

# 1. ATOMIC THEORY AND THE STRUCTURE OF THE ATOM

## The Learning Objectives

By the end of this Chapter, students should be able to describe the electronic structures and properties of atoms.

## 1.1. What Is a Theory?

Scientific problems are always checked by experimental work. If a large number of experiments all give similar results, the latter are then summarized into a single statement known as a **law**. Thus, a law is a summary of the results of a large number of separate experiments all giving the same conclusion. Further experiments are carried out to account for the law. This is done by proposing a **hypothesis**. If the results of the experiments agree with the hypothesis, those results are stated into what is called a **theory**.

## 1.2. Atomic Theory

The most important chemical theory was given by John Dalton (1766-1844). Initially, Dalton stated the hypothesis that all Substances consist of small particles of matter of several different kinds corresponding to the different elements. He called these particles **atoms** (from Greek: “atomos” which means indivisible). Dalton also said that elements consist of atoms and that atoms of one element are identical and compounds result from the combination of atoms of two or more elements each in a definite number. He assigned a weight of 1 (one) to a hydrogen atom and built a table of relative weights of elements and compounds (but see Section 1.4). This hypothesis was verified by further experimental work and so it became a theory. Thus Dalton’s atomic theory can be summarized into the following statements:

(a) All matter is made up of atoms that cannot be created or destroyed; that is, atoms are indivisible by ordinary chemical means

(b) Atoms of a particular element are identical in size, shape, mass<sup>1</sup> and all other properties and differ from other atoms in these properties.

## 1.3. Structure of the Atom

From various studies such as radioactivity and field emission, it was found that the atom consists of a

<sup>1</sup>It was later found that atoms of one element may have different masses depending on the number of neutrons present. Atoms of one element having different masses are called isotopes (see Section 1.5). Statement (b) therefore, does not hold for mass.

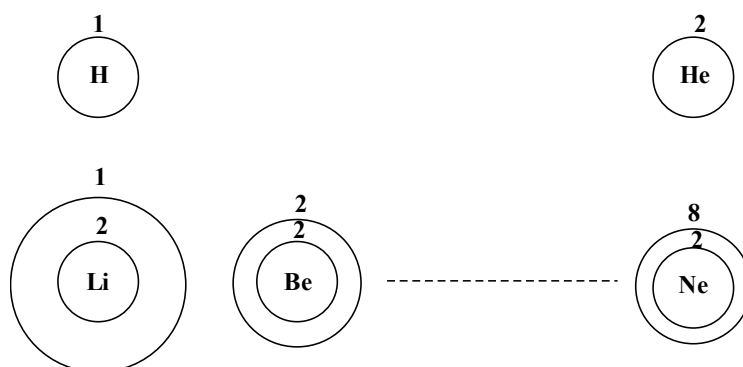
positively charged nucleus surrounded by negatively charged particles called **electrons**. In 1909, Ernest Rutherford studied the deflection patterns of alpha particles ( $\text{He}^{2+}$  ions) by thin metal foils and an analysis of the results led him to the conclusion that an atom has a tiny central nucleus that carries practically all the mass of the atom and that the electrons are around this nucleus. *The number of positive charges on the nucleus is called the **atomic number** (abbrev.  $Z$ ).* Since the atom is neutral, the number of positively charged particles must equal the number of negatively charged particles (electrons). Therefore, the number of electrons surrounding the nucleus in a neutral atom, must also be equal to the atomic number. The positively charged particles are called **protons**. The hydrogen atom for example, has one proton in its nucleus and carries one proton. The electrons are arranged around the nucleus in “**shells**”. Here, we imagine the first group of electrons to be on a small "circle" with the nucleus inside. The second group of electrons would be on a bigger circle with the smaller one inside it and so on. **Figure 1.1** illustrates this pattern.

Thus the successively added electrons first fill the innermost shell, then the next shell to it and so on. The innermost shell is called the **K** shell, the other shells in order of increasing size are called **L**, **M**, **N**, and so on. We shall see later that the K shell is the lowest in energy, the L shell is higher in energy than the K shell, the M shell is higher in energy than the L shell and so on.

#### 1.4. Relative Atomic Mass (RAM)

We have stated that an atom has some components. The electrons are negatively charged and each has a charge of  $-1.60206 \times 10^{-19}$  coulombs and a mass of  $9.109 \times 10^{-28}$  g. The electron charge is abbreviated “e” ( $-1.60206 \times 10^{-19} = e$ ) so that one electron has a charge of  $-e$  or just  $-1$ . It should be noted here that the minus ( $-$ ) sign does not mean that the electron is short of electric charge but that its electrical charge is of the type called negative. The protons are positively charged and each has a charge of  $+1.60206 \times 10^{-19}$  coulombs and a mass of  $1.672 \times 10^{-24}$  g. As for the electron, the charge on a proton is simplified to  $+1$ . All the atoms except hydrogen also have neutrons which are neutral (have a charge of zero) but have a mass of  $1.675 \times 10^{-24}$  g. The other components of an atom include neutrinos, positrons,  $\mu$ -mesons and pi-mesons among others but the detailed nature of these is beyond the scope of this book.

The absolute masses of atoms cannot be determined as the atoms are too light. Only the relative masses can be obtained. To get these relative masses, we need to assign a weight to one atom (the



**Figure 1.1.** Electron arrangements in the shells of atoms.

standard) and relate the masses of the others to it. Initially, hydrogen, which had been assigned a mass of one, was chosen as the standard. However, for some practical reasons a carbon atom with six protons and six neutrons (carbon-12) was later chosen as the new standard. The carbon-12 has a mass of exactly 12. The atomic masses of all the atoms were obtained with reference to a carbon-12 as the standard. However, with technological revolution in modern times, mass spectrometers are used to determine the relative masses of atoms directly. Note that the relative atomic masses are ratios hence have no units.

Since there are more than one atom for a particular element (isotopes, Section 1.5) with differing relative masses we need to calculate a weighted mean of their masses taking into account their relative abundances. *This weighted mean for the mass of a particular element is called the **atomic weight** of that element.* Therefore, we define the atomic weight of an element as the weighted mean of the relative masses of the isotopes of that particular element. For example, chlorine has two isotopes with the relative masses and abundances of 35 (75.5%) and 37 (24.5%). **Note that the sum of the relative abundances add up to 100%.** Thus the atomic weight (the relative atomic mass) of chlorine is:

$$\frac{35 \times 75.5}{100} + \frac{37 \times 24.5}{100} = 35.49$$

It must be noted here that there is no chlorine in nature with a mass of 35.49. The atomic unit is called the **Atomic mass unit** (amu, given the SI unit,  $\mu$ ). One atomic mass unit is equivalent to  $1.66 \times 10^{-24}$  g. Using this basis of measurement, the mass of an electron is  $9.109 \times 10^{-28}$  g  $\div 1.66 \times 10^{-24}$  g/amu = 0.000548 amu and that of a proton is  $1.672 \times 10^{-24}$  g  $\div 1.66 \times 10^{-24}$  g/amu = 1.00725 amu and that of a neutron is  $1.675 \times 10^{-24}$  g  $\div 1.66 \times 10^{-24}$  g/amu = 1.00861 amu. Atomic mass units are usually rounded off to whole numbers called *Mass Numbers* (abbrev. A). This means that the mass of an electron is 0 while that a proton and a neutron each has a mass of 1. The mass number (A) of an atom is the sum total of the number of protons and neutrons (since electrons are so light their contribution to the total mass is ignored). If we abbreviate the mass of neutrons N, then we have:

$$A = Z + N$$

where A is the mass number, Z is the number (=mass) of protons and N is the number (=mass) of neutrons.

