

1.1 Atomic structure

The Structure of the Atom

Mass Spectrometry

Electronic Structure

Ionisation Energies

THE STRUCTURE OF THE ATOM

a) Protons, neutrons and electrons

Atoms are made up of three fundamental particles: **protons**, **neutrons** and **electrons**.

Protons and neutrons are found in the nucleus and are collectively called **nucleons**. Electrons orbit the nucleus in a similar way to that in which planets orbit a sun. In between the electrons and nucleus there is nothing (empty space). The nucleus is very small; if an atom were the size of a football pitch, the nucleus would be the size of a drawing pin.

The basic properties of these three particles can be summarized in the following table:

Particle	Charge	Mass
Proton	+1 unit	Approx 1 unit
Neutron	No charge	Approx 1 unit
Electron	-1 unit	Approx 1/1840 units (very small)

1 unit of charge is 1.602×10^{-19} coulombs. A proton is given a charge of +1 and an electron a charge of -1. All charges are measured in these units.

1 unit of mass is 1.661×10^{-27} kg. This is also not a convenient number, so we use “atomic mass units”.

Since the mass of protons and neutrons varies slightly depending on the nucleus, then in order to define an “atomic mass unit” we need to choose one nucleus as a standard. For this purpose $^{12}_6\text{C}$, or “carbon-12”, was chosen because its mass per nucleon (1.661×10^{-27} kg) is around average, which means all the other nuclei have masses close to whole numbers. **An atomic mass unit is thus defined as 1/12th of the mass of one atom of carbon-12.** Everything else is measured relative to this quantity.

b) Atomic numbers, mass numbers and isotopes

An atom is named after the number of protons in its nucleus. If the nucleus of an atom has 1 proton, it is hydrogen; if it has two protons, it is helium; if it has 3, it is lithium etc. The number of protons in the nucleus of an atom is called the atomic number. It has the symbol Z.

The atomic number is the number of protons in the nucleus of an atom

Not all atoms of the same element have equal numbers of neutrons; this may vary slightly. The sum of the number of protons and neutrons in the nucleus of an atom is called its **mass number**. It is represented by the symbol A.

The **mass number** is the sum of the number of protons and neutrons in the nucleus of an atom

The nucleus of an atom can thus be completely described by its mass number and its atomic number. It is generally represented as follows:



Eg. ${}^9_4\text{Be}$, ${}^{12}_6\text{C}$, ${}^{24}_{12}\text{Mg}$

Atoms with the same atomic number but with different mass numbers (ie different numbers of neutrons) are called **isotopes**.

Isotopes are atoms with the same atomic number but with different mass numbers

Eg magnesium (atomic number 12) has 3 naturally occurring isotopes:

${}^{24}_{12}\text{Mg}$: 12 protons, 12 neutrons

${}^{25}_{12}\text{Mg}$: 12 protons, 13 neutrons

${}^{26}_{12}\text{Mg}$: 12 protons, 14 neutrons

In a neutral atom, the number of protons and electrons are the same. However, many elements do not exist as neutral atoms, but exist as **ions**. Ions are species in which the proton and electron numbers are not the same, and hence have an overall positive or negative charge. The number of electrons in a species can be deduced from its charge:

Eg

${}^{24}_{12}\text{Mg}^{2+}$: 12p, 12n, 10e

${}^{24}_{12}\text{Mg}^{+}$: 12p, 12n, 11e

${}^{24}_{12}\text{Mg}$: 12p, 12n, 12e

${}^{24}_{12}\text{Mg}^{-}$: 12p, 12n, 13e

c) Relative atomic mass

The mass of an atom is measured in atomic mass units, where one unit is $1/12^{\text{th}}$ of the mass of one atom of carbon-12.

The **relative isotopic mass** of an isotope is the ratio of the mass of one atom of that isotope to $1/12^{\text{th}}$ of the mass of one atom of carbon-12.

It is usually very close to a whole number ratio:

Isotope	Mass number	Relative isotopic mass
^1_1H	1	1.006
^4_2He	4	4.003
^9_4Be	9	9.012
$^{27}_{13}\text{Al}$	27	26.919
$^{59}_{27}\text{Co}$	59	58.933

The masses of protons and neutrons vary slightly from isotope to isotope, so the relative isotopic mass is not exactly a whole number.

The **relative atomic mass** of an atom is the ratio of the average mass of one atom of that element to $1/12^{\text{th}}$ of the mass of one atom of carbon-12.

The RAM is the average mass of all the isotopes, and is often not close to a whole number:

Element	Common mass numbers	Relative atomic mass
Mg	24, 25, 26	24.32
Cl	35, 37	35.45
Br	79, 81	79.91
Ba	134, 135, 136, 137, 138	137.33

Some elements and compounds exist as molecules; these also have a characteristic mass:

The **relative molecular mass** of a molecule is the ratio of the average mass of that molecule to $1/12^{\text{th}}$ of the mass of an atom of carbon-12.

