Established by Govt. of Arunachal Pradesh vide Act 9 of 2012, the Arunachal University of Studies Act, 2012 Recognized as per u/s 2(f) of University Grants Commission Act, 1956
NH-52, Namsai, Arunachal Pradesh -792103

MASTER OF SCIENCE (CHEMISTRY) – FOURTH SEMESTER

Fourth Semester			
S. No.	**Name of Subject**	**Credits**	**Total Marks**
1	Computers in Chemistry	2	100
2	Special paper – II(any one) 1. Bio-Inorganic Chemistry 2. Chemistry of Natural Products 3. Quantum Chemistry	4	100
3	Special paper – III(any one) 1. Structural Methods in Inorganic Chemistry 2. Application of Spectroscopy to Structural Analysis 3. Statistical Mechanics	4	100
4	Special paper – IV(any one) 1. Inorganic Rings, Chains, and Clusters 2. Reagents and Organic Synthesis 3. Chemical Kinetics	4	100
5	Project + Training	8	100
Total		**22**	

Subject Name: COMPUTERS IN CHEMISTRY

Co

mputer programming in FORTRAN.

Computer application in Chemistry: Development of small computer codes involving simple formulae in chemistry, such as van der Waals equation, pH titration, kinetics, radioactive decay. Evaluation of lattice energy and ionic radii from experimental data. Linear simultaneous equations to solve secular equations within the Hückel theory. Elementary structural features such as bond lengths, bond angles, dihedral angles etc., of molecules extracted from a database such as Cambridge database.

Use of computer programmes: Execution of linear regression, X-Y plot, numerical integration and differentiation as well as differential equation solution programmes. Monte Carlo and Molecular dynamics. Programmes with data preferably from physical chemistry laboratory.

Representation of molecules: Cartesian and Internal Assesment Coordinates; Geometry Optimization (Newton-Raphson), vibrational frequencies; ionization potential and electron affinities of molecules. BO

approximation, potential energy surface, SCF theory, Gaussian basis sets, Basic idea of Molecular Mechanics and force field; Molecular dynamics: basic concept, Verlet and Velocity-Verlat algorithm; Basic ideas of structure–activity relationship. Introduction to popular softwares (like Gaussian, GAMESS, MOPAC).

Recommended Texts:

1. Computational Chemistry by A. C. Norris, John Wiley

2. Numerical Recipes in FORTRAN/C by W. H. Press, S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, Cambridge University Press, 2nd Ed. 1996.

3. Fortran 77 and Numerical Methods by C. Xavier, New Age International, 2002.

4. Introduction to Computational Chemistry by Frank Jensen

5. Essentials of Computational Chemistry: Theories and Models by C. J. Cramer

6. Molecular Modeling: Principles and Applications by A. R. Leach, 2nd Ed. Pearson Education: England, 2001

7. Computational Chemistry Workbook by T. Heine, J-O. Joswig and A. Gelessus

Subject Name: INORGANIC CHEMISTRY SPECIALIZATION: - BIO-INORGANIC CHEMISTRY

Role of alkaline earth metal ions in biological systems: (i) Catalysis of phosphate transfer by Mg^{2+} ion, (ii) Ubiquitous regulatory role of Ca^{2+} in muscle contraction

Iron, copper and molybdenum proteins with reference to their oxygenation and oxidase activity: (i) Anti-oxidative functions: cytochrome P-450, catalases and peroxidases, (ii) Nitrate and nitrite reduction: NO_3 and NO_2 reductase, (iii) Electron transfer: cytochromes; blue copper proteins and iron-sulfur proteins and their Synthetic models, (iv) molybdo-enzymes – molybdenum cofactors: molybdenum-protien Complexes, (v) Nitrogen fixation through metal complexation, nitrogenase, (vi) Photosynthesis (PS-I and PS-II).

Metalloenzymes: Urease, Hydrogenase, and Cyanocobalamine

Interaction of metal complexes with DNA: DNA probe and chemotherapeutic agents

Iron storage and transport proteins: Ferritin, Transferritin and Hemosiderin

Recommended Texts:

1. M. N. Hughes, *Inorganic Chemistry of Biological Processes*, 2nd Ed.(1981), John-Wiley & Sons, New York.

2. W. Kaim and B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, An Introduction and Guide*, Wiley, New York (1995).
3. S. J. Lippard and J. M. Berg, *Principles of Bioinorganic Chemistry*, University Science Books, (1994).
4. I. Bertini, H. B. Grey, S. J. Lippard and J. S. Valentine, *Bioinorganic Chemistry*, Viva Books Pvt. Ltd., New Delhi (1998)

Subject Name: ORGANIC CHEMISTRY SPECIALIZATION: - Chemistry of natural products

Steroids:

Introduction, Occurrence, nomenclature, basic skeleton, spectral properties, Stereochemistry, isolation, synthesis, structure determination, reactions & Biosynthesis of steroids.
Bile acids, steroid hormones and corticosteroids.

