1.1 Atomic Structure

Details of the three sub-atomic (fundamental) particles

Particle	Position	Relative Mass	Relative Charge
proton	nucleus	1	+1
neutron	nucleus	1	0
electron	orbitals	1/1840	-1

An atom of Lithium (Li) can be represented as follows:

Mass number → **7** **Li** ← Atomic symbol
Atomic number → **3**

The **atomic number**, Z, is the number of protons in the nucleus.
The **mass number**, A, is the total number of protons and neutrons in the atom.

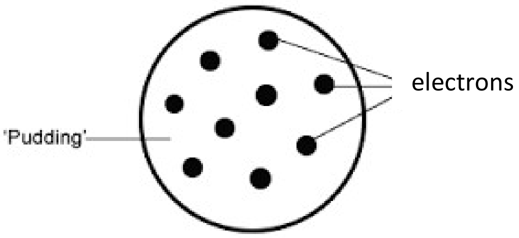
Number of neutrons = A - Z

History of Development of the Atom

Before the discovery of the electron atoms were thought to be tiny spheres that could not be divided

Plum-pudding model

The discovery of the electron led to the plum-pudding model of the atom. The **plum-pudding model** suggested that the atom was a ball of positive charge with negative electrons embedded in it.

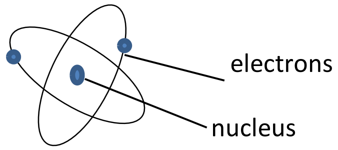


Nuclear model

The results from the Rutherford and Marsden's alpha scattering experiments led to the plum-pudding model being replaced by the nuclear model.
In this model the centre of the atom was called the nucleus.
This experiment showed:

- that **most** of the **mass of the atom** was in **the nucleus**.
- that all the **positive charge** of the atom was in the **nucleus**

The electrons were thought to orbit the nucleus, like planets around the sun.

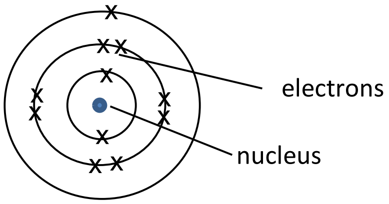


Nuclear model

In the experiment **most of the** alpha particles directed at thin gold foil passed through showing that that most of the **mass of the atom** was in **the nucleus**.
But a few were deflected or bounced back, suggesting the positive charge was concentrated at the centre of each gold atom in the nucleus.

Bohr Model

Neils Bohr adapted the nuclear model by suggesting that **electrons orbit** the **nucleus** at **specific distances**.
The electrons are on **energy levels** or shells.
The theoretical calculations of Bohr agreed with experimental observations.



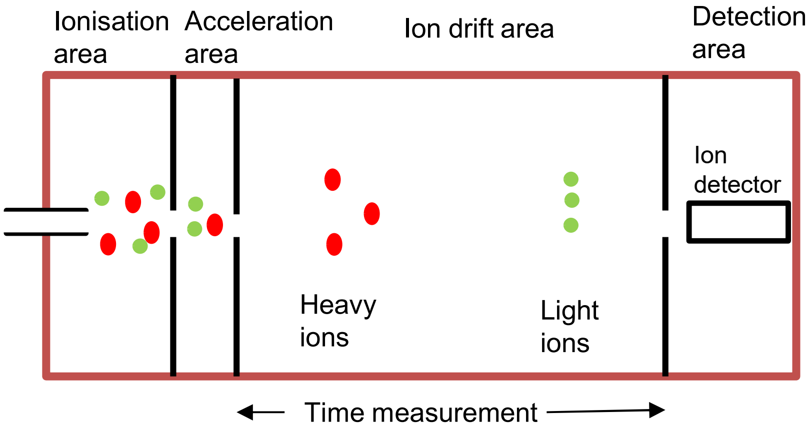
Bohr Model

Isotopes

Isotopes are atoms with the same number of protons, but different numbers of neutrons.

Isotopes have similar chemical properties because they have the same electronic structure. They may have slightly varying physical properties because they have different masses.

