

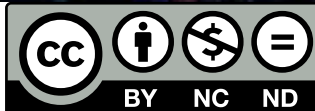
Introduction to Ocean Sciences

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*Water and Seawater***CRITICAL CONCEPTS USED IN THIS CHAPTER**

- CC1** Density and Layering in Fluids
- CC3** Convection and Convection Cells
- CC5** Transfer and Storage of Heat by Water
- CC6** Salinity, Temperature, Pressure, and Water Density
- CC7** Radioactivity and Age Dating
- CC8** Residence Time
- CC9** The Global Greenhouse Effect
- CC14** Phototrophy, Light, and Nutrients
- CC18** Toxicity



All known life forms on Earth depend on water and its unique properties. Although it is well known that plants and animals must take up or ingest water to survive, water is also important in many other ways. For example, the seawater in this photograph at Deacon's Reef, Papua New Guinea, is transparent to visible light. As a result, light energy can penetrate into the ocean, where it is used for photosynthesis. Many of the chemical elements and compounds invisibly dissolved in the seawater are essential to life. Water is important in many other subtle ways as well. For example, the organisms living in this reef ecosystem, and the terrestrial plants and animals that live on nearby land, thrive in a climate in which the temperature changes little between day and night. If water did not have a high heat capacity, these organisms would experience daily temperature variations and extremes comparable to those that occur in the middle of the largest deserts

Although most of us are aware that water is essential to life as we know it, the range of unique properties of water that make life possible is less well known. For example, the properties of water

- Help to create and control climate and weather
- Influence the formation and modification of the land and seafloor
- Enable essential chemicals to be transported to and within living organisms
- Control many features of our physical environment, such as rain, snow, and the waves on oceans and lakes
- Underlie the functioning of many aspects of modern society, ranging from cooling systems for automobile engines and

power plants, to ice cubes that keep drinks cold in summer

The dissolving power of water, the composition of seawater, and the processes that add or remove dissolved substances in ocean water are important to the studies of **sediments (Chap. 6)**, life in the oceans (**Chaps. 12, 14, 15**), and pollution (**Chap. 16**).

Water's unique physical properties are critically important to processes discussed in many chapters in this text, especially ocean–atmosphere interactions (**Chap. 7**) and the circulation of water in the oceans (**Chap. 10**). The behavior of sound and of **electromagnetic radiation**, including visible light, as they pass through seawater is important to ocean life (**Chap. 12**) and contributes to the difficulties faced by oceanographers in studying the oceans (**Chaps. 2, 3**). Light and sound transmission also influence the survival and reproduction strategies of marine **species (Chap. 14)**.

In this chapter, we will investigate the extraordinary properties of water that permit it to support life on our planet, we will discuss how water's dissolving ability affects the chemical composition of ocean water, and we will examine the most important physical properties of water and some of the ways that they influence the Earth and our **environment**.

ORIGINS AND DISTRIBUTION OF THE EARTH'S WATER

Early in its history, the Earth was hot and mostly molten. Heavy elements such as iron and nickel migrated toward the Earth's center, while lighter elements, such as silicon, aluminum, and oxygen, moved upward toward the surface. The lightest elements, which included hydrogen and oxygen, and compounds of light elements, including carbon dioxide, methane, and water vapor, migrated upward to form an atmosphere. The lightest gaseous elements, hydrogen and helium, were largely lost to space. After the Earth cooled, the **crust** solidified and water vapor in the atmosphere condensed into liquid water.

In the billions of years since the Earth's water first condensed, the temperature of the atmosphere apparently has changed relatively little. Hence, in addition to water vapor in the atmosphere, liquid and solid water probably were present in oceans and ice sheets throughout those billions of years. Volcanic activity released water that was trapped deep within the Earth's interior as the Earth solidified and continues to do so. However, the rate at which water has been released by volcanic activity since the Earth solidified is believed to be small in comparison with the volume of the oceans and ice sheets. Therefore, the amount of water at the Earth's surface probably has remained relatively unchanged for many millions of years.

Uniqueness of the Earth

The Earth is the only planet in the solar system with liquid water on its surface. The outer planets—Saturn, Jupiter, Uranus, and Neptune are cold, and any water present is vapor or ice. The surface of Mars is currently too cold to have liquid water, although it may have been warmer in the past. Certain features of the Martian surface suggest that liquid water was present at one time in its history, and we have direct evidence from instruments on robotic vehicles on the Martian surface that this was almost certainly the case. The surfaces of Mercury and Venus are hot and could have water only as a vapor. In addition, the mass and therefore the **gravity** of Mercury, Venus, and Mars are sufficiently small that much of the water formed during their early history has probably escaped into space.

Table 5-1 The World's Water

Location	Percentage of Total $2.0 \times 10^9 \text{ km}^3$
Oceans	96.5
Freshwater	
Ice caps and glaciers	1.78
Surface waters (lakes, rivers, streams)	0.013
Air and soil moisture	0.002
Groundwater	1.69
Total freshwater	3.5

There is evidence that liquid water does exist on other bodies in our solar system but not on their surface. Evidence suggests that there is liquid water under the frozen surfaces of three of Jupiter's four larger satellites: Callisto, Europa, and Ganymede. In the case of Ganymede, the water appears to be between 145 and 193 km below the surface. Water ice has also been detected on all of the major satellites of Saturn and Uranus.

Water is the only known substance that is present in all three physical forms—liquid, solid (ice), and gas (atmospheric water vapor)—within the range of temperatures and pressures found on the Earth's surface and in its atmosphere. The presence of water in all three forms and the conversion of water from one form to another are important to the maintenance of climatic conditions within the range we consider acceptable for human life and for the stability of the Earth's **ecosystems**.

Distribution of the Earth's Water

More than 96% of the world's water is in the oceans (**Table 5-1**). However, the tiny fractions of water in the atmosphere and in freshwater systems (lakes, rivers, streams, and **groundwater**) are disproportionately important to humanity. Freshwater may be the most precious and scarce natural resource supporting human civilization. Transport of water vapor from the oceans through the atmosphere to land as rain and snow determines the availability of the freshwater resource. The transfer of water between oceans and atmosphere determines critical aspects of our climate. In **Chapter 7** we learn more about the importance of the hydrologic cycle whereby water is exchanged among the oceans, atmosphere, freshwater, groundwater, and polar ice sheets.

THE WATER MOLECULE

To understand the unusual properties of water, we need to understand the structure of atoms and molecules, particularly the water molecule.

Atoms and Electrons

Atoms consist of negatively charged electrons orbiting in shells that surround a nucleus. The nucleus contains neutrons that have no charge and protons that are positively charged. The electrical charge of a proton is equal and opposite to that of an electron, and the number of protons in each atom is equal to the number of electrons. Hence, atoms are electrically neutral.

Each electron shell is capable of holding only a certain number of electrons. For example, the innermost shell holds a maximum of two electrons, and the second shell holds a maximum of eight. Elements that have their outermost shell filled are noble gases (helium, neon, argon, krypton, xenon), which are inert (that is, they do not react chemically with most atoms).

The atoms of most elements have an outermost electron

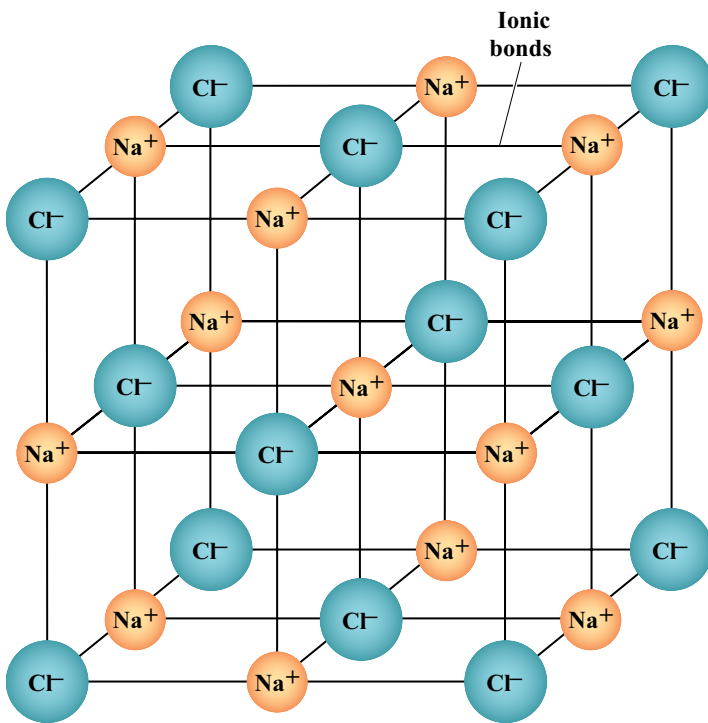


FIGURE 5-1 The sodium and chlorine atoms of common salt are held together in a salt crystal by ionic bonds. The ionic bond is an electrostatic attraction between the positively charged sodium ion (Na⁺) and the negatively charged chlorine ion (Cl⁻).

shell that is not completely filled with the maximum number of electrons. However, it is energetically favorable for each shell to be filled. Therefore, atoms of some elements, such as chlorine or oxygen, that have a nearly full outer electron shell, have a tendency to gain electrons in order to fill the shell. Atoms of other elements, such as sodium, that have outer electron shells less than half full, have a tendency to lose one or more electrons, producing an empty outer shell.

Chemical Bonds between Atoms

To fill their outer electron shells, two or more atoms of different elements can combine to create a molecule of a chemical compound. This can happen in two ways. First, one atom can donate one or more electrons to an atom of another element that has an incomplete outer shell. For example, a sodium atom can lose an electron, and a chlorine atom can gain this electron. Both now have completed outer electron shells. Sodium having lost an electron becomes a positively charged sodium **ion**, and chlorine becomes a negatively charged chloride ion. Because the two ions have opposite electrical charges, they are **electrostatically** attracted to each other and are bonded together by this attraction (**Fig. 5-1**). This type of bond is called an **ionic bond**.

The second way in which atoms of different elements can share electrons is called a **covalent bond**. One or more outer-shell electrons spend part of their time in the outer shell of each of the two atoms that are bonded. For example, each of two hydrogen atoms in the water molecule can share its single electron with an oxygen atom. To describe such electron sharing simply, each hydrogen electron orbits both its own hydrogen

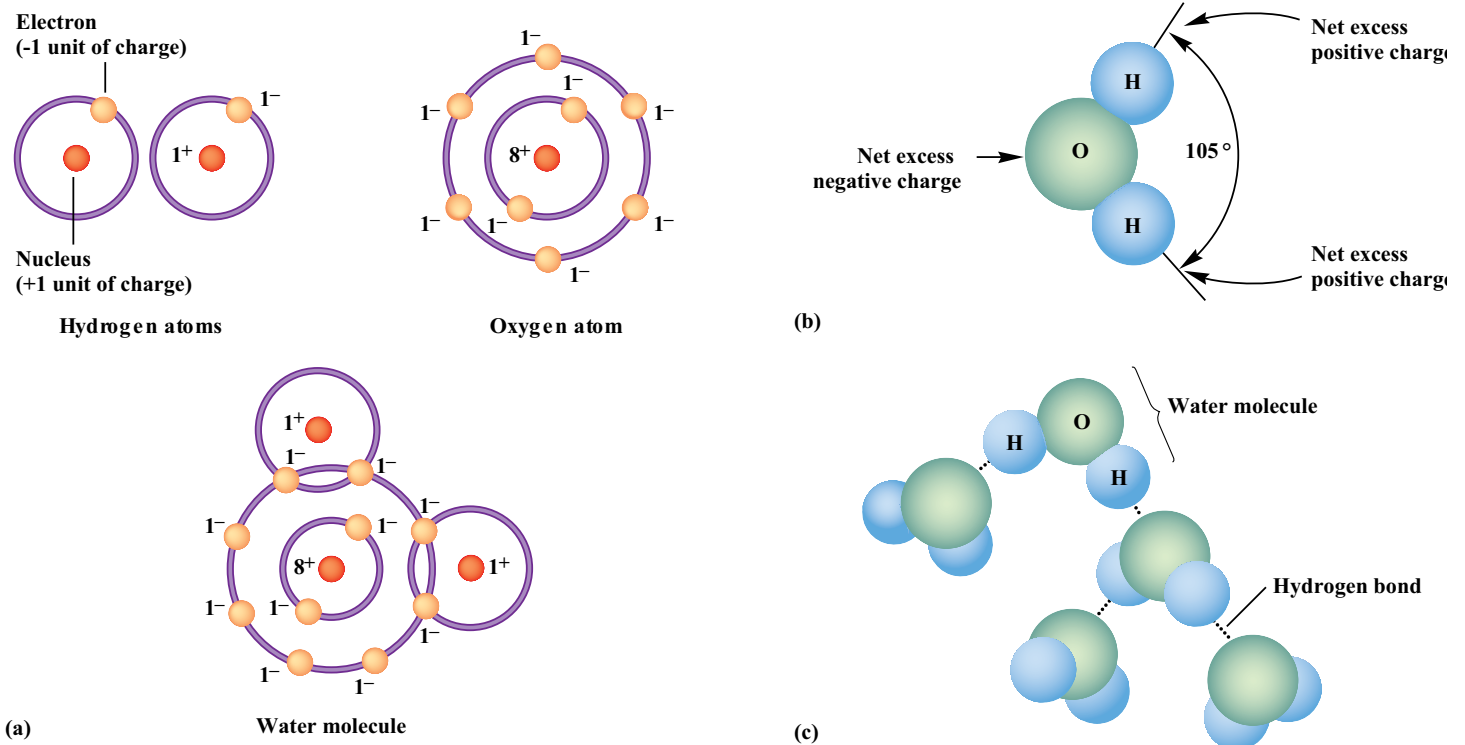


FIGURE 5-2 The water molecule consists of two hydrogen atoms and one oxygen atom. (a) The oxygen atom has six electrons in its outer shell. It lacks two electrons that would be needed to complete this shell. Each hydrogen atom has one electron and needs one more to complete its single shell. In a water molecule, the electrons from the hydrogen atoms and the six electrons from the outer shell of the oxygen atom are shared and orbit around both the oxygen and the hydrogen atoms. This is a covalent bond in which electron clouds from the bonded atoms partially overlap. (b) Both hydrogen atoms in a water molecule are on one side of the oxygen atom and are separated by an angle of 105°. The hydrogen electrons orbit partially around the oxygen atom, leaving the positive nucleus of each hydrogen atom partially “exposed” and giving this side of the water molecule a slight net positive charge. Similarly, the electrons orbiting the opposite side of the oxygen atom give that side of the molecule a slight net negative charge. Hence, water is a polar molecule. (c) Hydrogen bonds are formed between water molecules when the positive side of one molecule is attracted to the negative side of another.

Table 5-2 Anomalous Properties of Water and Their Importance

Property	Special Characteristic of Water	Importance
Heat capacity	Higher than that of any solid or liquid other than ammonia.	Water moderates climate in coastal regions. Currents transport large amounts of heat. Ocean water temperatures are relatively invariable in comparison with terrestrial temperatures.
Latent heat of fusion	Higher than that of any substance other than ammonia.	When ice forms, most of the energy lost is released to the atmosphere, and ice absorbs large amounts of heat in melting. Ice therefore acts as a thermostat to keep high-latitude water and atmosphere near freezing point all year.
Latent heat of vaporization	Higher than that of any other substance.	Heat is transported from the low-latitude ocean by evaporation and atmospheric circulation and released to the atmosphere through precipitation at higher latitudes.
Thermal expansion	Pure water has a density maximum at 4°C. The temperature at which the maximum occurs decreases as salinity increases; and there is no maximum at salinity >24.7.	Freshwater and low-salinity seawater stay unfrozen under ice in winter in lakes and estuaries.
Solvent property	Can dissolve more substances than any other liquid.	Water dissolves minerals from rocks and transports them to the oceans. Water is the medium in which the chemical reactions that support life occur.
Surface tension	Higher than that of any other liquid.	Surface tension controls the formation of droplets in the atmosphere and bubbles in the water. Some organisms use surface tension to anchor themselves to or walk on the surface.
Physical states	The only substance present as a gas, liquid, and solid within the temperature range at the Earth's surface.	Water vapor evaporated from the ocean helps transport heat from warm low latitudes to cold high latitudes. Liquid water also contributes to that transport through ocean currents. In polar regions, the presence of both ice and water moderates climate.

atom nucleus and within the outer shell of the oxygen atom electron cloud. At the same time, two electrons from the outer shell of the oxygen atom orbit within their own shell and around the hydrogen atoms (**Fig. 5-2a**). In this way, the oxygen has the extra electrons it needs to fill its outer electron shell for part of the time, and each of the two hydrogen atoms has two electrons to fill its outer electron shell for part of the time. Because the outer shell of each atom in the molecule is full at least part of the time, the bonded atoms form a stable molecule. Most covalent bonds are stronger than most ionic bonds. Consequently, atoms in a covalently bonded molecule usually are more difficult to break apart than those that are bonded by ionic bonds.

Van der Waals Force and the Hydrogen Bond

Molecules are electrically neutral. However, there is a weak attractive force between all molecules called the van der Waals force. It is caused by the attraction of the protons of one atom to the electrons of another. An additional attractive force or bond, called the hydrogen bond, is present between the molecules of water. In other chemical compounds, the hydrogen bond is either absent or weaker than it is in water. The strength of the hydrogen bond is what gives water most of its anomalous properties (**Table 5-2**).

Like other molecules, the water molecule is electrically neutral. However, the arrangement of atoms and electrons in the water molecule is such that the side of the molecule away from the hydrogen atoms has a small net negative charge, whereas the two areas where the hydrogen atoms are located have a small net

positive charge (**Fig. 5-2b**). Molecules that behave as though they have a positive and a negative side are called “polar molecules.” The reasons for the polarity are complicated, but they can be understood through a simplified example. The six electrons in the outer shell of the oxygen atom are arranged in pairs. The two hydrogen atoms are covalently bonded to the electrons in one of these pairs. This leaves two pairs of unshared orbiting electrons on the side of the oxygen atom opposite the hydrogen atoms, causing this side of the oxygen to have a negative charge bias. On the hydrogen side of the molecule, hydrogen electrons are shared with, and actually spend more time on, the oxygen atom, leaving the positively charged nucleus of each hydrogen atom “exposed.” Hence, this side of the molecule has a positive charge.

Because the water molecule is polar, the negatively charged side of one molecule is attracted to the positively charged side of an adjacent molecule. This attractive force is the hydrogen bond (**Fig. 5-2c**). It is relatively strong, but not as strong as ionic or covalent bonds. The relative strengths of bonds between atoms and molecules are listed in **Table 5-3**. The relative strength of a bond is an indication of how much energy is needed to break that bond. Substantially more energy is needed to break hydrogen bonds than is needed to counter van der Waals forces between molecules. The relatively high strength of the hydrogen bond is responsible for the anomalous properties of water.

THE DISSOLVING POWER OF WATER

Water can dissolve more substances and greater quantities of these substances than any other liquid. Its unique dissolving

power is related to the polar nature of the water molecule. Many inorganic chemical compounds—for example, sodium chloride (NaCl)—have ionic bonds. In such compounds, the two ions (Na^+ and Cl^- in the case of NaCl) are held together by the attraction of the two opposite electrical charges. If such a compound is placed in water, the electrostatic attraction is greatly reduced and the ionic bonds are broken by a process called **hydration**. Hydration occurs when a positive ion (e.g., Na^+) is surrounded by water molecules oriented with their negative sides toward the positive ion (Fig. 5-3). Conversely, a negative ion (e.g., Cl^-) is surrounded by water molecules oriented with their positive sides toward the negative ion. Thus, each ion becomes free to move independently of the other ion, and the compound dissolves. A variety of ionically bonded inorganic compounds, or “salts,” are dissolved in seawater. Many organic compounds also can be ionized and dissolved. Covalent compounds are generally less soluble in water than ionic compounds, although many covalent compounds, such as silica (SiO_2 , quartz, sand), dissolve in small quantities.

