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Chm 101

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Content

Atomic Theory and Structure

Pure substances are classified as elements or compounds, but just what makes a substance possess its unique properties? How small a piece of salt will still taste salty? Carbon dioxide puts out fires, is used by plants to produce oxygen, and forms dry ice when solidified. But how small a mass of this material still behaves like carbon dioxide? Substances are in their simplest identifiable form at the atomic, ionic, or molecular level. Further division produces a loss of characteristic properties.

What particles lie within an atom or ion? How are these tiny particles alike? How do they differ? How far can we can we continue to divide them? Alchemists began the quest, early chemists laid the foundation, and modern chemists continue to build and expand on models of the atom.

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 5.1). 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.

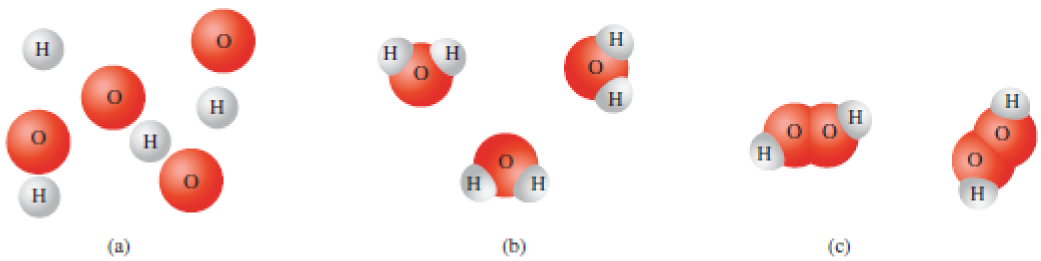


Fig 1.(a) Dalton's atoms were individual particles, the atoms of each element being alike in mass and size but different in mass and size from other elements. (b) and (c) Dalton's atoms combine in specific ratios to form compounds.

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 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 (see Figure 1c).

We often summarize our general observations regarding nature into a statement called a natural law. In the case of the composition of a compound, we use the law of definite composition, which 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 and for hydrogen peroxide H_2O_2as See Figure 1b and c.

The law of multiple proportions states atoms of two or more elements may combine in different ratios to produce more than one compound.

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:

$$F = kq_1q_2/ r^2$$

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

.**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 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.

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 structures and 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. 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 = $1x10^{-9}$ 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 $1x10^{6}$ 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 (Figure2). 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.

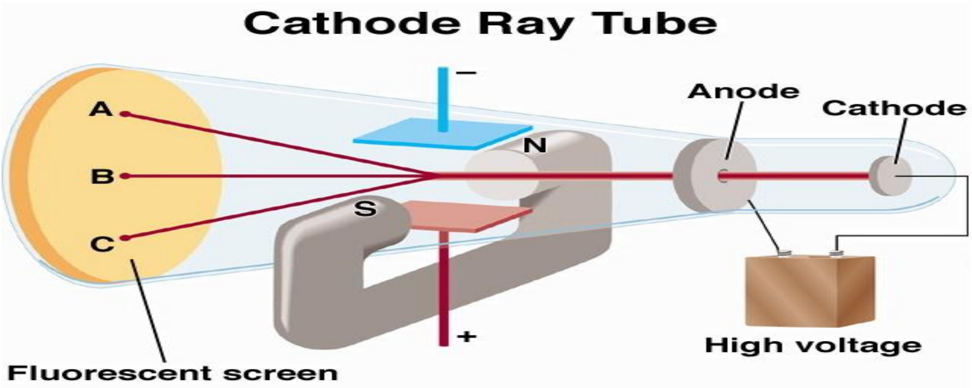


Fig 2.Crookes tube (cathode rays)

The electron**(e^-)** is a particle with a negative electrical charge and a mass of9.110 x 10^{-28} g. This mass is the mass1/1837 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 -1 of the size of an electron has not been determined exactly, but its diameter is believed to be less than10^{-12} cm. Protons were first observed by German physicist Eugen Goldstein (1850–1930) in1886. 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 its 1.673x10^{-24}*g*.relative charge is (+1) 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. 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 +1 of (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 3a).Negative ions were explained by assuming that additional electrons can be added to atoms. A net charge of (for example, or) is produced by the addition of one electron. A net charge of -1(for example, Cl^- or F^-) requires the addition of two electrons (Figure 3b).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 which is only very slightly greater than that of a proton. The properties of these three subatomic particles are summarized in Table 1.

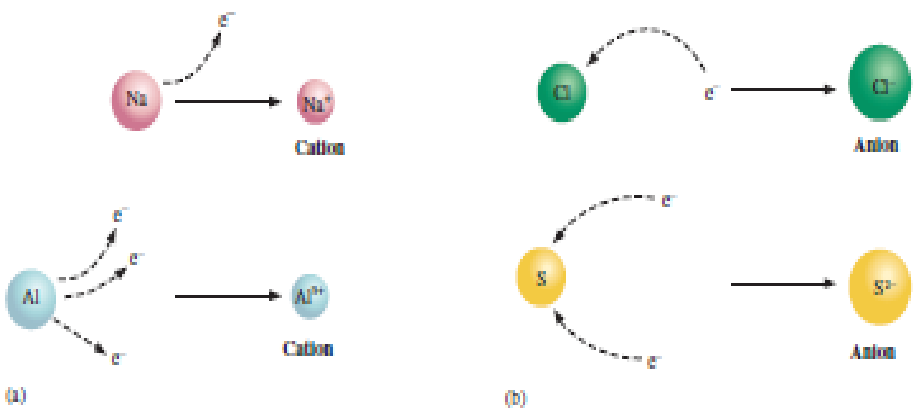


Fig. 3.Thomson model of the atom

Nearly all the ordinary chemical properties of matter can be explained in terms ofatoms consisting of electrons, protons, and neutrons. The discussion of atomic structurethat follows is based on the assumption

that atoms contain only these principalsubatomic 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 reactionsoccurring within the nucleus. The fields of atomic and high-energy physics haveproduced a long list of subatomic particles.

Ions:

Positive ions were explained by assuming that a neutral atom loses electrons.Negative ions were explained by assuming that atoms gain electrons

Table 1.Electrical charge and relative mass of electrons, protons and neutrons.

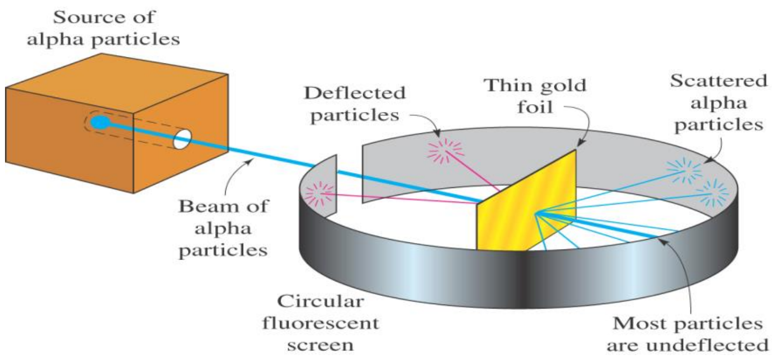
Particle	Symbol	Relative electrical charge	Actual mass (g)
Electron	e^-	−1	9.110×10^{-28}
Proton	p	+1	1.673×10^{-24}
Neutron	n	0	1.675×10^{-24}

The Nuclear Atom

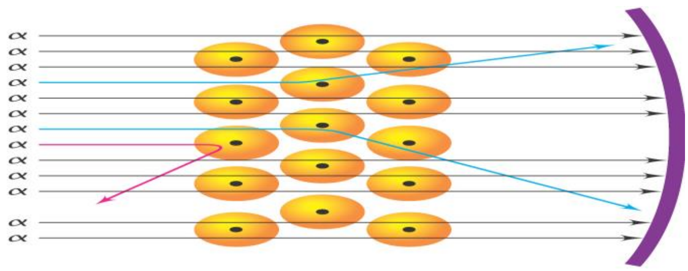
The discovery that positively charged particles are present in atoms came soon afterthe discovery of radioactivity by Henri Becquerel (1852–1908) in 1896. Radioactiveelements spontaneously emit alpha particles, beta particles, and gamma rays fromtheir nucleiBy 1907 Rutherford found that alpha particles emitted by certain radioactive elements were helium nuclei.

Rutherford experiment

In 1911 performed experiments that shot a stream of alpha particles at a gold foil.Most of the alpha particles passed through the foil with little or no deflection. He found that a few were deflected at large angles and some alpha particles even bounced back



An electron with a mass of 1/1837 amu could not have deflected an alpha particle with a mass of 4 amu. Rutherford knew that like charges repel.Rutherford concluded that each gold atom contained a positively charged mass that occupied a tiny volume. He called this mass the nucleus.Most of the alpha particles passed through the gold foil. This led Rutherford to conclude that a gold atom was mostly empty space.



General Arrangement of Subatomic Particles

Rutherford’s experiment showed that an atom had a dense, positively charged nucleus.Chadwick’s work in 1932 demonstrated that the atom contains neutrons.Rutherford also noted that light, negatively charged electrons were present in an atom and offset the positive nuclear charge.Rutherford put forward a model of the atom in which a dense, positively charged nucleus is located at the atom’s center. The negative electrons surround the nucleus. The nucleus contains protons and neutrons.

The atom and the location of its subatomic particles were devised in which each atom consists of a nucleussurrounded by electrons (see above). 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.

Atomic Numbers of the Elements

The atomic numberof an element is the number of protons in the nucleus of an atomof 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 inits nucleus. Every atom with an atomic number of 6 is a carbon atom; it contains 6 protonsin 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 ofpositive 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.

In the nuclear model of the atom,protons and neutrons are located inthe nucleus. The electrons are foundin the remainder of the atom (whichis mostly empty space becauseelectrons are very tiny).You don't need to memorize the atomic numbers of the elements because a periodictable is usually provided in texts, in laboratories, and on examinations. Theatomic numbers of all elements are shown in the periodic table on the inside front cover of this book and are also listed in the table of atomic masses on the inside front endpapers.

