Edexcel International AS Chemistry

Your notes

Electrons & Ions

Contents

Ionisation Energy – Definitions

Ionisation energy

- The **ionisation energy** (*IE*) of an element is the amount of energy required to remove **one mole** of electrons from **one mole** of gaseous atoms of an element to form **one mole** of gaseous ions
- Ionisation energies are measured under **standard conditions** which are 298 K and 101 kPa
- The units of IE are **kilojoules per mole** (kJ mol^{-1})
- The **first ionisation energy** (IE_1) is the energy required to remove **one mole of electrons** from one mole of gaseous atoms of an element to form one mole of gaseous 1+ ions
    - E.g. the first ionisation energy of gaseous calcium:

$$Ca (g) \rightarrow Ca^+ (g) + e^- \qquad IE_1 = +590 \text{ kJ mol}^{-1}$$

Second and third ionisation energies of an element

- More than one electron can be removed form an atom and each time you remove an electron there is a successive ionisation energy
- These are called second, third ionisation energy and so on
- The **second ionisation energy** (IE_2) is defined as
    - is the energy required to remove **one mole of electrons** from one mole of gaseous 1+ ions to form one mole of gaseous 2+ ions
- And can be represented as can be represented as

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

OR (for calcium)

$$Ca^+ (g) \rightarrow Ca^{2+} (g) + e^- \quad IE_2 = 1145 \text{ kJ mol}^{-1}$$

- **The third ionisation energy** (IE_3) of an element can be represented as

$$X^{2+} (g) \rightarrow X^{3+} (g) + e^-$$

OR (for calcium)

$$Ca^{2+} (g) \rightarrow Ca^{3+} (g) + e^- \quad IE_3 = 4912 \text{ kJ mol}^{-1}$$

Ionisation Energy – Considerations

Orbitals

- Subshells contain one or more **atomic orbitals**

- Orbitals exist at **specific** energy levels and electrons can only be found at these specific levels, **not** in between them
  - Each atomic orbital can be occupied by a maximum of **two** electrons with opposite spins
- This means that the number of orbitals in each subshell is as follows:
  - **s** : one orbital (1 x 2 = total of 2 electrons)
  - **p** : three orbitals (3 x 2 = total of 6 electrons)
  - **d** : five orbitals (5 x 2 = total of 10 electrons)
  - **f** : seven orbitals (7 x 2 = total of 14 electrons)
- 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 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**
  - The more protons there are in the nucleus, the more positively charged the nucleus is, and the more strongly electrons are attracted to it
- **Distance of outer electrons from the nucleus**
  - Attraction falls off very rapidly with distance. An electron close to the nucleus will be much more strongly attracted than one further away
- **Shielding effect of inner electrons**
  - As the number of shells between the valence electron and positive nucleus increases, the shielding increases. It then becomes easier to remove the valence electron as the shielding increases. This can occur within an orbit due to the presence of different subshells
- **Spin-pair repulsion**
  - Two electrons in the same orbital experience a bit of repulsion from each other. This offsets the attraction of the nucleus, so that paired electrons are removed more easily

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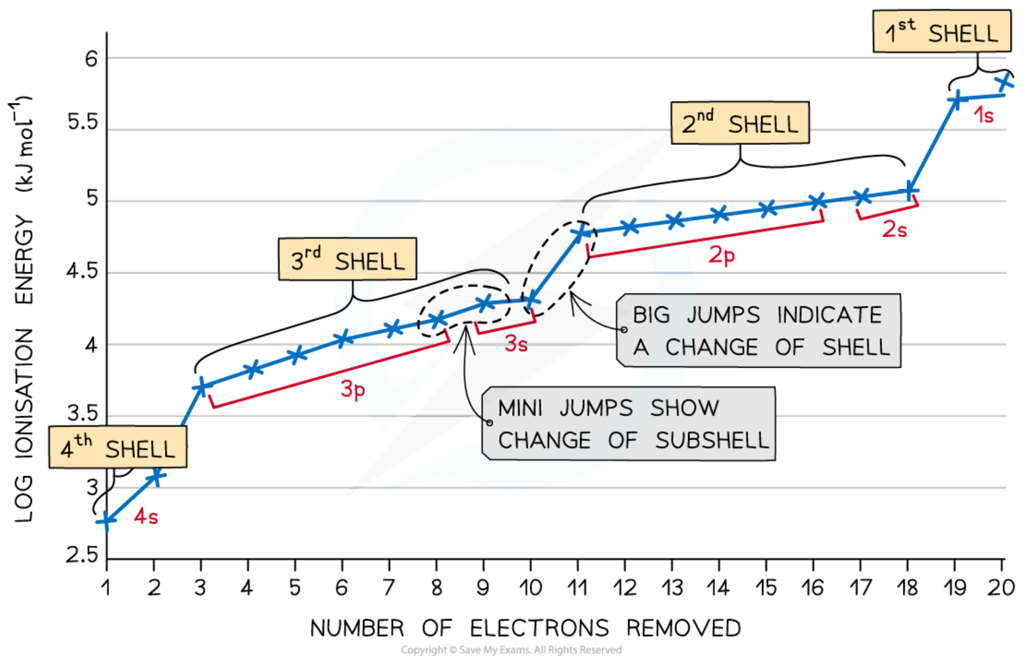
Ionisation Energy & Sub-shells

