Swami Ramanand Teerth Marathwada University, Nanded

PET Examination

(Chemistry)

Section-B:

1. Structure and Bonding: The periodic properties of elements, ionic radii, ionization potential, electron affinity, electronegativity, concept of hybridization. Molecular orbitals of homonuclear and heteronuclear diatomic molecules. Shapes of polyatomic molecules. VSEPR theory. Point groups for simple molecules. Bond lengths, bond angles, bond order and bond energies. Types of chemical bond (weak and strong). Intermolecular forces. Types of solids.
2. Acids and Bases : pH and pKa, acid-base concept in nonaqueous media, SHAB concept.
3. Surface Chemistry: Adsorption, mechanism of adsorption, factors affecting adsorption, difference between adsorption and absorption. Physical adsorption and chemical adsorption. Adsorption of gas by solid. Freundlich adsorption isotherm, Langmuir adsorption isotherm.
4. Introductory Energetics and Dynamics of Chemical Reactions : Law of conservation of energy. Energy and enthalpy of reactions. Entropy, free energy, relationship between free energy change and equilibrium. Rates of chemical reactions (first-and second-order reactions). Arrhenius equation and Concept of transition state, electron transfer reactions, catalysis Colligative properties of solutions.
5. Aspects of s, p, d, f Block Elements: General characteristics of each block. Coordination chemistry, Structural aspects, isomerism, octahedral and tetrahedral crystal-field spliting of d-orbitals. CFSE, magnetism and colour of transition metal ions. Sandwich compounds metal carbonyls and metal clusters. Rare gas compounds,
6. IUPAC Nomenclature of Organic and Inorganic Compounds.
7. Concept of Chirality: Recognition of symmetry elements and chiral structures. R-S nomenclature, diastereoisomerism in acyclic and cyclic-systems, E-Z isomerism.
8. Common Organic Reactions and Mechanisms: Reactive intermediates. Formation and stability of carbonium ions, carbenes, nitrenes, radicals and arynes. Nucleophilic, electrophilic, radical substitution, addition and elimination reactions. Familiar name reactions: Aldol, Perkin, Stobbe, Dieckmann condensations; Hofmann, Schmidt, Lossen, Curtius, Beckmann and Fries rearrangements, Reimer-Tiemann, Reformatsky and Grignard reactions. Diels-Alder reaction, Claisen rearrangement, Friedel-Crafts reaction, Witting reaction. Hydroboration,Oppenauer oxidation, Clemmensen, Wolf-Kishner, Meerwein- Ponndorf Verley and Birch reductions.
9. Data Analysis : Types of errors, accuracy and precision, least-square analysis, average standard diviation.
10. Qualitative and Quantitative analysis. Volumetric, gravimetric, complexometric, Spectrophotometric and therm ogravimetric analysis.
11. The distribution law – and its applications
12. Behaviors of ideal gases, real gases, the liquid state, the physical properties of liquids, The crystalline state, liquid crystals, the mesmeric state

UNIT-I:

1. Nuclear Chemistry: Radioactive decay and equilibrium. Nuclear reactions, Q value, cross sections, types of reactions. Chemical effects of nuclear transformations, fission and fusion, fission products and fission yields. Radioactive techniques, tracer techniques, neutron activation analysis, counting techniques such as G. M. ionization and proportional counters.

2. Chemistry of Transition Elements: Coordination chemistry of transition metal ions. Stability constants of complexes and their determination, stabilization of unusual oxidation states. Stereochemistry of coordination compounds. Ligand field theory, splitting of d-orbitals in low symmetry environments. Jahn-Teller effect, interpretation of electronic spectra including charge transfer spectra, spectrochemical series, nephelauxetic series. Dia-para-ferro and antiferromagentism, quenching of orbital angular moments, spin orbit coupling. Inorganic reaction mechanisms, substitution reactions, trans-effect and electron transfer reactions, photochemical eactions of chromium and ruthenium complexes. Fluxional molecules. Iso and heteropolyacids, metal clusters. Spin crossover in coordination compounds.

UNIT-II

1. Chemistry of Lanthanides and Acitindes: Position, Electronic configuration, Oxidation state, tendency to form complex compounds, Spectral and magnetic properties, use of lanthanide compounds as shift reagents

2. Physical characterization of inorganic compounds by UV, IR, Raman, NMR, ESR, Mössbauer, Mass, Electron spectroscopy and Atomic absorption spectroscopy. Application of atomic and molecular absorption and emmision spectroscopy in quantitative analysis. Light scattering techniques including nephelometry and Raman spectroscopy. Electroanalytical techniques, voltametry, cyclic voltametry, polarography, amperometry, coulometry and conductometry. Ion-selective electrodes. Anodic stripping voltametry, TGA, DTA, DSC and on-line analysers. Adsorption, partition, exclusion, electrochromatography. Solvent extraction and ion exchange methods.

UNIT III

1. Addition Reactions:

Addition to Carbon–Carbon Multiple Bonds: Mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, regioselectivity and chemoselectivity, orientation and reactivity.

Addition to Carbon–Hetero Multiple Bonds: Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acids, esters and nitriles. Addition of Grignard

reagents, Organo-zinc and organo-lithium reagents to carbonyl and unsaturated carbonyl compounds.

2. Elimination Reaction: The E^2, E^1 and E^1CB mechanisms and their spectrum. Orientation of the double bond. Reactivity: Effects of substrate structures, attacking base, the leaving group and the medium. Mechanism and orientation in pyrolytic elimination.