Atomic weights are recorded on various periodic tables (see Section 1.11) such as the one shown in the inside back cover of this book. It is possible to calculate the weight of an atom in grams or kilograms. Suppose, for example that  $6 \times 10^{23}$  hydrogen atoms weigh 1 g, *what is the weight of one hydrogen atom?* Simple proportion shows that one hydrogen atom weighs  $1 \text{ g} \div 6 \times 10^{23} = 1.66 \times 10^{-24}$  g. Note that the value obtained equals the weight of a single proton as given earlier. Since one hydrogen atom also weighs 1 amu, this confirms the fact that 1 amu equals  $1.66 \times 10^{-24}$  g. However, atomic weights are not usually expressed in grams or kilograms as the values become cumbersome in metric units.

Since  $6 \times 10^{23}$  hydrogen atoms weigh 1 g and one hydrogen atom weighs 1 amu, it follows that 1 g =  $6 \times 10^{23}$  amu. The figure  $6 \times 10^{23}$  (or more correctly  $6.0226 \times 10^{23}$ ) can be used to convert grams to atomic mass units. It is called the **Avogadro's Constant** (or **Number**) and its importance will be ap-

preciated in Chapter 3.

## 1.5. Isotopes

Atoms of a particular element all have the same atomic number and therefore, the same number of protons. However, most of the elements do not have all their atoms with the same number of neutrons. *Such atoms belonging to the same element but having different numbers of neutrons in their nuclei are called isotopes.* It is to be expected therefore that isotopes should have different masses (note the contrast with Dalton's postulate discussed earlier). This is indeed the case as shown by the example below for the isotopes of hydrogen.

<u>Name</u>	<u>Z</u>	<u>N</u>	<u>Mass Number (Z + N)</u>
Hydrogen	1	0	1
Deuterium	1	1	2
Tritium	1	2	3

## 1.6. Elements and Compounds

In the last section, we saw that elements consist of atoms. An element is a substance which contains only one kind of atom. **Table 1.1** shows the names of some elements and their symbols.

Note that the first letter in the name of some few elements is taken as a symbol of that particular element. For example, hydrogen is H, carbon is C, nitrogen is N and so on. However, because there are many more elements than the number of letters in the alphabet, some elements have two letters in their symbols. For these, the first letter is always in capitalized and the second one is written in small letter. For example, chlorine is Cl, magnesium is Mg, neon is Ne and so on. In the foregoing examples, the first letter is derived from the English name. In other cases, the symbols of the elements are derived from Latin or German names. For example, Antimony is Sb (from Latin, Stibnium), Copper is Cu (from Latin, Cuprum), Iron is Fe (from Latin, Ferrum), Sodium is Na (from German, Natrium), and potassium is K (from German, Kalium), sodium is Na (from German, Natrium) and potassium is K (from German, Kalium).

A compound is formed when atoms of two or more different elements combine. Examples of some compounds include water (H<sub>2</sub>O), methane (CH<sub>4</sub>), glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) and so on. The kind and number of atoms in a compound are described by a formula as shown in brackets after the names of those compounds. The usage of a formula can also be extended to an element if it naturally exists as a molecule. An example is dichloride (Cl<sub>2</sub>).

**Table 1.1. Some elements and their symbols.**

Name of element	Hydrogen	Nitrogen	Fluorine	Chlorine
Symbol	H	N	F	Cl

A formula indicates the relative numbers of atoms in a substance. There are three types of formulae; *empirical formula* is the simplest and gives a bare minimum information about a compound. Diamond for example, consists of an array of carbon atoms each covalently bonded to four other carbon atoms but the formula of diamond, C, does not indicate this. The other empirical formulae include, among others, NaCl (sodium chloride) and SiC (silicon carbide). In the general empirical formula of a compound,  $A_xB_y$  (where A and B are the atoms combined), the subscripts x and y are usually unity. The second is a *molecular formula*, which has more information about a compound than an empirical formula. In the general formula  $A_xD_y$ , (where A and D are the atoms combined), the subscripts x and y in a molecular formula, are the actual numbers of atoms in the compound. For example, water has two hydrogen atoms and one oxygen atom; its molecular formula is therefore  $H_2O$ . The third type is a *structural formula* which shows how the atoms are joined to each other. In this case, the dashes are used to represent bonds and the atomic symbols represent atoms. For example, the structural formula of water is H-O-H. We will encounter more structural formulae when we come to organic compounds later.

## 1.7. Relative Molecular and Formula Mass

In the last section, it was mentioned that compounds that exist as discrete entities, are described by a molecular formula. Such compounds are called molecules. Since the masses of atoms are relative, the masses of molecules are also relative. Each molecule has its own relative mass which is the sum of the relative atomic masses of the atoms in that molecule. We therefore define the *Relative Molecular Mass (RMM)* as the sum of the relative masses of the atoms in a molecular formula.

For example:

(a)  $H_2O$  has two hydrogen (H) atoms and one oxygen (O) atom

$$\begin{aligned} \text{Relative Molecular Mass of water} &= (2 \times \text{Relative Atomic Mass of H}) + (\text{Relative Atomic Mass of O}) \\ &= (2 \times 1) + 16 \\ &= 18 \end{aligned}$$

(b)  $N_2$  has two Nitrogen atoms

$$\begin{aligned} \text{Relative Molecular Mass of nitrogen molecule} &= (2 \times \text{Relative Atomic Mass of N}) \\ &= 2 \times 14 \\ &= 28 \end{aligned}$$

(c)  $C_6H_{12}O_6$  (glucose) has six carbon (C) atoms, 12 hydrogen (H) atoms and 6 oxygen (O) atoms

$$\begin{aligned} \text{Relative Molecular Mass of glucose} &= (6 \times \text{Relative Atomic Mass of C}) \\ &\quad + (12 \times \text{Relative Atomic Mass of H}) \end{aligned}$$

$$\begin{aligned}
 &+ (6 \times \text{Relative Atomic Mass of O}) \\
 &= 72 + 12 + 96 \\
 &= 180
 \end{aligned}$$

Compounds that do not exist as discrete entities however, do not form molecules and are represented by empirical formula. For these we do not assign a Relative Molecular Mass; instead a Relative Formula Mass (RFM) is used. *The relative formula mass is defined as the sum of the relative masses of the atoms in an empirical formula.* For example:

