Raffles Institution
Year 5 H2 Chemistry 2022
Lecture Notes 2 – Atomic Structure

Content

- The nucleus of the atom: neutrons and protons, isotopes, proton and nucleon numbers
- Electrons: electronic energy levels, ionisation energies, atomic orbitals, extranuclear structure

Learning Outcomes

Candidates should be able to:

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

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

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

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

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

(ii) distinguish between isotopes on the basis of different numbers of neutrons present

(f) describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the 4s and 4p orbitals

(g) describe the shapes of s, p and d orbitals [knowledge of wave functions is **not** required]

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

(i) explain the factors influencing the ionisation energies of elements (see the *Data Booklet*)

(j) deduce the electronic configurations of elements from successive ionisation energy data

(k) interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table

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

(m) describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity:

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

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

Lecture Outline

1 Atomic structure
2 The nucleus of the atom
3 The electronic structure of the atom
4 Electronic configurations
5 Electrostatic effects
6 Atomic radius
7 Ionic radius
8 Ionisation energies
9 Electronegativity

References

1 Chemistry for advanced level (by Peter Cann and Peter Hughes)
2 Chemistry in Context (by Hill and Holman)
3 Cambridge International AS and A Level Chemistry Coursebook (by Roger Norris, Lawrie Ryan & David Acaster)
4 Chemistry: The Molecular Nature of Matter and Change (by Martin S. Silberberg)
5 Website: http://www.chemguide.co.uk

1 ATOMIC STRUCTURE

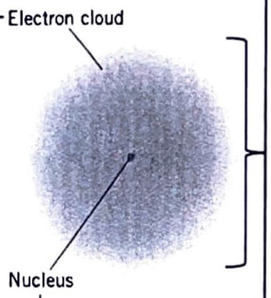
1.1 The atom

- An **atom** is the smallest particle found in an element that can take part in a chemical reaction.

Structure of an atom

electrons

- negatively charged
- concentrated in certain regions of space around the nucleus called **orbitals**
- The region around the nucleus where electrons move is mostly **empty space.**



atom

- contains a small, dense nucleus surrounded by electrons
- Atoms are very small. They have a diameter of about 10^{-10} m.
- The nucleus of an atom is even smaller. It has a diameter of 10^{-15} to 10^{-14} m

nucleus

- contains protons and neutrons (collectively known as *nucleons*)
- contains the bulk of the mass of an atom

protons

- positively charged

neutrons

- uncharged

1.2 The subatomic particles

- Three important subatomic particles found in an atom are the proton, the neutron and the electron.

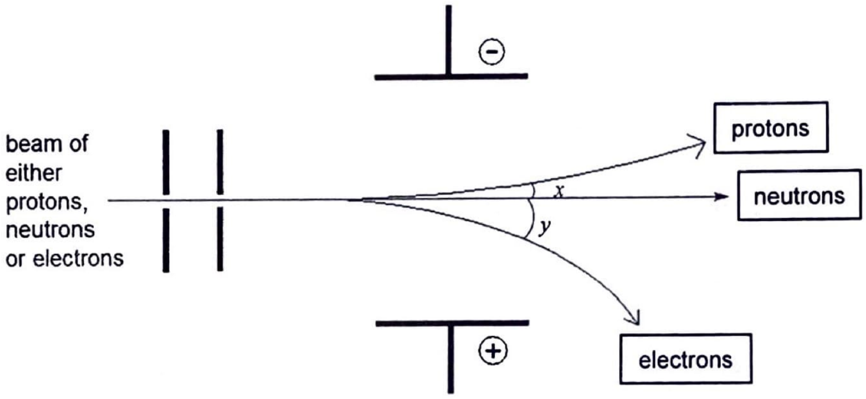
Sub-atomic particle	proton	neutron	electron
Location within the atom	in the nucleus	in the nucleus	around the nucleus
Actual mass / kg	1.67×10^{-27}	1.67×10^{-27}	9.11×10^{-31}
Relative mass	1	1	$\frac{1}{1840}$
Charge / C	$+1.60 \times 10^{-19}$	0	-1.60×10^{-19}
Relative charge	+1	0	−1
Symbol	$^{1}_{1}\mathrm{p}$	$^{1}_{0}\mathrm{n}$	$^{0}_{-1}\mathrm{e}$

1.3 Behaviour of the subatomic particles in an electric field

- Consider the following beams of subatomic particles all travelling at the same speed:
  - a beam of protons
  - a beam of neutrons
  - a beam of electrons

- When each of these beams is passed through an electric field, each beam is found to behave differently in the following aspects:
  - the direction of deflection and
  - the angle of deflection.

Behaviour of the subatomic particles in an electric field



Subatomic particle	Direction of deflection	Angle of deflection
proton (positively charged)	towards the negatively charged plate	x° ($x^\circ < y^\circ$)
neutron (uncharged)	not deflected	0°
electron (negatively charged)	towards the positively charged plate	y° ($y^\circ > x^\circ$)

- The direction of deflection is dependent on the **charge** on the subatomic particle.

- The angle of deflection is proportional to the magnitude of the $\frac{\textbf{charge}}{\textbf{mass}}$ ratio of the particle.

angle of deflection $\propto \left\lvert\frac{q}{m}\right\rvert$ where q = charge on particle m = mass of particle	• The **larger the charge q** of the particle, the stronger is the attraction towards the oppositely charged plate. ⇒ the **greater** the angle of deflection • The **larger the mass m** of the particle, the more difficult it is to cause it to deviate towards the oppositely charged plate. ⇒ the **smaller** the angle of deflection

Note: In this case, protons and electrons have the same charge in terms of magnitude. However, protons are heavier and hence the angle of deflection for the proton beam is smaller, i.e. $x^\circ < y^\circ$

Worked Example 1

Beams of charged particles are deflected by an electric field. In a particular experimental set-up, protons are deflected through an angle of +10°. Assuming an identical set of experimental condition, by what angles will the beam of each of the following particles (all travelling at the same speed) be deflected?

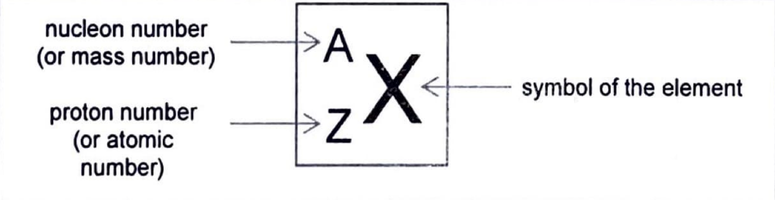
	Particle	$\left\|\frac{q}{m}\right\|$	angle of deflection
	$^{1}H^{+}$	1	+10°
(a)	$^{2}H^{+}$	$\frac{1}{2}$	$\frac{1}{2} \times 10^{\circ} = +5^{\circ}$
(b)	$^{18}O^{2-}$	$\frac{2}{18} = \frac{1}{9}$	$-\frac{1}{9} \times 10 = -1.11^{\circ}$
(c)	$^{9}Be^{2+}$	$\frac{2}{9}$	$\frac{2}{9} \times 10 = +2.22$

2 THE NUCLEUS OF THE ATOM

2.1 Representation of a Nuclide

- A **nuclide** is any species of given mass number and atomic number.

  The **nuclide** of an element is represented by



$^{A}_{Z}X$	$^{238}_{92}U$
Nucleon number (Total no. of protons and neutrons) = A No. of protons = Z No. of neutrons = A – Z	Nucleon number = 238 No. of protons = 92 No. of neutrons = 146
No. of electrons = No. of protons = Z	No. of electrons = 92

Note: The atomic number determines the **identity** of an atom.
For example, every atom with an atomic number of 6 is a carbon atom; it contains 6 protons in its nucleus.

- The **nuclide** of an element is named by its elemental name followed by its mass number.

  Examples:

$^{1}_{1}H$	$^{2}_{1}H$	$^{3}_{1}H$	$^{4}_{2}He$	$^{12}_{6}C$	$^{13}_{6}C$	$^{14}_{6}C$
hydrogen–1	hydrogen–2	hydrogen–3	helium–4	carbon–12	carbon–13	carbon–14

2.2 Isotopes

- Isotopes of an element are atoms that contain the **same number of protons** but **different number of neutrons** in the nucleus.

Example: Isotopes of chlorine

Nuclides	No. of protons	No. of electrons	No. of neutrons
$^{35}_{17}Cl$	17	17	18
$^{37}_{17}Cl$	17	17	20

- Isotopes have the **same number of electrons** and therefore the **same chemical properties**.

- Since isotopes have **different number of neutrons**, they have **different masses** and hence **different physical properties** such as density, melting point, etc.

Worked Example 2

Complete the following table.

	Nucleon number	No. of p	No. of n	No. of e⁻
$^{27}_{13}Al^{3+}$	27	13	14	10
$^{14}_{7}N^{3-}$	14	7	7	10

Worked Example 3

With the aid of the Periodic Table, identify **X** and **Y** below.

(a) Some isotopes are unstable and decompose naturally. An example is potassium–40 which undergoes decay by beta–particle emission as represented by the following equation: $^{40}_{19}K \rightarrow \mathbf{X} + ^{0}_{-1}e$.

(b) In 1937, O Hahn became the first person to obtain energy from 'splitting the atom'. He bombarded uranium–235 with neutrons. Each uranium–235 atom split into two smaller atoms and two neutrons with the release of energy as represented by the following equation: $^{235}_{92}U + ^{1}_{0}n \rightarrow \mathbf{Y} + ^{90}_{36}Kr + 2^{1}_{0}n$.

(a) $^{40}_{19}K \rightarrow \mathbf{X} + ^{0}_{-1}e$.

Nucleon number of **X** = 40

Proton number of **X** = 19 – (–1)

= 20

Hence **X** is $^{40}_{20}Ca$

(b) $^{235}_{92}U + ^{1}_{0}n \rightarrow \mathbf{Y} + ^{90}_{36}Kr + 2^{1}_{0}n$

Nucleon number of **Y** = 235 + 1 – 90 – 2

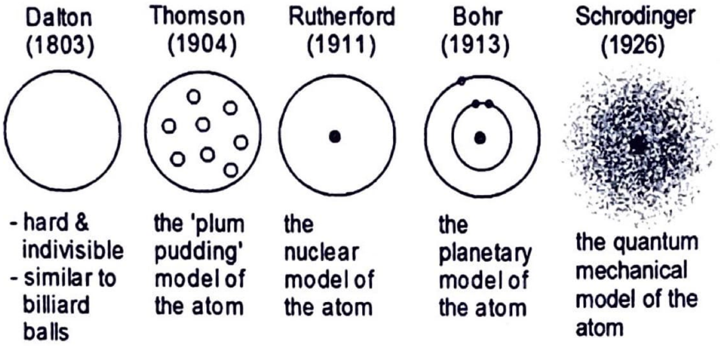
= 144

Proton number of **Y** = 92 – 36 = 56

Hence **Y** is $^{144}_{56}Ba$

3 THE ELECTRONIC STRUCTURE OF THE ATOM

3.1 Historical development of the atomic model



- In the practice of science, as more work is done, evidence collected and data accumulated, our understanding of the universe becomes better and clearer.

- Thus, more advanced models to understand nature develop as our knowledge expands.

This is also true of our understanding of the structure of atoms and matter.

The history of models developed is briefly summarized in the appendix.

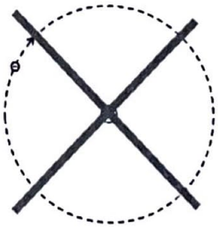
It is important that you refresh and update the way you think about atoms, and the way you write or illustrate atomic structure.

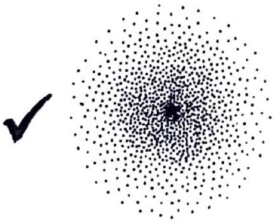
The rest of this topic will cover further details.

3.2 The electron

What do we know about electrons?

- Electrons in an atom do <u>not</u> occupy fixed positions around the nucleus. They do <u>not</u> move in orbits (or fixed circular/elliptical paths) around the nucleus.





- Electrons in an atom move in certain regions of space around the nucleus known as **atomic orbitals**.