The time of flight mass spectrometer



The mass spectrometer can be used to determine all the isotopes present in a sample of an element and to therefore identify elements.

It needs to be under a vacuum otherwise air particles would ionise and register on the detector

The following are the essential 4 steps in a mass spectrometer.

Learn all these steps carefully!

1. Ionisation

The sample can be ionised in a number of ways. Two of these techniques are electron impact and electrospray ionisation

Electron impact

- A vaporised sample is injected at low pressure
- An electron gun fires high energy electrons at the sample
- This knocks out an outer electron
- Forming **positive** ions with different charges e.g. $Ti (g) \rightarrow Ti^+ (g) + e^-$

Electron impact is used for elements and substances with low formula mass. Electron impact can cause larger organic molecules to fragment.

Electro spray Ionisation

- The sample is **dissolved** in a volatile, polar **solvent**
- then injected through a fine **needle** giving a fine mist or aerosol
- the tip of needle has **high voltage**
- at the tip of the needle the sample molecule, M, **gains a proton**, H^+, from the solvent forming MH^+
- $M(g) + H^+ \rightarrow MH^+(g)$
- The solvent evaporates away while the MH^+ ions move towards a negative plate

Electro spray ionisation is used preferably for larger organic molecules. The 'softer' conditions of this technique mean fragmentation does not occur.

2. Acceleration

- Positive ions are accelerated by an electric field
- To a constant kinetic energy

$KE = \frac{1}{2} mv^2$

KE = kinetic energy of particle (J)
m = mass of the particle (kg)
v = velocity of the particle (ms^{-1})

Rearranged gives $$v = \sqrt{\frac{2KE}{m}}$$

Given that all the particles have the same kinetic energy, the velocity of each particle depends on its mass. Lighter particles have a faster velocity, and heavier particles have a slower velocity.

You do not need to learn these equations but may be asked rearrange them and use them in a calculation.

3. Flight Tube

- The positive ions with smaller m/z values will have the same kinetic energy as those with larger m/z and will move faster.
- The heavier particles take longer to move through the drift area.
- The ions are distinguished by different flight times

$t = d/v$
t = time of flight (s)
d = length of flight tube (m)
v = velocity of the particle ($m\ s^{-1}$)

Combining the two equations gives you

$$t = d\sqrt{\frac{m}{2KE}}$$

4. Detection

The ions reach the detector and generate a small current, which is fed to a computer for analysis. The current is produced by electrons transferring from the detector to the positive ions. The size of the current is proportional to the abundance of the species

For each isotope the mass spectrometer can measure a **m/z (mass/charge ratio)** and an **abundance**

Sometimes two electrons may be removed from a particle forming a 2+ ion. $^{24}Mg^{2+}$ with a 2+ charge would have a m/z of 12

Example A sample of nickel was analysed and one of the isotopes found was ^{59}Ni. The ions were accelerated to have 1.000×10^{-16} J of kinetic energy and travelled through a flight tube that was 0.8000 m long.
Calculate the time one ion of $^{59}Ni^+$ would take to travel along the flight tube.
The Avogadro constant L = 6.022×10^{23} mol^{-1}

$$\text{Mass of one ion of } ^{59}Ni^+ = \frac{\text{Mass of one mole of } ^{59}Ni^+}{\text{The Avogadro constant}}$$

$= 59/ 6.022 \times 10^{23}$
$= 9.797\times10^{-23}$ g
$= 9.797\times10^{-26}$ **kg**

The most frequent error students make is to not convert the mass from g to kg

$$t = d\sqrt{\frac{m}{2KE}}$$

$t = 0.8000 \sqrt{(9.797\times10^{-26}/(2\times 1.000 \times 10^{-16}))}$
$t = 1.771\times10^{-5}$ s

Calculating Relative Atomic Mass

The relative atomic mass quoted on the periodic table is a weighted average of all the isotopes

