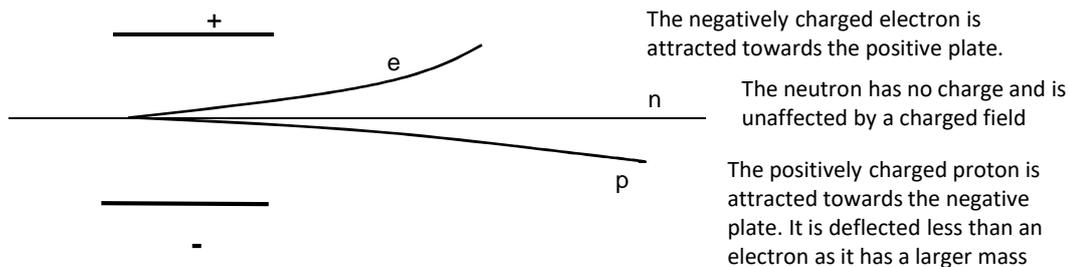


## 2 Atomic Structure

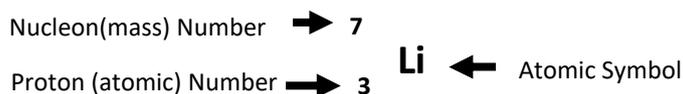
### Details of the three Sub-atomic (fundamental) Particles

| Particle | Position | Relative Mass | Relative Charge |
|----------|----------|---------------|-----------------|
| Proton   | Nucleus  | 1             | +1              |
| Neutron  | Nucleus  | 1             | 0               |
| Electron | Orbitals | 1/1840        | -1              |

### Behaviour of beams of protons, neutrons and electrons in electric fields



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



The **proton (atomic number)** ,Z, is the number of protons in the nucleus.

The **Nucleon (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.

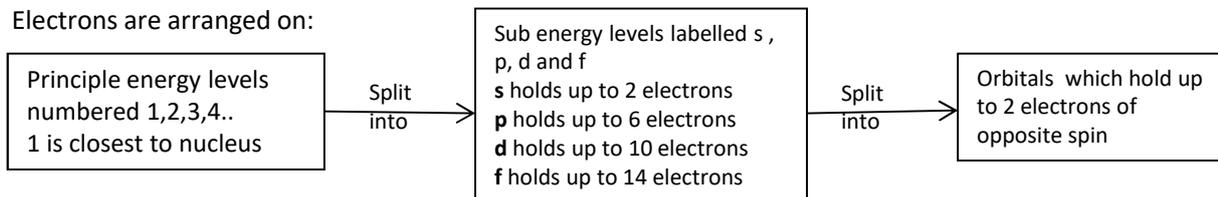
# Electronic Structure

## 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)

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

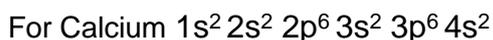
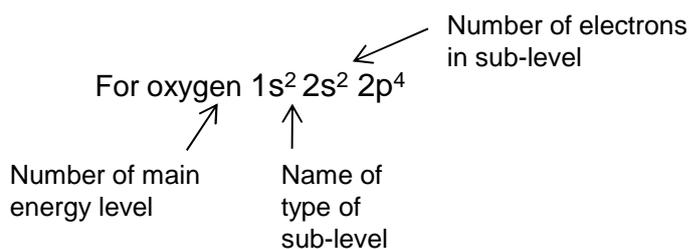
### Shapes of orbitals

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.

