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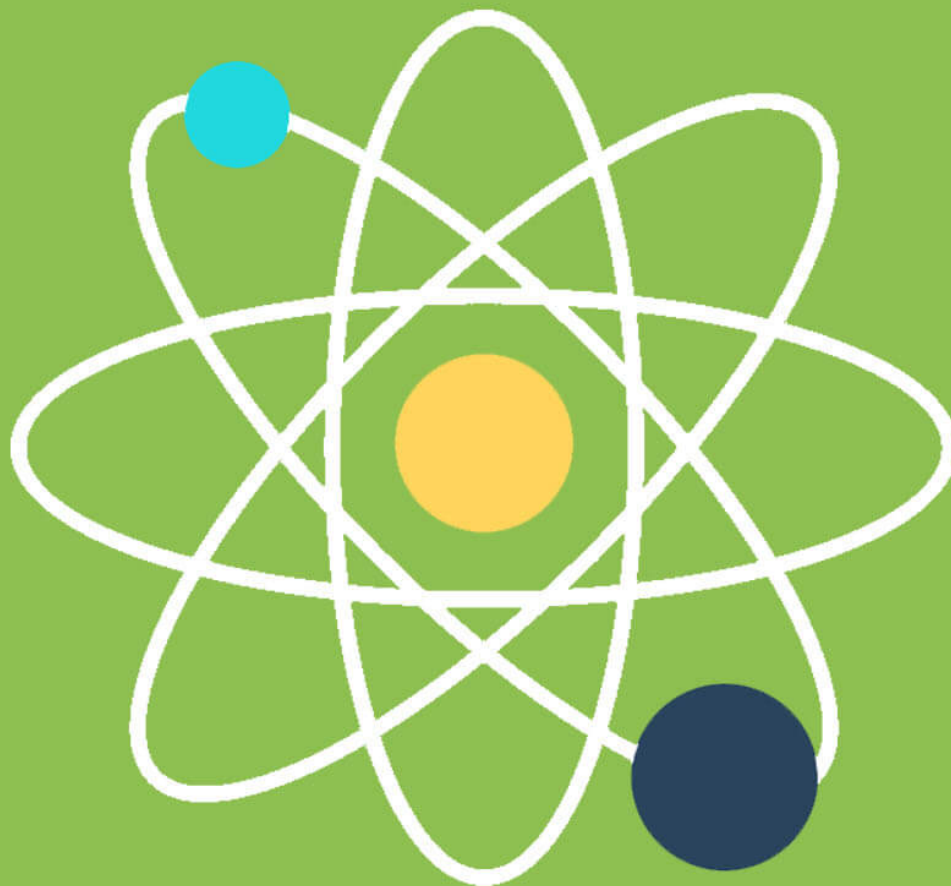
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12.1 Electrons in Atoms



IB Chemistry - Revision Notes

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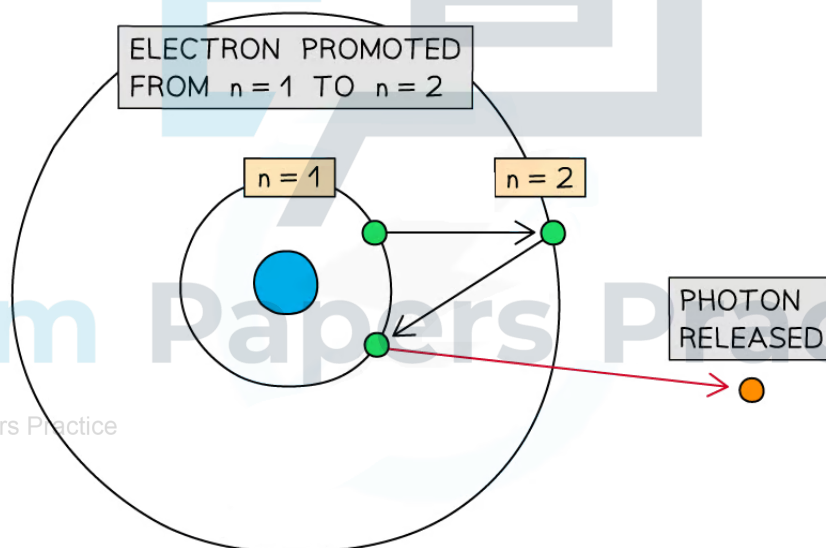


