# 2023 JC1 H2 CHEMISTRY (9729)
## CORE IDEA 1 – MATTER
## Topic 2: ATOMIC STRUCTURE

**Name:** ________________________________________ **Civics Group:** _________

**LEARNING OUTCOMES**

Students should be able to:

[From the topic of **Atomic Structure**]

(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 [knowledge of wave functions is not required]

(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 (see the Data Booklet)

(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

[From the topic of **The Periodic Table**]

(l) Recognise variation in the electronic configurations across a Period and down a Group

(m) Describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity:
 (i) Across a Period in terms of shielding and nuclear charge
 (ii) Down a Group in terms of increasing number of electronic shells, shielding and nuclear charge

## LECTURE CONTENT

## REFERENCES

1. **Chemistry (for CIE AS & A Level)** by Peter Cann & Peter Hughes 540 CAN
2. **Chemistry: The Molecular Nature of Matter & Change** by Martin S. Silberberg 540 SIL
3. **Calculations in A Level Chemistry (4th Edition)** by E.N. Ramsden 540 RAM
4. **Calculations for AS/A Level Chemistry** by Jim Clark 540 CLA

# 1 The Atom and the Subatomic Particles

## 1.1 Subatomic Particles

Learning Outcome:
- (a) Identify and describe protons, neutrons and electrons in terms of their relative charges and relative masses
- (c) Describe the distribution of mass and charges within an atom

An **atom** is the smallest particle found in an element that can take part in a chemical reaction. Particles that are smaller than the atom are called **subatomic particles**. The three main **subatomic particles** that form an atom are **protons**, **neutrons**, and **electrons**. Protons and neutrons are collectively known as **nucleons**. The centre of the atom is called the **nucleus**.

| Particles | Symbol | Position in atom | Relative Charge | Mass / amu* | Actual mass / kg |
|---|---|---|---|---|---|
| Protons | p | Nucleus | +1 | 1 | $1.67 \times 10^{-27}$ |
| Neutrons | n | Nucleus | 0 | 1 | $1.67 \times 10^{-27}$ |
| Electrons | e | Orbitals | −1 | $\frac{1}{1836}$ | $9.11 \times 10^{-31}$ |

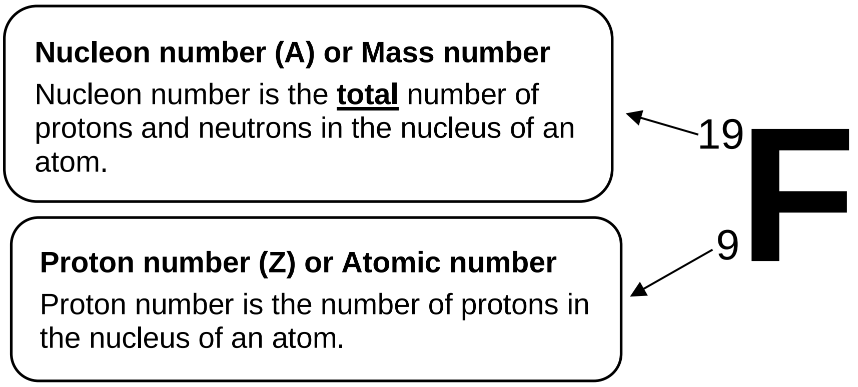
** Atomic mass units, or amu. It is defined as* $\frac{1}{12}$ *the mass of one atom of carbon-12.*

Almost the whole mass of the atom is concentrated in the nucleus, which takes up an extremely small space relative to the size of the whole atom. The size of an atom is easily more than 10,000 times that of the nucleus.

## 1.2 Nuclides and Isotopes

Learning Outcome:
- (d) Deduce the numbers of protons, neutrons and electrons present in both atoms and ions given protons 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

A nuclide is an atomic species whose proton and nucleon number are specified. It is usually represented in the manner below, using fluorine, F as an example:



**Nucleon number (A) or Mass number**

Nucleon number is the **<u>total</u>** number of protons and neutrons in the nucleus of an atom.

$${}^{19}_{9}\mathrm{F}$$

**Proton number (Z) or Atomic number**

Proton number is the number of protons in the nucleus of an atom.

The mass number (**A**) and atomic number (**Z**) give us information about the number of subatomic particles in the species.

In a **neutral atom**, no. of protons = **Z**
no. of neutrons = **A – Z**
no. of electrons = **Z**

In an **ion**, no. of protons = **Z**
no. of neutrons = **A – Z**
no. of electrons in an **anion**
= **Z + |charge number|**
no. of electrons in a **cation**
= **Z – |charge number|**

For example,

| | Number of protons | Number of neutrons | Number of electrons |
|---|---|---|---|
| $^{79}_{35}\text{Br}$ | | | |
| $^{56}_{26}\text{Fe}^{3+}$ | | | |
| $^{32}_{16}\text{S}^{2-}$ | | | |

Many elements consist of a mixture of isotopes. **Isotopes** are atoms of the same element with the **same number of protons** but **different number of neutrons**.

Isotopes of an element have the **same number and arrangement of electrons**. This leads to them having **similar chemical properties** as most chemical reactions only involve the transfer of electrons between different atoms, and leaves the nucleus of the atom intact. For example, both $^{35}\text{C}l$ and $^{37}\text{C}l$ atoms accept an electron from Na to give $\text{C}l^-$ in the formation of sodium chloride, $\text{Na}^+\ ^{35}\text{C}l^-$ and $\text{Na}^+\ ^{37}\text{C}l^-$ respectively.

However, since isotopes of an element have **different numbers of neutrons** and hence **different masses**, they will have **different physical properties** (e.g. melting and boiling points, density). For example, $^{37}\text{C}l_2$ has a higher density than $^{35}\text{C}l_2$ (as $^{37}\text{C}l_2$ has more neutrons, thus heavier than $^{35}\text{C}l_2$).

**Example 1A**

A Levels/2008/P1/Q4
*Use of Data Booklet is relevant to this question.*

Some isotopes are unstable and decompose naturally. In one type of decomposition, a neutron in the nucleus decomposes to form a proton, which is retained in the nucleus, and an electron, which is expelled from the atom.

Which change describes a process of this sort?

**A** $^{11}\text{C} \rightarrow\ ^{12}\text{C}$

**B** $^{23}\text{Na} \rightarrow\ ^{22}\text{Ne}$

**C** $^{32}\text{P} \rightarrow\ ^{31}\text{P}$

**D** $^{40}\text{K} \rightarrow\ ^{40}\text{Ca}$

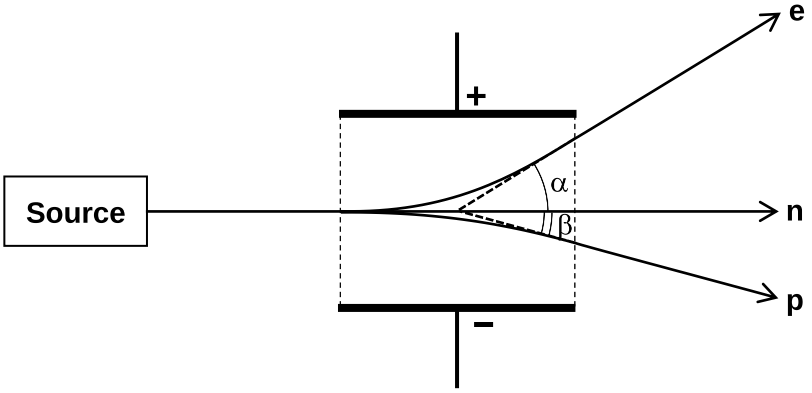
## 1.3 Behaviour of Subatomic Particles in an Electric Field

Learning Outcome:
(b) Deduce the behaviour of beams of protons, neutrons and electrons in an electric field

Protons, electrons and neutrons behave differently in an electric field due to differences in their **charges** and **relative masses**.

When beams of the three types of subatomic particles with the **same speed** are all travelling through an electric field of constant strength, each beam differs in their path travelled based on:

- **Direction** of deflection
- **Angle** of deflection



| Subatomic particles | Direction of deflection | Angle of deflection |
|---|---|---|
| Proton, p<br>(positively charged) | **curve** path towards the **negative** plate | β |
| Electron, e<br>(negatively charged) | **curve** path towards the **positive** plate | α |
| Neutron, n<br>(uncharged) | **undeflected** | zero |

Deflection of a beam of charged particles **only starts when the beam enters the electric field**. Since an attractive force continuously acts on the charged particles in the beam, the beam travels in a **curve path** as it undergoes acceleration.

Once **out of the electric field**, no attractive force acts on the charged particles in the beam. Hence, the beam continues its path in a **straight line**.

Although electrons and protons have the same magnitude of charge, **electrons are lighter**, and are hence **deflected to a greater extent** (i.e. $\alpha > \beta$).

