2023-2024

Chemistry I

First Year Science

Molecular Biotechnology

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Contents

1 Early Atomic Theory and Structure

1.1 Early Thoughts

The structure of matter has long intrigued and engaged us. The earliest models of the atom were developed by the ancient Greek philosophers. About 440 B.C. Empedocles stated that all matter was composed of four "elements"- earth, air, water, and fire. Democritus (about 470–370 B.C.) thought that all forms of matter were composed of tiny indivisible particles, which he called atoms, derived from the Greek word *atomos*, meaning "indivisible." He held that atoms were in constant motion and that they combined with one another in various ways. This hypothesis was not based on scientific observations. Shortly thereafter, Aristotle (384–322 B.C.) opposed the theory of Democritus and instead endorsed and advanced the Empedoclean theory. So strong was the influence of Aristotle that his theory dominated the thinking of scientists and philosophers until the beginning of the seventeenth century.

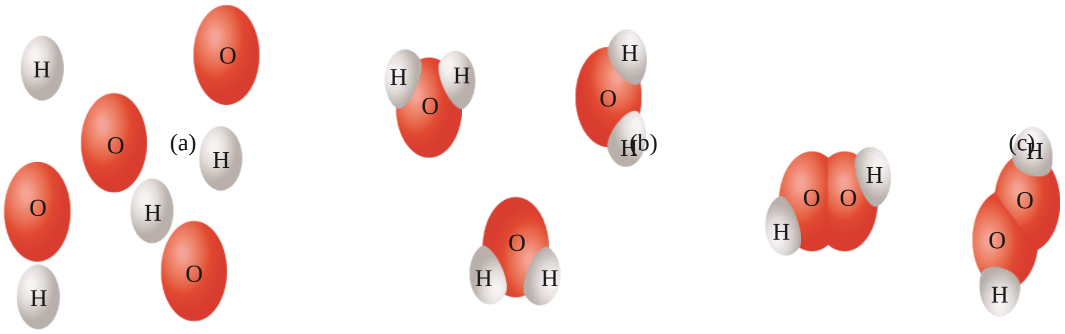
1.2 Dalton's Model of the Atom

More than 2000 years after Democritus, the English schoolmaster John Dalton (1766–1844) revived the concept of atoms and proposed an atomic model based on facts and experimental evidence (Figure 1.1). His theory, described in a series of papers published from 1803 to 1810, rested on the idea of a different kind of atom for each element. The essence of Dalton’s atomic model may be summed up as follows:

1) Elements are composed of minute, indivisible particles called atoms.
2) Atoms of the same element are alike in mass and size.
3) Atoms of different elements have different masses and sizes.
4) Chemical compounds are formed by the union of two or more atoms of different elements.
5) Atoms combine to form compounds in simple numerical ratios, such as one to one, one to two, two to three, and so on.
6) Atoms of two elements may combine in different ratios to form more than one compound.

Dalton’s atomic model stands as a landmark in the development of chemistry. The major premises of his model are still valid, but some of his statements must be modified or qualified because later investigations have shown that (1) atoms are composed of subatomic particles; (2) not all the atoms of a specific element have the same mass; and (3) atoms, under special circumstances, can be decomposed.

In chemistry we use models (theories) such as Dalton’s atomic model to explain the behavior of atoms, molecules, and compounds. Models are modified to explain new information. We frequently learn the most about a system when our models (theories) fail. That is the time when we must rethink our explanation and determine whether we need to modify our model or propose a new or different model to explain the behavior.



(a) **(b)** **(c)**

Figure 1.1 (a) Dalton’s atoms were individual particles, the atoms of each element being alike in mass and size but different in mass and size from other elements. (b) and (c) Dalton’s atoms combine in specific ratios to form compounds.

1.3 Composition of Compounds

A large number of experiments extending over a long period have established the fact that a particular compound always contains the same elements in the same proportions by mass. For example, water always contains 11.2% hydrogen and 88.8% oxygen by mass (see Figure 1.1b). The fact that water contains hydrogen and oxygen in this particular ratio does not mean that hydrogen and oxygen cannot combine in some other ratio but rather that a compound with a different ratio would not be water. In fact, hydrogen peroxide is made up of two atoms of hydrogen and two atoms of oxygen per molecule and contains 5.9% hydrogen and 94.1% oxygen by mass; its properties are markedly different from those of water (Figure 1.1c).

	Water	**Hydrogen peroxide**
Atomic composition	11.2% H 88.8% O 2 H + 1 O	5.9% H 94.1% O 2 H + 2 O

The law of definite composition

It states that *a compound always contains two or more elements chemically combined in a definite proportion by mass*.

Let’s consider two elements, oxygen and hydrogen, that form more than one compound. In water, 8.0 g of oxygen are present for each gram of hydrogen. In hydrogen peroxide, 16.0 g of oxygen are present for each gram of hydrogen. The masses of oxygen are in the ratio of small whole numbers, 16:8 or 2:1. Hydrogen peroxide has twice as much oxygen (by mass) as does water. Using Dalton’s atomic model, we deduce that hydrogen peroxide has twice as many oxygen atoms per hydrogen atom as water. In fact, we now write the formulas for water as H_2O and for hydrogen peroxide as H_2O_2. See Figure 1.1b and c.

The law of multiple proportions

It states that *atoms of two or more elements may combine in different ratios to produce more than one compound*. Some examples of the law of multiple proportions are given in Table 1.1. The reliability of this law and the law of definite composition is the cornerstone of the science of chemistry. In essence, these laws state that (1) the composition of a particular substance will always be the same no matter what its origin or how it is formed, and (2) the composition of different compounds formed from the same elements will always be unique.

Table 1.1 Selected Compounds Showing Elements That Combine to Give More Than One Compound

Compound	Formula	Percent composition
Copper(I) chloride	$CuCl$	64.2% Cu, 35.8% Cl
Copper(II) chloride	$CuCl_2$	47.3% Cu, 52.7% Cl
Methane	CH_4	74.9% C, 25.1% H
Octane	C_8H_{18}	85.6% C, 14.4% H
Methyl alcohol	CH_4O	37.5% C, 12.6% H, 49.9% O
Ethyl alcohol	C_2H_6O	52.1% C, 13.1% H, 34.7% O

1.4 The Nature of Electric Charge

You've probably received a shock after walking across a carpeted area on a dry day. You may have also experienced the static electricity associated with combing your hair and have had your clothing cling to you. These phenomena result from an accumulation of ***electric charge***. This charge may be transferred from one object to another. The properties of electric charge are as follows:

1) Charge may be of two types, positive and negative.

2) Unlike charges attract (positive attracts negative), and like charges repel (negative repels negative and positive repels positive).

3) Charge may be transferred from one object to another, by contact or induction.

4) The less the distance between two charges, the greater the force of attraction between unlike charges (or repulsion between identical charges). The force of attraction (F) can be expressed using the following equation:

$$\mathbf{F = kq_1q_2/r_2}$$

where q_1 and q_2 are the charges, r is the distance between the charges, and k is a constant.

1.5 Discovery of Ions

English scientist Michael Faraday (1791–1867) made the discovery that certain substances when dissolved in water conduct an electric current. He also noticed that certain compounds decompose into their elements when an electric current is passed through the compound. Atoms of some elements are attracted to the positive electrode, while atoms of other elements are attracted to the negative electrode. Faraday concluded that these atoms are electrically charged. He called them ***ions*** after the Greek word meaning “wanderer.”

Any moving charge is an electric current. The electrical charge must travel through a substance known as a conducting medium. The most familiar conducting media are metals formed into wires.

The Swedish scientist Svante Arrhenius (1859–1927) extended Faraday’s work. Arrhenius reasoned that an ion is an atom (or a group of atoms) carrying a positive or negative charge. When a compound such as sodium chloride (NaCl) is melted, it conducts electricity. Water is unnecessary. Arrhenius’s explanation of this conductivity was that upon melting, the sodium chloride dissociates, or breaks up, into charged ions, Na^+ and Cl^-. The Na^+ ions move toward the negative electrode (*cathode*), whereas the Cl^- ions migrate toward the positive electrode (*anode*). Thus positive ions are called ***cations***, and negative ions are called ***anions***.

From Faraday’s and Arrhenius’s work with ions, Irish physicist G. J. Stoney (1826–1911) realized there must be some fundamental unit of electricity associated with atoms. He named this unit the electron in 1891. Unfortunately, he had no means of supporting his idea with experimental proof. Evidence remained elusive until 1897, when English physicist J. J. Thomson (1856–1940) was able to show experimentally the existence of the electron.

1.6 Subatomic Parts of the Atom

The concept of the atom—a particle so small that until recently it could not be seen even with the most powerful microscope—and the subsequent determination of its structure stand among the greatest creative intellectual human achievements.

Any visible quantity of an element contains a vast number of identical atoms. But when we refer to an atom of an element, we isolate a single atom from the multitude in order to present the element in its simplest form. Figure 1.2 shows individual atoms as we can see them today.

What is this tiny particle we call the atom? The diameter of a single atom ranges from 0.1 to 0.5 nanometer (1 nm = 1 x 10^{-9} m). Hydrogen, the smallest atom, has a diameter of about 0.1 nm. To arrive at some idea of how small an atom is, consider this dot (•), which has a diameter of about 1 mm, or 1 x 10^{6} nm. It would take 10 million hydrogen atoms to form a line of atoms across this dot. As inconceivably small as atoms are, they contain even smaller particles, the **subatomic particles**, including electrons, protons, and neutrons.

The development of atomic theory was helped in large part by the invention of new instruments. For example, the Crookes tube, developed by Sir William Crookes (1832–1919) in 1875, opened the door to the subatomic structure of the atom (Figure 1.3). The emissions generated in a Crookes tube are called ***cathode rays***. J. J. Thomson demonstrated in 1897 that cathode rays (1) travel in straight lines, (2) are negative in charge, (3) are deflected by electric and magnetic fields, (4) produce sharp shadows, and (5) are capable of moving a small paddle wheel. This was the experimental discovery of the fundamental unit of charge—the electron.

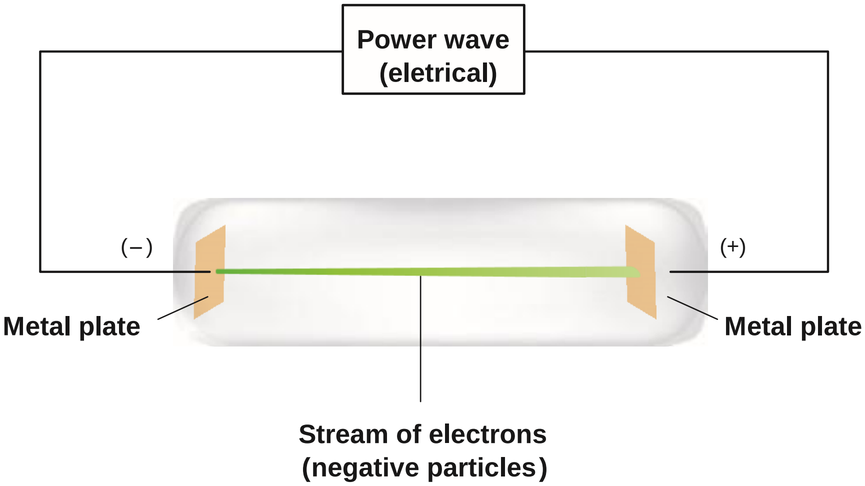


Figure 1.2 Cathode ray tube. A stream of electrons passes between electrodes. The fast-moving particles excite the gas inside the tube, creating a greenish glow between the electrodes.

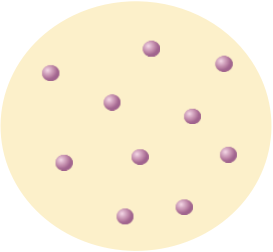


Figure 1.3 Thomson model of the atom. In this early model of the atom, negative particles (electrons) were thought to be embedded in a positively charged sphere. It is sometimes called the plum pudding model.

The **electron** (e^-) is a particle with a negative electrical charge and a mass of 9.110×10^{-28} g. This mass is 1/1837 the mass of a hydrogen atom. Although the actual charge of an electron is known, its value is too cumbersome for practical use and has therefore been assigned a relative electrical charge of -1. The size of an electron has not been determined exactly, but its diameter is believed to be less than 10^{-12} cm.

Protons were first observed by German physicist Eugen Goldstein (1850–1930) in 1886. However, it was Thomson who discovered the nature of the proton. He showed that the proton is a particle, and he calculated its mass to be about 1837 times that of an electron. The **proton** (p) is a particle with actual mass of 1.673×10^{-24} *g*. Its relative charge (+1) is equal in magnitude, but opposite in sign, to the charge on the electron. The mass of a proton is only very slightly less than that of a hydrogen atom.

Thomson had shown that atoms contain both negatively and positively charged particles. Clearly, the Dalton model of the atom was no longer acceptable. Atoms are not indivisible but are instead composed of smaller parts. Thomson proposed a new model of the atom.

In the **Thomson model of the atom**, the electrons are negatively charged particles embedded in the positively charged atomic sphere (see

Figure 1.4). A neutral atom could become an ion by gaining or losing electrons.

Positive ions were explained by assuming that the neutral atom loses electrons. An atom with a net charge of +1 (for example, Na^+ or Li^+) has lost one electron. An atom with a net charge of +3 (for example, Al^{3+}) has lost three electrons (Figure 1.5a).

Negative ions were explained by assuming that additional electrons can be added to atoms. A net charge of -1 (for example, Cl^- or F^-) is produced by the addition of one electron. A net charge of -2 (for example, O^{2-} or S^{2-}) requires the addition of two electrons (Figure 1.5b).

The third major subatomic particle was discovered in 1932 by James Chadwick (1891–1974). This particle, the **neutron** (n), has neither a positive nor a negative charge and has an actual mass (1.675 xx 10^{-24} g) which is only very slightly greater than that of a proton. The properties of these three subatomic particles are summarized in Table 1.2.

Nearly all the ordinary chemical properties of matter can be explained in terms of atoms consisting of electrons, protons, and neutrons. The discussion of atomic structure that follows is based on the assumption that atoms contain only these principal subatomic particles. Many other subatomic particles, such as mesons, positrons, neutrinos, and antiprotons, have been discovered, but it is not yet clear whether all these particles are actually present in the atom or whether they are produced by reactions occurring within the nucleus. The fields of atomic and high-energy physics have produced a long list of subatomic particles.

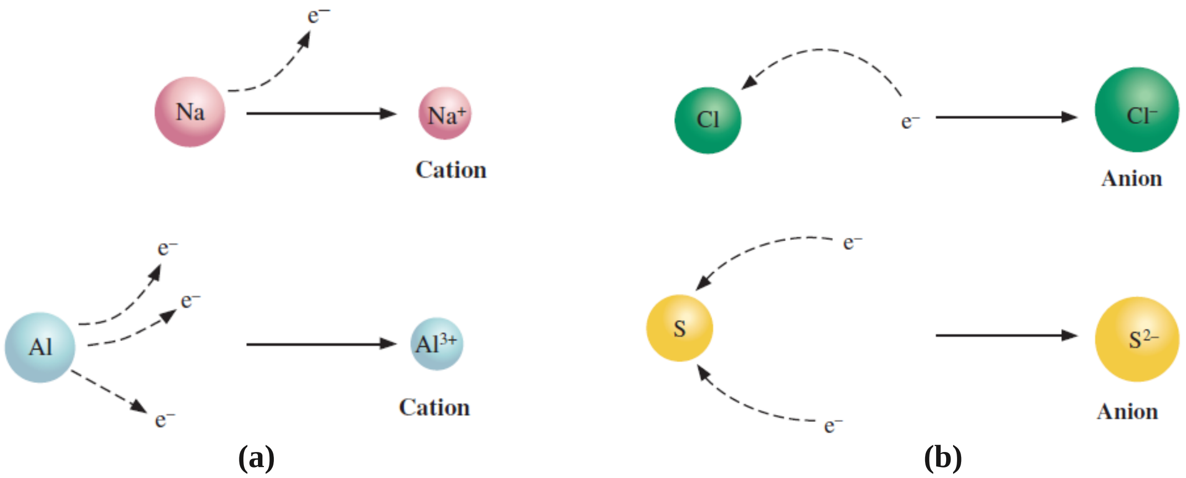


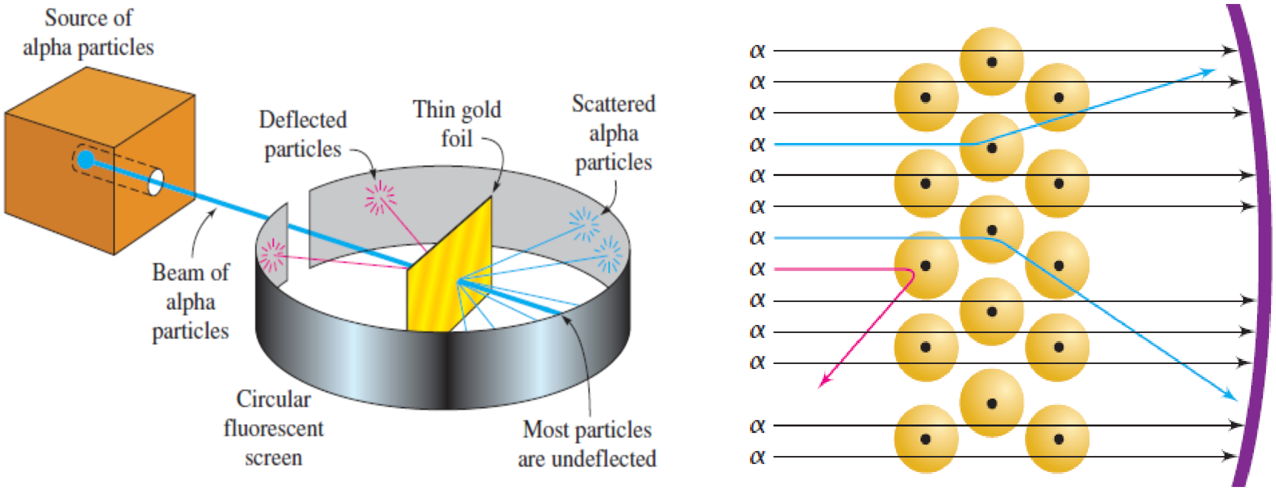
Figure 1.4 (a) When one or more electrons are lost from a neutral atom, a cation is formed. (b) When one or more electrons are added to a neutral atom, an anion is formed.

Table 1.2 Electrical Charge and Relative Mass of Electrons, Protons, and Neutrons

Subatomic Particle	Charge	Mass (g)	Mass (amu)	Mass (amu); Rounded to One Significant Figure	Location in an Atom
Proton	+1	1.6726×10^{-24}	1.0073	1	In the nucleus
Electron	−1	9.1094×10^{-28}	5.4858×10^{-4}	0.0005	Outside the nucleus
Neutron	0	1.6749×10^{-24}	1.0087	1	In the nucleus

1.7 The Nuclear Atom

The discovery that positively charged particles are present in atoms came soon after the discovery of radioactivity by Henri Becquerel (1852–1908) in 1896. Radioactive elements spontaneously emit alpha particles, beta particles, and gamma rays from their nuclei.



(a) (b)

Figure 1.5 a) Rutherford’s experiment on alpha-particle scattering, where positive alpha particles (α), a emanating from a radioactive source, were directed at a thin gold foil. (b) Deflection (red) and scattering (blue) of the positive alpha particles by the positive nuclei of the gold atoms.

By 1907 Ernest Rutherford (1871–1937) had established that the positively charged alpha particles emitted by certain radioactive elements are ions of the element helium. Rutherford used these alpha particles to establish the nuclear nature of atoms. In experiments performed in 1911, he directed a stream of positively charged helium ions (alpha particles) at a very thin sheet of gold foil (about 1000 atoms thick). See Figure 5.6a. He observed that most of the alpha particles passed through the foil with little or no deflection; but a few of the particles were deflected at large angles, and occasionally one even bounced back from the foil (Figure 1.6b). It was known that like charges repel each other and that an electron with a mass of 1/1837 amu could not possibly have an appreciable effect on the path of a 4-amu alpha particle, which is about 7350 times more massive than an electron. Rutherford therefore reasoned that each gold atom must contain a positively charged mass occupying a relatively tiny volume and that, when an alpha particle approaches close enough to this positive mass, it is deflected. Rutherford spoke of this positively charged mass as the nucleus of the atom. Because alpha particles have relatively high masses, the extent of the deflections (some actually bounced back) indicated to Rutherford that the nucleus is very heavy and dense. (The density of the nucleus of a hydrogen atom is about 10^{12} g/cm^3— about 1 trillion times the density of water). Because most of the alpha particles passed through the thousand or so gold atoms without any apparent deflection, he further concluded that most of an atom consists of empty space.

When we speak of the mass of an atom, we are referring primarily to the mass of the nucleus. The nucleus contains all the protons and neutrons, which represent more than 99.9% of the total mass of any atom (Table 1.1). By way of illustration, the largest number of electrons known to exist in an atom is 118. The mass of an atom therefore is primarily determined by the combined masses of its protons and neutrons.

General Arrangement of Subatomic Particles

The alpha-particle scattering experiments of Rutherford established that the atom contains a dense, positively charged nucleus. The later work of Chadwick demonstrated that the atom contains neutrons, which are particles with mass, but no charge. Rutherford also noted that light, negatively charged electrons are present and offset the positive charges in the nucleus. Based on this experimental evidence, a model of the atom and the location of its subatomic particles was devised in which each atom consists of a nucleus surrounded by electrons (see Figure 1.7). The nucleus contains protons and neutrons but does not contain electrons. In a neutral atom the positive charge of the nucleus (due to protons) is exactly offset by the negative electrons. Because the charge of an electron is equal to, but of opposite sign than, the charge of a proton, a neutral atom must contain exactly the same number of electrons as protons. However, this model of atomic structure provides no information on the arrangement of electrons within the atom.

A neutral atom contains the same number of protons and electrons.

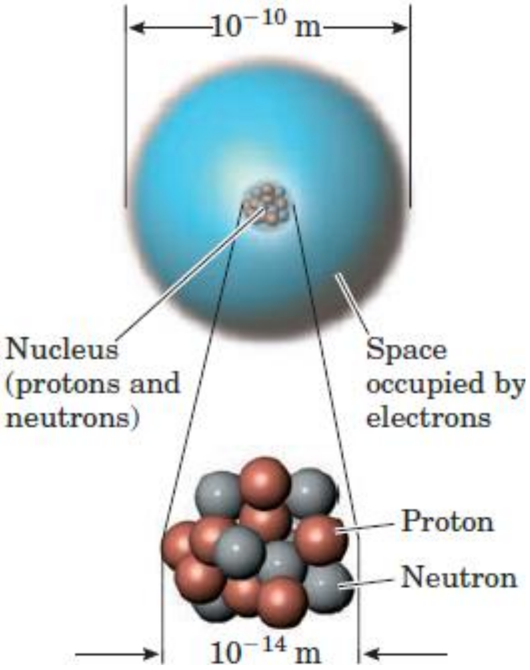


Figure 1.6 In the nuclear model of the atom, protons and neutrons are located in the nucleus. The electrons are found in the remainder of the atom (which is mostly empty space because electrons are very tiny).

Atomic Numbers of the Elements

The **atomic number** of an element is the number of protons in the nucleus of an atom of that element. The atomic number determines the identity of an atom. For example, every atom with an atomic number of 1 is a hydrogen atom; it contains one proton in its nucleus. Every atom with an atomic number of 6 is a carbon atom; it contains 6 protons in its nucleus. Every atom with an atomic number of 92 is a uranium atom; it contains 92 protons in its nucleus. The atomic number tells us not only the number of positive charges in the nucleus but also the number of electrons in the neutral atom, since a neutral atom contains the same number of electrons and protons.

Atomic number = Number of protons in the nucleus

1.8 Isotopes of the Elements

Shortly after Rutherford's conception of the nuclear atom, experiments were performed to determine the masses of individual atoms. These experiments showed that the masses of nearly all atoms were greater than could be accounted for by simply adding up the masses of all the protons and electrons that were known to be present in an atom. This fact led to the concept of the neutron, a particle with no charge but with a mass about the same as that of a proton. Because this particle has no charge, it was very difficult to detect, and the existence of the neutron was not proven experimentally until 1932. All atomic nuclei except that of the simplest hydrogen atom contain neutrons.

