

Chapter 6



An evaporate salt pond in Bonaire, Netherlands Antilles.

The Chemistry of Seawater

Chapter Outline

- | | |
|--|---------------------|
| 6.1 Salts 149 | Summary 164 |
| 6.2 Gases 155 | Key Terms 165 |
| Box: <i>Messages in Polar Ice</i> 158 | Study Questions 165 |
| 6.3 The pH of Seawater 160 | Study Problems 166 |
| 6.4 Other Substances 161 | |
| 6.5 Practical Considerations: Salt and Water 162 | |
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Learning Outcomes

After studying the information in this chapter students should be able to:

1. *sketch* the pattern of high and low sea surface salinity on a map of the world's oceans,
2. *explain* how sea surface salinity is modified by evaporation, precipitation, and runoff from the continents,
3. *review* the sources of major constituent ions in seawater,
4. *rank* the six most abundant constituent ions in seawater in order of their concentration,
5. *calculate* the residence time of an ion given its concentration and rate of supply,
6. *diagram* the distribution of oxygen and carbon dioxide with depth,
7. *describe* the pH scale and *explain* the role of carbon dioxide in buffering seawater pH,
8. *identify* the three ions considered important marine nutrients, and
9. *compare* and *contrast* two different methods of desalination.

Seawater is salt water, and historically, seawater has been valued for its salt. Until recently, salt was enormously important as a food preservative, and at one time, salt formed the basis for a major commercial trade. Today, although salt is still extracted from seawater, it is the water that has become increasingly valuable in many areas of the world. Seawater is also much more than salt water. Seawater is a complex solution containing dissolved gases, nutrient substances, and organic molecules as well as salts.

In this chapter, we investigate seawater, and we explore physical, chemical, and biological processes that regulate its composition. We also review the commercial extraction of salts from seawater and the possibilities of increasing our supply of fresh water by desalination.

6.1 Salts

Units of Concentration

Compounds can break apart into individual atoms or groups of atoms that have opposite electrical charges. A charged atom or group of atoms is an ion. An ion with a positive charge is a **cation**; an atom with a negative charge is an **anion**. The salts in seawater are present in dissolved form as cations and anions. For example, in a glass of seawater, you would find individual sodium cations (Na^+) and chloride anions (Cl^-). If the water was then left out in the sun to evaporate, these ions would combine to form a solid precipitate, the salt compound sodium chloride (NaCl).

The concentration of dissolved constituents in seawater can be expressed by weight, by volume, or in molar terms. Concentrations of different constituents vary by several orders of magnitude. When expressed by weight, concentrations are given as g/kg (parts per thousand), mg/kg (parts per million), or even $\mu\text{g}/\text{kg}$ (parts per billion), depending on the abundance of the constituent. Thus, 1 g/kg (1 part per thousand) = 1000 mg/kg (10^3 parts per million) = $1 \text{ million } \mu\text{g}/\text{kg}$ (10^6 parts per billion), or $1 \mu\text{g}/\text{kg}$ (1 part per billion) = 0.001 mg/kg (10^{-3} parts per million) = 0.000001 g/kg (10^{-6} parts per thousand). Similarly, measurements of concentration by volume are expressed as

g/l, mg/l, or $\mu\text{g}/\text{l}$. Since 1 liter of seawater weighs very nearly 1 kilogram (approximately 1.027 kilograms), concentrations measured by weight and by volume are numerically similar (the concentration of chloride in seawater is approximately 19.35 g/kg or 19.87 g/l).

For some purposes, it is useful to express the concentration of seawater constituents in molar terms. One mole of an element, or compound, has a mass in grams equal to the atomic (or ionic, or molecular) mass of the element or compound. A mole of sodium (Na^+) contains 23 g of sodium; a mole of sulfate (SO_4^{2-}) contains $32 + (16 \times 4) = 96 \text{ g}$ of sulfate; and a mole of bicarbonate (HCO_3^-) contains $1 + 12 + (16 \times 3) = 61 \text{ g}$ of bicarbonate. Once again, because 1 liter of seawater weighs nearly 1 kilogram, molar concentrations of a given dissolved constituent expressed as moles/kg and moles/l are numerically similar.

Ocean Salinities

In the major ocean basins, 3.5% of the weight of seawater is, on the average, dissolved salt and 96.5% is water, so a typical 1000 g or 1 kg sample of seawater is made up of 965 g of water and 35 g of salt. Oceanographers measure the salt content of ocean water in grams of salt per kilogram of seawater (g/kg), or parts per thousand (‰). The total quantity of dissolved salt in seawater is known as **salinity**, and the average ocean salinity is approximately 35‰. There are about 1338.5 million km^3 ($\sim 1.34 \times 10^9 \text{ km}^3$) of seawater in the oceans, with an average density of approximately 1.03 g/cm^3 ($1.03 \times 10^{12} \text{ kg/km}^3$) (see tables 2.4 and 5.3). The total weight of this seawater is about 1378.7 million trillion kg ($\sim 1.4 \times 10^{21} \text{ kg}$); the weight of the salt in the oceans is about 3.5% of the total weight, or approximately 48 million trillion kg ($\sim 1.1 \times 10^{20} \text{ lb}$, or $\sim 5.3 \times 10^{16} \text{ tons}$). If all the water in the oceans evaporated, this amount of salt would form a layer roughly 45.5 m (150 ft) thick over the entire surface of Earth.

The salinity of ocean surface water is associated with latitude. Latitudinal variations in evaporation and precipitation, as well as freezing, thawing, and freshwater runoff from the land, affect the amount of salt in seawater. The relationship among evaporation, precipitation, and mid-ocean surface

salinity with latitude is shown in figure 6.1. Notice the low surface salinities in the cool and rainy 40°–50°N and S latitude belts, high evaporation rates and high surface salinities in the desert belts centered on 25°N and S, and low surface salinities again in the warm but rainy tropics centered at 5°N. Sea surface salinities during the Northern Hemisphere summer are shown in figure 6.2.

In coastal areas of high precipitation and river inflow, surface salinities fall below the average. For example, during periods of high flow, the water of the Columbia River lowers the Pacific Ocean's surface salinity to less than 25‰ as far as 35 km (20 mi) at sea. Also, sailors have dipped up water fresh enough to drink from the ocean surface 85 km (50 mi) from the mouth of the Amazon River. In subtropic regions of high evaporation and low freshwater input, the surface salinities of nearly landlocked seas are well above the average: 40–42‰ in the Red Sea and the Persian Gulf and 38–39‰ in the Mediterranean Sea. In the open ocean at these same latitudes, the surface salinity is closer to 36.5‰. Surface salinities change seasonally in polar areas, where the surface water forms sea ice in winter, leaving behind the salt and raising the salinity of the water under the ice. In summer, a freshwater surface layer forms when the sea ice melts. Deep-water samples from the mid-latitudes are usually slightly less salty than the surface waters in part because the deep water is formed at the surface in high latitudes with high precipitation. The formation of these deep-water types is discussed in chapter 8.

Dissolved Salts

The atoms or groups of atoms that combine to form compounds can be held together by different kinds of bonds. The two hydrogen atoms and one oxygen atom in the water molecule are held together by covalent bonds in which electrons are shared between the atoms (see section 5.1). Other compounds, such as sodium chloride (NaCl), are held together by **ionic bonds** in which electrons are transferred from a metal atom (in this case, the metal sodium) to a nonmetal atom (in this case, the chlorine atom), creating ions of opposite charge that attract each other. As stated earlier, an ion with a positive charge is a cation; an ion with a negative charge is an anion. Ionic bonds are easily broken in water because of the polar nature of the water molecule. Thus, when salts are added to water, the salts dissolve, or dissociate (break apart), into ions. The dissolved salts in seawater are mostly present as cations and anions (see section 5.7).

When solid sodium chloride is added to water, the bonds between the ions break, and positively charged sodium ions and

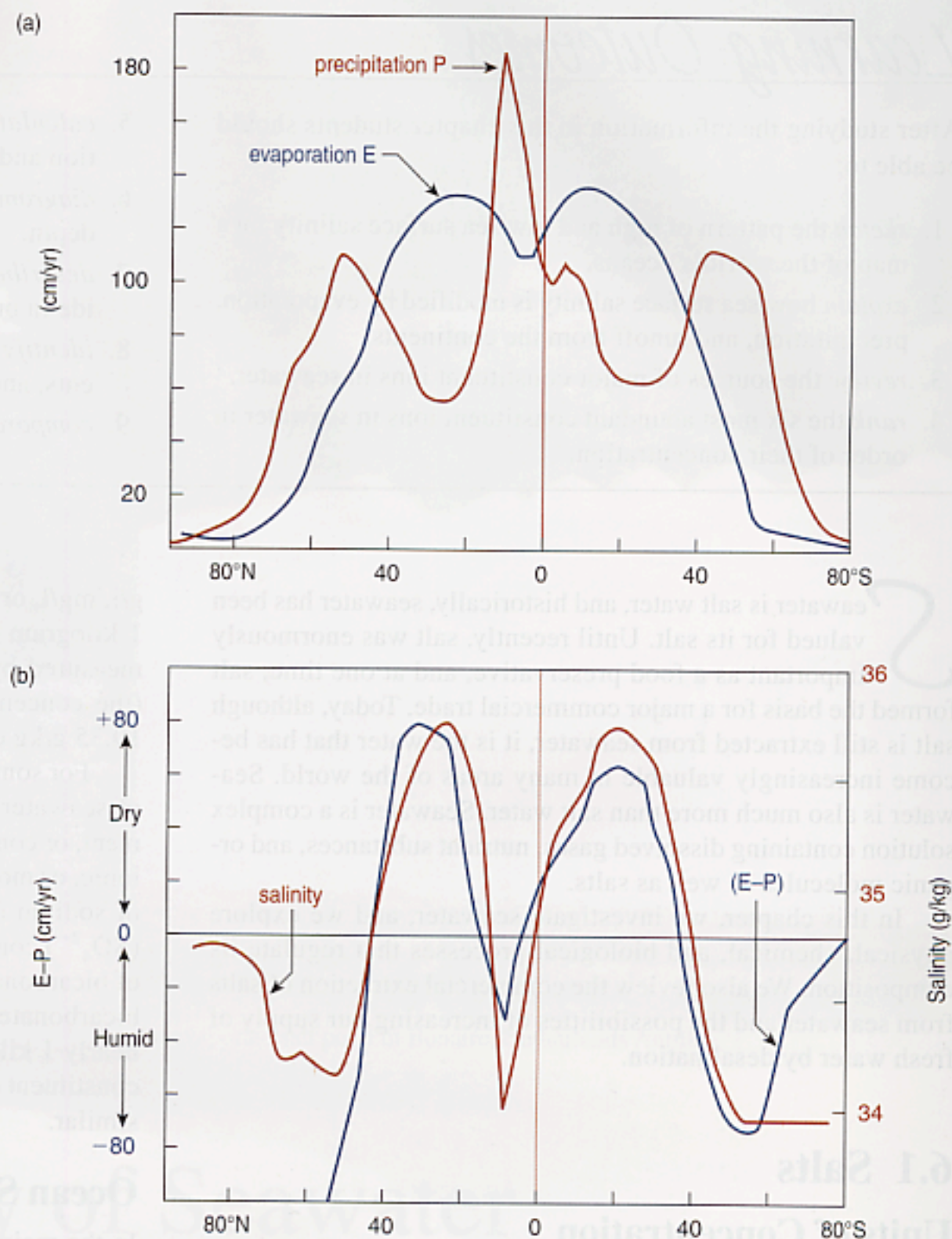
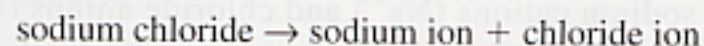
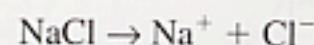


Figure 6.1 (a) Mid-ocean precipitation (red) and evaporation (blue) values as a function of latitude. (b) Mid-ocean average surface salinity values (red) match the average variation in [evaporation minus precipitation] values (blue) that occur with latitude.

negatively charged chloride ions are released into the water. This reaction can be written as



or it can be written with chemical abbreviations as



Six ions make up more than 99% of the salts dissolved in seawater. Four of these are cations: sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+); two are anions: chloride (Cl^-) and sulfate (SO_4^{2-}). Table 6.1 lists these six ions and five more, arranged in order of their abundance in seawater. The ions listed in table 6.1 are known as the **major constituents** of seawater. Note that sodium and chloride ions account for 86% of the salt ions in seawater.

