PAPER - I

....Phil. (Inorganic Chemistry)

Lectures: 60 Max. Marks: 100

NOTE: Ten questions will be set by the examiner selecting TWO from each unit. As far as possible, every question will be subdivided into two to three parts. The students shall attempt FIVE questions selecting ONE from each unit.

UNIT-I

Catalysis Involving Organometallic compounds: Homogeneous hydrogenation and hydroformylation of unsaturated compounds (Olefins). Asymmetric hydrogenation, hydroformylation, hydrosilylation of unsaturated compounds, hydrocyanation of alkenes; alkenes and alkynes metathesis.

UNIT-II

Co-ordination Addition Polymerisation: Zeigler Natta catalysts, composition, nature and mechanism of stereo specific placement in polymerisation, bimetallic and monometallic mechanism, stereoregulation, Supported metal oxide catalysts, polymerisation mechanism, boundion radical mechanism and bound-ion co-ordination mechanism. Metallocene based Zeigler Natta catalysts, catalysts composition, active centre and polymerisation mechanism.

UNIT-III

Separation Techniques in Analysis:- Ion exchange Chromato -graphy, types of ion-exchangers, ion exchange equillibria and factors effecting it, cation and anion exchange resins, ion-chromatography, instrumentation, detectors and methods of analysis. Solvent extraction, theory and mechanism of solvent extraction, synergistic extraction, solvent extraction with macromolecules (crown ethers, cryptands, calyx, arenes etc.) solid phase extraction and solid phase micro-extraction.

UNIT-IV

Voltammetric methods of analysis: Principle, excitation signals, mass transfer mechanism, instrumentation, methods of analysis and applications of pulse polarography, square wave polarography, cyclic voltammetry, hydrodynamic voltammetry and anode stripping voltammetry. Use of voltammetry for the determination of formal reduction potential and number of electron change for ferri/ferrocyanide couple and to study electrode mechanisms of electron reduction of nitrobenzene and voltammetry with microelectrodes.

UNIT-V

Chemistry of High Temperature Solvents – Introduction, structures, solutions of elements (metals and non-metals) in fused salts, reactions in fused salts (acid- base reactions, oxidation-reduction reactions, metathetic reactions), experimental methods (general discussion).

- 1. Advanced Polymer Chemistry- Manas Chanda
- 2. Fundamentals of Analytical Chemistry- Skoog, West, Holler and Crouch
- 3. Chemistry experiments for Instrumental methods- Sawer, Heineman and Beebe.
- 4. Electronic absorption spectroscopy and related techniques: D.N. Sathyanaray.
- 5. The Organometallic Chemistry of Transition metals: R.H. Crabtree.
- 6. Organometallic Chemistry-R.C.Mehrotra.
- 7. Homogeneous transition metal catalysis ó Christopher Masters
- 8. Homogeneous Catalysis ó Parshall
- 9. Principles and Application of HomogeneousCatalysis ó Nakamura and Tsutsui
- 10. Organotransition metal chemistry by S.G.Davis, Pergamon press 1982.
- 11. Principles and applications of organotransition metal chemistry by Ccollmen and Hegden

PAPER - II

....Phil. (Inorganic Chemistry)

Lectures: 60 Max. Marks: 100

NOTE: Ten questions will be set by the examiner selecting TWO from each unit. As far as possible, every question will be subdivided into two to three parts. The students shall attempt FIVE questions selecting ONE from each unit.

UNIT-I

- a) Role of Metal-ions in Biological Systems: Metal-ion-interactions with Nucleosides and Nucleotides, Metal-ion-interactions with DNA, Metal-ion-interactions with RNA.
- b) **Electron-Transfer Agents in Biological Systems**: Cytochromes, Iron sulphur proteins, Vitamin B_{12} and B_{12} Coenzymes Xanthane oxidase, Superoxide dismutase.

UNIT-II

- a) Supramolecular Reactions and Catalysis: Introduction, Catalysis by reactive macrocyclic cation receptor molecule, by reactive macrocyclic anion receptor molecule Supramolecular metallocatalysis.
- b) Supramolecular Assemblies: Introduction, Supramolecular solid materials, Molecular recognition at surfaces (Endoreceptors vs Exoreceptors), Molecular and Supramolecular Devices, Photonic, electronic and Ionic Devices.

