

Atomic Structure

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C1 Atomic Hypothesis (Dalton)

It assumed that –

- (i) an atom cannot be subdivided.
- (ii) atoms are neither created nor destroyed during chemical reactions.
- (iii) atoms of the same element are alike; in particular all atoms of an element have the same mass.
- (iv) atoms of different elements are not alike; in particular, their masses are different.

C2 Properties of Electron, Proton and Neutron

<u>Symbol</u>	<u>Proton (p)</u>	<u>Neutron (n)</u>	<u>Electron (e)</u>
Mass	1.67252×10^{-27} kg	1.67482×10^{-27} kg	9.1091×10^{-31} kg
Charge	1.60210×10^{-19} C	0	1.60210×10^{-19} C
Mass relative to the electron	1836	1839	1
Charge relative to the proton	+1	0	-1
Discovery	Goldstein	Chadwick	Thomson

C3 Some Sub-nuclear Particles

<u>Particle</u>	<u>mass</u>	<u>Charge</u>
Antiproton	Same as that of proton	Negative
μ -meson (muon)	210 times that of an electron	Positive and negative
π -meson (pion)	276 times that of an electron	Positive and negative
Neutrino	265 times that of an electron	Zero
Positron	Very much less than that of an electron	Zero
	Same as that of an electron	Positive

C4 Rutherford's Nuclear Model of Atom

- (i) **Rutherford's** scattering experiments disproved the Thomson model and led to the nuclear model of the atom in which positive charge is spread over a sphere of radius 10^{-15} m, the so-called nucleus, and that the outer most electron clouds are about 10^{-10} m from the centre of the nucleus.
- (ii) The positive charge of a nucleus is due to the positively charged particles called **protons**. But mass of the nucleus is due to the protons and neutrons.
- (iii) The total number of protons and neutrons in a nucleus determine the **nuclear mass**.

C5 Nature of Light and Electromagnetic Waves

Wave theory considers light to be a form of wave motion of wavelength λ , related to frequency ν and

velocity of light c be equation $\nu = \frac{c}{\lambda}$.

Light waves are also considered electromagnetic in nature (i.e, they are oscillations of electric and magnetic fields in space). Various types of electromagnetic radiations having various wavelengths (or frequencies) are known and they constitute the so-called electromagnetic spectrum.

By quantum theory put forward by planck $E = nh\nu = \frac{nhc}{\lambda}$.

where n is number of photons.

Practice Problems :

- Number of photons of light of wavelength 4000 \AA required to provide 1.00 J of energy is
(a) 2.01×10^{18} (b) 12.01×10^{31} (c) 1.35×10^{17} (d) none is correct
 - One quantum is absorbed per molecule of gaseous iodine for converting into iodine atoms. If light absorbed has wavelength of 5000 \AA , the energy required in kJmol^{-1} is
(a) 2.38×10^{-5} (b) 2.38×10^5 (c) 1.38×10^2 (d) none
 - A near ultraviolet photon of 300 nm is absorbed by a gas and then re-emitted as two photons. One photon is red with wavelength 760 nm . The wavelength of second photon is
(a) 300 nm (b) 460 nm (c) 760 nm (d) 495.65 nm
- [Answers : (1) a (2) b (3) d]

C6A Bohr Theory of H-atom

This theory is used to calculate the radius (r) and energy (E) of a permissible orbit for one-electron species like H, He^+ , Li^{2+} etc.

C6B Postulates of Borh Theory

- The electrons continue revolving in their respective orbits without losing energy. Thus each orbit is associated with a definite energy hence it is also called fixed energy levels.
- Angular momentum (mvr) of an electron in a given orbit is quantised.

$$mvr_n = \frac{nh}{2\pi} \dots$$

[m is the mass of electron, v is the velocity of electron, r is radius of orbit in which it is revolving, n is the number of orbit]

- Energy is emitted or absorbed by an atom only when an electron moves from one level to another. Thus

$$\Delta E = (E_{n_2} - E_{n_1}) = \frac{hc}{\lambda} \quad \text{where } E_{n_2} = \text{energy of the } n_2 \text{ level, } E_{n_1} = \text{energy of the } n_1 \text{ level}$$

Thus wave number $\bar{\nu}$ is $\bar{\nu} = \frac{1}{\lambda} = \frac{\Delta E}{hc}$

