



**UNIVERSITY OF KERALA**

**Syllabus for  
M. Sc. Programme in Branch IV  
ANALYTICAL CHEMISTRY**

**(Revised Syllabi under Semester System  
with effect from 2020 Admissions)**

## 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 2020 admission. There are two independent PG programmes in Chemistry, namely **M.Sc. Programme in Branch III–Chemistry and M.Sc. Programme in Branch IV–Analytical Chemistry**. Both these PG programmes are equivalent in all respect for employment and higher studies. Each of these two 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 two programmes are detailed below. The theory courses of the first three semesters and the practical courses of the first two semesters of the two programmes are common, and therefore, the examinations of these two 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 2020 admission in affiliated colleges of the university.

### M.Sc. PROGRAMME IN BRANCH IV – ANALYTICAL CHEMISTRY (Revised syllabus under semester system with effect from 2020 admission)

#### SYLLABUS AND SCHEME OF EXAMINATION

Course No and Title		Hours per week		Duration of ESA	Marks for CA	Marks for ESA	Total Marks
		L	P				
<b>SEMESTER I*</b>							
CL 211	Inorganic Chemistry I	5		3	25	75	100
CL 212	Organic Chemistry I	5		3	25	75	100
CL 213	Physical Chemistry I	5		3	25	75	100
CL 214	Inorganic Chemistry Practicals I		3	(To be continued in Semester II)			
CL 215	Organic Chemistry Practicals I		3	(To be continued in Semester II)			
CL 216	Physical Chemistry Practicals I		4	(To be continued in Semester II)			
<b>Total marks for Semester I</b>							<b>300</b>
*Distribution of teaching hours/week: Theory–15 hours, Practical's –10 hours							
<b>SEMESTER II*</b>							
CL 221	Inorganic Chemistry II	5		3	25	75	100
CL 222	Organic Chemistry II	5		3	25	75	100
CL 223	Physical Chemistry II	5		3	25	75	100

CL 214	Inorganic Chemistry Practicals II		3	6	25	75	100
CL 215	Organic Chemistry Practicals II		3	6	25	75	100
CL 216	Physical Chemistry Practicals II		4	6	25	75	100
<b>Total marks for Semester II</b>							<b>600</b>
*Distribution of teaching hours/week: Theory–15 hours, Practical’s –10 hours							
<b>SEMESTER III*</b>							
CL 231	Inorganic Chemistry III	5		3	25	75	100
CL 232	Organic Chemistry III	5		3	25	75	100
CL 233	Physical Chemistry III	5		3	25	75	100
CL 234	Inorganic Chemistry Practicals II		3	(To be continued in Semester IV)			
CL 235	Organic Chemistry Practicals II		3	(To be continued in Semester IV)			
CL 236	Physical Chemistry Practicals II		4	(To be continued in Semester IV)			
<b>Total marks for Semester III</b>							<b>300</b>
*Distribution of teaching hours/week: Theory–15 hours, Practical’s –10 hours							
<b>SEMESTER IV*</b>							
CL 241	Chemistry of Advanced Materials	5		3	25	75	100
CL 242	Applied Analytical Chemistry	5		3	25	75	100
CL 234	Inorganic Chemistry Practicals II		3	6	25	75	100
CL 235	Organic Chemistry Practicals II		3	6	25	75	100
CL 236	Physical Chemistry Practicals II		4	6	25	75	100
CL 243 (a)	Dissertation**					50	50
CL 243 (b)	Visit to R&D Centre					5	5
Comprehensive viva-voce						45	45
<b>Total marks for Semester IV</b>							<b>600</b>
<b>Grand Total (for semesters I – IV)</b>							<b>1800</b>
*Distribution of teaching hours/week: Theory–10 hours, Practical’s –10 hours , 5 hours for discussion on project							

\*\* 10 marks out of the 50 marks for dissertation will be for dissertation viva-voce. The remaining 40 marks is to be distributed as follows  
Introduction to the work/ Statement of the Problem – 5, Review of Literature – 5  
Materials and Methods – 5, Results and Discussion – 15, Language and style of presentation – 2, References – 3, Quality and Innovation – 5.

## **Programme Specific Outcomes**

- PSO 1 Develop a better understanding of the current chemical principles, methods and theories with the ability to critically analyse at an advanced level.
- PSO 2 Acquire solid knowledge of classical and modern experimental techniques and interpretation of results; thereby acquire the ability to plan and carry out independent projects
- PSO 3 Develop the qualities of time management and organization, planning and executing experiments.
- PSO 4 Have a good level of awareness of the problems associated with health, safety and environment
- PSO 5 Understand how chemistry relates to the real world and be able to communicate their understanding of chemical principles to a lay audience and as well apply the knowledge when situation warrants.
- PSO 6 Learn to search scientific literature and databases, extract and retrieve the required information and apply it in an appropriate manner
- PSO 7 Demonstrate proficiency in undertaking individual and/or team-based laboratory investigations using appropriate apparatus and safe laboratory practices.
- PSO 8 develop analytical solutions to a variety of chemical problems identified from application contexts; critically analyse and interpret qualitative & quantitative chemical information's.
- PSO 9 Set the scene to make use of the wide range of career options open to chemistry graduates.
- PSO 10 achieve an understanding and appreciation of the crucial role of analytical chemistry and its impacts on life, environmental and industrial processes

**M.Sc. PROGRAMME IN BRANCH III – CHEMISTRY**  
(Revised syllabus Under Semester System w.e.f. 2020 Admission)

**SEMESTER I**

**CL 211 INORGANIC CHEMISTRY I**

**Total 90 h**

<b>CO No.</b>	<b>Expected Course Outcomes</b> <i>Upon completion of this course, the students will be able to</i>	<b>Cognitive Level</b>	<b>PSO No.</b>
1.	employ crystal field theory in analysing the splitting of d orbitals in octahedral, tetragonal, square planar, tetrahedral, trigonal bipyramidal and square pyramidal fields, calculate Crystal Field Stabilization Energy and Interpret Octahedral Site Stabilization Energy.	Ap, An U	1
2.	apply Jahn-Teller theorem and demonstrate evidence for JT effect, static and dynamic JT effect.	Ap	1
3.	illustrate MOT for octahedral and tetrahedral complexes with and without pi bonds and construct MO diagrams.	An C	1
4.	critically evaluate data from a variety of analytical chemistry techniques and apply knowledge of the statistical analysis of data.	Ap, E	1, 2
5.	interpret complexometric titrations, redox titrations, gravimetric titrimetry and titrations in non-aqueous solvents.	E, U	1, 2
6.	apply TG, DTA and DSC in the study of metal complexes.	Ap, An	1, 2
7.	explain the functioning of the frontier materials in inorganic chemistry like Solid Electrolytes, Solid oxide fuel cells, Rechargeable battery materials, Molecular materials and fullerenes.	U	1, 4, 6
8.	explain the preparation, properties and structure of isopoly acids of Mo, W and V and heteropoly acids of Mo and W.	U	1
9.	explain preparation and properties of xenon fluorides, and noble gas compounds, aluminosilicates, zeolites and silicones and identify the importance of shape selectivity.	U	1
10.	identify the chemical processes occurring naturally in earth's atmospheric, aquatic and soil environments and evaluates the impacts of human perturbations to these processes.	An, E	4

PSO–Programme Specific Outcome

Cognitive Level: R–Remember  
An–Analyse

CO–Course Outcome

U–Understanding Ap–Apply  
E–Evaluate C–Create

<b>Module</b>	<b>Course Description</b>	<b>No. of Hrs</b>	<b>CO No.</b>
<b>1.0</b>	<b>Coordination chemistry-I: Theories of metal complexes</b>	<b>18</b>	
1.1	Crystal field theory: Splitting of d orbitals in octahedral, tetragonal, square planar, tetrahedral, trigonal bipyramidal and square pyramidal fields.	4	1
1.2	Jahn-Teller theorem, evidence for JT effect, static and dynamic JT effect.	2	2
1.3	Crystal Field Stabilization Energy. CFSE for $d^1$ to $d^{10}$ systems. Octahedral Site Stabilization Energy. Factors affecting the splitting parameter.	4	1
1.4	Spectrochemical series. Evidence of covalency in Metal-Ligand bond, introduction to Ligand field theory.	2	1
1.5	Molecular Orbital Theory. Sigma and pi bondings in complexes. MO diagrams of octahedral and tetrahedral complexes with and without pi bonds.	4	3
1.6	Experimental evidence of pi bond on the stability of sigma bond. Nephelauxetic effect.	2	3
<b>2.0</b>	<b>Analytical principles</b>	<b>18</b>	
2.1	Evaluation of analytical data: Accuracy and precision. Standard deviation, variance and coefficient of variation. Student 't' test, 'Q' test, and 'F' test. Confidence limits.	2	4
2.2	Errors: Classification, distribution, propagation, causes and minimization of errors. Significant figures and computation rules.	2	4
2.3	Correlation analysis: Scatter diagram. Correlation coefficient, r. Calculation of r by the method of least squares.	2	4
2.4	Volumetric methods: Classification of reactions in volumetry. Theory of indicators.	2	4
2.5	Complexometric titrations: Titration using EDTA-direct and back titration methods. Precipitation titrations. Redox titrations.	4	5
2.6	Titration in non-aqueous solvents. Organic reagents used in gravimetry: Oxine, dimethylglyoxime and cupferron.	2	5
2.7	Applications of TG, DTA and DSC in the study of metal complexes.	4	6
<b>3.0</b>	<b>Frontiers in Inorganic Chemistry</b>	<b>18</b>	
3.1	Solid Electrolytes: Mixed oxides, cationic, anionic solid electrolytes, mixed ionic-electronic conductors,	4	7
3.2	Solid Oxide Fuel Cells (SOFC), Rechargeable battery	3	7

	materials.		
3.3	Solid state chemistry of metal nitrides and fluorides, chalcogenides, intercalation chemistry and metal-rich phases.	4	7
3.4	Inorganic pigments, Inorganic phosphors.	3	7
3.5	Molecular materials and fullerides, basic idea of molecular materials chemistry like One dimensional metals, Molecular magnets and Inorganic liquid crystals.	4	7
<b>4.0</b>	<b>Isopoly &amp; Heteropoly acids, Silicon-Oxygen compounds, Xenon compounds</b>	<b>18</b>	
4.1	Isopoly: Preparation, properties and structure of isopoly acids of Mo, W and V.	4	8
4.2	Heteropoly acids: Heteropoly acids of Mo and W. Keggin Structure, Keggin anions, Polyoxometalates .	5	8
4.3	Silicon-oxygen compounds: Aluminosilicates, Zeolites as microporous materials and molecular sieves, Silicones and Polysiloxanes.	5	9
4.4	Xenon fluorides, Structure of XeF <sub>2</sub> (MO theory only), Perxenate ion, Organo xenon compounds, Coordination compounds of Xenon.	4	9
<b>5.0</b>	<b>Chemistry of Natural Environmental Processes</b>	<b>18</b>	
5.1	Chemistry of processes in atmosphere: Composition of the atmosphere. Automobile pollutants and the catalytic converter. Photochemical smog. Chemistry of the stratosphere. Catalytic destruction of ozone. Depletion of the ozone layer. Hazards of common air pollutants on the human health.	6	10
5.2	Chemistry of processes in hydrosphere: The hydrologic cycle. Cycling and purification. The unique properties of water. Acid-base properties.	6	10
5.3	Chemistry of processes in Lithosphere: Redox status in soil. pE, pH predominance diagrams for redox sensitive elements Fe and Cr. Acidity in soil materials. Acid neutralization capacity and the quantification of the soil acidity. Ion speciation in soil solution. Cation exchange capacity and exchange phase composition.	6	10

## References

1. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, John Wiley and Sons, 6th edition, 1999.
2. J. E. Huheey, Inorganic Chemistry- Principles of Structure and Reactivity, Harper Collins College Publishing, 4th edition, 2011.
3. K. F. Purcell and J. C. Kotz, Inorganic Chemistry, Saunders, 1977.
4. S. F. A. Kettle, Physical Inorganic Chemistry, Oxford University Press, 1st edition, 1998.

5. Shriver and Atkins, Inorganic Chemistry, Oxford University Press, 2010.
6. A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longman, 5th edition, 1989.
7. D. A. Skoog, D. M. West and F. J. Holler, Fundamentals of Analytical Chemistry, Saunders College Publishing, 7th edition, 1996.
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9. F.A. Cotton, Chemical Applications of Group Theory, Wiley Eastern, 3rd edition, 2009.
10. A. S. Kunju and G. Krishnan, Group Theory and its Applications in Chemistry, PHI Learning, 2010.
11. R. L. Carter, Molecular Symmetry and Group Theory, John Wiley & Sons, 1998.
12. E. James Girard, Principles of Environmental Chemistry, Jones and Bartlett Publishers, 3rd Edition, 2013
13. H.V. Jadhav, Elements of Environmental Chemistry, Himalya Publication House, 2010.
14. E. Michael Essington, Soil and water Chemistry, CRC Press, 2nd edition, 2015.

### CL 212 ORGANIC CHEMISTRY I

**Total 90 h**

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	write down the IUPAC name of polycyclic, spirocyclic and heterocyclic compounds and draw the structures from the IUPAC name of these compounds.	U	1
2.	determine R and S, P and M, E and Z configuration of compounds with chiral centres, biphenyls, allenes, spiranes and draw the configurations in dash and wedge formula, or zig –zag configurations.	E	1
3.	detect prochirality in a compound and explain relevance of prochirality .	U, An	1
4.	explain chiral centre, chiral axis and chiral plane with examples, stability of conformations, stereoselective and stereospecific reactions.	An, E	1
5.	calculate Cotton effect of a compound from its structure and configuration.	E	1
6.	explain different methods for generation of free radical and different types of free radical reactions- Predict the products in a free radical reaction.	U, An	1
7.	describe different types mechanism of substitution, elimination, hydrolysis and addition reactions.	Ap	1
8.	differentiate the rate, mechanism and stereochemistry influenced by solvent, substrate structure, intermediate stability.	An	1
9.	predict the products or reactants or reagents in selected	U	1



	types of reactions.		
10.	design the mechanism of selected reactions.	C	1

Module	Course Description	No. of Hrs	CO No.
<b>1.0</b>	<b>Stereochemistry</b>	<b>18</b>	
1.1	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.	3	1
1.2	Introduction to molecular symmetry and chirality, axial chirality, planar chirality and helicity, relative configuration, stereochemical nomenclature, R and S, E and Z (use only 3D formula, dash and wedge).	3	2
1.3	Prostereoisomerism, stereotopicity & stereoprojections. Prochiral centre and prochiral faces - Pro R and Pro S, Re face and Si face, Importance of prochirality in biological systems.	3	3
1.4	Axial stereochemistry: atropisomerism and its designation - biphenyls, allenes, spiranes- M and P configurations. Stereoselectivity: enantioselectivity, diastereoselectivity & stereoconvergence. Stereospecific and stereoselective synthesis.	2	4
1.5	Application of Cram's rule, Felkin-Ahn model. Basic introduction to chiral separation methods and estimation of enantiomeric excess, chiral pool, chiral auxiliary, chiral reagents, BINAP.	2	4
1.6	Conformational analysis of substituted cyclohexane, decalin and biased systems. Effect of conformation on reactivity of cyclohexanes.	2	4
1.7	Introduction to ORD, CD - their application in assigning configuration. Sector rules such as octant and axial haloketone rules. Cotton effect.	2	5
1.8	Importance of stereochemistry in drugs-Pthalidomide, Dopa, Ibuprofen.	1	2
<b>2.0</b>	<b>Reactions Involving Free Radicals, Nitrenes and Carbenes</b>	<b>18</b>	
2.1	Free radical Structure, stability and reactivity, Preparation of free radicals- Triphenyl methyl, TEMPO, AIBN, Dibenzoyl peroxide, NBS, Tributyl Tinhydride and AIBN.	5	6
2.2	Free radical reactions- Chlorination of alkane, addition of HX, SRN1 mechanism, Gomberg reaction, Pschorr	5	6

	ring closure, Hunsdieckers reaction, Ullman reaction, Kolbes electrolytic reaction.		
2.3	Acyloin condensation, Alkyne coupling reactions,. Mc Murry reaction, Pinacol coupling reaction.	3	6
2.4	Structure, formation, stability and reactions of carbenes and nitrenes (rearrangement reactions excluded).	5	6
<b>3.0 Nucleophilic substitution reaction</b>			
<b>3.0</b>	<b>Nucleophilic substitution reaction</b>	<b>18</b>	
3.1	Nucleophilic substitution at $sp^3$ carbon - $S_N1$ and $S_N2$ mechanisms. Competition between $S_N1$ and $S_N2$ reactions. Walden inversion, stereochemistry. Effect of solvent, leaving group and substrate structure on rates of $S_N1$ and $S_N2$ substitutions.	4	7, 8
3.2	Neighbouring group participation, Nonclassical carbocations, $S_N1'$ , $S_N2'$ , $S_Ni$ mechanisms.	3	7, 8
3.3	Mitsunobu reaction, Mechanism of esterification and ester hydrolysis-acid catalysed and base catalysed reactions.	3	7, 8
3.4	Aromatic Substitution reactions - Electrophilic substitution: mechanism and evidence- Reactions involving nitrogen, sulphur, carbon, halogen and oxygen electrophiles. Reimer-Tiemann, Vilsmeier-Haack reactions.	4	7, 8
3.5	Directive and rate controlling factors in aromatics with one or more substituents. Aromatic Nucleophilic Substitution reactions - $S_N1$ , $S_NAr$ , Elimination - Addition reactions (benzyne), evidence with examples, Chichibabin reaction.	4	7, 8
<b>4.0 Addition Reactions</b>			
<b>4.0</b>	<b>Addition Reactions</b>	<b>18</b>	
4.1	Addition of $H_2O$ , $X_2$ , $HX$ , and boranes to $C=C$ systems, (hydroboration followed by oxidation only), stereo aspects, effect of substituents on the rate of additions, iodo lactonisation, one or two examples.	5	9, 10
4.2	Prilezhaev reactions. Cis and trans hydroxylation of cycloalkenes. Nucleophilic addition to activated $C=C$ systems. Michael addition and Robinson Annulation.	5	9, 10
4.3	Aldol condensation (normal, crossed and directed), evidence for normal Aldol condensation. Stork enamine, Cannizzaro, Perkin, Ritter, Stobbe, Knoevenagel, Darzen, Reformatsky and benzoin condensations.	4	9, 10
4.4	Grignard, Mannich, Thorpe reactions, Dieckmann condensation, sulfur ylides (stabilized and unstabilised)-direct and conjugated addition to carbonyl. (Mechanisms expected for all reactions)	4	9, 10

<b>5.0</b>	<b>Elimination Reactions</b>	<b>18</b>	
5.1	Elimination reactions leading to C=C bond formation and their mechanisms. E <sub>1</sub> , E <sub>2</sub> and E <sub>1</sub> cb mechanisms.	5	9, 10
5.2	Stereo aspects of C=C bond formation in cyclic and acyclic systems. Regioselectivity in elimination, Hoffmann and Saytzeff elimination. Effect of basicity, temperature, leaving group and substrate structure.	5	9, 10
5.3	Elimination vs substitution, Shapiro reaction, Peterson and Julia olefination, Wittig and Wittig - Horner reaction-stereochemistry.	4	9, 10
5.4	Cis elimination-esters, sulfoxides, selenoxides, Chugaev reaction, Cope elimination, Stereo aspects of cis elimination - cyclic bicyclic systems Sodium in liquid ammonia and Lindlars catalyst in conversion of alkynes to alkenes.	4	9, 10

## References

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6. Maya Shankar Singh, Reactive Intermediates in Organic Chemistry-Structure, mechanism and reactions, Wiley-VCH, 2012.
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9. F. A. Carey and R. S. Sundberg, Advanced organic chemistry, Parts A and B," Fifth Edition, Springer, 2008.
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 18. R. O. C. Norman and J. M. Coxon, Principles of Organic Synthesis CRC press, 1993.

