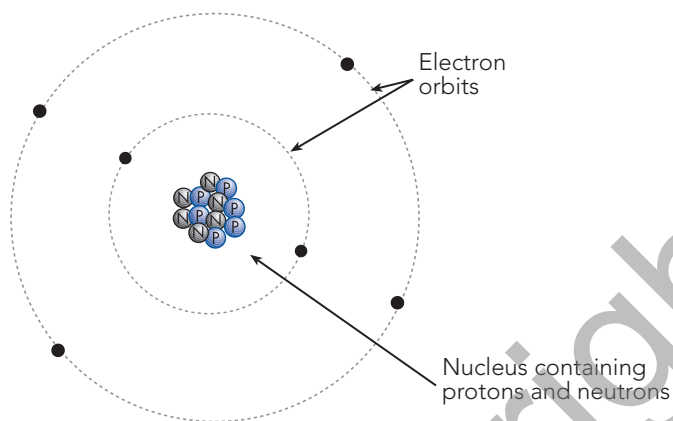


## Topics covered in this chapter:

- 1.1 Structure of the Atom
- 1.2 Atomic Number, Mass Number
- 1.3 Isotopes
- 1.4 The Mass Spectrometer
- 1.5 Atomic Structure and Light Spectra
- 1.6 Electron Arrangements in Atoms
- 1.7 Flame Tests
- 1.8 Atomic Emission Spectrometry (AES)
- 1.9 Atomic Absorption Spectrometry (AAS)
- 1.10 Electron Configurations and the Periodic Table
- 1.11 From Atoms to Ions
- 1.12 Electron Dot Diagrams
- 1.13 Ionisation Energy
- 1.14 Removal of Successive Electrons from Atoms
- 1.15 Trends and the Periodic Table

## 1.1 STRUCTURE OF THE ATOM



*Figure 1.1 Rutherford-Bohr model of the atom. The atom's mass is concentrated in the tiny nucleus while the electron cloud occupies most of the volume.*

In 1804, John Dalton first proposed the idea that tiny particles called atoms were the fundamental particles of nature. His atomic theory helped explain the experimental data available at that time and laid the foundations to our modern view of matter.

Part of Dalton's theory was that atoms of elements were solid and indivisible. However, work carried out by many other scientists such as Faraday, Thompson, Rutherford and Bohr established that in fact, atoms consist of protons, neutrons and electrons. Their discoveries led to a nuclear model of the atom and the following ideas:

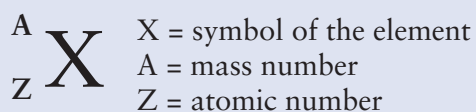
- Atoms consist basically of two regions, that is, a small dense nucleus surrounded by a cloud of electrons.
- The nucleus is positively charged and contains protons and neutrons. The very large majority of the mass of an atom is contained in the nucleus.
- The electrons are negatively charged and have a very small mass. They move rapidly in the region of space around the nucleus creating the effect of an electron cloud. This electron cloud makes up nearly all the volume of the atom.
- Atoms are electrically neutral. Hence the number of protons in any atom is equal to the number of electrons.

*Table 1.1 Properties of protons, neutrons and electrons.*

PARTICLE	LOCATION	MASS (kg)	RELATIVE MASS	RELATIVE CHARGE
proton	nucleus	$1.673 \times 10^{-27}$	1	+1
neutron	nucleus	$1.675 \times 10^{-27}$	1	0
electron	electron cloud	$9.11 \times 10^{-31}$	1/1836	-1

## 1.2 ATOMIC NUMBER, MASS NUMBER

Atoms can differ in atomic number and mass number. The atomic and mass numbers can be shown with the symbol of the element as follows.



e.g.  ${}^7_3\text{Li}$ ,  ${}^{12}_6\text{C}$ ,  ${}^{35}_{17}\text{Cl}$

- The **atomic number** ( $Z$ ) of an atom is the number of protons in the nucleus. All atoms of the same element have the same atomic number. For neutral atoms this is also equal to the number of electrons.
- The **mass number** ( $A$ ) is the total number of protons and neutrons.

Note also  $A = Z + N$  where  $N = \text{No. of neutrons}$

### Worked Example

#### 1.1 Determine the number and type of particles in a neutral atom of ${}^{23}_{11}\text{Na}$ :

Number of protons =  $Z = 11$

Number of neutrons =  $(A - Z) = 23 - 11 = 12$

Number of electrons = 11 (same as number of protons for a neutral atom).

## 1.3 ISOTOPES

All the atoms of a given element have the same number of protons but the number of neutrons may vary. Hence different forms of an element may have a different mass number ( $A$ ). These different forms of an element are called **isotopes**.

Isotopes of a particular element are chemically similar since they have the same number of electrons. This makes them difficult to separate as they only differ slightly in mass and density.

