9 The Periodic Table: chemical periodicity

This section on the Periodic Table and chemical periodicity builds on work covered in the first three chapters of this guide. In this chapter we will concentrate on Period 3 – the elements sodium to argon.

Physical properties of Period 3 elements

You need to know and be able to explain the variation of four key physical properties across the third period (sodium to argon). These are:

- atomic and ionic radius
- melting point
- electrical conductivity
- ionisation energy

Atomic and ionic radius

The Periodic Table is an arrangement of the chemical elements according to their proton numbers. The word ‘periodic’ suggests a regular recurrence of a feature. Look at the graph of atomic volume (which is linked directly to atomic radius) shown in Figure 9.1.

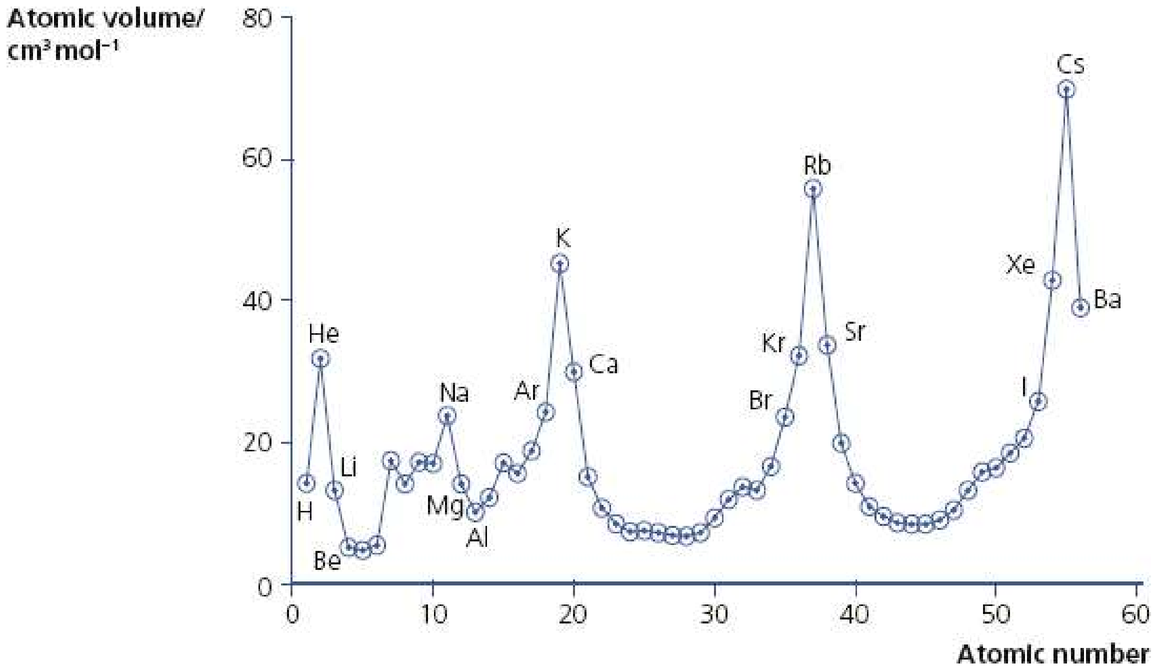

Figure 9.1 Relationship between atomic volume and atomic number

- A pattern is apparent – the Group 1 metals occur at peaks on the graph. The other thing that is noticeable is that atoms of the Group 1 metals get larger moving down the group.
- Moving across Period 3 from left to right, the ionic radii change (Figure 9.2). To begin with, elements lose electrons to form positive ions. The increasing positive charge pulls the remaining electrons closer to the nucleus to give a smaller ionic radius.
- Beyond silicon, Si^{4+}, the atoms form negative ions with a decreasing charge. The electrons gained fill the outer electron shell. This means that the ionic radius is much larger for phosphorus, P^{3-}, and then decreases steadily to chlorine, Cl^{-}.

