UNIVERSITY OF KERALA

POST GRADUATE PROGRAMME IN POLYMER CHEMISTRY

(Revised Syllabi under Semester System with effect from 2018 Admissions)

PREAMBLE

The syllabi of M.Sc programme in Polymer Chemistry offered in the affiliated colleges of the University under Semester system have been revised and the revised syllabi are to be effective from 2018 admission. There are five independent PG programmes in Chemistry, namely **M.Sc**. **Programme in Branch III - Chemistry**, **M.Sc. Programme in Branch IV - Analytical Chemistry, M.Sc. Programme in Branch V - Applied Chemistry, Branch VI Medicinal Chemistry and M.Sc. Programme in Branch VII – Polymer Chemistry**. All these five PG programmes are equivalent in all respect for employment and higher studies. Each of these five PG programmes shall extend over a period of two academic years comprising of four semesters, each of 450 hours in 18 weeks duration. The theory courses of the first three Semesters and the practical courses of the first two semesters of these five programmes are common, and therefore, the examinations of these five PG programmes are to be conducted with common question papers for the first three semesters by a common Board of Examiners. The syllabi of M.Sc. Branch VII –Polymer Chemistry are effective from 2018 admission in affiliated colleges of the university.

M.Sc. PROGRAMME IN BRANCH VII – POLYMER CHEMISTRY

(Revised syllabus under semester system with effect from 2018 admissions)

SYLLABUS AND SCHEME OF EXAMINATION

Course No. and Title	Hours per week		Duration of ESA in hours	Marks for CA	Marks for ESA	Total marks
	L	P				
SEMESTER I*						
PC 211 Inorganic Chemistry I	5		3	25	75	100
PC 212 Organic Chemistry I	5		3	25	75	100
PC 213 Physical Chemistry I	5		3	25	75	100
PC 214 Inorganic Practicals I		3	(To be continued in Semester II)			
PC 215 Organic Practicals I		3	(To be continued in Semester II)			
PC 216 Physical Practicals I		4	(To be continued in Semester II)			
			Total marks for semester 1			300
*Distribution of teaching hours/week: Theory- 15 hours, Practicals- 10 hours (1 hour for Seminar)						
SEMESTER II*						
PC 221 Inorganic Chemistry II	5		3	25	75	100
PC 222 Organic Chemistry II	5		3	25	75	100
PC 223 Physical Chemistry II	5		3	25	75	100
PC 214 Inorganic Practicals I		3	6	25	75	100
PC 215 Organic Practicals I		3	6	25	75	100
PC 216 Physical Practicals I		4	6	25	75	100
	Total marks for Semester II					600
*Distribution of teaching hours/week: Theory- 15 hours, Practicals- 10 hours (1 hour for Seminar)						

SEMESTER III*

PC 231 Inorganic Chemistry III	5		3	25	75	100
PC 232 Organic Chemistry III	5		3	25	75	100
PC 233 Physical Chemistry III	5		3	25	75	100
PC 234 Polymer Practicals I		3	(To be continued in Semester IV)			
PC 235 Organic Practicals II		3	(To be continued in Semester IV)			
PC 236 Physical Practicals II		4	(To be continued in Semester IV)			
			Total marks for semester III			300

*Distribution of teaching hours/week: Theory- 15 hours, Practicals- 10 hours (1 hour for Seminar)

SEMESTER IV*

PC 241 Polymer Chemistry I	5			25	75	100
PC 242 Polymer Chemsitry II	5		3	25	75	100
PC 234 Polymer Practicals II		3	6	25	75	100
PC 235 Organic Practicals II		3	6	25	75	100
PC 236 Physical Practicals II		4	6	25	75	100
PC 243(a) Dissertation	5				70	70
PC 243(b) Visit to R & D Centre					5	5
Comprehensive viva-voce					25	25
	Total marks for Semester IV					600
	Grand total (for semesters I-IV)					1800

**Distribution of teaching hours/week: Theory- 10 hours, 5 hours for discussion on project (1 hour for Seminar) **Each student has to choose either (a), (b), (c) as elective in accordance with the Dissertation chosen.

M.Sc. PROGRAMME IN BRANCH VII POLYMER CHEMISTRY

(Revised syllabus Under Semester System w.e.f. 2018 Admissions)

SEMESTER I

PC 211 INORGANIC CHEMISTRY I

Total 90 h

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

Types of ligands and complexes. Isomerism: Structural, geometrical and optical isomerism. Crystal field theory: Splitting of d orbitals in octahedral, tetragonal, square planar, tetrahedral, trigonal bipyramidal and square pyramidal fields. Jahn-Teller theorem, evidence for JT effect, static and dynamic JT effect. Crystal field stabilization energy (CFSE) and its calculations. Octahedral Site Stabilization Energy. Factors affecting the splitting parameter. Spectrochemical series. Evidence of covalency in Metal-Ligand bond, introduction to Ligand field theory. Molecular orbital theory. Sigma and pi bondings in complexes. MO diagrams of octahedral and tetrahedral complexes with and without pi bonds. Experimental evidence of pi bond on the stability of sigma bond. Nephelauxetic effect.

Unit II Analytical principles 18 h

Evaluation of analytical data: Accuracy and precision. Standard deviation, variance and coefficient of variation. Student ‘t’ test, ‘Q’ test, and ‘F’ test. Confidence limits. Errors: Classification, distribution, propagation, causes and minimization of errors. Significant figures and computation rules. Correlation analysis: Scatter diagram. Correlation coefficient,r. Calculation of r by the method of least squares. Volumetric methods: Classification of reactions in volumetry. Theories of indicators. Acid-base, redox, adsorption, metallochromic indicators. Complexometric titrations: Titration using EDTA-direct and back titration methods. Precipitation titrations. Redox titrations. Titrations in non-aqueous solvents. Organic reagents used in gravimetry: Oxine, dimethylglyoxime and cupferron. Principle and instrumentation of TG, DTA and DSC. Factors affecting TG and DTA curves. Applications of TG DTA and DSC in the study of metal complexes.

Unit III Molecular symmetry **18 h**

Symmetry and Character table: Symmetry elements and symmetry operation. Matrix representation of symmetry operations. Character of a matrix. Conditions for a set of elements to form a group. Point groups. Multiplication of operations. Group multiplication table. Similarity transformation and classification of symmetry operation, Matrix representation of point group. Reducible and Irreducible representations. The Great Orthogonality theorem. Rules derived from GOT (proof not required). 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. Hybridisation: identification of atomic orbitals taking part in hybridisation of triangular planar, square planar, trigonal bipyramidal, square pyramidal and tetrahedral molecules. Molecular symmetry and optical activity.

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

Preparation, properties and structure of isopoly acids of Mo,W and V and Heteropoly acids of Mo and W. Preparation and properties of Xenon fluorides and Krypton compounds ($KrCl_4$, KrF_4, KrF_2, $KrBr_6$, $Kr_2Cr_2O_7$, $KrCrO_4$ & KrO_2), structure of XeF_2 (MO theory only) . Preparation, bonding and uses of inter halogen compounds. Properties and structure of aluminosilicates and zeolites, shape selectivity. Preparation, properties and applications of silicones.

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

The 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. The Chemistry of processes in hydrosphere; The hydrologic cycle. Cycling and purification. The unique properties of water. Acid base properties. CO_2 in water. Alkalinity. O_2 consuming waste. DO, BOD and COD. The chemistry of processes in Lithosphere; Redox status in soil. pE, pH predominance diagrams for redox sensitive elements. 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.

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.
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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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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

PC 212 ORGANIC CHEMISTRY-I

Total 90 h

Unit I Stereochemistry of organic compounds 18h

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.

Introduction to molecular symmetry and chirality, Axial Chirality, Planar Chirality and Helicity, Relative configuration, Stereochemical nomenclature, *R* and *S*, *E* and *Z*. Prostereoisomerism, stereotopicity and stereoprojections. Non-carbon chiral centres – Nitrogen, phosphorus and sulfur as chiral centres.Axial stereochemistry:Atropisomerismand its designation, *M* and *P* configurations. Stereoselectivity: enatioseelctetivity, diastereeoselectivity and stereoconvergence. Basic introduction to chiral separation methods and estimation of enantiomeric excess.

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

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

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

Unit II Structure, reactivity and intermediates 18 h

Reaction coordinates- difference between transition state and intermediates, Homolytic and heterolyticbond fissions. Formation and structure of carbocations, carbanion and free radicals, Stability of intermediates, influence of field effect, inductive, mesomericand steric effects on controlling stability if carbocations, carbanions and carbon-centered radicals. Influence of structural features on acidity, basicity and reactivity of organic compounds. Alkyl, aralkyl and allylic cations –influence of substituents. General reactions of carbocations, carbanions and free radicals.Introduction to radical ions. Formation, structure, stability and chemical reactions of carbens, nitrenes and arynes.

Unit III Substitution reactions **18 h**

Nucleophilic substitution at sp^3carbon - S_N1 and S_N2 mechanisms.Walden inversion, stereochemistry.Effect of solvent,leaving group and substrate structure on rates of S_N1 and S_N2 substitutions.Neighbouring group participation, Non-classical carbocations, Competition between S_N^1 and S_N^2reactions.S_N1', S_N2', S_Ni mechanism.

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

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

Aromatic Nucleophilic Substitution reactions - S_N1, S_NAr, benzyne and $S_{RN}1$ mechanism and evidence with examples.

Unit IV Elimination and addition reactions **18h**

Elimination reactions leading to C=C bond formation and their mechanisms. E1, E2 and E1CB mechanisms.Stereoaspects of C=C bond formation. Effect of leaving group and substrate structure.Hoffmann and Saytzeff elimination.Cis elimination.Stereoaspects of the addition of H_2O, X_2, HX, and boranes to C=C systems**.**Effect of substituents on the rate of additions. Cis and trans hydroxylation of cycloalkenes. Nucleophilic addition to activated C=C systems. Structure of the transition state in the addition reactions. Michael addition:mechanism with evidence. Addition to Carbon-Heteroatom multiple bonds: Aldol condensation (normal, crossed and directed), Perkin, Stobbe, Knoevenagel, Darzen, Reformatsky and benzoin condensations. Grignard, Cannizzaro, Wittig and Wittig-Horner reactions.Application of Cram's rule, Felkin-Ann model.

Unit V Reagents in organic synthesis **18h**

Applications of hydrogenation catalysts, hindered boranes, bulky metal hydrides. $NaCNBH_3$ DIBAL, Li trialkylborohydrides, tri-*n*-butyltin hydride, diimide, Lindlar catalysts and aluminium alkoxide. Rosenmund reduction and McFadeyan-Stevens reaction. Oxidation using SeO_2, lead tetraacetate, ozone, peracids, DDQ, manganese (1V) oxide, silver carbonate and Cr(V1) reagents. Swern oxidation, Moffatt oxidation, allylic and benzylic

oxidation.Sommelet reaction.Elbs reaction.Oxidative coupling of phenols.Chemo and regioselectivity in reductions and oxidations.