In general,

- **Direction** of deflection is dependent on charge of a particle
- **Angle** of deflection is dependent on the charge to mass ratio of a particle

$$\boxed{\text{angle of deflection} \propto \left|\frac{q}{m}\right|}$$

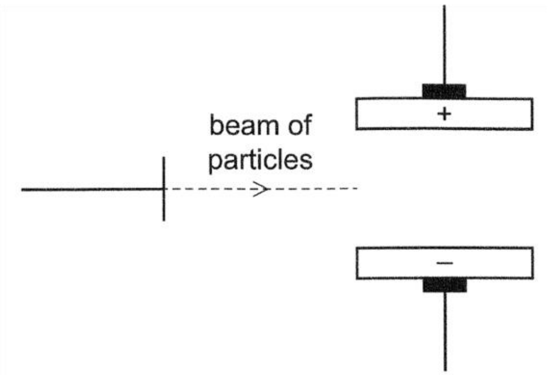
where q is the charge of the particle, m is the mass of the particle

Hence, particles with **smaller mass** and/or **higher charge** will be **deflected more** in the electric field.

### Example 1B

A Levels/2021/P1/Q1

In two separate experiments a beam of protons and a beam of electrons, travelling at the same velocity, pass through an electric field as shown.



Which statements are correct?

1 The electrons are deflected to a larger extent than the protons.

2 The electron beam is deflected in the opposite direction to the proton beam.

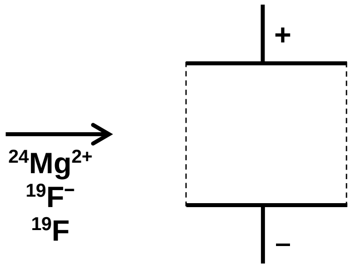
3 The proton beam travels in a straight path towards the negatively charged plate.

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

### Example 1C

Sketch the path which a $^{24}Mg^{2+}$ ion, a $^{19}F^{-}$ ion and a $^{19}F$ atom will take in an electric field.

| Particle | Charge | Relative Mass | Deflection | $\left\|\frac{q}{m}\right\|$ |
|---|---|---|---|---|
| **$^{24}Mg^{2+}$ion** | +2 | 24.0 | | |
| **$^{19}F^{-}$ ion** | −1 | 19.0 | | |
| **$^{19}F$ atom** | 0 | 19.0 | | |



***Note:***
- Deflection only occurs when beam passes into electric field
- Particles take a straight path again once out of the electric field

________ deflects at a larger angle as compared to __________ as it has a **larger** $\frac{q}{m}$ value.

**Self Check 1A**

Beams of charged particles are deflected by an electric field.

In an experiment, protons are deflected by an angle of +15º. In another experiment, under identical conditions, particle **X** is deflected by an angle of –5º.

What could be the composition of particle **X**?

| | protons | neutrons | electrons |
|---|---|---|---|
| **A** | 1 | 2 | 2 |
| **B** | 2 | 3 | 3 |
| **C** | 3 | 3 | 4 |
| **D** | 4 | 5 | 1 |

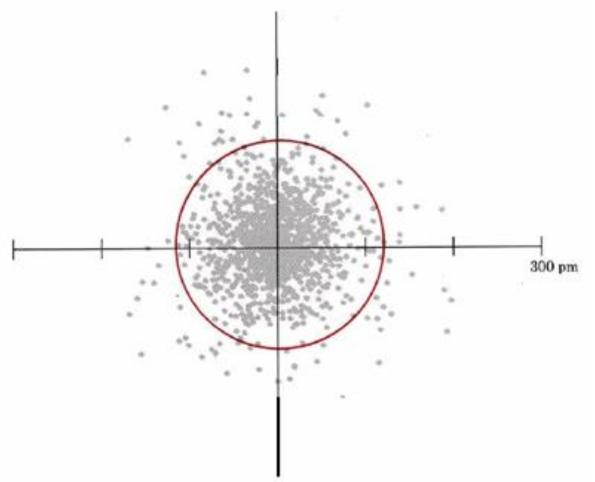
# 2 The Arrangement of Electrons

Electrons are not randomly distributed within an atom. Rather, they occupy specific volume regions, which have specific energies associated with them.

## 2.1 Atomic Orbitals

Learning Outcome:
(g) Describe the shapes of s, p and d orbitals. [knowledge of wave functions is not required]

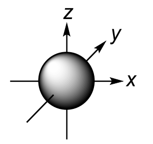
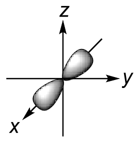
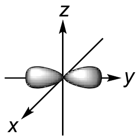
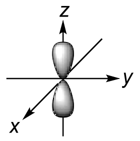
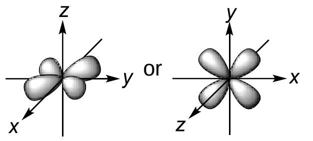
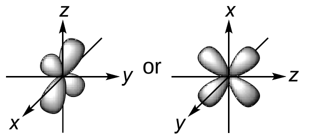
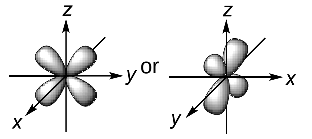
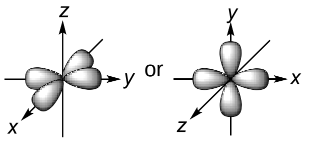
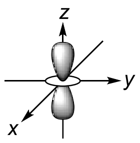
Knowing that electrons move around the nucleus, if we plot the position of a particular electron in a hydrogen atom every ten seconds over a period of time, we will see that the electron can be found anywhere within a spherical space around the nucleus, as shown in the diagram below.



The circle in the diagram demarcates the region of space in which you will be able to find the electron **95% of the time**. This region of **three dimensional space** is called an **orbital**.

In other words, an **orbital** is a region of space in which there is a high probability (95%) of finding an electron. Each orbital contains a maximum of 2 electrons. The energy of an orbital is the energy of the electrons occupying it.

There are different types of orbitals with different shapes and energies (further elaborated on in Section 2.2).

| type | shape | | description | |
|---|---|---|---|---|
| s orbital |  | | • s orbitals are **spherical**.<br>• There is only **one** s orbital in any subshell. | |
| p orbital |  | $p_x$ | • p orbitals are **dumbbell shaped**. Each orbital has two lobes of equal size.<br>• There are a total of **three** p orbitals in any subshell.<br>• The three p orbitals have **different orientations in space**. Each orbital is aligned along the axis corresponding to its subscript, e.g. the $p_x$ orbital is aligned along the x-axis. All p orbitals are **mutually perpendicular** to one another.<br>• The three p orbitals have the **same energy** i.e. they are **degenerate**.<br>• Putting all the three p orbitals together, we get a sphere. Hence, a p orbital is 1/3 the volume of a sphere. | |
| |  | $p_y$ | | |
| |  | $p_z$ | | |
| d orbital |  | $d_{xy}$ | Lobes point **between** axes | • There are a total of **five** d orbitals in any subshell.<br>• The five d orbitals have **different orientations in space**.<br>• The five d orbitals have the **same energy** i.e. they are **degenerate**.<br>• Putting all the five d orbitals together, we get a sphere. Hence, a d orbital is 1/5 the volume of a sphere. |
| |  | $d_{xz}$ | | |
| |  | $d_{yz}$ | | |
| |  | $d_{x^2-y^2}$ | Lobes point **along** axes | |
| |  | $d_{z^2}$ | | |

**Self Check 2A**

A Levels/2020/P1/Q1

The shape of each p-orbital is represented as two lobes.
How many 3d orbitals have four lobes?

**A** 2 **B** 3 **C** 4 **D** 5

*Visualising the shapes of orbitals*

## 2.2 Relationship between Principal Quantum Shells, Subshells and Orbitals

Learning Outcome:

(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.

Electrons are arranged in the following manner:

**Orbitals**

- Each orbital contains a **maximum of two** electrons.
- You will usually come across four types of orbitals: s, p, d and f.

**Subshells**

- Each subshell consists of a certain number of orbitals, depending on the **type** of subshell.

| Type of subshell | Type and number of orbital(s) |
|---|---|
| s | **one** s orbital |
| p | **three** p orbitals |
| d | **five** d orbitals |
| f | **seven** f orbitals |

- Orbitals in the same subshell have the **same energy** i.e. they are **degenerate** but they have **different orientation in space**.
- The **relative energies** of the subshells are in the order of **s < p < d < f** for the same principal quantum number.