Atomic number $_{1}H$ 1 proton in the nucleus

Atomic number $_{6}C$6 proton in the nucleus

Atomic number $_{92}U$92 proton in the nucleus

Isotopes of the Elements

Shortly after Rutherford's conception of the nuclear atom, experiments were performedto determine the masses of individual atoms. These experiments showed thatthe masses of nearly all atoms were greater than could be accounted for by simplyadding up the masses of all the protons and electrons that were known to be presentin an atom. This fact led to the concept of the neutron, a particle with no charge butwith 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 experimentallyuntil 1932. All atomic nuclei except that of the simplest hydrogen atomcontain neutrons.All atoms of a given element have the same number of protons. Experimental evidencehas shown that, in most cases, all atoms of a given element do not have identicalmasses. This is because atoms of the same element may have different numbersof neutrons in their nuclei.Atoms of an element having the same atomic number but different atomic massesare called isotopes of that element. Atoms of the various isotopes of an elementtherefore have the same number of protons and electrons but different numbers ofneutrons.

Three isotopes of hydrogen (atomic number 1) are known. Each has one proton inthe nucleus and one electron. The first isotope (protium), without a neutron, has amass 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 massnumber of 3.

The three isotopes of hydrogen may be represented by the symbols$_1^1H$, $_1^2H$ and $_1^3H$ andindicating an atomic number of 1 and mass numbers of 1, 2, and 3, respectively.This method of representing atoms is called isotopic notation. The subscript (*Z*) is theatomic number; the superscript (A) is the mass number, which is the sum of thenumber of protons and the number of neutrons in the nucleus. The hydrogen isotopesmay also be referred to as referred to as hydrogen-1, hydrogen-2, and hydrogen-3.

Mass number

(sumof protons andneutrons in the nucleus)

Z

E Symbol of element

A

Atomic number (number of protonsin the nucleus)

The mass number ofan element is the sum of theprotons and neutrons inthe 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 formother 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 $^{16}{}_8O$ $^{17}{}_8O$ and$^{18}{}_8O$, are stable. Of the fifteen known isotopes of arsenic, is the only one that is stable.$^{75}{}_{33}As$. is theonly one that is stable.

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 atomsexpressed in grams; therefore, a table of relative atomic masses using atomic mass unitswas devised. (The term atomic weight is sometimes used instead of atomic mass). Thecarbon isotope having six protons and six neutrons and designated carbon-12, or$^{12}_{6}C$, was chosen as the standard for atomic masses. This reference isotope was assigned avalue of exactly 12 atomic mass units (amu). Thus, 1 atomic mass unit is defined asequal to exactly of the mass of a carbon-12 atom. The actual mass of a carbon-12 atom is1.9927 x 10^{-23}*g*and that of one atomic mass unit is1.6606 x 10^{-24} g.

In the table of atomic masses, all elements then have values that are relative to themass assigned to the reference isotope, carbon-12.Hydrogenatoms,with a mass of about 1/12 that of a carbon atom, have an average atomicmass of 1.00794 amu on this relative scale. Magnesium atoms, which are about twiceas heavy as carbon, have an average mass of 24.305 amu. The average atomic mass ofoxygen is 15.9994 amu.

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

For example, the atomic mass of rubidium is 85.4678 amu, that of copper is63.546 amu, and that of magnesium is 24.305 amu. The deviation of an atomic massfrom a whole number is due mainly to the unequal occurrence of the various isotopesof an element.

The two principal isotopes of copper are $^{63}_{29}Cu$ and$^{65}_{29}Cu$. Copper used in everyday objects,and the Liberty Bell contains a mixture of these two isotopes. It is apparent thatcopper-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 copperisotopes observed by mass spectra determination are shown in the following table2:

Table 2.

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

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

(62.9298 amu)(0.6909) =43.48 amu

(64.9278 amu)(0.3091) =<u>20.07 amu</u>
63.55 amu

The atomic massof an element is the average relative mass of the isotopes of thatelement compared to the atomic mass of carbon-12 (exactly 12.0000 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 thenumber of neutrons in the nucleus of an atom of that isotope.For example, the fluorine atom(^{19}9F), atomic number 9, having a mass of 19 amu, contains 10 **neutrons:**

massnumber atomic number number of neutrons
19 9 10

The atomic masses given in the table on the front endpapers of this book are valuesaccepted by international agreement. You need not memorize atomic masses. Inthe calculations in this book, the use of atomic masses rounded to four significantfigures will give results of sufficient accuracy.

Modern Atomic Theory and the Periodic Table

Chemists have the same dilemma when they study the atom. Atoms are so verysmall that it isn't possible to use the normal senses to describe them. We are essentiallyworking in the dark with this package we call the atom. However, our improvementsin instruments (X-ray machines and scanning tunneling microscopes) andmeasuring devices (spectro-photometers and magnetic resonance imaging, MRI) aswell as in our mathematical skills are bringing us closer to revealing the secrets ofthe atom.

A Brief History

In the last 200 years, vast amounts of data have been accumulated to support atomictheory. When atoms were originally suggested by the early Greeks, no physical evidenceexisted to support their ideas. Early chemists did a variety of experiments, whichculminated in Dalton's model of the atom. Because of the limitations of Dalton'smodel, modifications were proposed first by Thomson and then by Rutherford, whicheventually led to our modern concept of the nuclear atom. These early models of theatom work reasonably well—in fact, we continue to use them to visualize a variety ofchemical concepts. There remain questions that these models cannot answer, includingan 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 andimproves upon the earlier atomic models.

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 electro-magnetic 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(3.00 x 10^8 m/s).

Light is one form of electromagnetic radiation and is usually classified by its wavelength,as shown in Figure 4. Visible light, as you can see, is only a tiny part of theelectromagnetic spectrum. Some examples of electromagnetic radiation involved inenergy transfer outside the visible region are hot coals in your backyard grill, whichtransfer infrared radiation to cook your food, and microwaves, which transfer energyto water molecules in the food, causing them to move more quickly and thus raisethe temperature of your food.

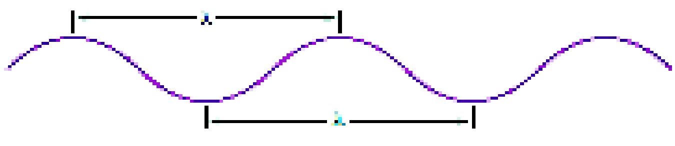


Fig. 4.

The Bohr Atom

As scientists struggled to understand the properties of electromagnetic radiation, evidencebegan to accumulate that atoms could radiate light. At high temperatures, orwhen 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 lightemitted by a gas is passed through a prism or diffraction grating, a set of brightly coloredlines called a line spectrumresults (Figure 5). These colored lines indicatethat the light is being emitted only at certain wavelengths, or frequencies, that correspondto specific colors. Each element possesses a unique set of these spectral lines that is different from the sets of all the other elements.

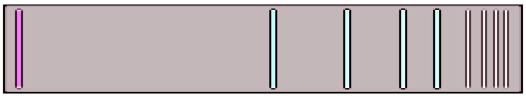


Fig. 5line spectrum

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

Bohr’s first paper in this field dealt with the hydrogen atom, which he described asa single electron revolving in an orbit about a relatively heavy nucleus. He applied theconcept of energy quanta, proposed in 1900 by the German physicist Max Planck(1858–1947), to the observed line spectrum of hydrogen. Planck stated that energyis never emitted in a continuous stream but only in small, discrete packets calledquanta.From this, Bohr theorized that electrons haveseveral possible energies corresponding to several possible orbits at different distancesfrom the nucleus. Therefore an electron has to be in one specific energy level; it cannotexist between energy levels. In other words, the energy of the electron is said tobe quantized. Bohr also stated that when a hydrogen atom absorbed one or morequanta 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 energylevels are available, the lowest of which is called the ground state. When anelectron 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 wavelength5. This light corresponds to one of the lines visible in the hydrogen spectrum(Figure 5). Several lines are visible in this spectrum, each one correspondingto a specific electron energy-level shift within the hydrogen atom.The chemical properties of an element and its position in the periodic table dependon electron behavior within the atoms. In turn, much of our knowledge of the behaviorof electrons within atoms is based on spectroscopy. Niels Bohr contributed a great dealto our knowledge of atomic structure by

(1)Suggesting quantized energy levels for electronsand

(2)Showing that spectral lines result from the radiation of small incrementsof energy (Planck's quanta) when electrons shift from one energy level to another.

Bohr'scalculations succeeded very well in correlating the experimentally observed spectral lineswith electron energy levels for the hydrogen atom. However, Bohr's methods of calculationdid not succeed for heavier atoms. More theoretical work on atomic structurewas needed.

In 1924, the French physicist Louis de Broglie suggested a surprising hypothesis:

All objects have wave properties. De Broglie used sophisticated mathematics to showthat the wave properties for an object of ordinary size, such as a baseball, are toosmall to be observed. But for smaller objects, such as an electron, the wave propertiesbecome significant. Other scientists confirmed de Broglie's hypothesis, showingthat electrons do exhibit wave properties. In 1926, Erwin Schrqdinger, an Austrianphysicist, created a mathematical model that described electrons as waves. UsingSchrqdinger's wave mechanics, we can determine the probabilityof finding an electronin a certain region around the nucleus of the atom.This treatment of the atom led to a new branch of physics called wave mechanics orquantum mechanics, which forms the basis for our modern understanding of atomicstructure. Although the wave-mechanical description of the atom is mathematical, itcan be translated, at least in part, into a visual model. It is important to recognize thatwe cannot locate an electron precisely within an atom; however, it is clear that electronsare not revolving around the nucleus in orbits as Bohr postulated.

Energy Levels of Electrons

One of the ideas Bohr contributed to the modern concept of the atom was that theenergy of the electron is quantized—that is, the electron is restricted to only certainallowed energies. The wave-mechanical model of the atom also predicts discrete principalenergy levelswithin the atom. These energy levels are designated by the letter*n*, where *n* is a positive integer (Figure 6). The lowest principal energy levelcorresponds to n= 1 the next to n= 2 and so on. As *n* increases, the energy of theelectron increases, and the electron is found on average farther from the nucleus.Each principal energy level is divided into sublevels, which are illustrated in Figure7. The first principal energy level has one sublevel. The second principal energy levelhas two sublevels; the third energy level has three sublevels, and so on. Each of thesesublevels contains spaces for electrons called orbitals.

