CHAPTER The Chemistry of Global Climate Change



This group of chimpanzees contributed minimally, or not at all, to global climate change and are not likely discussing the issue. However, they must adapt to the changes that will occur.

Unlike humans, chimpanzees, along with plants and other animals, don't argue with each other about whether climate is changing. They just attempt to adapt to the ever-changing world, which can affect their way of life including their access to food, water, and habitat. For example, as the climate changes, food availability shifts, thus forcing animals such as the chimpanzee to adapt in order to obtain enough calories to survive. The changes also affect their habitat, with variations due to differing weather patterns.

Like much of the planet, the salt water in the oceans has no voice, but it still responds to climate change and has a story to tell. In colder climates, it quietly freezes to form sea ice when temperatures drop. And perhaps more noisily, this ice breaks up with the return of warmer temperatures in the spring. This freeze-thaw cycle has been occurring for thousands of years, gradually shifting to form more or less ice as the temperatures on earth have shifted. In recent years, however, the freeze-thaw cycle has been more pronounced, and the waters in the Arctic have been free of ice for longer periods of time.

Might carbon dioxide be the culprit of changes witnessed in the Arctic? What about the shifts in plant and animal populations and habitats? No doubt you have heard about CO_2 in the news. As a greenhouse gas, carbon dioxide plays a role in keeping our planet comfortably warm and able to support life, but there can be too much of a good thing. Carbon dioxide isn't the only player, as we will see in this chapter. We also will talk about other gases, such as methane and water vapor, and how they contribute to the greenhouse effect.

What do you already know about CO₂? This next activity gives you an opportunity to assess your current knowledge.



As Consider This 3.1 pointed out, carbon dioxide is emitted by vehicles. As you'll see in this chapter and in the next, when hydrocarbons and other carbon-containing fuels burn, carbon dioxide is a product along with other air pollutants. No one argues about whether or not these gases are being emitted. Rather, they disagree about how much can be released without significant negative consequences to the Earth's climate or even if we should be concerned with these emissions.

In order to make an informed decision about emissions, we first need to examine the Earth's energy balance. We will do this by exploring how this balance can be altered, for example by investigating greenhouse gases and interpreting data collected from ice cores taken from the Earth's glaciers. We will also explain key chemistry concepts throughout this chapter such as energy balance, greenhouse gases and the greenhouse effect, molecular shape, molecular vibrations, the carbon cycle, atomic mass, moles, atmospheric gases, and aerosols to help you evaluate the effect of emissions on climate. The terms climate change and global warming are not the same but are closely related. We will use both in this chapter.

Chapter 3



Figure 3.1 Venus, as photographed by the Galileo spacecraft.

These and other types of electromagnetic radiation were introduced in Section 2.4.

In order to evaluate the effect of emissions on climate we cannot get ahead of ourselves. Ever wonder why Earth does not get too hot or too cold to sustain life? Let's find out as we begin thinking about climate change with a discussion of the energy balance of the Earth's atmosphere.

3.1 In the Greenhouse: Earth's Energy Balance

As we begin our journey into understanding **global climate change**, we need to understand first how the Earth is heated and cooled. The energy to heat the Earth comes mainly from the Sun. However, this is not the entire story. Based on the Earth's distance from the Sun and the amount of solar radiation the Sun emits, the average temperature on Earth should be -18 °C (0 °F), and the oceans should be frozen year round. Thankfully this is not true as Earth's average temperature is currently around 15 °C (59 °F).

Venus (Figure 3.1) is another planet whose temperature is inconsistent with its distance from the Sun. Considered by many to be the brightest and most beautiful body in the night sky, after our own moon, Venus has an average temperature of about 450 °C (840 °F). Based simply on its distance from the Sun, however, the average temperature on Venus would be 100 °C, the boiling point of water. What do Earth and Venus have in common that would explain these discrepancies? They both have an atmosphere. To see the role that our atmosphere plays, we now examine what happens when solar radiation reaches the Earth.

The energy processes that contribute to the Earth's energy balance appear in Figure 3.2. The Earth receives nearly all of its energy from the Sun (orange arrows), primarily in the form of ultraviolet, visible, and infrared radiation. Some of this incoming radiation is reflected back into space (blue arrows) by the dust and aerosol particles that are suspended in our atmosphere (25%). Other parts of this incoming radiation are reflected by the surface of the Earth itself, especially those regions white with snow or sea ice (6%). Thus, 31% of the radiation received from the Sun is reflected.

The remaining 69% of the radiation from the Sun is absorbed, either by the atmosphere (23%) or by the land masses and oceans (46%). We can account for all of the Sun's radiation by adding the reflected and absorbed radiation: 31% + 69% = 100%.

Your Turn 3.2 Light From the Sun

Consider these three types of radiant energy, all emitted by the Sun: infrared (IR), ultraviolet (UV), and visible.

- a. Arrange them in order of increasing wavelength.
- b. Arrange them in order of *increasing* energy.

Answer

```
a. ultraviolet, visible, infrared
```

In order to maintain Earth's energy balance, all of the radiation that is absorbed from the Sun must eventually go back into space. Figure 3.2 shows us that:

- 46% of the Sun's radiation is absorbed by the Earth
 - the Earth reemits all of the radiation it absorbs but at a longer wavelength (IR)
 part of what the Earth emits escapes into space (9%)
 - the remainder is absorbed by the atmosphere (37%)
- 54% of the Sun's radiation is absorbed by the atmosphere (23%), reflected from the atmosphere (25%), or reflected from the Earth's surface (6%)

The 60% of the radiation that is absorbed by the atmosphere, either directly from the Sun (23%) or from the Earth's surface (37%), eventually is emitted into space to complete the energy balance.

Again, the 46% of the Sun's radiation that is absorbed and eventually emitted by the Earth, 37% is absorbed in the atmosphere prior to its emission into space. This



Figure 3.2

The Earth's energy balance. Orange represents a mixture of wavelengths. Shorter wavelengths of radiation are shown in blue, longer ones in red. The values are given in percentages of the total incoming solar radiation.

Figures Alive! Visit Figures Alive! to learn more about the electromagnetic spectrum, Earth's energy balance, and the greenhouse effect.

process of absorption adds heat to the Earth's atmosphere because the radiation causes collisions between neighboring molecules, warming up the atmosphere. At any one time, 80% (or $37 \div 46 \times 100\%$) of Earth's emitted radiation will be absorbed in the atmosphere. As we hope you can see, the gases in Earth's atmosphere act like a greenhouse!

If you have ever parked a car with its windows closed on a sunny day, you probably have experienced firsthand how a greenhouse can trap heat. The car, with its glass windows, operates much the same way as does a greenhouse for growing plants. The glass windows transmit visible and a small amount of UV light from the Sun. This energy is absorbed by the car's interior, particularly by any dark surfaces. Some of this radiant energy is then reemitted as longer wavelength IR radiation (heat). Unlike visible light, infrared light is not easily transmitted through the glass windows and so becomes "trapped" inside the car. When you reenter the vehicle, a blast of hot air greets you. The temperature inside of a car can exceed 49 °C (120 °F) in the summer in certain climates! Although the physical barrier of the windows is not an exact analogy to the Earth's atmosphere, the effect of warming the car's interior is similar to the warming of the Earth.

The **greenhouse effect** is the natural process by which atmospheric gases trap a major portion (about 80%) of the infrared radiation radiated by the Earth. Again, Earth's average annual temperature of 15 °C (59 °F) is a result of the heat trapping gases in our atmosphere. The atmosphere of Venus acts in a similar manner, however it traps even more heat. This is because it is made up of nearly 96% carbon dioxide, which, as we will see, is a far greater concentration than in the Earth's atmosphere.



Refer to Figure 3.2 to answer these questions.

- a. Incoming solar radiation (100%) is either absorbed or reflected. Outgoing radiation from the Earth into space also can be accounted for (100%), as required for energy balance. Show how.
- **b.** What percent of the outgoing radiation is absorbed in the Earth's atmosphere? Calculate this by adding the percentage of incoming solar radiation absorbed in the atmosphere to that absorbed in the atmosphere after being radiated from Earth's surface. How does this value compare with the percentage emitted from the atmosphere?
- c. Suggest reasons why the different colors were used for incoming and outgoing radiation.

Carbon dioxide, which is present in the atmospheres of both Earth and Venus, is a greenhouse gas. **Greenhouse gases** are those gases capable of absorbing and emitting infrared radiation, thereby warming the atmosphere. In addition to carbon dioxide, other examples include water vapor, methane, nitrous oxide, ozone, and chlorofluorocarbons. The presence of those gases is essential in keeping our planet at habitable temperatures. The ability of the atmosphere to trap heat was first hypothesized by the French mathematician Jean-Baptiste Joseph Fourier (1768–1830) around 1800, but it took another 60 years for scientists to identify the molecules that were responsible. Irish physicist John Tyndall (1820–1893) first demonstrated that both carbon dioxide and water vapor absorb infrared radiation. We will explain this process in Section 3.4.

In our energy balance discussion, we showed that 80% of the Earth's absorbed solar radiation is emitted into the atmosphere. The exchange of energy between the Earth, atmosphere, and space results in a steady state and a continuous average temperature of the Earth. However, the increase in concentration of greenhouse gases that is taking place today is changing the energy balance and causing increased warming of the planet. The term **enhanced greenhouse effect** refers to the process in which atmospheric gases trap and return *more than* 80% of the heat energy radiated by the Earth. An increase in the concentration of greenhouse gases will very likely mean that more than 80% of the radiated energy will be returned to Earth's surface, with an accompanying increase in average global temperature. The popular term **global warming** often is used to describe the increase in average global temperatures that results from an enhanced greenhouse effect.

Why is the amount of greenhouse gases in the atmosphere increasing? One explanation considers **anthropogenic** influences on the environment, which stem from human activities such as industry, transportation, mining, and agriculture. These activities require carbon-based fuels, which produce carbon dioxide when burned. In the late 19th century, Swedish scientist Svante Arrhenius (1859–1927) considered the problems that increased industrialization might cause by building up CO_2 in the atmosphere. He calculated that doubling the concentration of CO_2 would result in an increase of 5–6 °C in the average temperature of the planet's surface. How are we adding CO_2 to the atmosphere?

Water vapor is the most abundant greenhouse gas in our atmosphere. However, contributions of water vapor from human activity are negligible compared with those from natural sources.

Another steady-state process, the Chapman cycle, was discussed in Section 2.6.

Section 1.9 described the chemistry of combustion. Look for more about coal (a fossil fuel) in Chapter 4.

Consider This 3.4 Evaporating Coal Mines

Writing in the London, Edinburgh, and Dublin Philosophical Magazine, Arrhenius described the phenomenon: "We are evaporating our coal mines into the air." Although the statement was effective in grabbing attention in 1898, what process do you think he really was referring to in discussing the amount of CO_2 being added to the air? Explain your reasoning.

To further investigate global climate change, we need answers to several important questions. For example, how have the atmospheric concentrations of greenhouse gases changed over time? Similarly, how has the average global temperature changed and how did we measure the changes? Can we determine if the changes in greenhouse gases and temperature are correlated? Can we distinguish natural climate variability from human influences? In the following section, we provide some data to help answer these questions.

3.2 Gathering Evidence: The Testimony of Time

Over the past 4.5 billion years, the approximate age of the Earth, both Earth's climate and its atmosphere have varied widely. Earth's climate has been directly affected by periodic changes in the shape of Earth's orbit and the tilt of Earth's axis. Such changes are thought to be responsible for the ice ages that have occurred regularly during the past million years. Even the Sun itself has changed. Its energy output half a billion years ago was 25–30% less than it is today. In addition, changes in atmospheric greenhouse gas concentrations affect the Earth's energy balance, and hence its climate. Carbon dioxide was once 20 times more prevalent in the atmosphere than it is today. Chemical processes lowered that level by dissolving much of the CO_2 in the oceans, or incorporating it in rocks such as limestone. The biological process of photosynthesis also radically altered the composition of our atmosphere by removing CO_2 and producing oxygen. Certain geological events like volcanic eruptions add millions of tons of CO_2 and other gases to the atmosphere.

Although these natural phenomena will continue to influence Earth's atmosphere and its climate in the coming years, we must also assess the role that human activities are playing. With the development of modern industry and transportation, humans have moved huge quantities of carbon from terrestrial sources like coal, oil, and natural gas into the atmosphere in the form of CO_2 . To evaluate the influence humans are having on the atmosphere, and hence on any enhanced greenhouse effect, it is important to investigate the fate of this large unnatural influx of carbon dioxide. Indeed, CO_2 concentrations in the atmosphere have increased significantly in the past half century. The best direct measurements are taken from the Mauna Loa Observatory in Hawaii (Figure 3.3). The red zigzag line shows the average monthly concentrations, with a small increase each April followed by a small decrease in October. The black line is a 12-month moving average. Notice the steady increase in average annual values from 315 ppm in 1960 to over 395 ppm in 2012. Later in this chapter, we will examine the evidence linking much of the added carbon dioxide to the burning of **fossil fuels**, combustible substances, of which coal, petroleum, and natural gas are the most common.





Figure 3.3

Carbon dioxide concentrations from 1958 to 2012, as measured at Mauna Loa, Hawaii. *Inset:* One year of the monthly variations.

Source: Scripps Institution of Oceanography, NOAA Earth System Research Laboratory, 2012.

Your Turn 3.5 The Cycles of Mauna Loa

- a. Calculate the percent increase in CO_2 concentration during the last 50 years.
- b. Estimate the variation in parts per million (ppm) CO₂ within any given year.
- c. On average, the CO₂ concentrations are higher each April than each October. Explain.

Answer

c. Photosynthesis removes CO₂ from the atmosphere. Spring begins in the northern latitudes in April; October is the start of spring in the southern latitudes. But the landmasses (and number of green plants) are greater in the northern hemisphere so the seasons in the northern hemisphere control the fluctuations.

How can we obtain data about the composition of our atmosphere farther back in time? Much relevant information comes from the analysis of ice core samples. Regions on the planet that have permanent snow cover contain preserved histories of the atmosphere, buried in layers of ice. Figure 3.4a shows a dramatic example of annual ice layers from the Peruvian Andes. The oldest ice on the planet is located in Antarctica, and scientists have been drilling and collecting ice core samples there for over 50 years (Figure 3.4b). Air bubbles trapped in the ice (Figure 3.4c) provide a vertical timeline of the history of the atmosphere; the deeper you drill, the farther back in time you go.

Relatively shallow ice core data show that for the first 800 years of the last millennium the CO_2 concentration was relatively constant at about 280 ppm. Figure 3.5 combines the Mauna Loa data (*red dots*) with data from a 200-meter ice core from the Siple station in Antarctica (*green triangles*), and a deeper core from the Law Dome, also in Antarctica (*blue squares*). Beginning about 1750, CO_2 began accumulating in the atmosphere at an ever-increasing rate, corresponding to the beginning of the Industrial Revolution and the accompanying combustion of fossil fuels that powered that transformation.

Skeptical Chemist 3.6 Checking the Facts on CO₂ Increases

- **a.** A recent government report states that the atmospheric level of CO_2 has increased 30% since 1860. Use the data in Figure 3.5 to evaluate this statement.
- b. A global warming skeptic states that the percent increase in the atmospheric level of CO₂ since 1957 has been only about half as great as the percent increase from 1860 to the present. Comment on the accuracy of that statement and how it could affect potential greenhouse gas emissions policy.



