

# 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

There are various models for atomic structure

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



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.

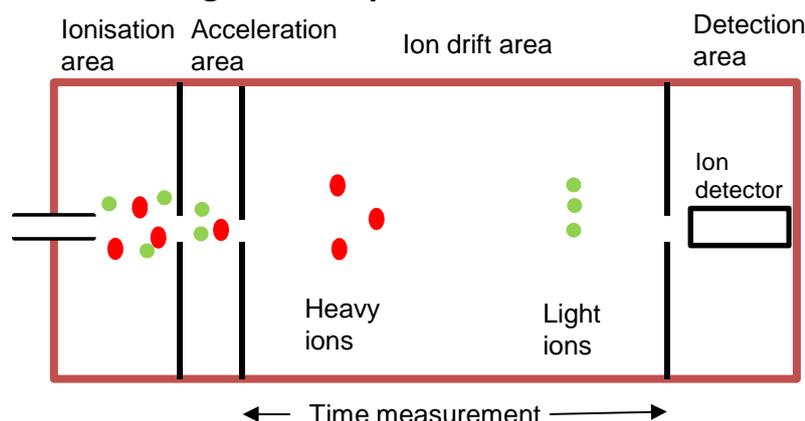
$$\text{Number of neutrons} = A - Z$$

### 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.

#### 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.  $\text{Ti} \rightarrow \text{Ti}^+ + \text{e}^-$

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
- injected through a fine hypodermic 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,  $\text{H}^+$ , from the solvent forming  $\text{MH}^+$
- $\text{M}(\text{g}) + \text{H}^+ \rightarrow \text{MH}^+(\text{g})$
- The solvent evaporates away while the  $\text{MH}^+$  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

Learn all these steps carefully!

## 2. Acceleration

- Positive ions are accelerated by an electric field
- To a constant kinetic energy  
 $KE = \frac{1}{2} m v^2$

$KE$  = kinetic energy of particle (J)

$m$  = mass of the particle (kg)

$v$  = velocity of the particle ( $\text{ms}^{-1}$ )

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 don't need to learn these equations but may be asked to 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 ( $\text{m s}^{-1}$ )

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.  $^{24}\text{Mg}^{2+}$  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  $^{59}\text{Ni}$ . The ions were accelerated to have  $1.000 \times 10^{-16}$  J of kinetic energy and travelled through a flight tube that was 0.8000 m long.

How long would one ion of  $^{59}\text{Ni}^+$  take to travel along the flight tube?

The Avogadro constant  $L = 6.022 \times 10^{23} \text{ mol}^{-1}$

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

$$= 59 / 6.022 \times 10^{23}$$

$$= 9.797 \times 10^{-23} \text{ g}$$

$$= 9.797 \times 10^{-26} \text{ kg}$$

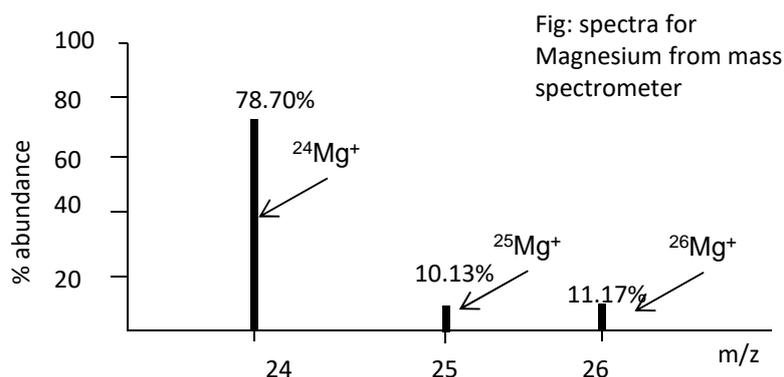
$$t = d \sqrt{\frac{m}{2KE}}$$

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

$$t = 1.771 \times 10^{-5} \text{ s}$$

## Calculating Relative Atomic Mass

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



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

$$\text{R.A.M} = \frac{\sum (\text{isotopic mass} \times \% \text{ abundance})}{100}$$