All atoms of a given element have the same number of protons. Experimental evidence has shown that, in most cases, all atoms of a given element do not have identical masses. This is because atoms of the same element may have different numbers of neutrons in their nuclei.

Atoms of an element having the same atomic number but different atomic masses are called **isotopes** of that element. Atoms of the various isotopes of an element therefore have the same number of protons and electrons but different numbers of neutrons.

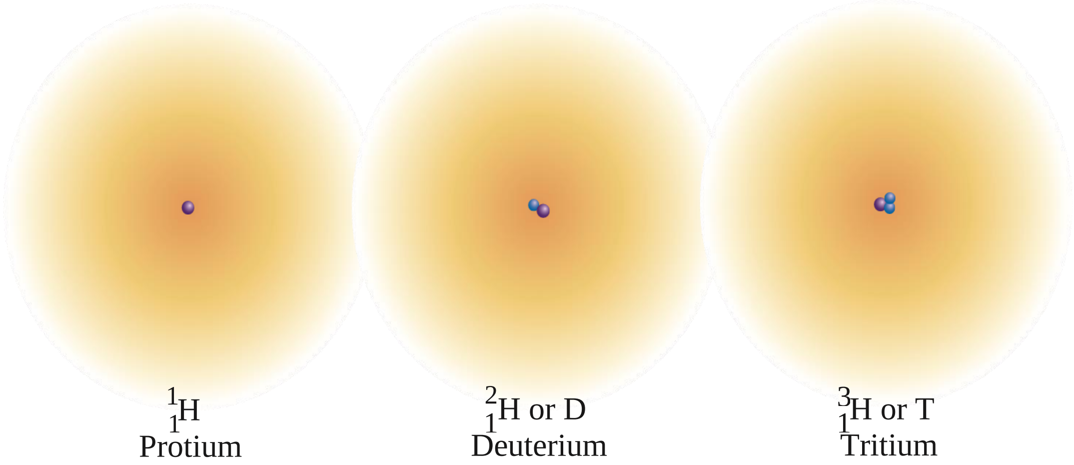


Figure 1.7 The isotopes of hydrogen. The number of protons (purple) and neutrons (blue) are shown within the nucleus. The electron (e-) exists outside the nucleus.

Three isotopes of hydrogen (atomic number 1) are known. Each has one proton in the nucleus and one electron. The first isotope (protium), without a neutron, has a mass number of 1; the second isotope (deuterium), with one neutron in the nucleus, has a mass number of 2; the third isotope (tritium), with two neutrons, has a mass number of 3 (Figure 1.7).

The three isotopes of hydrogen may be represented by the symbols ${}_{1}H^{1}$, ${}_{1}H^{2}$, and ${}_{1}H^{3}$, indicating an atomic number of 1 and mass numbers of 1, 2, and 3, respectively. This method of representing atoms is called ***isotopic notation*** ($\boldsymbol{{}^{A}_{Z}E}$) or ($\boldsymbol{{}_{Z}E^{A}}$). The subscript ($\boldsymbol{Z}$) is the ***atomic number***; the superscript ($\boldsymbol{A}$) is the ***mass number***, which is the sum of the number of protons and the number of neutrons in the nucleus. The hydrogen isotopes may also be referred to as hydrogen-1, hydrogen-2, and hydrogen-3.

The mass number of an element is the sum
of the protons and neutrons in the nucleus.

Most of the elements occur in nature as mixtures of isotopes. However, not all isotopes are stable; some are radioactive and are continuously decomposing to form other elements. For example, of the seven known isotopes of carbon, only two, carbon-12 and carbon-13, are stable. Of the seven known isotopes of oxygen, only three - $_8O^{16}$, $_8O^{17}$, and $_8O^{18}$ - are stable. Of the fifteen known isotopes of arsenic, $_{33}As^{75}$ is the only one that is stable.

1.9 Atomic Mass

The mass of a single atom is far too small to measure on a balance, but fairly precise determinations of the masses of individual atoms can be made with an instrument called a mass spectrometer. The mass of a single hydrogen atom is 1.673 x 10^{-24} g. However, it is neither convenient nor practical to compare the actual masses of atoms expressed in grams; therefore, a table of relative atomic masses using atomic mass units was devised (The term atomic weight is sometimes used instead of atomic mass). The carbon isotope having six protons and six neutrons and designated carbon-12, or $_6C^{12}$, was chosen as the standard for atomic masses. This reference isotope was assigned a value of exactly 12 atomic mass units (amu). Thus, 1 atomic mass unit is defined as equal to exactly 1/12 of the mass of a carbon-12 atom. The actual mass of a carbon12 atom is 1.9927 x 10^{-23} g, and that of one atomic mass unit is 1.6606 x 10^{-24} g. In the table of atomic masses, all elements then have values that are relative to the mass assigned to the reference isotope, carbon-12.

Hydrogen atoms, with a mass of about 1/12 that of a carbon atom, have an average atomic mass of 1.00794 amu on this relative scale. Magnesium atoms, which are about twice as heavy as carbon, have an average mass of 24.305 amu. The average atomic mass of oxygen is 15.9994 amu.

Since most elements occur as mixtures of isotopes with different masses, the atomic mass determined for an element represents the average relative mass of all the naturally occurring isotopes of that element. The atomic masses of the individual isotopes are approximately whole numbers, because the relative masses of the protons and neutrons are approximately 1.0 amu each. Yet we find that the atomic masses given for many of the elements deviate considerably from whole numbers.

For example, the atomic mass of rubidium is 85.4678 amu, that of copper is 63.546 amu, and that of magnesium is 24.305 amu. The deviation of an atomic mass from a whole number is due mainly to the unequal occurrence of the various isotopes of an element.

The two principal isotopes of copper are ${}_{29}Cu^{63}$ and ${}_{29}Cu^{65}$. Copper used in everyday objects. It is apparent that copper-63 atoms are the more abundant isotope, since the atomic mass of copper, 63.546 amu, is closer to

63 than to 65 amu. The actual values of the copper isotopes observed by mass spectra determination are shown in the following table:

Isotope	**Isotopic mass (amu)**	**Abundance (%)**	**Average atomic mass (amu)**
$_{29}Cu^{63}$	62.9298	69.09	63.55
$_{29}Cu^{65}$	64.9278	30.91	

The average atomic mass can be calculated by multiplying the atomic mass of each isotope by the fraction of each isotope present and adding the results. The calculation for copper is

$$(62.9298 \text{ amu})(0.6909) = 43.48 \text{ amu}$$

$$(64.9278 \text{ amu})(0.3091) = \underline{20.07 \text{ amu}}$$

$$63.55 \text{ amu}$$

The ***atomic mass*** of an element is the average relative mass of the isotopes of that element compared to the atomic mass of carbon-12 (exactly 12.000 amu).

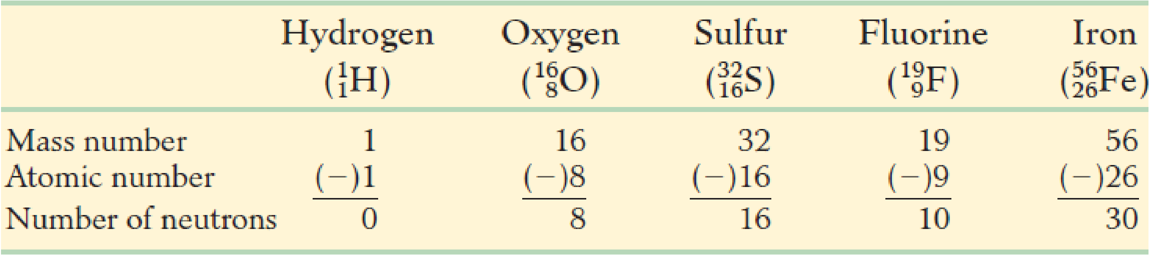
The relationship between mass number and atomic number is such that if we subtract the atomic number from the mass number of a given isotope, we obtain the number of neutrons in the nucleus of an atom of that isotope. Table 1.3 shows this method of determining the number of neutrons. For example, the fluorine atom ($_9F^{19}$), atomic number 9, having a mass of 19 amu, contains 10 neutrons:

mass number - atomic number = number of neutrons

19 - 9 = 10

The atomic masses given in the table on the front endpapers of this book are values accepted by international agreement. You need not memorize atomic masses. In the calculations in this book, the use of atomic masses rounded to four significant figures will give results of sufficient accuracy (See periodic table) .

Table 1.3 Determination of the Number of Neutrons in an Atom by Subtracting Atomic Number from Mass Number



	Hydrogen (^1_1H)	Oxygen ($^{16}_8O$)	Sulfur ($^{32}_{16}S$)	Fluorine ($^{19}_9F$)	Iron ($^{56}_{26}Fe$)
Mass number	1	16	32	19	56
Atomic number	(−)1	(−)8	(−)16	(−)9	(−)26
Number of neutrons	0	8	16	10	30

2 Modern Atomic Theory and the Periodic Table

2.1 A Brief History

In the last 200 years, vast amounts of data have been accumulated to support atomic theory. When atoms were originally suggested by the early Greeks, no physical evidence existed to support their ideas. Early chemists did a variety of experiments, which culminated in Dalton's model of the atom. Because of the limitations of Dalton's model, modifications were proposed first by Thomson and then by Rutherford, which eventually led to our modern concept of the nuclear atom. These early models of the atom work reasonably well—in fact, we continue to use them to visualize a variety of chemical concepts. There remain questions that these models cannot answer, including an explanation of how atomic structure relates to the periodic table. In this chapter, we will present our modern model of the atom; we will see how it varies from and improves upon the earlier atomic models.

2.2 Electromagnetic Radiation

Scientists have studied energy and light for centuries, and several models have been proposed to explain how energy is transferred from place to place. One way energy travels through space is by ***electromagnetic***

radiation. Examples of electromagnetic radiation include light from the sun, X-rays in your dentist's office, microwaves from your microwave oven, radio and television waves, and radiant heat from your fireplace. While these examples seem quite different, they are all similar in some important ways. Each shows wavelike behavior, and all travel at the same speed in a vacuum (3.0×10^8 m/s).

The study of wave behavior is a topic for another course, but we need some basic terminology to understand atoms. Waves have three basic characteristics: wavelength, frequency, and speed. **Wavelength** (lambda, λ) is the distance between consecutive peaks (or troughs) in a wave, as shown in Figure 2.1. **Frequency** (nu, ν) tells how many waves pass a particular point per second. **Speed** (v) tells how fast a wave moves through space.

Light is one form of electromagnetic radiation and is usually classified by its wavelength, as shown in Figure 2.2. Visible light, as you can see, is only a tiny part of the electromagnetic spectrum. Some examples of electromagnetic radiation involved in energy transfer outside the visible region are hot coals in your backyard grill, which transfer infrared radiation to cook your food, and microwaves, which transfer energy to water molecules in the food, causing them to move more quickly and thus raise the temperature of your food.

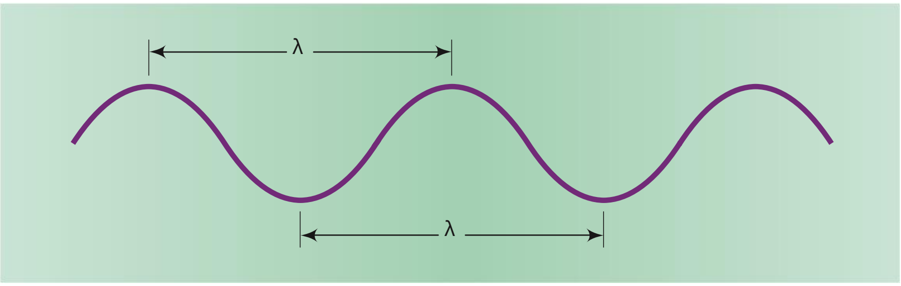


Figure 2.1 The wavelength of this wave is shown by λ. It can be measured from peak to peak or trough to trough.

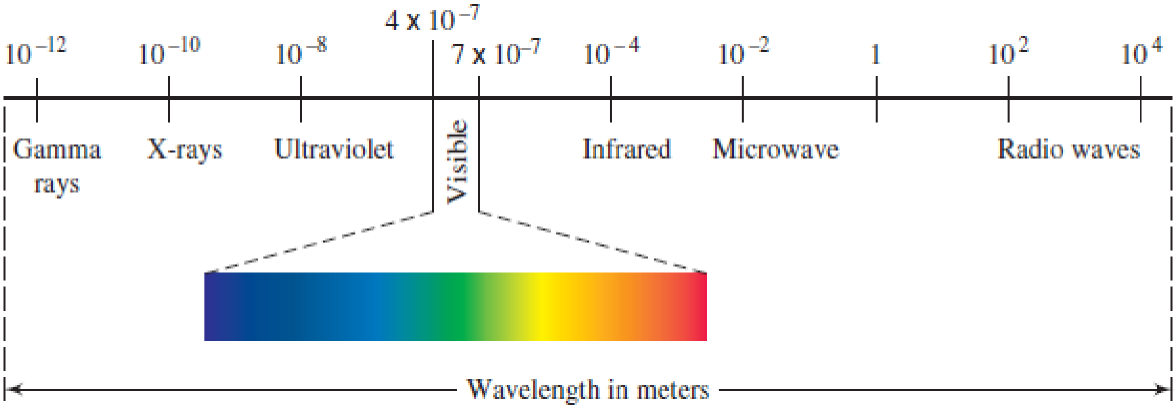


Figure 2.2 The electromagnetic spectrum.

We have evidence for the wavelike nature of light. We also know that a beam of light behaves like a stream of tiny packets of energy called photons. Scientists have agreed to explain the properties of electromagnetic radiation by using both wave and particle properties. Neither explanation is ideal, but currently these are our best models.

2.3 The Bohr Atom

As scientists struggled to understand the properties of electromagnetic radiation, evidence began to accumulate that atoms could radiate light. At high temperatures, or when subjected to high voltages, elements in the gaseous state give off colored light. Brightly colored neon signs illustrate this property of matter very well. When the light emitted by a gas is passed through a prism or diffraction grating, a set of brightly colored lines called a line spectrum results (Figure 2.3). These colored lines indicate that the light is being emitted only at certain wavelengths, or frequencies, that correspond to specific colors. Each element possesses a unique set of these spectral lines that is different from the sets of all the other elements.

Figure 2.3 Line spectrum of hydrogen. Each line corresponds to the wavelength of the energy emitted when the electron of a hydrogen atom, which has absorbed energy, falls back to a lower principal energy level.

In 1912–1913, while studying the line spectrum of hydrogen, Niels Bohr (1885–1962), a Danish physicist, made a significant contribution to the rapidly growing knowledge of atomic structure. His research led him to believe that electrons exist in specific regions at various distances from the nucleus. He also visualized the electrons as revolving in orbits around the nucleus, like planets rotating around the sun, as shown in Figure 2.4.

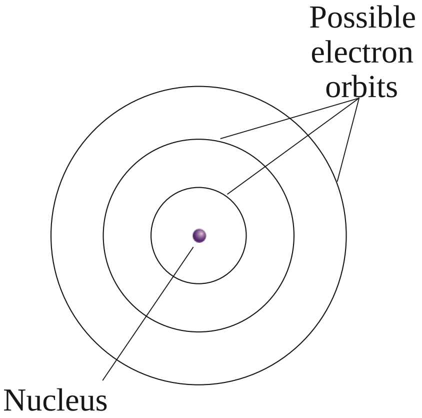


Figure 2.4 The Bohr model of the hydrogen atom described the electron revolving in certain allowed circular orbits around the nucleus.

Bohr's first paper in this field dealt with the hydrogen atom, which he described as a single electron revolving in an orbit about a relatively heavy nucleus. He applied the concept of energy quanta, proposed in 1900 by the German physicist Max Planck (1858–1947), to the observed line spectrum of hydrogen. Planck stated that energy is never emitted in a continuous stream but only in small, discrete packets called **quanta** (Latin, *quantus*, "how much"). From this, Bohr theorized that electrons have several possible energies corresponding to several possible orbits at different distances from the nucleus. Therefore an electron has to be in one specific energy level; it cannot exist between energy levels. In other words, the energy of the electron is said to be quantized. Bohr also stated that when a hydrogen atom absorbed one or more quanta of energy, its electron would “jump” to a higher energy level.

Bohr was able to account for spectral lines of hydrogen this way. A number of energy levels are available, the lowest of which is called the **ground state**. When an electron falls from a high energy level to a lower one (say, from the fourth to the second), a quantum of energy is emitted as light at a specific frequency, or wavelength (Figure 2.5). This light corresponds to one of the lines visible in the hydrogen spectrum (Figure 2.3). Several lines are visible in this spectrum, each one corresponding to a specific electron energy-level shift within the hydrogen atom.

The chemical properties of an element and its position in the periodic table depend on electron behavior within the atoms. In turn, much of our knowledge of the behavior of electrons within atoms is based on spectroscopy. Niels Bohr contributed a great deal to our knowledge of atomic structure by (1) suggesting quantized energy levels for electrons and (2) showing that spectral lines result from the radiation of small increments of energy (Planck’s quanta) when electrons shift from one energy level to another. Bohr’s calculations succeeded very well in correlating the experimentally observed spectral lines with electron energy levels for the hydrogen atom. However, Bohr's methods of calculation did not succeed for heavier atoms. More theoretical work on atomic structure was needed.

In 1926, Erwin Schrödinger, an Austrian physicist, created a mathematical model that described electrons as waves. Using Schrödinger's wave mechanics, we can determine the *probability* of finding an electron in a certain region around the nucleus of the atom.

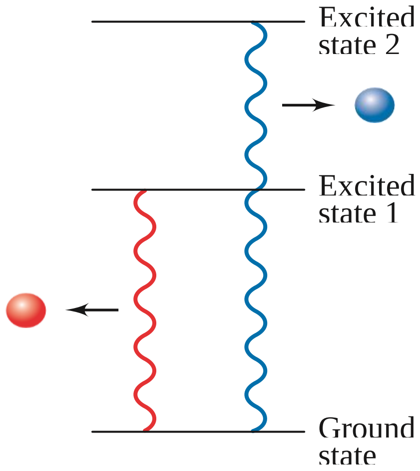


Figure 2.5 When an excited electron returns to the ground state, energy is emitted as a photon is released. The color (wavelength) of the light is determined by the difference in energy between the two states (excited and ground).

In 1924, the French physicist Louis de Broglie suggested a surprising hypothesis: All objects have wave properties. De Broglie used sophisticated mathematics to show that the wave properties for an object of ordinary size, such as a baseball, are too small to be observed. But for smaller objects, such as an electron, the wave properties become significant. Other scientists confirmed de Broglie's hypothesis, showing that electrons do exhibit wave properties.

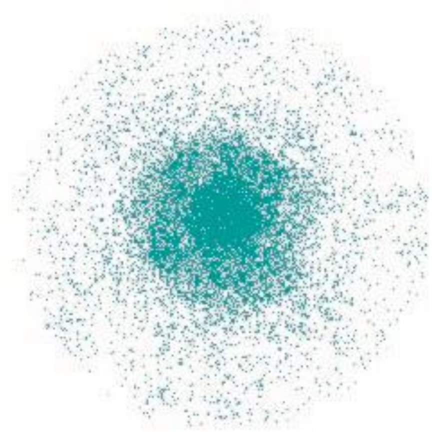


Figure 2.6 An orbital for a hydrogen atom. The intensity of the dots shows that the electron spends more time closer to the nucleus. orbital principal energy levels sublevels

This treatment of the atom led to a new branch of physics called *wave mechanics* or *quantum mechanics*, which forms the basis for our modern understanding of atomic structure. Although the wave-mechanical description of the atom is mathematical, it can be translated, at least in part, into a visual model. It is important to recognize that we cannot locate an electron precisely within an atom; however, it is clear that electrons are not revolving around the nucleus in orbits as Bohr postulated. The electrons are instead found in *orbitals*. An **orbital** is pictured in Figure 2.6 as a region in space around the nucleus where there is a high probability of finding a given electron.

2.4 Energy Levels of Electrons

One of the ideas Bohr contributed to the modern concept of the atom was that the energy of the electron is quantized—that is, the electron is restricted to only certain allowed energies. The wave-mechanical model of the atom also predicts discrete **principal energy levels** within the atom. These energy levels are designated by the letter *n*, where *n* is a positive integer (Figure 2.7). The lowest principal energy level corresponds to $n = 1$, the next to $n = 2$, and so on. As *n* increases, the energy of the electron increases, and the electron is found on average farther from the nucleus.

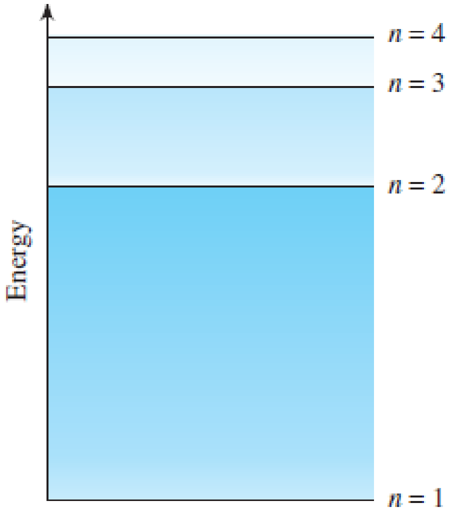


Figure 2.7 The first four principal energy levels in the hydrogen atom. Each level is assigned a principal quantum number n.

Each principal energy level is divided into **sublevels**, which are illustrated in Figure 2.8. The first principal energy level has one sublevel. The second principal energy level has two sublevels, the third energy level has three sublevels, and so on. Each of these sublevels contains spaces for electrons called orbitals.

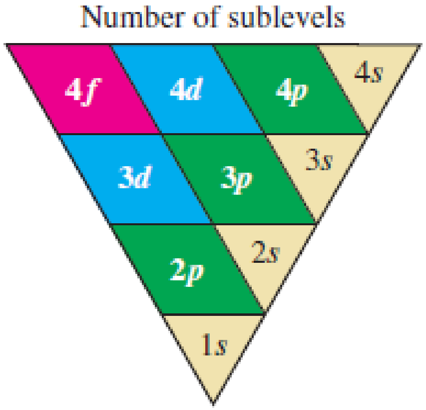


Figure 2.8 The types of orbitals on each of the first four principal energy levels.

In each sublevel the electrons are found within specified orbitals (*s*, *p*, *d*, *f*). Let's consider each principal energy level in turn. The first principal energy level (n = 1) has one sublevel or type of orbital. It is spherical in shape and is designated as 1*s*. It is important to understand what the spherical shape of the 1*s* orbital means.

The electron does not move around on the surface of the sphere, but rather the surface encloses a space where there is a 90% probability where the electron may be found. It might help to consider these orbital shapes in the same way we consider the atmosphere. There is no distinct dividing line between the atmosphere and “space.” The boundary is quite fuzzy. The same is true for atomic orbitals. Each has a region of highest density roughly corresponding to its shape. The probability of finding the electron outside this region drops rapidly but never quite reaches zero. Scientists often speak of orbitals as electron “clouds” to emphasize the fuzzy nature of their boundaries.

How many electrons can fit into a 1*s* orbital? To answer this question, we need to consider one more property of electrons. This property is called **spin**. Each electron appears to be spinning on an axis, like a globe. It can only spin in two directions. We represent this spin with an arrow: or . In order to occupy the same orbital, electrons must have *opposite* spins. That is, two electrons with the same spin cannot occupy the same orbital.

This gives us the answer to our question: An atomic orbital can hold a maximum of two electrons, which must have opposite spins. This rule is called the **Pauli exclusion principle**. The first principal energy level contains one type of orbital (1*s*) that holds a maximum of two electrons.

In the second principal energy level ($n = 2$) we find two sublevels, 2*s* and 2*p*. Like 1*s* in the first principal energy level, the 2*s* orbital is spherical in shape but is larger in size and higher in energy. It also holds a maximum of two electrons. The second type of orbital is designated by 2*p*. The 2*p* sublevel consists of three orbitals: $2p_x$, $2p_y$, and $2p_z$. The shape of *p* orbitals is quite different from the *s* orbitals, as shown in Figure 2.9.

