ATOMIC STRUCTURE

2

CORE

2.1 THE ATOM

2.1.1   State the position of protons, neutrons and electrons in the atom.

2.1.2   State the relative mass and relative charge of protons, electrons and neutrons.

2.1.3   Define the terms mass number (A), atomic number (Z) and isotopes of an element.

2.1.4   Deduce the symbol for an isotope given its mass number and atomic number.

2.1.5   Calculate the number of protons, neutrons and electrons in atoms and ions from the mass number, atomic number and charge.

2.1.6   Compare the properties of the isotopes of an element.

2.1.7   Discuss the use of radioisotopes

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In 1807 *John Dalton* proposed his **atomic theory** - that all matter was made up of a small number of different kinds of atoms, that were indivisible and indestructible, but which could combine in small whole numbers to form compounds.

From the point of view of chemical change this theory remains largely true, i.e. atoms, or most of the atom, remains intact throughout chemical reactions. We now know, however, that atoms are not indivisible and are in fact composed of many smaller subatomic particles. Even though much of the atom does not change in chemical reactions, the outermost part of the atom (known as the valence electron shell) is crucial to chemical interactions, so knowing about the atomic structure of atoms allows us to understand how atoms join together to form compounds and why different atoms react in different ways.

ATOMIC STRUCTURE

Three important types of **subatomic particles** are the proton, the neutron and the electron. The proton and neutron have a much greater mass than the electron and are very tightly bound together to form the nucleus of the atom. Hence the nucleus contains all the positive charge and nearly all the mass (>99.9%) of the atom. It is very much smaller than the atom - if the nucleus were 1 metre across, then the electrons would be about 10 kilometres away, so most of the atom is empty space. The electrons occupy shells around the nucleus. The proton and electron carry a single positive and a single negative charge respectively, whilst the neutron is electrically neutral. The

Particle	Proton	Neutron	Electron
Relative mass	1	1	$\frac{1}{1840} \approx 5 \times 10^{-4}$
Relative electrical charge	+1	0	1
Where found	In the nucleus	In the nucleus	Shells around the nucleus

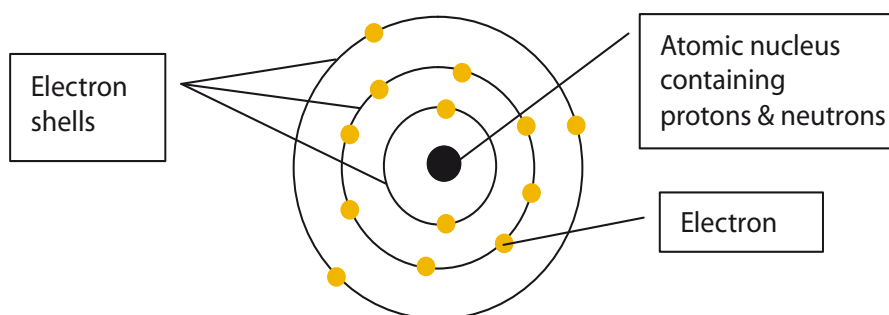*Figure 201   The subatomic particles*

Figure 202   A diagrammatic representation of the atom

characteristics of these subatomic particles are given in Figure 201 and a diagrammatic representation of the atom is given in Figure 202.

The fundamental difference between atoms of different elements lies in the number of protons in the nucleus. An element consists of atoms which have the same number of protons in their nuclei. This is known as the **atomic number** (Z) of the element. Each element has one more proton than the preceding element in the periodic table. The sum of the protons and neutrons in the nucleus is known as the **mass number** (A). The atomic number and mass number of an element may be indicated by a subscript and a superscript respectively, placed before the symbol for the element ($^{A}_{Z}X$), e.g. for aluminium:

Mass number $\longrightarrow$ 27
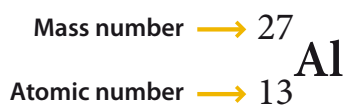
Atomic number $\longrightarrow$ 13 Al

This is sometimes written Al-27. The number of neutrons can be found by subtracting the atomic number from the mass number, e.g. in the case of aluminium there are 27–13 = 14 neutrons in the nucleus. For lighter elements, the numbers of protons and neutrons are approximately equal, but elements with many protons require a higher proportion of neutrons because of the greater repulsion between the larger number of protons. Lead, for example,

has 82 protons and (207–82) 125 neutrons (i.e. the p:n ratio is approximately 2:3).

In order to preserve electrical neutrality, the number of electrons in an atom is equal to the number of protons, so that aluminium has 13 electrons, which exist outside of the nucleus in shells of differing energies, as is discussed in greater detail later in Sections 2.3 and 2.4.

Atoms can gain or lose electrons to form ions, which have a net electrical charge because the numbers of protons and electrons are no longer equal. If an atom gains electrons, as non-metals tend to, then it will form a negatively charged ion (or anion), because there are now more electrons than protons. The ion will have one negative charge for each electron gained. For example an oxygen atom tends to gain two electrons to form the O^{2-} ion. An atom, especially of a metal, may also lose electrons to form a positive ion (or cation), because there are now more protons than electrons. The ion will have one positive charge for each electron lost. For example aluminium tends to lose three electrons to form the Al3+ ion. In chemical reactions, atoms **never** gain or lose protons. It is the interactions of the electrons that determine the chemical properties.

Knowing the atomic number (or name of the element), mass number and charge on a particle it is possible to calculate the numbers of protons, neutrons and electrons present.

What is the significance of the model of the atom in the different areas of knowledge? Are the models and theories that scientists create accurate descriptions of the natural world, or are they primarily useful interpretations for prediciton, explanation and control of the natural world? What is the purpose of a model? In what way, for example, would our perception of a new building change if we saw a model of it rather than just reading about its dimensions, or even looking at plans of it? Probably in some way it helps to make it more "real". We can better grasp what it is like and relate it to things we are more familiar with. Do theoretical models, like the chemical "model" of the atom, do the same thing as physical models? The answer is probably a qualified "yes". Models certainly help us to explain and have a better understanding of rather abstract concepts (actually, it is interesting to try to pin down just exactly what we mean by these words "explanation" and "understanding"!).

By a qualified yes I mean it is important not to stretch analogies too far. If we want to think of electrons as being rather like planets going around the sun, then probably, like planets, they have angular momentum, but we would probably not spend too much time looking for smaller particles going around the electrons just because many of the planets have moons! A model, or map (they have many similarities) is often only useful for its intended purpose. It would be difficult to use a street map of London to work out the best route between Holborn and Paddington on the train, just as the underground map would not be very helpful when working out how to walk from Piccadilly to Westminster Bridge. The particle model of light is really useful trying to explain the photo-electric effect, but not very helpful when it comes to interference patterns. Asking which light is really like is probably a bit like asking which of the two maps, London is really like!

For example in the ion $^{58}Ni^{2+}$ there will be 28 protons (because the atomic number of nickel must be 28), 30 neutrons (58 – 28) and 26 electrons (28 in a nickel atom minus 2 to give the +2 charge). Similarly in the ion $^{31}P^{3-}$ there will be 15 protons, 16 neutrons and 18 electrons.

Many elements are composed of slightly differing types of atoms known as **isotopes**. These atoms all have the same number of protons (which makes them still the same

element), but differ in the number of neutrons in the nucleus. Isotopes therefore have the same atomic number, but different mass numbers. Chlorine for example occurs naturally as a mixture of two isotopes. Both contain 17 protons, but one contains 18 neutrons and the other contains 20 neutrons, so the symbols for the two isotopes respectively are:

$$^{35}_{17}Cl \text{ and } ^{37}_{17}Cl$$
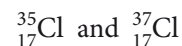
Both isotopes of chlorine have the same number of electrons and, as it is the number of electrons that determines the chemical properties of a substance, both isotopes have identical chemical properties. Physical properties often also depend on the mass of the particles and so different isotopes will often have slightly different physical properties such as density, rate of diffusion etc.

Natural chlorine contains approximately 75% ^{35}Cl and 25% ^{37}Cl. These percentages, known as the natural abundances of the isotopes, give the proportions of the different isotopes of chlorine, in the element and in all compounds of chlorine are often found by mass spectrometry (see Section 2.2). The existence of isotopes must therefore be taken into account in calculating the relative atomic mass of the element, which is the weighted mean. In chlorine, for example, out of 100 chlorine atoms, on average, 75 will have a mass of 35 and 25 will have a mass of 37, so the relative atomic mass of chlorine is:

$$\frac{(75 \times 35) + (25 \times 37)}{100} = 35.5$$

Similarly, if an element is only composed of two major isotopes and the molar mass is known, the natural abundances of the two isotopes can be calculated. For example iridium is composed almost entirely of 191Ir and ^{193}Ir. Knowing that its molar mass is 192.2 g mol^{-1}, the naturally occuring percentages of the two isotopes may be calculated:

Let the % of ^{191}Ir = x, then the % of ^{193}Ir = (100-x)

$$191 \frac{x}{100} + 193 \frac{(100-x)}{100} = 192.2$$

$$191x + 19300 - 193x = 192.2 \times 100$$
$$2x = 19300 - 19220$$
$$= 80$$
therefore $\quad x = 40$

Iridium is therefore 40% ^{191}Ir and 60% ^{193}Ir

Usually if an element has an atomic mass that is greater than 0.1 from being an integer, it is a sign that it is composed of a mixture of isotopes, though some elements that are composed of isotopes have atomic masses that are almost

integers. For example bromine consists of approximately equal amounts of ^{79}Br and ^{81}Br to give an atomic mass of almost exactly 80. Many elements have naturally occurring isotopes, but often these are only present in low percentages. This is the case in the isotopes of hydrogen (^2_1H - deuterium and ^3_1H - tritium) and carbon ($^{13}_{12}C$ and $^{14}_{12}C$).