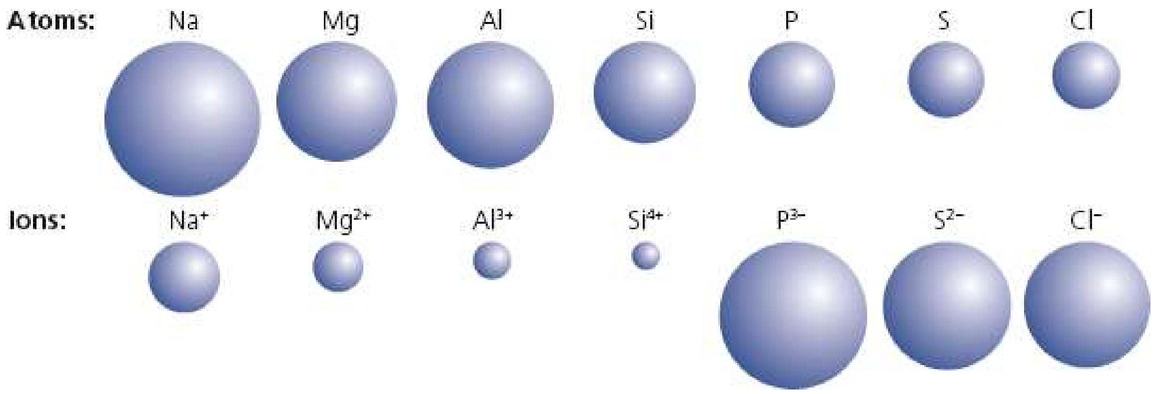

Figure 9.2 Atomic and ionic radii of Period 3 elements

Melting point

Period 3 contains different types of elements, from metals on the left-hand side through non-metallic solids to gases on the right-hand side. The melting points and boiling points of these elements are shown in Figure 9.3.

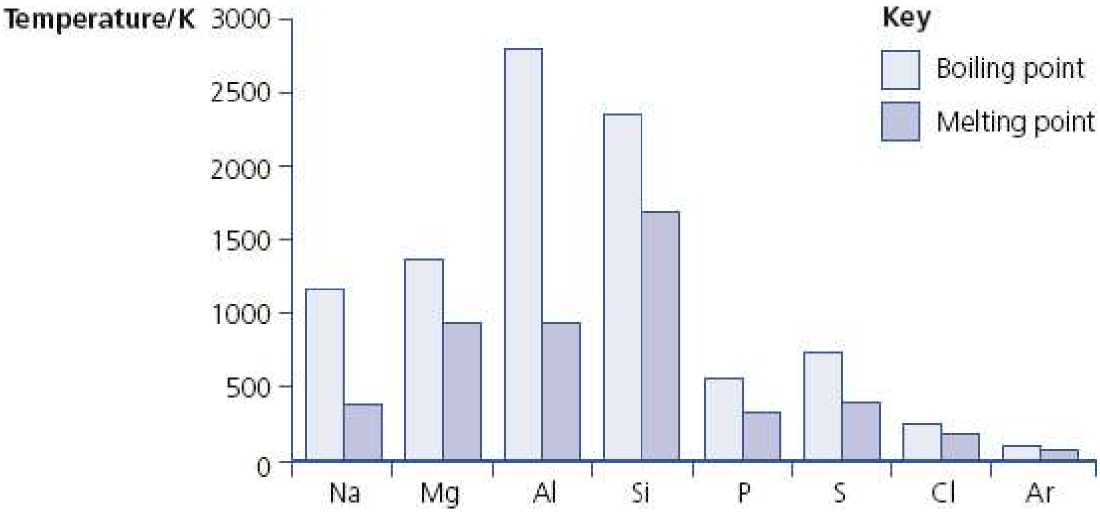

Figure 9.3 Melting points and boiling points of Period 3 elements

- The elements sodium, magnesium and aluminium are metals and their atoms are bonded using a 'sea' of delocalised electrons. The melting (and boiling) points increase because the number of electrons each atom contributes to the 'sea' increases.
- Silicon is a semi-conductor with a giant covalent structure (similar to that of diamond), so it has a high melting point.
- Phosphorus is a non-metal with four atoms in its molecules. To melt it, only van der Waals' forces have to be overcome, so phosphorus has a low melting point.
- Sulfur, another non-metal, is made up of S_8 molecules. Because the molecules are big, there are stronger van der Waals' forces between them than in phosphorus. So sulfur has a higher melting point than phosphorus.
- A chlorine molecule, Cl_2, has only two atoms so the melting point is lower than that of sulfur.
- Finally, argon consists of single atoms with very weak van der Waals' forces so argon has the lowest melting (and boiling) point in Period 3.

Electrical conductivity

Sodium, magnesium and aluminium are good electrical conductors because of the 'sea' of delocalised electrons they have. Silicon is a semi-conductor, but not as good a conductor as graphite. All the other elements are electrical insulators.

NOW TEST YOURSELF

1 An element in Period 3 of the Periodic Table is a poor conductor of electricity, has a low melting point and forms molecules containing four atoms.

What is the element?

First ionisation energy

Ionisation energy was discussed in Chapter 1. Figure 9.4 shows the changes in first ionisation energy across Period 3.