UNIT-III

Reactions at Coordinated Ligands:-Reactions due to metal ion polarization of co-ordinated ligands, Aldol Condensation, Imine formation, hydrolysis and substituent exchange. Template effect and macrocyclic ligands.

UNIT-IV

Electron-Transfer Reactions of Complexes: Electron-transfer theory, Outer-sphere exchange reaction. Bridge mechanism, Two-electron transfers, Non-complementary reactions. Replacement through Redox Mechanism, Photochemical Reactions of Chromium and Ruthenium complexes.

UNIT-V

Reactions of Oxyanions: Factors affecting rates, Oxygen exchange between phosphate and water, Induced Reactions, Chromate-Arsenite Reactions, Urea formation Reactions.

- 1. Elements of Bioinorganic Chemistry- G.N. Mukherjee and Arabinda Das (1993).
- 2. Inorganic Chemistry Purcell and Kotz.
- 3. The Inorganic Chemistry of Biological Process-M.N. Hughes (2nd Edn.)
- 4. Inorganic Reaction Mechanism- Edward.
- 5. Inorganic Reaction Mechanism Bassolo and Pearson.
- 6. Supramolecular Chemistry concepts and Perspectives- Jean-Marie Lehn(VCH-1995)

PAPER - I
Phil. (Organic Chemistry)
(Organic Synthesis)

Lectures: 60 Max. Marks: 100

NOTE: Ten questions will be set by the examiner selecting TWO from each unit. As far as possible, every question will be subdivided into two to three parts. The students shall attempt FIVE questions selecting ONE from each unit.

UNIT –I

Spectroscopy: Basic theory, Instrumentation and applications of UV spectroscopy, IR Spectroscopy, NMR Spectroscopy and Mass spectrometry in organic compounds. Problems based on IR, UV, NMR and mass spectral data.

UNIT - II

Reaction —**Mechanism:** Reaction and mechanism of following organic reactions: Stevens rearrangement, Cope rearrangement, Claisen rearrangement, Metathesis of olefins, Direction rearrangement, Hofmann-Loffler reaction, Sharpless assymetric epoxidation and Stork-enamine reaction

UNIT-III

Reagents in Organic Synthesis: Reagents in organic synthesis: Willkinson catalyst, Triphenylphosphine-alkyl halide reagent, Lithium dialkyl cuprates (Gilmanøs reagents), Lithium diisopropylamide (LDA), Dicyclohexylcarbobiimide (DCC), Tri-n-butyltinhydride. Nickel tetracarbonyl, Trimethylchlorosilane.

UNIT-IV

New Concepts in Organic Chemistry: Green Chemistry: Principles of green chemistry, green reagents, green catalysts: Bio-catalysts PTC and Crown ether, ionic liquids as solvent and catalysts. Organic synthesis in solid state: Michael addition and Aldol condensation, Combinatorial Chemistry: Concepts of Combinatorial chemistry and its use in organic synthesis, Combinatorial libraries. Click Chemistry: Concepts and uses in organic and polymer synthesis.

UNIT- V

Stereochemistry; Stereoselective and stereospecific reactions: Stereoselective reactions: Hydride reduction of cyclic ketones, catalytic hydrogenation, Stereoselective nucleophilic addition to acyclic carbonyl groups. Stereospecific reactions: Bromination of alkenes, Epoxidation and dihydroxylation of alkenes, Hydroboration oxidation. Analysis and separation of enantiomeric mixture: Chiral shift reagent and chiral solvating agents, Separation of enantiomers by chromatography. Enzymatic separation and desymmetrization using lipasases, proteases, Acylases and epoxide hydrolases.