Radioactive isotopes of all elements can be produced by exposing the natural element to a flux of slow moving neutrons in a nuclear reactor. This results in the nucleus of the atom capturing an additional neutron. These "radioisotopes" have many uses. Sometimes, as is the case with carbon-14, the rate of radioactive decay can be used to date objects. Naturally occurring carbon in living organisms contains a fixed proportion of carbon-14 owing to exchange with carbon in the atmosphere. On death this interchange stops and the proportion of carbon-14 starts to decrease. After about 5,700 years the proportion of carbon-14 will have fallen to about half its initial value.

Another use of radioisotopes is as "tracers". This relies on the fact that the radioactive isotopes behave chemically, and thus biologically, in an identical manner to the stable isotopes. For example the activity of the thyroid gland, which preferentially absorbs iodine, can be measured by monitoring the increase in radioactivity of the gland after taking a drink containing traces of iodine radioisotopes (typically ^{125}I and ^{131}I).

Some radiosotopes produce gamma rays and hence can be a source of quite intense radioactivity. Cobalt-60 is an example of this and radiation from cobalt-60 sources is used in radiation treatment for cancer and industrially in devices such as those monitoring the thickness of steel plate from a rolling mill.

Exercise 2.1

1. Which of the following are usually found in the nucleus of an atom?

   A   Electrons and neutrons only.
   B   Neutrons only.
   C   Protons neutrons and electrons.
   D   Protons and neutrons only.

2. The number of neutrons in an atom of $^{138}_{56}Ba$ is

   A   56
   B   82
   C   138
   D   194

3. How many electrons would have about the same mass as a proton or a neutron?

   A   200
   B   500
   C   2000
   D   5000

4. Which one of the following is not a common use of radioactive isotopes?

   A   As a fuel in fuel cells
   B   Irradiating tumours in patients with cancer.
   C   Measuring the rate of uptake of a drug that has been swallowed.
   D   Finding the age of rocks.

5. Radioisotopes of normally stable elements are

   A   chemically extracted from the natural element
   B   mined from scarce underground deposits.
   C   formed from the stable element in nuclear reactors.
   D   produced through chemical reactions of the stable element

6 Identify the following subatomic particles:

   a)   The particle that has a much lower mass than the others.
   b)   The particle that has no electrical charge.
   c)   The particle that is not found in the nucleus.
   d)   The number of these in the nucleus is equal to the atomic number.
   e)   The particle that is gained or lost when ions are formed

7. Calculate the numbers of protons, neutrons and electrons in the following:

Element	Mass No.	Protons	Neutrons	Electrons
Helium	4			
Nitrogen	14			
Aluminium	27			
Manganese	55			
Iodine	127			

8. Boron has atomic number 5. It comprises two isotopes, one with five neutrons, the other with six.

   a) Define the term "isotope".
   b) Calculate the mass numbers of the two isotopes and represent them in the form ^x_yB.
   c) In naturally occurring boron, 20% of the atoms contain five neutrons and 80% six neutrons. Calculate the relative atomic mass of boron.

9. Describe how you might use a sample of calcium phosphate, containing traces of a radioisotope of phosphorus, to measure the rate of uptake of phosphorus by the root systems of various plants.

10. Naturally occurring copper is a mixture of two isotopes. One of these has 29 protons and 34 neutrons, the other one two more neutrons. Complete the following table for both isotopes:

	No. Protons	No. Neutrons	No. Electrons	Atomic No.	Mass No.
Isotope 1	29	34			
Isotope 2					

   If the relative atomic mass of copper is 63.55, calculate the natural abundances of the two isotopes.

11. Give the numbers of protons, neutrons and electrons in the following isotopes:

Isotope	Number of		
	protons	neutrons	electrons
$^3_1$H			
$^{15}_7$N			
$^{57}_{26}$Fe			
$^{90}_{38}$Sr			
$^{235}_{92}$U			

12. Complete the following table:

Species	Number of		
	protons	neutrons	electrons
$^3\text{H}^-$			
$^{24}\text{Mg}^{2+}$			
	13	14	10
	16	18	18
$^{4+}$	22	26	

2.2 THE MASS SPECTROMETER

2.2.1 Describe and explain the operation of a mass spectrometer.

2.2.2 Describe how the mass spectrometer may be used to determine relative, atomic masses using the ^{12}C scale.

2.2.3 Calculate non-integer relative atomic masses and abundance of isotopes from given data

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A **mass spectrometer** is an instrument which separates particles according to their masses and records the relative proportions of these. In a mass spectrometer the substance is firstly converted to atoms or molecules in the vapour phase (A). These are then turned into positive ions (B) and accelerated (C). The fast moving ions are deflected (D) - the lighter the particle the greater the deflection. Finally particles of a particular mass, which can be adjusted, will be detected (E). The body of the instrument must be maintained at a high vacuum by a pump (F).

Region A contains the vapourised substance. If it is already a gas, then it will contain the gas at low pressure, if the sample is a solid or liquid, it must be heated to produce the vapour. This is connected to the rest of the mass spectrometer by a fine tube, or capillary, so that the transfer of material into the body of the instrument occurs very slowly. This is vital as the body of the mass spectrometer must be kept at a high vacuum for its correct operation, which depends on particles being able to pass through it without colliding with any other particles.

In region B, the particles are converted from neutral atoms or molecules into positive ions. This is usually done by bombarding them with fast moving electrons that are accelerated between the two plates shown. These electrons collide with electrons in the particle knocking them out and leaving a positive ion.

$$X\,(g) + e^- \longrightarrow X^+\,(g) + 2e^-$$
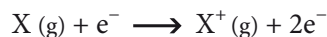
In region C, these positive ions are accelerated by the high electrical potential difference between the two parallel
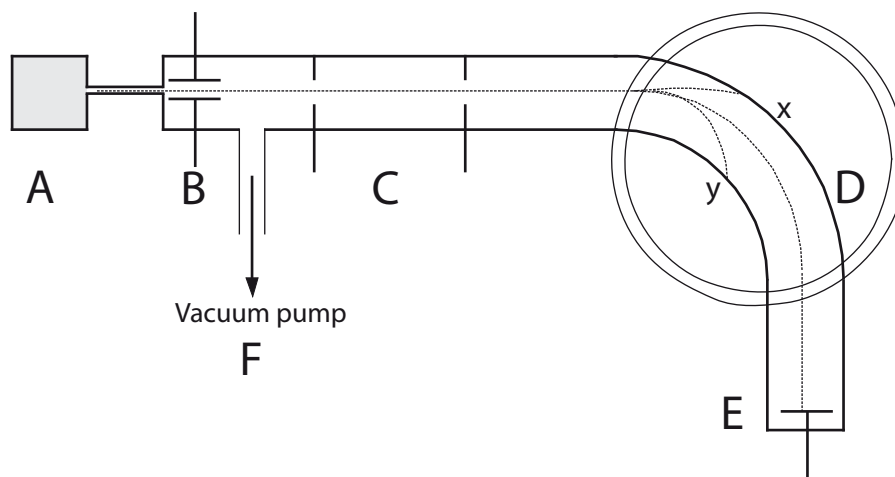

Figure 207   A diagram of a simple mass spectrometer

TOK   Reality or imagination?

None of these particles can be (or will be) directly observed. Which ways of knowing do we use to interpret indirect evidence, gained through the use of technology? Do we believe or know of their existence. Do we know electrons exist or do we believe electrons exist? Are they more like this book, for which most of us agree we have concrete evidence, or are they more like God, where (if we believe in Him, or Her, - English strikes again!) the evidence is more circumstantial? Let's go back to the discovery of the electron, late in the 19th Century; what was the necessity to come up with this hypothesis? Under certain circumstances rays could be observed, as a glow on a fluorescent screen, and these were easily deflected by electric or magnetic fields in a way that led to it being postulated they were caused by particles (under some circumstances you can observe single flashes of light) having a negative charge. Their production also seemed to leave much more massive particles with a positive charge. This was interpreted as evidence that atoms (already constraining ourselves within Dalton's paradigm) might be comprised of particles with unequal masses and opposite charges. Onward to the photo-electric effect, an electric current and the hydrogen atom spectrum; things we can observe directly for which we invoke the electron as an explanation.

Postulating the existence of the electron certainly allows us to relate many apparently unrelated phenomena, but is that existence? I guess it depends what you mean by exist? Postulating there is a publisher out there explains why I get e-mails enquiring why this chapter is late, why I sometime get large piles of proofs to read through and why, just occasionally, my bank account seems to have increased slightly. But is that the same sort of existence as meeting him in Melbourne (or at least me imagining that there is this person there at the same time as I am imagining that a place called Melbourne really exists and I am in it, at the same time as I have this wonderful sensation that seems to go with imagining I am enjoying a meal with him)?