**Principal Quantum Shells (Electronic Shells)**

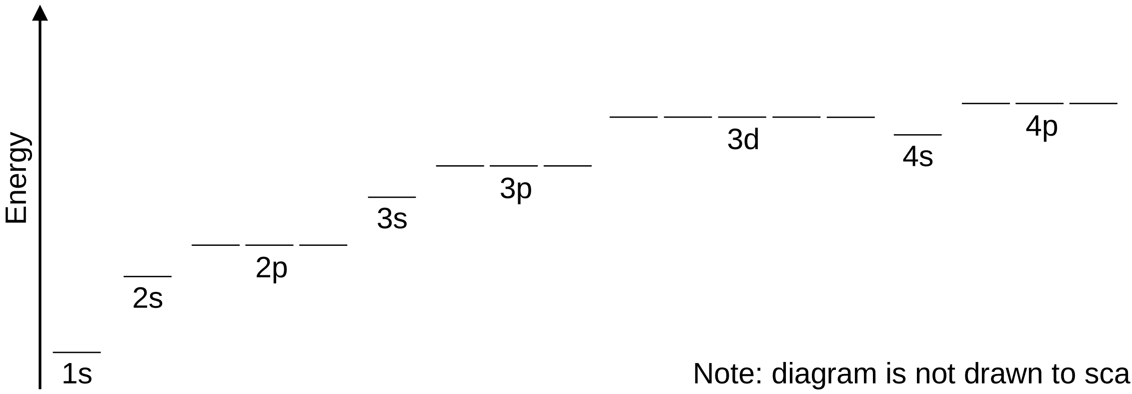
- Each shell consists of a certain number of subshells, depending on the **principal quantum number**, *n*, where *n* = 1, 2, 3, … (numbered **outwards** from the nucleus).

| *n* | Type of subshell(s) |
|---|---|
| 1 | s subshell |
| 2 | s subshell, p subshell |
| 3 | s subshell, p subshell, d subshell |
| 4 | s subshell, p subshell, d subshell , f subshell |

- The **higher** the value of *n*,
  - the **further** the electron is from the nucleus;
  - the **higher** the energy level of the electron;
  - the **less strongly** the electron is attracted to the nucleus;
  - the **larger and more diffused** (i.e. electron density spread over larger volume) the orbitals in the shell.

Putting everything together,

| **Principal quantum number, n** | Type of **subshell(s)** | Number of **orbital(s)** | Max number of electrons | |
|---|---|---|---|---|
| | | | in each **subshell** | in each **quantum shell** (max no. of electrons = $\underline{\mathbf{2n^2}}$) |
| 1 | s | 1 | 2 | 2 |
| 2 | s | 1 | 2 | 8 |
| | p | 3 | 6 | |
| 3 | s | 1 | 2 | 18 |
| | p | 3 | 6 | |
| | d | 5 | 10 | |
| 4 | s | 1 | 2 | 32 |
| | p | 3 | 6 | |
| | d | 5 | 10 | |
| | f | 7 | 14 | |



Note: diagram is not drawn to scale

# 3 Electronic Configuration

Learning Outcome:
(h) State the electronic configuration of atoms and ions given the proton number (and charge)

The **electronic configuration** of an element refers to the arrangement of electrons in the principal quantum shells, subshells and orbitals.

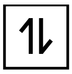
Knowing the electronic configuration enables us to identify the electron(s) to be removed in a chemical reaction. We will be able to know which orbital the electron to be removed resides in, and consequently the amount of energy required to remove it.

## 3.1 Rules for Arranging Electrons

**<u>Rule 1: Pauli's Exclusion Principle</u>**

Two electrons in the **same orbital** must have **<u>opposite spins</u>**.

Same spins
**WRONG!**



Opposite spins
**RIGHT!**

Electrons are often described with a special property known as spin. There are two possible orientations for electron spin, represented by arrows pointing in opposite directions.

***For your information***

Electron spin gives rise to the formation of magnetic fields. If two electrons in the same orbital have the same spin, the magnetic field created will be repulsive, causing the energy level of these two electrons to be higher, and thus being less stable as compared to a pair of electrons with opposite spins.

What exactly is the 'spin' of subatomic particles such as electrons and protons?

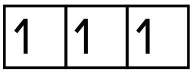
**<u>Rule 2: Hund's Rule</u>**

**Orbitals of a subshell** must be **<u>singly occupied first with parallel spins before pairing occurs</u>**.

For example, when filling **six** electrons into the **p subshell**,

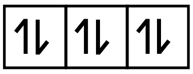
**After filling the <u>first three</u> electrons:**

- Orbitals are singly occupied, electrons have parallel spins



**After filling <u>all six</u> electrons:**

- Orbitals contain paired electrons with opposite spins



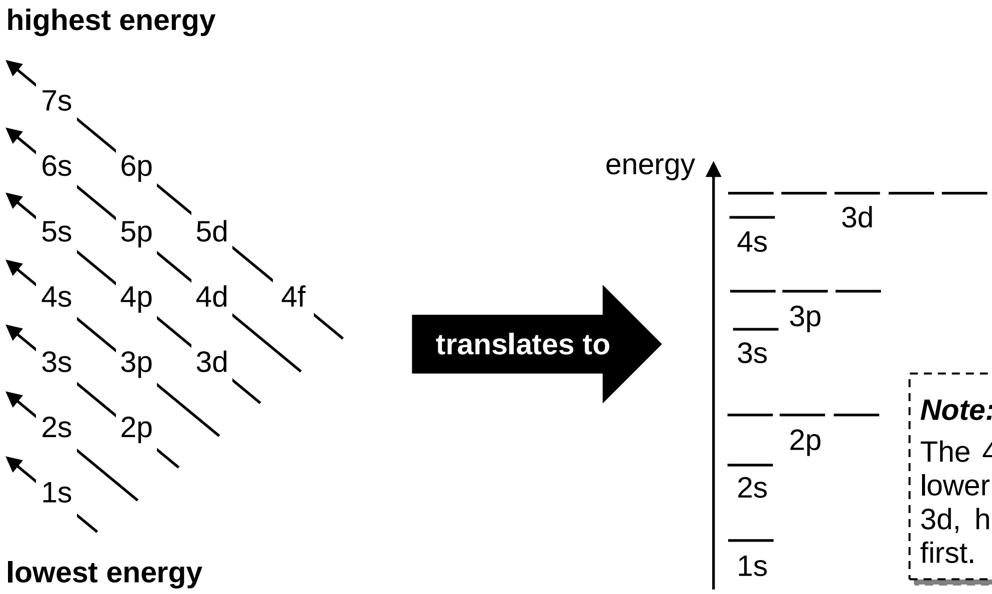
This happens as electrons repel one another electrostatically. Hence, they will want to remain as far apart as possible from one another by occupying different orbitals (i.e. different regions of space) first.

**<u>Rule 3: The Aufbau Principle</u>**

Place electrons into orbitals, **starting with those of the lowest energy** (nearest to the nucleus) **and then working upwards**.

Electrons in their lowest energy states is known as the **ground state** (i.e. when they are not excited). Energy can be supplied to move an electron from a lower energy state to a higher energy state (i.e. the excited state).

The following diagram is a convenient way to remember the sequence of orbitals from the lowest to highest in energy level.



***Note:***
The 4s subshell is at a lower energy level than 3d, hence will be filled first.

### 3.2 Electronic Configuration of an Atom

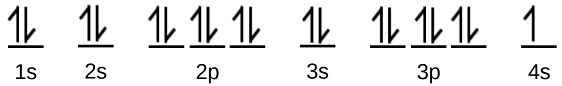
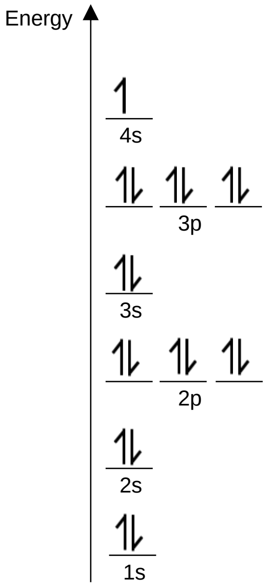
**<u>Steps for working out electronic configuration of an atom</u>**

1. Determine the **total number of electrons** in the atom.
2. Fill the orbitals **from the lowest energy upwards**, making sure that there are a **maximum of two electrons** in each orbital.
3. For subshells with more than one orbital i.e. p, d and f subshells, **fill all the orbitals with one electron each before putting in the second electron**.
4. If an orbital contains two electrons, the electrons must have **opposite spins**.

**Example 3A**

Represent the electronic configuration of the **potassium atom** in the ways stated in the table below.

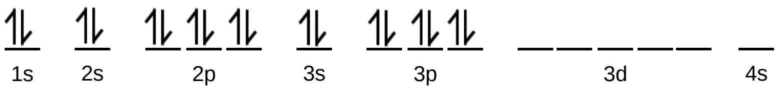
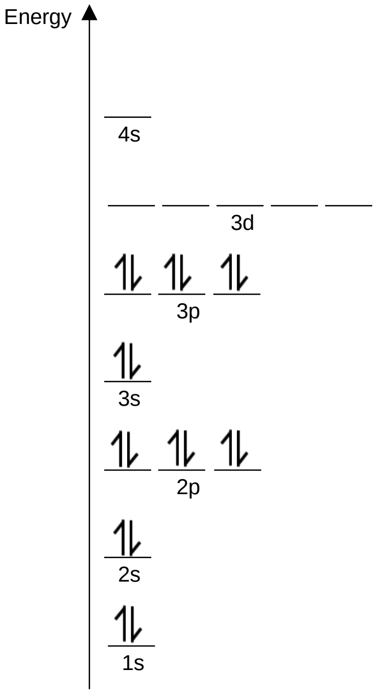
Potassium atom has **<u>19</u>** electrons.

| | |
|---|---|
| **Drawing** electronic configuration |  |
| **Writing/stating full** electronic configuration | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ |
| Writing/stating **short form notation** of electronic configuration | $[Ar]\ 4s^1$ |
| Drawing **energy level diagram** |  |

**Example 3B**

Represent the electronic configuration of the **scandium atom** in the ways stated in the table below.

