



**DEPARTMENT OF CHEMISTRY**  
**VIKRAMA SIMHAPURI UNIVERSITY: NELLORE – 524 004**

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**VSU-RECET 2010**  
**(Ph.D. Entrance Examination)**  
**Syllabus & Model Questions**

Time: 2 hours Max. Marks: 120  
*(Each question carries 1 mark. The candidate has to answer 30 questions from Section A, carrying 30 marks and 90 questions from Section B, carrying 90 marks).*

**SECTION - A**

**GENERAL APTITUDE (COMMON FOR ALL PG COURSES)**

Reasoning (includes mathematical): Number series; Letter series; Codes; Relationship; Classification. (5 Questions)

Logical Reasoning: Understanding the Structure of arguments; evaluating the distinguishing deductive and inductive reasoning; Verbal analogies: Word analogy – Applied analogy; Verbal Classification; Reasoning logical Diagrams: Simple Diagrammatic Relationship, Multi Diagrammatic Relationship; Venn diagram; Analytical Reasoning. (10 Questions)

Data Interpretation: Sources, acquisition and interpretation of data; Quantitative and qualitative data; Graphical representation and mapping of data. (5 Questions)

Information and Communication Technology (ICT): ICT: meaning, advantages, disadvantages and uses; General abbreviations and terminology; Basics of internet and e-mail. (5 Questions)

Research Aptitude: Research: Meaning, Characteristics and types; Steps of Research; Methods of Research; Research ethics. (5 Questions)

**SECTION - B**

**CO-ORDINATION COMPOUNDS**

Introduction to Crystal field Theory, CFSE and its calculation, Pairing energy, Splitting of 'd' orbitals in Trigonal bi pyramidal, square planar, square pyramidal and pentagonal bipyramidal geometries, Jahn -Teller effect, Application of CFT, OSSE, site Selection in Spinels, Shortcomings of CFT, Evidence for covalency -Nephelauxetic effect. MOT of coordinate Bonds -M.O. Diagrams for octahedral, tetrahedral and square planar complexes.

**REACTION MECHANISMS IN COMPLEXES**

Reactivity of metal complexes -inert and labile complexes- kinetics and Mechanisms of substitution reactions -Substitution reactions in octahedral complexes- Acid Hydrolysis - factors affecting Acid Hydrolysis - Base Hydrolysis-conjugate Base Mechanisms -Anation Reactions -Substitution Reactions in Square Planar complexes- Trans effect -Mechanisms of Trans effect -Electron Transfer Reaction-Inner Sphere and outer Sphere Mechanisms-Marcus theory.

## TRANSITION METAL H - COMPLEXES

Transition metal TC - complexes with unsaturated organic molecules - alkenes, alkynes, diene, dienyl and arene complexes- properties, nature of bonding and structural features - Important reactions relating to Nucleophilic and Electrophilic attack on ligands and to organic synthesis.

## ELECTRONIC SPECTRA OF COMPLEXES

Frank-Condon principle - Russel-Saunders coupling - Spectroscopic term symbols-Selection rules - Break - down of selection rules -Orgei Diagrams for  $d^1$  to  $d^9$  configurations in Octahedral and tetrahedral fields. Tanabe - Sugano diagrams of  $d^2$  to  $d^8$  configurations. - Spectra of octahedral and tetrahedral complexes of metal ions of  $d^1$  to  $d^9$  configurations. - Calculation of  $Dq$  and  $B^1$  parameters -Charge transfer spectra. Differences between ligand field spectra and charge transfer spectra.

## MAGNETIC PROPERTIES OF TRANSITION METAL COMPLEXES

Diamagnetism and paramagnetism-orbital and spin contributions, spin-orbit coupling, Hunds third rule and Energies of J levels - Curie law and Curie - Weiss law- Ferro magnet ism and antiferromagnetism - Temperature independent magnetism - Magnetic - Paramagnetism and crystalline fields - Ti (III), V (III),  $VO^{2+}$ , Cr (III), Mn (II), Fe (III), Co(II), Ni (II) and Cu (II). Magnetic Exchange in copper acetate and other dimmers - spin cross over in complexes.

