M.Sc. PROGRAMME IN BRANCH III CHEMISTRY

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

SEMESTER I

CH 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, triagonal 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.
2) J. E. Huheey , 'Inorganic Chemistry- Principles of Structure and Reactivity' , Harper Collins College Publishing
3) K. F. Purcell and J. C. Kotz, 'Inorganic Chemistry', Saunders.
4) S. F. A. Kettle, 'Physical Inorganic Chemistry', Oxford University Press.
5) Shriver and Attkins, 'Inorganic Chemistry', Oxford University Press.
6) A.I. Vogel, 'A Text Book of Quantitative Inorganic Analysis' , Longman.
7) D. A. Skoog, D. M. West and F. J. Holler, 'Fundamentals of Analytical Chemistry' Saunders College Publishing.
8) D. A. Skoog and D. M. West, 'Principles of Instrumental Analysis', Saunders College Publishing.
9) F.A.Cotton," Chemical Applications of Group Theory", Wiley Eastern
10) A.S.Kunju, G. Krishnan," Group Theory and its Applications in Chemistry", PHI Learning.
11) R.L.Carter,"Molecular Symmetry and Group Theory", John Wiley& Sons.
12) James E. Girard, Principles of Environmental Chemistry.
13) H.V. Jadhav, Elements of Environmental Chemistry.
14) Michael E. Essington Soil and water Chemistry.

CH 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 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 - Stereochemistry of nitrogen and phosphorus containing compounds. Atropisomerism and its designation. Stereoselectivity, enantiomeric excess and chiral separation methods.

Conformational analysis of alkanes and cycloalkanes , Biased systems. Effect of conformation on reactivity of cyclohexane and decalin derivatives.

Introduction to ORD, CD- configuration and their application in assigning configuration and conformation. 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 heterolytic fission. Formation and structure of carbocations, carbanion and free radicals, Stability of intermediates, influence of field effects – inductive effect, mesomeric effect, resonance effect and hyperconjugative effect, steric effects, 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 susbstitution at sp^3 carbon - S_N1 and S_N2 mechanism. Walden inversion, stereo specificity in S_N1 reaction. Effect of solvent, leaving group and substrate structure, Neighbouring group participation, Non-classical carbocations, Competition between S_N^1 and S_N^2 reactions. S_N1', S_N2', S_Ni mechanism.

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

Aromatic Substitution reactions - Electrophilic substitution, The mechanism and evidence-Reactions involving nitrogen, sulphur, carbon, halogen and oxygen electrophiles. Directive and rate controlling factors.

Aromatic Nucleophilic Substitution reactions - S_N1, S_NAr, benzyne and $S_{NR}1$ 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 X_2, HX, boranes and hydroxylation 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 of Aldol (normal, crossed and directed), Perkin, Stobbe, Knovenagel, Darzen, Reformatsky and benzoin condensations. Grignard, Cannizaro, Wittig and Wittig-Horner reactions. Mechanism and stereochemistry of addition to C=O systems. Cram's rule, Felkin-Anh model.

Unit V Reagents in organic synthesis 18 h

Applications of hydrogenation catalysts, hindered boranes, bulky metal hydrides. $NaCNBH_3$ DIBAL, Li trialkylborohydrides, tri-n-butyl tin 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. Sharpless asymmetric epoxidation. Chemo and regioselectivity in reductions and oxidations.

References

1. D. Hellwinkel, Systematic nomenclature of organic chemistry, Springer international edition
2. D. Nasipuri, "Stereochemistry of Organic compounds", Wiley Eastern.
3. Jonathan Clayden, Nick Greeves, and Stuart Warren , Organic Chemistry, OUP.
4. P.S. Kalsi, Sterochemistry, conformation and mechanism, New age.
5. Paula Yurkanis Bruice, " Organic chemistry", Third Edition, Pearson Education.
6. P. Sykes, " A guide book to mechanism in Organic chemistry", Longman.
7. S. N. Issacs, " Physical organic chemistry", Longman.
8. M.B. Smith, March's advanced organic chemistry" 5^{th} Edn, Wiley.
9. F. A. Carey and R. S. Sunderg, Advanced organic chemistry, part A and B", Kluwer, 4^{th}Edn.
10. M. A. Fox and J. K. Whitesell, " Organic chemistry", 2^{nd} Edn, Jones and Bartlett.

11. C. J. Moody and W. H. Whitham, " Reactive intermediates", Oxford University Press.
12. I. L. Finar, " Organic chemistry" Vol 2, Longman.
13. F. Carey, " Organic chemistry" 5th Edn, Mc Graw Hill.
14. M.B. Smith, Organic synthesis, McGraw Hill.
15. H.O. House, Modern synthetic reactions, Benjamin Cummins.
16. R.K. Mackie *et al*, Guide book to organic synthesis, Longman.
17. W. Carruthers, Modern methods in organic synthesis, Cambridge University.
18. R.O.C. Norman and A. Coxon, Modern synthetic reactions, Chapman and Hall.

CH213 PHYSICAL CHEMISTRY –I 90 h

Unit 1 Quantun Chemistry I 18 h

Failure of classical mechanics, 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 noncommuting 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. Spherical harmonics as eigen functions of angular momentum operators Lz and L^2

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

Unit II Surface Chemistry and Catalysis **18 h**

The Gas- solid inter phase, Types of adsorption. Heat of adsorption and its determination, Chemisorption- differences with physical adsorption Adsorption isotherms Classical Freundlich and Langmuir isotherms Thermodynamic and Statistical derivation of Langmuir adsorption isotherm Multilayer adsorption- the BET theory and Harkins- Jura theory.

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

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

Surface films: different types, Surface pressure and its measurement Surface potential and its measurements and interpretation. Measurement of surface area of solids: Harkins – Jura absolute method, entropy method and the point B method. Use of Langmuir, BET and Harkins – Jura isotherms for surface area determination.

Catalysis: Mechanism and theories of homogeneous and heterogeneous catalysis. Enzyme catalysis, 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 Free energy, Maxwell relations and significance, temperature dependence of free energy - Gibbs Helmholtz equation, applications of Gibbs Helmholtz equation.

Partial molar quantities, chemical potential, Gibbs-Duhem equations, determination of partial molar properties - molar volume and enthalpy. Fugacity, relation between fugacity and pressure, determination of fugacity of a real gas, variation of fugacity with temperature and

pressure Fugacity of liquid mixtures, fugacity of mixture of gases, Lewis randall rule. Activity, activity coefficients, dependence of activity on temperature and pressure. Determination of activity and activity coefficients of electrolytes and non electrolytes

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

Chemical affinity and thermodynamic functions, effect of temperature and pressure on chemical equilibrium- vant Hoff reaction isochore and isotherm.

Unit IV Chemical kinetics **18 h**

Theories of reaction rates: Collision theory-steric factor, potential energy surfaces. Conventional transition state theory-Eyring equation. Comparison of the two theories. Thermodynamic formulation of the two theories. Thermodynamic formulation of the reaction rates. Significance of $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$. Volume of activation.

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

Kinetics of complex reactions - parellel 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 N2O5. Rice-Herzfeld mechanism, branching chain reactions Hinshelwood mechanism of chain reactions and explosion.