NaCl has one sodium (Na) atom and one chlorine (Cl) atom

$$\begin{aligned}
 \text{Relative Formula Mass of NaCl} &= (1 \times \text{Relative Atomic Mass of Na}) + (1 \times \text{Relative Atomic Mass of Cl}) \\
 &= (1 \times 23) + (1 \times 35.5) \\
 &= 58.5
 \end{aligned}$$

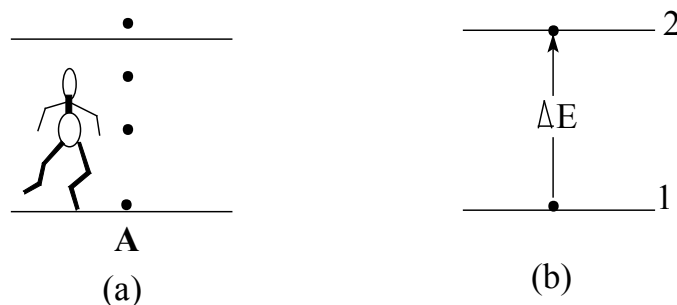
## 1.8. Pure Substances and Mixtures

A substance that contains only one kind of compound or element is said to be a pure substance. A bag of sugar, for example, contains only sugar molecules; therefore sugar is a pure substance. *Pure substances have got the same, definite composition. This means that the concentration of the substance in a pure compound is constant.*

When two or more different compounds (or elements) are put together and cannot react with each other, then we have a mixture. Air for example, which contains oxygen, nitrogen, water, carbon dioxide among others, is a mixture of gases. Unlike pure substances, *mixtures do not have definite compositions.* The composition of substances in air, for example, may vary depending on weather conditions. There are two types of mixtures; those in which the particles of each component are visibly present are called **heterogeneous mixtures**. An example is a mixture of say, salt and black pepper. The second type of mixture is where the particles of one component are evenly dispersed amongst those of the other. These are called **homogeneous mixtures**. They are also called **solutions** (see Chapter 3). Sugar or salt dissolved in water; methanol mixed with water; air on its own, are some examples of solutions.

## 1.9. Quantum Theory

It is common experience than when you hit a football, it will move to any distance depending on the amount of energy you give it. Consider **Figure 1.2(a)** as an example. Imagine a football player standing with a ball at position **A**. He can hit the ball from that point and depending on the amount of force that he applies, the ball can stop at any of the dark points indicated. The less the energy that he gives the ball, the shorter the distance the ball moves and vice versa. In this case, we say that the energy of the ball is continuous; That is, the ball can have any amount of energy. The motion of the ball here, is



**Figure 1.2.** Comparison of a football having any amount of energy (a) (classical physics) and another one having only enough energy to take it from one point to the next (b) (quantum physics).

a part of the physics called *classical physics*. Newton's Laws of motion are part of this physics. In reality, laws of classical physics apply to large particles such as the ball, automobiles, etc.

When classical physics was applied to atoms and other smaller particles, the results obtained were contrary to those expected. In 1900, Max Planck solved this mystery by stating that the energy of an object is not continuous; and that the object will only acquire enough energy to take it from one energy level to another. **Figure 1.2(b)** illustrates this. If we give energy to an object in state 1, the object will only move to state 2 if it has acquired enough energy equal to  $\Delta E = E_2 - E_1$  (where  $E_2$  is the energy of state 2 and  $E_1$  that of state 1). The energy in this case is in form of a packet or bundle and so, we speak of the energy being *quantized*. Thus the object can only have a certain definite energy value. Planck called this packet of energy ( $=\Delta E$ ) a **quantum of energy**. If the energy of the object in energy level 1 is less than  $\Delta E$ , the object will not move. This started a new branch of physics called *quantum physics* whose laws apply to tiny particles like atoms, electrons, etc.

On the basis of this quantum theory, Bohr in 1913 said that electrons move around the nucleus in circular orbits and as they do so, they emit or absorb energy that is quantized (it is now known that electrons do not actually behave this way).

The energy of an electron is governed by an integer called the **Principal Quantum Number** ( $n$ ). The principal quantum numbers are just arbitrary numbers which are introduced in order to make predictions match experiment. They are given numbers 1, 2, 3, 4, etc., increasing as an electron moves further away from the nucleus. In simple terms, the principal quantum numbers are the shell numbers; thus the K shell is principal quantum number 1, L shell is principal quantum number 2 and so on.

The modern quantum theory says that electrons move around the nucleus in a definite region of space. *The region of space in which the electron spends at least 95% of its time is called an orbital*. The orbitals are arranged in **shells** around the nucleus. For each principal quantum number ( $n$ ), there are  $n^2$  orbitals. These are shown in **Table 1.2**. Note that numbering starts from the innermost shell since the K shell is shell number 1 (that is principal quantum number 1).

Apart from the K shell which has one orbital (the s orbital), both theory and experiments have shown that the group of orbitals in each of the L, M, N, etc., shells do not have the same energies especially in a many-electron atom. In a hydrogen atom, which has only one electron, the orbitals in each group have the same energy. Such orbitals having the same energy are said to be **degenerate**. In

**Table 1.2. Shell symbols, orbitals and the maximum number of electrons in them for each principal quantum number.**

Shell number (n)	Symbol	Number of orbitals	Maximum number of electrons <sup>2</sup>
1	K	1	1
2	L	4	8
3	M	9	18
4	N	16	32
5	O	25	50
6	P	36	72

a many-electron atom, the L shell has two energy levels; the lower one has one orbital which is called an **s orbital**, the higher one has three identical orbitals which are degenerate and these are called **p orbitals**. The s orbital is spherical whereas the p orbitals are dumb-bell shaped situated at right angles to each other and in three dimensions along the x-, y- and z-axes; hence designated  $np_x$ ,  $np_y$  and  $np_z$  respectively, (where n is the principal quantum number) as shown in **Figure 1.3**.

The M shell has three energy levels; the lowest one consists of one orbital (also an s orbital), the second one has three orbitals which are identical and degenerate (also called p orbitals); and the third level consists of five degenerate orbitals called **d orbitals**. The N shell has four energy levels, s, p and d just like the M shell, but in addition, the highest one has seven degenerate orbitals called **f orbitals**.

Therefore, within a given shell, the energies increase in the order  $s < p < d < f^3$ , etc. It was stated earlier that the energy of the electron is governed by the principal quantum number n; this number also governs the size of the orbitals. As shown in **Figure 1.3**, an s orbital of principal quantum number one (denoted 1s) is smaller than an s orbital of principal quantum number two (denoted 2s). As we shall see in the next section, the orbitals can be specified by the “n” values in which they appear; thus we would talk of a 1s orbital to mean an s orbital of principal quantum number one. Similarly, a 2s or 3s orbital would mean an s orbital in principal quantum numbers two and three respectively. Analogously, 2p orbitals are those of principal quantum number two ( $2p_x$ ,  $2p_y$  or  $2p_z$ ). In the same way, we can also specify an electron in a particular orbital. Thus a 1s electron or a 3d electron means an electron in the s orbital of principal quantum number one or an electron in the d orbital of principal quantum number three, and so on.