### CL 213 PHYSICAL CHEMISTRY I

Total 90 h

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	outline the development of quantum mechanics and its tools and apply them in determining the wave functions and energies of moving particles.	U, Ap, An	1
2.	recognize the nature of adsorption and propose theories and choose theoretical and instrumental methods of measurements of surface property.	U, Ap, An	1
3.	understand theory and mechanism of catalytic action.	U	1
4.	correlate thermodynamic properties and apply them in systems.	U, Ap, An	1
5.	understand theories, mechanism and, kinetics of reactions and solve numerical problems.	U, Ap, An	1
6.	identify point groups and construct character table and predict hybridisation and spectral properties of molecules.	U, Ap, C	1

Module	Course Description	No. of Hrs	CO No.
<b>1.0</b>	<b>Quantum Chemistry I</b>	<b>18</b>	
1.1	Classical mechanics and its limitations –need of quantum mechanics, de Broglie relation and its experimental proof, uncertainty principle and its consequences.	1	1
1.2	Postulates of quantum mechanics: State function postulate: Born interpretation of the wave function, well behaved functions, orthonormality of wave functions.	2	1
1.3	Operator postulate: Operator algebra, linear and nonlinear operators, Laplacian operator, commuting and non-commuting operators, Hermitian operators and their properties.	2	1
1.4	Eigen value postulate: eigen value equation, eigen functions of commuting operators.	2	1
1.5	Expectation value postulate. Postulate of time Dependent Schrödinger equation, Quantization of angular momentum, quantum mechanical operators corresponding to angular momenta ( $L_x$ , $L_y$ , $L_z$ and $L^2$ ) - expression for ( $L_x$ , $L_y$ , $L_z$ and $L^2$ ) in polar coordinates.	2	1
1.6	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	3	1

	dimensional box three-dimensional box and cubical box-degeneracy.		
1.7	Particle with finite potential barriers, one potential barrier, two finite barriers. Quantum mechanical tunnelling (Qualitative concept only).	3	1
1.8	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 of wave functions, Harmonic oscillator model and molecular vibrations.	3	1
<b>2.0</b>	<b>Surface Chemistry and Catalysis</b>	<b>18</b>	
2.1	The gas-solid interphase, types of adsorption. Heat of adsorption and its determination, differences between chemisorptions and physisorption.	2	2
2.2	Adsorption isotherms - Freundlich and Langmuir isotherms. Thermodynamic and statistical derivation of Langmuir adsorption isotherm. Multilayer adsorption-the BET theory and Harkins-Jura theory.	3	2
2.3	Determination of surface area of solids-Harkins-Jura absolute method, point B method, Langmuir method and BET method.	2	2
2.4	Adsorption from solutions: Gibb's adsorption equation and its verification. Adsorption with dissociation. Adsorption with interaction between adsorbate molecules.	2	2
2.5	Different types of surfaces, properties of surface phase. Thermodynamics of surface. Surface tension of solutions. Surfactants and micelles. Examination of surfaces- Low Energy Electron Diffraction (LEED).	2	2
2.6	Photoelectron spectroscopy, ESCA, scanning probe microscopy, Auger electron spectroscopy, SEM and TEM.	3	2
2.7	Surface films-different types, surface pressure and its measurement.	2	3
2.8	Catalysis: Mechanism and theories of homogeneous and heterogeneous catalysis. Bimolecular surface reactions. Langmuir-Hinshelwood mechanism. Enzyme catalysis.	2	3
<b>3.0</b>	<b>Classical Thermodynamics</b>	<b>18</b>	
3.1	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.	2	4
3.2	Maxwell relations and significance, temperature	2	4

	dependence of free energy, Gibbs Helmholtz equation and its applications.		
3.3	Partial molar quantities - Chemical potential, Gibbs Duhem equations, determination of partial molar properties-partial molar volume and partial molar enthalpy.	2	4
3.4	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.	3	4
3.5	Activity, activity coefficients, dependence of activity on temperature and pressure. Determination of activity and activity coefficients of electrolytes and non-electrolytes.	2	4
3.6	Thermodynamics of mixing, Duhem-Margules equation, Konowaloff's first and second laws, Henry's law, excess thermodynamic functions-determination of excess enthalpy and volume.	4	4
3.7	Chemical affinity and thermodynamic functions, effect of temperature and pressure on chemical equilibrium-van't Hoff reaction isochore and isotherm.	3	4
<b>4.0</b>	<b>Chemical kinetics</b>	<b>18</b>	
4.1	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.	3	5
4.2	Theories of unimolecular reactions - Lindemann theory. Lindemann-Hinshelwood mechanism, qualitative idea of RRKM theory.	2	5
4.3	Kinetics of complex reactions- Parallel reactions, opposing reactions, consecutive reactions and chain reactions, steady state treatment, kinetics of $H_2-Cl_2$ and $H_2-Br_2$ reactions, decompositions of ethane, acetaldehyde and $N_2O_5$ . Rice-Herzfeld mechanism, branching chain reactions, Hinshelwood mechanism of chain reactions and explosion.	4	5
4.4	Fast reactions: Relaxation method, relaxation spectrometry, flow method, shock method, fast mixing method, field jump method, pulse method, flash photolysis and NMR method.	3	5
4.5	Reactions in solution: Factors affecting reaction rates in solutions, effect of dielectric constant and ionic strength, cage effect, Bronsted-Bjerrum equation.	3	5
4.6	Kinetic effects: Primary and secondary kinetic salt effect, influence of solvent on reaction rates,	3	5

	significance of volume of activation, linear free energy relationship. Hammett equation and Taft equation.		
<b>5.0</b>	<b>Molecular symmetry</b>	<b>18</b>	
5.1	Symmetry elements and symmetry operation. Matrix representation of symmetry operations. Block factored matrices, Character of a matrix. Conditions for a set of elements to form a group. Point groups and their systematic identification.	2	6
5.2	Multiplication of operations. Group multiplication table. Similarity transformation and classification of symmetry operation, Matrix representation of point group. Reducible and Irreducible representations.	3	6
5.3	The Great Orthogonality Theorem. Rules derived from GOT (proof not required).	1	6
5.4	Setting up of character table of $C_{2v}$ , $C_{3v}$ and $C_{2h}$ groups. Direct product representations. Reduction formula, reduction of reducible representation to IRs. Transformation properties of atomic orbitals. Molecular symmetry and optical activity.	4	6
5.5	Applications of character tables: Hybridisation-identification of atomic orbitals taking part in hybridisation of triangular planar, square planar, trigonal bipyramidal, square pyramidal and tetrahedral molecules.	4	6
5.6	Spectroscopy-Determination of number of active IR and Raman lines taking simple molecules belongs to $C_{2v}$ , $C_{3v}$ and $D_{4h}$ point groups as example.	4	6

### References

1. D. A. McQuarrie, Quantum Chemistry, University Science Books, 2008.
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24. L.H. Hall, Group Theory and Symmetry in Chemistry, McGraw Hill, 1969.
25. V. Ramakrishnan, M.S. Gopinathan, Group Theory in Chemistry, Vishal Publications, 1992.

### CL 214 INORGANIC CHEMISTRY PRACTICALS – I

**Total 125 h**

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	interpret data from an experiment, including the construction of appropriate graphs and the evaluation of errors.	U, E	3, 7, 8
2.	estimate volumetrically the concentration of Zn, Mg and Ni using EDTA and the volumetric estimation of Fe.	Ap, An	7, 8
3.	estimate volumetrically the hardness of water and concentration of Ca in water samples using EDTA.	Ap, An	7, 8
4.	estimate colorimetrically the concentration of Chromium – (using Diphenyl carbazide), Iron (using thioglycollic acid), Iron (using thiocyanate), Manganese (using potassium periodate), Nickel (using dimethyl glyoxime).	Ap, An	7, 8
5.	carry out the preparation of the metal complexes Potassium trioxalatochromate (III), Tetraammoniumcopper (II) sulphate, Hexamminecobalt (III) chloride.	Ap	7, 8
6.	record the UV spectra, IR spectra, magnetic susceptibility, TG, DTA and XRD of the complexes prepared.	Ap, An	2, 7, 8



Module	Course Description	No. of Hrs	CO No.
1.	Volumetric estimation using EDTA - Zn, Mg, Ni (back titration), Hardness of water, Ca (using murexide).	25	1, 2, 3
2.	Determine the hardness of water and the concentration of Ca in water samples using EDTA.	20	1, 2, 4
3.	Volumetric estimation of Fe.	10	1, 2, 3
4.	Colorimetric estimation of Chromium – (Diphenyl carbazide), Iron (thioglycollic acid), Iron (thiocyanate), Manganese (potassium periodate), Nickel (dimethyl glyoxime).	35	1, 2, 5
5.	Preparation of metal complexes - Record UV, IR, magnetic susceptibility, TG, DTA and XRD of the complexes prepared (a) Potassium trioxalatochromate (III) (b) Tetraammoniumcopper (II) sulphate (c) Hexamminecobalt (III) chloride	35	1, 2, 6, 7

### References

1. A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longman, 4th edition, 1978.
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3. D. A. Skoog and D. M. West, Analytical Chemistry: An Introduction, Saunders College Publishing, 4th edition, 1986.
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### CL 215 ORGANIC CHEMISTRY PRACTICALS – I

Total 125 h

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	interpret data from an experiment, including the construction of appropriate graphs and the evaluation of errors.	U, E	3, 7, 8
2.	determine the correct method for separation of a binary mixture and make the separated compounds in pure form.	An, E	2, 7, 8
3.	develop thin layer chromatogram of a compound and determine its purity.	C	2, 7, 8
4.	separate two compounds by column chromatography.	An	2, 7, 8
5.	utilize the synthetic procedures and reagents to convert a compound into another. Differentiate the products by spectroscopic methods.	An	2, 7, 8
6.	use green chemical principles in the synthesis.	Ap	2, 4
7.	solve GC MS and LC MS of a compound to ascertain purity and identity, apply the basic principles learned	Ap, E	2, 7

	through a practical example
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Module	Course Description	No. of Hrs	CO No.
1.	<p><b>Separation and identification of organic compounds-</b></p> <p>a. Quantitative wet chemistry separation of a mixture of two components by solvent extraction.</p> <p>b. 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<sub>f</sub> 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<sub>f</sub> Value, Drawing - in the form of a table.</p>	30	1, 4, 5
2.	<p><b>Separation of a mixture by column chromatography (not for end semester evaluation)</b></p> <p>a. Malachite green and methylene blue,</p> <p>b. o-nitroaniline and p-nitroaniline.</p>	20	1, 4
3.	<p><b>Preparation of compounds by two stages.</b></p> <ul style="list-style-type: none"> <li>▪ Recording UV, IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and EI mass spectra of synthesized compounds.</li> <li>▪ Record and interpret GC-MS and LC-MS of the purified compound.</li> <li>▪ TLC analysis-Stage 1 reactants and products on TLC plate 1 and stage 2 reactants and products on plate 2).</li> <li>▪ Record TLC in standard format as in separation.</li> </ul> <p><i>All preparations must be restricted to 1 g level</i></p> <p><b>I. Nitration</b></p> <p>(1) Acetanilide → p-nitroacetanilide → p-nitroaniline</p> <p>(2) Methylbenzoate → methyl m-nitrobenzoate → m-nitrobenzoic acid</p> <p><b>II. Bromination</b></p> <p>(3) Acetanilide → p-bromoacetanilide → p-bromoaniline <i>using CAN for bromination</i></p> <p><b>III. Aldol condensation- Synthesis of heterocycles.</b></p> <p>(4) Benzaldehyde → Dibenzylideneacetone → 1,5-Diphenyl-3-styryl-2-pyrazoline</p> <p><b>IV. Diazocoupling</b></p> <p>(5) Aniline → Diazoaminobenzene → p-aminoazobenzene</p> <p><b>V. Rearrangement</b></p> <p>(6) Pthalic anhydride → Pthalimide → Anthranilic acid</p> <p><b>VI. Synthesis of Dyes</b></p> <p>(7) N,N-Dimethylaniline → N,N-dimethyl-4-</p>	75 <i>(average 12.5 hrs for preparation and analysis of each)</i>	1, 5, 6, 7

	nitrosoaniline → methylene blue		
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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

1. B. S. Furniss, Vogel's text book of practical organic chemistry, 5th Edition, Longman, 1989.
2. D. L. Pavia, G. M. Lampman, G. S. Kriz and R. G. Engel, A microscale approach to organic laboratory techniques," Wadsworth Publishing, 5th Edition, 2012.
3. R. K. Bansal, Laboratory manual of organic Chemistry, Wiley Eastern, 1994.
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7. P. F Shalz, Journal of Chemical Education, 1996, 173: 267.
8. Monograph on green laboratory experiments, DST, Government of India, pp 1-79.
9. For spectral data of organic compounds, see:  
[http://sdfs.riodb.aist.go.jp/sdfs/cgi-bin/direct frame top.cgi](http://sdfs.riodb.aist.go.jp/sdfs/cgi-bin/direct%20frame%20top.cgi).

## CL 216 PHYSICAL CHEMISTRY PRACTICALS – I

**Total 125 h**

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	interpret data from an experiment, including the construction of appropriate graphs and the evaluation of errors.	U, E	3, 7, 8
2.	construct the Freundlich and Langmuir isotherms for adsorption of acetic/oxalic acid on active charcoal/alumina and determine the concentration of acetic/ oxalic acid	C, Ap, An	7, 8
3.	determine the rate constant, Arrhenius parameters, rate constant and concentration using kinetics	Ap	7, 8
4.	construct the phase diagram and determine the composition of an unknown mixture	Ap, An	7, 8
5.	construct the ternary phase diagram of acetic acid chloroform-water system and out the procedure in an unfamiliar situation to find out the composition of given homogeneous mixture.	C, Ap, An	7, 8
6.	construct the tie-line in the ternary phase diagram of acetic acid chloroform-water system	C, Ap, An	7, 8
7.	determine distribution coefficient using distribution law.	Ap	7, 8
8.	determine the equilibrium constant employing the	Ap	7, 8

	distribution law.		
9.	determine the coordination number of $\text{Cu}^{2+}$ in copper-ammonia complex.	Ap	7, 8
10.	determine $K_f$ of solid solvent, molar mass of non-volatile solute, mass of solvent and composition of given solution	Ap, An	7, 8
11.	determine $K_T$ of salt hydrate, molar mass of solute, mass of salt hydrate and composition of given solution.	Ap, An	7, 8
12.	determine surface tension and parachor of liquids.	Ap	7, 8
13.	ascertain the relationship between surface tension with concentration of a liquid and use this to find out the composition of given homogeneous mixture.	Ap, An	7, 8
14.	determine the concentration of given strong acid/alkali.	Ap, An	7, 8
15.	determine the heat of ionisation of acetic acid.	Ap, An	7, 8
16.	determine the heat of displacement of $\text{Cu}^{2+}$ by Zn.	Ap, An	7, 8

