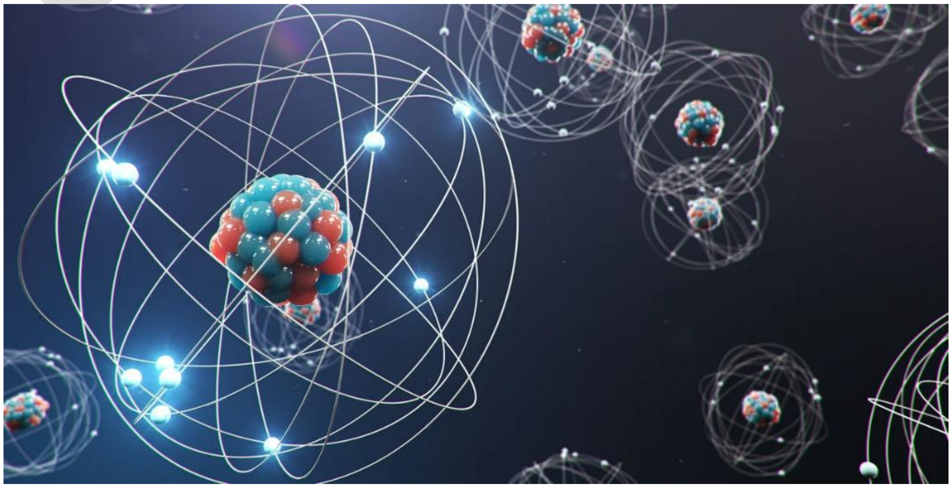
Cambridge
AS level
Chemistry

CODE: (9701)

Chapter 03

Electrons in atoms



Simple electronic structure

Electrons are arranged outside the nucleus in energy levels or quantum shells. These principal **energy levels** or **principal quantum shells** (symbol n) are numbered according to how far they are from the nucleus.

The arrangement of electrons in an atom is called its electronic structure or electronic configuration. The **electronic configurations** of lithium, carbon and neon are shown in Figure 3.2, together with a shorthand way of writing this structure.

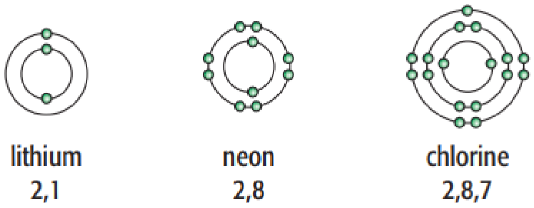


Figure 3.2 The simple electronic structures of lithium, neon and chlorine. The nuclei of the atoms are not shown.

Table 3.1 shows the number of electrons in each of the principal quantum shells (energy levels) for the first 11 elements in the Periodic Table. Each principal quantum shell can hold a maximum number of electrons:

- Shell 1 – up to 2 electrons
- Shell 2 – up to 8 electrons
- Shell 3 – up to 18 electrons
- Shell 4 – up to 32 electrons.

	Atomic number	Number of electrons in shell		
		n = 1	n = 2	n = 3
H	1	1		
He	2	2		
Li	3	2	1	
Be	4	2	2	
B	5	2	3	
C	6	2	4	
N	7	2	5	
O	8	2	6	
F	9	2	7	
Ne	10	2	8	
Na	11	2	8	1

Table 3.1 Simple electronic configurations of the first 11 elements in the Periodic Table.

Evidence for electronic structure

Ionization energy, ΔH_i

By firing high-speed electrons at atoms, scientists can work out how much energy must be supplied to form an ion by knocking out one electron from each atom. The energy change that accompanies this process is called ionization energy.

Ionization energies are measured under standard conditions. The general symbol for ionization energy is ΔH_i. Its units are $kJmol^{-1}$. The symbol for the 1st ionization energy is ΔHi1. calcium as an example:

$$\text{1st ionisation energy: } Ca(g) \longrightarrow Ca^{+}(g) + e^{-}$$

$$\Delta H_{i1} = 590\,kJ\,mol^{-1}$$

If a second electron is removed from each ion in a mole of gaseous 1+ ions, we call it the 2nd ionization energy, ΔH_{i2}. Again, using calcium as an example,