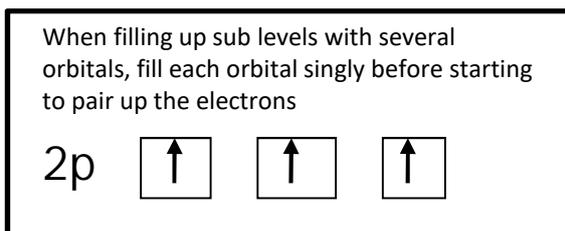
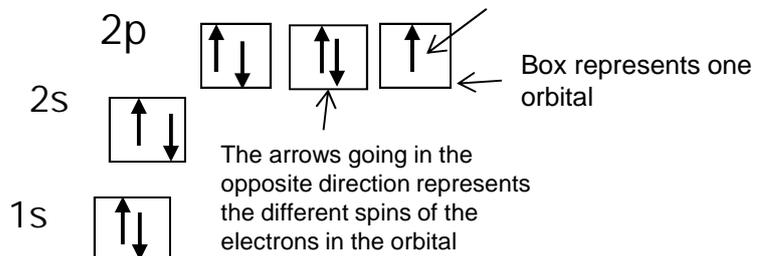
It is not possible to draw the shape of orbitals precisely.

### Writing electronic structure using letters and numbers

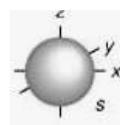


### Using spin diagrams

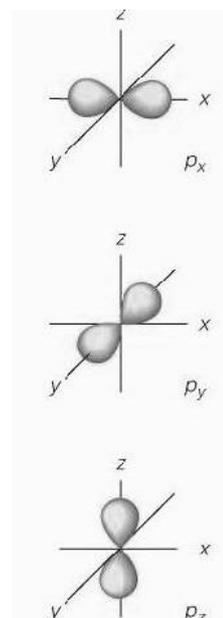
For fluorine



- s sublevels are spherical



- p sublevels are shaped like dumbbells

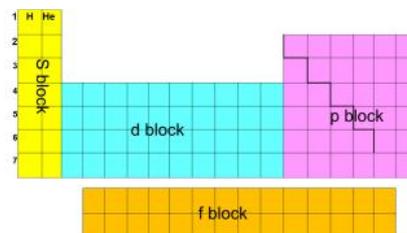


The periodic table is split into blocks.

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

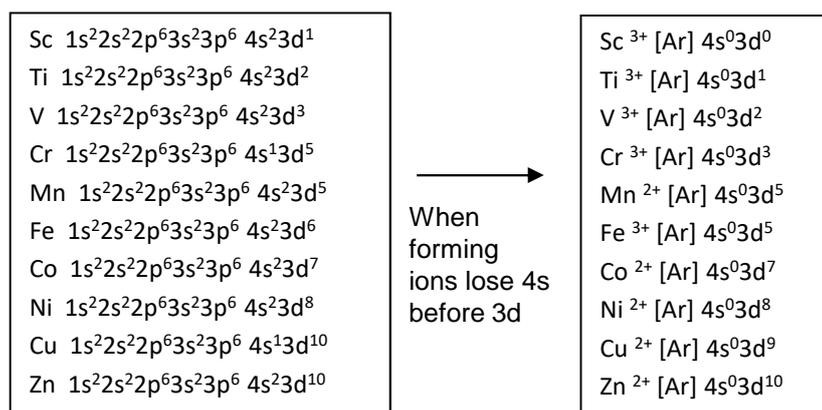
The electronic structure of the d-block has some complications. As mentioned earlier, conventionally we say that 4s fills before 3d and so we write them in that order. There is, however, disagreement in the scientific community about whether this is true.

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!



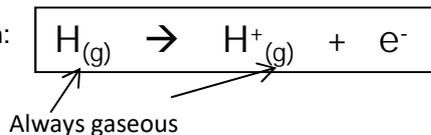
When forming ions lose 4s before 3d

## 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:



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



All values of ionisations are positive and therefore endothermic. This is because energy must be supplied to overcome the electrostatic attractive force between the nucleus and the electron.

