

FACULTY OF SCIENCES

SYLLABUS

FOR

B.Sc. (Hons) Chemistry

(Semester V-VI)

Session: 2018-19



KHALSA COLLEGE AMRITSAR

(An Autonomous College)

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Defaulters will be prosecuted.
(ii) Subject to change in the syllabi at any time.
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Scheme of Courses

Eligibility:-The candidate having passed 10+2 Examination (Medical and Non-Medical) from a recognized board.

SCHEME AND SCHEDULE OF COURSES

Semester-V				
S. No.	Course No.	Course Title	Max. marks	Hrs.
1.	BHCH-137	Physical Chemistry-V	50	45
2.	BHCH-138	Inorganic Chemistry-V	50	45
3.	BHCH-139	Organic Chemistry-V	50	45
4.	BHCH-140	Organic Chemistry-VI	50	45
5.	BHCH-141	Analytical Chemistry	50	45
6.	BHCH-142	Inorganic Lab II	50	45
7.	BHCH-143	Organic Lab III	50	45
Student PowerPoint Presentation/Seminar on a Subject Topic				
TOTAL			350	315
Semester-VI				
S. No.	Course No.	Course Title	Max. marks	Hrs.
1.	BHCH-144	Physical Chemistry-VI	50	45
2.	BHCH-145	Inorganic Chemistry-VI	50	45
3.	BHCH-146	Organic Chemistry-VII	50	45
4.	BHCH-147	Advanced Physical Chemistry	50	45
5.	BHCH-148	Advanced Chemistry	50	45
6.	BHCH-149	Inorganic Lab III	50	45
7.	BHCH-150	Physical Lab III	50	45
TOTAL			350	315

B.Sc. (Hons)

Chemistry

Semester-V

B.Sc. (Hons. School) Chemistry (Semester-V)
BHCH-137: Physical Chemistry-V

3 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

Instructions for paper setters and candidates

- I. Examiner will make five sections of paper namely Section-I, II, III, IV and V
- II. Examiner will set total of NINE questions comprising ONE compulsory question of short answer type covering whole syllabi and TWO questions from each unit.
- III. Section-I will consist of eight short questions carrying 1 Mark each.
- IV. Section-II, III, IV and V of paper will consist of EIGHT questions in total having TWO questions from each unit of the syllabus and each question carry 8 Marks.
- V. The students are required to attempt FIVE questions in all, taking ONE Compulsory question of section-I and one question from each section i.e. II, III, IV and V.

UNIT I

1. Equilibrium Thermodynamics:

(11 Hrs.)

Revision of zeroth, 1st, 2nd and 3rd Laws of thermodynamics. The work function and free energy relationships, the Gibbs Helmholtz equation, conditions of equilibrium, partial molar properties, physical significance of partial molar property, chemical potential, Gibb's Duhem equation, Duhem-Margles equation, variation of chemical potential with temperature and pressure, fugacity, determination by graphical method, use of equation of state, generalized method for determination of fugacity. Variation of fugacity with temperature and pressure, fugacity of solids and liquids, Numericals.

UNIT II

2. Non-Equilibrium Thermodynamics

(11 Hrs.)

Thermodynamic criteria for non-equilibrium states, entropy production for heat flow, matter flow and electric current flows. Rate of entropy production, phenomenological equations, flows and fluxes, Onsager reciprocity relations, Principles of microscopic reversibility, Principle of minimum entropy production, electrokinetic effects, diffusion, electric conduction. Applications of irreversible thermodynamics to biological systems.

UNIT III

3. Solutions and Their Properties:

(12 Hrs.)

Factors affecting solubility, types of solutions, thermodynamic properties of solutions, the solution process, condition for equilibrium between phases, equilibrium between a solution and its vapor phase, Ideal solution, the vapor pressure of ideal solution, vapor pressure of actual

liquid pairs, boiling point diagrams of miscible binary mixtures, distillation of binary miscible solutions, Azeotropes, the fractionating column, ratio of distillate to residue, solubility of partially miscible liquid pairs; Maximum, minimum, maximum & minimum solution temperature type, type without critical solution temperature, vapor pressure and distillation diagrams of partially miscible liquid pairs, vapor pressure and distillation of immiscible liquids, solubility of gases in liquids, the Nernst distribution law, solutions of solids in liquids, chemical equilibria in solutions.

Dilute Solutions: Henry's Law, Freezing points of dilute solutions, determination of M. Wts, the B. Pts of solutions, temperature and solubility in dil. solutions.

UNIT IV

4. Nanochemistry

(11 Hrs.)

