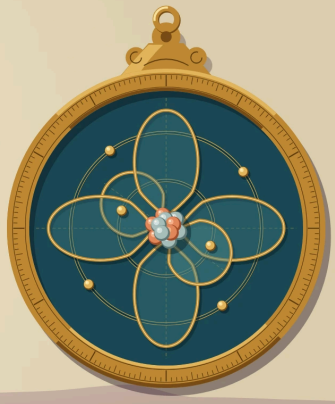
LEARNERS' ALLEY
Designed by Khow Willard

2 Atomic Structure

SINGAPORE JUNIOR CHEMISTRY OLYMPIAD



Everything else in chemistry depends on how atoms are built and how their electrons are arranged. This chapter builds the atom from its particles, arranges its electrons in shells and orbitals, and ends with the energy needed to remove them.

Learning objectives

By the end of this chapter, you can:

Foundation O LEVEL

- state the relative charge, mass and location of protons, neutrons and electrons
- deduce the particles in atoms and ions and write nuclide notation
- define isotopes and state how they differ

Core A LEVEL

- deduce how beams of charged particles deflect in an electric field
- describe the shapes and relative energies of s, p and d orbitals
- write electronic configurations of atoms and ions up to 4s
- explain the factors that affect ionisation energy and the dips across a period
- read successive ionisation energies to find the group

Prerequisites

Chapter 1: matter is made of particles, the difference between atoms and molecules, and between elements, compounds and mixtures, and how to read a formula such as H_2O. Fill in the blanks as the lesson goes.

2.1 The atom

An **atom** is the smallest particle of an element that still has the element's chemical properties. It is built from three **sub-atomic particles**. Protons and neutrons, together called **nucleons**, sit in the tiny central **nucleus**. Electrons move around it in shells (Figure 2.1).

particle	relative charge	relative mass	location
proton	_____	1	nucleus
neutron	_____	1	nucleus

electron	_____	about 1/1836	electron shells

- An atom is electrically neutral: number of protons = number of _____.
- The nucleus holds almost all the mass and all the positive charge. Electrons are held by the electrostatic attraction of the protons.
- The atom's radius is at least 100 000 times the radius of its nucleus. If the nucleus were a 1 cm marble, the atom would be about 1 km across, so an atom is mostly empty space.

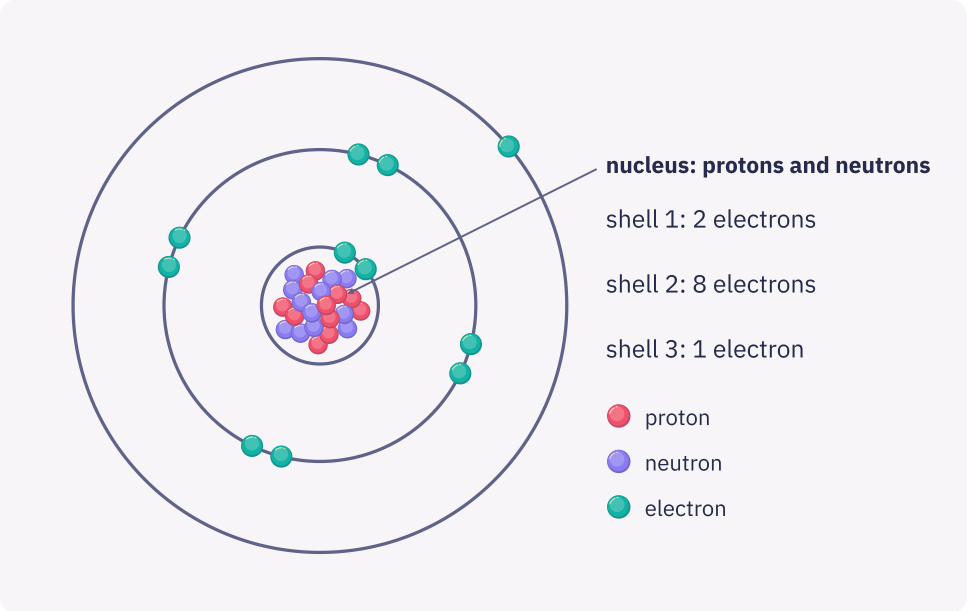


Figure 2.1 A sodium atom (not to scale: the nucleus is far smaller than shown). The shells hold 2, 8 and 1 electrons, and electrons sit in pairs where they can.