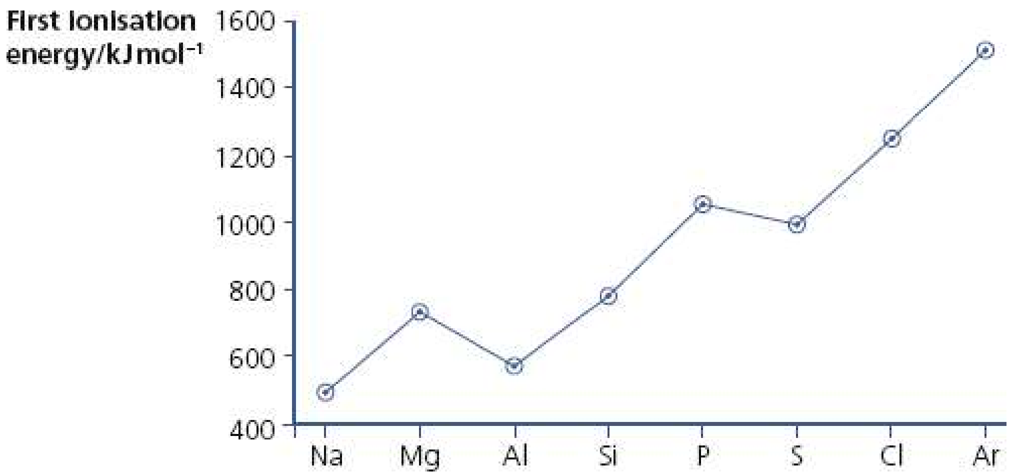

Figure 9.4 Changes in first ionisation energy across Period 3

There are four things that affect the size of the first ionisation energy:

- the charge on the nucleus
- the distance of the electron from the nucleus
- the number of electrons between the outer electrons and the nucleus
- whether the electron to be removed is alone or paired

Across Period 3, the charge on the nucleus increases by one unit for each element. In all cases, electrons are being removed from the third shell and these are screened by the $1s^2$, $2s^2$ and $2p^6$ electrons. The graph is not a straight line because of the orbitals the electrons are removed from.

The first ionisation energy of aluminium is lower than that of magnesium. This fall is because in aluminium the electron being removed is in a p-orbital and is, on average, further away from the nucleus than an electron in an s-orbital.

There is another drop between phosphorus and sulfur – this is caused by removing a paired electron in a p-orbital. The repulsion between these two electrons makes it easier to remove one of them than a single electron in a p-orbital.

NOW TEST YOURSELF

2 Why do the following affect the ionisation energy of an element?

a The charge on the nucleus.

b The distance from the nucleus of the electron being removed.

Chemical properties of Period 3 elements

You have to be able to recall the reactions of these elements with oxygen, chlorine and water, and to know about the reactions of any oxides and chlorides formed.

Reactions with oxygen

You have probably seen most of the Period 3 elements reacting with air, or perhaps with oxygen. The reactions are summarised in Table 9.1.

Table 9.1

Element	Reaction	Product(s)	Equation

Element	Reaction	Product(s)	Equation
Sodium	Burns with an orange-yellow flame to give white products	Sodium oxide and peroxide	$4Na + O_2 \rightarrow 2Na_2O$ $2Na + O_2 \rightarrow Na_2O_2$
Magnesium	Burns with a bright white flame to give a white product	Magnesium oxide	$2Mg + O_2 \rightarrow 2MgO$
Aluminium	Powder burns to give a white product	Aluminium oxide	$4Al + 3O_2 \rightarrow 2Al_2O_3$
Silicon	Burns if heated strongly	Silicon dioxide	$Si + O_2 \rightarrow SiO_2$
Phosphorus	Burns with a yellow flame producing clouds of white smoke	Phosphorus(III) oxide; phosphorus(V) oxide in excess O_2	$P_4 + 3O_2 \rightarrow P_4O_6$ $P_4 + 5O_2 \rightarrow P_4O_{10}$
Sulfur	Burns with a blue flame producing a colourless gas	Sulfur dioxide (sulfur trioxide is produced in the presence of a catalyst and excess O_2)	$S + O_2 \rightarrow SO_2$
Chlorine	Does not react directly with oxygen		
Argon	No reaction		

Reactions with chlorine

You may not have seen as many of the elements reacting with chlorine. The reactions are summarised in Table 9.2.