- 1. Practical NMR Spectroscopy, M.L. Martin, J.J. Delpeuch and G.J. Martin, Heyden.
- 2. Spectrometric Identification of Organic Compounds, R. M. Silverstein, G.C.Bassler and T.C.Morrill, John Wiley.
- 3. Introduction to NMR Spectroscopy, R.J. Abraham, J. Fisher and P. Loftus, Wiley.
- 4. Application of Spectroscopy of Organic Compounds, J.R. Dyer, Prentice Hall.
- 5. Spectroscopic Methods in Organic Chemistry, D.H. Williams, I. Fleming, Tata McGraw-Hill.
- 6. Organic spectroscopy by Jagmohan
- 7. Organic spectroscopy by W. Kemp.
- 8. Stereochemistry of Organic Compounds, D. Nasipuri, New Age International.
- 9. Stereochemistry of Organic Compounds, P.S. Kalsi, New Age International.
- 10. Organic Synthesis: Jagmohan Singh and Yadav.
- 11. Organic Reagents: Feiser and Feiser

PAPER - II
.....Phil. (Organic Chemistry)
(POLYMER CHEMISTRY)

Lectures: 60 Max. Marks: 100

NOTE: Ten questions will be set by the examiner selecting TWO from each unit. As far as possible, every question will be subdivided into two to three parts. The students shall attempt FIVE questions selecting ONE from each unit.

<u>UNIT-I</u>

Principle and Techniques of Polymerization: Importance of polymers. Chemical and geometrical structure of polymers, Polymerization: Chain polymerization, step growth polymerization, electrochemical, metathetical polymerization, group transfer polymerization, coordination polymerization. Concept of Copolymerization. Polymerization techniques, Kinetics of chain and step growth polymerization.

UNIT- II

Polymer Reactions: General introduction to the polymer reactions, Vulcanization, Chemical and radiation crosslinking, Derivatization of cellulose: etherification and esterification, Graft polymerization, Methods of Graft Copolymerization, Polymer as carriers or supports, polymeric reagents, polymeric substrates, polymeric catalysts and polymeric drugs

UNIT-III

Industrial Important Polymers: Chemistry and applications of cellulose, starch, gelatin, pectin, collagen, chitin and chitosan, Water soluble polymers: poly(acryamide), poly(acrylic acid), poly(methacrylic acid), poly(vinylpyrrolidone).

UNIT-IV

Synthesis and Applications of Commercial Polymers: Synthesis and application of following polymers Polyethylene, Polyvinyl chloride, Polyamides, Polyesters, Phenol- formaldehyde, ureaformaldehyde and epoxy resins, Biodegradable polymers (lactic and glycolic acid based). Conducting polymers (polyaniline and polypyrrole), applications of conducting polymers, Biomedical polymers.

UNIT- V

Polymer Characterization: Determination of molecular weight of polymers by colligative properties, viscosity measurement, end group analysis, sedimentation velocity and equilibrium method. Characterization of polymers by IR, NMR, TGA, DSC, XRD, SEM techniques.

- 1. Molecular Mechanics, U. Burkert and N.L. Allinger, ACS Monograph 177, 1982.
- 2. Organic Chemist

 Book of Orbitals. L. Salem and W.L. Jorgensen, Academic press.
- 3. Mechanism & Theory in Organic Chemistry, T.H.Lowry and K.C. Richardson, Harper & Row.
- 4. Introduction to Theoretical Organic Chemistry and Molecular Modeling, W.B. Smith, VCH, Weinheim.
- 5. Physical Organic Chemistry, N.S. Isaacs, ELBS/Longman.
- 6. Supramolecular Chemistry; Concepts and Perspectives, J.M. Lehn, VCH.
- 7. The Physical Basis of Organic Chemistry, H.Maskill, Oxford Univ. Press.
- 8. Textbook of Polymer Science, F.W. Billmeyer Jr. Wiley.
- 9. Polymer Science, V.R. Gowarikar, N.V. Visvanathan and J. Sreedhar, Wiley Eastern.
- 10. Functional Monomers & Polymers, K. Takemoto, Y. Inaki and R.M. Ottanbrite.



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stry, H.R. Alcock and F.W. Lambe, Prentice Hall. lers, J.M.G. Cowie, Blakie Academic and Professional.

