Kadi Sarva Vishwavidyalaya, Gandhinagar

PART-1 (BASIC AWARENESS AND APTITUDE ON RESEARCH) – 50 Marks

PART-2 Syllabus for Ph.D Entrance Test: Chemistry (Marks-50)

Unit -I: Inorganic Chemistry

Chemical periodicity: Electronic configuration, Bond parameters, Electronegativity and Magnitude, Fajan's rules. VSEPR Theory - Valence Bond Theory - Structure and bonding of hybridization and MOT Theory. Octet Rule and 18 electron rule.

Concepts of Acids and Bases: Theories (Arrhenius, Bronsted-Lowry, Lewis concept), Oswalt's Dilution Law. HSAB Concept. pH Scale, Buffer solution. Ionization constant. Relation between K_a and K_b, Non-Aqueous Solvents.

Group theory: Symmetry elements and symmetry operations, Types of Symmetry operations, Assigning Point groups with Illustrative examples, Group multiplication table of C_{2V} and C_{3V} for NH_3 molecule. Construction of character Tables- C_{2V} and C_{3V} point groups. Great Orthogonality theorem.

Main group elements and their compounds: Allotropy-graphite, diamond and bucky ball. Silicates. Synthesis, structure and bonding of Boranes, carbaborance, phosphazenes, oxy-acids of phosphorus and hexachlorocyclo triphosphazene, industrial importance of xenon compounds.

Transition elements: Electronic Configurations. General Properties - Physical, Magnetic, catalytic properties, Atomic and Ionic sizes, Ionization enthalpies, Oxidation state and chemical reactivity-. Oxides and Oxoanions of metals.

Coordination compounds: Nomenclature of Coordination Compounds. Important terms to co-ordination compound, Isomerism. Structure and Bonding Theories (CFT, LFT and VBT) Jahn-Teller theorem. Spectral and Magnetic Properties of Para, Dia, Ferro and Antiferro magnetism. Reaction Mechanisms - Trans Effect, Square-planar complex, Electron transfer reactions, Carbonyl complexes.

Inner-Transition elements: Electronic Configurations. Physical and Magnetic properties. Atomic and Ionic sizes and Oxidation states.Spectral and Magnetic Properties, Redox chemistry of Lanthanides and Actinides. Analytical applications- Shift Reagents, Separation of Lanthanides- Ion Exchange Method. Important applications.

References

1. F.A. Cotton, G. Wilkinson, F.A Murillo and M.Bochmann, **Advanced Inorganic Chemistry**, 6th Edition, John Wiley, 2007.
2. J.E. Huheey, E.A. Keiter, R.L. Keiter and O.K.Methi, **Inorganic Chemistry-Principles of structure and reactivity**, 4th ed. 5th Impression, Pearson-Education, 2009.

Unit II: Organic Chemistry

IUPAC nomenclature: Organic molecules including regio- and stereoisomers. Aliphatic and aromatic hydrocarbons with most important functional groups, poly functional compounds, bicyclic compounds, Spiro compounds. E/Z notation, R – S nomenclature.

Aromaticity: Benzenoid and non-benzenoid compounds – Huckle rule, Aromaticity, antiaromaticity, non aromaticity. Aromatic characters of Annulenes, fullerenes.

Principles of stereochemistry: Configurational isomerism-Enanitomers, Diastereomers. Conformational isomers. Homotopic, enentiotopic, enantioselectivity, diastereoselectivity. Concept of Chirality: Recognition of symmetry elements and chiral structures; diastereoisomerism in acyclic and cyclic systems. Conformational analysis of simple cyclic (chair and boat cyclo hexanes) and acyclic systems. Interconversion of Fischer, Newman and Sawhorse projections.

Organic reactive intermediates: Generation, stability and reactivity of carbocations, carbanions, free radicals, carbenes, benzynes and nitrenes. Sandmeyer reaction, Gomberg-Bachmann reaction, Pschorr reaction and Ullmann reaction, mechanism of Hunsdiecker reaction.

Organic reaction mechanisms: Addition, elimination E_1, E_2 and substitution reactions with electrophilic, nucleophilic or radical species. Determination of reaction pathways.

