CHAPTER 3

CHEMICALS IN THE “CLEAN” ATMOSPHERE

When you peer up at the sky, your eyes do not detect the huge number of chemical reactions taking place. These persistent reactions protect you from harmful solar radiation, rid the atmosphere of chemical wastes, and recycle the chemicals released in natural growth and decay cycles. It has taken billions of years for the atmospheric system to evolve into its current state, one that supports life as we know it.

Atmospheric chemists are helping us to understand the complexity of the chemical reactions occurring in the atmosphere. Some of the most important chemical compounds taking part in these reactions are present in exceedingly small concentrations. These compounds are highly reactive and critical in destroying pollutants and absorbing or reflecting photons from the Sun. Relatively small changes in the amounts of some atmospheric constituents alter delicate chemical balances. In order to understand the sensitivity of atmospheric processes to human activity, we must understand the chemical makeup of the atmosphere, the chemical characteristics of atmospheric components, and the processes that control the distribution of the various chemicals within the atmosphere.

The chemical structure of atmospheric components is important in determining what specific effect each of these components has on human health and on the human environment. Thus, the beginning of this chapter provides a fair amount of chemical detail, defining terms such as molecules, phases of matter, and chemical
formulas. It also explains why some atmospheric molecules that are present in relative small amounts are exceedingly critical in environmental problems.

Questions Answered in This Chapter

1. What is the chemical composition of the atmosphere?

2. What are the characteristics of atmospheric gases?

3. What is the chemical significance of atmospheric pressure and temperature?

4. Why do atoms come together to form atmospheric molecules?

5. Are there rules for predicting the stability of atmospheric molecules?

6. What causes atmospheric layers and the Earth’s wind patterns?

7. What critical chemical reactions occur in the upper layers of the atmosphere?

Molecules and Chemical Formulas

A **molecule** is a combination of a fixed number of atoms bonded together by chemical forces in a specific geometrical arrangement. A **chemical formula** represents the fixed atomic composition of a substance.

<table>
<thead>
<tr>
<th>Example 3-1</th>
<th>Information in chemical formulas</th>
</tr>
</thead>
<tbody>
<tr>
<td>What information does the formula for a water molecule convey?</td>
<td></td>
</tr>
</tbody>
</table>

We are all quite familiar with water, a highly variable atmospheric component. On humid days, there are a large number of water molecules in the atmosphere. On very dry days, the number of water molecules is relatively smaller. The chemical formula of water is H₂O, which conveys the information that every water molecule contains two hydrogen atoms and one oxygen atom. The composition and geometrical arrangement of these atoms is the same in each water molecule and is responsible for the special properties of water considered in detail in Chapter 4.

<table>
<thead>
<tr>
<th>Exercise 3-2</th>
<th>Information in chemical formulas</th>
</tr>
</thead>
<tbody>
<tr>
<td>What information is contained in the formulas of the following atmospheric molecules: oxygen (O₂), carbon dioxide (CO₂), nitrogen (N₂), and ammonia (NH₃).</td>
<td></td>
</tr>
</tbody>
</table>
Phases of Matter, Mixtures and Compounds

A gas is formally defined as one of the three fundamental phases of matter (solid, liquid, and gas). A gas completely fills and conforms to the shape of any containing vessel and is easily compressed. Atmospheric gases have outer space as part of their “container” because they are held to the surface of the Earth through gravitational forces.

A liquid is a phase of matter that flows easily, conforms to the shape of the confining vessel, and is relatively incompressible. Raindrops are examples of the formation of liquids from a gas (water vapor) in the atmosphere. Lakes are confined by depressions in the earth and the shoreline.

A solid is a phase of matter that has a definite volume and shape and resists forces that tend to change these properties. Atmospheric soot, ice clouds, and dust particles are finely divided solids.

Mixtures are combinations of two or more substances that are not chemically united, composed of any of the three phases of matter with no fixed amounts of each phase. For example, the atmosphere is really a mixture of gases, liquids, and solids. Salt and sand form a mixture. Salt dissolved in water forms a mixture. Lemon juice in tea forms a mixture. Because its water vapor content is highly variable, the composition of the atmosphere is not completely fixed. The amount of atmospheric dust and solids is variable in different parts of the Earth. Visible smoke coming from a chimney is a mixture of gases, solids, and sometimes liquids in the form of minute, visible droplets.

Chemical compounds are pure substances that are composed of two or more elements chemically combined in characteristic, fixed proportions. Water is a compound because there are exactly twice as many hydrogen atoms as oxygen atoms in every water molecule. Salt (NaCl) is a compound because there is always one Na for every Cl. However, salt is not composed of molecules but of positively and negatively charged ions, Na⁺ and Cl⁻ (Chapter 4).

<table>
<thead>
<tr>
<th>Exercise 3-3</th>
<th>Phases of matter &amp; mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characterize each of the following as a solid, a liquid, a gas, a mixture, or a pure compound: a cloud, distilled water, contaminated tap water, contents of a volcanic eruption, a rainstorm, fog, ice, ammonia (NH₃) gas, air, snow, mud, softball, walnut cookies, cookie dough ice cream, ice, salsa.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exercise 3-4</th>
<th>Chemical compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Which of the following is a chemical compound: oxygen (O₂), a soft drink, nitrogen (N₂), ocean water, carbon dioxide (CO₂), dirt, nitrous oxide (N₂O), milk, table salt, iced tea.</td>
<td></td>
</tr>
</tbody>
</table>
Valence Electrons and the Periodic Table

Isolated atoms are neutral. That is, they consist of one positively charged nucleus and a number of negatively charged electrons (−1 charge on each electron) equal to the atomic number of that atom. Not all electrons in atoms are equivalent with respect to their attraction to their atomic nucleus. Some electrons are more tightly held, and others, sometimes classified as the “outermost” electrons, are the least tightly held by the positive charge of their nucleus. Valence electrons are the only atomic electrons that are able to engage in chemical combination through the transferring or sharing of electrons between atoms. For many elements, the periodic table can be used to predict the number of valence electrons available either for sharing or for contributing to other atoms.

The Periodic Table

<table>
<thead>
<tr>
<th>1A</th>
<th>2A</th>
<th>3A</th>
<th>4A</th>
<th>5A</th>
<th>6A</th>
<th>7A</th>
<th>8A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>1H</td>
<td>2</td>
<td>Li</td>
<td>3</td>
<td>B</td>
<td>4B</td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>6B</td>
<td>7B</td>
<td>8B</td>
<td>9B</td>
<td>10B</td>
<td>11B</td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
</tr>
<tr>
<td>4</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
</tr>
<tr>
<td>5</td>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
</tr>
<tr>
<td>6</td>
<td>Cs</td>
<td>Ba</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
</tr>
<tr>
<td>7</td>
<td>Fr</td>
<td>Ra</td>
<td>Ac</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
</tr>
</tbody>
</table>

The periodic table above is arranged in rows and columns of elements. Each column is designated either with a numeral (black letters) or a numeral and a letter (red letters) identifying the elements below it. The number below an element’s symbol is the element’s atomic number (Z). We will discuss only the A elements in this chapter. The B elements in the periodic table will be considered in Chapter 8.

