Module P8.4 The periodic table and chemical bonding

Exit module

1 Opening items

1.1 Module introduction

One of the greatest triumphs of Western civilization has been the detailed understanding that scientists have obtained of everyday, large-scale phenomena in terms of the small-scale behaviour of atoms. Much of this understanding has been based on the theory of quantum mechanics developed in the mid-1920s, mainly by European physicists. However, the applications to atoms and molecules were based on ideas that had been formulated in the previous century by far-sighted chemists who understood more quickly than most physicists the reality of atoms and who appreciated that atomic ideas could be used to enable a profound understanding of the properties of the elements.

Most of this module is devoted to achieving an understanding of individual chemical elements and how they bond together to form compounds. This will lead us to consider some of the most important ideas in fundamental atomic science.

We begin by examining the *first ionization energies* of the elements and by demonstrating the information that these energies shed on the chemical properties of the elements. For example, the *noble gases*, which are very unreactive, have high values of first ionization energy, while the very reactive *alkali metals* have low values of first ionization energy. The relationship between the chemical reactivity of an atom and the arrangement of that atom's electrons in various *shells* and *subshells* (its *electronic structure*) is the main theme of Section 2.

A periodicity in the chemical properties of the elements was noticed by the Russian chemist Dmitri Mendeleev, who arranged the elements into a *periodic table* to reflect this. The modern form of Mendeleev's periodic table of the elements (Section 3) can be understood in terms of the distribution of electrons within the atom. The periodic table is arranged so that all elements with a similar outer shell of electrons (and hence similar chemical properties) appear in vertical columns, called *groups*, in which the *principal quantum number* of the outer shell of electrons increases down the column. The horizontal rows in the periodic table, the *periods*, typically contain several series of elements each of which is characterized by a common value of the principal quantum number. At both sides of the table are the columns of *typical* or *main group* elements. In between the main group elements are three series of *transition elements* (Subsection 3.2), a series of *lanthanides* (Subsection 3.3) and a series of *actinides* (Subsection 3.4).

Section 4 discusses the topic of *chemical bonding*. Simple theories of chemical bonding assume that the electronic configurations of the *noble gases* are especially stable, and that many elements tend to attain noble gas electronic configurations in chemical reactions. According to simple theories of bonding there are two ways in which atoms can attain this structure — *electron transfer* and *electron sharing*. This leads to the formation of *ionic* and *covalent* bonds, respectively, and these are discussed in Subsections 4.3, 4.4 and 4.5. Subsection 4.7 introduces a third kind of bonding, *metallic bonding*, in which each atom is presumed to share its bonding electron or electrons with every other atom in a crystal structure of positive ions.

Study comment Having read the introduction you may feel that you are already familiar with the material covered by this module and that you do not need to study it. If so, try the *Fast track questions* given in Subsection 1.2. If not, proceed directly to *Ready to study?* in Subsection 1.3.

1.2 Fast track questions

Study comment Can you answer the following *Fast track questions*?. If you answer the questions successfully you need only glance through the module before looking at the *Module summary* (Subsection 5.1) and the *Achievements* listed in Subsection 5.2. If you are sure that you can meet each of these achievements, try the *Exit test* in Subsection 5.3. If you have difficulty with only one or two of the questions you should follow the guidance given in the answers and read the relevant parts of the module. However, *if you have difficulty with more than two of the Exit questions you are strongly advised to study the whole module*.

Question F1

(a) What, in general, are the outer shell structures of noble gas atoms?

(b) Using your answer to part (a), write down the outer shell structure of the ground state of krypton, which is in the fourth period of the periodic table.

(c) Given that krypton has atomic number 36, write down the outer shell structure of the ground state of a bromine atom, which has atomic number 35. In which period and group of the periodic table would you expect bromine to lie?

Question F2

What is the essential distinguishing feature of the electronic structures of each of the following series of elements: (a) transition elements, (b) lanthanides, (c) actinides?

(Assume that the elements are in their ground states.)

Question F3

What is the charge of the oxygen ion in magnesium oxide?

Question F4

Sulphur (S) forms an oxide in which sulphur has a valency of six. What is the empirical formula of that oxide?

Question F5

Examine statements (a) to (c) below, which describe properties of carbon tetrachloride (CCl_4), fluorine oxide (F_2O), and rubidium oxide (Rb_2O). These substances are either ionic or covalent. Where you think a substance is ionic, assign charges to each ion. Where you think a substance is covalent, write a Lewis structure for it.

(a) CCl_4 is a liquid at room temperature and does not conduct electricity; it boils at 77 °C.

(b) F_2O is a gas at room temperature.

(c) Rb_2O is a solid with a high melting temperature. The structure of this oxide is such that each rubidium 'unit' is surrounded by four equidistant oxygen 'units', while each oxygen 'unit' is surrounded by eight equidistant rubidium 'units'.

Study comment

Having seen the *Fast track questions* you may feel that it would be wiser to follow the normal route through the module and to proceed directly to *Ready to study?* in Subsection 1.3.

Alternatively, you may still be sufficiently comfortable with the material covered by the module to proceed directly to the *Closing items*.

1.3 Ready to study?

Study comment In order to study this module you will need to understand the following terms: *atom*, *atomic number*, *chemical compound*, *electron*, *electric charge*, *electric current*, *element*, *ion*, *kelvin* (the SI unit of *temperature*), *molecule*, *nucleus*, *proton* and *voltage*. You should also be familiar with the use of *chemical symbols* to represent the chemical elements, and their combinations in *chemical formulae*, such as H_2O. (The symbols and atomic numbers of the elements are shown in Table 2). If you are uncertain about any of these terms, review them now by reference to the *Glossary*, which will also indicate where in *FLAP* they are developed. The following *Ready to study questions* will allow you to establish whether you need to review some of the topics before embarking on this module.

Question R1

The atomic number of argon is $Z = 18$. What information can you deduce about a neutral argon atom from this fact?

Question R2

In terms of their electrical charges, what is the key difference between a lithium ion and a helium atom?

(The atomic numbers of lithium and helium are 3 and 2, respectively.)

2 Chemical evidence for electron shells in atoms

In this section, we will consider patterns that are evident in the behaviour of chemical elements and how these patterns are related to the underlying atomic structures of the elements. We are thus following a standard scientific path by trying to understand behaviour on the large scale in terms of structure on a much smaller scale.

2.1 Periodicity in chemical reactivity

Let us begin with atoms, which generally consist of a tiny central nucleus that is in some sense ‘orbited’ by electrons (only hydrogen atoms contain a lone electron). When all the electrons in an atom have their lowest possible energy, the atom as a whole has its lowest energy and is said to be in its **ground state**. This is a very convenient ‘reference state’ and it is safe to assume that whenever the structure or behaviour of an atom is described in this module, that atom will be in its ground state unless you are told otherwise.

The minimum energy required to completely remove an electron from an atom in its ground state is called the **ionization energy**, a quantity that can readily be measured in the laboratory. The energy required to completely remove the *least tightly bound* electron from the influence of the atom is called the element's **first ionization energy**. This quantity is plotted against atomic number in Figure 1 for each element up to radon, Rn (Z = 86). Look carefully at this plot — it contains several important clues about atomic structure as we will now describe.

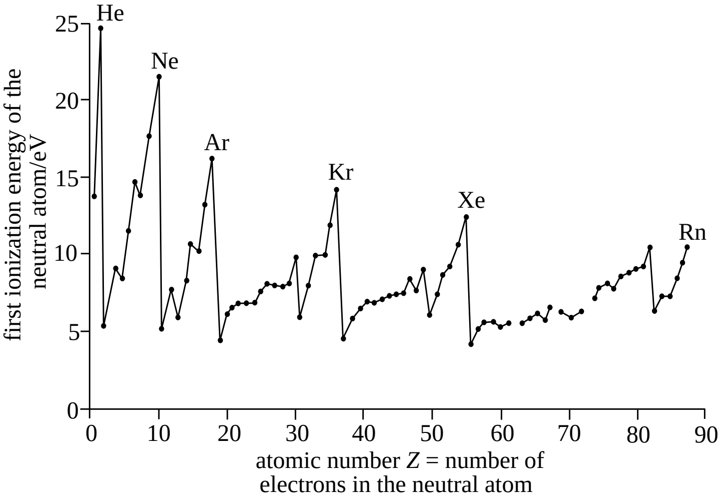


Figure 1 First ionization energies of elements up to radon.

You can see from Figure 1 that the first ionization energies form a regular pattern: there are a number of peaks, each followed by a deep trough. At the peaks are the elements helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). These elements, all gases at room temperature, are all inert, that is, they are very reluctant to combine with other elements. For this reason, they are collectively referred to as the **noble gases** (sometimes known as the **inert gases**).

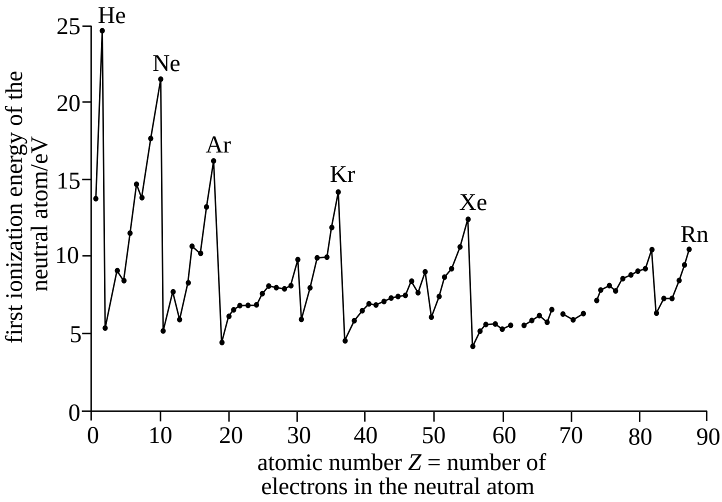


Figure 1 First ionization energies of elements up to radon.

The elements in the troughs that immediately follow the noble gases are lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr). These have similar properties to each other, but are very different from the noble gases: they are all highly reactive metals and are called the **alkali metals** because they react violently (or even explosively!) with water to form substances called *alkalies*. (These alkalies are compounds of an alkali metal with oxygen and hydrogen, examples are LiOH, NaOH, KOH, etc.)

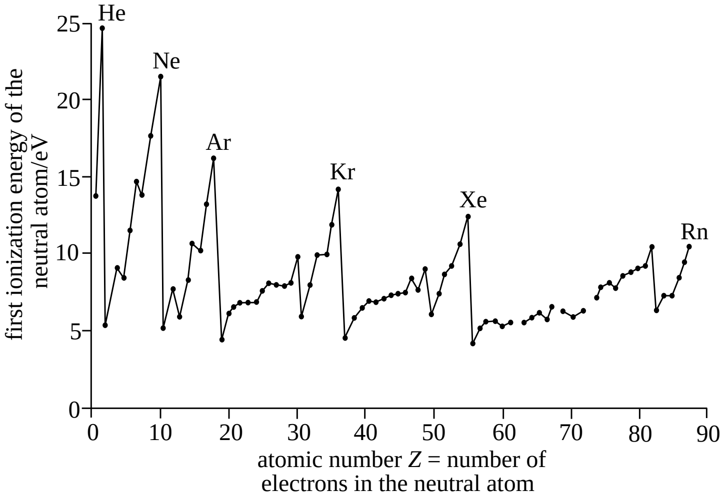


Figure 1 First ionization energies of elements up to radon.