Module	Course Description	No. of Hrs	CO No.
1.	<b>Adsorption</b> a) Freundlich and Langmuir isotherms for adsorption of acetic/oxalic acid on active charcoal/ alumina. b) Determination of concentration of acetic/ oxalic acid.	15	1, 2,
2.	<b>Kinetics</b> a) Determination of rate constant of acid hydrolysis of methyl acetate. b) Determination of Arrhenius parameters. c) Determination of concentration of given acid. d) Determination of rate constant of the saponification of ethyl acetate and evaluation of Arrhenius parameters. e) Determination of rate constant of reaction between $K_2S_2O_8$ and KI.	15	1, 3
3.	<b>Phase rule</b> <b>I. Solid-liquid equilibria</b> a) Construction of phase diagram and determination of the composition of unknown mixture (naphthalene/ biphenyl, naphthalene/ benzophenone, naphthalene/ diphenyl amine). b) Construction of phase diagram with simple eutectic - naphthalene/ metadinitrobenzene. <b>II. Partially miscible liquid pairs</b> a) CST of phenol-water system. b) 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.	16	1, 3, 4, 5, 6
4.	<b>Distribution law</b> a) Distribution coefficient of ammonia between hexane and water. Determination of equilibrium constant of copper - ammonia complex by partition method or coordination number of $Cu^{2+}$ in copper-ammonia complex. b) Distribution coefficient of benzoic acid between toluene and water. c) Distribution coefficient of iodine between hexane and water. d) Determination of the equilibrium constant of the reaction $KI + I_2 \rightleftharpoons KI_3$ and hence the concentration of given KI in hexane and water.	20	1, 7, 8, 9
5.	<b>Dilute Solutions</b> a) Determination of $K_f$ of solid solvent, molar mass of non-volatile solute, mass of solvent and composition	17	1, 10

	<p>of given solution (Solvent-Naphthalene/ Biphenyl/ Benzophenone etc. Solute-Naphthalene/ Biphenyl/ Diphenylamine etc.)</p> <p>b) Determination of vant Hoff's factor for benzoic acid in Naphthalene.</p> <p>c) Determination of atomicity of sulphur.</p>		
6.	<p><b>Transition temperature</b></p> <p>Determination of <math>K_T</math> of salt hydrate, molar mass of solute, mass of salt hydrate and composition of given solution (Solvent - <math>\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}</math>/<math>\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}</math>, Solutes glucose, sucrose, urea).</p>	12	1, 11
7.	<p><b>Surface tension</b></p> <p>a) Determination of surface tension of various liquids (water - ethanol, water - glycerol, water - sorbitol, nitrobenzene-toluene) by Stalagmometric method (drop number/ drop weight) and by Capillary rise method.</p> <p>b) Determination of parachors of molecules and various groups.</p> <p>c) Determination of concentration of a mixture.</p> <p>d) Determination of surface tension and parachor of liquids using double capillary method.</p> <p>e) Variation of surface tension with concentration. Unknown concentration of a mixture. Interfacial tension.</p> <p>f) Determination of surface excess and area per molecule.</p>	15	1, 12, 13
8.	<p><b>Thermochemistry</b></p> <p>a) Determination of the concentration of given strong acid/alkali.</p> <p>b) Thermometric titration of NaOH vs standard HCl.</p> <p>c) Heat of displacement of <math>\text{Cu}^{2+}</math> by Zn.</p> <p>d) Determination of the heat of ionisation of acetic acid.</p>	15	1, 14, 15, 16

### References

1. V. D. Athawal, Experimental Physical Chemistry, New Age International, 1st edn., 2001.
2. B. P. Levitt and J.A. Kitchener, Findlay's Practical Physical Chemistry, Longmans, London, 9th edn., 1973.
3. J. M. Newcombe, R. J. Denaro, A. R. Rickett & R.M.W Wilson, Experiments in Physical Chemistry Pergamon, 1962.
4. A.M. James and F.E. Pichard, Practical Physical Chemistry, Longman.
5. R.C. Das & Behera, Experimental Physical Chemistry, Tata McGraw Hill, 1983.
6. B. Viswanathan, Practical Physical Chemistry, Viva Publications, 2012.
7. P.S. Sindhu, Practicals in Physical Chemistry-A Modern Approach, McMillan India, 2005.

8. D. P. Shoemaker, C. W. Garland and J. W. Nibler. Experiments in Physical Chemistry.

### Model Question Papers

#### General Instruction to question paper setters

- There will be a 15 main questions in each question paper divided into 3 sections – A, B and C
- Each of the sections A, B and C will have 5 questions each, **1 from each module**.
- Each question in Section A will have 3 sub questions (a), (b) and (c), of which the candidate has to answer any two (2 marks each).
- Each question in Section B will have 2 sub questions (a) and (b), of which the candidate has to answer any one (5 marks each).
- Candidate should answer any three out of the five questions in Section C (10 marks each).
- Section A carries a total of 20 marks, Section B carries 25 marks, and Section 3 carries 30 marks.
- The maximum marks will be 75 and the duration of the exam will be 3 hrs.

**First Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 211: INORGANIC CHEMISTRY – I**  
(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

#### SECTION A

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

1. (a) Sketch the splitting of d orbitals in a trigonal bipyramidal complex.  
(b) Which among  $\text{CN}^-$  and  $\text{NH}_3$  have a higher nephelauxetic effect? Why?  
(c) Calculate the CFSE for a  $d^4$  ion.
2. (a) Differentiate accuracy from precision.  
(b) What are metallochromic indicators? Give an example.  
(c) What is a Student t test used for?
3. (a) CdS is an yellow pigment while CdSe is red. Given reason.  
(b) What is NASICON?  
(c) What are anti-stokes phosphors?
4. (a) What are zeolites? Explain their use as water softeners?  
(b) Determine the probable structure of perxenate ion using VSEPR theory.  
(c) What are polysiloxanes? Give it structure.
5. (a) List two conditions that favour the formation of photochemical smog.  
(b) Discuss briefly a method to quantify soil acidity.

(c) How does chlorine free radicals tamper the ozone layer?

[2 × 10 = 20]

### SECTION B

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

6. (a) State and illustrate Jahn-Teller distortion.  
(b) Discuss the factors affecting the magnitude of  $\Delta_o$ .
7. (a) What is a scatter diagram? What is its significance?  
(b) Discuss briefly the principle behind EDTA titrations.
8. (a) What are SOFCs?  
(b) Briefly discuss the structure of fullerenes.
9. (a) Zeolites find applications as microporous materials and molecular sieves. Substantiate this statement.  
(b) What are isopoly acids?
10. (a) List out five unique properties of water.  
(b) Discuss on the various air pollutants and their effect on human health.

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Describe the Molecular orbital energy level diagrams for octahedral metal complexes with and without  $\pi$ -bonds.
12. Explain the utility of TG, DTA and DSC in the study of metal complexes.
13. Detail the types of solid electrolytes giving due importance to structural aspects.
14. Elaborate the properties of the heteropoly acids of Mo and W.
15. What are pourbaix diagrams? Outline its role in explaining the chemistry of processes in lithosphere.

[10 × 3 = 30]

**First Semester M.Sc. Degree Examination – Model question paper**

**Branch III – Chemistry/ Branch IV – Analytical Chemistry**

**CH/CL 212: ORGANIC CHEMISTRY – I**

(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

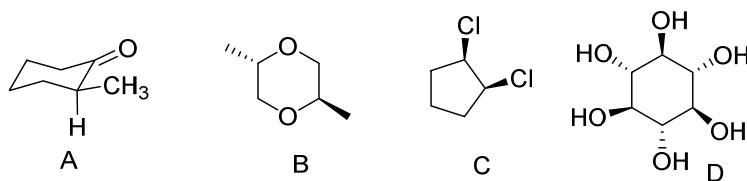
### SECTION A

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

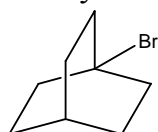
[23]



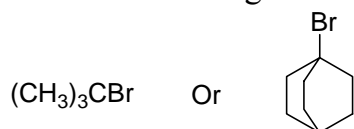
- Distinguish between conformation and configuration.
  - Draw the structure corresponding to diazabicyclo[2,2,2]octane.
  - Pick out the chiral/ achiral/ meso structures from the following.



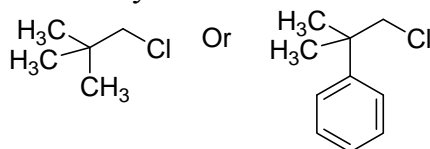
- What is AIBN?
  - Explain the peroxide effect in the addition of HBr to propene.
  - How you can synthesize the following molecule?



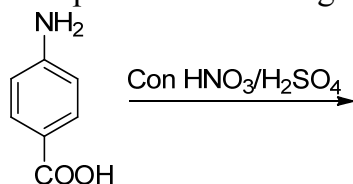
- Which of the following bromides will undergo a faster solvolysis? Explain



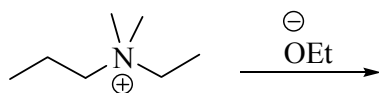
- Given below are two chlorides. Which among them will go through a faster solvolysis? Give reasons for your answer.



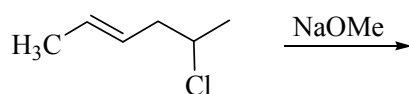
- Complete the following reaction.



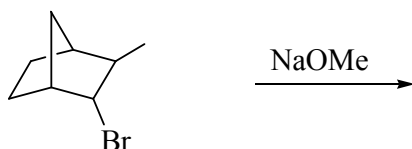
- Predict the product of the following reaction and indicate the major one. Give reasons.



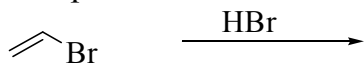
- What are the products obtained the reaction given below. Identify the major product in this case citing reasons.



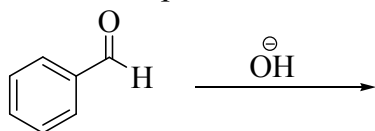
- Identify the major product in the following reaction. Substantiate your answer.



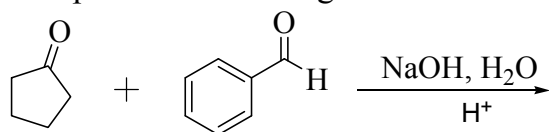
5. (a) Complete the reaction



- (b) Predict the products in the following reaction



- (c) Complete the following reaction

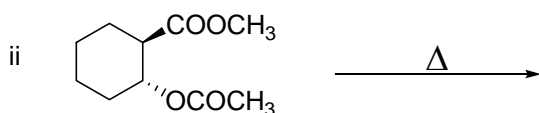
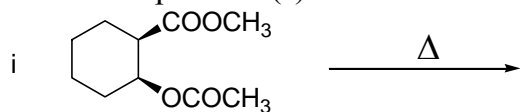


[2 × 10 = 20]

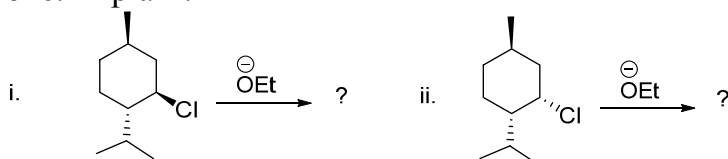
### SECTION B

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

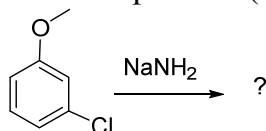
6. (a) Predict the product (s) of the following reactions



- (b) Predict the product (s) of the following reaction and indicate the major one. Explain?



7. (a) Give the product (s) with mechanism. Explain?

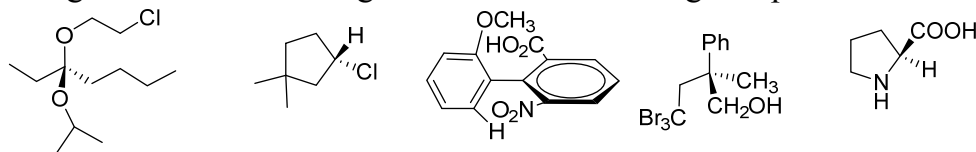


- (b) Discuss the mechanism of allylic bromination using NBS. Explain the stability of allyl radical.

8. (a) How will you convert isopropanol to n-propanol using a boron reagent? How does the addition of borane reagents to alkene differ from hydration? Illustrate with the help of an example.
- (b) Discuss benzoin condensation. What is the importance of cyanide in the

reaction?

9. (a) Assign the absolute configuration to the following compounds.



- (b) What are atropisomers? Explain why atropisomerism disappears at higher temperature?

10. (a) How does leaving group affect the rate of  $S_N^1$  and  $S_N^2$  reactions? Explain.  
(b) Give the major product obtained when methoxybenzene is nitrated.  
Discuss the directive effect with the help of resonance structures

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Discuss Cotton effect? What is octant rule? Explain ORD curve.
12. Discuss the structure, stability and reactions of carbenes. How will you distinguish between singlet and triplet carbenes by a chemical method?
13. Discuss the mechanism of  
a) Robinson Annulation                      b) Mannich reaction  
c) Thorpe reaction                            d) Ritter reaction and  
e) Darzen reaction
14. Neighbouring group participation results retention in configuration. Justify the given statement with the help of suitable examples. What is meant by anchimeric assistance?
15. Explain Wittig and Wittig –Horner reactions with stereochemistry. Compare Wittig reaction with Julia olefination.

[10 × 3 = 30]

**First Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 213: PHYSICAL CHEMISTRY – I**  
(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

### SECTION A

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

1. (a) Check whether the function  $e^{-x^2}$  is an eigen function for kinetic energy

[26]

- operator. If so what is the eigen value?
- (b) Show that the momentum of particle in 1D box is quantised.
  - (c) Write the general expression for Hermitte polynomial. Deduce first two polynomials.
2. (a) Distinguish between associative and dissociative chemisorption.
  - (b) Under what condition can multilayer adsorption become more important than monolayer adsorption?
  - (c) Explain one method of determination of surface pressure.
3. (a) Calculate  $\Delta S$  of mixing when 2 moles of  $H_2$ , 3 moles of He and 2 moles of  $O_2$  are mixed at fixed temperature assuming ideal behaviour and no chemical change.
  - (b) Write any two Maxwell's relations and give their significance.
  - (c) State 'Konowaloff's' rule.
4. (a) Give two reasons to show that conventional techniques are not suitable for the study of kinetics of fast reactions.
  - (b) Explain steady state principle?
  - (c) How volume of activation affects the reaction rate?
5. (a) Identify the symmetry elements present in the following and assign the point group  
(i)  $H_2$             (ii) HCl
  - (b) Explain improper axis of symmetry.
  - (c) Cyclic groups are abelian. Explain.

[2 × 10 = 20]

### SECTION B

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

6. (a) For a particle in 3D box with  $L_x = L_y = \frac{L_z}{2}$ , what would be the energy when  $n_x = 1$ ,  $n_y = 2$  and  $n_z = 2$  and when  $n_x = 1$ ,  $n_y = 1$  and  $n_z = 4$ . Use the calculations to explain the meaning of the term accidental degeneracy.
  - (b)  $H(x)$  is written as a power series in  $x$  as  $H(x) = \sum_{j=0}^n a_j x^j$ . Derive recursion formula.
7. (a) Write any two methods for the determination of surface area of a solid.
  - (b) Explain Langmuir-Hinshelwood mechanism of surface catalyzed reactions.
8. (a) Derive Van't Hoff isotherm. How is this useful in the study of chemical equilibria?
  - (b) Derive Gibbs-Duhem equation.
9. (a) Compare the rate constant as given by Arrhenius equation and collision

theory and show that  $E_a = E_0 + \frac{RT}{2}$

- (b) Derive the rate law for the decomposition of  $N_2O_5$ .
10. (a) Construct the group multiplication table for the symmetry operations of  $NH_3$  molecule.  
 (b) Determine the number of active IR and Raman lines in the vibrational spectrum of  $POCl_3$ .

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Set up the Schrodinger wave equation for a simple harmonic oscillator. Find the eigen functions and eigen values.
12. Explain any two instrumental techniques used for surface characterization.
13. Write a brief account of the methods for the determination of activity coefficient of electrolytes and non-electrolytes.
14. Explain chain reactions. Discuss Semionoff Henshelwood theory of branching chain reactions
15. a) Explain the hybridization scheme in  $BF_3$  molecule using group theory.  
 b) Show that the four elements of  $C_{2v}$  point groups forms 4 classes?

