Anderson Serangoon Junior College

H2 Chemistry

ATOMIC STRUCTURE

Content

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

Learning Outcomes

Students 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
(h) state the electronic configuration of atoms and ions given the proton number (and charge)
(i) (i) explain the factors influencing the ionisation energies of elements (see the *Data Booklet*)
(ii) explain the trends and variations in ionisation energies across a period and down a Group of the Periodic Table (see *The Periodic Table* lecture)
(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

References

1. Chemistry the Central Science (8th edition). Brown, LeMay, Bursten
2. A–level Chemistry. E.N Ramsden
3. Understanding Advanced Physical Inorganic Chemistry. Jeanne Tan, Chan Kim Seng
4. Chemistry for Advanced Level. Peter Cann, Peter Hughes
5. Cambridge International AS and A Level Chemistry. Lawrie Ryan and Roger Norris

Additional Activities – Learning Packages *on SLS*

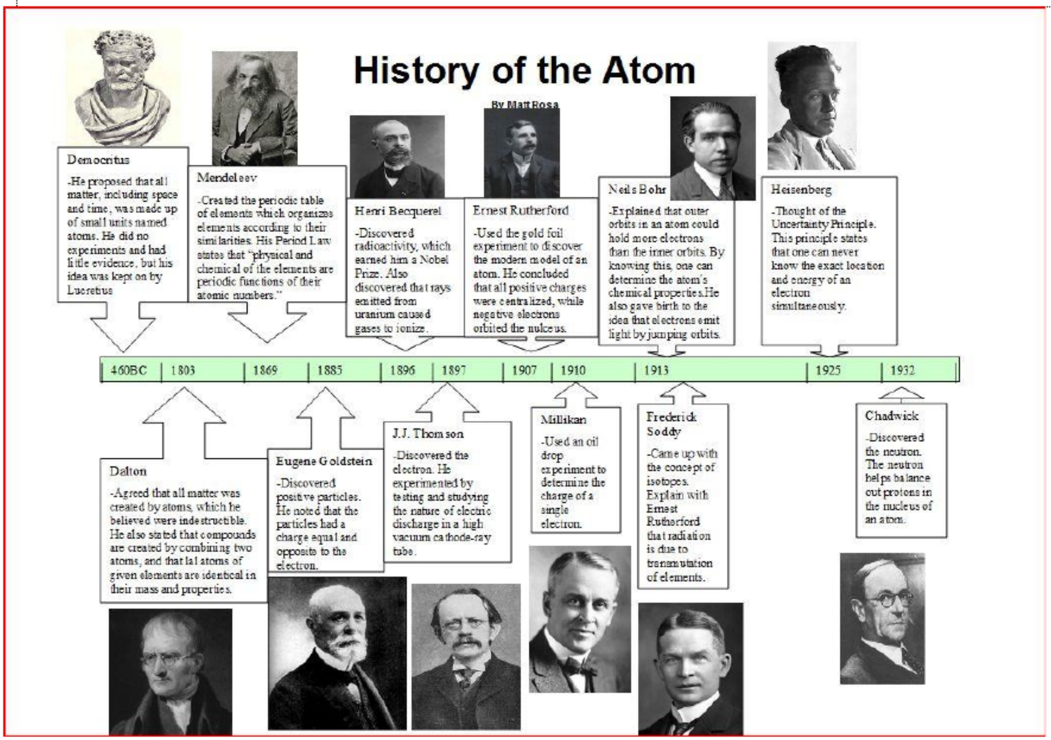
1. Protons, Neutrons and Electrons
2. Energy Levels of Orbitals in an Atom
3. Representing Electronic Configuration
4. Ionisation Energy

INTRODUCTION

How has the understanding of atomic structure developed and evolved?

http://bit.ly/1NT65ai

📖 *The **atomic model has changed over time** when **new evidence surfaced** through the various discoveries relating to the structure of an atom.*



History of the Atom

By Matt Rosa

Democritus

-He proposed that all matter, including space and time, was made up of small units named atoms. He did no experiments and had little evidence, but his idea was kept on by Lucretius

Mendeleev

-Created the periodic table of elements which organizes elements according to their similarities. His Period Law states that "physical and chemical of the elements are periodic functions of their atomic numbers."

Henri Becquerel

-Discovered radioactivity, which earned him a Nobel Prize. Also discovered that rays emitted from uranium caused gases to ionize.

Ernest Rutherford

-Used the gold foil experiment to discover the modern model of an atom. He concluded that all positive charges were centralized, while negative electrons orbited the nulceus.

Neils Bohr

-Explained that outer orbits in an atom could hold more electrons than the inner orbits. By knowing this, one can determine the atom's chemical properties.He also gave birth to the idea that electrons emit light by jumping orbits.

Heisenberg

-Thought of the Uncertainty Principle. This principle states that one can never know the exact location and energy of an electron simultaneously.

Dalton

-Agreed that all matter was created by atoms, which he believed were indestructible. He also stated that compounds are created by combining two atoms, and that lal atoms of given elements are identical in their mass and properties.

Eugene Goldstein

-Discovered positive particles. He noted that the particles had a charge equal and opposite to the electron.

J.J. Thomson

-Discovered the electron. He experimented by testing and studying the nature of electric discharge in a high vacuum cathode-ray tube.

Millikan

-Used an oil drop experiment to determine the charge of a single electron.

Frederick Soddy

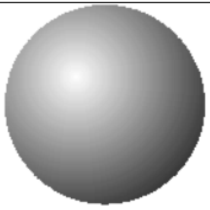
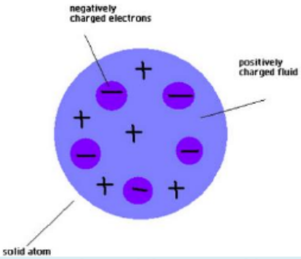
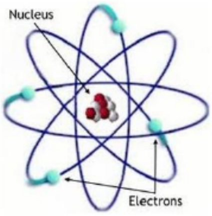
-Came up with the concept of isotopes. Explain with Ernest Rutherford that radiation is due to transmutation of elements.

Chadwick

-Discovered the neutron. The neutron helps balance out protons in the nucleus of an atom.

Source: https://www.tes.com/lessons/e_Cw_–QvqG1a9w/atomic–structure

From John Dalton's atomic theory, the development of atomic theory had come a long way and our understanding of the nature of matter and the structure of atoms were deepened with the works of scientists such as J. J. Thompson, Ernest Rutherford, James Chadwick, Niels Bohr, Louis de Broglie, Erwin Schrödinger and Werner Heisenberg, just to name a few.

		
Atomic model proposed by John Dalton	***Atomic model proposed by J. J. Thomson***	***Atomic model proposed by Ernest Rutherford***

Source: The history of Atom (http://thehistoryoftheatom.weebly.com/john–dalton.html)

PART 1: SUB–ATOMIC PARTICLES

1.1 Three Fundamental Sub–atomic Particles

	Proton	Neutron	Electron
Position within atom	In nucleus	In nucleus	Around nucleus
Actual Mass / g	1.673×10^{-24}	1.675×10^{-24}	9.109×10^{-28}
Mass / amu[i]	1.007	1.009	5.485×10^{-4}
Relative masses	1	1	1/1840
Charge	$+1.602 \times 10^{-19}$ C	0	-1.602×10^{-19} C
Relative charge	+1	0	–1

- Electrons are attracted to the protons in the nucleus by **electrostatic forces of attraction**.
- The protons and neutrons in the nucleus are drawn very close together by **nuclear forces**.
- These forces are only effective over a very short range because they do not pull the outer electrons into the nucleus.

[i] An atomic mass unit (amu) is defined as 1/12 the mass of one atom of carbon–12. It has the value of 1.6606×10^{-24} g.