Now consider the elements that occur just *before* the peaks in Figure 1 — fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). These elements, called the **halogens**, ☞ also have very similar chemical properties: each of them has a rather unpleasant odour and combines readily with many other elements. For example, each halogen combines with hydrogen to form an acid. (Narrowly defined, acids are compounds that include hydrogen and which form hydrogen ions when dissolved in water.) ☞

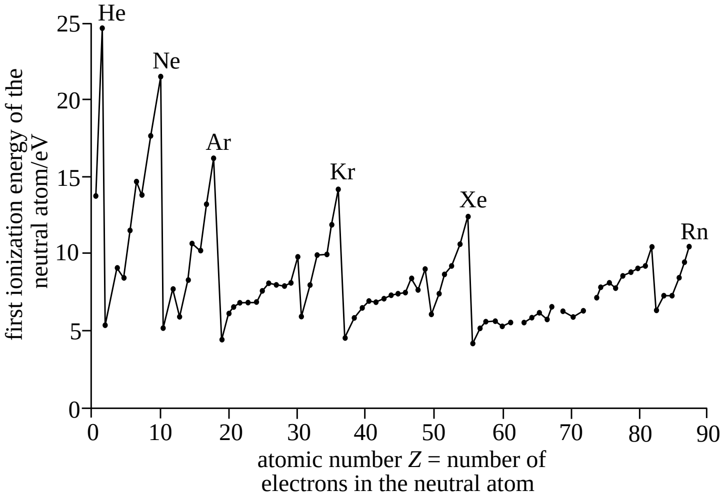


Figure 1 First ionization energies of elements up to radon.

The pattern in first ionization energies plainly indicates a corresponding pattern in the chemical behaviour of the elements. Long before ionization energies were measured or even thought of — indeed, well before it was realized that the atoms generally consist of a nucleus and electrons — several scientists had noticed a pattern in the chemical properties of the elements. The most important and famous insight was provided by the great Russian chemist Dmitri Mendeleev (1834–1907), who first arranged the elements in order of increasing atomic mass to form a **periodic table**.

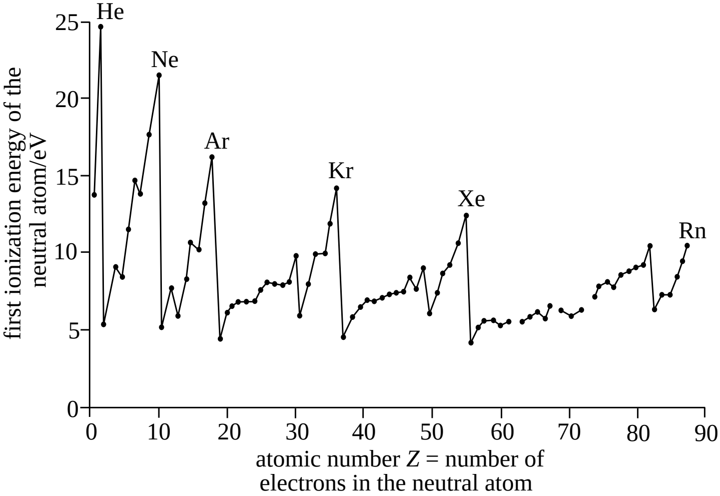


Figure 1 First ionization energies of elements up to radon.

To see why the idea of such a table seemed plausible to him, consider first the elements with *atomic numbers* from 2 to 9 inclusive:

He Li Be B C N O F

Although Mendeleev did not know their atomic numbers or anything about ionization energies, he did know the chemical formulae of some of the compounds formed by these elements, notably those with oxygen (*oxides*) and hydrogen (*hydrides*). Consider first the oxides of these elements. If we write the formulae of the oxides as M_2O_n, where M is any element from the list above, then from helium to boron (B), n takes the values 0, 1, 2 and 3 (the value zero for helium is appropriate because it does not form an oxide). The next two elements, carbon (C) and nitrogen (N), form more than one oxide. However, if you pick out the highest oxide, i.e. the oxide that contains the highest proportion of oxygen, you obtain $n = 4$ for carbon and $n = 5$ for nitrogen. Thus, the trend that runs from helium to boron continues to nitrogen. Beyond nitrogen, however, it peters out: F_2O_7, for example, does not exist.

In the case of hydrides, we can write the formula MH_n. Again if we restrict ourselves to the highest hydrides, i.e. those that contain the greatest proportion of hydrogen, then right across the row, n follows the sequence 0, 1, 2, 3, 4, 3, 2, 1: the values of n rise in steps of one until they reach a maximum value of four, before falling off in steps of one unit. Finally, the formulae of the highest *chlorides* (compounds formed with chlorine) follow the same trend as those of the highest hydrides.

Suppose we now look for patterns in the next eight elements, which we will write underneath the ones we have just discussed:

He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	Cl

This time the oxide trend is perfect. When the formulae of the highest oxides are written as M_2O_n, n takes the values 0, 1, 2, 3, 4, 5, 6, 7, from neon to chlorine. The trend in the formulae of the highest hydrides is exactly the same as in the first row, and so is that in the formulae of chlorides, except that at phosphorus (P), the higher chloride PCl_5, is formed. In this type of arrangement, elements with similar chemical properties (helium and neon, lithium and sodium) fall in vertical columns called **groups**. The horizontal rows are called **periods**.

In Mendeleev’s periodic table the group numbers are meant to represent the number of oxygen atoms that two atoms of the element are combined with in the highest oxide. For example, elements in group 2 form highest oxides of general formula MO, with two oxygen atoms combined with every two atoms of M.

2.2 Reactivity determined by outer electron configuration

Study comment This subsection includes a highly condensed introduction to some of the essential features of the *electronic configuration* of atoms. A more thorough and less condensed treatment of this topic is given elsewhere in *FLAP*. See the *Glossary* for details.

We have now established the structure of the periodic table, which neatly summarizes regularities in the chemical behaviour of chemical elements. In our discussion, we have often referred to the reactivity of the elements — how readily they combine with others to form new substances — but we have not yet explained *why* certain elements react in similar ways. This is the task of this subsection: once again, we will be explaining large-scale phenomena (chemical reactivity) in terms of small-scale structure.

An atom generally consists of a nucleus surrounded by electrons, so initial contact between atoms occurs in the vicinity of the outer electrons. Not surprisingly, therefore, it is the outer *electronic configuration* that strongly influences the way one kind of atom bonds to another.

Electrons in atoms are arranged in **shells**, characterized by the **principal quantum number** n ($n = 1$ corresponds to the first shell, $n = 2$ to the second, and so on); each shell contains one or more **subshells**, characterized by the **orbital angular momentum quantum number** l. In the nth shell there are n possible subshells, each of which corresponds to an integer (i.e. whole number) value of l in the range 0 to $n - 1$. The subshells corresponding to l values of 0, 1, 2 and 3 are often denoted by the letters s, p, d and f, respectively: so an electron with $n = 1$ and $l = 0$ is called a 1s electron, one with $n = 2$ and $l = 1$ a 2p electron, and so on. The quantum numbers of an electron are said to determine its **quantum state** and this, in turn, determines its **energy level**. To a first approximation, in any given atom, all the electrons in a given subshell have the same energy.

✦ What are the quantum numbers of an electron in the 3d state?

As we move from one element to another in order of increasing atomic number, the number of electrons increases. Fundamental principles of atomic physics, (particularly *Pauli's exclusion principle*), imply that the maximum number of electrons that can simultaneously occupy a subshell characterized by an orbital angular momentum quantum number l is $2(2l + 1)$. Hence no s subshell can contain more than two electrons, no p subshell more than six, no d subshell more than ten and no f subshell more than 14. This limitation plays a major part in determining the distribution of electrons across the various shells and subshells
— the **electronic configuration** of the atom.

In particular, the ground state electronic configurations, in which the electrons are distributed so as to minimize the atom's energy, tend to become more complicated as the atomic number increases. If we examine the precise way in which the electronic configuration changes as the atomic number increases we find that this too shows a periodic variation.

To see this let us consider part of the sequence of elements that we looked at in Subsection 2.1:

Li Be B C N O F Ne

(You may have noticed that helium has disappeared; it will come back later!)

The (ground state) electronic configuration of the lithium atom has two electrons in the s subshell of the $n = 1$ shell (the maximum number allowed) and one electron in the s subshell of the $n = 2$ shell. We represent this structure by writing it as $1s^22s^1$, the full size numbers indicate shells, the letters the subshells, and the superscripts show the number of electrons in each subshell. In beryllium there is a second 2s electron, so the electronic structure is $1s^22s^2$. No s subshell can contain more than two electrons, so in the boron atom the fifth electron must be a 2p electron, and the electronic configuration of boron is $1s^22s^22p^1$. From boron to neon, successive electrons are added to the 2p level, until at neon the configuration is $1s^22s^22p^6$. So the electronic configurations of the elements from lithium to neon are as shown in the margin. ☞

At neon, the 2p level is full because it contains its maximum quota of six electrons. The next highest energy level is 3s so the configuration of the element sodium, which contains one more electron than neon, is $1s^22s^22p^63s^1$. For the seven elements after sodium, the 3s and 3p levels are filled in the same way that the 2s and 2p levels are filled across the second period.

❖ What is the electronic configuration of the elements magnesium and aluminium, which contain respectively one and two more electrons than sodium?

You can therefore group the two rows (periods) as follows:

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

As you can see, this is very similar to the way that Mendeleev arranged the elements, except that the noble gases neon and argon are now at the *ends* of the rows whereas in our earlier arrangement neon was at the *beginning* of a row. This explains the mysterious disappearance of helium from our sample of elements —helium is an noble gas, like neon and argon, and therefore in our present arrangement should appear on the right of the table, above neon:

							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

As we will describe shortly, this arrangement makes more sense in terms of electronic configuration and is the one invariably adopted in modern versions of the periodic table.

❖ What common feature is shared by the electronic configurations of elements in the same vertical column?

Now let us pause to summarize what we have covered so far. The electronic configuration of atoms is a periodic property because when we set out the elements in order of atomic number, elements whose atoms have similar outer electronic configurations, such as carbon and silicon, occur at regular intervals. By grouping such elements in columns, we are constructing a periodic table that represents the periodicity in electronic configuration.

The elements in the two rows that we have set out have outer electronic configurations of the type $n\text{s}^1$, $n\text{s}^2$ and $n\text{s}^2n\text{p}^1$ to $n\text{s}^2n\text{p}^6$. Such elements are called **typical elements** or **main group elements**.