Figure 3.4

(a) Quelccaya ice cap (Peruvian Andes) showing the annual layers. (b) Ice core that can be used to determine changes in concentrations of greenhouse gases over time. (c) Microscopic air bubbles in ice.



Figure 3.5

Carbon dioxide concentrations over the last millennium as measured from Antarctic ice cores (*blue squares* and green triangles) and the Mauna Loa observatory (red dots).

Source: "Climatic Feedbacks on the Global Carbon Cycle," in The Science of Global Change: The Impact of Human Activities on the Environment, American Chemical Society Symposium Series, 1992.

What about further back in time? Drilling by a team of Russian, French, and U.S. scientists at the Vostok Station in Antarctica yielded over a mile of ice cores taken from the snows of 400 millennia. The atmospheric carbon dioxide concentrations going back over 400,000 years are shown in Figure 3.6, with the data from Figure 3.5 in the inset.

Most obvious from the graph are the periodic cycles of high and low carbon dioxide concentrations, which occur roughly in 100,000-year intervals. Although not shown on the graph, analysis of other ice cores indicate these regular cycles go back at least 1 million years. Two important conclusions can be drawn from these data. First, the current atmospheric CO_2 concentration is about 100 ppm *higher* than any time in the last million years. Also during that time, never has the CO_2 concentration risen as rapidly as it is rising today.





What about the global temperature? Measurements indicate that during the past 120 years or so, the average temperature of the planet has increased somewhere between 0.4 and 0.8 °C (0.7–1.1 °F). Figure 3.7 shows the changes in surface air temperature from 1880 to 2006. Nine of the ten warmest years since 1880 have occurred since the year 2000. Some scientists correctly point out that a century or two is an instant in the 4.5-billion-year history of our planet. They caution restraint in reading too much into short-term temperature fluctuations. Short-term changes in atmospheric circulation patterns like El Niño and La Niña events are certainly implicated in some of observed temperature anomalies.

Figure 3.7 also shows the temperature ranges within each year (*black error bars*) as well as the longer term trend (*blue line*). Although the general trend in temperatures over the last 50 years generally follows the increases in carbon dioxide concentrations, the temperature data from year to year are much less consistent. Whether the temperature increase is a consequence of the increased CO_2 concentration cannot be determined with absolute certainty.

It is important to realize that an increase in global average temperature does not mean that across the globe every day is now 0.6 °C warmer than it was in 1970. A map of the temperatures for 2011 compared with the average temperature between 1951 and 1980 is displayed in Figure 3.8. Many regions have experienced just a little warming, and some others have even cooled (*blue areas*). Yet there are other regions (*dark red areas*), particularly in the higher latitudes, that have experienced much more than the average warming. The increases are most drastic in the Arctic, where not surprisingly, much of the tangible effects of climate change have already been observed.

Ice cores also can provide data for estimating temperatures farther back in time because of the hydrogen isotopes found in the frozen water. Water molecules containing the most abundant form of hydrogen atoms, ¹H, are lighter than those that contain deuterium, ²H. The lighter H₂O molecules evaporate just a bit more readily than the heavier ones. As a result, there is more ¹H than ²H in the water vapor of the atmosphere than in the oceans. Likewise, the heavier H₂O molecules in the atmosphere condense just a bit more readily than the lighter ones. Therefore, snow that condenses from atmospheric water vapor is enriched in ²H. The degree of enrichment depends on temperature. The ratio of ²H to ¹H in the ice core can be measured and used to estimate the temperature at the time the snow fell.

When we look back into the past, we see that the global temperature has undergone fairly regular cycles, matching the highs and lows in CO_2 concentration quite remarkably (Figure 3.9). Other data show that periods of high temperature also have been characterized by high atmospheric concentrations of methane, another significant



Global surface temperatures (1880–2011). The red bars indicate the average temperature for each year, and the ranges for each year are shown as the black error bars. The blue line shows the 5-year moving average.

Source: National Oceanic and Atmospheric Administration National Climatic Data Center.

El Niño and La Niña are names given to natural cyclical changes in the oceanatmosphere system in the tropical Pacific. El Niño events lead to warmer ocean temperatures in the middle latitudes, and La Niña cycles produce cooler ocean temperatures.

> Isotopes of hydrogen (and other elements) were discussed in Section 2.2.



Figure 3.8

Change in global temperatures for 2011 (in °C) relative to the 1951–1980 average.

Source: NASA

greenhouse gas. The precision of these data do not allow an assignment of cause and effect. It is difficult to conclude whether increasing greenhouse gases caused the temperature increases, or vice versa. What is clear, however, is that the current CO2 and methane levels are much higher than any time in the last million years. Notice that the variation from hottest to coldest is only about 20 °F, yet that is the difference between the moderate climate we have today, and ice covering much of northern North America and Eurasia, as was the case during the last glacial maximum 20,000 years ago.

Over the past million years, Earth has experienced 10 major periods of glacier activity and 40 minor ones. Without question, mechanisms other than greenhouse gas concentrations are involved in the periodic fluctuations of global climate. Some of this temperature variation is caused by minor changes in Earth's orbit that affect the distance from Earth to the Sun and the angle at which sunlight strikes the planet. However, this hypothesis cannot fully explain the observed temperature fluctuations.



Figure 3.9

Carbon dioxide concentration (blue) and global temperatures (red) over the last 400,000 years from ice core data.

Source: Environmental Defense Fund.

Chapter 3

Orbital effects most likely are coupled with terrestrial events such as changes in reflectivity, cloud cover, and airborne dust, as well as CO_2 and CH_4 concentrations. The feedback mechanisms that couple these effects together are complicated and not completely understood, but it is likely that the effects from each are *additive*. In other words, the existence of natural climate cycles doesn't preclude the effect that increased concentrations of greenhouse gases would have on global climate.

We are a long way from the hothouse of Venus, but we face difficult decisions. These decisions will be better informed with an understanding of the mechanisms by which greenhouse gases interact with electromagnetic radiation to create the greenhouse effect. For that we must again take a submicroscopic view of matter.

3.3 Molecules: How They Shape Up

Carbon dioxide, water, and methane are greenhouse gases; in contrast, nitrogen and oxygen are not. Why the difference? The answer relates in part to molecular shape. In this section, we'll help you to put your knowledge of Lewis structures to work to predict shapes of molecules. In the next, we connect these shapes to molecular vibrations, which can help us to explain the difference between greenhouse gases and nongreenhouse gases.

In Chapter 2 you used Lewis structures to predict how electrons are arranged in atoms and molecules. Shape was not the primary consideration. Even so, in a few cases the Lewis structure did dictate the shape of the molecule. One example is for diatomic molecules such as O_2 and N_2 . Here, the shape is unambiguous because the molecule must be linear.

Even though different geometries are possible with larger molecules, Lewis structures still can help us with the process of predicting the shape. Therefore, the first step in predicting the shape of a molecule is to draw its Lewis structure. If the octet rule is obeyed throughout the molecule, each atom (except hydrogen) will be associated with four pairs of electrons. Some molecules include nonbonding lone-pair electrons, but all molecules must contain some bonding electrons or they would not be molecules!

Opposite charges attract and like charges repel. Negatively charged electrons are attracted to a positively charged nucleus. However, the electrons all have the same charge and therefore are found as far from each other in space as possible while still maintaining their attraction to the positively charged nucleus. Groups of negatively charged electrons repel one another. *The most stable arrangement is the one in which the mutually repelling electron groups are as far apart as possible.* In turn, this determines the atomic arrangement and the shape of the molecule.

We illustrate the procedure for predicting the shape of a molecule with methane, a greenhouse gas.

- 1. Determine the number of outer electrons associated with each atom in the molecule. The carbon atom (Group 4A) has four outer electrons; each of the four hydrogen atoms contributes one electron. This gives $4 + (4 \times 1)$, or 8 outer electrons.
- 2. Arrange the outer electrons in pairs to satisfy the octet rule. This may require single, double, or triple bonds. For the methane molecule, use the eight outer electrons to form four single bonds (four electron pairs) around the central carbon atom. This is the Lewis structure.

$$H: \overset{H}{C}: H \text{ or } H \overset{H}{-} \overset{H}{C} - H \overset{H}{-} H$$

1

Remember, the atmosphere is composed of 78% nitrogen and 21% oxygen.

Recall that Lewis structures and the octet rule were discussed in Section 2.3.

The octet rule applies for most atoms. Exceptions include hydrogen and helium. Although this structure seems to imply that the CH_4 molecule is flat, it is not. In fact, the methane molecule is tetrahedral, as we will see in the next step.

3. Assume that the most stable molecular shape has the bonding electron pairs as far apart as possible. (*Note:* In other molecules we need to consider nonbonding electrons as well, but CH₄ has none.) The four bonding electron pairs around the carbon atom in CH₄ repel one another, and in their most stable arrangement they are as far from one another as possible. As a result, the four hydrogen atoms also are as far from one another as possible. This shape is *tetrahedral*, because the hydrogen atoms correspond to the corners of a **tetrahedron**, a four-cornered geometric shape with four equal triangular sides, sometimes called a triangular pyramid.

One way to describe the shape of a CH_4 molecule is by analogy to the base of a folding music stand. The four C–H bonds correspond to the three evenly spaced legs and the vertical shaft of the stand (Figure 3.10). The angle between each pair of bonds is 109.5°. The tetrahedral shape of a CH_4 molecule has been experimentally confirmed. Indeed, it is one of the most common atomic arrangements in nature, particularly in carboncontaining molecules.



Figure 3.10

The legs and the shaft of a music stand approximate the geometry of the bonds in a tetrahedral molecule such as methane.

Consider This 3.7 Methane: Flat or Tetrahedral?

- a. If the methane molecule really were flat, as the two-dimensional Lewis structure seems to indicate, what would the H-C-H bond angle be?
- b. Offer a reason why the tetrahedral shape, not the two-dimensional flat shape, is more advantageous for this molecule.
- **c.** Consider the music stand shown in Figure 3.10. In the analogy of shape using a music stand, where would the carbon atom be located? Where would each of the hydrogen atoms lie?

Answer

a. 90° (at right angles). The two H atoms across from each other would be at 180°.

Chemists represent molecules in several different ways. The simplest, of course, is the chemical formula itself. In the case of methane, this is simply CH_4 . Another is the Lewis structure, but again this is only a two-dimensional representation that gives information about the outer electrons. Figure 3.11 shows these two representations as well as two others that are three-dimensional in appearance. One has a wedge-shaped line that represents a bond coming out of the paper in a direction generally toward the reader. The dashed wedge in the same structural formula represents a bond pointing away from the reader. The two solid lines lie in the plane of the paper. The other, a space-filling model, was drawn with a



Figure 3.11 Representations of CH₄. (a) Lewis structures and structural formula; (b) Space-filling model.

Chapter 3

molecular modeling program. Space-filling models enclose the volume occupied by electrons in an atom or molecule. Seeing and manipulating physical models, either in the classroom or laboratory, can also help you visualize the structure of molecules.

Not all outer electrons reside in bonding pairs. In some molecules, the central atom has nonbonding electron pairs, also called lone pairs. For example, Figure 3.12 shows the ammonia molecule in which nitrogen completes its octet with three bonding pairs and one nonbonding pair.



Section 2.9 discussed replacement of NH₃ as a refrigerant gas by CFCs. The role of ammonia in the nitrogen cycle is the subject of Section 6.9 and Section 11.12 describes the importance of NH₃ in agriculture.

Figure 3.12 Representations of NH₃.

(a) Lewis structures and structural formula; (b) Space-filling model.

A nonbonding electron pair effectively occupies greater space than a bonding pair of electrons. Consequently, the nonbonding pair repels the bonding pairs somewhat more strongly than the bonding pairs repel one another. This stronger repulsion forces the bonding pairs closer to one another, creating an H–N–H angle slightly less than the predicted 109.5° associated with a regular tetrahedron. The experimental value of 107.3° is close to the tetrahedral angle, again indicating that our model is reasonably reliable.

The shape of a molecule is described in terms of its arrangement of atoms, not electrons (Table 3.1). The hydrogen atoms of NH_3 form a triangle with the nitrogen atom above them at the top of the pyramid. Thus, ammonia is said to have a *trigonal pyramidal* shape. Going back to the analogy of the folding music stand

Table 3.1	Common Molecular Geometries		
# of Bonded Atoms to the Central Atom	# of Nonbonded Electron Pairs on Central Atom	Geometry	Illustration
2	0	linear	
2	2	bent	H ₂ O
3	1	trigonal pyramid	NH ₃
4	0	tetrahedral	CH₄

(see Figure 3.10), you could expect to find hydrogen atoms at the tip of each leg of the music stand. This places the nitrogen atom at the intersection of the legs with the shaft, with the nonbonded electron pair corresponding to the shaft of the stand.

The water molecule is *bent*, illustrating yet another shape. There are eight outer electrons on the central oxygen atom: one from each of the two hydrogen atoms plus six from the oxygen atom (Group 6A). These eight electrons are distributed in two bonding and two lone pairs of electrons (Figure 3.13a).



Figure 3.13 Representations of H₂O. (a) Lewis structures and structural formula; (b) Space-filling model.

If these four pairs of electrons were arranged as far apart as possible, we might predict the H–O–H bond angle to be 109.5° , the same as the H–C–H bond angle in methane. However, unlike methane, water has two nonbonding pairs of electrons. The repulsion between the two nonbonding pairs causes the bond angle to be less than 109.5° . Experiments indicate a value of approximately 104.5° .

Your Turn 3.8 Predicting Molecular Shapes, Part 1

Using the strategies just described, sketch the shape for each of these molecules.

- a. CCl₄ (carbon tetrachloride)
- b. CCl₂F₂ (Freon-12; dichlorodifluoromethane)
- **c**. H₂S (hydrogen sulfide)

Answer

a. Total outer electrons: 4 + 4(7) = 32. Eight of these electrons form 4 single bonds around the central C atom, one to each Cl atom. The other 24 are in 12 nonbonding pairs on the 4 Cl atoms. The bonding electron pairs on C arrange themselves to maximize the separation, and the molecule is tetrahedral.



We already looked at the structures of several molecules important for understanding the chemistry of climate change. What about the structure of the carbon dioxide molecule? With 16 outer electrons, the C atom contributes 4 electrons and 6 come from each of the 2 oxygen atoms. If only single bonds were involved, each atom would not have an octet. But the octet rule still can be obeyed if the central carbon atom forms a double bond with each of the 2 oxygen atoms, thus sharing 4 electrons.

What is the shape of the CO_2 molecule? Again, groups of electrons repel one another, and the most stable configuration provides the furthest separation of the negative charges. In this case, the groups of electrons are the double bonds, and these are furthest apart with an O=C=O bond angle of 180°. The model predicts that all three atoms in a CO_2 molecule will be in a straight line and that the molecule will be *linear*. This is, in fact, the case as shown in Figure 3.14. Revisit Section 2.3 for more about drawing Lewis structures for molecules with double bonds. Chapter 3



Figure 3.14 Representations of CO₂. (a) Lewis structures and structural formula; (b) Space-filling model.

We applied the idea of electron pair repulsion to molecules in which there are four groups of electrons (CH₄, NH₃, and H₂O) and two groups of electrons (CO₂). Electron pair repulsion also applies reasonably well to molecules that include three, five, or six groups of electrons. In most molecules, the electrons and atoms are still arranged to maximize the separation of the electrons. This logic accounts for the bent shape we associated with the ozone molecule.

