

# CHEMISTRY

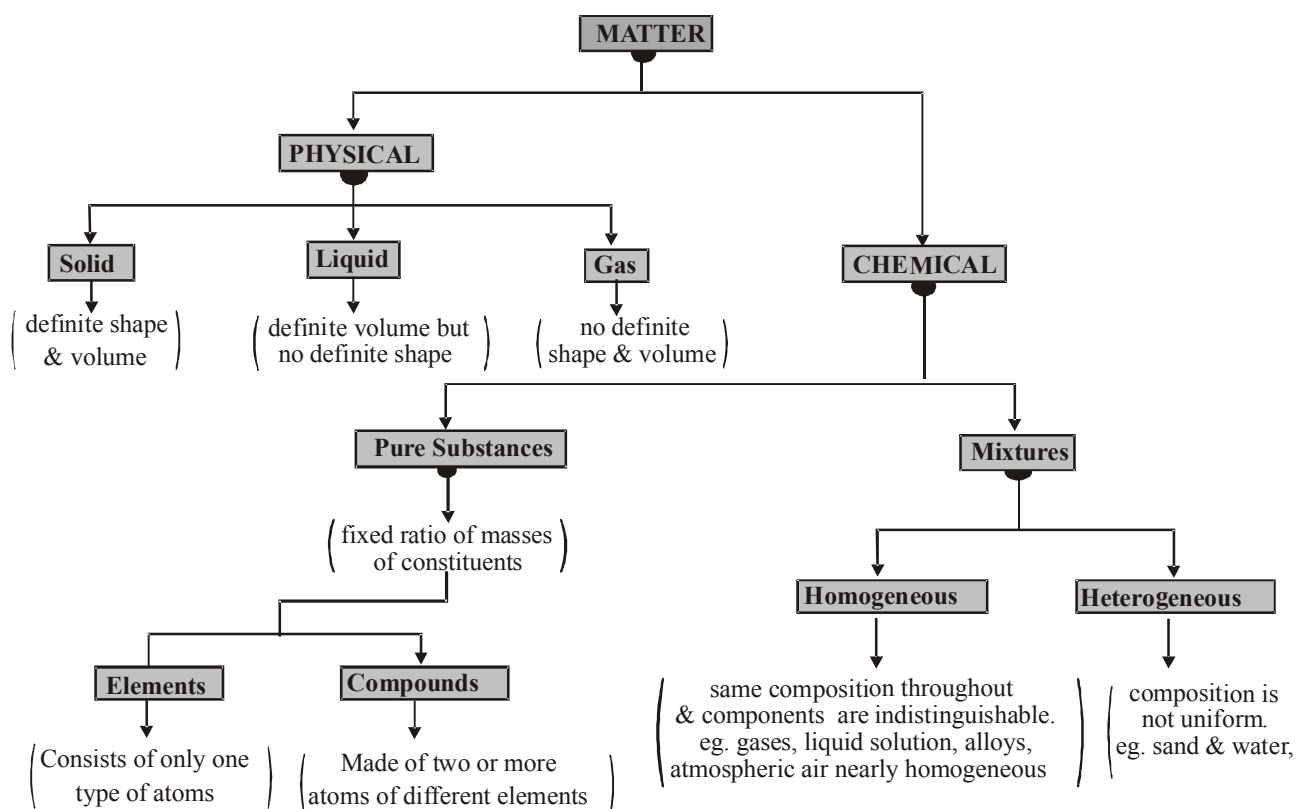
## ENTRANCE HUB ETHIOPIA REMEDIAL TUTORIAL STUDY MATERIAL

### CHAPTER ONE (ETHIO REMEDIAL)

### ATOMIC STRUCTURE AND PERIODICITY

#### 1.0 INTRODUCTION

Chemistry deals with the composition, structure and properties of matter. These aspects can be best described and understood in terms of basic constituents of matter: **atoms** and **molecules**. That is why chemistry is called the science of atoms and molecules. Can we see, weight and perceive these entities? Is it possible to count the number of atoms and molecules in a given mass of matter and have a quantitative relationship between the mass and number of these particles (atoms and molecules)? We will like to answer some of these questions in this Unit. We would further describe how physical properties of matter can be quantitatively described using numerical values with suitable units.



#### Classification of universe

Universe is classified into two types i.e. matter and energy.

**MATTER** : The thing which occupy space and having mass which can be felt by our five senses is called matter.

Matter is further classified into two categories :

(I) Physical classification

(II) Chemical classification

#### PHYSICAL CLASSIFICATION

It is based on physical state under ordinary conditions of temperature and pressure, **so on the basis of two nature of forces matter** can be classified into the following three ways :

(a) Solid

(b) Liquid

(c) Gas

**(a) Solid** : A substance is said to be solid if it possesses a definite volume and a definite shape.

**e.g.** Sugar, Iron, Gold, Wood etc.

**(b) Liquid** : A substance is said to be liquid if it possesses a definite volume but not definite shape. They take the shape of the vessel in which they are placed.

**e.g.** Water, Milk, Oil, Mercury, Alcohol etc.

**(c) Gas** : A substance is said to be gas if it neither possesses a definite volume nor a definite shape. This is because they completely occupy the whole vessel in which they are placed.

**e.g.** Hydrogen( $H_2$ ), Oxygen( $O_2$ ), Carbon dioxide( $CO_2$ ) etc.



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### ATOMIC STRUCTURE

Atom is a Greek word and its meaning is indivisible i.e. an ultimate particle which cannot be further subdivided. John Dalton considered that "all matter are composed of smallest indivisible particle called atom.

#### Dalton's Atomic Theory :

This theory is based on law of mass conservation and law of definite proportions. The salient features of this theory are :-

- (1) Each element is composed of extremely small particles called atoms.
- (2) Atoms of a particular element are like but differ from atoms of other element.
- (3) Atom of each element is an ultimate particle and it has a characteristic mass but is structureless.
- (4) Atoms are indestructible i.e. they can neither be created nor be destroyed.
- (5) Atoms of different elements take part in chemical reaction to form molecule.

### LAWS OF CHEMICAL COMBINATION

#### (a) Law of Mass Conservation (Law of Indestructibility of Matter)

"It was given by **Lavoisier** and tested by **Landolt**"

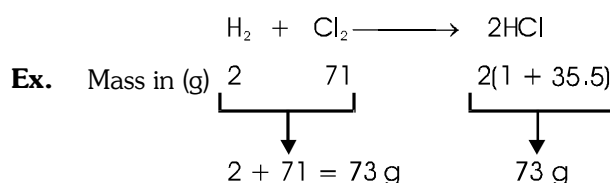
According to this law, the mass can neither be created nor be destroyed in a balanced chemical reaction or physical reaction. But one form is changed into another form is called as law of mass conservation.

If the reactants are completely converted into products, then the sum of the mass of reactants is equal to the sum of the mass of products.

**Total mass of reactants = Total mass of products.**

If reactants are not completely consumed then the relationship will be :

**Total mass of reactants = Total mass of products + Mass of unreacted reactants**



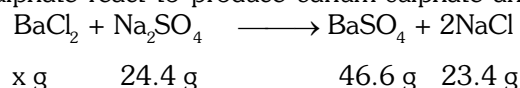
### EHpractice

#### EHpractice

What weight of  $\text{BaCl}_2$  would react with 24.4 g of sodium sulphate to produce 46.6 g of barium sulphate and 23.4 g of sodium chloride ?

#### Solution

Barium chloride and sodium sulphate react to produce barium sulphate and sodium chloride according to the equation :



Let the weight of  $\text{BaCl}_2$  be  $x \text{ g}$ . According to law of conservation of mass :

Total mass of reactants = Total mass of products

Total mass of reactants =  $(x + 24.4) \text{ g}$

Total mass of products =  $(46.6 + 23.4) \text{ g}$

Equating the two masses  $\Rightarrow x + 24.4 = 46.6 + 23.4$

$x = 46.6 + 23.4 - 24.4$  or  $x = 45.6 \text{ g}$

Hence, the weight of  $\text{BaCl}_2$  is 45.6 g

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EHpractice

10g of  $\text{CaCO}_3$  on heating gives 4.4 g of  $\text{CO}_2$  then determine weight of produced  $\text{CaO}$  in g.

Solution

$$\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$$

$$10 \text{ g} \qquad \qquad \qquad \text{x g} \qquad \qquad \qquad 4.4 \text{ g}$$

According to law of conservation of mass

$$10 = 4.4 + \text{x}$$

$$10 - 4.4 = \text{x}$$

$$\text{x} = 5.6 \text{ g}$$

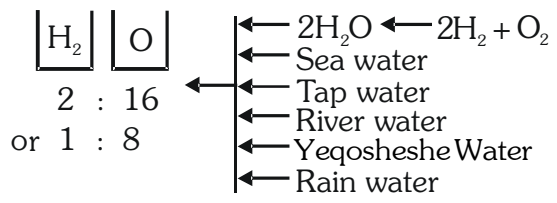
(b) Law of Definite Proportion / Law of Constant Composition

"It was given by **Proust**."

According to this law, a compound can be obtained from different sources. But the ratio of each component (by weight) remain same.i.e. it does not depend on the method of its preparation or the source from which it has been obtained.

For example :- molecule of ammonia always has the formula  $\text{NH}_3$ . That is one molecule of ammonia always contains, one atom of nitrogen and three atoms of hydrogen or 17 g of  $\text{NH}_3$  always contains 14 g of nitrogen and 3 g of hydrogen.

**Ex.** Water can be obtained from different sources but the ratio of weight of H and O remains same.



EHpractice

EHpractice

Weight of copper oxide obtained by treating 2.16 g of metallic copper with nitric acid and subsequent ignition was 2.70 g. In another experiment, 1.15 g of copper oxide on reduction yielded 0.92 g of copper. Show that the results illustrate the law of constant composition.

Solution

In I experiment

weight of  $\text{Cu}$  = 2.16 g

weight of  $\text{CuO}$  = 2.7 g

weight of Oxygen =  $2.7 - 2.16 = 0.54 \text{ g}$

$$\text{Cu} : \text{O}$$

$$2.16 : 0.54$$

$$\frac{2.16}{0.54} : \frac{0.54}{0.54}$$

$$4 : 1$$

In II experiment

weight of  $\text{CuO}$  = 1.15 g

weight of  $\text{Cu}$  = 0.92 g

weight of Oxygen =  $1.15 - 0.92 = 0.23 \text{ g}$

$$\text{Cu} : \text{O}$$

$$0.92 : 0.23$$

$$\frac{0.92}{0.23} : \frac{0.23}{0.23}$$

$$4 : 1$$

Thus the ratio of the masses of copper and oxygen in the two experiment are same. Hence the given data illustrate the law of constant proportion.





