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Chapter 1

Atomic structure

Background

e-Learning

Objectives

Chemistry is a science of change. Over the centuries people have heated rocks, distilled juices and probed solids, liquids and gases with electricity. From all this activity we have gained a great wealth of new materials – metals, medicines, plastics, dyes, ceramics, fertilisers, fuels and many others (Figure 1.1). But this creation of new materials is only part of the science and technology of chemistry. Chemists also want to understand the changes, to find patterns of behaviour and to discover the innermost nature of the materials.

Figure 1.1 All of these useful products, and many more, contain chemicals that have been created by applying chemistry to natural materials. Chemists must also find answers to problems caused when people misuse chemicals.

Our 'explanations' of the chemical behaviour of matter come from reasoning and model-building based on the evidence available from experiments. The work of scientists has shown us the following.

- All known materials, however complicated and varied they appear, can be broken down into the fundamental substances we call **elements**. These elements cannot be broken down further into simpler substances. So far, about 115 elements are known. Most exist in combinations with other elements in **compounds** but some, such as gold, nitrogen, oxygen and sulfur, are also found in an uncombined state. Some elements would not exist on Earth without the artificial use of nuclear reactions. Chemists have given each element a symbol. This symbol is usually the first one or two letters of the name of the element; some are derived from their names in Latin. Some examples are:

Element	Symbol
carbon	C
lithium	Li
iron	Fe (from the Latin *ferrum*)
lead	Pb (from the Latin *plumbum*)

- Groups of elements show patterns of behaviour related to their atomic masses. A Russian chemist, Dmitri Ivanovich Mendeleev, summarised these patterns by arranging the elements into a 'Periodic Table'. Modern versions of the Periodic Table are widely used in chemistry. (A Periodic Table is shown in the Appendix and explained, much more fully, in Chapter 7.)
- All matter is composed of extremely small particles, called atoms. About 100 years ago, the accepted model for atoms included the assumptions that (i) atoms were tiny particles, which could not be divided further or destroyed, and (ii) all atoms of the same element were identical. This model was very helpful, but gave way to better models, as science and technology produced new evidence. This evidence has shown scientists that atoms have other particles inside them – they have an internal structure.

Scientists now believe that there are two basic types of particles – 'quarks' and 'leptons'. These are the building blocks from which everything is made, from microbes to galaxies. For many explanations or predictions, however, scientists use a model of atomic structure in which atoms are made of electrons, protons and neutrons. Protons and neutrons are made from quarks, and the electron is a member of the family of leptons.

Discovering the electron

Electrolysis – the effect of electric current in solutions

When electricity flows in an aqueous solution of silver nitrate, for example, silver metal appears at the negative electrode (cathode). This is an example of *electrolysis* and the best explanation is that:

- the silver exists in the solution as positively charged particles known as **ions** (Ag^+)
- one silver ion plus one unit of electricity gives one silver atom.

The name 'electron' was given to this unit of electricity by the Irish scientist George Johnstone Stoney in 1891.

Study of cathode rays

At normal pressures gases are usually very poor conductors of electricity, but at low pressures they conduct quite well. Scientists, such as William Crookes, first studied the effects of passing electricity through gases at low pressures. They saw that the glass of the containing vessel opposite the cathode (negative electrode) glowed when the applied potential difference (voltage) was sufficiently high.

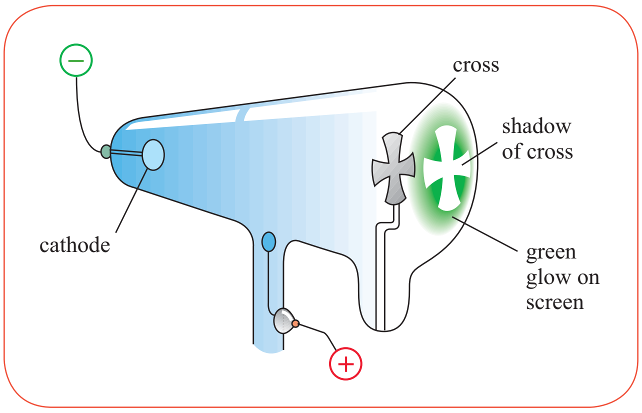

Figure 1.2 Cathode rays cause a glow on the screen opposite the cathode, and the 'Maltese Cross' casts a shadow. The shadow will move if a magnet is brought near to the screen. This shows that the cathode rays are deflected by a magnetic field. The term 'cathode ray' is still familiar today, as in 'cathode-ray oscilloscopes'.