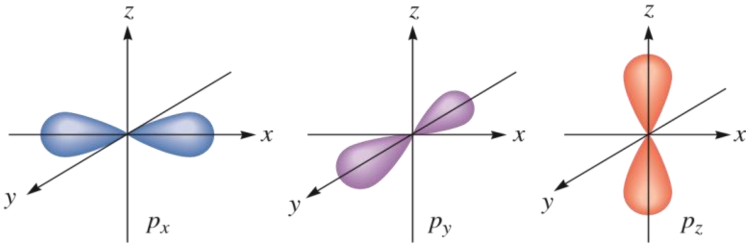


Figure 2.9 Perspective representation of the p_x, p_y, and p_z atomic orbitals.

Each *p* orbital has two “lobes.” Remember, the space enclosed by these surfaces represents the regions of probability for finding the electrons 90% of the time. There are three separate *p* orbitals, each oriented in a different direction, and each *p* orbital can hold a maximum of two electrons. Thus the total number of electrons that can reside in all three *p* orbitals is six. To summarize our model, the first principal energy level of an atom has a 1*s* orbital. The second principal energy level has a 2*s* and three 2*p* orbitals labeled $2p_x$, $2p_y$, and $2p_z$, as shown in Figure 2.10.

The third principal energy level has three sublevels labeled 3*s*, 3*p*, and 3*d*. The 3*s* orbital is spherical and larger than the 1*s* and 2*s* orbitals. The $3p_x$, $3p_y$, $3p_z$ orbitals are shaped like those of the second level, only larger. The five 3*d* orbitals have the shapes shown in Figure 2.11. You don’t need to memorize these shapes, but notice that they look different from the *s* or *p* orbitals.

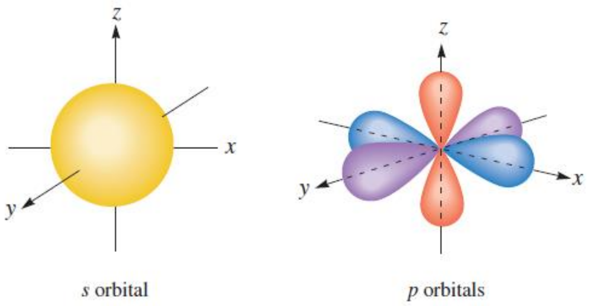


Figure 2.10 Orbitals on the second principal energy level are one *2s* and three *2p* orbitals.

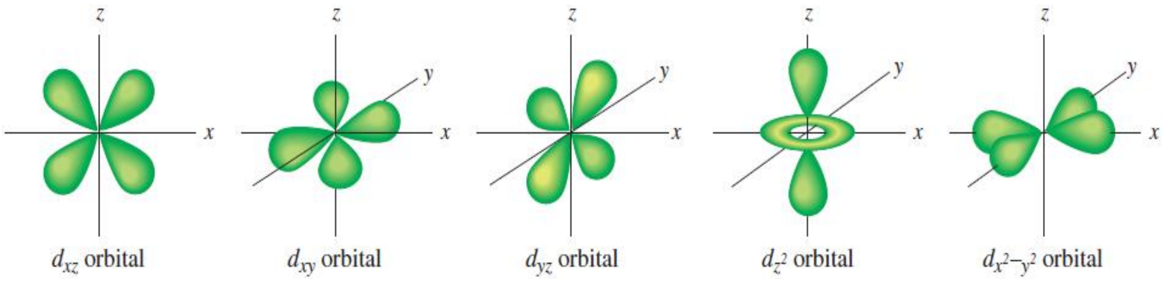


Figure 2.11 The five *d* orbitals are found in the third principal energy level along with one *3s* orbital and three *3p* orbitals.

Each time a new principal energy level is added, we also add a new sublevel. This makes sense because each energy level corresponds to a larger average distance from the nucleus, which provides more room on each level for new sublevels containing more orbitals.

The pattern continues with the fourth principal energy level. It has 4*s*, 4*p*, 4*d*, and 4*f* orbitals. There are one 4*s*, three 4*p*, five 4*d*, and seven 4*f* orbitals. The shapes of the *s*, *p*, and *d* orbitals are the same as those for lower levels, only larger. We will not consider the shapes of the orbitals. Remember that for all *s*, *p*, *d*, and *f* orbitals, the maximum number of electrons per orbital is two. We summarize each principal energy level:

***n* = 1**	**1*s***			
***n* = 2**	**2*s***	**2*p* 2*p* 2*p***		
***n* = 3**	**3*s***	**3*p* 3*p* 3*p***	**3*d* 3*d* 3*d* 3*d* 3*d***	
***n* = 4**	**4*s***	**4*p* 4*p* 4*p***	**4*d* 4*d* 4*d* 4*d* 4*d***	**4*f* 4*f* 4*f* 4*f* 4*f* 4*f* 4*f***

The hydrogen atom consists of a nucleus (containing one proton) and one electron occupying a region outside of the nucleus. In its ground state, the electron occupies a 1*s* orbital, but by absorbing energy the electron can become *excited* and move to a higher energy level.

The hydrogen atom can be represented as shown in Figure 2.12. The diameter of the nucleus is about 10^{-15} m, and the diameter of the electron orbital is about 10^{-10} m. The diameter of the electron cloud of a hydrogen atom is about 100,000 times greater than the diameter of the nucleus.

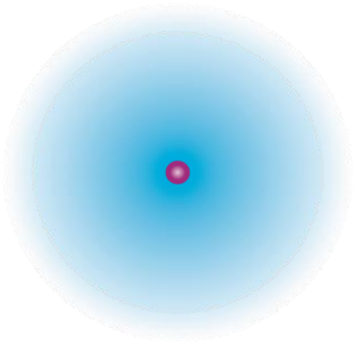


Figure 2.12 The modern concept of a hydrogen atom consists of a proton and an electron in an s orbital. The shaded area represents a region where the electron may be found with 90% probability.

2.5 Atomic Structures of the First 18 Elements

We have seen that hydrogen has one electron that can occupy a variety of orbitals in different principal energy levels. Now let’s consider the structure of atoms with more than one electron. Because all atoms contain orbitals similar to those found in hydrogen, we can describe the structures of atoms beyond hydrogen by systematically placing electrons in these hydrogen-like orbitals. We use the following guidelines:

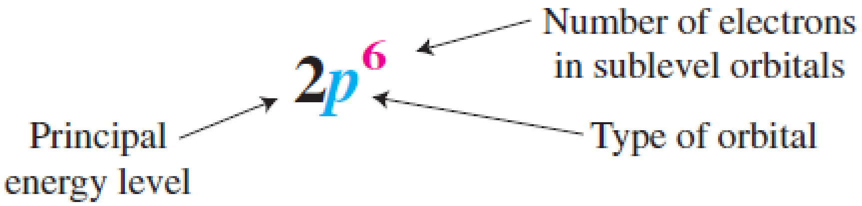
1) Electrons fill the orbitals in order of increasing orbital energy (**Aufbau Principle**). The number of electrons in a shell (n) = $2n^2$; with

max of 32 electrons. For the atoms beyond hydrogen, orbital energies vary as s < p < d < f for a given value of n.

2) Each orbital can hold up to two electrons with spins paired (**Pauli Exclusion Principal**).

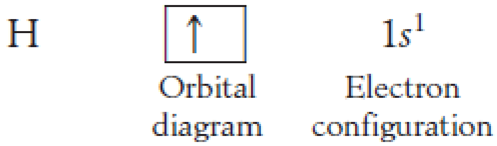
3) When there is a set of orbitals of equal energy, each orbital becomes half-filled before any of them becomes completely filled (**Hund's Rule**). For example, all three p orbitals must contain one electron before a second electron enters a p orbital.

We can use several methods to represent the atomic structures of atoms, depending on what we are trying to illustrate. We often are interested in showing the arrangement of the electrons in an atom in their orbitals. There are two ways to do this. The first method is called the **electron configuration**. In this method, we list each type of orbital, showing the number of electrons in it as an exponent. An electron configuration is read as follows:

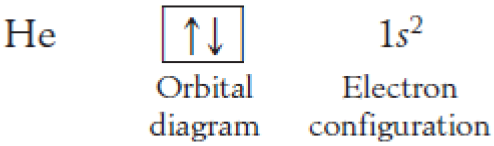


We can also represent this configuration with an **orbital diagram** in which boxes represent the orbitals (containing small arrows indicating the electrons). When the orbital contains one electron, an arrow, pointing upward (q), is placed in the box. A second arrow, pointing downward (p), indicates the second electron in that orbital.

Let's consider each of the first 18 elements on the periodic table in turn. The order of filling for the orbitals in these elements is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 4*s*. Hydrogen, the first element, has only one electron. The electron will be in the 1*s* orbital because this is the most favorable position (where it will have the greatest attraction for the nucleus). Both representations are shown here:



Helium, with two electrons, can be shown as

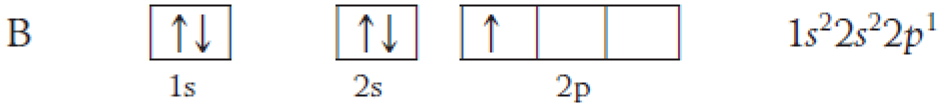


The first energy level, which can hold a maximum of two electrons, is now full. An atom with three electrons will have its third electron in the second energy level. Thus, in lithium (atomic number 3), the first two electrons are in the 1*s* orbital, and the third electron is in the 2*s* orbital of the second energy level.

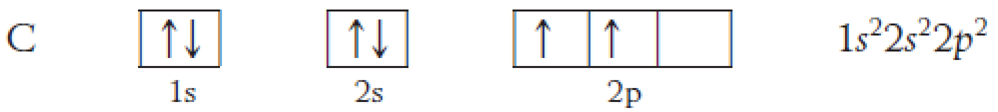
Lithium has the following structure:

All four electrons of beryllium are s electrons:

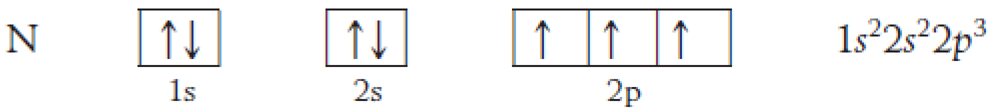
The next six elements illustrate the filling of the p orbitals. Boron has the first p electron. Because p orbitals all have the same energy, it doesn't matter which of these orbitals fills first:



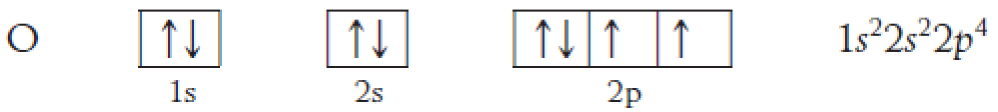
Carbon is the sixth element. It has two electrons in the 1s orbital, two electrons in the 2s orbital, and two electrons to place in the 2p orbitals. Because it is more difficult for the p electrons to pair up than to occupy a second p orbital, the second p electron is located in a different p orbital. We could show this by writing $2p_x{}^1\ 2p_y{}^1$, but we usually write it as $2p^2$; it is understood that the electrons are in different p orbitals. The spins on these electrons are alike, for reasons we will not explain here.



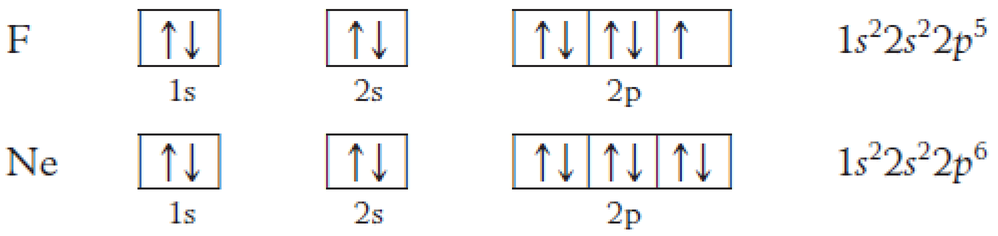
Nitrogen has seven electrons. They occupy the 1s, 2s, and 2p orbitals. The third p electron in nitrogen is still unpaired and is found in the $2p_z$ orbital:



Oxygen is the eighth element. It has two electrons in both the 1s and 2s orbitals and four electrons in the 2p orbitals. One of the 2p orbitals is now occupied by a second electron, which has a spin opposite the electron already in that orbital:

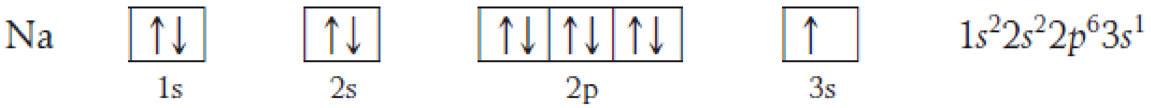


The next two elements are fluorine with nine electrons and neon with ten electrons:



With neon, the first and second energy levels are filled as shown in Table 2.1. The second energy level can hold a maximum of eight electrons, $2s^2$ $2p^6$.

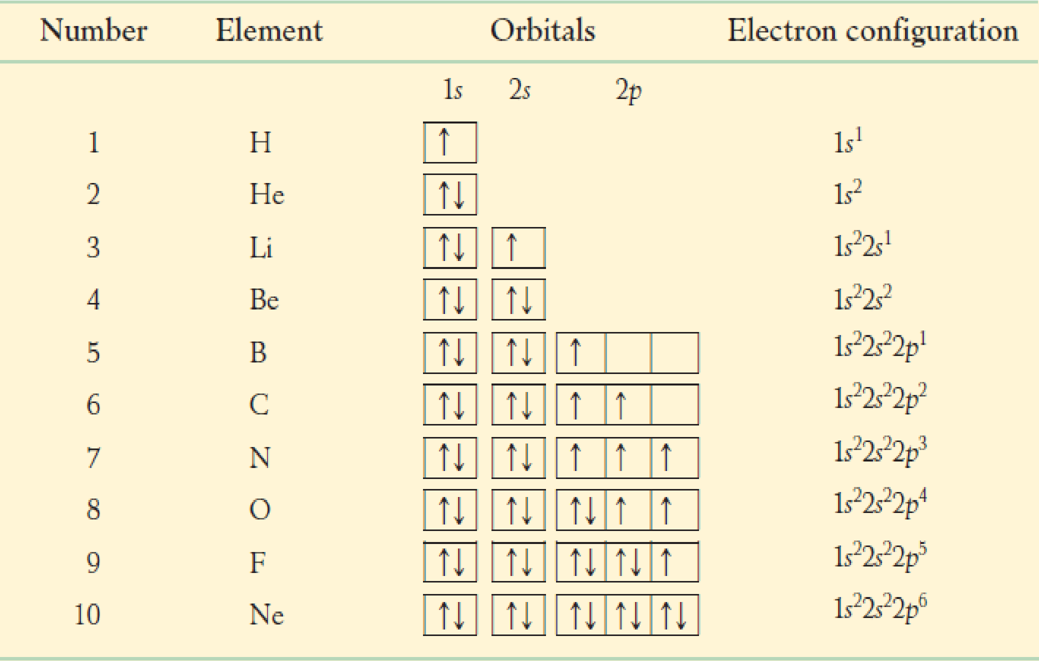
Sodium, element 11, has two electrons in the first energy level and eight electrons in the second energy level, with the remaining electron occupying the 3s orbital in the third energy level:



Magnesium (12), aluminum (13), silicon (14), phosphorus (15), sulfur (16), chlorine (17), and argon (18) follow in order. Table 10.2 summarizes the filling of the orbitals for elements 11–18.

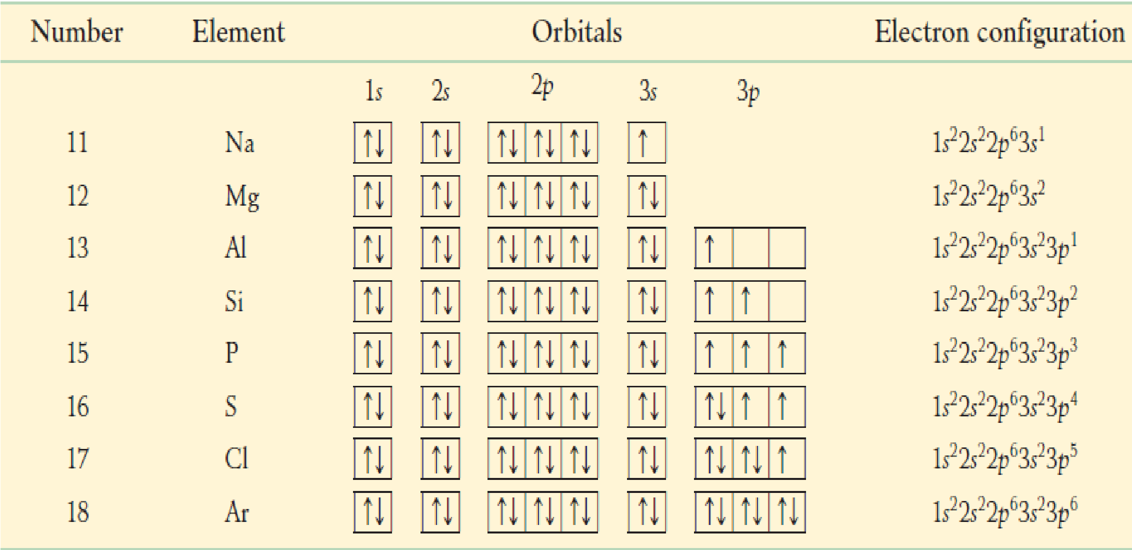
The electrons in the outermost (highest) energy level of an atom are called the valence electrons. For example, oxygen, which has the electron configuration of $1s^2$ $2s^2$ $2p^4$, has electrons in the first and second energy levels. Therefore the second principal energy level is the valence level for oxygen. The 2s and 2p electrons are the valence electrons. In the case of magnesium ($1s^2$ $2s^2$ $2p^6$ $3s^2$), the valence electrons are in the 3s orbital, since these are outermost electrons. Valence electrons are involved in bonding atoms together to form compounds and are of particular interest to chemists.

Table 2.1 Orbital Filling for the First Ten Elements



Number	Element	Orbitals 1s	Orbitals 2s	Orbitals 2p	Electron configuration
1	H	[↑]			$1s^1$
2	He	[↑↓]			$1s^2$
3	Li	[↑↓]	[↑]		$1s^2 2s^1$
4	Be	[↑↓]	[↑↓]		$1s^2 2s^2$
5	B	[↑↓]	[↑↓]	[↑][ ][ ]	$1s^2 2s^2 2p^1$
6	C	[↑↓]	[↑↓]	[↑][↑][ ]	$1s^2 2s^2 2p^2$
7	N	[↑↓]	[↑↓]	[↑][↑][↑]	$1s^2 2s^2 2p^3$
8	O	[↑↓]	[↑↓]	[↑↓][↑][↑]	$1s^2 2s^2 2p^4$
9	F	[↑↓]	[↑↓]	[↑↓][↑↓][↑]	$1s^2 2s^2 2p^5$
10	Ne	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	$1s^2 2s^2 2p^6$

Table 2.2 Orbital Filling for Elements 11-18



Number	Element	Orbitals 1s	Orbitals 2s	Orbitals 2p	Orbitals 3s	Orbitals 3p	Electron configuration
11	Na	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑]		$1s^2 2s^2 2p^6 3s^1$
12	Mg	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]		$1s^2 2s^2 2p^6 3s^2$
13	Al	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑][ ][ ]	$1s^2 2s^2 2p^6 3s^2 3p^1$
14	Si	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑][↑][ ]	$1s^2 2s^2 2p^6 3s^2 3p^2$
15	P	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑][↑][↑]	$1s^2 2s^2 2p^6 3s^2 3p^3$
16	S	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑][↑]	$1s^2 2s^2 2p^6 3s^2 3p^4$
17	Cl	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓][↑]	$1s^2 2s^2 2p^6 3s^2 3p^5$
18	Ar	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	$1s^2 2s^2 2p^6 3s^2 3p^6$

2.6 Electron Structures and the Periodic Table

We have seen how the electrons are assigned for the atoms of elements 1–18.

The periodic table represents the efforts of chemists to organize the elements logically. Chemists of the early nineteenth century had sufficient knowledge of the properties of elements to recognize similarities among groups of elements. In 1869, Dimitri Mendeleev (1834–1907) of Russia and Lothar Meyer (1830–1895) of Germany independently published periodic arrangements of the elements based on increasing atomic masses. Mendeleev's arrangement is the precursor to the modern periodic table, and his name is associated with it. The modern periodic table is shown in Figure 2.13.

Each horizontal row in the periodic table is called a period, as shown in Figure 2.13. There are seven periods of elements. The number of each period corresponds to the outermost energy level that contains electrons for elements in that period. Those in Period 1 contain electrons only in energy level 1, while those in Period 2 contain electrons in levels 1 and 2. In Period 3, electrons are found in levels 1, 2, and 3, and so on.

Elements that behave in a similar manner are found in groups or families. These form the vertical columns on the periodic table. Several systems exist for numbering the groups. In one system, the columns are numbered from left to right using the numbers 1–18. However, we use a system that numbers the columns with numbers and the letters A and B, as shown in Figure 2.13. The A groups are known as the representative elements. The B groups and Group 8 are called the transition elements. The groups (columns) of the periodic table often have family names. For example, the group on the far right side of the periodic table (He, Ne, Ar, Kr, Xe, and Rn) is called the noble gases. Group 1A is called the alkali metals, Group 2A the alkaline earth metals, and Group 7A the halogens.

We’ve just seen that the periods of the periodic table are associated with the energy level of the outermost electrons of the atoms in that period. Look at the valence electron configurations of the elements we have just examined (Figure 2.14). Do you see a pattern? The valence electron configuration for the elements in each column is the same. The chemical behavior and properties of elements in a particular family must therefore be associated with the electron configuration of the elements. The number for the principal energy level is different. This is expected since each new period is associated with a different energy level for the valence electrons.

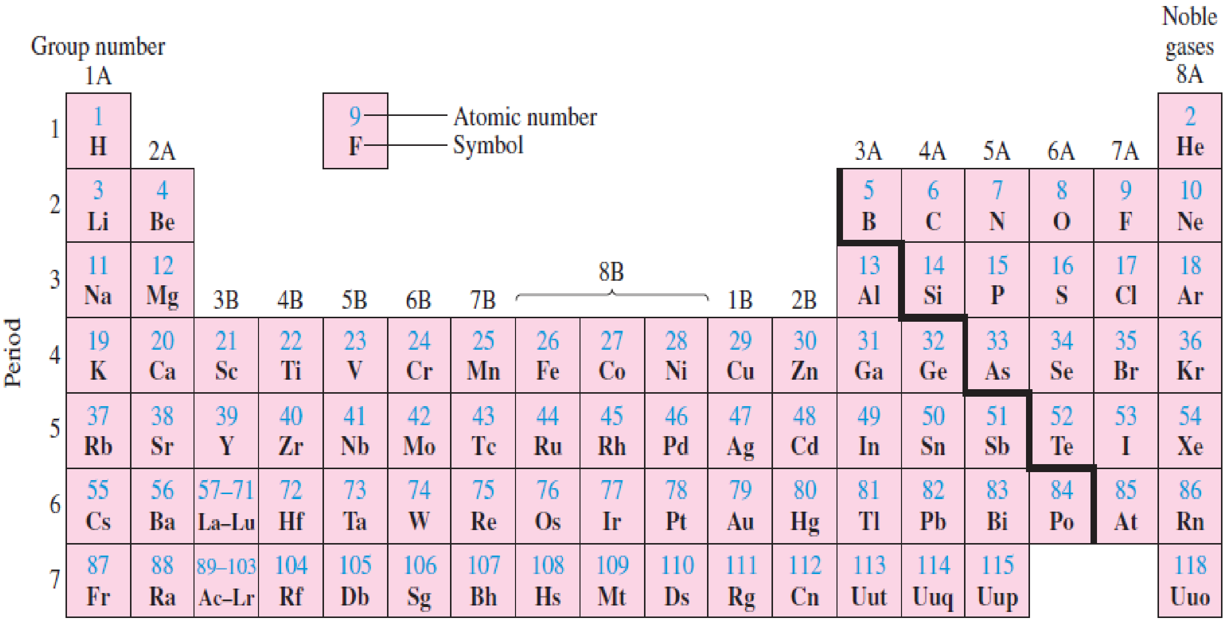


Figure 2.13 The periodic table of the elements.