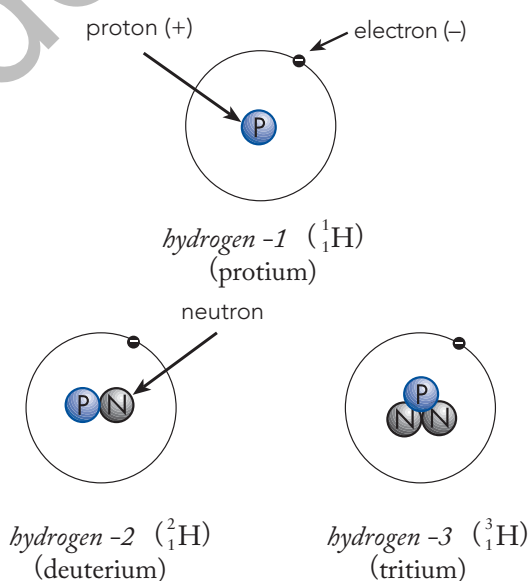


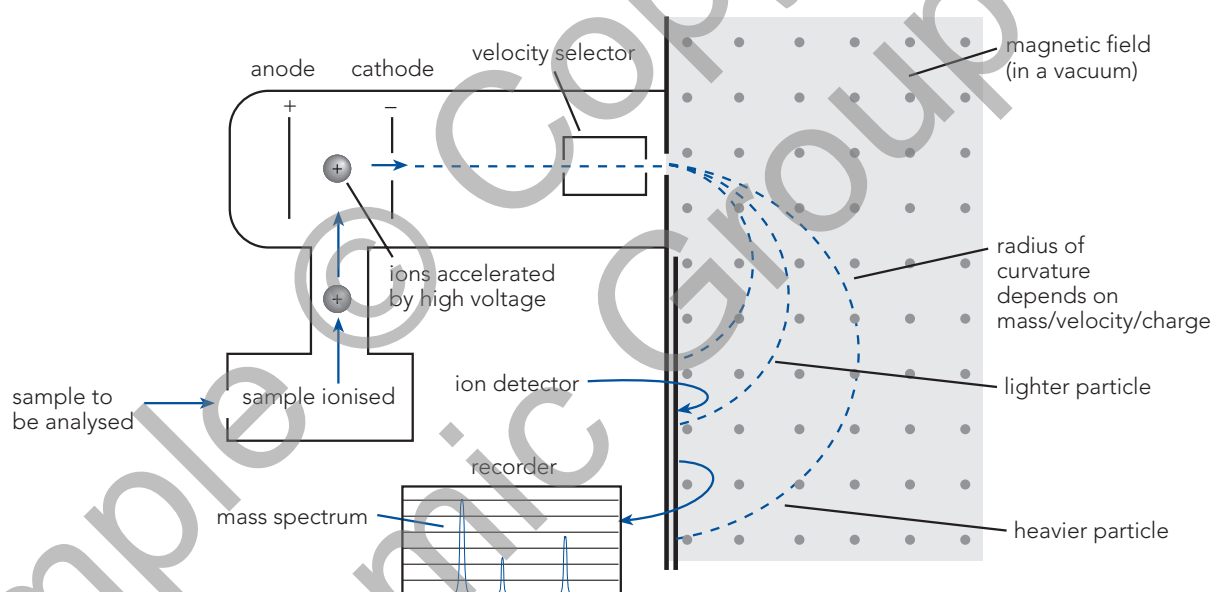
Figure 1.2 The three isotopes of hydrogen.

## 1.4 THE MASS SPECTROMETER

A mass spectrometer can be used to measure the masses and relative concentration of atoms and molecules. It can be used to determine the isotopic masses of naturally occurring elements and their relative abundance. This data can also be used to determine the relative atomic mass of that element.

A mass spectrometer consists of several components but essentially it uses a magnetic field in a vacuum to deflect the path of fast moving charged particles. The substance to be analysed is initially vaporised and then ionised by fast moving electrons. The resulting positive ions are then accelerated by an electric field, pass through a velocity selector and then enter the mass spectrometer.

The magnetic field then causes the ions to be deflected and separate depending on their mass and charge. Any difference in charge would give distinctly different results compared to small changes in mass and hence is easily accounted for. Effectively, the mass/charge ratio and relative concentration are recorded on the output chart.

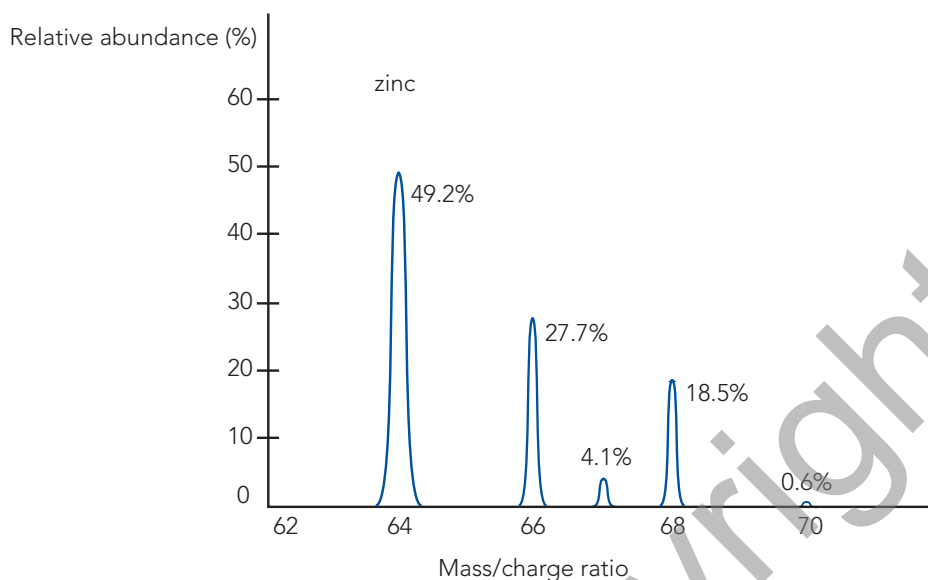


*Figure 1.3 Simplified view of the mass spectrometer. The sample to be analysed is firstly ionised and then its ions are accelerated. A velocity selector is used if just identifying masses. The mass spectrometer is essentially a strong magnetic field in a vacuum with suitable detectors. The mass spectrum gives distinctive peaks for each isotope.*

### Mass spectra and relative atomic mass

Typically, a mass spectrometer can be used to measure atomic masses, identify elements and generally help analyse small traces of unknown substances. Importantly, it can be used to determine the relative atomic mass of pure elements by identifying all of its isotopes and their relative abundance.