On the extreme left side of the periodic table, group 1A consists of hydrogen (H, Z=1), lithium (Li, Z=3), sodium (Na, Z=11), potassium (K, Z=19), etc. Each of these elements has only one valence electron that is chemically reactive. For example, the lithium atom contains three protons and three electrons, but has only one valence electron. The other two Li electrons are held so tightly that they essentially belong to the lithium nucleus and cannot be given away or shared with any other element. The red group number indicates how many valence electrons are available for bonding or sharing from each element in that column of the periodic table. The group of elements that is designated group 8A consists of the noble gases, so-called because they generally do not share their valence electrons and therefore are chemically inert. The elements with atomic numbers between 58 and 71 (the lanthanides) and between 90 and 103 (the actinides, which include uranium and plutonium) are not shown in the above table. Their number of valence electrons will not be dealt with here.
According to the quantum theory of the H atom (Chapter 2), electrons must be considered to have both wave-like and particle-like characteristics. Because of the Heisenberg uncertainty principle, we cannot follow the exact path of any electron in an atom. We can only predict and measure the relative probabilities of finding each electron in different regions around the nucleus. How, then, do we represent the hydrogen atom graphically?

A technique used in many dance shows is to strobe light the performer(s). The strobe light turns on for a very short period, locating the performer in a particular location in a particular pose. The light is turned off and the stage is completely dark. Following a short interval, the strobe light is illuminated again for another very short period, showing the performer in a different location in a different pose. The viewer can guess, but cannot necessarily predict exactly where the performer will be during each succeeding illumination interval.

In the same manner, we divide the space around the nucleus into very small cubes. Each of the cubes contains an electron detector that can detect when an electron at a designated moment is somewhere within the confines of that cube. The detector can only measure the presence or absence of an electron for a very short

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**Example 3-5**  **Calculating the number of valence electrons**

Give the atomic number, the total number of electrons, and the number of valence electrons for each of the following neutral atoms: C, N, O, F, Ne (in top row of the periodic table)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number (Z)</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Total number of electrons</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Number of valence electrons</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>0 (inert octet)</td>
</tr>
</tbody>
</table>

**Example 3-6**  **Number of valence electrons**

How many valence electrons are there in each of the following elements?:

- **Silicon Si (Z = 14)?**  
  Ans. Si is in group 4A and has 4 valence electrons, the same number as carbon, the element just above Si in the table.

- **Magnesium (Z = 12)?**  
  Ans. Mg is in group 2A and therefore has 2 valence electrons, the same as Beryllium (Be), also a group 2A element.

**Exercise 3-7**  **Number of valence electrons**

How many valence electrons are there in each of the following elements?: fluorine (F); oxygen (O); nitrogen (N); neon (Ne)

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### Electron Paths and the Quantum Theory

According to the quantum theory of the H atom (Chapter 2), electrons must be considered to have both wave-like and particle-like characteristics. Because of the Heisenberg uncertainty principle, we cannot follow the exact path of any electron in an atom. We can only predict and measure the relative probabilities of finding each electron in different regions around the nucleus. How, then, do we represent the hydrogen atom graphically?

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In the same manner, we divide the space around the nucleus into very small cubes. Each of the cubes contains an electron detector that can detect when an electron at a designated moment is somewhere within the confines of that cube. The detector can only measure the presence or absence of an electron for a very short
period, is turned off, and then turned on again in a regular strobe light fashion. An example of such an imaginary electron strobe detector is given in the following animation. Note that, at the end of the animation, the collection of dots in the animation represents the relative probabilities of finding the H atom electron at different distances from the H atom nucleus. The highest probability of finding the H atom electron is near the nucleus. The lowest probability is at a great distance from the nucleus.

This probability pattern is that for the most stable H atom in its lowest energy state. If the H atom absorbs a photon, adding the photon’s total energy to the stable H atom, the probability pattern changes to a more complex one where the probability of finding the electron is displaced farther away from the H atom proton nucleus. Quantum theory is able to predict the shape of the probability patterns for all of the different energy levels of the H atom, some of which are shown in figure 3-1.

However, atoms generally do not exist in nature in isolation. Certain atoms are attracted to each other, forming chemical compounds and thereby deforming atomic electron probability patterns. Let’s first examine the simplest chemical compound, the hydrogen molecule, H2 in the following animation.

**Chemical Bonds**

We now explore the interactions among atoms that lead to the formation of chemical compounds that are held together by chemical bonds. There are two basic types of strong chemical bonds, covalent and ionic, with intermediate bonds containing a mix of these two. A covalent bond forms when valence electrons are shared between nuclei. Pure covalent bonds are found in the major atmospheric molecules nitrogen (N2) and oxygen (O2). The valence electrons are equally shared between the nuclei in each of these two molecules. An ionic bond forms because of the attraction of the opposite net electrical charges on ions. Sodium chloride (NaCl) is a chemical substance made up exclusively of ionic bonds between Na+ and Cl− ions. Because covalent bonds formed by the sharing of valence electrons are found in all of the gaseous molecules in the atmosphere, we will focus in this chapter on covalent bonds.

The hydrogen molecule, H2, a major molecule found throughout the universe, but a minor constituent in the Earth’s atmosphere today, contains the simplest and the clearest example of a covalent bond. Each hydrogen atom has one proton as its nucleus and one electron in motion around that nucleus. Since hydrogen is in Group
1A of the periodic table, its only electron is also its lone valence electron. The four particles contained in the hydrogen molecule are shown in Fig. 3-2.

![Figure 3-2](Image)  
Oversimplified illustration showing a possible basis for chemical bonding. Electrons passing rapidly between nuclei both shield the positive nuclear charges and attract nuclei toward their negative charges. However, this representation of the covalent bond violates the uncertainty principle.

The two positively charged nuclei repel each other, and the two negatively charged electrons also repel each other. However, each of the electrons will be attracted to both nuclei and each nucleus will be attracted to the negative charges of both electrons. Electrons move very rapidly in comparison with the nuclei. If these attractive forces, averaged over time, are greater than the repulsive forces, averaged over time, there will be a chemical bond formed between the two H atoms. Such a bond is called a covalent bond because there is a cooperative sharing of both valence electrons between the two nuclei. The above is a “classical” explanation of a covalent bond because it ignores the quantum wave properties of both the electrons and the protons. Instead:

A valence electron can be attracted equally over time by several nuclei, as in the hydrogen (H₂) molecule, or it may be attracted unequally by different nuclei, as in the water molecule (Chapter 4). The covalent bond in the hydrogen molecule is known as a single bond, one that contains a single pair of valence electrons shared between two nuclei. In the O₂ and N₂ molecules, two and three pairs of valence electrons, respectively, are shared between these two nuclei, forming double and triple bonds. Counting pairs of available valence electrons from atoms helps predict what types of chemical bonds can be formed, as we will see later in this chapter.