- **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
  - We can look at **calcium** as an example
- The **first** electron removed in calcium has a low IE_1 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 that 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**

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



Successive ionisation energies for the element calcium

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

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

Na $1s^2 2s^2 2p^6$ $\mathbf{3s^1}$

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 $1s^2 2s^2 2p^6$ $\mathbf{3s^2}$

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**

Al $1s^2 2s^2 2p^6$ $\mathbf{3s^2 3p^1}$

Worked Example

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

IE_1 = **899** kJ mol^{-1}, IE_2 = **1757** kJ mol^{-1}, IE_3 = **14850** kJ mol^{-1}, IE_4 = **21005** 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 $\boldsymbol{IE_2}$ and $\boldsymbol{IE_3}$ which will correspond to a change in energy level.
  - Therefore the unknown element must be in **group 2**

Worked Example

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

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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 $\boldsymbol{IE_6}$ and $\boldsymbol{IE_7}$ meaning that the 7th electron is being removed from an energy level closer to the nucleus
  - Therefore element **X** must be group 6
  - If element **X** is in group 6 and in period 2 it must be **oxygen**

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The Shape of Orbitals

Orbitals

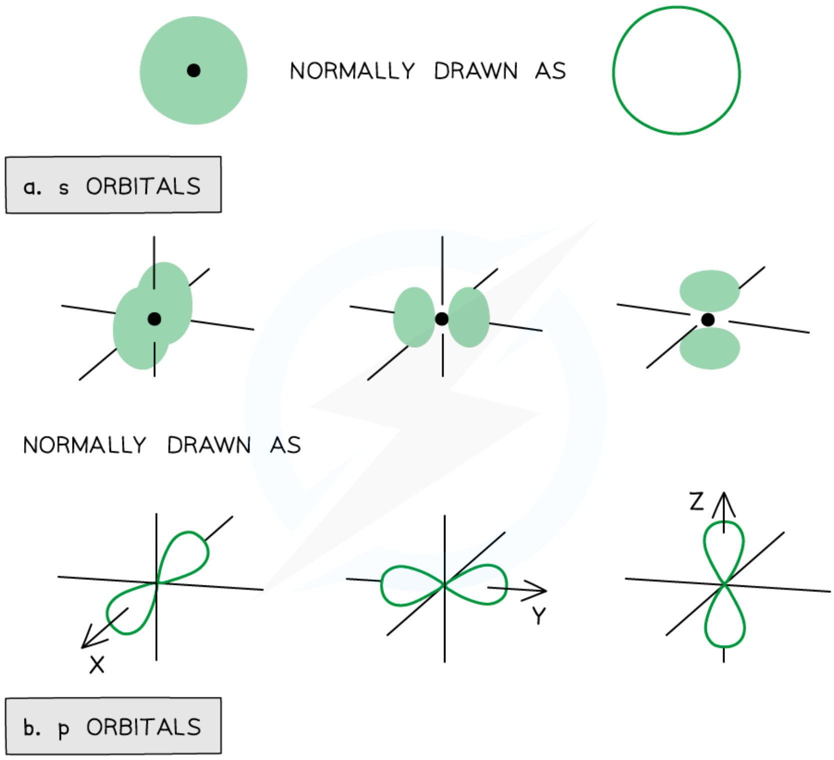
- We have seen before that the total number of electrons that each subshell in each orbital can hold are:
    - **s** : one orbital (1 x 2 = total of 2 electrons)
    - **p** : three orbitals (3 x 2 = total of 6 electrons)
    - **d** : five orbitals (5 x 2 = total of 10 electrons)
    - **f** : seven orbitals (7 x 2 = total of 14 electrons)
- The orbitals have specific 3-D shapes