C6C Results of Bohr Theory**1. Radius of nth orbit**

$$r_n = 0.53 \frac{n^2}{Z} \text{ \AA} \quad \text{where } Z = \text{atomic number}$$

2. Velocity of the electron in the nth orbit

$$v_n = \frac{Z}{n} \left(\frac{c}{137} \right) \quad \text{where } c = 3 \times 10^8 \text{ m/s}$$

3. Energy of the electron in the nth orbit

$$E_n = -13.6 \frac{Z^2}{n^2} \text{ eV}, \quad E_n = -(2.18 \times 10^{-18}) \frac{Z^2}{n^2} \text{ (J)}$$

$$E_T = K + U, \quad K = -E_T = -\frac{U}{2}, \quad U = 2E = -2K$$

4. Wavelength of photon emitted for a transition from n_2 to n_1

$$\frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where $R_H = 1.096 \times 10^7 \text{ m}^{-1}$ (Rydberg's constant)

5. Ionisation Energy

Energy required to remove the electron from the outermost orbit of the atom in gaseous phase is called ionisation energy (I.E.).

$E_\infty = 0$, thus the difference between the ground state of an atom and the excited state that correspond to $n_2 = \infty$ is called ionisation energy.

$$(\text{IE})_z = \frac{13.6 Z^2}{n^2} \text{ eV / atom}$$

6. Hydrogen Spectrum

Series	n_1	n_2	Region of Spectrum
Lyman	1	2, 3, ... ∞	Ultraviolet
Balmer	2	3, 4, ... ∞	Visible
Paschen	3	4, 5, ... ∞	Infrared
Brackett	4	5, 6, ... ∞	Infrared
Pfund	5	6, 7, ... ∞	Infrared

Practice Problems :

- The ratio of the energy of the electron in ground state of hydrogen to that of the electron in first excited state of Be^{3+} is :
 (a) 1 : 4 (b) 1 : 8 (c) 1 : 16 (d) 16 : 1
- If the shortest wavelength of H atom in Lyman series is x. then longest wavelength in Balmer series of He^+ is :
 (a) $\frac{9x}{5}$ (b) $\frac{36x}{5}$ (c) $\frac{x}{4}$ (d) $\frac{5x}{4}$
- The wavelength of the first line in Lyman series of hydrogen and that of the first line in Balmer series of lithium are in the ratio
 (a) 9 : 4 (b) 3 : 5 (c) 5 : 3 (d) 3 : 2

[Answers : (1) a (2) a (3) a]

C7A Particle and Wave Nature (Dual nature of Electron)

de Broglie based on Millikan's oil drop experiment (which showed particle nature) and diffraction study (which showed wave nature) suggested the dual nature of electron, both as a material particle and as a wave. According to de Broglie's equation.

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2m(\text{KE})}}, \text{ also } \lambda = \frac{h}{\sqrt{2m_e(\text{eV})}}$$

where $p (= mv = \sqrt{2m(\text{KE})})$ is called momentum of the particle of mass m moving with velocity v .

The circumference of n th orbit is equal to n times of wavelength of electrons.

$$2\pi r_n = n\lambda$$

Practice Problems :

- How fast is an electron moving if it have a wavelength equal to the distance it travels in one second ?
 (a) $\sqrt{\frac{h}{m}}$ (b) $\sqrt{\frac{m}{h}}$ (c) $\sqrt{\frac{h}{p}}$ (d) $\sqrt{\frac{h}{2(KE)}}$
 - A hydrogen molecule at 200°C is moving with a speed of 2.4×10^5 cm per sec. The de-Broglie's wave length is of the order of
 (a) 10,000 Å (b) 1. Å (c) 5.000 Å (d) 5Å
 - The accelerating potential is needed to produce an electron beam with an effective wavelength of 0.090 Å is
 (a) $(7.33 \times 10^{-23})/m_e q_e$ (b) $(7.33 \times 10^{-23})^2/m_e q_e$
 (c) $(7.33 \times 10)^2/m_e q_e$ (d) $(9.33 \times 10^{-23})^2/m_e q_e$
- [Answers : (1) a (2) b (3) b]