$$\text{2nd ionisation energy: } Ca^{+}(g) \longrightarrow Ca^{2+}(g) + e^{-}$$

$$\Delta H_{i2} = 1150\,kJ\,mol^{-1}$$

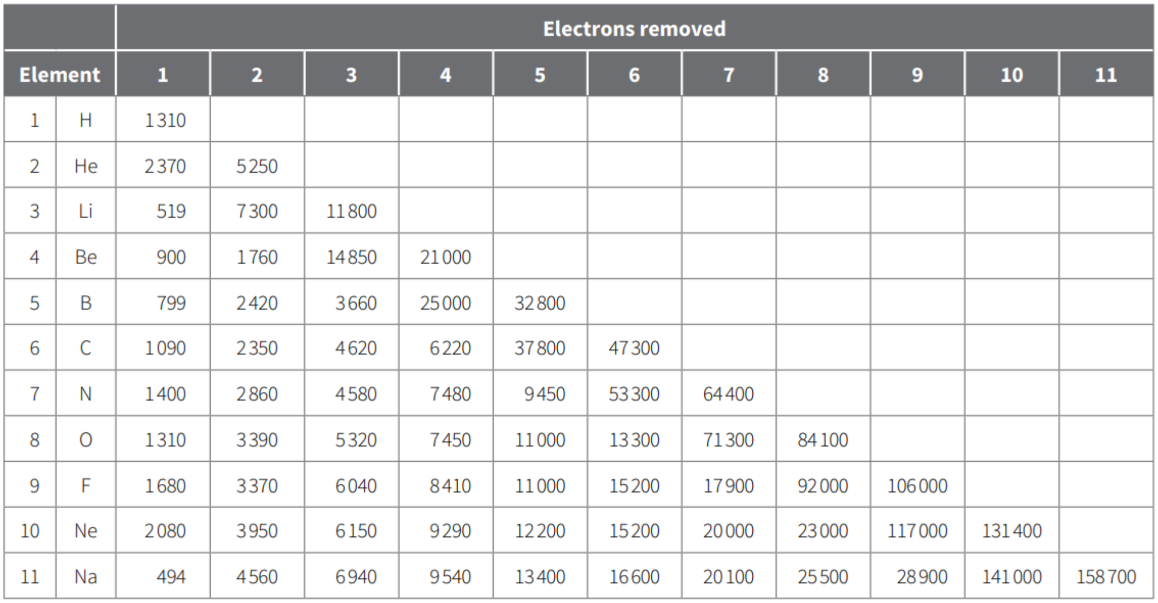
Removal of a third electron from each ion in a mole of gaseous 2+ ions is called the 3rd ionisation energy. Again, using calcium as an example:

$$\text{3rd ionisation energy: } Ca^{2+}(g) \longrightarrow Ca^{3+}(g) + e^{-}$$

$$\Delta H_{i3} = 4940\,kJ\,mol^{-1}$$

We can continue to remove electrons from an atom until only the nucleus is left. We call this sequence of ionisation energies**, successive ionisation energies**. The successive ionisation energies for the first 11 elements in the Periodic Table are shown in Table 3.2. The data in Table 3.2 shows us that:

■Ionization energies increase for each element due to the greater charge on the ion and the greater attractive force between positively charged protons and remaining negatively charged electrons, requiring more energy to overcome these forces.
■The ionisation energies of nitrogen and sodium show significant differences, with the second ionisation energy indicating electron removal from a principal quantum shell closer to the nucleus.



		Electrons removed										
Element		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
1	H	1310										
2	He	2370	5250									
3	Li	519	7300	11 800								
4	Be	900	1760	14 850	21 000							
5	B	799	2420	3660	25 000	32 800						
6	C	1090	2350	4620	6220	37 800	47 300					
7	N	1400	2860	4580	7480	9450	53 300	64 400				
8	O	1310	3390	5320	7450	11 000	13 300	71 300	84 100			
9	F	1680	3370	6040	8410	11 000	15 200	17 900	92 000	106 000		
10	Ne	2080	3950	6150	9290	12 200	15 200	20 000	23 000	117 000	131 400	
11	Na	494	4560	6940	9540	13 400	16 600	20 100	25 500	28 900	141 000	158 700

Table 3.2 Successive ionisation energies for the first 11 elements in the Periodic Table.

Three factors that influence ionisation energies

1) The size of the nuclear charge
As the atomic number (number of protons) increases, the positive nuclear charge increases. The bigger the positive charge, the greater the attractive force between the nucleus and the electrons. So, more energy is needed to overcome these attractive forces if an electron is to be removed.

■In general, ionisation energy increases as the proton number increases.