The mass spectrum of an element shows characteristic peaks for each of its isotopes. The position and height of these peaks indicates the relative mass and relative abundance of each isotope. To determine the percentage abundance of each isotope the peaks are carefully measured and their heights totalled. The height of each peak can then be considered as a fraction, or percentage, of the total height.



**Figure 1.4** The mass spectrum of Zinc showing the relative abundance of each of its five isotopes. The isotope  $^{64}\text{Zn}$  is the most abundant (49.2%) and its relative isotopic mass being 63.93. The relative atomic mass (atomic weight) of the element zinc can be calculated from the data in this spectrum. See worked example below.

### Worked Example

**1.2** Data determined from the mass spectrum for zinc is shown below. Use this to calculate the relative atomic mass ( $A_r$ ) for zinc.

ISOTOPE	ISOTOPIIC MASS	ABUNDANCE (%)
$^{64}\text{Zn}$	63.93	49.2
$^{66}\text{Zn}$	65.93	27.7
$^{67}\text{Zn}$	66.93	4.0
$^{68}\text{Zn}$	67.93	18.5
$^{70}\text{Zn}$	69.93	0.6

$$\begin{aligned}
 A_r(\text{Zn}) &= \sum (\text{isotopic mass} \times \text{abundance \%}) / 100 \\
 &= \sum ((63.93 \times 49.2) + (65.93 \times 27.7) + (66.93 \times 4.0) + (67.93 \times 18.5) + (69.93 \times 0.6)) / 100 \\
 &= 31.45 + 18.26 + 2.68 + 12.57 + 0.42 \\
 &= 65.38
 \end{aligned}$$

**1.3** The two isotopes of Lithium,  $^6\text{Li}$  and  $^7\text{Li}$ , have relative isotopic masses of 6.015 and 7.016. Their abundance in nature is 7.59% and 92.41%. Calculate the relative atomic mass ( $A_r$ ) for Lithium

$$\begin{aligned}
 A_r(\text{Zn}) &= \sum (\text{isotopic mass} \times \text{abundance \%}) / 100 \\
 &= \sum ((6.015 \times 7.59) + (7.016 \times 92.41)) / 100 \\
 &= 0.457 + 6.48 \\
 &= 6.94
 \end{aligned}$$

Table 1.2 Isotopes of some different elements.

Name of Isotope	Symbol	Abundance in nature %	Atomic Number (Z)	Mass Number (A)	Number of protons	Number of neutrons	Number of electrons in neutral atom
hydrogen – 1	${}^1_1\text{H}$	99.9885	1	1	1	0	1
hydrogen – 2	${}^2_1\text{H}$	0.0115	1	2	1	1	1
lithium – 6	${}^6_3\text{Li}$	7.59	3	6	3	3	3
lithium – 7	${}^7_3\text{Li}$	92.41	3	7	3	4	3
aluminium – 27	${}^{27}_{13}\text{Al}$	100.0	13	27	13	14	13
chlorine – 35	${}^{35}_{17}\text{Cl}$	75.76	17	35	17	18	17
chlorine – 37	${}^{37}_{17}\text{Cl}$	24.24	17	37	17	20	17
uranium – 235	${}^{235}_{92}\text{U}$	0.720	92	235	92	143	92
uranium – 238	${}^{238}_{92}\text{U}$	92.274	92	238	92	146	92

### Question 1.1

Indicate the number of protons, neutrons and electrons for the following neutral atoms:

- (a)  ${}^7_3\text{Li}$  \_\_\_\_\_ protons, \_\_\_\_\_ neutrons, \_\_\_\_\_ electrons
- (b)  ${}^{14}_7\text{N}$  \_\_\_\_\_ protons, \_\_\_\_\_ neutrons, \_\_\_\_\_ electrons
- (c)  ${}^{19}_9\text{F}$  \_\_\_\_\_ protons, \_\_\_\_\_ neutrons, \_\_\_\_\_ electrons
- (d)  ${}^{35}_{17}\text{Cl}$  \_\_\_\_\_ protons, \_\_\_\_\_ neutrons, \_\_\_\_\_ electrons

### Question 1.2

Complete the following table:

Isotope	Name of Isotope	Z Atomic No.	A Mass No.	Number of protons	Number of neutrons
${}^{12}_6\text{C}$	Carbon – 12	6	12	6	6
${}^{14}_6\text{C}$	Carbon – 14				
${}^{24}_{12}\text{Mg}$					
	Argon – 40	18	40		
${}^{27}_{13}\text{Al}$					
	Cobalt – 59	27			

### Question 1.3

The relative masses for the two isotopes of bromine and their abundance are:

Bromine-79 : 78.92 and 50.69%    Bromine-81 : 80.92 and 49.31%

Use this data to determine the relative atomic mass ( $A_r$ ) for bromine.