**Example 3-8**  
Sharing of valence electrons in bonds

There can be more than one pair of valence electrons shared between oxygen nuclei in the critical atmospheric molecule oxygen (O₂). Are these valence electrons shared equally between the two nuclei?

Indeed, they must be because the two oxygen nuclei have an identical positive charge. If they were between different nuclei, as in OH bonds in the water molecule, they would not equally share valence electrons.

**Exercise 3-9**  
Valence electrons in bonds

How many valence electrons can possibly be shared between the two nitrogen nuclei in the nitrogen molecule (N₂), the most abundant molecule in the atmosphere? How many electrons are there in this molecule? Are the valence electrons equally shared between the two nitrogen nuclei?
The Octet Rule (the Rule of Eight)

The sharing of electron pairs by atoms to achieve the stable electronic configuration of an un-reactive noble gas atom is a particular chemical trait first noted in 1916 by Gilbert N. Lewis. For example, when two hydrogen atoms share two electrons (one electron pair), there is the same number of electrons in this covalent bond as in the noble (un-reactive) gas helium (He). Thus, by sharing two electrons, each hydrogen atom in the hydrogen molecule is more stable than it is as an isolated hydrogen atom. Hydrogen atoms, with a single valence electron, are highly chemically reactive because of their single, unpaired electron. Indeed, the name of a chemical entity that has an unpaired electron is called an unstable “free radical.”

Lewis realized that the difference in atomic numbers between each successive pair of noble gas elements in the first three periods (rows) of the periodic table is eight (for Ne and He: 10 – 2 = 8; for Ar and Ne: 18 – 10 = 8). There are eight elements in the second and third rows (periods) of the periodic table, each row ending in a very stable noble gas group with eight valence electrons. For the lighter elements of the periodic table - except hydrogen - this number eight is a type of “magic” number of valence electrons. According to Lewis, this valence electron octet (group of eight), the so-called Lewis octet, is the desired arrangement in compounds for all lighter elements in the periodic table that are in the neighborhood of any noble gas other than helium. Thus, elements in the first, second, and third rows (periods) of the periodic table tend to surround themselves with a noble gas electronic configuration. For H atoms, this means sharing two valence electrons. Elements in the second and third rows of the periodic table can accomplish a noble gas valence electron configuration goal by sharing valence electrons with other elements in such a way that they each have eight valence electrons surrounding them, always counting both shared and unshared pairs of valence electrons.

Valence electrons can also be lost from an atom to create a noble gas electronic configuration. For example, the product of the loss of the single valence electron from the lithium atom (Li), the lithium ion Li⁺, contains the same number of electrons as helium, that is, two. However, these remaining electrons of the lithium ion are tightly bound and are not available for sharing with other elements. Therefore Li⁺ with no valence electrons is chemically un-reactive. However, the lithium atom (Li) with its single valence electron is a chemically reactive free radical.

The octet rule predicts the chemical structures of most atmospheric molecules. These are called either Lewis structures or electron dot structures.

In order to construct electron dot structures, you need to know the chemical formula and the spatial placement of each atom. This allows you to calculate the number of valence electrons contributed to the molecule by each atom. You should then arrange the atoms and valence electrons in such a way that hydrogen will share only one pair of electrons with another atom. Four pairs of either shared or unshared
valence electrons surround all other atoms, if possible. Although Lewis or electron dot structures may be arrived at by trial and error, one systematic way to arrive at a Lewis structure for compounds formed from elements in the first and second rows of the periodic table is:

1. **First, count all the valence electrons for each of the atoms, obtaining this information from the group number of the element in the periodic table.**

   For example, in H₂O, there are:

   - 2 valence electrons contributed by the two H atoms (2 x 1)
   - 6 valence electrons contributed by one O atom (1 x 6)
   - 8 valence electrons total (4 pairs of valence electrons).

2. **Write down the central atom and then distribute the remaining atoms around the central atom.** (You will be provided with information regarding relative atom positions in the molecule, e.g., the identity of the central atom.)

   For water, we are not only told the chemical formula, but are given the fact that water is a bent molecule whose atoms are arranged approximately as indicated below:

   \[
   \begin{array}{c}
   H \\
   O \\
   H
   \end{array}
   \]

3. **Connect pairs of atoms with a single electron pair. One shared pair of electrons constitutes a single covalent bond. Hydrogen can have a maximum of only one covalent bond; carbon, 4 bonds; nitrogen, 3; oxygen, 2; and fluorine, 1. Note that the maximum number of bonds for elements in the second row of the periodic table is equal to eight minus the group number. This is the number of electrons that can be shared with valence electrons contributed by other atoms.**

   Four valence electrons are used in forming two O–H bonds:

   \[
   \begin{array}{c}
   H : O \\
   \cdot \cdot \\
   H
   \end{array}
   \]

4. **Take the remaining valence electrons and place them on the atoms surrounding the central atom in such a manner as to obtain an octet around each outer atom other than hydrogen, which should have only two electrons in a single bond.**

   For water, there are four remaining valence electrons (8 total - 4 in the two bonds) that are used to complete the octet around the oxygen atom:

   \[
   \begin{array}{c}
   H : O : \\
   \cdot \cdot \\
   H
   \end{array}
   \]
5. Distribute any remaining electrons to the central atom; if there are fewer than eight electrons surrounding the central atom, create a multiple bond by moving one or more unshared electron pairs from one or more of the surrounding atoms to obtain an octet for the central atom.

For water, there are no remaining electrons, so the Lewis structure is that given in step 4 above, namely:

\[
\begin{array}{c}
\vdots \\
H : O : \\
\vdots \\
H \\
\end{array}
\]

Example 3-10  Electron dot structure of ammonia

Write the Lewis structure of the ammonia molecule, NH\textsubscript{3}. In ammonia, a minor, but quite important constituent of the atmosphere, three hydrogen atoms surround the central nitrogen atom.

Step 1: count valence electrons:

\[
\begin{array}{l}
\text{N: 5 valence electrons from the one nitrogen atom (1 x 5)} \\
\text{H: 3 valence electrons from the three hydrogen atoms (3 x 1)} \\
\text{8 valence electrons total (4 pairs)}
\end{array}
\]

Step 2: arrange the atoms as stated in the problem:

\[
\begin{array}{c}
H \\
\vdots \\
N \\
\vdots \\
H \\
H
\end{array}
\]

Step 3: draw single bonds (one pair of electrons each) from the N to each H:

\[
\begin{array}{c}
H : N : H \\
\vdots \\
H
\end{array}
\]

Step 4: add the remaining electrons (2) to complete an octet:

\[
\begin{array}{c}
H : N : H \\
\vdots \\
H
\end{array}
\]

Step 5: not needed, because there are no valence electrons are left.