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

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

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

Unit V Gaseous and liquid state **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 itsdetermination 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-Kwog equation, Claussious 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

Liquifaction of gases Critical phenomena, van der Waal's equation and critical state, principle of corresponding states, molar mass and density of real gases

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
2) D. A. McQuarrie, "Quantum Chemistry", Viva Publishers.
3) M. W. Hanna, "Quantum Mechanics in Chemistry", Benjamin.
4) R. K. Prasad, "Quantum Chemistry", New Age International Publishers
5) T. Angel, "Quantum Chemistry and Spectroscopy", Pearson Education.
6) P. W. Atkins, R.S.Friedman, "Molecular Quantum Mechanics", Oxford University Press.
7) J.P Lowe, K. Peterson, "Quantum Chemistry", New Age International
8) S. Glasstone, "Thermodynamics for Chemists",
9) G.W. Castellan, "Physical Chemistry", Addison-Lesley Publishing.
10) P.W. Atkins," Physical chemistry', Oxford University Press.

11) D. A . McQuarrie, J.D Simon,"Physical Chemistry- A Molecular Approach", Viva Publishers.
12) K.J Laidler, "Chemical Kinetics", McGraw Hill.
13) J.E. House, "Principles of Chemical Kinetics", Elsevier.
14) J. Rajaram, J.C Kuriakose," Kinetics and Mechanisms of Chemical Transformations", McMillan.
15) C. Kalidas, "Chemical Kinetic Methods: Principles of Fast reaction Techniques and Applications, New Age International.
16) K.K Rohatgi-Mukherjee, "Fundamentals of Photochemistry", New age International.
17) A.W. Adamson,"Physical Chemistry of Surfaces", 5th edition Wiley India.
18) D.K.Chakrabarty and B. Viswanathan, Heterogeneous catalysis, New Age Publications.
19) G.A.Somorjai.Y.Li,Introduction to Surface Chemistry and Catalysis.International
20) Puri, Sharma, Pathania,"Principles of physical Chemistry" Vishal publishing company
21) Gurdeep Raj "Advanced Physical Chemistry" GOEL Publishing House, Meerut.

CH 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.
2) A. I. Vogel, 'A Text Book of Qualitative Inorganic Analysis', Longman.
3) D.A. Skoog and D. M. West, 'Analytical Chemistry: An Introduction', Saunders College Publishing.
4) W. G. Palmer, 'Experimental Inorganic Chemistry,' Cambridge University P

CH 215 ORGANIC PRACTICALS-1

Total 125 h

A . Separation and identification of organic compounds

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

• Purification of the separated samples by boiling and crystallization.

• TLC of the purified samples along with the mixture in same TLC plates (if not possible use separate plates) and calculation of R_f values.

B. Separation of a mixture of by column chromatography

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

C. Preparation of compounds by two stages.

TLC analysis of the products and original compound in the same plate and measurement of Rf values. Recording UV, IR, NMR and mass spectrum of synthesized compounds.

• Acetanilide- ⟶ p-nitroacetanilide ⟶ p-nitroaniline

• Methylbenzoate ⟶ m-nitromethylbenzoate ⟶ m-nitrobenzoic acid

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

E. Green Organic Chemistry experiments

1) Acetanilide- ⟶ p-bromoacetanilide (KBr and CAN)

2) Benzophenone ⟶ Benzopinacol (photoreduction)

References

1) B S Furniss, Vogls text book of practical organic chemistry. Prentice hall
2) Raj K Bansal , Laboratory Manual of organic Chemistry, Wiley
3) Vishnoi, Practical Organic Chemistry, Vikas
4) R.M Silverstein, Spectrometric identification of Organic compounds
5) F G Mann and BC saunders, Practical Organic Chemistry, Pearson
6) Julius Berend Cohen, Practical organic chemistry, Mc Graw Hill
7) C.E Bella and DF Taber, Organic Chemistry laboratory, Thomson
8) Nelson Practical Biochemistry, wiley
9) P.F Shalz, J.Chem.Education, 1996, 173,267
10) P.D.L Lampman and Chriz, Introduction to organic Laboratory techniques, College publishing,
11) Monograph on green laboratory experiments, DST , Govt of India.
12) http://sdbs.riodb.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

CH 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 KT 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.

References

1) V. D. Athawal, "Experimental Physical Chemistry", New Age International.

2) B. P. Levitt and J.A. Kitchener,"Findlay's Practical Physical Chemistry", Longmans, London.

3) J. M. Newcombe, R. J. Denaro, A. R.Rickett, R.M.W Wilson,"Experiments in Physical Chemistry "Pergamon.

4) A.M. James, and F.E.Pichard, "Practical Physical Chemistry", Longman.

5) R.C. Das and Behera, "Experimental Physical Chemistry", Tata McGraw Hill.

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

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

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

CH 211 : INORGANIC CHEMISTRY- I

(2016 Admission Onwards)

(Common for CH/CL/CA/CM 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 g
   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 orthogonality theorem and explain.

9. a) Give an accont 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 can you 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/CM212: Organic Chemistry-I

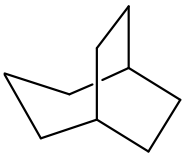
(2016 admission.)

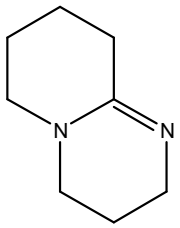
Time-3 hours **Maximum marks :75**

Section A

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

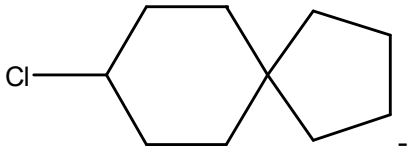
1 a) Write IUPAC names of the following





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

i) trans-1,4-dichlorocyclohexane-

ii) 

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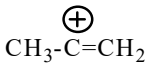
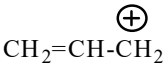
c)What is atropisomerism?

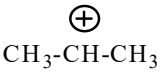
2 a) How arynes are formed?

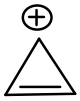
b)p-nitroaniline is less basic than m-nitroanile . explain.

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 classical carbocations

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

b)Write the mechanism of bebzoin 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 markonikoffs 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 acivity. 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
Branch-IV: Analytical Chemistry
Branch-V: Applied Chemistry
CH 213/CL 213/CA 213 : Physical Chemistry- 1
(2016 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 atn27^0C

   (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

CH 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-posphorous compounds:Molecular sulphides such as P_4S_3 , P_4S_7 , P_4S_9 and P_4S_{10} . Phophorous-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-paramgnetic 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 silminite.

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.
4) A. R. West, 'Solid State Chemistry and its Applications', Wiley Eastern.
5) H. J. Emeleus and A. G. Sharp, 'Modern Aspects of Inorganic Chemistry', Van Nostrand.
6) L. V. Azaroff, 'Introduction to Solids', Mcgraw-Hill.
7) S. Cotton, 'Lanthanides and Actinides', Macmillan.
8) Figgins and Hitchman, 'Ligand Field Theory and its Applications', Wiley-VCH.
9) A.Syamal and R. L.Datta, 'Elements of Magnetochemistry', Affiliated East-West Press.
10) C. Kittel, 'Introduction to Solid State Physics', Wiley and Sons.
11) Greenwood and E. Earnshaw, 'Chemistry of Elements', REPP Ltd.
12) E. Earnshaw, 'Introduction to Magnetochemistry', Academic Press.

CH 222 ORGANIC CHEMISTRY- II

Total 90 h

Unit I Molecular rearrangement and transformation reactions 18 h

Types of organic rearrangements. Anionic, cationotropic, prototropic, free radical, carbene, nitrene - 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 II 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 and fullerenes.