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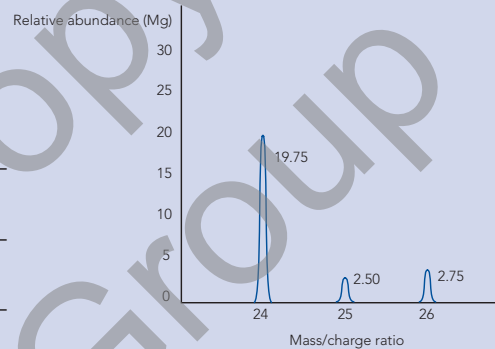
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### Question 1.4

The mass spectrum for magnesium is shown at right. The relative isotopic masses are  $^{24}\text{Mg}$  (23.99),  $^{25}\text{Mg}$  (24.99) and  $^{26}\text{Mg}$  (25.98).

Using the peak heights indicated determine:

- (a) Percentage abundance for each isotope
- (b) Relative atomic mass ( $A_r$ ) for Mg.



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### Question 1.5

An element X has two isotopes,  $^{69}\text{X}$  and  $^{71}\text{X}$ .

Draw a mass spectrum for these isotopes on the blank graph grid at right. The relative abundances are 60.1% and 39.9% and the isotopic masses 68.92 and 70.92 respectively. Determine  $A_r$  for element X

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### Question 1.6

There are two isotopes of copper; copper-63 and copper-65. Their isotopic masses are 62.93 and 64.93 respectively. The relative atomic mass for copper is 63.55. Use this data to determine the percentage abundance of each isotope of copper

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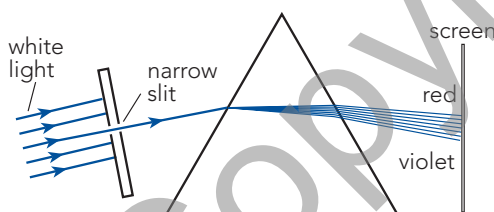
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## 1.5 ATOMIC STRUCTURE AND LIGHT SPECTRA

### The Nature of Light

We are all familiar with the colours of the rainbow and the multitude of colours in a fireworks display. But how are these different colours formed? The way electrons are arranged in atoms, and the ability of all atoms to absorb and emit energy, provides an answer. To better understand colour and spectra we need to briefly consider the nature of light.

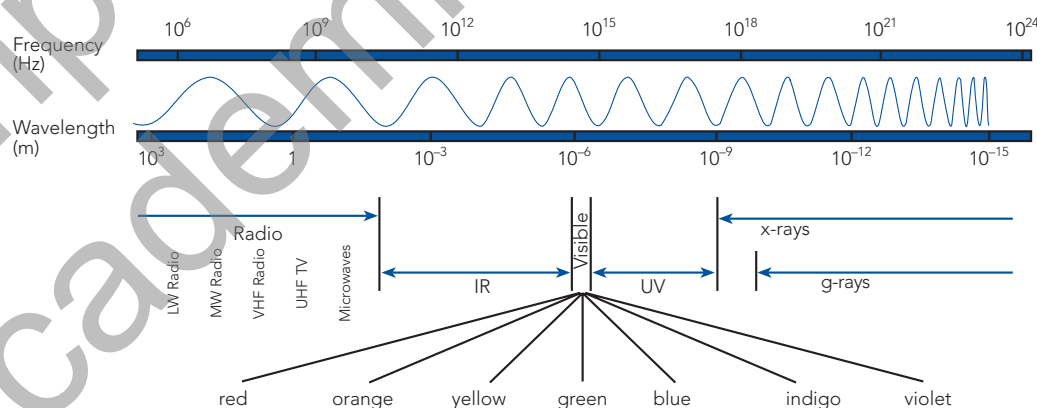
Light can be described as being both wave like and particle like in nature and makes up a small part of the overall electromagnetic spectrum (see below). Different colours of light, or other radiation, can all be considered as waves of a particular wavelength and frequency. It can also be said that each of the colours of light, or other radiation, are made up of a stream of particles called photons. Photon energies vary; the greater the frequency of the radiation, the greater the individual photon energies.



**Figure 1.5** Dispersion of white light by a prism. Light is a small part of the electromagnetic spectrum visible to the eye. The glass prism disperses the light into its component colours creating a continuous emission spectrum.

### The Electromagnetic Spectrum

Although not visible to the eye, there exists other radiation on either side of the visible spectrum. All radiation, like light, can travel through space. Radio waves, microwaves, ultraviolet waves and X-rays are all part of the electromagnetic spectrum and travel at the speed of light ( $3 \times 10^8 \text{ ms}^{-1}$  in a vacuum).

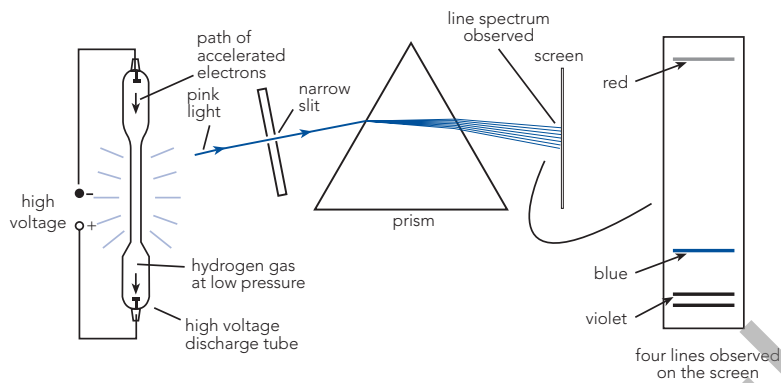


**Figure 1.6** The Electromagnetic Spectrum. All radiation travels at the speed of light. Relatively, radio waves have large wavelengths (low frequencies) while X-rays have very short wavelengths (very high frequencies). Photon energies increase with frequency, hence X-Rays can be considered to be made up of high energy photons while radio waves are made up of low energy photons.