### 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

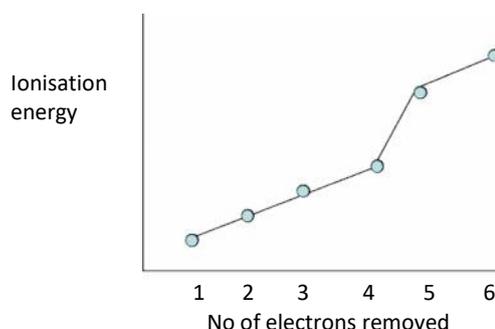
An element can have as many successive ionisation energies as it has electrons

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

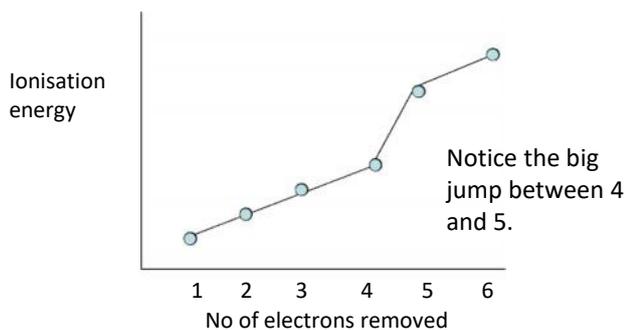
### Why are successive ionisation energies always larger?

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. Each successive ionisation energy is bigger than the previous one for the same reason.

Some of the increases are much bigger, however, and these big jumps gives us evidence for the main principle electron shells.



## How are ionisation energies linked to the main electron energy levels ?

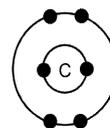


There is a big jump between the 4<sup>th</sup> and 5<sup>th</sup> ionisation energies.

### Explanation

The fifth electron is in an inner main 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 so is easier to remove.



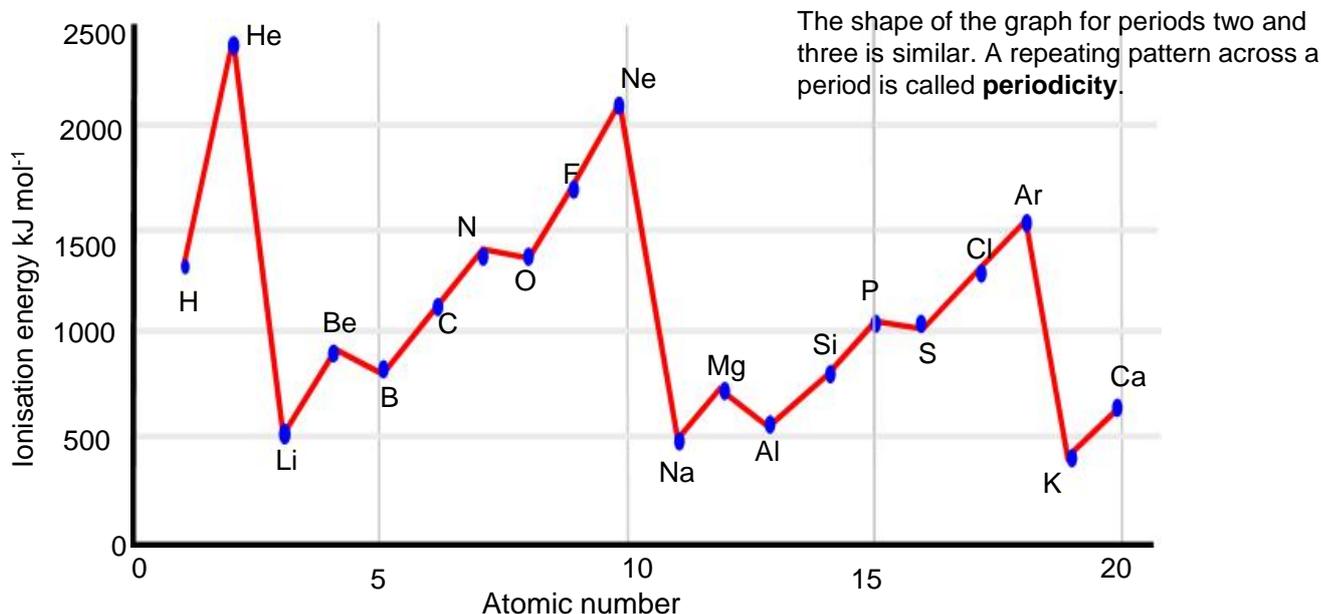
Example: What group must this element be in?