All the other elements dissolved in seawater are present in concentrations of less than one part per million and are called

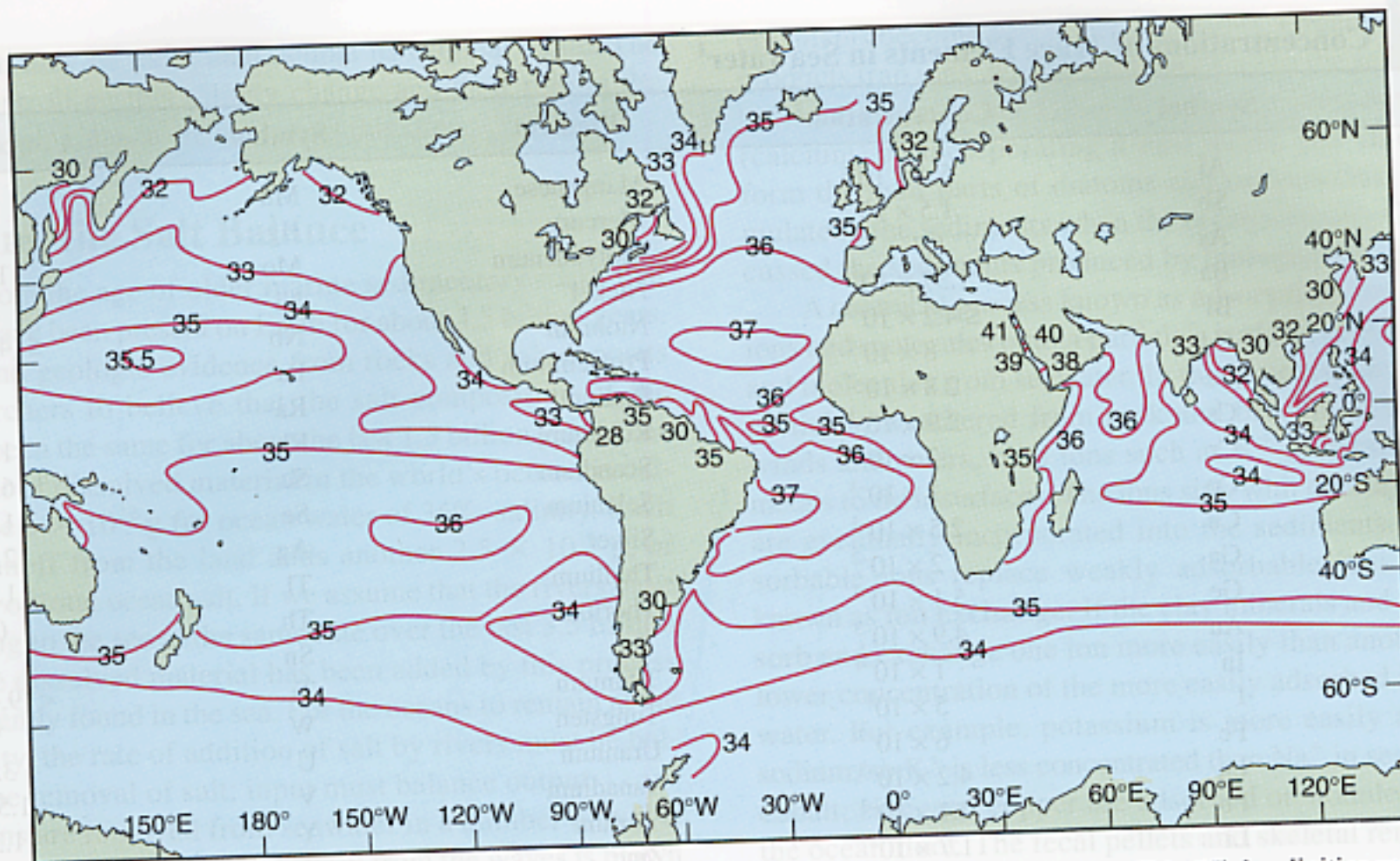


Figure 6.2 Average sea surface salinities in the Northern Hemisphere summer, given in parts per thousand (‰). (High salinities are found in areas of high evaporation; low salinities are common in coastal areas and regions of high precipitation.)

Table 6.1 Major Constituents of Seawater¹

Constituent	Symbol	Concentration in Seawater			Percentage by Weight
		g/kg	g/l	mole/l	
Chloride	Cl ⁻	19.35	19.87	0.560	55.07
Sodium	Na ⁺	10.76	11.05	0.481	30.62
Sulfate	SO ₄ ²⁻	2.71	2.78	0.029	7.72
Magnesium	Mg ²⁺	1.29	1.32	0.054	3.68
Calcium	Ca ²⁺	0.41	0.42	0.0105	1.17
Potassium	K ⁺	0.39	0.40	0.0102	1.10
Bicarbonate	HCO ₃ ⁻	0.14	0.144	0.0024	0.40
Bromide	Br ⁻	0.067	0.069	0.00086	0.19
Strontium	Sr ²⁺	0.008	0.008	0.00009	0.02
Boron	B ³⁺	0.004	0.004	0.00037	0.01
Fluoride	F ⁻	0.001	0.001	0.00005	0.02
Total		35.13	36.07	1.1485	99.99

1. Nutrients and dissolved gases are not included.

trace elements (table 6.2). Most trace elements are present in such small concentrations that it is common to report their concentrations at the parts per billion level. Some of these elements are important to organisms that are able to concentrate the ions. For example, long before iodine could be determined chemically as a trace element of seawater, it was known that shellfish and seaweeds were rich sources for this element, and seaweed was harvested for commercial iodine extraction.

Because the ratios of the major constituents of seawater do not change with changes in total salt content and because these constituents are not generally removed or added by living organisms, the major constituents are termed **conservative**

constituents. Certain of the ions present in much smaller quantities, some dissolved gases, and assorted organic molecules and complexes do change in concentrations because of biological and chemical processes that occur in some areas of the oceans; these are known as **nonconservative constituents**.

Sources of Salt

The original sources of sea salts include the crust and the interior of Earth. The chemical composition of Earth's rocky crust can account for most of the positively charged ions found in seawater. Large quantities of cations are present in rocks that

Table 6.2 Concentrations of Trace Elements in Seawater¹

Element	Symbol	Concentration ²	Element	Symbol	Concentration ²
Aluminum	Al	5.4×10^{-1}	Manganese	Mn	3×10^{-2}
Antimony	Sb	1.5×10^{-1}	Mercury	Hg	1×10^{-3}
Arsenic	As	1.7	Molybdenum	Mo	1.1×10^1
Barium	Ba	1.37×10^1	Nickel	Ni	5×10^{-1}
Bismuth	Bi	$\leq 4.2 \times 10^{-5}$	Niobium	Nb	$\leq (4.6 \times 10^{-3})$
Cadmium	Cd	8×10^{-2}	Protactinium	Pa	5×10^{-8}
Cerium	Ce	2.8×10^{-3}	Radium	Ra	7×10^{-8}
Cesium	Cs	2.9×10^{-1}	Rubidium	Rb	1.2×10^2
Chromium	Cr	2×10^{-1}	Scandium	Sc	6.7×10^{-4}
Cobalt	Co	1×10^{-3}	Selenium	Se	1.3×10^{-1}
Copper	Cu	2.5×10^{-1}	Silver	Ag	2.7×10^{-3}
Gallium	Ga	2×10^{-2}	Thallium	Tl	1.2×10^{-2}
Germanium	Ge	5.1×10^{-3}	Thorium	Th	(1×10^{-2})
Gold	Au	4.9×10^{-3}	Tin	Sn	5×10^{-4}
Indium	In	1×10^{-4}	Titanium	Ti	$< (9.6 \times 10^{-1})$
Iodine	I	5×10^1	Tungsten	W	9×10^{-2}
Iron	Fe	6×10^{-2}	Uranium	U	3.2
Lanthanum	La	4.2×10^{-3}	Vanadium	V	1.58
Lead	Pb	2.1×10^{-3}	Yttrium	Y	1.3×10^{-2}
Lithium	Li	1.7×10^2	Zinc	Zn	4×10^{-1}
			Rare earths		$(0.5-3.0) \times 10^{-3}$

1. Nutrients and dissolved gases are not included.

2. Parts per billion, or $\mu\text{g/kg}$.

Note: Parentheses indicate uncertainty about concentration.

are formed by the crystallization of molten magma from volcanic processes. The physical and chemical weathering of rock over time breaks it into small pieces and the rain dissolves out ions, which are carried to the sea by rivers. Anions are present in Earth's interior and may have been present in Earth's early atmosphere. Some anions may have been washed from the atmosphere by long periods of rainfall, but the more likely source of most of the anions is thought to have been Earth's mantle. During the formation of Earth, gases from the mantle are believed to have supplied anions to the newly forming oceans.

Acidic gases released during volcanic eruptions (for example, hydrogen sulfide, sulfur dioxide, and chlorine) dissolve in rainwater or river water and are carried to the oceans as Cl^- (chloride) and SO_4^{2-} (sulfate).

Tests show that the most abundant ions in today's rivers (table 6.3) are the least abundant ions in ocean water because the rivers have previously removed the most easily dissolved land salts and are now carrying the less soluble salts. Exceptions to this pattern are found in rivers used for irrigation. These rivers are flowing through arid soils that have not lost much of their salt content. The water is frequently used several times and passes through a number of irrigation projects on its way downriver, causing the water to become increasingly salty and unfit for irrigation purposes. This situation has produced years of continuous conflict between the United States and Mexico over the waters of the Colorado River and Rio Grande, which irrigate much of the agricultural land of the U.S. desert Southwest before becoming available to the farmlands of Mexico.

Table 6.3 Dissolved Salts in River Water

Ion	Symbol	Percentage by Weight
Bicarbonate	HCO_3^-	48.7
Calcium	Ca^{2+}	12.5
Silicon dioxide (nonionic)	SiO_2	10.9
Sulfate	SO_4^{2-}	9.3
Chloride	Cl^-	6.5
Sodium	Na^+	5.2
Magnesium	Mg^{2+}	3.4
Potassium	K^+	1.9
Oxides (nonionic)	$(\text{Fe}, \text{Al})_2\text{O}_3$	0.8
Nitrate	NO_3^-	0.8
Total		100.00

Note: Average river salt concentration is 0.120‰.

In addition, we know that hot-water vents located on the sea floor supply chemicals to the ocean water and also remove them. Hydrothermal activity found at the mid-ocean ridges and associated with hot spots and ridge formation may play an important role in stabilizing the ocean's salt composition. When hot magma is introduced, the cold crust cracks and becomes permeable. Pressure from the water above the sea floor is high (1 atm for every 10 m of water depth), and it forces water into cracks and voids, where it is heated to extremely high temperatures. The salinity of seawater entering the hydrothermal system is relatively constant worldwide, but the water emerging from hydrothermal vents has

a salinity that may be more than double its original value. The processes controlling this salinity change and their role in the ocean's total salt balance are unclear at this time.

Regulating the Salt Balance

We know from the age of older marine sedimentary rocks that the oceans have been present on Earth for about 3.5 billion years. Chemical and geologic evidence from rocks and salt deposits leads researchers to believe that the salt composition of the oceans has been the same for about the last 1.5 billion years. The total amount of dissolved material in the world's oceans is calculated to be 5×10^{22} g for ocean water of 36‰ salinity. Each year, the runoff from the land adds another 2.5×10^{15} g, or 0.000005% of total ocean salt. If we assume that the rivers have been flowing to the sea at the same rate over the last 3.5 billion years, more dissolved material has been added by this process than is presently found in the sea. For the oceans to remain at the same salinity, the rate of addition of salt by rivers must be balanced by the removal of salt; input must balance output.

Salt ions are removed from seawater in a number of ways; some are shown in figure 6.3. Sea spray from the waves is blown ashore, depositing a film of salt on land. This salt is later returned to the oceans by runoff from the land. Over geologic time, shallow arms of the sea have become isolated, the water has evaporated, and the salts have been left behind as sedimentary deposits called **evaporites**. Salt ions can also react with each other to form insoluble products that precipitate on the ocean floor. Biological processes concentrate salts, which are removed from the water if the organisms are harvested or if the

organisms become part of the sediments. Organisms' excretion products trap ions, which are transferred to the sediments or returned to the seawater. Other biological processes remove Ca^{2+} (calcium) by incorporating it into shells, and silica is used to form the hard parts of diatoms and radiolarians. These accumulate in the sediments when the organisms die. Chapter 4 discussed the sediments produced by biological processes.

