Collins

CHEMISTRY

AQA A-level Year 1 and AS

Student Book

Lyn Nicholls
Ken Gadd

CONTENTS

TO THE STUDENT

The aim of this book is to help make your study of advanced chemistry interesting and successful. It includes examples of modern issues, developments and applications that reflect the continual evolution of scientific knowledge and understanding. We hope it will encourage you to study science further when you complete your course.

USING THIS BOOK

Chemistry is fascinating, but complex – underpinned by some demanding ideas and concepts, and by a great deal of experimental data ('facts'). This mass of information can sometimes make its study daunting. So don't try to achieve too much in one reading session and always try to keep the bigger picture in sight.

There are a number of features in the book to help with this:

- Each chapter starts with a brief example of how the chemistry you will learn has been applied somewhere in the world, followed by a short outline of what you should have learned previously and what you will learn through the chapter.
- Important words and phrases are given in bold when used for the first time, with their meaning explained. There is also a glossary at the back of the book. If you are still uncertain, ask your teacher or tutor because it is important that you understand these words before proceeding.
- Throughout each chapter there are many questions, with the answers at the back of the book. These questions enable you to make a quick check on your progress through the chapter.
- Similarly, throughout each chapter there are checklists of key ideas that summarise the main points you need to learn from what you have just read.
- Where appropriate, worked examples are included to show how important calculations are done.
- There are many assignments throughout the book. These are tasks relating to pieces of text and data that show how ideas have been developed or applied. They provide opportunities to apply the science you have learned to new contexts, practise your maths skills and practise answering questions about scientific methods and data analysis.
- Some chapters have information about the 'required practical' activities that you need to carry out during your course. These sections provide the necessary background information about the apparatus, equipment and techniques that you need to be prepared to carry out the required practical work. There are questions that give you practice in answering questions about equipment, techniques, attaining accuracy, and data analysis.
- At the end of each chapter are practice questions. These are examination-style questions which cover all aspects of the chapter.

This book covers the requirements of AS Chemistry and the first year of A-level Chemistry. There are a number of sections, questions, assignments and practice questions that have been labelled 'Stretch and challenge', which you should try to tackle if you are studying for A-level. In places these go beyond what is required for the specification but they will help you build upon the skills and knowledge you acquire and better prepare you for further study beyond advanced level.

Good luck and enjoy your studies. We hope this book will encourage you to study chemistry further when you complete your course.

PRACTICAL WORK IN CHEMISTRY

While they may not all wear white coats or work in a laboratory, chemists and others who use chemistry in their work carry out experiments and investigations to gather evidence. They may be challenging established chemical ideas and models or using their skills, knowledge and understanding to tackle important problems.

Chemistry is a practical subject. Whether in the laboratory or in the field, chemists use their practical skills to find solutions to problems, challenges and questions. Throughout this course you will learn, develop and use these skills.

WRITTEN EXAMINATIONS

Your practical skills will be assessed in the written examinations at the end of the course. Questions on practical skills will account for about 15% of your marks at AS and 15% at A-level. The practical skills assessed in the written examinations are:

Independent thinking

- solve problems set in practical contexts
- apply scientific knowledge to practical contexts

Figure 1 *Most chemists and others who use chemistry in their work spend time in laboratories. Many also use their practical skills outside of a laboratory.*

Use and application of scientific methods and practices

- comment on experimental design and evaluate scientific methods
- present data in appropriate ways
- evaluate results and draw conclusions with reference to measurement uncertainties and errors
- identify variables including those that must be controlled

Numeracy and the application of mathematical concepts in a practical context

- plot and interpret graphs
- process and analyse data using appropriate mathematical skills
- consider margins of error, accuracy and precision of data

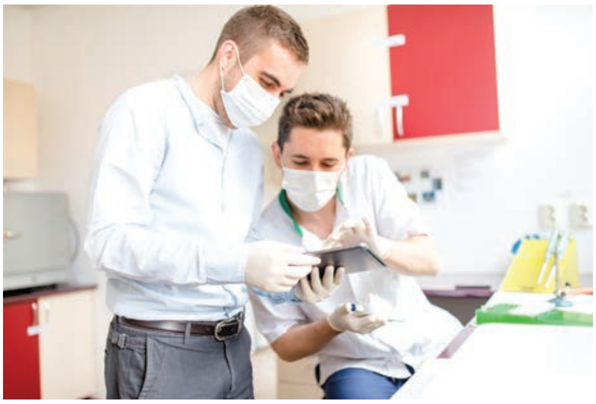


Figure 2 *Chemists record experimental data in laboratory notebooks. They also record, process and present data using computers and tablets.*

Instruments and equipment

- know and understand how to use a wide range of experimental and practical instruments, equipment and techniques appropriate to the knowledge and understanding included in the specification

Figure 3 *You will need to use a variety of equipment correctly and safely.*

Throughout this book there are questions and longer assignments that will give you the opportunity to develop and practise these skills. The contexts of some of the exam questions will be based on the 'required practical activities'.

ASSESSMENT OF PRACTICAL SKILLS

Some practical skills can only be practised when you are doing experiments. For A-level, these **practical competencies** will be assessed by your teacher:

- follow written procedures
- apply investigative approaches and methods when using instruments and equipment
- safely use a range of practical equipment and materials
- make and record observations and measurements
- research, reference and report findings

You must show your teacher that you consistently and routinely demonstrate the competencies listed above during your course. The assessment will not contribute to your A-level grade, but will appear as a 'pass' alongside your grade on the A-level certificate.

These practical competencies must be demonstrated by using a specific range of **apparatus and techniques**. These are:

- use appropriate apparatus to record a range of measurements (to include mass, time, volume of liquids and gases, temperature)
- use a water bath or electric heater or sand bath for heating
- measure pH using pH charts, or pH meter, or pH probe on a data logger
- use laboratory apparatus for a variety of experimental techniques including:
  - titration, using burette and pipette
  - distillation and heating under reflux, including setting up glassware using retort stand and clamps
  - qualitative tests for ions and organic functional groups
  - filtration, including use of fluted filter paper, or filtration under reduced pressure
- use a volumetric flask, including accurate technique for making up a standard solution
- use acid–base indicators in titrations of weak/strong acids with weak/strong alkalis

- purify:
  - a solid product by recrystallisation
  - a liquid product, including use of a separating funnel
- use melting point apparatus
- use thin-layer or paper chromatography
- set up electrochemical cells and measuring voltages
- safely and carefully handle solids and liquids, including corrosive, irritant, flammable and toxic substances
- measure rates of reaction by at least two different methods, for example:
  - an initial rate method such as a clock reaction
  - a continuous monitoring method

Figure 4 *Many chemists analyse material. They are called analytical chemists. Titration is a commonly used technique.*

Figure 5 *pH probe*

For AS, the above will not be assessed but you will be expected to use these skills and these types of apparatus to develop your manipulative skills and your understanding of the processes of scientific investigation.

REQUIRED PRACTICAL ACTIVITIES

During the A-level course you will need to carry out twelve **required practical** activities. These are the main sources of evidence that your teacher will use to award you a pass for your competency skills. If you are doing the AS, you will need to carry out the first six in this list.

1. Make up a volumetric solution and carry out a simple acid–base titration
2. Measurement of an enthalpy change
3. Investigation of how the rate of a reaction changes with temperature
4. Carry out simple test-tube reactions to identify:
   - cations – Group 2, NH_4^+
   - anions – Group 7 (halide ions), OH^-, CO_3^{2-}, SO_4^{2-}
5. Distillation of a product from a reaction
6. Tests for alcohol, aldehyde, alkene and carboxylic acid
7. Measuring the rate of reaction:
   - by an initial rate method
   - by a continuous monitoring method
8. Measuring the EMF of an electrochemical cell
9. Investigate how pH changes when a weak acid reacts with a strong base and when a strong acid reacts with a weak base
10. Preparation of:
    - a pure organic solid and test of its purity
    - a pure organic liquid
11. Carry out simple test-tube reactions to identify transition metal ions in aqueous solution
12. Separation of species by thin-layer chromatography

Information about the apparatus, techniques and analysis of required practicals 1 to 6 are found in the relevant chapters of this book, and 7 to 12 in Book 2.

You will be asked some questions in your written examinations about these required practicals.

Practical skills are really important. Take time and care to learn, practise and use them.

1 ATOMIC STRUCTURE

PRIOR KNOWLEDGE

You may know that substances are made from atoms and that an element is a substance made from just one sort of atom. You will probably have learnt that an atom consists of a nucleus, made up of protons and neutrons, with electrons moving around it in shells (or energy levels). You may also know about relative electrical charges and masses of protons, neutrons and electrons.

LEARNING OBJECTIVES

In this chapter, you will reinforce and build on these ideas and learn about more sophisticated models of atoms.

(Specification 3.1.1.1, 3.1.1.2, 3.1.1.3)

NASA's Curiosity Rover landed in the Gale Crater on Mars in August 2012. Its main mission was to investigate whether Mars has ever possessed the environmental conditions that could support life, as well as finding out about Martian climate and geology. Curiosity Rover contains an on-board science laboratory, equipped with a sophisticated range of scientific instruments. Many of these instruments have been specially designed for the mission.

The task of the on-board mass spectrometer is to investigate the atoms that are the building blocks of life – carbon, hydrogen, oxygen, phosphorus and sulfur. The spectrometer is making precise measurements of the carbon and oxygen isotopes found in carbon dioxide and methane from the atmosphere and the soil. After one Martian year (687 Earth days) of the mission, scientists have concluded that Mars once exhibited environmental conditions that were favourable for microbial life.

1.1 EARLY IDEAS ABOUT THE COMPOSITION OF MATTER

The nature of matter has interested people since the time of the early Greeks. The ideas that you have learnt about atomic structure have resulted from the work of many people over many centuries. You do not need to remember all of this information but here are some of the major events since 460BCE that led to our understanding of the atom.

Evidence for atomic structure

460–370BCE, Democritus

The Greek philosopher Democritus proposed that matter was made up of particles that cannot be divided further. They became known as atoms from the Greek word *atomos*, meaning ‘cannot be divided’.

His ideas were based on reasoning – you cannot keep dividing a lump of matter for ever.

384–322BCE, Aristotle

Aristotle was another ancient Greek philosopher, who proposed that all earthly matter was made from four elements: earth, air, fire and water. These elements have their natural place on Earth and when they are out of place, they move. So, rain falls and bubbles of air rise from water.

A tree grows in the earth, and it needs water and air. So, a tree is made from earth, water and air. Aristotle could analyse most matter in this way.

1627–1691, Robert Boyle

Robert Boyle was a Fellow of the Royal Society of London. His scientific ideas included the notion that matter is made up of tiny identical particles that cannot be subdivided. These tiny particles made up ‘mixt bodies’ (we now call them compounds). Putting the particles together in different ways made different compounds. Particles were in fixed positions in solids, but free to move in liquids and gases. Forces between particles made materials solid.

Boyle studied the nature and behaviour of gases, especially the relationship between volume and pressure. His theory of matter supported his experimental observations. He was the first scientist to keep accurate records.

1766–1844, John Dalton

John Dalton was an English chemist and physicist, who named the tiny particles **atoms**. His scientific idea was that atoms are indivisible and indestructible. All atoms of an element are identical and have the same mass and chemical properties. Atoms of different elements have different masses (he called them atomic weights) and different chemical properties. Atoms react together to form ‘compound atoms’. These later became known as molecules.