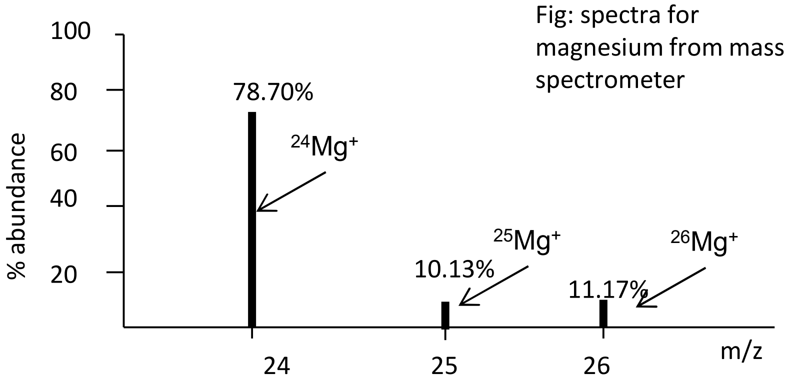


Fig: spectra for magnesium from mass spectrometer

If asked to give the species for a peak in a mass spectrum then give **charge** and **mass number** e.g. $^{24}Mg^+$

$$\text{R.A.M} = \frac{\Sigma\,(\text{isotopic mass x \% abundance})}{100}$$

Use these equations to work out the R.A.M

For above example of Mg
R.A.M = [(78.7 x 24) + (10.13 x 25) + (11.17 x 26)] /100 = 24.3

$$\text{R.A.M} = \frac{\Sigma\,(\text{isotopic mass x relative abundance})}{\text{total relative abundance}}$$

If relative abundance is used instead of percentage abundance use this equation

Example: Calculate the relative atomic mass of tellurium from the following abundance data:
124-Te relative abundance 2; 126-Te relative abundance 4; 128-Te relative abundance 7;
130-Te relative abundance 6

$$\text{R.A.M} = \frac{[(124\text{x}2) + (126\text{x}4) + (128\text{x}7) + (130\text{x}6)]}{19}$$
$$= 127.8$$

Example: Copper has two isotopes 63-Cu and 65-Cu. The relative atomic mass of copper is 63.5.
Calculate the percentage abundances of these two isotopes.

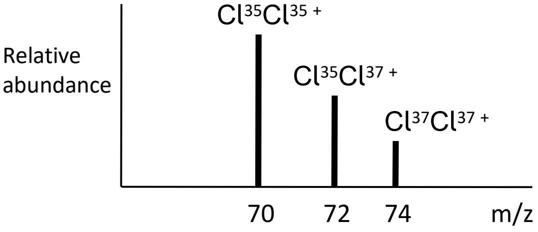
63.55 = y*x*63 + (1-y)*x*65
63.55 = 63y +65 -65y
63.55 = 65 -2y
2y = 1.45
y = 0.725

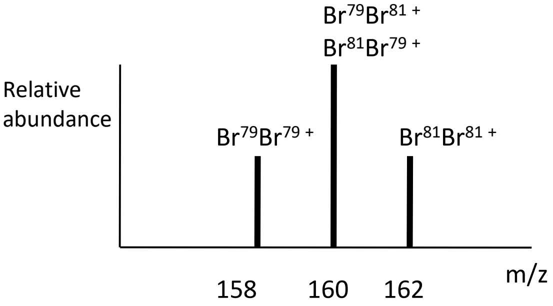
%abundance 63-Cu =72.5% %abundance 65-Cu = 27.5%

Mass spectra for Cl_2 and Br_2

Cl has two isotopes Cl^{35} (75%) and Cl^{37}(25%)   Br has two isotopes Br^{79} (50%) and Br^{81}(50%)

