Atomic structure and the periodic table

Subatomic particles and isotopes, mass spectrometry, ionisation energies, orbitals and electronic configurations, and periodic trends in Periods 2 and 3.

The atom

Particle	Relative mass	Relative charge
Proton	1	+1
Neutron	1	0
Electron	about $\frac{1}{1840}$	−1

The **atomic (proton) number** Z is the number of protons. The **mass number** A is the number of protons plus neutrons. For an atom or ion:

- protons $= Z$
- neutrons $= A - Z$
- electrons $= Z$ for an atom, $Z-$ charge for an ion (a 2+ ion has two fewer electrons)

Isotopes are atoms of the same element with the same number of protons but different numbers of neutrons. They have the same chemical properties, because they have the same electronic configuration, but slightly different physical properties such as mass.

Mass spectrometry

In a mass spectrometer a sample is vaporised and ionised, the ions are accelerated, deflected by a magnetic field and detected. The ions are separated by their mass-to-charge ratio, m/z.

- For an **element**, each peak is an isotope. The height is its relative abundance.
- For a **molecule**, the peak with the highest m/z (the molecular ion) gives the relative molecular mass.
- Some ions have a 2+ charge, giving a peak at half the expected m/z.

$$A_r = \frac{\sum(\text{isotopic mass} \times \text{abundance})}{\sum \text{abundance}}$$

> **TRY IT**
>
> A sample of boron has peaks at $m/z = 10$ (relative abundance 20) and 11 (80). Find A_r.

$$A_r = \frac{10 \times 20 + 11 \times 80}{100} = 10.8.$$

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Diatomic molecules

Chlorine has isotopes ^{35}Cl (75%) and ^{37}Cl (25%). The Cl_2 molecular ion has three peaks: $m/z = 70$ ($^{35}Cl^{35}Cl$), 72 ($^{35}Cl^{37}Cl$) and 74 ($^{37}Cl^{37}Cl$). Heights are in the ratio of probabilities: $0.75^2 : 2(0.75)(0.25) : 0.25^2 = 9 : 6 : 1$.

Ionisation energy

The **first ionisation energy** is the energy needed to remove one electron from each atom in one mole of gaseous atoms to form one mole of gaseous 1+ ions.

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

The **second ionisation energy** is the energy to remove one mole of electrons from one mole of gaseous 1+ ions, and so on. All ionisation energies are **endothermic**.

Ionisation energy depends on:

- **nuclear charge** (more protons, stronger attraction)
- **shielding** by inner electrons (more shielding, easier to remove)
- the **sub-shell** the electron is removed from (electrons in higher energy sub-shells are further out)

Evidence for shells and sub-shells

- **Successive ionisation energies** rise steadily, with a large jump when an electron is removed from a new, inner shell. The jump shows the group: if the big jump comes after 2 electrons are removed, the element is in Group 2.
- **First ionisation energies across a period** show dips. Boron is lower than beryllium because its outer electron is in a 2p sub-shell, which is higher in energy than 2s. Oxygen is lower than nitrogen because in oxygen two electrons share a 2p orbital and repel each other.

Orbitals and electronic configuration

An **orbital** is a region within an atom that can hold up to two electrons with opposite spins. Each sub-shell is made of orbitals:

Sub-shell	Orbitals	Maximum electrons
s	1	2
p	3	6
d	5	10

An **s** orbital is a sphere. A **p** orbital is a pair of lobes along an axis, and there are three at right angles (p_x, p_y, p_z).

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Filling the orbitals

1. Fill the lowest energy first. The order to remember is 1s, 2s, 2p, 3s, 3p, **4s**, 3d, 4p.
2. Orbitals of equal energy each take **one electron before any pairs up** (Hund's rule), with parallel spins.
3. Electrons in the same orbital have opposite spins.

> **TRY IT**
>
> Write the electronic configuration of nitrogen, iron and the Fe^{3+} ion.

N: $1s^2 2s^2 2p^3$, with the three 2p electrons in separate boxes. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. Fe^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$. The **4s** electrons are removed first.

> **NOTE**
>
> Chromium is $[Ar]3d^5 4s^1$ and copper is $[Ar]3d^{10} 4s^1$, because a half-full or full 3d sub-shell is more stable. Learn these two exceptions.

The Periodic Table is in blocks by the highest-energy sub-shell being filled: s-block (Groups 1 and 2), p-block (Groups 3 to 0) and d-block (the transition elements). Electronic configuration determines chemical properties.

Periodic trends

A **periodic property** repeats at regular intervals with increasing atomic number. A graph of the logarithm of first ionisation energy against atomic number for elements 1 to 36 shows the repeating pattern clearly.

Across a period (first ionisation energy)

There is a general increase as the nuclear charge increases while the shielding stays about the same, so the outer electrons are held more strongly. There are two dips in Period 2 and Period 3 (described above).

Down a group (first ionisation energy)

It **decreases** down a group. The outer electron is in a shell further from the nucleus and is more shielded by extra inner shells, which outweighs the greater nuclear charge.

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Melting and boiling temperatures in Periods 2 and 3

Elements	Structure	Melting temperature
Li, Be, Na, Mg, Al	Giant metallic	Rises from Group 1 to 3 as more electrons are delocalised and the ions have higher charge and are smaller
B, C, Si	Giant covalent	Very high, many strong covalent bonds to break
N, O, F, P, S, Cl	Simple molecules ($N_2, O_2, F_2, P_4, S_8, Cl_2$)	Low, only weak London forces to overcome
Ne, Ar	Single atoms	Lowest

Sulfur (S_8) is higher than phosphorus (P_4) and chlorine (Cl_2) because its larger molecules have stronger London forces.

When explaining melting temperature, name the structure, the particles, the forces broken, and say they are strong or weak. Never say covalent bonds break when a simple molecular substance melts.

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