SYLLABUS, TDC-III

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CHEMISTRY (HONOURS) PAPER-V

Time: 3 Hrs **F.M. : 100**

Nine questions to be set. Five questions to be answered. Short answer type questions are recommended. There may be several parts in a question and different units may be mixed in questions. While setting questions the entire syllabus may be covered as far as practicable.

1. **Electrochemistry:**

Galvanic cells, thermodynamics of Galvanic cells, chemical cells with and without transference, liquid junction potential, Glass electrode for the measurement of pH, Storage batteries, Lead accumulator, Polarisation, Hydrogen and oxygen overvoltage, Decomposition voltage in aqueous solution, Electrical double layer, corrosion of metals and its prevention.

2. **Wave Mechanics:**

Inadequacy of classical mechanics.Wave, quanta and motion of vibrating string, basic concept of quantum mechanics, postulates, eigen function and eigen value, physical properties of wave function, orthogonality and normalization of wave functions, Schrodinger wave equation and its importance, Treatment of free particle and particle in one , two and three dimensional boxes, rigid rotator-expression for energy rotational quantum number and degeneracy of states.

Elementary idea of H atoms, radial and angular parts of wave functions R, θ and ϕ, concept of quantum numbers and their significance, radial distribution functions, radial factors, Rnl-r, R^2nl-r and $4\pi r^2R^2$nl-r plots. Angular dependence of orbitals –shape of s,p and d orbitals, concept of electronic spin.

3. **Spectroscopy:**

Component of molecular energy and their quatization, different parts of electromagnetic radiation and their characterization, energy level spacings and relative population among levels, types of molecular spectra , band width,band intensity and position of spectral bands.

UV-visible spectra:

Frank-condon principle, selection rules, λ and ε max values, Qualitative description of σ, π and n molecular orbitals, transitions in H_2, ethylene, butadiene, formaldehydes, α, β, unsaturated carbonyl compounds. Red and blue Shifts, calculation of λmax, Woodward rules.

Infrared-spectra:

Energy levels of simple harmonic oscillator, selection rule, Hooke's law and force constant, qualitative relationship between force constant, bond length, bond angle, bond order, bond energy, and stretching frequency of molecules, vibrational spectra of H2O, NO2 and CO2, concept of group frequency.

4. Magnetic Resonance Spectra:

N.M.R. spectra, nuclear spin system, nuclear spin quantum number, nuclear spin angular momentum, nuclear magnetic moment, nuclear magneton, effect of magnetic field on system with nuclear spin, nuclear energy levels, magnetic quantum number for nuclear spin, energy level separation and resonance condition in a magnetic field N.M.R., chemical shift, factor affecting chemical shift, shielding and deshielding mechanisms, nuclear spin-, spin coupling, coupling constant and contributing factors to it, first order rules.

E.S.R. spectra: Electronic spin system, electronic spin quantum number, electron spin angular momentum, electron spin magnetic moment, Bohr magneton, effect of magnetic field on electronic spin system, electron spin energy levels, magnetic quantum number for electronic spin states, separation between energy levels caused by the presence of magnetic field, condition for electron spin resonance, selection rule, derivative curve, hyperfine coupling, hyperfine coupling constant, spectra of H_2 ,CH3 CH2OH,NO, C6H6.

5. Equilibrium Thermodynamics:

Maxwell relations, thermodynamic equation of state, free energy change in a chemical reaction and equilibrium constants, thermodynamic derivation of law of mass action, Denuder's concept of chemical equilibria and reaction potential, pressure and temperature dependence of equilibrium constant, van't Hoff equation. Nerst heat theorem, third law of thermodynamics and its experimental verification, entropy and probability.

6. Theories of Rate Process:

Derivation of Maxwell law of distribution of velocities of gaseous molecules. Average R.M.S. and most probable velocity, Collision theory of bimolecular reaction and its validity, Lindemann theory of unimolecular reaction. Hinselwood theory, Transition state theory-thermodynamic-traetment activation parameters viz volume of activation, free enegy of activation and Entropy of activation.

Steady state approximation and rate law for thermal decomposition of Ozone, N_2O_5 and non[photo chemical combinations of

$$H2 + Cl2 \rightarrow 2HCl$$

7. Photochemistry:

Primary and secondary photochemical processes, laws of photochemistry, Jablonski diagram, radiative and non-radiative transitions, quantum efficiency and its variation.

