



AQA
A-level

Chemistry

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Answers for the Test yourself questions and Activities in this book are available online at www.hoddereducation.co.uk/AQACchemistry. Chapters on practical skills (Chapter 34) and preparing for the examinations (Chapter 35) are also available online.

The following features have been included to help you get the most from this book.

This is a short list of topics that you should be familiar with before starting a chapter. The questions will help to test your understanding.

Key terms and formulae

These are highlighted in the text and definitions are given in the margin to help you pick out and learn these important concepts.

These highlight important facts, common misconceptions and signpost you towards other relevant topics.

Examples of questions or calculations are included to illustrate topics and feature full workings and sample answers.

These short questions, found throughout each chapter, are useful for checking your understanding as you progress through a topic.

EQUILIBRIUM SYSTEMS

TIP

It is always important to have a clear understanding of units in all quantities. If the volume was given as 600 cm^3 , this is equal to 0.6 dm^3 so the equilibrium moles should be divided by 0.6 to determine concentrations in mol dm^{-3} .

TEST YOURSELF 3

- 1.0 mol of A and 1.0 mol of B were mixed and allowed to reach equilibrium at a certain temperature.
 $2A + 2B \rightleftharpoons C + D$

- 0.2 mol of C were present at equilibrium mixture.
- Write an expression for the equilibrium constant, K_c , for this equilibrium and deduce its units.
- Calculate the amount, in moles, of A, B and D present in the equilibrium mixture.
- 10.0 mol of PCl₅ were allowed to reach equilibrium in a container of volume 2.5 dm^3 according to the equation.

- Write an expression for the equilibrium constant, K_c , for this reaction.
- Deduce the units for K_c .
- Calculate the amounts, in moles, of PCl₃ and Cl₂ in the equilibrium mixture.

- Calculate the concentration of PCl₅, PCl₃ and Cl₂ in the equilibrium mixture.

- Write an expression for the equilibrium constant, K_c , for this reaction:
 $NH_3 + SO_2 \rightleftharpoons N_2O + H_2O$

- Deduce the units for K_c .
- 2.00 mol of NH₃ and 5.50 mol of O₂ were present in the equilibrium mixture. 0.80 mol of NO were present in the equilibrium mixture.
- Calculate the amount, in moles, of NH₃, O₂ and H₂O present in the equilibrium mixture.
- The total volume is 20.0 dm^3 . Calculate the equilibrium concentrations of all reactants and products.

The equilibrium concentrations may be determined by dividing the equilibrium moles by the volume (see V if volume is not given). The equilibrium concentration may then be substituted into the K_c expression to calculate a value for K_c .

For a K_c expression which has no units, the volumes will cancel out as there are equal number of moles on each side of the equilibrium equation.

TIP

It is important to note that in this question, no volume is given as V/dm^3 is used as the volume and the equilibrium moles are divided by V to calculate the equilibrium concentrations in mol dm^{-3} .

TIP

K_c has no units. V cancels out in the equilibrium expression. It is acceptable to use equilibrium moles to calculate the value of a K_c which has no units but the use of V is better practice and appears in many mark schemes.

TIP

The answer has been given to 2 significant figures as all the initial data were given to 2 significant figures. This is good practice and you will notice this in mark schemes.

EXAMPLE 6

Nitrogen monoxide decomposes into nitrogen and oxygen according to the equilibrium:

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

- Write an expression for the equilibrium constant, K_c , for this equilibrium.
- Explain why K_c for this reaction has no units.
- 5.0 mol of nitrogen monoxide were allowed to come to equilibrium in a sealed container at a particular temperature. 1.5 mol of nitrogen were in the equilibrium mixture.
- Calculate the amount, in moles, of oxygen molecule and oxygen in the equilibrium mixture.
- Calculate a value for K_c for this equilibrium at this temperature.

Answers

- $K_c = \frac{[N_2][O_2]}{[NO]^2}$
- Equal numbers of moles on each side of the reaction so the concentrations cancel each other out in terms of units.

	mol	mol	mol
initial moles	5.0	0	0
reacting moles	-3.0	+1.5	+1.5
equilibrium moles	2.0	1.5	1.5
equilibrium concentrations	$\frac{2.0}{V}$	$\frac{1.5}{V}$	$\frac{1.5}{V}$
$K_c = \frac{[N_2][O_2]}{[NO]^2}$	$\frac{1.5}{2.0} \times \frac{1.5}{2.0}$	$\frac{2.75}{4.0}$ (no units)	

EXAMPLE 9

A reacts with B to form C and D according to the equilibrium below:

$$A + B \rightleftharpoons C + D$$

0.20 mol of A and 0.20 mol of B were mixed with 0.80 mol of C in a container of volume 10 dm^3 and the mixture was allowed to come to equilibrium at 500 K .

The equilibrium mixture contained 0.20 mol of A.

- Calculate the concentration, in mol dm^{-3} , of A, B, C and D in the equilibrium mixture.
- Write an expression for the equilibrium constant, K_c , for this reaction.
- Calculate a value for K_c for this equilibrium at 500 K and state its units, if any.

Activities

These practical-based activities will help consolidate your learning and test your practical skills.

In this edition the authors describe many important experimental procedures as “Activities” to conform to recent changes in the A-level curriculum. Teachers should be aware that, although there is enough information to inform students of techniques and many observations for exam-question purposes, there is not enough information for teachers to replicate the experiments themselves or with students without recourse to CLEAPSS Hazcards or Laboratory worksheets which have undergone a thorough risk assessment procedure.

EXAMPLE 1

Exhaust emissions from a petrol engine were found to contain traces of a molecule 'T' with the molecular formula C_7H_{14} .

- 1 Explain how this compound came to be present in the exhaust fumes.
- 2 Suggest other compounds which may be present in the fumes.
- 3 Write a balanced equation to show how 'T' is removed from the exhaust emissions, after passing through a catalytic converter.

Answers

The formula of 'T' conveys a lot of information. It is an alkene with seven carbon atoms. It belongs to the petrol fraction from the fractional distillation of crude oil. It is therefore used as a fuel in petrol engines. Some of this fuel will pass through the engine unburnt.

- 1 C_7H_{14} is unburnt hydrocarbon which is used as fuel for the petrol engine.
- 2 Oxides of nitrogen can be present (NO , NO_2) due to spark in the combustion engine. Sulfur oxides are present as the fuel may contain some sulfur-containing compounds.
- 3 You need to recall that the unburnt hydrocarbons are removed by reacting with nitrogen(III) oxide to produce nitrogen, carbon dioxide and water. Write the formulae in an equation form.

$$C_7H_{14} + NO \rightarrow N_2 + CO_2 + H_2O$$

To balance the equation, balance the C atoms and the H atoms followed by the O atoms before finally balancing the N atoms.

$$C_7H_{14} + 22NO \rightarrow 11N_2 + 7CO_2 + 8H_2O$$

TEST YOURSELF 5

- 1 a) What is the function of a catalytic converter?
b) Write balanced symbol equations to show how the following gases are removed from vehicle exhaust fumes.
i) CO
ii) NO_2
iii) NO
iv) C_2H_2
c) Why is the catalyst constructed in a honeycomb shape?
d) State two ways in which the cost of the catalytic converter is kept to a minimum when the metals used are very expensive.

ACTIVITY

Burning petrol in car engines

In a car engine, petrol vapour and air are compressed and ignited. The compression can cause pre-ignition which results in an undesirable knocking sound from the engine. Branched chain alkanes, such as that shown in Figure 12.17, are less likely to cause pre-ignition.

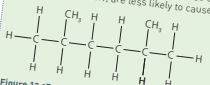


Figure 12.17

- 1 Name the alkane in Figure 12.17.
- 2 State the molecular formula of this alkane.
- 3 Draw and name a straight chain alkane isomer of this molecule.

Practice questions

- 1 How many branched chain isomers are there with the molecular formula C_6H_{14} ? (1)
A 4 B 5
C 7 D 8
- 2 Hexane is an alkane.
a) State the general formula of the alkanes. (1)
b) Give the molecular formula for hexane. (1)
c) Alkane A can be cracked to form one molecule of hexane and two molecules of propene, C_3H_6 . Deduce the molecular formula of A. (1)
- 3 Cracking is a process used in the petrochemical industry.
a) Explain what is meant by the term cracking. (1)
b) One type of cracking produces a high percentage of alkenes.
i) Name this type of cracking. (1)
ii) State the conditions used in this type of cracking. (2)
c) Give one economic reason why cracking is necessary. (1)

Practice questions

You will find practice questions, including multiple-choice questions, at the end of every chapter. These follow the style of the different types of questions with short and longer answers that you might see in your examination, and they are colour coded to highlight the level of difficulty.

- Green – Basic questions that everyone should be able to answer without difficulty.
- Orange – Questions that are a regular feature of exams and that all competent candidates should be able to handle.
- Purple – More demanding questions which the best candidates should be able to do.

Dedicated chapters for developing your **Maths** can be found for Year 1 (Chapter 17) and Year 2 (Chapter 33).

1

Atomic structure

PRIOR KNOWLEDGE

Protons have a positive charge (relative charge = +1), electrons have a negative charge (relative charge = -1) and neutrons have no charge at all (relative charge = 0).

The mass of an atom is centred in the nucleus as the mass of electrons are very much less than the mass of protons and neutrons.

The relative mass of a proton is 1; the relative mass of a neutron is 1 but the relative mass of an electron is $\frac{1}{1840}$.

Electrons are arranged in shells at increasing distances from the nucleus. There are a maximum number of electrons which each shell can hold. The shells closest to the nucleus fill first.

- The number of protons in the nucleus of an atom of a particular element is the same as the atomic number for that element.
- In an atom, the number of protons is equal to the number of electrons. This makes atoms electrically neutral (have no charge).
- The number of neutrons is equal to the mass number – atomic number.
- The mass number and atomic number are often written before the symbol for the element as for example, $^{23}_{11}\text{Na}$, where 11 is the atomic number for sodium and 23 is the mass number for this atom of sodium.
- Atoms of the same element with the same number of protons and a different number of neutrons are called isotopes. For example boron has two isotopes: $^{10}_5\text{B}$ and $^{11}_5\text{B}$. An atom of $^{10}_5\text{B}$ contains 5 protons, 5 electrons and 5 neutrons; an atom of $^{11}_5\text{B}$ contains 5 protons, 5 electrons and 6 neutrons.
- The electronic structure of an atom is determined from the number of electrons. The first shell can hold a maximum of 2 electrons, the second shell can hold 8 electrons and the third shell can hold a maximum of 8 electrons.
- For example an atom of sodium (atomic number 11, mass number 23) has 11 protons in the nucleus; 11 electrons arranged in shells and 12 (= 23 – 11) neutrons in the nucleus. The 11 electrons are arranged 2 in the first shell; 8 in the second shell and 1 in the third shell – this is often written as 2, 8, 1 for the electronic structure or electron configuration.

