

# ATOMIC STRUCTURE AND PERIODICITY

## Basic structure of the atom.

An atom contains protons, neutrons and electrons. The protons and neutrons are found in the nucleus of the atom while the electrons exist in the energy levels around the nucleus.

The characteristics of these basic particles are shown in the table

PARTICLE	RELATIVE MASS	RELATIVE CHARGE
Proton	1	+1
Electron	1/1840	-1
Neutron	1	None

The nucleus carries virtually all the mass of the atom and is positively charged.

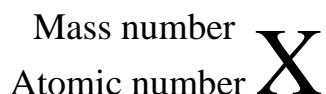
Number of protons in the nucleus = the atomic number of that atom.

The total number of particles in the nucleus is given by the mass number.

$$\text{Mass number} = \text{Protons} + \text{Neutrons}$$

$$\text{Number of neutrons in a nucleus} = \text{Mass number} - \text{Atomic number}$$

The atomic and mass numbers can be shown with the symbol of the atom:



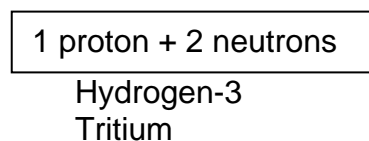
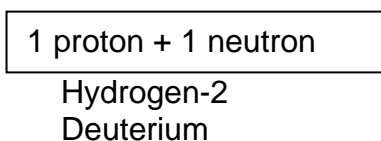
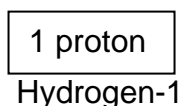
In a neutral atom, there will be no overall charge, so the no. of electrons = no. of protons.

The chemical nature of the atom is determined by the number of electrons it has and in particular the electron arrangement.

So the atomic number tells us what type of atom we have.

The number of neutrons in a particular type of atom often varies.

One example of this is in hydrogen



The atomic number for all these is 1 because they are all hydrogen atoms.

The mass number is different.

Atoms of the same type with different numbers of neutrons are called **isotopes**.

Carbon also has isotopes. C-12 is an important isotope in chemical definitions;

**Relative Atomic Mass** is the weighted mean of one mole of a normal sample of the element expressed on a scale on which one mole of the atoms of the C-12 isotope has a mass of exactly 12 units.

$$\text{R.A.M. } A_r = \frac{\text{mean* mass of 1 atom of the element}}{\text{one-twelfth of the mass of 1 atom of } ^{12}\text{C}}$$

Relative Molecular Mass and Relative Isotopic Mass are measured on the same scale.

**Relative Isotopic Mass** is the mass of one mole of an isotope of the element expressed on a scale on which one mole of the atoms of the C-12 isotope has a mass of exactly 12 units.

$$\text{R.I.M.} = \frac{\text{mass of 1 atom of the isotope}}{\text{one-twelfth of the mass of 1 atom of } ^{12}\text{C}}$$

**Relative Molecular Mass** is the weighted mean of one mole of a normal sample of the substance expressed on a scale on which one mole of the atoms of the C-12 isotope has a mass of exactly 12 units.

$$\text{R.M.M. } M_r = \frac{\text{mean mass of 1 **molecule** of the substance}}{\text{one-twelfth of the mass of 1 **atom** of } ^{12}\text{C}}$$

The term *relative molecular mass* should only be applied to substances which have covalently-bonded molecules e.g.  $\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{C}_8\text{H}_{18}$ . For ionic materials like  $\text{NaCl}$  and  $\text{CuSO}_4$  the term **relative formula mass** is preferred, though it is calculated in the same way, by adding up the R.A.M.s of all the atoms in the formula. *R.F.M.* can be used for molecular substances, too.