1.2 Representation of a Nuclide

- '**Nuclide**' refers to any species with a specified number of protons and neutrons.
- The nuclide of an element, X, is represented by: $\boxed{{}^{A}_{Z}\mathbf{X}}$

where

Z is atomic number / proton number
- number of **protons** in the nucleus of an atom
- unique for each element (thus, helping us to identify the element)
- isotopes of an element have the same proton number

A is the mass number / nucleon number
- sum of **protons** and **neutrons** in the nucleus of an atom
- isotopes of an element have different **mass numbers** due to different number of neutrons

Example 1

Determine the number of protons, neutrons and electrons of the following:

	^{35}Cl	^{40}Ar	^{40}K	$^{63}Cu^{+}$	$^{32}S^{2-}$
proton	**17**				
neutron	35–17 = **18**				
electron	**17**				

1.3 Isotopes

- Isotopes are atoms of an element that have the same number of **protons** but different number of **neutrons** and hence different **nucleon numbers (or mass number)**.

- The different mass numbers are known as **isotopic masses** (e.g. chlorine has two isotopes, chlorine–35 and chlorine–37.)

- They have the same number of electrons and thus, they show similar **chemical** properties. This is because in a chemical reaction, it is the **electrons** that are transferred between atoms. The nucleus remains intact.

- They have **different number of neutrons** and thus, **different masses.** Hence they show different **physical** properties (e.g. density).

- Not all isotopes are stable. Unstable isotopes undergo radioactive decay, sometimes producing a different isotope.

  - An example of an unstable isotope that undergoes radioactive (alpha) decay is uranium–238. In this process, the uranium atom ($^{238}_{92}U$) transmuted into an atom of thorium ($^{234}_{90}Th$) and, at the same time, gives off an alpha particle ($^{4}_{2}He$).

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He + \text{energy}$$

Example 2

Species	No. of protons	No. of neutrons	No. of electrons
A	16	18	16
T	17	18	17
O	17	20	17
M	17	18	18

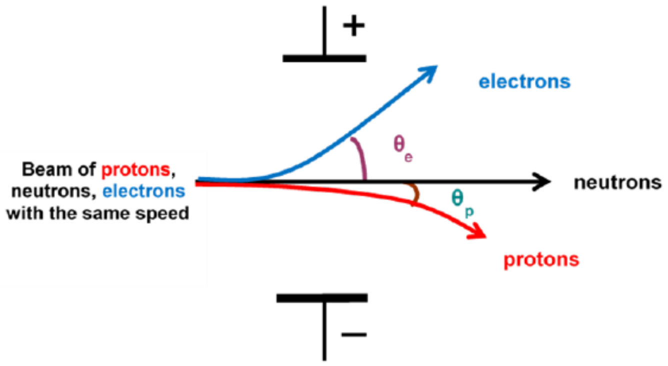
(a) Select a pair of isotopes.

(b) Which of the species are not from the same element as the rest?

(c) With reference to the Periodic Table, identify the species **A**, **T**, **O** and **M** by writing the symbols and show the nucleon numbers and charges.

1.4 Behaviour of Sub–atomic Particles in an Electric Field

When a beam comprising of protons, electrons and neutrons is passed through an electric field, the expected deflections are as shown below.



Particle	Charge of particle	Direction of deflection in electric field
Neutrons	Electrically neutral	Not deflected
Electrons	Negatively charged	Attracted towards the positively charged plate
Protons	Positively charged	Attracted towards the negatively charged plate

- Angle of deflection, θ, is proportional to the **charge** of the particle, but inversely proportional to its **mass**

$$\boxed{\theta\ \alpha\ \frac{\text{charge}}{\text{mass}}}$$

$\frac{q}{m}$ for a proton, $^{1}_{1}\mathrm{H}^{+} = \frac{1}{1} = \underline{\mathbf{1}}$ $\frac{q}{m}$ for an electron = $\frac{1}{\frac{1}{1840}}$ = **1840**

Thus, the angle of deflection for electrons is 1840 times more than protons ($\boldsymbol{\theta}_e > \boldsymbol{\theta}_p$).

- Particles with **smaller mass** and/or **higher charge** will be **deflected more**.

For your information

- *The **greater the charge of the particle**, the greater is the attractive force exerted on it from the oppositely charged plate, and the **greater is the deviation from its original direction of motion***

- *If two particles are moving at the same speed but one is more massive than the other, the heavier particle has a greater kinetic energy. Thus, more energy must be exerted on the heavier particle to cause it to deflect. Since the applied electric field is exerting the same amount of force on these two different particles with different masses, the **heavier particle is deflected to a lesser extent***

Example 3 (N96/I/1a)

Describe, by means of a diagram, how the paths of separate beams of

(i) protons
(ii) deuterons (a deuteron is an atomic nucleus containing a proton and a neutron)
(iii) hydrogen atoms

are affected on passing through an electric field which is at right angles to their direction of travel. You should relate clearly the **magnitude** and the **direction of deflection** of each beam to the others. *Give reasons for your answers.*

Solution

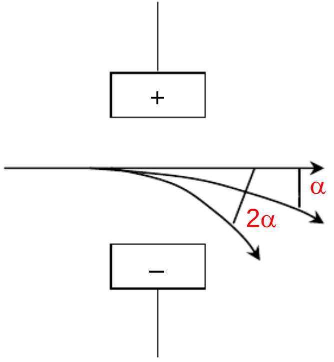
Approach:

a) *Determine the direction of deflection of each beam of particle..*

b) *To determine the magnitude of deflection of each particle, or compare the magnitude of deflection between 2 particles:*

  1) *calculate the q/m ratio for each particle*

  2) *use the relationship* $\text{ngle of deflection}, \theta \;\; \alpha \;\; \frac{\text{charge}}{\text{mass}}$



Working

Beams of	Mass number	Charge	Reason for direction of deflection
Protons			
Deuterons			
hydrogen atoms			

$\text{ngle of deflection}, \theta \;\; \alpha \;\; \frac{\text{charge}}{\text{mass}}$ (or q/m),

q/m ratio of proton =
q/m ratio of deuteron =

$\frac{\text{angle of deflection of deuteron}}{\text{angle of deflection of proton}} =$

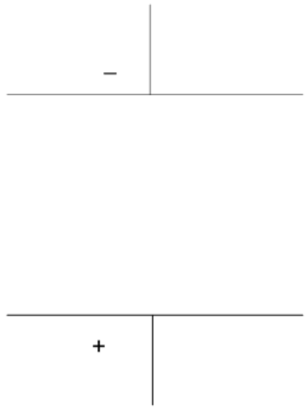
angle of deflection of deuteron =

Checkpoint 1

1(a) Five gaseous particles shown below are passed between two plates carrying a certain electric charge. One of the particles, $^{4}_{2}He^{2+}$, deflected through an angle of +8°. Complete the following table.

	Particles	$\frac{q}{m}$	Direction of deflection of particle in an electric field	Angle of deflection
1	$^{16}_{8}O^{2-}$			
2	$^{4}_{2}He^{2+}$			
3	$^{20}_{10}Ne$			
4	$^{31}_{15}P_4$			
5	$^{14}_{7}N_2^{+}$			

(b) Using answers in **(a)**, sketch the paths of particles **1**, **2** and **3** in an electric field on the same diagram, showing clearly the angle of deflection of each of the particles.



PART 2: THE ARRANGEMENT OF ELECTRONS

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

- It normally applies to atoms or ions in the **ground state** (i.e. **lowest possible energy level** available to it).

- The electronic configuration 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 **relative energies** of the electrons

- An electron in an atom is described by its **principal quantum number**, the **subshell**, and **orbital**.

2.1 Principal Quantum Number

- The electrons in an atom are arranged in **electronic shells**

- Each electronic shell is denoted by a **principal quantum number**, represented by the symbol ***n***, where **n** = 1, 2, 3, … (numbered outwards from the nucleus)

- The **larger** the principal quantum number,
    - ☞ the **further** is the shell from the nucleus (i.e. $n = 1$ is the innermost shell).
    - ☞ the **less strongly** the electron is **attracted** to the nucleus
    - ☞ the **higher** the **energy level** of the electron

2.2 Subshell

- Each electronic shell comprises one or more **subshells**.

