UNIVERSITY OF CALCUTTA

SYLLABI

FOR

THREE-YEAR B.Sc. HONOURS & GENERAL COURSES OF STUDIES

Chemistry

2010

w.e.f. 2010-2011

Chemistry Hons: Syllabus Scheme in modular form

Course names and distribution

PART – I (Year 1), total marks = 200 (Theory = 150, Practical = 50)

CHT	11a, 11b,	each 25 marks, Theory
CHT	12a, 12b,	each 25 marks, Theory
CHT	13a, 13b,	each 25 marks, Theory
CHP	14a+14b,	50 marks, Practical

PART – II (Year 2), total marks = 200 (Theory = 150, Practical = 50)

CHT	21a, 21b,	each 25 marks, Theory
CHT	22a, 22b,	each 25 marks, Theory
CHT	23a, 23b,	each 25 marks, Theory
CHP	24a+24b,	50 marks, Practical

PART – III (Year 3), total marks = 400 (Theory = 250, Practical = 150)

CHT	31a, 31b, 31c, 31d,	each 25 marks, Theory
CHT	32a, 32b, 32c,	each 25 marks, Theory
CHT	33a, 33b, 33c,	each 25 marks, Theory
CHP	34a, 34b,	25 and 50 marks, Practical
CHP	35a, 35b,	25 and 50 marks, Practical

Abbreviations:
CHP: Chem Hons Practical; CHT: Chem Hons Theory
First digit refers to year, second to paper.

Each CHT Exam = 1 hr for 25 marks, 2 hr for 50 marks, etc.
Each CHP Exam = 2-3 hr for 25 marks, 4 hr for 50 marks on each day

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Notes:
1. Each Theory module of 25 marks contains units I (marks = 15) and II (marks = 10).

2. Number of class hours = 25-35 for a 25-mark Theory module, 70-80 for a 25-mark Practical module.

Chemistry Hons: Course Description
Year 1
PART – I

CHT 11a

Unit-I. Radioactivity and Atomic Structure

Nuclear stability and nuclear binding energy. Nuclear forces: meson exchange theory. Nuclear models (elementary idea): Concept of nuclear quantum number, magic numbers. Nuclear Reactions: Artificial radioactivity, transmutation of elements, fission, fusion and spallation. Nuclear energy and power generation. Separation and uses of isotopes. Radio chemical methods: principles of determination of age of rocks and minerals, radio carbon dating, hazards of radiation and safety measures.

Bohr's theory to hydrogen-like atoms and ions; spectrum of hydrogen atom. Quantum numbers. Introduction to the concept of atomic orbitals; shapes, radial and angular probability diagrams of s, p and d orbitals (qualitative idea). Many electron atoms and ions: Pauli's exclusion principle, Hund's rule, exchange energy, Aufbau principle and its limitation. Electronic energy level diagram and electronic configurations of hydrogen-like and polyelectronic atoms and ions. Term symbols of atoms and ions for atomic numbers < 30.

Unit-II. Chemical periodicity I

Periodic table, group trends and periodic trends in physical properties. Classification of elements on the basis of electronic configuration. Modern IUPAC Periodic table. General characteristic of s, p, d and f block elements. Position of hydrogen and noble gases in the periodic table.

Effective nuclear charges, screening effects, Slater's rules, atomic radii, ionic radii (Pauling's univalent), covalent radii. Ionization potential, electron affinity and electronegativity (Pauling's, Mulliken's and Allred-Rochow's scales) and factors influencing these properties. Inert pair effect. Group trends and periodic trends in these properties in respect of s-, p- and d-block elements.

CHT 11b

Unit-I. Chemical Bonding and structure

Ionic bonding: Size effects, radius ratio rules and their limitations. Packing of ions in crystals, lattice energy, Born-lande equation and its applications, Born-Haber cycle and its applications. Solvation energy, polarizing power and polarizability, ionic potential, Fazan's rules. Defects in solids (elemementary idea).

Covalent bonding: Lewis structures, formal charge. Valence Bond Theory, directional character of covalent bonds, hybridizations, equivalent and non-equivalent hybrid orbitals, Bent's rule, VSEPR theory, shapes of molecules and ions containing lone pairs and bond pairs (examples from main groups chemistry), Partial ionic Character of covalent bonds, bond moment, dipole moment and electronegativity differences. Concept of resonance, resonance energy, resonance structures

Unit-II. Acid-Base reactions

Acid-Base concept: Arrhenius concept, theory of solvent system (in H_2O, NH_3, SO_2 and HF), Bronsted-Lowry's concept, relative strength of acids, Pauling rules. Amphoterism. Lux-Flood concept, Lewis concept. Superacids, HSAB principle. Acid-base equilibria in aqueous solution and p^H. Acid-base neutralisation curves; indicator, choice of indicators.

CHT 12a

Unit I. Acyclic stereochemistry

Representation of molecules in saw horse, Fischer, flying-wedge and Newman formulae and their inter translations, symmetry elements, molecular chirality.

Configuration: stereogenic units i) stereocentres: systems involving 1, 2, 3 centres, stereogenicity, chirotopicity. pseudoasymmetric (D/L and R/S descriptor, threo/erythro and syn/anti nomenclatures (for aldols) ii) stereoaxis: chiral axis in allenes & biphenyls, R/S descriptor; cis/trans, syn/anti, E/Z descriptors (for C=C, C=N).

Optical activity of chiral compounds: specific rotation, optical purity (enantiomeric excess), racemic compounds, racemisation (through cationic and anionic and radical intermediates), resolution of acids, bases and alcohols via diastereomeric salt formation.

Topicity of ligands and faces (elementary idea): Pro-R, Pro-S and Re /Si descriptors.