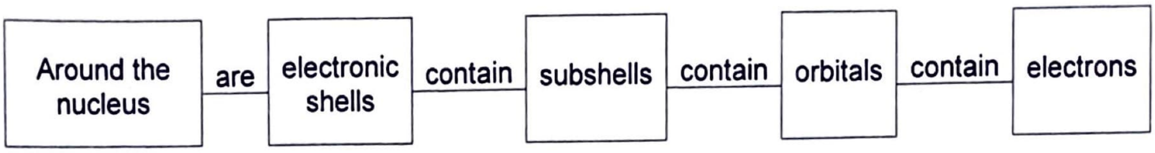
- Each electron has energy that is quantised (i.e. each electron has energy restricted to certain values). Each electron occupies a discrete energy level.

3.3 Arrangement of electrons in atoms

- The arrangement of electrons in an atom (or ion) is referred to its **electronic structure.**

The electronic structure provides us with the following information:
  - the **number of electrons** in the atom or ion
  - the **distribution of electrons** in the atom or ion
  - the **energies** of the electrons

It is important because it determines how the atom will react with other atoms to form ions or molecules.



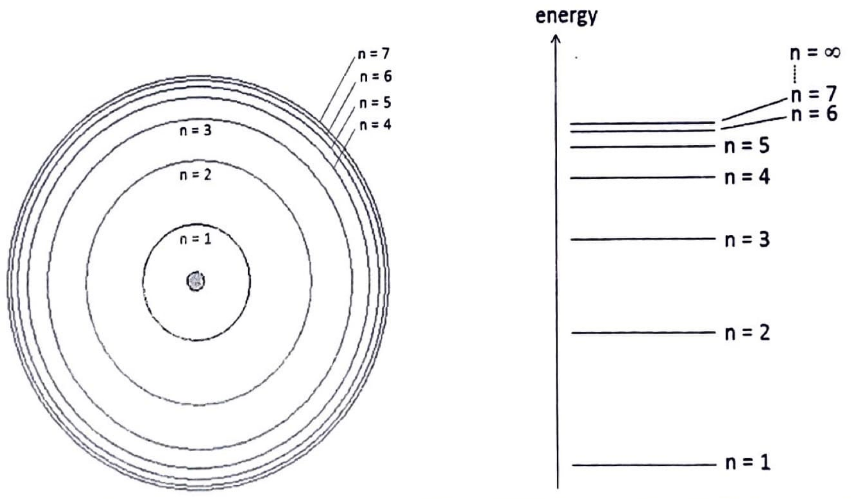
3.4 Electronic shells

- Electrons in atoms are arranged in a series of **shells** or **energy levels** surrounding the nucleus. Each shell is described by a number known as the **principal quantum number, n.**

- The principal quantum number n is a positive integer i.e. n = 1, 2, 3, ... (numbered outward from the nucleus).

  The greater the value of n,
  - the further the shell (or electron) is from the nucleus
  - the higher the energy level of the shell (or electron)
  - the weaker the electrostatic attraction between the nucleus and the electron
  - the larger the size of the orbital (or the orbital becomes more diffuse)

Diagrams showing shells or energy levels corresponding to the different principal quantum numbers



3.5 Subshells (sub-levels) and orbitals

- Each shell comprises one or more **subshells**. Each subshell, in turn, comprises one or more **orbitals**.

- An **orbital** represents a region in space in which there is a high probability (> 95%) of finding an electron.
  - Each orbital can accommodate **2 electrons**.
  - Each orbital has a distinctive geometrical shape (see Section 3.6).
  - The 'energy of an orbital' is the **energy of the electron** occupying the orbital.

Relationship between principal quantum number and subshells

Principal quantum number, n	Types of subshell
1	1s
2	2s, 2p
3	3s, 3p, 3d
4	4s, 4p, 4d, 4f

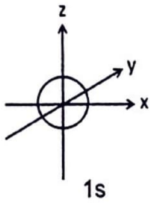
Note: The shell with principal quantum number n contains **n** subshells.

Relationship between subshells and orbitals

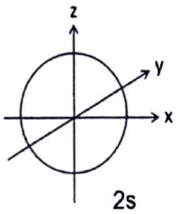
Subshell	No. of orbitals	Types of orbitals
s	1	s
p	3	p_x, p_y, p_z
d	5	$d_{xz}, d_{xy}, d_{yz}, d_{z^2}, d_{x^2-y^2}$
f	7	*(Read up on your own, if interested)*

3.6 Shapes of the orbitals

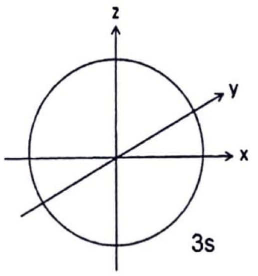
(a) The s orbital



1s



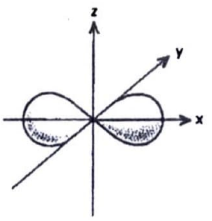
2s



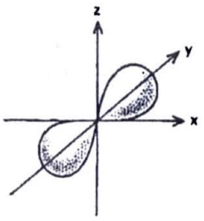
3s

- Shape of an s orbital: **spherical** shape
- s orbitals are **non–directional** as the electron density is not concentrated in any particular direction.
- s orbitals of different shells have the same spherical shape but different sizes.
- As **n** increases, the s orbital
  - increases in size, i.e. 1s < 2s < 3s < 4s
  - becomes **more diffuse**

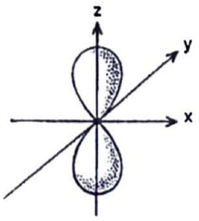
(b) The p orbitals



p_x



p_y



p_z

- Shape of a p orbital: **dumbbell** shape
- There are **three p orbitals** (i.e. p_x, p_y and p_z) in a **p subshell.**

- p orbitals are **directional** as the electron density is concentrated in certain directions along the x, y and z axes.
- The three p orbitals in the **same subshell** (with the same principal quantum number n are **<u>degenerate</u>** (i.e. they have the **same energy**).
- p orbitals of different shells have the same dumbbell shape but different sizes.
- As **n** increases, the p orbital
    - increases in size, i.e. 2p < 3p < 4p < 5p
    - becomes **more diffuse**

(c) The d orbitals

- There are **five d orbitals** (i.e. d_{xz}, d_{xy}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2}) in a d subshell.

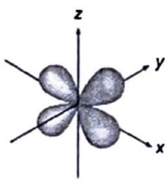
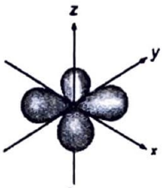
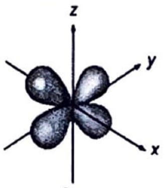
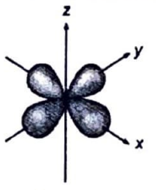
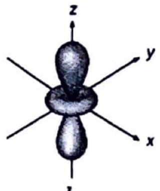
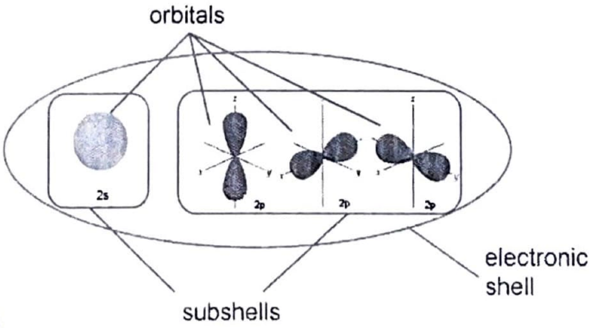
 d_{xz}  d_{xy}  d_{yz}	 $d_{x^2-y^2}$	 d_{z^2}
• These three orbitals have a similar 4–lobed shape. • These orbitals have their lobes **pointing between the axes.**	• This orbital also has a 4–lobed shape but it has its lobes **aligned along the x and y axes.**	• This orbital consists of a dumb–bell surrounded by a small doughnut shaped ring at its waist • This orbital is **aligned along the z axis.**

Diagram showing the relationship between electronic shell, subshells and orbitals



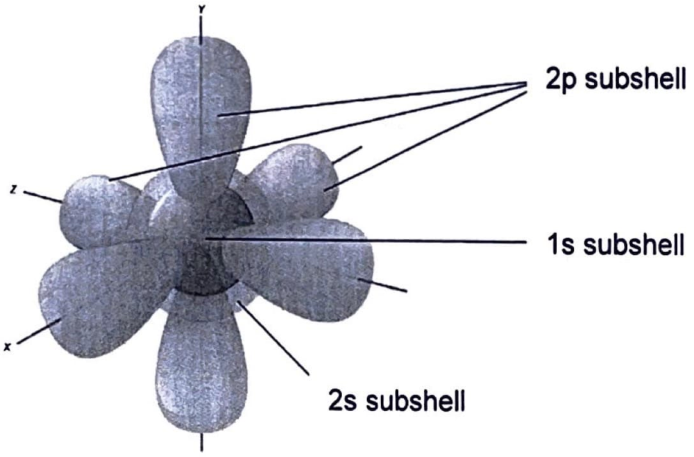
(using n = 2 as an example)

Each orbital has space for 2 electrons.

1) How many electrons can be placed in 2s subshell?	2
2) How many electrons can be placed in 2p subshell?	6
3) How many electrons can be placed in n=2 electronic shell, at maximum?	8

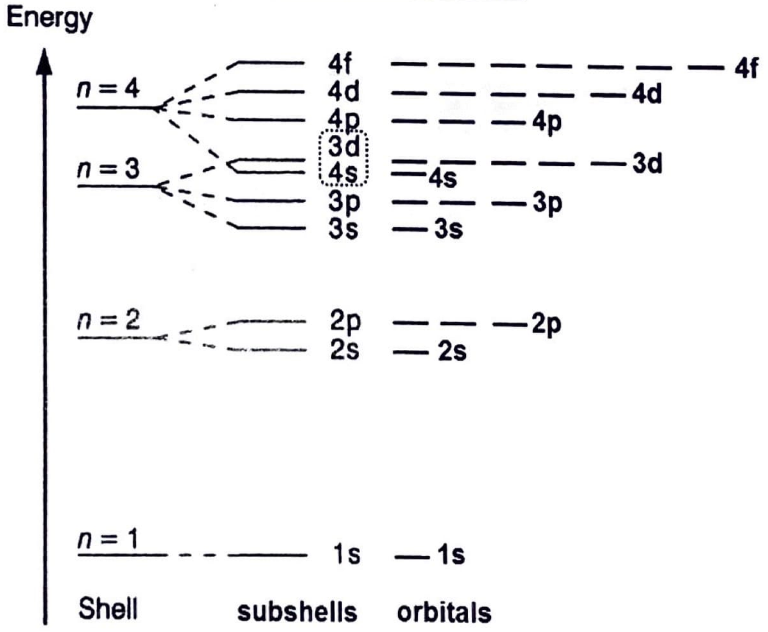
All the orbitals take up the space around the nucleus. As visualized in the diagram below:

- Orbitals found in inner electronic shells are smaller, and the electron density nearer the nucleus, compared to orbitals in the outer electronic shell (eg. n =1 compared to n = 2)
- Within the same electronic shell, the orbital from s subshell has electron density nearer to the nucleus than orbitals from p subshell. (eg. 2s orbital compared to 2p orbital)
- p orbitals are directional, s orbitals are not.