2.1.1 Proton number, nucleon number and ions

DEFINITION The **proton number**, Z, is the number of _____ in the nucleus. It fixes which element an atom is. The **nucleon number**, A, is the number of protons plus _____.

So the number of neutrons is A − Z. Nuclide notation writes A at the top left and Z at the bottom left of the symbol (Figure 2.2). An **ion** forms when an atom gains or loses electrons. Its protons and neutrons do not change. Each electron lost adds +1 to the charge and each electron gained adds −1. A positive ion is a **cation** and a negative ion is an **anion**. Particles with the same number of electrons, such as Na^+, Ne and F^-, are **isoelectronic**.

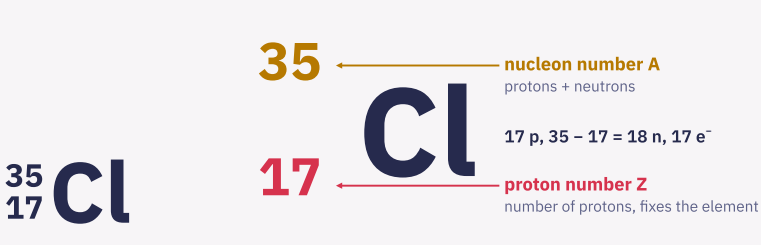


Figure 2.2 Nuclide notation for chlorine-35. Left: as it is written. Right: what each number means.

WORKED EXAMPLE How many protons, neutrons and electrons are in an atom of tungsten-184, $^{184}_{74}W$, and in a calcium ion, $^{40}_{20}Ca^{2+}$?

1. W: protons = Z = 74.	*Proton number gives the protons.*
2. W: neutrons = 184 − 74 = 110.	*Neutrons = A − Z.*
3. W: electrons = 74.	*The atom is neutral, so electrons = _____.*
4. Ca^{2+}: 20 protons, 40 − 20 = 20 neutrons.	*An ion keeps its protons and neutrons.*
Ca^{2+} has 20 − 2 = 18 electrons.	*The 2+ charge means _____ electrons were lost.*

2.1.2 Isotopes

DEFINITION **Isotopes** are atoms of the same element with the same proton number but different _____ numbers, so different numbers of _____.

	hydrogen-1	hydrogen-2	hydrogen-3
protons	1	1	1
neutrons	0	1	2
electrons	1	1	1
nucleon number	1	2	3

Isotopes have the same number of electrons, so they have the same electronic configuration and the same _____ reactions, because chemical reactions involve electrons and not the nucleus. Their masses differ, so their _____ properties, such as density, melting point, boiling point and rate of diffusion, differ. Name an isotope by its element and nucleon number, as in chlorine-35, ^{35}Cl or $^{2}_{1}H$ (Figure 2.3).

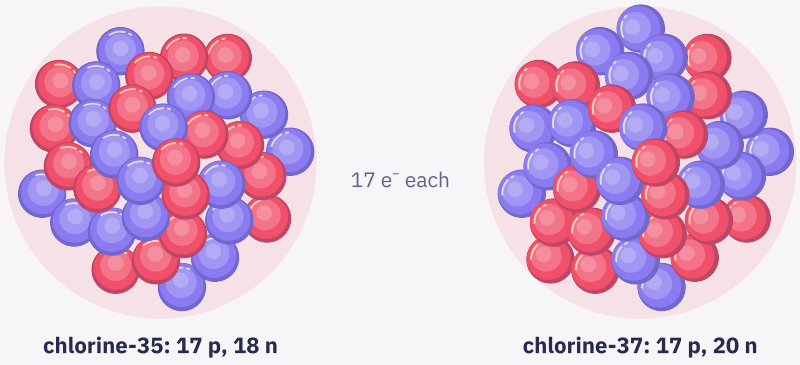


Figure 2.3 Two isotopes of chlorine. The extra two neutrons change the mass and nothing else about the chemistry.