Water’s exceptional dissolving power is the reason why most elements are present in seawater, even though many are in very low concentrations. Most of the dissolved substances occur as either **cations** (positively charged ions) or **anions** (negatively charged ions), each of which has a surrounding sphere of properly oriented water molecules. Ions dissolved in seawater are the source of elements needed for the growth of **phototrophic** marine bacteria and algae, on which most ocean life depends (Chap. 12). Note that **phototrophy** in the oceans is dominated by microscopic bacteria and **algae**. Plants exist only in some shallow ocean areas and account for a very tiny fraction of ocean life.

The dissolving power of water is also important to terrestrial life. Land plants obtain many of their needed elements from solution in water through their root systems. Animals, including humans, obtain many of the elements and other chemicals needed for their **biochemical** systems by dissolving these substances from their food through the digestion process. In fact, almost all processes that support the growth and function of living organisms on our planet depend on the dissolving power of water. Life as we know it would not exist if water did not have the ability to dissolve and separate the ions, enabling them to be moved in solution into and within living tissue.

SOURCES AND SINKS OF CHEMICALS DISSOLVED IN SEAWATER

Seawater is a solution of many different chemical compounds: cations, anions, and both organic and inorganic compounds that are not ionized. Concentrations of the compounds in ocean water are determined by their behavior in global **biogeochemical cycles** (Fig. 5-4) and by their abundance in the materials of the Earth’s crust. Compounds are both added to ocean water from sources

Table 5-3 Relative Strengths of Bonds between Atoms and Molecules

Type of Bond	Approximate Relative Strength
Van der Waals force (between molecules)	1
Hydrogen bond (between molecules)	10
Ionic bond (between atoms)	100
Covalent bond (between atoms)	Usually >1000

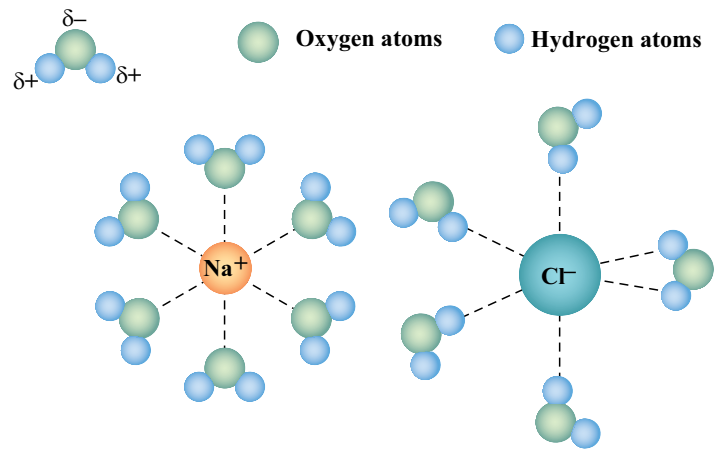


FIGURE 5-3 Compounds that are ionically bonded, such as common salt, are readily dissolved in water because both the positively charged ion (the sodium cation, Na^+) and the negatively charged ion (the chloride anion, Cl^-) are hydrated. Each ion is surrounded by polar water molecules oriented so that their positive sides (hydrogen atoms) face the anion and their negative sides (oxygen atom opposite the hydrogen atoms) face the cation. Hydration reduces the attraction between the cation and the anion and promotes their dispersal (solution) in the water.

such as river **runoff** and removed from seawater to sinks such as the seafloor sediments.

Biogeochemical Cycles

Continental rocks are **weathered** and transported to the oceans both as particles and as dissolved ions. The particles are deposited as ocean sediment. Many dissolved elements are used in biological processes and subsequently are incorporated in seafloor sediment in the form of the **hard parts** and **detritus** of marine organisms. Elements dissolved in seawater also can be precipitated directly or on particulate matter or they may be **adsorbed** by (adhere to) mineral grains and detritus and thus be removed to the sediment.

Over millions of years, ocean sediments are compacted by the weight of overlying sediments. Water is squeezed out and minerals precipitate between the grains, cementing the grains together to form sedimentary rock. Vast volumes of sedimentary rock and sediment eventually enter a **subduction zone**. Some of this material is scraped off the descending **lithospheric plate** edge and raised to form **sedimentary arc** islands, **continental margin** rocks, and **exotic terranes** (Chap. 4), where it is again weathered and **eroded**, thus continuing the biogeochemical cycle. Much of the sedimentary rock and sediment is **subducted** into the **mantle**, where some of it is melted and ejected through volcanoes as ash or **lava**. This material either reenters the oceans and returns to the ocean sediment directly, or collects on the land, where it is weathered and eroded to start a new cycle (Figure 5-4)

Biogeochemical cycles are actually much more complicated than Figure 5-4 indicates. For example, many elements used by marine organisms are rapidly recycled to seawater solution by the decomposition of detritus. Similarly, some elements from oceanic crustal rocks enter seawater in fluids discharged by **hydrothermal vents** at **oceanic ridges** (Chap. 15).

Steady-State Concentrations

The concentration of each element in ocean water is determined by the rate at which it enters the ocean water and the rate at which it is removed. If the rate of input exceeds the rate of removal, the concentration will rise, and vice versa. Although

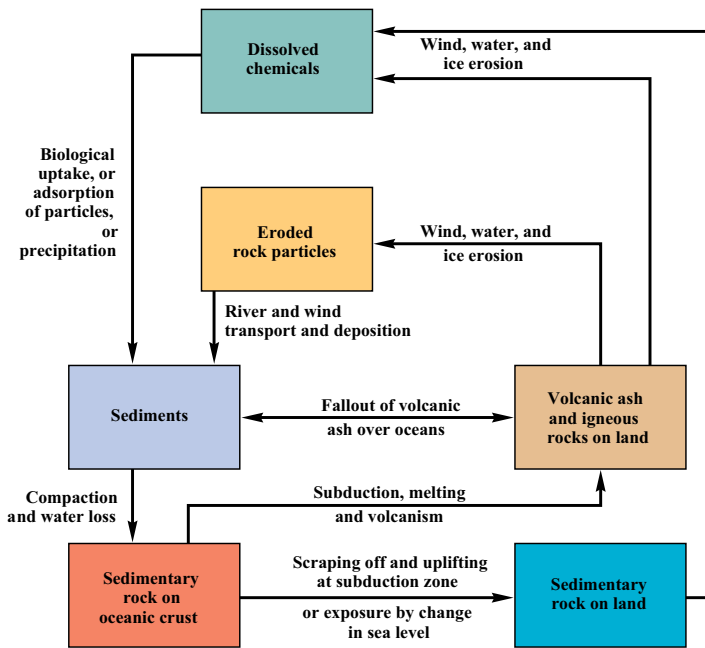


FIGURE 5-4 A simplified biogeochemical cycle.

global biogeochemical cycles include processes that take hundreds of millions of years, these cycles have been ongoing for billions of years and are thought to be at an approximate **steady state**. Steady state is achieved when the total quantity of an element in each of the compartments (square boxes) in Figure 5-4 remains approximately the same over time (its input rate equals its removal rate).

To see how a steady state is achieved, consider what would happen if an element's rate of input to the oceans were increased. The total quantity of an element within the global biogeochemical cycle does not change. Therefore, as the input to the oceans increases and the total quantity of the element in the oceans increases, the total quantity of the element in the other compartments must decrease. Consequently, less of the element is in the compartments that provide inputs to the oceans, and its input must decrease. If an element's input to the oceans (or any other compartment) increases, so do the rates of the various removal processes.

Here's a simple analogy: If we pour orange juice (the input) into a glass full of water and stir continuously, the glass will overflow. At first, the overflowing liquid (the output) is almost pure water, with only traces of orange juice mixed in it. The input of orange juice has increased, but neither the concentration in the glass nor that in the output reaches a new steady level instantly. As we continue to pour orange juice into the glass, the concentration of juice in the glass increases progressively to full concentration. The concentration of juice in the output also increases progressively in response to the change in concentration in the glass. When the concentrations of orange juice in the glass and in the output match the concentration of orange juice in the input, the system has reached a new steady state. Subsequently, unless we change the concentration of orange juice in the input, or alter

the output in some way (such as by allowing the orange juice pulp to settle and accumulate at the bottom of the glass), the input equals the output and the concentration of orange juice within the glass does not vary. Biogeochemical cycles are more complicated than our simple analogy because they have many inputs and outputs, and multiple "glasses" that empty into each other. However, they reach steady state in a similar way, and this steady state can be disturbed only by changes in one or more inputs or outputs.

Because the global biogeochemical cycles are approximately at steady state the rate of input of most elements to the oceans is approximately equal to the rate of removal. However, during Earth's long history changes such as plate tectonic movements and climate changes have altered the rates of input or output of the various elements to the oceans so the concentration of elements in the oceans has varied over long timescales.

Residence Time

The concentrations of elements in seawater are determined largely by the effectiveness of the processes that remove them from solution. Concentrations are high if the element is not removed rapidly or effectively from solution in ocean waters and if it is abundant in the Earth's crust. The effectiveness of removal is expressed by the **residence time (CC8)**, which is a measure of the mean length of time an atom of the element spends in the oceans before being removed to the sediment (or atmosphere).

The relationships of crustal abundance, residence time, and concentration in seawater for several elements are shown in Table 5-4. Note that the effectiveness of the removal processes, as expressed by residence time, is the principal determinant of concentration. Concentrations in this table are expressed both as $\text{mg}\cdot\text{kg}^{-1}$ the traditional units, that express weight of element per Kg of seawater and, **molality** units that reflect the relative number of atoms of each element in seawater rather than the total weight of the elements.

SALINITY

Many of the properties of water are modified by the presence of dissolved salts. The total quantity of dissolved salts in seawater is expressed as **salinity**. Until the early 1980s, salinity was expressed in grams of dissolved salts per kilogram of water or in parts per thousand, for which the symbol is ‰ (note that this is different from the percent symbol, %). The symbol ‰ is read as "per mil." Open-ocean seawater contains about 35 g of dissolved salts per kilogram of seawater and thus has a salinity of 35‰.

Table 5-4 Crustal Abundance, Oceanic Residence Time, and Seawater Concentration of Several Elements

Element	Crustal Abundance (%)	Oceanic Residence Time (years)	Concentration in Seawater	
			($\text{mg}\cdot\text{kg}^{-1}$)	($\text{pmol}\cdot\text{kg}^{-1}$)
Na (sodium)	2.4	55,000,000	10,780	$4.69\cdot 10^{11}$
Cl (chlorine as Cl^{-1})	0.013	87,000,000	19,360	$5.46\cdot 10^{11}$
Mg (magnesium)	2.3	13,000,000	1,280	$5.27\cdot 10^{10}$
K (potassium)	2.1	12,000,000	399	$1.02\cdot 10^{10}$
S (sulfur as sulfate, SO_4^{2-})	0.026	8,700,000	898	$2.80\cdot 10^{10}$
Ca (calcium)	4.1	1,100,000	412	$1.02\cdot 10^{10}$
Fe (iron)	2.4	200 to 500	0.00003	540
Al (aluminum)	6.0	200	0.00003	1,110
Mn (manganese)	0.5	60	0.00002	360
Pb (lead)	0.001	80	0.0000027	13

The original approach to measuring salinity was to evaporate water and weigh the salt residue. This tedious procedure was inaccurate because some dissolved ions, such as bromide and iodide, decomposed in the process and the elements were lost as gases. Various other methods have been used to determine salinity, including measuring the chloride concentration (which is closely related to total dissolved solids because seawater follows the principle of constant proportions, as discussed in the next section).

The most precise and widely used method of salinity determination is the measurement of **electrical conductivity**. Salinity is measured by comparison of the conductivity of two solutions, one of which has a precisely known salinity. Until the early 1980s, the comparison was made with a standard seawater whose salinity was determined precisely by a reference laboratory in Copenhagen, Denmark, and later in England. This method worked well but became very difficult as oceanography grew and the reference laboratory had to supply standard water samples to hundreds of laboratories worldwide. For this reason, and to improve the precision of salinity measurements, salinity has been redefined as a ratio of the electrical conductivity of the seawater to the electrical conductivity of a standard concentration of potassium chloride solution.

Because salinity is now defined as a ratio of electrical conductivities, it is no longer measured in parts per thousand but is expressed in “practical salinity units” (PSU). The average seawater salinity is now expressed as 35 without the ‰ symbol. However, seawater with a salinity of 35 PSU does have a concentration of almost exactly 35 g of dissolved salts per kilogram. All salinity values in this text are stated without the ‰ symbol, as is consistent with currently accepted practice. However, the symbol is still used in some publications.

Very small salinity changes can significantly alter seawater **density**. Consequently, salinity often must be measured to ± 0.001 , and to achieve that precision, conductivity must be measured to ± 1 part in 40,000. Such precision is readily achievable in the laboratory, and compact rapid reading conductivity sensors achieve nearly that precision when mounted in the CTD probes described in **Chapter 3**.

DISSOLVED CHEMICALS IN SEAWATER

The chemicals dissolved in seawater include most elements, a variety of naturally occurring and human-made **radionuclides (radioisotopes)**, and numerous organic compounds. Elements in solution are generally ionized. Many ions are compound ions, such as nitrate (NO_3^-) and phosphate (PO_4^{3-}), in which atoms of one element are combined with atoms of other elements. Hence, although we talk about dissolved nitrogen or phosphorus, we generally use the term “dissolved constituents,” not “dissolved elements.” Dissolved constituents are designated major, minor, or trace according to their concentration. Trace constituents include organic compounds, radionuclides, and trace elements. The term “trace elements” is widely used, although it is not accurate, because dissolved trace elements are present in seawater as simple or compound ions. Dissolved gases are generally considered separately.

Concentrations of dissolved constituents of seawater are usually measured in parts per million ($\text{mg}\cdot\text{kg}^{-1}$) or parts per billion ($\mu\text{g}\cdot\text{kg}^{-1}$). One part per million is roughly equivalent to one teaspoonful mixed into 5000 liters of water, or enough water to

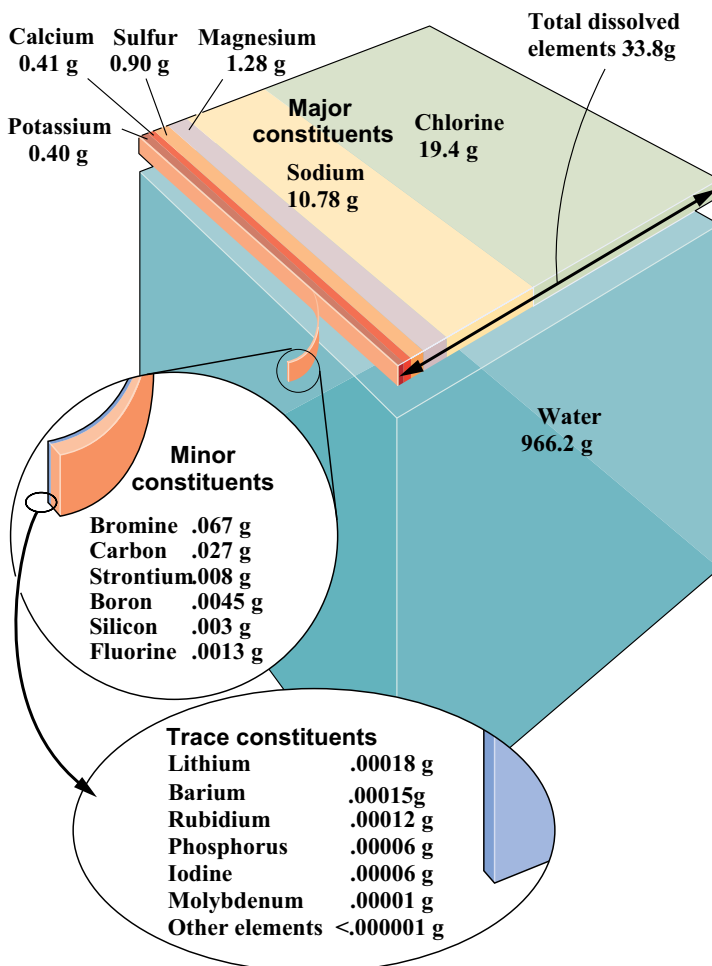


FIGURE 5-5 The dissolved elements in 1 kg of seawater. The total mass of dissolved elements is less than the total mass of dissolved salts (salinity) because the mass of dissolved salts includes the H^+ and OH^- ions associated with the dissolved species of some elements in seawater (see **Table 5-5**).

fill more than 14,000 cans of soda. One part per billion is roughly equivalent to mixing one teaspoonful into 5,000,000 liters of water, enough water to fill about five Olympic-size swimming pools. Some dissolved trace metal and organic constituents of seawater occur at concentrations in the parts per trillion range. One part per trillion is equivalent to one cent in 10 million dollars or one second in 31,700 years. Oceanographers now routinely express concentrations in molality units, discussed in **Chapter 1**.

Major Constituents

The major dissolved constituents have concentrations greater than 100 parts per million by weight. The six major constituents (**Table 5-5**) are chlorine, sodium, magnesium, sulfur (as sulfate), calcium, and potassium. They occur as the ions identified in **Table 5-5**. Together, these six ions constitute 99.28% of all dissolved salts in the oceans (**Fig. 5-5**), and sodium and chloride (the constituents of table salt) alone constitute more than 85%.

