HIMACHAL PRADESH UNIVERSITY, SHIMLA-171005

FACULTY OF PHYSICAL SCIENCES

REVISED SYLLABI

FOR Ph. D. CHEMISTRY COURSE WORK

(SEMESTER SYSTEM)
(SESSION 2019-20 AND ONWARDS)

HIMACHAL PRADESH UNIVERSITY
DEPARTMENT OF CHEMISTRY, SHIMLA-171005
INDIA

Annexure-"C"

A Detailed Scheme and Course Contents of the Syllabi for PhD . Chemistry Spread Over two Semesters (I-II) For Session 2019-20 and Onwards

SEMESTER-I			
Each candidate has to study three papers in first semester. Paper I (Research Methodology) is compulsory paper and two papers (optional Paper-II and III) from the respective specialization i.e. Inorganic Chemistry, or Organic Chemistry or Physical Chemistry. Each paper will be of 100 marks.			
Paper No.	**Title**	**Max. Marks**	
Paper 1	**Research Methodology** **Compulsory for all specialization)**	**100**	
	Inorganic Chemistry		
Paper -II	Inorganic Chemistry (Advanced Inorganic Chemistry)	100	
Paper -III	Inorganic Chemistry (Inorganic and Superamolecular Chemistry)	100	
Organic Chemistry			
Paper -II	Organic Chemistry (Organic Synthesis)	100	
Paper -III	Organic Chemistry (Polymer Chemistry)	100	
Physical Chemistry			
Paper -II	Physical Chemistry (Kinetics of Fast Reactions and Advanced Electrochemistry)	100	
Paper -III	Physical Chemistry (Non-Equilibrium Physical Chemistry and Theoretical and Applied Aspects of Surfactant System)	100	

Semester 1

M.Phil. Chemistry

Paper-I (Research Methodology)

Lectures: 60

Max. Marks: 100

Note: Examiner will set 10 questions, two from each section and the candidates will be required to attempt five questions in all selecting at least one question from each section. All questions will carry equal marks.

Section A

Research Methodology: Types and methods of research, classification of research, pure and applied research, exploring or formulative research, descriptive research, diagnostic research/study, Evaluation of research/study, action research, and experimental research-problem selection. Meaning, Scope, Primary sources of literature survey, Journals, patents etc., secondary sources of literature survey, Books, Reference books, Text books, listing of letters.

Section B

Scientific Writing : Scientific Document; Organization and writing of research paper, short communications, review articles, monographs, technical and survey reports, authored books, and edited books and dissertation. Abstracts and Journals in chemistry, Electronic forms of Journals, major libraries, subscribing Journals related to chemistry in the region and country and Patents and Patents writing.

Section C

Concepts of chemical safety: Chemical safety and ethical handling of chemicals, safe working procedure and protective environment, emergency procedure and first aid, laboratory ventilation, safe storage and use of hazardous chemicals, procedure for working with substances that pose hazards, flammable or explosive hazards, procedures for working with gases at pressures above or below atmosphere, safe storage and disposal of waste chemicals, recovery, recycling and reuse of laboratory chemicals.

Section D

Research ethics: Ethical issues, copy right, royalty, intellectual property rights, citation and acknowledgement. Reproducibility. Safety rules of laboratory acquaintance of experimental set up, importance of safety and security of data. Review of published research in the relevant field, training, field work.

Section E

Computer applications in research: Application and uses of common softwares in chemistry-origin, chemsketch, chemdraw, basic ideas on the use of internet in chemistry education.

Reference Books:

1 William Kemp, Organic Spectroscopy, ELBS London, 1987.

2 RM Silverstein, CG Bassler and TC Morril, Spectroscopic Identification of Organic Compounds, 4th Edition, John Wiley & Sons, New York, 1981.

3 Donald L Pavia, Gary M Lampman and George S Kriz, Introduction to Spectroscopy, 3 rd Edition, Saunders Golden Sunburst Series.

4 CN Banwell and Elaine M McCash, Fundamentals of Molecular Spectroscopy, 4th Edition.

5 Raymond Chang, Basic Principals of Spectroscopy, RE Krieger Publishing Co., Huntington, New York, 1978.

6 Paul D Leedy, Jeanne E Ormrod and Jeanne Ellis Ormrod, Practical Research: Planning and Design, Prentice Hall, 2004.

7 Robert V Smith, Graduate Research: A Guide for Students in the Sciences, University of Washington Press, 1998.

8 Anthony M Graziano and Michael L Rau, Research Methods: A Process of Inquiry, Prentice Hall, 2006.

9 Peter C Jurs, Computer Software Applications in Chemistry, 2nd Ed., John Wiley & Sons, New York, 1996.

10 Practical Skills in Chemistry, J. R. Dean, A. M. Jones, D. Holmes, R. Reed, J. Weyers and A Jones, Pearson Education Ltd. [Prentice Hall] (2002)

11. Research Methodology. Methods and Techniques : C. R. Kothari,

Semester 1

M.Phil. (Inorganic Chemistry)
PAPER – II (Advanced 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). 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, bound-ion radical mechanism and bound-ion co-ordination mechanism. Metallocene based Zeigler Natta catalysts, catalysts composition, active centre and polymerisation mechanism.

