MAA OMWAT DEGREE COLLEGE HASSANPUR (PALWAL)

Examination Notes

Class:- B.Sc 5th Sem(NEP)

Subject:- CHEMISTRY- Fundamental Chemistry – V

Bioinorganic Chemistry Metal ions present in biological system, classification based on action (essential, non-essential, trace, toxic), Na/K-pump, carbonic anhydrase and carboxypeptidase. Excess and deficiency of some trace metals. Toxicity of metal ions (Hg, Pb, Cd and As), reasons for toxicity, use of chelating agents in medicine. Metalloporphyrins with special reference to hemoglobin and myoglobin. Biological role of Na+ , K + , Ca+2, Mg+2, Fe+2 ions.

Chemistry of f-Block Elements Lanthanides: Electronic structure, oxidation states and ionic radii and lanthanide contraction, complex formation, occurrence and isolation, lanthanide compounds. Actinides: General features and chemistry of actinides, chemistry of separation of Np, Pu and Am from U, comparison of properties of lanthanides and actinides and transition elements

Photochemistry Interaction of radiation with matter, difference between thermal and photochemical processes. Laws of photochemistry: Grothus - Drapper law, Stark-Einstein law (law of photochemical equivalence), Jablonski diagram depicting various processes occurring in excited state, qualitative description of fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing), quantum yield, photosensitized reactions-energy transfer processes (simple examples).

Statistical Thermodynamics Introduction to statistical thermodynamics, types of statistics: Maxwell-Boltzmann statistics, BoseEinstein statistics and Fermi-Dirac statistics (derivation excluded). Maxwell-Boltzmann law, MaxwellBoltzmann law of distribution of energy and velocity, evaluation of energy. Derivation of equation of states for a monatomic ideal gas

Ultraviolet and Infra-Red spectroscopy Ultraviolet absorption spectroscopy-absorption laws (Beer-Lambert law), molar absorptivity, presentation and analysis of UV spectra, types of electronic transitions, effect of conjugation, concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. Molecular vibrations, Hooke's law, selection rules, intensity and position of IR bands, measurement of IR spectrum, fingerprint region, characteristic absorptions of various functional groups and interpretation of IR spectra of simple organic compounds.

Descriptive Notes on Bioinorganic Chemistry

Unit: Bioinorganic Chemistry

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1. Introduction to Bioinorganic Chemistry

Definition

Bioinorganic Chemistry is the branch of chemistry that studies the role of metal ions and inorganic elements in living organisms. It explains how metals participate in biological processes such as enzyme catalysis, oxygen transport, electron transfer, muscle contraction, nerve impulse transmission, and metabolism.

Importance

- Essential for life processes.
- Helps understand diseases caused by metal ion imbalance.
- Used in medicine, agriculture, and biotechnology.
- Plays an important role in drug design and diagnosis.

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2. Metal Ions Present in Biological Systems

Metal ions are indispensable components of biological systems. Approximately one-third of all proteins require metal ions for proper function.

Major Biological Metal Ions

Metal Ion	Biological Function
Na^+	Nerve impulse transmission, osmotic balance
K^+	Muscle contraction, intracellular electrolyte
Ca^{2+}	Bone formation, blood clotting, signaling
Mg^{2+}	ATP activation, enzyme cofactor
Fe^{2+}/Fe^{3+}	Oxygen transport, electron transfer
Zn^{2+}	Enzyme activation, DNA synthesis
Cu^{2+}	Oxidation-reduction reactions
Mn^{2+}	Photosynthesis, enzyme activity

Metal Ion	Biological Function
Co^{2+}	Vitamin B_{12} component
Mo	Nitrogen fixation
Ni	Urease enzyme

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3. Classification of Metal Ions Based on Their Biological Action

A. Essential Metals

These metals are absolutely necessary for normal growth and metabolism.

Examples

- Sodium (Na)
- Potassium (K)
- Calcium (Ca)
- Magnesium (Mg)
- Iron (Fe)
- Zinc (Zn)
- Copper (Cu)
- Manganese (Mn)
- Cobalt (Co)
- Molybdenum (Mo)

Characteristics

- Participate in enzyme activity.
- Maintain osmotic pressure.
- Essential for metabolism.
- Deficiency causes diseases.

B. Non-Essential Metals

These metals have no known biological function.

Examples

- Aluminum (Al)

- Silver (Ag)
- Gold (Au)
- Titanium (Ti)

Some may be used medicinally but are not required for life.

C. Trace Metals

Required only in minute quantities (less than 100 mg/day).

Examples

- Zn
- Cu
- Co
- Mn
- Mo
- Se

Functions:

- Enzyme cofactors
- Hormone synthesis
- Immune system
- DNA synthesis

D. Toxic Metals

These metals are poisonous even at low concentrations.

Examples:

- Mercury (Hg)
- Lead (Pb)
- Cadmium (Cd)
- Arsenic (As)

Effects:

- Damage proteins
- Inhibit enzymes

- Destroy nervous system
- Cause cancer

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4. Sodium–Potassium Pump (Na^+/K^+ Pump)

Definition

The sodium-potassium pump (Na^+/K^+-ATPase) is an ATP-dependent membrane protein that transports sodium and potassium ions across the cell membrane against their concentration gradients.

Mechanism

1. Three Na^+ ions bind inside the cell.
2. ATP is hydrolyzed.
3. Pump changes shape.
4. Three Na^+ ions move outside.
5. Two K^+ ions bind outside.
6. Pump returns to original shape.
7. Two K^+ ions enter the cell.

Overall Reaction

3 Na^+ (inside) → outside

2 K^+ (outside) → inside

Consumes 1 ATP

Functions

- Maintains membrane potential
- Nerve impulse transmission
- Muscle contraction
- Cell volume regulation
- Active transport

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5. Carbonic Anhydrase

Definition

Carbonic anhydrase is a zinc-containing metalloenzyme that catalyzes the reversible conversion of carbon dioxide and water into bicarbonate and hydrogen ions.

Reaction

$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

Metal Present

Zn^{2+}

Functions

- CO_2 transport in blood
- Regulation of blood pH
- Kidney acid-base balance
- Respiration

Clinical Importance

Carbonic anhydrase inhibitors are used in:

- Glaucoma
- Epilepsy
- Altitude sickness

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6. Carboxypeptidase

Definition

Carboxypeptidase is a zinc-containing digestive enzyme produced by the pancreas.

