

1ST SEM COMPLEMENTARY CHEMISTRY

CALICUT UNIVERSITY

GENERAL CHEMISTRY

2019 ADMISSION ONWARDS



Prepared by

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SEMESTER I
Course Code: CHE1C01
Complementary Course I:

Total Hours: 32; Credits: 2; Hours/Week: 2; Total Marks 75 (Internal 15 & External 60)

Objective(s): To provide the students a thorough knowledge about the chemistry of quantitative and qualitative analysis and the theories behind chemical bonding. It will also impart the ideas behind atomic nucleus and the importance of metals in biological systems.

Module I: Analytical Chemistry (10 hrs)

Atomic mass - Molecular mass - Mole concept – Molar volume - Oxidation and reduction – Oxidation number and valency - Equivalent mass. Methods of expressing concentration: Molality, molarity, normality and mole fraction. Calculation of concentration on dilution of given solution (problems).

Theory of volumetric analysis – Acid-base, redox and complexometric titrations – Acid-base, redox and complexometric indicators. Double burette method of titration: Principle and advantages.

Principles in the separation of cations in qualitative analysis - Applications of common ion effect and solubility product - Microanalysis and its advantages. Accuracy & Precision (mention only).

References

1. J. Mendham, R. C. Denney, J. D. Barnes, M. Thomas, *Vogel's Textbook of Quantitative Chemical Analysis*, 6th Edn., Pearson Education, Noida, 2013.
2. G. Svehla, *Vogel's Qualitative Inorganic Analysis*, 7th Edn., Prentice Hall, New Delhi, 1996.

Module II: Atomic Structure and Chemical Bonding (10 hrs)

Atomic Structure: -Bohr atom model and its limitations, de Broglie equation – Heisenberg uncertainty principle - Schrödinger wave equation (mention only) - Atomic orbitals - Quantum numbers and their significance - Pauli's Exclusion principle - Hund's rule of maximum multiplicity - Aufbau principle –Electronic configuration of atoms.

Chemical Bonding: Introduction – Type of bonds.

Ionic bond: Factors favouring the formation of ionic bonds - Lattice energy of ionic compounds and its application.

Covalent bond: Lewis theory – Coordinate bond.

VSEPR theory: Shapes of BeCl_2 , BF_3 , SnCl_2 , CH_4 , NH_3 , H_2O , NH_4^+ , SO_4^{2-} , PCl_5 , SF_4 , ClF_3 , XeF_2 , SF_6 , IF_5 , XeF_4 , IF_7 and XeF_6 .

Valence Bond theory- Hybridisation involving s, p and d orbitals: sp (acetylene), sp^2 (ethylene), sp^3 (CH_4), sp^3d (PCl_5), sp^3d^2 (SF_6).

Molecular Orbital theory: LCAO – Electronic configuration of H_2 , B_2 , C_2 , N_2 , O_2 and CO – Calculation of bond order – determination of HOMO and LUMO – Explanation of bond length and bond strength.

Intermolecular forces - Hydrogen bonding in H_2O - Dipole-dipole interactions.

References

1. C. N. R. Rao, *Understanding Chemistry*, Universities Press India Ltd., Hyderabad, 1999.
2. R. K. Prasad, *Quantum Chemistry*, 4th Edn., New Age International (P) Ltd., New Delhi, 2012.
3. Manas Chanda, *Atomic Structure and Chemical Bonding*, 4th Edn., Tata McGraw Hill Publishing Company, Noida, 2007.

4. R. Puri, L. R. Sharma K. C. Kalia, *Principles of Inorganic Chemistry*, 31st Edn., Milestone Publishers and Distributors, New Delhi, 2013.

Module III: Nuclear Chemistry (6 hrs)

Natural radioactivity – Modes of decay – Group displacement law.

Nuclear forces - n/p ratio - Nuclear stability - Mass Defect - Binding energy. Isotopes, isobars and isotones with examples.

Nuclear fission - Atom bomb - Nuclear fusion – Hydrogen bomb - Nuclear reactors

Application of radioactive isotopes – ¹⁴C dating, Rock dating, Isotopes as tracers, Radio diagnosis, radiotherapy.

References

1. H. J. Arnikar, *Essentials of Nuclear Chemistry*, 4th Edn., New Age International (P) Ltd., New Delhi, 1995 (Reprint 2005).
2. R. Gopalan, *Elements of Nuclear Chemistry*, Vikas Publ. House

Module IV: Bioinorganic Chemistry (6 hrs)

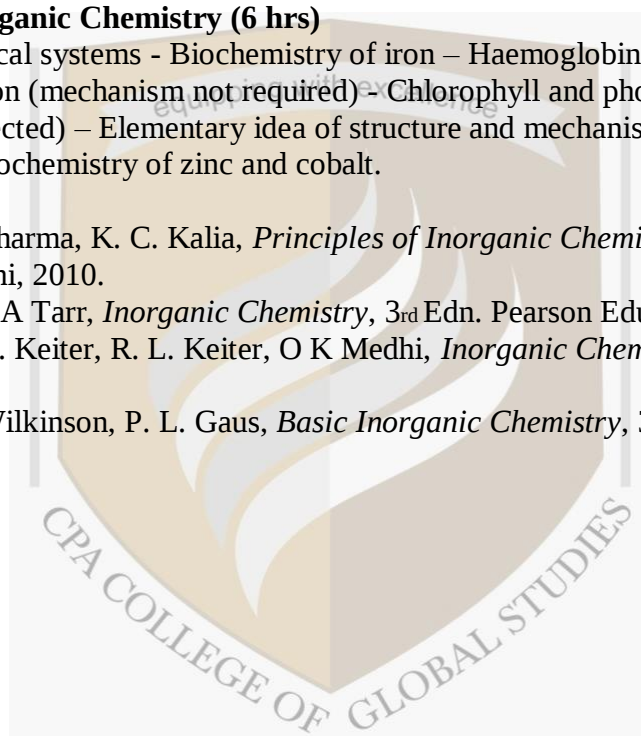
Metal ions in biological systems - Biochemistry of iron – Haemoglobin and myoglobin -O₂

and CO₂ transportation (mechanism not required) - Chlorophyll and photosynthesis

(mechanism not expected) – Elementary idea of structure and mechanism of action of sodium potassium pump - Biochemistry of zinc and cobalt.

References

1. B. R. Puri, L. R. Sharma, K. C. Kalia, *Principles of Inorganic Chemistry*, Milestone Publishers, New Delhi, 2010.
2. G. L. Meissler, D. A Tarr, *Inorganic Chemistry*, 3rd Edn. Pearson Education, 2004.
3. J. E. Huheey, E. A. Keiter, R. L. Keiter, O K Medhi, *Inorganic Chemistry*, 5th Edn. Pearson 2009.
4. F. A. Cotton, G. Wilkinson, P. L. Gaus, *Basic Inorganic Chemistry*, 3rd Edn, John – Wiley, 1995.



MODULE 1- ANALYTICAL CHEMISTRY

- Analytical chemistry is concerned with the theory and practice of methods for separation, identification and determination of the composition of a sample of matter.

PART I- SOME BASIC CHEMICAL CONCEPTS

Atomic mass

- It is the number showing how many times the mass of one atom of an element is heavier than $1/12$ th the mass of a C-12 atom.
- Atomic mass of an element =
$$\frac{\text{mass of one atom of the element}}{1/12 \text{ th the mass of C-12 atom}}$$

Atomic mass unit (amu)

- $1/12^{\text{th}}$ the mass of a C-12 atom is known as 1 amu. It is also known as Dalton (Da). Now a days, instead of writing 'amu', simplified 'u' is written which is known as unified mass.

- 6.02×10^{23} C-12 atom weighs 12g.

$$\text{Mass of 1 atom} = 12 / 6.02 \times 10^{23}$$

1 amu is $1/12$ th mass of a C -12 atom

$$\text{So, } 1 \times \frac{12}{6.02 \times 10^{23}} \text{ g}$$

$$= 1.66056 \times 10^{-27} \text{ kg}$$

- Atomic mass expressed in grams is called Gram atomic mass (GAM) or gam atom.

Eg: 1 GAM of C-12 is 12 g

1 GAM of oxygen is 16 g

Molecular mass

- The number showing how many times the mass of a molecule is heavier than $1/12$ th the mass of C-12 atom.

- Molecular mass =
$$\frac{\text{mass of a molecule}}{1/12^{\text{th}} \text{ mass of C-12 atom}}$$

- Eg: Molecular mass of $\text{O}_2 = 2 \times 16 \text{ u} = 32 \text{ u}$

Gram molecular mass

- Molecular mass expressed in grams is called gram molecular mass (GMM) or gram molecule or gram mole.

Eg: 1 GMM of water is 18 g.

Average atomic mass

- Atomic masses of most of the elements are non- integral values because we get weighted average of the atomic masses.

- Average atomic mass = $\Sigma (\% \text{ Abundance of the isotope} \times \text{Isotope mass})$

100

Mole concept

- One mole is defined as the amount of the substance which contains as many particles/entities as there are atoms in exactly 12 g of C-12.
- Number of particles in one mole of a substance is equal to 6.022×10^{23} and this number is known as Avogadro number.

Molar volume

- The volume occupied by one mole of a gas at a given temperature and pressure is called molar volume.
- Any gas occupies 22.414 L (dm^3) at STP. Thus, the molar volume at STP is 22.414 L

Equivalent weight/ Equivalent mass

- It is defined as the number of parts by mass of the element which combines or displaces with 1.008g of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine or one equivalent mass of any other element.
- Equivalent mass of an element = $\frac{\text{Atomic mass}}{\text{Valency}}$
- Equivalent mass expressed in grams is known as gram equivalent mass or gram equivalent or one equivalent of the substance.

Equivalent mass of an acid

- It is the number of parts by mass of the acid which contains 1.008 parts by mass of replaceable hydrogen .
- Equivalent mass of an acid = $\frac{\text{Molecular mass}}{\text{Basicity}}$

Basicity

- HCl contains one replaceable hydrogen atom. So, its equivalent mass is molecular mass itself.
- In the case of sulphuric acid (H_2SO_4) there are 2 replaceable hydrogen atoms. Thus it is a dibasic acid. so its equivalent mass = $\frac{\text{molecular mass}}{2}$

2

Equivalent mass of a base

- It is defined as number of parts by mass of the base required to neutralize one equivalent of an acid.

- Equivalent mass of base = $\frac{\text{molecular mass}}{\text{Acidity}}$
- The number of hydrogen ions with which one molecule of a base reacts is called its acidity. It is also equal to number of hydroxyl ions produced by one molecule of a base in aqueous solution.

Equivalent mass of an oxidising agent

- The number of parts by mass of an oxidising agent that gives one equivalent of oxygen (8 g) for oxidation or that which gets reduced with one mole of electrons.
- Equivalent mass of an oxidising agent = $\frac{\text{Molecular mass}}{\text{No. of electrons gained per molecule}}$
- Equivalent mass of an oxidant = $\frac{\text{molecular mass}}{\text{Decrease in oxidation number during the redox reaction}}$

Equivalent mass of a reducing agent

- It is the number of parts by mass of reducing agent which can be oxidised by one equivalent of oxygen or which furnishes one mole of electron for reduction.
- Equivalent mass of reducing agent = $\frac{\text{Molecular mass}}{\text{No. of electrons furnished per molecule}}$
- Equivalent mass of a reductant = $\frac{\text{Molecular mass}}{\text{Increase in oxidation number during the redox reaction}}$

Methods of expressing concentration of a solution

a) Molarity(M)

It is the number of moles of solute in one litre (dm³) of the solution.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of the solution in litres}}$$

$$\text{Molarity} = \frac{n_2}{V}$$

$$n_2 = \frac{\text{Mass of the solute (w}_2\text{)}}{\text{Molecular mass of the solute (M}_2\text{)}}$$

$$M = \frac{w_2}{M_2 \cdot V}$$

b) Molality(m)

- It is the number of moles of the solute present per 1000g (1kg) of the solvent.

- Molality= $\frac{\text{Number of moles of the solute}}{\text{Mass in kg of the solvent}}$
 $= \frac{\text{Number of moles of the solute}}{\text{Mass in g of the solvent}} \times 1000$

$$m = \frac{n_2 \times 1000}{w_1}$$

$$m = \frac{w_2 \times 1000}{M_2 \times w_1}$$

c) Mole fraction

- Mole fraction of any component is the ratio of the number of moles of that component to the total number of moles of the solution.

- Mole fraction of the solvent, $x_1 = \frac{n_1}{n_1 + n_2}$

Mole fraction of the solute, $x_2 = \frac{n_2}{n_1 + n_2}$

n_1 and n_2 are the number of moles of solvent and solute respectively.

- $x_1 + x_2 = 1$

d) Normality(N)

- Number of gram equivalents of the solute present per litre(dm³) of the solution.
- Normality= $\frac{\text{weight/litre}}{\text{Equivalent mass}}$

$$N = \frac{w_2}{E_2 \times V}$$

w_2 = mass of the solute

E_2 = Equivalent mass of the solute

V = Volume in litre(dm³)

- The weight required to prepare a solution of normality N and volume V is

$$w = \frac{NEV}{1000}$$

- Molality and normality depends on volume. As temperature changes volume changes. So, molarity and normality change on change of temperature. Mole fraction and molality are temperature independent.

Calculation of Normality of solution upon change of volume

- If 'V₁' is the volume of a solution and 'N₁' is the normality of a solution and let the volume changes to V₂, normality changes to N₂.

Then, $N_1V_1 = N_2V_2$

PART II-OXIDATION AND REDUCTION

- Oxidation is a process in which a species (atom/molecule/ion) losses electron.
- Reduction is a process in which a species gains electron.
- Oxidising agent is an electron gainer and reducing agent is an electron donor.

OXIDATION NUMBER

- It is the formal charge which an atom of an element appears to have when the electrons are counted according to the following rules.
 1. Electron shared between two like atoms(electronegativity same) are divided equally between atom.
 2. Electron shared between two unlike atoms are counted with more electronegative atom.

Rules for determining oxidation number

1. The oxidation number of elements in combined atom is zero.
2. Oxidation number of fluorine is -1. Halogens also have -1 oxidation number when bonded to less electronegative atom.
3. First group elements have oxidation number +1 (alkaline metal) and alkaline earth metals is +2 in their compounds.
4. Oxidation number of hydrogen in compounds is +1 except ionic hydrides.
5. Oxidation number of oxygen is -2 in compounds except peroxides where it is -1. In super oxides (KO₂) oxidation number of oxygen is -1/2, in F₂O it is +2 and in F₂O₂ it is +2.
6. In a molecule, the sum of oxidation number of all atoms is zero.
7. The oxidation number of ion is equal to charge of the ion.

Oxidation number concept for oxidation and reduction

- In oxidation, oxidation number increases and in reduction, oxidation number decreases.
- Oxidising agent is a substance whose oxidation number decreases and reducing agent is a substance whose oxidation number increases.