12.1.1 Emission Spectra & First Ionisation Energy

Convergence Limits on an Emission Spectrum

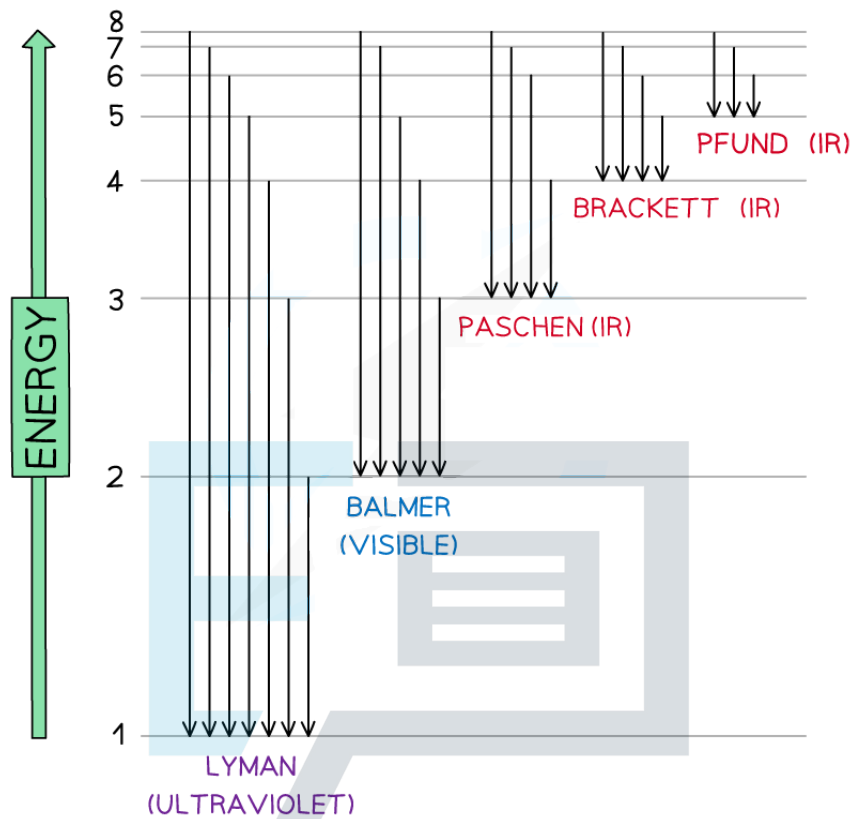
Emission Spectra

- Electrons move rapidly around the nucleus in energy shells
- Heat or electricity can be used to excite an electron to a higher main energy level
- These range from $n=1$ (ground state) to $n=\infty$
- When the electrons 'fall' back down they must lose the energy difference between the two energy levels. This loss of energy is performed by releasing electromagnetic energy in the form of infrared, visible light or ultraviolet radiation.
- When the electron falls back to $n=1$ (ground state) the energy released is in the ultraviolet region of the spectrum
- This corresponds to the **Lyman series**



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Promotion of an electron from the ground state ($n=1$) to $n=2$