s orbital shape

- The s orbitals are **spherical** in shape
- The **size** of the s orbitals increases with increasing shell number
    - E.g. the s orbital of the **third** quantum shell (n = 3) is bigger than the s orbital of the **first** quantum shell (n = 1)

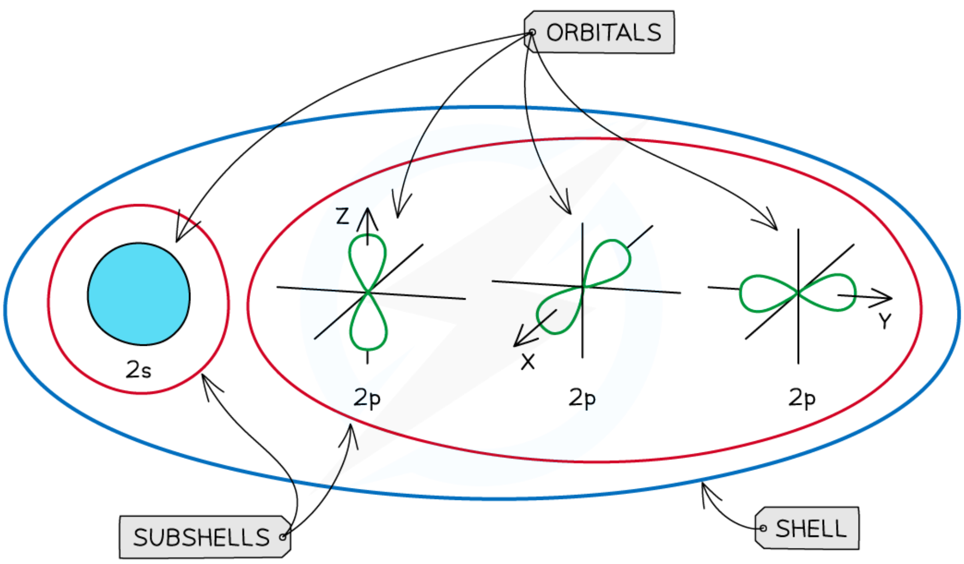
p orbital shape

- The p orbitals have a **dumbbell shape**
- Every shell has three p orbitals except for the first one (n = 1)
- The p orbitals occupy the x, y and z axes and point at right angles to each other, so are oriented **perpendicular** to one another
- The lobes of the p orbitals become **larger** and **longer** with increasing shell number



Representation of orbitals (the dot represents the nucleus of the atom) showing spherical s orbitals (a), p orbitals containing 'lobes' along the x, y and z axis

- Note that the shape of the d orbitals is **not** required



An overview of the shells, subshells and orbitals in an atom

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Populating Orbitals

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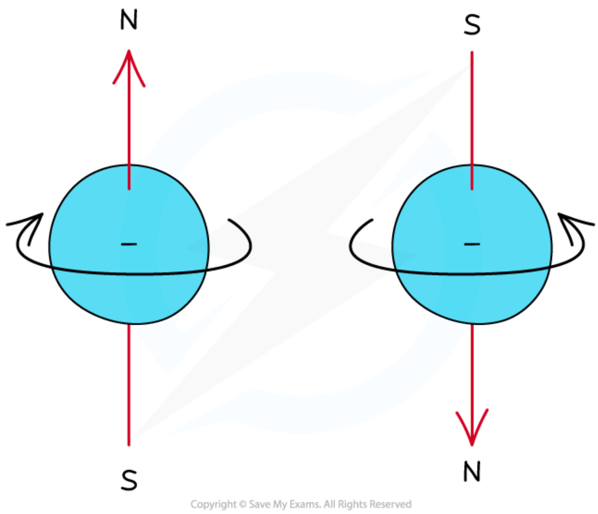
- Electrons can be imagined as small **spinning charges** which rotate around their own axis in either a **clockwise** or **anticlockwise direction**
  - The spin of the electron is represented by its direction
  - The spin creates a tiny magnetic field with N-S pole pointing up or down