- Subshells are represented by the letters: ***s***, ***p***, ***d*** and ***f***.

- The number of subshells in each electronic shell is equal to the **n** value.

Principal quantum number, n	No of subshells	Type of subshells
1	1	***s***
2	2	***s, p***
3	3	***s, p, d***
4	4	***s, p, d, f***

- Within the same electronic shell, the relative energies of the subshells are in the order: **s < p < d < f.**

2.3 Orbitals

❖ Electrons are not “fixed” in place; rather they are spread out around the nucleus as an **electron cloud** known as **orbital**.

❖ An orbital represents a three–dimensional volume of space around the nucleus in which there is a **high probability (> 95%) of finding an electron**.

Example: If we were to take instantaneous snapshots of the position of electrons over a period of time, a result similar to that shown below would be obtained for an s electron.

- Each subshell consists of **group of orbitals** with the **same energy level** (**degenerate**) but different orientation in space.

- The number of orbitals is determined by the type of subshell

Subshell	Number of orbitals
s	**1**
p	**3**
d	**5**
f	**7**

- Each orbital can contain a **maximum of two electrons** which must be of **opposite spin**.

Summary

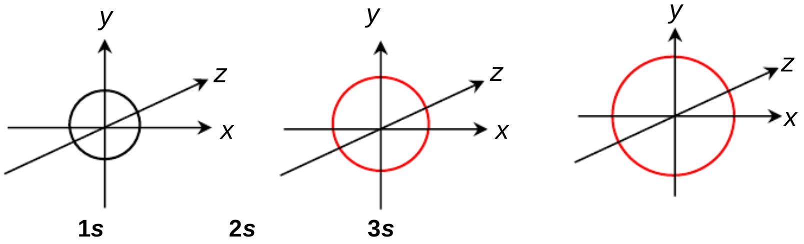
Principal quantum number (*n*)	**Type of subshells**	**No. of orbitals (n^2)**	**No. of electrons in subshell**	**Max. number of electrons in shell ($2n^2$)**
1	1s	1	2	2
2	2s	1	2	8
	2p	3	6	
3	3s	1	2	18
	3p	3	6	
	3d	5	10	
4	4s	1	2	32
	4p	3	6	
	4d	5	10	
	4f	7	14	

Note: From this table, it can be observed that in the ***n***th principal quantum number, there are ***n*** number of subshells consisting of n^2 number of orbitals with a maximum number of $2n^2$ electrons.

2.3.1 Shapes of Orbitals

(a) s orbitals

- The s orbital is **spherically symmetrical** about the nucleus.
- The probability of finding an electron at a distance r from the nucleus is the same in all directions.
- An s orbital is represented by drawing a circle.
- s orbitals from different principal electronic shells **differ in size**.



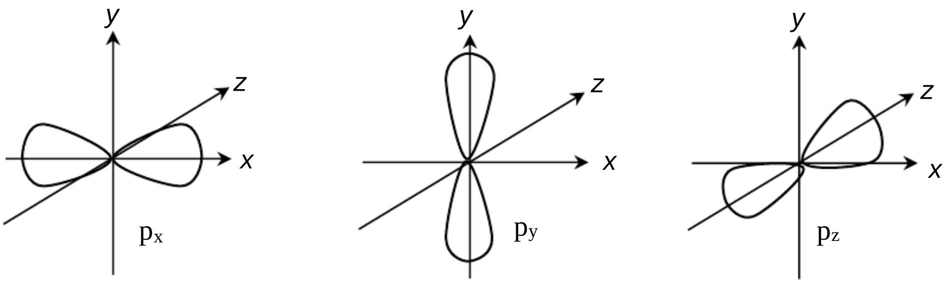
Why?

☞ As the principal quantum number, *n*, increases, the orbitals get **larger** and **more diffused**.

More detailed explanation
With a 2s orbital larger than a 1s orbital, the probability of finding an electron in a 2s orbital is spread across a greater region, and thus this electron is less strongly attracted by the nucleus as compared to one in the 1s orbital. As we view the electron as a negatively charged cloud, this means a lower electron density and hence a more diffused orbital.

(b) p orbitals: p_x, p_y and p_z

- A p subshell is made up of ***three*** **dumb–bell shaped** p orbitals mutually at **right angles** to each other.
- Each p orbital consists of two lobes with the atomic nucleus lying between them.
- p orbitals are **directional**, e.g. the p_x orbital will have 2 lobes of high electron density that lie along the x axis.
- All the three p orbitals are **degenerate**, i.e. they have the **same energy**.
- *p* orbitals from different electronic shell shells **differ in size**. Like s orbitals, the p orbitals get larger and more diffused as the principal quantum number, *n*, increases. i.e. 3p > 2p

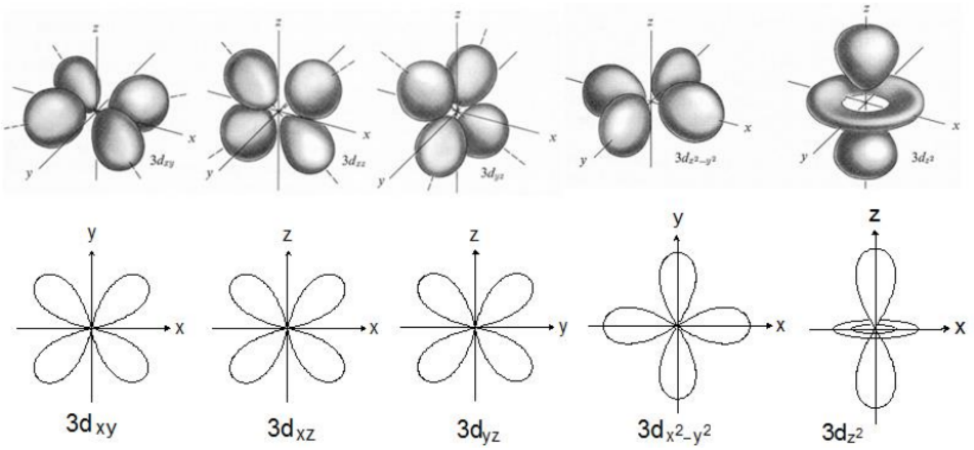


(c) d orbitals: d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}

- A d subshell consists of **5** orbitals which are **degenerate** (d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2}).

- Similar to other orbitals, d orbitals from different principal electronic shells **differ in size**.

- d orbitals are **directional**.
  - The d_{xy}, d_{yz} and d_{xz} orbitals each consists of 4 lobes of high electron density lying in the xy, yz and zx planes respectively. For example, in the case of d_{xy} orbital, the d_{xy} orbital has 4 lobes that lie in the xy plane in between the x and y axis.
  - The $dx^2–y^2$ orbital has 4 lobes of high electron density that lie along the axes of x and y.
  - The d_{z^2} orbital has two lobes along the z axis with a ring of high electron density in the xy plane.



2.3.2 Relative energies of the orbitals

- Each orbital is associated with a specific **energy level**, which is in turn associated with a specific distance of the electron from the nucleus.

- The “energy of an orbital” is the energy of the electron occupying that orbital.

- An electron that resides in an electron shell closer to the nucleus is more strongly attracted to it. It will have a lower potential energy and is thus more stable.

- A schematic representation of the energy levels is shown below, indicating the relative energies of the various orbitals.