Dalton studied the physical properties of air and gases. This led him to analytical work on ethene (olefiant gas), methane (carburetted hydrogen) and other gases. His atomic theory explained his chemical analyses. He summed up 150 years of ideas with his atomic theories.

1850–1930, Eugen Goldstein

The German physicist Eugen Goldstein’s scientific idea was that cathode rays contained negatively charged particles with mass. He assumed that these particles were produced when the gas particles in the cathode ray tube were split. Cathode rays could be deflected by a magnetic field. Goldstein also detected heavier positive particles.

He experimented with electrical discharge tubes – he passed an electric current between a cathode and an anode in a sealed tube containing gas at a very low pressure. He adapted his experiment, inserting a perforated cathode, as in Figure 1.

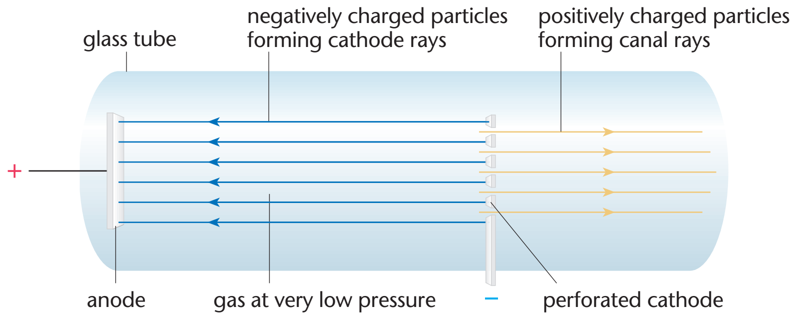


Figure 1 *An electrical discharge tube with a perforated cathode, as used by Goldstein*

1856–1937, Joseph John Thomson

Thomson's idea was that atoms contained **electrons**. He proposed that atoms could be divided into smaller particles. Electrons have very small mass, about one two-thousandths of the mass of a hydrogen atom. They are negatively charged. The negative charge is cancelled out by a sphere of positively charged material, as in Figure 2.

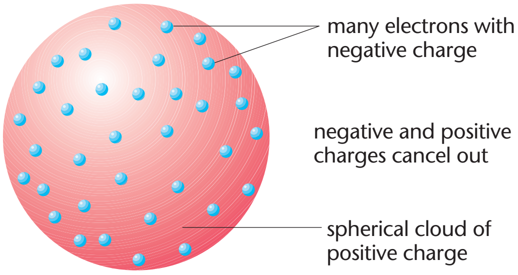


Figure 2 *Thomson's plum pudding model of the atom*

Thomson measured the deflection of the negative particles in cathode rays very accurately and calculated their mass. The cathode ray tubes he used were the forerunners of the cathode ray tubes used in televisions and monitors (Figure 3) before the development of flat screens.

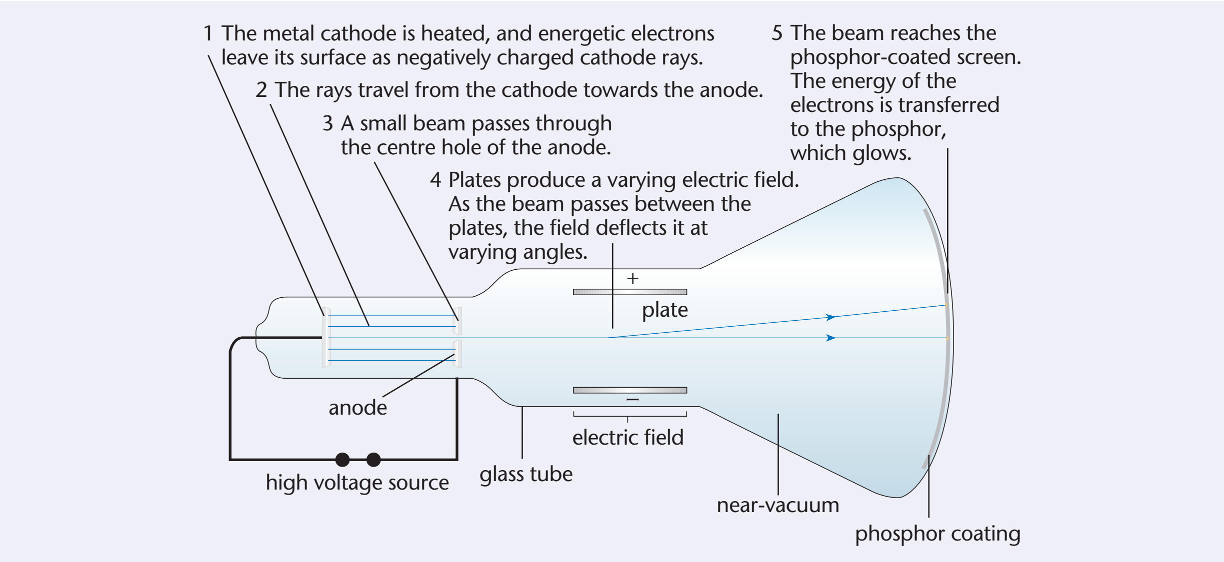


Figure 3 *Cathode ray tubes were used in televisions and computers before flat screens.*

Thomson's model of the atom became known as the 'plum pudding' model.

1871–1937, Ernest Rutherford

From work carried out in Manchester with his research students Hans Geiger and Ernst Marsden, Ernest Rutherford put forward the idea that the mass of the atom is not evenly spread. It is concentrated in a minute central region called the **nucleus**. Rutherford calculated the diameter of the nucleus to be 10^{-14} m.

All the positive charge of the atom is contained in the nucleus.

The electrons circulate in the rest of the atom, being kept apart by the repulsion of their negative charges.

These findings came from his interpretation of the results that are shown in Figure 4 (obtained from the experiment described in Figure 5).

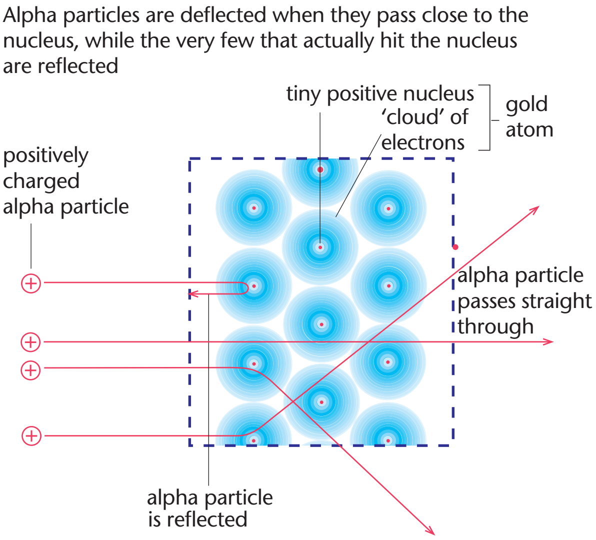


Figure 4 *Deflection of alpha particles by gold foil*

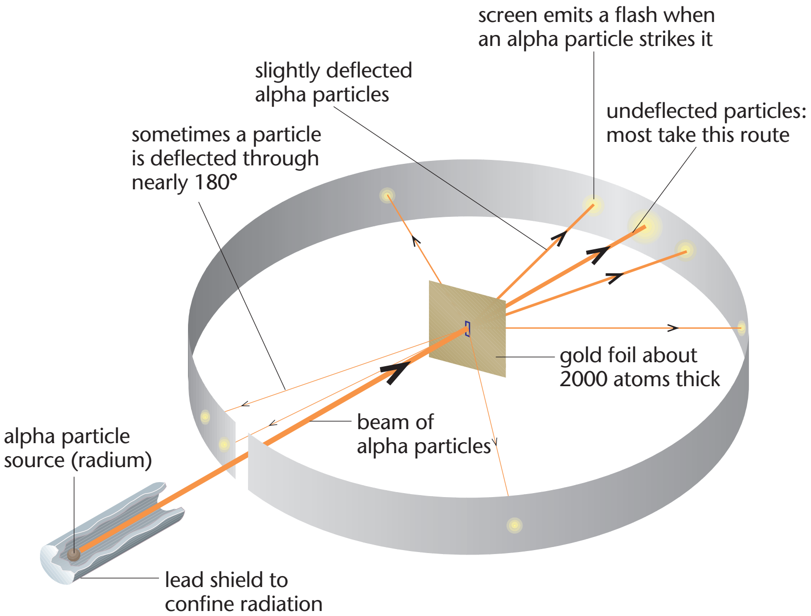


Figure 5 *Rutherford's experiment: the deflection of alpha particles through gold foil*

1888–1915, Henry Moseley and Ernest Rutherford

Rutherford continued the work that he had started, together with Moseley. Their idea was that the nucleus contained positively charged particles called **protons**. The number of protons (the atomic number) corresponds to the element's position in the Periodic Table. Protons make up about half the mass of the nucleus.

Moseley studied X-ray spectra of elements. Mathematically, he related the frequency of the X-rays to a number he called the **atomic number**. This corresponded to the element's position in the Periodic Table. Sadly, Moseley was killed in action at Gallipoli in World War 1. In 1919, Rutherford fired alpha particles at hydrogen gas and produced positive particles, which he called protons. His calculations also showed that the mass of the protons only accounted for half of the mass of the nucleus.

1891–1974, James Chadwick

Chadwick identified the **neutron** in 1932. Neutrons have no charge. They have the same mass as a proton.

He bombarded a beryllium plate with alpha particles and produced uncharged radiation on the other side of the plate. He placed a paraffin wax disc (which contains many hydrogen atoms) in the path of the radiation and showed that the radiation caused protons to be knocked out of the wax (Figure 6).

1885–1962, Niels Bohr

Bohr's scientific idea was that electrons orbit the nucleus in energy levels. Energy levels have fixed energy values – they are **quantised**. Electrons can only occupy these set energy levels.

Bohr studied emission spectra and produced explanations that incorporated the ideas of Einstein and Planck. Electrons orbited the nucleus in energy levels, where each energy level has a fixed energy value.

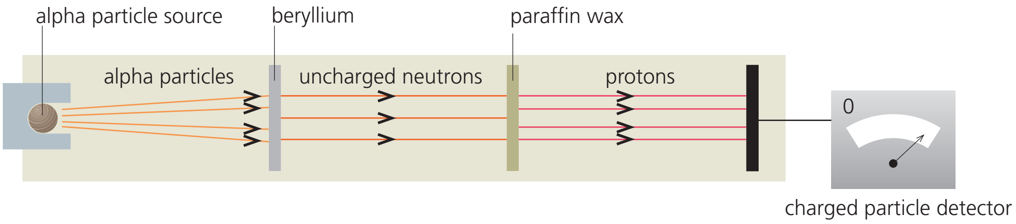


Figure 6 *Chadwick's experiment*

QUESTIONS

1. Aristotle's theory of earth, fire, air and water lasted for about 2000 years and was a major setback to ideas about atomic structure. Why did it last so long?
2. What evidence led to the discovery of:
   - **a.** the electron
   - **b.** the nucleus
   - **c.** the proton
   - **d.** the neutron?
3. Why was the neutron the last major subatomic particle to be discovered?