Electron jumps in the hydrogen spectrum

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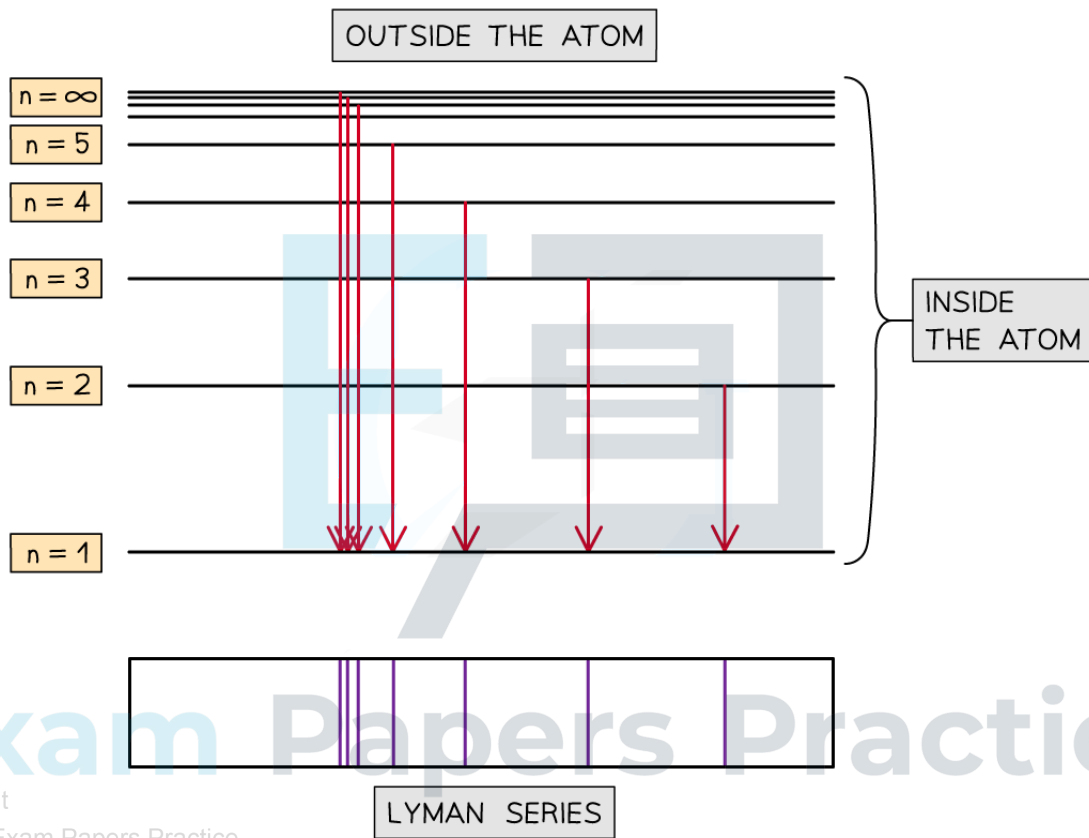
- This gives evidence for Bohr's model which is the idea that electrons exist in discrete energy levels so an exact amount of energy is required for an electron to 'jump' an energy level, a little like a ladder
- There are however limitations to this model
 - Assumes positions of electrons are fixed
 - Assumes energy levels are spherical in nature
 - Bohr limited calculations to hydrogen only, so does not explain the line spectra of other elements containing more than one electron

The Limit of Convergence

- As the line spectra is produced the lines will become closer together
 - Where the lines appear to meet is called the **limit of convergence**
 - The convergence limit is the frequency at which the spectral lines converge
 - The energy required for an electron to escape the atom, or reach the upper limit of convergence, is the ionisation energy



- The frequency of the radiation in the emission spectrum at the limit of convergence can be used to determine the first ionisation energy or IE_1
- In the **Lyman series** for the hydrogen atom (UV region), the frequency at the limit of convergence relates to the energy given out when an electron falls from $n = \infty$ to $n = 1$
- For hydrogen, the lines converge to a limit with a wavelength of 91.16 nm or $91.16 \times 10^{-9} \text{m}$



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Lyman series (ultra-violet radiation) corresponds to transitions between higher shells and the ground state ($n=1$)

Calculating First Ionisation Energy

Calculating First Ionisation Energy

- When dealing with the Lyman series the largest transitions represent the fall from the infinite level to $n=1$
- In reverse, it can be considered to be equal to the ionisation energy (note that ionisation energy is given per mole of atoms)
- Therefore, the first ionisation energy (I_1) of an atom can be calculated using the frequency (or wavelength) of the **convergence limit**
- We can do this by using the following equations

$$\Delta E = h\nu$$

$$c = \nu\lambda$$

- In order to calculate first ionisation energy (I_1) we must first calculate the **frequency** using the given data and rearranging:

$$c = \nu\lambda$$

as

$$\nu = c \div \lambda$$

- Once we know the frequency, we can use this to calculate the ionisation energy

E = ENERGY (J)

h = PLANCK'S CONSTANT (6.63×10^{-34} J s)

ν = FREQUENCY (s^{-1})

λ = WAVELENGTH (m)

c = SPEED OF LIGHT (3.00×10^8 m s^{-1})

Worked example

The convergence limit for the sodium atom has a frequency of $1.24 \times 10^{15} s^{-1}$. Calculate the first ionisation energy of sodium in $kJ mol^{-1}$.

Answer:

Step 1: Write out the equation to calculate the first ionisation energy (I_E)

$$\Delta E = h\nu$$

Step 2: Substitute in numbers from question and data booklet to give energy change **per atom**

$$I_E = 6.63 \times 10^{-34} \times 1.24 \times 10^{15}$$

$$I_E = 8.22 \times 10^{-19} \text{ J atom}^{-1}$$

Step 3: Calculate the first ionisation energy per mole by multiplying by **Avogadro's constant**

$$I_E = 8.22 \times 10^{-19} \times 6.02 \times 10^{23}$$

$$I_E = 494\,916 \text{ J mol}^{-1}$$

Step 4: Convert J mol^{-1} to kJ mol^{-1} by dividing by 1000

$$I_E = 495 \text{ kJ mol}^{-1}$$

So the first ionisation energy (I_E) of sodium has been calculated as **495 kJ mol⁻¹**

Worked example

The convergence limit for the hydrogen atom has a wavelength of 91.16 nm. Calculate the ionisation energy for hydrogen in kJ mol^{-1} .

