSORPTION IN THE OPEN OCEAN



(b) LIGHT ABSORPTION IN NEARSHORE WATERS

FIGURE B5-7

**Light absorption.** (a) The selective absorption of visible light by water permits the longer blue and green wavelengths to penetrate much deeper than the shorter red and yellow wavelengths. This effect imparts blue and green colors to the sea. No more than 1 percent of all sunlight penetrates to a water depth of 100 meters. This level separates the photic zone (where plants can photosynthesize) from the aphotic zone (where plants cannot photosynthesize). (b) Inshore water contains a high sediment load, which limits light penetration to a depth of no more than 20 meters below the sea surface. Note that the yellow and green wavelengths extend the deepest here and impart the green and yellow colors of coastal water. [Adapted from G. S. Levine, *Vision underwater*, *Oceanus* 23 (1980): 19–26.]

100 meters (~330 feet), and it is entirely in the blue part of the visible spectrum. Inshore waters tend to have high loads of suspended solids, both organic and inorganic. Here, light may not penetrate this turbid water any deeper than 20 meters (~66 feet) (sometimes less than 1 meter!) below the surface (**Figure B5-7b**). The color of nearshore water typically is green and yellow because suspended particles reflect these wavelengths (**Figure B5-8**).

Because light intensity diminishes with depth, it is useful to divide the water column into vertical domains (see Figure B5-7a). In the sunlit upper layer, termed the **photic zone**, plants receive adequate levels of sunlight and can photosynthesize. Below the illuminated photic zone lies the dark **aphotic zone**, where plants cannot survive. As

we shall discover later in the book, a large, diverse community of animals inhabits the unlit lower portions of the ocean, despite the absence of light and of live plants.

#### ■ SOUND TRANSMISSION

Sound is transmitted more effectively and rapidly in water than it is in air. In the sea, the velocity of sound averages about 1,445 meters per second (~3,237 mph), compared with about 334 meters per second (~748 mph) in air. It increases by about 1.3 meters per second (~29 mph) for every one ‰ increase in salinity, by 4.5 meters per second (~10.1 mph) for every 1°C increase in temperature, and by 1.7 meters per second (~3.8 mph) for every 100 meters (~330 feet) increase in water depth (in effect, an increase in water pressure).

