

## Atomic Structure

To succeed in this topic you need to:

- be able to use the periodic table to find atomic and mass numbers.

After working through this Factsheet you will be able to:

- describe and understand the accepted model of an atom
- interpret simple mass spectra
- understand the importance of ionisation energies of different elements, and use them as evidence in describing atomic structure
- assign electronic configurations to atoms
- understand the impact of electronic configuration on chemical properties
- define electron affinity

**Exam Hint:** A thorough understanding of atomic structure is essential for success throughout AS Chemistry. Questions often require candidates to

- work out the electronic configuration of an atom
- deduce chemical properties from electronic configuration
- describe and explain trends in ionisation energy
- interpret mass spectra

### Fundamental particles

An atom is the smallest particle of a chemical element. Atoms themselves consist of protons, neutrons (in the nucleus) and electrons (see Fig 1). The mass of an atom is concentrated in the nucleus. The nucleus is very small and massive, so therefore has an incredibly high density.

Fig 1. Fundamental particles of an atom

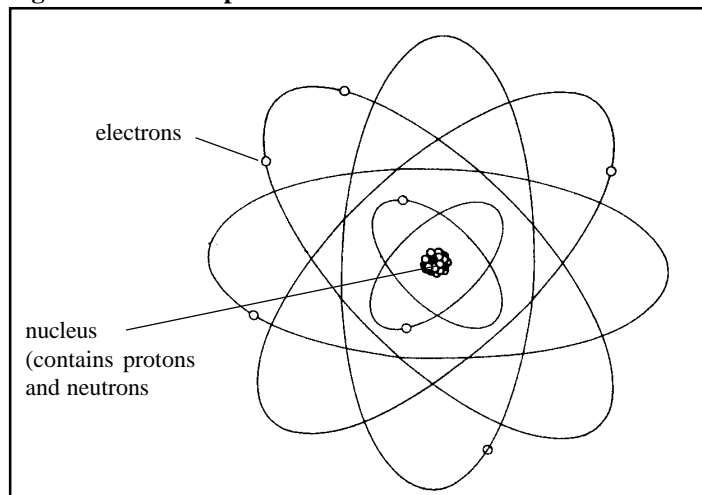


Table 1 Shows the **relative charge**, **relative mass** and position of atomic particles. (For most purposes, the mass of the electron is taken as 0).

Table 1. Atomic particles data

Particle	Relative mass	Relative charge	Position within atom
Proton	1	+1	nucleus
Neutron	1	0	nucleus
Electron	$\frac{1}{1850}$	-1	shells

The particles within a nucleus are drawn together by extremely powerful forces capable of overcoming the repulsion of the protons (+ve to +ve) However, these forces act over a short distance as they do not pull the electrons in.

The electrons are in constant motion, orbiting the nucleus.

### Atomic number, atomic mass number and isotopes



**Atomic number (Z):** the number of protons in an atom

**Mass number (A):** the number of protons + neutrons in an atom.

Remember also that the number of protons (+ve charges) will be equal to the number of electrons (-ve charges) in a **neutral** atom.

Given the information on the periodic table, it is possible to calculate the number of protons, neutrons and electrons present in an atom of any given element. Fig 2.

Fig 2.

Atomic number = 4                    ∴ number of protons = 4  
No. protons = no. electrons       ∴ number of electrons = 4  
Mass number = no. p + no. n       ∴ number of neutrons = 9 - 4 = 5

All atoms of the same element have the same atomic number - e.g atomic number of magnesium = 12, therefore **all** magnesium atoms contain 12 protons.

Mass numbers of atoms of the same element may, however, vary – due to different atoms containing different numbers of neutrons. These atoms are called **isotopes**.

**Remember** - Isotopes of one particular element are atoms which have the same atomic number and so the **same** number of **protons** (therefore are atoms of the same element) but different mass numbers, because they have **different** numbers of **neutrons**.

One example is hydrogen - there are three isotopes, all with atomic number 1, but with mass numbers 1, 2 and 3.

