

At the end of this topic, you should be familiar with:

- the structure of atoms
- the relative atomic mass scale
- the mass spectrometer
- electronic structure

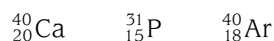
## A The structure of atoms

Atoms consist of a nucleus, comprising protons and neutrons, and electrons that move around the nucleus. Table 2.1 summarises important information regarding the relative charge and relative mass of each of the three particles from which atoms are made.

Particle	Relative charge	Relative mass
Proton	+1	1
Neutron	0	1
Electron	-1	1
		<u>2000</u>

Table 2.1

The atoms of the elements calcium, phosphorus and argon can be represented as:



where the larger number is called the mass number and the smaller number is called the atomic number.

For atoms, the atomic number is also equal to the number of electrons as the overall charge of an atom is zero (the number of positively charged protons must be equal to the number of negatively charged electrons).

Ions, i.e. particles with different numbers of protons and electrons, have an overall charge. Removing a negatively charged electron from a neutrally charged atom creates a positively charged ion and vice versa.

- **Mass number: the total number of protons and neutrons.**
- **Atomic number: the number of protons in the nucleus.**  
Each element has its own characteristic atomic number.

Referring to the above examples:

- a calcium atom has 20 protons, 20 electrons and 20 neutrons (40–20)
- a phosphorus atom has 15 protons, 15 electrons and 16 neutrons (31–15)
- an atom of argon has 18 protons, 18 electrons and 22 neutrons (40–18)

### 1 The structure of ions

Ions do not have the same number of protons and electrons. An atom of sodium (11 protons and 11 electrons) reacts by losing its outer shell electron. In doing so, it now forms a positively charged ion. Remember that the atom has a zero charge. The number of positively charged protons is equal to the number of negatively charged electrons, so the overall charge is zero. However, when the sodium atom loses its outer electron, it has lost one negatively charged electron; there are now only 10 electrons and 11 protons in the nucleus, so the overall charge is +1, that is 11–10. Table 2.2 lists some other ions with the numbers of protons, neutrons and electrons in each. Note that the atomic number is **always** equal to the number of protons, whether the particle is an atom or an ion.

The chemical properties of isotopes are identical since these depend on the outer electronic configuration of the atoms (isotopes differ in their nuclear composition only).

$^{12}\text{C}$  is the standard to which all other atom masses are compared.

Ions	Protons (+)	Neutrons (0)	Electrons (-)	Overall charge
$^{37}_{17}\text{Cl}^-$	17	20	18	-1
$^{35}_{17}\text{Cl}^-$	17	18	18	-1
$^{32}_{16}\text{S}^{2-}$	16	16	18	-2
$^{27}_{13}\text{Al}^{3+}$	13	14	10	+3

Table 2.2

## 2 Isotopes

Isotopes are atoms of an element with the same number of protons but different numbers of neutrons, i.e. atoms with the same atomic numbers but different mass numbers.

The element carbon has three different isotopes; all of its isotopes have the atomic number 6 but different mass numbers:

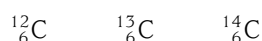


Table 2.3 shows the numbers of protons, neutrons and electrons in each of these three isotopes of carbon:

Isotopes	Protons	Neutrons	Electrons
$^{12}\text{C}$	6	6	6
$^{13}\text{C}$	6	7	6
$^{14}\text{C}$	6	8	6

Table 2.3

## B The relative atomic mass scale

The relative atomic mass (RAM) is the comparative mass of an atom of an element with  $\frac{1}{12}$  of an atom of  $^{12}\text{C}$  (the standard to which all other atoms are compared). On this scale,  $^{12}\text{C}$  assumes the relative atomic mass of 12 exactly. Note that the relative atomic mass does not have any units.

$$\text{relative atomic mass} = \frac{\text{average mass of an atom} \times 12}{\text{mass of an atom of } ^{12}\text{C}}$$

## 1 Isotopic considerations

The element chlorine has two isotopes with mass numbers of 35 and 37. How do we give chlorine a relative atomic mass, as a single number, when there is more than one isotope? All we do is calculate an average value for the relative atomic mass by multiplying the relative abundance of each isotope by the corresponding relative atomic mass.