Check your understanding

1. How many protons, neutrons and electrons are in the sulfide ion, $^{32}_{16}S^{2-}$?

2. Why do isotopes of an element react in the same way but differ in density?

2.1.3 Charged particles in an electric field CORE · A LEVEL

A beam of protons or electrons bends in an electric field, because they are charged. Neutrons carry no charge and go straight on. A positive particle bends towards the negative plate. A negative particle bends towards the positive plate (Figure 2.4).

RULE The angle of deflection is proportional to _____ ÷ _____. A larger charge bends the beam more and a larger mass bends it less.

An electron has the same size of charge as a proton but about 1/1836 of the mass, so its charge ÷ mass is far larger and it bends much more. Inside the field the path is curved. After the plates the beam travels in a straight line, and the angle is measured between this line and the original direction.

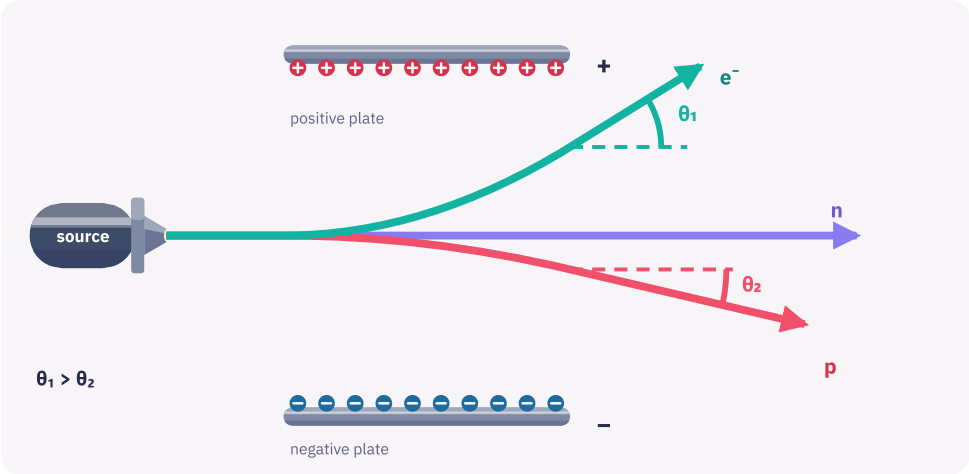


Figure 2.4 Beams of neutrons, protons and electrons in an electric field. The electron beam bends most, so $\theta_1 > \theta_2$.

WORKED EXAMPLE A beam of $^{241}Am^{+}$ ions is deflected +2° in an electric field. Under the same conditions, by what angle is a beam of $^{32}S^{-}$ ions deflected?

1. Angle = k × charge ÷ mass.	*The angle is _____ to charge ÷ mass.*
2. For Am^{+}: +2 = k × (+1) ÷ 241, so k = 482.	*Use the known beam to find k.*
3. For S^{-}: angle = 482 × (−1) ÷ 32 = −15.1.	*Charge is −1 and mass is 32.*
The S^{-} beam is deflected −15.1°.	*The minus sign means it bends the _____ way.*

Check your understanding

1. A beam of $^{1}H^{+}$ ions is deflected +4°. What is the deflection of a beam of $^{2}H^{+}$ ions under the same conditions?
2. Which beam bends more in the same field: $^{16}O^{2-}$ or $^{32}S^{2-}$? Explain.

2.2 Electrons in atoms

2.2.1 Shells

Electrons occupy shells at different distances from the nucleus. The inner shells have the lowest energy and fill first. For the first 20 elements, the first shell holds up to _____ electrons and the second and third shells up to _____ each. This gives the **electronic configuration**: sodium is 2.8.1 and potassium is 2.8.8.1.

