The periodic table 3

SUBSHELLS —— *contain* —— orbitals —— *types* —— s (spherical)
—— p (dumb-bell shaped)

p_x p_y p_z

s (max 2e⁻)
p (max 6e⁻)
d (max 10e⁻)
f (max 14e⁻)

increasing energy in a shell

example

The full electron configuration of an atom shows the distribution of its electrons over its subshells.

The **Pauli exclusion principle**: The maximum number of electrons in an orbital is 2. If there are 2 electrons in an orbital, they must have opposite spins.

Ge: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$

remember

Hund's rule: Electrons fill degenerate orbitals to give the maximum number of electrons with the same spin.

$_{24}$Cr: $[Ar]3d^5 4s^1$ $_{29}$Cu: $[Ar]3d^{10} 4s^1$

IONISATION ENERGY —— The electron with the highest energy is removed first. —— The 4s electrons are removed first from transition metals.

first ionisation energy (energy required to remove the first electron)

*n*th ionisation energy (energy required to remove the *n*th electron)

*n*th ionisation energy > (*n* – 1)th ionisation energy because the electron is removed from a more positive ion

(in general) increases across a period as the nuclear charge increases

large jump when an electron is removed from a new main energy level (shell)

The electron in the new energy level is closer to the nucleus and so more strongly attracted.

BUT!

B has a lower 1st ionisation energy than Be because the electrons are removed from different subshells.

O has a lower 1st ionisation energy than N because O has 2e⁻ paired in the same p orbital.
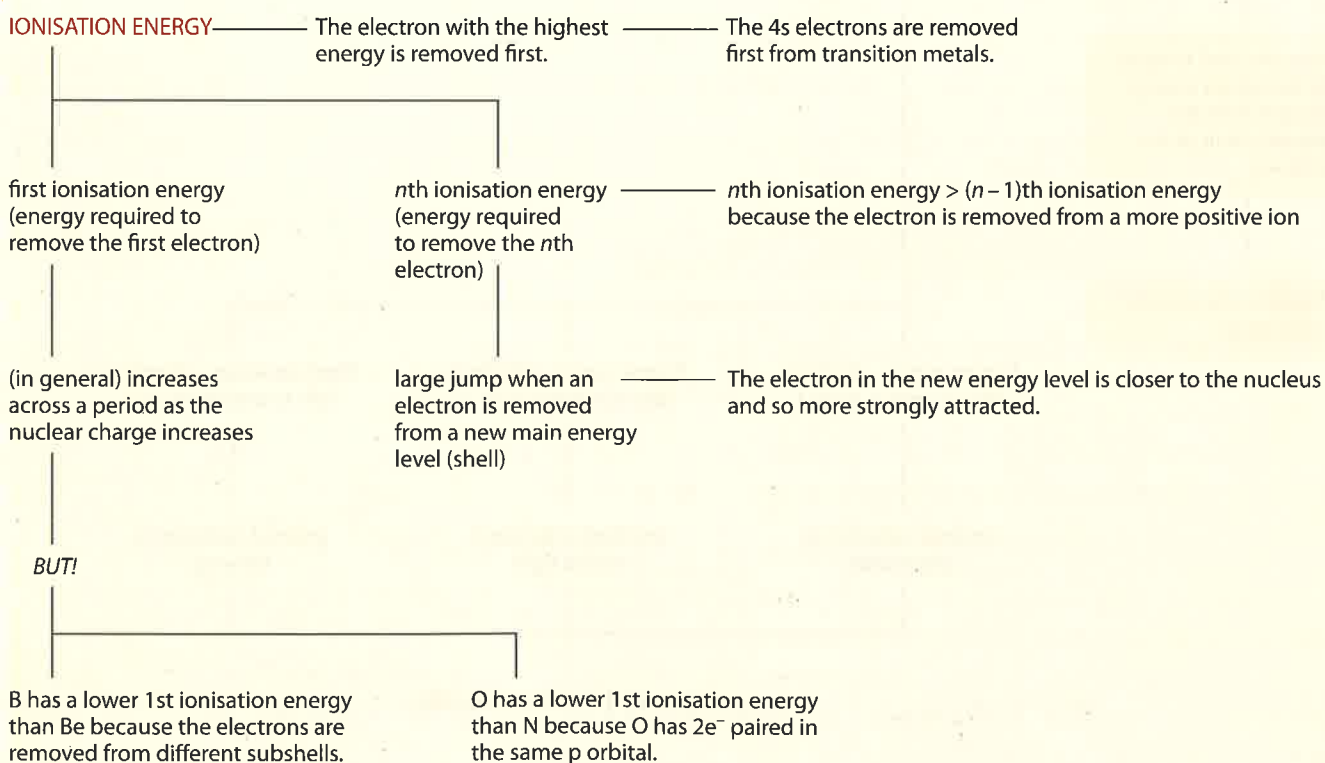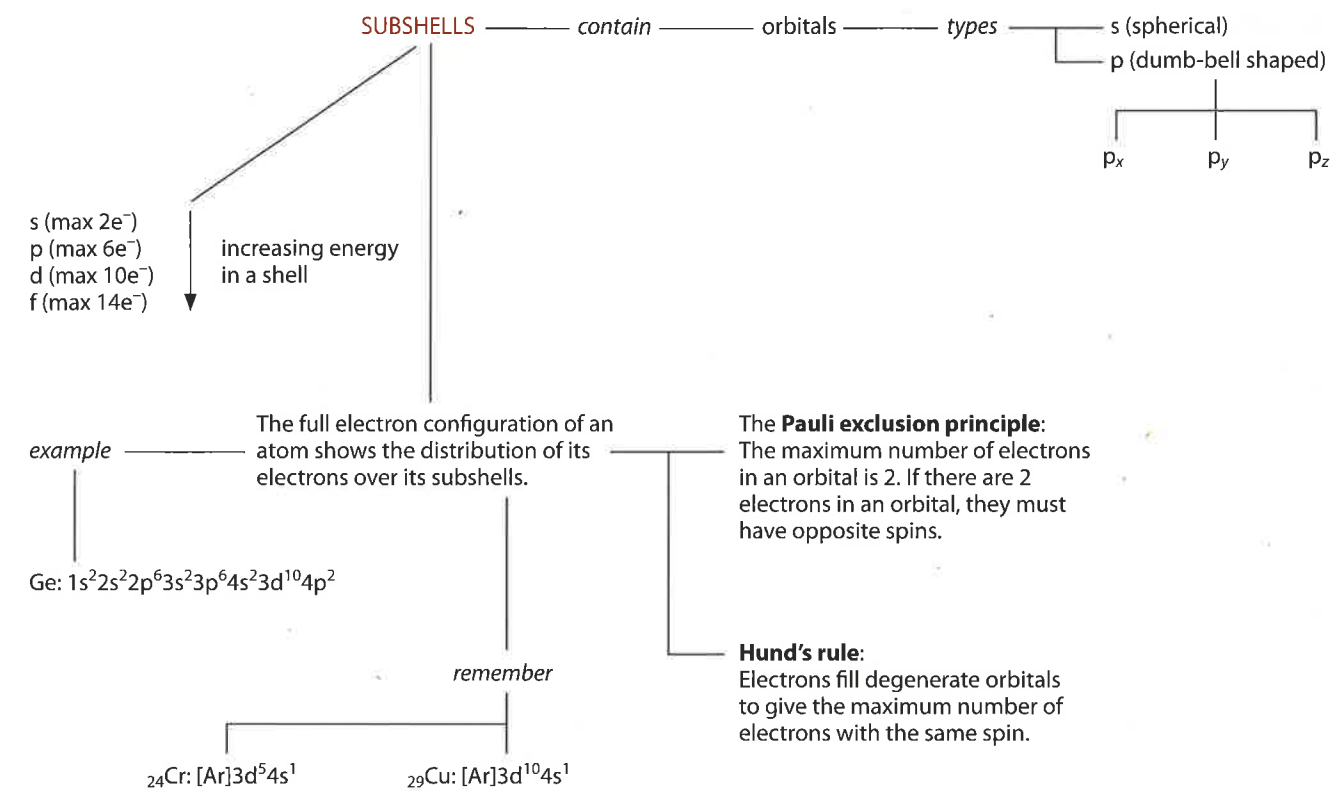
3.1 The periodic table

The elements in the periodic table are arranged in order of atomic number starting with hydrogen, which has atomic number 1. The **groups** are the vertical columns in the periodic table and the **periods** are the horizontal rows (Figure **3.1**).

Most of the elements in the periodic table are metals – these are shown in yellow in Figure **3.1**. The elements shown in pink are non-metals.

Learning objectives

- Understand how the elements in the periodic table are arranged
- Understand the terms **group** and **period**
- Understand how the electron configuration of an element relates to its position in the periodic table

Figure 3.1 The periodic table showing the distribution of metals, metalloids and non-metals.

There are some elements, such as Si, Ge and Sb, that have some of the properties of both metals and non-metals – these are called *metalloids* and are shaded green.

The symbols of the elements that are solid at room temperature and pressure are shown in black in Figure **3.1**, whereas those that are gases are in blue and liquids are in red.

Some of the groups in the periodic table are given names. Commonly used names are shown in Figure **3.2**. The noble gases are sometimes also called the 'inert gases'.

In the periodic table shown in Figure **3.1** it can be seen that the atomic numbers jump from 57 at La (lanthanum) to 72 at Hf (hafnium). This is because some elements have been omitted – these are the lanthanoid elements. The actinoid elements, which begin with Ac (actinium), have also been omitted from Figure **3.1**. Figure **3.2** shows a long form of the periodic table, showing these elements as an integral part.

There is some disagreement among chemists about just which elements should be classified as metalloids – polonium and astatine are sometimes included in the list.

Hydrogen is the most abundant element in the Universe: about 90% of the atoms in the Universe are hydrogen. Major uses of hydrogen include making ammonia and the hydrogenation of unsaturated vegetable oils.

Figure 3.2 The long form of the periodic table, with the names of some of the groups. Hydrogen, though sometimes placed in group 1, does not count as an alkali metal. The lanthanoids and actinoids are also often called 'lanthanides' and 'actinides'.

Mendeleev puzzled over the arrangement of elements in the periodic table until he had a dream in which he claims to have seen the arrangement. Kekulé also came up with the ring structure of benzene after a dream. Does it matter how a scientist comes up with a hypothesis? What is the difference between a scientific and a non-scientific hypothesis? Is it the origins of the hypothesis or the fact that it can be tested experimentally (is falsifiable) that makes it scientific?

Tin has a non-metallic allotrope (grey tin) and prolonged exposure of tin to low temperatures can bring about the transformation to the brittle non-metallic form. The transformation is sometimes called 'tin pest' and there are tales (not necessarily true!) that Napoleon lost the Russian campaign in 1812 because his soldiers had buttons made of tin – in the cold Russian winter the buttons became brittle and their trousers fell down!

Metallic properties

The metallic and non-metallic properties of elements can be related to ionisation energies (see later in this topic).

A metallic structure consists of a regular lattice of positive ions in a sea of delocalised electrons (page **160**). To form a metallic structure, an element must be able to lose electrons fairly readily to form positive ions. Going across a period the ionisation energy increases and so elements lose electrons less easily. So, metallic structures are formed by elements on the left-hand side of the periodic table, which have lower ionisation energies.

Going down a group in the periodic table, ionisation energy decreases, therefore elements are much more likely to exhibit metallic behaviour lower down a group. This can be seen especially well in group 14 going from non-metallic carbon at the top, through the metalloids (Si and Ge) to the metals tin and lead at the bottom.

> In general, metallic elements tend to have large atomic radii, low ionisation energies, less exothermic electron affinity values and low electronegativity.

3.1.1 The periodic table and electron configurations

Electrons in the outer shell (the highest main energy level) of an atom are sometimes called **valence electrons**. The group number of an element is related to the number of valence electrons. All the elements in group 1 have one valence electron (one electron in their outer shell); all the elements in group 2 have two valence electrons. For elements in groups 13–18, the number of valence electrons is given by (group number −10); so the elements in group 13 have three valence electrons and so on. The period number indicates the number of shells (main energy levels) in the atom – or which is the outer shell (main energy level).

The periodic table is divided into blocks according to the highest energy subshell (sub-level) occupied by electrons. So in the s block all the elements have atoms in which the outer shell electron configuration is ns^1 or ns^2 (where n is the shell number) and in the p block it is the p subshell that is being filled (Figure **3.3**).