Scandium is a **d-block element**. The scandium atom has **21** electrons.

| | |
|---|---|
| **Drawing** electronic configuration |  |
| **Writing/stating full** electronic configuration | |
| Writing/stating **short form notation** of electronic configuration | |
| Drawing **energy level diagram** |  |

**Note:**

For atoms of d-block elements,

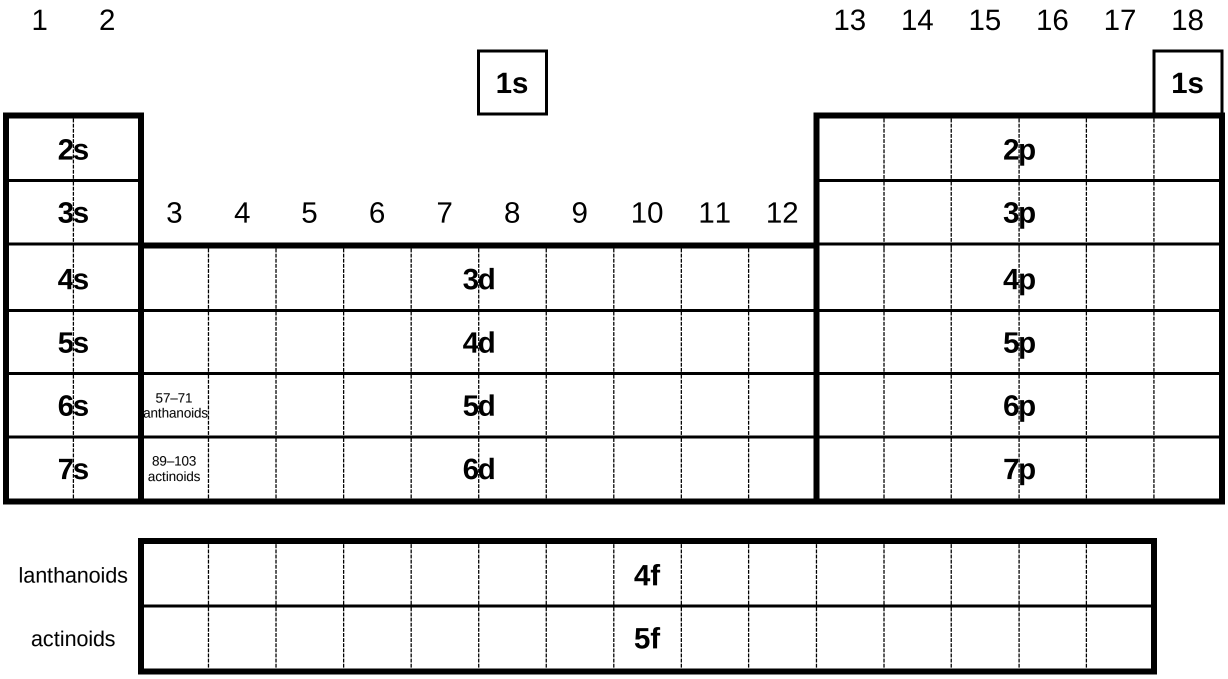
- **Fill** 4s orbital before 3d orbitals
- **Write/draw** 3d subshell before 4s subshell

*How do all the orbitals come together in the Sc atom? View the visualisation here.*

## 3.3 Electronic Configuration of Atoms and the Periodic Table

Learning Outcome:
(l) Recognise variation in the electronic configurations across a Period and down a Group

The Periodic Table is compartmentalised into blocks, namely the s block, p block, d block and f block. The **name of the block** indicates the **last occupied subshell** of the atom.



The **period number** indicates the **principal quantum number, n, of the valence (outermost) shell**. Elements in the same period have the same number of shells occupied with electrons.

The **group numbers** of the s and p block elements indicate the **number of electrons in the valence shell**. Elements in the same group have the same number of valence electrons and hence, same valence shell electronic configuration.

| | **Group 1** | **Group 2** | **Group 13** | **Group 14** | **Group 15** | **Group 16** | **Group 17** | **Group 18** |
|---|---|---|---|---|---|---|---|---|
| **valence shell electronic configuration** | $ns^1$ | $ns^2$ | $ns^2\ np^1$ | $ns^2\ np^2$ | $ns^2\ np^3$ | $ns^2\ np^4$ | $ns^2\ np^5$ | $ns^2\ np^6$<br>(except He) |
| | **s block** | | **p block** | | | | | |

**Example 3C**

An ion $X^+$ has the electronic configuration [Ne] $3s^2\ 3p^1$. Which group does X belong to?

**A** 1 **B** 2 **C** 13 **D** 14

### 3.4 Electronic Configuration of an Ion

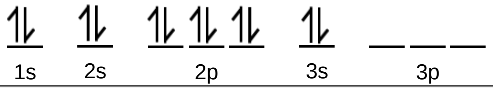
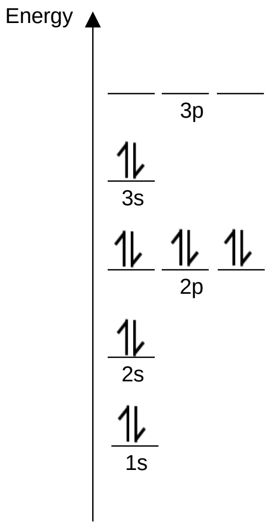
**Steps for working out electronic configuration of an ion**

1. Work out the electronic configuration of the **atom**.
2. For an **anion**, **add** the number of electrons equal to the negative charge **to the outermost shell**. For a **cation**, **remove** the number of electrons equal to the positive charge **from the outermost shell**.

**Example 3D**

Represent the electronic configuration of the **sulfur ion, $S^{2-}$** in the ways stated in the table below.

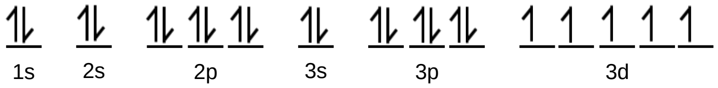
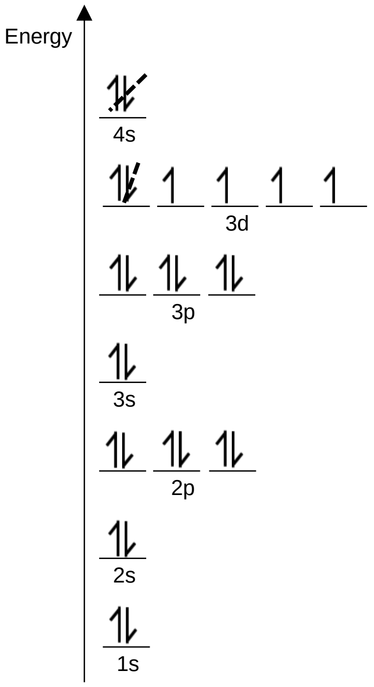
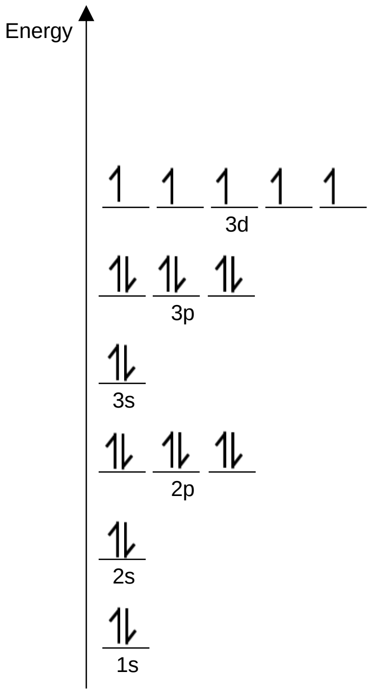
The S atom has **16** electrons. The $S^{2-}$ ion has **18** electrons.

| | |
|---|---|
| **Drawing** electronic configuration |  |
| **Writing/stating** electronic configuration | |
| Drawing **energy level diagram** |  |

**Example 3E**

Represent the electronic configuration of the **iron(III) ion, $Fe^{3+}$** in the ways stated in the table below.