In the final Lewis structure of ammonia above, there is an unshared pair of electrons. This pair can be shared with other atoms; this sharing is the basis for a very important concept in atmospheric chemistry.
Example 3-11  Electron dot structure of double bonds

What is the Lewis structure of carbon dioxide (CO$_2$), a minor, but very important greenhouse gas (Chapter 6) constituent of the atmosphere. Carbon dioxide is a linear molecule with the carbon atom placed between the two oxygen atoms.

Step 1: count valence electrons:

- C: 4 valence electrons from the one carbon atom (1 x 4)
- O: 12 valence electrons from the two oxygen atoms (2 x 6)

16 valence electrons total (8 electron pairs)

Step 2: arrange the atoms in the linear manner stated in the problem:

O     C     O

Step 3: draw single bonds (one pair of electrons each) from the C to each O:

O : C : O

Step 4: add remaining electrons (12, six pairs) to complete octets on all outer atoms:

.. O : C : O :

There is a problem with the above structure: even though each of the two oxygen atoms has an octet of valence electrons around it, the carbon atom has only four valence electrons surrounding it. We must therefore invoke rule 5 because we don’t have any valence electrons left to contribute.

Step 5: We can achieve octets around all three atoms by bringing in one pair of valence electrons from each of the oxygen atoms to form two double bonds, a **double bond** consisting of two pairs of electrons shared in a covalent bond between two nuclei:

: O : C : O :

↓

: O : : C : : O :

The Lewis structure predicts that there are two double bonds in carbon dioxide. Experimental results confirm this prediction.
Chemical Composition of the Atmosphere

After considering the electronic structure and bonding of a number of important atmospheric constituents, we now examine the overall composition of the atmosphere. The names and relative abundances of the various atmospheric gases are listed in Table 3-1. Over 99% of the mass of the atmospheric gases is contributed by nitrogen (N\(_2\)) and oxygen (O\(_2\)), with N\(_2\) being the dominant gas. The rest are called trace gases. The total amounts of N\(_2\) and O\(_2\), as well as some other trace gases present in very small concentrations, such as argon, neon, and other noble gases, have remained remarkably constant for the hundred or so years they have been accurately measured. The heavier noble gases (Ar, Kr, Xe) tend to be held closer the Earth because of gravitational forces. The lighter gases such as H\(_2\) are found in the highest elevations of the atmosphere and can even escape into outer space.

A number of minor constituents of the atmosphere vary in total amounts, the best known being water and carbon dioxide. The highly variable amount of water vapor in atmosphere is measured as the humidity level. The steadily increasing concentration of CO\(_2\), the most widely publicized of the greenhouse gases, is a cause for concern in terms of its potential for global warming and climate change, and is discussed extensively in Chapter 6.

Exercise 3-12
Electron dot structure of oxygen
Demonstrate that the Lewis structure of molecular oxygen, O\(_2\), can be written with a double bond consisting of two electron pairs between the two oxygen atoms. Oxygen is the second most abundant molecule in the atmosphere.

Exercise 3-13
Electron dot structure of nitrogen
Demonstrate that the electron dot structure of molecular nitrogen, N\(_2\), yields a triple bond consisting of three electron pairs between the two nitrogen atoms. Nitrogen is the most abundant molecule in the atmosphere. Nitrogen’s triple bond makes it a particularly stable molecule. That is, the two N atoms are very tightly bound in the N\(_2\) molecule. Therefore, it is a relatively chemically un-reactive molecule. Nevertheless, the N atom is a vital ingredient of living species. Often the raw material for making biologically important molecules is the N\(_2\) molecule. Some chemical reactants and additional energy must be provided to break this very strong chemical bond.
### Table 3-1
Composition of Clean Air Near Sea Level

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Chemical Formula</th>
<th>Percent by volume (in dry air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water vapor</td>
<td>H₂O</td>
<td>variable</td>
</tr>
<tr>
<td>Dry air</td>
<td>-----</td>
<td>100%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>78.084</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>20.948</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>0.934</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>0.032 (increasing)</td>
</tr>
<tr>
<td>Neon</td>
<td>Ne</td>
<td>0.0018</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>0.0005</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>0.0001</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>~0.00005</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N₂O</td>
<td>~0.00003</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>~0.00001</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>~0.000001</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>NO₂</td>
<td>~0.000001</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>SO₂</td>
<td>~0.0000002</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S</td>
<td>~0.0000002</td>
</tr>
<tr>
<td>Ozone</td>
<td>O₃</td>
<td>variable</td>
</tr>
</tbody>
</table>

### Properties of Gases

The human eye is incapable of seeing individual atmospheric atoms and molecules because they are so small. It takes very sophisticated scientific instruments to be able to observe single molecules. If we are to understand the properties of atmospheric gases consisting of molecules of low mass, we must accept the interpretations of many historic scientific studies. These demonstrate that a very large number of these minuscule gas molecules and atoms are moving randomly in space at many different speeds, (Fig. 3-3) some very fast, some relatively slow, with the bulk at intermediate speeds. Despite their very small size, these gas particles collide frequently with each other and with their surroundings because of their high

![Properties of a gas](image)

**Figure 3-3** Representation of the various species found in a collection of gas constituents in the atmosphere. A few move fast and a few move slowly, but the vast majority move around an average speed that is indicative of the atmospheric temperature.
speeds and their large number density (number of molecules in one cubic centimeter of the atmosphere).

One way you can confirm these collisions is to expose your skin to the atmosphere during a cold, windless day. Your skin will feel cold, in part, because a large number of these cold air molecules collide with your skin. However, they generally do not combine chemically with your skin. Instead, they bounce off your warm skin. A vast majority of the many departing atmospheric molecules take away some of the heat energy from your skin, thereby lowering the temperature of your skin and increasing their own average speed. Your lost body heat is helping to raise the temperature of the atmospheric gases surrounding your skin. Under such circumstances, the extent of temperature lowering of your skin exceeds by a significant amount the temperature gain of the atmosphere around you. This is because there are far more gas molecules in the cold atmosphere than those colliding with the warm surface of your skin. The gas molecules coming from collisions with your skin collide with other gas molecules and transfer body thermal energy to many other gas molecules in the atmosphere through subsequent collisions, increasing the atmospheric temperature by a very small amount, but causing “goose bumps” on you!