A chemical process known as **adsorption**, the adherence of ions and molecules onto a particle's surface, removes other ions and molecules from seawater. In this process, tiny clay mineral particles, weathered from rock and brought to the oceans by winds and rivers, bind ions such as K^+ (potassium) and trace metals to their surfaces. The ions sink with the clay particles and are eventually incorporated into the sediments. Strongly adsorbable ions replace weakly adsorbable ions in a process known as **ion exchange**. If the clay minerals and sediments adsorb and exchange one ion more easily than another, there is a lower concentration of the more easily adsorbed ion in the seawater. For example, potassium is more easily adsorbed than sodium, so K^+ is less concentrated than Na^+ in seawater. Nickel, cobalt, zinc, and copper are adsorbed on nodules that form on the ocean floor. The fecal pellets and skeletal remains of small organisms also act as adsorption surfaces. The settling of this organic debris transports metallic ions to the sediment, where they can be adsorbed on nodules. In these cases, the ions are removed from the water and are transferred to the sediments.

The process of forming the new crust at the ridge system of the deep-ocean floor (see chapter 3) participates in the input and output of the ions in seawater. Where molten rock rises from the mantle into the crust, magma chambers are formed. These

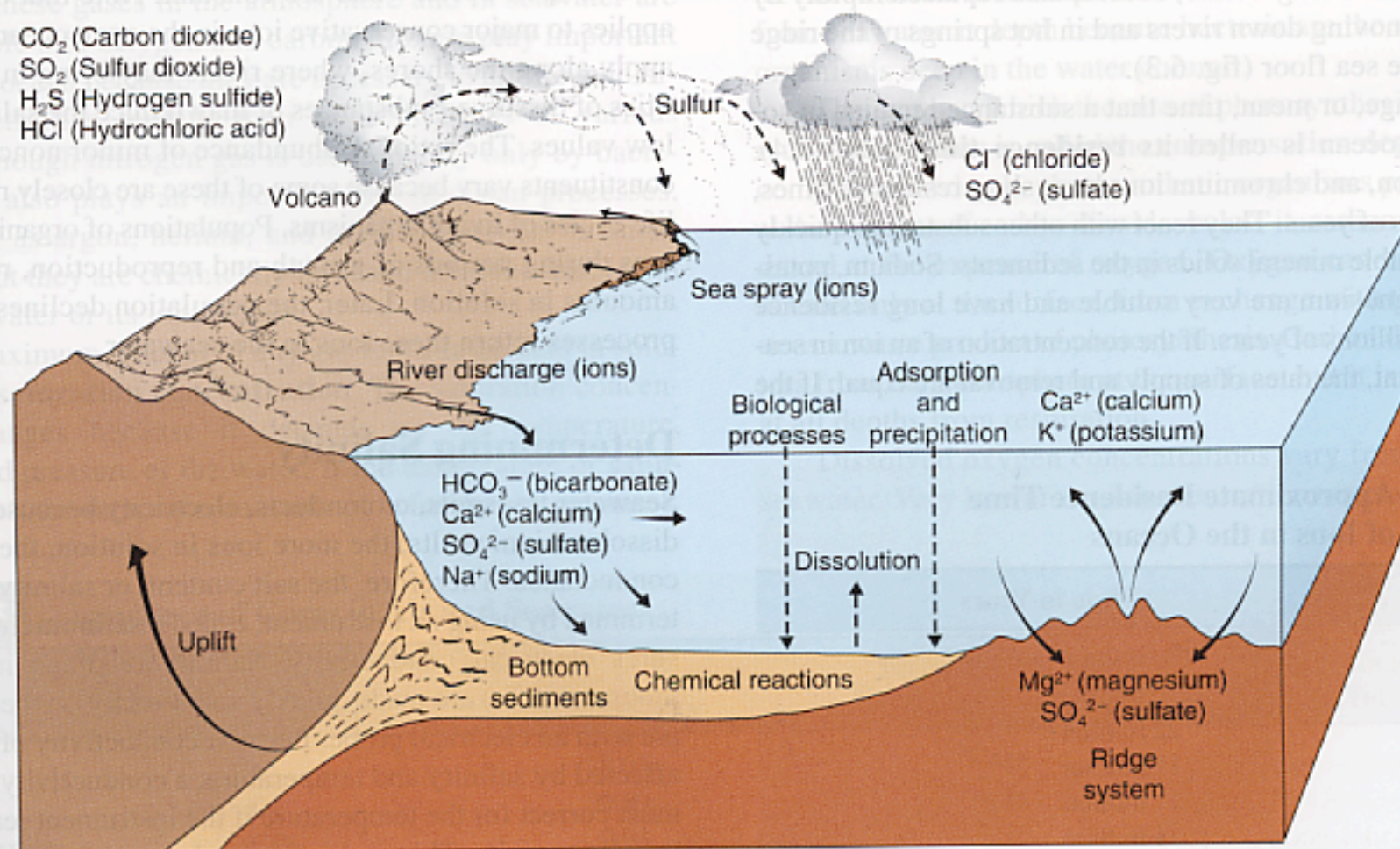


Figure 6.3 Processes that distribute and regulate the major constituents in seawater. Salt ions are added to seawater from rivers, volcanic events, ridge systems, and decay processes. Salt ions are removed from seawater by adsorption and ion exchange, spray, chemical precipitation, biological uptake, and addition to crustal rocks at ridge systems.

chambers are found mainly along plate boundaries but also above volcanic hot spots in the middle of plates. Cold water seeps down several kilometers through the fractured crust at a spreading center. The seawater becomes heated by flowing near the magma chamber. By convection, the heated water rises through the crust and reacts chemically with the rocks. Magnesium ions (Mg^{2+}) are transferred from the water to form minerals in the crust. At the same time, hydrogen ions (H^+) are released and the seawater solution becomes more acidic. Chemical reactions change sulfate (SO_4^{2-}) to sulfur and then to hydrogen sulfide (H_2S). The hot saline water dissolves metals from the crust, including copper, iron, manganese, and zinc, and releases potassium and calcium. It has been estimated that a volume of water equivalent to the entire mass of the oceans circulates through the crust at oceanic ridges every 10 million years.

The most important process for the removal of most elements from seawater is still adsorption of ions onto fine particles and their removal to the sediments. Ions deposited in the sediments are trapped there. They are not soon redissolved in the seawater, but geologic uplift elevates some marine sediments to positions above sea level. Erosion then works to dissolve and wash these deposits back to the sea.

Residence Time

The relative abundances of the salts in the sea are due in part to the ease with which they are introduced from Earth's crust and in part to the rate at which they are removed from the seawater. Sodium is moderately abundant in fresh water but is so highly soluble in seawater that it remains dissolved in the ocean. Calcium is removed rapidly from seawater to form limestone and the shells of marine organisms, but it is also replaced rapidly by calcium ions moving down rivers and in hot springs of the ridge systems on the sea floor (fig. 6.3).

The average, or mean, time that a substance remains in solution in the ocean is called its **residence time** (table 6.4). Aluminum, iron, and chromium ions have short residence times, in the hundreds of years. They react with other substances quickly and form insoluble mineral solids in the sediments. Sodium, potassium, and magnesium are very soluble and have long residence times, in the millions of years. If the concentration of an ion in seawater is constant, the rates of supply and removal are equal. If the

total amount of an ion present in the ocean is divided by either its rate of supply or its rate of removal, the residence time for that ion is known. For example, there are roughly 5.74×10^{20} g of Ca^{2+} in the oceans. It is estimated that Ca^{2+} is added to the oceans at a rate of about 5.4×10^{14} g per year. Therefore

$$\begin{aligned} \text{residence time } (\text{Ca}^{2+}) &= \left(\frac{5.74 \times 10^{20} \text{ g}}{5.55 \times 10^{14} \text{ g/yr}} \right) \\ &= 1.06 \times 10^6 \text{ years} \end{aligned}$$

Constant Proportions

Seawater is a well-mixed solution; currents and eddies in surface and deep water, vertical mixing processes, and wave and tidal action have all helped to stir the oceans through geologic time. Because of this thorough mixing, the ionic composition of open-ocean seawater is the same from place to place and from depth to depth. That is, the ratio of one major ion or seawater constituent to another remains the same. Whether the salinity is 40‰ or 28‰, the major ions exist in the same proportions. This concept was first suggested by the chemist Alexander Marcet in 1819. In 1865, another chemist, Georg Forchhammer, analyzed several hundred seawater samples and found that these constant proportions did hold true. During the world cruise of the *Challenger* expedition (1872–76), seventy-seven water samples were collected from different depths and locations. When chemist William Dittmar analyzed these samples, he verified Forchhammer's findings and Marcet's suggestion. These analyses led to the **principle of constant proportion** (or **constant composition**) of seawater, which states that regardless of variations in salinity, the ratios between the amounts of major ions in open-ocean water are constant. Note that the principle applies to major conservative ions in the open ocean; it does not apply along the shores, where rivers may bring in large quantities of dissolved substances or may reduce the salinity to very low values. The ratios of abundance of minor nonconservative constituents vary because some of these are closely related to the life cycles of living organisms. Populations of organisms remove ions during periods of growth and reproduction, reducing the amounts in solution. Later, the population declines, and decay processes return these ions to the seawater.

Determining Salinity

Seawater transmits, or conducts, electricity because it contains dissolved ionic salts; the more ions in solution, the greater the conductance. Therefore, the salt content, or salinity, can be determined by using an instrument, called a **salinometer**, that measures electrical conductivity. Salinity readings in parts per thousand (S‰) are made quickly and directly on the water sample with an electrical probe. Because conductivity of seawater is affected by salinity and temperature, a conductivity instrument must correct for the temperature if the instrument reads directly in salinity units. This correction is also necessary if the instrument reads conductance only. If conductance and temperature are measured separately, a computer program calculates the salinity. Other direct measurement techniques are discussed in chapter 8.

Table 6.4 Approximate Residence Time of Ions in the Oceans

Ion	Time in Years
Chloride	100 million–infinite
Sodium	210 million
Magnesium	22 million
Potassium	11 million
Sulfate	11 million
Calcium	1 million
Manganese	0.0014 million (1400)
Iron	0.00014 million (140)
Aluminum	0.00010 million (100)

To be sure that all salinity determinations are comparable, the world's oceanographic laboratories use a standard method of analysis and a standard seawater reference. At present, the Institute of Oceanographic Services in Wormly, England, is responsible for the production of standard seawater adjusted to both constant chloride content and electrical conductance to ensure standard calibration of laboratory instruments.

Historically, the quantity of chloride ions in a water sample was measured to establish the salinity of the sample. To do so, silver nitrate was added because the silver combines with the chloride ions. If the amount of silver required to react with all the chloride ions in a sample is known, the amount of chloride is known. The chloride concentration measured in this way is termed **chlorinity (Cl‰)** and is measured in parts per thousand or grams of chloride per kilogram of seawater. When the chlorinity of a sample is known, the concentration of any other major constituent can be calculated by using the principle of constant proportion.

Chlorinity and salinity are related by the equation

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

or

$$S‰ = 1.80655 \times Cl‰$$

6.2 Gases

Gases move between the sea and the atmosphere at the sea surface. Atmospheric gases dissolve in seawater and are distributed to all depths by mixing processes and currents. Abundant gases in the atmosphere and in the oceans are nitrogen (N₂), oxygen (O₂), and carbon dioxide (CO₂). The percentages of each of these gases in the atmosphere and in seawater are given in table 6.5. Oxygen and carbon dioxide play important roles in the ocean because they are necessary to all life, and biological activities modify their concentrations at various depths. Although nitrogen gas is used directly only by bacteria, its use also plays an important role in ocean processes. Gases such as argon, helium, and neon are present in small amounts, but they are chemically inert and do not interact with the ocean water or its inhabitants.

The maximum amount of any gas that can be held in solution is the **saturation concentration**. The saturation concentration changes because it depends on the temperature, salinity, and pressure of the water. If the temperature or salinity decreases, the saturation concentration for the gas increases.