These lead to the following spectra caused by the diatomic molecules





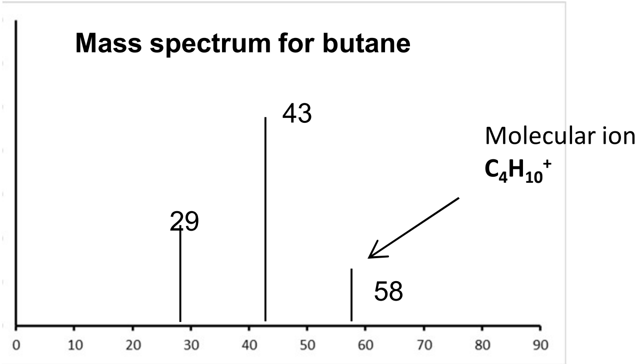
The 160 peak has double the abundance of the other two peaks because there is double the probability of 160 Br^{79}-Br$^{81\,+}$ as can be both Br^{79}-Br^{81} and Br^{81}-Br^{79}

Mass spectrometers have been included in planetary space probes so that elements on other planets can be identified. Elements on other planets can have a different composition of isotopes.

Measuring the M_r of a molecule

If a molecule is put through a mass spectrometer with an **Electron impact ionisation stage** it will often break up and give a series of peaks caused by the fragments. The peak with the largest m/z, however, will be due to the complete molecule and will be equal to the relative molecular mass, M_r ,of the molecule. This peak is called the parent ion or **molecular ion.**

Spectra for C_4H_{10}



If a molecule is put through a mass spectrometer with **electro spray ionisation** then fragmentation will not occur. There will be one peak that will equal the **mass of the MH^+ ion**. It will therefore be necessary to subtract 1 to get the M_r of the molecule. So if a peak at 521.1 is for MH^+, the relative molecular mass of the molecule is 520.1.

Electronic Structure

Models of the atom

An early model of the atom was the Bohr model (GCSE model) (2 electrons in first shell, 8 in second etc.) with electrons in spherical orbits. Early models of atomic structure predicted that atoms and ions with noble gas electron arrangements should be stable.

The A-level model

Electrons are arranged on:

Principle energy levels numbered 1,2,3,4..
1 is closest to nucleus

Split into →

Sub energy levels labelled s , p, d and f
s holds up to 2 electrons
p holds up to 6 electrons
d holds up to 10 electrons
f holds up to 14 electrons

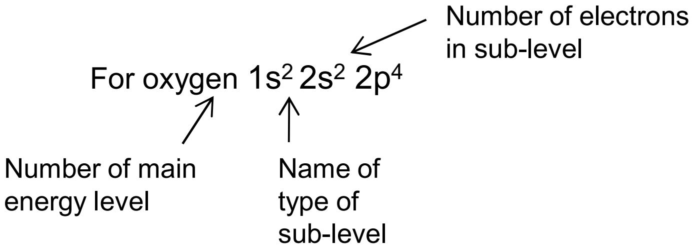
Split into →

Orbitals which hold up to 2 electrons of opposite spin

Principle level	1	2	3	4
Sub-level	1s	2s, 2p	3s, 3p, 3d	4s, 4p, 4d, 4f

An atom fills up the sub shells in order of increasing energy (note 3d is higher in energy than 4s and so gets filled after the 4s)
1s→2s→2p→3s→3p→ 4s→3d→4p→5s→4d→5p

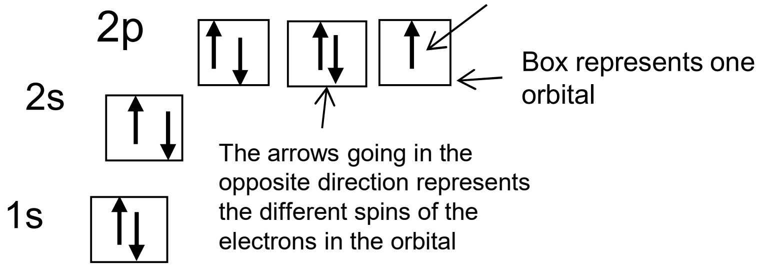
Writing electronic structure using letters and numbers


For oxygen $1s^2 2s^2 2p^4$

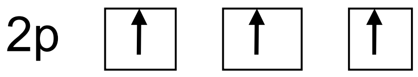
For calcium $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Using spin diagrams

For fluorine



When filling up sub levels with several orbitals, fill each orbital singly before starting to pair up the electrons

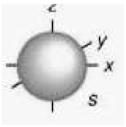


Shapes of orbitals
Orbitals represent the mathematical probabilities of finding an electron at any point within certain spatial distributions around the nucleus.