2) Distance of outer electrons from the nucleus the force of attraction between positive and negative charges decreases rapidly as the distance between them increases. So, electrons in shells further away from the nucleus are less attracted to the nucleus than those closer to the nucleus.

■The further the outer electron shell is from the nucleus, the lower the ionisation energy.

3) Shielding effect of inner electrons as all electrons are negatively charged, they repel each other. Electrons in full inner shells repel electrons in outer shells. Full inner shells of electrons prevent the full nuclear charge from being felt by the outer electrons. This is called shielding. The greater the **shielding** of outer electrons by the inner electron shells, the lower the attractive forces between the nucleus and the outer electrons.

■The ionisation energy is lower as the number of full electron shells between the outer electrons and the nucleus increases.

Interpreting successive ionisation energies

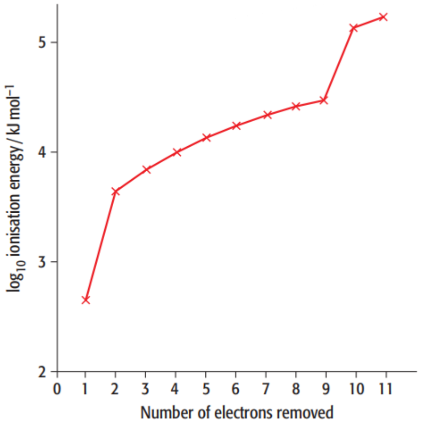


Figure 3.4 Graph of logarithm ($\log_{10}$) of ionisation energy of sodium against the number of electrons removed.

Figure 3.4 shows a graph of successive ionisation energies against the number of electrons removed for sodium. A logarithmic scale (to the base 10) is used because the values of successive ionisation energies have such a large range.

We can deduce the following about sodium from Figure 3.4:

■ The first electron removed has a low 1st ionisation energy, when compared with the rest of the data. It is very easily removed from the atom. It is therefore likely to be a long way from the nucleus and well shielded by inner electron shells.

■The second electron in sodium is more difficult to remove than the first, indicating a closer shell to the nucleus. The ionisation energy values for the first and second electrons suggest one electron in the outer shell.

■From the second to the ninth electrons removed there is only a gradual change in successive ionisation energies. This suggests that all these eight electrons are in the same shell

■The 10th and 11th electrons have high ionisation energies, suggesting proximity to the nucleus due to strong attraction and no inner electrons. The large increase in ionisation energy between the 9th and 10th electrons confirms the 10th electron's closer proximity to the nucleus.

Figure 3.5 shows this arrangement of electrons
We can use successive ionisation energies in this way to:

■Predict or confirm the simple electronic configuration of elements

■Confirm the number of electrons in the outer shell of an element and hence the group to which the element belongs.

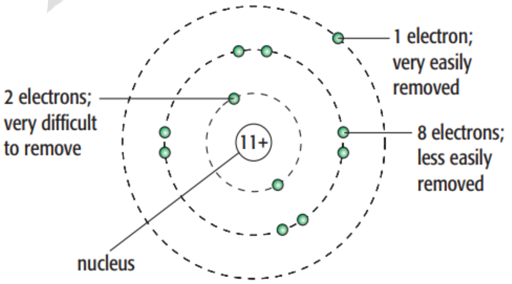


Figure 3.5 The arrangement of electrons in an atom of sodium can be deduced from the values of successive ionisation energies.

Subshells and atomic orbitals

Quantum subshells

Principal quantum shells are divided into subshells (sublevels), each with a different number of subshells (s, p, d). For elements with more than 57 electrons, there are f subshells. Figure 3.6 shows subshells for four principal quantum levels.

In any principal quantum shell, the energy of the electrons in the subshells increases in the order s < p < d. The maximum number of electrons that are allowed in each subshell is: s = 2 electrons, p = 6 electrons, d = 10 electrons.

■The first principal quantum level, n = 1, can hold a maximum of 2 electrons in an s subshell.

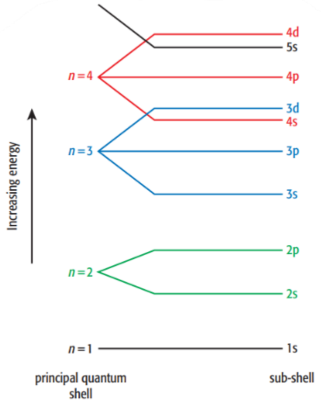


Figure 3.6 The subshells for the first four principal quantum shells.

■The second principal quantum level, n = 2, can hold a maximum of 8 electrons: 2 electrons in the s subshell and 6 electrons in the p subshell.