If the pressure decreases, the saturation concentration decreases. In other words, colder water holds more dissolved gas than warmer water, less-salty water holds more gas than more-salty water, and water under more pressure holds more gas than water under less pressure.

Distribution with Depth

During **photosynthesis**, plants, seaweeds, and phytoplankton use carbon dioxide, sunlight, and inorganic nutrients (see section 6.4) to produce organic matter. In the process of photosynthesis, oxygen is generated. Phytoplankton and seaweeds grow in surface waters where there is sufficient sunlight to carry out photosynthesis. This lighted portion of the ocean is referred to as the **euphotic zone** (euphotic means "well lit" in Greek). In coastal waters, the euphotic zone is relatively shallow and may extend to only about 15 to 20 m (49–66 ft). In the open ocean where there are less suspended particles, the euphotic zone extends much deeper to about 150 to 200 m (492–656 ft). Photosynthetic organisms produce oxygen and use carbon dioxide in surface waters. In contrast, heterotrophic organisms consume organic compounds as food and use respiration to derive energy from the consumed materials. During respiration, the organic matter is **oxidized** using oxygen to produce carbon dioxide. Thus, heterotrophic organisms consume oxygen and produce carbon dioxide. All living organisms, regardless of whether they are photosynthetic or heterotrophic, carry out respiration. As a consequence, respiration occurs at all depths within the ocean. Photosynthesis and respiration will be discussed in more detail in chapter 15. Bacteria also respire (although they, of course, do not breathe like humans). Bacterial respiration of organic matter becomes the most important factor in the removal of oxygen from seawater at depth because bacteria are the most abundant organisms deep in the water column.

The depth at which the rate of photosynthesis balances the rate of respiration is called the **compensation depth**. Above the compensation depth, photosynthetic organisms produce oxygen at the expense of carbon dioxide; below it, carbon dioxide is produced at the expense of oxygen. Oxygen can be added to the oceans only at the surface, from exchange with the atmosphere or as a waste product of photosynthesis. Carbon dioxide also enters from the atmosphere at the surface, but it is also produced at all depths from respiration.

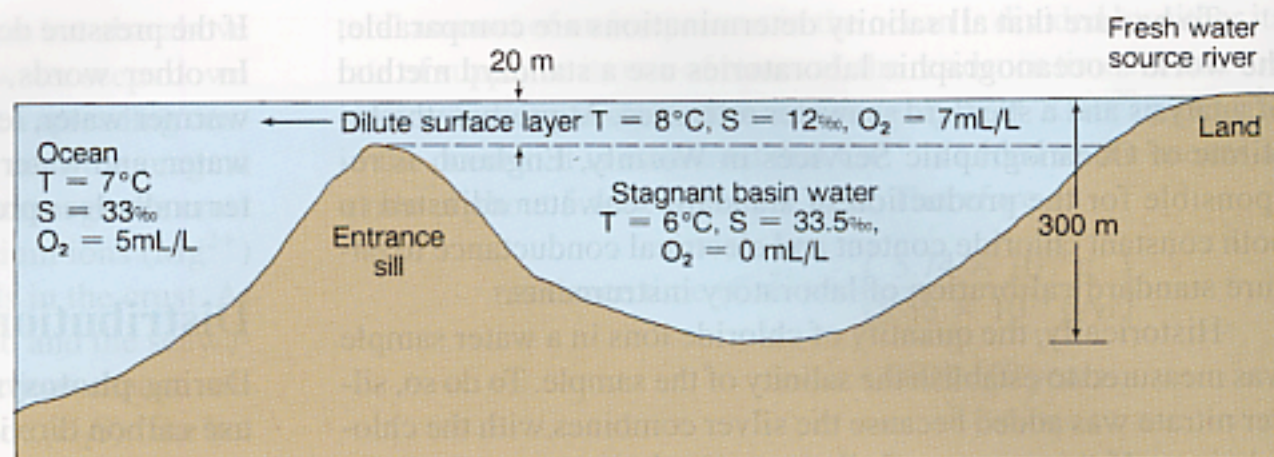
Dissolved oxygen concentrations vary from 0–10 ml/l of seawater. Very low or zero concentrations occur in the bottom

Table 6.5 Abundance of Gases in Air and Seawater

Gas	Symbol	Percentage by Volume in Atmosphere	Percentage by Volume in Surface Seawater ¹	Percentage by Volume in Total Oceans
Nitrogen	N ₂	78.03	48	11
Oxygen	O ₂	20.99	36	6
Carbon dioxide	CO ₂	0.03	15	83
Argon, helium, neon, etc.	Ar, He, Ne	0.95	1	
Totals		100.00	100	100

1. Salinity = 36‰, temperature = 20°C.

Figure 6.4 High-density ocean water is trapped behind the sill. The trapped water becomes anoxic at depth owing to continual respiration and decomposition. At the surface, sunlight enhances photosynthesis and the production of oxygen.



waters of isolated deep basins, which have little or no mixing with surface water. Such an area can occur at the bottom of a trench, in a deep basin behind a shallow entrance sill (as in the Black Sea), or at the bottom of a deep fjord (300–400 m; 900–1300 ft). If the deep water is only slowly flushed, respiration can use up the oxygen faster than the slow circulation to this depth is able to replace it. The bottom water becomes **anoxic**, or stripped of dissolved oxygen; **anaerobic** (or nonoxygen-using) bacteria live in such water. This condition is shown in figure 6.4. Because oxygen is more soluble in cold water than in warm water, more oxygen is found in surface waters at high latitudes than at lower latitudes. If the water is quiet, the nutrients and sunlight are abundant, and a large population of photosynthetic organisms is present, oxygen values at the surface can rise above the equilibrium (or saturation) value to 150% or more. This water is **supersaturated**. Wave action tends to liberate oxygen to the atmosphere and return the water to its 100% saturation state.

Figure 6.5 shows typical oxygen and carbon dioxide concentrations with depth. The concentration of both oxygen and carbon dioxide is influenced by biology. The concentration of oxygen is high and the concentration of carbon dioxide is low in surface waters because of photosynthesis. Below the euphotic zone, oxygen decreases as respiration of organic material removes the oxygen. The oxygen minimum occurs at about 800 m (2600 ft). Below this depth, the rate of removal of oxygen decreases because the population density of animals and the abundance of organic matter have decreased. The slow supply of oxygen to greater depths by water sinking from the surface gradually increases the concentration above that found at the oxygen minimum.

Carbon dioxide levels range between 45 and 54 ml/l throughout the oceans. The carbon dioxide concentration at the surface is low because it is used in photosynthesis. Below the surface layer, the concentration increases with depth as respiration continually produces carbon dioxide and adds it to the water. The deep water is able to hold high concentrations of CO_2 because the saturation value is high at low temperatures and high pressures. This is why calcareous oozes are preserved in the warmer, shallower water above the CCD and dissolved below it (review the discussion of biogenous sediments in chapter 4). At shallow depths, the concentration of CO_2 in the oceans is relatively low, in part because of high rates of photosynthesis and in part because the warm, shallow water has a low saturation value.

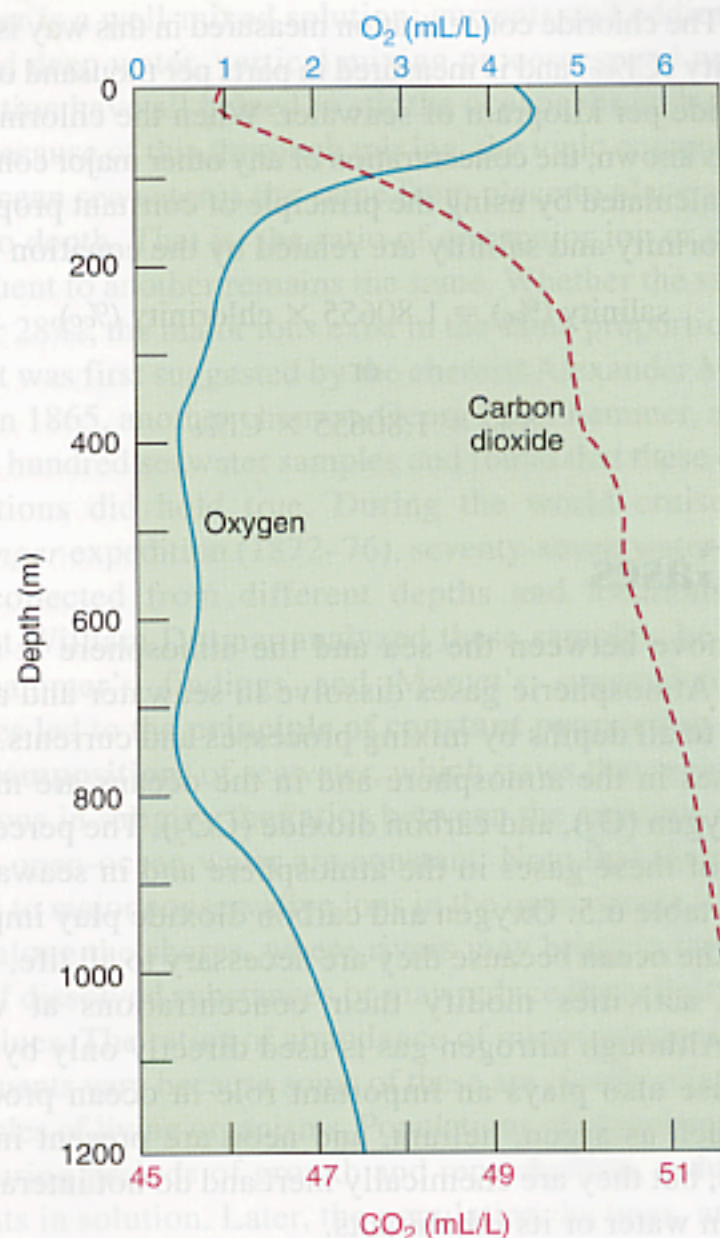


Figure 6.5 The distribution of O_2 and CO_2 with depth. Changes in O_2 concentration may exceed 400% from the surface to depth, whereas CO_2 concentrations change by less than 15%.

The Carbon Dioxide Cycle

At present, the net annual ocean uptake of carbon as carbon dioxide (CO_2) from the atmosphere is estimated to be 2 billion–3 billion metric tons per year. The rate at which the oceans absorb CO_2 is controlled by water temperature, pH (discussed in section 6.3), salinity, the chemistry of the ions (presence of calcium and carbonate ions), and biological processes, as well as mixing and circulation patterns (fig. 6.6).

The transfer of carbon from CO_2 to organic molecules by photosynthesis results in the addition of CO_2 to the intermediate and deep-ocean water when the organic material sinks and decays.