% abundance of  $^{35}_{17}\text{Cl}$  is 75.5% and % abundance of  $^{37}_{17}\text{Cl}$  is 24.5%



## The mass spectrometer

Using these figures, we obtain an average relative atomic mass for chlorine:

$$(75.5\% \text{ of } 35) + (24.5\% \text{ of } 37) = \left(\frac{75.5}{100} \times 35\right) + \left(\frac{24.5}{100} \times 37\right) \\ = 35.49 \text{ (no units)}$$

Therefore, 35.49 is the average relative atomic mass of the element chlorine on the relative atomic mass scale. Note that chlorine is quoted as having a relative atomic mass of 35.5 in most copies of the periodic table and now you can see why — it takes into account the abundance of the isotopes  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  (and this is also why other elements do not have whole number RAMs).

- Calculate the relative atomic mass for krypton, Kr, using the information in Table 2.4.

Isotopes	$^{78}_{36}\text{Kr}$	$^{80}_{36}\text{Kr}$	$^{82}_{36}\text{Kr}$	$^{83}_{36}\text{Kr}$	$^{84}_{36}\text{Kr}$	$^{86}_{36}\text{Kr}$
% abundance	0.35	2.3	11.6	11.5	56.9	17.4

Table 2.4

The average value for the relative atomic mass of krypton is therefore the sum of each percentage abundance multiplied by its respective mass number, i.e.

$$\left(\frac{0.35}{100} \times 78\right) + \left(\frac{2.3}{100} \times 80\right) + \left(\frac{11.6}{100} \times 82\right) + \left(\frac{11.5}{100} \times 83\right) + \left(\frac{56.9}{100} \times 84\right) + \left(\frac{17.4}{100} \times 86\right) \\ = 83.93 \text{ (no units)}$$

Note that on the relative atomic mass scale, the average value for carbon is often written as 12.011 and for hydrogen as 1.00797. These average values take account of the existence of other isotopes for these elements, that is  $^{12}\text{C}$ ,  $^{13}\text{C}$  and  $^{14}\text{C}$  as well as  $^1\text{H}$ ,  $^2\text{H}$  and  $^3\text{H}$ , all occurring in differing abundances.

Remember that the average RAM is the sum of each mass number multiplied by its respective percentage abundance.

Other modern spectroscopic techniques are discussed in Topic 19.

## The mass spectrometer

The mass spectrometer is a very powerful device that analyses a substance, whether an element or a compound, and measures the masses and the relative abundances of the components or fragmented parts. A mass spectrum is then produced that shows the mass-to-charge ratio ( $m/z$ ) of each fragment (on the  $x$ -axis) and the relative abundance of each respective component (on the  $y$ -axis). A diagram of a mass spectrometer is shown in Figure 2.1.

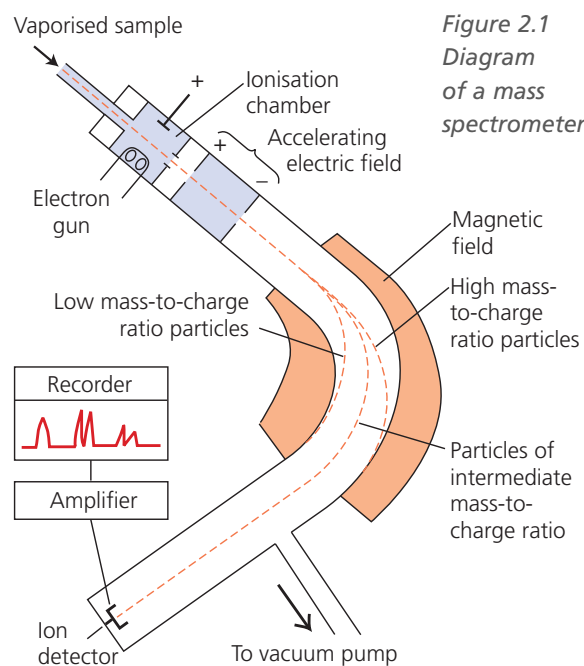


Figure 2.1  
Diagram of a mass spectrometer

Electrons are never gained by the vaporised particles to form negative ions.

All of the ionisation takes place in the gas phase — watch the state symbols.

Remember from your physics that 1 volt is the same as 1 joule per coulomb of charge, so all ions are supplied with the same degree of kinetic energy. Given that kinetic energy is equal to  $\frac{1}{2}mv^2$ , the ions with more mass will be moving with less velocity since the kinetic energy must be the same and vice versa for ions of low mass.