PART-III SOME ANALYTICAL CHEMISTRY TOPICS

1. THEORY OF VOLUMETRIC ANALYSIS

- **Volumetric analysis:** determination of volume of a solution of known concentration
- **Titration:** process carried out to determine the concentration of analyte solution.
- **Equivalence point:** point at which reaction is just completed in a titration
- **Indicator:** substance used to indicate the completion of the reaction
- **End point:** point of completion of reaction determined using an indicator.
- **Titre value:** the value obtained after titration.
- **Standard solution:** solution of accurately known concentration

Primary standards	Secondary standards
◆ Compound from which a standard solution can be prepared by direct weighing of a quantity followed by dilution to definite volume ◆ Examples: Na_2CO_3, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, Mohr's salt, $\text{K}_2\text{Cr}_2\text{O}_7$	◆ A substance from which direct preparation of standard solution is impossible but can be used as standard solutions if their concentrations are previously determined. ◆ Examples: NaOH, HCl, H_2SO_4, KMnO_4

Properties of a primary standard

- It must be easy to obtain, to purify, to dry and to preserve in pure state
- It should not be hygroscopic or deliquescent and must be stable in air
- Its composition should remain unaltered during storage
- It should have relatively high molar mass

- Substance must be readily soluble in water

(A) ACID-BASE TITRATIONS

- Titration in which acid solutions are titrated against standard alkali solutions and vice versa
- Acidimetry: titration of free bases against standard acid
- Alkalimetry: titration of free acids against standard base
- Neutralization reactions

Acid base indicators:

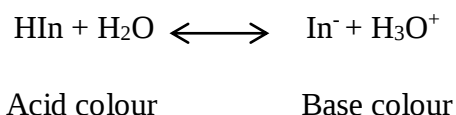
- Substances employed for visual detection of end point.
- They can change colour with changes in pH

Indicator	pH range and colour change
Thymol blue	← Red (1.2-1.8) yellow →
Methyl orange	← Red (3.1- 4.4) yellow →
Methyl red	← Red (4.2-6.3) yellow →
Bromothymol blue	← yellow (6.0-7.6) blue →
Cresol red	← yellow (7.2-8.8) red →
Phenolphthalein	← colourless (8-9.5) pink →
Alizarin yellow	← yellow (10.1-12) red →

Theories of acid base indicators:

a) Ostwald theory

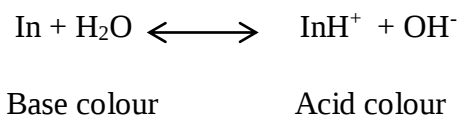
- An acid base indicator is a weak organic acid or weak organic base which has one colour in ionized form and another colour in unionized form
- Behavior of an acid type indicator



- The ionization constant (indicator constant) given by

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

- Behavior of base type indicator



- The ionization constant (indicator constant) given by

$$K_{In} = \frac{[InH^+][OH^-]}{[HIn]}$$

i. Action of phenolphthalein

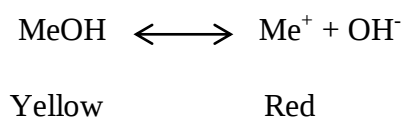
- Ionization equilibrium of phenolphthalein is given by



- In acidic solution presence of excess H_3O^+ ion suppresses the dissociation of phenolphthalein and the equilibrium lies very much to the left (HPh is practically unionized) and solution will be colourless.
- In alkaline solution excess OH^- will remove the H_3O^+ ions formed by dissociation of HPh and equilibrium lies very much to the right, resulting in accumulation of Ph^- (pink colour)

ii. Action of methyl orange

- Ionization equilibrium of phenolphthalein is given by

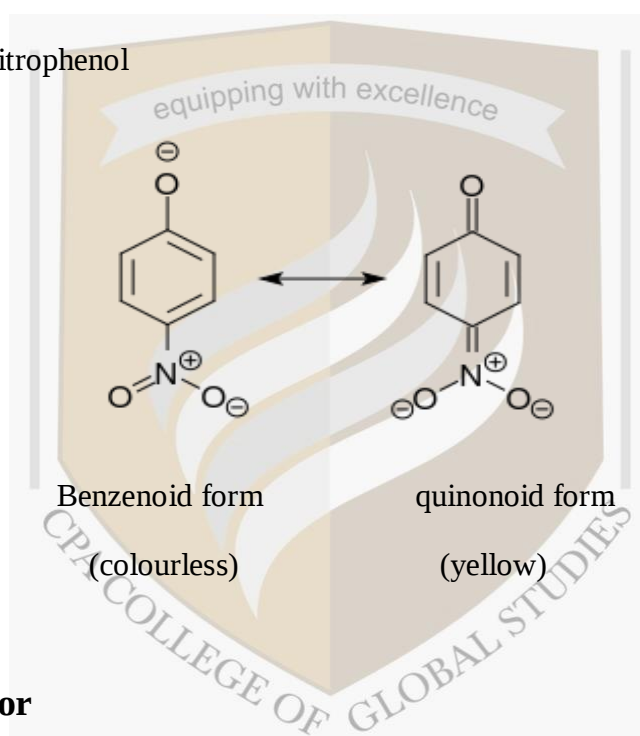


- In alkaline solution excess OH^- will suppresses ionization of methyl orange and equilibrium lies very much to left (yellow).

- In acidic solution excess H_3O^+ ions present combines with OH^- ions formed by dissociation of MeOH and hence equilibrium lies to right (red colour)

b) Quinonoid theory

- Acid base indicators exist as an equilibrium mixture of two tautomeric forms possessing different colours.
- Light coloured benzenoid form and bright coloured quinonoid form.
- One form exists in acid solution and the other in alkaline solution, imparting the corresponding colour to the solution.
- Example: 4-nitrophenol



Choice of indicator

Type	pH range	Indicators
Strong acid – strong base	4-10	Methyl red (4.2-6.3) Phenolphthalein(8-9.5) Methyl orange(3.1-4.4)
Weak acid – strong base	6.5-10	Phenolphthalein(8-9.5)
strong acid – weak base	3-7	Methyl orange(3.1-4.4) Methyl red (4.2-6.3)
Weak acid- weak base	No sharp point	Mixed indicators(neutral red – methylene blue)

B) REDOX TITRATIONS

- Redox reactions: chemical reactions which involve oxidation and reduction
- Redox titrations: oxidizing agents are titrated against reducing agents

a) Titrations involving potassium permanganate – Permanganometry

- Redox titrations which involve titration of potassium permanganate as the oxidant against reductants
- KMnO_4 is a powerful oxidizing agent in acidic medium and gets reduced to colourless manganous ion in redox reactions.



- Here reductants used are oxalic acid, oxalate, ferrous nitrate, sulphite, hydrogen peroxide etc.,
- KMnO_4 is a self-indicating agent.
- Example: hot oxalic acid can be titrated against KMnO_4 in presence of dilute H_2SO_4
- As KMnO_4 is not a primary standard it is standardized using standard oxalic acid or Mohr's salt solutions

b) Titrations involving potassium dichromate – dichrometry

- Redox titrations which involve titration of potassium dichromate as the oxidant against reductants
- $\text{K}_2\text{Cr}_2\text{O}_7$ is a powerful oxidizing agent in acidic medium and get reduced to green Cr^{3+}
- Here reductants used are ferrous sulphate, nitrate, sulphite, etc.,
- $\text{K}_2\text{Cr}_2\text{O}_7$ is a primary standard
- There are two methods for detection of end point in dichrometry of potassium dichromate against ferrous sulphate

i. External indicator method

- End point is detected externally by testing a drop of the solution with potassium ferricyanide.
- Ferrous ions give blue colour with ferricyanide. But at the end point no ferrous ions are present and test drop give no blue colour

ii. Internal indicator method

- End point is detected using suitable indicators
- Examples: N-phenyl anthranilic acid, diphenyl amine, sodium diphenylamine sulphonate

Redox indicators

- It is one which marks the end point of a redox titration by undergoing a colour change in response to the sudden change in potential that occur in the vicinity of the equivalence point
- Examples:
 - a. N-phenyl anthranilic acid (colourless to violet)
 - b. diphenyl amine (colourless to violet)

c) Titrations involving iodine and liberated iodine–iodimetry and iodometry

- Both involve titrations in which oxidizing agent is iodine.
- Iodimetry: direct titration of standard solution of iodine against a reducing agent
- Iodometry : titration of iodine liberated from a chemical reaction with a reducing agent.
- Reducing agents used are sodium thiosulphate, arsenious oxide, sodium arsenite etc.,
- Indicator used is starch solution, which is added near the end point so that the colour changes from blue to colourless at end point

(C) COMPLEXOMETRIC TITRATIONS

- Titrations are those which generally involve titrations of cations with suitable chelating agents.
- Chelating agents are multidentate ligands
- Most widely used chelating agent is EDTA(Ethylenediaminetetraacetic acid) – a hexadentate ligand
- EDTA is used as a titrant for the detection of various metal ions like Zn^{2+} , Mg^{2+} , Ca^{2+}
- Indicators used are Eriochrome black T (wine red to blue), murexide, calmagite etc.,

Double burette method of titration

- It makes use of two burettes

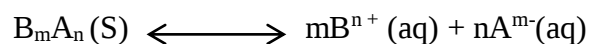
Advantages:

- Mouth pipetting can be avoided
- Saves significant amount of chemicals
- Only one drop indicator is needed and hence can use costly indicators for accurate results
- Saves time
- Since method is graphical more accurate result is obtained

2. PRINCIPLES IN SEPERATION OF CATIONS IN QUALITATIVE ANALYSIS

a) Solubility product

- Product of molar concentrations of its ions in a saturated solution of it at a given temperature
- Suppose a sparingly soluble salt B_mA_n is vigorously stirred with water, the equilibrium reaction will be



Equilibrium constant

$$K = \frac{[B^{n+}]^m [A^{m-}]^n}{[B_m A_n]}$$

$B_m A_n$ is a constant, therefore

Solubility product, $K_{sp} = [B^{n+}]^m [A^{m-}]^n$

b) Ionic product

- Product of molar concentrations of the constituent ions of a substance present in a solution of it at a given temperature.
- The precipitation of an ionic substance from solution occurs when the ionic product exceeds the value of its solubility product of the substance at that temperature.

c) Common ion effect

- The suppression of ionization of a weak electrolyte on the addition of a strong electrolyte containing a common ion.

d) Principles in the separation of cations in qualitative analysis

- Qualitative analysis is based on the principle of selective precipitation.
- Making use of principles of solubility product and common ion effect, a specific scheme has been prepared for the separation and analysis of cations through their selective precipitation

<i>Group</i>	<i>Cations</i>	<i>Group reagents</i>	<i>Precipitated as</i>
I	$Hg^+ Ag^+ Pb^{2+}$	Dil.HCl	Chlorides
II	$Hg^{2+} Bi^{3+} Cu^{2+} Cd^{2+}$	Dil.HCl + H_2S	Sulphides
III	$Al^{3+} Cr^{3+} Fe^{2+} Fe^{3+}$	$NH_4Cl + NH_4OH$	Hydroxides

IV	$\text{Co}^{2+} \text{ Ni}^{2+} \text{ Mn}^{2+} \text{ Zn}^{2+}$	$\text{NH}_4\text{Cl} + \text{NH}_4\text{OH} + \text{H}_2\text{S}$	Sulphides
V	$\text{Ba}^{2+} \text{ Sr}^{2+} \text{ Ca}^{2+}$	$\text{NH}_4\text{Cl} + \text{NH}_4\text{OH} + (\text{NH}_4)_2\text{CO}_3$	Carbonates
VI	$\text{Mg}^{2+} \text{ Na}^+ \text{ K}^+ \text{ NH}_4^+$		

e) Microanalysis and its advantages

- Quantitative and qualitative analysis of micro level.
- It promotes a green approach
- Example : spot tests

Advantages:

- Reduce cost of chemicals and equipments.
- Reduce consumption of chemicals and reduces wastage
- Minimizes environmental pollution
- Reduced health risks to analytes
- Reduces breakage of glasswares
- Reduces time
- Reduces storage area

3. COMPARISON OF RESULTS IN QUANTITATIVE ANALYSIS

a) True or most probable value

- There exists a degree of uncertainty with every type of measurement. Thus *true value* of a measurement can never be known with absolute certainty.
- The average of best results obtained by efficient and experienced workers are accepted as *most probable value* and generally it is taken as *true value*

b) Accuracy and precision

- *Accuracy* is the concordance between the observed value and the most probable value (accepted correct value)
- *Precision* is the concordance of a series of measurements of the same quantity.

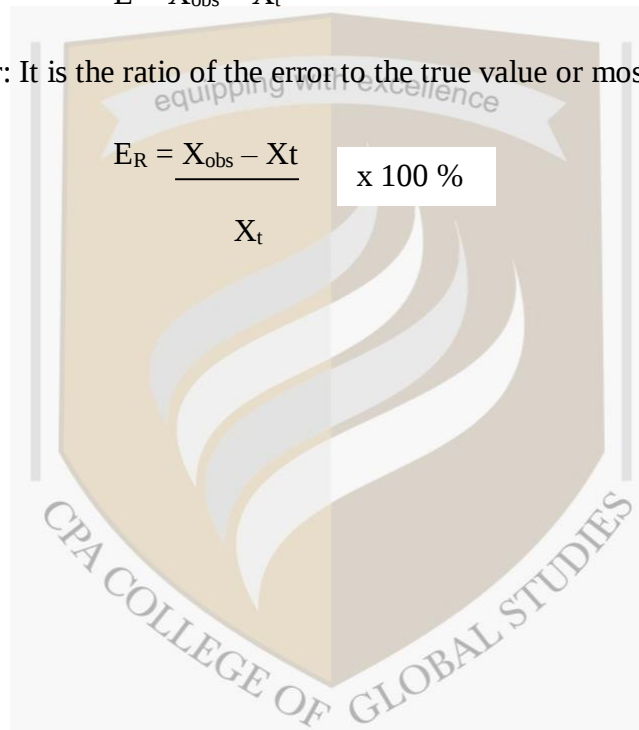
c) Errors

- Absolute error: difference between the observed value and the most probable value of the quantity measured.

$$E = X_{\text{obs}} - X_t$$

- Relative error: It is the ratio of the error to the true value or most probable value

$$E_R = \frac{X_{\text{obs}} - X_t}{X_t} \times 100 \%$$



MODULE-2- ATOMIC STRUCTURE AND CHEMICAL BONDING

BOHR ATOM MODEL

The main postulates of Bohr's atomic theory are:

1. The electrons revolve around a heavy positive central nucleus with a definite velocity in circular paths of fixed radius and energy. These circular paths are called orbits or stationary states.
2. The energy of revolving electrons remain constant while moving in a particular orbit. Since, each orbit is associated with a definite amount of energy, they are also called energy levels.
3. Only those orbits are permitted whose angular momentum is an integral multiple of $h/2\pi$. where h is the Planck's constant.

$$mvr = n \frac{h}{2\pi}$$

where, n = Principal quantum number

m = mass of electron

v = velocity of electron

r = radius of orbit.

4. Energy of electron increases with increasing distance from the nucleus.
5. An electron may jump from lower orbit (E_1) to higher one (E_2) by absorbing one quantum of energy or it may jump from higher orbit to lower one by emitting one quantum of energy. The frequency of radiation absorbed (ν) is

$$\begin{aligned}\nu &= \Delta E / h \\ &= E_2 - E_1 / h\end{aligned}$$

The above expression is called Bohr frequency rule.

The energy levels or shells with $n=1,2,3,4...$ are respectively called as K, L, M, N

Shells.

