AQA A Level Chemistry

Unit 1 – Physical Chemistry

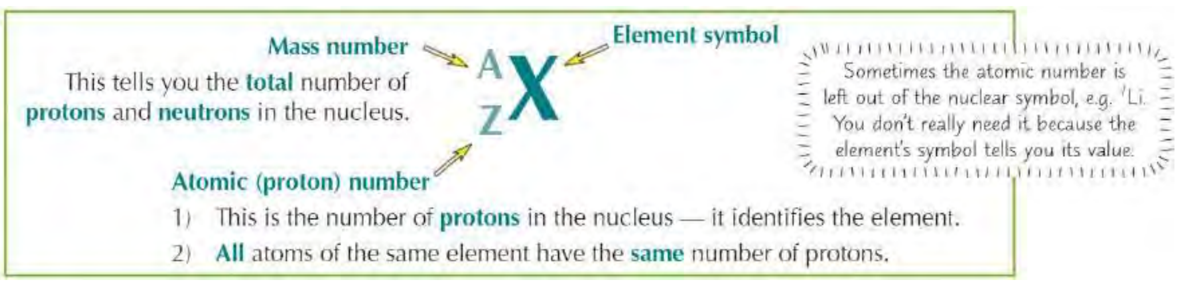
1.1 – Atomic Structure

1) What makes up an atom?

- All elements made up of atoms.
- Atoms made up of protons, neutrons, electrons.
- Most mass of atom in nucleus.
- Diameter of nucleus small compared to whole atom.

Subatomic particle	Relative mass	Relative charge
Proton	1	+1
Neutron	1	0
Electron, e^-	$\frac{1}{2000}$ (0.0005)	–1

2) Nuclear symbols.



For neutral atoms, num of electrons = num of protons.
Num of neutrons = Mass num – Atomic num

3) What are ions?

Ions formed when atoms lose or gain electrons.

Negative ions have more electrons than protons; positive ions have more protons than electrons.

4) What are isotopes?

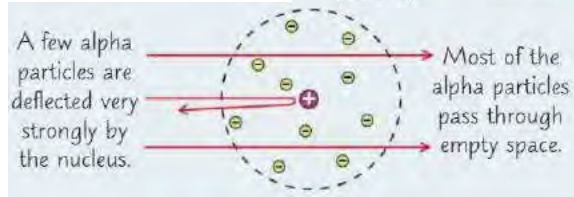
Isotopes of an element = Atoms with the same number of protons but different numbers of neutrons (so different mass numbers).

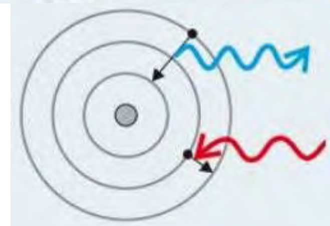
Isotopes of the same element have the same chemical properties, because the number and arrangement of electrons decide the chemical properties of elements.

They have different physical properties, as they depend on the mass of the atom.

5) Models of Atomic Structure changing over time.

1. Dalton – Atoms were solid spheres.
2. Thompson – Plum-pudding model; ball of positive charge with electrons dotted inside it.
3. Rutherford – Fired positive alpha particles at gold foil. Neutral plum pudding should get alpha pass through it. However, some alpha particles were deflected by nucleus. Atom was concluded to be mostly empty space, most mass in centre, nucleus is positive, and electrons orbit nucleus.
4. Bohr – Electrons orbit at specific distances; the further an electron is from the nucleus, the more energy it has. When electron loses energy, EM radiation is emitted and it jumps down a shell (and vice-versa).
5. Chadwick – Neutrons.
6. Not all electrons in shell have same energy – include sub shells.





6) Definitions of the three relative masses.

Relative Atomic Mass = the average mass of an atom compared to 1/12 mass of an atom of carbon-12 (^{12}C).

Relative Isotopic Mass = the mass of an atom of an isotope compared to 1/12 mass of an atom of carbon-12 (^{12}C).

Relative Molecular Mass = the average mass of a molecule compared to 1/12 mass of an atom of carbon-12 (^{12}C).

7) Electron Impact Ionisation.

- Sample vaporised and fired with high energy electrons from an electron gun, which knocks off one electron from each particle.
- + ions attracted to a negative plate when they are accelerated.
- Used for elements, and substances made of molecules with a low Mr.

