

Anglo-Chinese School (Independent)

Year 5 (2022) IBDP Chemistry HL



TOPIC 2 ATOMIC STRUCTURE

(IBDP syllabus Topic 2)

- 2.1 The nuclear atom
 - Essential Idea: the mass of an atom is concentrated in its minute positively charged nucleus.
- 2.2 Electron configuration
 - Essential Idea: the electron configuration of an atom can be deduced from its atomic number.

(IBDP syllabus Topic 12)

- 12.1 Electrons in atoms
 - Essential Idea: the quantized nature of energy transitions is related to the energy states of electrons in atoms and molecules

2.1 The nuclear atom

Essential idea: The mass of an atom is concentrated in its minute, positively charged nucleus.

Solution Nature of Science:

- Evidence and improvements in instrumentation—alpha particles were used in the development of the nuclear model of the atom that was first proposed by Rutherford. (1.8)
- Paradigm shifts—the subatomic particle theory of matter represents a paradigm shift in science that occurred in the late 1800s. (2.3)

Understandings:

- Atoms contain a positively charged dense nucleus composed of protons and neutrons (nucleons).
- Negatively charged electrons occupy the space outside the nucleus.
- The mass spectrometer is used to determine the relative atomic mass of an element from its isotopic composition.

Applications and skills:

- Use of the nuclear symbol notation ${}^{A}_{Z}X$ to deduce the number of protons, neutrons and electrons in atoms and ions.
- Calculations involving non-integer relative atomic masses and abundance of isotopes from given data, including mass spectra.

2.2 Electronic configuration

Essential idea: The electronic configuration of an atom can be deduced from its atomic number.

Solution Nature of Science:

- Developments in scientific research follow improvements in apparatus—the use of electricity and magnetism in Thomson's cathode rays.(1.8)
- Theories being superseded—quantum mechanics is among the most current models of the atom. (1.9)
- Use theories to explain natural phenomena—line spectra explained by the Bohr model of the atom. (2.2)

Understandings:

- Emission spectra are produced when photons are emitted from atoms as excited electrons return to a lower energy level.
- The line emission spectrum of hydrogen provides evidence for the existence of electrons in discrete energy levels, which converge at higher energies.
- The main energy level or shell is given an integer number, n, and can hold a maximum number of electrons, 2n².
- A more detailed model of the atom describes the division of the main energy level into s, p, d and f sub-levels of successively higher energies.
- Sub-levels contain a fixed number of orbitals, regions of space where there is a high probability of finding an electron.
- Each orbital has a defined energy state for a given electronic configuration and chemical environment and can hold two electrons of opposite spin.

Applications and skills:

- Description of the relationship between colour, wavelength, frequency and energy across the electromagnetic spectrum.
- Distinction between a continuous spectrum and a line spectrum.
- Description of the emission spectrum of the hydrogen atom, including the relationships between the lines and energy transitions to the first, second and third energy levels.
- Recognition of the shape of an s atomic orbital and the p_x , p_y and p_z atomic orbitals.
- Application of the Aufbau principle, Hund's rule and the Pauli Exclusion Principle to write electron configurations for atoms and ions up to Z = 36.

Guidance:

- Details of the electromagnetic spectrum are given in the data booklet in section 3.
- The names of the different series in the hydrogen line emission spectrum are not required.
- Full electron configurations (eg 1s²2s²2p⁶3s²3p⁴) and condensed electron configurations (eg [Ne] 3s²3p⁴) should be covered.
- Orbital diagrams should be used to represent the character and relative energy of orbitals.
- The electron configurations of Cr and Cu as exceptions should be covered.

12.1 Electronic configuration

Essential idea: The quantized nature of energy transitions is related to the energy states of electrons in atoms and molecules.

X Nature of Science:

• Experimental evidence to support theories – emission spectra provide evidence for the existence of energy levels.

Understandings:

- In an emission spectrum, the limit of the convergence at higher frequency corresponds to the first ionisation energy
- Trends in first ionisation energy across periods account for the existence of main energy levels and sub-levels in atoms.
- Successive ionisation energy data for an element give information that shows relations to electron configuration.

Applications and skills:

- Solving problems using E = hv
- Calculation of the value of the first ionisation energy from spectral data which gives the wavelength or frequency of the convergence limit.
- Deduction of the group of an element from its successive ionisation energy data.
- Explanation of the trends and discontinuities in the first ionisation energy across a period.

Guidance:

- The value of Planck's constant (*h*) and E = *hv* are given in the data booklet in sections 1 and 2.
- Use of the Rydberg formula is not expected in calculations of ionisation energy.

Important information for the topic

 $c = v\lambda$ E = hvSpeed of light = 3.00 × 10⁸ m s⁻¹ Planck's constant (h) = 6.63 × 10⁻³⁴ J s

2.1. The Nuclear Atom

2.1.1 The Subatomic Particles In An Atom

 β NOS - Background to atomic theory and Dalton's atomic theory.

ØNOS – Thomson's "plum-pudding" model of the atom.

ØNOS – Rutherford's gold foil experiment

An atom is the smallest component of an element. Atoms contain a positively charged dense nucleus composed of protons and neutrons (nucleons). Negatively charged electrons occupy the space outside the nucleus.



Scan me to view a video on the evolution of models of the atom

Relative masses and charges of the three subatomic particles:

Subatomic particle	Proton (p)	Neutron (n)	Electron (e)
Mass (kg)	1.672 ×10 ⁻²⁷	1.674 ×10 ⁻²⁷	9.109 ×10 ⁻³¹
Charge (× 10 ⁻¹⁹ C)	1.602 ×10 ⁻¹⁹	0	-1.602 ×10 ⁻¹⁹
Relative charge	+ 1	0	- 1

An atom can be represented by the nuclear symbol notation ${}^{A}_{Z}X$, where **X** is the symbol of the element.