The **relative formula mass** of a substance is:

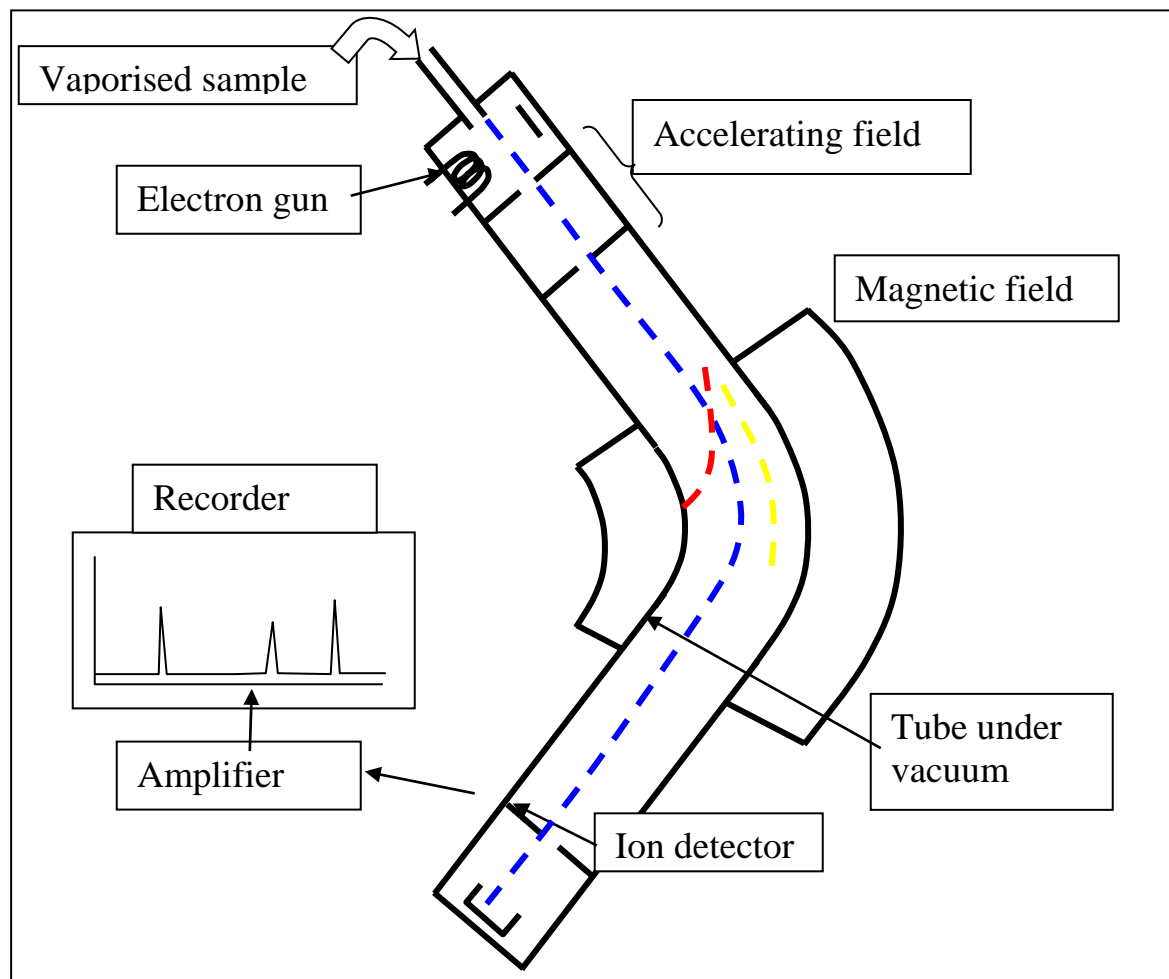
$$\text{R.F.M. } M_r = \frac{\text{the mean mass of one formula unit of the substance}}{\text{one twelfth of the mass of one atom of } ^{12}\text{C}}.$$

## The Mass Spectrometer

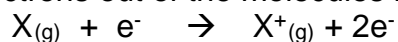
The mass spectrometer is a method of determining relative atomic and molecular masses.

The main processes involved are;

1. the sample is vaporised,
2. the sample is ionised,
3. the ions are accelerated by an electric field,
4. the accelerated ions pass through a magnetic field and are deflected,
5. the ions are detected and recorded.



The vaporised sample is fed into the ionisation chamber. Here it is bombarded by a stream of electrons which knock electrons out of the molecules in the sample.



These charged ions are then accelerated through an electric field and pass into a magnetic field. The magnetic field deflects the ions according to their mass and charge.