Back to solipsism - why am I even bothering to imagine I am writing all of this when I have no evidence at all (not even in my own brain!) that you the reader are out there reading it!

electrodes with holes in their centres. In region D these fast moving ions enter a magnetic field produced by an electromagnet. The poles, shown as circles, are above and below the plane of the diagram. This causes the fast moving ions to deflect, as shown. Particles of a certain mass (dependent on the field strength) will continue round the tube and strike the detector plate. Those with a greater mass will not be deflected as much and those with a smaller mass will be deflected more (deflection depends on the charge to mass ratio $\frac{m}{z}$). These will strike the wall of the instrument at (x) and (y) respectively. This means that only ions of a certain mass are detected at E, usually by means of the current flow required to neutralise the positive charge that they carry - the greater the number of particles of a given mass that are present, the greater the current.

By varying the strength of the magnetic field, ions of different masses can be brought to focus on the detector. In this way the relative abundances of ions of different masses produced from the sample can be determined. This is known as a mass spectrum. Usually the electron bombardment is adjusted to produce ions with only a single charge. Any doubly charged ions will be deflected more than the singly charged ions and will in fact behave in the same way as a singly charged ion of half the mass. That is why the x-axis is labelled $\frac{m}{z}$, where m is the relative mass of the species and z its relative charge. For example $^{32}S^{2+}$ will be observed at $\frac{m}{z} = 16$.

To summarise, the main operations are:

A   vapourised sample introduced
B   ionisation by electron bombardment
C   positive ions accelerated by electrical field
D   ions deflected by a magnetic field
E   detector records ions of a particular mass
F   vacuum prevents molecules colliding

The mass spectrometer has many applications, but one of the simplest is to determine the natural abundances of the isotopes of a particular element and hence allow
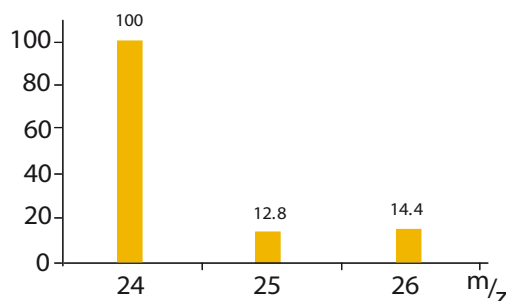

Figure 208   The mass spectrum of magnesium

calculation of its atomic mass. If for example a sample of magnesium was vapourised in the mass spectrometer, the resulting mass spectrum would be similar to that shown below.

The relative abundance is recorded so that either the most abundant isotope is given a value of 100 and the others recorded as a proportion of this, or the abundances are given as percentages of the whole.

The natural abundances of the three isotopes of magnesium and hence its relative atomic mass can be calculated from these data:

$$^{24}Mg = 100 \times \frac{100}{127.2} = 78.6\%$$

$$^{25}Mg = 100 \times \frac{12.8}{127.2} = 10.0\%$$

$$^{26}Mg = 100 \times \frac{14.4}{127.2} = 11.3\%$$

Relative atomic mass of magnesium =
$(24 \times 0.786) + (25 \times 0.100) + (26 \times 0.113) = 24.3$

With molecules, the relative molecular mass of the molecule can be found. The ionisation process often causes the molecule to break into fragments and the resulting 'fragmentation pattern' acts like a fingerprint to identify the compound.

Exercise 2.2

1. Describe briefly how in the mass spectrometer

   a)   the atoms are converted into ions.
   b)   the ions of different mass are separated.
   c)   the ions are detected.

2. Germanium (atomic number 32) contains 20% germanium-70, 27% germanium-71, 8% germanium-72, 37% germanium-73 and 8% germanium-74. Draw a graph of the mass spectrum that you would expect germanium to produce. If an atom of germanium-70 lost two electrons to become a doubly charged ion, at what $\frac{m}{z}$ would it appear?

3. The graph shows the mass spectrum of the element which contains 76 protons in its nucleus.

   a)   Write down, in the form $^{A}_{Z}X$, the isotopes that it is composed of with their natural abundances (as a %).
   b)   Calculate the relative atomic mass of the element.
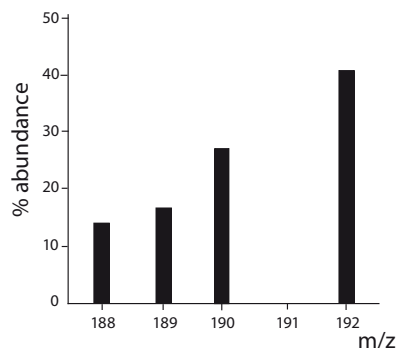
4. Lead has a molar mass of 207.2 g mol^{-1}. Assuming that it is composed entirely of ^{206}Pb, ^{207}Pb and ^{208}Pb, and that the percentages of the two lightest isotopes are equal, calculate the relative percentages of these isotopes in the natural element.

2.3 ELECTRON ARRANGEMENT

2.3.1   Describe the electromagnetic spectrum.

2.3.2   Distinguish between a continuous spectrum and a line spectrum.

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ATOMIC EMISSION SPECTRA

The study of the emission of light by atoms and ions is the most effective technique for deducing the electronic structure of atoms. Here the term "light" is being used rather loosely to indicate electromagnetic radiation. This covers radiation from gamma rays through to radio waves, as illustrated in Figure 210 below, that has many properties in common. Familiar visible light is just the very small region of this spectrum that our eyes happen to be sensitive to.

The best evidence for the fact that electrons in an atom surround the nucleus in certain allowed energy levels, or orbitals comes from a study of the emission spectra of elements. When an element is excited it will often emit light of a characteristic colour (e.g. the red of neon signs). In the case of gases this can be achieved by passing an electrical discharge through the gas at low pressure. For many metals the same effect can be observed when their compounds are heated directly in a Bunsen flame. This is the basis of the 'flame tests' for metals. For example, the alkali metals all impart a characteristic colour to the flame:
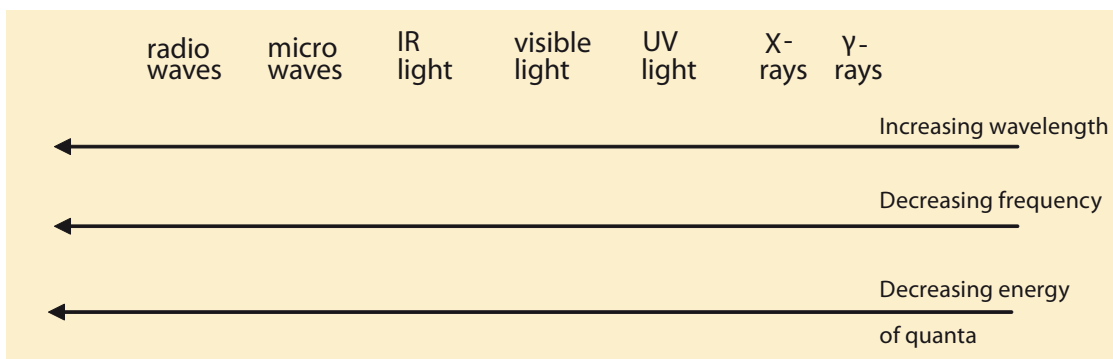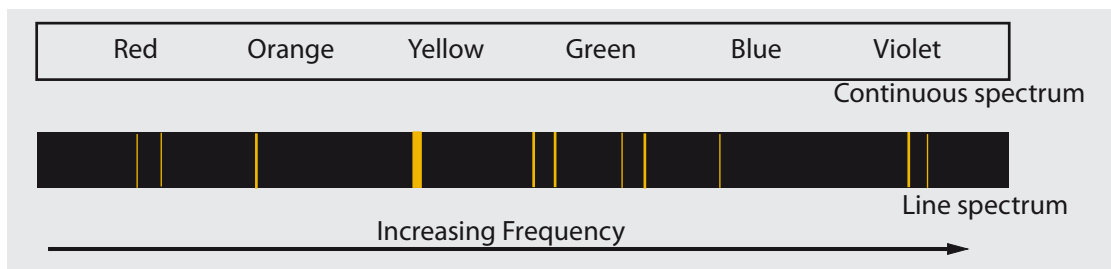
| radio waves | micro waves | IR light | visible light | UV light | X- rays | γ- rays |

Increasing wavelength

Decreasing frequency

Decreasing energy of quanta

Figure 210   The electromagnetic spectrum

| Red | Orange | Yellow | Green | Blue | Violet |

Continuous spectrum

Line spectrum

Increasing Frequency

Figure 211   Continuous and line spectra

n=5
n=4
n=3

Energy Difference ΔE

n=2

n=1

E

Electron in the atom gains energy from the excitation process.

Light of frequency f

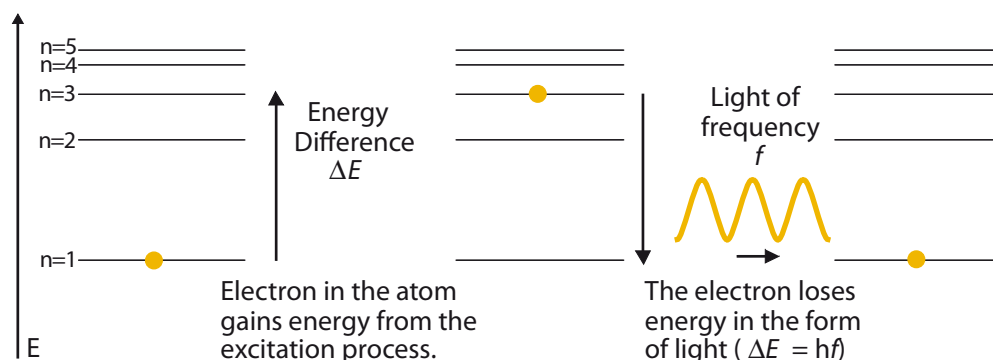The electron loses energy in the form of light (ΔE = hf)

Figure 212   The origin of line spectra

lithium - red, sodium - yellow, potassium – lilac, this is the basis of atomic absorption spectroscopy If the light is passed through a spectroscope, containing a prism or diffraction grating, to separate out the different colours, then what is observed is not a continuous spectrum (like a rainbow) as is observed with normal 'white' light, which contains all frequencies. Instead, it comprises very bright lines of specific colours with black space in between. This is known as a line spectrum and is illustrated in Figure 211. Each element has its own characteristic line spectrum that can be used to identify it.