The electron configurations for elements beyond these first 18 become long and tedious to write. We often abbreviate the electron configuration using the following notation:

$$\text{Na} \quad [\text{Ne}]3s^1$$

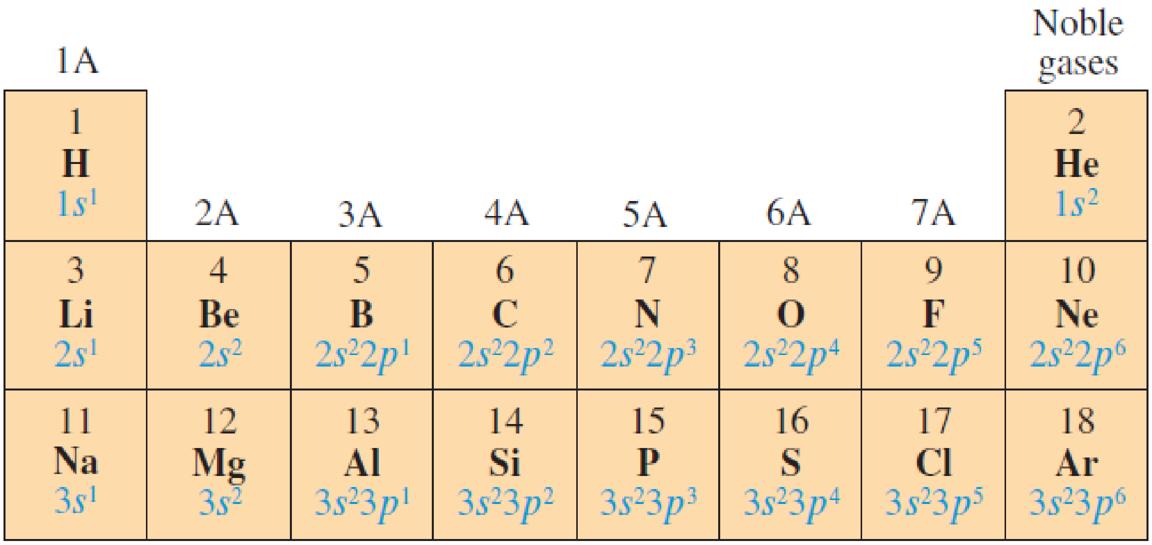
Look carefully at Figure 2.14 and you will see that the *p* orbitals are full at the noble gases. By placing the symbol for the noble gas in square brackets, we can abbreviate the complete electron configuration and focus our attention on the valence electrons. To write the abbreviated electron configuration for any element, go back to the previous noble gas and place its symbol in square brackets. Then list the valence electrons. Here are some examples:

B	$1s^2\ 2s^2\ 2p^1$	$[\mathrm{He}]2s^2\ 2p^1$
Cl	$1s^2$ 2s2 $2p^6\ 3s^2\ 3p^5$	$[\mathrm{Ne}]3s^2\ 3p^5$
Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$	$[\mathrm{Ne}]3s^1$

The sequence for filling the orbitals is exactly as we would expect up through the 3*p* orbitals. The third energy level might be expected to fill with 3*d* electrons before electrons enter the 4*s* orbital, but this is not the case. The behavior and properties of the next two elements, potassium (19) and calcium (20), are very similar to the elements in Groups 1A and 2A, respectively. They clearly belong in these groups. The other elements in Group 1A and Group 2A have electron configurations that indicate valence electrons in the *s* orbitals. For example, since the electron configuration is connected to the element's properties, we should place the last electrons for potassium and calcium in the 4*s* orbital.

Their electron configurations are:

K	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	**or**	$[\mathrm{Ar}]4s^1$
Ca	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	**or**	$[\mathrm{Ar}]4s^2$



1A	2A	3A	4A	5A	6A	7A	Noble gases
1 **H** $1s^1$							2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$	5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$	13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$

Figure 2.14 Valence electron configurations for the first 18 elements.

Elements 21–30 belong to the elements known as transition elements. Electrons are placed in the 3d orbitals for each of these elements. When the 3d orbitals are full, the electrons fill the 4p orbitals to complete the fourth period. Let’s consider the overall relationship between orbital filling and the periodic table. Figure 2.15 illustrates the type of orbital filling and its location on the periodic table. The tall columns on the table (labeled 1A–7A, and noble gases) are often called the representative elements. Valence electrons in these elements occupy s and p orbitals. The period number corresponds to the energy level of the valence electrons. The elements in the center of the periodic table are the transition elements where the d orbitals are being filled. Notice that the number for the d orbitals is one less than the period number. The two rows shown at the bottom of the table in Figure

2.15 are called the inner transition elements or the lanthanide and actinide series. The last electrons in these elements are placed in the orbitals. The number for the orbitals is always two less than that of the s and p orbitals. A periodic table is almost always available to you, so if you understand the relationship between the orbitals and the periodic table, you can write the electron configuration for any element. There are several minor variations to these rules.

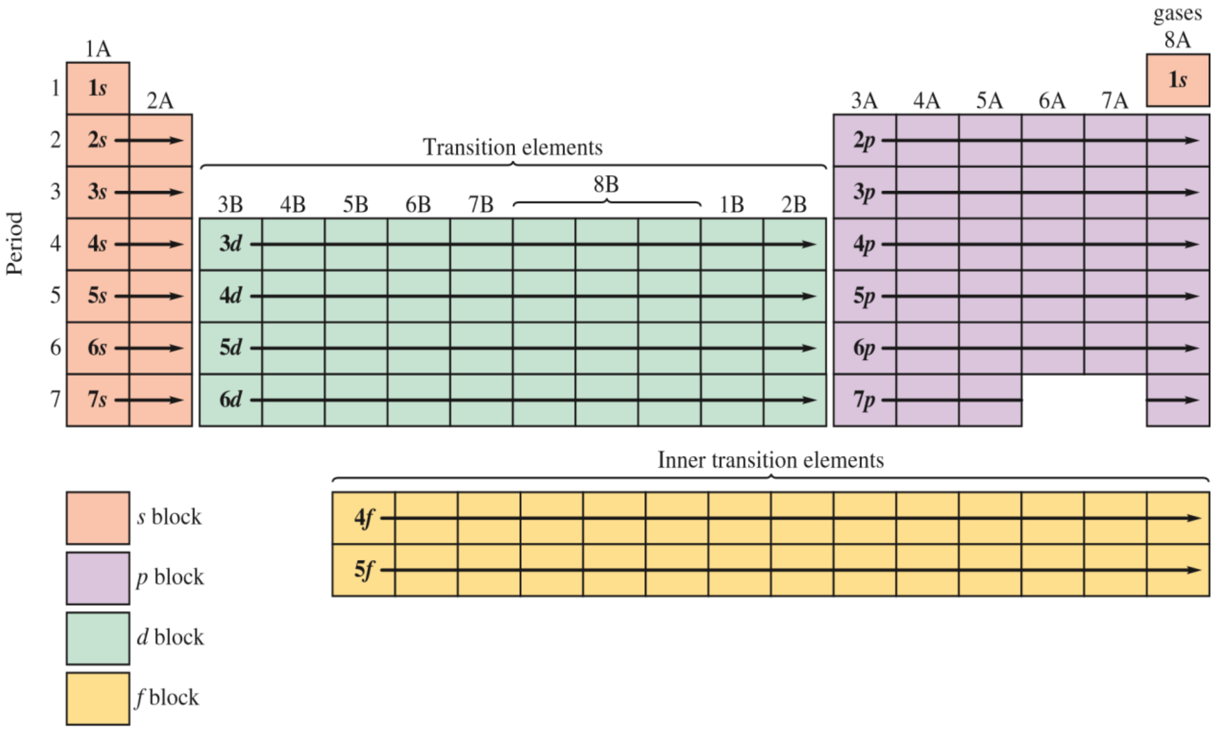
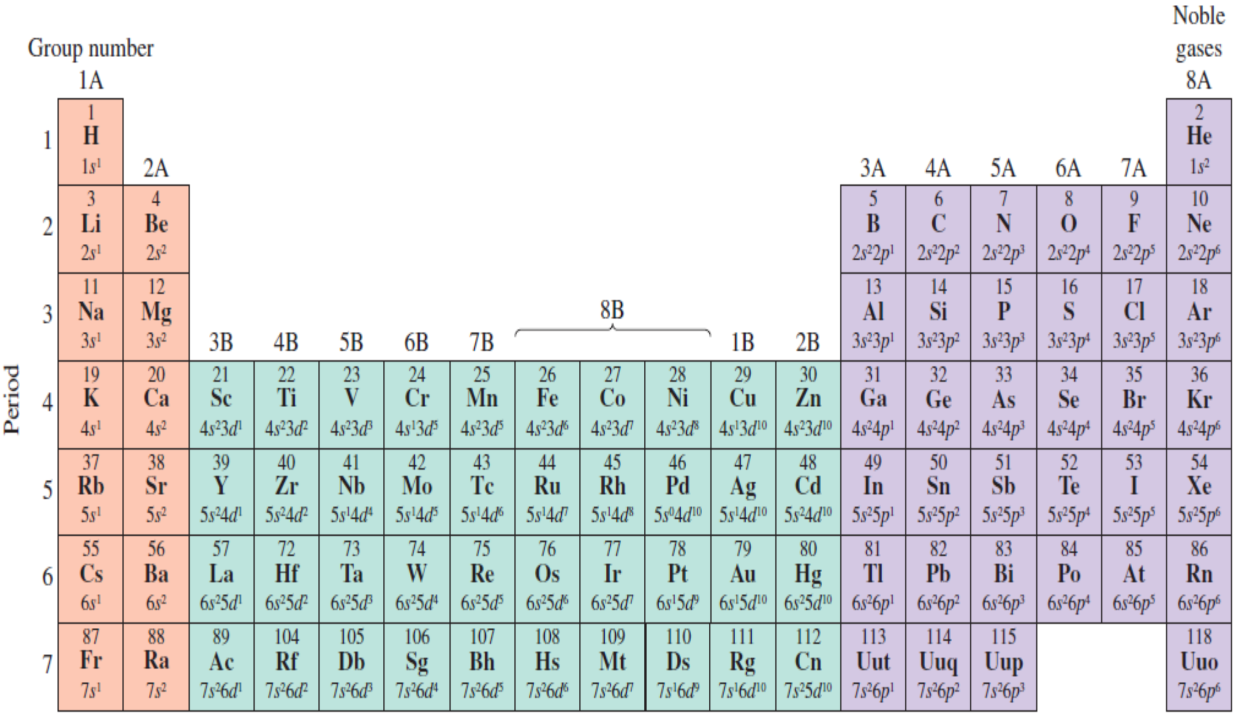


Figure 2.15 Arrangement of electrons according to sublevel being filled.

The early chemists classified the elements based only on their observed properties, but modern atomic theory gives us an explanation for why the properties of elements vary periodically. For example, as we “build” atoms by filling orbitals with electrons, the same orbitals occur on each energy level. This means that the same electron configuration reappears regularly for each level. Groups of elements show similar chemical properties because of the similarity of these outermost electron configurations.



Group number

Noble gases

Period	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^23d^1$	22 **Ti** $4s^23d^2$	23 **V** $4s^23d^3$	24 **Cr** $4s^13d^5$	25 **Mn** $4s^23d^5$	26 **Fe** $4s^23d^6$	27 **Co** $4s^23d^7$	28 **Ni** $4s^23d^8$	29 **Cu** $4s^13d^{10}$	30 **Zn** $4s^23d^{10}$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^24d^1$	40 **Zr** $5s^24d^2$	41 **Nb** $5s^14d^4$	42 **Mo** $5s^14d^5$	43 **Tc** $5s^14d^6$	44 **Ru** $5s^14d^7$	45 **Rh** $5s^14d^8$	46 **Pd** $5s^04d^{10}$	47 **Ag** $5s^14d^{10}$	48 **Cd** $5s^24d^{10}$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** $6s^25d^1$	72 **Hf** $6s^25d^2$	73 **Ta** $6s^25d^3$	74 **W** $6s^25d^4$	75 **Re** $6s^25d^5$	76 **Os** $6s^25d^6$	77 **Ir** $6s^25d^7$	78 **Pt** $6s^15d^9$	79 **Au** $6s^15d^{10}$	80 **Hg** $6s^25d^{10}$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** $7s^26d^1$	104 **Rf** $7s^26d^2$	105 **Db** $7s^26d^3$	106 **Sg** $7s^26d^4$	107 **Bh** $7s^26d^5$	108 **Hs** $7s^26d^6$	109 **Mt** $7s^26d^7$	110 **Ds** $7s^16d^9$	111 **Rg** $7s^16d^{10}$	112 **Cn** $7s^25d^{10}$	113 **Uut** $7s^26p^1$	114 **Uuq** $7s^26p^2$	115 **Uup** $7s^26p^3$			118 **Uuo** $7s^26p^6$

Figure 2.16 Outermost electron configurations.

In Figure 2.16, only the electron configuration of the outermost electrons is given. This periodic table illustrates these important points:

1. The number of the period corresponds with the highest energy level occupied by electrons in that period.
2. The group numbers for the representative elements are equal to the total number of outermost electrons in the atoms of the group. For example, elements in Group 7A always have the electron configuration ns2 np5. The d and f electrons are always in a lower energy level than the highest energy level and so are not considered as outermost (valence) electrons.
3. The elements of a family have the same outermost electron configuration except that the electrons are in different energy levels.
4. The elements within each of the s, p, d, f blocks are filling the s, p, d, f orbitals, as shown in Figure 2.15.
5. Within the transition elements, some discrepancies in the order of filling occur.

3. Chemical Bonds:

The Formation of Compounds from Atoms

3.1 Periodic Trends in Atomic Properties

Although atomic theory and electron configuration help us understand the arrangement and behavior of the elements, it’s important to remember that the design of the periodic table is based on observing properties of the elements. Before we use the concept of atomic structure to explain how and why atoms combine to form compounds, we need to understand the characteristic properties of the elements and the trends that occur in these properties on the periodic table. These trends allow us to use the periodic table to accurately predict properties and reactions of a wide variety of substances.

Metals and Nonmetals

Elements are classified as metals, nonmetals, or metalloids. The heavy stair-step line beginning at boron and running diagonally down the periodic table separates the elements into metals and nonmetals. Metals are usually lustrous, malleable, and good conductors of heat and electricity. Nonmetals are just the opposite; nonlustrous, brittle, and poor conductors. Metalloids are found bordering the heavy diagonal line and may have properties of both metals and nonmetals.

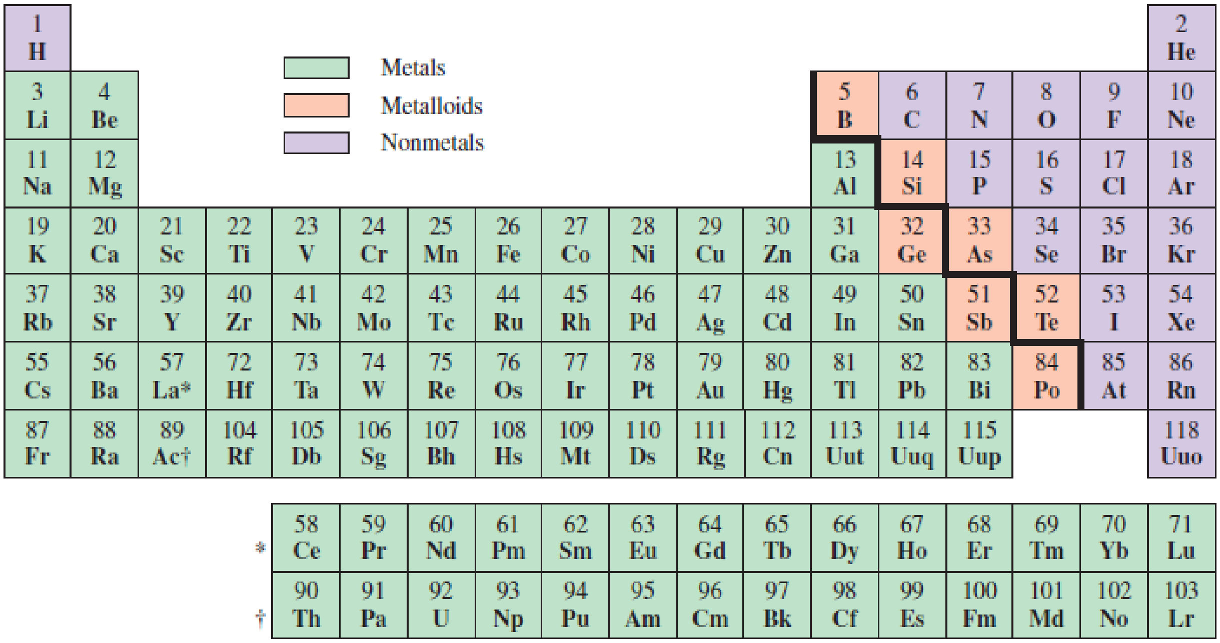
Most elements are classified as metals (see Figure 3.1). Metals are found on the left side of the stair-step line, while the nonmetals are located toward the upper right of the table. Note that hydrogen does not fit into the division of metals and nonmetals. It displays nonmetallic properties under normal conditions, even though it has only one outermost electron like the alkali metals. Hydrogen is considered to be a unique element.

It is the chemical properties of metals and nonmetals that interest us most. Metals tend to lose electrons and form positive ions, while nonmetals tend to gain electrons and form negative ions. When a metal reacts with a nonmetal, electrons are often transferred from the metal to the nonmetal.

Atomic Radius

The relative radii of the representative elements are shown in Figure 3.2. Notice that the radii of the atoms tend to increase down each group and that they tend to decrease from left to right across a period.

The increase in radius down a group can be understood if we consider the electron structure of the atoms. For each step down a group, an additional energy level is added to the atom. The average distance from the nucleus to the outside edge of the atom must increase as each new energy level is added. The atoms get bigger as electrons are placed in these new higher-energy levels.



🟩 Metals
🟥 Metalloids
🟪 Nonmetals

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac†	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup			118 Uuo
		*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		†	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Figure 3.1 The elements are classified as metals, nonmetals, and metalloids.

Understanding the decrease in atomic radius across a period requires more thought, however. As we move from left to right across a period, electrons within the same block are being added to the same principal energy level. Within a given energy level, we expect the orbitals to have about the same size. We would then expect the atoms to be about the same size across the period. But each time an electron is added, a proton is added to the nucleus as well. The increase in positive charge (in the nucleus) pulls the electrons closer to the nucleus, which results in a gradual decrease in atomic radius across a period.

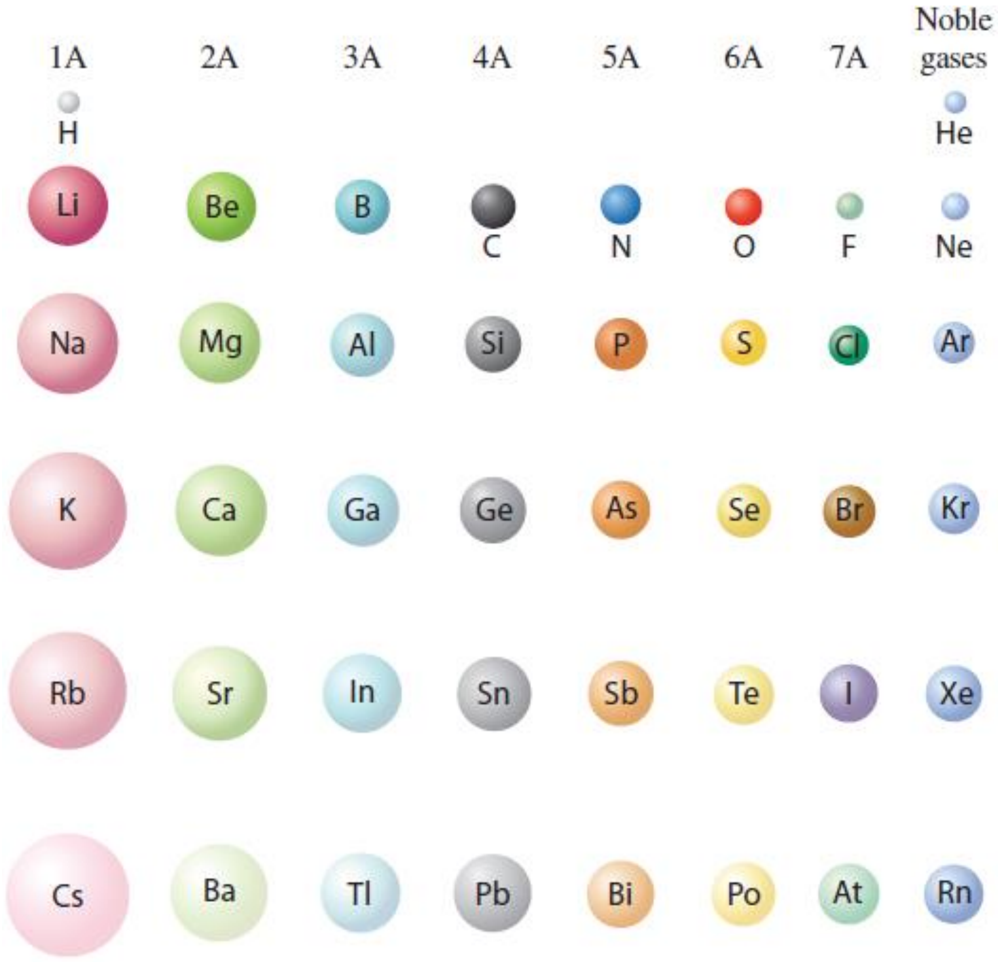


Figure 3.2 Relative atomic radii for the representative elements. Atomic radius decreases across a period and increases down a group in the periodic table.

Ionization Energy

The ionization energy of an atom is the energy required to remove an electron from the atom. For example,

$$\mathbf{Na + ionization\ energy \rightarrow Na^+ + e^-}$$

The first ionization energy is the amount of energy required to remove the first electron from an atom, the second is the amount required to remove the second electron from that atom, and so on. Table 3.1 gives the ionization energies for the removal of one to five electrons from several elements. The table shows that even higher amounts of energy are needed to remove the second, third, fourth, and fifth electrons. This makes sense because removing electrons leaves fewer electrons attracted to the same positive charge in the nucleus. The data in Table 3.1 also show that an extra-large ionization energy (blue) is needed when an electron is removed from a noble gas-like structure, clearly showing the stability of the electron structure of the noble gases.

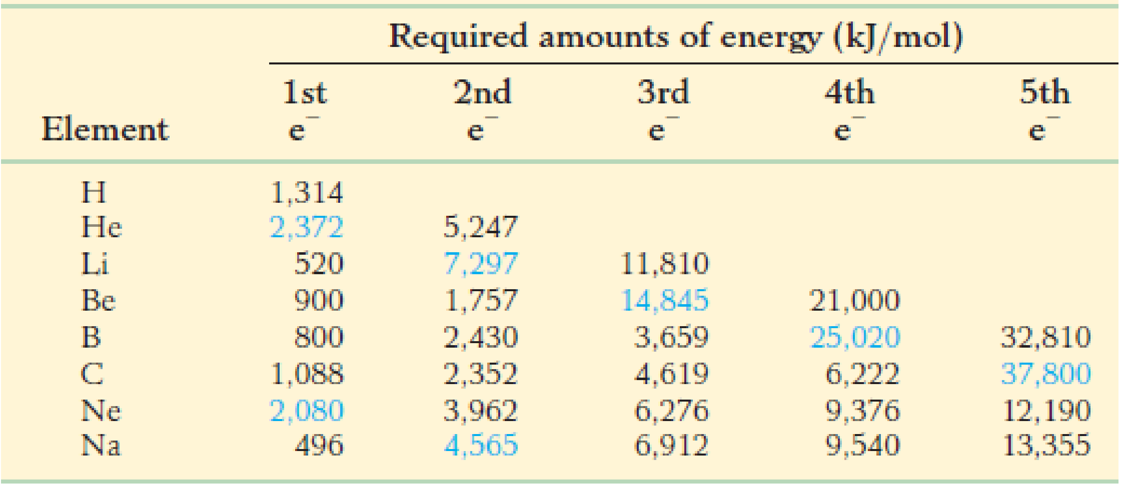
First ionization energies have been experimentally determined for most elements. Figure 3.3 plots these energies for representative elements in the first four periods. Note these important points:

1. Ionization energy in Group A elements decreases from top to bottom in a group. For example, in Group 1A the ionization energy changes from 520 kJ mol for Li to 419 kJ/mol for K.
2. Ionization energy gradually increases from left to right across a period. Noble gases have a relatively high value, confirming the nonreactive nature of these elements.