Table 9.2

Element	Reaction	Product	Equation
Sodium	Burns with a bright orange flame giving a white product	Sodium chloride	$2Na + Cl_2 \rightarrow 2NaCl$
Magnesium	Burns with a bright white flame giving a white product	Magnesium chloride	$Mg + Cl_2 \rightarrow MgCl_2$
Aluminium	Burns with a yellow flame giving a pale-yellow product	Aluminium chloride	$2Al + 3Cl_2 \rightarrow 2AlCl_3$
Silicon	Reacts when chlorine gas is passed over it to form a colourless liquid	Silicon tetrachloride	$Si + 2Cl_2 \rightarrow SiCl_4$
Phosphorus	Burns with a yellow flame to form a mixture of chlorides	Phosphorus(III) chloride and phosphorus(V) chloride	$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 10Cl_2 \rightarrow 4PCl_5$
Sulfur	Reacts when chlorine gas is passed over it to form an orange liquid	Disulfur dichloride	$2S + Cl_2 \rightarrow S_2Cl_2$
Chlorine	No reaction		
Argon	No reaction		

Reactions with water

Sodium reacts violently with water, releasing hydrogen gas and dissolving to form sodium hydroxide solution:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

Magnesium reacts slowly with cold water, forming magnesium hydroxide and hydrogen:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

It reacts vigorously if steam is passed over the heated metal, forming magnesium oxide and hydrogen:

$$Mg + H_2O \rightarrow MgO + H_2$$

NOW TEST YOURSELF

3 The table shows the reactions of two elements with oxygen and chlorine.

Element	Reaction with oxygen	Reaction with chlorine
X	Burns with a blue flame producing a colourless gas	Reacts to form an orange liquid
Y	Powder burns to give a white product	Burns giving a pale-yellow product

a What are elements X and Y?

b What could be the formula of the compound formed when these elements react together?

Oxidation numbers in oxides and chlorides

Figure 9.5 shows a plot of the oxidation numbers of the Period 3 elements in their oxides and chlorides.

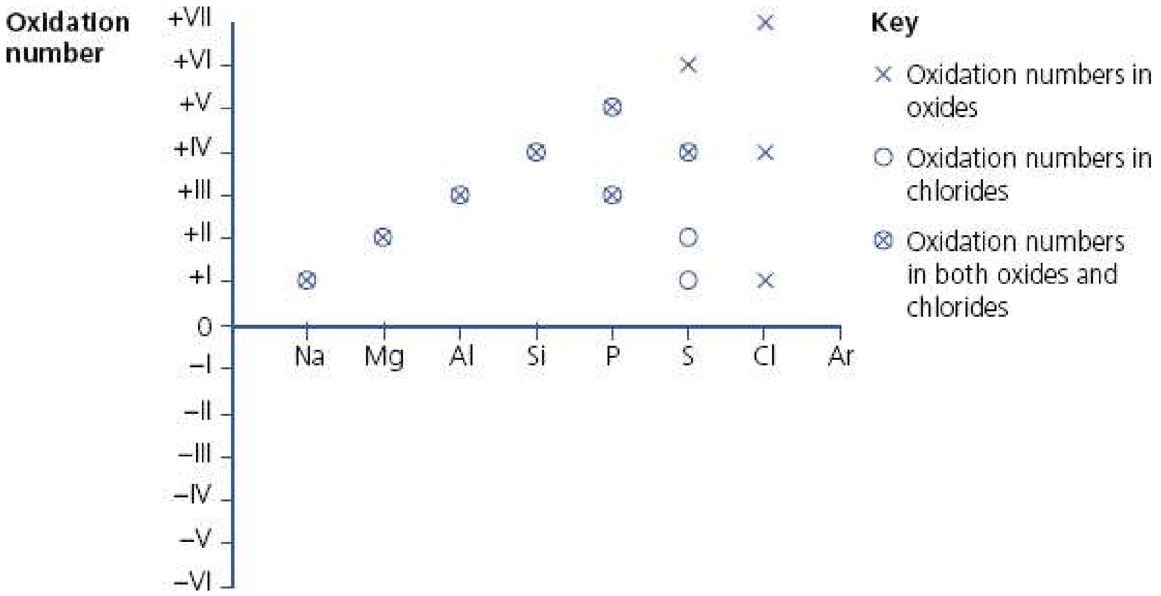

Figure 9.5 Oxidation numbers of the oxides and chlorides of Period 3 elements

- The first four elements have positive oxidation numbers that correspond to the loss of all their outer electrons (silicon can also gain four electrons in forming its hydride, SiH_4 – its oxidation number is still +4).
- Elements in Groups 15, 16 and 17 can also show positive oxidation numbers in their oxides and chlorides. You may think that it is unusual for non-metals to have positive oxidation numbers, but carbon has a positive oxidation number in carbon dioxide.

