

# **Mass Spectrometer & Atomic Structure**

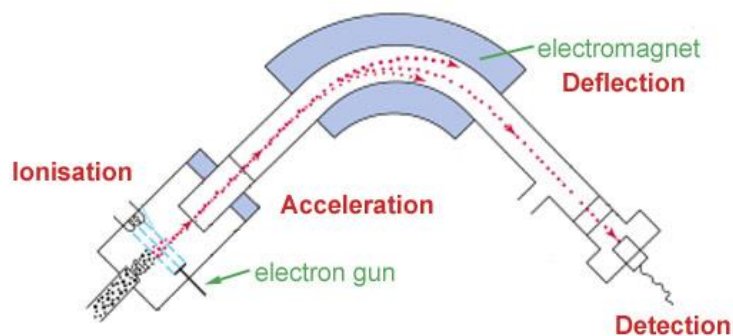
**By: Mahmoud Taha**

**Special thanks to Ms Williams and Ms Matrella for their constant  
support and inspiration**

Please note that these guides are a collation of my personal notes, teachers' notes, chemistry books, and websites such as chemguide, chemsheets, chemwiki and wikipedia.

### What is Mass Spectrometer?

"An analytical machine/device used to find out the relative masses of atoms and molecules"



1. In the mass spectrometer, the sample particle is entered into the ionization chamber. Note that the sample has to be in **gaseous form**.

2. The electron gun will shoot out electrons. These electrons are attracted to the other side of the chamber since due to the positive

plate.

3. The electrons bombard the sample causing it to form a positive ion. The next stage is acceleration.
4. Two negatively charged plates with an electric current causes the ionized particle to move quicker and be focused into a single beam. It will then enter into a magnetic field.
5. The electromagnet will cause the particle to deflect. Depending on mass to charge ratio ( $m/z$ ). A sample with a high mass and low charge will deflect less than a sample with a low mass with a high charge. Also note the strength of the magnetic field is affected by the electromagnet itself.
6. A tiny current is produced when each ion reaches the detector. The amount of current depends on the abundance of that ion.

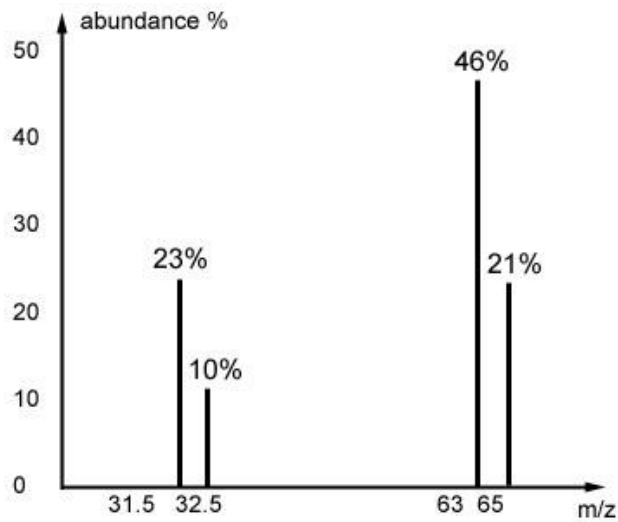
### Uses of Mass Spectrometer

The syllabus does mention that you need to:

"Describe some uses of mass spectrometers, e.g. in radioactive dating, in space research, in sport to detect use of anabolic steroids, in the pharmaceutical industry to provide an identifier for compounds synthesised for possible identification as drugs"

So keep that in mind because they may ask what are the uses of mass spec...

## The Graph (Elements)



To calculate the Relative Molecular Mass, the percentage abundance of each mass is divided by 100 and multiplied by the mass represented.

E.g.

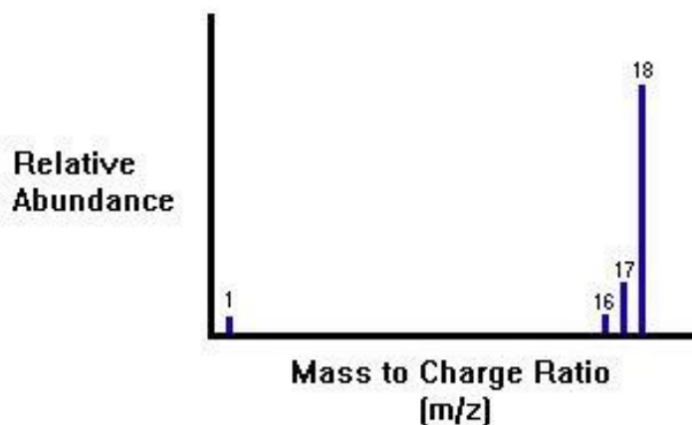
$$(0.23 \times 31.5) + (0.10 \times 32.5) + (0.46 \times 63) + (0.21 \times 65) = 63.62$$

All peaks need to be taken into account no matter how rare the isotope is.

