**Lecturer in Chemistry**
**Government Junior College of Arts, Commerce & Science.**
**Maharashtra Education Service , Group B (Collegiate Branch).**

**Standard** : Degree
**Medium** : English
**Nature of Paper** : Objective Type

**Total Marks** : 150
**Total Questions** : 150
**Duration** : 1 ½ Hours

**Part – I** **20 Questions**

**1. 1) Atomic Structure :**

Idea of De Broglie matter waves, Heisenberg uncertainty principle.
atomic orbitals, Schrodinger wave equation, significance of $\Psi_1$ & $\Psi_2$, quantum numbers, radial and angular wave functions and probability distribution curves, shapes of s, p, d orbitals. Aufbau and Pauli
exclusion principles, Hund's multiplicity rule. Electronic
configurations of the elements, effective nuclear charge.

**2) Chemical Bonding :**

**.01)** Covalent Bond - Valence bond theory and its limitations, directional characteristics of covalent bond, various types of hybridizations and shapes of simple inorganic molecules and ions. Valence shell electron pair repulsion (VSEPR) theory related to $NH_3$, $H_3O^+$, $SF_4$, $ClF_3$, $ICl_2$ and $H_2O$. MO theory and its applications to homonuclear and heteronuclear diatomic molecules, (CO and NO). Bond strength and bond energy, ionic character from dipole moment and electronegativity difference.

**.02)** **Ionic Solids:** Ionic structures, radius ratio effect and coordination number, limitation of radius ratio rule, lattice defects, semiconductors, lattice energy and Born-Haber cycle, solvation energy and solubility of ionic solids, polarizing power and polarisability of ions, Fajan's rule. Metallic bond- free electron, valence bond and band theories.

**.03)** Weak Interactions - Hydrogen bonding, Van der Waals forces.

**3) s-Block Elements :**

Comparative study, diagonal relationships, salient features of hydrides, solvation and complexation tendencies including their function in biosystems and introduction to alky and aryl compounds.

**4) p-Block Elements :**

**.01)** Comparative study diagonal relationships, compounds like hydrides, oxides and halides of elements with atomic number 13 to 17.

**.02)** Structure and bonding of Diborane, Silicates and tetrasulphar tetra-nitride.

**.03)** Basic properties of halogens, interhelogens and polyhalides.

**5) Chemistry of Elements of First, Second and Third Transition Series :**

General Characteristics, comparative treatment with their 3d-analogues in respect of ionic radii,oxidation states,magnetic behaviours,spectral properties and stereochemistry.

**6) Coordination Compounds :**

Werner's coordination theory and its experimental verification, effective atomic number concept, chelates, nomenclature of coordination compounds, isomerism in coordination compounds, valence bond theory of transition metal complexes.

**Part - II** **20 Questions**

**2. Metal-ligand Bonding in Transition Metal Complexes**

**1)** Limitations of valence bond theory, an elementary idea of crystal-field theory, crystal field splitting in octahedral, tetrahedral and square planar complexes, factors affecting the crystal-field parameters.

**2) Magnetic Properties of Transition Metal Complexes** :

Types of magnetic behaviour, methods of determining magnetic susceptibility, spin-only formula. L-S coupling, correlation of $\mu_s$ and $\mu_{eff}$ values, orbital contribution to magnetic moments, application of magnetic moment data for 3d-metal complexes.

**3) Electron Spectra of Transition Metal Complexes :**

Types of electronic transitions, selection rules for d-d transitions, spectroscopic ground states, spectrochemical series. Orgel-energy level diagram for $d_1$ and $d_9$ states, discussion of the electronic spectrum of $[Ti(H_2O)_6]^3$ complex ion.

4) **Chemistry of Lanthanide Elements :**
Electronic structure, oxidation states and ionic radii and lanthanide contraction, complex formation, occurrence and isolation, lanthanide compounds.

5) **Chemistry of Actinides :**
General features and chemistry of actinides, chemistry of separation of Np, Pu and Am from U.Similarities between the later actinides and the later lanthanides.

6) **Organometallic Chemistry :**
A brief account of metal-ethylenic complexes and homogeneous hydrogenation, mononuclear and polynuclear carbonyls and the nature of bonding in metal carbonyls.

**Part – III** **20 Questions**

**3. Bioinorganic Chemistry :**

1) Essential and trace elements in biological processes, metalloporphyrins with special reference to haemoglobin and myoglobin. Biological role of alkali (Na/K) ions with special reference to $Ca^{2+}$ and nitrogen fixation.