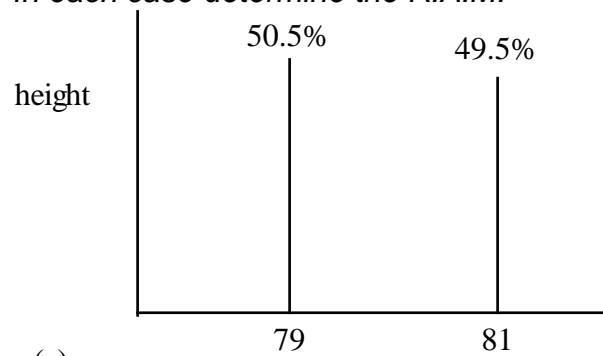
For a particular setting of electric and magnetic fields only particles of a certain mass reach the detector. Lower masses are deflected too much and higher masses too little.

The magnetic field strength is gradually altered changing the mass of particles which will reach the detector. The detector is connected to an amplifier and recorder so the mass of particles can be determined.

The mass spectrum of an element shows the relative isotopic mass and relative abundance of each isotope of the element being tested. In a mass spectrum the height of each peak = the relative abundance.

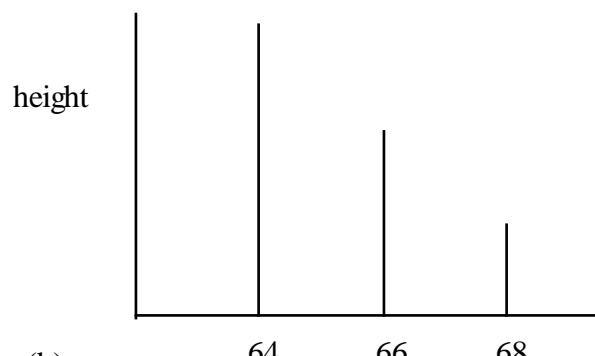
The **Relative Atomic Mass** of an element can be found by finding the sum of the products of the relative abundance of each isotope and its relative isotopic mass and then dividing by the total relative abundance.

*e.g. The two sketches show the mass spectra obtained from atoms of two different elements. In each case determine the R.A.M.*



(a)

mass/charge ratio



(b)

mass/charge ratio

(a) We assume the two peaks are due to atoms of two isotopes.

$$\text{Mean r.a.m.} = 79 \times \left(\frac{50.5}{100}\right) + 81 \times \left(\frac{49.5}{100}\right) = 79.99 = \underline{\underline{80.0}} \text{ (to 3 s.f.)}$$

(b) No scale is given, so we must use a ruler to measure the heights. Let us assume these are (from left to right) 3.8 cm, 2.4 cm, and 1.2 cm. Total = 7.4 cm

$$\text{Mean r.a.m.} = 64 \times \left(\frac{3.8}{7.4}\right) + 66 \times \left(\frac{2.4}{7.4}\right) + 68 \times \left(\frac{1.2}{7.4}\right) = \underline{\underline{65.3}} \text{ (to 3 s.f.)}$$

A very accurate version of the mass spectrometer can be used to **determine relative isotopic masses** to a high degree of accuracy: e.g.  $^{16}\text{O} = 15.99415$  and  $^{17}\text{O} = 16.99913$ .

## Mass Spectra of Molecules

The full mass spectrum of chlorine is more complicated than the examples shown on page 4. This is because chlorine is made up of diatomic molecules (molecules containing two atoms). Peaks occur at mass numbers 35, 37, 70, 72 and 74. The identity of these is as follows.

Peak at	Species responsible
35	$^{35}\text{Cl}^+$
37	$^{37}\text{Cl}^+$
70	$^{35}\text{Cl}_2^+$
72	$^{35}\text{Cl}^{37}\text{Cl}^+$
74	$^{37}\text{Cl}_2^+$

Peaks still occur at mass numbers 35 and 37 because molecules break up in the mass spectrometer.

Example

*Bromine has two isotopes of mass 79 and mass 81.*

*Predict the peaks you would expect to see in a mass spectrograph of bromine,  $\text{Br}_2$ .*

Peak	79	81	158	160	162
Species	$^{79}\text{Br}^+$	$^{81}\text{Br}^+$	$^{79}\text{Br}_2^+$	$^{79}\text{Br}^{81}\text{Br}^+$	$^{81}\text{Br}_2^+$

When molecules are passed through the mass spectrometer, the peak with the highest mass is caused by the ion formed from the whole molecule – this is called the **molecular ion** or **parent ion**.