## SPECTRAL TECHNIQUES OF INORGANIC COMPLEXES

Mossbauer spectroscopy, NQR spectroscopy, Electron spin resonance spectroscopy, photo electron spectroscopy.

## Aliphatic Nucleophilic substitutions and Aromatic Nucleophilic substitutions

Addition to Carbon - Carbon Multiple Bonds:  
Addition to Carbon - Hetero Multiple Bonds:  
Elimination reactions, esterification and hydrolysis  
Reagents in organic synthesis  
Stereochemistry and conformational analysis  
Optical isomerism:  
Conformational analysis  
Reactive intermediates

## METHODS OF ORGANIC SYNTHESIS

**Oxidations:** (i) Alcohols to carbonyls-Chromium (iv) oxidants-Dimethyl sulfoxide oxidation, periodate oxidation, Oppenauer oxidation, oxidation with manganese dioxide, oxidation with silver carbonate (ii) Alkenes to epoxides-peroxide induced epoxidations. (iii) Alkenes to diols-oxidation with potassium permanaganate, osmium tetraoxide, Prevost reaction (iv) Ketones to esters-Bayer-villiger oxidation (v) Oxidative bond cleavage-cleavage of alkenes by transition metals, (vi) Oxidation of alkyl or alkenyl fragments-selenium dioxide and chromium trioxide oxidations.

**Reductions:** Reduction with lithium aluminium hydride, sodium borohydride, alkoxides, bis-methoxy ethoxy aluminium hydride, Boron aluminium hydride and derivatives-catalytic hydrogenation-dissolving metal reductions, Non-Metallic reducing agents including enzymatic and microbial

**Organometallic reagents:**

Synthesis and applications of Grignard reagents - Organolithium, Zinc, Copper, Mercury, Palladium, Rhodium and Nickel compounds in Organic synthesis - Homogeneous catalytic reactions - Hydrogenation, Hydroformylation.

**APPLICATION OF SPECTRAL TECHNIQUES TO ORGANIC COMPOUNDS**

Ultra violet & Visible Spectroscopy, ORD, Circular Dichroism, Infrared Spectroscopy Nuclear magnetic resonance Spectroscopy ( $^1\text{H}$  nmr),  $^{13}\text{C}$  NMR Spectroscopy, mass Spectroscopy.

**QUANTUM CHEMISTRY -I**

**Introduction to Exact Quantum Mechanical Results:** Operator algebra. Eigen values and eigen functions. Operators for momentum and energy. The derivation of Schrodinger equation and the postulates of Quantum Mechanics. Discussion of solutions of the Schrodinger equation to some model systems, viz., particle in a box, harmonic oscillator, rigid rotor, hydrogen atom.

**Approximate Methods:** The Variation Theorem, Linear variation Principle, Perturbation Theory (first Order and non-degenerate), Application of Variation Method and Perturbation Theory to the helium atom.

**PHASE RULE**

Stokes and Roozeboom plots. Three component liquid systems - formation of one pair, two pairs and three pairs of partially miscible liquids; two salts and water - no chemical combination, double salt formation, one salt forms hydrate and two salts form hydrates.

**THERMODYNAMICS:**

Terms of Fugacity and its determination, partial molar properties, chemical potential, derivation of Gibbs-Duhem's equation, significance of partial molar properties, determination of partial molar volume. Concept of distribution, thermodynamic probability and most probable Distribution -Ensemble averaging, Postulates of ensemble averaging, canonical, grand canonical and micro-canonical ensembles. Partition functions - translational, rotational, vibrational and electronic partition functions, calculation of thermodynamic properties in partition functions -Heat capacity, chemical equilibria and equilibrium constant in terms of partition functions-Entropy of monatomic gases (Sackur-Tetrad equation).

**ELECTROCHEMISTRY**

**Irreversible Electrode Phenomenon:** Reversibility and irreversibility, Dissolution and deposition potentials. Decomposition voltage, overvoltage, diffusion overvoltage, charge transfer overvoltage, reaction overvoltage, concentration overvoltage-hydrogen and oxygen overvoltages, Tafel plots. Exchange current density and Transfer coefficient, Butler-Volmer equation for one electron transfer processes.

