

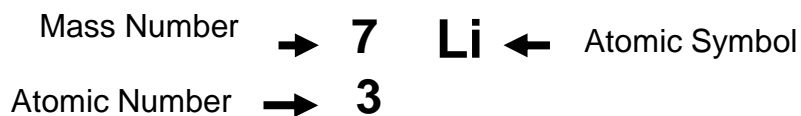
3. Atomic Structure and Periodic Table

Details of the three Sub-atomic (fundamental) Particles

Particle	Position	Relative Mass	Relative Charge
Proton	Nucleus	1	+1
Neutron	Nucleus	1	0
Electron	Orbitals	1/1800	-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.

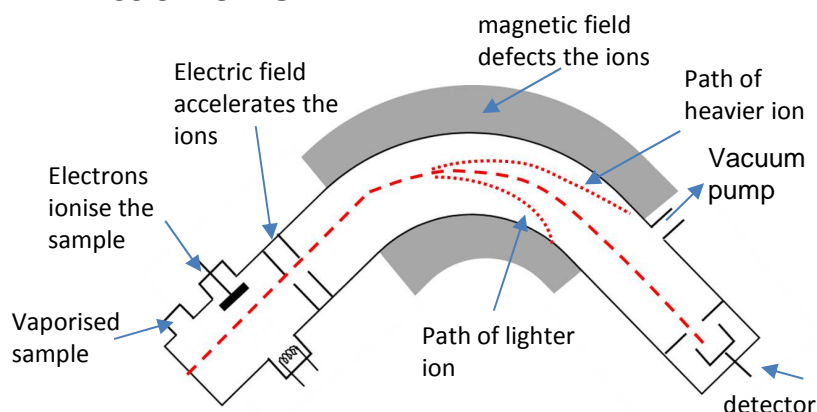
DEFINITION: **Relative isotopic mass** is the **mass** of one atom of an isotope compared to one twelfth of the mass of one atom of carbon-12

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

DEFINITION: **Relative atomic mass** is the **average mass** of one atom compared to one twelfth of the mass of one atom of carbon-12

DEFINITION: **Relative molecular mass** is the **average mass** of a molecule compared to one twelfth of the mass of one atom of carbon-12

THE 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

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

Learn all these steps carefully!

If the sample is not vaporized then vaporizing it would be the first step.

2. Acceleration

•A negative electric field accelerates the positive ions and makes them into a beam

3. Deflection

- The beam of positive ions is deflected by a strong magnetic field.
- The degree of deflection depends on the mass-to-charge ratio, m/z .
- The smaller this ratio the larger the deflection.
- By varying the magnetic field ratio, ions of different m/z ratios pass through the centre.