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 and cycloaddition reactions. FO analysis of [1, j] and [3, 3] migrations. 1, 3- dipolar cycloaddition. Stereo aspects of Diels- Alder reaction and Cope re arrangement. Fluxional molecules. Retro Diels-Alder, ene, cheletropic and cis elimination reactions and synthetic applications.

Unit III 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 reactions of acyclic ketones. Free radical reactions. Patterno-Buchi, Barton, photo-Fries and Di-π methane rearrangements. Photoreactions of Vitamin D. Photosynthesis, photochemistry of vision. Singlet oxygen generation and their reactions. Applications of photochemistry.

Unit IV 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 monoterpene, 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.

Unit V Physical organic chemistry **18 h**

Reactivity in relation to molecular structure and conformation. Steric effects. F strain. Ortho effect. Bond angle strain. The Hammett equation and its applications. Taft equation. Linear free energy relationships. 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. The Hammond postulate. Principle of microscopic reversibility. Marcus theory. Methods of determining reaction mechanisms. Phase transfer catalysis and its applications.

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5) P.Y. Bruice, Organic chemistry, Prentice Hall.
6) H. Arora, Organic photochemistry and Pericyclic reactions.
7) C.H. Dupuoy and O.L. Chapman, Molecular reactions and photochemistry, Prentice Hall.

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9) S.H. Pine, Organic chemistry, Mc-Graw Hill.

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11) J. Kagon, Organic photochemistry, Academic Press.

12) R.J. Simmonds, Chemistry of biomolecules, Royal society of chemistry.

13) J. Mann and others, Natural products- Their chemistry and biological significance, Longmann

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15) W. Kar, Medicinal chemistry, Wiley Eastern.

16) N.R. Krishnaswamy, Chemistry of natural products,A unified approach.

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18) K.G. Kres, D. Heussee and H. Wimmer, Spray reagents.

19) 18 J.B. Harborne, Phytochemical methods, Chapman and Hall.

CH 223 PHYSICAL CHEMISTRY –II 90 h

Unit I Quantum Chemistry II 18 h

Rotational motion: co-ordinate systems, 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 Atoms 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 atoms. 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 inter nuclear distance. Non-rigid rotors and centrifugal distortion. Rotational spectra of polyatomic molecules-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 vibrational modes into stretching (asymmetric, symmetric), bending, parallel and perpendicular vibrations. Finger print region and group frequencies. Introduction to FTIR and instrumentation.

Raman spectroscopy: Raman scattering, polarisability and classical theory of Raman spectrum. Rotational and vibrational Raman spectrum. Raman spectra of polyatomic molecules. 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 and rotational fine structure of electronic spectrum. Franck-Condon principle. Types of electronic transitions. Fotrat diagram. Predissociation . Calculation of heat of dissociation. Electronic spectra of polyatomic molecules: Electronic transition among molecular orbitals and 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,. Generalised equation for entropy production, Entropy production from heat flow. Matter flow and current flow.. Application of irreversible thermodynamics - to diffusion. Thermal diffusion, Thermo osmosis and thermomolecular pressure difference., electro kinetic effects, the Glansdorf- Pregogin equation. Far from equilibrium region. Principle of minimum entropy production, Le-Chatelier Brawn 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**

The Partition functions. Partition function for free linear motion, for free motion in a shared space, for linear harmonic vibration. Molecular partition functions. Translational, vibrational, rotational and electronic partition functions. Total partition functions Langevin function and its use for the determination of dipole moment.and molecular energies

Relationship 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. Mechanical description of molecular systems. Thermodynamic probability and entropy.

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

Unit V Electrochemistry 1 **18 h**

Ionics- Ions in solution. Deviation from ideal behaviour. Ionic activity. Ion-solvent interaction. Born equation. Ion-ion interaction. Strong electrolytes Debye-Huckel theory of strong electrolytes, Onsager equation. Limitation of the model Conductance at high frequencies 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-electrode interface. 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 over potentials. Butler-Volmer equation. Tafel and Nernst equation. Rate determining step in electrode kinetics. The hydrogen and oxygen over voltage. Theories of over voltage.

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9) R.P. Rastogi, R.r.Misra, "An Introduction to Chemical Thermodynamics", Vikas Publishing House.
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SECOND SEMESTER MSc.DEGREE EXAMINATION

Branch:Chemistry

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

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

CH 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 P4N 4Cl8 puckered and P4N4 F8 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 eg: 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) Eventhough d-d transitions are forbidden , why such transitions occur in many transition metal complexes? Illustrate with eg:.

8. a) Distinguish between spinels and inverse spinels with suitable eg:

   .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 eg: explain the phenomeneon of photoconductivity. What are it's 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 it's structure and compare the bonding with phosphazene molecule.

12 . Write an account on the selection rules and characterstics 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/CM222: Organic Chemistry-II

(Under Semester System w.e.f 2016 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 CholesterolI.

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 Lossen rearrangements.
12. Explain briefly on
    i) Sigmatropic reactions
    ii) 1, 3 - Dipolar and Ene reactions.
13. Discuss the following:
    i) Photochemistry of vision
    ii) Photoreaction of Vitamin D.
14. Explain the following:
    i) Structure of Estrone.
    ii) Chemical, spectroscopic and chiroptical methods for establishing carbon skeleton.
15. Discuss the following:
    i) Principles and applications of phase transfer catalysis.
    ii) Methods of determination of reaction mechanism.

[10x3=30 marks]

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

Branch-III Chemistry

Branch-IV: Analytical Chemistry

Branch-V: Applied Chemistry

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

(2016 Admission Onwards)

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

Section A

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

1. a) Set up the Schrodinger equation for a rigid rotator.
   b) Give plots of (a) radial probability distribution functions of 2S orbital and (b) angular plot of $2P_x$ 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

CH 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 capture 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.

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2. J. E. Huheey,' Inorganic Chemistry-Principles of Structure and Reactivity', Harper and Collins.
3. Ebsworth, Rankin and Cradock, 'Structural methods in Inorganic Chemistry'
4. K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordinaton Compounds', John Wiley.
5. Parish, 'NMR, NQR, EPR and Mossbauer Spectroscopy in Inorganic Chemistry'
6. G. Friedlander and J. W. Kennady, 'Introduction to Radio chemistry', John Wiley and Sons
7. H. J. Arnikar, ' Eessentials of Nuclear Chemistry' IV edition, New Age International, New Delhi.
8. F. Basalo and R. G. Pearson, 'Mechanism of Inorganic Reactions, John Wiley and Sons.
9. R. W. Hay, 'Bioinorganic Chemistry', Ellis Horwood.
10. P. Powell, 'Principles of Organometallic Chemistry, 2 nd Edn. Chapman and Hall.
11. Lippard S. J. and J. M. Berg, 'Principles of Bioinorganic Chemistry', Univ. Science Books.
12. D.E. Fenton, 'Biocoordination Chemistry', Oxford University Press.
13. R. C. Mehrothra and A.Singh, 'Organometallic Chemistry: A Unified Approach', Wiley eastern.
14. D. F. Shriver, P. W. Atkins and C. H. Langford, 'Inorganic Chemistry,' ELBS.
15. L. Bertin, H.B. Gray, S. J. lippard and J. S. Valentine, 'Bioinorganic Chemistry,' Viva Books Pvt. Ltd.

CH232 ORGANIC CHEMISTRY-III

Total 90 h

Unit I UV-Vis., IR and Mass spectrometry 18 h

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 quadruple mass analysers. Characteristic EIMS fragmentation modes and MS rearrangements. Mass spectral fragmentation patterns of long chain alkanes, alkenes, alkynes, aromatic compounds, carbonyl , nitro, amino and carboxy compounds.

