Raffles Institution
Year 5 H2 Chemistry 2017
Lecture Notes 2 – Atomic Structure

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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 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

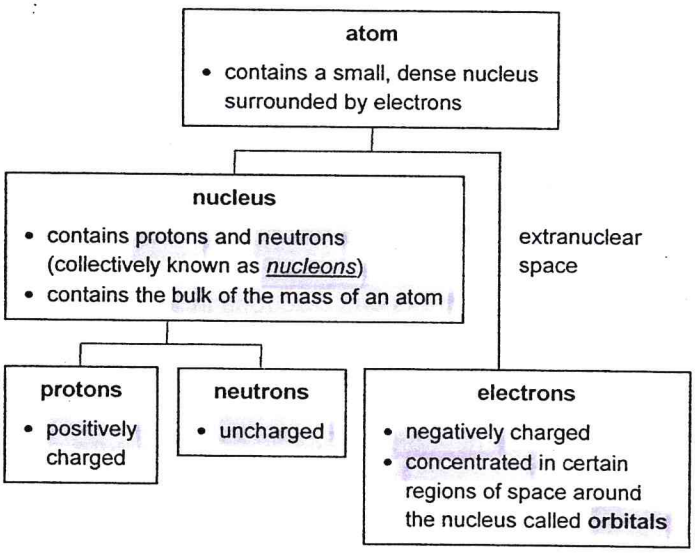
1 Chemistry for advanced level (by Peter Cann and Peter Hughes)
2 Chemistry in Context (by Hill and Holman)
3 Cambridge International AS and A Level Chemistry Coursebook (by Roger Norris, Lawrie Ryan & David Acaster)
4 Chemistry: The Molecular Nature of Matter and Change (by Martin S. Silberberg)
5 Website: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

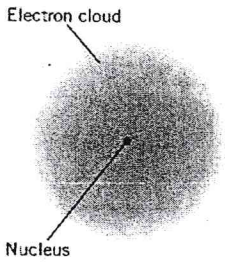
1 ATOMIC STRUCTURE

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





- 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.

⇒ The region around the nucleus where electrons move is mostly **empty space**.

1.2 The subatomic particles

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

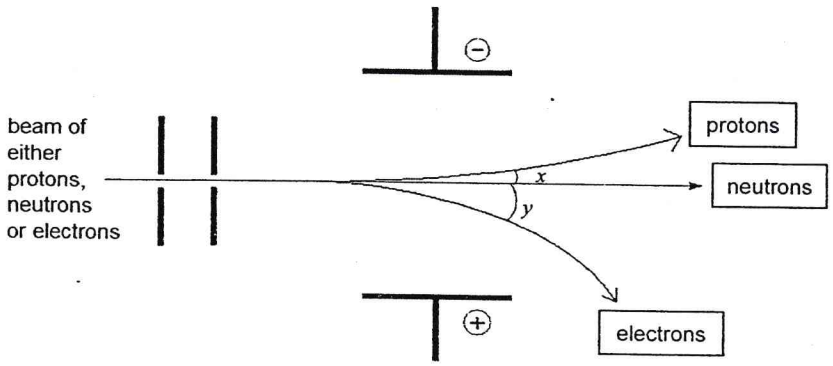
Sub-atomic particle	proton	neutron	electron
Discovered by	Ernest Rutherford (1911)	James Chadwick (1932)	Joseph John Thomson (1897)
Experiment	bombardment of gold foil with α particles	bombardment of beryllium with α particles	cathode ray experiment
Location within the atom	in the nucleus	in the nucleus	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	$^{1}_{1}\mathrm{p}$	$^{1}_{0}\mathrm{n}$	$^{0}_{-1}\mathrm{e}$

relative mass → $^{1}_{0}\mathrm{n}$ ← relative charge

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	$x°$ ($x° < y°$)
neutron (uncharged)	not deflected	0°
electron (negatively charged)	towards the positively charged plate	$y°$ ($y° > x°$)

- The direction of deflection is dependent on the **charge** on the subatomic particle.
- The angle of deflection is proportional to the magnitude of the $\frac{\text{charge}}{\text{mass}}$ 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. $x° < y°$

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)	$^{2}H^{+}$	$\frac{1}{2}$	5°
(b)	$^{18}O^{2-}$	$\frac{1}{9}$	1.11°
(c)	$^{9}Be^{2+}$	$\frac{2}{9}$	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

nucleon number (or mass number) → A proton number (or atomic number) → Z X ← symbol of the element	$^{238}_{92}U$
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 (proton 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 (27-13)	10 (13-3)
$^{14}_{7}N^{3-}$	14	7	7 (14-7)	10 (7+3)

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: $^{40}_{19}K \rightarrow \mathbf{X} + {}^{0}_{-1}e$. ← relative mass; ↖ relative charge

(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 $^{40}_{20}Ca$

(law of conservation of mass and charge).

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

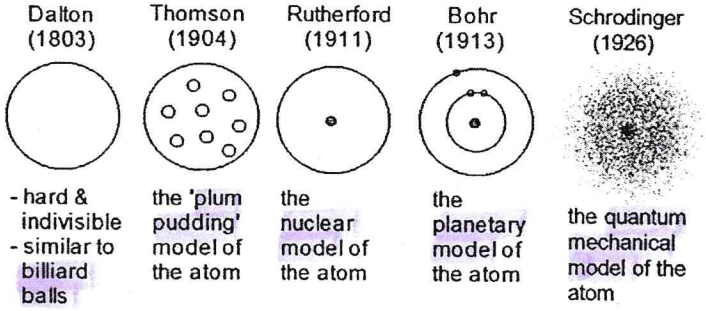
Nucleon number of **Y** = 235 + 1 – 90 – 2
= 144

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



1 The ancient Greeks (440 BC)
Leucippus originated the atom concept. He and his pupil, Democritus, refined and extended it in subsequent years.