The Lewis structure for the ozone (O_3) molecule with its 18 outer electrons contains a single bond and a double bond, and the central oxygen atom carries a nonbonding lone pair of electrons. Thus, the central O atom has three groups of electrons: the pair that makes up the single bond, the two pairs that constitute the double bond, and the lone pair. These three groups of electrons repel one another, and the minimum energy of the molecule corresponds to their farthest separation. This occurs when the electron groups are all in the same plane and at an angle of about 120° from one another. We predict, therefore, that the O₃ molecule should be bent, and the angle made by the three atoms should be approximately 120°. Experiments show the bond angle to be 117°, just slightly smaller than the prediction (Figure 3.15). The nonbonding electron pair on the central oxygen atom occupies an effectively greater volume than bonding pairs of electrons, causing a greater repulsion force responsible for the slightly smaller bond angle. Table 3.1 shows the molecular geometry for several molecules.



Figure 3.15

Representations of O₃.

(a) Lewis structures and structural formula for one resonance form; (b) Space-filling model.

Your Turn 3.9 Predicting Molecular Shapes, Part 2

Using the strategies just described, predict and sketch the shape of SO_2 (sulfur dioxide). *Hint:* Because S and O are in the same group on the periodic table, the structures for SO_2 and O_3 will be closely related.

As promised, in this section we helped you see that molecules have different shapes, ones that can be predicted. In the next, we return to our story of greenhouse gases, putting your knowledge of shapes to work to help you understand why not all gases are greenhouse gases.

The O₃ molecule is best represented by two equivalent resonance structures. Again see Section 2.3.

3.4 Vibrating Molecules and the Greenhouse Effect

How do greenhouse gases trap heat, keeping our planet at more or less comfortable temperatures? In part, the answer lies in how molecules respond to photons of energy. This topic is complex, but even so, we can give you enough basics so you can understand how the greenhouse gases in our atmosphere function. At the same time, we'll reveal why some gases do *not* trap heat.

We begin this topic by revisiting the interaction of ultraviolet (UV) light with molecules, as discussed in Chapter 2 in relation to the ozone layer. You saw that high energy photons (UV-C) could break the covalent bonds in O_2 and that photons of lower energy (UV-B) could break the bonds in O_3 . Put another way, both the ozone and the oxygen molecule can absorb UV radiation. When this absorption occurs, an oxygen-to-oxygen bond is broken.

Fortunately, infrared (IR) photons do not contain enough energy to cause chemical bonds to break. Instead, a photon of IR radiation can add energy to the vibrations in a molecule. Depending on the molecular structure, only certain vibrations are possible. The energy of the incoming photon must correspond exactly to the vibrational energy of the molecule for the photon to be absorbed. This means that different molecules absorb IR radiation at different wavelengths and thus vibrate at different energies.

We illustrate these ideas with the CO_2 molecule, representing the atoms as balls and the covalent bonds as springs. Every CO_2 molecule is constantly vibrating in the four ways pictured in Figure 3.16. The arrows indicate the direction of motion of each atom during each vibration. The atoms move forward and backward along the arrows. Vibrations **a** and **b** are stretching vibrations. In vibration **a**, the central carbon atom is stationary and the oxygen atoms move back and forth (stretch) in opposite directions away from the central atom. Alternatively, the oxygen atoms can move in the same direction and the carbon atom in the opposite direction (vibration **b**). Vibrations **c** and **d** look very much alike. In both cases, the molecule bends from its normal linear shape. The bending counts as two vibrations because it occurs in either of two possible planes. In vibration **c** the molecule is shown bending up and down in the plane of the paper on which the diagram is printed, whereas in vibration **d** the molecule is shown bending out of the plane of the paper.

If you ever examined a spring, you probably noticed that more energy is required to stretch it than to bend it. Similarly, more energy is required to stretch a CO_2 molecule than to bend it. This means that more energetic photons, those with shorter wavelengths, are needed to add energy to stretching vibrations **a** or **b** than to add energy to bending vibrations **c** or **d**. For example, absorption of IR radiation with a wavelength of 15.0 micrometers (μ m) adds energy to the bending vibrations (**c** and **d**). When that occurs, the atoms move farther from their equilibrium positions and move faster (on average) than they do normally. For the same thing to happen with vibration **b**, higher energy radiation having a wavelength of 4.3 μ m is required. Together, vibrations **b**, **c**, and **d** account for the greenhouse properties of carbon dioxide.





Figure 3.16

Molecular vibrations in CO_2 . Each spring represents a C=O double bond. Vibrations (a) and (b) are stretching vibrations; (c) and (d) are bending vibrations.



Figure 3.17

Infrared spectrum of carbon dioxide. The letters **(b)**, **(c)**, and **(d)** refer to the molecular vibrations shown in Figure 3.16.

In contrast, direct absorption of IR radiation does not add energy to vibration **a**. In a CO_2 molecule, the average concentration of electrons is greater on the oxygen atoms than on the carbon atom. This means that the oxygen atoms carry a partial negative charge relative to the carbon atom. As the bonds stretch, the positions of the electrons change, thereby changing the charge distribution in the molecule. Because of the linear shape and symmetry of CO_2 , the changes in charge distribution during vibration **a** cancel and no infrared absorption occurs.

The infrared (heat) energy that molecules absorb can be measured with an instrument called an infrared spectrometer. Infrared radiation from a glowing filament is passed through a sample of the compound to be studied, in this case gaseous CO_2 . A detector measures the amount of radiation, at various wavelengths, transmitted by the sample. High transmission means low absorbance, and vice versa. This information is displayed graphically, where the relative intensity of the transmitted radiation is plotted versus wavelength. The result is the *infrared spectrum* of the compound. Figure 3.17 shows the infrared spectrum of CO_2 .

The infrared spectrum shown in Figure 3.17 was acquired using a laboratory sample of CO_2 , but the same absorption takes place in the atmosphere. Molecules of CO_2 that absorb specific wavelengths of infrared energy experience different fates. Some hold that extra energy for a brief time, and then reemit it in all directions as heat. Others collide with atmospheric molecules like N₂ and O₂ and can transfer some of the absorbed energy to those molecules, also as heat. Through both of these processes, CO_2 "traps" some of the infrared radiation emitted by the Earth, keeping our planet comfortably warm. This is what makes CO_2 a greenhouse gas.

Any molecule that can absorb photons of IR radiation can behave as a greenhouse gas. There are many such molecules. Water is by far the most important gas in maintaining Earth's temperature, followed by carbon dioxide. Figure 3.18 shows the IR spectrum of H_2O molecules absorbing IR radiation. However, methane, nitrous oxide, ozone, and chlorofluorocarbons (such as CCl_3F) are among the other substances that help retain planetary heat.

Consider This 3.10

Bending and Stretching Water Molecules

- **a.** Use Figure 3.18 to estimate the wavelengths corresponding to the strongest IR absorbance for water vapor.
- **b.** Which wavelength do you predict represents bending vibrations and which represents stretching? Explain the basis of your predictions.

Hint: Compare the IR spectrum of H_2O with that of CO_2 .

The property of electronegativity, a measure of an atom's ability to attract bonded electrons, is discussed in Section 5.1.

Spectroscopy is the field of study that examines matter by passing electromagnetic energy through a sample.

You already learned about the role of CFCs in ozone depletion in Chapter 2. Nitrous oxide, N₂O, is also called dinitrogen monoxide. You will encounter this gas again in Chapter 6.



Infrared spectrum of water vapor.

Diatomic gases, such as N_2 and O_2 , are not greenhouse gases. Although molecules consisting of two identical atoms do vibrate, the overall electric charge distribution does not change during these vibrations. Hence, these molecules cannot be greenhouse gases. Earlier we discussed this lack of change in the overall electric charge distribution as the reason why stretching vibration **a** in Figure 3.17 was not responsible for the greenhouse gas behavior of CO_2 .

So far, you have encountered two ways that molecules respond to radiation. Highly energetic photons with high frequencies and short wavelengths (such as UV radiation) can break bonds within molecules. The less energetic photons (such as IR radiation) cause an increase in molecular vibrations. Both processes are depicted in Figure 3.19, but the figure also includes another response of molecules to radiant energy that is probably a good deal more familiar to you. Longer wavelengths than those in the IR range have only enough energy to cause molecules to rotate faster.



Molecular response to types of radiation.

For example, microwave ovens generate electromagnetic radiation that causes water molecules to spin faster. The radiation generated in such a device is of relatively long wavelength, about a centimeter. Thus the energy per photon is quite low. As the H_2O molecules absorb the photons and spin more rapidly, the resulting friction cooks your food, warms up the leftovers, or heats your coffee. The same region of the spectrum is used for radar. Beams of microwave radiation are sent out from a generator. When the beams strike an object such as an airplane, the microwaves bounce back and are detected by a sensor.



What might be handy to know about the carbon cycle? Three things are at the top of the list. First, *carbon is found in many places on our planet*. We call these reservoirs, as shown in Figure 3.20. For example, our atmosphere is a reservoir for carbon in the form of CO_2 (~400 ppm), CH_4 (~17 ppm), and CO (trace amounts, air pollutant). Another reservoir for carbon is carbonate-containing rocks. Plants and animals are a third place that you will find carbon, this time in the form of carbo-hydrates, proteins, and lipids.

Second, *carbon is on the move!* Through processes such as combustion, photosynthesis, and sedimentation, carbon moves from one reservoir to another. Michael B. McElroy of Harvard University estimated, "The average carbon atom has made the cycle from sediments through the more mobile compartments of the Earth back to sediments some 20 times over the course of Earth's history." CO_2 in the air today may have been released from campfires burning more than a thousand years ago. All of the processes illustrated in Figure 3.20 happen simultaneously, but at different rates.

Third, *where carbon ends up matters*. For example, the slow transformation of carbon from living organisms into fossil fuels millions of years ago is of great importance to us. Today's transfer of carbon back into the atmosphere by burning fossil fuel matters not only to us but also to those in future generations who must deal with the consequences of climate change. The next activity gives you a closer look at carbon reservoirs and the processes that move carbon between these reservoirs.

Your Turn 3.11 Understanding the Carbon Cycle

- a. Which processes add carbon (in the form of CO₂) to the atmosphere?
- b. Which processes remove carbon from the atmosphere?
- c. What are the two largest reservoirs of carbon?
- d. Which parts of the carbon cycle are most influenced by human activities?



Figure 3.20

The global carbon cycle. The numbers show the quantity of carbon, expressed in gigatonnes (Gt), that is stored in various carbon reservoirs (*black numbers*) or moving through the system per year (*red numbers*).

From Purves, Orians, Heller and Sadava, *Life, The Science of Biology*, 5th edition, 1998, page 1186. Reprinted with permission of Sinauer Associates, Inc.

Look for more about carbonate-containing rocks in Chapter 5 and more about the carbon basis of food in Chapter 11.

A gigatonne (Gt) is a billion metric tons, or about 2200 billion pounds. For comparison, a fully loaded 747 jet weighs about 800,000 lb. It would take nearly 3 million 747s to have a total mass of 1 Gt.



Figure 3.21 Global carbon dioxide emissions by end use.

Source: IPCC Fourth Assessment Report, Working Group III, 2007.

We hope that Your Turn 3.11 helped you to notice that the carbon cycle is a dynamic system. Notice the presence of both natural emission and removal mechanisms. Respiration adds carbon dioxide to the atmosphere, and photosynthesis removes it. Similarly, the oceans both absorb and emit carbon dioxide. As members of the animal kingdom, we *Homo sapiens* participate in the carbon cycle along with our fellow creatures. As is true for any animal, we inhale and exhale, ingest and excrete, live and die. In addition though, human civilization relies on processes that put much more carbon into the atmosphere than they remove (Figure 3.21). Widespread burning of coal for electricity production, of petroleum products for transportation, and of natural gas for home heating all transfer carbon from the largest underground carbon reservoir into the atmosphere.

Another human influence on CO_2 emissions is deforestation by burning, a practice that releases about 1.5 Gt of carbon to the atmosphere each year. It is estimated that forested land the size of two football fields is lost every second of every day from the rain forests of the world. Although firm numbers are rather elusive, Brazil continues as the country with the greatest annual loss of rain forest acreage; over 5.4 million acres of Amazon rain forest is vanishing each year. Trees, very efficient absorbers of carbon dioxide, are removed from the cycle through deforestation. If the wood is burned, vast quantities of CO_2 are generated; if it is left to decay, that process also releases carbon dioxide, but more slowly. Even if the lumber is harvested for construction purposes and the land is replanted in cultivated crops, the loss in CO_2 -absorbing capacity may approach 80%.

The total quantity of carbon released by the human activities of deforestation and burning fossil fuels is about 7.5 Gt per year. About half of this is eventually recycled into the oceans and the biosphere, however carbon dioxide is not always removed with the speed required by its rate of increase in the atmosphere. Much of the CO_2 emitted stays in the atmosphere, adding between 3.1 and 3.5 Gt of carbon per year to the existing base of 750 Gt noted in Figure 3.20. We are concerned primarily with the relatively rapid *increase* in atmospheric carbon dioxide, because *excess* CO_2 from this increase is implicated in global warming. Therefore, it would be useful to know the mass (Gt) of CO_2 added to the atmosphere each year. In other words, what mass of CO_2 contains 3.3 Gt of carbon, the midpoint between 3.1 Gt and 3.5 Gt? Answering this question requires that we return to some more quantitative aspects of chemistry.

Remember that the natural "greenhouse effect" makes life on Earth possible. Problems occur when the amount of greenhouse gases *increases* faster than it can be removed. The result is the *enhanced* greenhouse effect.

3.6 Quantitative Concepts: Mass

To solve the problem just posed, we need to know how the mass of C is related to the mass of CO₂. Regardless of the source of CO₂, its chemical formula is stubbornly the same. The mass percent of C in CO₂ is also unwavering, and therefore we must calculate the mass percent of C in CO₂, based on the formula of the compound. As you work through this and the next section, keep in mind that we are seeking a value for that percentage.

The approach requires the use of the masses of the elements involved. But this raises an important question: How much does an individual atom weigh? The mass of an atom is mainly attributable to the neutrons and protons in the nucleus. Thus, elements differ in mass because their atoms differ in composition. Rather than using absolute masses of individual atoms, chemists have found it convenient to employ relative masses in other words, to relate the masses of all atoms to some convenient standard. The internationally accepted mass standard is carbon-12, the isotope that makes up 98.90% of all carbon atoms. C-12 has a mass number of 12 because each atom has a nucleus consisting of 6 protons and 6 neutrons plus 6 electrons outside the nucleus.

The periodic table in the text shows that the atomic mass of carbon is 12.01, not 12.00. This is not an error; it reflects the fact that carbon exists naturally as three isotopes. Although C-12 predominates, 1.10% of carbon is C-13, the isotope with six protons and *seven* neutrons. In addition, natural carbon contains a trace of C-14, the isotope with six protons and *eight* neutrons. The tabulated mass value of 12.01 is often called by the name atomic mass, an average that takes into consideration the masses and percent natural abundance of all naturally occurring isotopes of carbon. This isotopic distribution and average mass of 12.01 characterize carbon obtained from any chemical source—a graphite ("lead") pencil, a tank of gasoline, a loaf of bread, a lump of limestone, or your body.