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### EHpractice

Carbon combines with hydrogen in P, Q and R. The % of hydrogen in P, Q and R are 25, 14.3, and 7.7 respectively. Which law of chemical combination is illustrated ?

### Solution

P	Q	R
H : C	H : C	H : C
25 : 75	14.3 : 85.7	7.7 : 92.3
$1 : \frac{75}{25}$	$1 : \frac{85.7}{14.3}$	$1 : \frac{92.3}{7.7}$
① : 3	① : 6	① : 12

Ratio of C in compounds P, Q and R is = 3 : 6 : 12 = 1 : 2 : 4

Which is a simple ratio so the data illustrate the law of multiple proportion.

### ATOMIC NUMBER AND MASS NUMBER

#### (a) Atomic Number

It is represented by Z. The number of protons present in the nucleus is called atomic number of an element.

For neutral atom : Number of electrons = Number of protons

For an ion : Number of electrons = Z - (charge on ion)

Z = number of protons only

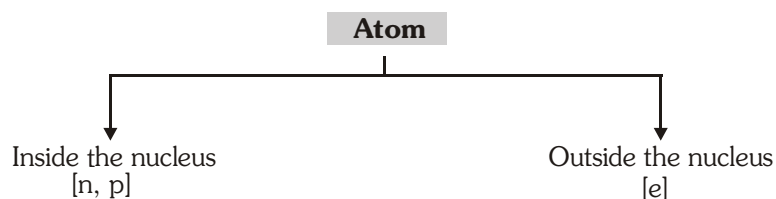
#### (b) Mass Number

It is represented by capital A. The sum of number of neutrons and protons is called the mass number of the element. It is also known as number of nucleons because neutrons & protons are present in nucleus.

**Formula :** A = number of protons + number of neutrons

Number of neutrons = A - Z

**Note :** A is always a whole number.

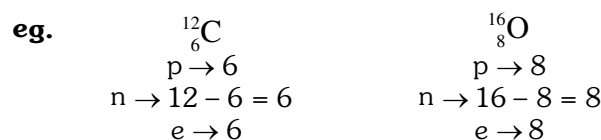
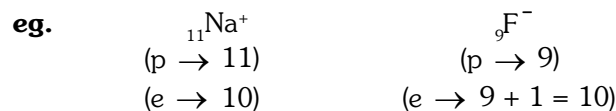


An atom of the element is represented by  ${}^A_ZX$

Where, X = Symbol of element

Z = Atomic number = no. of protons = no. of electrons (If atom is neutral)

A = Mass number = no. of neutrons + Atomic no.



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**Mass no. [A] and atomic weight** (amu= atomic mass unit)

Mass of Proton ( $m_p$ )	Mass of Neutron ( $m_n$ )	Mass of Electron ( $m_e$ )
$1.672 \times 10^{-27}$ kg	$1.675 \times 10^{-27}$ kg	$9.1 \times 10^{-31}$ kg
$1.672 \times 10^{-24}$ g	$1.675 \times 10^{-24}$ g	$9.1 \times 10^{-28}$ g
1.00727 amu	1.00866 amu	0.000549 amu

**Method for Analysis of atomic weight** →

eg.  $^{12}_6\text{C}$

$p \rightarrow 6$       Weight of proton =  $6 \times 1.00727$

$n \rightarrow 6$       Weight of neutron =  $6 \times 1.00866$

$e \rightarrow 6$        $\frac{\text{Weight of electron} = 6 \times 0.000549}{\text{Weight of } ^{12}_6\text{C atom} = 12.099 \text{ amu}}$

Mass no. of  $^{12}_6\text{C}$  atom = 12 [p and n]

**Note :** Mass no. of atom is always a whole no. but atomic weight may be in decimal.

### SOME IMPORTANT DEFINITIONS

(a) **Isotopes :** They are atoms of a given element which have the same atomic number but differ in their mass number.

eg.  $^{12}_6\text{C}$ ,  $^{13}_6\text{C}$ ,  $^{14}_6\text{C}$

$^{16}_8\text{O}$ ,  $^{17}_8\text{O}$ ,  $^{18}_8\text{O}$

$^1_1\text{H}$ ,  $^2_1\text{H}$ ,  $^3_1\text{H}$

**Explanation 1:**

$^{12}_6\text{C}$	$^{13}_6\text{C}$	$^{14}_6\text{C}$
$p \rightarrow 6$	6	6
$e \rightarrow 6$	6	6
$n \rightarrow 6$	7	8

[**Note :** Isotopes have the same number of protons but differ in the number of neutrons in the nucleus]

**Explanation 2:**

$^1_1\text{H}$	$^2_1\text{H}$	$^3_1\text{H}$ (Radioactive element)
Protium (H)	Deuterium (D)	Tritium (T)
$p \rightarrow 1$	1	1
$e \rightarrow 1$	1	1
$n \rightarrow 0$	1	2

- Neutron is not available in Protium
- No. of Nucleons = No. of Neutrons + No. of Protons  
= n + p

**Atomic Weight :** The atomic weight of an element is the average of mass of all the isotopes of that element.

- If an element have three isotopes  $y_1$ ,  $y_2$  and  $y_3$  and their isotopic weights are  $w_1$ ,  $w_2$ ,  $w_3$  and their percentage/possibility/probability/ratio of occurrence in nature are  $x_1$ ,  $x_2$ ,  $x_3$  respectively, then the average atomic weight of element is

$$\text{Average atomic weight} = \frac{w_1x_1 + w_2x_2 + w_3x_3}{x_1 + x_2 + x_3}$$

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eg.	$^{35}\text{Cl}$	$^{37}\text{Cl}$
Probability	75%	25%
ratio	3	1

$$\text{Average atomic weight} = \frac{35 \times 3 + 37 \times 1}{3 + 1} = \frac{142}{4} = 35.5$$

**(b) Isobars**  
Iso

& protons remains same.

<b>Ex.1</b>	$^3_1\text{H}$	$^3_2\text{He}$	<b>Ex.2</b>	$^{40}_{19}\text{K}$	$^{40}_{20}\text{Ca}$
	p = 1	p = 2		p = 19	p = 20
	e = 1	e = 2		e = 19	e = 20
	n = 2	n = 1		n = 21	n = 20
	p + n = 3	p + n = 3		n + p = 40	n + p = 40

**(c) Isoelectronic Species**

They are the atoms, molecules or ions which have the same number of electrons.

<b>Ex.1</b>	$\text{Cl}^-$	$\text{Ar}$
	18 e	18 e
<b>Ex.2</b>	$\text{H}_2\text{O}$	$\text{NH}_3$
	(2 + 8) = 10 e	(7 + 3) = 10 e
<b>Ex.3</b>	$\text{BF}_3$	$\text{SO}_2$
	(5 + 9 \times 3) = 32 e	(16 + 8 \times 2) = 32 e

### GOLDEN KEY POINTS

- Isotopes have same chemical property but different physical property.
- Isotopes do not have the same value of e/m.
- Isobars do not have the same chemical & physical property.
- Isobars do not have the same value of e/m

### EHpractice

**EHpractice** If the mass of neutron is doubled & mass of electron is halved then find out the new atomic mass of  $^{12}_6\text{C}$  and the percent by which it is increased.

**Solution**

**Step-1**  $^{12}_6\text{C} \rightarrow e = 6$

$$\left. \begin{array}{l} p = 6 = 6 \text{ amu} \\ n = 6 = 6 \text{ amu} \end{array} \right\} = 12 \text{ amu}$$

If the mass of neutron is doubled and mass of electron is halved then,

$$\left. \begin{array}{l} n = 12 \text{ amu} \\ p = 6 \text{ amu} \end{array} \right\} = 18 \text{ amu}$$

**Note :** mass of electron is negligible, so it is not considered in atomic mass.

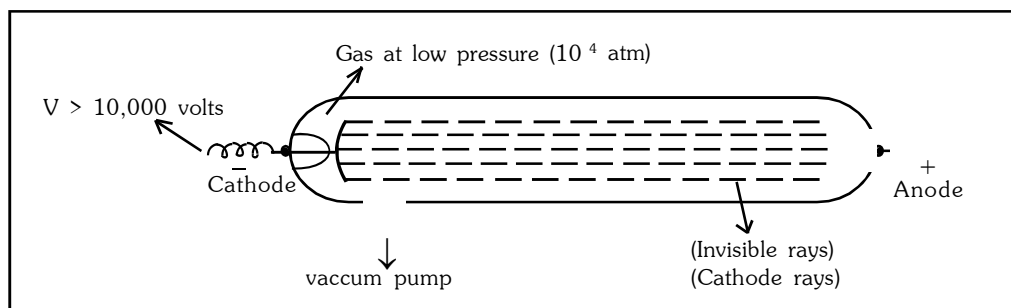
**Step-2** % Increment =  $\frac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \times 100 = \frac{18 - 12}{12} \times 100 = 50\%$



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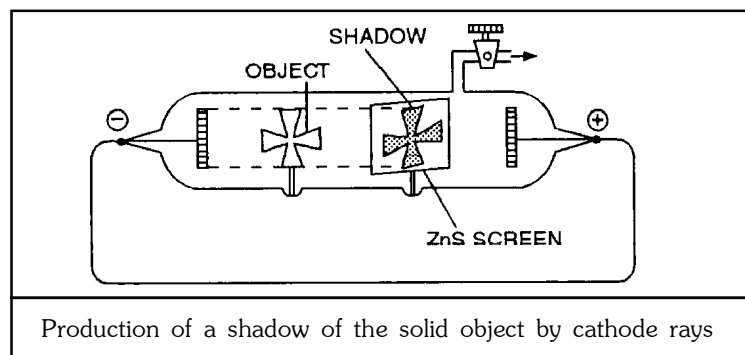
### ❑ CATHODE RAYS (Discovery of $e^-$ )