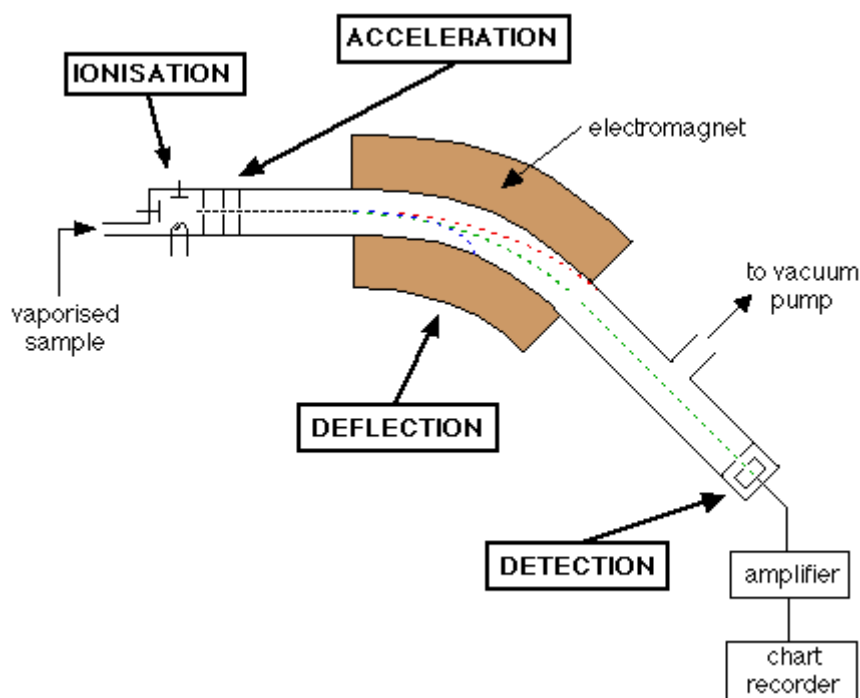
The relative molecular mass of a molecule is the sum of the relative atomic masses of its constituent atoms.

Eg The relative molecular mass of CO_2 is $12.0 + 16.0 + 16.0 = 44.0$

MASS SPECTROMETRY

The mass spectrometer is an instrument used for measuring the masses of atoms and molecules. It can also be used to measure the relative abundance of different isotopes and to predict the structure of more complex molecules.

1. How the mass spectrometer works



The workings of the mass spectrometer can be summarized in five stages:

- 1- Gaseous material released into ionization chamber
- 2- Particles bombarded with electrons and ionized, mostly to +1 ions (IONISATION)
A metal wire is heated until it starts emitting high energy electrons. These electrons hit the particles, knocking more electrons off. Most of the particles are ionized to +1 ions
- 3- Ions accelerated to uniform speed by electric field (ACCELERATION)
The positive ions are attracted to the negative plate and accelerate towards it
- 4- Ions deflected by magnetic field; deflection depends on m/e ratio (DEFLECTION)
The heavier the particle, the less the deflection
- 5- Electric current measured as ions land on plate (DETECTION)
The greater the abundance of the isotope, the larger the current

The degree of deflection depends on the mass and the charge; the greater the mass, the less the deflection, and the greater the charge, the greater the deflection. It can be shown that the deflection is inversely proportional to the m/e ratio.

In most cases, however, the charge is +1, so the deflection depends essentially on the relative mass of the species in the mass spectrometer. If the spectrometer is calibrated, the masses of all the species can be directly measured.

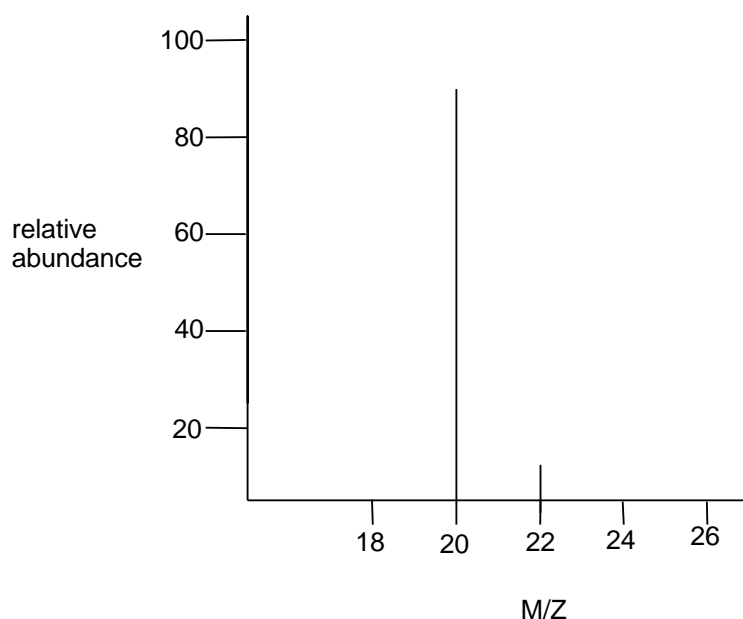
The greater the number of particles landing at a single point on the detector, the greater the electric current and the larger the peak. Thus the relative abundance of different isotopes can be measured.

