01 Atomic Structure & Physical Periodicity

GUIDING QUESTIONS

- What makes up an atom?
- How has the understanding of atomic structure developed and evolved?
- What is the evidence to show electrons in an atom exist in discrete energy levels?
- What do you understand by electronic configuration? How are the electrons arranged in the atoms of a given element?
- How is the arrangement of electrons of an element and its position in the Periodic Table related?
- What are the trends and variations in the physical properties in elements?
- How can the trends and variations in atomic and physical properties be explained?
- What are transition elements?
- Are there any trends/patterns in the properties of transition elements?

LEARNING OUTCOMES

Students should be able to:

- **1(a)** identify and describe protons, neutrons and electrons in terms of their relative charges and relative masses
- 1(b) deduce the behaviour of beams of protons, neutrons and electrons in an electric field
- **1(c)** describe the distribution of mass and charges within an atom
- **1(d)** deduce the numbers of protons, neutrons and electrons present in both atoms and ions given proton and nucleon numbers (and charge)
- **1(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
- 1(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
- **1(g)** describe the shapes of s, p and d orbitals (Refer also to Topic 23 Chemistry of the Transition Elements) [knowledge of wave functions is **not** required]
- **1(h)** state the electronic configuration of atoms and ions given the proton number (and charge)
- 1(i) explain the factors influencing the ionisation energies of the elements (see the *Data Booklet*)
- 1(j) deduce the electronic configurations of elements from successive ionisation energy data
- 1(k) interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table
- **5(a)** recognise variation in the electronic configurations across a Period and down a Group
- **5(b)** describe and explain qualitatively the general trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity (Refer also to Topic 2 Chemical Bonding for more on electronegativity)
 - (i) across a Period in terms of shielding and nuclear charge,
 - (ii) down a Group in terms of increasing number of electron shells, shielding and nuclear charge
- **6(a)** define the terms *relative atomic, isotopic,* molecular and formula mass (Refer to Topic 4 Reactions and Stoichiometry for molecular and formula mass)

- **6(c)** calculate the relative atomic mass of an element given the relative abundances of its isotopes
- **13(a)** explain that a transition element is a d block element whose atom has an incomplete d subshell, or which can give rise to cations with an incomplete d subshell
- **13(b)** state the electronic configuration of a first row transition element and its ions (see also 1(h))
- **13 (c)** explain why atomic radii and first ionisation energies of the transition elements are relatively invariant

REFERENCES

- 1. Peter Cann, Peter Hughes, Chemistry for Advanced Level, 1st Edition, John Murray, Chapter 2
- 2. E.N. Ramsden , A-level Chemistry, 4th Edition, Nelson Thornes, Chapter 2
- 3. Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 3rd Edition, McGraw Hill, Chapter 8
- 4. Gary L. Miessler, Donald A. Tarr, *Inorganic Chemistry*, 3rd Edition (international edition), Pearson Prentice Hall, Chapter 2, sections 2.2.3 & 2.2.4, pp. 34 to 43



1 THE STRUCTURE OF THE ATOM

1.1 The Discovery of the Subatomic Particles (Background Info)

The 5th century B.C. Greek philosopher *Democritus* proposed that one couldn't divide a piece of gold wire forever until there isn't any gold left as all matter consists of very small, indivisible particles. He called these particles *atomos*, meaning "uncuttable" or "indivisible". This concept remained undeveloped until nineteenth century.



Dalton's atomic theory may have been inspired by his favorite sport—lawn bowling.

In 1808, an English scientist and school teacher, *John Dalton* formulated the atomic theory that all matter is made up of atoms.

In 1897, J.J. Thomson proposed a model that described atoms as negatively charged electrons embedded in a sphere of positive charge, which was then known as the 'plum pudding' model.

In 1910, *Rutherford* observed that the majority of the α -particles passing through a thin sheet of gold foil went through with little deflection. But every now and then, he would observe great deflection. In some instances

the particle actually bounced back. This surprising discovery led to the theory that the positive charge in the atom is concentrated into an incredibly small nucleus right in the middle of it. The diameter of the nucleus is less than 10^{-5} of the atom.



Democritus believed in atoms a long time ago.

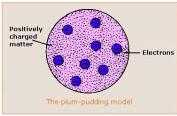


Figure 1. The plum-pudding model

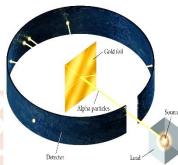


Figure 2. The gold foil experiment

Not until 1932 did the English physicist *James Chadwick* finally discover the neutron. He found it to be electrically neutral, having about the same mass as a proton. Together, the proton and neutron received the name "nucleon."



1.2 Atoms and the Properties of the Three Subatomic Particles

LO 1(a): identify and describe protons, neutrons and electrons in terms of their relative charges and relative masses

LO 1(c): describe the distribution of mass and charges within an atom

LO 1(d): deduce the numbers of protons, neutrons and electrons present in both atoms and ions given proton and nucleon numbers (and charge)

LO 1(e)(i): describe the contribution of protons and neutrons to atomic nuclei in terms of proton number and nucleon number

An **atom** is the smallest component of an element having the chemical properties of the element.

All atoms are made up of the same three subatomic particles - the electron, the proton and the neutron.

The protons and neutrons make up the nucleus of the atom while the electrons surround the nucleus. The protons and neutrons are sometimes referred to as **nucleons**.

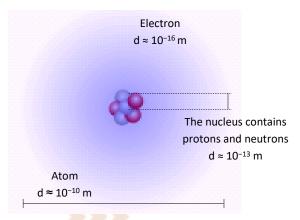


Figure 3. A schematic representation of an atom

The nucleus contains over 99.99% of the mass of an atom. This is due to the relatively large masses of the proton and neutron compared with the mass of the electron.

Table 1. Properties of the three subatomic particles.

property	proton	electron	neutron
relative charge	+1	-1	0
relative mass	17 9	1 1836	1

All atoms can be identified by the number of protons they contain. The chemical symbol is represented as



- A Nucleon number
- X Symbol for element
- Z Proton number

E.g., ¹⁶O has 8 protons, 8 electrons and 8 neutrons.

The proton number (Z) is the number of protons in the nucleus of each atom of an element.

In a neutral atom, the number of protons is equal to the number of electrons, so the proton number also indicates the number of electrons present in the atom. The chemical identity of an atom can be determined solely from its proton number.

The *nucleon number* (A), also called *mass number*, is the total number of neutrons and protons in the nucleus of an atom of an element.



1.3 Isotopes

LO 1(e)(ii): distinguish between isotopes on the basis of different numbers of neutrons present

Atoms of the same element do not all have the same mass. *Isotopes* are atoms of an element that have the same proton number but different nucleon numbers (or same number of protons but different number of neutrons).

