

Department of Chemistry/Industrial Chemistry
Vijayanagara Sri Krishnadevaraya University, Bellary

Ph.D Course Work

Revised Regulations [2014]

			IA	Exam	
Total					
Course-1	: Research Methodology,	03 hr/week	25	75	100
Course -II	: Cognate subject	03 hr/week	25	75	100
Course -II	: Field of Specialisation	03 hr/week	25	75	100

Note: Research methodology and cognate subject are compulsory to all the research students. Students can opt anyone of the specialized paper Course-II.

Question paper pattern

Q 1. Objective type; 8 questions of 2 marks each.	8X2=16
Q 2,3 & 4. With sub questions a,b if required c	3X15=45
Q 5 With sub questions a,b if required c	1X14=14

Question 1 should consist of two sub questions from each unit

Question 2,3,4 and 5 should consist of questions from Unit I,II,III and IV respectively.

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Course-1 : Research Methodology,

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3hrs/week

UNIT 1: Research sources 12 hrs

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- 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. Scientific ethics. Internet: Introduction to internet-web browsers-World Wide Web-Search engines-literature survey in Chemistry-popular website in chemistry-Database in chemistry. 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.

UNIT 2 : Research data presentation 12 hrs

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.. Preparation of synopsis and Thesis, Preparation of research project proposals. Patent: Introduction, patentable subject

UNIT 3: Purification and safety measures 12 hrs

Handling of chemicals; hazardous chemicals; air/water sensitive, corrosive, toxic, explosive, carcinogenic and radioactive materials. Safety measures in laboratory, Good laboratory practices (GLP). **Emergency response** : chemical spills, radiation spills, biohazard spills, leaking compressed gas cylinders, fires, medical emergency accident reporting; safety equipments, personal protective equipments, compressed gas safety, safety practices for disposal of broken glass wares.

Purification of compounds: General methods of isolation and purification of chemicals. Solvent extraction both cold and hot methods of crystallization, fractional crystallization, sublimation, Distillation; fractional distillation, distillation under reduced pressure, steam distillation, drying methods of solvents.

UNIT 4:Error Analysis in Chemical Measurements and results 12 hrs

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 mean with expected value, comparison of the results of the two different methods, comparison of precision of two methods- Linear regression, regression line, standard deviation, correlation coefficient – Multiple linear regression (one variable with two other variables).

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Course -II : Cognate subject

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48 hours

3hrs/week

Paper 1.2: SELECTED TOPICS IN CHEMISTRY

UNIT-1 Analytical and spectroscopic technique:

12 hrs

Chromatographic technique: Classification, basic principle, theory of chromatography, TLC, principle and applications.

Gas Chromatography and HPLC: Introduction, principle, instrumentation and applications.

UV-Vis spectroscopy: Principle. Beer's law, Deviation of Beers law, Instrumentation and applications.

IR Spectroscopy: Principle. Fingerprint region, Instrumentation and functional group analysis.

¹H NMR Spectroscopy : Introduction to NMR, quantum description of NMR, chemical shift, spin-spin coupling, coupling constant, instrumentation, applications, interpretation and limitations.

Mass spectroscopy: Principle. Fragmentation, Instrumentation and applications.

Spectroscopic applications: UV-visible, IR, ¹H NMR, ¹³C NMR, mass spectroscopy in structural elucidation of organic compounds. Problems on structural elucidation involving all the above spectroscopic methods.

UNIT- 2

12 hrs

Methods of determining rate laws, collision theory of reaction rates, steric factor, activated complex theory, Arrhenius equation and the activated complex theory, ionic reactions, Kinetic salt effects and steady state kinetics. Kinetic and thermodynamic control of reactions, treatment of unimolecular reactions. Spontaneous reactions, standard free energies change. The law of mass action, Reaction potential, Homogeneous equilibrium, temperature dependence of the equilibrium constant. The hydrodimerisation of acetonitrile, other commercial electro synthetic process, indirect electro synthesis, and the future electro synthesis. Electrochemical sensors. Synthesis of carbon nanotubes and its applications.