- *A* = total number of protons and neutrons (mass number or nucleon number)
- *Z* = number of protons (atomic number or proton number)
- (A Z) = number of neutrons.
- Atoms are electrically neutral as the number of protons is equal to the number of electrons.
- Isoelectronic: Atoms / ions that have the same number of electrons.
- Isotonic: Atoms / ions that have the same number of neutrons.

2.1.2 Isotopic Masses

Isotopes are atoms of the same element with a different number of neutrons. They have the same atomic number but different mass numbers.

- Isotopes have the same chemical properties but different physical properties.
- Isotopes of elements have different nucleon numbers, relative isotopic masses and numbers of neutrons.
- The isotope with more neutrons is referred to as the **heavier** isotope.
- Isotopes of some elements are radioactive as the nuclei of these atoms are unstable and breakdown spontaneously. When they break down, they emit radiation which may be alpha particles (α), beta particles (β) and gamma (γ) rays.
- Isotopes are used as biochemical tracers in nuclear medicine for diagnostics, treatment and research. They are also used as "chemical clocks" in geological and archaeological dating. In nuclear medicine, PET (positron emission tomography) scanners give three– dimensional images of tracer concentration in the body and are used to detect cancers.

The relative atomic mass (A_r) of an element is the weighted average atomic mass of its naturally occurring isotopes. Modern mass spectrometer is used to determine the relative atomic mass of an element from its isotopic composition. Each peak in the mass spectrum indicates an isotope of the element and m/z values can be used to identify the isotopes. The height of the peak in the mass spectrum indicates the relative abundance of the isotopes.

Mass spectrometry is an analytical technique which allows the determination of relative isotopic masses, relative molecular masses and structural features of organic compound as well as identification of unknown compounds, e.g. in forensic science.

Instrumentation and Operation of a Mass Spectrometer (Not required by the syllabus)

The essential functions of a mass spectrometer and the associated components are given below:



A: Vaporisation

The sample, in minute quantity, must be vaporised either before it is injected into the spectrometer or immediately after it has been injected.

 $\begin{array}{rll} \text{e.g.} & \mbox{Mg (s)} & \rightarrow & \mbox{Mg (g)} \\ & \mbox{H}_2 \mbox{O (l)} & \rightarrow & \mbox{H}_2 \mbox{O (g)} \end{array}$

B: Ionisation

The sample of a compound is ionized in the ionisation chamber, usually to unipositive cations by *loss of an electron*. This is achieved by bombarding the vapour with a stream of high-energy electrons. The positive ions can either be:

C: Acceleration

The positive ions produced are attracted and accelerated by using an electric field with a high negative potential applied across parallel plates. The ions are focused to produce a narrow beam of ions with high constant speed when they pass through slits in these plates.

D: Deflection

The accelerated ions passed through a magnetic field where they are deflected. The amount of deflection depends both on the **mass** (m) of the ion and its **charge** (z).

Angle of deflection
$$\infty$$
 $\frac{1}{mass / charge (m/z)}$ Radius of curvature ∞ $\frac{1}{deflection}$ ∞ $\frac{mass}{charge}$ or $\frac{m}{z}$

Heavier and less highly charged ions will be deflected less than the lighter and more highly charged ions. Ions with a particular mass-to-charge ratio are recorded on a detector. In other words, for particles with the same charge, the extent of deflection depends on mass—the larger the mass, the less is the angle of deflection.

E: Detector

lons impart a positive charge on collector plate. The charge is amplified and recorded as a peak on a moving chart. The **greater the abundance of the ions**, the greater the charge imparted on the plate, the greater the current produced, thus the **higher the peak** on the recorder.

By varying the strength of the electric or magnetic field, the various ion beams (charged particles of various masses) can be brought (or selected) to strike the collector plate and the results are displayed on a chart showing a series of peaks known as a mass spectrum.

Reading a mass spectrum:



Fragmentation of molecules usually occur in the ionisation chamber and the resulting mass spectrum tends to be complicated especially if isotopes and species with multiple charges are also present. Each peak indicates a molecular ion or fragment ion. Fragmentation usually begins with the molecular ion which breaks down to give a series of daughter ions or fragment ions. The process of fragmentation gives rise to characteristic patterns in the mass spectrum. These patterns can be used to elucidate the structure of a molecule.

The diagram below shows the mass spectra of pentan–2–one and pentan–3–one (isomers of pentanone).



(Reference: http://www.chemguide.co.uk/analysis/masspec/fragment.html#top)

Example 1:

Bromine contains 54.90% of $^{79}\mathrm{Br}$ and 45.10% of $^{81}\mathrm{Br},$ calculate the relative atomic mass of bromine.

A_r of Bromine = $\frac{(54.90 \times 79) + (45.10 \times 81)}{100} = 79.90$

Example 2:

Using the mass spectrum and relative abundance data below, calculate the relative atomic mass of neon.



m/z	Species present	Relative abundance	A r
20	²⁰ ₁₀ Ne	10	A_r (10 × 20) + (1 × 22)
22	²² ₁₀ Ne	1	=

Exercise 1

1. Fill in information in the table below:

Symbol	Mass No. (A)	Atomic No. (<i>Z</i>)	Protons	Neutrons	Electrons
Zn	65	30	30	35	30
Sr ²⁺	88	38	38	50	36
³⁵ ₁₇ Cl	35	17	17	18	17
³⁷ ₁₇ Cl	37	17	17	20	17
³⁷ ₁₇ Cl ⁻	37	17	17	20	18
$^{2}_{1}\text{H}^{+}$	2	1	1	1	0
$^{2}_{1}H^{-}$	2	1	1	1	2

2. Suggest why the isotopes of an element have the same chemical properties, though they have different relative isotopic masses?