C7B Photoelectric Effect : When a beam of light of suitable wavelength or frequency is allowed to fall on the surface of metal, the electrons are emitted from the surface of metal. This phenomena of emission of electrons is known as photoelectric effect. It was suggested that some portion of the photon energy is used up in removing the electrons from the surface by overcoming the attractive force of nucleus (known as threshold energy or work function of the metal) and rest portion is utilised in imparting velocity of these

electrons (into K.E. of the photoelectrons). $h\nu = W_0 + \frac{1}{2}mv^2$... [m, v is the mass and velocity of electron]

$W_0 = h\nu_0$. [where ν_0 is the threshold frequency]

Practice Problems :

- When a certain metal was irradiated with a light of frequency 3.2×10^{16} Hz, the photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light frequency 2.0×10^{16} Hz. Hence threshold frequency is
 (a) 1.6×10^{16} Hz (b) 0.8×10^{15} Hz (c) 8×10^{15} Hz (d) 8×10^{16} Hz
 - The threshold frequency for photo electric emission of electrons from platinum is $1.3 \times 10^{15} \text{ sec}^{-1}$. What is the minimum energy that photons of a particular radiation must possess to produce the photo electric effect with platinum metal ?
 (a) energy must be equal to $6.63 \times 10^{-34} \times 1.3 \times 10^{15} \text{ J}$
 (b) energy must be greater than $6.63 \times 10^{34} \times 1.3 \times 10^{15} \text{ J}$
 (c) energy corresponding to 400 nm
 (d) none of these
- [Answers : (1) c (2) b]

C8 Heisenberg's Uncertainty Principle

It is not possible to determine precisely both the position and the momentum (or velocity) of a small moving particle (e.g. electron, proton etc.)

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

where Δx , Δp and Δv are the uncertainties with regard to position, momentum and velocity respectively.

In terms of uncertainty in energy, ΔE and uncertainty in time Δt , this principle is written as,

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

Practice Problems :

- The uncertainty in the momentum of an electron is $1 \times 10^{-6} \text{ kg m sec}^{-1}$. The uncertainty in position would be
 (a) $1.05 \times 10^{-23} \text{ m}$ (b) $2.1 \times 10^{-25} \text{ m}$ (c) $1.05 \times 10^{-27} \text{ m}$ (d) $1.05 \times 10^{-25} \text{ m}$
- If a 1.0 gm body is travelling along x-axis at 100 m sec^{-1} within 1 m sec^{-1} . The theoretical uncertainty in its position is
 (a) $10^3/4\pi h$ (b) $10^3 h/4\pi$ (c) $h/4\pi$ (d) none

[Answers : (1) d (2) b]

C9A Schrodinger wave mechanical model :

As it was given by the Heisenberg that it is impossible to determine the position and velocity of e^- simultaneously. To overcome this a new model of atom was introduced which was based on dual behaviour of matter. It was introduced by **Erwin Schrodinger**.

He introduced a new concept for determining the position of e^- i.e., orbital.

C9B Orbital : It is the region in space where there is high probability of finding the electron.

Difference between orbit and orbital

- | <u>Orbit</u> | <u>Orbital</u> |
|--------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|
| 1. It is circular or elliptical path traced by an electron revolving round the nucleus of atom giving of the distance of e^- from the nucleus. | 1. It is the region in space where there is while high probability of finding the electron. fixed value |
| 2. It violates the Heisenberg principle | 2. It does not violate the Heisenberg principle |
| 3. It is not in accordance to the dual character of matter | 3. It is in accordance of dual character of matter. |

C9C Quantum numbers : Each orbitals is designated by three quantum number n , l and m .

The principle quantum number (n) :

- It determines the size and to a large extent the energy of the orbital.
- The larger the value of n , the larger the energy of the orbital.
- Principle quantum number also identifies the shell

i.e., $n = \underset{\substack{\uparrow \\ \text{K}}}{1}, \underset{\substack{\uparrow \\ \text{L}}}{2}, \underset{\substack{\uparrow \\ \text{M}}}{3}, \underset{\substack{\uparrow \\ \text{N}}}{4}$ shell.

- There are n^2 orbitals in a shell.
- All the orbitals of a given volume of n constitute a single shell of atom.
- Each shell consists of one or more subshells or sublevels.
- The number of subshells in a principal shell is equal to the value of n .