Function

Removes amino acids one by one from the C-terminal end of proteins.

Metal Present

Zn^{2+}

Biological Role

- Protein digestion
- Hydrolysis of peptide bonds
- Amino acid metabolism

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7. Excess and Deficiency of Trace Metals

Iron (Fe)

Deficiency

- Iron deficiency anemia
- Fatigue
- Weakness

Excess

- Hemochromatosis
- Liver damage
- Diabetes
- Heart disease

Zinc (Zn)

Deficiency

- Slow wound healing
- Hair loss
- Poor immunity
- Growth retardation

Excess

- Copper deficiency
- Nausea
- Vomiting

Copper (Cu)

Deficiency

- Anemia
- Bone abnormalities

Excess

- Wilson's disease
- Liver damage
- Neurological disorders

Iodine (I)

Deficiency

- Goiter
- Hypothyroidism

Excess

- Hyperthyroidism

Selenium (Se)

Deficiency

- Muscle weakness
- Cardiomyopathy

Excess

- Hair loss
- Brittle nails
- Garlic odor in breath

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8. Toxicity of Metal Ions

A. Mercury (Hg)

Sources

- Industrial waste
- Thermometers
- Fish

Toxic Effects

- Brain damage
- Kidney failure
- Nervous disorders
- Memory loss

Reason for Toxicity

Hg binds strongly with sulfhydryl (-SH) groups of proteins and enzymes.

B. Lead (Pb)

Sources

- Batteries

- Paint
- Pipes

Toxic Effects

- Anemia
- Brain damage
- Kidney disease
- Learning disability in children

Reason

Pb replaces calcium and interferes with enzyme activity.

C. Cadmium (Cd)

Sources

- Cigarette smoke
- Batteries
- Industrial pollution

Toxic Effects

- Kidney damage
- Bone disease
- Lung cancer

Reason

Cadmium binds to proteins and replaces zinc.

D. Arsenic (As)

Sources

- Contaminated groundwater
- Pesticides
- Mining

Toxic Effects

- Skin lesions
- Cancer
- Neuropathy
- Liver damage

Reason

Arsenic inhibits ATP production and enzyme activity.

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9. Reasons for Toxicity of Heavy Metals

Heavy metals become toxic because they:

- Bind to sulfur-containing enzymes.
- Replace essential metal ions.
- Generate reactive oxygen species (ROS).
- Damage DNA.
- Inhibit enzyme activity.
- Disturb protein structure.
- Cause oxidative stress.

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10. Chelating Agents in Medicine

Definition

Chelating agents are compounds that bind strongly with metal ions to form stable complexes that can be excreted from the body.

Medical Importance

Treatment of heavy metal poisoning.

Chelating Agent	Used For
EDTA	Lead poisoning

Chelating Agent	Used For
Dimercaprol (BAL)	Arsenic, Mercury
DMSA	Lead, Mercury
Penicillamine	Copper (Wilson's disease)
Deferoxamine	Iron overload

Advantages

- Removes toxic metals.
- Prevents organ damage.
- Increases metal excretion.
- Life-saving in poisoning.

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11. Metalloporphyrins

Definition

Metalloporphyrins are coordination compounds in which a metal ion is held within a porphyrin ring.

Examples

- Hemoglobin
- Myoglobin
- Cytochromes
- Chlorophyll (Mg)

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12. Hemoglobin

Definition

Hemoglobin is an iron-containing oxygen transport protein present in red blood cells.

Structure

- Four polypeptide chains
- Four heme groups
- One Fe^{2+} in each heme

Total iron atoms = **4**

Functions

- Oxygen transport
- Carbon dioxide transport
- Blood buffering

Oxygen Binding

$Hb + O_2 \rightleftharpoons HbO_2$

Binding is reversible.

Importance

- Maintains oxygen supply.
- Prevents tissue hypoxia.
- Essential for respiration.

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13. Myoglobin

Definition

Myoglobin is an iron-containing oxygen storage protein found in muscles.

Structure

- One polypeptide chain

- One heme group
- One Fe^{2+} ion

Functions

- Stores oxygen
- Supplies oxygen during exercise
- Facilitates oxygen diffusion

Difference Between Hemoglobin and Myoglobin

Hemoglobin	Myoglobin
Four chains	One chain
Four heme groups	One heme group
Oxygen transport	Oxygen storage
Blood	Muscle
Cooperative binding	Non-cooperative binding

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14. Biological Roles of Important Metal Ions

A. Sodium (Na^+)

Functions:

- Maintains extracellular fluid.
- Nerve impulse transmission.
- Osmotic pressure.
- Muscle contraction.
- Acid-base balance.

Deficiency:

- Hyponatremia
- Muscle cramps

B. Potassium (K^+)

Functions:

- Major intracellular ion.
- Nerve transmission.
- Heart rhythm.
- Muscle function.
- Protein synthesis.

Deficiency:

- Hypokalemia
- Muscle weakness
- Arrhythmia

C. Calcium (Ca^{2+})

Functions:

- Bone and teeth formation.
- Blood clotting.
- Muscle contraction.
- Hormone secretion.
- Cell signaling.

Deficiency:

- Osteoporosis
- Tetany

D. Magnesium (Mg^{2+})

Functions:

- ATP activation.
- Cofactor for over 300 enzymes.
- DNA and RNA synthesis.
- Muscle relaxation.
- Protein synthesis.

Deficiency:

- Muscle cramps
- Weakness
- Cardiac arrhythmias

E. Iron (Fe^{2+})

Functions:

- Oxygen transport.
- Electron transport chain.
- Hemoglobin synthesis.
- Myoglobin function.
- Enzyme cofactor.

Deficiency:

- Iron-deficiency anemia

Excess:

- Hemochromatosis

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15. Summary

Bioinorganic chemistry explores the indispensable roles of metal ions in living organisms. Essential metals such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and Fe^{2+} regulate physiological functions including nerve transmission, muscle contraction, oxygen transport, and enzyme catalysis. Zinc-containing enzymes like carbonic anhydrase and carboxypeptidase are vital for respiration and digestion. Heavy metals such as Hg, Pb, Cd, and As are toxic because they disrupt enzymes and cellular metabolism, but chelating agents provide effective treatment for metal poisoning. Metalloporphyrins, especially hemoglobin and myoglobin, illustrate how iron-containing complexes are fundamental for oxygen transport and storage. Understanding these concepts is essential for biochemistry, medicine, pharmacology, and environmental science.