Elements with isotopes do pose a problem when wanting to assign a mass number on for the element. An **average** atomic mass is calculated - called the **relative atomic mass**,  $A_r$ . The calculation of this average mass needs to take account of the relative abundance of each isotope; the method for doing this is illustrated in the following example:

For example, naturally occurring chlorine consists of 2 isotopes.

75% of the atoms have a mass of 35 (Cl-35)

25% of the atoms have a mass of 37 (Cl-37)

To work out  $A_r$ , we do  $\frac{75}{100} \times 35 + \frac{25}{100} \times 37 = 35.5$

The actual definition of relative atomic mass involves carbon - 12 - this must be **learnt**.



$$\text{Relative Atomic Mass } (A_r) = \frac{\text{mass of one atom of an element}}{1/12 \text{ mass of one atom of carbon-12}}$$

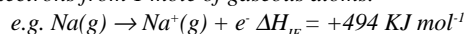
Carbon - 12 is used to because carbon is a common element and as a solid is easy to store and transport.

### Ionisation Energies

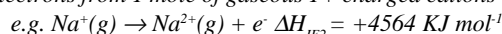
If an atom is supplied with enough energy, it will lose an electron, and additional supplies of energy may cause the loss of a second electron, then a third and so on. If a neutral atom loses an electron, it becomes a positively charged ion (cation).



**First Ionisation Energy** - the energy required to remove 1 mole of electrons from 1 mole of gaseous atoms.



**Second Ionisation Energy** - the energy required to remove 1 mole of electrons from 1 mole of gaseous 1+ charged cations

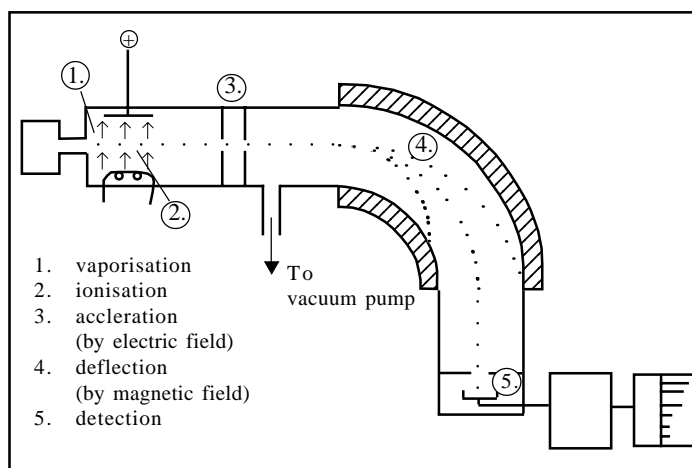


Examining successive ionisation energies for an element can give us further insight into atomic structure - specifically the arrangement of electrons (Fig 6 overleaf).

### The mass spectrometer

The mass spectrometer is a machine which provides chemists with a way to measure and compare masses of atoms and molecules (Fig 3.)

