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 22 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 electronic 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 what is meant by a transition element, in terms of d-block elements forming one or more stable ions with partially filled d subshells

13(b) state the electronic configuration of a first row transition element and its ion

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

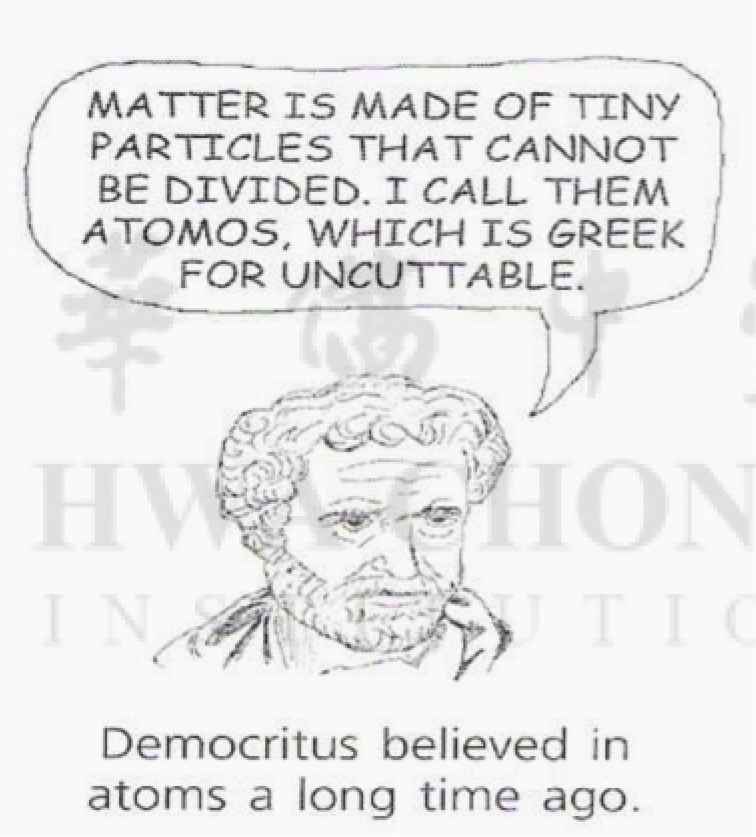
REFERENCES

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

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.

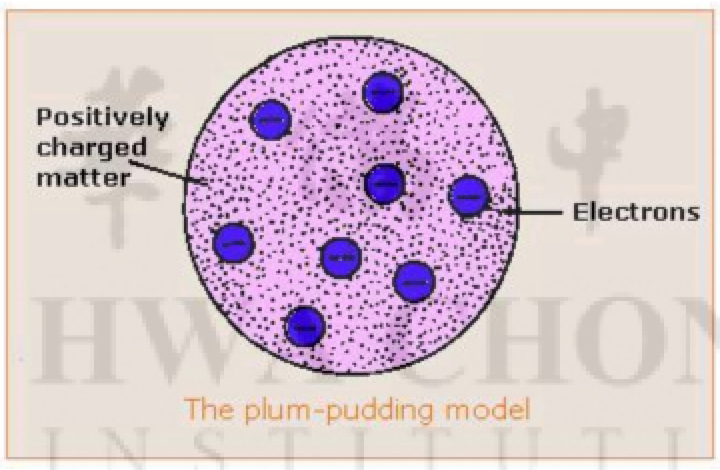


Figure 1. The plum-pudding model

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.

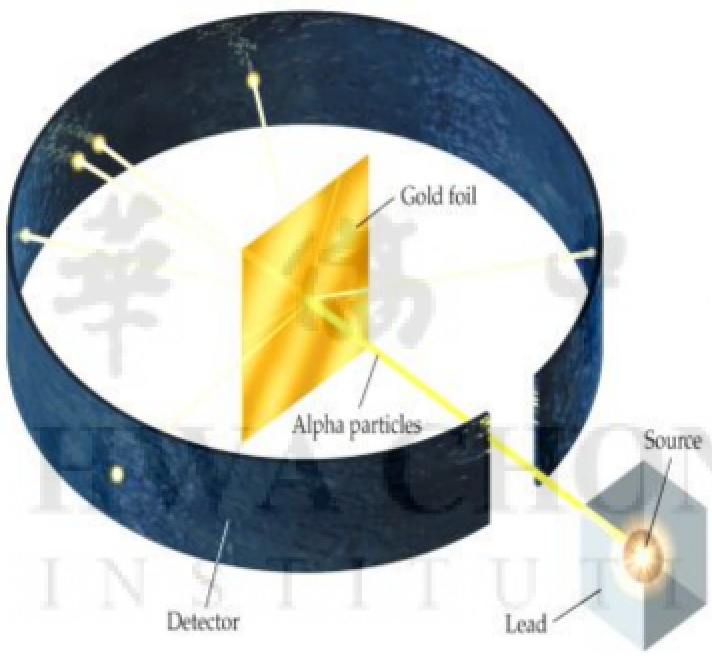


Figure 2. The gold foil experiment

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

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**.

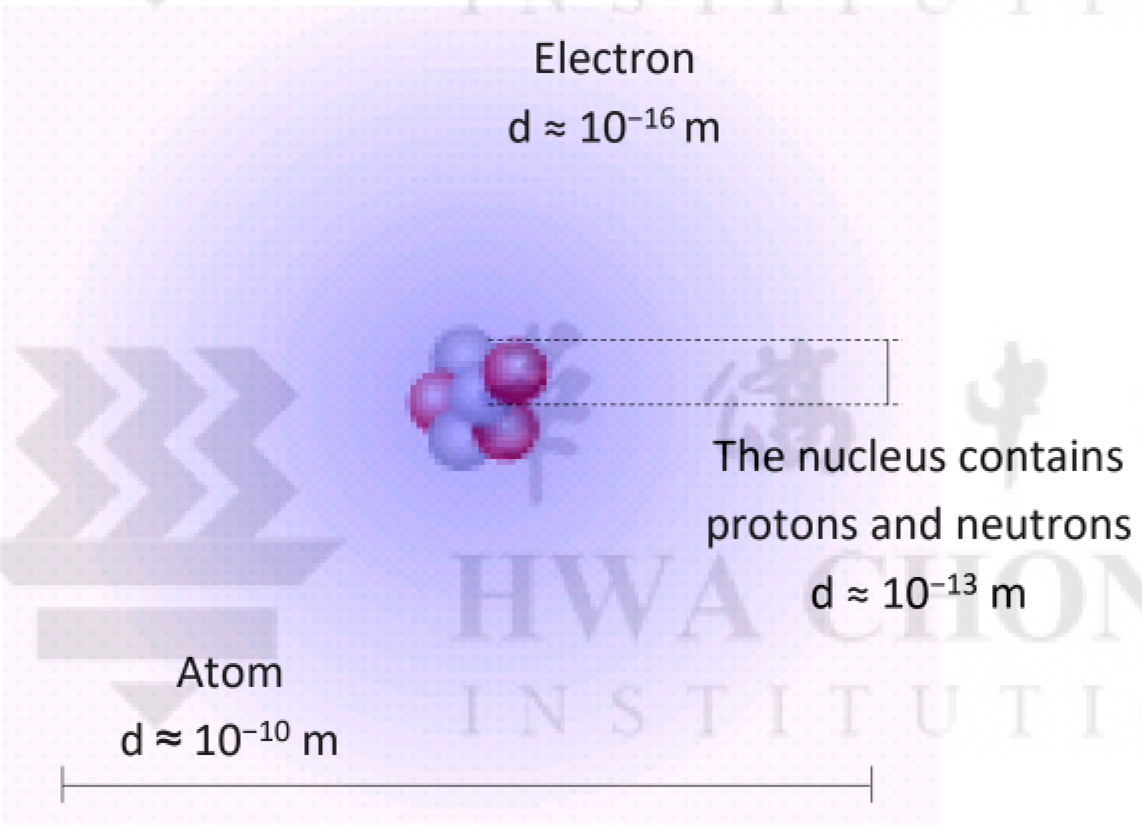


Figure 3. A schematic representation of an atom

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	1	$\frac{1}{1836}$	1

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

$${}^{A}_{Z}\mathrm{X}$$

A	Nucleon number
X	Symbol for element
Z	Proton number

E.g., ${}^{16}_{8}\mathrm{O}$ 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

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.

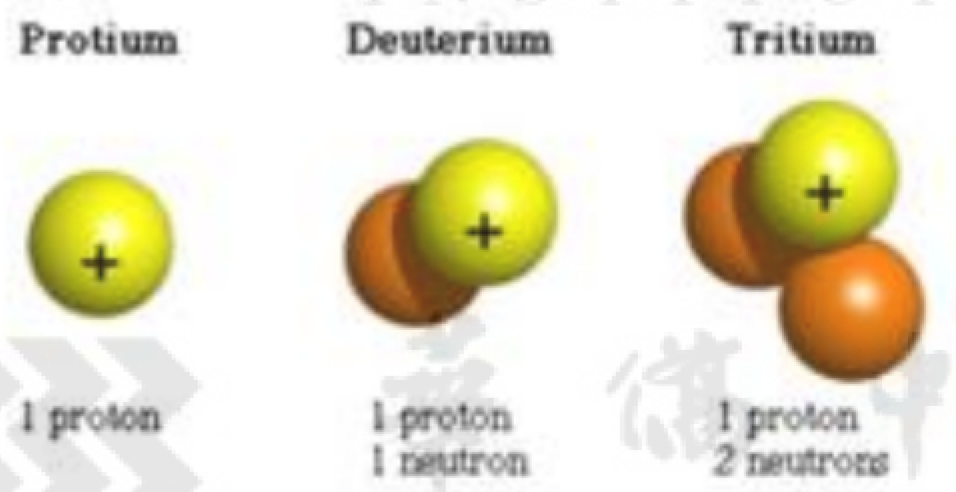


Figure 4. The nuclei of the three isotopes of hydrogen

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

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 ${}^{2}_{1}H$ for clarity's sake.