Fe is a **<u>d-block element</u>**. The Fe atom has **<u>26</u>** electrons. The $Fe^{3+}$ ion has **<u>23</u>** electrons.

| | |
|---|---|
| **Drawing** electronic configuration |  |
| **Writing/stating** electronic configuration | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$ |
| Drawing **energy level diagram** | ***(working)***<br>**<u>Fe atom:</u>**<br> <br>**<u>$Fe^{3+}$ ion:</u>**<br> |

### 3.5 Anomalous Electronic Configurations

For the Period 4 d-block elements i.e. Sc through Zn, the electronic configurations of the atoms generally take the form [Ar] $3d^n\ 4s^2$, where $n$ = 1 for scandium and $n$ = 10 for zinc. However, there are two exceptions:

1. Cr: **[Ar] $3d^5\ 4s^1$** instead of [Ar]$3d^4 4s^2$
2. Cu: **[Ar] $3d^{10}\ 4s^1$** instead of [Ar]$3d^9 4s^2$

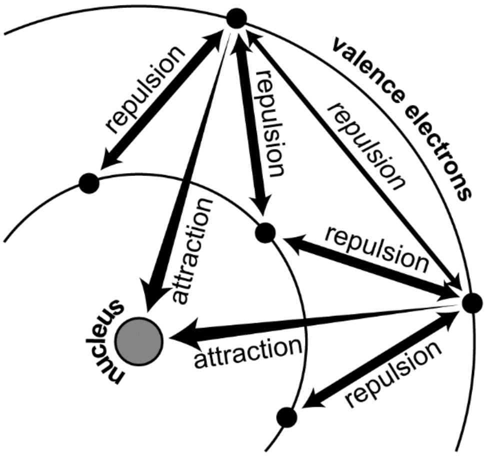
The **$3d^5$ (half-filled subshell)** and **$3d^{10}$ (fully-filled subshell)** are **energetically preferred** configurations due to the **symmetrical 3d electron cloud around the nucleus**. This allows for charges to be spread out evenly and as far apart as possible, leading to greater stability.

Note that at the 'A' Levels, we will consider the anomalous electronic configuration only for the Cr and Cu elements. For Fe atom which has an electronic configuration of [Ar]$3d^6 4s^2$, $Fe^{2+}$ will have the electronic configuration of [Ar]$3d^6$, and not [Ar]$3d^5 4s^1$.

# 4 Factors Affecting Atomic Properties and Periodic Trends

The elements in the periodic table are arranged in order of increasing atomic number. All of these elements display similar trends in:

- Ionisation Energy
- Atomic and Ionic Radius
- Electronegativity



The following factors affect the **electrostatic forces of attraction between the valence electrons and the nucleus**, giving rise to the various trends.

**1a. Charge of nucleus (nuclear charge)**

- More protons in nucleus, larger positive charge of nucleus
- Stronger electrostatic forces of attraction between the nucleus and the valence electrons

**1b. Number of electrons between valence electrons and nucleus (shielding or screening effect)**

**Shielding or screening effect** refers to the inter-electronic repulsion between the valence (outermost) electrons and inner shell electrons.

- Inner shell electrons confer the most significant shielding. Shielding by electrons within the same shell is generally more insignificant in comparison.
- Fewer electrons in the inner shells which leads to weaker shielding effect
- Stronger electrostatic forces of attraction between the nucleus and the valence electrons

Bringing together the effects of nuclear charge and shielding effect: **Effective Nuclear Charge**

The **effective nuclear charge** is the strength of the **net** electrostatic forces of **attraction** felt by the valence electrons after taking into account the shielding effect of the inner shell electrons.

**Effective nuclear charge = nuclear charge – shielding effect**
(det by no. of protons) (det by no. of inner shell electrons)

**2. Distance of electron from nucleus**

- Smaller distance between nucleus and valence electron
- Stronger electrostatic forces of attraction between the nucleus and the valence electron

# 5 Trends in Ionisation Energies

## 5.1 Ionisation Energy (I.E.)

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

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

E.g.
First ionisation energy of magnesium:
$Mg(g) \rightarrow Mg^+(g) + e^-$ 1st IE (Mg) = +736 kJ $mol^{-1}$

The **second** ionisation energy is the **energy required** to remove **1 mole of electrons** from **1 mole of singly charged gaseous cations** to form **1 mole of doubly charged gaseous cations**.

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

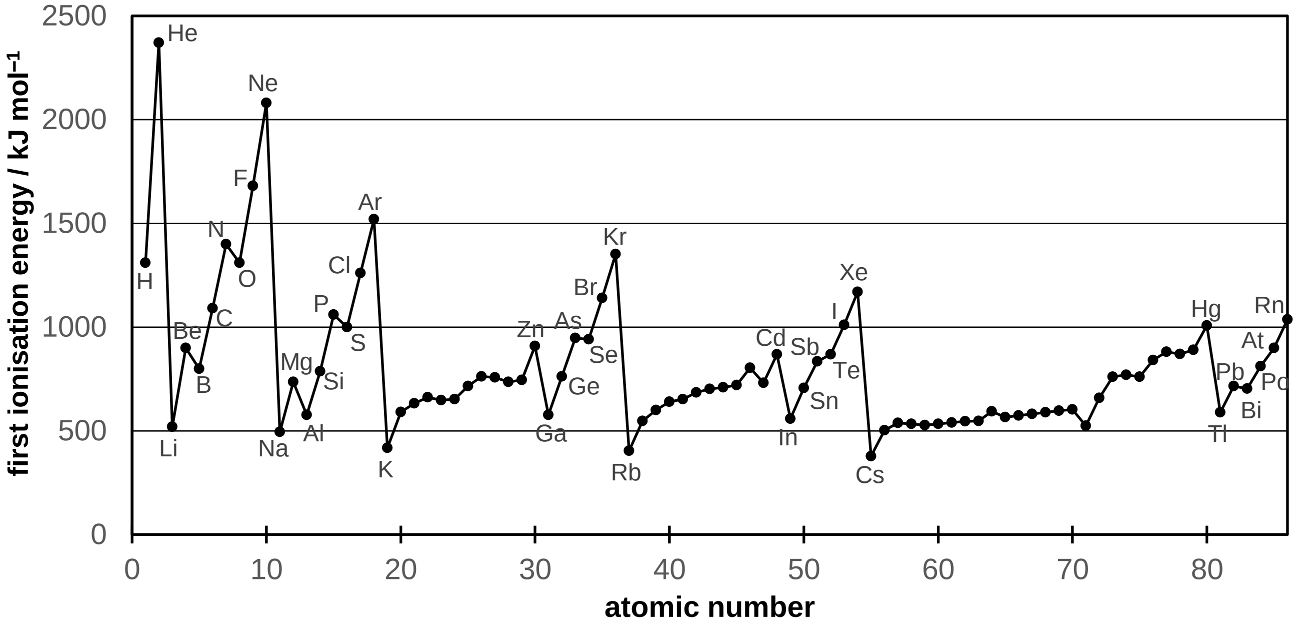
E.g.
Second ionisation energy of magnesium:
$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$ 2nd IE (Mg) = +1450 kJ $mol^{-1}$

Ionisation energy is always a **positive** value (i.e. **endothermic**) because energy is **required** to overcome the electrostatic forces of attraction between the nucleus and valence electrons.

## 5.2 Trends of 1st I.E.

Learning Outcome:
(l) Explain the factors influencing the ionisation energies of elements *(see the Data Booklet)*.
(m) Describe and explain qualitatively the trends and variations in first ionisation energy:
  (i) Across a Period in terms of shielding and nuclear charge
  (ii) Down a Group in terms of increasing number of electronic shells, shielding and nuclear charge

The following chart shows the 1st ionisation energies of elements with atomic numbers from 1 to 86.



### 5.2.1 Across the Period (e.g. Li, Be, B, C, O, N, F, Ne)

**General increase in 1st I.E. across the period**

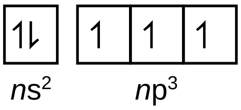
- Number of protons in the nucleus of the atom increases, thus **nuclear charge increases**
- Same number of inner shell electrons, thus **shielding effect is approximately constant**
- **Increase in effective nuclear charge**
- **Increase in electrostatic forces of attraction** between the nucleus and valence electron
- **More** energy needed to remove the valence electron
- **Increase** in 1st I.E. across the period

**Exception 1: Decrease in 1st I.E. from Group 2 to Group 13 (*e.g.* Be to B)**

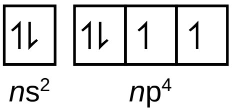
- Valence shell: Group 2: $ns^2$ Group 13: $ns^2\ np^1$
- ***n*p electron is of a higher energy level than the *n*s electron**
- **Less** energy is required to remove the valence *n*p electron from a Group 13 element

**Exception 2: Decrease in 1st I.E. from Group 15 to 16 (e.g. N to O)**

- Valence shell Group 15 :



Group 16 :



- There is **inter-electronic repulsion between the paired electrons in the same orbital** for a Group 16 element
- **Less** energy is required to remove the *n*p electron from Group 16 than Group 15