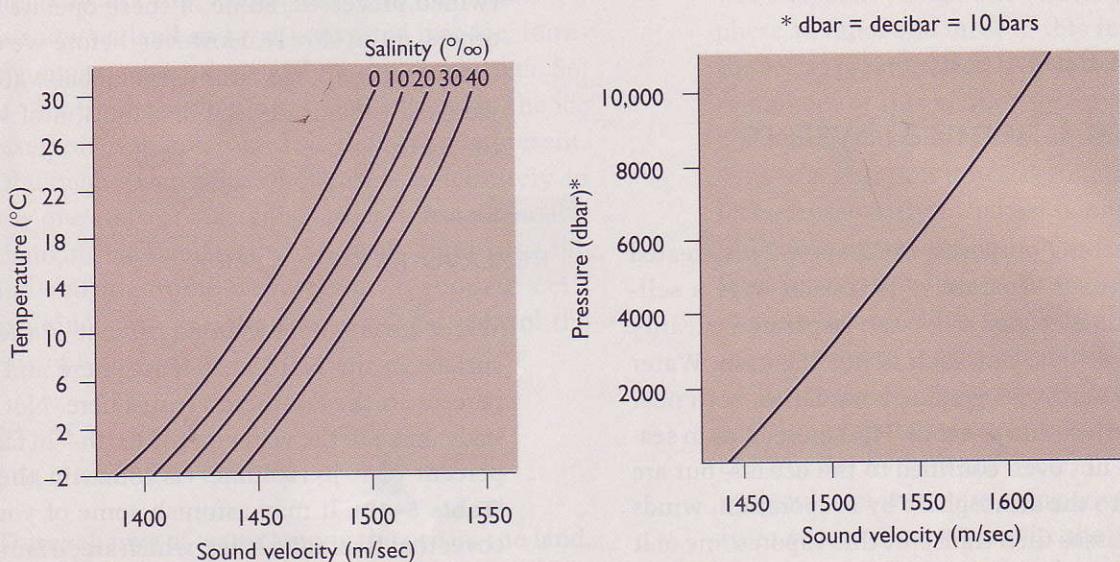


**FIGURE B5-8**

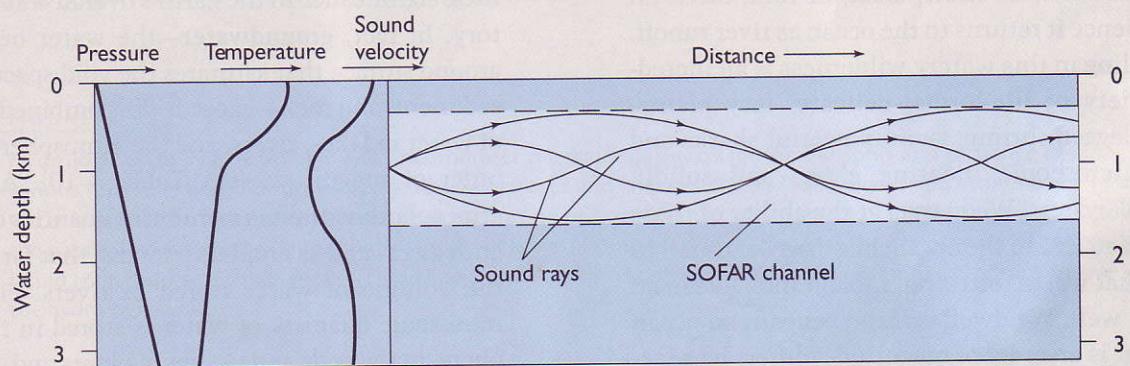
**Water color.** The different color tints of the water pouring out of the Sungai River into the ocean are created by the light-reflecting properties of different concentrations of suspended mud particles.

Because salinity varies slightly with water depth in most areas of the ocean, the speed of sound in water is affected mostly by temperature and pressure. Although pressure increases linearly with depth, temperature does not (**Figure B5-9a**). For example, the permanent thermocline marks a pronounced temperature gradient in the water column. In the surface water above the thermocline, sound velocity increases a bit with depth. The speed of sound drops sharply to a minimum value within the thermocline itself, but sound transmission increases in the water below the thermocline because of increasing water pressure. The result of these variations is a channel of minimum sound velocity at a water depth of about 1,000 meters (~3,300 feet) (see **Figure B5-9b**)—the so-called deep-sound channel or **SOFAR channel** (SOund Fixing And Ranging). Sound generated in this channel is focused as it is refracted (bent) from above and from below toward the center of the channel, where the speed is at a minimum. Because the sound waves are not spread vertically, there is little loss of energy, and even moderate amounts of sound energy can be focused and transmitted over great distances within the SOFAR channel. The sound in this zone is not dispersed; rather, it is trapped and confined to this relatively thin layer of the water column. Field tests have resulted in sound transmission along the SOFAR channel from Australia to Bermuda—a distance of 25,000 kilometers (~15,500 miles)!

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(a) VELOCITY OF SOUND



(b) SOFAR CHANNEL

FIGURE B5-9

Sound in seawater. (a) The speed of sound in water increases as salinity, temperature, and pressure increase. Note that temperature and pressure changes have a more marked effect on sound speed than salinity does. [Adapted from G. Neuman and W. J. Pierson, *Principles of Physical Oceanography* (Englewood Cliffs, N.J.: Prentice-Hall, 1966).] (b) Vertical variations in temperature and pressure create a zone of minimum sound velocity at a water depth of about 1 kilometer. Consequently, sound waves are bent toward the center of the zone, the SOFAR channel, so that the trapped sound energy is focused and can be transmitted over long distances. [Adapted from L. E. Kinsler and A. R. Frey, *Fundamentals of Acoustics* (New York: John Wiley, 1962).]

because water below the CCD is cold and acidic, and dissolves shells composed of  $\text{CaCO}_3$ .

5-7

## The Ocean as a Physical Chemical System

For teaching purposes, in Chapter 2 we treated the oceans separately, as if each were a self-contained basin of water, separated cleanly from the others. But such is not the case. Water does flow across geographic boundaries, both near the sea surface and at depth.  $\text{H}_2\text{O}$  molecules in seawater are not even confined to the oceans, but are passed into the atmosphere by evaporation; winds and air masses then transport this vapor, some of it across great distances. Eventually, the vapor condenses and falls as snow, sleet, or rain, often on land, whence it returns to the ocean as river runoff.