Four elements are named after the small village of Ytterby in Sweden – yttrium, terbium, erbium and ytterbium.
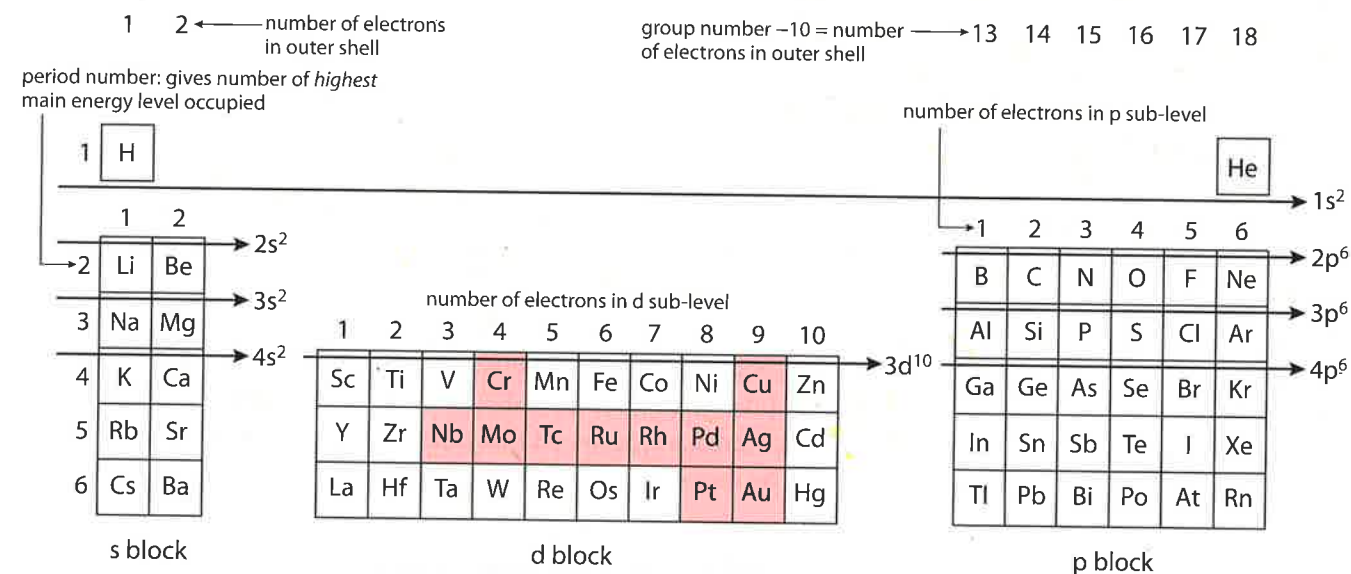

Figure 3.3 Division of the periodic table into blocks.

Consider sulfur – this element is in period 3 and group 16, and so has three shells (the highest occupied shell is the third) and $16 − 10 = 6$ electrons in its outer shell. It is in the p block – therefore its highest energy occupied subshell is a p subshell and the outer shell electron configuration is $3s^2 3p^4$ (six valence electrons).

The noble gases (group 18) have either two (He) or eight electrons (Ne–Rn) in their outer shell. Helium belongs in the s block because its highest energy occupied subshell is 1s, but it is usually put in group 18 with the other noble gases.

Scientists look for patterns in data. They gather evidence, not necessarily just from their own work but also from the published work of other scientists, and analyse the data to discover connections and to try to come up with general laws.

The modern periodic table has developed from one originally conceived by Russian chemist Dmitri Mendeleev in 1869. Mendeleev suggested that the elements were arranged in order of atomic weight (what we would now call relative atomic mass) and produced a table in which elements with similar chemical properties were arranged in vertical groups. Mendeleev took several risks when presenting his data – he suggested that some elements had not been discovered and left spaces for them in his table. Not only did he leave spaces but he also predicted the properties of these unknown elements – he made his hypotheses falsifiable, which added great weight to his theory. The predictions he made were later found to be extremely accurate – the mark of a good theory is that it should be able to be used to predict results that can be experimentally confirmed or refuted. He also suggested that the atomic weights of some elements were incorrect – he realised that tellurium (Te) belonged in the same group as O, S and Se but its atomic weight was higher than iodine and so it should be placed after iodine. Instead of abandoning his theory, he questioned the accuracy of the atomic weight of tellurium and placed it before iodine. This is, of course, the correct place, but Mendeleev's assumption that the atomic weight was lower than that of iodine was not correct.

Henry Moseley, working at the beginning of the 20th century established the connection between atomic number and the periodic table. Like Mendeleev he realised that there were still some elements to be discovered and proposed that three elements between Al and Au were yet to be discovered.

The development of science is not without controversy with regard to who has discovered what. Scientists publish work to make their material available to other scientists and also to establish prior claim on discoveries. For example, the German chemist Julius Lothar Meyer was working on the arrangements of elements at the same time as Mendeleev and came to very similar conclusions – so why is Mendeleev remembered as the father of the modern periodic table rather than Meyer?

Learning objectives

- Understand trends in atomic radius, ionic radius, first ionisation energy, electron affinity and electronegativity across a period
- Understand trends in atomic radius, ionic radius, first ionisation energy, electron affinity and electronegativity down a group

3.2 Physical properties

3.2.1 Variation of properties down a group and across a period

In the next few sections, we will consider how various physical properties vary down a group and across a period in the periodic table.

Atomic radius

The **atomic radius** is basically used to describe the size of an atom. The larger the atomic radius, the larger the atom.

The atomic radius is usually taken to be half the internuclear distance in a molecule of the element. For example, in a diatomic molecule such as chlorine, where two identical atoms are joined together, the atomic radius would be defined as shown in Figure **3.4**.

Atomic radius increases down a group.

This is because, as we go down a group in the periodic table the atoms have increasingly more electron shells. For example, potassium has four shells of electrons but lithium has only two (Figure **3.5**).
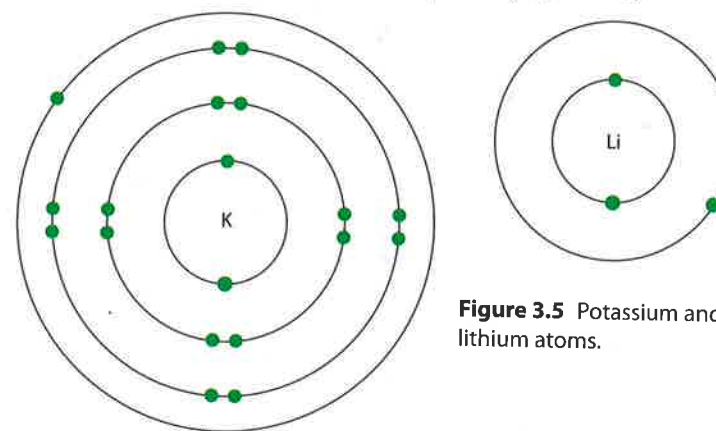

Figure 3.5 Potassium and lithium atoms.

Although the nuclear charge is higher for K, the number of electrons and hence the repulsion between electrons is also greater, and this counteracts any effects due to a greater number of protons in the nucleus.

Atomic radius decreases across a period.

Figure **3.6** shows the variation in atomic radius across period 3 in the periodic table. The reason that atomic radius decreases across a period is that nuclear charge increases across the period with no significant change in shielding. The shielding remains approximately constant because atoms in the same period have the same number of inner shells.

Sodium and chlorine (Figure **3.7**) have the same number of inner shells of electrons (and hence the amount of shielding is similar). However, chlorine has a nuclear charge of 17+ whereas sodium has a nuclear charge of only 11+. This means that the outer electrons are pulled in more strongly in chlorine than in sodium and the atomic radius is smaller.
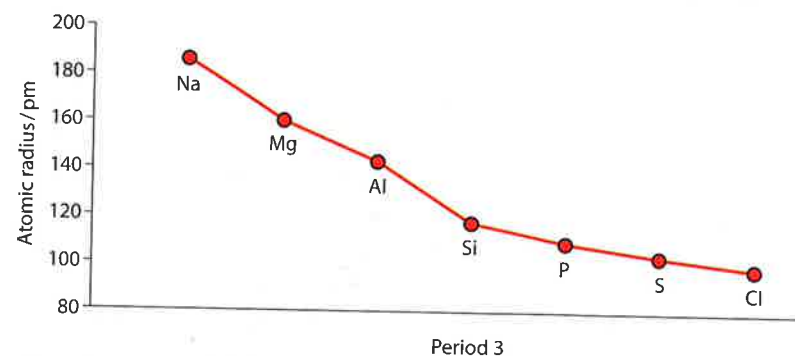

Figure 3.6 The variation in atomic radius across period 3. No atomic radius is shown for argon because it does not form covalent bonds and the internuclear distance between atoms bonded together therefore cannot be measured.
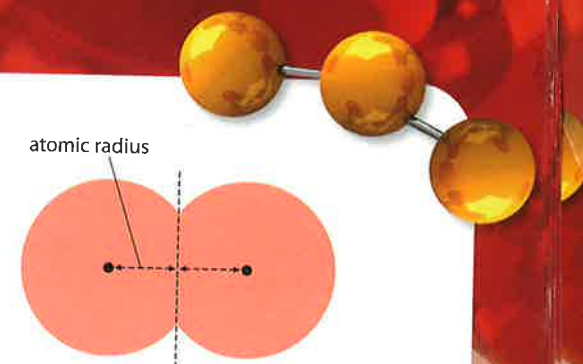

Figure 3.4 The atomic radius of chlorine atoms in a molecule.

Extension

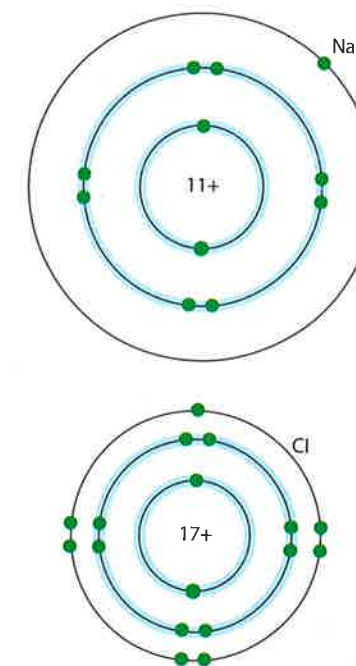It is possible to define two different atomic radii: the covalent radius and the van der Waals' radius.

Figure 3.7 Sodium and chlorine atoms. Inner shells, which shield the outer electrons, are highlighted in blue.

Extension

Although it is not possible to measure an atomic radius for Ar, it is possible to measure a value for the van der Waals' radius of this element.

Ionic radius

The ionic radius is a measure of the size of an ion.

> In general, the ionic radii of positive ions are smaller than their atomic radii, and the ionic radii of negative ions are greater than their atomic radii.

Figure **3.8** shows a comparison of the atomic and ionic radii (1+ ion) for the alkali metals. Each ion is smaller than the atom from which it is formed (by loss of an electron).
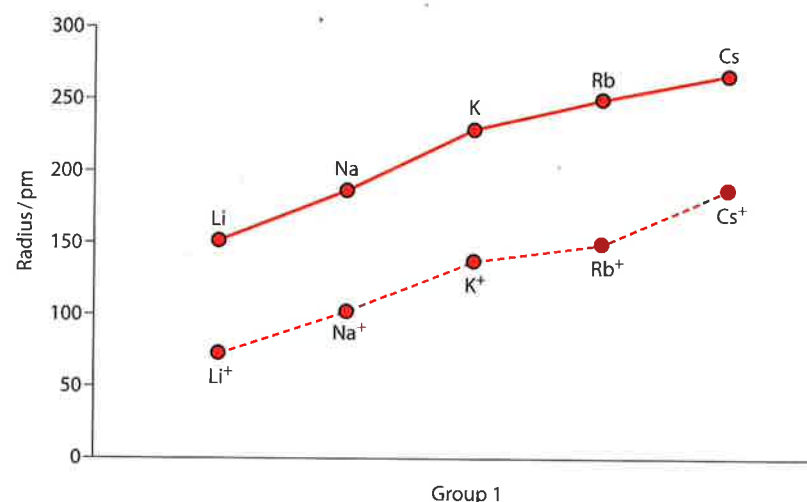
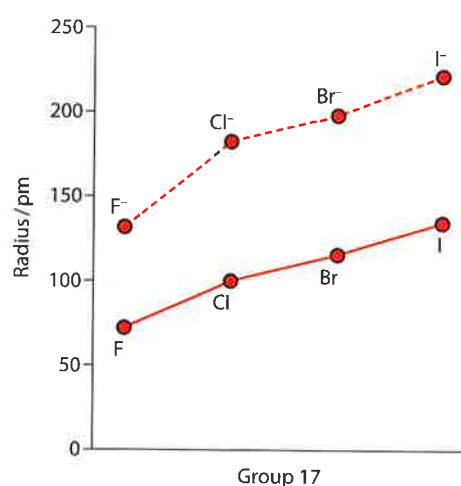**Figure 3.8** Atomic and ionic radii for the alkali metals.

Figure 3.9 A comparison of size between halogen atoms and their ions.

Na is larger than Na^+ because the former has one extra shell of electrons – the electron configuration of Na is 2,8,1, whereas that of Na^+ is 2,8. Also, they both have the same nuclear charge pulling in the electrons (11+), but there is a greater amount of electron–electron repulsion in Na because there are 11 electrons compared with only 10 in Na^+. The electron cloud is therefore larger in Na than in Na^+ because there are more electrons repelling for the same nuclear charge pulling the electrons in.