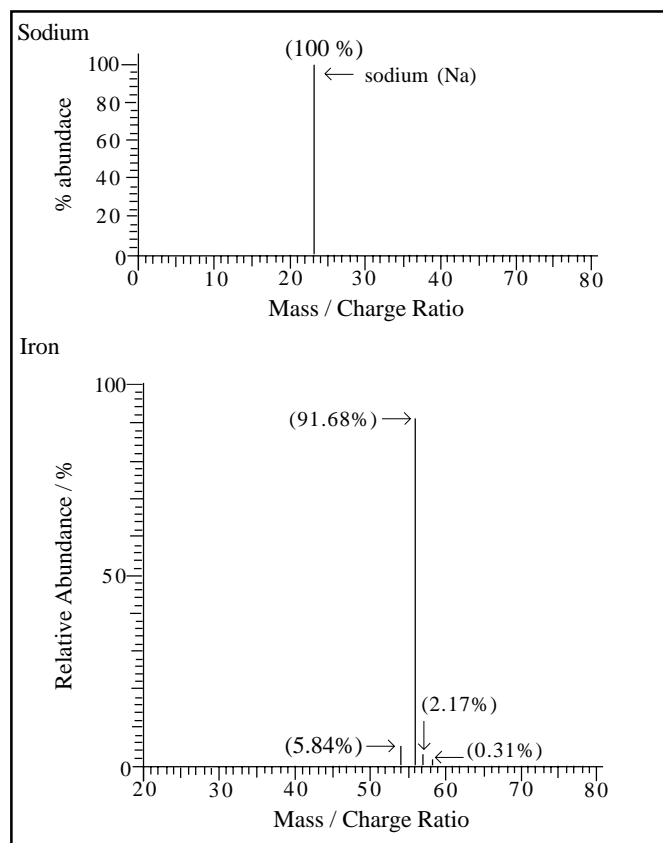
Fig 3. Mass Spectrometer



The way in which the mass spectrometer works can be broken down into 5 stages.

- 1. Vaporisation** - The sample being tested has to be turned into a gas, so individual atoms/molecules are separated.
- 2. Ionisation** - A heated filament gives out electrons into the ionisation chamber. As the sample enters the ionisation chamber, its atoms/molecules are bombarded by these electrons. The collisions cause electrons to be removed from the atoms/molecules of the sample, so positive ions are formed. (This is where fragmentation can occur - molecules may break into pieces.)
- 3. Acceleration** - An electric field is applied, which will accelerate the positive ions (as they are charged particles).
- 4. Deflections** - A magnetic field deflects the beam of ions. Ions with a high mass/charge ratio (eg. Heavy, 1+ charge) will be deflected less than ions with a low mass/charge (e.g. light 13+ charge)
- 5. Detection** - Those ions which have the correct mass/charge ratio will be detected. If the magnetic field is kept constant whilst the electric field causing acceleration is continuously varied, one species after another will be detected, so a complete spectrum, or trace, is obtained.

Fig 4. Mass spectrometer traces



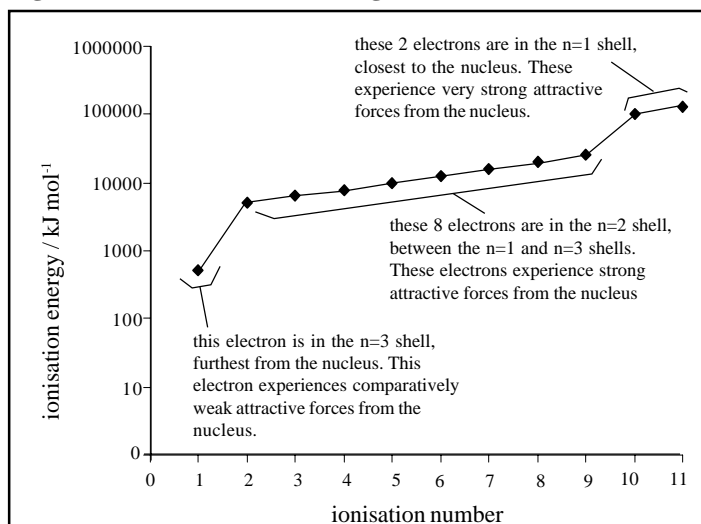
From the mass spectra shown, it is clear that the sodium sample tested consisted solely of sodium -23.

The sample of iron was a mixture of 4 isotopes, iron -54, iron -56, iron -57 and iron -58. The percentage abundancies are given (i.e. 91.68% iron -56, showing it to be the most common isotope) so now the relative atomic mass of iron can be calculated.

$$A_r = \text{avge mass} = \frac{5.84}{100} \times 54 + \frac{91.68}{100} \times 56 + \frac{2.17}{100} \times 57 + \frac{0.31}{100} \times 58 = 55.91$$

Note: many ions have a charge of +1, so the mass/charge (m/e) ratio is equal to the mass (m) of the ion.