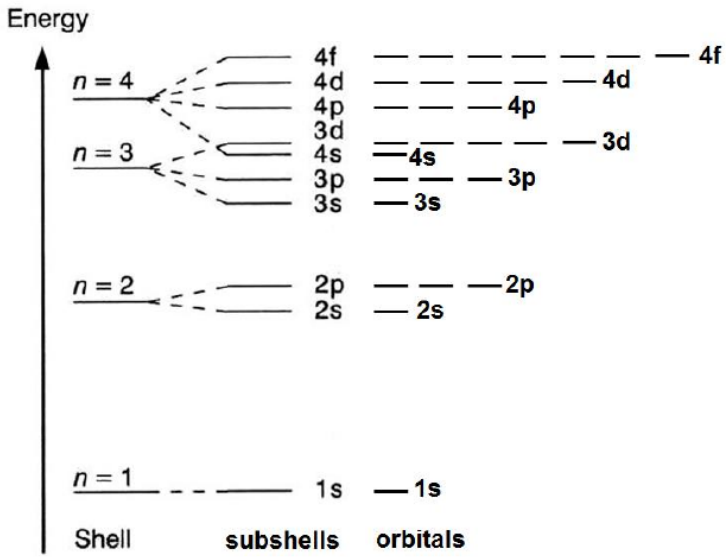


Figure: *The relative energies of the subshells for the first four principal quantum shells (Not to scale)*

1) In general, the greater the principal quantum number, the higher the energy of the electron.

2) The higher the energy of an electron, the less stable it is.

*3) Within the same electronic shell, the relative energies of the subshells are in the order **s < p < d < f.***
Why? For the same shell, by comparing the shapes of the orbital, electron in the s orbital is slightly closer to the nucleus than an electron in a p orbital, d orbital and f orbital, thus lower in energy.

4a) Why does the 4s subshell have a lower energy than the 3d subshell given that the n = 4 principal quantum number should have a higher energy than the n = 3 principal quantum number?

***Ans:** n = 4 **should** have a higher energy than n = 3. However, as the number of protons in the nucleus increases, the electrons in a particular orbital are attracted to it **more**. However, the decrease in energy is not regular and is not the same for all orbitals. In particular, electrons in the 4s and 4p orbitals decrease their energy faster than electrons in the 3d orbitals. As a result, 4s subshell having a lower energy than the 3d subshell.*

b) Does that mean that the 4s subshell is now closer to the nucleus than the 3d subshell?
***Ans:** No. On average, the n = 4 principal quantum number is still further away from the nucleus than n = 3.*

Checkpoint 2

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

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

2) Which diagram best shows the shapes and relative energies of 2s and 2p orbitals in carbon?

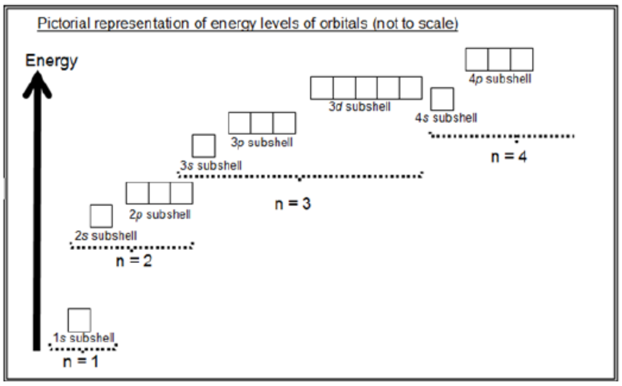
A	2p 2s		↑ energy	**C**	2p 2s		↓ energy
B	2p 2s		↑ energy	**D**	2p 2s		↓ energy

2.4 Filling the orbitals

- Electrons are arranged according to a set of rules:

Rule 1: The Aufbau Principle

- Electrons occupy the orbitals with the **lowest possible energy** first.
- This is because electrons that are closer to the nucleus are more strongly attracted to it. The potential energy will be lower and the system will be **more stable**.
- When the electrons in an atom occupy orbitals of lowest available energy, the atom is said to be in its **ground** state.



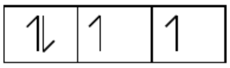
Rule 2: Pauli Exclusion Principle

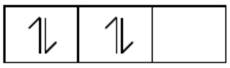
- Each orbital can hold a **maximum of 2 electrons.**
- The two electrons must have **opposite spins.**

not

Rule 3: Hund's Rule

- When filling a set of **degenerate** orbitals, electrons occupy the orbitals **singly with parallel spins** before any pairing occurs.
- This is because electrons tend to be as far apart as possible to **minimise inter–electronic repulsion**.





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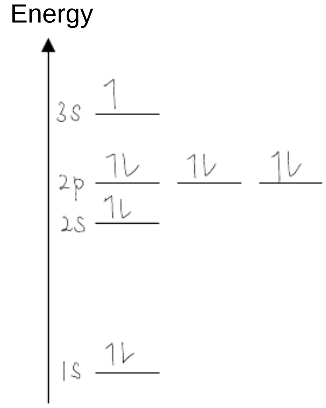
2.4.1 Representing Electronic Configurations

- Three ways of representing electronic configuration:

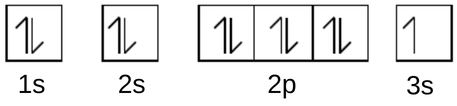
  1. Energy level diagram
  2. 'Electron–in–boxes' diagram
  3. Using '*spdf*' notation

Example for $_{11}$Na

(a) Using energy level diagram



(b) Using the 'electrons–in–boxes' diagram (where energy level is not required)



Use half arrow to represent a single electron

(c) Using the '*spdf*' notation

$_{11}$Na : $\mathbf{1s^2\ 2s^2\ 2p_x^2\ 2p_y^2 2p_z^2 3s^1}$ **OR**

$_{11}$Na : $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^1}$ ***most common form***

Sometimes, noble gas configuration (short–hand notation) is used:

Examples:

$_{9}$F	[He] $2s^2 2p^5$
$_{15}$P	[Ne] $3s^2 3p^3$
$_{20}$Ca	[Ar] $4s^2$

Noble gas configuration

He	$\mathbf{1s^2}$
Ne	$\mathbf{1s^2 2s^2 2p^6}$
Ar	$\mathbf{1s^2 2s^2 2p^6 3s^2 3p^6}$

***Note**: If the **full electronic configuration** is required by the question, the short–hand notation cannot be used.*

*E.g. the **full electronic configuration** of $_{15}$P should be $1s^2 2s^2 2p^6 3s^2 3p^3$ and **not** [Ne] $3s^2 3p^3$.*

Example 4

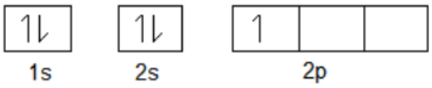
Write the **full** electronic configuration of the following atoms:

(a) lithium atom	(b) beryllium atom
(c) boron atom	(d) carbon atom
(e) nitrogen atom	(f) oxygen atom
(g) fluorine atom	(h) neon atom

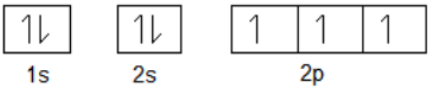
Example 5

Which diagram represents the arrangement of electrons in the ground state of a nitrogen atom? Explain why the other 3 options are incorrect.

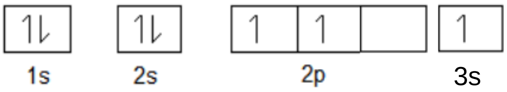
A



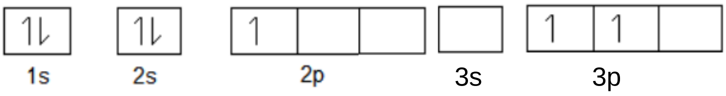
B



C



D



Explanation:

- A is ________ as there are 2 more electrons in N.
- C and D are ________. (Rule 1 is not fulfilled). These are examples of **excited state**.
- If an electron is promoted to an orbital of a higher energy level, the atom is **unstable** and is said to be in an **excited** state. There is **only one** ground state, but there are **many** excited states.