The fact that negative ions are larger than their parent atoms can be seen by comparing the sizes of halogen atoms with their ions (1−) in Figure **3.9**. Cl^- is larger than Cl because it has more electrons for the same nuclear charge and, therefore, greater repulsion between electrons. Cl has 17 electrons and 17 protons in the nucleus. Cl^- also has 17 protons in the nucleus, but it has 18 electrons. The repulsion between 18 electrons is greater than between 17 electrons, so the electron cloud expands as an extra electron is added to a Cl atom to make Cl^-.

The variation of ionic radius across a period is not a clear-cut trend, because the type of ion changes going from one side to the other – positive ions are formed on the left-hand side of the period and negative ions on the right-hand side.
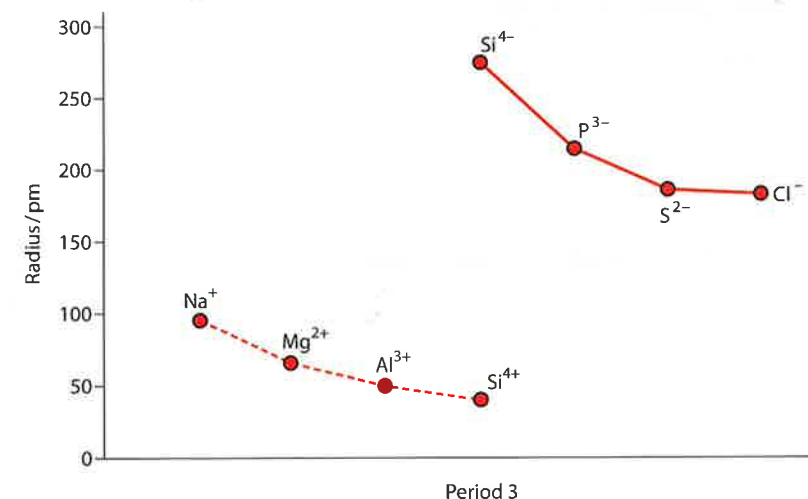
Figure 3.10 Variation of ionic radius of positive and negative ions across period 3.

For positive ions there is a decrease in ionic radius as the charge on the ion increases, but for negative ions the size increases as the charge increases (Figure **3.10**).

Let us consider Na^+ and Mg^{2+} – both ions have the same electron configuration, but Mg^{2+} has one more proton in the nucleus (Figure **3.11**). Because there is the same number of electrons in both ions, the amount of electron–electron repulsion is the same; however, the higher nuclear charge in Mg^{2+} means that the electrons are pulled in more strongly and so the ionic radius is smaller.

Now let us consider P^{3-} and S^{2-}. Both ions have the same number of electrons. S^{2-} has the higher nuclear charge and, therefore, because the amount of electron–electron repulsion is the same in both ions, the electrons are pulled in more strongly in S^{2-} (Figure **3.12**).
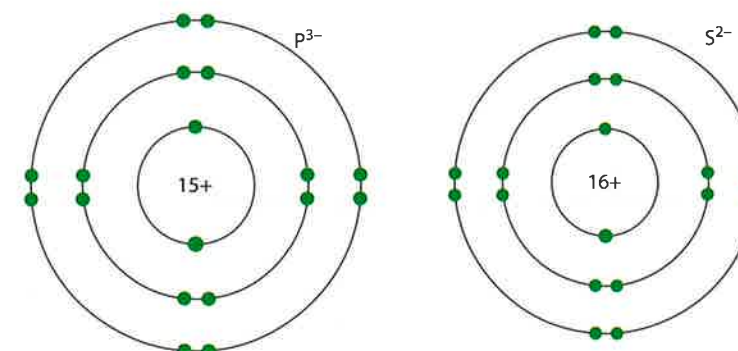
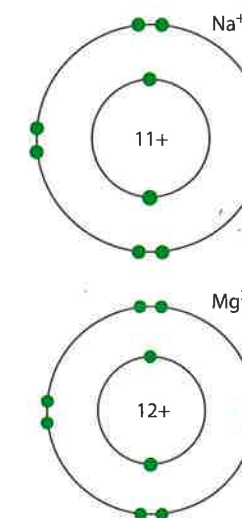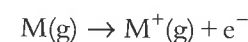**Figure 3.11** Mg^{2+} is smaller than Na^+.

Figure 3.12 S^{2-} is smaller than P^{3-}.

First ionisation energy

The first ionisation energy of an element is the energy required to remove the outermost electron from a gaseous atom – that is, the energy for the process:

$$M(g) \rightarrow M^+(g) + e^-$$

Variation in first ionisation energy down a group

> Down any group in the periodic table, the first ionisation energy decreases.

The decrease in first ionisation energy down a group is shown in Figure **3.13**. The size of the atom increases down the group so that the outer electron is further from the nucleus and therefore less strongly attracted by the nucleus (Figure **3.14**).

Although the nuclear charge also increases down a group, this is largely balanced out by an increase in shielding down the group, as there are more electron energy levels (shells). It is the increase in size that governs the change in first ionisation energy.
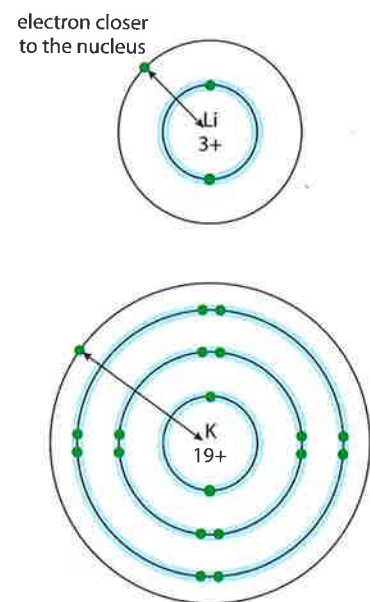
electron closer to the nucleus

Figure 3.14 Potassium has a lower first ionisation energy than lithium. Electrons that shield the outer electron are highlighted in blue.
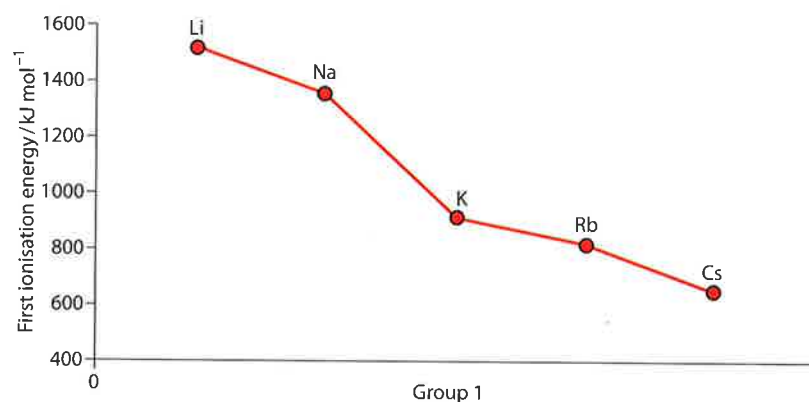

Figure 3.13 First ionisation energy for group 1.

Variation in first ionisation energy across a period

> The general trend is that first ionisation energy increases from left to right across a period. This is because of an increase in nuclear charge across the period.

The nuclear charge increases from Na (11+) to Ar (18+) as protons are added to the nucleus. The electrons are all removed from the same main energy level (third shell) and electrons in the same energy level do not shield each other very well. Therefore the attractive force on the outer electrons due to the nucleus increases from left to right across the period
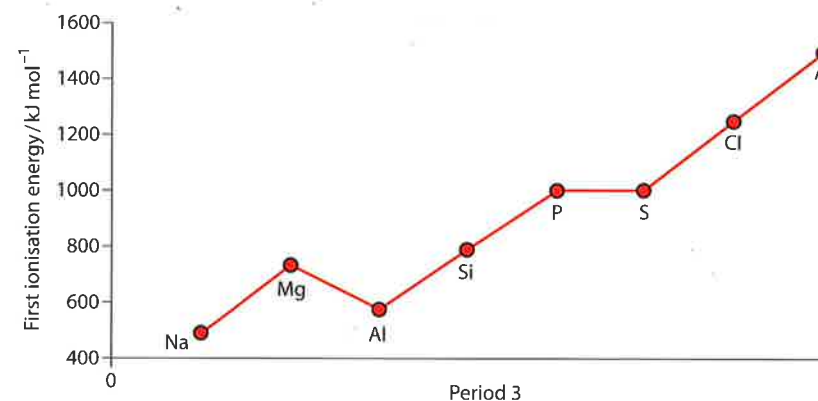

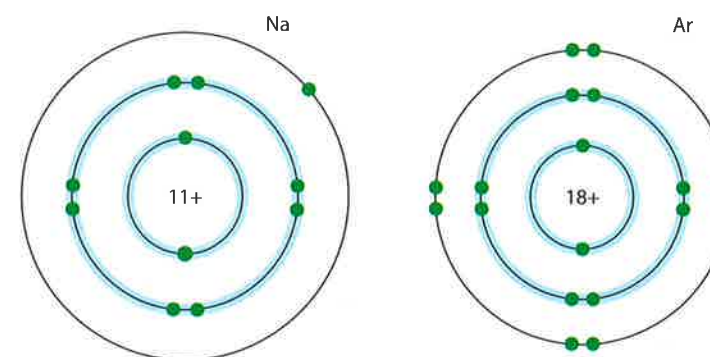**Figure 3.15** The variation in first ionisation energy across period 3 in the periodic table.

Figure 3.16 Sodium and argon atoms.

and the outer electron is more difficult to remove from an argon atom (Figure **3.16**). The argon atom is also smaller than the sodium atom and, therefore, the outer electron is closer to the nucleus and more strongly held.

There are two exceptions to the general increase in first ionisation energy across a period, and these are discussed on page **78**.

Electron affinity

The **first electron affinity** involves the energy change when one electron is added to a gaseous atom:

$$X(g) + e^- \rightarrow X^-(g)$$
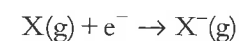
It is defined more precisely as the enthalpy change when one electron is added to each atom in one mole of gaseous atoms under standard conditions. Electron affinity is difficult to measure experimentally and data are incomplete.

The first electron affinity is exothermic for virtually all elements – it is a favourable process to bring an electron from far away (infinity) to the outer shell of an atom, where it feels the attractive force of the nucleus.

Exam tip
The exceptions to the trend are required knowledge for all students – refer to page **78**.

Variation of electron affinity down group 17

A graph of electron affinity down group 17 is shown in Figure **3.17**. The general trend is that electron affinity decreases down a group, but it can be seen that chlorine has the most exothermic value for electron affinity. A similar trend in electron affinity values is seen going down group 16 and group 14.

The electron affinity becomes less exothermic from Cl to I as the size of the atom increases. The electron is brought into the outer shell of the atom and as the atom gets bigger there is a weaker attraction between the added electron and the nucleus as it is brought to a position which is further from the nucleus.
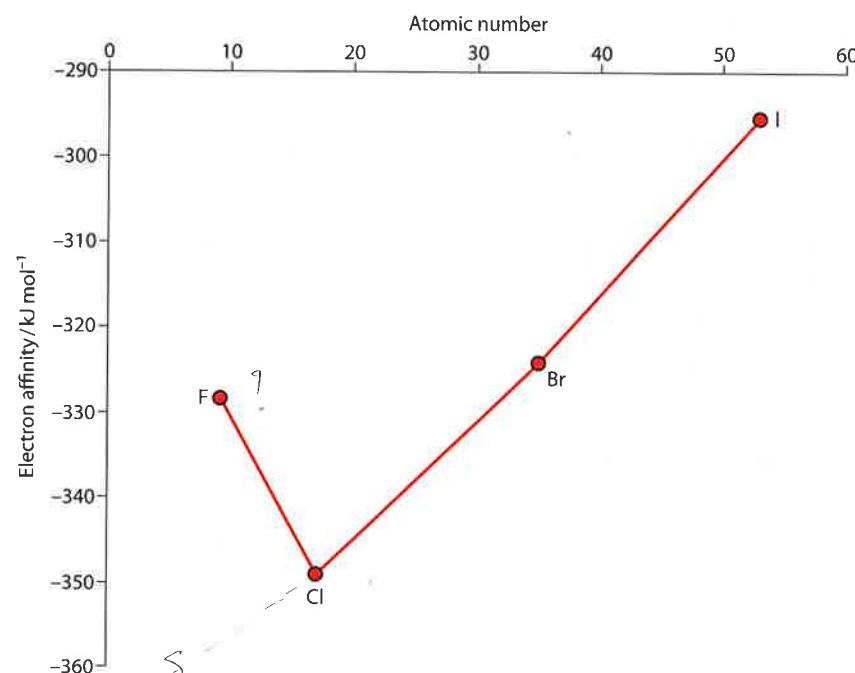

Figure 3.17 Electron affinity values of group 17 elements.