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$		
$A'_1$	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A'_2$	1	1	-1	1	1	-1	$R_z$	
$E'$	2	-1	0	2	-1	0	$(x, y)$	$(x^2 - y^2, xy)$
$A''_1$	1	1	1	-1	-1	-1		
$A''_2$	1	1	-1	-1	-1	1	$z$	
$E''$	2	-1	0	-2	1	0	$(R_x, R_y)$	$(xz, yz)$

[10 × 3 = 30]

## SEMESTER II

### CL 221 INORGANIC CHEMISTRY II

Total 90 h

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	obtain the term symbols of $d^n$ system and determine the splitting of terms in weak and strong octahedral and tetrahedral fields.	E	1
2.	explain the correlation diagrams for $d^n$ and $d^{10-n}$ ions in octahedral and tetrahedral fields and interprets electronic spectra of complexes.	U, E	1
3.	applies magnetic measurements in the determination of structure of transition metal complexes.	Ap	1
4.	relates crystalline structure to X-ray diffraction data and the reciprocal lattice and explains the diffraction methods	U	1
5.	explains crystal defects .	U	1
6.	elaborates the structure of selected compounds of $AX$ , $AX_2$ , $A_mX_2$ , $ABX_3$ and spinels.	C	1
7.	explains the electronic structure of solids using free electron theory and band theory.	E	1
8.	understands the differences in semiconductor and dielectric materials and their electrical and optical properties	U, E	1
9.	explain the structure and reactions of S–N, P–N, B–N, S–P compounds and boron hydrides.	U, E	1
10.	analyse the topological approach to boron hydride structure and estimates styx numbers and apply Wade's rules in borane and carboranes.	Ap, An, E	1
11.	identify the electronic configurations and term symbols of lanthanides and actinides.	Ap	1
12.	sketches the shapes of f orbital and shows their splitting in cubic ligand field.	U	1
13.	elaborates the importance of the beach sands of Kerala and their important components.	C	1

PSO–Programme Specific Outcome

Cognitive Level: R–Remember

An–Analyse

CO–Course Outcome

U–Understanding

E–Evaluate

Ap–Apply

C–Create

Module	Course Description	No. of Hrs	CO No.
1.0	<b>Coordination chemistry-II: Spectral and magnetic properties of transition metal complexes</b>	18	
1.1	Electronic spectra of metal complexes-Term symbols of $d^n$ system, Racah parameters, splitting of terms in weak and strong octahedral and tetrahedral fields.	4	1

1.2	Correlation diagrams for $d^n$ and $d^{10-n}$ ions in octahedral and tetrahedral fields (qualitative approach), d-d transition, selection rules for electronic transition, effect of spin orbit coupling and vibronic coupling.	3	2
1.3	Interpretation of electronic spectra of complexes- Orgel diagrams, Tanabe-Sugano diagrams, calculation of $Dq$ , $B$ and $\beta$ (Nephelauxetic ratio) values, charge transfer spectra.	3	2
1.4	Magnetic properties of complexes-paramagnetic and diamagnetic complexes, molar susceptibility, Gouy's method for the determination of magnetic moment of complexes, spin only magnetic moment.	4	3
1.5	Temperature dependence of magnetism. Temperature Independent Paramagnetism (TIP). Spin state crossover, Antiferromagnetism - inter and intra molecular interaction.	2	3
1.6	Application of magnetic measurements in the determination of structure of transition metal complexes.	2	3
<b>2.0 Crystalline state</b>			
2.1	Crystal symmetry- Introduction to point groups and space groups. Miller indices. Reciprocal lattice concept.	2	4
2.2	Close packed structures: BCC, FCC and HCP. Voids. Coordination number.	2	4
2.3	X-ray diffraction by crystals: Function of crystals. Transmission grating and reflection grating. Bragg's equation.	2	4
2.4	Diffraction methods: Powder and rotating crystal. Indexing and determination of lattice type and unit cell dimensions of cubic crystals.	3	4
2.5	Crystal defects: Perfect and imperfect crystals. Point, line and plane defects. Thermodynamics of Schottky and Frenkel defects.	2	5
2.6	Colour centers in alkali halide crystals. Defect clusters. Extended defects: Crystallographic shear structure and stacking faults. Dislocations and crystal structure.	3	5
2.7	Structure of compounds of AX (Zinc blende, Wurtzite), $AX_2$ (Rutile, fluorite, antiferroite), $A_mX_2$ (Nickel arsenide), $ABX_3$ (Perovskite, Ilmenite), Spinel. Inverse spinel structures.	4	6
<b>3.0 Solid state chemistry</b>			
3.1	Electronic structure of solids. Free electron theory, band theory. Refinements to simple band theory, k space and Brillouin zones.	4	7
3.2	Conductors, insulators and semiconductors. Band	3	7

	structure of conductors, insulators and semiconductors and their applications.		
3.3	Intrinsic and extrinsic semiconductors, doping of semiconductors and conduction mechanism, the band gap.	3	7
3.4	Temperature dependence of conductivity, carrier density and carrier mobility in semiconductors.	2	7
3.5	Superconductivity, Photoconductivity, Photovoltaic effect. Colour in inorganic solids.	3	7
3.6	Dielectric properties. Dielectric materials. Ferroelectricity, pyroelectricity, piezoelectricity and ionic conductivity. Applications of ferro, piezo and pyroelectrics.	3	8
<b>4.0 Compounds of S, N, P and B</b>			
4.1	Sulphur-Nitrogen compounds: $S_4N_4$ , $S_2N_2$ , $S_4N_2$ and polythiazyl $S_xN_y$ compounds. S-N cations and anions.	2	9
4.2	Sulphur-Phosphorus compounds: Molecular sulphides such as $P_4S_3$ , $P_4S_7$ , $P_4S_9$ and $P_4S_{10}$ .	2	9
4.3	Phosphorous-Nitrogen compounds: Phosphazines. Cyclo and linear phosphazines.	2	9
4.4	Boron-Nitrogen compounds: Borazine, substituted borazines and boron nitride.	2	9
4.5	Boron hydrides: Reactions of diborane. Structure and bonding. Polyhedral boranes: Preparation, properties, structure and bonding.	3	9
4.6	The topological approach to boron hydride structure. Styx numbers. Importance of icosahedral framework of boron atoms in boron chemistry. Closo, nido and arachno structures. Wade's rules.	5	10
4.7	Carboranes and metallocarboranes.	2	10
<b>5.0 Lanthanides and actinides</b>			
5.1	Lanthanides: Characteristic properties. Electronic configurations and term symbols. Occurrence and extraction. Separation techniques.	4	11
5.2	Oxidation states of lanthanides. Spectral and magnetic properties of lanthanides. Lanthanide complexes as shift reagents.	3	11
5.3	Shapes of f orbital and their splitting in cubic ligand field.	2	12
5.4	Actinides: Occurrence and general properties. Extraction of thorium and uranium. Electronic configuration and term symbol. Oxidation states. Spectral and magnetic	4	11



	properties.		
5.5	Comparative properties of lanthanides and actinides. Trans-uranium elements and their stabilities.	2	11
5.6	Applications of lanthanide and actinide compounds.	1	13
5.7	Comprehensive study of the beach sands of Kerala and their important components such as monazite, ilmenite, zircon and sillimanite.	2	13

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## CL 222 ORGANIC CHEMISTRY II

**Total 90 h**

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	discuss the fundamentals, operating principles and instrumentation of separation techniques.	R	1,
2.	differentiate the principle and applications of phase transfer catalysis with examples.	An	1
3.	describe the various methods of determining reaction mechanisms and basic thermodynamic principles of organic reactions.	U	1
4.	explain the Hammett parameters of reaction and design an experiment to confirm the mechanism of a reaction.	R, C	1
5.	identify different types of rearrangement reactions, determine the product of the reaction applying migratory aptitude, and reproduce the evidences for the mechanism of the reaction.	R, E	1

6.	understand that the outcomes of pericyclic reactions may be understood in terms of frontier orbital interactions, correlation diagram, Mobius and Huckel approach.	R	1
7.	recall and define the various types of pericyclic reaction; define such terms as 'conrotatory', 'suprafacial'.	R	1
8.	predict and rationalise the outcomes of pericyclic reactions including stereospecificity, regioselectivity, and stereoselectivity.	U	1
9.	state the synthetic importance of the above cycloaddition and rearrangement reactions, and give disconnections of target compounds corresponding to these reactions.	R	1
10.	describe the fate of excited molecule based on Jablonoski diagram, predict the course of an organic photochemical reaction and identify the product with the type of functional group.	R, An	1
11.	propose synthetic routes to a variety of molecules, starting from simple precursors with correct stereochemistry and reagents of selected reactions.	Ap	1

Module	Course Description	No. of Hrs	CO No.
<b>1.0</b>	<b>Separation Techniques</b>	<b>18</b>	
1.1	Classification of chromatographic methods. Theory of chromatography. Applications of chromatographic methods. Adsorption and partition chromatography. Paper, thin layer and column chromatographic methods.	4	1
1.2	Common Spray reagents and Developing agents in chromatography.	2	1
1.3	Centrifugal TLC, LC, pressure column chromatography, HPLC and GC, column matrices. Detectors. Affinity and chiral separations using HPLC.	4	1
1.4	GC MS and LC MS Principle, instrumentation and applications.	4	1
1.5	Normal and ultra-centrifugation. Gel and capillary electrophoresis and their applications.	2	1
1.6	Solvent extraction. Extraction using supercritical liquid CO <sub>2</sub> , Craig's technique of liquid-liquid extraction.	2	1
<b>2.0</b>	<b>Physical Organic Chemistry</b>	<b>18</b>	
2.1	Phase transfer catalysis and its applications.	2	2
2.2	Kinetic and thermodynamic control of reactions with examples.	1	3
2.3	Reaction coordinates- difference between transition state and intermediates, Energy profiles, Curtin – Hammet Principle, Hammond postulate. Principle of microscopic	3	3

	reversibility. Reactivity in relation to molecular structure and conformation. Steric effects, F strain. Ortho effect, Bond angle strain.		
2.4	Solvent polarity and parameters, Y, Z and E parameters and their applications. Primary, secondary, inverse kinetic isotope effects. Salt effects and special salt effects in SN reactions.	3	3
2.5	Methods of determining reaction mechanisms-Product analysis, Isotopic studies, Primary and secondary kinetic isotope effects, Isolation and detection of intermediates, Cross over experiments.	4	3
2.6	Linear Free Energy Relations, The Hammett equation and its applications. Significance of sigma ( $\sigma$ ) and rho ( $\rho$ ) reactions with negative and positive $\rho$ , low and high $\rho$ , abnormal Hammett plot, Taft equation. Hammett plot for aromatic nucleophilic, electrophilic, $S_N^1$ , $S_N^2$ , electrophilic addition, Wittig reactions.	5	4
<b>3.0</b>	<b>Molecular Rearrangement and Transformation Reactions</b>	<b>18</b>	
3.1	Types of organic rearrangements: Anionic, cationotropic, prototropic, rearrangements involving carbene and nitrene intermediates.	4	5, 11
3.2	Mechanism with evidence of Wagner – Meerwein, Pinacol, Demjanov, Hofmann, Curtius, Schmidt, Lossen, Beckmann.	3	5, 11
3.3	Mechanism with evidence of Fries, Fischer–Hepp, Hofmann–Martius, von-Richter, Orton, Bamberger, Smiles.	3	5, 11
3.4	Mechanism with evidence of Dienone–phenol, Benzilic acid, Benzidine, Favorskii, Stevens, Dakin.	3	5, 11
3.5	Bucherer reaction, Rupe, Stevens, Claisen rearrangement.	2	5, 11
3.6	Rearrangements involving diazomethane – Arndt Eistert reaction, Wolf rearrangement.	3	5, 11
<b>4.0</b>	<b>Aromaticity and Pericyclic Reactions</b>	<b>18</b>	
4.1	Aromaticity and antiaromaticity. Non aromatic, homoaromatic, hetero and non-benzenoid aromatic systems. Aromaticity of annulenes, mesoionic compounds, metallocenes, cyclic carbocations, carbanions.	2	6, 7
4.2	Influence of aromaticity on physical and chemical properties, Diamagnetic anisotropic – benzene and paracyclophane.	1	6, 7
4.3	Classification of pericyclic reactions, FMO, Correlation	4	6, 7,

	diagram, Mobius and Huckel theory of electrocyclic and cyclo addition reactions.		8, 9
4.4	Diels–Alder reaction–Stereo and regio selectivity , industrial applications–Aldrene, Dialdrene, endosulfan, anti stroke drug, Reserpine synthesis, fire retardant , Retro–Diels Alder, Alders ene, intramolecular Diels Alder reaction.	4	6, 7, 8, 9
4.5	1,3–Dipolar cycloaddition, nitrones, nitrile oxide, construction of heterocycles–oxazole, triazole, tetrazole, ozonide, Huisgen reaction.	3	6, 7, 8, 9
4.6	Sigmatropic rearrangement–classification [i,j], examples of [1,3], [1,5], [1,7], [3,3], [2,3] – FMO theory, stereochemistry of cope rearrangement, Claisen rearrangement.	4	6, 7, 8, 9
<b>5.0</b>	<b>Organic Photochemistry</b>	<b>18</b>	
5.1	Photochemical processes. Singlet and triplet states and their reactivity, Jablonski diagram, Energy transfer, sensitization and quenching.	3	10
5.2	Photoreactions of carbonyl compounds, enes, dienes and arenes. Norrish Type I and Type II reactions of acyclic ketones.	4	10
5.3	Patterno-Buchi and Barton reactions, Hofmann- Löffler-Freytag reaction, photo-Fries and Di- $\pi$ methane, oxa di- $\pi$ methane rearrangements.	4	10
5.4	Photoreactions of Vitamin D. Photosynthesis, photochemistry of vision.	3	10
5.5	Singlet oxygen generation and its reactions. Introduction to chemiluminescence.	2	10
5.6	Applications of photochemistry.	2	10

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### CL 223 PHYSICAL CHEMISTRY II

**Total 90 h**

<b>CO No.</b>	<b>Expected Course Outcomes</b> <i>Upon completion of this course, the students will be able to</i>	<b>Cognitive Level</b>	<b>PSO No.</b>
1.	apply quantum mechanical principles in solving both real and imaginary spherical harmonics systems-multi electron systems and analyse spectral lines.	U, Ap, An	1
2.	describe and explain the physical and chemical principles that underlie molecular structure determination techniques like microwave, vibrational, Raman and electronic spectroscopy.	R, U	1
3.	predict likely spectral characteristics of given molecular species, and be able to rationalise those characteristics on the basis of structural and electronic arguments.	Ap, An	1
4.	acquire knowledge of basics of statistical mechanics and compare statistical methods.	U, Ap	1
5.	understand and apply of theories of heat capacity.	U, Ap	1
6.	understand theories of electrolytes and electrochemical reactions.	R, U, Ap, An	1
7.	ascertain the application of electrochemistry in industrial fields.	An	1
8.	understand the theories and applications behind various types of analytical techniques in electrochemistry.	U	1
9.	acquire skill in solving numerical problems.	Ap	1

Module	Course Description	No. of Hrs	CO No.
<b>1.0</b>	<b>Quantum Chemistry II</b>	<b>18</b>	
1.1	Rotational motion: The wave equation in spherical polar coordinates-particle on a ring, the phi equation and its solution, wave functions in the real form.	3	1, 9
1.2	Non-planar rigid rotor and 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.	5	1, 9
1.3	Quantum Mechanics of Hydrogen-like systems: The wave equation in spherical polar coordinates: separation of variables – r, $\theta$ and $\phi$ equations and their solutions, wave functions and energies of hydrogen-like systems.	4	1, 9
1.4	Radial distribution functions, angular functions and their plots.	2	1
1.5	Wave functions for multi electron systems, wave equation for multi electron systems, symmetric and anti-symmetric wave functions, Pauli's anti-symmetry principle, and the postulate of spin. Spin orbitals. Spin-orbit coupling. Vector atom model-Term symbols, selection rules and explanation of spectral lines of hydrogen atom.	4	1
<b>2.0</b>	<b>Spectroscopy I</b>	<b>18</b>	
2.1	Rotational spectrum, selection rules, intensity of spectral lines, calculation of inter-nuclear distance.	2	2, 3
2.2	Non-rigid rotors and centrifugal distortion. Rotational spectra of polyatomic molecules-linear and symmetric top molecules. Introduction to instrumentation.	2	2, 3, 9
2.3	Vibrational spectra of harmonic and anharmonic oscillator. Selection rules. Morse curve, fundamentals and overtones. Determination of force constant.	3	2, 3, 9
2.4	Rotational fine structure, P, Q, R branches of spectra.	1	2, 3
2.5	Vibrational spectra of polyatomic molecules: Normal modes, classification of vibrational modes into stretching (asymmetric, symmetric), bending, parallel and perpendicular vibrations.	2	2, 3
2.6	Finger print region and group frequencies. Introduction to FTIR and instrumentation.	1	2, 3
2.7	Raman scattering, polarizability and classical theory of Raman spectrum.	1	2, 3
2.8	Rotational and vibrational Raman spectrum. Raman	2	2, 3

	spectra of polyatomic molecules. Complementarity of IR and Raman spectra. Mutual exclusion principle.		
2.9	Introduction to instrumentation. Laser Raman spectrum.	1	2, 3
2.10	Electronic spectra of diatomic molecules. Vibrational coarse structure and rotational fine structure of electronic spectrum. Franck-Condon principle.	2	2, 3, 9
2.11	Types of electronic transitions. Fortrat diagram. Predissociation.	1	2, 3
<b>3.0 Statistical Thermodynamics</b>			
		<b>18</b>	
3.1	Basic principle of permutation, combination, thermodynamic probability and entropy.	3	4
3.2	Microstates, concept of ensembles canonical and grand canonical ensemble.	1	4
3.3	Maxwell Boltzmann distribution.	2	4
3.4	Molecular partition functions - Translational (1D, 2D and 3D), vibrational, rotational and electronic partition functions. Total partition functions.	4	4
3.5	Relationship between partition functions and thermodynamic properties, Sackur-Tetrode equation. The principle of equi-partition of energy.	4	4
3.6	Chemical equilibrium, Law of mass action, Transformation of the equilibrium expressions. Statistical derivation.	4	4
<b>4.0 Quantum statistics</b>			
		<b>18</b>	
4.1	Bose-Einstein statistics, Thermodynamic probability, Bose Einstein distribution function. Examples of particles.	3	4
4.2	Fermi-Dirac statistics. Examples of particles- Fermi-Dirac distribution function. Thermionic emission	3	4
4.3	Relation between Maxwell Boltzmann, Bose Einstein and Fermi-Dirac statistics.	3	4
4.4	Quantum theory of heat capacity - calculation of heat capacity of gases; limitation of the method.	3	5
4.5	Heat capacity of solids. Dulong and Petit's law, Kopp's law; limitations.	2	5
4.6	Einstein theory of heat capacity; limitations.	2	5
4.7	The Debye theory of specific heat capacity of solids.	2	5
<b>5.0 Electrochemistry</b>			
		<b>18</b>	
5.1	Ionic: Activity and activity coefficient of electrolytes, determination of activity coefficient.	1	6
5.2	Debye-Huckel theory of strong electrolytes, Debye-Huckel-Onsager equation and its derivation, limitation of the model, conductance at high frequencies and high	2	6

	potentials –Wein effect and Debye - Falkenhagen effect.		
5.3	Ionic strength, Debye - Huckel limiting law, mean ionic activity coefficient.	1	6, 9
5.4	Electrodeics: Different type of electrodes. Electrochemical cells, EMF of concentration cells, liquid junction potential and its determination, cells without liquid junction potential.	2	6, 9
5.5	Calculation of thermodynamic properties. Electrical double layer and electro capillarity.	2	6, 9
5.6	Electrokinetic phenomena.	1	6, 7
5.7	Over potentials: Butler-Volmer equation. Tafel and Nernst equation, Tafel plot and its significance.	3	6 7
5.8	Fuel cells: H <sub>2</sub> -O <sub>2</sub> , zinc-air and solid oxide fuel cells.	1	7
5.9	Potentiometric titrations involving redox reaction. Conductometric titrations. Coulometric titrations.	2	8
5.10	Voltammetry: principle and method of polarography, cyclic voltammetry, stripping voltammetry and amperometry.	3	8

## References

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### **Model Question Papers**

#### **General Instruction to question paper setters**

- There will be a 15 main questions in each question paper divided into 3 sections – A, B and C
- Each of the sections A, B and C will have 5 questions each, **1 from each module.**
- Each question in Section A will have 3 sub questions (a), (b) and (c), of which the candidate has to answer any two (2 marks each).
- Each question in Section B will have 2 sub questions (a) and (b), of which the candidate has to answer any one (5 marks each).
- Candidate should answer any three out of the five questions in Section C (10 marks each).
- Section A carries a total of 20 marks, Section B carries 25 marks, and Section 3 carries 30 marks.
- The maximum marks will be 75 and the duration of the exam will be 3 hrs.