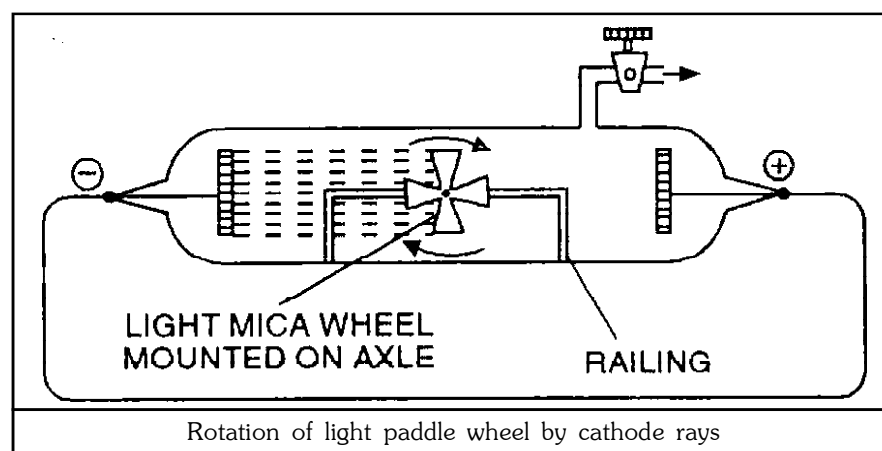
In 1859, **Julius plucker** started the study of conduction of electricity through gases at low pressure in a discharge tube. When a high voltage of the order 10, 000 volts or more was impressed across the electrodes, some sort of invisible rays moved from the -ve electrode to the +ve electrode. Since the -ve electrode is referred to as cathode, these rays were called cathode rays.

### ◆ Properties of Cathode rays

- (1) They travel in straight lines away from cathode with very high velocity ranging from  $10^7$  to  $10^9$  m/sec.
- (2) A shadow of metallic object placed in the path is cast on the wall opposite to the cathode.



- (3) They produce a **green glow** when strike the glass wall matter. Light is emitted when they strike the zinc-sulphide screen.
- (4) When a small pin wheel 10.0 is placed in their path, the blades of the wheel are set in motion. Thus the cathode rays consist of material particles which have mass and velocity.



- (5) They are deflected by the electric and magnetic fields. When the rays are passed between two electrically charged plates, these are deflected towards the positively charged plate. It shows that cathode rays carry -ve charge. These particles carrying negative charge were called **negatrons** by **Thomson**.

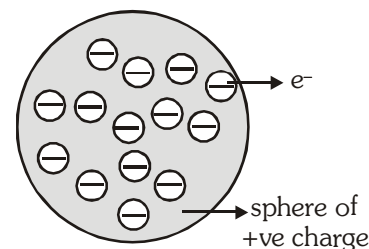
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### ATOMIC MODELS

#### Thomson's Model of Atom [1904]

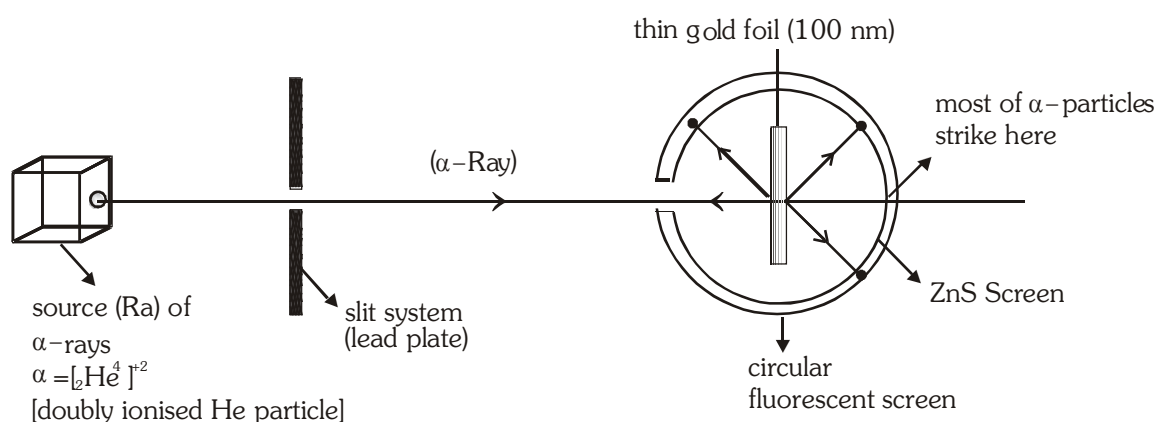
- Thomson was the first to propose a detailed model of the atom.
- Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are distributed more or less uniformly.
- This model of atom is known as "Plum-Pudding model" or "Raisin Pudding Model" or "Water Melon Model".



#### Drawbacks :

- An important drawback of this model is that the mass of the atoms is considered to be evenly spread over that atom.
- It is a static model. It does not reflect the movement of electron.
- It couldn't explain the stability of an atom.

### Rutherford's Scattering Experiment

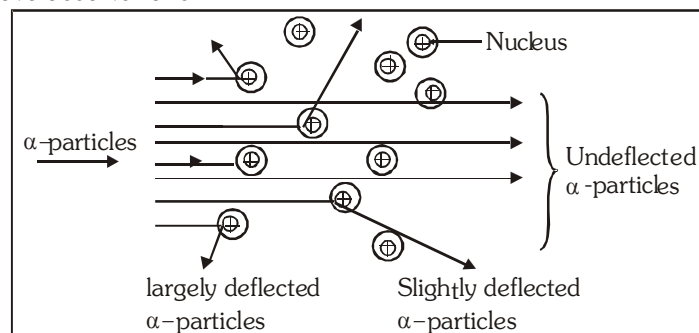


Rutherford observed that -

- Most of the  $\alpha$ -particles passed through the gold foil undeflected.
- A small fraction of the  $\alpha$ -particles were deflected by small angles.
- A very few  $\alpha$ -particles ( $\sim 1$  in 20,000) bounced back, that is, were deflected by nearly  $180^\circ$ .

Following conclusions were drawn from the above observations -

- Since most of the  $\alpha$ -particles went straight through the metal foil undeflected, it means that there must be very large empty space within the atom.
- Since few of the  $\alpha$ -particles were deflected from their original paths through moderate angles; it was concluded that whole of the +ve charge is concentrated and the space occupied by this positive charge is very small in the atom.



- When  $\alpha$ -particles come closer to this point, they suffer a force of repulsion and deviate from their paths.
  - The positively charged heavy mass which occupies only a small volume in an atom is called **nucleus**. It is supposed to be present at the centre of the atom.
- A very few of the  $\alpha$ -particles suffered strong deflections or even returned on their path indicating that the nucleus is rigid and  $\alpha$ -particles recoil due to direct collision with the heavy positively charged mass.

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### RUTHERFORD'S ATOMIC MODEL

On the basis of scattering experiments, Rutherford proposed model of the atom, which is known as nuclear atomic model. According to this model -

- An atom consists of a heavy positively charged nucleus where all the protons and neutrons are present. Protons & neutrons are collectively referred to as nucleons. Almost whole of the mass of the atom is contributed by these nucleons. The magnitude of the +ve charge on the nucleus is different for different atoms.
- The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of  $10^{-12}$  to  $10^{-13}$  cm and the atom has a diameter of the order of  $10^{-8}$  cm.

$$\frac{D_A}{D_N} = \frac{\text{Diameter of the atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5, \quad D_A = 10^5 D_N$$

Thus diameter (size) of the atom is  $10^5$  times the diameter of the nucleus.

- The radius of a nucleus is proportional to the cube root of the number of nucleons within it.

$$R \propto A^{1/3} \Rightarrow R = R_0 A^{1/3}$$

Where  $R_0 = 1.33 \times 10^{-13}$  cm (a constant) and  $A$  = mass number ( $p + n$ ) and  $R$  = radius of the nucleus.

$$R = 1.33 \times 10^{-13} \times A^{1/3} \text{ cm}$$

- There is an empty space around the nucleus called extra nuclear part. In this part electrons are present. The number of electrons in an atom is always equal to number of protons present in the nucleus. As the nuclear part of atom is responsible for the mass of the atom, the extra nuclear part is responsible for its volume.

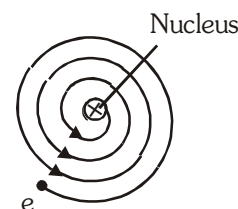
The volume of the atom is about  $10^{15}$  times the volume of the nucleus.

$$\frac{\text{Volume of the atom}}{\text{Volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = 10^{15}$$

- Electrons revolve around the nucleus in closed orbits with high speeds. The centrifugal force acting on the revolving electron is being counter balanced by the force of attraction between the electrons and the nucleus.
- This model was similar to the solar system, the nucleus representing the sun and revolving electrons as planets.

### Drawbacks of rutherford model -

- This theory could not explain the stability of atom. According to Maxwell, electron loose its energy continuously in the form of electromagnetic radiations. As a result of this, the  $e^-$  should loose energy at every turn and move closer and closer to the nucleus following a spiral path. The ultimate result will be that it will fall into the nucleus, thereby making the atom unstable.
- If the electrons loose energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies. Hence, the loss of energy by electron is not continuous in an atom.



- Each stationary orbit is associated with definite amount of energy therefore these orbits are also called as energy levels and are numbered as 1, 2, 3, 4, 5, .... or K, L, M, N, O, ..... from the nucleus outwards.