2) **Acids and Bases :**
Arrhenius, Bronsted-Lowry, the Lux-Flood, solvent system and Lewis concepts of acids and bases.

3) **Non-aqueous Solvents :**
Physical properties of a solvent, types of solvents and their general characteristics, reactions in non-aqueous solvents with reference to liquid $NH_3$ and liquid $SO_2$.

4) **Gaseous States :**
Postulates of kinetic theory of gases, deviation from ideal behaviour, Van der Waals equations of state, relationship between critical constant and Van der Waals constant, the law of corresponding states and reduced equation state.
Molecular velocities:Root mean square, average and most probable velocities. Qualitative discussion of the Maxwell's distribution of molecular velocities, collision number, mean free path and collision diameter. Liquifaction of gases based on Joule-Thomson effect.

5) **Liquid State :**
Intermolecular forces, structure of liquids (a qualitative description).
Structural differences between solids, liquids and gases.
Liquid crystals : Difference between liquid crystal, solid and liquid. Classification, structure of nematic and cholestric phases. Thermography and seven segment cell.

6) **Solid State :**
Definition of space lattice, unit cell, Laws of crystallography, Law of constancy of interfacial angles, Law of rationality of indices.
a) Law of symmetry. Symmetry elements in crystals and
X-ray diffraction by crystals. Derivation of Bragg's equation. Determination of crystal structure of NaCl, KCl, and CsCl by Laue's and powder methods.

7) **Colloidal State :**
Colloids: Definition, classification and applications.
Solids in liquids (sols) : properties: kinetic, optical and electrical. Stability of colloids, protective action, Hardy-Schulze law and gold number.
Liquids in liquids (emulsions): Types of emulsions, preparation, Emulsifier, General applications of emulsions.
Liquids in solids (gels) : classification, preparation, properties and general applications of gels.
Micelles : classification, structures and importance.

**Part - IV** **15 Questions**

**4. 1) Chemical Kinetics and Catalysis :**
Chemical Kinetics and its scope, rate of a reaction, factors influencing the rate of reaction - concentration, temperature, pressure, solvent, light and catalyst. Concentration dependence of rates, mathematical characteristics of simple chemical reactions - Zero order, first order, second order, pseudo order, half life and mean life. Determination of the order of reaction – differential, integration, method of half life period and isolation methods.
Radioactive decay as a first order phenomenon.

2) **Thermodynamics :**
First Law of Thermodynamics : statement, definition of internal energy and enthalpy. Heat

capacity, heat capacities at constant volume and pressure and their relationship. Joule's law, Joule - Thomson coefficient and inversion temperature.

Thermochemistry : Bond dissociation energy and its calculations from thermo-chemical data, temperature dependence of enthalpy. Kirchhoff's equation.

Second Law of thermodynamics : need for the law, different statements of the law. Carnot cycle and its efficiency. Carnot theorem. Thermodynamic scale of temperature.

Concept of entropy : entropy as a state function, entropy as a function of V & T, and of P & T, entropy change, Clausius inequality, entropy as a criteria of spontaneity and equilibrium. Entropy change in ideal gases and mixing of gases.

Third law of thermodynamics : Nernst heat theorem, statement and concept of residual entropy, evaluation of absolute entropy from heat capacity data. Gibbs and Helmnoltz functions; Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities, A & G as criteria for thermodynamic equilibrium and spontaneity, their advantage over entropy change.Variation of G and A with P, V and T.

3) **Chemical Equilibrium :**

Equilibrium constant and free energy. Thermodynamic derivation of law of mass action. Le Chatelier's principle.

Reaction isotherm and reaction isochore - Clapeyron equation and Clausius - Clapeyron equation and their applications.

4) **Phase Equilibrium :**

Statement and meaning of the terms - phase, component and degree of freedom. Derivation of Gibbs phase rule, phase equilibrium (phase diagram) of one component system - water and Carbon dioxide.

5) **Environmental Safety and Waste disposal :**

Air, water, soil and noise pollutions, Industrial toxins organic and inorganic treatment.

**Part - V** **20 Questions**

**5. Structure, Bonding and Reaction Mechanism :**

1) Hybridizations, bond lengths bond angles, bond energy, resonance, hyperconjugation, inductive field effects and hydrogen bonding, Green account of Reactive intermediates – carbocations, carbanions, free radicals, carbenes, arynes and nitrynes (with examples). Methods of determination of reaction mechanism : product analysis, testing and trapping of intermediates, isotopc effects, kinetic and stereochemical studies.

