

MAHARSHI DAYANAND SARASWATI UNIVERSITY AJMER



पाठ्यक्रम

SYLLABUS

SCHEME OF EXAMINATION AND COURSES OF STUDY

FACULTY OF SCIENCE

M.Sc. CHEMISTRY

SEMESTER I-II

सत्र 2015–16

महर्षिदयानंद सरस्वती विश्विद्यालय , अजमेर

M.Sc. CHEMISTRY
SEMESTER SCHEME OF EXAMINATION

1. The maximum marks of each Semester Examination will be 300 .There shall be two semesters in one year and four Semesters in all. It will necessary for a candidate to pass in the theory as well as in the practical examination separately.Criteria for pass percentage and division will be as per the university policy for Semester Scheme prescribed uniformly by the university.
2. There will be four papers in each of the four Semesters and 16 papers in all. Each paper will have maximum marks of 50 and examination will be of 3 hours duration. There will be one Practical Examination of 7 hours duration in one day with maximum of 100 marks in every Semester.
3. Each theory paper is assigned four hours per week of teaching. Practical classes are assigned three continuous periods of one hour each per day (18 hours per week). Seminars are assigned two hours per week which includes seminar presentation alongwith text submission.
4. Scheme of examination in Individual Semester and distribution of marks in each paper will be as under :

Curriculum & Scheme of Examination for M.Sc. Chemistry

Semester Number	And Paper Nomenclature	Total Marks
Semester I		
Paper – I	Inorganic Chemistry	50
Paper-II	Reaction Mechanism – I	50
Paper-III	Physical Chemistry – I	50
Paper-IV	Computer and Diffraction Methods	50
Paper V	Practicals (including Seminar of 15 marks)	100
Total		300

Semester II

Paper VI	Coordination Chemistry	50
Paper VII	Reaction Mechanism -II and Stereochemistry	50
Paper VIII	Physical Chemistry- II	50
Paper IX	Group Theory and Spectroscopy	50
Paper X	Practicals (including Seminar of 15 marks)	100
		Total 300

M.S.C. CHEMISTRY SEMESTER-I PAPER I- INORGANIC CHEMISTRY

Time: 3 Hours

Max. Marks:50

Note : Each paper is divided into three independent units. The question paper is divided into three parts, Part – A, Part-B and Part-C. Part A (10 marks) is compulsory and contains 10 questions (50 words each). Each question is of one mark. Part-B (10 marks) is compulsory and contains five questions at least one from each unit. Candidate is required to attempt all five questions. Each question is of two marks (100 words). Part-C (30 marks) contains six questions two from each unit. Candidate is required to attempt three questions - one from each Unit. Each question is of ten marks (400 words.).

Unit I

(a) Stereochemistry and Bonding in Main Group Compounds

VSEPR, Irregular Geometry of molecules. $d\pi-p\pi$ bonds, Bent rule and energetics of hybridization, some simple reactions of covalently bonded molecules.

(b) Metal Clusters

Higher boranes, carboranes, metalloboranes and metallocarboranes.

Unit II**Fundamentals of Transition Metal Complexes**

Energy profile of reaction, reactivity of metal complexes, inert and labile complexes, kinetic application of valence bond and crystal field theories, kinetics of octahedral substitution, acid hydrolysis, factors affecting acid hydrolysis, base hydrolysis, conjugate base mechanism direct and indirect evidences in favor of conjugate mechanism.

Unit III**Reaction Mechanism of Transition Metal Complexes**

Anation reactions, reactions without metal ligand bond cleavage. Substitution reactions in square planar complexes, the trans effect, mechanism of the substitution reaction. Redox reaction, electron transfer reactions, mechanism of one electron transfer reactions, outer-sphere type reactions, cross reactions and Marcus-Hush theory, inner sphere type reactions.

Books Suggested

1. Advanced Inorganic Chemistry, F.A. Cotton and Wilkinson. John Wiley.
2. Inorganic Chemistry, J.E. Huhey, Harpes & Row.
3. Chemistry of the Elements, N.N. Greenwood and A. Earnshaw, Pergamon.
4. Comprehensive Coordination Chemistry eds., G. Wilkinson, R.D. Gillars and J.A. McCleverty, Pergamon.
5. Reaction mechanism, Basalo Pearson, Academic Press.