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.

3 G. J. Stoney (1874)
- suggested the name 'electron' for tiny negative particles

4 Joseph John Thomson (1897)
- discovered the **electron** while working on cathode rays

5 Joseph John Thomson (1904)
- proposed **the 'plum pudding' model of the atom**, of electrons embedded in a sphere of positive charge

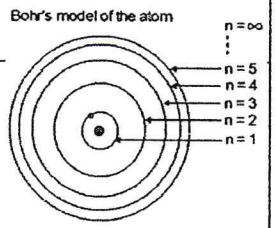
6 Ernest Rutherford (1911)
- discovered the **nucleus** while working on the gold foil experiment

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

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**

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**

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



11 Louis-Victor de Broglie (1923)
- proposed that electrons may behave as waves as well as particles – the theory of **wave-particle duality**

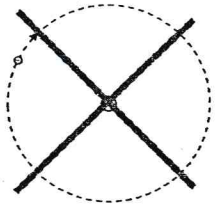
12 Werner Heisenburg (1927)
- proposed his **uncertainty principle** – it is impossible to know the position and momentum of the electron at the same instant in time
- there are inevitable uncertainties introduced in measuring two variables such as position and momentum of a particle at the same time

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

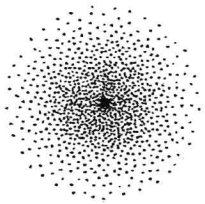
14 Quantum Mechanical Model of the Atom
- a mathematical model described by the Schrödinger equation
- solutions to the Schrödinger equation define regions of space where there is a high probability of finding an electron of a given energy – **atomic orbitals**
- no longer tells us where the electron 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**

3.2 The electron

What do we know about electrons?



- Electrons in an atom do **not** occupy fixed positions around the nucleus. They do **not** 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.

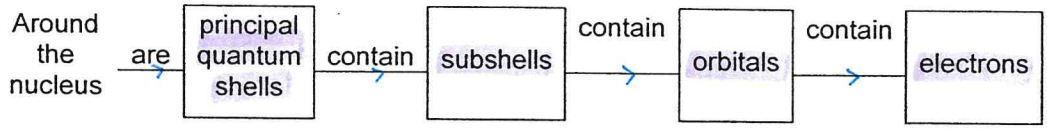
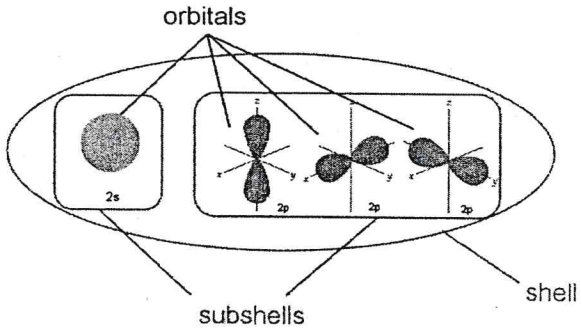


Diagram showing the relationship between shell, subshells and orbitals (using n = 2 as an example)



3.4 Electronic shells

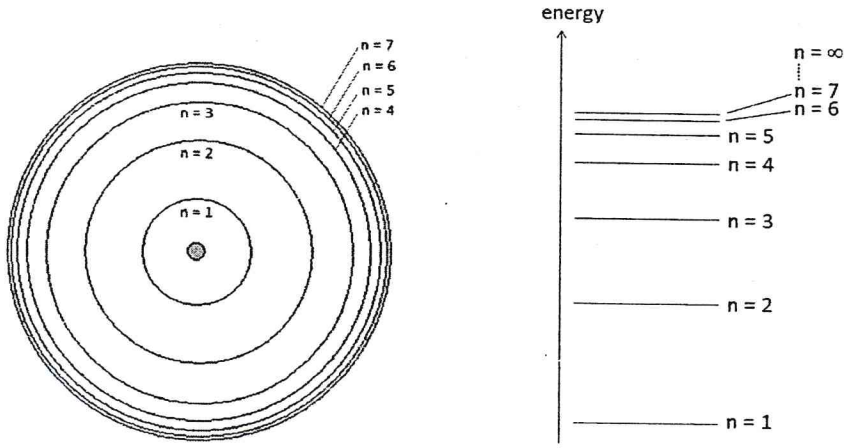
- Electrons in atoms are arranged in a series of **shells** or **energy levels** surrounding the nucleus. Each shell is described by a number known as the **principal quantum number, n**.

