Advanced Level

H2 Chemistry

(9476)

Book 1

A Complete Textbook for JC1

Low Kay Yong

Free sample — full book at jamescollins.com.sg

Contents

CHAPTER 1
Atomic Structure 1

1.1 Inside the atom 3
1.2 Subatomic particles in an electric field 4
1.3 Proton number, nucleon number and isotopes 6
1.4 Shells, subshells and orbitals 8
1.5 Shapes of s, p and d orbitals 9
1.6 Electronic configurations of atoms and ions 11
1.7 Ionisation energy and the factors affecting it 14
1.8 Successive ionisation energies 16
Chapter summary 20
Exam-style questions 21

CHAPTER 2
Chemical Bonding 26

2.1 Chemical bonds are electrostatic 28
2.2 Ionic bonding 31
2.3 Covalent and co-ordinate bonding 33
2.4 Orbital overlap: σ and π bonds 37
2.5 Shapes of molecules: VSEPR theory 39
2.6 Electronegativity and polarity 45
2.7 Intermolecular forces and hydrogen bonding 49
2.8 Bond energy, bond length and reactivity 54
2.9 Lattice structures of crystalline solids 57
2.10 Structure, bonding and physical properties 61
Chapter summary 64
Exam-style questions 65

CHAPTER 3
The Periodic Table 70

3.1 The Periodic Table and electronic configuration 72
3.2 Atomic radius and ionic radius 74
3.3 First ionisation energy and electronegativity 77
3.4 Melting point and electrical conductivity across Period 3 81
3.5 Physical properties down Group 2 and Group 17 84
3.6 Oxides and chlorides: oxidation number and bonding 86
3.7 Oxides and hydroxides: reactions with water, acids and bases 89
3.8 Chlorides with water; deducing structure 93
3.9 Group 2 reducing agents and Group 17 oxidising agents 97
3.10 Thermal stability of Group 2 carbonates and Group 17 hydrides 100
3.11 Using periodicity to predict and deduce 103
Chapter summary 106
Exam-style questions 107

CHAPTER 4
The Mole Concept, Stoichiometry and Gases 112

4.1 Relative masses 114
4.2 The mole and the Avogadro constant 116
4.3 Empirical and molecular formulae 118
4.4 Writing balanced equations 120
4.5 Reacting masses 122
4.6 Volumes of gases 124
4.7 Solutions and concentration 128
4.8 Titrations 130
4.9 Redox reactions 133
4.10 The kinetic theory and the gas laws 141
4.11 The ideal gas equation 144
4.12 Mixtures of gases 147
4.13 Real gases 149
Chapter summary 152
Exam-style questions 153

CHAPTER 5
Chemical Energetics 158

5.1 Energy changes in reactions 160
5.2 Energy profile diagrams 163
5.3 Standard enthalpy changes 165
5.4 Measuring enthalpy changes 168
5.5 Hess' Law and energy cycles 174
5.6 Atomisation, electron affinity and lattice energy 180
5.7 Born–Haber cycles 185
5.8 Dissolving ionic solids 188
5.9 Spontaneous change and entropy 192
5.10 Gibbs free energy and spontaneity 196
5.11 The limits of ΔG and the effect of temperature 198
Chapter summary 202
Exam-style questions 202

Free sample — full book at jamescollins.com.sg

CHAPTER 6
Reaction Kinetics 208

6.1 Rate of reaction 210
6.2 Rate equations, order and the rate constant 214
6.3 The initial-rates method 218
6.4 Concentration–time graphs and half-life 223
6.5 Reaction mechanisms and the rate-determining step 230
6.6 Designing a kinetics experiment 235
6.7 Collisions, activation energy and the Boltzmann distribution 240
6.8 Temperature and the rate constant 244
6.9 Catalysis 247
6.10 Enzymes 254
Chapter summary 257
Exam-style questions 258

CHAPTER 7
Chemical Equilibria 265

7.1 Reversible reactions and dynamic equilibrium 267
7.2 The equilibrium constant, K_c 270
7.3 Partial pressures and K_p 273
7.4 Calculating equilibrium constants 274
7.5 Calculating quantities at equilibrium 279
7.6 Le Chatelier's principle: concentration and pressure 280
7.7 Temperature and catalysts 285
7.8 The Haber process 289
Chapter summary 291
Exam-style questions 293

CHAPTER 8
Introduction to Organic Chemistry and Isomerism 297

8.1 Organic compounds and how they are classified 299
8.2 Formulae of organic compounds 301
8.3 Functional groups and naming 303
8.4 Hybridisation, shapes and σ and π bonds 307
8.5 Isomerism: constitutional isomers 312
8.6 Cis-trans isomerism 314
8.7 Chirality and enantiomers 317
8.8 Putting it together: isomers from a molecular formula 321
Chapter summary 322
Exam-style questions 324

CHAPTER 9
Organic Reactions and Mechanisms 328

9.1 Functional groups and degree of substitution 331
9.2 Bond breaking, reactive species and curly arrows 332
9.3 Types of organic reaction 337
9.4 What controls reactivity: delocalisation, electronic and steric effects 339
9.5 Alkanes: unreactivity and free-radical substitution 342
9.6 Alkenes and electrophilic addition 347
9.7 Benzene and electrophilic substitution 349
9.8 Halogenoalkanes and nucleophilic substitution 353
9.9 Carbonyl compounds and nucleophilic addition 360
9.10 Putting it together 363
Chapter summary 366
Exam-style questions 367

CHAPTER 10
Hydrocarbons 371

10.1 Hydrocarbons as fuels 373
10.2 Alkanes: free-radical substitution 375
10.3 Environmental consequences of burning hydrocarbons 377
10.4 Alkenes: electrophilic addition 380
10.5 Alkenes: reduction and oxidation 384
10.6 Benzene and methylbenzene: electrophilic substitution 387
10.7 Positions of substitution 391
10.8 The side chain 394
10.9 Telling hydrocarbons apart; reaction maps 397
Chapter summary 399
Exam-style questions 400

Weighted Assessment 1 405
Chapters 1–5

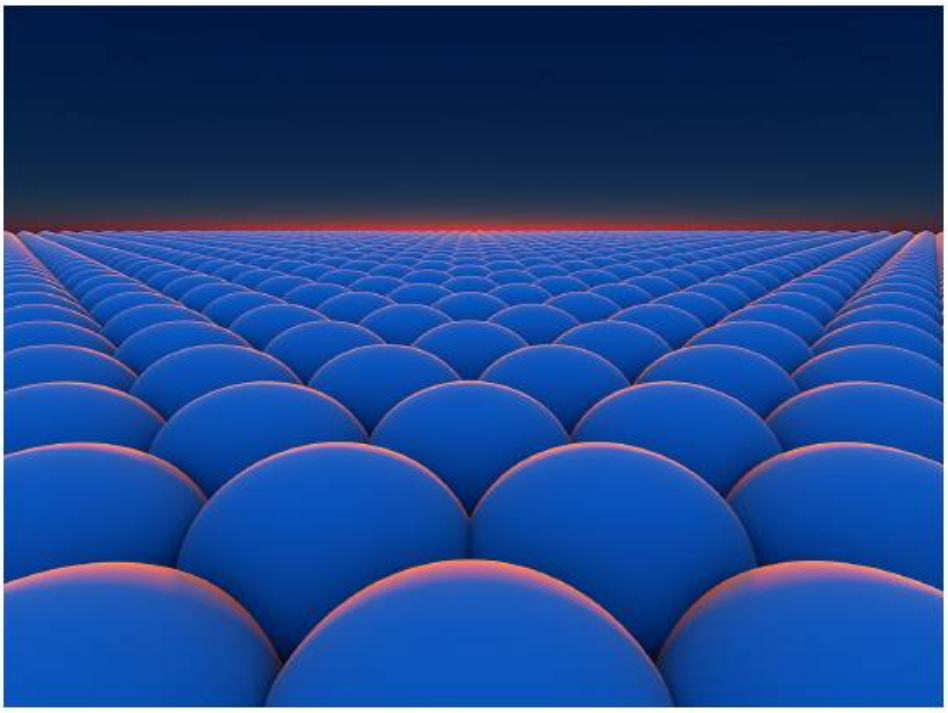
Weighted Assessment 2 408
Chapters 6–10

Index 410

Free sample — full book at jamescollins.com.sg

CHAPTER 1

Atomic Structure



Artist's impression of atoms packed in a regular pattern on a metal surface. With a scanning tunnelling microscope, scientists can image and even move individual atoms.

Why study atomic structure?

How electrons are arranged inside atoms decides how atoms bond and react, so the rest of the book builds on this chapter.

Where it matters	The atomic idea behind it
Computer chips: silicon is "doped" with traces of phosphorus or boron to control how it conducts electricity	The number of outer electrons in P (5) and B (3) compared with Si (4)
Medicines: some drugs are made with deuterium (^{2}H) in place of hydrogen so they break down more slowly in the body	Same electrons, so the same reactions; but the heavier ^{2}H makes C–^{2}H bonds break more slowly
Archaeology: the age of ancient wood or bone is found from its carbon-14 content	Isotopes of the same element differ only in neutron number
Reactive metals: sodium reacts violently with water, but gold does not react with water	How easily an atom loses its outer electrons (one measure is the ionisation energy)

Key questions

By the end of this chapter, you should be able to answer:

1. What is inside an atom, and how do we know?
2. How are the electrons in an atom arranged, and what shapes do their orbitals have?
3. Why do some elements lose electrons easily while others hold them tightly?
4. How can ionisation energy data tell us where an element sits in the

Free sample — full book at jamescollins.com.sg

Periodic Table?

Learning outcomes

By the end of this chapter, you should be able to:

(a) identify and describe protons, neutrons and electrons in terms of their relative charges and relative masses

(b) deduce the behaviour of beams of protons, neutrons and electrons in an electric field

(c) describe the distribution of mass and charges within an atom

(d) deduce the numbers of protons, neutrons and electrons present in both atoms and ions given proton and nucleon numbers (and charge)

(e) **(i)** describe the contribution of protons and neutrons to atomic nuclei in terms of proton number and nucleon number

(ii) distinguish between isotopes on the basis of different numbers of neutrons present

(f) describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the 4s and 4p orbitals

(g) describe the shapes of s, p and d orbitals

(h) state the electronic configuration of atoms and ions given the proton number (and charge)

(i) explain the factors influencing the ionisation energies of elements

(j) deduce the electronic configurations of elements from successive ionisation energy data

(k) interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table

Introduction

At O-Level, you used a simple model: a positive nucleus with electrons in circular shells. That model explains why sodium forms Na^+, but not why copper's electrons fill in an unexpected order, or why oxygen loses an electron more easily than nitrogen.