In each sublevel the electrons are found within specified orbitals (*s*, *p*, *d*, *f*). Let'sconsider each principal energy level in turn. The first principal energy level n= 1 hasone sublevel or type of orbital. It is spherical in shape and is designated as 1*s*. It is importantto understand what the spherical shape of the 1*s* orbital means. The electrondoes *not* move around on the surface of the sphere, but rather the surface encloses aspace where there is a 90% probability where the electron may be found.

It mighthelp 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 boundaryis quite fuzzy. The same is true for atomic orbitals. Each has a region of highest densityroughly corresponding to its shape. The probability of finding the electron outside

this region drops rapidly but never quite reaches zero. Scientists often speak of orbitalsas 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 toconsider one more property of electrons. This property is called spin. Each electronappears to be spinning on an axis, like a globe. It can only spin in two directions.

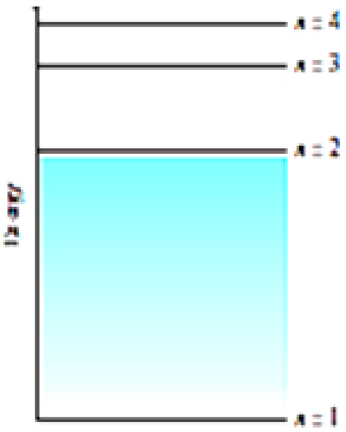


Fig.6

Fig.7

Werepresent this spin with an arrow ↑↓. In order to occupy the same orbital, electronsmust have opposite spins. That is, two electrons with the same spin cannot occupy thesame orbital. This gives us the answer to our question: An atomic orbital can hold amaximum of two electrons, which must have opposite spins. This rule is called thePauli exclusionprinciple. The first principal energy level contains one type of orbital (1s)that holds a maximum of two electrons.What happens with the second principal energy level (n=2). Here we find twosublevels, 2*s* and 2*p*. Like 1*s* in the first principal energy level, the 2*s* orbital is sphericalin 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 ofthree orbitals $2p_x$, $2p_y$, $2p_z$.and the shape of *p* orbitals is quite different from the *s*orbitals, as shown in Figure 8.

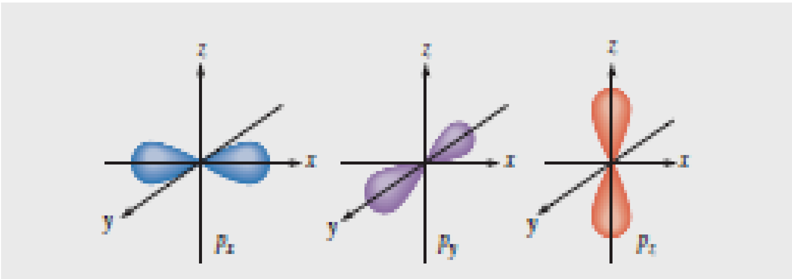


Fig.8

Each *p* orbital has two "lobes." Remember, the space enclosed by these surfacesrepresents the regions of probability for finding the electrons 90% of the time. Thereare three separate *p* orbitals, each oriented in a different direction, and each *p* orbitalcan hold a maximum of two electrons. Thus the total number of electrons that can residein 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 three2*p* orbitals labeled $2p_x$, $2p_y$ and$2p_z$, as shown in Figure 9.

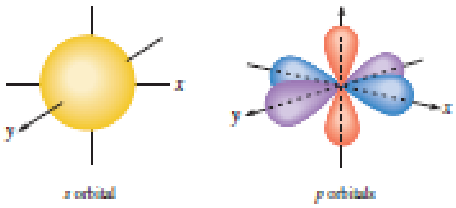


Fig.9

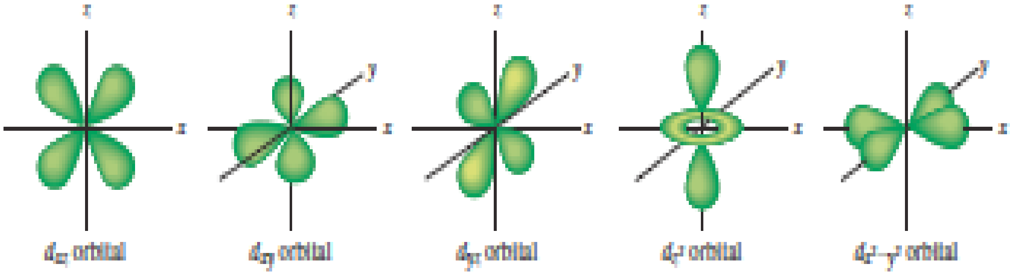


Fig.10.

The third principal energy level has three sublevels labeled 3s,3p 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 areshaped like those of the second level, only larger. The five 3*d* orbitals have the shapesshown in Figure 10. You don't need to memorize these shapes, but notice thatthey look different from the *s* or *p* orbitals.Each time a new principal energy level is added, we also add a new sublevel. Thismakes sense because each energy level corresponds to a larger average distance fromthe nucleus, which provides more room on each level for new sublevels containingmore orbitals.The pattern continues with the fourth principal energy level. It has 4*s*, 4*p*, 4*d*, and4f orbitals. There are one 4*s*, three 4*p*, five 4*d*, and seven 4f orbitals. The shapes of the *s*,*p*, and *d* orbitals are the same as those for lower levels, only larger. We will not considerthe shapes of the orbitals. Remember that for all *s*, *p*, *d*, and *f* orbitals, the maximumnumber 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 electronoccupying a region outside of the nucleus. In its ground state, the electron occupiesa 1*s* orbital, but by absorbing energy the electron can become excited and moveto a higher energy level.

Atomic Structures of the First 18 Elements

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

1. No more than two electrons can occupy one orbital.

2. Electrons occupy the lowest energy orbitals available. They enter a higher energyorbital only when the lower orbitals are filled. For the atoms beyond hydrogen,orbital energies vary as s<p<d<f for a given value of *n*.

3. Each orbital in a sublevel is occupied by a single electron before a second electronenters.

For example, all three *p* orbitals must contain one electron before a secondelectron enters a *p* orbital.We can use several methods to represent the atomic structures of atoms, dependingon what we are trying to illustrate. When we want to show both the nuclear makeupand the electron structure of each principal energy level (without orbital detail), we can use a diagram such as Figure 11.

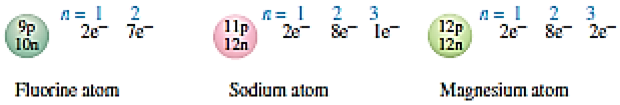
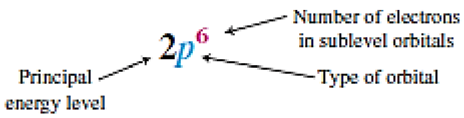


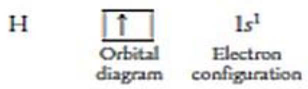
Fig. 11.

Often we are interested in showing the arrangement of the electrons in an atom intheir orbitals. There are two ways to do this. The first method is called the electronconfiguration. In this method, we list each type of orbital, showing the number ofelectrons in it as an exponent. An electron configuration is read as follows:

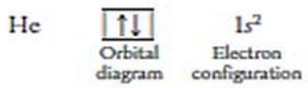


We can also represent this configuration with an in which boxesrepresent the orbitals (containing small arrows indicating the electrons when theorbital contains one electron, an arrow, pointing upward (↑) is placed in the box. Asecond arrow, pointing downward (↓) indicates the second electron in that orbital.

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

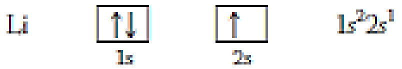


Helium, with two electrons, can be shown as



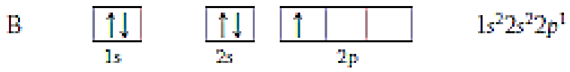
The first energy level, which can hold a maximum of two electrons, is now full. Anatom with three electrons will have its third electron in the second energy level. Thus,in lithium (atomic number 3), the first two electrons are in the 1*s* orbital, and thethird electron is in the 2*s* orbital of the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

Lithium has the following structure:

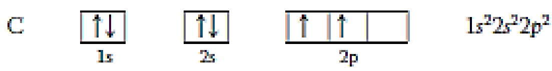


All four electrons of beryllium are *s* electrons:

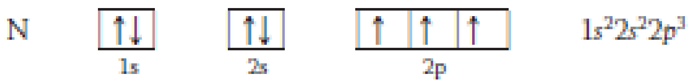
The next six elements illustrate the filling of the *p* orbitals. Boron has the first *p* electron.Because *p* orbitals all have the same energy, it doesn’t matter which of theseorbitals fills first:



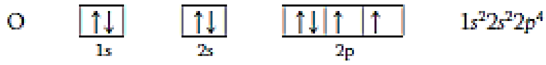
Carbon is the sixth element. It has two electrons in the 1*s* orbital, two electrons in the2*s* orbital, and two electrons to place in the 2*p* orbitals. Because it is more difficult forthe *p* electrons to pair up than to occupy a second *p* orbital, the second *p* electron islocated in a different *p* orbital. We could show this by writing $2p_x^1 2p_y^1$ but we usuallywrite it as $2p^2$: it is understoodthat the electrons are in different*p* orbitals. The spins on these electrons are alike, for reasons we will not explain here.



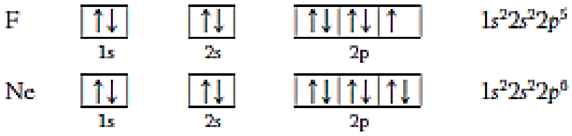
Nitrogen has seven electrons. They occupy the 1*s*, 2*s*, and 2*p* orbitals. The third *p*electron in nitrogen is still unpaired and is found in the $2p_z$ orbital:



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

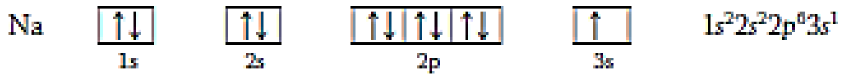


The next two elements are fluorine with nine electrons and neon with ten electrons:



With neon, the first and second energy levels are filled as shown in table 3. The secondenergy level can hold a maximum of eight electrons, $2s^22p^6$.