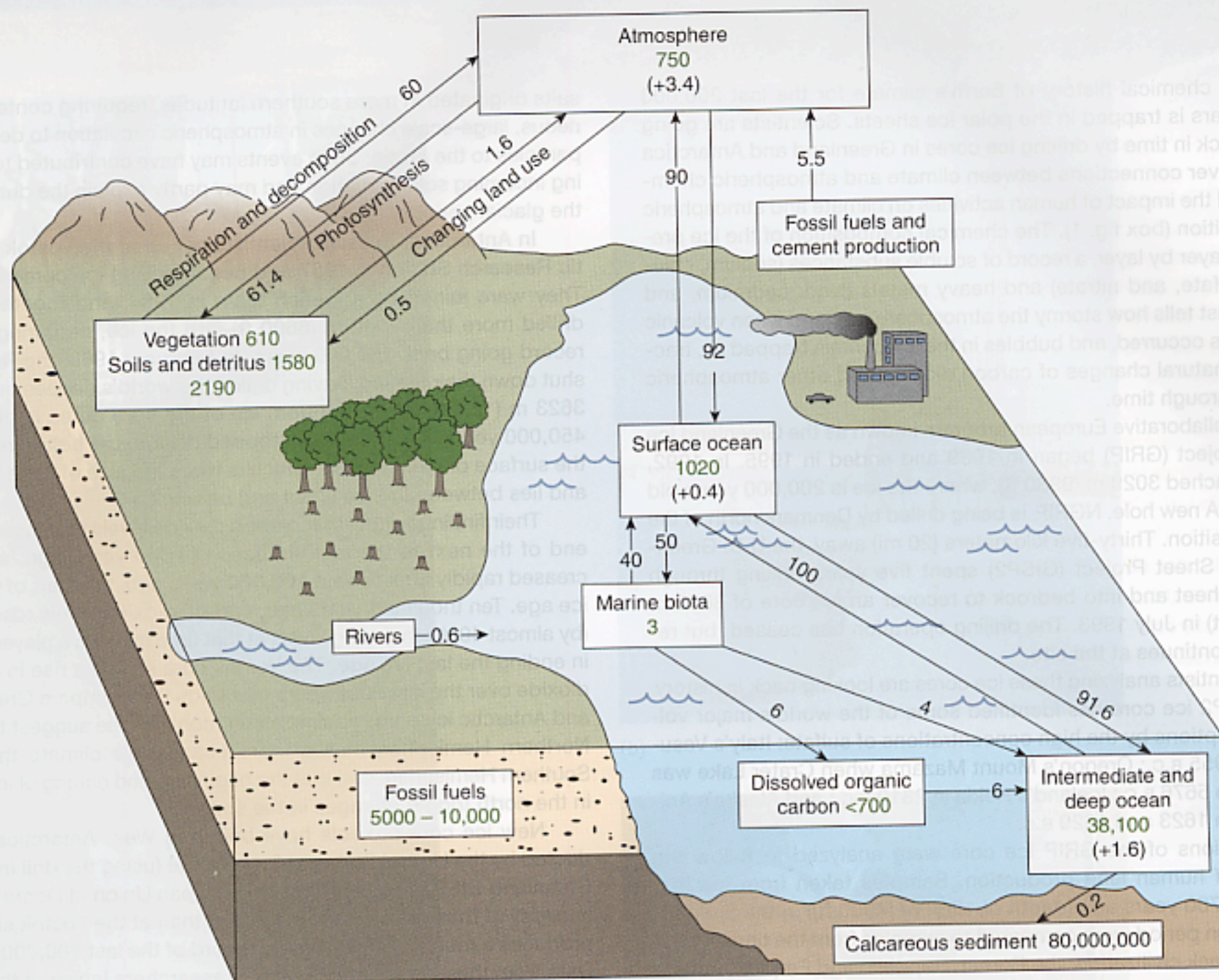


Figure 6.6 Major carbon dioxide pathways through Earth's environment. All numbers are given in billions of metric tons (1 metric ton = 10^6 g, 1 billion metric tons = 10^{15} g) of carbon. Numbers in *black* are rates of exchange per year between reservoirs. Numbers in *green* are total amounts stored in reservoirs. Numbers in *parentheses* are net annual changes in the total amount stored.

This process is often called the **biological pump**. Phytoplankton (see chapter 15) are responsible for about 40% of Earth's total production of organic material by photosynthesis. These organisms inhabit the shallow surface water, where sufficient sunlight is available for photosynthesis (see sections 5.8 and 15.2). About 90% of the phytoplankton organic matter is recycled in the euphotic zone as a result of consumption and respiration. Most of the remaining 10% (between 70% and 90%) is recycled before it reaches the sea floor, where the remainder is consumed by bottom-dwelling animals, decomposed by bacteria, or preserved in the sediment. This biochemical pump works along with the chemical solubility pump discussed previously to concentrate carbon in the deep ocean. The storage of CO_2 in Earth's reservoirs and the effect of increased production of CO_2 by the burning of fossil fuels are discussed further in chapter 7.

The Oxygen Balance

The oceans also play a large role in regulating the oxygen balance in Earth's atmosphere. Photosynthesis in the oceans releases oxygen, which is consumed by respiration and decay processes in

the same way as on land. However, some organic matter is incorporated into the seafloor sediments, preventing decay and decomposition. Therefore, oxygen is not consumed to balance the oxygen produced in photosynthesis, and 300 million metric tons of excess oxygen are produced each year. This excess amount of oxygen is not released into the atmosphere because the marine sediments are formed into rocks by Earth's geologic processes. Some of these rocks are uplifted onto land, and oxygen is eventually consumed in the weathering and oxidation of the materials in the rocks. This process balances the atmosphere's oxygen budget. The mechanisms that link and control the process are not well understood.

Measuring the Gases

The amount of dissolved oxygen in seawater samples can be measured by traditional chemical techniques in the laboratory. It is also possible to directly measure oxygen in the oceans by using specialized probes that send an electronic signal back to the ship or store the information in the testing unit. The concentration of dissolved carbon dioxide in seawater is very small. Nearly all of

Messages in Polar Ice

The chemical history of Earth's climate for the last 200,000 years is trapped in the polar ice sheets. Scientists are going back in time by drilling ice cores in Greenland and Antarctica to discover connections between climate and atmospheric chemistry and the impact of human activities on climate and atmospheric composition (box fig. 1). The chemical composition of the ice preserves, layer by layer, a record of soluble substances (sodium, chloride, sulfate, and nitrate) and heavy metals (lead, cadmium, and zinc). Dust tells how stormy the atmosphere was and when volcanic eruptions occurred, and bubbles in the ice contain trapped air, tracing the natural changes of carbon dioxide and other atmospheric gases through time.

A collaborative European program known as the Greenland Ice Core Project (GRIP) began in 1989 and ended in 1995. In 1992, GRIP reached 3029 m (9930 ft), where the ice is 200,000 years old or more. A new hole, NGRIP, is being drilled by Denmark north of the GRIP position. Thirty-five kilometers (20 mi) away, the U.S. Greenland Ice Sheet Project (GISP2) spent five years drilling through the ice sheet and into bedrock to recover an ice core of 3053 m (10,014 ft) in July 1993. The drilling operation has ceased, but research continues at the site.

Scientists analyzing these ice cores are looking back in history. The GISP2 ice core has identified some of the world's major volcanic eruptions by the high concentrations of sulfate: Italy's Vesuvius in 6955 B.C.; Oregon's Mount Mazama when Crater Lake was formed in 5676 B.C.; Iceland's Hekla in 2310 B.C.; and Alaska's Aniakchak in 1623 and 1629 B.C.

Sections of the GRIP ice core were analyzed to follow the history of human lead production. Samples taken from ice that formed 7760 years ago (depth of 1286 m [4000 ft]) in the prelead-production period were compared to samples from the times of the rise of Greek civilization, the Roman Republic and Empire, and the Medieval and Renaissance periods. Large-scale pollution from lead smelters during those periods contaminated even the Arctic, leaving the oldest documented record of human pollution.

Comparison of ice layers deposited before and after the Industrial Revolution shows that the concentration of sulfate from sulfuric acid tripled and that the concentration of nitrate from nitric acid doubled during the twentieth century. Lead continued to be a significant contaminant and increased dramatically as a byproduct of leaded-fuel combustion tied to the world's increased dependence on gasoline.

These ice cores tell us that climate changes have occurred more rapidly and more frequently than scientists had thought. Climate changes are recorded in the ice every few thousand years until the end of the last ice age, about 15,000 years ago. The climate warmed for the next 2000 years until a short period when Greenland temperatures decreased by 7°C, followed by very rapid warming, possibly over a period as short as three years, to the present interglacial stage that Earth enjoys today. These rapid, recent shifts in climate are thought to have been coupled with large shifts in the circulation of both the oceans and the atmosphere.

GISP2 core samples show massive changes in the quantities of dust and sea salt from aerosols that occur with the onset of glacial periods. When the ocean ice cover expanded, the dusts and

salts originated in more southern latitudes, requiring contemporaneous, large-scale changes in atmospheric circulation to deliver the particles to the Arctic. Such events may have contributed to blocking incoming solar radiation and may partly explain the duration of the glacial periods.

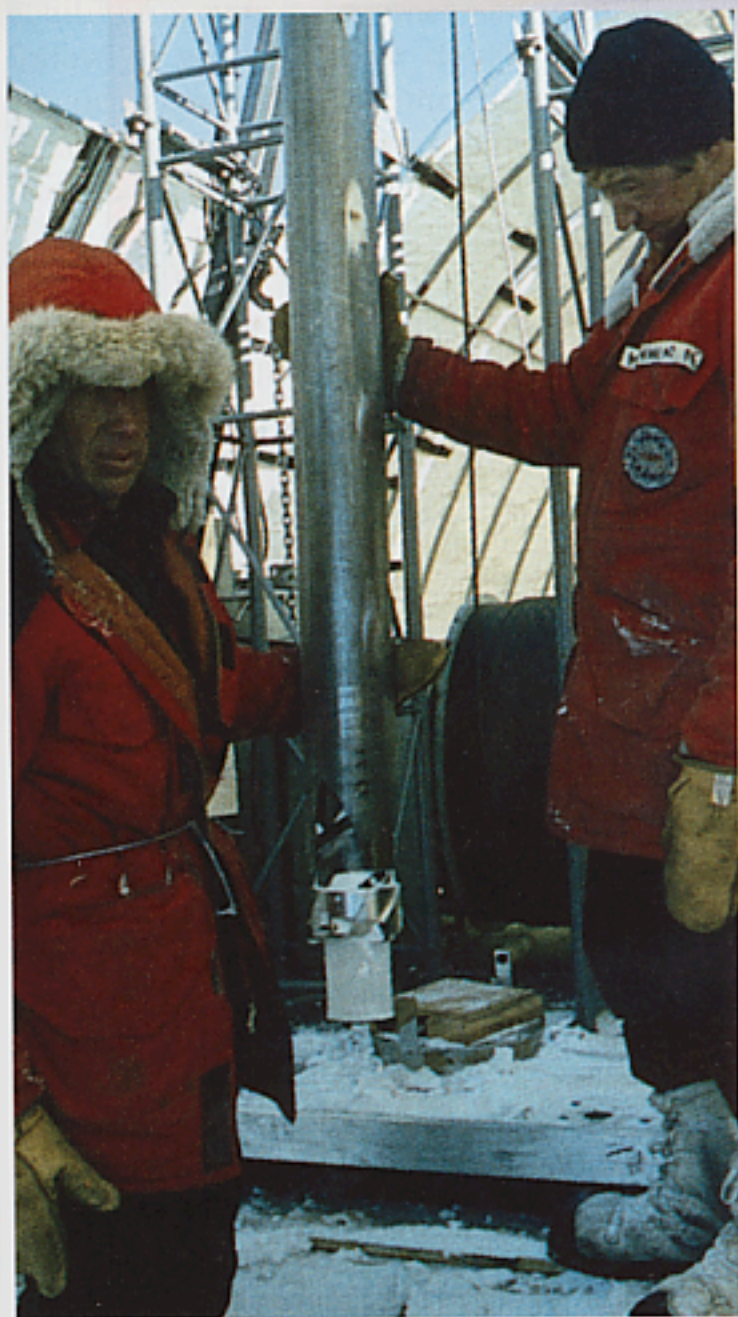
In Antarctica, Russian scientists set up at the Vostok Antarctic Research Station in 1957 and began drilling ice cores in 1972. They were joined by a French team in 1984, and together, they drilled more than 2000 m (6600 ft) into the ice, capturing an ice record going back 160,000 years. In February 1998, the Russians shut down their station, having drilled the world's deepest ice core, 3623 m (12,000 ft). The bottom ice of the core dates back about 450,000 years. The Russians stopped drilling just before reaching the surface of Lake Vostok, which is twice the size of Lake Ontario and lies between the ice sheet and bedrock.

Their findings show that carbon dioxide levels increased at the end of the next to the last ice age, 140,000 years ago, and decreased rapidly again about 100,000 years ago, the start of the last ice age. Ten thousand years ago, carbon dioxide levels rose again (by almost 40%); the rising levels at that time may have played a role in ending the last ice age. The Vostok core shows a rise in carbon dioxide over the last 2000 years. Methods that compare Greenland and Antarctic ice cores against a common timeline suggest that the Northern Hemisphere has a more changeable climate than the Southern Hemisphere and that the beginning and ending of ice ages in the north trigger changes in the south.

New ice core projects have begun in West Antarctica, conducted by the United States at Siple Dome (using the drill from the Greenland GISP2 hole) and by the European Union at Dome C. The snowfall at these sites is much heavier than at the Vostok site and produces a more detailed climate record of the last 100,000 years. Data from these new cores will help researchers interpret the Vostok data.