References

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2. D. Nasipuri, "Stereochemistry of Organic compounds", 2nd Edition, Wiley Eastern, 1994.
3. J. Clayden, N. Greeves, and S. Warren, "Organic Chemistry,"2nd Edition, Oxford University Press, 2012.
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18. R. O. C. Norman and J. M. Coxon, "Principles of organic synthesis," CRC Press, 1993.

PC 213 PHYSICAL CHEMISTRY –I

90 h

Unit 1- Quantum Chemistry I 18 h

Classical mechanics and its limitations, need of quantum mechanics, concept of matter wave,de Broglie relation and its experimental proof, uncertainty principle and its consequences.

Postulates of Quantum Mechanics

State function postulate:Born interpretation of the wavefunction, well behaved functions, orthonormality of wave functions. Operator postulate: operator algebra, linear and nonlinear operators, Laplacian operator, commuting and non-commuting operators, Hermitian operators and their properties, eigen functions and eigen values of an operator. Eigen value postulate: eigen value equation, eigen functions of commuting operators. Expectation value postulate. Postulate of time-dependent Schrödinger equation, Quantization of angular momentum, quantum mechanical operators corresponding to angular momenta (Lx, Ly, Lz and L^2)-commutation relations between these operators.

Application of Quantum mechanics to Exactly Solvable Model Problems

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

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

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

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

Unit II Surface Chemistry and Catalysis 18 h

The Gas- solid inter phase,types of adsorption. Heat of adsorption and its determination, differences betweenchemisorption and physisorption. Adsorption isotherms-classical, Freundlich and Langmuir isotherms. Thermodynamic and statistical derivation of Langmuir adsorption isotherm. Multilayer adsorption- the BET theory and Harkins- Juratheory.

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

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

Surface films-different types, surface pressure and its measurement,surface potential and its measurementsand interpretation.Measurement of surface area of solids - Harkins – Jura absolute method, entropy method andthe point B method. Use of Langmuir, BET and Harkins – Jura isotherms for surface areadetermination.

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

Unit 1II: Classical Thermodynamics 18 h

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

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

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

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

Thermodynamics of mixing, Duhem-Margules equation, Konowaloff'srule, Henry's law, excess thermodynamic functions- Determination of excess enthalpy and volume.

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

Unit IV Chemical kinetics **18 h**

Theories of reaction rates: Collision theory and its failure,. Transition state theory-Eyring equation. Comparison of the two theories. Thermodynamicformulation of the reaction rates. potential energysurfaces

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

Kinetics of complex reactions-parallel reactions,opposing reactions,consecutive reactions and chain reactions, steady state treatment, kinetics of 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.

Fast reactions: Relaxation method, relaxation spectrometry, flow method, shockmethod, fast mixing method, field jump method, pulse method, Flash photolysis and NMRmethod.

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

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

Unit V Gaseous and liquid state **18 h**

Maxwell's distribution of molecular velocities,influence of temperature on molecular velocities, types of molecular velocities-average velocity and most probable velocity and its determination from Maxwell's equation

Transport phenomena in gases-viscosity of gases, Chapman equation, determination of viscosity of gases, calculation of mean free path, Thermal conductivity, diffusion, Degrees of freedom of gaseous molecules - Transilational, Rotational and vibrational. Equation of state of real gases-van der Waal's equation, Other equation of states—Radlich-Kwong equation, Clausius equation, Virial equation, second virial coefficient and determination of diameter of a molecule.

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

Liquid state Liquid vapour equillibria, vapour pressure- methods of measuring vapour pressure - barometric method and dynamic method - equation of state for liquids, structure of

liquids, X-ray diffraction of liquids-vacancy model for a liquid, pair correlation function, surface tension , determination of surface tension, drop weight method and drop number method, viscosity, determination of coefficient of viscosity using Ostwald viscometer.

References

1. I.N. Levin, "Quantum Chemistry", Prentice Hall, New Jersey,Vth edn., 2000.
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PC 214 –INORGANIC CHEMISTRY PRACTICALS -1

Total 125 h

1. Separation and identification of rare/less familiar cations such as Ti, W, Mo, Th, Zr, V, U and Li
2. Volumetric estimation using EDTA, ammonium vanadate, ceric sulphate etc.
3. Colorimetric estimation of Cr, Fe, Mn, Ni, Cu etc.
4. Preparation of metal complexes: selection can be made from the following or any other from the existing literature.

    - $[Co(NH_3)_6]Cl_3$
    - $[Cu(NH_3)_4]SO_4$
    - $K_3[Cr(C_2O_4)_3]$
    - $K_3[Fe(C_2O_4)_3]$
    - Cis and trans isomers of $[Co(en)_2Cl_2]Cl$
    - $[Cr(en)_3]Cl_3$

References

1. A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longman, 4th edition, 1978.
2. A. I. Vogel, A Text Book of Qualitative Inorganic Analysis, Longman 5th edition, 1979.
3. D.A. Skoog and D. M. West, Analytical Chemistry: An Introduction, Saunders College Publishing, 4th edition, 1986.
4. W. G. Palmer, Experimental Inorganic Chemistry, Cambridge University, 1959.

PC 215 ORGANIC PRACTICALS-1

Total 125 h

A . Separation and identification of organic compounds

1. Quantitative wet chemistry separation of a mixture of two components by solvent extraction

2. TLC of the purified samples along with the mixture in same TLC **plates (component 1 with mixture and component 2 with mixture on separate TLC plate) and** calculation of $R_f$values- Reporting and recording TLC in standard formats- preparation of sample solution, adsorbent, dimensions of the plate, saturation time, developing time, visualization and detection, R_f Value, Drawing - in the form of a table.

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

1) Malachite green and methylene blue 2) *o*-nitroaniline and *p*-nitroaniline.

C. Preparation of compounds by two stages.

Recording/downloading UV,IR,^{1}H NMR and ^{13} C NMR and EI mass spectra of synthesized compounds.
TLC analysis- stage 1 reactants and products on TLC plate 1 and stage 2 reactants and products on plate 2)- Record TLC in standard format as in separation

All preparations must be restricted to 1 g level

Nitration

1) Acetanilide- ⟶ *p*-nitroacetanilide ⟶ *p*-nitroaniline

2) Methylbenzoate ⟶ methyl *m*-nitrobenzoate ⟶ *m*-nitrobenzoic acid

Bromination

3) Acetanilide- ⟶ *p*-bromoacetanilide ⟶ *p*-bromooaniline

Aldol condensation- Synthesis of heterocycles

4) benzaldehyde ⟶ Dibenzylideneacetone ⟶ 1,5-Diphenyl-3-styryl-2-pyrazoline

Diazocoupling

5) Aniline ⟶ Diazoaminobenzene ⟶ *p*-aminoazobenzene

Rerrangement

6) Pthalic anhydride - ⟶ Pthalimide ⟶ anthranilic acid

Synthesis of Dyes

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

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

References

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.
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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://sdbs.riodb.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi.

PC 216 PHYSICAL PRACTICALS –I 125 h

Adsorption

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

Kinetics

Determination of rate constant of acid hydrolysis of methyl acetate.

Determination of Arrhenius parameters.

Determination of concentration of given acid.

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

Determination of rate constant of reaction between $K_2S_2O_8$ and KI.

Study the kinetics of iodination of acetone in acid medium.

Phase rule

Solid-liquid equilibria

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

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

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

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

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

Distribution law

Distribution coefficient of ammonia between chloroform and water.

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

Distribution coefficient of benzoic acid between toluene and water.

Distribution coefficient of iodine between hexane and water/$CHCl_3$ and water/ CCl_4 and water

Determination of the equilibrium constant of the reaction $KI + I_2 \leftrightarrow [KI_3]$ and hence the concentration of given KI in hexane and water/$CHCl_3$ and water/ CCl_4 and water.

Determination of hydrolysis constant of anilinium hydrochloride.

Dilute Solutions

Determination of K_f of solid solvent, molar mass of non-volatile solute, mass of solvent and composition of given solution (Solvent- Naphthalene/Biphenyl/ Benzophenone etc. Solute- Naphthalene/ Biphenyl/ Diphenylanmine etc)

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

Determination of atomicity of sulphur.

Transition temperature

Determination of K_T of salt hydrate, molar mass of solute, mass of salt hydrate and composition of given solution (Solvent- $Na_2S_2O_3.5H_2O$/$CH_3COONa.3H_2O$, Solutes glucose,sucrose, urea)

Thermochemistry

Determination of the concentration of given strong acid/alkali.

Thermometric titration of NaOH Vs standard HCl.

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

Determination of the heat of ionisation of acetic acid.

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6) B.Viswanathan, "Practical Physical Chemistry",Viva Publications, 2012.

7) P.S.Sindhu, "Practicals in Physical Chemistry-A Modern Approach", MacMillanIndia, 2005.

8) D. P. Shoemaker, C. W. Garland & J. W. Nibler. "Experiments in Physical Chemistry

First Semester M.Sc. Degree Examination – Model question paper
Branch – Chemistry
PC 211 : INORGANIC CHEMISTRY- I
(2018 Admission Onwards)
(Common for CH/CL/CA/CM/PC 211)

Time : 3 Hrs Max. Marks: 75

SECTION A

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

1. a) What is meant by Nephelauxetic effect?

   b) Explain linkage isomerism with suitable example.

   c) What is meant by crystal field stabilization energy?

2. a) What do you mean by significant figure? How many significant figures are in the following?

   i) 0.0026
   ii) 6.023×10^{23}

   b) What are metallochromic indicators? Give an example.

   c) In a volumetric experiment the volumes of the titrant used are 9.98, 9.99, 9.98, 9.95, 10.00 and 10.02 mL. Calculate the standard deviation.

3. a) Identify the symmetry elements present in the following and assign the point group i) H_2O ii) HCl

   b) Explain improper axis of symmetry.

   c) What is meant by character table.

4. a) Explain the term ‘shape selectivity’.

   b) Give the preparation of $KrCl_4$ and KrO_2.

   c) What are zeolite? Explain their use as water softeners.

5. a) Brief the role of catalytic converters in automobiles.

   b) Explain the formation of photochemical smog.

   c) Mention the different regions of atmosphere. **(2x10= 20 marks)**

SECTION B

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

6. a) State and illustrate Jahn Teller effect.

   b) Explain the crystal field theory of octahedral complexes.

7. a) Give a brief note on scatter diagram and its significance.

   b) Explain the titrations in non-aqueous solvents.