With the exception of calcium, which is used by many marine organisms to build calcium carbonate hard parts of their bodies (**Chap. 6**), the major constituents are not utilized significantly in biological processes and do not interact readily with inorganic particles. Therefore, the primary process by which they are removed from the oceans is by the precipitation of salt deposits. This process occurs in shallow, partially enclosed **marginal seas** or embayments where the rate of removal of water by evapora-

TABLE 5.5 Concentrations and Speciation of the Elements in Seawater (Salinity 35)

Element	Chemical Symbol	Concentration (mg·kg ⁻¹)	Some Probable Dissolved Species
Chlorine	Cl	1.936 × 10 ⁴	Cl ⁻
Sodium	Na	1.078 × 10 ⁴	Na ⁺
Magnesium	Mg	1.28 × 10 ³	Mg ²⁺
Sulfur	S	8.98 × 10 ²	SO ₄ ²⁻ , NaSO ₄ ⁻
Calcium	Ca	4.12 × 10 ²	Ca ²⁺
Potassium	K	3.99 × 10 ²	K ⁺
Bromine	Br	67	Br ⁻
Carbon	C	27	HCO ₃ ⁻ , CO ₃ ²⁻ , CO ₂
Nitrogen	N	8.3	N ₂ gas, NO ₃ ⁻ , NH ₄
Strontium	Sr	7.8	Sr ²⁺
Boron	B	4.5	B(OH) ₃ , B(OH) ₄ ⁻ , H ₂ BO ₃
Oxygen	O	2.8	O ₂ gas
Silicon	Si	2.8	Si(OH) ₄
Fluorine	F	1.3	F ⁻ , MgF ⁺
Argon	Ar	0.62	Ar gas
Lithium	Li	0.18	Li ⁺
Rubidium	Rb	0.12	Rb ⁺
Phosphorus	P	6.2 × 10 ⁻²	HPO ₄ ²⁻ , PO ₄ ³⁻ , H ₂ PO ₄
Iodine	I	5.8 × 10 ⁻²	IO ₃ ⁻ , I ₂
Barium	Ba	1.5 × 10 ⁻²	Ba ²⁺
Molybdenum	Mo	1 × 10 ⁻²	MoO ₄ ²⁻
Uranium	U	3.2 × 10 ⁻³	UO ₂ (CO ₃) ₂ ⁴⁻
Vanadium	V	2.0 × 10 ⁻³	H ₂ VO ₄ ⁻ , HVO ₄ ²⁻
Arsenic	As	1.2 × 10 ⁻³	HAsO ₄ ²⁻ , H ₂ AsO ₄ ⁻
Nickel	Ni	4.8 × 10 ⁻⁴	Ni ²⁺
Zinc	Zn	3.5 × 10 ⁻⁴	ZnOH ⁺ , Zn ²⁺ , ZnCO ₃
Krypton	Kr	3.1 × 10 ⁻⁴	Kr gas
Cesium	Cs	3.1 × 10 ⁻⁴	Cs ⁺
Chromium	Cr	2.1 × 10 ⁻⁴	Cr(OH) ₃ , CrO ₄ ²⁻
Antimony	Sb	2.0 × 10 ⁻⁴	Sb(OH) ₆ ⁻
Neon	Ne	1.6 × 10 ⁻⁴	Ne gas
Copper	Cu	1.5 × 10 ⁻⁴	CuCO ₃ , CuOH ⁺
Selenium	Se	1.55 × 10 ⁻⁴	SeO ₃ ²⁻
Cadmium	Cd	7 × 10 ⁻⁵	CdCl ₂ ⁰
Xenon	Xe	6.6 × 10 ⁻⁵	Xe gas
Aluminium	Al	3 × 10 ⁻⁵	Al(OH) ₃ ⁻
Iron	Fe	3 × 10 ⁻⁵	Fe(OH) ₂ ⁺ , Fe(OH) ₄
Manganese	Mn	2 × 10 ⁻⁵	Mn ²⁺ , MnCl ⁺
Yttrium	Y	1.7 × 10 ⁻⁵	Y(OH) ₃
Zirconium	Zr	1.5 × 10 ⁻⁵	Zr(OH) ₄
Thallium	Tl	1.3 × 10 ⁻⁵	Tl ⁺
Tungsten	W	1 × 10 ⁻⁵	WO ₄ ²⁻
Niobium	Nb	5 × 10 ⁻⁶	Not known
Rhenium	Re	7.8 × 10 ⁻⁶	ReO ₄ ⁻
Helium	He	7.6 × 10 ⁻⁶	He gas
Titanium	Ti	6.5 × 10 ⁻⁶	Ti(OH) ₄

Element	Chemical Symbol	Concentration (mg·kg ⁻¹)	Some Probable Dissolved Species
Lanthanum	La	5.6 × 10 ⁻⁶	La(OH) ₃
Germanium	Ge	5.5 × 10 ⁻⁶	Ge(OH) ₄
Hafnium	Hf	3.4 × 10 ⁻⁶	Not known
Neodymium	Nd	3.3 × 10 ⁻⁶	Nd(OH) ₃
Lead	Pb	2.7 × 10 ⁻⁶	PbCO ₃ , Pb(CO ₃) ₂ ²⁻
Tantalum	Ta	<2.5 × 10 ⁻⁶	Not known
Silver	Ag	2 × 10 ⁻⁶	AgCl ₂ ⁻
Cobalt	Co	1.2 × 10 ⁻⁶	Co ²⁺
Gallium	Ga	1.2 × 10 ⁻⁶	Ga(OH) ₄
Erbium	Er	1.2 × 10 ⁻⁶	Er(OH) ₃
Ytterbium	Yb	1.2 × 10 ⁻⁶	Yb(OH) ₃
Dysprosium	Dy	1.1 × 10 ⁻⁶	Dy(OH) ₃
Gadolinium	Gd	9 × 10 ⁻⁷	Gd(OH) ₃
Praseodymium	Pr	7 × 10 ⁻⁷	Pr(OH) ₃
Scandium	Sc	7 × 10 ⁻⁷	Sc(OH) ₃
Cerium	Ce	7 × 10 ⁻⁷	Ce(OH) ₃
Samarium	Sm	5.7 × 10 ⁻⁷	Sm(OH) ₃
Tin	Sn	5 × 10 ⁻⁷	SnO(OH) ₃ ⁻
Holmium	Ho	3.6 × 10 ⁻⁷	Ho(OH) ₃
Lutetium	Lu	2.3 × 10 ⁻⁷	Lu(OH) ₃
Beryllium	Be	2.1 × 10 ⁻⁷	BeOH ⁺
Thulium	Tm	2 × 10 ⁻⁷	Tm(OH) ₃
Europium	Eu	1.7 × 10 ⁻⁷	Eu(OH) ₃
Terbium	Tb	1.7 × 10 ⁻⁷	Tb(OH) ₃
Mercury	Hg	1.4 × 10 ⁻⁷	HgCl ₄ ²⁻ , HgCl ₂
Indium	In	1 × 10 ⁻⁷	In(OH) ₂ ⁺
Rhodium	Rh	8 × 10 ⁻⁸	Not known
Palladium	Pd	6 × 10 ⁻⁸	Not known
Platinum	Pt	5 × 10 ⁻⁸	Not known
Tellurium	Te	7 × 10 ⁻⁸	Te(OH) ₃
Bismuth	Bi	3 × 10 ⁻⁸	BiO ⁺ , Bi(OH) ₂ ⁺
Thorium	Th	2 × 10 ⁻⁸	Th(OH) ₄
Gold	Au	9.85 × 10 ⁻⁹	AuCl ₂ ⁻
Ruthenium	Ru	5 × 10 ⁻⁹	Not known
Osmium	Os	2 × 10 ⁻⁹	Not known
Radium	Ra	1.3 × 10 ⁻¹⁰	Ra ²⁺
Iridium	Ir	1.3 × 10 ⁻¹⁰	Not known
Protactinium	Pa	5 × 10 ⁻¹¹	Not known
Radon	Rn	6 × 10 ⁻¹⁶	Rn gas

Note: Even for the more abundant constituents, concentration may vary slightly. For the rarer elements, the listed concentrations are uncertain and may be revised as analytical methods improve.

tion far exceeds its replacement by precipitation, river flow, and mixing with the open ocean (**Chap. 6**).

Inputs of major constituents from rivers and other sources are very small in comparison with the quantities in the oceans. Because concentrations of these constituents are not affected significantly by inputs or removal processes, their residence time is very long and the relative concentrations of these major constituents do not vary significantly. This principle of constant proportions is a cornerstone of chemical oceanography. The ratios of major constituent concentrations in seawater vary significantly only in enclosed seas, where evaporation leads to salt precipitation (**Chap.**

6), and in **estuaries**, where the ocean water is mixed with substantial quantities of river water. River water has a much more variable composition of the constituents.

Minor Constituents

The minor constituents of seawater include bromine, carbon, strontium, boron, silicon, and fluorine. They have concentrations between 1 part per million and 100 parts per million (**Table 5-5, Fig. 5-5**). Nitrogen and oxygen are not considered to be among the minor constituents, because they are present in seawater primarily as dissolved molecular oxygen (O₂) and nitrogen (N₂) gases. Dissolved gases are considered separately later in the chapter. To-

gether, the six major and six minor constituents constitute more than 99.6% of all the dissolved solids. Several minor constituents, notably carbon and silicon, are utilized extensively in biological processes. Therefore, the concentrations of these constituents in ocean waters are variable geographically and with time, changing in response to uptake by marine organisms and release during decay of organic matter. Such variations are discussed in **Chapter 12**.

Trace Elements

Other than the 12 major and minor constituents and the dissolved gases, all the elements listed in **Table 5-5** have concentrations in seawater of less than 1 part per million. Together, these trace elements constitute only about 0.4% of the total dissolved solids in seawater. Most trace elements are used extensively in biological processes or attach easily to particles that remove them from seawater. Many are introduced in significant quantities by hydrothermal vents, undersea volcanoes, decomposition of organic matter, atmospheric sources such as volcanic gases, river outflows, and release from seafloor sediment. Concentrations of the various trace constituents vary substantially in different parts of the ocean in response to variations in the input and removal processes.

Many trace elements are essential minerals for marine life, others are toxic, and many are essential for marine life at low concentrations but toxic at higher concentrations (**CC18**). Measurements of the concentrations of trace metals and observations of their **spatial** and temporal variations in the oceans are important to marine biological and pollution studies.

Many trace elements that are essential (e.g., iron, zinc, and copper) or toxic (e.g., lead and mercury) have seawater concentrations of about one part per billion (10^9) down to less than one part in 10^{13} (**Table 5-5**). Marine chemists have great difficulty measuring such extremely small concentrations. For many elements, the amount that dissolves from surfaces of samplers and sample bottles or is contributed by dust in laboratory air can be greater than the quantity in the water sample itself.

Radionuclides

A variety of naturally occurring and human-made radionuclides are present in seawater at extremely low concentrations (**CC7**). **Radioactivity** emanating from individual **isotopes** can be measured at exceedingly low levels, and sample contamination is generally a less critical problem than it is for trace metals. Therefore, determining even extremely small concentrations of radionuclides in seawater is relatively easy. In addition, many radionuclides are introduced to the oceans at known locations, and thus radionuclides can be used to trace the movements of ocean water (**Chap. 8**).

Radionuclides behave in biogeochemical cycles in ways that are virtually identical to those of the stable (nonradioactive) isotopes of their elements. Therefore, radionuclide distributions in seawater, sediments, and marine organisms, and movements of radionuclides among them, are used to infer movements of stable isotopes through the marine biogeosphere.

Organic Compounds

Thousands of different dissolved organic compounds are present in seawater. They include naturally occurring compounds such as proteins, carbohydrates, **lipids**, **amino acids**, vitamins, and petroleum hydrocarbons, as well as synthetic contaminants,

including **DDT** and **PCBs** (polychlorinated biphenyls). The number of organic compounds is so large that probably less than 1% of them have been identified. Most organic compounds are very difficult to study because they are present in the parts per trillion concentration range (one teaspoonful in 5000 Olympic-size swimming pools). However, we believe that marine algae and perhaps some animals cannot grow successfully without dissolved compounds, such as vitamins (**Chaps. 12, 13**). We also know that certain organic compounds are highly toxic, even at concentrations in the parts per trillion range.

Most organic compounds in seawater are naturally occurring compounds. Many are produced by marine organisms and released to seawater, either through **excretions** (similar to urine) or by being dissolved after the death and decomposition of the organism. Organic compounds are also transported from land to the ocean in rivers and through the atmosphere. In some areas, especially where runoff from **mangrove swamps** or **salt marshes** carries large quantities of organic matter, the concentrations of colored dissolved organic compounds (sometimes called “gelbstoff”) are high enough to make the water appear brownish yellow.

Some dissolved organic compounds are removed from solution by attachment to particles that sink to the seafloor. However, most such compounds are taken up by marine organisms or decomposed to their inorganic constituents in the water column, primarily by **bacteria** and **archaea** (**Chap. 12**).

Dissolved Gases

Gases are free to move between the atmosphere and the oceans at the ocean surface. The net direction of the exchange is determined by the **saturation solubility** and concentration of the gas in seawater. The saturation solubility is the maximum amount of the gas that can be dissolved in water at a specific temperature, salinity, and pressure. If seawater is undersaturated, a net transfer of gas molecules into the water occurs. If seawater is oversaturated, the net transfer is from the water into the atmosphere.

The atmosphere is composed primarily of nitrogen (78%) and oxygen (21%) and contains several other minor gases. Carbon dioxide constitutes about 0.037% of all atmospheric gases. The distribution of gases dissolved in ocean waters is very different (**Table 5-6**). The oceans have proportionally more oxygen and less nitrogen than the atmosphere because of differences in the saturation solubility of these gases. In addition, the ratios of carbon dioxide concentration to oxygen and nitrogen concentrations are much higher in seawater than in the atmosphere because carbon dioxide reacts with water in a complicated way to produce highly soluble carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) anions.

Oxygen and Carbon Dioxide

Gases can be exchanged between the ocean and the atmosphere only at the ocean surface. In the water column beneath the ocean surface, the proportions of dissolved gases are changed primarily by biochemical processes. In the shallow **photic zone** where light penetrates, carbon dioxide is consumed, and oxygen released during **photosynthesis**. However, in the much larger volume of deep-ocean waters where no photosynthesis occurs, the dominant process affecting dissolved gas concentrations is the consumption of oxygen through **respiration** and decomposition. The excess carbon dioxide produced by respiration and decomposition can escape to the atmosphere only at the ocean surface, and there is no mechanism for resupplying dissolved oxygen to the water below the photic zone. Therefore, deep-ocean water is

Table 5-6 Distribution of Gases in the Atmosphere and Dissolved in Seawater

Gas	Percentage of Gas Phase by Volume		
	Atmosphere	Surface Oceans	Total Oceans
Nitrogen (N ₂)	78	48	11
Oxygen (O ₂)	21	36	6
Carbon dioxide ^a	0.037	15	83

^a CO₂ in the atmosphere, CO₂ plus HCO₃⁻ plus CO₃²⁻ in the oceans.

depleted of oxygen and stores large quantities of carbon dioxide (Table 5-6).

The total quantity of carbon dioxide dissolved in the oceans is about 70 times as large as the total in the atmosphere. The processes that control oxygen and carbon dioxide concentrations at different depths and locations within the oceans are discussed in more detail in Chapter 12. The role of the oceans in absorbing and storing carbon dioxide is critical to the fate of carbon dioxide that has been, or will be, released by industrialized civilization, and to the severity of global climate change due to the enhanced greenhouse effect (CC9).

The saturation solubility of gases varies with pressure, temperature, and salinity. It increases with increasing pressure and decreasing temperature. Therefore, seawater at depth in the oceans can dissolve much higher concentrations of gases than surface seawater can. There is continuous movement of water from ocean surface layers to the deep layers and eventually back to the surface (Chap. 8). As water moves through the ocean depths, concentrations of dissolved gases are changed by biochemical processes and by mixing with other water masses that have different concentrations of the gases. Geological processes,

including the release of gases from undersea volcanoes and from decaying organic matter in sediments, can also change the concentrations of some gases, but those processes are generally of minor significance.

When water that is saturated with carbon dioxide sinks below the surface layer, gases can no longer be exchanged with the atmosphere. However, carbon dioxide is released into deep-ocean waters by respiration and by decay of organic matter. The added gas remains **dissolved** because the saturation solubility is increased by the higher pressures.

The increase in **solubility** caused by increased pressure is what keeps carbon dioxide dissolved in carbonated sodas. The carbon dioxide is dissolved in the soda under increased pressure at the bottling plant and then sealed in its container at the higher pressure. When the container is opened, the internal pressure is released, and the carbon dioxide bubbles out because the concentration exceeds the saturation solubility at the lower pressure.

The saturation solubility of gases generally increases as temperature decreases and is generally lower at ocean water salinities than in pure water (Fig. 5-6). Oxygen concentrations are higher in cold surface waters near the polar regions than in tropical waters. In tropical waters, the oxygen concentration is low enough that, under certain circumstances, it can be inadequate for the respiration needs of some marine species. For the same reason, tropical waters are more vulnerable to marine pollution by oxygen-consuming waste materials, such as sewage (Chap. 16).

Other Gases.

In addition to the major atmospheric gases, several other gases are present in seawater (Table 5-7). With the exception of sulfur dioxide, these gases are produced primarily by marine organisms, so surface waters are oversaturated and net movement of the gases is into the atmosphere (Table 5-7). The quantities of

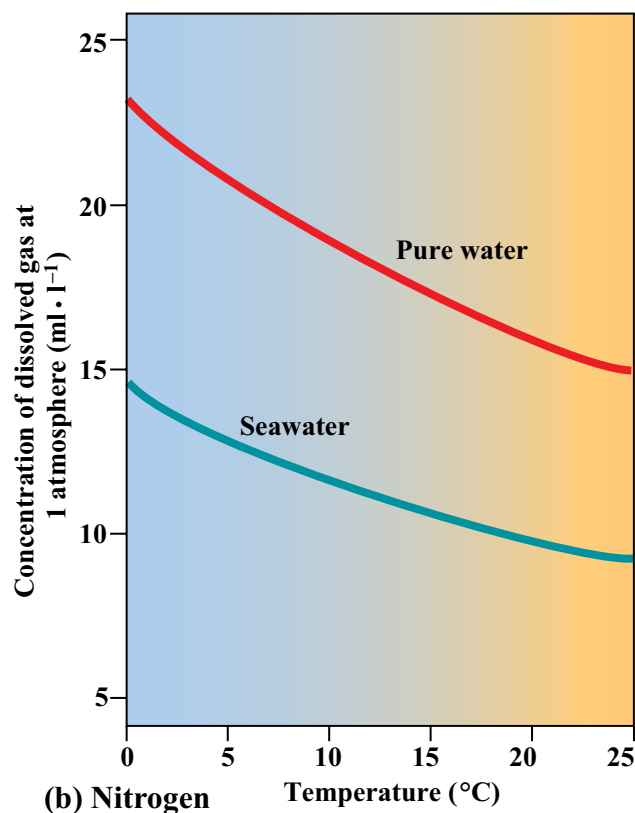
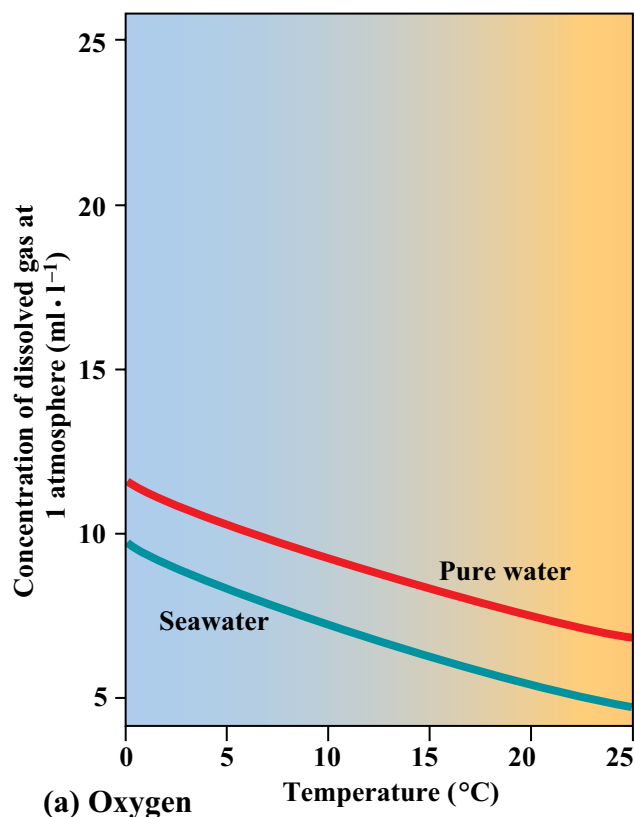


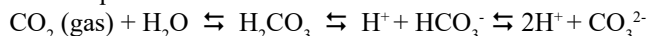
FIGURE 5-6 Solubility of oxygen (a) and nitrogen (b) in pure water and seawater. Note that the solubility of each gas is reduced as temperature increases and is lower at seawater salinity than in freshwater

such gases supplied to the atmosphere by the oceans are relatively small in comparison with those from other sources. However, the ocean concentrations of methane, for example, must be taken into account in global climate change studies because atmospheric methane contributes significantly to the greenhouse effect (CC9). Atmospheric sulfur dioxide comes primarily from fossil fuel burning, industrial processes, and volcanoes. Sulfur dioxide can be converted to sulfuric acid, the principal component of acid rain. The oceans act as a sink for this air contaminant by absorbing sulfur dioxide and the sulfate ions present in the runoff from acid rain.

pH and Buffering

The acidic or alkaline property of water is expressed as pH, which is a measure of the concentration of hydrogen ions (H^+). The pH increases as the hydrogen ion concentration decreases, and it is measured on a logarithmic scale of zero to 14: pH 0 is the most acidic, pH 14 is the most alkaline, and pH 7 is neutral. Pure water (free of dissolved carbon dioxide) is neutral, pH 7. Seawater normally is about pH 8, mildly alkaline. The near-neutral pH of natural waters is very important to aquatic biology. For example, persistent acid rain, which can be about pH 5, can severely damage or destroy aquatic life in lakes by reducing the natural pH of the lake water. In addition, the numerous marine species with calcium carbonate hard body parts cannot construct these parts if the water is even mildly acidic.