Isotopes of an element have the **same** electronic configuration and chemical properties. They have **different** relative isotopic masses and physical properties.

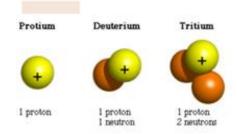


Figure 4. The nuclei of the three isotopes of hydrogen

Some common isotopes include: hydrogen (¹H, ²H, ³H), carbon (¹²C, ¹³C), oxygen (¹⁶O, ¹⁸O), sulfur (³²S, ³⁴S) and nitrogen (¹⁴N, ¹⁵N).

Isotopes may be stable or **unstable** (**radioactive**). E.g. the isotope 14 C decays by β -emission with a half-life of 5730 years.

When writing the chemical symbol for an element, it is not always necessary to write either or both the nucleon and proton numbers. E.g. ${}_{1}^{1}H$ may be written as ${}^{1}H$ or H. We assume the most abundant isotope is referred to when simply writing 'H' for example. However, when it is necessary to refer to a particular isotope of an element, the nucleon number as well as the proton number must be indicated e.g. if we want to refer to deuterium, then we should write ${}_{1}^{2}H$ for clarity's sake.

Exercise 1.1 (Worked Example)

Complete the following table with the no. of protons, neutrons and electrons for each particle.

		no. of protons	no. of electrons	no. of neutrons
(a	28 ₁₄ Si	THE CALCU		
(b	70 31Ga ³⁺	HWA CHUI	NG =	
(c	31 ₁₅ P ³⁻	INSTITUTI	O N	

Comments:

For each case, the subscript refers to the proton number (i.e. the number of protons present).

For (a), since it is a neutral atom, no. of protons = no. of electrons.

For (b), since it is positively charged, there should be 3 less electrons than protons. Hence, no. of electrons = 31 - 3 = 28.

For (c), since it is negatively charge, there should be 3 more electrons than protons. Hence, no. of electrons = 15 + 3 = 18.

The superscript refers to the nucleon number (i.e. the total number of protons and nucleons present). Thus, no. of neutrons = nucleon number - no. of protons.

For (a), no. of neutrons = 28 - 14 = 14

For (b), no. of neutrons = 70 - 31 = 39

For (c), no. of neutrons = 31 - 15 = 16

Answei	r:	F (197) T	35	
	Z ,,	no. of protons	no. of electrons	no. of neutrons
(a)	²⁸ Si	W A 14	14	14
(b)	⁷⁰ ₃₁ Ga ³⁺ <mark>↓</mark>	N S T I31 U T I	28	39
(c)	³¹ ₁₅ P ³⁻	15	18	16

Exercise 1.2

(a) Give the symbols of the elements (showing the nucleon numbers and charges) of the following three particles in the last column.

particle	protons	neutrons	electrons	answer
P	NSTITU	TIO ₈ N	6	
Q	7	7	10	
R	8	7	7	

(b) Use the *Data Booklet* to identify which are not the usual isotopes of the elements concerned.

[J00/I/1b]

Exercise 1.3 (Worked Example)

In 1999 Russian chemists claimed to be the first to identify atoms of a new element of proton number 114. This was produced by bombarding atoms of plutonium, Pu, with atoms of an isotope of a Group 2 element, **X**. The reaction taking place is as shown below.

$$^{244}_{94}$$
Pu + X $\rightarrow ^{289}_{114}$ [new element] + 3 neutrons $\binom{1}{0}$ n)

What is X?

A Mg B Ca C Sr D Ba

[N03/I/4]

Answer: B

Comments:

Interpreting the numbers given for the atom of plutonium, $^{244}_{94}$ Pu, we know that there are 94 protons (from the number at the bottom) and there are 150 neutrons.

If we look at the new element formed, we know that 20 protons (114 - 94) have been added into the new element. Referencing the periodic table, we can conclude that the element with proton number 20 is Calcium. The number of neutrons do not matter since the identity of an element is established by the number of protons.



..4 lons and deflection of charged particles

LO 1(b): deduce the behaviour of beams of protons, neutrons and electrons in an electric field

A **negative** ion (anion) has more electrons than protons. It is represented by ${}_{Z}^{A}X^{n-}$ where the number of electrons = Z + n.

E.g., ${}_{8}^{16}O^{2}$ has 8 + 2 = 10 electrons, 8 protons and 8 neutrons.

A **positive** ion (**cation**) has **fewer** electrons than protons. It is represented by ${}^{A}_{Z}X^{n+}$ where the number of electrons = Z - n.

E.g., $_{12}^{24}$ Mg²⁺has 12 – 2 = 10 electrons, 12 protons and 12 neutrons.

Because of their relative masses and charges, protons, electrons and neutrons behave differently when placed in an electric field. Protons are deflected to the **negative** plate, electrons deflected to the **positive** plate, and neutrons being neutral **pass straight through**.

Similarly, **cations** are deflected to the **negative** plate and **anions** are deflected to the **positive** plate.

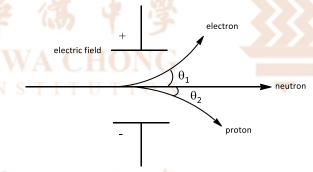


Figure 5. The behaviour of protons, neutrons and electrons in an electric field

In Figure 5, why is θ_1 greater than θ_2 ?

The electron has a much lower mass than the proton and is deflected to a much greater extent.

In general, we expect that the angle of deflection (θ) of a charged particle passing through an electric field to be directly proportional to the size of the charge (q), and inversely proportional to the mass (m).



Exercise 1.4 (Worked Example)

In a particular experimental set-up, protons are deflected through an angle of +15°. Assuming an identical set of experimental conditions, by what angles will the following particles be deflected? (D is deuterium, ²H, and T is tritium, ³H)

- D⁻
- T⁺
- He²⁺

[N12 /III/4(a)]

Strategy:

Since the angle of deflection is dependent on the $\frac{q}{m}$ ratio, you can present your answer in the form of a table, using the given angle of deflection of a proton as the reference point:

sp	ecies N S T I	TUTI <mark>q</mark> ratio	angle of deflection (θ)
proton, ¹ H ⁺		$\frac{q}{m} = \frac{+1}{1}$	θ = + 15° (given)
$D^- (= {}^2H^-)$. b 602	
$T^+ (= {}^3H^+)$	干的	7 7 3	
He ²⁺	HWA	CHONG	

Both D^- and He^{2+} have a $\frac{q}{m}$ ratio that is halved of that of ${}^1H^+$, thus the angle of deflection will be halved of that of ${}^1H^+$. However, as D^- is negatively charged, it will be deflected towards the positive plate (opposite to that of ${}^1H^+$). He^{2+} is positively charge and will be deflected towards the negative plate (similar to that of ${}^1H^+$).