This chapter refines that model. You will describe the particles in the atom and the definite shapes and energies of subshells and orbitals, and use ionisation energy data as evidence for how electrons are arranged. Bonding (Chapter 2) and transition elements (Chapter 18) build on these ideas.

What you already know

Try these before you start. If any feel unfamiliar, revise the O-Level topic first.

1. State the charge and location of each of the three subatomic particles.
2. Write the electron arrangement of a magnesium atom using the 2,8,... notation.
3. Explain why a sodium atom forms an ion with a 1+ charge.
4. What is the difference between the proton number and the nucleon number?

Key terms in this chapter: nucleon · proton number · nucleon number

Free sample — full book at jamescollins.com.sg

· isotope · principal quantum number · subshell · orbital · degenerate orbitals · Aufbau principle · Pauli exclusion principle · Hund's rule · isoelectronic · first ionisation energy · successive ionisation energies · shielding effect

1.1 Inside the atom

LEARNING OUTCOMES
1(a), 1(c)

An atom is made of three types of subatomic particle: **protons**, **neutrons** and **electrons**. Protons and neutrons form the **nucleus** at the centre of the atom and are together called **nucleons**. Electrons occupy the space around the nucleus.

The actual masses and charges of these particles are very small, so chemists compare them using relative values (**Table 1.1**).

Particle	Relative mass	Relative charge	Location
proton	1	+1	nucleus
neutron	1	0	nucleus
electron	1/1836	−1	around the nucleus

Table 1.1 *Relative masses and charges of the subatomic particles.*

Distribution of mass and charges

Almost all the mass of an atom is in the nucleus. Protons and neutrons are each about 1836 times heavier than an electron, so the electrons add very little to the total mass.

The nucleus carries all the positive charge of the atom. The negative charge of the electrons is spread through the space around the nucleus.

The nucleus is very small compared with the atom: about 10^{-15} m across, against about 10^{-10} m for the whole atom. Most of the atom is therefore empty space.

In Rutherford's gold foil experiment, most alpha particles (helium nuclei, He^{2+}: small, fast and positively charged) passed straight through the foil, but a few were deflected through large angles or bounced back; only a small, dense, positive nucleus could repel them so strongly.

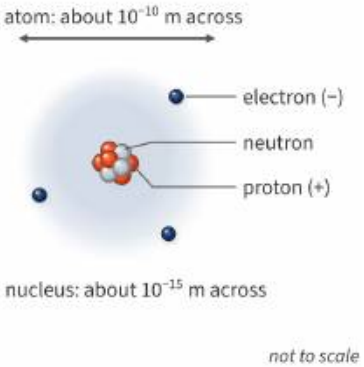


Figure 1.1 *Structure of an atom (not to scale): a tiny nucleus of protons and neutrons, about 10^{-15} m across, inside an atom about 10^{-10} m across.*

KEY POINT
In a neutral atom, the number of electrons equals the number of protons.

EXAM TIP
The relative mass of an electron is 1/1836, or "negligible". Some mark schemes do not accept zero.

Worked example 1.1

Question. A carbon-12 atom has 6 protons, 6 neutrons and 6 electrons. Calculate the percentage of its mass due to electrons.

Approach. Total the relative masses, then find the electrons' share.

Working. Nucleons = 12 × 1 = 12. Electrons = 6 × 1/1836 = 0.00327. Total = 12.00327. Percentage from electrons = (0.00327 ÷ 12.00327) × 100 = 0.0272%

Answer. 0.0272%. More than 99.9% of the mass is in the nucleus.

Check your understanding 1.1

1. Name the two subatomic particles that have almost the same mass.
2. Explain why an atom is electrically neutral.
3. Explain why almost all the mass of an atom is in its nucleus.
4. A hydrogen-1 atom has one proton and one electron. Calculate the

Free sample — full book at jamescollins.com.sg

percentage of its mass in the nucleus, to 3 significant figures.

PRACTICES OF SCIENCE
models change with evidence

Year	Scientist	Evidence or idea	Model
1803	Dalton	Elements combine in fixed ratios	Solid, indivisible atoms
1897	Thomson	Discovers the electron	Atoms contain small, negatively charged particles
1904	Thomson	Atoms are neutral overall	"Plum pudding": electrons in a sphere of positive charge
1911	Rutherford	Most alpha particles pass through gold foil; a few bounce back	Tiny, dense, positive nucleus
1913	Bohr	Atoms absorb and emit fixed amounts of energy	Electrons in fixed energy levels
1926 onwards	Schrödinger and others	Electrons behave as waves	Orbitals
1932	Chadwick	Discovers the neutron	Nucleus of protons and neutrons

Think about it: Which result of the gold foil experiment could the plum pudding model not explain?

LEARNING OUTCOME
1(b)

1.2 Subatomic particles in an electric field

When a beam of particles passes between two oppositely charged plates, charged particles are deflected and uncharged particles are not. The direction and size of the deflection reveal the sign of the charge and the charge-to-mass ratio (q/m).

Direction of deflection

A charged particle is attracted towards the oppositely charged plate (**Figure 1.2**):

- protons bend towards the **negative** plate
- electrons bend towards the **positive** plate
- neutrons are **not deflected**

The same rule applies to ions. Cations bend towards the negative plate, anions towards the positive plate. Neutral atoms and molecules pass straight through.

Size of deflection

The angle of deflection, θ, increases with the charge on the particle and decreases with its mass. For particles entering the field at the same speed:

$$\theta \propto q/m$$

Use relative charge, with its sign, for q and relative mass (for an ion, about equal to its nucleon number) for m. The sign of q/m gives the direction of deflection; its size gives the angle. In this book, a positive angle means deflection towards the negative plate.

Free sample — full book at jamescollins.com.sg

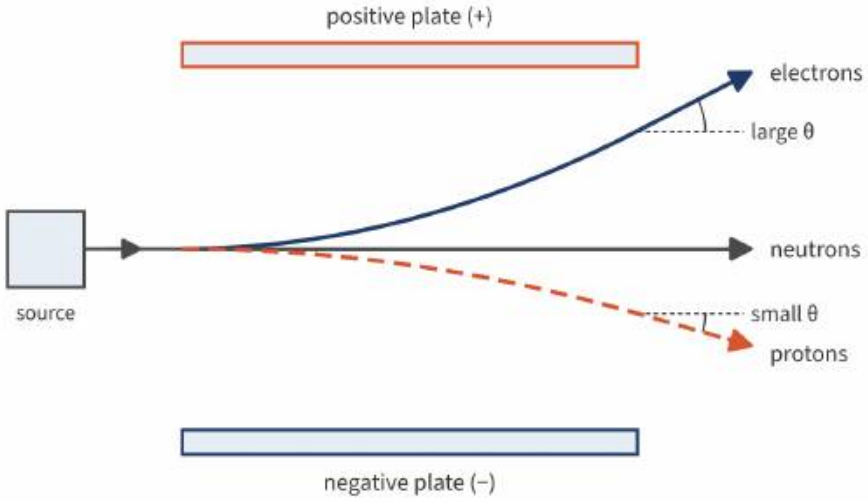


Figure 1.2 *Beams of electrons, neutrons and protons between charged plates. Electrons are deflected more than protons because the magnitude of their charge-to-mass ratio is larger; neutrons are not deflected.*

An electron has the same size of charge as a proton but 1/1836 of its mass. It is therefore deflected about 1836 times more than a proton, in the opposite direction.

KEY POINT
Larger charge → more deflection. Larger mass → less deflection.

Worked example 1.2

Question. Under certain conditions, a beam of $^{4}He^{2+}$ ions is deflected through +6.0°. Under the same conditions, calculate the angle of deflection for **(a)** $^{1}H^{+}$ **(b)** $^{3}He^{+}$ **(c)** $^{12}C^{2+}$ **(d)** $^{19}F^{-}$.

Approach. Find q/m for each particle. Since $\theta \propto q/m$, write $\theta = k \times q/m$. For $^{4}He^{2+}$, q/m = +2/4 = +0.5, so k = 6.0 ÷ 0.5 = 12 and $\theta = 12 \times q/m$.

Working.

Particle	q	m	q/m	θ
$^{4}He^{2+}$	+2	4	+0.500	+6.0° (given)
$^{1}H^{+}$	+1	1	+1.000	+12°
$^{3}He^{+}$	+1	3	+0.333	+4.0°
$^{12}C^{2+}$	+2	12	+0.167	+2.0°
$^{19}F^{-}$	−1	19	−0.053	−0.63°

Answer. **(a)** +12° **(b)** +4.0° **(c)** +2.0°, all towards the negative plate; **(d)** −0.63° towards the positive plate (q/m is negative).

EXAM TIP
Only electric fields are required, not magnetic fields. State the direction in words (towards the positive or negative plate) as well as the angle; the sign of an angle is only a convention.

EXAM TIP
The path is straight before the plates, curved between them, and straight again after leaving them. All beams start to bend at the same point.

COMMON ERROR
Comparing masses only. $^{12}C^{2+}$ is 12 times heavier than $^{1}H^{+}$ but has twice the charge, so it is deflected 1/6 as much, not 1/12.

Check your understanding 1.2

1. Sketch the paths of protons, neutrons and electrons passing between two charged plates. Label each path.
2. Explain why a beam of neon atoms passes straight through an electric field, but a beam of Ne^{+} ions is deflected.
3. Under certain conditions, $^{2}H^{+}$ is deflected through +3.0°. Under the same conditions, predict the angle for $^{4}He^{2+}$ and explain your answer.
4. X^{2+} and Y^{+} are deflected through the same angle under the same conditions. X^{2+} has relative mass 24. Deduce the relative mass of Y^{+}.