Seawater pH is buffered (maintained within a narrow range of pH 7.5 to 8.1) through the reactions of dissolved carbon dioxide. Dissolved carbon dioxide combines with water to form carbonic acid (H_2CO_3). The carbonic acid partially dissociates (separates into ions) to form a hydrogen ion and a bicarbonate ion (HCO_3^-), or two hydrogen ions and a carbonate ion (CO_3^{2-}). Carbon dioxide, carbonic acid, bicarbonate, carbonate, and hydrogen ions coexist in equilibrium in seawater:



The addition of acid to seawater increases the number of hydrogen ions, which reduces the pH of the seawater and forces the equilibrium to shift so that less carbonate and bicarbonate are present. This shift reduces the number of hydrogen ions present, which offsets the reduction of pH. The opposite shift occurs if alkali is added to seawater. Such buffering capacity partially protects the ocean waters from pH changes that otherwise might result from acid rain or from acidic or alkaline industrial effluents. However, the amount of carbon dioxide released by humans is so large that ocean pH is indeed changing slowly. Some of the

possible consequences of this change were discussed in Chapter 1.

HEAT PROPERTIES OF WATER

Of the properties of water, perhaps none are more important than the unique responses of water, ice, and water vapor to the application and removal of heat.

Heat Energy and Phase Changes

All substances can exist in three different phases: solid, liquid, or gas. In a solid, attractive forces between molecules (van der Waals forces, and hydrogen bonds if present) are strong enough to ensure that the molecules stay firmly fixed in place relative to each other, even though the molecules (or atoms in a pure element) vibrate. Heating the solid increases the strength of these vibrations. When the heat energy of each molecule is sufficient to overcome most of the attractive forces, the solid melts and becomes liquid. In a liquid, the molecules have enough energy to vibrate, rotate, and translate (temporarily move about in relation to each other). However, they do not have enough energy to escape completely from the attractive forces of their neighbors. If more heat is added to a liquid, each molecule eventually has enough energy to break free of the attractive forces. The compound then becomes a gas, in which each molecule is free to move about by itself. If heat is removed, the process is reversed; gas becomes liquid, and then solid, as heat is progressively lost.

Molecules of different chemical compounds have van der Waals forces of different strengths. As a result, each compound requires a certain characteristic quantity of heat energy to convert from solid to liquid or from liquid to gas. The stronger the attractive force between the molecules, the more heat energy each molecule must have to break free of this force. Therefore, the temperature at which a solid melts (the melting, or freezing, point) and the temperature at which a liquid vaporizes (the boiling, or condensation, point) increase as the van der Waals attractive force increases.

Freezing and Boiling Points

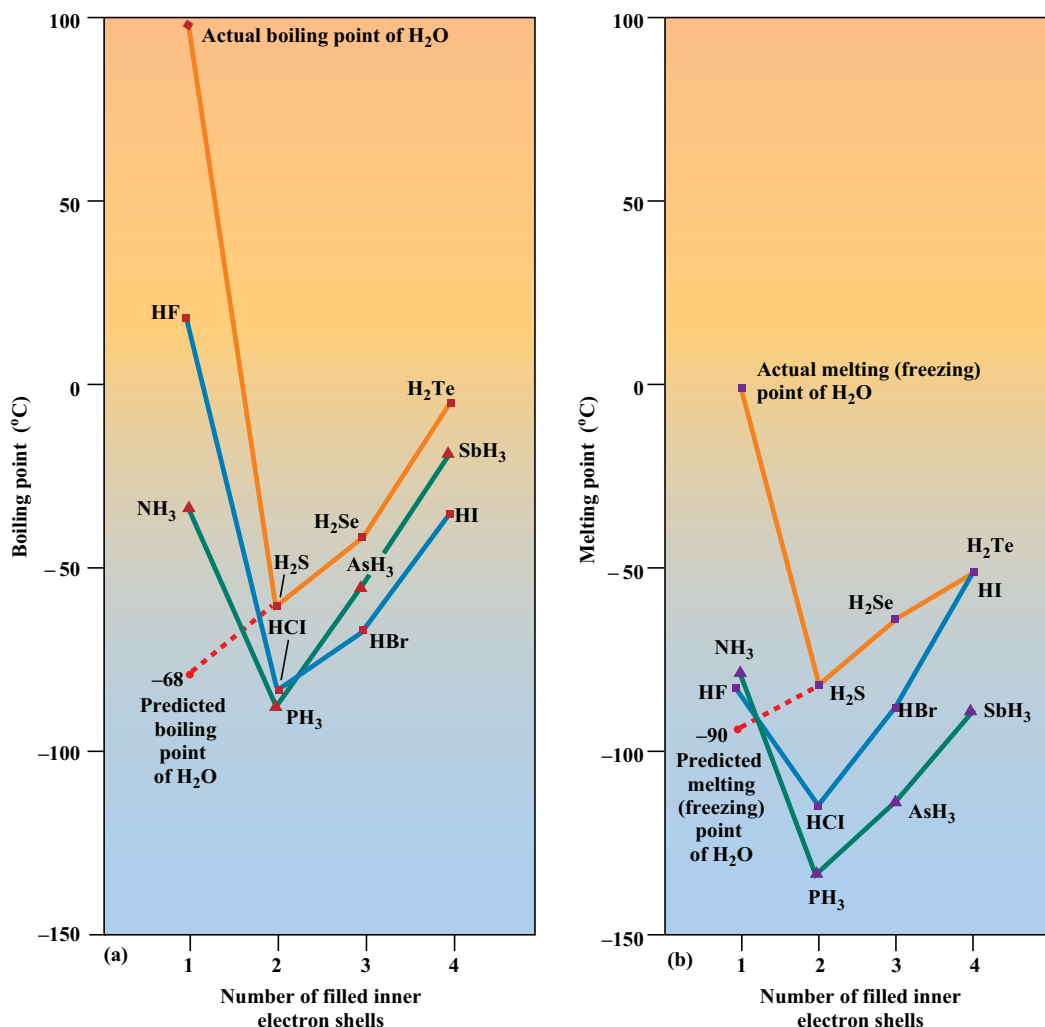
To convert solid water (ice) to liquid water and liquid water to gaseous water (water vapor), the heat energy supplied must overcome both the van der Waals attractive force and the much stronger attractive force of the hydrogen bond. Therefore, the amount of heat energy that each molecule of water must have to become free to rotate and move in relation to adjacent molecules (that is, to change from ice to water) is much greater than it would be if the hydrogen bond were not present. Similarly, the amount of heat energy that each water molecule must have to free itself completely and enter the gaseous state is much greater than it would be without the hydrogen bond.

The extra energy needed to break the hydrogen bond causes water's freezing point and boiling point temperatures to be anomalously high. If there were no hydrogen bond, water would freeze at about -90°C and boil at about -70°C , and all water on the Earth would be gaseous. There would be no oceans or life as we know it. Comparison of the boiling and freezing points of water with those of other hydrogen compounds that are formed with elements that, like oxygen, have two electrons short of a full outer electron shell

Table 5-7 Estimated Flux of Gases between Oceans and Atmosphere

Gas	Total Transfer ($\text{g}\cdot\text{yr}^{-1}$)	Direction of Net Transfer
Sulfur dioxide (SO_2)	1.5×10^{14}	Atmosphere to ocean
Nitrous oxide (N_2O)	1.2×10^{14}	Ocean to atmosphere
Carbon monoxide (CO)	4.3×10^{13}	Ocean to atmosphere
Methane (CH_4)	3.2×10^{12}	Ocean to atmosphere
Methyl iodide (CH_3I)	2.7×10^{11}	Ocean to atmosphere
Dimethyl sulfide ($\text{CH}_3)_2\text{S}$	4.0×10^{13}	Ocean to atmosphere

FIGURE 5-7 Freezing and boiling points of hydrogen compounds. The lines on the chart connect compounds of hydrogen with elements that have the same number of electrons in their outer shell but a different number of filled inner shells. If there were no hydrogen bond, both the boiling point and the melting point of compounds would be expected to increase progressively along these lines as the number of filled shells increased. However, water (H_2O), hydrogen fluoride (HF), and ammonia (NH_3) all have strong hydrogen bonds between their polar molecules, whereas there is no appreciable hydrogen bond in the compounds of hydrogen that are formed with sulfur (S), selenium (Se), tellurium (Te), chlorine (Cl), bromine (Br), iodine (I), phosphorus (P), arsenic (As), and antimony (Sb). In this latter group of compounds, the hydrogen bond is virtually absent because the atom combined with the hydrogen is much larger, and, therefore, the polarity of the molecules is much less. Since the hydrogen bond must be broken to convert solid to liquid or liquid to gas, the boiling points (a) and melting (freezing) points (b) of water, hydrogen fluoride, and ammonia are much higher than would be expected if they were not held by hydrogen bonds.



illustrates the anomalous nature of water (Fig. 5-7). Molecules in which hydrogen is combined with elements whose atoms are similar in size to oxygen but have a different number of outer-shell electrons (hydrogen fluoride, HF ; ammonia, NH_3) are also polar. They, too, have hydrogen bonds and anomalous melting and boiling points (Fig. 5-7).

As discussed later in this chapter, adding salt to water raises the boiling point and lowers the freezing point.

Heat Capacity and Latent Heat


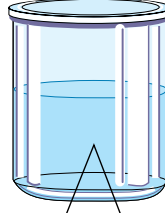
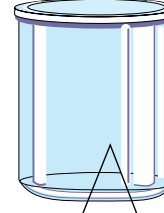
In addition to the freezing and boiling points, the numerical values of three other related heat properties of water are anomalously high because of the hydrogen bond: the **heat capacity**, the **latent heat of fusion**, and the **latent heat of vaporization**. These properties express the quantity of heat per specified quantity of a substance needed to raise the temperature, to convert solid to liquid, and to convert liquid to gas, respectively. Heat is a form of energy, and as such, it is quantified by a unit of energy. The SI unit of energy is the **joule** (abbreviated J). This SI unit is not yet in common usage in the United States, although it is widely used elsewhere. Many students will be more familiar with the **calorie** (abbreviated cal) widely used as the unit of energy in the United States. In this text, we will use the calorie, and we will also identify the equivalent value in joules.

To understand the concepts of heat capacity and latent heat, we can consider the sequence of events that occurs when we add heat to ice (Fig. 5-8). Within the solid ice, the individual mol-

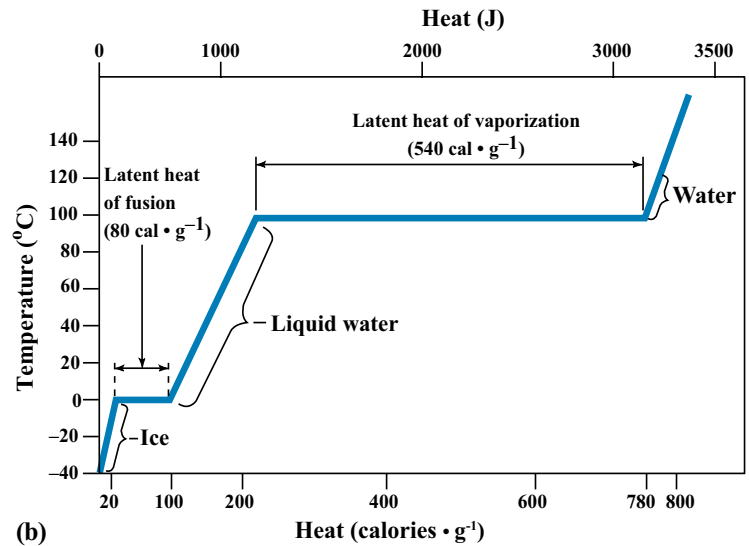
ecules vibrate, but the vibrations are suppressed by the hydrogen bonds. Adding heat energy to the ice increases the intensity of vibration of each water molecule and increases the temperature of the ice. The temperature of 1 g of ice is increased by 1°C when approximately 0.5 calorie (2.1 J) is added. As heat continues to be added, the temperature continues to rise until the ice reaches its melting point. Heat that raises (or lowers) the temperature of a substance to which it is added (or removed) is called **sensible heat**. The quantity of heat needed to increase the temperature of a specified quantity of a substance is called the “heat capacity.” For ice, the heat capacity is approximately $0.5 \text{ cal}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$ ($2.1 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$). That is, one-half of a calorie (2.1 J) is needed to raise the temperature of 1 gram of ice by 1°C .

After the ice has reached the melting point temperature, the temperature of the solid–liquid (ice–water) mixture does not increase again until an additional 80 calories (334 J) of heat energy has been added for each gram of ice (Fig. 5-8b,c). That is, as heat is added, the ice is progressively converted to water. Heat added to a substance that does not raise its temperature but instead changes its state (solid to liquid or liquid to gas) is called “latent” heat. The heat added to melt a specified quantity of ice is the latent heat of fusion (melting). The term *latent* is used because the heat is stored in the molecules of the liquid water and is released when the water is refrozen (fused). Hence, the latent heat of fusion of ice is $80 \text{ cal}\cdot\text{g}^{-1}$ ($334 \text{ J}\cdot\text{g}^{-1}$).

If we continue to add heat after all the ice is converted to water, the heat is again taken up as sensible heat and the tem-

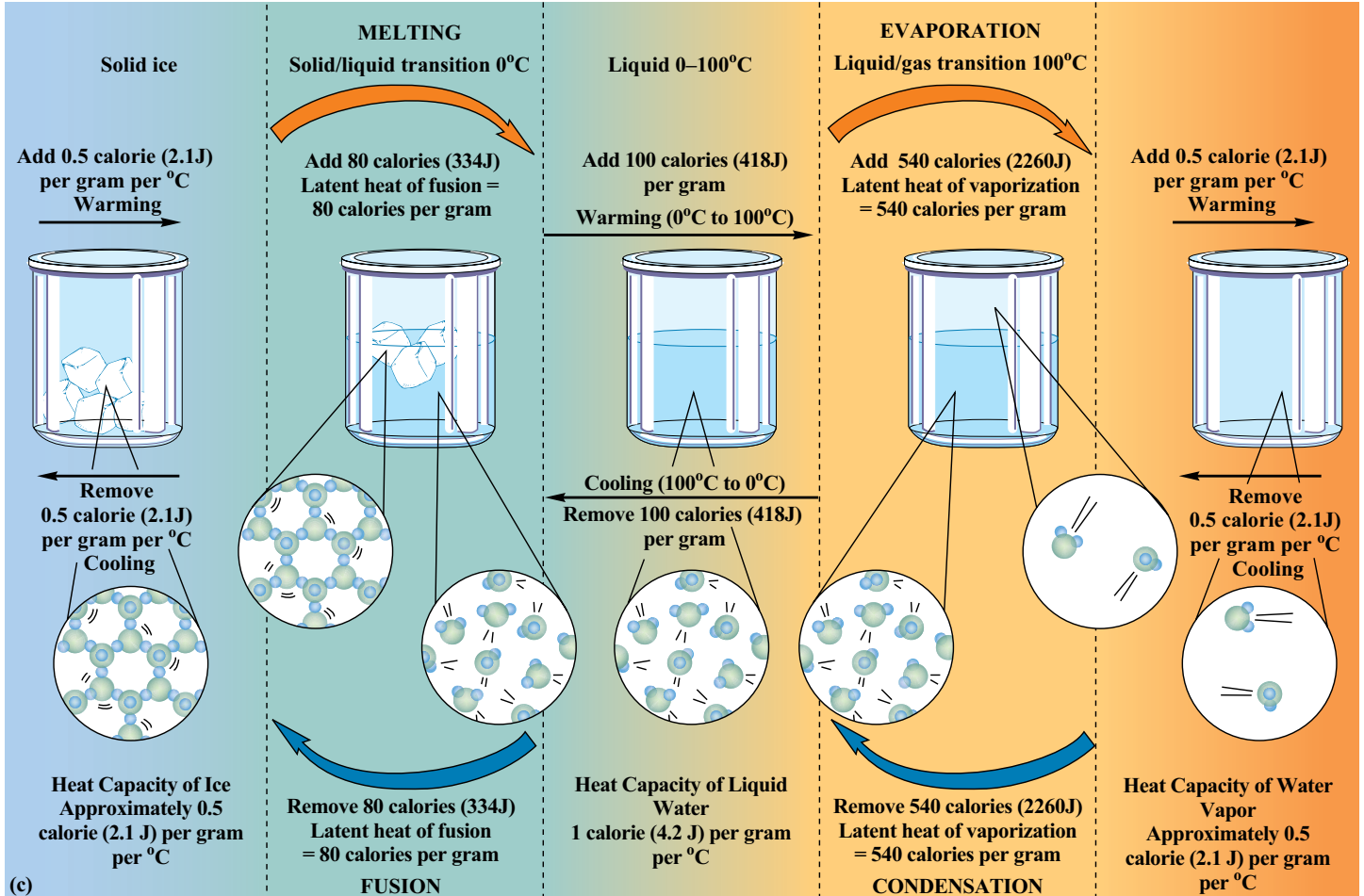
			
	SOLID (ice)	LIQUID	GAS (steam)
Motion	Motion limited to vibrations in almost fixed positions	Molecules moving around, can flow	Complete freedom of motion, can flow
Shape	Fixed, definite, rigid	Same as that of the lower part of the container, variable	Same as that of the closed container, variable
Volume	Almost constant; varies only slightly with temperature	Almost constant; varies slightly with temperature	Same as that of the closed container, variable

(a)



(b)

FIGURE 5-8 (a) Characteristics of solid, liquid, and gaseous water. (b, c) Water's latent heat of fusion (melting) is the amount of heat that must be added to convert ice to water at the freezing (melting) point temperature. Water's latent heat of vaporization is the amount of heat that must be added to water to convert water to water vapor at boiling point temperature. Both of these are high because of the need to provide energy to overcome the hydrogen bond attraction. As latent heat is added to change the phase, there is no change in temperature. In the reverse processes, the same amounts of latent heat that were added are released when water vapor condenses and when water freezes. The heat capacity of water is the amount of heat required to raise the temperature of 1 g of liquid water by 1°C and is measured in $\text{cal}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$ ($\text{J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$). The same amount of heat is released as water cools.



(c)

perature of the water rises. The heat capacity of water is about twice that of ice, or $1 \text{ cal} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$. That is, 1 calorie (4.2 J) of heat energy must be added to raise the temperature of 1 gram of water by 1°C .