The ions  $^{16}\text{O}^+$  and  $^{32}\text{S}^{2+}$  would be deflected equally since they have the same mass-to-charge ratio (both 16).

You must be familiar with the five major steps involved in its operation.

### Step 1: vaporisation

The sample is injected into the vaporisation chamber and heated. It undergoes a phase change and will emerge from the chamber in the form of a gas.

For example:

- bromine liquid to gaseous bromine solid,  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$
- solid benzoic acid to gaseous benzoic acid,  
 $\text{C}_6\text{H}_5\text{COOH}(\text{s}) \rightarrow \text{C}_6\text{H}_5\text{COOH}(\text{g})$

Note that ionic samples inevitably have much higher boiling points than organic molecules and this makes vaporisation very difficult.

### Step 2: electron bombardment (ionisation)

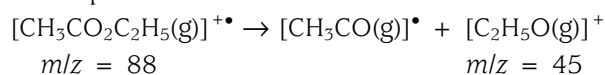
By increasing the potential difference across two plates, electrons are produced from the negative cathode and move across to the positively charged anode. Sometimes, this part of the spectrometer is called an electron gun. When the gaseous molecules or atoms diffuse past the electron beam, the high energy electrons may knock off one electron, or sometimes more, from the outer shell of the moving particles; this process is called ionisation.

For example:

- the ionisation of a gaseous sodium atom,  $\text{Na}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$
- the ionisation of an ethanol molecule,  $\text{C}_2\text{H}_5\text{OH}(\text{g}) \rightarrow [\text{C}_2\text{H}_5\text{OH}(\text{g})]^+ + \text{e}^-$

If molecules move past the electron gun, they will be ionised (as above) and then may undergo a fragmentation (a molecular split). In this process, a molecule with a positive charge (since it has lost one of its electrons) may rearrange its electron distribution and, in doing so, may break into two smaller fragments.

For example:



### Step 3: electrostatic acceleration

The positively charged ions are accelerated towards a negatively charged plate and as they do so their kinetic energy increases. The effect of the electrostatic acceleration is also to focus the positively charged ions into a beam prior to the next stage in the process.

### Step 4: magnetic deflection

The positive ions that have been electrostatically accelerated possess different masses and the majority of them have one positive charge (although other charges are possible). The ions are now 'sorted' according to their mass and their charge using a very strong magnetic field. The deflection depends on the mass-to-charge ratio of each ion or mass/charge ( $m/z$ ). **The smaller the ratio, the greater will be the deflection.**

**Low mass ions** undergo significant deflection and **high mass ions** undergo little deflection in the magnetic field. Ions with a **high charge** undergo a larger deflection than ions with a **low charge**.



The  $m/z$  of the ion  $M^{+•}$  gives the relative molecular mass of the original molecule — this is important when analysing the molecule.

### Step 5: detection

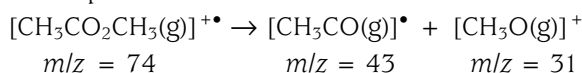
The positively charged ions have now been sorted according to their mass-to-charge ratio; they then move towards a detector. When the positively charged ions hit the detectors, they accept an electron and, in doing so, cause a current to flow. If there are two ions (of the same  $m/z$ ) that arrive at the same time, then twice the electrical current flows.

From each electrical conductor in the detector, an electrical current will be produced that is proportional to the number of ions of that particular mass-to-charge ratio that arrive per second. The current produced is called an **ion current**. The various ion currents are then amplified (magnified) so that they may be measured by a computer. The computer then produces a graph of ion current (% abundance) on the  $y$ -axis against mass-to-charge ratio on the  $x$ -axis; this is the mass spectrum.

**Figure 2.2** shows some mass spectra for (a) a monoatomic element, e.g. lead; (b) a diatomic element, e.g. bromine; and (c) an organic compound, e.g. ethanol.

In the case of organic compounds like methyl ethanoate, **fragmentations** are possible, producing fragments of different mass-to-charge ratios.

For example:



The mass-to-charge ratios of the fragments can often lead to their identification and hence the original molecule can be identified.