■The third principal quantum level, n = 3, can hold a maximum of 18 electrons: 2 electrons in the s subshell, 6 electrons in the p subshell and 10 electrons in the d subshell.

Figure 3.6 reveals that the order of subshells in terms of increasing energy does not follow a regular pattern after element argon, with the order appearing to overlap. The next element is potassium, with its outer electron in the 4s subshell, and the first element with an electron in the 3d subshell is element 21, scandium. The letters s, p, and d represent the lines observed when high-speed electrons hit gas particles at low pressure.

Atomic orbitals

Each subshell contains one or more atomic orbitals.

An atomic orbital is a region of space around the nucleus of an atom that can be occupied by one or two electrons.

As each orbital can only hold a maximum of two electrons, the number of orbitals in each subshell must be:
s – one orbital
p – three orbitals
d – five orbitals.

Shapes of the orbitals

Each orbital has a three-dimensional shape. Within this shape there is a high probability of finding the electron or electrons in the orbital. Figure 3.7 shows how we represent the s and p orbitals.

The s orbitals in the second principal quantum shell have a spherical shape, while the 2s orbitals in the first quantum shell have a spherical shape. The 2p orbitals in the second shell have an hourglass shape with two lobes, arranged at right angles along the x, y, and z axes. There are three 3p orbitals in the third quantum shell, each with the same energy. The d orbitals are more complex, with the idea of electron probability clouds arising from Louis de Broglie's 1925 suggestion that electrons behave like waves. Understanding the d-orbital shapes is essential for studying transition elements at the A level.

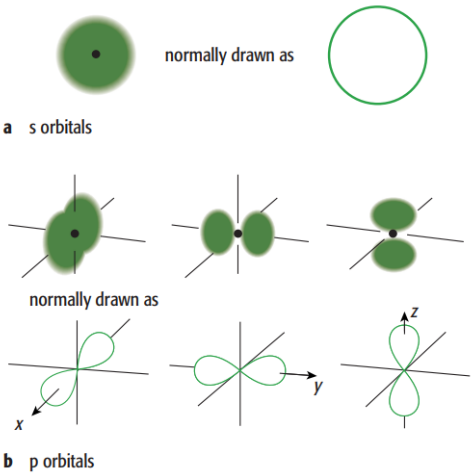


Figure 3.7 Representations of orbitals (the position of the nucleus is shown by the black dot): **a** s orbitals are spherical; **b** p orbitals, p_x, p_y and p_z, have 'lobes' along the *x*, *y* and *z* axes.

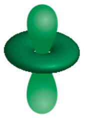


Figure 3.8 The shape of a dz^2 orbital.

Filling the shells and orbitals

The most stable electronic configuration of an atom is the one with the lowest energy. The order of filling subshells depends on their relative energy. The 1s subshell is filled first, followed by higher ones. The order of subshells does not follow a regular pattern, as shown in Figure 3.6.

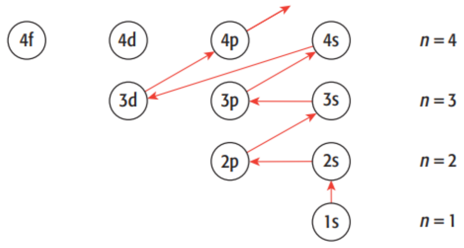
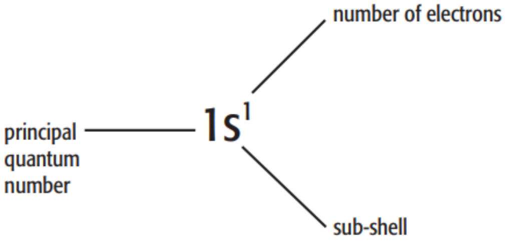


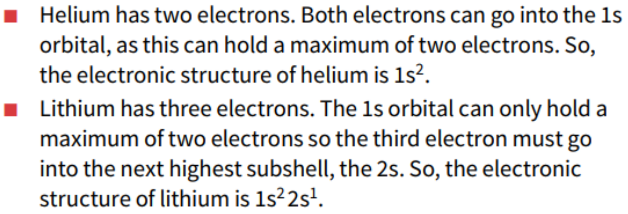
Figure 3.9 Diagram to show the order in which orbitals are filled up to shell *n* = 4.

Electronic configurations

Representing electronic configurations

A detailed way of writing the electronic configuration of an atom that includes information about the number of electrons in each subshell is shown below for hydrogen.