### The Hydrogen Spectrum

If an element such as hydrogen is heated by an electric current in a discharge tube, light is emitted. The spectra produced when this light is analysed through a prism is line emission spectra. In the visible range the spectra consists of four distinct coloured lines on a black background. Each of these coloured lines indicates light of a particular frequency, or energy, being given off by the atoms of hydrogen.

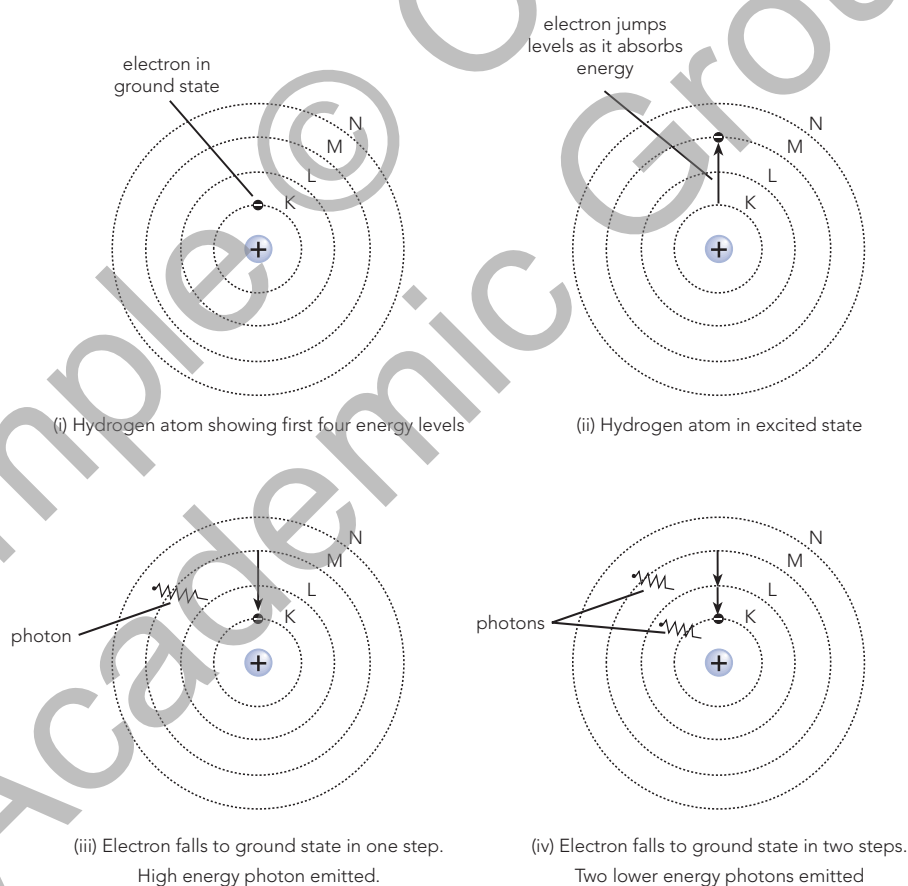




**Figure 1.7** Observing the line emission spectrum for Hydrogen.

### The Bohr model of the atom

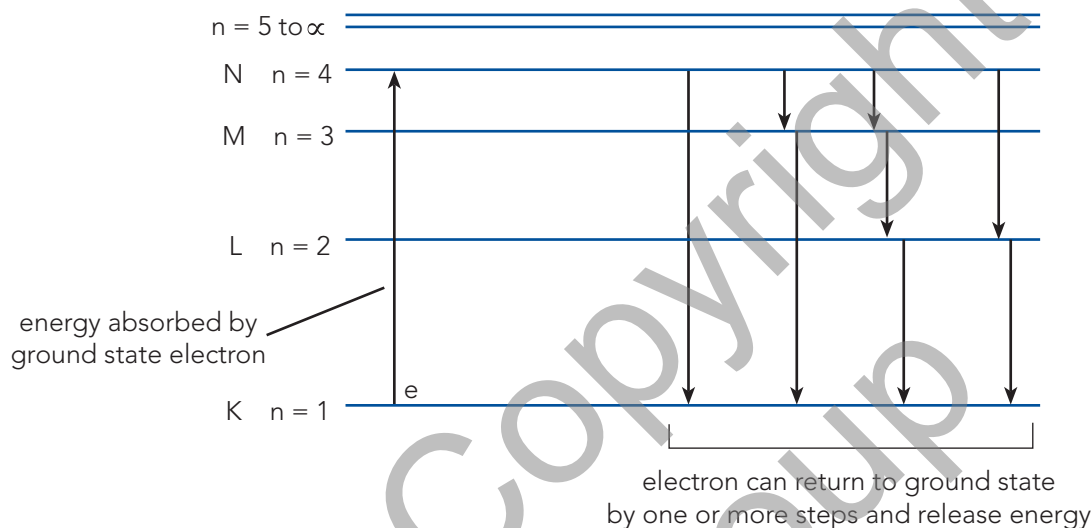
In developing his theory, Neils Bohr was particularly keen on being able to explain the line spectra he observed from a hydrogen discharge tube. He proposed that the spectra was due to the movement of excited electrons of the hydrogen atoms falling back to their normal, or stable state, within the atom. The atoms electrons must have been initially excited to higher energy levels by the collisions of the atoms with the electrons produced and accelerated by the discharge tube.