PAPER II- REACTION MECHANISM-I**Time: 3 Hours****Max. Marks:50**

Note : Each paper is divided into three independent units. The question paper is divided into three parts Part – A, Part-B and Part-C. Part A (10 marks) is compulsory and contains 10 questions (50 words each). Each question is of one mark. Part-B (10 marks) is compulsory and contains five questions at least one from each unit. Candidate is required to attempt all five questions. Each question is of two marks (100 words). Part-C (30 marks) contains six questions two from each unit. Candidate is required to attempt three questions- one from each Unit. Each question is of ten marks (400 words.).

Unit I**(a) Nature of Bonding in Organic Molecules**

Delocalized chemical bonding-conjugation, cross conjugation, resonance, hyperconjugation, bonding in fullerenes, tautomerism.

Aromaticity in benzenoid and non-benzenoid compounds, alternant and non-alternant hydrocarbons, Huckel's rule, energy level of π -molecular orbitals, annulenes, anti aromaticity, homo-aromaticity, PMO approach.

Bonds weaker than covalent – addition compounds, Crown ether complexes and cryptands, inclusion compounds.

(b) Reaction Mechanism: Structure and Reactivity

Types of mechanisms, types of reactions, thermodynamic and kinetic requirements, kinetic and thermodynamic control, Hammond's postulate, Curtin-Hammett principle. Potential energy diagrams.

Generation, structure, stability and reactivity of carbocations, carbanions free radicals, carbenes and nitrenes.

Effect of structure on reactivity-resonance and field effects, steric effect, the Hammett & Taft equation- linear free energy relationship. , substituent and reaction constants.

Unit II

(a) Aliphatic Nucleophilic substitution

The S_N2 S_N1 , mixed S_N1 and S_N2 and SET mechanism

(b) Aromatic Nucleophilic Substitution

The ArS_N1 , ArS_N2 , benzyne and $S_{RN}1$ mechanism. Reactivity-effect of substrate structure, leaving group and attacking nucleophile. The von Richter, Sommelet-Hauser and Smiles rearrangements.

(c) Aliphatic Electrophilic Substitution.

Bimolecular mechanism- S_E2 and S_{Ei} . The S_E1 mechanism, electrophilic substitution accompanied by double bond shifts. Effect of substrates, leaving group and the solvent polarity on the reactivity.

(d) Aromatic Electrophilic Substitution

The arenium ion mechanism, orientation and reactivity, energy profile diagrams. The ortho/para ratio, ipso attack, orientation in other ring system. quantitative treatment of reactivity in substrates and electrophiles. Diazonium coupling, Vismier reaction, Gattermann-koch reaction.

UNIT – III

Free Radical Reactions

Types of free radical reactions, free radical substitution mechanism, mechanism at an aromatic substrate, neighbouring group assistance. Reactivity for aliphatic and aromatic substrates at a bridgehead. Reactivity in the attacking radicals. The effect of solvent on reactivity.

Allylic halogenations (NBS), oxidation of aldehydes to carboxylic acids, auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts, Sandmeyer reaction. Free radical rearrangement, Hunsdiecker Reaction

Books Suggested

1. Advanced Organic Chemistry-Reactions, Mechanism and Structure, Jerry March, John Wiley.
2. Advanced Organic Chemistry, F.A. Carey and R.J. Sundberg, Plenum.
3. A guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman
4. Structure and Mechanism in Organic Chemistry, C.K. Ingold Cornell University Press.
5. Organic Chemistry, T.R. Morrison and R.N. Boyd, Prentice-Hall
6. Modern Organic Reactions, H.O. Housee, Benjamin.
7. Principles of Organic Synthesis, R.O.C. Norman and J.M. Coxon, Blackie Academic & Professional.
8. Pericyclic Reactions S.M. Mukherji, Macmillan, India.
9. Reaction Mechanism in Organic Chemistry, S.M. Mukherji and S.P. Singh, Macmillan.
10. Stereochemistry of Organic Compounds, D. Nasipuri, New Age International.
11. Stereochemistry of Organic Compounds, P.S. New Age International.
12. Quantum Chemistry by Zimmerman Academic Press.

