

For the post of Written Recruitment Test for the post of Postgraduate Assistants in Tamil Nadu Higher Secondary Educational Service.

**Syllabus: CHEMISTRY** (Subject Code: P05)

**Unit-I**

Periodic properties – Atomic radius – ionic radius, ionization potential, electron affinity and electronegativity – Their significance in chemical bonding.

VB theory, MO theory – applications – Comparison of VB and MO theories – VSEPR theory – Bond order – Bond energy – Bond length Bond polarity – Partial ionic character of bonds – The concept of multi-centre bond – Electron deficient compounds – Hydrogen bond – Its influences.

Non aqueous solvents – A general study of typical reactions in non aqueous media – comparison with reactions in aqueous media.

Solid state chemistry – Ionic bonding – Lattice energy – Born equation – Born Haber cycle – Radius ratio rule – Born Meyer equation – Kapustinski's Modification – energetics of the dissolution of ionic compounds in polar solvents – different types of electrostatic interactions.

Structural aspects of solids – Fourier synthesis and analysis structure factors – scattering factors – Spinels and Inverse spinels – defects in stoichiometric and Non stoichiometric crystals.

Electrical properties of solids – Band theory semi conductors – Junction devices – Super conductivity – Ionic conductivity – Optical properties of solids – Lasers and phosphors – Photovoltaic effect – solar energy.

Magnetic properties of solids – Different types – dia, para, ferro, antiferro and ferri Magnetism – Magnetic hysteresis.

**Unit II**

Co-ordination chemistry – Methods of preparation of complexes – isomerism in complexes – applications of complex formation in analytical chemistry – complexes and their stability chelate effect Stability constants – Their determination – complexes of Metals in different oxidation states and their stability.

Optical activity and concept of chirality – Different kinds of optically active compounds – configuration – Fischer, sawhorse and Newman projections – Absolute configuration R and S Notations – Methods with more than one chiral center – Asymmetric synthesis – optical purity.

Geometrical isomerism resulting from double bonds – The E,Z. system of nomenclature – Geometrical isomerism of monocyclic compounds and fused ring systems – Stereospecific and stereoselective reactions with examples.

Conformational analysis – conformation and reactivity in acyclic and cyclo – hexane systems – conformation of decalins, cyclohexane and cyclohexanone.

**Unit III**

Organic reaction mechanisms – General methods of investigating reaction mechanisms – kinetic and non-kinetic methods – different types of reaction intermediates.

Aliphatic nucleophilic substitution SN<sub>1</sub>, SN<sub>2</sub> and SN<sub>i</sub> reactions – substitution at vinylic and benzylic carbon – stereo chemistry of nucleophilic reaction – solvents and substituent effects – Nucleophilicity Neighboring group participation.

Addition to double and triple bonds – Mechanism Hydration – Hydroboration – Hydroxylation – epoxidation.

Elimination reactions E1, E2, E<sub>1cB</sub> Mechanism – Orientation effects in elimination reactions – stereo chemistry of elimination reactors - dehydration of alcohols – dehydro halogenation – cope elemination.

Heterocyclics – synthesis and reactivity of furan, thiophene, pyrrole pyridine, quinoline, isoquinoline, Indole, flavenes, and anthocyanins – skrap synthesis – Fischer indole synthesis.

The chemistry ;of natural products structure elucidations and Biogenesis of the following:

Alkaloids : Reticulene, Reserpine, Morphine

Terpenoids : Zingiberene, Squalene, Lanosterol

Steroids : Cholesterol, Oestrone, Progesterone

Carbohydrates: Maltose, Starch, Cellulose (biogenis not expected)

Structure and functions of biopolymer such as proteins and Nucleic acids – Primary, Secondary and tertiary structures of proteins – Mechanism of Enzyme action – DNA and RNA.

#### Unit IV

The old quantum theory – Inadequacy of classical mechanics – Failure of classical mechanics – success of quantum hypothesis explaining black body radiation – Photo electric effect – the hydrogen spectrum – Bohr's explanation of hydrogen spectrum – Failure of Bohr's model.

De broglie's postulates of Matter waves – experimental observation of matter waves – Heisenberg's uncertainly principle – wave particle dualism – Davisson, Garmer experiments – Postulates of quantum mechanics – Time dependent schrodinger equation – Needs of an acceptable wave function – Physical significance of Psi function.

Operators in quantum mechanics. Operator algebra – Linear and Hermitian operators –m Eigen functions and Eigen values – Hamiltonian operators – Angular momentum.

Application of schrodinger equation – particle in one and three dimensional boxes – quantum mechanical results for a simple harmonic oscillaltor and rigid rotator - approximation methods – perturbation methods – variation method – VB and MO methods.

Symmetry elements and symmetry operations – Point groups – representation of groups reducible and irreducible representations characters tables – Orthogonality theorem and its consequences.

Symmetry selection rule for IR and Ramanspectra – Systematic procedure for determining symmetries of normal modes of vibration – symmetry applied to MO theory and orbital hybridization.

#### Unit V

Thermodynamic equations of state – closed and open systems – partial molal quantities – chemical potential with temperature and pressure – third law of thermodynamics.

Fugacity – methods of determination – activity and activity co-efficient – standard states for gases, liquids – solids and solutions – mean activity co-efficients of electrolytes.

Maxwell's distribution of molecular velocities – derivation of expression for average, most probable and rcot mean square velocities – Microstates Macrostates – partial functions – Sackur tetrode equation – statistical approach to the third law of Thermodynamics – Maxwell Boltzmann – Bose Einstein and Fermi

Dirac statistics – Heat capacities of solids – Einstein and Debye Models Low temperature – Negative absolute temperature.