Free sample — full book at jamescollins.com.sg

5. Under the conditions of Worked example 1.2 ($\theta = 12 \times q/m$), a particle is deflected through 1.5° towards the positive plate. Which of these could it be? **(i)** 8 protons, 8 neutrons, 10 electrons **(ii)** 9 protons, 10 neutrons, 10 electrons **(iii)** 16 protons, 16 neutrons, 18 electrons. Show your working.

LEARNING OUTCOMES
1(d), 1(e)(i), 1(e)(ii)

1.3 Proton number, nucleon number and isotopes

The nucleus of an atom is described by two numbers: how many protons it contains, and how many nucleons in total.

DEFINITION:
The **proton number (Z)** is the number of protons in the nucleus of an atom.

DEFINITION:
The **nucleon number (A)** is the total number of protons and neutrons in the nucleus of an atom.

The proton number, also called the atomic number, identifies the element: every atom with 11 protons is sodium. The nucleon number is also called the mass number, because protons and neutrons supply almost all the mass.

The number of neutrons follows from these two numbers:

$$\textbf{number of neutrons} = A - Z$$

Writing nuclide symbols

A nuclide is an atom of one particular kind, identified by its proton number and nucleon number; $^{23}_{11}\mathrm{Na}$ and $^{37}_{17}\mathrm{Cl}$ are nuclides.

A particle is written with its nucleon number at the top left, its proton number at the bottom left and any charge at the top right.

For example, $^{23}_{11}\mathrm{Na}^{+}$ and $^{35}_{17}\mathrm{Cl}^{-}$.

The number of electrons depends on the charge. A neutral atom has Z electrons. A positive ion with charge n+ has lost n electrons, so it has Z − n electrons. A negative ion with charge n− has gained n electrons, so it has Z + n electrons.

Worked example 1.3

Question. State the numbers of protons, neutrons and electrons in:
(a) $^{27}_{13}\mathrm{Al}^{3+}$ **(b)** $^{59}_{27}\mathrm{Co}^{2+}$ **(c)** $^{37}_{17}\mathrm{Cl}^{-}$ **(d)** $^{78}_{34}\mathrm{Se}^{2-}$.

Approach. Protons = Z. Neutrons = A − Z. Electrons = Z − (positive charge) or Z + (size of the negative charge).

Working.

Species	Protons	Neutrons	Electrons
$^{27}_{13}\mathrm{Al}^{3+}$	13	27 − 13 = 14	13 − 3 = 10
$^{59}_{27}\mathrm{Co}^{2+}$	27	59 − 27 = 32	27 − 2 = 25
$^{37}_{17}\mathrm{Cl}^{-}$	17	37 − 17 = 20	17 + 1 = 18
$^{78}_{34}\mathrm{Se}^{2-}$	34	78 − 34 = 44	34 + 2 = 36

COMMON ERROR
Using the nucleon number to count electrons. Electrons depend only on Z and the charge.

Free sample — full book at jamescollins.com.sg

Isotopes

DEFINITION:
Isotopes are atoms of the same element with the same number of protons but different numbers of neutrons, and so different nucleon numbers.

Isotopes of an element have the same proton number but different nucleon numbers. Hydrogen has three isotopes (**Table 1.2**).

Isotope	Symbol	Protons	Neutrons	Electrons
hydrogen-1 (protium)	$^{1}_{1}H$	1	0	1
hydrogen-2 (deuterium, D)	$^{2}_{1}H$	1	1	1
hydrogen-3 (tritium)	$^{3}_{1}H$	1	2	1

Table 1.2 *The isotopes of hydrogen.*

Isotopes have the **same chemical properties** because they have the same number of electrons and the same electronic configuration. Chemical reactions involve electrons, not neutrons.[1] For the same reason, isotopes have the same ionisation energies: the nuclear charge and the arrangement of electrons are the same.

Isotopes have **slightly different physical properties**, such as density, melting point and rate of diffusion, because their atoms have different masses.

KEY POINT
Same electrons → same chemistry. Different neutrons → different mass → different physical properties.

LINK
Most elements exist as a mixture of isotopes. You will use isotopic abundances to calculate relative atomic mass in Chapter 4.

Worked example 1.4

Question. Three particles, labelled 1 to 3, contain the subatomic particles shown. Identify each particle and write its full symbol.

Particle	Protons	Neutrons	Electrons
1	20	20	18
2	16	18	18
3	20	24	20

Approach. Protons give the element. A = protons + neutrons. Charge = protons − electrons.

Working. Particle 1: Z = 20 (Ca), A = 40, charge = 20 − 18 = +2. Particle 2: Z = 16 (S), A = 34, charge = 16 − 18 = −2. Particle 3: Z = 20 (Ca), A = 44, charge 0.

Answer. 1 is $^{40}_{20}Ca^{2+}$, 2 is $^{34}_{16}S^{2-}$, 3 is $^{44}_{20}Ca$. Particles 1 and 3 both have 20 protons but different nucleon numbers (40 and 44), so particle 1 is an ion of the isotope ^{40}Ca and particle 3 is an atom of the isotope ^{44}Ca.

EXAM TIP
Define isotopes in terms of particles: atoms of the same element with the same number of protons but different numbers of neutrons. "Different masses" alone is not enough; say protons and neutrons.

Check your understanding 1.3

1. State the numbers of protons, neutrons and electrons in $^{31}_{15}P^{3-}$ and $^{66}_{30}Zn^{2+}$.
2. A particle has 12 protons, 13 neutrons and 10 electrons. Write its full symbol.
3. Explain why ^{24}Mg and ^{26}Mg react in the same way with oxygen.
4. State one physical property that differs between H_2O and D_2O, and

Free sample — full book at jamescollins.com.sg

explain why it differs.

5. The ammonium ion, NH_4^+, contains one ^{14}N atom and four ^{1}H atoms. **(a)** State the total numbers of protons, neutrons and electrons in one ammonium ion. **(b)** Under the conditions of Worked example 1.2 ($\theta = 12 \times q/m$), calculate the angle of deflection of a beam of these ions and state its direction.

Notes

[1] Not required by the 9476 syllabus. Isotopes do react at slightly different rates, because a bond to a heavier isotope is slightly harder to break. The effect is largest for hydrogen, where ^{2}H has twice the mass of ^{1}H: this is why deuterated medicines break down more slowly.

LEARNING OUTCOME
1(f)

1.4 Shells, subshells and orbitals

Electrons in an atom can only have certain fixed energies. These energies are grouped into shells, subshells and orbitals.

Principal quantum shells

Electrons occupy principal quantum shells, numbered by the principal quantum number, n = 1, 2, 3, 4 and so on. As n increases, the shell is further from the nucleus and its electrons generally have higher energy.

COMMON ERROR
Stating that the third shell holds 8 electrons. That is only true of the 3s and 3p subshells together, which fill before 4s. The full third shell holds 18.

Subshells

Each shell is divided into **subshells**, labelled s, p, d and f. Shell n contains n types of subshell:

Shell (n)	Subshells
1	1s
2	2s, 2p
3	3s, 3p, 3d
4	4s, 4p, 4d, 4f (4d and 4f not required)

The 9476 syllabus covers subshells up to 3d, plus 4s and 4p.

EXAM TIP
Use the three terms precisely: a shell (n) contains subshells (s, p, d), and a subshell contains orbitals. Mixing them up makes a definition wrong.

Orbitals

DEFINITION:
An **atomic orbital** is a region of space around the nucleus where there is a high probability of finding an electron.

Each orbital holds a maximum of **two electrons**, and these must have opposite spins (spin is a property of an electron; the two possible spins are shown by the arrows ↑ and ↓). Each type of subshell contains a fixed number of orbitals (**Table 1.3**).

Subshell	Number of orbitals	Maximum electrons
s	1	2
p	3	6
d	5	10

Table 1.3 *Orbitals and electrons in each type of subshell.*

The orbitals within one subshell have the same energy. Orbitals of equal energy are called **degenerate orbitals**. For example, the three 2p orbitals are degenerate.

Shell n contains n^2 orbitals and can hold a maximum of $2n^2$ electrons: 2 in

Free sample — full book at jamescollins.com.sg

shell 1, 8 in shell 2 and 18 in shell 3.

Relative energies of subshells

Within a shell, energy increases in the order s < p < d. The shells also overlap: in atoms such as K and Ca, the 4s subshell is slightly lower in energy than 3d, so it fills first. The order of filling is:

1s → 2s → 2p → 3s → 3p → 4s → 3d → 4p

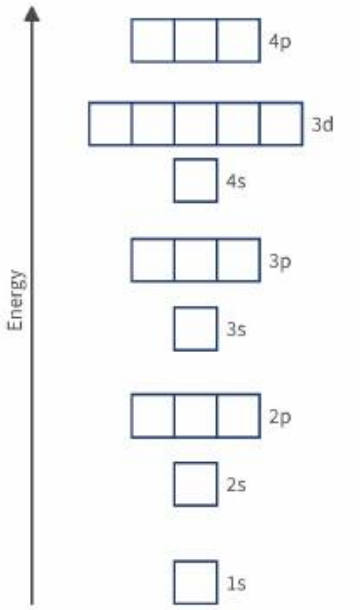


Figure 1.3 *Order in which subshells fill when building up atoms, with energy increasing upwards (energies as shown apply up to calcium; see Figure 1.8).*

KEY POINT

4s fills before 3d because 4s is lower in energy in atoms up to calcium. You will see in Section 1.6 how this affects the configurations of ions.

Worked example 1.5

Question. For the third shell (n = 3), state **(a)** the subshells present **(b)** the total number of orbitals **(c)** the maximum number of electrons.

Working. (a) 3s, 3p, 3d. **(b)** 1 + 3 + 5 = 9 orbitals (= n^2). **(c)** 9 × 2 = 18 electrons (= $2n^2$).

Answer. 3s, 3p and 3d; 9 orbitals; 18 electrons.

Check your understanding 1.4

1. State the number of orbitals in a 4p subshell and the maximum number of electrons it can hold.
2. Explain what is meant by degenerate orbitals, giving one example.
3. Arrange in the order in which they fill when building up atoms: 3d, 4p, 3p, 4s.
4. Calculate the maximum number of electrons in the second shell, and show how it is made up from its subshells.