Dwelling in this watery wilderness is an incredible variety of life-forms: delicate, lacy plants, spindly-legged shrimp, swift, powerful sharks and tuna, microscopic, floating algae, and solidly anchored oysters. We marvel at the ability of these creatures to live in the ocean, but many of us fail to realize that we, as terrestrial inhabitants, live in an ocean as well. We dwell on land beneath an ocean of air that is an order of magnitude (differs by a factor of 10) deeper than the deepest seas and that, because of its weight, exerts considerable pressure on us. (For those of you who are technically inclined, atmospheric pressure at sea level is about 1,013 millibars, or

$$\sim 1,013 \times 10^6 \text{ dynes/cm}^2,$$

or

$$\sim 10 \text{ metric tons/m}^2.)$$

This transparent envelope of fluid—the gaseous atmosphere—is in direct contact with the surface of all the land and oceans and is a crucial element of the planet's water cycle. The atmosphere and hydrosphere, which enclose the Earth's crust, interact through a vast network of processes. Powered by the energy of the sun, water is exchanged among

the oceans, the atmosphere, and the landmasses through evaporation, precipitation, river flow, groundwater (subterranean water) percolation, ocean circulation, and a host of related and intertwined processes. Some of these operate quickly; others, quite slowly. However, before we examine the workings of this immense global water cycle, we need to consider the distribution of water on the Earth.

### RESERVOIRS OF WATER

Water covers more than 60 percent of the Earth's surface in the Northern Hemisphere and over 80 percent in the Southern Hemisphere. Not surprisingly, most of the water on the Earth—in fact, 97.25 percent of it by volume—is found in the oceans (**Table 5-10**). It may astonish some of you to discover that rivers and lakes, which are so familiar and so indispensable to the activities of humans, are of little significance in the Earth's overall water inventory. In fact, **groundwater**—the water below the ground surface that saturates the void space in soil, sediment, and rock—exceeds the combined volume of water in lakes, rivers, and the atmosphere by one order of magnitude (see Table 5-10). Also, the atmosphere contains a significant quantity of water, both as gas and as droplets (clouds), that far exceeds the volume of water stored in rivers. Finally, a minuscule quantity of water is stored in the biosphere, in the cells and tissues of plants and animals.

Although the values cited in Table 5-10 are accurate for the present, they do not reflect the

TABLE 5-10

Earth's water reservoirs

| Reservoir   | Water Volume ( $10^6 \text{ km}^3$ ) | Total Water (%) |
|-------------|--------------------------------------|-----------------|
| Oceans      | 1370                                 | 97.25           |
| Ice masses  | 29                                   | 2.05            |
| Groundwater | 9.5                                  | 0.68            |
| Lakes       | 0.125                                | 0.01            |
| Atmosphere  | 0.013                                | 0.001           |
| Rivers      | 0.0017                               | 0.0001          |
| Biosphere   | 0.0006                               | 0.00004         |
| Total       | 1408.64                              | 99.99           |

Source: Adapted from E. K. Berner and R. A. Berner, *The Global Water Cycle* (Englewood Cliffs, N.J.: Prentice-Hall, 1987).

quantities that existed in some of these reservoirs in the geologic past. During glacial ages, for example, seawater that evaporated from the oceans fell as snow on land and was converted into ice, forming enormous ice caps and mountain glaciers. So, at that time, the volume of water stored in the ice reservoir was much greater than it is at present. Obviously, water does not reside indefinitely in any one state or reservoir; rather, it is continually changing back and forth, from gas to liquid to solid, and shifting from one reservoir to another. Let's examine some specific processes that control the flux of water on the Earth.