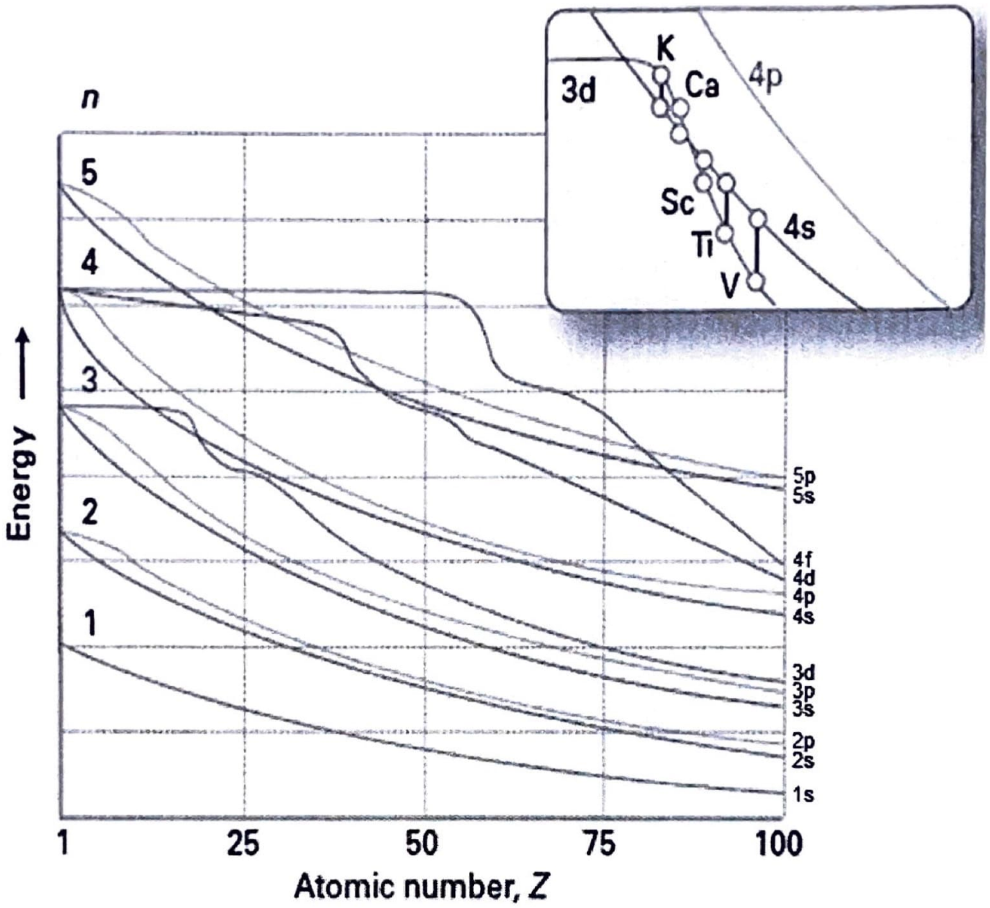
3.7 Relative energies of the orbitals

Diagram showing the relative energy levels of the orbitals (not to scale) in a multi–electron atom



- For orbitals in the same shell (i.e. with the same value of n), their relative energies increase in the following order: **s < p < d < f**
  e.g. 4s < 4p < 4d < 4f

Diagram showing the decrease in orbital energy with increasing atomic number



By observing the trend,

- As the atomic number increases, the energies of all the orbitals decrease, i.e. the energies of the electrons occupying those orbitals decrease.

- Due to their proximity to the nucleus, the spherically symmetrical s orbitals are affected to a greater degree than are the more angular p and d orbitals, and so their energies decrease more rapidly than the other types of orbitals.

- By n = 4, there is, in fact **an overlap between the 3rd and 4th shells.** As seen from the graph above, **the energy of the 4s subshell has already become less than that of the 3d subshell** at Z = 18 (argon).

- In summary, fill **4s before 3d**, as seen later in section 4.1 and 4.2

3.8 Summary

→ Increasing distance from nucleus

→ Increasing energy level

(generally)

Principal quantum number	n = 1	n = 2		n = 3			n = 4			
Subshells (s, p, d, f)	one subshell	two subshells		three subshells			four subshells			
	1s	**2s**	**2p**	**3s**	**3p**	**3d**	**4s**	**4p**	**4d**	**4f**
Orbitals (s, p, d, f)	one 1s orbital	one 2s orbital	three 2p orbitals	one 3s orbital	three 3p orbitals	five 3d orbitals	one 4s orbital	three 4p orbitals	five 4d orbitals	seven 4f orbitals
	$1s$	$2s$	$2p_x$ $2p_y$ $2p_z$	$3s$	$3p_x$ $3p_y$ $3p_z$	$3d_{xz}$ $3d_{xy},$ $3d_{yz}$ $3d_{z^2}$ $3d_{x^2-y^2}$	$4s$	$4p_x$ $4p_y$ $4p_z$	$4d_{xz}$ $4d_{xy},$ $4d_{yz}$ $4d_{z^2}$ $4d_{x^2-y^2}$	**Read up on your own, if interested**
No. of orbitals per shell	1	1 + 3 = 4		1 + 3 + 5 = 9			1 + 3 + 5 + 7 = 16			
Max. no. of e^- per subshell	2	2	6	2	6	10	2	6	10	14
Max. no. of e^- per shell	2	8		18			32			

Note: Each orbital can accommodate a maximum of **2 electrons**.

In the **nth shell**,

- number of subshells = n
- number of orbitals = n^2
- maximum number of electrons that can be accommodated = $2n^2$

Example 1: In the **3rd shell**,

- number of subshells = 3
- number of orbitals = 9
- maximum number of electrons that can be accommodated = $(2)(3^2) = 18$

Example 2: In the **4th shell**,

- number of subshells = 4
- number of orbitals = 16
- maximum number of electrons that can be accommodated = $(2)(4^2) = 32$

4 ELECTRONIC CONFIGURATIONS

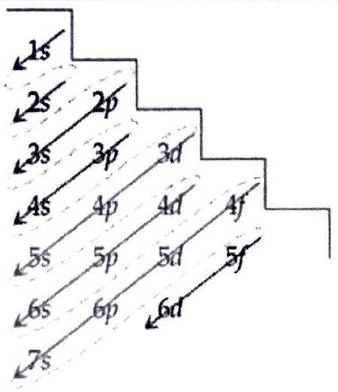
- The **electronic configuration** of an atom (or ion) refers to how its electrons are distributed among the various atomic orbitals i.e. how its electrons are arranged in the shells, subshells and orbitals.

- Different ways of writing electronic configurations

(i)	Using shells/energy levels notation	Si:	2.8.4 (not usually used at "A" levels)
(ii)	Using the s, p, d, f notation	Si:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ or *[Ne] $3s^2\ 3p^2$ *[Ne] represents $1s^2\ 2s^2\ 2p^6$
(iii)	Using electrons-in-boxes diagram	Si:	[↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑][↑][ ] 1s 2s 2p 3s 3p

4.1 The basic rules to writing electronic configurations

- The principles that govern the distribution of electrons in the orbitals are:

1	**The Aufbau (building-up) Principle**	- Electrons fill orbitals **from the lowest energy orbital upwards**.		
			- Order of filling up of orbitals: 1s → 2s → 2p → 3s → 3p → **4s → 3d** → 4p → 5s → 4d → … - Electrons occupy the **4s orbital first** before the 3d because the 4s orbitals are at a **lower energy level** than the 3d orbitals (see page 11).	
2	**Hund's Rule**	- Orbitals of a **subshell** (i.e. orbitals of the same energy) must be occupied **singly** by electrons of **parallel spins** before pairing can occur. This helps to minimise inter–electronic repulsion.		
		[↑][↑][↑] ✓ 2p	[↑][↑][↓] ✗ 2p	[↑↓][↑][ ] ✗ 2p
3	**The Pauli Exclusion Principle**	- Each orbital can hold a maximum of **two electrons** and they must be of **opposite spins**.		
		[↑↓] ✓	[↑↑] ✗	[↓↓] ✗
		Note: Paired electrons can only be stable when they spin in opposite directions so that the magnetic attraction which results from their **opposite spins** can counterbalance the electrical repulsion which results from their identical charges.		

4.2 Writing electronic configurations

principal quantum number ber

$1s^1$

number of electrons in subshell

type of subshell

(a) The first twenty elements (Z = 1 to Z = 20)

Element	'Electrons–in–boxes' diagram	Electronic configuration
$_{1}$H	[↑] 1s	$1s^1$
$_{2}$He	[↑↓] 1s	$1s^2$
$_{3}$Li	[↑↓] [↑] 1s 2s	$1s^2\ 2s^1$
$_{4}$Be	[↑↓] [↑↓] 1s 2s	$1s^2\ 2s^2$
$_{5}$B	[↑↓] [↑↓] [↑][ ][ ] 1s 2s 2p	$1s^2\ 2s^2\ 2p^1$
$_{6}$C	[↑↓] [↑↓] [↑][↑][ ] 1s 2s 2p	$1s^2\ 2s^2\ 2p^2$
$_{7}$N	[↑↓] [↑↓] [↑][↑][↑] 1s 2s 2p	$1s^2\ 2s^2\ 2p^3$
$_{8}$O	[↑↓] [↑↓] [↑↓][↑][↑] 1s 2s 2p	$1s^2\ 2s^2\ 2p^4$
$_{9}$F	[↑↓] [↑↓] [↑↓][↑↓][↑] 1s 2s 2p	$1s^2\ 2s^2\ 2p^5$
$_{10}$Ne	[↑↓] [↑↓] [↑↓][↑↓][↑↓] 1s 2s 2p	$1s^2\ 2s^2\ 2p^6$

Element	Electronic configuration
$_{11}$Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$
$_{12}$Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$
$_{13}$Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
$_{14}$Si	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
$_{15}$P	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
$_{16}$S	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
$_{17}$Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
$_{18}$Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
$_{19}$K	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
$_{20}$Ca	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

(b) The first row d-block elements (Z = 21 to Z = 30)

Using [Ar] to represent

1s	2s	2p			3s	3p		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Element	'Electrons-in-boxes' diagram							Electronic configuration
		3d					4s	
$_{21}$Sc	[Ar]	↑					↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^1\ 4s^2}$
$_{22}$Ti	[Ar]	↑	↑				↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^2\ 4s^2}$
$_{23}$V	[Ar]	↑	↑	↑			↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^3\ 4s^2}$
$_{24}$Cr *	[Ar]	↑	↑	↑	↑	↑	↑	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^5\ 4s^1}$
$_{25}$Mn	[Ar]	↑	↑	↑	↑	↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^5\ 4s^2}$
$_{26}$Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^6\ 4s^2}$
$_{27}$Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^7\ 4s^2}$
$_{28}$Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^8\ 4s^2}$
$_{29}$Cu *	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^{10}\ 4s^1}$
$_{30}$Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^{10}\ 4s^2}$

Note: Electrons occupy the 4s orbital first before the 3d orbitals because the 4s orbital is at a lower energy level than the 3d orbitals

4.3 Anomalous electronic configurations of Cr and Cu

- The electronic configuration of Cr is $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1}$.

			3d	4s		
$_{24}$Cr	Expected electronic configuration	[Ar]	↑ ↑ ↑ ↑ ☐	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$ less stable	✗
	Actual electronic configuration	[Ar]	↑ ↑ ↑ ↑ ↑	↑	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ **more stable**	✓

Reason: 3d and 4s orbitals are about equal in energy by the time Cr is reached.
By having one electron each in the 3d and 4s orbitals, **inter–electronic repulsion** is minimised.

- The electronic configuration of Cu is $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1}$.

			3d	4s		
$_{29}$Cu	Expected electronic configuration	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$ • less stable	✗
	Actual electronic configuration	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ • **more stable**	✓

Reason: The **fully filled** 3d subshell is unusually stable due to the symmetrical charge distribution around the metal centre.

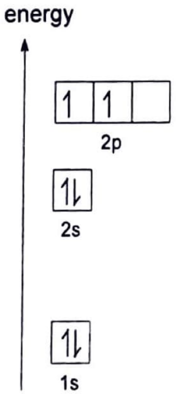
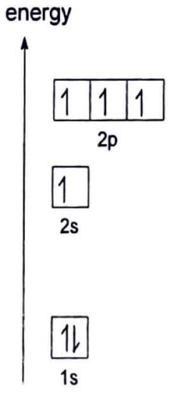
Summary:

- Order of **filling** up electrons: 1s → 2s → 2p → 3s → 3p → **4s** → **3d** → 4p → 5s
  (Electrons occupy the **4s** orbital **first** before the 3d orbitals)
- Order of **writing** electronic configuration follows the order of the principal quantum shell
  (i.e. 1s → 2s → 2p → 3s → **3p** → **3d** → **4s** → **4p** →5s)
- Each orbital can fill up to **2** electrons
- Degenerate orbitals of a subshell must be occupied **singly** and with **parallel spins**
- Both **Cr** and **Cu** have **anomalous** electronic configuration.

Note: there is an easier way of figuring out and writing electronic configuration based on Periodic Table (refer in section 4.7)

4.4 Ground state and excited state

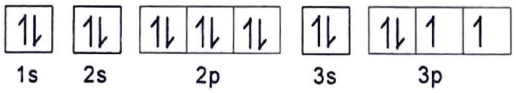
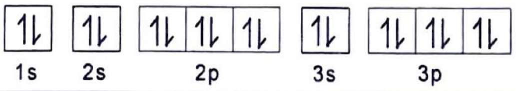
- An atom is in the **ground state** when the electrons are in the orbitals of **lowest available energy level**. Most atoms are in their ground state at room temperature.
- The electronic configurations written so far on the earlier pages are all **ground state electronic configurations** (i.e. the most stable electronic configurations).
- An atom is in the **excited state** when one or more electrons **absorb energy** and are promoted to a **higher energy level**. Excited atoms are **unstable** and can emit energy to return to the ground state.