## 1.10. Electronic Structures

Electrons are added to each atom, one at a time across a period. The lowest energy orbitals fill first and once those are full, the next lower energy ones fill and so on. Structures which show the n-values and their orbitals that are occupied, together with the number of electrons in them are called **electronic structures**. The question one can ask at this point is: “how many electrons can a single orbital accommodate?”. The answer to this question was arrived at by Wolfgang Pauli, who introduced a restriction on the number of electrons which can go into a single orbital. The restriction called the *Pauli*

<sup>2</sup>The maximum number of electrons allowed for each n-value is  $2n^2$  (see Section 1.10).

<sup>3</sup>The symbols s, p, d and f arise from electronic transitions in spectroscopy; s for Sharp, p for Principal, d for Diffuse and f for Fundamental (see for example, the more advanced references 1 and 4).



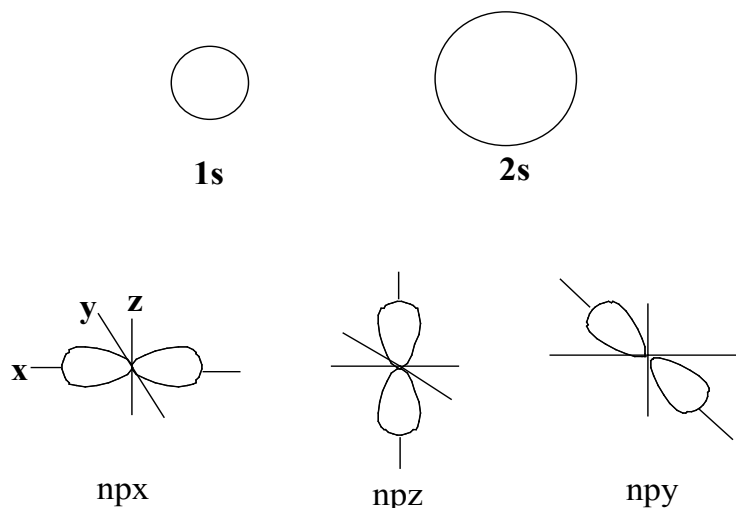
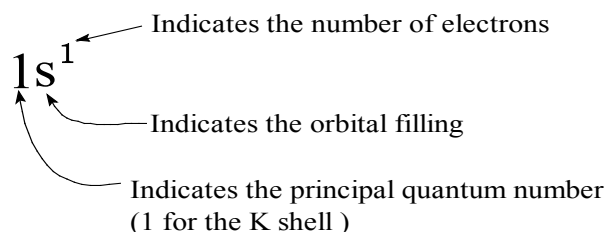


Figure 1.3. s and p orbitals of an atom.

*Exclusion Principle* states that “**any orbital will not hold more than two electrons**”. This means that any orbital can hold 0, 1 or 2 electrons but not more than 2. Therefore, the maximum number of electron allowed for each  $n$  value will be equal to  $2n^2$  (see **Table 1.2**).

In any atom the K shell is the lowest in energy followed by the L and then the M and so on. Within a shell, the s orbital is the lowest in energy followed by the p orbitals and then the d orbitals and so on. *The lowest energy shell and the lowest energy orbital in that shell fills first.* With this and the Pauli Exclusion Principle in mind, we can now write the electronic structures for some of the atoms. We begin with the simplest atom, hydrogen. This atom has got only one electron, and this will therefore, go into the s orbital of the K shell. The electronic structure we can write for hydrogen is therefore,  $1s^1$ .



The lowest energy level of an atom is called the **ground state** of that atom. For example, we have seen above that in hydrogen the electron normally resides in the 1s orbital. The electronic state  $1s^1$  is the lowest energy state for hydrogen and it is therefore the ground state. However, the electron in hydrogen can also move to higher levels, say to a 2s orbital. Such states of higher energy are called **excited states** of the atom.

Note that the s orbital of the K shell of hydrogen is half-full so that in the next atom, helium, an added electron will go into the same orbital and the electronic structure for helium is therefore  $1s^2$ . At this point, the s orbital of the K shell is full in accord with Pauli Exclusion Principle. In the next atom, lithium (Li), the L shell starts filling and the electron will go into the s orbital of this shell ( $n = 2$ ). The electronic structure of lithium is therefore,  $1s^2 2s^1$  and that of beryllium (Be) is  $1s^2 2s^2$ . The s orbital of the L shell is now filled up, and in the next atom boron (B), the p orbitals of the L shell start filling so

that the electronic structure of boron is  $1s^2 2s^2 2p^1$ . Since there are three p orbitals, six electrons are required to fill them completely and the atoms B, C, N, O, F and Ne all fill up the 2p orbitals with Ne having the electronic structure  $1s^2 2s^2 2p^6$ . The trend is the same in the third row of the periodic table. The s orbital fills first for this row (note: this is the s orbital of the M shell) in Na and Mg, followed by the p orbitals. The d orbitals are not filled. In the fourth row, the s orbital of the N shell fills first (in K and Ca). In the next atom scandium (Sc), the d orbitals of row three become lower in energy than the p orbitals of row four, and so they start filling. The electronic structure we can write for scandium is therefore,  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ . The d orbitals require ten electrons (for the five of them) and the ten atoms Sc to Zn fill these orbitals. After the 3d orbitals are filled, the p orbitals of the fourth row start filling. Again, note that the d and f orbitals of the fourth row are not filled at this point. The d orbitals for row four are filled in the fifth row after the s orbital of that row is filled. In the sixth row, the s orbital of that row fills first and then the next electron in La (atom 57) enters the 5d orbital after which, the f orbitals of row four (elements Ce-Lu) start filling. These require fourteen electrons (for the seven of them) and so we see a group of fourteen atoms normally written at the bottom of the table. After the 4f orbitals are filled, the 5d orbitals continue filling in the remaining nine atoms (Hf-Hg; note that one 5d electron went into La) followed by the 6p orbitals. The filling up of electrons into orbitals becomes complicated as we go down the table so that we will not continue any further. From the foregoing discussion, we note that the orbitals are filled in the order:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p \dots$$

The electronic structures are also written in the same order. There are three points to be noted in these structures. The first is that *the sum of the superscripts in the electronic structure gives the atomic number of the atom*. For example, in the electronic structure of oxygen,  $1s^2 2s^2 2p^4$ , the sum of the superscripts is 8 ( $2 + 2 + 4$ ), so the atomic number of oxygen is 8. This means that once we know the atomic number of an atom, we can easily write its electronic structure and vice versa. The second is that *the sum of the electrons in the highest principal quantum number, especially for the main group atoms, gives the group number of that atom*. For example, in the electronic structure of oxygen, the highest principal quantum number is 2, and there are 6 electrons there ( $2 + 4 = 6$ ). So oxygen is a group 6A element. Finally, *the highest principal quantum number in the electronic structure gives the period in which that atom appears*. In the example of oxygen, the highest principal quantum number in its electronic structure is 2, so oxygen is in period 2.