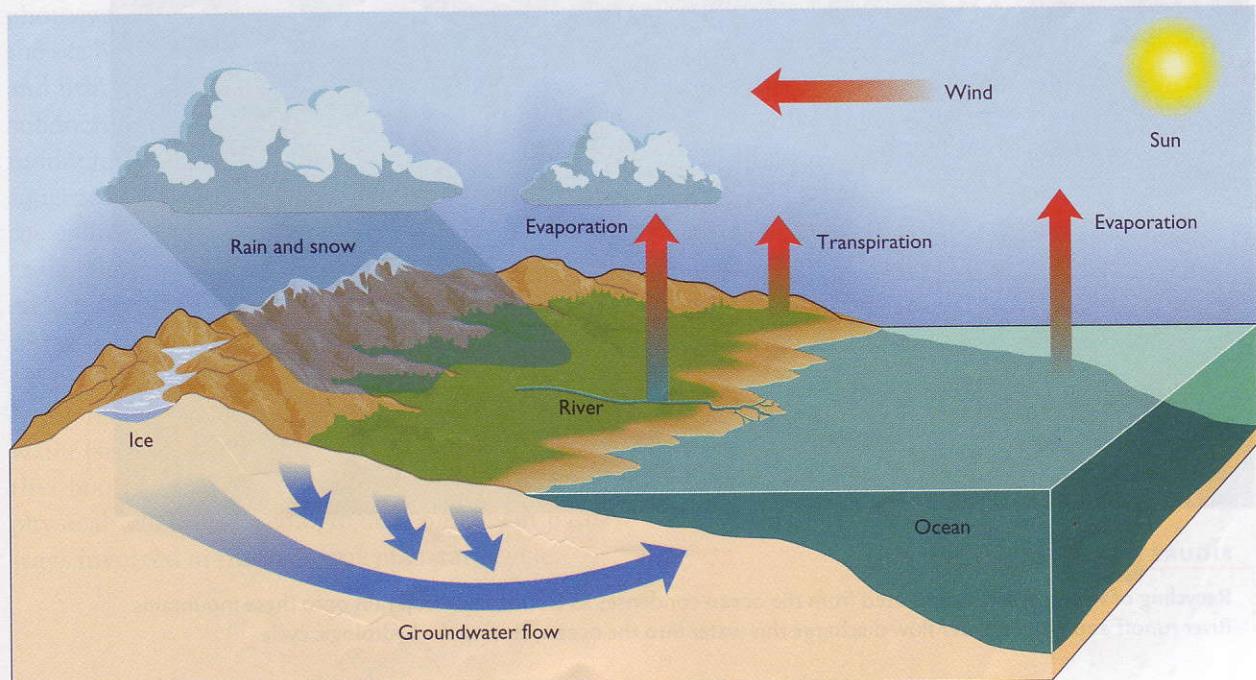
## THE GLOBAL WATER CYCLE

The exchange of water among the ocean, the land, and the atmosphere is termed the **hydrologic cycle** (Figure 5-20). The sun's heat evaporates sur-

face water from the ocean and the land. (Just leave a glass of water in sunlight for a few days and see what happens!) Evaporated water enters the atmosphere as vapor and most of this returns directly to the sea as precipitation. Air currents transport the remainder of this water vapor over land, where it condenses and falls as rain or snow (Figure 5-21). This precipitation flows as runoff into rivers, collects temporarily in lakes, ponds, and wetlands, infiltrates the ground (groundwater) only to emerge later in rivers and lakes, or remains in solid form as snow or ice. With time, all of this water finds its way back to the oceans, either as river outflow, melting glaciers and icebergs, groundwater seepage, or evaporation and precipitation, thereby closing the hydrologic cycle. In effect, the same molecules of water are being continually recycled from reservoir to reservoir, the rates of flux and the quantity exchanged and stored depending on climate.

FIGURE 5-20

**Hydrologic cycle.** The hydrologic cycle incorporates the major pathways for the transport and exchange of water among the various reservoirs of the earth. Basically, water circulates and changes phases (solid, liquid, gas) continually. In the gaseous state, water is supplied to the atmosphere by the evaporation of surface liquid water, much of it from the oceans, and by transpiration, the passage of water vapor through the surface of leaves. Condensation then causes the atmosphere to release this water as a liquid (rain) and as a solid (snow). These liquid and solid forms of water eventually return to the oceans by river runoff, closing the hydrologic cycle.



Over the oceans, evaporation exceeds precipitation, and the balance of water is maintained by river inflow. On all the land combined, in contrast, precipitation far exceeds evaporation, and the excess water travels to the ocean by river and groundwater flow. Estimates of these various fluxes are summarized in **Table 5–11**. These calculations assume that the total volume of water on the planet is fixed on a global scale (a perfectly reasonable supposition on a short time scale), so that precipitation and evaporation are balanced for the planet as a whole.