The radioactive isotope carbon-14, although present only in trace amounts, provides direct evidence that the combustion of fossil fuels is the *predominant* cause of the rise in atmospheric CO₂ concentrations over the past 150 years. In all living things, only 1 out of 10^{12} carbon atoms is a C-14 atom. A plant or animal constantly exchanges CO₂ with the environment, and this maintains a constant C-14 concentration in the organism. However, when the organism dies, the biochemical processes that exchange carbon stop functioning and the C-14 is no longer replenished. This means that after the death of the organism, the concentration of C-14 decreases with time because it undergoes radioactive decay to form N-14. Coal, oil, and natural gas are remnants of plant life that died hundreds of millions of years ago. Hence, in fossil fuels, and in the carbon dioxide released when fossil fuels burn, the level of C-14 is essentially zero. Careful measurements show that the concentration of C-14 in atmospheric CO₂ has recently decreased. This strongly suggests that the origin of the added CO₂ is indeed the burning of fossil fuels, a decidedly human activity.

Your Turn 3.12 Isotopes of Nitrogen

Nitrogen (N) is an important element in the atmosphere and in biological systems. It has two naturally occurring isotopes: N-14 and N-15.

- a. Use the periodic table to find the atomic number and atomic mass of nitrogen.
- b. What is the number of protons, neutrons, and electrons in a neutral atom of N-14?
- c. Compare your answers for part ${\bf b}$ with those for a neutral atom of N-15.
- d. Given the atomic mass of nitrogen, which isotope has the greatest natural abundance?

Having reviewed the meaning of isotopes, we return to the matter at hand—the masses of atoms and particularly the atoms in CO₂. Not surprisingly, it is impossible to weigh a single atom because of its extremely small mass. A typical laboratory balance can detect a minimum mass of 0.1 mg; this corresponds to 5×10^{18} carbon atoms, or 5,000,000,000,000,000 carbon atoms. An atomic mass unit is far too small to measure in a conventional chemistry laboratory. Rather, the gram is the chemist's mass

Isotopes and the relative masses of subatomic particles were discussed in Section 2.2.

You may notice that no units are used with the atomic masses. These are in atomic mass units (amu), which equals 1.66 × 10⁻¹⁷ kg.

You will learn to write equations for nuclear reactions in Section 7.2.

unit of choice. Therefore, scientists use exactly 12 g of carbon-12 as the reference for the atomic masses of all the elements. We define **atomic mass** as the mass (in grams) of the same number of atoms that are found in exactly 12 g of carbon-12. This number of atoms is, of course, *very* large. This important chemical number is named after an Italian scientist with the impressive name of Count Lorenzo Romano Amadeo Carlo Avogadro di Quaregna e di Ceretto (1776–1856). (His friends called him Amadeo.) **Avogadro's number** is the number of atoms in exactly 12 g of C-12. Avogadro's number, if written out, is 602,000,000,000,000,000,000,000. It is more compactly written in scientific notation as 6.02×10^{23} . This is the incredible number of atoms in 12 g of carbon, no more than a tablespoonful of soot!

Avogadro's number counts a large collection of atoms, much like the term *dozen* counts a collection of eggs. It does not matter if the eggs are large or small, brown or white, "organic" or not. No matter, for if there are 12 eggs, they are still counted as a dozen. A dozen ostrich eggs has a greater mass than a dozen quail eggs. Figure 3.22 illustrates this point with a half-dozen tennis and a half-dozen golf balls. Like atoms of different elements, the masses of a tennis ball and a golf ball differ. The number of balls is the same—six in each bag, a half dozen.

Skeptical Chemist 3.13 Marshmallows and Pennies

Avogadro's number is so large that about the only way to hope to comprehend it is through analogies. For example, one Avogadro's number of regular-sized marshmallows, 6.02×10^{23} of them, would cover the surface of the United States to a depth of 650 miles. Or, if you are more impressed by money than marshmallows, assume 6.02×10^{23} pennies were distributed evenly among the approximately 7 billion inhabitants of the Earth. Every man, woman, and child could spend \$1 million every hour, day and night, and half of the pennies would still be left unspent at death.

Can these fantastic claims be correct? Check one or both, showing your reasoning. Come up with an analogy of your own.

Knowledge of Avogadro's number and the atomic mass of any element permit us to calculate the average mass of an individual atom of that element. Thus, the mass of 6.02×10^{23} oxygen atoms is 16.00 g, the atomic mass from the periodic table. To find the average mass of just one oxygen atom, we must divide the mass of the large collection of atoms by the size of the collection. In chemist's terms, this means dividing the atomic mass by Avogadro's number. Fortunately, calculators help make this job quick and easy.

 $\frac{16.00 \text{ g oxygen}}{6.02 \times 10^{23} \text{ oxygen atoms}} = 2.66 \times 10^{-23} \text{ g oxygen/oxygen atoms}$

This very small mass confirms once again why chemists do not generally work with small numbers of atoms. We manipulate trillions at a time. Therefore, practitioners of this art need to measure matter with a sort of chemist's dozen—a very large one, indeed. To learn about it, read on . . . but only after stopping to practice your new skill.

Your Turn 3.14 Calculating Mass of Atoms

- a. Calculate the average mass in grams of an individual atom of nitrogen.
- **b.** Calculate the mass in grams of 5 trillion nitrogen atoms.
- c. Calculate the mass in grams of 6 \times 10¹⁵ nitrogen atoms.

Answer

a. $\frac{14.01 \text{ g nitrogen}}{6.02 \times 10^{23} \text{ nitrogen atoms}} = 2.34 \times 10^{-23} \text{ g nitrogen/nitrogen atom}$

Figure 3.22 Six tennis balls have a greater mass

than six golf balls.

Calculation Tip

Predict:

Will the answer be a large or a small number?

Check:

Does your answer match your prediction, and is it reasonable?

127

Chapter 3



Chemists have another way of communicating the number of atoms, molecules, or other small particles present. This is to use the term **mole** (**mol**), defined as containing an Avogadro's number of objects. The term is derived from the Latin word to "heap," or "pile up." Thus, 1 mol of carbon atoms consists of 6.02×10^{23} C atoms, 1 mol of oxygen gas is made up of 6.02×10^{23} oxygen molecules, and 1 mol of carbon dioxide molecules corresponds to 6.02×10^{23} carbon dioxide molecules.

As you already know from previous chapters, chemical formulas and equations are written in terms of atoms and molecules. For example, reconsider the equation for the complete combustion of carbon in oxygen.

$$C + O_2 \longrightarrow CO_2$$
 [3.1]

This equation tells us that one atom of carbon combines with one molecule of oxygen to yield one molecule of carbon dioxide. Thus it reflects the *ratio* in which the particles interact. It is equally correct to say that 10 C atoms react with 10 O₂ molecules (20 O atoms) to form 10 CO₂ molecules. Or, putting the reaction on a grander scale, we can say 6.02×10^{23} C atoms combine with 6.02×10^{23} O₂ molecules (12.0×10^{23} O atoms) to yield 6.02×10^{23} CO₂ molecules. The last statement is equivalent to saying: "one *mole* of carbon plus one *mole* of oxygen yields one *mole* of carbon dioxide." Thus the numbers of *atoms and molecules* taking part in a reaction are proportional to the numbers of *moles* of the same substances. The ratio of two oxygen atoms to one carbon atom remains the same regardless of the number of carbon dioxide molecules, as summarized in Table 3.2.

In the laboratory and the factory, the quantity of matter required for a reaction is often measured by mass. The mole is a practical way to relate number of particles to the more easily measured mass. The **molar mass** is the mass of Avogadro's number, or one *mole*, of whatever particles are specified. For example, from the periodic table we can see that the mass of one mole of carbon atoms, rounded to the nearest tenth of a gram, is 12.0 g. A mole of oxygen atoms has a mass of 16.0 g. But we can also speak of a mole of O_2 molecules. Because there are two oxygen atoms in each oxygen, O_2 . Consequently, the molar mass of O_2 is 32.0 g, twice the molar mass of O. Some refer to this as the molecular mass or molecular weight of O_2 , emphasizing its similarity to atomic mass or atomic weight.

The same logic for the molar mass of the element O_2 applies to compounds, such as carbon dioxide. The formula, CO_2 , reveals that each molecule contains one carbon atom and two oxygen atoms. Scaling up by 6.02×10^{23} , we can say that each mole of CO_2 consists of 1 mol of C and 2 mol of O atoms (see Table 3.2). But remember that we are interested in the molar mass of carbon dioxide, which we obtain by adding the molar mass of carbon to twice the molar mass of oxygen:

$$1 \mod CO_2 = 1 \mod C + 2 \mod O$$
$$= \left(1 \mod C \times \frac{12.0 \text{ g C}}{1 \mod C}\right) + \left(2 \mod O \times \frac{16.0 \text{ g O}}{1 \mod O}\right)$$
$$= 12.0 \text{ g C} + 32.0 \text{ g O}$$

 $1 \bmod \mathrm{CO}_2 = 44.0 \mathrm{g} \mathrm{CO}_2$

Table 3.2	Ways to Interpret a Chemical Equation		
С	+	O ₂	\longrightarrow CO ₂
1 atom		1 molecule	1 molecule
6.02×10^{23}	atoms	6.02×10^{23} molecule	s 6.02×10^{23} molecules
1 mol		1 mol	1 mol

When used together with a number, *mol* is an abbreviation for *mole*.

There are 2 mol of oxygen atoms, O, in every mole of oxygen molecules, O₂. This procedure is routinely used in chemical calculations, where molar mass is an important property. Some examples are included in Your Turn 3.15. In every case, you multiply the number of moles of each element by the corresponding atomic mass in grams and add the result.

Your Turn 3.15 Molecular Molar Mass

Calculate the molar mass of each of these greenhouse gases.

- **a.** O_3 (ozone)
- b. N₂O (dinitrogen monoxide or nitrous oxide)
- c. CCl₃F (Freon-11; trichlorofluoromethane)

Answer

a. $1 \mod O_3 = 3 \mod O$ = $3 \mod O \times \frac{16.0 \text{ g O}}{1 \mod O}$ = 48.0 g O_3

We started out on this mathematical excursion so that we could calculate the mass of CO₂ produced from burning 3.3 Gt of carbon. We now have all the pieces assembled. Out of every 44.0 g of CO₂, 12.0 g is C. This mass ratio holds for all samples of CO₂, and we can use it to calculate the mass of C in any known mass of CO₂. More to the point, we can use it to calculate the mass of CO₂ released by any known mass of carbon. It only depends on how we arrange the ratio. The C-to-CO₂ ratio is $\frac{12.0 \text{ g C}}{44.0 \text{ g CO}_2}$, but it is equally true that the CO₂-to-C ratio is $\frac{44.0 \text{ g CO}_2}{12.0 \text{ g O}}$.

For example, we could compute the number of grams of C in 100.0 g CO_2 by setting up the relationship in this manner.

$$100.0 \text{ g-CO}_2 \times \frac{12.0 \text{ g-C}}{44.0 \text{ g-CO}_2} = 27.3 \text{ g-C}$$

The fact that there is 27.3 g of carbon in 100.0 g of carbon dioxide is equivalent to saying that the mass percent of C in CO_2 is 27.3%. Note that carrying along the units "g CO_2 " and "g C" helps you do the calculation correctly. The unit "g CO_2 " can be canceled, and you are left with "g C." Keeping track of the units and canceling where appropriate are useful strategies in solving many problems. This method is sometimes called unit or dimensional analysis.

Your Turn 3.16 Mass Ratios and Percents

- **a.** Calculate the mass ratio of S in SO_2 .
- **b.** Find the mass percent of S in SO_2 .
- c. Calculate the mass ratio and the mass percent of N in N_2O .

Answers

a. The mass ratio is found by comparing the molar mass of S with the molar mass of SO₂.

$$\frac{32.1 \text{ g S}}{64.1 \text{ g SO}_2} = \frac{0.501 \text{ g S}}{1.00 \text{ g SO}_2}$$

b. To find the mass percent of S in SO₂, multiply the mass ratio by 100.

$$\frac{0.501 \text{ g S}}{1.00 \text{ g SO}_2} \times 100 = 50.1\% \text{ S in SO}_2$$

To find the mass of CO_2 that contains 3.3 gigatonnes (Gt) of C, we use a similar approach. We could convert 3.3 Gt to grams, but it is not necessary. As long as we use the same mass unit for C and CO_2 , the same numerical ratio holds. Compared with our

Calculation Tip

Predict:

Will the answer be larger or smaller than the given value? What are the units?

Check:

Does the answer match your prediction? Have units canceled, leaving the one needed for the answer?

Chapter 3

last calculation, this problem has one important difference in how we use the ratio. We are solving for the mass of CO_2 , not the mass of C. Look carefully at the units this time.

$$3.3 \,\text{GtC} \times \frac{44.0 \,\text{GtCO}_2}{12.0 \,\text{GtC}} = 12 \,\text{GtCO}_2$$

Once again the units cancel, and we are left with Gt of CO_2 .

Our burning question, "What is the mass of CO_2 added to the atmosphere each year from the combustion of fossil fuels?" has finally been answered: 12 gigatonnes. Of course, we also managed to demonstrate the problem-solving power of chemistry and to introduce five of its most important ideas: atomic mass, molecular mass, Avogadro's number, mole, and molar mass. The next few activities provide opportunities to practice your skill with these concepts.

Your Turn 3.17 SO₂ from Volcanoes

- **a.** It is estimated that volcanoes globally release about 19×10^6 t (19 million metric tons) of SO₂ per year. Calculate the mass of sulfur in this amount of SO₂.
- b. If 142×10^6 t of SO₂ is released per year by fossil-fuel combustion, calculate the mass of sulfur in this amount of SO₂.

Answer

a. The mass ratio of S to SO₂ is known from Your Turn 3.16.

 $19 \times 10^{6} \pm SO_{2} \times \frac{32.1 \times 10^{6} \pm S}{64.1 \times 10^{6} \pm SO_{2}} = 9.5 \times 10^{6} \pm S$

If you know how to apply these ideas, you have gained the ability to critically evaluate media reports about releases of C or CO_2 (and other substances as well) and judge their accuracy. One can either take such statements on faith or check their accuracy by applying mathematics to the relevant chemical concepts. Obviously, there is insufficient time to check every assertion, but we hope that you develop questioning and critical attitudes toward all statements about chemistry and society, including those found in this book.

Skeptical Chemist 3.18 Checking Carbon from Cars

A clean-burning automobile engine emits about 5 pounds of C in the form of CO₂ for every gallon of gasoline it consumes. The average American car is driven about 12,000 miles per year. Using this information, check the statement that the average American car releases its own weight in carbon into the atmosphere each year. List the assumptions you make in solving this problem. Compare your list and your answer with those of your classmates.

3.8 Methane and Other Greenhouse Gases

Concerns about an enhanced greenhouse effect are based primarily on increases in concentrations of atmospheric CO_2 . However, other gases also play a role. Methane, nitrous oxide, chlorofluorocarbons, and even ozone all take part in trapping heat in the atmosphere.

Our level of concern regarding each of these gases is related to their concentration in the atmosphere but also to other important characteristics. The **global atmospheric lifetime** characterizes the time required for a gas added to the atmosphere to be removed. It is also referred to as the "turnover time." Greenhouse gases also vary in their effectiveness in absorbing infrared radiation. This is quantified by the **global warming potential (GWP),** a number that represents the relative contribution of a molecule of the atmospheric gas to global warming. The GWP of carbon dioxide is assigned the reference value of 1; all other greenhouse gases are indexed with respect to it. Gases with relatively short lifetimes, such as water vapor, tropospheric ozone,

Global atmospheric lifetime values, although useful for comparison, are best thought of as approximations.