Stretch and challenge

4. Describe how ideas about atomic structure changed from 1897 to 1932.

1.2 RELATIVE MASS AND RELATIVE CHARGE OF SUBATOMIC PARTICLES

Further experiments established the masses and charges of protons, electrons and neutrons. These are summarised in Table 1.

Because the values for mass are so small, the idea of **relative mass** is used. The relative mass of a proton is 1 and that of a neutron is 1. The relative mass of the electron is 5.45×10^{-4} or $\frac{1}{1837}$.

Charges on subatomic particles are also given relative to one another. A proton has a relative charge of $+1$ and an electron has a relative charge of -1. A neutron has no charge. The protons and neutrons together are called **nucleons**. Protons in the nucleus do not repel each other because a strong nuclear force acts over the small size of the nucleus and binds all the nucleons together.

Since atoms of any element are neutral, the number of protons (positive charge) must equal the number of electrons (negative charge). The atoms of all elements, except hydrogen, contain these three fundamental particles.

Particle	Mass/kg	Charge/C	Relative mass	Relative charge
Electron	9.109×10^{-31}	1.602×10^{-19}	5.45×10^{-4}	-1
Proton	1.672×10^{-27}	1.602×10^{-19}	1	$+1$
Neutron	1.674×10^{-27}	0	1	0

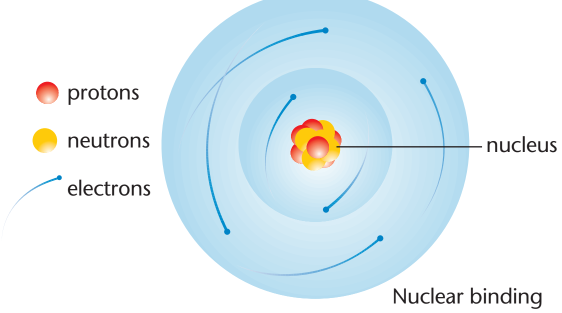
Note: The mass of the electron is so small compared to the mass of the proton and neutron that chemists often take it to be zero.

Table 1 *The fundamental atomic particles, their mass and charge*

KEY IDEAS

- All matter is composed of atoms.
- The nucleus of an atom contains positive protons, with a relative mass of 1 and relative charge of $+1$, and neutral neutrons (except hydrogen), with a relative mass of 1 and no charge.
- Electrons orbit the nucleus in energy levels (shells). An electron has a very small mass and relative charge of -1.
- The number of electrons in an atom equals the number of protons, to give an uncharged atom.

The electrons are kept apart by their negative charge.



Nuclear binding forces allow protons to be close together.

Figure 7 *This diagram summarises the model of the atom that scientists often use nowadays.*

1.3 WORKING WITH VERY SMALL AND VERY LARGE NUMBERS

Working with very small numbers can be confusing. To help avoid this, scientists use standard form and standard prefixes when communicating their numerical work.

Standard form

Numbers with many zeros are difficult to follow, so scientists tend to express these in **standard form**. Standard form is a number between one and 10. So, how is the number 769 000 expressed in standard form?

- Locate the decimal point: 769 000.0
- Move the decimal point to give a number between 1 and 10: 7.69000
- Multiply the number by ten raised to the power x, where x is the number of figures the decimal point was moved: 7.69×10^5

Sometimes the decimal point may move the other way. Take the mass of the electron (0.000 545 units) as an example.

- Find the decimal point and move it. This time it goes to the right: 00005.45
- Multiply the number by ten raised to the power x, where x is the number of figures the decimal point was moved. But, this time, the index will be negative: 5.45×10^{-4}

Calculations using standard form

Standard form makes multiplication and division of even the most complex numbers much easier to handle. When you multiply two numbers in standard form, you multiply the numbers and add the indices. For example:

$(3 \times 10^2) \times (2 \times 10^3) = 6 \times 10^5$

If you divide numbers in standard form, you divide the standard number and subtract the indices. For example:

$$\frac{8 \times 10^4}{4 \times 10^2} = 2 \times 10^2$$

Units and standard prefixes

Science is based on observations and measurements. When making measurements, it is essential to use the correct units.

Again, to make numbers more manageable, scientists use prefixes that usually have intervals of a thousand. For example, attaching preferred prefixes to the unit metre, you have kilometre, millimetre and nanometre. But other intervals can be used if they are convenient for the task in hand.

A system of prefixes is used to modify units. Prefixes that are commonly used are listed in Table 2.

Prefix	Symbol	Multiplier	Meaning
mega	M	10^6	1 000 000
kilo	k	10^3	1000
deci	d	10^{-1}	0.1
centi	c	10^{-2}	0.01
milli	m	10^{-3}	0.001
micro	µ	10^{-6}	0.000 001
nano	n	10^{-9}	0.000 000 001
pico	p	10^{-12}	0.000 000 000 001

Table 2 *Standard prefixes*

Significant figures

When carrying out calculations based on measurements made, you must be confident that the answers you give are as precise as the measurements allow. This is done by counting the number of significant figures (sig figs) in the number given for a measurement. So, for example, a measured mass of:

3.4 g (two sig figs) means you are confident to the nearest 0.1 g

3.40 g (three sig figs) means you are confident to the nearest 0.01 g

3.400 g (four sig figs) means you are confident to the nearest 0.001 g.

Worked example 1

Using data from Table 1, calculate how many electrons have the same mass as a nucleus containing one proton and one neutron.

mass of nucleus $= (1.672 \times 10^{-27}) + (1.674 \times 10^{-27})$

number of electrons with the same mass

$$= \frac{(1.672 \times 10^{-27}) + (1.674 \times 10^{-27})}{9.109 \times 10^{-31}}$$

answer given on calculator = 3673.290153

Since the mass of each particle is given to four significant figures, the answer must contain no more than four significant figures. The answer must be rounded up or down. The answer is 3673 electrons.

(Maths Skills 0.0, 0.1, 0.2, 0.4, 1.1)

Remember:

- Do not round calculations up or down until you reach the final answer because errors can be carried through.
- The answer to a chemical calculation must not have more significant figures than the number used in the calculation with the fewest significant figures.

Fact	Example
all non-zero digits are significant	275 has three sig figs
zero between non-zero digits is significant	205 has three sig figs
zero to the left of the first non-zero digit is not significant	301 has three sig figs, 0.31 has two sig figs
zero to the right of the decimal point is significant	2.9 has two sig figs, 2.90 has three sig figs
numbers ending in zero to the left of the decimal point: the zero may or may not be significant	a mass of 840 g has two sig figs if the balance is accurate to ± 10 g, and three sig figs if the balance is accurate to ± 1 g

Table 3 *Significant figures*

ASSIGNMENT 1: SIZE, SCALE AND SIGNIFICANT FIGURES

(MS 0.0, 0.1, 0.2; PS 1.1, 1.2, 3.2)

A single carbon atom measures about one ten-billionth of a metre across, a dimension so small that it is impossible to imagine. The nucleus is a thousand times smaller again, and the electron a hundred thousand times smaller than that!

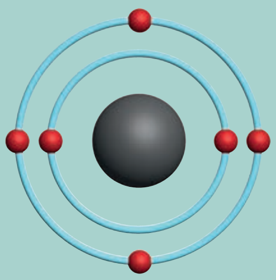


Figure A1 *A single carbon atom measures about one ten-billionth of a metre across.*

Because the numbers are so unimaginably small, scientists do not use grams and metres to describe atoms and subatomic particles. They use a different set of units.

You have already come across the idea of relative masses. Protons and neutrons both have a relative mass of 1. We say these have a mass of 1 relative mass unit. The electron is a mere 0.000545 relative mass units. Clearly, even with relative masses you have some awkward numbers.

Questions

Give your answers to the appropriate number of significant figures, and in standard form where appropriate.

A1. **a.** An atom of hydrogen contains only a proton and an electron. Calculate the mass of the hydrogen atom in kilograms.

b. A molecule of hydrogen contains two atoms. Calculate the mass of a hydrogen molecule in grams.

c. How many electrons have the same mass as a single neutron?

A2. Convert these quantities into measurements in grams, expressed in standard form:

a. The mass of a neutron.

b. 200 million electrons.

c. 10 gold coins weighing a total of 0.311 kg.

A3. A uranium atom contains 92 electrons. Calculate the mass, in kilograms, of protons in the atom.

A4. How many times heavier is the nucleus of a helium atom (two protons and two neutrons) than its electrons?

1.4 ATOMIC NUMBER, MASS NUMBER AND ISOTOPES

Different elements have different numbers of electrons, protons and neutrons in their atoms. It is the number of protons in the nucleus of an atom that identifies the element. Remember that, if an atom forms an ion by gain or transfer of electrons, it is still an ion of the same element. An atom can also have one or two more or fewer neutrons and still remain the same element. Using this information, you can define an element using two numbers: the atomic number and the mass number (Figure 8).

Atomic (proton) number (*Z*). The atomic number of an element is the number of protons in the nucleus of the atom. It has the symbol *Z* and is also known as the proton number. Its value is placed in front of the element's symbol, below its mass number. Since atoms are neutral, the number of protons equals the number of electrons orbiting the nucleus. All atoms of the same element have the same atomic number.

Mass number (*A*). The mass number of an element is the total number of protons and neutrons in the nucleus of an atom. It is a measure of its mass compared with other types of atom. Even in heavy atoms, the electron's mass is so small that it makes little difference to the overall mass of the atom. Protons and neutrons both have a mass of 1, so:

$$\text{mass number } (A) = \text{number of protons } (Z) + \text{number of neutrons } (n)$$

$$A = Z + n$$

The symbol for the mass number is *A*, and its value goes above the atomic number in front of the element's symbol.

You can calculate the number of neutrons in the nucleus using:

$$\text{number of neutrons } (n) = \text{mass number } (A) - \text{atomic number } (Z).$$

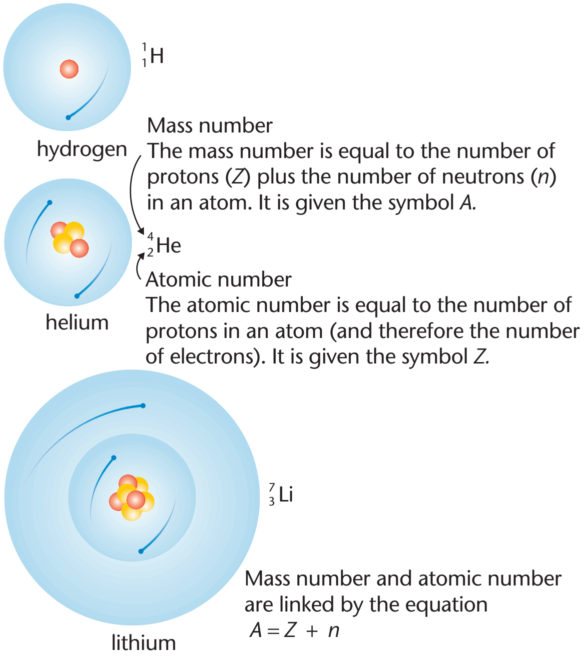


Figure 8 *Mass number and atomic number*

QUESTIONS

5. How many protons, neutrons and electrons do the following atoms and ions have?
    - **a.** An element with mass number 19 and atomic number 9.
    - **b.** An element with mass number 210 and atomic number 85.
    - **c.** An ion with one positive charge, a mass number of 23 and atomic number 11.
    - **d.** An ion with three negative charges, a mass number of 31 and atomic number 15.
    - **e.** An ion with three positive charges, a mass number 52 and atomic number 24.