- Helium has two electrons. Both electrons can go into the 1s orbital, as this can hold a maximum of two electrons. So, the electronic structure of helium is $1s^2$.
- Lithium has three electrons. The 1s orbital can only hold a maximum of two electrons so the third electron must go into the next highest subshell, the 2s. So, the electronic structure of lithium is $1s^2 2s^1$.

Electrons are added one by one for successive elements, filling each subshell in order of increasing energy. The electronic configurations of the first 18 elements are shown in Table 3.5.

A question about this type of detailed notation will often be stated like this: ‘Use 1s2 notation to give the electronic configuration …’

Table 3.6 displays the electronic configurations of elements after argon, represented by [Ar]. The 'noble gas core' represents argon's configuration, 1s2, 2s2, 2p6, 3s2, 3p6. This method is a shorthand for writing atoms with many electrons but should be prepared for exams.

You should note the following:

■ Electronic configuration of potassium Potassium has the electronic structure 1s2 2s2 2p6 3s2 3p6 4s1. The outer electron goes into the 4s subshell rather than the 3d subshell because the 4s is below the 3d in terms of its energy.

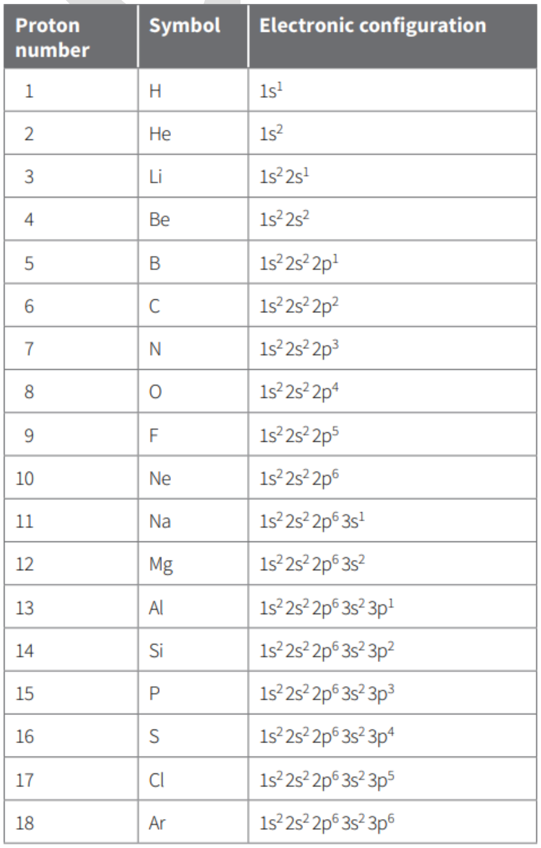
■Filling the 3d subshell After calcium, a new subshell becomes occupied. The next electron goes into a 3d subshell rather than a 4p subshell.

Scandium has an electronic configuration of [Ar] 3d1 4s2, due to electrons occupying the lowest energy orbitals, resulting in a pattern ending with zinc.

■ Chromium and copper

Chromium and copper exhibit unusual electronic configurations, differing from the expected pattern of [Ar]3d4 4s1 and [Ar]3d10 4s1, requiring understanding as exceptions.

■ Gallium to krypton
The electrons add to the 4p subshell because this is the next highest energy level above the 3d.



Proton number	Symbol	Electronic configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	$1s^2 2s^1$
4	Be	$1s^2 2s^2$
5	B	$1s^2 2s^2 2p^1$
6	C	$1s^2 2s^2 2p^2$
7	N	$1s^2 2s^2 2p^3$
8	O	$1s^2 2s^2 2p^4$
9	F	$1s^2 2s^2 2p^5$
10	Ne	$1s^2 2s^2 2p^6$
11	Na	$1s^2 2s^2 2p^6 3s^1$
12	Mg	$1s^2 2s^2 2p^6 3s^2$
13	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$
14	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$
15	P	$1s^2 2s^2 2p^6 3s^2 3p^3$
16	S	$1s^2 2s^2 2p^6 3s^2 3p^4$
17	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$

Table 3.5 Electronic configurations for the first 18 elements in the Periodic Table.

Orbitals and the Periodic Table

The arrangement of elements in the Periodic Table reflects the electronic structure of the elements. The Periodic Table can be split into blocks of elements (Figure 3.10).

■Elements in Groups 1 and 2 have outer electrons in an s subshell.