Conformation: Conformational nomenclature, eclipsed, staggered, gauche and anti; dihedral angle, torsion angle, energy barrier of rotation, relative stability of conformers on the basis of steric effect, dipole-dipole interaction, H-bonding; conformational analysis of ethane, propane, n-butane, haloethane, 1,2-haloethane, 1,2-glycol, 1,2-halohydrin; invertomerism of trialkylamines.

Unit II. Bonding and physical properties

Valence bond theory: concept of hybridisation, resonance (including hyperconjugation), orbital pictures of bonding (sp^3, sp^2, sp: C-C, C-N & C-O system). Inductive effect, bond polarization and bond polarizability, steric effect, steric inhibition of resonance.

MO theory: sketch and energy levels of MOs of i) acyclic p orbital system (C=C, conjugated diene and allyl systems) ii) cyclic p orbital system (neutral system: [4], [6] annulenes; charged system: 3,4,5-ring system); Frost diagram, Huckel's rules for aromaticity & antiaromaticity; homoaromaticity.

Physical properties: bond distance, bond angles, mp/bp & dipole moment in terms of structure and bonding (covalent & non covalent). Heat of hydrogenation and heat of combustion.

CHT 12b

Unit I. General treatment of reaction mechanism

Mechanistic classification: ionic, radical and pericyclic; heterolytic bond cleavage and heterogenic bond formation, homolytic bond cleavage and homogenic bond formation; representation of mechanistic steps using arrow formalism.

Reactive intermediates: carbocations (cabenium and carbonium ions), carbanions, carbon radicals, carbenes – structure using orbital picture, electrophilic/nucleophilic behaviour, stability, generation and fate (elementary idea)

Reaction thermodynamics: free energy and equilibrium, enthalpy and entropy factor, intermolecular & intramolecular reactions. Application of thermodynamic principles in tautomeric equilibria [keto-enol tautomerism, composition of the equilibrium in different systems (simple carbonyl, 1,3 and 1,2- dicarbonyl systems, phenols and related system), substituent and solvent effect].

Concept of acids and bases: effect of structure, substituent and solvent on acidity and basicity.

Reaction kinetics: transition state theory, rate const and free energy of activation, free energy profiles for one step and two step reactions, catalyzed reactions, kinetic control and thermodynamic control of reactions, isotope effect , primary kinetic isotopic effect (k_H/k_D), principle of microscopic reversibility, Hammond postulate.

Unit II. Nucleophilic substitution reactions

Sustitution at sp^3 centre - Mechanism: S_N1, S_N2, S_N2', S_Ni mechanisms, effect of solvent, substrate structure, leaving group, nucleophiles including ambident nucleophiles (cyanide & nitrite) substitution involving NGP; relative rate & stereochemical features [systems: alkyl halides, allyl halides, alcohols, ethers, epoxides].

Halogenation of alkanes and carbonyls.

Substitution at sp^2 carbon (carbonyl system) - Mechanism: $B_{AC}2$, $A_{AC}2$, $A_{AC}1$, $A_{AL}1$ (in connection to acid and ester). Systems: amides, anhydrides & acyl halides [formation and hydrolysis]

CHT 13a

Unit I. Kinetic theory and the gaseous state

Concept of pressure and temperature. Nature of distribution of velocities in one, two and three dimensions. Maxwell's distribution of speeds. Kinetic energy distribution in one, two and three dimensions, calculations of average, root mean square and most probable values in each case; calculation of number of molecules having energy $\geq \varepsilon$, Principle of equipartition of energy and its application to calculate the classical limit of molar heat capacity of gases.

Collision of gas molecules; collision diameter; collision number and mean free path; frequency of binary collisions (similar and different molecules); wall collision and rate of effusion.

Deviation of gases from ideal behaviour; compressibility factor; Andrew's and Amagot's plots; van der Waals equation and its characteristic features. Existence of critical state. Critical constants in terms of van der Waals constants. Law of corresponding state and significance of second virial coefficient. Boyle temperature. Intermolecular forces (Debye, Keesom and London interactions; Lennard-Jones potential, elementary idea).

Unit II. Thermodynamics – I

Importance and scope, definitions of system and surroundings; type of systems (isolated, closed and open). Extensive and intensive properties. Steady state and equilibrium state. Concept of thermal equilibrium and the zeroth-law of thermodynamics. Thermodynamic coordinates, state of a system, equation of state, state functions and path functions. Partial derivatives and cyclic rule. Concept of heat and work (IUPAC convention). Graphical explanation of work done during expansion and compression of an ideal gas. Reversible and irreversible processes and work done.

First law of thermodynamics, internal energy (U) as a state function. Enthalpy as a state function. Heat changes at constant volume and constant pressure; relation between C_P and C_V using ideal gas and van der Waals equations. Joule's experiment and its consequence. Explanation of term $(\delta U/\delta V)_T$. Isothermal and adiabatic processes.

Thermochemistry: heat changes during physicochemical processes at constant pressure/volume. Kirchoff's relations. Bond dissociation energies. Changes of thermodynamic properties in different chemical changes.

CHT 13b

Unit I. Thermodynamics – II

Second law of thermodynamics – need for a Second law. Concept of heat reservoirs and heat engines. Kelvin – Planck and Clausius statements and equivalence of the two statements with entropic formulation. Carnot cycle and refrigerator. Carnot's theorem; thermodynamic scale of temperature.

Physical concept of entropy. Entropy as a measure of the microscopic but not macroscopic disorder. Values of §dQ/T and Clausius inequality. Entropy change of systems and surroundings for various processes and transformations. Entropy change during the isothermal mixing of ideal gases. Entropy and unavailable work. Auxiliary state functions (G and A) and their variation with T, P and V. Criteria for spontaneity and equilibrium.