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



Magnesium (12), aluminum (13), silicon (14), phosphorus (15), sulfur (16), chlorine(17), and argon (18) follow in order. Table 4 summarizes the filling of the orbitalsfor elements 11–18.The electrons in the outermost (highest) energy level of an atom are called thevalence electrons. For example, oxygen, which has the electron configuration of? $1s^22s^22p^4$ has electrons in the first and second energy levels. Therefore the secondprincipal energy level is the valence level for oxygen. The 2*s* and 2*p* electrons are thevalence electrons. In the case of magnesium($1s^22s^22p^63s^1$) the valence electrons arein the 3*s* orbital, since these are outermost electrons.

Table.3

Number	Element	Orbitals			Electron configuration
		1s	2s	2p	
1	H	[↑]			$1s^1$
2	He	[↑↓]			$1s^2$
3	Li	[↑↓]	[↑]		$1s^22s^1$
4	Be	[↑↓]	[↑↓]		$1s^22s^2$
5	B	[↑↓]	[↑↓]	[↑][ ][ ]	$1s^22s^22p^1$
6	C	[↑↓]	[↑↓]	[↑][↑][ ]	$1s^22s^22p^2$
7	N	[↑↓]	[↑↓]	[↑][↑][↑]	$1s^22s^22p^3$
8	O	[↑↓]	[↑↓]	[↑↓][↑][↑]	$1s^22s^22p^4$
9	F	[↑↓]	[↑↓]	[↑↓][↑↓][↑]	$1s^22s^22p^5$
10	Ne	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	$1s^22s^22p^6$

Table. 4.

Number	Element	Orbitals					Electron configuration
		1s	2s	2p	3s	3p	
11	Na	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑]		$1s^22s^22p^63s^1$
12	Mg	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]		$1s^22s^22p^63s^2$
13	Al	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑][ ][ ]	$1s^22s^22p^63s^23p^1$
14	Si	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑][↑][ ]	$1s^22s^22p^63s^23p^2$
15	P	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑][↑][↑]	$1s^22s^22p^63s^23p^3$
16	S	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑][↑]	$1s^22s^22p^63s^23p^4$
17	Cl	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓][↑]	$1s^22s^22p^63s^23p^5$
18	Ar	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	$1s^22s^22p^63s^23p^6$

Electron Structures and the Periodic Table

We have seen how the electrons are assigned for the atoms of elements 1–18. How dothe electron structures of these atoms relate to their position on the periodic table?

To answer this question, we need to look at the periodic table more closely.The periodic table represents the efforts of chemists to organize the elements logically.Chemists of the early nineteenth century had sufficient knowledge of the propertiesof elements to recognize similarities among groups of elements. In 1869, DimitriMendeleev (1834–1907) of Russia and Lothar Meyer (1830–1895) of Germany independentlypublished periodic arrangements of the elements based on increasingatomic masses. Mendeleev’s arrangement is the precursor to the modern periodictable, and his name is associated with it. The modern periodic table is shown in Figure12 and on the inside front cover of the book.Each horizontal row in the periodic table is called a period, as shown in Figure12. There are seven periods of elements. The number of each period correspondsto the outermost energy level that contains electrons for elements in that period. Thosein Period 1 contain electrons only in energy level 1, while those in Period 2 contain electronsin 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. Theseform the vertical columns on the periodic table. Several systems exist for numbering thegroups. In one system, the columns are numbered from left to right using the numbers1–18. However, we use a system that numbers the columns with numbers and the lettersA and B, as shown in Figure 12.

The A groups are known as the representativeelements. The B groups and Group 8 are called the transition elements. In this notebook we will focus on the representative elements. The groups (columns) of the periodictable often have family names. For example, the group on the far right side of theperiodic table (He, Ne, Ar, Kr, XeandRn) is called the noble gases. Group 1A is calledthe alkali metals, Group 2A the alkaline earth metals, and Group 7A the halogens.How is the structure of the periodic table related to the atomic structures of the elements?

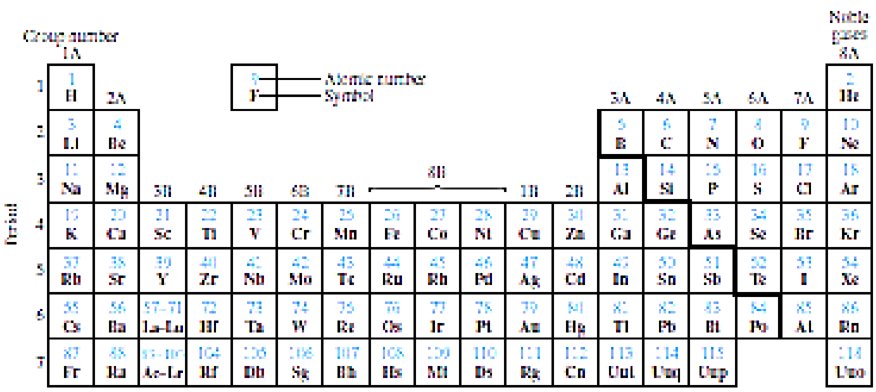


Fig. 12

The chemical behavior and properties of elements in a particular familymust therefore be associated with the electron configuration of the elements. Thenumber for the principal energy level is different. This is expected since each new periodis associated with a different energy level for the valence electrons.The electron configurations for elements beyond these first 18 become long and tediousto write. We often abbreviate the electron configuration using the following notation:

Na $[Ne]3s^1$

Look carefully at Figure 14 and you will see that the *p* orbitals are full at the noblegases. By placing the symbol for the noble gas in square brackets, we can abbreviatethe complete electron configuration and focus our attention on the valence electrons.Towrite 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	$1s^22s^22p^1$	$[He]2s^22p^1$
Cl	$1s^22s^22p^63s^23p^5$	$[Ne]3s^23p^5$
Na	$1s^22s^22p^63s^1$	$[Ne]3s^1$

The sequence for filling the orbitals is exactly as we would expect up through the3*p* orbitals. The third energy level might be expected to fill with 3*d* electrons beforeelectrons enter the 4*s* orbital, but this is not the case. The behavior and properties ofthe next two elements, potassium (19) and calcium (20), are very similar to the

1A							Noble gases
1 H $1s^1$	2A	3A	4A	5A	6A	7A	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 $3s^23p^6$

Fig.13.

elements in Groups 1A and 2A, respectively. They clearly belong in these groups. Theother elements in Group 1A and Group 2A have electron configurations that indicatevalence electrons in the *s* orbitals(Figure 13).

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 elementsvary 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 configurationreappears regularly for each level. Groups of elements show similar chemicalproperties because of the similarity of these outermost electron configurations.

This periodic table illustrates these important points:

1. The number of the period corresponds with the highest energy level occupied byelectrons in that period.

2. The group numbers for the representative elements are equal to the total numberof outermost electrons in the atoms of the group. For example, elements in Group7A always have the electron configuration nS^2,$nP^{5.}$ The d and f electrons are alwaysin a lower energy level than the highest energy level and so are not considered asoutermost (valence) electrons.

3. The elements of a family have the same outermost electron configuration exceptthat the electrons are in different energy levels.

Metals, Nonmetals, and Metalloids

The elements can be classified as metals, nonmetals, and metalloids. Most of the elementsare metals. We are familiar with them because of their widespread use intools, construction materials, automobiles, and so on. But nonmetals are equally usefulin our everyday life as major components of clothing, food, fuel, glass, plastics, andwood. Metalloids are often used in the electronics industry.The metals are solids at room temperature (mercury is an exception). They have high luster, are good conductors of heat and electricity, are malleable (can be rolledor hammered into sheets), and are ductile (can be drawn into wires). Most metalshave a high melting point and a high density. Familiar metals are aluminum, chromium,copper, gold, iron, lead, magnesium, mercury, nickel, platinum, silver, tin, andzinc. Less familiar but still important metals are calcium, cobalt, potassium, sodium,uranium, and titanium.

Metals have little tendency to combine with each other to form compounds. Butmany metals readily combine with nonmetals such as chlorine, oxygen, and sulfur toform compounds such as metallic chlorides, oxides, and sulfides. In nature, mineralsare composed of the more reactive metals combined with other elements. A fewof the less reactive metals such as copper, gold, and silver are sometimes found in anative, or free, state. Metals are often mixed with one another to form homogeneousmixtures of solids called alloys. Some examples are brass, bronze, steel, and coinagemetals.

Nonmetals, unlike metals, are not lustrous, have relatively low melting points anddensities, and are generally poor conductors of heat and electricity. Carbon, phosphorus,sulfur, selenium, and iodine are solids; bromine is a liquid; and the rest of thenonmetals are gases. Common nonmetals found uncombined in nature are carbon(graphite and diamond), nitrogen, oxygen, sulfur, and the noble gases (helium, neon, argon, krypton, xenon, and radon).Nonmetals combine with one another to form molecular compounds such as carbondioxide methane butane and sulfur dioxide Fluorine,the most reactive nonmetal, combines readily with almost all other elements.

Several elements (boron, silicon, germanium, arsenic, antimony, tellurium, and polonium)are classified as **metalloids** and have properties that are intermediate betweenthose of metals and those of nonmetals. Certain metalloids, such as boron, silicon, and germanium, are theraw materials for the semiconductor devices that make the electronics industry possible.

The Formationof Compounds from Atoms

Periodic Trends in Atomic Properties

Although atomic theory and electron configuration help us understand the arrangementand behavior of the elements, it’s important to remember that the design of theperiodic table is based on observing properties of the elements. Before we use theconcept of atomic structure to explain how and why atoms combine to form compounds,we need to understand the characteristic properties of the elements and thetrends 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 varietyof substances (Fig. 14).

In above section, we classified elements as metals, nonmetals, or metalloids.The heavy stair-step line beginning at boron and running diagonally down the periodictable separates the elements into metals and nonmetals. Metals are usuallylustrous, malleable, and good conductors of heat and electricity. Nonmetals arejust the opposite—nonlustrous, brittle, and poor conductors. Metalloids are foundbordering the heavy diagonal line and may have properties of both metals andnonmetals.Most elements are classified as metals. Metals are found on theleft side of the stair-step line, while the nonmetals are located toward the upper rightof the table. Note that hydrogen does not fit into the division of metals and nonmetals.It displays nonmetallic properties under normal conditions, even though ithas only one outermost electron like the alkali metals. Hydrogen is considered to bea unique element.It is the chemical properties of metals and nonmetals that interest us most. Metalstend to lose electrons and form positive ions, while nonmetals tend to gain electronsand form negative ions. When a metal reacts with a nonmetal, electrons areoften transferred from the metal to the nonmetal.