**Temperature**

Temperature is a difficult quantity to define. It is a property of a collection of molecules, atoms or ions. One way to define temperature is that if one object has a higher temperature than another object and we place the two objects in direct contact, heat will flow from the hotter to the colder object until there is no net flow of heat between the objects. At this point, the temperatures of the two objects are equal. It is much easier to describe how we can measure temperature. Newer digital methods include converting electrical measurements of solid materials into direct temperature readings. Temperature has been measured historically in terms of the length of a tube of liquid mercury or colored liquid in a thermometer, which is calibrated at the freezing point (0 °C, 32 °F) and boiling point of water (100 °C, 212 °F). °C refers to degrees Celsius, a temperature scale used commonly by scientists, and °F refers to degrees Fahrenheit, an English system still in use. Because there are 180 Fahrenheit degrees for every 100 Celsius degrees, one Celsius degree is 100/180 (or 5/9) of a Fahrenheit degree. Conversion of Fahrenheit to Celsius requires the adjustment for the fact that the freezing points of the two temperature measurement scales are 32 degrees apart. These facts are used in deriving the conversion equations from Fahrenheit (°F) to Celsius (°C) and vice versa:

\[
°C = \frac{5}{9} (°F - 32) \quad \text{and} \quad °F = \left(\frac{9}{5} °C + 32\right)
\]
The temperature of the atmosphere is a collective property of a large number of atmospheric atoms and molecules. If we were to measure the speed of just one of these molecules at a given moment, we could not determine a temperature of the gas that contains that molecule. One molecule doesn't have a temperature. At any moment, a molecule may have a very high speed or it may have a very low speed. What we are concerned about when we talk about the atmospheric temperature is related to the average speed of a collection of atmospheric molecules. The emphasis on average properties is important because atmospheric molecules have a wide distribution of velocities. At any given instant, there is a small portion moving very slowly or very rapidly, with the vast majority moving near the average speed. As temperature changes, the shape of this speed distribution changes, shifting to higher average speeds with increasing temperatures.

If the average speed of the gas molecules in a certain atmospheric region is high, a thermometer placed in that region will register a high temperature. If the average speed is lower, the temperature will be lower. Average speeds of gaseous air molecules at room temperature are on the order of a thousand miles (1700 kilometers) per hour. Despite the large average space between molecules at atmospheric pressure, these molecules collide frequently (Fig. 3-4) with each other because of their high speeds, high number densities, and the small, but finite, sizes of the molecules. At high temperatures, the collisions between atmospheric molecules are

<table>
<thead>
<tr>
<th>Example 3-14</th>
<th>Temperature conversions</th>
</tr>
</thead>
<tbody>
<tr>
<td>What is the temperature in °C of a room whose temperature measures 72 °F?</td>
<td></td>
</tr>
<tr>
<td>°C = ( \frac{5}{9} ) (72 - 32)</td>
<td></td>
</tr>
<tr>
<td>°C = ( \frac{5}{9} ) (40) = ( \frac{200}{9} ) = 22.2 °C (room temperature in Centigrade)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exercise 3-15</th>
<th>Temperature conversions</th>
</tr>
</thead>
<tbody>
<tr>
<td>The temperature of water in a glass is measured as 36 °C. What is its Fahrenheit temperature?</td>
<td></td>
</tr>
<tr>
<td>°C = ( \frac{5}{9} ) (72 - 32)</td>
<td></td>
</tr>
<tr>
<td>°C = ( \frac{5}{9} ) (40) = ( \frac{200}{9} ) = 22.2 °C (room temperature in Centigrade)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-3 Molecular speed distributions at two different temperatures of a gas. Blue is at a lower temperature, and red is at a higher temperature. “u” is the average speed.
generally quite elastic, that is, they bounce apart much like billiard or tennis balls do when they collide. Compare this type of collision with the collision of two ripe tomatoes, which are “mushier” and much less elastic.

At lower temperatures, the collisions between slower moving atmospheric molecules are “sticky,” in some ways like collisions between two tennis balls covered with Velcro™ or sticky glue. At certain critical temperatures, the slower moving particles tend to adhere to each other when they collide, especially if there are three molecules in a collision or if an atmospheric dust particle is present to carry away energy generated by the formation of weak bonds between the colliding molecules. Ultimately, such collisions form a condensed form of matter such as a liquid or a solid. Individual atmospheric water molecules can form liquid droplets in the form of clouds. If the temperature is low enough, for example, in Antarctica, solid water in the form of ice clouds can form. These types of ice clouds are important in understanding the formation of the “ozone hole” (Chapter 7). The two condensed states of matter, liquid and solid, are collections of atoms, molecules or ions in which these chemical species are much more closely spaced than in atmospheric gases.

**Pressure of Atmospheric Gases**

When a gas is confined to a limited space, such as in a balloon filled with air, the trapped gas molecules collide with the inside wall of the balloon. If we focus on one square inch or square centimeter of an air-filled balloon, there are more collisions of air molecules per minute with the inside surface than with the outside surface during one minute. **Pressure** can be defined as the force exerted by these collisions in one specific area of the balloon in one minute. In this example, the pressure is greater inside the balloon than outside the balloon. If you insert a needle into the balloon, you see the consequences of this large difference in pressure: the inside pressure is suddenly lowered as the air rushes out of the balloon to equalize the inside and outside pressures.

The pressure of a gas increases with: (1) increasing numbers of molecules at a given temperature and volume; (2) increasing absolute temperature (degrees K = the number of degrees Celsius + 273°) for a fixed number of molecules and volume; (3)
decreasing volume for a fixed number of molecules and temperature. These three statements can be combined to yield a single quantitative relationship stating that pressure of a gas is directly proportional to the number (n) of gas molecules (or atoms) and the absolute temperature T, and inversely proportional to the volume (V) of the gas. A mathematical equation stating the above word statement is:

\[ P = \frac{nRT}{V} \]

where R is a proportionality constant. This equation holds true for gases that are at relatively low pressures and reasonably high temperatures and that consist of molecules that do not have a very high affinity for each other, that is, they do not undergo "sticky" collisions. Such gases are called "ideal gases," primarily because they behave according to the above **ideal gas equation**.

---

**Example 3-16**

**Atmospheric Pressure**

When a large metal can is connected to a vacuum pump and air is withdrawn, the can crumples inward into a much smaller volume. Why?

Because there is a partial vacuum on the inside of the can, there are very few gas molecules bombarding the inside surface of the can per second to counterbalance the many more molecules bombarding it on the outside. The sum total of all of these outside collisions of atmospheric molecules push in on the can with such force that the can collapses.

---

**Exercise 3-17**

**Airplane pressure differences**

Humans operate best in an air pressure close to that present near sea level. Yet airplanes operate at altitudes at which the outside air pressure is far lower than that at sea level. How is this accomplished? Compare the number of collisions per second of air molecules on the inside and outside of the window of a jet. (Remember to compare the speed of the airplane with the speed of the molecules in air.)