Important Examination Questions

1. Define Bioinorganic Chemistry. Discuss the importance of metal ions in biological systems.
2. Classify metal ions into essential, non-essential, trace, and toxic metals with examples.
3. Explain the mechanism and biological significance of the Na^+/K^+ pump.
4. Describe the structure and functions of carbonic anhydrase.
5. Explain the role of zinc in carboxypeptidase.
6. Discuss the deficiency and excess effects of trace metals.
7. Explain the toxicity of Hg, Pb, Cd, and As and their mechanisms of action.
8. What are chelating agents? Discuss their medical applications.
9. Describe the structure and functions of hemoglobin and myoglobin.
10. Explain the biological roles of Na^+, K^+, Ca^{2+}, Mg^{2+}, and Fe^{2+} ions.

Descriptive Notes on Chemistry of f-Block Elements

Unit: Lanthanides and Actinides

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1. Introduction to f-Block Elements

Definition

The **f-block elements** are those elements in which the last electron enters the **(n−2)f subshell**. They are placed separately at the bottom of the periodic table and are commonly known as **inner transition elements**.

The f-block consists of:

1. **Lanthanides (4f series):** Atomic numbers **58–71** (Cerium to Lutetium)
2. **Actinides (5f series):** Atomic numbers **90–103** (Thorium to Lawrencium)

General electronic configuration:

[
(n-2)f^{1-14}(n-1)d^{0-1}ns^2
]

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2. Lanthanides

Definition

Lanthanides are the fourteen elements following lanthanum in which the **4f orbitals are progressively filled**.

Elements

Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

They are commonly called **Rare Earth Elements (REEs)** because they occur together in nature and are difficult to separate.

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3. Electronic Structure of Lanthanides

General Electronic Configuration

[
[Xe],4f^{1-14}5d^{0-1}6s^2
]

Examples:

Element	Electronic Configuration
La	[Xe]$5d^1 6s^2$
Ce	[Xe]$4f^1 5d^1 6s^2$
Pr	[Xe]$4f^3 6s^2$
Nd	[Xe]$4f^4 6s^2$
Gd	[Xe]$4f^7 5d^1 6s^2$
Lu	[Xe]$4f^{14} 5d^1 6s^2$

Characteristics

- Filling of 4f orbitals.
- Electrons are poorly shielded.
- Similar chemical properties.
- Mostly electropositive metals.

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4. Oxidation States of Lanthanides

The most common oxidation state is:

+3

Reason:

- Loss of two 6s electrons and one 5d/4f electron gives a stable configuration.

Other oxidation states:

Element	Oxidation States
Ce	+3, +4
Pr	+3, +4
Eu	+2, +3
Sm	+2, +3
Yb	+2, +3
Tb	+3, +4

Stability

+3 > +2 > +4

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5. Ionic Radii and Lanthanide Contraction

Definition

The gradual decrease in the ionic and atomic radii of lanthanide elements from **La^{3+} to Lu^{3+}** is called **Lanthanide Contraction**.

Cause

- Poor shielding by 4f electrons.
- Increase in nuclear charge.
- Greater attraction between nucleus and electrons.

Consequences

1. Similar sizes of 4d and 5d transition elements.
2. Difficulty in separating lanthanides.
3. Decrease in basic strength of hydroxides.
4. Increased density and hardness.
5. Similar chemistry among lanthanides.

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6. Complex Formation in Lanthanides

Lanthanides form complexes due to:

- High positive charge.
- Small ionic size.
- Availability of vacant orbitals.

Common ligands:

- EDTA
- Fluoride (F^-)
- Oxalate ($C_2O_4^{2-}$)
- Citrate
- Nitrate

Examples:

- $[La(EDTA)]^-$
- $[Ce(NO_3)_6]^{2-}$

Characteristics

- Mostly ionic.
- High coordination numbers (8–12).
- Weak crystal field effects.

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7. Occurrence of Lanthanides

Lanthanides occur together in minerals.

Important ores:

Mineral	Composition
Monazite	Rare earth phosphates
Bastnäsite	Rare earth fluorocarbonates
Xenotime	Yttrium phosphate

Major producing countries include China, Australia, India and the USA.

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8. Isolation of Lanthanides

Since lanthanides have very similar chemical properties, their separation is difficult.

Methods

(A) Fractional Crystallization

Based on slight differences in solubility.

(B) Fractional Precipitation

Based on differences in precipitation.

(C) Ion Exchange Method

Uses ion-exchange resins.

Advantages:

- High purity
- Most commonly used

(D) Solvent Extraction

Uses organic solvents.

Suitable for industrial-scale separation.

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9. Lanthanide Compounds

Important compounds include:

(1) Oxides

General formula:

[
Ln_2O_3
]

Properties:

- Basic
- High melting point
- Thermally stable

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(2) Hydroxides

Formula:

$$
\mathrm{Ln(OH)_3}
$$

Properties:

- Basic
- Basicity decreases across the series due to lanthanide contraction.

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(3) Halides

Examples:

- $\mathrm{CeCl_3}$
- $\mathrm{LaF_3}$

Properties:

- Mostly ionic
- High melting points

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(4) Nitrates

Formula:

$$
\mathrm{Ln(NO_3)_3}
$$

Used in laboratory chemistry and industrial processes.

10. Actinides

Definition

Actinides are fourteen elements following actinium in which the **5f orbitals are progressively filled**.

Elements:

Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr.

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11. General Features of Actinides

Electronic Configuration

[
[Rn],5f^{1-14}6d^{0-1}7s^2
]

Properties

- Radioactive.
- Heavy metals.
- Dense and electropositive.
- Many are synthetic.
- Show several oxidation states.
- Readily form complexes.

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12. Chemistry of Actinides

Oxidation States

Unlike lanthanides, actinides show many oxidation states.

Element Common Oxidation States

Element	Common Oxidation States
Th	+4
Pa	+5
U	+3, +4, +5, +6
Np	+3 to +7
Pu	+3 to +7
Am	+2 to +6

Reason:

Small energy difference between 5f, 6d and 7s orbitals.