Explanation of line spectrum of Hydrogen

- When a solid element is heated or when electricity is passed, light is emitted from them. When this light is resolved using a spectroscope, a discontinuous spectrum is obtained. The spectrum consists of a series of lines. Each line correspond to a particular wavelength. This is known as line spectrum.
- The Hydrogen spectrum consist of 5 series of lines appearing in different regions of electromagnetic spectrum. They are

Series	n_1	n_2	Appearance
Lyman Series	1	2,3,4...	UV region
Balmer Series	2	3,4,5...	Visible region
Paschen series	3	4,5,6...	IR region

Brackett series	4	5,6,7...	IR
Pfund series	5	6,7,8...	IR

- The wave number of lines in the series is given by Rydberg formula

$$\bar{\nu} = 1/\lambda = R_H [1/n_1^2 - 1/n_2^2]$$

where, R_H = Rydberg constant ($1.097 \times 10^7 \text{ m}^{-1}$)

- When energy is supplied to hydrogen atom, the electron in the ground state may absorb one quantum of energy and jump into higher energy level. When this electron returns to the lower level it emits radiation of definite frequency. Each transition causes the formation of lines of that frequency in the spectrum.
- Bohr's theory can also explain the line spectrum of hydrogen-like atomic species like He^+ and Li^{2+} ions.

Limitations of Bohr's theory

- Bohr's theory cannot explain the formation of fine spectrum of hydrogen.
- It cannot explain the complex line spectra of elements whose atoms contain several electrons.
- It cannot explain the details of bond formation and also the shapes of molecules.
- Bohr's assumption that electrons revolve in well-defined orbits around the nucleus is against de-Broglie's concept and Heisenberg's uncertainty principle.
- Bohr's theory cannot explain Zeeman effect and Stark effect.

De-Broglie equation

- Matter shows wave character in addition to particle nature. This is referred to as wave-particle duality of matter and the proposal is called de-Broglie hypothesis.
- The equation which relates wave properties to particle properties is called de-Broglie equation.

$$\lambda = h/mv$$

where λ = Wave length of particle

m = mass of particle

v = velocity of particle.

mv = P , momentum of the particle

$$\lambda = h/P$$

Significance of the de Broglie equation

- For moving macroscopic objects, mass is very large, so the wavelength is negligibly small and its wave properties cannot be observed.
- For moving microscopic particles, mass is extremely small, so the wavelength would be considerably high. It shows wave character significantly.

Derivation of de Broglie equation

- The energy of a photon, $E = h\nu = hc/\lambda$ _____ (i)

Where ν , c and λ are the frequency, velocity and wavelength of radiations respectively.

Einstein's mass- energy relationship is $E = mc^2$. _____ (ii)

From (i) and (ii)

$$hc/\lambda = mc^2$$

$$\lambda = h/mc$$

de Broglie argued that the above equation can be applied to matter also. So, velocity of light, c can be replaced with velocity of particle, v

$$\lambda = h/mv$$

OR

$$\lambda = h/p$$

- Electron possess wave nature and particle nature.

Heisenberg's uncertainty principle

- It states that "it is impossible to determine simultaneously the position and momentum (or velocity) of a small moving particle like electron at any given instant with absolute certainty".
- Mathematically, it can be expressed as

$$\Delta x \times \Delta p_x \geq h/4\pi$$

Δp_x is the uncertainty in momentum along x- direction.

Δx is the uncertainty in position.

$$\text{But, } p_x = mv_x$$

If Δv_x is the uncertainty in velocity, then

$$\Delta x \times m\Delta v_x \geq h/4\pi$$

Significance of the uncertainty principle

- Bohr had predicted well defined paths or orbits for electrons to revolve around the nucleus. The path of any revolving object is determined by its position and velocity. But according to Heisenberg uncertainty principle, it is impossible to determine both position and velocity simultaneously. So, this principle rules out the existence of definite paths or trajectories for moving subatomic particles.

Schrodinger wave equation

- Schrodinger proposed a wave equation describing the electron's motion analogous to that used to describe a standing wave system. This equation is called Schrodinger wave equation.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

Second derivative with respect to Z Schrodinger wave Function
 Position Energy Potential Energy

- Ψ is a measure of the amplitude of the matter wave.
- Significance of ψ and ψ^2 - the wave function ψ is the measure of amplitude and has no physical significance. The square of the wave function $|\psi|^2$, is known as probability density and is proportional to probability of finding the particle within the space.
- The wave function for an electron is found by solving Schrodinger wave equation and the acceptable values of ψ can be obtained only for certain energies. Thus, energy of an electron is quantized.

ORBITALS

- Orbital is a three dimensional region of space around the nucleus where there is maximum probability of finding an electron.
- All orbitals except s-orbital have directional character.

QUANTUM NUMBERS

- They are a set of numbers which specify the location and energy of electron in an atom.

i) Principle Quantum number(n):

- It denotes the main energy level in which the electron is present
- It specifies the average distance of electron from the nucleus.
- Greater the value of n, higher the energy and farther will be the electron from the nucleus.
- The value of n=1,2,3(positive integer).

ii) Azimuthal Quantum number(l)

- It specify the orbital angular momentum of electron.
- It can have values from 0 to n-1.
- It denotes the subshell in which the electron is present.

iii) Magnetic Quantum number(m)

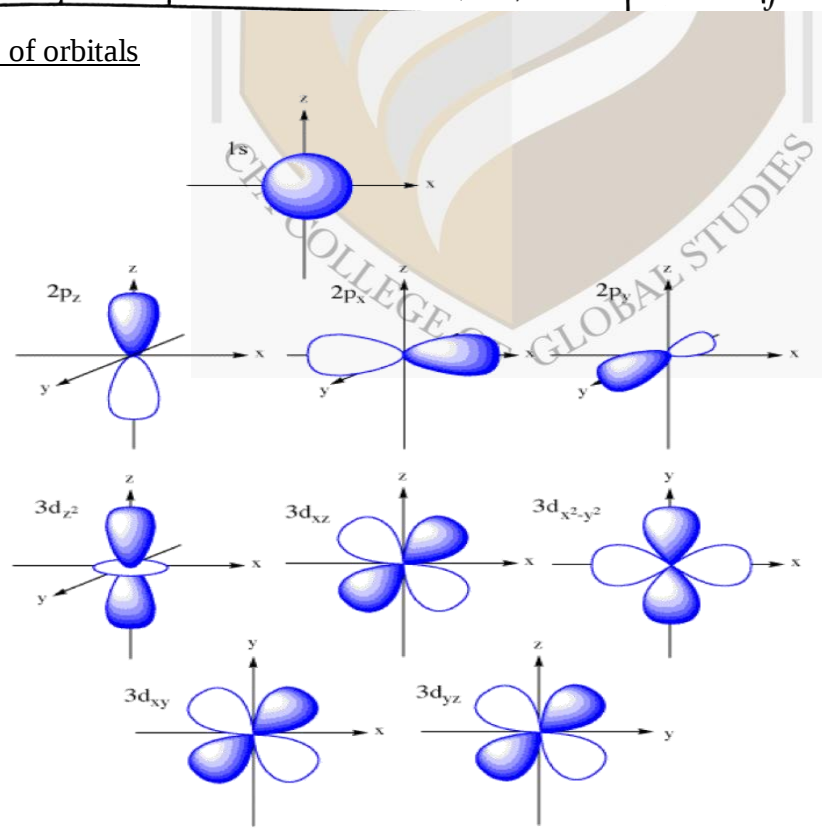
- It specify the spatial orientation of electron in a magnetic field.
- It can have $(2l+1)$ values ranging from $-l$ to $+l$ including zero.

iv) **Spin Quantum number(s)**

- It specifies the spin angular momentum of electron and its orientation in space.
- The possible values of 's' are +1/2 and -1/2 which correspond to clockwise and anti-clockwise spin.

n	l	m	Designation of the sublevel	No. of orbitals
1	0	0	1s	One
2	0	0	2s	One
	1	-1, 0, +1	2p	Three
3	0	0	3s	One
	1	-1, 0, +1	3p	Three
	2	-2, -1, 0, +1, +2	3d	Five
4	0	0	4s	One
	1	-1, 0, +1	4p	Three
	2	-2, -1, 0, +1, +2	4d	Five
	3	-3, -2, -1, 0, +1, +2, +3	4f	Seven

Shapes of orbitals



Electron arrangement in atoms

i) Pauli's exclusion principle:

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

Or

- An orbital can accommodate a maximum of 2 electrons only, and those two electrons should have opposite spin.

ii) Aufbau principle:

- In the ground state of an atom, electrons are filled into various orbitals in the increasing order of their energies.
- The order of orbitals in the increasing order of energies are
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p,

iii) Hund's rule of maximum multiplicity

- In the filling of orbitals of a degenerate set,
 - i) Electron pairing is not possible until all the orbitals of the set contain one electron each.
 - ii) The unpaired electrons in the orbitals of the set have parallel spins.

Stability of configuration with completely filled and half-filled orbitals

- Extra stability of half-filled and completely filled orbitals are due to the following reasons.
 - i) Greater the symmetry, higher is the stability. The completely filled and half-filled configurations are more symmetrical and higher is the stability.
 - ii) Greater the exchange energy, greater is the stability. Electrons with parallel spin in a given subshell can exchange their position mutually. During this process, some energy is released and this energy is called exchange energy.

Cr(24)- $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Cu(29)- $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

CHEMICAL BONDING

Ionic bond/ Electrovalent bond

- It refers to strong electrostatic force of attraction that hold together the oppositely charged ions formed by transfer of one or more electrons.

Eg: Formation of NaCl, $MgCl_2$.

Conditions favouring ionic bond formation:

- Low ionisation energy of electron-donating atom.
- A high value of electron affinity of the electron accepting atom.
- A large negative value of lattice energy of the compound formed.

- A large electronegativity difference between combining elements.

Lattice energy:

- Lattice energy of an ionic compound is the energy released when 1 mole of ionic compound is formed from its constituent ions.

Born-Lande equation

$$U^\circ = - \frac{N_0 A Z^+ Z^- e^2}{4\pi\epsilon_0 r_0} [1 - 1/n]$$

U° = Lattice energy

N_0 = Avagadro no.

A = Madelung constant.

n = Born exponent

r_0 = equilibrium distance between positive and negative ions in the crystal.

Z^+ and Z^- are positive integers representing +ve and -ve charges of cations and anions.

e = charge of electron

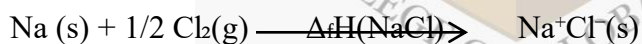
ϵ_0 = permittivity of free space

Born-Haber Cycle

- It is the thermochemical method of calculating lattice energy based on Hesse's law of constant heat summation.

Eg: Formation of NaCl

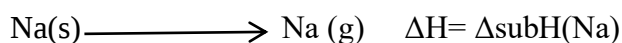
Thermochemical equation is



Enthalpy change during the formation of 1 mole of NaCl from the elements sodium and chlorine is known as enthalpy of formation of NaCl, $\Delta_f H(\text{NaCl})$.

The enthalpy change in each step is as follows

- 1) Sublimation of solid sodium metal to give sodium vapour.



The energy change is the enthalpy of sublimation.(positive value)

- 2) Formation of sodium ions from its gaseous atoms.



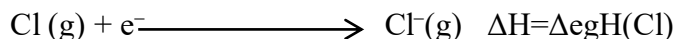
The energy change is the ionisation enthalpy.(positive value)

- 3) Dissociation of chlorine molecules to give chlorine atoms.



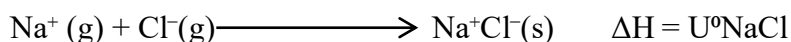
The energy change in this step is the bond dissociation enthalpy. (positive value)

- 4) Addition of an electron to chlorine atom to form chloride ion.



The energy change in this process is electron gain enthalpy. (negative value)

- 5) The formation of solid NaCl from the gaseous ions.



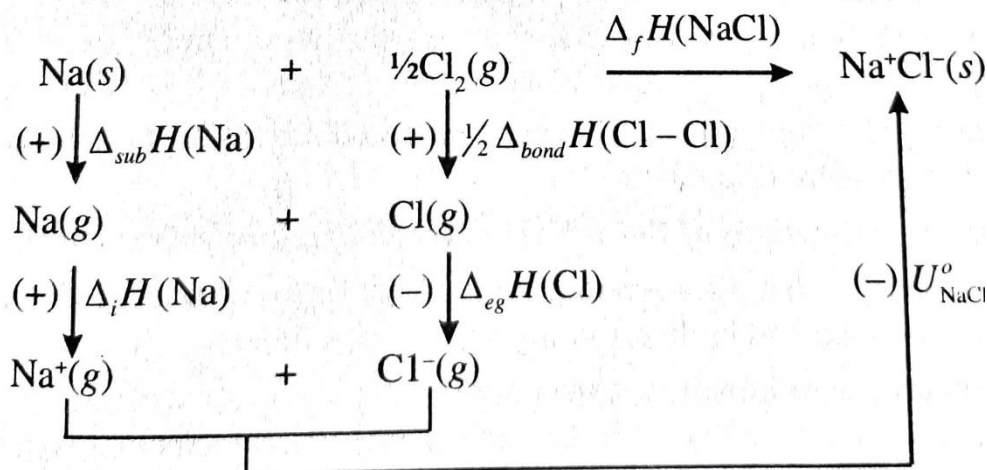
The energy change during this process is equal to lattice energy of sodium chloride. (negative value)

Applying Hesse's law,

$$\Delta_f H (\text{NaCl}) = \Delta_{\text{sub}} H(\text{Na}) + \Delta_i H(\text{Na}) + \frac{1}{2} \Delta_{\text{bond}} H(\text{Cl}_2) + \Delta_{\text{eg}} H(\text{Cl}) + U^\circ \text{NaCl}$$

$$\text{Or, } U^\circ \text{NaCl} = \Delta_f H(\text{NaCl}) - \Delta_{\text{sub}} H(\text{Na}) - \Delta_i H(\text{Na}) - \frac{1}{2} \Delta_{\text{bond}} H(\text{Cl}_2) - \Delta_{\text{eg}} H(\text{Cl})$$

The above steps can be expressed in the form of cycle



Application of lattice energy determination

- a) Determination of enthalpy of formation:

The enthalpy of formation of an ionic compound can be calculated with the help of Born-Haber cycle. The value of lattice energy is calculated using Born-Landé equation.

- b) Calculation of enthalpy of solution of ionic compounds:

When an ionic solute dissolves in water, there occurs breaking of crystal lattice and then hydration of ions occurs. Dissolution is an endothermic process and hydration of ions is an exothermic process.

Enthalpy of solution = -Lattice energy + sum of enthalpies of hydration of ions.

Knowing the lattice energy, the enthalpy of solution can be calculated.

- c) Lattice energy calculations determined using Born-Haber cycle help in estimating the stability of ionic compounds and helps in determining the stoichiometry.
- d) Lattice energy helps in accounting the stabilities of metal hydrides, polyhalides, peroxides, and superoxides.
- e) Lattice energy helps in evaluation of crystal field stabilization energies.
- f) It helps in predicting and comparing the solubilities of ionic compounds.
- g) It helps in determining the electron affinities of elements.

COVALENT BOND

Lewis theory-

- According to Lewis theory, atoms combine with each other by sharing one or more pair of electrons and they achieve stable octet configuration.
- A bond formed between two atoms by sharing a pair of electrons is called a covalent bond.

Eg: Formation of F_2 molecule.

COORDINATE BOND

- Bond formed between two atoms by sharing an electron pair which is contributed by one of the atoms is called coordinate bond or dative bond or donor- acceptor bond.

Eg: Interaction between ammonia and BF_3

VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR THEORY)

Features/Postulates

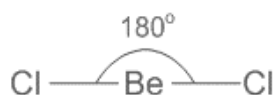
- Geometry of a molecule is determined by number of valence shell electron pairs around the central atom.
- Electron pairs in the valence shell repel each other.
- Valence shell electron pairs orient in such a way to minimize the repulsion.
- The valence shell is considered spherical and the electron pairs are assumed to localize on the spherical surface at maximum distance.
- The magnitude of electron pair repulsion is in the order
Lone pair-lone pair repulsion > lone pair- bond pair repulsion > bond pair- bond pair repulsion
These repulsions result in deviation from their shapes and bond angles.
- A multiple bond is treated as single bond.