8. a) Construct the multiplication table for the symmetry operations of NH_3 molecule.

   b) State and explain orthogonality theorem.

9. a) Give an account of inter halogen compounds.

   b) Write a short note on silicones.

10. a) List out the major pollutants. Outline how they affect human health?

    b) Describe how we can quantify soil acidity.

(5x5= 25 marks)

SECTION C

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

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

(10x3= 30 marks)

FIRST SEMESTER MSc.DEGREE EXAMINATION

BRANCH - CHEMISTRY

CH/CL/CA/CM/PC212: Organic Chemistry-I

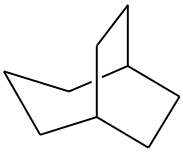
(2018 admission)

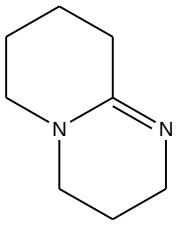
Time: 3 hours **Maximum marks:75**

Section A

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

1 a) Write IUPAC names of the following.

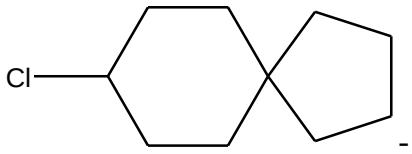




b) Indicate the element of symmetry present in each of the following molecules.

i)*trans*-1,4-dichlorocyclohexane-

ii)



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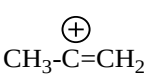
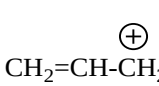
c)What is atropisomerism?

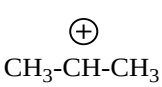
2. a) How arynes are formed?

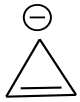
b)*p*-Nitroaniline is less basic than *m*-nitroanile, explain.

c)Arrange the following carbocations in order of increasing stability and give reasons.









3. a) What is SNi reaction?

b) Alkaline hydrolysis of $Et_2NCH(Cl)CH_2CH_3$ produces $Et_2NCH(Et)CH_2OH$. Account for this observation

c) Write two examples of non classicalcarbocations.

4 a) How would you prepare trans-1,2-dihydroxycyclohexane from cyclohexene?

b)Write the mechanism of benzoin condensation.

c) How can the E1CB pathway be distinguished from the kinetically indistinguishable E2 pathway?

5 a) Write two important reaction of $NaCNBH_3$

b) Explain the importance of DDQ in organic synthesis.

c) Explain Swern Oxidation **(2x10= 20 marks)**

Section B

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

6 a) Compare ORD and CD and explain their relationship

b) Write a note on stereochemistry of nitrogen compounds

7 a) Explain the Felkin-Ann model with an example

b)How carbenes are generated? Explain its structure and properties

8 a) Explain why anti Markonikoff's addition is not exhibited by HCl or HI when reacted with 1-butene?

b) After standing in aqueous acid *R*-2-butanol is found to have lost its optical activity. Account for this observation.

9 a) Write a note on cis and trans hydroxylation of alkenes

b) State Crams rule.Explain it with suitable example

10 a)Write a note on oxidation using SeO_2

b) Explain briefly the role of Lead tetra acetate in organic synthesis (**5x5= 25 marks)**

Section C

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

11. Give a brief account on stereoselectivity, enantiomeric excess and chiral separation.

12 Explain the following

a. S_NAr mechanism , b) Orientation effect in aromatic electrophilic substitution

13. Discuss the following
a) competition between S_N1 and S_N2 b) Stereochemistry of nucleophilic substitution

14. Describe the following

a) Mechanism with evidences of aldol condensation

b) Wittig reactions and applications

15. Write a note on a) Sharpless asymmetric epoxidation

b) Chemoselectivity in reduction reactions **(10x3= 30 marks)**

First Semester M.Sc. Degree Examination (Model Question Paper)

Branch-III Chemistry
CH 213/CL 213/CA 213/PC 213 : Physical Chemistry- 1
(2018 Admission Onwards)
I

Time: 3 h Max.Marks:75

Section A

Answer any two from **a,b,c**, of each question. Each sub question carries **2** marks.

(10 x 2 = 20 marks)

1. (a)Calculate de Broglie wave length of mass 1 mg moving with a velocity of 10 m s^{-1}

   (b) What is an operator? Give example.

   (c) Write spectroscopic term symbol for the ground state of O atom

2. (a) What is the principle of photoelectron spectroscopy?

   (b) Write the B.E.T theory of multilayer adsorption kjhh

   (c) Write the different types of adsorption? Explain

3. (a) Define chemical potential

   (b) State Lewis –Randall rule of fugacity

   (c) Write Konowaloff's rule

4. (a) How is nmr spectroscopy made use of in the study of fast reactions?

   (b) What is steady state approximation?

   (c) Define quantum yield

5. (a) What is the effect of temperature on the distribution of molecular velocities of a gas? Explain.

   (b) Calculate the root mean square velocity of nitrogen at 27^0C

   (c) Write the virial equation of state. Explain the terms

Section B

Answer either **a** or **b** of each question. Each question carries **5** marks.

(5 x 5 = 25 marks)

6. (a) Explain Quntaum mechanical Tunneling

   (b) Write kinetic energy operator. Show that it is a Hermition operator

7. (a) Write any two methods for the determination of surface area of a solid

   (b) Explain Langmuir-Hinshelwood mechanism of surface catalysed reaction

8. (a) Define fugacity. Write the method for the determination of fugacity of a gas

   (b) Derive Gibbs Duhem equation

9. (a) Explain Jabalonski diagram

   (b) Derive the rate law for the decomposition of N_2O_5

10. (a) Calculate the viscosity of O_2 at 25^0C. The molecular diameter is 3.6A

    (b) Write any one method for the determination of surface tension of liquid

Section C

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

(3 x 10 = 30 marks)

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

12. Explain any two methods using for surface analysis

13. Write a brief account of the methods for the determination of activity coefficient of electrolytes and non electrolytes

14. Explain chain reactions. Discuss Seminoff Henshelwood theory of branching chain reactions

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

SEMESTER II

PC 221 INORGANIC CHEMISTRY –II

Total 90 h

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

Sulphur-nitrogen compounds: Tetrasulphur tetranitride, disulphur dinitride and polythiazyl S_xN_y compounds. S-N cations and anions. Sulphur-phosphorus compounds: Molecular sulphides such as P_4S_3 , P_4S_7 , P_4S_9 and P_4S_{10} . Phosphorous-nitrogen compounds: Phosphazines. Cyclo and linear phosphazines. Boron-nitrogen compounds: Borazine, substituted borazines and boron nitride. Boron hydrides: Reactions of diborane. Structure and bonding. Polyhedral boranes: Preparation, properties, structure and bonding. 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. Carboranes and metallocarboranes.

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

Electronic spectra of metal complexes- Term symbols of d^n system, Racah parameters, splitting of terms in weak and strong octahedral and tetrahedral fields. 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 Interpretation of electronic spectra of complexes- Orgel diagrams, Tanabe-Sugano diagrams, Calculation of *Dq* , *B* and β (Nephelauxetic ratio) values, charge transfer spectra. 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. Temperature dependence of magnetism. Temperature Independent Paramagnetism (TIP). Spin state crossover, Antiferromagnetism-inter and intra molecular interaction. Application of magnetic measurements in the determination of structure of transition metal complexes.

Unit III Crystalline state **18 h**

Crystal systems and lattice types. Bravais lattices. Crystal symmetry- Introduction to point groups and space groups. Miller indices. Reciprocal lattice concept. Close packed structures: BCC, FCC and HCP. Voids. Coordination number. Crystal binding: Molecular, covalent, metallic and hydrogen bonded crystals. X- Ray diffraction by crystals: Function of crystals. Transmission grating and reflection grating. Braggs equation. Diffraction methods: Powder and rotating crystal. Indexing and determination of lattice type and unit cell dimensions of cubic crystals. Crystal defects: Perfect and imperfect crystals. Point, line and plane defects. Thermodynamics of Schottky and Frenkel defects. Colour centers in alkali halide crystals. Defect clusters. Extended defects: Crystallographic shear structure and stacking faults. Dislocations and crystal structure. Structure of compounds of AX (Zinc blende, Wurtzite) , AX_2 (Rutile, fluorite, antifluorite), A_mX_2 (Nickel arsenide), ABX_3 (Perosvskite, Ilmenite). Spinels. Inverse spinel structures.

Unit IV Lanthanides and actinides **18 h**

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

Unit V Solid state chemistry **18 h**

Electronic structure of solids. Free electron theory, band theory. Refinements to simple band theory, k space and Brillouin zones. Conductors, insulators and semiconductors. Band structure of conductors, insulators and semiconductors and their applications. Intrinsic and extrinsic semiconductors, doping of semiconductors and conduction mechanism, the band gap, temperature dependence of conductivity, carrier density and carrier mobility in semiconductors, Superconductivity, Photoconductivity, Photovoltaic effect. Colour in

inorganic solids. Dielectric properties. Dielectric materials. Ferroelectricity, pyroelectricity, piezoelectricity and ionic conductivity. Applications of ferro, piezo and pyroelectrics.

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3. S. F. A. Kettle, Physical Inorganic Chemistry, Oxford University Press, 1st edition, 1998.
4. A. R. West, Solid State Chemistry and its Applications, Wiley Eastern, 1990.
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12. A. Earnshaw, Introduction to Magnetochemistry, Academic Press, 1968.

PC 222 ORGANIC CHEMISTRY- II

Total 90 h

Unit I Physical organic chemistry 18 h

Reactivity in relation to molecular structure and conformation.Steric effects.*F* strain.Ortho effect, Bond angle strain.Linear free energy relationships.The Hammett equation and its applications.Taft equation.Solvent polarity and parameters.Y, Z and E parameters and their applications.Primary and secondary kinetic isotope effects.Salt effects and special salt effects in SN reactions.Kinetic and thermodynamic control of reactions. Energy profiles, Hammond postulate. Principle of microscopic reversibility.Marcus theory.Methods of determining reaction mechanisms. Phase transfer catalysis and its applications.

Unit II Molecular rearrangement and transformation reactions 18h

Types of organic rearrangements: Anionic, cationotropic, prototropic, free radical, carbene and nitrene intermediates. Mechanism with evidence of Wagner-Meerwein, Pinacol, Demjanov, Hofmann, Curtius, Schmidt, Lossen, Beckmann, Wolf, Fries, Fischer-Hepp, Hofmann-Martius, von-Richter, Orton, Bamberger, Smiles, Dienone-phenol, Benzilic acid, Benzidine, Favorskii, Stevens, Wittig, Sommelet-Hauser, Bayer-Villiger rearrangements.