Fig 5. Successive ionisation energies for sodium



The pattern shows us that sodium has 11 electrons arranged in 3 shells, or energy levels. The first electron is relatively easy to remove as:

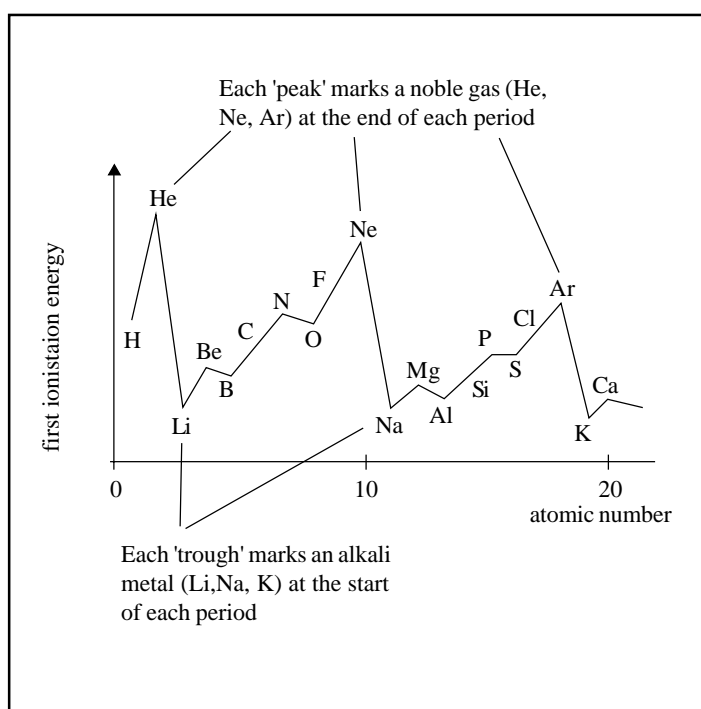
- it exists further from the nucleus
- the electrons orbiting closer to the nucleus 'shield' it from the positive centre so the attractive forces are comparatively weak.

The next 8 electrons have similar ionisation energies (as they are all a similar distance from the nucleus) but do get successively slightly harder to remove, as the **relative positive charge** in the ion is increasing. The last 2 electrons are very difficult to remove as they exist very close to an unshielded nucleus.

### Ionisation Energy and the Periodic Table

- alkali metals are the easiest to ionize
- noble gases are the hardest to ionize
- As we move across a period, the first IE tends to increase, as
  - nuclear charge increases
  - electrons are added to the same shell, the same distance from the nucleus with the same degree of shielding

Fig 6. First ionisation energies for the first 20 elements



Notice that within a period, sets of elements with similar first ionisation energies exist, consisting of 2, 3, 3, members - within period 2, this is (Li, Be) (B, C, N) and (O, F, Ne). These are explained by the existence of **subshells** - see later.

There is also a trend in first IEs down any group - there is a general **decrease** due to the increased distance and shielding of the outer electrons from the nucleus.

### Electronic Configurations

You are aware that electrons exist in different energy levels (or quantum shells).

Electrons can also be split **within** a quantum shell, into **subshells**.

e.g. in the second shell (referred to as " $n=2$ ") there are 8 electrons in a full shell. This can be split into 2 subshells:

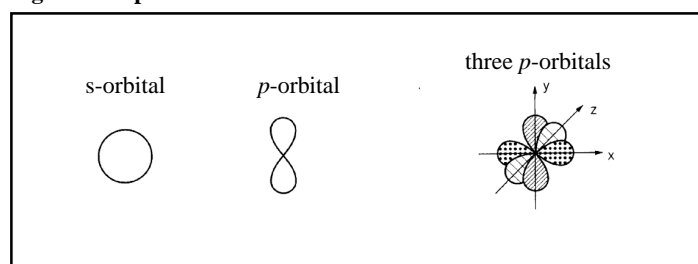
- 2s - containing 2 electrons slightly harder to remove
- 2p - containing 6 electrons slightly easier to remove.