UNIT-III

Synthesis of Coordination compounds:- Theoratical consideration: Labile and Inert Coordination compounds, synthesis of mixed ligand complexes by co-proprtionation, chelate effect, trans effect (Peyrone's rule, Jorgonson's rule and Kurnakov's rule), Cis effect, Geometric isomerization of square planer platinum(II) and Palladium(II) complexes, hard-soft acid-base (HSAB) principle, factors affecting the acid base properties of coordination compounds, ligand effects on redox potentials of coordination compounds.

UNIT-IV

Voltammetric methods of analysis: Principle, excitation signals, mass transfer mechanism, instrumentation, methods of analysis and applications of pulse polarography, cyclic voltammetry and anode stripping voltammetry. Use of cyclic 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).

Books Recommended:

1. Homogeneous transition metal catalysis – Christopher Masters
2. Principles and Application of HomogeneousCatalysis – Nakamura and Tsutsui
3. Advanced Polymer Chemistry- Manas Chanda
4. Synthetic Coordination Chemistry: Principles and Practice- J.A. Davies, C.M. Hockensmith, V.Y.Kukushkin and Y.N. Kukushkin.
5. Fundamentals of Analytical Chemistry- Skoog, West, Holler and Crouch
6. Chemistry experiments for Instrumental methods- Sawer, Heineman and Beebe.
7. Electronic absorption spectroscopy and related techniques: D.N. Sathyanaray.
8. The Organometallic Chemistry of Transition metals: R.H. Crabtree.
9. Principles and applications of organotransition metal chemistry by Ccollmen and Hegden

Semester 1

M.Phil. (Inorganic Chemistry)
PAPER – III (Inorganic and Superamolucular 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.

Books Recommended:

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 (2^{nd} Edn.)
4. Inorganic Reaction Mechanism- Edward.
5. Inorganic Reaction Mechanism - Bassolo and Pearson.
6. Supramolecular Chemistry concepts and Perspectives- Jean-Marie Lehn(VCH-1995)

Semester 1

M.Phil. (Organic Chemistry)

PAPER – II (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, Di- π methane rearrangement, Hofmann-Loffler reaction, Sharpless assymatric epoxidation and Stork-enamine reaction.

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

UNIT–III

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,

Click Chemistry: Concepts and uses in organic and polymer synthesis.

UNIT- IV

Stereochemistry; Stereoselective and stereospecific reactions: Stereoselective reactions: Hydride reduction of cyclic ketones, catalytic hydrogenation, Stereoselective nucliophilic addition to acyclic carbonyl groups stereospecific reactions :Bromination of alkene, 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.

UNIT- V

Drug design and development: Pharmacokinetics and Pharmacodynamics: Introduction to drug absorption, distribution, metabolism, elimination using pharmacokinetics. Importance of pharmacokinetics in drug development. Drug design, concepts of lead compound and lead modification, Example: Development of cimetidine-A rational approach to drug design: Anti ulcer therapy, Biological activity of cimetidine ,Structure and activity of cimetidine, Metabolism of cimetidine, cimetidine analogues.

Books Recommended:

1. Practical NMR Spectroscopy, M.L.Martin, J.J. delpeuch and G.J.Martin, Heyden.
2. Spectrophotometric 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. Fischer and P. Loftus, Wiley.
4. Appliation 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 Synthesis: Feiser and Feiser.
12. An Introduction to Medicinal Chemistry, Graham L. Patrick.
13. Medicinal Chemistry: Principles and Practice Edited by F.D. King.
14. Textbook of Organic Medicinal and Pharmaceutical Chemistry, Edited by Charles O. Wilson, et al.
15. Introduction to Medicinal Chemistry, Alex Gringuage.

Semester 1

M.Phil. (Organic Chemistry)
PAPER – III (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.

UNIT-I

Polymer Synthesis: Kinetic and mechanism of radical, cationic, and anionic addition polymerization, Living polymerization. Significance of chain transfer reactions, Chemistry and kinetics of inhibition and retardation.

Miscellaneous polymerization reactions: Monomers with two different polymerizable groups, Hydrogen transfer polymerization, Polymerization and cyclotrimerization of isocyanates, Monomers with triple bonds, Ring opening polymerization: Scope, polyermerizability, polymerization mechanism and kinetics, examples of cyclic amide and ethers; Monomers containing the same functional groups, Monomers containing different functional groups, Zwitterionic copolymerization.

UNIT –II

Copolymer Synthesis: Principles of polymer reactivity, factors affecting polymer reactivity , Chain transfer copolymerization, Chemistry and methods of graft copolymerization, radical graft copolymerization, ionizing and UV radiation and redox initiation, and other grafting systems.

Block copolymer formation, sequential monomer addition, charge formation reactions, telechelic polymers, Reactions of block copolymers, mechanochemical bond scission, special initiators.