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

For above example of Mg

$$\text{R.A.M} = [(78.7 \times 24) + (10.13 \times 25) + (11.17 \times 26)] / 100 = 24.3$$

$$\text{R.A.M} = \frac{\sum (\text{isotopic mass} \times \text{relative abundance})}{\text{total relative abundance}}$$

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

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

**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.

$$63.55 = y \times 63 + (1-y) \times 65$$

$$63.55 = 63y + 65 - 65y$$

$$63.55 = 65 - 2y$$

$$2y = 1.45$$

$$y = 0.725$$

%abundance 63-Cu = 72.5%

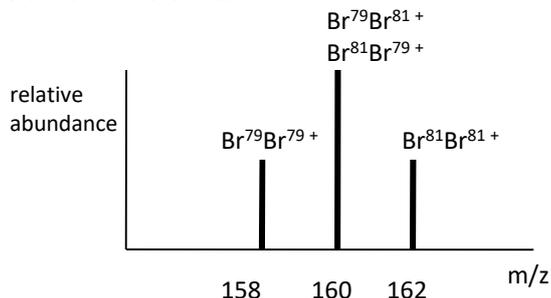
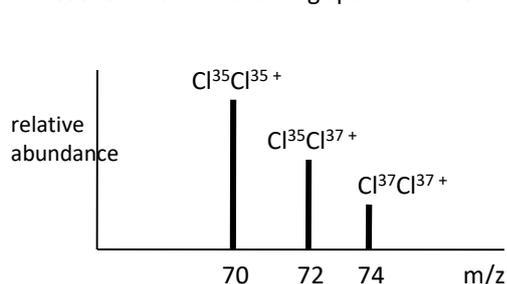
%abundance 65-Cu = 27.5%

## Mass spectra for Cl<sub>2</sub> and Br<sub>2</sub>

Cl has two isotopes Cl<sup>35</sup> (75%) and Cl<sup>37</sup> (25%)

Br has two isotopes Br<sup>79</sup> (50%) and Br<sup>81</sup> (50%)

These lead to the following spectra caused by the diatomic molecules



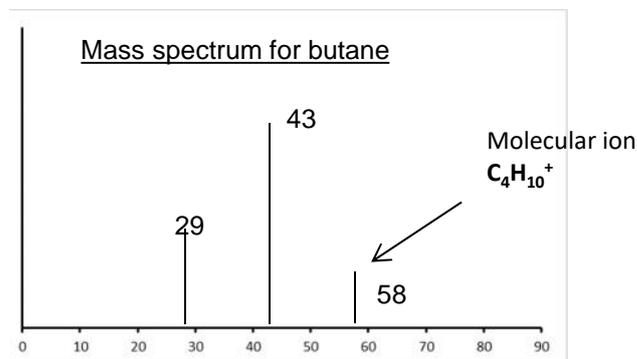
The 160 peak has double the abundance of the other two peaks because there is double the probability of 160 Br<sup>79</sup>-Br<sup>81</sup> + as can be Br<sup>79</sup>-Br<sup>81</sup> and Br<sup>81</sup>-Br<sup>79</sup>

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<sub>r</sub> 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<sub>r</sub>, of the molecule. This peak is called the parent ion or **molecular ion**

### Spectra for C<sub>4</sub>H<sub>10</sub>



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<sup>+</sup> ion**. It will therefore be necessary to subtract 1 to get the M<sub>r</sub> of the molecule. So if a peak at 521.1 is for MH<sup>+</sup>, the relative molecular mass of the molecule is 520.1.