---

**Layers of the Atmosphere**

Atmospheric pressure decreases with increasing altitude because of the Earth's decreasing gravitational attraction for the atmospheric molecules with increasing elevation. Gravitational forces decrease the velocity of molecules moving away from the Earth in much the same way it does of a ball thrown up into the air. There are fewer molecules at high altitudes; therefore, the pressure of the atmosphere decreases with altitude.
Clouds at different elevations show different characteristics. This is because of the different moisture content, temperature and wind patterns at the different layers of the atmosphere. Atmospheric layers exist because of the way in which the temperature varies with altitude.

Figure 3-5 Atmosphere pressure and temperature as a function of height, showing different layers.

The temperature of the atmospheric layer closest to the Earth, the troposphere, decreases with height in the manner illustrated in Fig. 3-5. We know that the air temperature decreases when we climb a mountain. We intuitively feel that
the temperature of the atmosphere should continue to decrease with altitude. However, if we were to switch to a balloon at the top of the mountain and take temperature readings while floating up to about 20 kilometers (12 miles), into a region called the tropopause, we would find that instead of decreasing with increasing altitude, the already cold temperature actually starts to increase with further increases in altitude. Two more reversals in the temperature-altitude profile occur above the stratopause and the mesopause. With each reversal of the temperature-altitude trend, there is a new layer of the atmosphere. These reversals in temperature vs. altitude trends, known as temperature inversions, are explained by the interaction of incoming solar and cosmic radiation from outside the Earth, and result in the division of the atmosphere into different zones including the troposphere (below the tropopause), stratosphere (below the stratopause) (Fig. 3-5). The majority of the molecules of the atmosphere are in the troposphere and stratosphere. Ninety-nine percent of the 5,500 trillion tons of gases that compose the atmosphere are contained in a 19-mile (32 km) high band above the Earth’s surface.

The nature of the temperature-altitude profile of the troposphere and the weather patterns of the Earth lead to very efficient mixing of all gases contained within the troposphere, the atmospheric layer immediately above the Earth’s surface. However, this efficient mixing ceases at the tropopause. The reversal in the temperature-altitude trend results in very inefficient vertical mixing in the stratosphere. This means that material injected into a particular region of the stratosphere at a particular altitude tends to stay at that altitude for years, even though it may be horizontally mixed in a very efficient manner, for example, being spread around the world. Gases and particles from major volcanic eruptions into the stratosphere are carried around the Earth many times in this fashion at the altitude of their injection, sometimes significantly affecting global weather for long periods. All of the temperature inversions described above are large, persistent features of the Earth’s atmosphere, although the exact height of the atmospheric boundaries of these layers can vary according to locations and season. During certain weather patterns in regions of the lower troposphere, there are also localized, transient temperature inversions much closer to the earth’s surface, caused by local geographic features. These inversions can lead to severe air pollution episodes. The air below the temperature inversion does not mix readily with the upper air. Pollutants in the air parcel below the temperature inversion layer are trapped until the inversion disappears. In the same manner, but on a much larger scale, the entire troposphere traps most long-lived air pollutants. However, there is a very slow transfer of long-lived pollutants from the troposphere into the stratosphere. Tropospheric pollutants such as CFCs (chlorofluorocarbons) are believed to affect the protective layer in the stratosphere known as the ozone layer. This layer is created from the interaction of ultraviolet radiation from the sun with O2 in the stratosphere. The chemistry of the ozone layer will be described below and in chapter 7.

Most turbulent weather occurs in the troposphere, so most commercial jets fly in the region of the troposphere where there is little turbulence. Sometimes there is an “overshoot into the troposphere, and this is felt by airplane passengers.
Interaction of Light with the Atmosphere

Why is the sky blue? This blue color is the result of sunlight scattered by invisible atmospheric molecules. Shorter wavelength violet to blue-green light from the sun is more strongly scattered than longer wavelength light by these molecules. Therefore, colors around blue are more effectively scattered than other colors in the visible spectrum. Because of the different efficiencies of the color sensing cells in the eye, the brain interprets these scattered photons of sunlight from all parts of the sky as a blue sky (Figure 3.6).

Clouds also scatter sunlight, but because they are composed of much larger clusters of liquid water molecules, they efficiently reflect the entire visible spectrum of sunlight and therefore appear white. Clouds observed below through an airplane window are white,

Fig. 3.6 The sky looks blue everywhere because of the stronger scattering of blue light from the sun than of other colors. Everywhere the observer looks, the sky looks blue because the blue component of sunlight is being scattered toward the observer from all directions. The poorly scattered red light is responsible for the redness of the setting sun when the observer is viewing the sun on the horizon, when most of the blue light has been scattered away from the distant observer.

indicating that they reflect all wavelengths of visible sunlight back out into space. Reflected light from clouds is quite important in global warming considerations (Chapter 6). On a sunny day, most clouds seen from the ground are also white, indicating that they are reflecting the full visible spectrum of the Sun toward the observer’s eyes from the cloud. Raindrops can cause the white sunlight to be broken
up (refracted) into its components, thereby causing rainbows, which display the same into a spectrum of visible light as when white light passes through a prism (Fig. 2-7).

The gases contained in the Earth's atmosphere are nearly all transparent to visible radiation, but only certain wavelengths of ultraviolet and infrared radiation penetrate atmospheric gases and are able to bombard the surface of the Earth directly. All other radiations are absorbed in different regions of the atmosphere, some heating the Earth’s atmosphere, some causing chemical reactions. Two critical phenomena arise from the absorption of infrared and ultraviolet radiation in different parts of the atmosphere: the greenhouse effect (Chapter 6) and stratospheric ozone layer formation and destruction.

**Formation of the ozone layer**

Short wavelength ultraviolet radiation from the Sun never reaches the Earth’s surface because it is absorbed in the stratosphere. It is dangerous to expose living organisms to this radiation because such high-energy ultraviolet radiation can disrupt the chemical bonds of biologically important molecules. Some atmospheric gases are capable of absorbing, and thereby filtering out, this harmful radiation. For example, molecular nitrogen (N₂) absorbs some very high energy UV radiation. Molecular oxygen (O₂) and ozone (O₃) also are important molecular participants in this UV filtration process. O₂ is released directly by plants into the troposphere, whereas O₃ arises from the interaction of UV radiation with oxygen molecules in the stratosphere. Ozone is also produced at ground level during smog formation (Chapter 5).

What are the chemical reactions responsible for the stratospheric ozone layer? The first is the reaction of a UV photon with O₂. The increased molecular energy in O₂ due to the photon absorption (Fig. 3-8) is observed primarily as vibration energy of the O₂ molecule. This energy-rich, vibrationally excited, oxygen molecule (O₂*) dissociates, i.e., vibrates so strongly that it comes apart into oxygen atoms (Fig. 3-8). Reactions (3-1) and (3-2) below represent the same processes illustrated in Fig. 3-8 in the form of chemical equations.