To Learn More About Messages in Polar Ice

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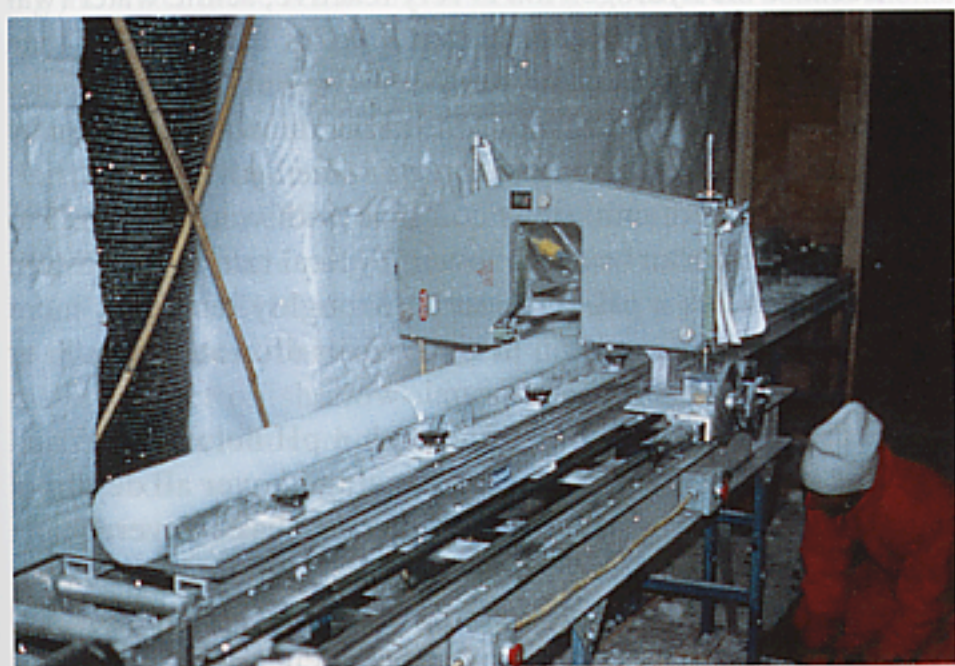
(a)



(b)



(d)



(c)

Box Figure 1 (a) Scott-Amundsen Base, 90°S, November–December 1982. Cores 10 cm (4 in) in diameter were drilled to 227 m (745 ft) with a mechanical drill. The ice at the bottom of the core is approximately 2200 years old. (b) Greenland Ice Sheet Project 2 (GISP2) drilling station, summer 1990. The tunnel houses laboratories and leads to the drilling site. The boxes at the tunnel entrance hold core sections ready for shipment to cold storage at the scientists' home laboratories. (c) A lengthwise slab is removed from a core section for analysis in the tunnel lab. (d) GISP2, July 1989. The layering of this ice core was inspected and photographed before it was analyzed for gas and particle content, chemistry, and conductivity. The core was 13 cm (5 in) in diameter.

the carbon dioxide in seawater reacts with water to form carbonic acid and its dissociation products (see section 6.3). Consequently, carbon dioxide concentrations can either be measured directly or determined by measuring the pH of the water.

6.3 The pH of Seawater

The water molecule, H_2O , can dissociate (break apart) to form a hydrogen cation, H^+ , and a hydroxide anion, OH^- . Consequently, in any water solution, there will always be a combination of H_2O molecules, H^+ ions, and OH^- ions. The concentration of H_2O molecules always greatly exceeds the concentrations of the two ions. In a pure water solution (one in which there is only water molecules) at $25^\circ C$, a very small fraction of the water molecules, about 10^{-7} , will spontaneously dissociate into H^+ and OH^- ions. In other words, the concentration of both H^+ and OH^- ions will be 10^{-7} , as one in every 10 million (10^7) water molecules breaks apart. Solutions in which the concentrations of these two ions are equal are called neutral solutions.

In solutions that are not pure water, chemical reactions can remove or release hydrogen ions, making the concentrations of H^+ and OH^- unequal. The concentrations of H^+ and OH^- in a water solution are inversely proportional to each other. In other words, a tenfold increase in the concentration of one ion results in a tenfold decrease in the concentration of the other. An imbalance in the relative concentrations of these ions results in either an acidic solution (if there are more H^+ cations than OH^- anions) or an alkaline, also called basic, solution (if there are more OH^- anions than H^+ cations).

The acidity or alkalinity of a solution is measured using the **pH** scale, which ranges from a low of 0 to high of 14 (fig. 6.7). The pH scale is a logarithmic scale that measures the concentration of the hydrogen ion (written $[H^+]$) in a solution. The formal definition of pH is:

$$pH = -\log_{10}[H^+]$$

In pure water, where the concentrations of H^+ and OH^- are both 10^{-7} , the pH is equal to 7,

$$pH = -\log_{10}[10^{-7}] = -(-7) = 7,$$

and the solution is neutral. If the concentration of the hydrogen ion is increased by a factor of ten to 10^{-6} , or one part in 1 million instead of one part in 10 million, the pH drops to 6 and the solution is slightly acidic. Solutions with pH less than 7 (high H^+ concentrations) are acidic and those with pH greater than 7 (low H^+ concentrations) are alkaline, or basic.

Solutions with lower pH are more acidic than solutions with higher pH. For example, the following statements are all equivalent:

$$pH = 1 \text{ is more acidic than } pH = 3, \text{ or}$$

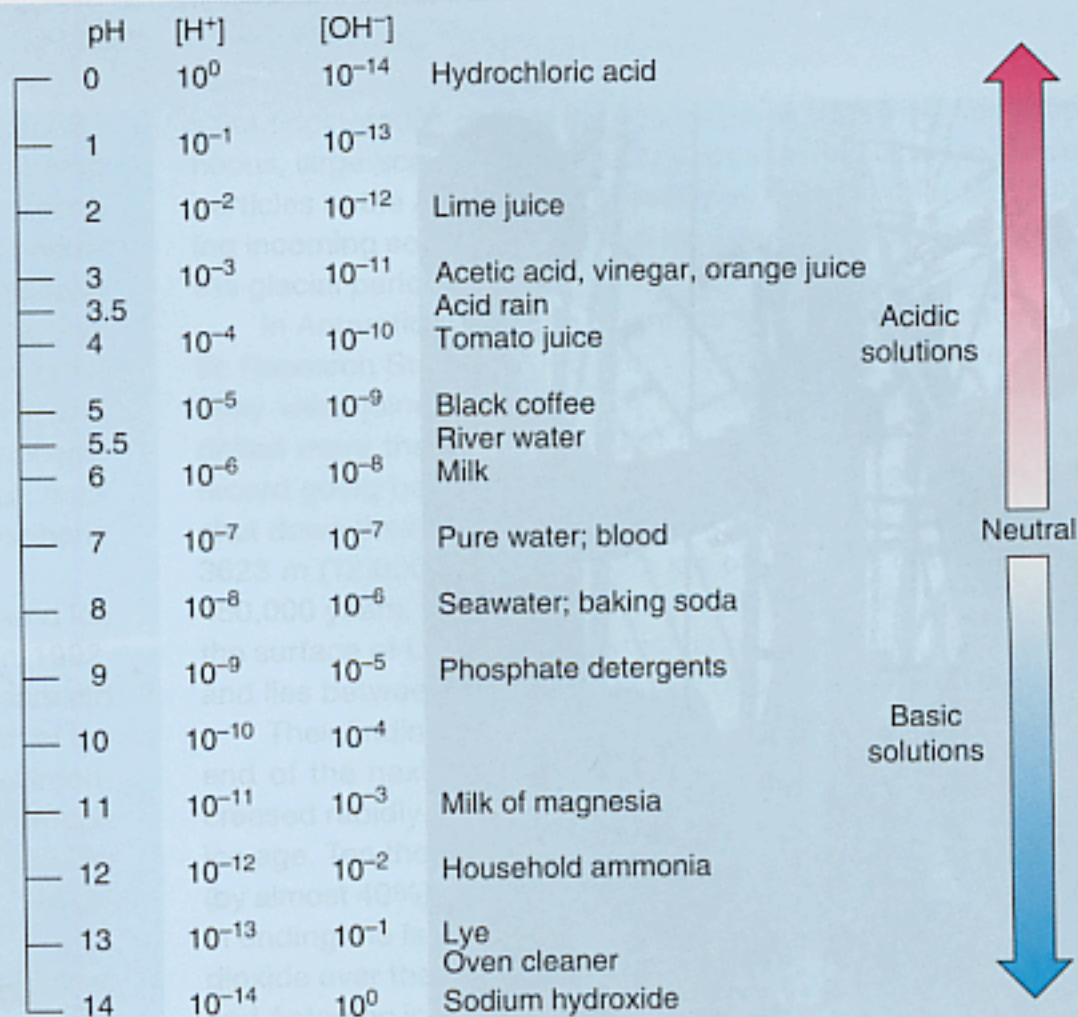


Figure 6.7 The pH scale is a measure of the concentration of hydrogen ions in a solution. A neutral solution has a pH of 7. Acidic solutions have a pH less than 7, and alkaline, or basic, solutions have a pH greater than 7.

$[H^+] = 10^{-1}$ is more acidic than $[H^+] = 10^{-3}$, or

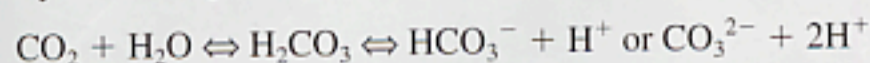
$[H^+] = 0.1$ is more acidic than $[H^+] = 0.001$

Similarly, solutions with higher pH are more alkaline than solutions with lower pH.

Because the hydrogen ion is very reactive, acidic water (water with a relatively high concentration of H^+ and pH less than 7) is an effective chemical weathering agent capable of decomposing and dissolving rock. The pH of rainwater is normally about 5.0–5.6 (slightly acidic), but in some heavily industrialized regions where emissions combine with water droplets to form acid rain, it can be much lower. Typical rain in the eastern United States has a pH of about 4.3, roughly ten times more acidic than normal, and can in some cases drop as low as 3, or 100 times more acidic than normal.

Seawater is slightly alkaline with a pH between 7.5 and 8.5. The pH of the world's oceans averaged over all depths is approximately 7.8. Surface water currently has an average pH of about 8.2. The pH of seawater remains relatively constant because of the buffering action of carbon dioxide in the water. A **buffer** is a substance that prevents sudden, or large, changes in the acidity or alkalinity of a solution. If some process changes the concentration of hydrogen ions in seawater, causing the pH to rise above or fall below its average, or mean value, the buffer becomes involved in chemical reactions that release or capture hydrogen ions, returning the pH to normal. When carbon dioxide dissolves in seawater, the CO_2 combines with the water to form carbonic acid (H_2CO_3). The carbonic acid rapidly dissociates into bicarbonate (HCO_3^-) and a

hydrogen ion (H^+), or carbonate (CO_3^{2-}) and two hydrogen ions ($2 H^+$). The CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-} exist in equilibrium with each other and with H^+ , as shown in the following equation. The double arrows indicate that the reactions can move in either direction, either producing or removing hydrogen ions as is necessary to maintain a relatively constant pH.



If seawater becomes too alkaline, or basic, then the reactions in this equation progress to the right, releasing hydrogen ions and decreasing the pH. If seawater becomes too acidic, then the reactions progress to the left, removing free hydrogen ions from the water and increasing the pH. This buffering capacity of carbon dioxide in seawater is important to organisms requiring a relatively constant pH for their life processes and to the chemistry of seawater, which is controlled, in part, by its pH.

From the reactions described, it is clear that the pH of seawater strongly depends on the concentration of CO_2 in the water. The higher the concentration of CO_2 in the water, the lower its pH and the more acidic it becomes. While the average pH of seawater tends to be fairly constant, it does vary with changes in the concentration of CO_2 in the water, as discussed in section 6.2.

Because the pH of seawater is inversely proportional to the concentration of CO_2 , the pH of the surface water tends to be slightly higher (about 8.2 on average), or more alkaline, than average (refer back to fig. 6.5). The pH at the ocean surface may be as high as 8.5 if the water is warm and if the rate of primary production, or photosynthesis, is high. Raising the pH of the water releases carbonate ions, CO_3^{2-} , that bond with the abundant Ca^{2+} in solution to form calcium carbonate $CaCO_3$. In cold, deep water, where the concentration of CO_2 is high, the pH drops, making the water more acidic and dissolving calcium carbonate shells.

