

Atoms, Molecules, Chemical Arithmetic and Atomic Structure

Atoms, Molecules and Chemical Arithmetic

Significant figures

The total number of digits in a number including the last digit whose value is uncertain is called the number of significant figures e.g. 12.4267 ± 0.0001 has six significant figures.

Rules for determining the number of significant figures

(1) All non-zero digits as well as the zeros between the non-zero digits are significant e.g. 5004 has four significant figures.

(2) Zeros to the left of the first non-zero digit in a number are not significant e.g. 0.0045 has two significant figures.

(3) If a number ends in zeros but these zeros are to the right of the decimal point, then these zeros are significant e.g. 2.500 has four significant figures.

(4) If a number ends in zeros but these zeros are not to the right of a decimal point, these zeros may or may not be significant e.g. 10500 written as 1.05×10^4 has three significant figures but written as 1.050×10^4 has four significant figures and so on.

(5) The result of an addition or subtraction should be reported to the same number of decimal places as that of the term with least number of decimal places e.g. sum $4.525 + 2.3 + 6.24 = 13.063$ will be reported as 13.1.

(6) The result of multiplication or division should be reported to the same number of significant figures as is possessed by the least precise term e.g. $4.327 \times 2.8 = 12.1156$ will be reported as 12.

(7) If calculation involves a number of steps, the result should contain the same number of significant figures as that of the least precise number involved, other than the exact numbers.

Rounding off non significant figures

It implies as follows

(1) If the digit just next to the last digit to be retained is less than 5, the last digit is taken as such and all other digits to its right are dropped e.g. $1.234 = 1.23$.

(2) If the last digit is greater than 5, the digit to be retained is increased by 1 and all other digits on its right are dropped e.g. $1.236 = 1.24$.

(3) If the digit just next to the last digit to be retained is equal to 5, the last significant figure is left unchanged if it is even and is increased by 1 if it is odd e.g. $1.235 = 1.24$, $1.225 = 1.22$.

S.I. Units

Seven basic SI units for physical quantities are as follows

| Length | Mass | Time | Temperature | Electric Current | Luminous Intensity | Amount of substance |
|-----------------------|---------------------------|------------|---------------------|---------------------|-----------------------|---------------------|
| metre (<i>m</i>) | Kilogram (<i>kg</i>) | Second (s) | Kelvin (<i>K</i>) | Ampere (<i>A</i>) | Candela (<i>Cd</i>) | Mole (<i>mol</i>) |

Some derived units : Volume = m^3 , Velocity = ms^{-1} , Acceleration = ms^{-2} , Force = $kg\ ms^{-2}$ = newton (N)
Pressure = $kg\ m^{-1}\ sec^{-2}$ = pascal (Pa), Energy = $kg\ m^2\ s^{-2}$ = joule (J), Density = $kg\ m^{-3}$.

Some prefixes used for subsidiary units : These are either multiples or fractions of the base units
e.g. deci = 10^{-1} , centi = 10^{-2} , milli = 10^{-3} , micro = 10^{-6} , nano = 10^{-9} , pico = 10^{-12} , femto = 10^{-15} ,
(fermi = $10^{-13}\ cm = 10^{-15}\ m$), deca = 10^{-1} , hecta = 10^{-2} , kilo = 10^3 , Mega = 10^6 , giga = 10^9 , tera = 10^{12} , peta = 10^{15} , exa = 10^{18}

Some useful conversion factors : $1\ \text{\AA} = 10^{-10}\ m$, $1\ nm = 10^{-9}\ m$, $1\ pm = 10^{-12}\ m$, $1\ litre = 10^{-3}\ m^3 = 1\ dm^3$, $1\ atm = 760\ mm\ or\ torr = 101,325\ pa\ or\ Nm^{-2}$, $1\ bar = 10^5\ Pa$, $1\ calorie = 4.184\ J$, $1\ electron\ volt\ (eV) = 1.6022 \times 10^{-19}\ J$.

Atom and Molecules

Atom : It is the smallest particle of an element that takes place in a chemical reaction. It may or may not be capable of free existence.

Molecule : It is the smallest particle of an element or a compound that is capable of free existence.

(i) The term molecule was given by Avogadro. (ii) The term element was given by Robert Boyle.

Laws of chemical combinations

Based on the quantitative results of chemical reactions dealing with the *weight-weight* and *weight-volume* relationships, few laws were formulated which are -

Law of conservation of mass : "In all physical and chemical changes, the total mass of the reactants is equal to that of the products" or "Matter can neither be created nor destroyed".

Law of constant composition or definite proportions : "A chemical compound is always found to be made up of the same elements combined together in the same fixed ratio by weight"

Law of multiple proportions : "When two element combine together to form two or more chemical compounds, then the weights of one of the elements which combine with a fixed weight of the other bear a simple ratio to one another."

Law of Reciprocal Proportions : The ratio of the weights of two elements A and B which combine with a fixed weight of the third element C is either the same or a simple multiple of the ratio of the weights of A and B which directly combine with each other.

Note : □ Law of reciprocal proportion can be used to obtain equivalent weights of elements.

Hence it is also called law of equivalent proportion.

Gay Lussac's law of gaseous volumes : "When gases react together, they always do so in volumes which bear a simple ratio to one another and to the volumes of the products, if gaseous, all measurements are made under the same conditions of temperature and pressure.

Dalton's Atomic Theory

It was based on laws of chemical combinations. The different assumptions of the theory are.