UNIT- 3 :

12 hrs

Aromatic nitro compounds; Mechanism of nitration, nitro compounds, charge transfer complexes, aromatic nitroso compounds, reduction products of nitro compounds.

Aromatic amino compounds: Strength of bases, Hofmann- Martius rearrangement, Fischer-Hepp rearrangement, Orton rearrangement, Ullmann reaction and diamines.

Diazonium salts:

Diazotization, reactions of diazonium salts, diazoamino and aminoazo compounds. Azoxybenzene, azobenzene, hydrozobenzene, benzidine rearrangement.

Reactions and rearrangement: Arndt- Eistert reaction, Baeyer- Villiger rearrangement, Mannich reaction, Oppenauer oxidation, Reformatsky reaction, Sommelet reaction, Stobbe condensation, Witting reaction, Wolf rearrangement, Michael reaction.

Heterocyclic compounds: Synthesis and reactivity of furan, thiophene pyrrole, benzofuran, indole, benzothiophene, imidazole, pyrazoles, isoxazoles oxazoles, thiazoles, quinoline, isoquinoline and pyrimidine.

UNIT-4

12 hrs

Co-ordination chemistry : Introduction of co-ordination compounds, Structural elucidation of coordination compounds by UV- visible, magnetic susceptibility, IR, ¹H NMR and TGA methods.

Industrial applications of Organometallic compounds: Homogeneous catalysis, hydrogenations of olefins, oxo-process, Waker process, water gas shift reactions, carbonization. Heterogeneous catalysis, Fischer- Tropics reaction, Ziegler-Natta polymerization.

Metal complexes in medicine: Interaction of metal complexes with nucleic acids, metal ion deficiency effects, toxicity of metal ions and treatment of toxicity, chelating agents in medicine, bacterial agents, antiviral agents and anticancer agents, metal complexes as drugs and therapeutic agents.

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Course-III : Field of Specialization-Inorganic Chemistry and Nanoscience

Unit-I: Metal complexes: **12hrs**

Synthesis of Metal Complexes, Characterization by UV, IR, NMR and Mass spectrometry .

Unit-II: Bioinorganic chemistry **12hrs**

Essential and trace metals. Metalloproteins as enzymes, vitamin B12, synthetic model compounds,

Unit-III: Nanomaterials **12hrs**

Synthesis : Reduction, Sol- gel method, Reverse micelles, combustion method, microwave and co-precipitation method.

Characterization: Powder X-ray diffraction (PXRD), Scanning Probe Microscopy (SEM), Transmission electron microscopy(TEM), Atomic force microscopy(AFM)

Unit-IV: Properties and Application of nanomaterials **12hrs**

Properties of Nanomaterials: role of size in nanomaterials, Electronic Properties:, Dielectric Properties, Magnetic Properties: Diamagnetic, Paramagnetic, Ferromagnetic and Antiferromagnetic, Optical Properties, Semiconductor nanoparticles, Luminescence in Semiconductor nanoparticles: Photoluminescence, Cathodoluminescence and Thermoluminescence.

Applications: Automobiles, Textiles, Cosmetics, Domestic Appliances, Biotechnology and Medical field, Space and Defence, Nanotechnology and Environment

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Course-III : Field of Specialization –Physical Chemistry

48 hrs

Unit-I: Introduction to Thermodynamics

The first and second laws of thermodynamics. Thermodynamic functions, heat capacity, enthalpy, entropy. Equilibrium in one phase system, real gasses, the reactions between gases, reactions of solid-state phases, reaction kinetics, rate equations.

Theory of Solution and related topics

The theory of solutions, Free energy as a function of composition. Methods for calculation of thermodynamic equilibrium. Electrochemical processes.