Chemical Properties

- Highly reactive.
- Form oxides and halides.
- Readily undergo oxidation.
- Strong complex-forming tendency.

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13. Separation of Np, Pu and Am from Uranium

Spent nuclear fuel contains:

- Uranium (U)
- Neptunium (Np)
- Plutonium (Pu)
- Americium (Am)

Principle

Separation is based on differences in oxidation states and solvent extraction.

PUREX Process (Plutonium Uranium Redox Extraction)

Step 1

Spent fuel is dissolved in concentrated nitric acid.

Step 2

Extraction with tributyl phosphate (TBP) in kerosene.

TBP selectively extracts:

- Uranium
- Plutonium

Americium remains in the aqueous phase.

Step 3

Redox reactions are used to separate uranium and plutonium.

Example:

$Pu^{4+} \rightarrow Pu^{3+}$

Pu^{3+} is not extracted by TBP and returns to the aqueous layer.

Step 4

Neptunium is separated by adjusting its oxidation state.

Step 5

Americium is recovered using ion exchange or solvent extraction methods.

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14. Comparison of Lanthanides, Actinides and Transition Elements

Property	Lanthanides	Actinides	Transition Elements
Orbital filled	4f	5f	d-orbitals
Oxidation states	Mainly +3	+3 to +7	Variable
Radioactivity	Mostly non-radioactive (except Pm)	All radioactive	Mostly non-radioactive
Complex formation	Moderate	Strong	Strong
Magnetic behavior	Paramagnetic	Strongly paramagnetic	Paramagnetic/Ferromagnetic
Color	Pale-colored ions	Deep-colored ions	Colored ions
Shielding	Poor (4f electrons)	Poor (5f electrons)	Better than f-block
Covalent character	Less	Greater	Moderate
Chemical reactivity	Less reactive	More reactive	Moderate
Separation	Difficult	Easier than lanthanides	Comparatively easy

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15. Similarities Between Lanthanides and Actinides

- Both are f-block elements.
- Both are electropositive metals.
- Both exhibit contraction across the series.
- Both form complexes.
- Both have high coordination numbers.
- Both readily form oxides and halides.

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16. Differences Between Lanthanides and Actinides

Lanthanides	Actinides

Lanthanides	Actinides
4f orbitals filled	5f orbitals filled
Mostly +3 oxidation state	Variable oxidation states
Mostly non-radioactive	All radioactive
Less complex formation	Greater complex formation
Less covalent	More covalent
More stable	Less stable
Rare earth elements	Mostly synthetic heavy elements

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17. Applications of Lanthanides

- Catalysts in petroleum refining.
- Permanent magnets (Nd–Fe–B magnets).
- Optical glass and lasers.
- Phosphors in LEDs and fluorescent lamps.
- MRI contrast agents (Gd compounds).
- Rechargeable batteries.

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18. Applications of Actinides

- Uranium as nuclear fuel.
- Plutonium in nuclear reactors and weapons.
- Americium in smoke detectors.
- Thorium for potential nuclear fuel cycles.
- Radioisotopes in scientific research and medicine.

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19. Summary

The **f-block elements** consist of **lanthanides** and **actinides**, characterized by the filling of **4f** and **5f** orbitals, respectively. Lanthanides predominantly exhibit the **+3 oxidation state**, show **lanthanide contraction**, and possess very similar chemical properties, making their separation difficult. They form oxides, halides, hydroxides, and coordination compounds and have important technological applications in magnets, catalysts, lasers, and medical imaging.

Actinides, in contrast, are **all radioactive** and display a much wider range of oxidation states because of the comparable energies of the 5f, 6d, and 7s orbitals. Their chemistry is more

complex, with stronger covalent character and greater tendency to form complexes. Industrial separation of **neptunium (Np), plutonium (Pu), and americium (Am)** from uranium is commonly achieved using the **PUREX (Plutonium Uranium Redox Extraction) process**, which exploits differences in oxidation states and solvent extraction behavior. A comparative study of lanthanides, actinides, and transition elements highlights the distinctive chemical behavior of the f-block and its significance in modern chemistry, nuclear science, and advanced materials.

Important Examination Questions

1. Define f-block elements and explain the electronic configuration of lanthanides.
2. Discuss the oxidation states of lanthanides with suitable examples.
3. Explain **lanthanide contraction**, its causes, and its consequences.
4. Describe the occurrence and methods of isolation of lanthanides.
5. Explain the important compounds and complex formation of lanthanides.
6. Discuss the general features and chemistry of actinides.
7. Describe the **PUREX process** for the separation of uranium, neptunium, plutonium, and americium.
8. Compare the properties of **lanthanides, actinides, and transition elements**.
9. Differentiate between lanthanides and actinides.
10. Write short notes on the applications of lanthanides and actinides.

Photochemistry – Descriptive Notes

1. Photochemistry

Photochemistry is the branch of chemistry that deals with **chemical reactions initiated by the absorption of light (radiation)**. The absorbed light provides energy to molecules, causing them to reach an excited state where they can undergo chemical or physical changes.

Characteristics

- Involves ultraviolet (UV), visible, or infrared (IR) light.
- Reactions occur only after light absorption.
- Products often differ from those obtained by heating.

Examples

- Photosynthesis in plants.
- Formation of vitamin D in skin.
- Photography.
- Decomposition of silver bromide in photographic films.

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2. Interaction of Radiation with Matter

When electromagnetic radiation strikes a substance, several processes may occur.

(a) Absorption

- A molecule absorbs a photon if the photon's energy matches the energy difference between two molecular energy levels.
- The molecule is promoted from the **ground state (S_0)** to an **excited state (S_1 or S_2).**

[
E = h\nu = \frac{hc}{\lambda}
]

Where:

- **E** = energy of photon
- **h** = Planck's constant
- **ν** = frequency
- **c** = speed of light

- λ = wavelength

(b) Reflection

Some light is reflected from the surface.

(c) Transmission

Light passes through the material without being absorbed.

(d) Scattering

Light changes direction due to interaction with particles.

(e) Emission

Excited molecules return to lower energy states by emitting light (fluorescence or phosphorescence).