Metals don’t behave in exactly the same manner. Some metals give up electrons much more easily than others. In the alkali metal family, cesium gives up its 6s electron much more easily than the metal lithium gives up its 2s electron. This makes sense when we consider that the size of the atoms increases down the group. The distance between the nucleus and the outer electrons increases and the ionization energy decreases. The most chemically active metals are located at the lower left of the periodic table.

Nonmetals have relatively large ionization energies compared to metals. Nonmetals tend to gain electrons and form anions. Since the nonmetals are located at the right side of the periodic table, it is not surprising that ionization energies tend to increase from left to right across a period. The most active nonmetals are found in the upper right corner of the periodic table (excluding the noble gases).

Table 3.1 Ionization Energies for Selected Elements



Element	Required amounts of energy (kJ/mol) 1st e^-	2nd e^-	3rd e^-	4th e^-	5th e^-
H	1,314				
He	2,372	5,247			
Li	520	7,297	11,810		
Be	900	1,757	14,845	21,000	
B	800	2,430	3,659	25,020	32,810
C	1,088	2,352	4,619	6,222	37,800
Ne	2,080	3,962	6,276	9,376	12,190
Na	496	4,565	6,912	9,540	13,355

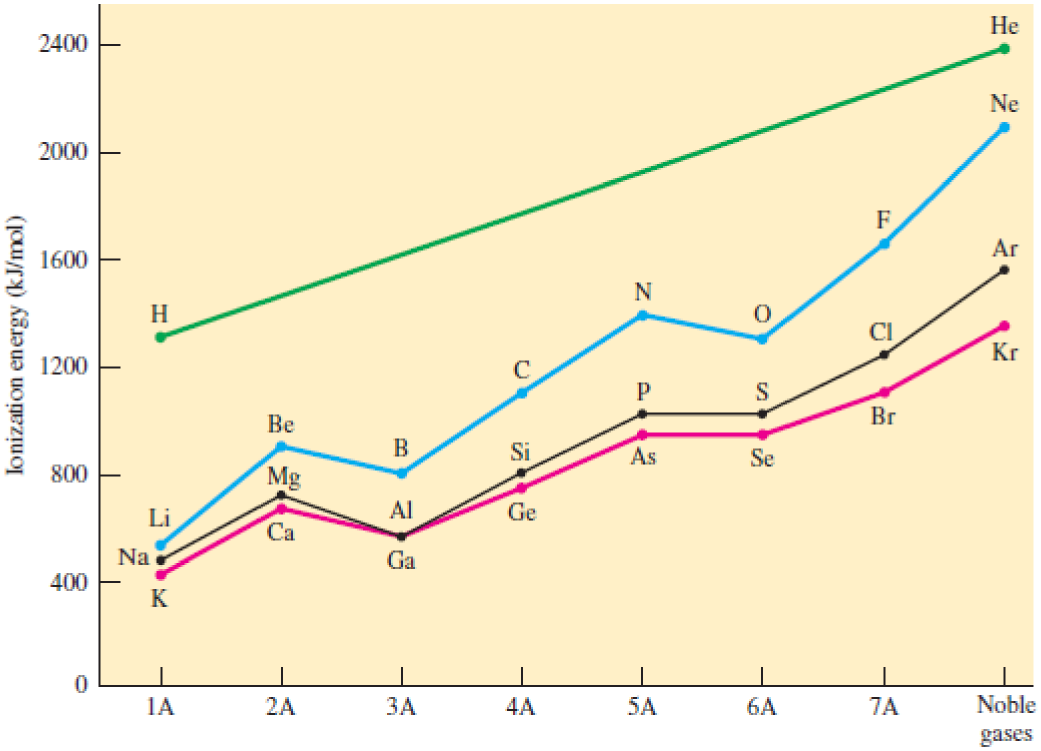
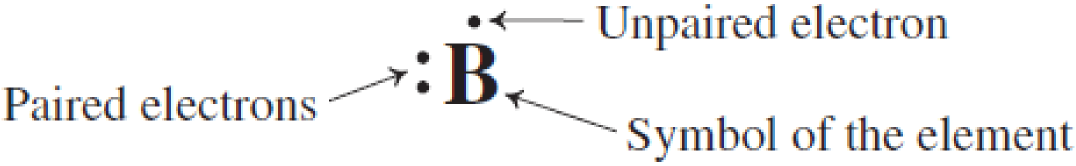


Figure 3.3 Periodic relationship of the first ionization energy for representative elements in the first four periods.

3.2 Lewis Structures of Atoms

Metals tend to form cations (positively charged ions) and nonmetals form anions (negatively charged ions) in order to attain a stable valence electron structure. For many elements this stable valence level contains eight electrons (two s and six p), identical to the valence electron configuration of the noble gases. Atoms undergo rearrangements of electron structure to lower their chemical potential energy (or to become more stable). These rearrangements are accomplished by losing, gaining, or sharing electrons with other atoms. For example, a hydrogen atom could accept a second electron and attain an electron structure the same as the noble gas helium. A fluorine atom could gain an electron and attain an electron structure like neon. A sodium atom could lose one electron to attain an electron structure like neon.

The valence electrons in the outermost energy level of an atom are responsible for the electron activity that occurs to form chemical bonds. The Lewis structure of an atom is a representation that shows the valence electrons for that atom. American chemist Gilbert N. Lewis (1875–1946) proposed using the symbol for the element and dots for electrons. The number of dots placed around the symbol equals the number of s and p electrons in the outermost energy level of the atom. Paired dots represent paired electrons; unpaired dots represent unpaired electrons. For example, **H·** is the Lewis symbol for a hydrogen atom, $1s^1$; **:B·** is the Lewis symbol for a boron atom, with valence electrons $2s^2$ $2p^1$. In the case of boron, the symbol B represents the boron nucleus and the $1s^2$ electrons; the dots represent only the $2s^2$ $2p^1$ electrons.



The Lewis method is used not only because of its simplicity of expression but also because much of the chemistry of the atom is directly associated with the electrons in the outermost energy level. Figure 3.4 shows Lewis structures for the elements hydrogen through calcium.

A quick way to determine the correct number of dots (electrons) for a Lewis structure is to use the Group number. For the A groups on the periodic table, the Group number is the same as the number of electrons in the Lewis structure.

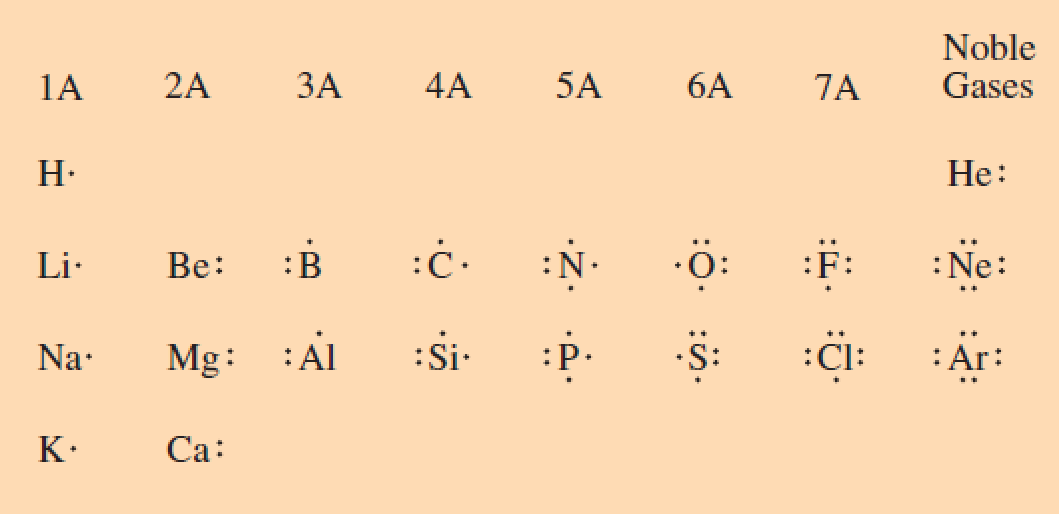


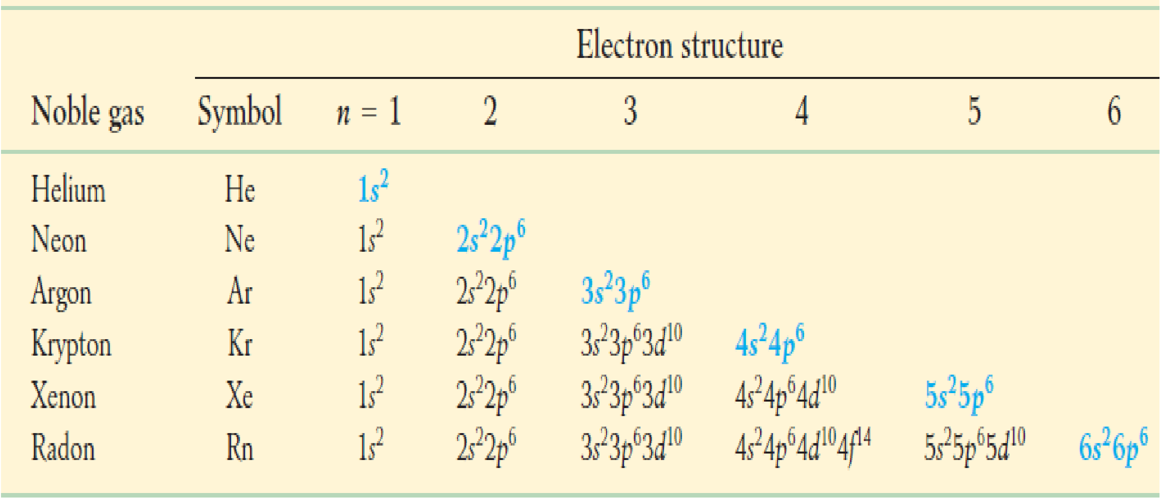
Figure 3.4 Lewis structures of the first 20 elements. Dots represent electrons in the outermost energy levels only.

3.3 The Ionic Bond: Transfer of Electrons From One Atom to Another

The chemistry of many elements, especially the representative ones, is to attain an outer electron structure like that of the chemically stable noble gases. With the exception of helium, this stable structure consists of eight electrons in the outermost energy level (Table 3.2).

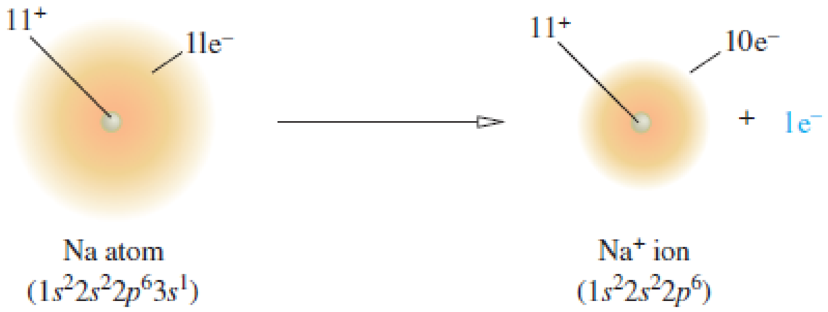
Let's look at the electron structures of sodium and chlorine to see how each element can attain a structure of 8 electrons in its outermost energy level. A sodium atom has 11 electrons: 2 in the first energy level, 8 in the second energy level, and 1 in the third energy level. A chlorine atom has 17 electrons: 2 in the first energy level, 8 in the second energy level, and 7 in the third energy level. If a sodium atom transfers or loses its 3s electron, its third energy level becomes vacant, and it becomes a sodium ion with an electron configuration identical to that of the noble gas neon. This process requires energy.

Table 3.2 Arrangement of Electrons in the Noble Gases

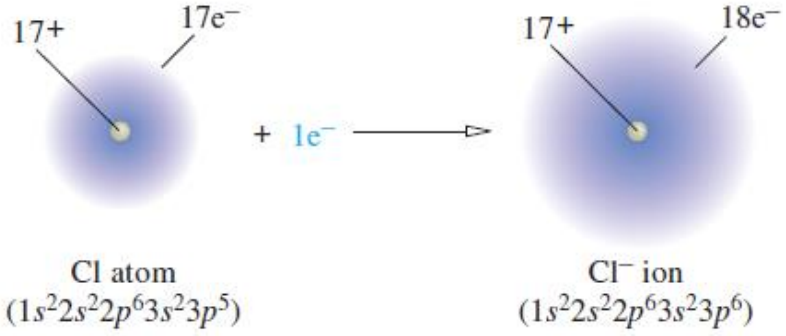


	Electron structure						
Noble gas	Symbol	$n = 1$	2	3	4	5	6
Helium	He	$1s^2$					
Neon	Ne	$1s^2$	$2s^22p^6$				
Argon	Ar	$1s^2$	$2s^22p^6$	$3s^23p^6$			
Krypton	Kr	$1s^2$	$2s^22p^6$	$3s^23p^63d^{10}$	$4s^24p^6$		
Xenon	Xe	$1s^2$	$2s^22p^6$	$3s^23p^63d^{10}$	$4s^24p^64d^{10}$	$5s^25p^6$	
Radon	Rn	$1s^2$	$2s^22p^6$	$3s^23p^63d^{10}$	$4s^24p^64d^{10}4f^{14}$	$5s^25p^65d^{10}$	$6s^26p^6$

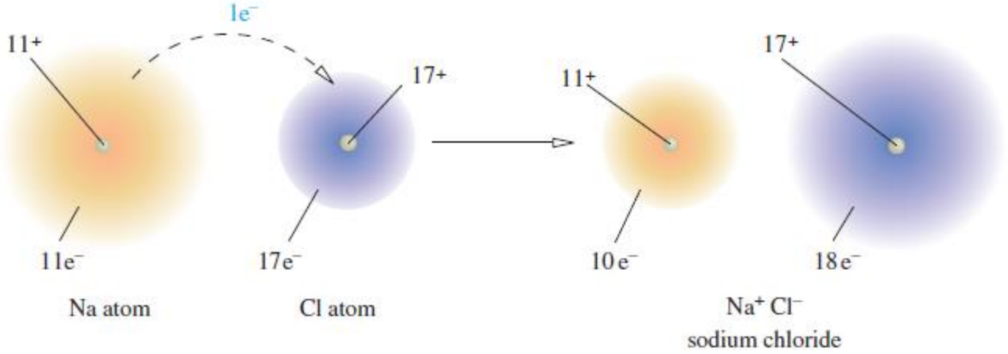
An atom that has lost or gained electrons will have a positive or negative charge, depending on which particles (protons or electrons) are in excess. Remember that a charged particle or group of particles is called an ion By losing a negatively charged electron, the sodium atom becomes a positively charged particle known as a sodium ion. The charge, +1, results because the nucleus still contains 11 positively charged protons, and the electron orbitals contain only 10 negatively charged electrons. The charge is indicated by a plus sign (+) and is written as a superscript after the symbol of the element (Na^+).



A chlorine atom with seven electrons in the third energy level needs one electron to pair up with its one unpaired 3p electron to attain the stable outer electron structure of argon. By gaining one electron, the chlorine atom becomes a chloride ion (Cl^-), a negatively charged particle containing 17 protons and 18 electrons. This process releases energy:



Consider sodium and chlorine atoms reacting with each other. The 3s electron from the sodium atom transfers to the half-filled 3p orbital in the chlorine atom to form a positive sodium ion and a negative chloride ion. The compound sodium chloride results because the Na^+ and Cl^- ions are strongly attracted to each other by their opposite electrostatic charges. The force holding the oppositely charged ions together is called an ionic bond.



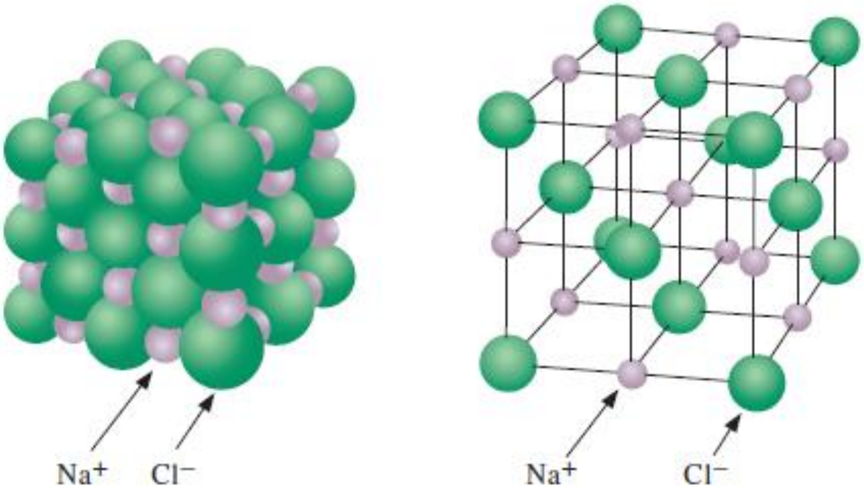
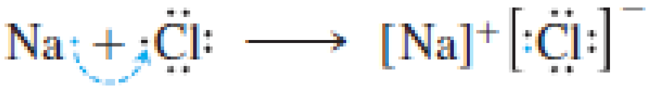


Figure 3.5 Diagram represents a small fragment of sodium chloride, which forms cubic crystals. Each sodium ion is surrounded by six chloride ions, and each chloride ion is surrounded by six sodium ions. The tiny NaCl crystals show the cubic crystal structure of salt.

The Lewis representation of sodium chloride formation is



The chemical reaction between sodium and chlorine is a very vigorous one, producing considerable heat in addition to the salt formed. When energy is released in a chemical reaction, the products are more stable than the reactants. Note that in NaCl both atoms attain a noble gas electron structure.

Sodium chloride is made up of cubic crystals in which each sodium ion is surrounded by six chloride ions and each chloride ion by six sodium ions, except at the crystal surface. A visible crystal is a regularly arranged aggregate of millions of these ions, but the ratio of sodium to chloride ions is 1:1, hence the formula NaCl. The cubic crystalline lattice arrangement of sodium chloride is shown in Figure 3.5.

Figure 3.6 contrasts the relative sizes of sodium and chlorine atoms with those of their ions. The sodium ion is smaller than the atom due primarily to two factors:

(1) The sodium atom has lost its outermost electron, thereby reducing its size; and (2) the 10 remaining electrons are now attracted by 11 protons and are thus drawn closer to the nucleus. Conversely, the chloride ion is larger

than the atom because (1) it has 18 electrons but only 17 protons and (2) the nuclear attraction on each electron is thereby decreased, allowing the chlorine atom to expand as it forms an ion.

We've seen that when sodium reacts with chlorine, each atom becomes an ion. Sodium chloride, like all ionic substances, is held together by the attraction existing between positive and negative charges. An ionic bond is the attraction between oppositely charged ions.

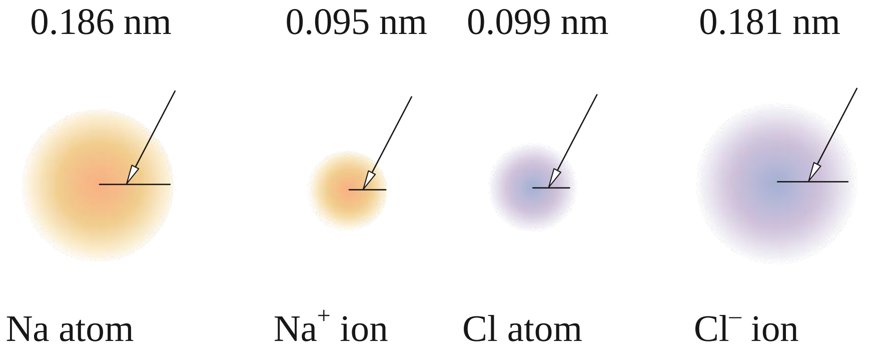
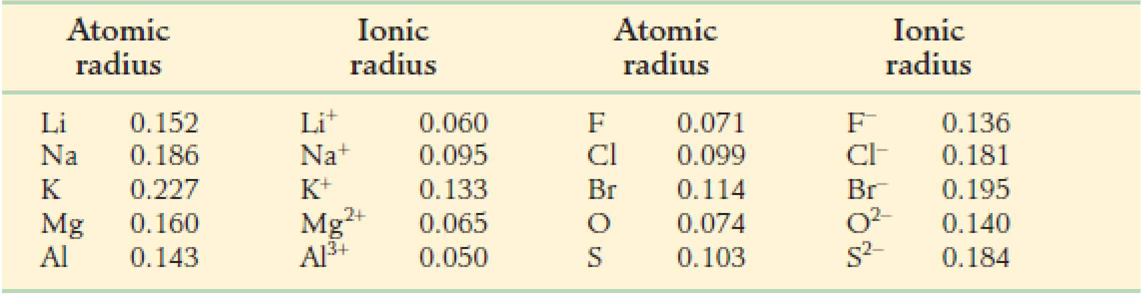


Figure 3.6 Relative radii of sodium and chlorine atoms and their ions.

Ionic bonds are formed whenever one or more electrons are transferred from one atom to another. Metals, which have relatively little attraction for their valence electrons, tend to form ionic bonds when they combine with nonmetals.

Table 3.3 Change in Atomic Radii (nm) of Selected Metals and Nonmetals



Atomic radius		Ionic radius		Atomic radius		Ionic radius	
Li	0.152	Li^+	0.060	F	0.071	F^-	0.136
Na	0.186	Na^+	0.095	Cl	0.099	Cl^-	0.181
K	0.227	K^+	0.133	Br	0.114	Br^-	0.195
Mg	0.160	Mg^{2+}	0.065	O	0.074	O^{2-}	0.140
Al	0.143	Al^{3+}	0.050	S	0.103	S^{2-}	0.184

It’s important to recognize that substances with ionic bonds do not exist as molecules. In sodium chloride, for example, the bond does not exist solely between a single sodium ion and a single chloride ion. Each sodium ion in the crystal attracts six near-neighbor negative chloride ions; in turn, each negative chloride ion attracts six near-neighbor positive sodium ions (Figure 3.5).

A metal will usually have one, two, or three electrons in its outer energy level. In reacting, metal atoms characteristically lose these electrons, attain the electron structure of a noble gas, and become positive ions. A nonmetal, on the other hand, is only a few electrons short of having a noble gas electron structure in its outer energy level and thus has a tendency to gain electrons. In reacting with metals, nonmetal atoms characteristically gain one, two, or three electrons; attain the electron structure of a noble gas; and become negative ions. The ions formed by loss of electrons are much smaller than the corresponding metal atoms; the ions formed by gaining electrons are larger than the corresponding nonmetal atoms. The dimensions of the atomic and ionic radii of several metals and nonmetals are given in Table 3.3.

3.4 Predicting Formulas of Ionic Compounds

In previous examples, we learned that when a metal and a nonmetal react to form an ionic compound, the metal loses one or more electrons to the nonmetal. Group 1A metals always form +1 cations, whereas Group 2A form +2 cations. Group 7A elements form -1 anions and Group 6A elements form -2 anions.

It stands to reason, then, that this pattern is directly related to the stability of the noble gas configuration. Metals lose electrons to attain the electron configuration of a noble gas (the previous one on the periodic table). A nonmetal forms an ion by gaining enough electrons to achieve the electron configuration of the noble gas following it on the periodic table. These observations lead us to an important chemical principle:

In almost all stable chemical compounds of representative elements, each atom attains a noble gas electron configuration. This concept forms the basis for our understanding of chemical bonding.