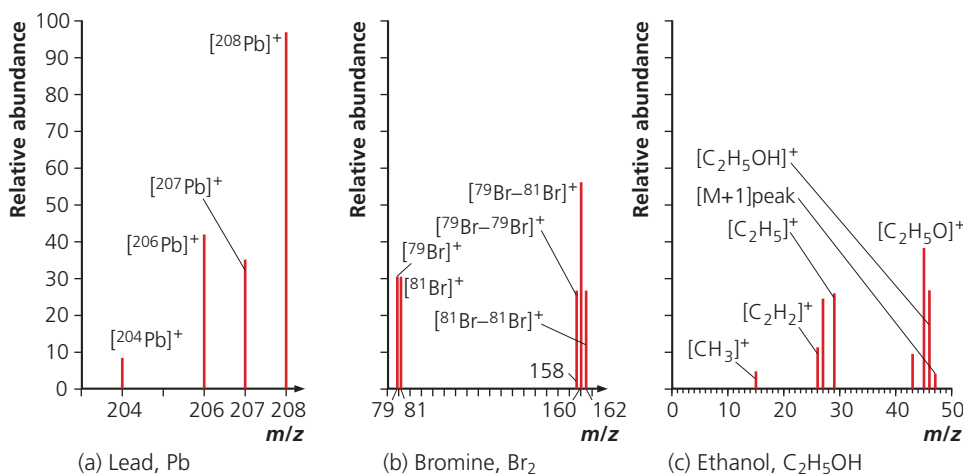


Figure 2.2 Examples of mass spectra

The **molecular ion peak** (the peak of highest mass-to-charge ratio containing  $^{12}\text{C}$ ) can lead directly to the identification of the molecule. A peak at  $(M + 1)$  is usually due to the presence of one  $^{13}\text{C}$  atom isotope in the molecule.

## D Electronic structure of atoms

At GCSE you would have been taught the idea of the electronic configuration. This simply arranges the available number of electrons into shells (in which

Ionisation energies are measured in the gas phase.

Ionisation energies are always endothermic since energy must be supplied for an electron to overcome the nuclear attraction.

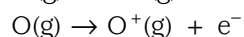
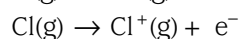
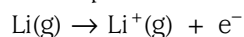
## 1

## Electron shells

Ionisation enthalpies can be used to provide evidence for the electronic structure of atoms.

- **The standard first ionisation enthalpy is defined as the heat energy required to remove a mole of electrons from a mole of gaseous atoms in order to form a mole of gaseous ions all with a single positive charge at 298 K and 1 atmosphere pressure.**

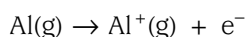
For example:



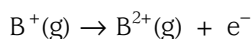
It is possible to measure the ionisation enthalpy required to remove further electrons from the same element. These are called the second ionisation enthalpy (to remove the second mole of electrons) and the third ionisation enthalpy (to remove the third mole of electrons), and so on.

For example:

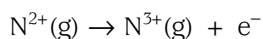
- the first ionisation enthalpy of aluminium



- the second ionisation enthalpy of boron



- the third ionisation enthalpy of nitrogen



If we consider one element only, and plot the consecutive ionisation energies for that element, the resulting graph yields some important information about electronic structure. For example, Table 2.5 lists the consecutive ionisation energies for the element oxygen.

Ionisation enthalpy/kJ mol <sup>-1</sup>	Ionisation involved	
1 310	$\text{O(g)} \rightarrow \text{O}^{\text{+}}(\text{g}) + \text{e}^{-}$	1st ionisation
3 390	$\text{O}^{\text{+}}(\text{g}) \rightarrow \text{O}^{\text{2+}}(\text{g}) + \text{e}^{-}$	2nd ionisation
5 320	$\text{O}^{\text{2+}}(\text{g}) \rightarrow \text{O}^{\text{3+}}(\text{g}) + \text{e}^{-}$	3rd ionisation
7 450	$\text{O}^{\text{3+}}(\text{g}) \rightarrow \text{O}^{\text{4+}}(\text{g}) + \text{e}^{-}$	etc.
11 000	$\text{O}^{\text{4+}}(\text{g}) \rightarrow \text{O}^{\text{5+}}(\text{g}) + \text{e}^{-}$	etc.
13 300	$\text{O}^{\text{5+}}(\text{g}) \rightarrow \text{O}^{\text{6+}}(\text{g}) + \text{e}^{-}$	etc.
71 000	$\text{O}^{\text{6+}}(\text{g}) \rightarrow \text{O}^{\text{7+}}(\text{g}) + \text{e}^{-}$	etc.
84 100	$\text{O}^{\text{7+}}(\text{g}) \rightarrow \text{O}^{\text{8+}}(\text{g}) + \text{e}^{-}$	etc.