- 13. Supramolecular Chemistry, Edited by Alberto Ciferri, Taylor and Francis
- The chemistry of Nanomaterials Vol.I and Vol II, Edited by C. N. R. Rao, A Muller, A.K.Cheetham, Wiley VCH. 2005
- 15. Metal-Polymer Nanocomposites, Edited L. Nicolais and G Carotenuto, Wiley Interscience 2005.
- Polymer Chemistry and Physics of Modern Materials, J.M.G. Cowie NAd V.Arrighi, Taylor and Francis Group 2008
- 17. Designing Safer Polymers by P.T.Anastas, P.H. Bickart, M.M. Kirchhoff , Wiley Interscience, 2001

PAPER - I

Phil. (Physical Chemistry)

(Kinetics of Fast Reactions and Advanced Electrochemistry)

Lectures: 60 Max. Marks: 100

NOTE: Ten questions will be set by the examiner selecting TWO from each unit. As far as possible, every question will be subdivided into two to three parts. The students shall attempt FIVE questions selecting ONE from each unit.

Kinetics of Fast Reactions

UNIT - I

Basic Principles of Chemical Relaxation Techniques: Relaxation time and its significance, determination of rate constants from relaxation data. Evaluation of relaxation time form a relaxation oscillogram. Relaxation time in multi step systems. Chemical relaxation in two and multi step systems. Thermodynamic aspects in relation to chemical relaxation; Gibbs free energy, affinity of a reaction and advancement of a reaction.

UNIT - II

Experimental Techniques for the Study of Relaxation Kinetics (Theory and Applications):

- **Pressure Jump Technique:** Application to mechanistic investigation of relaxation behaviour in Beryllium Sulphate solution and determination of thermodynamic quantities from amplitude data of relaxation oscillogram.
- **Temperature Jump Technique:** Application to mechanism of water addition to carbonyl functional group of organic carbonyl compounds.
- Electric Field Jump Technique: Application to neutralization reaction.
- Ultrasonic Relaxation Technique: Application to ion ó association (ultrasonic absorption in aqueous solutions of MnSO₄), and inter and intra molecular proton transfer reaction.

Advanced Electrochemistry

UNIT - III

Physical Chemistry of Ionic Solution: Ion ó Solvent and Ion ó Ion interactions: Ion ó quadrupole model of ion ó solvent interactions, ion ó induced dipole interactions in primary salvation sheath. Heats and entropy changes accompanying hydration. Hydrophobic effect in salvation. Debye ó Huckel Theory of ion ó ion interactions. Poissonøs equation and Debye ó Huckel Theory of charge distribution around ions (Linearzation of Boltzmann equation), and linearized Poisson ó Boltzmann equation and its solution. Debye ó Huckel ionic ó cloud model and Debye ó Huckel length.

UNIT - IV

Physical Chemistry of Ion – Transport in Solution: The driving force for diffusion, Fickøs law of steady ó state diffusion, and diffusion ó coefficient. The Einstein ó Smoluchowski equation. Gross view of non ó steady ó state diffusion (Fickøs second law). Diffusion process stimulated by a constant current (or Flux). Einstein relation between absolute ion mobility and diffusion coefficient. The interdependence of ionic drifts: the Onsager Phenomenological Equations, diffusion potential and the Planck ó Henderson equation.

he electrified interface, introduction and basic facts of electrocapillarity, thermodynamics of the electrocapillary effect. Thermodynamic treatment of polarizable interface, determination of charge density on the electrode (Lippmann equation), determination of surface excess (variation of surface tension with solvent composition of electrochemical system). The structure of electrified surfaces. The Helmholtz ó Perrin theory, the Gouy ó Chapman Diffuse ó Charge Model of double layer and Stern Model. Isotherms of adsorption in electrochemical systems. The Temkin isotherm, ionic isotherm for heterogeneous surfaces and thermodynamic analysis of adsorption isotherm.