Shapes of Molecules

a) Molecules containing bond pairs only-

1. BeCl₂

In BeCl₂, the central atom has 2 bond pairs and no lone pairs. The molecule is linear and the bond angle is 180°.



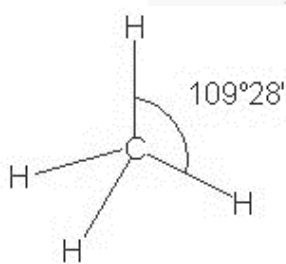
2. BF₃

In BF₃, the central atom has 3 bond pairs and no lone pairs. The molecule is trigonal planar with the bond angle 120°.



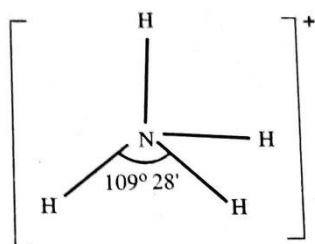
3. CH₄

In CH₄, the central atom has 4 bond pairs and no lone pairs. The molecule is tetrahedral with the bond angle 109°28'.



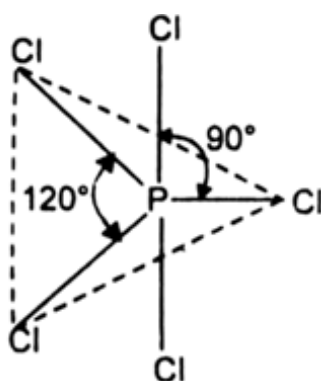
4. NH₄⁺

In NH₄⁺, the central atom N has 4 bond pairs and no lone pairs. The molecule is tetrahedral with bond angle 109°28'.



5. PCl_5

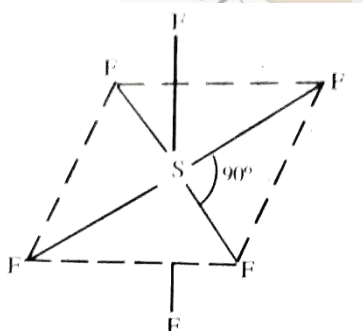
In PCl_5 , the central atom P has 5 bond pairs and no lone pairs. The molecule has trigonal bipyramidal shape. There are 2 types of bonds- axial and equatorial. The equatorial bond angles are 120° and the angle between equatorial and axial bond is 90° .



Trigonal bipyramidal

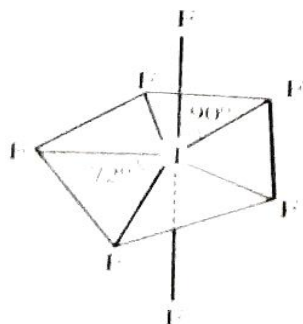
6. SF_6

In SF_6 , the central atom S has 6 bond pairs and no lone pairs. The molecule is octahedral and the bond angle is 90° .



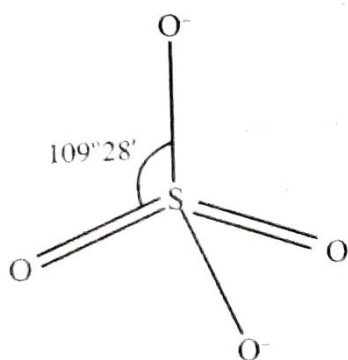
7. IF_7

In IF_7 , the central atom I has 7 bond pairs and no lone pairs. The molecule is pentagonal bipyramidal and the bond angle is 72° and 90° .



8. SO_4^{2-}

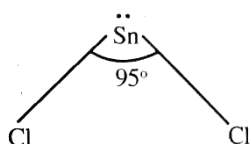
The central atom is S. In applying VSEPR theory, multiple bonds are considered as single bonds. So, there are four bond pairs and no lone pairs. The sulphate ion is tetrahedral with bond angle $109^\circ 28'$.



b) Molecules containing bond pairs and lone pairs

1. SnCl_2

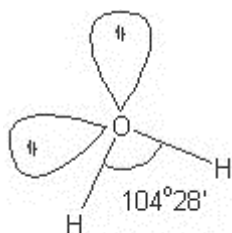
In SnCl_2 , there are 2 bond pairs and 1 lone pair around the central atom (Sn). According to VSEPR theory these tend to stay as far as possible to minimise repulsion. They tend to stay as far as possible to minimise repulsion. Hence, they arrange in trigonal planar fashion. But, since one corner is occupied by lone pair, and the l.p-b.p repulsion is greater than b.p-b.p repulsion the actual geometry is bent or angular shape (v-shape). Bond angle is 95° .



2. H_2O

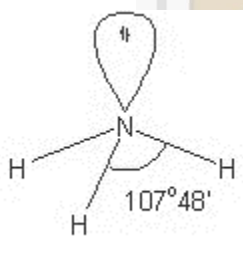
In H_2O , central atom is oxygen. There are 6 valence electrons- 2 bond pair and 2 lone pair around central atom. To minimise repulsion, they stay as far as possible and

arrange in tetrahedral manner. Since two corners are occupied by lone pairs, the actual geometry is bent or angular (V- shape). The bond angle decreases to $104^{\circ}27'$.



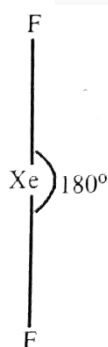
3. NH_3

In NH_3 , the central atom N has 5 valence electrons (3 b.p and 1 l.p). To avoid repulsion, they tend to stay as far as possible. They arrange themselves in tetrahedral manner. Since one corner is occupied by lone pair, the actual geometry is trigonal pyramidal. The bond angle decreases to 107° .



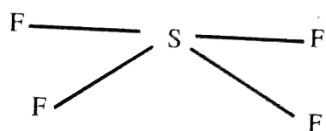
4. XeF_2

In XeF_2 , there are two bond pairs and three lone pairs around the central atom Xe. To avoid repulsion they tend to stay as far as possible and are arranged in trigonal bipyramidal manner. Lone pairs occupy equatorial positions and bond pairs are in axial position. The actual geometry of the molecule is linear with bond angle 180° .



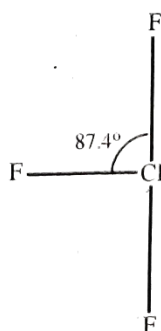
5. SF_4

In SF_4 , there are four bond pairs and one lone pair around the central atom S. To minimise the repulsion they tend to stay as far as possible and are arranged in trigonal bipyramidal fashion. The lone pairs occupy the equatorial position and the four bond pairs occupy two equatorial and two axial positions. The molecule is see-saw shaped.



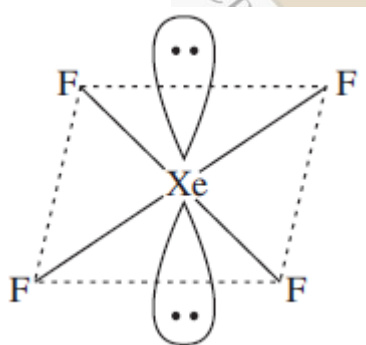
6. ClF_3

In ClF_3 , there are three lone pairs and two lone pairs around the central atom Cl. To minimise the repulsion they tend to stay as far as possible and are arranged in trigonal bipyramidal fashion. The two lone pairs occupy two equatorial position and 3 bond pairs occupy one equatorial and two axial positions. The molecule is T shaped. The bond angle between axial and equatorial bond is 87.4° .



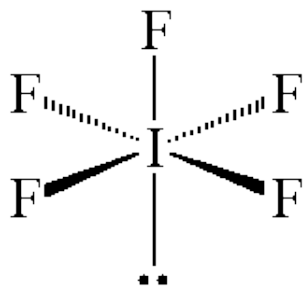
7. XeF_4

In XeF_4 , there are four bond pairs and two lone pairs around the central atom Xe. They tend to stay as far as possible to minimize the repulsion and are arranged in octahedral fashion. The 2 lone pairs occupy axial positions and four bond pairs are in four coplanar positions. The bond angle is 90° .



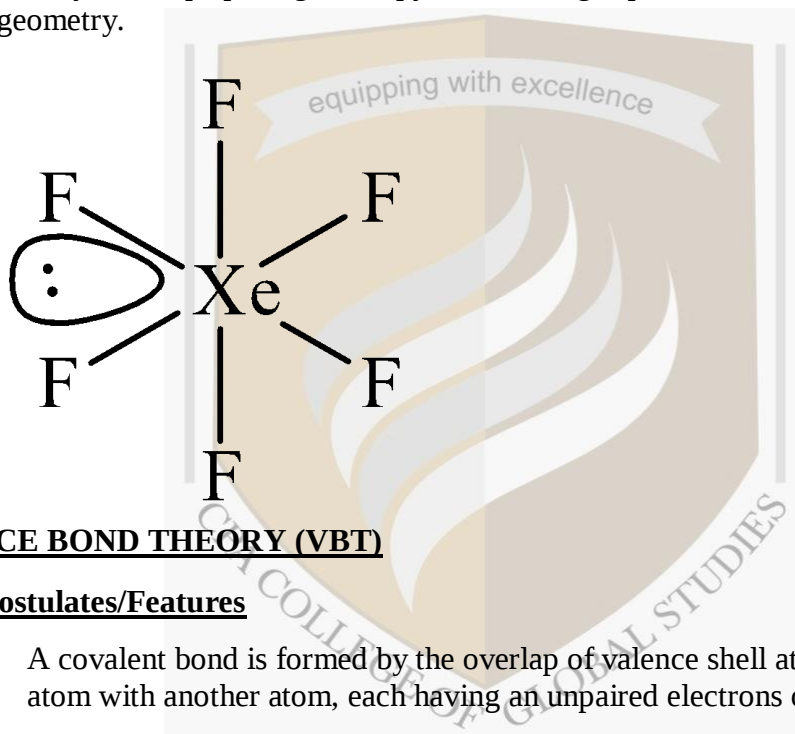
8. IF_5

In IF_5 , there are 5 bond pairs and one lone pair around the central atom I. They tend to stay as far as possible to minimize the repulsion and are arranged in octahedral fashion. One corner is occupied by lone pair, the actual geometry of the molecule is square pyramidal. The bond angle reduces to 81.9° .



9. XeF_6

In XeF_6 , there are 6 bond pairs and one lone pair around the central atom Xe. They tend to stay as far as possible to minimize the repulsion. According to VSEPR Theory, its shape pentagonal bipyramidal. In gas phase, it has distorted octahedral geometry.



VALENCE BOND THEORY (VBT)

- **Postulates/Features**

1. A covalent bond is formed by the overlap of valence shell atomic orbitals of one atom with another atom, each having an unpaired electrons of opposite spins.
2. The electron pairs occupy molecular orbitals (bond orbitals) formed by overlapping of atomic orbitals.
3. Overlapping causes maximum electron density between the nuclei of two atoms.
4. There is a fall of potential energy during overlapping. This stabilizes the system.
5. Strength of covalent bond is proportional to extend of overlapping.
6. Between two orbitals of same energy, the one more directionally concentrated would form stronger bonds.
7. The overlapping of orbitals with particular orientations give directional characteristics to the covalent bond.

- The positive overlap between the orbitals result in bonding interaction.
- The negative overlap corresponds to antibonding interaction.

- Zero overlap corresponds to non-bonding interaction.

Types of overlapping

- Depending on type of overlapping of atomic orbitals, covalent bonds are classified into two

i)Sigma bond-

- Formed by head on overlap/axial overlap/end-to-end overlap of atomic orbitals along internuclear axis.
- σ bond is a strong bond and is symmetrical around the axis.
- Sigma bond can be formed by s-s, s-p or p-p overlap.

ii)Pi bond

- It is formed by sideways /lateral/sidewise overlap of atomic orbitals.
- π bond is a weak bond.
- Pi bond is unsymmetrical about internuclear axis.
- Pi bond consist of two electron clouds, one above and one below the plane of atomic nuclei.

HYBRIDISATION

- The process of intermixing of various atomic orbitals of slightly different energies to yield a new set of orbitals of equivalent energy and shapes is called hybridisation.
- A hybrid orbital is a linear combination of atomic orbitals of the same atom.

Features of hybridisation

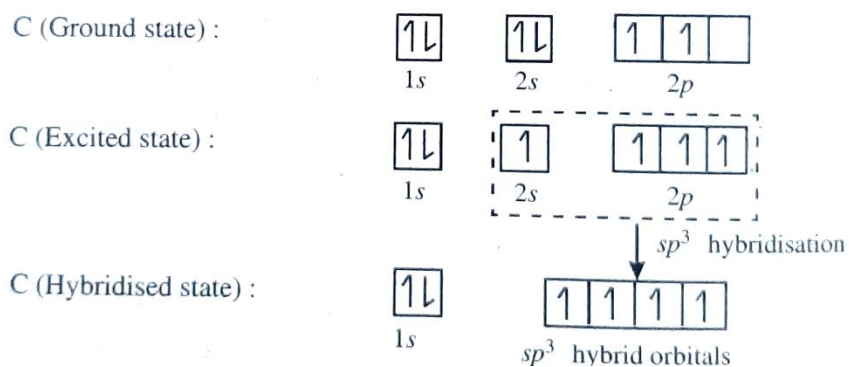
- Number of hybrid orbitals produced is equal to number of atomic orbitals taking part in hybridisation.
- Hybrid orbitals are equivalent in energy and shape.
- A hybrid orbital is better oriented than a pure orbital.
- Hybrid orbitals oriented in space such that there is least repulsion between electron pairs. The type of hybridisation determines the geometry of molecules.

sp³ hybridisation

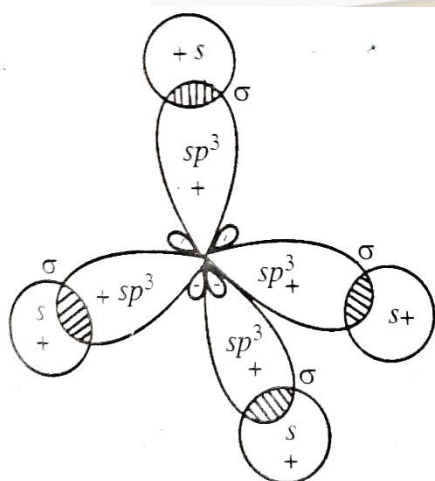
- The s and p orbitals of the valence shell of an atom mix with redistribution of energy.

Eg: Methane(CH₄)

- Central atom is carbon. Ground state electronic configuration is $1s^2 2s^2 2p^2$.
- For attaining valency four, one of the 2s electron is promoted to 2p orbital to give an excited state. Then the 2s and three 2p orbitals undergo hybridisation to form four new sp³ hybrid orbitals.



- The four hybrid orbitals are equivalent in energy and shape. They are arranged in tetrahedral manner. These orbitals overlap with 1s orbital of hydrogen to form four C-H sigma bonds.
- Thus, CH_4 molecules has tetrahedral geometry with bond angle $109^\circ 28'$.