Extension

Electron–electron repulsion also affects the electron affinity and as the atom gets smaller the electrons are, on average, closer together and there is more electron–electron repulsion. This means that the electron affinity should be less exothermic when an electron is added to a smaller atom. Going from F to Cl the electron affinity becomes more exothermic because the decrease in electron–electron repulsion outweighs the fact that there is less attraction between the electron and the nucleus.

Variation in electron affinity across a period

The general trend in electron affinity from group 13 to group 17 is shown in Figure **3.18**.
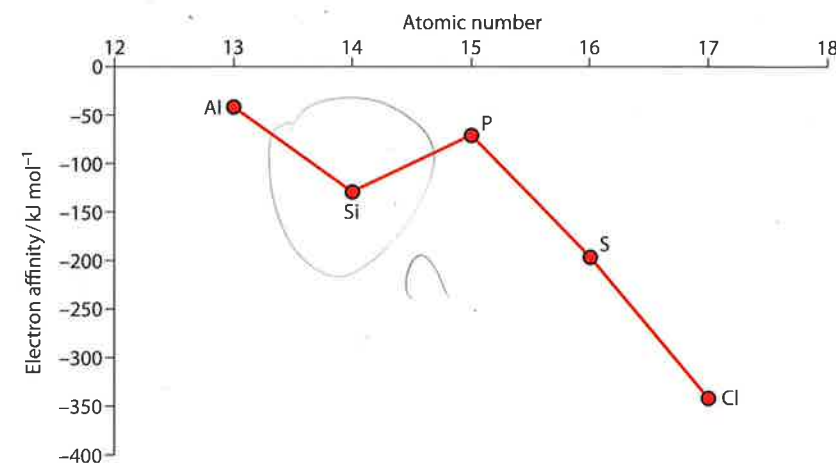

Figure 3.18 Electron affinity values across period 3.

The general trend is that the electron affinity becomes more exothermic. This is because of an increase in nuclear charge and a decrease in atomic radius from left to right across the period. For instance, F has a higher nuclear charge and a smaller radius than O and so the electron will be more strongly attracted when it is brought into the outer shell of the F atom.

Extension

Phosphorus has a less exothermic electron affinity than silicon because of its electron configuration. P has three unpaired electrons in three separate p orbitals and when one electron is added this electron must be paired up in the same p orbital as another electron – this introduces an extra repulsion term that is not present in Si. The arguments being used here are very similar to those for the variation of first ionisation energy across a period discussed in Topic **2**.

Electronegativity

Electronegativity is a measure of the attraction of an atom in a molecule for the electron pair in the covalent bond of which it is a part.

In a covalent bond between two different atoms, the atoms do not attract the electron pair in the bond equally. How strongly the electrons are attracted depends on the size of the individual atoms and their nuclear charge.

Electronegativity decreases down a group – this is because the size of the atoms increases down a group. Consider hydrogen bonded to either F or Cl (Figure **3.19**). The bonding pair of electrons is closer to the F nucleus in HF than it is to the Cl nucleus in HCl. Therefore the electron pair is more strongly attracted to the F nucleus in HF and F has a higher electronegativity than Cl.
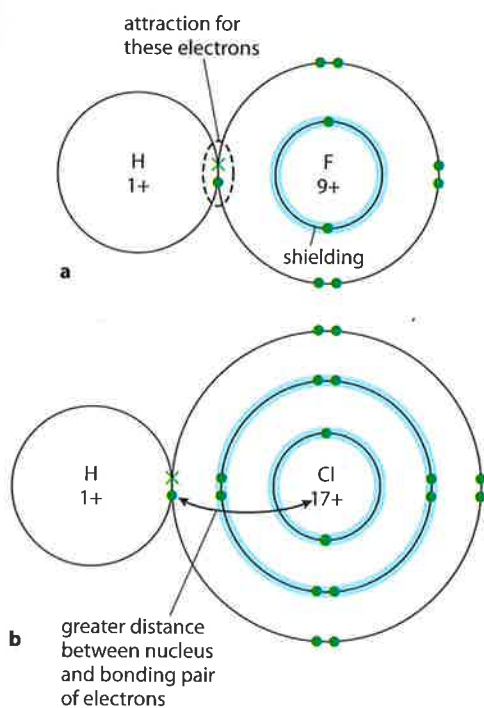
Figure 3.19 Hydrogen bonded to **a** fluorine and **b** chlorine.
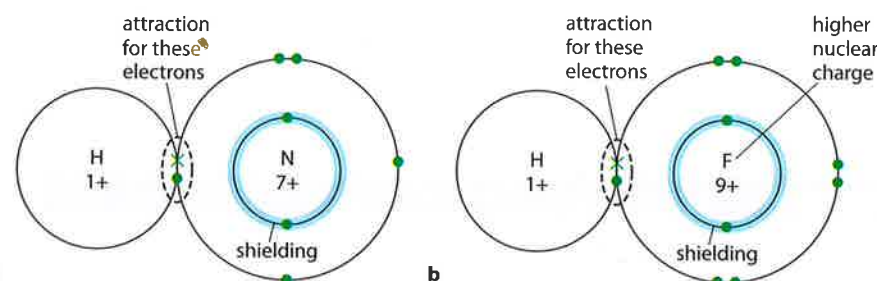
Chlorine's higher nuclear charge does not make it more electronegative than fluorine because the shielding from inner shells (shown with blue shading in Figure **3.19**) increases from F to Cl such that the effective nuclear charge felt by the bonding electrons is approximately the same in each case (+7 if shielding were perfect).

Electronegativity increases across a period – the reason for this is the increase in nuclear charge across the period with no significant change in shielding. The shielding remains approximately constant because atoms in the same period have the same number of inner shells.

So, if an N–H bond is compared with an F–H bond (Figure **3.20**), the electrons in the N–H bond are attracted by the seven protons in the nucleus, but the electrons in the F–H bond are attracted by the nine protons in the F nucleus. In both cases the shielding is approximately the same (because of two inner shell electrons).

Figure 3.20 Hydrogen bonded to **a** nitrogen and **b** fluorine.

? Test yourself

1 Give the names of the following elements:
   a the element in period 3 and group 14
   b the element in period 5 and group 16
   c the element in the same group as sulfur but in period 6
   d a halogen in period 5
   e an element in the same period as potassium that has five outer shell electrons

2 State whether the following properties increase or decrease across a period:
   a electronegativity
   b atomic radius

3 Arrange the following in order of increasing radius (smallest first):
   a Ba   Mg   Sr   Ca
   b O^{2-} Na^+ F^-
   c Na Na^+ K Al^{3+}
   d S   Cl I^- Cl^- S^{2-}

4 Are the following **true** or **false**?
   a A germanium atom is smaller than a silicon atom, but silicon has a higher first ionisation energy.
   b Selenium has a higher first ionisation energy and electronegativity than sulfur.
   c Antimony has a higher first ionisation energy and electronegativity than tin.
   d Cl^- is bigger than Cl, but Se^{2-} is smaller than Se.
   e Iodine has a higher electronegativity than tellurium but a lower electronegativity than bromine.

5 Based on the following data, which element (**X** or **Y**) is more likely to be a metal?

	First ionisation energy / kJ mol^{-1}	Atomic radius / nm	Electronegativity
X	736	0.136	1.3
Y	1000	0.104	2.6

3.2.2 Properties of elements in group 1 and group 17

Group 1 elements

The elements in group 1 are known as the **alkali metals**. They are all highly reactive, soft, low melting point metals (Table **3.1**). They are placed together in group 1 for two reasons – they all have one electron in their outer shell and they react in very similar ways (similar chemical properties).

> The reactions of an element are determined by the number of electrons in the outer shell (highest main energy level) of their atoms. Because elements in the same group in the periodic table have the same number of electrons in their outer shell, they react in basically the same way.

The bonding in all these elements is metallic. The solid is held together by electrostatic attraction between the positive ions in the lattice and the delocalised electrons (see page **160**).

The attraction for the delocalised, negatively-charged, electrons is due to the nucleus of the positive ion. As the ions get larger as we go down the group, the nucleus becomes further from the delocalised electrons and the attraction becomes weaker (Figure **3.22**). This means that less energy is required to break apart the lattice going down group 1.

> Melting point decreases down group 1 (Figure **3.21**).

> Liquid sodium is used as a coolant in some nuclear reactors.

Element	Symbol	Atomic number	Electron configuration	Density / g cm^{-3}	Melting point / °C	Boiling point / °C
lithium	Li	3	[He]2s^1	0.53	180	1330
sodium	Na	11	[Ne]3s^1	0.97	98	890
potassium	K	19	[Ar]4s^1	0.86	64	774
rubidium	Rb	37	[Kr]5s^1	1.53	39	688
caesium	Cs	55	[Xe]6s^1	1.87	29	679

Table 3.1 Similarities in alkali metal properties.
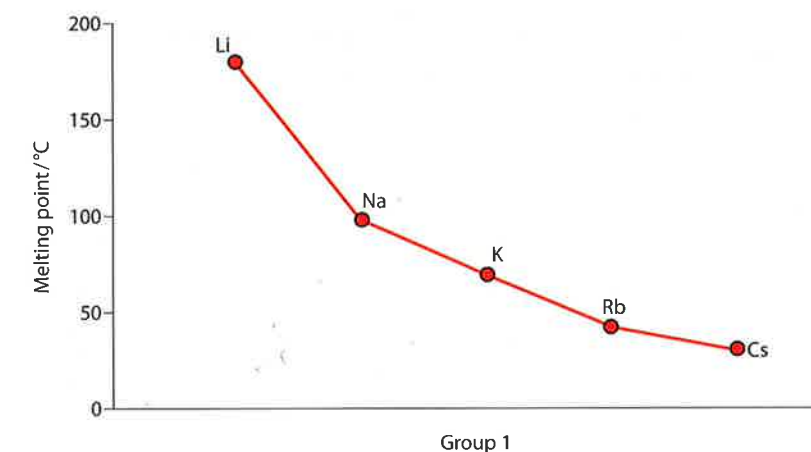
Figure 3.21 Variation in melting point in group 1.
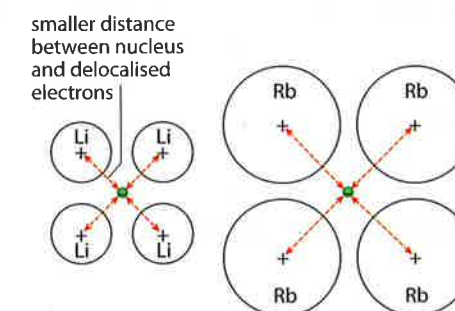
Figure 3.22 The delocalised electrons are attracted more strongly in lithium than in rubidium.

Reactions of the elements in group 1

The elements in group 1 are all reactive metals that react readily with, among other things, oxygen, water and halogens. The atoms all have one electron in their outer shell, and virtually all reactions involve the loss of this outer shell electron to form a positive ion, M^+. The reactions become more vigorous going down the group because the ionisation energy decreases as the size of the atom increases. This means that, for example, caesium loses its outer electron to form a positive ion much more easily than sodium and will react more vigorously.

Reaction with oxygen

The alkali metals react vigorously with oxygen and all tarnish rapidly in air. The general equation for the reaction is:

$$4M(s) + O_2(g) \rightarrow 2M_2O(s)$$
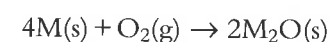
Reaction with water

The alkali metals react rapidly with water. The general equation for the reaction is:

$$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$$
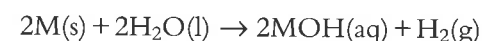
An alkaline solution is formed. The alkali metal hydroxides are strong bases and ionise completely in aqueous solution (page **321**).

The reaction with water becomes more vigorous going down the group – sodium melts into a ball, fizzes rapidly and moves around on the surface of the water; potassium bursts into flames (lilac); and caesium explodes as soon as it comes into contact with water.

M_2O is a basic oxide that will dissolve in water to form an alkaline solution, containing M^+ and OH^- ions.

Lithium, sodium and potassium are all less dense than water.

Group 17 elements

The elements in group 17 are known as the **halogens**. They are all non-metals consisting of diatomic molecules (X_2). Some properties are given in Table **3.2**.

Element	Symbol	Atomic number	Electron configuration	Colour	Melting point/°C	Boiling point/°C	Physical state at room temperature and pressure
fluorine	F	9	$[He]2s^2 2p^5$	pale yellow	−220	−188	gas
chlorine	Cl	17	$[Ne]3s^2 3p^5$	yellow–green	−101	−35	gas
bromine	Br	35	$[Ar]3d^{10}4s^2 4p^5$	deep red liquid, orange vapour	−7	59	liquid
iodine	I	53	$[Kr]4d^{10}5s^2 5p^5$	grey shiny solid, purple vapour	114	184	solid

Table 3.2 Properties of halogens.