**Second Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 221: INORGANIC CHEMISTRY – II**  
(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

**SECTION A**

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

1. (a) Which among  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$  has an intense d–d transition ? Why?  
(b) The effective magnetic moment of a complex is 4.90 BM. Calculate the number of unpaired electrons per unit complex.  
(c) The electronic spectra of metal complexes are broad. Why?
2. (a) Differentiate H-centre from V-centre in NaCl crystals.  
(b) What effects do Schottky and Frenkel defects have on the density of a crystal?  
(c) What are spinels? Give the general formula of spinels.
3. (a) What is meant by band gap of a substance?  
(b) The conductance of metals decreases with increase in temperature. Why?  
(c) What are intrinsic and extrinsic semiconductors
4. (a) Complete the reactions given below  
(i)  $\text{B}_2\text{H}_6 + \text{H}_2\text{O} \rightarrow$   
(ii)  $\text{S}_4\text{N}_4 + \text{Cl}_2 \rightarrow$   
(b) Which undergoes addition reactions faster – Benene or Borazine? Why?  
(c) Clasify the following into closo, nido and archano.  
 $\text{B}_2\text{H}_6$ ,  $\text{C}_2\text{B}_9\text{H}_{11}$ ,  $\text{B}_{12}\text{H}_{12}^{2-}$ ,  $\text{B}_5\text{H}_{11}$ ,
5. (a) Actinides form oxocations but lanthanides don't. Give reason?  
(b) What is misch metal?  
(c) Which among lanthanides and actinides has a higher tendency to form complexes? Why?

[2 × 10 = 20]

**SECTION B**

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

6. (a) Discuss the Orgel diagram and electronic spectra of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ .  
(b) What is meant by a charge transfer spectra?
7. (a) Detail the line and plane defects in solids.  
(b) Describe the principle and procedure of X-ray diffraction method.
8. (a) Examine the various types of dielectric properties exhibited by crystals.  
(b) What is photovoltaic effect? Which type of materials exhibit this?

9. (a) How is polythiazyl synthesized? Describe its structure. Why is it treated as a one dimensional conductor?  
(b) Obtain the styx number of  $B_4H_9$ .
10. (a) Detail the ion exchange method employed in the separation of lanthanides.  
(b) Briefly describe the industrial importance of the beach sands of Kerala.

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Explain the Guoy's methods used to determine magnetic susceptibility. How is it important in structure determination?
12. Discuss in detail the perovskite structure by taking  $SrTiO_3$  as the example.
13. Discuss the salient features of the band theory of solids and compare it with the free electron theory of solids.
14. What are carboranes? How are they obtained?
15. Compare the spectral and magnetic properties of lanthanides and actinides.

[10 × 3 = 30]

**Second Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 222: ORGANIC CHEMISTRY – II**  
(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

### SECTION A

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

1. (a) What is retention time? Explain its significance.  
(b) Write any two spraying reagents for detection of alkaloids.  
(c) What is meant by reversed phase HPLC.
2. (a) What is F strain?  
(b) Explain microscopic reversibility.  
(c) Describe Taft equation and its terms?
3. (a) Show how vicinal diols are converted to ketones by rearrangement?  
(b) Give the mechanism of Curtius rearrangement.  
(c) Briefly explain Fisher-Hepp reaction.
4. (a) Why is [10] annulene a non aromatic compound?

- (b) Azulene possesses dipole moment of 1.4 D. Why?  
 (c) State Woodward and Hoffman rules for pericyclic reaction?
5. (a) What is photo-Fries rearrangement?  
 (b) Distinguish singlet and triplet states in photochemistry.  
 (c) Write an example for Barton reaction.

[2 × 10 = 20]

### SECTION B

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

6. (a) Describe the instrumentation of GC-MS  
 (b) What are the information's obtained from a LC-MS chromatogram?
7. (a) Design a cross over experiment for Claisen rearrangement and predict your observation.  
 (b) Hammett  $\rho$  value of nitration of benzene is negative while that of Wittig reaction is positive Explain.
8. (a) Explain the migratory aptitude in Baeyer-Villiger rearrangement with three examples  
 (b) Discuss the mechanism and applications of Dienone-phenol rearrangement
9. (a) Write the product of photochemical ring closure of 2E, 4E hexadiene with correct stereochemistry and FMO explanation  
 (b) Draw a correlation diagram to show that supra-supra 4+2 cycloaddition is thermally allowed.
10. (a) Discuss the chemistry behind the process of vision.  
 (b) Explain Paterno-Buchi reaction

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Describe the experimental procedures for thin layer chromatography and column chromatography.
12. Explain any four reactions where isotopic studies support the mechanism.
13. Describe with evidences the mechanism of  
 a) Wagner-Meerwein rearrangement      b) Pinacol rearrangement  
 c) Demjanov rearrangement                d) Hofmann rearrangement
14. Describe the stereoselectivity and regioselectivity of Diels-Alder reactions
15. Write a note on fate of excited state molecule with a Jablonski diagram and photochemistry of vitamin-D.

[10 × 3 = 30]

**Second Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 223: PHYSICAL CHEMISTRY – II**  
(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

**SECTION A**

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

1. (a) Write the determinantal form of wave function for lithium atom.  
(b) By inspecting the hydrogen like wave function,  
$$\varphi_{nlm} = \frac{\sqrt{2}}{81\sqrt{\pi}} Z^{3/2} (6 - Zr) Zr \exp(-Zr/3) \cos\theta$$
, find the quantum numbers  $n$ ,  $l$  and  $m$ .  
(c) What is a radial distribution function? Mention its importance.
2. (a) How would one determine the theoretical force constant of the C–C bond?  
(b) Anti-stokes lines are usually weak. Why?  
(c) What is the effect of nuclear spin on the intensity of spectral lines?
3. (a) Differentiate between Bosons and Fermions.  
(b) Explain the concept of ensembles and give the difference in properties of each category  
(c) How can you explain partition function is a measure of number of available energy levels?
4. (a) Calculate the value of  $C_v$  for any element when its temperature is equal to the Debye characteristics temperature.  
(b) What is Sterling's approximation? How this approximation helps to arrive at thermodynamic probability.  
(c) Distinguish between Dulong Pettit law and Kopps law.
5. (a) Draw the graph and explain the theory of conductometric titration of a weak acid against a strong base.  
(b) What is the significance of half-wave potential?  
(c) Calculate the mean activity coefficient of 0.01 M  $\text{BaCl}_2$  in water at  $25^\circ\text{C}$ .

[2 × 10 = 20]

**SECTION B**

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

6. (a) Verify that  $F = 1/\sqrt{2} \pi \exp(iM\phi)$  constitute an orthonormal set for particle in a ring.  
(b) Write the Schrodinger equation for hydrogen atom in polar coordinates and separate the variables.

7. (a) Spacing between adjacent lines in HCl molecule is  $10 \text{ cm}^{-1}$ . Force constant is  $1.38 \times 10^{-23} \text{ JK}^{-1}$ , Calculate maximum population at room temperature.  
(b) Explain the origin of P and R branches in rotational-vibrational spectrum.
8. (a) Deduce Sackur-Tetrode relation using Partition function.  
(b) State and prove Boltzman's theorem connecting entropy and probability.
9. (a) Considering free electrons in a metal to form a Fermi gas. Obtain the Richardson – Dushman equation for thermionic emission for electrons.  
(b) Deduce Fermi-Dirac distribution law; hence obtain an expression for energy.
10. (a) Explain the term ionic mobility. The  $\text{H}^+$  ion because of its heavy hydration and consequent large size and shape, should have a low mobility but actually its mobility is very high. How would you account for it? Why does  $\text{H}^+$  ion move about 50 times more rapidly in ice than in liquid water.  
(b) The exchange current density of a Pt/ $\text{H}_2$ ,  $\text{H}^+(\text{aq})$  electrode is  $0.79 \text{ mA cm}^{-2}$ . What current flows through a standard electrode of total area  $5 \text{ cm}^2$  when the potential difference across the electrode is  $5 \text{ mV}$ , the temperature  $25^\circ\text{C}$  and the proton activity unity?

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. 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 orthogonality condition.  
(7+3)
12. (i) The rotational Raman spectrum recorded for  $^{14}\text{N}_2$  molecule using monochromatic laser source of wave length  $336.86 \text{ nm}$ , first three Stokes lines were observed respectively at  $28677.3$ ,  $29669.3$  and  $29661.4 \text{ cm}^{-1}$ . Find the bond length of the molecule.  
(ii) How is the rotational spectrum of a diatomic molecule affected by isotopic substitution?  
(5+5)
13. (i) How thermo dynamic functions like internal energy, entropy and specific heat capacity are related to partition function? Derive the relation.  
(ii) Explain Maxwell-Boltzman distribution law.  
(7+3)
14. What are the limitations of Einstein's theory of heat capacity? How Debye theory attempted to rectify this? Discuss Debye theory of specific heat capacity of solids.

15. (i) What is exchange current density? How the concept is understood using Butler-Volmer equation?  
(ii) Describe the theory and application of cyclic voltametry.

(5+5)

[10 × 3 = 30]

## SEMESTER III

### CL 231 INORGANIC CHEMISTRY III

Total 90 h

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	demonstrate knowledge of advanced content in the areas of inorganic chemistry such as in organometallic compounds, bioinorganic compounds, spectroscopic methods in inorganic Chemistry and nuclear chemistry.	U	1
2.	examine the bonding in simple and polynuclear carbonyls with and without bridging and complexes with linear $\pi$ donor ligands.	U, An	1
3.	explain the structure and bonding of ferrocene and dibenzenechromium with the help of MO theory.	U, An, C	1
4.	understand fundamental reaction types and mechanisms in organometallics and to employ them to understand selected catalytic processes in industry.	U, An, C	1
5.	contrasts the thermodynamic and kinetic stability of complexes, analyses the factors affecting stability of complexes and explains the methods of determining stability constants.	An, E	1
6.	classifies ligand substitution reactions and explains its kinetics and various mechanisms.	U, E	1
7.	analyze the chemical and physical properties of metal ions responsible for their biochemical action as well as the techniques frequently used in bioinorganic chemistry such as oxygen transport, e-transfer, communication, catalysis, transport, storage etc.	U, An	1
8.	explain the principles of spectroscopic methods employed in inorganic chemistry and their applications in the study of metal complexes.	An, E	1
9.	demonstrate a knowledge of fundamental aspects of the structure of the nucleus, radioactive decay, nuclear reactions, counting techniques.	R, U	1
10.	evaluate the role of nuclear chemistry to find the most suitable measures, administrative methods and industrial solutions to ensure sustainable use of the world's nuclear resources.	U, E, C	1, 4

PSO–Programme Specific Outcome

Cognitive Level: R–Remember

An–Analyse

CO–Course Outcome

U–Understanding

E–Evaluate

Ap–Apply

C–Create

Module	Course Description	No. of Hrs	CO No.
1.0	Organometallic compounds	18	



1.1	Nomenclature of organometallic compounds. Hapto nomenclature. 18 and 16 electron rule, isoelectronic and isolobal analogy.	2	1
1.2	Metal carbonyls, bonding in metal carbonyls. Synthesis, structure and bonding of polynuclear carbonyls with and without bridging.	2	2
1.3	Complexes with linear $\pi$ donor ligands: Olefins, acetylenes, dienes and allyl complexes. Complexes with cyclic $\pi$ donors: Cyclopentadiene, benzene complexes.	2	2
1.4	Structure and bonding of ferrocene and dibenzenechromium complexes (MO treatment).	4	3
1.5	Oxidative addition and reductive elimination, insertion and elimination reactions	3	4
1.6	Catalysis by organometallic compounds: Alkene hydrogenation using Wilkinson's catalyst, hydroformylation of olefins using cobalt and rhodium catalyst, polymerization reaction by Ziegler-Natta catalyst, Monsanto acetic acid process, Palladium catalysed oxidation of ethylene-the Wacker process.	5	4
<b>2.0</b>	<b>Coordination chemistry-III: Reactions of metal complexes</b>	<b>18</b>	
2.1	Energy profile of a reaction - Thermodynamic and kinetic stability, Stability of complex ions in aqueous solutions: Formation constants. Stepwise and overall formation constants. Factors affecting stability of complexes.	2	1, 5
2.2	Determination of stability constants: spectro photometric, polarographic and potentiometric methods.	3	1, 5
2.3	Stability of chelates. Thermodynamic explanation, macrocyclic effects.	1	1, 5
2.4	Classification of ligand substitution reactions-kinetics and mechanism of ligand substitution reactions in square planar complexes, trans effect theory and synthetic applications.	3	1, 6
2.5	Kinetics and mechanism of octahedral substitution-water exchange, dissociative mechanism, associative mechanism - Eigen-Wilkins mechanism, Eigen - Fuoss equation, base hydrolysis, racemisation and isomerisation reactions.	3	1, 6
2.6	Electron transfer reactions: Outer sphere mechanism-Marcus theory, inner sphere mechanism - Taube mechanism.	3	1, 6
2.7	Photochemical reactions-substitution and redox reactions of Cr(III), Ru(II), and Ru(III) complexes. Photo-isomerisation and photo-aquation reactions of metal complexes.	3	1, 6

<b>3.0</b>	<b>Bioinorganic chemistry</b>	<b>18</b>	
3.1	Essential and trace elements in biological systems, structure and functions of biological membranes, mechanism of ion transport across membranes, sodium-potassium pump.	2	1, 7
3.2	Photosynthesis, porphyrin ring system, chlorophyll, PS I and PS II. Synthetic model for photosynthesis.	2	1, 7
3.3	Role of calcium in biological systems - blood coagulation, muscle contraction.	1	1, 7
3.4	Oxygen carriers and oxygen transport proteins-haemoglobin and myoglobin.	2	1, 7
3.5	Non-haeme iron-sulphur proteins involved in electron transfer-ferredoxin and rubredoxin.	3	1, 7
3.6	Iron storage and transport in biological systems ferritin and transferrin.	3	1, 7
3.7	Redox metalloenzymes-cytochromes, cytochrome P-450, peroxidases and superoxide dismutase and catalases. Nonredox metalloenzymes- Carboxypeptidase A - structure and functions.	3	1, 7
3.8	Nitrogeases, biological nitrogen fixation. Vitamin B <sub>12</sub> and coenzymes. Toxic effects of metals (Cd, Hg, Cr and Pb).	2	1, 7
<b>4.0</b>	<b>Spectroscopic Methods in Inorganic Chemistry</b>	<b>18</b>	
4.1	Infrared spectra of coordination compounds. Structural elucidation of coordination compounds containing the following molecules/ ions as ligands- NH <sub>3</sub> , H <sub>2</sub> O, CO, NO, OH <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , CN <sup>-</sup> , SCN <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> and X <sup>-</sup> (X=halogen). Changes in ligand vibration on coordination with metal ions.	5	1, 8
4.2	Vibrational spectra of metal carbonyls-CD and ORD spectra of metal complexes.	3	1, 8
4.3	ESR spectra: Application to Cu(II) complexes and inorganic free radicals such as PH <sub>4</sub> , F <sub>2</sub> <sup>-</sup> and [BH <sub>3</sub> ] <sup>-</sup> .	3	1, 8
4.4	Nuclear Magnetic Resonance Spectroscopy: The contact and pseudocontact shifts, some applications including biological systems, an overview of NMR of metal nuclides with emphasis on <sup>11</sup> B, <sup>31</sup> P and <sup>19</sup> F NMR.	4	1, 8
4.5	Mossbauer Spectroscopy: Application of the technique to the studies of iron and tin complexes.	3	1, 8
<b>5.0</b>	<b>Nuclear Chemistry</b>	<b>18</b>	
5.1	Nuclear structure, mass and charge. Nuclear moments. Binding energy. Semiempirical mass equation. Stability rules. Magic numbers.	3	1, 9

5.2	Nuclear models: Shell, Liquid drop, Fermi gas, collective and optical models.	3	1, 9
5.3	Equation of radioactive decay and growth. Half life and average life. Radioactive equilibrium. Transient and secular equilibria.	3	1, 9
5.4	Nuclear reactions: Direct nuclear reactions, heavy ion induced nuclear reactions, photonuclear reactions. Neutron captures cross section and critical size.	3	1, 9
5.5	Nuclear fission as a source of energy, Nuclear chain reacting systems. Principle of working of the reactors of nuclear power plants. Breeder reactor. Nuclear fusion reaction, stellar energy.	3	1, 10
5.6	Principles of counting technique such as G.M. counter, proportional, ionization and scintillation counters. Cloud chamber.	3	1, 9

### References

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### CL 232 ORGANIC CHEMISTRY III