PAPER III – PHYSICAL CHEMISTRY- I

Time: 3 Hours

Max. Marks:50

Note : Each paper is divided into three independent units. The question paper is divided into three parts Part – A, Part-B and Part-C. Part A (10 marks) is compulsory and contains 10 questions (50words each).Each question is of one mark. Part-B (10 marks) is compulsory and contains five questions at least one from each unit. Candidate is required to attempt all five questions. Each question is of two marks (100 words). Part-C (30 marks) contains six questions two from each unit. Candidate is required to attempt three questions one from each Unit. Each question is of ten marks (400 words.).

Unit I**(a) Quantum Chemistry**

Schrodinger equation to some model systems viz., harmonic oscillator, the rigid rotor, the hydrogen atom. Applications of variation method and perturbation theory to the Helium atom.

(b) Molecular Orbital Theory

Huckel theory of conjugated systems, bond order and charge density calculations. Applications to ethylene, butadiene, cyclopropenyl radical, cyclobutadiene etc.

Unit II**Thermodynamics**

Concept of fugacity and determination of fugacity. Non-ideal systems, Excess functions for non-ideal solutions, Activity, Activity coefficient, Debye Huckel theory for activity coefficient for electrolytic solution; determination of activity and activity coefficient; ionic strength. Application of phase rule to three component system – acetic acid + chloroform + water.

Unit III**A. Chemical Dynamics**

Collision theory of reaction rates, steric factor, activated complex theory, ionic reactions, kinetic salt effects, steady state kinetics, kinetic and thermodynamic control of reactions, methods of determining mechanism, isotope effects.

Dynamic chain (hydrogen-bromine reactions, pyrolysis of acetaldehyde, decomposition of ethane), photochemical (hydrogen-bromine reaction), acid base catalysis, kinetics of enzyme reactions, general features of fast reactions, study of fast reactions by flow method, flash photolysis, dynamics of unimolecular reactions (Lindemann Theory, Hinshelwood Modifications).

Books Suggested :

1. Physical Chemistry, P.W. Atkins, ELBS
2. Introduction to Quantum Chemistry, A.K. Chandra, Tata McGraw Hill.
3. Quantum Chemistry, Ira N. Levine, Prentice Hall.
4. Coulson's Valance, R McWeeny, ELBS
5. Chemical Kinetics, K.J.Laidler, MacGraw-Hill
6. Kinetics and Mechanism of Chemical transformations, J. Rajaram and J. Kuriacose, McMillan.
7. Micelles, Theoretical and Applied Aspects, V.Moroi, Plenum.

8. Modern Electrochemistry Vol.I and Vol.II J.O.M. Bockris and A.K.N. Reddy, Plenum.
9. Introduction to Polymer Science, V.R. Gowarikar, N.V. Vishwanathan and J. Sridhar, Wiley Eastern.
10. Phase Rule by Bowden.
11. Phase Rule by Y.K. Gupta.

PAPER IV COMPUTER AND DIFFRACTION METHODS

Time: 3 Hours

Max. Marks:50

Note : Each paper is divided into three independent units. The question paper is divided into three parts Part – A, Part-B and Part-C. Part A (10 marks) is compulsory and contains 10 questions (50 words each). Each question is of one mark. Part-B (10 marks) is compulsory and contains five questions at least one from each unit. Candidate is required to attempt all five questions. Each question is of two marks (100 words). Part-C (30 marks) contains six questions two from each unit. Candidate is required to attempt three questions one from each Unit. Each question is of ten marks (400 words.).

Unit I

(a) Introduction to Computers and Computing

Basic structure and functioning of computers with a PC as an illustrative example. Memory, I/O devices. Secondary Storage. Computer language. Operating systems with DOS as an example. Introduction to UNIX and WINDOWS. Data Processing, principles of programming. Algorithms and flow-charts.

(b) Computer Programming in C

Overview of C, Constants., Variable and Data Types, Operators and Expression, Managing Input and output Operators, Decision Making and Branching, IF statement, IF....ELSE statement, GO TO statement, Decision Making and Looping, WHILE statement, DO statement and FOR Statement, Jumps in loop.

Unit-II

(a) Programming in Chemistry

Development of small computer codes involving simple formulae in chemistry, such as Vander waals equation, titration, kinetics, radioactive decay. Evaluation of lattice energy and ionic radii from experimental data.

(b) Electron Diffraction:

Scattering intensity Vs. scattering angle, Wierl equation, measurement technique, elucidation of structure of simple gas phase molecules, Low energy electron diffraction and structure of surfaces.