- (1) All types of matter is composed of atoms.
- (2) Atoms are extremely small, invisible and indestructible, *i.e.* atom can neither be destroyed nor created.
- (3) Atoms of the same are alike in properties.
- (4) Atoms combine in small whole numbers to form compound atoms (known as molecule).
- (5) Compound atoms of a substance are alike possess similar properties.

Berzelius and Avogadro's hypothesis

Berzelius Hypothesis : Equal volumes of all gases contain equal number of atoms under same conditions of temperature and pressure. When applied to law of combining volumes, this hypothesis predicts that atoms are divisible and hence it is contrary to Dalton's atomic theory.

Avogadro's hypothesis : "Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules." Avogadro hypothesis is used in

- (1) Deriving the molecular formula of gases. (2) Determining atomicity of gases.
- (3) In deriving the relation, molecular wt. = $2 \times$ vapour density

Atomic and Molecular mass

Atomic Mass : It is the average relative mass of its atoms as compared with an atom of carbon -12 isotope taken as 12.

$$\text{Atomic mass} = \frac{\text{Average mass of an atom}}{1/12 \times \text{Mass of an atom of } C^{12}}$$

Average atomic mass : If an element exists in two isotopes having atomic masses 'a' and 'b' in the ratio $m : n$, then average atomic mass = $\frac{(m \times a) + (n \times b)}{m + n}$.

Since the atomic mass is a ratio, it has no units and is expressed in *amu*, $1 \text{ amu} = 1.66 \times 10^{-24} \text{ g}$.

Following are the important methods for determining atomic mass:

- (a) Dulong and Petit's method
- (b) Specific heat method
- (c) Volatile chloride formation method
- (d) Isomorphism method

Molecular mass : Molecular mass of a substance is the average relative mass of its molecules as compared with an atom of C-12 isotope taken as 12. Thus, molecular mass is a ratio and hence has no units. It is expressed in *amu*.

$$\text{Molecular mass} = \frac{\text{Mass of one molecule of the substance}}{1/12 \times \text{Mass of one atom of } C^{12}}$$

Following are the important methods for determining molecular mass;

- (a) Vapour density method, (b) Diffusion method, (c) Colligative properties and (d) Victor Mayer method

Difference between atomic mass and actual mass of an atom

The atomic mass of an atom (element) is not its actual mass. It is relative mass as compared with an atom of carbon taken as 12. It is expressed in *amu*. The actual mass of an atom means its mass in grams which is obtained by dividing the atomic mass of the element by Avogadro's number (6.02×10^{23}) because one gram atom contains Avogadro's number of atoms.

Gram atomic & Molecular mass

Gram atomic Mass (GAM) : The atomic mass of an element expressed in grams is called gram atomic mass. This amount of the element is called one gram atom.

Gram molecular mass or molar mass (GMM) : The molecular mass of a substance expressed in gram is called gram molecular mass or molar mass. This amount of the substance is called one gram molecule.

(1) Aston, Dalton and avogram are the other names of 1 *amu*.

(2) Accurate determination of atomic weights and relative abundance of the isotopes can be determined with the help of an instrument known as mass spectrometer. Developed by Aston.

(3) In the beginning John Dalton determined the atomic weight with respect to hydrogen.

Mole concepts

Mole is unit which represents 6.022×10^{23} particles (atoms molecules or ions, etc.) irrespective of their nature. The number 6.022×10^{23} is called Avogadro's number and is represented by N_0 . Avogadro's number of gas molecules occupy a volume of $22,400 \text{ cm}^3$ at S.T.P. The number of molecules in 1 cm^3 of gas at STP is called Loschmidt number. Its value is 2.688×10^{19} . The calculation of this number is based on the Faraday's law of electrolysis.

Note : A mole any substance is related to mass of a substance, number of particles and volume of a gaseous substance

Equivalent weights

The equivalent weight of a substance is the number of parts by weight of the substance that combine with or displace directly or indirectly 1.008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35.5 parts by weight of chlorine.

$$\text{Eq. wt. of an element} = \frac{\text{Atomic mass}}{\text{Valency}} ;$$

$$\text{Eq. wt. of an acid} = \frac{\text{Mol. wt. of the acid}}{\text{Basicity}}$$

$$\text{Eq. wt. of a base} = \frac{\text{Mol. wt. of the base}}{\text{Acidity}} ;$$

$$\text{Eq. wt. of a salt} = \frac{\text{Formula weight}}{\text{Total +ve charge or -ve charge}}$$

$$\text{Eq. wt. of radical} = \frac{\text{Formula weight of radical}}{\text{No. of units of charge}}$$

$$\text{Eq. wt. of an oxidizing or reducing agent} = \frac{\text{Mol. wt. of the substance}}{\text{Number of electrons gained or lost by one molecules}}$$

Basicity is the number of displaceable H^+ ions from one molecule of the acid (e.g. 1 for HCl , 2 for H_2SO_4 , 3 for H_3PO_4).

Acidity is the number of displaceable OH^- ions from one molecule of the base (e.g. 1 for $NaOH$, 2 for $Ca(OH)_2$ etc).

Following are the important methods of determining equivalent weight

(1) Hydrogen displacement method (for metals which can displace hydrogen from acids) –

$$\text{Eq. wt. of metal} = \frac{\text{weight of metal}}{\text{weight of hydrogen displaced}}$$

$$(2) \text{Oxide method} - \text{Eq. wt. of metal} = \frac{\text{weight of metal}}{\text{weight of oxygen}} \times 8.0$$

$$(3) \text{Chlorine method} - \text{Eq. wt. of metal} = \frac{\text{weight of metal}}{\text{weight of chlorine}} \times 35.5$$

Stoichiometry

Calculation based on chemical equation is called stoichiometry. The chemical equation gives us important information regarding –

- (1) Molar ratio between reactants and products.
- (2) Mass ratio between reactant and products.
- (3) Volumes ratio between gaseous reactants and products.