1.5 Shapes of s, p and d orbitals

LEARNING OUTCOME

1(g)

Each type of orbital has a characteristic shape. The shape shows the region where an electron is most likely to be found. You need to draw and describe these shapes, but not the mathematics behind them.

s orbitals

An s orbital is **spherical**, centred on the nucleus, so it is non-directional. Every shell has one s orbital. The s orbitals get larger as n increases, so a 3s orbital is bigger than a 2s, which is bigger than a 1s. Orbitals in the same shell, such as 2s and 2p, are about the same size; p orbitals also get larger as n increases.

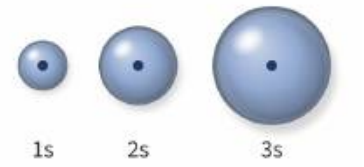


Figure 1.4 *The 1s, 2s and 3s orbitals: spheres centred on the nucleus, larger as n increases.*

p orbitals

A p orbital is **dumbbell-shaped** and directional: two lobes on opposite sides of the nucleus. The three p orbitals in a subshell point along the three axes at right angles to each other, so they are labelled $\mathbf{p_x}$, $\mathbf{p_y}$ and $\mathbf{p_z}$. The three orbitals are degenerate.

d orbitals

A d subshell has five orbitals. Their shapes fall into two sets: three **non-axial** orbitals with lobes between the axes, and two **axial** orbitals with lobes along the axes (**Table 1.4**).

Free sample — full book at jamescollins.com.sg

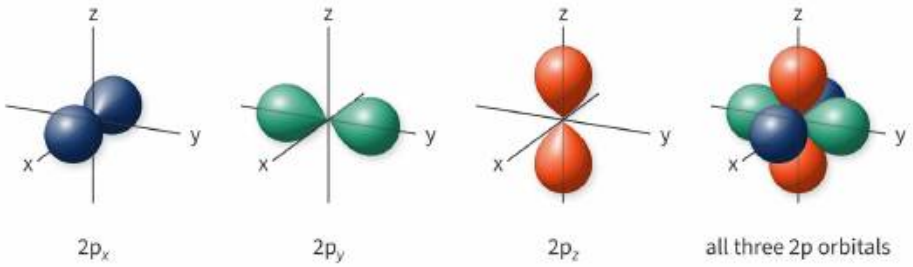


Figure 1.5 *The three 2p orbitals, each a dumbbell along one axis, shown separately and together.*

Orbital	Shape	Where the lobes lie
d_{xy}	four lobes	between the x and y axes
d_{xz}	four lobes	between the x and z axes
d_{yz}	four lobes	between the y and z axes
$d_{x^2-y^2}$	four lobes	along the x and y axes
d_{z^2}	two lobes and a ring	lobes along the z axis; ring in the xy plane

Table 1.4 *The five d orbitals.*

KEY POINT
Three d orbitals have lobes **between** the axes; two have lobes **along** the axes. This difference is important for the colours of transition metal complexes (Chapter 18, Book 2).

EXAM TIP
Draw and label the axes and name each orbital (e.g. 3d_{xz}); a d orbital without axes cannot be identified. An s orbital is spherical (not circular); a p orbital is dumbbell-shaped (not figure-of-eight).

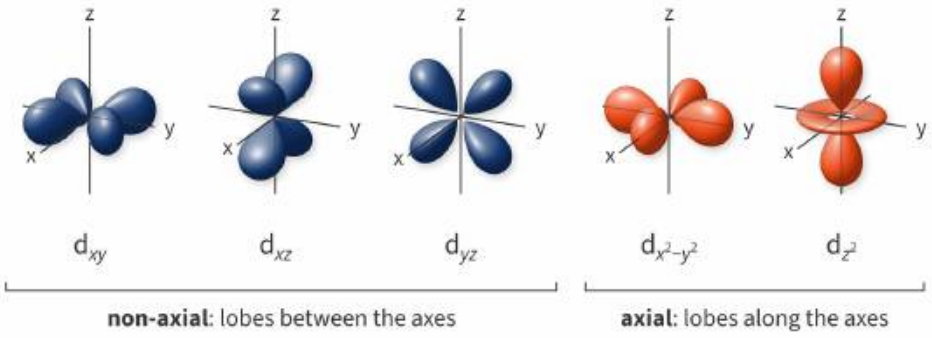


Figure 1.6 *The five 3d orbitals: in d_{xy}, d_{xz} and d_{yz} the lobes lie between the axes; in $d_{x^2-y^2}$ and d_{z^2} they lie along the axes.*

Worked example 1.6

Question. **(a)** Sketch a $2p_y$ orbital. **(b)** Which two d orbitals have lobes pointing along the axes?

Working. **(a)** Draw x, y and z axes; draw two lobes along the y axis, one each side of the nucleus. **(b)** From **Table 1.4**: $d_{x^2-y^2}$ has lobes along the x and y axes; d_{z^2} has lobes along the z axis. The other three point between the axes.

Answer. **(a)** Dumbbell along the y axis, axes labelled. **(b)** $d_{x^2-y^2}$ and d_{z^2}.

COMMON ERROR
Drawing d_{z^2} with four lobes. It has two lobes along the z axis plus a ring.

Check your understanding 1.5

1. State one similarity and one difference between **(a)** a 1s and a 3s orbital, **(b)** a 2s and a 2p orbital.
2. Sketch the three 2p orbitals, each on its own set of labelled axes.
3. Name the three d orbitals whose lobes lie between the axes.
4. Sketch a $d_{x^2-y^2}$ orbital and a d_{xy} orbital, and state one difference between them.

Free sample — full book at jamescollins.com.sg

1.6 Electronic configurations of atoms and ions

LEARNING OUTCOME
1(h)

The **electronic configuration** of an atom shows how its electrons are distributed among the orbitals. In the lowest-energy arrangement, the **ground state**, electrons are placed according to three rules.

Three rules for filling orbitals

Aufbau principle: Electrons fill orbitals in order of increasing energy, lowest first.

Pauli exclusion principle: An orbital holds at most two electrons, and they must have opposite spins.

Hund's rule: Electrons occupy degenerate orbitals singly, with parallel spins, before any pairing occurs.

Hund's rule applies because electrons repel each other. Two electrons in separate orbitals are further apart than two in the same orbital, which gives a lower energy.

Beyond the syllabus, but used in Chapter 8: if an electron absorbs energy and moves to a higher-energy orbital, the atom is in an excited state. For example, $1s^2\ 2s^1\ 2p^3$ is an excited state of carbon (ground state $1s^2\ 2s^2\ 2p^2$): it has the correct number of electrons, but one 2s electron has been promoted to 2p.

Writing configurations

There are five ways to show the same configuration. For sulfur (Z = 16):

Notation	Sulfur
Full	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
Noble gas core	[Ne] $3s^2\ 3p^4$
Each orbital separately	[Ne] $3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$
Electrons-in-boxes	[Ne] 3s: ↑↓ · 3p: ↑↓ ↑ ↑
Energy-level diagram	Boxes drawn at heights that show their energy, increasing upwards (as in **Figure 1.3** up to calcium; **Figure 1.8** once 3d is occupied), filled with arrows

In the noble gas core, [Ne] stands for the configuration of neon, $1s^2\ 2s^2\ 2p^6$ ([Ar] stands for $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$). In the electrons-in-boxes diagram, each box is an orbital and each arrow an electron. Sulfur's 3p subshell has one pair of electrons and two unpaired electrons, as Hund's rule predicts. In the third row, which lists each p orbital separately, $3p_x^2$ is the pair.

From potassium onwards, 4s fills before 3d, because in K and Ca the 4s subshell is lower in energy.[2] In the written configuration, however, subshells are grouped by shell number, so 3d is written before 4s:

Element	Z	Configuration
K	19	[Ar] $4s^1$
Ca	20	[Ar] $4s^2$
Sc	21	[Ar] $3d^1\ 4s^2$
Fe	26	[Ar] $3d^6\ 4s^2$
Zn	30	[Ar] $3d^{10}\ 4s^2$
Ga	31	[Ar] $3d^{10}\ 4s^2\ 4p^1$
Kr	36	[Ar] $3d^{10}\ 4s^2\ 4p^6$

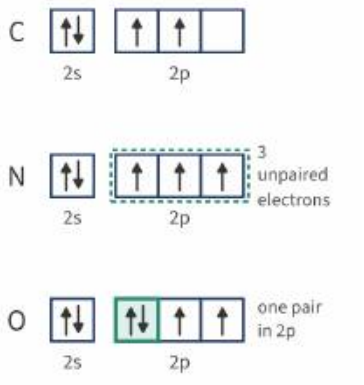


Figure 1.7 *Electrons-in-boxes diagrams for C, N and O: nitrogen has three unpaired 2p electrons; oxygen has one pair.*

Free sample — full book at jamescollins.com.sg

Chromium and copper

Two elements in Period 4 do not follow the expected pattern:

Element	Expected	Actual
Cr (Z = 24)	[Ar] $3d^4\ 4s^2$	**[Ar] $3d^5\ 4s^1$**
Cu (Z = 29)	[Ar] $3d^9\ 4s^2$	**[Ar] $3d^{10}\ 4s^1$**

EXAM TIP
Learn Cr and Cu as exceptions. Do not move a 4s electron into 3d for any other atom.

The 3d and 4s subshells are very close in energy, so a small change in arrangement can lower the overall energy. In Cr, $3d^5\ 4s^1$ places all six 3d and 4s electrons unpaired in separate orbitals, so there is less repulsion between them than in $3d^4\ 4s^2$, where two electrons share the 4s orbital. This arrangement is often described as a "stable half-filled" 3d subshell. In Cu, $3d^{10}\ 4s^1$ gives a completely filled 3d subshell, whose electron charge is spread evenly (symmetrically) around the nucleus; this arrangement has a lower overall energy than $3d^9\ 4s^2$. A common way to state this is "a fully filled 3d subshell is more stable".

Configurations of ions

COMMON ERROR
Writing Fe^{2+} as [Ar] $3d^4\ 4s^2$. The 4s electrons go first.

KEY POINT
A memory aid: 4s fills first and empties first.

