

# VIJAYANAGARA SRI KRISHNADEVARAYA UNIVERSITY, BALLARI

## **Ph. D. Entrance Examination Syllabus**

### (2019-20)

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### VIJAYANAGARA SRI KRISHNADEVARAYA UNIVERSITY, BALLARI DEPARTMENT OF CHEMISTRY

#### Syllabus for Entrance examination of Ph.D. degree

Note: The entrance examination is of 3 hours duration and consists of 100 marks. Out of 100 marks **60 marks are from the Chemistry core subject syllabus** and **40 % marks from the Research Methodology syllabus**. The questions are of multiple choice type. Marks distribution for each unit is mentioned at the right side after the end of each unit.

#### **Research Methodology** (4 Units- Total 40 Marks)

#### UNIT 1

#### **Introduction to Research**

Nature and importance of research - aims, objective, principles and problems; types of research, Selection of research problems and literature survey: primary sources- Journals periodicals, abstracts; Secondary listing of titles, reviews –annual Treatises, serials, monographs and text books, encyclopedia, catalogues, index of tabulated data. Research ethics.

(10 Marks)

#### UNIT 2

#### **Research sources and copyright**

Science citation index- Searching the chemical literature-location of journal article- materials on a given topic- information about specific compound- Choosing a problem-abstract of a research paper. Internet: Introduction to internet-web browsers-World Wide Web-Search enginesliterature survey in Chemistry-popular website in chemistry-Database in chemistry. Scientific ethics and its importance; Plagiarism, Protection of research data. Patent: Introduction, patentable subject; Copyright. (10 Marks)

#### UNIT 3

#### **Research sources and data presentation**

usage of packages (e.g. ORIGIN; EXCEL) for data analysis; basics of computer operations; using windows – directory structures – command structure (document preparation, EXCEL, Power Point Presentation); E-Mail: Introduction to e-mail- creating e-mail-Receiving and sending e-mail; Research manuscript preparation Full length research paper, short communication, letters, reviews, popular science articles in magazines, Few case studies with reference to journals and periodicals. Presentation of research papers: Oral and poster presentation in seminars, workshops and conferences etc.. (10 Marks)

#### Error analysis and safety requirements

Classification of errors-Accuracy-Precision-Minimization of errors-Significant figures. Statistical treatment of data: Mean and Standard Deviation-distribution of random and normal errors-Reliability of results-Confidence interval-Comparison of mean results students t-distribution and t-tests-Comparison of precision of two methods, comparison of precision of two methods- Linear regression, regression line, standard deviation, correlation coefficient-Multiple linear regression(one variable with two other variables).

Safety requirements in laboratory and data management; Good laboratory practices Sampling- Significance, types of sampling and sampling of solid, liquid and gaseous samples

(10 Marks)

#### **Core Subject- (8 Units – Total 60 Marks)**

#### <u>Unit – I</u>

#### **Concepts in Organic chemistry**

**Chemical bonding and Stereochemistry:** Atomic and molecular orbits, concepts of bonding, anti bonding and non bonding molecular orbitals, hybridization  $- \text{sp,sp}^2 \& \text{sp}^3$ , geometry and shape of simple molecules, bond length, bond angel and bond energies. Bonding in fullerenes, H-bonding. Bond polarity, dipole moment.

**Aromaticity**: in benzenoid and non benzenoid compounds, Huckl's rule, annulenes. Aromaticity, antiaromaticity, nonaromaticity of organic systems(3-7 numbered rings & ring ions).

**Stereo Chemistry:** Elements of symmetry, concepts of chirality, optical isomerism, projection formulae, Fisher, Saw horse, Newman and Flying wedge formulae and their inter conversion, optical isomerism due to one or more than one chiral centres.

Threo and erythro isomer, enantiomers, diastearic isomers and epimers. D-L and R-S conversions. Geometrical isomerism – cis-trans, syn-anti and E-Z nomenclature, isomerism in ketoximes and aldoximes, Beckmann rearrangement.

#### **Reaction Mechanisms, Reactive Intermediates & Named reactions:**

Types of mechanism, methods of determination of reaction mechanism – cross over experiments, product analysis, presences of intermediates. Formation, structure and stability of carbocations, carboanions, free radicals, carbenes, nitrenes and aryne intermediates. [8 Marks]

#### UNIT 2

#### **Coordination and Organometallic chemistry**

#### Geometry, Magnetic and Spectral Properties of Metal Complexes:

*Geometry of Metal Complexes*: Stereochemistry, coordination numbers, 3 to 8, isomerism in metal complexes, geometrical isomerism, optical isomerism, coordination isomerism, ionization isomerism, linkages isomerism.

*Magnetic Properties of Metal Complexes:* Magnetic susceptibility, types of magnetic behavior, diamagnetic corrections, orbital contribution, spin-orbit coupling, ferro and anti-ferromagnetism.

**Organometallic Chemistry:** Classification & nomenclature of organometallic compounds – 16 & 18 electron rules – electron counting by neutral atom & oxidation state method.

Transition metal alkyls (synthesis and stability), metal carbonyls, nitrosyls, carbenes (Fischer and Shock) synthesis and bonding. (10 Marks)

#### UNIT 3

#### Thermodynamics and electrochemistry

#### **Chemical Thermodynamics:**

A brief resume of laws of thermodynamics (combined form of 1<sup>st</sup> and 2<sup>nd</sup> laws), entropy as a measure of unavailable energy, concept of fugacity and free energy. Variation of free energy with T & P. Maxwell's relations. Third law of thermodynamics- free energy of mixing, partial molar quantities, partial molar volume and free energy (chemical potential). Gibbs- Duhem and Duham-Margules equations.