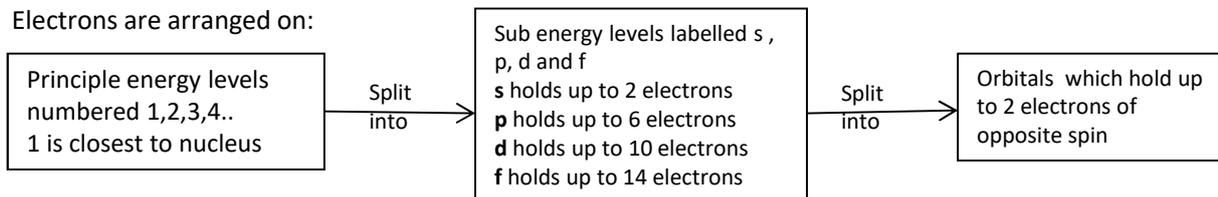
# Electronic Structure

## 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 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)  
 $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p$

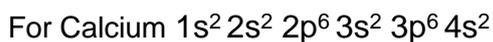
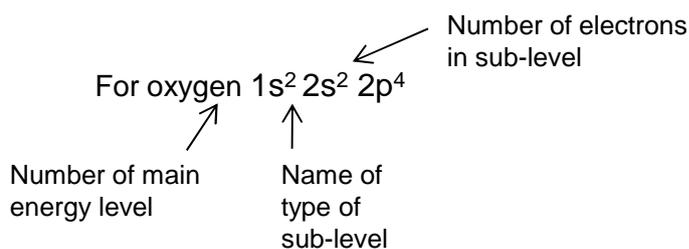
### Shapes of orbitals

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.

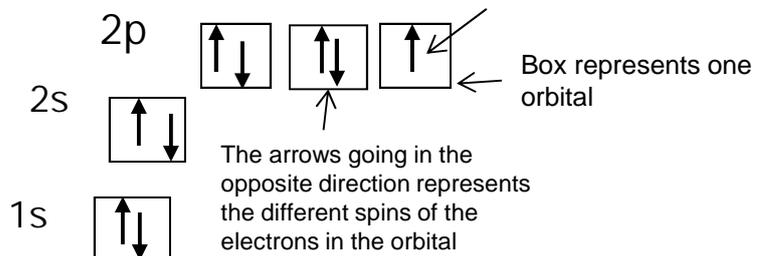
It is not possible to draw the shape of orbitals precisely.

### Writing electronic structure using letters and numbers



### Using spin diagrams

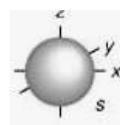
For fluorine



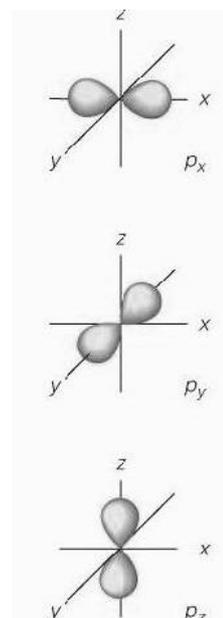
When filling up sub levels with several orbitals, fill each orbital singly before starting to pair up the electrons

2p  $\uparrow \uparrow \uparrow$

- s sublevels are spherical



- p sublevels are shaped like dumbbells

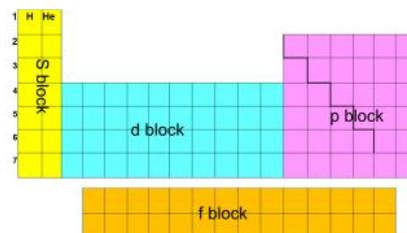


The periodic table is split into blocks.