Table 3.3	Examples of Greenhouse Gases				
Name (Chemical Formula)	Preindustrial Concentration (1750)	Concentration in 2011	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
carbon dioxide CO ₂	270 ppm	396 ppm**	50-200*	Fossil fuel combustion, deforestation, cement production	1
methane CH ₄	700 ppb	1816 ppb	12	Rice paddies, waste dumps, livestock	21
nitrous oxide N ₂ O	275 ppb	324 ppb	120	Fertilizers, industrial production, combustion	310
CFC-12 CCl ₂ F ₂	0	0.53 ppb	102	Liquid coolants, foams	8100

*A single value for the atmospheric lifetime of CO₂ is not possible. Removal mechanisms take place at different rates. The range given is an estimate based on several removal mechanisms.

**The carbon dioxide value is from 2012 and the value has surpassed 400 ppm at several points during 2013.

tropospheric aerosols, and other ambient air pollutants, are distributed unevenly around the world. It is difficult to quantify their effect, and therefore GWP values are not usually assigned. Table 3.3 lists four greenhouse gases, their main sources, and their important properties in the climate change conversation.

Your Turn 3.19 Greenhouse Gases on the Rise

Using the data in Table 3.3, calculate the percentage increases for CO_2 , CH_4 , and N_2O since 1750. Rank the three in order of their percentage increase.

The current atmospheric concentration of CH_4 is about 50 times lower than that of CO_2 , but as an infrared absorber, methane is about 20 times more efficient than carbon dioxide. Fortunately, CH_4 is quite readily converted to other chemical species by interaction with tropospheric free radicals, and therefore has a relatively short lifetime. By comparison, carbon dioxide is much less reactive. The primary removal mechanisms for CO_2 are dissolution in oceans, photosynthesis by plants, and the much longer process of mineralization into carbonate rocks.

Methane emissions arise from both natural and human sources. About 40% of total CH_4 emissions come from natural sources, of which emanations from wetlands are by far the largest contributor. These marshy habitats are perfectly suited for **anaerobic bacteria**, those that can function without the use of molecular oxygen. As they decompose organic matter, many types of anaerobic bacteria produce methane, which then escapes into the atmosphere. In Alaska, Canada, and Siberia, however, much of the methane produced from thousands of years of decomposition has remained trapped underground by the permafrost. There is concern that melting of the surface in the northern latitudes might trigger a massive release of methane into the atmosphere. There is geological evidence that such a release has occurred in the past and led to higher global temperatures.

Methane is also released from the oceans, where a substantial amount of it appears to be trapped in "cages" made of water molecules. Such deposits are referred to as methane hydrates. Australia's Commonwealth Scientific and Industrial Research Organization (CSIRO) has taken a series of ocean core drillings to gather evidence about methane hydrates and their role in global warming (Figure 3.23). There is concern that if some of these hydrates become unstable then large amounts of methane might rapidly be released to the atmosphere.

Termites are another natural source of methane. These ubiquitous insects have special bacteria in their guts that allow them to metabolize cellulose, the main component of wood. But instead of making water and CO_2 , termites produce methane and CO_2 . Not only can they inflict direct damage to homes, but they also add to greenhouse gas concentrations. The sheer number of termites is staggering, estimated to be more than half a metric ton for every man, woman, and child on the planet!



Figure 3.23

(a) A floating drilling platform used by the CSIRO.(b) A sample of methane hydrate from the continental shelf off the coast of Florida.

The major human source of CH_4 is agriculture, with the biggest culprits being rice cultivation and the raising of livestock. Rice is grown with its roots under water, where, again, anaerobic bacteria produce methane. Most of the methane is released to the atmosphere. Additional agricultural CH_4 comes from an increasing number of cattle and sheep. The digestive systems of these ruminants (animals that chew their cud) contain bacteria that break down cellulose. In the process, methane is formed and released through belching and flatulence—about 500 liters of CH_4 per cow per day! The ruminants of the Earth release a staggering 73 million metric tons of CH_4 each year.

Landfills add another large quantity of methane to the atmosphere. The chemistry occurring within our buried garbage is controlled by the same anaerobic bacteria found in wetlands and produces the same result. Some of this methane is captured (biogas) and burned as a fuel, but the vast majority is released into the atmosphere.

The other main anthropogenic source of methane originates from our extraction of fossil fuels. Methane is often found with oil and coal deposits, and drilling and mining procedures release most of that methane to the atmosphere while recovering the liquid or solid products. There are also significant losses from transporting, purifying, and using natural gas.

Consider This 3.20 Methane Concentrations Stabilizing?

In recent years, scientists observed methane concentrations leveled off. Is this the case currently? Use the resources of the Internet to support your answer.

Another gas that contributes to global warming is nitrous oxide, also known as "laughing gas." It has been used as an inhaled anesthetic for dental and medical purposes. Its sources and sinks are not as well established as are those for carbon dioxide and methane. The majority of N_2O molecules in the atmosphere come from the bacterial removal of nitrate ion (NO_3^-) from soils, followed by removal of oxygen. Agricultural practices, again linked to population pressures, can speed up the removal of reactive compounds of nitrogen from soils. Other sources include ocean upwelling and stratospheric interactions of nitrogen compounds with high-energy oxygen atoms. Major anthropogenic sources of N_2O are automobile catalytic converters, ammonia fertilizers, biomass burning, and certain industrial processes (nylon and nitric acid production). In the atmosphere, a typical N_2O molecule persists for about 120 years,

For more information on using methane as a fuel, check Section 4.10.

The role of N₂O in destroying stratospheric ozone was discussed in Section 2.8.

Table 3.4	Climate Change and Ozone Depletion: A Comparison			
		Climate Change	Ozone Depletion	
Region of atmosp	here	primarily the troposphere	the stratosphere	
Major players		$H_2O,CO_2,CH_4,andN_2O$	O ₃ , CFCs, HCFCs, and halons	
Interaction with radiation		Molecules absorb IR radiation. This causes them to vibrate and return heat energy to the Earth.	Molecules absorb UV radiation. This causes one or more bonds in the molecule to break.	
Nature of problem	m	Greenhouse gases are increasing in concentration. In turn this is trapping more heat, causing an increase in the average global temperatures.	CFCs are causing a decrease in concentrations of O_3 in the stratosphere. In turn, this is causing an increase in the UV radiation that reaches the surface of the Earth.	

absorbing and emitting infrared radiation. Over the past decade, global atmospheric concentrations of N_2O have shown a slow but steady rise.

A few comments need to be made about ozone, a gas we encountered in Chapter 2. Often there is confusion between the phenomena of climate change and ozone depletion. Both are often in the news, both involve complex atmospheric processes, and both have anthropogenic as well as natural sources. In fact, ozone itself can act like a greenhouse gas, but its efficiency depends very much on its altitude. It appears to have its maximum warming effect in the upper troposphere. Therefore, depletion of ozone has a *slight cooling effect* in the stratosphere, and it may also promote slight cooling at Earth's surface. Other differences are summarized in Table 3.4.

Depletion of the stratospheric ozone layer is *not* a principal cause of climate change. However, stratospheric ozone depletion and climate change are linked in an important way, through ozone-depleting substances. CFCs, HCFCs, and halons, all implicated in the depletion of stratospheric ozone, also absorb infrared radiation and are all greenhouse gases. Emissions of these synthetic gases rose by 58% from 1990–2005, although their concentrations are still very low.

Consider This 3.21 Global Warming Potential As the Clock Ticks

Although Table 3.3 reports a single value of Global Warming Potential (GWP) for each greenhouse listed, in actuality different values are possible, depending on the time frame. For example:

	20 years	100 years	500 years
CH ₄	72	21	7.6
N ₂ O	289	310	156
C 1 1 (C	<i>c</i>	C 1 1	1 10 01

The reason for the differences is a function of the estimated atmospheric lifetime of the gas.

- a. Compare the GWPs for methane for 20 and 100 years. Explain why these values are consistent with an estimated atmospheric lifetime of about 12 years for methane.
- **b.** For both methane and nitrous oxide, the GWP values are lower for 500 years than for 100 years. Propose an explanation.

3.9 How Warm Will the Planet Get?

"Prediction is very difficult, especially about the future." Niels Bohr, one of the foremost contributors to our modern view of the atom, spoke these words years ago. His words still hold true today! 133

HCFCs were discussed in Section 2.12.

Consider This 3.22 Sun Skeptics?

Some people have stated that changes in the Sun are causing global climate change. What are your thoughts?

Although admittedly a difficult task, we still need to make predictions. To this end, in 1988, the United Nations Environment Programme and the World Meteorological Organization teamed up to establish the UN Intergovernmental Panel on Climate Change (IPCC). The IPCC was charged with assembling and assessing the climate change data, including socioeconomic data. Thousands of international scientists were involved in this review. In their fourth and most recent report published in 2007, the vast majority of scientists agreed on several key points:

- The Earth is getting warmer.
- Human activities (primarily the combustion of fossil fuels and deforestation) are responsible for much of the recent warming.
- If the rate of greenhouse gas emissions is not curtailed, our water resources, food supply, and even our health will suffer.

A fifth report was scheduled for release in 2014.

The challenge, however, is to understand current climate change well enough to *predict* future changes and by doing so, to determine the decrease in emissions required to minimize harmful changes. To make predictions, scientists work with models. They design computer models of the oceans and the atmosphere that take into account the ability of each to absorb heat as well as to circulate and transport matter (Figure 3.24). If that weren't difficult enough, the models must also include astronomical, meteorological, geological, and biological factors, ones that are often incompletely understood. Human influences, such as population, industrialization levels, and pollution emissions must also be included. Dr. Michael Schlesinger, who directs climate research at the University of Illinois, remarked: "If you were going to pick a planet to model, this is the *last* planet you would choose."

Climate scientists call the factors (both natural and anthropogenic) that influence the balance of Earth's incoming and outgoing radiation by the term **radiative forcings**. Negative forcings have a cooling effect; positive forcings a warming effect. The primary forcings used in climate models are solar irradiance, greenhouse gas concentrations, land use, and aerosols. The effects of these forcings on the Earth's energy balance are summarized in Figure 3.25. Red, orange, and yellow bars represent positive forcings, and blue bars indicate negative ones. Each forcing has an error bar associated with it; the larger the error bar, the more uncertain the value.

Solar Irradiance ("solar brightness")

We can directly observe the natural seasonal variations in sunlight intensity. In the higher latitudes, temperatures are warmer in the summer. Compared to winter months, the Sun is higher in the sky and stays up longer. Across the globe, these variations essentially cancel, because when it is winter in the Northern Hemisphere it is summer in the Southern Hemisphere.

Subtle periodic changes occur in the brightness of the Sun. The Earth's orbit oscillates slightly over a 100,000-year period, changing its shape. In addition, the magnitude of the tilt of the Earth's axis and the direction of that tilt both change over the course of several tens of thousands of years, affecting the amount of solar radiation hitting the Earth. Neither of these occurs on a time scale short enough to explain the recent warming, however.

Additionally, sunspots occur in large numbers about every 11 years. You might think that dark spots on the Sun would mean a smaller amount of radiation hitting the Earth, but exactly the opposite is true. Sunspots occur when there is increased magnetic activity in the outer layers of the Sun, and the stronger magnetic fields stir up a larger amount of charged particles that emit radiation. Notably, the 17th and 18th centuries,

The IPCC received the 2007 Nobel Peace Prize (shared with former U.S. Vice President Al Gore) for its work in understanding global warming.

The unique properties of water, including its unusually large specific heat, will be described in Chapter 5.



Figure 3.24 Climate scientists use computer

simulations to understand future climate change.

Periodic orbital eccentricities are a possible cause of the ice age oscillations shown in Figure 3.9.



Figure 3.25

Selected radiative forcings of climate from 1750 to 2005. The units are in watts per square meter (W m⁻²), the light energy hitting a square meter of the Earth's surface every second.

Source: Adapted from Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.

sometimes called the "Little Ice Age" because of the below average temperatures in Europe, were preceded by a period of almost no sunspot activity. However, the solar brightness over those 11-year cycles varies only by about 0.1%. As you can see from Figure 3.25, this natural variability is the *smallest* of any positive forcing listed.

Your Turn 3.23 Radiation from the Sun

Sunlight strikes the Earth continually. Which types of light are emitted by the Sun? Which one makes up the largest percentage of sunlight? *Hint:* Refer back to Figure 2.8.

Greenhouse Gases

These are the dominant anthropogenic forcings. Largest among these is CO_2 , constituting about two thirds of the warming from all greenhouse gases. However, as we explained in the previous section, methane, nitrous oxide, and other gases do contribute. Notice the relatively small contribution from "halocarbons" (CFCs and HCFCs) as shown in Figure 3.25. It has been estimated that without the ban on CFC production imposed by the Montreal Protocol, by 1990 the forcings from CFCs would have outweighed those from CO_2 . In sum, the positive forcings from greenhouse gases are more than 30 times greater than the natural changes in solar irradiance.

Land Use

Changes in land use drive climate change because these changes alter the amount of incoming solar radiation that is absorbed by the surface of the Earth. The ratio of electromagnetic radiation *reflected* from a surface relative to the amount of radiation *incident* on it is called the **albedo**. In short, albedo is a measure of the reflectivity of a surface. The albedo of the Earth's surface varies between about 0.1 and 0.9, as you can see from the values listed in Table 3.5. The higher the number, the more reflective the surface.

During periods of high sunspot activity, the aurora borealis ("northern lights") is more spectacular because of the greater number of charged particles striking the Earth's atmosphere.

The Montreal Protocol was discussed in Section 2.11.

Earth has an average albedo of 0.39. In contrast, that of the Moon is about 0.12.

Table 3.5	Albedo Values for Different Ground Covers	
Surface		Range of Albedo
fresh snow		0.80-0.90
old/melting snow		0.40-0.80
desert sand		0.40
grassland		0.25
deciduous trees		0.15–0.18
coniferous forest		0.08–0.15
tundra		0.20
ocean		0.07–0.10

As the seasons change, so does the albedo of the Earth. When a snow-covered area melts, the albedo decreases and more sunlight is absorbed, creating a positive feedback loop and additional warming. This effect helps to explain the greater increases in average temperature observed in the Arctic, where the amount of sea ice and permanent snow cover is decreasing. Similarly, when glaciers retreat and expose darker rock, the albedo decreases, causing further warming.

Human activity also can change the Earth's albedo, most notably through deforestation in the tropics. The crops we plant reflect more incoming light than does the dark green foliage of the rain forests, causing an increase in the albedo and hence resulting in *cooling*. In addition, sunlight is more consistent in the tropics, so changes in land use at low latitudes produce greater effects than changes in the polar regions. The conversion of tropical rain forest to crop and pastureland has more than offset the decrease in the amount of sea ice and snow cover near the poles. Therefore, the changes in the Earth's albedo have caused a net *cooling* effect.

Consider This 3.24 White Roofs, Green Roofs

- a. In 2009, U.S. Energy Secretary Steven Chu suggested that painting roofs white would be one way to combat global warming. Explain the reasoning behind this course of action.
- **b.** The idea of "green roofs" is also attracting attention. Planting gardens on rooftops has benefits in addition to those of white roofs. But such gardens also have limitations. Explain.

Aerosols

A complex class of materials, aerosols have a correspondingly complex effect on climate. Many natural sources of aerosols exist, including dust storms, ocean spray, forest fires, and volcanic eruptions. Human activity also can release aerosols into the environment in the form of smoke, soot, and sulfate aerosols from coal combustion.