The **RFM** of a compound can be found from the mass value of the molecular ion.

Molecules of a particular compound will always break up in the same way and in the same proportion when passed through a mass spectrometer. This means that a given compound will always produce the same pattern in a mass spectrum. This can be used to identify the presence of compounds in analysis.

This has been used as follows.

- In sport to detect the use of anabolic steroids
- By pharmaceutical industries to identify synthesized compounds as possible potential drugs

### **Independent research:**

Research how the mass spectrometer used in space research.

## Electronic Structure of the atom

The electronic structure of an atom that determines its chemical properties.

Electrons can be regarded as having certain energy levels. The lower levels fill before the higher levels are occupied.

The simple theory you learnt at IGCSE, pictures the atom as having shells, the shell of lowest energy being closest to the nucleus. The next shell can hold up to eight electrons. The third shell also holds up to eight electrons.

Bonding is explained in terms of atoms trying to obtain a stable electrons arrangement by;

- (i) transfer from electron rich atoms(metals) to electron deficient atoms(non-metals);
- (ii) sharing electrons between electron deficient atoms.

This model on its own is not sophisticated enough for understanding A level work fully and does not explain how the atoms arrange electrons above a number of twenty.

The simple bonding theory which comes from the model cannot explain the structure of molecules such as  $\text{PCl}_5$  or  $\text{SF}_6$ .

### Electronic Configuration

- The **shells** used in the simple view of the atom are divided into **subshells**.

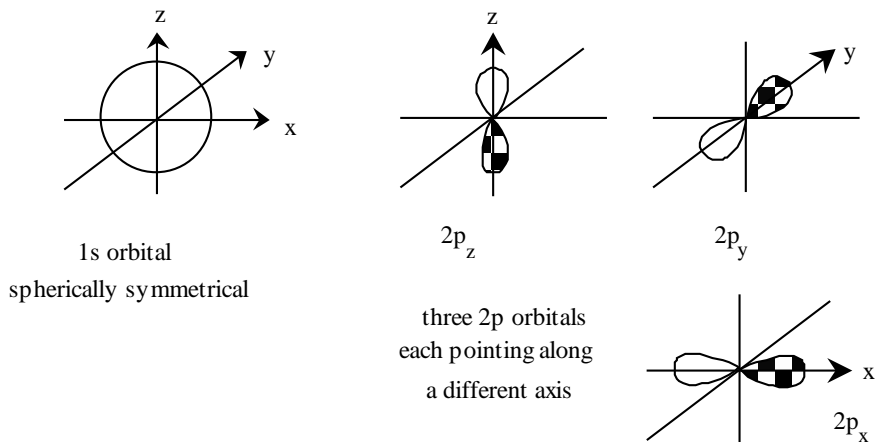
Shell	Subshells
1	s
2	s p
3	s p d
4	s p d f

- The higher the energy of the shell, the more subshells it contains.

Electrons inside the atom should be thought of as waves rather than particles.

The area occupied by an electron wave is called the **orbital**.

An orbital has no edge: the electron density just tails off more and more. However, we can calculate the surface which would contain a given percentage (say, 95%) of the electron density, and use this to gain an idea of the shape of the orbital (below).



It is important to remember that the electron density is not uniform within this shape. The s-orbital is always spherically symmetrical, while the three 2p orbitals each point along one particular axis, at right angles to the other two. Remember that when one electron occupies a 2p orbital it occupies both halves; when two electrons occupy it, they **both** occupy both halves.

Each electron in an atom is different from all the other electrons.

### The s subshell

s orbitals can contain a maximum of two electrons.

These have the same energy value, but are said to have opposite spin values.

### The p subshell

There are three p orbitals, each of which can contain a maximum of two electrons.

### The d subshell

There are five d orbitals, each of which can contain a maximum of two electrons.