Since the position at which an ion appears on the detector depends on its mass, different isotopes appear at different points on the detector. The magnitude of the peak gives the relative abundance of the isotope.

Thus the relative atomic mass of the element can be calculated from its mass spectrum.

An example of a simple mass spectrum is shown below:

Mass spectrum of Ne



The peak at 20 is $^{20}\text{Ne}^+$, and the peak at 22 is $^{22}\text{Ne}^+$

2. Calculating relative atomic masses

The relative atomic mass can be calculated by the formula:

$$\frac{\Sigma (\text{percentage abundance of each isotope} \times \text{mass of each isotope})}{100}$$

eg Using the mass spectrum of neon above:

$$\text{ram} = (90 \times 20 + 10 \times 22) / 100 = 20.2$$

All relative atomic masses have been found in this way.

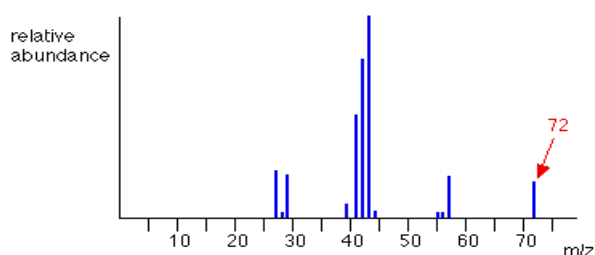
3. Deducing relative molecular masses

It is also possible to put molecules into the mass spectrometer. Because the conditions inside a mass spectrometer are very extreme, the molecules often break up into smaller pieces. This is known as fragmentation.

The mass spectrum of a molecule can thus look quite complicated:

Mass spectrum of pentane (C_5H_{12})

simplified mass spectrum of pentane - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



Many of these peaks result from fragmentation of the molecule, but the peak with the largest m/e ratio comes from the unbroken molecular ion, in this case $\text{C}_5\text{H}_{12}^+$, and is called the **molecular ion peak**. The m/e ratio of this peak (72) will be the relative molecular mass of the molecule.

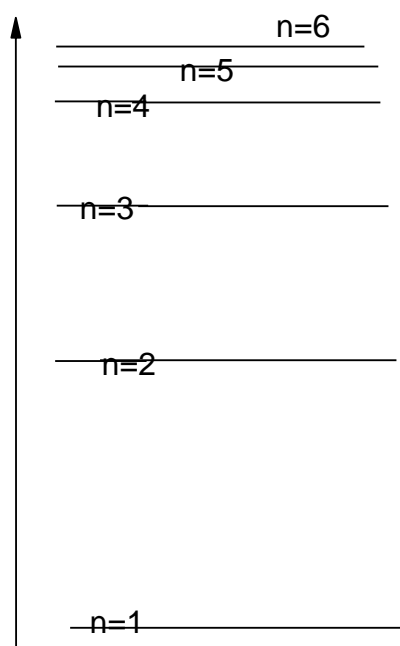
The relative molecular mass of a molecule is obtained by looking at the peak in the spectrum with the largest m/e ratio (ie the peak furthest to the right).

ELECTRONIC STRUCTURE

i) Energy levels

Electrons do not orbit the nucleus randomly; they occupy certain fixed energy levels. Each atom has its own unique set of energy levels, which are difficult to calculate but which depend on the number of protons and electrons in the atom.

Energy levels in an atom can be numbered 1,2,3,... To infinity. 1 is the lowest energy level (closest to the nucleus) and energy level infinity corresponds to the energy of an electron which is not attracted to the nucleus at all. The energy levels thus converge as they approach infinity:



ii) Orbitals and sub-levels

Electrons do not in fact orbit the nucleus in an orderly way. In fact they occupy areas of space known as **orbitals**. The exact position of an electron within an orbital is impossible to imagine; an orbital is simply an area of space in which there is a high probability of finding an electron.

Orbitals can have a number of different shapes, the most common of which are as follows:

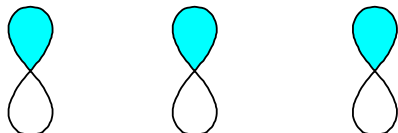
s-orbitals: these are spherical.



Every energy level contains one s-orbital.
An s-orbital in the first energy level is a 1s orbital.

An s-orbital in the second energy level is a 2s orbital, etc

p-orbitals: these are shaped like a 3D figure of eight. They exist in groups of three:



Every energy level except the first level contains three p-orbitals. Each p-orbital in the same energy level has the same energy but different orientations: x, y and z.

A p-orbital in the second energy level is a 2p orbital ($2p_x$, $2p_y$, $2p_z$)

A p-orbital in the third energy level is a 3p orbital ($3p_x$, $3p_y$, $3p_z$), etc

In addition, the third and subsequent energy levels each contain five d-orbitals, the fourth and subsequent energy levels contain seven f-orbitals and so on. Each type of orbital has its own characteristic shape.