Haemoglobin, chlorophyll and phthalocyanines:

Introduction, degradation products of Haemoglobin; spectral properties and synthesis of porphyrins.

Chlorophyll: introduction, structure, degradation products of chlorophyll.

Phthalocyanines: Introduction, preparation & structure of phthalocyanines.

Vitamins: Introduction to vitamin B complex, vitamin B1,B2,B12,Pantothenic acid, Folic acid, Biotins, Pyridoxine.
Vitamin E and K group.

Carotenoids:
Introduction; Geometrical isomerism, Characterization and biosynthesis of carotenoids.
Anthocyanins:

Recommended Texts:

1. Nitya Anand, J.S. Bindra and S. Ranganathan, *Art in organic synthesis*,2nd ed.(1970),Holden Day,San Francisco.
2. S .W .Pelletier, *Chemistry of Alkaloids*, Van Nostrand Reinhold Co. New York (1970).
3. I.L. Finar,*Organic Chemistry*,Vol.II,5th ed.(1975),Reprinted in 1996,ELBS and Longman Ltd, New Delhi.
4. J.W.Apsimon, *Total synthesis of Natural Products* ,Vol. 1-6,Wiely-Interscience Publications,New York,(Vol. 1, 1973).
5. J.S.Bindra and R. Bindra, *Creativity in Organic synthesis,* Academic Press,NY(1975).

Subject Name: PHYSICAL CHEMISTRY SPECIALIZATION: - QUANTUM CHEMISTRY

Fundamentals: Review of classical mechanics, general formulation of quantum mechanics, review of angular momentum, harmonic oscillator problem.

Approximation methods: Stationary perturbation theory for non-degenerate and degenerate systems with examples, time-dependent perturbation theory, radiative transitions, Einstein coefficients.

Many Electron atoms: Electron correlation, addition of angular momenta, Clebesch Gordan series, total angular momentum and spin-orbit interaction.

Group Theory: Review and applications**.**

Ab initio methods for closed shell systems: Review of molecular structure calculations, Hartree-Fock SCF method for molecules, Roothaan-Hartree-Fock method, selection of basis sets. Density functional method: energy as a functional of charge density, Kohn-Sham equations.

Recommended Texts:

1. *Molecular Quantum Mechanics,* P.W. Atkins and R.S. Friedman, 3rd edition (1997), Oxford University Press. Oxford.
2. *Quantum Chemistry,* H. Eyring, J. Walter and G.E. Kimball, (1944) John Wiley, New York.
3. *Quantum Chemistry*, I.N. Levine, 5th edition (2000), Pearson Educ., Inc., New Delhi.

4. Modern Quantum Chemistry: Introduction to Advanced Electronic Structure, A. Szabo and N. S. Ostlund, (1982), Dover, New York.

Subject Name: INORGANIC CHEMISTRY SPECIALIZATION: - STRUCTURAL METHODS IN INORGANIC CHEMISTRY

NMR Spectroscopy: (i) Use of Chemical shifts and spin-spin couplings for structural determination, (ii) Double resonance, and Dynamic processes in NMR, (iii) Decoupling phenomenon, Nuclear Overhauser Effect, DEPT spectra and structural applications in 13C NMR, (iv) Use of Chemicals as NMR auxiliary reagents (shift reagents and relaxation reagents) (v) 1H NMR of paramagnetic substances. (vi) NMR of Metal nuclei.

Electron Spin Resonance Spectroscopy: Basic principle, Hyperfine Splitting (isotropic systems); the *g*-value and the factors affecting thereof; interactions affecting electron energies in paramagnetic complexes (Zero-field splitting and Kramer's degeneracy); Electron-electron interactions, anisotropic effects (the *g*-value and the hyperfine couplings); Structural applications to transition metal complexes.

Vibrational Spectroscopy: Applications of vibrational spectroscopy in investigating the stretching and bending modes of molecules (AB3 and AB4 types).

Recommended Texts:

1. E. A. V. Ebsworth, D. W. H. Rankin and S. Cradock, *Structural Methods in Inorganic Chemistry*, 1st Edn.(1987), Blackwell Scientific Publications, Oxford, London.
2. R. S. Drago, *Physical Methods in Chemistry*, International Edition (1992), Affiliated East West Press, New Delhi.
3. R. S. Drago, *Physical Methods in Inorganic Chemistry*, 1st Edn.(1971), Affiliated East West Press, New Delhi.
4. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn. (1986), John Wiley & Sons, New York.
5. W. Kemp, *Organic Spectroscopy*, 3rd Edn. (1991), Macmillan, London.
6. G. Aruldhas, *Molecular Structure and spectroscopy*, Prentice Hall of India Pvt. Ltd., New Delhi (2001).

