

TAMIL NADU PUBLIC SERVICE COMMISSION

CHEMISTRY (PG DEGREE STANDARD)

Code No.228

FOR THE POST OF JUNIOR SCIENTIFIC OFFICER

Unit – I : Quantum Chemistry :Quantum mechanical postulates – Eigen value and function – the Schrodinger wave equation – elementary applications of Schrodinger's equation – the particle in a box (one, two and three dimensional cases) – particle in a ring. The harmonic oscillator –the rigid rotor – the hydrogen atom – the Schrodinger equation for hydrogen atom – angular momentum – term symbols – Approximation methods – perturbation and variation method – application to hydrogen and helium atoms – R.S. coupling and term symbols for atoms in the ground state – Slater orbital and HF – SCF methods Born open – Heimer approximation – valence bond theory for hydrogen molecule – LACO – MO theory for di and polyatomic molecules – concept of hybridization – Huckel theory for conjugated molecules (ethylene butadiene and benzene) – semi empirical methods.

Unit – II: Chemical Kinetics and Thermodynamics: Rate laws – rate constant for first, second, third and zero order reaction – Half life period Temperature dependence on rate – Arrhenius theory – collision theory – Absolute reaction rate theory – ionic reaction – salt effect – catalysis – Laws of photo chemistry, quantum efficiency - photo physical processes of electronic excited molecules.

Partial molar properties – Chemical Potential – Partial molar volume and molar heat content – significance and determination – Thermodynamics of real gases - gas mixture – fugacity definition – determination of fugacity variation of fugacity with temperature and pressure – concept of thermodynamic probability – distribution of distinguishable and non – distinguishable particles. Maxwell – Boltzmann, Fermi-Dirac and Bose Einstein statistics – modes of contribution to energy – partition function – translational, vibrational and rotational partition functions for mono, diatomic and polyatomic ideal gases.

Unit – III : Nuclear Chemistry : Nuclear properties –nuclear spin and moments, origin of nuclear forces, salient features of liquid drop and shell models. Types of radioactive decay: Orbital electron capture, nuclear isomerism, internal conversion, detection and

determination of activity by cloud chamber, nuclear emulsion, bubble chamber, G.M., Scintillation and Cherenkov counters; Accelerators – Linear and Cyclotron. Nuclear reaction: Types, reaction cross section, Q-value, threshold energy, compound nucleus theory: nuclear fission and fusion reactions as energy sources: photonuclear and thermo nuclear reactions. Components of nuclear reactor – the fast breeder reactor – nuclear reactors in India. Radioactive tracer – principles of tracer technique – application of tracers in the study of reaction mechanism and in analytical chemistry – neutron activation analysis, isotope dilution analysis – radio chemical determination of age of geological specimen. Tracers as applied to industry and agriculture – radioactive tracer in the diagnosis and treatment in the field of medicine.

Unit- IV: Electrochemistry : Mean ionic activity and activity coefficient: concept of ionic strength, Debye-Huckel theory of strong electrolytes – activity coefficient of strong electrolytes-determination – Debye Huckel limiting law at appreciable concentration of electrolytes – Debye Huckel Bronsted equation – qualitative and quantitative verification. PH & PKa of acids and bases – determents and buffer actions conductometric and potentiometric tirations Mechanism of electrode reaction – polarization and overpotential. Corrosion and passivation of metals: Pourbaix and Evans diagrams – fuel cells – electrodeposition – principle, applications and anticorrosion techniques.

Unit – V : Spectroscopy

Electromagnetic radiations and quantization of energy: Rotational spectra of diatomic molecules – isotopic substitution and rotational constants – vibrations spectra of linear symmetric, linear asymmetric and bent tri atomic molecules – electronic spectra – selection rules – nuclear magnetic resonance – chemical shifts – spin – spin coupling – election spin resonance and hyperfine splitting theoretical principles of mass spectroscopy. Application's of UV, IR, NMR, ESR and mass spectroscopy for structural elucidation of organic compounds, inorganic complexes and free radicals.

Unit – VI : Organometallic compounds, Bio inorganic chemistry and Polymers:

Metal carbonyls, Metal nitrosyls, metal alkyl, alkenes and arene compounds – organic metallic compounds in catalysis – Chemistry of porphyrins – chlorophyll hemoglobin, myoglobin, ferredoxin, rubredoxin and cytochromes.