A solid object, placed between the cathode and the glow, casts a shadow (Figure 1.2). They proposed that the glow was caused by rays coming from the cathode and called these *cathode rays*.

At the time there was some argument about whether cathode rays are waves, similar to visible light rays, or particles. The most important evidence is that they are strongly deflected by a magnetic field. This is best explained by assuming that they are streams of electrically charged particles. The direction of the deflection shows that the particles in cathode rays are negatively charged.

J. J. Thomson's *e*/*m* experiment

The great leap in understanding came in 1897, at the Cavendish Laboratory in Cambridge (Figure 1.3 and Figure 1.4). J. J. Thomson measured the deflection of a narrow beam of cathode rays in both magnetic and electric fields. His results allowed him to calculate the charge-to-mass ratio (e/m) of the particles. Their charge-to-mass ratio was found to be exactly the same, whatever gas or type of electrode was used in the experiment. The cathode-ray particles had a tiny mass, only approximately 1/2000th of the mass of a hydrogen atom. Thomson then decided to call them **electrons** – the name suggested earlier by Stoney for the 'units of electricity'.

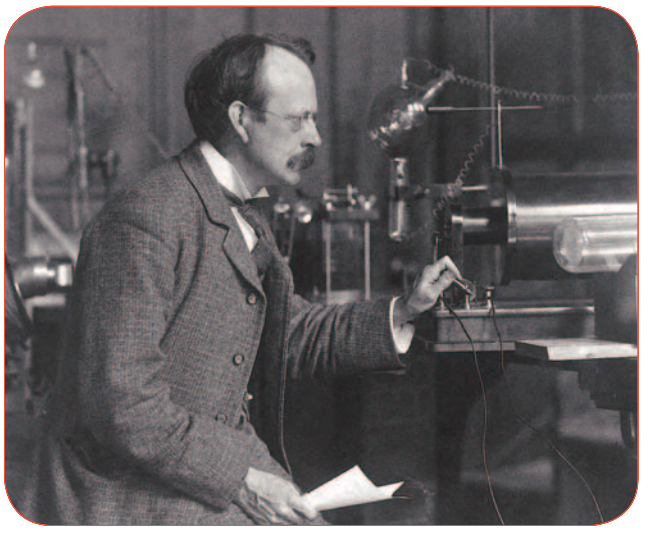

Figure 1.3 Joseph (J.J.) Thomson (1856–1940) using his cathode-ray tube.

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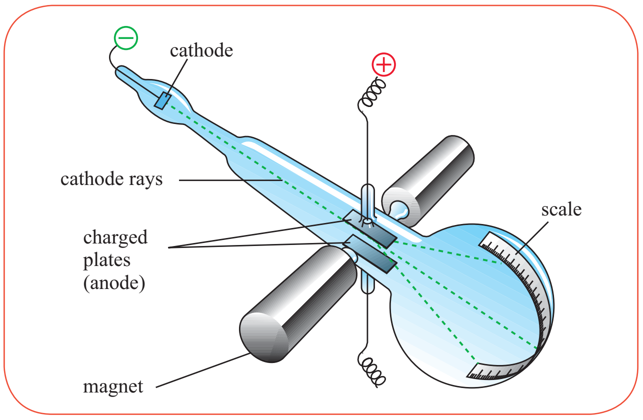

Figure 1.4 A drawing of Thomson's apparatus. The electrons move from the hot cathode (negative) through slits in the anode (positive).

Millikan's 'oil-drop' experiment

The electron charge was first measured accurately in 1909 by the American physicist Robert Millikan using his famous 'oil-drop' experiment (Figure 1.5). He found the charge to be 1.602×10^{-19} C (coulombs). The mass of an electron was calculated to be 9.109×10^{-31} kg, which is 1/1837th of the mass of a hydrogen atom.