It is now plain that the members of certain families of elements which we introduced earlier have similar outer electronic configurations and are included among the typical elements. Thus, the alkali metals, which include lithium and sodium, have outer electronic configurations of the type $n\text{s}^1$. Again, the noble gases, with the exception of helium, have outer electronic configurations of the type $n\text{s}^2n\text{p}^6$.

The electronic configuration of these elements is shown in Table 1. They are known as group 0 elements.

Because these elements have the maximum possible number of electrons in their highest-energy quantum states (i.e. they each have a full outer subshell), they are very unreactive.

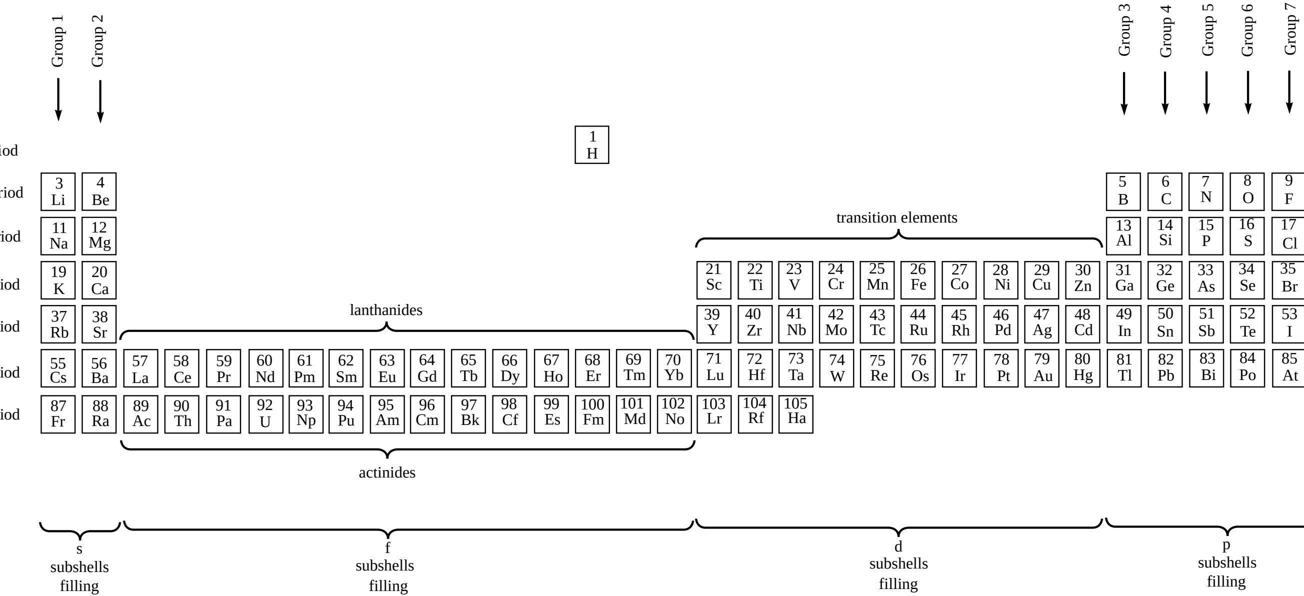
The number of electrons in the outer subshell increases across a period from left to right across the periodic table, and so the natural place for this particular group of noble gases is at the extreme right-hand side of the table.

Table 1 Ground states of group 0 elements (noble gases). All group 0 elements (except helium) have outer shell configuration of $ns^2\,n\mathrm{p}^6$.

Element	Symbol	Outer shell
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	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

3 The periodic table

The formulation of the periodic table was undoubtedly one of the most important events in the history of science. It introduced a powerful framework for all subsequent work in chemistry — a colossal achievement in itself — and it brought order to a bewildering diversity of data on the elements. In this section, we will look more closely at the periodic table and you will be able to see clearly its power as a means of organizing information about the chemical elements.



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

Figure 2 The periodic table of the elements.

Table 2a Ground state electronic configurations of the elements. Typical elements (i)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
1	H	1																	
2	He	2																	
3	Li	2	1																
4	Be	2	2																
5	B	2	2	1															
6	C	2	2	2															
7	N	2	2	3															
8	O	2	2	4															
9	F	2	2	5															
10	Ne	2	2	6															

Table 2b Ground state electronic configurations of the elements. Typical elements (ii)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
11	Na	2	2	6	1														
12	Mg	2	2	6	2														
13	Al	2	2	6	2	1													
14	Si	2	2	6	2	2													
15	P	2	2	6	2	3													
16	S	2	2	6	2	4													
17	Cl	2	2	6	2	5													
18	Ar	2	2	6	2	6													
19	K	2	2	6	2	6		1											
20	Ca	2	2	6	2	6		2											

Table 2c Ground state electronic configurations of the elements. Transition elements (i)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
21	Sc	2	2	6	2	6	1	2											
22	Ti	2	2	6	2	6	2	2											
23	V	2	2	6	2	6	3	2											
24	Cr	2	2	6	2	6	5	1											
25	Mn	2	2	6	2	6	5	2											
26	Fe	2	2	6	2	6	6	2											
27	Co	2	2	6	2	6	7	2											
28	Ni	2	2	6	2	6	8	2											
29	Cu	2	2	6	2	6	10	1											
30	Zn	2	2	6	2	6	10	2											

Table 2d Ground state electronic configurations of the elements. Typical elements (iii)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
31	Ga	2	2	6	2	6	10	2	1										
32	Ge	2	2	6	2	6	10	2	2										
33	As	2	2	6	2	6	10	2	3										
34	Se	2	2	6	2	6	10	2	4										
35	Br	2	2	6	2	6	10	2	5										
36	Kr	2	2	6	2	6	10	2	6										
37	Rb	2	2	6	2	6	10	2	6			1							
38	Sr	2	2	6	2	6	10	2	6			2							

Table 2e Ground state electronic configurations of the elements. Transition elements (ii)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
39	Y	2	2	6	2	6	10	2	6	1		2							
40	Zr	2	2	6	2	6	10	2	6	2		2							
41	Nb	2	2	6	2	6	10	2	6	4		1							
42	Mo	2	2	6	2	6	10	2	6	5		1							
43	Tc	2	2	6	2	6	10	2	6	6		1							
44	Ru	2	2	6	2	6	10	2	6	7		1							
45	Rh	2	2	6	2	6	10	2	6	8		1							
46	Pd	2	2	6	2	6	10	2	6	10									
47	Ag	2	2	6	2	6	10	2	6	10		1							
48	Cd	2	2	6	2	6	10	2	6	10		2							

Table 2f Ground state electronic configurations of the elements. Typical elements (iv)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
49	In	2	2	6	2	6	10	2	6	10		2	1						
50	Sn	2	2	6	2	6	10	2	6	10		2	2						
51	Sb	2	2	6	2	6	10	2	6	10		2	3						
52	Te	2	2	6	2	6	10	2	6	10		2	4						
53	I	2	2	6	2	6	10	2	6	10		2	5						
54	Xe	2	2	6	2	6	10	2	6	10		2	6						
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1			
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2			

Table 2g Ground state electronic configurations of the elements. The Lanthanides

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2			
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2			
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2			
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2			
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2			
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2			
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2			
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2			
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2			
68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2			
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6			2			
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2			

Table 2h Ground state electronic configurations of the elements. Transition elements (iii)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	9					
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2			

Table 2i Ground state electronic configurations of the elements. Typical elements (v)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2

Table 2j Ground state electronic configurations of the elements. The Actinides

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
99	Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
100	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
101	Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
102	No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2

Table 2k Ground state electronic configurations of the elements. Transition elements (iv)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
103	Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
104	Rf	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2	2
105	Ha	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	3	2

3.1 Noble gases, halogens and alkali metals

Figure 2 shows the modern version of the periodic table. You will probably find it helpful to look at this figure in conjunction with Table 2, which shows the electronic configurations of the elements (up to element 105). ☞

The periodic table is arranged so that all elements with a similar outer shell electronic configuration (and hence similar chemical properties) appear in vertical columns, groups, in which the principal quantum number of the outer shell increases as you step down the column. Thus the horizontal rows (periods) in the periodic table contain all the elements with the same principal quantum number in the outer shell. The subshells fill up as you move from left to right across the rows.

We can now discuss the properties of the elements in the light of their position in the table. The noble gases, the group 0 elements, appear in a column down the right hand side of the table . In Subsection 2.1 we mentioned two of the groups in the periodic table which contain particularly reactive elements. The group 7 elements, known as halogens, all have outer shell electronic configuration $n\mathrm{s}^2n\mathrm{p}^5$, as you would expect since they appear one column to the left of the noble gases. Thus, all group 7 elements have one vacant space in their outer p subshell. This space is easily filled by a spare electron resulting in a negatively charged ion which is then very reactive on account of its electrostatic properties. The group 1 elements on the other hand (the alkali metals) all have an outer shell structure $n\mathrm{s}^1$. This outer electron is weakly bound, which is manifest in the low ionization energies of these elements, and hence easily removed to leave a positively charged ion. Very often, of course, positively charged alkali metal ions combine with negatively charged halogen ions to form *salts* such as sodium chloride (NaCl), the chemical name for table salt.

3.2 The transition elements

The two elements that follow argon in the periodic table are potassium and calcium. These are typical elements, because their outer electronic configurations are $4s^1$ and $4s^2$, respectively. Potassium can be grouped under sodium, and calcium under magnesium. The next element is scandium Sc, which is certainly not a typical element: when the 4s level is full, the 3d level begins filling rather than the 4p. As Tables 2c, 2e, 2h and 2k show, this pattern of the d subshell in the *n*th shell filling *after* the s subshell in the n + 1th shell is repeated in each of the later periods in the periodic table.

Table 2c Ground state electronic configurations of the elements. Transition elements (i)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
21	Sc	2	2	6	2	6	1	2											
22	Ti	2	2	6	2	6	2	2											
23	V	2	2	6	2	6	3	2											
24	Cr	2	2	6	2	6	5	1											
25	Mn	2	2	6	2	6	5	2											
26	Fe	2	2	6	2	6	6	2											
27	Co	2	2	6	2	6	7	2											
28	Ni	2	2	6	2	6	8	2											
29	Cu	2	2	6	2	6	10	1											
30	Zn	2	2	6	2	6	10	2											

Figure 3 gives the subshell energy level diagram

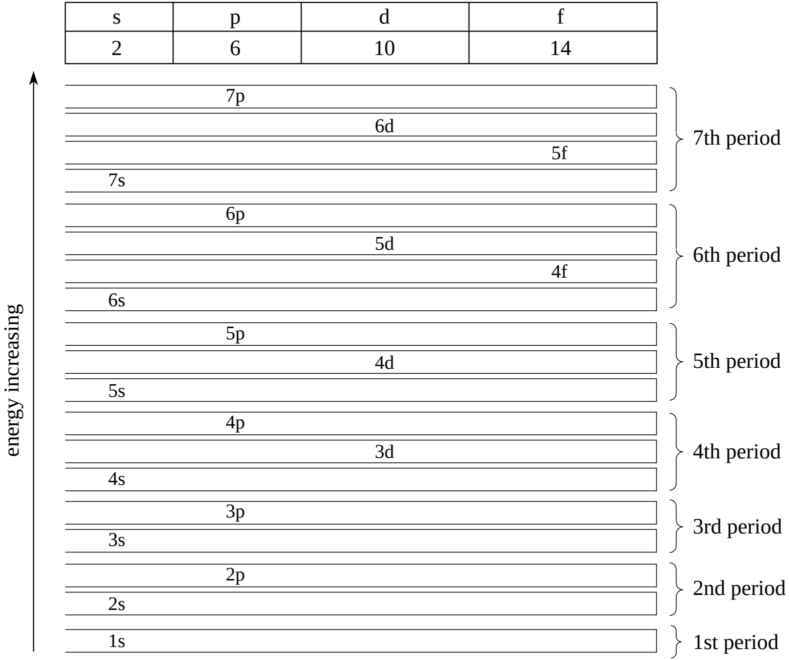


Figure 3 Subshell energy level diagram.

and Figure 4 displays the order of ascending subshells.