$_{6}$C (ground state) $1s^2\ 2s^2\ 2p^2$	$_{6}$C* (excited state) $1s^2\ 2s^1\ 2p^3$	Other possible electronic configurations of C in the excited state:
		$1s^2\ 2s^2\ 2p^1\ 3s^1$ or $1s^2\ 2s^1\ 2p^1\ 3s^1\ 3p^1$ *Note that the electrons in the 1s orbital do not usually get promoted (energy gap between n=1 and n=2 is too wide)

4.5 Electronic configurations of ions

- Ions are formed when atoms gain or lose electrons.

(a) Anions (negative ions)

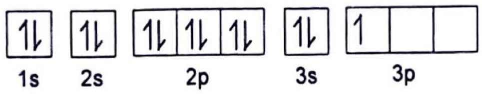
General rule:	Electrons are added to the **next available orbital** (i.e. the next energetically accessible orbital) in the atom during the formation of an anion.	
Example: $_{16}$S		$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
$_{16}S^{2-}$		$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

(b) Cations (positive ions)

General rule:	Electrons are first removed from the orbitals with the **highest energy**.

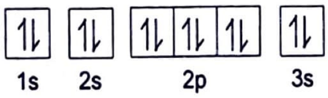
Example: Cations from the main groups (e.g. Al)

$_{13}$Al



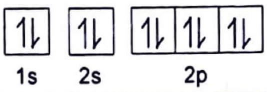
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

$_{13}$Al$^+$



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

$_{13}$Al^{3+}



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

Example: Cations from the d–block (e.g. Fe)

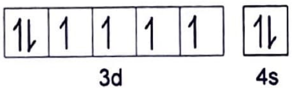
Note: 4s electrons are lost before the 3d electrons
(with reference to the first row transition elements)

Electrons occupy the 4s orbital first because the 4s orbital is at a lower energy level than the 3d orbitals.

*Once electrons occupy the **inner 3d orbitals**, they (i.e. the 3d electrons) provide some shielding for the **outermost 4s electrons**. They repel the 4s electrons to a slightly higher energy level.*

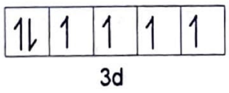
Hence in the formation of cations, **the 4s electrons are lost before the 3d electrons**.

$_{26}$Fe [Ar]



$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

$_{26}$Fe^{2+} [Ar]



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

Note: when writing electronic configuration of ions, first figure out the original electronic configuration of the relevant atoms and modify to give the ionic electronic configuration.

4.6 Electronic configurations and isoelectronic species

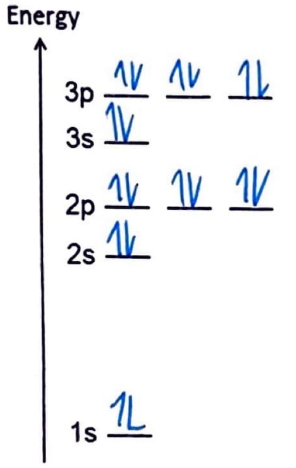
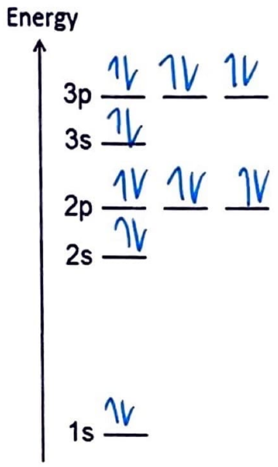
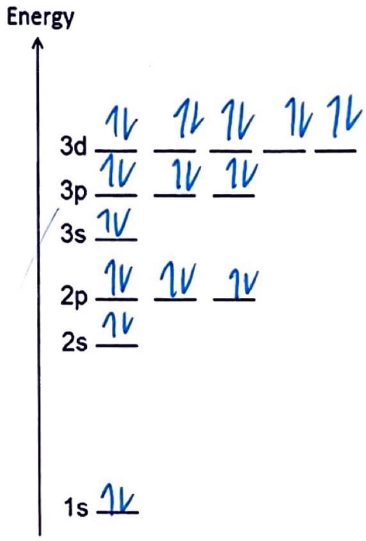
- Isoelectronic species are species with the **same total number of electrons**.

Examples of isoelectronic species:

Atoms or ion	Electronic configuration	Total number of electrons
N^{3-}, O^{2-}, F^-, Ne, Na^+	$1s^2 2s^2 2p^6$	10
Cr	$1s^2 2s^2 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$	24
Mn^+	$1s^2 2s^2 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$	24
Fe^{2+}	$1s^2 2s^2 2p^6\ 3s^2\ 3p^6\ 3d^6$	24

Worked Example 4

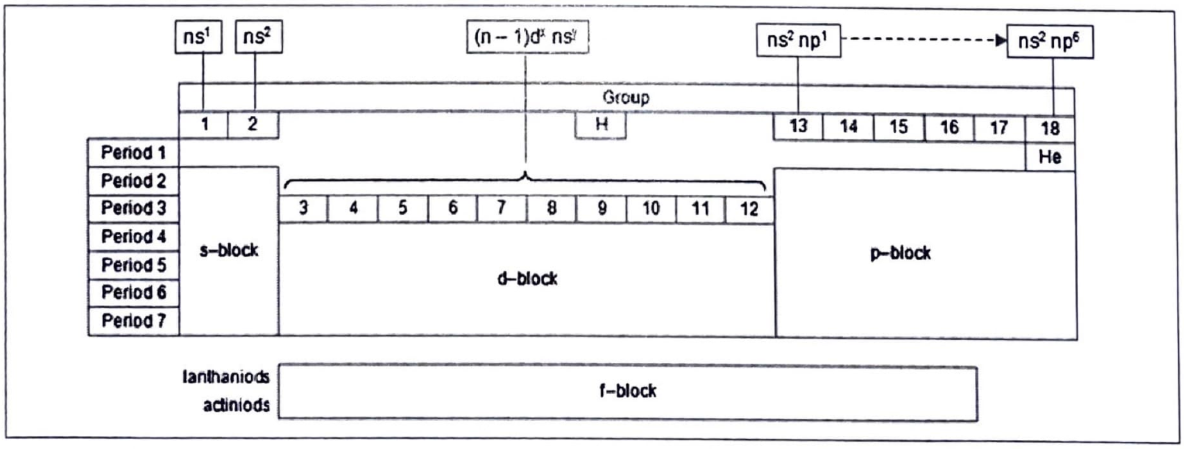
Write down the electronic configuration of each of the following species and draw **an energy level diagram** to illustrate each electronic configuration.

(a) S^{2-}	**(b) Ca^{2+}**	**(c) Cu^{+}**
S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ S^{2-}: $1s^2\ 2s^2\ 2p^6$ $3s^2\ 3p^6$	Ca: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ Ca^{2+}: $1s^2\ 2s^2\ 2p^6$ $3s^2\ 3p^6$	Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ Cu^{+}: $1s^2\ 2s^2\ 2p^6\ 3s^2$ $3p^6\ 3d^{10}$
		

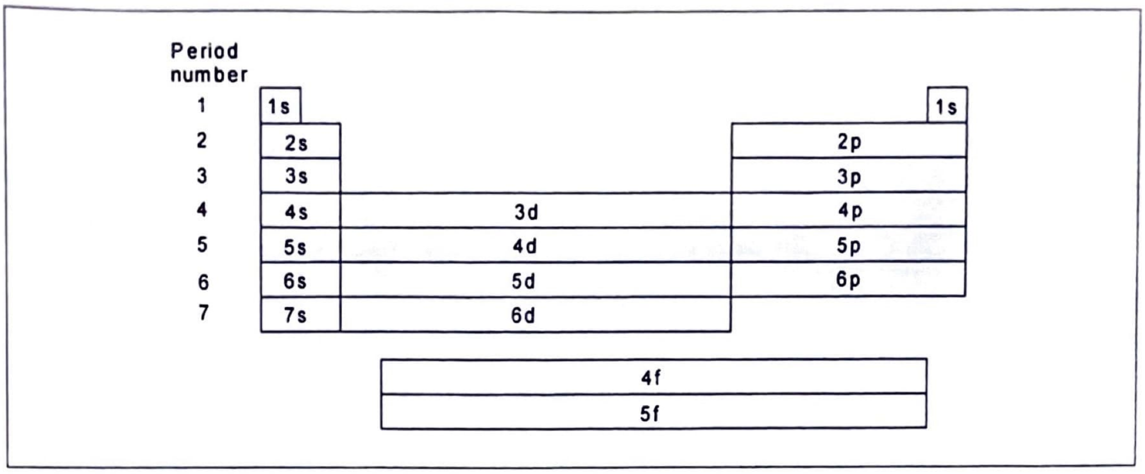
4.7 Electronic configurations and the Periodic Table

- Based on the electronic configurations of the elements, the elements in the Periodic Table are grouped into four blocks, the **s, p, d and f blocks**, as shown below.

- The name of each block is determined by whether an s, p, d or f subshell is being filled in successive elements of that block.



Period no = outer/valence shell
Group no = y for groups 1 and 2 and (10 + y) for groups 13 to 18 where y = no of valence electrons
x-block = highest energy subshell filled



- **Horizontal rows** in the Periodic Table are called **<u>periods</u>**. Elements in the same period have the same number of electronic shells. The period number of an element is the number of electronic shells occupied with electrons in an atom of that element.

- **Vertical columns** in the Periodic Table are called **<u>groups</u>**. Elements in the same group have the same number of valence electrons and hence similar outer electron configurations.

	Group							
Group number	1	2	13	14	15	16	17	18
Group name	alkali metals	alkaline earth metals			pnicogens	chalcogens	halogens	noble gases
Electronic configuration of valence shell	ns^1	ns^2	$ns^2\ np^1$	$ns^2\ np^2$	$ns^2\ np^3$	$ns^2\ np^4$	$ns^2\ np^5$	$ns^2\ np^6$

Example:

Bromine is a Group 17 element ⇒ electronic configuration of valence shell is **$ns^2\ np^5$**
(position in group gives the outer shell electronic confuration)

Bromine is a Period 4 element ⇒ n = 4 (**Period gives the no. of shells)**

Hence the electronic configuration of bromine is **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^{10} 4s^2 4p^5$**

5 ELECTROSTATIC EFFECTS

- Electrostatic effects – attraction of opposite charges and repulsion of like charges – play a major role in determining the energy states of atoms and hence influence their atomic properties, such as atomic size and ionisation energies.

- The main factors that affect the strength of the electrostatic attraction between the nucleus and the electrons are:

1. **Number** of **electronic shells**

   If the **number of shells** increases,
   - the principal quantum number, n, of the outermost (valence) shell **increases**
   - distance between the nucleus and the valence electron **increases**
   - electrostatic attraction between the nucleus and the valence electron **decreases**

2. **Nuclear charge, Z**

   If the number of protons increases,
   - **nuclear charge increases**
   - electrostatic attraction between the nucleus and the valence electron **increases**

3. **Shielding effect (or screening effect)** by **inner electrons**

   If the **number of inner shell electrons** increases
   - shielding effect experienced by the valence electron **increases**
   - electrostatic attraction between the nucleus and the valence electron **decreases**

2* Effective nuclear charge, (Z_{eff})

The effective nuclear charge is the resultant positive charge experienced by the valence electrons in a multi-electron atom taking into consideration the shielding effect of the inner electrons.

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

where Z = proton number
and S = shielding (constant)

If **effective nuclear charge** increases,
- electrostatic attraction between the nucleus and the valence electron **increases**

When discussing the trend of the atomic properties **across a period**, it is common to consider factors 2 and 3 together and state their combined net effect using the term, **effective nuclear charge**.