TEST YOURSELF ON PRIOR KNOWLEDGE 1

- 1 What is meant by the term atomic number?
- 2 State the relative mass and relative charge of: a) a proton; b) an electron and c) a neutron?
- 3 $^{35}_{17}\text{Cl}$ and $^{37}_{17}\text{Cl}$ are isotopes of chlorine.
 - a) What is meant by the term isotopes?
 - b) Calculate the number of protons, electrons and neutrons in an atom of $^{37}_{17}\text{Cl}$.
- 4 Write electron configurations for the following atoms:
 a) P b) Li c) O d) K e) Ar f) He g) Al
- 5 Identify the element which has atoms with 15 electrons and 16 neutrons.

The development of theories about atoms and their structure has spanned centuries. The model of the atom that will be familiar from previous study is of a heavy nucleus containing protons (and neutrons) surrounded by electrons orbiting in shells. Many scientists contributed to the development of theories of atomic structure.

The basics of atomic structure

An atom is the smallest particle of an element which has the characteristic properties of the element. The symbol for an element can represent an atom of that element. For example, Mg represents an atom of magnesium, C represents an atom of carbon.

Relative mass of subatomic particles

Atoms are composed of subatomic particles called electrons, protons and neutrons. The table below shows the relative mass, relative charge and location of the subatomic particles. The actual mass of a proton is $1.67262178 \times 10^{-27}$ kg. For ease of calculation the masses of the subatomic particles are measured relative to the mass of a proton, which is given a value of 1. The mass of a neutron is the same and the mass of an electron is 1840 times less. The same idea of a relative scale is used with charge. The charge on a proton is given a value of +1 and the charge on an electron has the same magnitude but it is oppositely charged.

Particle	Relative mass	Relative charge	Location in the atom
Proton	1	+1	nucleus
Neutron	1	0	nucleus
Electron	$\frac{1}{1840}$	-1	energy levels

As the relative mass of an electron is substantially smaller than the mass of a proton and a neutron, most of the mass of an atom is concentrated in the nucleus. The nucleus occupies only a small fraction of the total volume of the atom.

The incredibly high density within the nucleus suggests that the particles within it are drawn very close together by extremely powerful forces. These

forces are obviously so powerful that they can overcome the repulsion which the protons have for each other as they are positively charged. Neutrons have no charge and are not involved in the repulsion in the nucleus.

Atomic number and mass number

- The **atomic number** is equal to the number of protons in the nucleus of an atom.
- The **mass number** is the total number of protons and neutrons in the nucleus of an atom.
- Atoms of the same element can have different masses. For example an atom of hydrogen can have a mass number of 1, 2 or 3.
- Atoms of the same element, which have different mass numbers, are called **isotopes**.
- All the isotopes of an element have the same atomic number as they have the same number of protons in the nucleus.

TIP

The number of protons defines the element. Any particles with 17 protons are particles of the element chlorine – they may be ions or atoms.



Figure 1.1 The explosive power of a hydrogen bomb results from an uncontrolled, chain reaction in which isotopes of hydrogen – namely deuterium and tritium combine under extremely high temperatures. What element do you think is produced?

Isotopes

Isotopes should be written as shown below.

$$\begin{array}{l} \text{Mass number} \rightarrow A \\ \text{Atomic number} \rightarrow Z \end{array} \text{E}$$

where E is the symbol for the element. A is often used to represent the mass number and Z is used to represent the atomic number. The atomic number can also be called the proton number.

There are three isotopes of hydrogen which can be written as:

- ${}^1_1\text{H}$ Mass Number 1, Atomic Number 1, called protium
 ${}^2_1\text{H}$ Mass Number 2, Atomic Number 1, called deuterium
 ${}^3_1\text{H}$ Mass Number 3, Atomic Number 1, called tritium

From the mass number and atomic number, it is possible to determine the quantities of the various subatomic particles in an atom of each isotope, using the formulae:

$$\text{Mass Number} = \text{Number of protons} + \text{Number of neutrons}$$

$$\text{Atomic Number} = \text{Number of protons}$$

So

$$\text{Number of neutrons} = \text{Mass Number} - \text{Atomic Number}$$

$$\text{Number of electrons} = \text{Number of protons [in a neutral atom]}$$

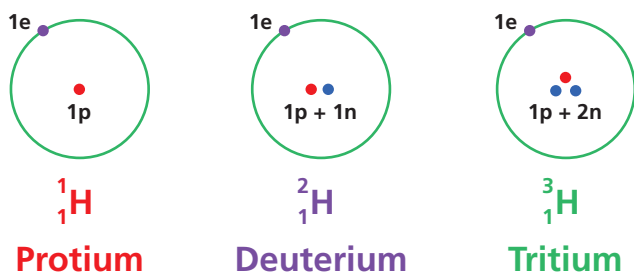


Figure 1.2 The three isotopes of hydrogen, showing their subatomic particles.

	Number of protons	Number of electrons	Number of neutrons
Protium ${}^1_1\text{H}$	1	1	0
Deuterium ${}^2_1\text{H}$	1	1	1
Tritium ${}^3_1\text{H}$	1	1	2

Not all isotopes of elements have individual names, for example, with the two isotopes of chlorine:

$^{35}_{17}\text{Cl}$ (often called chlorine-35): Mass Number 35, Atomic Number 17

$^{37}_{17}\text{Cl}$ (often called chlorine-37): Mass Number 37, Atomic Number 17

The table below shows the numbers of subatomic particles for the two isotopes of chlorine.

	Number of protons	Number of electrons	Number of neutrons
Chlorine-35	17	17	18
Chlorine-37	17	17	20



Figure 1.3 Analysis of carbon isotope ratios ($^{13}\text{CO}_2$: $^{12}\text{CO}_2$) in the breath of paediatric patients on ventilators can lead to early detection of sepsis. Sepsis is a whole-body inflammation caused by severe infection, which can lead to death.

TIP

Often the atomic number is not included when identifying isotopes but the mass number should always be written. Chlorine-35 may be written as $^{35}_{17}\text{Cl}$ or ^{35}Cl .

Isotopes have the same number and arrangement of electrons and so the atoms of each isotope will have the same chemical properties. However due to the different numbers of neutrons, the atoms have different masses and hence different physical properties. For example pure $^{37}_{17}\text{Cl}_2$ will have a higher density, higher melting point and higher boiling point than pure $^{35}_{17}\text{Cl}_2$.

Two important isotopes of carbon are ^{12}C and ^{13}C .

The carbon-12 standard

The masses of all atoms are measured relative to the mass of an atom of carbon-12, which is given a value of 12.0000. In all the following definitions the term relative means that the mass is measured against $\frac{1}{12}$ the mass of an atom of carbon-12.

The reason for the choice of carbon as the standard is an historical one and a practical one. Originally hydrogen was chosen as the standard against which the masses of all other elements was measured, however when the accuracy of atomic mass measurement reached 0.00001, it was realised that elements were a mixture of atoms of different masses. So it was decided to choose one isotope of an element as the standard. $^{12}_6\text{C}$ was chosen for the practicality of carrying a solid around as opposed to a gas.

The **relative isotopic mass** is the mass of a single isotope of an element relative to $\frac{1}{12}$ the mass of an atom of carbon-12. This is most often derived from mass spectrometry where the mass of the individual isotopes can be determined. This will be explained in the next section. For all purposes the value of the relative isotopic mass is the same as the mass number for a particular isotope of an element.

The **relative atomic mass** (A_r) is the average mass of an atom of an element relative to $\frac{1}{12}$ the mass of an atom of carbon-12. A_r is often used as shorthand for relative atomic mass.

Calculating relative atomic mass

Naturally occurring elements are composed of a mixture of different isotopes. These isotopes occur in different proportions.

If the proportion of each isotope were to be changed, the relative atomic mass of the element would change. The following hypothetical example shows what would happen if the proportion of the two isotopes of chlorine were different.

% chlorine-35	100.0	75.0	50.0	25.0	0.0
% chlorine-37	0.0	25.0	50.0	75.0	100.0
Relative atomic mass	35.0	35.5	36.0	36.5	37.0

EXAMPLE 1

In a naturally occurring sample of chlorine, 75% is ^{35}Cl and the remainder (25%) is ^{37}Cl . Calculate the relative atomic mass of the sample of chlorine.

Assuming 100 atoms of chlorine.

Answer

Total mass of ^{35}Cl atoms = $75 \times 35 = 2625$

Total mass of ^{37}Cl atoms = $25 \times 37 = 925$

Total mass of 100 atoms = $(75 \times 35) + (25 \times 37) = 3550$

Average mass = $\frac{3550}{100} = 35.5$

Relative atomic mass of chlorine = 35.5.

The relative abundance of the two isotopes may not be given as a percentage. The relative atomic mass is calculated in the same way. Multiply the mass by the relative abundance for each isotope. Add these values together and divide by the total of all the relative abundances.

EXAMPLE 2

This table shows the relative abundances of the three different isotopes of magnesium. Calculate the relative atomic mass of magnesium to one decimal place.

Isotope	Relative abundance
^{24}Mg	15.8
^{25}Mg	2.0
^{26}Mg	2.2

For each isotope multiply the mass by the relative abundance and add these together. Finally divide this number by the sum of the relative abundances.

Answer

$$\begin{aligned}
 \text{Relative atomic mass} &= \frac{(15.8 \times 24) + (2.0 \times 25) + (2.2 \times 26)}{15.8 + 2.0 + 2.2} \\
 &= \frac{379.2 + 50 + 57.2}{20} \\
 &= \frac{486.4}{20} = 24.32
 \end{aligned}$$

The answer to one decimal place is 24.3.