The effect of aerosols on climate is probably the least well understood of the forcings listed in Figure 3.25. Tiny aerosol particles ($<4 \mu$ m) are efficient at scattering incoming solar radiation. Other aerosols absorb incoming radiation, and still other particles both scatter and absorb. Both processes decrease the amount of radiation available for absorption by greenhouse gases and therefore have a cooling effect (negative forcing). In a dramatic example, the 1991 eruption of Mt. Pinatubo in the Philippines spewed over 20 million tons of SO₂ into the atmosphere. In addition to providing spectacular sunsets for several months, the sulfur dioxide caused temperatures around the world to drop slightly. The results provided the climate modelers a mini-control experiment. The most reliable models were able to reproduce the cooling effect caused by the eruption.

In addition to that direct cooling effect, aerosol particles can serve as nuclei for the condensation of water droplets and hence promote cloud formation. Clouds reflect

The term *aerosol* was defined in Section 1.11. The role of aerosols in acid rain will be discussed in Section 6.6.



Mt. Pinatubo eruption, 1991.



Figure 3.26

Climate model predictions of annual global mean surface temperatures for the 20th century. Black lines display temperature data relative to the average temperature for the years 1901–1950. The blue bands indicate the predicted temperature range using natural forcings only. The pink bands indicate the predicted temperature range using *both* natural and anthropogenic forcings.

Source: Adapted from Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.

incoming solar radiation, although the effects of increased cloud cover are more complex than this. Therefore, in both direct and indirect ways, aerosols *counter* the warming effects of greenhouse gases.

Given the complexity inherent in all the forcings that we have just described, you can appreciate that assembling these forcings into a climate model is no easy task. Furthermore, once a model has been built, scientists have difficulty assessing its validity. However, scientists do have one trick in their back pockets. They can test climate models with known data sets as a means to tease apart the contributions of different forcings. For example, we know the temperature data of the 20th century. In Figure 3.26, the black lines represent the known data. Next examine the blue bands. These represent temperature ranges that were predicted by the climate model using *only* natural forcings. As you can see, the natural forcings do not map well onto the actual temperatures. Finally, examine the pink bands to see that when anthropogenic forcings are included, the temperature increases of the 20th century can be accurately reproduced. So although the last 30 years of warming were *influenced* by natural factors, the actual temperatures cannot be accounted for without including the effects of human activities.

Your Turn 3.25 Assessing Climate Models

Between 1950 and 2000, the climate models that used natural forcings only (blue bands in Figure 3.26) showed an overall cooling effect and thus did not match the observed temperatures.

- a. Name the forcings included in the models that only included natural forcings.
- **b.** List two additional forcings included in the models that more accurately recreate the temperatures of the 20th century (pink bands in Figure 3.26).

Answer

a. Aerosols (such as those from volcanic eruptions), solar irradiance.

The magnitude of future emissions, and hence the magnitude of future warming, depends on many factors. As you might expect, one is population. As of 2012, the global population stood at about 7 billion. Assuming that there will be more feet on the planet in the future, we humans are likely to have a larger **carbon footprint**, an estimate of the amount of CO_2 and other greenhouse gas emissions in a given time frame, usually a year. Having more people to feed, clothe, house, and transport will require the consumption of more energy. In turn, this translates to more CO_2 emissions, at least if using current fuels. In addition, scientists who create climate models have to include values for two factors: (1) the rate of economic growth, and (2) the rate of development of "green" (less carbon-intensive) energy sources. Again, as you might expect, both are difficult to predict.

Chapter 0 introduced the concept of an ecological footprint. Carbon footprints are a subset of the more general term.



Figure 3.27

Four model projections for temperature scenarios in the 21st century based on different socioeconomic assumptions. The black line is the data for the 20th century with the gray regions indicating the uncertainty in those values. The four dark lines represent projected 21st-century temperatures, with the wider lighter colored bands representing the uncertainty range for each scenario.

Source: Adapted from Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.

So what, if anything, can computer models tell us about the Earth's future climate? Given the uncertainties that we have listed, hundreds of different projected temperature scenarios for the 21st century are possible. Figure 3.27 shows four of these, together with the actual temperature data for the 20th century.

The four scenarios for 21st-century temperatures are based on different assumptions. The orange line assumes that emissions levels are kept at 2000 levels, admittedly an unrealistic target given the increases that already have occurred since 2000. Even with this most optimistic scenario, some additional warming will take place due to the persistence of CO_2 in the atmosphere for years to come. Both the blue and green lines assume that the global population will increase to 9 billion by 2050 but then gradually decrease. However, the blue line includes the more rapid development of energy-efficient technologies, leading to lower CO_2 emissions. The red line assumes a continually increasing population combined with a slower and less globally integrated transition to new, cleaner technologies.

All of the lines point in the same direction—up. With some amount of future warming virtually ensured, we now turn our discussion to the consequences of climate change.

3.10 The Consequences of Climate Change

Considering even the most extreme predictions of warming described in the last section, you may be thinking, "So what?" After all, the temperature changes predicted in Figure 3.27 are only a few degrees. At any single spot on the planet, the temperature fluctuates several times that amount daily.

An important distinction needs to be made between the terms *climate* and *weather*. Weather includes the daily high and low temperatures, the drizzles and downpours, the blizzards and heat waves, and the fall breezes and hot summer winds, all of which have relatively short durations. In contrast, **climate** describes regional temperatures, humidity, winds, rain, and snowfall over decades, not days. And while the weather varies on a daily basis, our climate has stayed relatively uniform over the last 10,000 years. The values quoted for the "average global temperature" are but one measure of climate phenomena. The key point is that relatively small changes in average global temperature can have huge effects on many aspects of our climate.

In addition to modeling various future temperature scenarios (see Figure 3.27), the 2007 IPCC report estimated the likelihood of various consequences. The report employed descriptive terms ("judgmental estimates of confidence") to help both policy makers and the general public better understand the inherent uncertainty of the data.

Table 3.6	Judgmental Estimates of Confidence	
Term		Probability That a Result Is True (%)
virtually certain		>99
very likely		90-99
likely		66–90
medium likelihood		33–66
unlikely		10–33
very unlikely		1–10

Source: Adapted from Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.

Subsequent updates to the IPCC reports will use these terms, along with their assigned probabilities, which are found in Table 3.6.

Conclusions from the 2007 IPCC report are listed in Table 3.7. For example, it was judged *very unlikely* that all of the observed global warming was due to natural climate variability. Rather, the scientific evidence strongly supports the position that human activity factors significantly in the increase in average global temperature observed over the last century. Furthermore, from the scientific evidence for global warming, it was judged *virtually certain* that human activities were the main drivers of recent warming. Check Table 3.7 for other conclusions relevant to any discussion of global climate change.

Many scientific organizations, including the American Association for the Advancement of Science and the American Chemical Society, also have recognized the threats posed by climate change. In an open letter to United States senators, the organizations cited sea level rise, more extreme weather events, increased water scarcity, and disturbances of local ecosystems as likely eventualities of a warmer planet. To conclude this section, we describe these and other outcomes we might expect, including sea ice disappearance, more extreme weather, changes in ocean chemistry, loss of biodiversity, and harm to human health.

Table 3.7IPCC Conclusions, 2007

Virtually Certain

Main drivers of recent warming are human activities.

Very Likely

- Human-caused emissions are the main factor causing warming since 1950.
- Higher maximum temperatures are observed over nearly all land areas.
- Snow cover decreased about 10% since the 1960s (satellite data); lake and river ice cover in the middle and high latitudes of the Northern Hemisphere was reduced by 2 weeks per year in the 20th century (independent ground-based observations).
- In most of the areas in the Northern Hemisphere, precipitation has increased.

Likely

- Temperatures in the Northern Hemisphere during the 20th century have been the highest of any century during the past 1000 years.
- Arctic sea ice thickness declined about 40% during late summer to early autumn in recent decades.
- An increase in rainfall, similar to that in the Northern Hemisphere, has been observed in tropical land areas falling between 108° North and 108° South.
- Summer droughts have increased.

Very Unlikely

The observed warming over the past 100 years is due to climate variability alone, providing new and even stronger evidence that changes must be made to stem the influence of human activities.

Each of the potential consequences can be considered in the context of the tragedy of the commons, which we encountered in Chapters 1 and 2.



Figure 3.28

The extent of Arctic ice in September 2012 in comparison to the 30-year average sea ice minimum (yellow line).

Source: Earth Observatory, NASA.

Sea Ice Disappearance

As shown in Figure 3.8, the temperatures in the Arctic are rising faster than anywhere else on Earth. One result is that sea ice is shrinking (Figure 3.28). A record low for ice cover was set in September 2012. Summer sea ice has declined about 40% from when satellites started tracking ice coverage in the late 1970s. A new analysis that uses both computer models and data from actual conditions in the Arctic region forecasts that most of the Arctic sea ice will be gone in 30 years. Not only would significant populations of wildlife be endangered, but the accompanying decrease in albedo would lead to even more warming.

Sea-Level Rise

Warmer temperatures result in an increase in sea level. This increase occurs primarily because as water warms, it expands. A smaller effect is caused by the influx of freshwater into the ocean from glacier runoff. According to a 2008 study published in the journal *Nature*, the increase was about 1.5 millimeters each year (about 7.5 cm during the past 50 years) between 1961 and 2003. However, the increases are not seen uniformly across the globe. In addition, they are influenced by regional weather patterns. Even so, these small increases in sea levels can cause erosion in coastal areas and the stronger storm surges associated with hurricanes and cyclones.

Consider This 3.26 External Costs

The consequences described earlier and later on are examples of what are known as external costs. These costs are not reflected in the price of a commodity, such as the price of a gallon of gasoline or a ton of coal, but nevertheless take a toll on the environment. The external costs of burning fossil fuels often are shared by those who emit very little carbon dioxide, such as the people of the island nation of Maldives. Although a rise of sea level of just a few millimeters may not seem like much, the effects could be catastrophic for nations that lie close to sea level. Use the resources of the Internet to investigate how the people of Maldives are preparing for rising sea levels. Also comment on how this is an example of the tragedy of the commons.

More Extreme Weather

An increase in the average global temperature could cause more extreme weather, including storms, floods, and droughts. In the Northern Hemisphere, the summers are predicted

Albedo and positive feedback were discussed in Section 3.9.

to be drier and the winters wetter. Over the past several decades, more frequent wildfires and floods have occurred on every continent. The severity (although not the frequency) of cyclones and hurricanes also may be increasing. These tropical storms extract their energy from the oceans; a warmer ocean provides more energy to feed the storms.

Changes in Ocean Chemistry

"Over the past 200 years, the oceans have absorbed approximately 550 billion tons of CO_2 from the atmosphere, or about a third of the total amount of anthropogenic emissions over that period," reports Richard A. Feely, a senior scientist with the National Pacific Marine Environmental Laboratory in Seattle. Scientists estimate that a million tons of CO_2 is absorbed into the oceans every hour of every day! In their role as carbon sinks, the world's oceans have mitigated some of the warming that carbon dioxide would have caused had it remained in the atmosphere. However, this absorption has come with a cost. Critical changes are already occurring in the oceans, as we will further explore in Chapter 6. For example, carbon dioxide is slightly soluble in water and dissolves to form carbonic acid. In turn, this is affecting marine organisms that rely on a constant level of acidity in the ocean to maintain the integrity of their shells and skeletons. The increase in carbon dioxide concentrations in the atmosphere (and also in the corresponding concentration of carbonic acid in the oceans) is putting entire marine ecosystems at risk.



Coral bleaching caused by El Nino, a consequence of global warming, Maldives, Indian Ocean, Asia.

Consider This 3.27 Plankton and You

Plankton are microscopic plant– and animal–like creatures found in both salt and freshwater systems. Many plankton species have shells made of calcium carbonate that could be weakened by more acidic environments. Although humans do not eat plankton, many other marine organisms do. Construct a food chain to show the link between plankton and humans.

Look for more about carbon dioxide and ocean acidification in Chapter 6.

Loss of Biodiversity

Climate change already is affecting plant, insect, and animal species around the world. Species as diverse as the California starfish, Alpine herbs, and checkerspot butterflies all have exhibited changes in either their ranges or their habits. Dr. Richard P. Alley, a Pennsylvania State University expert on past climate shifts, sees particular significance in the fact that animals and plants that rely on each other will not necessarily change ranges or habits at the same rate. Referring to affected species, he said, "You'll have to change what you eat, or rely on fewer things to eat, or travel farther to eat, all of which have costs." In extreme cases, those costs can cause the extinction of species. Currently, the rate of extinction worldwide is nearly 1000 times greater than at any time during the last 65 million years! A 2004 report in the journal *Nature* projects that about 20% of the plants and animals considered will face extinction by 2050, even under the most optimistic climate forecasts.

Vulnerability of Freshwater Resources

Like polar and sea ice, glaciers in many parts of the world are shrinking due to increased average temperatures (Figure 3.29). Billions of people rely on glacier runoff for both drinking water and crop irrigation. The 2007 report of the IPCC predicts that a 1 °C increase in global temperature corresponds to more than half a billion people experiencing water shortages that they have not known before. The redistribution of freshwater also has implications in food production. Drought and high temperatures could reduce crop yields in the American Midwest, but the growing range might extend farther into Canada. It is also possible that some desert regions could get sufficient rain to become arable. One region's loss may well become another locale's gain, but it is too early to tell.



Many different species of checkerspot butterflies exist. This one is found in parts of Wisconsin.

For more on the chemistry of water availability and use, see Section 5.3.



Human Health

We may all be losers in a warmer world. In 2000, the WHO attributed over 150,000 premature deaths worldwide to the effects of climate change. Those effects included more frequent and severe heat waves, increased droughts in already water-stressed regions, and infectious diseases in regions where they had not occurred before. Further increases in average temperatures are expected to expand the geographical range of mosquitoes, tsetse flies, and other disease-carrying insects. The result could be a significant upturn in illnesses such as malaria, yellow and dengue fevers, and sleeping sickness in new areas, including Asia, Europe, and the United States.

3.11 What Can (or Should) We Do About Climate Change?

The debate over climate change has shifted in the last 20 years. Today's scientific data leave little room for doubt about whether it is occurring. For example, measurements of higher surface and ocean temperatures, retreating glaciers and sea ice, and rising sea levels are unequivocal. In addition, the carbon isotopic ratio found in atmospheric CO_2 (discussed in Section 3.6) leaves little doubt that human activity is responsible for much of the observed warming. However, at issue is what we *can* do and what we *should* do about the changes that are occurring.

Consider This 3.28 Carbon Footprint Calculations

Investigate three websites that calculate your carbon footprint.

- **a.** For each site, list the name, the sponsor, and the information requested in order to calculate the carbon footprint.
- b. Does the information requested differ from site to site? If so, report the differences.
- c. List two advantages and two disadvantages of doing a carbon footprint calculation.

Figure 3.29

A view of the Exit Glacier in Kenji Fjords National Park, Alaska, in 2008. The sign in the foreground marks the extent of the ice flow in 1978.

For more on food metabolism as a source of energy, see Section 11.9. Energy is essential for every human endeavor. Personally, you obtain the energy you need by eating and then metabolizing food. As a community or nation, we meet our energy needs in a variety of ways, including by burning coal, petroleum, and natural gas. The combustion of these carbon-based fuels produces several waste products, including carbon dioxide. The countries with large populations and those that are highly industrialized tend to burn the largest quantities of fuels and as a result emit the most CO_2 . According to the Carbon Dioxide Information Analysis Center (CDIAC) of Oak Ridge National Laboratory, in 2008, the top CO_2 emitters were China, the United States, the Russian Federation, India, and Japan. Which other nations rank high on the list? The next activity shows you how to find out.