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

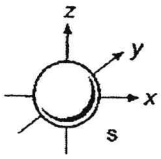
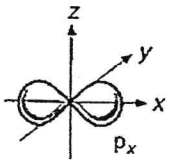
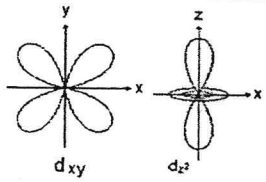
Principal quantum number, n	Types of subshell
1	1s
2	2s, 2p
3	3s, 3p, 3d
4	4s, 4p, 4d, 4f

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

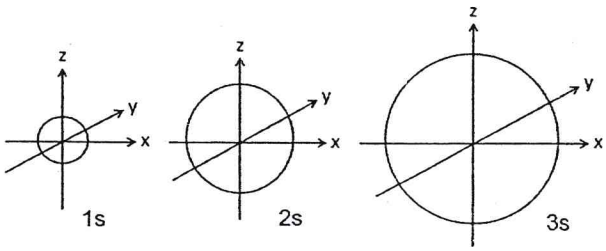
Relationship between subshells and orbitals

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

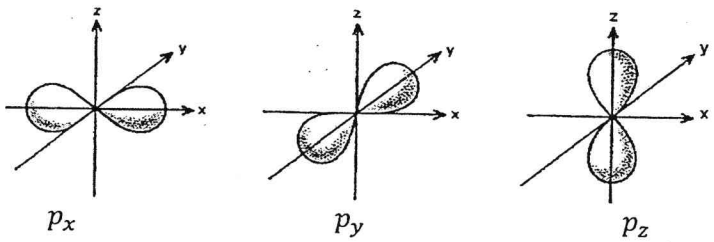
Types of orbitals	s orbital	p orbitals (p_x, p_y, p_z)	d orbitals (d_{xz}, d_{xy}, d_{yz}, $d_{x^2-y^2}$, d_{z^2})
Shape of orbital			
	spherical shape	dumb–bell shape	various shapes

(a) The s orbital



- 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**

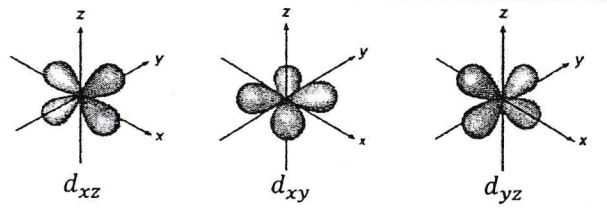
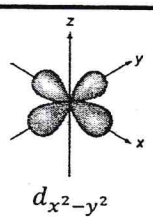
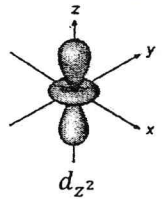
(b) The p orbitals



- 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 with the same principal quantum number n are **degenerate** (i.e. they have the same energy).
- p orbitals of different shells have the same dumb–bell shape but different sizes.
- As **n** increases, the p orbital
  - increases in size, i.e. 2p < 3p < 4p < 5p
  - becomes **more diffuse**