■ Elements in Groups 3 to 18 (apart from He) have outer electrons in a p subshell.

■Elements that add electrons to the d subshells are called the d-block elements. Most of these are transition elements.

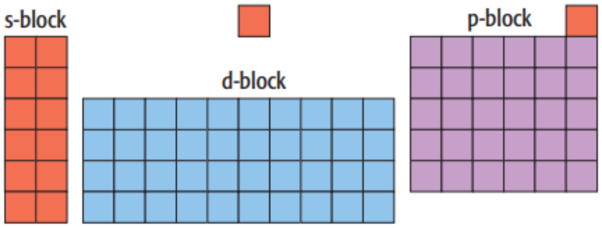


Figure 3.10 Some of the blocks of elements in the Periodic Table.

Filling the orbitals A useful way of representing electronic configurations is a diagram that places electrons in boxes (Figure 3.11).

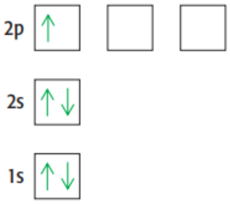


Figure 3.11 The electronic configuration of boron in box form.

■Each box represents an atomic orbital.

■The boxes (orbitals) can be arranged in order of increasing energy from bottom to top.

■An electron is represented by an arrow.

■The direction of the arrow represents the 'spin' of the electron. (We imagine an electron rotating around its own axis either in a clockwise or anticlockwise direction.)

■When there are two electrons in an orbital, the 'spins' of the electrons are opposite, so the two arrows in this box point in opposite directions.

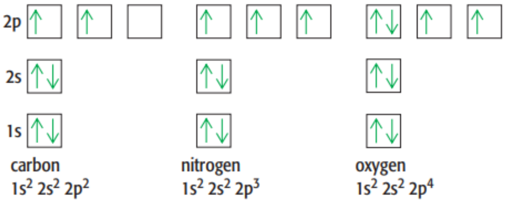


Figure 3.12 When adding electrons to a particular subshell, the electrons are only paired when no more empty orbitals are available.

Electrons repel each other due to their same charge, so they occupy separate orbitals in the same subshell to minimize repulsion. They have a'spin' in the same direction. When empty orbitals are available, electrons are paired, with opposite spins to minimize repulsion.

Electronic configuration of ions

Positive ions form when electrons are removed from atoms, like sodium ions with 10 electrons and sulfide ions with 18 electrons. The electronic configuration of sodium ions is 1s2 2s2 2p6, like neon. Negative ions form when atoms gain electrons, like sulfide ions with 18 electrons. Electrons in the outer subshell are typically removed when metal ions form positive ions. However, d-block elements behave differently, with the 4s subshell filling before the 3d subshell.

Patterns in ionisation energies in the Periodic Table

Patterns across a period

Figure 3.13 shows how the first ionisation energy, ΔHi1, changes across the first two periods. We can explain the form of the graph mainly by referring to the factors that influence ionisation energies.

1) ΔHi1 generally increases over periods, including Period 1 (hydrogen and helium), Period 2 (lithium to neon), and other periods, as nuclear charge increases, but electron removal comes from the same shell.

So, the force of attraction between the positive nucleus and the outer negative electrons increases across the period because:

i the nuclear charge increases

ii the distance between the nucleus and the outer electron remains reasonably constant

iii the shielding by inner shells remains reasonably constant.

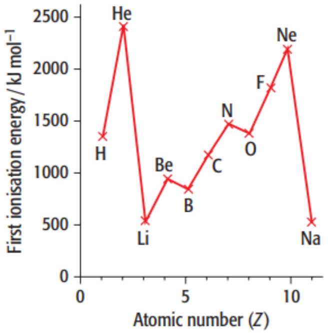


Figure 3.13 A graph of the first ionisation energies of the elements hydrogen to sodium plotted against atomic number.

2) The ionisation energy decreases rapidly between elements, with lithium having a smaller ΔH_{i1} than helium due to its three electrons in the second quantum shell, whereas helium has two electrons in the first.
So, the force of attraction between the positive nucleus and the outer negative electrons decreases because,

i the distance between the nucleus and the outer electron increases

ii the shielding by inner shells increases

iii these two factors outweigh the increased nuclear charge.

3) The ΔH_{i1} decreases slightly between beryllium and boron, despite boron having one more proton. This decrease occurs when the outer electron is removed. Beryllium has the electronic structure 1s2 2s2, while boron has the structure 1s2 2s2 2p1.