Unit II NMR spectroscopy and structural elucidation 18 h

Theory of NMR spectroscopy, chemical shifts, anisotropic effects and coupling constant. Spin-spin interactions in typical systems. First order and second order spectra. Simplification methods of complex spectra by high field NMR, shift reagents, chemical exchange and doule resonance. Theories of FT NMR (1D NMR), ^{13}C NMR spectroscopies. ^{13}C NMR chemical shifts. Applications of NOE, DEPT, INEPT. 2D NMR- 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, Riemer-Tiemann, Simon-Smith, Vilsmeier-Hack, Ullmann and Chichibabin reactions. Ring formation by Dieckmann, Kostanecki, Thorpe, Pschorr and acyloin condensations. Stork enamine, Shapiro, Peterson, Heck, Stille, Ritter and Prilezhaev reactions. Synthesis of small rings. Simon-Smith reaction. Reduction and oxidation in synthesis. Catalytic hydrogenation. Alkali metal reduction, Birch reduction, Wolff-Kishner reduction and Clemmenson reduction. Huang-Milon modification. Boranes,
LAH and sodiumborohydride as reductants. Hydrogenations, Oppenauer oxidation, Jones oxidation. Applications of HIO_4, OsO_4 and mCPBA. Organo palladium catalysts -Heck, Negoshi, Sonagiri and Susuki coupling

Unit IV Methods in organic synthesis 18 h

Retrosynthetic analysis and disconnection approach. Synthetic strategy and synthons. Regioselectivity in enol and enamine alkylation. Sterospecific and steroselective synthesis, Sharpless asymmetric epoxidation, Chiral pool, chiral auxiliary, Chiral reagents, BINAP,

Mitsunobu reaction. 1,3-dipolar cycloaddition in the construction of rings. Story synthesis. Olefin synthesis by extrusion reactions. Olefin metathesis. Umpolung. Reductive coupling reactions. Epoxide to alkene. Introduction to combinatorial synthesis. Electrochemical reduction of organic halogen, nitro and carbonyl compounds. Electrochemical Kolbe oxidation. 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 iquid liquid extraction.

References

1. D.H. Williams and I. Fleming, Spectroscopic methods in organic chemistry, Wiley
2. W. Kemp, Organic spectroscopy, Longman
3. Pavia, Lampman *etal*, Spectroscopy, Cengage Learning.
4. N.S. Issacs. Physical organic chemistry, Longman.
5. R.A.Y. Jones, Physical and mechanistic organic chemistry, Cabridge University Press.
6. J. Hine, Physical organic chemistry, Academic.
7. M.B. Smith, Organic synthesis, McGraw Hill.
8. H.O. House, Modern synthetic reactions, Benjamin Cummins.
9. R.K. Mackie *et al*, Guide book to organic synthesis, Longman.
10. W. Carruthers, Modern methods in organic synthesis, Cambridge University.
11. Jagadamba Singh, LDS yadav, Organic Synthesis, Pragati prakashan.
12. Jonathan Clayden, Nick Greeves, and Stuart Warren , Organic Chemistry, OUP.
13. D. A. Skoog, D. M. West and F. J. Holler, " Fundamentals of analytical chemistry", Saunders college publishing.
14. D. J. Holme and H. Perk, " Analytical Biochemistry", Blackie

CH 233 Physical Chemistry -III

90 Hrs

Unit I Chemical Bonding 18 h

Approximate methods: method of Variation - Variation theorem and its proof. Linear and non 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 diatomic molecules 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^3 Hybridisation. 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 18h

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

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.

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

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.

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

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 **18h**

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**

Quantum statistics: Bose Einstein Statistics, Bose Einstein distribution. Thermodynamic probability, Bose Einstein distribution function. Examples of particles. Theory of Para magnetism. Bose Einstein condensation, Liquid Helium. Supercooled liquid.

Fermi- Dirac Statistics. Fermi- Dirac Distribution, Examples of particles Fermi Dirac Distribution function Thermionic emission. Relation between Maxwell Boltzmann, Bose Einstein and Fermi -Dirac Statistics

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 18h

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 metals.

Conductometry: principle and method. Conductometric titrations.

Coulometry: Principle and method. Coulometric titrations. principle and method of polarography, **Voltametry**: 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.

References

1. I.N.Levin, “Quantum Chemistry”, Prentice Hall.
2. D.A. McQuarrie, ”Physical Chemistry- A Molecular Approach”, Viva Publishers.
3. T. Engel,”Quantum Chemistry and Spectroscopy”, Pearson.
4. M. W. Hanna, “Quantum Mechanics in Chemistry”, Benjamin.
5. R. K. Prasad, “Quantum Chemistry”, New Age International Publishers.
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7. J.P Lowe, K. Peterson, “Quantum Chemistry”, New Age International
8. E. Lewars, “Computational Chemistry- Introduction to the Theory and Applications of Molecular and Quantum Mechanics”, Springer.
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11. G. Aruldhas, “Molecular Structure and Spectroscopy”,Prentice Hall of India.
12. R.S. Drago, “Physical Methods in Chemistry”, Saunders College.
13. W. Kemp, “NMR in Chemistry”, McMillan
14. F.W. Sears and G.L. Salinger, An Introduction to Thermodynamics, Kinetic Theory of Gases and Statistical Mechanics”, Addison wisely.
15. L. K. Nash, “Elements of Statistical Thermodynamics”, Addison Wesley Publishing Co.

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17. G.W Castellan, ”Physical Chemistry”, Addison-Lesley Publishing.
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21. D.A. Skoog, D.M.West and F.J.Holler,” Fundamentals of Analytical Chemistry” Saunders College.
22. Puri, Sharma, Pathania,”Principles opf physical Chemistry”Vishal publishing company.
23. Gurdeep Raj “Advanced Physical Chemistry” GOEL Publishing House, Meerut.
24. F.W. Sears and G.L. Sailinger” Thermodynamics, Kinetic Theory, and Statistical Thermodynamics” Third edition. Narosa publishing House , New Delhi.

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

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

References

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2. A. I. Weining and W. P. Schoder, ‘Technical Methods of Ore analysis’.
3. W. R. Schoder and A. R. Powell, ‘Analysis of Minerals and Ores of Rare Elements’.
4. Willard , Merrit and Dean, ‘Instrumental Methods of Analysis,’

5. W. W. Wendlandt, 'Thermal Methods of Analysis,' Inter-Science.
6. B. A. Skoog and D. M. west, 'Principles of Instrumental Analysis,' Saunders College.
7. R. S. Drago, 'Physical Methods in Inorganic Chemistry', Van Nostrand.
8. K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordinaton Compounds', John
9. E. A. O. Ebsworth, 'Structural methods in chemistry' Blackwell Scientific Publications.
10. D. F. Shriver and P. W. Atkins and C. H. Langford, 'Inorganic Chemistry', ELBS.
11. A. K. Galway, 'Chemistry of Solids,' Chapman and Hall.
12. N. B. Hanna, 'Solid State Chemistry,' Prentice Hall.

CH 235 ORGANIC PRACTICALS-II

Total 125 h

A.**Volumetric estimation** of

1) Aniline 2) Phenol 3) glucose

4) Iodine value and saponification value of coconut oil

B). **Colorimetric estimation** of 1) Aniline 2) Glucose 3) Cholesterol 4) Ascorbic acid 5) Streptomycin or Aspirin.