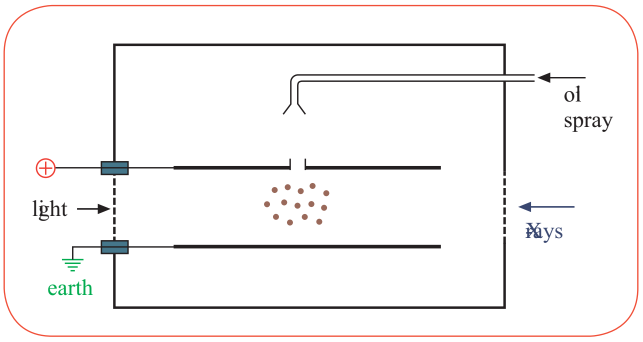

Figure 1.5 Oil drops which were sprayed into the container acquired a negative charge. The drops remained stationary when the upward force of attraction to the positive plates equalled the downward force due to gravity. Calculations on the forces allowed Millikan to find the charges on the drops. These were multiples of the charge on an electron.

Discovering protons and neutrons

New atomic models: 'plum-pudding' or 'nuclear' atom

Before electrons were discovered every atom was believed to be indivisible and to be made of the same 'material' all the way through – like a snooker ball. The discoveries about electrons demanded new models for atoms. If there are negatively charged electrons in all electrically neutral atoms, there must also be a positively charged part. For some time the most favoured atomic model was J. J. Thomson's 'plum-pudding', in which electrons (the 'plums') were embedded in a 'pudding' of positive charge (Figure 1.6).

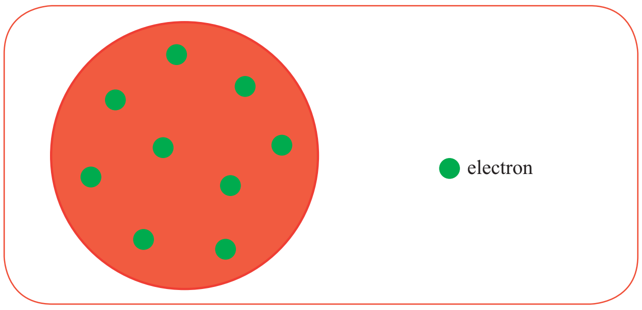

Figure 1.6 J. J. Thomson's 'plum-pudding' model of the atom. The electrons (plums) are embedded in a sphere of uniform positive charge.

Then, in 1909, came one of the experiments that changed everything. Two members of Ernest Rutherford's research team in Manchester University, Hans Geiger and Ernest Marsden, were investigating how α-particles (α is the Greek letter alpha) from a radioactive source were scattered when fired at very thin sheets of gold and other metals (Figure 1.7).

They detected the α-particles by the small flashes of light (called 'scintillations') that they caused on impact with a fluorescent screen. Since (in atomic terms) α-particles are heavy and energetic, Geiger and Marsden

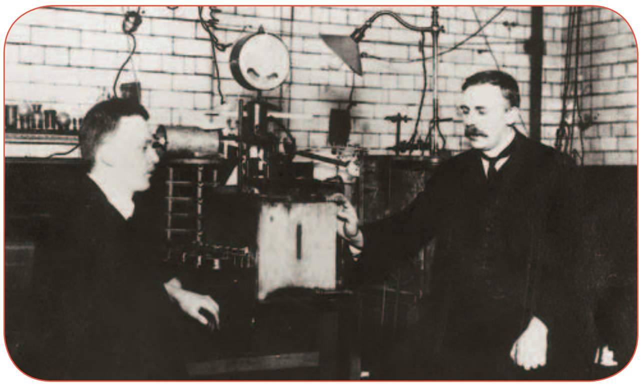

Figure 1.7 Ernest Rutherford (right) and Hans Geiger using their apparatus for detecting α-particle deflections. Interpretation of the results led Rutherford to propose the nuclear model for atoms.

were not surprised that most particles passed through the metal with only slight deflections in their paths. These deflections could be explained, by the ‘plum-pudding’ model of the atom, as small scattering effects caused while the positive α-particles moved through the diffuse mixture of positive charge and electrons.

However, Geiger and Marsden also noticed some large deflections. A few (about one in 20 000) were so large that scintillations were seen on a screen placed on the same side of the gold sheet as the source of positively charged α-particles. This was unexpected. Rutherford said: ‘it was almost as incredible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you!’ (Figure 1.8).