There is less attraction between the fifth electron in boron and the nucleus because:

i the distance between the nucleus and the outer electron increases slightly

ii the shielding by inner shells increases slightly

iii these two factors outweigh the increased nuclear charge

4) The decrease in ΔH_{i1} between nitrogen and oxygen is due to the spin-pairing of electrons. Nitrogen has one more proton than nitrogen, and the electron removed is in the same 2p subshell. The extra repulsion between the electrons in the oxygen orbital results in less energy needed to remove an electron.
So, ΔH_{i1} for oxygen is lower, because of spin-pair repulsion.

Patterns down a group the first ionisation energy decreases as you go down a group in the Periodic Table. For example, in Group 1 the values of ΔH_{i1} are:

■Li = 519kJmol^{-1}

■Na = 494kJmol^{-1}

■K = 418kJmol^{-1}

■Rb = 403kJmol^{-1}

As you go down the group, the outer electron removed is from the same type of orbital but from a successively higher principal quantum level – 2s from lithium, 3s for sodium and 4s for potassium.

Although the nuclear charge is increasing down the group there is less attraction between the outer electron and the nucleus because:

1.the distance between the nucleus and the outer electron increases

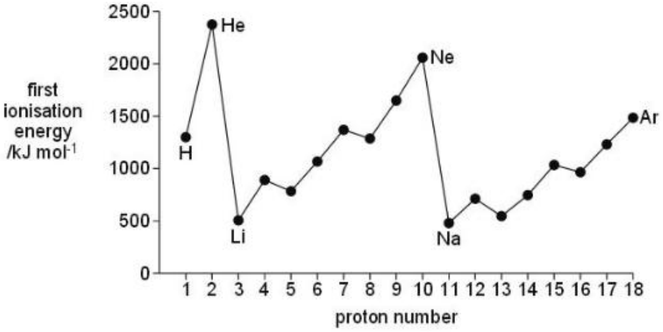
2. the shielding by complete inner shells increases

3. these two factors outweigh the increased nuclear charge

Revision questions

The Periodic Table we currently use is derived directly from that proposed by Mendeleev in 1869 after he had noticed patterns in the chemical properties of the elements he had studied.

The diagram below shows the first ionisation energies of the first 18 elements of the Periodic Table as we know it today.



(a) Give the equation, including state symbols, for the first ionisation energy of fluorine.
(b) Explain why there is a general increase in first ionisation energies from sodium to argon.
(c) (i) Explain why the first ionisation energy of aluminium is less than that of magnesium.
(ii) Explain why the first ionisation energy of sulphur is less than that of phosphorus.

(3) Copper and titanium are each used with aluminium to make alloys which are light, strong and resistant to corrosion.
Aluminium, Al, is in the third period of the Periodic Table; copper and titanium are both transition elements.
(a) Complete the electronic configuration of aluminium and of titanium, proton number 22.

Phosphorus is a very reactive non-metallic element which readily forms ionic compounds with metals such as calcium and covalent compounds with non-metals such as chlorine and oxygen.

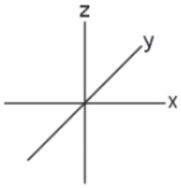
(a) (i) Write an equation, with state symbols, for the second ionisation energy of calcium.
(ii) Use the Data Booklet to calculate the enthalpy change that occurs when one mole of gaseous calcium ions, Ca2+, is formed from one mole of gaseous calcium
atoms.
Include a sign in your answer.

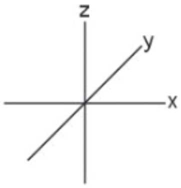
Al	$1s^2$
Ti	$1s^2$

(4) In the 19th and 20th centuries, experimental results showed scientists that atoms consist of a positive, heavy nucleus which is surrounded by electrons.
Then in the 20th century, theoretical scientists explained how electrons are arranged in orbitals around atoms.
(a) The diagram below represents the energy levels of the orbitals present in atoms of the second period (Li to Ne).
(i) Label the energy levels to indicate the principal quantum number and the type of orbital at each energy level.

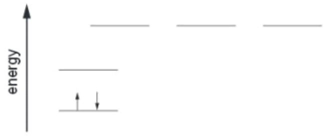
Label each type.

(ii) On the axes below, draw a sketch diagram of one of each different type (shape)
of orbital that is occupied by the electrons in a second-period element.