The **Periodic Table** lists the elements in order of proton number (Figure 2.5). Its rows are **periods** and its columns are **groups**, numbered 1 to 18. Groups 3 to 12 begin only in Period 4.

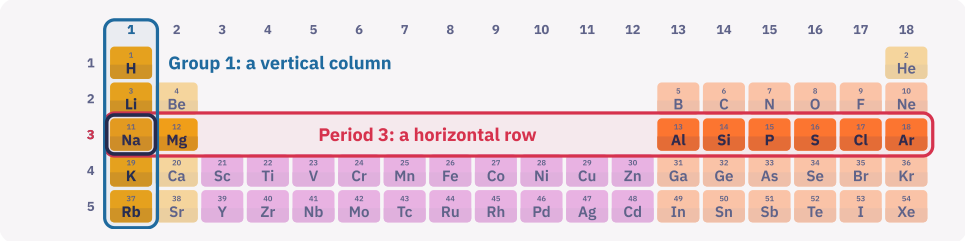


Figure 2.5 The Periodic Table to Period 5. The number above each symbol is the proton number.

- The outer shell is the **valence shell**, and its electrons are valence electrons. A full valence shell is stable, which is why the noble gases are unreactive.
- Period number = number of occupied shells. For Groups 1 and 2, group number = valence electrons. For Groups 13 to 18, valence electrons = group number − 10. Helium has 2.
- Elements in the same group have the same number of valence electrons and so similar chemical properties.

This 2.8.8 pattern breaks down after calcium. The finer description below explains why, and is what A Level and the olympiad use.

2.2.2 Subshells and orbitals CORE · A LEVEL

Each shell is a **principal quantum shell**, numbered n = 1, 2, 3, 4. Shell n is made of subshells, and each subshell is made of orbitals.

DEFINITION An **orbital** is a region of space with a high probability (about 95%) of finding an _____. Each orbital holds at most _____ electrons.

An electron has no fixed path. Marking its position again and again builds a cloud that is dense near the nucleus and thins out further away. The orbital is the region that contains most of that cloud.

shell n	subshells	orbitals	maximum electrons
1	1s	1	2
2	2s, 2p	1 + 3 = 4	8
3	3s, 3p, 3d	1 + 3 + 5 = 9	18
4	4s, 4p, 4d, 4f	16	32

An s subshell has 1 orbital, a p subshell 3 and a d subshell 5. Shell n holds up to $2n^2$ electrons. The 4f subshell is not needed in this course.

Energies. Energy rises with n: 1s < 2s < 3s < 4s. Within a shell the order is s < p < d. Orbitals in the same subshell have the same energy and are called **degenerate**. The levels crowd together as n increases, so the 4s orbital is _____ in energy than 3d and fills first (Figure 2.6).

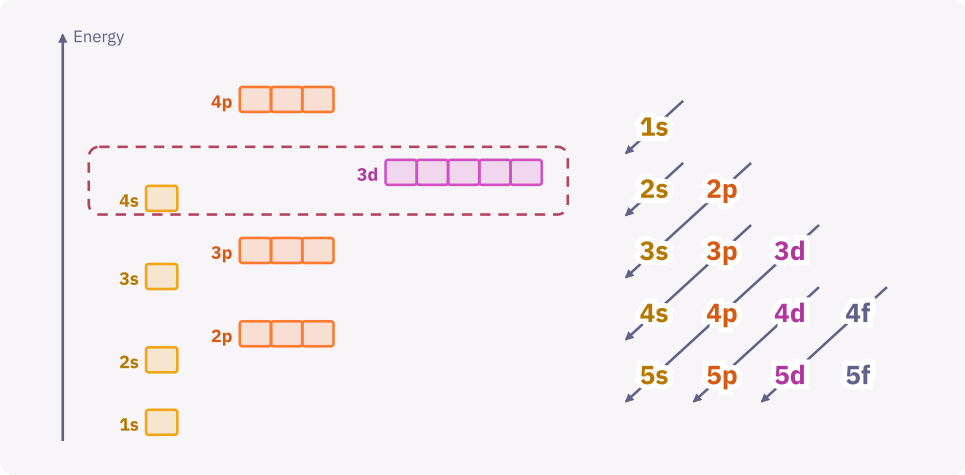


Figure 2.6 Left: relative energies of the orbitals, with energy increasing upwards. Right: the diagonal rule. Follow the arrows to read the order of filling: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p.