## Mass Spec of Compounds

Mass specs can also be used to measure the RMM of a compound. The compound will be the sample in this case. It enters the machine and gets ionized, deflected and detected. The ion with the greatest mass to charge ratio ( $m/z$ ) is the so called parent ion. The mass of this ion is considered to be the RMM of the compound.

For example, this is the mass spec of water. The first ion is only  $H^+$ . The second one is  $O^{2-}$ . The third one is  $OH^-$ . Finally the last one is  $H_2O$ . That last ion is the parent ion, i.e. it is the molecule of water therefore its mass is considered the RMM of water. The other ions are called fragment ions. Note that the parent ion doesn't have to be the highest peak on the graph.



Refresher:

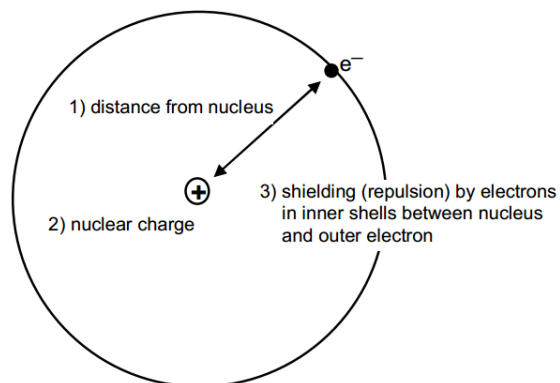
Keyword	Definition
Relative atomic mass (RAM)	The average mass of its isotopes compared with the mass of an atom of carbon-12
Relative isotopic mass (RIM)	The mass of the isotope compared with the mass of an atom of carbon-12
1 amu (or) Atomic mass of hydrogen	The mass of a carbon-12 atom divided by 12
Relative molecular mass (RMM or Mr)	The sum of the relative atomic masses of all the atoms in the chemical formula

## Ionisation Energy

1<sup>st</sup> ionisation energy is the energy required to remove one electron from each atom in a mole of gaseous atoms producing one mole of 1+ gaseous ions. Note that 2<sup>nd</sup> ionisation energy is the energy required to remove the second electron.

4 factors affect the ionisation energy:

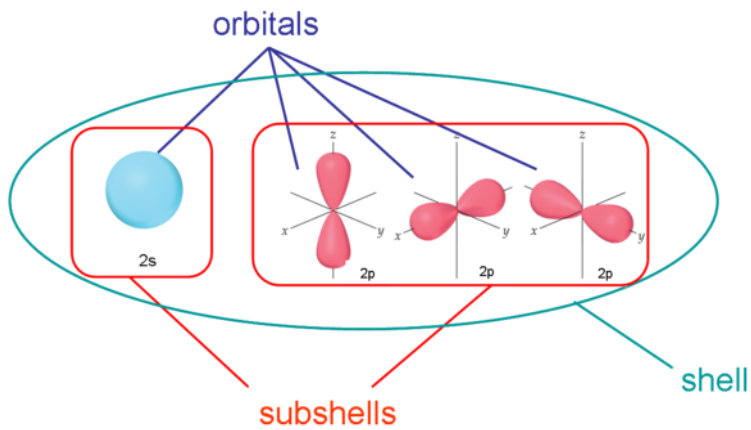
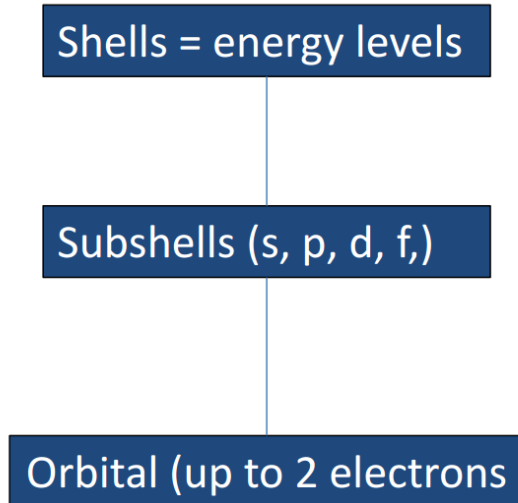
- Distance from nucleus (atomic radius): The further an electron is the less attracted to the nucleus.
- Nuclear Charge: This is essentially the number of protons in the nucleus. The more, the better :P  
More protons lead to stronger attraction theoretically.