**SYMMETRY AND GROUP THEORY**

Symmetry Elements and Symmetry operation, Definitions of a group, sub-group. Relation between orders of a finite group and its sub-group-Conjugacy Relation and classes- point symmetry group, Schonflies symbols-Representation of groups by matrices (representation for  $C_n$ ,  $C_{nv}$ ,  $D_{nh}$ , etc. groups to be worked out explicitly), character of a representation. The great orthogonality theorem (without proof)- Character tables.

## **POLYMERS- STRUCTURE AND PROPERTIES**

Morphology and order in crystalline polymers, configuration of Polymer chains, crystal structures and polymers. Stain induced morphology, morphology of crystalline polymers, crystallization and melting- polymer structure and physical properties, crystalline melting point,  $T_m$ -melting point of homogeneous series, effect of chain flexibility and other steric factors- entropy and heat effusion, the glass transition temperature,  $T_g$ , relationship between  $T_m$  and  $T_g$  effects of molecular weight, diluents, chemical structure, chain topology, branching and cross linking.

## MODEL QUESTIONS

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#### SECTION – A GENERAL APTITUDE

- 1) 196, 256, 324, 400, 484, \_\_\_\_\_  
A) 576      B) 441      C) 529      D) 625
- 2)  $1/9, 2/27, 8/81, \text{_____}, 1024/729$   
A)  $32/243$       B)  $128/243$       C)  $256/243$       D)  $64/243$
- 3) A man walks 30m towards south. Then Turning to his right, he walks 30m. Then turning to his left, he walks 20m. Again, he turns to his left and walks 30m. How far is the from his initial position?  
A) 20m B) 30m C) 60m D) 50m
- 4)  $64:16::70: \text{_____}$   
A) 17.5 B) 18.5 C) 21.5 D) 20.5
- 5) Solve the given equation  
 $X^2+Y^2=34; \quad X^2-Y^2=544$   
The value of X and Y are  
A)  $\pm 4, \pm 3$       B)  $\pm 5, \pm 3$       C)  $\pm 3, \pm 5$       D)  $\pm 3, \pm 4$
- 6) Mathematical standard deviation is represented by  
A)  $\sigma = \sqrt{\frac{\sum Xi - \bar{X}}{N}}$       B)  $\sigma = \frac{\sum Xi - \bar{X}}{N}$       C)  $\sigma = \sqrt{\frac{(\sum Xi - \bar{X})^2}{N}}$   
D)  $\sigma = \sqrt{\frac{(\sum Xi + \bar{X})^2}{N^2}}$
- 7) Which of the following is not an Internet Browser?  
A) Internet Explorer      B) Netscape      C) Opera      D) AQL
- 8) Data transfer rate in Modems is measured in  
A) Bits per minute      B) Bits per Second  
C) Band Width      D) None of the Above
- 9) Basic steps of research process includes  
A) Problem definition      B) Research Design      C) Data Collection      D) All
- 10) Which of the following comes under quantitative objective of Research?  
A) A study of estimate the demand of product  
B) A study of testing the effect of level of education  
C) A Study on the impulse buying behavior of customers  
D) None

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30)

## SECTION-B

31. Carbonyl Compounds can be converted into alkene by the following reaction
- Wittig reaction
  - Clemmensen reduction
  - Wolf – Kishner reduction
  - None of the Above
32. In NMR- $H^1$  the aldehydic proton can be observed at
- 8 PPM
  - 6 PPM
  - 9 PPM
  - 12 PPM
33. Calamine is the ore of
- Aluminium
  - Zinc
  - Iron
  - Copper
34. How many ions are produced from complex  $Co(NH_3)_6Cl_2$  in solution
- 6
  - 4
  - 3
  - 2
35. During an isothermal expansion of an ideal gas its:
- Internal energy increases
  - Enthalpy decreases
  - Enthalpy remains unaffected
  - Enthalpy reduces to Zero
36. If the initial concentration of the reactant is doubled, time for half reaction is also doubled, the order of reaction is
- Zero
  - First
  - Second
  - Third

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120)