UNIT IV

1. Nucleophilic Substitution:

Aliphatic Nucleophilic Substitution: SN^2, SN^1, mixed SN^1 and SN^2 and SET mechanism. Neighbouring group participation by π and σ-bonds, Anchimeric assistance. The SN^i mechanism. Nucleophilic substitutions at an allylic, Aliphatic and a vinylic carbon.
Aromatic nucleophilic Substitution: SN^{Ar} , SN^1, Benzyne and SNR^1 mechanism. Reactivity: Effect of substrate, Leaving group and attacking nucleophile.

2. Electrophilic Substitution:

a) Aliphatic Electrophilic Substitution: SE^2 and SE^i and SE^1 mechanism, Effect of substrates, Leaving group and the solvent polarity on the reactivity.

b) Aromatic Electrophilic Substitution: The ortho/para ratio, ipso attack. Quantitative treatment of reactivity in substrates and electrophiles. Diazonium coupling, Vilsmeir reaction, Gattermann-Koch reaction.

UNIT-V

1. Stereochemistry and Conformational Analysis: Conformational analysis of acyclic and cyclic (mono and di substitutted cyclohexanes) systems, Interconverison of Fischer, Newman and Sawhorse projections. Newer methods of assymetric synthesis (including enzymatic and catalytic nexus), enantio-and diastereo selective synthesis. Effects of conformation on reactivity in acylic compounds and cyclohexanes.

2. Spectroscopy: Physical characterizations of organic compounds by UV, IR, NMR, and Mass for structural elucidation of compounds.

UNIT-VI

1. Pericyclic Reactions: Molecular orbital symmetry, Classification, Woodward-Hoffmann correlation diagrams, Electrocyclic reactions, Cycloadditions. Sigmatropic, Claisen, Cope and aza-Cope rearrangements.

2. Photochemistry: Principles–photochemical theory, electronic excitation, singlet and triplet states, Jablonski diagram. Energy transfer, quantum efficiency. Photochemistry of carbonyl compound and olefins. Photo-fries reaction of anilides, Photo-rearrangements, Barton reaction singlet molecular oxygen reaction photochemical formulation of smog photo-degradation of polymers, photochemistry of vision, nπ - pπ rearrangement.

UNIT VII

1. Reagents in Organic Synthesis: Grignard reagents, Organolithium reagents, Gilman's Reagent (Lithium Dimethyl cuprate), Lithium Diisoproplamide (LDA), Trimethylsilyl iodide, Diazomethane, Polyphosphoric acid, DCC (Dicyclohexylcarbodiimide), Enamines, Phosphorus, sulfur and nitrogen ylides. Complex metal hydride, Woodward and Prevost hydroxylation, Osmium tetraoxide, DDQ, Selenium dioxide.

2. Transformations, Rearrangements and Name reactions: Favorskii reaction, Strok enamine reaction, Michael addition, Mannich reaction, Sharpless asymmetric expoxidation, Ene reaction, Barton reaction, Hofmann Loffler-Freytag reaction, Shapiro reaction, Baeyer-Villiger reaction, Chichibabin reaction. Von Richter, Sommelet-Hauser and Smiles rearrangements.

UNIT-VIII

1. Quantum Chemistry: Planck's quantum theory, wave-particle duality, Uncertainty principle, operators and commutation relations, postulates of quantum mechanics and Schrodinger equation, free particle, particle in a box, degeneracy, harmonic oscillator, rigid rotator and the hydrogen atom. Application of Schrödinger equation to hydrogen atom. The variation theorem, linear variation principle. Perturbation theory (first order and non degenerate). Applications of variation method and perturbation theory to the Helium atom. Ordinary angular momentum, generalized angular momentum, eigen functions for angular momentum, eigen values of angular momentum. Spin, anti-symmetry and Pauli's exclusion principle, commutation relation, zeeman splitting, Spin orbital coupling. Operator using ladder operators, addition of angular momentum.

2. Phase Rule: Recapitulation of phase rule and terms involved in it. Three component system: representation of ternary systems. Partially miscible three liquid systems:-1) system composed of three liquid components, one partially miscible pairs, two partially miscible , three partially miscible pairs. 2) System composed of two solid and a liquid components:- formation of eutectic systems, crystallisation of pure components only, formation of binary compounds, one double salt formation. Formation of binary compounds hydrate formation, formation of ternary compounds, formation of solid solutions, partially miscibility of Phases.

UNIT-IX

1. Classical Thermodynamics: laws of thermodynamics. Free energy and entropies. Concept of fugacity and determination of fugacity by graphical method and from equation of state. Debye-Huckel theory for activity coefficient of electrolytic solutions determination of activity

and activity coefficients by 1) solubility 2) E.M.F. method.3) vapour pressure method, Ionic strength.

2. Statistical Thermodynamics : Concept of distribution, thermodynamics probability, ensemble averaging, postulates of ensemble avaranging. Canonical, grand canonical and micro-canonical ensembles. Partition functions: Translational, rotational, vibrational and electronic partition functions. calculation of thermodynamic properties in terms of partition functions. Applications of partition functions.

UNIT-X

1.Chemical Dynamics: Methods of determining rate laws, collision theory of reaction rates, steric factor, Arrhenius activated complex theory, Arrhenius equation and the activated complex theory, ionic reactions, kinetic salt effects.

Dynamic chain, Photochemical and oscillatory reactions. Homogeneous catalysis, kinetics of enzyme reactions. General features of fast reactions, study of fast reaction by flow method. Flash photolysis and the nuclear magnetic resonance method. Dynamics of unimolecular reactions.

2. Electrochemistry : DH-0nsager theory ,Kohlrausch's law & it's applications , conductometric & Potentiomentric titrations, Nernst Equation, concentration cells –with and without transference, applications of EMF, over- voltage & it's applications, corrosion of metals, polarography.