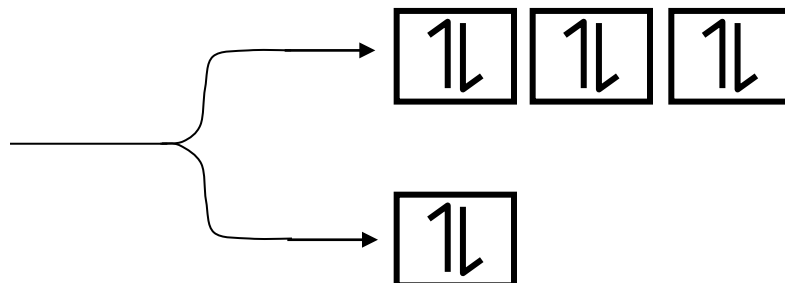
## Electron shells

- The first shell holds two electrons in an s subshell. **1s**
- The electrons have the same energy value, but are said to have opposite spin values.



- The second shell holds eight electrons.
- These are split into two energy levels;
  - the lower level has two electrons in the 's' subshell **2s**
  - the higher level has six electrons in the 'p' subshell. **2p**
- The electrons in the 'p' subshell are found in three different regions of the atom which are called 'x', 'y' and 'z'.

**Second shell**  
8 electrons



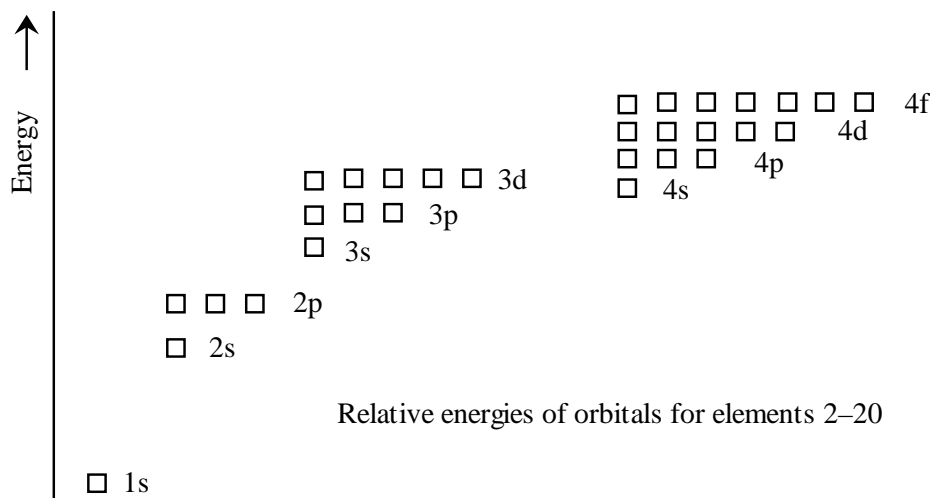
- The third shell holds eighteen electrons.
- These are split into three energy levels;
  - the lower level has two electrons in the 's' subshell **3s**
  - the next highest level has six electrons in the 'p' subshell. **3p**
  - the highest level has ten electrons in the 'd' subshell. **3d**

Note - In the higher shells there is overlap between the energy levels of the subshells. E.g. The 4s subshell is filled before the 3d subshell.

## Electronic configurations

Electronic Configuration can be predicted. If the following rules are followed:

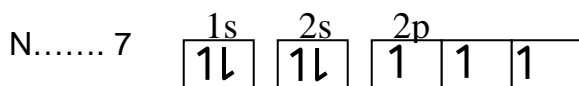
- Electrons go into lower energy levels before higher ones.
- Electrons go into lower sub-shells before higher ones.
- Electrons occupy orbitals with 1 electron rather than 2 if possible.
- Electrons can only occupy the same orbital if they have opposite spins.
- The orbital order 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p



e.g.

Atom	No of electrons	Configuration
Si	14	$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
K	19	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
Mn	25	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$
Ge	32	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^2$
Kr	36	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6$

Another way of representing electronic configuration giving greater detail is as “electrons in boxes”



When writing the electron configurations of ions, it is important to take into account the number of electrons lost or gained.  $\text{Ca}^{2+} 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

An exactly half full or full d subshell is particularly stable. This gives chromium and copper what is at first sight an unexpected electronic configuration.

The extra stability of the exactly half full or full d subshell means that an electron from the 4s goes to the 3d to give a half full subshell for chromium and a full subshell for copper.

Element	Initially expected but wrong	Correct electron configuration
Chromium, Cr	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^4$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$
Copper, Cu	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^9$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$



## Configurations and the Periodic Table

### s, p and d-block elements

All s-block elements have their highest energy electrons in s-orbitals.