Introduction, Self assembling of materials, material self assembling, Molecular vs material self assembling, Two dimensional assemblies, Mesoscale assemblies, coercing colloids, nanocrystals, supramolecular structures, nanoscale materials, carbon nanotubes, nanowires, fullerenes, Applications of nanomaterials, Future perspectives

Books Recommended:

1. Principles of Physical Chemistry, C.F. Prutton and S.H. Maron.
2. Physical Chemistry by G.W. Castellan.
3. Thermodynamics for Chemists, S.Glasstone.
4. Physical Chemistry, P.W. Atkins, 6th edn. Oxford.
5. The Thermodynamics of Biological Processes, D.Jou and J.E. Llebot.
6. Physical Chemistry, W.J. Moore.
7. Physical Chemistry: A Molecular Approach, D.A. MCMarrie & J. D. Simon.
8. L. E. Foster, Nanotechnology, Science Innovation and Opportunity, Pearson Edu., 2007

B.Sc. (Hons. School) Chemistry (Semester-V)
BHCH-138: Inorganic Chemistry-V

3 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

Instructions for paper setters and candidates

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UNIT-I

1. Chemical Bonding-III (Ionic bond)

(11 Hrs.)

Factors affecting the stability of ionic compounds. Lattice energy, Born Lande equation and its applications, Madelung constant, Born-Haber cycle, applications of lattice energy, covalent character in ionic compounds, polarizing power and polarizability, Fajan's rules, Ionic radii, Factors affecting the radii of ions, Radii of polyatomic ions, Efficiency of packing and crystal lattices, Radius ratio rule, calculation of some limiting radius ratio values for different coordination members, Structure of crystal lattices, NaCl, CaCl₂, ZnS (Zinc blende and Wurzite), fluorite, rutile and cadmium iodide. Predictive power of thermochemical calculations on ionic compounds.

UNIT-II

2. Perfect and imperfect crystals:

(11 Hrs.)

Intrinsic and extrinsic defects, point defects, line and plane defects, vacancies-Schottky and Frenkel defects. Thermodynamics of Schottky and Frenkel defect formation, colour centres, non-stoichiometry and defects. Metals, insulators and semiconductors, Band theory, Band structure of metals, intrinsic and extrinsic semiconductors, doping semiconductors, p-n junctions, High temperature super conductors.

UNIT-III

3. Crystal field theory

(12 Hrs.)

The splitting of d-orbitals in different fields (octahedral, tetrahedral, tetragonally distorted octahedral, square planar, trigonal bipyramidal), Consequences and applications of orbital splitting, crystal field stabilization energy, magnetic properties, Factors affecting extent of splitting and spectrochemical series, colour of transition metal complexes. Structural effect of

crystal field splitting; ionic radii, Jahn-Teller effect in octahedral and tetrahedral complexes. Thermodynamic effects of crystal field splitting, enthalpies of hydration of M^{2+} ions, lattice energies of MCl_2 compounds, etc. Evidence of covalence and adjusted crystal field theory. Molecular orbital treatment of octahedral complexes and bonding; complexes with no bonding and complexes with bonding. Molecular orbital diagrams for tetrahedral and square planar complexes.

UNIT-IV

4. Electronic Spectra of Transition Metal Complexes:

(12 Hrs.)

Basis of electron absorption spectroscopy, Term Symbols, Spin-spin, orbital-orbital and spin orbital coupling, L.S. and jj coupling schemes, Russell-Saunders coupling scheme, determination of all the spectroscopic terms of p^n , d^n ions, determination of ground state terms for p^n , d^n , f^n ions using L.S. scheme, determination of total degeneracy of terms, order of interelectronic repulsions and crystal field strength in various fields, two type of electron repulsion parameters. spin orbit coupling parameters energy separation between different j states. Orgel diagrams; weak field splitting, Intermediate and strong field splitting. Tanabe and Sugano diagrams. Electronic spectra of d^1 - d^9 metal complexes and f type compounds. Calculation of D_q of d^1 , d^2 & d^8 configurations.

Books Recommended

1. Cotton F. A., Wilkinson G., Murillo C. A., Bochmann M., Advanced Inorg. Chemistry, 6th edn., Pubs: John Wiley India. (2003).
2. Shriver D. F., Atkins F. W. and Langford C. M., Inorganic Chemistry, 3rd edn., Pubs: Oxford University Press, 1999.
3. Huheey J. E., Keiter E. A., Keiter R. L., Inorganic Chemistry : Principles of Structure and Reactivity; 4th edn, Pubs: Harper Collins, 1993.

B.Sc. (Hons. School) Chemistry (Semester-V)
BHCH-139: Organic Chemistry-V
Organic Aspects of Spectroscopy

3 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

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UNIT-I

1. Electromagnetic Spectrum: Absorption Spectra

(11 Hrs)

Ultraviolet (UV) absorption spectroscopy – absorption laws (Beer-Lambert law), molar absorptivity, presentation and analysis of UV spectra, types of electronic transitions, effect of conjugation. Concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. UV spectra of conjugated enes and enones.

Infrared (IR) absorption spectroscopy – molecular vibrations, Hooke's law, selection rules, intensity and position of IR bands, measurement of IR spectrum, fingerprint region, characteristic absorptions of various functional groups and interpretation of IR spectra of simple organic compounds.