All the isotopes have same number of protons and electron configurations. As the chemical properties are dependent on the electron configurations, hence they will have the same chemical properties.

- **3.** The species $^{104}_{44}$ Ru contains
 - A. 44 neutrons and 44 electrons
 - B. 44 protons and 44 electrons
 - C. 44 protons and 104 neutrons
 - D. 60 neutrons and 60 electrons

Answer: B

Mass number = 104 Atomic number = 44 Number of protons = atomic number = 44 Number of electrons = number of protons = 44 (since the element is not charged) Number of neutrons = 104 - 44 = 60

- **4.** Chlorine occurs as two natural isotopes, chlorine–35 and chlorine–37. Which of the following statements about chlorine atoms is false?
 - A. All chlorine atoms have the same nuclear charge.
 - B. The nuclei have diameters which are approximately 1/10000 of the diameter of chlorine atoms.
 - C. Some naturally occurring chlorine nuclei contain 18 protons.
 - D. Some naturally occurring chlorine nuclei contain 20 neutrons.

Answer: C

Atoms of all chlorine isotopes contain 17 protons. Atoms that contain 18 protons will be argon. Atoms of chlorine–37 contain (37 – 17) = 20 neutrons.

5. Iridium has a relative atomic mass of 192.2. Its isotopes are ¹⁹¹Ir and ¹⁹³Ir. Calculate the percentage abundances of the two isotopes.

Let the percentage of 191 lr = x and percentage of 193 lr = 100 - x. $\frac{(x \times 191) + [(100-x) \times 193]}{100} = 192.2$ $\frac{191x + 19300 - 193x = 192.2 \times 100}{2x = 19300 - 19220}$ x = 40Iridium is 40% of 191 lr and 60% 193 lr.

6. A sample of the element rubidium (symbol: Rb) contains two isotopes, ⁸⁵Rb and ⁸⁷Rb, in the ratio of 18 : 7. Calculate the relative atomic mass of rubidium.

Relative atomic mass of rubidium = $\frac{(18 \times 85) + (7 \times 87)}{25} = 85.56$

2.2 Electron Configuration

2.2.1 Electromagnetic Spectrum

The different electromagnetic radiations have different wavelengths. The visible light region contains radiation having wavelengths between 400 nm - 700 nm and the different colours correspond to radiations of different wavelengths. In addition to visible light there are many other electromagnetic radiations, such as X–rays, ultraviolet rays (uv), infra–red rays (IR), microwaves and radio waves.

The arrangement of all the electromagnetic radiations in the increasing order of their wavelengths or decreasing order of their frequencies is termed the **electromagnetic spectrum**.



The frequency of the radiation can be determined using the equation:

 $c = \lambda v$

where c is the speed of light = $3.00 \times 10^8 \text{ m s}^{-1}$

A photon is characterised by either wavelength, denoted by λ or energy, by *E*. The inverse relationship between the energy of a photon (*E*) and the wavelength of the light (λ) is shown in the equation:

$$E = \frac{hc}{\lambda}$$

where *h* is the Planck's constant = $6.63 \times 10^{-34} \text{ J s}$

The inverse relationship means that light consisting of high energy photons has a short wavelength. Light consisting of low energy photons has a long wavelength.

As
$$c = v\lambda$$
, the equation $E = \frac{hc}{\lambda}$ can also be written as:
 $E = hv$

Example 3:

A certain energy source emits radiation of wavelength 500.0 nm. What is the energy of one photon of this radiation?

500.0 nm = 500.0 x 10^{-9} m = 5.000 x 10^{-7} m c = λv (5.000 x 10^{-7} m) (v) = 3.00 x 10^8 m s⁻¹ v = 6.00 x 10^{14} s⁻¹ E = hv $E = (6.63 x <math>10^{-34}$ J s) (6.00 x 10^{14} s⁻¹) $E = 3.978 x 10^{-19}$ J

2.2.2 Energy Level and Bohr Model

In atomic physics, the Bohr model, introduced by Niels Bohr in 1913, depicts the atom as a small, positively charged nucleus surrounded by electrons that travel in circular orbits around the nucleus—similar in structure to the solar system, but with attraction provided by electrostatic forces rather than gravity. Bohr modified the Rutherford model by requiring that the electrons move in orbits of fixed size and energy. According to Bohr's model, the energy of the electron in an atom is quantized. Quantization means that a quantity cannot vary continuously to have any arbitrary value but can change only discontinuously to have specific or discrete values.

Bohr found that the electron had the least energy when n = 1 which corresponds to the first Bohr energy level. This lowest energy state is called the ground state and electrons in this energy level are closest to the nucleus.

 β NOS – Models of the atom and electron arrangements.

 β NOS – The quantum mechanical model of the atom.

2.2.3 Hydrogen Emission Spectrum

When a sample of gaseous hydrogen atoms at low pressure is subjected to a high amount of energy, such as from an electric discharge or heat, the atoms will be able to emit electromagnetic radiation. The electron in the hydrogen atom may absorb energy and undergo an electronic transition ('jump') to higher energy levels. The electron at the higher energy level is said to be in an *excited* state. Then when the electron returns to a lower energy level, energy is emitted in the form of light/ photon. For example, an electron may return from n = 5 to n = 4 then to n = 2 and finally to n = 1 or it may be from n = 3 to n = 1. The electron cannot change its energy in a continuous way, in the same way you cannot stand in between the steps; it can only change in discrete amounts.



view a simulation on the hydrogen emission spectrum



Source: http://www.cas.miamioh.edu/~varrisim/F06101incl.html

The emitted photon from the atom on passing through a very thin slit (diffraction grating) and then through a prism. The emission lines correspond to photons of energies that are emitted when the excited electrons transit from higher energy levels (e.g. n = 4, 5, 6) to a lower energy level (e.g. n = 2 or n = 1).