### THE OCEAN AS A BIOGEOCHEMICAL SYSTEM

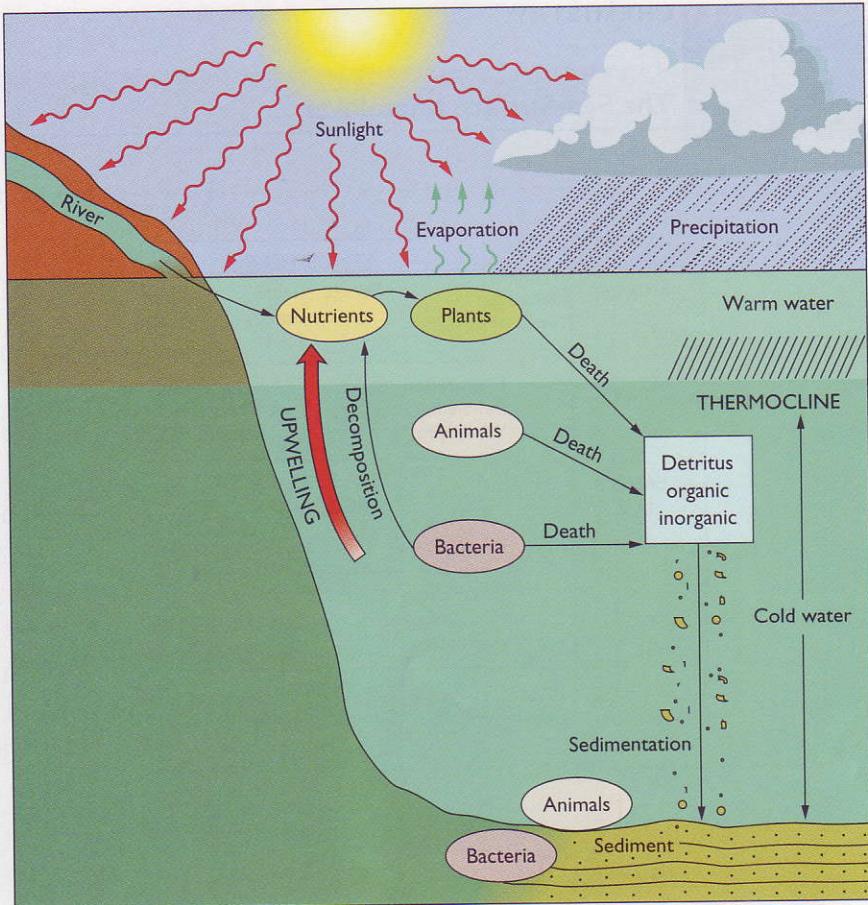
Now that we have examined the chemistry of seawater and the physical nature of the water column, we can combine them into a generalized biogeochemical system (**Figure 5–22**). Rivers supply the ocean with most of its dissolved ions, these being derived mainly from the chemical weathering of

rocks on land. The driving force underlying the ocean's biogeochemical system is the sun. Solar radiation absorbed by ocean water raises its temperature and stratifies the water column. A thermocline, separating the warm surface water from the cold deep water, forms. In addition sunlight is used by plants to convert carbon dioxide and nutrients into organic compounds (food) by photosynthesis. Small marine animals that graze on the multiplying plants in turn serve as food for even larger animals. This results in the transfer of energy (radiation from the sun) and matter (nutrients from rocks) through biological systems. When marine organisms die, they sink below the permanent thermocline, taking with them nutrients (phosphorus and nitrogen compounds) that are so crucial to plant photosynthesis. Bacteria decompose this dead organic matter, freeing these substances and producing nutrient-rich water. The vertical mixing of ocean water then slowly transports this water and its dissolved load of chemicals upward, reinfusing



**FIGURE 5–21**

**Recycling of water.** Water evaporated from the ocean condenses as clouds that drop rain onto these mountains. River runoff and groundwater flow discharge this water into the ocean, closing the hydrologic cycle.



**FIGURE 5-22**

Biochemical recycling of matter. Inorganic nutrients are converted into food by plant photosynthesis in the surface-water layer of the ocean. Animals eat plants and one another. When plants and animals die, their organic matter settles through the water column, where it is converted into simple nutrients by bacterial decomposition. This nutrient-charged water is then returned slowly to the surface by upwelling currents, completing the biochemical recycling of key nutrients. [Adapted from D. J. Repeta, G. Eglinton, and C. Lee, Marine organic geochemistry, *Oceanus* 35, no. 1 (1992): 38–46.]

the sunlit surface layer with nutrients that, once again, are incorporated into living plant tissue by photosynthesis. Some of these materials collect on the sea bottom as oozes, where they become buried and lithified into rock, and, by the process of plate subduction, are deformed and raised to form a mountain belt (see Figure 5–7). As these rocks are squeezed and uplifted by the tremendous forces of the colliding plates, they undergo chemical weathering and mechanical erosion until the chemicals are released once more and are transported by rivers to the ocean. The result is a continuous biochemical recycling of elements between living and non-living matter, and between surface and subsurface water (see Figure 5–22). Much of the remainder of this book is devoted to examining the different physical, chemical, geologic, and biological pathways involved in this majestic planetary cycle.