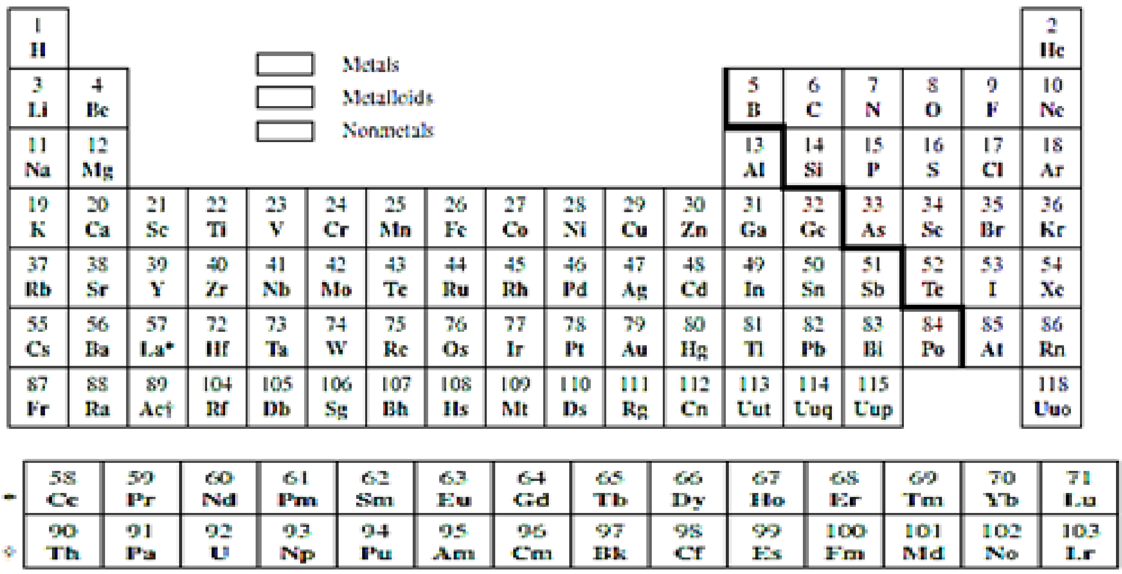


Fig. 14.

Atomic Radius;

The relative radii of the representative elements are shown in Figure 15. Notice thatthe radii of the atoms tend to increase down each group and that they tend to decreasefrom left to right across a period.

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

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 blockare being added to the same principal energy level. Within a given energy level, we expectthe orbitals to have about the same size. We would then expect the atoms to beabout the same size across the period. But each time an electron is added, a proton isadded to the nucleus as well. The increase in positive charge (in the nucleus) pulls theelectrons closer to the nucleus, which results in a gradual decrease in atomic radiusacross a periodas seen from the following:

Fig.15

Ionization Energy:

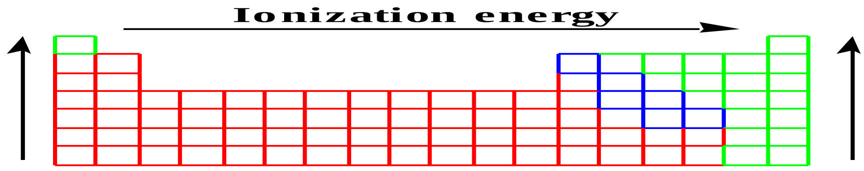
The **ionization energy** of an atom is the energy required to remove an electron fromthe atom. For example,

Na + ionization energy → Na^{-} + e^{-}

The first ionization energy is the amount of energy required to remove the first electronfrom an atom, the second is the amount required to remove the second electron from that atom, and so on.

Table 8 gives the ionization energies for the removal of one to five electronsfrom several elements. The table shows that even higher amounts of energy are neededto remove the second, third, fourth, and fifth electrons. This makes sense becauseremoving electrons leaves fewer electrons attracted to the same positive charge in thenucleus. The data in Table 5 also show that extra-large ionization energy (blue)is needed when an electron is removed from a noble gas-like structure, clearly showingthe stability of the electron structure of the noble gases.

First ionization energies have been experimentally determined for most elements.



Metals don’t behave in exactly the same manner. Some metals give up electronsmuch more easily than others. In the alkali metal family, cesium gives up its 6*s* electronmuch more easily than the metal lithium gives up its 2*s* electron. This makessense when we consider that the size of the atoms increases down the group. The distancebetween the nucleus and the outer electrons increases and the ionization energydecreases. The most chemically active metals are located at the lower left of theperiodic table.

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

Table .5.

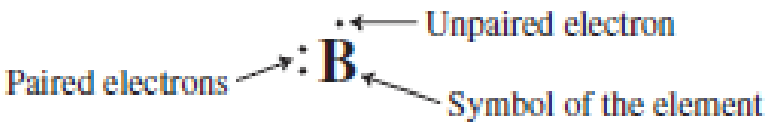
Element	Required amounts of energy (kJ/mol) 1st e^-	2nd e^-	3rd e^-	4th e^-	5th e^-
H	1,314				
He	2,372	5,247			
Li	520	7,297	11,810		
Be	900	1,757	14,845	21,000	
B	800	2,430	3,659	25,020	32,810
C	1,088	2,352	4,619	6,222	37,800
Ne	2,080	3,962	6,276	9,376	12,190
Na	496	4,565	6,912	9,540	13,355

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. Formany elements this stable valence level contains eight electrons (two *s* and six *p*),identical to the valence electron configuration of the noble gases. Atoms undergorearrangements of electron structure to lower their chemical potential energy (orto become more stable). These rearrangements are accomplished by losing, gaining,or sharing electrons with other atoms. For example, a hydrogen atom could accepta second electron and attain an electron structure the same as the noble gashelium. A fluorine atom could gain an electron and attain an electron structurelike neon. A sodium atom could lose one electron to attain an electron structurelike neon.The valence electrons in the outermost energy level of an atom are responsible forthe electron activity that occurs to form chemical bonds.

The Lewis structureofan atom is a representation that shows the valence electrons for that atom. Americanchemist Gilbert N. Lewis (1875–1946) proposed using the symbol for the elementand dots for electrons. The number of dots placed around the symbol equalsthe number of *s* and *p* electrons in the outermost energy level of the atom. Paireddots 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 symbolfor a boron atom, with valence electrons $2S^2$, $2P^1$

In the case of boron, the symbolrepresents the boron nucleus and the $1S^2$ electrons ; the dots represent only theelectrons $2S^2$, $2P^1$



The Lewis method is used not only because of its simplicity of expression but alsobecause much of the chemistry of the atom is directly associated with the electronsin the outermost energy level. Figure 16 shows Lewis structures for the elements hydrogenthrough calcium.

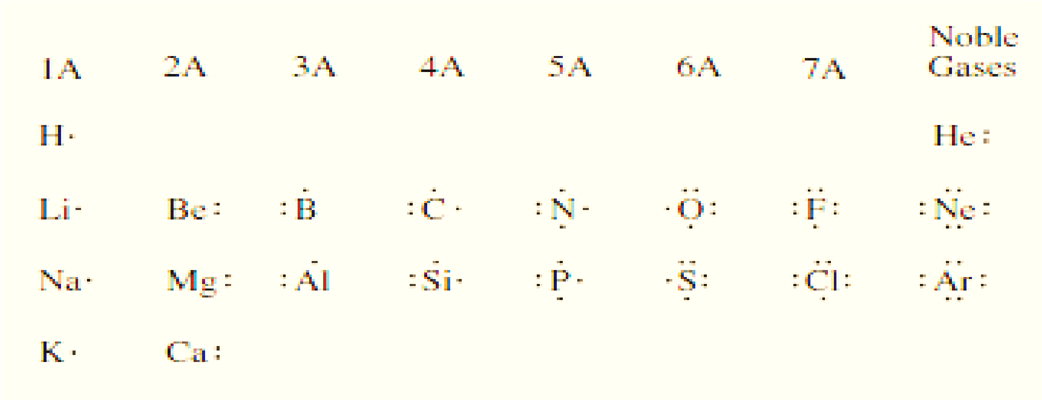


Fig.16

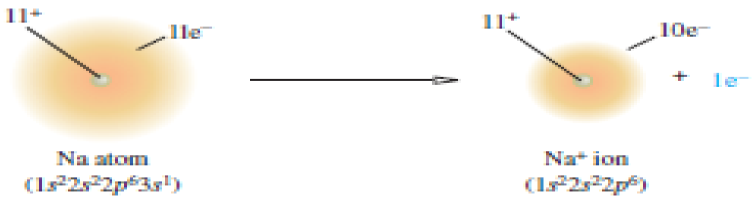
The ionic bond:

The chemistry of many elements, especially the representative ones, is to attain anouter electron structure like that of the chemically stable noble gases. With theexception of helium, this stable structure consists of eight electrons in the outermostenergy level (Figure 6).

Table.6.

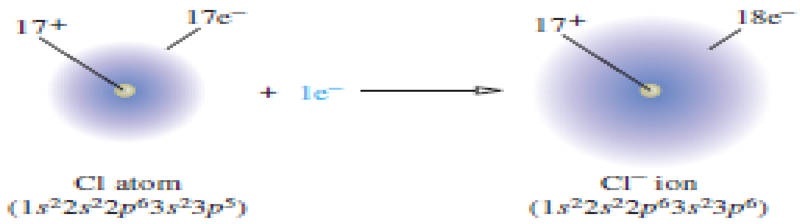
		Electron structure					
Noble gas	Symbol	$n = 1$	2	3	4	5	6
Helium	He	$1s^2$					
Neon	Ne	$1s^2$	$2s^2 2p^6$				
Argon	Ar	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6$			
Krypton	Kr	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6$		
Xenon	Xe	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6 4d^{10}$	$5s^2 5p^6$	
Radon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

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



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 positivelycharged particle known as a sodium ion. The charge +1, results because the nucleus stillcontains 11 positively charged protons and the electron orbitals contain only 10 negativelycharged electrons. The charge is indicated by a plus + signs and is written as asuperscript after the symbol of the element Na^+.A chlorine atom with seven electrons in the third energy level needs one electronto pair up with its one unpaired 3*p* electron to attain the stable outer electron structureof argon. By gaining one electron, the chlorine atom becomes a chloride ion Cl^-a negatively charged particle containing 17 protons and 18 electrons. Thisprocess releases energy:



Consider sodium and chlorine atoms reacting with each other. The3*s* electron fromthe sodium atom transfers to the half-filled 3*p* orbital in the chlorine atom to form apositive sodium ion and a negative chloride ion. The compound sodium chlorideresults because the Na^+ and Cl^- ions are strongly attracted to each other by theiropposite electrostatic charges. The force holding the oppositely charged ions togetheris called an ionic bond (Figure 17).