Thermodynamic relations: Maxwell's relations, thermodynamic equation of state. Gibbs- Helmholtz equation, Joule-Thomson experiment and its consequences; inversion temperature. Joule-Thomson coefficient for a van der Waals gas. General heat capacity relations.

Unit II. Chemical kinetics

Introduction of reaction rate in terms of extent of reaction; rate constants, order and molecularity of reactions. Reactions of zero order, first order, second order and fractional order. Pseudo first order reactions (example using acid catalyzed hydrolysis of methyl acetate). Determination of order of a reaction by half-life and differential method. Rate-determining and steady-state approximation – explanation with suitable examples.

Opposing reactions, consecutive reactions and parallel reactions (with explanation of kinetic and thermodynamic control of products; all steps first order).

Temperature dependence of rate constant: Arrhenius equation, energy of activation. Homogeneous catalysis with reference to acid-base catalysis. Enzyme catalysis: Michaelis-Menten equation, turn-over number.

CHP 14a+14b

Qualitative inorganic analysis of mixtures containing not more than 4 radicals from the following:

Cation Radicals: Na^+, K^+, Ca^{+2}, Sr^{+2}, Ba^{+2}, Al^{+3}, Cr^{+3}, Mn^{+2}, Fe^{+3}, Co^{+3}, Ni^{+3}, Cu^{+2}, Zn^{+2}.
Anion Radicals: F^-, Cl^-, Br^-, BrO_3^-, I^-, SCN^-, S^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, NO_3^-, NO_2^-, PO_4^{3-}, BO_3^{3-}, CrO_4^{2-}/ $Cr_2O_7^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$.
Insoluble Materials: Al_2O_3, Fe_2O_3, Cr_2O_3, SnO_2, $SrSO_4$, $BaSO_4$, CaF_2.

Experiment A: Preliminary Tests for acid and basic radicals in given samples.
Experiment B: Wet tests for Acid and Basic radicals in given samples.
Experiment C: Confirmatory tests.

Notes:
At least 10 unknown samples are to be analyzed by each student during the laboratory session. Oxide, hydroxide, carbonate and bicarbonate should not be reported as radicals.

Chemistry Hons: Course Description

Year 2

PART – II

CHT 21a

Unit I. Chemical Periodicity II

General trends of variation of electronic configuration, elemental forms, metallic nature, magnetic properties (if any), catenation and catalytic properties (if any), oxidation states, inert pair effect (if any), aqueous and redox chemistry in common oxidation states, properties and reactions of important compounds such hydrides, halides, oxides, oxy-acids (if any), complex chemistry (if any) in respect of the following elements:

(i) s-block elements: Li-Na-K, Be-Mg-Ca-Sr-Ba.

(ii) p-block elements: B-Al-Ga-In-Tl, C-Si-Ge-Sn-Pb, N-P-As-Sb-Bi, O-S-Se-Te, F-Cl-Br-I, He-Ne-Ar-Kr-Xe

Unit II. Other Types of Bonding

Molecular orbital concept of bonding (elementary pictorial approach):sigma and pi-bonds, multiple bonding, MO diagrams of H_2, F_2, O_2, C_2, B_2, CO, NO, CN^-, HF, and H_2O; bond orders, bond lengths, Walsh Diagram. Coordinate bonding: Lewis acid-base adducts (examples), double salts and complex salts, Werner theory of coordination compounds. Ambidentate and polydentate ligands, chelate complexes. IUPAC nomenclature of coordination compounds (up to two metal centers). Coordination numbers, constitutional isomerism. Stereoisomerism in square planar and octahedral complexes.

Hydrogen bonding and its effects on the physical properties of compounds of the main group elements.

Metallic bonding: qualitative idea of band theory, conducting, semi conducting and insulating properties with examples from main group elements.

CHT 21b

Unit I. Chemistry of s- and p-block Elements

(i) Structure, bonding and reactivity of B_2H_6; $(SN)_x$ with x = 2, 4; phosphazines; interhalogens. (ii) Structure of borates, silicates, polyphosphates, borazole, boron nitride, silicones, thionic acids. (iii) Reactivity of polyhalides, pseudo halides, fluorocarbons, freons and NO_x with environmental effects. (iv) Chemistry of hydrazine, hydroxylamine, N_3^-, thio- and per-sulphates.

Noble gases from air; oxides, fluorides and oxofluorides of xenon; chemical and photochemical reactions of ozone.

Unit II. Precipitation and Redox Reactions

Solubility product principle, common ion effect and their applications to the precipitation and separation of common metallic ions as hydroxides, sulfides, phosphates, carbonates, sulfates and halides. Ion-electron method of balancing equation of redox reaction. Elementary idea on standard redox potentials with sign conventions, Nernst equation (without derivation). Influence of complex formation, precipitation and change of pH on redox potentials; formal potential. Feasibility of a redox titration, redox potential at the equivalence point, redox indicators. Redox potential diagram (Latimer and Frost diagrams) of common elements and their applications. Disproportionation and comproportionation reactions (typical examples).

CHT 22a

Unit I. Addition reactions

Electrophilic addition to C=C: Mechanism, reactivity, regioselectivity and stereoselectivity. Reactions: halogenations, hydrohalogenation, hydration, hydrogenation, epoxidation, hydroxylation, ozonolysis, electrophiilic addition to diene (conjugated dienes and allenes). Radical addition: HBr addition. Dissolving metal reduction of alkynes and bezenoid aromatics (Birch). Pericyclic addition: Diels-Alder reaction. Addition of singlet and triplet carbenes.