UNIT-II

2. NMR Spectroscopy

(12 Hrs)

Introduction. The nuclear spin, precessional motion. Larmor frequency, the NMR isotopes, population of nuclear spin levels, spin –spin and spin –lattice relaxation, measurement techniques (CW and FT methods). Solvent used, Chemical Shift, shielding constant, range of typical chemical shifts simple applications of chemical shift ring currents and aromaticity, shifts of ^1H and ^{13}C , inductive effect, ring current effect and anisotropy chemical bonds, intermolecular forces effecting the chemical shifts. Spin –spin interactions, low and high resolution NMR with various examples. Correlation for H bonded to Carbon. 1H bond to other nuclei such as nitrogen, oxygen and sulphur. Complex spin –spin interaction. Interaction

between two or more nuclei, splitting due to vicinal and geminal protons, long range coupling. ABX and ABC systems with their coupling constants, shifts reagents. Effects of chemical exchange, fluxional molecules, Hindered rotation on NMR spectrum, Karplus relationship. Nuclear magnetic double resonance, spin decoupling, Nuclear overhauser Effect (NOE). ^{13}C ^1H coupling, ^{13}C spectra, Differences from ^1H nmr, DEPT, Intensities of lines in ^{13}C .

UNIT-III

3. Mass Spectroscopy

(11 Hrs)

Basic Principles. Methods of ionization E1 & C1, Laser desorption, Fast Atom Bombardment (FAB). Molecular ions, isotope ions, fragment ions of odd and even electron types, Nitrogen rule, Factors affecting cleavage patterns, simple cleavage, cleavages at a hetero atom, multicentre fragmentations, rearrangements, Diels–Alder fragmentation, Mc Lafferty rearrangement. Cleavage associated with common functional groups, Aldehydes, ketones cyclic and acyclic esters, alcohols, olefins, aromatic compounds amine.

UNIT-IV

4. Application of UV, IR, NMR and Mass Spectroscopy

(11 Hrs)

Structure elucidation by combined application of UV, IR, NMR and mass spectra.

Books:

1. W. Kemp, "Organic Spectroscopy".
2. D.L. Pavia, G.M. Lampan, G.S. Kriz, Introduction to Spectroscopy
3. D.H. Williams, I. Fleming, "Spectroscopic Methods in Organic Chemistry
4. R. S. Drago, "Physical Methods in Chemistry"
5. R.M. Silverstein, G.C. Bassler, T.C. Morr. Spectrometric Introduction of Organic Compounds".
6. R.C. Banks, E.R. Matjeka, G. Mercer, "Introductory Problems in Spectroscopy".
7. C.N. Banwell "Fundamentals of Molecular Spectroscopy".

B.Sc. (Hons. School) Chemistry (Semester-V)
BHCH-140: Organic Chemistry-VI
(Reaction Mechanisms)

3 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

Instructions for paper setters and candidates

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UNIT-I

1. Aliphatic Nucleophilic Substitution

(11 Hrs)

The S_N^1 , S_N^2 , mixed S_N^1 and S_N^2 and SET mechanisms.

The neighbouring group mechanism, neighbouring group participation by π and σ bonds, anchimeric assistance. Nucleophilicity and S_N^2 reactivity based on curve cross model.

Classical and nonclassical carbocations, phenonium ions, norbornyl system, common carbocation rearrangements. Application of NMR spectroscopy in the detection of carbocations. Relationship between polar and electron transfer reactions.

The S_N^1 mechanism.

Nucleophilic substitution at an allylic, aliphatic trigonal and a vinylic carbon. Reactivity effects of substrate structure, attacking nucleophile, leaving group and reaction medium, phase transfer catalysis and ultrasound, ambident nucleophile, regioselectivity.

UNIT-II

2. Aromatic Nucleophilic Substitution

(6 Hrs)

The S_NAr , S_N1 , benzyne and $S_{RN}1$ mechanisms, Reactivity –effect of substrate structure, leaving group and attacking nucleophile. The von Richter, Sommelet-Hauser, and Smiles rearrangements.

3. Free Radical Substitution

(6 Hrs)

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

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

UNIT-III

4. Aliphatic Electrophilic Substitution (5 Hrs)

Bimolecular mechanisms- S_E2 and S_{Ei} . The S_{E1} mechanism, electrophilic substitution accompanied by double bond shifts. Effect of substrates, leaving group and the solvent polarity on the reactivity.

5. Aromatic Electrophilic Substitution (6 Hrs)

Arenium ion mechanism The S_{E1} mechanism, orientation and ortho/para ratio, Ipso attack, Mechanism of nitration, Amination, halogenation, sulphonation, mercuration, Vilsmeier-Haack reaction and Friedel-Crafts reaction. Energy profile diagrams. Activating and deactivating substituents.

UNIT-IV

6. Addition to Carbon-Carbon Multiple Bonds (6 Hrs)

Mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, regio- and chemoselectivity, orientation and reactivity. Addition to cyclopropane ring. Hydrogenation of double and triple bonds, hydrogenation of aromatic rings. Hydroboration. Michael reaction. Sharpless asymmetric epoxidation.

7. Addition to Carbon-Hetero Multiple Bonds (5 Hrs)

Addition of water, H_2S , alcohol, amines and Grignard reagent to carbonyl compounds, imine, isocyanate, nitriles, carbon disulfide, Mannich reaction, Reformatsky reaction.