The calculation based on chemical equation are of three types namely –

- (i) Mass-mass relationship,
- (ii) Mass-volume relationship,
- (iii) Volume-volume relationship

The various steps involved in solving problems based on chemical equations are.

- (i) Write balanced equations for the reactions involved.
- (ii) Write the relative number of moles or relative masses of the reactants and products involved in the problem below their formulae.
- (iii) In case of a gaseous substance, write down 22.4 L at STP below the formula in place of 1 mol (if volume is involved).
- (iv) Apply unitary method to make the required calculations.

Empirical and molecular formulas

Empirical formula - It is the simplest formula of a compound which gives the simplest whole number ratio of the atoms of the various elements present in one molecule of the compound e.g. empirical formula of glucose ($C_6H_{12}O_6$) is CH_2O .

Calculation of empirical formulas

First calculate % of oxygen = 100 – Sum of % of all other elements. Then E.F. is calculated through the following steps :

$$\text{Element} \rightarrow \% \text{ of element} \rightarrow \text{Atomic mass} \rightarrow \text{Relative no. of atoms} = \frac{\%}{\text{At. mass}} \rightarrow \text{Simplest atomic ratio} \rightarrow \text{Simplest whole no. ratio}$$

Molecular formula - It is the actual formula of a compound which gives the actual number of atoms of various elements present in one molecule of the compound e.g. molecular formula of glucose is $C_6H_{12}O_6$.

Relationship between empirical formula and molecular formula

Molecular formula = $n \times$ Empirical formula

$$\text{Where } n \text{ is any integer such as } 1, 2, 3, \dots \text{ etc. } n = \frac{\text{Molecules mass}}{\text{Empirical formula mass}}$$

Volumetric Analysis

(1) Normality of a solution is the number of gram equivalents of the solute present in one litre of the solution.

(2) Molarity of a solution is the number of moles of the solute present in one litre of the solution.

$$(3) \text{ No. of gram equivalents} = \frac{\text{Wt. of the solute in grams}}{\text{Eq. wt. of the solute}}$$

$$(4) \text{ No. of moles} = \frac{\text{Wt. of the substance in grams}}{\text{Mol. wt. of the substance}}$$

(5) When a solution is diluted, we can apply normality equation or molarity equation.

$$N_1 \times V_1 = N_2 \times V_2 \quad \text{or} \quad M_1 \times V_1 = M_2 \times V_2$$

(Before dilution) (After dilution) (Before dilution) (After dilution)

(6) When the solutions of two substances (an acid and a base or an oxidizing and a reducing substance) react completely, we apply normality equation viz.

$$\begin{matrix} N_1 \times V_1 \\ \text{(solution 1)} \end{matrix} = \begin{matrix} N_2 \times V_2 \\ \text{(Solution 2)} \end{matrix}$$

(7) In terms of molarity equation, for the reaction $n_1A + n_2B \rightarrow \text{Products}$, we apply $\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$

Important formula used for numerical problems

- Mass of one atom of element = $\frac{GAM}{N_0}$.

□ Mass of 1 molecule of a substance = $\frac{GMM}{N_0}$.

□ No. of atoms in 'w' gram of element = $\frac{w}{GMM} \times N_0$.

□ No. of moles of element for X atom = $\frac{X}{N_0}$.

□ No. of molecules in 'n' moles of substance = $n \times N_0$.

□ Moles in 'n' atoms = $\frac{n}{N_0} \times \text{atomicity}$.

□ For elements with atomicity > 1, The formula can be modified as; Atoms in 'n' moles = $n \times N_0 \times \text{atomicity}$.

□ Weight % of an element = $\left(\frac{\text{At. wt.} \times \text{No. of atoms per molecule}}{\text{Mol. wt. of the compound}} \right) \times 100$.

□ According to Dulong and Petit's rule for any element Atomic wt. \times Specific heat = 6.4 (approx.) or
 Approx. Atomic weight = $\frac{6.4}{\text{Specific heat}}$

□ Mass of X atoms of element = $\frac{GAM}{N_0} \times X$.

□ Mass of X molecule of a substance = $\frac{GMM}{N_0} \times X$.

□ No. of atoms in 'n' moles of element = $n \times N_0$.

□ No. of molecules in 'w' gm. of substance = $\frac{w}{GMM} \times N_0$.

□ No. of moles in X molecules = $\frac{X}{N_0}$.

□ Eq wt. = $\frac{\text{Atomic weight}}{\text{Valency}}$.

Atomic Structure

Structure of Atom

(1) John Dalton 1801, believed that matter is made up of extremely minute indivisible particles, called atoms.