Nucleophilic addition to C=O: Mechanism, reactivity, equilibrium and kinetic control. Reactions with alcohols, amines, thiols, HCN, bisulfate, Wittig reaction. Carbonyl Reduction: hydride addition, Wolff-Kishner reduction, dissolving metal (Bouveault-Blanc reduction, Clemmensen Reduction), Cannizzaro reaction, Tischenko reaction, aldol condensation, benzoin condensation. Hydrolysis of nitriles and isonitriles. Nucleophilic addition to α,β-unsaturated carbonyl system (general principles).

Unit II. Elimination and aromatic substitution

Elimination - Mechanisms: E1, E2 and E1cB; reactivity, orientation (Saytzeff/ Hofmann) and stereoselectivity; substitution vs elimination,

Electrophilic aromatic substitution: Mechanisms, orientation and reactivity. Reactions: nitration, nitrosation, sulfonation, halogenation, Friedel-Crafts reactions, one-carbon electrophiles (reactions: chloromethylation, Gatterman-Koch, Gatterman, Hoesch, Vilsmeier-Haack reaction, Reimer-Tiemann, Kolbe-Schmidt).

Nucleophilic aromatic substitution: Addition-elimination mechanism, S_N1 mechanism, benzyne mechanism.

CHT 22b

Unit I. Nitrogen compounds and Organometallics

Nitrogen compounds: amines (aliphatic & aromatic) [preparation, separation and identification of primary, secondary and tertiary amines], E. Clarke reaction, enamines, Mannich reaction, diazomethane, diazoacetic ester, aromatic nitro compounds, aromatic diazonium salts, nitrile and isonitrile.

Organometallics: preparation of Grignard reagent and organo lithium. Reactions: addition of Grignard and organo lithium to carbonyl compounds, substitution on -COX, conjugate addition by Gilman cuprates, Reformatsky reaction.

Unit II. Reactions: Rearrangements

1,2-shift: Rearrangement to electron-deficient carbon (Wagner-Meerwein rearrangement, pinacol rearrangement, dienone-phenol; Wolff rearrangement in Arndt-Eistert synthesis, benzil-benzilic acid rearrangement).

Electron-deficient nitrogen (Beckmann rearrangement, Schmidt rearrangement, Hofmann rearrangement, Lossen rearrangement, Curtius rearrangement).

Electron-deficient oxygen (Baeyer-Villiger oxidation, hydroperoxide rearrangement (cumene hydroperoxide-phenol rearrangement), Dakin reaction.

Aromatic rearrangements [migration from oxygen to ring carbon (Fries rearrangement, Claisen rearrangement); migration from nitrogen to ring carbon (Hofmann-Martius rearrangement**,** Fischer-Hepp rearrangement, N-azo to C-azo rearrangement, Bamberger rearrangement, Orton rearrangement, benzidine rearrangement.

CHT 23a

Unit I. Thermodynamics and Equilibrium

Open system, chemical potential and activity, partial molar quantities, chemical potential in terms of Gibb's free energy and other thermodynamic state functions and its variation with temperature and pressure. Gibbs-Duhem equation; fugacity of gases and fugacity coefficient.

Thermodynamic conditions for equilibrium, degree of advancement. van't Hoff's reaction isotherm (deduction from chemical potential). Explanation of the free energy versus degree of advancement plot . Equilibrium constant and standard Gibbs free energy change. Definitions of K_P, K_C and K_x ; van't Hoff's reaction isobar and isochore from different standard states. Shifting of equilibrium due to change in external parameters e.g. temperature and pressure. Le Chatelier's principle and degree of advancement.

Activity and activity coefficients of electrolyte / ion in solution. Debye-Huckel limiting law (statement and applications only). Solubility equilibrium and influence of common ions and indifferent ions thereon. P^H, buffer solution, buffer capacity, salt hydrolysis (detailed treatment).

Unit II. Liquid State and Viscosity of Fluids

Nature of the liquid state, (short range order and long range disorder). Vapor pressure. Surface tension, surface energy, excess pressure, capillary rise and measurement of surface tension. Work of cohesion and adhesion, spreading of liquid over other surface. Vapour pressure over curved surface. Temperature dependence of surface tension.

General features of fluid flow (streamline flow and turbulent flow). Reynold number, nature of viscous drag for streamline motion, Newton' equation, viscosity coefficient. Poiseuille's equation (with derivation), temperature dependence of viscosity, principle of determination of viscosity coefficient of liquids by falling sphere method.

Viscosity of gases vs. liquids and kinetic theory of gas viscosity.

CHT 23b

Unit I. Quantum Chemistry I

Wave-particle duality, light as particles: photoelectric and Compton effects; electrons as waves and the de Broglie hypothesis.

Elementary concepts of operators, eigenfunctions and eigenvalues. Linear operators. Commutation of operators, fundamental commutator and uncertainty relation (without proof). Expectation value. Hermitian operator. Schrodinger time-independent equation: nature of the equation, acceptability conditions imposed on the wave functions and probability interpretations of wave function.

Particle in a box: setting up of Schrodinger equation for one-dimensional box and its solution. Comparison with free particle eigenfunctions and eigenvalues. Properties of PB wave functions (normalisation, orthogonality, probability distribution). Expectation values of x, x^2, p_x and p_x^2 and their significance in relation to the uncertainty principle. Extension of the problem to two and three dimensions and the concept of degenerate energy levels.