2) **Stereochemistry of Organic Compounds :**

**Optical isomerism :** elements of symmetry, chiral and achiral molecules with two stereogenic centres, diastereoisomers, threo and erythro diastereoisomers, meso compounds, resolution of enantiomers, inversion, retention and racemization, R & S systems of nomenclature.

**Geometrical isomerism :** determination of configuration of geometric isomers. E & Z system of nomenclature, geometric isomerism in oximes and alicyclic compounds.

Conformations of cyclohexane and mono substituted cyclohexane derivatives. Baeyer's strain theory.

3) **Absorption Spectroscopy - Theory, principle and applications :**

.01) **Ultraviolet (UV) absorption spectroscopy** - Absorption laws (Beer-Lambert law), types of electronic transitions, effect of conjugation. Concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. UV spectra of conjugated enes and enones.

.02) **(1) Infrared (IR) absorption spectroscopy** - Molecular vibrations, Hooke's law, selection rules, intensity and position of IR bands, finger print regulation characteristic absorpotions of various functional groups and interpretation of IR spectra of simple organic compounds.

.03) **Rotational Spectrum :** Diatomic molecules. Energy levels of a rigid rotor (semi-classical principles), selection rules, spectral intensity, distribution using population distribution (Maxwell-Boltzmann distribution) determination of bond length, qualitative description of non-rigid rotor, isotopic effect.

.04) **Nuclear magnetic resonance (NMR) spectroscopy** : Proton magnetic resonance ($^1$H NMR) spectroscopy, nuclear shielding and deshielding, chemical shift, spin-spin splitting and coupling constants, areas of signals, interpretation of PMR spectra of simple organic molecules such as ethyl bromide, ethanol, acetaldehyde, 1,1,2-tribromoethane, ethyl acetate, toluene and acetophenone. (Problems pertaining to the structure elucidation of simple organic compounds using UV, IR and PMR spectroscopic data.)

**4) Alkenes, Dienes and Alkynes :**

**.01)** Methods of formation, mechanisms of dehydration of alcohols and dehydrohalogenation of alkyl halides, regioselectivity in alcohol dehydration. The Saytzev and Hoffmann rules, of elimination reactions and relative stabilities of alkenes. Chemical reactions of alkenes: mechanisms involved in hydrogenation, electrophilic and free radical additions, Markownikov rule, hydroboration, oxidation, oxymercuration-reduction, epoxidation, ozonolysis, hydration, hydroxylation and oxidation with $KM_nO_4$. Polymerization of alkenes, substitution at the allylic and vinylic positions of alkenes. Industrial applications of ethylene and propane.

**.02)** **Nomenclature and classification of dienes :** Chemical reactions - 1, 2 and 1, 4 additions, Diels-Alder reaction. Alkynes: methods of formation. Chemical reactions of alkynes, acidity of alkynes. Mechanism of electrophilic and nucleophilic additions, hydroboration and oxidation, metal-ammonia reduction and polymerization.

## Part - VI — 20 Questions

**6. 1) Arenes and Aromaticity :**

Aromaticity : the Huckel rule, aromatic ions.

Aromatic electrophilic substitutions: Mechanism of nitration, halogenation, sulphonation, mercuration and Friedel - Crafts reaction. Energy profile diagrams. Activating and deactivating substituents, orientation and ortho/para ratio, Birch reduction

**2) Alcohols and Phenols :**

Chemical reactions of vicinal glycols : Oxidative cleavage [$Pb(OAC)_4$ and $HIO_4$] and Pinacol-pinacolone rearrangement. Reactions of phenols: electrophilic aromatic substitutions. Mechanism of Fries rearrangement, Claisen rearrangement, Gatteman synthesis, Hauben-Hoesch reaction and Reimer-Tiemann reaction.

**3) Aldehydes and Ketones :**

Reactions of aldehycdes and ketones : Mechanism of nucleophilic additions to carbonyl group with particular emphasis on benzoin, Aldol, Perkin and Knoevenagel reactions. Condensation with ammonia and its derivatives. Witting and Mannich reaction. Use of acetals as protecting group. Oxidation of aldehydes, Baeyer-Villiger oxidation of ketones, Cannizzaro reaction. Meerwein Ponndorf Verley (MPV), Clemmensen, Wolff-Kishner, $LiAlH_4$, and $NaBH_4$ reductions. Halogenation of enolizable ketones.

**4) Carboxylic Acids :**

Preparation and reactions of carboxylic acids. Hell-Volhard- Zelinsky reaction. Synthesis of acid chlorides, esters and amides. Mechanism of reduction, decarboxylation, esterification and hydrolysis of carboxylic acids.