TIP

Often you may be asked to quote the answer to a specific number of decimal places. The answer above to 1 decimal place is 24.3. 24.48 to 1 decimal place becomes 24.5. 48.775 to 2 decimal places becomes 48.78. If you are unsure about decimal places see Chapter 17.

TEST YOURSELF 2

1 State the number of protons, electrons and neutrons present in the following atoms:

- a) ${}_{19}^{39}\text{K}$ b) ${}_{9}^{19}\text{F}$ c) ${}_{56}^{137}\text{Ba}$ d) ${}_{88}^{226}\text{Ra}$

2 Bromine has two isotopes which are detailed in this table.

Isotope	Atomic number	Mass number	% abundance
${}_{35}^{79}\text{Br}$			
	35	81	49.5

- a) Copy and complete the table above.
 b) Calculate the relative atomic mass of bromine.
- 3 Copper exists as two isotopes, ${}^{65}\text{Cu}$ and ${}^{63}\text{Cu}$. ${}^{65}\text{Cu}$ has an abundance of 30.8%.
- a) Calculate the relative abundance of ${}^{63}\text{Cu}$.
 b) Calculate the relative atomic mass of copper to two decimal places.
- 4 Silver has two isotopes, ${}^{107}\text{Ag}$ and ${}^{109}\text{Ag}$. 52% of silver is ${}^{107}\text{Ag}$. Determine the relative atomic mass of silver.
- 5 92.0% of lithium is ${}^7\text{Li}$ and the remainder is ${}^8\text{Li}$. Determine the relative atomic mass of lithium to 1 decimal place.
- 6 Boron has two isotopes, ${}^{10}\text{B}$ and ${}^{11}\text{B}$. The relative atomic mass of boron is 10.8. Calculate the percentage abundance of each of the two isotopes.

Mass spectrometry

Mass spectrometry can be used to determine information about elements and compounds. It can determine the relative isotopic masses of the isotopes of elements and their relative abundance. It shows the different isotopes of an element. This information is used to calculate the relative atomic mass (A_r) of an element. For compounds, mass spectrometry can identify unknown purified compounds by comparing the mass spectrum obtained to those in a database. The mass spectrum of a compound also gives its relative molecular mass (M_r).

Time-of-flight (TOF) mass spectrometer

A TOF mass spectrometer is used to analyse elements and compounds. The sample is dissolved in a polar, volatile solvent and pumped through a narrow capillary tube to create droplets of the solution. A polar volatile solvent is used to ensure that it evaporates.

The five processes which occur in a TOF mass spectrometer are:

1 Electrospray ionisation

A high voltage is applied to the tip of the capillary to produce highly charged droplets. The solvent evaporates from these droplets to produce gaseous charged ions. All the ions in this simple treatment of TOF mass spectrometry are considered to be mononuclear ions (with a single positive charge).

2 Acceleration

An electric field is applied to give all the ions with the same charge a constant kinetic energy. As kinetic energy $= \frac{1}{2}mv^2$, it depends on the mass of the particles (m) and their velocity (v , or speed). As all particles are given the same kinetic energy, heavier particles (larger M_r) move more slowly than lighter particles.

3 Ion drift

The ions enter a region with no electric field called the flight tube. Here the ions are separated based on their different velocities. The smaller fast ions travel through the flight tube much more rapidly and arrive at the detector first.

4 Ion detection

The detector records the different flight times of the ions. The positively charged ions arrive at the detector and cause a small electric current because of their charge.

5 Data analysis

The flight times are analysed and recorded as a mass spectrum by the data analyser. The mass spectrum obtained is a plot of relative abundance against mass to charge ratio (m/z).

General information about a mass spectrum

The trace from the mass spectrometer (the mass spectrum) is a series of peaks on a graph where the vertical axis is relative abundance (which is the same as the electric current from the detector) and the horizontal axis is the mass to charge ratio.

The relative abundance is a measure of how many of each ion is present. Often the highest peak is given a value of 100 and the other peaks are worked out relative to this value.

The mass/charge ratio for single charge ions is equivalent to the mass of the ion, as mass divided by 1 = mass. The horizontal axis should be labelled ' m/z ' but it may also be labelled ' m/e ' or 'mass to charge ratio'. The m/z values for isotopes of an element are the relative isotopic masses for these isotopes.

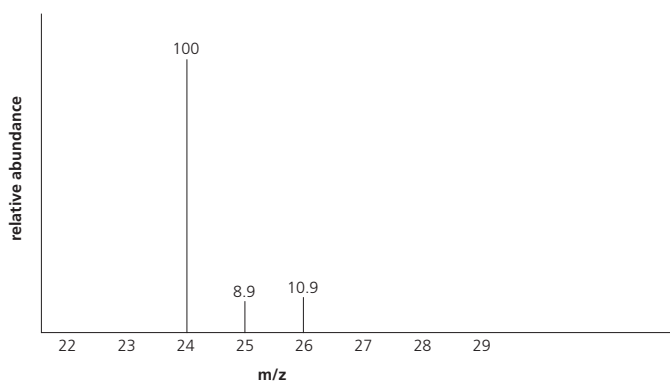


Figure 1.4 Mass spectrum of magnesium.

Mass spectrum of an element

Below is an example of a mass spectrum of naturally occurring magnesium (an element). The numbers above the peaks indicate the relative abundance of each ion detected. Sometimes it is given like this and for other examples the relative abundance may have to be read from the scale on the vertical axis.

TIP

If you are asked to calculate the relative atomic mass of magnesium to an appropriate level of precision, the answer must be given to 2 significant figures as this is the least accurate level of measurement. All of the relative isotopic abundance data are given to 2 significant figures. The relative abundance data are given to 2 (8.9) and 3 (100 and 10.9) significant figures. Any calculation in which the appropriate level of precision in an answer is required should have its answer quoted to the number of significant figures of the lowest level of precision of the data used.

The peaks in the spectrum are caused by the isotopes of magnesium.

The mass spectrum tells us several things:

- 1 Magnesium has three isotopes as there are three peaks on the spectrum corresponding to each of the isotopes.
- 2 The relative isotopic masses of these isotopes are 24, 25 and 26 as these are the m/z values for each of the isotopes.
- 3 The most abundant isotope of magnesium has a relative isotopic mass of 24. This is the m/z value for the peak with the highest relative abundance.
- 4 The ion responsible for the peak at 24 is $^{24}\text{Mg}^+$; the ion responsible for the peak at 25 is $^{25}\text{Mg}^+$; the ion responsible for the peak at 26 is $^{26}\text{Mg}^+$.
- 5 The relative atomic mass (A_r) of magnesium can be calculated from the information in the mass spectrum.

The relative atomic mass of magnesium is simply the average mass of all the atoms of the different isotopes. This calculation is carried out by multiplying the relative isotopic mass by the relative abundance for each peak. These are then added together and the total is divided by the total of all the relative abundances.

Working this out

$$\text{relative atomic mass} = \frac{(100 \times 24) + (8.9 \times 25) + (10.9 \times 26)}{119.8} = 24.26$$

To 1 decimal place this is 24.3 as given on the Periodic Table of the Elements supplied in the Data Booklet with examinations.

TIP

The mass spectrum of magnesium shows that the most abundant isotope is ^{24}Mg and the heavier ^{25}Mg and ^{26}Mg occur in smaller proportions. Even without a calculator it is possible to predict that the relative atomic mass of magnesium would be close to 24 but slightly above it due to the presence of the heavier isotopes.

EXAMPLE 3

Cubic zirconia, the cubic crystalline form of zirconium dioxide is extensively used in gems as a cheap alternative to diamond. It is artificially manufactured and contains the element zirconium, a transition metal which has four isotopes.

The mass spectrum on page 9 is for zirconium. Determine the relative atomic mass of zirconium to one decimal place.

Figure 1.5 Cubic zirconia resembles diamond, and sparkles with brilliance. Can you compare its chemical composition and properties with that of diamond?



Answer

There are four isotopes of zirconium with relative isotopic masses of 90, 91, 92 and 94.

The relative abundances of the isotopes are: $^{90}\text{Zr} = 9.0$; $^{91}\text{Zr} = 2.0$; $^{92}\text{Zr} = 3.0$; $^{94}\text{Zr} = 3.0$.

relative atomic mass

$$= \frac{(90 \times 9.0) + (91 \times 2.0) + (92 \times 3.0) + (94 \times 3.0)}{9 + 2 + 3 + 3}$$

$$= \frac{1550}{17} = 91.2 \text{ (to 1 decimal place)}$$

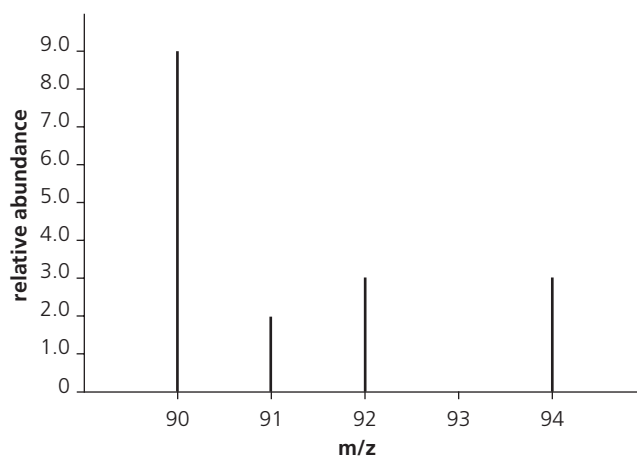


Figure 1.6 Mass spectrum of zirconium.

TIP

The element in Example 3 could have been an unknown element and you may have had to identify it from its relative atomic mass. In the Periodic Table provided with your examination, zirconium has a relative atomic mass of 91.2.

TIP

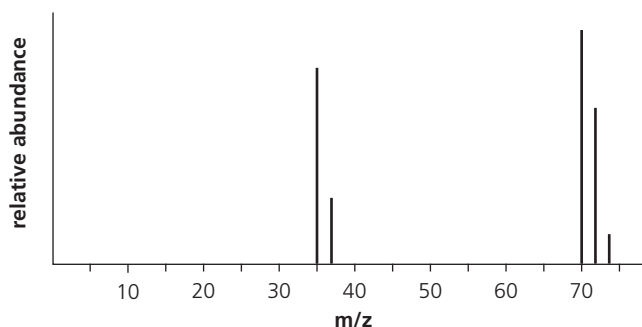
The ability to read data from a graph or in this case a spectrum and to translate these data into numerical form is an important skill throughout Chemistry. Use the level of precision given on the graph/spectrum – in this case both the m/z values and the relative abundance values are given to two significant figures. If you were asked for an appropriate level of precision in the answer, it should also be to two significant figures.