Photochemical reactions:

$$H2 + Cl2 \rightarrow 2HCl$$

$$H2 + Br2 \rightarrow 2HBr$$

Decompositionof HI, fluorescence and phosphorescence, photosensitization.

Reference Books:-

(1) Physical Chemistry **P.W. Atkins** Oxford University Press
(2) Advanced Physical Chemistry **Gurdeep Raj** Goel Publication House
(3) Quantum Chemistry **Donald A.** McQuarrie Viva Books

CHEMISTRY PAPER: VI

Time: 3 Hrs **F.M.: 100**

Nine questions to be set. Five questions to be answered. Short answer type questions are recommended. There may be several parts in a question and different units may be mixed in questions. While setting questions the entire syllabus may be covered as far as practicable.

1. **Molecular orbital and valence bond methods:**
Principles of linear combination, criteria of maximum overlapping for effective combination, Energy and probability plots of bonding and anti bonding molecular orbitals in H_2^+, energy versus internuclear separation in H2 both for attractive and repulsive states, non-bonding M.O. and three centre bonding, valence bond wave functions of H2 molecule, quantitative description of sp, sp^2 and sp^3 hybrid orbitals and inter orbital, comparison between V.B. and M.O. methods.

2. **Magnetic Properties:**
Diamagnetic, paramagnetic, ferromagnetic and antiferro-magnetic behaviour. Paramagnetic susceptibility and method of its determination, Variation of magnetic susceptibility with temperature, Curie and Neel temperature, Ground Term Symbols and Hund's rule, dependence of magnetic moment value on L.S. and J quantum numbers, spin only magnetic moment, quenching of orbital angular momentum, magnetic moment data in case of transition metal complexes.

3. **Metal Ligand Bonding in Transition Metal Complexes:**
V.B. model of M-L bonding and its limitations, crystal field model d-orbital splitting in o_h and T_d environments, crystal field splitting parameter (10Dq) and factors affecting it, crystal field stabilization energy, magnetic properties and colour of complexes, variation of ionic radii of M^{2+} ions in 3d series. Thermodynamic stability constants and factors affecting stability of complexes, chelate effect, entropy effect.

4. **Nuclear Chemistry:**
   Nuclear stability and binding, artificial radioactivity, positron emission and β-decay process, Nuclear fission, Liquid drop model, nuclear chain reaction, moderator, nuclear fusion reactions, neutron activation analysis, isotope dilution method, isotope effect and isotope exchange reactions.
5. **Electronic Spectra of Transition Metal Cmplexes:**
   Types of electronic transition, selection rules for electronic transition, spectrochemical series, Free ion ground terms and Orgel diagram for d^1 to d^9.systems in octahedral and tetrahedral fields, Visible spectra of $[Ti(H2O)6]^{3+}$ ions.
6. **Hard and Soft Acid and Bases:**
   Classification of metals into A and B, acid-base behaviour of hard and soft acids and bases, classification, their acid-base strength, hardness-softness, symbiosis, theory of hardness and softness, electronegativity and hardness and softness.
7. **Inorganic Polymers:**
   Classification of polymers, chemistry of inorganic ring and chain compounds containing boron, nitrogen, phosphorous and silicon atoms.
8. **Methods of Analysis**:

   (a) Complexometric titration using EDTA, estimation of Mg^{2+} ion and Ca^{2+}.
   (b) Chromatographic technique: Principles of TLC and gas chromatography, determination of Rf value.
   (c) Introduction of Colourimetry coulometry and flame photometry.

Reference Books:-

(1) Inorganic Chemistry **Huheey**, Medhi Pearson
(2) Concise Coordination Chemistry **R. Gopalan, V.Ramalingam** Vikas Pub House Ltd
(3) Selected Topics Chemistry **G.D. Tuli, S.K. Basu, R.D. Madan** Bharti Bhawan

CHEMISTRY PAPER: VII

Time: 3 Hrs **F.M. : 100**

Nine questions to be set. Five questions to be answered. Short answer type questions are recommended. There may be several parts in a question and different units may be mixed in questions. While setting questions the entire syllabus may be covered as far as practicable.