When an atom is excited its electrons gain energy and move to a higher energy level. In order to return to lower energy levels, the electron must lose energy. It does this by giving out light. This is illustrated in Figure 212.

The frequency (f), and hence colour, of the light depends on the amount of energy lost by the electron (ΔE), according to the equation:

$$\Delta E = h f \qquad (h \text{ is Planck's constant})$$

The colour of light is sometimes defined by its wavelength (λ) rather than its frequency (f). The two are related by the equation $c = f.\lambda$ ($c = 3 \times 10^{-8}$ m s^{-1}, the velocity of light) i.e. the greater the frequency, the shorter the wavelength.

Because there are only certain allowed energy levels within the atom, there are a limited number of amounts of energy (ΔE) that the electron can lose. This means that only certain frequencies of light can be emitted, hence the line spectrum. A continuous spectrum would imply that an electron in an atom could have any energy.
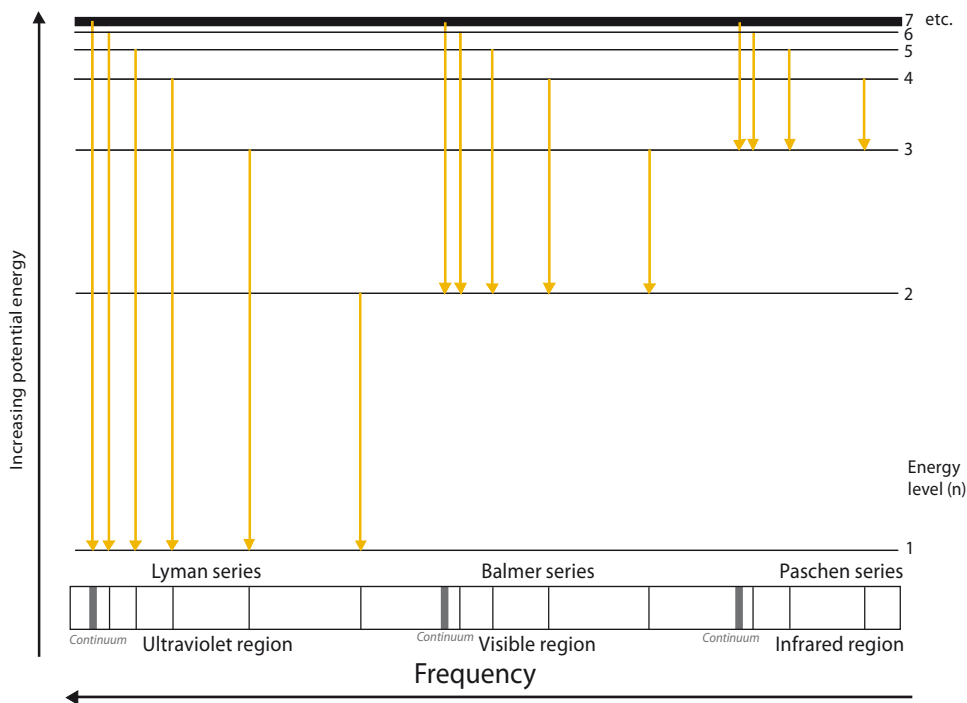
Figure 213   Explanation of the atomic emission spectrum of hydrogen

By studying the frequencies of the lines in the emission spectrum of an element, the energies of the various energy levels in its atoms may be found. The situation is not quite as simple as has been portrayed because there are sub-levels within the main allowed levels and this makes the spectra significantly more complex, nevertheless they may still be used to determine the allowed energy levels for electrons within an atom. It is found that the energy levels are not evenly spaced, like the rungs of a ladder, but that the higher the energy, the smaller the difference in energy between successive energy levels becomes (See Figure 212). This means that the lines in a spectrum will converge (i.e. get closer together) with increasing frequency. The limit of this convergence indicates the energy required to completely remove the electron from the atom (i.e. to ionise it) and so it may be used to determine the ionisation energy.

> 2.3.3   Explain how the lines in the emission spectrum of hydrogen are related to the energy levels of electrons.
>
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THE ATOMIC EMISSION SPECTRUM OF HYDROGEN

The **emission spectrum** of the hydrogen atom is the simplest emission spectrum, because having only one electron, there is none of the electron-electron repulsion which causes the principal energy levels to split into different sub-levels. When a potential difference is applied across hydrogen gas at low pressure, electromagnetic radiation is emitted. As explained above, this is not uniform but concentrated into bright lines, indicating the existence of only certain allowed electron energy levels within the atom. It was by a study of these lines that the electronic structure of the hydrogen was deduced, though it is simpler to start, as below, with the accepted electronic structure and show how this results in the observed spectrum.

The spectrum is divided into a number of distinct series, named after the people who discovered them, which occur in different spectral regions as shown (there are also further series at longer wavelengths which are not shown). Each series corresponds to transitions in which the electron falls to a particular energy level. The reason

I'm so old I even remember back to when we thought that being able to reproduce music via a groove on a piece of vinyl that rotated at $33^1/_3$ rpm was a pretty neat idea! It prompts me to go even further back in time and muse upon what it is that we really mean by "technology". Is using a stick to dig up roots applying technology? What is the cut-off point? Dictionary definitions seem to hinge around applying scientific discoveries to manufacturing, so maybe "using technology to further science"? (but since it comes out of science anyway, it sounds a bit circular!) Can we consider knowledge as being "manufactured", as opposed to being "discovered"? Now there's a fundamental difference that it's probably worth devoting some thought to!

If we have two solutions of potassium manganate(VII) (permanganate – it forms purple solutions) we can tell at a glance which is the more concentrated (making a couple of assumptions on the way?). Is this knowledge essentially different to that we would obtain from putting them in a spectrophotometer and reading that at 525 nm (in the green region – why here when the solution is purple?) one had an absorbance of 1.374 and the other an absorbance of 0.867? (Maybe there would be a couple more assumptions to add!) How do the knowledge implications change again if we shift the wavelength to 280 nm (in the ultraviolet region) and take two apparently colourless solutions of benzoic acid and find one has an absorbance greater than the other? Both look the same so are we sure there's a difference? (Yet more assumptions – how many do we need to make us start to feel uneasy?)

There's a saying that "seeing is believing" (or did they mean "knowing"?), but from TOK classes on perception we probably now know the pitfalls that lie there. Wassabe and Guacamole are a very similar shade of green, and remembering a recent horrendous mistake in which millions of taste buds died, maybe we shouldn't put too much faith in any one sense?

why they occur in different spectral regions is that as the energy levels increase, they converge (i.e. get closer together in energy). This means that all transitions to the n=1 level include the large n=1 to n=2 energy difference and so they are all high energy transitions found in the ultraviolet region. For similar reasons all transitions to the n=2 level are in the visible region etc.

Each series has a very similar structure of lines that become closer together going towards higher frequencies. This is another result of the convergence of energy levels. Each series ends in a brief continuum at the high frequency end where the lines become too close together to be separated. The cut off of this is the energy emitted when an electron completely outside the atom (n=∞) falls to the particular level involved. In the case of the Lyman series, this corresponds to the ionisation energy of the hydrogen atom, which can be found from the high frequency cut off of the continuum.

The reverse can happen, that is a hydrogen atom can absorb light of a particular frequency and this will excite an electron from a lower energy level to a higher one. This is known as an absorption spectrum. It appears as black lines (caused because a particular frequency is absorbed) in a continuous spectrum. Only the Lyman series (in the ultraviolet region) is observed in the absorption spectrum

because in hydrogen atoms the electrons are normally in the lowest energy level (n=1) and so can only move to higher energy levels from that energy level.

2.3.4   Deduce the electron arrangement for atoms and ions up to Z = 20.

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ELECTRONIC STRUCTURE AND THE PERIODIC TABLE

The most stable energy levels, or shells, are those closest to the nucleus and these are filled before electrons start to fill the higher levels. There is a maximum number of electrons that each energy level can hold. The first can hold up to two electrons, the second up to eight electrons. Beyond this the situation becomes more complex. The number of electrons in each orbital is known as the electronic structure of the atom. For example aluminium has 13 electrons so its electronic structure is 2.8.3. i.e. it has 2 electrons in the first level, 8 in the second (so both of these are filled) and the remaining 3 in the third. Different isotopes of an element have the same number of electrons

H			B	C	N	O	F	He
1								2
Li	Be		B	C	N	O	F	Ne
2,1	2,2		2,3	2,4	2,5	2,6	2,7	2,8
Na	Mg		Al	Si	P	S	Cl	Ar
2,8,1	2,8,2		2,8,3	2,8,4	2,8,5	2,8,6	2,8,7	2,8,8
K	Ca							
2,8,8,1	2,8,8,2							

Figure 214   Electronic structure in relation to the periodic table

---

TOK   Which ways of knowing allow us access to the microscopic world?"