Consider This 3.29 Carbon Emissions by Nation

CDIAC publishes a list of the top 20 nations for CO_2 emissions.

- **a.** From what you already know, predict any five of the nations (in addition to those listed in the previous paragraph) that are on this list. Check how accurate your predictions were by using the Internet.
- b. How would these rankings change if they were listed per capita?

In a 2008 address, John Holdren summarized our options in dealing with climate change with three words: mitigation, adaptation, and suffering. "Basically, if we do less mitigation and adaptation, we're going to do a lot more suffering," he concluded. But who will be responsible for the mitigation? Who will be forced to adapt? Who will bear the brunt of the suffering? It is likely that significant disagreements will arise regarding answers to these questions. But we can agree that any practical solution must be global in nature and include a complicated mix of risk perception, societal values, politics, and economics.

Climate mitigation is any action taken to permanently eliminate or reduce the long-term risk and hazards of climate change to human life, property, or the environment. The most obvious strategy for minimizing anthropogenic climate change is to reduce the amount of CO_2 emitted into the atmosphere in the first place. Take a look back at Figure 3.21. It is difficult to imagine curtailing any of these "necessities" to any great extent. Therefore decreasing our energy consumption will not be easy, at least in the short term. The simplest and least expensive approach is to improve energy efficiency. Due to the inefficiencies associated with energy production, saving energy on the consumer end multiplies its effect on the production end three to five times. However, relying on the individual consumers worldwide to buy the right goods and do the right things will not be sufficient to hold CO_2 emissions below dangerous levels.

A developing technology aimed at slowing the rate of carbon dioxide emissions is to capture and isolate the gas after combustion. **Carbon capture and storage (CCS)** involves separating CO_2 from other combustion products and storing (sequestration) it in a variety of geologic locations. If the CO_2 is properly immobilized, it cannot reach the atmosphere and contribute to global warming. In addition to the large technological challenges posed by CCS, high start-up costs, usually in excess of \$1 billion per power plant, so far are limiting this approach as a mitigation strategy.

Although at least two dozen projects are in development worldwide, as of 2009, only four industrial-scale CCS projects were in operation. Three remove CO_2 from natural gas reservoirs and store it in various underground geologic formations (Figure 3.30). The fourth and largest project, located in Saskatchewan, Canada, takes CO_2 captured from a coal-fired power plant in North Dakota and injects it into a depleted oil field. By doing so, additional oil is forced up through the existing wells for recovery. The benefits of enhancing oil recovery combined with CO_2 sequestration could become a model for other types of projects. Combined, these CCS efforts store about 5 million metric tons of carbon dioxide annually.

We will present more thoughts from John Holdren in the conclusion.

Chapter 4 focuses on energy from fossil fuels, Chapter 7 on nuclear energy, and Chapter 8 on some alternative energy sources such as wind and solar power.



Figure 3.30

Methods for carbon dioxide sequestration.

Your Turn 3.30 Carbon Capture Limitations

Refer back to the global carbon cycle in Figure 3.20. What percent of global carbon dioxide emissions from fossil fuel burning is captured by current CCS technology?

Critics of CCS technology dispute its ultimate efficacy for slowing atmospheric CO_2 buildup, citing high costs as well as the long time frame for commercial implementation. Others contend that pursuing CCS simply delays and distracts attention from developing carbon-free energy sources. Finally, there is the sheer magnitude of the problem. According to the International Energy Agency, in order for CCS to make a meaningful contribution to mitigation efforts by 2050, it would require nearly 6000 installations *each* injecting a million metric tons of CO_2 per year into the ground.

A low-tech sequestration strategy is to reverse the extensive deforestation activities that are occurring predominantly in the world's tropical rainforests. Started in 2006 by the United Nations Development Programme and the World Agroforestry Center, the "Billion Trees Campaign" seeks to slow climate change by planting trees in depleted forests. During the first 18 months of the program, over 2 billion trees were planted, mostly in Africa. By 2012, over 12 billion trees were planted. If this number of trees seems like a lot, remember the scale of deforestation; in 2005, forest area equal to about 35,000 football fields was cleared *every day*!

Your Turn 3.31 Trees as Carbon Sinks

An average-sized tree absorbs 25 to 50 pounds of carbon dioxide each year. In the United States, the average annual per capita CO_2 emission is 19 tons.

- **a.** How many trees would be required to absorb the annual CO_2 emissions for an average U.S. citizen?
- b. What percentage of annual global emissions from burning fossil fuels could be absorbed by 12 billion trees?

Hint: Refer back to Figure 3.20.

Regardless of any potential decreases in future emissions, some effects of climate change are unavoidable. As mentioned previously, many of the CO_2 molecules emitted today will remain in the atmosphere for centuries. **Climate adaptation** refers to the ability of a system to adjust to climate change (including climate variability and extremes) to moderate potential damage, to take advantage of opportunities, or to cope with the consequences. Some adaptive methods include developing new crop varieties and shoring up or constructing new coastline defense systems for low-lying countries and islands. The further spread of infectious diseases could be minimized by enhanced public health systems. Many of these strategies are win–win situations that would benefit societies even in the absence of climate change challenges.

Compared with the scientific consensus on understanding the role greenhouse gases play in the Earth's climate, there is much less agreement among governments regarding what actions should be taken to limit greenhouse gas emissions. One outcome from the Earth Summit held in 1992 in Rio de Janeiro was the Framework Convention on Climate Change. The goal of this international treaty was "to achieve stabilization of greenhouse gas concentrations in the atmosphere at a low enough level to prevent dangerous anthropogenic interference with the climate system." Not only was this treaty nonbinding, but also there was no agreement about what "dangerous anthropogenic interference" meant, or what level of greenhouse gas emissions would be necessary to avoid it.

In 1997, the first international treaty imposing legally binding limits on greenhouse gas emissions was written by nearly 10,000 participants from 161 countries gathered in Kyoto, Japan. The result has come to be known as the Kyoto Protocol. Binding emission targets based on 1990 levels were set for 38 developed nations to reduce their emissions of six greenhouse gases. The gases regulated include carbon dioxide, methane, nitrous oxide, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride. The United States was expected to reduce emissions to 7% below its 1990 levels, the European Union (EU) nations 8%, and Canada and Japan 6% by 2012.

Consider This 3.32 The British Experience

The British Labour Party in 1997, under the leadership of Tony Blair, committed to cut British greenhouse gas emissions 20% by 2010. This is significantly more than the 12.5% required by the Kyoto treaty. Did Britain meet its goal? Research this question and write a short report on the British experience in reducing greenhouse gases. Have other countries been able to reduce their emissions significantly since 1997?

Although the treaty went into effect in 2005 (when ratified by the Russian Federation), the United States never opted to participate. One reason was the belief that meeting the reduction requirements set by the protocol would cause serious harm to the U.S. economy. Another reason for not ratifying the protocol was concern about the lack of emissions limitations on developing nations, mainly China and India; those countries are expected to show the most dramatic increases in carbon dioxide emissions in the coming years. The administration of President George W. Bush argued that such unequal burdens between developed and developing countries would be economically disastrous to the United States.

The United States has also resisted domestic legislation to restrict CO_2 emissions on similar economic grounds. Voluntary reduction programs implemented during the early 2000s proved insufficient to reduce emissions for a variety of reasons. One "problem" is that fossil fuels are too cheap. A second problem is that any mitigation measures entail significant up-front costs, and just as importantly, the cost of mitigation is not known with certainty, making it difficult for corporations to plan effectively. The world's current energy infrastructure cost \$15 trillion to develop and distribute, and reducing carbon dioxide emissions will mean replacing much of that infrastructure. A final problem lies in the fact that the benefits of emissions reductions will not be felt for decades because of the long residence time of CO_2 molecules in the atmosphere.

Chapter 3

Now, 20 years after the Earth Summit, scientific consensus is beginning to focus on determining what levels of CO_2 are considered "dangerous." At the United Nations Climate Conference in 2007, participating scientists concluded that greenhouse gas emissions need to peak by about 2020, and then be reduced to well below half of current levels by 2050. In absolute terms, that means that annual global emissions must be decreased by about 9 billion tons. To give you a scale of the magnitude of this goal, reducing emissions by 1 billion tons requires one of the following changes.

- Cutting energy usage in the world's buildings by 20–25% below business-as-usual.
- Having all cars get 60 mpg instead of 30 mpg.
- Capturing and sequestering carbon dioxide at 800 coal-burning power plants.
- Replacing 700 large coal-burning power plants with nuclear, wind, or solar power.

Clearly, implementation of any one of those (and the projected goal is 9 billion tons) will not be accomplished on a purely voluntary basis. In the United States and elsewhere, there is a burgeoning realization that laws and regulations are needed to reduce greenhouse gas emissions. One example is a "cap-and-trade" system, such as the one that has been successful in reducing the emission of oxides of both sulfur and nitrogen in the United States. The "trade" part of the cap-and-trade system works through a system of allowances. Companies are assigned allowances that authorize the emission of a certain quantity of CO_2 , either during the current year or any year thereafter. At the end of a year, each company must have sufficient allowances to cover its actual emissions. If it has extra allowances, it can trade or sell them to another company that might have exceeded their emissions limit. If a company has insufficient allowances, it must purchase them. The "cap" is enforced by creating only a certain number of allowances each year.

Here's an example of how cap-and-trade works. Without emission restrictions, Plant A emits 600 tons of CO_2 and Plant B emits 400 tons. To get under the imposed cap, they are required to reduce their combined emissions by 300 tons (30%). One way to accomplish this is for each to reduce their own emissions by 30%, each accruing the associated costs. It is likely, however, that one of the plants (Plant B in Figure 3.31) would be more efficient in their emissions reductions, and lower their emissions below the prescribed 30%. In that case, Plant A can purchase some unused emissions permits from Plant B, at a cost less than that required for Plant A to comply with the 30% emissions reduction. The *overall* emissions reductions are then arrived at in the most financially beneficial way for both plants.



Figure 3.31

The emissions cap-and-trade concept.

Source: EPA, Clearing the Air, The Facts About Capping and Trading Emissions, 2002, page 3.

Section 6.11 describes in detail the damage caused by the oxides of nitrogen and sulfur. The cap-and-trade system has some possible disadvantages, including a potentially volatile market for the emissions permits. Energy providers might experience wide, often unpredictable swings in their energy costs. Those swings would result in large fluctuations in consumer costs. As an alternative to cap-and-trade, some advocate a carbon tax instead of a cap-and-trade program. Instead of limiting emissions and letting the market decide how "best" to comply, a carbon tax simply increases the cost of burning fossil fuels. Placing an additional cost based on the amount of carbon contained in a certain quality of fuel is intended to make alternative energy sources more competitive in the near term. Of course, levying a tax on carbon fuels or emissions will mean higher prices for consumers as well.

Consider This 3.33 Climate Change Insurance?

Mitigation of climate change can be seen as a risk-benefit scenario. As such, uncertainty about future effects may discourage governments from taking financially costly actions. Another way of tackling climate change is to view it as a risk-management problem, analogous to the reasons we buy insurance. Having car insurance doesn't reduce the likelihood of being involved in an accident, but it can limit the costs if an accident should occur. How might the insurance analogy fit in with climate change actions and policies?

Although the U.S. federal government has been slow to produce binding climate change legislation, individual states have taken matters into their own hands. The 10 northeastern states that make up the Regional Greenhouse Gas Initiative (RGGI) signed the first U.S. cap-and-trade program for carbon dioxide. The program began by capping emissions at current levels in 2009 and then reducing emissions 10% by 2019. The Midwestern Regional Greenhouse Gas Reduction Accord states developed a multi-sector cap-and-trade system to help meet a long-term target of 60–80% below current emissions levels. Western Climate Initiative states, as well as British Columbia and Manitoba (the first participating jurisdictions outside of the United States), agreed to mandatory emissions reporting, as well as regional efforts to accelerate development of renewable energy technologies.

More locally, the U.S. Mayors Climate Protection Agreement included 227 cities committed to cutting emissions to meet the targets of the Kyoto Protocol. The cities represented include some of the largest in the Northeast, the Great Lakes region, and West Coast, and their mayors represent some 44 million people.

Skeptical Chemist 3.34 Drop in the Bucket?

Critics suggest that actions made by individual states or countries, even if successful, cannot possibly have a significant effect on global emissions of greenhouse gases. Proponents for immediate action, such as NASA climate scientist James Hansen, take a different approach. "China and India have the most to lose from uncontrolled climate change because they have huge populations living near sea level. Conversely then, they also have the most to gain from reduced local air pollution. They must be a part of the solution to global warming, and I believe they will be if developed nations such as the United States take the appropriate first steps." After studying this chapter, which side do you fall on? Explain.

Consider This 3.35 Carbon Dioxide Revisited

After reading this chapter, what facts do you now know about carbon dioxide? List them. Also list the sources of carbon dioxide in the atmosphere. Compare these lists to those from Consider This 3.1. Have they changed? Explain.

Conclusion

We began our journey into global climate change by stating that chimpanzees attempt to adapt to changes in climate without arguing whether change is happening. How are humans noticing and adapting to climate change? Let's look at the following assertion.

John Holdren, director of the White House Office of Science and Technology Policy, has said several times, "Global warming is a misnomer, because it implies something that is gradual, something that is uniform, something that is quite possibly benign. What we are experiencing with climate change is none of those things."

The first assertion is that global warming isn't gradual. By this he means that in comparison with the past, the climate changes we are seeing today are occurring much more rapidly. Natural climate changes are part of our planet's history. Glaciers, for example, have advanced and retreated numerous times, and global temperatures have been both much higher and much lower than the temperatures we currently experience. But the geologic evidence indicates these past changes occurred over millennia, not decades as they are today. So Holdren is correct. Global warming is not gradual, at least not in comparison with the geologic time frames of the past.

Second, he asserts that global warming does not occur uniformly across the globe. Holdren is right again. To date, the most dramatic effects have been observed at the poles. These include quickly receding glaciers, shrinking sea ice, and melting permafrost. So far, the more densely populated lower latitudes have experienced far smaller effects from climate change.

His third assertion, that global warming might not be benign, is the most difficult to assess. The issue is complicated in part because we cannot predict with certainty which aspects of our planet global warming will affect and to what degree. It is further complicated because we cannot easily understand why only a few degrees of warming might be catastrophic.

As evidenced by Holdren's points, global climate change is an extremely complicated phenomenon. Like it or not, we are in the midst of conducting a planetwide experiment, one that will test our ability to sustain both our economic development and our environment.