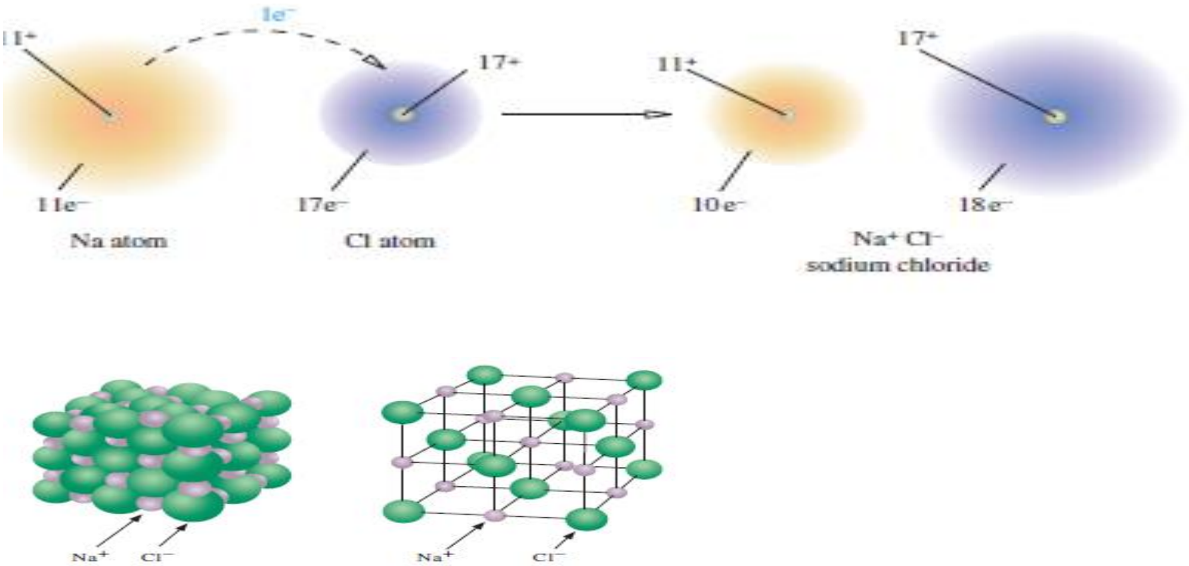


Fig.17.

The Lewis representation of sodium chloride formation is;

$$Na\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow Na^+ + [:\ddot{\underset{\cdot\cdot}{Cl}}:]^-$$

The chemical reaction between sodium and chlorine is a very vigorous one, producingconsiderable heat in addition to the salt formed. When energy is released in achemical reaction, the products are more stable than the reactants. Note that in NaClboth atoms attain a noble gas electron structure.Sodium chloride is made up of cubic crystals in which each sodium ion is surroundedby six chloride ions and each chloride ion by six sodium ions, except at thecrystal surface. A visible crystal is a regularly arranged aggregate of millions ofthese 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 18.

Figure 18 contrasts the relative sizes of sodium and chlorine atoms with thoseof 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 drawncloser 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 eachelectron is thereby decreased, allowing the chlorine atom to expand as it formsan ion.

We have seen that when sodium reacts with chlorine, each atom becomes an ion.Sodium chloride, like all ionic substances, is held together by the attraction existingbetween positive and negative charges. An ionic bondis the attraction between oppositelycharged ions.

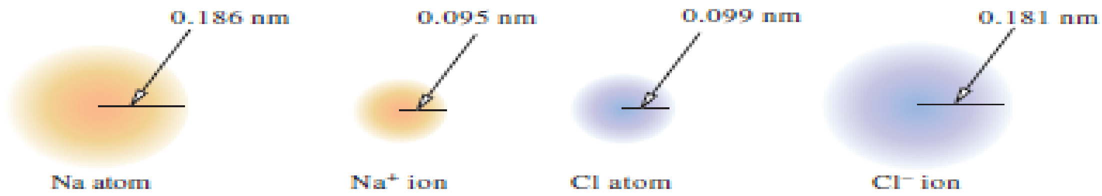


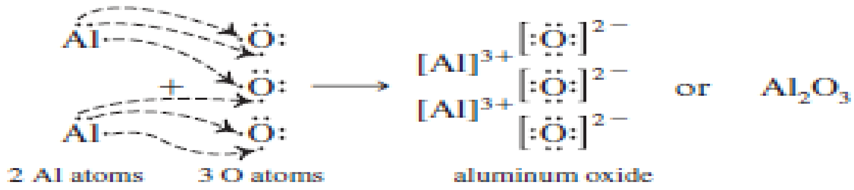
Fig. 18.

Table.7.

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

Ionic bonds are formed whenever one or more electrons are transferred from oneatom to another. Metals, which have relatively little attraction for their valence electrons,tend to form ionic bonds when they combine with nonmetals.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 singlesodium ion and a single chloride ion. Each sodium ion in the crystal attracts sixnear-neighbor negative chloride ions; in turn, each negative chloride ion attracts sixnear-neighbor positive sodium ions (see Figure 18).A metal will usually have one, two, or three electrons in its outer energy level. Inreacting, metal atoms characteristically lose these electrons, attain the electron structureof a noble gas, and become positive ions. A nonmetal, on the other hand, is onlya few electrons short of having a noble gas electron structure in its outer energy leveland thus has a tendency to gain electrons. In reacting with metals, nonmetal atomscharacteristically gain one, two, or three electrons; attain the electron structure of anoble gas; and become negative ions. The ions formed by loss of electrons are muchsmaller than the corresponding metal atoms; the ions formed by gaining electrons arelarger than the corresponding nonmetal atoms. The dimensions of the atomic andionic radii of several metals and nonmetals are given in Table 7.

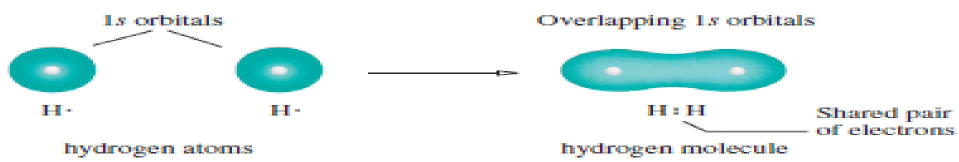
Formation of aluminum oxide Al_2O_3 from its elements.



The covalent bond: sharing electrons

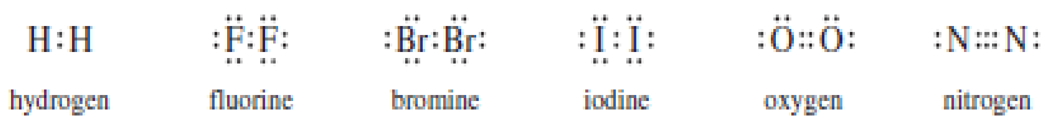
Some atoms do not transfer electrons from one atom to another to form ions. Insteadthey form a chemical bond by sharing pairs of electrons between them. A covalentbondconsists of a pair of electrons shared between two atoms. This bonding conceptwas introduced in 1916 by G. N. Lewis. In the millions of known compounds,the covalent bond is the predominant chemical bond.True molecules exist in substances in which the atoms are covalently bonded. It isproper to refer to molecules of such substances as hydrogen, chlorine, hydrogen chloride,carbon dioxide, water, or sugar. These substances contain only covalentbonds and exist as aggregates of molecules. We don't use the term moleculewhen talking about ionic ally bonded compounds such as sodium chloride, becausesuch substances exist as large aggregates of positive and negative ions, not as molecules(Figure 18).

A study of the hydrogen molecule gives us an insight into the nature of the covalentbond and its formation. The formation of a hydrogen molecule H_2involves theoverlapping and pairing of 1*s* electron orbitals from two hydrogen atoms.



Each atom contributes one electron of the pair that is shared jointly by twohydrogen nuclei. The orbital of the electrons now includes both hydrogen nuclei, butprobability factors show that the most likely place to find the electrons (the point ofhighest electron density) is between the two nuclei. The two nuclei are shielded fromeach other by the pair of electrons, allowing the two nuclei to be drawn very close toeach other.

The formula for chlorine gas Cl_2 is when the two atoms of chlorine combine toform this molecule; the electrons must interact in a manner similar to that shown inthe hydrogen example. Each chlorine atom would be more stable with eight electronsin its outer energy level. But chlorine atoms are identical, and neither is able to pullan electron away from the other. What happens is this: The unpaired 3*p* electron orbitalof one chlorine atom overlaps the unpaired 3*p* electron orbital of the other atom, resulting in a pair of electrons that are mutually shared between the two atoms. Eachatom furnishes one of the pair of shared electrons. Thus, each atom attains a stablestructure of eight electrons by sharing an electron pair with the other atom. The pairingof the *p* electrons and the formation of a chlorine molecule is illustrated in figure19. Neither chlorine atom has a positive or negative charge, because bothcontain 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 betweentwo atoms are hydrogen H_2 oxygen nitrogen O_2fluorine F_2bromine $Br_2$and iodine I_2.Note that more than one pair of electrons may beshared between atoms:



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

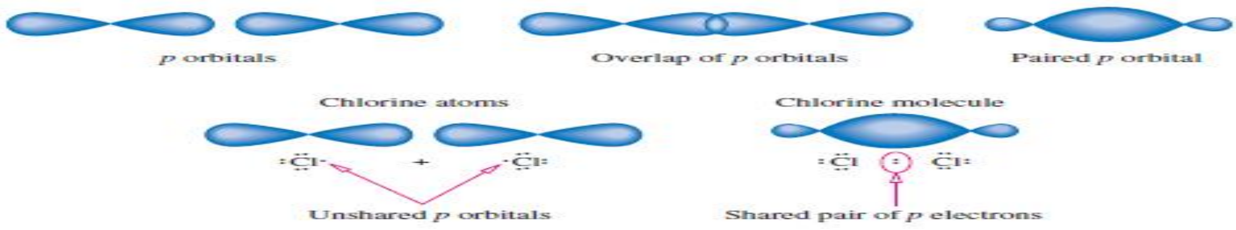


Fig.19

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

The ionic bond and the covalent bond represent two extremes. In ionic bonding theatoms are so different that electrons are transferred between them, forming a chargedpair of ions. In covalent bonding, two identical atoms share electrons equally. Thebond is the mutual attraction of the two nuclei for the shared electrons. Betweenthese extremes lie many cases in which the atoms are not different enough for a transferof 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 covalentbond.