Note: We will be making use of these factors in explaining the trends and variations in:

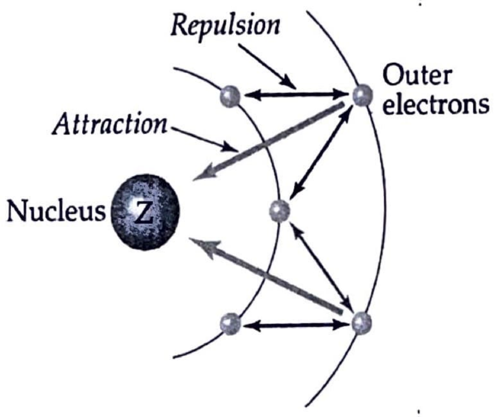
- atomic radius and ionic radius
- first ionisation energies across a period
- first ionisation energies down a group
- successive ionisation energies of an element
- electronegativity

- What is meant by shielding?

Since all electrons are negatively charged, they repel each other. The **electrons in inner shells repel the electrons in outer shells** and prevent them from experiencing the full effect of the actual nuclear charge. This is called **shielding**.

$$\underbrace{1s^2\,2s^2\,2p^6}_{\text{inner shell electrons}}\ \underbrace{3s^2\,3p^3}_{\text{valence electrons}}$$

The greater the shielding of outer electrons **by the inner shell electrons,** the weaker the attractive forces between the nucleus and the outer electrons.



Note:
Electrons in the **same shell** provide very **poor shielding effect** for one another.

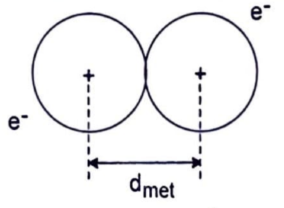
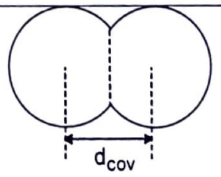
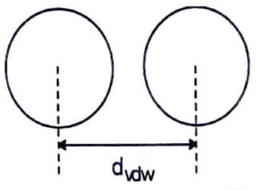
For a given shell n, **shielding ability of electrons decreases** in the following order: **s > p > d > f**

d and f electrons usually **provide poor shielding effect** for outermost electrons from the nuclear charge because the **d and f orbitals are rather diffuse**.

6 ATOMIC RADIUS

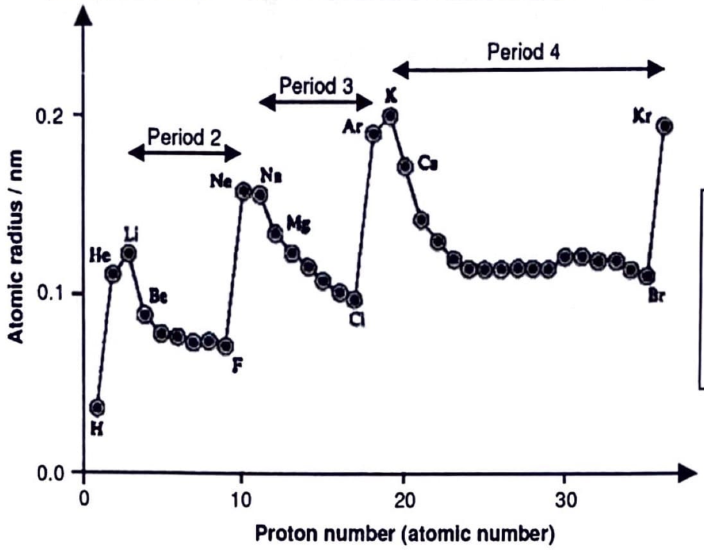
6.1 Definitions

- **Atomic radius** is defined as half the shortest inter–nuclear distance found in the structure of the element. This observed 'radius' of the atom depends upon *how the atom bonds or interacts with its neighbours.*

Atomic radius	The metallic radius of an atom is half the inter–nuclear distance between **two neighbouring atoms** in the **metal**. • Metallic radius is obviously restricted to those elements that form metallic lattices. Example: r_{Mg} = 0.160 nm	 metallic radius = $\frac{1}{2}d_{met}$
	The covalent radius of an atom is half the inter–nuclear distance between two **covalently bonded atoms**. • Covalent radius may be measured for most elements Example: r_{Cl} = 0.099 nm	 covalent radius = $\frac{1}{2}d_{cov}$
	The van der Waals' radius of an atom is half the inter–nuclear distance between **atoms** which are **<u>not</u> chemically bonded**. • Van der Waal's radius is most easily determined for non-metals, and is particularly useful for the lighter noble gases which do not form chemical bonds. Example: r_{Ar} = 0.192 nm	 van der Waals' radius = $\frac{1}{2}d_{vdw}$

6.2 Variation in atomic radii

Diagram showing the atomic radii of the elements



*Note: the values of Ne, Ar and Kr are van der Waals' radius

6.2.1 Trend in atomic radii across a Period

Group	1	2	13	14	15	16	17	18
Period 3 elements	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic radius / nm	0.186	0.160	0.143	0.117	0.110	0.104	0.099	0.190
Note: Data are obtained from the Data Booklet.								

Trend:	Atomic radii **decrease** across a period. (with reference to Period 2 and 3.)
Explanation:	Across a period, • the number of shells remain the same. • number of protons increases and hence **nuclear charge increases.** • number of electrons also increases but these electrons are added to the same outermost shell, and hence **shielding effect remains approximately constant**. • effective nuclear charge increases. • electrostatic attraction between the nucleus and the valence electrons **increases**, resulting in a **decrease** in the size of the electron cloud. Hence atomic radii **decrease** across a period.

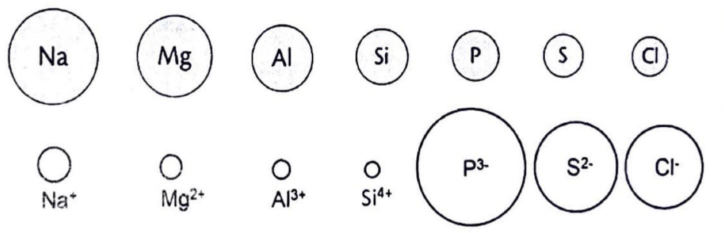
6.2.2 Trend in atomic radii down a Group

Group 17 elements	F	Cl	Br	I	At
Atomic radius / nm	0.072	0.099	0.114	0.133	0.140
Trend:	Atomic radii **increase** down a group.				

Explanation:	Down a group, - the **number of electronic shells increases** - distance between the nucleus and the valence electrons **increases** - shielding experienced by valence electrons **increases** Despite the increasing nuclear charge, - electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in an **increase** in the size of the electron cloud. Hence atomic radii **increase** down a group.

7 IONIC RADIUS

The ionic radius of an ion can be defined as the radius of the spherical ion in an ionic compound.

Group	**1**	**2**	**13**	**14**	**15**	**16**	**17**	**18**
Period 3 elements	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic radius / nm	0.186	0.160	0.143	0.117	0.110	0.104	0.099	0.192
Ion	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	P^{3-}	S^{2-}	Cl^-	--
Ionic radius / nm	0.095	0.065	0.050	0.041	0.212	0.184	0.181	--
								

7.1 Cationic radius ($r_{cation} < r_{atom}$)

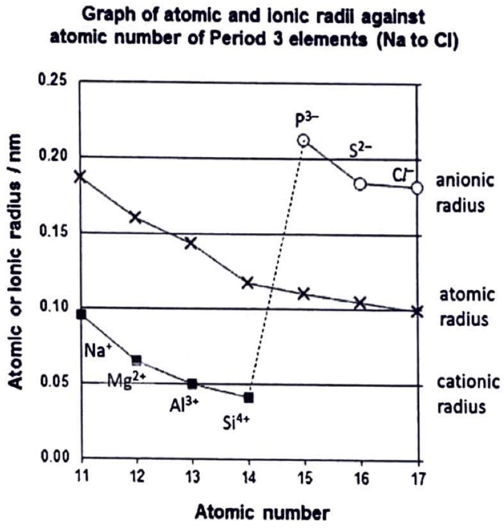
Observation:	The radius of a cation is always **smaller** than that of the parent atom.	
Example:	Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ r_{Mg}: 0.160 nm	Mg^{2+}: $1s^2\ 2s^2\ 2p^6$ $r_{Mg^{2+}}$: 0.065 nm
Explanation:	- Both the cation and its parent atom have the same number of protons and hence have the **same nuclear charge**. - However, the cation has **one less electronic shell** than its parent atom Electrostatic attraction between the nucleus and the valence electrons **increases**, resulting in a **decrease** in size of the electron cloud.	

7.2 Anionic radius ($r_{atom} < r_{anion}$)

Observation:	The radius of an anion is always **greater** than that of the parent atom.
Example:	S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ r_S: 0.104 nm S^{2-}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ $r_{S^{2-}}$: 0.184 nm
Explanation:	• Both the anion and its parent atom have the same number of protons and hence have the **same nuclear charge**. • However, the anion has **more electrons** than its parent atom. • With more electrons, **electron–electron repulsion increases** • Electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in an **increase** in the size of the electron cloud.

7.3 Ionic radii of isoelectronic species

Observation:



Ionic radii of isoelectronic ions **decrease** across a period.

Example:

Trend	$Na^+ > Mg^{2+} > Al^{3+}$		
Ions	Na^+	Mg^{2+}	Al^{3+}
No. of p	11	12	13
No. of e⁻	10	10	10
Electronic configuration	$1s^2\ 2s^2\ 2p^6$		

$P^{3-} > S^{2-} > Cl^-$		
P^{3-}	S^{2-}	Cl^-
15	16	17
18	18	18
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$		

Explanation:

- Na^+, Mg^{2+} and Al^{3+} are isoelectronic species and hence their valence electrons experience the **same shielding effect**.
- However, **nuclear charge increases** from Na^+ to Al^{3+}.
- Effective nuclear charge **increases** from Na^+ to Al^{3+}
- Electrostatic attraction between the nucleus and the valence electrons **increases**, resulting in the **decrease** in the size of the electron cloud.

Explanation for the trend observed from P^{3-} to Cl^- is the same as above.

- Additional point to note:

Observation:	There is a sharp increase in ionic radius from Al^{3+} to P^{3-}.
Example:	Al^{3+}: $1s^2\ 2s^2\ 2p^6$ P^{3-}: $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^6}$
Explanation:	From Al^{3+} to P^{3-}, • **nuclear charge and shielding effect increase**. As the **number of electronic shells increases**, • distance between the nucleus and the valence electrons **increases** • electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in an **increase** in the size of the electron cloud. Hence the ionic radius of P^{3-} is bigger than that of Al^{3+}.

---

8 IONISATION ENERGIES

8.1 Definitions

first ionisation energy	The first ionisation energy of an element M is the energy required to remove **1 mole of electrons** from **1 mole of gaseous M atoms** to form **1 mole of gaseous M⁺ ions**.	
	Equation: $M(g) \rightarrow M^+(g) + e^-$	ΔH = 1st ionisation energy
	Example: $Ca(g) \rightarrow Ca^+(g) + e^-$	$\Delta H = +590\ kJ\ mol^{-1}$
second ionisation energy	The second ionisation energy of an element M is the energy required to remove **1 mole of electrons** from **1 mole of gaseous M^+ ions** to form **1 mole of gaseous M^{2+} ions**.	
	Equation: $M^+(g) \rightarrow M^{2+}(g) + e^-$	ΔH = 2nd ionisation energy
	Example: $Ca^+(g) \rightarrow Ca^{2+}(g) + e^-$	$\Delta H = +1150\ kJ\ mol^{-1}$

- Ionisation is an **endothermic** process and ionisation energies are positive values since energy is absorbed during ionisation to overcome the attraction between the electron and the nucleus.

- Ionisation energies affect the type of bond formed by the atom with other atoms. Elements with low ionisation energies will find it easy to lose an electron to form a cation, resulting in ionic bonds being formed.

Worked Example 5

(a) Write an equation to represent the reaction in which its enthalpy change is equal to the third ionisation energy of sodium.

