# AURCET - 2013 SYLLABUS
# TEST NO. – 10: INORGANIC & ANALYTICAL CHEMISTRY, ORGANIC & FOOD, DRUGS, & WATER CHEMISTRY, PHYSICAL NUCLEAR CHEMISTRY & CHEMICAL OCEANOGRAPHY, ENGINEERING CHEMISTRY

## PAPER - II

### GENERAL CHEMISTRY

### MOLECULAR SPECTROSCOPY:

Basic concepts of symmetry and group theory – symmetry elements – axioms of group theory – classification of molecules into point groups – representation of point groups – matrix representation – reducible and irreducible representations – reduction of a reducible representation to an irreducible one – orthogonality theorem – character table and its anatomy (character table not to be derived) – use of character tables – application of group theoretical concepts to vibrational spectroscopy (infra-red and Raman).

### ROTATIONAL AND VIBRATIONAL SPECTRA:

Rotational spectra of diatomic molecules – isotope effect-selection rules.

Infra-red spectra of diatomic molecules – isotope effect – selection rules – anharmonic oscillator – normal modes of vibration – simultaneous vibrations – rotational spectra-combination bands – overtones – Fermi resonance – concept of group frequencies – Raman effect (classical approach) – applications of IR and Raman spectra.

Electronic spectrum of a diatomic molecule – coars structure – classification of bands – fine structure – band head and band shading – types of electronic transitions in molecules applications of electronic spectra – charge transfer spectra.

### INORGANIC CHEMISTRY

Term symbols – Russell – Saunders coupling – Derivation of terms Symbols for various configurations.

Chemical Bonding : Application of VB, MO and VSEPR theories in explaining the structure of simple molecules – role of 'P' and 'd' orbitals in hybridization and bonding.

Chemistry of main group elements: General trends in properties – boron hydrides. Carboranes, intercalation compounds, nitrogen – phosphorous, boron – nitrogen and sulphur – nitrogen cyclic compounds.

Chemistry of transition elements: Comparative study of the first, second and third transition series. Metal cluster compounds – Favorable conditions for formation – Structure and bonding in halide and carboxlate metal compounds.

Chemistry of Inner Transition elements: Chemistry of Lanthanides – electronic configurations, Oxidation states – Lanthanide contraction and its consequences – magnetic and spectral properties – separation of lanthanides.

Chemistry of actinides – Synthesis of transuranium elements electronic configurations, oxidation states – position in the periodic table – actinide contraction – comparison of magnetic and spectral properties with those of lanthanides.

Coordination compounds: Crystal field theory – crystal field splitting patterns in octahedral, tetrahedral, tetragonal, square planar, square pyramidal and trigonal bipyramidal geometries – Determination of crystal field splitting energy-calculation of crystal field stabilization energies – Factors affecting crystal field splitting energies – spectrochemical series – Jahn – Teller effect – Ligand field theory.

Electronic spectra of transition metal complexes – Selection rules – break down of selection rules – Orgel and Tanabe – Sugano diagrams – Spectra of octahedral and tetrahedral complexes.

Magnetic properties of free ions – spin and orbital moment and spin – orbit coupling Quenching of orbital momentum by crystal fields in complexes.

Stability of complexes – Factors affecting stability – chelate effect – Determination of stability constants of complexes – Spectrophotometric method and pH metric method.

Inorganic reaction mechanisms: Inert and liable complexes – Explanation of liability on the basis of CFSE.

Substitution reactions of metal complexes – Id Ia and A mechanism – Ligand replacement reactions of octahedral complexes-Acid hydrolysis, Anation and Base hydrolysis of

cobalt(III) Complexes Ligand displacement reactions of square planar complexes of platinum(II) – Trans effect – Mechanism of trans effect (theories) – Electron transfer reactions of complexes – Inner and outer sphere mechanisms.

## ORGANIC CHEMISTRY

Structure and reactivity – localized and delocalized covalent bond – concent of resonance and aromaticity – Huckel's rule aromaticity in benzenoid and non-benzenoid compounds – anti aromaticity and homo aromaticity, Naature of Organic reaction – energy and kinetic considerations – types of Organic reactions – reagents – reactive intermediates, their formation and stabilization – inductive and mesomeric effects.

Stereochemistry and stereoisometrism – conformational isomerism and analysis in acyclic and simple cyclic systems – substituted ethanes, cyclopentane, cyclohexane, cyclohexane, cyclooctance and decalins – Optical isomerism – optical activity molecular dissymmetry and chirality – elements of symmetry.

Fischer's projection – D.L. and R.S. – configurations – relative and absolute configuration

– optical isomerism due to a symmetric carbon atoms optical isomerism in biphenyl, allenes and spirans – optical isomerism of nitrogenous compounds – recemisation and resolution – geometrical isomerism and E.Z. configurations Properties of geometrical isomers.

Aromatic substitution reactions – electrophilic, nucleophilic and through benzynes – radical substitution of arenes – orientation Nucleophilic substitution at a saturated carbon, SNI, SN2, ENi – reaction – effect of structure of nucleophile, leaving group, solvent and neighbouring groups. Addition Reactions: Addition to C=C and C=O double bond. Additions involving electrophiles, nucleophiles and free radicals.

Elimination reactions – E1, E1CB, E2 reactions – elimination versus substitution reactions.

Machanisms of some name reactions – aldol, Parkin, Benzoin, Cannizaro, Witting, Griganard Reformatsky, Wagner – Meerwein – Hofmann, Clasen and Favorsky, rearrangements – Hydroboration – Openauer Oxidation, Clemmensen reduction, Wolf- Kischner reduction – Meerwein – Pondorf and Varley and Birch reductions.

Spectra and structure – application of organic spectroscopy UV IR – HNMR and Mass spectral data.

Alkaloids – priperine, apropine, cocaine, nicotins, papverine and quinine Purines – caffions.

## PHYSICAL CHEMISTRY

SOLIDS: X-ray diffraction studies – crystal structure determination – lattice types and lattice dimensions – crystal defects – linear point and edge defects – Band theory of solids

– Theories of specific heats of solids – semiconductors and their properties. Physical Methods for the elucidation of molecular structure – magnetic properties of molecules – theories of magnetic susceptibility- Application of magnetic susceptibility measurements to coordination compounds – spin-spin interactions – Chemical shift and its origin –

experimental methods – application of NMR studies in structural-elucidation – application to structure of ethanol, acetophenone, aceltamide, dimethyl formamide and styrene – electron spin resonance –principle and experimental technique – line shapes and line widths – g-value – hyperfine interactions – application of ESR Studies to the structure of free radical, metal complexes and biological systems.

THERMODYNAMICS : Free energy, entropy and enthalpy – Chemical equilibrium – thermodynamic criteria of the chemical equilibrium – effect of temperature on equilibrium constant – Vant Hoff isochore – Maxwell relations – Gibbs-Duhem equation Duheme – Margules equation – classius –clapeyron equation – Nernst heat theorem and third law of thermodynamics – determination of absolute entropy.

KINETICS: Theories of reaction rates – collision and transition state theories – study of fast reactions using flow and relaxation methods – Kinetic isotope effects – reactions in solution – primary and secondary kinetic salt effects – Effect of dielectric constant – elementary ideas of linear free energy relations – Hammett and Taft equations – Chain reactions – consecutive, parallel and opposing reactions involving uni-molecular steps only – catalysis – homogeneous and heterogeneous – acid-base and redox catalysis.