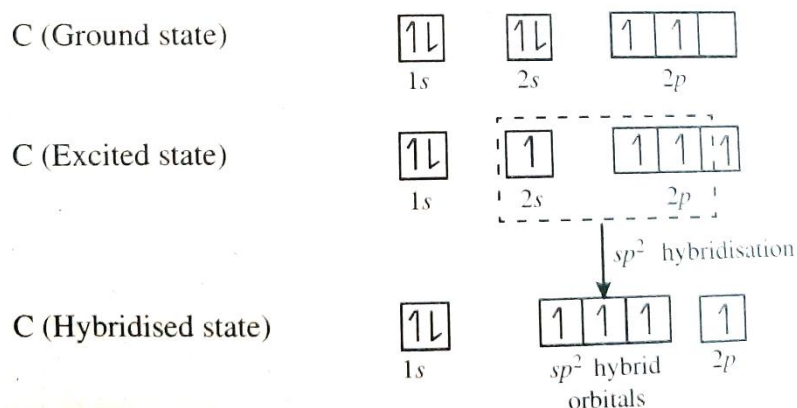


sp^2 hybridisation

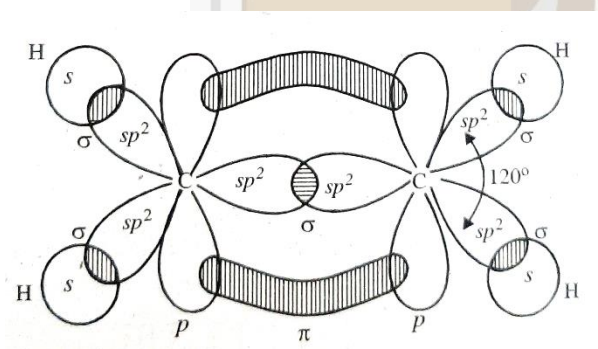
- The s and two p orbitals (p_y and p_z) of valence shell of an atom mix with redistribution of energy.

Eg: Ethelene(C_2H_4)

- Ground state electronic configuration of C is $1s^2 2s^2 2p^2$.
- During excited state, one electron from 2s orbital is promoted to vacant 2p orbital.
- The 2s and two 2p orbitals mix to form three new sp^2 hybrid orbitals.



- The hybrid orbitals are oriented in planar triangular fashion and unhybridised p-orbital lie perpendicular to the plane containing hybrid orbitals.
- One of the sp^2 orbitals overlap with sp^2 orbital of other C atom forming C-C sigma bond. The remaining two sp^2 hybrid orbitals on each C atom overlap with 1s orbital of H forming four C-H sigma bonds.
- The unhybridised p-orbital containing unpaired electron overlap in sidewise manner to form pi bond.

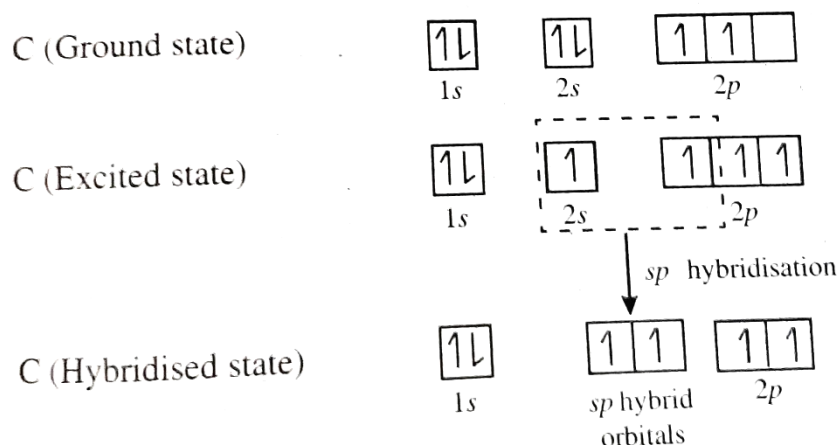


sp hybridisation

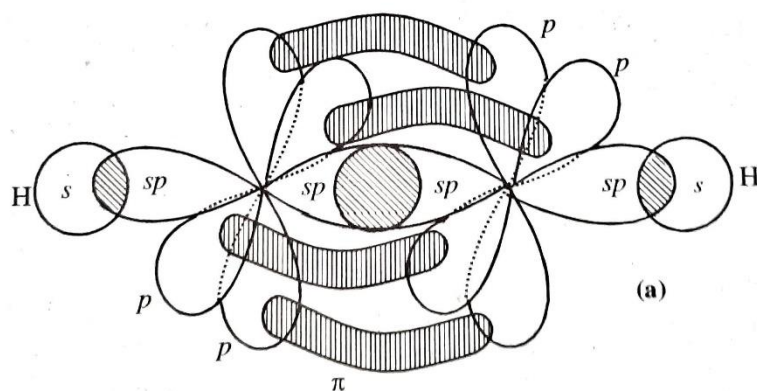
- One s and one p orbital overlap with redistribution of energy to form sp hybrid orbital.

Eg: Acetylene(C_2H_2)

- Ground state electronic configuration of C is $1s^2 2s^2 2p^2$.
- During excited state, one electron from 2s orbital is promoted to vacant 2p orbital.
- The 2s and one 2p orbital mix to form two sp hybrid orbitals.



- The hybrid orbitals are oriented in linear fashion. The two unhybridised p- orbitals lie perpendicular to the plane containing hybrid orbitals.
- One of the *sp* orbital of one carbon overlap with *sp* orbital of other carbon to form C-C sigma bond. The remaining *sp* orbitals on each C atom overlap with 1s orbital of H to form two C-H sigma bonds.
- The two unhybridised p-orbital on each carbon atom overlap in sidewise manner to form two pi bonds.

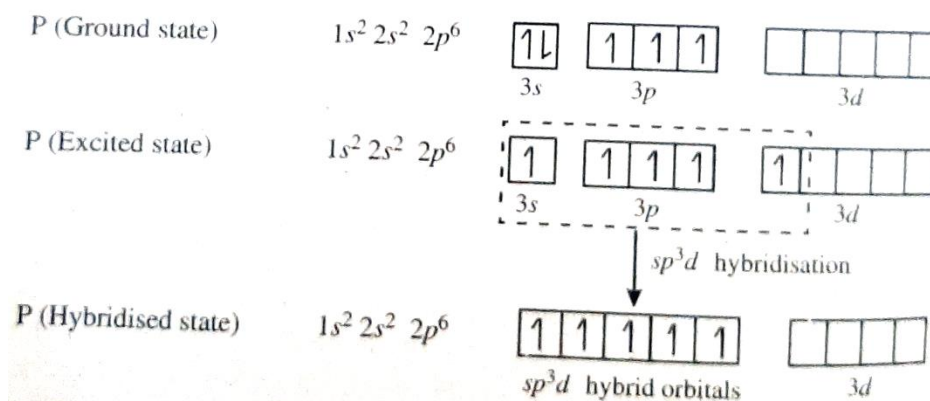


sp³d hybridisation

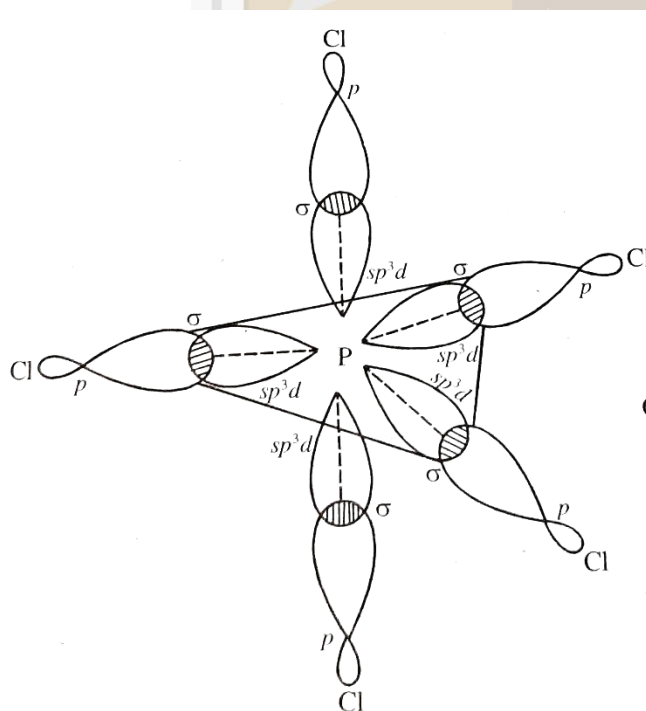
- One s, three p and one d orbital overlap to form 5 sp³d hybrid orbitals.

Eg: PCl₅

- The ground state electronic configuration of P (15) is $1s^2 2s^2 2p^6 3s^2 3p^3$.
- During excited state, one electron from 3s is promoted to vacant d- orbital.
- The 3s, 3p and one of 3d orbital mix together to form five sp³d orbitals.



- The five sp^3d hybrid orbitals are oriented in trigonal bipyramidal manner making bond angle 120° and 90° .
- The hybrid orbitals overlap with 3p orbital of chlorine atom to form 5 P-Cl sigma bonds. Out of these, three P-Cl bond lie in triangular plane making bond angle 120° . They are called equatorial bonds. The remaining two bonds are perpendicular to the equatorial plane. They are called axial bonds.



- Repulsive interaction between axial and equatorial bond pairs are greater. Therefore, axial bonds are longer and weaker than equatorial. Therefore, PCl_5 is a reactive molecule.

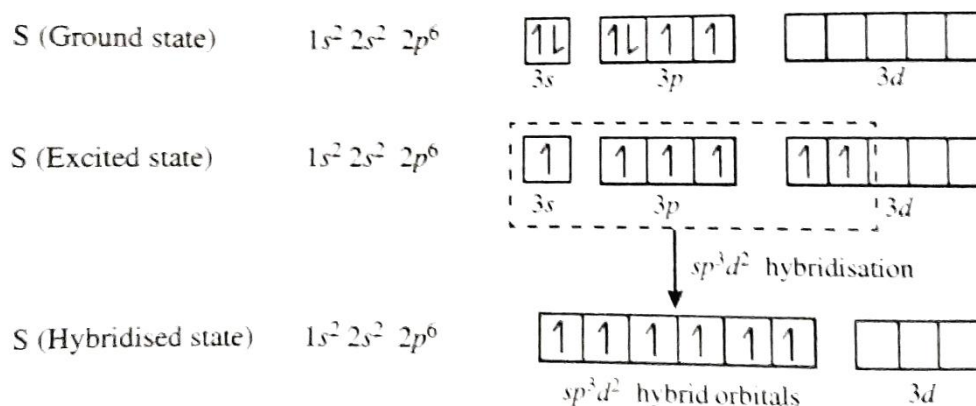
sp^3d^2 hybridisation

- One s, three p and two d-orbitals overlap to form six sp^3d^2 hybrid orbitals.

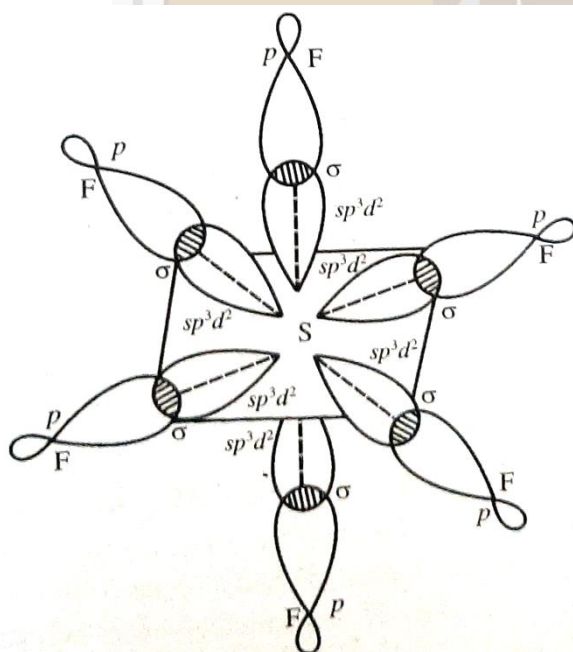
Eg: SF_6

- The ground state configuration of S(16) atom is $1s^2 2s^2 2p^6 3s^2 3p^4$

- During excited state, one electron from 3s and 3p is promoted to vacant d- orbital. Then, the 3s, 3p and two 3d orbitals mix to form six sp^3d^2 hybrid orbitals.



- The six sp^3d^2 hybrid orbitals are oriented in octahedral manner making bond angle of 90° .
- The six hybrid orbitals overlap with 3p orbital of F atom to form six S-F sigma bonds.



MOLECULAR ORBITAL THEORY (MOT)

- Describes covalent bonds in terms of molecular orbitals.

Basic concepts/postulates of MOT

- When nuclei of 2 atoms come close, their atomic orbitals interact leading to the formation of molecular orbitals.
- Each molecular orbital is described by a wave function ψ known as molecular orbital wave function.

- ψ^2 represents the probability density of finding the electron in a given volume element $d\tau(dx,dy,dz)$.
- Each molecular orbital wave function is associated with a set of quantum numbers which determine energy and shape of molecular orbitals.
- Each wave function is associated with definite energy values and the total energy of the molecule is the sum of energies of occupied molecular orbitals.
- Electrons fill the molecular orbitals following Aufbau principle, Hund's rule and Pauli's exclusion principle.
- Each electron in molecular orbital belongs to all nuclei present in the molecule, ie, they are polycentric.

LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO METHOD)

- By LCAO method, addition and subtraction of wave function yield molecular orbitals ψ_+ and ψ_- respectively.

$$\psi_+ = \Psi_A + \Psi_B$$

$$\psi_- = \Psi_A - \Psi_B$$

- ψ_+ formed by addition of wave function are called 'bonding molecular orbitals'.

ψ_- formed by subtraction of wave function are called 'anti bonding molecular orbitals'.

$$\psi_+^2 = (\psi_+ + \psi_-)^2 = \psi_A^2 + 2\psi_A\psi_B + \psi_B^2$$

$$\psi_-^2 = (\Psi_+ - \psi_-)^2 = \psi_A^2 - 2\psi_A\psi_B + \psi_B^2$$

- ψ_A^2 and ψ_B^2 represent the probability density and $\psi_A\psi_B$ represent the probability of finding the electron in internuclear region.
- The electrons in bonding molecular orbitals are in between the nuclei, They tends to hold the nuclei together and stabilize the molecule.
- Electrons placed in anti- bonding molecular orbitals destabilize the molecule because the mutual repulsion between electron is high.
- Hence, bonding molecular orbital has lower energy and anti- bonding molecular orbitals have higher energy.

$\sigma, \sigma^*, \pi, \pi^*$ molecular orbitals

- Molecular orbitals in which electron density is concentrated symmetrically around inter nuclear axis is called σ molecular orbital.
- In σ bonding molecular orbital, electron density is concentrated between the nuclei while in σ anti bonding (σ^*) molecular orbital electron density is depleted from the region between the nuclei.
- Molecular orbitals in which electron density is concentrated unsymmetrically about the internuclear axis is called π molecular orbital.
- A π bonding molecular orbital has electron density in between the nuclei but distributed unsymmetrically about the internuclear axis.

- A π antibonding molecular orbital (π^*) has electron density depleted from the region between the nuclei and unsymmetrically distributed about the internuclear axis.

BOND ORDER

- It is the half of difference between number of bonding electrons and number of anti-bonding electrons.

$$\text{B.O} = \frac{1}{2} [\text{Nb} - \text{Na}]$$

- If $\text{Nb} > \text{Na}$, i.e, when bond order > 0 , the molecule is stable.
- If $\text{Nb} = \text{Na}$ / $\text{Nb} < \text{Na}$, the molecule is unstable and does not exist.
- Bond order is directly proportional to bond strength and inversely proportional to bond length.