We can apply this principle in predicting the formulas of ionic compounds. To predict the formula of an ionic compound, we must recognize that chemical compounds are always electrically neutral. In addition, the metal will lose electrons to achieve noble gas configuration and the nonmetal will gain electrons to achieve noble gas configuration. Consider the compound formed between barium and sulfur. Barium has two valence electrons, whereas sulfur has six valence electrons:

$$\mathbf{Ba\ [Xe]6s^2 \qquad S\ [Ne]3s^2\ 3p^4}$$

If barium loses two electrons, it will achieve the configuration of xenon. By gaining two electrons, sulfur achieves the configuration of argon. Consequently, a pair of electrons is transferred between atoms. Now we have Ba^{2+} and S^{2-}. Since compounds are electrically neutral, there must be a ratio of one Ba to one S, giving the formula BaS.

The same principle works for many other cases. Since the key lies in the electron configuration, the periodic table can be used to extend the prediction even further. Because of similar electron structures, the elements in a family generally form compounds with the same atomic ratios. In general, if we know the atomic ratio of a particular compound (e. g., NaCl) we can predict the atomic ratios and formulas of the other alkali metal chlorides. These formulas are LiCl, KCl, RbCl, CsCl, and FrCl (Table 3.4).

Similarly, if we know that the formula of the oxide of hydrogen is H_2O, we can predict that the formula of the sulfide will be H_2S, because sulfur has the same valence electron structure as oxygen. Recognize, however, that these are only predictions; it doesn’t necessarily follow that every element in a group will behave like the others or even that a predicted compound will actually exist. For example, knowing the formulas for potassium chlorate, bromate, and iodate to be $KClO_3$, $KBrO_3$, and KIO_3, we can correctly predict the corresponding sodium compounds to have the formulas $NaClO_3$, $NaBrO_3$, and $NaIO_3$. Fluorine belongs to the same family of elements (Group 7A) as chlorine, bromine, and iodine, so it would appear that fluorine should combine with potassium and sodium to give fluorates with the formulas KFO_3 and $NaFO_3$. However, potassium and sodium fluorates are not known to exist.

In the discussion in this section, we refer only to representative metals (Groups 1A, 2A, and 3A). The transition metals (Group B) show more complicated behavior (they form multiple ions), and their formulas are not as easily predicted.

Table 3.4 Formulas of Compounds Formed by Alkali Metals

Lewis structure	Oxides	Chlorides	Bromides	Sulfates
$Li^{\cdot}$	Li_2O	$LiCl$	$LiBr$	Li_2SO_4
$Na^{\cdot}$	Na_2O	$NaCl$	$NaBr$	Na_2SO_4
$K^{\cdot}$	K_2O	KCl	KBr	K_2SO_4
$Rb^{\cdot}$	Rb_2O	$RbCl$	$RbBr$	Rb_2SO_4
$Cs^{\cdot}$	Cs_2O	$CsCl$	$CsBr$	Cs_2SO_4

3.5 The Covalent Bond: Sharing Electrons

Some atoms do not transfer electrons from one atom to another to form ions. Instead they form a chemical bond by sharing pairs of electrons between them. A **covalent bond** consists of a pair of electrons shared between two atoms. This bonding concept was introduced in 1916 by G. N. Lewis. In the millions of known compounds, the covalent bond is the predominant chemical bond.

True molecules exist in substances in which the atoms are covalently bonded. It is proper to refer to molecules of such substances as hydrogen, chlorine, hydrogen chloride, carbon dioxide, water, or sugar (Figure 3.7). These substances contain only covalent bonds and exist as aggregates of molecules. We don’t use the term molecule when talking about ionically bonded compounds such as sodium chloride, because such substances exist as large aggregates of positive and negative ions, not as molecules (Figure 3.7).

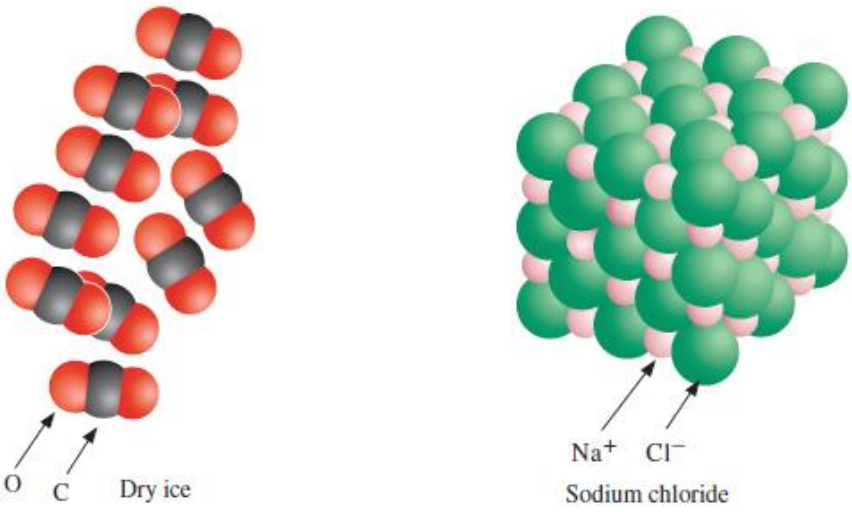


Figure 3.7 Solid carbon dioxide (dry ice) is composed of individual covalently bonded molecules of CO_2 closely packed together. Table salt is a large aggregate of Na^+ and Cl^- ions instead of molecules.

A study of the hydrogen molecule gives us an insight into the nature of the covalent bond and its formation. The formation of a hydrogen molecule (H_2) involves the overlapping and pairing of 1s electron orbitals from two hydrogen atoms, shown in Figure 3.8. Each atom contributes one electron of the pair that is shared jointly by two hydrogen nuclei. The orbital of the electrons now includes both hydrogen nuclei, but probability factors show that the most likely place to find the electrons (the point of highest electron density) is between the two nuclei. The two nuclei are shielded from each other by the pair of electrons, allowing the two nuclei to be drawn very close to each other.

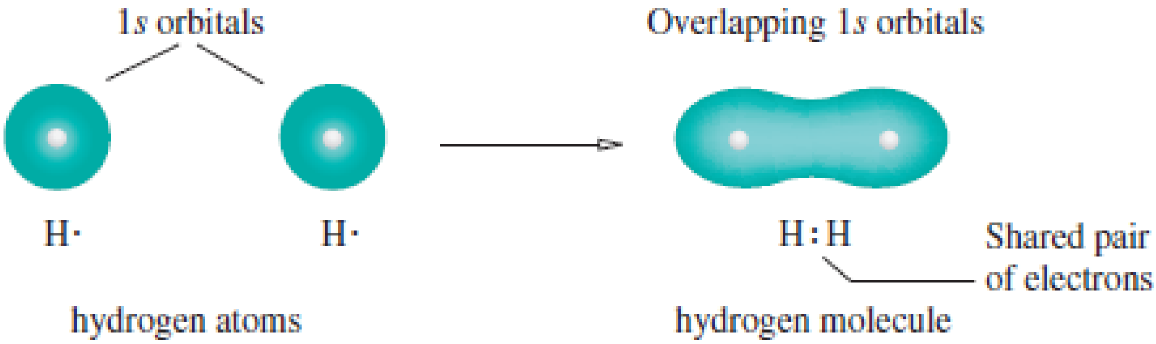


Figure 3.8 The formation of a hydrogen molecule from two hydrogen atoms. The two 1s orbitals overlap, forming the H_2 molecule. In this molecule the two electrons are shared between the atoms, forming a covalent bond.

The formula for chlorine gas is Cl_2. When the two atoms of chlorine combine to form this molecule, the electrons must interact in a manner similar to that shown in the hydrogen example. Each chlorine atom would be more stable with eight electrons in its outer energy level. But chlorine atoms are identical, and neither is able to pull an electron away from the other. The unpaired 3p electron orbital of one chlorine atom overlaps the unpaired 3p electron orbital of the other atom, resulting in a pair of electrons that are mutually shared between the two atoms. Each atom furnishes one of the pair of shared electrons. Thus, each atom attains a stable structure of eight electrons by sharing an electron pair with the other atom. The pairing of the p electrons and the formation of a chlorine molecule are illustrated in Figure 3.9.

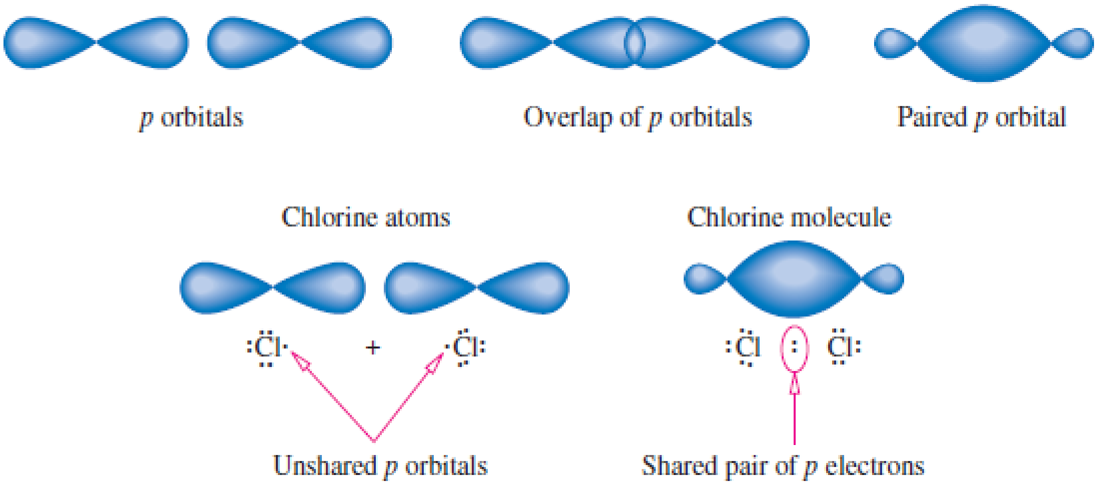
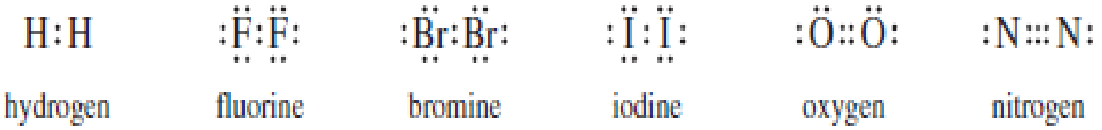


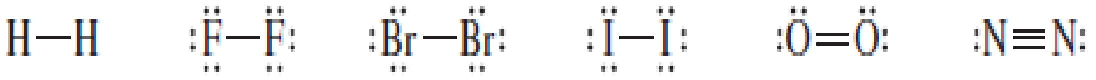
Figure 3.9 Pairing of p electrons in the formation of a chlorine molecule.

Neither chlorine atom has a positive or negative charge, because both contain the same number of protons and have equal attraction for the pair of electrons being shared. Other examples of molecules in which electrons are equally shared between two atoms are hydrogen (H_2), oxygen (O_2), nitrogen (N_2), fluorine (F_2), bromine (Br_2), and iodine (I_2). Note that more than one pair of electrons may be shared between atoms:



The Lewis structure given for oxygen does not adequately account for all the properties of the oxygen molecule.

In writing structures, we commonly replace the pair of dots used to represent a shared pair of electrons with a dash (—). One dash represents a single bond; two dashes, a double bond; and three dashes, a triple bond. The six structures just shown may be written thus:



The ionic bond and the covalent bond represent two extremes. In ionic bonding the atoms are so different that electrons are transferred between them, forming a charged pair of ions. In covalent bonding, two identical atoms share electrons equally. The bond is the mutual attraction of the two nuclei for the shared electrons. Between these extremes lie many cases in which the atoms are not different enough for a transfer of electrons but are different enough that the electron pair cannot be shared equally. This unequal sharing of electrons results in the formation of a polar covalent bond.

3.6 Coordinate Covalent Bond

The coordinate covalent bond is a kind of two-center, two-electron covalent bond in which the two electrons derive from the same atom. It is also known as a dative bond, dipolar bond, or coordinate bond. It is commonly found in coordination compounds. It is usually by an arrow → directing from the donating atom to the receiving one. The bonding of metal ions to ligands involves this kind of interaction. Examples are carbon monoxide CO, ammonium ion NH_4^+, and hydronium ion H_3O^+.

Another example of a dative covalent bond is provided by the interaction between a molecule of ammonia, with a lone pair of electrons on the nitrogen atom, and boron trifluoride, in which the boron atom having an incomplete octet of electrons (see Figure 3.10).

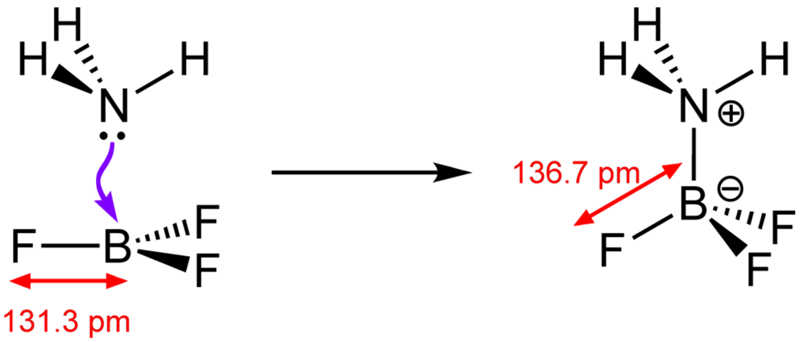


Figure 3.10 Coordinate bonding in the reaction NH_3 with BF_3.

3.7 Electronegativity and Polarity of Molecules

When two different kinds of atoms share a pair of electrons, a bond forms in which electrons are shared unequally. One atom assumes a partial positive charge and the other a partial negative charge with respect to each other. This difference in charge occurs because the two atoms exert unequal attraction for the pair of shared electrons. The attractive force that an atom of an element has for shared electrons in a molecule or polyatomic ion is known as its electronegativity. Elements differ in their electronegativities. For example, both hydrogen and chlorine need one electron to form stable electron configurations. They share a pair of electrons in hydrogen chloride (HCl). Chlorine is more electronegative and therefore has a greater attraction for the shared electrons than does hydrogen. As a result, the pair of electrons is displaced toward the chlorine atom, giving it a partial negative charge and leaving the hydrogen atom with a partial positive charge. Note that the electron is not transferred entirely to the chlorine atom (as in the case of sodium chloride) and that no ions are formed. The entire molecule, HCl, is electrically neutral. A partial charge is usually indicated by the Greek letter delta, .δ. Thus, a partial positive charge is represented by δ + and a partial negative charge by δ -. $^{+\delta}\ \mathrm{H\,:Cl}\ ^{-\delta}$

A scale of relative electronegativities, in which the most electronegative element, fluorine, is assigned a value of 4.0, was developed by the Nobel Laureate (1954 and 1962) Linus Pauling (1901–1994). Table 3.5 shows that the relative electronegativity of the nonmetals is high and that of the metals is low. These electronegativities indicate that atoms of metals have a greater tendency to lose electrons than do atoms of nonmetals and that nonmetals have a greater tendency to gain electrons than do metals. The higher the electronegativity value, the greater the attraction for electrons. Note that electronegativity generally increases from left to right across a period and decreases down a group for the representative elements. The highest electronegativity is 4.0 for fluorine, and the lowest is 0.7 for francium and cesium. It’s important to remember that the higher the electronegativity, the more strongly an atom attracts electrons.

The polarity of a bond is determined by the difference in electronegativity values of the atoms forming the bond (Table 3.6). If the electronegativities are the same, the bond is nonpolar covalent and the electrons are shared equally. If the atoms have greatly different electronegativities, the bond is very polar. At the extreme, one or more electrons are actually transferred and an ionic bond results.

A dipole is a molecule that is electrically asymmetrical, causing it to be oppositely charged at two points. A dipole is often written as . A hydrogen chloride molecule is polar and behaves as a small dipole. The HCl dipole may be written as $\mathrm{H}{+\!\!\!\longrightarrow}\mathrm{Cl}$. The arrow points toward the negative end of the dipole. Molecules of H_2O, HBr, and ICl are polar (see Figure 3.11).

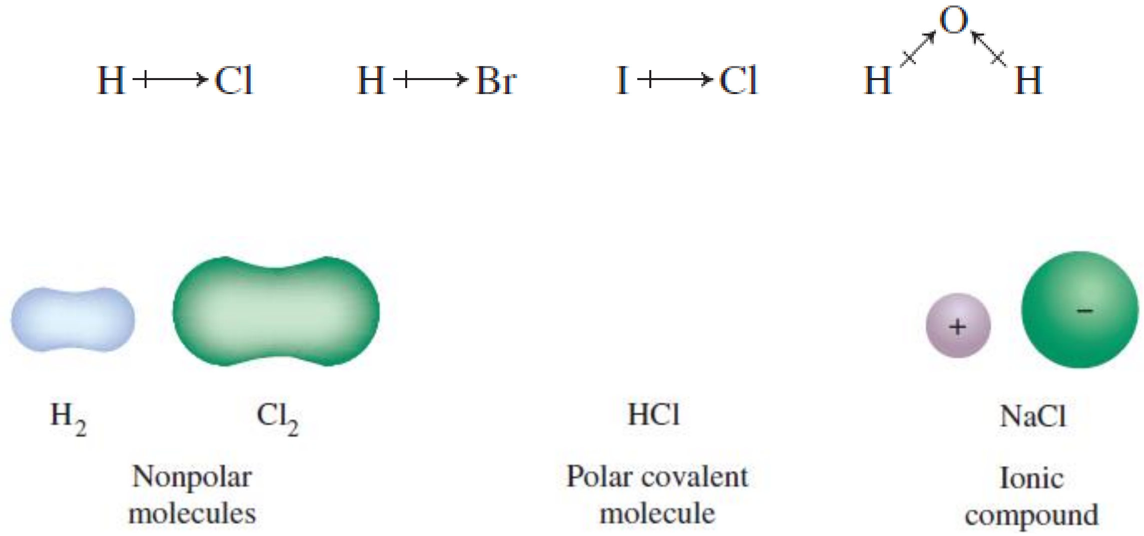
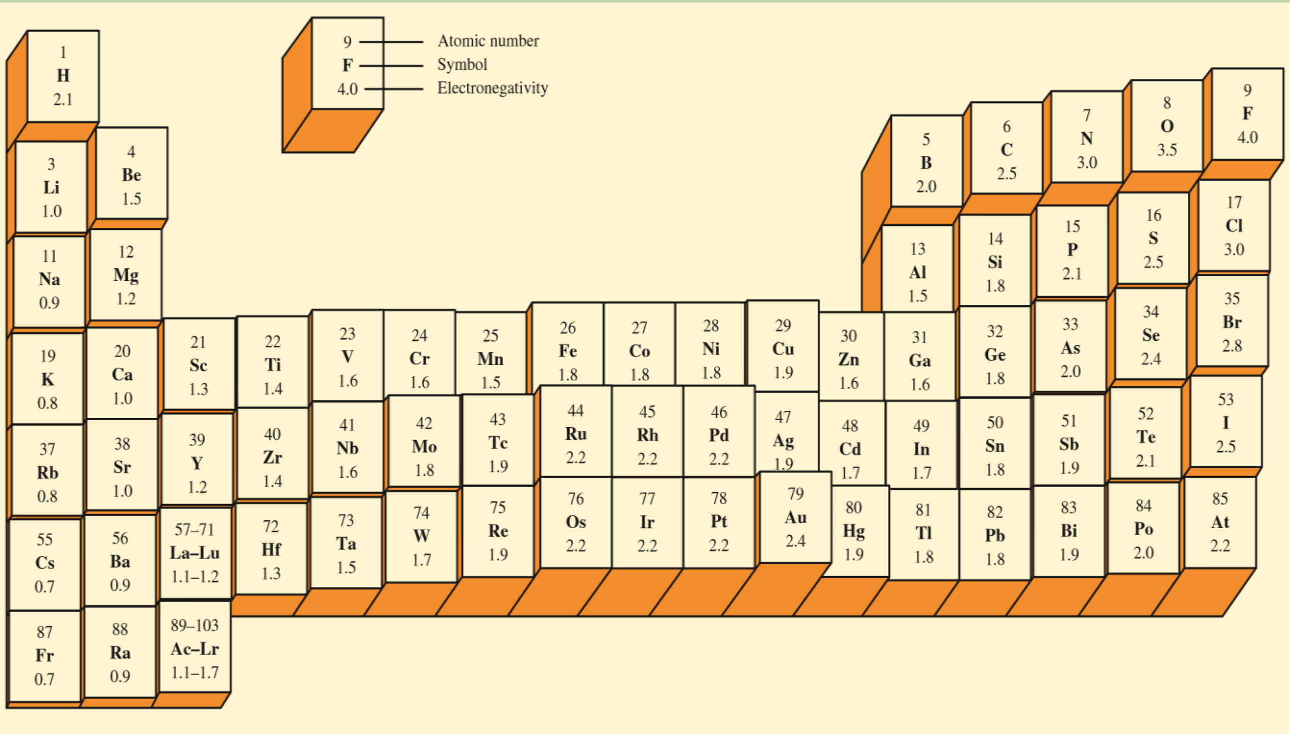


Figure 3.11 Nonpolar, polar covalent, and ionic compounds.

Table 3.5 Three-Dimensional Representation of Electronegativity



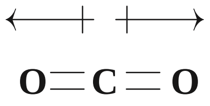
1 H 2.1																
3 Li 1.0	4 Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0
11 Na 0.9	12 Mg 1.2											13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3.0
19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.4	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.8	28 Ni 1.8	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8
37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5
55 Cs 0.7	56 Ba 0.9	57–71 La–Lu 1.1–1.2	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.8	83 Bi 1.9	84 Po 2.0	85 At 2.2
87 Fr 0.7	88 Ra 0.9	89–103 Ac–Lr 1.1–1.7														

How do we know whether a bond between two atoms is ionic or covalent? The difference in electronegativity between the two atoms determines the character of the bond formed between them. As the difference in electronegativity increases, the polarity of the bond (or percent ionic character) increases.

In general, if the electronegativity difference between two bonded atoms is greater than 1.7–1.9, the bond will be more ionic than covalent.

If the electronegativity difference is greater than 2.0, the bond is strongly ionic. If the electronegativity difference is less than 1.5, the bond is strongly covalent.

Care must be taken to distinguish between polar bonds and polar molecules. A covalent bond between different kinds of atoms is always polar. But a molecule containing different kinds of atoms may or may not be polar, depending on its shape or geometry. Molecules of HF, HCl, HBr, HI, and ICl are all polar because each contains a single polar bond. However, CO_2, CH_4, and CCl_4 are nonpolar molecules despite the fact that all three contain polar bonds. The carbon dioxide molecule O=C=O is nonpolar because the carbon–oxygen dipoles cancel each other by acting in opposite directions.



dipoles in opposite directions

Carbon tetrachloride (CCl_4) is nonpolar because the four C¬Cl polar bonds are identical, and since these bonds emanate from the center to the corners of a tetrahedron in the molecule, their polarities cancel one another. Methane has the same molecular structure and is also nonpolar.

We have said that water is a polar molecule. If the atoms in water were linear like those in carbon dioxide, the two O¬H dipoles would cancel each other, and the molecule would be nonpolar. However, water is definitely polar and has a nonlinear (bent) structure with an angle of 105° between the two O¬H bonds.

The relationships among types of bonds are summarized in Table 3.6. It is important to realize that bonding is a continuum; that is, the difference between ionic and covalent is a gradual change.

Table 3.6 Relating bond type to electronegativity difference between atoms.

Electronegativity Difference (Δ)	Bond
$\Delta \geq 2$	Ionic
$0.4 < \Delta < 2$	Polar covalent
$\Delta \leq 0.4$	Nonpolar covalent

3.8 Lewis Structures of Compounds

As we have seen, Lewis structures are a convenient way of showing the covalent bonds in many molecules or ions of the representative elements. In writing Lewis structures, the most important consideration for forming a stable compound is that the atoms attain a noble gas configuration.

The most difficult part of writing Lewis structures is determining the arrangement of the atoms in a molecule or an ion. In simple molecules with more than two atoms, one atom will be the central atom surrounded by the other atoms. Thus, Cl_2O has two possible arrangements, Cl¬Cl¬O or Cl¬O¬Cl. Usually, but not always, the single atom in the formula (except H) will be the central atom.