The hydrogen **emission spectrum** is a **line** spectrum and the lines in the spectrum correspond to the photons of a particular wavelength (frequency). For each element, the emission spectrum is characteristic and unique to the element and it can be used to identify the element. (Similar to a flame test of cations). The emission spectrum **provides crucial evidence for the existence of electrons in discrete energy levels** which converge at higher energies (frequencies). The energy level is said to be **quantised**. If energy of an atom is not quantised, the emission spectrum would be continuous.

The spectrum formed from white light contains **all colours or frequencies** and is known as a **continuous spectrum**. Continuous spectra are produced by all incandescent solids and liquids and by gases under high pressure.



Source: http://astro.unl.edu/naap/hr/hr background1.html

The hydrogen emission spectrum consists of four coloured lines separated by dark bands. The wavelengths of the four lines are 656.3 nm (red), 486.1 nm (blue-green), 434.0 nm (indigo) and 410.1 nm (violet). This set of coloured lines is found in the visible region, are associated with electron transitions to n = 2 energy level.

There are other sets of lines (series) in the ultraviolet and infrared red region, they are associated with electronic transitions to n = 1 and n = 3 energy level respectively.



Each series in the hydrogen emission spectrum consists of lines of fixed frequencies. This shows that the energy of the electron is quantised, i.e. it has a fixed amount of energy as the electron is in a **discrete energy level**. These energy levels are characterized by a whole number called the principal quantum number, *n*.



The hydrogen emission spectrum above shows that with an increase in frequency, the spacing between adjacent lines in the emission spectrum decreases. The lines are closer to each other and each series converges to a limit, called the convergence or series limit. The lines are so close together in that region that the spectrum looks continuous.

The gap between the lines in the spectrum indicates that the energy levels of the atom. There is a convergence of the energy levels at higher frequencies and wider energy gaps when the energy level is closer to the nucleus.

Further Reading: Fireworks

The colours of fireworks are the result of emissions of light (photons) by energetically excited metal atoms. The gun powder used in fireworks heats and excites the electrons in metal. A fraction of a second later, these excited electrons return to the ground state and energy is released as light of various colours.

Exercise 2

- 1. Which of the following statements is/are consistent with the Bohr model?
 - I. The lowest energy level is closest to the nucleus.
 - II. An electron can transit from n = 2 energy level to n = 3 energy level by emitting a photon of definite energy.
 - III. An electron can remain in a particular energy level as long it emits a radiation of a constant frequency.
 - A. I only
 - B. II only
 - C. III only
 - D. I and II only

Answer: A

I is true. II is false as energy is absorbed for an electron to move from a lower to a higher energy level. III is false as an electron has a fixed amount of energy (quantisation).

- 2. The emission spectrum of an atom appears as a
 - A. continuous spectrum.
 - B. series of dark lines in an otherwise continuous spectrum.
 - C. series of evenly-spaced bright lines.
 - D. series of bright lines that converge at high frequency.

Answer: D

- 3. What is the energy of a photon with a wavelength of 586 nm?
 - A. 3.39×10^{-28}
 - B. 3.39×10^{-26}
 - C. 3.39×10^{-19}
 - D. 3.39×10^{-17}

Answer: C

```
3 \times 10^8 = \nu \times 586 \times 10^{-9}

\nu = 5.12 \times 10^{14} Hz

E = 6.626 \times 10^{-34} \times 5.12 \times 10^{14} = 3.392 \times 10^{-19} J
```

- **4.** The spectral line that corresponds to the electronic transition from n = 3 to n = 2 in the hydrogen atom is red in colour. What type of electromagnetic radiation will be emitted during an electronic transition from n = 2 to n = 1?
 - A. Ultraviolet
 - B. Red light
 - C. Infrared
 - D. Radio waves

Answer: A

Transition to n = 1 is in the ultraviolet range.

5. If it takes 3.36 x 10⁻¹⁹ J of energy to eject an electron from the surface of a certain metal, calculate the longest possible wavelength, in nanometers, of light that can ionise the metal.

3.36 x $10^{-19} = (6.626 \text{ x } 10^{-34}) (v)$ v = 5.071 x 10^{14} s^{-1} $\lambda v = \text{c}$ (λ) (5.071 x 10^{14}) = 3.00 x 10^8 $\lambda = 592 \text{ nm}$

2.2.4 Energy Levels, Sub–Levels, Orbitals and Electron Spin

The Bohr model is the idea of a main energy level, described by n, which is called the principal quantum number. n determines the energy and the average distance of an electron from the nucleus. The main energy level or shell is given an integer number and can hold a maximum of $2n^2$ electrons.

The main energy level or shell is divided into s, p, d and f sub-levels. Sub-levels contain a fixed number of orbitals which are regions of space with a high probability of finding an electron. Each orbital can hold a maximum of 2 electrons. According to Pauli Exclusion Principle, the two electrons occupying the same orbital must have different spin states.

Sub-level	Number of orbitals in sub-level	Maximum number of electrons
S	1	2
р	3	6
d	5	10
f	7	14

Each orbital has a defined energy state for a given configuration and chemical environment. It may be noted that all the orbitals of a particular energy level will have the same energy. For example, all the 2p orbitals have the same energy. Orbitals having equal energy are termed **degenerate**.