- **Anions:** add electrons to the next available orbital. O^{2-} is $1s^2\ 2s^2\ 2p^6$.
- **Cations:** remove electrons from the outer shell first; within that shell, p electrons go before s electrons (e.g. Br^+ is [Ar] $3d^{10}\ 4s^2\ 4p^4$).
- **d-block cations:** remove **4s electrons before 3d**. Once 3d is occupied, it is lower in energy than 4s, so 4s is the highest-energy occupied subshell. Its electrons are also further from the nucleus, so they are lost first.

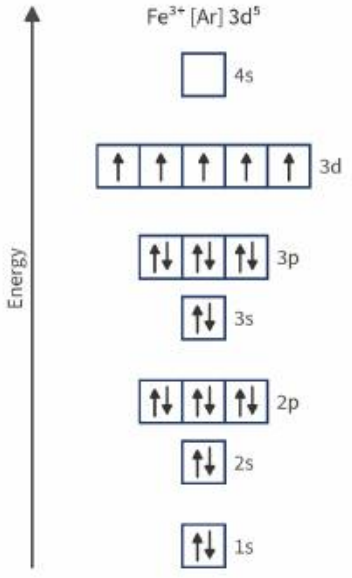


Figure 1.8 *Energy-level diagram for Fe^{3+}, [Ar] $3d^5$: once 3d is occupied it lies below 4s, which is empty in the ion.*

EXAM TIP
"Write" or "state" a configuration: give it in full (spdf), e.g. $1s^2\ 2s^2\ 2p^6\ 3s^1$, not [Ne] $3s^1$, unless asked for the noble gas core. "Draw": electrons-in-boxes or energy-level diagram, every subshell labelled.

Worked example 1.7

Question. Write the electronic configurations, using the noble gas core, of **(a)** Fe^{2+} **(b)** Fe^{3+} **(c)** Cr^{3+} **(d)** Cu^+.

Approach. Write the atom first, then remove 4s electrons before 3d.

Working.

Ion	Atom	Electrons removed	Ion configuration
Fe^{2+}	[Ar] $3d^6\ 4s^2$	$4s^2$	[Ar] $3d^6$
Fe^{3+}	[Ar] $3d^6\ 4s^2$	$4s^2$, then one 3d	[Ar] $3d^5$
Cr^{3+}	[Ar] $3d^5\ 4s^1$	$4s^1$, then two 3d	[Ar] $3d^3$
Cu^+	[Ar] $3d^{10}\ 4s^1$	$4s^1$	[Ar] $3d^{10}$

3d and 4s on an energy-level diagram. Once 3d holds electrons, it is lower in energy than 4s. In an energy-level diagram of any atom or ion from scandium onwards with electrons in 3d (e.g. Fe, Br, Fe^{3+}), draw the 3d boxes below the 4s box; in an ion such as Fe^{3+}, leave 4s empty. **Figure 1.3** shows the filling order for building up atoms; it is not the order of energies in these atoms and ions. This does not change the configurations: Fe is still [Ar] $3d^6\ 4s^2$, because electrons in the compact 3d orbitals repel each other more strongly (Note 2).

Isoelectronic species

DEFINITION:
Isoelectronic species have the same number of electrons.

N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+} and Al^{3+} each have 10 electrons, arranged

Free sample — full book at jamescollins.com.sg

$1s^2\ 2s^2\ 2p^6$. They differ only in nuclear charge, which affects their size (Chapter 3).

For s- and p-block species, the same number of electrons also means the same configuration. For d-block species it may not: Cr, Mn^+ and Fe^{2+} each have 24 electrons, but Cr and Mn^+ are [Ar] $3d^5\ 4s^1$, while Fe^{2+} is [Ar] $3d^6$.

Blocks of the Periodic Table

An element's block is the type of subshell its last electron enters in the filling (Aufbau) order:

- **s-block:** Groups 1 and 2, and helium
- **p-block:** Groups 13 to 18, except helium
- **d-block:** scandium to zinc, and the elements below them

The period number equals the principal quantum number, n, of the outer shell. For s- and p-block elements, the outer-shell configuration gives the group: ns^1 is Group 1, ns^2 is Group 2, and $ns^2\ np^1$ to $ns^2\ np^6$ are Groups 13 to 18. Helium ($1s^2$) is the exception: it is placed in Group 18 with the other noble gases.

For example, a silicon atom has 4 outer electrons ($3s^2\ 3p^2$), boron has 3 and phosphorus has 5. Traces of P or B change how silicon conducts electricity in computer chips because P has one more outer electron than Si and B has one fewer.

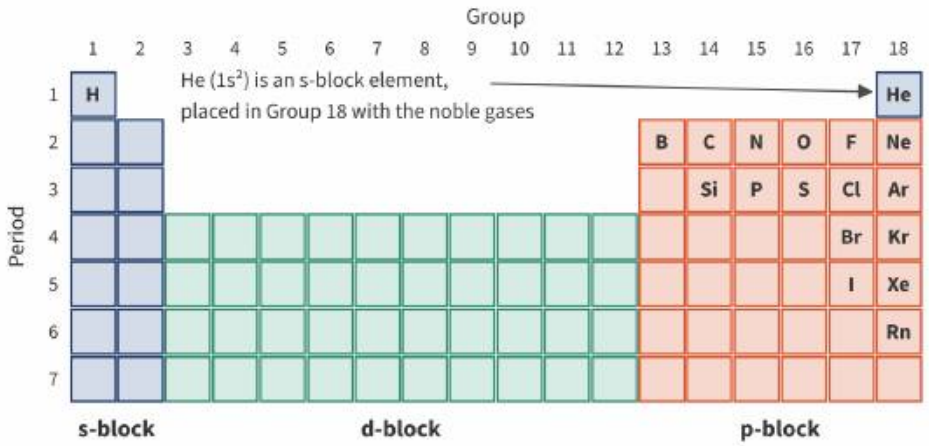


Figure 1.9 *Blocks of the Periodic Table. Helium ($1s^2$) is an s-block element placed in Group 18.*

Check your understanding 1.6

1. State the full electronic configuration of phosphorus. Draw its electrons-in-boxes diagram, starting from 1s, and state the number of unpaired electrons.
2. Write the configurations of Ni and Ni^{2+} using the noble gas core.
3. Draw electrons-in-boxes diagrams for the 3d and 4s orbitals of Cr and Cu.
4. Explain why the Co^{2+} ion is [Ar] $3d^7$ and not [Ar] $3d^5\ 4s^2$.
5. The ion X^+ has the configuration [Ar] $3d^{10}\ 4s^2\ 4p^2$. Deduce the period and group of X and identify X.

Free sample — full book at jamescollins.com.sg

Notes

[2] Not required by the 9476 syllabus. From scandium onwards, 3d is lower in energy than 4s, yet 4s is still occupied (by two electrons, except in Cr and Cu, which have $4s^1$). The 3d orbitals are more compact than 4s, so electrons in them repel each other more strongly; keeping two electrons in the more spread-out 4s orbital gives the lower total energy.

LEARNING OUTCOME
1(i)

1.7 Ionisation energy and the factors affecting it

Ionisation energy (IE) measures how strongly an atom holds its electrons, so IE data are evidence for how electrons are arranged.

DEFINITION:
The **first ionisation energy** of an element is the energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of gaseous singly charged positive ions.

For sodium:

$$Na(g) \rightarrow Na^+(g) + e^- \quad \Delta H = +494 \text{ kJ mol}^{-1}$$

EXAM TIP
Always include the state symbol (g) for the atoms and ions in an ionisation energy equation.

Ionisation energies are always positive (endothermic), because energy is needed to overcome the attraction between the nucleus and the electron. The first four ionisation energies of selected elements are listed in the Data Booklet (the booklet of data provided in the examination).

Factors affecting ionisation energy

The ionisation energy depends on how strongly the nucleus attracts the electron being removed.

DEFINITION:
The **shielding effect** is the reduction in attraction between the nucleus and an outer electron, caused by repulsion from electrons in inner shells.

Factor	Effect on ionisation energy
Nuclear charge	More protons → stronger nuclear attraction for the electron → higher IE
Distance from nucleus	Electron in a higher shell is further away → weaker nuclear attraction for the electron → lower IE
Shielding	Inner-shell electrons shield the outer electron, so it feels a smaller effective nuclear charge → weaker nuclear attraction for it → lower IE
Subshell	A p electron is higher in energy than an s electron in the same shell → weaker nuclear attraction for it → less energy needed to remove it → lower IE
Inter-electronic repulsion	An electron sharing an orbital with another is repelled by it → less energy needed to remove it → lower IE

Table 1.5 *Factors that affect ionisation energy.*

KEY POINT
The effective nuclear charge is the nuclear charge reduced by shielding. To explain IE, compare nuclear charge with shielding, name the shell or subshell, then compare the electrostatic attraction and the energy needed.

Using the factors

Down a group, IE decreases. For example, K (418 kJ mol^{-1}) has a lower first IE than Na (494 kJ mol^{-1}). Potassium's outer electron is in shell 4: K has one more inner shell of electrons than Na, so its outer electron is further from

Free sample — full book at jamescollins.com.sg

the nucleus and more shielded. The electrostatic attraction between it and the nucleus is therefore weaker and less energy is needed to remove it. The increase in nuclear charge is outweighed by these effects.

The first IE falls sharply from a noble gas to the next Group 1 element, for example from Ne (2080 kJ mol^{-1}) to Na (494 kJ mol^{-1}). The outer electron of Na is in a new shell, further from the nucleus and shielded by two inner shells, so the electrostatic attraction between it and the nucleus is much weaker and much less energy is needed to remove it, even though Na has one more proton.

In Period 4, the first IE of Ga (577 kJ mol^{-1}) is slightly lower than that of Ca (590 kJ mol^{-1}), even though Ga has 11 more protons: the 4p electron removed from Ga is higher in energy than the 4s electron removed from Ca, so the electrostatic attraction between it and the nucleus is weaker and less energy is needed to remove it.

Across a period, IE generally increases. Nuclear charge increases while electrons are added to the same shell, so shielding remains approximately constant. The effective nuclear charge therefore increases, the electrostatic attraction between the nucleus and the outer electrons is stronger, and more energy is needed to remove an electron. Two exceptions provide evidence for subshells.

Worked example 1.8

Question. Explain why the first ionisation energy of **(a)** aluminium (577 kJ mol^{-1}) is lower than that of magnesium (736 kJ mol^{-1}) **(b)** oxygen (1310 kJ mol^{-1}) is lower than that of nitrogen (1400 kJ mol^{-1}).