If we write out the subshells in the order of increasing energy, then the electronic configuration of scandium is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$. The 4p level only begins filling at gallium Ga (element 31), when the 3d level has been filled. Typical elements thus reappear in the table at gallium (Table 2d).

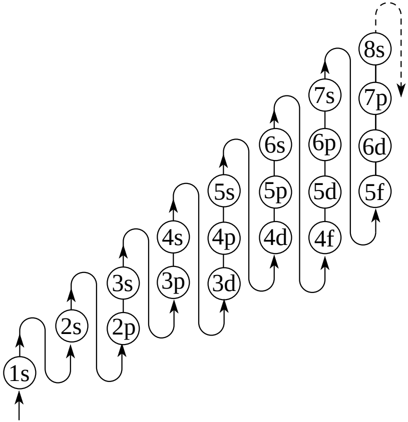


Figure 4 Order of ascending energy for the subshells.

The elements between calcium and gallium (Table 2c) span the region in which the 3d shell is filling up. There are ten of them, because the 3d level can accommodate up to ten electrons. Because their configurations are of this type, they cannot be grouped under typical elements, so the block of typical elements is usually separated between calcium and gallium, and the ten elements are inserted there.

Table 2c Ground state electronic configurations of the elements. Transition elements (i)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
21	Sc	2	2	6	2	6	1	2											
22	Ti	2	2	6	2	6	2	2											
23	V	2	2	6	2	6	3	2											
24	Cr	2	2	6	2	6	5	1											
25	Mn	2	2	6	2	6	5	2											
26	Fe	2	2	6	2	6	6	2											
27	Co	2	2	6	2	6	7	2											
28	Ni	2	2	6	2	6	8	2											
29	Cu	2	2	6	2	6	10	1											
30	Zn	2	2	6	2	6	10	2											

The elements scandium Sc ($Z = 21$) to zinc Zn ($Z = 30$) are called **transition elements** because they form a bridge between two blocks of typical elements.

We define transition elements as the elements that span a region in which a d shell is filling.

❖ In the scandium to zinc series, what is the most common outer electronic configuration of the transition elements?

Two of the ten transition elements, chromium (Cr) and copper (Cu), do not have outer electronic configurations of the type $4s^23d^x$. Their outer electronic configurations are, respectively, $4s^13d^5$ and $4s^13d^{10}$. We will not go into the detailed causes of these exceptions, but they reflect the fact that, in the scandium to zinc region, the 3d and 4s energy levels are very close in energy.

The periodic table in Figure 2 clearly sets the transition elements apart from the typical elements, and there is strong experimental support for this — the transition elements have properties different from those of the typical elements. Among the characteristics of transition elements are the following:

(a) They are all metals.

(b) Their compounds are often strongly coloured (for example, many copper compounds are a characteristic blue-green and many manganese compounds are pink).

(c) They often form more than one compound with other elements. In particular, they often form two or more halides with the formula type MX_n (where M represents any metal and X represents a particular halogen element) and two or more oxides with the formula type M_2O_n. In such cases the values of n usually differ by one. Thus iron forms a dichloride $FeCl_2$, and a trichloride $FeCl_3$, which are pale green and yellow-brown, respectively. Chromium forms the following fluorides: CrF_2 (green), CrF_3 (green), CrF_4 (green), CrF_5 (red) and CrF_6 (yellow), and copper yields the oxides Cu_2O and CuO. By contrast, typical elements form two or more chlorides or oxides less often, and when they do the values of n usually differ by two. Thus lead forms just two chlorides, $PbCl_2$ and $PbCl_4$.

(d) Magnetism is often associated with transition elements. For example, the strongly magnetic metals (Fe, Co, Ni) all lie in the first transition region.

Table 2d Ground state electronic configurations of the elements. Typical elements (iii)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
31	Ga	2	2	6	2	6	10	2	1										
32	Ge	2	2	6	2	6	10	2	2										
33	As	2	2	6	2	6	10	2	3										
34	Se	2	2	6	2	6	10	2	4										
35	Br	2	2	6	2	6	10	2	5										
36	Kr	2	2	6	2	6	10	2	6										
37	Rb	2	2	6	2	6	10	2	6			1							
38	Sr	2	2	6	2	6	10	2	6			2							

After the series of transition elements has been completed, as we have said, the 4p level begins filling at gallium ($Z = 31$). When the 4p level becomes full at the noble gas krypton ($Z = 36$), the fourth period ends.

In terms of the electronic configurations of its elements, the fifth period is a straightforward repeat of the fourth. From Figures 3 and 4 you can see that the 5s level is filled first (rubidium, Rb, and strontium, Sr), after which the filling of the 4d level generates a second series of transition elements, from yttrium (Y) to cadmium (Cd).

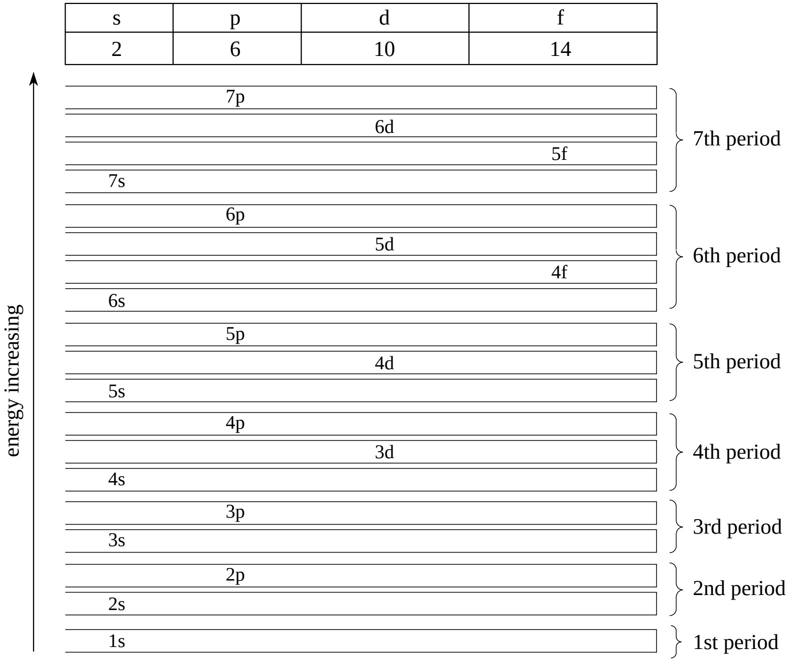


Figure 3 Subshell energy level diagram.

Typical elements reappear with the filling of the 5p level at indium (In), and the period ends when the 5p level is full at the noble gas xenon.

Table 2f Ground state electronic configurations of the elements. Typical elements (iv)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
49	In	2	2	6	2	6	10	2	6	10		2	1						
50	Sn	2	2	6	2	6	10	2	6	10		2	2						
51	Sb	2	2	6	2	6	10	2	6	10		2	3						
52	Te	2	2	6	2	6	10	2	6	10		2	4						
53	I	2	2	6	2	6	10	2	6	10		2	5						
54	Xe	2	2	6	2	6	10	2	6	10		2	6						
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1			
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2			

3.3 The lanthanides

The sixth period begins with the elements caesium (Cs) and barium (Ba). If we represent the electronic configuration of the noble gas, xenon, by the symbol [Xe], then the electronic configurations of caesium and barium are [Xe]$6s^1$ and [Xe]$6s^2$, respectively. The atomic number of barium is 56.

Question T1

Use Figure 3 to predict the electronic configurations of the following elements (their atomic numbers are given in brackets):
lanthanum (57),
praseodymium (59),
terbium (65),
ytterbium (70),
lutetium (71). ❑

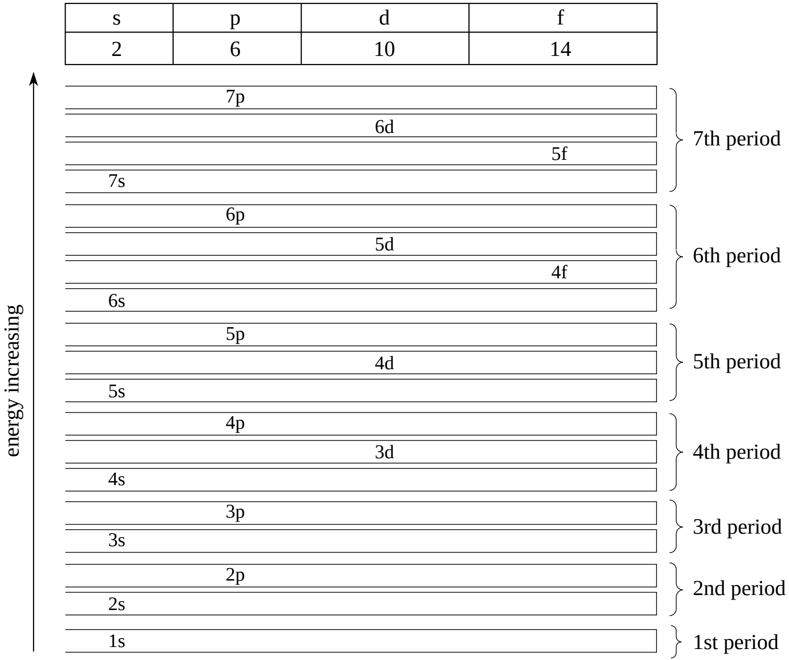


Figure 3 Subshell energy level diagram.

The answer to Question T1 suggests that, after barium, a new series of elements appears in which the 4f shell is being filled. There will be 14 elements in this new series because f shells can accommodate 14 electrons. The 4f shell becomes full at ytterbium, which has the configuration $[Xe]6s^24f^{14}$.

We will therefore define the new series as the fourteen elements from lanthanum to ytterbium, inclusive. The fourteen elements that follow barium are called **lanthanides** and their characteristic electronic configuration is $[Xe]6s^24f^x$.