(c) Neutron diffraction

Scattering of neutrons by solids and liquids, magnetic scattering, measurement techniques. Elucidation of structure of magnetically ordered unit cell.

Unit - III

X-ray Diffraction

Debye-Scherrer method of X-ray structural analysis of crystal, index reflections, identification of unit cells from systematic absences in diffraction pattern. Structure of simple lattices and X-ray intensities, structural factor and its relation to intensity and electron density, phase problem. Description of the procedure for an X-ray structure analysis, absolute configuration of molecules. Ramchandran diagram.

Books Suggested

1. Modern Spectroscopy, J.M. John Wiley.
2. Applied Electron Spectroscopy for chemical Analysis Ed. H. Windawi and F.L. No, Wiley Interscience.
3. NMR, NQR, EPR and Mossbauer Spectroscopy in Inorganic Chemistry, R.V. Parish, Ellis Harwood.
4. Physical Methods in Chemistry R.S. Drago, Saunders College.
5. Chemical Application of Group Theory, F.A. Cotton.
6. Introduction to Molecular Spectroscopy, R. Chang, McGraw Hill.
7. Basic Principles of Spectroscopy, R. Chang, McGraw Hill
8. Theory and Applications of UV Spectroscopy, H.H. Jaffe and M. Orchin, IBH-Oxford.
9. Introduction of Photoelectron Spectroscopy, P.K. Ghosh, John Wiley.
10. Introduction to Magnetic Resonance., A Carrington and A.D. Carrington and A.D. Maclachalan, Harper & Raw.
11. Programming inAnsiC-E. Balagursamy

PAPER V -PRACTICALS**Time : 07 Hours****Max Marks-100****A. Inorganic****Preparations (Any five of the following preparations)**

- (1) Tris(thiourea)copper (II)sulphate.
- (2) Cis –Potassium Diaquatrioxalatochromate(III).
- (3) Sodium Diamminetetrathiocynatochromate(III).
- (4) Tris(acetylacetonato)manganese(II).
- (5) Potassium Trioxalatoferrate(III).
- (6) Prussian Blue.
- (7) Hexamminecobalt(III) Hexanitro-N-cobaltate(III).
- (8) Vanadyl acetylacetonate
- (9) Dichloridobis(pyridine)cobalt(II).
- (10) Hexamminenickel(II) chloride.
- (11) Bis(dimethylglyoximato)nickel (II).
- (12) Tetramminecopper(II) sulphate.

B. Organic**(a) Qualitative Analysis**

Separation, purification and identification of compounds of binary mixture (two solids).

(b) Quantitative Analysis (any three)

- (i) Estimation of amines/phenols using bromide solution/or acetylation method.
- (ii) Determination of Iodine value of an oil sample.
- (iii) Determination of Acid Value of an oil sample.
- (iv) Determination of Saponification value of an oil sample.

C. Physical Chemistry

(Students are required to perform at least five experiments from the following experiments.)

1. Determination of the effect of (a) change of temperature (b) change of concentration of reactants and catalyst and (c) Ionic strength of the media on the velocity constant of hydrolysis of an ester/ionic reactions.
2. Determination of strength of acid in gm/l conductometrically using following combinations (i) SA-WB (ii) WA-SB (iii) WA-WB (iv) SA-SB {S-Strong, W-Weak, A-Acid, B-Base }
3. Determination of the velocity constant, order of the reaction and energy of activation of saponification of ethyl acetate by sodium hydroxide conductometrically.

4. Determination of solubility and solubility product of sparingly soluble salts (e.g. PbSO_4 , BaSO_4) conductometrically.
5. Determination of the strength of strong and weak acids in a given mixture conductometrically.
6. To study the effect of solvent on the conductance of AgNO_3 /acetic acid and to determine the degree of dissociation and equilibrium constant in different solvents and in their mixture (DMSO, DMF, dioxane, acetone, water) and to test the validity of Debye-Huckel-Onsager theory.
7. Determination of the dissociation constant of acetic acid in DMSO, DMF acetone and dioxane by titrating it with KOH.
8. Determination of the dissociation constant of monobasic/dibasic acid.