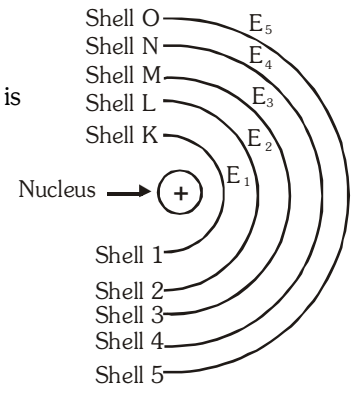
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### 6<sup>th</sup> Postulate

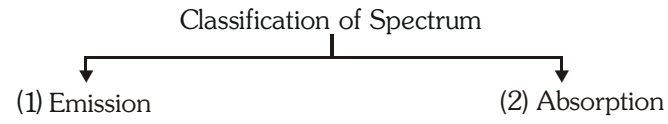
- The emission or absorption of energy in the form of photon can only occur when electron jumps from one stationary state to another & it is
 
$$\Delta E = E_{\text{higher}} - E_{\text{lower}} = E_{n_2} - E_{n_1} = \text{Energy of a quantum}$$

$$= h\nu = \text{Bohr's frequency condition}$$
- Energy is absorbed when electron jumps from inner to outer orbit and is emitted when electron moves from outer to inner orbit.
- $n_2 > n_1$  whether emission or absorption of energy will



### SPECTRUM

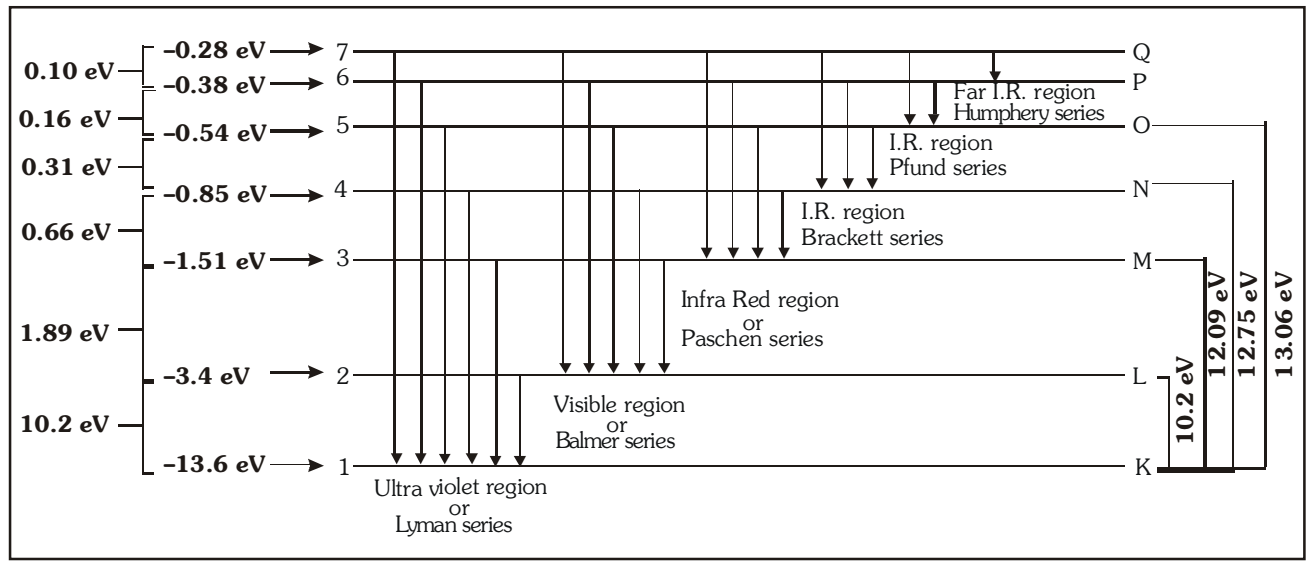
When a radiation is passed through a spectroscope (prism) for the dispersion of the radiation, the pattern (photograph) obtained on the screen (photographic plate) is called as spectrum of the given radiation



### HYDROGEN SPECTRUM

When an electric excitation is applied on hydrogen atomic gas at low pressure, a bluish light is emitted. When a ray of this light is passed through a prism, a spectrum of several isolated sharp lines is obtained. The wavelength of various lines show that spectrum lines lie in Visible, Ultraviolet and Infra red region. These lines are grouped into different series.

Series	Discovered by	regions	$n_2 \rightarrow n_1$	No. of lines
Lyman	Lyman	U.V. region	$n_2 = 2, 3, 4 \dots / n_1 = 1$	$n_2 - 1$
Balmer	Balmer	Visible region	$n_2 = 3, 4, 5 \dots / n_1 = 2$	$n_2 - 2$
Paschen	Paschen	Infra red (I.R.)	$n_2 = 4, 5, 6 \dots / n_1 = 3$	$n_2 - 3$
Brackett	Brackett	I.R. region	$n_2 = 5, 6, 7 \dots / n_1 = 4$	$n_2 - 4$
Pfund	Pfund	I.R. region	$n_2 = 6, 7, 8 \dots / n_1 = 5$	$n_2 - 5$
Humphery	Humphery	Far I.R. region	$n_2 = 7, 8, 9 \dots / n_1 = 6$	$n_2 - 6$





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### QUANTUM NUMBERS

To obtain complete information about an electron in an atom 4 identification numbers are required and these identification numbers are called as quantum numbers.

- (a) Principal quantum number (n) → Shell (Orbit)
- (b) Azimuthal quantum number (ℓ) → Sub shell
- (c) Magnetic quantum number (m) → Orbital
- (d) Spin quantum number (s) → Spin of electron

#### (a) Principal Quantum Number (n)

Given By → Bohr

- It represents the name and energy of the shell to which electron belongs and size of orbital.
- The value of n lies between 1 to ∞  
i.e n = 1,2,3,4,-----∞ corresponding name of shells are K, L, M, N, O, -----
- Greater the value of n, greater is the distance from the nucleus.

$$r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$

$$r_1 < r_2 < r_3 < r_4 < r_5 \text{ -----}$$

- Greater the value of n, greater is the energy of shell

$$E = -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom}$$

$$E_1 < E_2 < E_3 < E_4 \text{ -----}$$

- Velocity of electron  $v = 2.18 \times 10^6 \frac{Z}{n} \text{ m/s}$   
 $v_1 > v_2 > v_3 \text{ .....}$

- The angular momentum of a revolving electron is  $mvr = \frac{nh}{2\pi}$

Where n = Principal quantum number.

- The number of electrons in a particular shell is equal to  $2n^2$

#### (b) Azimuthal quantum number / Angular quantum number / Secondary quantum number / Subsidiary quantum number (ℓ)

Given by – Sommerfeld

- It represents the name of the subshell, shape of orbital and orbital angular momentum
- Possible values of 'ℓ' are :-

$$\text{i.e } \ell = 0, 1, 2 \text{ ----- } (n-1)$$

$$\ell = 0 \text{ (s Subshell)}$$

$$\ell = 1 \text{ (p Subshell)}$$

$$\ell = 2 \text{ (d Subshell)}$$

$$\ell = 3 \text{ (f Subshell)}$$

- Value of ℓ lies between 0 to (n – 1) in a particular n<sup>th</sup> shell :-

**Ex.** If n = 1 then ℓ = 0 ⇒ 1s i.e. in n = 1 shell, only one subshell 's' is present.

If n = 2 then ℓ = 0, 1 ⇒ 2s, 2p i.e. in n = 2 shell, two subshell 's' & 'p' are present.

If n = 3 then ℓ = 0, 1, 2 ⇒ 3s, 3p, 3d i.e. in n = 3 shell, three subshell 's', 'p' & 'd' are present.

If n = 4 then ℓ = 0, 1, 2, 3 ⇒ 4s, 4p, 4d, 4f i.e. in n = 4 shell, four subshell 's', 'p', 'd' & 'f' are present.

- If the value of n is same then the order of energy of the various subshell will be  
 $s < p < d < f$  [valid only for multi-electron species]

$$\text{Ex. } 4s < 4p < 4d < 4f, \quad 3s < 3p < 3d, \quad 2s < 2p$$

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- If Value of  $\ell$  is same but value of  $n$  is different then the order of energy will be.  
**Ex.**  $1s < 2s < 3s < 4s < 5s < 6s$   
 $3d < 4d < 5d < 6d$   
 $4p < 5p < 6p$
- The orbital angular momentum =  $\sqrt{\ell(\ell+1)} \frac{h}{2\pi}$  or  $\sqrt{\ell(\ell+1)} \hbar$   $\left\{ \because \hbar = \frac{h}{2\pi} \right\}$  {  $\hbar$  is called as 'hash' }  
 Orbital angular momentum : For s subshell = 0  
 For p subshell =  $\sqrt{2} \frac{h}{2\pi}$  or  $\sqrt{2} \hbar$
- The number of electrons in a particular subshell is equal to  $2(2\ell+1)$   
 for s subshell number of electrons = 2 e  
 for p subshell number of electrons = 6 e  
 for d subshell number of electrons = 10 e  
 for f subshell number of electrons = 14 e
- Shape of the orbital :
 

s	→	spherical
p	→	dumb bell shape
d	→	double dumb bell shape
f	→	complex shape

### (c) Magnetic Quantum Number /Orientation Quantum Number (m) :

Given by linde

- It represents the orientation of electron cloud (orbital)
- Under the influence of magnetic field each subshell is further subdivided into orbitals ( The electron cloud is known as orbital)  
 Magnetic quantum number describe these different distributions of electron cloud.
- Value of  $m$  = all integral value from  $-\ell$  to  $+\ell$  including zero.  
 i.e. Value of  $m = -\ell$  to  $+\ell$

**Orbital :** 3D space around the nucleus where the probability of finding electrons is maximum is called an orbital. An orbital can be represented by 3 set of quantum numbers

$$= \Psi_{n,\ell,m}$$

Ex. 1 :  $2p_x$ ;  $n=2, \ell=1, m=-1$  or  $m=+1$

Ex. 2 :  $3d_z$ ;  $n=3, \ell=2, m=0$

Ex. 3 :  $\Psi_{(3,2,0)}$ ;  $n=3, \ell=2, m=0$ ;  $3d_{z^2}$

### (d) Spin Quantum number (s) :

Given by **Goudsmit** and **Uhlenbeck**

- It represents the direction of electron spin around its own axis
- For clockwise spin/spin up( $\uparrow$ ) electron  $\rightarrow \pm \frac{1}{2}$
- For anti-clockwise spin/spin down( $\downarrow$ ) electron  $\rightarrow \mp \frac{1}{2}$

Spin angular momentum of an electron =  $\sqrt{s(s+1)} \cdot \frac{h}{2\pi}$  or  $\sqrt{s(s+1)} \hbar$

- Each orbital can accomodate 2 electrons with opposite spin or spin paired.