Each sub-shell is a collection of orbitals:

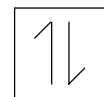
Sub-shell	orbitals	max e-
s	1	2
p	3	6
d	5	10
f	7	14

Fig 7 shows the orbitals for the s and p sub-shells

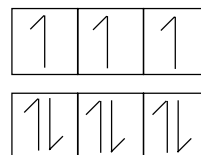
Fig 7. s and p orbitals



Each orbital can hold up to 2 electrons, but electrons in a pair must have opposing **spin**. We represent each orbital by a box, and the electrons by half-arrows. One half arrow points up and one down, to represent the different spins of the two electrons



When electron sub shells are filling up, one electron is placed in each available orbital first; the electrons only pair up when no more orbitals are available in that sub-shell.

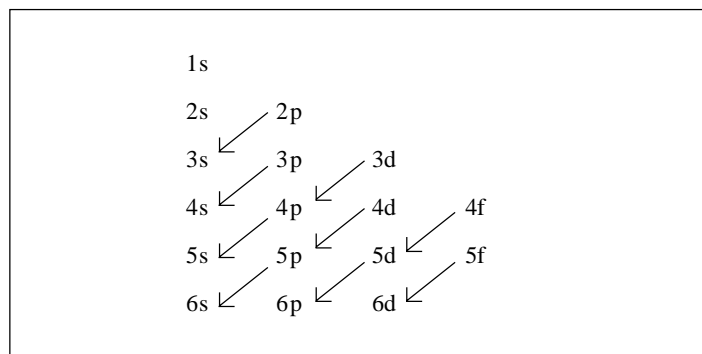


#### Exam Hint:

- You need to be able to draw the shapes of the s and p orbitals, but not of d or f orbitals.
- You need to know the number of orbitals - and hence number of electrons - in each sub-shell.

**Order of filling of sub-shells**

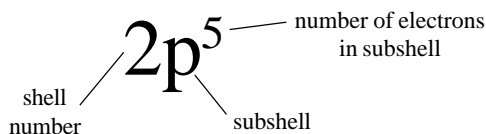
We already know that the electrons in an atom fill up the first shell before going into the second, and fill that before going into the third shell. We now need to look at the order in which the sub-shells fill up. This is described by Fig 9.

**Fig 9. Order of filling of sub-shells**

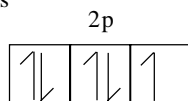
Using the diagram, the order in which the subshells fill is:

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p .... etc

We are now able to write out electronic configurations in more detail, using the following notation:



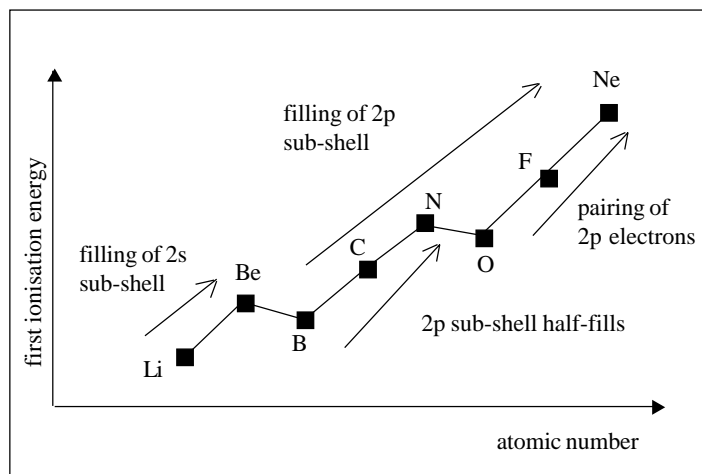
or using arrows in boxes



Using the principles covered so far, we can now find the electronic configurations of the first 36 elements (Table 2)

**Evidence for sub-shells from ionisation energies**

Whilst there is a **general** increase in IE across the period, this is not a smooth trend, which can be explained by the existence of sub-shells.