**Figure 1.8** Atomic energy levels and spectra. Atoms can absorb energy through heating, light or electrical discharge. Only specific amounts of energy are absorbed by the electrons as they move to possible higher levels. In the excited state atoms are unstable and electrons return to their ground state within a few nanoseconds. They can fall in one step or more but in each case a photon of light is emitted. The photon energy is the same as that lost by the electron falling. In the case shown above there are three possible photon energies created corresponding to three distinct spectral lines or colours.

Bohr proposed that the electrons of atoms can only exist in specific energy levels. These levels, also referred to as shells, are denoted 1, 2, 3, ... or K, L, M, .... as we go outward from the nucleus. Electrons in atoms are normally in their lowest possible energy level or ground state. However, they can absorb energy and jump to higher levels in which case the atom is said to be in an excited, but unstable, state. The electrons quickly fall back to their ground state, sometimes in more than one step, and emit light of a specific frequency corresponding to the energy jump.

Some possible electron transitions for the hydrogen atom are shown below.



**Figure 1.9** Electron transitions in hydrogen and spectra. When hydrogen atoms absorb energy its electron can jump to any of the available energy levels including leaving the atom altogether (ionisation). In the example above an electron absorbs energy and jumps to the  $n = 4$  level. Since it is not stable at this level it returns to the ground state. It can do so in a variety of steps. When considering a large number of atoms all possible pathways occur and we observe all the characteristic spectral lines for hydrogen.

#### Question 1.7

- (a) Which visible colour is least refracted by a prism? \_\_\_\_\_
- (b) Which has the greater photon energy; IR or UV? \_\_\_\_\_
- (c) Which is the longest wavelength light; blue or orange? \_\_\_\_\_
- (d) How many visible lines are in the hydrogen spectrum? \_\_\_\_\_

#### Question 1.8

An excited electron in a hydrogen atom can return to its ground state directly or by a sequence of steps. Photons of different energies are emitted depending on the difference in energies between the levels traversed. Determine the number of possible photon energies emitted if an electron is initially excited to the:

- (a) third level (n = 3) \_\_\_\_\_
- (b) fourth level (n = 4) \_\_\_\_\_
- (c) fifth level (n = 5) \_\_\_\_\_

## 1.6 ELECTRON ARRANGEMENTS IN ATOMS

The way that electrons are arranged in atoms is very important as it determines chemical behaviour. The nucleus is not involved in chemical reactions and is not affected by them.

Although they cannot say exactly where an electron is and how fast it is moving, scientists have established that electrons can only exist in specific **energy levels** within the atom. In 1912 Danish physicist Niels Bohr proposed a theory of the atom which was able to explain more clearly the behaviour of electrons in atoms and was consistent with quantum theory. He proposed that:

- electrons can only exist in specific energy levels
- electrons could be excited from one level to another by specific amounts of energy corresponding to the difference in energy levels
- energy, in the form of photons, is emitted whenever an electron moves from a high energy level to a lower one.

The Bohr theory helped explain the observation of emission and absorption spectra and is still the basis of today's atomic theory. However, a refinement of the Bohr model of the atom based on quantum mechanics (Erwin Schrodinger, 1926) better describes the nature of atoms, particularly multi electron atoms.

This refined model of the atom states that electrons move in regions of space called orbitals rather than in specific orbits. The quantum mechanical model of the atom states that within an atom there exists:

- principal energy levels, or shells, denoted 1, 2, 3, ... or K, L, M, ...
- a maximum number of electrons for any level given by the formula  $2n^2$ , where  $n$  is the energy level number
- energy sublevels, or subshells, denoted s, p, d, f, ...
- orbitals that make up the sublevels: s (1 orbital), p (3 orbitals), d (5 orbitals) and f (7 orbitals)
- each orbital can hold a maximum of 2 electrons.

*Table 1.3 Shells, subshells and orbitals in atoms*

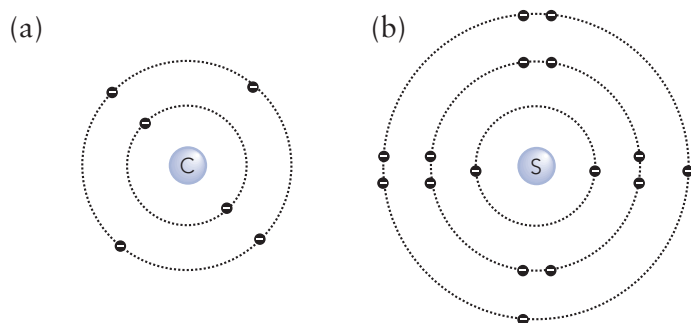
Energy level (first 4)	Shell Symbol	Subshell*	Number of orbitals in subshell*	Maximum number of electrons ( $2n^2$ )
1	K	1s	1	2
2	L	2s 2p	1 3	8
3	M	3s 3p 3d	1 3 5	18
4	N	4s 4p 4d 4f	1 3 5 7	32

\* May not be required for your course.