**5) Organic Compounds of Nitrogen :**

Amine salts as phase-transfer catalysts. Preparation of alkyl and aryl amines (reduction of nitro compounds nitriles), reductive amination of aldehyde and keto compounds. Gabriel phthalimide synthesis of amines, Hoffmann bromamide reaction, reactions of amines with nitrous acid. Synthetic transformations of aryl diazonium salt, azo coupling.

**6) Organosulphur and Heterocyclic Compounds containing nitrogen atom :**

Methods of formation and chemical reactions of thiols, thioethers, sulphonic acids, sulphonamides and sulphaguanidine. Preparation and reactions of pyridine indole, quinoline and isoquinoline with special reference to Fisher indole synthesis. Skraup synthesis and Bischler-Napieralski synthesis. Mechanism of electrophilic substitution reactions of indole, quinoline and isoquinoline.

## Part - VII — 20 Questions

**7. Organic Synthesis via Enolates :**

**1)** Alkylation of diethyl malonate and ethyl acetoacetate. Synthesis of ethyl acetoacetate : the Claisen condensation. Alkylation of 1,3-dithianes. Alkylation and acylation of enamines.

**2) Carbohydrates :**

Configuration of monosaccharides. Determination of ring size of monosaccharides. Cyclic structure of D(+) glucose. An introduction to disaccharides (maltose, sucrose and lactose) and polysaccharides (starch and cellulose) without structure determination.

**3) Amino Acids, Peptides, Proteins and Nucleic Acids :**

Classification of proteins, structure determination, end group analysis, selective hydrolysis of peptides. Classical peptide synthesis, solid-phase

peptide synthesis. Structures of peptides and proteins.

Nucleic acids : Introduction, Constituents of nucleic acids, ribonucleosides and ribronucleotides. The double helical structure of DNA.

4) **Synthetic Polymers :**

Addition polymerization: Free radical vinyl, ionic vinyl and Ziegler-Natta polymerization.

Condensation polymerization. Polyesters, polyamides, phenol formaldehyde resins, urea formaldehyde resins, epoxy resins and polyurethanes.

Natural and synthetic rubbers.

5) **Synthetic Dyes :**

Colour and constitution (electronic concept). Classification of dyes. Chemistry and synthesis of Methyl orange red, Malachite green, Crystal violet, Phenolphthalein, Fluorescein, Alizarin and Indigo.

6) **Green Chemistry :**

Introduction, concept of atom economy, hazard reductin, importance of solvent, role of catalysts, biological alternatives. Applications of Green Chemistry.

**Part - VIII** **15 Questions**

**8. Electrochemistry :**

**1)**

**.01)** Migration of ions and Kohlrausch law,Arrhenius theory of electrolytic dissociation and its limitations,weak and strong electrolytes,Ostwald's dilution law its uses and limitations.Debye-Huckel-Onsager equation for strong electrolytes(elementary treatment only).

**Applications of conductivity measurements :** determination of degree of dissociation, determination of $k_a$ of acids, determination of solubility product of a sparingly soluble salt, conductometric titrations.

**Types of reversible electrodes:** gas-metal ion, metal-metal ion, metal-insoluble salt-anion and redox electrodes. Electrode reactions, Nernst equation, derivation of cell E.M.F. and single electrode potential, standard hydrogen and reference electrodes, electrode potential, electrochemical series and its significance.

**.02)** Electrolytic and Galvanic cells, reversible and irreversible cells, conventional representation of electrochemical cells.

EMF of a cell and its measurement. Computation of cell EMF.Calculation of thermodynamic quantities of cell reactions ($\Delta G$, $\Delta H$ and $K_{eq}$), Decomposition potential and over voltage.

Definition of pH and pKa, determination of pH using hydrogen, quinhydrone and glass electrodes by potentiometric methods.

**Buffers:** mechanism of buffer action, Henderson-Hazel equation. Hydrolysis of salts. **Corrosion:** types, theories and methods of its prevention.

Energy Sources, Alkaline Batteries, Ni-Cd and Li-cells, Fuelcells: $H_2$ /$O_2$ and ethanol Fuel cells, Solar cells

2) **Elementary Quantum Mechanics :**

Hamiltonian operator, Schrodinger wave equation and its importance, physical interpretation of the wave function, postulates of quantum mechanics, particle in a one dimesional box.

Schrodinger wave equation for H-atom, separation into three equations (without derivation), quantum numbers and their importance.

3) **Photochemistry :**

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

4) **Computers :**

Basic concepts, use of computers in Chemistry.Computer simulations and Molecular Modelling.

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