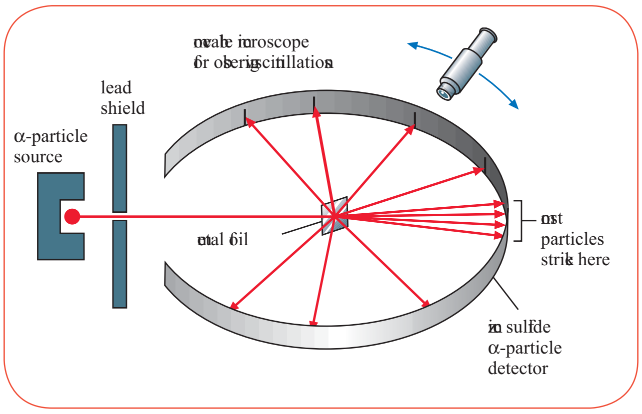

Figure 1.8 Geiger and Marsden’s experiment, which investigated how α-particles are deflected by thin metal foils.

The plum-pudding model, with its diffuse positive charge, could not explain the surprising Geiger–Marsden observations. However, Rutherford soon proposed his convincing nuclear model of the atom. He suggested that every atom consists largely of empty space (where the electrons are) and that the mass is concentrated into a very small, positively charged, central core called the **nucleus**. The nucleus is about 10 000 times smaller than the atom itself – similar in scale to a marble placed at the centre of an athletics stadium.

Most α-particles will pass through the empty space in an atom with very little deflection. When an α-particle approaches on a path close to a nucleus, however, the positive charges strongly repel each other and the α-particle is deflected through a large angle (Figure 1.9).

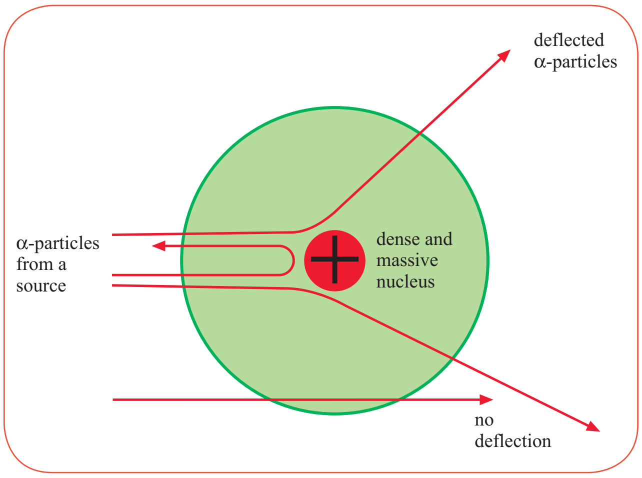

Figure 1.9 Ernest Rutherford’s interpretation of the Geiger–Marsden observations. The positively charged α-particles are deflected by the tiny, dense, positively charged nucleus. Most of the atom is empty space.

Nuclear charge and ‘atomic’ number

In 1913, Henry Moseley, a member of Rutherford’s research team in Manchester, found a way of comparing the positive charges of the nuclei of atoms of different elements. The charge increases by one unit from element to element in the Periodic Table. Moseley showed that the sequence of elements in the Table is related to the nuclear charges of their atoms, rather than to their relative atomic masses (see Chapter 7). The size of the nuclear charge was then called the **atomic number** of the element. Atomic number defined the position of the element in the Periodic Table.

Particles in the nucleus

The proton

After he proposed the nuclear atom, Rutherford reasoned that there must be particles in the nucleus which are responsible for the positive nuclear charge. He and Marsden fired α-particles through hydrogen, nitrogen and other materials. They detected new particles with positive charge and the approximate mass of a hydrogen atom. Rutherford eventually called these particles **protons**. A proton carries a positive charge of 1.602×10^{-19} C, equal in size but opposite in sign to the charge on an electron. It has a mass of 1.673×10^{-27} kg, about 2000 times as heavy as an electron.

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Each electrically neutral atom has the same number of electrons outside the nucleus as there are protons within the nucleus.

The neutron

The mass of an atom, which is concentrated in its nucleus, cannot depend only on protons; usually the protons provide around half of the atomic mass. Rutherford proposed that there is a particle in the nucleus with a mass equal to that of a proton but with zero electrical charge. He thought of this particle as a proton and an electron bound together.