**Figure 3-8** Illustration of the absorption of UV-radiation by molecular oxygen (O₂) to form a vibrationally-excited electronic state molecule, which readily dissociates into oxygen atoms.
\[
\begin{align*}
O_2 + UV & \rightarrow O_2^* \text{ (excited molecule)} \quad (3-1) \\
O_2^* & \rightarrow O + O \quad \text{(2 oxygen atoms)} \quad (3-2)
\end{align*}
\]

The resulting oxygen atoms are chemically very reactive because they each have unpaired valence electrons and combine with oxygen molecules (O₂). If the oxygen atom and the oxygen molecule come together, they react to form a highly excited ozone molecule (O₃*), which is so energy-rich that, unless some energy is taken away from O₃*, it falls apart again (3-3) into an oxygen atom and an oxygen molecule.

\[
O_2 + O \rightarrow O_3^* \rightarrow O_2 + O \quad (3-3)
\]

The only way that the ozone molecule can survive is if it reacts in the presence of another molecule, arbitrarily designated as “M,” that can absorb the excess energy of the O₃*. M is any molecule or other collection of atoms that increases its vibrational or rotational energy (Chapter 6) upon collision with O₃* before it decomposes. Thus, the close proximity of M during a collision of O with O₂ is a requirement to form a stable ozone molecule, as shown in Fig. 3-9 and equation (3-4). However by participating in reaction (3-4), M absorbs energy from the excited ozone molecules and is itself excited and is designated M*. The M* has excess energy that it transmits to other surrounding molecules during collisions with them. Some of this energy is transformed into increased speeds of molecules, and the average temperature of the atmospheric region in which M* molecules are located is increased. Transfer of energy from M* species to their surroundings is the reason for the heating of the upper layers of the stratosphere where the UB radiation from the Sun is absorbed and is also the cause of the temperature inversion responsible for the stratospheric layer.

![Fig. 3-9](Ch_3_Ozone_Layer/p.3)  
Stabilization, by molecule M, of the highly-excited ozone molecule by transfer of energy to the M molecule, which can be any molecule, e.g., N₂ or even another O₂ molecule.

The chemical equation corresponding to Fig. 3-9 is represented below:

\[
O + O_2 + M \rightarrow [MO_3]^* \rightarrow O_3 \text{ (ozone)} + M^* \quad (3-4)
\]
The newly formed ozone molecule strongly absorbs ultraviolet (UV) light in a slightly shorter wavelength region of the electromagnetic spectrum than that absorbed by the oxygen molecule (UV-B; Chapter 6). The ozone molecule that absorbs this UV radiation decomposes to give an oxygen molecule and an electronically excited oxygen atom, as demonstrated in Fig. 3-10 and in equation (3-5):

\[
O_3 + UV \rightarrow O_3^* (excited) \rightarrow O_2 + O^* \quad (3-5)
\]

Note that reaction (3-5) represents the destruction of an ozone molecule created in reaction (3-4). The oxygen atom (O*) has excess energy and collides with any molecule M to form M* (Fig. 3-11), which dissipates its excess energy by collisions with other molecules thereby also causing an increase in the stratospheric temperature. Reaction (3-6) represents this energy transfer reaction.

\[
O^* + M \rightarrow O + M^* \quad (3-6)
\]

The resulting de-excited oxygen atom, O, can then react with O₂ to form another ozone molecule, as indicated in reaction (3-4). Thus, ozone is continuously created in the stratosphere following the interaction of UV with O₂ molecules and destroyed due to the absorption of sunlight by the ozone molecules, releasing heat in the stratosphere and causing a temperature inversion that is responsible for the formation of the stratosphere.

This series of reactions illustrates the transformation of sunlight energy into molecular vibration energy into heat energy. The total amount of energy absorbed in this series of reactions from the Sun is equal to the amount of heat energy released by
the chemical reactions as thermal energy, as it must be because of the First Law of Thermodynamics (Chapter 9).

The ozone generated by reaction (3-4) has its highest concentration in the middle to lower region of the stratosphere, which is called the “ozone layer,” where the ozone concentration is the highest in the entire atmosphere. This ozone layer removes a significant portion of the harmful UV radiation entering the Earth’s atmosphere from the Sun through the chemical reactions listed above.

Ozone molecules are also found closer to the Earth’s surface in the troposphere but at much lower concentrations than in the stratosphere. The chemistry of the production of ozone is different in these two atmospheric regions. Chapter 5 will deal with the chemistry of tropospheric smog, a primary component of which is ozone. The ozone layer is found in the stratosphere (see Chapter 7 for further discussion of the ozone “hole”).

**The Origin of Winds**

Wind disperses air pollutant chemicals as well as carrying them for long distances from their source (Chapter 5). More of the Sun’s energy is absorbed per square foot of the Earth’s surface near the equator than at either the North or South Poles. Sun-warmed tropical air is less dense than cold air and therefore rises. This air is replaced by cooler air masses moving in from both north and south of the equator. But these colder air masses ultimately come from the North and South Poles. Fig. 3-12a illustrates the global air circulation patterns that would be expected from this simple air circulation pattern. In Chapter 9, we will find a fundamental principle that states that heat always flows from warm regions to cold regions. The wind
circulation pattern shown in Fig. 3-12a demonstrates how excess heat absorbed at the equator could be delivered to the North and South Polar regions by the wind pattern set up by the rising tropical air masses, except for one complicating factor - the Earth rotates.

As the Earth turns, it causes forces similar to those experienced on a merry-go-round or carrousel. It is difficult to walk in a straight line toward the center on an operating merry-go-round. Parcels of air experience similar types of forces as the Earth turns on its axis, giving rise to the complex wind patterns of easterlies, westerlies, trade winds, and jet streams (Fig. 3-12b).

Because of these global wind patterns, the transport of long-lived air pollutants is worldwide. However, the transport times of these pollutants from one region of the Earth to another may be anywhere from days to months to years, depending on the location of the source and on the wind patterns at the time of a release. Note that a pollutant might have a difficult time getting from the northern hemisphere into the southern hemisphere, and vice versa. However, there is relatively efficient transport of gases such as ozone from the equator to the North and South Poles. It is for this reason that there is less ozone at the equator than there is in the region of the Poles. The ozone hole (Chapter 7) is a seasonal depletion of the ozone concentration in the ozone layer of the stratosphere over Antarctica. Ozone initially generated in the tropics is destroyed in the Antarctic.