Shapes. An s orbital is a sphere. A p orbital is a dumb-bell, and the three p orbitals point along the x, y and z axes. Of the five d orbitals, $d_{x^2-y^2}$ and d_{z^2} point along the axes, and d_{xy}, d_{xz} and d_{yz} point between the axes (Figure 2.7). Four of the d orbitals have four lobes. The d_{z^2} orbital has two lobes and a ring around its middle. Orbitals of the same type get larger as n increases.

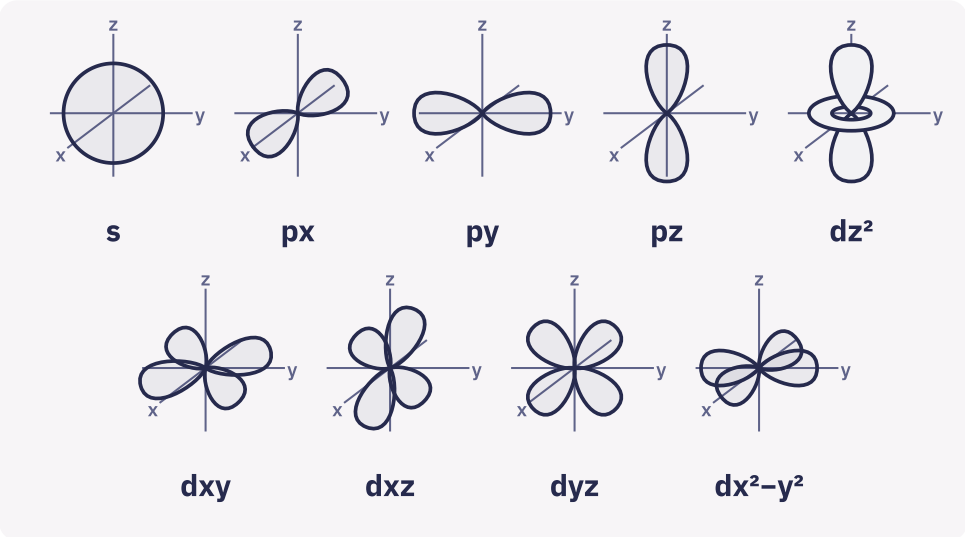


Figure 2.7 Shapes of the s, p and d orbitals on x, y and z axes.

2.2.3 Writing electronic configurations CORE · A LEVEL

Fill the orbitals of an atom in its ground state, the state with every electron in the lowest available energy level, using three rules.

1. **Aufbau principle:** an electron goes into the empty orbital of _____ energy first. After 3p, the 4s orbital fills **before** 3d.
2. **Hund's rule:** in a subshell, orbitals fill _____ first, with parallel spins, before any pairs form. This keeps repulsion between electrons low.
3. **Pauli exclusion principle:** an orbital holds at most 2 electrons, and they must have _____ spins.

Write each subshell with its number of electrons as a superscript, in order of increasing n (so 3d comes before 4s). Oxygen is $1s^2\ 2s^2\ 2p^4$: the 2 in 2p is the shell, the p is the subshell and the 4 is the number of electrons. The same configuration is drawn as boxes, with a box for each orbital and a half arrow for each electron (Figure 2.8). Label the boxes with the subshell only.



Figure 2.8 Electrons in boxes. Each 2p orbital of nitrogen holds one electron (Hund's rule). The fourth 2p electron of oxygen pairs up with opposite spin (Pauli).

A shorter form shows the inner electrons as the symbol of the previous noble gas, as in bromine, [Ar] $3d^{10}$ $4s^2$ $4p^5$. The position in the Periodic Table also shows the last subshell filled. Sodium is in Period 3 and the s block, so it ends $3s^1$. Phosphorus is the third element of the p block in Period 3, so it ends $3p^3$.