- 1. Modren Electrochemistry Vol. 1 & 2: J.OøM Bockris, A.K.N. Reddy and M.G.- Aldeco
- 2. Physical Chemistry of Surfaces: A.W. Adamson
- 3. Electrochemistry: S. Glasstone
- 4. Chemical Kinetic Method: Principles and Applications: C. Kalidas

PAPER - II

Phil. (Physical Chemistry)

(Non ó Equilibrium Physical Chemistry and Theoretical and Applied Aspects of Surfactant System)

Lectures: 60 Max. Marks: 100

NOTE: Ten questions will be set by the examiner selecting TWO from each unit. As far as possible, each question will be divided into two to three parts. The students shall attempt FIVE questions selecting ONE from each unit.

(A) NON – EQUILIBRIUM PHYSICAL CHEMISTRY

UNIT - I

Linear Non – Equilibrium Thermodynamics (LNT): Basic principles of non - equilibrium thermodynamics: a review. Applications of Non ó Equilibrium Thermodynamics to linear steady state phenomena: membrane transport (osmosis) thermodynamic theory of thermo ó osmosis, thermodynamic theory of non ó reacting gaseous mixtures, kinetic theory of thermo ó osmosis (a brief introduction to some experimental results). Electro - osmosis phenomena: non ó equilibrium steady ó states. Theories based on models of uncharged and charged membranes (a brief introduction to some experimental results).

UNIT - II

Non Linear Steady States: Non ó linear flux equations in respect of electro ó kinetic phenomena (expressions as well as some qualitative insight to some experimental results). Non ó linear flux equation and non ó linear steady state in chemical reactions (i) linear (rate) and non linear flux equation for a single reversible reaction and (ii) linear phenomennlogical relation and non ó linear flux equation for coupled reactions.

(B) THEORETICAL AND APPLIED ASPECTS OF SURFACTANT SYSTEMS

UNIT - III

Micelle formation, critical micelle concentration, monodisperse micelles of ionic and non ó ionic surfactants and thermodynamics of micelle formation (Mass Action Model). Counterion binding to micelles (Evan and Ninham - model). Kinetics of micelle formation. Effect of temperature and pressure on micelle formation (a qualitative insight). Micelle Temperature Range (MTR) or Kraft phenomenon, physicochemical meaning of MTR and effect of salt on MTR.

UNIT - IV

Micellar Solubilization:

Representation of solubilization results (definition of partion coóefficients). Thermodynamics of solubilization, distribution of solubilizate molecules among micelles. Factors effecting solubilization. Solubilization in micellar liquid chromatography (MLC): partition theory, and application of MLC to drug and protein analysis (brief outline only). Electrokinetic chromatography on micellar solubilization (MEKC): theory of separation and applications of MEKC: biological system, environment and drug analysis (brief outline only). Interactions between amphiphiles and polymers/proteins; Analytical model for binding (Scathchard binding equation), Necklace bead model for Polymer / protein surfactant complex (qualitative insight only).



istry of Micellar System:

Effect of micelles on chemical reactions, micelle catalyzed reactions, distribution of reactants among micelles: Poisson and Gaussian distributions. Inhibition in micellar solutions. Determination of CMC by fluorescence probe method (Qualitative view) and micellar aggregation number by fluorescence probe method (Static and dynamic methods), Kinetics of redox reaction.

- 1. Introduction to Non ó Equilibrium Physical Chemistry: R.P. Rastogi
- 2. Thermodynamics: R.C. Srivastava, S.K. Saha and A.K. Jain
- 3. Solubilization in Surfactant Aggregates: Eds S.D. Christian and J.F. Scamehorn (Surfactant Science Series Vol. 55)
- 4. Polymer ó Surfactant System: Ed. J.C.T. Kwak (Surfactant Science Series Vol. 77)
- 5. Micelles (Theoretical and Applied Aspects): Y. Moroi
- 6. Non ó equilibrium Thermodynamics: C. Kalidas
- 7. Non ó equilibrium Thermodynamics: I. Prigogene
- 8. Studies in Interface Science, Ser. (Elsevier) No.13, Surfactants: Chemistry, Interfacial Properties, Applicatios: V.B. Fainerman, D. Mobius and R. Millar Eds.
- Surface Active Behaviour of Performance Surfactants, Annual Surfactant Review Vol. 3 D.R. Karsa Ed.