Table 2.5



## Electronic structure of atoms

It is not easy to see evidence for the sub-shells using these graphs (only the shells). The energy between sub-shells within a shell is relatively small.

Make sure that you use the correct words in the correct context.

Look for the biggest jump. The point at which the jump starts indicates the group number. So, if the ionisation enthalpies are 502, 966, 3390, 4700, 6000, 7700, 9000, 10 200, then this element is in group 2.

The third electron would require too much energy, an investment of energy that would not be recovered by the lattice energy when the new ions bonded to form their lattice structure.

If a graph is plotted of  $\log_{10}$  of the ionisation energy against the number of the electron being removed, it is clear from the graph (see Figure 2.3) that six of the eight electrons are removed a lot more easily than the two that are closest to the nucleus. Therefore, in an atom of oxygen, two electrons are in the first shell and six are in the outer shell.

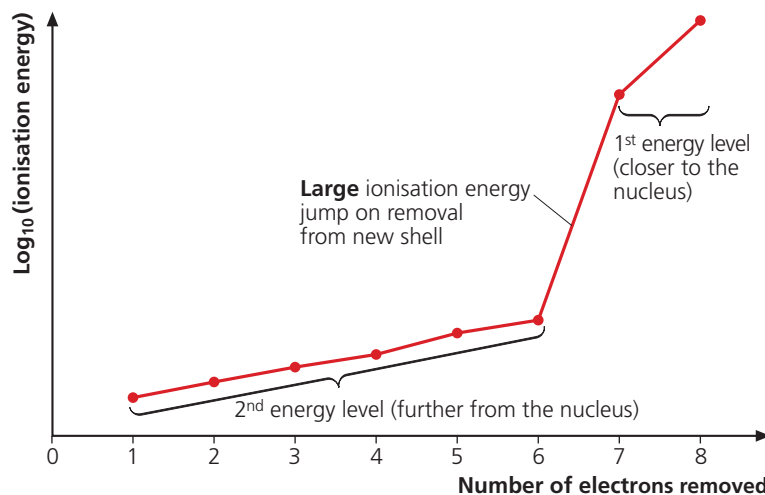


Figure 2.3  
Graph of  $\log_{10}$  ionisation energy versus number of the electron being removed for oxygen

It can be seen that of the eight electrons, two electrons are closer to the nucleus than the other six. There are therefore six outer electrons. We can analyse other ionisation energy plots for other elements and find that a similar pattern seems to be present.

Each **shell** is divided into **sub-shells** (or sub-levels) and then each sub-shell is made up of **orbitals**. An orbital is allowed to contain a maximum of two electrons.

The ionisation energies may be given in numerical form rather than as a graph. For example, the first six consecutive ionisation enthalpies for the elements X, Y and Z are shown in Table 2.6.

	1st	2nd	3rd	4th	5th	6th
<b>X</b>	1090	2350	4610	6220	37 800	47 000
<b>Y</b>	590	1150	4940	6480	8120	10 700
<b>Z</b>	966	1950	2730	4850	6020	12 300

Table 2.6

● **In which groups of the periodic table would X, Y and Z be found?**

In X, there is a large jump in ionisation enthalpies from electron number 4 to electron number 5. This indicates that electron 5 is more tightly bound by the nucleus and it is likely to be the start of a new shell of electrons closer to the nucleus. There are four electrons in the outer shell of X, so it is in group 4 of the periodic table.

In Y, the largest jump is between electron 2 and electron 3. This means that there are two electrons in the outer shell of Y, so Y is in group 2. The electrons that are easier to remove are those that Y loses when it reacts to form an ion.

In Z, there are five electrons in the outer shell, so we place Z in group 5.

2

## Order of filling sub-shells

If a copy of the periodic table is available in the examination, it can be used to determine the order of electron filling of the sub-shells within an atom, as shown in Figure 2.4.

Move horizontally through the 1s and then into the 2s and the 2p and so on. This is the order in which the sub-shells fill, lowest energy first.