After $100 \text{ cal} \cdot \text{g}^{-1}$ ($418 \text{ J} \cdot \text{g}^{-1}$) of heat energy has been added to the water (starting as melted ice water at 0°C), the water temperature reaches the boiling point. With the continued addition of heat, the temperature does not rise again until an additional $540 \text{ cal} \cdot \text{g}^{-1}$ ($2,260 \text{ J} \cdot \text{g}^{-1}$) of heat energy has been added and all the water has been converted to a gas. Hence, the latent heat of vaporization of water is $540 \text{ cal} \cdot \text{g}^{-1}$ ($2,260 \text{ J} \cdot \text{g}^{-1}$). Finally, if we add more heat to the gaseous water (water vapor), its temperature rises by about 1°C for each additional $0.5 \text{ cal} \cdot \text{g}^{-1}$ ($2.1 \text{ J} \cdot \text{g}^{-1}$), so the heat capacity of water vapor is about $0.5 \text{ cal} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ ($2.1 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$).

The latent heats and heat capacity of water are very high primarily because the hydrogen bond is stronger than van der Waals forces. More heat energy is needed to overcome the attraction between molecules in solid, liquid, and gaseous forms of water than in substances whose molecules are bound only by van der Waals forces. Consequently, the heat capacity of liquid water is the highest of all liquids other than liquid ammonia and is higher than that of all solids; the latent heat of fusion of water is the highest of all substances other than ammonia; and the latent heat of vaporization of water is the highest of all known substances.

Implications of the High Heat Capacity and Latent Heats of Water

The anomalously high heat capacity and latent heats of water have many implications. In our everyday experience, we rely on the high latent heat of fusion to keep our iced drinks cold. When we add ice cubes to a cold drink, the drink remains cold for a long time, until all the ice has melted. The drink, a mixture of ice and water, remains cold as it gains heat from its surroundings, until it has absorbed 80 calories (334 J) for each gram of ice, converting the ice to water. Subsequently, when all the ice has melted, the drink warms quickly because each calorie (each 4.2 J) gained can raise the temperature of 1 g of water by 1°C .

The high heat capacity of water is illustrated by the behavior of hot drinks. A hot drink cools much more slowly than, for example, an empty cup or glass taken out of a hot dishwasher. The reason is that more heat must be lost per unit weight of water than of any other substance (other than liquid ammonia) to lower its temperature by a given number of degrees.

The high heat capacity of water allows large amounts of heat energy from the sun to be stored in ocean waters without causing much of a temperature change. The heat is released to the atmosphere when atmospheric temperatures fall. Because water has this heat-buffering capability, coastal locations have milder **climates** than inland locations (**Chap. 7**). The heat-buffering capacity of the oceans and the transfer of latent heat between ice, oceans, and atmosphere are important to global climatic control and to studies of the effects of releases of gases that contribute to the **greenhouse effect** (**Chap. 7**).

In the polar ocean and coastal regions, water's high latent heat of fusion acts to control the air and water temperatures in much the same way that ice cubes cool an iced drink. During winter, latent heat is released to the atmosphere as water freezes to form more sea ice. Conversely, in summer, heat added to the polar regions is used to melt the ice. Because the heat lost or

gained is latent heat, not sensible heat, the ocean surface water and sea ice remain at or close to the freezing point throughout the year. Because air temperatures are partially controlled by ocean temperatures, the annual climatic temperature ranges in polar ocean regions are small (**Chap. 7, CC5**)

Evaporation

Liquids, such as water, can be converted to a gas at temperatures below their boiling point by a process known as "evaporation." For example, puddles of cold water can evaporate from the ground after a rainstorm. Although the average energy level of water molecules remains the same unless there is a change of temperature, the energy level of individual molecules varies around this average. Some molecules that temporarily possess higher amounts of energy can overcome their hydrogen bonds and escape completely from the liquid phase (evaporate).

Water evaporating from the oceans carries its latent heat of vaporization into the atmosphere and releases it when the water subsequently condenses as rain. Because the latent heat of vaporization is high, water can transport large quantities of heat energy from ocean to atmosphere, where that energy can be redistributed geographically. For example, areas of the Earth where evaporation is slow and precipitation is high are warmed, and areas where evaporation is high are cooled (**Chap. 7, CC5**).

Water's high latent heat of vaporization facilitates cooking and can be observed in a kitchen. If we heat a saucepan of water on a stove, the water can be brought to a boil quickly, but then, even if we do not change the heat setting, it takes much longer for the pan to boil dry. It takes only $100 \text{ cal} \cdot \text{g}^{-1}$ ($418 \text{ J} \cdot \text{g}^{-1}$) to heat water from its freezing point to its boiling point, but more than five times as much, $540 \text{ cal} \cdot \text{g}^{-1}$ ($2,260 \text{ J} \cdot \text{g}^{-1}$), to vaporize or convert the water to steam. Water's high latent heat of vaporization is also apparent when we bake food for substantial lengths of time at temperatures well above 100°C and find that the food is still moist.

Because evaporating molecules gain the energy to escape by colliding with molecules that remain behind in the liquid, the average energy level (temperature) of the water molecules that remain behind is reduced. This is why we feel colder when we first climb out of a swimming pool or shower. While we are wet, water molecules evaporate, using heat energy gained from our skin and the air and leaving behind colder skin. After toweling off, we have less water on our skin and the amount of evaporation is reduced. Another example of this phenomenon is the wind chill factor used in **weather** forecasts. Increasing the speed of wind blowing across a wet or damp surface, such as the skin, increases the evaporation rate and thus increases the rate of surface cooling.

At temperatures below the boiling point, the average water molecule has less energy than it does at the boiling point. Therefore, more heat must be supplied to evaporate each molecule of water than is needed to vaporize it at the boiling point, and the latent heat of vaporization increases with decreasing temperature. For example, the latent heat of vaporization at 20°C is $585 \text{ cal} \cdot \text{g}^{-1}$ ($2,449 \text{ J} \cdot \text{g}^{-1}$) which is $45 \text{ cal} \cdot \text{g}^{-1}$ ($189 \text{ J} \cdot \text{g}^{-1}$) higher than at 100°C .

EFFECTS OF PRESSURE, TEMPERATURE, AND DISSOLVED SALTS ON SEAWATER DENSITY

Many of the movements of water masses in the oceans are driven by differences in density. Solid objects that have higher density than water sink, and those that have lower density rise

and float. Liquid water can also rise or sink if its density is different from that of the surrounding water (CC1, CC3). Water density is controlled by changes in pressure, temperature (CC6), and concentration of dissolved constituents (salinity).

Pressure

Because water molecules in a liquid form can be forced together only slightly as pressure increases, seawater is virtually incompressible, and its volume decreases and density increases only very slightly with pressure. Therefore, pressure changes are not as important to controlling water density in the oceans as changes in temperature and salinity are. However, the pressure at the greatest depths in the oceans is more than 1000 times as great as atmospheric pressure. This pressure change causes seawater density to be approximately 2% higher than it is in shallow water at the same temperature and salinity. This small difference must be taken into account in some research studies. Like all other gases, water vapor is compressible, and its density varies substantially with pressure.

Temperature

Increasing temperature adds energy that enables the molecules of solids and liquids to vibrate, rotate, and/or translate more vigorously. Thus, the average distance between the molecules generally increases. As the same number of molecules occupies a larger volume (the material expands), increasing the temperature causes the density to decrease. Ice is no exception to this rule. However, pure water (but not seawater, as discussed later) behaves anomalously, because liquid water has a density maximum at 4°C. Between 0°C and 4°C, water density actually increases with increasing temperature (Fig. 5-9). In the rest of liquid water's temperature range—4°C to 100°C—pure water behaves normally and density decreases with increasing temperature.

The reason for the anomalous effect of temperature on water density is the hydrogen bond. Water molecules form clusters in which the molecules are arranged in a lattice-like structure. The atoms in the cluster are held in place by hydrogen bonds (Fig. 5-10). The structure is similar to that of ice, and the molecules of water in a cluster occupy a larger volume than molecules that are not clustered. The ordered clusters remain together for only a few ten-millionths of a second, but they are continuously forming, breaking, and re-forming. Both the number of clusters present at any time and the number

FIGURE 5-10 The hydrogen bond plays a major role in the properties of ice and water. (a) Molecules in the ice crystal lattice are bonded to each other by hydrogen bonds and arranged in a hexagonal lattice. The resulting structure is very open, which explains the low density of ice. (b) Water molecules constantly form clusters that are temporarily held together by hydrogen bonds. The clusters consist of chains or networks of water molecules arranged in hexagons. The representation here shows this hexagonal form but, for simplicity, does not show the hydrogen bonds. (c) When water molecules are unclustered, the molecules are closer to each other than they are in clusters. Clusters are more likely to form and may persist longer at low temperatures, which is why water's density decreases below 3.98°C.

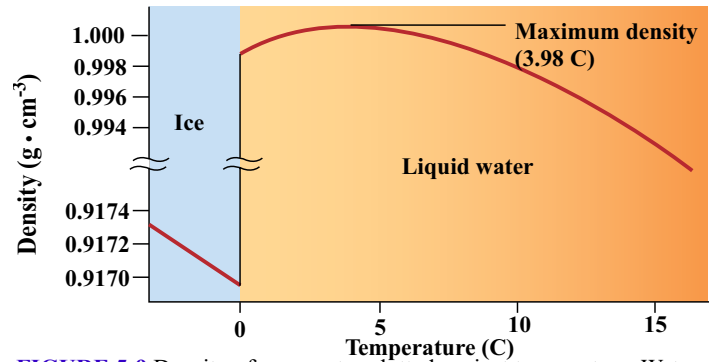
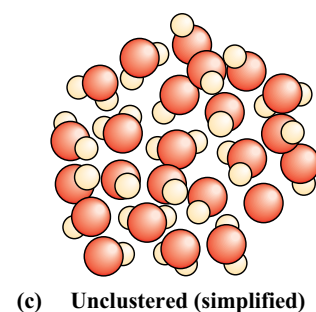
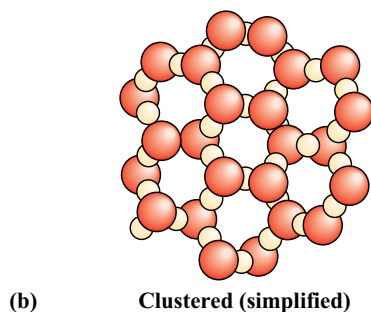
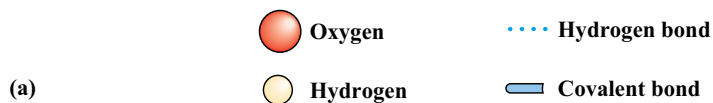
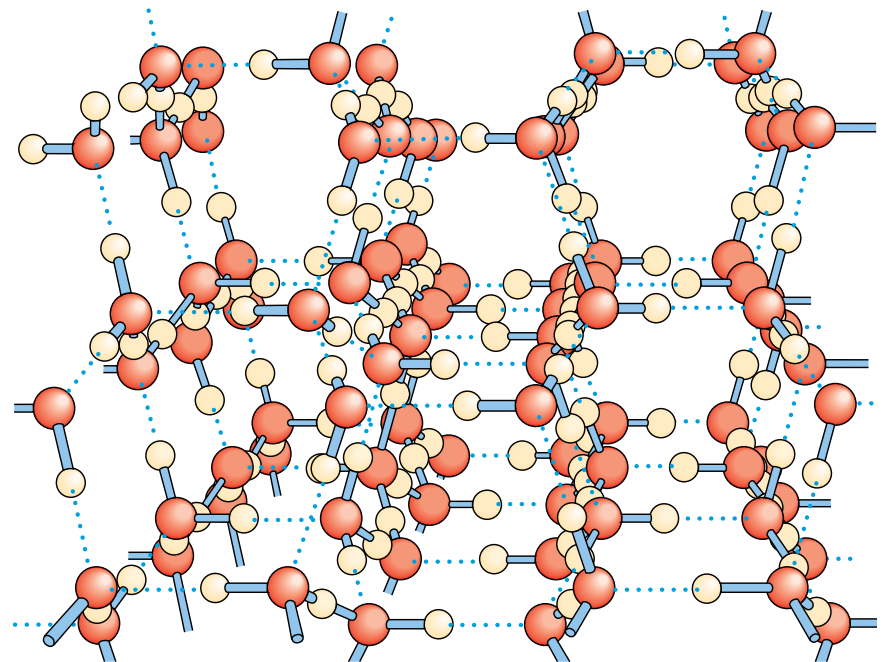


FIGURE 5-9 Density of pure water plotted against temperature. Water with no dissolved salts has a maximum density at 3.98°C. At lower temperatures, water density decreases until the freezing point is reached. There is a discontinuity in the density scale. The density of ice is much less than that of liquid water because of the open structure of the ice crystal lattice. When solid ice and liquid water occur together at 0°C, the ice floats on the water because its density is less than that of the water

of molecules in each cluster increase as the temperature decreases (more unbroken hydrogen bonds are present). Because clustered molecules occupy a greater volume than unclustered molecules, an increase in the number of clusters and in the number of molecules per cluster decreases the density of the water. Above 4°C, there are too few clusters to counteract completely the normal



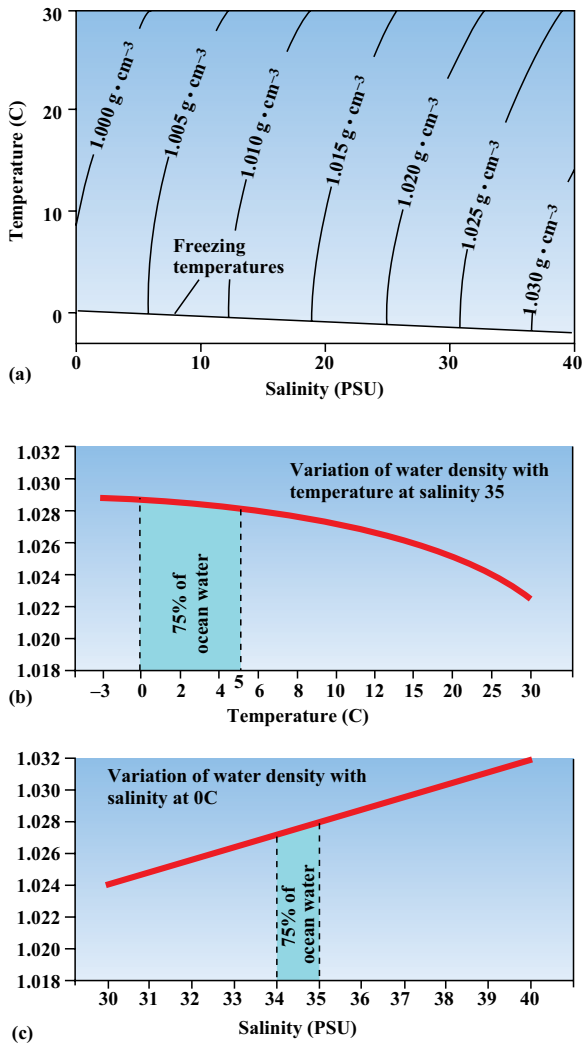


FIGURE 5-11 The effects of temperature and salinity on the density of water. (a) The relationships among salinity, temperature, and density are complex. The effects of temperature and salinity individually are more obvious if we examine (b) the relationship of temperature (-3°C to 30°C) to density at a fixed salinity, and (c) the relationship of salinity (30 to 40 PSU) to density at fixed temperature. The shaded sections of the plots in (b) and (c) represent the narrow ranges of salinity and temperature present in most ocean water.

temperature effect on density. Below 4°C (actually 3.98°C), however, clustering increases fast enough that the decrease in density caused by the clustering is faster than the increase caused by the normal temperature effect.

Dissolved Salts and Density

Salts dissolved in water increase the water density for several reasons. First, the **ions** or molecules of most substances dissolved in seawater have a higher density than water molecules. Dissolved substances also reduce the clustering of the water molecules, further increasing the density, particularly at temperatures near the freezing point.

Combined Effects of Salinity and Temperature

The density of ocean waters is determined primarily by salinity and temperature. **Figure 5-11a** shows the relationships among the salinity, temperature, and density of seawater. Raising the temperature of freshwater from 4°C to 30°C (the range between the temperature of maximum density and the highest temperature generally found in surface waters) decreases its density by about 0.0043 (from 1.0000 to 0.9957), or about 0.4%. At a constant

temperature, changing the salinity from 0 to 40 (approximately the range of salinity in surface waters) changes the density by about 0.035, or about 3.5%. These observations suggest that salinity is more important than temperature as a determinant of density. This is often true in rivers and **estuaries** where the water has a wide range of salinity, but the range of salinity in open-ocean waters is much smaller. In fact, 99% of all ocean water has salinity between 33 and 37, and 75% has salinity between 34 and 35 (**Fig. 5-12**). Similarly, 75% of ocean water has a temperature between 0°C and 5°C , and the rest has a much wider temperature range, between about -3°C and 30°C .

With the exception of water discharged by **hydrothermal vents**, the highest temperatures in the oceans are in surface waters in tropical regions. **Figure 5-11b,c** relates salinity, temperature, and seawater density, and shows that, in most of the ocean, temperature and salinity are of approximately equal importance in determining the density of ocean waters. However, their relative importance varies with location and depth. For example, temperature changes are more important to density variations in the tropical water column, where salinity variation is relatively small but temperature variation with depth is relatively large. In contrast, salinity is more important in some high-**latitude** regions, where salinity variations are relatively large as a result of high volumes of freshwater **runoff** and the formation and melting of ice, but temperatures are generally uniform and near the freezing point.

ICE FORMATION

When surface water is cooled to the freezing point, the behavior of ice and water in lakes and oceans is determined by two

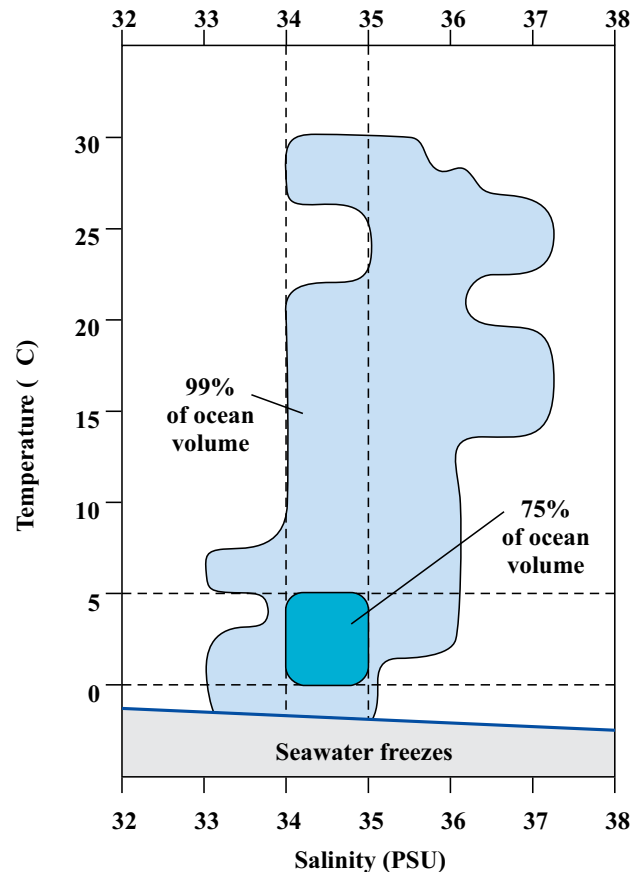


FIGURE 5-12 Temperature and salinity characteristics of ocean waters. Ninety-nine percent of all ocean water has salinity and temperature within the range shown by the larger shaded area. Seventy-five percent of all ocean water has the much narrower range of salinity and temperature within the inner darker-shaded area.

factors: the relative density of ice and water, and the variations of water density with salinity at temperatures near the freezing point.