Books Suggested:

1. Advanced Organic Chemistry-Reactions, Mechanism and Structure, Jerry March, John Wiley.
2. Advanced Organic Chemistry, F.A. Carey and R.J. Sundberg, Plenum.
3. Modern Physical organic chemistry Eric V. Anslyn /Deniis A.Doughutes. P 637-655 (2004) University, Science Books.
4. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman.
5. Structure and Mechanism in Organic Chemistry, C.K. Ingold, Cornell University Press.
6. Organic Chemistry, R.T. Morrison and R.N. Boyd, Prentice Hall
7. Modern Organic Reactions, H.O. House, Benjamin.
8. Principles of Organic Synthesis, R.O.C. Norman and J.M. Coxon, Blackie Academic & Professional.
9. Reaction Mechanism in Organic Chemistry, S.M. Mukherji and S.P. Singh, Macmillan.

B.Sc. (Hons) Chemistry Semester-V
BHCH-141: Analytical Chemistry

3 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

Instructions for paper setters and candidates

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- V. The students are required to attempt FIVE questions in all, taking ONE Compulsory question of section-I and one question from each section i.e. II, III, IV and V.

UNIT-I

1. Electro Analytical Methods:

(11 hrs.)

Electrolytic and galvanic cell, Cell components, D.C. & A.C. current in a cell, Reversible and irreversible cells. Nature of electrodes potentials. Description of standard hydrogen electrode. Measurement of potentials. Sign conventions. E° values and their calculations. Effect of concentration on cell potentials. Concept of Liquid Junction potential. Ohmic potential (IR drop). Polarization (overvoltage) phenomenon and its theories. Limitation of the use of standard electrode potentials.

UNIT-II

2. Potentiometric Methods:

(7 Hrs.)

Reference electrodes (Calomel, Ag/AgCl, Tl/TlCl) Metallic indicator electrodes (first, second and third type). Metallic Redox indicator electrode: Membrane and ion –selective Electrodes: Principle and design: Glass electrode. Gas sensing probes. Enzyme electrode: Ion Sensitive Field Effect Transistors (ISFETS) Principal and Potentiometer methods.

3. Electrogravimetry and Coulmetry:

(5 Hrs.)

Current voltage relationship, electrolysis at constant applied voltage, constant current

electrolysis, coulometric methods of Analysis, potentiostatic coulmetry, Amperostatic Coulmetry, application of coulmetric titrations.

UNIT-III

4. Voltammetry and Polarography (11 Hrs.)

General introduction, theoretical consideration of classical polarography, polarographic currents, effect of capillary characteristics on diffusion current, residual current, half wave potential. Effect of complex formation on polarographic waves and mixed anodic cathodic waves, oxygen waves, instrumentation, cell, electrodes and their modifications. Application of polarography. Modified voltametric methods, viz.; current sampled polarography, (TAST), pulse polarography square wave, Fast linear sweep, Cyclic voltammetry, Hydrodynamic Voltametric, stripping methods, amperometric titrations and their applications.

UNIT-IV

5. Conductometric Methods: (7 Hrs.)

Electrolytic conductance, relationships used in conductometry, variation of equivalent conductance with concentration, measurement of conductance, conductometric titrations, Applications to various types of titrations for detection of end points.

6. Turbidimetry and Nephelometry: (4Hrs.)

Theory of Nephelometry and Turbidimetry, Instrumentation, applications.

Books:

1. D.A. Skoog and D.M. West: Principles of Instrumental Methods of Analysis.
2. D.A.Skoog and D.M. West, F.J.Hollar: Fundamentals of Analysis Chemistry.
3. G.W.Ewing: Instrumental Methods of Analysis.
4. H.H. Willard, L.L. Marritt & J.A. Dean: Instrumental Methods of Analysis.

Recommended for Further Readings:

1. B.H. Vassos and G.W.Ewing: Electro Analytical Chemistry.
 2. J.A. Plamberk: Electro Analytical Chemistry.
- H.A. Flaschka, A.J. Barnard and P.E. Strurrock, Analytical Chemistry.

B.Sc. (Hons) Chemistry Semester-V
BHCH-142: Inorganic Lab-II

4 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

Quantitative Analysis

1. Volumetric Analysis

- a. Determination of acetic acid in commercial vinegar using NaOH.
- b. Determination of alkali content-antacid tablet using HCl.
- c. Estimation of calcium content in chalk as calcium oxalate by permanganometry.
- d. Estimation of hardness of water by EDTA.
- e. Estimation of ferrous and ferric by dichromate method.
- f. Estimation of copper using sodiumthiosulphate.

2. Synthesis and Analysis

- (a) Preparation of Sodium trioxalatoferrate (III)
- (b) Preparation of Ni-DMG Complex
- (c) Preparation of Copper tetrammine complex
- (d) Preparation of cis-bisoxalatodiaquachromate (III) ion
- (e) Preparation of bisethylenediammine cobalt (III) chloride
- (f) Preparation of trans-bisoxalatodiaquachromate (III) ion

Book:

1. Synthesis and techniques in inorganic chemistry. R. J. Angelici, Pubs: SGS series London, (1977).
2. Vogel's Inorganic Quantitative book on Analysis.