I was intrigued reading this one – what is the implication of the phrase "image of an invisible world"? Does it imply that we believe this image we have is in some way real? Probably that depends a lot on what we mean by real and whether we think that reality is "out there" or "in here" (i.e. in our minds)? Making a sharp turn to avoid a return to solipsism, even if we accept there is a physical world out there, is the world you perceive the same as the world I perceive? If I say "Eiffel Tower", is what pops up as my mental image the same as what pops up as your mental image and can we claim either of them corresponds to reality? In that case if I say "electrons in "sodium" probably the image we see in our brain does not correspond to reality either, just to a model we find useful?

What about our ways of knowing about this world? If "us" means you or me (unless you're a Nobel Laureate) the answer is probably maily through our eyes (reading books like this one as well as looking at things you access on your computer) and ears (listening to what your teacher tells you in class, or what you hear on television). These are ways we have of finding out what other people think, or have thought – in other words we get second hand knowledge on Authority. We then process that in our brains, hopefully applying logic and critical thinking skills and maybe

a little creativity, to construct our world referred to in the previous paragraph. Sometimes we will note inconsistencies and enquire further to resolve these – we "stand on the shoulders of giants" as Newton would have it. That might enable us (especially if we are called Newton or Einstein) to have an effect on the way the other "us" (i.e. the human race) knows about the invisible world, by doing science experiments, prompted by our rational thoughts, that change the accepted knowledge that everybody else learns.

Once again in cutting edge science the primary path of perception is vision – we read meters, note numbers on digital displays, look at the chemicals in test tubes. It's very rarely that we engage any of our other senses. But that is obtaining data, which is a long way from obtaining knowledge (think how they are related, and what about 'information'?). Again knowing is probably what happens to all of these things we see when they whizz round in our brain and interact, perhaps allowing us to suggest new and better models for what seems to be out there. Just be careful that your world view is not too different from that of everybody else. It could make for a very uncomfortable life - they have special places where they put people like that!

and the same electronic structure, hence they exhibit identical chemical properties.

It is the electrons, especially those in the outermost shell, or valence shell, that determine the physical and chemical properties of the element. For example elements with three or less electrons in the valence level, with the exception of boron, are metals, the others non-metals. It is therefore not surprising that the **electronic structure** of an element is closely related to its position in the periodic table, which can therefore act as a memory aid for electronic structure. The period (horizontal row) gives the number of energy levels that contain electrons and the group (number of vertical columns from the left) gives the number of electrons in the valence level. This is shown in Figure 214.

Phosphorus, for example is in the third period, so it has electrons in the first three energy levels, and in the fifth group, so it has five electrons in the valence level. Its electronic structure is therefore 2,8,5.

Example

List the electron arrangement of chlorine and identify the element with n = 2 that has the same number of valence (outer shell) electrons.

Solution

The electron arrangement of chlorine is 2.8.7. Fluorine is the element with n = 2 that also has 7 valence electrons since both chlorine and fluorine are in group 7/17.

Exercise   2.3

1. An atom has an atomic number of 13 and a mass number of 27. How many electrons will it have in its valence level?

    A   1
    B   2
    C   3
    D   5

2. Which of the following would produce a line spectrum rather than a continuous spectrum?

    A   A yellow (sodium) street light.
    B   A normal filament light bulb.
    C   Sunlight.
    D   A white hot piece of steel.

3. Which of the following colours corresponds to light of the highest energy

    A   Yellow
    B   Red
    C   Green
    D   Blue

4. Which one of the following is not a valid electronic structure?

    A   2,8,4
    B   2,6
    C   2,9,1
    D   2,8,8,2

5. Which one of the following electron transitions in a hydrogen atom would produce light in the visible region of the spectrum?

    A   n=2 to n=1
    B   n=5 to n=4
    C   n=6 to n=2
    D   n=4 to n=1

6. Which one of the following is not true for both absorption and an emission spectra?

    A   They are the result of the movement of electrons between energy levels.
    B   The electrons can move between any two energy levels.
    C   The frequency of the light is related to the difference in the energy levels.
    D   There is a convergence towards the high frequency end.

7. Which of the following transitions in the hydrogen atom would produce light of the shortest wavelength?

    A   n=2 to n=1
    B   n=5 to n=4
    C   n=6 to n=2
    D   n=4 to n=1

8. Given the atomic numbers of the following elements, write their simple electronic structures:

    a) Beryllium (At. No. = 4)
    b) Aluminium (At. No. = 13)
    c) Fluorine (At. No. = 9)
    d) Argon (At. No. = 18)
    e) Sulfur (At. No. = 16)

9. Two particles have the following composition:

    A: 37 protons; 38 neutrons, 37 electrons
    B: 37 protons; 40 neutrons, 37 electrons

    a) What is the relationship between these particles?
    b) These two particles have very similar chemical properties. Explain why.

10. Explain why, in the hydrogen atom spectrum:

    a) only light of certain frequencies is observed.
    b) different series are observed in different spectral regions.
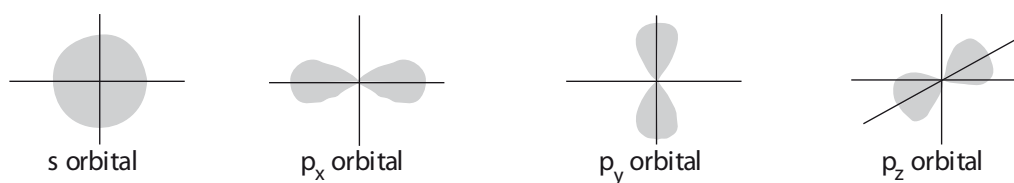   c) these series all converge at the high frequency end.

s orbital p_x orbital p_y orbital p_z orbital

Figure 215   An illustration of the electron distribution in s- and p-orbitals
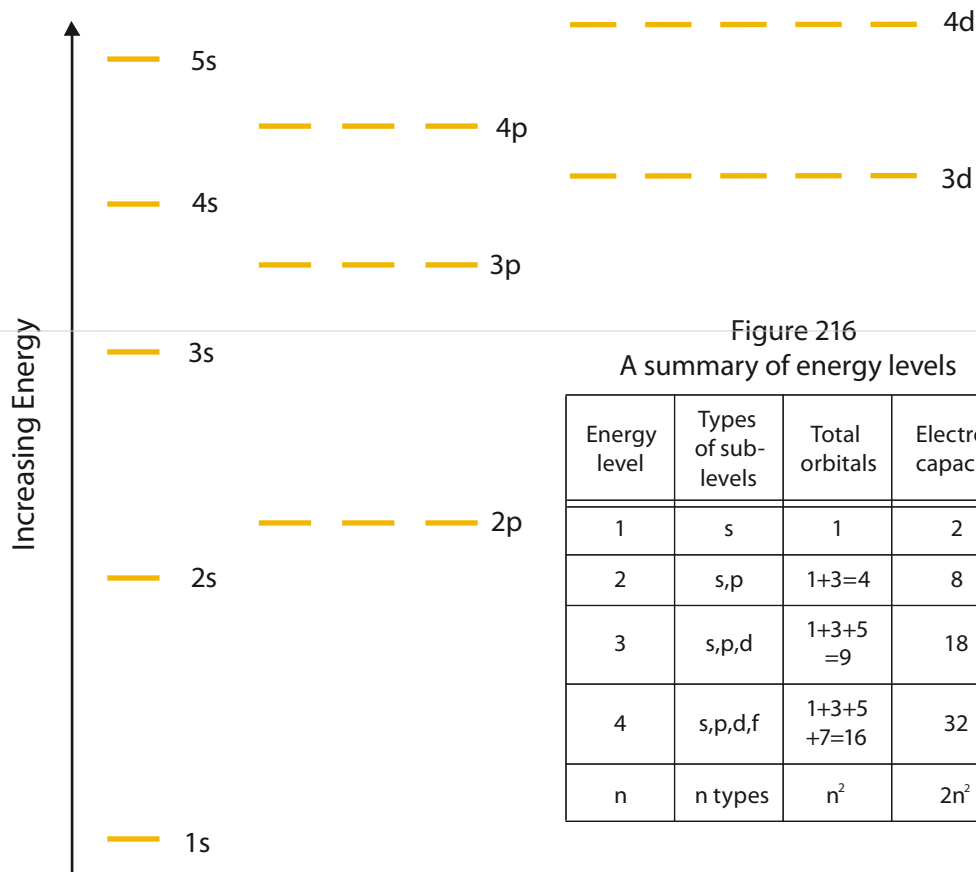
Figure 216
A summary of energy levels

Energy level	Types of sub-levels	Total orbitals	Electron capacity
1	s	1	2
2	s,p	1+3=4	8
3	s,p,d	1+3+5 =9	18
4	s,p,d,f	1+3+5 +7=16	32
n	n types	n^2	$2n^2$

Figure 216   The electron energy levels in a typical atom

AHL

HIGHER LEVEL
12.1 ELECTRON CONFIGURATION (AHL)

The nucleus of the atom is surrounded by electrons arranged in specific energy levels and sub-levels. The different sub-levels differ in the shape of the electron distribution. Each energy sub-level is divided into orbitals each of which can contain up to two electrons, which must have opposite spins, as a consequence of the Pauli exclusion principle, which says that no two electrons in an atom can be in exactly the same state (that is, they cannot be in the same place at the same time). The evidence to support this model of electronic structure, illustrated in Figure 2.16, comes mainly from the study of atomic spectra, as described above.