Correct  $\uparrow\downarrow$  Spin paired e

Wrong  $\uparrow\uparrow$  Spin parallel e

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### EHpractice

- EHpractice** Calculate the value of  $n$ ,  $\ell$  and  $m$  for  $7p_y$  orbital ?
- Solution**  $n = 7, \ell = 1, m = +1 \text{ or } -1$
- EHpractice** Calculate the value of  $n$ ,  $\ell$  and  $m$  for  $3s$  orbital ?
- Solution**  $n = 3, \ell = 0, m = 0$
- EHpractice** Calculate the value of  $n$ ,  $\ell$  and  $m$  for  $5d_{z^2}$  orbital ?
- Solution**  $n = 5, \ell = 2, m = 0$
- EHpractice** Which of the following set of quantum numbers is not possible ?
- (a)  $n = 2, \ell = 0, m = -1, s = -\frac{1}{2}$
- (b)  $n = 3, \ell = 2, m = 0, s = \pm\frac{1}{2}$
- (c)  $n = 2, \ell = 3, m = -2, s = \pm\frac{1}{2}$
- Solution** (a) not possible (b) possible (c) not possible

### WAVE MECHANICAL MODEL OF AN ATOM

This model consists of following

- (A) de-Broglie concept (Dual nature of Matter)
- (B) Heisenberg's Uncertainty principle.

#### (A) THE DUAL NATURE OF MATTER (THE WAVE NATURE OF ELECTRON)

In 1924, a French physicist, **Louis de-Broglie** suggested that if the nature of light is both that of a particle and of a wave, then this dual behavior should be true also for the matter.

- (1) The wave nature of light rays and X-rays is proved on the basis of their interference and diffraction and many facts related to radiations can only be explained when the beam of light rays is regarded as composed of energy corpuscles or photons whose velocity is  $3 \times 10^{10} \text{ cm/s}$ .
- (2) According to de-Broglie, the wavelength  $\lambda$  of an electron is inversely proportional to its momentum  $p$ .

$$\lambda \propto \frac{1}{p} \quad \text{or} \quad \lambda = \frac{h}{p} \quad (\text{Here } h = \text{Planck's constant, } p = \text{momentum of electron})$$

$$\therefore \text{Momentum } (p) = \text{Mass } (m) \times \text{Velocity } (v) \quad \therefore \lambda = \frac{h}{mv}$$

- (3) The above relation can be proved as follows by using Einstein's equation, Planck's quantum theory and wave theory of light.

Einstein's equation,  $E = mc^2$  where  $E$  is energy,  $m$  is mass of a body and  $c$  is its velocity.

$$\therefore E = hv = h \times \frac{c}{\lambda} \quad (\text{According to Planck's quantum theory}) \quad \dots(i)$$

$$\text{and } c = v\lambda \quad (\text{According to wave theory of light}) \quad \therefore v = \frac{c}{\lambda}$$

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But according to Einstein's equation  $E = mc^2$  ... (ii)

$$\text{From equation (i) \& (ii) : } mc^2 = h \times \frac{c}{\lambda} \text{ or } mc = \frac{h}{\lambda} \text{ or } p = \frac{h}{\lambda} \text{ or } \boxed{\lambda = \frac{h}{p}}$$

- (4) It is clear from the above equation that the value of  $\lambda$  decreases on increasing either  $m$  or  $v$  or both. The wavelength of many fast-moving objects like an aeroplane or a cricket ball, is very low because of their high mass.

### Bohr's theory and de-broglie concept :

- (1) According to de-Broglie, the nature of an electron moving around the nucleus is like a wave that flows in circular orbits around the nucleus.
- (2) If an electron is regarded as a wave, the quantum condition as given by Bohr in his theory is readily fulfilled.
- (3) If the radius of a circular orbit is  $r$ , then its circumference will be  $2\pi r$ .
- (4) We know that according to Bohr theory,  $mvr = \frac{nh}{2\pi}$

$$\text{or } 2\pi r = \frac{nh}{mv} \quad (\because mv = p \text{ momentum})$$

$$\text{or } 2\pi r = \frac{nh}{p} \quad \left( \because \frac{h}{p} = \lambda \text{ de-Broglie equation} \right)$$

$$\therefore 2\pi r = n\lambda \text{ (where } n = \text{total number of waves } 1, 2, 3, 4, 5, \dots, \infty \text{ and } \lambda = \text{Wavelength)}$$

$$(5) \quad \therefore 2\pi r = \frac{nh}{mv} \text{ or } mvr = \frac{nh}{2\pi} \quad \therefore mvr = \text{Angular momentum}$$

Thus  $mvr = \text{Angular momentum}$ , which is a integral multiple of  $\frac{h}{2\pi}$ .

- (6) It is clear from the above description that according to de-Broglie there is similarity between wave theory and Bohr theory.

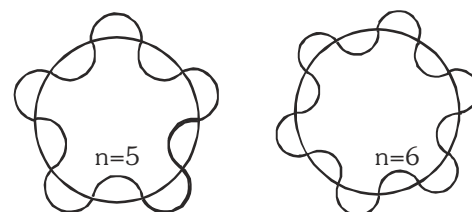


figure : Similarity between de-Broglie waves and Bohr's orbit

### (B) HEISENBERG UNCERTAINTY PRINCIPLE

Bohr's theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de-Broglie, it is not possible to ascertain simultaneously the exact position and velocity of the electron more precisely at a given instant since the wave extends throughout a region of space.

In 1927, Werner Heisenberg presented a principle known as Heisenberg uncertainty principle which states that : "It is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron."

The uncertainty in measurement of position,  $(\Delta x)$ , and the uncertainty in momentum  $(\Delta p)$  are related by Heisenberg's relationship as

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$$F \times \Delta t \times \Delta x \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta E \times \Delta t \geq \frac{h}{4\pi}$$

where  $h$  is Planck's constant.

- (i) When  $\Delta x = 0$ ,  $\Delta v = \infty$
- (ii) When  $\Delta v = 0$ ,  $\Delta x = \infty$  So, if the position is known quite accurately, i.e.,  $\Delta x$  is very small,  $\Delta v$  becomes large and vice-versa.

### EHpractice

**EHpractice** The mass of a particle is 1 mg and its velocity is  $4.5 \times 10^5$  cm per second. What should be the wavelength of this particle if  $h = 6.652 \times 10^{-27}$  erg second.

(1)  $1.4722 \times 10^{-24}$  cm (2)  $1.4722 \times 10^{-29}$  cm (3)  $1.4722 \times 10^{-32}$  cm (4)  $1.4722 \times 10^{-34}$  cm

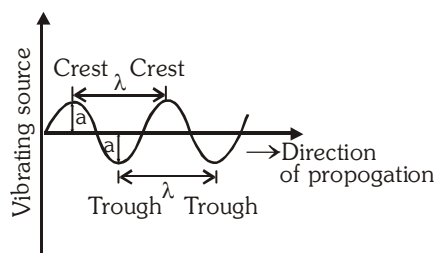
**Solution** Given that  $m = 1 \text{ mg} = 1 \times 10^{-3} \text{ g}$ ,  $v = 4.5 \times 10^5 \text{ cm s}^{-1}$ ,  $h = 6.652 \times 10^{-27} \text{ erg s}$ .

$$\therefore \lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-27} \text{ erg s}}{1 \times 10^{-3} \text{ g} \times 4.5 \times 10^5 \text{ cm s}^{-1}} = 1.4722 \times 10^{-29} \text{ cm}$$

### ELECTROMAGNETIC WAVES (EM WAVES) OR RADIANT ENERGY

According to this theory, the energy is transmitted from one body to another in the form of waves and these waves travel in the space with the same speed as light ( $3 \times 10^8$  m/s). These waves are known as Electro magnetic waves or radiant energy. **Ex** : Radio waves, micro waves, Infra red rays, visible rays, ultraviolet rays, X-rays, gamma rays.

- The radiant energy do not need any medium for propagation.
- The radiant energy have electric and magnetic fields and travel at right angle to these fields.
- The upper most point of the wave is called crest and the lower most point is called trough.



Some of the terms employed in dealing with the waves are described below.

- (1) **Wavelength ( $\lambda$ ) (Lambda)** : It is defined as the distance between two nearest crest or trough. It is measured in terms of Å (Angstrom), pm (picometre), nm (nanometer), cm (centimetre), m (metre)  
 $1 \text{ Å} = 10^{-10} \text{ m}$ ,  $1 \text{ pm} = 10^{-12} \text{ m}$ ,  $1 \text{ nm} = 10^{-9} \text{ m}$ ,  $1 \text{ cm} = 10^{-2} \text{ m}$
- (2) **Wave number ( $\bar{\nu}$ ) (nu bar)** : It is the reciprocal of the wavelength, that is number of waves present in unit length  

$$\bar{\nu} = \frac{1}{\lambda}$$
It is measured in terms of  $\text{cm}^{-1}$ ,  $\text{m}^{-1}$  etc.
- (3) **Frequency ( $\nu$ ) (nu)** : Frequency of a wave is defined as the number of waves which pass through a point in 1 s. It is measured in terms of Hertz (Hz),  $\text{s}^{-1}$  or cycle/s(cps) ( $1 \text{ Hertz} = 1 \text{ s}^{-1}$ )
- (4) **Time period (T)** : Time taken by a wave to pass through one point. 
$$T = \frac{1}{\nu} \text{ second}$$



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- (5) **Velocity (c)** : Velocity of a wave is defined as distance covered by a wave in 1 second

$$c = \lambda / T = \lambda \nu \text{ or } \nu = c / \lambda \text{ or } c = \nu (\text{s}^{-1}) \times \lambda (\text{m}) \text{ or } c = \nu \lambda (\text{m s}^{-1})$$

Since c is constants i.e. frequency is inversely proportional to  $\lambda$

- (6) **Amplitude (a)** : The amplitude of a wave is defined as the height of crest or depth of trough.