Electrons can spin either in a clockwise or anticlockwise direction around their own axis

- Electrons with the same **spin** repel each other which is also called **spin-pair repulsion**
  - Therefore, electrons will occupy separate orbitals in the same subshell first to minimise this repulsion and have their **spin** in the same direction
  - They will then pair up, with a second electron being added to the first p orbital, with its spin in the **opposite** direction
- This is known as **Hund's Rule**
  - E.g. if there are three electrons in a **p subshell**, one electron will go into each p_x, p_y and p_z orbital

Electron configuration: three electrons in a p subshell

- The principal quantum number indicates the energy level of a particular shell but also indicates the energy of the electrons in that shell

    - A 2p electron is in the second shell and therefore has an energy corresponding to n = 2
- Even though there is repulsion between negatively charged electrons, they occupy the same region of space in orbitals
- An orbital can only hold two electrons and they must have opposite spin - the is known as the **Pauli Exclusion Principle**
- This is because the energy required to jump to a higher empty orbital is **greater** than the inter-electron repulsion
- For this reason, they pair up and occupy the lower energy levels first

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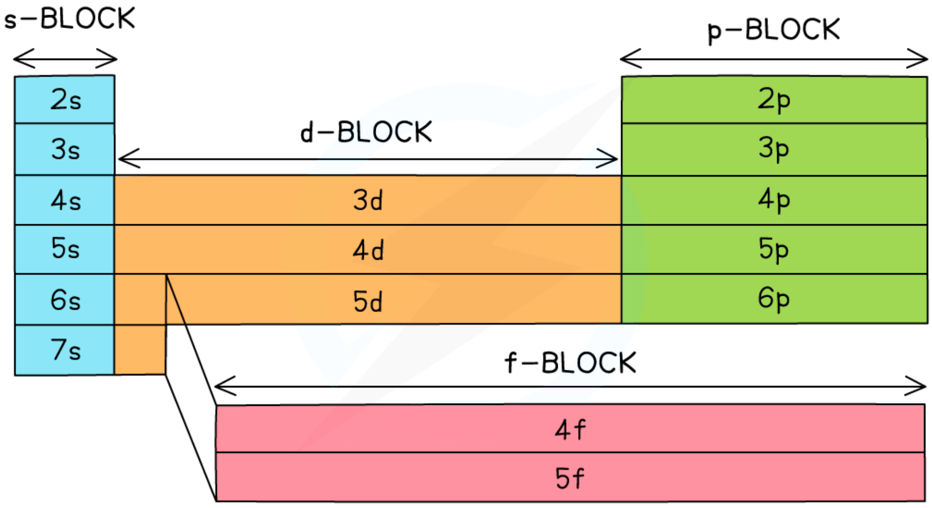
Predicting Electronic Configurations

- The Periodic Table is split up into four main blocks depending on their electron configuration
- Elements can be classified as an s-block element, p-block element and so on, based on the position of the outermost electron:
  - s block elements - Have their valence electron(s) in an s orbital
  - p block elements - Have their valence electron(s) in a p orbital
  - d block elements - Have their valence electron(s) in a d orbital
  - f block elements - Have their valence electron(s) in an f orbital



- The **principal quantum shells** increase in energy with increasing **principal quantum number**
  - E.g. $n = 4$ is higher in energy than $n = 2$
- The **subshells** increase in energy as follows: s < p < d < f
  - The only exception to these rules is the 3d orbital which has slightly higher energy than the 4s orbital
  - Because of this, the 4s orbital is filled before the 3d orbital
- All the orbitals in the **same** subshell have the same energy and are said to be **degenerate**
  - E.g. p_x, p_y and p_z are all equal in energy