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3. Difference Between Thermal and Photochemical Processes

Thermal Process	Photochemical Process
Initiated by heat	Initiated by light
Molecules gain energy from collisions	Molecules gain energy by absorbing photons
Reactants remain in ground state	Excited-state molecules participate
Rate increases with temperature	Depends mainly on light intensity and wavelength
Requires activation energy from heating	Activation energy supplied by light
Example: Combustion	Photosynthesis

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4. Laws of Photochemistry

(A) Grotthuss–Draper Law

Statement

Only the light that is absorbed by a substance can produce a photochemical change.

Explanation

- Light that is reflected or transmitted cannot initiate a photochemical reaction.
- Absorption is essential before any photochemical reaction can occur.

Example

Silver bromide decomposes only after absorbing light.

[
2AgBr \rightarrow 2Ag + Br_2
]

(B) Stark–Einstein Law (Law of Photochemical Equivalence)

Statement

Each molecule that absorbs one photon is activated for a photochemical reaction.

or

One absorbed photon excites only one molecule.

Explanation

- One photon transfers its entire energy to one molecule.
- The excited molecule may undergo reaction or lose energy by other processes.

Importance

- Forms the basis for calculating quantum yield.
- Explains primary photochemical processes.

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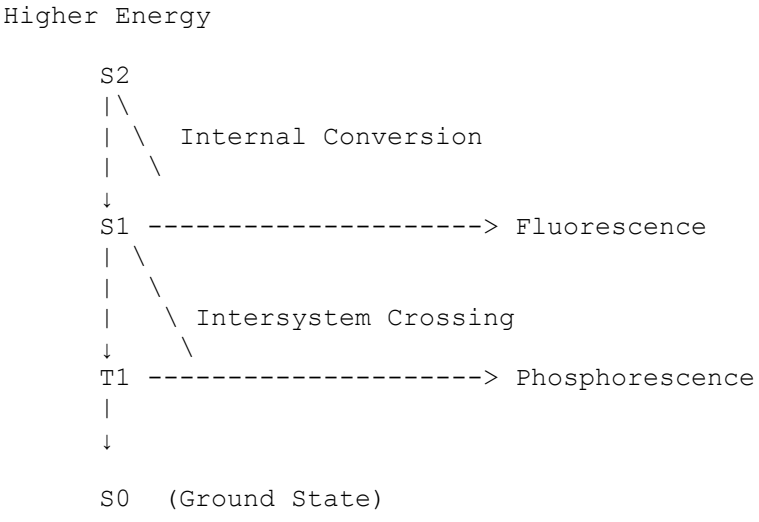
5. Jablonski Diagram

The Jablonski diagram represents the electronic states of molecules and the transitions between them.



Electronic States

- $\mathbf{S_0}$ = Ground singlet state
- $\mathbf{S_1}$, $\mathbf{S_2}$ = Excited singlet states
- $\mathbf{T_1}$ = Excited triplet state

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6. Processes Occurring in the Excited State

(A) Fluorescence

Definition

Fluorescence is the **rapid emission of light** when an excited molecule returns from the **excited singlet state (S_1)** to the **ground singlet state (S_0).**

Characteristics

- Very fast.
- Lifetime: $\mathbf{10^{-9}}$ **to** $\mathbf{10^{-7}}$ **s**
- Stops immediately when light source is removed.
- Emitted light has longer wavelength than absorbed light (Stokes shift).

Examples

- Fluorescent dyes
- Fluorescent lamps

(B) Phosphorescence

Definition

Phosphorescence is the emission of light when a molecule returns from the **triplet state (T_1)** to the **ground state (S_0).**

Characteristics

- Slow process.
- Lifetime: milliseconds to hours.
- Continues even after the light source is removed.

Examples

- Glow-in-the-dark materials
- Luminous paints

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7. Non-Radiative Processes

These processes involve **loss of energy without emission of light.**

(A) Internal Conversion (IC)

Definition

Internal conversion is the transition between two electronic states of the **same spin multiplicity** without emission of radiation.

Example:

[
S_2 \rightarrow S_1
]

or

$$
S_1 \rightarrow S_0
$$

Characteristics

- No light emitted.
- Energy converted into heat.

(B) Intersystem Crossing (ISC)

Definition

Intersystem crossing is the transition from an excited singlet state to an excited triplet state.

Example:

$$
S_1 \rightarrow T_1
$$

Characteristics

- Spin changes during transition.
- Leads to phosphorescence.
- Non-radiative process.

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8. Quantum Yield (Quantum Efficiency)

Definition

Quantum yield is the ratio of the number of molecules reacting (or events occurring) to the number of photons absorbed.

Formula

$$
\phi=\frac{\text{Number of molecules reacted}}{\text{Number of photons absorbed}}
$$

or

$$
\phi=\frac{\text{Number of events}}{\text{Number of photons absorbed}}
$$

Interpretation

- **φ = 1** → One molecule reacts per absorbed photon.
- **φ > 1** → Chain reactions occur.
- **φ < 1** → Some excited molecules lose energy without reacting.

Factors Affecting Quantum Yield

- Wavelength of light.
- Temperature.
- Presence of quenchers.
- Solvent.
- Oxygen concentration.

---

9. Photosensitized Reactions

Definition

A photosensitized reaction is a photochemical reaction in which a **photosensitizer** absorbs light first and then transfers its energy to another molecule that actually undergoes the reaction.

Photosensitizer

A substance that absorbs light but is regenerated after transferring energy.

Examples:

- Benzophenone
- Acetone
- Chlorophyll
- Rose Bengal

Energy Transfer Process

The sensitizer (S) absorbs light:

$$
S + h\nu \rightarrow S^*
$$

The excited sensitizer transfers energy:

$$
S^* + A \rightarrow S + A^*
$$

The excited acceptor reacts:

$$
A^* \rightarrow Products
$$

Where:

- **S** = Sensitizer
- **A** = Acceptor molecule

Simple Examples of Photosensitized Reactions

Example 1: Photosynthesis

- **Sensitizer:** Chlorophyll
- Chlorophyll absorbs sunlight.
- Energy is transferred to drive the conversion of carbon dioxide and water into glucose and oxygen.

Example 2: Formation of Singlet Oxygen

- **Sensitizer:** Rose Bengal (or methylene blue)
- The sensitizer absorbs light and transfers energy to molecular oxygen.

- Ground-state oxygen is converted into highly reactive **singlet oxygen**, which is used in photodynamic therapy and oxidation reactions.