Atom consists of two parts

| | | |
|---|---|-----------------------|
| Nucleus : Neutron (n) +Proton (p) | } | Fundamental particles |
| Extra nuclear part : Electron (e) only. | | |

(2) The characteristics of fundamental particles are given below.

| Particle | Symbol | Mass in amu | Mass in Kg | Charge in esu | Charge in coulomb | e/m | Discovery |
|----------|--------------|-------------|--------------------------|--------------------------|--------------------------|--------------------------------|--------------------|
| Electron | ${}_{-1}e^0$ | 0.000548 | 9.1091×10^{-31} | -4.803×10^{-10} | -1.602×10^{-19} | $1.76 \times 10^8 \text{ c/g}$ | Thomson |
| Proton | ${}_{+1}P^1$ | 1.00757 | 1.6725×10^{-27} | $+4.803 \times 10^{-10}$ | $+1.602 \times 10^{-19}$ | $9.58 \times 10^4 \text{ c/g}$ | Goldstein (1886) |
| Neutron | ${}_0n^1$ | 1.00893 | 1.6748×10^{-27} | 0 | 0 | 0 | J. Chadwick (1932) |

Note : □ The mass of electron given above is the rest mass. It is $1/1837$ times the mass of a hydrogen atom.

(3) Other fundamental particles and Antiparticles

Bryons : These are heavy particles and include protons, neutrons etc.

Mesons : These are particles of intermediate mass.

Leptons : These are lighter particles viz. electron, μ particles and neutrinos.

Positron : C.D. Anderson (1932) discovered it. It has same negligible mass and same amount of charge as of the electron. But charge is +ve and of short life 10^{-8} sec.

Meson : Yukawa (1935) discovered it. It has mass in between that of proton and electron in cosmic rays. The charge may be +ve, -ve or zero.

Neutrino (ν): Pauli (1927) suggested the existence of a particle called neutrino. It has a variable mass less than that of an electron. The charge on this particle is zero. Allen and Rodebeek (1952), showed their free existence.

Antiproton (p^-): Segre (1956) discovered it. It has mass equal to that of a proton but with a negative charge.

Allotropy : When the element exists in 2 or more forms in the same state that differ in physical properties, it is said to exhibit allotropy, while these forms are called allotropes of that element.

Note : □ The mass (m) of a particle (electron) at high speed is given by:

$$m = \frac{m_{\text{rest}}}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}, \quad \text{Where, } v = \text{velocity of particle, } c = \text{velocity of light}$$

If $v = c$, then $m = \infty$.

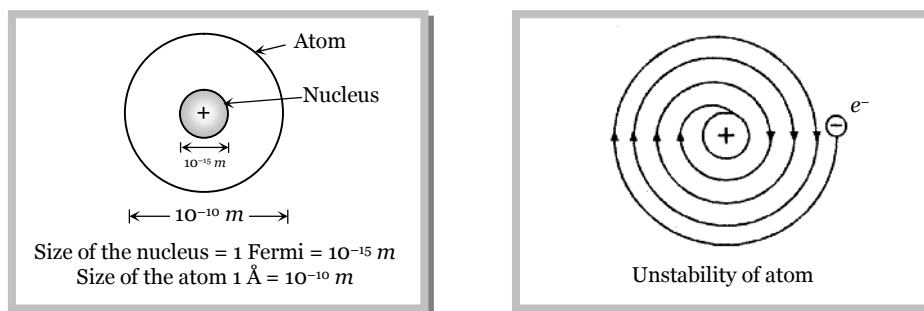
(4) **Rutherford's Experiment :** In 1911, Rutherford observed that when α - particles emitted from Ra struck thin metallic sheets, many of them passed through the sheet with no change in their path but a few of them got deflected 90° or through larger angles. He concluded that :

(i) As most of the α -particles passed undeflected, the atom must predominantly consists of empty space.

(ii) As a few α - particles carrying +ve charge are strongly deflected there must be a heavy +ve charged body present in each atom and the volume occupied by this is only a minute fraction of the total volume of an atom an atom. He called this +vely charged body as nucleus. It is surrounded by small negatively charged particles called electrons, at relatively large distances form the nucleus.

In order to explain why the electrons do not fall into the nucleus due to electrostatic attraction, Rutherford proposed that electrons are revolving round the nucleus at high velocities. The centrifugal force arising from this motion just balances the force of electrostatic attraction.

Objections to Rutherford's Model : When ever an electric charge is subjected to acceleration, it emits radiation and loses energy. As a result of this, the orbit will become smaller and the electrons will drop on the nucleus. This, however, does not happen. This model also fails to explain the line spectrum of hydrogen.



(5) Atomic number and Mass number

Atomic number (Z) : Mosley denoted atomic no. of element by Z representing the no. of protons in the nucleus of an element.

$\therefore Z = \text{No. of protons in the nucleus of an atom} = \text{No. of electrons in the extra nuclear part of neutral atom.}$

Mass number (A) : It is equal to sum of numbers of protons and no. of neutrons in an atom.

$$A = p + n, \text{ or } A = Z + n, \text{ or } A - Z = n$$

An element X having mass no. (*At. wt.*) A and *At. no.* Z , is represented as ${}_Z X^A$

Note : Actual mass of atom is not equal to the sum of mass of e , p and n present in it, e.g., for Chlorine $({}_{17}Cl^{35}) = 17(1.007276) \text{ amu} + 18(1.008665) \text{ amu} + 17(0.0005486) \text{ amu} = 35.289005 \text{ amu}$. However, the mass of chlorine has been accurately determined as 34.96885 amu . This difference between the two values $(35.28901 \text{ amu} - 34.96885 \text{ amu}) = 0.32016 \text{ amu}$ is known as mass defect.

This difference, expressed in its energy equivalent, is called the binding energy of the nucleons (neutrons + protons) in the nucleus of the atom in question.