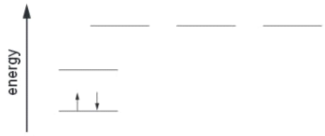




(iii) Complete the electronic configurations of nitrogen atoms and oxygen atoms on the energy level diagrams below.
Use arrows to represent electrons.



nitrogen



oxygen

(b) (i) Use the Data Booklet to state the value of the first ionisation energy of nitrogen and of oxygen.
(ii) Explain, with reference to your answer to (a) (iii), the relative values of these two
ionisation energies.

(5) The alkali metals are a series of six elements in Group I of the Periodic Table. The first ionisation energy of these elements shows a marked trend as the Group is descended.
(a) Define the term first ionisation energy.

(b) (i) State and explain the trend in first ionisation energy as Group I is descended.
(ii) Suggest how this trend helps to explain the increase in the reactivity of the elements as the Group is descended.
(c) In a redox reaction, 0.83 g of lithium reacted with water to form 0.50 dm^3 of aqueous lithium hydroxide.

$2Li(s) + 2H_2O(l) \rightarrow\rightarrow 2LIOH\ (aq) + H_2(g)$

(i) Calculate the amount, in moles, of lithium that reacted.

(6) The first six ionisation energies of an element X are given below.

ionisation energy / kJ mol^{-1}					
first	second	third	fourth	fifth	sixth
950	1800	2700	4800	6000	12300

(a) Define the term first ionisation energy.

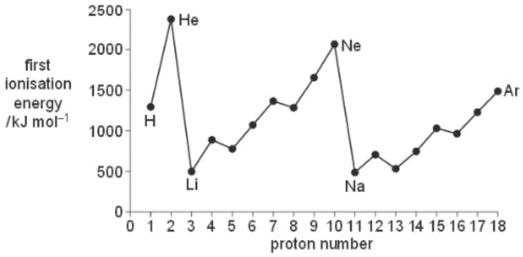
(b) Write an equation, with state symbols, for the second ionisation energy of element X.
(c) Use the data given above to deduce in which Group of the Periodic Table element X is placed. Explain your answer.
The first ionisation energies (I.E.) for the elements of Group IV are given below.

element	C	Si	Ge	Sn	Pb
1st I.E. / kJ mol^{-1}	1090	786	762	707	716

(d) Explain the trend shown by these values in terms of the atomic structure of the elements.

(7) The Periodic Table we currently use is derived directly from that proposed in 1869 by Mendeleev who had noticed patterns in the physical and chemical properties of the elements he had studied.

The diagram below shows the first ionisation energies of the first 18 elements of the Periodic Table.



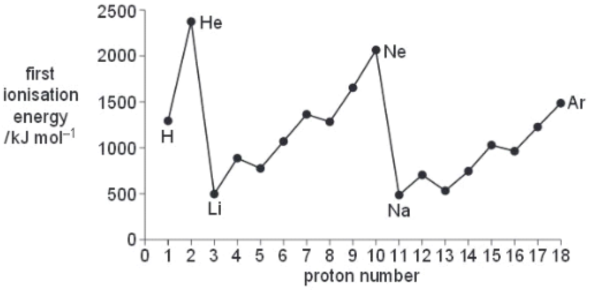
(a) Give the equation, including state symbols, for the first ionisation energy of sulfur.

(b) Explain why there is a general increase in first ionisation energies across the Period from sodium to argon.

(c) (i) Explain why the first ionisation energy of magnesium is greater than that of aluminium.
(ii) Explain why the first ionisation energy of phosphorus is greater than that of sulfur.

(8)The Periodic Table we currently use is derived directly from that proposed in 1869 by Mendeleev who had noticed patterns in the physical and chemical properties of the elements he had studied.

The diagram below shows the first ionisation energies of the first 18 elements of the Periodic Table.



(a) Give the equation, including state symbols, for the first ionisation energy of carbon.
(b) (i) Explain why sodium has a lower first ionisation energy than magnesium.
(ii) Explain why magnesium has a higher first ionisation energy than aluminium.
(iii) Explain why helium, He, and neon, Ne, occupy the two highest positions on the diagram.
(iv) Explain why the first ionisation energy of argon, Ar, is lower than that of neon, which is lower than that of helium.
(c) (i) The first ionisation energies of the elements Na to Ar show a variation. Some physical properties show similar variations.
The atomic radius of the elements decreases from Na to C7.
Give a brief explanation of this variation.

(ii) The cations formed by the elements Na to Al are smaller than the corresponding atoms.
Give a brief explanation of this change.