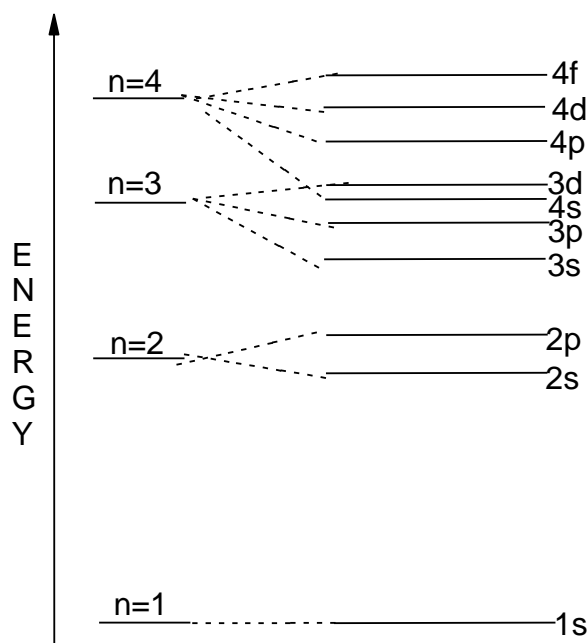
s, p and d orbitals do not all have the same energy. In any given energy level, s-orbitals have the lowest energy and the energy of the other orbitals increases in the order $p < d < f$ etc. Thus each energy level must be divided into a number of different sub-levels, each of which has a slightly different energy.

The number and type of orbitals in each energy level can thus be summarised as follows:

Energy level	Number and type of orbital				
	1 st sub-level	2 nd sub-level	3 rd sub-level	4 th sub-level	5 th sub-level
1	1 x 1s				
2	1 x 2s	3 x 2p			
3	1 x 3s	3 x 3p	5 x 3d		
4	1 x 4s	3 x 4p	5 x 4d	7 x 4f	
5	1 x 5s	3 x 5p	5 x 5d	7 x 5f	9 x 5g

iii) Shells

Since the different sub-levels have different energies, and the energies of the different levels get closer together with increasing energy level number, the high energy sub-levels of some energy levels soon overlap with the low energy sub-levels of higher energy levels, resulting in a more complex energy level diagram:



Starting with the lowest energy, the orbitals can thus be arranged as follows:

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f
 5d 6p 7s 5f 6d

Many of these sub-levels have similar energy, and can be grouped together. A collection of sub-levels of similar energy is called a **shell**.

1s | 2s 2p | 3s 3p | 4s 3d 4p | 5s 4d 5p | 6s 4f 5d 6p

The arrangement of shells and the maximum number of electrons in each can be summarised as follows:

Shell number	Orbitals in shell
1	1 x 1s
2	1 x 2s, 3 x 2p
3	1 x 3s, 3 x 3p
4	1 x 4s, 5 x 3d, 3 x 4p
5	1 x 5s, 5 x 4d, 3 x 5p
6	1 x 6s, 7 x 4f, 5 x 5d, 3 x 6p

iv) Electrons

Electrons repel each other. In a small space such as an orbital, it is impossible to put more than two electrons.

Since electrons are charged particles, and moving charges create a magnetic field, it is possible to create a small magnetic attraction between two electrons if they are spinning in opposite directions in the same orbital. This is the reason two electrons, and not one, are permitted in the same orbital.

It is thus possible to calculate the maximum possible number of electrons in each sub-level, and thus in each energy level:

Shell	Number of electrons in each sub-level	Max. no of electrons
1	2 x 1s	2
2	2 x 2s, 6 x 2p	8
3	2 x 3s, 6 x 3p	8
4	2 x 4s, 10 x 3d, 6 x 4p	18
5	2 x 5s, 10 x 4d, 6 x 5p	18
6	2 x 6s, 14 x 4f, 10 x 5d, 6 x 6p	32

v) Electron arrangement in orbitals

There are three rules which determine the way in which electrons fill the orbitals

1. Aufbau/building principle: electrons always fill the lowest energy orbitals first.
2. Hund's rule: electrons never pair up in the same orbital until all orbitals of the same energy are singly occupied, and all unpaired electrons have parallel spin.
3. Pauli exclusion principle: only two electrons may occupy the same orbital, and they must do so with opposite spin.

The arrangement of electrons in an atom is known as its **electronic configuration**. It can be represented in two ways:

The **arrow and box method** represents each orbital as a box and each electron as an arrow. The direction of spin is shown by the orientation of the arrow.