Approach. Write the configurations and identify the electron removed.

Working.

(a) Mg: [Ne] $3s^2$. Al: [Ne] $3s^2\ 3p^1$. The electron removed from Al is a 3p electron, which is higher in energy than the 3s electron removed from Mg. Less energy is needed to remove it.

(b) N: $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. O: $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. In O, the electron removed is from a doubly occupied 2p orbital. Inter-electronic repulsion between the paired electrons means less energy is needed to remove it.

Answer. (a) Al loses a 3p electron, which is higher in energy than the 3s electron lost by Mg, so the electrostatic attraction between it and the nucleus is weaker and less energy is needed to remove it. This outweighs its greater nuclear charge. **(b)** O loses one of the two electrons in its $2p_x$ orbital; inter-electronic repulsion between these paired electrons means less energy is needed to remove it than to remove an unpaired 2p electron from N. This outweighs its greater nuclear charge.

PRACTICES OF SCIENCE
evidence for subshells

The simple shell model predicts a smooth rise in IE across a period. The dips at Mg → Al and N → O do not fit it. Chemists explained these anomalies by proposing s and p subshells and electron pairing.

LINK
Trends in IE across Period 3 and down Group 2 are covered in full in Chapter 3.

COMMON ERROR
Explaining an IE by a "stable octet", "noble gas configuration" or "half-filled subshell" (S vs P). These describe arrangements, not causes. Compare nuclear charge, shielding and the subshell (or paired electron) removed.

Free sample — full book at jamescollins.com.sg

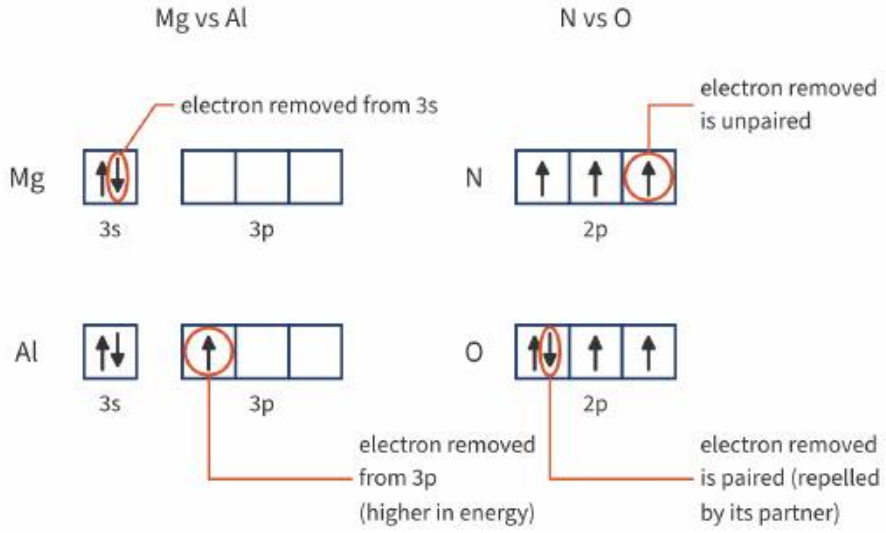


Figure 1.10 *Electrons-in-boxes diagrams for Mg and Al, and for N and O, with the electron removed on ionisation circled.*

Check your understanding 1.7

1. Write an equation, with state symbols, for the first ionisation energy of magnesium.
2. Explain why the first ionisation energy of lithium is greater than that of sodium.
3. Explain why the first ionisation energy of sulfur is lower than that of phosphorus.
4. Explain why neon has a higher first ionisation energy than fluorine.
5. Cl^-, Ar and K^+ are isoelectronic. Arrange them in order of increasing energy needed to remove one electron, and explain your order.

LEARNING OUTCOMES
1(j), 1(k)

1.8 Successive ionisation energies

Electrons can be removed from an atom one at a time. The energy needed for each step is a **successive ionisation energy**. An atom of proton number Z has Z electrons, so it has Z successive ionisation energies. The pattern of these values shows how many electrons are in each shell.

DEFINITION:
The **second ionisation energy** is the energy required to remove one mole of electrons from one mole of gaseous singly charged positive ions to form one mole of gaseous doubly charged positive ions.

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

COMMON ERROR
Writing the second IE as $X(g) \rightarrow X^{2+}(g) + 2e^-$. That equation represents the sum of the first and second IEs.

The third, fourth and later ionisation energies follow the same pattern: each removes one mole of electrons from one mole of gaseous ions that are already positive. For example, the third ionisation energy is the energy required to remove one mole of electrons from one mole of gaseous X^{2+} ions to form one mole of gaseous X^{3+} ions: $X^{2+}(g) \rightarrow X^{3+}(g) + e^-$.

To remove more than one electron, add the successive IEs. For $O(g) \rightarrow O^{3+}(g) + 3e^-$,

Free sample — full book at jamescollins.com.sg

$\Delta H = IE_1 + IE_2 + IE_3 = +(1310 + 3390 + 5320) = +10\,020$ kJ mol^{-1}. For a different amount, multiply by the number of moles of atoms: 0.0200 mol of O(g) needs $0.0200 \times 10\,020 = 2.00 \times 10^2$ kJ.

Why successive IEs increase

Each successive IE is larger than the one before, because every electron is removed from an increasingly positive ion. With fewer electrons, shielding decreases and there is less inter-electronic repulsion, while the nuclear charge stays the same. Each remaining electron therefore feels a larger effective nuclear charge, so the electrostatic attraction between it and the nucleus is stronger and more energy is needed to remove the next electron.

Worked example 1.9

Question. The second ionisation energy of chromium is 1590 kJ mol^{-1} and that of manganese is 1510 kJ mol^{-1} (Data Booklet). Explain why the second IE of chromium is higher, even though manganese has the larger nuclear charge.

Approach. Write the configuration of each 1+ ion, then identify the subshell the second electron comes from.

Working.

Cr: [Ar] $3d^5\,4s^1$, so Cr^+ is [Ar] $3d^5$. Mn: [Ar] $3d^5\,4s^2$, so Mn^+ is [Ar] $3d^5\,4s^1$.

The second electron removed from Cr comes from the 3d subshell (in shell 3), which is closer to the nucleus and lower in energy than 4s once 3d is occupied.

The second electron removed from Mn comes from 4s, which is higher in energy and further from the nucleus, so the electrostatic attraction between it and the nucleus is weaker and less energy is needed to remove it.

Answer. Cr^+ loses a 3d electron from the $3d^5$ subshell; in Cr^+, 3d is lower in energy and closer to the nucleus than 4s, so the electrostatic attraction between this electron and the nucleus is stronger and more energy is needed to remove it. Mn^+ loses a 4s electron, which is higher in energy and further from the nucleus, so the electrostatic attraction between it and the nucleus is weaker and less energy is needed to remove it. These effects outweigh the extra proton in manganese, so the second IE of Cr is higher.

Large jumps show a change of shell

A **large jump** between two successive IEs means the next electron comes from a shell closer to the nucleus; it is less shielded, so the electrostatic attraction between it and the nucleus is stronger and far more energy is needed to remove it. For p-block elements in Period 4, the jump into the full 3d subshell is smaller than usual. For Ga (577, 1980, 2960 and 6190 kJ mol^{-1}), the largest ratio, 3.4, is IE_2/IE_1, but the first large jump in the differences (1403, 980 and 3230 kJ mol^{-1}) is between IE_3 and IE_4, which correctly gives Group 13.

The number of electrons removed before the first large jump equals the number of outer-shell electrons. For s- and p-block elements, this gives the

Free sample — full book at jamescollins.com.sg

group number (d-block elements are covered in Chapter 18):

Electrons before first large jump	Group
1	1
2	2
3 to 8	13 to 18

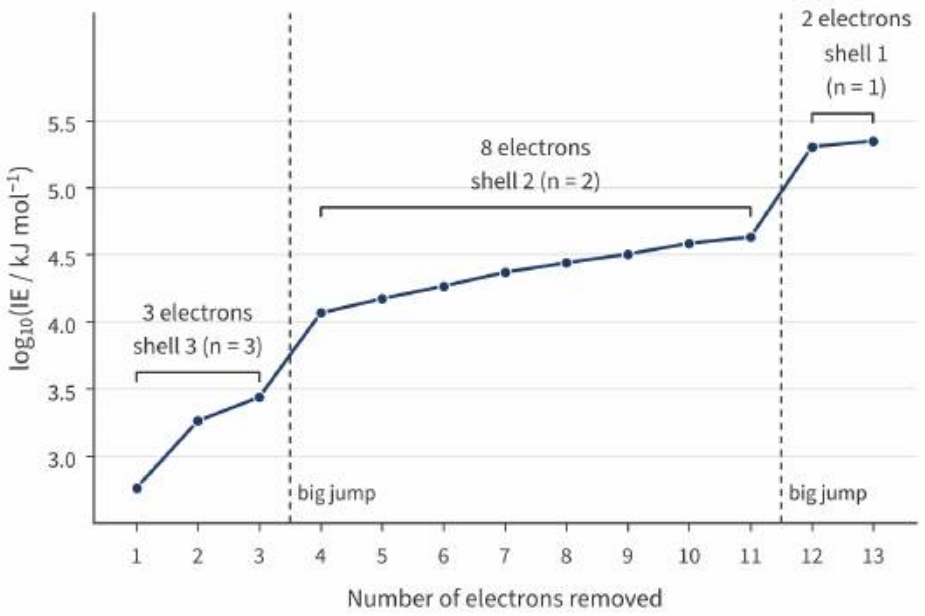


Figure 1.11 *Successive ionisation energies of aluminium (log scale): two large jumps split the 13 electrons into shells of 3, 8 and 2.*[3]

A log scale is used because the values range from about 600 to over 200 000 kJ mol^{-1}. Smaller jumps within a shell, such as between the 2p and 2s electrons, can show the subshells, although they are not always clear.

On a graph of all the successive IEs of an atom, the large jumps split the values into sets, and the number of sets equals the number of occupied shells. This gives the period number: aluminium has three sets of points (**Figure 1.11**), so it is in Period 3.