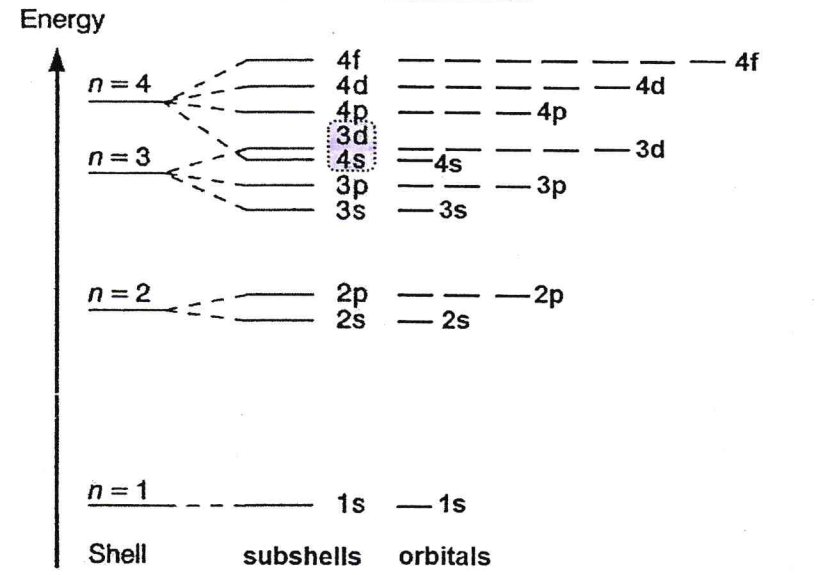
(c) The d orbitals

- 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.**

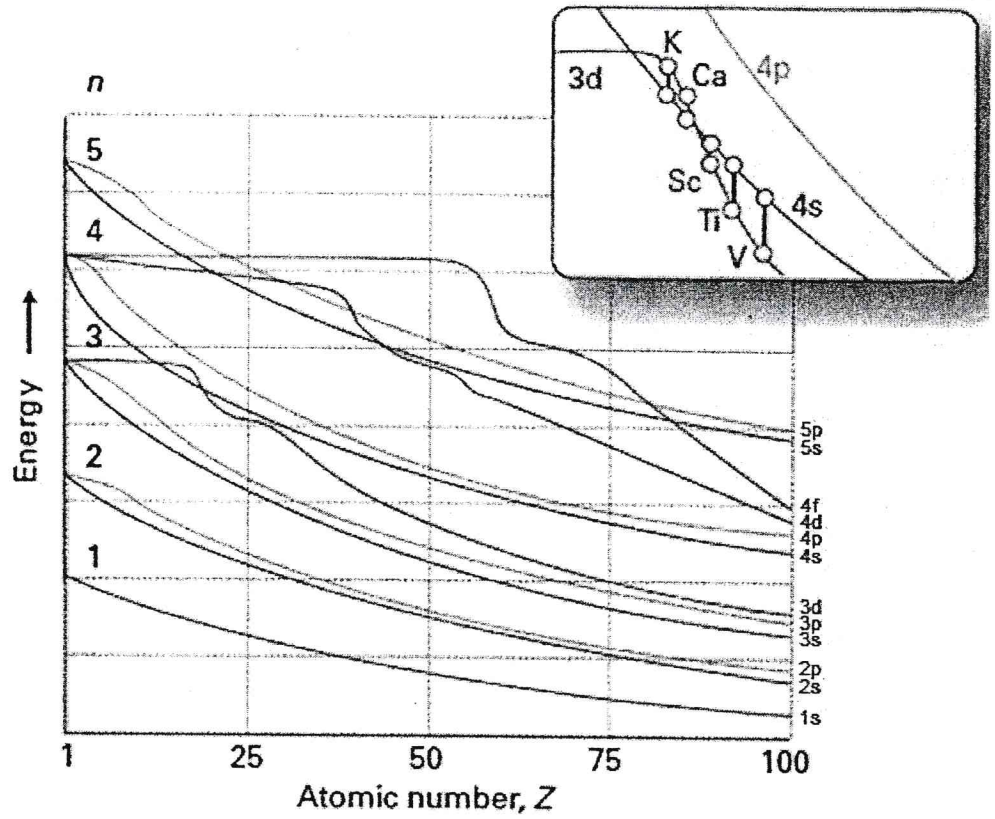
3.7 Relative energies of the orbitals

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



- As the nuclear charge 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 orbital has already become less than that of the 3d orbital** at Z = 18 (argon).
    - Affects how electrons are filled (The Aufbau Principle) in *section 4.1*

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 **n^{th} shell**,

- number of subshells = n
- number of orbitals = n^2
- maximum number of electrons that can be accommodated = $2n^2$ max. no. of electrons

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**,

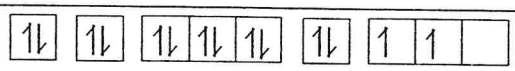
- number of subshells = 4
- number of orbitals = 16
- maximum number of electrons that can be accommodated = $(2)(4^2) = 32$

- A **shell** contains a group of orbitals with the same principal quantum number.
- A **subshell** is a group of orbitals with the same energy level but differ in their orientation in space.

4 ELECTRONIC CONFIGURATIONS

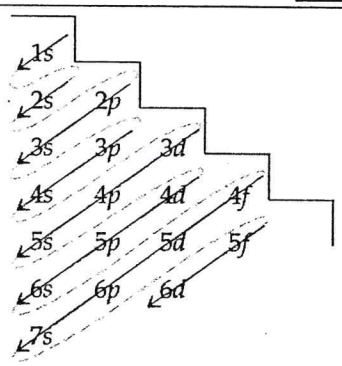
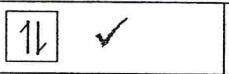
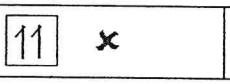
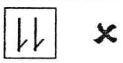
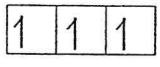
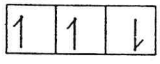
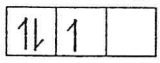
- The **electronic configuration** of an atom (or ion) refers to how its electrons are distributed among the various atomic orbitals i.e. how its electrons are arranged in the shells, subshells and orbitals.

- Different ways of writing electronic configurations

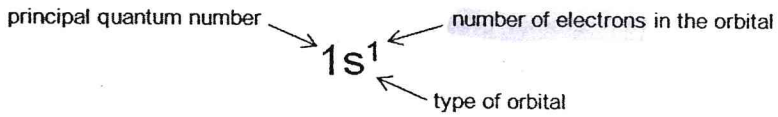
(i)	Using shells/energy levels notation	Si:	2.8.4
(ii)	Using the s, p, d, f notation	Si:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ or *[Ne] $3s^2\ 3p^2$ *[Ne] represents $1s^2\ 2s^2\ 2p^6$
(iii)	Using electrons-in-boxes diagram	Si:	

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 is at a **lower energy level** than the 3d orbitals (see page 11).
2	**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.	
3	**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.	
		 ✓	 ✗  ✗

4.2 Writing electronic configurations



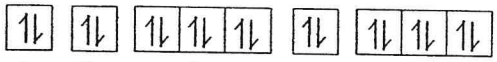
(a) The first twenty elements (Z = 1 to Z = 20)

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

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 (see page 11).

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

Using [Ar] to represent 

Element	'Electrons-in-boxes' diagram	Electronic configuration
	[Ar] 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] ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
$_{30}$Zn	[Ar] ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^{10}\ 4s^2}$

4.3 Anomalous electronic configurations of Cr and Cu

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

$_{24}$Cr	Expected electronic configuration	[Ar] ↑ ↑ ↑ ↑ ⬜ ↑↓ (3d 4s)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$ less stable	✗
	Actual electronic configuration	[Ar] ↑ ↑ ↑ ↑ ↑ ↑ (3d 4s)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ **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 **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$**.

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

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.

$_6C$ (ground state) $1s^2\ 2s^2\ 2p^2$	$_6C^*$ (excited state) $1s^2\ 2s^1\ 2p^3$	Other possible electronic configurations of C in the excited state:
energy 2p 2s 1s	energy 2p 2s 1s	$1s^2\ 2s^2\ 2p^1\ 3s^1$ 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.