The electronic configuration of the first 18 elements using the arrow in box method is as follows:

	1s	2s	2p	3s	3p
H	<div>↑</div>				
He	<div>↑↓</div>				
Li	<div>↑↓</div>	<div>↑</div>			
Be	<div>↑↓</div>	<div>↑↓</div>			
B	<div>↑↓</div>	<div>↑↓</div>	<div>↑</div> <div></div> <div></div>		
C	<div>↑↓</div>	<div>↑↓</div>	<div>↑</div> <div>↑</div> <div></div>		
N	<div>↑↓</div>	<div>↑↓</div>	<div>↑</div> <div>↑</div> <div>↑</div>		
O	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑</div> <div>↑</div>		
F	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑</div>		
Ne	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>		
Na	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	<div>↑</div>	
Mg	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	<div>↑↓</div>	
Al	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	<div>↑↓</div>	<div>↑</div> <div></div> <div></div>
Si	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	<div>↑↓</div>	<div>↑</div> <div>↑</div> <div></div>
P	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	<div>↑↓</div>	<div>↑</div> <div>↑</div> <div>↑</div>
S	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑</div> <div>↑</div>
Cl	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑</div>
Ar	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>

The **orbital method** indicates the number of electrons in each orbital with a superscript written immediately after the orbital.

The electronic configurations of the first eighteen elements can be shown with the orbital method as follows:

H:	$1s^1$
He:	$1s^2$
Li:	$1s^2 2s^1$
Be:	$1s^2 2s^2$
B:	$1s^2 2s^2 2p^1$
C:	$1s^2 2s^2 2p^2$ or $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$
N:	$1s^2 2s^2 2p^3$ or $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
O:	$1s^2 2s^2 2p^4$ or $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
F:	$1s^2 2s^2 2p^5$
Ne:	$1s^2 2s^2 2p^6$
Na:	$1s^2 2s^2 2p^6 3s^1$
Mg:	$1s^2 2s^2 2p^6 3s^2$
Al:	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si:	$1s^2 2s^2 2p^6 3s^2 3p^2$ or $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$
P:	$1s^2 2s^2 2p^6 3s^2 3p^3$ or $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
S:	$1s^2 2s^2 2p^6 3s^2 3p^4$ or $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
Cl:	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ar:	$1s^2 2s^2 2p^6 3s^2 3p^6$

A shorthand form is often used for both the above methods. Full shells are not written in full but represented by the symbol of the element to which they correspond, written in square brackets.

Eg. $1s^2 2s^2 2p^6$ is represented as [Ne] and $1s^2 2s^2 2p^6 3s^2 3p^6$ is represented as [Ar].

The shorthand electronic configuration of the elements with atomic numbers 18 to 36 can be written as follows:

	4s	3d	4p
K	[Ar] ↑		
Ca	[Ar] ↑↓		
Sc	[Ar] ↑↓	↑ 	
Ti	[Ar] ↑↓	↑ ↑ 	
V	[Ar] ↑↓	↑ ↑ ↑ 	
Cr	[Ar] ↑	↑ ↑ ↑ ↑ ↑	
Mn	[Ar] ↑↓	↑ ↑ ↑ ↑ ↑	
Fe	[Ar] ↑↓	↑↓ ↑ ↑ ↑ ↑	
Co	[Ar] ↑↓	↑↓ ↑↓ ↑ ↑ ↑	
Ni	[Ar] ↑↓	↑↓ ↑↓ ↑↓ ↑ ↑	
Cu	[Ar] ↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	
Zn	[Ar] ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	
Ga	[Ar] ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑
Ge	[Ar] ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑ ↑
As	[Ar] ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑ ↑ ↑
Se	[Ar] ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑ ↑
Br	[Ar] ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑
Kr	[Ar] ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓

Note the unusual structures of chromium and copper.

The difference in energy between the 3d and 4s electrons is very small, and in chromium the energy required to promote an electron from 4s to 3d is recovered in the reduced repulsion which results from the fact that they are no longer paired. Thus the $4s^1 3d^5$ structure in Cr is preferred.

In copper, the 3d orbitals are actually lower in energy than the 4s orbital, so the $4s^1 3d^{10}$ structure in Cu is preferred.

v) Electron arrangement in ions

The electronic configuration of ions can be deduced by simply adding or removing the appropriate number of electrons. The order in which electrons are to be removed can be deduced from the following rules:

- remove outer shell electrons first
- remove p-electrons first, then s-electrons and then d-electrons
- remove paired electrons before unpaired electrons in the same sub-level

vi) Effect of electronic configuration on chemical properties

The chemical properties of an atom depend on the strength of the attraction between the outer electrons and the nucleus. These in turn depend on the number of protons and on the electronic configuration, and so it follows that these two factors are instrumental in determining the chemical properties of an atom.

This is in contrast with the neutron number however, which has no effect on the chemical properties of an atom. Neutrons have no charge and hence exert no attractive force on the nucleus.

Isotopes, therefore, tend to have very similar chemical properties since they have the same atomic number and the same electronic configuration. They differ only in number of neutrons, which do not directly influence the chemical properties of an element.