Unit III Aromaticity and symmetry controlled reactions 18 h

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

Symmetry properties of MOs. Classification of pericyclic reactions.Mechanism and stereochemistry of electrocyclic, cycloaddition and sigmatropic reactions. Woodward-Hoffmann rules. FO, CD and Huckel-Mobius analysis of electrocyclic, cycloaddition and sigmatropic reactions.FO analysis of [1, j] and [3, 3] migrations. 1,3-dipolar cycloaddition. Stereo aspects of Diels-Alder reaction and Cope re arrangement.Intramolecular Diels-Alder, Retro Diels-Alder, Alder-ene, retro-ene andcheletropicreactions.Synthetic applications of Diels-Alder reactions.Fluxional molecules.

Unit IV Organic photochemistry **18 h**

Photochemical processes**.**Energy transfer, sensitization and quenching.Singlet and triplet states and their reactivity.Photoreactions of carbonyl compounds, enes, dienes and arenes.Norrish Type I and Type II reactions of acyclic ketones. Free radical reactions:Patterno-Buchi and Barton reactions, photo-Fries and Di-π methane rearrangements. Photoreactions of Vitamin D. Photosynthesis, photochemistry of vision.Singlet oxygen generation and their reactions.Introduction to chemiluminescence.Applications of photochemistry.

Unit V Chemistry of natural products and biomolecules **18 h**

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

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1. L. M. Harwood, “Polar rearrangements,” Oxford University Press 1995.
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   J. Clayden, N. Greeves, and S. Warren, “Organic Chemistry,” 2ndEdition, Oxford University Press, 2012.
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PC 223 PHYSICAL CHEMISTRY –II 90 h

Unit I

Quantum Chemistry II

18 h

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

Quantum Mechanics of Hydrogen-like systems-Potential energy 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. Orbitals-radial functions, radial distribution functions, angular functions and their plots**.** Wave equation for multielectron systems**.** Hartree-Fock Self- Consistent Field (HF-SCF) method for atoms, Hartree-Fock equations (derivation not required) & the Fock operator.

Unit II Spectroscopy –I **18 h**

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

Vibrational Spectroscopy: Vibrational spectra of harmonic and anharmonic oscillator.Selection rules. Morse curve, fundamentals and overtones. Determination of force constant.Rotational fine structure, P,Q,R branches of spectra.Vibrational spectra of polyatomic molecules: Normal modes, classification of vibrationalmodes into stretching (asymmetric, symmetric), bending, parallel and perpendicularvibrations. Finger print region and group frequencies. Introduction to FTIR andinstrumentation.

Raman spectroscopy: Raman scattering, polarisability and classical theory of Ramanspectrum. Rotational and vibrational Raman spectrum. Raman spectra of polyatomicmolecules. Complementarity of IR and Raman spectra. Mutual exclusion principle.Introduction to instrumentation. Laser Raman spectrum.

Electronic spectra. Electronic spectra of diatomic molecules. Vibrational coarse structure androtational fine structure of electronic spectrum. Franck-Condon principle. Types of

electronictransitions. Fotrat diagram. Predissociation. Calculation of heat of dissociation.Electronic spectra of polyatomic molecules: Electronic transition among molecular orbitalsand absorption frequencies. Effect of conjugation. Introduction to instrumentation.Simultaneous determination of two components.

Unit III Applications of Thermodynamics 18 h

Thermodynamics of irreversible processes: Simple examples of irreversible processes. General theory of non equilibrium processes The phenomenological relations. Onsager reciprocal relation. Generalized equation for entropy production, Entropy production from heat flow, matterflow and current flow. Application of irreversible thermodynamics to diffusion. Thermal diffusion, Thermo osmosis and thermomolecular pressure difference. Electro kinetic effects, the Glansdorf- Pregogine equation. Far from equilibrium region. Principle of minimum entropy production, Le-Chatelier Bra(u)wn Principle.

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.

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

Unit IV Statistical Mechanics –I 18 h

Microstates. Concept of ensembles Canonical and Grand canonical ensemble. Classical distribution of particles-Maxwell Boltzmann distribution.

Bose-Einstein statistics, Bose-Einstein distribution. Thermodynamic probability, Bose Einstein distribution function. Examples of particles. Theory of Para magnetism. Bose Einstein condensation, Liquid Helium. Super cooled liquid.

Fermi- Dirac Statistics. Fermi- Dirac distribution, examples of particles Fermi-Dirac distribution functionThermionic emission. Relation between Maxwell Boltzmann, Bose Einstein and Fermi -Dirac Statistics.

.**Unit V Electrochemistry** 1 **18 h**

Ionics- Ions in solution. Deviation from ideal behaviour. Ionic activity. Ion-solventinteraction. Born equation. Ion-ion interaction. Strong electrolytes Debye-Huckel theory of strong electrolytes,Onsager equation. Limitation of the model Conductance at highfrequencies and high potentials –Wein effect--Activity coefficient and its determination.

Ionic strength, Debye-Huckel limiting law. Equation for appreciable concentration. Osmotic coefficient. Activities in concentrated solutions. Ion associations. Ion transport.

Electrodics: Different type of electrodes. Origin of electrode potential, Electrochemical cells, Concentration cells and activity coefficient determination. Liquid junction potential. evaluation of thermodynamic properties, the electrode double layer, Electrode-electrodeinterface. Theory of multilayer capacity. Electrocapillarity. Lippmann potential and membrane potential.

Electrokinetic phenomena. Mechanism of charge transfer at electrode- electrolyte interface. Electrolysis. Current- potential curve. Dissolution, deposition and decomposition potentials.Energy barriers at metal –electrolyte interface. Different types of overpotentials. Butler-Volmer equation. Tafel and Nernst equation. Rate determining step in electrode kinetics. The hydrogen and oxygen over voltage. Theories of overvoltage.

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SECOND SEMESTER MSc.DEGREE EXAMINATION

Branch:Chemistry

(Common for CH/CL/CA/CM/PC 221)

(Under Semester System w.e.f 2018 Admissions)

PC 221- INORGANIC CHEMISTRY-II

Time:3 h **Max marks:75**

SECTION-A

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

1. a) Classify the following as closo, nido, arachno or hypho.

   1) B_5H_9 2) B_5H_{11} 3) B_6H_{12} 4) B_9H_{15}.

   b) Which sulphur –nitrogen compound is known as 'one-dimensional' metal? Why is it called so?

   c) Why are $P_4N_4Cl_8$ puckered and $P_4N_4F_8$ planar?

2. a) How would you distinguish between ferro magnetic and anti ferromagnetic material?

   b) Explain non-crossing rule.

   c) The effective magnetic moment of a complex is 4.90 BM. Calculate the no: of unpaired electron per unit complex.

3. a) What is the type of defect observed in AgBr crystals? Why?

   b) Give one example each for molecular, covalent, metallic and H-bonded crystals.

   c) Differentiate between H-centre and v-centre in NaCl crystals.

4. a) Write any two differences between 4f and 5f orbitals.

   b) Give the term symbols for Eu^{3+} and Lu^{3+}.

   c) Explain why Actinides have greater tendency for complex formation than lanthanides?

5 . a) What is band gap?

   b) Draw the first Brillouin zone for a primitive cubic lattice?

   c) Conductivity of metals decreases with increase of temperature. Explain.

[2 x 10 = 20 marks]

SECTION-B

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

6. a) How is diborane prepared? Discuss the structure and bonding in diborane.

   b) Write a note on metallocarboranes.

7. a) Describe the Guoy's method to determine magnetic susceptibility . How are these measurements used to calculate effective magnetic moments?

   b) Even though d-d transitions are forbidden, why such transitions occur in many transition metal complexes? Illustrate with examples.

8. a) Distinguish between spinels and inverse spinels with suitable examples.

   .b) Write briefly on line and plane defects in solids.

9. a) Briefly discuss the basis of the ion-exchange method for the separation of Lanthanides.

   b) Compare the spectral and magnetic properties of Lanthanides and Actinides.

10. a) With suitable examples explain the phenomenon of photoconductivity. What are its applications?

    b) Write a short note on the applications of ferro, piezo and pyroelectrics.

[5x 5 = 25 marks]

SECTION-C

Answer any three questions and each question carries 10 marks.

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

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

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

14. a) Correlate the oxidation states and ionic radii with electronic configuration of lanthanides.

    b) Write a short note on the beach sands of kerala.

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

[10x3 = 30 marks]

SECOND SEMESTER MSc. DEGREE EXAMINATION

BRANCH - CHEMISTRY

CH/CL/CA/CM/PC222: Organic Chemistry-II

(Under Semester System w.e.f 2018 Admissions)

Time-3 hours **Maximum marks :75**

Section A

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

1. a) Give the mechanism of rearrangement of aryl hydroxylamines to aminophenols.

   b)Describe Stevens rearrangement.

   c)Show the mechanism involved in the rearrangement of an unsubstituted amide to a primary amine.

2. a) Explain why cyclodecapentaene with 10 π electrons is not aromatic.

   b)Write briefly on Homoaromaticity.

   c) State Woodward Hoffmann rules.

3. a) Explain Phosphorescence.

   b) Write a short note on Norrish type I reaction.

   c) Describe anyone method of generation of singlet oxygen.

4. a) Explain von Braun reaction.

   b)Show the products formed when Quercetin is treated with dimethyl sulphate followed by boiling with ethanolic KOH.

   c)Draw the structure of CholesteroI.

5. a) Explain Taft equation

   b) Describe salt effect in substitution reaction

   c) State Marcus theory

[2x10=20 marks]

Section B

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

6. a) Discuss the mechanism and applications of Baeyer Villiger reaction.

   b) Discuss the mechanism of Benzidine rearrangement. Also write proof to support the mechanism.

7. a) Explain the acidity of Cyclopentadiene and Cycloheptatriene.

b) Explain briefly Claisen rearrangement.

8. a) Briefly explain Barton reaction.

b) Explain the photochemistry of olefins.

9. a) Discus the structure elucidation of Carotene.

b) Briefly describe the biosynthesis of terpenes.

10. a) Explain kinetic and thermodynamic control in reactions involving ketones.

b)Explain the reason for the difficulty in the hydrolysis of 2, 6 - disubstituted benzoic acid esters.

[5x5=25 marks]

SECTION-C

Answer **any three** questions and **each** question carries 10 marks.

11. i) Discuss the mechanism and applications of Beckmann rearrangement.

ii) Discuss the similarity in the intermediates of Curtius, Schmidt and Lossenrearrangements.

12 Explain briefly on

i) Sigmatropic reactions

ii) 1, 3 - Dipolar and Ene reactions.

13.Discuss the following:

i) Photochemistry of vision

ii) Photoreaction of Vitamin D.

14. Explain the following:

i) Structure of Estrone.

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

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15. Discuss the following:

i) Principles and applications of phase transfer catalysis.

ii) Methods of determination of reaction mechanism.