C). Spectral identification (UV, IR, ^{1}H NMR, ^{13}C NMR, EI mass) of Organic compounds

from a library of organic compounds
D. Separations of mixtures by Paper Chromatography
1) Separation of amino acids 2) Separation of dyes
E) Three stage preparation
1)Benzaldehyde → Benzoin(green synthesis with thiamine HCl) → benzil → benzilic acid
2) Phthalic acid → Phthalic anhydride → pthalimide → anthranilic acid

References

1. B S Furniss, Vogls text book of practical organic chemistry. Prentice hall
2. Raj K Bansal , Laboratory Manual of organic Chemistry, Wiley
3. Vishnoi, Practical Organic Chemistry, Vikas
4. R.M Silverstein, Spectrometric identification of Organic compounds
5. F G Mann and BC saunders, Practical Organic Chemistry, Pearson
6. Julius Berend Cohen, Practical organic chemistry, Mc Graw Hill
7. C.E Bella and DF Taber, Organic Chemistry laboratory, Thomson
8. Nelson Practical Biochemistry, wiley
9. P.F Shalz, J.Chem.Education, 1996, 173,267
10. P.D.L Lampman and Chriz, Introduction to organic Laboratory techniques, College publishing,
11. Monograph on green laboratory experiments, DST , Govt of India.
12. http://sdbs.riodb.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

CH 236 PHYSICAL PRACTICALS –II

125 hrs

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 Kholrads 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.

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.

2) B. P. Levitt and J.A. Kitchener,”Findlay's Practical Physical Chemistry”, Longmans, London.

3) J. M. Newcombe, R. J. Denaro, A. R.Rickett, R.M.W Wilson,”Experiments in Physical Chemistry”Pergamon.

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

5) R.C.Das and Behera, “Experimental Physical Chemistry”, Tata McGraw Hill.

6) B.Viswanathan, ‘’Practical Physical Chemistry”, Viva Publications.

7) P.S.Sindhu, “Practicals in Physical Chemistry-A Modern Approach”, MacMillan India.

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

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

Branch – Chemistry

CH/CL/CA 231 : INORGANIC CHEMISTRY- III

(2016 Admission Onwards)

Time : 3 Hrs Max. Marks: 75

SECTION A

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

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

   b) How does 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 MSc.DEGREE EXAMINATION

BRANCH - CHEMISTRY

CH/CL/CA232: Organic Chemistry-III

(2016 admission ownwards.)

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.

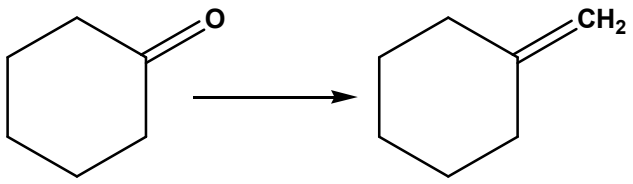
c) Explain how the presence of bromine atom in a molecule can be detected by mass spectrum.

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 pentyl chloride $(CH^a_3)_3CH^b_2$ Cl.

3 a) Suggest a method for conversion



b) What is Clemmenson reduction

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?

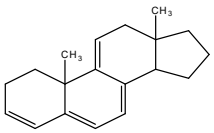
c) Outline the applications of Gel electrophoresis.

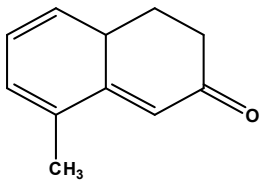
(2x10= 20 marks)

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

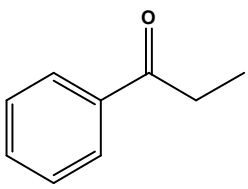




b) How IR spectrum can be used to distinguish

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

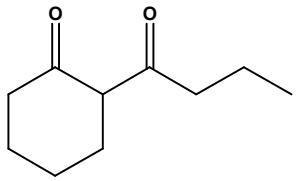


b) Explain the paramagnetic anisotropy of alkenic, aldehydic and aromatic protons.

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 using umpolung

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

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

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 CH 233 – Physical Chemistry III

(2016 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

CH 241-Chemistry of Advanced materials

Unit I Introduction to Nanomaterials 18 h

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

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

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

Unit II The basic tools and applications of nanotechnology 18 h

Basic principles and applications of Scanning electron microscopy (SEM), transmission Electron Microscopy(TEM) , Atomic Force Microscopy (AFM) and Energy Dispersive X-ray Spectroscopy(EDAX)-Powder X-ray diffraction and determination of

particle size- UV-Visible spectroscopy and determination of band gap-Application of IR spectroscopy in the analysis of nanomaterials

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

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

Unit III Polymerization processes **18 h**

Free radical addition polymerization - kinetics and mechanism. Chain transfer. Molecular weight distribution and molecular weight control. Cationic and anionic polymerization: Kinetics and mechanism. Step growth polymerization - Linear Vs cyclic polymerization. Other methods of polymerization - bulk, solution, melt, suspension, emulsion and dispersion techniques. Polymer stereochemistry: Configuration and conformation. Tacticity. Chiral polymers.Polymer characterization-Molecular weights - Methods for determining molecular weights - static, dynamic, viscometry, light scattering and GPC.Crystalline and amorphous states-glassy and rubbery States. Glass transition temperature and crystalline melting of polymers.Degree of crystallinity - X-ray diffraction.Thermal stability of polymers- Application of DSC.

Unit IV Speciality Polymers **18 h**

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

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

Unit V Smart materials **18 h**

Piezoelectric,magnetostrictive, halochromic, electrochromic,thermochromic,magnetocaloricandthermoelectric materials.Chemistry behindphotochromism in spiropyrans, spirooxazines,diarylethenes, azobenzenes, quinones. Examples for Photochromic Coordination Compounds.

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

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CH 242 (a) INORGANIC CHEMISTRY IV

Total 90 h

Unit I Applications of group theory — 18 h

Hybrid orbitals and molecular orbitals for simple molecules. Transformation properties of atomic orbitals. Hybridastion schemes for σ and π bonding with examples. MO

theory for AB_n type molecules. Molecular orbitals for regular octahedral, tetrahedral and metal sandwich compounds. Ligand field theory: Splitting of d orbitals in different environments using group theoretical considerations. Construction of energy level diagrams. Correlation diagram. Method of descending symmetry. Tanabe-Sugano diagrams. Selection rules for electronic spectra. Molecular orbitals in octahedral complexes. Formation of symmetry adapted group orbitals of ligands. MO diagram. Symmetry and selection rules: Symmetry properties of common orbitals. Application of character tables to infrared and Raman spectroscopy. Infrared and Raman active modes for C_{2v}, C_{3v} and D_{4h}

Unit II Supramolecular Chemistry 18 h

Concepts and language. Molecular recognition: Molecular receptors for different types of molecules, design and synthesis of coreceptors and multiple recognition. Strong, weak and veryweak Hydrogen bonds.Utilisation of H-bonds to create supramolecular structures. Use of H bonds in crystal engineering and molecular recognition. Supramolecular reactivity and catalysis. Transport processes and carrier design.Supramolecular devices. Supramolecular photochemistry, supramolecular electronic, ionic andswitching devices Some examples of self- assembly in supramolecular chemistry.