Without any charge to make it 'perform' in electrical fields, detection of this particle was very difficult. It was not until 12 years after Rutherford's suggestion that, in 1932, one of his co-workers, James Chadwick, produced sufficient evidence for the existence of a nuclear particle with a mass similar to that of the proton but with no electrical charge (Figure 1.10). The particle was named the **neutron**.

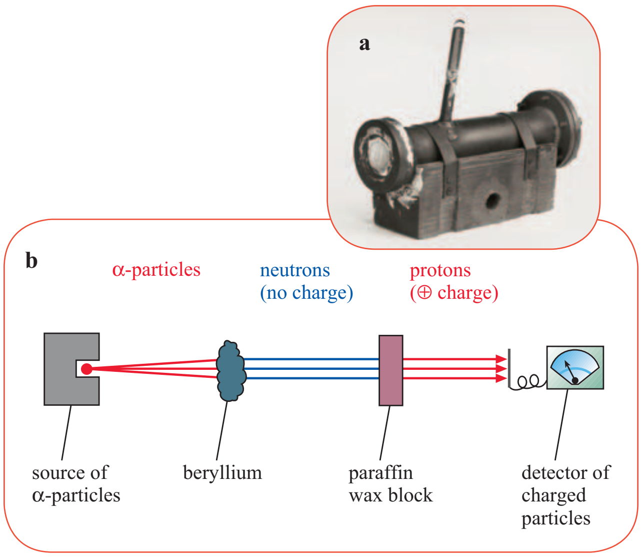

Figure 1.10 a Using this apparatus, James Chadwick discovered the neutron.
b Drawing of the inside of the apparatus. Chadwick bombarded a block of beryllium with α-particles ($^{4}_{2}He$). No charged particles were detected on the other side of the block. However, when a block of paraffin wax (a compound containing only carbon and hydrogen) was placed near the beryllium, charged particles were detected and identified as protons (H^+). Alpha-particles had knocked neutrons out of the beryllium, and in turn these had knocked protons out of the wax.

Atomic and mass numbers

Atomic number (*Z*)

The most important difference between atoms of different elements is in the number of protons in the nucleus of each atom. The number of protons in an atom determines the element to which the atom belongs. The atomic number of an element shows:

- the number of protons in the nucleus of an atom of that element
- the number of electrons in a neutral atom of that element
- the position of the element in the Periodic Table.

Mass number (*A*)

It is useful to have a measure for the total number of particles in the nucleus of an atom. This is called the **mass number**. For any atom:

- the mass number is the sum of the number of protons and the number of neutrons.

Summary table

Particle name	Relative mass	Relative charge
electron	negligible (about 1/2000th the mass of a proton)	–1
proton	1	+1
neutron	1	0

Isotopes

In Rutherford's model of the atom, the nucleus consists of protons and neutrons, each with a mass of one atomic unit. The relative atomic masses of elements should then be whole numbers. It was thus a puzzle why chlorine has a relative atomic mass of 35.5.

The answer is that atoms of the same element are not all identical. In 1913, Frederick Soddy proposed that atoms of the same element could have different atomic masses. He named such atoms **isotopes**. The word means 'equal place', i.e. occupying the same place in the Periodic Table and having the same atomic number.

The discovery of protons and neutrons explained the existence of isotopes of an element. In isotopes of

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one element, the number of protons must be the same, but the number of neutrons will be different.

Remember:

atomic number (Z) = number of protons

mass number (A) = number of protons + number of neutrons

Isotopes are atoms with the same atomic number, but different mass numbers. The symbol for isotopes is shown as:

$^{\text{mass number}}_{\text{atomic number}}\text{X}$ or $^{A}_{Z}\text{X}$

For example, hydrogen has three isotopes:

	Protium	Deuterium	Tritium
	$^{1}_{1}\text{H}$	$^{2}_{1}\text{H}$	$^{3}_{1}\text{H}$
protons	1	1	1
neutrons	0	1	2

It is also common practice to identify isotopes by name or symbol plus mass number only. For example, uranium, the heaviest naturally occurring element (Z=92), has two particularly important isotopes of mass numbers 235 and 238. They are often shown as uranium-235 and uranium-238, as U-235 and U-238 or as ^{235}U and ^{238}U.