The increase in CO_2 in the atmosphere has resulted in a corresponding increase in the concentration of the gas in the oceans as CO_2 is absorbed by seawater. The increasing concentration of CO_2 in the water is producing a decrease in the pH of the water, an effect that is referred to as "ocean acidification." The average pH of the oceans is predicted to fall by up to 0.5 units by 2100 if global emissions of CO_2 continue to rise at present rates. This increase in ocean acidity could have a major impact on shallow-water marine organisms that build shells of calcium carbonate, which could dissolve rapidly in more acidic water.

The most important sources of CO_2 in seawater are direct transfer of the gas from the atmosphere, the respiration of marine organisms, and the oxidation of organic matter.

6.4 Other Substances

Nutrients

Ions required for plant or phytoplankton growth are known as nutrients; these are the fertilizers of the oceans. As on land, phytoplankton require nitrogen and phosphorus in the form of nitrate (NO_3^-) and phosphate (PO_4^{3-}) ions. A third nutrient

Table 6.6 Nutrients in Seawater

Element	Concentration $\mu\text{g}/\text{kg}^1$	Relative Molar Abundance
Nitrogen (N)	500	16
Phosphorus (P)	70	1
Silicon (Si)	3000	40

1. Parts per billion.

required in the oceans is the silicate ion (SiO_4^{4-}), which is needed to form silica (SiO_2), the hard outer wall of the single-celled diatoms and the skeletal parts of some protozoans. These three nutrients are among the dissolved substances brought to the sea by the rivers and land runoff. Despite their importance, they are present in very low concentrations (table 6.6).

The concentrations of nutrient ions vary because some of these ions are closely related to the life cycles of organisms. The relative molar abundance of carbon, nitrogen, and phosphorus in marine phytoplankton is C:N:P = 106:16:1. This relationship is called the **Redfield Ratio**. Analysis of the composition of siliceous marine organisms makes it possible to calculate a Redfield Ratio for silicon as well: C:Si:N:P = 106:40:16:1. The consumption, decomposition, and recycling of organic matter as it sinks through the water column result in an increase in carbon:nutrient ratios as nutrients are released to the water. Nutrients are removed from the water as the plant populations grow and reproduce, temporarily reducing the amounts in solution. Later, when the populations decline, death and decay return the ions to the seawater. Nutrients are cycled to different consumers as zooplankton feed on phytoplankton. The zooplankton are in turn eaten by other consumers, and eventually the nutrients are returned to the oceans by death and bacterial decomposition. Excretory products from zooplankton and larger animals are also added to the seawater, broken down, and used by a new generation of zooplankton and phytoplankton. Nutrients are non-conservative; they do not maintain constant ratios in the way most major salt ions do. The cyclic nutrient pathways for nitrogen and phosphorus are discussed in chapter 15.

Organics

A wide variety of organic substances are present in seawater. Proteins, carbohydrates, lipids (or fats), vitamins, hormones, and their breakdown products are all present. Some are eventually oxidized or broken down into smaller molecules; others are used directly by organisms and are incorporated into their systems. Another portion of the organic matter accumulates in the sediments, where over geologic time it may slowly provide hydrocarbon molecules to form deposits of oil and gas. In the areas of the ocean that are high in plant and animal life, the surface layer may take on a green-yellow color owing to the presence of organic decay products. The incorporation of soluble organics into glacial ice at the Antarctic ice shelves is related to the formation of green ice.

6.5 Practical Considerations: Salt and Water

Chemical Resources

About 30% of the world's table salt is extracted from seawater. The industrially produced energy required to remove the water is kept to a minimum to keep extraction costs low. In warm, dry climates, seawater is allowed to flow into shallow ponds and evaporate down to a concentrated brine solution. More seawater is added, and the process is repeated several times, until a dense brine is produced. Evaporation continues until a thick, white salt deposit is left on the bottom of the pond. Several different salts are in the deposit. These salts form in the order listed in table 6.7. The salt deposit is collected and refined to separate out sodium chloride (halite), or table salt. This technique is used in southern France, Puerto Rico, and California (fig. 6.8).

In cold climate areas, salt has been recovered by freezing the seawater in similar ponds. The ice that forms is nearly fresh; the salts are concentrated in the brine beneath the ice. The brine is removed and heated to remove the last of the water.

Of the world's supply of magnesium, 60% comes from the sea, and so does 70% of the bromine. There are vast amounts of dissolved constituents in the world's seawater, including 10 million tons of gold and 4 billion tons of uranium, but the concentration is very low (one part per billion or less). In the case of gold, no method has been devised in which the cost of extraction does not exceed the value of the recovered element. At one time or another, Japan, Germany, and the United States have expressed an interest in extracting uranium. Japan set up a land-based test plant in 1986 to produce 10 kg (26 lb) of uranium from seawater each year, but the operation proved to be too expensive.

Desalination

Desalination is the process of obtaining fresh water from salt water. There are three main desalination methods:

1. processes involving a change of state of the water—liquid to solid or liquid to vapor;
2. processes requiring ion exchange columns; and
3. processes using a semipermeable membrane—electrodialysis and reverse osmosis.

Table 6.7 Sequence of Salts Formed from Evaporation of Seawater

Order of Precipitation	Solid	% of Total Solid
1	$\text{CaCO}_3 + \text{MgCO}_3$	1
2	CaSO_4 (gypsum)	3
3	NaCl (halite)	70
4	Na-Mg-K-SO_4 and KCl , MgCl_2	26



Figure 6.8 The southern end of San Francisco Bay was diked into shallow ponds, where seawater is evaporated to obtain salt. Most of these ponds are being converted back to “natural” conditions.

The simplest process involving a change of state is a solar still (fig. 6.9). In this process, a pond of seawater is capped by a low plastic dome. Solar radiation penetrates the dome and evaporates the seawater. The evaporated water condenses on the undersurface of the dome and trickles down to be caught in a trough, where it accumulates and flows to a freshwater reservoir. The rate of production is slow, and a very large system is needed to supply the water requirements of even a small community.

When water is distilled by boiling, evaporation proceeds at a rapid rate and large quantities of fresh water are produced, but the energy requirement is high. If water is introduced to a chamber with a reduced air pressure, the boiling occurs at a much lower temperature and therefore uses less energy. Change of state by freezing can also be used to recover fresh water from seawater. The energy requirement is approximately one-sixth of that needed for evaporation, but the mechanical separation of the freshwater ice from the salt brine remains difficult.

Columns containing ion exchange resins that extract ions from salt water work well with water of low salinity, but the resins need to be replaced periodically (fig. 6.10b). Small ion exchange units are manufactured for household use to improve drinking water quality.

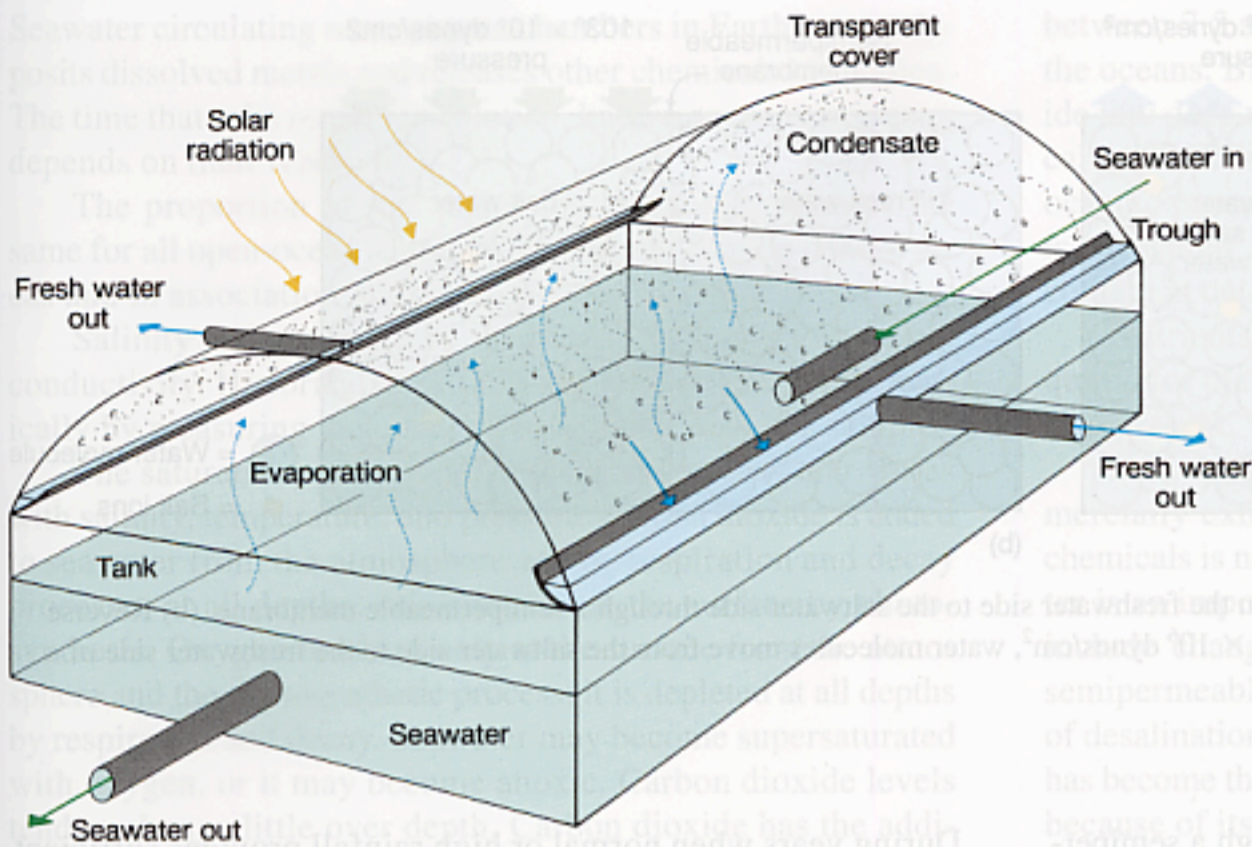


Figure 6.9 Solar energy is used to evaporate fresh water from seawater. Solar radiation penetrates the transparent cover over the seawater contained in the tank.