IONISATION ENERGIES

i) First ionisation energy

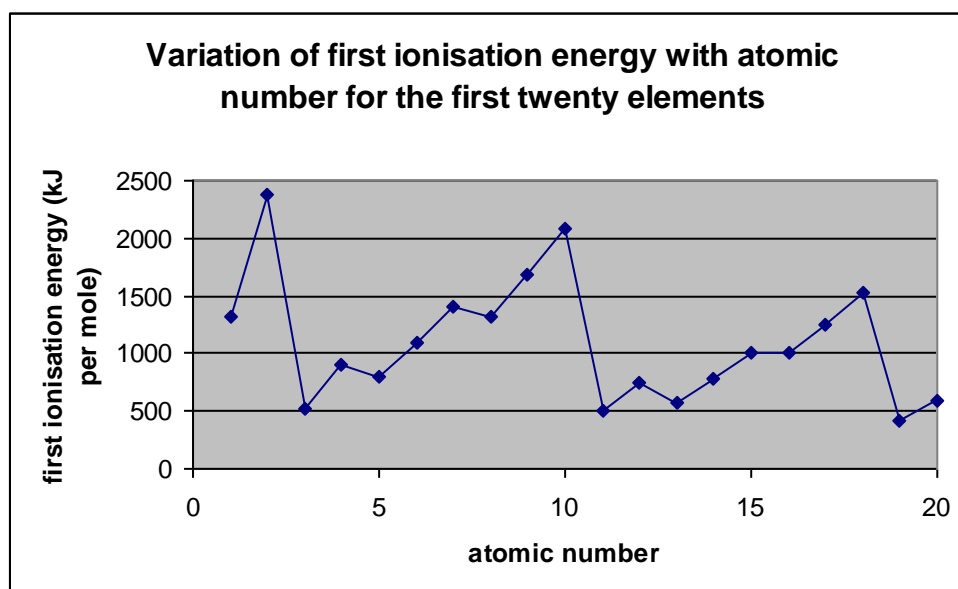
The first ionisation energy of an element is the energy required to remove one electron from each of a mole of free gaseous atoms of that element.

It can also be described as the energy change per mole for the process:



The amount of energy required to remove an electron from an atom depends on the number of protons in the nucleus of the atom and on the electronic configuration of that atom.

The first ionisation energies of the first 20 elements in the periodic table is shown below:



There are various trends in this graph which can be explained by reference to the proton number and electronic configuration of the various elements. A number of factors must be considered:

- Energy is required to remove electrons from atoms in order to overcome their attraction to the nucleus. The greater the number of protons, the greater the attraction of the electrons to the nucleus and the harder it is to remove the electrons. The number of protons in the nucleus is known as the **nuclear charge**.
- The effect of this nuclear charge, however, is cancelled out to some extent by the other electrons in the atom. Each inner shell and inner sub-shell electron effectively cancels out one unit of charge from the nucleus. This is known as **shielding**.
- The outermost electrons in the atom thus only feel the residual positive charge after all inner shell and inner sub-shell electrons have cancelled out much of the nuclear charge. This residual positive charge is known as the **effective nuclear charge**.

- Electrons repel each other, particularly when they are in the same orbital. The degree of **repulsion** between the outermost electrons affects the ease with which electrons can be moved.

When considering trends in ionisation energies, it is thus necessary to consider 4 factors:

- nuclear charge
- shielding
- effective nuclear charge
- electron repulsion

The trends in first ionisation energies amongst elements in the periodic table can be explained on the basis of variations in one of the four above factors.

Trend across period 1

Compare the first ionisation energies of H and He. Neither have inner shells, so there is no shielding. He has two protons in the nucleus; H only has one. Therefore the helium electrons are more strongly attracted to the nucleus and hence more difficult to remove.

The first ionisation energy of He is thus higher than that of H.

Since H and He are the only atoms whose outer electrons are not shielded from the nucleus, it follows that He has the highest first ionisation energy of all the elements. All elements (except H) have outer electrons which are shielded to some extent from the nucleus and thus are easier to remove.

So Helium has the highest first ionisation energy of all the elements.

Trends across period 2

Compare now the first ionisation energies of He ($1s^2$) and Li ($1s^2 2s^1$). Li has an extra proton in the nucleus (3) but two inner-shell electrons. These inner-shell electrons cancel out the charge of two of the protons, reducing the effective nuclear charge on the 2s electron to +1. This is lower than the effective nuclear charge on the He 1s electrons, +2, and so the electrons are less strongly held and easier to remove.

The first ionisation energy of Li is thus lower than that of He.

Compare the first ionisation energies of Li ($1s^2 2s^1$) and Be ($1s^2 2s^2$). Be has one more proton in the nucleus than Li, and no extra inner-shell electrons, so the effective nuclear charge on Be is higher and the Be electrons are more strongly attracted to the nucleus.

The first ionisation energy of Be is thus higher than that of Li.

In general, the first ionisation energy increases across a period because the nuclear charge increases but the shielding remains the same.

Compare the first ionisation energies of Be ($1s^2 2s^2$) and B ($1s^2 2s^2 2p^1$). B has one more proton in the nucleus than Be but there are also 2 extra inner sub-shell electrons. These cancel out the charge of two more of the protons, leaving an effective nuclear charge of only +1. This is less than Be (+2) so the electrons are less strongly attracted to the nucleus and thus less difficult to remove.