Although Lewis structures for many molecules and ions can be written by inspection, the following procedure is helpful for learning to write them:

Problem-Solving Strategy: Writing a Lewis Structure

1. Obtain the total number of valence electrons to be used in the structure by adding the number of valence electrons in all the atoms in the molecule or ion. If you are writing the structure of an ion, add one electron for each negative charge or subtract one electron for each positive charge on the ion.

2. Write the skeletal arrangement of the atoms and connect them with a single covalent bond (two dots or one dash). Hydrogen, which contains only one bonding electron, can form only one covalent bond. Oxygen atoms are not normally bonded to each other, except in compounds known to be peroxides. Oxygen atoms normally have a maximum of two covalent bonds (two single bonds or one double bond).

3. Subtract two electrons for each single bond you used in Step 2 from the total number of electrons calculated in Step 1. This gives you the net number of electrons available for completing the structure.

4. Distribute pairs of electrons (pairs of dots) around each atom (except hydrogen) to give each atom a noble gas structure.

5. If there are not enough electrons to give these atoms eight electrons, change single bonds between atoms to double or triple bonds by shifting unbonded pairs of electrons as needed. Check to see that each atom has a noble gas electron structure (two electrons for hydrogen and eight for the others). A double bond counts as four electrons for each atom to which it is bonded.

Example 1:

How many valence electrons are in each of these atoms: Cl, H, C, O, N, S, P, I?

Solution:

You can look at the periodic table to determine the electron structure, or, if the element is in Group A of the periodic table, the number of valence electrons is equal to the group number:

Atom	Group	Valence electrons
Cl	7A	7
H	1A	1
C	4A	4
O	6A	6
N	5A	5
S	6A	6
P	5A	5
I	7A	7

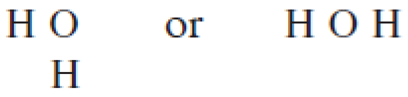
Example 2:

Use the Writing a Lewis Structure Problem-Solving Strategy for water (H_2O).

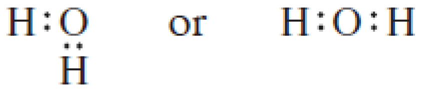
Solution:

1. The total number of valence electrons is eight, two from the two hydrogen atoms and six from the oxygen atom.

2. The two hydrogen atoms are connected to the oxygen atom. Write the skeletal structure:

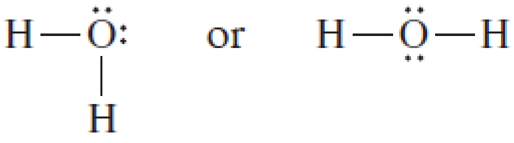


Place two dots between the hydrogen and oxygen atoms to form the covalent bonds:



3. Subtract the four electrons used in Step 2 from eight to obtain four electrons yet to be used.

4. Distribute the four electrons in pairs around the oxygen atom. Hydrogen atoms cannot accommodate any more electrons:



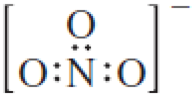
These arrangements are Lewis structures because each atom has a noble gas electron structure. Note that the shape of the molecule is not shown by the Lewis structure.

3.9 Complex Lewis Structures

Most Lewis structures give bonding pictures that are consistent with experimental information on bond strength and length. There are some molecules and polyatomic ions for which no single Lewis structure consistent with all characteristics and bonding information can be written.

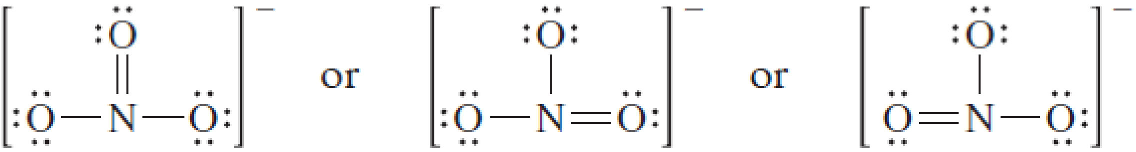
For example, consider the nitrate ion, NO_3^-. To write a Lewis structure for this polyatomic ion, we use the following steps.

1. The total number of valence electrons is 24: 5 from the nitrogen atom, 6 from each oxygen atom, and 1 from the -1 charge.
2. The three O atoms are bonded to a central N atom. Write the skeletal structure and place two electrons between each pair of atoms. Since we have an extra electron in this ion, resulting in a -1 charge, we enclose the group of atoms in square brackets and add a - charge as shown.



3. Subtract the 6 electrons used in Step 2 from 24 (found in Step 1) to obtain 18 electrons yet to be placed.
4. Distribute the 18 electrons around the N and O atoms:

5. One pair of electrons is still needed to give all the N and O atoms a noble gas structure. Move the unbonded pair of electrons from the N atom and place it between the N and the electron-deficient O atom, making a double bond.

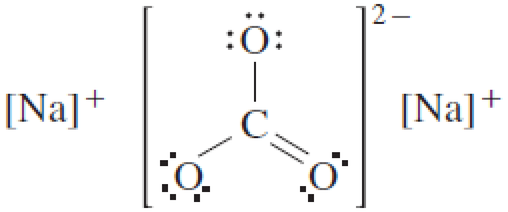


Are these all valid Lewis structures? Yes, so there really are three possible Lewis structures for $NO^{3-.}$

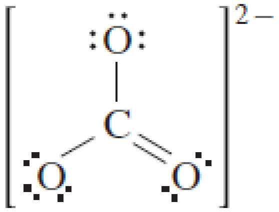
A molecule or ion that has multiple correct Lewis structures shows ***resonance***. Each of these Lewis structures is called a ***resonance structure***. In this book, however, we resonance structure will not be concerned with how to choose the correct resonance structure for a molecule or ion. Therefore any of the possible resonance structures may be used to represent the ion or molecule.

3.10 Compounds Containing Polyatomic Ions

A polyatomic ion is a stable group of atoms that has either a positive or a negative charge and behaves as a single unit in many chemical reactions. Sodium carbonate, Na_2CO_3, contains two sodium ions and a carbonate ion. The carbonate ion (CO_3^{2-}) is a polyatomic ion composed of one carbon atom and three oxygen atoms and has a charge of -2. One carbon and three oxygen atoms have a total of 22 electrons in their outer energy levels. The carbonate ion contains 24 outer electrons and therefore has a charge of -2. In this case, the 2 additional electrons come from the two sodium atoms, which are now sodium ions:



sodium carbonate



carbonate ion

Sodium carbonate has both ionic and covalent bonds. Ionic bonds exist between each of the sodium ions and the carbonate ion. Covalent bonds are present between the carbon and oxygen atoms within the carbonate ion. One important difference between the ionic and covalent bonds in this compound can be demonstrated by dissolving sodium carbonate in water. It dissolves in water, forming three charged particles—two sodium ions and one carbonate ion—per formula unit of Na_2CO_3:

$$Na_2CO_3(s) \xrightarrow{\text{water}} 2\,Na^+(aq) + CO_3^{2-}(aq)$$

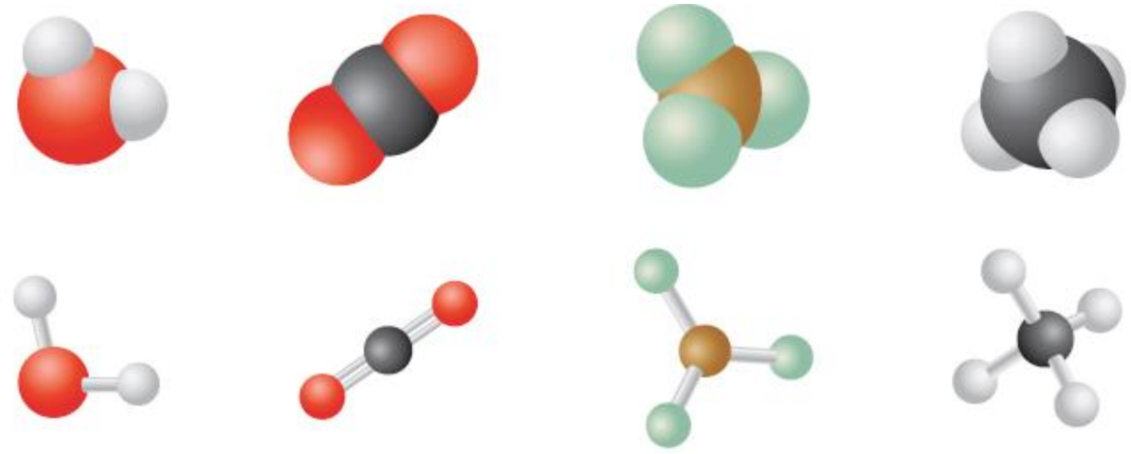
The CO_3^{2-} ion remains as a unit, held together by covalent bonds; but where the bonds are ionic, dissociation of the ions takes place. Do not think, however, that polyatomic ions are so stable that they cannot be altered. Chemical reactions by which polyatomic ions can be changed to other substances do exist.

3.11 Molecular Shape

So far in our discussion of bonding we have used Lewis structures to represent valence electrons in molecules and ions, but they don't indicate anything regarding the molecular or geometric shape of a molecule. The three-dimensional arrangement of the atoms within a molecule is a significant feature in understanding molecular interactions. Let's consider several examples illustrated in Figure 3.12.

Water is known to have the geometric shape known as "bent" or "V-shaped." Carbon dioxide exhibits a linear shape. BF3 forms a third molecular shape called trigonal planar since all the atoms lie in one plane in a triangular arrangement. One of the more common molecular shapes is the tetrahedron, illustrated by the molecule methane (CH_4).

How do we predict the geometric shape of a molecule? We will now study a model developed to assist in making predictions from the Lewis structure.



Water
H_2O
(V-shaped)

Carbon dioxide
CO_2
(linear shape)

Boron trifluoride
BF_3
(trigonal planar)

Methane
CH_4
(tetrahedral)

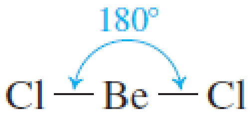
Figure 3.12 Geometric shapes of common molecules. Each molecule is shown as a ball-and-stick model (showing the bonds) and as a space filling model (showing the shape).

3.12 The Valence Shell Electron Pair Repulsion (VSEPR) Model

The chemical properties of a substance are closely related to the structure of its molecules. A change in a single site on a large biomolecule can make a difference in whether or not a particular reaction occurs.

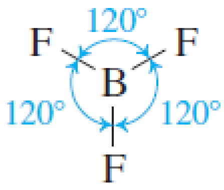
Instrumental analysis can be used to determine exact spatial arrangements of atoms. Quite often, though, we only need to be able to predict the approximate structure of a molecule. A relatively simple model has been developed to allow us to make predictions of shape from Lewis structures.

The VSEPR model is based on the idea that electron pairs will repel each other electrically and will seek to minimize this repulsion. To accomplish this minimization, the electron pairs will be arranged around a central atom as far apart as possible. Consider $BeCl_2$, a molecule with only two pairs of electrons surrounding the central atom. These electrons are arranged 180° apart for maximum separation:



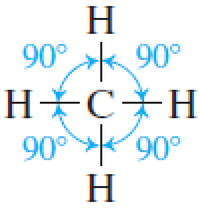
This molecular structure can now be labeled as a linear structure. When only two pairs of electrons surround a central atom, they should be placed 180° apart to give a linear structure.

What occurs when there are only three pairs of electrons around the central atom? Consider the BF_3 molecule. The greatest separation of electron pairs occurs when the angles between atoms are 120°:

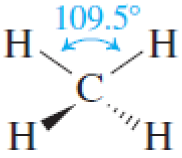


This arrangement of atoms is flat (planar) and, as noted earlier, is called trigonal planar structure. When three pairs of electrons surround an atom, they should be placed 120° apart to show the trigonal planar structure.

Now consider the most common situation (CH_4), with four pairs of electrons on the central carbon atom. In this case the central atom exhibits a noble gas electron structure. What arrangement best minimizes the electron pair repulsions? At first, it seems that an obvious choice is a 90° angle with all the atoms in a single plane:



However, we must consider that molecules are three-dimensional. This concept results in a structure in which the electron pairs are actually 109.5° apart:



In this diagram the wedged line seems to protrude from the page, whereas the dashed line recedes. Two representations of this arrangement, known as tetrahedral structure, are illustrated in Figure 3.13. When four pairs of electrons surround a central atom, they should be placed 109.5° apart to give them a tetrahedral structure.

The VSEPR model is based on the premise that we are counting electron pairs. It's quite possible that one or more of these electron pairs may be nonbonding (lone) pairs. What happens to the molecular structure in these cases?

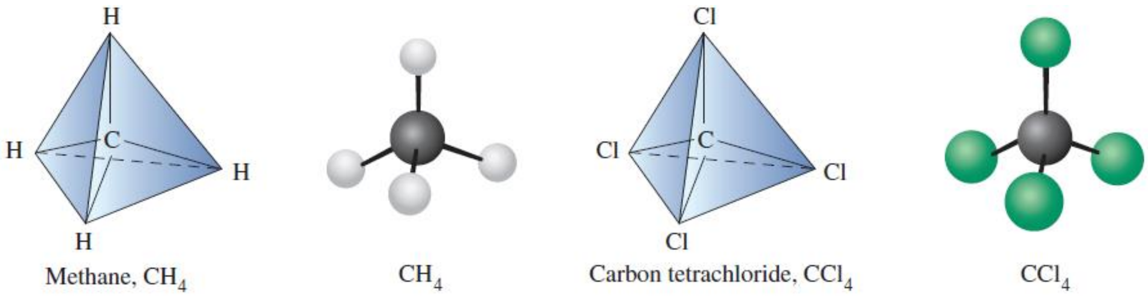


Figure 3.13 Ball-and-stick models of methane and carbon tetrachloride. Methane and carbon tetrachloride are nonpolar molecules because their polar bonds cancel each other in the tetrahedral arrangement of their atoms. The carbon atoms are located in the centers of the tetrahedrons.

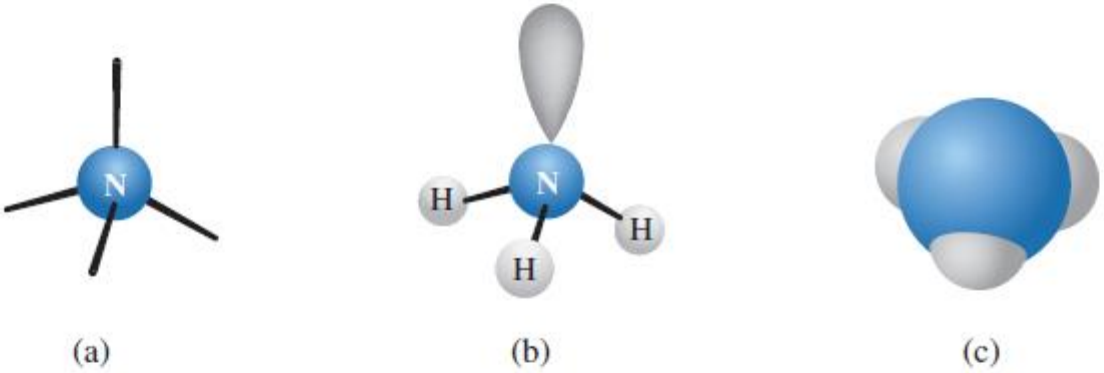
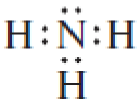


Figure 3.14 (a) The tetrahedral arrangement of electron pairs around the N atom in the NH_3 molecule. (b) Three pairs are shared and one is unshared. (c) The NH_3 molecule is pyramidal.

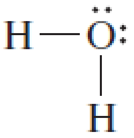
Consider the ammonia molecule. First we draw the Lewis structure to determine the number of electron pairs around the central atom:



$$\begin{array}{ccc}\mathrm{H} & :\overset{\cdot\cdot}{\mathrm{N}}: & \mathrm{H}\\ & \overset{\cdot\cdot}{\mathrm{H}} & \end{array}$$

Since there are four pairs of electrons, the arrangement of electrons around the central atom will be tetrahedral (Figure 3.14a). However, only three of the pairs are bonded to another atom, so the molecule itself is pyramidal. It is important to understand that the placement of the electron pairs determines the shape but the name for the molecule is determined by the position of the atoms themselves. Therefore, ammonia is pyramidal (Figure 3.14c).

Now consider the effect of two unbonded pairs of electrons in the water molecule. The Lewis structure for water is



$$\begin{array}{ccc}\mathrm{H} & - & \overset{\cdot\cdot}{\mathrm{O}}:\\ & & | \\ & & \mathrm{H}\end{array}$$

The four electron pairs indicate that a tetrahedral electron arrangement is necessary (Figure 3.15a). The molecule is not called tetrahedral because two of the electron pairs are unbonded pairs. The water molecule displays a bent structure. Let’s summarize the VSEPR model.

Problem-Solving Strategy: Determining Molecular Shape Using VSEPR

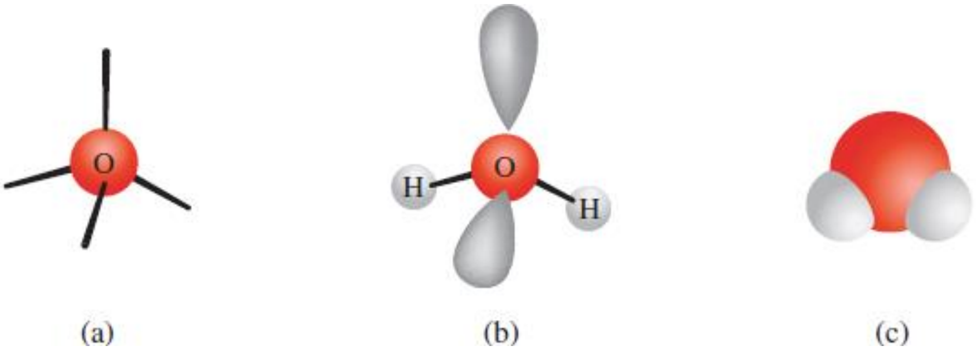
1. Draw the Lewis structure for the molecule.

2. Count the electron pairs around the central atom and arrange them to minimize repulsions (as far apart as possible). This determines the electron pair arrangement.

3. Determine the positions of the atoms.

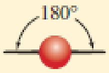
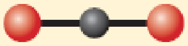
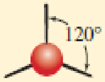
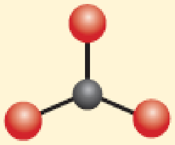
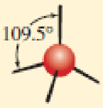
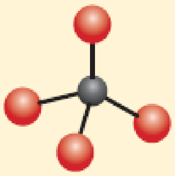
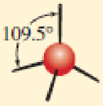
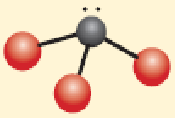
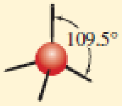
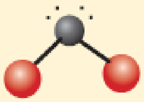
4. Name the molecular structure from the position of the atoms.

It is important to recognize that the placement of the electron pairs determines the structure but the name of the molecular structure is determined by the position of the atoms. Table 3.7 shows the results of this process. Note that when the number of electron pairs is the same as the number of atoms, the electron pair arrangement and the molecular structure are the same. But when the number of atoms and the number of electron pairs are not the same, the molecular structure is different from the electron pair arrangement. This is illustrated when the number of electron pairs is four (a tetrahedral arrangement) in Table 3.7.



Fgure 3.15 (a) The tetrahedral arrangement of the four electron pairs around oxygen in the H_2O molecule.(b) Two of the pairs are shared and two are unshared. (c) The H_2O molecule is bent.

Table 3.7 Arrangement of Electron Pairs and Molecular Structure

Number of electron pairs	Electron pair arrangement	Ball-and-stick model	Bonds	Molecular structure	Molecular structure model
2	Linear		2	Linear	
3	Trigonal planar		3	Trigonal planar	
4	Tetrahedral		4	Tetrahedral	
4	Tetrahedral		3	Trigonal pyramidal	
4	Tetrahedral		2	Bent	

Problems:

1) Use the Writing a Lewis Structure Problem-Solving Strategy for a molecule of carbon tetrachloride (CCl_4).
2) Use the Writing a Lewis Structure Problem-Solving Strategy for CO_2.
3) Predict the molecular shape for these molecules: H_2S, CCl_4 , $AlCl_3$.

3.13 The Valence Bond Model

Lewis structures cannot explain the relative strengths and lengths of covalent bonds (each bond is simply two electrons shared by two atoms). Valence Bond Theory describes the covalent bond as the overlap of atomic orbitals and two electrons (of opposite spins) are situated in this overlap region. The strength and length of a covalent bond depends on the nature of the orbitals that overlap.

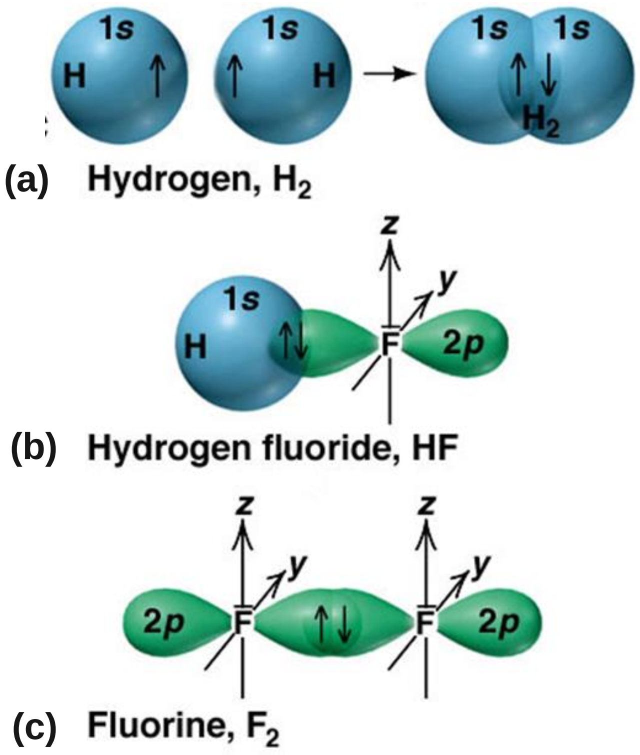


Figure 3.16 (a) For H_2, there is the overlap of two 1s orbitals, one from each H. (b) For HF, there is the overlap of a 1s orbital from H and a 2p orbital from F. (c) For F_2, there is the overlap of two 2p orbitals, one from each F.

3.14 Hybridization

Hybridization is the combination of at least two non-equivalent atomic orbitals. The hybrid orbitals produced are very different from the pure atomic orbitals. It is used to explain the observed geometries, i.e., hybridization is not used to predict a geometry. It does not apply to isolated atoms. It is used to explain the orientation of bonds and lone pairs in a molecule.

The number of hybrid orbitals formed equals the number of pure atomic orbitals that participate in the hybridization. Hybridization requires an energy input which is compensated for by the energy released during the formation of the bonds. Covalent bonds in polyatomic molecules are formed by the overlap of hybrid orbitals together or hybrid orbitals with non-hybrid orbitals. The bonds obtained through hybridization fit within the valence bond model.

Types of Hybrid Orbitals

1. The sp Hybridization

The sp hybridization is used to describe the covalent bonds around a central atom in a linear molecule. The excitation of an electron from the s orbital to a p orbital is necessary so that, in each bond, an electron from the central atom is coupled with an electron from the terminal atom (see Figure 3.17).

The used energy is offset by the energy released by the formation of the two bonds. Orbital box diagram for sp hybridization of beryllium in gaseous beryllium chloride $BeCl_2$ is shown in Figure 3.18.

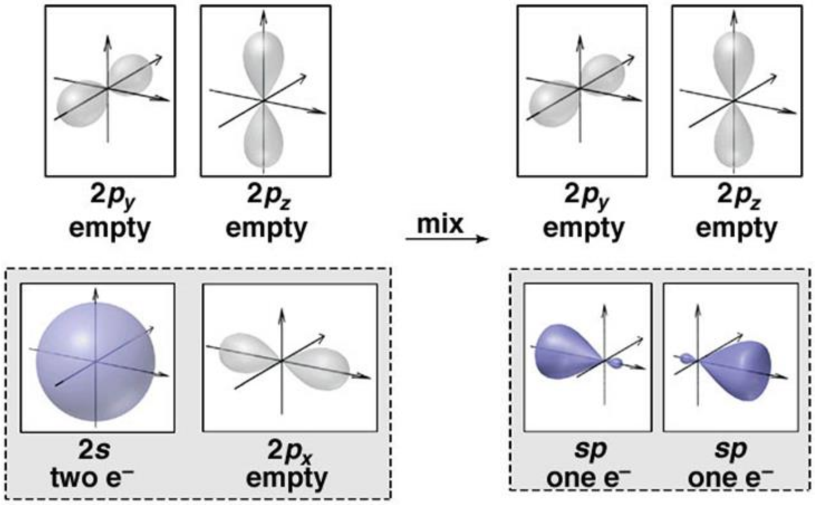


Figure 3.17 Hybridization of 2s with $2p_x$ orbitals.