Subject Name: ORGANIC CHEMISTRY SPECIALIZATION: - APPLICATION OF SPECTROSCOPY TO STRUCTURAL ANALYSIS

PMR Spectroscopy: Interpretation of spectra, chemical shift, shielding mechanism and anisotropic effects, chemical exchange and chemical shifts in chiral molecules. Spin-spin, spin-lattice relaxations, Spin-spin interactions, naming spin systems, magnitude of coupling constant: Germinal, vicinal and long range couplings. Simplification of Complicated Spectra: Aromatic induced shifts spin decoupling, deuterium exchange, spectra at higher fields. Hindered rotation and rate processes. Nuclear Overhauser effect.

CMR Spectroscopy: General considerations, chemical shift, calculation of approximate chemical shift values, coupling constants. Interpretation of simple CMR spectra. DEPT spectrum. 2 DNMR: COSY, NOESY and HETCOR.

Mass Spectrometry: Introduction, ion production, fragmentation, single and multiple bond cleavage, rearrangements, cleavage associated with common functional groups, molecular ion peak, metastable ion peak, Nitrogen rule and interpretation of mass spectra

Problems: Structure elucidation based on spectroscopic data (IR, UV, NMR and Mass).

Recommended Texts:

1. J. R. Dyer, *Application of Absorption Spectroscopy of Organic Compounds,* Prentice Hall, New Delhi (1978).
2. R.M. Silverstein and F.X. Webster, *Spectroscopic Identification of Organic Compounds*, 6th Edition (2003) John Wiley, New York.
3. D.H. Williams and I.F. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th Edition(1988), Tata-McGraw Hill, New Delhi.
4. P.Y Bruice, *Organic Chemistry*, 2nd Edition (1998) Prentice – Hall, New Delhi.

Subject Name: PHYSICAL CHEMISTRY SPECIALIZATION: - STATISTICAL MECHANICS

Basic statistical mechanics: Phase space, equal a priori probability, ensemble (canonical, micro-canonical and grand canonical), Liouville theorem, entropy, Gibbs paradox.

Partition function: Rotational, vibrational, translational, electronic and nuclear partition functions, application of partition functions to specific heat of solids and chemical equilibrium.

Bose-Einstein and Fermi-Dirac distributions: Einstein condensation, thermodynamic properties of ideal BE gas, degenerate Fermi gas, application of FD statistics to electron gas in metals.

Fluctuations: Means square deviation and fluctuations in ensembles, concentration fluctuations in quantum statistics.

Recommended Texts:

1. Statistical Mechanics (1988), B.K. Agarwal and M. Eisner, Wiley Eastern, New Delhi
2. Statistical Mechanics (2000), D.A. Mcquarrie, California University Science Books
3. Statistical Mechanics (1996), R. K. Patharia, Butterworth, Heinemann, Elsevier
4. Statistical Mechanics (1962), N. Davidson, Mc Graw Hill Book Co. New York

Subject Name: INORGANIC CHEMISTRY SPECIALIZATION: - INORGANIC RINGS, CHAINS, AND CLUSTERS

Clusters and element-element bonds: Polyhedral boranes: Electron deficiency *vs* sufficiency. Types and IUPAC nomenclature. Wade's polyhedral skeleton electron pair theory (PSEPT). W. N. Lipscomb's styx rules and semi-topological structures of boranes. Equivalent and resonance structures. Wade's vs Lipscomb's methods of studying higher boranes.

Heteroboranes: Types of heteroboranes with special reference to carboranes, structure, bonding and IUPAC nomenclature. Metallaboranes, Metallacarboranes, metal σ and μ bonded borane/carborane clusters. Resemblance of Metallaboranes/ Metallacarboranes with ferrocene and related compounds. Applications of Metallaboranes / Metallacarboranes as drug delivery system. Applications of PSEPT over heteroboranes.

Principle of Isolobility: Development and formulation of the concept of isolobility and its applications in the understanding of structure and bonding of heteroboranes.

Metal Clusters: Metal-metal bonds. Concept of quadrupolar bond and its comparison with a C-C bond; Types of metal clusters and multiplicity of M-M bonds. Simple and condensed metal carbonyl clusters. Applications of PSEPT and Wade's-Mingo's and Lauhr's rule over metalcarbonyl clusters. Metal halide and metal chalcogenide clusters: Bloomington schuffle in dinuclear tungsten clusters.

Heteropoly and Isopoly acids: Structural principles and their applications.