The energy level closest to the nucleus only contains one sub-level and one orbital. This orbital has spherical symmetry and as orbitals of this shape are known as 's' orbitals, it is referred to as the 1s orbital. It can hold two electrons of opposite spins which are conventionally illustrated as upward and downward pointing arrows..

The second energy level has two sub-levels. The 's' sub-level has one 's' orbital, with spherical symmetry, and the 'p' sub-level has three 'p' orbitals, which have a "figure of eight" electron distribution. These all have the same energy under normal conditions and differ in that one is oriented along the x-axis, a second along the y-axis and the third along the z-axis (see Figure 210). Each orbital can again hold two electrons making six p-electrons and a total of eight in the second level. Owing to increased electron-electron repulsion, the p-orbitals are at a slightly higher energy than the s- orbitals in all atoms except hydrogen.

The third energy level has three sub-levels. The 's' and 'p' sub-levels contain two s-electrons and six p-electrons respectively. It also has five 'd' orbitals, all of the same energy (unless in the presence of ligands), but with even more complex shapes. The d-orbitals can therefore hold ten electrons, giving a total of eighteen for the third level. There is however a complication in that the 3d-orbitals are at a higher energy than the 3p-

orbitals and they occur, in most atoms, at a slightly higher energy than the 4s-orbital. In the fourth energy level, as well as the s-orbital, the three p-orbitals and the five d-orbitals, there are also seven 'f'-orbitals. These orbitals (up to and including the 4d) and their relative energies for a typical atom are shown in Figure 211.

FILLING ELECTRON ENERGY LEVELS

The electrons in atoms always adopt the lowest energy configuration possible by filling one sub-level completely before starting to fill the sub-level of next highest energy. This is known as the *'Aufbau'* (building up) principle. In hydrogen therefore, the electron occupies the 1s orbital and in helium this is doubly filled; the two electrons are paired, and drawn as ↑↓ (showing opposite spins). nl^x notation is used to describe the electron configuration of an atom where n is the main energy level, l the sub-level, and x is the number of electrons in the sub-level, hence the electronic structures of these atoms can be written as $1s^1$ and $1s^2$ respectively. The first energy level is now full, so in lithium, the third electron must occupy the s-orbital of the second level, and with beryllium this is doubly filled (paired electrons) so that their respective electronic structures are $1s^2 2s^1$ and $1s^2 2s^2$. The fifth electron in boron now occupies one of the 2p orbitals, giving an electronic structure of $1s^2 2s^2 2p^1$. Carbon has six electrons so there is the possibility of these electrons occupying separate p-orbitals, with similar spins (217 a), separate p-orbitals with opposite spins (217 b) or the same p-orbital with opposite spins (217 c):
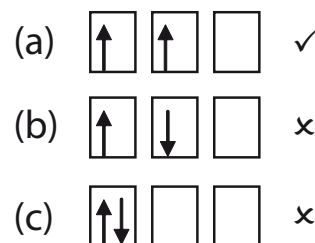

Figure 217   Possible ways for two electrons to occupy orbitals of the same energy

It turns out that (217 a) is the most stable configuration (this is known as **Hund's rule**, or the principle of 'maximum multiplicity'; sub-level orbitals are singly occupied as far as possible by electrons with the same spin) and so in carbon the two outer electrons singly occupy two of the p-orbitals and in nitrogen all three p-orbitals are singly occupied, the electronic structures being $1s^2\,2s^2\,2p^2$ and $1s^2\,2s^2\,2p^3$ respectively. Going from oxygen, through fluorine to neon, these orbitals are each doubly filled, the electronic structures in this order being $1s^2\,2s^2\,2p^4$, $1s^2\,2s^2\,2p^5$ and $1s^2\,2s^2\,2p^6$. The arrangement of electrons in the p-orbital of some of these atoms is illustrated in Figure 218.
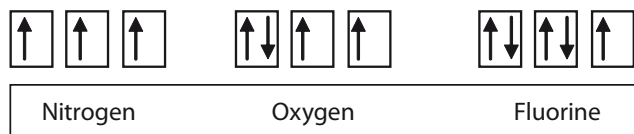

| Nitrogen | Oxygen | Fluorine |

Figure 218   Occupancy of the 2p orbitals in some atoms

At sodium the outer electrons start to occupy the third energy level in a manner totally analogous to the filling of the second energy level until argon ($1s^2\,2s^2\,2p^6\,3s^2\,3p^6$) is reached. At this point, the 4s level is at a lower energy than the 3d level and so this is the next to be filled in potassium and calcium. With longer electronic structures, an abbreviated form may be written in which the symbol for a noble gas in square brackets indicates filled inner shells as for that gas, so the abbreviated electronic structure of potassium can be written as $[Ar]\,4s^1$ and the full electronic structure as $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$. The electronic structure for calcium can be similarly written as $[Ar]\,4s^2$ or $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$.

Starting at scandium the 3d orbitals are gradually filled, each orbital being first singly occupied (Hund's rule), as far as manganese ($[Ar]\,3d^5\,4s^2$) and then doubly filled (thought chromium and copper are exceptions to this, see below), until at zinc ($[Ar]\,3d^{10}\,4s^2$) the 3d and 4s sub-levels are both fully filled. From gallium to krypton the 4p orbital is filled in the usual manner. The order in which the orbitals of an atom are filled according to the Aufbau principle is also illustrated in Figure 219.
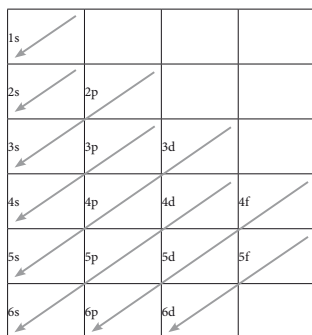

Figure 219   The order of electrons filling sub-levels

There are two exceptions to the filling of the 3d orbital, both associated with a 4s-electron being used to generate the additional stability associated with a half-filled and fully filled 3d orbital. Chromium is $[Ar]\,3d^5\,4s^1$ rather than $[Ar]\,3d^4\,4s^2$ and copper $[Ar]\,3d^{10}\,4s^1$ rather than $[Ar]\,3d^9\,4s^2$. A peculiarity of these (first row d-block) elements, with both d and s electrons in the valence shell, is that when the elements between scandium and zinc form cations, the first electrons that they lose are the 4s electrons, even though this orbital was filled before the 3d orbitals. This is a consequence of a change in the relative stabilities of the 3d and 4s orbitals, which occurs as the 3d orbital starts to fill, that means that the ion with the most d-electrons is the more stable. Therefore, for example, the electronic structure of the iron(II) ion, formed by the loss of two electrons from an iron atom ($[Ar]\,3d^6\,4s^2$) is $[Ar]\,3d^6$ not $[Ar]\,3d^4\,4s^2$. The 3d and 4s sublevels are close in energy, so that once the $4s^2$ electrons are lost, the 3d electrons also behave as valence electrons, for example, Fe^{3+} is $[Ar]\,3d^5$. This accounts for many of the unique properties of these elements.

The electronic structures of the elements are related to the position of the element in the periodic table. In the elements on the far left of the periodic table, the s-orbitals are being filled up, so this is known as the s-block. Similarly in the middle d-block of the periodic table the d-orbitals are being filled and in the right hand p-block, the p-orbitals are being filled. The f-block is traditionally separated from the main table, though it should be placed between the s-block and the d-block, as is found in the "long form" of the table, as shown diagrammatically in Figure 220.
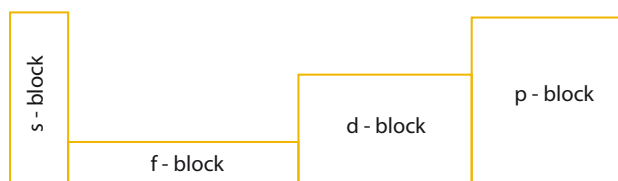

Figure 220   The 'long form' of the periodic table

Value of *l*	0	1	2	3
Value of *m*	0	−1 0 +1	−1 −1 0 +1 +2	−3 to +3
Value of *n* 1	1s ↑↓			
2	2s ↑↓	2p ↑↓ ↑↓ ↑↓		
3	3s ↑↓	3p ↑↓ ↑↓ ↑↓	3d ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	
4	4s	4p ↑↓ ↑↓ ↑↓	4d ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	4f 7 × ↑↓

Figure 221   Interpretation of orbitals in terms of quantum numbers table

QUANTUM NUMBERS

Electrons have a wave as well as a particle nature. Their wave-like nature in atoms can be described by the **Schrödinger wave equation**. This involves four constants, called quantum numbers, and a solution for the equation is only possible if the values of these quantum numbers lie within certain limits. The principal quantum number (n) must be a positive integer. The azimuthal (or subsidiary) quantum number (l) can have integer values from zero to (n – 1). The magnetic quantum number (m) can have integer values from –l to +l (including zero), whilst the spin quantum number (s) can be ±½. This interpretation corresponds exactly with the electron orbital concept outlined above. The principal quantum number dictates the main or principal energy level, the azimuthal quantum number the sub-level ($l=0$ is an s-sublevel; $l=1$ is a p-sublevel; $l=2$ is a d-sublevel; $l=3$ is an f-sublevel etc.), the magnetic quantum number the particular orbital within the sub-level (i.e. p_x, p_y and p_z) with the spin quantum number differentiating between the two electrons in that orbital. This correspondence is shown in Figure 221 in which ↑ represents s=+½ and ↓ represents s=−½:

A more precise statement of the **Pauli exclusion principle** is that no two electrons in a given atom can have the same four quantum numbers.
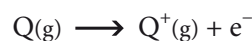
IONISATION ENERGIES

12.1.1 Explain how evidence from first ionization energies across periods accounts for the existence of the main energy levels and sub-levels in an atom.