1.4 Ions and deflection of charged particles

A **negative** ion (**anion**) has **more** electrons than protons. It is represented by ${}^{A}_{Z}X^{n-}$ where the number of electrons = Z + n.
E.g., ${}^{16}_{8}O^{2-}$ 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., ${}^{24}_{12}Mg^{2+}$ 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.

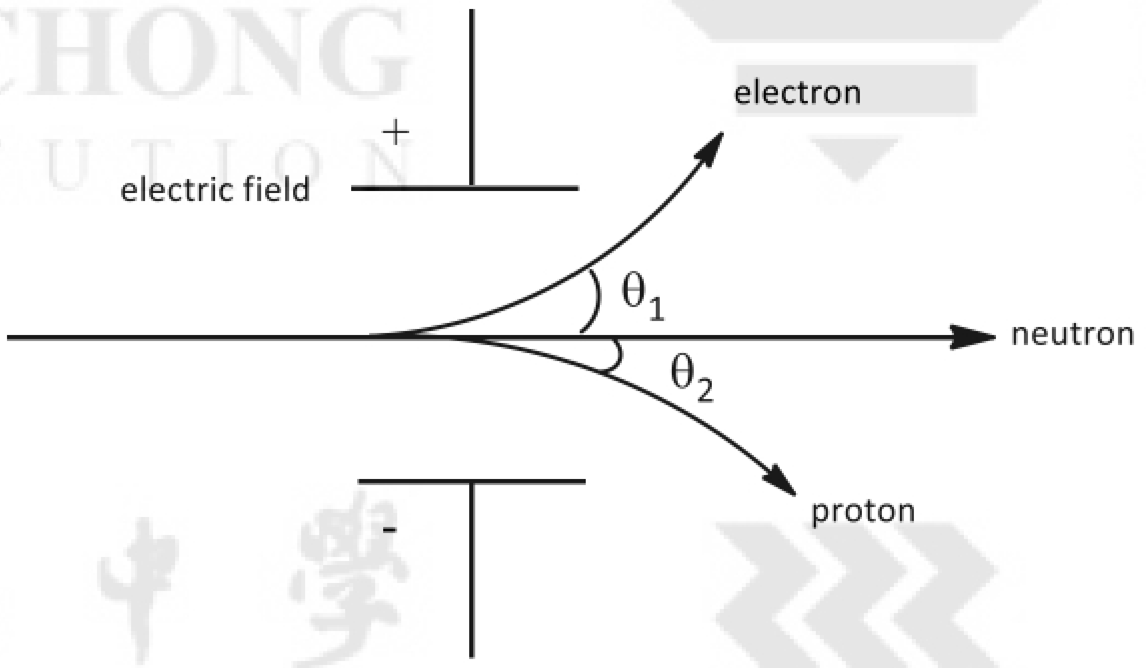


Figure 5. The behaviour of protons, neutrons and electrons in an electric field

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).

$$\boxed{\theta \propto \frac{q}{m}}$$

The angles of deflection may be calculated as given in the example below:

Lecture Exercise 1.1

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, ^{2}H, and T is tritium, ^{3}H)

- D^{-}
- T^{+}
- He^{2+}

[N12 /III/4(a)]

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

Self-Practice 1.1

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)	$^{28}_{14}Si$			
(b)	$^{70}_{31}Ga^{3+}$			
(c)	$^{31}_{15}P^{3-}$			

Self-Practice 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	6	8	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]

Self-Practice 1.3

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.

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

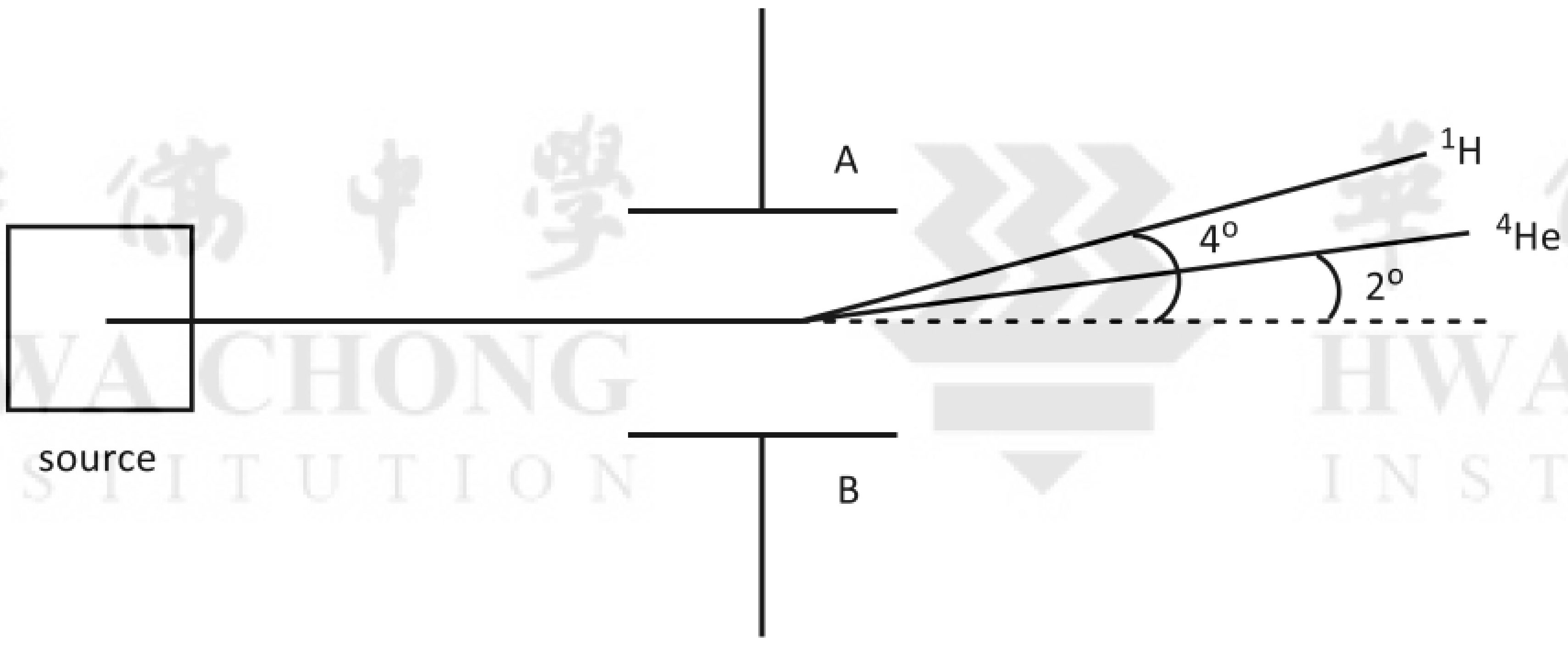
What is **X**?

A Mg **B** Ca **C** Sr **D** Ba

[N03/I/4]

Self-Practice 1.4

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, ^{1}H and ^{4}He nuclei are deflected as follows:



Giving reasons for your answers, suggest

(i) the polarity of plate **A**,

(ii) why ^{1}H is deflected twice as much as ^{4}He,

(iii) the angles of deflection (to 1 decimal place) of **I**: ^{2}H nuclei,
II: ^{3}He nuclei.

[J00/I/1 (c)]

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
p	3	6
d	5	10
f	7	14

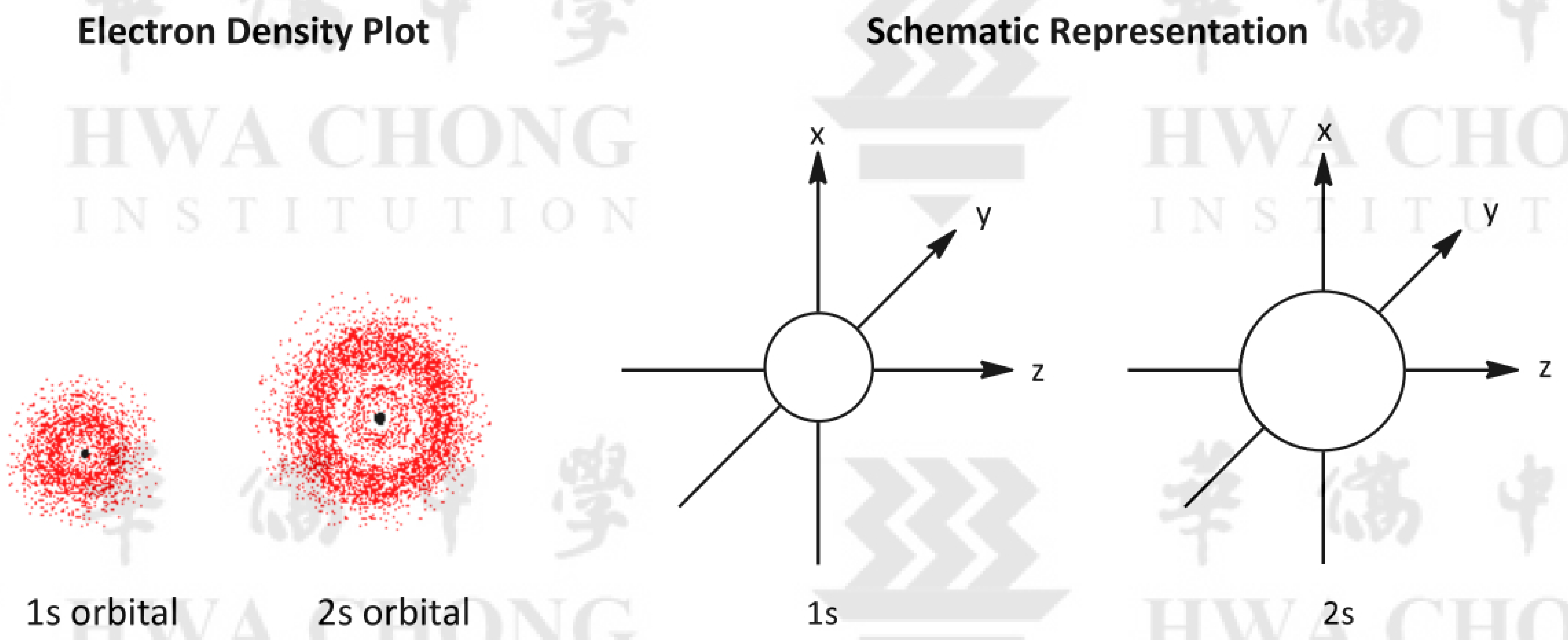
The table below summarises the relationships among principal quantum shells, subshells, orbitals and number of electrons.