Books Suggested :

1. Vogel's Textbook of Quantitative Analysis, revised, J. Bassett, R.C. Denney, G.H. Jeffery and J. Mendham, ELBS.
2. Synthesis and Characterization of Inorganic Compounds, W.L. Jolly, Prentice Hall.
3. Experiments and Techniques in Organic Chemistry, D.Past, C.Johnson and M. Miller, Prentice Hall.
4. Macroscale and Microscale Organic Experiments, K.L. Williamson, D.C. Health.
5. Systematic Qualitative Organic Analysis, H. Mideleton, Adward Arnold.
6. Handbook of Organic Analysis-Qualitative and Quantitative, H. Clark, Adward Arnold.
7. Vogel's Textbook of Practical Organic Chemistry, A.R. Tatchell John Wiley.
8. Practical Physical Chemistry, A.M. James and F.E. Prichard, Longman.
9. Findley's Practical Physical Chemistry, B.P. Levitt, Longman.
10. Experiments in Physical Chemistry, R.C. Das and B. Behera. Tata McGraw Hill.

INSTRUCTIONS FOR PRACTICALS**Max Marks: 100****Time:07 Hours**

The Board of Examiners will constitute of one External Examiner and one Internal Examiner.

	Marks
(A)Inorganic	
Inorganic Preparations	- 15
(B)Organic	
(a)Qualitative Analysis	- 15
(b) Quantitative Analysis	- 15
(C) Physical	
1. One experiment is to be performed	- 20
(D)Viva	- 10
(E)Record	- 10
(F)Seminar	- 15
Grand Total	100

M.Sc.CHEMISTRY
SEMESTER-II

PAPER VI – COORDINATION CHEMISTRY**Time: 3 Hours****Max. Marks:50**

Note : Each paper is divided into three independent units. The questions paper is divided into three parts Part – A, Part-B and Part-C. Part A (10 marks) is compulsory and contains 10 questions (50words each).Each question is of one mark. Part-B (10 marks) is compulsory and contains five questions at least one from each unit. Candidate is required to attempt all five questions. Each question is of two marks (100 words). Part-C (30 marks) contains six questions two from each unit. Candidate is required to attempt three questions one from each Unit. Each question is of ten marks (400 words.).

Unit I**(a) Metal-Ligand Equilibria in Solution**

Stepwise and overall formation constants and their interaction, trends in stepwise constants, factors affecting the stability of metal complexes with reference to the nature of metal ion and ligand, chelate effect and its thermodynamic origin, determination of binary formation constants by pH-metry and spectrophotometry.

(b) Metal Ligand Bonding

Limitation of crystal field theory, molecular orbital theory, octahedral, tetrahedral and square planar complexes, π – bonding and molecular orbital theory.

Unit II**Electronic Spectra and Magnetic Properties of Transition Metal Complexes**

Spectroscopic ground state, correlation, Orgel and Tanabe-Sugano diagrams for transition metal complexes (d^1 - d^9 States). Calculations of Dq , B and β parameters, charge transfer spectra, anomalous magnetic moments, magnetic exchange coupling and spin crossover.

Unit III**Metal π -Complexes.**

Metal carbonyls, structure and bonding. Vibrational spectra of metal carbonyls for bonding and structural elucidation, important reactions of metal carbonyls; preparation, bonding structure and important reactions of transition metal nitrosyl, dinitrogen and dioxygen complexes; tertiary phosphine as ligand..

Books Suggested

1. Advanced Inorganic Chemistry, F.A.Cotton and Wilkinson. John Wiley.
2. Inorganic Chemistry, J.E. Huhey, Harpes & Row.
3. Chemistry of the Elements, N.N. Greenwood and A. Earnshaw, Pergamon.
4. Inorganic Electronic Spectroscopy, A.B.P. Lever, Elsevier.
5. Magnetochemistry, R.L. Carlin, Springer Verlag.
6. Comprehensive Coordination Chemistry eds., G. Wilkinson, R.D. Gillars and J.A. McCleverty, Pergamon.
7. Reaction mechanism, Basalo Pearson, Academic Press.