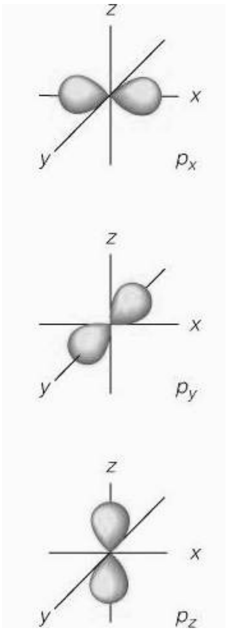
Each orbital has its own approximate, three dimensional shape.

It is not possible to draw the shape of orbitals precisely.

•s sublevels are spherical



• p sublevels are shaped like dumbbells

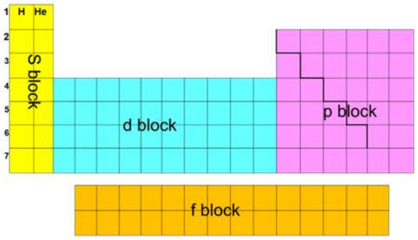


The periodic table is split into blocks.

A **s** block element is one whose outer electron is filling a s-sub shell e.g. sodium $1s^2\,2s^2\,2p^6\,3\mathbf{s}^1$

A **p** block element is one whose outer electron is filling a p-sub shell e.g. chlorine $1s^2\,2s^2\,2p^6\,3s^2\,3\mathbf{p}^5$

A **d** block element is one whose outer electron is filling a d-sub shell e.g. vanadium $1s^22s^22p^63s^23p^6\,4s^23d^3$



Electronic structure for ions

When a positive ion is formed electrons are lost from the outermost shell.
Mg is $1s^2\,2s^2\,2p^6\,3s^2$ becomes Mg^{2+} is $1s^2\,2s^2\,2p^6$

When a negative ion is formed electrons are gained
O is $1s^2\,2s^2\,2p^4$ becomes O^{2-} is $1s^2\,2s^2\,2p^6$

Electronic structure of d-block elements

The electronic structure of the d-block has some complications. As mentioned earlier, conventionally we say that 4s fills before 3d and so we write them in that order. There is, however, disagreement in the scientific community about whether this is true.
If you look at the electronic structures below you will see both chromium and copper have an unusual arrangement in having a half filled 4s sub shell.
You will also see that when d-block elements form ions they **lose** the **4s electrons first**.
You may find if you research different reasons for these observations. It may well be many of the reasons are false and we have to accept that some things in chemistry don't neatly follow patterns we can explain.
You do need to learn these electronic structure though!

Sc $1s^22s^22p^63s^23p^6\,4s^23d^1$
Ti $1s^22s^22p^63s^23p^6\,4s^23d^2$
V $1s^22s^22p^63s^23p^6\,4s^23d^3$
Cr $1s^22s^22p^63s^23p^6\,4s^13d^5$
Mn $1s^22s^22p^63s^23p^6\,4s^23d^5$
Fe $1s^22s^22p^63s^23p^6\,4s^23d^6$
Co $1s^22s^22p^63s^23p^6\,4s^23d^7$
Ni $1s^22s^22p^63s^23p^6\,4s^23d^8$
Cu $1s^22s^22p^63s^23p^6\,4s^13d^{10}$
Zn $1s^22s^22p^63s^23p^6\,4s^23d^{10}$

$\longrightarrow$

When forming ions **lose 4s before 3d**

Sc^{3+} [Ar] $4s^03d^0$
Ti^{3+} [Ar] $4s^03d^1$
V^{3+} [Ar] $4s^03d^2$
Cr^{3+} [Ar] $4s^03d^3$
Mn^{2+} [Ar] $4s^03d^5$
Fe^{3+} [Ar] $4s^03d^5$
Co^{2+} [Ar] $4s^03d^7$
Ni^{2+} [Ar] $4s^03d^8$
Cu^{2+} [Ar] $4s^03d^9$
Zn^{2+} [Ar] $4s^03d^{10}$