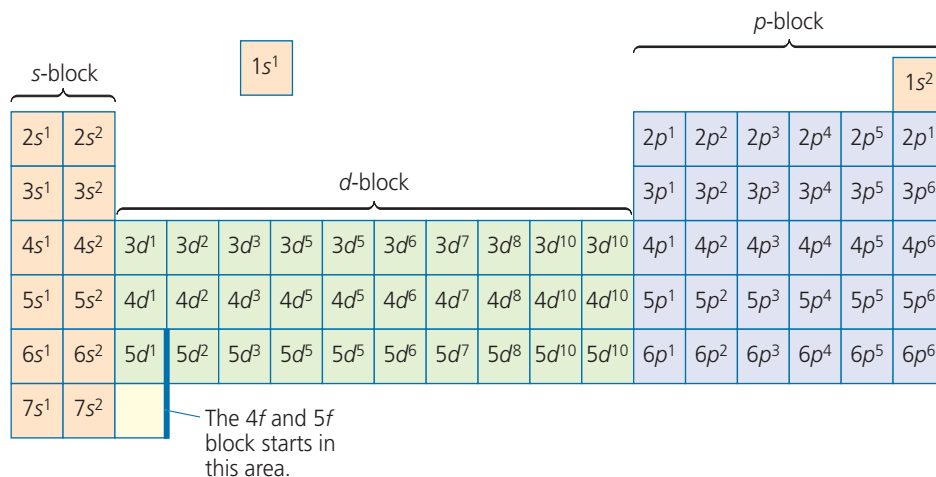


Figure 2.4 The periodic table with outer electron configuration shown

If a periodic table is not available, then there is a way of recalling the order in which the sub-shells are filled. Remember the arrangement of sub-shells in Figure 2.5.

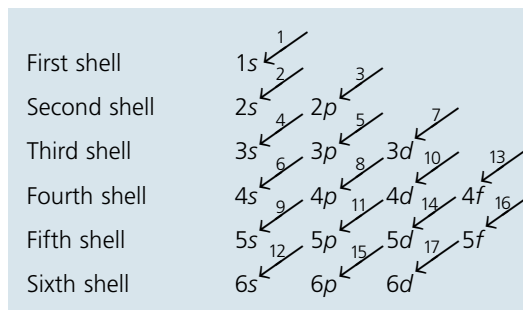


Figure 2.5 Arrangement of sub-shells

Draw diagonal lines, like those shown, and gradually move along the lines downwards (starting at number 1). The lines should cross, in order, the sub-shell that fills up next. The result should be as follows, in order of lowest energy first:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, etc.

Note that the periodic table is arranged in the order in which the sub-shells fill with electrons, that is the sub-shells from lowest energy to highest energy. So, it should be of little surprise that the order starts with the 1s since this is the orbital closer to the nucleus, and lower in energy, and then the 2s and then the 2p (although the latter two sub-shells are relatively close in energy compared with the 1s and 2s sub-shell difference in energy). After the 3s is filled with two electrons, the 3p is filled with six electrons. Then the 4s is filled before the 3d.

Table 2.7 gives examples of electronic configurations.

The Aufbau (or building) Principle: electrons enter the lowest energy available.



Table 2.7

Element	Atomic number	Electronic configuration
Sodium, Na	11	$1s^2, 2s^2, 2p^6, 3s^1$
Na <sup>+</sup>		$1s^2, 2s^2, 2p^6$
Potassium, K	19	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
K <sup>+</sup>		$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
Sulphur, S	16	$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$
S <sup>2-</sup>		$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
Gallium, Ga	31	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^1$
Ga <sup>3+</sup>		$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$
Krypton, Kr	36	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6$

3

### Relationship between the periodic table and the electronic configuration

Lithium has an electronic configuration of  $1s^2, 2s^1$ , with its outer electron in an s-orbital, so it is in the s-block. Its outer electron is in the second shell, so lithium is in period 2 of the periodic table.

- The **sub-shell** containing the outer electrons determines the **block** of the periodic table in which the element is placed.
- The **group number** of the element will be same as the number of electrons in the **outer shell**.

4

### Orbital box diagrams

A box represents an atomic orbital. Only a maximum of two electrons is allowed in an orbital; this is the Pauli Exclusion Principle.