(6) Different types of atomic species

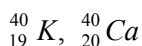
Isotopes : Atoms of an element having the same atomic no. but different at. wt. are called isotopes.

$$\text{eg } {}_{17}^{35}Cl \text{ and } {}_{17}^{37}Cl, {}_1^1H, {}_1^2D \text{ and } {}_1^3T, {}_8^{16}O, {}_8^{17}O \text{ and } {}_8^{18}O$$

Isotopes have the same no. of protons and electrons but different no. of neutrons. They have the same chemical properties. The fractional at. wt. of an element is due to the different proportions in which various isotopes are present in it, eg. chlorine has two isotopes ${}_{17}Cl^{35}$ and ${}_{17}Cl^{37}$ present in the ratio 3:1.

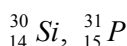
$$\text{Average at. wt.} = \frac{3 \times 35 + 1 \times 37}{4} = 35.5 \text{ amu}$$

Isobars : Atoms of different elements having different at. no. but the same at. wt. are called isobars. eg.

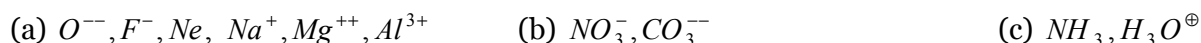


Isobars have different no. of protons, neutrons and electrons, but the sum of no. of protons and neutrons is same. They have different chemical properties.

Isotones : Atoms having the same no. of neutrons but different no. of protons are called Isotones. eg.



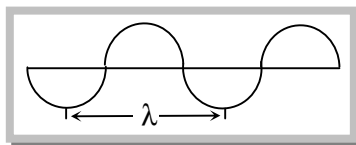
Isoelectronic ions or molecules : Species having same no. of electron but different charge on nucleus are known as isoelectronic ions.



Isodiaphers : Species with same isotopic number *i.e.* $(A-2Z)$ or $(n-Z)$

(7) **Electromagnetic radiations** : “Electromagnetic radiations is a form of energy transported in the forms of waves from any source continuously with the velocity of light and consists of electric and magnetic fields oscillating perpendicular to each other and to the direction of propagation”. Every wave has following five characteristics, viz,

Wavelength (λ) : The distance between two neighbouring troughs or crests. Expressed in *cm*, *nm*, \AA units. $1\text{\AA} = 1 \times 10^{-10} \text{ nm} = 10^{-8} \text{ cm}$.



Frequency (ν) : The number of times a wave passes through a given point in one second. Expressed in *cps* or *Hz*. $1\text{Hz} = 1\text{cps}$.

Velocity (c) : The distance travelled by the wave in one second. All waves have same velocity *i.e.* $3 \times 10^{10} \text{ cm s}^{-1} = 3 \times 10^8 \text{ m s}^{-1} = 186,000 \text{ miles s}^{-1}$.

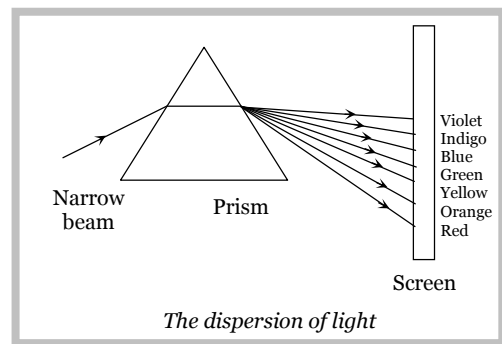
Wave number ($\bar{\nu}$) : The number of wavelengths per *cm*. Expressed in cm^{-1} .

Amplitude (α) : The height of the crest or depth of trough of a wave. It determines the intensity or brightness of the light beam.

Relation between wave characteristic : $\nu = \frac{c}{\lambda} = c\bar{\nu}$

(8) **Electromagnetic spectrum** : When sunlight is passed through a prism, it absorbs wavelength range of black colour radiation and other splits into a series of colour bands known as emission spectrum and black colour band which is known as absorption spectrum.

The splitting of light into seven colours is called emission **Spectrum**. The characteristic range of wavelength of electromagnetic radiation situated in an increasing or decreasing order called **electromagnetic spectrum**.



Wavelengths and frequencies of electromagnetic radiation's

| Electromagnetic radiation | Wavelength(Å) | Frequency (Hz or sec ⁻¹) |
|---------------------------|---------------------------------------|--|
| Radiowaves | 3×10^{13} to 3×10^9 | 1×10^5 to 1×10^9 |
| Microwaves | 3×10^9 to 6×10^6 | 1×10^9 to 5×10^{11} |
| Infra red (IR) | 6×10^6 to 7600 | 5×10^{11} to 3.95×10^{14} |
| Visible | 7600 to 3800 | 3.95×10^{14} to 7.9×10^{14} |
| Ultraviolet (UV) | 3800 to 150 | 7.9×10^{14} to 2×10^{16} |
| X-Rays | 150 to 0.1 | 2×10^{16} to 3×10^{19} |
| Gamma rays | 0.1 to 0.01 | 3×10^{19} to 3×10^{20} |
| Cosmic rays | 0.01 to zero | 3×10^{20} to infinity |

↓
 Decreasing λ
 Increasing ν, E

Limitations of electromagnetic waves : Electromagnetic wave theory was successful in explaining the properties of light such as interference, diffraction etc. but it could not explain the phenomena of 'Black body radiation', and 'Photoelectric effect.'

(9) **Planck's quantum theory :** This theory was proposed by Max Planck to explain black body radiations and photoelectric effect. According to this theory,

"Radiant energy is emitted or absorbed only in discrete units or packets of energy called photon (quantum). the energy 'E' associated with a quantum is given by $E = h\nu$, where h is Planck's constant and ν is frequency of radiations".