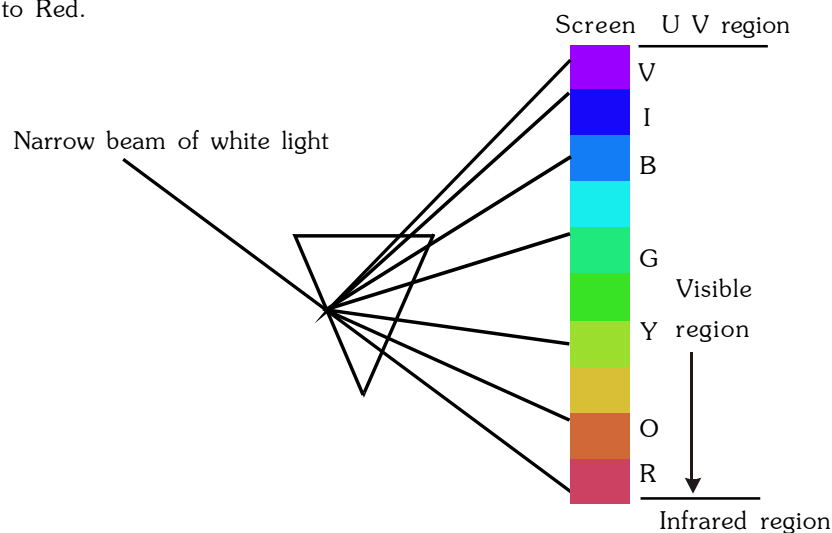
**Important note :**  $\nu = \frac{c}{\lambda} = c\bar{\nu} \quad \left( \bar{\nu} = \frac{1}{\lambda} \right)$

### Electromagnetic spectrum or EM spectrum :

The arrangement obtained by arranging various types of EM waves in order of their increasing frequency or decreasing wave length is called as EM SPECTRUM

	( )							
low( $\nu$ )	RW	MW	IR	Visible Rays	U.V	X-rays	$\gamma$ -rays	high( $\nu$ )
low(E)								high(E)
longer( $\lambda$ )								shorter( $\lambda$ )
	$3 \times 10^9 \text{\AA}$		$7600 \text{\AA}$		$150 \text{\AA}$			
	$3 \times 10^{14} \text{\AA}$	$6 \times 10^6 \text{\AA}$		$3800 \text{\AA}$	$0.1 \text{\AA}$	$0.01 \text{\AA}$		

When a narrow beam of white light is passed through a prism, it is dispersed into 7 colours from violet to Red.



### EHpractice

ETHIO BISRAAT of All ETHIOPIA Radio broadcasts on a frequency of 1368 kilo hertz. Calculate the wavelength of the electromagnetic waves emitted by the transmitter.

### Solution

As we know velocity of light ( $c$ ) =  $3 \times 10^8 \text{ m/s}$

Given  $\nu$  (frequency) = 1368 kHz =  $1368 \times 10^3 \text{ Hz} = 1368 \times 10^3 \text{ s}^{-1}$

$$\therefore \lambda = \frac{c}{\nu} \quad \therefore \lambda = \frac{3 \times 10^8 \text{ ms}^{-1}}{1368 \times 10^3 \text{ s}^{-1}} = 219.3 \text{ m}$$

### EHpractice

Calculate  $\bar{\nu}$  in  $\text{cm}^{-1}$  and  $\nu$  of yellow radiation having a wavelength of  $5800 \text{ \AA}$

### Solution

$$\text{As we known } \bar{\nu} = \frac{1}{\lambda} = \frac{1}{5800 \text{ \AA}} = \frac{1}{5800 \times 10^{-8} \text{ cm}} = \frac{10^8}{5800} \text{ cm}^{-1} = 17241.37 \text{ cm}^{-1}$$

$$\nu = c\bar{\nu} = 3 \times 10^{10} \text{ cm s}^{-1} \times 1.7 \times 10^4 \text{ cm}^{-1} = 3 \times 1.7 \times 10^{14} = 5.1 \times 10^{14} \text{ s}^{-1}$$

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**EHpractice** A particular radiostation broadcast at a frequency of 1120 kilo hertz. Another radio station broadcast at a frequency of 98.7 mega hertz. What are the wavelength of radiations from each station.

**Solution** Station 1<sup>st</sup>  $\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ ms}^{-1}}{1120 \times 10^3 \text{ s}^{-1}} = 267.86 \text{ m}$

Station 2<sup>nd</sup>  $\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ ms}^{-1}}{98.7 \times 10^6 \text{ s}^{-1}} = 3.0395 \text{ m}$

**EHpractice** . How long would it take a radio wave of frequency  $6 \times 10^3 \text{ s}^{-1}$  to travel from mars to earth, that is a distance of  $8 \times 10^7 \text{ km}$  ?

**Solution** Distance to be travelled from mars to earth =  $8 \times 10^7 \text{ km} = 8 \times 10^{10} \text{ m}$

$\therefore$  Velocity of EM waves =  $3 \times 10^8 \text{ m/s}$

$\therefore$  Time =  $\frac{\text{Distance}}{\text{Velocity}} = \frac{8 \times 10^{10} \text{ m}}{3 \times 10^8 \text{ m/s}} = 2.66 \times 10^2 \text{ s} = 4 \text{ min } 26 \text{ s}$

### PLANCK'S QUANTUM THEORY

According to planck's quantum theory :

- (1) The radiant energy emitted or absorbed by a body not continuously but discontinuously in the form of small discrete packets of energy and these packets are called quantum.
- (2) In case of light, the smallest packet of energy is called as 'photon' but in general case the smallest packet of energy is called as quantum.
- (3) The energy of each quantum is directly proportional to frequency of the radiation i.e.

$$E \propto \nu \quad \Rightarrow \quad E = h\nu \quad \text{or} \quad E = \frac{hc}{\lambda} \left\{ \because \nu = \frac{c}{\lambda} \right\}$$

$h$  is proportionality constant or Planck's constant

$$h = 6.626 \times 10^{-37} \text{ kJ s} \quad \text{or} \quad 6.626 \times 10^{-34} \text{ J s} \quad \text{or} \quad 6.626 \times 10^{-27} \text{ erg s}$$

- (4) Total amount of energy transmitted from one body to another will be some integral multiple of energy of

a quantum.  $E = nh\nu = \frac{nhc}{\lambda} = nhc\bar{\nu}$

where  $n$  = Positive integer

= Number of quanta

### EHpractice

**EHpractice** Calculate the energy of a photon of sodium light of wave length  $5.862 \times 10^{-16} \text{ m}$  in joule.

**Solution**  $\lambda = 5.886 \times 10^{-16} \text{ m}, \quad c = 3 \times 10^8 \text{ m s}^{-1}$

$$E = nh\nu \quad \text{or} \quad \frac{nhc}{\lambda} \quad \{ \because n = 1 \}$$

$$\therefore E = \frac{hc}{\lambda} = \frac{1 \times 6.6 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ ms}^{-1}}{5.862 \times 10^{-16} \text{ m}} = \frac{6.6 \times 3}{5.862} \times 10^{-10} \text{ J} = 3.38 \times 10^{-10} \text{ J}$$

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EHpractice

Calculate the frequency & energy of a photon of wave length 4000 Å.

Soluiton

(a) Calculation of frequency :  $\lambda = 4000 \text{ Å} = 4000 \times 10^{-10} \text{ m}$

$$\therefore \nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m/s}}{4 \times 10^{-7} \text{ m}} = 0.75 \times 10^{15} \text{ s}^{-1} = 7.5 \times 10^{14} \text{ s}^{-1}$$

(b) Calculation of energy :

$$E = h\nu = 6.626 \times 10^{-34} \text{ joule second} \times 7.5 \times 10^{14} \text{ s}^{-1} = 4.96 \times 10^{-19} \text{ joule}$$

EHpractice

Calculate the  $\lambda$  and frequency of a photon having an energy of 2 electron volt

Soluiton

$\therefore 1\text{eV} = 1.602 \times 10^{-19} \text{ J} \therefore 2\text{eV} = 3.204 \times 10^{-19} \text{ J} = E$

(a) Calculation of wavelength ( $\lambda$ ) :  $E = \frac{hc}{\lambda}$  or  $\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{3.204 \times 10^{-19} \text{ J}}$

$$= 6.204 \times 10^{-7} \text{ m}$$

(b) Calculation of frequency ( $\nu$ ) :  $\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{6.204 \times 10^{-7} \text{ m}} = 0.49 \times 10^{15} \text{ s}^{-1} = 4.9 \times 10^{14} \text{ s}^{-1}$

EHpractice

Which has a higher energy ?

(a) A photon of violet light with wave length 4000 Å

(b) A photon of red light with wave length 7000 Å

Soluiton

(a) Violet light :  $E_{\text{violet}} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{4000 \times 10^{-10} \text{ m}} = 4.97 \times 10^{-19} \text{ joule}$

(b) Red light :  $E_{\text{red}} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{7000 \times 10^{-10} \text{ m}} = 2.8 \times 10^{-19} \text{ joule}$

$$\text{So, } E_{\text{violet}} > E_{\text{red}}$$

### RULES FOR FILLING OF ELECTRONS

(a) Aufbau Principle

(b) (n + l) rule

(c) Hund's maximum multiplicity principle

(d) Pauli's exclusion principle

#### (a) Aufbau Principle

Aufbau is a German word and its meaning is 'Building up'

- Aufbau principle gives a sequence in which various subshell are filled up depending on the relative order of the energies of various subshell.
- Principle : The subshell with minimum energy is filled up first when this subshell obtained maximum quota of electrons then the next subshell of higher energy starts filling.
- The sequence in which various subshell are filled are as follows.

1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>6</sup>, 4s<sup>2</sup>, 3d<sup>10</sup>, 4p<sup>6</sup>, 5s<sup>2</sup>, 4d<sup>10</sup>, 5p<sup>6</sup>, 6s<sup>2</sup>, 4f<sup>14</sup>, 5d<sup>10</sup>, 6p<sup>6</sup>, 7s<sup>2</sup>, 5f<sup>14</sup>, 6d<sup>10</sup>, ....