Unit III Metal-metal bonds and metal clusters 18 h

Metal-metal bonds: Factors affecting the formation of metal-metal bond. Dinuclear compounds of Re , Cu and Cr, metal-metal multiple bonding in $(Re_2X_8)^{2-}$, Trinuclear clusters, tetranuclear clusters, hexanuclear clusters. Polyatomic zintl anion and cations. Infinite metal chains. Metal carbonyl clusters. Anionic and hydrido clusters. LNCCs and HNCCs. Isoelectronic and isolobal relationships. Hetero atoms in metal clusters: Carbide and nitride containing clusters. Electron counting schemes for HNCCs. Capping rule. Chalcogenide clusters. Chevrel phases.

Unit IV Selected topics in Bioinorganic Chemistry 18 h

Copper on biochemical systems. Oxidase activity, super oxide dismutase activity. Electron transport in biology. Structure and function of copper proteins in electron transport process. Oxygen transport copper proteins. Hemocyanin- copper transport, copper enzymes-Azurin, plastocyanin. Inorgnic medicinal chemistry. Metals in medicine. Metal deficiency and

diseases. Toxic effects of metals. Effect of deficiency and excess of essential metal ions. Toxicity due to non essential elements and speciation. Detoxification mechanism. Role of lithium and aluminium in biological systems. Chelation therapy and chemotherapy. Anticancer drugs and vanadium based diabetics drugs.

Unit V Acids and Bases and Non-aqueous Solvents **18 h**

Acid base concept in non aqueous media-HSAB concept, solvent effects, linear free energy relationship-mechanism and methods of determination, super acids Reactions in non-aqueous solvents. Ammonia - solutions of metals in liquidammonia. Protonic solvents: anhydrous sulfuric acid, hydrogen halides. Aprotic solvents: non-polar solvents, non-ionizable polar solvents, polar solvents undergoing autoionization, liquid halogens, inter halogen compounds, oxy halides, dinitrogen tetroxide, sulphur dioxide.

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17. D. A. Phipps, 'Metals and Metabolism,' Clarendon Press, Oxford.
18. **I.** Bertini, H. B. Gray, S. J. Lippard and J. S. Valentine, 'Bioinorganic chemistry

CH242 (b) - ORGANIC CHEMISTRY-IV

Unit I Organometallic chemistry 18 h

Preparation of organo Mg, Al, Li, Cu, Zn, Cr, Fe, Ce and sulphur stabilised compounds. Reactions of Grignard reagents in organic synthesis. Alkylation, oxirane addition, carbon dioxide addition, carbonyl addition, enone addition (1,2 and 1,4additions), reduction, conjugate addition and enolisation reactions. Selectivity in Grignard reactions. Reactions of organo Li reagents, Li exchange reaction, its use in the preparation of RLi compounds, addition to C=O, COOH and $CONR_2$, Li dialkyl cuprates (Gilman reagent)- preparation and reaction with alkyl halides, aryl halides, with enones. Alkynyl Cu(1) reagents, Glaser coupling. Dialkyl Cd compounds- preparation and reaction with acyl halides. Benzenetricarbonyl chromium- preparation and reaction with carbanions. Tebe reagent, Silane carbanion and its reactions.

Unit II Molecular recognition and supramolecular chemistry 18 h

Introduction to supramolecular chemistry. One-pot reactions.The concepts of molecular recognition, host, guest and receptor systems. Forces involved in molecular recognition. Hydrogen bonding, ionic bonding, π-stacking, Vander Walls and hydrophobic interactions. Introduction to molecular receptors. Tweezers, cryptands and carcerands. Cycophanes, cyclodextrins and calixarenes- typical examples. Non-covalent interactions in biopolymer structure organization. Role of self organization and self association in living nature. Importance of molecular recognition in DNA and protein structure, their function and protein biosynthesis. Supramolecular systems like Organic zeolite, Clathrate hydrates of gases, Helicates. Nanotubes, liquid crystals, nanotechnology and other industrial applications of

supramolecular chemistry.

Unit III Medicinal chemistry **18 h**

Combinatorial organic synthesis, introduction, methodology, automation, solid supported and solution phase synthesis, study of targeted or focused libraries and small molecule libraries, Applicaion- drug discovery.

Drug design and development-Discovery of a drug, a lead compound. Development of drug-Pharmaccophore identification, modification of structure, structure-activity relationship, structure modification to increase potency. The Hammet equation, Taft equation and lipophilicity. Computer assisted drug design. Receptors and drug action. Natural products and drug development. Different classes of drugs with examples. Synthesis of paracetamol, phenobarbital, diazepam, sulphamethoxazole, benzyl penicillin, chloramphenicol.

Unit IV Chemistry of biopolymers and polymers **18 h**

Peptide bond formation methods.SPPS, Mechanism, Amino and carboxy protection in SPPS. Synthesis of tripeptides, A, G, C, T, U, adenosine, ADP and ATP. Automated polypeptide and oligonucleotide synthesis. Structure organization of proteins and poly nucleotides. Protein sequencing by Edmans method. Protein denaturation. Structure of polysaccharides including starch, cellulose, glycogen and chitin .Synthesis of stereo regular polymers. Ziegler-Natta catalyst.Polymers in organic synthesis- supports, reagents and catalysts. Bio degradable polymers.

Unit V Green chemistry **18 h**

Twelve principles of green chemistry. Green chemical strategies for sustainable development- Reaction mass balance, atom economy evaluation for chemical reaction efficiency, green solvents, reaction media- Synthesis under water, solventless, fluorous and ionic liquid media. Synthesis using scavenger resins, catalysis and biocatalysis. Green computation. Green processes-. Microwave synthesis- fundamentals of microwave synthesis-Two Principal Mechanisms for Interaction With Matter- The Microwave Effect with examples - Single-Mode and Multimode Microwave cavities. Microwave technology-Techniques and applications in MORE chemistry. Sonochemical synthesis. Applications of

sonication in the synthests of organic compounds

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FOURTH SEMESTER M.Sc. DEGREE EXAMINATION

Branch : CHEMISTRY
(Under Semester System w.e.f 2016 Admissions)
CH 241-Chemistry of Advanced materials

Time: 3 h Max. Marks: 75

Section A

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

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

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

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

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

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

[2 x 10 = 20 marks]

Section B

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

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

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

8 a) Explain the kinetics of free radical addition polymerization.

b) Explain DSC method for determination of Glass transition temperature.

9 a) Explain in detail the synthesis of polyacetylenes.

b) Explain in detail the synthesis of polythiophenes.

10 a) Explain the concept of pseudo elasticity.

b) Write a note on shape-memory polymers. [5x 5 = 25 marks]

Section C

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

11 Explain in detail SEM and TEM.

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

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

14 Explain the application of Polymers in catalysis.

15 Write a note on the chemistry behind photochromism in spiroprans, spirooxazines, diarylethenes and azobenzenes. [10x3 = 30 marks]

FOURTH SEMESTER M.Sc. DEGREE EXAMINATION

Branch:Chemistry

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

CH 242(a)- INORGANIC CHEMISTRY-IV

Time:3 hrs Max marks:75

SECTION-A

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

1. a) What is the point group of NO 3-? How does it's symmetry change when complexed as unidentate ligand?

   b) Give the splitting of d-orbitals in a square pyramidal geometry?

   c) Demonstrate that C 3 and C 3 2 belong to the same class in C 3v point group.

2. a) What is meant by macrocyclic effect?

   b) Give any two eg: of self-assembly in supramolecular chemistry.

   c) What are the 3 basic functions of supramolecular species?

3. a) What are anionic clusters? Give eg:.

   b) Explain Wade's rules to calculate the no: of frame work electrons in crystals.

   c) Clusters of Co (CO) 12 and Co3 FeH(CO)12 are isolobal to each other. Explain.