2.2.4 Chromium and copper

Chromium and copper break the pattern. Cr is [Ar] $3d^5$ $4s^1$ and Cu is [Ar] $3d^{10}$ $4s^1$. A half-filled or full 3d subshell is more stable than $3d^4$ $4s^2$ or $3d^9$ $4s^2$, and 3d and 4s are so close in energy that moving one electron costs little (Figure 2.9).

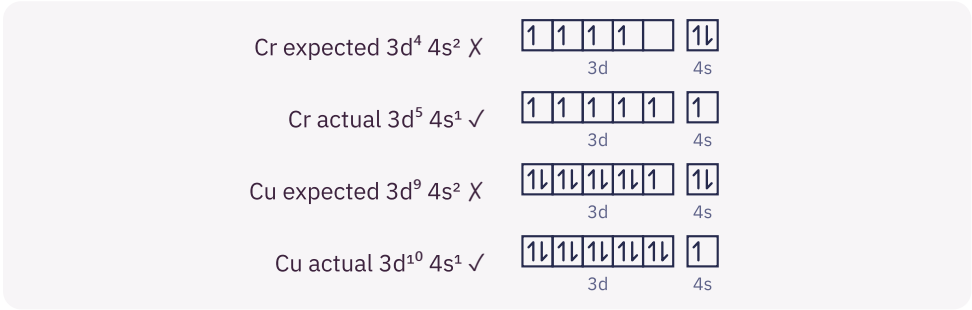


Figure 2.9 One 4s electron moves into 3d in chromium and copper.

2.2.5 Ions

Write the atom's configuration first. For a cation, remove electrons from the _____ shell, taking them from 4s before 3d. For an anion, add electrons to the empty or part-filled valence orbitals. This is the trap: 4s fills first but also **empties** first, because once 3d holds electrons, 4s (n = 4) is the outermost shell (Figure 2.10).

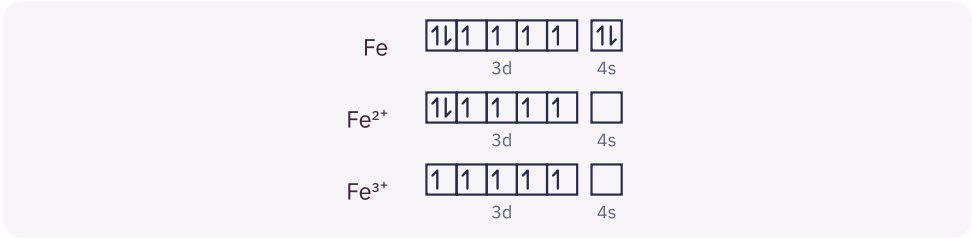


Figure 2.10 Iron and its ions. The two 4s electrons leave first, then one 3d electron.

WORKED EXAMPLE Write the electronic configuration of (a) S^{2-}, (b) Fe^{2+}, (c) Fe^{3+}.

(a) S is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^4$. Add 2 electrons to 3p. *An anion gains electrons in the outer shell.*

S^{2-}: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ *The same as argon.*

(b) Fe is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^6$ $4s^2$. Remove 2 electrons from _____. *4s empties before 3d.*

Fe^{2+}: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^6$ *The 4s electrons go.*

(c) **Fe^{3+}: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^5$** *The third electron comes from 3d.*

Check your understanding

1. Write the full electronic configuration of the calcium ion, Ca^{2+}.
2. How many unpaired electrons are in a nitrogen atom, and in an oxygen atom?
3. Explain why the configuration of chromium is $3d^5\ 4s^1$ and not $3d^4\ 4s^2$.
4. Which element has the ground state valence configuration $4s^2\ 4p^4$?

2.3 Ionisation energy

CORE · A LEVEL

DEFINITION The **first ionisation energy** is the energy needed to remove _____ of electrons from 1 mole of gaseous atoms, to form 1 mole of singly charged gaseous cations.