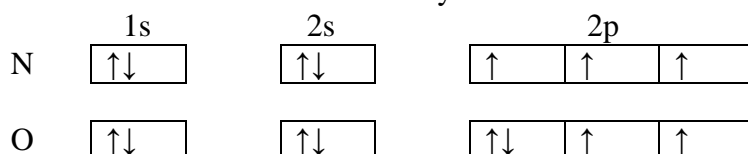
The first ionisation energy of B is thus lower than that of Be.

Ionisation energies decrease from group II to group III because in group III the electrons are removed from a p-orbital, so it is shielded by the s-electrons in the outer shell. Thus the effective nuclear charge decreases.

From B ($1s^2 2s^2 2p^1$) to N ($1s^2 2s^2 2p^3$) the proton number increases, but the number of electrons shielding the nuclear charge remains the same at 4. Thus the effective nuclear charge increases from B to N and the electrons become progressively harder to remove.

The first ionisation energy thus increases from B to N.

So far the concepts of effective nuclear charge and shielding have been used to explain the trend in first ionisation energies for the first 7 elements. They cannot, however, explain the fall between N and O. The electronic configurations of N and O must be considered more carefully:



Note that in N the electron is removed from an unpaired orbital, but in O it is removed from a paired orbital. In a paired orbital, the two electrons share a confined space and so repel each other. They are therefore less stable and easier to remove. This repulsion effect outweighs the higher effective nuclear charge in O.

The first ionisation energy of O is thus lower than that of N.

First ionisation energies decrease from group V to group VI, since the electron removed from the group VI atom is paired, so there is more repulsion between the electrons and the electron is easier to remove.

The first ionisation energies increase as expected from O to Ne, due to the increase in effective nuclear charge.

The trend in first ionisation energies across period 2 can thus be summarised as follows:

1. There is a general increase across the period as the nuclear charge increases and the shielding remains the same.
2. There is a drop from Be to B because in B a 2p electron is being removed and the extra shielding from the 2s subshell actually causes a fall in the effective nuclear charge.
3. There is also a drop from N to O because the electron in O is being removed from a paired orbital. The repulsion of the electrons in this orbital makes them less stable and easier to remove.

The same trend can also be found in Period 3 (Na - Ar). There is a general increase, but a drop between Mg and Al and also between P and S.

Trend down a group

The above graph also shows a clear decrease in first ionisation energy on descending a group. This can be explained in the following way:

On descending a group, the effective nuclear charge stays the same but the number of inner shells increases. The repulsion between these inner shells and the outer electrons makes them less stable, pushes them further from the nucleus and makes them easier to remove.

ii) Successive ionisation energies

The second ionisation energy of an atom is the energy required to remove one electron from each of a mole of free gaseous unipositive ions.

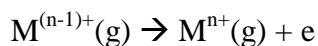


Other ionisation energies can be defined in the same way:

The third ionisation energy of an atom is the energy required to remove one electron from each of a mole of bipositive ions.



The nth ionisation energy can be defined as the energy required for the process



It always becomes progressively more difficult to remove successive electrons from an atom; the second ionisation energy is always greater than the first, the third always greater than the second and so on. There are two satisfactory explanations for this:

As more electrons are removed from an atom, the number of electrons remaining in the atom decreases. The repulsion between these electrons therefore decreases, while the number of protons remains the same. The remaining electrons are thus more stable and increasingly difficult to remove.

The difference in successive ionisation energies, however, varies widely and depends on the electronic configuration of the atom in question. The difference in successive ionisation energies of an atom can be predicted qualitatively by consideration of the effective nuclear charge on the electron to be removed and the shielding of that electron by the inner shell and inner sub-shell electrons.

Consider the successive ionisation energies of aluminium, $1s^2 2s^2 2p^6 3s^2 3p^1$:

The 1st ionisation energy is fairly low because the 3p electron is shielded by all the other electrons, and the effective nuclear charge is only +1.

The 2nd and 3rd ionisation energies are significantly higher than the 1st because 3s electrons are being removed and the effective nuclear charge on these electrons is +3.

1st: 578 kJmol^{-1} , 2nd: 1817 kJmol^{-1} , 3rd: 2745 kJmol^{-1}

There is a huge jump to the 4th ionisation energy, since a 2p electron is now being removed. The shielding has fallen and the effective nuclear charge has risen to +9. The 5th and 6th ionisation energies are also high.

4th: 11578 kJmol^{-1} , 5th: 14831 kJmol^{-1} , 6th: 18378 kJmol^{-1}

There is another significant jump to the 7th ionisation energy, since an unpaired 2p electron is now being removed.