1. Synthesis of adipic acid starting from cyclohexanol.
2. Synthesis of p-nitroacetanilide from acetanilide.
3. Synthesis of p-bromoaniline by bromination of acetanilide and subsequent hydrolysis.
4. Isolation of caffeine from tea leaves.
5. Synthesis of aniline from nitrobenzene.
6. Synthesis of 2-phenylindole by Fischer indole synthesis approach.
7. Synthesis of diethylbarbituric acid from diethyl malonate.
8. Synthesis of Fluorescein.
9. Cannizzaro reaction of 4-chlorobenzoic acid.
10. Synthesis of ethyl benzoate from benzoic acid.
11. Dihydroxylation of cyclohexene with peracids and KMnO_4 –Product distribution by TLC
J. Chem Edu., **2008**, 85, p959.
12. Prepare a sample of Ibuprofen and record its ^1H , ^{13}C NMR spectra
13. Reduction of 3-nitroacetophenone using i) NaBH_4 ii) using Sn and HCl. Identification of the products with NMR, UV, IR spectra
14. Preparation of oil of Wintergreen from commercial aspirin tablets *J. Chem Edu.*, **2009**, 86, p475

B.Sc. (Hons)
Chemistry

Semester-VI

B.Sc. (Hons. School) Chemistry (Semester-VI)
BHCH-144: Physical Chemistry-VI

3 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

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UNIT I

1. Thermodynamics of diffusion:

(11Hrs.)

Thermodynamic view of diffusion, Relation between transport properties. Einstein relation, Nernst-Einstein relation, stoke's Einstein relation. Diffusion in non-steady state. Fick's second law of diffusion. Theory of diffusion in liquids.

UNIT II

2. Photochemistry

(11 Hrs.)

Interaction of radiation with matters, difference between thermal and photochemical processes, Lamber's law, Lambert-beer law, laws of photochemistry: Grothus-Drapper law, Stark-Einstien law, Jablonski diagram, qualitative description of fluorescence and phosphorescence and non-radiative processes, Stern-Volmer equation, quantum yield and its determination, photosensitized reaction, energy transfer processes, Flash photolysis.

UNIT III

3. Solid State

(12 Hrs.)

Classification of solids: Crystalline and amorphous, covalent, ionic, metallic and molecular solids, Unit cell and space lattice, Crystallographic system, Bravais lattices, laws of crystallography, symmetry elements in crystals, X-ray diffraction by crystals, derivation of Bragg's law, determination of crystal structure of NaCl, KCl by use of powder method; Laue's method.

UNIT IV

4. Nuclear Chemistry

(11 Hrs.)

Introduction, Theories of radioactive decay, modes of decay, group displacement laws, Kinetics of radioactive decay, radioactive equilibrium, radioactive disintegration series, artificial radioactivity, artificial transmutation, Nuclear models, nuclear fission and nuclear fusion, radioactive detection: GM counter, Scintillation counter, applications of radioactivity. Tracer techniques,

Books Recommended:

1. Principles of Physical Chemistry, C.F. Prutton and S.H. Maron.
2. Physical Chemistry by G.W. Castellan.
3. Thermodynamics for Chemists, S.Glasstone.
4. Physical Chemistry, P.W. Atkins, 6th edn. Oxford.
5. Physical Chemistry, W.J. Moore.
6. Physical Chemistry: A Molecular Approach, D.A. MCMarrie & J. D. Simon.
1. Friedlander G., Kennedy J.W., Macias E.S. and Miller J.M., Nuclear and Radiochemistry, 3rd Edition, Pubs: John Wiley and Sons (1981).
2. Arnikar H.J., Essentials of Nuclear Chemistry, 2nd Edition, Pubs: Wiley Eastern Limited (1987),

B.Sc. (Hons. School) Chemistry (Semester-VI)
BHCH-145: Inorganic Chemistry-VI

3 Hrs./Week

45 hrs.

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UNIT-I

1. Organometallics:

(12 Hrs.)

Importance of organometallic chemistry in modern times: Definition and terminologies. 18-electron rule, Preparation of metal carbonyls, binary carbonyls, mixed metal polynuclear carbonyls, chemical reactions of metal carbonyls, nitrosyl compounds, Dinitrogen and dioxygen complexes, Metal Alkyls, Carbenes, Carbynes and Carbides,

2. Catalysis by Organometallic compounds:

Alelene Hydrogenation, Tolman Catalytic loop, Hydroformylation, Monsanto Acetic Acid Process, The Wacker Process, Ziegler-Natta catalysis

UNIT-II

(11 hrs)

3. Alkali metal and alkaline earth metal chelators: Macrocyclic ligands, macrocyclic effect, crown ethers and podands, coronands, cryptands, structure of 18 crown-6 complex with KNCS, ion cavity complex, effect of anion and cation type on complex structure, simultaneous complexation of metal ion and water or of two metal ions, sandwich formation, cryptands and their cation complexes, podands with aromatic donors and groups.