Figure 3.18 Orbital box diagram of sp hybridization of beryllium in gaseous beryllium chloride.

2. The sp^2 Hybridization

The sp^2 hybridization is used to describe covalent bonds around a central atom in a trigonal planar molecule To form three bonds, an electron must be excited from the s orbital to an empty p orbital.

As an example, the sp^2 hybridization of boron in boron trifluoride BF_3 is shown in Figure 3.19.

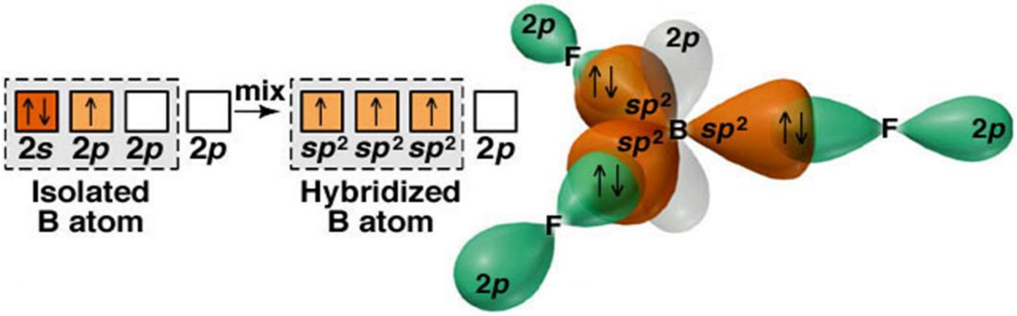


Figure 3.19 The sp^2 hybrid orbitals of boron in boron trifluoride.

3. The sp^3 Hybridization

The sp^3 hybridization is used to describe covalent bonds around a central atom in a tetrahedral molecule. To form four bonds, an electron must be excited from the s orbital to an empty p orbital as shown in Figure 3.20 for carbon atom in methane CH_4 molecule.

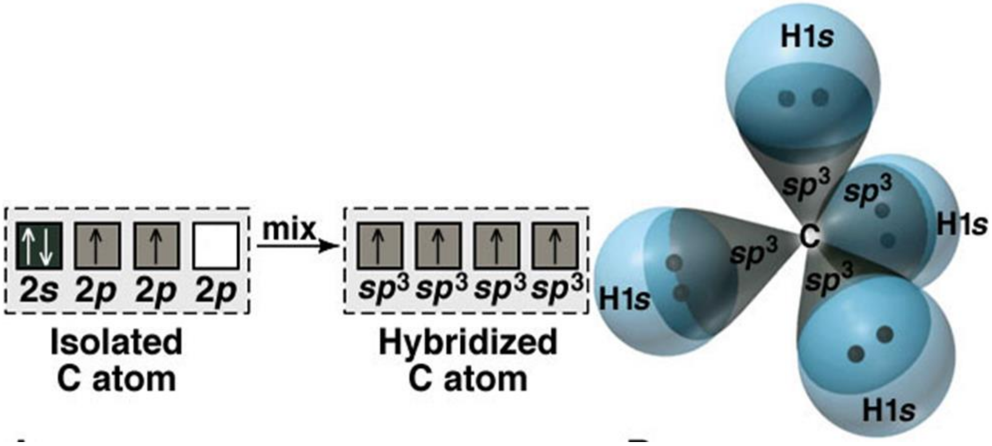


Figure 3.20 The sp^3 hybrid orbitals of carbon in methane.

4. The sp^3d Hybridization

The sp^3d hybridization is used to describe covalent bonds around a central atom in a trigonal bipyramidal molecule. To form five bonds, an electron must be excited from the s orbital to an empty d orbital. An example is the hybridization of phosphorus in phosphorus pentachloride PCl_5 (see Figure 3.21).

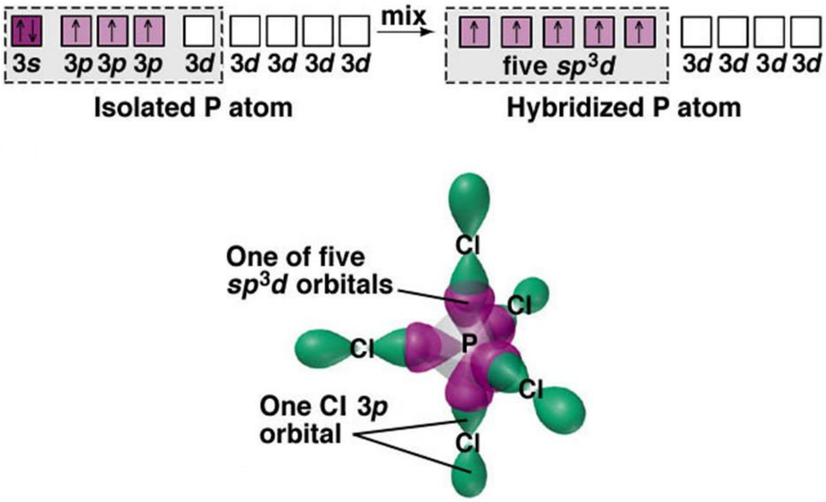


Figure 3.21 The sp^3d hybrid orbitals of phosphorus in phosphorus pentachloride.

5. The sp^3d^2 Hybridization

The sp^3d^2 hybridization is used to describe covalent bonds around a central atom in an octahedral molecule. To form six bonds, two electrons must be excited; one from the s orbital and other from a p orbital, to two empty d orbitals. An example is the hybridization of sulfur in sulfur hexafluoride (see Figure 3.22).

The composition and orientation of the resulting hybrid orbitals are summarized in Table 3.8.

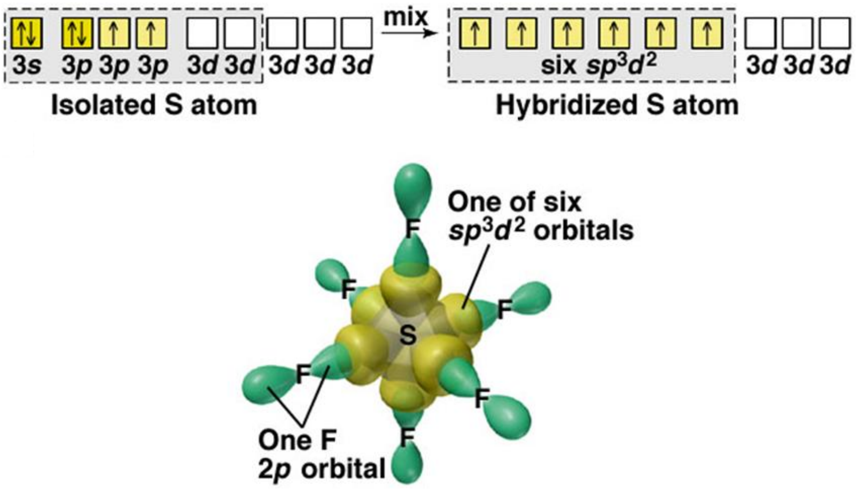
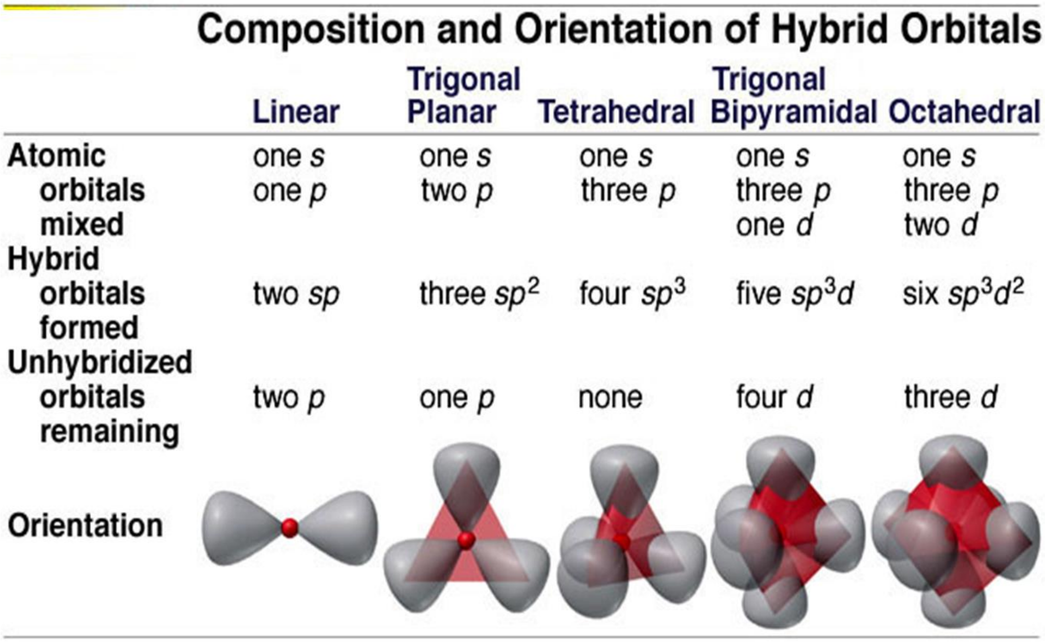


Figure 3.22 The sp^3d^2 hybrid orbitals of sulfur in sulfur hexafluoride.

Table 3.8 The composition and orientation of hybrid orbitals.



Composition and Orientation of Hybrid Orbitals

	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one *s* one *p*	one *s* two *p*	one *s* three *p*	one *s* three *p* one *d*	one *s* three *p* two *d*
Hybrid orbitals formed	two *sp*	three sp^2	four sp^3	five sp^3d	six sp^3d^2
Unhybridized orbitals remaining	two *p*	one *p*	none	four *d*	three *d*
Orientation					

3.15 Molecular Orbital (MO) Theory

A molecule is viewed as a collection of nuclei surrounded by delocalized molecular orbitals. Atomic wave functions are summed to obtain molecular wave functions. If wave functions support each other, a bonding MO is formed (region of high electron density exists between the nuclei).

If wave functions cancel each other, an antibonding MO is formed (a node of zero electron density occurs between the nuclei) (see Figure 3.23).

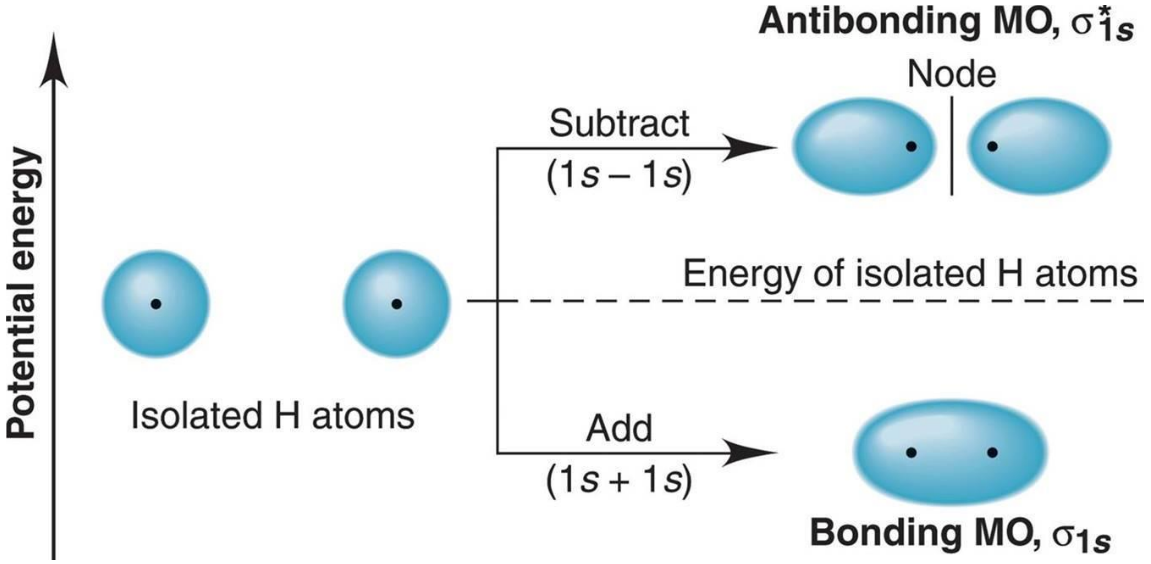


Figure 3.23 The Formation of H_2 molecular orbitals from atomic orbitals.

During forming molecular orbitals, the following rules should be taken into consideration:

- Number of combined AOs = number of produced MOs.
- Bonding MOs have lower in energy than isolated atoms

- Antibonding MOs have higher in energy than isolated atoms.
- To form MOs, AOs must have similar energy and orientation.
- Sigma (σ) and pi (π) bonds are denoted as before; a star (*) is used to denote antibonding MOs.
- Bonding and antibonding MOs for core electrons cancel each other and have no net contribution to bonding.
- Only MO diagrams showing MOs created by combining valence-electron AOs are important.
- ***MO bond order (BO) = 1/2 [(no. of electrons in bonding MOs) - (no. of electrons in antibonding MOs)].***
- Higher bond order means stronger bond.
- MOs are filled in the same sequence as for AOs (aufbau, exclusion principles, and Hund’s rule).
- Relative energies are: $\sigma 2p < \pi 2p < \pi^*2p < \sigma^*2p$
- End-to-end interaction is more effective than side-to-side interaction in bonding MOs.

Molecular orbitals of hydrogen molecule is shown in Figure 3.24 using diagram from which we can calculate the bond order as BO = 1/2(2-0) = 1.

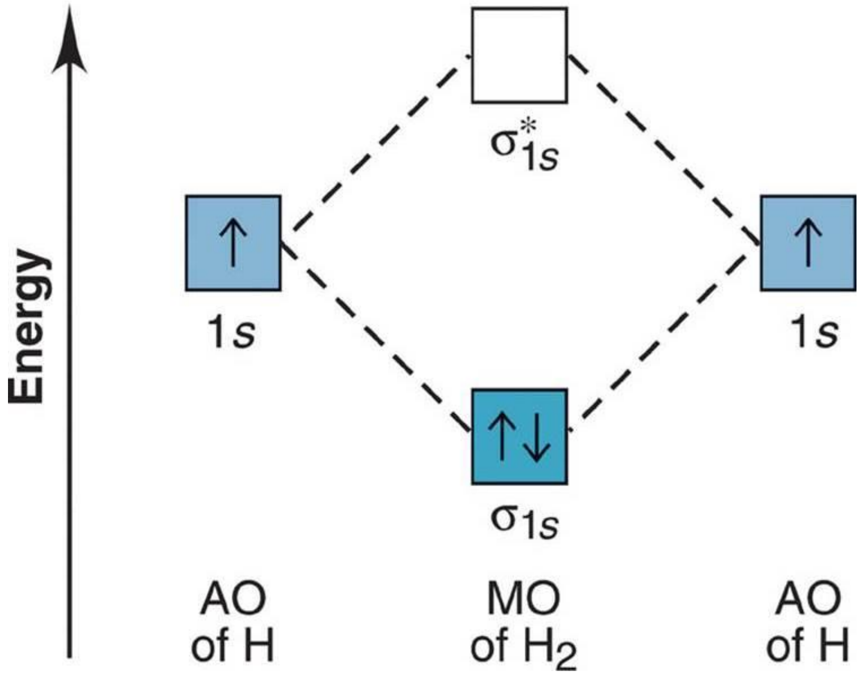


Figure 3.24 Molecular orbital diagram of H_2.

3.16 Intermolecular Forces

Intermoleculear forces are forces of attraction/repulsion that exist between molecules. The ones need to be overcome to change the state of the substance. Covalent Bonds are not *inter*molecular forces. They are *intra*molecular forces. The stronger the intermolecular interaction, the stronger molecules are held together.

Intermoleculear forces include the following types:

1. **Van der Waals Forces:** Discovered by the Dutch physicist, Van der Waals and named in his honor. They are weak interactions between molecules and divided into *Dipole–Dipole* and *Ion-Dipole* interactions.

Dipole–Dipole occurs when a molecule has a permanent dipole moment (molecule is polar),where the negative end of one molecule will sit closer to the positive end of its neighbor (see Figure 3.25).

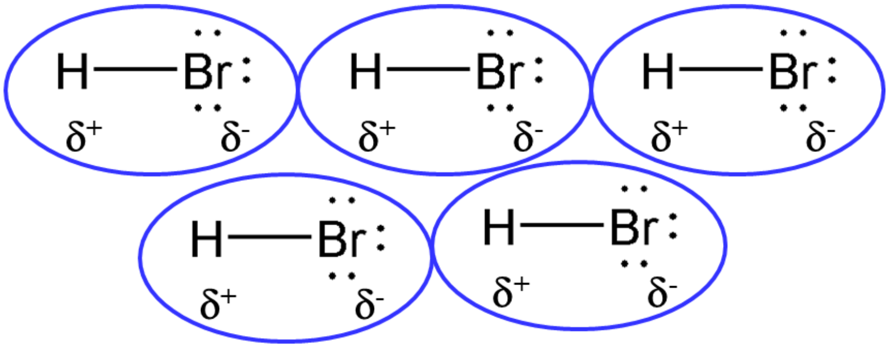


Figure 3.25 Dipole-dipole interaction between hydrogen bromide molecules.

Ion-Dipole force exists when an ionic compound is dissolved in a polar solvent, like H_2O. The δ- end of H_2O is attracted to a cation (+). The δ+ end of H_2O is attracted to an anion (-). An example is dissolving sodium chloride salt NaCl in water (see Figure 3.26).

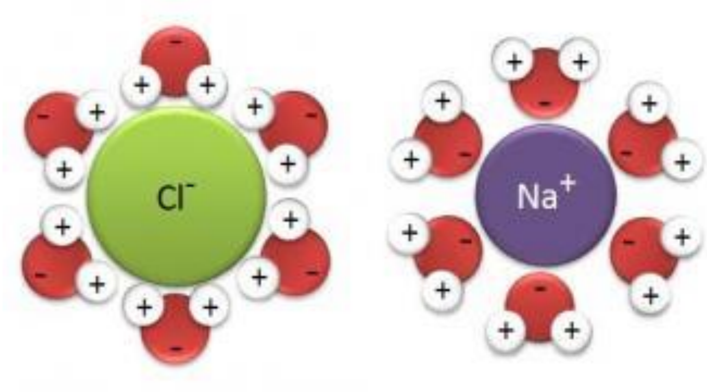
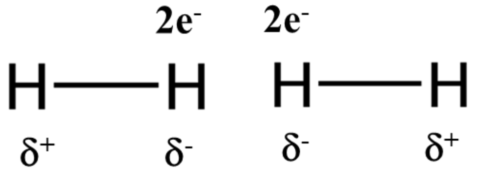


Figure 3.26 Ion-dipole interaction when sodium chloride is dissolved water.

2. **London Forces:** The weakest of all intermolecular forces. Temporary shifts in electron density within a molecule. Caused by the natural vibrations of the electrons in the bond, there is no permanent dipole moment. The dominant intermolecular force exists in non-polar substances. For instance the two electrons shared in H_2, located on one H atom rather than the other.



Hydrogen Bonding

It occurs when H is involved in a strongly polar bond with O, N or F. The hydrogen atom nucleus (just a proton) is attracted to the lone pairs of these highly electronegative atoms. The result is a network of strong intermolecular interactions between H atoms and available lone pairs. It can exist between molecules of same compound or different compounds (intermolecular) or between atoms in the same molecule (intramolecular).

It exists for example in water (see figure 3.27), ammonia and hydrofluoric acid. It is the primary reason for unique properties of water in the known universe. Water expands when it freezes however everything else contracts. Water floats when it freezes but generally solids have higher density than liquids.

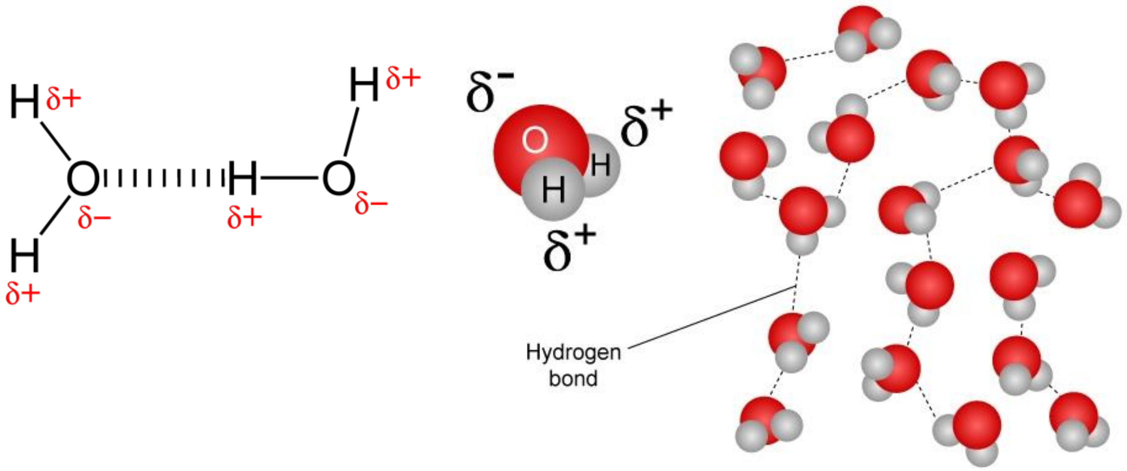


Figure 3.27 Hydrogen bonding in water.

3.17 Metallic Bond

It is the force that holds atoms together in a metallic compounds. The valence electrons in metals are delocalized, capable of freely moving throughout the entire crystal. The atoms that lost the electrons become positive ions, and the interaction between such ions and valence electrons gives rise to the binding force that holds the metallic crystal together (see figure 3.28). In other words, metallic bond results from the electrostatic attraction between metal cations and delocalized electrons.

The “Sea of Electrons” Model is used to explain this bond. According to this model bond occurs due to: low electronegativities, low effective nuclear charges and large diffuse orbitals. Thus, electrons can flow freely from one atom to the next. The nature of metallic bonding accounts for many of the physical properties of metals, such as conductivity and malleability.

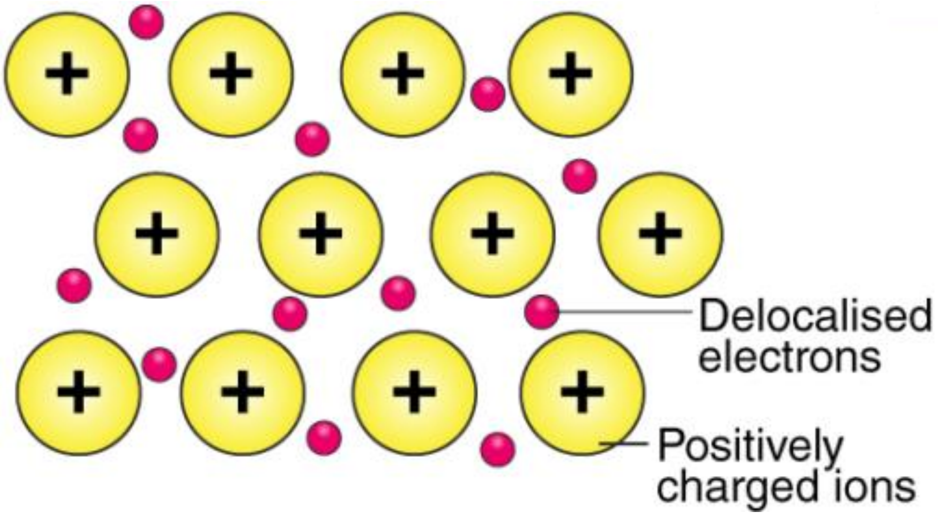


Figure 3.28 Metallic bonding in metals.