Copyright **Answer:**

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Step 1: Calculate the frequency of the convergence limit, **converting wavelength into m (nm to m = $\times 10^{-9}$)**

$$c = \nu\lambda$$

$$\nu = c \div \lambda$$

$$\nu = 3.00 \times 10^8 \div 91.16 \times 10^{-9}$$

$$\nu = 3.29 \times 10^{15} \text{ s}^{-1}$$

Step 2: Substitute into the equation to calculate I_E for one atom of hydrogen in J mol^{-1}

$$\Delta E = h\nu$$



$$IE_1 = 6.63 \times 10^{-34} \times 3.29 \times 10^{15}$$

$$IE_1 = 2.18 \times 10^{-18} \text{ J atom}^{-1}$$

Step 3: Calculate IE_1 for 1 mole of hydrogen atoms

$$IE_1 = 2.18 \times 10^{-18} \times 6.02 \times 10^{23}$$

$$IE_1 = 1313491 \text{ J mol}^{-1}$$

Step 4: Convert J mol^{-1} to kJ mol^{-1}

$$IE_1 = 1313 \text{ kJ mol}^{-1}$$

So the first ionisation energy (IE_1) of hydrogen has been calculated as **1313 kJ mol⁻¹**

 **Exam Tip**

These equations are found in the data booklet so you don't need to learn them. Also, be careful to calculate the first ionisation energy (IE_1) per mole by using **Avogadro's constant (N_A)** 6.02×10^{23} and converting units to kJ mol^{-1} . Finally, when working through calculations, keep the numbers in your calculator to avoid rounding up too early.

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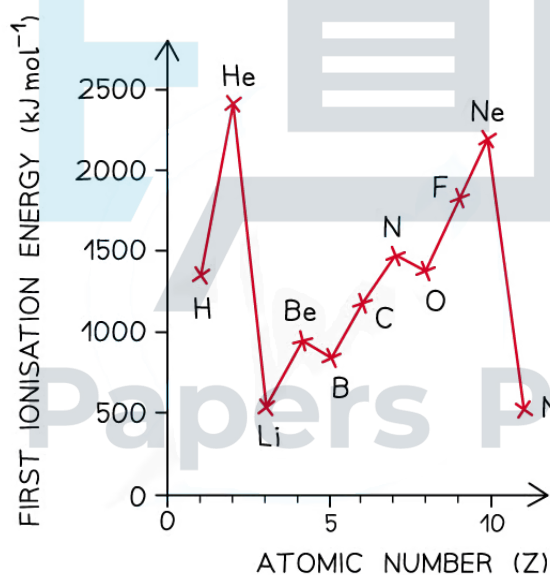
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12.1.2 Ionisation Energy Trends

Trends Across a Period

- Ionisation energies show **periodicity** – a trend across a period of the Periodic Table
- As could be expected from their electron configuration, the group 1 metals have a relatively low ionisation energy, whereas the noble gases have very high ionisation energies
- The size of the first ionisation energy is affected by four factors:
 - **Size of the nuclear charge**
 - **Distance of outer electrons from the nucleus**
 - **Shielding effect of inner electrons**
 - **Spin-pair repulsion**
- First ionisation energy **increases** across a period and **decreases** down a group



A graph showing the ionisation energies of the elements hydrogen to sodium

Ionisation energy across a period

- The ionisation energy across a period generally **increases** due to the following factors:
 - Across a period the **nuclear charge increases**
 - This causes the **atomic radius** of the atoms to **decrease**, as the outer shell is pulled closer to the nucleus, so the distance between the nucleus and the outer electrons **decreases**



- The **shielding** by inner shell electrons remain reasonably constant as electrons are being added to the same shell
- It becomes **harder to remove an electron** as you move across a period; **more energy** is needed
- So, the ionisation energy increases