Mass spectrum of a molecular element

Elements like chlorine exist as diatomic molecules. In the mass spectrometer the molecules of an element like chlorine can form ions with a single positive charge but also the mass spectrometer can break up the molecule into atoms, which can also form single positively charged ions.

Chlorine has two different isotopes: ^{35}Cl and ^{37}Cl

There are five different possible ions which should be detected in the mass spectrometer:



- $^{35}\text{Cl}^+$
- $^{37}\text{Cl}^+$
- $(^{35}\text{Cl}-^{35}\text{Cl})^+$
- $(^{35}\text{Cl}-^{37}\text{Cl})^+$
- $(^{37}\text{Cl}-^{37}\text{Cl})^+$

There should be peaks seen at m/z values of 35, 37, 70, 72 and 74 on a mass spectrum of molecular chlorine.

The mass spectrum of molecular chlorine is shown in Figure 1.7.

Figure 1.7 Mass spectrum of molecular chlorine.

- As predicted there are peaks at 35, 37, 70, 72 and 74.
- As the ratio of $^{35}\text{Cl}:^{37}\text{Cl}$ is 3:1 the relative abundance of the peaks at m/z values of 35 and 37 are in a 3:1 ratio.
- The ratio of the peaks at m/z values of 70:72:74 are 9:6:1.

TIP

It is also important to be able to translate data in a graphical form like a mass spectrum to numerical data, which can be used in a calculation. Look at the labels on the axes (and any units present) to see what data can be obtained from a graphical representation.

TIP

There are two atoms and the ratio for the individual isotopes is 3:1. The probability of two atoms being ^{35}Cl is $(\frac{3}{4} \times \frac{3}{4} = \frac{9}{16})$.
The probability of two atoms being ^{37}Cl is $(\frac{1}{4} \times \frac{1}{4} = \frac{1}{16})$
and the probability of either $(^{35}\text{Cl} - ^{37}\text{Cl})$ or $(^{37}\text{Cl} - ^{35}\text{Cl})$ is $\frac{6}{16}(1 - \frac{9}{16} - \frac{1}{16})$.
This gives a ratio of 9:6:1.

Mass spectrum of a compound

For a compound, the last major peak at the highest m/z value is the **molecular ion**. This means it is caused by the molecular ion formed from the whole molecule. **The m/z value of this peak is the relative molecular mass (M_r) of the compound.**

The **relative molecular mass** is the mass of a molecule relative to $\frac{1}{12}$ the mass of an atom of carbon-12. The relative molecular mass is often written as M_r . It can be calculated by adding up the relative atomic masses of all the atoms in a compound.

When a molecule is put through a mass spectrometer, the molecule breaks up. This process is called fragmentation. The fragments of the molecule form ions and these are detected. The pattern of peaks caused by these fragments is called the fragmentation pattern.

Figure 1.8 shows the spectrum of ethanol, $\text{C}_2\text{H}_5\text{OH}$. The molecular ion peak (often written as M^+) is at an m/z value of 46. This is the last major peak in the spectrum of the highest m/z value. There is a small peak at 47 and this is caused by the presence of one ^{13}C atom.

The peak with the greatest abundance is usually not the molecular ion peak. The peak with the greatest abundance is called the base peak (in this case the one at an m/z value of 31) and in computer generated mass spectra, the height of this peak is usually taken as 100 and all other peaks are measured relative to it.

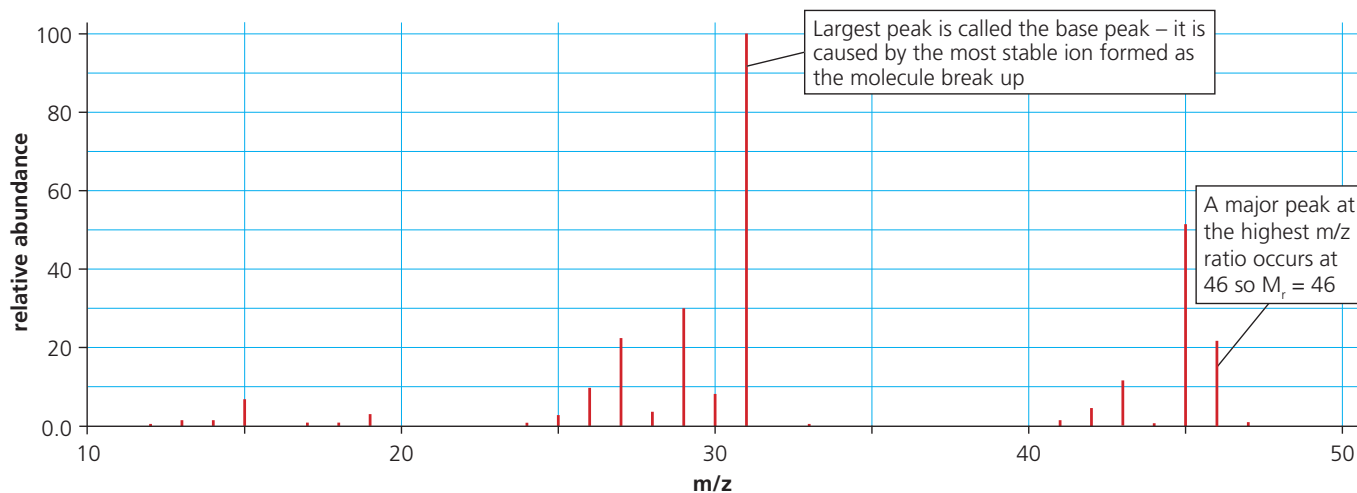


Figure 1.8 Mass spectrum of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$.

EXAMPLE 4

A sample of an unknown compound was analysed in a time-of-flight (TOF) mass spectrometer. The spectrum obtained is shown in Figure 1.9. What is the M_r of this compound and what is the m/z value of the base peak?

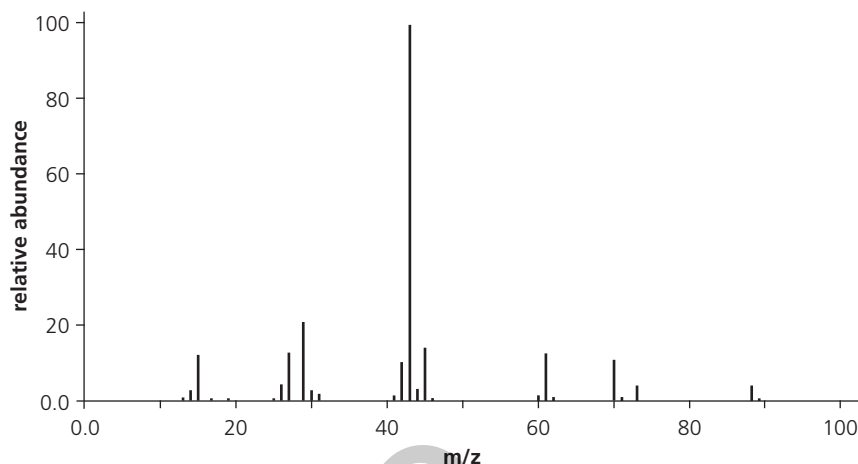


Figure 1.9 Spectrum of unknown compound.

Answer

The M_r of the compound is 88. This is the highest m/z of a peak in the spectrum and corresponds to the molecular ion.

The peak at an m/z value of 43 is the base peak and corresponds to the most stable ion as the molecule breaks up in the mass spectrometer.

Identification of elements (and compounds)

A mass spectrum is obtained, and information about the peak heights and m/z values are fed into a computer. This computer compares the spectrum of the unknown element (or compound) with those in its data banks and can identify the element (or compound). The fragmentation pattern of a compound is the same and acts like a fingerprint for that compound. An exact match is required for identification and this requires a pure sample.

TEST YOURSELF 3

- 1** The mass spectrum of an element is shown in Figure 1.10. Calculate the relative atomic mass of the element to one decimal place and identify the element.

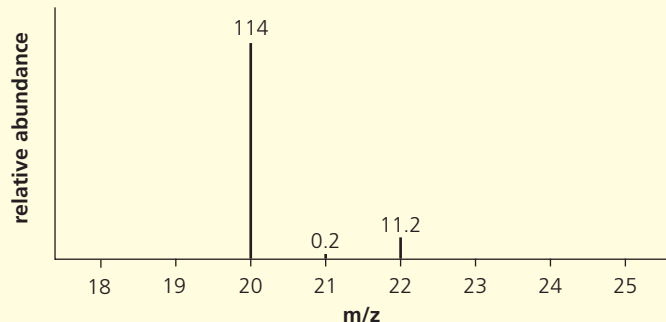


Figure 1.10

- 2** The mass spectrum of lead is shown in Figure 1.11. Calculate the relative atomic mass of the lead.

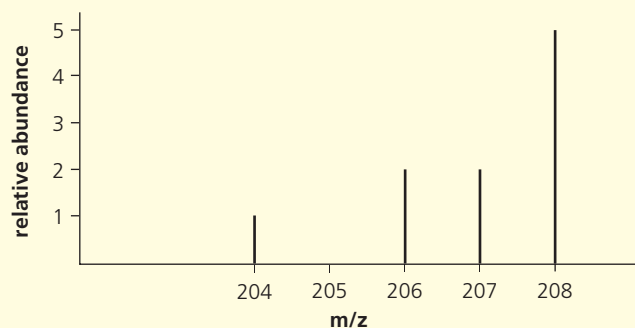


Figure 1.11

- 3 The spectrum in Figure 1.12 is for an unknown alkane. All alkanes have the general formula C_nH_{2n+2} .

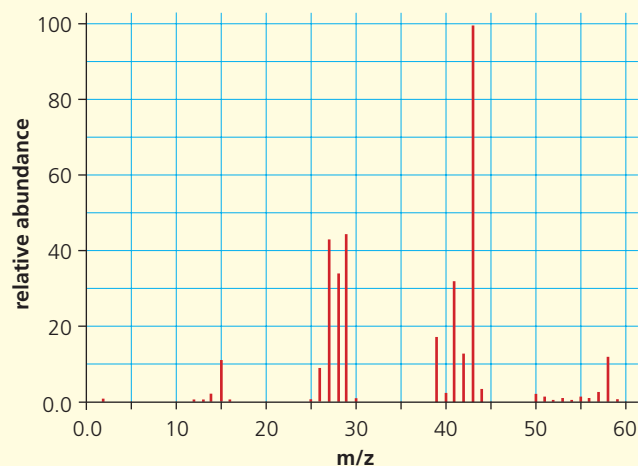


Figure 1.12 Spectrum for unknown alkane.