Ionisation Energies

Definition: First ionisation energy

The first ionisation energy is the enthalpy change when one mole of gaseous atoms forms one mole of gaseous ions with a single positive charge

Remember these definitions very carefully

This is represented by the equation: $H_{(g)} \rightarrow H^{+}_{(g)} + e^{-}$

Always gaseous

The equation for 1st ionisation energy always follows the same pattern.
It does not matter if the atom does not normally form a +1 ion or is not gaseous

Definition: Second ionisation energy

The second ionisation energy is the enthalpy change when one mole of gaseous ions with a single positive charge forms one mole of gaseous ions with a double positive charge

This is represented by the equation: $Ti^{+}_{(g)} \rightarrow Ti^{2+}_{(g)} + e^{-}$

Factors that affect ionisation energy

There are three main factors
1.The attraction of the nucleus
(The more protons in the nucleus the greater the attraction)
2. The distance of the electrons from the nucleus
(The bigger the atom the further the outer electrons are from the nucleus and the weaker the attraction to the nucleus)
3. Shielding of the attraction of the nucleus
(An electron in an outer shell is repelled by electrons in complete inner shells, weakening the attraction of the nucleus)

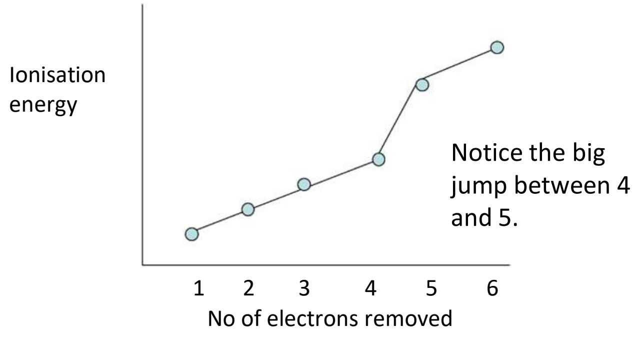
Many questions can be answered by application of these factors

Successive ionisation energies

The patterns in successive ionisation energies for an element give us important information about the electronic structure for that element.

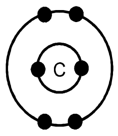
Why are successive ionisation energies always larger?
The second ionisation energy of an element is always bigger than the first ionisation energy.
When the first electron is removed a positive ion is formed.
The ion increases the attraction on the remaining electrons and so the energy required to remove the next electron is larger.

How are ionisation energies linked to electronic structure?



Notice the big jump between 4 and 5.

Explanation
The fifth electron is in a inner shell closer to the nucleus and therefore attracted much more strongly by the nucleus than the fourth electron.
It also does not have any shielding by inner complete shells of electron

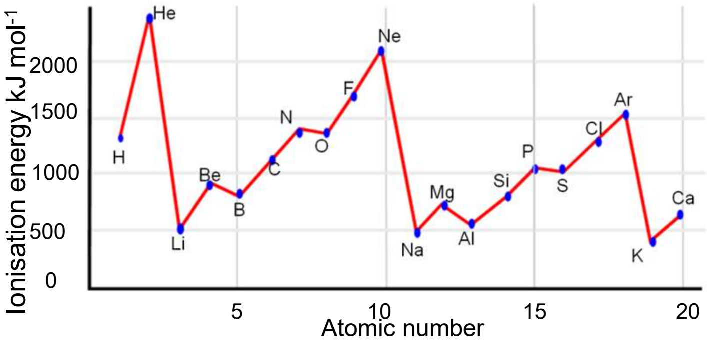


Example: What group is this element in?