2.4.2 Electronic Configurations involving More Than 18 Electrons

- When filling electrons into the orbitals, the **4s orbital is filled first before the 3d orbitals**. *(Refer to page 18 on using periodic Table to decide on the relative subshell energies)*

$_{19}$K : $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^1$

$_{20}$Ca : $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$

$_{21}$Sc : $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ **$3d^1$** **$4s^2$**

Note: The electronic configuration is always written in the order of **increasing** principal quantum number e.g. for $_{26}$Fe it should be $1s^2 2s^2 2p^6 3s^2 3p^6$**$3d^6 4s^2$** but ***not*** $1s^2 2s^2 2p^6 3s^2 3p^6$**$4s^2 3d^6$**.

2.4.3 Anomalous Electronic Configurations

The electronic configurations for chromium ($_{24}$Cr) and copper ($_{29}$Cu) are anomalous.

(a) Chromium: [Ar] **$3d^5$** $4s^1$ *not* [Ar] $3d^4$ $4s^2$

(b) Copper: [Ar] **$3d^{10}$** **$4s^1$** *not* **[Ar] $3d^9$ $4s^2$**

Electronic configurations with **half–filled** or **fully filled 3d subshells** are unusually **stable** due to the **symmetrical distribution of charge around the nucleus**.

If similar charges are distributed symmetrically, this means that all charges are spread out evenly and as far apart as possible. This results in similar amount of electrostatic repulsion at each point in space. Such a state has lower energy (thus more stable) as compared to a state of asymmetrical distribution.

2.5 Electronic Configurations involving ions

2.5.1 Cations/ positively charged ions

- Electrons are first removed from orbitals with the highest energy.

  Note:
  - For atoms / ions with **more than 20** electrons, the 4s electrons are removed first before the 3d electrons even though the 4s orbital is filled before the 3d orbitals.
  - This is because the 3d subshell is closer to the nucleus. Once the 3d subshell is occupied by electrons, the inner 3d electrons repel the 4s electrons further from the nucleus and cause the latter to be at a higher energy level.

Example 6

Determine the electronic configuration of the following ions:

(a) Na^+ ion

($Na : 1s^2 2s^2 2p^6 3s^1$)
Na^+ :

(b) Ca^{2+} ion

($Ca: 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$)
Ca^{2+} :

(c) Iron(II) ion

($Fe : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$)
Fe^{2+} :

(d) Iron(III) ion

($Fe : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$)
Fe^{3+} :

2.5.2 Anions/ Negatively charged ions

☞ Anions are formed when atoms **gain electrons**.

☞ Electrons are added to the **next available lowest energy orbital** in the atom.

Example 7

Determine the electronic configuration of the following ions:

(a) Oxide ion

($O : 1s^2 2s^2 2p^4$)
O^{2-} :

(b) Chloride ion

($Cl : 1s^2 2s^2 2p^6 3s^2 3p^5$)
Cl^- :

2.6 Electronic Configurations involving isoelectronic species

- When 2 different species (atoms or ions) have the **same** number of electrons (or electronic configuration), they are said to be **isoelectronic** with one another.

  For example, the following species are isoelectronic:

  ${}_9F^-$ $\mathbf{1s^2 2s^2 2p^6}$ ${}_{10}Ne$ $\mathbf{1s^2 2s^2 2p^6}$ ${}_{11}Na^+$ $\mathbf{1s^2 2s^2 2p^6}$

Checkpoint 3

1 Gallium has the electronic configuration [Ar] $3d^{10} 4s^2 4p^1$, where [Ar] represents the configuration of argon.

In which order are the electrons lost in forming the Ga^{4+} ion?

	1st	*2nd*	*3rd*	*4th*
A	3d	4p	4s	4s
B	3d	4s	4s	4p
C	4s	4s	4p	3d
D	4p	4s	4s	3d

N95/IV/4

2 Which of the following species have three unpaired electrons?

A A*l*

B Ti^{3+}

C Zn^{2+}

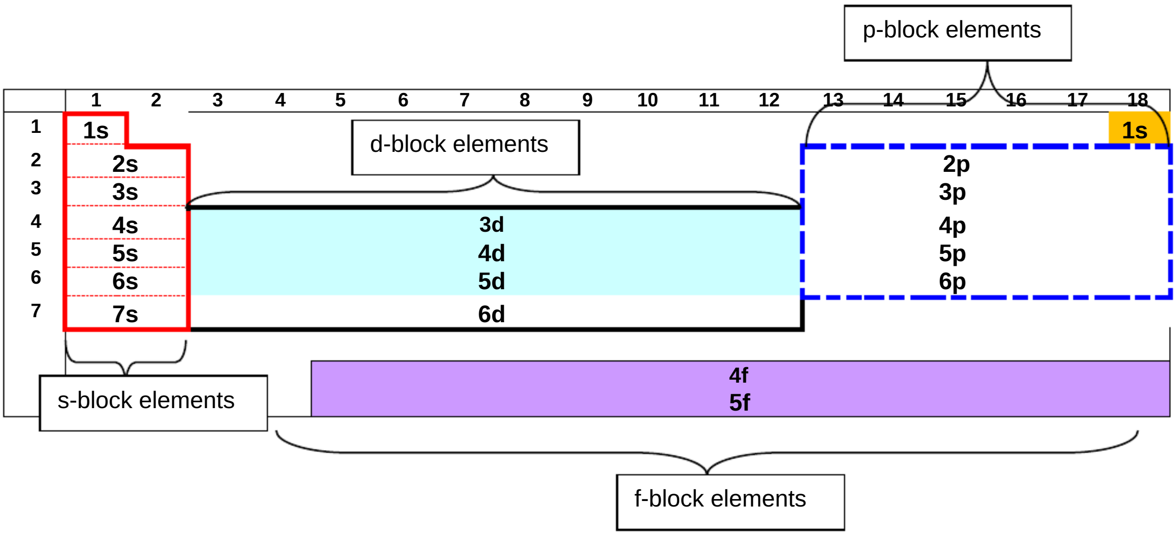
D Cr^{3+}

2.7 The Periodic Table

In the Periodic Table,

- elements are arranged in order of increasing **atomic (proton)** number
- elements in the same **Period** (row) have electrons occupying the same outermost shell (or have the same number of electron shells).
- elements in the same **Group** (column) have the same number of valence (outermost) electrons and thus, same electronic configuration in the valence (outermost) shell in their atoms.

Regions of the Periodic Table



How can we easily decide the relative energy levels of the subshells?

The Periodic Table is divided into blocks of 2, 6, 10 and 14 columns which reflects the *number of electrons that occupy s, p d and f subshells*.

As we proceed through the elements in the periodic table in order of increasing atomic number, we will be able to determine the *relative energies* of the subshells and hence deduce the *order of filling* up the subshells.

PART 3: IONISATION ENERGY

3.1 Definition of first ionisation energy (1^{st} I.E.):

The **first ionisation energy** of an element is the energy **needed** to remove **one mole** of electrons from **one mole** of the **gaseous atoms** to form **one mole of singly charged gaseous cations**.

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

E.g. The 1st I.E. for sodium can be represented by the following equation:

$$Na(\mathbf{g}) \longrightarrow Na^{+}(\mathbf{g}) + e^{-} \qquad \Delta H = +494 \text{ kJ mol}^{-1}$$

- The magnitude of ionisation energy is a measure of the **strength of attraction** between the **positively charged nucleus** (due to the protons present) and the **valence electron** that is to be removed.

- Ionisation energies have positive values (**endothermic**) because energy is **absorbed** during ionisation to overcome this attractive force.

- When we carry out ionisation, the species must be **gaseous** atoms. In the gaseous state, atoms have very minimal interactions with one another. Thus, the energy absorbed would solely be responsible for removing the electrons and not for overcoming other type of interactions.