The energies of the orbitals depend not only upon the nuclear charge but also upon the other electrons present in the atom. We have to consider the attraction between the electrons and the nucleus as well as the repulsive interactions between the electrons.

An electron in an atom is stable when the total attractive interactions are greater than the total repulsive interactions.

2.2.5 Types of Orbitals

The *s* orbitals have spherical shape and they are non–directional. For every quantum shell, there is only one *s* orbital and the size of the *s* orbital increases with the principal quantum number.



The p orbitals have dumb-bell shape and they are directional – the three p orbitals have different directions in space. The size of the p orbitals also increases with the principal quantum number.



d ,,,

d,,

d

d ,2 ... 2

d ,2



Note: 4*s* orbital (when empty) has lower energy than the 3*d* orbitals despite its higher quantum number.

For a given main energy level, the energy of d-orbitals > p-orbitals > s-orbitals.

2.2.6 Aufbau Principle, Hund's Rule and Pauli Exclusion Principle

Orbital diagrams refer to arrow-in-box diagrams and they are used to represent the character and relative energy of orbitals. Electrons are arranged in orbitals according to a set of rules.

If the above rules are followed, electrons occupy the lowest possible energy and the resultant arrangement of electrons is known as **ground state electronic configuration** (i.e. lowest **energy state**). When one or more electrons absorb energy and are promoted to higher energy level(s), the atom is said to be in an **excited state**.

Rule 1: *Aufbau* Principle

Electrons are added progressively to the orbitals starting with the lowest energy.



Order of orbitals in terms of increasing energy: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, etc.

Rule 2: Pauli Exclusion Principle

Each orbital can hold a maximum of two electrons. Paired electrons can only be stable when they spin in opposite directions so that the magnetic attraction which results from their opposite spins counterbalances the electrical repulsion.



Rule 3: Hund's Rule

When filling a sub-level, each orbital must be occupied singly before they are occupied in pairs i.e. electrons only 'pair-up' when each sub-level is already half-filled.



Element	Total Electrons	Orbital Diagram	Electron Configuration
		1s 2s 2p 3s	
Li	3	11 1	$1s^2 2s^1$
Be	4	11 11	$] 1s^2 2s^2$
В	5	11 11 1	$] 1s^2 2s^2 2p^1$
С	6	11 11 1	$] 1s^22s^22p^2$
N	7	11 11 1 1	$] 1s^2 2s^2 2p^3$
Ne	10	11 11 11 11 1	$] 1s^2 2s^2 2p^6$
Na	11	11 11 11 11 1	$1s^22s^22p^63s^1$

The electronic configuration of an atom or ion refers to the arrangement of electrons in its main energy levels, sub–levels and orbitals.

Notation for writing electronic configuration:



Exceptions to the Aufbau principle

At higher principal quantum numbers, the energy difference between certain sub–levels is smaller than that between the 3*d* and 4*s* sub–levels. As a result, there are some exceptions to the *Aufbau* principle among the heavier transition elements.

Element	Symbol	Atomic no.	Electron configuration
Scandium	Sc	21	[Ar] 3d ¹ 4s ²
Titanium	Ti	22	$[Ar] 3d^2 4s^2$
Vanadium	V	23	[Ar] $3d^3 4s^2$
Chromium	Cr	24	[Ar] 3d ⁵ 4s ¹
Manganese	Mn	25	$[Ar] 3d^5 4s^2$
Iron	Fe	26	[Ar] 3d ⁶ 4s ²
Cobalt	Co	27	$[Ar] 3d^7 4s^2$
Nickel	Ni	28	[Ar] 3d ⁸ 4s ²
Copper	Cu	29	[Ar] 3 <i>d</i> ¹⁰ 4s ¹
Zinc	Zn	30	[Ar] $3d^{10} 4s^2$

From the electron configuration of the transition metals, it may be noted that chromium and copper atoms have 5 and 10 electrons in the 3*d* orbitals instead of 4 and 9 electrons respectively. The reason is because fully–filled orbitals and half–filled orbitals have extra stability. Thus, p^3 , p^6 , d^5 , d^{10} , f^7 and f^{14} configurations which are either fully–filled or half–filled are more stable. Therefore, to acquire greater stability, one of the 4*s* electron enters the 3*d* orbitals so that the set of 3*d* orbitals become half–filled or fully–filled as seen in the configurations of chromium and copper atoms, respectively.

The extra stability of half-filled and fully-filled electronic configurations can be explained in terms of symmetry and exchange energy (see enrichment for explanation on exchange energy).

Symmetrical arrangement

The electronic configurations in which all the orbitals of same sub–shell are either fully–filled or half–filled will have a relatively more symmetrical distribution of electrons and therefore greater stability.



Enrichment: Exchange energy

The half–filled or fully–filled degenerate orbitals have a greater number of exchanges and consequently, they have larger **exchange energy of stabilization**. The "exchange" refers to shifting electrons from one orbital to another within the same sub–level. Let us compare the number of exchanges in the $3d^4 4s^2$ and in the $3d^5 4s^1$ configuration in chromium.

In the $3d^4$ arrangement, there are 6 electron exchanges which imply that there are six possible arrangements with parallel spin in $3d^4$ configurations. Whereas in the $3d^5$ arrangement, there are 10 electron exchanges which imply that there are ten possible arrangements with parallel spin in the $3d^5$ configurations. It is quite evident from the above description that the total number of electron exchanges in the $3d^5$ arrangement is larger; which lends it relatively greater stability.