Dissolved Salts and Freezing

Increasing the salinity lowers the freezing point of water (Fig. 5-13). This is why salt is used to de-ice roads. Increasing the concentration of dissolved salts also inhibits the clustering of water molecules and therefore lowers the temperature at which the density maximum occurs (Fig. 5-13). As salinity increases, the temperature of the water density maximum decreases more rapidly than the freezing point temperature. Therefore, as salinity increases, the difference between the temperature of maximum density (4°C in pure water) and the freezing point is narrowed. At a salinity of 24.7, the density maximum and the freezing point are the same temperature (-1.36°C). At any salinity above 24.7, the freezing point is reached before a density maximum occurs. Since open-ocean water generally has a salinity above 24.7, seawater does not have an anomalous density maximum.

Because freshwater has a maximum density at 4°C and seawater has no maximum density, lakes and rivers behave differently from the oceans when freezing. As winter begins, the surface water of a freshwater lake cools and its density increases. This cold, dense surface water sinks and displaces bottom water upward to be cooled in its turn. This **convection** process is called “overturning” (CC3). Convection continues until all the water in the lake is 4°C and is at the maximum density. As the surface layer of water cools below 4°C , its density no longer increases. Instead, it actually decreases. Therefore, this water does not sink. The water in this surface layer continues to cool until it reaches 0°C and then the water freezes. The resulting ice has a lower density than water and floats. With further cooling, the lake water continues to lose heat, but because of the density maximum there

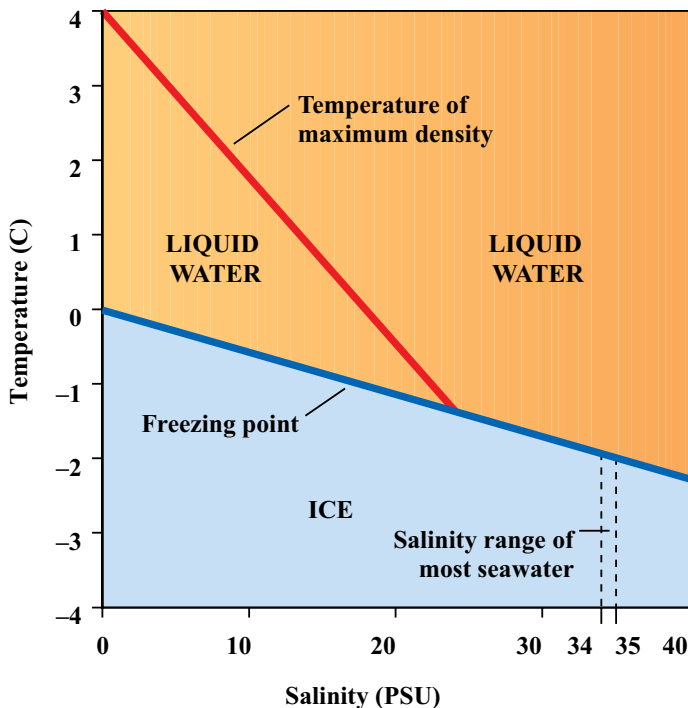


FIGURE 5-13 Increasing the concentration of dissolved salts in water reduces both the freezing point and the temperature at which the anomalous density maximum occurs. However, the temperature of maximum density is reduced more rapidly than the freezing point as salt concentration increases. Consequently, seawater (99% of which has salinity greater than 33) has no anomalous density maximum.

is no convection, so the heat is lost by **conduction** through the overlying ice layer. As heat continues to be lost, the water immediately under the ice cools to 0°C and freezes. Therefore, the ice layer grows progressively thicker from underneath. Ice is not a very good conductor of heat. In addition, a large amount of heat must be lost to convert water to ice because of the high latent heat of fusion. Consequently, the ice layer on a lake surface will grow to a thickness of at most only a meter or two, depending on the length and severity of the winter. If the lake is deep enough, a pool of liquid water at 4°C will remain below the ice of the lake throughout the winter. Many freshwater organisms that cannot tolerate being frozen survive the winter in such pools of water.

In contrast to freshwater, as seawater (salinity greater than 24.7) cools, its density increases continuously until it reaches its freezing point of about -2°C . Cooling water continues to sink away from the surface until ice forms. This is why most of the deep water in the oceans is cold, generally below 4°C (Chap. 10). As seawater freezes, most of the dissolved salts are excluded from the ice and remain in the unfrozen water. Therefore, salinity increases in the remaining water, and as a result, the freezing point decreases (Fig. 5-13). If freezing occurs quickly, or if winds break up the surface ice and splash water onto the ice surface, isolated pockets or pools of liquid water can be present within the ice. The water in the pockets has high salinity, and its temperature may be several degrees below the freezing point of seawater with normal salinity. Some microscopic algae, bacteria and animals survive the Arctic and Antarctic winters in such isolated pockets of liquid inside the sea ice.

Density of Ice

Most substances have higher density in the solid phase than in the liquid phase. Water is an exception to this rule. Ice at 0°C has a density of $0.917\text{ g}\cdot\text{cm}^{-3}$, about 8% less than the density of water of the same temperature. Hence, water expands when it freezes. The reason is that the ice crystal has an open lattice structure, and fewer water molecules are packed into the volume that they would occupy as water (Fig. 5-10). In winter, expansion of water as it freezes bursts water pipes, breaks up rocks, and causes potholes in street surfaces when small cracks are filled with water and then freeze.

Ice floats because it is less dense than water. If ice did not float, it would sink to the bottoms of ponds and lakes as they froze, and surface water would continue to freeze and sink until no liquid water was left. Hence, aquatic organisms would have no liquid water refuge below the ice in which to survive the winter. In addition, sea ice formed in the polar regions would sink to the floor of the oceans and accumulate. Because there would be no way to bring the ice to the surface to remelt it, the oceans would have a warm-water surface layer over a solid ice layer extending to the seafloor.

SURFACE TENSION AND VISCOSITY

As we have seen, hydrogen bonding plays an important role in several thermal properties of water. Hydrogen bonding also contributes to the high **surface tension** of water and its relatively high **viscosity**. Surface tension and viscosity are major factors in determining the behavior of waves and controlling the processes by which water molecules are transported across biological membranes.

Surface Tension

Molecules within a liquid are subject to attractive forces that pull them toward all adjacent molecules. Moreover, molecules

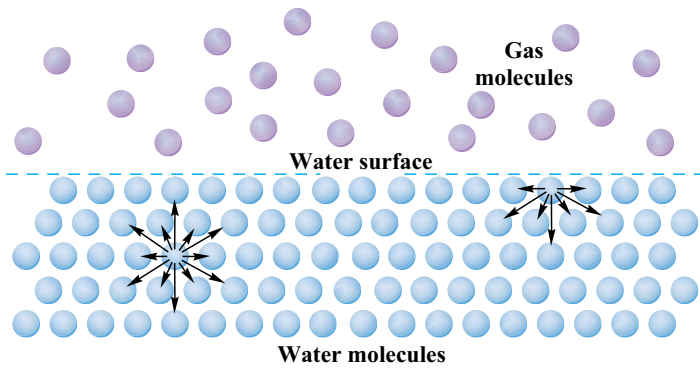


FIGURE 5-14 All molecules in a liquid are attracted to each other by van der Waals forces. Liquids have surface tension because the molecules at the surface are attracted more strongly to other molecules of the liquid than to the gas molecules above, which are more dispersed and thus, on average, farther away. Molecules at the surface have a net inward attraction that makes the surface behave somewhat like the rubber of an inflated balloon. The surface tension of water is particularly high because the water molecules are attracted to each other by both van der Waals forces and the much stronger hydrogen bond.

at the surface of a liquid are attracted much more strongly to their neighboring liquid molecules than to the more remote gas molecules above the surface (Fig. 5-14). Therefore, all molecules on the surface are pulled toward the interior of the liquid. The attractive force tends to minimize the number of molecules at the surface and creates a surface tension that pulls the liquid surface into a configuration with the minimum possible surface area. Because of the strong hydrogen bond attraction between water molecules, the surface tension of water is higher than that of any known liquid other than mercury.

Surface tension tends to pull water droplets into a spherical shape because a sphere has the lowest possible ratio of surface area to volume. We can see the approximately spherical shape in beads of water on a newly waxed automobile, and in drips from a leaky faucet.

If we pour water into one side of a saucepan (or ocean), **gravity** distributes the water so that all parts of the water surface are at the same level. Similarly, if we disturb a surface—say, by sloshing the saucepan—the water will quickly return to its original state, in which its surface is flat and horizontal. Surface tension “pulls” the surface into the minimum area possible, which in the saucepan is a flat horizontal plane. For this reason, the high surface tension of water critically affects the generation and dissipation of small waves on the ocean surface (Chap. 11).

If an object is to break through a water surface, it must be heavy enough to push aside the water molecules and break the surface tension. Any object with a density greater than that of water can be made to float on the water surface if its weight per unit of water surface area is too low to break the surface tension. For example, a steel sewing needle can be positioned to float on the water surface. Similarly, insects such as the water strider can walk on water because of its high surface tension.

The high surface tension of water has significant effects on the formation and behavior of gas bubbles and spray, which are created in the oceans primarily by breaking waves. Once they have formed in water, small gas bubbles cannot easily break through the ocean surface to escape to the atmosphere. When bubbles do break through the surface, a large number of small water droplets are ejected into the air. Because of their high surface tension,

the droplets do not readily combine into larger drops that would fall back to the water surface faster. The high surface tension of water helps to retain gas bubbles in the water and water droplets in the air, enhancing the efficiency of gas transfer between oceans and atmosphere. Because small droplets have large surface areas in relation to their volume, evaporation from the oceans is also enhanced.

Because of the high surface tension of water, many small aquatic organisms, such as mosquito **larvae**, can anchor themselves from below in a very thin surface water layer called the **surface microlayer**. The surface microlayer is just a few molecules thick.

Viscosity

Viscosity is a measure of a liquid’s internal resistance to flow or the resistance of the liquid to the movement of an object through it. A low-viscosity liquid flows easily, whereas a high-viscosity, or “viscous,” liquid flows slowly. Water has a lower viscosity than many liquids, such as honey or motor oil. However, the viscosity of water is high enough to provide substantial resistance to minute organisms that swim or sink in water. To these tiny organisms, moving through water is equivalent to our swimming through tomato ketchup. In fact, many microscopic organisms rely on the viscosity of water to prevent them from sinking out of the upper layers of ocean water where they live.

Water viscosity varies with salinity and temperature. Viscosity increases as temperature decreases (slightly less than 1% per °C within the normal range of ocean water temperatures) because more structured water molecule clusters are present at lower temperatures. The clusters do not move out of the way as easily as individual molecules do. Hence, microscopic organisms in warm tropical waters have more difficulty in avoiding sinking than do organisms in cold polar waters. Many tropical microorganisms have compensated by evolving elongated spines or frilled appendages that increase “drag” as they move through the water. Related polar species generally do not have these ornate features.

Viscosity also increases as salinity increases, because the component ions of the dissolved salts are very effective in surrounding themselves with water molecules to form clusters that resemble water molecule clusters. However, the change in viscosity caused by dissolved salts is small within the range of salinity in freshwater and the oceans. Viscosity increases by less than 1% from freshwater to salinity-35 seawater at the same temperature.

TRANSMISSION OF LIGHT AND OTHER ELECTROMAGNETIC RADIATION

Light is a form of electromagnetic radiation emitted by the sun and stars. However, visible light occupies only a small segment of the very wide electromagnetic radiation spectrum (Fig. 5-15). Ultraviolet light, X-rays, and gamma rays have progressively shorter **wavelengths** than visible light, whereas infrared light, microwaves, and radio waves have progressively longer wavelengths.

Absorption

Water absorbs electromagnetic radiation, but the depth of water penetrated varies with the intensity of the radiation and with wavelength. At most wavelengths, absorption is so effective that, even at very high intensity, the radiation can penetrate only a few centimeters or meters of water. Absorption is less effective within the narrow range of wavelengths of visible light and for very long-wavelength radio waves. However, even at the wavelengths

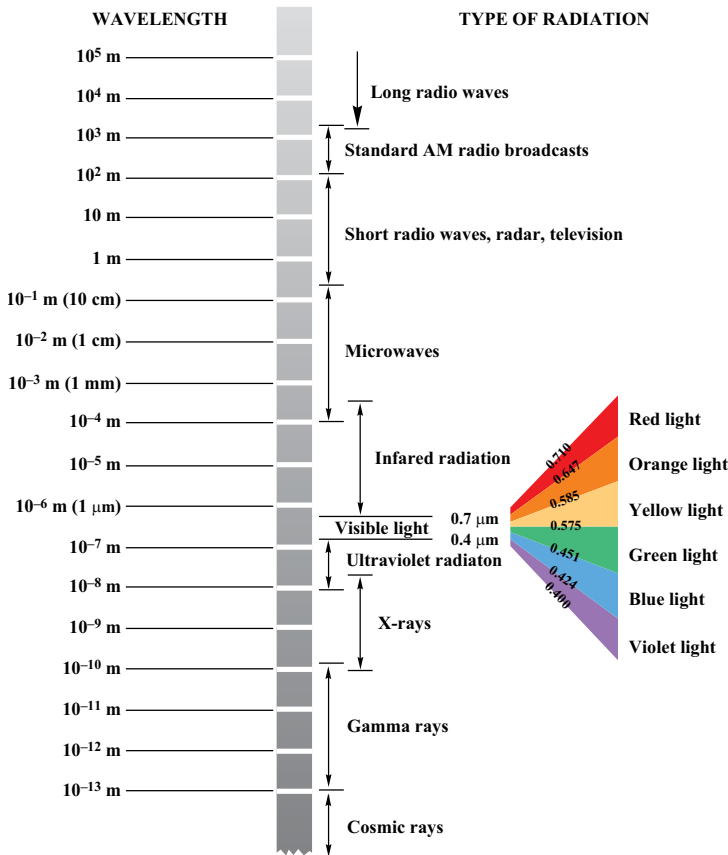


FIGURE 5-15 The electromagnetic radiation spectrum

of lowest absorption, the most intense radiation (e.g., **lasers**) cannot penetrate more than a few tens or hundreds of meters of water. For this reason, oceanographers cannot use electromagnetic radiation, such as radar, radio waves, or laser light, to “see” through the oceans in the same way that radar can see through clouds to the Earth’s surface or even the surface of Venus.

Because radio waves and other forms of electromagnetic radiation do not penetrate far through water, they cannot be used for underwater communication. For example, long-range communication with submarines is a considerable problem. Very low-**frequency** radio waves can penetrate a few tens of meters into the ocean and are used to communicate with submarines near the surface. Because intense visible light can penetrate up to several hundred meters below the ocean surface, satellite-mounted lasers also are used to communicate with submarines at shallow depths. The inability of electromagnetic radiation, such as radar, to penetrate ocean water is the principal reason why submarines are among the best places to hide strategic missiles. Detection of submarines relies primarily on sound waves, which are transmitted easily through ocean water.

The greater transmissibility of visible light through water (compared to other electromagnetic wavelengths) is critically important to life in the oceans (**Chaps. 12, 13**). Like life on the land, most non-**microbial** life in the oceans depends on algae and bacteria that need light to grow by **photosynthesis (CC14)**.

Some wavelengths of visible light are better absorbed by water than others (**Fig. 5-16a**). Wavelengths at the red end of the visible spectrum are the most rapidly absorbed, and violet wavelengths also are absorbed relatively quickly; blue and green light penetrate farthest. Outside the visible light spectrum, infrared radiation (wavelengths longer than red light) and ultraviolet

radiation (wavelengths shorter than violet light) are strongly absorbed by water

As light penetrates the ocean, it is absorbed not only by water molecules, but also by suspended particles. Accordingly, light penetrates deeper in clear ocean waters than in high-**turbidity** coastal waters with high **suspended sediment** loads or high **plankton** concentrations (**Fig. 5-16b–d**).

Scattering and Reflection

We are all familiar with the idea that light is reflected by smooth “shiny” surfaces such as the silvered surface of a mirror. Light is also reflected when it encounters a rough surface. However, individual light rays meet different parts of the rough surface at different angles, and as a result, they are reflected in different directions. When this occurs, the light is said to be **scattered**.

As light penetrates the ocean water column, scattering occurs when some of the photons of light bounce off water molecules, molecules of dissolved substances, or suspended particles. The light scatters in all directions, but some is directed upward and is said to be **backscattered**. In very clear ocean waters with few suspended particles or plankton, most of the red and yellow light is absorbed rather than scattered (**Fig. 5-16b–d**). Light of blue wavelengths has a greater probability of being backscattered because blue light travels through a greater length of the water column. Therefore, most of the backscattered light in clear ocean waters is of blue wavelengths, and it is this backscattered light that gives the ocean its deep blue color.

In waters with more suspended particles or plankton, there is a higher probability of backscattering of all visible wavelengths. Hence, in more turbid waters, the backscattered light comprises a much wider range of wavelengths, and the water appears not blue, but green or brownish. The specific color is determined by the nature of the suspended particles. All particles absorb light more effectively at some wavelengths, and their color is determined by which wavelengths of the light they do not absorb. Light of these nonabsorbed wavelengths is scattered and, therefore, constitutes the wavelengths we see when looking at the particles. Most particles in the oceans are either green, such as many **phytoplankton** cells, or brown, such as sand and other mineral particles. Ocean waters with large phytoplankton populations (**Chap. 14**) tend to appear greenish, whereas coastal waters with large loads of suspended mineral grains appear muddy brown. Therefore, color variations of the ocean surface indicate the quantity of particulate material and phytoplankton in the near-surface water. Ocean surface color measured by sophisticated sensors aboard satellites (**Fig. 5-17**) is used to investigate distributions of the living and nonliving particles in the oceans (**Chaps. 6, 12**).

The underwater world seen in movies or video is a blaze of colored creatures. However, **scuba** divers see such colors only in very shallow water. Just a few meters below the surface, the red and yellow wavelengths of natural sunlight are absorbed, so bright red fishes appear black and most objects appear blue or bluish green. The true colors are revealed only when lights with a full spectrum of visible wavelengths are shone on the marine life. For this reason, underwater photographers or videographers must carry powerful lights.