12.1.2 Explain how successive ionisation energy data is related to the electron configuration of an atom.

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The **ionisation energy** of an atom is the minimum amount of energy required to remove a mole of electrons from a mole of gaseous atoms to form a mole of gaseous ions, that is, using Q as the symbol for the element, it is the energy required for the change:

$$Q(g) \longrightarrow Q^+(g) + e^-$$

The second ionisation energy is similarly the energy required to remove a second mole of electrons from the ion produced by the loss of one electron, that is the energy required for the change:

$$Q^+(g) \longrightarrow Q^{2+}(g) + e^-$$
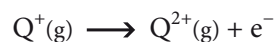
Note that these are both endothermic changes, because work has to be done to remove a negatively charged

electron from the attraction of a positively charged nucleus. The magnitude of the ionisation energy will depend on the charge on the nucleus. This will be counteracted by the repulsion, or "shielding" of electrons in filled inner orbitals. To a first approximation, each electron in a filled inner shell will cancel one unit of nuclear charge and after these have been subtracted, the remaining nuclear charge is referred to as the effective nuclear charge (ENC see Figure 222). The third factor that affects the ionisation energy is the repulsion that the electron experiences from other electrons within the same shell.
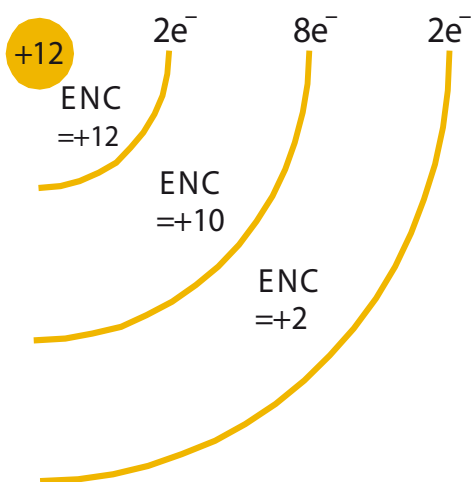

Figure 222   The effective nuclear charge (ENC) for the electrons in magnesium

SUCCESSIVE IONISATION ENERGIES

The more electrons that have been removed from an atom, the greater the energy required to remove the next electron. When the successive electrons are all in the same energy level this is because of a reduction in the amount of electron-electron repulsion and hence the greater nuclear-electron attraction that results causes the remaining electrons to move closer to the nucleus. Consider for example the successive ionisation energies for the magnesium atom, shown in Figure 223 below. The two outer electrons experience the same effective nuclear charge. The first one to be removed is also repelled by the other valence electron, but this force is absent when the second electron is removed. After the first electron is lost, the second outer electron is attracted closer to the nucleus, hence the higher ionisation energy.

Similarly, from the third to the tenth ionisation energy the electrons are being removed from the second energy level, where again the electrons all experience the same effective nuclear charge (+10). In the case of the third ionisation energy this nuclear attraction is counteracted by the repulsion of seven other electrons in the same valence shell, but in the case of the fourth ionisation energy there are only six other electrons repelling the electron being lost, so the remaining valence electrons are now attracted closer to the nucleus and the ionisation energy increases. This trend continues as the remaining second shell electrons are removed. The last two electrons in the second shell have slightly higher ionisation energies than would be anticipated from this trend because they are being removed from the s sub-shell which is slightly more stable than the p sub-shell.
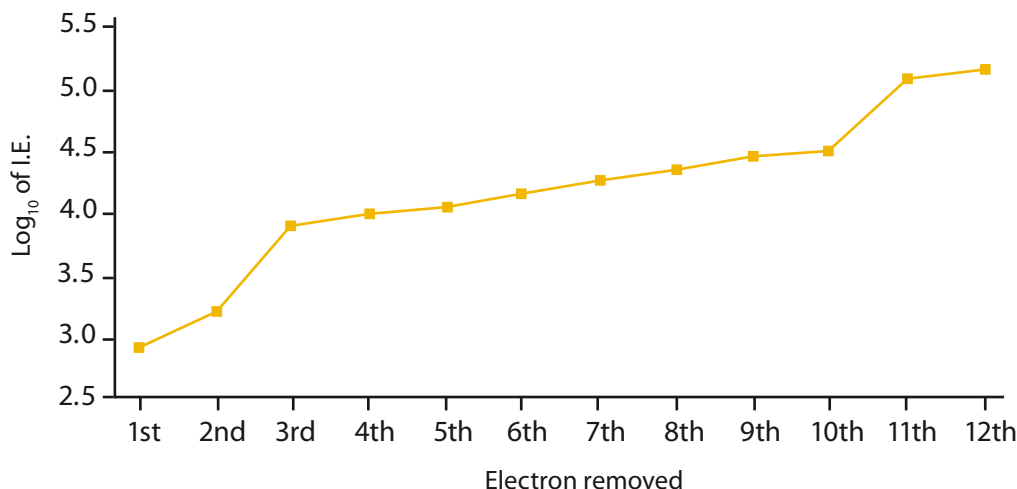

Figure 223   The energy required for the removal of successive electrons from a magnesium atom.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Group	1	2	13	14	15	16	17	0
Electronic structure	2.8.1	2.8.2	2.8.3	2.8.4	2.8.5	2.8.6	2.8.7	2.8.8
1st IE	496	738	578	789	1,010	1,000	1,251	1,520
2nd IE	4,560	1,450	1,820	1,580	1,900	2,250	2,300	2,670
3rd IE	6,910	7,730	2,750	3,230	2,910	3,360	3,820	3,930
4th IE	9,540	10,500	11,600	4,360	4,960	4,560	5,160	5,770
5th IE	13,400	13,600	14,800	16,100	6,270	7,010	6,540	7,240
6th IE	16,600	18,000	18,400	19,800	21,269	8,500	9,360	8,780
7th IE	20,100	21,700	23,300	23,800	25,400	27,100	11,000	12,000
8th IE	25,500	25,700	27,500	29,300	29,900	31,700	33,600	13,800
9th IE	28,900	31,600	31,900	33,900	35,900	36,600	38,600	40,800
10th IE	141,000	35,400	38,500	38,700	41,000	43,100	44,000	46,200

(Note all values are kJ mol^{-1} correct to 3 sig fig.)

Figure 224   Ionisation data for thel elements from sodium (Na) to argon (Ar)

Sometimes with successive ionisation energies the next electron must be removed from a filled inner energy level, so that this electron will experience a much higher effective nuclear charge (see Fig. 222) and there is a sudden large rise in ionisation energy. This is the case for the third and the eleventh electrons to be removed from magnesium. Note the use of the logarithmic scale in Figure 223. This makes the shell structure more obvious because, if a linear scale were used, all of the first ten ionisation energies would lie very close to the x-axis.

Consider the detailed ionisation energy data for the period sodium to argon shown below in Figure 224. Looking at these data it can be seen that the sudden increase in ionization energy (see shaded cells), corresponding to starting to remove electrons from the 2p sub-shell, occurs after the removal of one more electron going across the period. Similarly the very high 10th ionization of sodium corresponds to removing an electron from the 1s orbital. Apart from these, the data shows that there is a steady increase in successive ionization energies for every element (decrease in e$^-$-e$^-$ repulsion) and a steady increase going across the period (increase in nuclear charge).

VARIATION OF IONISATION ENERGY

WITHIN THE GROUP

Going down a group of the periodic table, the ionisation energy of the elements decreases. This is because whilst the effective nuclear charge remains approximately constant (the extra nuclear charge being approximately cancelled out by an extra filled electron shell), the electrons that are being lost are in successively higher energy levels and hence further from the nucleus.

An example would be the first ionisation energy of the elements of Group 1, the alkali metals, given in Figure 225). In lithium, for example, the electron is lost from the 2s sub-shell at a distance of 152 pm from the nucleus. In sodium it is lost from the 3s sub-shell which is 186 pm from the nucleus, hence the lower ionisation energy (see Figure 226).

This trend can be seen for these elements and perhaps even more clearly for the noble gases, the peak ionisation energies, in Figure 227.