All p-block elements have their highest energy electrons in p-orbitals.

All d-block elements have their highest energy electrons in d-orbitals.

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

## Evidence for Electron shells and subshells

### Ionisation Energies

An electron is attracted to the positive charge in the nucleus of the atom. It is possible to remove an electron from an atom. The process of removing an electron from an atom to form a positive ion is called **ionisation**. The energy required to remove one electron from an atom is the first ionization energy.

The size of the ionisation energy is an indication of the strength of attraction between the outer electrons and the nucleus.

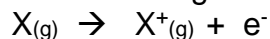
Energy changes in chemistry are generally measured as heat energy or enthalpy.

The definition of the first ionisation energy is:

The energy required to remove one electron from each atom in one mole of mole of gaseous atoms producing one mole of gaseous ions with one positive charge.

or

The enthalpy change for the following reaction:



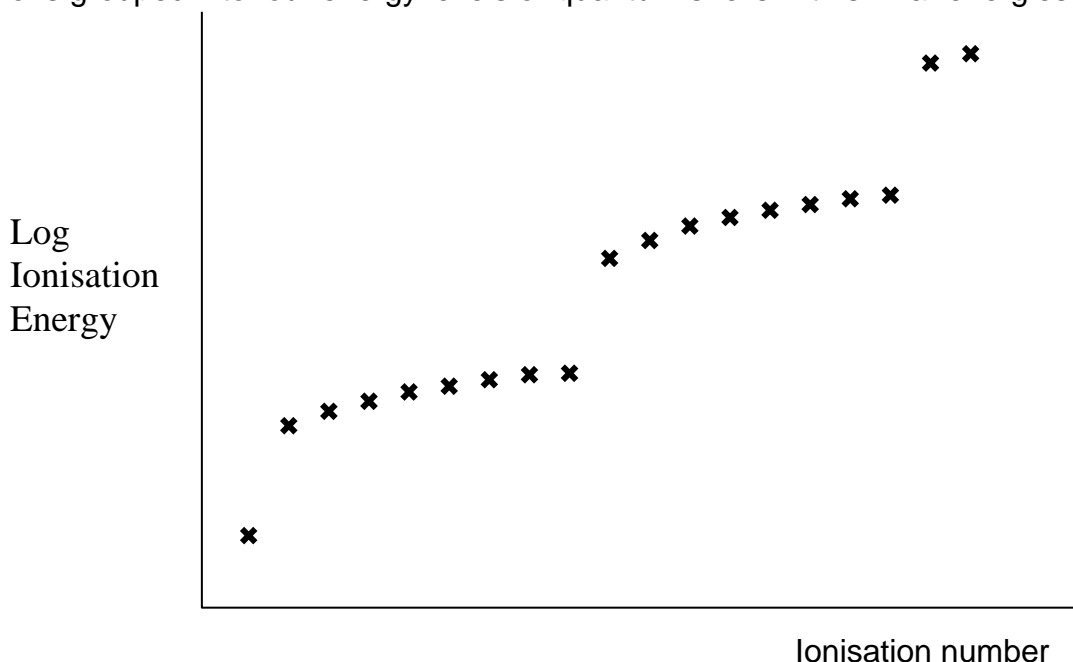
Examples

The first ionization energy of chlorine  $Cl_{(g)} \rightarrow Cl^{+}_{(g)} + e^{-}$

The second ionization energy of sodium  $Na^{+}_{(g)} \rightarrow Na^{2+}_{(g)} + e^{-}$

## Successive ionisation energies

The graph of successive ionisation energies against number for potassium (At No 19) shows electrons grouped into four energy levels or quantum shells with similar energies.



To remove the second electron it is necessary to break into a complete shell, so a lot more energy needed. Similarly with the tenth electron there is an increase in the energy required for its removal as this has to come from a complete shell.

From successive ionization energies it is possible to tell which group of the Periodic table an element is in. The table below shows successive ionisation energies for an element. Energy values are given in  $\text{kJ mol}^{-1}$ .

1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>	6 <sup>th</sup>
577	1820	2740	11600	14800	18400

Notice that there is a large increase after the third ionisation energy – so the fourth electron is much more difficult to remove.