8) Electrospray Ionisation.

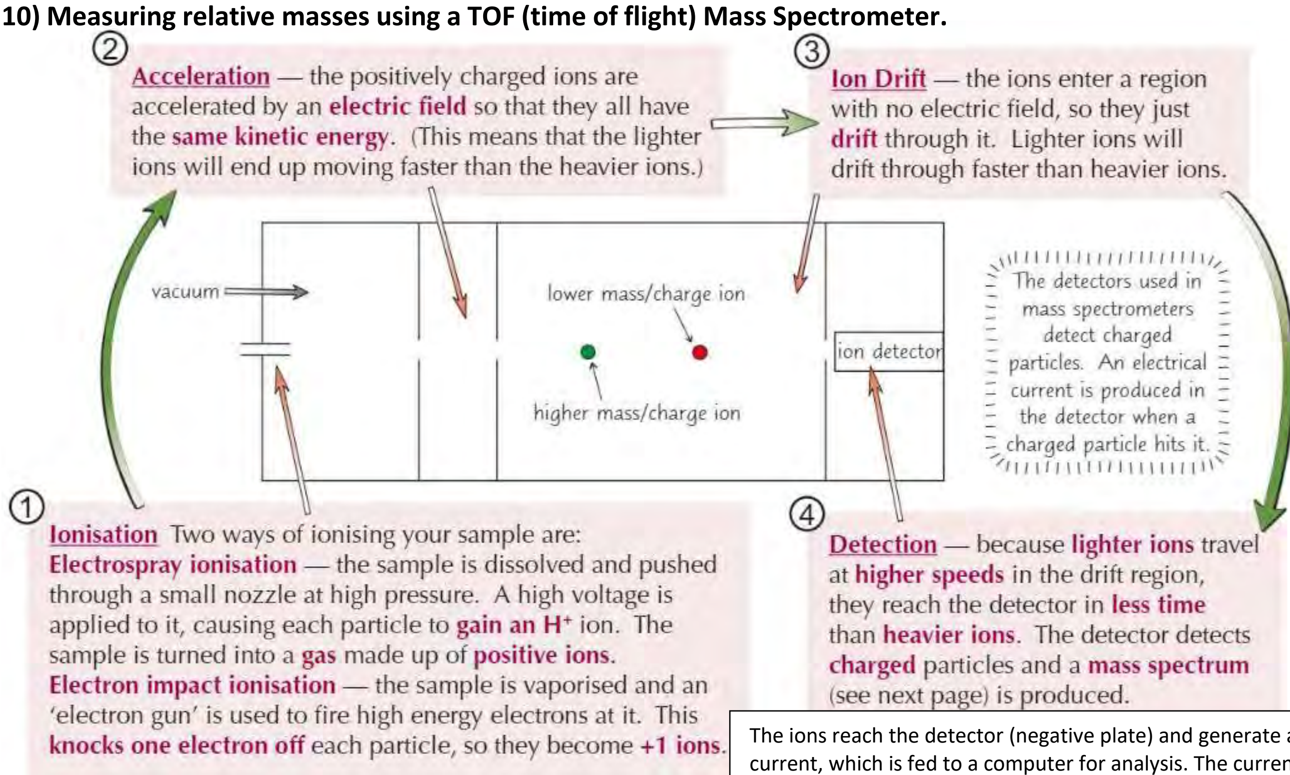
- Sample dissolved in a volatile solvent and injected through a needle to give a fine mist.
- Tip of the needle attached to the positive terminal of a high voltage power supply. Particles are ionised by gaining a proton (H+) from the voltage as they leave the needle.
- Ions formed attracted to a negative plate where they are accelerated.
- Used for substances made of molecules with a high Mr – biological molecules (EG: proteins).

9) Equations for Electron Impact Ionisation and Electrospray Ionisation.