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

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,…



Electron Density Plot **Schematic Representation**

1s orbital 2s orbital 1s 2s

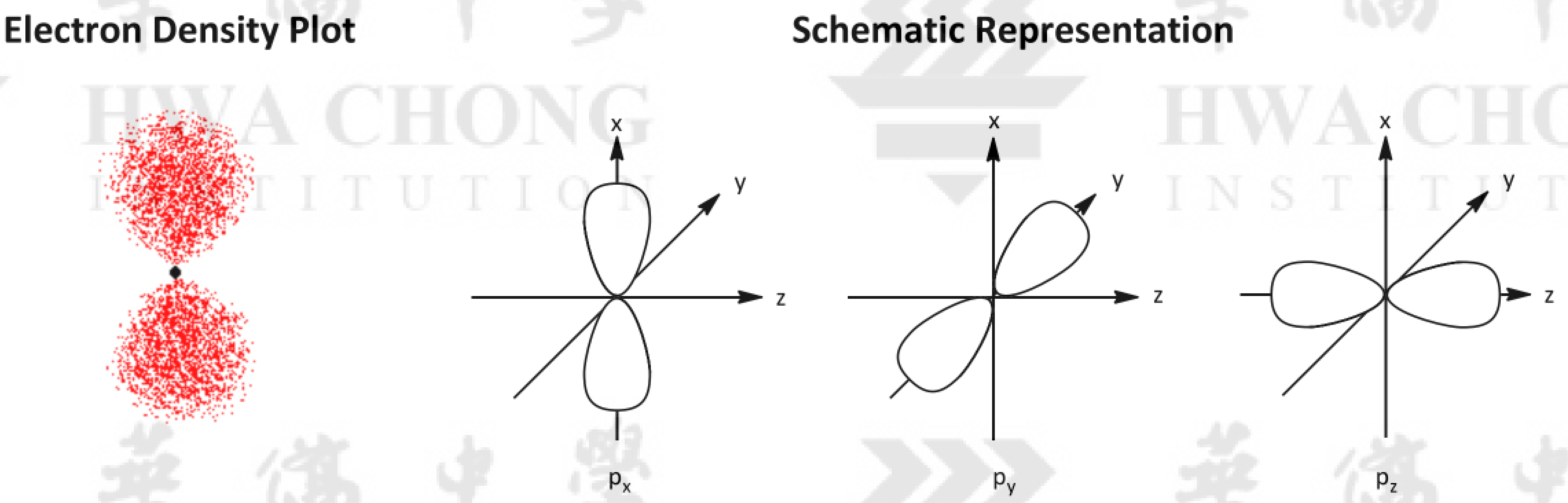
Figure 7. The s orbital

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.



Electron Density Plot **Schematic Representation**

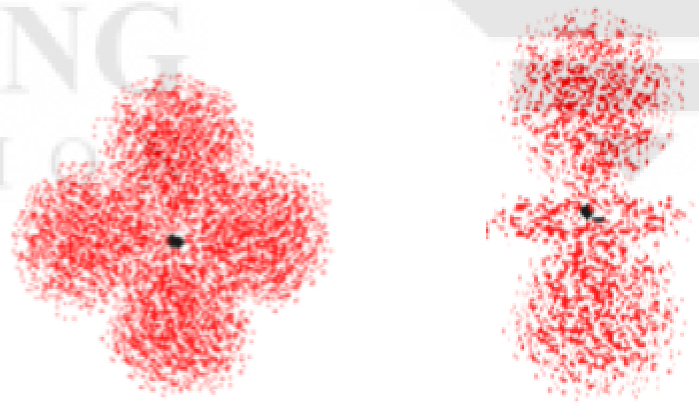
p_x p_y p_z

Figure 8. The p orbital

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 …

Electron Density Plot



Schematic Representation

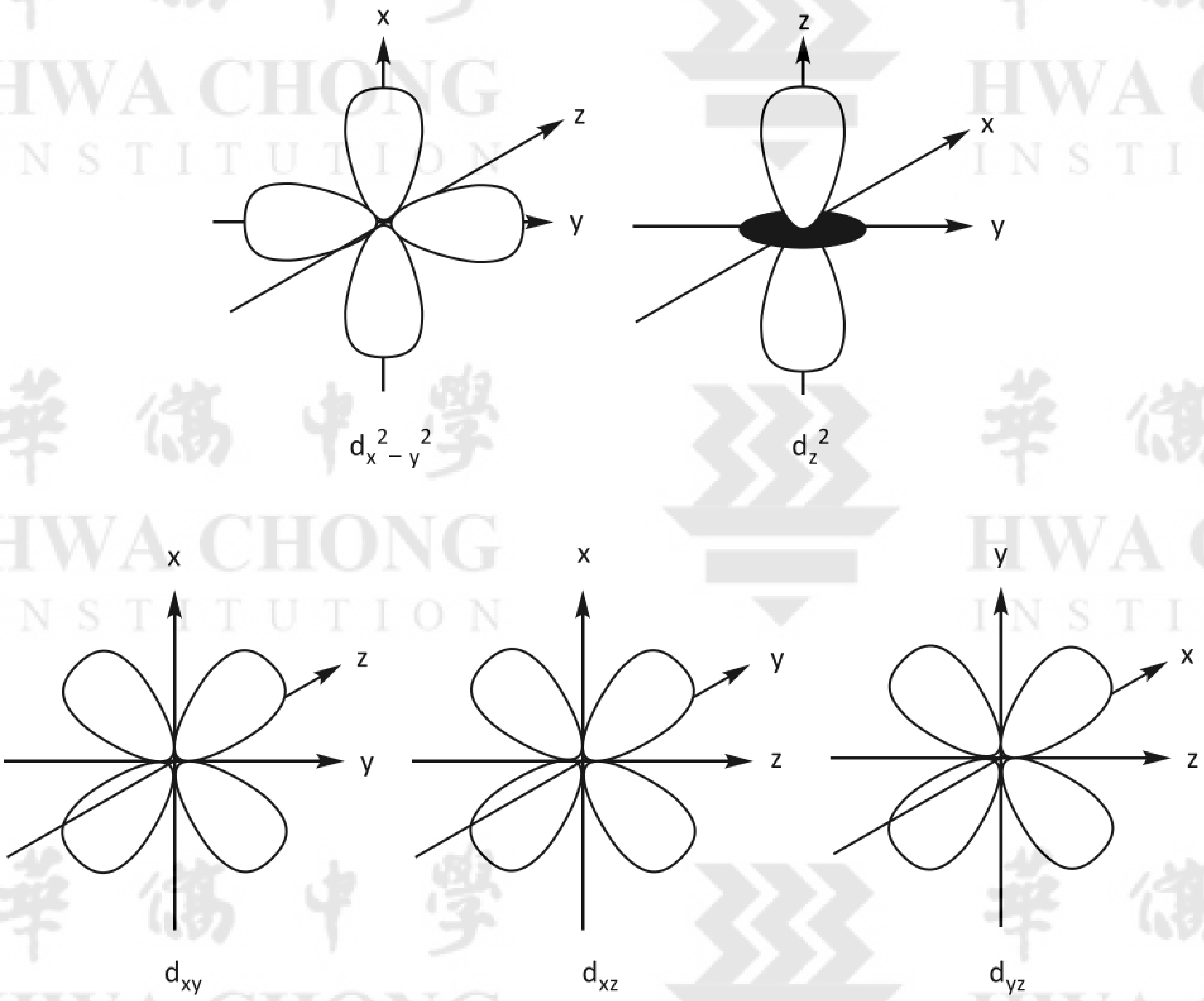


Figure 9. The d orbitals

Lecture 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 $1s^2$ $2s^2$ $2p^3$.