**Fig 10. First ionisation energies across period 2****Table 2. Electronic arrangement of the elements from hydrogen to krypton**

Element	Atomic number	1s	2s	2p	3s	3p	3d	4s	4p
Hydrogen	1	<b>1</b>							
Helium	2	<b>2</b>							
1s level full									
Lithium	3	2	<b>1</b>						
Beryllium	4	2	<b>2</b>						
2s level full									
Boron	5	2	2	<b>1</b>					
Carbon	6	2	2	<b>2</b>					
Nitrogen	7	2	2	<b>3</b>					
Oxygen	8	2	2	<b>4</b>					
Fluorine	9	2	2	<b>5</b>					
Neon	10	2	2	<b>6</b>					
2p level full									
Sodium	11	2	2	6	<b>1</b>				
Magnesium	12	2	2	6	<b>2</b>				
3s level full									
Aluminium	13	2	2	6	2	<b>1</b>			
Silicon	14	2	2	6	2	<b>2</b>			
Phosphorus	15	2	2	6	2	<b>3</b>			
Sulphur	16	2	2	6	2	<b>4</b>			
Chlorine	17	2	2	6	2	<b>5</b>			
Argon	18	2	2	6	2	<b>6</b>			
3p level full									
Potassium	19	2	2	6	2	6		<b>1</b>	
Calcium	20	2	2	6	2	6		<b>2</b>	
4s level full									
Scandium	21	2	2	6	2	6	<b>1</b>	2	
Titanium	22	2	2	6	2	6	<b>2</b>	2	
Vanadium	23	2	2	6	2	6	<b>3</b>	2	
Chromium	24	2	2	6	2	6	<b>5</b>	1	**
Manganese	25	2	2	6	2	6	<b>5</b>	2	
Iron	26	2	2	6	2	6	<b>6</b>	2	
Cobalt	27	2	2	6	2	6	<b>7</b>	2	
Nickel	28	2	2	6	2	6	<b>8</b>	2	
Copper	29	2	2	6	2	6	<b>10</b>	1	**
Zinc	30	2	2	6	2	6	<b>10</b>	2	
3d level full									
Gallium	31	2	2	6	2	6	10	2	<b>1</b>
Germanium	32	2	2	6	2	6	10	2	<b>2</b>
Arsenic	33	2	2	6	2	6	10	2	<b>3</b>
Selenium	34	2	2	6	2	6	10	2	<b>4</b>
Bromine	35	2	2	6	2	6	10	2	<b>5</b>
Krypton	36	2	2	6	2	6	10	2	<b>6</b>
4p level full									

**Note:** a) how the 4s level fills up before the 3d level,  
 b) for chromium and copper (labelled \*\*) the sequence is out of step; you will meet this point again when studying the transition elements.

You will be required to write the electronic arrangement (or **configuration**) for elements and there are two accepted ways for doing this. For example, the electronic arrangement for iron could be written:  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$  or  $[\text{Ar}] 3d^6, 4s^2$  where [Ar] represents the electronic arrangement of the noble gas argon.

You will notice from Fig 10 that the first ionisation energy decreases from Be to B and from N to O. A similar phenomenon occurs between groups 2 to 3 and 5 to 6 in the other periods. This can be explained by examining the electron configurations of the elements:

### Comparing Be and B



Beryllium has **full-subshell stability**, as the highest occupied subshell is complete. Boron has one electron in a higher (2p) sub-shell, which is easier to remove, hence its 1<sup>st</sup> IE is lower than that of Be

### Comparing N and O



Nitrogen has **half-shell stability**.

Oxygen has one 2p orbital which has a pair of electrons and paired electrons repel, so one of these electrons is easier to remove, hence it has a lower 1<sup>st</sup> IE than that of nitrogen.

### Electronic Structure and Chemical Properties

Chemical reactions involve the making and/or breaking of bonds. Bond involve the movement of electrons.

e.g. Covalent bond - sharing of electrons  
Ionic bond - transfer of electrons

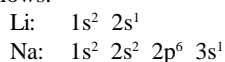
It makes sense therefore that the electronic configuration of an atom has an impact on its chemical properties.

Any group on the periodic table can be considered a 'family of elements' as the elements in that group will exhibit similar chemical properties. This is due to each member of the group having the **same number of electrons in its outer shell**.