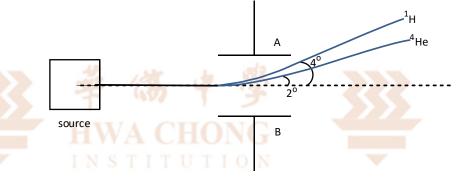
 T^+ has a $\frac{q}{m}$ ratio that is 1/3 of that of ${}^1H^+$, thus the angle of deflection will be 1/3 of that of ${}^1H^+$. Having a positive charge, it will be deflected to the negative plate.

Answer:

Allowel.		
species	q m ratio	angle of deflection (θ)
proton, ¹ H ⁺	$\frac{q}{m} = \frac{+1}{1}$	θ = +15° (given)
D ⁻ (= ² H ⁻)	$\frac{q}{m} = \frac{-1}{2}$	$\theta = \frac{-1}{2} \times 15 = -7.5^{\circ}$
T ⁺ (= ³ H ⁺)	$\frac{q}{m} = \frac{+1}{3}$	$\theta = \frac{+1}{3} \times 15 = +5.0^{\circ}$
He ²⁺	$\frac{q}{m} = \frac{+2}{4} = \frac{+1}{2}$	$\theta = \frac{+1}{2} \times 15 = +7.5^{\circ}$

Exercise 1.5

A plasma is a gaseous mixture in which the atoms have been completely stripped of their electrons, leaving bare nuclei. Because of possible use in controlled nuclear fusion reactions, plasma behaviour has been intensively studied. When passed between two plates carrying a certain electric charge, ¹H and ⁴He nuclei are deflected as follows:



Giving reasons for your answers, suggest

- (i) the polarity of plate A,
- (ii) why ¹H is deflected twice as much as ⁴He,
- (iii) the angles of deflection (to 1 decimal place) of

I: ²H nuclei,

II: ³He nuclei.

[J00/I/1 (c)]







2 QUANTIFYING THE MASSES OF ATOMS

In Section 1.2, we have looked at the composition of the atom. While the protons, neutrons and electrons have masses, they are so small such that it is impossible to weigh atoms individually except for highly specialised equipment. For day-to-day use in a laboratory, an easier way to quantify the masses of atoms is needed. And so we usually measure the *relative* masses of atoms, or how heavy one atom is compared to another atom.

2.1 Relative Masses of Atoms

LO 6(a)part: define the terms relative atomic, isotopic masses

We call this relative mass the relative atomic mass of an atom. We measure all relative masses against the mass of carbon-12, the most abundant isotope of carbon. Hence, the definition of relative atomic mass would look like the following:

Relative atomic mass,
$$A_{\rm r}=\frac{{\rm average\ mass\ of\ one\ atom\ of\ an\ element}}{\frac{1}{12}}\,{\rm x\ the\ mass\ of\ one\ atom\ of\ }^{12}{\rm C}$$

Note that the word 'average' is used in the definition above as the atomic mass of an atom takes into account the relative abundance of all possible isotopes of that element. We will deal with the idea of relative abundance of isotopes in the next section.

In cases where we want to deal very specifically with the atomic mass of one of the possible isotopes of an element, then we would call this the relative isotopic mass. The definition would look like the following:

Relative isotopic mass =
$$\frac{\text{mass of one atom of an isotope of an element}}{\frac{1}{12} \text{ x the mass of one atom of }^{12}\text{C}}$$

2.2 Relative Abundance of Isotopes

LO 6(c): calculate the relative atomic mass of an element given the relative abundances of its isotopes

Most elements consist of mixtures of isotopes. The abundance of each isotope in a mixture is called the *isotopic abundance* or the *relative abundance*.

For instance, chlorine has two isotopes: ^{35}Cl and ^{37}Cl (note that isotopes of the same element have the same atomic number). Naturally occurring samples of chlorine are found to contain ^{35}Cl and ^{37}Cl in a ratio of 3:1. Hence, the relative abundance of ^{35}Cl is 75% and the relative abundance of ^{35}Cl is 25%.

The relative atomic mass of an element is also the sum of the relative isotopic masses of each isotope multiplied by their relative abundances.



Using chlorine as an example,

Relative atomic mass, A_r of $Cl = \sum$ (relative isotopic mass x isotopic abundance)

$$= (35 \times 0.75) + (37 \times 0.25)$$

17 Cl chlorine 35.5

Exercise 2.1 (Worked Example)

The relative atomic mass of boron, which consists of the isotopes ${}^{10}_{5}B$ and ${}^{11}_{5}B$ is 10.8. What is the percentage of ${}^{11}_{5}B$ atoms in the isotopic mixture?

Solution:

Let α be the relative abundance of $^{11}_{5}B$ atoms.

∴ Relative abundance of 10 B atoms = (1 - a)

$$a(11) + (1 - a)(10) = 10.8$$

$$11a + 10 - 10a = 10.8$$

∴
$$a = 0.8$$

∴ Percentage of ${}^{11}_{5}B$ atoms in the mixture = 80.0%

Comments:

The relative abundances of ${}^{10}_{5}B$ and ${}^{11}_{5}B$ should add up to 1.

The sum of the relative isotopic masses of each isotope multiplied by their relative abundances will give the relative atomic mass of 10.8.

Exercise 2.2

1. The five isotopes of krypton occur in the following abundances:

isotopic mass	% abundance
80	2
T T 82 T O	12
83	12
84	57
86	17

Use these data to calculate a value, to one decimal place, for the A_r of atmospheric krypton.

2. Naturally occurring gallium, Ga, is a mixture of two isotopes, gallium-69 and gallium-71. Use this information, together with the *Data Booklet*, to calculate the percentage abundance of each isotope.



3 THE ARRANGEMENT OF THE ELECTRONS

LO 1(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

3.1 Principal Quantum Shell

In order to understand chemical reactions, one must understand how electrons are arranged in atoms. Much about what we know of electrons comes from quantum theory, which states that electrons can be described by four *quantum numbers*. (The only one required in the A-level syllabus is the principal quantum number, n, of only integer value of 1, 2, 3, ...)

The principal quantum number, n, describes the main energy level of an electron. It also indicates the relative size of the orbital and therefore relative distance of the electron from the nucleus. The larger the value of n, the higher the energy level and the further the electron is from the nucleus.

All atomic orbitals of the same value of n are said to be in the same quantum shell.

The **maximum** number of electrons that can occupy each principal quantum shell can be obtained by the formula **2n**².

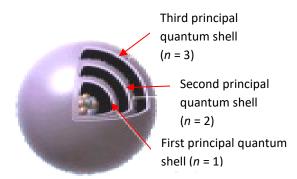


Figure 6. Principal quantum shells of an atom

Table 2 - Maximum number of electrons for each principal quantum shell.

principal quantum number (n)	1	2	3	4
maximum number of electrons (2n²)	2	8	18	32

3.2 Subshells

Each principal quantum shell can be subdivided into one or more **subshells** (or sub levels). The number of subshells in a principal quantum shell is the same as its principal quantum number.