[10x3=30 marks]

Second Semester M.Sc. Degree Examination (Model Question Paper)

Branch-III Chemistry

CH 223/CL 223/CA 223/PC 223 : Physical Chemistry- II

(2018 Admission Onwards)

Time : 3 Hours **Max mark : 75**

Section A

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

1. a) Set up the Schrodinger equation for a rigid rotator.
   b) Give plots of (a) radial probability distribution functions of 2S orbital and (b) angular plot of $2P_x$ orbital.
   c) Write the expression for fock operator and explain the terms
2. a) What are overtones? Why are they weak?
   b) State and explain the rule of mutual exclusion with one example.
   c) State Franck-Condon principle.
3. a) Explain the terms 'Force' and 'Flux' with reference to irreversible thermodynamics.
   b) Show the influence of temperature on the miscibility curve in a three component system forming a pair of partially miscible liquids.
   c) What are the conditions under which linear relations are valid to understand irreversible processes.
4. a) Derive ideal gas law from translational partition function.
   b) Explain the term canonical ensemble.
   c) Electron would never follow Maxwell Boltzmann statistics. Why?
5. a) What is Lippmann potential? How does it arise?
   b) Calculate the mean activity coefficient of 0.01M $BaCl_2$ in water at 25^oC.
   c) Explain the origin of concentration overpotential.

(10 X 2 = 20 Marks)

Section- B

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

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

b) Explain the origin of P and R branches in rotational-vibrational spectrum.

8. a) Derive generalized equation for entropy production from heat flow.
   b) Give the Onsagar-reciprocal relations. What are its applications?
9. a) Apply Fermi-Dirac statistics to understand paramagnetism in solids.
   b) Derive the expression for partition function for particle executing (i) free linear motion and (ii) free linear harmonic vibration.
10. a) Derive Debye-Huckel limiting law.
    b) Discuss the various models for electrical double layer.

(5 X 5 = 25 Marks)

Section-C

Answer **any three** questions and **each** question carries **10** marks

11. (i) Apply Schrodinger equation for particle in a ring. Find eigen values and eigen functions.
    (ii) Show that any two associated Legendre functions satisfy orthonormality condition.
12. (i) Give an account of rotation spectra of diatomic molecules. Explain the effect of nonrigidity of the bond on the spectra.
    (ii) How is the rotational spectrum of a diatomic molecule affected by isotopic substitution?
13. (i) Draw the phase diagram of a three component liquid system with three pairs of partially miscible liquids. Explain.
    (ii) How would you understand (a) thermo osmosis and (b) thermal diffusion from irreversible thermodynamics?
14. Derive the expression for the distribution function of a Boson and Bose-Einstein condensation.
15. (i) Derive Butler-Volmer equation. Deduce the expression for the low and high field limits of this equation.
    (ii) Discuss the application of Debye-Huckel Onsagar equation as applied to strong electrolytes and point out its limitations.

(10 x 3 = 30Marks)

SEMESTER III

PC 231 INORGANIC CHEMISTRY- III

Total 90 h

Unit I Organometallic compounds 18h

Nomenclature of organometallic compounds. Hapto nomenclature. 18 and 16 electron rule, isoelectronic and isolobal analogy. Types of metal complexes. Metal carbonyls, bonding in metal carbonyls. Bonding in metal nitrosyls and cyanides. Synthesis, structure and bonding of polynuclear carbonyls with and without bridging. Complexes with linear π donor ligands: Olefins, acetylenes, dienes and allyl complexes. Complexes with cyclic π donors: Cyclopentadiene, benzene complexes, structure and bonding of ferrocene and dibenzenechromium complexes (MO treatment). Oxidative addition and reductive elimination, insertion and elimination reactions Catalysis by organometallic compounds: Alkene hydrogenation using Wilkinson's catalyst, hydroformylation of olefins using cobalt catalyst and polymerization reaction by Ziegler-Natta catalyst. Fluxional molecules.

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

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. Determination of stability constants: spectrophotometric, polarographic and potentiometric methods. Stability of chelates. Thermodynamic explanation, macrocyclic effects. Classification of ligand substitution reactions -kinetics and mechanism of ligand substitution reactions in square planar complexes, trans effect- theory and synthetic applications. Kinetics and mechanism of octahedral substitution- water exchange, dissociative mechanism, associative mechanism- Eigen-Wilkins mechanism, Eigen-Fuoss equation, base hydrolysis, racemisation and isomerisation reactions. Electron transfer reactions: Outer sphere mechanism- Marcus theory, inner sphere mechanism- Taube mechanism. Photochemical reactions- substitution and redox reactions of Cr(III) , Ru(II) , and Ru(III) complexes. Photo-isomerisation and photo-aquation reactions of metal complexes

Unit III Bioinorganic chemistry **18 h**

Essential and trace elements in biological systems, structure and functions of biological membranes, mechanism of ion transport across membranes, sodium-potassium pump. Photosynthesis, porphyrin ring system, chlorophyll, PS I and PS II. Synthetic model for photosynthesis. Role of calcium in biological systems. Oxygen carriers and oxygen transport proteins- haemoglobin and myoglobin. Non-haeme iron-sulphur proteins involved in electron transfer-ferredoxin and rubredoxin. Iron storage and transport in biological systems- ferritin and transferrin. Redox metalloenzymes-cytochromes, peroxidases and superoxide dismutase and catalases. Nonredox metalloenzymes- CarboxypeptidaseA- structure and functions. Nitrogeases, biological nitrogen fixation. Vitamin B_{12} and coenzymes. Toxic effects of metals(Cd, Hg, Cr and Pb).

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

Infrared spectra of coordination compounds. Structural elucidation of coordination compounds containing the following molecules/ ions as ligands- NH_3, H_2O, CO, NO, OH^-, $SO4^{2-}$, CN^-, SCN^-, NO_3^-, NO_2^- CH_3COO^- and X^- (X= halogen). Changes in ligand vibration on coordination with metal ions. Vibrational spectra of metal carbonyls- CD and ORD spectra of metal complexes. ESR spectra : Application to Cu(II) complexes and inorganic free radicals such as PH_4, F_2^- and $[BH_3]^-$. Nuclear Magnetic Resonance Spectroscopy :The contact and pseudocontact shifts, some applications including biological systems, an overview of NMR of metal nuclides with emphasis on $_{31}P$ and $_{19}F$ NMR. Mossbauer Spectroscopy : Application of the technique to the studies of iron and tin complexes.

Unit IV Nuclear chemistry **18 h**

Nuclear structure, mass and charge. Nuclear moments. Binding energy. Semiempirical mass equation. Stability rules. Magic numbers. Nuclear models: Shell, Liquid drop, Fermi gas, collective and optical models. Equation of radioactive decay and growth. Half life and average life. Radioactive equilibrium. Transient and secular equilibria. Nuclear reactions: Direct nuclear reactions, heavy ion induced nuclear reactions, photonuclear reactions. Neutron captures cross section and critical size. 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. Principles of counting technique such as G.M. counter, proportional, ionization and scintillation counters. Cloud chamber.

References

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6. G. Friedlander and J. W. Kennady, Introduction to Radio chemistry, John Wiley and Sons New York, 1949.
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15. L. Bertin, H.B. Gray, S. J. lippard and J. S. Valentine, Bioinorganic Chemistry, Viva Books Pvt. Ltd, New Delhi, 1998.

PC 232 ORGANIC CHEMISTRY-III

Total 90 h

Unit IUV-Vis and IR Spectroscopy and Mass spectrometry 18h

Electronic transitions and analysis of UV spectra of enes, enones and arenes.Woodward-Fieser rules.Effect of solvent polarity on UV absorption.Principle of characteristic group frequency in IR.Identification of functional groups and other structural features by IR, Hydrogen bonding and IR bands.Sampling techniques.Mass spectrometry- 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. Mass spectral fragmentation patterns of long chain alkanes, alkenes, alkynes, alcohols, ethers, thiols, aromatic compounds, aldehydes, ketones, acids, amides, nitro, amino and halo compounds.

Unit II NMR spectroscopy and structural elucidation 18h

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

Unit III Organic synthesis 18 h

C-C and C=C bond forming reactions. Mannich, Reimer-Tiemann, Synthesis of small rings.Simmons-Smith, Vilsmeier-Haack, Ullmann and Chichibabin reactions. Ring formation by Dieckmann, Kostanecki, Thorpe, Pschorr and acyloin condensations. Stork enamine, Shapiro, Peterson, Heck, Stille, Ritter and Prilezhaev reactions.Reduction and oxidation in synthesis.Catalytic hydrogenation.Alkali metal reduction, Birch reduction, Clemmensen reduction and Wolff-Kishner reduction, Huang-Minlon modification.Boranes,LAH and sodiumborohydride as reductants.Hydrogenation, Oppenauer oxidation, Jones oxidation.Applications of HIO_4, OsO_4 and mCPBA.Organo palladium catalysts -Heck, Negishi, Sonagashiraand Suzuki coupling

Unit IV Methods in organic synthesis **18 h**

Retrosynthetic analysis and disconnection approach. Synthetic strategy and synthons.Regioselectivity in enol and enamine alkylation.Stereospecific and steroselective synthesis, Sharpless asymmetric epoxidation, Chiral pool, chiral auxiliary, Chiral reagents, BINAP, Mitsunobu reaction. 1,3-dipolar cycloaddition in the construction of rings. Olefin synthesis by extrusion reactions.Olefin metathesis – first and second generation Grubbs' catalysts.Umpolung concept, functional group equivalents.Reductive coupling reactions.Epoxide to alkene.Introduction to combinatorial synthesis.Electrochemical reduction of organohalogen, nitro and carbonyl compounds.Electrochemical Kolbe oxidation.Protecting group strategy: Tetrahydropyranyl, silyl, *t*-butyl, trichloroethyl, acetal and thioacetal as hydroxyl, thiol, carboxyl and carbonyl protecting groups in synthesis.

Unit V Separation techniques **18 h**

Classification of chromatographic methods.Theory of chromatography.Applications of chromatographic methods.Adsorption and partition chromatography.Paper, thin layer and column chromatographic methods.Centrifugal TLC, LC, Pressure column chromatography, HPLC and GC.Column matrices.Detectors.Affinity and chiral separations using HPLC.Normal and ultra-centrifugation.Gel and Capillary electrophoresis and their applications.Solvent extraction.Extraction using supercritical liquid CO_2, Craig's technique of liquid-liquid extraction.

References

1. D. H. Williams and I. Fleming, "Spectroscopic methods in organic chemistry," 6thEdition, Tata McGraw Hill, 2011
2. W. Kemp, "Organic spectroscopy,"3rd Edition, Palgrave Macmillan, 1991
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14. D. J. Holme and H. Perk, “Analytical Biochemistry,” 3rd Edition, Prentice Hall, 1998.