Table 2g Ground state electronic configurations of the elements. The Lanthanides

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2			
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2			
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2			
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2			
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2			
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2			
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2			
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2			
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2			
68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2			
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6			2			
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2			

In general then, we can say that the lanthanides are typified by the outer electronic configuration $6s^24f^{\,x}$, where x runs from 1 to 14. ☞

Because they cannot be grouped beneath elements that we have considered up until now, we must pull the periodic table apart again, and insert them after barium (Figure 2). After the 4f level has been filled at ytterbium (Yt), lutetium (Lu), which has the configuration $[Xe]6s^24f^{14}5d^1$, begins a new series of transition elements.

Table 2g Ground state electronic configurations of the elements. The Lanthanides

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2			
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2			
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2			
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2			
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2			
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2			
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2			
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2			
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2			
68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2			
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6			2			
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2			

The lanthanides behave very similarly in many chemical reactions, so similarly that only since 1945 has it become possible to separate them completely from each other and obtain pure samples of each.

For nearly all of them, the highest oxide has formula M_2O_3, and for all fourteen of them, the highest chloride is MCl_3. ☞

Table 2g Ground state electronic configurations of the elements. The Lanthanides

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2			
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2			
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2			
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2			
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2			
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2			
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2			
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2			
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2			
68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2			
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6			2			
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2			

As we have already stated, after the 4f level has been filled at ytterbium, lutetium begins a new series of transition elements. The new transition series is completed with element number 80, mercury (Hg), and more typical elements then appear as the 6p level begins to fill. When the 6p level is filled at the noble gas radon, the sixth period is complete.

Table 2h Ground state electronic configurations of the elements. Transition elements (iii)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	9					
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2			

The lanthanides and transition elements play a key role in high-temperature superconductivity, one of the most important areas of research to have begun in the 1980s. **Superconductors** are extremely unusual in that, below their characteristic critical temperatures, they can carry electricity with zero resistance. The phenomenon was discovered in 1911 by the Dutch physicist Heike Kammerlingh Onnes (1853–1926) who demonstrated that lead and mercury were superconductors when they are cooled to the temperature of liquid helium (4.2 K).

For almost 75 years, there seemed little hope of finding materials that were superconductors at temperatures much higher than about 23 K. However, in 1986 K. Alex Müller (1927–) and Georg Bednorz (1950–) discovered at the IBM research laboratories in Zurich that a certain form of barium lanthanum copper oxide was a superconductor up to about 35 K. Soon afterwards, Ching-Wu Chu and his team at the University of Houston discovered that a related class of ceramic materials, a particular form of yttrium barium copper oxide exhibited superconductivity up to an astonishing 84 K, well above the temperature of liquid nitrogen. Because liquid nitrogen is comparatively inexpensive (it is cheaper than beer!), these discoveries hold the promise of making superconductors available for commercial use.

Bednorz and Müller, the midwives of the new field of high-temperature superconductivity, were jointly awarded the 1987 Nobel Prize for Physics.

3.4 The actinides

The seventh period begins as usual with an alkali metal, francium (Fr), and a group 2 metal, radium (Ra), as the 7s level is filled. The elements beyond this point are classified with the lanthanide elements. This similarity of the elements beyond radium to the lanthanides became obvious only during the wartime programme for the manufacture of atomic bombs in the United States, when teams of scientists under the direction of Glen Seaborg (1912–) succeeded in making new elements with atomic numbers greater than that of uranium (U).

Table 2j Ground state electronic configurations of the elements. The Actinides

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
99	Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
100	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
101	Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
102	No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2

Among these elements is element number 94, plutonium (Pu), which can be made by neutron bombardment of uranium in a nuclear reactor.

At a certain point beyond uranium, marked by atomic numbers 95 and 96 (americium, Am, and curium, Cm), it was found that the elements began to behave like lanthanides. Thus americium and the elements immediately following it all form a highest chloride of formula MCl_3.

Table 2j Ground state electronic configurations of the elements. The Actinides

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
99	Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
100	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
101	Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
102	No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2

This analogy with the lanthanides prompted Seaborg to propose in 1945 that actinium, and the thirteen elements following it, spanned a region in which the 5f level is filling. (Notice that this is consistent with Figure 4.) These fourteen elements are therefore grouped beneath the lanthanides in Figure 2; they are called the **actinides**.

Table 2j Ground state electronic configurations of the elements. The Actinides

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
99	Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
100	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
101	Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
102	No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2

Further confirmation of this idea has come with the preparation of elements 104–107. These were made by Soviet and American scientists between 1976 and 1986. These elements behave like transition elements rather than like actinides or lanthanides.

Table 2k Ground state electronic configurations of the elements. Transition elements (iv)

Z		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
103	Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
104	Rf	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2	2
105	Ha	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	3	2

This suggests that the 5f level is full at nobelium (No), element 102, and that stepwise filling of the 6d level begins at element 103, lawrencium (Lr) (Figure 4).

Question T2

(a) Use Figures 3 and 4 to work out the electronic configurations of the elements that have atomic numbers 16 and 28, respectively.

(b) Are these typical elements, transition elements, lanthanides or actinides?

(c) In what periods do they lie?

(d) Refer to the periodic table in Figure 2. In what group of the table does element 16 fall? What are the names of the two elements? ❏

4 Chemical bonding

Our discussion so far has mainly concerned individual chemical elements and their properties. Now it is time to consider how they combine, or bond, to form other substances.

4.1 Valency

When two elements react to form a chemical compound, experiment shows that their atoms tend to combine in a particular ratio. For example, sodium and chlorine react to yield sodium chloride NaCl, not $NaCl_2$ or $NaCl_3$. Likewise, the product of the reaction of hydrogen and oxygen is H_2O, not HO or HO_2. Why is there such a strong preference for certain combinations such as NaCl and H_2O?

Theories of chemical bonding supply answers to questions like this, and we will discuss them shortly. First, however, we will focus on the relationship between the numbers of atoms that combine in different compounds. An examination of this relationship leads to a property called **valency**, which is useful in predicting the formulae of certain compounds.

Consider the following three formulae:

HCl, NH_3, NCl_3

Notice that in HCl the elements hydrogen and chlorine combine with each other in the atomic ratio 1:1. Each of these two elements combines with nitrogen in the same ratio of 3:1 in NH_3 and NCl_3. There appears to be a relationship between the three formulae. This kind of observation for sets of compounds led chemists to suggest that the formula of a compound is determined by some inherent property of the constituent elements. This property, valency, determines the relative numbers of atoms of elements in compounds.

If each element had only a single value of its valency, the formulae of compounds could be readily predicted from a knowledge of those valencies. Unfortunately, many elements have several values of valency, which reduces the predictive power of the concept. Nevertheless, provided we steer clear of complicated cases, and show due caution, we can use the concept of valency to predict the formulae of many compounds quite straightforwardly.

The rules for determining the valency of an element are quite simple, particularly for *binary compounds* (those that contain only two elements), and we will restrict the discussion to these compounds. Because valency is linked to chemical formulae, it is concerned with the relative numbers of atoms in compounds. For this reason, some arbitrary reference element is chosen as the basis of values of valency. This element is hydrogen, and by definition its valency is taken to be one.

> If an element forms a binary compound with hydrogen, its valency is equal to the number of atoms of hydrogen that combine with one atom of that element.

For example, in hydrogen chloride (HCl) one atom of chlorine combines with one atom of hydrogen, so the valency of chlorine is one.

✧ Nitrogen can combine with hydrogen to form the chemical ammonia, which has the chemical formula NH_3. On the basis of this formula, what do you deduce to be the valency of nitrogen?

Knowing that nitrogen and chlorine have valencies of 3 and 1, respectively, (at least in the simple cases considered above), we can predict that they will jointly form the binary compound NCl_3, which is indeed the case. The existence of NCl_3 demonstrates that it is not necessary to rely on compounds of hydrogen in order to determine the valency of an element. For example, if the valency of chlorine in HCl is the same as that of hydrogen, i.e. one, the valency of nitrogen is equal to the number of atoms of chlorine that combine with one atom of nitrogen. In NCl_3, therefore, the valency of nitrogen is three, the same value as we deduced from the existence of ammonia NH_3.

To take another example, hydrogen and oxygen combine as water, which has the formula H_2O.

Question T3

What is the valency of oxygen in H_2O? ❏

As the examples above illustrate, the idea that elements have a fixed valency, is useful in predicting chemical formulae even though it must be treated with caution.

In general, if element A has valency *x*, and element B has valency *y*, then if A and B combine to form a compound, *y* atoms of A will combine with *x* atoms of B.

Of course, there are limitations to the generality of these predictions and to the information that valency provides. Valency alone gives no indication of the nature of the interaction between atoms, which is the subject of the following subsections. While you are reading them, you may find it helpful to refer to Table 3, which gives the valencies of ten common elements.

Question T4

In forming compounds, silicon (Si) generally exhibits a valency of four.

(a) What is the formula of the simplest substance that silicon can form with hydrogen ?

(b) What is the formula of the simplest substance that silicon can form with oxygen (O), which has a valency of two? ❏

Table 3 Valencies of ten common elements.

Element	Valency
hydrogen (H)	1
carbon (C)	4
nitrogen (N)	3
oxygen (O)	2
fluorine (F)	1
sodium (Na)	1
magnesium (Mg)	2
chlorine (Cl)	1
potassium (K)	1
calcium (Ca)	2

4.2 A simple theory of chemical bonding

To form a compound, the different atoms have to bond together. An atom consists of a nucleus surrounded by electrons, so initial contact between atoms involves the outer electrons. Not surprisingly, therefore, the outer electronic configuration strongly influences the way one kind of atom bonds to another.

The simplest theories of **chemical bonding** are based on the observation that the elements of group 0, the noble gases, are extraordinarily unreactive. These elements are helium, neon, argon, krypton, xenon and radon. They are all monatomic gases: that is, they exist as single helium atoms or single neon atoms, not as He_2 or Ne_2 molecules. They do not react with the common laboratory chemicals. Indeed, they are all unaffected by molten sodium, which is usually extremely reactive, and helium, neon and argon do not even react with hot fluorine, a substance that attacks nearly every other element. Since 1962 some compounds of xenon, krypton and radon have been prepared, for example XeF_4, XeO_3 and KrF_2, but the overall impression of a chemically very unreactive group is correct.

We describe this chemical inertness of the group 0 elements by saying that the noble gases are stable with respect to chemical reactions. Now when atoms react, their outer electronic configurations are disturbed. It follows that the electronic configurations of the noble gases must be especially stable to disturbance.

As we noted at the beginning of this module, the ionization energies of the noble gases are unusually large (Figure 1), so removal of an electron from a noble gas atom is especially difficult. This suggests that the electronic configuration of a noble gas is particularly stable with respect to the loss of an electron.

Simple theories of chemical bonding assume that the electronic configurations of the noble gases are especially stable, and that many elements tend to attain noble gas electronic configurations in their chemical reactions.