Isotopes

All atoms of the same element have the same number of protons and the same atomic number, *Z*. However, they may have a different number of neutrons and so a different mass number, *A*. Atoms of the same element with different mass numbers are called **isotopes**. Nitrogen has two isotopes, $^{14}_{7}N$ and $^{15}_{7}N$. Both isotopes have seven protons, but $^{14}_{7}N$ has seven neutrons and $^{15}_{7}N$ has eight neutrons. The notation for an isotope shows the mass number and the atomic number:

The isotopes of carbon and their sub atomic particles are summarised in Table 4.

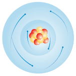
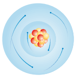
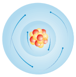
Name		No. of protons	No. of neutrons	No. of electrons	Relative abundance %
carbon-12		6	6	6	98.93
carbon-13		6	7	6	1.07
carbon-14		6	8	6	10^{-10}

Table 4 *Isotopes of carbon*

Properties of isotopes

The chemical properties of an element depend on the number and arrangement of the electrons in its atoms. Since all the isotopes of an element have the same number and arrangement of electrons, they also all have the same chemical properties. However, because of the difference in mass, isotopes differ slightly in their physical properties, such as in the rate of diffusion (which depends on mass), and their nuclear properties, such as radioactivity.

Isotopes that are not radioactive, such as chlorine-35 and chlorine-37, are called **stable isotopes**. Data books give you the relative abundance of each isotope present in such stable, naturally occurring elements.

KEY IDEAS

- The atomic (proton) number, *Z* is equal to the number of protons in the nucleus.
- The mass number, *A* is equal to the number of protons plus the number of neutrons in the nucleus.
- Isotopes of an element have the same number of protons but different numbers of neutrons.

Relative abundance of isotopes

Most elements have isotopes. The percentage of each isotope that naturally occurs on Earth is referred to as its **relative isotopic abundance**. Chlorine has two isotopes, $^{35}_{17}Cl$ and $^{35}_{17}Cl$. Any sample of naturally occurring chlorine will contain 75.53% of chlorine-35 and 24.47% of chlorine-37.

Hydrogen has three isotopes: $^{1}_{1}H$, $^{2}_{1}H$ (called deuterium) and $^{3}_{1}H$ (called tritium). Elements that occur in space may contain different percentages of isotopes. These percentages are known as its **isotope signature**.

Mass spectrometry

Performance enhancing drugs are illegal in most sports and most organisations use drug tests to ensure that the competition is fair. An athlete may be asked to produce a urine sample and, sometimes, a blood sample. This is sent to a testing facility. The drug tests detect the presence of compounds that are produced by chemical reactions in the body as it processes the drug. **Mass spectrometers** are used to help analyse the sample. Drug analysis is just one of a vast range of applications of mass spectrometry in analytical chemistry.

There are several different types of mass spectrometer. They can be used to identify the mass of an element, an isotope or a molecule. Knowing the mass of a particle helps scientists to identify the particle. One type of spectrometer is called a **time-of-flight mass spectrometer** (Figure 11).

ASSIGNMENT 2: ISOTOPE DETECTIVE

(MS 0.0, 0.1; PS 1.1, 1.2, 3.2)

Human beings have long been obsessed with the idea that life might exist or have existed on Mars, one of the closest planets to Earth. In 2003 the European Mars Express detected methane gas, CH_4. We use methane to heat our homes and for cooking food. On Earth, 90% of all methane comes from living things, such as the decay of organic material. This is how the gas in our homes originated. The remaining 10% was produced from geological activity.

The big question is: ‘What is the origin of the methane gas on Mars?’. Perhaps it was formed by the decay of organic material billions of years ago. Or maybe it is being given off by present-day microbes that exist under the surface in areas heated by volcanic activity. Alternatively, was the methane gas a result of geological processes? The answer may be found in isotopes.

Carbon has three isotopes: carbon-12, carbon-13 and carbon-14. Their abundances on Earth, as shown by the isotopic signature of methane, are given in Table A1.

Hydrogen has two naturally occurring isotopes: hydrogen-1, which has a 99.9885% abundance on Earth, and hydrogen-2, which has a 0.01115% abundance. (The other hydrogen isotope, hydrogen-3, is not naturally occuring. It is produced in nuclear reactors.)

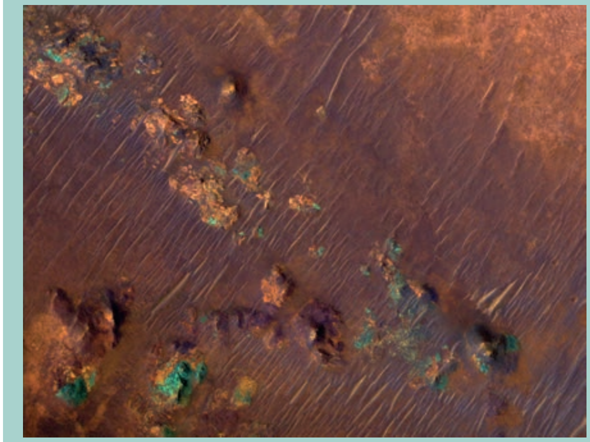


Figure A1 *Nili Fossae, one of the regions on Mars emitting methane. Are the plumes of methane gas evidence for life on Mars?*

Chemical reactions involve electrons; the presence of extra neutrons in isotopes does not affect these reactions. So, methane molecules may contain a mixture of these different isotopes. The three most common methane molecules are formed when one carbon-12 combines with four hydrogen-1 atoms, one atom of carbon-13 combines with four hydrogen-1 atoms, and when one atom of carbon-12 combines with three hydrogen-1 atoms and one hydrogen-2 atom. These can be written as:

$^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$ respectively. (D stands for deuterium, which is the name given to hydrogen-2.)

Methane formula	Natural percentage abundance on Earth
$^{12}CH_4$	0.99827
$^{13}CH_4$	0.01110
$^{12}CH_3D$	0.00062

Table A1 *The isotopic signature of naturally occurring methane on Earth*

When scientists determine the isotopic signature of Martian methane, they can compare it with that on Earth. They may then be a step nearer to deciding its origin.

Questions

A1. What are the atomic numbers and mass numbers of:

- **a.** the isotopes of carbon
- **b.** the isotopes of hydrogen?

A2. Why is carbon-14 ignored in possible methane formulae?

A3. What is the difference in mass between $^{12}CH_4$ and $^{13}CH_4$?

A4. What is the difference in mass between $^{12}CH_4$ and $^{12}CH_3D$?

A5. Which form of methane is most common and why?

A6. Suggest a formula for an extremely rare type of methane.

A7. When scientists compare the isotopic signature of Martian methane with that of methane on Earth, what assumptions are they making?

Figure 9 *Athletes undergo drugs tests during training and competition. Any found using performance enhancing drugs face bans from the sport.*

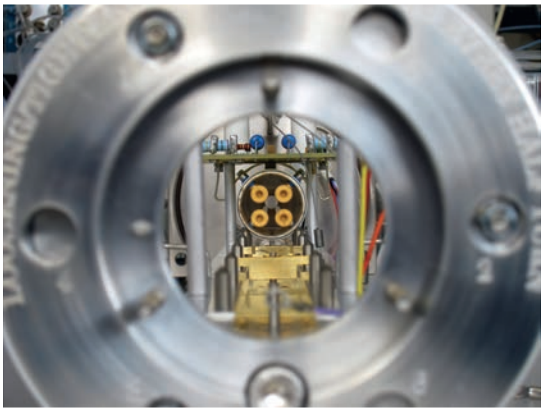


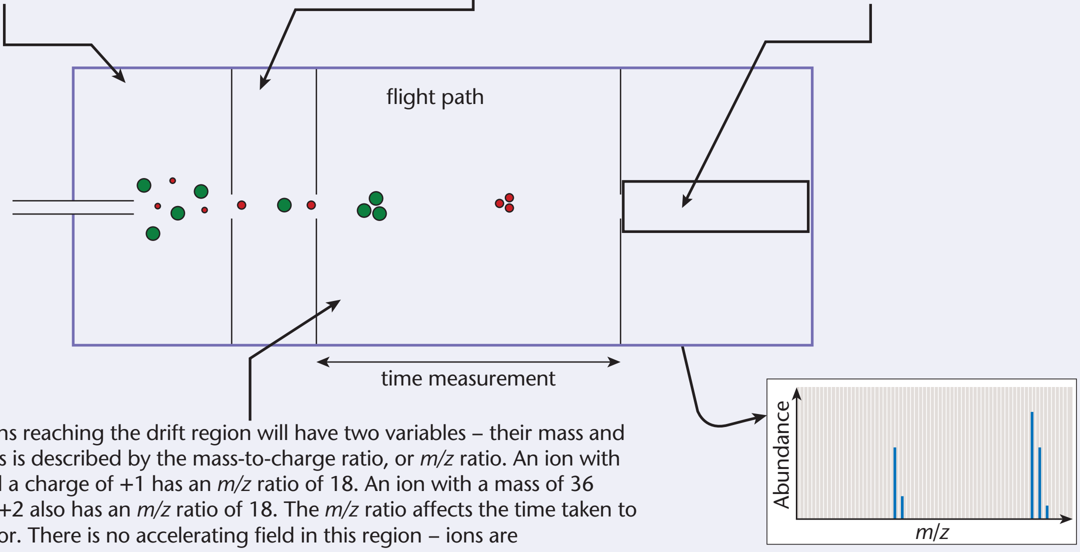
Figure 10 *Inside the flight tube of a triple quadrupole time-of-flight mass spectrometer*

Electrospray ionisation. The sample being tested is vaporised and injected into the spectrometer. A beam of electrons is fired at the sample and knocks out electrons to produce ions. A technique called electrospray ionisation is used because this reduces the number of molecules that break up or fragment. Most atoms or molecules lose just one electron, but a few lose two. Positively charged ions are produced. Only the most energetic electrons can knock out two electrons, so most ions have a single positive charge. If M is a molecule of the sample, then:

$M(g) \rightarrow M^{+}(g) + e^{-}$ or, $M(g) \rightarrow M^{2+}(g) + 2e^{-}$.

Acceleration. The electric field has a fixed strength – the potential difference is constant. It accelerates the ions so that all the ions with the same charge have the same kinetic energy – they are travelling at the same speed.

Ion detector. The ions are distinguished by different flight times at the ion detector. The electronic signal is used by computer software to produce a mass spectrum. The position of each peak on the mass spectrum is related to the *m*/*z* charge of the ions. Since most ions have a +1 charge, this will be the same as the mass of the ion. The size of each peak is proportional to the abundance of the ion in the sample.



Ion drift. The ions reaching the drift region will have two variables – their mass and their charge. This is described by the mass-to-charge ratio, or *m*/*z* ratio. An ion with a mass of 18 and a charge of +1 has an *m*/*z* ratio of 18. An ion with a mass of 36 and a charge of +2 also has an *m*/*z* ratio of 18. The *m*/*z* ratio affects the time taken to reach the detector. There is no accelerating field in this region – ions are 'free-wheeling'. Heavier ions move slower than lighter ions and singularly charged ions move slower than ions with two or more charges. The time taken to reach the ion detector is called the 'flight time'. For example, if the flight path is 0.6 m long and an ion has a mass of 26 atomic units, the flight time will be 6×10^{-6} seconds.