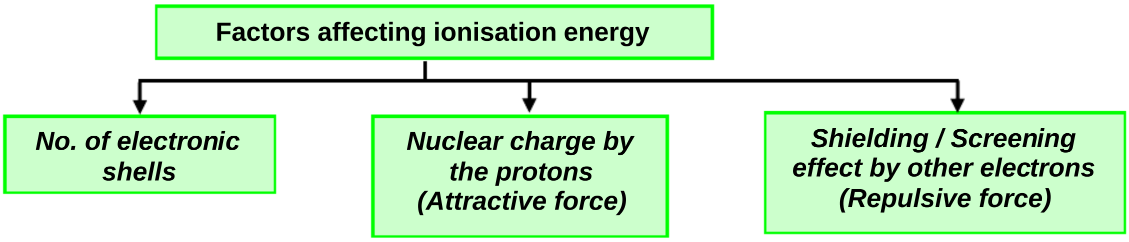
Example 8

Which equation is used to define the first ionisation of bromine?

A $Br(g) \rightarrow Br^{-}(g) - e^{-}$
B $Br(g) \rightarrow Br^{+}(g) + e^{-}$
C $\frac{1}{2}Br_2(g) \rightarrow Br^{+}(g) + e^{-}$
D $\frac{1}{2}Br_2(l) \rightarrow Br^{+}(g) + e^{-}$

Modified N96/IV/1; N99/III/2

3.2 Factors Affecting Ionisation Energy (I.E.)



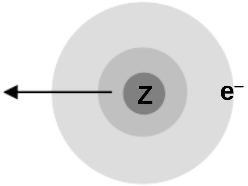
3.2.1 Nuclear Charge

- As the number of protons increases, the nuclear charge **increases**.
  - ☞ The attraction of the positively charged nucleus for the negatively charged valence electrons **becomes stronger**.
  - ☞ **More** energy is required to remove the valence electrons.
  - ☞ Hence, the ionisation energy **increases**.

3.2.2 Shielding effect by other electrons

- Electrons in the **inner** electronic shells **repel** those in the outer shell away from the nucleus.
- The inner (core) electrons **partially cancel** the attraction between the valence electrons and the nucleus, i.e. the inner electrons **shield** or **screen** the valence electrons from the attraction of the nucleus. Hence, the actual attraction of the nucleus experienced by the valence electrons is lessened.

Shielding by inner shell of electrons

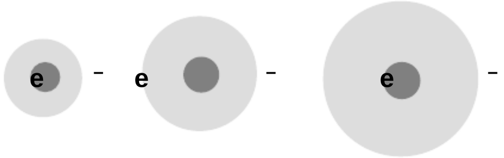


The valence electron, **e⁻** does not "experience" the full attraction of the nuclear charge, **Z**, from the nucleus

- ☞ Shielding/screening effect **increases** with an **increase** in the **number of inner electronic shells**.
- ☞ Thus the electrostatic **attraction** between the valence electron and the nucleus **becomes weaker**.
- ☞ **Less energy** is required to remove the valence electron
- ☞ Hence the ionisation energy **decreases**.

3.2.3 No. of electronic shells (distance)

- As the number of electron shells **increases**, the valence electrons are **further away** and **more shielded** from the nucleus.



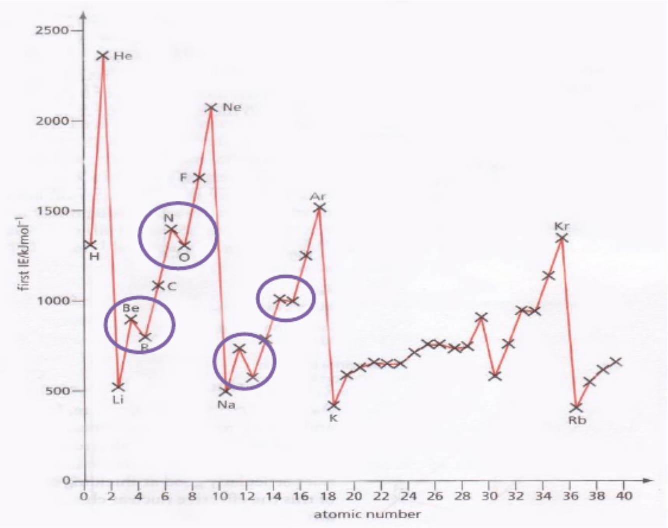
  ☞ The attraction of the positively charged nucleus for the negatively charged electrons **becomes weaker**.

  ☞ **Less** energy is required to remove the valence electrons.

  ☞ Hence, the ionisation energy **decreases**.

3.3 Trends in First Ionisation Energy

The figure below shows how the **first ionisation energy** of elements vary with atomic number.



First ionisation energies for the first 40 elements

Observations from the graph above,

(a) First ionisation energies generally increase across a period

Examples	From Li to Ne (Period 2 elements) From Na to Ar (Period 3 elements)
Reason	• Across a period, number of protons increases and hence **nuclear charge increases.** • Across a period, number of electrons also increases but these electrons are added to the same outermost electron shell and hence **number electron shell remains the same** and **shielding effect remains approximately constant.** • Electrostatic **attraction** between the valence electrons and the nucleus **becomes stronger**. • Hence **more energy** is required to remove a valence electron from an atom across a period. • First ionisation energies **generally increase** across a period.

(b) Exceptions to the General Trend across the Period

(i) Between Groups 2 and 13

Example 1	Across period 3: The first ionisation energy of A*l* (577 kJ mol^{-}) is **lower** than that of Mg (736 kJ mol^{-1}).
Reason	Mg: $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2}$ A*l*: $1s^2\ 2s^2\ 2p^6\ 3s^2\ \mathbf{3p^1}$ • Nuclear charge of A*l* is higher than Mg. • However, the 3p electron to be removed from A*l* is at a **higher energy level** and **less strongly attracted to the nucleus** than the 3s electron to be removed from Mg. • Hence **less energy** is required to remove the 3p electron in A*l* than the 3s electron in Mg. • Consequently the first ionisation energy of A*l* is **lower** than that of Mg.
Example 2	Across period 2: The first ionisation energy of B (799 kJ mol^{-1}) is **lower** than that of Be (900 kJ mol^{-1}).
Reason	Be: $1s^2\ \mathbf{2s^2}$ B: $1s^2\ 2s^2\ \mathbf{2p^1}$ • Nuclear charge of B is higher than Be. • However, the 2p electron to be removed from B is at a **higher energy level** and **less strongly attracted to the nucleus** than the 2s electron to be removed from Be. • Hence **less energy** is required to remove the 2p electron in B than the 2s electron in Be. • Consequently the first ionisation energy of B is **lower** than that of Be.

(ii) Between Groups 15 and 16

Example 1	The first ionisation energy of S (1000 kJ mol^{-1}) is **lower** than that of P (1060 kJ mol^{-1}).
Reason	P : $1s^2\ 2s^2\ 2p^6\ 3s^2$ **$3p^3$** S : $1s^2\ 2s^2\ 2p^6\ 3s^2$ **$3p^4$** • Nuclear charge of S is higher than P. • However, 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 3p electron from S. • Hence the first ionisation energy of S is **lower** than that of P.
Example 2	The first ionisation energy of O (1310 kJ mol^{-1}) is **lower** than that of N (1400 kJ mol^{-1}).
Reason	N : $1s^2\ 2s^2$ **$2p^3$** O : $1s^2\ 2s^2$ **$2p^4$** • Nuclear charge of O is higher than N. • However, the 2p electron to be removed from O is a **paired electron** while that to be removed from N is an **unpaired electron**. • Due to **inter–electronic repulsion** between paired electrons in the same orbital, **less energy** is required to remove the 2p electron from O. • Hence the first ionisation energy of O is **lower** than that of N.