Electronegativity:

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 agreater attraction for the shared electrons than does hydrogen. As a result, thepair of electrons is displaced toward the chlorine atom, giving it a partial negativecharge and leaving the hydrogen atom with a partial positive charge. Note thatthe electron is not transferred entirely to the chlorine atom (as in the case of sodiumchloride) and that no ions are formed. The entire HCl molecule is electrically neutral. A partial charge is usually indicated by the Greek letter delta, δ.

Electron Affinity

The amount of energy released or spent when an electron is added to a neutral atom or molecule in the gaseous state to form a negative ion.

$$\mathbf{X + e^{-} \rightarrow X^{-} + energy}$$

- If the two atoms that constitute a covalent bond are identical, then there is equal sharing of electrons.
- This is called nonpolar covalent bonding.
- If the two atoms that constitute a covalent bond are not identical, then there is unequal sharing of electrons.
- This is called polar covalent bonding.
- One atom assumes a partial positive charge and the other atom assumes a partial negative charge.

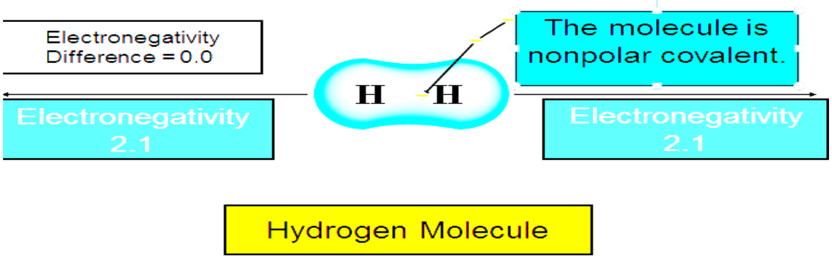
This charge difference is a result of the unequal attractions the atoms have for their shared electron pair.

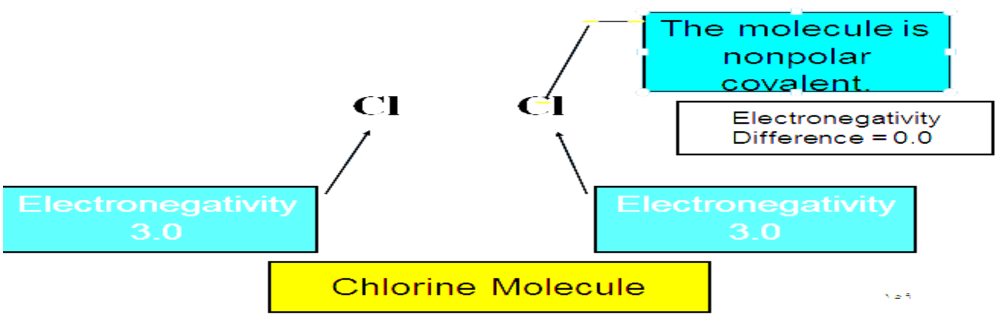
Relating bond type to electronegativity difference

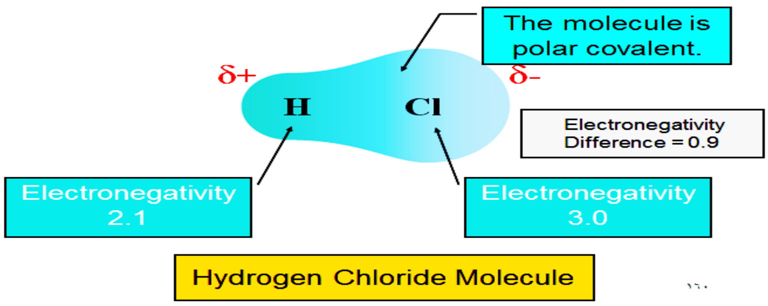
The polarity of a bond is determined by the difference in electronegativity values of the atoms forming the bond.

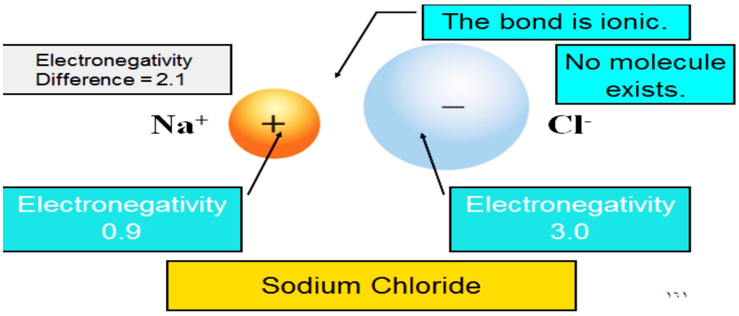
Electronegativity Difference (Δ)	Bond
Δ ≥ 2	Ionic
0.4 < Δ < 2	Polar covalent
Δ ≤ 0.4	Nonpolar covalent

If the electronegativities are the same, the bond is nonpolar covalent and the electrons are shared equally.









Molecular Polarity:

Polar bonds occur when two bonded atoms differ in their electronegativities**.** Such is the case in HCl where chlorine is more electronegativethan hydrogen resulting in a polar H-Cl bond. As seen in Figure 21,the partial negative charge (- δ) is on the more electronegative atom (Cl); the partial positive charge (+δ) resides on the less electronegative atom (H). The bondpolarity is indicated by an arrow (↔), with the plus sign indicating the partial positivecharge (+δ) on the less electronegative atom, and the arrow pointing tothe partial negative charge (- δ) end of the bond. A molecule that has polar bondsmay or may not be polar. If electron density is concentrated at one end of the molecule,as in HCl, the result is a polar molecule**.** A polar molecule is a permanentdipole with a partial negative charge (- δ) where the electron density is concentrated,and a partial positive (+δ) charge at the opposite end, as illustrated in Figure 20. Ifthe polar bonds are oriented so that their polarities cancel each other, such as in CO_2,a nonpolar moleculeresults.

Fig.20

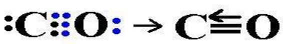
The net dipole moment of a molecule is the sum of its bond dipoles. A diatomicmolecule is, of course, linear. If its atoms differ in electronegativity, then the bondand the molecule will be polar, with the partial negative charge at the more electronegative atom, as in HCl (figure 20).

Polarity of Molecules:

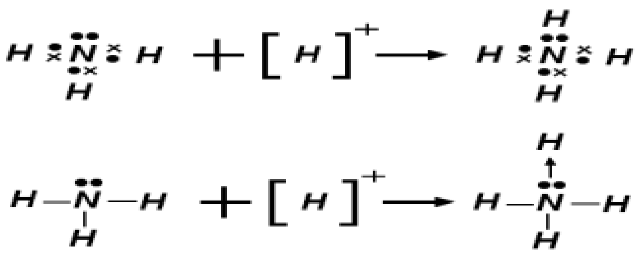
Water, H_2O, has two polar bonds and, because of its geometry, is a polar molecule

The coordinate covalent bond:

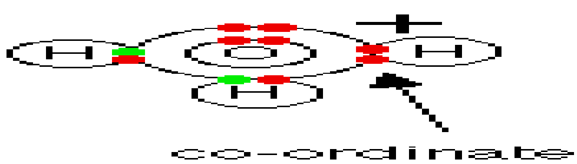
A covalent bond (dative) in which one of the atoms donates both electrons.Properties do not differ from those of a normal covalent bond.A coordinate covalent bond is usually shown with an arrow.

Example 1: 

Example 2: Ammonium ion NH_4^+



Example 3: Hydronium ion H_3O^+



London (Dispersion) Forces:

London forces, also known as dispersion forces, occur in all molecular substances.They result from the attraction between the positive and negative ends ofinduced (nonpermanent) dipoles in adjacent molecules. An induced dipole iscaused in one molecule when the electrons of a neighboring molecule are momentarilyunequally distributed, resulting in a temporary dipole in the first molecule.

Figure 21, illustrates how one H_2 molecule with a momentary unevenness in itselectron distribution can induce a dipole in a neighboring H_2 molecule. This kindof shift in electron distribution in a molecule is known as polarization.

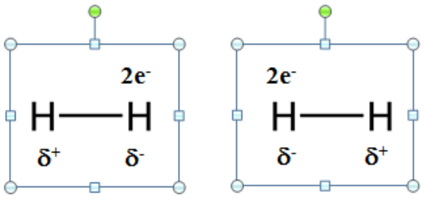


Fig. 21

Due topolarization, even noble gas atoms, molecules of diatomic gases such as oxygen,nitrogen, and chlorine (all of which must be nonpolar), and nonpolar hydrocarbonmolecules such as CH_4 and C_2H_6 have these fleeting dipoles. Such London forcesare the only noncovalent interactions among nonpolar molecules.

London forces range in energy from approximately 0.05 to 40 kJ/mol. Theirstrength depends on how readily electrons in a molecule can be polarized, whichdepends on the number of electrons in a molecule and how tightly they are held bynuclear attraction. In general, electrons are more easily polarized when the moleculecontains more electrons and the electrons are less tightly attracted to thenucleus; London forces increase with increased number of electrons in a molecule.Thus, large molecules with many electrons, such as Br_2 and I_2, are relativelypolarizable. In contrast, smaller molecules (F_2, N_2, O_2) are less polarizable becausethey have fewer electrons.When we look at the boiling points of several groups of nonpolar molecules(Table 8), the effect of the total number of electrons becomes readily apparent:

Boiling points increase as the total number of electrons increases. (This effect alsocorrelates with molar mass—the heavier an atom or molecule, the more electronsit has.) For a liquid to boil, its molecules must have enough energy to overcomemonovalent intermolecular attractive forces among the molecules.

Table 8.