Even within groups, trends in reactivity can be explained by electronic configuration:

e.g.1 For Group 1 – the alkali metals – reactivity **increases** down the group.

If we consider lithium and sodium, their electron configurations are as follows:



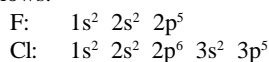
Both Li and Na require to lose 1 electron to gain a stable noble gas electronic configuration. It is difficult to remove the outer electron from lithium as it is close to the nucleus and experiencing little shielding. These factors mean lithium:

- has a higher 1<sup>st</sup> IE than sodium
- is less reactive than sodium

This trend continues down the group.

e.g.2 For Group 7 – the halogens – reactivity **decreases** down the group.

If we consider fluorine and chlorine, their electron configurations are as follows:



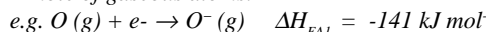
Both F and Cl need to gain 1 electron to acquire a stable noble gas electronic configuration. An electron would be more strongly attracted to F rather than the larger Cl, as it could join a lower energy level closer to the nucleus with less shielding from it. Therefore, the smaller the halogen atom, the more reactive it is. So reactivity decreases down the group.

### Electron Affinities

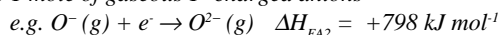
As shown with the halogens, it is possible to **add** electrons to an atom, forming a negative ion (anion). The energy required to do this is the **electron affinity**.



**First Electron Affinity** - the energy required to add 1 mole of electrons to 1 mole of gaseous atoms.



**Second Electron Affinity** - the energy required to add 1 mole of electrons to 1 mole of gaseous 1- charged anions

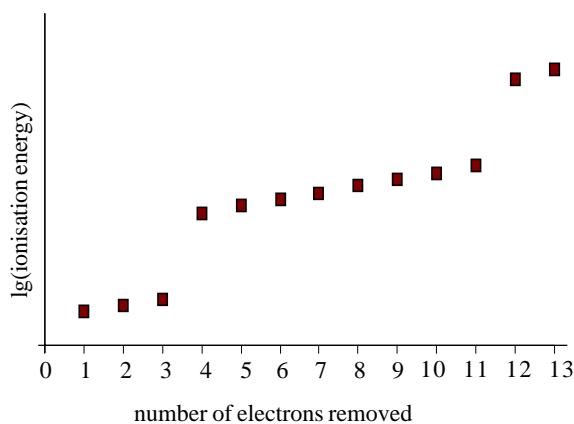


The 1<sup>st</sup> EA is always exothermic (energy is released) because the electron goes into a vacancy in the outer energy level. This is 'bond-making' so energy is released.

However, this creates a 1- ion so to put the second electron into the vacant site needs energy to be put in to overcome the repulsion (-ve to -ve) between the ion and the electron - so the 2<sup>nd</sup> EA is always endothermic (energy is absorbed).

### Questions

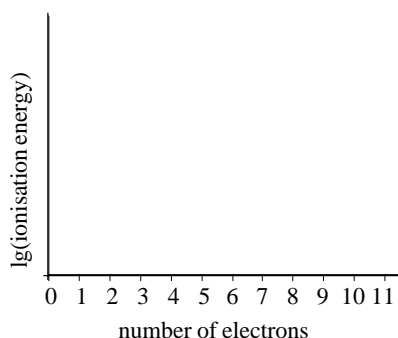
- a) Define the terms first ionisation energy.
- b) The graph shows a plot of lg (ionisation energy) vs number of the electron removed for aluminium.



Explain the form of this graph in terms of the electron structure of aluminium.

- a) Define the terms
  - atomic number
  - mass number
  - relative atomic mass
  - isotope
- b) Describe in detail the five stages in the operation of a mass spectrometer.
- c) The mass spectrometer analysis of neon shows it exists of two isotopes of different relative abundances ie. 20 (90%) and 22 (10%). Calculate the relative atomic mass of neon.