**TABLE 5-11**

Water fluxes

| Process                      | Water Flux ( $\text{km}^3/\text{yr}$ ) |
|------------------------------|----------------------------------------|
| Evaporation from land        | 72,900                                 |
| Precipitation on land        | 110,300                                |
| Precipitation on oceans      | 385,700                                |
| Evaporation from oceans      | 423,100                                |
| Total precipitation on Earth | 496,000                                |
| Total evaporation on Earth   | 496,000                                |

Source: Adapted from E. K. Berner and R. A. Berner, *The Global Water Cycle* (Englewood Cliffs, N.J.: Prentice-Hall, 1987).



## The Sea-Surface Microlayer

The seawater interface is a unique surface where chemicals are exchanged between the ocean and the atmosphere. This actual surface, called the **surface microlayer**, is incredibly thin—a few hundred micrometers ( $\sim 0.0039$  inch)—and, although regarded as being important for the chemistry of the upper ocean, has not been examined extensively because of the difficulties of sampling such a tiny vertical section of the water column. However, it represents a critical link between the atmosphere and the ocean (Figure B5–10). The surface microlayer receives and transmits energy, gases, and solids and collects matter transported by winds from above and by water from below. Ferren MacIntyre (1974) aptly states, “Through the ocean’s 360 million square kilometers of surface pass 70 percent of the solar energy that the earth absorbs, most of its supply of freshwater, a large fraction of the annual production of carbon dioxide and oxygen, a huge tonnage of particulate matter and unmeasured volumes of man-made pollutants.” Clearly, an understanding of the chemical and physical processes that occur across the surface microlayer of the ocean is essential for an understanding of processes of global proportion.

What exactly is meant by the ocean’s surface? In other words, how thick is this surface? Actually, providing an answer to this question is not a simple matter. The definition of the surface microlayer is quite loose and depends on the research interests of the chemists, physicists, and biologists who study ocean phenomena at the air-sea interface. Most oceanographers would probably agree that the surface microlayer extends from 3 Angstroms ( $10^{-10}$  meters), the diameter of a water

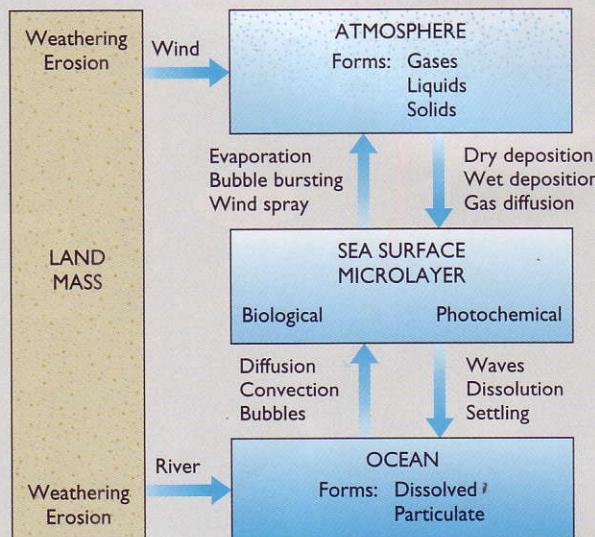
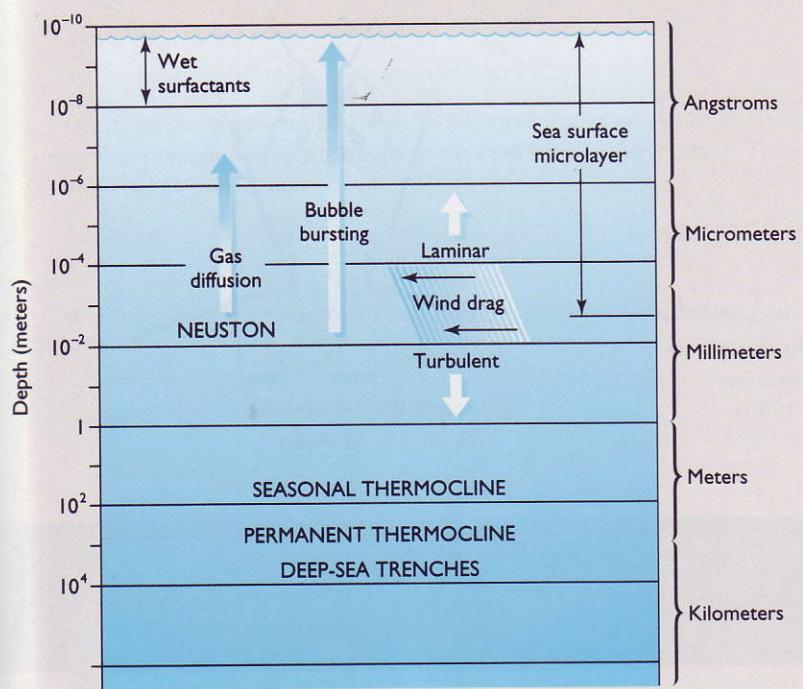