–

(c) First ionisation energy decreases down the Group

<table>
<tr>
<td>Data</td>
<td>
<table>
<tr><th>Group 1</th><th>1st ionisation energy / kJ mol^{-1}</th></tr>
<tr><td>Li</td><td>519</td></tr>
<tr><td>Na</td><td>494</td></tr>
<tr><td>K</td><td>418</td></tr>
<tr><td>Rb</td><td>403</td></tr>
<tr><td>Cs</td><td>376</td></tr>
</table>
<table>
<tr><th>Group 17</th><th>1st ionisation energy / kJ mol^{-1}</th></tr>
<tr><td>F</td><td>1680</td></tr>
<tr><td>Cl</td><td>1260</td></tr>
<tr><td>Br</td><td>1140</td></tr>
<tr><td>I</td><td>1010</td></tr>
<tr><td>At</td><td>920</td></tr>
</table>
</td>
</tr>
<tr>
<td>Reason</td>
<td>Down a group,

Nuclear charge increases.
However, number of electron shells increase, which result in valence electron further away and is more shielded from the nucleus
Electrostatic attraction between the valence electron and the nucleus becomes weaker.
Less energy is required for the removal of the valence electron

Hence first ionisation energies of the elements generally decrease down a group.</td>
</tr>
</table>

(d) Additional points to take note

1. The first ionisation energy of the noble gas is the **highest** within each period.

- Within each period, the noble gas has the largest number of protons compared to any one of the preceding elements and hence it has the **largest nuclear charge**.
- Within each period, the noble gas has the same number of shell. It also has the largest number of electrons but these additional electrons are added to the **same outermost shell and they provide relatively poor shielding** for one another. Hence the valence electrons in the noble gas atom experience **approximately the same shielding effect** as those of any of the preceding elements.
- Thus the electrostatic **attraction** between the valence electron and the nucleus is the **greatest** for the noble gas atom.
- Hence the **largest amount of energy** is required to remove an electron from the noble gas atom than from any other element within each period, leading the noble gas having the highest first ionisation energy.

2. There is a **sharp drop** in first ionisation energy from **He to Li**, from **Ne to Na** and from **Ar to K**.

The first ionisation energy of K is **lower** than that of Ar.

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

- Though the nuclear charge of K is larger than that of Ar, the 4s electron to be removed from K is **further away from the nucleus** than the 3p electron in Ar. This 4s electron experiences significantly **more shielding** due to more inner electrons.
- The 4s electron in K is **less strongly attracted** by the nucleus and requires **less energy** to be removed compared to the 3p electron in Ar.
- Hence the first ionisation energy of K is lower than that of Ar.

Example 9

Why is the first ionisation energy of Ne higher than that of F?

A Fluorine is more electronegative than neon.
B Neon has a complete octet, but fluorine does not.
C The atomic radius of fluorine is less than that of neon.
D The nuclear charge in neon is greater than that in fluorine.

Example 10

Why is the first ionisation energy of sulfur lower than that of phosphorus?

A Sulfur is more electronegative than phosphorus.
B Sulfur forms anions more readily.
C The electron to be lost is paired with another electron.
D The sulfur atom is larger than the phosphorus atom.

3.4 Trend in Successive Ionisation Energies of an Element

Definition of second ionisation energy (2nd I.E.):

The **second ionisation energy** of an element is the energy needed to remove **one mole** of electrons from **one mole** of **singly charged gaseous** cations to form **one mole** of **doubly charged gaseous** cations.

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

- Successive ionisation energies refer to the energies required to remove electrons one after another from a gaseous ion.
- During ionisation, electrons are always removed from the **valence** (outermost) shell.
- The successive ionisation energies of an element **increase** with the removal of each electron.

nth ionisation energy : $\mathbf{X^{(n-1)+}(g) \longrightarrow X^{n+}(g) + e^{-}}$

For example:

$$Mg(g) \longrightarrow Mg^{+}(g) \longrightarrow Mg^{2+}(g) \longrightarrow Mg^{3+}(g) \longrightarrow Mg^{4+}(g)$$

I.E. (kJ mol^{-1}) = 736 1450 7740 10500

Reason:	**General increase in successive I.E.:** • as electrons are successively removed from the atom • number of protons **remains the same** ⇒ **nuclear charge remains the same** • number of electrons decreases ⇒ **shielding effect decreases** ***(But note:*** *The change in shielding effect is not significant if the number of inner shell electrons remains the same.)* • **remaining electrons experience stronger attraction** by the nucleus • **more energy** is required to remove the electron leading to an **increase** in I.E.

Why is the 3rd IE significantly larger than the 2nd IE (1450 vs 7740)?

Reason:	Mg^{+} : $1s^2\,2s^2\,2p^6\,\mathbf{3s^1}$ Mg^{2+} : $1s^2\,2s^2\,\mathbf{2p^6}$ • **The 3rd electron is removed from an inner electron shell** which is **nearer to** and **less shielded** from the nucleus • Thus **the electron experiences even stronger attraction by the nucleus** • **even more energy** is required to remove the electron leading to a **larger increase** in I.E.

3.5 Deducing the Position of an Element within the Periodic Table from Successive Ionisation Energy Data

1. Data of successive ionisation energies of an element **provides evidence** for the existence of principal quantum shells (energy levels) and subshells (sub–levels) in an atom.

2. **Large difference (i.e. big jump)** between two successive ionisation energies
⇒ removal of electrons from **different principal quantum shells**

3. **Moderate difference (i.e. small jump)** between two successive ionisation energies
⇒ removal of electrons from **different subshells**

Example 11

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

940 (1st)   2100   3100   4100   7100   7900   15000   16000

State and explain the group of the Periodic Table to which **X** is likely to belong.

Solution

Approach:
a) Compute the differences between successive ionisation energies.
b) Why is there a large jump?
c) How many electrons in the outermost (valence) shell?
d) Predict the group number of the element

I.E.	**kJ mol^{-1}**	**Difference with previous I.E.**
1st	940	–
2nd	2100	1160
3rd	3100	1000
4th	4100	1000
5th	7100	3000
6th	7900	800
7th	15000	**7100**
8th	16000	1000

Reason:

☞ The largest difference is between the ___ **and** ___ **I.E.**

☞ The 7th electron is ____________________ by the nucleus.

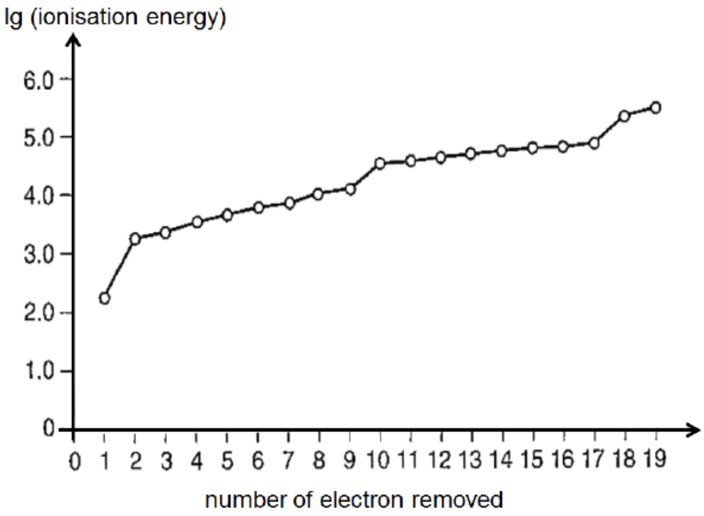
☞ because it is removed from an ______ electron shell that is closer to the nucleus and hence less shielded from the nucleus.

☞ Therefore, there are ___ electrons in the outermost (valence) shell.

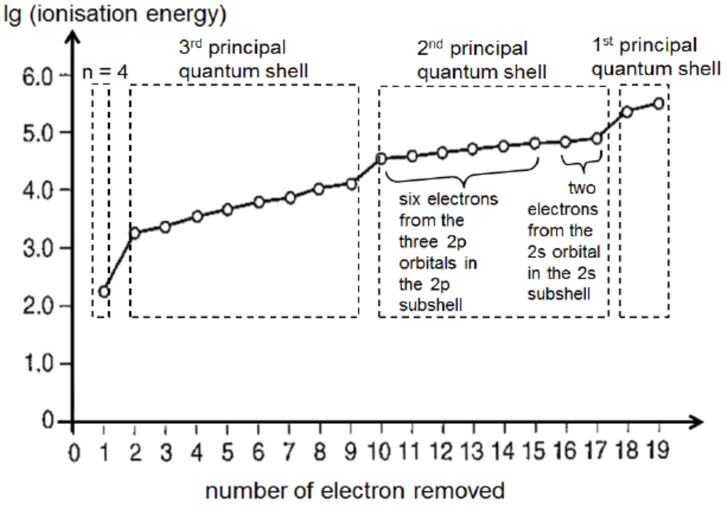
☞ Thus, **X** is likely to be in ________ .