Unit II. Electrochemistry

Conductance and measurement of conductance, cell constant, specific conductance and molar conductance. Variation of specific and equivalent conductance with dilution for strong and weak electrolytes. Kohlrausch's law of independent migration of ions, ion conductance and ionic mobility. Equivalent and molar conductance at infinite dilution and their determination for strong and weak electrolytes. Ostwald's dilution law. Debye-Huckel model (physical idea only). Application of conductance measurement (determination of solubility product and ionic product of water). Conductometric titrations. Determination of transport number by moving boundary method.

Types of electrochemical cells and examples , cell reactions, emf and change in free energy, ΔH and ΔS of cell reactions from emf measurements. Thermodynamic derivation of Nernst equation. Standard cells. Half-cells / electrodes, different types of electrodes (with examples). Standard electrode potential (IUPAC convention) and principles of its determination. Types of concentration cells. Liquid junction potential and its minimisation.

Glass electrode and determination of pH of a solution. Potentiometric titrations: acid-base and redox.

CHP 24a

Analytical Estimations

1. Iodometry/iodimetry: Vitamin C.
2. Permanganometry: Fe^{III} and Mn^{II} in a mixture.
3. Dichromatometry: Fe^{III} and Cu^{II} in a mixture; Fe^{III} and Cr^{III} in a mixture.
4. Complexometry (EDTA): $CaCO_3$ and $MgCO_3$ in mixture; Mg^{II} and Zn^{II} in mixture.

CHP 24b

Instrumental Estimations

1. Spectrophotometry: Mn^{II}; $p^{K}{}_{in}$.
2. Conductometry: HCl-AcOH mixture; dibasic acid.
3. Potentiometry: Halide ion.
4. p^{H}-metry: HCl-AcOH mixture; dibasic acid.
5. Ion-exchanger: Cation content of a sample by cation exchanger

Chemistry Hons: Course Description

Year 3

PART – III

CHT 31a

Unit I. Chemistry of coordination compounds

Isomerism, reactivity and stability: Determination of configuration of cis- and trans- isomers by chemical methods. Labile and inert complexes, substitution reaction on square planer complexes, trans effect (example and applications). Stability constants of coordination compounds and their importance in inorganic analysis.

Structure and bonding: VB description and its limitations. Elementary Crystal Field Theory: splitting of d^n configurations in octahedral, square planar and tetrahedral fields, crystal field stabilization energy in weak and strong fields; pairing energy. Jahn-Teller distortion. Metal-ligand bonding (MO concept, elementary idea), sigma- and pi-bonding in octahedral complexes (qualitative pictorial approach) and their effects on the oxidation states of transitional metals (examples).

Magnetism and Colour: Orbital and spin magnetic moments, spin only moments of d^n ions and their correlation with effective magnetic moments, including orbital contribution; quenching of magnetic moment: super exchange and antiferromagnetic interactions (elementary idea with examples only); d-d transitions; L-S coupling; qualitative Orgel diagrams for $3d^1$-$3d^9$ ions and their spectroscopic ground states; selection rules for electronic spectral transitions; spectrochemical series of ligands; charge transfer spectra (elementary idea).

Unit II. Chemistry of d- and f- block elements

General comparison of 3d, 4d and 5d elements in term of electronic configuration, elemental forms, metallic nature, atomization energy, oxidation states, redox properties, coordination chemistry, spectral and magnetic properties.

f-block elements: electronic configuration, ionization energies, oxidation states, variation in atomic and ionic (3+) radii, magnetic and spectral properties of lanthanides, comparison between lanthanide and actinides, separation of lanthanides (by ion-exchange method).

Chemistry of some representative compounds: $K_2Cr_2O_7$, $KMnO_4$, $K_4[Fe(CN)_6]$, $K_2[Ni(CN)_4]$, H_2PtCl_6, $Na_2[Fe(CN)_5NO]$.

CHT 31b

Unit I. Organometallic Compounds

18-electron rule and its applications to carbonyls (including carbonyl hydrides and carbonylates), nitrosyls, cyanides, and nature of bonding involved therein. Simple examples of metal-metal bonded compounds and metal clusters. Metal-olefin complexes: zeises salt (preparation, structure and bonding), Ferrocene (preparation, structure and reactions). Hapticity(η) of organometallic ligands, examples of mono tri and penta-hapto cyclopentadienyl complexes. Simple examples of fluxional molecules. Coordinative unsaturation: oxidative addition and insertion reactions. Homogeneous catalysis by organometallic compounds: hydrogenation, hydroformylation and polymerization of alkenes (Ziegler-Natta catalysis).

Unit II. Bioinorganic Chemistry

Elements of life: essential major, trace and ultratrace elements. Basic chemical reactions in the biological systems and the role of metal ions (specially Na+, K+, Mg2+, Ca2+, Fe3+/2+, Cu2+/+, and Zn2+).Metal ion transport across biological membrane Na+-ion pump, ionophores. Biological functions of hemoglobin and myoglobin, cytochromes and ferredoxins, carbonate bicarbonate buffering system and carbonicanhydrase. Biological nitrogen fixation, Photosynthesis: Photosystem-I and Photosystem-II. Toxic metal ions and their effects, chelation therapy (examples only), Pt and Au complexes as drugs (examples only), metal dependent diseases.

CHT 31c

Unit I. Electrochemical and spectral analysis, and analytical separation

Electrochemical methods: Conductometry, Potentiometry, pH-metry. Electrogravimetry, Coulometry. Spectrophotometry: Lambert-Beer law, Limits to Beer's law, Principle of spectrophotometric estimation of iron, manganese and phosphorous. Principles and instrumentations of atomic absorption and atomic emission spectrometry; estimation of sodium and potassium in water samples.

Ion exchange resins and their exchange capacities, principle and simple applications of ion exchange separation. Chromatographic separations: General description and classification of chromatographic methods, thin layer, paper and column chromatographic techniques and their simple applications, Rf-values and their significance, elution in column chromatography, migration rates of solutes, band broadening and column efficiency, column resolution.