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

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

A **d** block element is one whose outer electron is filling a d-sub shell e.g. vanadium  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$



## 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

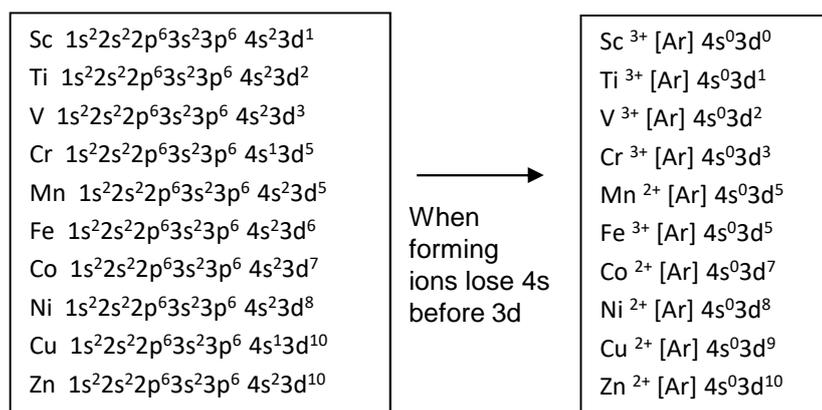
The electronic structure of the d-block has some complications. As mentioned earlier, conventionally we say that 4s fills before 3d and so we write them in that order. There is, however, disagreement in the scientific community about whether this is true.

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!

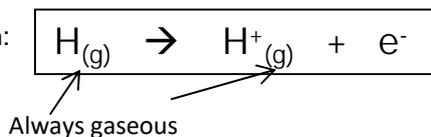


## Ionisation Energies

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

This is represented by the equation:



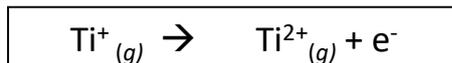
Remember these definitions very carefully

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:



### 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.

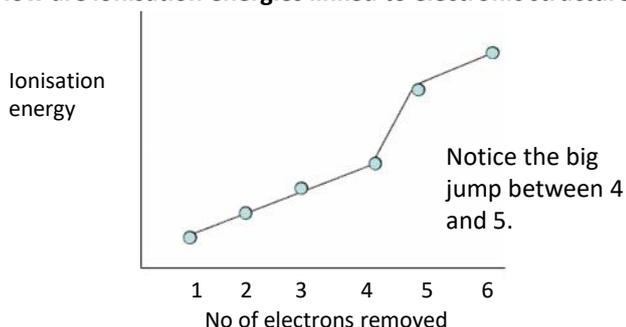
#### Why are successive ionisation energies always larger?

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.

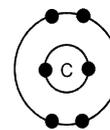
#### How are ionisation energies linked to electronic structure?



#### Explanation

The fifth electron is in an 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

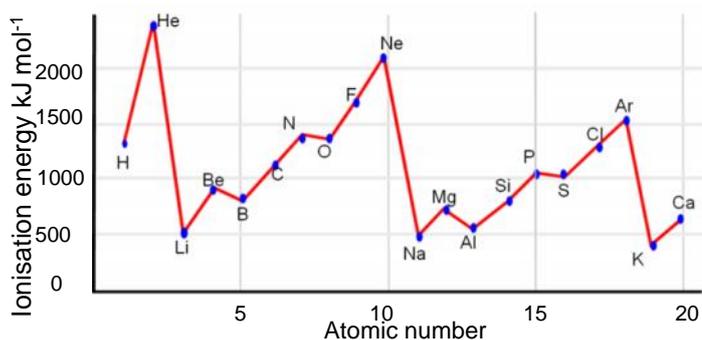


Example: What group must this element be in?

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

Here there is a big jump between the 2<sup>nd</sup> and 3<sup>rd</sup> ionisations energies which means that this element must be in group 2 of the periodic table as the 3<sup>rd</sup> 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. Its first electron is in the first shell closest to the nucleus and has no shielding effects from inner shells. He has a bigger first ionisation energy than H 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 of 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.

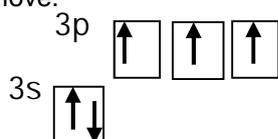
### Q. Why is there a small drop from Mg to Al?

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

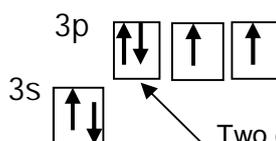
### Q. Why is there a small drop from P to S?

With sulphur 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.



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



Two electrons of opposite spin in the same orbital

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

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