Numbers of protons, neutrons and electrons

It is easy to calculate the composition of a particular atom or ion:

number of protons = Z

number of neutrons = $A-Z$

number of electrons in neutral atom = Z

number of electrons in positive ion = Z − charge on ion

number of electrons in negative ion = Z + charge on ion

For example, magnesium is element 12; it is in Group 2, so it tends to form doubly charged (2+) ions. The ionised isotope magnesium-25 thus has the full symbol:

$^{25}_{12}\text{Mg}^{2+}$,

and

number of protons = 12

number of neutrons = 13

number of electrons = 10

SAQ

1 a What is the composition (numbers of electrons, protons and neutrons) of neutral atoms of the two main uranium isotopes, U-235 and U-238? Hint

b What is the composition of the ions of potassium-40 (K^+) and chlorine-37 (Cl^-)? (Use the Periodic Table in the Appendix for the atomic numbers.) Hint

Answer

Counting atoms and molecules

If you have ever had to sort and count coins, you will know that it is a very time-consuming business! Banks do not need to count sorted coins, as they can quickly check the amount by weighing. Chemists are also able to count atoms and molecules by weighing them. This is possible because atoms of different elements also have different masses.

We rely on tables of relative atomic masses for this purpose. *The* **relative atomic mass**, *A_r, of an element is the mass of the element relative to the mass of carbon-12; one atom of this isotope* (see page 5) *is given a relative isotopic mass of exactly 12.* The relative atomic masses, A_r, of the other elements are then found by comparing the average mass of their atoms with that of the carbon-12 isotope. Notice that we use the *average* mass of their atoms. This is because we take into account the abundance of their naturally occurring isotopes. Thus the precise relative atomic mass of hydrogen is 1.0079, whilst that of chlorine is 35.45. (Accepted relative atomic masses are shown on the Periodic Table in the Appendix.)

We use the term **relative isotopic mass** for the mass of an isotope of an element relative to carbon-12. For example, the relative isotopic mass of carbon-13 is 13.003. If the natural abundance of each isotope is known, together with their relative isotopic masses, we can calculate the relative atomic mass of the element as follows.

Chlorine, for example, occurs naturally as chlorine-35 and chlorine-37 with percentage natural abundances 75.5% and 24.5% respectively. So

$$\text{relative atomic mass} = \frac{(75.5 \times 35) + (24.5 \times 37)}{100}$$
$$= 35.5$$

SAQ

2 Naturally occurring neon is 90.9% neon-20, 0.3% neon-21 and 8.8% neon-22. Use these figures to calculate the relative atomic mass of naturally occurring neon.

Hint

Answer

The masses of different molecules are compared in a similar fashion. The **relative molecular mass**, M_r, of a compound is the mass of a molecule of the compound relative to the mass of an atom of carbon-12, which is given a mass of exactly 12.

To find the relative molecular mass of a molecule, we add up the relative atomic masses of all the atoms present in the molecule. For example, the relative molecular mass of methane, CH_4, is $12 + (4 \times 1) = 16$.

Where compounds contain ions, we use the term **relative formula mass**. Relative molecular mass refers to compounds containing molecules.

SAQ

3 Use the Periodic Table in the Appendix to calculate the relative formula mass of the following:

a magnesium chloride, $MgCl_2$

b copper sulfate, $CuSO_4$

c sodium carbonate, $Na_2CO_3.10H_2O$ ($10H_2O$ means ten water molecules).

Answer

Building with atoms

Nanotechnology is the design and creation of objects that are so small we measure them in nanometres.

It is difficult for us to imagine a nanometre (nm). The tiny dimensions involved in nanotechnology are mind-boggling. The nanometre is the unit of measurement used on an atomic level:

$1\,\text{nm} = 10^{-9}\,\text{m}$

In other words, a nanometre is a billionth of a metre (or a millionth of a millimetre, check your ruler!).

Nanotechnologists are now making machines that are less than 100 nm in size. The skills and techniques to manipulate atoms, and position them where we want them, have only recently been developed.

The possibilities are very exciting. Imagine tiny machines patrolling your bloodstream. They could eventually check out cells in our bodies and deliver medication exactly to where it is needed. However, the use of nanoparticles, in for example cosmetics, is worrying some people. They believe the particles might pass through layers of skin, allowing substances designed for your skin to get inside the body. So they want tougher rules for the testing of these products.

