SYLLABUS FOR

M. Sc. PROGRAMME IN BRANCH V
APPLIED CHEMISTRY

(Revised Syllabi under Semester System
with effect from 2016 Admission)
PREAMBLE

The syllabi of M.Sc programmes in Chemistry offered in the affiliated colleges of the University under Semester system have been revised and the revised syllabi are to be effective from 2016 admission. There are four independent PG programmes in Chemistry, namely M.Sc. Programme in Branch III - Chemistry, M.Sc. Programme in Branch IV - Analytical Chemistry and M.Sc. Programme in Branch V - Applied Chemistry and Branch VI Medicinal Chemistry. All these four PG programmes are equivalent in all respect for employment and higher studies. Each of these four PG programmes shall extend over a period of two academic years comprising of four semesters, each of 450 hours in 18 weeks duration. The syllabi and scheme of examinations of these four programmes are detailed below. The theory courses of the first three Semesters and the practical courses of the first two semesters of the four programmes are common, and therefore, the examinations of these four PG programmes are to be conducted with common question papers for the first three semesters by a common Board of Examiners. These syllabi are effective from 2016 admission in affiliated colleges of the university.

M.Sc. PROGRAMME IN BRANCH V – APPLIED CHEMISTRY
(Revised syllabus under semester system with effect from 2016 admission)
SYLLABUS AND SCHEME OF EXAMINATION

<table>
<thead>
<tr>
<th>Course No. and Title</th>
<th>Hours per week</th>
<th>Duration for ESA in hours</th>
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*Distribution of teaching hours/week: Theory- 15 hours, Practicals- 10 hours
### SEMESTER III*

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*Distribution of teaching hours/week: Theory- 15 hours, Practicals- 10 hours

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Total marks for Semester IV: 600

Grand total (for semesters I-IV): 1800

*Distribution of teaching hours/week: Theory- 10 hours, 5 hours for discussion on project

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**M.Sc. PROGRAMME IN BRANCH V- APPLIED CHEMISTRY**

(Revised syllabus Under Semester System w.e.f. 2016 Admissions)

### SEMESTER I

**CA 211 INORGANIC CHEMISTRY I**

**Total 90 h**

**Unit I  Coordination chemistry-I: Theories of metal complexes  18 h**


**Unit II Analytical principles** 18 h


**Unit III Molecular symmetry** 18 h


**Unit IV Isopoly and heteropoly acids, Noble gases, interhalogens** 18 h

Preparation, properties and structure of isopoly acids of Mo, W and V and Heteropoly acids of Mo and W. Preparation and properties of Xenon fluorides and Krypton compounds (KrCl$_4$, KrF$_4$, KrF$_2$, KrBr$_6$, Kr$_2$Cr$_2$O$_7$, KrCrO$_4$ & KrO$_2$), structure of XeF$_2$ (MO theory only). Preparation, bonding and uses of interhalogen compounds. Properties and structure of aluminosilicates and zeolites, shape selectivity. Preparation, properties and applications of silicones.

**Unit V Chemistry of Natural Environmental Processes** 18 h


**References**

Unit I Stereochemistry of organic compounds

Nomenclature of organic compounds - Cyclic, fused polycyclic and bridged polycyclic hydrocarbons, Bridged and fused hydrocarbon systems, Spirocyclic hydrocarbon systems, Heterocyclic systems containing Nitrogen and Oxygen.


Conformational analysis of alkanes and cycloalkanes, Biased systems. Effect of conformation on reactivity of cyclohexanes – conformation of decalin.

Introduction to ORD, CD- their application in assigning configuration. Sector rules such as octant and axial haloketone rules. Cotton effect.

Chiral drugs: Ibuprofen, Methyldopa, and Thalidomide – Structure, chirality and activity (Basic concepts only)

Unit II Structure, reactivity and intermediates

Unit III Substitution reactions 18 h

Nucleophilic substitution at sp³ carbon - Sₙ₁ and Sₙ₂ mechanisms. Walden inversion, stereochemistry. Effect of solvent, leaving group and substrate structure on rates of Sₙ₁ and Sₙ₂ substitutions. Neighbouring group participation, Non-classical carbocations, Competition between Sₙ₁ and Sₙ₂ reactions. Sₙ₁', Sₙ₂', Sₙᵢ mechanism.

Mechanism of esterification and ester hydrolysis-acid catalysed and base catalysed reactions.

Aromatic Substitution reactions - Electrophilic substitution: mechanism and evidence. Reactions involving nitrogen, sulphur, carbon, halogen and oxygen electrophiles. Directive and rate controlling factors in aromatics with one or more substituents.

Aromatic Nucleophilic Substitution reactions - Sₙ₁, Sₙ₂, Ar, benzyne and Sₙᵢ mechanism with examples.

Unit IV Elimination and addition reactions 18 h


Unit V Reagents in organic synthesis 18 h


References


CA 213 PHYSICAL CHEMISTRY – I

Unit I- Quantum Chemistry I


Postulates of Quantum Mechanics

State function postulate: Born interpretation of the wavefunction, well behaved functions, orthonormality of wave functions. Operator postulate: operator algebra, linear and nonlinear operators, Laplacian operator, commuting and non-commuting operators, Hermitian operators and their properties, eigen functions and eigen values of an operator. Eigen value postulate: eigen value equation, eigen functions of commuting operators. Expectation value postulate. Postulate of time-dependent Schrödinger equation, Quantization of angular momentum, quantum mechanical operators corresponding to angular momenta (Lx, Ly, Lz and L²)-commutation relations between these operators.

Application of Quantum mechanics to Exactly Solvable Model Problems

Translational motion: free particle in one-dimension, particle in a box with infinite potential barrier- one dimensional box, three dimensional box and cubical box - degeneracy - particle with finite potential barriers-one potential barrier, two finite barriers, potential barriers of definite thickness-Quantum mechanical tunneling (Qualitative concept only)

Vibrational motion: one-dimensional harmonic oscillator (complete treatment), Hermite equation (solving by method of power series), Hermite polynomials, recursion relation, wave functions and energies- important features, Harmonic oscillator model and molecular vibrations.

Symmetric and antisymmetric wave functions, Pauli’s antisymmetry principle, the postulate of spin. Spin orbitals. Spin-orbit coupling.

Vector atom model- Term symbols, explanation of spectral lines (for sand p blocks only)

Unit II Surface Chemistry and Catalysis


Adsorption from solutions: Gibb’s adsorption equation and its verification. Adsorption with dissociation. Adsorption with interaction between adsorbate molecules.

Different types of surfaces, Properties of surface phase. Thermodynamics of surface. Surface tension of solutions. Surfactants and micelles. Examination of surfaces using low energy electron diffraction, photoelectron spectroscopy, ESCA, scanning probe microscopy, Auger electron spectroscopy, SEM and TEM.

**Catalysis:** Mechanism and theories of homogeneous and heterogeneous catalysis. Enzymecatalysis, bimolecular surface reactions. Langmuir – Hinshelwood mechanism, instrumental methods of catalyst characterization—diffraction and thermal methods, spectroscopic and microscopic techniques.

**Unit III: Classical Thermodynamics**

Entropy—dependence of entropy on variables of a system (S, T and V; S, T and P). Thermodynamic equations of state. Criteria for equilibrium and spontaneity, Euler’s relation, Gibbs and Helmholtz free energy, Maxwell relations and significance, temperature dependence of free energy, Gibbs Helmholtz equation and its applications.

**Partial molar quantities:** chemical potential, Gibbs-Duhem equations, determination of partial molar properties—partial molar volume and partial molar enthalpy.

Fugacity—relation between fugacity and pressure, determination of fugacity of a real gas, variation of fugacity with temperature and pressure. Fugacity of liquid mixtures, fugacity of mixture of gases, Lewis Randall rule.

Activity, activity coefficients, dependence of activity on temperature and pressure. Determination of activity and activity coefficients of electrolytes and non electrolytes

Thermodynamics of mixing, Duhem-Margules equation, Konowaloff’s rule, Henry’s law, excess thermodynamic functions—determination of excess enthalpy and volume.

Chemical affinity and thermodynamic functions, effect of temperature and pressure on chemical equilibrium—van’t Hoff reaction isochore and isotherm.