Table 3 - The subshells in each principal quantum shell

principal quantum number, n	number of subshell	types of subshells	notation for subshells
1	WA CHO	S	1s
2	STI ² THTI	s, p	2s , 2p
3	3	s, p, d	3s , 3p , 3d,
4	4	s, p, d, f	4s , 4p, 4d, 4f

Subshells within a given quantum shell differ slightly in energy, with the energy of the subshell increasing according to the following order: s, p, d, f, i.e., energy of 4s < 4p < 4d < 4f.

3.3 Atomic Orbitals

Electrons are not randomly distributed in the region of space around the nucleus. They occupy specific volume regions, called **orbitals**, which have specific energies associated with them. According to the current quantum mechanical model of the atom, electrons in an atom **do not** remain in specific positions. They move in spaces defined by the Schrödinger's equation and Heisenberg's Uncertainty Principle (*NOT in A-level syllabus*). Instead of predicting the precise location for each electron in an atom, each electron is assigned to an energy level and orbital as it can only possess specific quantities of energy.

An atomic orbital is defined as the region of space with a 90% probability (or more) of finding an electron. This distribution of the probability of finding an electron at a certain position is the electron density.

- Each subshell (s, p, d, f) has one or more orbitals at the same energy level (degenerate) but different orientations in space.
- Each orbital can contain up to a **maximum of 2 electrons**. These electrons are of opposite spins.

Table 4.The number of orbitals and maximum number of electrons in each subshell

subshell	number of orbitals	maximum number of electrons in each subshell
S	1	2
р	3	6
d	5	10
f	7	14

The table below summarises the relationships among principal quantum shells, subshells, orbitals and number of electrons.

Table 5. Summary of the relationship between principal quantum shells, subshells and orbitals

principal quantum number, n	subshell	number of orbitals	maximum number of electrons in each principal quantum shell, $2n^2$
1	1s	1	2
2	2s 2p	1 3	8
3	3s 3p 3d	1 3 5	18
4	4s 4p 4d 4f	1 3 5 7	32

LO 1(g): describe the shapes of s, p and d orbitals (Refer also to Topic 23 Chemistry of the Transition Elements) [knowledge of wave functions is **not** required]

3.3.1 The s Orbital

Each **s subshell** has **only one s orbital**. All s orbitals are **spherical** in shape with no nodal plane (region of zero electron density). The probability of finding an electron at a given distance from the nucleus is the same regardless of the direction from the nucleus. The size of s orbitals increases with the principal quantum number, i.e., 1s < 2s < 3s,...

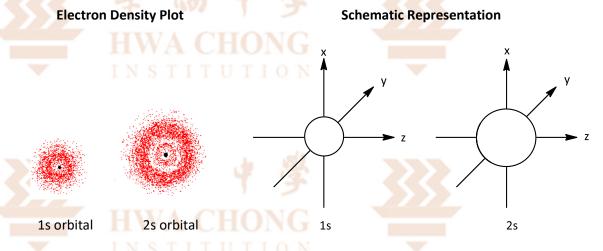


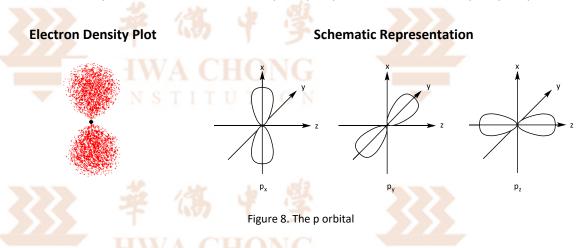
Figure 7. The s orbital

3.3.2 The p Orbital

Each **p subshell** has **three p orbitals.** Since each orbital can hold up to **2** electrons, each p **subshell** can hold up to **6** electrons. There are no p orbitals in the first quantum shell.

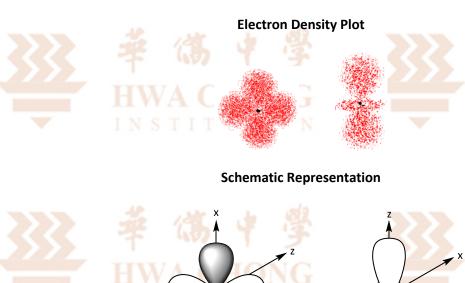
The **p orbital** is **dumb-bell** in shape. Each p orbital consists of two lobes with a region of zero electron density (node) between them centered on the nucleus.

The three p orbitals in a certain quantum shell are **identical** in **size** and **shape** but differ in their **spatial orientation**. The three p orbitals are represented as p_x , p_y , p_z , where the subscripts denote the axes along which the orbitals are orientated. The three p orbitals are **degenerate**, i.e. at the same energy level. The size of p orbitals increases with the principal quantum number, i.e. 2p < 3p < 4p.



3.3.3 The d Orbital

Each **d subshell** has **five d orbitals.** Since each orbital can hold **a maximum of 2** electrons, each d **subshell** can hold up to **10** electrons. There are **five** d orbitals: d_{xy} , d_{xz} , d_{yz} , d_{z}^2 , $d_{x^2-y}^2$. The five d orbitals are also **degenerate**. The size of d orbitals increases with the principal quantum number, i.e. 3d < 4d < 5d ...



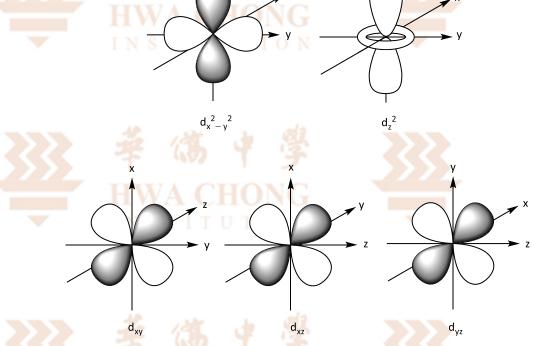


Figure 9. The d orbitals (Note: It is not necessary to colour/shade the orbitals)

Exercise 3.1

What kind of orbital must an electron with the principal quantum number n = 2 occupy?

- A a spherically-shaped orbital
- B either an s or p orbital
- **C** the orbital closest to the nucleus
- D a dumb-bell-shaped orbital

[N1995/IV/3; N2000/III/2]

3.4 Electronic Configuration

The electronic configuration of an atom shows the distribution of electrons in various orbitals in an atom.

Rule 1: The Aufbau or 'Building-up' Principle

Electrons in their ground states (i.e. when they are not excited) occupy orbitals **in order of energy levels**. The orbital with the **lowest** energy is always filled **first**.