Electron Impact Ionisation = $X_{(g)} + e^- \rightarrow X^+_{(g)} + 2e^-$

Electrospray Ionisation = $X_{(g)} + H^+ \rightarrow XH^+_{(g)}$

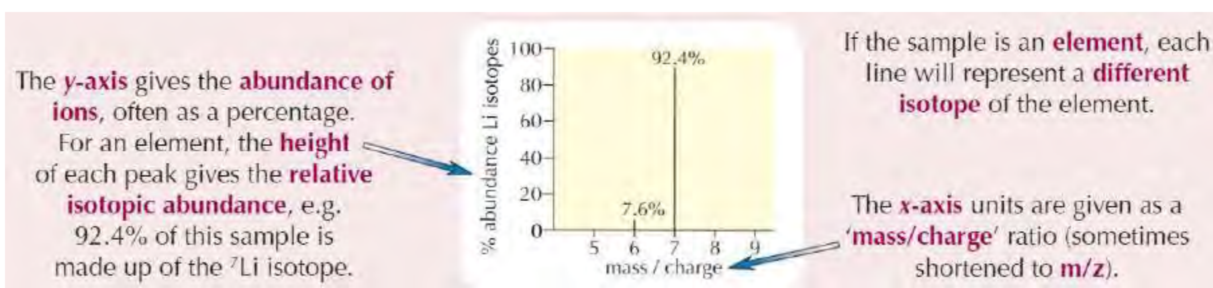
10) Measuring relative masses using a TOF (time of flight) Mass Spectrometer.



The ions reach the detector (negative plate) 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 (ions gain an e-). The size of the current is proportional to the abundance of the species, as current of an ion can be compared relatively to the current produced by other ions, causing m/z to be measured.

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

11) 5th Step – Data analysis – Mass Spectrum created from Electron Impact Ionisation.



Spectrum above produced using electron impact ionisation:

- Detector plate is negative.
- One electron knocked off each particle, turning them to +1 ions – so that the mass/charge ratio of each peak is the same as the relative mass of that isotope.

- If electrospray ionisation had been used instead, an H+ ion would have been added to each particle to form +1 ions – so that the mass/charge ratio of each peak would be one greater than the relative mass of each isotope.

12) Advantages and Disadvantages of Electron Impact Ionisation and Electrospray Ionisation.

Electron Impact Ionisation:

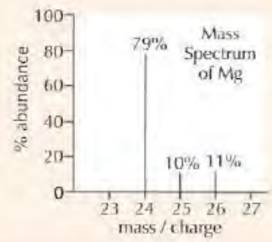
- ✗ Molecule often fragmented – many peaks. Peak with the highest m/z is the molecule Mr.

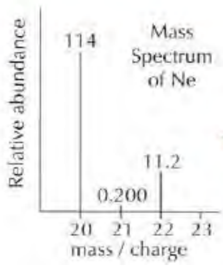
Electrospray Ionisation:

- ✓ Molecules rarely fragmented – one peak, minus the m/z by 1 to get the molecule Mr.
- ✗ Resulting ions have a Mr one unit higher due to the gain of a proton.
- ✗ Can't be used if particles aren't capable of gaining a proton.

13) Working out Relative Atomic Mass from a mass spectrum (EG: Mg).

1) For each peak, read the **% relative isotopic abundance** from the y-axis and the **relative isotopic mass** from the x-axis. **Multiply** them together to get the total mass for each isotope: $79 \times 24 = 1896$; $10 \times 25 = 250$; $11 \times 26 = 286$
2) **Add** up these totals: $1896 + 250 + 286 = 2432$
3) **Divide by 100** (as percentages were used):
$A_r(Mg) = 2432 \div 100 = 24.32 =$ **24.3 (3 s.f.)**





If the relative abundance is **not** given as a percentage, the total abundance may not add up to 100. In this case, don't panic. Just do steps 1 and 2 as above, but then divide by the **sum of the relative abundances** instead of 100 — like this:

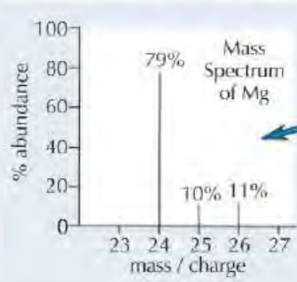
$$A_r(Ne) = \frac{(114 \times 20) + (0.2 \times 21) + (11.2 \times 22)}{114 + 0.2 + 11.2} = 20.2 \text{ (3 s.f)}$$

14) Identifying elements from a mass spectrum.

Elements with different **isotopes** produce more than one line in a mass spectrum because the isotopes have **different masses**. This produces characteristic patterns which can be used as '**fingerprints**' to **identify** certain **elements**.