|  | 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

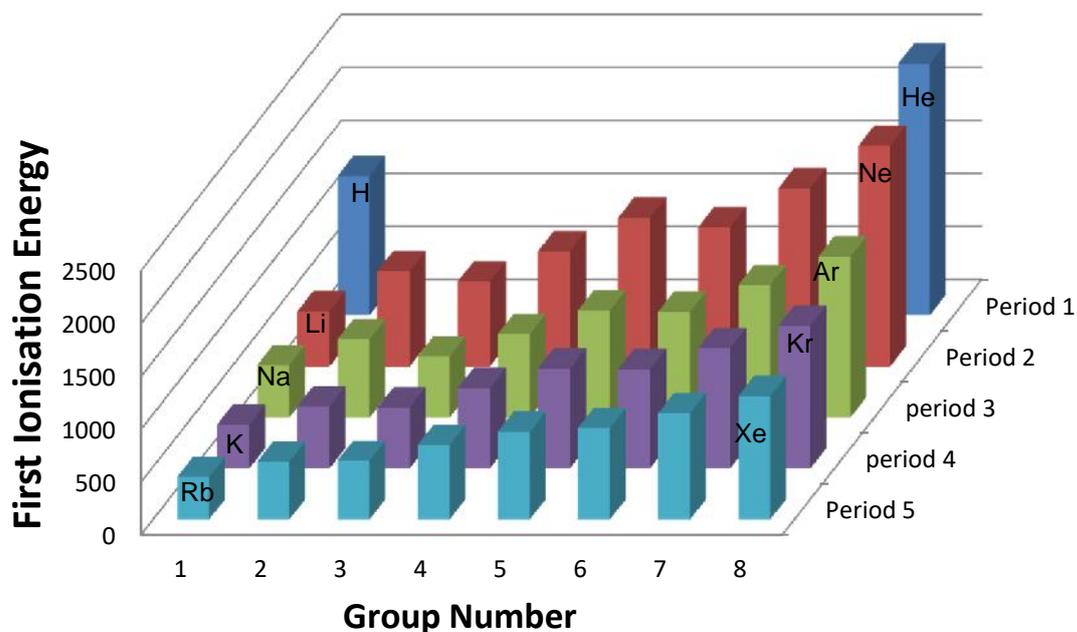
The pattern in the first ionisation energy of each successive element in the periodic table also gives us useful information about electronic structure



### Evidence for the main electron energy levels

The noble gases are always at the maximum peak for each period, but there is a decrease in ionisation energy down the group. (true of all groups). This is because as one goes down the group the outer electrons become further from the nucleus and become more shielded from the nuclear pull by complete inner shells

There is a large drop each time between the group 0 elements and the group 1 elements. This is because the element in group 1 will have its outer electron in a new shell further from the nucleus and is more shielded. So the group 1 element is easier to remove and has a lower ionisation energy.



Notice the drop in ionisation energy down each group

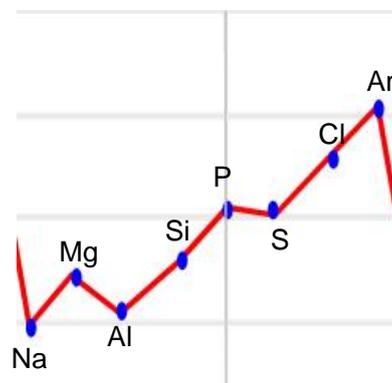
As one goes down a group, the outer electrons are found in shells further from the nucleus and are more shielded so the attraction of the nucleus becomes smaller

Helium has the biggest first ionisation energy because 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.

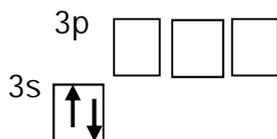
### Evidence for the electron sub energy levels

There is in general an increase in ionisation energy across a period. This is because 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.