A graph of second IE against proton number has a similar shape to the graph of first IE (which peaks at each noble gas and falls sharply at the next Group 1 element; Chapter 3), moved one element to the right. This is because the X^+ ion has the same number of electrons as the atom of the element before X. So the second IE peaks at a Group 1 element, whose X^+ ion loses an inner-shell electron, and it falls sharply at the Group 2 element that follows. Likewise, a graph of third IE peaks at a Group 2 element and falls sharply at the element that follows (Group 13 in Periods 2 and 3; scandium in Period 4).

Worked example 1.10

Question. The first five ionisation energies of a Period 3 element, Y, are (in kJ mol^{-1}): 786, 1580, 3230, 4360, 16 100.[4] Deduce the group of Y, its electronic configuration and its identity.

Approach. Find the difference between each pair of successive IEs and locate the first large jump.

Free sample — full book at jamescollins.com.sg

Working.

IE	1st	2nd	3rd	4th	5th
Value / kJ mol^{-1}	786	1580	3230	4360	16 100
Difference from previous / kJ mol^{-1}	–	794	1650	1130	11 740
Ratio to previous	–	2.0	2.0	1.3	3.7

The first large jump, 11 740 kJ mol^{-1} (ratio 3.7), is between the 4th and 5th IEs, so the 5th electron comes from an inner shell, which is closer to the nucleus and less shielded; the electrostatic attraction between it and the nucleus is therefore much stronger, and much more energy is needed to remove it. Y therefore has 4 outer electrons and is in Group 14. In Period 3, the outer shell is n = 3.

In shell 3, the 1st and 2nd electrons come from 3p and the 3rd and 4th from 3s. Within a shell the differences are all small (794–1650 kJ mol^{-1}; ratios 1.3–2.0) compared with the jump to the inner shell (11 740 kJ mol^{-1}; ratio 3.7), so here the change from 3p to 3s does not show up clearly.

Answer. Group 14; $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$; Y is silicon.

EXAM TIP
Find the first large jump from the differences between successive IEs: look for one clearly larger than all those before it. A small IE_1 can make IE_2/IE_1 look large when no shell changes.

Worked example 1.11

Question. The first three ionisation energies of calcium are 590, 1150 and 4940 kJ mol^{-1}. **(a)** Write an equation for the second IE. **(b)** Explain the large increase from the second to the third IE.

Working. (a) $Ca^+(g) \rightarrow Ca^{2+}(g) + e^-$. **(b)** Ca is [Ar] $4s^2$. The first two electrons come from 4s. The third comes from 3p, in shell 3, which is closer to the nucleus and less shielded, so the electrostatic attraction between it and the nucleus is much stronger and much more energy is needed to remove it. The increase from IE_2 to IE_3 is 4940 − 1150 = 3790 kJ mol^{-1}.

Check your understanding 1.8

1. The first four IEs of an element are 418, 3070, 4600 and 5860 kJ mol^{-1}. State its group and explain your answer.
2. Sketch a graph of $\log_{10}$(IE) against number of electrons removed for sodium (Z = 11). Show the pattern only; values are not needed.
3. Explain why the second IE of potassium (3070 kJ mol^{-1}) is much larger than the second IE of calcium (1150 kJ mol^{-1}).
4. The second ionisation energy of aluminium (1820 kJ mol^{-1}) is higher than that of silicon (1580 kJ mol^{-1}), although silicon has the greater nuclear charge. Explain this, using the configurations of Al^+ and Si^+.
5. Element A (Period 5) has the first four IEs of 548, 1060, 4120 and 5440 kJ mol^{-1}. Element B (Period 2) has the first seven IEs of 1310, 3390, 5320, 7450, 11 000, 13 300 and 71 300 kJ mol^{-1} (the 5th–7th are reference values). Deduce the groups of A and B and the formula of the ionic compound they form.
6. These are all the ionisation energies of an atom: 900, 1760, 14 800

Free sample — full book at jamescollins.com.sg

and 21 000 kJ mol^{-1}. Deduce the number of occupied shells, and hence the period and group of the element.

7. The second ionisation energies, in kJ mol^{-1}, of eight consecutive elements, numbered 1 to 8 in order of increasing proton number, are 2860, 3390, 3370, 3950, 4560, 1450, 1820 and 1580. Identify which numbered element is in Group 1, and explain the sharp fall in second IE at the element after it.
8. The second ionisation energy of oxygen (3390 kJ mol^{-1}) is higher than that of fluorine (3370 kJ mol^{-1}), although fluorine has the greater nuclear charge. Explain this, using the configurations of O^+ and F^+.
9. The 2nd to 6th ionisation energies of an element in Period 3 are 1820, 2740, 11 600, 14 800 and 18 400 kJ mol^{-1} (the 5th and 6th are reference values). Deduce the group of the element and identify it.
10. Refer to your sketch for sodium in question 2. Explain **(a)** why each ionisation energy is larger than the one before, and **(b)** why there is a large jump after the 1st electron and again after the 9th electron.
11. Magnesium has 12 electrons. State which of its 12 successive ionisation energies remove an electron from a subshell that is completely filled just before that electron is removed.
12. Two Period 2 elements, Q and R, are in Groups 15 and 16. Their first four IEs, in kJ mol^{-1}, are Q: 1400, 2860, 4590, 7480 and R: 1310, 3390, 5320, 7450. Use the differences between successive IEs to deduce which element is in Group 15. Explain your answer.

Notes

[3] **Figure 1.11** uses Data Booklet values for the 1st–4th ionisation energies of aluminium (577, 1820, 2740 and 11 600 kJ mol^{-1}). The Data Booklet stops at the 4th, so the 5th–13th are standard reference values (CRC Handbook of Chemistry and Physics / NIST).

[4] Worked example 1.10 uses Data Booklet values for the 1st–4th ionisation energies of element Y. The 5th is a standard reference value (NIST), rounded to 3 significant figures.

Chapter summary

- Atoms contain protons (relative mass 1, charge +1), neutrons (1, 0) and electrons (1/1836, −1). Nearly all the mass and all the positive charge are in the tiny nucleus.
- In an electric field, protons bend towards the negative plate, electrons towards the positive plate, and neutrons are not deflected. The angle of deflection $\theta \propto q/m$.
- Proton number Z identifies the element; nucleon number A = protons + neutrons; neutrons = A − Z. Electrons = Z − positive charge or Z + size of negative charge.
- Isotopes have the same number of protons but different numbers of neutrons. They have the same chemical properties but slightly different physical properties.
- Shells (n) contain subshells (s, p, d), which contain orbitals (1, 3, 5). Each orbital holds at most two electrons, of opposite spin. Filling order: 1s → 2s → 2p → 3s → 3p → 4s → 3d → 4p.
- s orbitals are spherical; p orbitals are dumbbells along x, y, z; three d orbitals lie between the axes and two ($d_{x^2-y^2}$, d_{z^2}) along them.

Free sample — full book at jamescollins.com.sg

- Configurations follow the Aufbau principle, Pauli exclusion principle and Hund's rule. Cr is [Ar] $3d^5\ 4s^1$ and Cu is [Ar] $3d^{10}\ 4s^1$. d-block atoms lose 4s electrons before 3d.
- Across a period, first IE generally increases: nuclear charge increases while shielding remains approximately constant. First IE decreases with distance, shielding, higher subshell energy and inter-electronic repulsion.
- Successive IEs always increase. A large jump marks a change to an inner shell; for s- and p-block elements, the number of electrons before the first large jump gives the group, and the number of sets of values (shells) gives the period.

Exam-style questions

Values not in the Data Booklet are reference values.

Section A: Multiple-choice questions

For each question, choose one answer from A to D.

M1 Which species contains more electrons than neutrons?

A $^{19}F^-$

B $^{16}O^{2-}$

C $^{23}Na^+$

D $^{24}Mg^{2+}$

M2 Which pair of species has the same number of electrons and the same number of neutrons?

A $^{19}F^-$ and ^{20}Ne

B $^{23}Na^+$ and $^{27}Al^{3+}$

C $^{16}O^{2-}$ and $^{19}F^-$

D $^{35}Cl^-$ and ^{40}Ar

M3 Under certain conditions, a beam of $^1H^+$ is deflected through +8° by an electric field. Under the same conditions, which ion is deflected through +2°?

A $^2H^+$

B $^4He^{2+}$

C $^4He^+$

D $^6Li^+$

M4 Use of the Data Booklet is relevant to this question. How many orbitals contain at least one electron in a ground-state silicon atom?

A 5

B 7

C 8

D 14

M5 For the elements potassium to zinc, which subshell fills immediately after 4s?

A 3d

B 4p

C 4d

D 3p

M6 Which orbital has lobes lying along both the x and y axes?

A d_{xy}

B $d_{x^2-y^2}$

C d_{z^2}

D p_z

M7 Which ground-state electronic configuration is correct?

A Cr: [Ar] $3d^4\ 4s^2$

B Cu^+: [Ar] $3d^9\ 4s^1$

C Fe^{3+}: [Ar] $3d^5$

D Ti^{2+}: [Ar] $4s^2$

Free sample — full book at jamescollins.com.sg

M8 Use of the Data Booklet is relevant to this question. How many unpaired electrons are there in a ground-state Co^{2+} ion?

A 1
B 3
C 5
D 7

M9 Which equation represents the second ionisation energy of aluminium?

A $Al(g) \rightarrow Al^{2+}(g) + 2e^-$
B $Al^+(aq) \rightarrow Al^{2+}(aq) + e^-$
C $Al^{2+}(g) \rightarrow Al^{3+}(g) + e^-$
D $Al^+(g) \rightarrow Al^{2+}(g) + e^-$

M10 Use of the Data Booklet is relevant to this question. Which element has the highest first ionisation energy?

A boron
B carbon
C nitrogen
D oxygen

M11 The first six ionisation energies of an element, in kJ mol^{-1}, are 1060, 1900, 2920, 4960, 6270 and 21 300. In which group of the Periodic Table is the element?

A 14
B 15
C 16
D 17

M12 Which statements about ^{35}Cl and ^{37}Cl atoms are correct?

1 They have the same number of electrons.
2 They have the same chemical properties.
3 They have the same nucleon number.

A 1 and 2 only
B 1 and 3 only
C 2 and 3 only
D 1, 2 and 3

M13 Which species have the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$?