**Unit IV Chemical kinetics**

**Theories of reaction rates:** Collision theory and its failure, Transition state theory—Eyring equation. Comparison of the two theories. Thermodynamic formulation of the reaction rates. Potential energy surfaces

Theories of unimolecular reactions—Lindemann theory, Lindemann-Hinshelwood mechanism, qualitative idea of RRKM theory,

**Kinetics of complex reactions**—parallel reactions, opposing reactions, consecutive reactions and chain reactions, steady state treatment, kinetics of H₂-Cl₂ and H₂-Br₂ reactions, decompositions of ethane, acetaldehyde and N₂O₅. Rice-Herzfeld mechanism, branching chain reactions Hinshelwood mechanism of chain reactions and explosion.

**Fast reactions:** Relaxation method, relaxation spectrometry, flow method, shock method, fast mixing method, field jump method, pulse method, Flash photolysis and NMR method.

**Reactions in solution:** Factors affecting reaction rates in solutions, effect of dielectric constant and ionic strength, cage effect, Bronsted-Bjerrum equation, primary and secondary kinetic salt effect, influence of solvent on reaction rates, significance of volume of activation, linear free energy relationship. Hammet equation and Taft equation.

**Photochemistry:** Effect of radiation on the rate of reaction, Jabalonski diagram, Laws of photochemistry. Quantum yield. Experimental determination of quantum yield. Fluorescence and phosphorescence, Quenching of fluorescence, Stern-Volmer equation.

**Unit V Gaseous and liquid state**

Maxwell’s distribution of molecular velocities, influence of temperature on molecular velocities, types of molecular velocities—average velocity and most probable velocity and its determination from Maxwell’s equation
Transport phenomena in gases—viscosity of gases, Chapman equation, determination of viscosity of gases, calculation of mean free path, Thermal conductivity, diffusion, Degrees of freedom of gaseous molecules - Translational, Rotational and vibrational. Equation of state of real gases—van der Waal's equation, Other equation of states—Radlich-Kwong equation, Clausius equation, Virial equation, second virial coefficient and determination of diameter of a molecule.

**Inter molecular forces**—dipole-dipole interaction, induced dipole- dipole, induced dipole-induced dipole interactions

**Liquid state** Liquid vapour equilibria, vapour pressure- methods of measuring vapour pressure - barometric method and dynamic method - equation of state for liquids, structure of liquids, X-ray diffraction of liquids-vacancy model for a liquid, pair correlation function, surface tension , determination of surface tension, drop weight method and drop number method, viscosity, determination of coefficient of viscosity using Ostwald viscometer.

**References**

5. T. Angel, “Quantum Chemistry and Spectroscopy”, Pearson Education IIIrd edn..
CA 214 – INORGANIC CHEMISTRY PRACTICALS -1

Total 125 h

1. Separation and identification of rare/less familiar cations such as Ti, W, Mo, Th, Zr, V, U and Li
2. Volumetric estimation using EDTA, ammonium vanadate, ceric sulphate etc.
3. Colorimetric estimation of Cr, Fe, Mn, Ni, Cu etc.
4. Preparation of metal complexes: selection can be made from the following or any other from the existing literature.
   - \([\text{Co(NH}_3\text{)}_6\text{]}\text{Cl}_3\)
   - \([\text{Cu(NH}_3\text{)}_4\text{]}\text{SO}_4\)
   - \(\text{K}_3[\text{Cr(C}_2\text{O}_4\text{)}_3]\)
   - \(\text{K}_3[\text{Fe(C}_2\text{O}_4\text{)}_3]\)
   - Cis and trans isomers of \([\text{Co(en)}_2\text{Cl}_2]\text{Cl}\)
   - \([\text{Cr(en)}_3]\text{Cl}_3\)

References


CA 215 ORGANIC PRACTICALS-1

Total 125 h

A. Separation and identification of organic compounds

1. Quantitative wet chemistry separation of a mixture of two components by solvent extraction
2. TLC of the purified samples along with the mixture in same TLC plates (component 1 with mixture and component 2 with mixture on separate TLC plate) and calculation of \(R_f\) values- Reporting and recording TLC in standard formats- preparation of sample solution, adsorbent, dimensions of the plate, saturation time, developing time, visualization and detection, \(R_f\) Value, Drawing - in the form of a table.

B. Separation of a mixture of by column chromatography (not for End semester evaluation)

1) Malachite green and methylene blue 2) \(\alpha\)-nitroaniline and \(\rho\)-nitroaniline.

C. Preparation of compounds by two stages.

Recording/downloading UV, IR, \(^1\)H NMR and \(^{13}\)C NMR and EI mass spectra of synthesized compounds.

TLC analysis- stage 1 reactants and products on TLC plate 1 and stage 2 reactants and products on plate 2) - Record TLC in standard format as in separation

All preparations must be restricted to 1 g level

Nitration

1) Acetanilide –> \(\rho\)-nitroacetanilide –> \(\rho\)-nitroaniline
2) Methylbenzoate –> methyl \(m\)-nitrobenzoate –> \(m\)-nitrobenzoic acid
Bromination

3) Acetanilide → p-bromoacetanilide → p-bromooaniline

Aldol condensation - Synthesis of heterocycles

4) benzaldehyde → Dibenzylideneacetone → 1,5-Diphenyl-3-styril-2-pyrazoline

Diazocoupling

5) Aniline → Diazoaminobenzene → p-aminoazobenzene

Rerrangement

6) Phthalic anhydride → Phthalimide → anthranilic acid

Synthesis of Dyes

7) N,N-Dimethylaniline → N,N-dimethyl-4-nitrosoaniline → methylene blue

The board of examiners have to select either TLC of separated components OR TLC of preparation for an examination. But both TLC examinations are to be practiced and entered in the record of experiments.

References

8. Monograph on green laboratory experiments, DST, Government of India, pp 1-79.
9. For spectral data of organic compounds, see: http://sdb.siodb.aist.go.jp/sdbs/cgi-bin/direct frame top.cgi.

CA 216 PHYSICAL PRACTICALS –I

125 h

Adsorption

Freundlich and Langmuir isotherms for adsorption of acetic/oxalic acid on active charcoal.

Determination of concentration of acetic/oxalic acid.

Kinetics

Determination of rate constant of acid hydrolysis of methyl acetate.

Determination of Arrhenius parameters.

Determination of concentration of given acid.

Determination of rate constant of the saponification of ethyl acetate and evaluation of Arrhenius parameters.

Determination of rate constant of reaction between K_2 S_2 O_8 and KI.

Study the kinetics of iodination of acetone in acid medium.
Phase rule
Solid-liquid equilibria

Construction of phase diagram and determination of the composition of unknown mixture (naphthalene/biphenyl, naphthalene/benzophenone, naphthalene/diphenyl amine)

Construction of phase diagram with congruent melting point- naphthalene/metadinitrobenzene

Partially miscible liquid pairs- CST of phenol-water system.

Effect of impurities (KCl/NaCl/succinic acid) on the miscibility temperature of phenol-water system and hence the determination of concentration of given unknown solution.

Three component system- Construction of ternary phase diagram of acetic acid chloroform-water system and hence the composition of given homogeneous mixture. Construction of tie-line.

Distribution law

Distribution coefficient of ammonia between chloroform and water.

Determination of equilibrium constant of copper-ammonia complex by partition method or coordination number of Cu$^{2+}$ in copper-ammonia complex.

Distribution coefficient of benzoic acid between toluene and water.

Distribution coefficient of iodine between hexane and water/CHCl$_3$ and water/CCl$_4$ and water

Determination of the equilibrium constant of the reaction KI + I$_2$ "$!$[KI$_3$] and hence the concentration of given KI in hexane and water/CHCl$_3$ and water/CCl$_4$ and water.

Determination of hydrolysis constant of anilinium hydrochloride.

Dilute Solutions

Determination of K$_f$ of solid solvent, molar mass of non-volatile solute, mass of solvent and composition of given solution (Solvent-Naphthalene/Biphenyl/Benzophenone etc.

Solute-Naphthalene/Biphenyl/Diphenylanmine etc)

Determination of vant Hoff’s factor for benzoic acid in Naphthalene.

Determination of atomicity of sulphur.

Transition temperature

Determination of K$_s$ of salt hydrate, molar mass of solute, mass of salt hydrate and composition of given solution (Solvent-Na$_2$S$_2$O$_3$.5H$_2$O/CH$_3$COONa.3H$_2$O, Solutes glucose,sucrose, urea)

Thermochemistry

Determination of the concentration of given strong acid/alkali.