The heavier an ion the less it is deflected

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

Calculating relative atomic mass

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

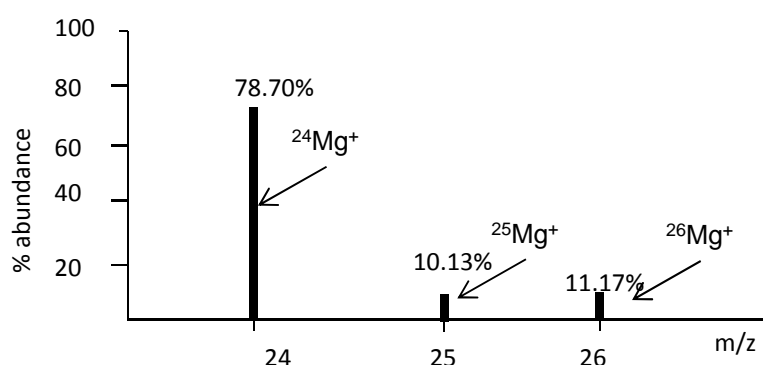


Fig: spectra for Magnesium from mass spectrometer

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

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

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

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

For above example of Mg

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

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

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

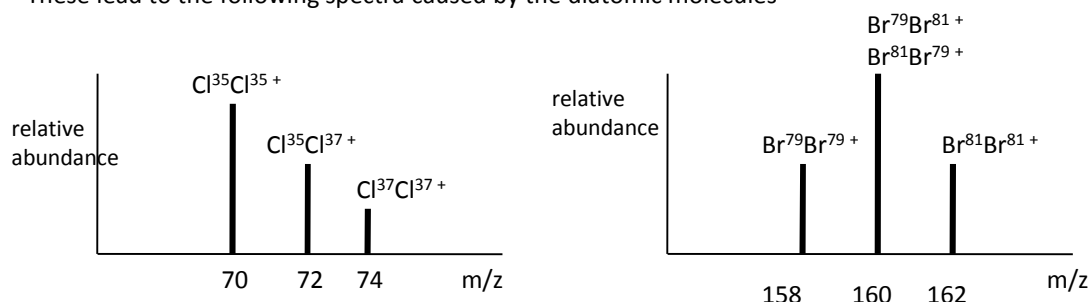
If relative abundance is used instead of percentage abundance use this equation

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%)

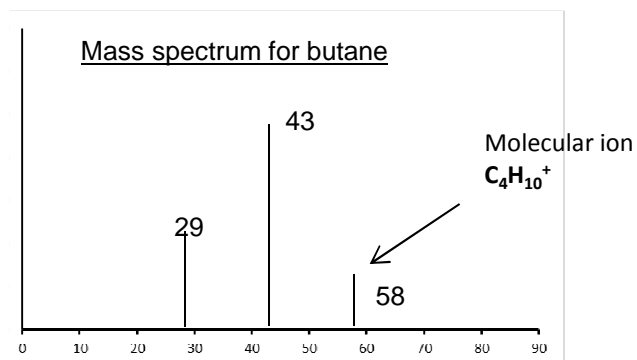
These lead to the following spectra caused by the diatomic molecules



Measuring the M_r of a molecule

If a molecule is put through a mass spectrometer 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 M_r of the molecule. This peak is called the parent ion or **molecular ion**

Spectra for C_4H_{10}



Uses of Mass spectrometers

- 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.
- Drug testing in sport to identify chemicals in the blood and to identify breakdown products from drugs in body
- quality control in pharmaceutical industry and to identify molecules from sample with potential biological activity
- radioactive dating to determine age of fossils or human remains

Radioactive Carbon Dating

All living things have small amounts of the radioactive Carbon-14 isotope. When a living thing dies no more ^{14}C is produced and it starts to decay. The object becomes less radioactive over time.

Measure the abundance of ^{14}C in the material to be tested. By use of the half-life of ^{14}C work out how old the object is by working out how much it has decayed.

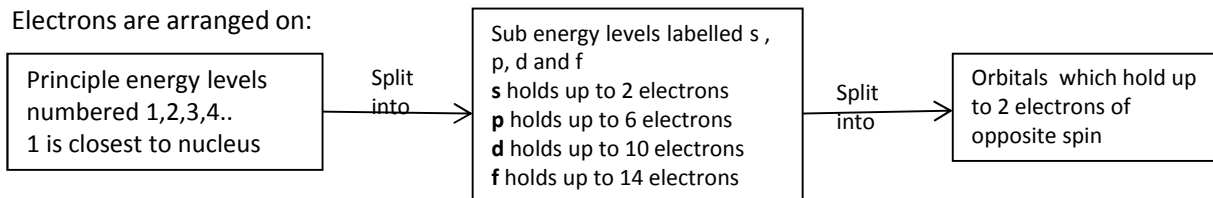
Electronic Structure

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

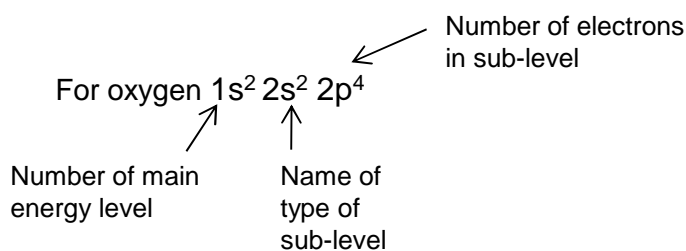
Shapes of orbitals

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

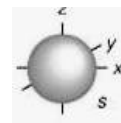
Each orbital has its own approximate, three dimensional shape.