Magnesium has three isotopes with the percentage abundance shown here.

Mg Isotopes	% Abundance
^{24}Mg	79
^{25}Mg	10
^{26}Mg	11



If a sample being analysed contains magnesium, this isotopic distribution will show up in the mass spectrum.

Many elements only have one stable isotope. They can still be identified in a mass spectrum by looking for a line at their **relative atomic mass**.

15) Identifying molecules using mass spectrometry.

- A molecular ion, M+, is formed in the mass spectrometer when one electron is removed from the molecule.
- This gives a peak in the spectrum with a mass/charge ratio equal to the relative molecular mass of the molecule.
- This is used to identify any unknown compounds.

Example: A sample of a straight-chain alcohol is analysed in a mass spectrometer. The mass/charge ratio of its molecular ion is 46.0. Identify the alcohol.

The table on the right shows the M_r of the first three straight-chain alcohols. The mass/charge ratio of the molecular ion must **equal** the M_r of the alcohol in the sample. So the alcohol must be **ethanol, C_2H_5OH**.

Alcohol	M_r
methanol CH_3OH	32.0
ethanol C_2H_5OH	46.0
propanol C_3H_7OH	60.0

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%

16) Electron shells made up of sub-shells and orbitals.

- Electrons have fixed energies, moving around the nucleus in areas called shells (or energy levels).
- Each shell is given a principal quantum number.
- The further a shell is from the nucleus, the higher its energy, and the larger its principal quantum number.
- Experiments show that not all the electrons in a shell have exactly the same energy.
- The atomic model explains why shells are divided up into sub-shells that have slightly different energies.
- The sub-shells have different numbers of orbitals, which can each hold up to 2 electrons.
- The two electrons in each orbital spin in opposite directions.

This table shows the number of electrons that fit in each type of sub-shell.

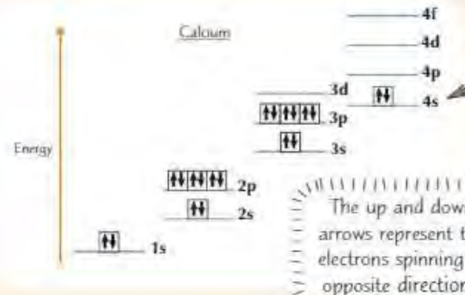
Sub-shell	Number of orbitals	Maximum electrons
s	1	$1 \times 2 = 2$
p	3	$3 \times 2 = 6$
d	5	$5 \times 2 = 10$
f	7	$7 \times 2 = 14$

And this one shows the sub-shells and electrons in the first four energy levels.

Shell	Sub-shell	Total number of electrons
1st	1*s*	2
2nd	2*s* 2*p*	$2 + (3 \times 2) = 8$
3rd	3*s* 3*p* 3*d*	$2 + (3 \times 2) + (5 \times 2) = 18$
4th	4*s* 4*p* 4*d* 4*f*	$2 + (3 \times 2) + (5 \times 2) + (7 \times 2) = 32$

17) Working out Electron Configurations.

1) Electrons fill up the **lowest** energy sub-shells first.



There's always got to be an exception to mess things up. The 4s sub-shell has a lower energy level than the 3d sub-shell, even though its principal quantum number is bigger. This means the 4s sub-shell fills up first.

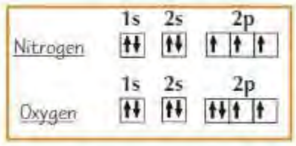
The up and down arrows represent the electrons spinning in opposite directions.

Sub-shell notation is the main way of showing electron configuration.
The electron configuration of **calcium** is:

$$1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2$$

Energy level / shell (principal quantum number) — Sub-shell — Number of electrons

2) Electrons fill orbitals **singly** before they start sharing.



See the next page for more on the s and p blocks.

3) For the configuration of **ions** from the **s** and **p** blocks of the periodic table, just **remove or add** the electrons to or from the highest energy occupied sub-shell.
E.g. Mg = $1s^2\ 2s^2\ 2p^6\ 3s^2$, so Mg^{2+} = $1s^2\ 2s^2\ 2p^6$. Cl = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$, so Cl^- = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

Watch out — **noble gas symbols**, like that of argon (Ar), are sometimes used in electron configurations. For example, calcium ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$) can be written as $[Ar]4s^2$, where $[Ar] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

First ionisation energy of oxygen atoms less than that of nitrogen atoms as two of the electrons in the outer p subshell of oxygen occupy the same orbital. Therefore, there is repulsion between the two electrons, lowering the first ionisation energy of oxygen.