This means that there are three electrons in the outer shell, so the element is in group 3.

### Example

Here are successive I.E. values in  $\text{kJ mol}^{-1}$  for two elements:

element X 1010 1900 2900 5000 6300 **21300** 25400 29800

element Y 590 1150 **4940** 6480 8120 10700 12300 14600 18200 20400 57100.

In what group of the periodic table are X and Y?

For X there is a sharp rise between the 5<sup>th</sup> and the 6<sup>th</sup> values, so X must have five electrons in its outer shell. X is a Group 5 element.

Y shows a jump between the second and third values, so it is in Group 2.

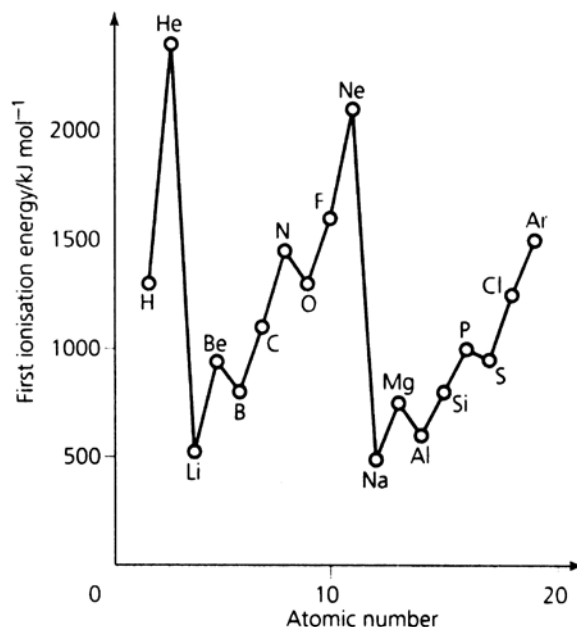
## First ionisation energy

The first ionisation energy is energy required to remove one electron from an atom.

The factors which affect ionisation energies are:

- the **nuclear charge**,
- the **distance away from the nucleus** of the electron,
- the **shielding of the nucleus by other electrons**.  
(Being spherical s subshells are much better at shielding than p subshells).

If first ionisation energy is plotted for a number of elements the results provide evidence for the existence of subshells.



- Lithium has the lowest first ionisation energy of the second period.
- It is more difficult to remove an electron from Beryllium since the charge on the nucleus has increased Beryllium having a 4+ nuclear charge, whereas lithium is only 3+.
- Although Boron also has a higher nuclear charge, it has lower first ionisation energy because the electron is now in the 'p' subshell, and the inner 's' subshell shields it from the nucleus.
- The ionisation energy increases again to Carbon and Nitrogen as the nuclear charge increases.
- Oxygen has a higher nuclear charge, but the first ionisation energy is lower because the extra electron now has to pair up in an orbital (in Nitrogen each p orbital has an electron in it) so the extra electron is repelled and it is easier to remove it.
- The values increase after oxygen as the nuclear charge increases.
- The pattern repeats itself for the next period of the periodic table – First ionization energy is a **periodic property**.

## Periodicity

Periodicity is the regular occurrence of a trend across a period (or down a group) in the periodic table.

Many periodic properties can be explained in terms of structure and bonding.

e.g. Explaining trends physical properties in period 3 from sodium to argon.

	Na	Mg	Al	Si	P	S	Cl	Ar
atom* radius / nm	0.157	0.140	0.126	0.117	0.110	0.104	0.099	–
ion radius / nm	0.098	0.065	0.054	no ion	0.212	0.184	0.181	–
ion charge	+1	+2	+3		–3	–2	–1	–
structure	metal	metal	metal	diamond	P <sub>4</sub> <sup>†</sup>	S <sub>8</sub>	Cl <sub>2</sub>	atomic
melting point / K	371	923	932	1683	317 <sup>†</sup>	392	172	84
boiling point / K	1163	1390	2720	2630	553 <sup>†</sup>	718	239	87
relative conductivity	1	1.23	1.96	semi	0	0	0	0
first I.E / kJ mol <sup>–1</sup>	500	740	580	790	1010	1000	1260	1520

<sup>†</sup>white P — red P, a polymer, sublimates at 863

### (a) Atomic radii:

The radius of an atom depends on whether it is bonded to another one, and on the nature of the bonding (metallic, ionic, covalent). If we compare similar types of radius, the general trend is for atoms to get smaller across a period.