7th: 23296 kJmol^{-1} , 8th: 27460 kJmol^{-1} , 9th: 31862 kJmol^{-1}

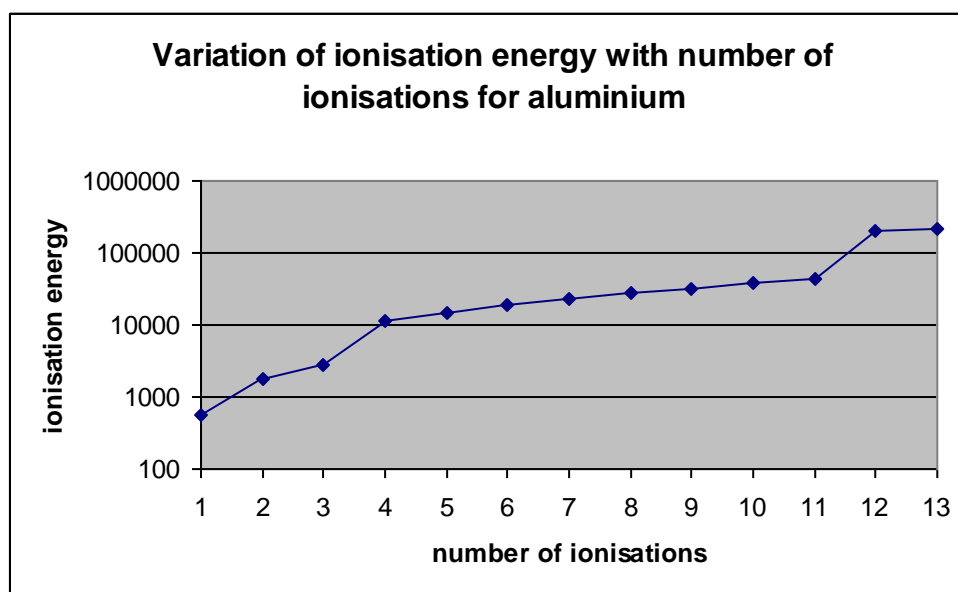
The next significant jump is between the 9th and 10th ionisation energies, since the 10th requires the removal of a 2s electron.

10th: 38458 kJmol^{-1} , 11th: 42655 kJmol^{-1}

There is a huge jump to the 12th ionisation energy, since a 1s electron is now being removed.

12th: $201276 \text{ kJmol}^{-1}$, 13th: $222313 \text{ kJmol}^{-1}$.

These ionisation energies could be plotted on a graph as follows:



Note that the largest jumps by far occur between the 3rd and 4th ionisation energies, and between the 11th and 12th ionisation energies. In practice only large jumps such as this are visible on such a graph.

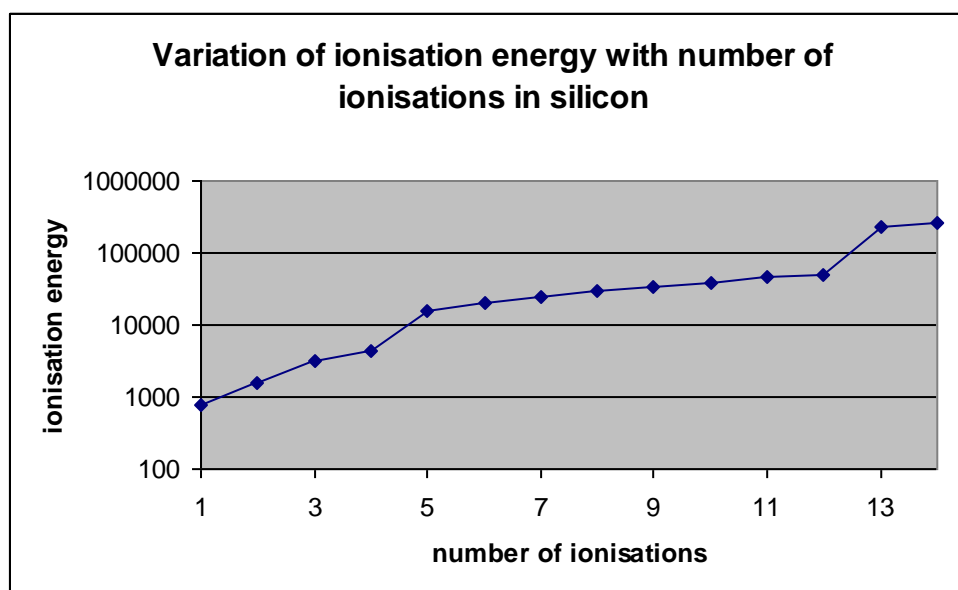
The relative values of successive ionisation energies are therefore a direct indicator of the electronic configuration of the atom in question.

The trends can be summarised as follows:

1. The successive ionisation energies of an atom always increase. The more electrons that are removed, the fewer the number electrons that remain. There is therefore less repulsion between the electrons in the resulting ion. The electrons are therefore more stable and harder to remove.
2. By far the largest jumps between successive ionisation energies come when the electron is removed from an inner shell. This causes a large drop in shielding, a large increase in effective nuclear charge and a large increase in ionisation energy

By applying the above principles in reverse, it is also possible to predict the electronic structure of a species by analysis of the successive ionisation energy data:

Eg Si:



Large jumps occur between 4th and 5th and between 12th and 13th.

Therefore there are three shells: The first contains 2 electrons, the second 8 and the third 4.