**Chemical Kinetics:** definition of rate, order and molecularity. Half-life period, theory of reaction rates

#### **Electrochemistry of Solutions:**

Electrical double layer and its thermodynamics. A brief survey of Helmholtz – Perrin, Gouy – Champman and Stern electrical double layer, EMF cells, liquid junction potential and its determination. Energetics of cell reactions, effect of temperature, pressure and concentration on energetics of cell reactions

**Electrochemical energy sources** – Batteries, classification, characteristics, primary, secondary and Fuel cells. [10 Marks]

#### UNIT 4

#### **Analytical Chemistry**

Acid base titrations: Principle, titration curves; equivalence point – theory acid base indicators applications.

**Complexometric Titrations:** Introduction, a simple complexation titration, selectivity, masking and demasking agents, metal ion indicators, some practical considerations.

**Oxidation** –**Reduction Titrations:** Redox process, titration curves, redox indicators and applications.

**Separation techniques:** Introduction, basics to separation and chromatographic techniques; classification of chromatographic techniques.

**Paper and thin layer Chromatography:** General principles and classification of chromatographic methods-paper, thin layer, column and liquid chromatography.

**Ion Exchange Chromatography:** Definitions, requirements for ion exchange resin, types of ion exchange resins, principle, ion exchange capacity, applications of ion exchange chromatography.

Gas Liquid Chromatography: Principle, apparatus-columns, detectors, applications.

HPLC Principles: Instrumentation-columns, stationary phase and matrices, applications.

Thermal Methods of Analysis: Principle, working and applications of TGA, DSC and DTA

[10 Marks]

#### UNIT 5

#### **Spectroscopic Techniques**

**Electromagnetic radiation:** regions of electromagnetic radiation spectrum – interaction electromagnetic radiation with matter

**UV-Visible Spectroscopy:** Quantitative aspects of absorption – Beer- Lambert's law. Criteria for spectrophotometric determinations with examples (Fe, Mo and Ni). Limitations of the law, Types of absorption bands, simple chromophoric –auxochrome theory. Wood-Ward and Fischer rules for conjugated diens, trienes, Quantitative applications.

**Infra Red Spectroscopy:** Introduction – Molecular vibrations –, calculation of vibrational frequencies, instrumentation-– FT – IR Spectrometer. Sampling techniques, interpretation of IR spectra, important regions in the IR spectrum; applications of IR spectroscopy in the structural elucidation of organic compounds.

**HNMR Spectroscopy:** Introduction – Nuclear spin and magnetic moment, origin of NMR spectra, interpreparation of NMR spectrum, chemical shifts(down field and up field), factors influencing chemical shifts, spin-spin relaxations, use of HNMR spectrum in structural elucidation.

**Mass Spectroscopy:** Introduction – Basic theory, types of ions, factors affecting fragmentation, Mc Laffarty rearrangement, nitrogen rule, applications of mass spectrometry.

[10 Marks]

#### UNIT 6

#### **Heterocyclic and Natural Products**

**Heterocyclic Chemistry:** IUPAC nomenclature of heterocyclic ring systems (3-7 memberd rings and simple fused systems) comparative aromaticity of pyrrole, furan, thiophene, pyridine-electorphilic and nucleophilic substitutions reactions.

Alkaloids – classifications, occurrence, and synthesis of quinine, and morphine.

**Terpenoids** – occurrence, stereo Chemistry, isoprene rule .

**Carbohydrates, Proteins and Nucleic acids:** -Determination of ring structures of monosaccharide and disaccharides with reference to glucose, fructose, maltose and sucrose.

**Proteins** – Amino acids, peptides, peptide synthesis using blocking reagents. Structure of proteins – primary structure, sequence of amino acids in proteins.

Nucleic acids- chemical and enzymatic hydrolysis of nucleic acids, purine & pyrimidine bases,

[8 Marks]

#### UNIT-7

#### **Environmental and Green Chemistry**

**Principles & concept of green chemistry :** Introduction –Concept and Principles-development of Green Chemistry- Atom economy reactions – Selection of starting materials, Designing biodegradable products, Green reaction conditions, Green catalysis, Heterogeneous catalysis:

Biocatalysis: -toxicity measures- Need of Green Chemistry in our day to day life.

**Renewable resources :** Biomass –Renewable energy – Fossil fuels-Energy from Biomass-Solar Power-Fuel Cells-Alternative economics- Syngas economy- hydrogen economy-

Air Pollution: Air pollutants, prevention and control, Green house effect and acid rain. CO – industrial and transportation sources. So<sub>x</sub>- sources, ambient concentration, control techniques – Ozone hole. Photochemical smog and PAN.  $NO_x$  – sources, ambient concentration, control techniques. Bhopal gas tragedy.

**Soil pollution:** Composition of soil – Inorganic and organic components in soil, micro and macro nutrients.

Water quality: Safe drinking water, public health significance, Determination of BOD, COD and TOC. [10 Marks]

#### UNIT 8

#### **Polymers and Nanoscience**

#### Importance of polymers. Basic Concepts:

Monomers, degree of polymerization. Classification of polymers. Polymerization: Condensation, addition, radical chain-ionic and co-ordination and co-polymerization

. **Polydispersion-average molecular weight concept:** Number, weight and viscosity average molecular weights, practical significance of molecular weight. Measurement of molecular weights.

**Morphology and order in crystalline polymers** - configurations of polymer chains. Crystal structures of polymers. Morphology of crystalline polymers. Polymer structure and physical properties-crystalline melting point  $T_m$ -melting points of homogenous series, The glass transition temperature.

Polymer processing: Plastics, elastomers and fibres, compounding. Processing techniques.

Electrically conducting polymers and Biomedical polymers: Properties and applications.

Chemistry of nanomaterials : Introduction: Synthesis, properties and Scope and importance of nanoscience and nanotechnology. [10 Marks]