Unit 2. Statistical methods in chemical analysis and environmental analysis

Errors in chemical analysis: Accuracy and precision of measurements, determinate indeterminate, systematic and random errors in chemical analysis with examples, absolute and relative errors; source, effect and detection of systematic errors; distribution of random errors, normal error curve, standard deviations, standard deviation of calculated results- sum or difference, product or quotient, significant figures, rounding and expressing results of chemical computations.

Principles for determination of BOD, COD, DO, TDS, in water samples.
Detection and estimation of As, Hg, Cd, Pb, NH_4^+, and F^-, NO_3^-, NO_2^- in water sample.
Detection, collection and principles of estimation of CO, NOx, SO_2, H_2S and SPM in air samples.

CHT 31d

Unit I: Gravimetric and tritimetric methods of analysis

Requirements of gravimetry: properties of precipitates and precipitating regents, particle size and filterability of precipitates, colloidal and crystalline precipitates coprecipitation and post-precipitation drying and ignition of precipitates, principles of gravimetric estimation of chloride, phosphate, zinc, iron, aluminum and magnesium singly.

Primary and secondary standard substances in acid-base, redox, complexometric (EDTA) and argentometric titrations. Principle and application of redox tritimetric estimation based on the use of the following reagents: $KMNO_4$, $K_2Cr_2O_7$, I_2, $Na_2S_2O_3.5H_2O$, $KH(IO_3)_2$ and $KBrO_3$. Principle of argentimetric estimation of chloride using adsorption indicators.

Principle of complexometric EDTA titration, metal ion indicators (examples), masking and demasking reactions, estimation of Cu-Zn, Fe-Al and Ca-Mg mixture by EDTA titration methods.

Dissolution, scheme of analysis and principles of estimation of the constituents of the following materials: dolomite, pyrolusite, chalchopyrites, Portland cement, basic slag, brass, steel and type metal.

Unit II. Thermodynamics of dissolution

Acidities of cations, factors influencing acidities (effects of charge and size); basicities of anions, factors influencing basicities (size and charge effects). Hydration energies of ions, Born-equation, enthalpy change associated with dissolution, solubility rules, thermodynamic interpretations of the rules; application of the rules for precipitation reactions, uses of the rules in quantitative and qualitative analysis, complexation reactions and their roles in dissolution processes.

CHT 32a

Unit I. Carbanion chemistry and cyclic stereochemistry

Carbanions: formation of enols and enolates (metal), alkylation of enolates, reactions of enolates with carbonyls (aldehydes, ketones and esters), conjugate addition of enolates.

Cyclic Stereochemistry: Baeyer strain theory.

Conformational analysis: cyclohexane, mono and disubstituted cyclohexane, symmetry properties and optical activity. Conformation & reactivity in cyclohexane system: elimination (E2), rearrangement, nucleophilic substitution (S_N1, S_N2, NGP), oxidation of cyclohexanol, esterification, saponification, lactonisation.

Unit II. Spectroscopy UV, IR, NMR (elementary)

UV Spectra*:* Electronic transition (σ-σ*, n-σ*, π-π* and n-π*), relative positions of λ_{max} considering conjugative effect, steric effect, solvent effect, red shift (bathochromic shift), blue shift (hypsochromic shift), hyperchromic effect, hypochromic effect (typical examples).

IR Spectra: Modes of molecular vibrations, application of Hooke's law, characteristic stretching frequencies of O-H, N-H, C-H, C-D, C=C, C=N, C=O functions; factors effecting stretching frequencies (H-bonding, mass effect, electronic factors, bond multiplicity, ring size).

PMR Spectra: Nuclear spin, NMR active nuclei, principle of proton magnetic resonance, equivalent and non-equivalent protons, chemical shift δ), shielding / deshielding of protons, up-field and down-field shifts. NMR peak area (integration), diamagnetic anisotropy, relative peak positions of different kinds of protons (alkyl halides, olefins, alkynes, aldehyde H), substituted benzenes (toluene, anisole, nitrobenzene, halobenzene, dinitrobenzenes, chloronitrobenzene), first order coupling (splitting of the signals: ordinary ethanol, bromoehane, dibromoehanes), coupling constants.

CHT 32b

Unit I. Synthetic strategies and Asymmetric synthesis

Retrosynthetic analysis: disconnections, synthons, donor and acceptor synthons, functional group interconversion, C-C disconnections and synthesis [one group and two-group (1,2 to 1,6-dioxygenated], reconnection (1,6-di carbonyl), natural reactivity and umpolung, protection-deprotection strategy [alcohol, amine, carbonyl, acid]

Strategy of ring synthesis: thermodynamic factor, synthesis through enolate anion chemistry and carbonyl condensation reactions (including acetoaceticester & malonic ester synthesis) ,synthesis through rearrangement (including pinacol, Favorski), synthesis of large rings, high dilution technique and acyloin reaction, Stobbe condensation.

Asymmetric synthesis: stereoselective and stereospecific reactions, diastereo-selectivity and enantioselectivity (only definition), diastereoselectivity: addition of nucleophiles to C=O, adjacent to a stereogenic centre (Felkin-Anh model).

Unit II. Carbohydrate chemistry

Monosaccharides: Aldoses upto 6 carbons, structure of D-glucose & D-fructose (configuration & conformation), anomeric effect, mutarotation.
reactions: osazone formation, bromine – water oxidation, stepping–up (Kiliani method) and stepping–down (Ruff's & Wohl's method)of aldoses.

Disaccharides: glycosidic linkages, structure of sucrose.