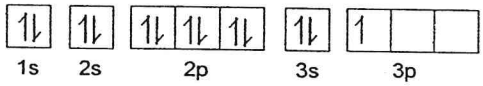
(a) Anions (negative ions)

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 2s 2p 3s 3p	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
$_{16}S^{2-}$	1s 2s 2p 3s 3p	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

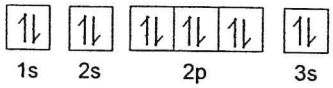
(b) Cations (positive ions)

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

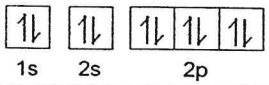
Example: Cations from the main groups (e.g. Al)

$_{13}Al$  $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

1s 2s 2p 3s 3p

$_{13}Al^+$  $1s^2\ 2s^2\ 2p^6\ 3s^2$

1s 2s 2p 3s

$_{13}Al^{3+}$  $1s^2\ 2s^2\ 2p^6$

1s 2s 2p

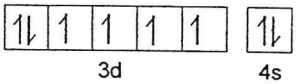
Example: Cations from the d–block (e.g. Fe)

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

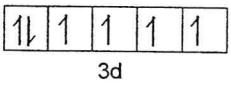
Electrons occupy the 4s orbital first because the 4s orbital is at a lower energy level than the 3d orbitals.

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

3d 4s

$_{26}Fe^{2+}$ [Ar]  $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ (4s) lost 2e

3d

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.

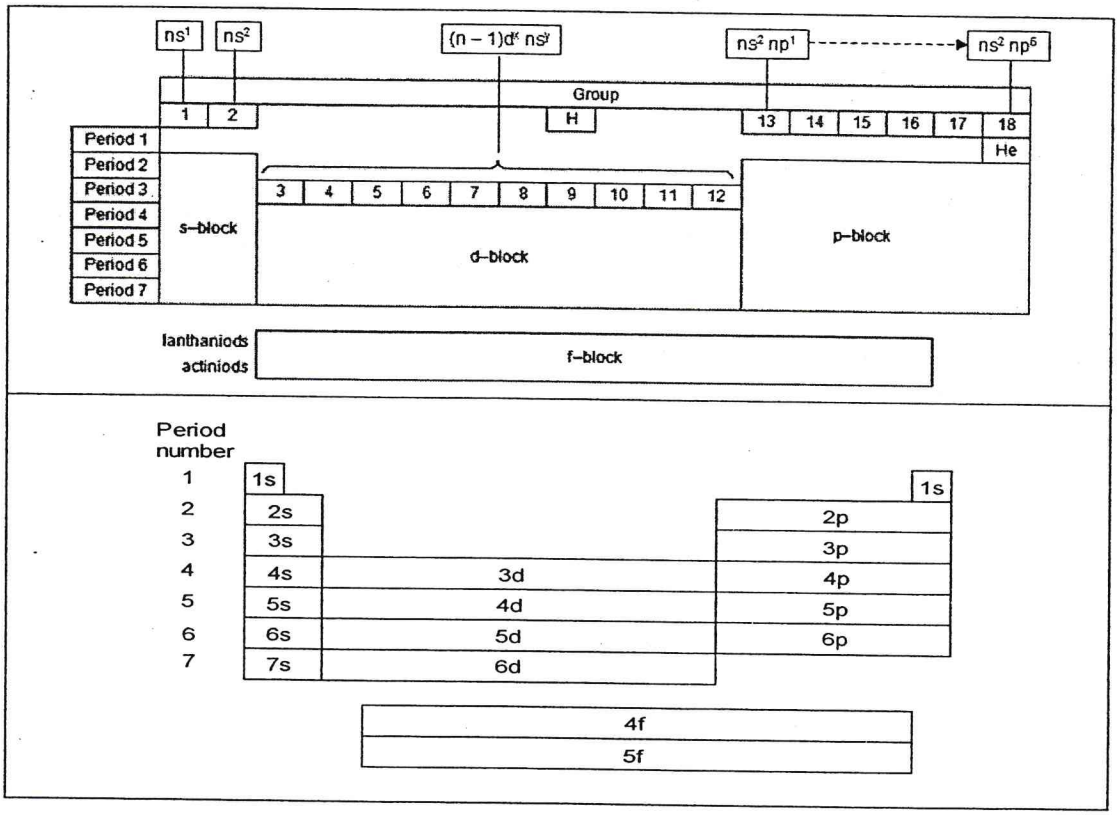
(a) S^{2-}	(b) Ca^{2+}	(c) Cu^{+}
S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ S^{2-}: $1s^2 2s^2 2p^6 3s^2 3p^6$	Ca: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ Ca^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6$	Cu: $1s^2 2s^2 2p^6 3s^2 3d^{10} 4s^1$ Cu^{+}: $1s^2 2s^2 2p^6 3s^2 3d^{10}$
Energy 3p ↿⇂ ↿⇂ ↿⇂ 3s ↿⇂ 2p ↿⇂ ↿⇂ ↿⇂ 2s ↿⇂ 1s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

* Add or remove electrons : 4s before 3d

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.