Variation of melting point in group 17

The melting points of the halogens increase going down the group (Figure **3.23**).
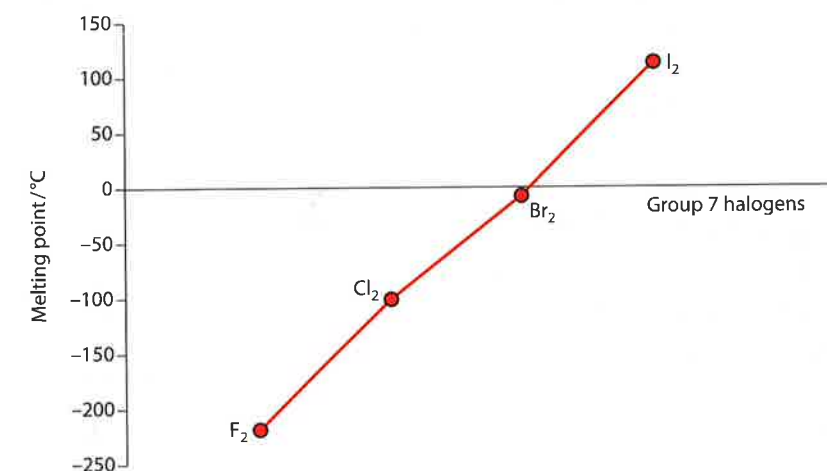

Figure 3.23 Variation in melting point in group 17.

As the relative molecular masses of the X_2 halogen molecules increase, the London forces (page **148**) between molecules get stronger. This means that more energy must be supplied to separate the molecules from each other.

Reactions of the elements in group 17

All the atoms of the elements in group 17 have seven electrons in their outer shell and react either by gaining an electron to form X^- ions or by forming covalent compounds. Reactivity decreases down the group, and fluorine is the most reactive element known, reacting directly with virtually every other element in the periodic table. The variation in reactivity of the halogens cannot be as easily explained as for the alkali metals. The very high reactivity of fluorine can be explained in terms of an exceptionally weak F–F bond and the strength of the bonds it forms with other atoms. The reactivity in terms of the formation of X^- ions can be related to a decrease in electron affinity (energy released when an electron is added to a neutral atom) going down the group as the electron is added to a shell further away from the nucleus, but this is only part of the story and several factors must be considered when explaining the reactivity of the halogens.

The halogens all react with the alkali metals to form salts. The general equation is:

$$2M(s) + X_2(g) \rightarrow 2MX(s)$$
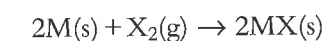
The salts formed are all white/colourless, fairly typical ionic compounds. They contain M^+ and X^- ions. All alkali metal chlorides, bromides and iodides are soluble in water and form colourless, neutral solutions.

Chlorine is produced by the electrolysis of brine. Worldwide annual production is about 60 million tonnes. Chlorine and its compounds are involved in the production of about 90% of the most important pharmaceuticals. Its biggest single use is in the production of PVC.

How vigorous the reaction is depends on the particular halogen and alkali metal used – the most vigorous reaction occurs between fluorine and caesium, and the least vigorous between lithium and iodine.

Displacement reactions of halogens

These are reactions between a solution of a halogen and a solution containing halide ions – they are discussed in more detail on page **404**. A small amount of a solution of a halogen is added to a small amount of a solution containing a halide ion, and any colour changes are observed (see Table **3.3**). Potassium chloride, bromide and iodide solutions are all colourless. The colours of chlorine, bromine and iodine solutions are shown in Figure **3.24**.

Orange colour, due to the production of bromine.

Red-brown colour, due to the production of iodine.

	KCl(aq)	KBr(aq)	KI(aq)
Cl_2(aq)	no reaction	orange solution	dark red–brown solution
Br_2(aq)	no reaction	no reaction	dark red–brown solution
I_2(aq)	no reaction	no reaction	no reaction

Table 3.3 Results of reactions between halogen solutions and solutions containing halide ions.

The reactions that occur are:

$$Cl_2(aq) + 2KBr(aq) \rightarrow 2KCl(aq) + Br_2(aq)$$

Ionic equation: $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

$$Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$$

Ionic equation: $Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$

$$Br_2(aq) + 2KI(aq) \rightarrow 2KBr(aq) + I_2(aq)$$

Ionic equation: $Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$

The more reactive halogen displaces the halide ion of the less reactive halogen from solution – chlorine displaces bromide ions and iodide ions from solution, and bromine displaces iodide ions from solution.

These reactions are all **redox reactions** (Topic **9**), in which a more reactive halogen oxidises a less reactive halide ion. Chlorine is a stronger oxidising agent than bromine and iodine; it will oxidise bromide ions to bromine, and iodide ions to iodine. Bromine is a stronger oxidising agent than iodine and will oxidise iodide ions to iodine. In terms of electrons, chlorine has the strongest affinity for electrons and will remove electrons from bromide ions and iodide ions.
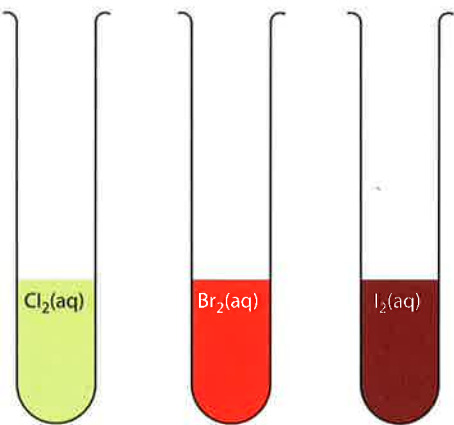
Figure 3.24 Chlorine solution is pale yellow–green (almost colourless if it is dilute), bromine solution is orange, and iodine solution is red–brown.
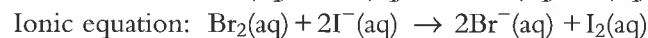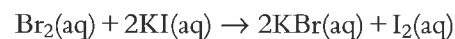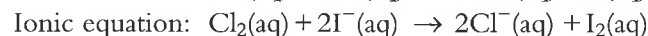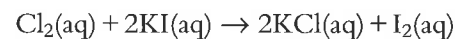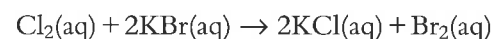
Cl_2(aq) Br_2(aq) I_2(aq)

## 3.2.3 Oxides of period 2 and period 3 elements

Oxides of elements may be classified as basic, acidic or amphoteric. The nature of the oxides changes across a period and Table **3.4** shows how the oxides change from basic to amphoteric to acidic across period 3.

In general, metallic oxides are **basic** and non-metallic oxides are **acidic**.

A basic oxide is one that will react with an acid to form a salt and, if soluble in water, will produce an alkaline solution. Sodium oxide reacts with water to form sodium hydroxide:

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

Sodium oxide reacts with acids such as sulfuric acid to form salts:

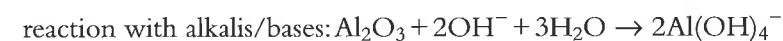$$Na_2O(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$$
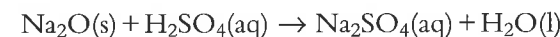
Magnesium oxide, because of the relatively high charges on the ions, is not very soluble in water but it does react to a small extent to form a solution of magnesium hydroxide, which is alkaline:

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$$
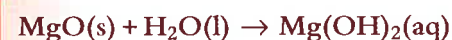
Aluminium is on the dividing line between metals and non-metals and forms an amphoteric oxide – these have some of the properties of a basic oxide and some of an acidic oxide. Aluminium is exhibiting properties between those of a metal (basic) oxide and those of a non-metal (acidic) oxide.

Aluminium oxide does not react with water but it does display amphoteric behaviour in that it reacts with both acids and bases to form salts:

reaction with acids: $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$

reaction with alkalis/bases: $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$
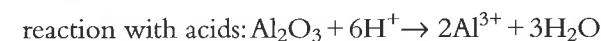
Amphoteric oxides react both with acids and with bases.

Learning objectives

- Describe the changes from basic to acidic oxides across a period
- Write equations for the reactions of oxides with water and predict the acidity of the resulting solutions

Exam tip
Reactions highlighted like this must be learnt for examinations.

	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulfur
Formula of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2 SO_3
Nature of element	metal			non-metal		
Nature of oxide	basic		amphoteric	acidic		
Reaction with water	soluble, reacts	sparingly soluble, some reaction	insoluble		soluble, reacts	
Solution formed	alkaline	slightly alkaline	–		acidic	

Table 3.4 The acid–base nature of some period 3 oxides.

The remaining oxides in Table **3.4** are all acidic oxides. An acidic oxide is one that reacts with bases/alkalis to form a salt and, if soluble in water, will produce an acidic solution.
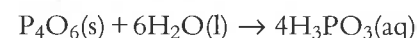
P_4O_6 (phosphorus(III) oxide) and P_4O_{10} (phosphorus(V) oxide) form phosphoric(III) and phosphoric(V) acid, respectively, when they react with water:

$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

SO_2 (sulfur(IV) oxide) and SO_3 (sulfur(VI) oxide) form sulfuric(IV) and sulfuric(VI) acid, respectively, when they react with water:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$
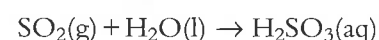
Nitrogen oxides

There are many oxides of nitrogen, ranging in formula from N_2O to N_2O_5. Two of the most environmentally important are nitrogen(II) oxide (NO) and nitrogen(IV) oxide (NO_2).

Nitrogen reacts with oxygen at very high temperatures to form NO (nitrogen monoxide, nitric oxide or nitrogen(II) oxide):

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$
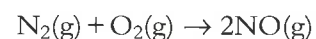
This reaction occurs in the internal combustion engine. NO is virtually insoluble in water and is classified as a neutral oxide.

NO can be oxidised in the atmosphere to NO_2, which can react with water to produce nitric(V) acid (HNO_3), which is one of the acids responsible for acid deposition (see Subtopic **8.5**). NO_2 can be classified as an acidic oxide:

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

N_2O (nitrogen(I) oxide, nitrous oxide) is another neutral oxide. N_2O is also known as laughing gas and major uses include as an anaesthetic and as the propellant in 'squirty cream'.

Phosphoric(V) acid is an ingredient of Coca-Cola®.

Non-metal oxides such as SO_2 are produced in various industrial processes and when coal is burnt. This can be responsible for **acid rain**, which can, among other things, kill fish in lakes and trees in forests.

Nitrogen oxides (NO_x) may be formed in internal combustion engines, and these are involved in the formation of photochemical smog in cities (Figure **3.25**).

Figure 3.25 A photochemical smog over Hong Kong.

Nature of science

Science and the technology that develops from it have been used to solve many problems – but it can also *cause* them. The development of industrial processes that produce acidic gases led to acid rain being a major environmental problem. Acid rain, and its associated problems, is important to people across the world and it is vital that scientists work to improve the public understanding of the issues involved. Scientists also work as advisors to politicians in developing policies to solve these problems.

Advancements in science have often arisen from finding patterns in data. An understanding of the patterns in physical and chemical properties of elements in the periodic table has allowed chemists to make new substances. For instance, the knowledge that sulfur formed a range of compounds with nitrogen probably led scientists to attempt to make selium–nitrogen and tellurium–nitrogen compounds.

Test yourself

6 Write balanced equations for the following reactions:
  a rubidium with water
  b potassium with bromine
  c chlorine solution with potassium bromide solution
  d sodium oxide with water
  e sulfur(VI) oxide with water

7 State whether trends down the group in each of the following properties are the same or different when group 1 and group 17 are compared:
  a electronegativity
  b reactivity
  c melting point
  d ionisation energy

8 State whether an acidic or alkaline solution will be formed when each of the following is dissolved in/reacted with water:
  a SO_3
  b MgO
  c Na

Learning objectives

- Describe the characteristic properties of transition metals
- Explain why transition metals have variable oxidation numbers
- Explain the formation and describe the shape of complex ions
- Explain why transition metal complex ions are coloured
- Explain the factors that affect the colour of a transition metal complex
- Understand the magnetic properties of transition metal atoms and ions
- Describe some uses of transition metals and their compounds as catalysts

Exam tip

Remember that chromium and copper have slightly different electron configurations.

Figure 3.26 Zinc is not a transition element but the classification of scandium is more controversial.

Exam tip

Scandium is regarded as a transition element on the syllabus.

The 'transition elements' are often called the 'transition metals'.

3.3 First-row d-block elements (HL)

3.3.1 The transition elements (d block)

The first-row d-block elements are:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30

There are also two other rows of d-block elements.