FIGURE B5-10

Box model of the sea-surface microlayer. This simple model shows how the sea-surface microlayer connects the atmosphere with the ocean. [Adapted from P. S. Liss, in *Chemical Oceanography*, J. P. Riley and G. Skirrow, eds. (New York: Academic Press, 1975), 193–243.]

molecule, to a depth of about 3 millimeters ( $\sim 0.1$  inch) or so, the lower limit of nonturbulent (smooth or laminar) water flow in the absence of a wind. Using a log scale to plot a vertical profile of the ocean lets us expand the surface microlayer, so that it occupies about half the water depth on that diagram (Figure B5–11). Some chemists and physicists believe that this 3-millimeter-thick ( $\sim 0.1$ -inch) surface layer may provide as many research problems as has the remainder of the ocean! Biologists refer to the organisms that inhabit the surface microlayer as the **neuston** and that thin habitat as the **neuston layer** (see Figure B5–11).

Three processes transport matter to the ocean’s surface from below: molecular diffusion, convective motion, and rising air bubbles. *Diffusion* is a slow process and comes about by the random motion of molecules. *Convection* refers to the vertical circulation of water that results in the transfer of heat and both dissolved and particulate matter. The most significant process in the surface microlayer by far is, however, the ascent and bursting of *bubbles*. Bubbles created by waves and wind rise through seawater because of their buoyancy and adsorb or scavenge inorganic and organic matter in both dissolved and solid states. When the bubble bursts, a portion of the scavenged material is



**FIGURE B5-11**

**Profile of the ocean.** This cross section of ocean depth is plotted on a logarithmic scale that expands the sea-surface microlayer, which actually extends no more than 3 millimeters below the sea surface, relative to the remainder of the water column.

ejected into the air, while the remainder collects in the surface microlayer. Material also is added to the sea surface from the atmosphere either as “wet” precipitation (rainfall and snowfall) or as “dry” deposition (particle settlement and gas diffusion). The result of this atmospheric and oceanic flux of material is the enrichment of both dissolved and particulate matter in the surface microlayer. The concentrated materials represent a surface coating that can reduce significantly the transfer of gases and water vapor across the air-sea interface, an effect that influences the chemistry of the lowermost atmosphere and the uppermost ocean and, quite possibly, climate in the long run.

The processes that occur within the surface microlayer can be divided into biological and **photochemical effects**. Sampling indicates that bacteria and plankton are more numerous in the surface microlayer than they are in the water immediately below. These organisms consume and produce a large variety of organic and inorganic substances and, presumably, influence the chemistry of this surface film of water. Evidence suggests that, when microorganisms living in the surface microlayer wiggle their tiny flagella (whiplike appendages), the tiny currents they induce can increase the rate of evaporation by as much as a factor of 3. Field experiments have demonstrated

that microorganisms are scavenged by rising air bubbles and are ejected into the air when the bubble bursts. Ultraviolet radiation is not attenuated in the surface microlayer, and, in theory, this should lead to photochemical reactions, such as the oxidation of organic compounds. For example, it has been suggested that photochemical reactions, as well as microbial processes, are responsible for the production of much of the carbon monoxide (CO) in the surface microlayer.