### 1.10.1. Hund's Rule

The Pauli Exclusion Principle stated earlier tells us exactly how many electrons can go into a particular orbital; *an orbital will not have more than two electrons*. With this principle, we can straight away write the electronic structure of for example, carbon as,  $1s^2 2s^2 2p^2$ . In Section 1.9, we saw that there are three degenerate p orbitals designated  $np_x$ ,  $np_y$ ,  $np_z$ . The question now arises: "how do the two 2p electrons of carbon enter the three p orbitals?". There are two possibilities; either both can go into the  $2p_x$  orbital (*i.e.*,  $1s^2 2s^2 2p_x^2$ , with the  $2p_y$  and  $2p_z$  orbitals empty) or one can go into the  $2p_x$  and the other one into the  $2p_y$  (*i.e.*,  $1s^2 2s^2 2p_x^1 2p_y^1$  with the  $2p_z$  orbital empty). **Friedrich Hund** came up with a rule that is used to decide which electronic structure will be the most stable. The rule, called Hund's rule states that "**electrons will occupy degenerate orbitals singly if those orbitals are empty**". This

means that as long as there is a set of orbitals with the same energy, the electrons will go in separate orbitals until each such orbital has one electron. After that, additional electrons will start pairing up in accord with the Pauli Principle. With this, we can write the most stable electronic structure of carbon as:  $1s^2 2s^2 2p_x^1 2p_y^1$  (**note**: the choice of which orbital is occupied *i.e.*, whether the  $2p_x$ ,  $2p_y$  or  $2p_z$ , is pure arbitrary). The electronic structure of nitrogen, oxygen, fluorine and neon are: **N**:  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ , **O**:  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ , **F**:  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$ , **Ne**:  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$ . Note that nitrogen has one electron in each of the p orbitals in accord with Hund's rule and that pairing starts in oxygen. The same trend applies to the d orbitals and also, the f orbitals.

### 1.10.2. Paramagnetism and Diamagnetism

The electronic structure of carbon given above has two unpaired electrons in the p orbitals while nitrogen has three such electrons. Oxygen and fluorine have two and one unpaired electrons respectively, while neon has no unpaired electrons. Elements such as carbon, with unpaired electrons, tend to be attracted by a magnet and are said to be **paramagnetic**. Elements such as neon with all the electrons paired tend to be repelled by a magnet and are said to be **diamagnetic**.

## 1.11. Periodic Table

The periodic table groups elements with similar chemical and physical properties together. Initially, the Russian chemist, Dmitri Mendeleev grouped elements in order of increasing atomic weights but this arrangement was later changed to one which grouped the elements in order of increasing atomic numbers. It was observed that if elements were arranged in order of increasing atomic numbers, elements with similar chemical properties recurred periodically and at regular intervals. This so called *periodic law* was used in the construction of the periodic table whose widely used version is shown on the inside of the back cover. In that table, there are eighteen (18) vertical columns which are called **groups** and about seven (7) rows, called **periods**. *All the members of a group have the same outer shell electron configuration, apart from the "n" value which is different.* For example, the lithium group elements all have the  $ns^1$  outer shell configuration. Members of a group also have similar chemical properties (see Section 1.12). *Group 1a elements are called **alkali elements** (hydrogen is not included in this group). Group 2a elements are called **alkaline earth elements**, and these have the  $ns^2$  outer shell structure. Group 7a elements are called **halogens** with an outer shell configuration of  $ns^2 np^5$ . Group 8a elements are called **rare gases** or **noble gases**.* Another way of naming the different groups of elements depends on the outer shell orbital which the different groups fill. *Thus, groups 1a and 2a elements are called **s-block elements**. Groups 3a-8a elements are called **p-block elements**.* Groups 1a to 7a which have incompletely filled s and p orbitals of the highest n-value are also referred to as **representative (or main group) elements** while the noble gases have a completely filled p orbital of highest n-value. *Groups 1b-8b in which the d orbitals are filled are called **d-block elements**. Groups 1b, 3b-8b have incompletely filled d orbitals and these are referred to as **transition elements**.* Group 2b, with a completely filled d orbital is not normally included in the group of transition elements. *The elements Ce-Lu, in which the 4f orbitals are filled, are called **rare earth elements** or **lanthanides**. The elements Th-Lr, in which the 5f orbitals are filled, are called **actinides** (another group of rare earth elements). The lanthanides and actinides together are called the **inner-transition elements** or **f-block elements**.*

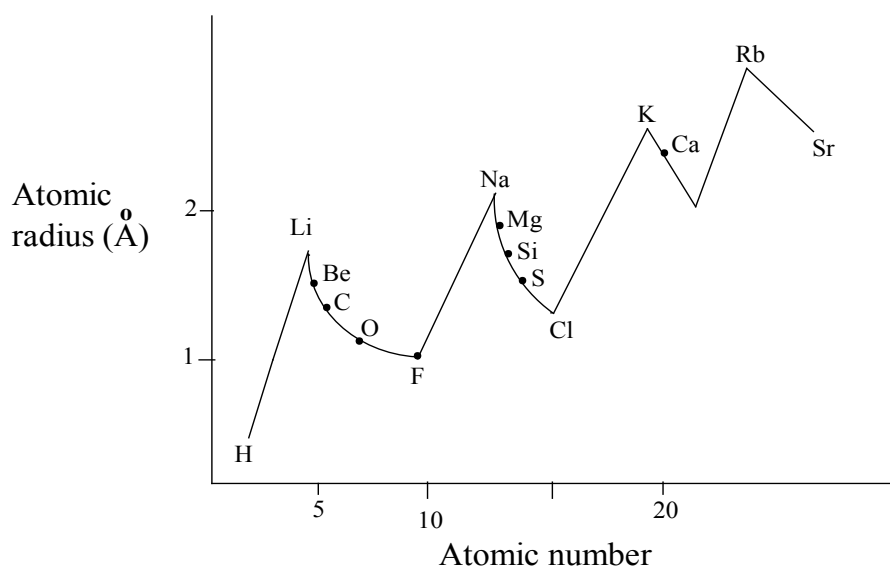
### 1.11.1. Periodicity

As it has been mentioned in the previous section, the periodic table groups elements with similar outer shell electronic configurations together. This periodicity leads to elements with similar chemical properties falling in the same group. A few examples will illustrate this periodicity.

Atomic sizes of atoms can be used to show the variation of chemical properties. The atomic radius is a good indication of the size of an atom. In both the diatomic molecules such as chlorine and the metals, the atomic radius is obtained by taking half the distance between the two nuclei of the atoms that are “touching”. Now if atomic radii of various atoms are plotted against their respective atomic numbers, then **Figure 1.4** results.

