

BHARATI VIDYAPEETH
(DEEMED TO BE UNIVERSITY), PUNE, INDIA
PhD Entrance Test – 2020
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 : Electronic Spectroscopy & Raman Spectroscopy:

A)Electronic spectra of diatomic molecules Born-oppenheimer approximation, Vibrational coarse structure, Franck-Condon Principle, Dissociation energy and dissociation products, rotational fine structure of electronic and vibrational transition, Fortrat Diagramm. Predissociation, electronic structure of diatomic molecules, M.O. theory, Shapes of molecular orbitals, Molecular.

B)Scattering of light and Raman Spectrum, Rayleigh scattering and Raman Effect, Classical and Quantum theory of Raman Effect, Pure rotational Raman Spectra, Linear, Symmetric top and asymmetric top molecules. Vibrational Raman Spectra Raman activity of vibrations, Rule of Mutual Exclusion Overtone and combination vibrations, Vibrational Raman Spectra, Rotational fine structures, Polarization of light and Raman Effect. Vibration of spherical top molecules structure determination from Raman and Infrared spectra.

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 ringsystems, 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 reactions.

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 :**

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

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