CHT 32c

Unit I. Carbocycles and Heterocycles

Polynuclear hydrocarbons: syntheses and reactions of naphthalene, anthracene and phenanthrene.

Heterocyclic compounds: reactivity, orientation and important reactions of furan, pyrrole, pyridine, indole, synthesis (including retrosynthetic approach) pyrrole: Knorr pyrrole synthesis and Hantzsch synthesis. Hantzsch pyridine synthesis. Indole: Fischer, Madelung and Reissert synthesis, Skaurp quinoline and Bischler-Napieralski Synthesis of isoquinoline.

Unit II. Amino acids, peptides and nucleic acids

Amino acids: Synthesis: (Strecker, Gabriel, acetamido malonic ester, azlactone); isoelectric point, ninhydrin reaction.

Peptides: peptide linkage, syntheses of peptides using N-protection & C-protection, solid phase synthesis; peptide sequence: C–terminal and N–terminal unit determination (Edmann, Sanger & dansyl chloride).

Nucleic acids: pyrimidine & purine bases (only structure & nomenclature), nucleosides and nucleotides, DNA: Watson-Crick model, complimentary base –pairing in DNA.

CHT 33a

Unit I. Properties of solids, interfaces and dielectrics

Crystal, crystal planes, law of rational indices, Calculation of fraction occupied for simple cubic, bcc, and fcc. Miller indices. Bragg's law and its applications for the determination of crystal structure for cubic system single crystal. Crystal structures of NaCl and KCl.

Special features of interfaces compared to bulk. Surface dynamics: Physical and chemical adsorption. Freundlich and Langmuir adsorption isotherms; multilayer adsorption and BET isotherm (no derivation required). Gibbs adsorption isotherm and surface excess. Heterogeneous catalysis (single reactant).

Colloids: lyophobic and lyophilic sols. Origin of charge and stability of lyophobic colloids. Coagulation and Schultz-Hardy rule. Zeta potential and Stern double layer (qualitative idea). Tyndall effect. Electrokinetic phenomenon (qualitative idea only).

Electrical properties of molecules: Polarizability of atoms and molecules, dielectric constant and polarisation, molar polarisation for polar and non-polar molecules. Clausius-Mosotti equation and Debye equation (both with derivation) and their application. Determination of dipole moments.

Unit II. Quantum Chemistry – II

Simple Harmonic Oscillator: setting up of the Schrodinger stationary equation, energy expression (without derivation), expression of wave function for n = 0 and n = 1 (without derivation) and their characteristic features.

Stationary Schrodinger equation for the H-atom in polar coordinates, separation of radial and angular (θ, φ) parts. Solution of φ-part and emergence of quantum number 'm'; energy expression (without derivation), degeneracy. Hydrogenic wave functions up to n = 2 (expression only); real wave function. Concept of orbitals and shapes of s and p orbitals.

CHT 33b

Unit I. Phase equilibrium and colligative properties

Definitions of phase, component and degrees of freedom. Phase rule and its derivations. Definition of phase diagram. Phase equilibria for one component system – water, CO_2. First order phase transition and Clapeyron equation; Clausius-Clapeyron equation - derivation and use.

Liquid vapour equilibrium for two component systems. Ideal solution at fixed temperature and pressure. Principle of fractional distillation. Duhem-Margules equation. Henry's law. Konowaloff's rule. Positive and negative deviations from ideal behaviour. Azeotropic solution. Liquid-liquid phase diagram using phenol-water system. Solid-liquid phase diagram. Eutectic mixture. Nernst distribution law. Solvent extraction.

ΔG, ΔS ΔH and ΔV of mixing for binary solutions. Vapour pressure of solution. Ideal solutions, ideally diluted solutions and colligative properties. Raoult's law. Thermodynamic derivation of colligative properties of solution (using chemical potentials) and their inter-relationships. Abnormal colligative properties.

Unit II. Statistical thermodynamics and the third law

Macrostates and microstates, thermodynamic probability, entropy and probability, Boltzmann distribution formula (with derivation). Applications to barometric distribution. Partition function and Einstein’s theory of heat capacity of solids. Limitations of Einstein’s theory and Debye's modification (qualitative).

Nernst heat theorem. Approach to zero kelvin, adiabatic demagnetisation. Planck's formulation of third law and absolute entropies.

CHT 33c

Unit I. Kinetics and photochemistry

Collision theory (detailed treatment); outline of Transition State theory. Primary kinetic salt effect. Lindemann theory of unimolecular reaction.

Potential energy curves (diatomic molecules), Frank-Condon principle and vibrational structure of electronic spectra. Bond dissociation and principle of determination of dissociation energy (ground state). Decay of excited states by radiative and non-radiative paths. Fluorescence and phosphorescence, Jablonsky diagram.

Laws of photochemistry: Grotthus-Draper law, Stark-Einstein law of photochemical equivalence and Lambert-Beer's law; quantum yield and its measurement for a photochemical process, actinometry. Photostationary state. Photosensitized reactions. Kinetics of HI decomposition, H_2-Br_2 reaction, dimerisation of anthracene.

Unit II. Spectroscopy

Rotational spectroscopy of diatomic molecules: rigid rotor model, selection rules, spectrum, characteristic features of spectral lines (spacing and intensity). Determination of bond length, effect of isotopic substitution.

Vibrational spectroscopy of diatomic molecules: SHO model, selection rules, spectra; anharmonicity and its consequences on energy levels, overtones, hot bands.

Raman Effect. Characteristic features and conditions of Raman activity with suitable illustrations. Rotational and vibrational Raman spectra. Rule of mutual exclusion with examples.