- State the m/z value of the molecular ion peak.
- State the m/z value of the peak with the highest relative abundance.
- What is the relative molecular mass (M_r) of this alkane?
 - Suggest a formula for the alkane using the M_r .

TIP

For some work in bonding and structure, GCSE notation of electrons in shells is still used, particularly in dot and cross diagrams and shapes of molecules.

Electron configuration

The shells which may be familiar from GCSE are now called **energy levels**. Each energy level may be divided into sub-shells.

The evidence for the existence of **sub-shells** comes from evidence of ionisation energies of elements. Ionisation energies will be examined in the next part of this topic but before this can be done we need to understand electron configuration.

Basic information

- The first energy level (moving out from the nucleus) is called $n=1$; the second $n=2$ and so on. This number is called the principal quantum number.
- The energy levels get closer together as you move further from the nucleus. The difference between the first energy level ($n=1$) and the second energy level ($n=2$) is larger than the distance between the second energy level ($n=2$) and the third energy level ($n=3$). This continues further from the nucleus.
- Each energy level is divided into sub-shells.
- A sub-shell is an orbital or a combination of orbitals.
- An orbital is a three-dimensional space and each orbital can hold up to two electrons.
- Two electrons in the same orbital spin in opposite directions to minimise repulsions.
- There are four main types of orbitals: s, p, d and f, but at this level only s, p and d orbitals are studied.
- There is only one s orbital at each energy level.
- There are three p orbitals at each energy level starting at $n=2$ making up a p sub-shell.
- There are five d orbitals at each energy level starting at $n=3$ making up a d sub-shell.

TIP

Although the 4s fills before the 3d, in written form the 3d should always be written before the 4s. This means a scandium atom would be $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$. Sub-shells at the same energy level should be written together in sequence.

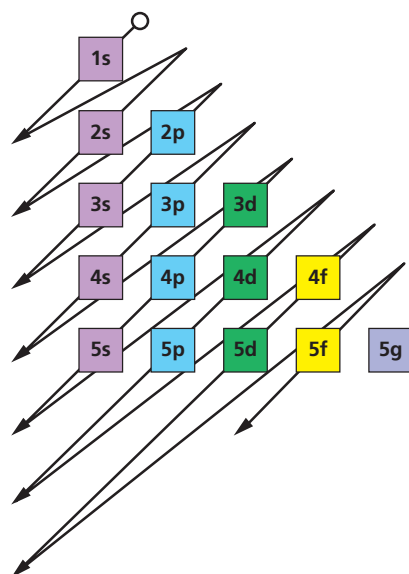


Figure 1.14 Diagram to remember the order in which sub-shells are filled. Follow the arrow!

Sub-shells

A sub-shell is always written as the energy level (principal quantum number) and then the type of orbital which makes up that sub-shell.

For example:

- The s orbital at energy level $n=1$ is written as 1s; this is the 1s sub-shell
- The s orbital at energy level $n=2$ is written as 2s; this is the 2s sub-shell
- The p orbital at energy level $n=2$ is written as 2p; this is the 2p sub-shell
- The s orbital at energy level $n=3$ is written as 3s; this is the 3s sub-shell and so on

Writing notation for electrons in sub-shells

When electrons are placed in a sub-shell, a number (written as a superscript) is written after the sub-shell notation. If there are no electrons in a particular sub-shell, it does not again have to be written.

For example:

- One electron in the 1s sub-shell is written as $1s^1$
- Two electrons in the 1s sub-shell is written as $1s^2$
- Three electrons in the 2p sub-shell is written as $2p^3$
- Six electrons in the 2p sub-shell is written as $2p^6$

The 3d sub-shell is at a slightly higher energy level than the 4s sub-shell as energy levels overlap slightly but by convention the 3d should be written before the 4s.

Sub-shells available at each energy level

- The $n=1$ energy level can have two electrons in the same sub-shell (1s).
- The $n=2$ energy level can have two electrons in one sub-shell (2s) and six electrons in a slightly higher sub-shell (2p).
- The $n=3$ energy level can have two electrons in one sub-shell (3s), six electrons in a slightly higher sub-shell (3p) and ten electrons in a sub-shell slightly higher again (3d).
- The $n=4$ energy level can have two electrons in one sub-shell (4s), six electrons in a slightly higher sub-shell (4p), ten electrons in the next sub-shell (4d) and 14 electrons in a sub-shell slightly higher again (4f).

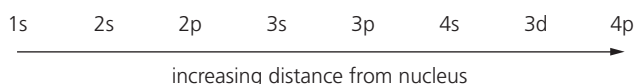


Figure 1.13 Sub-shells filling order.

Filling order of sub-shells

The sub-shells fill in the following order shown in Figure 1.13.

A typical sub-shell diagram

Figure 1.15 shows the electron configuration of a potassium atom.

At this stage it is important to note the following from Figure 1.15:

- the distance between the energy levels decreases further from the nucleus
- the $n=3$ and $n=4$ energy levels overlap so that the 4s sub-shell is at a lower level than the 3d sub-shell
- electrons fill the sub-shells closest to the nucleus first
- in a potassium atom there is one electron in the outer 4s sub-shell and all other sub-shells closer to the nucleus are full

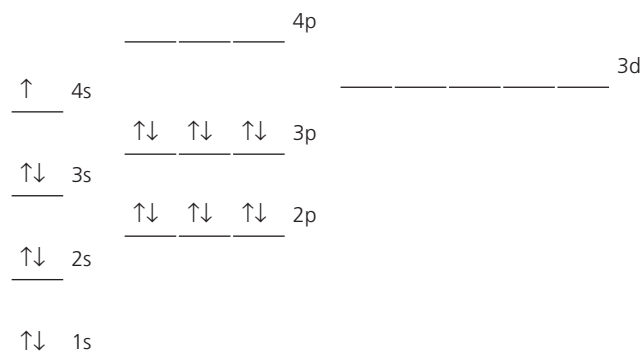


Figure 1.15 The electron configuration of a potassium atom.

- the electrons are indicated by an up arrow (\uparrow) and a down arrow (\downarrow); the up and down arrows represent the different directions of spin of the electrons in an orbital to minimise repulsions
- the 3d and 4p sub-shells are not occupied by electrons and so are not written in the electron configuration
- the electron configuration of a potassium atom is written as: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$.
- when electrons are in their lowest possible energy levels, the atom is said to be in the ground state.

TIP

Remember it is convention to write the 3d before the 4s even though the 4s fills first. The principal quantum numbers are kept together.

Writing electron configurations

Electrons repel each other and so when forming pairs in an orbital, they will only do this when they must.

An s sub-shell has only one orbital so two electrons will occupy this (spinning in opposite directions).

A p sub-shell has three p orbitals. If two electrons are placed in a p sub-shell they will go into different orbitals which make up the sub-shell.

EXAMPLE 5

Write the electron configuration of a nitrogen atom.

Answer

An electron in box notation diagram helps to show this as it shows the electrons at each of the energy levels. Nitrogen atoms (atomic number = 7) have full 1s and 2s sub-shells and there are three more electrons to place in the 2p sub-shell. There is one electron in each of the three 2p orbitals that make up the 2p sub-shell. The three electrons are shown to be spinning in the same direction (all as \uparrow) in the electron in box notation diagram (Figure 1.16).

The electron configuration of nitrogen is written $1s^2 2s^2 2p^3$.

Nitrogen atoms have three unpaired electrons.

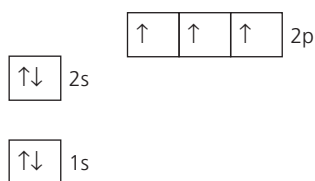


Figure 1.16 The three electrons are shown to be spinning in the same direction (all as \uparrow) in the electron in box notation diagram.

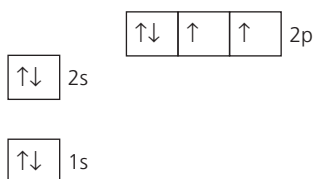


Figure 1.17 The electron configuration of oxygen is written $1s^2 2s^2 2p^4$.

EXAMPLE 6

Write the electron configuration of an oxygen atom.

Answer

The atomic number of oxygen is 8.

The 1s and 2s sub-shells are full and this leaves 4 electrons to place in the 2p sub-shell. There is one orbital with 2 electrons (spinning in opposite directions shown as ↑↓) and the other two 2p orbitals in this sub-shell have one electron (both shown as ↑).

Oxygen atoms have only two unpaired electrons as one of the 2p orbitals has a pair of electrons which spin in opposite directions to minimise their repulsion for each other.

EXAMPLE 7

Write the electron configuration of a vanadium atom.

Answer

The atomic number of vanadium is 23. For 23 electrons once again the $1s^2 2s^2 2p^6 3s^2 3p^6$ sub-shells are full (18 electrons in total). This leaves five electrons to place in the 4s and 3d sub-shells. The 4s fills first taking two electrons and then the remaining three electrons are placed in the 3d (all spinning in the same direction in different orbitals).

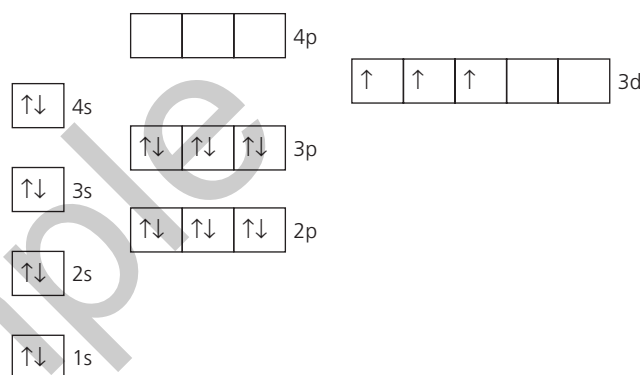


Figure 1.18 The electron configuration of a vanadium atom is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$.