### 5.2.2 Down the Group (e.g. He, Ne, Ar, Kr, Xe, Rn)

**Decrease in 1st I.E. down the group**

- **Both nuclear charge and shielding effect increase**.
- However, valence electrons are located in a shell with a larger principal quantum number, n, and are **further away from the nucleus**
- **Decrease in electrostatic forces of attraction** between the nucleus and the valence electron
- **Less** energy needed to remove the valence electron
- **Decrease** in 1st I.E. down the group

## 5.3 Successive I.E. of an Atom

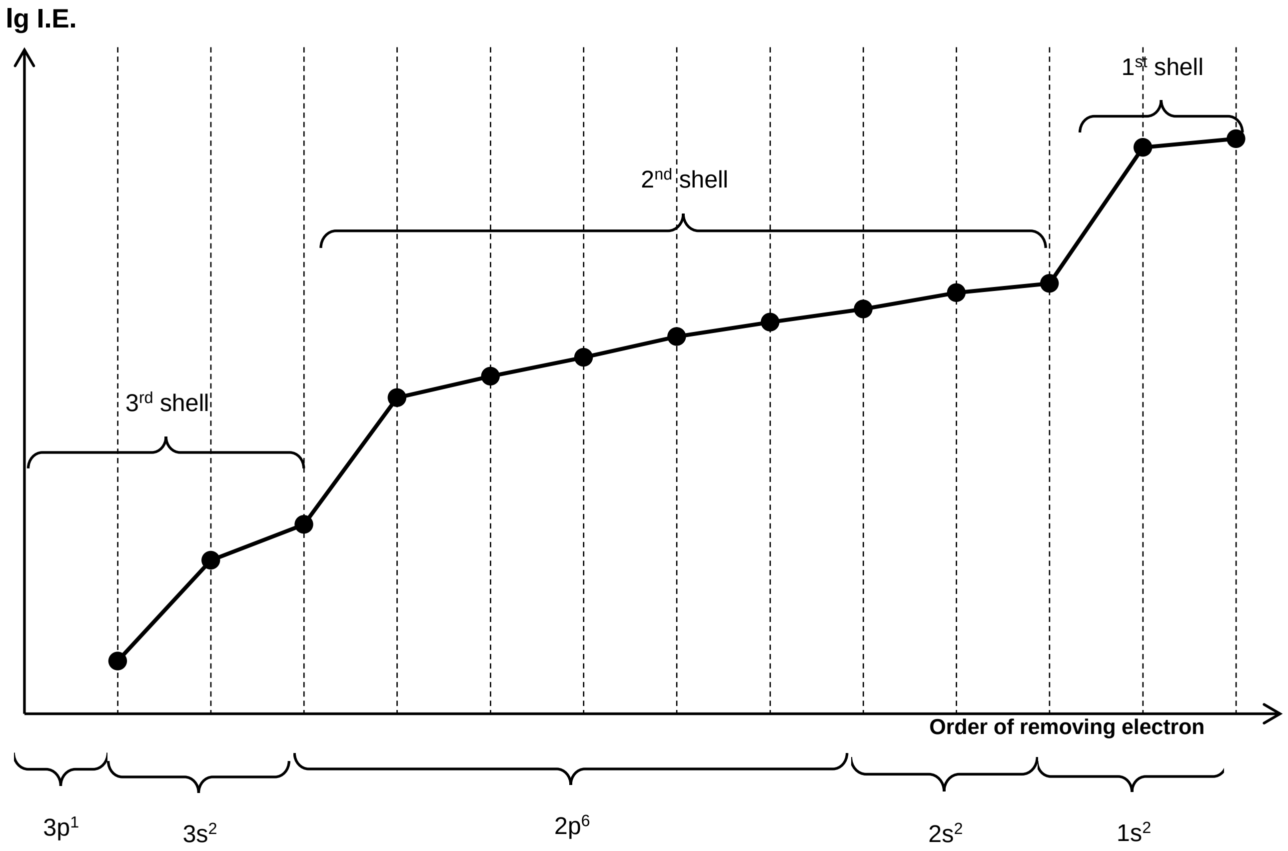
Learning Outcome:
(j) Deduce the electronic configurations of elements from successive ionisation energy data
(k) Interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table

**General Trend:**

- **Shielding effect decreases** as electrons are removed
- **Nuclear charge remains the same**, hence **effective nuclear charge increases**
- Resulting in **increase in electrostatic forces of attraction** between the nucleus and the **remaining** electrons
- **More** energy needed for subsequent removal of electrons
- Successive I.E. of an atom **always increases**

### 5.3.1 Deducing Electronic Configuration Using Successive I.E.

The following graph and table show the successive ionisation energies of an **aluminium** atom (A*l*: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$).



| Order of removal | 1st | 2nd | 3rd | 4th | 5th | 6th | 7th | 8th | 9th | 10th | 11th | 12th | 13th |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **I.E. / kJ mol$^{-1}$** | 577 | 1820 | 2740 | 11600 | 14800 | 18400 | 23300 | 27500 | 31900 | 38500 | 42600 | 201000 | 222000 |

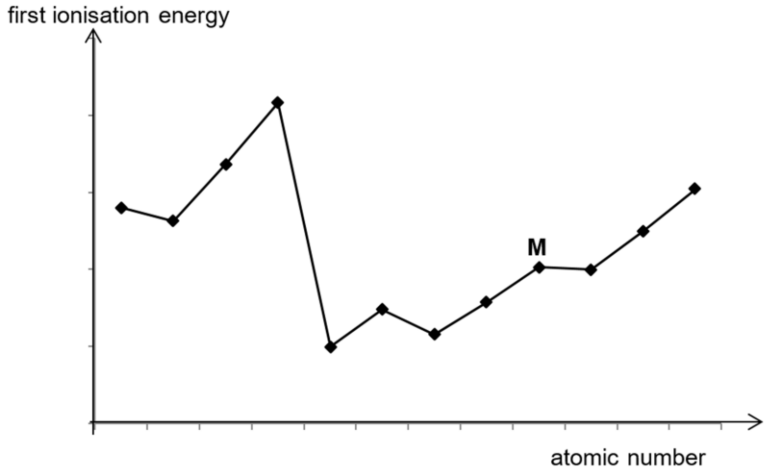
Difference btw successive I.E.: 1243 920 **8860** 3200 3600 4900 4200 4400 6600 4100 **158400** 21000

3rd shell 2nd shell 1st shell

- A **large increase** in I.E. represents a **change in principal quantum shell**.
  - Electron is removed from an inner principal quantum shell which is **closer to the nucleus**, and hence experiences **stronger** electrostatic forces of attraction.
- The **number of electrons that are removed** before the **first large increase** in I.E. indicates the **number of valence electrons** in the atom, and hence the **group** the element is in.
- Using these pieces of information, the **valence shell electronic configuration of the atom** can be deduced.

**Example 5A**

NJC/2015/P1/Q3 (modified)
The diagram below shows the first ionisation energy of some elements with atomic numbers less than 20.



Which is the most likely formula of the chloride of **M**?

**A** $\mathbf{M}Cl$ **B** $\mathbf{M}Cl_2$ **C** $\mathbf{M}Cl_3$ **D** $\mathbf{M}Cl_4$

**Example 5B**

HCI/2014/P1/Q3
The successive ionisation energies of two elements, **P** and **Q**, are given below.

| **Ionisation energies / kJ mol$^{-1}$** | **1st** | **2nd** | **3rd** | **4th** | **5th** | **6th** | **7th** | **8th** |
|---|---|---|---|---|---|---|---|---|
| **P** | 740 | 1450 | 7720 | 10540 | 13630 | 18020 | 21700 | 25660 |
| **Q** | 1011 | 1907 | 2910 | 4960 | 6270 | 21270 | 25431 | 29872 |

What is the formula of the compound formed when **P** reacts with **Q**?

A $\mathbf{P}_2\mathbf{Q}_3$ B $\mathbf{P}_3\mathbf{Q}_2$

C $\mathbf{P}_2\mathbf{Q}_5$ D $\mathbf{P}_5\mathbf{Q}_2$

# 6 Trends in Atomic Radius, Ionic Radius, and Electronegativity

Learning Outcome:
(m) Describe and explain qualitatively the trends and variations in atomic radius, ionic radius and electronegativity:
  (i) Across a Period in terms of shielding and nuclear charge
  (ii) Down a Group in terms of increasing number of electronic shells and nuclear charge

Apart from ionisation energies, electronic configuration can help us to understand **atomic radius**, **ionic radius**, and **electronegativity**. This is because these properties are also **dependent on the strength of attraction between the nucleus and the valence electrons or the shared electrons in a covalent bond**.

**Atomic radius** is defined as *half the distance* between the centres of two adjacent atoms found in the structure of the element.