UNIT-III

4. Molecular Orbital Theory:

(10 Hrs)

Evidence for covalent character in Bonding, MOEL diagram for octahedral and tetrahedral complexes involving bonding, charge transfer transitions.

5. π Acid Ligands: Definition Carbon monoxide complexes, bonding in linear MCO groups,

polynuclear metal carbonyls, vibrational spectra, Reactions, carbonyl hydrides and halides. Metal-metal bonding metal-metal multiple bonding,

UNIT-IV

6. Bioinorganic Chemistry

12 Hrs.

Essential and trace elements in biological processes, Metal storage and transport: Fe, Cu, Zn and V, metalloporphyrins and special reference to haemoglobin and myoglobin. Biological role of alkali and alkaline earth metal ions with special reference to Ca^{2+} , Metallothioneins: transporting some toxic metals, Biological redox processes

Books:

1. Cotton F. A., Wilkinson G., Murillo C. A., Bochmann M., Advanced Inorg. Chemistry, 6th edn., Pubs: John Wiley India. (2003).
2. Gupta B. D. and Elias A. J. Basic Organometallic Chemistry. Pubs: University Press (2010)
3. Huheey J. E., Keiter E. A., Keiter R. L., Inorganic Chemistry : Principles of Structure and Reactivity; 4th edn, Pubs: Harper Collins, 1993.
4. B.E. Douglas and D.H. McDaniel, Concepts and Models of Inorganic Chemistry.
5. R. Hilgenfeld and W. Saengar, Topics in current chemistry Vol-II.
6. Elschenbroich C., Organometallics. Pubs: Wiley VCH Verlag GmbH.

3 Hrs./Week

45 hrs.

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- IV. Section-II, III, IV and V of paper will consist of EIGHT questions in total having TWO questions from each unit of the syllabus and each question carry 8 Marks.
- V. The students are required to attempt FIVE questions in all, taking ONE Compulsory question of section-I and one question from each section i.e. II, III, IV and V.

UNIT-I

1. Stereochemical Principles; conformation, steric and stereoelectronic effects (11 Hrs)

Enantiomeric relationships, Diastereomeric relationships, Dynamic stereochemistry, Prochiral relationships, Conformations of Acyclic molecules, cyclohexane derivatives, Rings other than six membered, Conformational effects on reactivity, angle strain and its effects on reactivity, Relationship between ring size and facility of ring closure. Torsional strain and related stereo electronic effects. Asymmetric synthesis. optical activity in absence of chiral carbon (biphenyls, allenes and spiranes), chirality due to helical shape. Stereochemistry of the compounds containing nitrogen, sulphur and phosphorus.

UNIT-II

2. Reactive Intermediates: Structure and Reactivity (6 Hrs)

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

Reaction of electron-deficient intermediates

Carbenes: Addition, insertion, rearrangement reactions; Wolff rearrangement and Arndt-Eistert synthesis.

Nitrines: generation of carboalkoxynitrenes from alkazidoformates.

3. Rearrangement reactions (5 Hrs)

Rearrangement of electron-deficient nitrogen compounds: Beckmann, Curtius, Hofmann, Schmidt rearrangements (Bayer-villiger rearrangement)

Rearrangement of Carbocations: Pinacoles, Tiffeneau-Demjanov rearrangement, Carbon-carbon bond formation involving carbocations, Polyolefin cyclisation, Fragmentation reactions.

UNIT-III

4. Oxidation Reactions

(6Hrs)

Oxidation of alcohols to aldehydes, ketones or carboxylic acids Transition metal oxidants: Cr(VI) Oxidants, MnO_2 and ruthenium tetraoxide. Other oxidants: DMSO-DCC, DMSO/ Ac_2O , Dimethyl sulphide/ N-chloro succinimide, DMSO/ Cl_2 . Addition of oxygen at carbon-carbon double bonds. Transition metal oxidants. KMnO_4 , OsO_4 . Cleavage of carbon-carbon double bonds by transition metal oxidants; KMnO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7/\text{Ac}_2\text{O}$, CrO_3/AcOH .

5. Reduction Reactions

(6 Hrs)

Reduction of Carbonyl group Addition of hydrogen. Catalytic hydrogenation, Group III hydride-transfer rearrangements. Reduction of carbonyl groups, halides, sulphonates, epoxides, acetylenes; Group IV hydride donors: Reduction of alcohols, aromatic ketones, Carboxylic acids and esters with silanes, Cannizzaro reaction. Hydrogen atom donors, reductive dehydrogenation of alkyl halides and acid chlorides and deoxygenation of alcohols with tributyl tin hydride. Dissolving metal reduction: addition of hydrogen, reductive deoxygenation of carbonyl groups, Clemmensen reduction, Wolff-Kishner reduction. Tosylhydrazone reduction, thioketal desulphurization.

UNIT-IV

6. Organic Synthesis via Enolates

(6 Hrs)

Acidity of α -hydrogens, alkylation of diethyl malonate and ethyl acetoacetate. Synthesis of ethylacetoacetate: the Claisen condensation. Keto-enol tautomerism of ethyl acetoacetate. Alkylation of 1,3-dithianes. Alkylation and acylation of enamines.