## Worked Example

### 1.4 Show the electron arrangement around: (a) carbon and (b) sulfur



These are sometimes called electron energy level diagrams. Energy level diagrams are sometimes drawn with electrons in pairs, showing they occupy the same orbital. This is only done if an energy level contains more than 4 electrons. An abbreviated way of writing the electron structure of an atom is to give its electron configuration. For example, as shown in Table 1.4, the electron configuration for sodium is given as 2, 8, 1.

### 1.5 Write the electron configuration for the two atoms in example 1.4.

- (a) carbon            2 , 4  
(b) sulfur            2 , 8 , 6

### 1.6 How many electrons are there in the outermost energy level for the atoms nitrogen, fluorine and sodium?

Determine electron configurations first. Hence:

- N    2 , 5    ∴    5 electrons in outer level  
O    2 , 6    ∴    6 electrons in outer level  
Na   2 , 8 , 1 ∴    1 electron in outer level

#### Question 1.9

Write the electron configuration for the following elements. To help you, use the periodic table to determine the atomic number ( $Z$ ) of each element and hence the number of electrons for a neutral atom of that element.

- (a) Carbon \_\_\_\_\_ (d) Fluorine \_\_\_\_\_  
(b) Chlorine \_\_\_\_\_ (e) Calcium \_\_\_\_\_  
(c) Magnesium \_\_\_\_\_ (f) Boron \_\_\_\_\_

#### Question 1.10

How many electrons are there in the outermost energy level of:

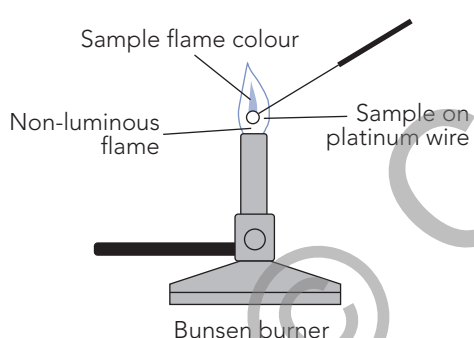
- (a) Silicon \_\_\_\_\_ (d) Fluorine \_\_\_\_\_  
(b) Aluminium \_\_\_\_\_ (e) Chlorine \_\_\_\_\_  
(c) Sulfur \_\_\_\_\_ (f) Carbon \_\_\_\_\_

## 1.7 FLAME TESTS

As we have learnt, the colours we may observe in a flame are due to electron transitions within excited gaseous atoms. A flame test can be used to identify, although only qualitatively, a range of metal ions due to the characteristic colours produced when their salts are burnt. A small amount of the substance being tested is placed on a platinum wire and burnt in a very hot non-luminous Bunsen flame. Typical flame colours are yellow for sodium, red for barium and blue/green for copper.

Only a small number of metal ions can be distinguished in this way as a Bunsen flame is not hot enough to excite the electrons of many atoms. It is also difficult to distinguish between very similar colours. For example, reddish colours are produced by calcium, strontium and lithium compounds. The colours may also be affected by the presence of traces of other ions. However the use of reference flames of known compounds burnt under the same conditions will help. Observation of the flames in a darkened room using a spectroscope will also provide more certainty.

*Table 1.5 Typical flame colours for some metals.*



*Figure 1.11 Flame testing. Samples placed in a hot non-luminous flame give characteristic colours for different metallic ions.*

METAL IONS	FLAME COLOUR
Boron	Bright green
Barium	Pale green
Calcium	Orange/Red
Copper	Blue/Green
Iron	Gold
Lithium	Red/Crimson
Potassium	Violet/Lilac
Sodium	Yellow
Strontium	Deep red

### Question 1.11

Use your understanding of atomic structure to explain how different colours are produced when different salts are placed in a hot Bunsen flame.

### Question 1.12

Two different salts, sodium chloride and sodium nitrate, each give an intense yellow colour when flame tested. Explain why the same colour is observed.

### Question 1.13

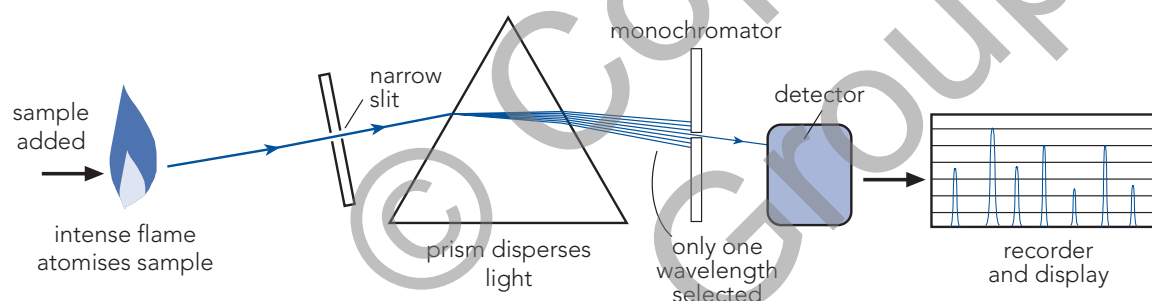
Describe a simple test that would distinguish between calcium nitrate and barium chloride salts.

## 1.8 ATOMIC EMISSION SPECTROMETRY (AES)

As mentioned above the use of a spectroscope for the visual observation of spectra from coloured flames is very useful. However it is largely qualitative and is limited only to the visible spectrum. A more efficient and quantitative method of analysing elements in a flame is the use of the atomic emission spectrometer.