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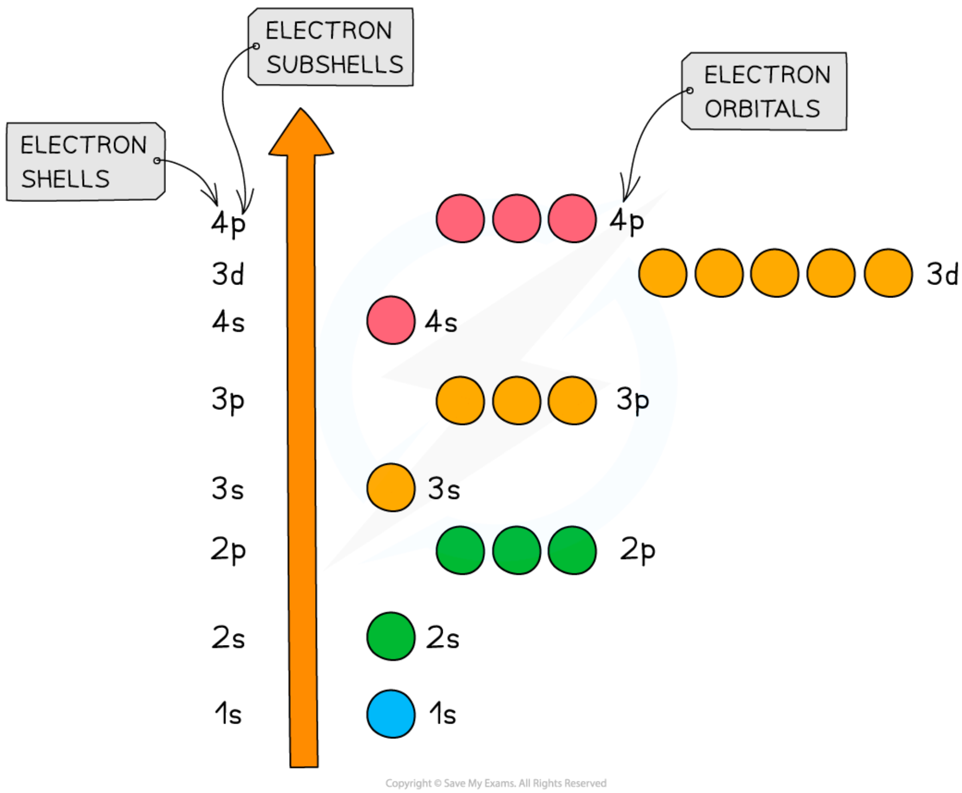
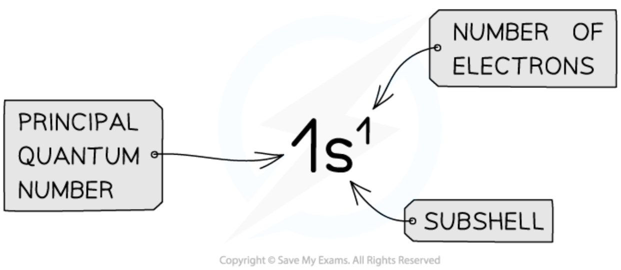


Relative energies of the shells and subshells

- The **electron configuration** gives information about the number of electrons in each **shell, subshell** and **orbital** of an atom
- The subshells are filled in order of increasing energy



The electron configuration shows the number of electrons occupying a subshell in a specific shell

- Writing out the **electron configuration** tells us how the electrons in an atom or ion are arranged in their shells, subshells and orbitals
- This can be done using the **full** electron configuration or the **shorthand** version
  - The **full** electron configuration describes the arrangement of all electrons from the 1s subshell up

    - The **shorthand** electron configuration includes using the symbol of the **nearest preceding noble gas** to account for however many electrons are in that noble gas
- **Ions** are formed when atoms **lose** or **gain** electrons
    - Negative ions are formed by **adding** electrons to the outer subshell
    - Positive ions are formed by **removing** electrons from the outer subshell
    - The transition metals **fill** the 4s subshell before the 3d subshell but **lose** electrons from the 4s first and not from the 3d subshell (the 4s subshell is lower in energy

Full Electron Configurations

- Hydrogen has 1 single electron
    - The electron is in the s orbital of the first shell
    - Its electron configuration is $1s^1$
- Potassium has 19 electrons
    - The first 2 electrons fill the s orbital of the first shell
    - They then continue to fill subsequent orbitals and subshells in order of increasing energy
    - The 4s orbital is lower in energy than the 3d subshell, so it is therefore filled first
    - The full electron configuration of potassium is **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$**

Shorthand Electron Configurations

- Using potassium as an example again:
    - The nearest preceding noble gas to potassium is **argon**
    - This accounts for 18 electrons of the 19 electrons that potassium has
    - The shorthand electron configuration of potassium is **[Ar] $4s^1$**