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

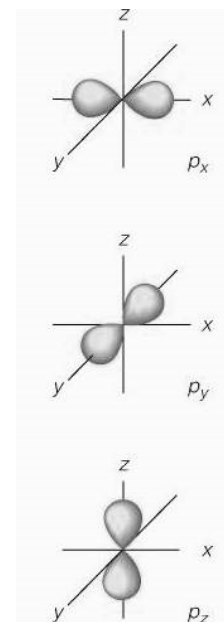
Writing electronic structure using letters and numbers



- s sublevels are spherical

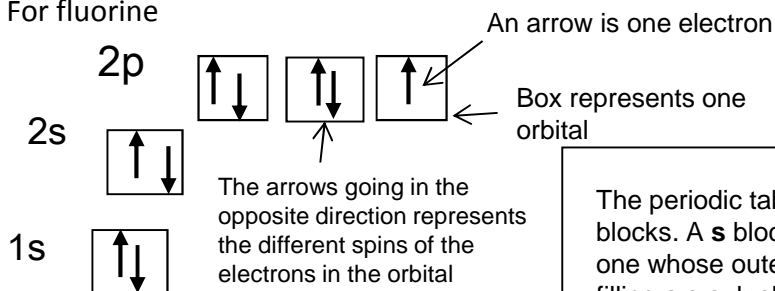


- p sublevels are shaped like dumbbells



Using spin diagrams

For fluorine



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



The periodic table is split into blocks. A s block element is one whose outer electron is filling a s-sub shell

Electronic structure for ions

When a positive ion is formed electrons are lost
Mg is $1s^2 2s^2 2p^6 3s^2$ but Mg^{2+} is $1s^2 2s^2 2p^6$

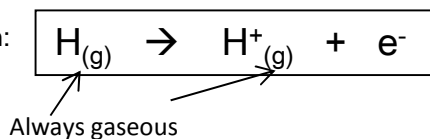
When a negative ion is formed electrons are gained
O is $1s^2 2s^2 2p^4$ but O^{2-} is $1s^2 2s^2 2p^6$

Ionisation Energies

Definition :First ionisation energy

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

This is represented by the equation:



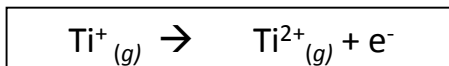
Remember these definitions very carefully

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 energy required 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.

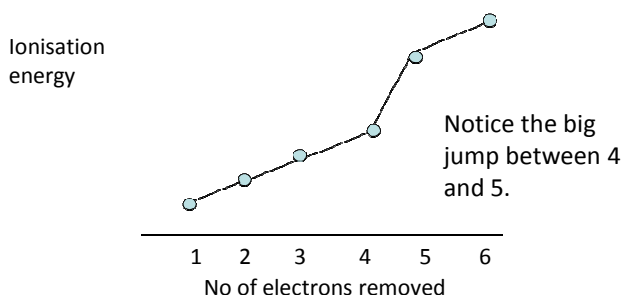
Why are successive ionisation energies always larger?

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.

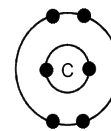
How are ionisation energies linked to electronic structure?



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

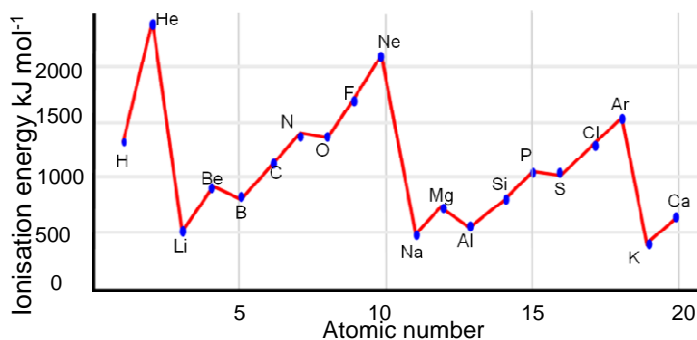


Example: What group must this element be in?

	1	2	3	4	5
Ionisation energy 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. 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 number of protons increases making the effective attraction of the nucleus greater. The electrons are being added to the same shell which has the same shielding effect and the electrons are pulled in closer to the nucleus.

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.

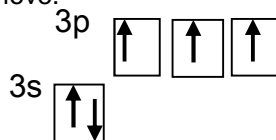
Q. Why is there a small drop from Mg to Al?

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

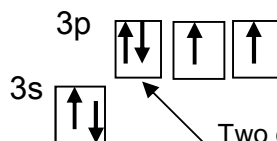
Q. Why is there a small drop from P to S?