- Shielding Effect: This causes the outermost electron to experience less attraction to the nucleus. Why?  
Because the inner energy shells lessen the attraction between the valency electron and its nucleus. Think of looking a person directly or through 10 rows of people. The more the rows the harder it is to spot the person.
- Pairing Effect: if an electron is on its own in the orbital or paired up also affects. Two electrons in the same orbital experience a bit of repulsion from each other. This offsets the attraction of the nucleus, so paired electrons are removed more easily than expected.

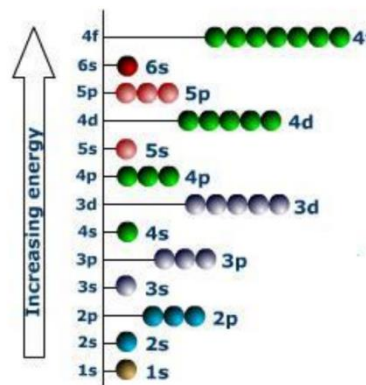
Note the first ionisation energy of an element is always lower than its second due to the increasing pull of the protons. After one electron is take away, the ion is positively charged overall and hence the attraction between the nucleus and the valency electron. Also note that effective nuclear charge is taking into account nuclear charge and shielding while nuclear charge doesn't take into account the shielding effect.

# Electron arrangement



## Orbitals of Electrons

Electrons are arranged in a particular order in any ion or atom. First electrons fill up the first sub shell (i.e. the s orbital) in the first energy level. Then they fill the 2s, 2p, 3s, etc... When they fill the orbitals, they fill it on their own first then if more electrons still need an orbital they then start to pair up. This is essentially Hund's rule.



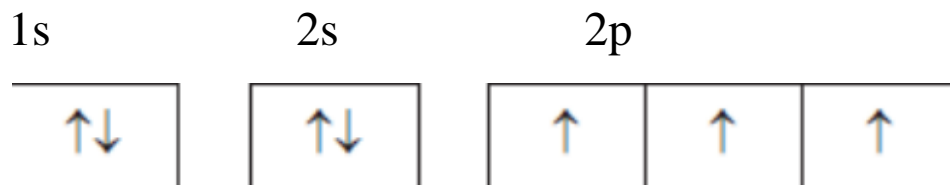
This can be demonstrated using the electron-in-box notation

For example to represent the N atom (which has 7 electrons) you should do the following:

The first 2 electrons go to the 1s subshell. Note how the paired electrons face opposite each other.

Then the next 2 go to the 2s subshell.

Now here is where stuff start to get tricky, in the p, d and f subshells you have to insert the electrons 1 in each orbital, then if you have any left overs, put one in each orbital (from left to right) to fill it. If all the orbitals are filled, move on to the next subshell. In this case we didn't need to as the last 3 electrons took an orbital each and there was no need to pair any electrons in the p subshell.



## Exceptions

*(May not be in the syllabus, I have included it just in case, better to have a read)*

There is however 2 exceptions to how normal elements arrange their electrons. In the case of Chromium (Cr) the electrons are arranged in the following format:

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ . The part in bold shows how one of the electrons in Cr goes from the 4s sub shell to the 3d sub shell. This happens because of the following: 2 subshells half filled are more stable than 1 subshell filled and the other subshell not completely filled. When the s subshell has 1 electron, it is half filled. When the d subshell has 5 electrons, it is half filled resulting in 2 half filled sub shells while if there were 2 electrons in s subshell then it will be completely filled and 4 electrons in d subshell will result in it being incompletely filled.

The other exception would be Cu. Its electron configuration is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ . Certain arrangements of shells are more stable than others. Fully-filled shells are obviously very stable. Half-filled shells are also quite stable (though not as stable as fully filled ones), while other fillings are rather unstable. The [Ar] means  $1s^2 2s^2 2p^6 3s^2 3p^6$ , which is Argon electrons configuration...please don't use [Ar] in the exam.