PAPER VII –REACTION MECHANISM- II AND STEREOCHEMISTRY**Time: 3 Hours****Max. Marks:50**

Note : Each paper is divided into three independent units. The question paper is divided into three parts Part – A, Part-B and Part-C. Part A (10 marks) is compulsory and contains 10 questions (50 words each). Each question is of one mark. Part-B (10 marks) is compulsory and contains five questions at least one from each unit. Candidate is required to attempt all five questions. Each question is of two marks (100 words). Part-C (30 marks) contains six questions two from each unit. Candidate is required to attempt three questions- one from each Unit. Each question is of ten marks (400 words.).

Unit I**a) Addition to Carbon-Hetero Multiple Bonds**

Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acids, esters and nitriles. Addition of Grignard reagents, organozinc and organolithium reagents to carbonyl and unsaturated carbonyl compounds. Wittig reaction.

Mechanism of condensation reaction involving enolates-Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe reactions. Hydrolysis of esters and amides, ammonolysis of esters.

b) Addition to Carbon-Carbon Multiple Bonds

Mechanism and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, regio- and chemo-selectivity, orientation and reactivity.

Addition to cyclopropane ring. Hydrogenation of double and triple bonds, hydrogenation of aromatic rings. Hydroboration. Michael reaction. Sharpless asymmetric epoxidation.

Unit II

(a) Stereochemistry Elements of symmetry, Chirality, molecules with more than one chiral center, threo and erythro isomers, methods of resolution, optical purity, enantiotopic and diastereotopic atoms, groups and faces, stereospecific and stereoselective synthesis. Asymmetric synthesis. Optical activity in the absence of chiral carbon (biphenyls, allenes and spiranes), chirality due to helical shape.

Stereochemistry of the compounds containing nitrogen, sulphur and phosphorus.

(b) Conformational analysis of cycloalkanes, decalins, effect of conformation on reactivity, conformation of sugars, steric strain due to unavoidable crowding.

Unit III**Pericyclic Reactions**

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1,3,5-hexatriene and allyl system. Classification of pericyclic reaction. Woodward-Hoffmann correlation diagrams. FMO and PMO approach Electrocyclic reactions-conrotatory and disrotatory motions, $4n$, $4n+2$ and allyl systems. Cycloadditions-antarafacial and suprafacial additions, $4n$, $4n+2$ systems, $2+2$ addition of ketenes, 1,3 dipolar cycloaddition and cheletropic reactions.

Sigmatropic rearrangements-suprafacial and antarafacial shifts of P sigmatropic shifts involving carbon moieties, 3,3-and 5,5-sigmatropic rearrangements. Claisen, Cope and aza-Cope rearrangements, Ene reaction.

Books Suggested:

1. Advanced Organic Chemistry-Reactions, Mechanism and Structure, Jerry March, John Wiley.
2. Advance Organic Chemistry, F.A. Carey and R.J. Sundberg, Plenum.
3. A guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman
4. Structure and Mechanism in Organic Chemistry, C.K. Ingold Cornell University Press.
5. Organic Chemistry, T.R. Morrison and R.N. Boyd, Prentice-Hall
6. Modern Organic Reactions, H.O. House, Benjamin.
7. Principles of Organic Synthesis, R.O.C. Norman and J.M. Coxon, Blackie Academic & Profesional.
8. Pericyclic Reactions S.M. Mukherji, Macmillan, India.
9. Reaction Mechanism in Organic Chemistry, S.M. Mukherji and S.P. Singh, Macmillan.
10. Stereochemistry of Organic Compounds, D. Nasipuri, New Age International.
11. Stereochemistry of Organic Compounds, P.S. New Age International.
12. Quantum Chemistry by Zimmerman Academic Press.

PAPER VIII –PHYSICALCHEMISTRY - II**Time: 3 Hours****Max. Marks:50**

Note : Each paper is divided into three independent units. The questions paper is divided into three parts Part – A, Part-B and Part-C. Part A (10 marks) is compulsory and contains 10 questions (50words each).Each question is of one mark. Part-B (10 marks) is compulsory and contains five questions at least one from each unit. Candidate is required to attempt all five questions. Each question is of two marks (100 words). Part-C (30 marks) contains six questions two from each unit. Candidate is required to attempt three questions one from each Unit. Each question is of ten marks (400 words.).

Unit I**Electrochemistry**

Electrochemistry of solutions, Debye-Huckel-Onsager treatment and its extension, ion solvent interactions. Debye-Huckel-Bjerrum model. Thermodynamics of electrified interface equations, methods of determination. Semiconductor interfaces-theory of double layer at semiconductor, electrolyte solution interfaces, structure of double layer interfaces. Effect of light at semiconductor solution interface.