EXAMPLE 8

Write the electron configuration of a chromium atom.

Answer

The atomic number of chromium is 24.

24 electrons means the $1s^2 2s^2 2p^6 3s^2 3p^6$ are full as before (18 electrons in total). This leaves six electrons to place in the 4s and 3d sub-shells. By moving one electron from the 4s to the 3d the chromium atom can have a half-filled 3d sub-shell ($3d^5$). A half-filled or filled sub-shell is more stable so this is a more stable electron configuration for the chromium atom.

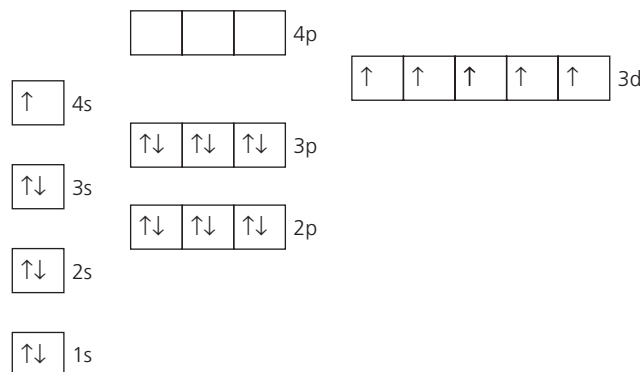


Figure 1.19 The electron configuration of a chromium atom is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$.

EXAMPLE 9

Write the electron configuration of a copper atom.

Answer

The atomic number of copper is 29.

29 electrons means the $1s^2 2s^2 2p^6 3s^2 3p^6$ are full (18 electrons in total). This leaves 11 electrons to place in the 4s and 3d sub-shells. As with chromium, copper has an unusual electron configuration as one electron moves from the 4s to the 3d sub-shell giving a more stable full 3d sub-shell.

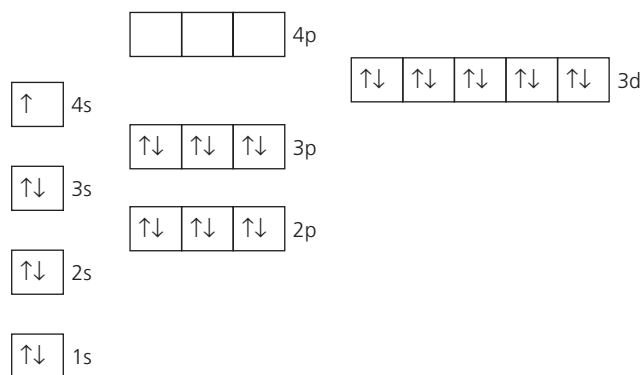


Figure 1.20 The electron configuration of a copper atom is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$.

TIP

When you go into any chemistry exam you should put a star at chromium and copper on the Periodic Table as their atoms have unusual electron configurations.

The atoms of chromium and copper have an unusual electron configuration because of the stability of filled and half-filled sub-shells. Chromium is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ instead of $3d^4 4s^2$. This is because one electron in each of the orbitals of the 3d sub-shell makes it more stable – they are symmetrical around the nucleus. Copper is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ instead of $3d^9 4s^2$ as would have been expected. Again the ten electrons in the 3d sub-shell make it more stable due to symmetry around the nucleus.

Electron configuration of simple ions

When atoms form simple ions they can either lose or gain electrons.

Ions formed from metal atoms

- Metal atoms tend to lose electrons to become positive ions.
- The number of electrons they lose is the same as the positive charge on the ion.
- The name of a positive ion is the same as the atom, e.g. Na is a sodium atom and Na^+ is a sodium ion; Al is an aluminium atom and Al^{3+} is an aluminium ion.
- When metal atoms lose electrons they lose them from the outermost level except atoms of d block elements.
- Atoms of d block elements lose their 4s electrons first then their 3d.

Ions formed from non-metal atoms

- Non-metal atoms tend to gain electrons to become negative ions.
- The number of electrons they gain is the same as the negative charge on the ion.
- The name of a negative ion is the atom stem with '-ide' on the end, e.g. O is an oxygen atom and O^{2-} is an oxide ion; Br is a bromine atom and Br^- is a bromide ion.

Hydrogen

- A hydrogen atom has only one 1s electron.
- A hydrogen atom can either lose this electron to become a hydrogen ion, H^+ or it can gain an electron to become a hydride ion, H^- .

TIP

Atoms on elements in the main groups (not transition metals) form ions which have the electron configuration of the nearest Noble gas. For example nitride ions, N^{3-} , have the same electron configuration as Ne atoms.

EXAMPLE 10

Write the electron configuration of an iron(III) ion.

Answer

- Atoms of iron have 26 electrons.
- An iron(III) ion is Fe^{3+} .
- The electrons in an atom of iron are arranged $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$.
- Iron is a d block element.
- Atoms of d block elements lose their 4s electrons first.
- An iron atom loses three electrons to become Fe^{3+} so it loses two electrons from the 4s and one electron from the 3d.
- The electron configuration of an iron(III) ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$.

EXAMPLE 11

Write the electron configuration of a sulfide ion, S^{2-} .

Answer

Atoms of sulfur have 16 electrons, arranged $1s^2 2s^2 2p^6 3s^2 3p^4$.

When sulfur atoms form sulfide ions, they gain two electrons to give them the same electron configuration as argon.

The electron configuration of a sulfide ion is $1s^2 2s^2 2p^6 3s^2 3p^6$.

Isoelectronic

- Particles which are **isoelectronic** have the same electron configuration.
- An atom of neon has an electron configuration of $1s^2 2s^2 2p^6$.
- An oxide ion, O^{2-} , also has an electron configuration of $1s^2 2s^2 2p^6$.
- A neon atom has 10 protons and an oxide ion has 8 protons. This is what makes them different despite the fact they have the same electron configuration (are isoelectronic).

TEST YOURSELF 4

1 Write electron configurations in spd format for the following ions:

- i) Li^+ ii) Cl^- iii) O^{2-} iv) Na^+ v) Fe^{2+}
vi) Fe^{3+} vii) Ni^{2+} viii) Cu^{2+} ix) Cr^{3+} x) Br^-

2 Which of the following ionic compounds contains ions that are isoelectronic (have the same electron configuration)?

- A sodium chloride
B aluminium oxide
C potassium fluoride
D zinc oxide

3 Using the following electron configurations:

- A $1s^2 2s^2 2p^6$
B $1s^2$
C $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
D $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
E $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Give the letter (A to E) which represents the electron configuration of the following atoms and ions.

- i) H^- ii) N^{3-} iii) Zn iv) Ga^+ v) Mg^{2+} vi) Kr
vii) Se^{2-} viii) Rb^+ ix) Li^+ x) He xi) O^{2-} xii) Sr^{2+}

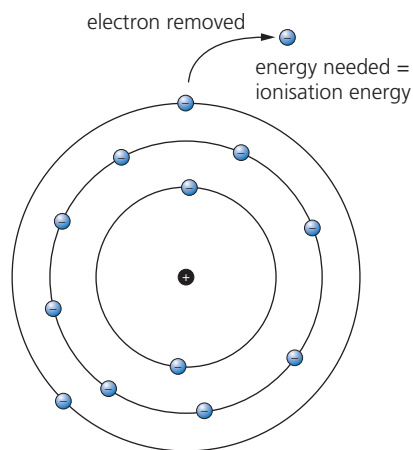


Figure 1.21 What element is being ionised in this diagram?

Ionisation energies

The electrons in atoms and ions are attracted to the positive nucleus. Energy is required to overcome this attraction and remove electrons. The process of removing electrons from atoms and ions is called **ionisation**. The ionisation energy is the energy required to remove electrons.

The **first ionisation energy** is the energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of gaseous 1+ ions.

Successive ionisations give the first, second, third, fourth, etc. ionisation energies. Only one mole of electrons is removed with each ionisation.

For example for sodium

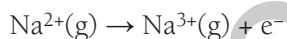
The first ionisation of sodium is represented by the equation:



The second ionisation of sodium is represented by the equation:



The third ionisation of sodium is represented by the equation:



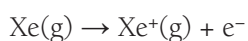
TIP

Equations for ionisation energies are often asked for. You must include state symbols. The atoms and ions must be in the gaseous state.



Figure 1.22 Ionisation in plasma televisions.

Ionisation occurs in plasma screen televisions. The screen consists of two glass panels with millions of tiny cells containing xenon and neon gas, sandwiched in between. When energy in the form of an electrical voltage is supplied, the atoms become ionised into a mixture of positive ions and negative electrons, which is called a plasma.



In a plasma with an electrical current running through it, positively charged ions collide with electrons, exciting the gas atoms in the plasma and causing them to release ultraviolet photons that interact with the phosphor material coated on the inside of the cell, and gives off visible light.

Values for ionisation energies

Ionisation energies are measured in kJ mol^{-1} (kilojoules per mole). The units include per mole (mol^{-1}) as it is the energy per mole of gaseous atoms. The first ionisation energy of sodium is $+496 \text{ kJ mol}^{-1}$. 496 kJ of energy are required to convert 1 mole of Na(g) to 1 mole of $\text{Na}^+(\text{g})$ by removing 1 mole of electrons.

Often this is written as:



TIP

Only 1 mole of electrons is removed with each ionisation, even though the ions formed may look odd, for example $\text{Cl}^+(\text{g})$ or $\text{Al}^{2+}(\text{g})$.

All ionisation energy values will be positive as they are endothermic as energy is required to remove an electron from the attractive power of the nucleus. The higher the value, the more energy is required to remove 1 mole of electrons. The first ionisation energy for magnesium is $+738 \text{ kJ mol}^{-1}$. 738 kJ of energy are required to convert 1 mole of Mg(g) to 1 mole of $\text{Mg}^+(\text{g})$ by removing 1 mole of electrons. There are trends in ionisation energy values in the Periodic Table that provide evidence for the existence of electron arrangement in energy levels and in sub-shells.