Inorganic Polymers: Classification, Types of Inorganic Polymerization, Comparison with organic polymers, Boron-oxygen and boron-nitrogen polymers, silicones, coordination polymers, sulphur-nitrogen, sulphur-nitrogen-fluorine compounds, - binary and multicomponent systems, haemolytic inorganic systems.

Recommended Texts:

1. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 6th Edn. (1999), JohnWiley & Sons, New York.
2. James E. Huheey, *Inorganic Chemistry*, 4th Edn. (1993), Addison Wesley Pub. Co., New York
3. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd Edn. (1997), Butterworth Heinemann, London.

Subject Name: ORGANIC CHEMISTRY SPECIALIZATION: - REAGENTS AND ORGANIC SYNTHESIS

Oxidation : (i) Oxidation with peracids: Oxidation of carbon-carbon double bonds carbonyl compounds, allylic carbon-hydrogen bonds, (ii) Oxidation with selenium dioxide and Osmium tetraoxide, (iii) Oxidation with lead tetraacetate, mercuric acetate (iv) hypervalent iodine

Reagents and Reactions: (i) Gilman's reagent – Lithium dimethylcuprate, (ii) Lithium diisopropylamide (LDA), (iii) Dicyclohexyl carbodiimide (DDC), (iv) 1,3-Dithiane (Umpolung reagent), (v) Peterson's synthesis, (vi) Baker's yeast, (vii) DDQ, (viii) Palladium catalysed reactions, (ix) Woodward and Prevost hydroxylation, (x) Iodotrimethyl silane and (xi) Ionic liquids

Recommended Texts:

1. H.O. House, *Modern Synthetic Reactions*, 2nd Edition (1972), Benjamin/Cummings Publishing Company, California.

2. L.F. Fieser and M. Fieser, *Reagents for Organic Synthesis,* Vol. 1-16 (Vol. 1, 1967), WileyInterscience, New York.

3. M.B. Smith and J. March, *March's Advanced Organic Chemistry – Reactions, Mechanisms & Structure*, 5th ed. (2001), Wiley-Interscience, New York.

4. M. B. Smith, *Organic Synthesis,* McGraw Hill Inc., New York (1995).

5. J. Clayden, N. Greeves, S. Warren, and E. Wothers, *Organic Chemistry,* Oxford Univ. Press, Oxford (2001).
6. P. R. Jenkins, *Organometallic Reagents in Synthesis,* Oxford science Publ., Oxford (1992).

Subject Name: PHYSICAL CHEMISTRY SPECIALIZATION: - CHEMICAL KINETICS

Transition state theory: Application of statistical mechanics to transition state theory, comparison of transition state theory with experimental results, thermodynamic treatment of TST, theories of unimolecular reactions - treatments of: Lindmann, Hinshelwood, Rice Ramsperger- Kassel (RRK), and Rice-Ramsperger-Kassel-Marcus (RRKM).

Reactions in solution: Reaction between ions, effect of solvent (single & double sphere models), interpretation of frequency factor and entropy of activation, influence of ionic strength, salt effect, reactions involving dipoles, influence of pressure on reaction rates in solution.

Molecular collisions: Intermolecular potential and centrifugal barrier, impact parameter, collision cross section and rate, energy threshold, opacity function and reaction cross section.

Experimental probes of reactive collisions: IR chemiluminescence, laser-induced fluorescence. Features of potential energy surfaces (PES), enhancement of reaction.

Molecular beams: Stripping and rebound mechanism.

Dynamics with femtosecond laser techniques: Detection of activated complex.

Recommended Texts:

1. *Reaction Kinetics* (1998), M. J. Pilling and A.P.W, Seakins, Oxford Science Publication, New York
2. *Chemical Kinetics*, 3rd Edition (1967), K.J. Laidler, Harper & Row Publishers, New York.
3. *Kinetics and Mechanism of Chemical Transformation*, Ist Edition (1993), J. Rajaram and J.C. Kuriacose, MacMillan India Ltd., New Delhi.
4. *Modern Liquid Phase Kinetics* (1994), B. G. Cox, Oxford University Press, Oxford.
5. *Molecular Reaction Dynamics and Chemical Reactivity* (1987), R. D. Levine and R. B. Bernstein, Oxford University Press, Oxford.

6. *Femtochemistry-Ultrafast Dynamics of the Chemical Bond* (1994), A. H. Zewail, vols. I and II, World Scientific, New Jersey, Singapore.

Subject Name: PROJECT WORK

Research project approved by the Supervisor, preparation of the dissertation and presentation of results, and viva-voce examination by a board of examiners.

Note: The Normal Rule and Regulation pertaining to the Examination and other issues will be applicable in Faculty of Science as per Arunachal University of Studies Act 2012, Subsequent Statute and Rules & Regulations.