The samples to be analysed are heated to much higher temperatures and the characteristic light is passed through a prism or diffraction grating, much like the spectroscope. However, instead of viewing all the spectra as a whole, a device called a monochromator allows only single wavelengths at a time to pass through. The spectra can then be detected and recorded in various ways.

The intensity of each spectral line can be recorded on film using a spectrograph or more conveniently as a graphic display using a spectrometer. In the spectrograph the darkness on the negative for a particular wavelength indicates intensity and the abundance of the element causing it. In the spectrometer the detected light from the monochromator is converted to an electrical current and then displayed digitally or graphically. Hence the atomic emission spectrometer provides a more practical and quantitative method for identifying most metalloid elements (see figure 1.12 below).



*Figure 1.12 The atomic emission spectrometer. The sample solution is drawn into the flame as a very fine spray and becomes vaporised and atomised. The excited atoms emit light which is characteristic of the elements in the sample. The prism disperses the light into its characteristic spectra with the monochromator allowing each wavelength to be detected and recorded separately.*

## 1.9 ATOMIC ABSORPTION SPECTROMETRY (AAS)

### Absorption Spectra

As we have seen, white light can be dispersed by a prism and a continuous emission spectrum is produced (figure 1.5). However, if the white light passes through a gas sample before being dispersed, then the resulting spectra will have dark lines present within an otherwise continuous spectrum. The dark lines (really an absence of light) are in the exact position that bright lines would appear in the emission spectrum of the sample gas used. This is called absorption spectra and can be used to identify the gaseous elements through which the light has passed.

A classic example of absorption spectra are the dark lines, called Fraunhofer lines, which appear within the continuous spectrum of sunlight. The cause of the dark lines is the absorption of specific frequencies of radiation as the light from the sun passes through its large gaseous atmosphere. In this way the presence of both hydrogen and helium on the sun were identified.

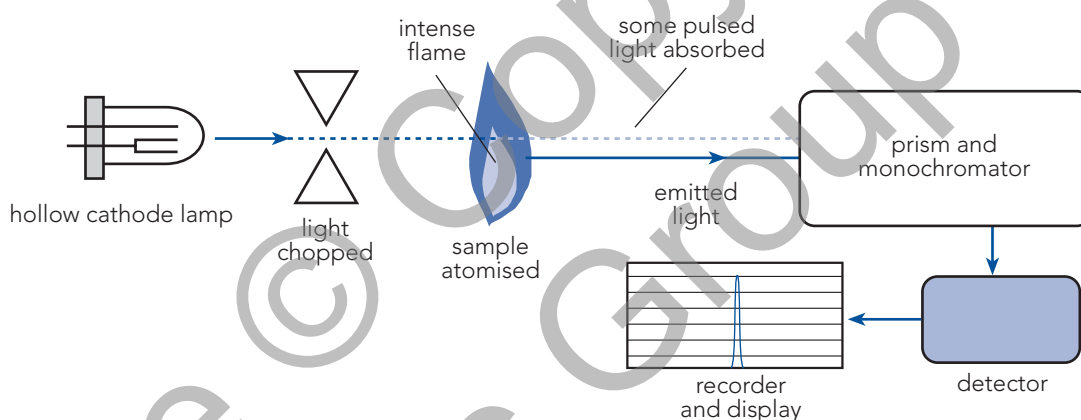
### Atomic Absorption Spectrometer

Both emission and absorption spectroscopy are a useful means of analysing substances. However the accurate measurement of very small concentrations of metallic elements is quite difficult. In 1952 a very sensitive technique, called atomic absorption spectrometry, was developed by Alan Walsh, an Australian scientist of the CSIRO division of Chemical Physics. The technique did not

involve the usual absorption from white light as a source, but rather, absorption of light emitted by the element being analysed.

The atomic absorption spectrometer (AAS) was first demonstrated at the Melbourne University in 1954. An essential component of the spectrometer is the hollow cathode lamp whose cathode is coated with the metal being investigated (see figure 1.13 below). Hence the light which passes through the atomised sample contains the exact wavelengths that can be absorbed by the metal being analysed. The amount of cathode light absorbed by the metal atoms gives a measure of their concentration. Importantly, the detectors are able to distinguish between the cathode light left over after absorbance and the light naturally emitted by the gaseous atoms in the flame returning to their ground state. This is achieved by pulsing (or chopping) the light from the cathode so that the detector can distinguish it from the continuous beam from the flame.

The atomic absorption spectrometer is one of the most important scientific instruments developed in Australia. It provides a sensitive and high speed technique for the measurement of small traces of metals down to a few parts per billion. Today it is an essential analytical tool used in agriculture, mining, industry, hospitals and chemical laboratories.



*Figure 1.13 The atomic absorption spectrometer. Light from the hollow cathode lamp has the specific wavelengths that the metal being analysed can absorb. The detector effectively measures the amount of this light which is absorbed and this indicates the concentration of the metal atoms in the sample.*

#### Question 1.14

Explain the purpose of each of the following in the atomic emission spectrometer.

- (a) Prism \_\_\_\_\_
- (b) Monochromator \_\_\_\_\_

#### Question 1.15

Explain the reason of each of the following in the atomic absorption spectrometer.

- (a) The cathode of the lamp is coated with the metal being analysed.  
\_\_\_\_\_
- (b) Light from the lamp is pulsed \_\_\_\_\_