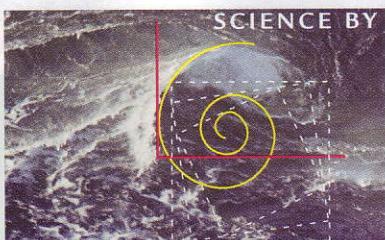
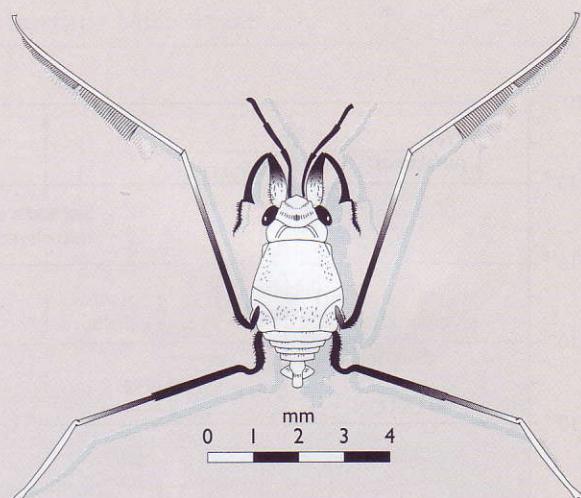
Besides bacteria and plankton, the neuston includes macroscopic organisms. The snail *Janthina prolongata* is such a member, and apparently it feeds directly on the organics that collect in the surface coating. Insects that abound on land are uncommon in the ocean. However, five species of sea striders, *Halobates* (Figure B5-12), live on top of the surface microlayer, floating because air is trapped in their body hair. Apparently, they feed on small organisms that they encounter in the surface film.

Some marine chemists believe that human pollutants may be enriched in the surface microlayer and these are rapidly dispersed far from their point of origin. For example, in the past, DDT, a toxic chlorinated hydrocarbon, was used extensively in North America as a pesticide to enhance crop yield. Some fraction of the DDT sprayed by planes on croplands remained airborne, and winds transported this load westward, where it rained down in the North Atlantic Ocean. Scientists surmise that much of the DDT likely remained in the surface microlayer and became concentrated in neuston organisms. Wilson’s petrel, allegedly the most abundant bird in the world, transported DDT to the high latitudes of the Southern Hemisphere. It accomplished this

because it is a long-distance migrant that feeds in the North Atlantic and breeds on the Antarctic continent. By this mechanism, DDT was dispersed rapidly across the globe, so that even the ostensibly isolated Antarctic fauna (birds and seals) became contaminated with the exceedingly toxic pollutant.

FIGURE B5-12

The sea strider *Halobates*. This is a sketch of one of the few marine species of insects that strides atop the sea-surface microlayer. [Adapted from P. M. David, *Endeavor* 24 (1965): 95–100.]



### Order of Magnitude

A concept used by scientists is the order of magnitude. A difference of one order of magnitude between two measurements means that they vary by a factor of 10. For example, a current that is flowing at 2.3 meters per second is one order of magnitude faster than a current with a speed of 0.6 meters per second.

Perhaps we can see this better if we express both current velocities as a power of 10 (see Math Box, “Powers of Ten”). Let’s do that.

$$2.3 \text{ m/sec} = 2.3 \times 10^0 \text{ m/sec}$$

$$0.6 \text{ m/sec} = 6.0 \times 10^{-1} \text{ m/sec}$$

The order of magnitude difference is 1, that is,  $10^0$  is larger than  $10^{-1}$  by a factor of 10.

If three fish are, respectively, 0.12, 0.43, and 1.88 meters in length, the first two values are of the same order of magnitude, and both are one order of magnitude smaller than the third value. Do you agree? It may help you to express each measurement of length as a power of 10.

$$0.12 = 1.20 \times 10^{-1}$$

$$0.43 = 4.30 \times 10^{-1}$$

$$1.88 = 1.88 \times 10^0$$

This shows clearly that the first two measurements are one order of magnitude smaller than the third ( $10^{-1}$  versus  $10^0$ ), which means simply that they vary by a factor of 10.

To see if you grasp the concept, try this problem. The average depth of the ocean is 4 kilometers (4,000 meters). How many orders of magnitude is this greater than the depth of the shelf break, which averages about 130 meters? Try to solve this problem on your own before continuing.