Example 3: Benzophenone-Sensitized Reaction

- Benzophenone absorbs UV light.
- It transfers energy to an organic substrate, initiating reactions such as isomerization or hydrogen abstraction.

Summary

- **Photochemistry** studies chemical reactions initiated by light.
- **Only absorbed light** causes photochemical change (Grotthuss–Draper law).
- **One absorbed photon excites one molecule** (Stark–Einstein law).
- The **Jablonski diagram** illustrates excitation, fluorescence, phosphorescence, internal conversion, and intersystem crossing.
- **Fluorescence** is fast light emission from the singlet excited state, while **phosphorescence** is slower emission from the triplet state.
- **Internal conversion** and **intersystem crossing** are non-radiative pathways that dissipate energy without light emission.
- **Quantum yield (φ)** measures the efficiency of a photochemical process by comparing reacted molecules (or events) to absorbed photons.
- In **photosensitized reactions**, a sensitizer absorbs light and transfers energy to another molecule, enabling reactions such as photosynthesis and singlet oxygen generation.

Statistical Thermodynamics – Descriptive Notes

1. Introduction to Statistical Thermodynamics

Statistical thermodynamics is the branch of physical chemistry that explains the **macroscopic properties** of matter (such as pressure, temperature, entropy, and internal energy) in terms of the **microscopic behavior** of atoms and molecules.

It combines the principles of **thermodynamics**, **statistics**, and **quantum mechanics** to describe the distribution of molecules among different energy levels.

Basic Concepts

- A gas contains a very large number of molecules moving randomly.
- Individual molecular motion is unpredictable, but the average behavior of all molecules can be described statistically.
- Statistical thermodynamics relates molecular properties to measurable thermodynamic quantities.

Importance

- Explains molecular distribution among energy levels.
- Provides the basis for calculating thermodynamic functions.
- Helps understand gases, solids, and liquids at the molecular level.
- Connects microscopic behavior with macroscopic observations.

---

2. Types of Statistics

Depending on the nature of particles, three types of statistical distributions are used.

(A) Maxwell–Boltzmann Statistics (MB Statistics)

Definition

Maxwell–Boltzmann statistics describe the distribution of **classical particles** that are **distinguishable** and do not obey quantum restrictions.

Characteristics

- Particles are distinguishable.
- Any number of particles can occupy the same energy level.
- Applicable at high temperatures and low densities.
- Used for ideal gases.

Applications

- Ideal gases
- Gas kinetics
- Molecular velocity distribution

(B) Bose–Einstein Statistics (BE Statistics)

Definition

Bose–Einstein statistics describe **bosons**, particles having **integral spin** (0, 1, 2, ...).

Characteristics

- Particles are indistinguishable.
- Many particles may occupy the same quantum state.
- Responsible for Bose–Einstein condensation.

Examples

- Photons
- Helium-4 atoms
- Phonons

(C) Fermi–Dirac Statistics (FD Statistics)

Definition

Fermi–Dirac statistics describe **fermions**, particles having **half-integral spin**.

Characteristics

- Particles are indistinguishable.
- Obey the **Pauli Exclusion Principle**.
- Only one particle can occupy a given quantum state.

Examples

- Electrons
- Protons
- Neutrons

Comparison of the Three Statistics

Property	Maxwell–Boltzmann	Bose–Einstein	Fermi–Dirac
Particle type	Classical	Bosons	Fermions
Distinguishable	Yes	No	No
Same energy state	Unlimited particles	Unlimited particles	Only one particle
Quantum effects	Negligible	Important	Important
Examples	Gas molecules	Photons	Electrons

---

3. Maxwell–Boltzmann Law

Statement

The Maxwell–Boltzmann law states that **gas molecules are distributed among different energy states according to probability**, and most molecules possess intermediate energies while only a few have very low or very high energies.

Significance

- Explains the distribution of molecular energies.
- Forms the basis of kinetic theory.
- Used in calculating thermodynamic properties.

---

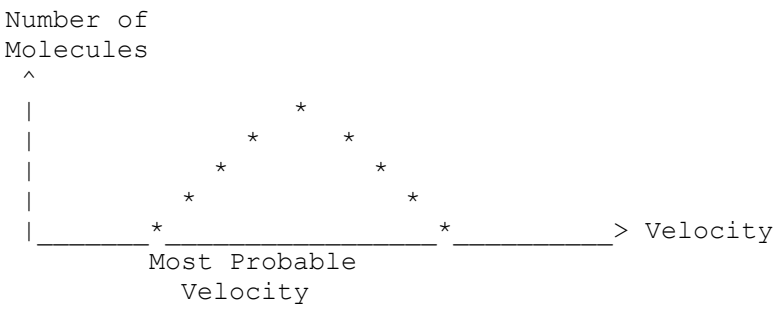
4. Maxwell–Boltzmann Distribution of Molecular Velocity

The Maxwell–Boltzmann distribution describes the fraction of molecules having different molecular velocities.

Characteristics

- Very few molecules have zero velocity.
- Number of molecules increases with velocity.
- Maximum number occurs at the **most probable velocity**.
- Number decreases at higher velocities.

Distribution Curve



Types of Molecular Velocities

(a) Most Probable Velocity

The velocity possessed by the largest number of molecules.

$$
v_{mp}=\sqrt{\frac{2RT}{M}}
$$

(b) Average Velocity

Average of the velocities of all molecules.

$$
v_{avg}=\sqrt{\frac{8RT}{\pi M}}
$$

(c) Root Mean Square (RMS) Velocity

Square root of the average of the squares of molecular velocities.

$$
v_{rms}=\sqrt{\frac{3RT}{M}}
$$

Relationship

$$
v_{rms}>v_{avg}>v_{mp}
$$

---

5. Maxwell–Boltzmann Distribution of Energy

The Maxwell–Boltzmann distribution also describes how molecules are distributed among different energy levels.

Characteristics

- Few molecules possess very low energy.
- Most molecules possess moderate energy.
- Very few molecules possess high energy.

Effect of Temperature

- At low temperature, the distribution is narrow.
- At high temperature, the curve becomes broader.
- More molecules possess higher energy as temperature increases.

---

6. Evaluation of Energy

For a monatomic ideal gas, only **translational kinetic energy** contributes to the internal energy.