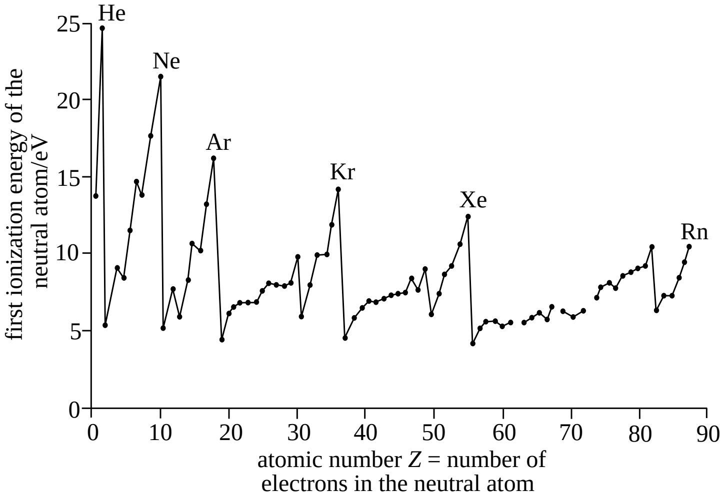


Figure 1 First ionization energies of elements up to radon.

According to this assumption, the noble gases are chemically inert because they already have the noble gas electronic configurations. How can one element attain the electronic configuration of another? According to the simple theories of bonding there are two ways: *electron transfer* and *electron sharing*.

4.3 Ionic bonding

The alkali metals, the group 1 elements, all have the electronic configuration of a noble gas plus one extra electron. If this electron is removed in a chemical reaction, a positively charged ion (called a **cation**) will be formed and this ion will have the electronic configuration of a noble gas atom. Thus, for example, lithium has the electronic configuration $1s^22s^1$; by losing its 2s electron, it forms the lithium ion Li^+ and attains the noble gas configuration of helium ($1s^2$). This reaction can be written as

$$\mathrm{Li} \rightarrow \mathrm{Li}^+ + e^-$$

Question T5

What is the electronic configuration of the sodium ion Na^+? To what noble gas does this configuration correspond ? ❏

Consider now the group 7 elements, the halogens. They all have the electronic configuration of a noble gas *less* one electron. By addition of one electron, for example in a chemical reaction, a negatively charged ion (called an **anion**) will be formed, which will have the electronic configuration of a noble gas atom. Thus, for example, fluorine ($1s^22s^22p^5$) will form a fluoride ion F^-, with the electronic configuration ($1s^22s^22p^6$) of neon.

Question T6

What is the electronic configuration of the chloride ion, Cl^-? To what noble gas does this configuration correspond? What does the superscript minus stand for? ❏

Thus you can envisage that when the metal lithium and the gas fluorine react to form lithium fluoride (LiF), a colourless compound that resembles common salt, an electron is transferred from each lithium atom to each fluorine atom, with the formation of the following ions:

$$2\text{Li} + \text{F}_2 \rightarrow 2\text{Li}^+ + 2\text{F}^-$$

The electrostatic attraction between the positive lithium ions and negative fluoride ions in lithium fluoride gives rise to **ionic bonding**.

We now know that lithium ions have a single positive charge, and fluoride ions have a single negative charge because these charges give each ion a noble gas electronic configuration. At the same time, this explains why lithium fluoride has the formula LiF: the compound must be neutral and this can only be achieved by combining equal numbers of the oppositely charged ions.

Question T7

Write down the electronic configuration of magnesium. How could magnesium most easily attain the electronic configuration of a noble gas? What therefore is the symbol for the magnesium ion? What is the formula for magnesium fluoride? ❏

The alkali metals (group 1) form compounds containing singly charged positive ions, whereas magnesium in group 2 forms compounds containing the ion Mg^{2+}, and the halogens (group 7) form compounds containing singly charged negative ions (generally called halide ions). All these ions have noble gas electronic configurations. Their charges are such that the alkali metals must form halides of the type M^+X^-, and group 2 metals like magnesium, halides of the type $M^{2+}(X^-)_2$.

Ionic substances have a structure in which the ions tend to surround themselves with ions of opposite charge, and in which discrete molecules cannot be legitimately identified. Because there are strong electrostatic forces between the ions, ionic substances are generally solids at room temperature and they have comparatively high melting and boiling temperatures.

Another characteristic property of ionic substances is that when they melt they conduct electricity, because of the presence of charged ions. Also, if these substances dissolve significantly in water, they usually form solutions that readily conduct electricity.

4.4 Covalent bonding

Many substances, for example, oxygen (O_2), carbon tetrachloride (CCl_4) and ammonia (NH_3), have properties that cannot be understood in terms of ions. Instead, they have a structure in which discrete molecules, with the same chemical formula as that of the substance, are separated from each other by what are relatively large distances on a molecular scale. The form of bonding that accounts for the existence of these molecules is known as **covalent bonding**, and the substances composed of such molecules are said to be *molecular covalent substances*.

At room temperature, these substances exist as solids, liquids and gases, and most of them have relatively low melting and boiling temperatures. They do not conduct electricity simply because they do not consist of ions.

Other examples of this type of substance are chlorine (Cl_2), hydrogen (H_2), nitrogen (N_2), water (H_2O), nitrogen trichloride (NCl_3), methane (CH_4) and carbon dioxide (CO_2). Each of them comprise discrete molecules with the formula indicated. All of these formulae can be understood easily by assigning a fixed valency to the atoms of nitrogen, oxygen, hydrogen, chlorine and carbon: one to hydrogen and chlorine, two to oxygen, three to nitrogen and four to carbon.

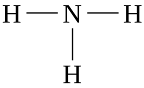
The molecules H_2, Cl_2, NH_3 and NCl_3 can be represented as shown in structures I to IV.

$H—H$

I

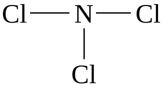
$Cl—Cl$

II



$$\begin{array}{ccccc} H & — & N & — & H \\ & & | & & \\ & & H & & \end{array}$$

III



$$\begin{array}{ccccc} Cl & — & N & — & Cl \\ & & | & & \\ & & Cl & & \end{array}$$

IV

In these molecular diagrams, the constituent atoms are linked by bonds that are represented by lines. The number of bonds issuing from each atom is equal to its valency, which determines the ways in which the atom can link with others. For example, because three bonds spring out of each nitrogen atom, whenever the nitrogen bonds with other atoms all three of its bonds must link with those of other atoms. One way in which this can be easily achieved is by bonding with three hydrogen atoms to form a molecule of ammonia, NH_3.

Question T8

Represent molecules of the compounds hydrogen chloride (HCl), methane (CH_4), carbon tetrachloride (CCl_4) and water (H_2O) using a diagram that makes clear the valencies of each constituent atom. ❏

The atoms in the molecular diagrams or structures that you have met so far have been linked by single valency lines or single bonds, but this is by no means always the case. Consider, for example, the oxygen (O_2) and carbon dioxide (CO_2) molecules. The molecules are drawn as in structures V and VI

$\mathrm{O{=}O}$

V

$\mathrm{O{=}C{=}O}$

VI

in order to ensure that oxygen has a valency of two and that carbon has a valency of four.

In these examples, atoms are linked by *two* valency lines: they are said to be held together by **double bonds**.

✥ Draw a diagram of the N_2 molecule in which nitrogen has its common valency of three.

You now know how to draw diagrams of the molecules in molecular covalent compounds in which each atom forms a number of bonds equal to its assigned valency. What is the nature of the bonds which hold the atoms together, and *why* do the carbon, chlorine, hydrogen, nitrogen and oxygen atoms have their characteristic valencies?

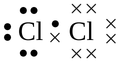
The properties of chlorine, Cl_2, are nothing like those of an ionic substance such as NaCl. However, even if we ignore this and try to give the Cl_2 molecule an ionic form, we cannot do so consistently. For instance, suppose we say that one of the chlorine ‘units’ in the Cl_2 molecule is a Cl^- ion with the electronic configuration of argon.

❖ What will be the electric charge and electronic configuration of the other chlorine ‘unit’?

In 1916, a solution to this sort of problem was proposed by Gilbert Lewis (1875–1946), the American chemist also famous for naming the photon (the quantum of electromagnetic radiation) in 1923. Lewis suggested that bonds could be formed between atoms by *sharing* pairs of electrons and that each shared pair constituted a *covalent bond*. He pointed out that this provided a means by which atoms in many compounds could attain noble gas structures. Thus, we can represent two chlorine atoms by the symbols given in structure VIII

VIII

where the dots on one atom and the crosses on the other represent the seven outer electrons ($3s^23p^5$). We then write the chlorine molecule Cl_2 as in IX.



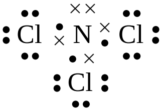
IX

This type of diagram is now called a **Lewis structure**. By convention, the outer electrons around the atoms are grouped in pairs. The pair of electrons that falls between the two chlorines is counted towards the electronic configurations of both atoms. The pair of electrons thus shared between the atoms constitutes a chemical bond.

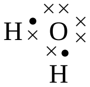
✧ What electronic configuration is thereby achieved by the two chlorines in the Cl_2 molecule?

Because one pair of electrons is involved in the Lewis structure, the bond is a single bond. The shared electron pair is therefore an electronic interpretation of the single bond line drawn between the two chlorine atoms in structure II.

As further examples, consider the molecules NCl_3 and H_2O. Nitrogen has five outer electrons ($2s^22p^3$), hydrogen has one ($1s^1$), and oxygen has six ($2s^22p^4$). Suppose that we represent the outer electrons on the nitrogen and oxygen atoms by crosses, and those on the hydrogen and chlorine atoms by dots. Then each atom attains a noble gas electronic configuration in the Lewis structures are given in X and XI.



X



☞

XI

❖ What noble gas electronic configurations are attained by nitrogen, oxygen and hydrogen in these structures?

Question T9

Draw a Lewis structure for the methane molecule, CH_4. ❏

So far, any two atoms in our Lewis structures have been held together by just one electron-pair bond. Sometimes, however, two or three pairs may be involved.

❖ Draw the Lewis structure corresponding to structure VI for CO_2.

$$O{=}C{=}O$$

VI

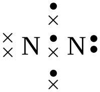
The presence of two electron pairs between each oxygen ‘unit’ and the central carbon ‘unit’ allow us to interpret each carbon–oxygen double bond in structure VI. As the examples of CO_2 and CH_4 demonstrate, carbon has a valency of four because it attains the neon electronic configuration when it exercises that valency.

As noted earlier, an example of a triple bond is supplied by the nitrogen molecule, $\mathrm{N{\equiv}N}$ (structure VII).

$$\mathrm{N{\equiv}N}$$

VII

The Lewis structure for nitrogen molecules is given as structure XIII.