Thermometric titration of NaOH Vs standard HCl.

Heat of displacement of Cu$^{2+}$ by Zn.

Determination of the heat of ionisation of acetic acid.

References

4) A.M.James, and F.E.Pichard, “Practical Physical Chemistry”, Longman.
1. a) What is meant by Nephelauxetic effect?
   b) Explain linkage isomerism with suitable example.
   c) What is meant by crystal field stabilization energy?

2. a) What do you mean by significant figure? How many significant figures are in the following?
   i) 0.0026
   ii) $6.023 \times 10^{23}$
   b) What are metallochromic indicators? Give an example.
   c) In a volumetric experiment the volumes of the titrant used are 9.98, 9.99, 9.98, 9.95, 10.00 and 10.02 mL. Calculate the standard deviation.

3. a) Identify the symmetry elements present in the following and assign the point group
   i) $\text{H}_2\text{O}$
   ii) $\text{HCl}$
   b) Explain improper axis of symmetry.
   c) What is meant by character table.

4. a) Explain the term ‘shape selectivity’.
   b) Give the preparation of $\text{KrCl}_4$ and $\text{KrO}_2$.
   c) What are zeolite? Explain their use as water softeners.

5. a) Brief the role of catalytic converters in automobiles.
   b) Explain the formation of photochemical smog.
   c) Mention the different regions of atmosphere.

6. a) State and illustrate Jahn Teller effect.
   b) Explain the crystal field theory of octahedral complexes.

7. a) Give a brief note on scatter diagram and its significance.
   b) Explain the titrations in non-aqueous solvents.

8. a) Construct the multiplication table for the symmetry operations of $\text{NH}_3$ molecule.
   b) State and explain orthogonality theorem.
9. a) Give an account of inter halogen compounds.
   b) Write a short note on silicones.
10. a) List out the major pollutants. Outline how they affect human health?
    b) Describe how we can quantify soil acidity.  

SECTION C

Answer any three questions. Each question carries 10 marks

11. Explain the bonding in octahedral complexes with and without pi bonds using MO Theory.
12. Briefly explain the principle, instrumentation and applications of TG and DTA.
13. Construct the character table for $C_{2v}$ and explain.
14. Write a short note on the preparation and properties of heteropoly acids of Mo and W.
15. What are Pourbaix diagrams? Outline its role in explaining the chemistry of processes in lithosphere.  

FIRST SEMESTER MSc.DEGREE EXAMINATION
BRANCH – APPLIED CHEMISTRY
CH/CL/CA/CM 212: Organic Chemistry-I
(2016 admission)

Time: 3 hours  
Maximum marks: 75

Answer any two among (a), (b) and (c) from each question. Each sub question carries 2 marks

1. a) Write IUPAC names of the following.

   ![Structures](image)

   b) Indicate the element of symmetry present in each of the following molecules.
   i) trans-1,4-dichlorocyclohexane-

   ![Structure](image)

   ii) -

   c) What is atropisomerism?

2. a) How aryynes are formed?
   b) $p$-Nitroaniline is less basic than $m$-nitroaniline, explain.
   c) Arrange the following carbocations in order of increasing stability and give reasons.

   ![Structures](image)
3. a) What is SNi reaction?
b) Alkaline hydrolysis of Et₂NCH(Cl)CH₂CH₃ produces Et₂NCH(Et)CH₂OH. Account for this observation
c) Write two examples of non classical carbocations.
4. a) How would you prepare trans-1,2-dihydroxycyclohexane from cyclohexene?
b) Write the mechanism of benzoin condensation.
c) How can the E1CB pathway be distinguished from the kinetically indistinguishable E2 pathway?
5. a) Write two important reaction of NaCNBH₃
b) Explain the importance of DDQ in organic synthesis.
c) Explain Swern Oxidation

Section B
Answer either (a) or (b) from each question. Each sub question carries 5 marks

6. a) Compare ORD and CD and explain their relationship
b) Write a note on stereochemistry of nitrogen compounds
7. a) Explain the Felkin-Ann model with an example
b) How carbenes are generated? Explain its structure and properties
8. a) Explain why anti Markonikoff’s addition is not exhibited by HCl or HI when reacted with 1-butene?
b) After standing in aqueous acid R-2-butanol is found to have lost its optical activity. Account for this observation.
9. a) Write a note on cis and trans hydroxylation of alkenes
b) State Cram’s rule. Explain it with suitable example
10. a) Write a note on oxidation using SeO₂
b) Explain briefly the role of Lead tetra acetate in organic synthesis

Section C
Answer any three questions. Each question carries 10 marks

11. Give a brief account on stereoselectivity, enantiomeric excess and chiral separation.
12. Explain the following
   a. SₐrAr mechanism, b) Orientation effect in aromatic electrophilic substitution
13. Discuss the following
   a) competition between Sₐ₁ and Sₐ₂, b) Stereochemistry of nucleophilic substitution
14. Describe the following
   a) Mechanism with evidences of aldol condensation
   b) Wittig reactions and applications
15. Write a note on a) Sharpless asymmetric epoxidation
   b) Chemoselectivity in reduction reactions
First Semester M.Sc. Degree Examination (Model Question Paper)
Branch-V: Applied Chemistry
CH 213/CL 213/CA 213: Physical Chemistry-1
(2016 Admission Onwards)

Time: 3 h                              Max.Marks:75

Section A
Answer any two from a,b,c, of each question. Each sub question carries 2 marks.  
(10 x 2 = 20 marks)

1. (a) Calculate de Broglie wave length of mass 1 mg moving with a velocity of 10 m s⁻¹
   (b) What is an operator? Give example.
   (c) Write spectroscopic term symbol for the ground state of O atom

2. (a) What is the principle of photoelectron spectroscopy?
   (b) Write the B.E.T theory of multilayer adsorption
   (c) Write the different types of adsorption? Explain

3. (a) Define chemical potential
   (b) State Lewis –Randall rule of fugacity
   (c) Write Konowaloff’s rule

4. (a) How is nmr spectroscopy made use of in the study of fast reactions?
   (b) What is steady state approximation?
   (c) Define quantum yield

5. (a) What is the effect of temperature on the distribution of molecular velocities of a gas? Explain.
   (b) Calculate the root mean square velocity of nitrogen at 27°C
   (c) Write the virial equation of state. Explain the terms

Section B
Answer either a or b of each question. Each question carries 5 marks.  
(5 x 5 = 25 marks)

6. (a) Explain Quantum mechanical Tunneling
   (b) Write kinetic energy operator. Show that it is a Hermition operator

7. (a) Write any two methods for the determination of surface area of a solid
   (b) Explain Langmuir-Hinshelwood mechanism of surface catalysed reaction

8. (a) Define fugacity. Write the method for the determination of fugacity of a gas
   (b) Derive Gibbs Duhem equation

9. (a) Explain Jabalonski diagram
   (b) Derive the rate law for the decomposition of N₂O₅

10. (a) Calculate the viscosity of O₂ at 25°C. The molecular diameter is 3.6Å
     (b) Write any one method for the determination of surface tension of liquid

Section C
Answer any three questions. Each question carries 10 marks.  
(3 x 10 = 30 marks)

11. Apply Schrodinger Wave equation for a simple harmonic oscillator. Find eigen values and eigen functions

12. Explain any two methods using for surface analysis
13. Write a brief account of the methods for the determination of activity coefficient of electrolytes and non-electrolytes.


15. Discuss viscosity of a gas and Chapman equation. How can we calculate mean free path and collision diameter from viscosity determination.

**SEMESTER II**

**CA 221 INORGANIC CHEMISTRY –II**

Total 90 h

**Unit I Sulphur, nitrogen, phosphorus and boron compounds** 18 h


**Unit II Coordination chemistry-II: Spectral and magnetic properties of transition metal complexes** 18 h


**Unit III Crystalline state** 18 h


**Unit IV Lanthanides and actinides** 18 h

Lanthanides: Characteristic properties. Electronic configurations and term symbols. Occurrence and extraction. Separation techniques. Oxidation states. Spectral and magnetic properties. Shapes of f-orbital and
their splitting in cubic ligand field. Lanthanide complexes as shift reagents. Actinides: Occurrence and general properties. Extraction of thorium and uranium. Electronic configuration and term symbol. Oxidation states. Spectral and magnetic properties. Comparative properties of lanthanides and actinides. Trans-uranium elements and their stabilities. Applications of lanthanide and actinide compounds. Comprehensive study of the beach sands of Kerala and their important components such as monazite, ilmenite, zircon and sillimanite.