PC 233 Physical Chemistry -III 90 h

Unit I Chemical Bonding 18 h

Approximate methods: method ofVariation - Variation theorem and its proof. Linear variation functions. Secular equations and secular determinants.Perturbation method-Successive correction to an unperturbed problem. Detailed treatment of first order non-degenerate case only.

Treatment of molecules- The Born- Oppenheimer approximation- LCAO-MO Theory- MO theory of H_2 and H_2^+. MO treatment of other homo diatomicmolecules Li_2, Be_2, B_2, C_2, O_2 and F_2. MO treatment of hetero diatomic molecules LiH,CO, NO and HF. Spectroscopic term symbols for homo diatomic molecules.

Valance bond theory of diatomic molecules H_2, O_2 and F_2. Comparison of MO and VB theories, Quantum mechanical treatment of SP, SP^2 and SP^3Hybridisation.HMO theory of conjugated systems. Bond order and charge density calculations,Free valance.Application of HMO method to ethylene, allyl system, butadiene and benzene.

Unit II Computational Chemistry 18 h

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

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

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

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

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

Construction of Z-matrix for simple molecules. H_2O, H_2O_2, H_2CO, CH_3CHO, NH_3 and CO_2.

Unit III Spectroscopy II **18 h**

Resonance spectroscopy: Nuclear Magnetic resonance Spectroscopy, Nuclear spin.Interaction between nuclear spin and applied magnetic field. Proton NMR . Population of energy levels. Nuclear resonance. Chemical shift. Relaxation methods. Spin-spin coupling.Fine structure. Elementary idea of 2D and 3D NMR. Introduction to instrumentation.

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

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

NQR spectroscopy - Principle and application

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

Unit IV Statistical Mechanics II **18 h**

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

Relation ship between Partition functions and thermodynamic properties, The principle of equipartition of energy. Chemical equilibrium. Law of mass action. Transformation of the equilibrium expressions. Statistical derivation.Thermodynamic probability and entropy.

Equipartition principle Quantum theory of heat capacity. Calculation of heat capacity of gases, limitation of the method. Heat capacity of solids. Dulong and Petit's law, Kopp's law, Classical theory and its limitation. The vibrational properties of solids. Einstein theory of heat capacity. The spectrum of normal modes. Limitations of Einstein's theory. The Debye theory, the electronic specific heat.

Unit V Electro Analytical and Spectrophotometric methods. **18 h**

Potentiometric methods: Reference electrodes and indicator electrodes. The hydrogen,calomel, Ag-AgCl electrode. The glass electrode- its structure, performance and limitations.Measurement of pH. Potentiometric titrations- redox and precipitation titrations.

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

Conductometry: Principle and method. Conductometric titrations.

Coulometry: Principle andmethod. Coulometric titrations.

Voltametry: principle and method of polarography, cyclicvoltammetry, stripping voltammetry and amperometry.

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

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24. F.W. Sears and G.L. Sailinger” Thermodynamics, Kinetic Theory, and Statistical Thermodynamics” Third edition. Narosa publishing House , New Delhi.

PC 234- Polymer Chemistry Practicals –I **Total-125 h**

1. Dry Rubber and Latex Analysis

   Determination of DRC, Total solid, Estimation of anmmonia, KOH number, VFA Number, Estimation of Mg^{2+}, coagulant content, ash content, sludge content, filler content, silica content and volatiles in dry rubber article.

2. Quantitative Analysis of polymers

   Determination of molecular mass by solution viscosity, end group analysis, determination of swelling characteristics of cross linked polymers, UV, IR and thermal analysis of polymers for characterization, Study of polymerchelation by spectrophotometry. Potentiometric titration of polyelectrolytic solutions, pH measurements of polyelectrolyte solution.

3. Measurements of Physical properties of Polymers

   Thermal. Rheological, electric and optical analysis: TG, DTA, DSC, and TMA, Dielectric strength, volume resistivity, surface resistivity, arc resistance, MFI, capillary rheometer testing. Scorth and cure time determination.

4. Preparation of thermoplastics/thermosetting plastics

   1. Polyacrylamide (Suspension)
   2. Crosslinked polyacrylamide
   3. Aniline-formaldehyde resin
   4. Phenol-formaldehyde resin
   5. Glyptal resin

References

1. E. M. McCaffery, Laboratory preparations for macromolecular chemistry, macgrow-Hill
2. E. A. Collins, J. Bares, F. W. Billmeyer, Experiments in polymer science, Wiley.
3. D. Braun, H. Cherdron adn W. Kern, Technologies of polymer synthesis and characterizarion, Wiley.
4. S. H. Pinner, A practical course in polymer chemistry, Pergamon.
5. D. Braun, H. Cherdron adn W. Kern, Pracical molecular organic chemistry, Harward Academic.
6. S. R. Sandler, and M. Karo, Polymer synthesis, Vol 1-3, Academic.
7. E. M. Pearce, Macromolecular synthesis, JohnWiley.

PC 235 ORGANIC PRACTICALS-II Total 125 h

A.**Volumetric estimation** of
1) Aniline 2) Phenol 3) glucose 4) Ascorbic acid 5) Aspirin

B). **Colorimetric estimation**
6) paracetamol with potassium ferricyanide
7protein by biuret method
8) Ascorbic acid by folin-phenol reagent or phosphotungstic acid methods

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

D. Separations of mixtures by Paper Chromatography
10) Identification of amino acids

E) Single stage preparation of organic compounds by green chemistry

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

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

References

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://sdbs.riodb.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

PC 236 PHYSICAL PRACTICALS –II 125 h

Conductometry

Determination of strength of strong and weak acids in a mixture

Determination of strength of a weak acid.

Determination of solubility product of a sparingly soluble salt ($PbSO_4$, $BaSO_4$ etc.)

Hydrolysis of NH_4Cl or CH_3COONa or aniline hydrochloride

Determination of order of reaction, rate constant and energy of activation for saponification of ethyl acetate

Precipitation titrations.

Determination of critical micellar concentration (CMC) of sodium lauryl sulphate from measurement of conductivities at different concentrations.

Equivalent conductance at infinite dilutions and verification of Kohlrausch's law.

Determination of Onsager constants.

Potentiometry

Determination of emf of Daniel cell.

Determination of the emf of various $ZnSO_4$ solutions and hence the concentration of unknown $ZnSO_4$ solution.

Determination of valency of mercurous ion.

Determination of temperature dependence of EMF of a cell

Determination of stoichiometry and formation constant of silver-ammonia complex.

Determination of activity and activity constant of electrolytes.

Determination of thermodynamic constants of reactions.

pH metric titrations.

Acid alkali titrations using Quinhydrone electrode.

Titrations(double) involving redox reactions – Fe^{2+} Vs $KMnO_4$, $K_2Cr_2O_7$, $Ce(NH_3)SO_4$ and KI Vs $KMnO_4$

Determination of strengths of halides in a mixture.

Determination of pH of buffer solutions and hence to calculate the E^0 of quinhydrone electrode

Spectrophotometry

Verification of Beer-Lambert’s law.

Absorption spectra of conjugated dyes.

Determination of concentration of potassium dichromate and potassium permanganate in a mixture.

To study the complex formation between Fe^{3+} and salicylic acid.

Determination of pKa of an indicator.

Polarimetry

Measurement specific rotation of glucose.

Determination of specific rotation of sucrose

Determination of unknown concentration of glucose solution. and rate constant of its hydrolysis in presence of HCl

Polarography :

Determination of half wave potential E ½ and unknown concentration of Cd^{2+} ion.

Determination of concentrations of metal ions in a mixture.

Surface tension

Determination of surface tension of various liquids (water-ethanol, water-glycerol, water-sorbitol, nitrobenzene- toluene) by Stalagmometric method (drop number/ drop weight)

Determination of parchors of molecules and various groups.

Determination of concentration of a mixture.

Determination of surface tension and parachor of liquids using double capillary method. Variation of surface tension with concentration. Unknown concentration of a mixture. Interfacial tension. Determination of surface excess and area per molecule.

Viscosity: Viscosity of liquids and mixtures of liquids. Verification of Kendall's equation. Composition of unknown mixtures. Determination of molecular masses polymers by viscosity measurements.

Refractometry

Determination of molar refraction of pure liquids

Determination of concentration of KCl solution/glycerol solution

Determination of solubility of KCl in water.

Determination of molar refraction of solid KCl

Study the stoichiometry of potassium iodide-mercuric iodide complex.

Determination of concentration of KI solution.

References

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 and 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”, MacMillan India, 2005.

8) D. P. Shoemaker, C. W. Garland & J. W. Nibler. “Experiments in Physical Chemistry” McGraw Hill, 2003.

9. Dr.J.N. Gurthu and Amit Gurthu, “Advanced Physical Chemistry experiments” Pragati Prakashan.

10. J.B. Yadav, “Advanced Practical Physical Chemistry” Goel Publishing House , Meerut.

Third Semester M.Sc. Degree Examination – Model question paper

Branch – Chemistry

CH/CL/CA/PC 231 : INORGANIC CHEMISTRY- III

(2018 Admission Onwards)

Time : 3 Hrs Max. Marks: 75

SECTION A

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

1. a) Draw the structure of $Rh_4(CO)_2$.

   b) How do sigma allyl complexes differ from pi allyl complexes?

   c) What are fluxional molecules?

2. a) What are the factors affecting the stability of complexes?

   b) Explain Macrocyclic effect?

   c) What is anation reaction? Give an example.

3. a) Why electron transfer process in photosynthesis is called an uphill process?

   b) Explain the mechanism of oxygen binding in haemocyanin.

   c) What is Na^+ - K^+ pump? How does it function?

4. a) What is group frequency concept? Illustrate with example.

   b) Why are solid samples used for recording Mossbauer spectra?

   c) What is Dopplar broadening? Explain with an example.

5. a) Explain binding energy.

   b) What is compound nucleus? How is it formed?

   c) Give a note on breeder reactors.

(2x10= 20 marks)

SECTION B

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

6. a) What are metal carbonyls? Explain the structure and bonding in $Ni(CO)_4$

   b) Discuss the mechanism of polymerization of Zeigler- Natta catalyst.

7. a) Explain Trans effect with suitable examples.

   b) Give an account of photochemical reactions of complexes.

8. a) Discuss the role of calcium in blood clotting process.

   b) Explain the structural features of haemoglobin.

9. a) How does IR spectroscopy help for the structural elucidation of complexes containing ammonia and water as ligands.

   b) Explain CD and ORD spectra of complexes.

10. a) Distinguish between Transient and Secular equilibria.

    b) What is meant by half life period? How is it related to decay constant? The $t_{1/2}$ of a radio nuclide is 20 years. If a sample of this nuclide has an initial activity of 8000 disintegrations per minute today, what will be its activity after 80 years?