- **Horizontal rows** in the Periodic Table are called **periods**. 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 **groups**. 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:

Chlorine is a Group 17 element $\Rightarrow$ Electronic configuration of valence shell is $\mathbf{ns^2\ np^5}$
Chlorine is a Period 3 element $\Rightarrow$ n = 3

Hence the electronic configuration of chlorine is $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5}$

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**

Note: 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**

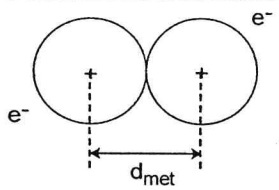
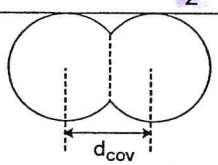
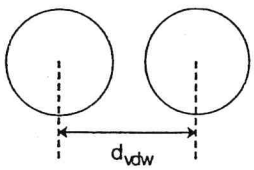
d and f electrons usually **provide poor shielding effect** for outermost electrons from the nuclear charge because the **d and f orbitals are rather diffuse.**

→ spread over a large area, not concentrated.

6 ATOMIC RADIUS

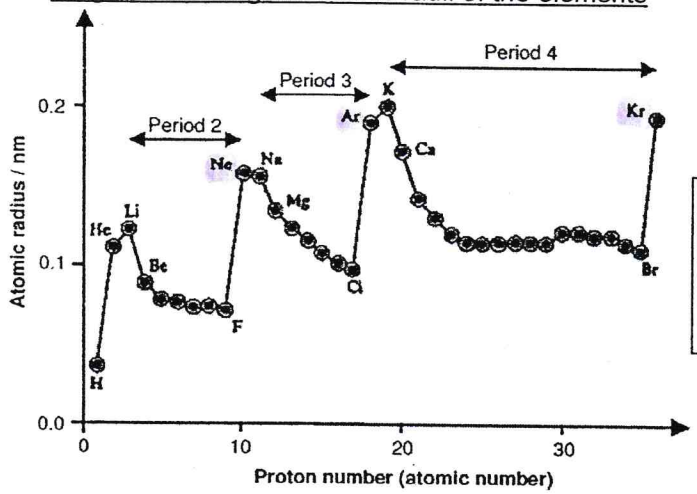
6.1 Definitions

- **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 **not 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 = $\frac{1}{2}d_{vdw}$

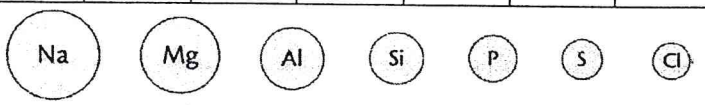
6.2 Variation in atomic radii

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	0.192
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.

* Across period atomic radii : ↓
* Down a group atomic radii : ↑

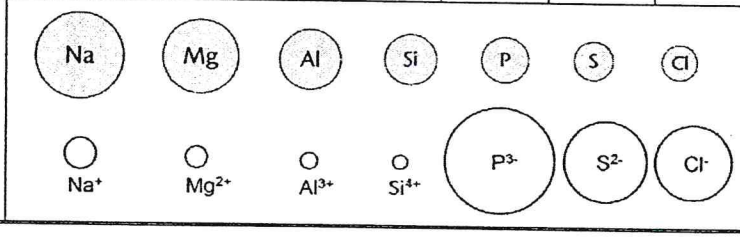
6.2.2 Trend in atomic radii down a Group

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** 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 ($r_{cation} < r_{atom}$)

positive ions (lost electrons)

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 ($r_{atom} < r_{anion}$)

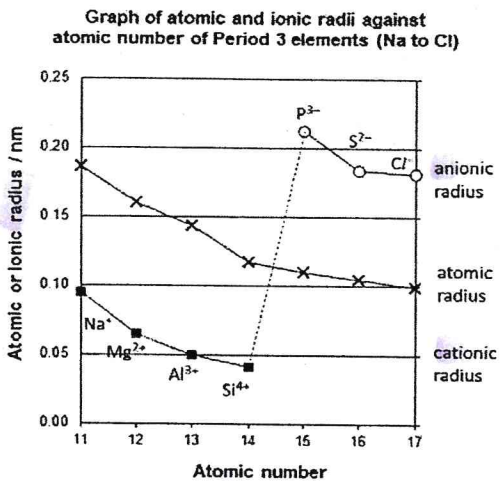
negative ions (move $\bar{e}$)

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.

same no. of e⁻

7.3 Ionic radii of isoelectronic species

Observation:



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

Example:

Trend	**$Na^+ > Mg^{2+} > Al^{3+}$**				**$P^{3-} > S^{2-} > Cl^-$**		
Ions	Na^+	Mg^{2+}	Al^{3+}		P^{3-}	S^{2-}	Cl^-
No. of p	11	12	13		15	16	17
No. of e^-	10	10	10		18	18	18
Electronic configuration	$1s^2\ 2s^2\ 2p^6$				$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$		

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:	• P^{3-} has one more electronic shell than Al^{3+}. • Despite the increase in nuclear charge, the valence electrons of P^{3-} are less strongly attracted by the nucleus. • Consequently 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** (absorb energy) 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.