Unit V Solid state chemistry 18 h


References


CA 222 ORGANIC CHEMISTRY- II

Unit I Physical organic chemistry 18 h


Unit II Molecular rearrangement and transformation reactions 18h

Unit III Aromaticity and symmetry controlled reactions 18 h

Aromaticity and antiaromaticity. Homo, hetero and non-benzenoid aromatic systems. Aromaticity of annulenes, mesoionic compounds, metalloccenes, cyclic carbocations, carbanions.


Unit IV Organic photochemistry 18 h


Unit V Chemistry of natural products and biomolecules 18 h

Introduction to primary and secondary metabolites in plants. Extraction methods of chemical constituents from plants, such as fractionation using solvents, specific extraction of alkaloids and supercritical fluid extraction. Characterizations of isolated compounds (terpenes, sterols, alkaloids, carbohydrates, flavonoids and poly phenols) by colour reactions and spray reagents. Biosynthesis of terpenes from mevalonic acid and sterols from squalene. Structure elucidation of ocimene, classification of pigments, structure elucidation of β-carotene. Structural differences between a triterpene and a sterol. Synthesis of quercetin, synthesis of testosterone, androsterone, estrone and progesterone. Determination of carbon skeleton of alkaloids (Hofmann, Emde and Von Braun degradation methods). Structural elucidation of ephedrine, nicotine, atropine.

References

CA 223 PHYSICAL CHEMISTRY –II 90 h

Unit I

Quantum Chemistry II 18 h

Rotational motion: Cartesian and spherical polar coordinates. The wave equation in spherical polar coordinates - particle on a ring, the phi equation and its solution, wave functions in the real form. Non-planar rigid rotor (or particle on a sphere)-separation of variables, the phi and the theta equations and their solutions, Legendre and associated Legendre equations, Legendre and associated Legendre polynomials. Spherical harmonics (imaginary and real forms)-polar diagrams of spherical harmonics.


Unit II Spectroscopy –I 18 h

Microwave spectroscopy: Rotational spectrum, intensity of spectral lines, calculation of internuclear distance. Non-rigid rotors and centrifugal distortion. Rotational spectra of polyatomic molecules-linear and symmetric top molecules. Introduction to instrumentation.


Unit III Applications of Thermodynamics 18 h

difference. Electro kinetic effects, the Glansdorff-Pregogine equation. Far from equilibrium region. Principle of minimum entropy production, Le-Chatelier Bra(u)wn Principle.


Solid-Liquid systems: Two salts and water systems- no chemical combination, double salt formation, one salt forms a hydrate, double salt forms hydrate, Isothermal evaporation.

Unit IV Statistical Mechanics –I 18 h


Unit V Electrochemistry 1


References


SECOND SEMESTER M.Sc. DEGREE EXAMINATION
Branch: V- Applied Chemistry
(Common for CH/CL/CA/CM 221)
(Under Semester System w.e.f 2016 Admissions)
CA 221- INORGANIC CHEMISTRY-II

Time: 3 h Max marks: 75

SECTION-A

Answer any two among (a), (b), and (c) from each question. Each sub-question carries 2 marks.

1. a) Classify the following as closo, nido, arachno or hypho.
   1) B \(_5\) H \(_9\)  
   2) B \(_5\) H \(_{11}\)  
   3) B \(_6\) H \(_{12}\)  
   4) B \(_9\) H \(_{15}\).

   b) Which sulphur–nitrogen compound is known as ‘one-dimensional’ metal? Why is it called so?
   c) Why are P \(_4\) N \(_4\) C \(_18\) puckered and P \(_4\) N \(_4\) F \(_8\) planar?

2. a) How would you distinguish between ferromagnetic and anti ferromagnetic material?
   b) Explain non-crossing rule.
   c) The effective magnetic moment of a complex is 4.90 BM. Calculate the no. of unpaired electron per unit complex.

3. a) What is the type of defect observed in AgBr crystals? Why?
   b) Give one example each for molecular, covalent, metallic and H-bonded crystals.
   c) Differentiate between H-centre and v-centre in NaCl crystals.

4. a) Write any two differences between 4f and 5f orbitals.
   b) Give the term symbols for Eu \(^{3+}\) and Lu \(^{3+}\).
   c) Explain why Actinides have greater tendency for complex formation than lanthanides?

5. a) What is band gap?
b) Draw the first Brillouin zone for a primitive cubic lattice?
c) Conductivity of metals decreases with increase of temperature. Explain.  

\[ 2 \times 10 = 20 \text{ marks} \]

**SECTION-B**

Answer either (a) or (b) of each question carries 5 marks.

6. a) How is diborane prepared? Discuss the structure and bonding in diborane.
   b) Write a note on metalloocarboranes.

7. a) Describe the Guoy’s method to determine magnetic susceptibility. How are these measurements used to calculate effective magnetic moments?
   b) Even though d-d transitions are forbidden, why such transitions occur in many transition metal complexes? Illustrate with examples.

8. a) Distinguish between spinels and inverse spinels with suitable examples.
   b) Write briefly on line and plane defects in solids.

9. a) Briefly discuss the basis of the ion-exchange method for the separation of Lanthanides.
   b) Compare the spectral and magnetic properties of Lanthanides and Actinides.

10. a) With suitable examples explain the phenomenon of photoconductivity. What are its applications?
    b) Write a short note on the applications of ferro, piezo and pyroelectrics.

\[ 5 \times 5 = 25 \text{ marks} \]

**SECTION-C**

Answer any three questions and each question carries 10 marks.

11. How is Borazine prepared? Discuss its structure and compare the bonding with phosphazene molecule.

12. Write an account on the selection rules and characteristics of d-d transition and application of each electronic spectra in elucidating the structure of metal complexes.

13. Discuss briefly on the packing of atoms and ions in solids.

14. a) Correlate the oxidation states and ionic radii with electronic configuration of lanthanides.
    b) Write a short note on the beach sands of kerala.

15. Discuss the salient features of band theory of solids and compare it with the free electron theory of solids.

\[ 10 \times 3 = 30 \text{ marks} \]
b) Write briefly on Homoaromaticity.
c) State Woodward Hoffmann rules.

3. a) Explain Phosphorescence.
b) Write a short note on Norrish type I reaction.
c) Describe anyone method of generation of singlet oxygen.

4. a) Explain von Braun reaction.
b) Show the products formed when Quercetin is treated with dimethyl sulphate followed by boiling with ethanolic KOH.
c) Draw the structure of Cholesterol.

5. a) Explain Taft equation
b) Describe salt effect in substitution reaction
c) State Marcus theory

Section B

Answer either a) or b) of each question, and each question carries 5 marks.

6. a) Discuss the mechanism and applications of Baeyer Villiger reaction.
b) Discuss the mechanism of Benzidine rearrangement. Also write proof to support the mechanism.

7. a) Explain the acidity of Cyclopentadiene and Cycloheptatriene.
b) Explain briefly Claisen rearrangement.

8. a) Briefly explain Barton reaction.
b) Explain the photochemistry of olefins.

9. a) Discuss the structure elucidation of Carotene.
b) Briefly describe the biosynthesis of terpenes.

10. a) Explain kinetic and thermodynamic control in reactions involving ketones.
b) Explain the reason for the difficulty in the hydrolysis of 2, 6 - disubstituted benzoic acid esters.

Section-C

Answer any three questions and each question carries 10 marks.

11. i) Discuss the mechanism and applications of Beckmann rearrangement.
    ii) Discuss the similarity in the intermediates of Curtius, Schmidt and Lossen rearrangements.

12 Explain briefly on
i) Sigmatropic reactions
ii) 1, 3 - Dipolar and Ene reactions.

13. Discuss the following:
   i) Photochemistry of vision
   ii) Photoreaction of Vitamin D.

14. Explain the following:
i) Structure of Estrone.

ii) Chemical, spectroscopic and chiroptical methods for establishing carbon skeleton.

15. Discuss the following:

i) Principles and applications of phase transfer catalysis.

ii) Methods of determination of reaction mechanism.  

[10x3=30 marks]

Second Semester M.Sc. Degree Examination (Model Question Paper)
Branch-V: Applied Chemistry
CH 223/CL 223/CA 223: Physical Chemistry- II
(2016 Admission Onwards)

Time : 3 Hours                            Max mark : 75

Section A

Answer any two among (a), (b) and (c) from each question. Each sub-division carries 2 marks.