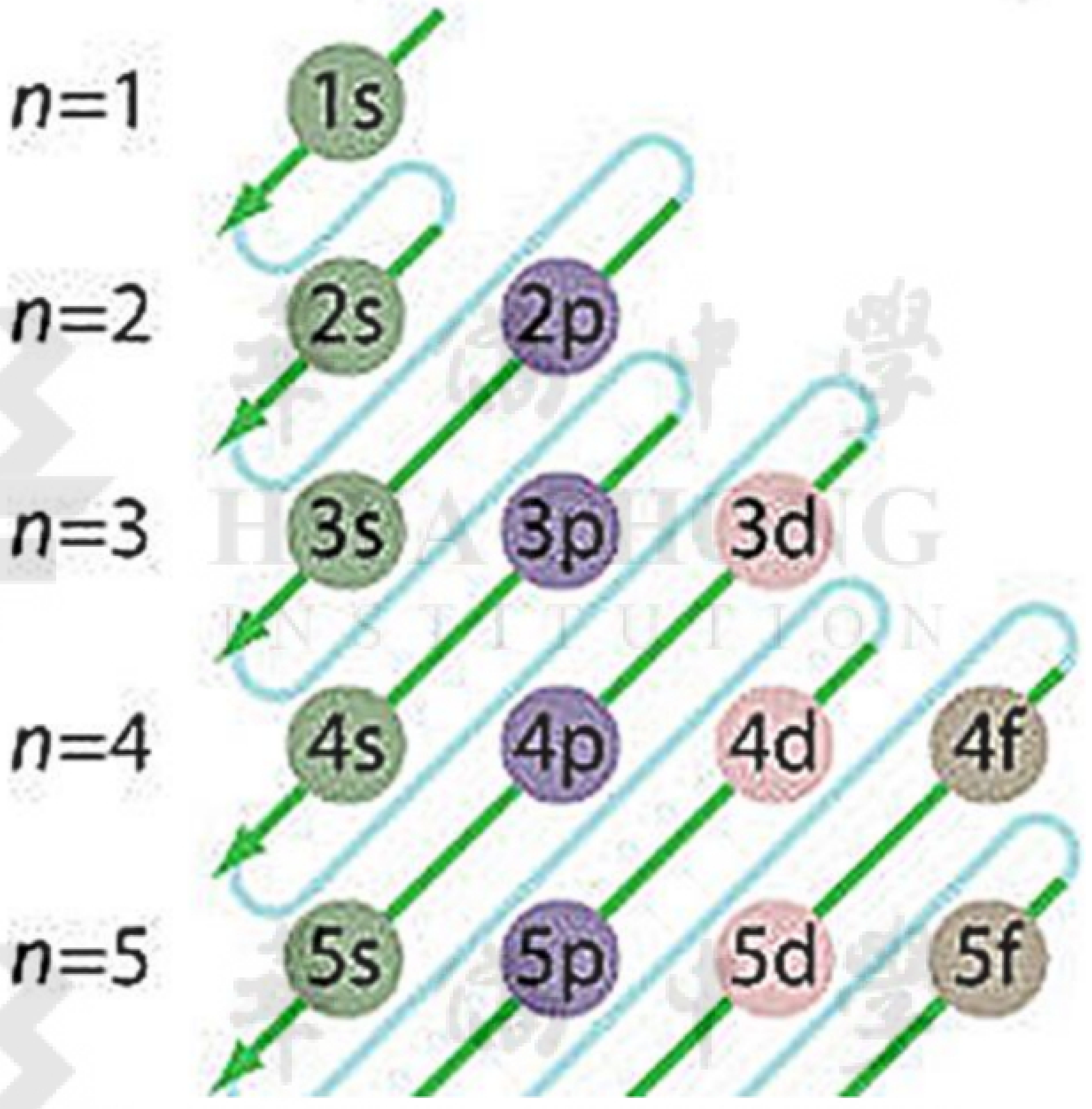


Figure 11. Mnemonic for the order of filling electrons into the orbitals

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

Period 2	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
	$[\mathrm{He}]2s^{1}$	$[\mathrm{He}]2s^{2}$	$[\mathrm{He}]2s^{2}2p^{1}$	$[\mathrm{He}]2s^{2}2p^{2}$	$[\mathrm{He}]2s^{2}2p^{3}$	$[\mathrm{He}]2s^{2}2p^{4}$	$[\mathrm{He}]2s^{2}2p^{5}$	$[\mathrm{He}]2s^{2}2p^{6}$
Period 3	**Na**	**Mg**	***Al***	**Si**	**P**	**S**	***Cl***	**Ar**
	$[\mathrm{Ne}]3s^{1}$	$[\mathrm{Ne}]3s^{2}$	$[\mathrm{Ne}]3s^{2}3p^{1}$	$[\mathrm{Ne}]3s^{2}3p^{2}$	$[\mathrm{Ne}]3s^{2}3p^{3}$	$[\mathrm{Ne}]3s^{2}3p^{4}$	$[\mathrm{Ne}]3s^{2}3p^{5}$	$[\mathrm{Ne}]3s^{2}3p^{6}$

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

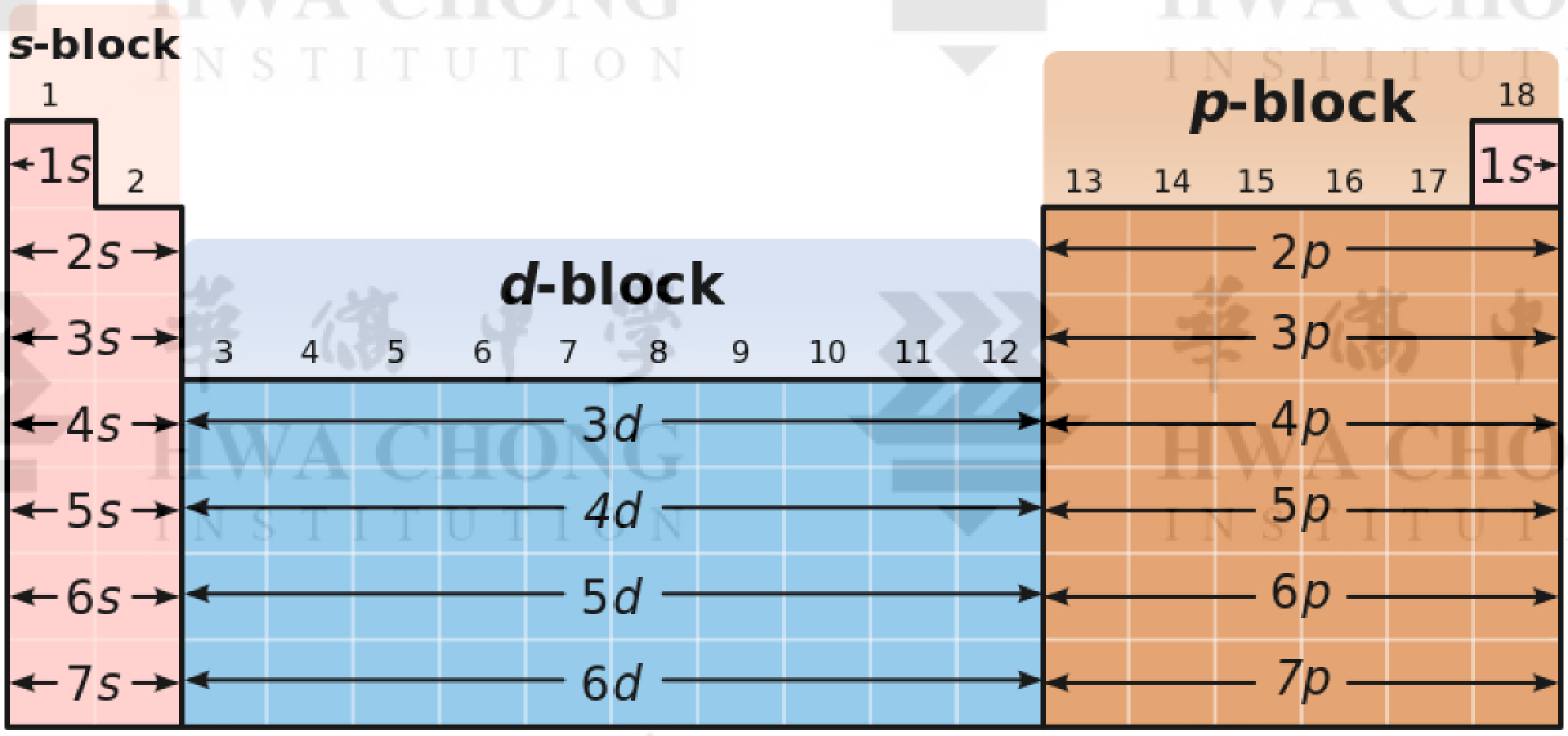


Figure 12. Periodic table illustrating how elements are grouped according to their valence subshells

By definition,

> A **transition metal** is a *d*-block element that forms some compounds containing its ion with an incomplete d-subshell.

As a result, *d*-block elements such as scandium and zinc are not considered to be transition elements because:

- scandium forms only the Sc^{3+} which has the $3d^0$ configuration
- zinc forms only Zn^{2+} ion which has $3d^{10}$ configuration

Lecture 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?

A $1s^2\ 2s^1$ **B** $2s^1\ 2p^2$ **C** $3p^3$ **D** $4s^2\ 4p^1$

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

4 PERIODIC TRENDS IN ATOMIC AND IONIC RADII

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

(i) **number of quantum shells**
(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.

Hence, $$Z_{eff} = Z - S$$

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

**For example, shielding of p electrons by s or p electrons in the same quantum shell does occur. 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.*

4.1 Trend in Atomic Radius

Down the Group:

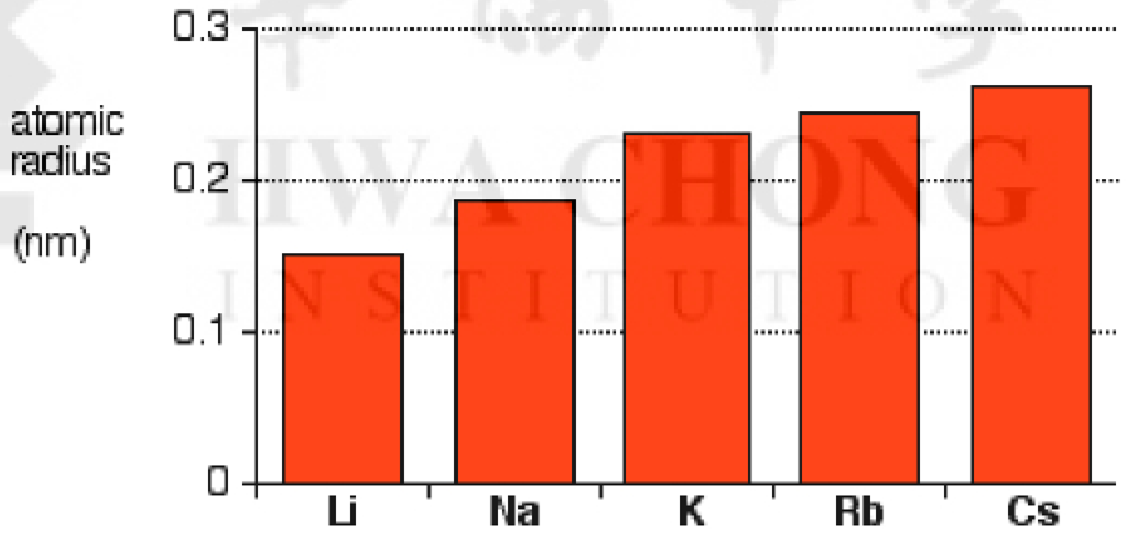


Figure 13. Atomic radii of Group 1 elements

General Trend:

Atomic radius increases down the group.