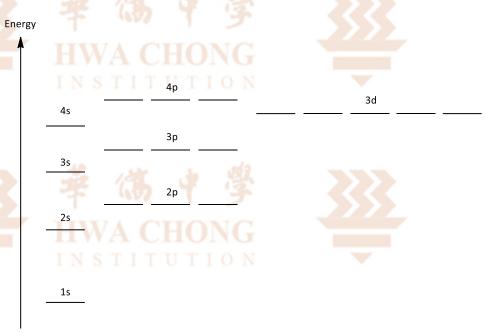
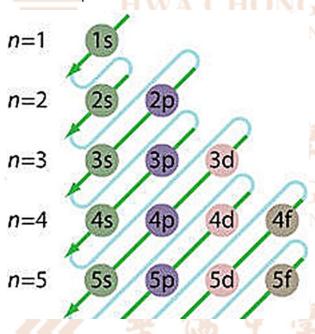


Figure 10. Relative energies of the orbitals for the first 20 elements

Figure 11 below shows the **sequence** in which the electron orbitals are populated with electrons in an atom as the proton number increases.



The 1s subshell is the first to be filled, then the 2s orbital, the 2p orbitals and then the 3s orbitals and so on. Electrons only enter higher energy levels after lower energy levels have been filled.

For example, nitrogen, N, with atomic number 7 will have 2 electrons in 1s orbital and 2 electrons in 2s orbital and 3 electrons in 2p orbitals.

The electronic configuration of N is represented as 1s² 2s² 2p³.

Figure 11. Mnemonic for the order of filling electrons into the orbitals

Rule 2: Hund's Rule of Multiplicity

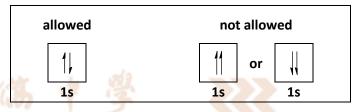
When filling subshells that contain more than one orbital with the same energy (p, d and f subshells), each orbital must be singly occupied before electrons are paired.

E.g. for $_7N$, each of the three 2p orbitals will be filled with 1 electron. To reflect this, we can write the electronic configuration of N as $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$.

Rule 3: Pauli Exclusion Principle

An orbital cannot hold more than two electrons and the two electrons sharing the same orbital must have **opposite spins**. This can be shown in an electron-in-box diagram where the **box** represents the **orbital** and the **arrows** within it represent the **electrons**. The direction of the arrow (up or down) indicates the spin of the electron.

Thus,



				7
Exercise	3.2 (Work	d Example)		20
Element	electronic configuration	INCT	electron-in-box diagram	-
₆ C	1s ² 2s ² 2p ²	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1	Tt.
8O	1s ² 2s ² 2p ⁴	1) 1) 1) 1s 2s 2p	<u>, </u>	101
₁₂ Mg	1s ² 2s ² 2p ⁶ 3s ²	1 1 1 1 1 1 1 1 1 2 2 2 2 p		t I
21 S C	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹ 4s ²	1 1 1 1 1 1 1 1 1 2s 2p		ner
₂₅ Mn	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁵ 4s ²	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		m
₂₄ Cr*	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁵ 4s ¹	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		SS
₂₇ C0	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁷ 4s ²	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	07
₂₉ Cu*	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ¹	1) 1) 1) 1s 2s 2p		Tr
35Br	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ² 4p ⁵	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		, I

Chromium and copper are two exceptions to this general pattern:

- Electronic configuration of Cr is 1s²2s²2p⁶3s²3p⁶3d⁵4s¹ (not 1s²2s²2p⁶3s²3p⁶3d⁴4s²)
- Electronic configuration of Cu is 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹ (not 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁹ 4s²)

The explanation for these exceptions are not required in the A-level syllabus but they are a result of the effects of increasing nuclear charge on the 3d and 4s orbitals and the repulsions between electrons sharing the same orbital. For a full explanation with references to the published papers, please refer to 'Inorganic Chemistry, 3rd Ed, G.L. Miessler & D.A. Tarr, Pearson, Prentice Hall, Chapter 2, sections 2.2.3 & 2.2.4, pgs 34 to 43.

LO 1(h): state the electronic configuration of atoms and ions given the proton number (and charge)

When writing the electronic configuration of a cation:

- first write the electronic configuration of the atom,
- then **remove** the number of electrons equal to the positive charge, starting from the highest energy (outermost) subshell.
- From Scandium onwards, the 4s electrons are removed first in the formation of positive ions. E.g., the electronic configuration of 29Cu is 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹ while that of 29Cu²⁺ is 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁹.

When writing the electronic configuration of an anion:

- first write the electronic configuration of the atom,
- then **add** <u>number of electrons equal to the negative charge</u>, starting from orbitals of lowest energy available.

E.g., the electronic configuration of $_{16}S$ is $1s^2 2s^2 2p^6 3s^2 3p^4$, while that of $_{16}S^{2-}$ is $1s^2 2s^2 2p^6 3s^2 3p^6$.

Exercise 3.3 (Worked Example)

Complete the table below.

ion	electronic configuration of atom	electronic configuration of ion		
₁₁ Na ⁺	STITUTION			
₂₆ Fe ²⁺				
₁₇ C <i>l</i> ⁻				

Comments

The electronic configurations of the atoms and ions can be obtained by applying the rules stated above.

For Na⁺ and Fe²⁺, remove 1 and 2 electrons respectively from the highest energy subshell. One 3s electron will be removed from Na and two 4s electrons will be removed from Fe.

Answer:

ion	electronic configuration of atom	electronic configuration of ion			
₁₁ Na ⁺	1s ² 2s ² 2p ⁶ 3s ¹	1s ² 2s ² 2p ⁶			
₂₆ Fe ²⁺	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁶ 4s ²	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁶			
₁₇ C <i>l</i> -	1s ² 2s ² 2p ⁶ 3s ² 3p ⁵	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶			

Exercise 3.4

Which of the following particles would, on losing an electron, have a half-filled set of p orbitals?

Α

 $\mathsf{C}^{\scriptscriptstyle{-}}$

.

 N^-

C

O⁺

D

0-

[J93/IV/2]

.5 Electronic Configuration and Periodicity

LO 5(a): recognise variation in the electronic configurations across a Period and down a Group

In the Periodic Table, the arrangement of the elements was proposed according to their electronic configurations. It is divided into the s-block, the d-block and the p-block. The electronic configurations of elements will affect their physical and chemical properties.