7. Coupling Reactions

(5 Hrs)

Reaction and mechanism of Diazo coupling, Glaser coupling, Heck reaction, Mcmurry reaction, Stille coupling, Suzuki coupling, Sonogashira reaction. Negishi and Hiyama coupling.

Suggested Books

1. Carey F.A. and Sundberg R.J., Advance Organic Chemistry, part A and part B, 2nd Edn., Pubs: Plenum Press, New York, 1984.
2. Morrison R.T. and Boyd P.S., Organic Chemistry, 5th Edn., Pubs: Allyn and Bacon Inc., Boston (1992).
3. March J., Advanced Organic Chemistry, 3rd Edn., Pubs: Wiley Interscience, 1985.
4. Streitwieser A., Jr. and Heathcock C.H., Introduction to Organic Chemistry 3rd Edn., Pubs: MacMillan Pub. Co., N.Y, 1992.
5. Isaccs N.S., Physical Organic Chemistry, Pubs: Longman Scientific & Technical, 1987.

B.Sc. (Hons. School) Chemistry (Semester-VI)
BHCH-147: Advance Physical Chemistry

3 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

Instructions for paper setters and candidates

- I. Examiner will make five sections of paper namely Section-I, II, III, IV and V
- II. Examiner will set total of NINE questions comprising ONE compulsory question of short answer type covering whole syllabi and TWO questions from each unit.
- III. Section-I will consist of eight short questions carrying 1 Mark each.
- IV. Section-II, III, IV and V of paper will consist of EIGHT questions in total having TWO questions from each unit of the syllabus and each question carry 8 Marks.
- V. The students are required to attempt FIVE questions in all, taking ONE Compulsory question of section-I and one question from each section i.e. II, III, IV and V.

UNIT-I

1. Molecular Interactions and other topics:

(11 Hrs.)

Electrical properties: Polar and Non polar Crystals, Capacitance, Dielectric Properties, Dipole moment, polarization, polarizability and electrical susceptibility, Clausius Mossoti and Debye Equations.

Magnetic properties: magnetic susceptibility, permanent magnetic moment, induced magnetic moment. Liquid crystals, difference between liquid crystals solid and liquid, classification, structure of nematic and cholestric phases, movement in liquids, Ionic solids.

Molecular reaction dynamics: Collision theory, Diffusion controlled reactions Activated complex theory; reaction co-ordinates and transition state, formation and decay of the activated complex, Derivation and use of Eyring equation. Thermodynamic aspects; reactions between ions.

UNIT-II

2. Helium atom, Schrödinger Equation

(11 Hrs.)

Approximate solutions, variation method and its application to ground state of hydrogen atom, Pauli exclusion principle, two electron spin functions, Slater determinants and Pauli principle, excited state of helium atom, Lithium atom.

UNIT-III

3. Periodic table, Atomic term symbols

(11 Hrs.)

Spin-orbit coupling, vector model of atom, Hund's rules, atomic spectra and selection rules, j-j coupling. Molecular electronic structure, Born-Oppenheimer approximation, ionic and covalent bonding. The hydrogen molecule ion, Molecular orbital description of hydrogen molecule. Other homonuclear diatomic molecules, heteronuclear diatomic molecule; polyatomic molecules. Huckel molecular orbital theory, unsaturated molecules and aromatic hydrocarbons. Metals, insulators and semiconductors, Valence bond theory.

UNIT-IV

4. Statistical Thermodynamics

(12 Hrs.)

Molecular energy levels and the Boltzmann distribution: configurations and weights, most probable configuration; the molecular partition function, physical interpretation of the partition function. The canonical ensemble, canonical partition function and its relation to molecular partition function for independent particles. The statistical entropy; heat, work and entropy; entropy and partition function, entropy of a monoatomic gas. Factorization of partition function; calculation of translational, rotational vibrational and electronic contributions, the overall partition function.

Suggested Books

1. Physical Chemistry by P.W. Atkins 7th Edn. (1994).
2. Physical Chemistry by I.N. Levine 4th ed. (1993).
3. Physical Chemistry by Donald C. McQuarrie (1983).
4. Introductory Quantum Chemistry by A.K. Chandra (1988).
5. Molecular Quantum Mechanis by P.W. Atkins and R. S. Friedman, Oxford University Press, 2004.

FURTHER READING:

1. Physical Chemistry by G.M.B. Barrow V. Edition (1985).
2. Physical Chemistry by Walter J. Moore V.Ed. (1976).
3. Physical Chemistry by Alberty and Silbey, Wiley (1992).

B.Sc. (Hons. School) Chemistry (Semester-VI)
BHCH-148: Advance Chemistry

3 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

Instructions for paper setters and candidates

- I. Examiner will make five sections of paper namely Section-I, II, III, IV and V
- II. Examiner will set total of NINE questions comprising ONE compulsory question of short answer type covering whole syllabi and TWO questions from each unit.
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UNIT-I

1. Elementary Quantum Chemistry:

(11Hrs.)

Historical background, classical ideas of energy and particle trajectory. Blackbody radiation and Planck's hypothesis of quantization of energy, photoelectric effect. Line spectra of atoms, diffraction of electrons, wave-particle duality. De Broglie's relation Heisenberg's uncertainty principle.