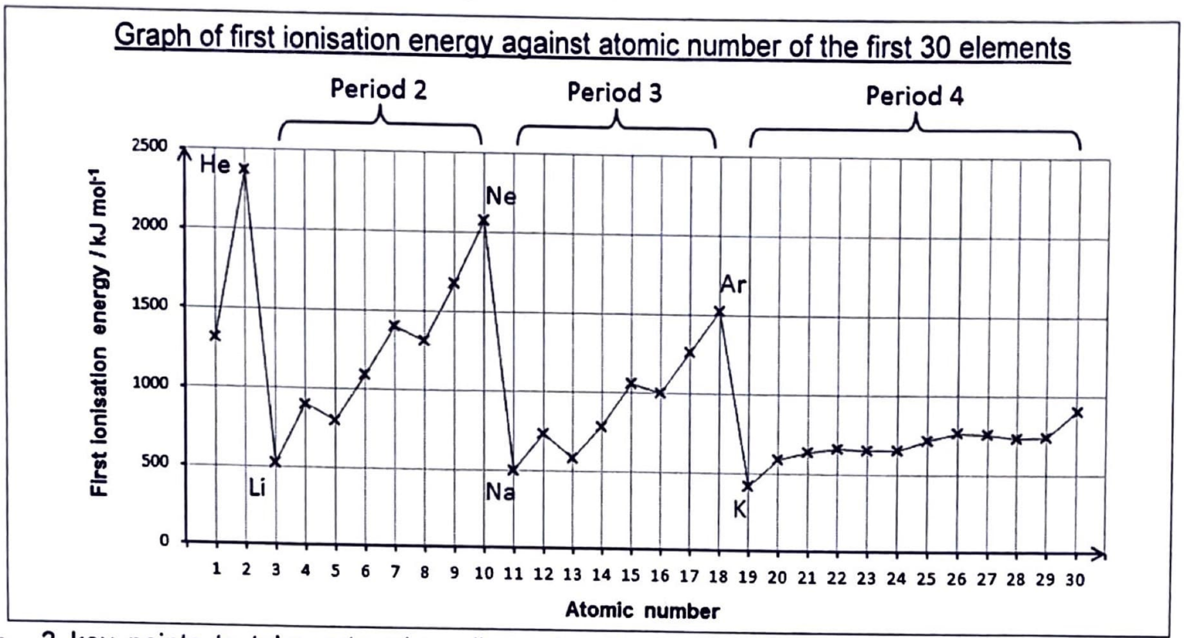
$Na^{2+}(g) \rightarrow .\ Na^{3+}(g) + e^-$

(b) Name the enthalpy change for the following reaction: $O(g) \rightarrow O^{3+}(g) + 3e^-$.

1st + 2nd + 3rd IE of O.

8.2 Trends in ionisation energies

8.2.1 Trend in first ionisation energies across a Period



- 3 key points to take note when discussing the trend of first ionisation energies across a period.
  (i) general increment across a period (Period 2 & 3)
  (ii) irregularity 1 – **due to higher energy p electron vs s electron** of Group 13 vs Group 2
  (iii) irregularity 2 – **due to repulsion experienced by the paired p electron of** Group 16 vs **unpaired p electron of** Group 15

  When answering a question, you need to decide between (i), (ii) or (iii) by examining the electronic configuration.

(i) General increment across a period

Trend:	The first ionisation energies of elements **<u>generally increase</u>** across a period.
Explanation:	Across a period, • the number of shells remain the same. • number of protons increases and hence **<u>nuclear charge increases.</u>** • number of electrons also increases but these electrons are added to the same outermost shell, and hence **<u>shielding effect remains approximately constant</u>**. • **effective nuclear charge increases.** • electrostatic attraction between the nucleus and the valence electrons **<u>increases</u>**, resulting in an **<u>increase</u>** in the energy required to remove the valence electron from an atom. Hence the 1st IE of the elements **<u>generally increase</u>** across a period.

(ii) Irregularity 1 – Group 2 & Group 13

Examples:	The first ionisation energy of B is **lower** than that of Be. The first ionisation energy of Al is **lower** than that of Mg.
Explanation:	Mg: $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2}$ Al: $1s^2\ 2s^2\ 2p^6\ 3s^2\ \mathbf{3p^1}$ The 3p electron to be removed from Al is at a **<u>higher energy level</u>** than the 3s electron to be removed from Mg. • Hence **<u>less energy</u>** is required to remove the 3p electron in Al than the 3s electron in Mg. • First ionisation energy of Al is **<u>lower</u>** than that of Mg.

(iii) Irregularity 2 – Group 15 & Group 16

Examples:	The first ionisation energy of O is **lower** than that of N. The first ionisation energy of S is **lower** than that of P.
Explanation:	P: [Ne] [↿⇂] [↿ | ↿ | ↿] (3s, 3p) S: [Ne] [↿⇂] [↿⇂ | ↿ | ↿] (3s, 3p) • The 3p electron to be removed from S is a **paired electron** while that to be removed from P is an **unpaired electron**. • Due to **inter–electronic repulsion** between paired electrons in the same orbital, **less energy** is required to remove the paired 3p electron from S. • Hence the first ionisation energy of S is **lower** than that of P.

8.2.2 Trend in first ionisation energies down a Group

Group 1	1st I.E. / kJ mol^{-1}
Li	519
Na	494
K	418
Rb	403
Cs	376

Group 17	1st I.E. / kJ mol^{-1}
F	1680
Cl	1260
Br	1140
I	1010
At	920

Trend:	The first ionisation energies of the elements generally **decrease** down a group.
Explanation:	Down a group, • the **number of electronic shells increases** • distance between the nucleus and the valence electrons **increases** • shielding experienced by valence electrons **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in an **decrease** in the energy required to remove a valence electron. Hence first ionisation energies **decrease** down a group.

With reference to graph of 1st IE against atomic number on page 26, it is noted that there is a great decease in 1st IE between Ne & Na and between Ar & K. Why?

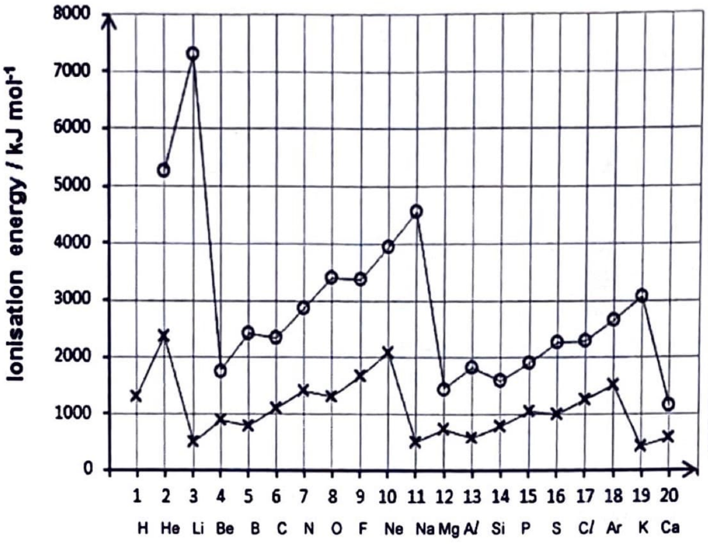
Ne: $1s^2\ 2s^2\ \mathbf{2p^6}$ **vs** Na: [Ne]$\mathbf{3s^1}$ Ar: [Ne]$3s^2\mathbf{3p^6}$ K: [Ar]$4s^1$

- In both cases, electron removed from gp 1 element is from larger electron shell compare to preceeding gp 18 element
- distance between the nucleus and the valence electrons **increases**
- shielding experienced by valence electrons **increases**

Despite the increasing nuclear charge,

- electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in an **decrease** in the energy required to remove a valence electron.
- Hence first ionisation energies of Na is much lower than Ne, and K much lower than Ar

Graph of first (x) and second ionisation energies (o) against atomic number of the first 20 elements



- Second IE > first IE because more energy is required to remove an electron from a positive ion.
- Right–upward shift of graph observed: every element has one less electron, thus the 2nd IE trends in the same way as 1st IE of the previous element.

For any **n^th^ IE**, element with n valence electrons still has an outer shell electron to lose
The preceding element (with n-1 valence electrons) loses an inner shell electron, since it has already lost all its valence electrons), hence much higher IE.
The succeeding element will have higher IE due to increasing effective nuclear charge.
For the graph of variation of nth IE against atomic number, **the element with n valence electrons has much lower nth IE than the preceding element**. Hence, the element at the lowest point of the nth IE trend is from Group n (for n = 1 or 2) or 10+n (for n > 2).

Worked Example 6

For each pair of species below, predict and explain which has a higher *second* ionisation energy.

Hint: Always figure out the electronic configuration of the species first, in order to determine which factor is to be compared; if (i) p vs s electrons, or (ii) paired vs unpaired p electrons are removed, an irregular trend is predicted. Otherwise, usually effective nuclear charge, which explains the general periodic trend is the main consideration.

(a) Al and Si	(b) O and F
Al^+: $1s^2\ 2s^2\ 2p^6\ 3s^2$ Si^+: $1s^2\ 2s^2\ 2p^6$ $3s^2,\ 3p^1$ *Note: ns^2 vs $ns^2\ np^1$*	O^+: $1s^2\ 2s^2\ 2p^3$ F^+: $1s^2\ 2s^2\ 2p^4$ *Note: $ns^2\ np^3$ vs $ns^2\ np^4$*
• The 3p electron to be removed from Si^+ is at a higher **energy level** than the 3s electron to be removed from Al^+. • Hence **less energy** is required to remove the 3p electron in Si^+ than the 3s electron in Al^+. ∴ Al has a higher 2nd I.E. than Si.	• Due to inter-electronic repulsion between paired electrons in the same 2p orbital, **less energy** is required to remove the 2p electron from F^+, compared to the unpaired 2p electron from O^+. ∴ O has a higher 2nd I.E. than F.

8.2.3 Trend in successive ionisation energies of an element

	1st	2nd	3rd	4th	5th	6th
Ionisation energies of K / kJ mol^{-1}	418	3070	4600	5860	7980	9650

Trend:	Successive ionisation energies of an element **increase**.
Explanation:	This is because once the first electron is removed from the neutral atom, each successive electron is removed from an ion of **increasing positive charge** which attracts the electrons more strongly.
Alternative explanation:	$K(g) \longrightarrow K^+(g) \longrightarrow K^{2+}(g) \longrightarrow K^{3+}(g) \longrightarrow K^{4+}(g) \longrightarrow K^{5+}(g) \longrightarrow K^{6+}(g)$ • number of protons remains the same and hence **nuclear charge remains the same** • number of electrons **decreases** • electrostatic attraction between the nucleus and the remaining electrons **increases**, resulting in an **increase** in energy required to remove each subsequent electron.

8.2.4 Deducing group number from successive ionisation data

1st ionisation energy:	$K(g) \rightarrow K^+(g) + e^-$	$\Delta H_1 = +418$ kJ mol^{-1}
2nd ionisation energy:	$K^+(g) \rightarrow K^{2+}(g) + e^-$	$\Delta H_2 = +3070$ kJ mol^{-1}

Observation:	Large jump in the 1st and 2nd I.E. of K.
Explanation:	K: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ K$^+$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ • K belongs to Group 1 and has 1 valence electron. • Significantly more energy is required to remove the 2nd electron from K as the 2nd electron is located in a different shell, one that is inner and **nearer to the nucleus**, and hence experiences a stronger electrostatic attraction to the nucleus.

Worked Example 7

The first eight ionisation energies (in kJ mol^{-1}) of an element **E** are as follows:

703 1610 2460 4350 5400 8500 10300 12300

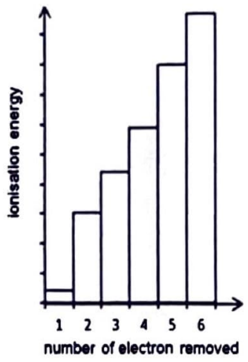
Difference: 907 850 1890 1050 3100 1800 2000

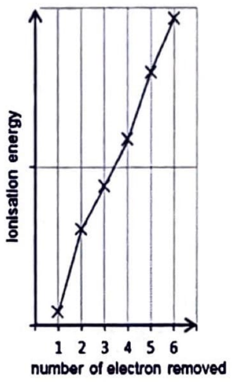
State the group of the Periodic Table to which **E** is likely to belong. State your reasoning clearly.

- A large jump in the 5th and 6th ionisation energies is observed.
- Significantly more energy is required to remove the 6th electron as it is located in an inner shell.
  ∴ There are 5 electrons in the valence shell. ⇒ **E** is likely to be in Group 15.

Worked Example 8

The graphs of the first six successive IE of an element **X** are shown below.





Deduce the group in the Periodic Table **X** is likely to belong to.