Azinuthal or Subsidiary quantum number : (l)

Each subshell in a shell is designated by l . l can have n values ranging from 0 to $(n - 1)$ e.g. when $n = 1$, $l = 0$, $n = 2$, $l = 0, 1$ etc. i.e. for $n = 1$, $l = 0$ it means there is one subshell for $n = 2$, $l = 0, 1$. It means there are two subshell.

Subshells corresponding to different values of l are represented by following symbols

$l =$	0, 1, 2, 3, 4, 5
notations	s, p, d, f, g, h

Each subshell consists of one or more orbitals.

The number of orbitals in a subshell is given by $(2l + 1)$.

e.g. In any $l = 0$ subshell, there are $2(0) + 1 = 1$ orbitals.

For $l = 1$ subshell there are $2(1) + 1 = 3$ orbitals.

In any $l = 2$ subshell, there are $2(2) + 1 = 5$ orbitals.

In other words,

subshell notation	=	s, p, d, f, g
value of l	=	0, 1, 2, 3, 4
Number of orbitals	=	1, 3, 5, 7, 9

$$\text{The orbital angular momentum} = \sqrt{l(l+1)} \frac{h}{2\pi}$$

The quantum number l also gives the shape of the orbital in the subshell.

Magnetic quantum number (m) :

It gives information about the orientation of the orbital.

For any subshell (defined by l values), $(2l + 1)$ values of m are possible and these values are given as

$$m = -l, -(l-1), \dots, 0, \dots, +(l-1), +l$$

e.g. for $l = 2$ (d), m can have total $= 2(2) + 1 = 5$ values.

These values are $-2, -1, 0, +1, +2$ [Five orbitals]

For $l = 1$ (p) $m = 2(1) + 1 = 3$ values.

These values are $-1, 0, +1$ [Three orbitals]

i.e., there are three preferred orientation of p in space.

Thus each orbital is defined by set of values of n, l and m

e.g. If 4s is given then $n = 4, l = 0$

If 5p is given then $n = 5, l = 1$

Spin quantum number : Electrons spin about the axes.

Some spinning in one direction and some in other direction.

Two orientation of electron which is possible is one is in clockwise direction and other one is in anticlockwise direction.

They are represented by two arrows \uparrow (spin up) and \downarrow (spin down)

The two spins have either $+\frac{1}{2}$ value or $-\frac{1}{2}$ value.

Practice Problems :

- Correct set of quantum numbers for the unpaired electron in chlorine atom is

(a) $n = 2, l = 1, m = 0$	(b) $n = 2, l = 1, m = 1$
(c) $n = 3, l = 1, m = 1$	(d) $n = 3, l = 0, m = 0$
- Arrange the electrons represented by the following sets of quantum numbers in the decreasing order of energy for a multi-electron atom

(i) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$	(ii) $n = 3, l = 1, m = 1, s = -\frac{1}{2}$
(iii) $n = 3, l = 2, m = 0, s = +\frac{1}{2}$	(iv) $n = 3, l = 0, m = 0, s = -\frac{1}{2}$
(a) (iii) > (ii) > (i) > (iv)	(b) (iii) > (iv) > (i) > (ii)
(c) (i) > (ii) > (iii) > (iv)	(d) (iii) > (i) > (ii) > (iv)
- For a d-electron the orbital angular momentum is

(a) $\sqrt{6} \hbar$	(b) $\sqrt{2} \hbar$	(c) \hbar	(d) $2\hbar$
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- Among the following the possible orbitals are 1p, 2s, 2p and 3f.

(a) 1p, 2s	(b) 1p, 3f	(c) 3f, 2p	(d) 2s, 2p
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- The number of electrons in an atom having the following quantum numbers are respectively

(1) $n = 4, m_s = -\frac{1}{2}$	(2) $n = 3, l = 0$		
(a) 16, 9	(b) 32, 18	(c) 16, 2	(d) 9, 16

6. The lowest value of n that allows g orbitals to exist is
 (a) 2 (b) 3 (c) 4 (d) 5
7. An electron is in one of the $3d$ orbital. The possible values of n, l and m_l for this electron are respectively
 (a) 3, 1, 1 (b) 3, 2, -2 (c) 3, 0, 2 (d) 3, 1, -1
- [Answers : (1) c (2) d (3) a (4) d (5) d (6) d (7) b]

C9D Electronic configuration of atoms : The distribution of electrons into orbitals of atom is called its electronic configuration.