18) Behaviour of Transition Metals.

- Chromium and copper donate one of their 4s electrons to the 3d sub-shell, as it's more stable with a full or half-full d sub-shell.
- When transition metals become ions, they lose their 4s electrons before their 3d electrons – when 4s is filled, it becomes higher than 3d, because 3d (more electrons) has a stronger attraction with the nucleus.

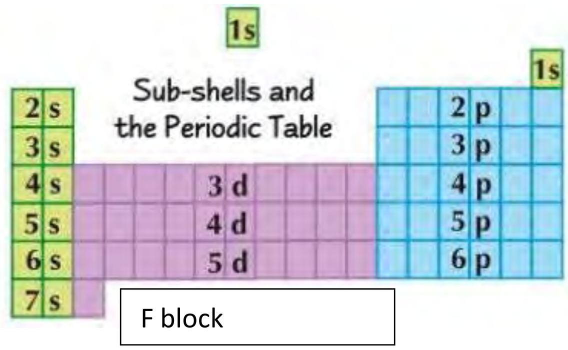
Transition Metals Behave Unusually

1) **Chromium** (Cr) and **copper** (Cu) are badly behaved. They donate one of their **4s** electrons to the **3d sub-shell**. It's because they're happier with a **more stable** full or half-full d sub-shell.
Cr atom (24 e^-): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ Cu atom (29 e^-): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

2) And here's another weird thing about transition metals — when they become **ions**, they lose their **4s** electrons **before** their 3d electrons.
Fe atom (26 e^-): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$ → Fe^{3+} ion (23 e^-): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

It's OK to write the 3d and 4s sub-shells the other way round if you prefer.

19) Chemical Properties of an element decided by their electronic structure (number of outer shell electrons).



- The s block elements (Groups 1 and 2) have 1 or 2 outer shell electrons, which are easily lost to form positive ions with an inert gas configuration.
- The elements in Groups 5, 6 and 7 (in p block) can gain 1, 2 or 3 electrons to form negative ions with an inert gas configuration. Groups 4 to 7 can also share electrons when they form covalent bonds.
- Group 0 (the noble/inert gases) have completely filled s and p sub-shells – completely inert.
- Transition metals (d block elements) lose s and d electrons to form positive ions.

20) Ionisation.

Ionisation = the removal of one or more electrons.

First ionisation energy = the energy needed to remove 1 electron from each atom in 1 mole of gaseous atoms to form 1 mole of gaseous 1+ ions.

It is an endothermic process, and you have to put energy in to ionise an atom or molecule.

You can write **equations** for this process — here's the equation for the **first ionisation of oxygen**:

$O_{(g)} \rightarrow O^{+}_{(g)} + e^{-}$ **1st ionisation energy = +1314 kJ mol⁻¹**

Here are a few rather important points about ionisation energies:

1) You **must** use the gas state symbol, **(g)**, because ionisation energies are measured for gaseous atoms.
2) Always refer to **1 mole** of atoms, as stated in the definition, rather than to a single atom.
3) The **lower** the ionisation energy, the **easier** it is to form an ion.

21) Factors affecting ionisation energy.

Nuclear Charge:

- The more protons there are in the nucleus, the more positively charged the nucleus is and the stronger the attraction for the electrons.

Distance from Nucleus (Atomic Radius):

- Attraction falls off very rapidly with distance.
- An electron close to the nucleus will be much more strongly attracted than one further away.

Shielding:

- As the number of electrons between the outer electrons and the nucleus increases, the outer electrons feel less attraction towards the nuclear charge.
- The lessening of the pull of the nucleus by inner shells of electrons is called shielding (or screening).

A high ionisation energy means there's a high attraction between the electron and the nucleus, and so more energy is needed to remove the electron.

22) Successive Ionisation Energies involve removing additional electrons.

You can remove all the electrons from an atom, leaving only the nucleus. Each time you remove an electron, there's a successive ionisation energy.