MOLECULAR ORBITAL ELECTRONIC CONFIGURATION OF SOME MOLECULES

a) H₂ molecule

- The molecular orbital electronic configuration is $\sigma 1s^2$.

- Bond order = $\frac{1}{2}(\text{Nb} - \text{Na})$

$$= \frac{1}{2}(2 - 0)$$

$$= 1$$

- Bond order is positive, the molecule is stable.
- There are no unpaired electrons. The molecule is diamagnetic

b) B₂ molecule

- The MO electronic configuration is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 = \pi 2p_y^1$

- Bond order = $\frac{1}{2}(\text{Nb} - \text{Na})$

$$= \frac{1}{2}(6 - 4)$$

$$= 1$$

- The molecule is stable and paramagnetic.

c) C₂ molecule

- The MO electronic configuration is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2$

- Bond order = $\frac{1}{2} (\text{Nb} - \text{Na})$

$$= \frac{1}{2} (8 - 4)$$

$$= 2$$

- The molecule is stable and diamagnetic

d) N₂ molecule

- The MO electronic configuration is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$

- Bond order= $\frac{1}{2} (N_b - N_a)$

$$= \frac{1}{2} (10 - 4)$$

$$= 3$$

- The molecule is stable and diamagnetic

e) O₂ molecule

- The MO electronic configuration is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$

- Bond order= $\frac{1}{2} (N_b - N_a)$

$$= \frac{1}{2} (10 - 6)$$

$$= 2$$

- The molecule is stable and paramagnetic.

f) CO molecule

- The MO electronic configuration is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$

- Bond order=3

- The molecule is stable and diamagnetic

- In hetero nuclear diatomic molecules, $\Psi_{mo} = \Psi_A + \lambda \Psi_B$ where $\lambda \neq 1$

The molecular orbitals will not be symmetric about the plane bisecting the internuclear axis.

HOMO AND LUMO OF MOLECULES

- HOMO is the Highest occupied Molecular Orbital of a molecule and LUMO is the Lowest Unoccupied Molecular Orbital.
- HOMO and LUMO are collectively called Frontier Orbitals.

Eg: In the MO diagram of CO, HOMO is $\sigma 2p_z$ whereas LUMO is $\pi^* 2p_x$ and $\pi^* 2p_y$ are LUMO.

- The energy difference between HOMO and LUMO is called HOMO-LUMO gap. They are of great importance in determining the spectral characteristics of a molecule. It is also used to predict the strength and stability of transition metal complexes and the colours they produce in solution.

INTERMOLECULAR FORCES

- The force of attraction and repulsion between atoms/molecules in a gas, liquid or solid.
- Attractive or cohesive intermolecular forces are called Vandewaal's force.
- They include dipole-dipole forces, dipole- induced dipole forces, induced dipole- induced dipole forces.

Dipole- Dipole forces

- They act between molecules possessing permanent dipole moment. Eg: HCl
- The +ve end of one dipole will attract the negative end of other dipole.
- They are weaker than ionic or covalent bonds.
- The interaction energy of dipole- dipole interaction is given by the equation
$$V = -\frac{2}{3kT} \left(\frac{\mu_1 \mu_2}{4\pi\epsilon_0} \right) \frac{1}{r^6}$$
; μ_1 and μ_2 are dipole moments.
- The dipole-dipole interaction is inversely proportional to temperature.
- Greater the magnitude of dipole- dipole forces, greater will the melting and boiling points.

HYDROGEN BOND

- The weak attractive force between hydrogen atom and highly electronegative atom (F, O, N) with non- bonding electron pairs is called hydrogen bond.
- It is a type of dipole- dipole interaction.
- When hydrogen atom is bound to more electronegative atom, a partial charge separation occurs and molecule become polar. The hydrogen which is positive interact with negative end of neighbouring molecule and form a bridge.
- It is weaker than covalent bond.
- Two types-

Intermolecular hydrogen bonding- Hydrogen bonding between different molecules of same substance or different substance.

Intramolecular hydrogen bonding- Hydrogen bonding present within the same molecule.

Hydrogen bonding in water

- The unique properties of water arises from its polarity. Water molecule has two bond pairs and two lone pairs around the oxygen atom and there is large electronegativity difference between H and O atoms. H₂O molecule is bent and highly polar.
- Water forms intermolecular hydrogen bonding in a unique manner. Each water molecule forms hydrogen bonding with four of its neighbours.

Unique properties of water

- Water is an exceptionally good solvent

The great solvent power of water is the result of its polarity and exceptional H-bonding ability. It has a high dielectric constant and it dissolves ionic compounds through ion-dipole forces that separate the ions from their crystals and disperse them in solution. Water also dissolves many polar non-ionic substances. Eg: ethanol.

- Water has high specific heat and high heat Of vaporization

The extensive association through H-bonding gives water a high specific heat capacity because the added heat gets utilized to break the hydrogen bonds instead of increasing the temperature. Water has an exceptionally high heat of vaporization.

- Water shows high surface tension and high capillarity

The extensive intermolecular H-bonding present in it is responsible for its high surface tension and high capillarity. This phenomenon helps land plants, it enables the ground-water absorbed by the plant roots to rise by capillary action. The spherical shape of liquid drop is due to its high surface tension.

- Water has the highest boiling point and melting point among the hydrides of group 16 elements

The extensive association of water molecules through intermolecular hydrogen bonding is responsible for the unexpectedly high boiling point and melting point of water because a large amount of energy has to be expended to break these hydrogen bonds. Such association through hydrogen bonding is not present in H_2S , H_2Se and H_2Te .

- Ice has lower density than liquid water

Each water molecule gets connected to four other water molecules in tetrahedral manner through hydrogen bonding. In ice, continuation of tetrahedral pattern through many molecules in a fixed array leads to open hexagonal three dimensional structure with several cavities. The large spaces within ice give ice a lower density than liquid water. As a result, ice floats on water.

- Water shows anomalous variation of density between 0°C and 40°C .

When ice melts at 0°C , its tetrahedral network arrangement breaks down, and the freed molecules pack much more closely, filling spaces in the cavity. This decrease in volume continues up to about 4°C . As a result, water shows its highest density at 4°C . With further increase in temperature, the density decreases through normal thermal expansion.

MODULE-7- NUCLEAR CHEMISTRY

Nuclear Chemistry

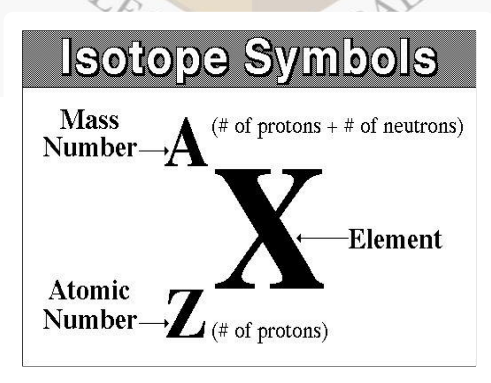
- Branch of chemistry deals with properties of the nuclei and changes in nuclei.

The Nucleus

- Radius : femtometers ($1\text{fm} = 10^{-15}\text{m}$)
- The nucleus is composed of nucleons
 - ◆ Protons (+ ve)
 - ◆ Neutrons (chargeless)
- Most of the mass is concentrated at nucleus. Hence it has high density.
- A nucleus is characterized by two numbers
 - ◆ atomic number (Z; number of protons)
 - ◆ mass number(A; total no. of nucleons)

Nuclide

- Species of atom characterized by the constitution of its nucleus



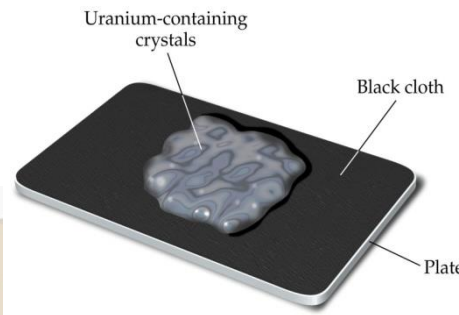
E.g., ${}_{13}^{27}\text{Al}$

- total number of nucleons is 27
- total number of protons is 13

- the number of neutrons is 14 (27-13)

Radioactivity

- Discovered by Antoine Henri Becquerel in 1896
- He saw that photographic plates developed bright spots when exposed to uranium metals (potassium uranyl sulphate).



- Marie Curie and Pierre Curie discovered that the emission of radiation from U is a consequence of nuclear process and certain elements like Th also have this property
- They identified 2 new elements, Po and Ra.

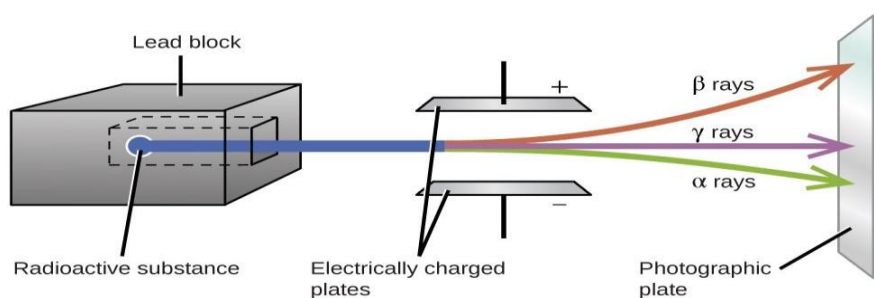
Radioactivity – definition and properties

- spontaneous emission of certain active rays by certain nuclides
- Independent of chemical state of element
- Physical conditions such as temperature pressure etc.

Natural radioactivity

- Radioactivity associated with naturally occurring materials.

Types of radioactive decays



1. Alpha particle

- ❖ Composition – Alpha particles, same as helium nuclei
- ❖ Symbol – Helium nuclei, He , α
- ❖ Charge – positively charged ($2+$)
- ❖ Mass (amu) – 4
- ❖ Approximate energy – 5 MeV
- ❖ Penetrating power – least (even stopped by 0.05 mm thick Al foil)
- ❖ Ionising power-because of high momentum they can ionize the gases which they are passing
- ❖ Action on photographic plate– can affect

2. Beta particle

- ❖ Composition – Beta particles, same as an electron
- ❖ Symbol – e^- , β
- ❖ Charge – negatively charged ($1-$)
- ❖ Mass (amu) – $1/1837$ (practically 0)
- ❖ Approximate energy – 0.05 – 1 MeV
- ❖ Penetrating power – moderate (Can penetrate through 5 mm thickness or more)
- ❖ Ionising power - because of smaller size, less than that of alpha rays
- ❖ Action on photographic plate – can affect

3. Gamma particle

- ❖ Composition – High-energy electromagnetic radiation
- ❖ Symbol – γ
- ❖ Charge – 0

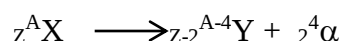
- ❖ Mass (amu) – 0
- ❖ Approximate energy – 1 MeV
- ❖ Penetrating power – high (penetrates through 25cm thick iron block)
- ❖ Ionising power- least
- ❖ Action on photographic plate – can affect

Modes of decay-Theory of radioactive disintegration

- The atoms of all radioactive elements undergo spontaneous disintegration with the emission of alpha and beta particles to yield atoms of new elements.
- Two modes by which unstable radioactive elements decay are
 - ❖ Alpha emission
 - ❖ Beta emission

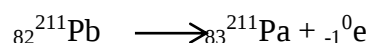
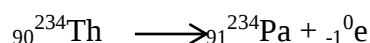
1. Alpha emission

- When a radio nuclide decays by emitting an alpha particle there occurs a decrease of 2 in atomic number and decrease in 4 units in the mass number

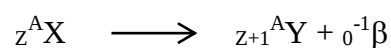


2. Beta emission

- When a radio nuclide decays by emitting a beta particle there occur an increase of 1 in atomic number and no change in the mass number.



- Ejection of a high speed electron from the nucleus.

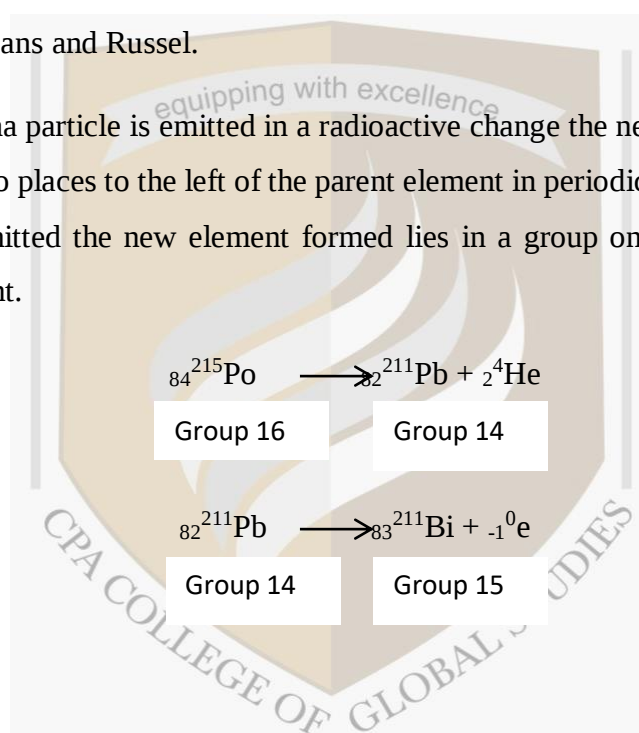


3. Gamma Emission

- Emission of high energy electromagnetic radiation.
- Usually occurs after emission of a decay particle forms a metastable nucleus.
- Does not change the isotope or element.

Group displacement law

- By Soddy Fajans and Russel.
- When an alpha particle is emitted in a radioactive change the new element formed lies in a group two places to the left of the parent element in periodic table and when a beta particle is emitted the new element formed lies in a group one place to the right of parent element.



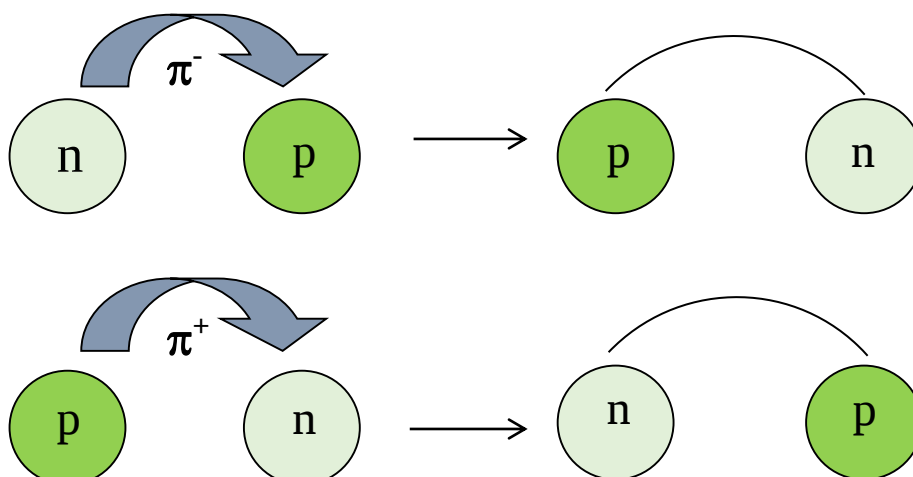
Nuclear forces

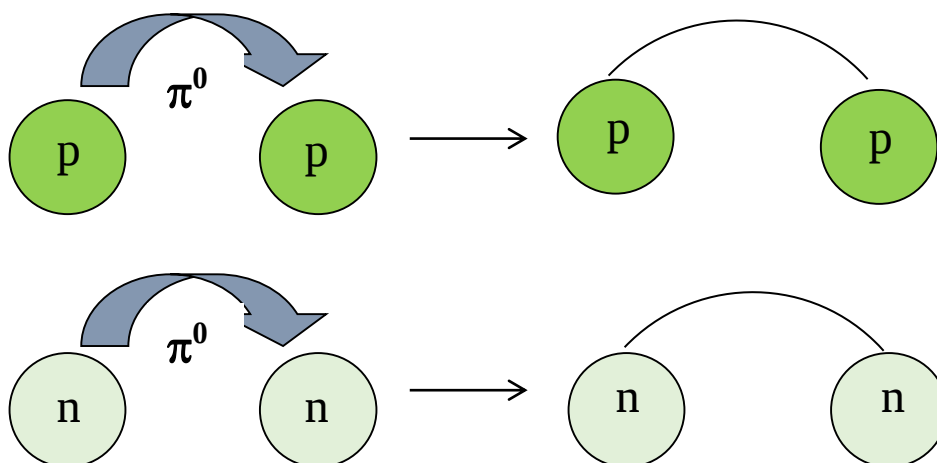
- The attractive forces that bind the nucleons together.
- A nucleus will be stable if attractive forces > repulsive forces.
- Nucleon - nucleon attractive forces are not electrostatic in nature. Because there are not oppositely charged particles.
- Short range forces (1-3 fm).
- Hence each nucleon attracts only those in its immediate vicinity and does not interact with distant ones - saturation character.