Worked Example

Write down the full and shorthand electron configuration of the following elements:

1. Calcium
2. Gallium
3. Ca^{2+}

Answer

Answer 1:

- Calcium has 20 electrons so the **full electronic configuration** is:
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
- The 4s orbital is lower in energy than the 3d subshell and is therefore filled first

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- The **shorthand** version is [Ar] $4s^2$ since argon is the nearest preceding noble gas to calcium which accounts for 18 electrons

Answer 2:

- Gallium has 31 electrons so the **full electronic configuration** is:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p1$

[Ar] $3d^{10}\ 4s^2\ 4p^1$

- Even though the 4s is filled first, the full electron configuration is often written in numerical order. So, if there are electrons in the 3d sub-shell, then these will be written before the 4s

Answer 3:

- What this means is that if you ionise calcium and remove two of its outer electrons, the electronic configuration of the Ca^{2+} ion is identical to that of argon

Ca^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Ar is also $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Exceptions

- Chromium and copper have the following electron configurations, which are different to what you may expect:
    - Cr is [Ar] $3d^5\ 4s^1$ **not** [Ar] $3d^4\ 4s^2$
    - Cu is [Ar] $3d^{10}\ 4s^1$ **not** [Ar] $3d^9\ 4s^2$
- This is because the [Ar] $3d^5\ 4s^1$ and [Ar] $3d^{10}\ 4s^1$ configurations are **energetically stable**

Presenting the Electron Configuration

- Electrons can be imagined as small **spinning charges** which rotate around their own axis in either a **clockwise** or **anticlockwise direction**
    - The spin of the electron is represented by its direction
- Electrons with similar **spin** repel each other which is also called **spin-pair repulsion**
- Electrons will therefore occupy separate orbitals in the same subshell where possible, to minimize this repulsion and have their **spin** in the same direction
    - E.g. if there are three electrons in a **p subshell**, one electron will go into each p_x, p_y and p_z orbital

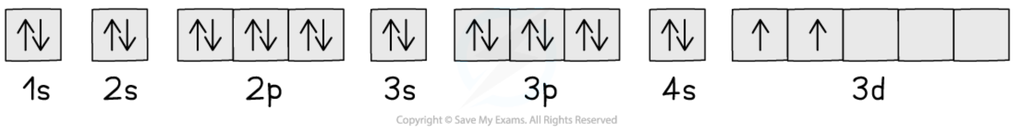
Electron configuration: three electrons in a p subshell

- Electrons are only paired when there are no more empty orbitals available within a subshell, in which case the spins are the **opposite** spins to minimize repulsion
  - E.g. if there are four electrons in a p subshell, one p orbital contains 2 electrons with opposite spin and two orbitals contain one electron only
  - The first 3 electrons fill up the empty p orbitals one at a time, and then the 4th one pairs up in the p_x orbital

Electron configuration: four electrons in a p subshell

Box Notation

- The **electron configuration** can be represented using the **electrons in boxes** notation
- Each box represents an **atomic orbital**
- The boxes are arranged in order of **increasing** energy from bottom to top
- The electrons are represented by opposite arrows to show the **spin** of the electrons
  - E.g. the box notation for titanium is shown below
  - Note that since the 3d subshell cannot be either full or half full, the second 4s electron is not promoted to the 3d level and stays in the 4s orbital



The electrons in titanium are arranged in their orbitals as shown. Electrons occupy the lowest energy levels first before filling those with higher energy

Chemical Properties

- The way an element reacts with other elements is determined by an number of factors, but in particular the **electronic configuration** of its atoms
- The Periodic Table is arranged in **periods (horizontal**) and **groups (vertical)**
  - All the elements in the same period have the same number of shells (principle quantum number)
  - All the elements in the same group have the same number of outer electrons

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- The elements in each group of period show particular trends and characteristics in their chemical and physical properties that can be explained in terms of their atomic numbers
- This provides valuable information about what is **likely to happen** when particular elements react
- The properties of the elements are a function of their atomic numbers
- Using this information as well as the location of the elements in the different blocks we can predict the properties
- For example:
    - Helium, neon and argon all have electronic structures with full sub shells as well as high ionisation energies
        - This confirms that the electronic arrangement is very stable explaining why they rarely react with other chemicals

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