Scuba divers can observe scattering and absorption of light by particles by noting changes in the visibility and lighting of the water. In turbid water with more particles, daylight does not penetrate very far. In addition, at shallow levels to which some

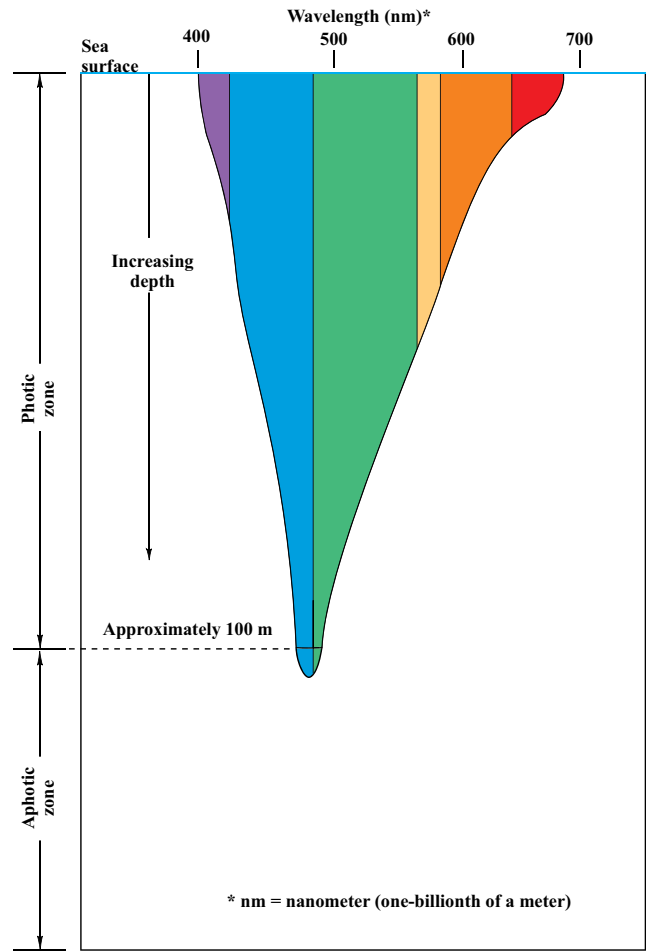
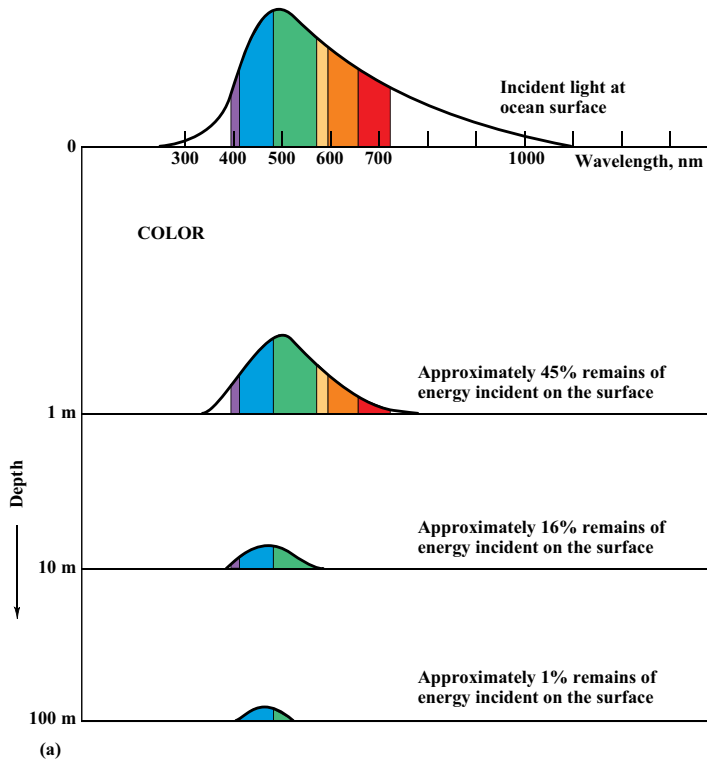
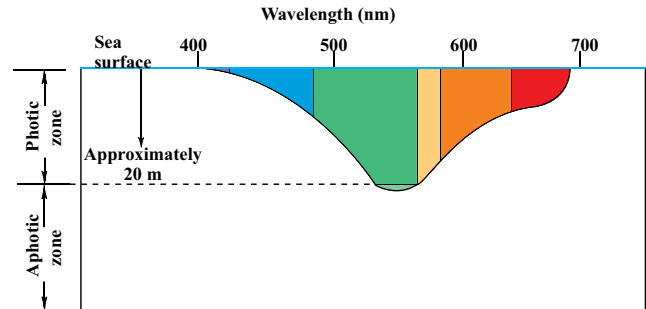
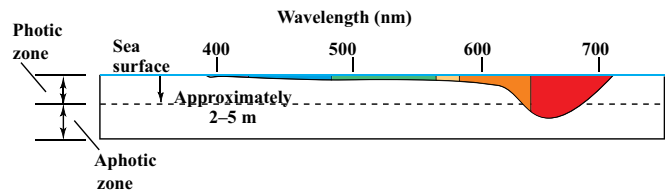


FIGURE 5-16 (Above and right) Light penetration and absorption in ocean waters. (a) Absorption of electromagnetic energy by ocean water. Note that energy in the infrared (about 700–1000 nm) and ultraviolet (about 300–400 nm) wavelengths is absorbed very rapidly compared to energy in the visible light wavelengths (400–680 nm). Also, energy at longer wavelengths of visible light (red/orange) is absorbed more quickly than energy at shorter (blue/green) wavelengths. The remaining parts of the figure show the depth at which light of visible wavelengths is reduced to less than 1% of the intensity at the surface in (b) clear open-ocean water, (c) coastal-ocean water, and (d) estuarine water. The aphotic zone begins at the depth where the ambient light intensity is approximately 1% of that at the surface. Note that the photic zone depth is much reduced in coastal and estuarine waters. Below the photic zone, light is insufficient for phytoplankton to produce enough organic matter by photosynthesis to survive. Note also that the wavelength range of light reaching the lower part of the photic zone moves from the blue/green part of the spectrum toward the red end of the spectrum in coastal and estuarine waters. This is the reason why open-ocean waters usually appear blue while coastal and estuarine waters do not.

(b) Clear open-ocean water



(c) Coastal ocean water



(d) Estuarine water

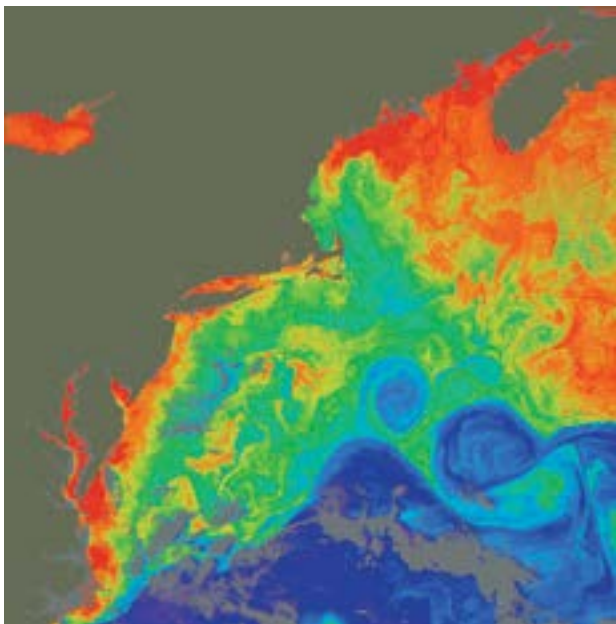


FIGURE 5-17 (Left) This image of the Northwest Atlantic Ocean shows data obtained from a satellite-mounted instrument called the Coastal Zone Color Scanner, which measures the intensity of light reflected or backscattered by the Earth's surface. The data are from a narrow wavelength band, in which the intensity of the light received by the scanner from the ocean surface increases with increasing concentrations of chlorophyll-containing phytoplankton in the photic zone. Intensities of light in this wavelength band are depicted by the false colors in this image. Red colors show the areas of highest chlorophyll and phytoplankton concentration; and progressively lower concentrations are depicted by the orange, yellow, green, and blue shades. Note that the highest concentrations of chlorophyll are found in the coastal region and that the image reveals the complex patterns associated with different water masses.

natural light penetrates, horizontal visibility is reduced. Just as daylight is blocked from penetrating vertically into the water by scattering and absorption, light traveling from an object horizontal to the diver is absorbed and scattered. If the absorption and scattering are substantial, the light from distant objects does not reach the diver and the objects cannot be seen. When light is scattered equally in all directions, a scuba diver may not be able to visually distinguish between up and down.

Refraction

The speed of light in seawater is less than that in air. As light waves pass from air into water or from water into air, they are **refracted** (their direction is changed because of the change in speed) (Fig. 5-18a). An easy way to see refraction is to sight down the length of a ruler and dip the end of the ruler into a tumbler of water (Fig. 5-18b). The tip of the ruler appears to be bent upward as it passes into the water. Refraction causes fishes in an aquarium to appear bigger and closer than they really are. Similarly, fishes and other objects seen through a scuba mask appear larger and closer than they are.

Refraction between air and water increases as salinity increases. Therefore, measurements of refraction are often used to determine approximate salinity.

TRANSMISSION OF SOUND

Electromagnetic radiation travels both through a vacuum and through substances such as air and water. Sound is fundamentally different because it cannot be transmitted through a vacuum. The sound effects in space movies are pure fantasy, because sound cannot travel across the vacuum of space. Sound is transmitted as a vibration in which adjacent molecules are compressed in sequence. One molecule is pushed into the next, increasing the “pressure” between the two molecules. The second molecule pushes on a third, increasing the pressure between the second and third molecules and relieving the pressure between the first two molecules, and so on. Hence, sound waves are pressure waves transmitted through gases, liquids, and solids. The pressure waves can range from very high frequencies, which the human ear cannot hear (ultrasound), to low frequencies below the audible range that we sometimes feel as vibrations from our surroundings.

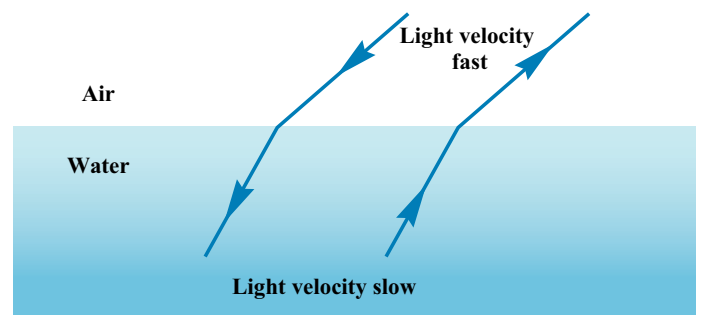
Sound waves are absorbed, reflected, and scattered as they pass through water much less than electromagnetic radiation is. Therefore, sound travels much greater distances in water and sound waves are the principal tools of communication and remote sensing for both oceanographers and marine animals.

Sound Velocity

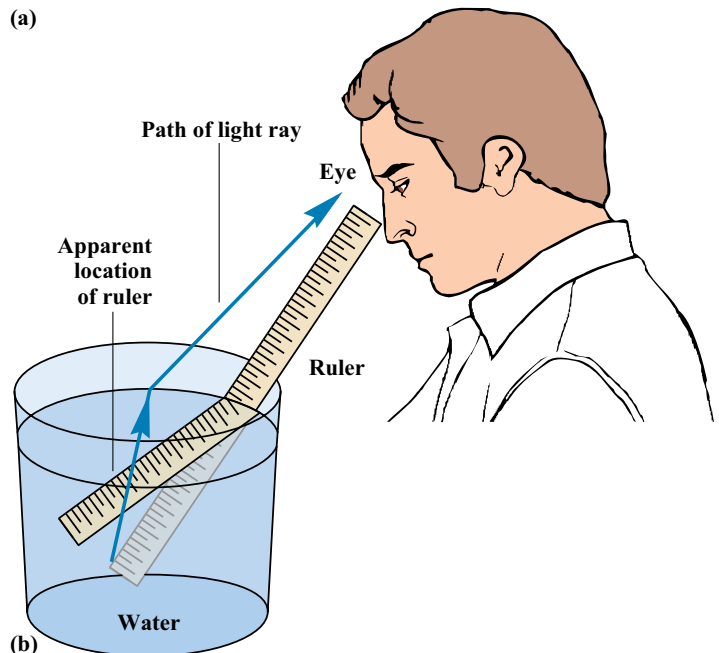
The speed of sound is about four times greater in water than in air. In seawater, the speed of sound increases with increases in salinity, pressure, and temperature (Fig. 5-19a,b). However, the changes due to salinity variations are relatively small within the range of salinities in ocean waters. Thus, sound velocity generally decreases with depth in the upper layers of the oceans, where the temperature change is large, but then increases again with depth in the deep layers, where temperature variations are small and pressure changes are more important (Fig. 5-19c). Sound velocity in the oceans can be determined if the salinity, temperature, and depth (pressure) are known.

Sonar

Sound velocity is important because sound waves are used to measure distances in water. Sound pulses sent through water



(a)



(b)

FIGURE 5-18 (a) Light rays are bent, or refracted, when they pass between air and water. (b) Inserting a ruler or stick through a water surface at an angle illustrates the distortion in the way refraction makes objects appear. The ruler looks as if it is bent at the point it enters the water.

bounce off objects and the seafloor. If the sound velocity at all points within the sound path is known and the time taken for the sound to go out and the echo to return is measured, the distance to the object or seafloor can be calculated. This is the principle of **sonar**.

Sonar systems send and receive sound pulses to measure ocean depths or to measure the distance and direction of objects that reflect sound, such as submarines. **Schools** of fish, concentrations of tiny animals called **zooplankton** on which fishes feed, and concentrations of suspended mineral grains also can be detected with sonar.

Different frequencies are employed for different applications. For example, low frequencies are used for deep-ocean **sound-ing**. Higher frequencies allow smaller particles (or animals) to be detected, but higher-frequency sound is more effectively absorbed by water. Therefore, higher frequencies are used in applications involving small objects in shallow water, such as finding fishes and tracing plumes of particles from river discharges or ocean dumping. Dolphins use their natural sonar to locate objects such as fishes, and they can tune the sound frequencies they use: low frequencies for long distance, and higher frequencies for more detailed echo “vision” at shorter distances.

Sound Refraction and the Sound Channel

Just as light is refracted as it passes between air and water (Fig. 5-18a), sound waves are refracted as they pass between

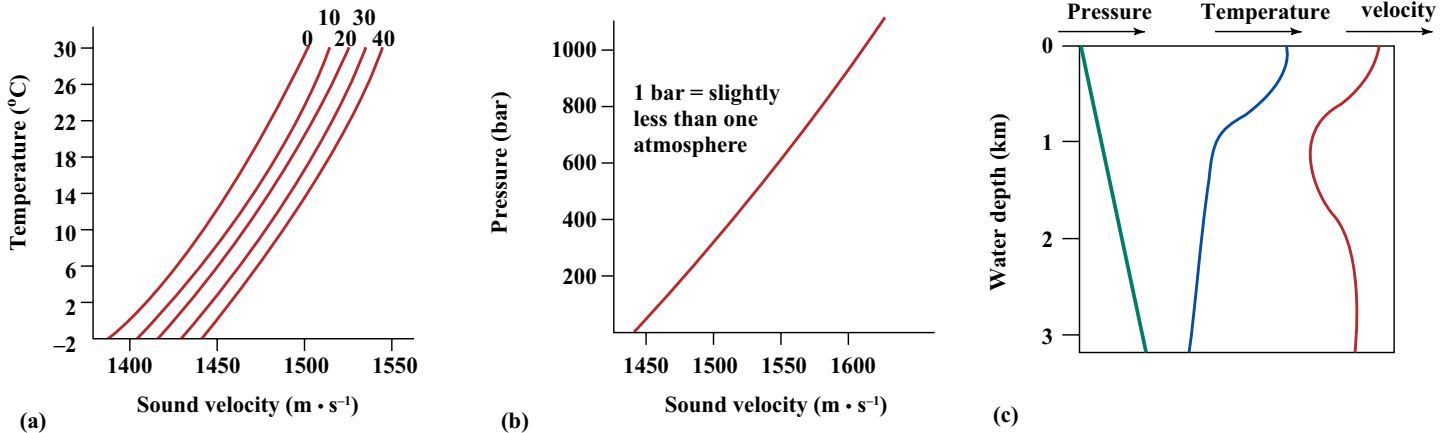


FIGURE 5-19 The velocity of sound in ocean water varies with temperature, pressure, and salinity. Sound velocity increases with (a) increasing temperature or salinity and (b) increasing pressure. Salinity is comparatively less important in determining sound velocity than temperature or pressure. (c) Variations of pressure and temperature with depth in the oceans produce changes in the sound velocity that are sometimes complex. Generally sound velocity decreases with depth until it reaches a minimum at about 1000 m (1 km) and then increases as depth increases.

air and water (Fig. 5-20a), or through water in which the sound velocity varies. At any specific ocean depth, the parameters that determine sound velocity are fairly constant over great distances (Chap. 10). Hence, sound waves that travel horizontally are little affected by refraction. Sound waves that travel vertically are also not affected significantly by refraction, because they pass perpendicularly to the horizontal layers of varying sound velocity. In contrast, sound waves that pass through the ocean at any angle other than horizontal or vertical are refracted in complicated

curving paths. The paths are determined by the initial direction of the sound waves and their varying velocity in the waters through which they pass (Fig. 5-20b).

Two important consequences of sound refraction in the oceans are of interest. First, sonar sound pulses sent out by a vessel at any downward angle not close to the vertical are refracted away from a zone called the “shadow zone” (Fig. 5-20b). The zone starts at a depth where sound velocity is at a maximum, being slower at both shallower and deeper levels. Such a maximum is

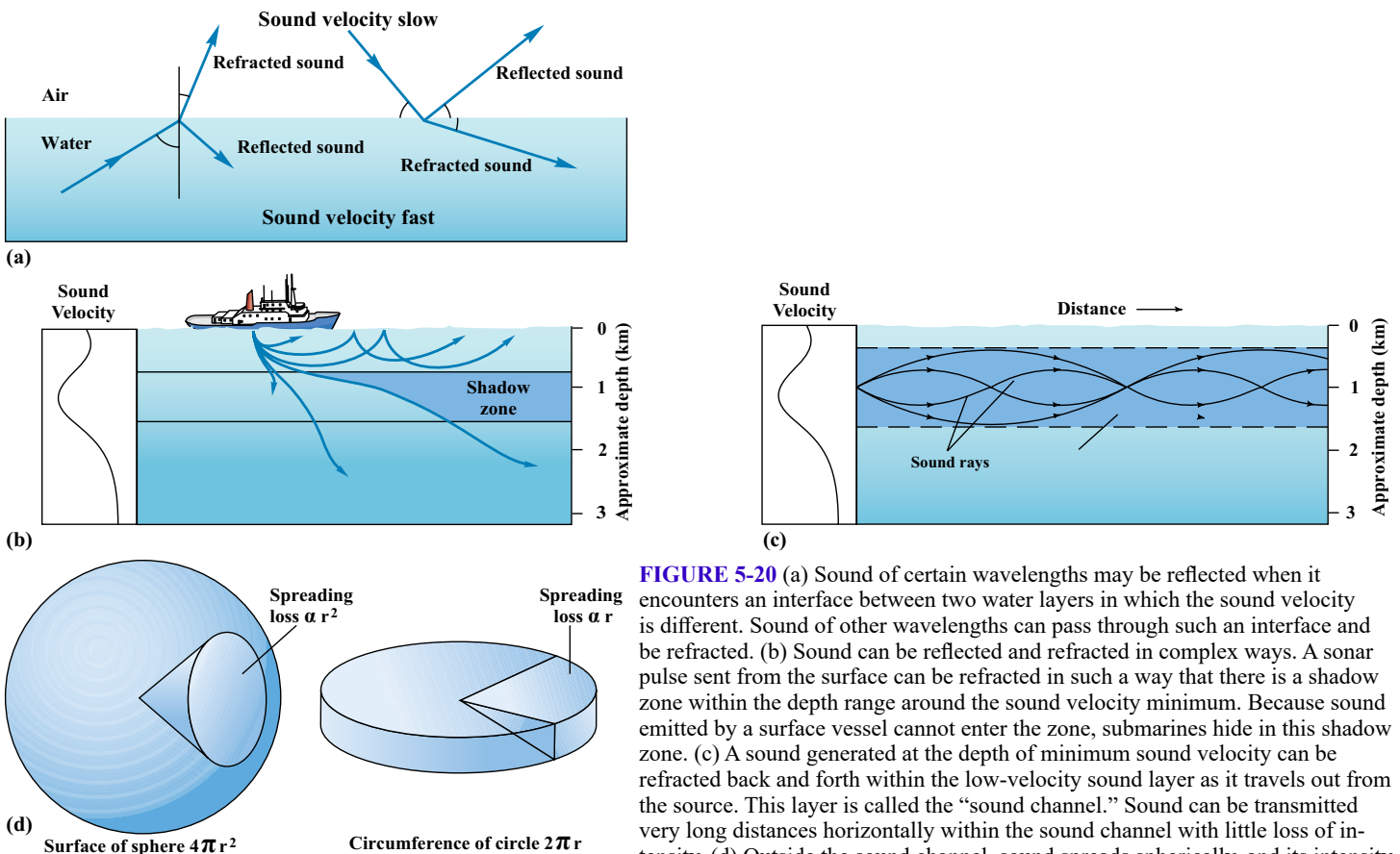


FIGURE 5-20 (a) Sound of certain wavelengths may be reflected when it encounters an interface between two water layers in which the sound velocity is different. Sound of other wavelengths can pass through such an interface and be refracted. (b) Sound can be reflected and refracted in complex ways. A sonar pulse sent from the surface can be refracted in such a way that there is a shadow zone within the depth range around the sound velocity minimum. Because sound emitted by a surface vessel cannot enter the zone, submarines hide in this shadow zone. (c) A sound generated at the depth of minimum sound velocity can be refracted back and forth within the low-velocity sound layer as it travels out from the source. This layer is called the “sound channel.” Sound can be transmitted very long distances horizontally within the sound channel with little loss of intensity. (d) Outside the sound channel, sound spreads spherically, and its intensity is reduced in proportion to the square of the distance from the source. Within the sound channel, sound spreads cylindrically and loses intensity only in proportion to the distance from the source.

present within submarine operating depths in many parts of the oceans. Hence, submarines can hide from sonar detection if they can remain in the shadow zone. This is one reason why the navies of the world continuously monitor changes in the temperature and salinity of the upper few hundred meters of the ocean throughout their operating areas. Small changes in these characteristics can change the location and effectiveness of the shadow zone. Because sound travels in complicated curved paths between the sources and echoing objects, knowledge of salinity and temperature distributions is essential in determining the sound velocity distribution and estimating the location and depth of an object detected by sonar.