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

NOTE A **mole** is a fixed number of particles, 6.02×10^{23}, used because single atoms are far too small to count. kJ mol^{-1} means kilojoules for one mole of atoms. Chapter 4 uses the mole in calculations.

The second ionisation energy removes an electron from $X^+(g)$ to give $X^{2+}(g)$, and so on. Every ionisation energy is **positive** (endothermic: energy is taken in) because energy is needed to pull the electron away from the nucleus. Gaseous atoms are far apart, so the energy measured is only that of removing the electron. The (g) after each formula is a state symbol meaning gas, and it is part of the equation.

2.3.1 Trends in first ionisation energy

Three factors decide how strongly the outer electron is held: the _____, the _____ by inner shells, and the distance from the nucleus. Inner electrons repel the outer electron and cancel part of the pull of the nucleus. What is left is the **effective nuclear charge**, Z_{eff} = Z − shielding. Electrons in the same shell shield each other very little (Figure 2.11).

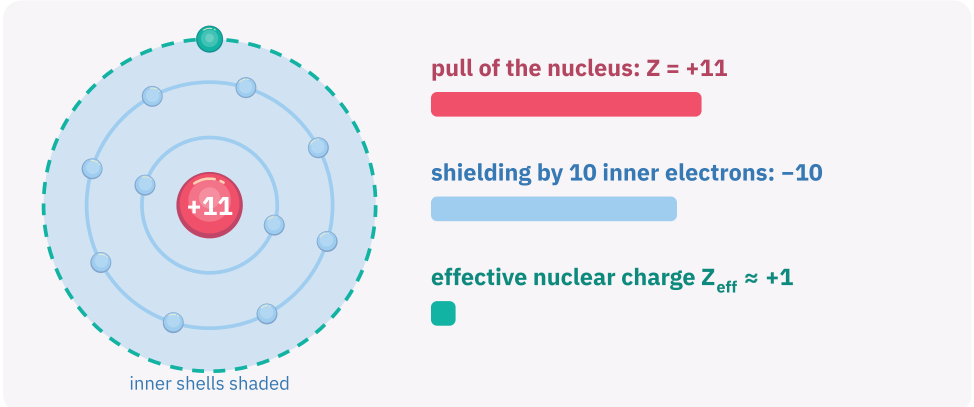


Figure 2.11 Sodium: a nuclear charge of +11 less the shielding of 10 inner electrons leaves an effective nuclear charge of about +1 for the outer electron.

- **Across a period**, the first ionisation energy generally increases. Nuclear charge rises while the electrons enter the same shell, so shielding stays about the same, the effective nuclear charge rises and the atom shrinks. The outer electron is held more strongly, so more energy is needed to remove it.
- **Down a group**, it decreases. The atom has more shells, so the outer electron is further out and more shielded. This largely cancels the rise in nuclear charge, so the outer electron is held more weakly and less energy is needed.

In an answer, state the effect on the **attraction** and then on the **energy required**. Figure 2.12 shows the pattern for the first 20 elements. Two small dips interrupt the rise across Periods 2 and 3.



Figure 2.12 First ionisation energy of the elements 1 to 20 in kJ mol^{-1}. The coloured points are the dips.

dip	values (kJ mol^{-1})	reason
Mg to Al (and Be to B)	736 then 577	Al's outer electron is in a 3p orbital, higher in energy and less strongly attracted than Mg's 3s electron, so less energy is needed.
P to S (and N to O)	1060 then 1000	S loses a paired 3p electron. The repulsion between the two electrons in one orbital makes it easier to remove than P's unpaired 3p electron.



Figure 2.13 The two dips. Left: B loses a higher-energy 2p electron. Right: O loses an electron from a pair.

2.3.2 Successive ionisation energies

Successive ionisation energies always _____. The number of protons stays the same while the number of electrons falls, so each remaining electron is held more strongly. The size of each step shows the shell structure (Figure 2.14).