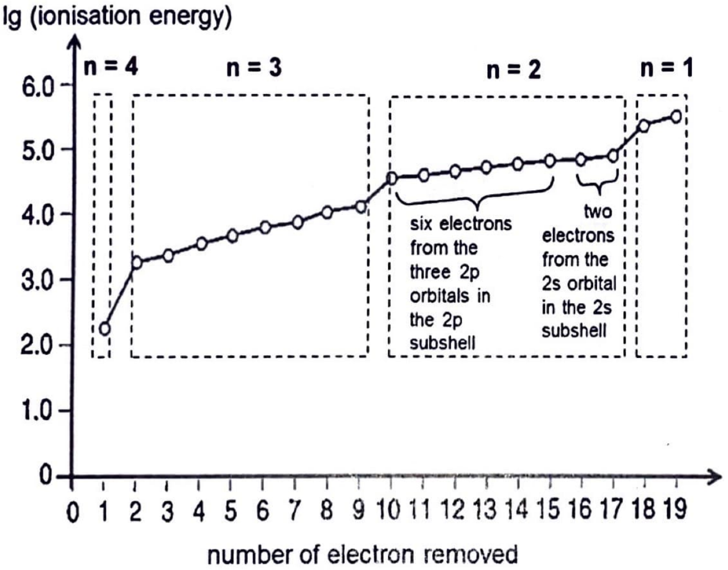
State your reasoning clearly.

- A large jump in the **1st** and **2nd** ionisation energies is observed.
- Significantly more energy is required to remove the 2nd electron as it is located in an inner shell.

  ∴ There is 1 electron in the valence shell. ⇒ **X** is likely to be in Group 1.

8.2.5 Deducing electronic configuration & other information from successive ionisation data

Graph showing successive ionisation energies for an element **X**



Note:
It is common to have **lg (ionisation energy)** instead of ionisation energy as the vertical axis. This is to **allow the large range of ionisation energies** to be fitted conveniently on the vertical scale and also to make any large difference between successive ionisation energies more apparent.

- Information which can be obtained from the above graph of successive IE

  (i) There are **a total of 19 electrons** present in an atom of the element.

  The electronic configuration of the element **X** is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$.

  (ii) There are **4 electronic shells**.

  A **large jump** in ionisation energies is observed when an electron is removed from a **different shell**, one that is **inner and nearer to the nucleus**, and hence experiences a stronger electrostatic attraction to the nucleus.

  The graph shows 3 such large increases in ionisation energies corresponding to the removal of the **2nd**, **10th** and **18th** electron
  ⇒ there are **4 different electronic shells**.

(iii) There is **1 valence electron** and hence the element belongs to **Group 1** of the Periodic Table.

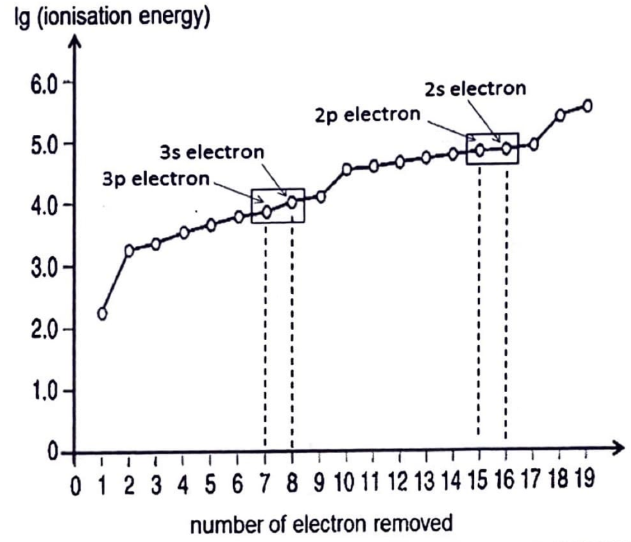
A **large jump** between the 1st and 2nd ionisation energies is observed.

⇒ significantly more energy is required to remove the 2nd electron as it is located in a **different shell**, one that is inner and **nearer to the nucleus**, and hence experiences a stronger electrostatic attraction to the nucleus.

⇒ there is **1 valence electron**

⇒ the element belongs to **Group 1** of the Periodic Table

- Points to take note:
  - Data of successive ionisation energies of an element provides evidence for the existence of electronic shells of different principal quantum numbers (energy levels) and subshells (sub-levels) in an atom.
  - Large jump observed in two successive ionisation energies
    ⇒ removal of electrons from different shells
  - Moderate difference (i.e. small jump) between two successive ionisation energies
    ⇒ removal of electrons from different subshells



- The **small jump** between 7th and 8th ionisation energies is due to the removal of electrons from **different subshells**.
- The energy gap between subshells is not as big as that between shells and is sometimes **not discernible**.

  For example, a small jump is expected between the 15th and 16th ionisation energies (due to the removal of electrons from different subshells) but this is **not observed** in the graph.

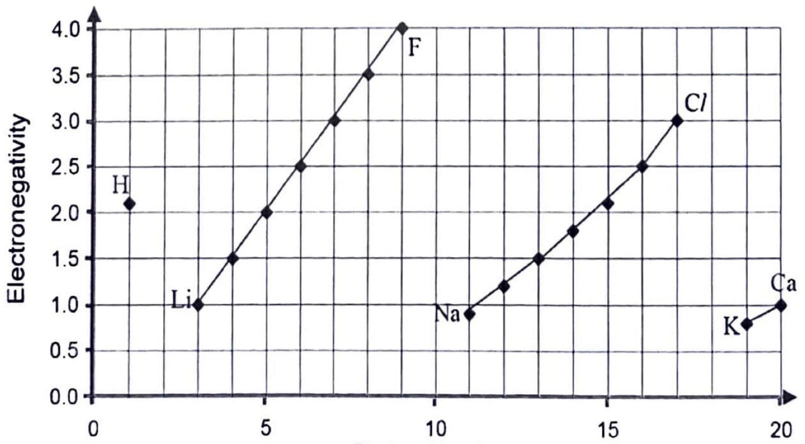
---

9 ELECTRONEGATIVITY

9.1 Definition

The **electronegativity** of an atom in a molecule is a relative measure of its ability to attract bonding electrons.

9.2 Variation in electronegativity

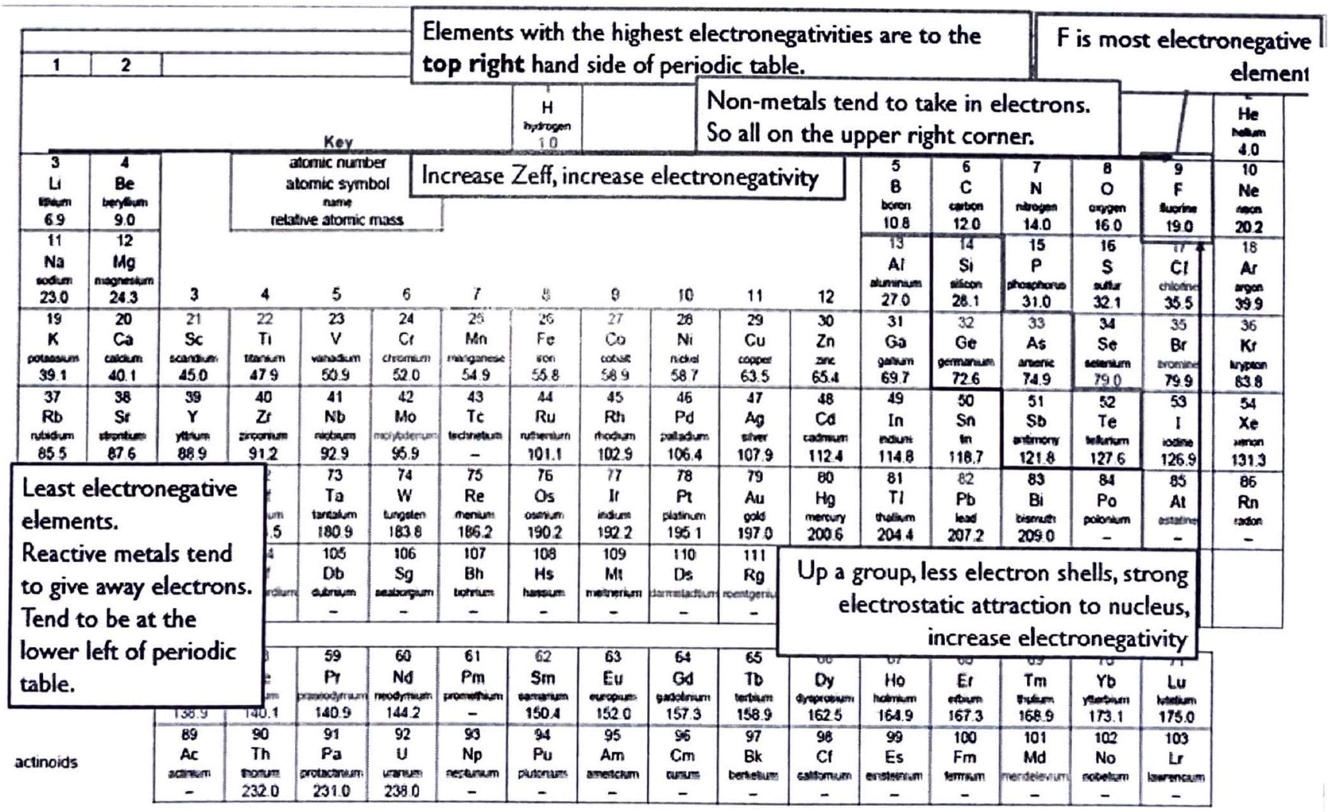


9.2.1 Trend in electronegativity across a period

Trend:	Electronegativity **increases** across a period.
Explanation:	Across a period, • the number of shells remain the same. • number of protons increases and hence **nuclear charge increases.** • number of electrons also increases but these electrons are added to the same outermost shell, and hence **shielding effect remains approximately constant**. • effective nuclear charge increases. • electrostatic attraction between the nucleus and the bonding electrons **increases** Hence electronegativity **increases** across a period.

9.2.2 Trend in electronegativity down a group

Trend:	Electronegativity **decreases** down a group.
Explanation:	Down a group, • the **number of electronic shells increases** • distance between the nucleus and the bonding electrons **increases** • shielding experienced by bonding electrons **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the • bonding electrons **decreases** Hence electronegativity **decreases** down a group.



Elements with the highest electronegativities are to the **top right** hand side of periodic table.

F is most electronegative element

Non-metals tend to take in electrons. So all on the upper right corner.

Increase Zeff, increase electronegativity

Least electronegative elements. Reactive metals tend to give away electrons. Tend to be at the lower left of periodic table.

Up a group, less electron shells, strong electrostatic attraction to nucleus, increase electronegativity

9.2.3 Significance of Electronegativity (Refer to Chemical Bonding)

- When two atoms of similar electronegativity are covalently bonded, a non–polar bond is formed.
- If the difference between the electronegativities of the two bonding atoms increases, the covalent bond becomes more polar.
- At the same time, the ionic character of the bond also increases. With sufficient difference in electronegativity, the two atoms will form an ionic bond instead.
- In general,

ΔEN	**Bond type**
$\Delta EN < 0.5$	Nonpolar covalent
$0.5 < \Delta EN < 1.6$	Polar covalent
$2.0 < \Delta EN$	Ionic

Note: Metals have low electronegativities, and tend to lose electrons, while non–metals have high electronegativity, and tend to gain electrons. In fact, electronegativity can be correlated to metal, metalloid, or non-metal, properties of an element.

SUMMARY

Effective nuclear charge is very important in explaining periodic trends

- (Zeff =Z – S)

Across a period,

- number of **protons increases** and hence **nuclear charge increases.**
- number of electrons also increases but these **electrons are added to the same outermost shell,** and hence **shielding effect remains approximately constant.**
- **effective nuclear charge increases.**
- electrostatic attraction between the nucleus and the valence electrons **increases,**

Electrons pulled closer to nucleus, **atomic radii** decrease across period

Electrons pulled closer to nucleus, **ionic radii (for isoelectronic ions)** decrease across period

More energy required to overcome electrostatic attraction **Ionisation energy generally** increases across period

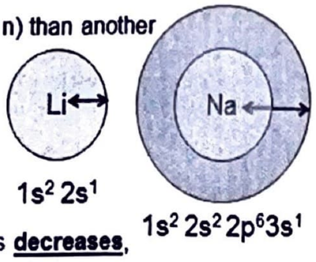
Tend to pull bonding electrons to itself, **electronegativity generally** increases across period

When comparing atoms/ions with different number of electron shells, this becomes the most important consideration.