1 S^{2-}
2 Ca^{2+}
3 Ti^{4+}
4 Cl

A 1 and 2 only
B 1 and 4 only
C 2, 3 and 4 only
D 1, 2 and 3 only

M14 Which factors help to explain why the first ionisation energy of potassium is lower than that of sodium?

1 The outer electron of potassium is further from the nucleus.
2 The outer electron of potassium experiences more shielding.
3 Potassium has a smaller nuclear charge.

A 1 only
B 2 only
C 1 and 2 only
D 1, 2 and 3

M15 The second ionisation energy of a Period 3 element, X, is about nine times its first ionisation energy. Which statements are correct?

1 X is in Group 1.
2 X readily forms an X^+ ion.
3 The second electron is removed from a 2p orbital.

A 1 only
B 1 and 2 only
C 1 and 3 only
D 1, 2 and 3

M16 For a ground-state Fe^{3+} ion (Fe, proton number 26), which row is correct?

	Number of unpaired electrons	Number of fully occupied orbitals
A	5	9
B	5	10
C	4	9
D	3	11

Free sample — full book at jamescollins.com.sg

M17 Why is the first ionisation energy of magnesium higher than that of aluminium?

A Magnesium has a greater nuclear charge than aluminium.

B The electron removed from aluminium is in a higher-energy 3p orbital.

C The outer electron of aluminium is in a doubly occupied orbital.

D Magnesium has a completely filled outer shell.

M18 The first four ionisation energies of element E, in kJ mol^{-1}, are 736, 1450, 7740 and 10 500. E reacts with chlorine to form an ionic compound. What is the formula of this compound?

A ECl

B ECl_2

C ECl_3

D E_2Cl

M19 W, X, Y and Z are four consecutive elements in the Periodic Table, in order of increasing proton number. Their first ionisation energies, in kJ mol^{-1}, are W 1000, X 1260, Y 1520 and Z 418. Which element is in Group 18?

A W

B X

C Y

D Z

M20 Use of the Data Booklet is relevant to this question. Which atom or ion has a half-filled p subshell after it gains one electron?

A germanium atom, Ge

B gallium atom, Ga

C arsenic atom, As

D selenium ion, Se^+

M21 Which expression gives the energy needed for $Al(g) \rightarrow Al^{3+}(g) + 3e^-$?

A the third ionisation energy of aluminium

B 3 × the first ionisation energy of aluminium

C the third ionisation energy minus the first ionisation energy

D the sum of the first, second and third ionisation energies

Section B: Structured questions

1 Nickel has two common isotopes, ^{58}Ni and ^{60}Ni.

(a) Define the term *isotopes*. [1]

(b) State the numbers of protons, neutrons and electrons in a $^{60}_{28}Ni^{2+}$ ion. [2]

(c) A sample of nickel is enriched in ^{60}Ni. Predict whether its reaction with dilute acid gives different products from that of ordinary nickel. Explain your answer. [2]

[Total: 5]

2 A beam of $^7Li^+$ ions is deflected through +2.0° by an electric field.

(a) Under the same conditions, calculate the angles of deflection of $^6Li^+$ and $^9Be^{2+}$. [2]

(b) An ion X^{2-} is deflected through −1.75° under the same conditions. Deduce the relative mass of X^{2-} and suggest its identity. [2]

(c) State and explain how a beam of electrons would be deflected under the same conditions, compared with the $^7Li^+$ beam. [2]

[Total: 6]

3 **(a)** Sketch a d_{z^2} orbital and a d_{xy} orbital, each on a labelled set of axes. [2]

(b) State the total number of orbitals in the n = 2 shell. [1]

(c) Arrange these subshells in the order in which they fill when building up atoms: 4s, 3s, 3d, 2p. [1]

[Total: 4]

4 Write the electronic configuration, using the noble gas core, of:

(a) V (proton number 23) [1]

(b) V^{3+} [1]

(c) Cu^{2+} [1]

(d) Se^{2-} (proton number 34) [1]

(e) State the number of unpaired electrons in V^{3+}. [1]

[Total: 5]

5 **(a)** Define the *first ionisation energy* of

Free sample — full book at jamescollins.com.sg

chlorine, and write an equation to represent it. [2]

(b) The first ionisation energy of boron (799 kJ mol^{-1}) is lower than that of beryllium (900 kJ mol^{-1}). Explain this, with reference to their electronic configurations. [2]

(c) The first ionisation energy of selenium (941 kJ mol^{-1}) is slightly lower than that of arsenic (944 kJ mol^{-1}). Explain this. [2]

[Total: 6]

6 The first eight ionisation energies of a Period 3 element, R, are (in kJ mol^{-1}): 1260, 2300, 3850, 5150, 6540, 9360, 11 000, 33 600.

(a) Deduce the group of R. Explain your answer. [2]

(b) Give the full electronic configuration of R and identify it. [2]

(c) Calculate the energy needed to convert 0.0400 mol of gaseous R atoms into $R^{3+}(g)$ ions. [2]

[Total: 6]

7 The first ionisation energies of the Period 4 elements outside the d-block are shown in Table 7.1.

Table 7.1

Element	K	Ca	Ga	Ge	As	Se	Br	Kr
proton number	19	20	31	32	33	34	35	36
first ionisation energy / kJ mol^{-1}	418	590	577	762	944	941	1140	1350

(a) Describe and explain the general trend in first ionisation energy from Ga to Kr. [2]

(b) Explain why the first ionisation energy of Ga is slightly lower than that of Ca, even though Ga has a much larger nuclear charge. [2]

(c) Zinc (proton number 30) comes just before gallium. Explain why the first ionisation energy of gallium (577 kJ mol^{-1}) is lower than that of zinc (908 kJ mol^{-1}). [2]

(d) Rubidium (proton number 37) follows krypton. Predict whether its first ionisation energy is higher or lower than that of K. Explain your answer. [2]

(e) Write the electronic configuration of Ge using the noble gas core, and state the number of unpaired electrons. [2]

[Total: 10]

8 Manganese (proton number 25) forms Mn^{2+} and Mn^{3+} ions.

(a) Write the electronic configurations of Mn, Mn^{2+} and Mn^{3+} using the noble gas core. [2]

(b) Draw an electrons-in-boxes diagram for the 3d and 4s orbitals of Mn^{2+}. State the number of unpaired electrons. [2]

(c) In a certain complex of Mn^{2+}, six molecules or ions approach the ion along the positive and negative x, y and z axes. Name the two 3d orbitals whose lobes point directly at these molecules or ions, and sketch one of them on labelled axes. [3]

(d) Suggest one reason why Mn^{2+} is more difficult to oxidise to Mn^{3+} than Fe^{2+} is to Fe^{3+}. [1]

[Total: 8]

Section C: Extended questions

9 Boron has two stable isotopes, ^{10}B and ^{11}B.

(a) (i) State the numbers of protons, neutrons and electrons in a $^{11}B^{3+}$ ion. [2]

(ii) Under certain conditions, a beam of $^{10}B^{+}$ ions is deflected through +3.3° by an electric field. Calculate the angles of deflection of $^{11}B^{+}$ and $^{11}B^{3+}$ under the same conditions. [2]

(iii) Explain why a beam of ^{11}B atoms is not deflected. [1]

(b) (i) Write the full electronic configurations of B and B^{3+}. [1]

(ii) Sketch the shape of the orbital that contains the highest-energy electron in a boron atom. Label the axes. [1]

(iii) State the number of unpaired electrons in a boron atom. [1]

(c) The first five ionisation energies of

Free sample — full book at jamescollins.com.sg

boron are 799, 2420, 3660, 25 000 and 32 800 kJ mol^{-1}.

(i) Write an equation for the third ionisation energy of boron. [1]

(ii) The fourth ionisation energy of boron is much larger than the fourth ionisation energy of carbon (6220 kJ mol^{-1}). Explain this. [2]

(iii) The ratio IE_2/IE_1 (3.0) is larger than the ratio IE_3/IE_2 (1.5). Explain this in terms of subshells. [2]

(d) The first ionisation energy of aluminium is 577 kJ mol^{-1}. Explain why it is lower than that of boron. [2]

(e) Sketch a graph of $\log_{10}$(ionisation energy) against the number of electrons removed, using all five values in **(c)**. Use your sketch to deduce the number of electrons in each shell of a boron atom, and hence state the period and group of boron. [3]

[Total: 18]

10 Iron and copper are d-block metals.

(a) Iron has four stable isotopes: ^{54}Fe, ^{56}Fe, ^{57}Fe and ^{58}Fe.

(i) State one similarity and one difference between the nuclei of ^{54}Fe and ^{58}Fe. [2]

(ii) Beams of $^{54}Fe^{2+}$ and $^{58}Fe^{3+}$ ions enter the same electric field at the same speed. Calculate the ratio of their angles of deflection, $\theta(^{58}Fe^{3+}) : \theta(^{54}Fe^{2+})$. [1]

(iii) A beam of $^{58}Fe^{2+}$ ions is then passed through the same field. State which of $^{54}Fe^{2+}$ and $^{58}Fe^{2+}$ is deflected more. [1]

(b) (i) Write the electronic configurations of Fe, Fe^{2+} and Fe^{3+} using the noble gas core. [3]

(ii) Draw an electrons-in-boxes diagram for the 3d and 4s orbitals of Fe^{2+}, and state the number of unpaired electrons. [2]

(iii) State one reason why iron loses its 4s electrons before its 3d electrons. [1]

(iv) Sketch a d_{xz} orbital on labelled axes. [1]

(c) The third ionisation energy of iron is 2960 kJ mol^{-1} and that of cobalt is 3230 kJ mol^{-1}.

(i) Write an equation for the third ionisation energy of iron. [1]

(ii) Explain why the third ionisation energy of cobalt is higher than that of iron, by referring to the electronic configurations of the ions involved. [2]

(d) (i) Write the electronic configurations of Cu^+ and Zn^+ using the noble gas core. [2]

(ii) The second ionisation energy of copper (1960 kJ mol^{-1}) is higher than that of zinc (1730 kJ mol^{-1}). Explain this difference. [2]

[Total: 18]

Free sample — full book at jamescollins.com.sg