

BHARATI VIDYAPEETH
(DEEMED TO BE UNIVERSITY), PUNE, INDIA
PhD Entrance Test – 2023
SECTION-II: CHEMISTRY - 50 Marks

Unit-I : Microwave Spectroscopy & IR Spectroscopy :

A) Rotation of molecules, Rotational spectra of rigid diatomic molecules, selection rules, interaction of spectral lines, determination of bond lengths, effect of isotope substitution, non – rigid rotator and its spectrum, Linear polyatomic molecules, symmetric and asymmetric top molecules.

B) Vibrating diatomic molecule, energy levels of a diatomic molecule, simple harmonic and an harmonic oscillator, Diatomic vibrating rotator, vibration – rotation spectra of carbon – monoxide, determination of force constant and bond strengths, interaction of radiation and vibrations, P, Q and R branches, fundamental vibration and overtone frequencies. Linear molecules, influence nuclear spin, Symmetric top molecules.

Unit-II : A) Surface-, Electro- chemistry and Materials Chemistry : Adsorption, Freundlich and Langmuir adsorption isotherms, multilayer adsorption and BET theory, surface area determination, Temkin isotherm, adsorption in solution, surface excess, Gibbs adsorption equation, 2D gas law, phase rule and its applications, Electrochemical cells, half-cell reactions, Nernst equation, overvoltage, liquid junction potential, strong and weak electrolytes, Debye Huckel theory, principles underlying polymer chemistry, chain and branched polymers, determination of molecular weight (number and mass average) of polymers, introductory nanoscience, synthesis and characterization of nanomaterials.

B) Solid state Chemistry:

crystalline and amorphous solids, crystal structure types, unit cell, Miller indices, Bragg equation, Bravais lattices, defects in crystals, Frenkel and Schottky defects, Band theory of solids.

Unit-III: Coordination Chemistry & Chemistry of Transition elements:

A) Introduction, Bonding in transition metal complexes, Valence bond theory, Crystal field theory, Molecular orbital theory. Electronic spectra and magnetic properties of transition metal compounds.

B) Introduction, occurrence & recovery, High oxidation states, structural trends, mononuclear oxocomplexes, polyoxometallates, intermediate oxidation states, metal-metal bonded compounds, noble character.

Unit-IV: Reaction mechanisms of d-metal complexes, Lanthanides, Actinides and Transactinide elements:

A) Introduction, Ligand substitution reactions, classification of mechanisms. The substitution of square-planar complexes, substitution of octahedral complexes, Rate law and their interpretation, Activation of octahedral complexes, stereochemistry, Isomerization reactions, Redox reactions, classification & theory of redox reactions, photochemical reactions, d-d and charge-transfer reactions, Transitions in metal-metal bonded systems.

B) Lanthanides: Introduction, methods of separation of Lanthanides, Lanthanide contraction, applications of Lanthanides. Actinides: Introduction, methods of preparation and separation of actinides, applications of actinides. Transactinide elements: Introduction, applications of transactinide elements.

Unit-V: **Electrophilic & Nucleophilic Substitutions:**

A) SN1, SN2, SNi, SN1', SN2' & SNi' with respect to mechanism and stereochemistry. Nucleophilic substitutions at an allylic, aliphatic and vinylic carbons. Reactivity, effect of substrate structure, effect of attacking nucleophiles, leaving groups and reaction medium. Ambident nucleophiles. Neighbouring group participation by σ , π and aromatic ring systems.

B) Introduction, specificity of the reactions, SNAr, Aromatic SN1 and Aryne mechanism. Effect of substrate structure, leaving group, attacking group, base & solvent.

C) Introduction, concept of Aromaticity, Arenium ion mechanism, orientation and reactivity in Nitration, Sulphonation, Halogenation, Friedel – Craft reactions in aromatic systems. Energy profile diagrams. The ortho / para ratio, ipso attack orientation in ring systems, Diazo-Coupling, Jakobsen, Haworth, Henkel and halogen dance reaction.

Unit-VI: **Rearrangements, Stereochemistry and Spectroscopy :**

A) Beckmann, Hoffmann, Schmidt, Curtius, Lossen, Claisen, Fries, Benzilic acid, Favorskii and Wolf rearrangements.

B) Concept of chirality: Recognition of symmetry elements and chiral structures, prochiral relationship, enantiomers, diastereomers, racemic modification and their resolution, R/S nomenclature, geometrical isomerism, E & Z nomenclature, conformational analysis of mono and disubstituted cyclohexanes.

C) Problems based on UV-VIS, IR, NMR & Mass spectroscopy.

Unit-VII: **Chromatography and Electro-analytical techniques**

A) General principles, Classification, Partition Chromatography, Adsorption Chromatography. Principles, Techniques and applications of Paper, Thin-Layer, Column, HPLC, Gas Chromatography and Electro Chromatography.

B) Voltammetry, cyclic voltammetry, polarography, amperometry, coulometry and conductometry. Ion-selective electrodes. TGA, DTA, DSC and on-line analysers

BOOKS RECOMMENDED

- 1) Fundamentals of molecular spectroscopy, C.N. Banwell and E. McCasj, Tata McGraw Hill (1994)
- 2) Concise Inorganic chemistry, J.D. Lee, 5th Edition, ELBS (1986).
- 3) Advanced Inorganic Chemistry: F.A. Cotton, R.G. Wilkinson, John Wiley (1984).
- 4) Advanced organic chemistry (Part-A) by F.A. Carey and R.J. Sundberg, 3rd edition, Plenum Press, New York and London, 1990.
- 5) Spectroscopic methods in organic chemistry by Williams & Fleming, Tata – McGraw Hill, 4th edition, 1988.
- 6) Spectroscopic Identification of organic compounds by R.M. Silverstein and G.C. Bassler, 5th edition, 1991.
- 7) Instrumental methods of Analysis (Can Nostrand). Willard Merritt and Dean