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Summary

Glossary

- Our current theory of the atom has developed from simpler theories; those early theories were changed or modified in the light of experimental results.
- Any atom has an internal structure with almost all of the mass in the nucleus, which has a diameter very much smaller than the diameter of the atom.
- The nucleus contains protons (positively charged) and neutrons (uncharged). Electrons (negatively charged) exist outside the nucleus.
- All atoms of the same element have the same atomic number (Z); that is, they have equal numbers of protons in their nuclei.
- The mass number (A) of an atom is the total number of protons and neutrons. Thus the number of neutrons = $A - Z$.
- The isotopes of an element are atoms with the same atomic number but different mass numbers. If neutral, they have the same number of protons and electrons but different numbers of neutrons.
- Atomic, isotopic and molecular masses are given relative to carbon-12, which has a mass of exactly 12.

Questions

1 Antimony, Sb, is a metal used in alloys to make lead harder. Bullets contain about 1% of antimony for this reason.

a Antimony has two main isotopes.

i What do you understand by the term isotopes? [1]

ii Copy and complete the table below to show the properties of particles that make up isotopes. [2]

Hint

	Proton	**Neutron**	**Electron**
Relative mass			
Relative charge			

b Relative atomic mass, A_r, can be used to compare the masses of atoms of different elements.

Hint

i Explain what you understand by the term *relative atomic mass*. [3]

ii The antimony in a bullet was analysed by a forensic scientist to help solve a crime. The antimony was found to have the following percentage composition by mass: ^{121}Sb, 57.21%; ^{123}Sb, 42.79%.
Calculate a value for the relative atomic mass of the antimony. Give your answer to four significant figures. [2]

OCR Chemistry AS (2811) June 2006 [Total 8]

Answer

continued

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2 Sulfur and sulfur compounds are common in the environment.

a A sample of sulfur from a volcano contained 88.0% by mass of ^{32}S and 12.0% by mass of ^{34}S. Copy and complete the table below to show the atomic structure of each isotope of sulfur. [2]

	Number of		
Isotope	**protons**	**neutrons**	**electrons**
^{32}S			
^{34}S			

b Calculate the relative atomic mass of the volcanic sulfur. Your answer should be given to three significant figures. [2]

OCR Chemistry AS (2811) June 2001 [Total 4]

Answer

3 Analysis of a sample of bromine in a mass spectrometer showed that it contained a mixture of the ^{79}Br and ^{81}Br isotopes in the proportions: ^{79}Br, 55.0%; ^{81}Br, 45.0%.
Calculate the relative atomic mass of bromine in this sample. [2]

OCR Chemistry AS (2811) Jan 2002 [Total 2]

Answer

4 A sample of element **B** was analysed in a mass spectrometer. The relative atomic mass of element **B** can be calculated from the results shown in the table below.

	Isotope 1	**Isotope 2**	**Isotope 3**
relative isotopic mass	58.0	60.0	62.0
percentage composition / %	68.2	27.3	4.5

Using the information in the table, calculate the relative atomic mass of this sample of **B**. Give your answer to three significant figures. [2]

OCR Chemistry AS (2811) June 2003 [Total 2]

Answer

5 Chemists use a model of an atom that consists of sub-atomic particles (protons, neutrons and electrons). The particles in each of the following pairs differ only in the number of protons or neutrons or electrons. Explain what the difference is within each pair.

a ^{6}Li and ^{7}Li [1]

b ^{32}S and $^{32}S^{2-}$ [1]

c $^{39}K^{+}$ and $^{40}Ca^{2+}$ [1]

[Total 3]

Answer

continued

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6 Here is one way in which scientists work:

- observations are made, usually from experiments
- a theory is suggested to explain these observations
- new observations are made – they either confirm or disprove the theory
- if the observations disprove the theory, a new theory is suggested.

Re-read the start of this chapter. Use the development of modern atomic theory to produce an essay that explains 'how science works'. The title of your essay is 'How scientists developed the modern theory of atomic structure'.

You should include:

– the original model of the atom
– the observations made by Crookes, Thomson and Millikan that led to the 'plum pudding' model
– the observations made by Geiger and Marsden that led to the 'nuclear atom' model
– Rutherford's ideas and Chadwick's observations that led to the 'protons, neutrons and electrons' model studied today at GCSE.

[Total max 10]

Answer