They are called 'd-block' elements because the subshell being filled across this series is the 3d subshell. The electron configurations range from $[Ar]4s^2 3d^1$ for scandium to $[Ar]4s^2 3d^{10}$ for zinc:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$[Ar]4s^1 3d^1$	$[Ar]4s^2 3d^2$	$[Ar]4s^2 3d^3$	$[Ar]4s^1 3d^5$	$[Ar]4s^2 3d^5$	$[Ar]4s^2 3d^6$	$[Ar]4s^2 3d^7$	$[Ar]4s^2 3d^8$	$[Ar]4s^1 3d^{10}$	$[Ar]4s^2 3d^{10}$

The **transition elements** can be defined as different from 'the d-block elements', and the definition we will use here is:

> a transition element is an element that forms at least one stable ion with a partially filled d subshell

According to this definition, zinc is not counted as a transition element because the only ion it forms is the 2+ ion, with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (full d subshell). Zinc (Figure **3.26**) does not exhibit some of the typical characteristic properties of transition metals detailed below (e.g. it does not form coloured compounds). The inclusion/exclusion of scandium as a transition element according to this definition is much more controversial. In virtually every compound scandium has oxidation number +3 (no d electrons) however, it also forms a couple of compounds (ScH_2 and $CsScCl_3$) with formal oxidation number +2, but the bonding in these compounds is more complicated and they do not necessarily contain the 2+ ion.

Properties of the transition elements

We have already studied the variation in properties of a set of eight elements across the periodic table when we looked at the properties of period 3 elements. The transition elements also form a set of eight elements across the periodic table, but these are much more similar to each other than the elements across period 3. For instance, they are all metals rather than showing a change from metal to non-metal.

The variation in first ionisation energy and atomic radius of the transition elements and period 3 elements are compared in Figures **3.27** and **3.28**. It can be seen that the variation of ionisation energy and atomic radius across the series of the transition elements is much smaller than across period 3.
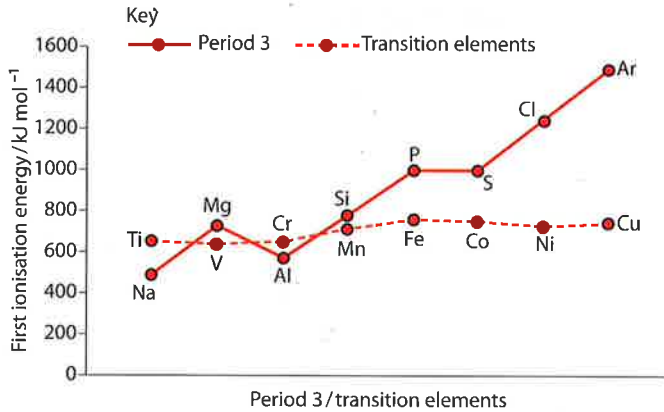
Figure 3.27 A comparison of the variation of first ionisation energy across period 3 with that across the transition metal series.
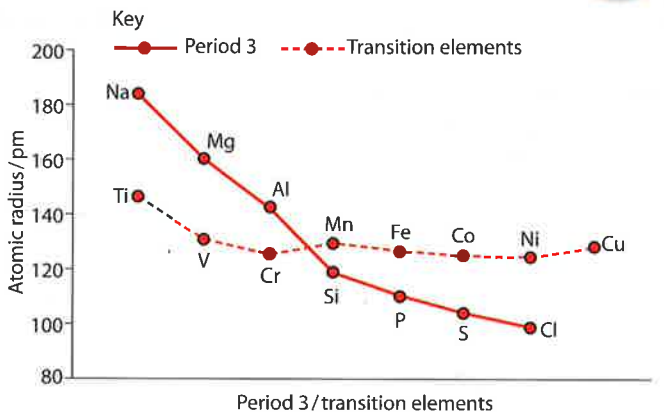
Figure 3.28 A comparison of the variation of atomic radius across period 3 with that across the transition metal series.

Because of their similarity it is possible to draw up a list of characteristic properties of transition elements:

- Transition elements are all typical metals – they have high melting points and densities.
- Transition elements can exhibit more than one oxidation number in compounds/complexes.
- Transition elements form complex ions.
- Transition elements form coloured compounds/complexes.
- Transition elements and their compounds/complexes can act as catalysts in many reactions.
- Compounds of transition elements can exhibit magnetic properties.

Exam tip

The last five properties are the most important for examinations.

Ionisation of transition elements

Transition elements form positive ions. The electron configurations of some transition metal ions are shown in Table **3.5**.

The 4s electrons are always removed before the 3d electrons when an ion is formed.

Element	Electron configuration	Ion	Electron configuration
Cr	$[Ar]4s^1 3d^5$	Cr^{2+}	$[Ar]3d^4$
		Cr^{3+}	$[Ar]3d^3$
Mn	$[Ar]4s^2 3d^5$	Mn^{2+}	$[Ar]3d^5$
Fe	$[Ar]4s^2 3d^6$	Fe^{2+}	$[Ar]3d^6$
		Fe^{3+}	$[Ar]3d^5$
Co	$[Ar]4s^2 3d^7$	Co^{2+}	$[Ar]3d^7$
Cu	$[Ar]4s^1 3d^{10}$	Cu^+	$[Ar]3d^{10}$
		Cu^{2+}	$[Ar]3d^9$

Table 3.5 Electron configurations of transition metals and their ions.

Oxidation number and oxidation state are often used interchangeably.

3.3.2 Variable oxidation numbers

The positive oxidation numbers (oxidation states) exhibited by the transition elements are shown in Figure **3.29**. The greatest number of different oxidation numbers and the highest oxidation numbers are found in the middle of the series. From titanium to maganese there is an increase in the total number of electrons in the 4s and 3d subshells, so the maximum oxidation number increases. Maganese has the electron configuration $[Ar]4s^23d^5$ and therefore a maximum oxidation number of +7. Iron has eight electrons in the 4s and 3d subshells and would be expected to have a maximum oxidation number of +8, but the ionisation energy increases from left to right across the transition elements series and it becomes more difficult to reach the highest oxidation numbers towards the right-hand side of the series. The chemistry of copper and nickel is, for the same reason, dominated by the lower oxidation numbers.

All transition metals show oxidation number +2. In most cases this is because they have two electrons in the 4s subshell, and removal of these generates an oxidation number of +2.

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
			7				
		6	6	6			
	5	5	5	5			
4	4	4	4	4	4	4	4
3	3	3	3	3	3	3	3
2	2	2	2	2	2	2	2
1	1	1	1	1	1	1	1
0	0	0	0	0	0	0	0

Figure 3.29 Oxidation numbers of transition metals in compounds. Not all oxidation numbers are common.

Why more than one oxidation number?

The 4s and 3d subshells are close in energy, and there are no big jumps in the successive ionisation energies when the 4s and 3d electrons are removed. Therefore the number of electrons lost will depend on a variety of factors such as lattice enthalpy, ionisation energy and hydration enthalpy. Electrons are not removed in order to generate the nearest noble gas electron configuration. The graph in Figure **3.30** shows a comparison of the first seven ionisation energies of magnesium and manganese. It can be seen that there is a very large jump between the second and third ionisation energies of magnesium, but that there are no such jumps for manganese.
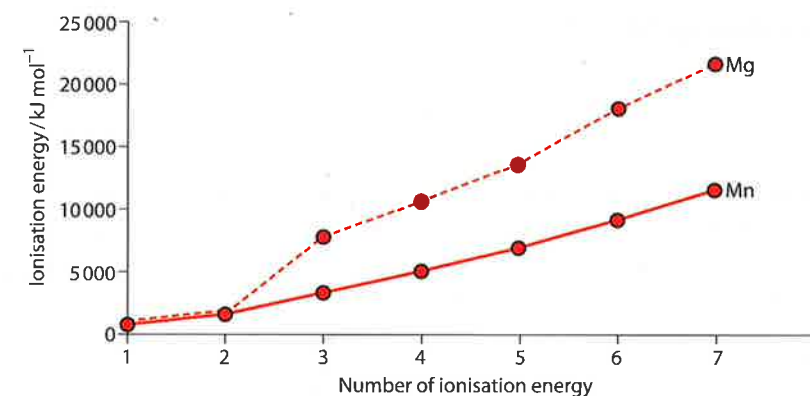

Figure 3.30 Comparison of successive ionisation energies of magnesium and manganese.

## Magnetic properties of transition metal compounds

There are two forms of magnetism we need to be concerned with – **paramagnetism** and **diamagnetism**.

Paramagnetism is caused by unpaired electrons – paramagnetic substances are attracted by a magnetic field.

Diamagnetism is caused by paired electrons – diamagnetic substances are repelled slightly by a magnetic field.

All substances have some paired electrons and so all substances exhibit diamagnetism. However, the diamagnetic effect is much smaller than the paramagnetic effect and so, if there are any unpaired electrons present, the paramagnetic effect will dominate and the substance will be paramagnetic overall and attracted by a magnetic field. The more unpaired electrons, the greater the paramagnetism (magnetic moment).

Consider the electron configurations of two transition metal ions:
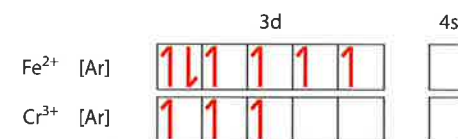
Both contain unpaired electrons and their compounds are paramagnetic – so both $FeCl_2$ and $CrCl_3$ are paramagnetic. Because an Fe^{2+} ion has four unpaired electrons and a Cr^{3+} ion has only three, the iron(II) compound is more paramagnetic (higher magnetic moment).

The Cu^+ ion has the following electron configuration:
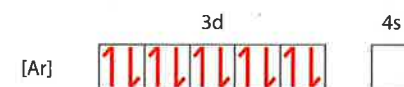
All the electrons are paired so compounds of copper(I), such as $CuCl$, are diamagnetic only.
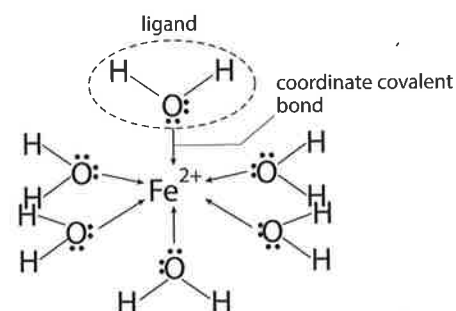
A ligand is a Lewis base.

Figure 3.31 A complex ion is formed when ligands bond to a transition metal ion. The ligands donate lone pairs into vacant orbitals (3d, 4s or 4p) on the transition metal ion.

Extension

There is a strong case for considering the bonding in a transition metal complex ion as having a significant ionic component. Crystal field theory and ligand field theory consider the bonding from a more ionic point of view.

Complex ions

A complex ion consists of a central metal ion surrounded by **ligands** – transition metal ions form many complexes.

Ligands are negative ions or neutral molecules that have lone pairs of electrons. They use the lone pairs to bond to a metal ion to form a complex ion. **Coordinate covalent bonds** (dative bonds) are formed between the ligand and the transition metal ion.

The structure of $[Fe(H_2O)_6]^{2+}$ is shown in Figure **3.31**. H_2O is the ligand in this complex ion. The shape of this complex ion is octahedral and it is called the hexaaquairon(II) ion. Other ways of drawing this are shown in Figure **3.32**.
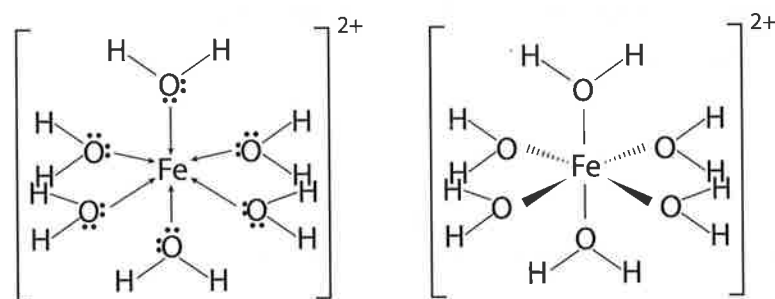

Figure 3.32 Alternative representations of the $[Fe(H_2O)_6]^{2+}$ complex ion.

All transition elements, with the exception of titanium, form an octahedral complex ion with the formula $[M(H_2O)_6]^{2+}$ in aqueous solution.

Complex ions can have various shapes depending on the number of ligands. However, shapes cannot be worked out using the valence shell electron-pair repulsion theory (see page **137**) because more subtle factors also govern the overall shape. If a complex ion contains 6 ligands it will almost certainly be octahedral, but complexes containing 4 ligands may be tetrahedral or square planar (Figure **3.33**).
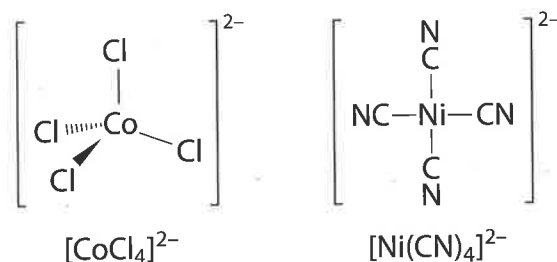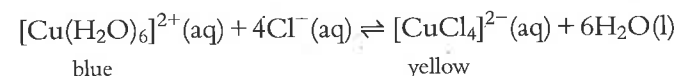

$[CoCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$

Figure 3.33 $[CoCl_4]^{2-}$ is tetrahedral but $[Ni(CN)_4]^{2-}$ is square planar.