Figure 11 *The basic principles of a time-of-flight mass spectrometer*

The mass spectrum of magnesium

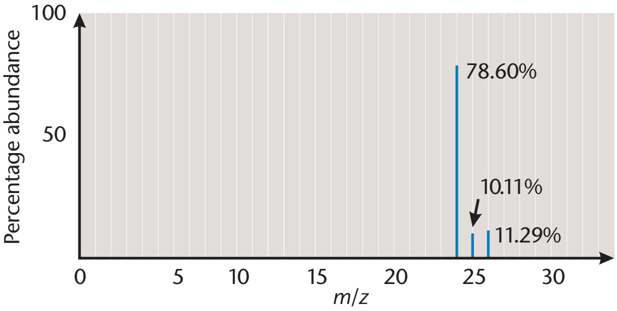


Figure 12 *Mass spectrum of magnesium*

The chart produced by a mass spectrometer is called a mass spectrum (plural: mass spectra).

When a sample of magnesium vapour is fed into the mass spectrometer, it is bombarded by high energy electrons in the **ionisation region**. These fast-moving, energetic electrons knock electrons off the magnesium atoms to produce positively charged magnesium ions, Mg^+.

$Mg(g) \rightarrow Mg^+(g) + e^-$

If bombarded with very high energy electrons, some magnesium ions lose a second electron:

$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$

These positively charged magnesium ions pass through the spectrometer and are accelerated by an electric field to give all ions with the same charge the same kinetic energy. The sample then passes into the drift region. Magnesium has three isotopes: magnesium-24, magnesium-25 and magnesium-26. If ions of all isotopes have the same charge, then the lighter magnesium-24 will take a shorter time to reach the ion detector than the heavier ions. The flight time will be less.

A mass spectrum is produced. The *y*-axis is the percentage abundance. The *x*-axis is the mass/charge (or *m*/*z*) ratio (Figure 12).

The spectrum of magnesium has three lines. These correspond to the three isotopes of magnesium. The heights of the lines are proportional to the amounts of each isotope present. The sample in Figure 12 contains 78.60% of magnesium-24, 10.11% of magnesium-25 and 11.29% of magnesium-26.

The mass spectrum of an element shows:

- the mass number of each isotope present (since mass numbers are masses compared with carbon-12, this number is called the relative isotopic mass)
- the relative abundance of each isotope.

Calculating the relative atomic mass from isotopic abundance

You can use information from mass spectra to calculate the **relative atomic mass**, A_r, of an element (see Section 1.5).

For magnesium, the isotopes ^{24}Mg, ^{25}Mg and ^{26}Mg are present in the ratio 78.60 : 10.11 : 11.29. This means that the mass of 100 magnesium atoms will be:

$(78.60 \times 24) + (10.11 \times 25) + (11.29 \times 26)$

The average mass of one magnesium atom will be:

$$\frac{(78.60 \times 24) + (10.11 \times 25) + (11.29 \times 26)}{100}$$

$= 24.3$ (to one decimal place)

This is the relative atomic mass of magnesium. The A_r value for magnesium in your data book is 24.3.

Note that atoms of magnesium with this actual mass do not exist. This is the *average* mass of all the naturally occurring isotopes of magnesium, taking abundance into account.

The mass spectrum of lead

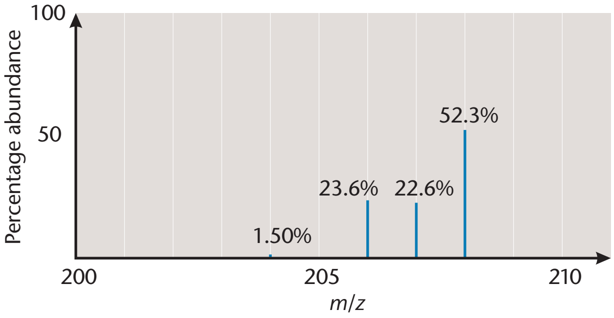


Figure 13 *Mass spectrum of lead*

The mass spectrum of lead (Figure 13) shows that lead has four isotopes with mass numbers of 204, 206, 207 and 208. The heights of the lines show that these are in the ratio of 1.50 : 23.6 : 22.6 : 52.3. These are percentage abundances and add up to 100.

To calculate the relative atomic mass of lead:

mass of 100 atoms

$= (1.540 \times 204) + (23.6 \times 206) + (22.6 \times 207) + (52.3 \times 208)$

relative atomic mass

$$= \frac{(1.540 \times 204) + (23.6 \times 206) + (22.6 \times 207) + (52.3 \times 208)}{100}$$

$= 207.2$

QUESTIONS

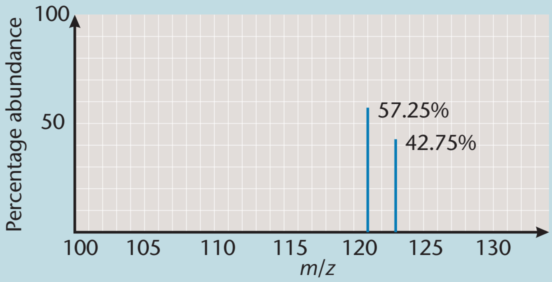


Figure 14 *Mass spectrum of antimony*

6. Look at the mass spectrum of a sample of antimony (Figure 14).

  a. How many isotopes does antimony have?

  b. What are their mass numbers?

  c. What is the percentage abundance of each isotope?

  d. Calculate the relative atomic mass of antimony from this spectrum.

7. Find the relative atomic mass of naturally occurring uranium that contains 0.006% uranium-234, 0.72% uranium-235 and 99.2% uranium-238.

8. Silver has two isotopes, silver-107 and silver-109. These are present in the ratio of 51.35 : 48.65 in naturally occurring silver. Calculate the relative atomic mass of silver.

ASSIGNMENT 3: ANALYSING HAIR

(MS 1.1, 1.2; PS 1.1, 1.2, 3.2)

Figure A3 *Scientists analyse hair to provide forensic evidence.*

Hair grows at a fairly uniform rate. Its composition depends partly on diet and the water you drink. The ratios of different isotopes in the water supply vary with your location and the rocks the water percolates through. For example, the isotopes of strontium (^{87}Sr and ^{88}Sr) and the isotopes of oxygen (^{16}O, ^{17}O and ^{18}O) vary all over the world. As your hair grows, the isotope ratios from your environment are captured in your hair.

For the forensic scientist, analysing the isotopes in a sample of your hair can tell where you are from and where you have been. This is a very useful tool in cases such as deciding whether a terrorist suspect has been to a particular location.

Questions

A1. Strontium has an atomic number of 38. How many protons, neutrons and electrons are in one atom of strontium-87 and in one atom of strontium-88?

A2. Naturally occurring strontium has four isotopes with these percentage abundances:

Strontium isotope	Percentage abundance
strontium-84	0.56
strontium-86	9.86
strontium-87	7.00
strontium-88	82.58

Table A2

  a. Sketch strontium's mass spectrum.

  b. Calculate the relative atomic mass of strontium.

A3. The data given in Table A2 for strontium isotopes are average figures for all naturally occurring strontium isotopes on Earth. What information do forensic scientists need when using hair analysis to track people?

1.5 RELATIVE ATOMIC MASS, A_r

Atoms have very small masses, from 10^{-24} g to 10^{-22} g. Instead of using these masses, scientists use **relative atomic mass** (symbol A_r). Relative here means the mass of one atom compared with another. Originally, the mass of each atom was compared with the mass of a hydrogen atom, where hydrogen had a mass of one. As mass spectroscopy developed and gave more accurate values for the masses of atoms, it was discovered that hydrogen's mass is slightly more than one.

Relative atomic mass is now defined as the average mass of an atom compared with $\frac{1}{12}$ the mass of a carbon-12 atom.

relative atomic mass, A_r =

$$\frac{\text{average mass of one atom of an element}}{\frac{1}{12}\text{ the mass of one carbon-12 atom}}$$

Relative atomic masses have no units because they show how many times heavier one atom is compared with another. Books give different numbers of decimal places for these values. The A_r for magnesium is given as 24 in most GCSE Periodic Tables. You will now need to use the more precise value of 24.3 for most calculations.

Remember, relative atomic mass is the average mass of all isotopes of an element, taking relative abundance into consideration. These values can be found using mass spectroscopy and the calculations you did earlier.

1.6 RELATIVE MOLECULAR MASS, M_r

In chemistry, you also need to know the mass of molecules. The same relative atomic mass scale is used. The **relative molecular mass** is the mass of a molecule compared with $\frac{1}{12}$ the mass of a carbon-12 atom.

relative molecular mass, M_r =

$$\frac{\text{average mass of one molecule}}{\frac{1}{12}\text{ the mass of one carbon-12 atom}}$$

Finding M_r values

The mass spectrometer can also be used to find relative molecular mass values. This is dealt with in more detail in Chapter 16. If a sample of vaporised molecules is introduced into the mass spectrometer, the bombarding electrons can knock an electron off a molecule in the same way as they did with a sample of atoms. This produces a positively charged ion called the **molecular ion, M^+**.

$$M(g) \rightarrow M^+(g) + e^-$$

Most of these molecular ions are now split into fragments by the bombarding electrons, but some remain intact.

The line produced by these molecular ions on the mass spectrum represents the relative molecular mass of the sample – if the atoms in the molecule have isotopes, there will be more than one molecular ion peak. The mass spectrum of methane (Figure 15) shows the molecular ion peak at $m/z = 16$ and another at $m/z = 17$. The one at 16 is due to $^{12}CH_4{}^+$ and the much smaller one at 17 is due to $^{13}CH_4{}^+$. These can be used to calculate the relative molecular mass of methane.

You will find more information about relative atomic mass and relative molecular mass in Chapter 2.

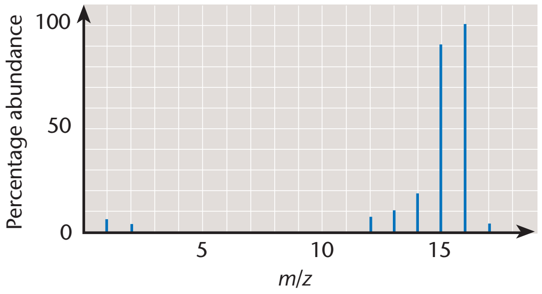


Figure 15 The mass spectrum of methane, CH_4

KEY IDEAS

- In a time-of-flight mass spectrometer, samples are ionised, accelerated to constant kinetic energy, allowed to drift and detected.
- A mass spectrum can be used to find the relative isotopic mass and abundance of isotopes of an element.
- The mass spectrum of a compound can be used to find its M_r and provide clues about its structure.
- Relative atomic mass is the average mass of an atom compared with $\frac{1}{12}$ the mass of a carbon-12 atom.
- Relative molecular mass is the average mass of a molecule compared with $\frac{1}{12}$ the mass of a carbon-12 atom.