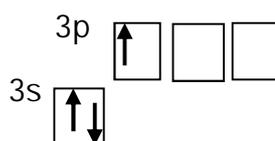
There are two small drops in the general trend, however, that provide further evidence for the existence of sub energy levels.



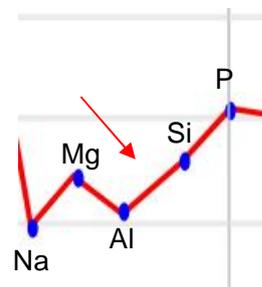
Notice the small drop between the group 2 elements and group 3 elements (Be + B, Mg + Al). Al is starting to fill a 3p sub shell, whereas Mg has its outer electrons in the 3s sub shell. The electrons in the 3p subshell are slightly easier to remove because the **3p electron sub shell is slightly higher in energy** and they are also slightly shielded by the 3s electrons.



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

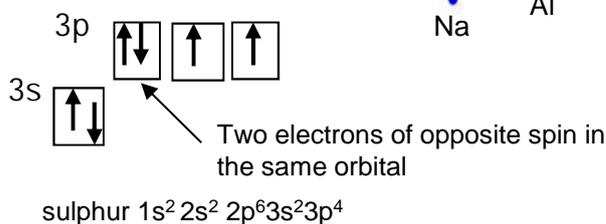
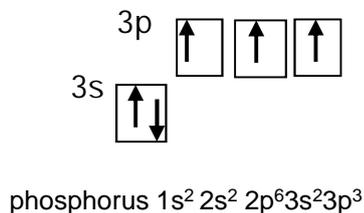
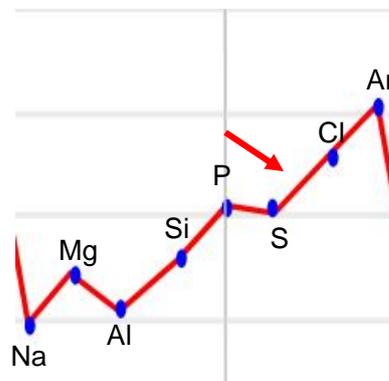


Aluminium  
 $1s^2 2s^2 2p^6 3s^2 3p^1$



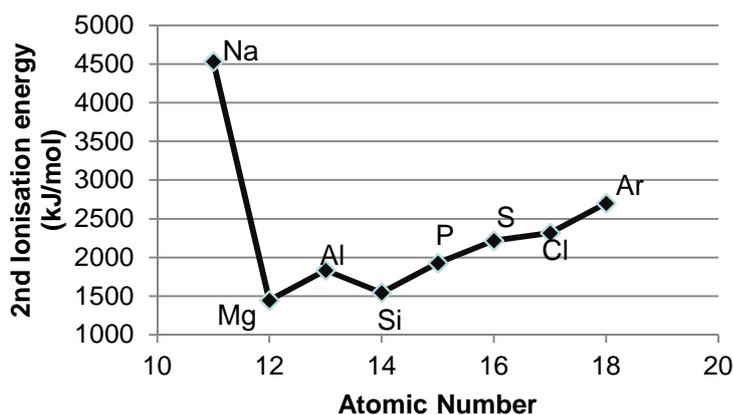
## Why is there a small drop from P to S?

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.



## 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.

### First Electron affinity

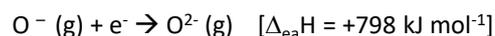
The first electron affinity is the enthalpy change that occurs when 1 mole of gaseous atoms gain 1 mole of electrons to form 1 mole of gaseous ions with a  $-1$  charge



The first electron affinity is exothermic for atoms that normally form negative ions because the ion is more stable than the atom and there is an attraction between the nucleus and the electron

### Second Electron affinity

The second electron affinity is the enthalpy change when one mole of gaseous  $1^-$  ions gains one electron per ion to produce gaseous  $2^-$  ions.



The second electron affinity for oxygen is **endothermic** because it takes energy to overcome the **repulsive force** between the **negative ion and the electron**