4. a) What is cisplatin? What is it's importance?

b) What is the role of Lithium in biological systems?

c) Write any two diseases caused by the deficiency of copper in the body.

5 .a) Give eg: of room –temperature molten salts that could be used as non-aqueous solvents?

b) What is meant by leveling effect of solvent?

c) Which species would act as a base in (1) BrF 2 and (2) liq SO 2. Why?

[2 x 10 = 20 marks]

SECTION-B

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

6. a) Give the salient features of Tanabe-Sugano diagram taking d 5 ion as an eg:.

b) Discuss the application of group theory in arriving at the selection rules for the electronic spectrum of metal complexes.

7. a) Explain the importance of supramolecular chemistry in the field of catalysis.

b) What are the advantages and applications of supramolecular chemistry in Nanotechnology?

8. a) Explain the concept of chevel phases.

b) What are LNCC's? Give eg: Discuss their structures.

9. a) The toxicity of metals have been variously correlated with their (1) electronegativity , (2) insolubility of sulphides and (3) stability of chelates. Discuss.

b) What are dismutation reactions? Give eg: What type of metal is in superoxide dismutase?

10. a) What are the advantages and disadvantages of using aprotic solvents as non-aqueos solvents?

b) Write a note on the reactions in liquid HF.

[5x 5 = 25 marks]

SECTION-C

Answer any three questions and each question carries 10 marks.

11. Deduce the normal modes of trans-N_2F_2 molecule and predict the IR and Raman activity of the modes. Given the character table for C_{2h}.

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_Z	x^2,y^2,z^2,xy
B_g	1	-1	1	-1	R_X,R_Y	xz,yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x,y	

12. Discuss with suitable eg: the different types of interaction in supramolecular compounds.
13. Discuss and draw the structure and bonding of $[Re_2 Cl_8]^{2-}$.
14. Explain the structure and functions of hemocyanin and plastocyanin.
15. Write a detailed account of the reactions in the following non-aqueous solvents:
    (1) $N H_3$ and (2) N_2O_4.

[10x3 = 30 marks]

FOURTH SEMESTER MSc.DEGREE EXAMINATION

BRANCH - CHEMISTRY

CH242 (b): Organic Chemistry-IV

(Under Semester System w.e.f 2016 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) Describe any one method for preparation of organo zinc reagents.
   b) Describe the preparation of benzenetricarbonyl chromium.
   c) Write short note on Tebbe reagent.
2. a) Explain host-guest system with an example
   b) Explain the importance of Hydrogen bonding in molecular recognition
   c) What are cryptands?
3. a) Draw the structure of benzyl pencillin and diazepam
   b) What is in vitro and in vivo analysis of drugs?
   c) What is meant by lead in drug analysis?
4. a) Write the examples of amino protecting groups .How it can be deprotected?
   b) What is the difference between nucleotide and nucleoside?
   c) How cellulose is different from chitin?
5. a) What is biodiesel?
   b) What is meant by sonochemical synthesis? Give an application.
   c) Write few examples of green solvents. [2 x 10 = 20 marks]

Section B

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

6 a) What is Tebbe reagent? How it is prepared? Mention any two applications

b) llustrate the uses of Grignard reagent in organic synthesis.

7 a) Write short note on a) Molecular tweezers, b) Calixarene c) cyclodextrins

b) Explain the structure and importance of cyclodextrins

8 a) Describe the synthesis-of paracetamol

b) Explain a) pharmacophore b) lead compound with examples

9 a) Explain the role of polymers in organic synthesis.

b) Write any two techniques used in protein sequencing

10 a) Explain atom economy with aldol condensation as example.

b) Write a note on sonochemistry in organic synthesis. [5x 5 = 25 marks]

Section C

Answer ant three questions.Each question carries 10 marks

11. Write notes on the preparation and application of the following:

a) Dialkyl Cd compounds. b)Benzenetricarbonyl chromium.

12. Describe the importance of molecular recognition in DNA and protein structure.

13. Explain the structure-activity relation in the development of drugs.

14. Write an SPPS method for synthesis of Phe-ala-gly, explaining each step and advantages of SPPS

15. Explain the twelve basic principles of green chemistry.

[10x3 = 30 marks]

CH 242 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)

SEMESTER IV

Analytical Chemistry

CL 241 APPLIED ANALYTICAL CHEMISTRY

Total 90 hrs

Unit I

Separation techniques **18h**

Chromatography: definition and classification, techniques used in paper, thin layer and column chromatography. Gas Chromatography (GC): classification, migration rates of solutes, preparation of column and column materials, temperature, effects, chiral stationary phases and applications. HPLC: principle, instrumentation- sample injection, columns, solvent selection and detectors.Introduction to GCMS and LCMS.Ion exchangechromatography: principle, technique and applications. Solvent extraction: principle and techniques, role of chelating ligands, crown ethers, calixarenes and cryptands in solvent extraction. Introduction to Solid phase extraction (SPE) and Microwave assisted extraction (MAE). Applications. Membrane separation processes: operating principles and applications of microfiltration, ultra-filtration, reverse osmosis, dialysis and electro-dialysis.

Unit II

Thermal and Radiochemical methods of Analysis **18h**

Principle, theory and instrumentation ofThermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA).Principle and applications of Differential Scanning Calorimetry (DSC), Thermo mechanical analysis (TMA) and Dynamic mechanical analysis (DMA). Thermometric titrimetry – theory, applications.

Radiochemical methods of analysis: radioactive tracer techniques and its applications, principle and applications of isotope dilution analysis, neutron activation analysis and its applications. Radiometric titration: principle, techniques based on complex formation and precipitation, radiometric titration curves for estimation of ions from their mixture. Applications of radio isotopes in industry, medicine, autoradiography, radio pharmacology, radiation safety precaution, nuclear waste disposal.

Unit III

Food and Forensic Analysis **18 h**

Food analysis: general methods for the determinationofmoisture, ash, crude protein, fat, crude fibre, carbohydrate, calcium, potassium, sodium, and phosphates in food. Food adulteration – common adulterants in food and their determination. Contamination of food stuffs. Analysis of milk for fat and added water. Oils and fats and their analysis: iodine value, iodine bromine value, saponification value and acid value and their significances. Rancidity-detection and determination (peroxide number). Pesticide residues in foods-determination of chlorinated organic pesticides.

Forensic analysis: basic principles and significance, sampling, sample storage, sample dissolution.General discussion of poisons with special reference to mode of action ofcyanide and organophosphates. Classification of poisons, Lethal dose, significance of LD 50 and LC 50.Estimation of poisonous materials such as lead, mercury, chromium and arsenic in biological materials. Physiological effects of natural poisons such as morphine, hashish and nicotinoids. Health hazards and Remedial measures.

Unit IV

Instrumental Methods of Chemical analysis **18 h**

Flame spectrometry: introduction, elementary theory, instrumentation, type of burners,type of interferences, background correction method and applications.Atomic absorption spectroscopy:principle, instrumentation, production of atoms and ions, burners, detectors, HCL,TGL, EDL, advantage and disadvantage of AAS.Atomic emission spectrometry: introduction, equipment, qualitative and quantitative analysis with AES, plasma emission spectrometry, ICP-AES, sample introduction and measurements.X-ray Photoelectron spectroscopy (XPS): introduction and basic theory, instrumentation, XPS imaging.Molecular fluorescence and X-ray fluorescence: **i**ntroduction and basic theory, instrumentation and applications.