Table 6(a). The valence electronic configuration of each group in the periodic table

group Number	valence shell electronic configuration	block
7 1 (197)	ns¹	s block
2	ns²	s-block
13	ns ² np ¹	
14	ns²np²	p-block
15	ns²np³	
16	ns²np⁴	
17	ns²np⁵	
18	ns²np ⁶	

Table 6(b). The valence electronic configuration for elements in Periods 2 & 3

Period	Li	Be	В	С	N	0	F	Ne
2	[He]2s ¹	[He]2s ²	[He]2s ² 2p ¹	[He]2s ² 2p ²	[He]2s ² 2p ³	[He]2s ² 2p ⁴	[He]2s ² 2p ⁵	[He]2s ² 2p ⁶
Period	Na	Mg	Al	Si	Р	S	C <i>l</i>	Ar
3	[Ne]3s ¹	[Ne]3s ²	[Ne]3s ² 3p ¹	[Ne]3s ² 3p ²	[Ne]3s ² 3p ³	[Ne]3s ² 3p ⁴	[Ne]3s ² 3p ⁵	[Ne]3s ² 3p ⁶

Note: For simplicity, [He] and [Ne] are used to represent the configuration $1s^2$ and $1s^22s^22p^6$ respectively. Do not use these symbols when asked to write electronic configuration in examinations.

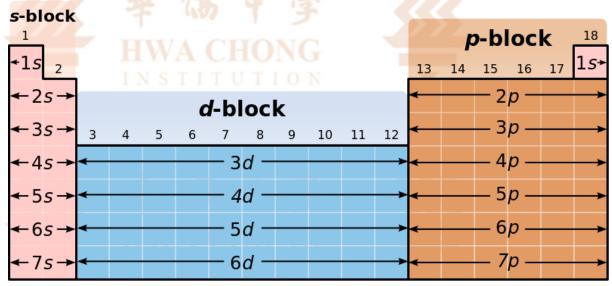


Figure 12. Periodic table illustrating how elements are grouped according to their valence subshells



LO 13(a): explain that a transition element is a d block element whose atom has an incomplete d subshell, or which can give rise to cations with an incomplete d subshell

LO 13(b): state the electronic configuration of a first row transition element and its ions (see also 1(h))

By definition,

A **transition element** is a <u>d block element</u> whose <u>atom</u> has an <u>incomplete d subshell</u>, or which can give rise to cations with an incomplete d subshell.

As a result, even though Zn is a d-block element, it is not considered to be a transition element because Zn has 3d¹⁰ configuration and forms only Zn²⁺ ion which has 3d¹⁰ configuration.

Exercise 3.5

Which of the following corresponds to the configuration of the three electrons of highest energy for the ground state of an element in Group 13?

 $1s^2 2s^1$

В

 $2s^1 2p^2$

C

 $3p^3$

 $4s^2 4p^1$ D

[N1985/III/3; J1989/III/3]





PERIODIC TRENDS IN ATOMIC AND IONIC RADII

LO 5(b)part: describe and explain qualitatively the general trends and variations in atomic radius, ionic radius, first ionisation energy

(i) across a Period in terms of shielding and nuclear charge,

(ii) down a Group in terms of increasing number of electron shells, shielding and nuclear charge

In explaining periodic trends in atomic and ionic radii, two fundamental considerations are important:

(i) number of quantum shells

The **number of quantum shells** determine how far the outermost electron is from the nucleus. The further the outermost electron is from the nucleus, the weaker the attraction between the outermost electron and the nucleus.

(ii) effective nuclear charge

The **effective nuclear charge**, **Z**_{eff}, is the **net nuclear charge** experienced by an **outer electron**. It is dependent on:

- (a) **Nuclear charge (Z)**: The nuclear charge is dependent on the number of protons. The larger the number of protons, the greater the nuclear charge and the attraction for the outermost electrons by the nucleus.
- (b) **Shielding** or **screening effect (S)**: Presence of inner-shell electrons reduces the electrostatic attraction between the outermost electrons and the nucleus.

Electrons in the same quantum shell do exert some shielding effect on each other.*

*For example, electrons in the 2p subshell are slightly shielded by electrons in the 2s subshell. Electrons in the same orbital also provide a little shielding effect on each other due to inter-

electronic repulsion.

However this shielding effect is small compared to that by the inner core electrons.

*Order of shielding effect by electrons in the same quantum shell: s > p > d > f.

Since shielding effect decreases the attraction between the outer shell electron and the nucleus, $\mathbf{Z}_{\text{eff}} = \mathbf{Z} - \mathbf{S}$.

4.1 Trend in Atomic Radius

Down the Group:

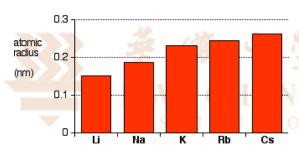


Figure 13. Atomic radii of Group 1 elements

General Trend:

Atomic radius increases down the group.

Reason:

As the number of quantum shells increases the outermost electrons are further away from the nucleus, hence the atomic radius increases. Both the nuclear charge and shielding effect increase down the group, hence the effective nuclear charge differs little down the group.

Hence the number of quantum shells is the more important factor.

Across Periods 2 and 3:

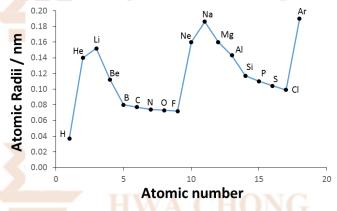


Figure 14. Atomic radii of period 2 & 3 elements

Why are the atomic radii of the noble gases so large?

The term atomic radius does not mean the same thing for every element. The atomic radii given for He, Ne and Ar in the *Data Booklet* are labelled van der Waals' radii, rather than covalent radii (see Chapter 02 Section 4.2 for explanation). Ar, for instance, does not form compounds, so it will not have a covalent radius. The van der Waals' radius of an atom is always larger than the covalent radius, which explains the anomalously high atomic radii of the noble gases in the graph above.

General Trend:

Atomic radius decreases across the period.

Reason:

- nuclear charge increases due to the increase in the number of protons in the nucleus
- shielding effect remains relatively constant (as the electrons are added to the same outermost shell)
- effective nuclear charge increases, resulting in stronger electrostatic forces of attraction between the nucleus and the outermost electron
- outermost electrons are pulled closer to the nucleus and hence a decrease in the atomic radius

Across the First Row Transition Elements:

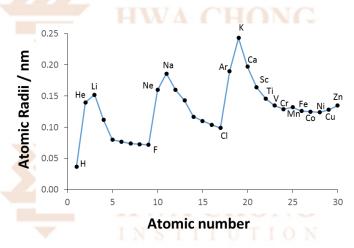


Figure 15. Atomic radii across periods 2, 3 and the first row transition elements

General Trend:

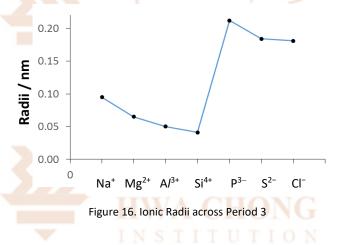
Atomic radius is relatively invariant.