- **Gradual increase:** the electrons removed come from the same subshell.
- **Small jump:** the next electron comes from a subshell of lower energy in the same shell, for example from s after p.
- **Big jump:** the next electron comes from an _____ shell, which is much closer to the nucleus, less shielded and held much more strongly.

The big jump gives the group. The number of electrons removed before it equals the valence electrons.

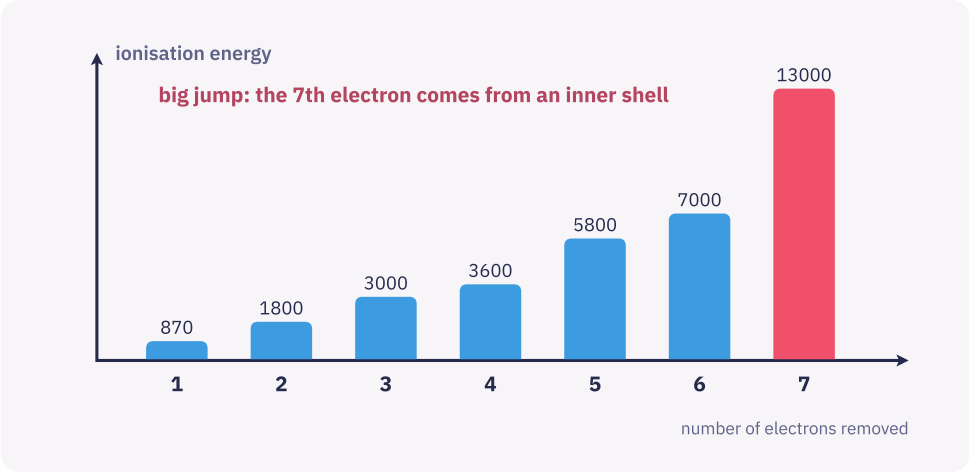


Figure 2.14 The first seven ionisation energies of X (kJ mol^{-1}). The big jump after the sixth means 6 valence electrons.

WORKED EXAMPLE The first seven ionisation energies of element X in kJ mol^{-1} are 870, 1800, 3000, 3600, 5800, 7000 and 13 000. State the group of X, giving a reason.

1. The largest jump is from the 6th to the 7th.	*13 000 is far above 7000.*
2. The 7th electron comes from an inner shell, so there are 6 valence electrons.	*A big jump means a new* _____.
X is in Group 16.	*Valence electrons = 16 − 10.*

Check your understanding

1. The first seven ionisation energies of element J in kJ mol^{-1} are 1020, 1950, 2730, 4580, 6020, 12 300 and 15 400. Which group is J in?

2. Explain why the second ionisation energy of sodium is much greater than its first.

3. Explain why the first ionisation energy of aluminium is lower than that of magnesium.

Answers to Check your understanding

2.1

1. 16 protons, 32 − 16 = 16 neutrons and 16 + 2 = 18 electrons.
2. Isotopes have the same number of electrons, so they react in the same way. They have different numbers of neutrons, so their masses differ, and with them their physical properties such as density.
3. The angle is proportional to charge ÷ mass. Charge is unchanged and the mass doubles, so the angle halves to +2°.
4. O^{2-} bends more. Both have charge −2, and the mass of 16 is less than 32, so charge ÷ mass is larger for oxygen.

2.2

1. Ca is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. Remove both 4s electrons: Ca^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.
2. Nitrogen has 3, one in each 2p orbital. Oxygen has 2, because the fourth 2p electron pairs up.

3. A half-filled 3d subshell with one electron in 4s is more stable than $3d^4\ 4s^2$, and 3d and 4s are close in energy.
4. Selenium. The valence configuration $4s^2\ 4p^4$ is in Period 4 and Group 16.

2.3

1. The big jump is between the 5th and 6th, so J has 5 valence electrons and is in Group 15.
2. The first electron comes from the outer 3s subshell. The second must be removed from the inner 2p subshell of Na^+, which is closer to the nucleus and more strongly attracted.
3. The electron lost by Al is a 3p electron, higher in energy and less strongly attracted to the nucleus than Mg's 3s electron, so less energy is needed.