XIII

The existence of covalent bonds is not confined to neutral molecules. Such bonds also hold together *polyatomic ions*, that is ions that comprise modifications of *several* atoms. For example, when sodium hydroxide dissolves in water it forms ions of $\mathrm{Na^+}$ and $\mathrm{(OH)^-}$. Chemists indicate this by writing:

$$\mathrm{NaOH(s) = Na^+(aq) + (OH)^-(aq)}$$ ☞

This shows that sodium hydroxide is an ionic compound, $\mathrm{Na^+(OH)^-}$, but the *hydroxide ion* $\mathrm{(OH)^-}$ it contains is held together by a covalent bond. We can put an $\mathrm{(OH)^-}$ ion together by bonding an $\mathrm{O^-}$ ion to a hydrogen atom.

✦

A neutral oxygen atom contains six electrons ($2s^22p^4$). How many outer electrons will an $\mathrm{O^-}$ ion have ?

✦

Draw a Lewis structure for $\mathrm{(OH)^-}$.

The negative charge is now part of the whole oxygen–hydrogen complex, so it is placed outside brackets drawn around the Lewis structure.

At this point, you could be forgiven for thinking that the bonding and formulae of all chemical compounds can be explained by assuming that the atoms tend to attain noble gas electronic configurations. This is very far from being the case. For instance, the theory cannot account for the existence of transition element compounds such as $FeCl_2$ and CuO, or for sulphur trioxide SO_3. Nevertheless it can be usefully applied to many substances, and we now emphasize this by extending it to a new type of material.

4.5 Extended covalent bond

Our study of covalent substances has so far been confined to compounds or elements that are composed of discrete molecules. However not all covalent substances are built in this way.

This point can be demonstrated by diamond, one of the forms of the element carbon. Although a different kind of covalent substance, its structure can be understood using the principles of the previous section. Diamonds are held together by C–C covalent bonds. Each carbon atom will form four such bonds; carbon has a valency of four, and in forming four single covalent bonds, attains the electronic configuration of neon.

In diamond, each atom forms four C–C electron-pair bonds, which point towards the corners of a regular tetrahedron (a pyramid with triangular base and sides). A fragment of the diamond structure is shown in Figure 5.

The C–C bonds are very strong, and you will notice that they spread out symmetrically through the structure in all directions. It is therefore very difficult to break into the structure with, say, a chisel.

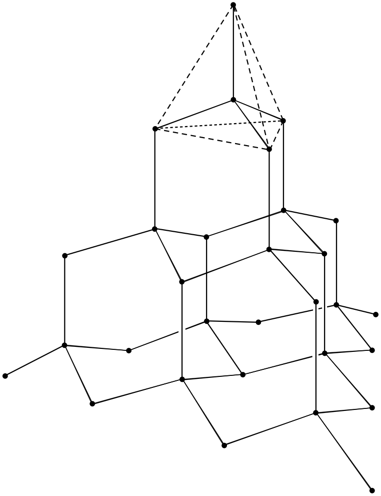


Figure 5 The structure of diamond. Each carbon atom is surrounded by four others located at the corners of a tetrahedron. The length of the C–C bond is 1.54×10^{-10} m.

Diamond is the hardest substance known and has a melting temperature (under pressure) of over 3500 °C. This extremely high melting point, together with the fact that it contains no discrete molecules, distinguishes diamond from the covalent compounds we have met so far. ☞

The absence of discrete molecules means that the C–C bonds must be broken if the structure is to be dismembered, and this accounts for the high melting temperature. Because the C–C bonds consist of shared electron pairs, diamond is covalent, but it is not molecular covalent in the sense we described earlier. We could argue to the contrary only if we were prepared to concede that entire diamond crystals could be regarded as giant molecules, which is contrary to experimental evidence.

The element silicon occurs in the same group of the periodic table as carbon, and it provides another example of an extended covalent substance — silicon dioxide (SiO_2) which resembles carbon dioxide (CO_2) only in its formula. Carbon dioxide is a gas at room temperature and comprises 0.03% of air by volume. It consists of discrete molecules and its Lewis structure shows that it is held together by carbon–oxygen double bonds (O|C|O). The physical properties of SiO_2 are, however, very different from those of CO_2.

The structure of quartz, a form of silicon dioxide, is shown in Figure 6. Here, both the silicon and oxygen atoms have noble gas electronic configurations. Each silicon ‘unit’ forms four single (electron-pair) bonds directed towards the corners of a tetrahedron and attains the electronic configuration of argon; each oxygen forms two single bonds and attains the configuration of neon.

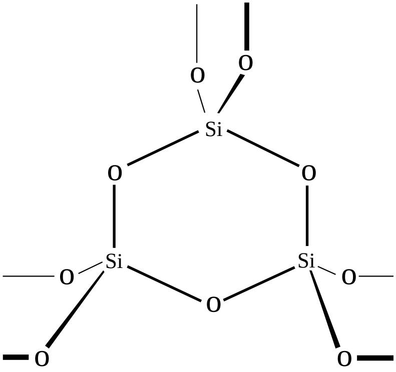


Figure 6 Simplified structure of quartz (silicon dioxide). The length of the Si–O bond is 1.61 × 10^{-10} m.

The overall ratio of silicon to oxygen atoms in silica is 1: 2. The structure is a three-dimensional network of Si–O bonds: there are no discrete molecules. Like diamond, it is an extended substance and it is not molecular covalent. Silicon dioxide (SiO_2) should be a solid, and if the Si–O bonds are strong, as they are, the solid should be hard and it should melt at a high temperature. In fact, silicon dioxide SiO_2 (or silica) occurs as the common mineral quartz, which is very hard, and it has the expected high melting temperature (1710 °C).

This brief comparison of silicon dioxide and carbon dioxide has highlighted the differences between extended and molecular covalent substances and it has demonstrated how profoundly the physical properties of a compound are affected by the type of chemical bonding between its constituents.

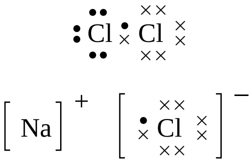
4.6 Electronegativity

When the atoms of non-metallic elements from the extreme right of the periodic table combine, they form covalent substances. However, combination of the atoms of a metallic element from the extreme left of the table with atoms of a non-metallic element from the extreme right, yields an ionic compound. Consider, for example, the third period, which runs from sodium to argon.

Na Mg Al Si P S Cl Ar

When two chlorine atoms combine, covalent Cl_2 molecules of chlorine *gas* are formed. However, chlorine atoms combine with sodium atoms to form a *solid*, the ionic compound Na^+Cl^-. Let us look at this contrast from an electronic point of view.

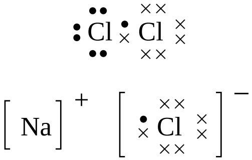
In structure XV, the Lewis structure of the Cl_2 molecule is juxtaposed with a representation of the ions in sodium chloride.



XV

The chloride ion has the electronic configuration of argon, with eight outer electrons, and the electron transferred from the sodium atom is marked by a black dot. Following the convention earlier, the outer electrons are grouped in pairs.

Notice that in both of these structures, the formation of a chemical bond involves the formation of a new electron pair in the outer electron configuration of chlorine. However, in Cl_2, because the two atoms are identical, the electron pair must be equally shared between the two atoms whereas in NaCl it resides completely on the resulting chloride ion. According to this picture, ionic and covalent bonding are simply different aspects of the same process, because both involve the formation of electron pairs: *the difference between them lies only in the extent to which those electron pairs are shared between atoms*.



XV

Atoms towards the right of the periodic table form covalent compounds when they interact; atoms towards the left behave somewhat differently. To explain this, we need to introduce the idea of *electronegativity*.

The **electronegativity** of an element is the power of an atom of the element to attract electrons to itself *when entering into chemical combination* (see Table 4) ☞. In the Cl_2 molecule, the two identical atoms have an equal appetite for electrons: their electronegativities are equal, so the electron pair is shared equally between the two atoms. Now consider sodium chloride.

✦ Which atom is the more electronegative, sodium or chlorine?

Table 4 Typical values for the electronegativities of ten elements.

Element	Electronegativity
sodium (Na)	0.9
lithium (Li)	1.0
silicon (Si)	1.8
hydrogen (H)	2.1
carbon (C)	2.5
bromine (Br)	2.8
nitrogen (N)	3.0
chlorine (Cl)	3.0
oxygen (O)	3.5
fluorine (F)	4.0

This argument suggests that the electronegativity of chlorine, near the end of the third period, is greater than that of sodium at the beginning.

A further hint that this is correct comes from the ionization energies of some elements (see Figure 1). If an element has a low ionization energy, then an electron is removed from its atom with relative ease, and this suggests that the electronegativity of the element should be comparatively low. By the converse argument, high electronegativities are associated with high ionization energies; the ionization energy of chlorine, like its electronegativity, is greater than the corresponding value for sodium.

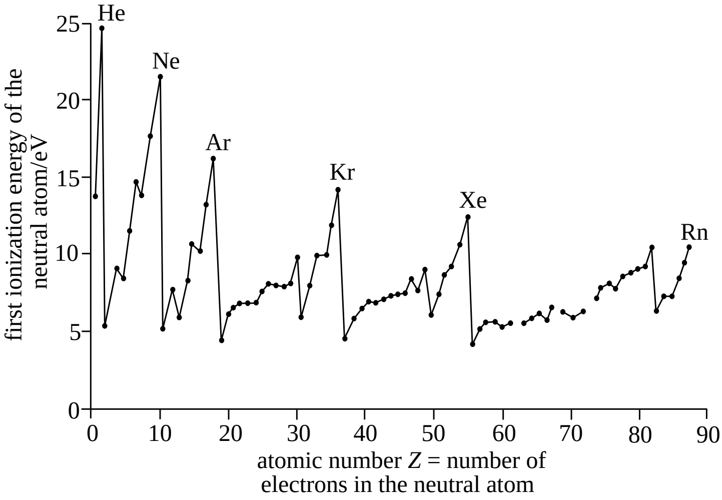


Figure 1 First ionization energies of elements up to radon.

More advanced theoretical arguments suggest that electronegativity increases steadily across the third period from sodium to chlorine. Within the periodic table in general, electronegativity usually increases from left to right across a period, and decreases from the top to bottom of a group. The most electronegative elements are in the top right-hand corner of the table — the top of groups and the end of periods. Ignoring helium, neon and argon, which form no chemical compounds, the most electronegative elements are first, fluorine, followed by oxygen, chlorine and nitrogen.

These trends in electronegativity can help us to predict whether one substance is more likely to be ionic than another. When atoms of high but similar electronegativity from the right-hand side of the periodic table bond together, covalent substances are formed. However, when atoms of high electronegativity combine with atoms of *low* electronegativity at the extreme *left* of the periodic table, ionic compounds tend to be formed.

It remains to consider what happens when atoms of low but similar electronegativity on the *left* of the periodic table combine with each other. This is the topic of the next subsection.