SUMMARY

Down a group/ or when any species has a larger electronic shell (larger n) than another

- the **number of electronic shells increases**
- distance between the nucleus and the valence electrons **increases**
- shielding experienced by valence electrons **increases**



Despite the increasing nuclear charge,

- electrostatic attraction between the nucleus and the valence electrons **decreases**,

Increase in the size of the electron cloud.

atomic radii increase down group

Increase in the size of the electron cloud.
ionic radii of anion larger than cation

Less energy required to remove electron

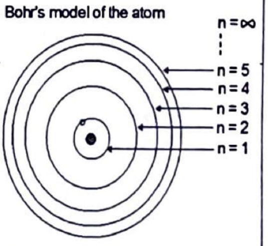
Ionisation energy decreases down the group

Less ability to pull bonding electrons to itself

electronegativity decreases down the group

Apppendix

Development of scientific models of matter, the atom and atomic structure.

1 The ancient Greeks (440 BC) Leucippus originated the atom concept. He and his pupil, Democritus, refined and extended it in subsequent years.	**8 Max Planck (1900)** • introduced the idea that matter absorbs and emits energy in discrete units called **quanta** • each fixed quantity of energy emitted is called a **quantum** of energy • ... the first step towards **quantum theory**
2 John Dalton's Atomic Theory (1803) • All matter consists of indivisible particles called atoms. • Atoms of one element cannot be converted into atoms of another element. • Atoms of an element are identical and are different from the atoms of any other element. • Compounds result from chemical combination of a specific ratio of atoms from different elements.	**9 Albert Einstein (1905)** • worked on the photoelectric effect • proposed that light may behave as a particle as well as a wave • extended the quantum concept to include light • light consists of discrete units called **photons**
3 G. J. Stoney (1874) • suggested the name 'electron' for tiny negative particles	Bohr's model of the atom  **10 Niels Bohr (1913)** • proposed the **planetary model of the hydrogen atom** in which the electron moves in certain allowed circular orbits around the nucleus • used the idea of quantized electronic energy levels • can explain the emission spectrum of the hydrogen atom but fails to explain the spectra of atoms more complex than hydrogen • is built on the false assumption that the electron exists as a solid particle of matter in an atom
4 Joseph John Thomson (1897) • discovered the **electron** while working on cathode rays	**11 Louis-Victor de Broglie (1923)** • proposed that electrons may behave as waves as well as particles – the theory of **wave-particle duality**
5 Joseph John Thomson (1904) • proposed **the 'plum pudding' model of the atom**, of electrons embedded in a sphere of positive charge	**12 Werner Heisenburg (1927)** • proposed his **uncertainty principle** – it is impossible to know the position and momentum of the electron at the same instant in time • there are inevitable uncertainties introduced in measuring two variables such as position and momentum of a particle at the same time
6 Ernest Rutherford (1911) • discovered the **nucleus** while working on the gold foil experiment	**13 Erwin Schrödinger (1926)** • applied the idea of electron as a wave to work out a wave theory of the atom • developed the wave equation, popularly called the Schrödinger equation
7 Ernest Rutherford (1911) • described his **nuclear model of the atom**: an atom consists of a tiny dense, positively charged central nucleus surrounded by the negatively charged electrons	**14 Quantum Mechanical Model of the Atom** • a mathematical model described by the Schrödinger equation • solutions to the Schrödinger equation define regions of space where there is a high probability of finding an electron of a given energy – **atomic orbitals** • no longer tells us where the electron is; it only tells us where it might be • introduces the idea of the probability of finding the electron in a certain volume: **the orbital**

Raffles Institution
Year 5 H2 Chemistry 2022
Tutorial 2 – Atomic Structure

Self-check Questions

1 Complete the following table with the aid of a Periodic Table.

Particle	No. of protons	No. of neutrons	No. of electrons
	6	8	6
	7	7	10
	8	7	7
$^{31}P^{3-}$			
^{14}N			

2 This question is concerned with various properties of the following five ions.

$$^{31}_{15}V^{3-},\ ^{32}_{15}W^{2-},\ ^{31}_{16}X^{2-},\ ^{31}_{15}Y^{-},\ ^{35}_{17}Z^{-}$$

(Note: The symbols, **V**, **W**, **X**, **Y** and **Z** are not the atomic symbols of the elements concerned.)

(a) Which of the above ions would be deflected the most when a beam is passed through an electric field?

(b) Which of the above ions would be deflected the least when a beam is passed through an electric field?

3 Write the full ground state electronic configuration for each:

(a) C*l* **(b)** Si **(c)** Cr

4 Write the full electronic configuration of the Period 2 element with the following successive ionisation energies (in kJ mol^{-1}):

799 2420 3660 25000 33000

Discussion Questions

N2012/3/4(a),(b)

5 Beams of charged particles are deflected by an electric field. If the particles are all traveling at the same speed, through an electric field of constant strength, the angle of deflection is proportional to their charge/mass ratio.
In a particular experimental set-up, protons are deflected through an angle of +15°.

(a) Assuming an identical set of experimental conditions, by which angles will the following particles be deflected? (D is deuterium, ^{2}H, and T is tritium, ^{3}H)

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

[3]

(b) Under identical conditions, a beam of particles, **R**, each having 12 times the mass of a proton, was deflected by an angle of +5°.

(i) Suggest the overall charge on a particle of **R**.

(ii) Given that a particle of **R** contains 6 protons, deduce the number of neutrons and electrons in a particle of **R**.

[3]

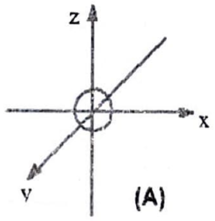
6 **(a)** The orbitals of the first two principal quantum numbers are illustrated below. The diagrams are of the same scale but not necessarily placed in any order.

(i) Label all the orbitals.

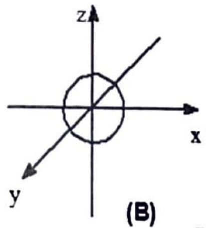
(ii) List 2 differences between orbital **(A)** and **(B)**.

(iii) Describe and compare the shapes of **(B)** and **(C)**.

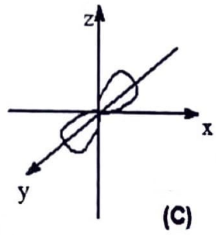
(iv) Which orbital(s) will be empty in an isolated atom of lithium?



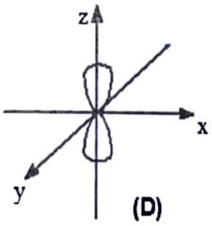
(A)



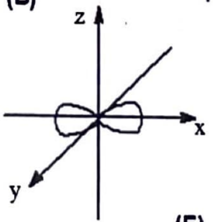
(B)



(C)



(D)



(E)

(b) In an isolated atom of element Y, orbitals **(A)**, **(B)** and **(C)** are completely filled with electrons and **(D)** is half full.

(i) State, with reasoning, if you would expect **(E)** to be empty?

(ii) Given that Y only forms a negative ion of formula Y^-, how many electrons would you expect to find in **(E)**?

(c) Give the atomic number(s) of the elements (with Z = 1 to 10) whose isolated atoms
  (i) contain no unpaired electrons
  (ii) contain the largest number of unpaired electrons

(d) In an isolated atom of element X, orbitals **(A)**, **(B)**, **(C)** are fully filled, but orbitals **(D)** and **(E)** are only half-filled. Sketch the trend of successive ionisation energies for the first seven electrons.

7 **(a)** Write down the electronic configurations of the following species:

(i) ${}_{33}As^{3-}$ **(ii)** ${}_{31}Ga^{3+}$ **(iii)** ${}_{36}Kr$ **(iv)** ${}_{22}Ti^{2+}$

(b) Which of these are isoelectronic to each other?

(c) Give the electronic configuration of an excited state for the krypton atom.

(d) Sketch an energy level diagram to illustrate the ground state electronic configuration of a titanium atom.

8 For each pair of elements listed below, state and explain which element has the higher first ionisation energy.

- **(a)** Lithium and sodium
- **(b)** Beryllium and boron
- **(c)** Nitrogen and oxygen
- **(d)** Fluorine and neon
- **(e)** Neon and sodium

9 **(a)** Sketch, on the same axes, the general trends for the following properties of the elements (Na to C*l*) across the third period of the Periodic Table

(i) atomic radius **(ii)** ionic radius

(b) Explain why the ionic radius of P^{3-} is larger than the atomic radius of P.

(c) Explain why the ionic radius of Mg^{2+} is less than that of Na^{+}.

10 The first five successive ionisation energies (in kJ mol^{-1}) of an element **Q** are as follows:

1090, 2400, 4600, 6200, 37800

(a) State and explain which group of the Periodic Table element **Q** belongs to:

(b) Write the outermost shell electronic configuration for **Q**.

(c) With the aid of an equation, state what is meant by the sixth ionisation energy of **Q**.

(d) Predict, with reasoning, if the value of the sixth ionisation energy of **Q** would be greater than the fifth.

11 **(a)** The table shows the ionisation energies, I.E. (in kJ mol^{-1}), of 4 unknown elements denoted by **P**, **Q**, **R** and **S**.

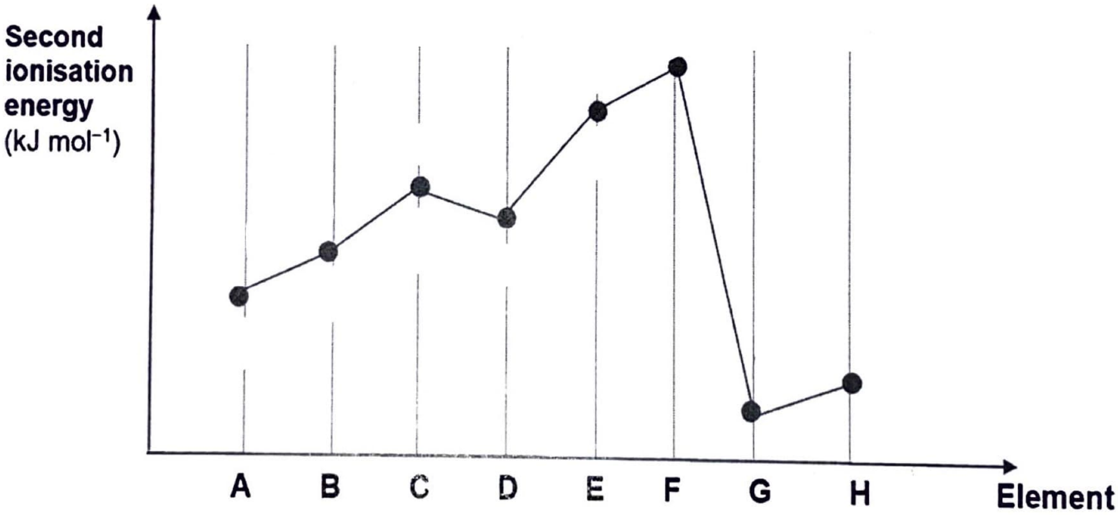
Element	1st I.E.	2nd I.E.	3rd I.E.	4th I.E.	5th I.E.
P	740	1450	7730	10500	13700
Q	500	4600	6910	9540	13400
R	420	3050	4420	5900	8000
S	580	1820	2750	11600	14900

(i) With reference to element **P**, explain why the difference between the 2nd and 3rd ionisation energies is much greater than that between the 1st and 2nd ionisation energies.

(ii) Deduce whether element **Q** is a Period 2 element.

(iii) Calculate the energy required to remove 0.06 moles of electrons from 0.02 moles of gaseous **R** atoms. **[4]**

(b) The following diagram shows the second ionisation energies of eight consecutive elements **A** to **H** in the Periodic Table. The atomic numbers of these elements are less than 18.



(i) Write an equation to represent the *second ionisation energy* of element **A**.

(ii) Sketch a graph of the first six successive ionisation energies of element **B**.

(iii) Explain why the second ionisation energy of element **D** is lower than that of element **C**.

(iv) Write the electronic configuration of element **H**. **[4]**