In a similar way, it can be established that the number of exchanges in $3d^{10}$ configurations is larger than in $3d^9$ configurations which makes the $3d^{10}$ configurations relatively more stable.

2.2.7 Electron Configurations of lons

lons are formed when the atom loses or gains electron(s). A positive ion (cation) is formed when an atom loses electron(s) whereas a negative ion (anion) is formed when an atom gains electron(s).

The electron configuration of ions is written using the same rules as the atoms. However, it must be noted that when forming cations, the electrons are lost from the orbital with the highest energy. The anions are formed by adding electrons to vacant orbital of highest energy.

Example 4:

Write the electron configuration of Fe^{2+} and Fe^{3+} ions.

 $\begin{array}{rll} {}_{26}{\sf Fe} & : 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,{\rm 4s^2} \\ {}_{26}{\sf Fe^{2+}} & : 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,{\rm 3d^6} \\ {}_{26}{\sf Fe^{3+}} & : 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,{\rm 3d^5} \end{array}$

Exercise 3

- 1. Which principles or rules are violated in the following electron configurations of atoms? Write the correct electron configuration for each of the elements.
 - (a) boron: $1s^2 2s^3$

Pauli's exclusion principle: each orbital can hold 2 electrons (spin pair) Boron atom: 1s² 2s² 2p¹

(b) nitrogen: $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$

Hund's rule: no of unpaired electrons is maximized within a subshell/orbital Nitrogen atom: $1s^2 2s^2 2p^3$ (2 p_x^1 , $2p_y^1$ and $2p_z^1$)

(c) beryllium: $1s^2 2p_x^2$

Aufbau principle: fill the orbitals in order of increasing potential energy Beryllium atom: 1s² 2s²

- 2. Write the full electron configurations for the following ions and draw their orbital diagrams (electron–in–box diagram).
 - (a) ₂₄Cr³⁺

1s² 2s² 2p⁶ 3s² 3p⁶ 3d³

(b) ₂₉Cu⁺

1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰

- **3.** For each of the following, decide whether the electron configurations shown represent a neutral atom, a positive ion or a negative ion of the element shown, (a) $H : 1 s^2$
 - (a) H : 1*s*²

H⁻ (hydride ion) (ground state)

(b) S: $1s^2 2s^2 2p^6 3s^2 3p^4$

Atom (ground state)

(c) N : $1s^2 2s^1 2p^3$

N⁺ (unipositive ion) (excited state)

(d) F: $1s^2 2s^2 2p^5 3s^1$

F⁻(fluoride ion) (excited state)

Enrichment: Quantum Numbers

Four quantum numbers, n, l, m_l , and m_s , define the electron's position in the atom.

The principal quantum number, *n*, represents the main energy levels, or shells, the electrons can occupy in an atom, and the whole-number values 1, 2, 3....

The secondary quantum number, l, represents sub-levels and it has value ranging from 0 to n -1, and the letters s, p, d, f. l describes the shape of the orbital

The magnetic quantum number, m_l , describes the amount of energy levels in a sub-levels and has values -l to +l. It determines the number of orbitals and their orientation within a sub-level.

The spin quantum number, m_s , represents electron spin and has values + $\frac{1}{2}$ or - $\frac{1}{2}$. The Pauli Exclusion Principle states that no two electrons in an atom can have the same set of four quantum numbers (n, *l*, m_l , and m_s).

TOK – Historical development in the discovery of the structure of atom.

NOS – Determining the wavelengths of lines in spectra.

12.1 Electrons in an atom (AHL – Topic 12)

12.1.1 Ionisation Energy

When enough energy is supplied to move the electron in hydrogen atom from the ground state to $n = \infty$, the ionisation of hydrogen atom takes place. In an emission spectrum, the limit of convergence at higher frequency corresponds to the first ionisation energy. The 1st ionisation energy per electron is therefore a measure of the distance between the n = 1 level and $n = \infty$ level.

The 1st ionisation energy is defined as the minimum energy required in removing one mole of valence electrons from one mole of gaseous atoms to form 1 mole of singly positively charge gaseous ion.

The second ionisation energy $(2^{nd} IE)$ is defined as the energy required in removing one mole of electrons from one mole of its gaseous ions $M^+(g)$ in its ground state. Ionisation energies always have positive values (endothermic) since energy is required to remove an electron.

In general,

l,	$X(g) \rightarrow$	X+ (g) +	e⁻	$\Delta H_1 = 1^{st} IE$
	$X^{+}\left(g ight) \ ightarrow$	X ²⁺ (g) +	e⁻	$\Delta H_2 = 2^{nd} IE$
	$X^{2+}(g) \rightarrow$	X ³⁺ (g) +	e⁻	$\Delta H_3 = 3^{rd} IE$
	$X(g) \rightarrow$	X ³⁺ (g) +	3e-	ΔH = summation of the 1 st , 2 nd & 3 rd IE

Example 5:

Calculate the 1st IE of hydrogen using the list of the frequencies of the seven most widely spaced lines in the Lyman series.

v (Hz)			
2.467 x 10 ¹⁵			
2.924 x 10 ¹⁵			
3.084 x 10 ¹⁵			
3.158 x 10 ¹⁵			
3.198 x 10 ¹⁵			
3.223 x 10 ¹⁵			
3.238 x 10 ¹⁵			

$$E = hv$$

= 6.63 × 10⁻³⁴ × 3.238 × 10¹⁵
= 2.147 × 10⁻¹⁸ J
1st IE = $\frac{2.147 \times 10^{-18} \times 6.02 \times 10^{23}}{1000}$

12.1.2 Factors Affecting Ionisation Energy

(a) Nuclear charge

- Nuclear charge is the total charge of the protons in the nucleus. This is also the same as the number of protons.
- Given atoms or ions with the same number of filled quantum shells, the greater the nuclear charge, the greater the ionisation energy.