Second ionisation energy = the energy needed to remove 1 electron from each ion in 1 mole of gaseous 1+ ions to form 1 mole of gaseous 2+ ions.

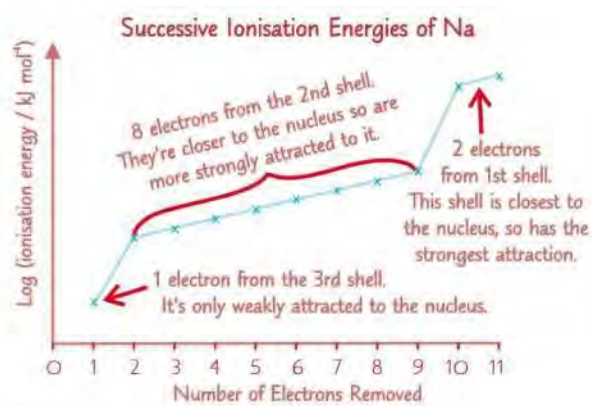
And here's the equation for the **second ionisation of oxygen**: $O^{+}_{(g)} \rightarrow O^{2+}_{(g)} + e^{-}$ **2nd ionisation energy = +3388 kJ mol⁻¹**

The equation for the ***nth*** **ionisation energy** is.... $X^{(n-1)+}_{(g)} \rightarrow X^{n+}_{(g)} + e^{-}$

23) Successive Ionisation Energies show Shell Structure.

A **graph** of successive ionisation energies (like this one for sodium) provides evidence for the **shell structure** of atoms.

1) **Within each shell**, successive ionisation energies **increase**. This is because electrons are being removed from an **increasingly positive ion** — there's **less repulsion** amongst the remaining electrons, so they're **held more strongly** by the nucleus.
2) The **big jumps** in ionisation energy happen when a new shell is broken into — an electron is being removed from a shell **closer** to the nucleus.



1) Graphs like this can tell you which **group** of the periodic table an element belongs to. Just count **how many electrons are removed** before the first big jump to find the group number.

   E.g. In the graph for sodium, **one electron** is removed before the first big jump — sodium is in **group 1**.

2) These graphs can be used to predict the **electronic structure** of elements. Working from **right to left**, count how many points there are before each big jump to find how many electrons are in each shell, starting with the first.

   E.g. The graph for sodium has **2 points** on the right-hand side, then a jump, then **8 points**, a jump, and **1 final point**. Sodium has **2 electrons** in the first shell, **8** in the second and **1** in the third.

24) Trends in First Ionisation Energies.

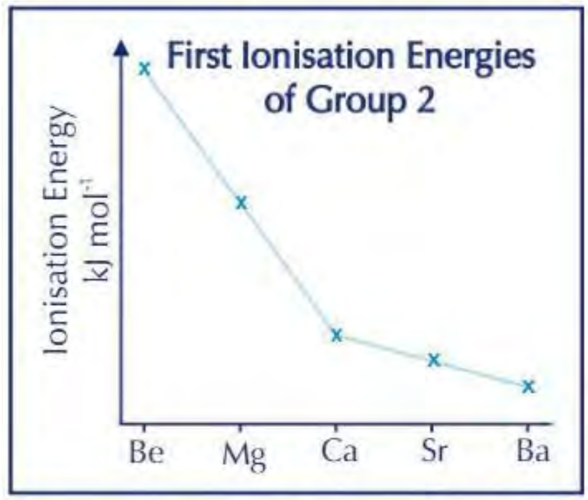
- The first ionisation energies of elements down a group of the periodic table decrease.
- The first ionisation energies of elements across a period generally increase.

25) Ionisation trend of Group 2.

Ionisation energy decreases down group 2:

- If each element down Group 2 has an extra electron shell compared to the one above, the extra inner shells will shield the outer electrons from the attraction of the nucleus.
- Also, the extra shell means that the outer electrons are further away from the nucleus, so the nucleus's attraction will be greatly reduced.

Both these factors make it easier to remove outer electrons, resulting in a lower ionisation energy.



26) Ionisation trend of a Period.

Ionisation energy increases across a period:

- Number of protons increases, so a stronger nuclear attraction.
- All the extra electrons at around the same energy level, even if the outer electrons are in different orbital types; meaning there's little extra shielding effect or extra distance to lessen the attraction from the nucleus.