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### For Example

${}^1\text{H}$	$\rightarrow$	$1s^1$
${}^2\text{He}$	$\rightarrow$	$1s^2$
${}^3\text{Li}$	$\rightarrow$	$1s^2, 2s^1$
${}^4\text{Be}$	$\rightarrow$	$1s^2, 2s^2$
${}^5\text{B}$	$\rightarrow$	$1s^2, 2s^2, 2p^1$
${}^6\text{C}$	$\rightarrow$	$1s^2, 2s^2, 2p^2$
${}^7\text{N}$	$\rightarrow$	$1s^2, 2s^2, 2p^3$
${}^8\text{O}$	$\rightarrow$	$1s^2, 2s^2, 2p^4$
${}^9\text{F}$	$\rightarrow$	$1s^2, 2s^2, 2p^5$
${}^{10}\text{Ne}$	$\rightarrow$	$1s^2, 2s^2, 2p^6$
${}^{11}\text{Na}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^1$
${}^{12}\text{Mg}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2$
${}^{13}\text{Al}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
${}^{14}\text{Si}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
${}^{15}\text{P}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^3$
${}^{16}\text{S}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$
${}^{17}\text{Cl}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
${}^{18}\text{Ar}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
${}^{19}\text{K}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
${}^{20}\text{Ca}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
${}^{21}\text{Sc}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
${}^{22}\text{Ti}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$
${}^{23}\text{V}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
${}^{24}\text{Cr}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$ [Exception]
${}^{25}\text{Mn}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$
${}^{26}\text{Fe}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
${}^{27}\text{Co}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$
${}^{28}\text{Ni}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$
${}^{29}\text{Cu}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$ [Exception]
${}^{30}\text{Zn}$	$\rightarrow$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

### Electronic configuration can be written by following different methods :

- ${}^{26}\text{Fe} \rightarrow$ 
  - $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
  - $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$
  - $1s^2, 2s^2p^6, 3s^2p^6d^6, 4s^2$   
 $\quad\quad\quad 2\quad\quad 8\quad\quad 14\quad\quad 2$
  - $[\text{Ar}] 4s^2 3d^6$

- ${}^{26}\text{Fe} \rightarrow$ 

$$1s^2 \quad \underbrace{2s^2 2p^6}_{(n-2)} \quad \underbrace{3s^2 3p^6 3d^6}_{(n-1)} \quad \underbrace{4s^2}_n$$

$n \rightarrow$  Outer most Shell or Ultimate Shell or Valence Shell

In this Shell electrons are called as Valence electrons or this is called core charge

$(n-1) \rightarrow$  Penultimate Shell or core or pre valence Shell

$(n-2) \rightarrow$  Pre Penultimate Shell

- If we remove the last 'n' Shell (ultimate Shell) then the remaining shells are collectively called as Kernel.

Ex.  ${}^{26}\text{Fe} \rightarrow \underbrace{1s^2 2s^2 2p^6 3s^2 3d^6 3p^6}_{\text{Kernel}} 4s^2$

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### (b) (n + ℓ) Rule (For multi electron species)

According to it the sequence in which various subshell are filled up can also be determined with the help of (n + ℓ) value for a given subshell.

#### Principle of (n+ℓ) rule :

The subshell with lowest (n+ℓ) value is filled up first. When two or more subshell have same (n+ℓ) value then the subshell with lowest value of n is filled up first.

#### In case of H-atom :

Energy only depends on principal quantum number

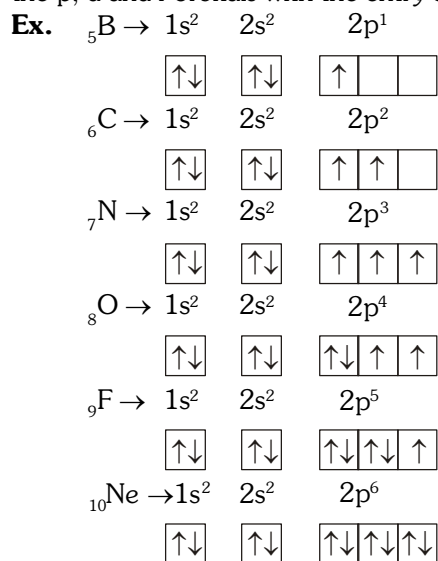
$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots\dots\dots$$

Sub Shell	n	ℓ	n + ℓ
1s	1	0	1
2s	2	0	2
2p	2	1	3
3s	3	0	3
3p	3	1	4
4s	4	0	4
3d	3	2	5
4p	4	1	5
5s	5	0	5
4d	4	2	6
5p	5	1	6
6s	6	0	6

**Order :** 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>6</sup>, 4s<sup>2</sup>, 3d<sup>10</sup>, 4p<sup>6</sup>, 5s<sup>2</sup>, 4d<sup>10</sup>, 5p<sup>6</sup>, 6s<sup>2</sup>, 4f<sup>14</sup>, 5d<sup>10</sup>, 6p<sup>6</sup>, 7s<sup>2</sup>, 5f<sup>14</sup>, 6d<sup>10</sup>, ....

### (c) Hund's Maximum Multiplicity Rule (Multiplicity : Many of the same kind)

- This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called degenerate orbitals).
- It states : pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.
- Since there are three p, five d and seven f orbitals, therefore, the pairing of electrons will start in the p, d and f orbitals with the entry of 4th, 6th and 8th electron, respectively.



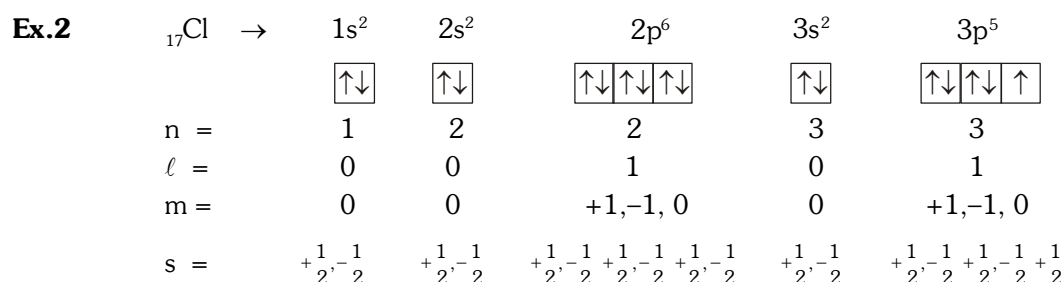
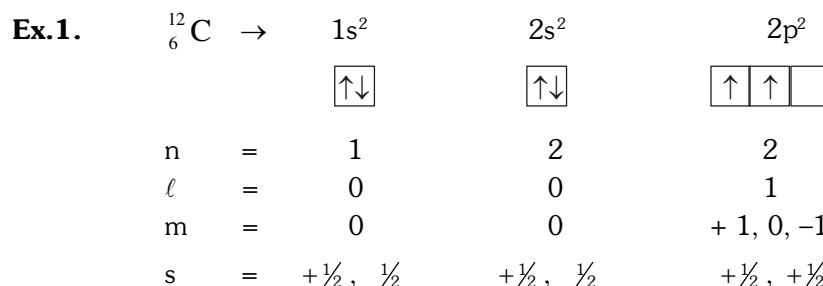


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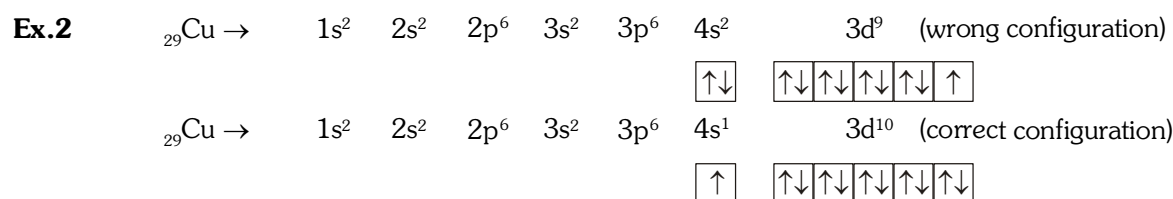
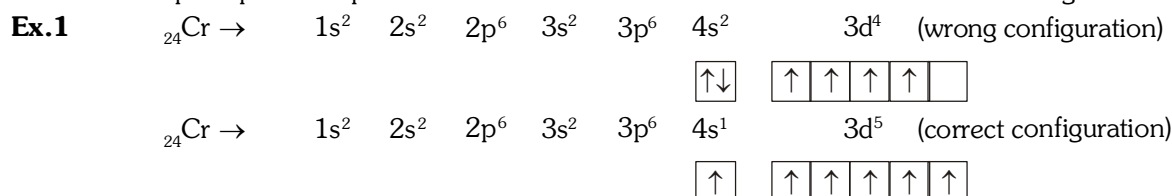
### (d) Pauli's Exclusion Principle

In 1925 Pauli stated that no two electron in an atom can have same values of all four quantum numbers i.e., an orbital can accommodate maximum 2 electrons with opposite spin.



### Exception of Aufbau principle :

In some cases it is seen that the electronic configuration is slightly different from the arrangement given by Aufbau principle. A simple reason behind this is that half filled & full filled subshell have got extra stability.



### EHpractice

- EHpractice Solution** Calculate the number of unpaired electrons in Cr
- ${}^{24}_{24}\text{Cr} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$   
in  ${}^{24}_{24}\text{Cr}$ , 6 electrons are unpaired.
- EHpractice Solution** The number of unpaired electrons in  $\text{Cr}^{+3}$
- $\text{Cr}^{+3} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^3$   
in  $\text{Cr}^{+3}$ , 3 electrons are unpaired.
- EHpractice Solution** The number of unpaired electrons in 3d subshell of  $\text{Cr}^{+3}$
- 3
- EHpractice Solution** The number of unpaired electrons in  $\text{Fe}^{+2}$  &  $\text{Fe}^{+3}$
- $\text{Fe}^{+2} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^6 = 4$  unpaired electrons  
 $\text{Fe}^{+3} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5 = 5$  unpaired electrons

## Extended or Long Form of the Periodic Table

[illegible]

IUPAC designations of groups of elements are given in brackets



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### PERIODICITY

(A) In a period, the ultimate orbit remain same, but the number of  $e^-$  gradually increases.

In a group, the number of  $e^-$  in the ultimate orbit remains same, but the values of  $n$  increases.

(B) **Causes of periodicity :**

- The cause of periodicity in properties is due to the same outermost shell electronic configuration coming at regular intervals.
- In the periodic table, elements with similar properties occur at intervals of 2, 8, 8, 18, 18 and 32. These numbers are called as magic numbers.

### ATOMIC RADIUS

The average distance of valence shell  $e^-$  from nucleus is called atomic radius. It is very difficult to measure the atomic radius because –

- The isolation of single atom is very difficult.
- There is no well defined boundary for the atom. (The probability of finding the  $e^-$  is 0 only at infinity).

So, the more accurate definition of atomic radius is –

- Half the inter-nuclear distance( $d$ ) between two atoms in a homoatomic molecule is known as atomic radius.
- This inter-nuclear distance is also known as bond length. Inter-nuclear distance depends upon the type of bond by which two atoms combine.