Chemical equilibrium – thermodynamic derivation of equilibrium constant – standard free energy – calculations.

Phase equilibrium – thermodynamic derivation of phase rule application of phase rule – three component systems.

Chromatography – column, paper, thinlayer, gas-liquid, High pressure liquid chromatography HPLC principle and applications.

Thermal analysis – differential thermal analysis (DTA) – Principle and applications – thermogravimetric analysis (TGA) Principle and application.

Chemical crystallography – Diffraction methods – X ray Neutron, electron diffraction methods. Principle and applications.

Polarimetry – Circular dichroism – Optical Rotatory dispersion (ORD) Principle and applications.

## Unit VI

Nuclear – chemistry – Nuclear spins and moments – Nuclear structure – Nuclear forces – Nuclear stability – Nuclear modes – Modes of Radioactivity decay. Nuclear isomerisation Nuclear Reaction Energy – Coulomb barrier cross section – excitation function – Radioactive Equilibria – Types of Nuclear reactions – Nuclear fission Nuclear Reactors – Atomic Power Project in India – Radiation hazards – Radiation dosimetry – Nuclear fusion – Stellar Energy.

Application of Radioactivity – Tracer Techniques – Neutron Activation analysis – Isotope Dilution Analysis – Interaction of radiation with matter – Range of alpha and beta particles – Absorption coefficient.

Organometallic compounds – Metallocenes – Arene complexes – Nonaromatic olefins and acetylenes complexes – catalysis by organometallic compounds Wilkinson's catalyst – Oxidation – Ziegler process – Ziegler – Natta catalysis.

Inorganic photo chemistry – Photochemical reactions of coordination and organometallic compounds – Properties of excited states – charge transfer photo Oxidation, photo reduction, photo substitution, photo isomerisation - Photo chemical conversion – Solar energy.

## Unit VII

Term symbols and term states –  $d_n$  - ions energy levels – Diagrams weakfield and strong field and strong field concepts – spin orbit coupling – The Nephelauxetic effect charge transfer spectra – Applications of UV, IR, NMR, BSR and Mossbauer spectroscopy techniques in the study of coordination chemistry.

Magnetic interactions – Magnetic susceptibilities determination – application in coordination chemistry. Application of VB, MO, CF and LF theories in coordination chemistry – Group theoretical approach – splitting of d-orbitals – spectro-chemical series – concept of weak and strong fields – Thermodynamic and chemical effect of d-orbitals splitting – Jahn Teller distortion.

Nuclear Magnetic Resonance Spectroscopy – Theory – Study of PMR – chemical shift – Type of shielding – Spin-spin coupling spin decoupling – applications to simple natural products.

Electron spin resonance spectroscopy – paramagnetism – Nuclear hyperfine structure – Hyperfine coupling.

### Unit VIII

Huckel's rule and concept of aromaticity – aromaticity of Benzenoid – Nonbenzenoid aromatics. The annulenes - Aromaticity in charged rings and fused ring systems. Aromatic electrophilic substitution – Mechanism and reactivity, Typical reactions to include diazonium coupling – Halogenation, sulphonation. Friedal craft alkylation and acylation. Aromatic Nucleophilic substitution – Benzyne mechanism – Examples. Oxidation – Reduction reactions – Mechanisms – selectivity in oxidations and reductions.

Molecular rearrangements – Rearrangements with Carbon to Nitrogen, Carbon to Oxygen and Carbon migrations. Curtius, Lossen, Schmitts Baeyer – Villiger, Pinacol – Pinacolone, Benzoin – Benzilic acid, Benzidine, Favorski and Fries rearrangements – sigmatropic rearrangements – Claisen and Cope. Pericyclic reactions, selection rules – orbital symmetry – Electrocyclic reactions – cycloadditions sigmatropic reactions.

Modern synthetic reactions – Diels Alder reaction Wittig reactions – Stork Enamine reactions – Mannich reactions, Birch reductions.

### Unit IX

Theories of reaction rates – simple collision theory – absolute reaction rate theory (ARRT) – Reaction co-ordinate – Potential energy surfaces. Hammett – Taft equation – Hammett acidity function – Acid base catalysis Bronsted relation Enzyme catalysis – Michaelis Menton Law – influence of pH and temperature. Surface phenomenon – Heterogeneous catalysis – Absorption isotherms. Electrolytic conductance – applications – solubility product – Interionic attraction theory – Debye – Huckel – Onsager equation – equivalent conductivity of electrolytes.

Electro potentials – Electrochemical cells – electrode – electrolyte interface – electrical double layer electro capillary phenomena – electro kinetic Phenomena – Membrane potential – Polarisation – over potential – Polarography – concentration polarization – electro chemical polarization – Butler – Volmer equation.

### Unit X

Theory and applications of the following spectroscopic methods; electronics spectra-UV-Visible spectra – IR spectra – Raman spectra – Laser – Raman spectra – NMR – WCR- ESR Spectra – Mossbauer spectroscopy – photoelectron spectroscopy – Poly

merisation reactions – Mechanism – stereochemical aspects. Types of polymers – organic and inorganic polymers – preparation – properties – structure – polystyrene – Polyvinylchloride – Polyesters – Nylon – Phenol resin – amino resins – epoxy resins. Phosphonitrilic compounds – silicones – Borazines applications of polymers.