1. a) Set up the Schrodinger equation for a rigid rotator.
   b) Give plots of (a) radial probability distribution functions of 2S orbital and (b) angular plot of 2Px orbital.
   c) Write the expression for fock operator and explain the terms

2. a) What are overtones? Why are they weak?
   b) State and explain the rule of mutual exclusion with one example.
   c) State Franck-Condon principle.

3. a) Explain the terms ‘Force’ and ‘Flux’ with reference to irreversible thermodynamics.
   b) Show the influence of temperature on the miscibility curve in a three component system forming a pair of partially miscible liquids.
   c) What are the conditions under which linear relations are valid to understand irreversible processes.

4. a) Derive ideal gas law from translational partition function.
   b) Explain the term canonical ensemble.
   c) Electron would never follow Maxwell Boltzmann statistics. Why?

5. a) What is Lippmann potential? How does it arise?
   b) Calculate the mean activity coefficient of 0.01M BaCl₂ in water at 25°C.
   c) Explain the origin of concentration overpotential.

(10 X 2 = 20 Marks)

Section- B

Answer either (a) or (b) of each question and each question carries 5 marks

6. a) Explain self-consistent field method to solve many electron systems.
   b) Write the Schrodinger equation for hydrogen atom in polar coordinates and separate the variables.

7. a) Explain the principle and application of Laser Raman Spectrum.
   b) Explain the origin of P and R branches in rotational-vibrational spectrum.

8. a) Derive generalized equation for entropy production from heat flow.
   b) Give the Onsagar-reciprocal relations. What are its applications?

9. a) Apply Fermi-Dirac statistics to understand paramagnetism in solids.
   b) Derive the expression for partition function for particle executing (i) free linear motion and (ii) free linear harmonic vibration.
10. a) Derive Debye-Huckel limiting law.
b) Discuss the various models for electrical double layer. \( (5 \times 5 = 25 \text{ Marks}) \)

Section-C

Answer any three questions and each question carries 10 marks

11. (i) Apply Schrodinger equation for particle in a ring. Find eigen values and eigen functions.
   (ii) Show that any two associated Legendre functions satisfy orthonormality condition.

12. (i) Give an account of rotation spectra of diatomic molecules. Explain the effect of nonrigidity of the bond on the spectra.
   (ii) How is the rotational spectrum of a diatomic molecule affected by isotopic substitution?

13. (i) Draw the phase diagram of a three component liquid system with three pairs of partially miscible liquids. Explain.
   (ii) How would you understand (a) thermo osmosis and (b) thermal diffusion from irreversible thermodynamics?

14. Derive the expression for the distribution function of a Boson and Bose-Einstein condensation.

15. (i) Derive Butler-Volmer equation. Deduce the expression for the low and high field limits of this equation.
   (ii) Discuss the application of Debye-Huckel Onsager equation as applied to strong electrolytes and point out its limitations. \( (10 \times 3 = 30 \text{ Marks}) \)

SEMESTER III
CA 231 INORGANIC CHEMISTRY- III

Unit I Organometallic compounds 18h


Unit II Coordination chemistry-III: Reactions of metal complexes 18h

reactions of Cr(III), Ru(II), and Ru(III) complexes. Photo-isomerisation and photo-aquation reactions of metal complexes.

**Unit III Bioinorganic chemistry** 18 h


**Unit IV Spectroscopic Methods in Inorganic Chemistry** 18 h

Infrared spectra of coordination compounds. Structural elucidation of coordination compounds containing the following molecules/ ions as ligands- NH\textsubscript{3}, H\textsubscript{2}O, CO, NO, OH\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, CN\textsuperscript{-}, SCN\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-}, CH\textsubscript{3}COO\textsuperscript{-} and X (X= halogen). Changes in ligand vibration on coordination with metal ions. Vibrational spectra of metal carbonyls- CD and ORD spectra of metal complexes. ESR spectra: Application to Cu(II) complexes and inorganic free radicals such as PH\textsubscript{4}+, F\textsuperscript{2-} and [BH\textsubscript{3}]. Nuclear Magnetic Resonance Spectroscopy: The contact and pseudocontact shifts, some applications including biological systems, an overview of NMR of metal nuclides with emphasis on \textsuperscript{31}P and \textsuperscript{19}F NMR. Mossbauer Spectroscopy: Application of the technique to the studies of iron and tin complexes.

**Unit IV Nuclear chemistry** 18 h


**References**


CA 232 ORGANIC CHEMISTRY-III

Unit I UV-Vis and IR Spectroscopy and Mass spectrometry 18h


Unit II NMR spectroscopy and structural elucidation 18h

Theory of NMR spectroscopy, chemical shifts, anisotropic effects and coupling constant. Spin-spin interactions in typical systems. First order and higher order spectra. Simplification methods of complex spectra by high field NMR, shift reagents, chemical exchange and double resonance. 13C NMR chemical shifts. Applications of NOE, DEPT, and 2D techniques such as COSY, HSQC, HMQC and HMBC. Spectral interpretation and structural elucidation. Solving of structural problems on the basis of numerical and spectrum based data.

Unit III Organic synthesis 18h


Unit IV Methods in organic synthesis 18h

Retrosynthetic analysis and disconnection approach. Synthetic strategy and synths. Regioselectivity in enol and enamine alkylation. Stereospecific and stereoselective synthesis. Sharpless asymmetric epoxidation, Chiral pool, chiral auxiliary, Chiral reagents, BINAP, Mitsunobu reaction. 1,3-dipolar cycloaddition in the

Unit V  Separation techniques 18 h

References

CA 233 Physical Chemistry –III 90 h
Unit I Chemical Bonding 18 h

Treatment of molecules - The Born- Oppenheimer approximation- LCAO-MO Theory- MO theory of H₂ and H⁻ . MO treatment of other homo diatomic molecules Li₂, Be₂, B₂, C₂, O₂ and F₂. MO treatment of hetero diatomic molecules LiH, CO, NO and HF. Spectroscopic term symbols for homo diatomic molecules.
Valence bond theory of diatomic molecules H\textsubscript{2}, O\textsubscript{2} and F\textsubscript{2}. Comparison of MO and VB theories, Quantum mechanical treatment of SP, SP\textsuperscript{2} and SP\textsuperscript{3} Hybridisation. HMO theory of conjugated systems. Bond order and charge density calculations, Free valence. Application of HMO method to ethylene, allyl system, butadiene and benzene.

Unit II Computational Chemistry 18 h

Introduction to computational chemistry: as a tool and its scope. Potential energy surface - stationary point, saddle point or transition state, local and global minima. Slater and Gaussian functions and its properties. Basis sets: minimal, double zeta, triple zeta basis sets, contracted basis sets, Pople’s style basis sets and their nomenclature. Basis functions - Roothan’s concept, Slater type orbitals (STO) and Gaussian type orbitals (GTO). Slater determinants

Quantum mechanical computational methods - Ab initio methods: Introduction to SCF. Wave functions for open shell state, RHF, ROHF and URHF. (no calculation). Electron correlation and introduction to post HF methods.

Semiempirical methods. Huckels and extended Huckel methods. Strengths and weaknesses. PPP, ZDO and CNDO approach. (Mentioning only).

Density functional theory - Hohenberg-Kohn theorems, Exchange co-relational functional. (Only the basic principles and terms to be introduced).

Non-quantum mechanical computational methods - Molecular mechanics: Force fields, bond stretching, angle bending, torsional terms, non-bonded interactions, electrostatic interactions and the corresponding mathematical expressions. Names of some commonly used force fields.

Construction of Z-matrix for simple molecules. H\textsubscript{2}O, H\textsubscript{2}O\textsubscript{2}, H\textsubscript{2}CO, CH\textsubscript{3}CHO, NH\textsubscript{3} and CO\textsubscript{2}.

Unit III Spectroscopy II 18 h


ESR spectroscopy: Electron spin. Interaction with magnetic field. Kramer’s rule. The g factor. Determination of g values. Fine structure and hyperfine structure. Elementary idea of ENDOR and ELDOR.

Mossbauer spectroscopy: Basic principles. Doppler effect, chemical shift, recording of spectrum, application. Quadrupole effect.

NQR spectroscopy - Principle and application

Photoelectron spectroscopy. Introduction to UV photoelectron and X-ray photoelectron spectroscopy.