Ionisation energies as evidence for energy levels

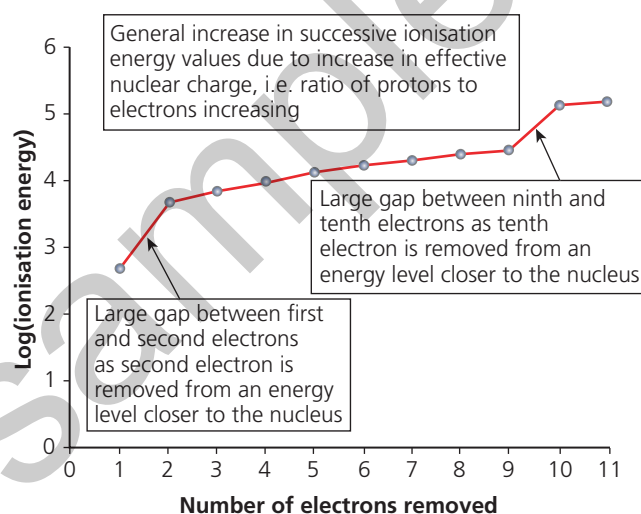


Figure 1.23 The $\log(\text{ionisation energy})$ against the number of electrons removed from a sodium atom.

The graph in Figure 1.23 shows the successive ionisation energies of a sodium atom, it becomes clear that there is a distinct set of energy levels. The diagram shows the $\log(\text{ionisation energy})$ against the number of electrons removed from a sodium atom.

The log of the ionisation energy is used to condense the diagram as the ionisation energies vary across a wide range of values.

The existence of energy levels is proven by the large gaps in the successive ionisation energies as these correspond to the removal of electrons from energy levels closer to the nucleus and so more energy is required to remove the electron.

The general increase in successive ionisation energies is caused by the increase in the ratio of protons to electrons as successive electrons are removed. This is often called effective nuclear charge.

Using successive ionisation energies

Successive ionisation energies are an indicator of the group to which an element belongs.

EXAMPLE 12

The first five successive ionisation energies for four different elements are given in the table.

Element	Ionisation energy (kJ mol^{-1})				
	First	Second	Third	Fourth	Fifth
W	+496	+4562	+6912	+9543	+13353
X	+1087	+2353	+4621	+6223	+37831
Y	+578	+1817	+2745	+11577	+14842
Z	+738	+1451	+7733	+10543	+13630

- 1 State which element belongs to Group 4.
- 2 Which element would form a simple ion with a charge of $2+$?
- 3 Which element would have one electron in its outer energy level?
- 4 Which element would form an oxide with the formula M_2O_3 where M represents the element?

Answers

- 1 Element X has a large increase in ionisation energy after the fourth electron has been removed (+6223 to remove the fourth electron and +37831 to remove the fifth electron). This would suggest four electrons in the outer energy level and the fifth electron in an energy level closer to the nucleus. So, element X has four electrons in the outer energy level, which is characteristic of an element in Group 4. Element X is actually carbon.
- 2 An element in Group 2 would form a simple ion with a charge of $2+$. Element Z has a large increase in ionisation energy after the second electron has been removed (+1451 to remove the second electron and +7733 to remove the third electron). This would suggest there are two electrons in the outer energy level and the third electron is in an energy level closer to the nucleus. So, element Z has two electrons in its outer energy level, which is characteristic of an element in Group 2. Element Z is actually magnesium.
- 3 One electron in the outer energy level would suggest a Group 1 element. Element W has a large increase in ionisation after the first electron has been removed (+496 to remove the first electron and +4562 to remove the second electron). This would suggest one electron in the outer energy level and the second electron in an energy level closer to the nucleus. So, element W has one electron in the outer energy level, which is characteristic of an element in Group 1. Element W is actually sodium.
- 4 An element which forms an oxide with the formula M_2O_3 would suggest an element in Group 3. Element Y has a large increase in ionisation energy after the third electron has been removed (+2745 to remove the third electron and +11577 to remove the fourth electron). This would suggest three electrons in the outer energy level and the fourth electron in an energy level closer to the nucleus. So, element Y has three electrons in the outer energy level, which is characteristic of an element in Group 3. Element Y is actually aluminium.

TIP

All of the above questions are different ways of getting you to place an element in a particular group.

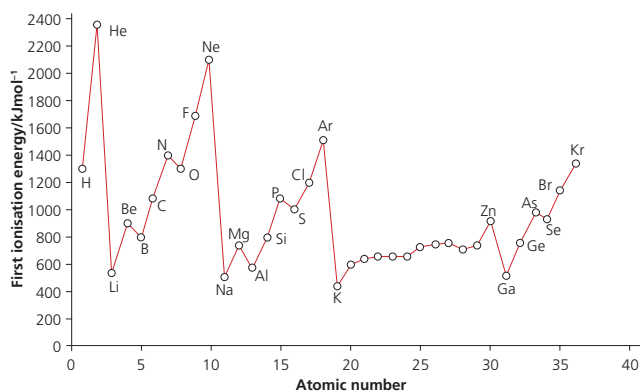


Figure 1.24 First ionisation energies for the elements, hydrogen (atomic number 1) to krypton (atomic number 36).

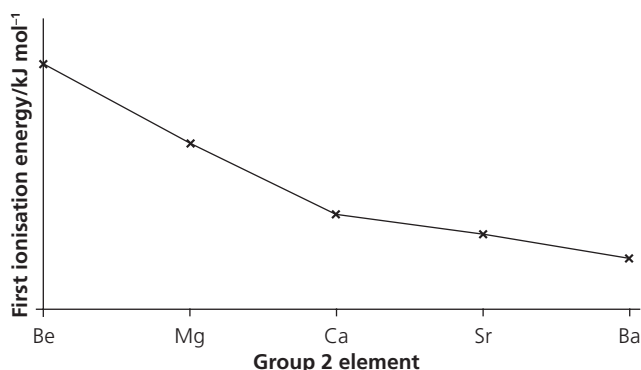


Figure 1.25 Graph of first ionisation energy of the Group 2 elements.

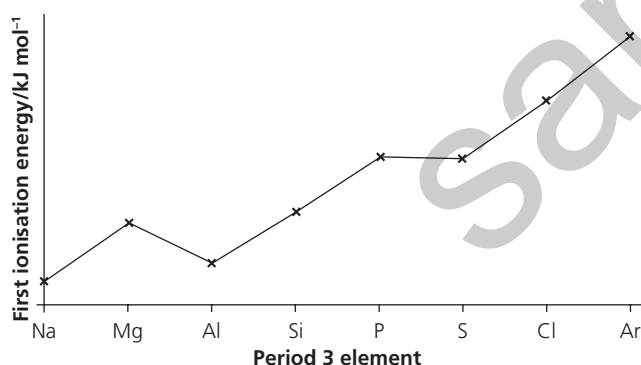


Figure 1.26 First ionisation energies of Period 3 elements.

Ionisation energy pattern for elements 1 to 36

The graph in Figure 1.24 shows the pattern in first ionisation energies for the elements, hydrogen (atomic number 1) to krypton (atomic number 36).

There are three general patterns which should be apparent from this diagram:

1 Ionisation energy decreases down a group.

Look at the decrease from helium to neon to argon and then krypton. The same pattern is clear for Group 2.

This is seen more clearly by examining a graph of first ionisation energies of the Group 2 elements (Figure 1.25).

2 Ionisation energy shows a general increase across a period.

From sodium to argon there is a general increase in first ionisation energy.

The graph in Figure 1.26 shows the first ionisation energies of the Period 3 elements from sodium to argon.

3 Within the short periods (periods 2 and 3), there is a zig-zag pattern.

The first ionisation drops below the general increase for elements in Group 3 (boron and aluminium) and Group 6 (oxygen and sulfur) (Figure 1.26).

Explaining trends in ionisation energies

The patterns in ionisation energies can be explained by the electronic structure of the atoms. There are three main factors which can be used to explain these patterns:

- 1 Atomic radius (how far the outer electrons are from the attractive power of the nucleus).
 - The atomic radius of beryllium is less than the atomic radius of magnesium.
 - Atomic radius increases down a group and decreases across a period.
 - The further an outer electron is from the attractive power of the nucleus the less energy is required to ionise it.
- 2 Nuclear charge (how many protons are attracting the outer electron).
 - The greater the number of protons, the greater the nuclear charge.
 - A greater nuclear charge leads to a stronger attraction to the outer electron so more energy is required to ionise it.



Figure 1.27 Lithium is used in batteries. Why is a low ionisation energy important?

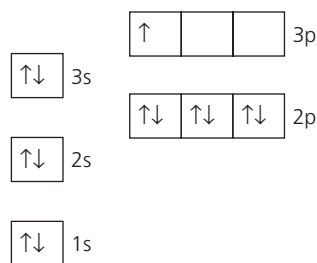


Figure 1.28 Electron configuration of aluminium.

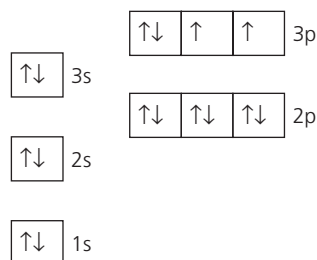


Figure 1.29 Electron configuration of sulfur.

3 Shielding by inner electrons (how many electrons are between the nucleus and the outer electron so shielding the attractive power of the nucleus).

- The attractive power of the nucleus can be shielded by inner electrons.
- The more inner electrons there are, the more the nucleus is shielded and the less energy is required to ionise the outer electron.

First ionisation energy decreases down a group

This pattern is due to the existence of energy levels within the atom. As a group is descended, the outer electrons are further away from the nucleus (at higher energy levels) and so are more easily removed as the positive nucleus has less of a hold on them. This factor is called atomic radius.

Also as the outer electron is at a higher energy level, there are more electrons between it and the positive nucleus so this shields the attractive power of the nucleus from the outer electrons. This factor is called shielding by inner electrons. The charge of the nucleus also increases as a group is descended and so works against the other two factors to hold the electron more firmly. This factor is called nuclear charge. However, the combination of the three factors causes the ionisation energy to decrease as the group is descended.

First ionisation energy increases across a period

The pattern of a general increase in ionisation energy as the period is crossed from left to right is caused by the increase in nuclear charge.

Also the atomic radius decreases across the period. The outer electron is closer to the nucleus with a greater nuclear charge holding it so more energy is required to remove it.

There is no increased shielding (as the electron being removed is in the same energy level).

Group 1 elements, such as lithium, have low ionisation energies and are likely to form positive ions. Lithium's low ionisation energy, for example, is important for its use in lithium-ion computer backup batteries where the ability to lose electrons easily makes a battery that can quickly provide a large amount of energy.