Although the atomic radius is a physical property, it has a profound effect on chemical properties. In **Figure 1.4**, note that the alkali elements have large atomic radii. This is because these elements always “see” the beginning of a new shell, *i.e.*, an additional electron starts filling a new shell as we move from one period to the next.

The periodicity here is shown by the fact that the group 1 elements have the largest radii (hence sizes), the elements in the middle of the table have smaller sizes and so a repeating pattern is obtained with successive periods. In **Figure 1.4**, the elements Lithium (Li) to Fluorine (F), are in the same period (have the same number of shells) as are sodium (Na) to chlorine (Cl). Taking period two (with atoms Li to F) as an example, we notice that the atomic radius decreases as we move from Li to F, *i.e.*, from left to right in that row. *Why is this so?* In answering this question, let’s first consider the force of attraction between the outer shell electron and the nucleus. We will take lithium as our example. This atom has two electrons in the inner (K) shell and one electron in the outer (L) shell. Its nuclear charge is +3. The electron(s) in the K shell prevent the outer electron from experiencing the full attractive force of the nucleus. We say that the outer shell electron in lithium is shielded from the nucleus by the two inner shell electrons. The consequence of this is that the net force of attraction experienced by the outer shell electron from the nucleus, is as if the two inner electrons were placed at the nucleus



**Figure 1.4.** Variation of atomic radii of the elements with atomic number.

where there is also a +3 positive charge. The net force of attraction of the outer shell electron to the nucleus is therefore +1 (*i.e.*,  $+3 - 2$ ). We say therefore that the **effective nuclear charge of lithium is +1**. If we make similar calculations for all the atoms in a period, we find that the effective nuclear charge increases from +1 to +8 across a period. Since the number of shells is the same in a period, the effect of increased effective nuclear charge as we move from left to right is that the radii become smaller and smaller.

Another example to illustrate the periodicity is to look at the first ionization energy (see Section 1.13). A plot of these energies against atomic number is given in **Figure 1.5**.

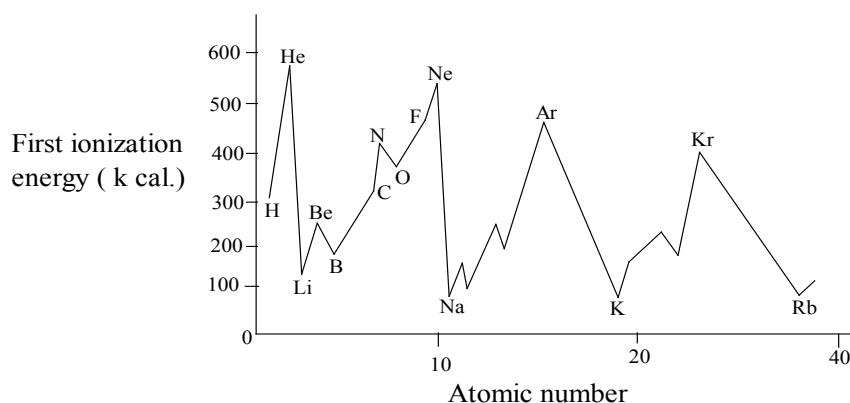
The above graph resembles that of **Figure 1.4** in shape. A few things should be noted from graph. As we move along a period of the periodic table (e.g., from Li to Ne), there is a rise in the first ionization energy. This rise is due to increasing effective nuclear charge in the atoms; +1 in Li to +8 in Ne, so that less energy is required to remove an electron from an atom with a smaller effective nuclear charge (e.g., of +1) than from an atom with a larger effective nuclear charge (e.g., of +8). Note that the atoms in the same period have the same number of shells. From one period to the next one below (e.g., from He to Li), there is a general drop in the ionization energy. This is because as a new period starts, a new shell begins to fill (see **Figure 1.1**) and this results in an instant increase in the radius of the first atom. Since alkali elements always “see” the beginning of a new shell, these elements have the lowest first ionization energies. Note that these elements are at the bottom of the curve in **Figure 1.5**.

Within a group, there is also a general drop of the first ionization energy. This is due to increasing atomic radius from top to bottom (e.g., He to Kr). The periodic recurrence of atoms with similar electronic configurations has been illustrated with the two examples above. We shall see later that this periodic recurrence of similar configurations leads to periodic recurrence of chemical and physical properties as well.

## 1.12. Some Representative Elements of Importance

### 1.12.1. Group 1a Elements: Li, Na, K, Rb, Cs, Fr

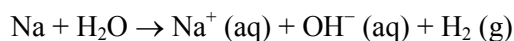
These elements have one outer shell electron, with the  $ns^1$  structure. Group 1a elements are called **alkali elements**. These elements are so reactive that they are rarely found in elemental. They are soft,



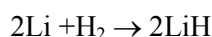
**Figure 1.5. Variation of the first ionization energy with atomic number.**

malleable and have a silver luster and being metals, they are good conductors of heat and electricity. They have low melting points which decrease down the group from 180°C in lithium to 28.7°C in cesium. Francium (Fr) occurs only in small amounts and most of its isotopes are radioactive (see footnote on page 16).

Alkali elements all have similar chemical properties. They are strong reducing agents as shown by their violent reaction with water, exemplified by sodium:



The hydroxides produced are high melting solids which are soluble in water. The great reactivity of these elements is reflected in their atomic structure and their large atomic radius. The atoms lose the outer electron to acquire the electronic configuration of the nearest inert gas. *Since their radii increase down the group, the outer electron in the heavier elements, such as cesium, is loosely held by the nuclear charge compared to the outer electron in the lighter elements such as lithium. Consequently, reactivity of the alkali elements increases as we go down the group.* The reaction of potassium with water is more vigorous than that of sodium with water, for this reason. Alkali elements also react with hydrogen to give hydrides, for example,



Alkali elements also react with oxygen to form oxides. Simple monoxides of the form  $\text{M}_2\text{O}$  are only formed with lithium. Sodium gives  $\text{Na}_2\text{O}_2$ , a peroxide on direct reaction with oxygen. The other metals give superoxides of the form  $\text{MO}_2$ .

### 1.12.2. Group 2a Elements: Be, Mg, Ca, Sr, Ba, Ra

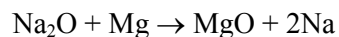
These elements have two outer shell electrons, with the  $ns^2$  structure, with the exception of helium which belongs to group 8a. Group 2a elements are called **alkaline earth elements**. These elements are also rarely found in the elemental state. They are hard, dense, with high melting and boiling points and being metals, are good conductors of heat and electricity. Radium is radioactive (see footnote on page 16). Compared with group 1a elements, group 2a elements have larger nuclear charges hence, their atomic sizes are smaller than those of group 1a elements.

Alkaline earths react with water only at high temperatures (compare, group 1a) to form hydroxides:



These elements are, like group 1a elements, very reactive. Their reactivities also increase down the group for the same reason as the alkali elements. Unfortunately, *elements like magnesium, readily react with oxygen in the air and form a thin layer of metal oxide on the surface of the metal. This greatly reduces their reactivity.* Magnesium is therefore, much less reactive with say, cold water than calcium is, unless the water is heated up.