CHP 34a

Spectroscopic Analysis of Organic Compounds

A. Assignment of labelled peaks in the ^{1}H NMR spectrum of the known organic compounds explaining the relative ∂ values and splitting pattern.

B. Assignment of labeled peaks in the IR spectrum of the same compound.

(C-H, O-H, N-H, C=C, C=O, NO_2 stretching frequencies)

At least 10-15 compounds from among the list given below are to be chosen:

(i) p-Bromoacetanilide (ii) p-Methyl-α-bromoacetophenone (iii) Vanillin (iv) Cinnamic acid (v) p-Aminobenzoic acid (vi) Salicylamide (vii) o-Hydroxy acetophenone (viii) 4-keto pentanoic acid (ix) Benzylacetate (x) Diethylmaleate (xi) Diethylfumarate (xii) p-Nirtobenzaldehyde (xiv) Mesityl oxide (xv) o-Hydroxybenzaldehyde (xvi) p-Nitroaniline

A separate laboratory workbook should be maintained for these experiments.

CHP 34b

Experiment -1. Qualitative analysis of single solid organic compounds

A. Detection of special elements (N, Cl, S) by Lassaigne's test

B. Solubility and Classification (solvents: H_2O, 5% HCl, 5% $NaHCO_3$, 5% NaOH)

C. Detection of the following functional groups by systematic chemical tests:
Aromatic amino ($-NH_2$), aromatic nitro ($-NO_2$), Aimdo ($-CONH_2$, including imide), Phenolic –OH, Carboxylic acid (-COOH), Carbonyl (>C=O); only one test for each functional group is to be reported.

Each student, during laboratory session, is required to carry out qualitative chemical tests for all the special elements and the functional groups in known and unknown (at least 5) organic compounds.

Experiment - 2. Organic preparations

A. The following reactions are to be performed, noting the yield of the crude product:
1. Nitration of aromatic compounds
2. Condesation reactions
3. Hydrolysis of amides/ imides/ esters
4. Acetylation of phenols / aromatic amines
5. Benzoylation of phenols / aromatic amines
6. Side chain oxidation of aromatic compounds
7. Diazo coupling reactions of aromatic amines
8. Bromination of anilides
9. Redox reaction
10. Green 'multi-component –coupling' reaction

B. Purification of the crude product is to be made by crystallisation (water/alcohol, crystallisation after charcoal treatment, or sublimation, whichever is applicable).

C. MP of the purified product is to be noted.

Note: Each student is required to perform ALL the experiments cited above (in A, B and C) in classes.

CHP 35a

Experiments:
1. Determination of surface tension of a given solution by drop weight method using a stalagmometer, considering aqueous solutions of NaCl, acetic acid, ethanol etc, as systems.
2. Determination of viscosity coefficient of a given solution with Ostwald's viscometer considering aqueous solutions of cane-sugar, glycerol, ethanol, etc.
3. Determination of solubility of sparingly soluble salts in water and various Electrolyte medium by titrimetric method. KHTa as sparingly soluble salt in water, KCl, $NaNO_3$ may be used.

4. Determination of partition coefficient of Iodine or Acetic acid in water and an immiscible organic solvent.
5. Determination of the rate constant for the first order acid catalyzed hydrolysis of an ester (V_0 and V_∞ be supplied).
6. Determination of rate constant of decomposition of H_2O_2 by acidified KI solution using clock reactions.

A separate laboratory workbook should be maintained for these experiments.

CHP 35b

Experiments:
1. To study the kinetics of inversion of sucrose using polarimeter.
2. To study the phase diagram of a binary system (Phenol + water) and the effect of impurities (e.g. NaCl).
3. Determination of ionization constant of a weak acid by conductometric method.
4. To study the kinetics of saponification of ester by conductometric method.
5. Determination of the equilibrium constant of the reaction $KI + I_2 = KI_3$ by partition method (partition coefficient to be supplied).
6. Determination of E_0 of Fe^{+3}/Fe^{2} couple in the hydrogen scale by potentiometric titration of ferrous ammonium sulfate solution using $KMnO_4$, or, $K_2Cr_2O_7$ as standard.
7. Determination of concentration of (i) $AgNO_3$ solution and (ii) solubility product of AgCl by potentiometic titration of standard KCl solution against $AgNO_3$ solution.
8. Determination of pK values of weak monobasic, dibasic and polybasic acid by pH-metric method (e.g. using, acetic acid, succinic acid, oxalic acid, phosphoric acid, etc.).
9. Study of the kinetics of the reaction $I^- + S_2O_8^{2-}$ by colorimetric method.

Chemistry General: Syllabus Scheme in modular form

Course names and distribution

PART – I (Year 1), total marks = 100 (Theory = 100)

CGT	11a, 11b	each 25 marks, Theory
CGT	12a, 12b	each 25 marks, Theory

PART – II (Year 2), total marks = 200 (Theory = 100, Practical = 100)

CGT	21a, 21b	each 25 marks, Theory
CGT	22a, 22b	each 25 marks, Theory
CGP	23	50 marks, Practical
CGP	24	50 marks, Practical

PART – III (Year 3), total marks = 100 (Theory = 75, Practical = 25)

CGT	31a, 31b, 31c	each 25 marks, Theory
CGP	32	25 marks, Practical

Abbreviations:
CGT: Chem General Theory; CGP: Chem General Practical
First digit refers to year, second to paper

Each CGT Exam = 1½ hr for 50 marks, or as stated later
Each CGP Exam = 3 hr for 25/50 marks on each day, or as stated later

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Notes:
1. A Theory module of 25 marks would contain units I (marks = 15) and II (marks = 10).

2. Number of class hours = number of marks (Theory)
   Number of class hours = 2-3 times the number of marks (Practical)