Unit IV Statistical Mechanics II 18 h

Molecular partition functions. Translational (1D, 2D and 3D), vibrational, rotational and electronic partition functions. Total partition functions Langevin function and its use for the determination of dipole moment and molecular energies.


Unit V Electro Analytical and Spectrophotometric methods. 18 h


**Electrogravimetry:** Principle and method. Determination of Copper. Separation of metal ions.

**Conductometry:** Principle and method. Conductometric titrations.

**Coulometry:** Principle and method. Coulometric titrations.

**Voltammetry:** Principle and method of polarography, cyclic voltammetry, stripping voltammetry and amperometry.

**Flame emission and atomic absorption spectrometry.** Instrumentation for AAS. The flame characteristics. Atomiser used in spectroscopy. Hollow cathode lamp. Interference in AAS. Application of AAS.

**References**

CA 234- Inorganic Chemistry Practicals -II  
Total-125 h

1. Estimation of simple mixture of ions (involving quantitative separation) by volumetric and Gravimetric methods.
2. Analysis of typical alloys and ores
3. Ion exchange separation of binary mixtures.
4. Spectral Interpretation of metal complexes using IR, UV-Vis. spectral data. Supplementary information like metal estimation, CHN analysis, conductivity measurements and magnetic measurements to be provided to the students. Assessment is based on arriving at the structure of the complex and assignment of IR spectral bands.
5. Interpretation of TG and DTA curves of metal oxalate hydrates. Assessment is based on the identification of various stages.

References

CA 235 ORGANIC PRACTICALS-II  
Total 125 h

A. Volumetric estimation of

1) Aniline 2) Phenol 3) glucose 4) Ascorbic acid 5) Aspirin

B. Colorimetric estimation

6) paracetamol with potassium ferricyanide
7) protein by biuret method
8) Ascorbic acid by folin-phenol reagent or phosphotungstic acid methods
C). Spectral identification

9) UV, IR, $^1$H NMR, $^{13}$C NMR, EI mass spectral identification of Organic compounds from a library of organic compounds (Each student has to record the spectral analysis of a minimum of 40 compounds)

D. Separations of mixtures by Paper Chromatography

10) Identification of amino acids

E) Single stage preparation of organic compounds by green chemistry

11) Preparation of $p$-bromoacetanilide using CAN
12) Radical coupling – 1,1-Bis-2-naphthol
13) Synthesis of dihydropyrimidinone
14) Synthesis of dibenzalacetone with lithium hydroxide
15) Photoreduction of benzophenone to benzopinacol (not for end semester evaluation)

The board of examiners have to choose the combination of a volumetric estimation, a colorimetric estimation, a green synthesis OR paper chromatography and spectral analysis. The choice of experiments should change every year.

References

8. Monograph on green laboratory experiments, DST, Government of India, pp 1-79.
9. For spectral data of organic compounds, see: [http://sdds.riodb.aist.go.jp/sdds/cgi-bin/direct_frame_top.cgi](http://sdds.riodb.aist.go.jp/sdds/cgi-bin/direct_frame_top.cgi)

**CA 236 PHYSICAL PRACTICALS –II**

125 h

**Conductometry**

- Determination of strength of strong and weak acids in a mixture
- Determination of strength of a weak acid.
- Determination of solubility product of a sparingly soluble salt (PbSO$_4$, BaSO$_4$, etc.)
- Hydrolysis of NH$_4$Cl or CH$_3$COONa or aniline hydrochloride
- Determination of order of reaction, rate constant and energy of activation for saponification of ethyl acetate

**Precipitation titrations.**

- Determination of critical micellar concentration (CMC) of sodium lauryl sulphate from measurement of conductivities at different concentrations.
- Equivalent conductance at infinite dilutions and verification of Kohlrausch’s law Determination of Onsager constants.
Potentiometry

Determination of emf of Daniel cell.
Determination of the emf of various ZnSO₄ solutions and hence the concentration of unknown ZnSO₄ solution.
Determination of valency of mercurous ion.
Determination of temperature dependence of EMF of a cell
Determination of stoichiometry and formation constant of silver-ammonia complex.
Determination of activity and activity constant of electrolytes.
Determination of thermodynamic constants of reactions.

pH metric titrations.

Acid alkali titrations using Quinhydrone electrode.
Titrations(double) involving redox reactions – Fe²⁺ Vs KMnO₄, K₂Cr₂O₇, Ce(NH₃)SO₄ and KI Vs KMnO₄
Determination of strengths of halides in a mixture.
Determination of pH of buffer solutions and hence to calculate the E⁰ of quinhydrone electrode

Spectrophotometry

Verification of Beer-Lambert’s law.
Absorption spectra of conjugated dyes.
Determination of concentration of potassium dichromate and potassium permanganate in a mixture.
To study the complex formation between Fe³⁺ and salicylic acid.
Determination of pKa of an indicator.

Polarimetry

Measurement specific rotation of glucose.
Determination of specific rotation of sucrose
Determination of unknown concentration of glucose solution and rate constant of its hydrolysis in presence of HCl

Polarography :

Determination of half wave potential E ½ and unknown concentration of Cd²⁺ ion.
Determination of concentrations of metal ions in a mixture.

Surface tension

Determination of surface tension of various liquids (water-ethanol, water-glycerol, water-sorbitol, nitrobenzene-toluene) by Stalagmometric method (drop number/ drop weight)
Determination of parchors of molecules and various groups.
Determination of concentration of a mixture.
Determination of surface tension and parchor of liquids using double capillary method.
Variation of surface tension with concentration. Unknown concentration of a mixture. Interfacial tension. Determination of surface excess and area per molecule.

Refractometry

Determination of molar refraction of pure liquids
Determination of concentration of KCl solution/glycerol solution
Determination of solubility of KCl in water.
Determination of molar refraction of solid KCl
Study the stoichiometry of potassium iodide-mercuric iodide complex.
Determination of concentration of KI solution.

References
4) A.M. James, and F.E. Pichard, “Practical Physical Chemistry”, Longman.

Third Semester M.Sc. Degree Examination – Model question paper
Branch – V- Applied Chemistry

CH/CL/CA 231 : INORGANIC CHEMISTRY- III
(2016 Admission Onwards)

Time : 3 Hrs                            Max. Marks: 75

SECTION A

Answer two among (a), (b) and (c) from each question carries 2 marks

1. a) Draw the structure of Rh$_2$(CO)$_2$.
   b) How do sigma allyl complexes differ from pi allyl complexes?
   c) What are fluxional molecules?
2. a) What are the factors affecting the stability of complexes?
   b) Explain Macrocyclic effect?
   c) What is anation reaction? Give an example.
3. a) Why electron transfer process in photosynthesis is called an uphill process?
   b) Explain the mechanism of oxygen binding in haemocyanin.
   c) What is Na$^+$ - K$^+$ pump? How does it function?
4. a) What is group frequency concept? Illustrate with example.
   b) Why are solid samples used for recording Mossbauer spectra?
   c) What is Doppler broadening? Explain with an example.
5. a) Explain binding energy.
    b) What is compound nucleus? How is it formed?
    c) Give a note on breeder reactors. (2x10= 20 marks)

SECTION B
Answer either among (a) or (b) from each question carries 5 marks

6. a) What are metal carbonyls? Explain the structure and bonding in Ni(CO)₄
    b) Discuss the mechanism of polymerization of Zeigler- Natta catalyst.
7. a) Explain Trans effect with suitable examples.
    b) Give an account of photochemical reactions of complexes.
8. a) Discuss the role of calcium in blood clotting process.
    b) Explain the structural features of haemoglobin.
9. a) How does IR spectroscopy help for the structural elucidation of complexes containing ammonia and water as ligands.
    b) Explain CD and ORD spectra of complexes.
10. a) Distinguish between Transient and Secular equilibria.
    b) What is meant by half life period? How is it related to decay constant? The t₁/₂ of a radio nuclide is 20 years. If a sample of this nuclide has an initial activity of 8000 disintegrations per minute today, what will be its activity after 80 years? (5x5= 25 marks)

SECTION C
Answer any three questions. Each question carries 10 marks

11. Explain the bonding of ferrocene by MO Theory.
12. Briefly explain outer sphere and inner sphere mechanism of electron transfer reactions
13. i) Discuss the function of PS-I and PS-II in photosynthetic activity.
    ii) Outline the probable mechanistic pathways Nitrogenase activity in nitrogen fixation.
14. i) Discuss the application of ESR spectroscopy to Cu(II) complexes.
    ii) Explain how Mossbauer spectroscopy helps to the studies of iron and tin complexes
15. Discuss about different types of nuclear reactions with suitable examples. (10x3= 30 marks)

THIRD SEMESTER M.Sc.DEGREE EXAMINATION
BRANCH – V- APPLIED CHEMISTRY
CH/CL/CA232: Organic Chemistry-III
(2016 admission onwards)

Time-3 hours Maximum marks :75

Section A – Answer any two among (a), (b) and (c) from each question.
Each sub question carries 2 marks

1. a) Explain how CH stretching vibrations of sp, sp\(^2\), sp\(^3\) hybridised carbon varies.
   b) Polar solvents usually produce a red shift in the \(\delta^{1}\delta\) transition explain.
   c) Explain how the presence of bromine atom in a molecule can be detected by mass spectrum.