Complex ions can undergo substitution reactions in which, for example, H_2O ligands are replaced by other ligands. For example, in the addition of concentrated hydrochloric acid to blue copper(II) sulfate solution:

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$$
     blue   yellow

As the acid is added, the yellow $[CuCl_4]^{2-}$ complex ion is formed. So, the solution changes colour from blue to green (a mixture of blue and yellow). According to Le Chatelier's principle (see Topic **7**) the position of equilibrium shifts to the right as Cl^- is added.

The oxidation number of a transition metal in a complex ion

The oxidation number of a transition metal in a complex ion can be worked out from the charges on the ligands. Ligands may be either neutral or negatively charged (see Table **3.6**).

In $[Fe(H_2O)_6]^{2+}$ all the ligands are neutral water molecules. The overall charge on the ion is just due to the iron ion, so the oxidation number of iron must be +2.

In $[Ni(CN)_4]^{2-}$ all the ligands have a 1− charge, so the total charge from all four ligands is 4−. The overall charge on the ion is 2−; so, the oxidation number of nickel must be +2 to cancel out 2− from the 4− charge.

Working out the overall charge on a complex ion

If the oxidation number (charge) of the central transition metal ion and the charges on the ligands are known, the overall charge on the complex ion can be worked out.

Neutral ligands	1− ligands
H_2O	Cl^-
NH_3	CN^-
CO	Br^-

Table 3.6 Charges on ligands.

Exam tip
Oxidation numbers are discussed in more detail in Topic **9**.

Worked example

3:1 Platinum(II) can form a complex ion with 1 ammonia and 3 chloride ligands. What is the overall charge and formula of the complex ion?

Platinum(II) has a charge of 2+
Ammonia is a neutral ligand (NH_3)
Chloride has a 1− charge (Cl^-)

The overall charge is $(2+) + (0) + 3(1-) = 1-$

The formula of the complex ion is: $[Pt(NH_3)Cl_3]^-$

Catalytic ability

Transition elements and their compounds/complexes can act as catalysts. For example, finely divided iron is the catalyst in the **Haber process** in the production of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
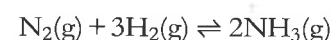
Iron in the above reaction is a heterogeneous catalyst (one that is in a different physical state to the reactants) but transition metal compounds often act as homogeneous catalysts (ones that are in the same phase as the reactants). The ability to act as a catalyst relies on a transition metal atom or ion having varying oxidation numbers and also being able to coordinate to other molecules/ions to form complex ions.

Some scientists believe that the bonding between a transition metal and a ligand is purely ionic. All scientists have the same experimental data available to them – to what extent is scientific knowledge objective and to what extent is it a matter of interpretation and belief?

Nature of science

Science is about finding patterns and these patterns allow us to make predictions. However, it is not always the patterns that are most interesting and careful observation is essential to spot anomalies and exceptions to patterns that could lead to new discoveries and theories. Zinc can be regarded as anomalous in the first row of the d block, for instance, it does not generally form coloured compounds; this has resulted in it not being included as a transition element.

3.4 Coloured complexes (HL)

The colours of some complex ions are shown in Table **3.7**.

In a gaseous transition metal ion, all the 3d orbitals have the same energy – that is, they are degenerate. However, when the ion is surrounded by ligands in a complex ion, these d orbitals are split into two groups. In an octahedral complex ion there are two orbitals in the upper group and three orbitals in the lower groups (Figure **3.34**).
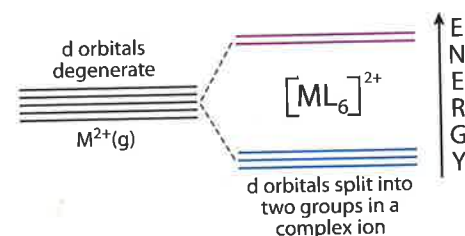
Complex ion	Colour
$[Cu(H_2O)_6]^{2+}$	blue
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	deep blue/violet
$[Fe(SCN)(H_2O)_5]^{2+}$	blood red
$[Ni(H_2O)_6]^{2+}$	green

Table 3.7 The colours of some complex ions.

Extension

All the d orbitals in a complex ion are higher in energy than the d orbitals in an isolated gaseous ion.

Extension

The electrons in d_{z^2} and $d_{x^2-y^2}$ orbitals are repelled more by the ligand electrons because they point directly at the ligands – greater repulsion leads to higher energy.

Extension

The d orbitals are split in different ways in different-shaped complex ions.

Figure 3.34 The splitting of d orbitals in a complex ion.

The splitting may be regarded as being caused by the repulsion between the electrons in the metal ion d orbitals and the lone pairs on the ligands. Two of the metal ion d orbitals point directly at the ligands and so are raised in energy, whereas the other three d orbitals point between the ligands and are lowered in energy relative to the other two d orbitals.

Energy in the form of a certain frequency of visible light can be absorbed to promote an electron from the lower set of orbitals to the higher set (Figure **3.35**).
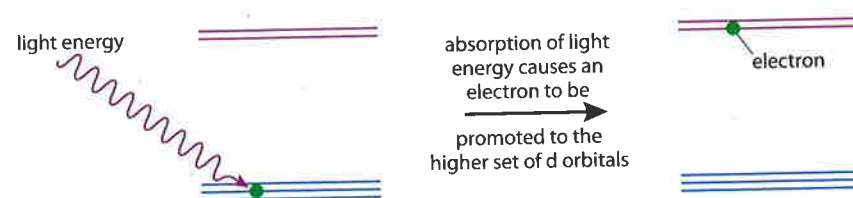

Figure 3.35 Absorption of light by a complex ion.

When white light passes through copper sulfate solution (Figure **3.36**), orange light is absorbed, promoting an electron from the lower set of d orbitals to the higher set. This means that the light coming out contains all the colours of the spectrum except orange and so appears blue, the complementary colour to orange.
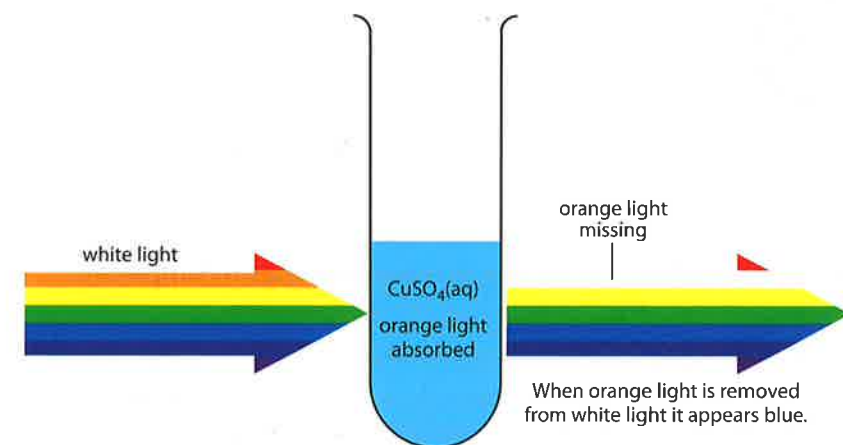
Figure 3.36 Colour and absorption.
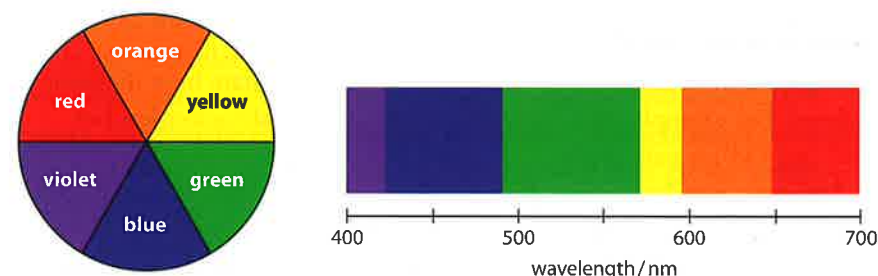
Figure 3.37 A colour wheel – along with the approximate wavelengths of visible light. Complementary colours are opposite each other in the colour wheel, therefore blue is complementary to orange and green is complementary to red.

> For a substance to appear coloured, certain frequencies of light in the visible region of the spectrum must be absorbed.

The colour of a substance will appear to an observer as the **complementary colour** to the light that is absorbed. A colour wheel (Figure **3.37**) shows which pairs of colours are complementary (opposite each other in the colour wheel). If we know the colour of the complex ion, the colour of light that is absorbed can be worked out, and vice versa. For example, because a solution of nickel(II) chloride is green, it must absorb red light – the complementary colour to green.

> The formation of coloured substances requires the presence of a partially filled d subshell.

Let us consider the Sc^{3+} ion or the Ti^{4+} ion. These both have no electrons in the 3d subshell and so are colourless, as it is not possible to absorb energy to promote a 3d electron.

White light is a mixture of all colours (frequencies) of visible light.

Extension

$Cr_2O_7^{2-}$ (orange), CrO_4^{2-} (yellow) and MnO_4^- (purple) are all very highly coloured, but they have no d electrons. They are coloured because of a different mechanism from the one described here.

Figure 3.38 A Cu^+ or Zn^{2+} ion has ten 3d electrons.

The Cu^+ ion and the Zn^{2+} ion both have ten 3d electrons (Figure 3.38), and as there is no space in the upper set of orbitals it is not possible to promote an electron to the upper set of orbitals. No light in the visible region of the spectrum is absorbed and these ions are colourless.

> What do we mean when we say that a solution of copper sulfate is blue? Is blueness a property of copper sulfate solution, or is the blueness in our minds? What colour would copper sulfate solution be in orange light? Or in the dark?

Most aqueous solutions of Fe^{3+} are actually yellow, but they do not contain $[Fe(H_2O)_6]^{3+}$(aq).

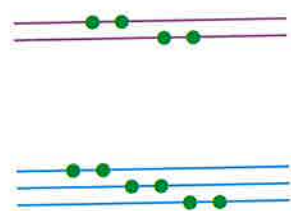In general, for complex ions containing the same metal and the same ligands, the greater the oxidation number of the transition metal, the greater the splitting of the d orbitals.

Factors that affect the colour of transition metal complexes

At the simplest level, the colours of transition metal complexes can be related to the amount of splitting of the d orbitals. For example, if there is a greater difference in energy between the lower and higher set of d orbitals then a higher frequency (shorter wavelength) of light will be absorbed and the complementary colour will be different. The following factors all have a part to play.

Identity of the metal

Complexes of different metals in the same oxidation state have different colours. For example, Mn^{2+}(aq) ($3d^5$) is very pale pink/colourless but Fe^{2+}(aq) ($3d^6$) is pale green.

Different metal ions have different electron configurations and, because colours are caused by electron transitions, different arrangements of electrons give rise to different colours due to different amounts of repulsion between electrons.

If **isoelectronic** (same number of electrons) transition metal ions complexes are considered, such as $[Mn(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ (both metal ions have five 3d electrons) then there will be a greater amount of splitting of d orbitals in $[Fe(H_2O)_6]^{3+}$. A higher nuclear charge on the metal ion (26+ for Fe and 25+ for Mn) for the same number of electrons causes the ligands to be pulled in more closely in an Fe^{3+} complex, so that there is greater repulsion between the ligand electrons and the d electrons of the transition metal ion – and therefore greater splitting of the d orbitals.

Oxidation number

The same metal has different colours in different oxidation states. For example:

$[Fe(H_2O)_6]^{2+}$(aq) is pale green and

$[Fe(H_2O)_6]^{3+}$(aq) is pale violet.

There are two reasons for this:
- the electron configurations of the ions are different
- a higher charge on the metal ion causes the ligands to be pulled in more closely, so that there is greater repulsion between the ligand electrons and the d electrons of the transition metal ion – and therefore greater splitting of the d orbitals.

Nature of the ligand

The same metal ion can exhibit different colours with different ligands. This is mainly because of the different splitting of the d orbitals caused by different ligands.

Ligands can be arranged into a **spectrochemical series** according to how much they cause the d orbitals to split:

$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CO \approx CN^-$$
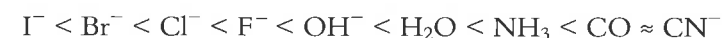
So a chloride ion causes greater splitting of the d orbitals than an iodide ion, and an ammonia molecule causes greater splitting of the d orbitals than a water molecule.

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ has a larger energy gap between the two sets of d orbitals than $[Cu(H_2O)_6]^{2+}$ and absorbs a shorter wavelength (higher frequency) of light (Figure 3.39). $[Cu(NH_3)_4(H_2O)_2]^{2+}$(aq) is dark blue/violet and absorbs more in the yellow–green (higher frequency) region of the visible spectrum.

A full explanation of the spectrochemical series is difficult at this level. The fact that fluoride ions cause greater splitting of d orbitals than iodide ions can be explained in terms of **charge density** (charge per unit volume) of the ligand – both F^- and I^- have the same charge but the F^- ion is much smaller and therefore causes greater repulsion of the metal ion d electrons and greater splitting of the d orbitals. This explanation cannot, however, be extended to the rest of the spectrochemical series – as can be seen by the fact that CO, a neutral ligand, causes greater splitting of d orbitals than negatively charged ligands that would be expected to have a higher charge density. However, the spectrochemical series can

Ligands that cause greater splitting of d orbitals are called stronger field ligands.