**Contributions of Biological Processes to the “Clean” Atmosphere**

Living matter contains many different elements of importance that are released into the atmosphere. Among these elements are carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S). Many compounds from organisms in the soil and in natural waters are exchanged...
with the atmosphere (Fig. 3-13). For instance, plants take carbon dioxide (CO₂) and water (H₂O) from the air and release oxygen (O₂) as well as carbon dioxide. Carbon monoxide (CO) and nitrogen (N₂) are also removed from the atmosphere by small plants and organisms in the soil. Organisms on the Earth are continually generating many trace gases present in the atmosphere. Among these gases are CO₂, H₂O, methane (CH₄), ammonia (NH₃), nitrous oxide (N₂O), N₂, and nitric oxide (NO). One interesting compound released naturally from the oceans is dimethylsulfide, or DMS [(CH₃)₂S]. This compound is generated by plankton and is said to be a major contributor to marine cloud formation, an important factor in global warming considerations (Chapter 6). Methane (CH₄), a major greenhouse gas and an important contributor to atmospheric chemistry, is generated by bacteria in termites and in some farm animals such as cows and in certain decay processes in wetlands. Many trees, especially pines, emit complex organic molecules, called terpenes (related to turpentine), into the atmosphere. Particulate matter of biological origin also is found in the air. Wind suspends resilient bacteria to heights of four miles above the ground. In addition, pollen, algae, dandruff, and other natural biological particles have been found in the atmosphere.

Upon the death of an organism, decomposition initiates the recycling of all the elements contained in that organism into the atmosphere or into the ground in chemical forms that can be employed in the chemical and biological synthesis of new organisms. Thus, the atmosphere is continually exchanging chemical raw materials, acting as a medium for recycling atoms and molecules in both living and decomposing matter. From a chemical point of view, the atmosphere is a very busy and very important part of the Earth system!

**SUMMARY**

1. **What is the chemical composition of the atmosphere?**

   Two gases, oxygen and nitrogen, make up the bulk of the mass of the gases in the dry atmosphere. However, the chemical characteristics of the atmosphere are also critically dependent on trace gases, present at relatively low concentration, such as water, carbon dioxide, methane, and ozone.

2. **What are the characteristics of atmospheric gases?**

   Atmospheric gases consist of exceedingly small, randomly moving molecules and atoms that collide often, exchange energy and move at a wide variety of speeds, which average thousands of kilometers per hour. In the atmosphere, there is a large amount of space between molecules in comparison with their size.

3. **What is the significance of the pressure and temperature of the atmosphere?**
A gas’s temperature is related to the average speed of its constituent molecules. Faster average speeds correspond to higher temperatures. Pressure is a measure of the force of molecular impacts per unit area on the surface of a gas container. Atmospheric pressure and molecular density decrease with increasing altitude.

4. Why do atoms come together to form atmospheric molecules?

Nearly all atmospheric molecules are held together by the sharing of valence electrons in covalent bonds, thereby attracting atomic nuclei to one another. Valence electrons are among the weakest held electrons of the atoms making up an atmospheric molecule.

5. Are there rules for predicting the stability of atmospheric molecules?

Electronic structures of simple molecules can be predicted with the Lewis octet structure rules, which combine knowledge of numbers of valence electrons of constituent atoms, electron pairing, and the propensity of many elements to surround themselves with noble gas electronic structures. With the exception of hydrogen and lithium, nearly all of the low atomic number atoms tend toward an octet of shared and unshared valence electrons in molecules.

6. What causes the layers of the atmosphere and the Earth’s wind patterns?

The temperature decreases with increasing altitude in the troposphere. Because of the absorption of radiation from the sun to form the ozone layer, the temperature increases with altitude in the stratosphere. These opposite temperature vs. altitude trends are responsible for the bottom two layers of the atmosphere. Winds arise because more sunlight is absorbed in the equator region than at the Poles and winds help transport the resulting excess heat energy from warm tropical regions to the cold Polar regions. Wind patterns are made more complex because of the rotation of the Earth.

7. What critical chemical reactions occur in the different layers of the atmosphere?

The most important chemical reactions in the stratosphere are those responsible for the production and destruction of the ozone layer. There are also many other important chemical reactions occurring in the troposphere that help to eliminate air pollutants.

Review Questions

1. Name three characteristics of a gas. Which of these is related to the temperature of the gas?

2. Name at least three characteristics the rare (noble) gases share?
3. What is the chemical difference between the row number (period) and the group number of an atom in the periodic table? For example, N (row 2, Group 5), and P (row 3, Group 5).

4. Describe in detail all of the forces among the various charged particles in the hydrogen molecule (H₂) leading to the formation of the covalent bond in that molecule.

5. What are the different types of electromagnetic radiation that emanate from the Sun, and which of these make it through the atmosphere and are able to bombard the land and water surface of the Earth? Which radiations are absorbed in the Earth’s atmosphere? In what region are they absorbed?

6. What feature of the atmosphere is responsible for its separation into the troposphere and the stratosphere?

7. Specifically, what defines a temperature inversion in the atmosphere?

8. Write the chemical reaction(s) responsible for the formation of the ozone layer and the reaction(s) responsible for the destruction of ozone in the ozone layer?

9. Why is the ozone concentration in the ozone layer not larger than it is, despite the fact that huge concentrations of ozone molecules are continually being formed during daylight hours?

Problems

10. What are the electronic structures of the five most abundant molecules in the atmosphere?

11. How many atoms of carbon and oxygen are present in each carbon dioxide molecule?

12. How many atoms of hydrogen and oxygen are there in hydrogen peroxide (H₂O₂) and in a water molecule?

13. Distinguish which of the following chemical species are atoms and which are molecules: O, CO₂, N₂, C, NO₂, H₂O, H, O₂.

14. In what ways are all molecules of atmospheric carbon dioxide the same? In what ways can they differ?

15. Draw appropriate Lewis structures for CH₄, N₂O, NH₃, and CO, all gases found in the atmosphere. (Carbon is the central atom in CH₄ surrounded by four H atoms; N is the central atom in the linear N₂O molecule).
16. Write the Lewis structure for H$_2$Se. (Reason by analogy to predict the arrangement of the atoms in H$_2$Se. Because Se and O are in the same group of the periodic table, the Lewis structures of H$_2$O and H$_2$Se should be intimately related.)

17. How many atoms of each element are contained in a CFC molecule with the formula C$_2$F$_4$Cl$_2$? How many total atoms are there in this molecule?

18. How many atoms are there in 10 molecules of ammonia (NH$_3$)? How many hydrogen and nitrogen atoms are there in 10 NH$_3$ molecules?

**Discussion Questions**

19. Discuss why atmospheric pressure should decrease with increasing height from the point of view of gravitational forces felt by a single oxygen molecule. Predict its path through the atmosphere for a very long time and describe its height, speed, surroundings, and fate in chemical reactions. Include an excursion into the stratosphere in this molecular journey through the atmosphere.

20. Repeat the same exercise with respect to atmospheric temperature trends with increasing height. What limitations must this model have because of the division of the atmosphere into different regions such as troposphere, stratosphere, etc.?

**Group Project**

21. Search the Internet using one of the Web browsers as well as the library for additional material on the atmosphere under the following topics: astronauts and atmosphere, atmosphere, stratosphere, pressure, wind, etc. Be on the lookout for information that conflicts with the text or adds further details to the material in the text. Inform your instructor in writing of your findings.

**Readings**