Crosslinking processes, chemical and radiation crosslinking, vulcanization. Halogenations reactions, aromatic substitution and cyclization of aromatic polymers.

UNIT- III

Polymer Characterization: Determination of molecular weight of polymers by colligative properties, viscosity measurement, end group analysis, sedimentation velocity and equilibrium method.

Analysis and Characterization of polymers by chemical analysis, FTIR, NMR,TGA, GPC, DSC, XRD, SEM techniques.

UNIT- IV

Special Polymer Reactions : General introduction to the polymer reactions, Derivatization reactions of biopolymers – cellulose, chitosan, starch and natural gums

Polymer as carriers or supports, polymeric reagents, polymeric substrates, polymeric catalysts, immobilized enzymes.

Polymer stability and degradation: Type of degradation, mechanism, ultrasonic, photo, high energy and oxidative degradation, Fire retardants, UV stabilizers and absorbers. Biodegradation by alkali, acid, ionic liquids and enzymes, hydrolytic reactions of biopolymers and their special technological potential with respect to bio-ethanol .

UNIT-V

Specialty Polymers: Biodegradable polymers (lactic and glycolic acid based). Conducting polymers, applications of conducting polymers. Hydrogels. Biomedical polymers, contact lenses, dentures, implants, artificial – heart, kidney and blood.

Polymers and environment: Environmental aspects of polymers, energy and feedstock utilization, Problems of non-degradability of synthetic polymers, biomass utilization, bioplastics.

Books Recommended

1. Textbook of Polymer Science, F.W. Billmeyer Jr. Wiley.
2. Polymer Science, V.R. Gowarikar, N.V. Visvanathan and J. Sreedhar, Wiley Eastern.
3. Functional Monomers & Polymers, K. Takemoto, Y. Inaki and R.M. Ottanbrite.
4. Contemporary Polymer Chemistry, H.R. Alcock and F.W. Lambe, Prentice Hall.
5. Physics & Chemistry of Polymers, J.M.G. Cowie, Blakie Academic and Professional.
6. Supramolecular Chemistry , Edited by Alberto Ciferri, Taylor and Francis.
7. The chemistry of Nanomaterials Vol.I and Vol II, Edited by C. N. R. Rao, A Muller, A.K. Cheetham, Wiley VCH. 2005.
8. Metal-Polymer Nanocomposites, Edited L. Nicolais and G Carotenuto, Wiley Interscience 2005.
9. Polymer Chemistry and Physics of Modern Materials, J.M.G. Cowie and V. Arrighi,Taylor and Francis Group 2008.
10. Designing Safer Polymers by P.T.Anastas, P.H. Bickart, M.M. Kirchhoff , Wiley Interscience, 2001.

Semester 1

M.Phil. (Physical Chemistry)

PAPER – II (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 and 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.

Advanced Electrochemistry

UNIT - III

Physical Chemistry of Ionic Solution: Ion – Solvent and Ion – Ion interactions: Ion – quadrupole model of ion – solvent interactions, ion – induced dipole interactions in primary salvation sheath. Heats and entropy changes accompanying hydration. Hydrophobic effect in salvation. Poisson's equation and Debye – Huckel Theory of charge distribution around ions (Linearzation of Boltzmann equation).

UNIT - IV

Physical Chemistry of Ion – Transport in Solution: The driving force for diffusion, Fick's law of steady – state diffusion, and diffusion – coefficient. The Einstein – Smoluchowski equation. Gross view of non – steady – state diffusion (Fick's second law). Diffusion process stimulated by a constant current (or Flux). Einstein relation between absolute ion mobility and diffusion coefficient.

UNIT – V

Surface Electrochemistry: The 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 – Perrin theory, the Gouy – Chapman Diffuse – Charge Model of double layer and Stern Model.

Books Recommended:

1. Modren Electrochemistry Vol. 1 & 2: J.O'M 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

Semester 1

M.Phil. (Physical Chemistry)

PAPER – III (Non – 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. Each question will be subdivided into two to three parts. The students shall attempt FIVE questions selecting ONE from each unit.

UNIT – I

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

UNIT – II

Non Linear Steady States: Non – linear flux equations in respect of electro – kinetic phenomena (expressions as well as some qualitative insight to some experimental results). Non – linear flux equation and non – 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 – linear flux equation for coupled reactions.

UNIT – III

Micelle formation, critical micelle concentration, monodisperse micelles of ionic and non – 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 treatment). Micelle Temperature Range (MTR) or Kraft phenomenon, physicochemical meaning of MTR and effect of salt on MTR.

UNIT – IV

Micellar Solubilization: Thermodynamics of micellar solubilization, distribution of solubilizate molecules among micelles. Factors affecting 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).

UNIT - V

Micellar Catalysis and Photochemistry 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).

Books Recommended:

1. Introduction to Non – 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 – Surfactant System: Ed. J.C.T. Kwak (Surfactant Science Series Vol. 77)
5. Micelles (Theoretical and Applied Aspects): Y. Moroi
6. Non – equilibrium Thermodynamics: C. Kalidas
7. Non – equilibrium Thermodynamics: I. Prigogene