(b) Shielding effect by inner electrons

- Electrons in the inner shells repel the valence electrons, giving rise to the shielding effect. Shielding effect is usually given by the number of electrons in the inner quantum shells.
- The greater the shielding effect, the lower will be the ionisation energy.

The nuclear charge of an atom serves to attract the electrons towards the nucleus but the shielding effect of the inner core electrons serves to shield the electrostatic forces of attraction of the nucleus on the valence electrons. This balance can be roughly measured by the effective nuclear charge. Effective nuclear charge (Z_{eff}) is difference between nuclear charge and shielding effect. This gives a measure of the actual nuclear charge experienced by electrons in the valence shell, hence how tightly the electrons are attracted to the nucleus.

12.1.3 Successive Ionisation Energy

The successive ionisation energies of an atom increase with the removal of each electron, 1st IE < 2nd IE < 3rd IE.

Reason:

The general increase in successive ionisation energy is due to increasing amount of energy required to remove successive electrons from an increasingly positive ion due to an increasing electrostatic force of attraction between the nucleus and valence electrons.

The electron configurations of atoms can be investigated by experimentally measuring the successive ionisation energies. A large increase in ionisation energy indicates that the electron removed was more strongly held by the nucleus than the earlier ones; i.e. it could have come from an inner quantum shell.

Example 6:

Deduce the electron configuration of potassium using its successive ionisation energies.



The potassium atom has a total of 19 electrons which fall into four groups:

- 1. The first electron (valence electron) is relatively easy to remove.
- 2. The next eight electrons are more difficult to remove (closer to the nucleus) and require higher energy.
- 3. The next subsequent group of eight electrons are even more difficult to remove (even closer to the nucleus) and require even higher energy.
- 4. The last two electrons are most difficult to remove as they are closest to the nucleus.

This suggests that the potassium atom has two electrons closest to the nucleus (in quantum shell, n = 1), eight electrons further out (in quantum shell, n = 2). It also has another eight electrons even further out (in quantum shell, n = 3) and one valence (in quantum shell, n = 4). Hence, the electron arrangement in potassium is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

Example 7:

Consider the successive Ig IE values of the third quantum shell of a period 4 main group element:



There is a steady rise in the Ig IE values for the successive removal of the first six electrons, followed by a larger increase in the Ig IE value. This indicates that the last two electrons are more strongly attracted to the nucleus. This larger increase is a result of the 7th and 8th electrons being removed from a sub–level of lower energy. This therefore shows that the third quantum shell is further divided into sub–levels (3s sub–level and 3p sub–level).

Example 8:

The first seven ionisation energies (in kJ mol⁻¹) of an element are as follows:

1012 1903 2912 4956 6273 22233 25397

Deduce the group number of the element and explain your answer.

- Biggest increase between 5th and 6th ionisation energy.
- 6th electron is removed from an inner quantum shell which is closer to the nucleus.
- Hence, there is much stronger electrostatic attraction between the 6th electron and the nucleus hence a lot more energy is thus required to remove it.
- 1st 5 electrons are removed from the valence shell.
- There are 5 valence electrons in the valence shell.
- Thus, the element is in Group 15.

12.1.4 Trends in the 1st Ionisation Energy

The diagram below shows the graph of the 1st IE of some elements.



Across a period (from left to right),

- There is an **increase** in effective nuclear charge, Z_{eff}. This is because nuclear charge increases but shielding effect remains relatively constant since the inner quantum shells of electrons remain the same.
- The valence electrons are drawn closer to the nucleus, so the electrostatic attractions between the valence electrons and the nuclei increase.
- More energy is required to remove a valence electron from the gaseous atom.

Down a group,

- The number of filled quantum shells increases and the size of the atoms increase.
- The valence electrons occupy energy levels that are increasingly further from the nucleus.
- This increased distance reduces the electrostatic attractions between the protons in the nuclei and the valence electrons.
- Hence the electrostatic forces of attraction of the nucleus for the valence electrons decreases and less energy is required to remove them.

The diagram shows **two deviations from the 1**st **IE general trend**:

1. The first ionisation energy of aluminium is lower than that of magnesium.

 $\begin{array}{rll} Mg: & 1s^2\,2s^2\,2p^6\,3s^2\\ Al: & 1s^2\,2s^2\,2p^6\,3s^2\,3p^1 \end{array}$

It is because less energy is required to remove a 3p electron in the aluminium atom than a 3s electron in the magnesium atom as the 3p sub–level is of higher energy than the 3s sub–level and the 3p electron is further from the nucleus. The 3p electron also experiences shielding by the 3s electrons. As a result, the 3p electron experiences a weaker electrostatic force of attraction from the nucleus.

2. The first ionisation energy of the sulfur atom is lower than that of a phosphorus atom.



It is because in a sulfur atom, there are two electrons occupying the same 3p orbital and this gives rise to inter–electronic repulsion. Thus, less energy is required to remove a paired 3p electron from a sulfur atom compared to the energy required to remove an unpaired 3p electron from a phosphorus atom.