1. **Reaction Mechanism:**
   Methods of determination of reaction mechanism (product analysis,

intermediates, use of isotopes, Cross over experiment, kinetic and stereochemical studies).Mechanism of nucleophilic substitution reactions at saturated carbon atom SN^1, SN^2 and SN^i. Relative reactivities of alkyl halides, allyl, vinyl and aryl halides, α- and β- Elimination reaction. E1 and E2 mechanism and their region and stereo selectivities. Electrophilic additions to carbobn-carbon multiple bonds, Regio and stereo selectivities, Nucleophilic additions to carbon-oxygen double bond..

2. **Reagents use in organic synthesis:**
   Diazomethane, Lithium aluminium hydride, Sodium borohydride, Diborane, Nbromo succinimide, Raney Nickel, Aluminium isoproxide, Periodic acid, Lead tetraacetate, Lithium dialkylcuprate and Osmium tetroxide. Discussion on specificity of the reagents and mechanism involved

3. **Organic Reactions and Molecular Rearrangements:**
   i) Mannich reaction ii) Michael additionreaction
   iii) Hofmann exhaustive Methylation and elimination
   iv) Wagner-Meerwein rearrangement
   v) Wolf rearrangement
   vi) Hofmann rearrangement vii)Beckmann rearrangement viii) Curtius rearrangement
   ix) Schmidt rearrangement
   x) Pinacol-Pinacolon rearrangement

4. **Polynuclear Hydrocarbons:**

   Preparation, properties and structure determination of naphthalene, anthracene and phenanthrene..

5. **Heterocyclic compounds:**
   (a) Five membered, heterocyclics: Preparation, properties and aromatic character of pyrrole, furan and thiophene.
   (b) Six membered heterocyclics: Preparation, properties and aromatic character of pyridine.
   (c) Condensed heterocyclics: Preparation, properties of quinoline and isoquinoline.

6. **Dyes:**
   Classification, correlation of colour with constitution. Chemistry of the following dyes: methyl orange, Congo-red, Malachite green, Crystal violet, Phenolphthalein, Fluorescein, Alizarin and Indigo.

7. **Ureides:**
   Purines, Isolation, structure and synthesis of Uric acid..

8. **(a) Amino Acids and Proteins:**:

i) Classification, structure and stereo chemistry of amino acids, Acid base behaviour, isoelectric point and electro-phoresis, preparation and reactions of α-amino acids.

ii) Peptide linkage, Basic idea about primary and secondary structure of proteins.

(b) Nucleic Acids

(i) Brief knowledge of purine and pyridine bases.

(ii) D-Ribose and de-ribose.

(iii) Constitution of nucleic acid and basic idea of double helix structure of DNA.

Reference Books:-

(1) Organic Chemistry **S.M. Mukherji, S.P.Singh** Bharti Bhawan

(2) Advanced Organic Chemistry **Jerry March** Wiley

(3) Organic Chemistry **Jagdamba Singh, L.D.S. Yadav** Pragati Prakashan

(4) A Text Book of Organic Chemistry **Bahl & Bahl** S. Chand

CHEMISTRY PRACTICAL

Time: 6 Hrs **F.M. : 100**

The following exercises are to be performed**: Physical** (1 to 7):

1. To determine the specific reaction rate of hydrolysis of methyl acetate catalyzed by H^+ ion at room temperature.
2. To compare strength of HCl andH2SO4 by studying the kinetics of hydrolysis of ethyl acetate.
3. To determine the distribution coefficient of iodine between waterand CCl4.
4. To determine the surface tension of a liquid.
5. To determine the heat of neutralization of NaOH with HCl.
6. To determine enthalpy of neutralization of acetic acid using NaOH solution and determine enthalpy of ionization.
7. To determine the viscosity of a liquid.
8. Synthesis of organic compounds:
   (i) Acetylation of salicylic acid
   (ii) Benzoylation of aniline
   (iii) Nitration of monobenzene to m-dinitrobenzene.
   (iv) Selective reduction of m-dinitrobenzene to m-nitroaniline.

Distribution:

One experiment from physical	**60**
One experiment from organic out of exercise in item 8	**20**
Note Book	**05**
Viva-Voce	**15**

Reference books:

(1) Elementary Practical Organic Chemistry Small Scale preparation Part I Arthur I. Vogel Pearson India
(2) Practical Chemistry **Dr. O.P.Pandey, D.N. Bajpai, Dr. S. Giri** S.Chand
(3) Text book of Quantitative chemical Analysis **J Mendham, R C Denney, J D Barnes, M** Thomas Pearson