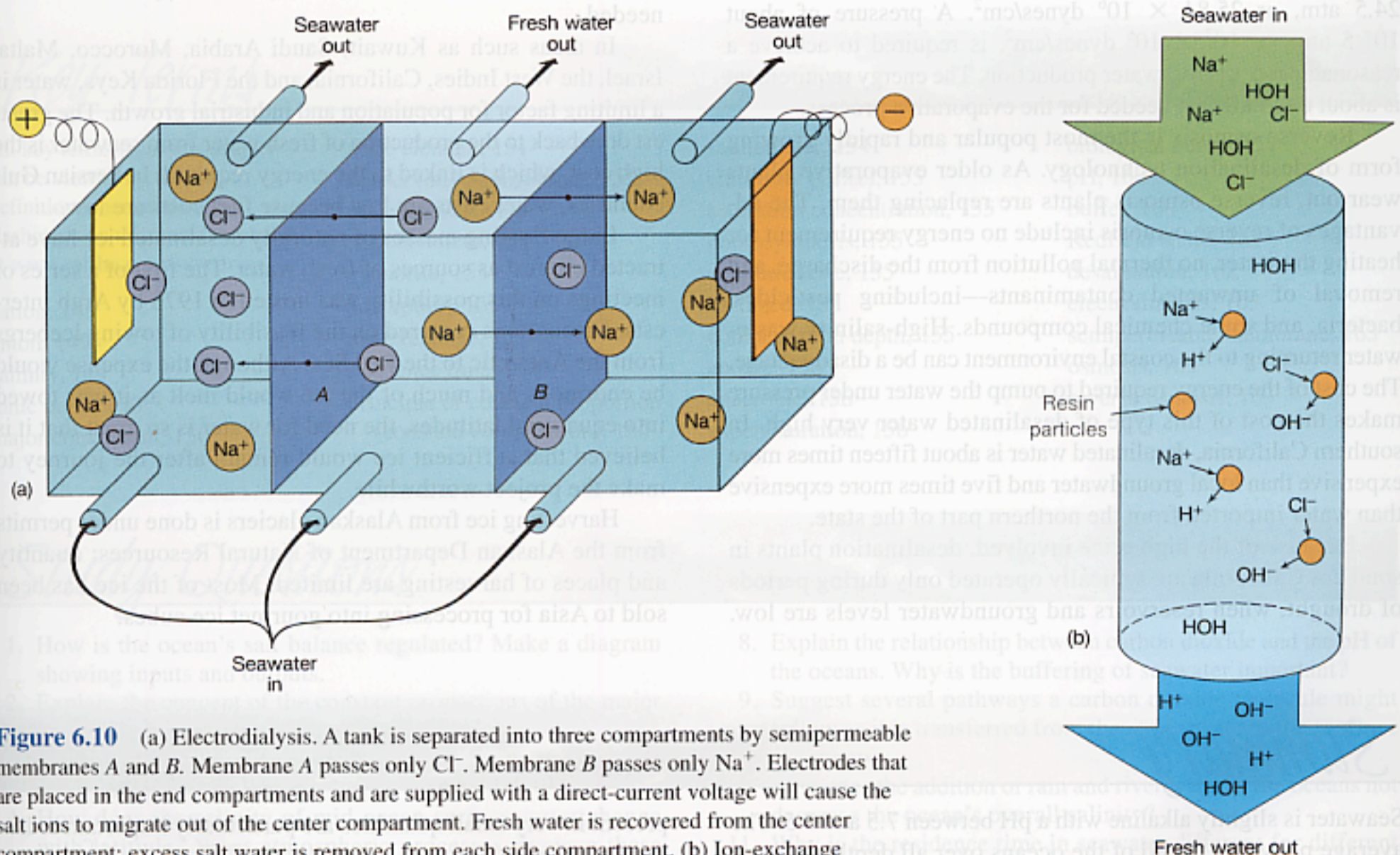


Figure 6.10 (a) Electrodes. A tank is separated into three compartments by semipermeable membranes A and B. Membrane A passes only Cl^- . Membrane B passes only Na^+ . Electrodes that are placed in the end compartments and are supplied with a direct-current voltage will cause the salt ions to migrate out of the center compartment. Fresh water is recovered from the center compartment; excess salt water is removed from each side compartment. (b) Ion-exchange column. Seawater passes through a column of resin particles that exchange H^+ for Na^+ and Cl^- for OH^- to produce HOH , or fresh water (H_2O).

Electrodialysis uses an electrical field to transport ions out of solution and through **semipermeable membranes**; this technique also works best in low-salinity (or brackish) water (fig. 6.10a).

Osmosis is the movement of water across a semipermeable membrane; the water moves from the side with the higher con-

centration of water molecules (or low salinity) to the side with the lower concentration of water molecules (or high salinity); this movement creates a higher pressure on the low-water concentration (or high-salinity) side of the membrane (fig. 6.11a). **Reverse osmosis** produces fresh water from seawater by applying pressure

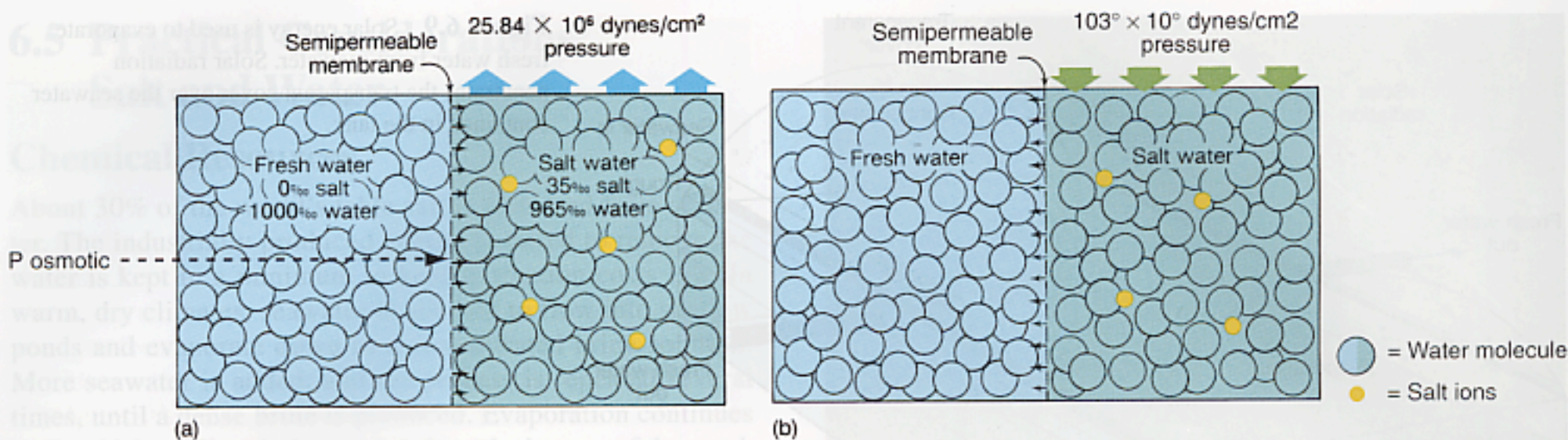


Figure 6.11 (a) Osmosis. Water molecules move from the freshwater side to the saltwater side through a semipermeable membrane. (b) Reverse osmosis. When pressure on the salt water exceeds 25.84×10^6 dynes/cm², water molecules move from the saltwater side to the freshwater side of a semipermeable membrane.

to seawater and forcing the water molecules through a semipermeable membrane, leaving behind the salt ions and other impurities (fig. 6.11b). The pressure applied to the seawater must exceed 24.5 atm, or 25.84×10^6 dynes/cm². A pressure of about 101.5 atm, or $10^3 \times 10^6$ dynes/cm², is required to achieve a reasonable rate of freshwater production. The energy requirement is about one-half that needed for the evaporative process.

Reverse osmosis is the most popular and rapidly growing form of desalination technology. As older evaporative plants wear out, reverse osmosis plants are replacing them. The advantages of reverse osmosis include no energy requirement for heating the water, no thermal pollution from the discharge, and removal of unwanted contaminants—including pesticides, bacteria, and some chemical compounds. High-salinity wastewater returning to the coastal environment can be a disadvantage. The cost of the energy required to pump the water under pressure makes the cost of this type of desalinated water very high. In southern California, desalinated water is about fifteen times more expensive than local groundwater and five times more expensive than water imported from the northern part of the state.

Because of the high price involved, desalination plants in southern California are typically operated only during periods of drought, when reservoirs and groundwater levels are low.

During years when normal or high rainfall provides sufficient fresh water, the plants are shut down and only maintenance-level work is done to ensure that they will be operational when needed.

In areas such as Kuwait, Saudi Arabia, Morocco, Malta, Israel, the West Indies, California, and the Florida Keys, water is a limiting factor for population and industrial growth. The greatest drawback to the production of fresh water from seawater is the high cost, which is linked to the energy required. In Persian Gulf countries, water costs are low because fuel costs are low.

Large floating masses of naturally desalinated ice have attracted interest as sources of fresh water. The first of a series of meetings on this possibility was hosted in 1978 by Arab interests. Discussions centered on the feasibility of towing icebergs from the Antarctic to the Red Sea. Although the expense would be enormous and much of the ice would melt as it was towed into equatorial latitudes, the need for water is so great that it is believed that sufficient ice would remain after the journey to make the project worthwhile.

Harvesting ice from Alaskan glaciers is done under permits from the Alaskan Department of Natural Resources; quantity and places of harvesting are limited. Most of the ice has been sold to Asia for processing into gourmet ice cubes.

Summary

Seawater is slightly alkaline with a pH between 7.5 and 8.5. The average pH value for all of the oceans over all depths is about 7.8. Seawater pH remains fairly constant because of the buffering action of carbon dioxide in the water.

The average salinity of ocean water is 35‰. The salinity of the surface water changes with latitude and is affected by evaporation, precipitation, and the freezing and thawing of sea ice. Soluble salts are present as ions in seawater. Positive ions are cations; negative ions are anions. Six major constituent ions make up 99% of the salt in seawater. Trace elements that are

present in very small quantities are particularly important to living organisms.

Most of the positively charged ions come from the weathering and erosion of Earth's crust and are added to the sea by rivers. Gases from volcanic eruptions are dissolved in river water as anions. Because the average salinity of the oceans remains constant, the salt gain must be balanced by the removal of salt; input must equal output. Salts are removed as sea spray, evaporites, and insoluble precipitates, as well as by biological reactions, adsorption, chemical reactions, and uplift processes.

Seawater circulating near magma chambers in Earth's crust deposits dissolved metals and releases other chemicals in solution. The time that salts remain in solution, known as residence time, depends on their reactivity.

The proportion of one major ion to another remains the same for all open-ocean salinities. Ratios may vary in coastal areas and in association with biological processes.

Salinity is determined by measuring a sample's electrical conductivity. Historically, salinity has been determined chemically by measuring the quantity of chloride ions in a sample.

The saturation value of gases dissolved in seawater varies with salinity, temperature, and pressure. Carbon dioxide is added to seawater from the atmosphere and by respiration and decay processes at all depths; it is removed at the surface by photosynthesis. Oxygen is added only at the surface from the atmosphere and the photosynthetic process; it is depleted at all depths by respiration and decay. Seawater may become supersaturated with oxygen, or it may become anoxic. Carbon dioxide levels tend to change little over depth. Carbon dioxide has the additional role of buffer in keeping the pH range of ocean water

between 7.5 and 8.5. Large quantities of CO_2 are absorbed by the oceans. Biological processes pump carbon as carbon dioxide into deep water, where it is fixed in the marine sediments as calcium carbonate. Atmospheric oxygen is regulated by oceanic processes. The amount of oxygen present in seawater is measured chemically and electronically. Carbon dioxide content is determined from the pH of the water.

Nutrients include the nitrates, phosphates, and silicates required for plant growth. A wide variety of organic products are also present.

Salt, magnesium, and bromine are currently being commercially extracted from seawater. Direct extraction of other chemicals is neither economic nor practical at present. Fresh water is an important product of seawater. Desalination methods include change-of-state processes, movement of ions across semipermeable membranes, and ion exchange. The practicality of desalination is determined by cost and need. Reverse osmosis has become the most popular option; it is nonpolluting but costly because of its energy requirements.

Chapter

Key Terms

All key terms from this chapter can be viewed by term or definition when studied as flashcards on this book's website at www.mhhe.com/sverdrup10e.

cation, 149

anion, 149

salinity, 149

ionic bond, 150

major constituent, 150

trace element, 151

conservative constituent, 151

nonconservative constituent, 151

evaporite, 153

adsorption, 153

ion exchange, 153

residence time, 154

principle of constant proportion (constant composition), 154

salinometer, 154

chlorinity ($\text{Cl}\%$), 155

saturation concentration, 155

photosynthesis, 155

euphotic zone, 155

oxidized, 155

compensation depth, 155

anoxic, 156

anaerobic, 156

supersaturation, 156

biological pump, 157

pH, 160

buffer, 160

Redfield Ratio, 161

desalination, 162

electrodialysis, 163

semipermeable membrane, 163

osmosis, 163

reverse osmosis, 163

Study Questions

- How is the ocean's salt balance regulated? Make a diagram showing inputs and outputs.
- Explain the concept of the constant proportions of the major ions in seawater.
- What is the least expensive method of desalination? Where is it most likely to be used?
- How does the salinity of mid-ocean surface water change with latitude? What atmospheric processes produce these changes?
- List the sources of the salts found in seawater. How is their input regulated?
- Silicate is a nonconservative constituent of seawater and does not obey the principle of constant proportions. Explain why.
- Compare the distributions of oxygen and carbon dioxide to depth in seawater. What processes are responsible for the distribution of each gas?
- Explain the relationship between carbon dioxide and the pH of the oceans. Why is the buffering of seawater important?
- Suggest several pathways a carbon dioxide molecule might follow as it is transferred from the atmosphere to the seafloor sediments.
- Why does the addition of rain and river water to the oceans not decrease the ocean's overall salinity?
- Why is the residence time in seawater different for different salts?
- Explain reverse osmosis and how it produces fresh water from seawater.
- What is the significance of the compensation depth to photosynthetic organisms?
- Why does the concentration of dissolved substances in river water differ from the concentration of the same substances in seawater?
- Why are nutrients considered to be nonconservative materials?