1.7 DESCRIBING ELECTRONS

Main shell	Sub-shell	Max no. electron pairs in sub-shell	Max no. electrons in sub-shell	Max. no. electrons in main shell
1	s	1	2	2
2	s	1	2	8
	p	3	6	
3	s	1	2	18
	p	3	6	
	d	5	10	
4	s	1	2	32
	p	3	6	
	d	5	10	
	f	7	14	

Figure 16 *Shells, sub-shells and number of electrons*

Electrons are arranged in **electron shells** around the nucleus. Each electron shell has a particular energy value. Electrons can be described as being in a particular shell. Within each shell, there are sub-shells (or orbitals). The number of sub-shells in each shell is shown in Figure 16. The sub-shells are given the letters s, p, d and f. The letters come from words used to describe emission spectral lines (this is discussed further a little later in this chapter). Figure 16 shows that the first shell has a maximum of two electrons and that they are both in sub-shell s. The second electron shell has a maximum of eight electrons, two of which are in sub-shell s and six in sub-shell p. This sequence of sub-shells corresponds to an increase in energy (Figure 17). Each additional electron goes into the sub-shell with the next lowest energy. The order of filling is the same as the order of the elements in the Periodic Table.

Electron orbitals

Electrons are constantly moving, and it is impossible to know the exact position of an electron at any given time. However, measurements of the density of electrons as they move round the nucleus show that there are regions where it is highly probable to find an electron. These regions of high probability are called **orbitals**. Each s, p, d and f sub-shell corresponds to a differently shaped orbital.

The shapes of s and p orbitals are shown in Figure 18. Each orbital can hold two electrons, which spin in opposite directions. Table 5 shows the numbers of electrons and orbitals in the sub-shells.

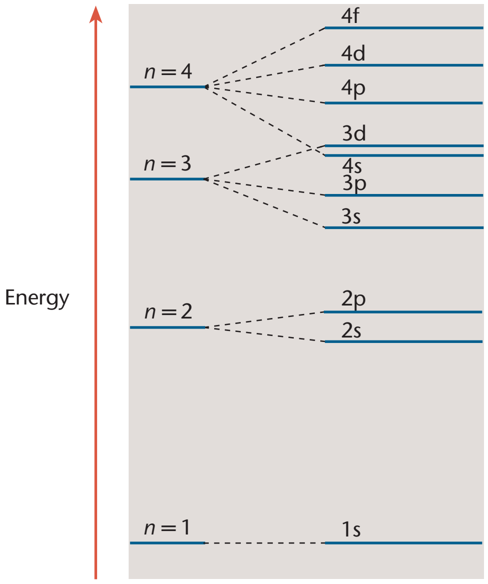


Figure 17 *The energies of the sub-shells in an atom with many electrons*

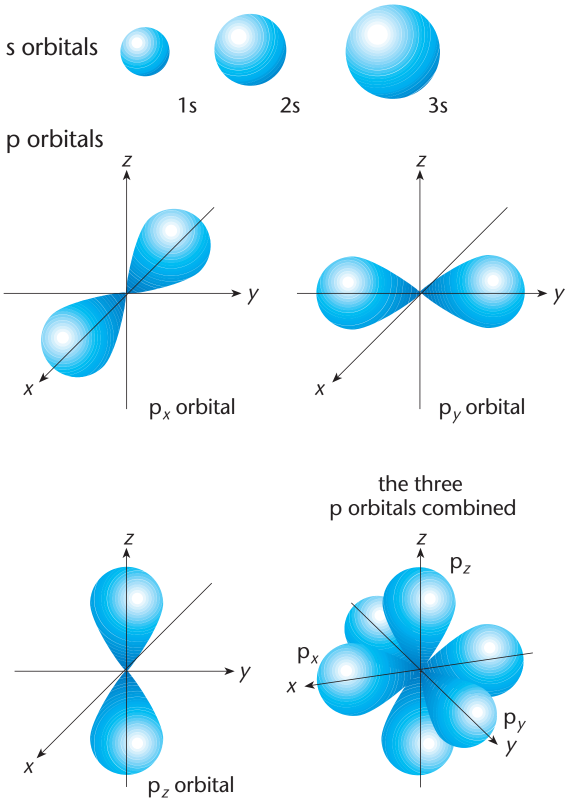


Figure 18 *The three-dimensional (3D) shape of the s and p orbitals*

Sub-level	s	p	d	f
Number of orbitals in sub-shell	1	3	5	7
Maximum number of electrons	2	6	10	14

Table 5 *Number of orbitals and maximum number of electrons per sub-shell*

Emission spectra and electrons

When an electrical voltage is applied to a gas at low pressure in a discharge tube, radiation in the visible part of the spectrum is emitted. This light can be split into its component colours using a spectroscope, an instrument designed by Robert Bunsen (the same Bunsen as in Bunsen burner).

One theory of light considers it to consist of particles, called photons, that move in a wave-like motion. Each photon has its own amount of energy, depending on the wavelength of the photon. The shorter the wavelength, the more energetic the photon and the higher the energy. Ultraviolet (UV) radiation has a shorter wavelength than infrared (IR) radiation, so a photon of UV radiation has more energy than a photon of IR radiation.

Many advertising signs are gas-discharge tubes, which are often filled with neon. When neon absorbs electrical energy, electrons become excited to higher energy levels. As the electrons fall back, radiation in the yellow part of the visible spectrum is emitted. Other colours are usually obtained by using tinted glass.

The electrons in the atoms of gas in the discharge tube absorb electrical energy. This excites the electrons and they move into a higher energy level. This is not a stable arrangement and the electrons fall back to their original position, called the ground state, in one or more steps. You can see this in Figure 19. As the electron returns to a lower energy level (or shell), energy is emitted as radiation. If this radiation is in the visible range, you see it as coloured light. A spectroscope will split this radiation into lines of a particular colour. The energy gaps between the energy levels in the atom determine the wavelength of the radiation emitted. All the lines for an element make up its emission spectrum.

If the energies of electrons were not fixed, the **emission spectra** would be continuous, with no lines.

Niels Bohr suggested that electrons could only exist at fixed energies. He gave each energy level (shell) the symbol n and numbered them 1, 2, 3, and so on, so that $n = 1$ is the first energy level and the ground state for hydrogen's 1 electron (see Figure 19).

Each line in hydrogen's emission spectrum represents the difference between the energy of the level to which the electron becomes excited and the level to which it falls back.

This is the basis of the **quantum theory**. Whereas Rutherford thought that the electron moved smoothly, Bohr showed that it moved in small jumps, or quanta.

Emission spectra provide evidence for electrons in shells. You will read about other evidence later in this chapter.

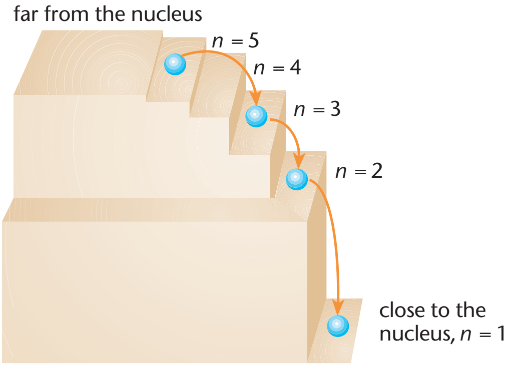


Figure 19 *The staircase model for the levels of the energies emitted by the hydrogen electron. As shown, energy jumps can be down one step or more than one step.*

QUESTIONS

Stretch and challenge

9. Why did Bohr suggest that electrons have fixed amounts of energy?
10. Draw a hydrogen atom with seven energy levels (shells). Show hydrogen's electron in the first shell. Annotate your diagram to show what happens when the electron absorbs energy and moves to $n = 3$ before falling back to the ground state. Label your diagram to show the outcome.

Electron configuration of atoms

The arrangement of electrons in an atom can be written as symbols in an **electron configuration**. The electron configuration includes sub-shells as well as shells, and shows the number of electrons in each.

- Hydrogen has one electron in shell 1, sub-shell s. Its electron configuration is 1s.
- Helium has two electrons with opposite spin. Its electron configuration is $1s^2$.
- Lithium has two electrons in 1s and one in 2s. Its electron configuration is $1s^2\ 2s^1$.

You can also draw a **spin diagram** for each sub-shell that shows the direction of spin of all the electrons. So, you can represent the 12 electrons in the shells/sub-shells of magnesium in two ways, electron configuration or a spin diagram.

	Shells/sub-shells			
	1s	2s	2p	3s
Electron configuration	$1s^2$	$2s^2$	$2p^6$	$3s^2$
Spin diagram	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓

Between hydrogen and argon, electrons of increasing energy are added, one per element, in sub-shell order 1s, 2s, 2p, 3s, 3p. Then, for potassium, the next electron skips sub-shell 3d and goes into 4s. Though shell three energies are lower overall than shell four energies, the 3d sub-shell has a higher energy than the 4s sub-shell as shown in Table 6 (and Figure 17). The order of filling is the order of elements in the Periodic Table and 4s is filled before 3d. Later, you will see that the chemical properties of elements reflect the energy levels of electrons.

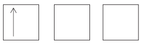
Filling orbitals

You have seen that the arrows in electron spin diagrams indicate their direction of spin and whether there are one or two electrons per orbital. The electrons fill the orbitals in a set order.

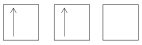
Electrons organise themselves so that they remain unpaired and fill the maximum number of sub-shells possible.

As you have seen, for the p sub-shells, this means that electrons first occupy empty orbitals and are parallel spinned. When these orbitals each have one electron, additional electrons are spin-paired; the second electron in an orbital will spin in the opposite direction.

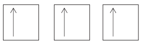
Electron $2p^1$ in boron is:



Electrons $2p^2$ in carbon are:

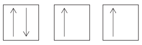


Electrons $2p^3$ in nitrogen are:

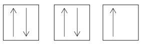


There is now one electron in each orbital. The next electron goes into the first orbital and spins in the opposite direction, so that:

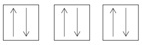
Electrons $2p^4$ in oxygen are:



Electrons $2p^5$ in fluorine are:



Electrons $2p^6$ in neon are:



In Table 6, shell one in helium is filled. The next element with a filled level is neon, which has the electron configuration $1s^2\ 2s^2\ 2p^6$.

Since the outermost shell is complete, these elements are very stable and are known as the noble gases. Noble gas configurations are used to write abbreviated electron configurations. For example, the full electron configuration for potassium is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$. The abbreviated form is $[Ar]\ 4s^1$.

Similarly, the abbreviated electron configuration for phosphorus is $[Ne]\ 3s^2\ 3p^3$.

QUESTIONS

11. Use Table 6 to help you write abbreviated electron configurations for:

- **a.** sulfur
- **b.** aluminium
- **c.** calcium
- **d.** scandium
- **e.** silicon
- **f.** iron
- **g.** krypton
- **h.** copper.