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \quad \left(\because \frac{1}{\lambda} = \bar{\nu} \right) \quad \text{Where } h \text{ is Planck's constant} =$$

$$6.625 \times 10^{-34} \text{ J sec} = 6.625 \times 10^{-27} \text{ erg sec}$$

$$c \text{ is velocity of light} = 3.0 \times 10^8 \text{ m sec}^{-1} = 3.0 \times 10^{10} \text{ cm sec}^{-1}$$

$$\nu \text{ is frequency of light in sec}^{-1}; \bar{\nu} \text{ is wave no. in } m^{-1} \text{ or } cm^{-1}.$$

It is thus clear that energy of photon decreases with increase in λ .

$\xrightarrow{\text{VIBGYOR}} \lambda$ increases and E decreases

Note : □ Energy 'E' associated with a photon can also be written as

$$E = \frac{12375}{\lambda} \text{ eV. where } E \text{ is energy in eV and } \lambda \text{ is wavelength of light in } \text{\AA}.$$

(10) **Neil's Bohr Atomic Theory (1913) :** it is based on the following assumptions.

(i) The electron moves around the +vely charged nucleus in a circular orbit, the centripetal force for this motion is balanced by the electrostatic attraction.

(ii) The electron can rotate only in certain orbits which are known as stationary or quantized orbits for which the angular momentum is an integral multiple of $\frac{h}{2\pi}$. When the electron moves in these orbits it cannot emit any radiation.

(iii) The electron radiates a quantum of energy of frequency ν only when it jumps from an orbit of higher energy to an orbit of low energy. If E_1 and E_2 are the energies of the electron in two successive orbits, then $E_2 - E_1 = h\nu$ (h is Planck's constant = 6.62×10^{-27} ergs).

$$\nu = \frac{c}{\lambda}; \quad c = 3 \times 10^{10} \text{ cm/s}, \quad \lambda = \text{wavelength}$$

The energy of the electron in an orbit characterised by quantum number ' n '

$$E_n = -\frac{20\pi^2 Z^2 e^4 m}{h^2 n^2} = \frac{-13.6 Z^2}{n^2} \text{ eV atm}^{-1} = \frac{1311.8 Z^2}{n^2} \text{ KJmol}^{-1}$$

Where, Z is atomic number; m and e are mass and charge of the electron respectively.

The radius of the paths in which an electron can revolve is given by;

$$r = \frac{n^2 h^2}{4\pi^2 m e^2} = 0.53 n^2 \text{ \AA}$$

$$(1 \text{ \AA} = 10^{-8} \text{ cm})$$

Putting $n = 1, 2, 3, 4$ etc., the radii of the first five orbits of H - atom are:

| Orbit (n) | 1 | 2 | 3 | 4 | 5 |
|-------------------------|-------|-------|-------|-------|--------|
| Radius (\AA) | 0.529 | 2.116 | 4.761 | 8.464 | 13.225 |

When an electron jumps from an outer orbit in which its quantum number is ' n_2 ' to an inner orbit in which it is ' n_1 '; the energy emitted as radiation is given by

$$E_{n_2} - E_{n_1} = \frac{2\pi^2 Z^2 e^4 m}{h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

and the frequency expressed in wave number will be

$$\bar{\nu} = \frac{2\pi^2 Z^2 e^4 m}{h^3 c} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where R is the Rydberg constant. For hydrogen R is 109677.8 cm^{-1} .

Bohr's model explains successfully the spectrum of hydrogen atom and species having one electron. It explains the appearance of five series of lines in hydrogen spectrum.

Comparative study of important spectral series of Hydrogen atom

| S.No. | Spectral series | Lies in the region | Transition | $\lambda_{\max} = \frac{n_1^2 n_2^2}{(n_2^2 - n_1^2)R}$ | $\lambda_{\min} = \frac{n_1^2}{R}$ | $\frac{\lambda_{\max}}{\lambda_{\min}} = \frac{n_2^2}{n_2^2 - n_1^2}$ |
|-------|-----------------|--------------------|---|--|--|---|
| 1. | Lyman series | Ultraviolet region | $n_1 = 1$ $n_2 = 2, 3, 4, \dots, \infty$ | $n_1 = 1$ and $n_2 = 2$ $\lambda_{\max} = \frac{4}{3R}$ | $n_1 = 1$ and $n_2 = \infty$ $\lambda_{\min} = \frac{1}{R}$ | $\frac{\lambda_{\max}}{\lambda_{\min}} = \frac{4}{3}$ |