Exercise 4

1. Deduce the group number of the elements **A** to **D** using the ionisation energies.

	Ionisation Energy / kJ mol ⁻¹						
Element	1st 2nd 3rd 4th						
Α	500 4600		6900	9500			
В	740	1500	7700	10500			
С	900 1800		14800	21000			
D	580	1800	2700	11600			

- A Group 1 (large 'jump' after 1st IE)
- B Group 2 (large 'jump' after 2nd IE)
- C Group 2 (large 'jump' after 2nd IE)
- D Group 13 (large 'jump' after 3rd IE)

Summary

- All atoms of the same element have the same atomic number (Z); that is, they have equal numbers of protons in their nuclei.
- The mass number (A) of an atom is the total number of protons and neutrons. Thus the number of neutrons = A Z.
- The isotopes of an element are atoms with the same atomic number but different mass numbers. They have the same number of protons and electrons, but different numbers of neutrons.
- Mass spectra of elements enable isotopic abundances and relative atomic masses to be determined.
- If an atom is given sufficient energy (electrical or thermal), electrons can be excited from a lower energy level to a higher energy level. When the excited electron falls from a higher to a lower energy level, a quantum (photon) of electromagnetic radiation is emitted. This can be seen as a line in the emission spectrum of the element.
- Electrons can occupy a discrete energy level and gain or lose quanta ('packets') or photons of energy. When they return from higher energy levels to a lower energy level, a photon of energy is emitted.
- The main energy levels or shells are given principal quantum numbers n = 1, 2, 3, 4, etc. The first shell (n=1) is closest to the nucleus.
- The quantum shell is divided into sub–levels known as *s*, *p*, *d* or *f* and each sub–levels consists of atomic orbitals (solutions to the Schrodinger equation).
- Sub-level *s*, *p*, *d* and *f* have 1, 3, 5 and 7 orbitals, respectively. *s* orbitals are spherical and *p* orbitals are dumb–bell shaped.
- Each orbital holds a maximum of two electrons and the two electrons in an orbital are spin paired.
- The first ionisation energy of an element is the minimum energy required to remove one mole of electrons from a mole of gaseous atoms to form one mole of singly charged gaseous cations. Ionisation energies data gives crucial evidence to the existence of main energy level and sub–levels.

Suggested Answers

Exercise 1

1.

Symbol	Mass No. (A)	Atomic No. (<i>Z</i>)	Protons	Neutrons	Electrons
Zn	(35 + 30) = 65	30	30	35	30
Sr ²⁺	(38 + 50) = 88	38	38	50	36
³⁵ ₁₇ Cl	35	17	17	(35 – 17) =18	17
³⁷ ₁₇ Cl	37	17	17	(37 – 17) = 20	17
³⁷ ₁₇ Cl ⁻	37	17	17	(37 – 17) = 20	18
$^{2}_{1}\text{H}^{+}$	2	1	1	1	0
$^{2}_{1}\text{H}^{-}$	2	1	1	1	2

2. All the isotopes have same number of protons and electron configurations. As the chemical properties are dependent on the electron configurations, hence they will have the same chemical properties.

3. B

The species ${}^{104}_{44}$ Ru contains 44 protons, 44 electrons and (104 - 44) = 60 neutrons.

4. C

Atoms of all chlorine isotopes contain 17 protons. Atoms that contain 18 protons will be argon. Atoms of chlorine–37 contain (37 - 17) = 20 neutrons.

5. Let the percentage of ¹⁹¹Ir = x and percentage of ¹⁹³Ir = 100 - x. $\frac{(x \times 191) + [(100-x) \times 193]}{100} = 192.2$ $191x + 19300 - 193x = 192.2 \times 100$ 2x = 19300 - 19220 x = 40Iridium is 40% of ¹⁹¹Ir and 60% ¹⁹³Ir.

6. Relative atomic mass of rubidium =
$$\frac{(18 \times 85) + (7 \times 87)}{25} = 85.56$$

Exercise 2

1. A

I is true; II is false – energy is absorbed and III is false – they have a fixed amount of energy (quantisation).

2. D

3.

C $3 \times 10^8 = v \times 586 \times 10^{-9}$ $v = 5.12 \times 10^{14}$ Hz $E = 6.626 \times 10^{-34} \times 5.12 \times 10^{14} = 3.392 \times 10^{-19}$ J

4. A

Transition to n = 1 is in the ultraviolet range.

5. $3.36 \times 10^{-19} = (6.626 \times 10^{-34}) (v)$ $v = 5.071 \times 10^{14} \text{ s}^{-1}$ $\lambda v = c$ $(\lambda) (5.071 \times 10^{14}) = 3.00 \times 10^{8}$ $\lambda = 592 \text{ nm}$

Exercise 3

- (a) Pauli's exclusion principle: each orbital can hold 2 electrons (spin pair) Boron atom: 1s² 2s² 2p¹
 - (b) Hund's rule: no of unpaired electrons is maximized within a subshell/orbital Nitrogen atom: 1s² 2s² 2p³ (2 p_x¹, 2p_y¹ and 2p_z¹)
 - (c) Aufbau principle: fill the orbitals in order of increasing potential energy Beryllium atom: 1s² 2s²
- **2.** (a) [Ar] $3d^3$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
 - (b) [Ar] $3d^{10}$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
- **3.** (a) H atom is 1s¹
 - (b) S atom is $1s^2 2s^2 2p^6 3s^2 3p^4$
 - (c) N atom is $1s^2 2s^2 2p^3$
 - (d) F atom is $1s^2 2s^2 2p^5$
- Exercise 4
- **1.** A Group 1 (large 'jump' after 1st IE)
 - B Group 2 (large 'jump' after 2nd IE)
 - C Group 2 (large 'jump' after 2nd IE)
 - D Group 3 (large 'jump' after 3rd IE)
- atom (ground state) N⁺ (unipositive ion) (excited state)
- F^{-} (fluoride ion) (excited state)

H⁻ (hydride ion) (ground state)