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

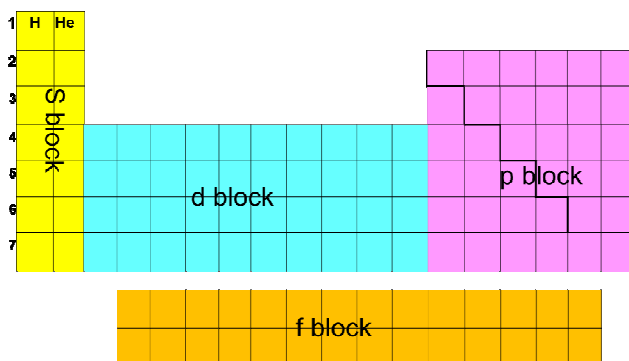
PERIODICITY

Classification of elements in s, p, d blocks

Elements are classified as s, p or d block, according to which orbitals the highest energy electrons are in.

Period 2 = Li, Be, B, C, N, O, F, Ne

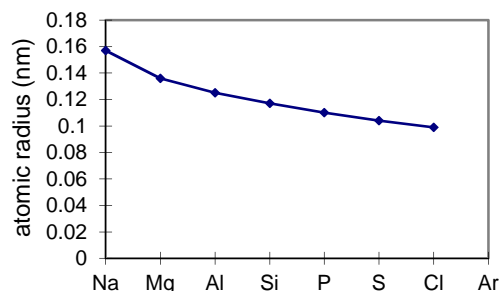
Period 3 = Na, Mg, Al, Si, P, S, Cl, Ar



Atomic radius

Atomic radii **decrease** as you move from left to right across a period, because the **increased number of protons** create more positive charge attraction for **electrons which are in the same shell** with similar shielding.

Exactly the same trend in period 2

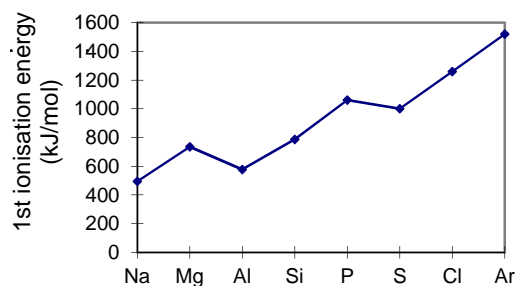


1st ionisation energy

There is a **general trend** across is to **increase**. This is due to **increasing number of protons** as the electrons are being added to the same shell

There is a **small drop between Mg + Al**. Mg has its outer electrons in the 3s sub shell, whereas **Al is starting to fill the 3p** subshell. Al's electron is slightly easier to remove because the **3p electrons are higher in energy**.

There is a **small drop** between **phosphorous** and **sulphur**. Sulphur's outer electron is being **paired up** with an another electron in the **same 3p orbital**. When the second electron is added to an orbital there is a slight **repulsion** between the two negatively charged electrons which makes the second electron easier to remove.



Exactly the same trend in period 2 with drops between Be & B and N to O for same reasons- make sure change 3s and 3p to 2s and 2p in explanation!

Melting and boiling points

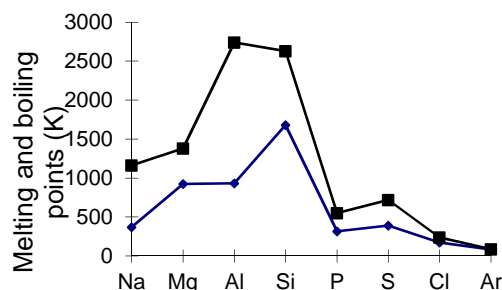
For **Na, Mg, Al- Metallic** bonding : strong bonding – gets stronger the more electrons there are in the outer shell that are released to the sea of electrons. A smaller positive centre also makes the bonding stronger. High energy is needed to break bonds.

Si is Macromolecular: many strong covalent bonds between atoms high energy needed to break covalent bonds– very high mp +bp

Cl₂(g), S₈(s), P₄(s)- simple Molecular : weak London forces between molecules, so little energy is needed to break them – low mp+ bp

S₈ has a higher mp than P₄ because it has more electrons (S₈=128)(P₄=60) so has stronger London forces between molecules

Ar is monoatomic weak **London Forces** between atoms



Similar trend in period 2
 Li,Be metallic bonding (high mp)
 B,C macromolecular (very high mp)
 N₂,O₂ molecular (gases! Low mp as small London Forces)
 Ne monoatomic gas (very low mp)