- Independent of charge on the nucleus and are the same for all three types of nucleon pairs – (n-n), (n-p), (p-p)
- The short range attractive forces that bind the nucleons together are a kind of exchange forces resulting from meson exchange interactions.

Yukawa's meson exchange theory

- According to meson theory of nuclear forces, a ceaseless rapid exchange of a nuclear - particle called a **π meson** or **pion** occurs between neighboring nucleons.
- Pions may be positively charged (π^+), negatively charged (π^-) or neutral (π^0)
- Their masses are 273, 273, 264 times that of an electron ($m_e = 9.1 \times 10^{-31}$ kilograms).
- The neutron - proton interactions occur with their interconversion by exchange of π^+ and π^- mesons
- A neutron emits a negative pion (π^-) which is taken up by a proton.
- Proton emits a positive pion (π^+) which is taken up by a neutron.
- In either case a proton becomes a neutron and vice versa.
- A (p-p), (n-n) interactions occur by the transfer of a neutral pion (π^0).
- These rapid exchanges between close neighbors result in attractive forces between nucleons, which bind them together.



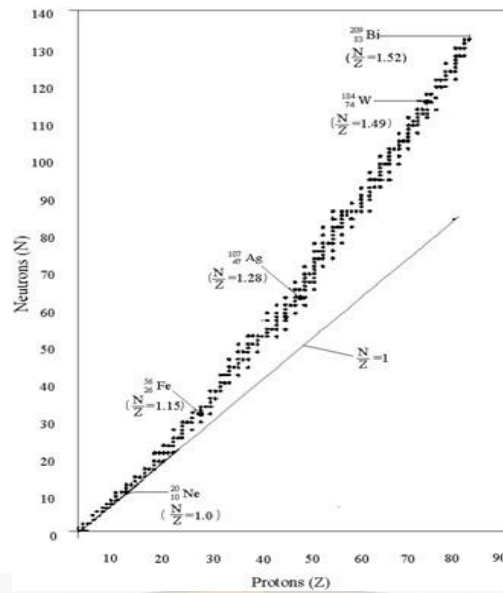


N/P Ratio (N/Z ratio) and nuclear stability

- Stability of nucleus is determined by no. of protons and neutrons.
- In the stable nuclides of lower atomic number (up to 29) $N/P = 1$. i.e., $N = P$
- For nuclides of higher atomic numbers, ($N/P > 1$) tend to have more neutrons than protons.
- For heaviest nuclides such as Pb and Bi, N/P ratio > 1.5
- All nuclides larger than Bi are unstable and radioactive

Conclusion

- Nuclides having N/P ratio in the range 1 to 1.6 are stable
- For lower Z nuclides (up to 20) all points fall on or close to the line ($N=P$)
- At higher atomic numbers – increasingly curved, (N/P) ratio increases.
- The points in the plot thus lie in a region of stability or belt of stability.
- Any nuclide whose N/P ratio falls outside the belt stability would be unstable and undergo spontaneous radioactive disintegration in an attempt to attain a favorable N/P ratio.



Mass Defect

- Mass of an atom is less than the sum of masses of its components (p, n, e)
- The difference is called mass defect.
- Mass defect is equal to the mass lost as an equivalent amount of energy during the formation of a nucleus from its components
- mass defect: $\Delta m = \text{mass nucleons} - \text{mass nucleus}$

$$\text{Mass defect } \Delta M = [Zm_p + Zm_e + (A-Z) m_n] - M$$

- Z- atomic number
- A-mass number
- m_p - mass of proton
- m_e - mass of electron
- m_n - mass of neutron
- M- expected total mass

Binding Energy

- The mass lost in the formation a nucleus is converted into energy according to Einstein's mass - energy relationship $E=mc^2$
- The energy released in the formation of a nucleus from its component nucleons is called the binding energy of nucleus.

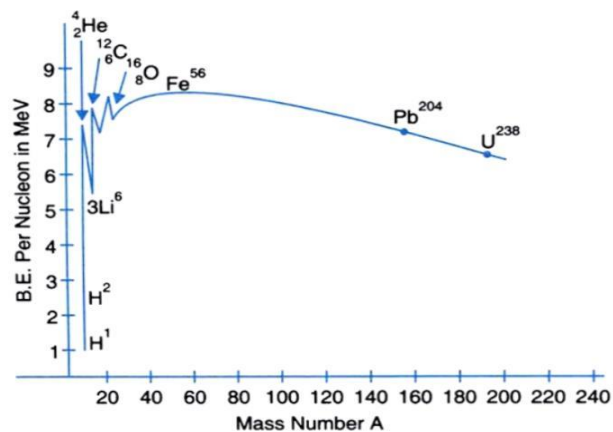
◆ $BE = \Delta m \times c^2$ joule (Δm - Kg)

(C -velocity of light)

◆ $BE = \Delta m \times 931.5$ MeV (Δm -amu)

$$\text{Binding energy per nucleon} = \frac{\text{Total binding energy}}{\text{Number of nucleons}}$$

Binding Energy Curve



- Over a considerable range of mass numbers BE/nucleon is close to 8 MeV.
- Graph peaks at A=56
- The more BE released per nucleon, the more stable the nucleus
- Mass number of 56 is maximum possible stability (Fe)

Isotopes, Isobars and Isotones

1. Isotopes

- Atoms having same atomic number but different mass numbers.
- Same number of protons and electrons - atoms of same element.
- Same chemical properties but different physical properties.

E.g., protium (${}_1^1\text{H}$), deuterium (${}_1^2\text{H}$) and tritium (${}_1^3\text{H}$) – isotopes of hydrogen.

2. Isobars

- Atoms having same mass number but different atomic number.
- Atoms of different elements.
- Different physical and chemical properties.

E.g., ${}_{18}^{40}\text{Ar}$, ${}_{19}^{40}\text{K}$, ${}_{20}^{40}\text{Ca}$ are isobars.

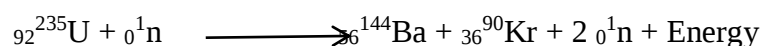
3. Isotones

- Atoms that have same number of neutrons in their nuclei but different mass numbers.
- Atoms of different elements.
- Different physical and chemical properties.

E.g., ${}_{14}^{30}\text{Si}$, ${}_{15}^{31}\text{P}$, ${}_{16}^{32}\text{S}$ are isotones.

Nuclear fission

- Splitting of a heavy nucleus, when bombarded with a suitable particle (neutron), into fragments of comparable masses with the release of huge amount of energy.
- E.g., ${}_{92}^{235}\text{U}$ undergoes fission when bombarded with thermal neutrons.



Fissile nuclides

- Nuclei which undergo fission on bombardment with slow / thermal neutrons.

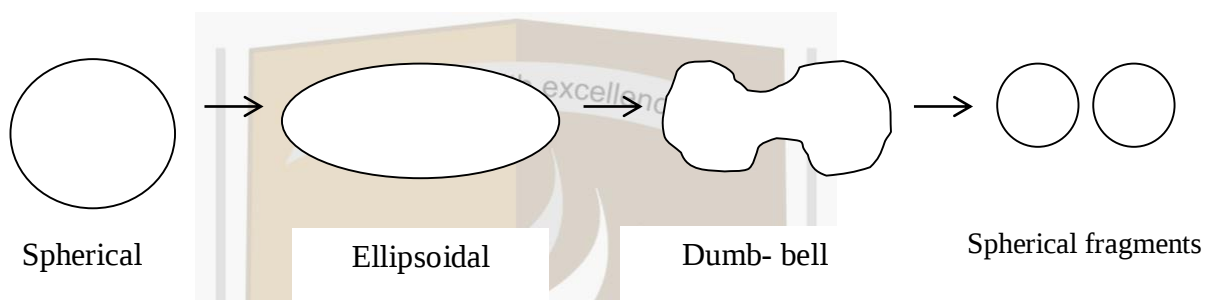
- E.g., ${}_{92}^{233}\text{U}$, ${}_{94}^{239}\text{Pu}$

Fissionable nuclides

- Nuclei which undergo fission with fast neutrons. (e.g., ${}_{91}^{232}\text{Pa}$, ${}_{90}^{232}\text{Pu}$)

Fission mechanism: nuclear liquid drop model

- Fission mechanism is comparable to the breaking up of a spherical liquid drop to two smaller droplets on applying a large deforming force.



- During fission target nucleus combines with projectile neutron and form high energy compound nucleus.
- It gets deformed to a dumb- bell shape.
- Due to repulsive force between positive charges on two segments the system cleaves to two separate smaller nuclei.
- During fission, some mass is always lost and it is converted into energy by the equation $E = mc^2$
- Hence a lot of energy is released during the reaction.
- Fission nucleus will produce two to three neutrons, each of which can initiate fission.
- These secondary neutrons may thus propagate the fission; it is called *nuclear chain reaction or fission chain reaction*.

Critical mass

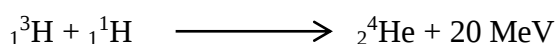
- The minimum amount of the target material required to sustain a fission chain reaction at a constant rate.

Applications

Atomic bomb, nuclear reactors, constructive purposes etc.

Nuclear fusion

- The process in which two lighter nuclei fuse together to form a heavier nucleus with release of a huge amount of energy.



- Some mass is lost during fusion, it is converted to energy by Einstein's equation $E=mc^2$
- Fusion can take place only at high temperatures of the order of million degree centigrade.
- It is also called thermonuclear reactions because the combining nuclei have high kinetic energy to overcome their mutual repulsion.
- Common in interior of stars
- Net reaction in sun is



Distinction between fission and fusion

<i>Nuclear fission</i>	<i>Nuclear fusion</i>
• Process in which heavy nucleus split into two fragments when bombarding with a suitable sub atomic particle. • Can take place at ordinary temperatures.	• Process in which two lighter nuclei fuse to form a heavier nuclei. • Require high temperature of the order of 10^6 K

- | | |
|--|--|
| <ul style="list-style-type: none"> • Mass of product nuclei is lower than that of parent nuclei. • Fission energy released per unit mass of the material that undergoing fission is large. | <ul style="list-style-type: none"> • Product nucleus is heavier than the fusing nuclei • Energy released per unit mass of the combining nuclides is larger than that in fission. |
|--|--|

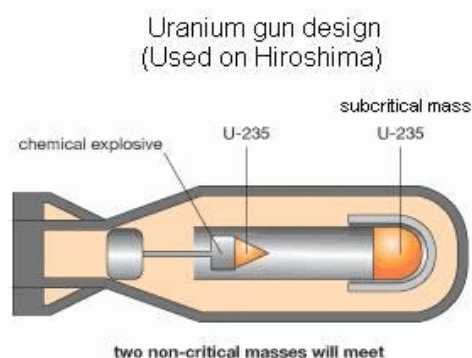
Applications of nuclear fission and fusion

1. Atom bomb

Principle:

- When a nuclear fission chain reaction is allowed to occur in an uncontrolled manner within a small volume, an enormous amount of fission energy would be released in a small time interval in an explosive manner.
- Fissile material used – U-235, Pu-239 or combination of the two.
- Fission of ~1kg of U-235 or Pu-239 release an energy equivalent to that from about 15000 to 20000 tons of TNT.
- Nature of explosion depends upon,
 - ❖ Fissile material.
 - ❖ Geometry and design of bomb.

Gun barrel type atom bomb- working



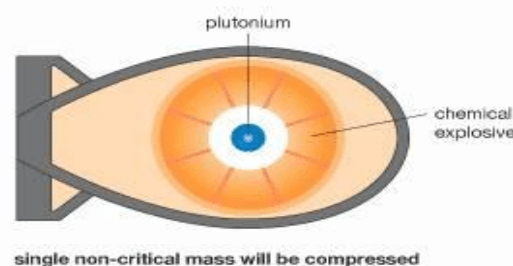
- Little boy – used in Hiroshima

- Contains two pieces of fissile materials U-235, each of a sub-critical mass.
- One is called *wedge* and the other is called *target*.
- Using a chemical explosive like TNT, wedge is fired down from the gun barrel into the target.
- They form a super- critical mass.
- The fission chain reaction is started by neutrons, from a source at the centre of the device.
- An uncontrolled fission chain reaction occurs, and enormous heat energy is released explosively.

Fat Man –Nagasaki



Plutonium Implosion design
(used on Nagasaki)



- Rounder and fatter
- Fissile material used – Pu-239
- Implosion type bomb- the two sub critical portions of fissile material are packed into a spherical case
- To cause chain reaction, these two units are forced and compressed into each other at the centre.

2. Hydrogen bomb

- Thermonuclear bomb

Principle:

- Nuclear fusion initiated by uncontrolled fission chain reaction.

Working:

- Fusion of hydrogen nuclei to form helium nuclei.
- A fission type bomb, namely an atom bomb, is arranged at the centre of the device and its explosion acts as a source of heat and neutrons.
- It is surrounded by a mixture of deuterium (^2H) and ^6Li .
- The explosion of atom bomb is triggered off first.
- The neutrons from the fission chain reaction convert the ^6Li isotope to tritium (^3H).



- Heat from fission initiates fusion. Possible fusion reactions are,



- No restrictions of critical size of fusible materials
- Since, the energy released per unit mass of the material during fusion is very much greater than that in fission; a hydrogen bomb is 1000 times more powerful than an atom bomb.
- Often referred as *fission – fusion* bomb.

3. Nuclear reactor

- Arrangement in which release of nuclear energy through a self- propagating fission chain reaction is achieved at a controlled rate.
- The fission produce secondary neutrons and they are responsible for the propagation of the process.

- It is possible that some of the secondary neutrons may be lost either by leakage from the system or through capture by the nuclei of the system for processes other than fission.

Critical size:

- Minimum condition for maintaining a fission chain reaction is that for each nucleus undergoing fission at least one neutron on the average is produced, which causes fission of other nucleus. For a system, there is a limiting minimum size that is required to satisfy this condition which is called critical size.

Critical mass:

- Minimum amount of fissile material present to sustain a fission chain reaction at a constant rate.