Noble Gases			Halogens			Hydrocarbons		
	No. e's	bp (°C)		No. e's	bp (°C)		No. e's	bp (°C)
He	2	−269	F_2	18	−188	CH_4	10	−161
Ne	10	−246	Cl_2	34	−34	C_2H_6	18	−88
Ar	18	−186	Br_2	70	59	C_3H_8	26	−42
Kr	36	−152	I_2	106	184	C_4H_{10}*	34	0

Thus, the boiling point of a liquid depends on the nature and strength of intermolecular forces.If more energy is required to overcome the intermolecular attractions between moleculesof liquid A than the intermolecular attractions between molecules of liquidB, then the boiling point of A will be higher than that of B. As noted in Table 11,such is the case for Cl_2 (bp =34 °C) compared with F_2 (bp =188 °C) due toweaker London forces between diatomic fluorine molecules than between diatomicchlorine molecules. Conversely, weaker intermolecular attractions result in lowerboiling points. For example, the boiling point of Br_2 (59 °C) is higher than that ofCl_2 (-34 °C), indicating stronger London forces among Br_2 molecules than amongCl_2 molecules.

Interestingly, molecular shape can also play a role in London forces. Two of theisomers of pentanestraight-chain pentane and 2,2-dimethylpropane (both withthe molecular formula C_5H_{12})differ in boiling point by 27 °C. The linear shape ofthe pentane molecule allows close contact with adjacent molecules over its entirelength, resulting in stronger

London forces, while the more compact 2,2-dimethylpropanemolecule does not allow as much close contact.

Dipole-Dipole Attractions:

Because polar molecules have permanent dipoles, a noncovalent interaction calleda dipole-dipole attraction is created between two polar molecules or betweentwo polar groups in the same large molecule. Molecules that are permanent dipolesattract each other when the partial positive region of one is close to the partial negativeregion of another.

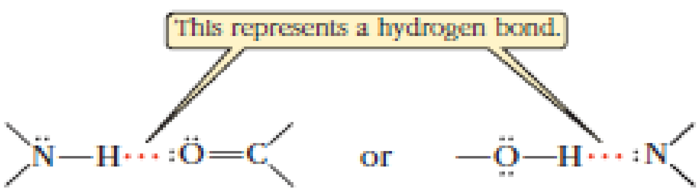
The boiling points of several nonpolar and polar substances with comparablenumbers of electrons, and therefore comparable London forces, are given in Table 9. In general, the more polar its molecules, the higher the boiling point of a substance,provided the London forces are similar (molecules with similar numbersof electrons). The lower boiling points of nonpolar substances compared withthose of polar substances in Table 9.4 reflect this relationship. Dipole-dipole forcesrange from 5 to 25 kJ/mol, but London forces (0.05to 40 kJ/mol) can be stronger. For example, the greater London forces in HI cause it to have a higher boiling point(-36 °C) than HCl (-85 °C), even though HCl is more polar. When London forcesare similar, however, a more polar substance will have stronger intermolecularattractions than a less polar one. An example of this is the difference in boilingpoints of polar Cl_2 (97 °C) with dipole-dipole attractions and nonpolar Br_2 (59 °C)with only London forces, even though the substances have approximately the sameLondon forces due to their similar number of electrons (Table 12).

Table.9.

Nonpolar Molecules			Polar Molecules		
	No. e's	bp (°C)		No. e's	bp (°C)
SiH_4	18	−112	PH_3	18	−88
GeH_4	36	−90	AsH_3	36	−62
Br_2	70	59	ICl	70	97

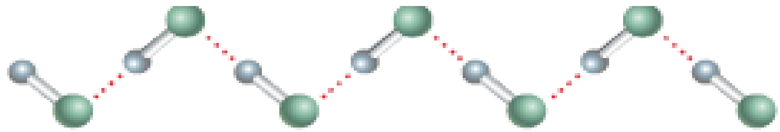
Hydrogen Bonds:

A hydrogen bond is an especially significant type of noncovalent interaction due to a special kind of dipole-dipole force. A hydrogen bond is the attractionbetween a partially positive hydrogen atom covalently bonded to F, N, or O anda lone electron pair on a small, very electronegative atom (generally F, O, or N).The H atom and the lone pair may be in two different molecules or in differentparts of the same large molecule. Electron density within molecules shifts towardF, O, or N because of their high electronegativity, giving these atoms partial negativecharges. As a result, a hydrogen atom bonded to the nitrogen, oxygen, orfluorine atom acquires a partial positive charge. In a hydrogen bond, a partiallypositive hydrogen atom bonded covalently to one of the electronegative atoms(X) is attracted electrostatically to the negative charge of a lone pair on the otheratom (Z). Hydrogen bonds are typically shown as dotted lines (. . .) between theatoms:



The hydrogen bond forms a “bridge” between a hydrogen atom and a highly electronegativeatom. This type of bridge from hydrogen to a lone pair on nitrogen oron oxygen plays an essential role in determining the

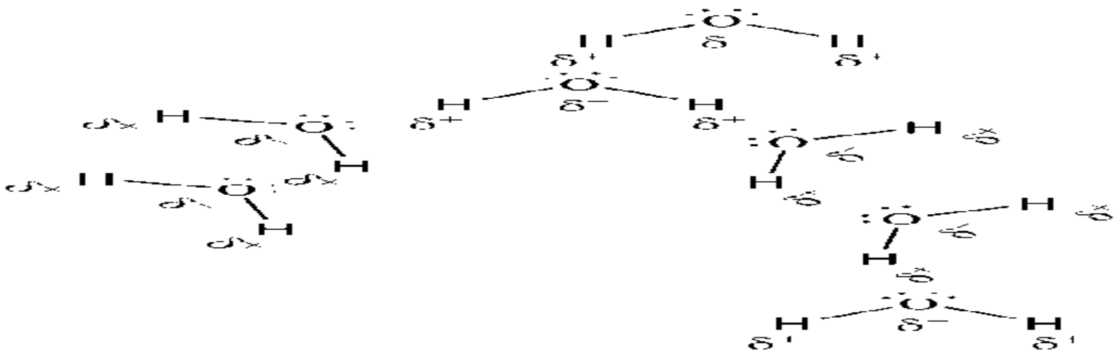
folding (three-dimensionalstructure) of large protein molecules.The greater the electronegativity of the atom connected to H, the greater the partialpositive charge on H and hence the stronger the hydrogen bond.
The H atom is very small and its partial positive charge is concentrated in a verysmall volume, so it can come very close to the lone pair to form an especially strongdipole-dipole force through hydrogen bonding. Hydrogen-bond strengths rangefrom 10 to 40 kJ/mol, which is less than for covalent bonds. However, a great manyhydrogen bonds often occur in a sample of matter, and the overall effect can be verydramatic. An example of this effect can be seen in the melting and boiling points ofethanol. This chapter began by noting the very different melting and boiling pointsof ethanol and dimethyl ether, both of which have the same molecular formula,C_2H_6O, and thus the same number of electrons and roughly the same London forces.Both molecules are polar (dipole moment-0), so there are dipole-dipole forces ineach case. The differences in melting and boiling points arise because of hydrogenbonding in ethanol. The OH bonds in ethanol make intermolecular hydrogenbonding possible, while this is not possible in dimethyl ether because it has noO - H bonds.The hydrogen halides also illustrate the significant effects of hydrogen bonding(Figure 22). The boiling point of hydrogen fluoride, HF, the lightest hydrogenhalide, is much higher than expected. This is attributed to hydrogen bonding,which does not occur significantly in the other hydrogen halides.



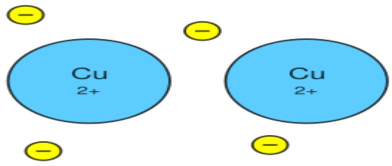
Hydrogen bonding in solid HF

Fig.22

Hydrogen bonding is especially strong among water molecules and is responsiblefor many of the unique properties of water. Hydrogen compoundsof oxygen’s neighbors and family members in the periodic table are gasesat room temperature: CH_4, NH_3, H_2S, H_2Se, H_2Te, PH_3, HF, and HCl. But H_2O is a liquidat room temperature, indicating a strong degree of intermolecular attraction.



Metallic BondingThe “Sea of Electrons” Model:



Due to low electronegativities, low effective nuclear charges and large diffuse orbitals, electrons can flow freely from one atom to the next.

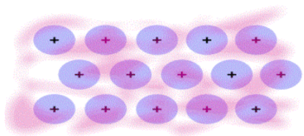


Fig.23.

Metals behave as though metal cations exist in a “sea” of mobile electrons—thevalence electrons of all the metal atoms. Metallic bonding is the nondirectionalattraction between positive metal ions and the surrounding sea of negative charge(valence electrons). Each metal ion has a large number of near neighbors. Thevalence electrons are spread throughout the metal’s crystal lattice, holding the positivemetal ions together. When an electric field is applied to a metal, these valenceelectrons move toward the positive end of the field, and the metal conducts electricity.The mobile valence electrons provide a uniform charge distribution in a metallattice, so the positions of the positive ions can be changed without destroying theattractions among positive ions and electrons. Thus, most metals can be bent anddrawn into wire. Conversely, when we try to deform an ionic solid, which consistsof a lattice of positive and negative ions, the crystal usually shatters because the balanceof positive ions surrounded by negative ions, and vice versa, is disrupted.

To visualize how bonding electrons behave in a metal, first consider thearrangement of electrons in an individual atom far enough away from any neighborso that no bonding occurs. In such an atom the electrons occupy orbitals that havedefinite energy levels. In a large number of separated, identical atoms, all of theenergy levels are identical. If the atoms are brought closer together, however, theybegin to influence one another. The identical energy levels shift up or down and
become bands of energy levels characteristic of the large collections of metal atoms(Figure 23). An energy band is a large group of orbitals whose energies are closely spaced and whose average energy is the same as the energy of the corresponding orbital in an individual atom. In some cases, energy bands for different types of electrons (s, p, d, and so on) overlap; in other cases there is a gap between different energy bands.

Within each band, electrons fill the lowest energy orbitals much as electrons fill-orbitals in atoms or molecules. The number of electrons in a given energy band depends on the number of metal atoms in the crystal. In considering conductivity and other metallic properties, it is usually necessary to consider only valence electrons, as other electrons all occupy completely filled bands in which two electrons occupy every orbital. In these bands, no electron can move from one orbital to another, because there is no empty spot for it.