Total 90 h

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	describe and explain the physical and chemical principles that underlie molecular structure determination techniques such as UV-visible, IR, mass and NMR spectroscopy.	U, An	1
2.	apply knowledge of molecular structure determination using UV-visible, IR, mass and NMR spectroscopic techniques to identify and/or characterise chemical compounds from experimental data.	Ap, An	1, 8
3.	calculate $\lambda_{\max}$ of a compound, apply IR frequency table to determine the functional groups present in the molecule, interpret mass spectrum of compound from fragmentation.	U, Ap	1, 8
4.	predict likely spectral characteristics of given molecular species; solve the structures of unknown molecules using appropriate spectroscopic techniques.	U, Ap, An	1, 8
5.	devise a 2 D NMR of a compound based on learned principles and solve the structure of a compound based on NMR data.	C, Ap	1, 8
6.	discuss organic transformations with organometallic compounds and predict the products of the reactions.	U	1
7.	propose the retro synthetic pathways to a variety of molecules	U, Ap, C	1
8.	propose mechanisms for chemical reactions, given starting materials, reagents, conditions, and/or products.	U, Ap, C	1
9.	compare the reactions and mechanism and determine the products of a selected set of reactions; identify protecting group strategies.	Ap, E	1
10.	devise combinatorial method to create a library of compounds.	C	1, 6
11.	give examples of stereoselective, regioselective and chemoselective reductions and oxidations.	U	1

Module	Course Description	No. of Hrs	CO No.
<b>1.0</b>	<b>UV-vis and IR Spectroscopy and Mass spectrometry</b>	<b>18</b>	
1.1	Electronic transitions and analysis of UV spectra of enes, enones and arenes. Woodward Fieser rules. Effect of solvent polarity on UV absorption.	4	1, 2, 3

1.2	Principle of characteristic group frequency in IR. Identification of functional groups and other structural features by IR, Hydrogen bonding and IR bands. Sampling techniques.	4	1, 2, 3
1.3	Mass spectrometry-Soft and hard ionization techniques; EI, CI, FAB, Electrospray and MALDI ion sources. Magnetic, High resolution (Double focusing), TOF and quadrupole mass analysers. Characteristic EIMS fragmentation modes and MS rearrangements.	6	1, 2, 3
1.4	Mass spectral fragmentation patterns of long chain alkanes, alkenes, alkynes, alcohols, ethers, thiols, aromatic compounds, aldehydes, ketones, acids, amides, nitro, amino and halo compounds.	4	1, 2, 3
<b>2.0 NMR spectroscopy and Structural elucidation 18</b>			
2.1	Theory of NMR spectroscopy, chemical shifts, anisotropic effects and coupling constant. Spin-spin interactions in typical systems. First order and higher order spectra.	5	1, 2,
2.2	Simplification methods of complex spectra by high field NMR, shift reagents, chemical exchange and double resonance.	5	1, 2
2.3	<sup>13</sup> C NMR chemical shifts. Applications of NOE, DEPT, and 2D techniques such as COSY-HSQC, HMQC and HMBC (basic principles only).	5	1, 2, 5
2.4	Spectral interpretation and structural elucidation. Solving of structural problems on the basis of numerical and spectrum based data.	3	1, 4
<b>3.0 Organometallic compounds in organic synthesis 18</b>			
3.1	Preparation of organo Mg, Al, Li, Cu, Zn, Cr, Grignard reagents in organic synthesis. Alkylation, oxirane addition, carbon dioxide addition, carbonyl addition, enone addition (1,2 - and 1,4 - additions), reduction, and enolisation reactions. Selectivity in Grignard reactions.	5	6, 8
3.2	Reactions of organo Li reagents, Li exchange reaction, its use in the preparation of RLi compounds, addition to C=O, COOH and CONR <sub>2</sub> , Li dialkylcuprates (Gilman reagent)-preparation and reaction with alkyl halides, aryl halides and enones.	5	6, 8
3.3	Alkynyl Cu(I) reagents, Glasier coupling. Dialkyl cadmium compounds preparation and reaction with acyl halides.	4	6, 8
3.4	Benzene tricarbonyl chromium - preparation and reaction with carbanions. Tebbe's reagent, Silane carbanion and its reactions.	4	6, 8

<b>4.0</b>	<b>Methods in organic synthesis</b>	<b>18</b>	
4.1	Retrosynthetic analysis and disconnection approach-synthons, synthetic strategy, reliable reaction, disconnect after heteroatom, chemoselectivity, two group disconnections (use of epoxide), creation of cis and trans double bonds, retro synthesis of amines.	3	7, 9
4.2	Regioselectivity in enol alkylation, Lithium enolates, Zimmerman-Taxler model, enamine alkylation, aza enolate, silyl enol ether, alkylation of nitriles, nitro compounds, acids, ketones, aldehydes.	3	7, 9
4.3	Olefin metathesis – first and second generation Grubbs' catalysts. Umpolung concept-1,3-Dithiane, benzoin condensation.	3	7, 9
4.4	Coupling reactions - Heck, Negishi, Sonagashira, Kumada and Suzuki coupling, Stepens-Castro coupling, Stille coupling,	4	7, 9
4.5	Protecting group strategy: Tetrahydropyranyl, silyl, t-butyl, trichloroethyl, acetal and thioacetal as hydroxyl, thiol, carboxyl and carbonyl protecting groups in synthesis.	3	7, 9
4.6	Introduction to combinatorial synthesis - split and pool method only.	2	10
<b>5.0</b>	<b>Oxidation and Reduction reactions in organic chemistry</b>	<b>18</b>	
5.1	Reduction using boranes and hindered boranes - 9 BBN, disiamylborane, pinacolborane	2	11
5.2	Sodium borohydride and lithium aluminium hydride, NaCNBH <sub>3</sub> DIBAL-H, bulky metal hydrides, Li trialkylborohydrides, tri-n-butyltin hydride, diimide, and aluminium alkoxide.	4	11
5.3	Birch reduction, Clemmensen reduction and Wolff - Kishner reduction, Huang - Minlon modification, Rosenmund reduction.	3	11
5.4	McFadayan-Stevens reaction, allylic and benzylic oxidation, Sharpless epoxidation, oxidation using SeO <sub>2</sub> , manganese (IV) oxide, lead tetraacetate, ozone, peracids, DDQ, silver carbonate and Cr(VI) reagents.	5	11
5.5	Jones oxidation, chemo and region selectivity in reductions and oxidations. Swern oxidation, Moffatt oxidation, Sommelet reaction. Applications of HIO <sub>4</sub> , Dess-Martin periodinane, OsO <sub>4</sub> and mCPBA.	4	11

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5. Y. R. Sharma, Elementary Organic Spectroscopy, S. Chand Publishing, 2010.
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7. G. Aruldhas, Molecular Structure and Spectroscopy, Prentice Hall of India, 2001.
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24. Mc Murry, Organic chemistry, 9th edition, Cengage Learning, 2015.

### CL 233 PHYSICAL CHEMISTRY III

Total 90 h

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	understand the theories of chemical bonding and their application with help of approximate methods predict the nature of orbitals and molecular spectra.	U, Ap, An	1

2.	compare MO and VBT.	An	1
3.	understand the properties of gases and liquids and the nature of the intermolecular forces in them.	U, Ap, An	1
4.	describe the principle behind the determination of surface tension and coefficient of viscosity.	U	1
5.	describe and explain the physical and chemical principles that underlie molecular structure determination techniques like NMR, ESR, Mossbauer, NQR and PES spectroscopy.	U, Ap, An	1
6.	judge the degrees of freedom of systems and understand theories of irreversible thermodynamic systems.	U, Ap, An, E	1
7.	understand the quantum mechanical and non-quantum mechanical methods in computational chemistry, potential energy surface and basis functions.	U, An	1
8.	write the Z matrix of simple molecules.	U, Ap	1
9.	acquire skill in solving numerical problems.	Ap	1

Module	Course Description	No. of Hrs	CO No.
<b>1.0</b>	<b>Approximate methods and Chemical Bonding</b>	<b>18</b>	
1.1	Approximate methods: Method of Variation-variation theorem and its proof. Linear variation functions. Secular equations and secular determinants.	2	1
1.2	Method of Perturbation-successive correction to an unperturbed problem. Detailed treatment of first order non-degenerate case only. Hartree-Fock Self-Consistent Field (HF-SCF) method for atoms, Hartree-Fock equations (derivation not required) & the Fock operator.	3	1
1.3	MO theory- The Born-Oppenheimer approximation -MO Theory-LCAO MO method applied to H <sub>2</sub> and H <sub>2</sub> <sup>+</sup> .	2	1
1.4	MO diagram of homo nuclear diatomic molecules Li <sub>2</sub> , Be <sub>2</sub> , B <sub>2</sub> , C <sub>2</sub> , O <sub>2</sub> and F <sub>2</sub> and hetero nuclear diatomic molecules LiH CO, NO and HF.	2	1
1.5	Spectroscopic term symbols for homodiatomc molecules, selection rules for molecular spectra.	1	1
1.6	Valance bond theory - VB treatment of hydrogen molecule only.	2	1
1.7	Comparison of MO and VB theories.	1	2
1.8	Quantum mechanical treatment of sp, sp <sup>2</sup> and sp <sup>3</sup> hybridisation.	2	1
1.9	HMO theory of conjugated systems. Bond order and charge density calculations, free valance. Application of HMO method to ethylene, allyl, butadiene and benzene systems.	3	1, 9
<b>2.0</b>	<b>Gaseous and Liquid State</b>	<b>18</b>	
2.1	Maxwell's distribution of molecular velocities,	4	3, 9



	influence of temperature, types of molecular velocities-derivation of molecular velocities from Maxwell's equation.		
2.2	Transport phenomena in gases – viscosity of gases, Chapman equation, determination of viscosity of gases, calculation of mean free path.	3	4, 9
2.3	Thermal conductivity, diffusion	3	3
2.4	Degrees of freedom of gaseous molecules - Translational, Rotational and vibrational.	1	3
2.5	Equation of state of real gases- van der Waal's equation, Other equation of states - Virial equation, second virial coefficient and determination of diameter of a molecule.	3	3, 9
2.6	Inter molecular forces - Dipole-dipole interaction, induced dipole-dipole, induced dipole-induced dipole interactions.	1	3
2.7	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-short range order.	1	3
2.8	X-ray diffraction of liquids. Vacancy model for a liquid, radial distribution function.	1	3
2.9	Surface tension - determination of surface tension by drop weight method and drop number method. Viscosity - determination of coefficient of viscosity by Ostwald viscometer.	1	4, 9
<b>3.0</b>	<b>Spectroscopy II</b>	<b>18</b>	
3.1	Resonance spectroscopy: Nuclear Magnetic resonance Spectroscopy, Nuclear spin. Interaction between nuclear spin and applied magnetic field.	2	5
3.2	Proton NMR. Population of energy levels.	1	5
3.3	Nuclear resonance. Chemical shift. Relaxation methods. Spin-spin coupling. Fine structure.	2	5
3.4	Introduction to instrumentation Fourier Transformation (FT) NMR Spectroscopy: Instrumentation - experimental aspects magnets, radio frequency transmitter, NMR probe and computer. Radio frequency pulses effect of pulses, rotating frame reference, FID, FT technique - data acquisition and storage, signal averaging. Pulse sequences- pulse width, spins and magnetisation vector.	3	5, 9
3.5	ESR spectroscopy: Electron spin. Interaction with magnetic field. Kramer's rule. The g factor. Fine structure and hyperfine structure. Analytical applications of ESR, Determination of reaction rates and mechanisms by ESR, Structural determination by ESR. Elementary idea of ENDOR and ELDOR.	4	5, 9

3.6	Mossbauer spectroscopy: Basic principles. Doppler effect, chemical shift, recording of spectrum, application. Quadrupole effect, Effect of magnetic field.	3	5
3.7	NQR spectroscopy- Principle and application.	2	5
3.8	Photoelectron spectroscopy: Introduction to UV photoelectron and X-ray photoelectron spectroscopy.	1	5
<b>4.0 Applications of Thermodynamics</b>			
4.1	Simple examples of irreversible processes.	1	6
4.2	General theory of non-equilibrium processes. The phenomenological relations. Onsager reciprocal relation. Principle of minimum entropy production.	2	6
4.3	Generalized equation for entropy production, Entropy production from heat flow, matter flow and current flow.	3	6, 9
4.4	Application of irreversible thermodynamics to diffusion. Thermal diffusion, thermo osmosis and thermo-molecular pressure difference.	4	6
4.5	Electro-kinetic effects, the Glansdorf-Pregogine equation. Far from equilibrium region.	3	6
4.6	Three component systems: Graphical representation. Three component liquid systems with one pair of partially miscible liquids. Influence of temperature. Systems with two pairs and three pairs of partially miscible liquids.	3	6
4.7	Solid- liquid system: Two salts and water systems-no chemical combination, double salt formation, one salt forms hydrate, double salt forms hydrate, Isothermal evaporation.	2	6
<b>5.0 Computational Chemistry</b>			
5.1	Introduction to computational chemistry: As a tool and its scope. Potential energy surface-stationary point, saddle point or transition state, local and global minima. Basis functions-Slater type orbitals (STO) and Gaussian type orbitals (GTO).	3	7
5.2	Basis sets: minimal, split valence, polarized and diffuse basis sets, contracted basis sets, Pople's style basis sets and their nomenclature.	2	7
5.3	Quantum mechanical computational methods - Abinitio methods: Introduction to SCF. RHF, ROHF and URHF. (no need of calculation). Wave functions for open shell state, Slater determinants, Roothan concept.	2	7
5.4	Semi empirical methods: Huckels and extended Huckel methods. Strengths and weaknesses. PPP, ZDO, NDDO, INDO, MNDO (AM1, PM3) and CNDO	2	7

	approach.(Mentioning only).		
5.5	Density functional theory methods (DFT) - Electron correlation and introduction to post HF methods. Hohenberg-Kohn theorems, Exchange correlational functional Kohn-Sham orbitals, Local density approximation. Generalized gradient approximation (Only the basic principles and terms to be introduced).	2	7
5.6	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. Commonly used forcefields - AMBER and CHARMM.	2	7
5.7	Construction of Z-matrix for simple molecules. H <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> CO, CH <sub>3</sub> CHO, NH <sub>3</sub> and CO <sub>2</sub> .	2	8
5.8	Structure drawing and energy calculation (geometry optimization) using free software Arguslab, Tinker, NAMD, DL-POLY	3	7

## References

- 1 I. N. Levine, Quantum Chemistry, 6th Edn, Pearson Education Inc., 2009.
- 2 P.W. Atkins, R.S. Friedman, Molecular Quantum Mechanics. 4th Edn., Oxford University Press, 2005.
- 3 D.A. McQuarrie, Quantum Chemistry, University Science Books, 2008.
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- 23 A. Leach, Molecular Modelling: Principles and Applications, 2nd Edn., Longman, 2001.
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## CL 234 INORGANIC CHEMISTRY PRACTICALS – II

**Total 125 h**

<b>CO No.</b>	<b>Expected Course Outcomes</b> <i>Upon completion of this course, the students will be able to</i>	<b>Cognitive Level</b>	<b>PSO No.</b>
1.	interpret data from an experiment, including the construction of appropriate graphs and the evaluation of errors.	U, An	3, 7, 8
2.	estimate a simple mixture of ions (involving quantitative separation) by volumetric and gravimetric methods.	An	7, 8
3.	perform COD, BOD, DO, TDS analysis.	Ap, An	4, 7, 8
4.	predict likely spectral characteristics of given metal complexes solve the structures of unknown metal complexes using appropriate spectroscopic techniques and magnetic measurements .	Ap, An	6, 8
5.	analyse the XRD of simple substances.	An	8
6.	interpret TG and DTA curves.	An	8

<b>Module</b>	<b>Course Description</b>	<b>No. of Hrs</b>	<b>CO No.</b>
1.	Estimation of simple mixture of ions (involving quantitative separation) by volumetric and gravimetric methods. a) Iron (gravimetric) and Chromium (volumetric) b) Iron (gravimetric) and Zinc (volumetric) c) Copper (volumetric) and Nickel (gravimetric) d) Iron and Copper	40	1, 2

	e) Copper and Nickel		
2.	Environmental Analysis – COD, BOD, DO, TDS	20	1, 3
3.	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.	25	4
4.	Analysis of XRD of simple substances.	15	5
5.	Interpretation of TG and DTA curves .	25	6

### References

1. A. I. Vogel, A Text Book of Quantitative inorganic Analysis, Longman, 4th edition, 1978.
2. Willard , Merrit and Dean, Instrumental Methods of Analysis, 7th edition, 1986.
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5. R. S. Drago, Physical Methods in Inorganic Chemistry, Van Nostrand, 1992.
6. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordinaton Compounds, John Wiley & Sons, 6th edition, 2008.
7. D. F. Shriver, P. W. Atkins and C. H. Langford, Inorganic Chemistry, ELBS, 1990.
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## CL 235 ORGANIC CHEMISTRY PRACTICALS – II

**Total 125 h**

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	interpret data from an experiment, including the construction of appropriate graphs and the evaluation of errors.	U, An	3, 7, 8
2.	predict likely spectral characteristics of given molecular species; solve the structures of unknown molecules using appropriate spectroscopic techniques	Ap, An	6, 7, 8
3.	develop paper chromatogram of a compound and determine its purity	C	7, 8
4.	estimate quantitatively the Aniline, Phenol, glucose, Ascorbic acid and Aspirin in a sample	Ap	7, 8
5.	estimate colorimetrically paracetamol, protein and ascorbic acid	Ap	7, 8
6.	use green chemical principles in the synthesis	Ap	4, 7, 8

Module	Course Description	No. of Hrs	CO No.
A.	<b>Volumetric estimation of</b> 1) Aniline 2) Phenol 3) Glucose 4) Ascorbic acid 5) Aspirin	25	4
B.	<b>Colorimetric estimation</b> 6) paracetamol with potassium ferricyanide 7) protein by biuret method 8) Ascorbic acid by folin-phenol reagent or phosphotungstic acid methods	25	5
C.	<b>Spectral identification</b> 9) UV, IR, <sup>1</sup> H NMR, <sup>13</sup> C NMR, EI mass spectral identification of Organic compounds from a library of organic compounds (Each students have to record the spectral analysis of a minimum of 40 compounds)	40	1, 2
D.	<b>Separations of mixtures by Paper Chromatography</b> 10) Identification of amino acids	10	3
E.	<b>Single stage preparation of organic compounds by green chemistry</b> 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).	25	4
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.			