Preparation and uses of polyethylene and uses of polyethylene, poly butylenes PVC, Nylon – Ziegler – Natta catalysts – Inorganic Polymers such as silicones, Borazines and phosphonitrilic compounds.

Unit – VII : Organic reaction mechanism and Stereochemistry: General methods of reaction mechanisms (Kinetic and non kinetic) S_N1 , S_N2 mechanisms – addition substitution, elimination and rearrangements – free radical mechanism – aromatic substitution – formation and stability of reactive intermediates – The arenium ion mechanism. Orientation and reactivity (ortho, meta and para directing groups). Typical reactions to be studied – nitration, halogenations, alkylation, acylation and diazonium coupling. Formylation – Gatterman, Gatterman-Koch, Vilsmeier-Hack & Reimer-Tiemann, Ziegler alkylation, Chichibabin, Aldol condensation – Claisen condensation – Perkin, Cannizzaro, Friedel Craft, Favorski, Stork enamine – Michael addition – Baeyer – villiger – Chichibabin. Pericyclic reactions – classification and examples Woodward and Hoffmann rules – use of OsO_4 , diborane, $NaBH_4$, $LiAlH_4$ in organic synthesis. Photo Chemistry of ketones, photo oxygenation, photo reduction, photocycloaddition, Paterno - Buchi reaction, Di- π -methane rearrangement. Cis-trans isomerisation, Barton reaction and photo-Fries reaction.

Elements of symmetry – optical and geometric isomerism E,Z and R,S notation's – Conformational analysis simple cyclic and acyclic systems – Effects of conformation on reactivity in acyclic compounds and cyclohexanes. Relative stabilities of cis – trans isomers.

Unit – VIII: Natural Products and Drugs : Carbohydrates - Classification – configuration and general reactions of monosaccharides – Chemistry of glucose, fructose, sucrose and maltose, important compounds in Chemistry – Dyes – azo triphenylmethane and phthalein groups – indigo – alizarin vitamins, hormones, proteins – structural determination –Terpenoids – classification, isolation, general properties of citral, α -Terpineol, menthol, camphor.

Alkaloids and Flavonoids – Nomenclature and classification general properties – colour reactions, structure for Nicotine, atropine, cocaine, quinine, morphine and Heroin.

Drugs: Pharmacological actions, therapeutic uses and screening tests of the following drugs – opium alkaloids – morphine, heroin, antibiotics – synthetic analgesics – pethidine, methadone – barbiturates – tranquilizers – phenothiazines, meprobamate, diazepam – stimulants – amphetamines, imipramines – hallucinogens – cannabinoids, LSD – hypnosis and sedatives – antipyretics, analgesic, antiseptics and disinfectants – Alcohol - manufacture of ethyl alcohol and liquors – constituents of liquors – estimation of alcohol contents in liquors – denaturation, denaturants, industrial alcohol and power alcohol.

Unit - IX : Poisons and Pesticides : Definition of poisons – Mode of action of poisons – Extraction and purification of poisons in toxicological analysis – Volatile poisons – metallic poisons – non-volatile organic poisons – water soluble compounds – protein precipitation methods. Estimation of the following poisons – Carbon monoxide, cyanide, formaldehyde, methanol, chloral, chloroform, phenols, cresols, phosphorus and amphetamines - Signs and symptoms of H_2SO_4 , HNO_3 , CO_2 , H_2S poisoning. Analytical methods for the estimation of ethyl alcohol. Metallic poison – signs, symptoms of arsenic, mercury, lead and copper – Reinch test - Marsch Berzelius and Gutzeit tests – volumetric, colorimetric and instrumental methods of analysis of the above metals. Pesticides & Insecticides – Definition – general properties poisonous nature – detection & isolation.

Unit – X : Analytical Chemistry and Instrumental methods: Significant figures – precision & accuracy – Errors - minimizing methods – estimation of errors – rejection of observation.

Absorption, partition chromatography – Gas Chromatography – HPLC – Solvent extraction and ion exchange methods – atomic absorption spectroscopy – Electron analytical techniques voltammetry, cyclic voltammetry, polarography, amperometry, Coulometry and conductometry, ion-Selective electrodes – TGA, DTA and DSC.