4.7 Metallic bonding

When the atoms of elements on the left of the periodic table come together, metals are formed. Because all the atoms have low electronegativities, they are prepared to surrender electrons to other atoms, either by electron transfer or electron-pair sharing. However, because the atoms have low electronegativity, none of them will readily accept these electrons, either by forming a negative ion, or by accepting a share in electron-pair bonds. In consequence, a pool of free electrons is created, which is like hot money — they are passed quickly from hand to hand, and can find no permanent home! Within this pool resides an array of positive ions formed from the atoms that supplied it (Figure 7). Ultimately, each atom shares its bonding electron or electrons with every other atom in the crystal. This is a simple but very useful model of **metallic bonding**.

Consider a specific example. When sodium atoms combine with one another, sodium metal is formed. Each sodium atom contributes one electron to the pool of free electrons, so each atom forms an Na^+ ion with the noble gas configuration of neon.

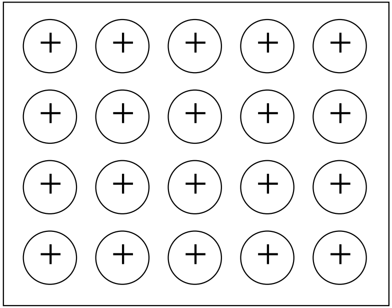


Figure 7 A simple model of metallic bonding: in metallic elements and alloys, an array of positive ions is steeped in a pool of negatively charged free electrons. An alloy is a combination of elements, usually metallic elements in various proportions.

According to this model, therefore, sodium metal consists of an array of Na^+ ions immersed in a pool of free electrons. The metal is held together by the ‘free’ electrons. It is energetically more favourable for the ions to be in close proximity with the sea of delocalized electrons rather than discrete atoms.

Because there is only one bonding electron per metal atom in sodium, the bonding is quite weak, and the melting point is low (98 °C). With magnesium, the next element in the period, the ion with a noble gas configuration is Mg^{2+}. This double positive charge now interacts with the negative charge of the two free electrons per metal atom. The bonding is therefore stronger, and the melting point is correspondingly higher (650 °C).

You will of course be familiar with the distinctive properties of metals such as iron, aluminium, copper, silver and tin. Metals often have a lustrous appearance, and are good conductors of heat and electricity. The free electrons, which roam throughout the metal structure, account for the electrical conductivity. When a voltage is applied across two points on a piece of metal, the electron motion becomes less random, there is an overall movement of electrons between the two points, and an electric current flows.

Study comment We have discussed so far some of the simple theories of chemical bonding. There are more complex models which give a more complete description of chemical behaviour. One such model involves the concept of electrons occupying orbitals.

4.8 Summary of Section 4

Many substances are formed by atoms bonding together in order to attain the highly stable electronic configurations of the noble gases. Three main types of chemical bonding have been discussed:

○ Ionic bonding, in which ions with noble gas configurations are formed by electron transfer.

○ Covalent bonding, in which atoms achieve noble gas configurations by sharing electron pairs.

○ Metallic bonding, in which positive ions with noble gas configurations are held together by a pool of free electrons.

These three kinds of bonding give rise to the distinctive properties of ionic, covalent and metallic substances. Whether a substance is ionic, covalent, or metallic is strongly influenced by the electronegativity of the atoms of which it is composed. In general, electronegativity increases from left to right across periods of the periodic table, and decreases down groups from the top to the bottom. This variation means that the non-metallic elements on the extreme right of the periodic table have high electronegativities; metallic elements at the extreme left have low electronegativities.

When non-metallic elements combine with themselves, or with each other to form binary compounds, their high but similar electronegativities result in the formation of shared electron-pair bonds. In other words, they form covalent substances. In many cases these substances can be represented by Lewis structures in which each non-metallic atom attains the electronic configuration of the noble gas at the end of its period.

When non-metallic elements from the extreme right of the periodic table form binary compounds with metallic elements from the extreme left, the large difference in electronegativity tends to generate ionic compounds. Such compounds can often be represented as assemblies of ions in which the metallic element has formed a positive ion with the electronic configuration of the preceding noble gas, and the non-metallic element had formed a negative ion with the electronic configuration of the following noble gas.

When elements from the left of the periodic table combine with themselves, or with each other, their low electronegativities generate assemblies of positive ions within a pool of free electrons. These free electrons account for the metallic properties of such elements, and also of the substances that they form by combination which are called *alloys*.

Question T10

Consider the compounds IBr, $CaCl_2$ and $CaMg_2$. One is ionic, one is covalent, and one is metallic. Identify which is which, and then match each compound to one of the three descriptions (a) to (c) below:

(a) White solid that melts at 772 °C. It is a poor conductor of electricity in the solid state, but a good one when melted or dissolved in water.

(b) Brown-black solid that melts at 41 °C to give a liquid with low electrical conductivity.

(c) Silvery looking solid that melts at 720 °C. Whether solid or molten, it is an excellent conductor of electricity. ❏

5 Closing items

5.1 Module summary

1 The *first ionization energy* of an atom is the energy required to remove its least tightly bound electron. When these values are plotted against atomic number, they trace a regular pattern. At the peaks are the *noble* (or *inert*) *gases*; just after the peaks are the very reactive *alkali metals*; and just before the peaks are the *halogens*, also very reactive.

2 The observed periodicity in the chemical properties of the elements enables them to be arranged in the form of a *periodic table*. The modern form of the table can be understood in terms of the *electronic configuration* of atoms, that is the distribution of the electrons across the various *shells* and *subshells* that they may occupy. No s subshell can contain more than two electrons, no p subshell more than six, no d subshell more than ten and no f subshell more than 14.

3 The periodic table is arranged so that all elements with similar outer electronic configurations (and hence similar chemical properties) appear in vertical columns, known as *groups*, in which the *principal quantum number* of the outer shell increases down the column. The horizontal rows in the periodic table, known as *periods*, typically contain several series of elements, each of which corresponds to the filling of a specific subshell.

4 At each end of the periodic table are groups of *typical* or *main group elements*. In between the main group elements are three series of *transition elements* (corresponding to the filling of d subshells) and the *lanthanides* and *actinides* (corresponding to the filling of f subshells).

5 Simple theories of *chemical bonding* assume that the electronic configurations of the noble gases are especially stable, and that many elements tend to attain noble gas electronic configurations in their chemical reactions.

6 *Valency* is a property of an element that describes its ability to combine with other elements; it is helpful in predicting the formulae of certain compounds.

7 *Ionic bonding* involves the transfer of electrons from one atom to another, forming ions which have the outer electronic configuration of a noble gas. Ionic compounds consist of ions which in the solid state are held together by strong electrostatic forces; ionic compounds therefore tend to have comparatively high melting temperatures.

8 *Covalent bonding* involves the sharing of electrons between atoms so that the atoms each attain the outer electronic configuration of a noble gas. Covalent compounds are often made up of discrete molecules; the forces between these are in general less than the forces between ions, so the melting temperatures of covalent compounds tend to be less than those of ionic compounds. *Extended covalent bonding*, in which there are no discrete molecules, also arises.

9 The concept of *electronegativity* provides a link between ionic and covalent bonding. The electronegativity of an element is the power of an atom of the element to attract electrons to itself when entering into chemical combination.

10 *Metallic bonding* involves each atom sharing its bonding electron or electrons with every other atom in a crystal structure of positive ions.

5.2 Achievements

Having completed this module, you should be able to:

A1 Define the terms that are emboldened and flagged in the margins of the module.

A2 Outline the structure of the periodic table, and explain its relationship to the electronic configuration of atoms.

A3 Describe the main features and consequences of the electronic configuration of groups 0, 1 and 7 of the periodic table, together with those of the transition elements, the lanthanides and the actinides.

A4 Use the concept of valency to predict the structure of simple chemical compounds.

A5 Describe the characteristics of ionic, molecular covalent, extended covalent, and metallic bonding.

A6 Explain the relationship between the nature of the bonding in a compound and the properties of that compound.

A7 Draw Lewis structures for simple covalent compounds.

A8 Explain how the concept of electronegativity determines whether two atoms will combine to form an ionic, covalent or metallic compound.

Study comment You may now wish to take the *Exit test* for this module which tests these Achievements. If you prefer to study the module further before taking this test then return to the *Module contents* to review some of the topics.

5.3 Exit test

Study comment Having completed this module, you should be able to answer the following questions each of which tests one or more of the Achievements.

Question E1

(*A2* and *A3*) Radon, atomic number 86, marks the point in Figure 4 where the 6p level has become full. Use Figure 4 to predict the electronic configurations of the unknown elements 114, 118 and 119. (Use the symbol [Rn] for the electronic configuration of radon 86.)

Which, if any, of these three elements is (a) a typical element, (b) a transition element, (c) an alkali metal, (d) a noble gas, (e) an actinide?

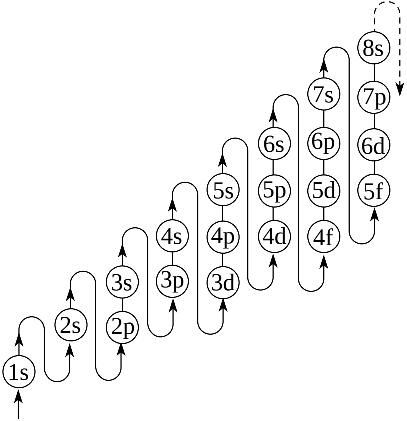


Figure 4 Order of ascending energy for the subshells.

Question E2

(*A4*) (a) Aluminium has valency three. What are the chemical formulae of the simplest chemical compounds that it forms with the following elements:

(i) nitrogen, which has valency 3;

(ii) oxygen, which has valency 2;

(iii) carbon, which has valency 4.

(b) What are the valencies of the noble gases? Explain your answer.

Question E3

(*A2*, *A5* and *A6*) An element Z is a solid that is a poor conductor of electricity. Z forms two fluorides with the formulae ZF_4 and ZF_6. The compound ZF_6 is a colourless gas.

(a) In which group of the periodic table does Z lie? Explain how you deduce your answer from the properties described. What can you say about the electronic configuration of Z?

(b) What would you predict for the formula of the highest oxide of Z? Would you expect this oxide to be an ionic or covalent substance ? Explain your reasoning.

(c) Deduce, as far as possible, the range of candidates for the identity of element Z.

Question E4

(*A4* and *A7*) Nitrogen forms the compounds nitrosyl chloride (NOCl) and hydrazine (N_2H_4), which consist of discrete molecules. For each compound, draw diagrams of the molecules in which bonds are represented by lines, and each kind of atom has its common valency: nitrogen (3), oxygen (2), chlorine (1) and hydrogen (1). Then, for each case, draw the corresponding Lewis structure.

Question E5

(*A8*) Consider the following pairs of fluorides: (a) AlF_3 and PF_3; (b) CF_4 and SnF_4. One member of each pair is classified as an ionic substance, the other as a covalent substance. State which is which, expressing your reasons in terms of the electronegativities of the elements concerned.

Study comment This is the final *Exit test* question. When you have completed the *Exit test* go back to Subsection 1.2 and try the *Fast track questions* if you have not already done so.

If you have completed **both** the *Fast track questions* and the *Exit test*, then you have finished the module and may leave it here.