Since only two electrons are allowed per orbital, the orbital is sometimes represented as a box in which two electrons, represented by half arrows, are placed. So a full 1s orbital would be represented as  $\boxed{\uparrow\downarrow}$  and a full 2p as  $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$  and a full 3d as  $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$  and so on.

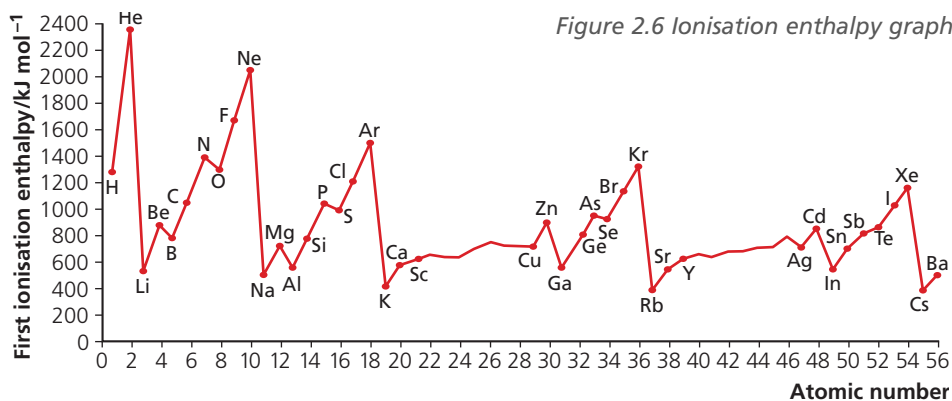
The electronic configuration for the element phosphorus would be written as:  $1s^2, 2s^2, 2p^6, 3s^2, 3p^3$  or, using box notation:  $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$   
 $\text{1s} \quad \text{2s} \quad \text{2p} \quad \text{3s} \quad \text{3p}$

5

### Trends and patterns in ionisation enthalpies

Ionisation enthalpy questions are common in examinations. Make sure that you learn to explain the trends and patterns as well as the blips.

As we saw earlier, consecutive ionisation enthalpies for a particular element yield some very important information regarding the electronic structure of the atom. When plotting a graph of the first ionisation energy for the elements against atomic number (see Figure 2.6), a regular repeating pattern is produced. This is an example of **periodicity** (a pattern in properties repeating itself at regular intervals).



There is some important information that you must know from this graph and you should also be able to explain the variations using your knowledge and understanding of electronic structure gained so far.

**Your explanations should focus on:**

- the distance between the electron and the nucleus
- the nuclear charge
- the shielding, from the nuclear charge, provided by the inner shells on the outer electron
- any electron–electron repulsion taking place within an orbital

The following explanations illustrate how these ideas may be applied to certain changes in ionisation enthalpy.

***Variation down a group of the periodic table, e.g. lithium and sodium***

Trend: a decrease

Explanation:

- despite the increased nuclear charge, the electron being removed is in a new shell progressively further from the nucleus
- the extra electron shell provides extra shielding for the removed electron from the attraction of the positively charged nucleus
- the net effect is to decrease the ionisation energy

***Variation across a period from left to right***

Trend: a general increase

Explanation:

- the electrons are being removed from the **same** electron shell
- the outer electron is experiencing slightly more shielding by the inner electron shells
- the nuclear charge is increasing since more protons are being added from left to right
- the electron experiences a greater attraction as the element increases in atomic number

Although the general trend is for ionisation energy to increase from left to right across a period, there are two notable small decreases.

***From group 2 to group 3, e.g. magnesium to aluminium or beryllium to boron***

Explanation:

- despite the increased nuclear charge, the added electron is in a new *p* sub-shell of slightly higher energy
- this is slightly further from the nucleus
- the  $s^2$  electrons, for the group 3 element, provide some shielding
- the overall effect is for the ionisation energy to decrease

***From group 5 to group 6, e.g. nitrogen to oxygen or phosphorus to sulphur***

Explanation:

- despite the increased nuclear charge, the electron from the group 6 element is being removed from a  $p^4$  configuration
- if there are four electrons in a *p* sub-shell, two of the electrons must be paired
- this inter-electron repulsion lowers the attraction between the electron and the nucleus, so the electron is easier to remove

Do not forget the number of protons in the nucleus; it is not just about the electrons.

Remember, 'inter-electronic repulsion' for the group 5 to 6 ionisation enthalpies drops.