Overpotentials, exchange current density, derivation of Butler-Volmer equation, Tafel Plot.

Polarography theory, Ilkovic equation; half wave potential and its significance.

Corrosion – Types, mechanism and inhibition.

Unit II**Surface Chemistry****(a) Adsorption**

Pressure difference across curved surface (Laplace equation), vapour pressure of droplets (Kelvin equation), Gibbs adsorption isotherm, estimation of surface area (BET equation without derivation), mechanism of surface catalytic reactions.

(b) Micelles

Surface active agents, classification of surface active agents, micellization, hydrophobic interaction, critical micellar concentration (CMC), factors affecting the CMC of surfactants, counter ion binding to micelles, thermodynamics of micellization, solubilization, micro emulsion, reverse micelles.

(c) Macromolecules

Electrically conducting, fire or heat resistant, liquid crystal polymers

UNIT III**Statistical Thermodynamics**

Concept of distribution, thermodynamic probability and most probable distribution. Ensemble averaging, postulate of ensemble and averaging. Canonical, grand canonical and micro canonical ensembles. Partition functions-translational, rotational, vibrational and electronic partition functions, calculation of thermodynamic properties in terms of partition functions. Applications of partition functions. Chemical equilibria and equilibrium constant in terms of partition functions, Fermi-Dirac statistics.

Bose-Einstein statistics-distribution law and application to helium in brief.

Books Suggested :

1. Physical Chemistry, P.W. Atkins, ELBS
2. Introduction to Quantum Chemistry, A.K. Chandra, Tata McGraw Hill.

3. Quantum Chemistry, Ira N. Levine, Prentice Hall.
4. Coulson's Valance, R McWeeny, ELBS
5. Chemical Kinetics, K.J.Laidler, MacGraw-Hill
6. Kinetics and Mechanism of Chemical transformations, J. Rajaraman and J. Kuriacoose, McMillan.
7. Micelles, Theoretical and Applied Aspects, V.Moroi, Plenum.
8. Modern Electrochemistry Vol.I and Vol.II J.O.M. Bockris and A.K.N. Reddy, Plenum.
9. Introduction to Polymer Science, V.R. Gowarikar, N.V. Vishwanathan and J. Sridhar, Wiley Eastern.
10. Phase Rule by Bowden.
11. Phase Rule by Y.K. Gupta.

PAPER IX – GROUP THEORY AND SPECTROSCOPY

Time: 3 Hours

Max. Marks:50

Note : Each paper is divided into three independent units. The question paper is divided into three parts Part – A, Part-B and Part-C. Part A (10 marks) is compulsory and contains 10 questions (50words each).Each question is of one mark. Part-B (10 marks) is compulsory and contains five questions at least one from each unit. Candidate is required to attempt all five questions. Each question is of two marks (100 words). Part-C (30 marks) contains six questions two from each unit. Candidate is required to attempt three questions one from each Unit. Each question is of ten marks (400 words.).

Unit I

(a) Symmetry and Group Theory in Chemistry

Symmetry elements and symmetry operation, definitions of group, sub-group, relation between orders of a finite group and its subgroup Conjugacy relation and classes. Point symmetry group.

(b) Raman Spectroscopy

Classical and quantum theories of Raman effect. Pure rotational, vibrational and vibrational-rotational Raman spectra, selection rules, mutual exclusion principle.Resonance Raman spectroscopy, coherent anti Stokes Raman spectroscopy (CARS).

Unit II**(a)Molecular spectroscopy**

Energy levels, molecular orbitals, vibrational transitions, vibration progression and geometry of the excited states, Franck-Condon Principle, electronic spectra of polyatomic molecules, Emission spectra, radiative and non-radiative decay, internal conversion, spectra of transition metal complexes, charge-transfer spectra.

(b) Photoelectron Spectroscopy

Basic principles; photo-electric effect, ionization process, Koopman's theorem. Photoelectron spectra of simple molecules. ESCA. Chemical information from ESCA. Auger electron spectroscopy-basic idea. Photoacoustic Spectroscopy:, Basic principle of photoacoustic spectroscopy (PAS), PAS-gases and condensed systems, chemical and surface applications.