| | | | | | | |
|----|-----------------|------------------|---|--|---|---|
| 2. | Balmer series | Visible region | $n_1 = 2$ $n_2 = 3, 4, 5, \dots, \infty$ | $n_1 = 2$ and $n_2 = 3$ $\lambda_{\max} = \frac{36}{5R}$ | $n_1 = 2$ and $n_2 = \infty$ $\lambda_{\min} = \frac{4}{R}$ | $\frac{\lambda_{\max}}{\lambda_{\min}} = \frac{9}{5}$ |
| 3. | Paschen series | Infra red region | $n_1 = 3$ $n_2 = 4, 5, 6, \dots, \infty$ | $n_1 = 3$ and $n_2 = 4$ $\lambda_{\max} = \frac{144}{7R}$ | $n_1 = 3$ and $n_2 = \infty$ $\lambda_{\min} = \frac{9}{R}$ | $\frac{\lambda_{\max}}{\lambda_{\min}} = \frac{16}{7}$ |
| 4. | Brackett series | Infra red region | $n_1 = 4$ $n_2 = 5, 6, 7, \dots, \infty$ | $n_1 = 4$ and $n_2 = 5$ $\lambda_{\max} = \frac{16 \times 25}{9R}$ | $n_1 = 4$ and $n_2 = \infty$ $\lambda_{\min} = \frac{16}{R}$ | $\frac{\lambda_{\max}}{\lambda_{\min}} = \frac{25}{9}$ |
| 5. | Pfund series | Infra red region | $n_1 = 5$ $n_2 = 6, 7, 8, \dots, \infty$ | $n_1 = 5$ and $n_2 = 6$ $\lambda_{\max} = \frac{25 \times 36}{11R}$ | $n_1 = 5$ and $n_2 = \infty$ $\lambda_{\min} = \frac{25}{R}$ | $\frac{\lambda_{\max}}{\lambda_{\min}} = \frac{36}{11}$ |

(11) **Sommerfeld theory (1915)** : It states that :

- (i) The orbits in which the electrons move are in most cases elliptical.
- (ii) The orbits are capable of interpenetrating and electrons in these orbits are spinning like a top.
- (iii) The orbits are further divided into sub-orbits or sub-states which are denoted as 's', 'p', 'd', 'f' orbitals.

A result of sommerfeld model suggests that $\frac{n}{k} = \frac{\text{length of major axis}}{\text{length of minor axis}}$

e.g., if principal quantum no. $n = 4$.

The values of k can be 1, 2, 3, 4 only, since k is an integer

\therefore 4th shell have 4 subshells.

Total spin and magnetic moment : The total spin (s) of an atom is given by $s = \frac{1}{2} \times n$, where n is number of unpaired electrons.

The spin magnetic moment (μ) of electron (excluding orbital magnetic moment) in Bohr magneton (B.M.) is given by : $\mu_{\text{effective}} = \sqrt{4s(s+1)}$

If $s = 1/2 \times n$; $\therefore \mu_{\text{effective}} = \sqrt{n(n+2)} B.M.$

To derive the possible no. of λ in line spectrum, when an electron de-excites from one o level to other.

Say an electron is in 4th shell in H atom. It is to be de-excited to ground state level, i.e., I shell.

The possible no. of λ given out = $\Sigma \Delta n = \Sigma(4-1) = \Sigma 3 = 1 + 2 + 3 = 6$

(12) **Photoelectric effect** : The phenomenon of ejection of electrons from the surface of a metal when light of suitable frequency strikes on it, is called as photoelectric effect. The emitted electrons are called photoelectrons.

Threshold energy is a character of a particular metal, therefore

$$h\nu = x + \frac{1}{2}m\nu^2$$

If the threshold frequency is ν_0 , then Threshold energy, $x = h\nu_0$, so that

$$h\nu = h\nu_0 + \frac{1}{2}m\nu^2 \text{ or } \frac{1}{2}m\nu^2 = h\nu - h\nu_0$$

Therefore kinetic energy of ejected electron ($\frac{1}{2}m\nu^2$)

$$K.E. = h\nu - h\nu_0$$

In this equation $h\nu$ = energy of incidental photon and $h\nu_0$ = minimum value of energy required to eject the electron.

(13) Particle and wave nature of electron i.e. dual nature : de Broglie proposed a relationship between λ of a moving particle with its velocity on the basis of quantum theory.

$$\lambda = \frac{h}{mu} = \frac{h}{p} = \frac{h}{\sqrt{2m(KE)}} \quad (\because KE = \frac{1}{2}mu^2)$$

Where m is mass of moving particle, u is its velocity

P is momentum of particle equal to μ or $\sqrt{2m(KE)}$, h is Planck's constant.

The circumference of the n th orbit (if closed) is equal to integer multiple of wavelength.

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

Also, Frequency of matter wave $= \frac{u}{\lambda} = \frac{u}{h/mu} = \frac{mu^2}{h} = \frac{2KE}{h}$

(14) Heisenberg's uncertainty principle : According to this principle, it is impossible to determine momentum and position of a subatomic particle precisely and simultaneously.

$$\Delta p \cdot \Delta x \geq \frac{h}{4\pi} \quad \text{Where } \Delta p \text{ is uncertainty in momentum}$$

$$m \cdot \Delta u \cdot \Delta x \geq \frac{h}{4\pi} \quad \begin{array}{l} \Delta x \text{ is uncertainty in position} \\ \Delta u \text{ is uncertainty in velocity.} \end{array}$$

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

(15) Schrodinger wave equation : Bohr treated electron as a particle. However, de Broglie suggested that e^- has a dual nature, i.e., it behaves both as a particle as well as wave. The wavelength λ of moving particle is

$$\lambda = \frac{h}{m\nu} \quad \dots(1)$$

Where ν and m are the velocity and mass of moving particle respectively. If r is radius of the wave, $2\pi r$ its circumference, then

$$\lambda n = 2\pi r \quad \dots(2)$$

Thus according to wave theory, an electron is a stationary wave moving around the nucleus in a circular path. The wave character was later on confirmed by Davison, Germer (1927) and Thomson (1928).