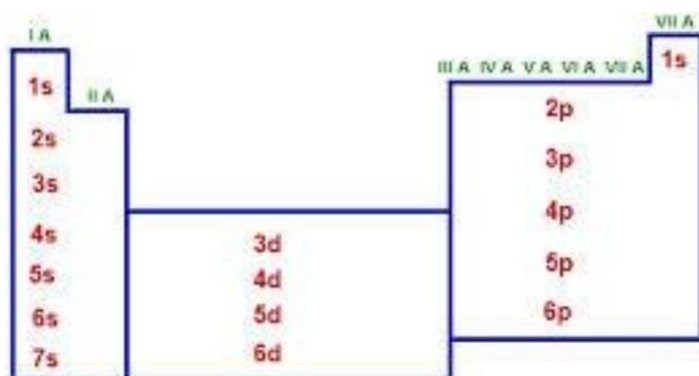
As a result, we can compare the two different electron configuration for copper:

[Ar]  $4s^2 3d^9$ : Contains a fully-filled s-shell (very stable) and one non-filled d-shell (unstable)

[Ar]  $4s^1 3d^{10}$ : Contains a fully-filled d-shell (very stable) and a half-filled s-shell (stable)

Hence in both cases, the atom prefers to have the most stable configuration. Note that [Ar] refers to the electron configuration of Argon which is  $1s^2 2s^2 2p^6 3s^2 3p^6$ .

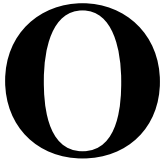

The following diagram shows on which energy sub shell does the valency electron 'sits'. This will be useful when predicting the ionisation energy trends.





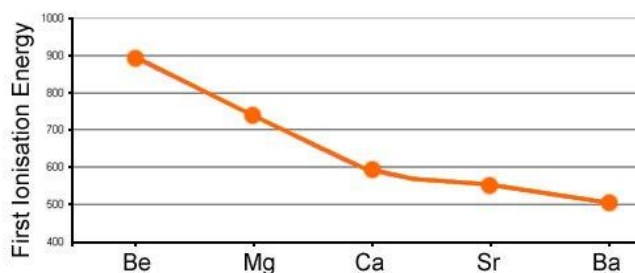
## Shapes of the orbitals

The two main shapes you have to be familiar with are the s orbital and the p orbital:

	
S orbital	P orbital (note the is a possible p orbital, it could also be horizontal or diagonal)

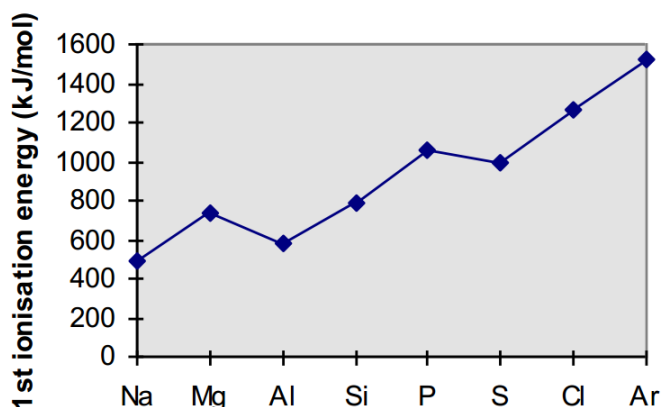
## Trends

So what are the trends that form across the periodic table? Well, let's start with a general look down a group. As the atomic number increases, so does the electron number. So how does that affect the first ionisation energy? Well, having more protons should have more attraction to the nucleus hence the ionisation energy should overall decrease right? However that's not the case. As the graph shows, the ionisation energy decreases. Why? Because more electron shells are present each time. Hence more shielding effect will take place. Also, the atomic radius will increase. Both of these will decrease the effective nuclear charge which in turn decreases the attraction between the nucleus and the valency electron. Therefore the outermost electron is more easily removed.



The next trend to look at is across a period. By referring to the graph we can see that as you go across a period the ionisation energy increases. This happens because there is more protons present each time, yet the effect of shielding doesn't significantly increase. However there are 2 exceptions for the general trend.

Al has a lower ionisation energy than Mg. This is due to the valency electron of Al sitting in a higher energy level (the p sub shell) so it is further away from the nucleus and it's easier to be removed.



The other exception would be Phosphorus and Sulphur. Phosphorus has electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^3$ , note that in the p sub shell, all the electron are not paired. Sulphur on the other hand has electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^4$ , the 4th electron in the p subshell is paired up. This pairing causes a slight repulsion between the electrons because they like to be in an orbit of their own. Hence it is easier to lose that paired up electron.

A very likely question to come in the exam is why Ar has a higher ionisation energy than Na. This is because Ar has more protons and hence more attraction of its electrons towards the nucleus than Na. We don't take shielding into consideration as the difference is insignificant since Na and Al has the same number of electron shells.