Chapter Summary

Having completed this chapter you should be able to:

- Understand the different processes that take part in Earth's energy balance (3.1)
- Compare and contrast the Earth's natural greenhouse effect and the enhanced greenhouse effect (3.1)
- Understand the major role that certain atmospheric gases play in the greenhouse effect (3.1–3.2)
- Explain the methods used to gather past evidence of greenhouse gas concentrations and global temperatures (3.2)
- Use Lewis structures to determine molecular geometry and bond angles of molecules (3.3)
- Relate molecular geometry to absorption of infrared radiation (3.4)
- List the major greenhouse gases and explain why each has the appropriate molecular geometry to be a greenhouse gas (3.4)
- Explain the roles that natural processes play in the carbon cycle and climate change (3.5)
- Evaluate how human activities contribute to the carbon cycle and climate change (3.5)
- Understand how molar mass is defined and used (3.6)

- Calculate the average mass of an atom using Avogadro's number (3.6)
- Demonstrate the usefulness of the chemical mole (3.7)
- Assess the sources, relative emission quantities, and effectiveness of greenhouse gases other than CO₂ (3.8)
- Evaluate the roles of natural and anthropogenic climate forcings (3.9)
- Recognize the successes and limitations of computerbased models in predicting climate change (3.9)
- Correlate some of the major consequences of climate change with their likelihood (3.10)
- Evaluate the advantages and disadvantages of proposed greenhouse gas regulations (3.11)
- Provide examples of climate mitigation and climate adaptation strategies (3.11)
- Analyze, interpret, evaluate, and critique news stories on climate change (3.1–3.12)
- Take an informed position with respect to issues surrounding climate change (3.1–3.12)

Questions

Emphasizing Essentials

- 1. The chapter concluded with a quote from John Holdren: "Global warming is a misnomer, because it implies something that is gradual, something that is uniform, something that is quite possibly benign. What we are experiencing with climate change is none of those things." Use examples to:
 - a. explain why climate change is not uniform.
 - b. explain why it is not gradual, at least in comparison to how quickly social and environmental systems can adjust.
 - c. explain why it probably will not be benign.
- 2. The surface temperatures of both Venus and Earth are warmer than would be expected on the basis of their respective distances from the Sun. Explain.
- 3. Using the analogy of a greenhouse to understand the energy radiated by Earth, of what are the "windows" of Earth's greenhouse made? In what ways is the analogy not precisely correct?
- 4. Consider the photosynthetic conversion of CO_2 and H_2O to form glucose, $C_6H_{12}O_6$, and O_2 .
 - a. Write the balanced equation.
 - b. Is the number of each type of atom on either side of the equation the same?
 - c. Is the number of molecules on either side of the equation the same? Explain.
- 5. Describe the difference between climate and weather.
- 6. a. It is estimated that 29 megajoules per square meter (MJ/m²) of energy comes to the top of our atmosphere from the Sun each day, but only 17 MJ/m² reaches the surface. What happens to the rest?
 - b. Under steady-state conditions, how much energy would leave the top of the atmosphere?
- 7. Consider Figure 3.9.
 - a. How does the present concentration of CO₂ in the atmosphere compare with its concentration 20,000 years ago? With its concentration 120,000 years ago?
 - b. How does the present temperature of the atmosphere compare with the 1950–1980 mean temperature? With the temperature 20,000 years ago? How does each of these values compare with the average temperature 120,000 years ago?
 - c. Do your answers to parts **a** and **b** indicate causation, correlation, or no relation? Explain.

- 8. Understanding Earth's energy balance is essential to understanding the issue of global warming. For example, the solar energy striking the Earth's surface averages 168 watts per square meter (W/m²), but the energy leaving Earth's surface averages 390 W/m². Why isn't the Earth cooling rapidly?
- 9. Explain each of these observations.
 - a. A car parked in a sunny location may become hot enough to endanger the lives of pets or small children left in it.
 - b. Clear winter nights tend to be colder than cloudy ones.
 - c. A desert shows much wider daily temperature variation than a moist environment.
 - d. People wearing dark clothing in the summertime put themselves at a greater risk of heatstroke than those wearing white clothing.
- 10. Construct a methane molecule (CH₄) from a molecular model kit (or use Styrofoam balls or gumdrops to represent the atoms and toothpicks to represent the bonds). Demonstrate that the hydrogen atoms would be farther from one another in a tetrahedral arrangement than if they all were in the same plane (square planar arrangement).
- **11.** Draw the Lewis structure and name the molecular geometry for each molecule.
 - a. H₂S
 - b. OCl₂ (oxygen is the central atom)
 - c. N₂O (nitrogen is the central atom)
- 12. Draw the Lewis structure and name the molecular geometry for these molecules.
 - a. PF_3
 - b. HCN (carbon is the central atom)
 - c. CF_2Cl_2 (carbon is the central atom)
- **13.** a. Draw the Lewis structure for methanol (wood alcohol), H₃COH.
 - b. Based on this structure, predict the H–C–H bond angle. Explain your reasoning.
 - c. Based on this structure, predict the H–O–C bond angle. Explain your reasoning.
- a. Draw the Lewis structure for ethene (ethylene), H₂CCH₂, a small hydrocarbon with a C=C double bond.
 - b. Based on this structure, predict the H–C–H bond angle. Explain your reasoning.
 - c. Sketch the molecule showing the predicted bond angles.

15. Three different modes of vibration of a water molecule are shown. Which of these modes of vibration contributes to the greenhouse effect? Explain.



- 16. If a carbon dioxide molecule interacts with certain photons in the IR region, the vibrational motions of the atoms are increased. For CO_2 , the major wavelengths of absorption occur at 4.26 μ m and 15.00 μ m.
 - **a.** What is the energy corresponding to each of these IR photons?
 - b. What happens to the energy in the vibrating CO₂ species?
- 17. Water vapor and carbon dioxide are greenhouse gases, but N_2 and O_2 are not. Explain.
- 18. Explain how each of these relates to global climate change.
 - a. volcanic eruptions
 - b. CFCs in the stratosphere
- **19.** Termites possess enzymes that allow them to break down cellulose into glucose, $C_6H_{12}O_6$, and then metabolize the glucose into CO_2 and CH_4 .
 - a. Write a balanced equation for the metabolism of glucose into CO₂ and CH₄.
 - b. What mass of CO₂, in grams, could one termite produce in one year if it metabolized 1.0 mg glucose in one day?
- 20. Consider Figure 3.21.
 - a. Which sector has the highest CO₂ emission from fossil-fuel combustion?
 - b. What alternatives exist for each of the major sectors of CO₂ emissions?
- **21.** Silver has an atomic number of 47.
 - a. Give the number of protons, neutrons, and electrons in a neutral atom of the most common isotope, Ag-107.

- b. How do the numbers of protons, neutrons, and electrons in a neutral atom of Ag-109 compare with those of Ag-107?
- 22. Silver only has two naturally occurring isotopes: Ag-107 and Ag-109. Why isn't the average atomic mass of silver given on the periodic table simply 108?
- 23. a. Calculate the average mass in grams of an individual atom of silver.
 - b. Calculate the mass in grams of 10 trillion silver atoms.
 - c. Calculate the mass in grams of 5.00×10^{45} silver atoms.
- 24. Calculate the molar mass of these compounds. Each plays a role in atmospheric chemistry.
 - **a.** H₂O
 - **b.** CCl_2F_2 (Freon-12)
 - c. N_2O
- 25. a. Calculate the mass percent of chlorine in CCl_3F (Freon-11).
 - b. Calculate the mass percent of chlorine in CCl_2F_2 (Freon-12).
 - c. What is the maximum mass of chlorine that could be released in the stratosphere by 100 g of each compound?
 - d. How many atoms of chlorine correspond to the masses calculated in part **c**?
- 26. The total mass of carbon in living systems is estimated to be 7.5×10^{17} g. Given that the total mass of carbon on Earth is estimated to be 7.5×10^{22} g, what is the ratio of carbon atoms in living systems to the total carbon atoms on Earth? Report your answer in percent and in ppm.
- 27. Consider the information presented in Table 3.3.
 - a. Calculate the percent increase in CO₂ when comparing 2012 concentrations with preindustrial concentrations.
 - b. Considering CO₂, CH₄, and N₂O, which has shown the greatest percentage increase when comparing 2011 concentrations with preindustrial concentrations?
- **28.** Other than atmospheric concentration, what two other properties are included in the calculation of the global warming potential for a substance?
- 29. Total greenhouse gas emissions in the United States rose 16% from 1990 to 2005, growing at a rate of 1.3% a year since 2000. How is this possible when CO₂ emissions grew by 20% in the same time period? *Hint:* See Table 3.3.

Concentrating on Concepts

- 30. John Holdren, quoted in the conclusion of the chapter, suggests that we use the term *global climatic disruption* rather than *global warming*. After studying this chapter, do you agree with his suggestion? Explain.
- 31. The Arctic has been called "our canary in the coal mine for climate impacts that will affect us all."
 - a. What does the phrase "canary in the coal mine" mean?
 - b. Explain why the Arctic serves as a canary in a coal mine.
 - c. The melting of the tundra accelerates changes elsewhere. Give one reason.
- 32. Do you think the comment made in the cartoon is justified? Explain.



about global warming "

Source: From The Wall Street Journal. Permission by Cartoon Features Syndicate.

- **33.** Given that direct measurements of Earth's atmospheric temperature over the last several thousands of years are not available, how can scientists estimate past fluctuations in the temperature?
- 34. A friend tells you about a newspaper story that stated, "The greenhouse effect poses a serious threat to humanity." What is your reaction to that statement? What would you tell your friend?
- 35. Over the last 20 years, about 120 billion tons of CO_2 has been emitted from the burning of fossil fuels, yet the amount of CO_2 in the atmosphere has risen only by about 80 billion tons. Explain.

- 36. Carbon dioxide gas and water vapor both absorb IR radiation. Do they also absorb visible radiation? Offer some evidence based on your everyday experiences to help explain your answer.
- 37. How would the energy required to cause IR-absorbing vibrations in CO_2 change if the carbon and oxygen atoms were connected by single rather than double bonds?
- 38. Explain why water in a glass cup is quickly warmed in a microwave oven, but the glass cup itself warms much more slowly, if at all.
- **39.** Ethanol, C₂H₅OH, can be produced from sugars and starches in crops such as corn or sugarcane. The ethanol is used as a gasoline additive and when burned, it combines with O₂ to form H₂O and CO₂.
 - a. Write a balanced equation for the complete combustion of C_2H_5OH .
 - b. How many moles of CO_2 are produced from each mole of C_2H_5OH completely burned?
 - c. How many moles of O_2 are required to burn 10 mol of C_2H_5OH ?
- 40. Explain whether each of the radiative forcings described in Section 3.9 is positive or negative and rank them in terms of importance to overall climate change predictions.
- 41. Why is the atmospheric lifetime of a greenhouse gas important?
- 42. Compare and contrast stratospheric ozone depletion and climate change in terms of the chemical species involved, the type of radiation involved, and the predicted environmental consequences.
- 43. Explain the term *radiative forcings* to someone unfamiliar with climate modeling.
- **44.** It is estimated that Earth's ruminants, such as cattle and sheep, produce 73 million metric tons of CH_4 each year. How many metric tons of carbon are present in this mass of CH_4 ?
- 45. Nine of the ten warmest years since 1880 have occurred since the year 2000. Does this *prove* that the enhanced greenhouse effect (global warming) is taking place? Explain.
- 46. A possible replacement for CFCs is HFC-152a, with a lifetime of 1.4 years and a GWP of 120. Another is HFC-23, with a lifetime of 260 years and a GWP of 12,000. Both of these possible replacements have a significant effect as greenhouse gases and are regulated under the Kyoto Protocol.
 - a. Based on the given information, which appears to be the better replacement? Consider only the potential for global warming.
 - b. What other considerations are there in choosing a replacement?

Chapter 3

47. The emissions of CO₂ from fossil fuel burning can be reported in different ways. For example, the Carbon Dioxide Information Analysis Center (CDIAC) reported in 2009 that China, the United States, and India ranked highest among world nations:

		Metric tons
Ranking	Nation	of CO ₂
#1	China (mainland)	2,096,295
#2	United States	1,445,204
#3	India	539,794

- a. Would the rankings change if expressed on a per capita basis? If so, which nation would rank first?
- b. CDIAC reports the per capita rankings on the basis of metric tons carbon emitted, rather than metric tons CO_2 . Qatar leads the world in per capita emissions at 12.01 metric tons carbon. Would this value be higher or lower if expressed on the basis of metric tons of CO_2 emitted? Explain.
- 48. Compare and contrast a cap-and-trade system with a carbon tax.
- 49. When Arrhenius first theorized the role of atmospheric greenhouses, he calculated that doubling the concentration of CO₂ would result in an increase of 5–6 °C in the average global temperature. How far off was he from the current IPCC modeling?
- 50. Now that you have studied air quality (Chapter 1), stratospheric ozone depletion (Chapter 2), and global warming (Chapter 3), which do you believe poses the most serious problem for you in the short run? In the long run? Discuss your reasons with others and draft a short report on this question.

Exploring Extensions

- 51. Former vice president Al Gore writes in his 2006 book and film, An Inconvenient Truth: "We can no longer afford to view global warming as a political issue rather, it is the biggest moral challenge facing our global civilization."
 - a. Do you believe that global warming is a moral issue? If so, why?
 - b. Do you believe that global warming is a political issue? If so, why?
- 52. China's growing economy is fueled largely by its dependence on coal, described as China's "double-edged sword." Coal is both the new economy's "black gold" and the "fragile environment's dark cloud."

- a. What are some of the consequences of dependence on high-sulfur coal?
- b. Sulfur pollution from China may slow global warming, but only temporarily. Explain.
- c. What other country is rapidly stepping up its construction of coal-fired power plants and is expected to have a larger population than China by the year 2030?
- 53. The quino checkerspot butterfly is an endangered species with a small range in northern Mexico and southern California. Evidence reported in 2003 indicates that the range of this species is even smaller than previously thought.
 - a. Propose an explanation why this species is being pushed north, out of Mexico.
 - b. Propose an explanation why this species is being pushed south, out of southern California.
 - c. Propose a plan to prevent further harm to this endangered species.
- 54. Data taken over time reveal an increase in CO_2 in the atmosphere. The large increase in the combustion of hydrocarbons since the Industrial Revolution is often cited as a reason for the increasing levels of CO_2 . However, an increase in water vapor has *not* been observed during the same period. Remembering the general equation for the combustion of a hydrocarbon, does the difference in these two trends *disprove* any connection between human activities and global warming? Explain your reasoning.
- 55. In the energy industry, 1 standard cubic foot (SCF) of natural gas contains 1196 mol of methane (CH₄) at 15.6 °C (60 °F). *Hint:* See Appendix 1 for conversion factors.
 - a. How many moles of CO_2 could be produced by the complete combustion of 1 SCF of natural gas?
 - b. How many kilograms of CO₂ could be produced?
 - c. How many metric tons of CO₂ could be produced?
- 56. An international conference on climate change was held in Copenhagen in December 2009. Write a brief summary of the outcomes of this conference.
- 57. A solar oven is a low-tech, low-cost device for focusing sunlight to cook food. How might solar ovens help mitigate global warming? Which regions of the world would benefit most from using this technology?
- 58. In 2005, the European Union adopted a cap-and-trade policy for carbon dioxide. Write a short report on the outcomes of this policy, both in terms of the economic result and the effect it has had on European greenhouse gas emissions.

- 59. The world community responded differently to the atmospheric problems described in Chapters 2 and 3. The evidence of ozone depletion was met with the Montreal Protocol, a schedule for decreasing the production of ozone-depleting chemicals. The evidence of global warming was met with the Kyoto Protocol, a plan calling for targeted reduction of greenhouse gases.
 - a. Suggest reasons why the world community dealt with the issue of ozone depletion *before* that of global warming.
- b. Compare the current status of the two responses. When was the latest amendment to the Montreal Protocol? How many nations have ratified it? Has the level of chlorine in the stratosphere dropped as a result of the Montreal Protocol? How many nations have ratified the Kyoto Protocol? What has happened since it went into effect? Have any other initiatives been proposed? Have levels of greenhouse gases dropped as a result of the Kyoto Protocol?