The filling of electron into different orbitals takes place according to following three rules :

1. **Aufbau Principle :** In the ground state of the atoms, the orbitals are filled in order of their increasing energies.

In other words, electrons first occupy the lowest energy orbital available to them and then enter to higher energy orbital.

The order of increase of energy of orbitals can be calculated by $(n + l)$ rule.

Lower the value of $(n + l)$ for an orbital, the lower is its energy.

If two orbitals have the same $(n + l)$ value, the orbital with lower value of n has the lower energy.

2. **Pauli Exclusion Principle :** The number of electrons to be filled in various orbitals is restricted by this principle.

No two electrons in an atom can have the same set of four quantum numbers.

e.g. If an electron in an atom has particular set of quantum number say $n = 1, l = 0, m = 0, s = +\frac{1}{2}$ then no other electron in an atom can have this set of quantum number.

3. **Hund's Rule of maximum multiplicity :** This rule deals with the filling of electrons into orbitals belonging to same subshell.

Orbital of same subshells like p_x, p_y, p_z are of equal energy and these are called as degenerate orbitals.

Similarly d has five orbitals of same energy i.e., $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$, f has 7 degenerate orbitals etc.

Hund's Rule States that : pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not takes place until each orbital belonging to that subshell has got one electron each i.e. is singly occupied.

↑ ↑ ↑
 e.g. p_x, p_y, p_z as there are 3-orbitals the pairing of electron starts in p with the entry of 4th electron.

4. **Magnetic Moment $\mu = \sqrt{n(n+2)}$, $n \rightarrow$ number of unpaired electron.**

Practice Problems :

1. A compound of vanadium has magnetic moment of 1.73 B.M. The electronic configuration of vanadium in the compound is

(a) $[Ar]3d^1$ (b) $[Ar]3d^3$ (c) $[Ar]3d^2$ (d) $[Ar]3d^0$

2. The ground state electronic configuration of Nitrogen ($z = 7$) atom. Can be represented as

(a) $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow}$ (b) $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\downarrow} \boxed{\uparrow}$

(c) $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\downarrow} \boxed{\downarrow}$ (d) $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\downarrow}$

3. If Hund's rule is not followed, magnetic moment of Fe^{2+}, Mn^+ and Cr all having 24 electrons will be in order :

(a) $Fe^{2+} < Mn^+ < Cr$ (b) $Fe^{2+} = Cr < Mn^+$
 (c) $Fe^{2+} = Mn^+ < Cr$ (d) $Mn^{2+} = Cr < Fe^{2+}$

4. Magnetic moment of X^{n+} ($Z = 26$) is $\sqrt{24}$ B.M. Hence number of unpaired electrons and value of n respectively are :

(a) 4, 2 (b) 2, 4 (c) 3, 1 (d) 0, 2

[Answers : (1) a (2) a (3) b (4) a]

C10 Isotopes

Atoms of the same element having same atomic numbers but different mass numbers are called isotopes e.g., ${}_{92}\text{U}^{238}$, ${}_{92}\text{U}^{235}$, ${}_{84}\text{Po}^{213}$, ${}_{84}\text{Po}^{216}$.

Isobars : Atoms of different elements having same mass numbers but different atomic numbers are called isobars, e.g., Po^{216} and ${}_{85}\text{At}^{216}$, ${}_{88}\text{Ra}^{228}$, ${}_{89}\text{Ac}^{228}$ and ${}_{90}\text{Th}^{228}$.

Isosters : Molecules having same number of atoms and same number of electrons are called Isosters.

For e.g., CO and N_2 , each has two atoms and the total number of electrons are 14.

Isodiaphers : Atoms having the same difference of neutrons and protons or same isotopic numbers. It is noticed that nucleide and its decay product after α emission are isodiaphers. e.g., ${}_{92}\text{U}^{235}$ and ${}_{90}\text{Th}^{231}$, ${}_{29}\text{Cu}^{65}$ and ${}_{24}\text{Cr}^{55}$.

Isotones : Nucleides having same no. of neutrons are known as isotones ${}_{2}\text{N}^{14}$ & ${}_{8}\text{O}^{15}$, ${}_{54}\text{Xe}^{136}$ & ${}_{56}\text{Ba}^{139}$, ${}_{50}\text{Ce}^{140}$ ${}_{59}\text{Pr}^{141}$.