Dips in the trend

- There is a slight **decrease** in I_1 between **beryllium** and **boron** as the fifth electron in boron is in the 2p subshell, which is further away from the nucleus than the 2s subshell of beryllium
 - **Beryllium** has a first ionisation energy of **900 kJ mol⁻¹** as its electron configuration is **1s² 2s²**
 - **Boron** has a first ionisation energy of **800 kJ mol⁻¹** as its electron configuration is **1s² 2s² 2p_x¹**
- There is a slight **decrease** in I_1 between **nitrogen** and **oxygen** due to **spin-pair repulsion** in the 2p_x orbital of oxygen
 - **Nitrogen** has a first ionisation energy of **1400 kJ mol⁻¹** as its electron configuration is 1s² 2s² 2p_x¹ 2p_y¹ 2p_z¹
 - **Oxygen** has a first ionisation energy of **1310 kJ mol⁻¹** as its electron configuration is 1s² 2s² **2p_x²** 2p_y¹ 2p_z¹
 - In oxygen, there are 2 electrons in the 2p_x orbital, so the repulsion between those electrons makes it slightly easier for one of those electrons to be removed

From one period to the next

- There is a large **decrease** in ionisation energy between the **last** element in one period, and the **first** element in the next period
- This is because:
 - There is increased **distance** between the nucleus and the outer electrons as you have added a new shell
 - There is increased **shielding** by inner electrons because of the added shell
 - These two factors outweigh the increased **nuclear charge**

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Successive Ionisation Energies

Successive ionisation energies of an element

- The **successive** ionisation energies of an element **increase**
- This is because once you have removed the outer electron from an atom, you have formed a **positive ion**
- Removing an electron from a positive ion is **more difficult** than from a neutral atom
- As more electrons are removed, the **attractive forces increase** due to decreasing shielding and an increase in the proton to electron ratio
- The increase in ionisation energy, however, is not constant and is dependent on the atom's electronic configuration
- Taking calcium as an example:

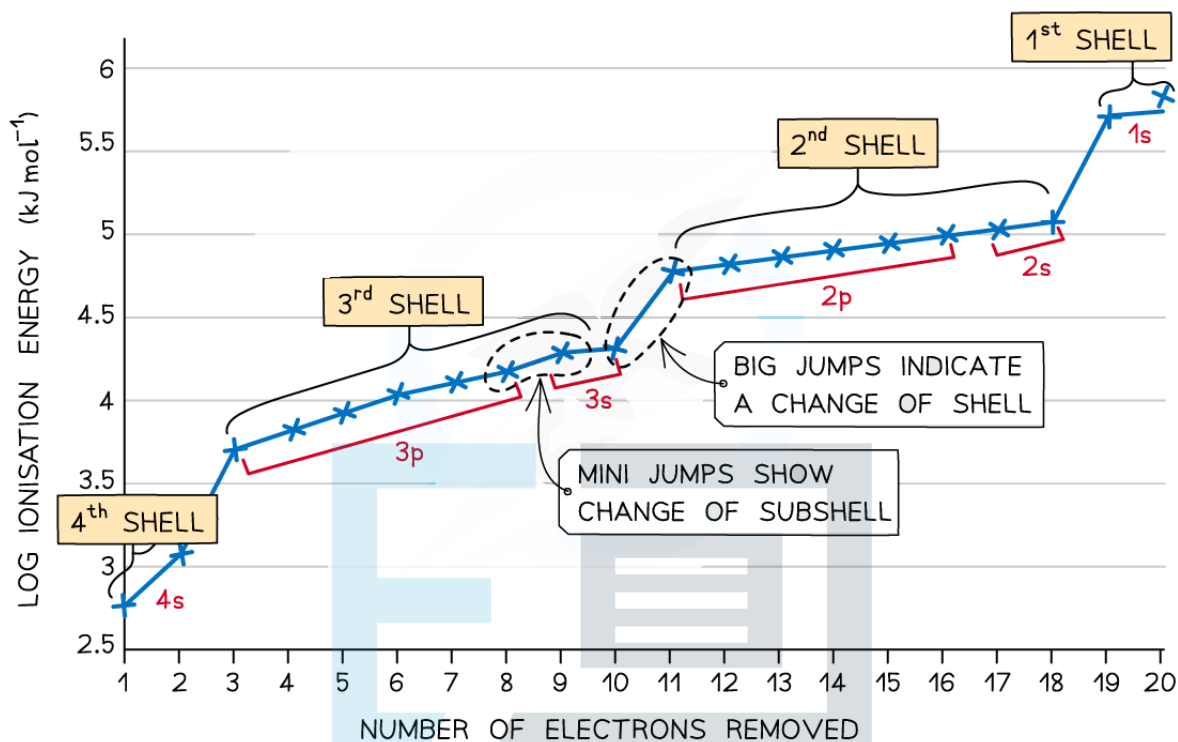
Ionisation Energies of Calcium Table

Electronic Configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$1s^2 2s^2 2p^6 3s^2 3p^6$	$1s^2 2s^2 2p^6 3s^2 3p^5$
IE	First	Second	Third	Fourth
IE (kJ mol^{-1})	590	1150	4940	6480