### References

1. B. S. Furniss, Vogel's text book of practical organic chemistry, 5th Edition, Longman, 1989.
2. D. L. Pavia, G. M. Lampman, G. S. Kriz and R. G. Engel, A microscale approach to organic laboratory techniques, Wadsworth Publishing, 5th Edition, 2012.
3. R. K. Bansal, Laboratory manual of organic Chemistry, Wiley Eastern, 1994.
4. N. K. Vishnoi, Advanced Practical Organic Chemistry, 3rd Edition, Vikas.
5. F. G. Mann and B. C. Saunders, Practical Organic Chemistry, Pearson Education, 2009.
6. J. B. Cohen, Practical organic chemistry, Forgotten Books, 2015.
7. P. F Shalz, Journal of Chemical Education 1996, 173: 267.
8. Monograph on green laboratory experiments, DST, Government of India, pp 1-79.
9. For spectral data of organic compounds, see: [http://sdfs.riodb.aist.go.jp/sdfs/cgi-bin/direct\\_frame\\_top.cgi](http://sdfs.riodb.aist.go.jp/sdfs/cgi-bin/direct_frame_top.cgi)

## CL 236 PHYSICAL CHEMISTRY PRACTICALS – II

Total 125 h

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	interpret data from an experiment, including the construction of appropriate graphs and the evaluation of errors.	U, E	3, 7, 8
2.	determine the strength of strong/ weak acids by conductometric titrations.	Ap	7, 8
3.	verify Onsager equation and Kohlraush's law conductometrically .	An, E	7, 8
4.	determine the activity and activity coefficient of electrolyte.	Ap, An	7, 8
5.	determine the concentration of a solution potentiometrically or pH metrically.	Ap, An	7, 8
6.	employ spectrophotometry in determining unknown concentration.	Ap, An	7, 8
7.	determine the viscosity of liquid mixtures and use this in determining the concentration of a component in a mixture.	Ap, An	7, 8
8.	determine the concentration of a liquid mixture using a refractometer .	Ap, An	7, 8
9.	determine the unknown concentration of a given glucose solution.	Ap, An	7, 8

Module	Course Description	No. of Hrs	CO No.
1.	<b>Conductometry</b> a) Determination of strength of strong and weak acids in a mixture b) Determination of strength of a weak acid. c) Precipitation titration ( $\text{BaCl}_2 \times \text{K}_2\text{SO}_4$ ) d) Titration of dibasic acid ( $\text{H}_2\text{C}_2\text{O}_4/\text{H}_2\text{SO}_4$ ). e) Verification of Onsager equation. f) Verification Kohlraush's law. g) Determination of activity and activity coefficient of electrolyte.	20	1, 2, 3, 4
2.	<b>Potentiometry</b> a) Determination of emf of Daniel cell and temperature dependence of emf of a cell. b) Titrations involving redox reactions – $\text{Fe}^{2+}$ vs $\text{KMnO}_4$ , $\text{K}_2\text{Cr}_2\text{O}_7$ , $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_2$ and $\text{KI}$ vs $\text{KMnO}_4$ c) Determination of the emf of various $\text{ZnSO}_4$ solutions and hence the concentration of unknown $\text{ZnSO}_4$	20	1,5

	<p>solution.</p> <p>d) Determination of activity and activity constant of electrolytes.</p> <p>e) Determination of thermodynamic constants of reactions.</p>		
3.	<p><b>pH metric titrations.</b></p> <p>a) Acid alkali titrations using Quinhydrone electrode.</p> <p>b) Titrations(double) involving redox reactions – <math>\text{Fe}^{2+}</math> vs <math>\text{KMnO}_4</math>, <math>\text{K}_2\text{Cr}_2\text{O}_7</math>, <math>(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_2</math> and <math>\text{KI}</math> vs <math>\text{KMnO}_4</math></p> <p>c) Determination of strengths of halides in a mixture.</p> <p>d) Determination of pH of buffer solutions and hence to calculate the <math>E^\circ</math> of quinhydrone electrode</p>	15	1, 5
4.	<p><b>Spectrophotometry</b></p> <p>a) Verification of Beer-Lambert's law.</p> <p>b) Absorption spectra of conjugated dyes (malachite green, methylene blue).</p> <p>c) Determination of concentration of potassium dichromate and potassium permanganate in a mixture.</p> <p>d) To study the complex formation between <math>\text{Fe}^{3+}</math> and salicylic acid.</p> <p>e) Determination of pKa of an indicator.</p>	20	1, 6
5.	<p><b>Polarimetry</b></p> <p>a) Measurement specific rotation of glucose.</p> <p>b) Determination of specific rotation of sucrose</p> <p>c) Determination of unknown concentration of glucose solution and rate constant of its hydrolysis in presence of HCl</p>	15	1, 7
6.	<p><b>Viscosity:</b></p> <p>a) Viscosity of liquids and mixtures of liquids.</p> <p>b) Verification of Kendall's equation.</p> <p>c) Composition of unknown mixtures.</p> <p>d) Determination of molecular masses polymers by viscosity measurements (Mark-Houwink equation)</p>	15	1, 8
7.	<p><b>Refractometry</b></p> <p>a) Determination of molar refraction of pure liquids</p> <p>b) Determination of concentration of KCl solution/glycerol solution</p> <p>c) Determination of solubility of KCl in water.</p> <p>d) Determination of molar refraction of solid KCl</p> <p>e) Study the stoichiometry of potassium iodide-mercuric iodide complex.</p> <p>f) Determination of concentration of KI solution.</p>	20	1, 9



## References

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## Model Question Papers

### General Instruction to question paper setters

- There will be a 15 main questions in each question paper divided into 3 sections – A, B and C
- Each of the sections A, B and C will have 5 questions each, **1 from each module.**
- Each question in Section A will have 3 sub questions (a), (b) and (c), of which the candidate has to answer any two (2 marks each).
- Each question in Section B will have 2 sub questions (a) and (b), of which the candidate has to answer any one (5 marks each).
- Candidate should answer any three out of the five questions in Section C (10 marks each).
- Section A carries a total of 20 marks, Section B carries 25 marks, and Section C carries 30 marks.
- The maximum marks will be 75 and the duration of the exam will be 3 hrs.

**Third Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 231: INORGANIC CHEMISTRY – III**  
(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

### SECTION A

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

1. (a) Represent diagrammatically the dative bonding seen in metal-cyano complexes.  
(b) Give an example each for a hexahapto ligand and a heptahapto ligand.

- (c) Verify whether  $[\text{IrBrCO}(\text{PPh}_3)_2]$  obeys 18 electron rule or not.
2. (a) List the factors that affect the stability of coordination compounds.  
 (b) What is meant by trans effect?  
 (c) What is the Kurnakovs test?
3. (a) Give two examples for metallo-enzymes containing iron.  
 (b) Briefly discuss the coordination environment of the metal ion in Vitamin  $\text{B}_{12}$ .  
 (c) Explain the mechanism of oxygen binding in haemocyanin.
4. (a) Explain doppler broadening with an example.  
 (b) What is superhyperfine splitting in esr spectra?  
 (c) How many signals are obtained in the  $^{19}\text{F}$  nmr spectra of the following  
 (i)  $\text{SF}_6$       (ii)  $\text{SF}_4$       (iii)  $\text{XeOF}_4$ . Give reasons for your answer
5. (a) List any two differences between GM counter and Proportional counter.  
 (b) Distinguish between half life and average life. How are they related?  
 (c) Summarise the liquid drop model of the nucleus.

[2 × 10 = 20]

### SECTION B

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

6. (a) IR spectroscopy provides vital information in during the study of metal carbonyls. Explain.  
 (b) Discuss the characteristics of oxidative addition and reductive elimination reactions of organometallic compounds.
7. (a) Give an account of the photochemical reactions of complexes.  
 (b) Using  $[\text{PtCl}_4]^{2-}$  as the starting material, how can the cis and trans isomers of  $[\text{PtCl}_2(\text{NH}_3)(\text{PPh}_3)]$  and  $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]^-$  be prepared
8. (a) Explain the role played by calcium in blood clotting.  
 (b) Briefly discuss nitrogen fixation.
9. (a) Discuss the application of ESR spectroscopy to Cu (II) complexes.  
 (b) Discuss the utility of Mossbauer spectroscopy in the study of complexes of iron.
10. (a) Give a brief note on nuclear shell model  
 (b) What is meant by radioactive equilibrium? The ratio between atoms of two radioactive elements A & B at equilibrium was found to be  $3.1 \times 10^9:1$ . If the half life period of A is  $2 \times 10^{10}$  years what is the half life of B.

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Construct the MO diagram of dibenzene chromium and explain the bonding using MOT.
12. What are inner sphere and outer sphere reactions? Explain the salient features.
13. Discuss in detail the function of PS-I and PS-II in photosynthetic activity.
14. How is CD and ORD employed in the structure determination of metal complexes?
15. Explain the principle involved in the working of the reactors in nuclear power plants

[10 × 3 = 30]

**Third Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 232: ORGANIC CHEMISTRY – III**  
 (2020 Admission Onwards)

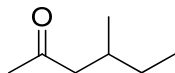
Time: 3 Hrs

Max. Marks: 75

**SECTION A**

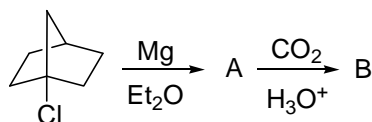
Answer **two** among (a), (b) and (c) from each. Each sub question carries 2 marks

1. (a) What is the effect of solvent polarity on n- $\pi^*$  transition?  
 (b) How will you distinguish between Intramolecular hydrogen bonding and intermolecular hydrogen bonding using IR spectroscopy?  
 (c) Predict the fragmentation pattern of the following molecule

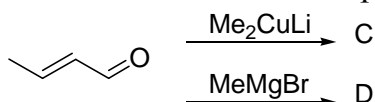


2. (a) How many peaks do you expect in the nmr spectrum of N,N-dimethyl formamide? Explain.  
 (b) How does the coupling constant differ between a geminal and vicinal hydrogens?  
 (c) What are shift reagents? Give an example

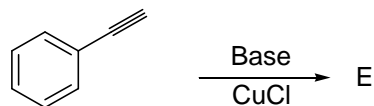
3. (a) Complete the reaction



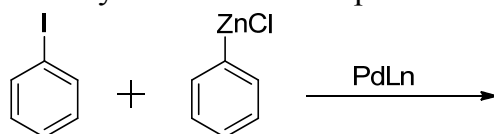
- (b) Predict the structure of the products C and D in the reaction given below



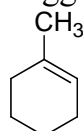
- (c) Write the structure of the compound E in the reaction given below



4. (a) Identify the reaction and predict the product

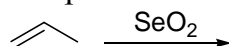


- (b) Suggest a retrosynthetic route for the following compound

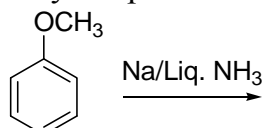


- (c) Give any two protecting groups for hydroxyl group.

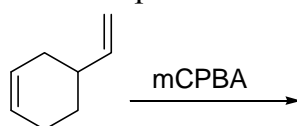
5. (a) Complete the reaction



- (b) Identify the product in the reaction given below



- (c) What is the product obtained in the following reaction?

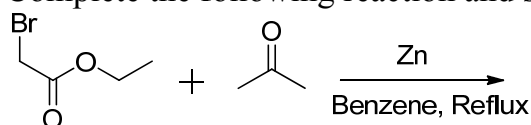


[2 × 10 = 20]

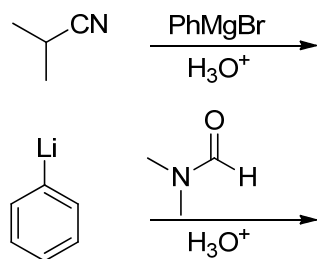
### SECTION B

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

6. (a) Discuss the principle and applications of MALDI.  
 (b) Give the mass fragmentation pattern of toluene and phenol.
7. (a) Explain the anomaly in the chemical shift value of acetylene and benzene.  
 (b) Write on any two 2D NMR technique.
8. (a) Complete the following reaction and suggest a suitable mechanism



- (b) Predict the product (s) of the following reactions with mechanism



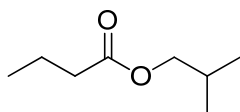
9. (a) Convert benzaldehyde to ethylbenzene using umpolung strategy.  
 (b) Discuss the mechanism for Stille coupling with the help of an example.
10. (a) Illustrate Sharpless asymmetric epoxidation with the help of an example.  
 (b) Give a brief outline of four Cr(VI) reagents used for oxidation reactions.

[5 × 5 = 25]

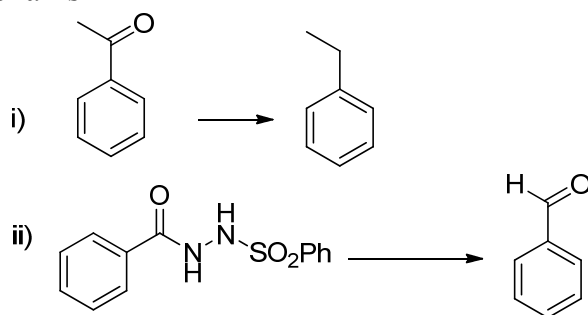
### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. a) Discuss the mass spectral fragmentation pattern of aromatic compounds, ketones and amides.  
 b) Write on FAB.
12. a) <sup>1</sup>H NMR spectrum of a compound gives the following spectral data.  
 $\delta$ 9.78(1H, s), 7.75(2H, d), 6.90(2H, d), 3.8(3H, s). Identify the compound  
 b) Discuss DEPT nmr of



13. a) Discuss the preparation and reactivity of Tebbe's reagent.  
 b) Illustrate the synthetic utility of silyl carbanions using examples
14. a) Discuss Suzuki and Heck coupling with the help of mechanism.  
 b) Write in brief on olefin metathesis
15. a) Comment on the reactivity of various bulky metal hydrides using suitable examples.  
 b) How will you bring about the following conversion? Suggest a suitable mechanism



[10 × 3 = 30]

**Third Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 233: PHYSICAL CHEMISTRY – III**  
(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

**SECTION A**

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

1. (a) Arrange  $O_2$ ,  $O_2^+$ ,  $O_2^-$  in the increasing order of stability. Justify your answer.  
(b) Write briefly about 'Perturbation theory'.  
(c) Write the Hamiltonian for He atom and suggest a suitable trial wave function for it.
2. (a) Predict and justify the condition at which a real gas obeys the following equation of state  $PV = RT + Pb$ .  
(b) The van der Waals constant  $a$  for two gases are 4.17 and  $0.024 \text{ dm}^6 \text{ atm mol}^{-2}$  respectively. Explain which is easily liquefiable and why?  
(c) At what pressure does the mean free path of argon gas at  $25^\circ\text{C}$  become comparable to the diameter of the atoms themselves? Given  $\sigma = 0.36 \text{ nm}^2$ .
3. (a) The shift in frequency shown by a proton from TMS is 180 Hz, when measured on a 100 MHz instrument. Calculate the chemical shift in ppm.  
(b) Calculate the ESR frequency of an unpaired electron in a magnetic field 0.33 Tesla. Given for free electron  $g=2$ ,  $\beta=9.273 \times 10^{-27} \text{ J/T}$ .  
(c) Explain the basic principle of X-ray photo electron spectroscopy.
4. (a) Apply phenomenological equation in thermal diffusion.  
(b) How is temperature influence the miscibility curve of a three-component system forming one pair of partially miscible liquids?  
(c) What are the conditions under which linear relations are valid to understand irreversible processes?
5. (a) How do parameterization techniques help to reduce the task of computation?  
(b) Construct the z-matrix of  $\text{CO}_2$  molecule.  
(c) Differentiate STO and GTO.

[2 × 10 = 20]

**SECTION B**

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

6. (a) Calculate the first order correction to the energy levels for a one dimensional box with a slanted bottom whose potential energy varies as  $v_x/a$  where  $a$  is the length of the box.

- (b) Apply HMO theory to butadiene molecule and discuss the molecular orbitals and their corresponding energy levels.
7. (a) Calculate  $C_v$  for the following gases at room temperature.  
 i) He            ii) HCl            iii) CO<sub>2</sub>  
 Discuss the principle of equipartition of energy.  
 (b) Which among CO<sub>2</sub> and O<sub>2</sub> undergo effusion faster. Justify your answer.
8. (a) Write a brief account of NMR spectroscopy.  
 (b) Discuss the application of Mossbauer spectroscopy.
9. (a) Derive expressions for entropy production in the case of system contains both the matter flow and current flow.  
 (b) Verify the Onsager reciprocal relation in the case of simple chemical reaction  $A \rightleftharpoons B$ .
10. (a) Write a note on non-quantum mechanical method of energy calculation.  
 (b) What is potential energy surface? Explain its significance.