The average kinetic energy of one molecule is

$$
E=\frac{3}{2}kT
$$

where:

- **E** = average kinetic energy per molecule
- **k** = Boltzmann constant
- **T** = absolute temperature

For one mole,

$$
E=\frac{3}{2}RT
$$

where:

- **R** = gas constant

For **n moles**,

$$
E=\frac{3}{2}nRT
$$

Thus, the internal energy of a monatomic ideal gas depends **only on temperature**.

---

7. Derivation of the Equation of State for a Monatomic Ideal Gas

Using the kinetic theory of gases:

Step 1: Pressure due to Molecular Motion

The pressure exerted by gas molecules is

$$
P=\frac{1}{3}\rho c_{rms}^{2}
$$

where:

- **P** = pressure
- **ρ** = density
- $\mathbf{c_{rms}}$ = root mean square velocity

Step 2: Density

Density is

$$
\rho=\frac{Nm}{V}
$$

where:

- **N** = number of molecules
- **m** = mass of one molecule
- **V** = volume

Substituting,

$$
PV=\frac{1}{3}Nm c_{rms}^{2}
$$

Step 3: Kinetic Energy

Average kinetic energy of one molecule

$$
\frac{1}{2}mc_{rms}^{2}=\frac{3}{2}kT
$$

Therefore,

$$
mc_{rms}^{2}=3kT
$$

Substituting into the pressure equation,

$$
PV=NkT
$$

Since

$$
N=nN_A
$$

and

$$
R=N_Ak
$$

we obtain

$$
\boxed{PV=nRT}
$$

This is the **equation of state for a monatomic ideal gas**, also known as the **Ideal Gas Equation**.

---

8. Assumptions of an Ideal Monatomic Gas

1. Gas molecules are treated as point particles.
2. Molecular volume is negligible compared to the container volume.
3. Molecules move randomly in straight lines.
4. Collisions between molecules are perfectly elastic.
5. No intermolecular forces act except during collisions.
6. Average kinetic energy depends only on absolute temperature.

---

9. Applications of Statistical Thermodynamics

- Explains gas behavior.
- Derives the ideal gas equation.
- Calculates entropy and free energy.
- Predicts molecular energy distributions.
- Explains heat capacities of gases.
- Studies molecular motion and reaction rates.

Summary

- **Statistical thermodynamics** connects molecular behavior with macroscopic thermodynamic properties.
- **Maxwell–Boltzmann statistics** apply to distinguishable classical particles, **Bose–Einstein statistics** to bosons, and **Fermi–Dirac statistics** to fermions.
- The **Maxwell–Boltzmann law** describes the distribution of molecules among energy and velocity states.
- Molecular velocities are characterized by the **most probable**, **average**, and **RMS** velocities, with (v_{rms} > v_{avg} > v_{mp}).
- The average translational kinetic energy of a monatomic ideal gas is (\frac{3}{2}kT) per molecule or (\frac{3}{2}nRT) for (n) moles.
- From kinetic theory, the **equation of state** for a monatomic ideal gas is:

[
\boxed{PV=nRT}
]

which relates pressure, volume, temperature, and the amount of gas.

Ultraviolet (UV) and Infrared (IR) Spectroscopy – Descriptive Notes

---

1. Spectroscopy

Spectroscopy is the study of the interaction of **electromagnetic radiation** with matter. It is widely used to identify compounds, determine molecular structure, and analyze chemical composition.

The two most important spectroscopic techniques in organic chemistry are:

- **Ultraviolet (UV) Spectroscopy**
- **Infrared (IR) Spectroscopy**

PART A: ULTRAVIOLET (UV) ABSORPTION SPECTROSCOPY

2. Introduction

Ultraviolet spectroscopy is based on the **absorption of ultraviolet or visible light** by molecules, causing electrons to move from lower-energy molecular orbitals to higher-energy orbitals.

UV Region

- **Ultraviolet:** 200–400 nm
- **Visible:** 400–800 nm

Principle

When UV radiation passes through a sample, molecules absorb energy if the photon energy matches the energy difference between two electronic energy levels.

[
E=h\nu=\frac{hc}{\lambda}
]

This absorption causes **electronic excitation**.

---

3. Beer–Lambert Law

The Beer–Lambert law relates the absorption of light to the concentration of the absorbing substance.

Statement

The absorbance of a solution is directly proportional to:

- Concentration of the solution
- Path length of the sample

Equation

[
A=\varepsilon cl
]

where:

- **A** = Absorbance
- **ε** = Molar absorptivity (L mol^{-1} cm^{-1})
- **c** = Concentration (mol L^{-1})
- **l** = Path length (cm)

Importance

- Used to determine unknown concentrations.
- Basis of quantitative UV analysis.

---

4. Molar Absorptivity (Molar Extinction Coefficient)

Definition

Molar absorptivity is the absorbance of a **1 mol L^{-1}** solution measured in a **1 cm** cell.

Unit

[
L,mol^{-1},cm^{-1}
]

Significance

- Indicates how strongly a compound absorbs UV light.
- Larger ε means stronger absorption.

---

5. Presentation of UV Spectrum

A UV spectrum is a graph of:

- **X-axis:** Wavelength (nm)
- **Y-axis:** Absorbance or Molar absorptivity

Information Obtained

- Maximum absorption wavelength (**λmax**)
- Intensity of absorption
- Presence of conjugation
- Identification of chromophores

---

6. Analysis of UV Spectrum

UV spectra provide information about:

- Degree of conjugation
- Presence of aromatic rings
- Unsaturated functional groups
- Electronic transitions

The longer the conjugated system, the larger the wavelength of absorption.

---

7. Types of Electronic Transitions

Electronic transitions occur when electrons absorb UV energy.

(A) σ → σ*

- Electron moves from σ bonding orbital to σ* antibonding orbital.
- Highest energy transition.
- Found in saturated compounds.

Example:

- Alkanes

(B) n → σ*

- Lone-pair electron moves to σ* orbital.

Occurs in:

- Alcohols
- Amines
- Halides

(C) π → π*

- Electron moves from π bonding orbital to π* orbital.

Occurs in:

- Alkenes
- Carbonyl compounds
- Aromatic compounds

Strong absorption.

(D) n → π*

- Lone-pair electron moves to π* orbital.

Occurs in:

- Aldehydes
- Ketones
- Carboxylic acids

Weak absorption.