Reason:

- The effect of an increase in nuclear charge (due to the increase in the number of protons in the nucleus) is nullified by the increasing shielding effect (due to the increase in the number of inner-shell electrons), resulting in effective nuclear charge to be approximately the same. Hence, the number of quantum shells is the more important factor to consider
- As the number of quantum shells **increases** (as additional electrons are added to a new principal quantum shell), the outermost **electrons are further away** from the nucleus, hence the atomic radius **increases**

4.2 Trend in Ionic Radius

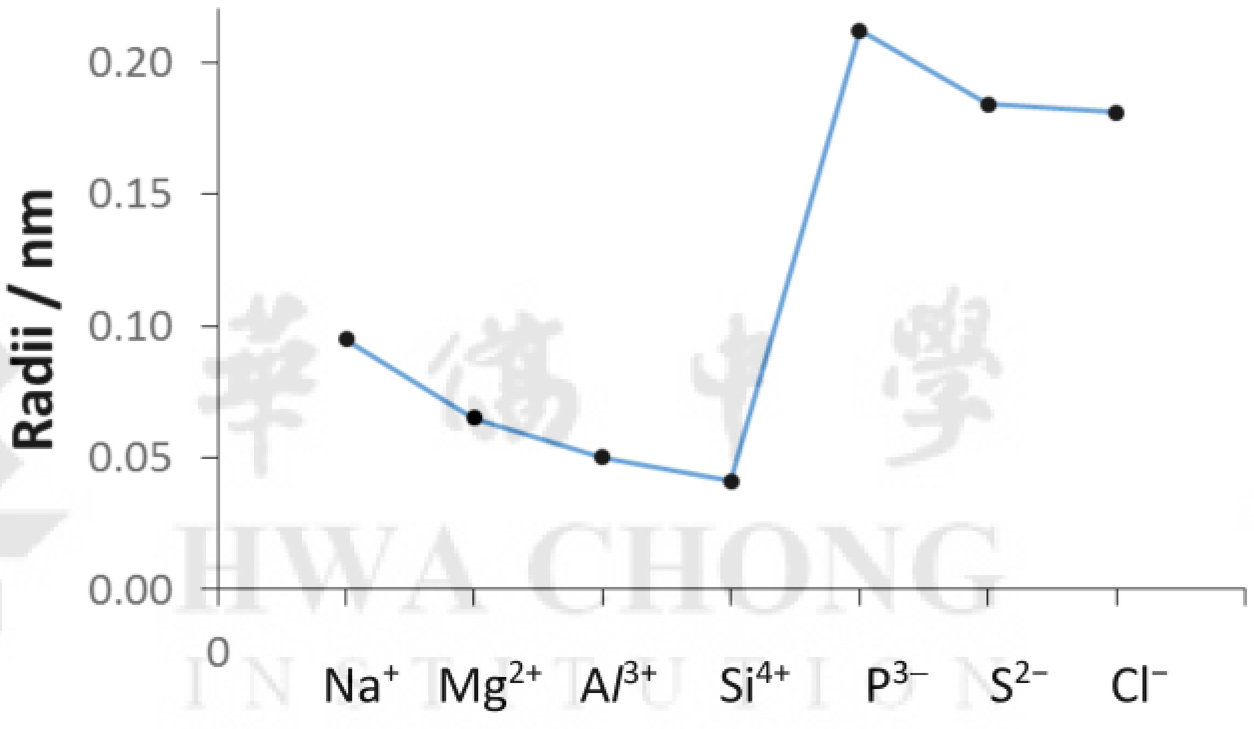


Figure 16. Ionic Radii across Period 3

Ionic radius of cations:

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

Ionic radius of anions:

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

The ions, Na^+, Mg^{2+}, Al^{3+} and Si^{4+} are said to be **isoelectronic** as they have the **same number of electrons**, which is 10. Similarly P^{3-}, S^{2-} and Cl^- are **isoelectronic** as they have 18 electrons each. Across the two isoelectronic series (Na^+ to Si^{4+} and P^{3-} 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 Si^{4+} to the anionic series of P^{3-} 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.

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

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.

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

Examples:

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

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

Similarly, nth **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.

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

Factors affecting ionisation energy of an atom:

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

5.2 Trend in the Successive Ionisation Energies of the Same Element

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

$IE_1 < IE_2 < IE_3 < IE_4 < \ldots$

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

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 $1s^2\ 2s^2\ 2p^6\ 3s^2$.

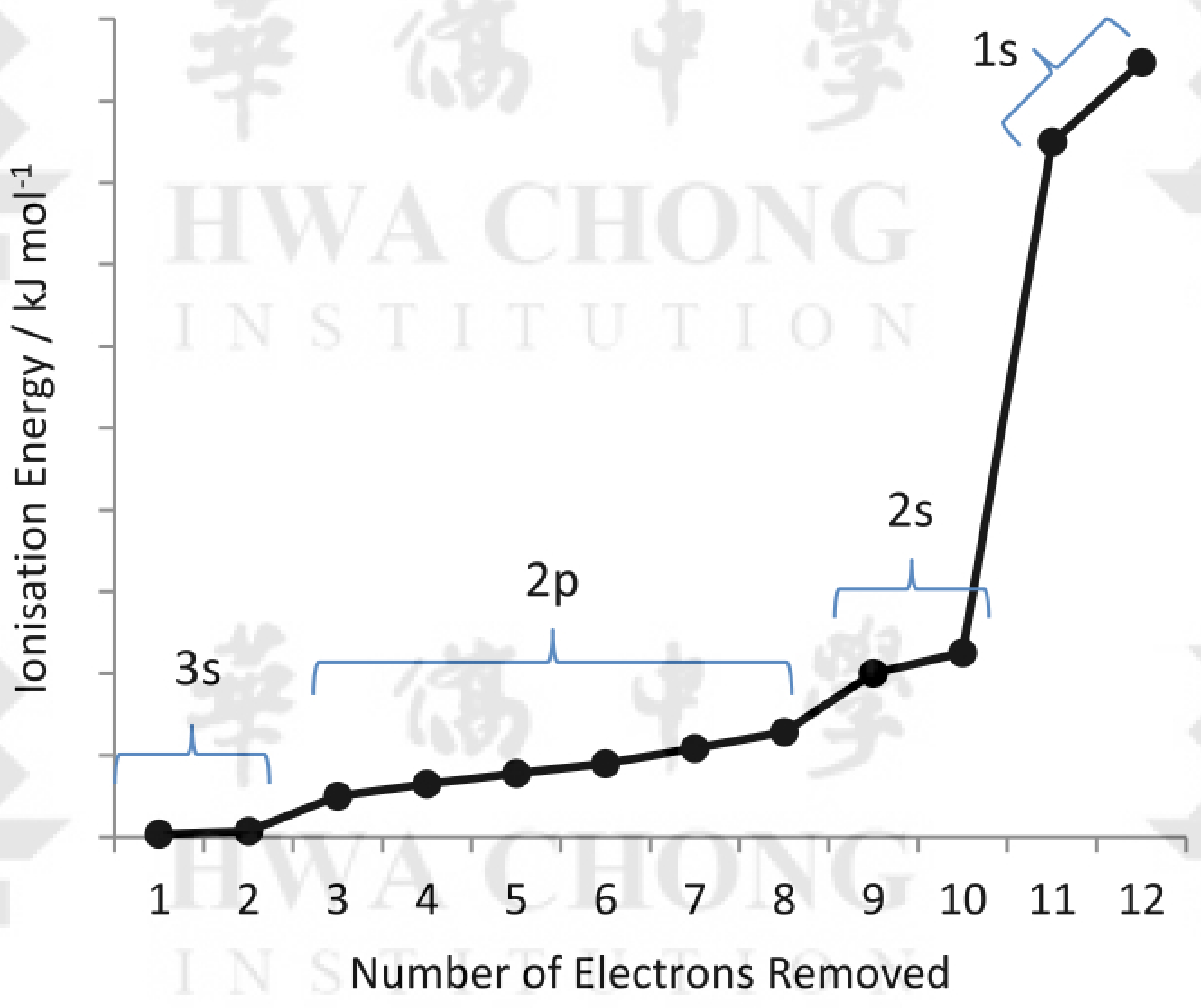


Figure 17. Successive ionisation energies of magnesium

- 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 **8th** to **9th** ionisation energies as more energy is required to remove the **2s** electrons, which are closer to the nucleus compared to the **2p** electrons.