Reason:

- nuclear charge increases due to increasing number of protons
- electrons are added to the inner
 3d subshell, which contributes to
 the shielding effect
- shielding effect increases thereby nullifying, to a considerable extent, the influence of each additional proton in the nucleus
- effective nuclear charge remains almost constant















Ionic radius of cations:

$$Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$$

Ionic radius of anions:

$$P^{3-} > S^{2-} > Cl^{-}$$

The ions, Na⁺, Mg²⁺, A l^{3+} and Si⁴⁺ are said to be **isoelectronic** as they have the **same number of electrons**, which is 10. Similarly P³⁻, S²⁻ and Cl^- are **isoelectronic** as they have 18 electrons each. Across the two isoelectronic series (Na⁺ to Si⁴⁺ and P³⁻ to Cl^-), nuclear charge **increases** and **shielding effect** is the same (due to same number of electrons).

This results in an **increase** in the effective nuclear charge and a stronger attraction between the outermost electrons and the nucleus, hence a **decrease** in ionic size across each series.

There is a sharp increase in ionic radius from the cationic series of Na⁺ to Si⁴⁺ to the anionic series of P³⁻ to Cl⁻, because the anions have one more quantum shell of electrons than the cations.



5 Ionisation Energy (IE)

5.1 Definitions

First ionisation energy is the energy needed to remove 1 mole of electrons from 1 mole of gaseous atoms to form 1 mole of unipositively charged gaseous ions.

$$X(g) \rightarrow X^{+}(g) + e^{-}$$
 1st IE

Examples:
$$Na(g) \rightarrow Na^{+}(g) + e^{-}$$
 1st IE of Na

$$Fe(g) \rightarrow Fe^+(g) + e^-$$
 1st IE of Fe

Second ionisation energy is the energy required to remove 1 mole of electrons from 1 mole of unipositively charged gaseous ions to form 1 mole of gaseous ions with double positive charge.

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

Examples:
$$Na^+(g) \rightarrow Na^{2+}(g) + e^ 2^{nd}$$
 IE of Na $Fe^+(g) \rightarrow Fe^{2+}(g) + e^ 2^{nd}$ IE of Fe

Similarly, n^{th} ionisation energy is the energy needed to remove 1 mole of electrons from 1 mole of gaseous ions with (n-1)+ charge to form 1 mole of gaseous ions with n^+ charge.

$$X^{(n-1)+}(g) \to X^{n+}(g) + e^ n^{th} IE$$

Factors affecting ionisation energy of an atom:

- number of quantum shells
 The <u>larger the number of quantum shells in an atom</u>, the further the electron is from the nucleus and hence experiences weaker nuclear attraction and is easier to remove, hence the <u>lower the ionisation energy</u>.
- effective nuclear charge, Z_{eff}
 The <u>higher the effective nuclear charge</u>, the stronger the attractive forces between the nucleus and the electrons to be removed, hence the <u>greater the ionisation energy</u>.

5.2 Trend in the Successive Ionisation Energies of the Same Element

For the same element, ionisation energies always increase in the following order:

$$|E_1 < |E_2 < |E_3 < |E_4 < ...$$

Reason:

When an electron is removed from a neutral atom, the number of protons that exert an attraction for the remaining electrons remains the same. However, the shielding effect (or mutual electrostatic repulsion) among the remaining electrons in the outermost shell is reduced since there is now one less electron. Hence effective nuclear charge increases. More energy is needed to remove another electron from the more positively charged ion, and hence a higher ionisation energy.

Application of successive ionisation energy values

LO 1(j): deduce the electronic configurations of elements from successive ionisation energy data
LO 1(k): interpret successive ionisation energy data of an element in terms of the position of that element within the
Periodic Table

Successive ionisation energy values can be used to determine the electronic configuration of atoms and hence the identity of the element.

E.g., the ground state electronic configuration of magnesium is 1s² 2s² 2p⁶ 3s².

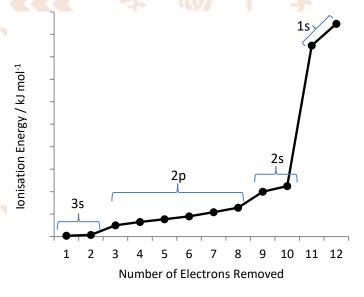


Figure 17. Successive ionisation energies of magnesium







- the **first big** increase from the **2**nd to **3**rd ionisation energies:
 - implies that the **third** electron is in an **inner** quantum shell, and thus there are **two** electrons in the outermost or valence 3s subshell.

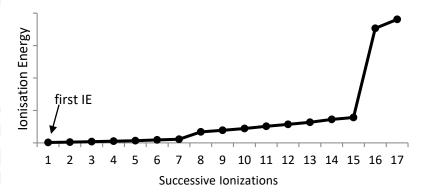
Conclusion: Mg is a Group 2 element.

- the gradual increase from the 3rd to 10th ionisation energies:
 - implies that the next 8 electrons are removed from the second quantum shell.
 - a **slightly** greater increase from the **8**th to **9**th ionisation energies as more energy is required to remove the **2s** electrons, which are closer to the nucleus compared to the **2p** electrons.
- the second big increase from the 10th to 11th ionisation energies
 - implies that the **last** two electrons are in the first (**inner most**) quantum shell.

Exercise 5.1 (Worked Example)

Identify the group number of the element for each set of ionisation energies.

(i) A



- (ii) **B**: successive ionisation energies (in kJ mol⁻¹): 1060, 1900, 2920, 4960, 6280, 21 200
- (iii) **C**: successive ionisation energies (in kJ mol⁻¹): 687, 1577, 3232, 4355, 16 091, 19 784.

Answers:

- (i) A: Group 17
- (ii) B: Group 15
- (iii) C: Group 14

Comments:

For this question, look for the first big increase in ionisation energy which would signal that there is a change in quantum shell.

In (i), the first big increase in ionisation energy between electron 7 and 8, indicating that there are 7 electrons in the outer most shell of **A**.

For (ii) and (iii) find the difference between each successive ionisation.

For (ii), the biggest increase in ionisation energy occurs between electron 5 and 6. This shows that there are 5 electrons in the outermost quantum shell.

Similarly for (iii), there are 4 electrons in the outermost quantum shell.

Exercise 5.2

The use of the Data Booklet is relevant to this question.

The successive ionisation energies, in kJ mol⁻¹, of an element X are given below:

870 1800 3000 3600 5800 7000 13200

What is X?