The second important consequence of sound refraction in the oceans is that sound emitted at or about the depth of a sound velocity minimum is focused in what is called the “sound channel” (Fig. 5-20c). With the exception of sound waves traveling out vertically (or nearly so) from such a source, all sound waves are refracted back and forth as they pass alternately up and down across the depth of the velocity minimum. A sound velocity minimum, and therefore a sound channel, is present at a depth of several hundred meters throughout most of the world’s oceans. Sound normally spreads out spherically (in all directions), and the loss in intensity (attenuation) due to the spreading is proportional to the square of the distance from the source (Fig. 5-20d). In contrast, sound is focused in the sound channel and spreads cylindrically, so that the attenuation is proportional only to the distance from the source. Hence, sound can travel very large distances within the sound channel with relatively little attenuation. For example, sounds of small underwater explosions in the sound channel near Australia have been detected as far away as Bermuda in the North Atlantic Ocean.

Acoustic Thermometry

The vast distance over which sound can travel in the sound channel is the basis of an experiment, begun in 1991, that provides a sensitive means to determine of average ocean temperature.

Determining whether the Earth’s average surface and/or atmospheric temperature has recently changed or is now changing as a result of greenhouse effect enhancement is very difficult.

Changes of only one-tenth of a degree per year in the global average temperature could drastically change the Earth’s climate in just a few decades. However, because of the high temporal and **spatial** variability of temperatures in the ocean, land surface, and atmosphere, the best measurements currently possible from conventional thermometers or satellites are not accurate enough to identify changes in the global average temperature of less than about a tenth of a degree. In contrast, changes of only a few thousandths of a degree per year in the average temperature of ocean water can be identified by measurement of the travel times of sounds over distances of thousands of kilometers in the sound channel. This method of monitoring is known as “**acoustic thermometry**.”

The principle of acoustic thermometry is simple and was proven in 1991 with a preliminary experiment, the Acoustic Thermometry of Ocean Climate (ATOC) program. A large underwater transducer (a sound producer like a loudspeaker) is lowered into the sound channel. In the preliminary experiment, the transducer was placed in the ocean near Heard Island in the southern Indian Ocean (Fig. 5-21). The transducer transmits low-frequency sound pulses into the sound channel. At several locations tens of thousands of kilometers away, sensitive **hydrophones** detect the incoming sound and precisely record its arrival time. The travel time is measured to within a fraction of a second and used to compute the average speed of sound between transducer and receiver.

The speed of sound in seawater increases with increasing temperature. Therefore, if the travel time between a transducer and a listening point in the system decreases from year to year, it indicates that the average temperature within the sound channel between those two points has increased (unless the average salinity or average depth of the sound channel has changed). An experimental acoustic array with the sound source located just north of the Hawaiian Islands and receiving stations surrounding the Pacific Ocean basin at distances of 3000 to 5000 km from this source has demonstrated that average ocean temperature measurements can be made with a precision of about 0.006°C. Results from this program have revealed surprisingly large seasonal and other short-term variations of average temperatures. The program operated between 1996 and 2006 but did not continue

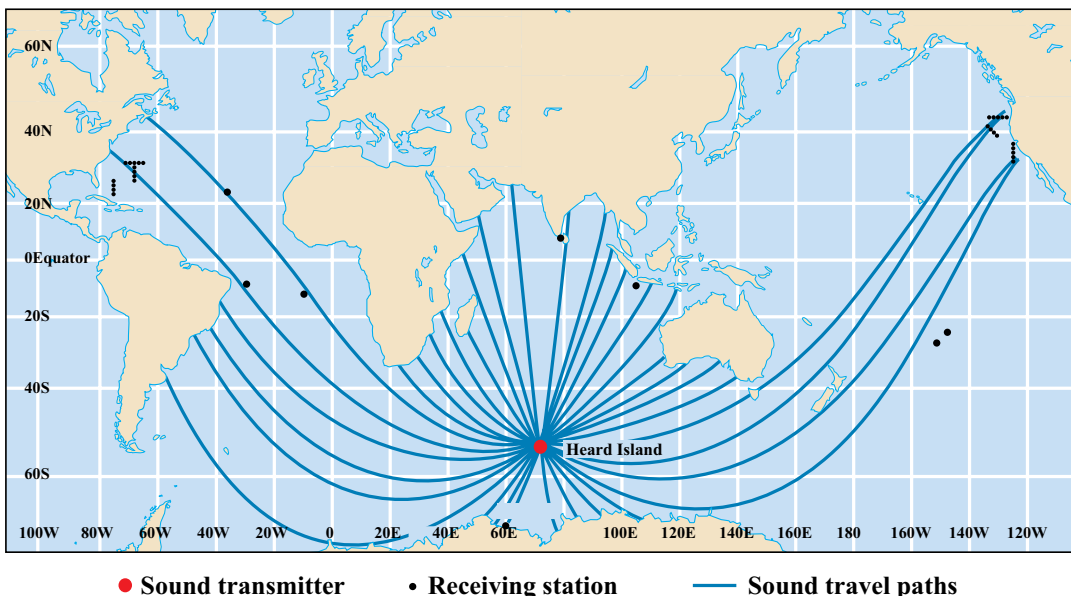


FIGURE 5-21 The Heard Island experiment. Sound pulses were emitted from a source in the sound channel at Heard Island, and the time of travel to the various receiving sites (shown by the black dots) was measured very precisely. Because the travel time of sound would change if the average temperature of the ocean water in the sound channel changed, arrays such as this could be used to monitor changes in the average temperature of ocean waters at the depth of the sound channel.

long enough to reveal any long-term trends. The program was abandoned, at least in part, by controversies concerning the possible effects of the sounds produced on marine species, especially whales, dolphins, and other **marine mammals**.

Recently the idea of monitoring ocean temperatures by acoustic thermometry has been revived by studies of acoustic waves that are created by earthquakes and that travel in the sound channel. Results obtained using this technique have identified temperature fluctuations in the East India Ocean on timescales of 12 months, 6 months and approximately 10 days and an estimate of the decadal warming trend that is consistent with but significantly higher than the trend estimated from Argo float data. As with all environmental measurements, the existence of two independent techniques for measuring trends and assessing temporal variability promises to substantially improve the accuracy and detail of ocean water temperature change monitoring studies.

Ocean Noise

Scuba divers know that the undersea world is not silent. Besides the sounds of breathing regulators and boat propellers, an observant scuba diver hears a variety of other noises. They often sound like a well-known snap-crackle-pop cereal. The natural sources of sound in the oceans are many and varied, but generally they fit into three categories: noises from breaking waves and bursting air bubbles, noises from vessels and other human mechanical equipment, and biological noises. Each of the sources produces sounds across a wide range of frequencies.

Biological sounds are produced by many species and through various means. For example, whales and dolphins use sound to locate objects, such as prey, and to communicate with each other. Dolphins may also use intense bursts of sound to confuse or stun their prey. Certain **crustaceans** (shrimp, crabs, and lobsters) make clicking noises as they close their claws, and certain fishes make sounds by inflating and deflating the **swim bladder** (a gas sac used to control **buoyancy**).

Natural sounds and the sounds of human activities, both of which are always present in the ocean, constitute a background noise above which the sonar sound probes used by oceanographers or navies must be strong enough to be heard. Submarines can be detected easily if they send out sonar signals to locate vessels that are searching for them, so instead they use sensitive directional microphones to detect the noise of ships' propellers.

Because sound can travel very long distances in water, sensitive microphones can pick up sounds made hundreds or even thousands of kilometers away. Using sensitive microphone arrays, navies obtain data that are analyzed by supercomputers to separate the sounds of submarine or ship engines and other ship noises from background noise. This technology has become highly sophisticated. In some cases, the listening arrays can identify a specific submarine or surface vessel by its own specific sound "fingerprint" and can determine the vessel's location precisely and track its movements across oceans. This capability has been extended so that the system can now identify and track some species in the oceans including whales. Individual whales can even be identified and tracked as each whale makes its own unique sounds.

CHAPTER SUMMARY

Origins and Distribution of the Earth's Water.

The Earth is the only planet known to have water in all three states: solid (ice), liquid, and gas (atmospheric vapor). The

oceans contain 97% of the Earth's water.

The Water Molecule.

Water has many unusual properties related to the polar nature of its molecule and the resulting hydrogen bond between water molecules.

The Dissolving Power of Water.

Water can dissolve more substances than any other known liquid. Water molecules can surround and hydrate negatively and positively charged ions, allowing the oppositely charged ions of a compound to move independently within the surrounding water molecules.

Salinity.

Various properties of water depend on the concentration of dissolved salts, expressed as salinity. Salinity is usually determined by the measurement of electrical conductivity.

Composition of Seawater.

Seawater is a complex solution containing almost all naturally occurring elements, many radionuclides, numerous organic compounds, and dissolved gases. Elements are present primarily as ions and are classified as major, minor, or trace constituents according to concentration. Dissolved gases, including oxygen, nitrogen, and carbon dioxide, can move freely between surface seawater and the atmosphere. Concentrations of elements in seawater are in an approximate steady state. These concentrations are determined by the crustal abundance of the elements and their behavior in biogeochemical cycles. Ratios of major ions are generally almost constant, although the total dissolved constituent concentration (salinity) varies.

Dissolved carbon dioxide is present as carbonate, bicarbonate, and molecular carbon dioxide in a complex equilibrium that allows more carbon dioxide to be dissolved than would otherwise be the case. This is one reason why the oceans contain about 70 times as much carbon dioxide as the atmosphere. Carbon dioxide is produced by respiration and decomposition of organic matter throughout the ocean depths. Most organic matter in the oceans is produced through photosynthesis, which uses carbon dioxide and releases oxygen. Photosynthesis requires light energy and occurs only in upper layers of ocean waters.

Heat Properties of Water.

Water has anomalously high freezing and boiling points. Hence, water can be present in solid, liquid, and vapor phases in the range of temperatures found at the Earth's surface. Water also has anomalously high heat capacity, latent heat of fusion, and latent heat of vaporization. These anomalous properties enable water to store and transport large amounts of heat through the oceans and atmosphere. Without these properties, the Earth's climate would be much more extreme.

Effects of Pressure, Temperature, and Dissolved Salts on Seawater Density.

Pure water has an anomalous density maximum at 4°C, but the maximum disappears with increasing salt concentration and is not present in seawater of normal salinity. Seawater density increases with increasing salinity and with decreasing temperature. Water expands as it freezes, so ice is less dense than water and floats. As seawater freezes, the salts are excluded and left in solution.

Surface Tension and Viscosity.

Water has an anomalously high surface tension. This property

affects the behavior of the sea surface, including the creation and dissipation of small waves and the formation and behavior of gas bubbles and spray droplets in breaking waves. Water has a high viscosity relative to many other liquids. This high viscosity allows microscopic organisms that are more dense than water to remain in the surface layers of the oceans, because water provides a relatively high resistance to their motion including sinking.

Transmission of Light and Other Electromagnetic Radiation.

Water effectively absorbs electromagnetic radiation. Absorption is less effective at the wavelengths of visible light. Visible light can penetrate up to several hundred meters into clear ocean waters and is the energy source for phototrophy which includes photosynthesis. Blue and green wavelengths of light are absorbed less than red, yellow, and violet wavelengths.

Suspended particles absorb, scatter, and reflect light. The depth to which light penetrates to support phototrophy is reduced as the concentration of suspended particles increases.

Transmission of Sound.

Sound is absorbed much less effectively by water than electromagnetic radiation is. Sound travels long distances through water with little loss of intensity, and it is used by oceanographers and marine animals for communication and remote sensing in the oceans. The principal use of sound by oceanographers is to measure ocean depth and seafloor **topography** with sonar.

Sound velocity varies slightly with salinity, temperature, and depth (pressure). Very accurate measurements of ocean depth by sonar require detailed knowledge of salinity and temperature variations in the water column. Sound pulses can be used to make very precise measurements of year-to-year changes in average ocean water temperature based on the time sound takes to travel from a source to receiving microphones thousands of kilometers away.

KEY TERMS

You should recognize and understand the meaning of all terms that are in boldface type in the text. All those terms are defined in the Glossary. The following are some less familiar key scientific terms that are used in this chapter and that are essential to know and be able to use in classroom discussions or exam answers.

acoustic	latent heat of vaporization
adsorbed	nutrient
alkaline	pH
anion	photic zone
backscattered	photosynthesis
biogeochemical cycle	phototroph
calorie	phototrophy
cation	plankton
conduction	radionuclide (radioisotope)
contaminant	refracted
convection	residence time
covalent bond	respiration
density	runoff
detritus	salinity
electrical conductivity	salt marsh
electromagnetic radiation	saturation solubility
eroded	scattered
estuary	sediment
excretion	sensible heat
frequency	solubility
groundwater	sonar

hard parts	sounding
heat capacity	spatial
hydration	steady state
hydrogen bond	surface tension
hydrophone	suspended sediment
hydrothermal vent	turbidity
ion	van der Waals force
ionic bond	viscosity
isotope	water mass
joule	weathered
latent heat of fusion	

STUDY QUESTIONS

1. What are the principal sources and sinks of elements dissolved in seawater? Explain why the totals of these sources and sinks must be approximately balanced.
2. Why are some elements present in high concentrations in seawater, whereas others are present in much lower concentrations?
3. Why is the solubility of carbon dioxide in seawater so high?
4. The water molecule is polar. Why does this property give water a high latent heat of vaporization?
5. In Florida citrus groves, growers often try to encourage ice crystals to grow on the trees and fruit during unusually cold nights when the air temperature drops below freezing. Explain how the physical properties of water and ice make this an effective method for protecting the citrus fruit from being frozen and damaged.
6. Why is it easier for a person to float in the ocean than in freshwater?
7. If ice were dense enough that it always sank, how would lakes behave in winter? How might the oceans be different?
8. What is surface tension, and why is this property of water important in the ocean? Why is the high surface tension of water important in our everyday life? The surface tension of water is reduced by the addition of detergents. How and why is that effect useful to us?
9. Why is it dark deep in the oceans? Why can we not easily see the bottoms of streams and rivers?
10. What do we need to know about the properties of the ocean water beneath a ship if we want to use sonar to measure the depth accurately? Why does sound travel long distances in ocean water?

CRITICAL THINKING QUESTIONS

1. Describe all the ways that you can think of in which the Earth would be different if the water molecule were not polar.
2. Continental rocks and soils are constantly leached as freshwater dissolves ions and gases in rocks and transports them to the oceans. However, it is thought that the concentration and composition of dissolved salts in the oceans has remained approximately the same for hundreds of millions of years. Explain how this stability is possible and explain why the hundreds of millions of years of leaching have not depleted the concentrations of such soluble elements as sodium and potassium in terrestrial rocks.
3. In this chapter the concept of steady-state processes is illustrated by an analogy of pouring orange juice into a glass filled with water. (a) List some processes that occur in our homes, industry, or economy that are steady-state processes in the sense that the outputs change in response to changes in

the inputs (or vice versa). (b) How quickly does this response lead to a new steady state in the examples you have given, and how would changes in inputs or outputs in your example produce temporal changes equivalent to the changes in “concentration” of the “substance” in the “box” discussed in **CC8**?

4. If water’s heat capacity and latent heat of vaporization were much lower, would we still have rain, and would puddles of rainwater behave differently? Explain your answer. Describe some of the things that would be different in your everyday life.
5. If we look through the water of a swimming pool, we can see the bottom. If the water surface is calm, the tiles and lane markings appear clear and sharp. However, if the surface is disturbed, even if only by tiny ripples, these markings appear indistinct and seem to shimmer. Why?

CRITICAL CONCEPTS REMINDERS

CC1 Density and Layering in Fluids: Water in the oceans is arranged in layers according to the water density. Many movements of water masses in the oceans are driven by differences in water density.

CC3 Convection and Convection Cells: Fluids, including ocean water, that are cooled from above or heated from below, sink or rise because their density is increased or reduced respectively. This establishes convection processes that are a primary cause of vertical movements and the mixing of ocean waters.

CC5 Transfer and Storage of Heat by Water: Water’s high heat capacity allows large amounts of heat to be stored in the oceans and released to the atmosphere without much change of ocean water temperature. Water’s high latent heat of vaporization allows large amounts of heat to be transferred to the atmosphere in water vapor and then transported elsewhere. Water’s high latent heat of fusion allows ice to act as a heat buffer reducing climate extremes in high latitude regions. .

CC6 Salinity, Temperature, Pressure, and Water Density: Sea water density is controlled by temperature, salinity, and to a lesser extent pressure. Density is higher at lower temperatures, higher salinities, and higher pressures. Movements of water below the ocean surface layer are driven primarily by density differences

CC7 Radioactivity and Age Dating: Seawater contains naturally occurring and man-made radioisotopes of many elements at very low concentrations. These are useful for tracing movements of the elements through biogeochemical cycles.

CC8 Residence Time: The residence time of an element in seawater is the average length of time atoms of the element spend in the oceans and it depends, to a large extent, on the rate of processes that remove them from solution. Residence time is a major factor in determining the concentration of elements in seawater.

CC9 The Global Greenhouse Effect: The oceans play a major part in studies of the greenhouse effect because the oceans store large amounts of carbon dioxide and are a source of other greenhouse gases including methane.

CC14 Phototrophy, Light, and Nutrients: Phototrophy, that includes photosynthesis, the major processes in the production of living matter, depend on the availability of light. Thus, the transmission of light through ocean water limits the depth to which phototrophy may occur.

CC18 Toxicity: Many dissolved constituents of seawater become toxic to marine life at concentrations above their natural levels in seawater. A number of these constituents are nutrients that can limit primary production if their concentrations are too low. Thus, life depends on the relatively invariable concentrations of dissolved chemicals in the oceans.

CREDITS

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