3. Sketch a graph on the axes below to show the successive ionisation energies of sodium.



Give reasons for the shape of the line you draw.

4. For each of the following elements give the electronic configuration in terms of s, p and d orbitals:
- phosphorus
  - carbon

5. Explain the trend in first ionisation energies and the reasons for it:

- down a group
- across a period

6. a) Why is the first ionisation energy of nitrogen higher than that of oxygen?

- b) Write equations which represent for oxygen:

- the first electron affinity
- the second electron affinity

7. Give reasons for each of the following:

- sodium is more reactive than magnesium
- potassium is more reactive than sodium
- chlorine is less reactive than fluorine

### Answers

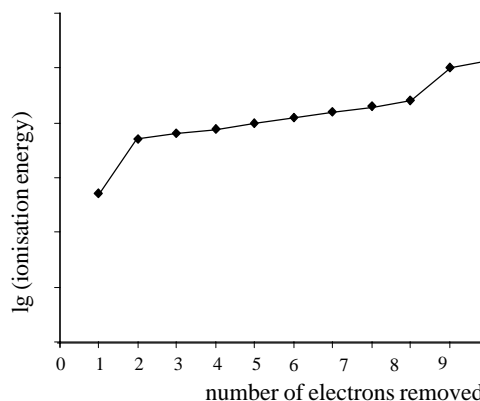
1. a) The energy needed to remove one mole of electrons from 1 mole of gaseous atoms.  
 b) Al has a 2, 8, 3 configuration ie. 3 outer electrons, 8 electrons in the next orbital and 2 electrons in the inner orbital.

2. a) (i) number of protons in the nucleus  
 (ii) number of protons and neutrons in the nucleus  
 (iii) the mass of an atom compared to 1/12 mass of an atom of carbon 12  
 (iv) atoms with the same atomic number but different mass numbers/  
 atoms with the same number of protons but different numbers  
 of neutrons

- b) Vaporisation – heating the sample to turn it into a gas  
 Ionisation – bombarding the gaseous sample with an electron beam to remove electrons and produce positive ions.  
 Acceleration – attraction of the positive ions to an electrical field.  
 Deflection – passing the ions through a magnetic field to deflect them according to mass/charge ratio.  
 Detection – ions being measured according to mass/charge ratio and their relative abundance being calculated.

- c) 20.20

3.



Na is 2, 8 1. There is one electron in the outer orbit, 8 electrons in the next orbit and 2 in the innermost orbit.

4. a) P = 15  $1s^2 2s^2 2p^6 3s^2 3p^3$   
 b) C = 6  $1s^2 2s^2 2p^2$

5. a)  $1^{st}$  I.E's decrease down a Group.

The outer electron is further from the nucleus and the inner electron orbitals shield the pull of the nucleus on the outer electrons. The outer electrons are easier to remove.

- b)  $1^{st}$  I.E's increase across a Period.

The outer electrons go into the same outer orbital so the shielding effect is the same across the Period. At the same time one extra proton is added, increased the nuclear charge. This makes the outer electrons increasingly more difficult to remove.

6. a) N is  $1s^2 2s^2 2p^3$  O is  $1s^2 2s^2 2p^4$   
 Half-shell stability of  $p^3$ , compared to O where the p electron is more easily removed.

- b) (i)  $O(g) + e^- \rightarrow O^-(g)$   
 (ii)  $O^-(g) + e^- \rightarrow O^{2-}(g)$

7. a) Na only has to lose one electron to gain the Noble Gas configuration, and its  $1^{st}$  I.E. is lower than for magnesium. The Na single electron is lost more easily, so sodium is more reactive.

- b) K has a bigger atomic number so more electron orbits. Increased shielding on an electron further from the nucleus means the outer electron is easier to remove than the one for Na.

- c) F has a smaller atomic number so less electron orbits so less shielding of the pull of the nucleus for the electron needed to complete is outer orbital. The F atom therefore has more pull on electrons so is more reactive than Cl.

### Acknowledgements:

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