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Discuss the bonding in H<sub>2</sub> molecule by valence bond theory.
12. Discuss about the transport properties of gas. Show that the ratio of thermal conductivity to that of coefficient of viscosity =  $C_v/M$
13. a) Explain the principle and applications of NQR spectroscopy.  
 b) When N<sub>2</sub> gas is excited with radiation of energy 21.22 eV from a helium lamp, electrons are ejected with kinetic energies 5.63eV and 4.53 eV. What are their binding energies?  
 (7+3)
14. a) Draw the phase diagram of a three-component liquid system with three pairs of partially miscible liquids. Explain.  
 b) How would you understand (i) thermo osmosis and (ii) thermal diffusion from irreversible thermo dynamics?  
 (5+5)
15. a) Write briefly on ab-initio methods used in computational chemistry? What are the merits and demerits of the method?  
 b) Explain the terms i) force field ii) contracted Gaussians.  
 (7+3)

[10 × 3 = 30]

## SEMESTER IV

### CL 241 CHEMISTRY OF ADVANCED MATERIALS

**Total 90 h**

<b>CO No.</b>	<b>Expected Course Outcomes</b> <i>Upon completion of this course, the students will be able to</i>	<b>Cognitive Level</b>	<b>PSO No.</b>
1.	understand dimensions, synthesis, physicochemical properties of nanomaterials and its applications.	U, Ap, An	1
2.	understand and apply characterization tools for analysing nano structures.	U, Ap, An	1
3.	outline and recognize the types of polymerization, kinetics and mechanisms.	U, Ap, An	1
4.	understand the stereochemical aspects and methods for the determination of molecular weights of polymers.	U, Ap, An	1
5.	discuss the synthesis and applications of selected classes of speciality polymers.	U, Ap, An	1, 5
6.	distinguish the types and important applications of smart materials.	U, Ap, An	1, 5

PSO–Programme Specific Outcome

CO–Course Outcome

Cognitive Level: R–Remember

U–Understanding

Ap–Apply

An–Analyse

E–Evaluate

C–Create

<b>Module</b>	<b>Course Description</b>	<b>No. of Hrs</b>	<b>CO No.</b>
<b>1.0</b>	<b>Introduction to Nanomaterials and Nanotechnology</b>	<b>18</b>	
1.1	Nanomaterials: 0D, 1D, 2D and 3D nanomaterials-fundamental physicochemical principles - size dependence of the properties of nanomaterials - quantum confinement. Nanocomposites.	3	1
1.2	Synthesis of nanomaterials: Sol-Gel, colloidal precipitation, co-precipitation, hydrothermal, vapour deposition, and sonochemical method.	3	1
1.3	Carbon nanostructures and clusters: Graphenes, carbon nanotubes and fullerenes (C <sub>60</sub> ) - Synthesis, properties and applications.	4	1
1.4	Metal nanoparticles: Synthesis and properties (optical, electronic, magnetic), surface plasmon resonance.	3	1
1.5	Evolving interfaces of nanotechnology: Nanobiotechnology, nanoelectronics, nano sensors, nano-biosensors, nano tweezers, elementary ideas about nano catalysts, nano photocatalysts, nanofiltration.	3	1
1.6	Nanomedicines-nanoparticles for medical imaging and targeting cancer cells and nano encapsulation for drugdelivery to tumours. Nanotoxicology.	2	1



<b>2.0</b>	<b>Characterization Tools in Nanotechnology</b>	<b>18</b>	
2.1	Electron microscopies: Scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HR-TEM).	4	2
2.2	Probe microscopies: Atomic Force Microscopy (AFM), Scanning tunnelling microscopy (STM), Scanning tunnelling electron microscopy (STEM).	4	2
2.3	X-ray methods: X-ray diffraction (XRD), X-ray Photoelectron spectroscopy (XPS), Energy Dispersive X-ray Spectroscopy(EDAX), X-ray Fluorescence (XRF)	4	2
2.4	Laser scattering method: Dynamic light scattering (DLS)	1	2
2.5	Spectroscopic techniques: IR spectroscopy for surface functionalization of nanoparticles, UV-visible - Diffused reflectance spectroscopy, photoluminescence, Raman spectroscopy. (Basic understanding of each technique with special emphasis on characterization at nano scale).	5	2
<b>3.0</b>	<b>Polymerization processes</b>	<b>18</b>	
3.1	Free radical addition polymerization-kinetics and mechanism. Chain transfer. Cationic and anionic polymerization: Kinetics and mechanism. Step growth polymerization - Polymer characterization – Molecular weights.	3	3
3.2	Linear vs cyclic polymerization. Other methods of polymerization - bulk, solution, melt, suspension, emulsion and Dispersion techniques.	3	3
3.3	Polymer stereochemistry: Configuration and conformation, Tacticity, Chiral polymers.	3	4
3.4	Molecular weight distribution and molecular weight control. Methods for determining molecular weights-static, dynamic, viscometry, light scattering and GPC.	4	4
3.5	Crystalline and amorphous states - Glassy and rubbery states. Glass transition temperature and crystalline melting of polymers. Degree of crystallinity - X-ray diffraction.	3	4
3.6	Thermal stability of polymers - Application of DSC.	2	3
<b>4.0</b>	<b>Speciality Polymers</b>	<b>18</b>	
4.1	Industrial Polymers: carbon chain and hetero chain polymers-synthesis and applications. Polymeric reagents, catalysts and substrates.	3	5
4.2	Conducting polymers: Synthesis & applications of polyacetylenes, polyanilines, polypyrroles & polythiophines.	3	5

4.3	Photo responsive and photorefractive polymers. Polymers in optical lithography.	3	5
4.4	Drug delivery - Drug carriers - Polymer based nanoparticles.	3	5
4.5	Basic concepts about polymer based LEDs and lithium-polymer batteries.	3	5
4.6	Liquid crystalline polymers - Main chain and side chain liquid crystalline polymers. Phase morphology.	3	5
<b>5.0</b>	<b>Smart materials</b>	<b>18</b>	
5.1	Piezoelectric, magnetostrictive, halochromic, chromogenic, electrochromic, thermochromic, magnetocaloric and thermoelectric materials.	4	6
5.2	Chemistry behind photochromism in spiropyrans, spirooxazines, diarylethenes, azobenzenes, quinones. Examples for photochromic coordination compounds.	4	6
5.3	Shape-memory polymers, pH-sensitive polymers, Temperature-responsive polymers, dielectric elastomers.	4	6
5.4	Self-healing polymers and concept of mechanophores.	3	6
5.5	Introduction to ferrofluids, concept of pseudo elasticity.	3	6

## References

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### CL 242 APPLIED ANALYTICAL CHEMISTRY

**Total 90 h**

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	explain the thermal and radiochemical methods used in analytical chemistry.	U, An	1, 2
2.	explain the application of radio isotopes and the need for a safe disposal of nuclear waste.	U, An	1, 4
3.	explain the principle underlying the methods used in food analysis.	U, An	1, 10
4.	carryout the detection of food adulterants.	U, Ap, An	1, 7, 10
5.	explain the basic principles of forensic analysis.	U, An	1
6.	explain the nature of poisons and suggest possible antidotes.		1, 10
7.	explain the importance of DNA finger printing and ballistics in forensic analysis.	U, An	1, 10
8.	explain the methods of analysis and the principles involved in the analysis of biological fluids, enzymes, drugs and alcoholic beverages.	U, An	1, 10
9.	explain the instrumentation and working principle of Flame spectrometry, AAS, AES, XPS and X-ray fluorescence.	U, An	1, 2

PSO–Programme Specific Outcome

CO–Course Outcome

Cognitive Level: R–Remember

U–Understanding

Ap–Apply

An–Analyse

E–Evaluate

C–Create

Module	Course Description	No. of Hrs	CO No.
<b>1.0</b>	<b>Thermal and Radiochemical methods of Analysis</b>	<b>18</b>	
1.1	Principle, theory and instrumentation of Thermo mechanical analysis (TMA) and Dynamic mechanical analysis (DMA). Thermometric titrimetry – theory,	4	1

	applications.		
1.2	Radiochemical methods of analysis: radioactive tracer techniques and its applications, principle and applications of isotope dilution analysis, neutron activation analysis and its applications.	5	1
1.3	Radiometric titration: principle, techniques based on complex formation and precipitation, radiometric titration curves for estimation of ions from their mixture.	5	1
1.4	Applications of radio isotopes in industry, medicine, autoradiography, radio pharmacology, radiation safety precaution, nuclear waste disposal.	4	2
<b>2.0</b>	<b>Food Analysis</b>	<b>18</b>	
2.1	Food analysis: Determination of moisture (Oven drying Karl-Fischer Titration, Colorimetry), Ash (Dry and Wet ash method), crude protein (Kjeldahl's method, Dumas method and Biuret method), Fat (Soxhlet method; Mojonnier Method, Gerber method), Crude fibre, carbohydrate (Phenol-Sulfuric Acid method for determination of total carbohydrates; Nelson-Somogyi method for determination of reducing sugars; Enzymatic method), calcium, potassium, sodium, phosphates and vitamins (A, B <sub>1</sub> , B <sub>2</sub> , C, E) in food.	6	3
2.2	Food adulteration – common adulterants in food and their determination. Contamination of food stuffs. Analysis of milk for fat and added water.	4	4
2.3	Oils and fats and their analysis: iodine value, iodine bromine value, saponification value and acid value and their significances. Rancidity-detection and determination (peroxide number).	4	3, 4
2.4	Pesticide residues in foods determination of chlorinated organic pesticides.	4	3, 4
<b>3.0</b>	<b>Forensic Analysis</b>	<b>18</b>	
3.1	Forensic analysis: basic principles and significance, sampling, sample storage, sample dissolution.	3	5
3.2	Analysis of biological substances – blood, saliva and urine.	2	6
3.3	General discussion of poisons with special reference to mode of action of cyanide and organophosphates. Classification of poisons, Lethal dose, significance of LD <sub>50</sub> and LC <sub>50</sub> . Diagnosis of poisons in the living and the dead—clinical symptoms – postmortem appearances. Antidotes for common poisons. Estimation of poisonous materials such as lead, mercury, chromium and arsenic in biological materials.	5	6
3.4	Physiological effects of natural poisons such as	2	6

	morphine, hashish and nicotinoids. Health hazards and Remedial measures.		
3.5	DNA Finger printing, Steps involved, DNA Finger printing for tissue identification in dismembered bodies, Detecting steroid consumption in athletes.	3	7
3.6	Ballistics: internal and terminal ballistics – small arms. Bullets and bullet wounds, composition of bullets and detecting powder burn, detection of powder residue by chemical tests.	3	7
<b>4.0 Analysis of selected materials</b>			
<b>4.0</b>	<b>Analysis of selected materials</b>	<b>18</b>	
4.1	Principles of estimation of biological fluids: Estimation and interpretation of data for blood sugar, haemoglobin, urea and cholesterol.	3	8
4.2	Biological significance, analysis and assay of enzymes: pepsin, monoaminoxidase, and tyrosinase.	3	8
4.3	Analysis of drugs and pharmaceuticals: quality control, official methods, classical and modern methods of drug analysis.	4	8
4.4	Analysis of common drugs: analgesics, antipyretics, antimalarial, antiallergic (anti-histamines) and antibiotics.	4	8
4.5	Analysis of alcoholic beverages: determination of quality parameters such as original extract, alcohol, extract, CO <sub>2</sub> , O <sub>2</sub> . Brix, degree of inversion, pH value, ethyl carbamate, carbohydrate, and dissolved oxygen	4	8
<b>5.0 Instrumental Methods of Chemical Analysis</b>			
<b>5.0</b>	<b>Instrumental Methods of Chemical Analysis</b>	<b>18</b>	
5.1	Flame spectrometry: introduction, elementary theory, instrumentation, type of burners, type of interferences, background correction method and applications.	4	9
5.2	Atomic absorption spectroscopy: principle, instrumentation, production of atoms and ions, burners, detectors, HCL, TGL, EDL, advantage and disadvantage of AAS.	4	9
5.3	Atomic emission spectrometry: introduction, equipment, qualitative and quantitative analysis with AES, plasma emission spectrometry, ICP-AES, sample introduction and measurements.	4	9
5.4	X-ray Photoelectron spectroscopy (XPS): introduction and basic theory, instrumentation, XPS imaging.	3	9
5.5	Molecular fluorescence and X-ray fluorescence: introduction and basic theory, instrumentation and applications.	3	9

## References

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### CL 243 (a) Dissertation

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	demonstrate an advanced theoretical and technical knowledge of chemistry as a creative endeavour; analyse, interpret and critically evaluate scientific information.	Ap, An	1
2.	present information, articulate arguments and conclusions, in a variety of modes, to audiences in their field of research.	E, C	5, 8

3.	as part of a team or individually, design, conduct, analyse and interpret results of an experiment, and effectively communicate these in written reports and other formats.	Ap, An	3, 7
4.	develop an understanding of the requirements to undertake independent research in a chemistry field.	U	6, 9
5.	demonstrate an understanding of the relationship between scientific research and the progress of new knowledge in a global scenario.	An	5, 6, 9

### CL 243 (b) Visit to R & D Centre

CO No.	Expected Course Outcomes <i>Upon completion of this course, the students will be able to</i>	Cognitive Level	PSO No.
1.	Understand the relevance of independent supervised research in a chemistry field and the need of well-developed judgement, adaptability and accountability as a practitioner or learner	U, An	2, 9

### Model Question Papers

#### General Instruction to question paper setters

- There will be a 15 main questions in each question paper divided into 3 sections – A, B and C.
- Each of the sections A, B and C will have 5 questions each, **1 from each module**.
- Each question in Section A will have 3 sub questions (a), (b) and (c), of which the candidate has to answer any two (2 marks each).
- Each question in Section B will have 2 sub questions (a) and (b), of which the candidate has to answer any one (5 marks each).
- Candidate should answer any three out of the five questions in Section C (10 marks each).
- Section A carries a total of 20 marks, Section B carries 25 marks, and Section 3 carries 30 marks.
- The maximum marks will be 75 and the duration of the exam will be 3 hrs.

**Fourth Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 241: CHEMISTRY OF ADVANCED MATERIALS**  
 (2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

### SECTION A

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

1. (a) What is meant by quantum confinement?  
 (b) Explain the synthesis of metal nanoparticles with an example.  
 (c) Write a short note on nano toxicology?

2.
  - (a) What is EDAX?
  - (b) How XPS is used in nano technology?
  - (c) How diffused reflectance spectroscopy is used in characterisation of nanoparticles?
  
3.
  - (a) What do you mean by chain transfer in polymerization process?
  - (b) Mention two advantages and two disadvantages of solution polymerization over bulk polymerization.
  - (c) Explain briefly “auto acceleration” in radical polymerization? Why does it happen?
  
4.
  - (a) What are conducting polymers?
  - (b) Name any two polymeric reagents.
  - (c) Which are the polymers used in optical lithography?
  
5.
  - (a) What are halochromic materials?
  - (b) Write a note on pH-sensitive polymers.
  - (c) What are piezo electric materials?

[2 × 10 = 20]

### SECTION B

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

6.
  - (a) Explain the relation between size and properties of nano-materials.
  - (b) Explain the CVD method used in the preparation of nanoparticles.
  
7.
  - (a) Explain the use of powder XRD in determination of particle size of nanomaterials.
  - (b) How is electron microscopy used as characterisation techniques?
  
8.
  - (a) What are chain transfer agents? Describe their effect on rate expression and molecular weight obtained in the presence of chain transfer agent.
  - (b) Unlike radical polymerisation both cationic and anionic polymerization show a marked dependence on the type of solvent used. Discuss on this.
  
9.
  - (a) Discuss the structure and working principle of lithium polymer batteries.
  - (b) Explain in detail the synthesis of polythiophenes.
  
10.
  - (a) Explain the chemistry of photochromism in spirooxazines and quinones.
  - (b) Write short note on synthesis and application of ferrofluids.

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Explain application and role of metal nano particles in catalysis with examples.
  
12. Discuss the applications of DLS and IR spectroscopy in the analysis of nanomaterials.



13. Elaborate any two methods to determine the molecular weight of polymers.
  14. Explain the application of polymers in drug delivery and in catalysis.
  15. Describe with proper examples:
    - (a) magnetostrictive materials
    - (b) thermoelectric materials
    - (c) self-healing polymers
    - (d) dielectric elastomers.
- [10 × 3 = 30]

**Fourth Semester M.Sc. Degree Examination – Model question paper**  
**Branch IV – Analytical Chemistry**  
**CL 242: APPLIED ANALYTICAL CHEMISTRY**  
(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

**SECTION A**

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

1.
  - (a) Explain the principle behind thermo mechanical analysis?
  - (b) What is meant by radiotracer technique? Give its applications
  - (c) List out any two methods adopted for radiation safety.
2.
  - (a) Differentiate food adulteration from contamination.
  - (b) What is meant by rancidity?
  - (c) How is fat content in milk determined?
3.
  - (a) Distinguish LD<sub>50</sub> and LC<sub>50</sub>.
  - (b) What are antidotes? Which is the antidote used for treatment of pesticidal poisoning due to malathion?
  - (c) What is meant by a false positive in forensic analysis? Give an example.
4.
  - (a) Give the principle for the estimation of blood sugar.
  - (b) Write a short note on Brix.
  - (c) What are the modern methods of drug analysis?
5.
  - (a) Flame emission spectroscopy is temperature dependent whereas AAS is not. Why?
  - (b) List out two advantages and disadvantages of AAS.
  - (c) What is the role of nebuliser in flame photometry?

[2 × 10 = 20]

**SECTION B**

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

6.
  - (a) Examine briefly the methods and concerns of nuclear waste disposal
  - (b) Discuss the principle behind Dynamic Mechanical Analysis.

7. (a) Explain the Phenol-Sulfuric Acid method for the determination of total concentration of carbohydrates present in food samples.  
(b) How is the presence of chlorinated organic pesticides determined in food?
8. (a) What is a presumptive test in forensic analysis? Briefly explain the presumptive test used in the identification of saliva?  
(b) What are suicidal and homicidal poisons? What are the characteristics of ideal suicidal and homicidal poisons? Give examples.
9. (a) Explain the determination of alcohol content and CO<sub>2</sub> in alcoholic beverages.  
(b) Point out the biological significance of pepsin and monoaminoxidase.
10. (a) Give an account of the working of a hollow cathode lamp.  
(b) Explain the interferences in AAS.

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Discuss in detail the neutron activation analysis in radio chemistry citing its applications.
12. Explain the Kjeldahl's methods for the determination of proteins in food citing its advantages and disadvantages.
13. Discuss briefly on DNA finger printing as an analytical tool in forensic chemistry.
14. Give and principle and detail the method of estimation of cholesterol in biological samples.
15. Explain the theory and instrumentation of X-ray fluorescence.

[10 × 3 = 30]