Unit III**Electron SpinResonance Spectroscopy**

Basic principles, zero field splitting and Kramer's degeneracy, factors affecting the "g" value Isotropic and anisotropic hyperfine coupling constants, spin Hamiltonian, spin densities and McConnell relationship, measurement techniques, spin polarization for atoms and transition metal ions, spin-orbit coupling and significance of g-tensors, application to transition metal complexes (having one unpaired electron) including biological systems and to inorganic free radicals such as PH_4 F_2 and $[\text{BH}_3]$.

Books Suggested

1. Modern Spectroscopy, J.M. John Wiley.
2. Applied Electron Spectroscopy for chemical Analysis Ed. H. Windawi and F.L. No, Wiley Interscience.
3. NMR, NQR, EPR and Mossbauer Spectroscopy in Inorganic Chemistry, R.V. Parish, Ellis Harwood.
4. Physical Methods in Chemistry R.S. Drago, Saunders College.
5. Chemical Application of Group Theory, F.A. Cotton.
6. Introduction to Molecular Spectroscopy, R. Chang, McGraw Hill.
7. Basic Principles of Spectroscopy, R. Chang, McGraw Hill
8. Theory and Applications of UV Spectroscopy, H.H. Jaffe and M. Orchin, IBH-Oxford.
9. Introduction of Photoelectron Spectroscopy, P.K. Ghosh, John Wiley.
10. Introduction to Magnetic Resonance., A Carrington and A.D. Carrington and A.D. Maclachalan, Harper & Raw.

PAPER X-PRACTICALS**Time : 07 Hours****Max Marks-100****A. Inorganic**

Separation and determination of two metal ions Cu-Ni, Ni-Mg, Cu-Fe, Cu-Ba etc. involving volumetric and gravimetric methods.

B. Organic**(a) Organic Synthesis (any five)**

- (i) Acetylation: Acetylation of cholesterol and separation of cholesteryl acetate by column chromatography.
- (ii) Oxidation: Adipic acid by chromic acid oxidation of cyclohexanol.
- (iii) Aldol condensation: Dibenzal acetone from benzaldehyde.
- (iv) Sandmeyer reaction: p-chlorotoluene from p-toluidine.
- (v) Cannizzaro reaction: 4-chlorobenzaldehyde as substrate.
- (vi) Friedel Crafts Reaction: β -Benzoylpropionic acid from succinic anhydride and benzene.
- (vii) Aromatic electrophilic substitutions: Synthesis of p-nitroaniline and p-bromoaniline

(b) Quantitative Analysis (any two)

- (i) Determination of DO of a water sample.
- (ii) Determination of COD of a water sample.
- (iii) Determination of BOD of a water sample.

C. Physical Chemistry

(Students are required to perform at least five experiments from the following experiments.)

1. Determination of congruent composition and temperature of a binary system (e.g. diphenylamine-benzophenone system).
2. To construct the phase diagram for three component system (e.g., chloroform-acetic acid-water).
3. Determination of the velocity constant of hydrolysis of an ester/ionic reaction in micellar media.
4. Determination of the rate constant for the oxidation of iodide ions by hydrogen peroxide studying the kinetics as an iodine clock reaction.
5. Determination of the primary salt effect on the kinetics of ionic reactions and testing of the Bronsted relationship (iodine ion is oxidized by persulphate ion).
6. Determination of strengths of halides in a mixture potentiometrically.

7. Determination of the strengths of strong and weak acids in a given mixture using a potentiometer/pH meter.
8. Determination of the formation constant of silver-ammonia complex and stoichiometry of the complex potentiometrically.
9. Acid-base titration in a non-aqueous media using a pH meter.
10. Determination of activity and activity coefficient of electrolytes.
11. Determination of partition coefficient of I_2 between water and CCl_4 .

INSTRUCTIONS FOR PRACTICALS

Max Marks: 100

Time: 07 Hours

The Board of Examiners will constitute of one External Examiner and one Internal Examiner.

Marks

(A) Inorganic

Separation and determination of two metals involving volumetric and gravimetric methods. - 20

(B) Organic

(a) Organic Synthesis - 10
(b) Quantitative Analysis - 15

(C) Physical

1. One experiment is to be performed - 20

(D) Viva - 10

(E) Record - 10

(F) Seminar - 15

Grand Total 100