From eq. (1) and (2), we have

$$2\pi r = \frac{nh}{mv} \quad \text{or} \quad mvr = \frac{nh}{2\pi}$$

According to Schrodinger, the electron does not move round the nucleus in fixed orbits, but may, in fact, be anywhere with different probabilities. The probability of its presence near the nucleus is greatest and as the distance from nucleus increases the probability decreases. Schrodinger from mathematical treatment of wave motion gave a general wave equation describing the behaviour of a small particle. Consider a system such as a stretched string. For its vibration,

$\Psi = A \sin \frac{2\pi x}{\lambda}$. Where $x =$ displacement, $\Psi =$ wave function, $A =$ amplitude of the wave, $\lambda =$ wavelength

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - P.E.)\Psi = 0$$

Ψ^2 for an electron at a given point indicates the probability of occurrence of the electron at that point.

(16) **The quantum numbers** : The quantum numbers are results of Schrodinger wave equation.

(i) **Principal quantum no.**

- Denoted by 'n'
- The values of n are from 1 to n

$$n = 1 \quad K \text{ shell}; \quad n = 2 \quad L \text{ shell}$$

$$n = 3 \quad M \text{ shell}; \quad n = 4 \quad N \text{ shell}$$

- 'n' signify for the size and energy level of major energy shell.

(ii) **Azimuthal or angular quantum no.**

- Denoted by 'l'
- The values of l are from 0 to $n - 1$

$$l = 0 \text{ for } s \text{ subshell}; \quad l = 1 \text{ for } p \text{ subshell}$$

$$l = 2 \text{ for } d \text{ subshell}; \quad l = 3 \text{ for } f \text{ subshell}$$

- 'l' signify for shape and energy level of subshells.

(iii) **Magnetic quantum no.**

- Denoted by 'm'

- The values of ' m ' are from $\pm l$ to $\pm l$

| | | | | |
|-----|---------|----------------|-------------------------|-----------------------------|
| Let | $l = 1$ | $m = -1$ | 0 | +1 |
| | | p_x or p_y | p_z | p_y or p_x |
| Let | $l = 2$ | $m = -2$ | -1 | 0 |
| | | d_{xy} or | d_{xz} or d_{z^2} , | d_{yz} or $d_{x^2-y^2}$, |
| | | $d_{x^2-y^2}$ | d_{yz} | d_{xz} or d_{xy} |

- ' m ' signify for the possible no. of orientations of subshells.

(iv) Spin quantum no

- Denoted by s

- The values of s are $+\frac{1}{2}$ or $-\frac{1}{2}$

- ' s ' Signify for the direction of spin of electron in a sub- subshell or orbital.

◇ Angular momentum

$$\text{Angular momentum of an electron in an orbital} = n \frac{h}{2\pi}$$

$$\text{Angular momentum of an electron in an orbital} = \frac{h}{2\pi} \times \sqrt{[(l+1)l]}$$

(17) Pauli's exclusion principle

(i) It is impossible for two electrons of an atom to have all their four quantum no. same.

(ii) e.g. $\boxed{\uparrow\downarrow}$ is correct for $1s^2$

$\boxed{\uparrow\uparrow}$ is wrong for $1s^2$

(iii) Following results have been obtained by Pauli's exclusion principle.

- Maximum no. of electrons in a shell can be $2n^2$.
- Maximum no. of electrons in a subshell can be 2, 6, 10, 14 in s, p, d, f respectively.
- Maximum no. of electrons in a sub-subshell (orbital) is 2 only.

(18) **Rules for writing electronic configuration** : The electronic configuration is written on the basis of following rules :

(i) **Aufbau principle** : The electrons in a poly electronic atom are filled one by one in order of increasing energy level.

e.g. ${}_1H$: $1s^1$ is correct, $2s^1$ is wrong because energy level of $1s < 2s$.

(ii) **Hund's rules** : In filling a group of orbitals of equal energy (or subshells) it is preferred to assign electrons to empty orbitals rather than pair them in a particular subshell, because the former arrangement leads to lower energy level. Same spin of unpaired electrons in sub-subshell also gives rise to lower energy level.

e.g. ${}_{7}\text{N} : 1s^2, 2s^2 2p^3$

for $2p^3$

| | | |
|----|---|---|
| ↑ | ↑ | ↑ |
| ↑↓ | ↑ | |
| ↑ | ↓ | ↑ |

is correct
is wrong
is wrong

(iii) **($n + l$) rule** : The subshell with lower values of ($n + l$) possesses lower energy level and should be filled first. e.g., ${}_{19}\text{K} : 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$ is correct

$n + l$ of $4s = 4 + 0 = 4$

$n + l$ of $3d = 3 + 2 = 5$

Thus, $4s$ should be filled first.

If ($n + l$) is same for two subshells, the one with lower values of n possess lower energy and should be filled first. e.g. ${}_{21}\text{Sc} : 1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 4p^1$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1, 4s^2$ is correct

$n + l$ of $4p = 4 + 1 = 5$

$n + l$ of $3d = 3 + 2 = 5$

Thus, $3d$ should be filled first.

$\therefore n$ of $3d < n$ of $4s$

(iv) A subshell having nearly full filled or nearly half filled configuration tends to acquire exactly full filled or exactly half filled nature in order to attain stability i.e. lower energy level.

e.g. ${}_{24}\text{Cr} : 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^4, 4s^2$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$ is correct

${}_{29}\text{Cu} : 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9, 4s^2$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$ is correct

${}_{46}\text{Pd} : 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^8, 5s^2$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}$ is correct

Number of nodes : Total number of nodes in a shell = ($n - 1$)

Angular nodes = l

Spherical nodes = $n - l - 1$