(5x5= 25 marks)

SECTION C

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

11. Explain the bonding of ferrocene by MO Theory.
12. Briefly explain outer sphere and inner sphere mechanism of electron transfer reactions
13. i) Discuss the function of PS-I and PS-II in photosynthetic activity.

    ii) Outline the probable mechanistic pathways Nitrogenase activity in nitrogen fixation.
14. i) Discuss the application of ESR spectroscopy to Cu(II) complexes.

    ii) Explain how Mossbauer spectroscopy helps to the studies of iron and tin complexes

15. Discuss about different types of nuclear reactions with suitable examples.

(10x3= 30 marks)

THIRD SEMESTER M.Sc.DEGREE EXAMINATION

BRANCH - CHEMISTRY

CH/CL/CA/PC232: Organic Chemistry-III

(2018 admission onwards)

Time-3 hours Maximum marks :75

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

Each sub question carries 2 marks

1 a) Explain how CH stretching vibrations of sp, sp^2, sp^3 hybridised carbon varies.

b) Polar solvents usually produces a red shift in the $\pi \rightarrow \pi$ transition explain.

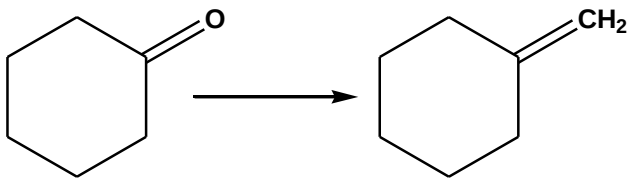
c) Explain how the presence of bromine atom in a molecule can be detected by mass spectrum.

2 a) Explain why acetylenic hydrogens are more upfield than vinylic hydrogens.

b) What multiplicities are observed for the signals of off resonance decoupled ^{13}C spectrum of 2-chloropropene?

c) Account for the fact that splitting is observed between Hydrogens "a" and b in 2-methyl propene $(CH^a_3)_2C=CH^b_2$ and not in neo pentylchloride $(CH^a_3)_3CH^b_2$ Cl.

3 a) Suggest a method for conversion



b) What is Clemmensonreduction

c) What are enamines? Write one synthetic application of enamine

4 a) Explain the use of silyl group as protecting group in organic synthesis.

b) Explain the term combinatorial synthesis

c) What is umpolung?

5 a) What is the principle of chromatography

b) What is paper chromatography? How is it helpful in identifying various alpha amino acids?

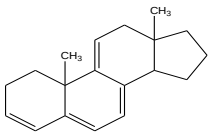
c) Outline the applications of Gel electrophoresis.

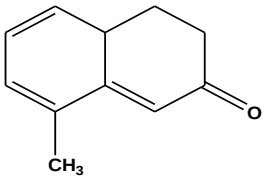
(2x10= 20 marks)

Section B

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

6 a) By using Woodward Fieser rules calculate the λ max values

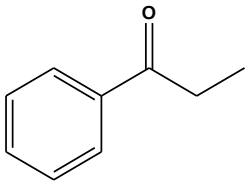




b) How IR spectrum can be used to distinguish

i) Primary amine from primary amide ii)) Ethyl benzene from o-xylene

7 a) Deduce the identity of the compound $C_9H_{10}O$ that has an IR absorption at 1688 cm-1 and 1 H NMR signals at 1.22 (triplet, 3 H), 2.98 (quartet) and 7.28-7.95 (multiplet, 5H).Assign the data

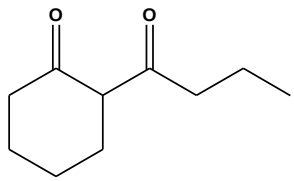


b) Explain the paramagnetic anisotropy of alkenic, aldehydic and aromatic protons.

8 a) Discuss Vilmeier-Hack reaction.

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

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



b) Discuss the synthesis of β-hydroxy ketones and aldehydes usingumpolung

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

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

Sectiion C

Answer any three questions.Each question carries 10 marks

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

12. Write short notes on

i) DEPT spectra, ii) Nuclear Overhauser effect, iii) Shift reagents in NMR,
iv) Double resonance NMR

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

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

15. With a schematic diagram explain the principle, instrumentation, and applications of GC

(10x3= 30 marks)

THIRD SEMESTER M Sc. CHEMISTRY DEGREE EXAMINATION

BRANCH – CHEMISTRY

CH/CL/CA/PC 233 – Physical Chemistry III

(2018 admission ownwards.)

Time : 3 Hours Max. Marks : 75

Section A

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

Each sub question carries 2 marks

1) A) Arrange O_2, O_2^+, O_2^- in the increasing order of stability. Justify your answer
   B) Write briefly about "Perturbation theory"
   C) Explain the more dipole moment in ethyl chloride than in chlorobenzene.
2) A) Construct the z-matrix of CH_3CHO.
   B) Name any two chemistry related software.
   C) Write the determinantal wavefunction for the configuration $1S_2$ 2Pz
3) A) Write the expression for chemical shift in Mossbauer spectroscopy and explain the terms.
   B) Calculate the ESR frequency of an unpaired electron in a magnetic field 0.33 Tesla. Given for free electron g=2, $\beta=9.273\times10^{-27}$ J/T
   C) Explain the basic principle of X-ray photoelectron spectroscopy.
4) A) Calculate the value of ln6! with and without Stirling's theorem. Find the difference between the values if any. Comment on the result.
   B) What is meant by the law of equipartition of energy?
   C) State and explain Dulong Petit's law. Explain its limitations.
5) A) What are the requirements for choosing a reference electrode?
   B) Define half wave potential. Explain its significance.
   C) Why do we use three electrodes in cyclic voltametry.

(2x10= 20 marks)

Section B

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

6) A) Derive the expression for the bond angle and wave function in sp^2 hybridisation.
   B) Apply HMO theory to butadiene molecule and discuss the molecular orbitals and their corresponding energy levels.
7) A) Differentiate between Slater type orbitals and Gaussian type orbitals
   B) What is potential energy surface? Explain its significance.

8) A) Write a brief account of 2D-NMR spectroscopy.
   B) What is Kramer's degeneracy? Discuss.
9) A) B) Give comparison between Bose-Einstein, Maxwell-Boltzmann and Fermi-Dirac statistics.
   B) Explain briefly how heat capacity of gases can be calculated?
10) A) Explain the working of glass electrode.
   B) Discuss the advantages and disadvantages of amperometric titrations.

(5x5= 25 marks)

Section C

Answer any three questions.Each question carries 10 marks

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

SEMESTER IV

PC 241 – POLYMER CHEMISTRY- I

Total 90 h

Unit I Synthesis of Macromolecules – Molecular Mass of Polymers 18h

Concept of macromolecules, Classification, Functionality and principles of polymerization, Different polymerization techniques, Kinetic chain length, gelation, Branching and crosslinking, Stepgrowth polymerization, Carothers Equation, Ring opening polymerization, Plasma polymerization, Copolymer-Copolymer equation, Monomer reactivity ratio, Q-e scheme. Molecular mass of Polymers: Molecular mass distribution 90wd/, Distribution curve, Polysdispersity, Molecular mass average determination, Absolute nad relative methods. Colligative properties: ebullioscopy, cryoscopy,end group analysis, Membrane Osmometry, Vapour phase osmometry, Light scattering, Ultracentrifugation. Solution viscosity - Intrinsic viscosity, Determination of viscosity average molecular weight, Mark-Howink equation, determination of k and a, Fractionation of polymers- Gel permeation chromatography (GPC), Relation of chromatogram shape and MWD.

Unit II Investigation of Polymers – Structure and configuration 18 h

Chiral polymers, tacticity, conformation of single molecules, freely jointed chain, random flight model, Average chain dimension. End to end distance, Restirction due to bond angles, Conformation in crystal and microconformation. Secondary bond forces, chain configuration, Spectral methods for the investigation of structure and configuration: IR, NMR (^{1}H and ^{13}C) and ESR, UV-VIS, Raman, Fluoresence and Mass spectroscopic techniques. Basic determination of polymer properties: Ring structure and its significance, chain flexibility and factors affecting it. Property requirements and polymer utilization-Elastomers, fibers and plastics.

Unit III Theory of Polymer Solution: Ideal and Nonideal Solution 18 h

Thermodynamics of polmer solution- Entropy, enthalpy, and free energy of mixing. Lattice model-solubility parameter, Free volume theory, Excluded volume, Flory-Huggins Theory, Flory-Krigbaum theory, Huggins and Kraemer equation, Phase equillibria in

polymeric systems. Critical solution temperature, LCST and UCST behaviour, Experimental results in binary systems involving polymer blends.

Unit IV Polymer blend alloys and composites 18 h

Importance of polymer blending-Blending techniques. Miscible and immiscible blends, Miscibility through specific interactions. Polymer alloys, Phase diagram of polymers, polymer systems. Blend morphology, characteristics of FTIR, Flourescent spectroscopy, microscopy, Compatibilization of miscible blends, Addition of graft or copolymers. Types of compatibilities: in situ fomerd, separately added polymers. Polymer composites: Role of fiber and matrix in improving composite properties bonding between fiber and matrix. Critical fiber length in short fiber composites. Role of composites in aerospace application. Composite fabrication techniques: Open model process, vacuum bag molding, centrifugal casting, pultrusion. Closed model process-matefed die molding, thermofoaming injection molding.

Unit IV Polymer degradation and stabilization 18 h

Chemical degradation, physical degradation, ageing, crazing, degradation by micro organisms, Biodegradable polymers, Mechanism of degradation, secondary chain reaction, Self reaction, depolymerisation, metal catalysed degradation, Thermal oxidation, Photooxidation, Mechanical degradation, Degradation by ionizing radiation, ozone attack. Degradation of special polymers: Polyolefins, PVC, PS, PMMA. Stabilization: Chain breaking antioxidants, bound antioxidants, Radiation protection, Stabilization against biodegradation.

References

16. F. Rodriguez, rinciples ofpolymer systems, MacGraw Hill.
17. H. G. Elias, Macromolecules, Plenum.
18. P. J. Florey, Principles of polymer chemistry, Cornell Univ.
19. F. A. Bovey, Polymer configuration and conformations, Academic.
20. R. J. Young, Introduction to polymer science, Wiley.
21. G. Odian, Principles of polymerization, Wiley.
22. F. W. Billmayer, Text book of polymer science, Wiley.
23. K. K. Chawla, Composite materials, Springer
24. D. R. Paul and Newman, Polymer blends, Vol 1 and 2, Academic.
25. O. Olabisi, Polymer-polymer miscibility, Academic.