2. a) Explain why acetylenic hydrogens are more upfield than vinylic hydrogens.
   b) What multiplicities are observed for the signals of off resonance decoupled \(^1\)C spectrum of 2-chloropropene?
   c) Account for the fact that splitting is observed between Hydrogens “a” and b in 2-methyl propene \((\text{CH}_3)_2\text{C} = \text{CH}_2\) and not in neo pentylchloride \((\text{CH}_3)_2\text{CH}^b\text{Cl}\).

3. a) Suggest a method for conversion

4. a) Explain the use of silyl group as protecting group in organic synthesis.
   b) Explain the term combinatorial synthesis.
   c) What is umpolung?

5. a) What is the principle of chromatography
   b) What is paper chromatography? How is it helpful in identifying various alpha amino acids?
   c) Outline the applications of Gel electrophoresis. \((2\times10=20 \text{ marks})\)

**Section B**

Answer either (a) or (b) from each question. Each sub question carries 5 marks

6. a) By using Woodward Fieser rules calculate the \(\varepsilon_{\text{max}}\) values

   \[
   \begin{align*}
   \text{C}_{19}\text{H}_{24}\text{O} & \quad \text{IR absorption at 1688 cm}^{-1} \\
   \text{H}_3 & \quad \text{NMR signals at 1.22 (triplet, 3 H), 2.98 (quartet) and 7.28-7.95 (multiplet, 5H). Assign the data}
   \end{align*}
   \]

   b) How IR spectrum can be used to distinguish
      i) Primary amine from primary amide
      ii) Ethyl benzene from o-xylene

7. a) Deduce the identity of the compound C\(_9\)H\(_{10}\)O that has an IR absorption at 1688 cm\(^{-1}\) and 1 H NMR signals at 1.22 (triplet, 3 H), 2.98 (quartet) and 7.28-7.95 (multiplet, 5H). Assign the data
b) Explain the paramagnetic anisotropy of alkenic, aldehydic and aromatic protons.

8 a) Discuss Vilmeier-Hack reaction.

b) Write short notes on important metal hydrides used as reducing agents in organic synthesis

9 a) Explain the regioselective synthesis of the following compound from cyclohexanone

[Chemical structure of a compound]

b) Discuss the synthesis of â-hydroxy ketones and aldehydes using umpolung

10 a) Explain the principle of gas chromatography and ion exchange chromatography. What type of substances are analysed using the above?

b) Describe the principle and instrumentation of HPLC (5x5= 25 marks)

Section C

Answer any three questions. Each question carries 10 marks

11. Discuss the functional group and fingerprint regions in the IR spectrum. How the IR spectrum is useful in distinguishing the inter and intra molecular hydrogen bonding

12. Write short notes on
   i) DEPT spectra, ii) Nuclear Overhauser effect, iii) Shift reagents in NMR, iv) Double resonance NMR

13. Explain the following named reactions with mechanism and example
   i) Mannich reactions  ii) Robinson annulations reactions iii) Suzuki coupling

14. Explain olefin metathesis and Mitsonobu reaction with applications of each

15. With a schematic diagram explain the principle, instrumentation, and applications of GC (10x3= 30 marks)

THIRD SEMESTER M Sc. CHEMISTRY DEGREE EXAMINATION
BRANCH –V- APPLIED CHEMISTRY
CH/CL/CA/CM 233 – Physical Chemistry III
(2016 admission onwards.)

Time : 3 Hours 
Max. Marks : 75

Section A

Answer any two among (a), (b) and (c) from each question.

Each sub question carries 2 marks

1) A) Arrange O₂, O²⁺, O²⁻ in the increasing order of stability. Justify your answer
   B) Write briefly about “Perturbation theory”
   C) Explain the more dipole moment in ethyl chloride than in chlorobenzene.

2) A) Construct the z-matrix of CH₃CHO.
   B) Name any two chemistry related software.
C) Write the determinantal wavefunction for the configuration 1S₂ 2Pz

3) A) Write the expression for chemical shift in Mossbauer spectroscopy and explain the terms.
B) Calculate the ESR frequency of an unpaired electron in a magnetic field 0.33 Tesla. Given for free electron g=2, ħ=9.273×10⁻²⁷ J/T
C) Explain the basic principle of X-ray photoelectron spectroscopy.

4) A) Calculate the value of ln6Å with and without Stirling’s theorem. Find the difference between the values if any. Comment on the result.
B) What is meant by the law of equipartition of energy?
C) State and explain Dulong Petit’s law. Explain its limitations.

5) A) What are the requirements for choosing a reference electrode?
B) Define half wave potential. Explain its significance.
C) Why do we use three electrodes in cyclic voltametry. (2x10= 20 marks)

Section B

Answer either (a) or (b) from each question. Each sub question carries 5 marks

6) A) Derive the expression for the bond angle and wave function in sp² hybridisation.
B) Apply HMO theory to butadiene molecule and discuss the molecular orbitals and their corresponding energy levels.

7) A) Differentiate between Slater type orbitals and Gaussian type orbitals
B) What is potential energy surface? Explain its significance.

8) A) Write a brief account of 2D-NMR spectroscopy.
B) What is Kramer’s degeneracy? Discuss.

9) A) B) Give comparison between Bose-Einstein, Maxwell-Boltzmann and Fermi-Dirac statistics.
B) Explain briefly how heat capacity of gases can be calculated?

10) A) Explain the working of glass electrode.
B) Discuss the advantages and disadvantages of amperometric titrations. (5x5= 25 marks)

Section C

Answer any three questions. Each question carries 10 marks

11) Write a note on the secular equations.
12) Discuss Density functional theory and give its advantages and limitations.
13) Explain the principle and applications of NQR spectroscopy.
14) Derive Einstein’s heat capacity equation for solid.
15) Describe the theory and instrumentation of AAS. (10x3= 30 marks)
SEMESTER IV

CA 241-Chemistry of Advanced materials

Unit I Introduction to Nanomaterials 18 h

Nanomaterials: 0D, 1D, 2D and 3D nanomaterials-fundamental physicochemical principles - size dependence of the properties of nanomaterials- quantum confinement

Synthesis of nanomaterials-Sol-Gel, colloidal precipitation, co-precipitation, hydrothermal, vapour deposition, and sonochemical method

Metal nanoparticles: Size control, characterization, and properties (optical, electronic, magnetic) Surface Plasmon resonance and its applications, role in catalysis, alloy nanoparticles.

Unit II The basic tools and applications of nanotechnology 18 h

Basic principles and applications of Scanning electron microscopy (SEM), transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Energy Dispersive X-ray Spectroscopy (EDAX)-Powder X-ray diffraction and determination of particle size- UV-Visible spectroscopy and determination of band gap-Application of IR spectroscopy in the analysis of nanomaterials

Carbon nano structures: Fullerenes: C60, C80 and C240-Synthesis, Properties and applications (mechanical, optical and electrical) of C60. Functionalisation and reactivity of carbon nanotubes.

Nanosensors: Nanosensors based on quantum size effects, electrochemical sensors and nano bio sensors. Nano tweezers, Applications of nano technology in effluent treatment and photo catalysis.