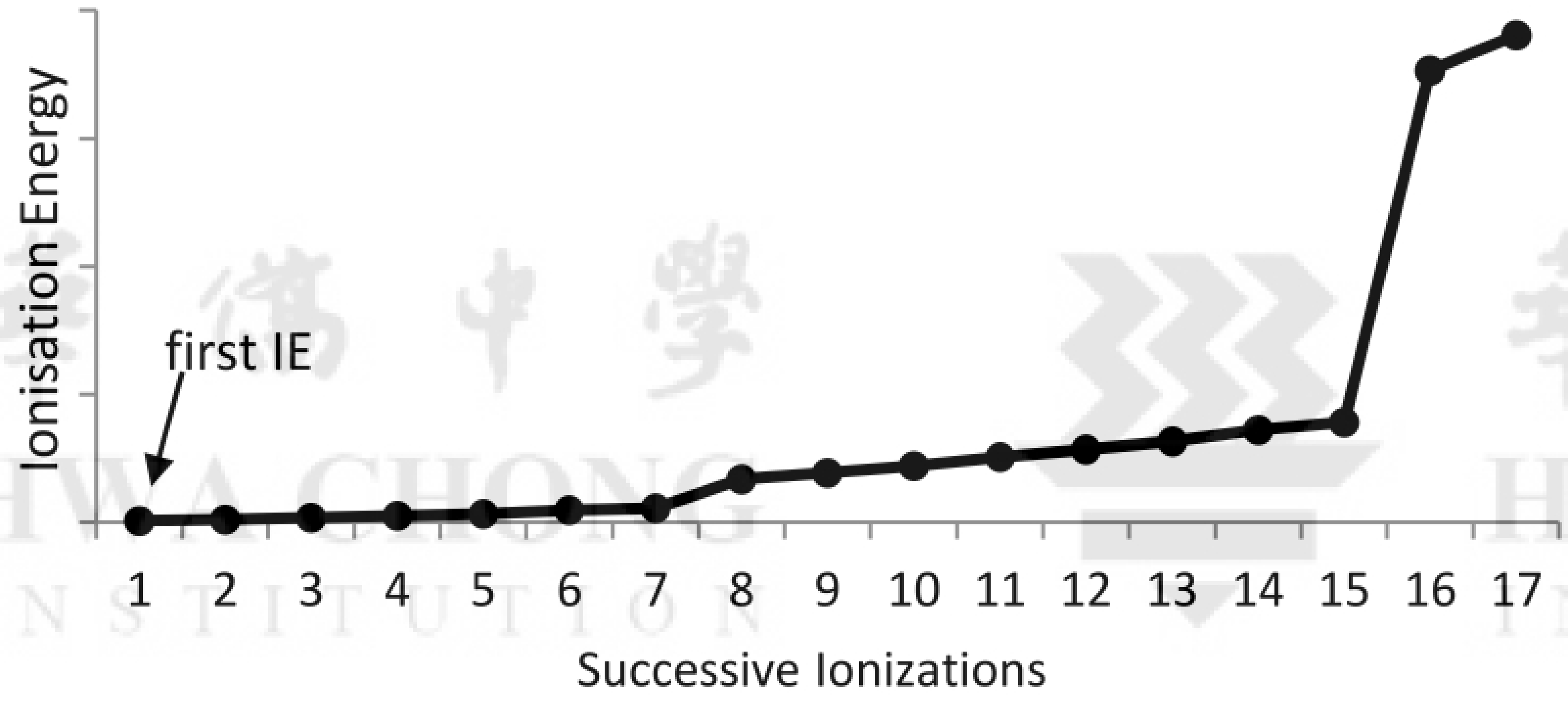
- the **second big** increase from the **10th** to **11th** ionisation energies

  - implies that the **last** two electrons are in the first (**inner most**) quantum shell.

Self-Practice 5.1

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.

Self-Practice 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**?

A $_{33}$As **B** $_{40}$Zr **C** $_{52}$Te **D** $_{53}$I

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

5.3 Trend in the First Ionisation Energies of Different Elements

Down the Group:

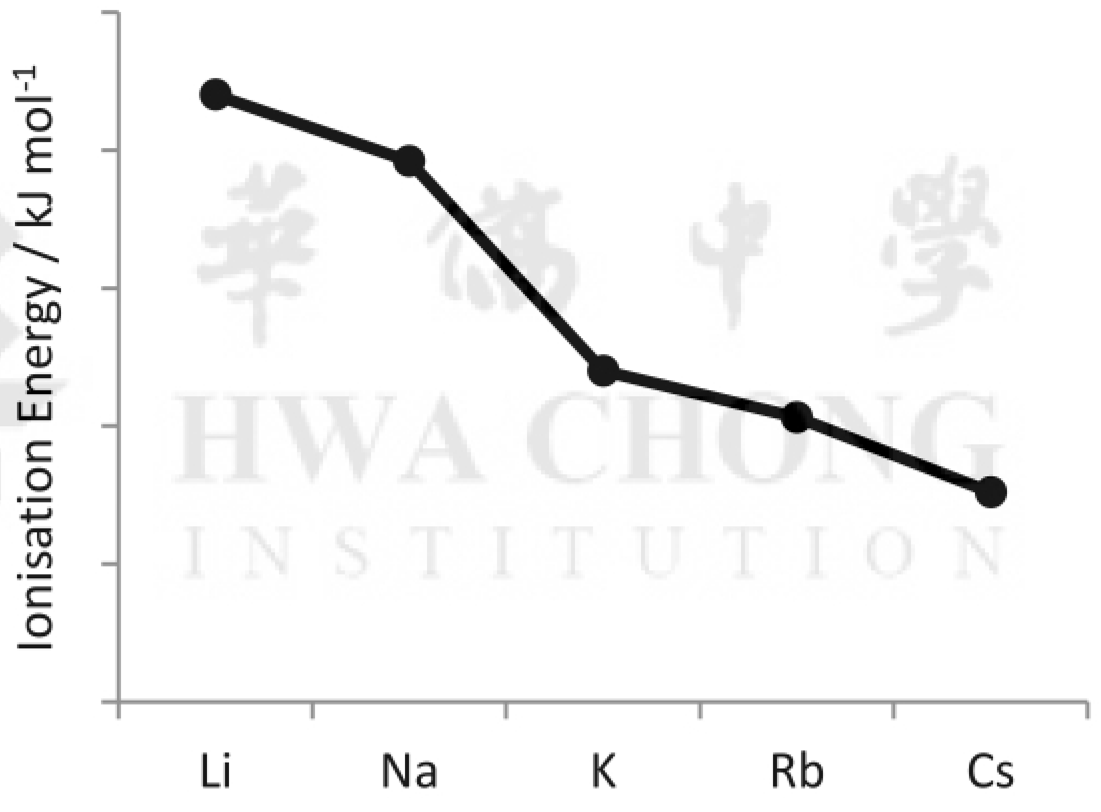


Figure 18. First ionisation energy trend down a group

General Trend:

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

Reason:

Down the group, the effect of increasing nuclear charge is nullified by the increase in shielding effect, resulting in effective nuclear charge to be approximately the same. The increase in the number of quantum shells of electrons means that the outermost electrons are further from the nucleus.

Therefore, the electrostatic forces of attraction between the nucleus and the outermost electron are weaker and less energy is required to remove this electron.

Across Periods 2 and 3:

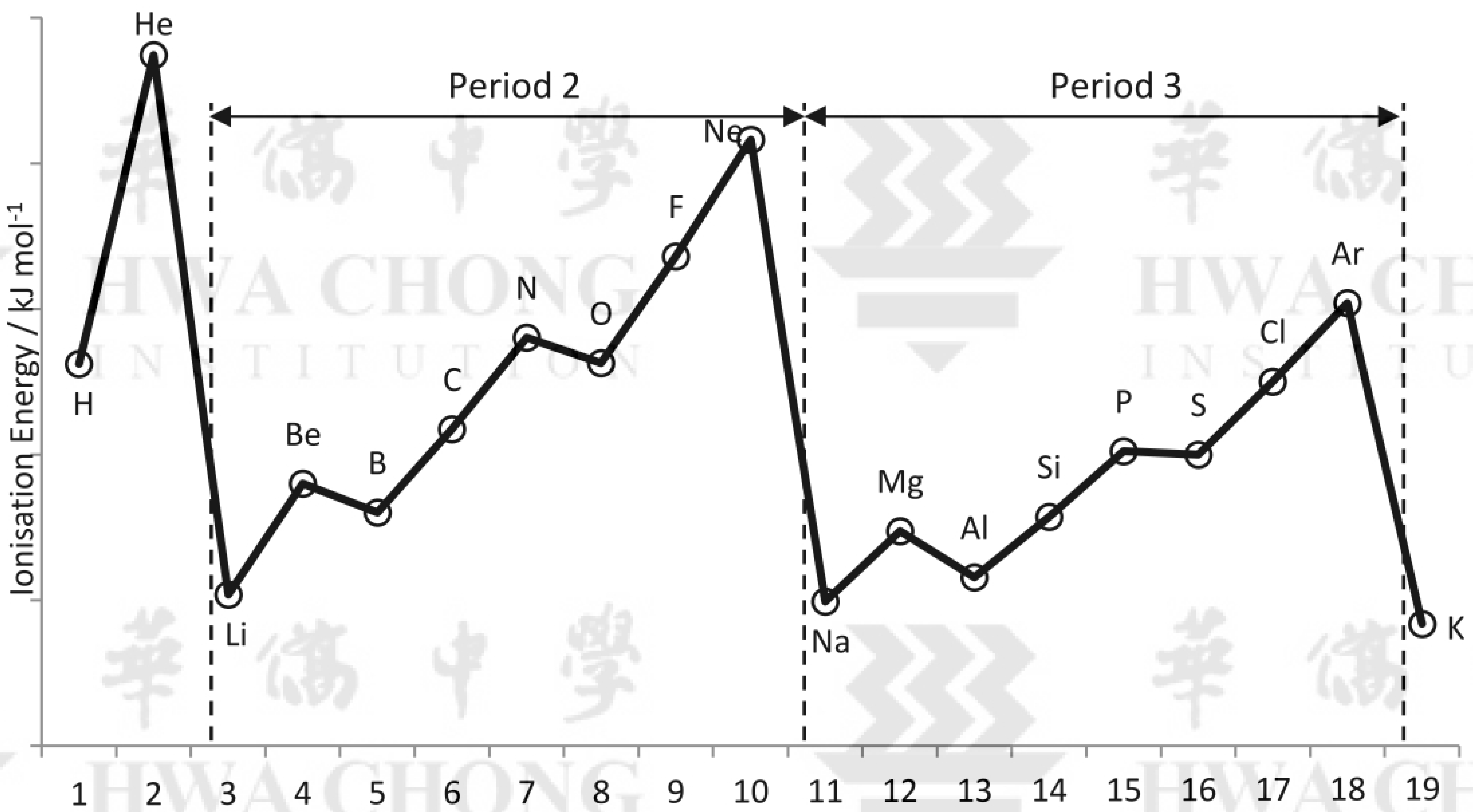


Figure 19. First ionisation energy trend across Periods 2 & 3

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:

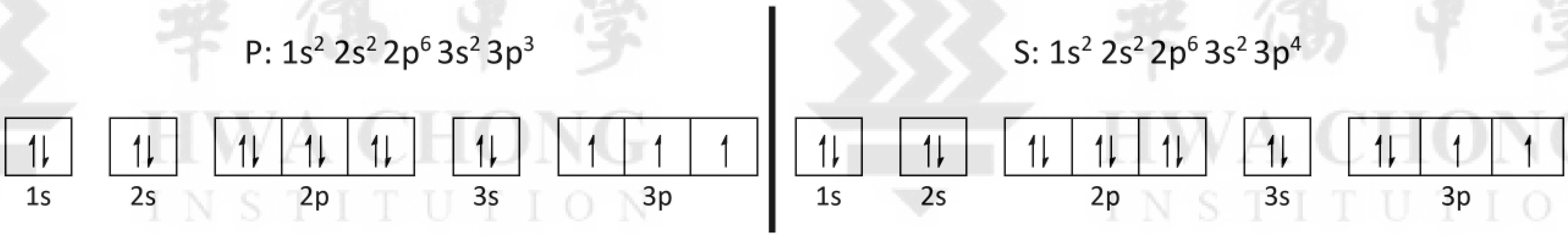
- **Small dip between Group 2 and Group 13 elements**
  A*l* has lower 1st ionisation energy than Mg.

  Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ A*l*: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

  The 3p subshell of A*l* 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 A*l*, resulting in a lower ionisation energy for A*l*.

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

  Consider the electronic configurations of P and S.



P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

All the 3p electrons in P are **unpaired**. In S, two of the 3p electrons are **paired**. There is some **inter-electronic 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:

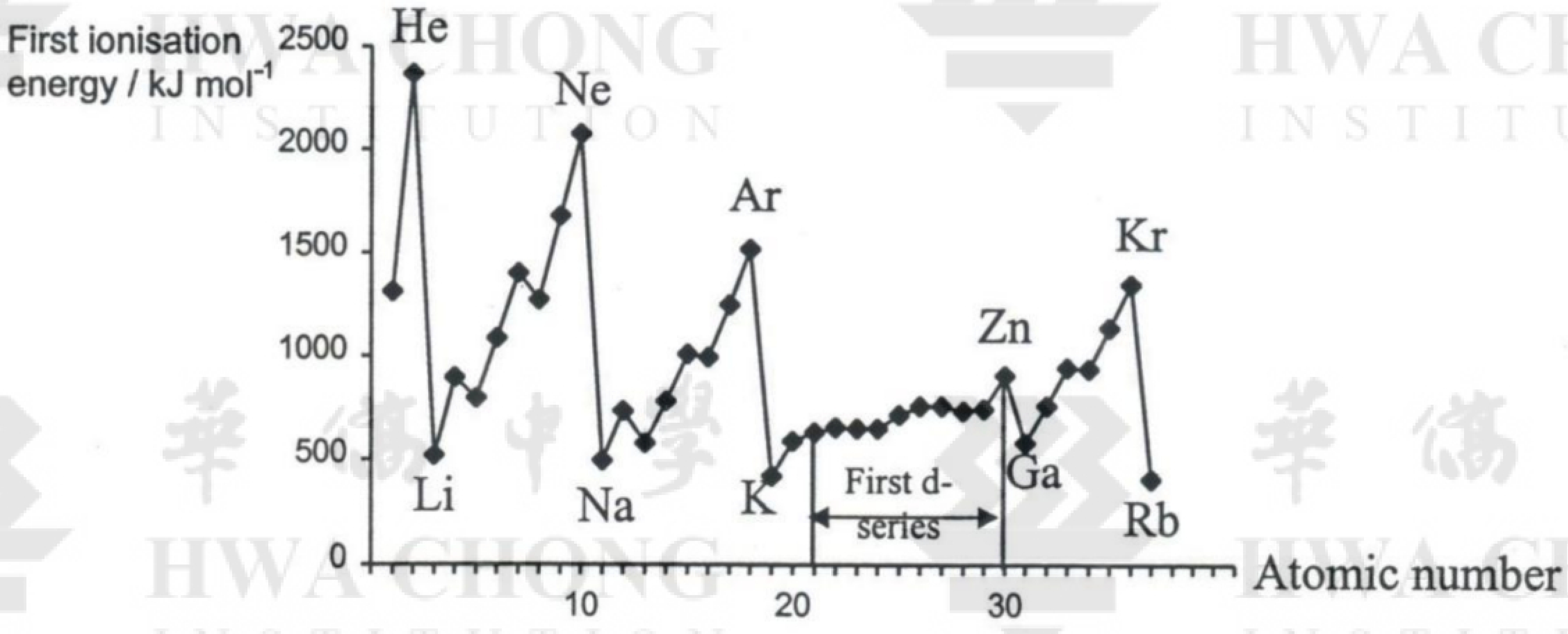


Figure 20: First ionisation energy trend across the first transition elements series

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

Self-Practice 5.3

The diagram shows part of the Periodic Table.

						H											He
Li	Be											B	C	N	O	F	Ne
Na	Mg											A*l*	Si	P	S	C*l*	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

Which element in the diagram has the largest atomic radii?

A Br **B** K **C** Kr **D** Sc

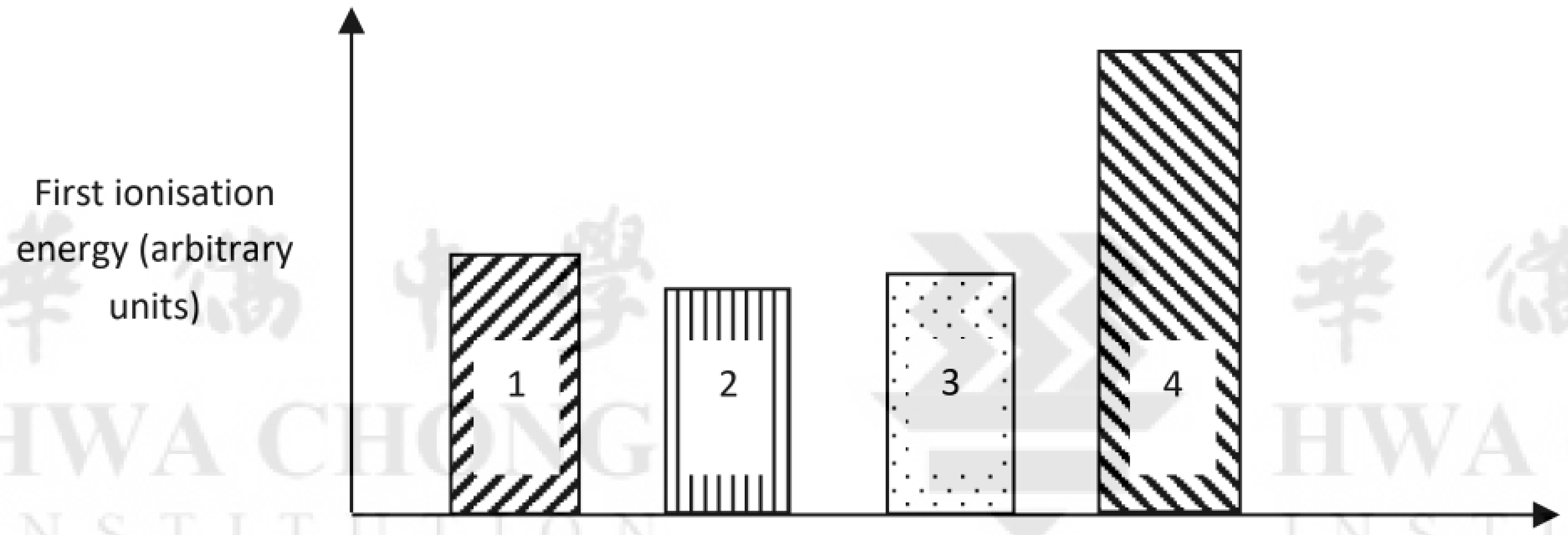
[N10/I/1]

Self-Practice 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?

A B, C, N, O
B Co, Ni, Cu, Zn
C Mg, Ca, Sr, Ba
D 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.

MODERN MASS SPECTROSCOPY

A SIMPLIFIED THEORETICAL BASIS**

In 1886, Eugen Goldstein, when studying the cathode ray tube, observed rays in gas discharges under low pressure that travelled away from the anode and through channels in a perforated cathode, opposite to the direction of negatively charged cathode rays (which travel from cathode to anode). Goldstein called these positively charged anode rays "kanalstrahlen"; the standard translation of this term into English is "canal rays". Wilhelm Wien found that strong electric or magnetic fields deflected the canal rays and, in 1899, constructed a device with parallel electric and magnetic fields that separated the positive rays according to their charge-to-mass ratio (q/m). Wien found that the charge-to-mass ratio depended on the nature of the gas in the discharge tube. English scientist J.J. Thomson later improved on the work of Wien by reducing the pressure to create the mass spectrograph.