### Ionic Radius

(i) **Cationic Radius**

- When an neutral atom loses  $e^-$  it converts into cation (+ve charged ion)
- Cationic radius is always smaller than atomic radius **because** after losing  $e^-$  number of  $e^-$  reduces, but number of protons remains same, due to this  $Z_{eff}$  increases, hence electrons are pulled towards nucleus and atomic radius decreases, moreover after losing all the electrons from the outer most shell, penultimate shell becomes ultimate shell which is nearer to nucleus so size decreases.

$$(c) \text{ Size of cation } \propto \frac{1}{\text{Magnitude of the charge or } Z_{eff}}$$

**Ex.** (i)  $Fe > Fe^{+2} > Fe^{+3}$

(ii)  $Pb^{+2} > Pb^{+4}$

(iii)  $Mn > Mn^{+2} > Mn^{+3} > Mn^{+4} > Mn^{+5} > Mn^{+6} > Mn^{+7}$

### Metallic/Crystal Radius

- Half of the inter nuclear distance between two adjacent metallic atoms in crystalline lattice structure.
- there is no overlapping of atomic orbitals, So **Metallic radius > Covalent radius**

$$(c) \text{ Metallic radius } \propto \frac{1}{\text{Metallic bond strength}}$$

### Vander Waal's Radius

- Those atoms (like noble gases) which are not bonded with each other, experiences a weak attractive force to come nearer.
- Half of the distance between the nuclei of adjacently placed atoms in solid state of a noble gas is Vander Waal's radius.
- Inert gas have only Vander Waal radius.
- In molecules of nonmetals solid both covalent and van der Waal's radius exists.

$$\text{Vander Waal's radius} \cong 2 \times \text{covalent radius}$$

$$\text{Vander Waal's radius} > \text{Metallic radius} > \text{Covalent radius}$$

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### ● Factors affecting atomic size are :

#### (a) In a period

$$\text{Atomic radius} \propto \frac{1}{Z_{\text{eff}}} \propto \frac{\text{negative charge}}{\text{positive charge}}$$

$$\text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$$

#### (b) In a group

$$\text{Atomic radius} \propto \text{number of shells}$$

$$\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$$

### ● Periodic variation of atomic size :

(i) **Across a period** : It decreases from left to right in a period as effective nuclear charge ( $Z_{\text{eff}}$ ) increases

$$\text{Ex. } \text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$$

(ii) **In a group** : It increases from top to bottom in a group as number of shell increases

$$\text{Ex. } \text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$$

**Exceptions** : Transition elements

$$\begin{array}{c} \text{Sc} \quad \text{Ti} \quad \text{V} \quad \text{Cr} \quad \text{Mn} \\ \hline Z_{\text{eff}} > \text{Screening effect} \end{array}$$

$$\begin{array}{c} \text{Fe} \quad \text{Co} \quad \text{Ni} \\ \hline Z_{\text{eff}} \approx \text{Screening effect} \end{array}$$

$$\begin{array}{c} \text{Cu} \quad \text{Zn} \\ \hline Z_{\text{eff}} < \text{Screening effect} \end{array}$$

$$\text{Order of covalent radius : Sc} > \text{Ti} > \text{V} > \text{Cr} > \text{Mn} > \text{Fe} \approx \text{Co} \approx \text{Ni} < \text{Cu} < \text{Zn}$$

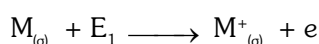
### IONISATION POTENTIAL OR IONISATION ENERGY OR IONISATION ENTHALPY (IP / IE)

(i) Minimum energy required to remove most loosely bonded outer most shell e in ground state from an isolated gaseous atom is known as ionization energy.

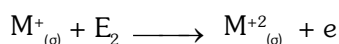
(Isolated → Without any bonding with other atom)

#### (ii) Successive Ionization Energy

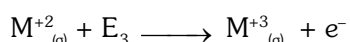
(a) For an atom  $M_{(g)}$  successive ionization energies are as follows -



$$E_1 = \text{I}^{\text{st}} \text{ Ionization energy}$$



$$E_2 = \text{II}^{\text{nd}} \text{ Ionization energy}$$



$$E_3 = \text{III}^{\text{rd}} \text{ ionization energy}$$

$$\boxed{E_1 < E_2 < E_3 \dots \dots \dots} \text{ (Always for an element)}$$

(b) Electron can not be removed from solid state of an atom, it has to be convert into gaseous form, Energy required for conversion from solid state to gaseous state is called Sublimation energy.

(c) For any neutral atom ionization energy is always an endothermic process ( $\Delta H = +ve$ )

(d) It is measured in eV/atom (electron volt/atom) or Kcal/mole or KJ/mole

### FACTORS AFFECTING IONISATION ENERGY

#### In a period

##### (i) Effective nuclear charge ( $Z_{\text{eff}}$ )

$$\text{Ionisation Energy} \propto Z_{\text{eff}} \propto \frac{\text{positive charge}}{\text{negative charge}}$$

Ion with high positive oxidation state will have high ionisation energy.

$$\text{Ex. } \text{Fe}^{+3} > \text{Fe}^{+2} > \text{Fe}$$

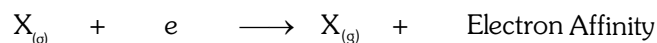


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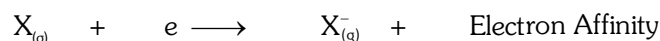
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### ELECTRON AFFINITY/ELECTRON GAIN ENTHALPY ( $EA/\Delta H_{eg}$ )

- (1) The amount of energy released when an electron is added to the valence shell of an isolated gaseous atom known as Electron affinity.

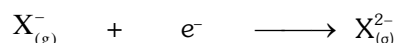


- (2) Generally first electron addition of an isolated gaseous atom is an exothermic process (except stable electronic configuration)

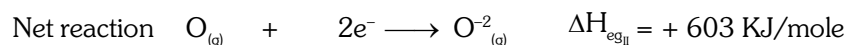
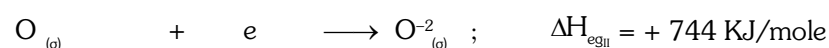
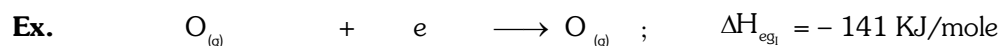


$$\Delta H_{egI} \text{ (first electron gain enthalpy)} = -ve$$

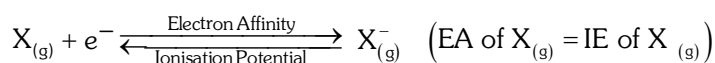
- (3) Second electron addition of an isolated gaseous atom is always an endothermic process due to inter electronic repulsion.



$$\Delta H_{egII} \text{ (second electron gain enthalpy)} = \text{positive}$$



- (4) Formation of poly negative anion like  $O^{2-}$ ,  $N^{3-}$ ,  $C^{4-}$  etc. is always an endothermic process.  
 (5) Electron affinity of neutral atom is equal to ionisation energy of its anion.



### ELECTRONEGATIVITY (EN)

- (i) The tendency of a covalently bonded atom to attract shared pair of electrons towards itself is called electronegativity.  
 (ii) A polar covalent bond of A – B may be broken as  
 $A - B \longrightarrow A^{\delta-} - B^{\delta+}$  (Electronegativity A > Electronegativity B)  
 depending on their tendency to attract bonded electron.  
 (iii) **Difference between electronegativity and Electron Affinity :**

Electronegativity	Electron Affinity
<ul style="list-style-type: none"> <li>Tendency of an atom in a molecule to attract the bonded electrons</li> <li>It is not an energetic term</li> <li>It regularly increases in a period because not depend on stable electronic configuration</li> <li>It has no unit</li> </ul>	<ul style="list-style-type: none"> <li>Energy released when an electron is added to neutral isolated gaseous atom</li> <li>It is an energetic term</li> <li>It does not increases regularly in a period because depend on stable electronic configuration</li> <li>It is measured in eV/atom or KJ mol<sup>-1</sup> or K cal mole<sup>-1</sup></li> </ul>

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(iv) EN was explained by Pauling for the first time

Electronegativity of some other elements are as follows –

Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	H 2.1
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	F 4.0
K 0.8						Br 2.8
Rb 0.8						I 2.5
Cs 0.7						
Fr 0.7						

In Pauling's scale, elements having almost same electronegativity are-

N = Cl = 3.0  
C = S = I = 2.5  
P = H = 2.1  
Be = Al = 1.5  
K = Rb = 0.8  
Cs = Fr = 0.7

**Note :** Small atoms are normally having more electronegativity than larger atoms.

(v) **FACTORS AFFECTING ELECTRONEGATIVITY :**

(A) **Atomic size**

$$\text{Electronegativity} \propto \frac{1}{\text{Atomic size}}$$

**Ex.** F > Cl > Br > I

(B) **Effective nuclear charge ( $Z_{\text{eff}}$ )**

$$\text{Electronegativity} \propto Z_{\text{eff}} \propto \frac{\text{positive charge}}{\text{negative charge}}$$

**Ex.**  $\text{Mn}^{+2} < \text{Mn}^{+4} < \text{Mn}^{+7}$   
 $\text{O}^{-2} < \text{O}^{-1} < \text{O} < \text{O}^{+1} < \text{O}^{+2}$   
 $\text{Fe} < \text{Fe}^{+2} < \text{Fe}^{+3}$

----->  
 $Z_{\text{eff}} \uparrow \text{EN} \uparrow$

(C) **% s - character**

$$\text{Electronegativity} \propto \%s\text{-Character}$$

(vi) **PERIODIC TABLE & ELECTRONEGATIVITY :**

(A) Electronegativity decreases down the group.

(B) In period on moving from left to right electronegativity increases.

(C) Electronegativity of Cs and Fr are equal, it is because from  ${}_{55}\text{Cs}$  to  ${}_{87}\text{Fr}$  only one shell increases but nuclear charge (No. of proton) increases by +32, so effect of nuclear charge balanced the effect of increase in number of shell.

**Electronegativity of F > Cl but Electron affinity of Cl > F**

(D) In IIIA group, value of electronegativity is irregular when going down the group, because of transition contraction

**Electronegativity of Ga > Electronegativity of Al**

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