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Successive ionisation energies for the element calcium

- The **first** electron removed has a low I_{E1} as it is easily removed from the atom due to the spin-pair repulsion of the electrons in the 4s orbital
- The **second** electron is more difficult to remove than the first electron as there is no **spin-pair repulsion**
- The **third** electron is much more difficult to remove than the second one corresponding to the fact that the third electron is in a **principal quantum** shell which is closer to the nucleus (3p)
- Removal of the **fourth** electron is more difficult as the orbital is no longer full, and there is less **spin-pair repulsion**
- The graph shows there is a large increase in successive ionisation energy as the electrons are being removed from an increasingly positive ion
- The big jumps on the graph show the change of **shell** and the small jumps are the change of **subshell**

Deducing the Group

- **Successive ionisation data** can be used to:
 - Predict or confirm the simple electronic configuration of elements
 - Confirm the number of electrons in the outer shell of an element
 - Deduce the group an element belongs to in the Periodic Table
- By analysing where the large jumps appear and the number of electrons removed when these large jumps occur, the **electron configuration** of an atom can be determined
- Na, Mg and Al will be used as examples to deduce the electronic configuration and positions of elements in the Periodic Table using their successive ionisation energies

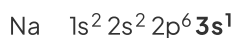
Successive Ionisation Energies Table

Element	Atomic Number	Ionisation Energy (kJ mol ⁻¹)			
		First	Second	Third	Fourth
Na	11	494	4560	6940	9540
Mg	12	736	1450	7740	10500
Al	13	577	1820	2740	11600

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Sodium

- For sodium, there is a huge **jump** from the **first** to the **second** ionisation energy, indicating that it is much easier to remove the first electron than the second
- Therefore, the first electron to be removed must be the last electron in the **valence shell** thus Na belongs to group I
- The large jump corresponds to moving from the 3s to the full 2p subshell



Magnesium

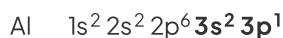
- There is a huge increase from the **second** to the **third** ionisation energy, indicating that it is far easier to remove the first two electrons than the third



- Therefore the **valence shell** must contain only two electrons indicating that magnesium belongs to group II
- The large jump corresponds to moving from the 3s to the full 2p subshell
Mg $1s^2 2s^2 2p^6 3s^2$

Aluminium

- There is a huge increase from the **third** to the **fourth** ionisation energy, indicating that it is far easier to remove the first three electrons than the fourth
- The 3p electron and 3s electrons are relatively easy to remove compared with the 2p electrons which are located closer to the nucleus and experience greater **nuclear charge**
- The large jump corresponds to moving from the **third shell** to the **second shell**



Worked example

Values for the successive *IE*s of an unknown element are:

- $IE_1 = 899 \text{ kJ mol}^{-1}$,
- $IE_2 = 1757 \text{ kJ mol}^{-1}$,
- $IE_3 = 14850 \text{ kJ mol}^{-1}$,
- $IE_4 = 21005 \text{ kJ mol}^{-1}$

Deduce which group of the periodic table of elements you would expect to find the unknown element.

Answer:

The largest jump is between IE_2 and IE_3 which will correspond to a change in energy level.

Copyright Therefore, the unknown element must be in **group 2**.

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Worked example

The table shows successive ionisation energies for element **X** in period 2.

SUCCESSIVE IONISATION ENERGIES OF UNKNOWN ELEMENT

Ionisation number	1	2	3	4	5	6	7	8
Ionisation energy (kJ mol ⁻¹)	1314	3388	5301	7469	10989	13327	71337	84080

Identify element **X**.

Answer:

- The largest jump in ionisation energy is between IE_6 and IE_7 meaning that the 7th electron is being removed from an energy level closer to the nucleus
- Therefore, element **X** must be group 16 (6)
- If element **X** is in group 16 (6) and in period 2, it must be **oxygen**