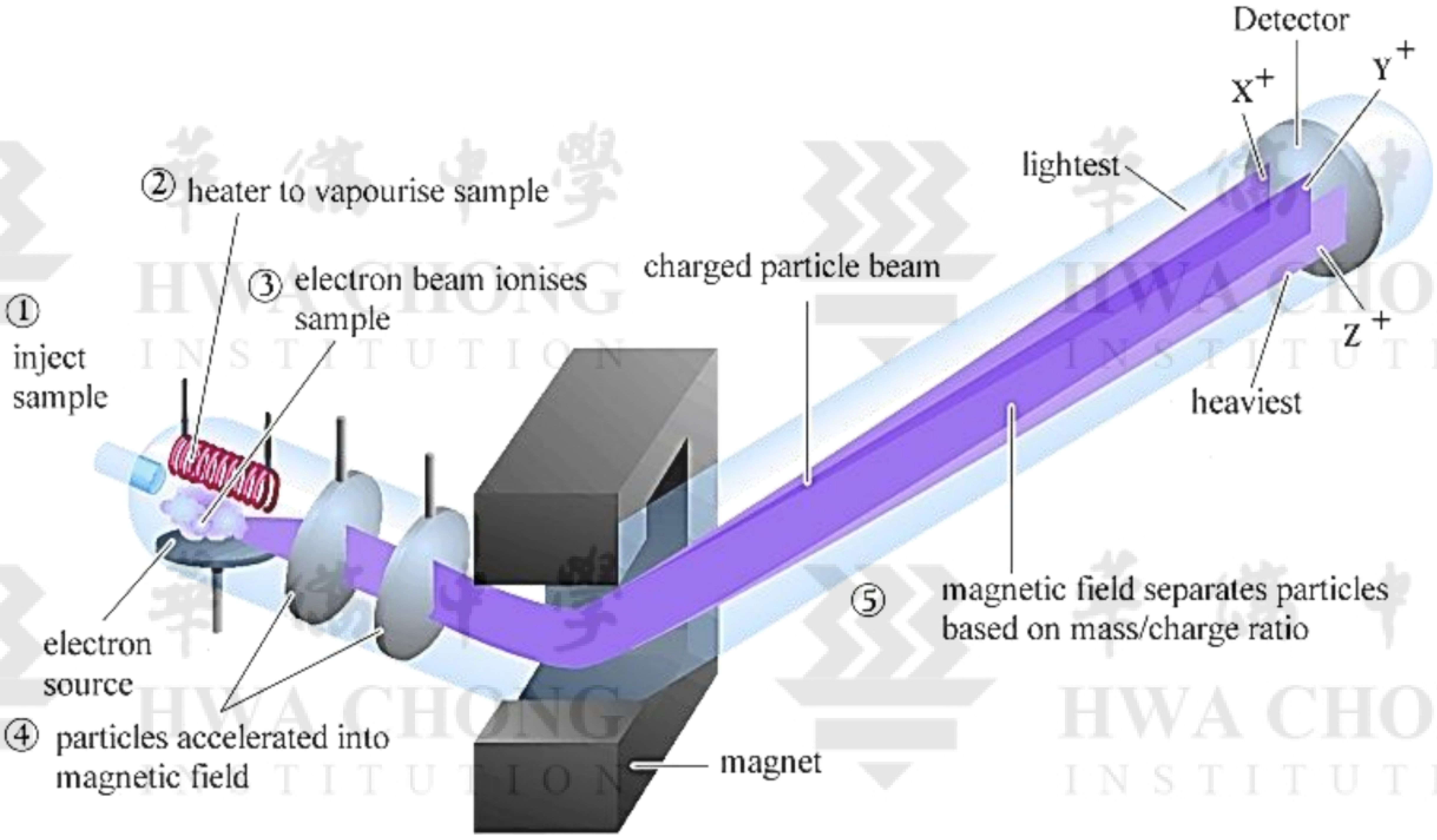


Figure 2. A schematic of a modern day mass spectrometer***

***Adapted from http://www.mhhe.com/physsci/chemistry/carey/student/olc/ch13ms.html

1) Ionisation Chamber (Points θ,ω & ε)

The ionisation chamber or ion source is the part of the mass spectrometer that ionises the material under analysis (the analyte). This chamber is kept under very low pressure or even vacuum conditions so that the ions created do not interact with the air in the chamber and dissipate before they can be analysed. Techniques for ionisation include electron ionization and chemical ionization. These are generally used for analytes which form gases and vapours (created by heating a volatile sample). In electron ionisation, the analyte is bombarded by a stream of high energy electrons which knock off an electron from the atom or molecule, creating an ion. In chemical ionisation techniques, the analyte is ionized by chemical ion-molecule reactions during collisions in the source. Two more sophisticated techniques often used with liquid and solid samples include electrospray ionization and matrix-assisted laser ionization.

** Adapted from https://en.wikipedia.org/wiki/Mass_spectrometry

2) Ion Acceleration and Beam Focusing (Point ρ)

The ions created in the ionisation chamber are then transported by magnetic or electric fields to the mass analyser. The stream of ions is accelerated by passing them through an ion accelerator. Energy is imparted to the stream of ions so that the ions can be passed through a mass analyser and have enough energy to reach the detector at the end of the spectrometer. The stream of ions are then focused into a narrow beam and passed through a slit so that random unwanted ions are excluded from the mass analyser downstream.

3) Mass Analyser (Point τ)

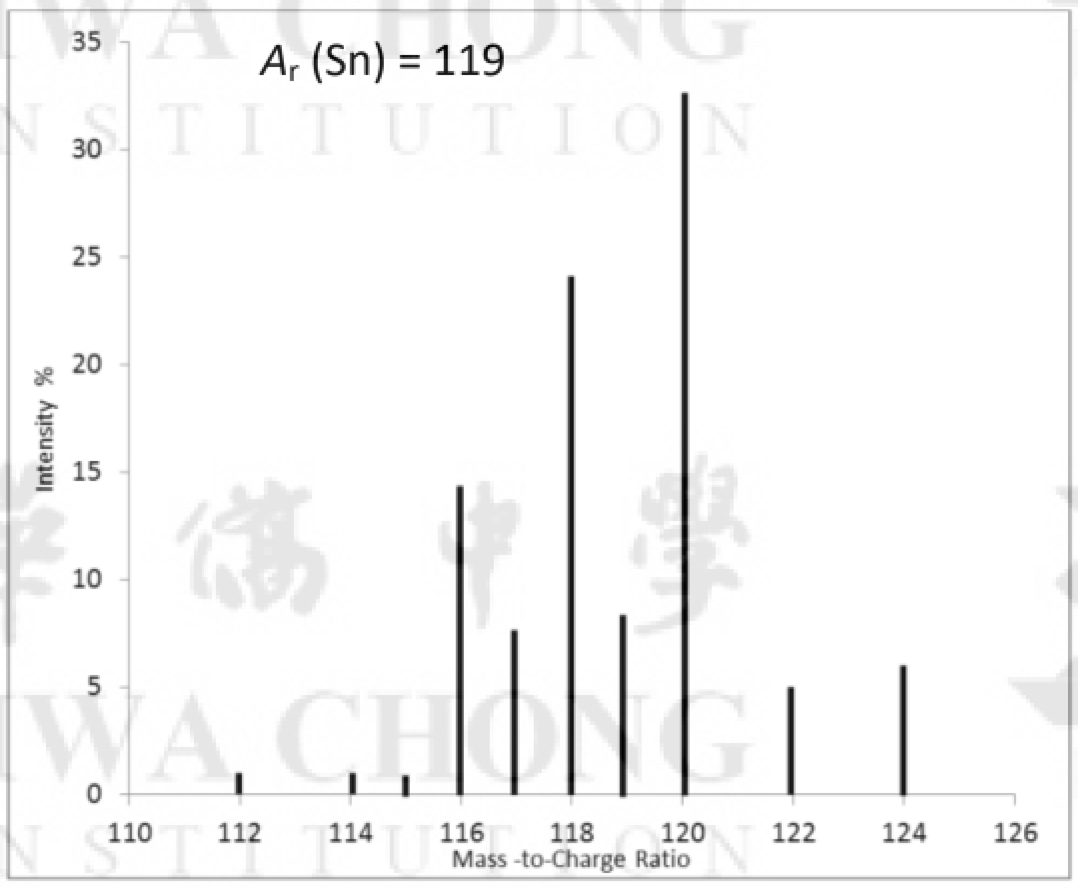
Mass analysers separate the ions according to their charge-to-mass ratio. The dynamics of the ions in electric and magnetic fields in vacuum are governed by Lorentz Force Law and Newton's Second Law of Motion. In general, this charge-to-mass ratio represents the ratio of the number of elementary charges of the ion (for example, $^{A}_{Z}M^{n+}$, the charge being n+) to the nucleon number (which is A in this example). The ability of the mass analyser to distinguish between two ions of slightly different q/m ratio is called the mass resolving power. Hence a good mass analyser (or a high resolution analyser) will be able to distinguish between very small differences in the q/m ratio. The detection of isotopes would require a high resolution mass analyser since the difference between isotopes could differ only by one nucleon number.

4) Detector

The final element of the mass spectrometer is the detector. The detector records either the charge induced or the current produced when an ion passes by or hits a surface. A modern day detector employs a scanning technique where the instrument scans through a range of q/m values (preset) and any signal produced in the detector during the course of the scan will be captured. Repeated scans will produce a mass spectrum, a record of ions as a function of their q/m (or more commonly m/q ratio as it is easier to read) versus the signal intensity of the relevant q/m ratios. Because the number of ions leaving the mass analyser at a particular instant is typically quite small, considerable amplification is often necessary to get a signal.

5) Mass Spectrum

The result of the separation of ions of different charge-to-mass ratio is usually expressed as a mass spectrum as shown below. Note mass-to-charge is preferred as it gives values > 1 and makes the spectrum easier to read. The spectrum shows the different isotopes of tin and their relative abundances. A weighted average of these isotopic abundances gives the relative atomic masses in the Period Table.



m/q	intensity
112	0.97
114	0.66
115	0.34
116	14.54
117	7.68
118	24.22
119	8.59
120	32.58
122	4.63
124	5.79