12 hrs

Unit-II: Polymer Chemistry and Technology

Monomers, repeat units, degree of polymerization. Linear, branched and network polymers. Classification of polymers. Polymerization: Condensation, addition, radical chain-ionic and coordination and co-polymerization. Polymerization conditions and polymer reactions. Polymerization in homogenous and heterogeneous systems, Polymerization Techniques. Number, weight and viscosity average molecular weights. Polydispersity and molecular weight distribution. The practical significance molecular weight. Measurement of molecular weights. End-group, viscosity, light scattering, osmotic and ultracentrifugation methods. Analysis and testing of polymers-chemical analysis of polymers, spectroscopic methods, X-ray diffraction study. Microscopy. Thermal analysis and physical testing-tensile strength. Fatigue, impact. Tear resistance. Hardness and abrasion resistance. Electropolymerization, Drug delivery systems.

12 hrs

Unit – III Electrochemistry and applications (Related to Research Guide)

Introduction of electrochemistry, reversible and irreversible cells, Nernt's theory of electrode potential, standard electrode potential, measurement of electrode potential, rate of electrode processes, concentration cells, liquid-liquid junction potential or diffusion potential, applications of EMF measurements, oxidation and reduction systems, Electromotive series or potential series, decomposition voltage or decomposition potential, over voltage, potentiometric titrations, polarography, cyclic voltammetry, theory, instrumentation and applications, solvent effects, supporting electrolytes, reference electrode, working electrode, auxillary electrode, modified electrodes, differential pulse voltammetry, square wave voltammetry, stripping voltametry, coulometry, amperometric titrations, Introduction, fundamentals of batteries, classification of batteries, sizes of batteries, battery characteristics, primary batteries, dry cell, alkaline MnO₂

batteries and other batteries. Secondary batteries - lead-acid, alkaline storage batteries-battery charging theory and practice. Energy economics. Fuel cells - types - electrochemistry of fuel cells. 12 hrs

Unit IV: Quantum Chemistry

Brief review of Quantum chemistry, Schrodinger equation- Application to one and three dimensional box.

Surface chemistry, Theories of adsorption. 12 hrs

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Course –III- Field of Specialization- Organic Chemistry

48 Hrs

[3Hrs/Week]

UNIT-I

12 Hrs

A. Separation and Purification Techniques:

Principle of:

1. Re crystallization : using various solvents and mixture of solvents
2. Fractional crystallization: e.g. Separation of naphthalene and diphenyl
3. Fractional distillation : e.g. Separation of Benzene, acetone, ethyl alcohol etc.
4. Steam distillation
5. Soxhlet Extraction.

B. Biological and Pharmacological Screening of compounds

Principle, material and methodology for the following activities:

1. Antimicrobial (Antibacterial, antifungal and antiviral)
2. Analgesic
3. Anti-inflammatory
4. Anthelmintic
Mechanism of action

UNIT-II

12 Hrs

A. Oxidations and Reductions in Organic Synthesis

Oxidation reactions involving – Chromium and manganese compounds, air, ozone, hydrogen peroxide, per acids, periodic acid, N-Bromo succinimide

Reduction reactions involving- Catalytic hydrogenation, Complex metal

hydrides, dissolving metals.

B. Reagents in Organic Synthesis

1. Gilman reagent
2. Lithium diisopropyl amide (LDA)

- | | |
|------------------------------------|-----------------------------------|
| 3. Dicyclohexyl carbodiimide (DCC) | 4. 1,3-Dithiane |
| (Reactivity umpolung) | |
| 5. Trimethyl silyl iodide | 6. Tri-n-butyl hydride (TNBH) |
| 7. DDQ | 8. Woodward-Prevost hydroxylation |
| 9. Osmium tetroxide | 10. Stannic chloride |
| 11. Selenium dioxide | 12. Phase transfer catalyst |
| 13. Crown ether | 14. Merrifield resin |
| 15. Bakers yeast | 16. Peterson synthesis |

UNIT-III : Heterocyclic compounds

12 hrs

Bio significant heterocyclic molecules (Pyrimidine, Pyridine, indole and Purine).
Synthetic heterocycles as chemotherapeutic agents. (Related to indoles and benzofurans).