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

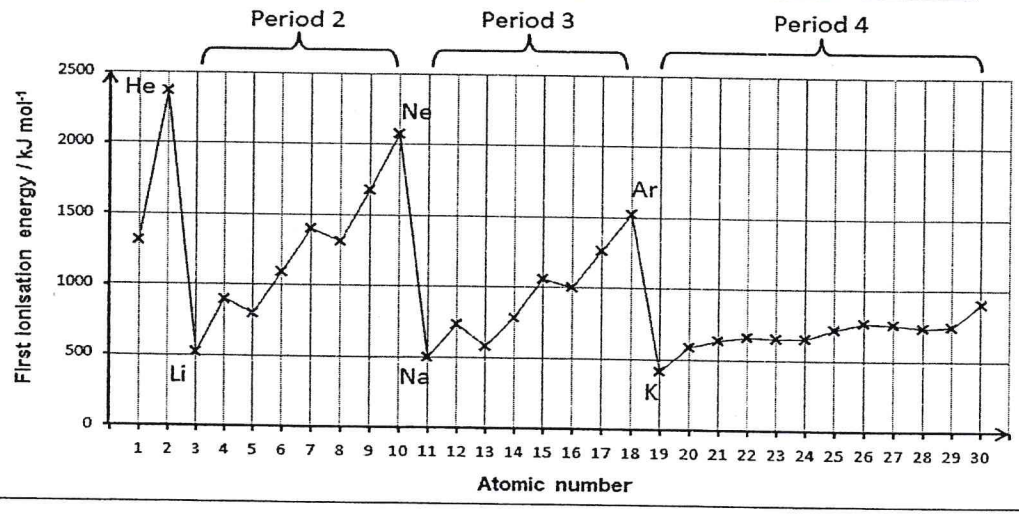
(b) Name the enthalpy change for the following reaction: $O(g) \rightarrow O^{3+}(g) + 3e^-$.

1st + 2nd + 3rd ionisation energies of oxygen (sum).

8.2 Trends in ionisation energies

8.2.1 Trend in first ionisation energies across a Period

Graph of first ionisation energy against atomic number of the first 30 elements



- 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 – between Group 2 and Group 13 elements
  (iii) irregularity 2 – between Group 15 and Group 16 elements

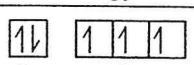
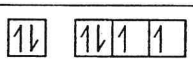
(i) General increment across a period

Trend:	The first ionisation energies of the elements **generally increase** 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 valence electrons **increases**, resulting in an **increase** in the energy required to remove the valence electron from an atom. Hence the first ionisation energies of the elements **generally increase** across a period.

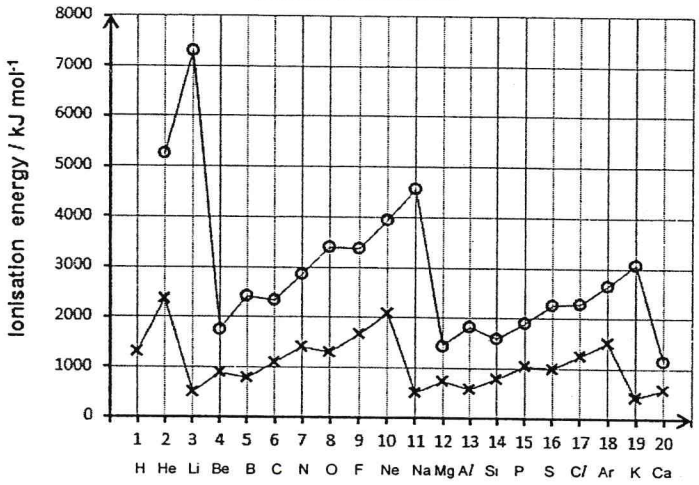
(ii) Irregularity 1 – Group 2 & Group 13

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 **higher energy level** than the 3s electron to be removed from Mg. • Hence **less energy** is required to remove the 3p electron in Al than the 3s electron in Mg. • First ionisation energy of Al is **lower** 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.

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



Note:
The maxima for the two graphs occur at different atomic numbers.

2^{nd} I.E. > 1^{st} I.E. because more energy is required to remove an electron from a positive ion

(a) Identify the similarities and differences between the variations of first ionisation energies and that of second ionisation energies.
(b) Account for your observations in (a).

8.2.2 Trend in first ionisation energies down a Group

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

Group 17	1^{st} 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 electron **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in a **decrease** in the energy required to remove the valence electron from an atom. Hence the first ionisation energies of the elements generally **decrease** down a group.

Worked Example 6

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

(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 $ns^2\ np^1$* • 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.	O^+: $1s^2\ 2s^2\ 2p^3$ F^+: $1s^2\ 2s^2\ 2p^4$ *Note: $ns^2\ np^3$ vs $ns^2\ np^4$* • Due to inter-electronic repulsion between paired electrons in the same 2p orbital, **less energy** is required to remove the 2p electron from F^+. ∴ 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

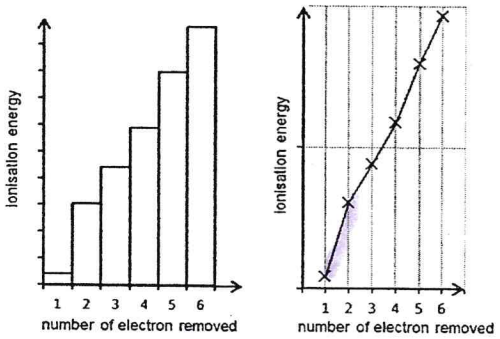
State the group of the Periodic Table to which **E** is likely to belong. State your reasoning clearly.

- 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 ionisation energies of an element **X** are shown below.