At high temperatures, the elements in their metallic form can reduce other compounds as in the following example:



The resulting oxides are strong bases which react with acids and to some extent, water. In the latter solvent, the oxides form hydroxides (e.g., magnesium hydroxide, also known as *milk of magnesia*  $\text{Mg}(\text{OH})_2$ ). The solubilities of the hydroxides in water increase in the order:  $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg} > \text{Be}$ .

### 1.12.3. Group 4a Elements: C, Si, Ge, Sn, Pb

Group 4a elements have four outer shell electrons with the  $ns_2np^2$  structure. Carbon is a non-metal, silicon and germanium are metalloids (such elements with properties between non-metals and metals are also termed *semi-metals*) and tin and lead are metals. Large amounts of carbon are found in living systems (plants and animals). There are two forms (different forms of the same element are also called **allotropes**) of carbon: graphite, which is widely used for making pencil leads, is an extended multi-layered structure. In this structure, carbon atoms form six-membered rings which in turn, are joined to each other to form a planar structure. Several of these layers are then stuck together by Van der Waals forces (see Chapter 2). Graphite conducts electricity in plane parallel to the plane but not perpendicular to it. The other allotrope of carbon is diamond in which each carbon is covalently bonded to four other carbons to form a three dimensional network which is hard. Carbon is somehow unique in group 4a in that it is able to form compounds in which several carbon atoms are bonded to each other to form chains or rings. This property of carbon is called catenation and is responsible for the variety of organic compounds. Organic compounds are discussed in Chapters 11 - 14.

Silicon occurs in silica ( $\text{SiO}_2$ ) and silicate minerals. Silicon is widely used in the manufacture of computer chips and transistors. Lead occurs mostly in the metallic form. It is used for making electrodes in car batteries and also as an oil additive in the form of tetraethyllead ( $(\text{CH}_3\text{CH}_2)_4\text{Pb}$ ). Group 4a elements can form are able to form four covalent bonds in their compounds. Examples include the hydrides (e.g.,  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{PbH}_4$ ), chlorides (e.g.,  $\text{CCl}_4$ ,  $\text{SnCl}_4$ ) and oxides (e.g.,  $\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{GeO}_2$ ). However, from silicon downwards, the elements can also form six covalent bonds. For example,  $\text{SiF}_6^{2-}$ ,  $\text{Pb}(\text{OH})_6^{2-}$ .

### 1.12.4. Group 5a Elements: N, P, As, Sb, Bi

Elements in this group have five outer shell electrons. The outer shell configuration is  $ns^2np^3$ . Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids while bismuth is a metal. Nitrogen occurs in abundance in the atmosphere as a diatomic molecule,  $\text{N}_2$ . Phosphorus exists in rock phosphates ( $\text{Ca}_3(\text{PO}_4)_2$ ). Arsenic and antimony occur mostly as sulphite minerals while bismuth exists in pure form as a metal.

There are three allotropes of phosphorus: the reactive white phosphorus has a tetrahedral structure ( $\text{P}_4$ ), red phosphorus exists as a polymer and the third form, black phosphorus is a layer structure much like graphite. Arsenic and antimony also have tetrahedral structure  $\text{As}_4$  and  $\text{Sb}_4$  respectively.

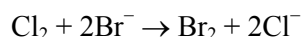
Group 5a elements form various compounds including hydrides (e.g.,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{SbH}_3$ ,  $\text{BiH}_3$ ), oxides (e.g.,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{As}_4\text{O}_6$ ,  $\text{Bi}_2\text{O}_3$ ) and halides (e.g.,  $\text{NF}_3$ ,  $\text{PCl}_3$ ). The hydrides are basic compounds and this basicity decreases as we go down the group.



### 1.12.5. Group 7a Elements: F, Cl, Br, I and At

These elements have seven outer shell electrons, *i.e.*, the  $ns^2np^5$  structure. Group 7a elements are called the halogens and unlike groups 1a and 2a elements which are metals, these are non-metals. Astatine<sup>4</sup> is a radioactive element. Fluorine is the most electronegative (see Section 1.13.3) of the elements and usually has an oxidation number of  $-1$  (see Chapter 8). The other elements are also electronegative but unlike fluorine, they exhibit both negative as well as positive oxidation numbers. Halogens are very reactive and they act as oxidants in most of their reactions. Their strength as oxidants decreases as the atomic number increases. *Unlike group 1a and 2a elements, halogens gain electrons when they react. This means that the smaller the volume of the element, the easier it will grab the electrons. Consequently, reactivity in the halogens increases as we go up the group, with fluorine being the most reactive.* For example, the reaction of potassium with fluorine is more vigorous than that of potassium with chlorine. Halogens are colored, poisonous molecules with unpleasant smell; fluorine is a yellow gas, chlorine is green/yellow gas, bromine is red and iodine is a purple solid.

Group 7a elements react with metals to form metal halides. Large metals, with low oxidation numbers (e.g.,  $+1$  or  $+2$ ), form ionic halides whereas small metals with high oxidation numbers result in semi metallic halides. Halogens also react with each other as shown by the oxidation of bromide ( $\text{Br}^-$ ) by chlorine—a reaction that is used to recover bromine from sea water.



### 1.12.6. Group 8a Elements: He, Ne, Ar, Kr, Xe, Rn

Group 8a elements have eight outer shell electrons with the  $ns^2np^6$  structure except helium which has the  $s^2$  structure. Group 8a elements are called **rare, inert or noble gases**. Since they have a complete octet, their structures are very stable, hence the name inert. The word inert is however, a misnomer since compounds of some of these elements have been detected such as xenon difluoride ( $\text{XeF}_2$ ) and xenon oxyfluoride ( $\text{XeOF}_2$ ), among others. *It is perhaps important to note that it is only this group of elements that has atoms which exist in nature as single-atomed molecules.* This property is a reflection of the stable electronic configurations of these elements.

## 1.13. Some Atomic Properties of the Elements of the Periodic Table

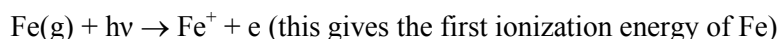
In the preceding section, we have looked at only four of the groups of concern at this stage. In order to increase depth on the other groups, the student is advised to consult the reference books given in this chapter. For the mean time, we turn our discussion to some properties of elements of the periodic table.

<sup>4</sup>Radioactivity is a spontaneous emission of radiation and particles from an unstable nucleus of an atom. For example, uranium-238 is an unstable element which emits  $\alpha$ -radiation ( $\text{He}^{2+}$  ions with a mass of 4) and the remaining particle has a mass of 234 and atomic number 90, according to the equation  ${}_{92}^{238}\text{U} \rightarrow {}_{90}^{234}\text{Th} + {}_2^4\text{He}$ . The atom with a mass of 234 and atomic number 90 is thorium.