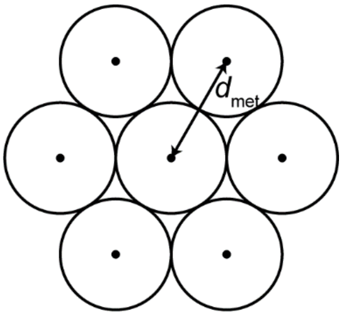
Due to differences in inter-atomic bonding in different elements, the way atomic radius is measured for each element may be different:

**metallic radius**

- The metallic radius of an atom is half the distance between the **centres of two adjacent atoms in the metal**.

$$r_{\text{met}} = \frac{d_{\text{met}}}{2}$$

- Metallic radius is obviously restricted to those elements that form **metallic lattices.**

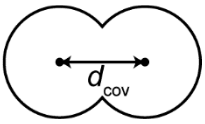


**covalent radius**

- The covalent radius of an atom is half the distance between the **centres of two adjacent atoms that are covalently bonded**.

$$r_{\text{cov}} = \frac{d_{\text{cov}}}{2}$$

- Covalent radius may be measured for **most non-metal elements**.

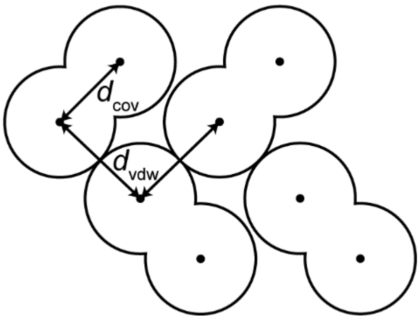


**van der Waals radius**

- The van der Waals' radius of an atom is half the distance between the **centres of two adjacent atoms which are not chemically bonded**.

$$r_{\text{vdw}} = \frac{d_{\text{vdw}}}{2}$$

- van der Waal's radius is most easily determined for **non-metals**, and is particularly useful for the **noble gases**.

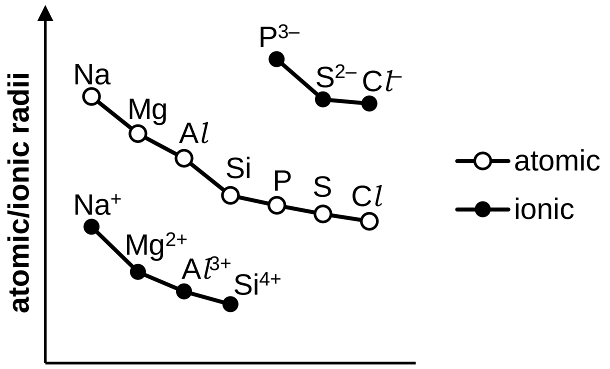


**Ionic radius** is defined as the average distance between the nuclei of two adjacent ions of the same element.

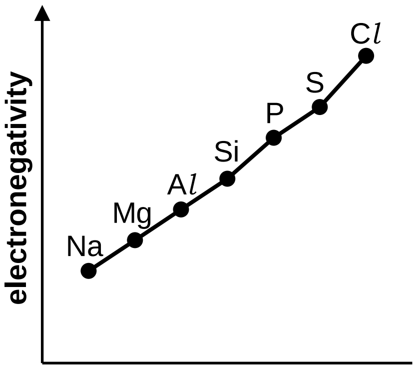
**Electronegativity** refers to the ability of an atom to attract the shared pair(s) of electrons in a covalent bond.

## 6.1 Trends Across the Period

<table>
<tr>
<th>atomic and ionic radii</th>
<th>electronegativity</th>
</tr>
<tr>
<td>



</td>
<td>



</td>
</tr>
<tr>
<td>

**Atomic radius decreases across the period**

- Number of protons in the nucleus of the atom increases, thus **nuclear charge increases**
- Same number of inner shell electrons, thus **shielding effect is approximately constant**
- **Increase in effective nuclear charge**
- **Increase in electrostatic forces of attraction** between the nucleus and valence electron

**Cationic radii decreases from $Na^+$ to $Si^{4+}$**

- Nuclear charge **increases**
- **Same** shielding effect since the cations are isoelectronic (same number of electrons)
- **Stronger** electrostatic forces of attraction between the nucleus and the valence electrons

**Anion radii decreases from $P^{3-}$ to $Cl^-$**

- Nuclear charge **increases**
- **Same** shielding effect since the anions are isoelectronic (same number of electrons)
- **Stronger** electrostatic forces of attraction between the nucleus and the valence electrons

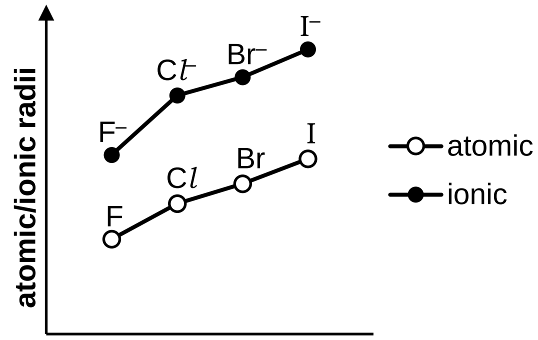
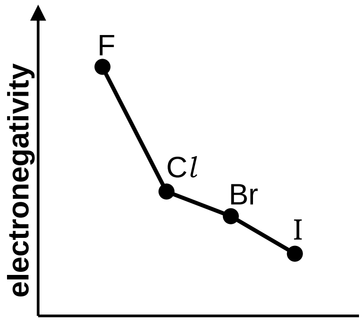
</td>
<td>

**Electronegativity increases across the period**

- Number of protons in the nucleus of the atom increases, thus **nuclear charge increases**
- Same number of inner shell electrons, thus **shielding effect is approximately constant**
- **Increase in effective nuclear charge**
- **Increase in electrostatic forces of attraction** between the nucleus and valence electron

</td>
</tr>
</table>

## 6.2 Trends Down the Group

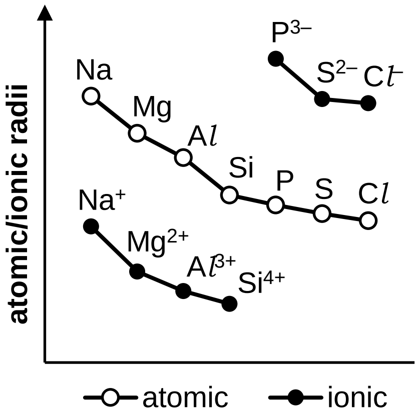
<table>
<tr><th>atomic and ionic radii</th><th>electronegativity</th></tr>
<tr><td>
</td><td>
</td></tr>
<tr><td><b><u>Atomic and ionic radii increase down the group</u></b><br>• <b><u>Both nuclear charge and shielding effect increase</u></b><br>• However, valence electrons are located in a shell with a larger principal quantum number, n, and are <b><u>further away from the nucleus</u></b><br>• <b><u>Decrease in electrostatic forces of attraction</u></b> between the nucleus and the valence electron</td><td><b><u>Electronegativity decreases down the group</u></b><br>• <b><u>Both nuclear charge and shielding effect increase</u></b><br>• However, valence electrons are located in a shell with a larger principal quantum number, n, and are <b><u>further away from the nucleus</u></b><br>• <b><u>Decrease in electrostatic forces of attraction</u></b> between the nucleus and the valence electron</td></tr>
</table>

## 6.3 More Observations About Ionic Radii

**Cations are smaller than their corresponding atoms**

*E.g.* Electronic configurations of Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$
Electronic configurations of $Na^+$: $1s^2\ 2s^2\ 2p^6$

- Nuclear charge **remains the same**
- Cation has **fewer electrons** than the atom
- Shielding effect **decreases**
- **Increase** in the electrostatic forces of attraction between the nucleus and the valence electrons in cation



**Anions are larger than their corresponding atoms**

*E.g.* Electronic configurations of Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
Electronic configurations of $Cl^-$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

- Nuclear charge **remains the same**
- Anion has **more electrons** than the atom
- Shielding effect **increases**
- **Decrease** in the electrostatic forces of attraction between the nucleus and the valence electrons in anion

**The anions ($P^{3-}$, $S^{2-}$ and $Cl^-$) are larger than the cations ($Na^+$, $Mg^{2+}$, $Al^{3+}$, $Si^{4+}$)**

*E.g.* Electronic configurations of $Na^+$, $Mg^{2+}$, $Al^{3+}$, $Si^{4+}$: $1s^2\ 2s^2\ 2p^6$
Electronic configurations of $P^{3-}$, $S^{2-}$ and $Cl^-$: $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^6}$

- Anions have **one more filled principal quantum shell** compared to cations
- Valence electrons in anions are **further** from the nucleus than those in cations
- **Weaker** electrostatic forces of attraction between the nucleus and valence electrons in anions than in cations

# KEY IDEAS

## The Atom and the Subatomic Particles

What are the relative charges and relative masses of protons, neutrons and electrons?
Where are these subatomic particles found in an atom? What is the definition of nucleon number and proton number?
How do these subatomic particles behave in an electric field?
Can you deduce the number of protons, neutrons and electrons in atoms and ions given proton and nucleon number (and charge)?