Conditions for the designing of a nuclear reactor

1. Presence of fissile material equal to or greater than the critical mass
 2. Occurrence of a controlled slow neutron chain reaction – by using a suitable substance to reduce the speed of the neutrons- *moderator* (graphite or heavy water)
 3. Inserting control rods of neutron absorbers such as Cd or B
 4. Optimum use of the fission neutrons of each generation- By minimizing neutron loss by any factor and by ascertaining that the size of the fuel-moderator system is equal to or above the critical size but with as minimum surface area possible.
- First nuclear reactor – *Chicago chain reacting pile*
 - Fuel used – *natural uranium (and uranium oxide)*
 - Moderator – *graphite*
 - control rods – *cadmium*

General features of a nuclear reactor

1. Fuel

- U – 235, U – 233, and Pu – 239

- Typical example is natural uranium containing 0.72% of U – 235.
- Enriched uranium contain a greater amount of U – 235
- Part of reactor containing fuel is called *reactor core*

2. Moderator

- Used to slow down fast secondary neutrons through collision.
- Graphite, heavy water (D₂O), beryllium oxide, water

3. Control material

- Used to absorb thermal neutrons.
- Cadmium, boron etc. are used as control rods.

4. Reactor coolant

- To remove heat generated by fission chain reaction.
- Coolant is pumped through the reaction core to take up heat from fission products.
- Water, heavy water, liquid sodium, organic polyphenyls, etc. and gases like air and carbon dioxide are commonly used coolants.

5. Reactor shield

- Shield covering of whole reactor protects the persons in the vicinity from hazardous gamma rays and neutrons coming from the reactor.
- High power reactors have two shields
 - ◆ Thermal shield: made of iron or steel close to the core, which absorbs gamma rays and protects the outer shield from damage
 - ◆ Biological shield: absorbs both gamma rays and neutrons, usually consists of a layer of concrete of several feet thickness.

Breeder reactor

- U -235 is the only fissile material present in nature and which is only about 0.7% of natural uranium.
- Since there is no known method to generate U – 235, we use alternate fissile materials, U -233 and Pu - 239.
- They are not naturally available but can be produced from neutron bombardment of more available U – 238 and Th – 232 respectively.
- Consider conditions are so adjusted that, of the secondary neutrons produced by fission of U – 235 in a natural uranium reactor, one is used for propagating the reaction and the rest are made to undergo capture by U – 238 to produce Pu – 239. Hence the proportion of Pu - 239 produced would be greater than that of U- 235 consumed.
- i.e., as the process continues, more fissile material is produced than that of consumed. –breeding and such reactor is *breeder reactor*.

Applications of radioactive isotopes

1. C-14 dating

- Technique used for determining the age of archeological carbonaceous objects (woods and animal fossils) by measuring the radioactivity of ^{14}C present in them.
- Age of the sample can be calculated by the equation

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N_t}$$

* t- age

* N_0 - initial activity

* N_t - final activity

* λ - decay constant

2. Rock dating

- Method of determining age of rocks and minerals of uranium thorium etc.
- Age can be calculated using the equation

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N_t}$$

* t - age

* N_0 - initial activity

* N_t - final activity

* λ - decay constant

3. Isotopes as tracers

- The isotope used for tagging or labeling an element so that its fate in a physical or chemical change can be traced is called a tracer.
- Uses of *radio isotopes* are
 - i. Radiophosphorous (^{32}P) – tracer in agriculture to study uptake of phosphatic fertilizers by different plants
 - ii. β rays from a source like ^{90}Sr – measuring thickness of coatings, layers, paper, metal sheets, rubber sheets etc.
- Limitations of radioisotopes are health hazards to users and also to living organisms.
- Uses of *non - radioactive isotopes* are
 - i. Stable ^{18}O – used to establish a multistage mechanism of photosynthesis. Using it as tracer it was established that the oxygen liberated in the process came from photodissociation of water not from CO_2
- Limitation of non- radioactive isotopes as tracers is the need for employing a mass spectrometer which is complicated, expensive instrument.

4. Use of radiotraceas tracers for radiodiagnosis

Various radioisotopes are used for diagnostic purposes in medicines

- i. Radioactive ^{131}I – diagnosis of thyroid disorders
- ii. Radioactive ^{24}Na – detect obstructions in blood circulation
- iii. ^{74}As – locating brain tumors.
- iv. ^{32}P – detecting skin cancer.
- v. ^{58}Co – determining uptake of vitamin B_{12} .
- vi. ^{51}Cr – determining volume of RBC and total volume of blood.

vii. ^{59}Fe – measure rate of formation and life time of RBC.

5. Use of radioisotopes in radiotherapy

- i. High energy γ rays from isotopes of Ra and Co – destroy cancer cells.
- ii. ^{131}I – treatment of thyroid cancer.
- iii. ^{32}P – treatment of blood cancer.
- iv. ^{90}Sr – treatment of corneal cancer.



MODULE-4- BIOINORGANIC CHEMISTRY

BIOINORGANIC CHEMISTRY

Interdisciplinary scientific branch examines the chemistry of inorganic entities within biological and biochemical systems.

1. The study of naturally occurring inorganic elements in biochemical systems.
2. The artificial introduction of metals into biological systems as probes to determine the structure and function of biomolecules and as drugs to treat diseases.
3. Investigation of inorganic elements in nutrition.
4. Research on the toxicity of inorganic species .etc.

Essential elements:

1. **Bulk elements:** Required by living organisms in large quantities.

Eg.; O, C, H, N, S, P, Na, K, Mg, Ca, Cl

2. **Trace elements:** Required by living organisms in minute amounts

Eg.; Fe, Cu, Zn, Mn, Mo, Co, Cr, V, Ni, Cd, Sn, Pb, Li, B, F, I, Se, Si,

As

Functions of metal ions in biochemical process:

1. As cofactors in enzymes
2. As structural entities
3. In the control of metabolic pathways and other mechanisms
4. As oxygen carriers
5. Maintenance of osmotic pressure and pH, and regulatory action

Biochemistry of Iron

1. Iron acts as an **oxygen carrier** in the blood of mammals, birds and fish (haemoglobin)
2. For **oxygen storage** in muscle tissues(myoglobin)
3. As an electron carrier in plants ,animals and bacteria(cytochromes) and for electron transfer in plants and bacteria
4. For storage and scavenging of iron in animals (ferretin, transferrin, haemosiderin)
5. As nitrogenase
6. As a part of number of enzymes like aldehyde oxidase, catalase and peroxidase.

Haemoglobin and myoglobin

- Both haemoglobin and myoglobin are metal porphyrins which contain heme group in their structure.
- Heme group: contain an iron atom coordinated to 4 nitrogen atoms of porphyrin-IX

(Porphyrins are derivatives of porphine in which four pyrrole units are linked by four methane bridges)

Heme group in haemoglobin and myoglobin

Fe is present at the centre of 4 macrocyclic N.

There are 4 pyrrole rings which are conjugated with the heme centre

Haemoglobin (Transport of oxygen)

- Tetramer
- Molar mass about 64500.
- Each sub units of hemoglobin contains a polypeptide chain and heme group coordinated through the N atom of histidine group of its polypeptide chain
- The four sub units of hemoglobin are linked with one another through salt bridges present between the four polypeptide chains.
- Deoxyhemoglobin: Hemoglobin not taken up oxygen

- Oxyhemoglobin: Oxygenated hemoglobin

Myoglobin: (storage of oxygen)

- Monomer
- Only one heme unit is present.
- Heme group is embedded in a crevice formed by the coiling of its polypeptide chain containing 150-160 amino acids.
- molar mass-17000
- Deoxymyoglobin- myoglobin which has not taken oxygen
- Oxymyoglobin- oxygenated myoglobin

Structure of Hb

- There are four heme groups and Fe is situated at the centre of the core
- Hence it is a tetramer
- Heme group is attached to a protein in both haemoglobin and myoglobin through a coordinated histidine-nitrogen atom.
- Heme group contain Fe at the centre of porphyrin ring.
- The 4 N atoms of the ring are coplanar with Fe
- The fifth position of Fe is occupied by N atom of histidine
- The sixth position is occupied by water or oxygen.

Transport of O₂ and CO₂

- Hb has high affinity for O₂ at high O₂ pressures
- In lungs P of O₂ is very high- Hb reversibly combines with O₂ to form oxyhaemoglobin
- In arteries O₂ P is low, Hb dissociates and release O₂
- O₂ is stored in Mb

- Tissues- need for O_2 is high and there will be CO_2
- CO_2 lowers pH – Hb release more O_2 to Mb
- When O_2 is removed from Hb in muscles – replaced by H_2O
- The CO_2 diffuses from plasma to Hb and it combine with H_2O and produce HCO_3^- and H^+
- The HCO_3^- ions diffuse to blood plasma from Hb – the blood returns to heart through veins
- It is pumped into lungs where HCO_3^- convert back to H^+ and CO_2 – exhaled through lungs.

Mechanism of oxygen binding

- In oxy Hb – Fe^{3+} - low spin state, paramagnetic
- In deoxy Hb - Fe^{2+} - high spin state, diamagnetic.
- 5th position of deoxyhaemoglobin is fitted with a histidine
- In this Fe is sitting above the porphyrin ring
- The radius of Fe^{2+} is $0.77\text{\AA}$. Hence it cannot exactly fit in the cavity
- So it will sit outside the porphyrin ring.
- when it binds with oxygen, Fe^{2+} is gets oxidizes to Fe^{3+}
- Fe^{3+} is almost fit to the cavity because its radius is small. ($0.69\text{\AA}$)
- Hence the shape of complex change from square pyramidal to octahedral

Coopractivity

- The phenomenon where the addition of O_2 to one heme group facilitates the addition of O_2 to other heme groups of Hb.

Bohr's effect

- under acidic pH, the equilibrium between deoxyHb and oxyHb is shifted in favour of the deoxygenation process

Photosynthesis

- Photophysical processes and oxidation reduction reactions are photosensitized by many pigments like chlorophyll.

chlorophyll

- Photosensitizer in photosynthesis.
- Two common types
- Chlorophyll a, chlorophyll b

Structure

- Tetrapyrrole ring system coordinated to central magnesium (+2 oxidation state) via ring nitrogens and long lipid soluble hydrocarbon tail.
- Main photosynthetic pigment - Chlorophyll a – directly involved in light reactions.
- Accessory pigments – chlorophyll b, xanthophylls, carotenoids – do not directly involved in photosynthesis- absorb light and pass the energy to chlorophyll a.

Mechanism of photosynthesis

- Combination of water and carbon dioxide photosensitized by chlorophyll to form carbohydrates.
- $n\text{CO}_2 + n\text{H}_2\text{O} + \text{energy} \longrightarrow (\text{CH}_2\text{O})_n + n\text{O}_2 ; \Delta H = +x \text{ KJ}$
- Eg: $6\text{CO}_2 + 6\text{H}_2\text{O} + \text{energy} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + n\text{O}_2 ; \Delta H = +2861 \text{ KJ/mol}$
-
- Endergonic reaction

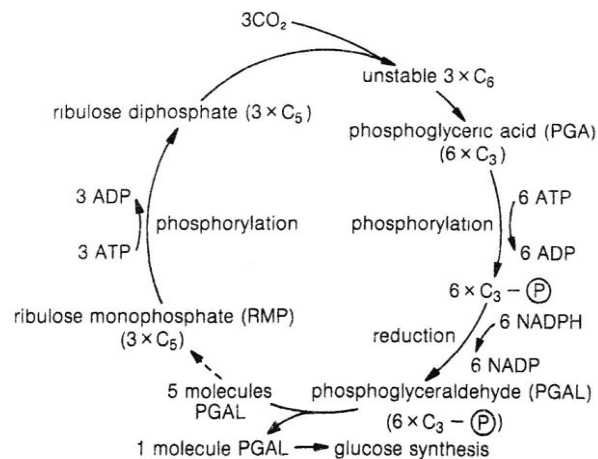
- Plants capture light energy from sun using chlorophyll (found in chloroplasts).
- Chloroplasts form the photosynthetic site for plants and algae.
- Two stages

1. Light reactions

- Occur with absorption of light, include formation of high energy chemical intermediates ATP and NADPH, water splitting and oxygen formation.
- These reactions occur in grana.

2. Dark reactions

- Do not need light to occur.
- Involves the utilization of energy rich products ATP and NADPH of light reactions to fix CO_2 into carbohydrates. In calvin cycle.
- These occur in stroma



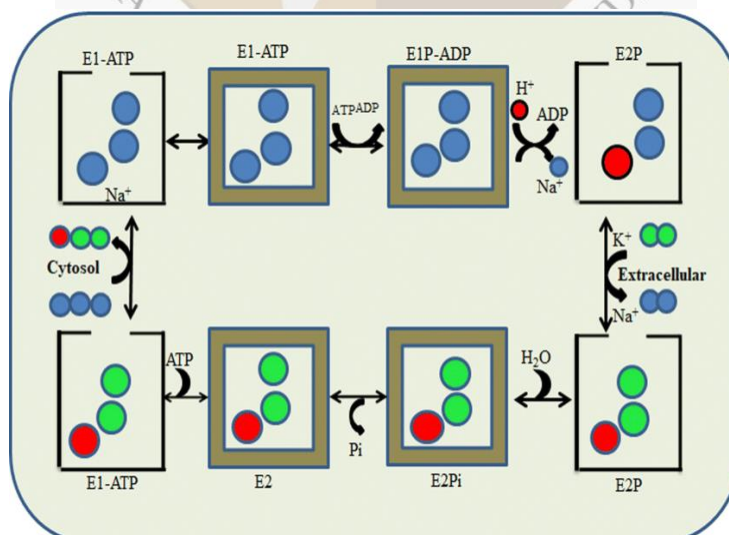
Sodium potassium pump

- Sodium concentration within animal cell has to be kept about 10 times lower than that in extracellular fluids,

- Potassium concentration within cell is about 30 times higher than in extracellular fluids.
- This concentration gradient across cell membrane is maintained by sodium potassium pump.
- The energy required for Na^+ and K^+ pumping is provided by ATP generated during metabolic reactions inside the cell.

Mechanism

- An ATP and 3 Na^+ ions inside the cell attach to the cell membrane-bound enzyme adenosine triphosphatase (E_1).
- Enzyme is phosphorylated in presence of Na^+ and Mg^{2+} ions to give a phosphoenzyme E_1P
- E_1P undergoes eversion to give E_2P
- E_2P undergoes dephosphorylation in a K^+ dependant process and three Na^+ ions are replaced by 2 K^+
- The loss of ATP triggers conformational change ($\text{E}_2 - \text{E}_1$) and carries two K^+ ions to interior of cell where they released.



Biochemistry of zinc

- Main constituent in enzymes – carbonic anhydrase, carboxypeptidase, alcohol dehydrogenase, aldolases, peptidases, proteases, DNA and RNA polymerases, transcarbamylase etc.

1. Carbonic anhydrase :

- Present in RBC, involved in respiration.
- Speed up the absorption of CO₂ by RBC in muscles and other tissues and reverse reaction involving the release of CO₂ in lungs, it also regulates pH.

2. Carboxy peptidase:

- Present in pancreatic juice – protein metabolism
- CP - A - Catalyses the hydrolysis of terminal peptide link at the carbonyl end of the peptide chain
- CP – B – splits carboxyl terminal lysine and arginine residues only.

3. Alcohol dehydrogenase:

- Alcohol metabolism

4. Dehydrogenase and aldoses : sugar metabolism

5. Alkaline phosphatase : energy releasing reactions

Biochemistry of cobalt

1. *Cyanocobalamin* (vitamin B 12)
2. *Adenosyl cobalamin*
3. *Methyl cobalamin*