Group 3 and Group 6 first ionisation energies

The zig-zag pattern gives us evidence for the existence of sub-shells in energy levels.

The atoms of Group 3 elements, such as aluminium, show a lower than expected first ionisation energy. This is due to the division of the energy level into sub-shells. Aluminium has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^1$. The $3p^1$ electron is further from the nucleus and has additional shielding from the $3s^2$ inner electrons so it requires less energy to ionise it.

The atoms of Group 6 elements, such as sulfur, show a lower than expected first ionisation energy. This is due to the pairing of electrons in the p sub-shell. The $3p^4$ electron configuration of sulfur ($1s^2 2s^2 2p^6 3s^2 3p^4$) means that two electrons are paired in a p orbital in this sub-shell. The repulsion between these two electrons lowers the energy required to remove one of the electrons and this decreases first ionisation energy.

The fact that the atoms of elements in Group 3 and Group 6 show a lower first ionisation energy than would be expected provides evidence that the second and third energy levels are divided into two sub-shells, the first taking two electrons and the second taking six. This would explain the decrease in first ionisation energy from Group 2 to Group 3 and also the decrease from Group 5 to Group 6.



Figure 1.30 Why is helium safe to use in a diver's tank?

Group 1 and Group 0 elements

Atoms of Group 1 elements have the lowest first ionisation energy in every period as they have the greatest atomic radius and the lowest nuclear charge in a particular period.

Atoms of Group 0 elements have the highest first ionisation energy in every period for the opposite reasons – they have the smallest atomic radius and the highest nuclear charge in a period.

The increased pressure that scuba divers experience far below the water's surface can cause too much oxygen to enter their blood, which would result in confusion and nausea. To avoid this, divers sometimes use a gas mixture called heliox – oxygen diluted with helium. Helium's high ionisation energy ensures that it will not react chemically in the bloodstream.

Summary of patterns in ionisation energy and their explanation

1 First ionisation energy decreases down a group

- Atomic radius increases
- Shielding by inner electron increases
- So less energy required to remove the electron.

2 First ionisation energy increases across a period

- Atomic radius decreases
- Nuclear charge increases
- Shielding by inner electrons is the same
- More energy required to remove the electrons.

3 Lower first ionisation energy than expected for elements in Group 3 and 6

- Group 3 atoms have an $s^2 p^1$ arrangement
- Outer p^1 electron is further from the nucleus
- Inner s^2 electrons increase shielding so less energy is required to ionise the outer p^1 electron
- Group 6 atoms have a p^4 arrangement – the repulsion of two electrons in the same p orbital leads to less energy being required to ionise the outer electron.

Patterns in second ionisation energies

The patterns in first ionisation energy are shifted one to the left when the patterns of second ionisation energy are considered. Where a Group 1 element would have the lowest first ionisation energy, it would have the highest second ionisation energy.

TIP

The pattern in ionisation energies for Group 2 can be applied to any group in the Periodic Table. The patterns in Period 3 can be applied to Period 2.

Table 1.1 shows the first and second ionisation energies for the Period 3 elements.

Group 1 elements have the highest second ionisation energy in a particular period as the second electron is being removed from an energy level closer to the nucleus. Group 2 elements have the lowest second ionisation energy in a particular period.

Table 1.1 First and second ionisation energies for the Period 3 elements.

Element	First ionisation energy/ kJ mol^{-1}	Second ionisation energy/ kJ mol^{-1}
Na	496	4560
Mg	738	1450
Al	577	1816
Si	786	1577
P	1060	1890
S	1000	2260
Cl	1256	2295
Ar	1520	2665

TEST YOURSELF 5

- 1 What is the definition of first ionisation energy?
- 2 What are the units of ionisation energy?
- 3 Write equations for the following ionisations including state symbols:
 - a) first ionisation of silicon
 - b) second ionisation of potassium
 - c) third ionisation of carbon
- 4 The first six successive ionisation energies, in kJ mol^{-1} , of an element M are:
578, 1817, 2745, 11 578, 14 831, 18 378
What is the formula of the oxide of M?

Practice questions

1 Which of the following represents the second ionisation of magnesium?

- A $\text{Mg(s)} \rightarrow \text{Mg}^{\text{+}}(\text{s}) + \text{e}^{-}$
- B $\text{Mg(s)} \rightarrow \text{Mg}^{2+}(\text{g}) + 2\text{e}^{-}$
- C $\text{Mg}^{\text{+}}(\text{g}) \rightarrow \text{Mg}^{2+}(\text{g}) + \text{e}^{-}$
- D $\text{Mg}^{\text{+}}(\text{g}) \rightarrow \text{Mg}^{2+}(\text{s}) + \text{e}^{-}$

(1)

2 Which of the following is the electron configuration of an iron(II) ion?

- A $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^6 4\text{s}^2$
- B $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^6$
- C $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^5 4\text{s}^1$
- D $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^5$

(1)

3 An unknown element in Period 3 has the following successive ionisation energies in kJ mol^{-1} .

First ionisation energy	+1000
Second ionisation energy	+2252
Third ionisation energy	+3357
Fourth ionisation energy	+4456
Fifth ionisation energy	+7004
Sixth ionisation energy	+8496
Seventh ionisation energy	+27 107
Eighth ionisation energy	+31 719

To which group of the Periodic Table does the element belong?

- A Group 3 B Group 4
- C Group 5 D Group 6

(1)

4 Write equations to represent the following ionisations:

- a) First ionisation of aluminium (1)
- b) Third ionisation energy of lithium (1)
- c) Explain why there is no fourth ionisation of lithium (1)

5 Figure 1.31 shows the first ionisation energies of the elements hydrogen to sodium.

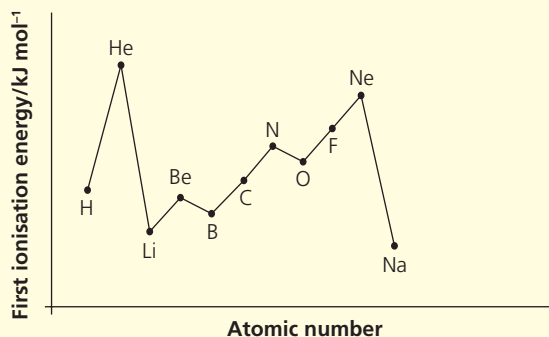


Figure 1.31

- a) Write an equation for the first ionisation of boron including state symbols. (1)
- b) Explain why the first ionisation energy of sodium is less than that of lithium. (3)
- c) Explain why the first ionisation energy of oxygen is less than the first ionisation energy of nitrogen. (2)
- d) Continue the graph in Figure 1.31 for the next three elements after sodium. (3)
- e) Explain why the Noble gases have the highest ionisation energy in each period. (3)

6 Figure 1.32 shows the first ionisation energies of the elements lithium (atomic number 3) to neon (atomic number 10).

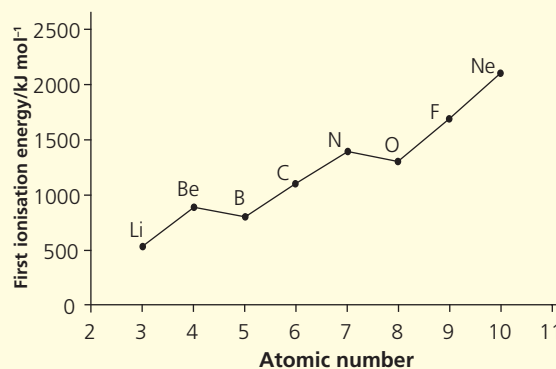


Figure 1.32

- a) Explain why there is a general increase in first ionisation energy across the period. (3)
- b) Explain why the value for the first ionisation energy of boron is lower than the value for beryllium. (2)
- c) Write the electron configuration of an atom of nitrogen. (1)

- 7 An element was analysed using a TOF (time-of-flight) mass spectrometer. The spectrum showed that there were four isotopes. The relative isotopic masses and relative abundances are given in the table below.

Relative isotopic mass	Relative abundance
50	9.4
52	72.5
53	14.5
54	3.6

- Calculate the relative atomic mass of the element to one decimal place. (2)
- Identify the element. (1)
- Identify the species responsible for the peak at 54. (1)

- 8 The spectrum in Figure 1.33 is for ethanoic acid.

- State the m/z value of the peak with the highest relative abundance. (1)
- What is the relative molecular mass (M_r) of this compound? (1)

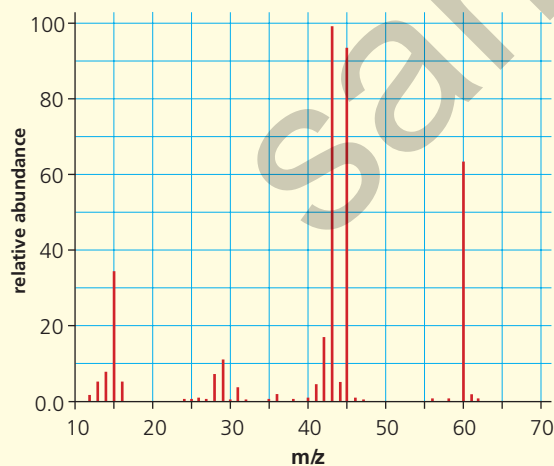
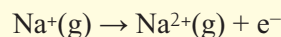


Figure 1.33

- 9 The second ionisation of sodium is represented by the equation:



- Explain why the second ionisation energy is greater than the first ionisation energy of sodium. (2)
- Write an equation for the first ionisation of sodium. (1)
- Which element in Period 3 would be expected to have the lowest second ionisation energy? (1)
- The electron configuration of an ion is shown in Figure 1.34:

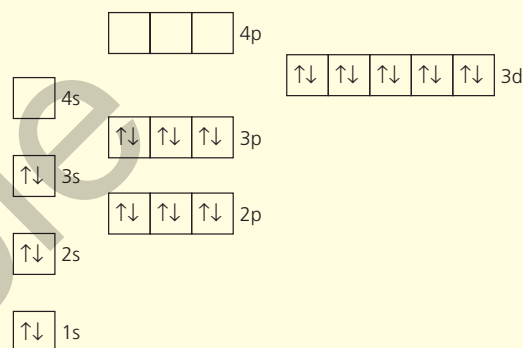


Figure 1.34

- Write the electron configuration. (1)
- An ion of zinc and an ion of copper have this electron configuration. Write the formulae of these two ions. (2)