Heterocyclic agrochemicals. Naturally accruing heterocycles of physiological importance.
Biosynthesis of typical nitrogen and oxygen heterocycles.

Recent developments in the chemistry of indoles, benzofurans and benzothiophenes and their comparative study.

UNIT-IV : Stereochemistry

12 hrs

Topocity and prochirality, Asymmetric synthesis and asymmetric induction, double diastereo selection and double asymmetric induction, diastereo selection in cyclic systems, enantio selective alkylation of ketobne via hydrozones.

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Course –III- Field of Specialization- Inorganic Chemistry

Course-III Paper 1.3 : Field of specialization: 48 hrs

CHEMISTRY OF COORDINATION COMPOUNDS. 3hrs/week

Unit - I: Properties of Coordination Compounds. 12hrs

Objective, nomenclature of metal complexes, EAN.

Spectral properties:-

Types of electronic spectra, selection rules for electronic transitions, charge transfer spectra, d-d transition spectra, energy levels in tetrahedral field, Tanabe-Sugano diagrams.

Magnetic properties of the Complexes:

Origine of magnetic moment, magnetic permability and susceptibility, diamagnetism, paramagnetism, ferromagnetism and anti ferromagnetism.

Unit-II: Theories of Coordinate Bond 12hrs

The Valence Bond Theory; modification of Paulings VBT, drawbacks of VBT,

Crystal Field Theory (CFT); Splitting of d-orbitals in octahedral field, CFSE for tetrahedral symmetry, tetrahedral distortion in octahedral symmetry, square planar coordination, orbital splitting in other fields, adoption of geometrical arrangements, magnitude of $10Dq$, evidence for CFSE in complexes.

The crystal field model. Molecular Orbital theory: MOT for sigma bonding in complexes, MOT and other geometries, $\pi(\pi)$ bonding and MOT. Adjusted Crystal Field Theory. A review of theories.

Unit-III : Thermodynamic Stability of the Metal Complexes: 12hrs

Kinetics and thermodynamic stability of the metal complexes, factors affecting the metal complexes, chelate and macro cycle effects, structural equilibria of complexes and mixed ligand complexes. Calculation of ΔG° and ΔH° , factors influencing the stability of complexes, correlation between the properties of ligand and stability of metal complexes, Determination of stability by spectrophotometric- Job's, mole-ratio, slope ratio, p^H metric (potentiometric), polarigraphic, solvent-extraction and ion-exchange method.

Unit-IV: Isomerism of Metal Complexes 12hrs

Isomerism of Metal Complexes:

Ionization isomerism, solvent isomerism, linkage isomerism, coordination isomerism, ligand isomerism, polymerization isomerism.

Stereoisomerism: cis-trans isomerism, optical isomerism.

Identification of isomeric metal complexes: By conductivity measurement, by electrolysis, by freezing point depression, by IR, by XRD, by Dipolement, by NMR spectroscopy, by mass spectroscopy and by Chemical method.

REFERENCES:

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2. Theoretical Principles of Inorganic Chemistry, G.S.Manku, Tata McGraw Hill Publishing Company Limited, New Delhi, Sixteenth reprint-2012.
3. Text Book of Inorganic Chemistry, R.Gopalan, Universities Press, Hyderabad-2012.
4. Concise Coordination Chemistry, R.Gopalan and V.Ramalingam, Vikas Publishing House Pvt.Ltd., New Delhi, Reprint-2012.
5. Advanced Inorganic Chemistry, O.P.Agarwal, Dhanpat Rai and Sons, New Delhi, Eighth Edition-2012.
6. Chemistry of Complex, Equilibria, M.T.Beck, Reinhold, London-1990.
7. Inorganic Chemistry, J.E.Huheey, E.A.Keiter and R.L.Keiter, 4th Edition-1993.
8. Magneto Chemistry, R.L.Carlin, Springer Verlag.
9. Basic Inorganic Chemistry, F.A.Cotton, G.Wilkinson and P.L.Gau, John Wiley and Sons, Inc., Edition-1999.