Energy Order

[
\sigma\rightarrow\sigma^*

n\rightarrow\sigma^*

\pi\rightarrow\pi^*

n\rightarrow\pi^*
]

---

8. Effect of Conjugation

Conjugation means alternating single and double bonds.

Effects

- Lowers energy gap.
- Increases wavelength of absorption (λmax).
- Increases absorption intensity.

Example:

Ethylene absorbs around **171 nm**.

1,3-Butadiene absorbs around **217 nm** because of conjugation.

---

9. Chromophore

Definition

A chromophore is an atom or group of atoms responsible for absorption of UV or visible light.

Examples

- C=C
- C≡C
- C=O
- N=N
- NO_2
- Benzene ring

---

10. Auxochrome

Definition

An auxochrome is a group that **does not absorb strongly by itself** but increases the intensity or shifts the absorption of a chromophore.

Examples

- –OH
- $–NH_2$
- –OR
- –SH

---

11. Spectral Shifts

(A) Bathochromic Shift (Red Shift)

Shift of absorption toward **longer wavelength**.

Occurs due to:

- Increased conjugation

- Addition of auxochromes

Example:

Benzene → Aniline

(B) Hypsochromic Shift (Blue Shift)

Shift toward **shorter wavelength**.

Occurs due to:

- Loss of conjugation
- Protonation

(C) Hyperchromic Effect

Increase in absorption intensity.

Caused by:

- Auxochromes
- Increased conjugation

(D) Hypochromic Effect

Decrease in absorption intensity.

Caused by:

- Steric hindrance
- Loss of conjugation

PART B: INFRARED (IR) SPECTROSCOPY

12. Introduction

Infrared spectroscopy studies the interaction of infrared radiation with molecules.

IR absorption causes **molecular vibrations** rather than electronic excitation.

IR Region

4000–400 cm^{-1}

---

13. Molecular Vibrations

A molecule continuously vibrates.

Two main types are:

(A) Stretching Vibrations

Change in bond length.

Types:

- Symmetric stretching
- Asymmetric stretching

(B) Bending Vibrations

Change in bond angle.

Types:

- Scissoring
- Rocking
- Wagging
- Twisting

---

14. Hooke's Law

The vibration of a chemical bond follows Hooke's law, treating the bond like a spring.

The vibrational frequency depends on:

- Bond strength (force constant)
- Mass of the bonded atoms

Stronger bonds vibrate at higher frequencies, while heavier atoms vibrate at lower frequencies.

---

15. Selection Rule

A vibration is IR active only if it causes a **change in the dipole moment** of the molecule.

Examples:

- HCl → IR active
- CO_2 symmetric stretch → IR inactive
- O_2 → IR inactive

---

16. Intensity and Position of IR Bands

Position

Depends upon:

- Bond strength
- Atomic masses

Strong bonds absorb at higher wavenumbers.

Intensity

Depends upon:

- Magnitude of dipole moment change

Greater dipole moment change gives stronger absorption bands.

17. Measurement of IR Spectrum

Instrument

IR spectrophotometer

Procedure

- IR radiation passes through the sample.
- Molecules absorb specific frequencies.
- Detector records transmitted radiation.

The spectrum is plotted as:

- **X-axis:** Wavenumber (cm^{-1})
- **Y-axis:** % Transmittance or Absorbance

---

18. Fingerprint Region

Range

1500–400 cm^{-1}

Characteristics

- Highly complex.
- Unique for every compound.
- Used for compound identification.
- No two different compounds have identical fingerprint regions.

---

19. Characteristic IR Absorptions of Functional Groups

Functional Group	Wavenumber (cm^{-1})	Appearance
O–H (Alcohol)	3200–3600	Broad

Functional Group	Wavenumber (cm^{-1})	Appearance
O–H (Carboxylic acid)	2500–3300	Very broad
N–H	3300–3500	Medium
C–H (Alkane)	2850–2960	Strong
C–H (Alkene)	3000–3100	Medium
C≡C	2100–2260	Weak
C≡N	2210–2260	Strong
C=C	1620–1680	Medium
C=O	1650–1750	Very strong
NO_2	1500–1600 and 1300–1400	Strong
C–O	1000–1300	Strong

---

20. Interpretation of IR Spectra of Simple Organic Compounds

Alcohol

- Broad O–H band around **3200–3600 cm^{-1}**
- C–O stretch around **1000–1300 cm^{-1}**

Aldehyde

- Strong C=O band around **1720 cm^{-1}**
- Weak aldehydic C–H bands near **2720–2820 cm^{-1}**

Ketone

- Strong C=O absorption around **1715 cm^{-1}**
- No O–H band

Carboxylic Acid

- Broad O–H band from **2500–3300 cm^{-1}**
- Strong C=O band around **1700–1725 cm^{-1}**

Amine

- N–H stretch around **3300–3500 cm^{-1}**
- C–N stretch around **1020–1250 cm^{-1}**

Ester

- Strong C=O band around **1735–1750 cm^{-1}**
- Strong C–O band around **1050–1300 cm^{-1}**

Advantages of UV Spectroscopy

- Simple and rapid.
- Non-destructive.
- Suitable for quantitative analysis.
- Detects conjugated systems.
- Widely used in pharmaceutical and biochemical analysis.

Advantages of IR Spectroscopy

- Identifies functional groups.
- Requires a small sample.
- Non-destructive.
- Useful for purity testing.
- Confirms molecular structure.

Summary

- **UV spectroscopy** measures the absorption of ultraviolet/visible light and involves **electronic transitions** such as $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$.
- The **Beer–Lambert law** states that absorbance is proportional to concentration and path length: (A = \varepsilon cl).

- **Chromophores** are light-absorbing groups, while **auxochromes** modify the wavelength and intensity of absorption.
- **Bathochromic**, **hypsochromic**, **hyperchromic**, and **hypochromic** effects describe changes in the position or intensity of absorption bands.
- **IR spectroscopy** measures molecular vibrations in the **4000–400 cm^{-1}** region.
- Only vibrations that produce a **change in dipole moment** are IR active.
- The **fingerprint region (1500–400 cm^{-1})** is unique for each compound and is invaluable for identification.
- Characteristic absorption bands allow the identification of functional groups such as **O–H, N–H, C=O, C=C, C≡N, and C–O**, making IR spectroscopy a powerful tool for structural analysis of organic compounds.