Unit III Polymerization processes 18 h


Unit IV Speciality Polymers 18 h

Industrial Polymers: carbon chain and hetero chain polymers- synthesis and applications-Polymeric reagents, catalysts and substrates

Conducting polymers - Synthesis & applications of polyacetylenes, polyanilines, polypyrroles & polythiophenes. Photoresponsive and photorefractive polymers. Polymers in optical lithography - Drug delivery - Drug carriers - Polymer based nanoparticles. Polymer based LEDs, lithium-polymer batteries, Liquid crystalline polymers - Main chain and side chain liquid crystalline polymers. Phase morphology

Unit V Smart materials 18 h

Piezoelectric,magnetostrictive, halochromic, electrochromic,thermochromic, magnetocaloric and thermoelectric materials. Chemistry behind photochromism in spiropyrans, spirooxazines,diarylethenes, azobenzenes, quinones. Examples for Photochromic Coordination Compounds.

Shape-memory polymers, pH-sensitive polymers, Temperature-responsive polymers, dielectric elastomers, self-healing polymers and concept of mechanophores, polymorphism in polycaprolatone, introduction to ferrofluids, concept of pseudoelasticity.

References:

SEMESTER IV
CA 242 APPLIED CHEMISTRY
Total 90 h

UNIT I – Water treatment
18 h


UNIT II– Soaps & Detergents
18 h

Soap manufacture: raw materials, characteristics of cold process, semi boiled process and boiled process, additives of soap, detergent action of soap, influence of fatty acid composition of the oil on properties of soap, manufacture of soap for different purposes-laundry soaps, toilet soaps, liquid soaps, transparent soaps, baby soaps, shaving soaps, medicated soaps, textile soaps, naphtha soaps, marine soaps. Chemical analysis of anionic, cationic, amphoteric and nonionic detergents used in modern industries and for household purposes-their chemistry, manufacture and applications.

UNIT III - Corrosion and Protective Coatings
18 h

Corrosion and its Control: Nernst Theory, Standard Electrode Potential, Galvanic Series, Concentration cell, Types of corrosion: Uniform and Galvanic, Erosion, Crevice, Pitting, Exfoliation and Selective leaching, Inter-angular Stress, Waterline, Soil, Microbiological. Theories of corrosion: Acid, Direct Chemical attack, Electrochemical, Corrosion reactions, Factors affecting corrosion, Protective measures


UNIT IV - Applied Inorganic Chemistry
18 h

Introduction to chemical industry. Flow sheet preparation. Flow sheets and engineering aspects of the manufacture of sulfuric acid, ammonia, urea and glass.

Refractories: Definition, Classification with Examples; Criteria of a Good Refractory Material; Causes for the failure of a Refractory Material. Flow sheet and engineering aspect of the manufacture of Refractories.

Unit V – Applied Organic Chemistry 18h

Raw materials and routes to major organic products. Flow sheets and engineering aspects of the manufacture of nitrobenzene, vinyl chloride, soaps, detergents and hydrogenation of oils.

Homogeneous Catalysis. Stoichiometric reactions for catalysis and homogeneous catalytic hydrogenation, Zeigler-Natta polymerization of olefin, catalytic reactions involving hydrocarbonylation of olefins (oxo reaction), activation of C-H bonds.

Polymers: Types of Polymerization. Thermoplastics & thermosetting polymers. Preparation, properties and applications of the Polyethylene, Teflon, PVC, Nylon, Phenol formaldehyde & Urea Formaldehyde, Elastomers: Natural rubber, Vulcanization of rubber & Synthetic rubber.

References


CA 243 DISSERTATION

Instructions to Question Papers Setters

The Syllabus of each theory has five units. While setting the question papers, equal weight is to be given to each of the Units for choosing the questions. Each question paper is of 3 hours duration and has three Sections, namely Section A, Section B and Section C constituting a total 75 marks as detailed.

Section A Five questions, one from each Unit containing three short answer questions marked (a), (b), and (c), each of which has 2 marks. One has to answer any two of (a), (b) or (c) from each of the five questions. (2x10=20 marks)

Section B Five questions, one from each unit containing two short essay questions marked (a) and (b), each of which has marks. One has to answer either (a) or (b) from each of the five questions. (5x5=25 marks)

Section C Five essay questions, one from each unit having 10 marks. One has to answer any three questions from the five questions asked.(10x3=30 marks)

Structures should be in chemdraw or ISIS/ draw
FOURTH SEMESTER M.Sc. DEGREE EXAMINATION
Branch: V- APPLIED CHEMISTRY
(Under Semester System w.e.f 2016 Admissions)
CA 241-Chemistry of Advanced materials

Time: 3 h  Max. Marks: 75

Section A
(Answer any two among (a), (b) and (c) from each question. Each sub question carries 2 marks)

1 a) What is surface plasmon resonance?
   b) What is meant by quantum confinement?
   c) What are alloy nanoparticles?

2 a) What is EDAX?
   b) What are fullerenes?
   c) What are nano tweezers?

3 a) What do you mean by chain transfer in polymerization process?
   b) What is meant by tacticity of a polymer?
   c) What is GPC?

4 a) What are conducting polymers?
   b) Name any two polymeric reagents.
   c) What are photo responsive polymers?

5 a) What are piezo electric materials?
   b) What are halochromic materials?
   c) Write examples of any two photochromic coordination compounds.

[2 x 10 = 20 marks]

Section B
(Answer either (a) or (b) of each question. Each question carries 5 marks)

6 a) Explain the relation between size and properties of nano-materials.
   b) Explain CVD method for preparing nano particles.

7 a) Explain the use of powder XRD in determination of particle size of nano materials.
   b) Explain how SWCNTs and MWCNTs are synthesized.

8 a) Explain the kinetics of free radical addition polymerization.
   b) Explain DSC method for determination of Glass transition temperature.

9 a) Explain in detail the synthesis of polyacetylenes.
   b) Explain in detail the synthesis of polythiophenes.

10 a) Explain the concept of pseudo elasticity.
     b) Write a note on shape-memory polymers.

[5 x 5 = 25 marks]

Section C
(Answer any three question and each question carries 10 marks)

11 Explain in detail SEM and TEM.

12 Explain in detail nano synthesis using Sol-Gel and Hydrothermal methods

13 Explain determination of molecular weights by viscometry and light scattering methods.

14 Explain the application of Polymers in catalysis.

15 Write a note on the chemistry behind photochromism in spiroprans, spirooxazines, diarylethenes and azobenzenes.

[10x3 = 30 marks]
Fourth Semester M.Sc. Degree Examination
Branch – V- Applied Chemistry
CA 242 Applied Chemistry
(2016 Admission Onwards)

Time: 3 h                                                                                                                     Total Marks: 75

Section A.
Answer any two among (a), (b) and (c) from each question carries 2 marks
1 (a) What are the disadvantages of sludge formation?
(b) Explain the difference between coagulation and flocculation?
(c) What is foaming?
2 (a) What is saponification value?
(b) Explain the mechanism of action of soap
(c) What are naphtha soaps
3 (a) Rusting of iron is quicker in saline water than in ordinary water. why?
(b) What is Galvanic corrosion? How can it avoided
(c) What are sacrificial anodes? Give examples
4 (a) What are the constituents of Portland Cement? Why Portland cement so named?
(b) Explain the structure and synthesis of Urea
(c) What is glass? How is soft glass prepared?
5 (a) Define vulcanization of rubber. How vulcanization is is carried out?
(b) Give the Color chemicals Added to Food and soft drinks and explain its health hazards
(c) Explain the manufacture of BHC

Section B.
Answer either among (a) or (b) from each question carries 5 marks
6 (a) Point out the essential differences between hard and soft water
(b) Explain anyone method for the determination of alkalinity of water
7 (a) Explain the influence of fatty acid composition on the properties of soaps
(b) Explain cold, semiboiled and boiled processe in the manufacture of soap.
8 (a) How much rust will be formed when 100 kg of iron have completely rusted away.
(b) Write a note on the various factors affecting corrosion.
9 (a) What are refractories. Explain the criteria for a good refractory material.
(b) Explain the dry and wet process for the manufacture of cement.
10 (a) Explain the synthesis of paracetamol.
(b) Give a note on cosmetics.

Section C
Answer any three questions. Each question carries 10 marks
11. Explain the various processes for softening of water
12. Write an essay on the manufacture, chemistry and applications of detergents
13. With the help of Flow chart diagram explain the manufacture of sulphuric acid
14. Describe the method of preparation, properties and applications of (i) PVC (ii) Nylon (iii) Urea formaldehyde and (iv) Teflon
15. Write a note on protective coatings.

(10x3=30 marks)