Schrödinger-wave equation, concept of wave function (ψ) physical significance of ψ and ψ^2 , normalization of ψ constraints on ψ . Free particle, particle in a one dimensional box, translational energy, energy levels, quantization of energy, wave functions for particle in a box, comparison with classical theory, concepts of orthogonality and orthonormality. Kronecker delta. Particle in a three dimensional box, cubical box and concept of degeneracy of energy levels. Operators, definitions, linear operators, eigenvalue operators, operators for various observables, concept of Hermitian operators, orthogonality. Postulates of quantum mechanics, time dependent Schrödinger equation, expectation values, applications of particle in a box model.

UNIT-II

(12 Hrs.)

2. Quantum Mechanics II. Vibrational motion, classical one-dimensional harmonic oscillator. Quantum mechanical harmonic oscillator, Energy and energy levels of simple harmonic oscillator (no derivation), wave functions for simple harmonic oscillator, tunnel effect. Hermite polynomials as even and odd functions, average kinetic energy and average potential energy of simple harmonic oscillator, virial theorem.

Rotational motion: two dimensional rotation (particle on a ring), energy levels, angular momentum and position of particle on a ring. Rotation of a particle in three dimensions, Schrödinger equation and its

elementary solution, spherical harmonics, applications to diatomic molecule (rigid rotator). Schrödinger equation for hydrogen-like atoms, elementary discussion of its solution, energy levels for hydrogen like atoms, wave functions for hydrogen atom, electron spin, concept of spin orbitals, spectral selection rules for one-electron atoms, spectrum of hydrogen atom.

UNIT III

3. Inorganic Polymers

(11Hrs.)

Introduction, Types of inorganic polymers

Polyphosphazenes: Introduction, synthesis route, ring opening polymerization mechanism, molecular structure of phosphazene, nature of bonding in phosphazene, structure property relationship (crystalline vs. amorphous polymers, hydrophobic vs. hydrophilic, water stable vs. water erodible and material structure imposed by side group stacking) , advanced elastomers, polyphosphazene as biomedical material

UNIT-IV

4. Silicones and polysiloxanes

(11 Hrs.)

Introduction, Nomenclature, Preparation of monomers, ring opening polymerization, copolymerization, structural features, formation of cross linked silicones, general properties, reactive homopolymers, random copolymers, block copolymers, silicones elastomers, silicones resins, applications.

Books Recommended

1. James E. Mark, Harry R. Allcock, Robert West, Inorganic Polymers
2. Malcolm P.Stevens, Polymer Chemistry an Introduction, Third edition Oxford University Press
3. P.Ghosh, Polymer science and Technology of Plastics and Rubbers
4. Molecular Quantum Mechanics by P.W. Atkins and R. S. Friedman,Oxford University Press, 2004.
5. Introduction to Nuclear Chemistry by H.J.Arnikaar, New Age Publishers (1981)

4 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internal Assessment)

1. Determine nickel (II) in a given sample gravimetrically using dimethylglyoxime.
2. Determine copper (II) in a given sample gravimetrically using ammonium/sodium thiocyanate.
3. Estimate the iron as its ferric oxide from a given solution of ferrous ammonium sulfate gravimetrically.
4. Estimate chromium (III) as its lead chromate.
5. Estimate lead as its lead molybdate gravimetrically.
6. Estimate cobalt as mercury tetraisothiocyanatocobalt (II) $[\text{HgCo}(\text{NCS})_4]_n$.
7. Determine silver (I) as its chloride gravimetrically.
8. Determine barium (II) as its chromate gravimetrically.
9. Determine cadmium (II) as $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_2]$ gravimetrically.

Book: Vogel's Quantitative Inorganic Analysis

B.Sc. (Hons. School) Chemistry (Semester-VI)
BHCH-150: Physical Lab III

4 Hrs./Week

45 hrs.

Max. Marks: 40+10(Internl Assessment)

Conductometry

1. Determination of the solubility of a sparingly soluble substance.
2. Determination of the degree of hydrolysis of NH_4Cl and CH_3COONa .
3. To study the kinetics of saponification of ethyl acetate by sodium hydroxide.

Potentiometry

4. Potentiometric titrations of dibasic acid, oxalic acid and malonic acid with base.
5. To determine potentiometrically the solubility and solubility product of a sparingly soluble salt.
6. Determination of heat of reaction, equilibrium constant and other thermodynamic functions of the reaction.



Polarimetry

7. To study the kinetics of inversion of cane sugar by means of polarimetry.

Chemical Kinetics

8. To determine activation energy of a reaction by studying its temperature dependence.
9. To study the reaction between potassium iodide and potassium peroxodisulphate. .

Determination of Molecular Masses by Cryoscopy

10. To determine molar depression constant (K_f) for a given solvent.
11. To determine cryoscopically the apparent degree of dissociation of KCl and $\text{Ca}(\text{NO}_3)_2$ in water.

pH-metry:

12. To titrate a base against a strong acid and determine the ionization constant of the weak base