## The Arrangement of Electrons

What is a principal quantum shell, subshell and orbital?
Can you draw the energy level diagram of the orbitals from n=1 to n=4?
Can you draw and describe the shape of s, p and d orbitals correctly?

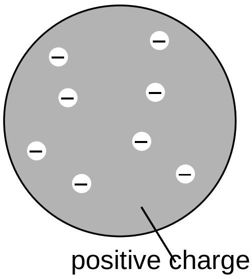
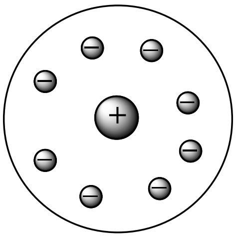
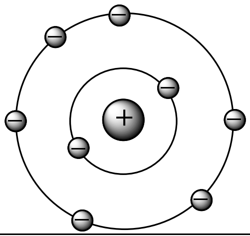
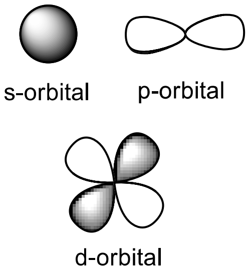
## Electronic Configuration

How does electronic configuration change across a period and down a group?
Can you write/draw the electronic configuration and energy level diagram of an atom and ions?
How do you deduce electron configuration given successive ionisation energy data?

## Trends in Ionisation Energies, Atomic and Ionic Radii, and Electronegativity

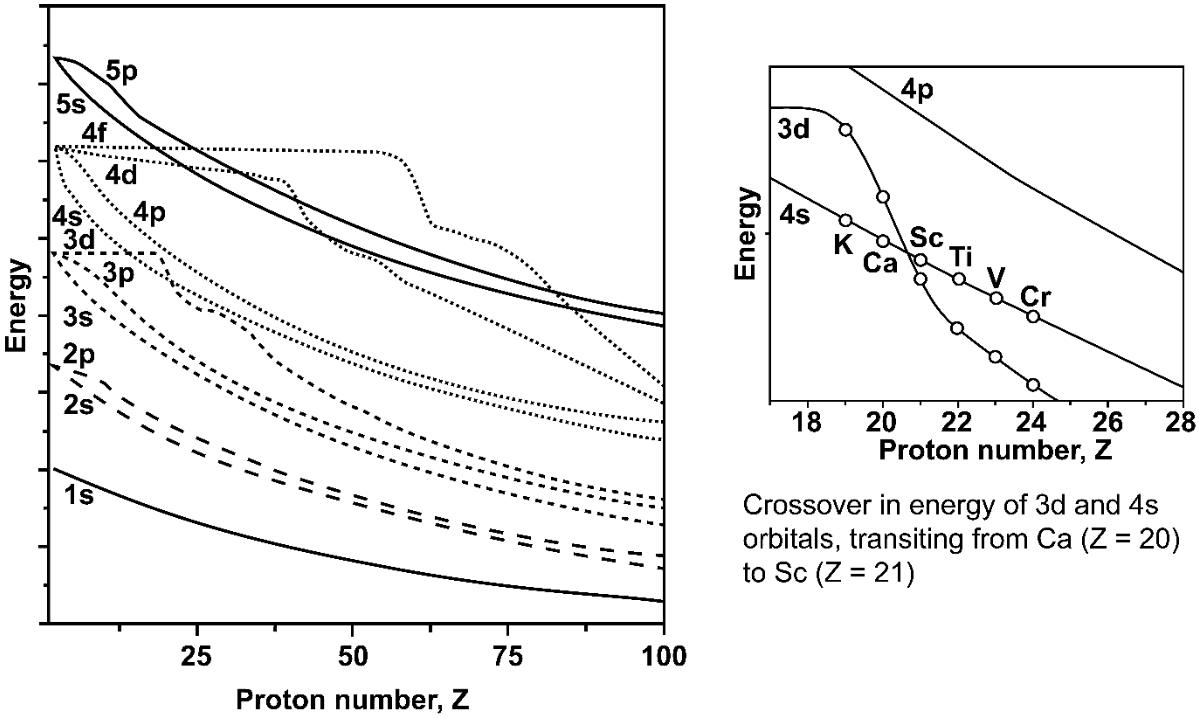
Can you define ionisation energy, atomic radius, ionic radius and electronegativity?
What are the factors that affect atomic properties (ionisation energy, atomic radius, ionic radius and electronegativity)?
How do these factors change across the period and down a group?
How do these atomic properties change across the period and down a group? Draw the graphs for these trends.
What are the anomalies in the trend of 1st IE across a period?
Can you compare between the radii of corresponding atoms and ions?

# ANNEX 1 HISTORICAL PERSPECTIVE OF ATOMIC STRUCTURE

| When? | Who? | What? | Diagram |
|---|---|---|---|
| 500BC | Democritus | • Postulated ***Particle*** theory of matter:<br>• Matter composed of small, indivisible particles called atoms. | – |
| 1803 | John Dalton | Postulated ***Atomic*** theory of matter.<br>• All matter is composed of atoms.<br>• Atoms cannot be made or destroyed.<br>• All atoms of the same element are identical.<br>• Different elements have different types of atoms. | – |
| 1897 | JJ Thomson | • Discovered ***electrons***.<br>• Proposed a ‘Plum Pudding’ model of the atom: electrons embedded in a cloud of positive charge.<br>Discovery of electrons:<br>Cathode Ray Tube Experiment<br>Millikan’s Oil Drop Experiment |  |
| 1911 | Ernest Rutherford | • Discovered ***protons***.<br>• Proposed that most of the mass of the atom is concentrated in a very small volume known as *nucleus*.<br>• Rutherford’s model of an atom depicts a nucleus at the centre of the atom, with electrons moving around the nucleus, like planets orbiting around a sun.<br>Discovery of protons:<br>Rutherford’s Gold Foil Experiment |  |
| 1913 | Niels Bohr | • Modifying Rutherford’s model, Bohr stated that **electrons** are **confined to well-defined circular orbits**, each having **discrete energy level**.<br>**(This is the model described at ‘O’ Level.) |  |
| 1927 | Erwin Schrodinger | • Using Louis de Broglie's 1924 proposal that **electrons behave as waves** in an atom, Schrodinger wrote out a wave equation for the electrons in an atom.<br>• Solutions of the Schrodinger equation describe the **energy level of each electron** and the **region an electron is likely to be found (called orbitals)** around the nucleus.<br>**(For ‘A’ Level, students need to know the shapes and relative energies of these orbitals.) |  <br>**one of the d-orbitals** |
| 1932 | James Chadwick | • Discovered ***neutrons***.<br>• Neutrons are **electrically neutral** particles **found in the nucleus of an atom, having the same mass as protons**. | – |

# ANNEX 2 ELECTRONIC CONFIGURATIONS OF D-BLOCK ELEMENTS

Up till Ca, the 4s orbital is lower in energy compared to the 3d orbitals. However, **from Sc** onwards, there is a crossover between the energies of the 3d and 4s orbitals (see Figure A below), and the **4s** becomes the **outermost (highest energy) orbital**, while the **3d** orbital is **penultimate** (2nd from the last). Hence, **when representing the electronic configuration** in writing, **3d is written before 4s**.



Crossover in energy of 3d and 4s orbitals, transiting from Ca (Z = 20) to Sc (Z = 21)

Figure A Crossover between energy of 3d and 4s orbitals between Ca and Sc

However, **when filling up the orbitals of an atom of a d-block element**, the **4s orbital is filled before the 3d**. For example, spectroscopic results show that Sc has the electronic configuration [Ar] $3d^1$ $4s^2$, instead of [Ar] $3d^3$ or [Ar] $3d^2$ $4s^1$. This is due to the **3d subshell being more compact than the diffuse 4s orbital**. The most probable distance of a 3d electron from the nucleus is less than that of a 4s electron i.e. the 3d electrons are more likely to be found closer to the nucleus (see Figure B), so two 3d electrons repel each other more strongly than two 4s electrons. Hence, **the more electrons occupying the 3d subshell, the larger the electron repulsion**.

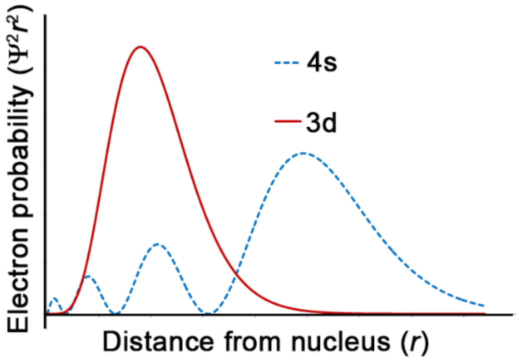


Figure B

Probability of finding an electron at different distances from the nucleus

For Sc, electronic configuration [Ar] $3d^1$ $4s^2$ is more favourable as it minimises the strong electron-electron repulsions in the 3d orbitals. Even though energy is required to have electrons populate the higher energy 4s orbital, the total energy of the atom is the least.