26. F. R. Jones, Handbook of polymer fiber composites, Longman.
27. H. Williard, L. Merritt, J. Dean and F. Settle, Instrumental methods of analysis, Van Nostrand.
28. P. K. Mallick, Fiber reinforced composites, Marcel dekker.

PC 242 - POLYMER CHEMISTRY II

Total 90 h

Unit I Polymer synthesis and Nanotechnology **18 h**

Polymerization initiated by metal catalysts, Atom transfer radical polymerization(ATRP), Chain transfer polymerization, Plasma polymerization, nanotechnology: importance of polymer nanoparticles, processing, characterization of polymer nanostructure, metla polymer nanocomposite synthesis, Polymer coated coreshell nanopartcles, Importance of subnanometer and micrometer sized organic and iinorganc particles coated with polymer. Polystyrene capped gold nanoparticles -synthesis, gold nanoshells in blood immunoassay. Polymer supports: Reactivity of functional group polymers, Functionilization of polystyrene, polymers as reagents and reactants, Effect of crosslinking on the reactivity of functional groups, Solid state peptide synthesis. Immobilized application. Polymer bound catalysts.

Unit II Biopolymers and biomedical applications **18 h**

Nucleic acids-nucleocides, nucleotides, RNA, DNA- structural aspects, Biological significance-coading of aminoacids, Heredity, NA-Finger printing, gene technology, Applicaion of genetic engineering techniques in agriculture, biology and medicine, Biomedical application of polymers: polymers as drug ca polymersrriers, polymers for surgery and plasma substitution. Polymeric drugs, polymersas artificial enzymes, synzymes, Biometric chemistry.

Unit III Speciality Polymers **18 h**

Conduction polymers, conduction mechanism applications, Polyacytelene, polyparaphenylenes, polyanilines, polypyrrole, Photoconductive polymers, polymers in nonlinear optics, polymers with piezoelectric, pyroelectric and ferroelectric properties, Polyvinylidine fluoride. Photoresists for semiconductor applications, Negative Photoresists, Positive photoresists, Plasma reversible photoresistors, Electron beam lithography, Liquid crystalline polymers: preparation, properties, and applications, Chiral thermometric liquid crystal polymers, Nematic, liquid crystal polymers, Ionic Polymers: ionic crosslinking, Bound polymers and counter ion.

Unit IV Polymer Physics **18 h**

Crystallization and melting, strain induced morphology, Polymer single crystals, Transition temperature, Boyer-Baeman rule, Transport phenomenon: Mass transport principles in polymeric materials, measurement of mass transport Permeation and sorption methods, Factors affecting mass transport, Fick's law, Henry's law, polymer viscoelasticity: generelised linear viscoelasticity, creep, stress relaxation, stress experiments in polymer solids, apolymer melt rheology, Newtonian and non-newtonian fluids, Bingham and Pseudoplastics, Rheopectic, and thioxotropic behaviour, melt viscosity, melt flow index polymer rheology, Mechanical properties: Tensile, resilience, compression, impact and creep properties of polymers, shear strength, abrasion and fatigue. Fibre forming polymers: tenacity, denier, moisture content, moisture regain, fibre drawing, heat setting, texturising of fibre.

Unit V Polymer Technology **18 h**

Compounding: additive for thermoplastic and thermosets, Mastication, vulcanization, compounding of latex, Plasticization-Fillers, thermal stabilizers, with special emphasis to PVC, UV stabilizers, antioxidants, flame retardation, Two roll mixing and extruder mixing - advantage of twin – screw extruder Molding: Extrursion, die swell injection molding of thermoplastics and thermosets, transfer molding of thermosets, Plunger molding, blow molding, thermoforming, vacuum forming, casting, calendering, laminating, film production, Industrial polymers: Polyolefins, polyvinyl carbazides, poly acrylics, PMMA, poly methacrylics, polyacrylonitrile. Flourocarbon polymers: PTFE, PCTFE, surface graft treatment, thermosets, epoxy resins, alkyd resins, polyimides, unsaturated polyester, epoxy resins as coating materials. Heat resistant polymers: Poly phenylene oxide (PPO), polysulphide, thermoplastic elastomers involving natural, synthetic rubber, butyl rubber, hypalon rubber, EPDM, Neoprene.

References

1. S. Kobayashi, et. Al. New frontiers in polmersynthesis.
2. J. H. Koo, Polymer nanocomposites-aprocessing, characterization and applications, MacGraw Hill.
3. L. Nicolais, G. Garotenuto, Metal polymer nanocomposites, Wiley Intersceicne.
4. F. Daniels et. al. Experimental physical chemistry, MacGraw Hill.
5. D. L. Nelson, M. M. Cox, Lehninger princliples of biochemistry, W. H. Freeman.
6. G. Odian, principles of polymerization, Wiley.

7. C. S. Harper, Handbook of plastics, elastomers,and composites, MacGraw Hill.
8. M. Morron, Rubber Technology, Kluwer.
9. E. W. Madge, Latex foam rubber, Maclaren and Sons.
10. R. W. Dyson, Speciality Polymers, Chapman Hall.
11. A. F. Diar, K. Kanazawa, J. I. Castillo and J. A. Logan, Conducting polymers, Plenum
12. L. Hollidary, Ionic Polymers, Applied Science.
13. A. Blumstein, Liquid cryatlline order in polymers, Academic.

PC 243(a) DISSERTATION

Each of the students has to carry out original research in a topic in accordance with the Elective paper chosen for Semester IV under the guidance and supervision of a teacher in the concerned Department of the College.

Instructions to Question Papers Setters

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

Section A Five questions, one from each Unit containing three short answer questions marked (a), (b), and (c), each of which has 2 marks. One has to answer any two of (a), (b) or (c) from each of the five questions. (2x10=20 marks)
Section B Five questions, one from each unit containing two short essay questions marked (a) and (b), each of which has marks. One has to answer either (a) or (b) from each of the five questions. (5x5=25 marks)
Section C Five essay questions, one from each unit having 10 marks. One has to answer any three questions from the five questions asked.(10x3=30 marks)

Structures should be in chemdraw or ISIS/ draw

FOURTH SEMESTER M.Sc. DEGREE EXAMINATION

Branch VII: POLYMER CHEMISTRY
(Under Semester System w.e.f 2018 Admissions)

PC 241- POLYMER CHEMISTRY - I

Time: 3 h Max. Marks: 75

SECTION A

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

1 a) What is the effect of size and polarity of the monomers on its reactivity ratio?

b) Why is an optimum molecular weight necessary for polymers to be commercially useful?

c) Why does the light scattering technique provide weight average molecular weight?

2 a) Explain tacticity taking the example of polypropylene.

b) How cyclisation reaction is related to the size of the ring?

c) How NMR is useful in the determination of absolute configuration?

3 a) What is critical solution temperature?

b) Write Huggins and Kramer equation and explain

c) Brief about excluded volume.

4 a) What are the factors to be considered when two polymers are blended together?

b) What are the advantages and disadvantages of short fibre reinforced composites?

c) Explain pultrusion technique.

5 a) Why most of the polymers are prone to degradation?

b) What are the differences between oxidative and ozone degradation?

c) What is the type of degradation taking place in PMMA

[2 X 10 = 20 marks]

SECTION B

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

6 a) Explain Q-e scheme. What is the application of Q-e scheme?

b) Describe the membrane osmometry technique for determining the molecular weight of polymers.

7 a) What is the principle of Fluorescence spectroscopy? What are its important applications?

b) Explain configuration and conformation taking suitable examples.

8 a) What is solubility parameter? Explain one method for the determination of solubility parameter.

b) What are the effects of entropy and enthalpy is mixing of polymer solutions?

9 a) Why solution mixing is not commercially used for blending of two polymers? What are the advantages of polymer blends?

b) What are the commonly used methods for improving the compatibility of two polymers? Discuss briefly any one method.

10 a) Which are the methods used for checking biodegradability of a polymer? Explain briefly one method for checking the biodegradability of a polymer.

` b) Explain how metals catalyse degradation of polymer.

[5 X 5 = 25 marks]

Section C

Answer any three questions.Each question carries 10 marks

11 Derive the kinetic equation for a co-polymerization reaction. How can you predict the structure of a co-polymer.

12 Explain briefly the principle of ESR and Raman spectroscopic techniques.

13 Explain briefly critical solution temperature – LCST and UCST behaviour.

14 Explain briefly the different theories of compatibilisation of two polymers. What is the role of the fibre in improving the properties of a composite.

15 Explain in detail the thermo oxidative degradation of natural rubber. What are the commonly used chemicals for preventing the degradation of polymers. What are the changes taking place in a polymer during oxidative degradation.

[10 X 3 = 30 marks]

FOURTH SEMESTER M.Sc. DEGREE EXAMINATION

Branch VII :Polymer Chemistry

(Under Semester System w.e.f 2018 Admissions)

PC 242- POLYMER CHEMISTRY-II

Time:3 hrs Max marks:75

SECTION A

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

1 a) Which are the different types of nanomaterials?
b) What are the advantages of ATRP?
c) What is the advantage of immobilized enzymes?

2 a) What are the important applications of biomaterials?

b) What are the important applications of gene technology in medicine?

c) What are artificial enzymes?

3 a) How are liquid crystalline polymers classified?

b) What is meant by photoconductivity?

c) What are the advantages of conducting polymers over metals?

4 a) State and Explain Baeyer – Baeman rule.

b) What is meant by transition temperature?

c) Describe briefly pseudo plastics.

5 a) List out the advantages of twin – screw extrudere.

b) What is meant by calendaring? Explain.

c) What are plasticizers? Explain.

[2 X 10 = 20 marks]

SECTION B

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

6 a) Explain briefly the normal kinetics of ATRP polymerization.

b) What are the different types of solid supports used in peptide synthesis.

7 a) Explain the microbial attack of polyaminoacids.

b) What are requirements of a polymer to be used as a biomaterial?

8 a) What are liquid crystalline polymers? What are its important applications/

b) What is the mechanism of conducting in conjugated polymers? Explain the conducting mechanism of polyaniline.

9 a) State and explain Fick's law.

b) Explain Newtonian and non-Newtonian fluids with suitable examples.

10 a) Explain the extenders and fillers used in plastics.

b) Discuss plunger moulding and reciprocating screw moulding with illustration.

[5 X 5 = 25 marks]

Section C

Answer any three questions.Each question carries 10 marks

11 Explain briefly the solid state synthesis for the production of peptides.

12 Compare RNA and DNA in structure, properties and function.

13 Explain the structure, properties and applications of polyaniline, polyacetylene and polyparaphenylene.

14 Explain briefly the intermolecular bonding in polymers taking suitable examples. What are the requirements for a polymer to undergo strain induced crystallization.

15 Explain briefly the mixing process in a single extruder and a twin screw extruder. Compare its advantages and disadvantages.

[10 X 3 = 30 marks]