What information can be obtained from a successive ionisation energies graph?

The graph below shows **all** the successive ionisation energies for element **X**.

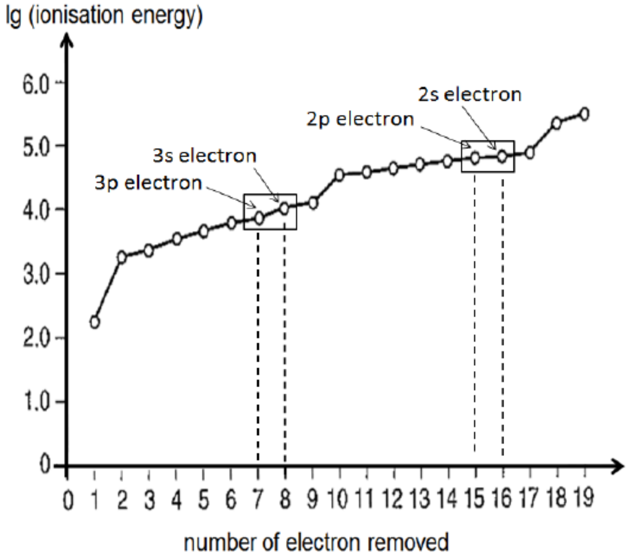


The following information can be obtained from the graph.

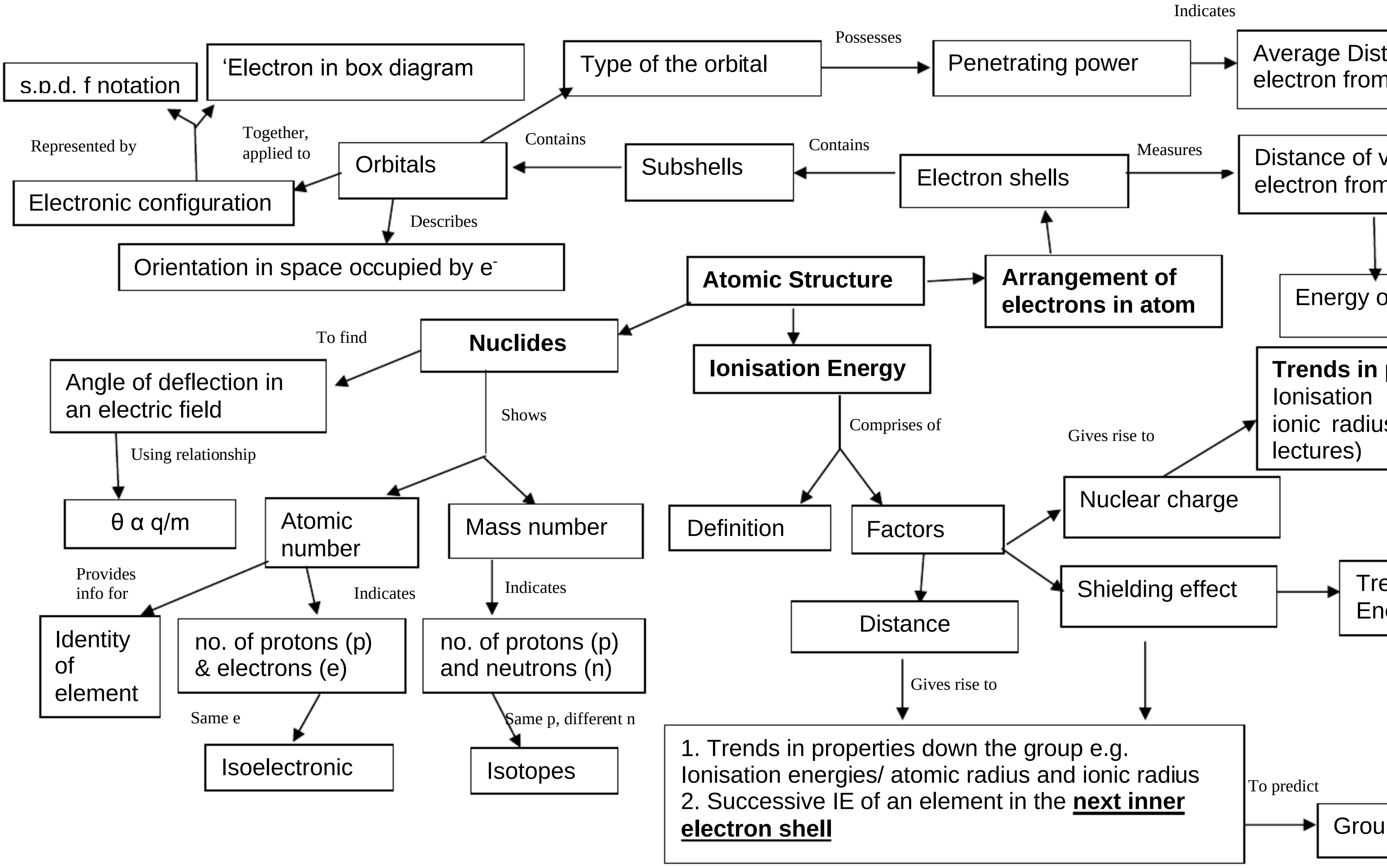
<table>
<tr><td>1</td><td>There are a total of 19 electrons present in an atom of the element.
The electronic configuration of the element X is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$.</td></tr>
<tr><td>2</td><td>


There are **4 principal quantum shells**.

- A **large increase** (i.e. big jump) in ionisation energy is observed when an electron is removed from a **different electron shell**, one that is **nearer to and less shielded from the nucleus** (i.e. at a lower energy level).
- The graph shows **3 such large increases** in ionisation energies corresponding to the removal of the **2nd**, **10th** and **18th** electron. Therefore, there are **4 different shells of electrons**
</td></tr>
</table>

	• Example: **large difference** between the 9th and 10th ionisation energies ⇒ **more energy** is required to remove the 10th electron ⇒ the 10th electron is removed from an **inner electron shell** that is closer to the nucleus and hence less shielded from the nucleus ⇒ the 10th electron is more strongly attracted by the nucleus
3	There is **1 valence electron** and hence the element belongs to **Group 1** of the Periodic Table. • There is a **large difference** between the 1st and 2nd ionisation energies ⇒ **more energy** is required to remove the 2nd electron ⇒ the 2nd electron is removed from an inner electron shell, one that is closer to the nucleus and less shielded from the nucleus ⇒ the 2nd electron is more strongly attracted by the nucleus
4	 • 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 principal quantum shells. • **Sometime, this observation is 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.

END


Indicates
Possesses
s.p.d. f notation
'Electron in box diagram
Type of the orbital
Penetrating power
Average Dist
electron from
Represented by
Together, applied to
Contains
Contains
Measures
Electronic configuration
Orbitals
Subshells
Electron shells
Distance of v
electron from
Describes
Orientation in space occupied by e-
Atomic Structure
Arrangement of electrons in atom
Energy o
To find
Nuclides
Ionisation Energy
Trends in
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Comprises of
Gives rise to
Using relationship
θ α q/m
Atomic number
Mass number
Definition
Factors
Nuclear charge
Provides info for
Indicates
Indicates
Shielding effect
Tre
En
Identity of element
no. of protons (p) & electrons (e)
no. of protons (p) and neutrons (n)
Distance
Same e
Same p, different n
Gives rise to
Isoelectronic
Isotopes
1. Trends in properties down the group e.g. Ionisation energies/ atomic radius and ionic radius
2. Successive IE of an element in the next inner electron shell
To predict
Grou