Z	Element	Electron configuration	Electron spin diagram																	
			1s	2s	2p			3s	3p			3d					4s	4p		
1	H	$1s^1$	↑																	
2	He	$1s^2$	↑↓																	
3	Li	$1s^2 2s^1$	↑↓	↑																
4	Be	$1s^2 2s^2$	↑↓	↑↓																
5	B	$1s^2 2s^2 2p^1$	↑↓	↑↓	↑	☐	☐													
6	C	$1s^2 2s^2 2p^2$	↑↓	↑↓	↑	↑	☐													
7	N	$1s^2 2s^2 2p^3$	↑↓	↑↓	↑	↑	↑													
8	O	$1s^2 2s^2 2p^4$	↑↓	↑↓	↑↓	↑	↑													
9	F	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑↓	↑↓	↑													
10	Ne	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓	↑↓	↑↓													
11	Na	$1s^2 2s^2 2p^6 3s^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑												
12	Mg	$1s^2 2s^2 2p^6 3s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓												
13	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	☐	☐									
14	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	☐									
15	P	$1s^2 2s^2 2p^6 3s^2 3p^3$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑									
16	S	$1s^2 2s^2 2p^6 3s^2 3p^4$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑									
17	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑									
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓									
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	☐	☐	☐	☐	☐	↑			
20	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	☐	☐	☐	☐	☐	↑↓			
21	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	☐	☐	☐	☐	↑↓			
22	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	☐	☐	☐	↑↓			
23	V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	☐	☐	↑↓			
24	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	↑	↑	↑			
25	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	↑	↑	↑↓			
26	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	↑	↑↓			
27	Co	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	↑↓			
28	Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑↓			
29	Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑			
30	Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓			
31	Ga	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	☐	☐
32	Ge	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	☐
33	As	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑
34	Se	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑
35	Br	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Table 6 *Electron configurations and spin diagrams for the first 30 elements*

Electron configuration of ions

An ion is an atom in which either:

- one or more electrons have been removed, producing a positively charged ion, or
- one or more electrons have been added, producing a negatively charged ion.

Worked example

What is the electron configuration of the sodium ion, Na^+?

The electron configuration of the sodium atom is $1s^2\ 2s^2\ 2p^6\ 3s^1$.

In Na^+ the outermost electron, $3s^1$, has been removed.

This is the electron of highest energy in sodium, and so takes the least energy to remove. The electron configuration of Na^+ is $1s^2\ 2s^2\ 2p^6$. Inner electron shells have the effect of shielding outermost electrons from the positive charge of the nucleus. A full shell has a strong shielding effect on a single outermost electron, which is then easy to remove, as in the case of Na^+.

QUESTIONS

12. Explain the meaning of 2, p and 6 in $2p^6$.

13. Write the electron configuration for each of:

- **a.** Ca^{2+}
- **b.** Cl^-
- **c.** Al^{3+}
- **d.** Br^-
- **e.** N^{3-}

KEY IDEAS

- Electrons in an atom are arranged in shells, with the first shell closest to the nucleus and with least energy.
- Each shell consists of one or more sub-shells, also called orbitals, of which there are four types: s, p, d and f.
- An orbital contains a maximum of two electrons spinning in opposite directions.
- The electron configuration of an atom specifies the number of electrons in each shell and sub-shell.

1.8 IONISATION ENERGIES

The energy required to remove an electron from an atom in its gaseous state is called the **ionisation energy**. The energy required to remove the first electron is called the **first ionisation energy** and can be written as:

$$M(g) \rightarrow M^+(g) + e^-$$

The energy required to remove the second electron from an atom is called the second ionisation energy and can be written as:

$$M^+(g) \rightarrow M^{2+}(g) + e^-$$

Ionisation energy values for removing the second and subsequent electrons are called **successive ionisation energies**.

The ionisation energy for one atom is so small that, for convenience, ionisation energies are measured per mole of atoms, in $kJ\ mol^{-1}$.

QUESTIONS

14. Write equations, using M, to show the third and fourth ionisation energies.

The first ionisation energy is the enthalpy change (energy change) when one mole of gaseous atoms forms one mole of gaseous ions with a single positive charge.

Ionisation energies have been calculated for all but a few of the very heavy elements in the Periodic Table. Figure 20 shows the first ionisation energies for the elements from hydrogen to caesium.

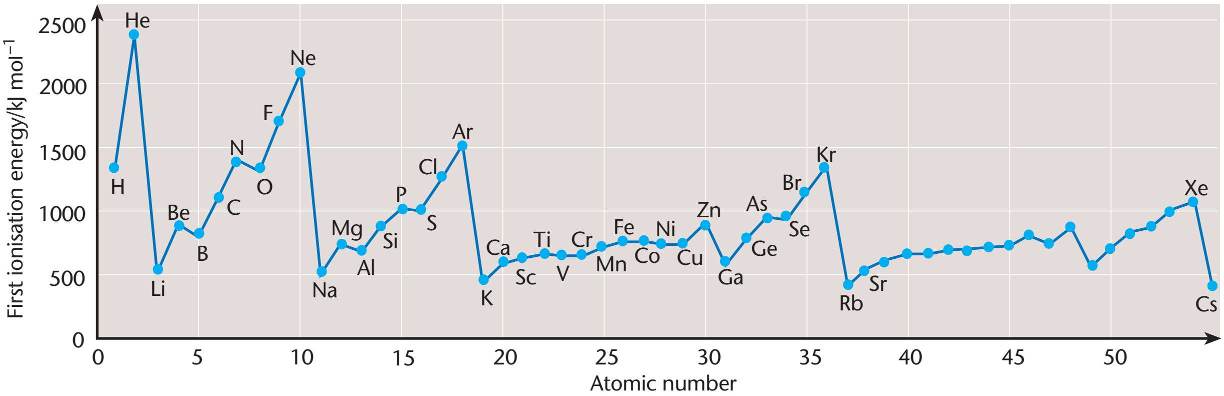


Figure 20 *First ionisation energies of the elements, from hydrogen to caesium*

1.9 EVIDENCE FOR SHELLS AND SUB-SHELLS

Patterns in first ionisation energies provide evidence for the existence of electron shells and sub-shells. You can see this if you look at the first ionisation energies down Group 2 and across Period 3. Successive ionisation energies of an element provide further evidence.

First ionisation energies of Group 2 elements

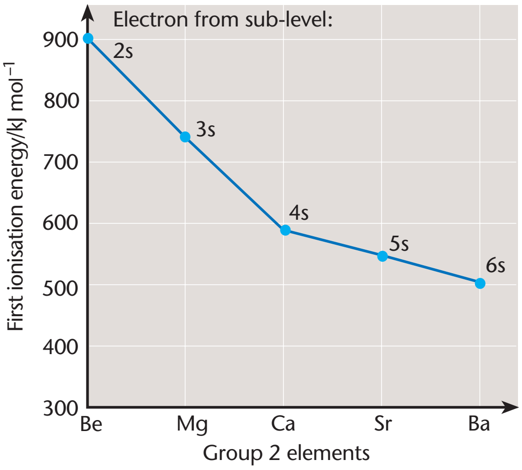


Figure 21 *First ionisation energies of Group 2 elements, from beryllium to barium*

The Group 2 elements, beryllium to barium, are reactive metals. They are also known as the alkaline earth metals because they react with water to form an alkaline solution. The outer sub-shells of these elements contain a pair of electrons in an s orbital. The first ionisation energy measures how much energy is needed to remove one mole of these electrons from a mole of atoms.

Figure 21 shows how the first ionisation energies decrease down Group 2. That means that the first electron becomes easier to remove. This is because:

- the number of electron shells between the outer electron and the nucleus is increasing; the electron shells shield the outer electron from the attraction of the nucleus, and
- the radius of each atom is increasing as you go down Group 2; the distance between the outer electron and the nucleus is increasing.

So, the outer electrons are easier to remove and the first ionisation energies decease. This is evidence for the existence of electron shells.

First ionisation energies of Period 3 elements

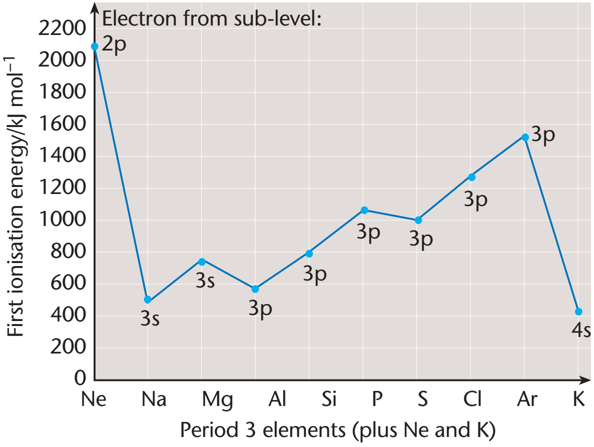


Figure 22 *First ionisation energies of Period 3 elements, from sodium to argon*

As you move across Period 3, each element has one more electron than the last. This electron fills the first available empty orbital. The electron for sodium fills the 3s orbital. The electrons in the first and second shells shield the 3s electron from the positive charge of the nucleus and it is relatively easy to remove.

Magnesium has one more electron than sodium, and this completes the 3s orbital and spins in the opposite direction. Magnesium also has an extra proton, so the positive charge on the nucleus has increased. More energy is needed to remove magnesium's first electron. Magnesium's first ionisation energy is higher than sodium's.

The extra electron that aluminium has compared with magnesium is the first to fill a 3p orbital. p orbitals have higher energy than s orbitals. Aluminium's first electron is easier to remove than the 3s electron of magnesium. The first ionisation energy drops.

The extra electron that silicon has compared with aluminium, and that phosphorus has compared with silicon, fill the remaining empty 3p orbitals. At the same time, the positive charge on the nucleus is increasing and more energy is needed to remove these electrons. The first ionisation energies increase from aluminium to phosphorus.

Sulfur's first electron enters a 3p orbital already containing one electron. These spin in opposite directions and repel each other. It takes less energy to remove the first electron from sulfur than to remove the first electron from phosphorus. Its first ionisation energy is lower.

The electrons for chlorine and argon fill the remaining 3p orbitals. The positive charge on the nucleus continues to increase and the first ionisation energy increases as more energy is needed to remove an electron.

The general trends for first ionisation energy are:

- A sharp fall in ionisation energy between neon and sodium and between argon and potassium as electrons enter a new shell. This is evidence that the outer electron is on its own in a new shell and is shielded from the charge on the nucleus by electrons in the inner shells.
- An overall increase in the first ionisation energy across Period 3 as the positive charge on the nucleus increases and electrons are attracted more strongly.
- An increase in ionisation energy for each sub-shell as the charge on the nucleus increases and electrons are attracted more strongly.
- A fall in ionisation energy between magnesium and aluminium as electrons start to fill a new sub-shell, 3p. This is evidence that a new sub-shell is being filled.
- A fall in ionisation energy between phosphorus and sulfur as electrons start to pair up in the 3p sub-shells. This is evidence that electrons are pairing up in sub-shells.

Successive ionisation energies

Magnesium has the electron configuration 2,8,2. Its first three successive ionisation energies are:

$Mg(g) \rightarrow Mg^{+}(g) + e^{-}$
first ionisation energy = $+738\ kJ\ mol^{-1}$

$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$
second ionisation energy = $+1451\ kJ\ mol^{-1}$

$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^{-}$
third ionisation energy = $+7733\ kJ\ mol^{-1}$

Figure 23 shows a graph of the $\log_{10}$ successive (ionisation energy) against the number of the electron removed (ionisation number) for magnesium. We use $\log_{10}$ to make the numbers easier to handle.