 $\label{eq:alpha} \textbf{A} \qquad _{33} As \qquad \qquad \textbf{B} \qquad _{40} Zr \qquad \qquad \textbf{C} \qquad _{52} Te \qquad \qquad \textbf{D} \qquad _{53} I$

[J92/IV/4; N2002/I/14; J2003/I/4]



.3 Trend in the First Ionisation Energies of Different Elements

LO 1(i): explain the factors influencing the ionisation energies of the elements (see the Data Booklet)

Down the Group:

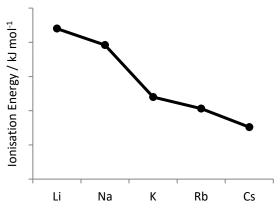


Figure 18. First ionisation energy trend down a group

General Trend:

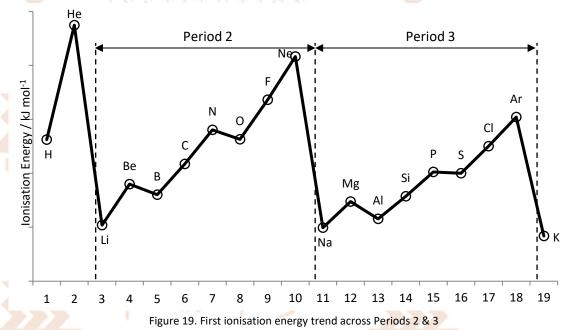
In general, **first ionisation energy** of elements **decreases** down a group.

Reason:

Down the group, the number of quantum shells of electrons increases, hence the outermost electrons are further from the nucleus. Therefore, the electrostatic forces of attraction between the nucleus and the outermost electron is weaker and less energy is required to remove this electron.

Both the nuclear charge and shielding effect increase down the group, so the effective nuclear charge differs little down the group. Hence, the number of quantum shells is the more important factor.

Across Periods 2 and 3:



General Trend:

In general, first ionisation energy of elements increases across a period.

Reason:

Across the period, nuclear charge **increases** and shielding effect remains **relatively the same**. Hence the effective nuclear charge **increases** and the electrostatic forces of attraction between the outermost electrons and the nucleus **become stronger**, so more energy is required to remove the outermost electron.



Two Anomalies:

• Small dip between Group 2 and Group 13 elements

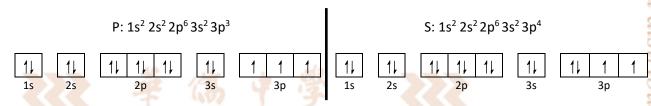
Al has lower 1st ionisation energy than Mg.

Al:
$$1s^2 2s^2 2p^6 3s^2 3p^1$$

The 3p subshell of Al is **further away** from the nucleus than the 3s subshell. There is weaker attraction between the nucleus and the outermost electron. Hence less energy is required to remove the 3p electron from Al, resulting in a lower ionisation energy for Al.

• Small dip between Group 15 and Group 16 elements S has lower 1st IE than P.

Consider the electronic configurations of P and S.



All the 3p electrons in P are **unpaired**. In S, two of the 3p electrons are **paired**. There is some **interelectronic repulsion** between the paired electrons in the 3p subshell in S. Thus, less energy than expected is required to remove one of these paired electrons from S.

Across Transition Elements:

LO 13(c): explain why atomic radii and first ionisation energies of the transition elements are relatively invariant

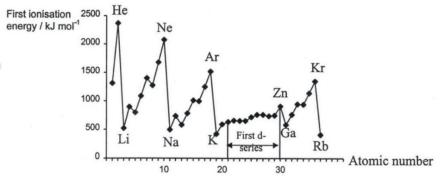


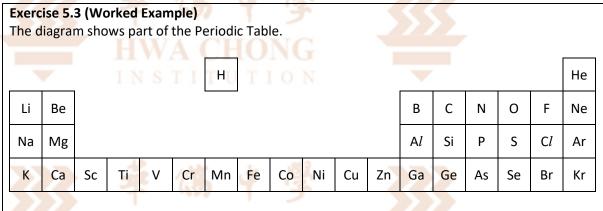
Figure 20: First ionisation energy trend across the first transition elements series

General Trend:

First ionisation energy remains relatively invariant.

Reason:

- 1st ionisation energy involves removal of a 4s electron
- The nuclear charge increases due to increasing number of protons while additional electrons are added to the inner 3d subshell, which contributes to the shielding effect. The shielding effect increases thereby nullifying, to a considerable extent, the influence of each additional proton in the nucleus
- Effective nuclear charge remains almost constant. Thus, energy required to remove the outermost electron of each succeeding element remains relatively invariant



Which element in the diagram has the largest atomic radii?

B K

Sc

[N10/I/1]

Answer: B

Comments:

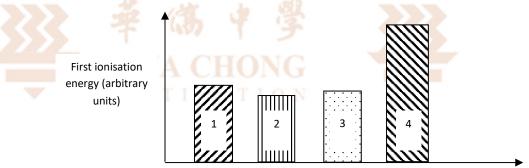
The atomic radius of an atom decreases across the period due to the increasing effective nuclear charge. K is the only group 1 element here, thus the answer is B.

Exercise 5.4

Use of the Data Booklet is relevant to this question.

The bar chart gives some information about the first ionisation energies of elements, numbering from 1 to 4.

The elements are adjacent to one another in the Periodic Table with increasing proton number either across a period from left to right, or down a group.



What could these elements be?

B, C, N, O Α

Co, Ni, Cu, Zn В

C Mg, Ca, Sr, Ba

Si, P, S, C*l*

[N09/I/17]



LOOKING AHEAD

In this topic, we have looked at the structure of the atoms, the shapes and energies of the atomic orbitals, as well as the energies associated with removal of electrons from isolated gaseous atoms. In the following topic, we will be applying these concepts to help us understand how atoms interact to form chemical bonds.

A particularly important and useful concept is that of effective nuclear charge. We have used this concept of effective nuclear charge quite extensively in this last section of Topic 1. So far, we have only considered isolated gaseous atoms and discussed the impact of the effective nuclear charge on removing electrons from these atoms. In reality, the electrostatic forces due to the effective nuclear charge of the atom extend beyond its outermost electron.

When two atoms are in proximity, the nucleus of each atom exerts an attractive force on its own electrons as well as the electrons of the other atom. The same nucleus also exerts a repulsive force on the nucleus of the other atom. This attraction and repulsion on the electrons and nucleus of the other atom by the first atom result in a net attractive force on the electrons of the other atom. It is quite clear then that the effective nuclear charge of the first atom would play a significant role in attracting the electrons of the other atom.

This attraction was first referred to as 'oxygenicity' in 1809 by Avogadro and Bezelius adopted the term 'electronegativity' in 1811. The concept of 'electronegativity' was finally defined and quantified by Linus Pauling in 1932. (Interesting fact: Linus Pauling is the only person to be awarded two unshared Nobel Prizes.)

Electronegativity quantifies the attractive force one atom exerts on the electrons of another atom in a chemical bond. A larger number implies a larger force of attraction towards the electrons. We will have a more thorough discussion of the concept of electronegativity when we deal with chemical bonding in Topic 2.