A water molecule is more polar than an ammonia molecule and there would be expected to be a higher charge density on the O in H_2O than the N in NH_3.
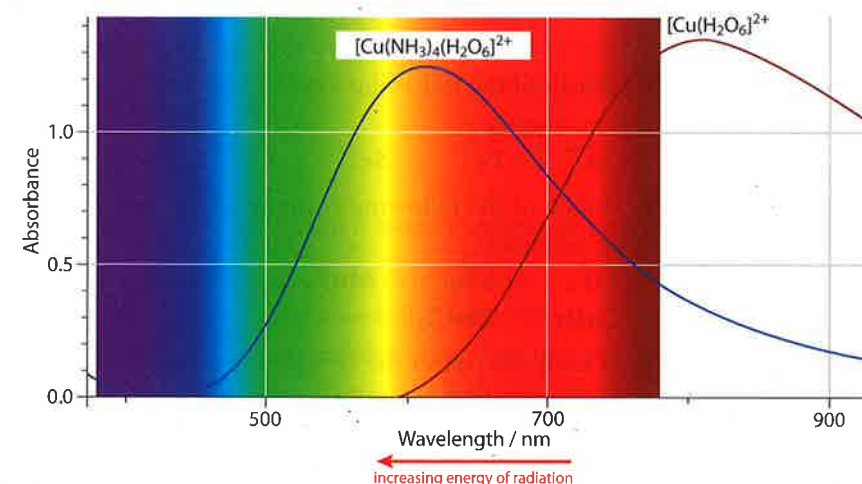
Figure 3.39 $[Cu(H_2O)_6]^{2+}$(aq) is blue and absorbs mostly at the red–orange end of the spectrum. $[Cu(NH_3)_4(H_2O)_2]^{2+}$(aq) is dark blue/violet and absorbs more in the yellow–green (shorter wavelength) region of the visible spectrum.

be explained to a certain extent in terms of π bonding (see Topic 4) between the ligand and the transition metal ion. Such π overlap of a lone pair on F^- with ligand d orbitals causes the splitting of the d orbitals to be reduced. Ligands that have extra lone pairs of electrons (beyond that required to bond to the transition metal ion), such as water, should cause less splitting of d orbitals than those without extra lone pairs (such as ammonia) due to this π electron donation effect. The CO ligand is a π acceptor and this is why it causes greater splitting of d orbitals.

Nature of science

Models are abstract constructions that allow us to visualise or make sense of theories about particular scientific phenomena. Here we are using a very simple model, in terms of promotion of an electron from a low-energy d orbital to a higher energy d orbital, to explain the colour of transition metal complexes. This model has limited value because it explains *some* aspects of colour but not others. For instance, it does not explain anything about the intensities of the colours absorbed, why transition metal complexes can absorb more than one wavelength of light or why complexes such as MnO_4^- are coloured.

There are, however, much more sophisticated models that have greater explanatory power. Models are a very powerful tool in understanding the real world and making predictions. Models may be qualitative, as here, or quantitative and developed in terms of mathematical equations. When developing a model there is always a balance between simplicity and explanatory/predictive power.

? Test yourself

9 Give the full electron configuration of the following ions:
   a Ni^{2+} **c** V^{3+}
   b Co^{3+} **d** Mn^{4+}

10 Give the oxidation number of the transition metal in each of these complex ions:
   a $[Ni(H_2O)_6]^{2+}$ **e** $[Co(NH_3)_5Br]^{2+}$
   b $[Fe(CN)_6]^{4-}$ **f** $[Co(NH_3)_4Br_2]^+$
   c $[MnCl_4]^{2-}$ **g** $[FeO_4]^{2-}$
   d $[Co(NH_3)_6]^{3+}$ **h** $Ni(CO)_4$

11 Which of the following ions will be paramagnetic?
   Cu^{2+} Fe^{2+} Sc^{3+} Co^{3+} Mg^{2+}

12 Which of the following compounds are likely to be coloured?
   TiF_4 VF_5 MnF_3 CoF_2
   $CuBr$ $ZnCl_2$

13 In each case, select the complex ion that would be expected to absorb the longer wavelength of light:
   a $[Co(H_2O)_6]^{2+}$ or $[Co(H_2O)_6]^{3+}$
   b $[Fe(H_2O)_6]^{2+}$ or $[Fe(NH_3)_6]^{2+}$

Exam-style questions

1 The element in group 13 and period 5 is:
   A Y   **B** In   **C** Tl   **D** P

2 Which of the following properties decrease in value down group 17?
   A electronegativity and first ionisation energy
   B melting point and electronegativity
   C melting point and atomic radius
   D ionic radius and first ionisation energy

3 Which of the following is a transition element?
   A Te   **B** Np   **C** Ta   **D** Sm

4 Which of the following forms an alkaline solution when added to water?
   A SO_3 **B** Na_2O **C** P_4O_{10} **D** SiO_2

5 Which of the following is true for two elements in the same group in the periodic table?
   A they have the same physical properties
   B they have similar chemical properties
   C they have the same electronegativity
   D they have the same number of shells of electrons

6 A non-metallic element, X, forms a gaseous oxide with the formula X_2O that reacts with water to form an acidic solution. The element X is most likely to be:
   A Na   **B** S   **C** Cl   **D** P

HL 7 Which of the following is **not** a characteristic property of transition metals?
   A they form complex ions
   B they have full d subshells
   C they exhibit more than one oxidation number in compounds
   D they form coloured compounds

HL 8 What is the oxidation number of chromium in $K_3[Cr(CN)_6]$?
   A +6   **B** −6   **C** +3   **D** −3

HL 9 Which of the following complex ions would be expected to be colourless?
   A $[Ni(H_2O)_6]^{2+}$ **C** $[Cu(H_2O)_6]^{2+}$
   B $[Zn(H_2O)_6]^{2+}$ **D** $[Co(H_2O)_6]^{2+}$

10 Which compound will be diamagnetic?

      A $CrCl_3$ **B** $CuCl_2$ **C** $TiCl_4$ **D** VCl_2

11 **a** The atomic and ionic radii of some elements are given in the table:

Element	Atomic radius / pm	Ionic radius / pm
Na	186	98
Al	143	45
Cl	99	181
K	231	133

    i Explain why the atomic radius of aluminium is smaller than that of sodium.   **[2]**

    ii Explain why the ionic radius of aluminium is smaller than its atomic radius but the atomic
radius of chlorine is larger than its atomic radius.   **[4]**

    iii Explain why the ionic radius of potassium is smaller than that of chlorine.   **[2]**

  b **i** Write equations for the first electron affinity of chlorine and the first ionisation energy of magnesium. **[2]**

    ii Explain why the first electron affinity of chlorine is more exothermic than the first electron affinity of
bromine.   **[2]**

    iii Explain why chlorine has a higher first ionisation energy than magnesium.   **[2]**

12 **a** Write the full electron configuration of:

    i a Cu atom;   **ii** a Cu^{2+} ion   **[2]**

  b One characteristic property of transition metals is that they can form complex ions with ligands.
Explain what is meant by the term *ligand*.   **[2]**

  c What is the oxidation number of copper in the complex ion $[CuCl_4]^{2-}$?   **[1]**

  d Explain whether CuBr is diamagnetic or paramagnetic.   **[2]**

  e **i** Explain why solutions containing the complex ion $[Cu(H_2O)_6]^{2+}$ are coloured.   **[3]**

    ii Explain why solutions containing the complex ion $[Cu(NH_3)_2]^+$ are colourless.   **[2]**

    iii When concentrated hydrobromic acid is added to an aqueous solution of copper(II) sulfate the
following reaction occurs:
$$[Cu(H_2O)_6]^{2+} + Br^- \rightarrow [Cu(H_2O)_5Br]^+ + H_2O$$
State and explain any differences in the wavelength of light absorbed by $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_5Br]^+$.   **[2]**

Summary

The periodic table summary diagram:

for groups 1 and 2, number of outer shell electrons = group number

for groups 13–18, number of outer shell electrons = group number – 10

Electron affinity generally becomes less exothermic down a group.

Electronegativity and 1st ionisation energy decrease down a group.

Atomic radius and ionic radius increase down a group.

elements arranged in order of atomic number — *arranged in* — **groups** – vertical columns

Positive ions are smaller than the parent atom.

Negative ions are larger than the parent atom.

examples

Reactivity increases and melting point decreases down group.

group 1 – the **alkali metals**   group 17 – the **halogens**

Melting point increases and reactivity decreases down group.

React vigorously with water:
$2M + 2H_2O \rightarrow 2MOH + H_2$

Alkali metals react with halogens:
$2M + X_2 \rightarrow 2MX$

A more reactive halogen displaces a less reactive halogen, for example
$Cl_2(aq) + 2KBr(aq) \rightarrow 2KCl(aq) + Br_2(aq)$

To TRANSITION METALS on next page

periods – horizontal rows — *example* — period 3

Electronegativity and 1st ionisation energy increase across a period.

Electron affinity becomes more exothermic across a period.

Atomic radius decreases across a period.

oxides

basic:
Na_2O — $Na_2O + H_2O \rightarrow 2NaOH$
MgO — $MgO + H_2O \rightarrow Mg(OH)_2$

amphoteric: Al_2O_3

acidic:
SiO_2
P_4O_6
P_4O_{10} — $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
SO_2 — $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$
SO_3 — $SO_3 + H_2O \rightarrow H_2SO_4$
NO_2 — $2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$

HL

TRANSITION METALS — can have more than one oxidation number in compounds or complexes — At least one ion has a partially filled d subshell.

One of the oxidation numbers is always +2.

can exhibit magnetic properties

examples —
- Cu: +1, +2
- Fe: +2, +3
- Mn: +2, +4, +7
- Cr: +2, +3, +6

The 4s electrons are always removed before the 3d electrons.

unpaired electrons cause paramagnetism

can form **complex ions** with ligands — **Ligands** are either negative ions or neutral molecules with lone pairs of electrons.

use lone pairs to bind to metal through coordinate covalent bonds

form coloured compounds and complexes — The presence of ligands causes d orbitals to split into two groups with different energy levels. — A certain frequency of visible light is absorbed to promote an electron to a higher d orbital – the complementary colour is transmitted.

complementary colours can be determined from a colour wheel

colour depends on:
- identity of the metal
- oxidation number of the metal ion
- nature of the ligand

ligands can be arranged into a spectrochemical series according to how much they split d orbitals

can act as catalysts in form of elements or compounds

Chemical bonding and structure 4

Bonding

Compounds can be divided into two main classes according to the bonding in them – they are either **ionic** or **covalent**. The type of bonding present can usually be deduced by looking at the formula of the compound. Covalent compounds are those formed between two or more non-metallic elements, whereas ionic compounds are usually formed between a metallic element and a non-metallic one. For example, NaCl is an ionic compound but CH_4 is covalent.

There are some compounds for which the distinction is not so clear. For instance, ammonium chloride does not contain any metallic elements but has ionic bonding between the ammonium ions (NH_4^+) and the chloride ions (Cl^-). In addition to this, within the NH_4^+ ion there is covalent bonding.

Generally, as a rough rule of thumb, elements that are close together in the periodic table form covalent compounds but elements that are far apart in the periodic table form ionic compounds. Thus elements from groups 1 and 17 combine to form ionic compounds (CsF being the most ionic) but elements from groups 14, 15, 16 and 17 combine to form covalent compounds. This is discussed in terms of electronegativity on page **129**.

Ionic compound: **metal** and **non-metal**
Covalent compound: **two or more non-metals**

4.1 Ionic bonding and structure

Positive ions are usually formed by metallic elements by the loss of valence (outer shell) electrons. For example, magnesium loses the two electrons in its highest energy level (outer shell) to form a 2+ ion:

$$Mg \rightarrow Mg^{2+} + 2e^-$$

Negative ions are usually formed by non-metallic elements by the gain of electrons. For example, oxygen gains two electrons to fill up its outer shell (highest occupied energy level):

$$O + 2e^- \rightarrow O^{2-}$$
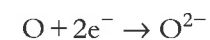
At the simplest level, when elements in the main groups of the periodic table (groups 1, 2, 13 (to a certain extent), 15, 16 and 17) form ions, electrons are gained or lost to achieve the electron configuration of the nearest **noble gas**. That is, electrons are gained or lost to make an ion that is **isoelectronic** (same number of electrons) with the nearest noble gas.

Another way of saying this is that electrons are lost or gained to achieve a full outer shell of electrons. Although this is true for the first 20 elements, it is not generally true after that because of the existence of transition metals (and d orbitals).

Learning objectives

- Recognise the formulas of ionic compounds
- Understand how ions are formed and recall the formulas of some common ions
- Work out the formulas of ionic compounds from the charges on the ions
- Describe the structure of sodium chloride as an example of an ionic lattice
- Explain the physical properties of ionic compounds in terms of structure and bonding