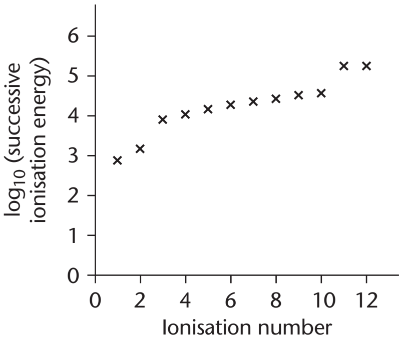


Figure 23 *The trend in the successive ionisation energies of magnesium*

The first two electrons are removed from the third or outer shell. The increase between the second and third electron is because the third electron is taken from the second shell. The gradual increase from the third to the tenth electron shows electrons being removed from the second shell. The large increase between the tenth electron and eleventh electron is because the eleventh electron is taken from the first shell.

QUESTIONS

Stretch and challenge

15. Use Table 7 (which gives the successive ionisation energies for magnesium) to plot a graph of successive ionisation energy divided by the charge on the remaining ion against the number of electrons removed.

16. Using your knowledge of shells and sub-shells, explain the shape of the graph you obtained.

17. These are the first five successive ionisation energies for elements X, Y and Z:

X	578, 1817, 2745, 11578, 14831
Y	496, 4563, 6913, 9544, 13352
Z	738, 1451, 7733, 10541, 13629

In which group of the Periodic Table are these elements found?

Ionisation	Ionisation energy/kJ mol^{-1}
1	738
2	1451
3	7733
4	10 543
5	13 630
6	18 020
7	21 711
8	25 661
9	31 653
10	35 458
11	169 988
12	189 368

Table 7 *The successive ionisation energies of magnesium*

ASSIGNMENT 4: WHY DO SCIENTISTS THINK ELECTRONS ARE ARRANGED IN SHELLS AND SUB-SHELLS?

(MS 3.1, 3.2)

One piece of evidence for this theory came from patterns from ionisation energy plots. These are the first ionisation energies for Period 2:

Element	Li	Be	B	C	N	O	F	Ne
First ionisation energy/kJ mol^{-1}	520	899	801	1087	1402	1313	1681	2080

Questions

A1. Plot a graph of first ionisation energy against atomic number, *Z*.

A2. Why is there an overall increase across Period 2 from lithium to neon?

A3. Why is the first ionisation energy of beryllium higher than that of lithium?

A4. Why are there dips in the pattern at boron and oxygen?

A5. Why is there an increase in the first ionisation energy between:

- **a.** boron and nitrogen
- **b.** oxygen and neon?

A6. If there was a regular increase in the first ionisation energy across Period 2, what might scientists conclude about the existence of sub-shells?

A7. What is the evidence for the existence of:

- **a.** electron shells
- **b.** electron sub-shells?

A8. How does lithium's first ionisation energy help to predict its reactivity?

A9. How does neon's first ionisation energy help to predict its stability and/or lack of reactivity?

KEY IDEAS

- The first ionisation energies decrease down Group 2 because the outermost electrons are increasingly shielded from the attraction of the nucleus.
- There is an overall increase in the first ionisation energy across a period because of the increasing nuclear charge.
- The first ionisation energies provide evidence for the existence of shells and sub-shells.

PRACTICE QUESTIONS

1. The element rubidium exists as the isotopes ^{85}Rb and ^{87}Rb.

a. State the number of protons and the number of neutrons in an atom of the isotope ^{85}Rb.

b. i. Explain how the gaseous atoms of rubidium are ionised in a mass spectrometer.

ii. Write an equation, including state symbols, to show the process that occurs when the first ionisation energy of rubidium is measured.

c. Table Q1 shows the first ionisation energies of rubidium and some other elements in the same group.

Element	Sodium	Potassium	Rubidium
First ionisation energy/kJ mol^{-1}	494	418	402

Table Q1

State one reason why the first ionisation energy of rubidium is lower than the first ionisation energy of sodium.

d. i. State the block of elements in the Periodic Table that contains rubidium.

ii. Deduce the full electron configuration of a rubidium atom.

e. A sample of rubidium contains the isotopes ^{85}Rb and ^{87}Rb only. The isotope ^{85}Rb has an abundance 2.5 times greater than that of ^{87}Rb. Calculate the relative atomic mass of rubidium in this sample. Give your answer to one decimal place.

f. By reference to the relevant part of the mass spectrometer, explain how the abundance of an isotope in a sample of rubidium is determined.

AQA June 2012 Unit 1 Question 1

2. The element nitrogen forms compounds with metals and non-metals.

a. Nitrogen forms a nitride ion with the electron configuration $1s^2\ 2s^2\ 2p^6$. Write the formula of the nitride ion.

b. An element forms an ion Q with a single negative charge that has the same electron configuration as the nitride ion. Identify the ion Q.

c. Use the Periodic Table and your knowledge of electron arrangement to write the formula of lithium nitride.

AQA Jan 2012 Unit 1 Question 5a, b

3. Mass spectrometry can be used to identify isotopes of elements.

a. i. In terms of fundamental particles, state the difference between isotopes of an element.

ii. State why isotopes of an element have the same chemical properties.

b. Give the meaning of the term relative atomic mass.

(Continued)

c. The mass spectrum of element X has four peaks. Table Q2 gives the relative abundance of each isotope in a sample of element X.

m/z	64	66	67	68
Relative abundance	12	8	1	6

Table Q2

- **i.** Calculate the relative atomic mass of element X. Give your answer to one decimal place.
- **ii.** Use the Periodic Table to identify the species responsible for the peak at *m/z* = 64.

d. Explain how the detector in a mass spectrometer enables the abundance of an isotope to be measured.

AQA June 2011 Unit 1 Question 1

4. Indium is in Group 3(13) in the Periodic Table and exists as a mixture of the isotopes ^{113}In and ^{115}In.

a. Use your understanding of the Periodic Table to complete the electron configuration of indium.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$ ______

b. A sample of indium must be ionised before it can be analysed in a mass spectrometer.

- **i.** State what is used to ionise a sample of indium in a mass spectrometer.
- **ii.** Write an equation, including state symbols, for the ionisation of indium that requires the minimum energy.
- **iii.** State why more than the minimum energy is not used to ionise the sample of indium.
- **iv.** Give two reasons why the sample of indium must be ionised.

c. A mass spectrum of a sample of indium showed two peaks at *m/z* = 113 and *m/z* = 115. The relative atomic mass of this sample of indium is 114.5

- **i.** Give the meaning of the term *relative atomic mass*.
- **ii.** Use these data to calculate the ratio of the relative abundances of the two isotopes.

d. State and explain the difference, if any, between the chemical properties of the isotopes ^{113}In and ^{115}In.

AQA Jan 2011 Unit 1 Question 2

5. a. Copy and complete Table Q3.

	Relative mass	Relative charge
Proton		
Electron		

Table Q3

b. An atom has twice as many protons and twice as many neutrons as an atom of ^{19}F. Deduce the symbol, including the mass number, of this atom.

c. The Al^{3+} ion and the Na^+ ion have the same electron arrangement.

- **i.** Give the electron arrangement of these ions in terms of s and p electrons.
- **ii.** Explain why more energy is needed to remove an electron from the Al^{3+} ion than from the Na^+ ion.

d. The first ionisation energies of a group of elements provides evidence for the existence of electron shells.

- **i.** Describe the trend in first ionisation energies down Group 2.
- **ii.** Explain how the trend you have described in d.i. provides evidence for the existence of electron shells.

e. First ionisation energies across a period provide evidence for the existence of electrons in sub-shells.

- **i.** Describe the trend in first ionisation energies in Period 3.
- **ii.** Explain how the trend you have described in e.i. provides evidence for the existence of electron sub-shells.

AQA January 2007 2 Unit 1 Question 1

6. a. Copy and complete Table Q4.

	Relative mass	Relative charge
Proton		
Electron		

Table Q4

(Continued)

b. An atom of element Q contains the same number of neutrons as are found in an atom of ^{27}Al. An atom of Q also contains 14 protons.

  i. Give the number of protons in an atom of ^{27}Al.

  ii. Deduce the symbol, including mass number and atomic number, for this atom of element Q.

c. Define the term *relative atomic mass* of an element.

d. Table Q5 gives the relative abundance of each isotope in a mass spectrum of a sample of magnesium.

m/z	24	25	26
Relative abundance	73.5	10.1	16.4

Table Q5

Calculate the relative atomic mass of this sample of magnesium, using the data in Table Q5. Give your answer to one decimal place.

e. State how the relative molecular mass of a covalent compound is obtained from its mass spectrum.

AQA June 2004 Unit 1 Question 1

7. A sample of iron from a meteorite was found to contain the isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe.

a. The relative abundances of these isotopes can be determined using a time-of-flight (TOF) mass spectrometer. In the mass spectrometer, the sample is first vaporised and then ionised.

  i. State what is meant by the term *isotopes*.

  ii. Give an equation to show a gaseous iron atom producing one electron and an iron ion in the ionisation area.

  iii. State the two variables that determine the time taken for an ion to move across the drift area.

  iv. Explain why it is difficult to distinguish between an $^{56}\text{Fe}^{+}$ ion and a $^{112}\text{Cd}^{2+}$ ion in a mass spectrometer.

b. i. Define the term *relative atomic mass of an element*.

  ii. The relative abundances of the isotopes in this sample of iron are shown in Table Q6.

m/z	54	56	57
Relative abundance	5.8	91.6	2.6

Table Q6

Calculate the relative atomic mass of iron in this sample, using the data in Table Q6. Give your answer to one decimal place.

AQA June 2005 Unit 1 Question 1

8. a. Titanium is a d block element in Period 4.

  i. State what is meant by a d block element.

  ii. Write the full electron configuration for titanium in terms of s, p and d electrons.

b. Titanium has five stable isotopes, with ^{48}Ti being the most abundant.

  i. State one difference and two similarities between the stable isotopes of titanium.

  ii. Explain why stable isotopes of titanium have the same chemical properties.

c. Mass spectroscopy can be used to determine the relative abundance of titanium isotopes. Why is it difficult to distinguish between $^{48}\text{Ti}^{2+}$ and $^{24}\text{Mg}^{+}$ ions on a mass spectrum?

Stretch and challenge

9. Scandium is a d block element and is used in alloys to make sporting equipment such as golf clubs and fishing rods.

a. Give the electron configuration for scandium.

(Continued)

b. When d block elements form ions, the s electrons are lost first, then d electrons. Most d block elements form ions with more than one charge, but the scandium ions has a $+3$ charge in most of its compounds.

   i. Give the electron configuration for the Sc^{3+} ion.

   ii. Suggest why most d block elements have ions with a $+2$ charge.

c. Like scandium, zinc only forms one type of ion. It has a $+2$ charge. Give the electron configuration for a Zn^{2+} ion.

d. Iron forms ions with a $+2$ charge and with a $+3$ charge. Give the electron configuration for the Fe^{3+} ion.

Multiple choice

10. Which element has an isotope with an atomic number of 35 and a mass number of 79?

A. Chlorine
B. Gold
C. Bromine
D. Selenium

11. How many neutrons are present in an atom of $^{27}_{13}Al$?

A. 13
B. 27
C. 14
D. 40

12. What is 0.00859 in standard form?

A. 8.59×10^{-1}
B. 8.59×10^{-2}
C. 8.59×10^{-3}
D. 8.59×10^{-4}

13. What determines the flight time of ions in the drift region of a time-of-flight spectrometer?

A. Mass only
B. Charge only
C. *m*/*z* ratio
D. The number of electrons removed by electrospray ionisation only