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

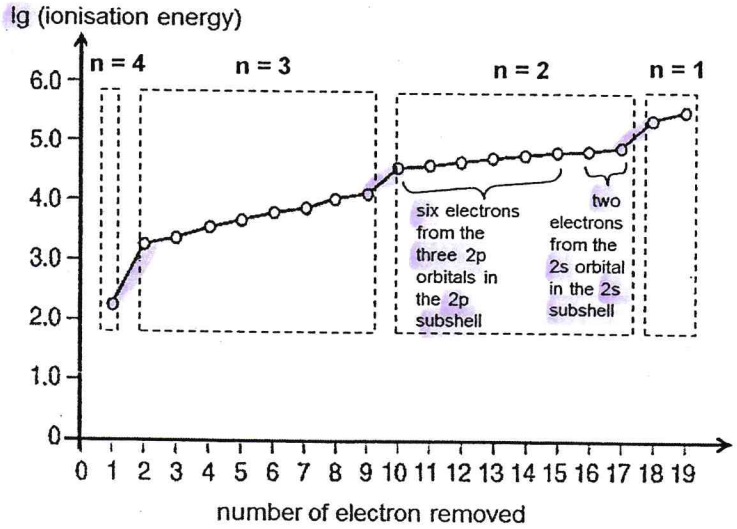
State your reasoning clearly.

- 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 ionisation energies

  (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**.

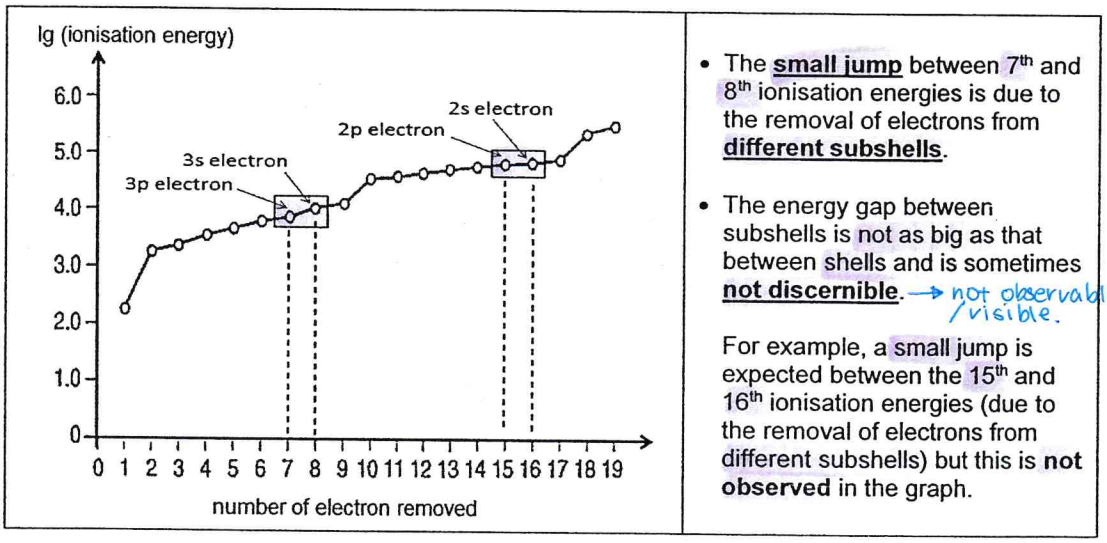
  A **large jump** in ionisation energies is observed when an electron is removed from a **different shell**, one that is **inner and nearer to the nucleus**, and hence experiences a stronger electrostatic attraction to the nucleus.

  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**. → not observable / visible.

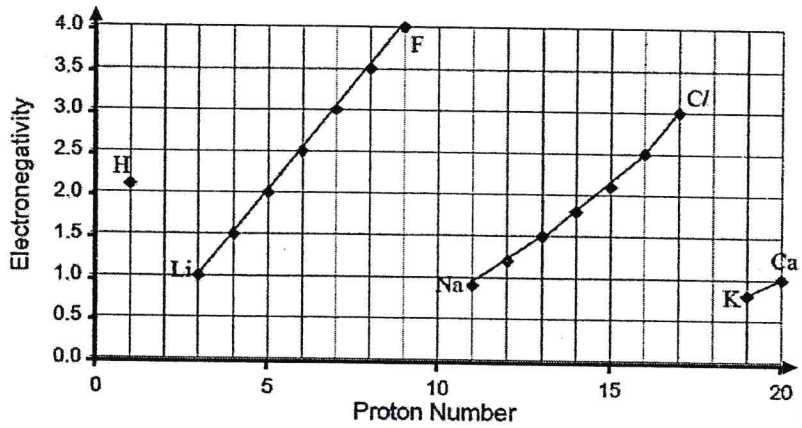
  For example, a small jump is expected between the 15th and 16th ionisation energies (due to the removal of electrons from different subshells) but this is **not observed** in the graph.

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 shells increases.** • distance between the nucleus and the bonding electrons **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the bonding electrons **decreases** Hence electronegativity **decreases** down a group.

9.2.3 Significance of Electronegativity (Refer to (f) of 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
ΔEN < 0.5	Nonpolar covalent
0.5 < ΔEN < 1.6	Polar covalent
2.0 < ΔEN	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.

ionic bonds are about electron transfer

dot and cross : only draw valence electrons..

Low lying orbital → energetically accessible

electrons are lost from less electronegative element

more electronegative gains the electron

S can expand octet — accomodate more than 8 electrons

period 3 and above can expand.