### 1.13.1. Ionization Energy

Ionization energy is defined as *the minimum energy required to remove an electron from a gaseous atom to form a gaseous ion*. There can be the first ionization energy corresponding to the removal of the first electron from the atom. Similarly, the second, third and so on, ionization energies can be obtained corresponding to the removal of the second, third, etc., electrons respectively. For example, when iron is exposed to a high energy radiation  $h\nu$  (where  $h$ , is Planck's constant equal to  $6.63 \times 10^{-34}$  Joules second per molecule and  $\nu$ , is the frequency of radiation), it is possible for an electron to be removed from the gaseous iron atom to form  $\text{Fe}^+(\text{g})$  (a gaseous iron ion), viz:



and subsequently, we can have:



and so on.

We have already discussed the periodicity in the values of the first ionization energies in Sub-Section 1.11.1. We saw that within a period, the first ionization energy increases across a row due to increasing effective nuclear charge. This trend starts again in the next period and so on.

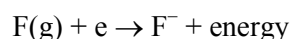
There is one striking observation in **Figure 1.5** however, which needs some clarification. While we say that ionization energies increase from left to right within a period, we note that there are some breaks or drops somewhere in the rows. In other words, the trend is not smooth. For example, in the second period, (Li to Ne), boron (B) has lower first ionization energy than beryllium (Be). Similarly, we notice that oxygen (O) has lower first ionization energy than the preceding atom, nitrogen (N). Taking the first pair of atoms (B and Be) first, the electronic structures of these elements are Be:  $1s^2 2s^2$  and B:  $1s^2 2s^2 2p^1$ . The lower first ionization energy of boron is a result of the fact that the p orbital in this element is higher in energy than the s orbital of the same principal quantum number. This means then that less energy is required to remove the "2p" electron in boron than the "2s" electron in beryllium.

Electrons are negatively charged and so they repel each other. When the electrons occupy orbitals, **the Pauli Exclusion Principle and Hund's rule** (Section 1.10) will apply. With these two rules in mind, (*i.e.*, Hund's and Pauli's principle), the electronic structure of nitrogen (see also Sub-Section 1.10.1) is  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$  (note that there are three of the p orbitals all degenerate and situated at right angles to each other along the x-, y- and z-axes). When another electron goes into oxygen, it will go into one of the p orbitals already containing an electron (recall that a maximum of six electrons are required for the p orbitals each one taking two electrons in accord with Pauli Exclusion Principle). The two electrons will thus repel each other; this repulsion is in fact, far more than the increased nuclear charge from nitrogen to oxygen. As a result, it is easier to remove the first electron in oxygen than that in nitrogen. This explains the lower first ionization energy of oxygen than that of nitrogen.

### 1.13.2. Electron Affinity

The electron affinity is *the energy released when an electron is added to a gaseous atom*. For example,

when an electron is added to a gaseous fluorine atom, energy is given out, viz:



The resulting ion in the above equation (an anion) is called a fluoride ion. There can be the first, second, third, etc., electron affinities corresponding to the addition of the first and so on, electrons. Energy will be given off when an electron is added to an atom as in the example above, so that the electron affinity for say, fluorine will be a negative quantity. *The more negative the electron affinity, the more stable the resulting ion formed. In other words, the more negative the values, the greater the tendency of the gaseous atom to grab an electron.* Positive values then mean that the gaseous atom involved, does not readily grab electrons. In this case the ion formed would be unstable.

When a second electron is added to the fluoride ion ( $\text{F}^-$ ), there will be repulsion between the first added electron and the second one, so that the second electron affinity will be positive. Some selected electron affinities are given in **Table 1.3**.

A Few things need to be noted here. The electron affinity of an atom will equal to the first ionization energy of the corresponding anion. In the case of fluorine, for example, the electron affinity of  $\text{F(g)}$  will be equal to the first ionization energy of  $\text{F}^-(\text{g})$ . This is an example of the law of conservation of energy. In **Table 1.3**, it can be seen that halogens have the highest electron affinities compared to the other elements, implying that the ions (halides) formed from these elements are quite stable. Although the trends in the values of the electron affinities are not distinct, in general non-metals have higher values than metals. Also, the values tend to increase across a period as atomic number increases but they tend to decrease down a group.

### 1.13.3. Electronegativity

Electronegativity *is the power with which an atom will attract electrons to itself in a molecule.* Electronegativity values are obtained by considering the energy released when a bond breaks. The values have been adjusted so that fluorine, the most electronegative element, has a value of 4.0. As such, electronegativities are relative numbers rather than measurable quantities like electron affinities. An atom that tends to acquire rather than lose electrons is said to be electronegative. It will be seen in Chapter 2 that electronegativity plays an important role in determining the polarity of bonds, *i.e.*, whether the bond between two atoms is covalent, ionic or metallic. Electronegativity values for some elements are given in **Table 1.4**.

**Table 1.3. Some selected electron affinities (kJ/mole).**

<b>H</b>					
-72					
<b>Li</b>	<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>
-52	-29	-120	-3	-141	-333
<b>Na</b>		<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>
-71		-180	-70	-201	-343
				<b>I</b>	
				-295	

**Table 1.4. Electronegativity values of selected elements.**

<b>H</b>						
2.1						
<b>Li</b>	<b>Be</b>	<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>
1.0	1.5	2.0	2.5	3.0	3.5	4.0
<b>Na</b>	<b>Mg</b>	<b>Al</b>	<b>Si</b>	<b>p</b>	<b>S</b>	<b>Cl</b>
0.9	1.2	1.5	1.8	2.1	2.5	3.0
<b>K</b>	<b>Ca</b>					
0.8	1.0					

As **Table 1.4** shows, electronegativity values tend to increase across a period and decrease down the group. The halogens have the highest values and so they are the most electronegative of all the elements in the periodic table. In contrast, the metals have the lowest values. Also, note that electronegativity values show more periodicity.

### Suggested Reading Texts

1. Chang, R. (2005) Chemistry. 8th Edition, International Edition, McGraw-Hill, Inc., Boston.
2. Ebbing, D.D. and Gammon, S.D. (1999) General Chemistry. 6th Edition, International Student Edition, Houghton Mifflin Co., New York.
3. McMurry, J. and Castellion, M.E. (2003) Fundamentals of General Organic and Biological Chemistry. Pearson Education Inc., New Jersey.
4. Bodner, G.M. and Pardue, H.L. (1995) Chemistry: An Experimental Science. 2nd Edition, John Willey and Sons Inc., New York.
5. Atkins, P.W., Clugstonm, M.J., Frazerm, M.J. and Jonesm, R.A.Y. (1988) Chemistry: Principles and Applications. Longman, London.

### More Advance Texts

1. Mahan, B.H. (1974) University Chemistry. 3rd Edition, Addison-Wesley Pub. Co., Boston.
2. Banwell, C.N. (1983) Fundamentals of Molecular Spectroscopy. 3rd Edition, McGraw-Hill Book Co., Boston.