	1	2	3	4	5
Ionisation energy kJ mol^{-1}	590	1150	4940	6480	8120

Here there is a big jump between the 2nd and 3rd ionisations energies which means that this element must be in group 2 of the periodic table as the 3rd electron is removed from an electron shell closer to the nucleus with less shielding and so has a larger ionisation energy

The first ionisation energy of the elements



The shape of the graph for periods two and three is similar. A repeating pattern across a period is called **periodicity**.

The pattern in the first ionisation energy gives us useful information about electronic structure

You need to carefully learn the patterns

Q. Why has helium the largest first ionisation energy?

A. Helium's first electron is in the first shell closest to the nucleus and has no shielding effects from inner shells. Helium has a bigger first ionisation energy than hydrogen as it has one more proton.

Many questions can be answered by application of the 3 factors that control ionisation energy

Q. Why do first ionisation energies decrease down a group?

A. As one goes down a group, the outer electrons are found in shells further from the nucleus and are more shielded, so the attraction from the nucleus becomes smaller.

Q. Why is there a general increase in first ionisation energy across a period?

A. As one goes across a period, the electrons are being added to the same shell which has the same distance from the nucleus and same shielding effect. The number of protons increases, however, making the effective attraction of the nucleus greater.

Q. Why has Na a much lower first ionisation energy than neon?

This is because Na will have its outer electron in a 3s shell further from the nucleus and is more shielded. So Na's outer electron is easier to remove and has a lower ionisation energy.

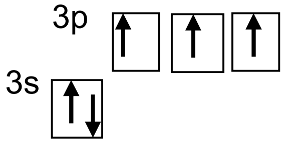
Q. Why is there a small drop from Mg to Al?

Al is starting to fill a 3p sub shell, whereas Mg has its outer electrons in the 3s sub shell. The electrons in the 3p subshell are slightly easier to remove because the 3p electrons are higher in energy and are also slightly shielded by the 3s electrons

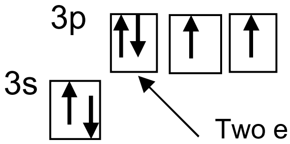
Q. Why is there a small drop from P to S?

With sulfur there are 4 electrons in the 3p sub shell and the 4th is starting to doubly fill the first 3p orbital.
When the second electron is added to a **3p orbital** there is a slight **repulsion** between the two negatively charged electrons which makes the second electron easier to remove.

Learn carefully the explanations for these two small drops as they are different to the usual factors



phosphorus $1s^2 2s^2 2p^6 3s^2 3p^3$

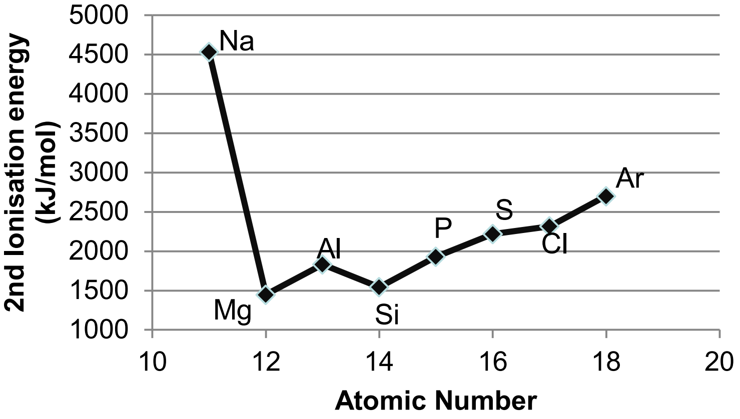


Two electrons of opposite spin in the same orbital

sulfur $1s^2 2s^2 2p^6 3s^2 3p^4$

Patterns in the second ionisation energy.

If the graph of second ionisation or each successive element is plotted then a similar pattern to the first ionisation energy is observed but all the elements will have shifted one to the left.



The group 1 elements are now at the peaks of the graph

Lithium would now have the second largest ionisation of all elements as its second electron would be removed from the first 1s shell closest to the nucleus and has no shielding effects from inner shells. Li has a bigger second ionisation energy than He as it has more protons.