Element	Li	Na	K	Rb	Cs
I.E. (kJ mol^{-1})	526	502	425	409	382

Figure 225   First ionisation energies for the alkali metals

Lithium   Sodium

Nucleus has +3 charge

Nucleus has +11 charge

152 pm

186 pm

Outer electron experiences ENC of 1 (=3 – 2)

Same ENC, but electron is closer to nucleus in Li

Outer electron experiences ENC of 1 (=11 – 10)
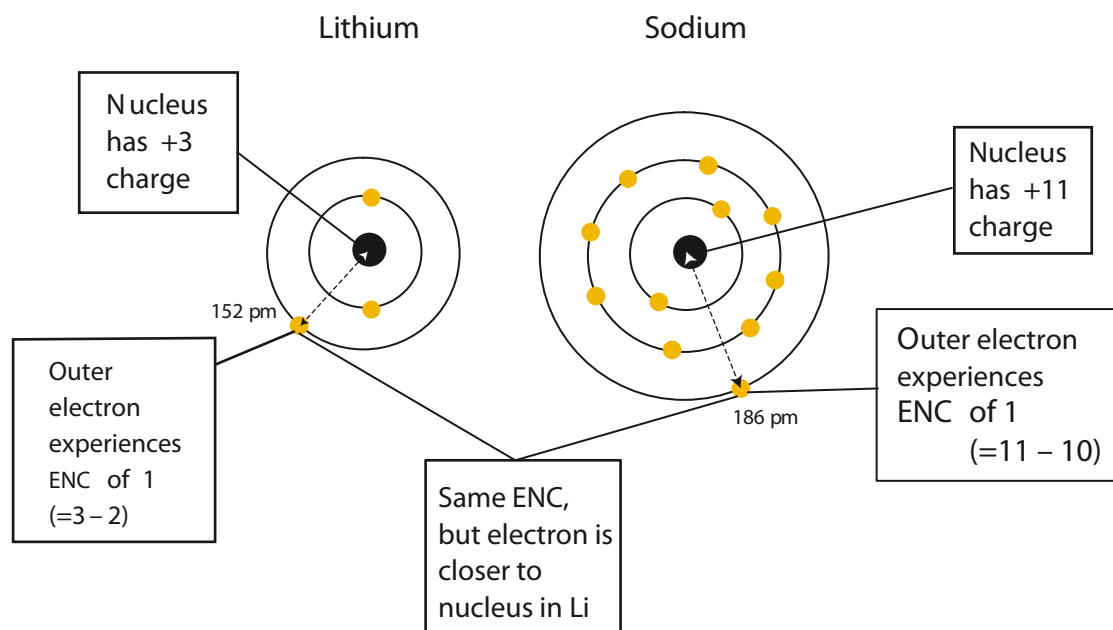
Figure 226   A simplified electronic structure of lithium and sodium illustrating effective nuclear charges

F=1680

Cl=1260

Si=786

Period 2

Period 3

H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar K Ca

Ionisation Energy / kJ mol^{-1}
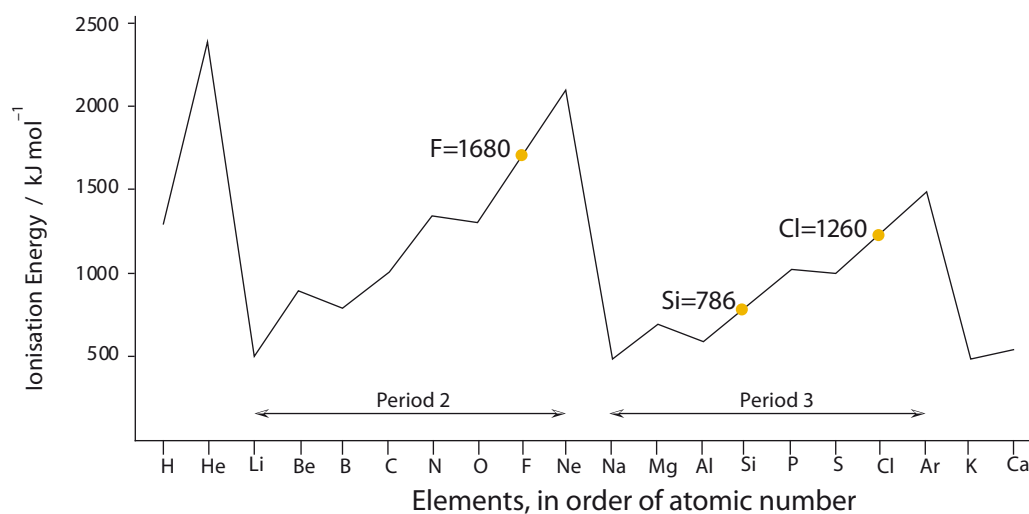
Elements, in order of atomic number

Figure 227   The variation of first ionisation energy with atomic number

THE VARIATION OF IONISATION ENERGY

ACROSS A PERIOD

The ionisation energies of successive elements (in kJ mol^{-1}) is shown in Figure 224.

Overall, going across a period (for example period 2 from Li to Ne, or period 3 from Na to Ar), it can be seen that the ionisation energy increases. This is because of the increase in the charge on the nucleus which, as the electrons being removed are all in the same energy level, increases the effective nuclear charge, and hence the ionisation energy.

The increase is not however a smooth one. Going from the second to the third element in each period (Be to B and Mg to Al) there is a decrease. This is because the electron removed from the third element is in a p-subshell (e.g. B is $1s^2\,2s^2\,2p^1$) whereas that being lost from the second element is from an s-subshell (e.g. Be is $1s^2\,2s^2$). The p-subshell is at a slightly higher energy than the s-subshell and this more than counteracts the effect of the increase in nuclear charge, so the result is a decrease in ionisation energy.

There is also a slight decrease going from the fifth to the sixth element in each period (N to O and P to S). This is because in the fifth element each of the p-orbitals is singly filled, whereas with the sixth element one of these must be doubly filled as shown in Figure 228.

Nitrogen   Oxygen

Figure 228   The 2p electron structure in nitrogen and oxygen

There is greater electron-electron repulsion between the two electrons that share the same orbital, which more than counteracts the effect of the increase in nuclear charge, hence oxygen has a lower ionisation energy than nitrogen.

Isoelectronic species are those which have the same electronic structure. For example S^{2-}, Cl^-, Ar, K^+, and Ca^{2+} all have an electronic stucture $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$. In the order shown the charge on the nucleus gradually increases (from +16 for S to +20 for Ca), so that the attraction for the electrons becomes greater and the ionisation energies gradually increase.

1.   The electronic structure $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ would be found in

    A   neon atoms
    B   sodium ions
    C   sulfide ions
    D   chlorine atoms

2.   Which one of the following elements has the lowest first ionisation energy?

    A   Argon
    B   Magnesium
    C   Sodium
    D   Lithium

3.   How many 3d electrons are present in the ground state of a cobalt atom?

    A   6
    B   7
    C   8
    D   9

4.   The first three ionisation energies of aluminium (in kJ mol^{-1}) are 584, 1823 & 2751. The fourth ionisation energy (in kJ mol^{-1}) is most likely to be about:

    A   3000
    B   5000
    C   10 000
    D   100 000

5.   The first ionisation energy of aluminium is slightly lower than that of magnesium because

    A   magnesium has a higher nuclear charge.
    B   the outer electron in aluminium is in a p-orbital not an s-orbital.
    C   in aluminium the electron is being lost from a doubly filled orbital.
    D   the radius of the aluminium atom is greater than the magnesium atom.

6.   Which one of the following atoms would have the highest fourth ionisation energy?

    A   C
    B   N
    C   Si
    D   P

7. How many unpaired electrons are there in the Cr^{3+} ion?

   A   0
   B   1
   C   3
   D   6

8. Which one of the following would require the most energy for the removal of one more electron?

   A F^-
   B   Ne
   C Na^+
   D Mg^{2+}

9. Write the complete electron configurations of:

   a)   Mn   b)   S
   c) Mg^{2+} d) Fe^{3+}
   e)   Cu

10. Arrange the following in order of increasing ionisation energy

   Li   Na   Ne   N   O

11. a) Sketch a graph to show how you would expect the successive ionisation energies of silicon to vary with the number of electrons removed.
    b) Explain how this provides evidence that the electrons in atoms are arranged in distinct energy levels.
    c) Explain why, within one of these levels, the amount of energy required to remove an electron varies with the number of electrons removed.

12. Explain why

    a) the first ionisation energy of lithium is greater than that of sodium.
    b) the first ionisation energy of oxygen is less than that of nitrogen.
    c) the first ionisation energy of beryllium is greater than that of boron.

13. A particular metal cation M^{3+} has the electronic structure [Ar] $3d^2$.

    a) Identify the metal concerned.
    b) Write the electronic structure of the metal atom.

c) Explain why the electronic structure of the ion could not be the electronic structure of a neutral atom.

14. The graph below shows the logarithm of the successive ionisation energies of a particular element with atomic number less than or equal to 20.
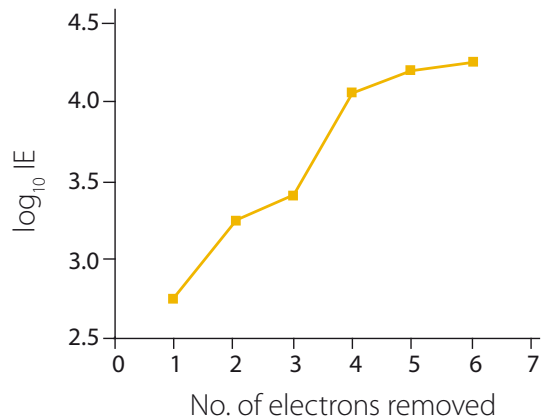
a) Identify the element.
b) Predict the approximate value of the logarithm of the seventh ionisation energy.
c) How would you expect the equivalent successive ionisation energies of the element immediately above it in the periodic table to compare in magnitude?

15. The table below gives successive ionisation data for a number of elements in kJmol^{-1}.

Element	First IE	Second IE	Third IE	Fourth IE
A	580	1800	2700	11600
B	900	1800	14800	21000
C	2080	4000	6100	9400
D	590	1100	4900	6500
E	420	3600	4400	5900

a) Which two elements are probably in the same group of the periodic table?
b) Which element is probably in group 3 of the periodic table? How can you tell?
c) Which two elements probably have consecutive atomic numbers?
d) Which element is most probably a noble gas? Give two pieces of evidence for this.