Unit V

Analysis of selected materials **18 h**

Principles of estimation of biological fluids.**:** Estimation and interpretation of data for blood sugar, haemoglobin, urea and cholesterol. Biological significance, analysis and assay of enzymes: pepsin, monoaminoxidase, and tyrosinase.Analysis of drugs and pharmaceuticals: quality control, official methods, classical and modern methods of drug

analysis.Analysis of common drugs:analgesics, antipyretics, antimalarial, antiallergic (anti-histamines) and antibiotics. Analysis of alcoholic beverages: determination of quality parameters such as original extract, alcohol, extract, CO_2, O_2, Brix, degree of inversion, pH value, ethyl carbamate, carbohydrate, and dissolved oxygen.

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20. Soil Pollution: origin, monitoring and remediation, AbrahimMirsal, Springer (2010)
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22. Essentials of Forensic Medicine and Toxicology, K. S. Narayana Reddy, 2002.
23. Analytical Chemistry Principles, John H. Kennedy, 2nd edition, Saunders College Publishing, California, 1990.
24. Food Analysis: Theory and practice, YeshajahuPomeranz, Clifton E. Meloan, Springer.
25. Food Analysis, Edited by S. Suzanne Nielsen, Springer
26. Analysis of food and beverages, George Charalanbous, Academic press 1978

Fourth Semester M.Sc. Degree Examination

Branch:Analytical Chemistry

CL 242:Applied Analytical Chemistry

(2016 Admission Onwards)

Time: 3 Hours **Max. Marks: 75**

SECTION-A

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

1. (a) What are the applications of crown ethers in extraction?

   (b) What is meant by R_f value? Indicate its significance.

   (c) Give the characteristics of an ideal detector used in gas chromatography.

2. (a) Write a short note on activation analysis.

   (b)What is the principle of thermo mechanical analysis?

   (c) What is meant by radiotracer technique? Give its applications.

3. (a) Differentiate food adulteration and contamination.

   (b) Explain the term rancidity.

   (c) How will you determine fat in milk?

4. (a) Flame emission spectroscopy is temperature dependent whereas AAS is not. Why?

   (b)What is the principle of XPS?

(c) Explain how fluorescence can be employed for nano level detection.

5. (a) Give the principle for the estimation of blood sugar.

(b) Write a short note on Brix.

(c) What are the modern methods of drug analysis?

SECTION-B

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

6. (a) Write a note on the classification of chromatographic methods.

(b) Explain the development of TLC plates.

7. (a) Compare and contrast TG and DTA

(b) What is isotopic dilution analysis? How is it useful in the determination of concentration of an unknown sample?

8. (a) How is poisonous elements such as lead and mercury present in food identified and how is it determined?

(b) Give one method each for the determination of iodine-bromine value an saponification value of an oil sample indicating their significance.

9. (a) Write a note on GC-MS and LC-MS

(b) Give an account of the working ofa hollow cathode lamp.

10.(a) Describe briefly the modern methods of drug analysis.

(b) Explain the determination of alcohol content and CO_2 in alcoholic beverages.

SECTION-C

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

11. Describe the principle, basic instrumentation and applications of HPLC.

12. Give an account on the principle, instrumentation, application and factors affecting the curve in differential scanning calorimetry.

13. What is meant by Forensic analysis? How does it differ from normal chemical analysis? Discuss the special features of forensic analysis such as sampling,

sample dissolution and sample storage.

14. (a) Explain the interferences in AAS.

(b) Explain briefly the principle and applications of Fluorimetry.

15. (a) Write explanatory notes on biological significance of pepsin and monoaminoxidase.

(b) Describe the principles of estimation of biological fluids.

SEMESTER IV

CA 241 APPLIED CHEMISTRY

Total 90 h

UNIT I – Water treatment 18h

Technology of water Standards for drinking water, Methods of Treatment of water for domestic and industrial purposes: Sedimentation, Coagulation, Filtration, Sterilization, Break point chlorination. Determination of alkalinity of water, Hardness of water: Units, determination. Demineralization of water.

Softening of water: Lime-soda Process, Ion exchange process, Zeolite process.

Boiler Troubles: Carry Over, Priming, Foaming, Scale, Sludge, Corrosion, Caustic Embrittlement. Internal treatment of water: Carbonate conditioning, Phosphate conditioning, Colloidal conditioning, Calgon conditioning.

UnitII-Soaps& Detergents 18h

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

UNIT III - Corrosion and Protective Coatings 18h

Corrosion and its Control: Nernst Theory, Standard Electrode Potential, Galvanic Series, Concentration cell, Types of corrosion: Uniform and Galvanic, Erosion, Crevice,

Pitting, Exfoliation and Selective leaching, Inter-angular Stress, Waterline, Soil, Microbiological. Theories of corrosion: Acid, Direct Chemical attack, Electrochemical, Corrosion reactions, Factors affecting corrosion, Protective measures

Protective Coatings : Paints : Constituents, functions & mechanism of drying, varnishes and Lacqers, surface preparation for metallic coatings, electroplating of gold and electrodeless plating of Nickel, anodizing, phosphate coating, powder coating & antifouling coating.

UNIT IV - Applied Inorganic Chemistry 18h

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

Portland Cement: Manufacture of cement, Dry and Wet process, Important process parameters for manufacturing a good cement clinker. Characteristics of the constitutional compounds of cement. Additives for cement, Properties, General composition, Testing of cement, Chemical & physical requirement.

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

Unit V – Applied Organic Chemistry 18h

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

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

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

References

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Fourth Semester M.Sc. Degree Examination

Branch – Chemistry

CA 241 Applied Chemistry

(2016 Admission Onwards)

Time: 3 h **Total Marks: 75**

Section A.

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

1 (a) What are the disadvantages of sludge formation?

(b) Explain the difference between coagulation and flocculation?

(c)What is foaming?

2 (a) what is saponification value?

(b) Explain the mechanism of action of soap

(c) What are naphtha soaps

3 (a) Rusting of iron is quicker in saline water than in ordinary water. why?

(b)What is Galvanic corrosion? How can it avoided

(c)What are sacrificial anodes? Give examples

4 (a) What are the constituents of Portland Cement? Why Portland cement so named?

(b) Explain the structure and synthesis of Urea

(c) What is glass? How is soft glass prepared?

5 (a) Define vulcanization of rubber. How vulcanization is is carried out?

(b) Give the Color chemicals Added to Food and soft drinks and explain its health hazards

(c) Explain the manufacture of BHC (2x10=20 marks)

Section B.

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

6 (a) Point out the essential differences between hard and soft water
(b)Explain anyone method for the determination of alkalinity of water

7 (a) Explain the influence of fatty acid composition on the properties of soaps
(b) Explain cold, semiboiled and boiled processe in the manufacture of soap.

8 (a) How much rust will be formed when 100kg of iron have completely rusted away.
(b) Write a note on the various factors affecting corrosion.

9 (a) What are refractories. Explain the criteria for a good refractory material.
(b) Explain the dry and wet process for the manufacture of cement.

10 (a) Explain the synthesis of paracetamol.

(b) Give a note on cosmetics. (5x5=25 marks)

Section C

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

11. Explain the various processes for softening of water

12. Write an essay on the manufacture,chemistry and applications of detergents

13. With the help of Flow chart diagram explain the manufacture of sulphuric acid

14. Describe the method of preparation, properties and applications of (i) PVC (ii) Nylon (iii) Urea formaldehyde and (iv)Teflon

15. Write a note on protective coatings.

(10x3=30 marks)