NOW TEST YOURSELF

4 Study Figure 9.5 and then explain the pattern of oxidation numbers for the chlorides.

Reactions of oxides with water and their acid–base behaviour

The general trend is that alkalis are formed on the left-hand side of the period, aluminium and silicon oxides are almost insoluble, and acids are formed on the right-hand side (Table 9.3).

Table 9.3

Oxide	Reaction	pH of solution	Equation
Sodium	Dissolves exothermically	14	$Na_2O + H_2O \rightarrow 2NaOH$
Magnesium	Slight reaction	9	$MgO + 2H_2O \rightarrow Mg(OH)_2$
Aluminium	No reaction		
Silicon	No reaction		
Phosphorus	Phosphorus(III) oxide reacts with cold water	1–2	$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$
	Phosphorus(V) oxide reacts violently	1–2	$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
Sulfur	Sulfur dioxide dissolves readily	1	$SO_2 + H_2O \rightarrow H_2SO_3$
	Sulfur trioxide reacts violently	0	$SO_3 + H_2O \rightarrow H_2SO_4$
Chlorine	Does not react directly with oxygen		
Argon	No reaction		

Aluminium oxide is **amphoteric**. This means that it reacts with both acids and alkalis. Aluminium oxide contains oxide ions, so it reacts as a base with acids, in a similar way to magnesium oxide:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

It also has significantly acidic tendency, reacting with alkalis, such as sodium hydroxide, to form an aluminate:

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

Reactions of the chlorides with water

The reactions of the chlorides of Period 3 elements with water (Table 9.4) give clues about the bonding present.

This is linked to the electronegativity of the element. As you saw in Chapter 3, the bigger the difference in electronegativity, the more polar is the bond. Sodium and chlorine have a difference of 2.1 whereas sulfur and chlorine have a difference of only 0.5.

Table 9.4

Chloride	Bonding	Electronegativity	Reaction	Equation
Sodium	Ionic (electrovalent)	0.9	Dissolves to give Na^+ and Cl^- ions	
Magnesium	Ionic (electrovalent)	1.2	Dissolves to give Mg^{2+} and Cl^- ions	
Aluminium	Mainly covalent	1.5	Hydrolyses	$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$
Silicon	Covalent	1.8	Hydrolyses	$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$
Phosphorus	Covalent	2.1	Hydrolyses	$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

Chloride	Bonding	Electronegativity	Reaction	Equation
Sulfur	Covalent	2.5	Hydrolyses	$2S_2Cl_2 + 2H_2O \rightarrow SO_2 + 4HCl + 3S$
Chlorine	No reaction	3.0		
Argon	No reaction			

Bonding and electronegativity

In studying the trends in behaviour described above we need to consider the reasons for the trends. In order to make sense of these we think about the bonds being formed in the compounds and the electronegativity of the elements concerned.

As we go from left to right across the period, the bonding in both the oxides and the chlorides changes from ionic to covalent. Electronegativity increases across the period and thus the difference in electronegativity between the element and oxygen or the element and chlorine decreases.

Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

NOW TEST YOURSELF

5 Oxygen has an electronegativity of 3.5.

- **a** For each of the oxides Na_2O to SO_2 calculate the difference in electronegativity.
- **b** What do you notice about these?
- **c** Use Table 9.4 to predict the type of bonding in each oxide.

6 An element J in Period 3 reacts vigorously with oxygen when in powder form. It forms a liquid chloride that hydrolyses in water to give an acidic solution and an insoluble solid.

Identify J and write balanced equations for the three reactions described.

REVISION ACTIVITY

a Sketch a graph to show how the first ionisation energy changes across Period 3 from sodium to argon.

b For the elements in Period 3:

- **i** Write the formulae of two oxides that do not react with water.
- **ii** Identify the element that can exist in oxidation states +3 and +5.
- **iii** Identify the element whose oxide forms a very strong giant covalent lattice.
- **iv** Identify the element that reacts with nitrogen when it is burned in air.

c Write equations to show that aluminium oxide is amphoteric.

END OF CHAPTER CHECK

By now you should be able to:

- describe qualitatively the variation in physical properties of the elements in Period 3
- describe, explain and write equations for the reactions of the elements in Period 3 with oxygen and for the reactions of these oxides with water
- describe, explain and write equations for the reactions of the chlorides of elements in Period 3 with water
- explain the variation and trends in the above reactions in terms of bonding and electronegativity
- predict the characteristic properties of an element in a given group; deduce the nature and possible position in the Periodic Table of an unknown element based on physical and chemical properties