This is because the nuclear charge is increasing, and the extra electrons being added go into the same outer shell.

On the whole, electrons in the same shell do not shield one another very efficiently, and the size contracts as the effective nuclear charge increases.

The alkali metal, in Group 1, is the largest atom, and the halogen, in group 7, is the smallest.

### (b) Ionic radii:

Ionic radii depend on the charge. Positive ions are always smaller than the neutral atoms, and higher charges make cations smaller still. Negative ions are much larger than neutral atoms, and larger still if the charge is higher.

From the table, it is clear that although Na atoms are larger than Cl, Na<sup>+</sup> ions are much smaller than Cl<sup>–</sup> ions.

### (c) Melting points:

These depend on the type of bonding, and the structures of the solids.

Generally, going across a period metallic bonding at first increases in strength (Na<Mg<Al) as successive atoms have more valence electrons, and then gives way to a giant covalent structure (Si – like diamond), and then to molecular solids (P<sub>4</sub>, S<sub>8</sub>, Cl<sub>2</sub>, Ar).

Melting points therefore tend to increase, reaching a maximum in the middle, and fall sharply to a minimum on the right (see table).

Values for the four molecules reflect the size of the molecule, and so the intermolecular forces (i.e. S<sub>8</sub> > P<sub>4</sub> > Cl<sub>2</sub> > Ar).

#### (d) Boiling points:

These are less dependent on crystal structure, and so give a better idea of the forces between the particles.

Again we can note the increase in metallic bonding from Na to Mg to Al; the high value for the giant molecule Si; the remainder are simple molecular structures.

For these, intermolecular forces again depend on size of molecule:  $P_4 < S_8$ ; then there is a fall to  $Cl_2$  and Ar, since they have weaker dispersion forces and lower boiling points.

#### (e) Electrical conductivity:

Along the series Na–Mg–Al the number of outer shell electrons which can be delocalised in metallic bonding increases, and the electrical conductivity increases accordingly.

By Si, however, the effective nuclear charge is too high to allow electron delocalisation, and Si is not a metal, although it is a semiconductor because an electron can be torn free relatively easily.

The remainder are non-metallic insulators: their effective nuclear charges are too great to allow electrons to escape under normal conditions.

#### (f) Ionisation energies:

The **effective nuclear charge** is the charge “seen” by an outer electron, after allowing for the effect of shielding. Thus for sodium (element 11), which has the configuration [Ne]  $3s^1$ , ten of the nuclear charges are effectively shielded by the neon shells, and the effective nuclear charge on the outer electron is close to +1.

The first ionisation energies for the first 13 elements are shown below:

The general trend **across a period** in the Periodic Table, from Li to Ne, is for the values to increase sharply.

This is because, while the nuclear charge is increasing by one each time, the additional electron is being added in the same outer shell, and generally it is not shielded completely by the others.

However, there are two “kinks”. In Group 3 boron,  $2s^2 2p^1$ , is lower than expected. This is because its 2p electron is sufficiently shielded by the  $2s^2$  pair for the effective nuclear charge to be lower than it was in Be.

In Group 6 oxygen,  $2s^2 2p^4$ , is also low. This is attributed to the fact that the fourth p electron has to be spin-paired, and so it is partly repelled by the other electron in the same orbital (also of note is that, once an electron is lost,  $O^+$  has a half-filled 2p sub-shell, and in general half-filled and completely filled sub-shells are particularly stable).

A similar pattern is followed in Period 3, with low values in Group 3 and Group 6. [Note that if *second* ionisation energies are plotted, the pattern is again similar, but this time shifted along one element e.g.  $Li^+(1s^2)$  is high, while  $Be^+(1s^2 2s^1)$  is low.]

The general trend **down a group** is for ionisation energies to fall by a small amount. Although the nuclear charge increases, this is cancelled out by the addition of another closed shell, so the effective nuclear charge on the outer electron is similar, but the electron is further away from the nucleus, since it is being removed from a higher quantum number shell.