Named reactions and rearrangements: Aldol, Perkin, Stobbe, Dieckmann condensations; Holmann, Schmidt, Lossen, Curtius, Backmann and Fries rearrangements; Reimer – Tiemann, Reformatsky and Grignard reactions. Diels – Aider reactions; Clasien rearrangements; Friedeal – Crafts reactions; Witting reactions; and robinson annulation. Routine functional group transformations and interconversions of simple functionalities. Hydroboration, Oppenaur oxidations; Clemmensen, Wolff-Kishner, Meerwein – Ponndorf – Veriey and Birch reductions.

Concepts in organic synthesis: Retrosynthesis, disconnection approach of C-C disconnection and C-X disconnection, synthons, linear and convergent synthesis, umpolung of reactivity and protecting groups.

Pericyclic reactions: Electrocyclisation, cycloaddition, sigmatropic

rearrangements and other related concerted reactions. 1,3 and 1,5–hydrogen shifts - Cope and Claisen rearrangements; 1,3 -dipolar additions and Diels - Alder reaction.

Photochemical reactions in organic chemistry: Principles and applications- Jablonski diagram - Photochemical reactions of Ketones - Norrish I and II type reactions - Photoreduction -Paterno-Buchi reaction - Photosensitization - Reactions of alpha beta-unsaturated ketones - isomerization and cycloadditions - cis-trans isomerisation of simple olefins - di-pi-methane rearrangement - Photooxidation - Oxidative coupling - Barton reaction.

Heterocyclic compounds Synthesis and reactivity of common heterocyclic compounds containing one or two heteroatoms (O, N, S). Imidazole, oxazole, thiazole and indole, Anthocyanidins, pyrimidines, purines.

Chemistry of natural products: Carbohydrates, proteins and peptides, fatty acids, nucleic acids, terpenes, steroids and alkaloids, cholesterol and hormones. Function and application of enzymes and coenzymes.

References

1. R.T. Morrison and R. N. Boyd's, **Organic Chemistry**, 6thed., Spring 2008.
2. I.L. Finar, **Organic Chemistry Vol. I & II**, 5th ed, Pearson Education, Singapore, 2004.
3. Micheal B.Smith and Jerry March, **March's Advanced Organic Chemistry Reactions, Mechanishms and Structure**, 6thed., JohnWiley&Sons Inc., New Jersey, 2007.
4. Peter Skyes, **A Guide book to Mechnism in Organic Chemistry**, Orient Longman Private Limited., New Delhi, 2003.
5. I.L. Finar, **Organic Chemistry Vol. I & II**, 5th ed, Pearson Education, Singapore, 2004.
6. J.M.Coxon and B. Halton, **Organic Photochemistry**, 2nd edition, Cambridge University Press, 2011.
7. Jagdamba Singh, **Photochemistry and Pericyclic Reactions**, 3rd edition, New Age Science, 2009.

Unit III: Physical Chemistry

Chemical kinetics: Empirical rate laws and temperature dependence; complex reactions; steady state approximation; determination of reaction mechanisms; collision and transition state theories of rate constants; unimolecular reactions; enzyme kinetics; salt effects; homogeneous catalysis.

Chemical Thermodynamics: First and II laws of thermodynamics Concept of entropy-entropy,Entropy changes in various processes Nernst heat thermodynamics applications to gaseous system, Third law of thermodynamics and its application to evaluate absolute entropies of solids, liquids and gases; Partial molar quantities and their determination, Gibbs-

Duhem equation, Gibbs Duhem-Margules equation and its application, Chemical potential and its applications, Activity and activity co-efficients , Methods of determination of activity and activity coefficients, Concept of Fugacity and its determination methods.

Surface Chemistry: Physical and Chemical adsorption, Adsorption isotherms, Multi molecular theory or B.E.T. Adsorption Isotherm, Gibbs Adsorption Equation, Surface active agent OR Surfactants, Micellisation, Critical Micelle Concentration(CMC)

Nuclear Chemistry: Nuclear energy and Reactions-Transmutation, Chain Reaction, Spallation reaction, thermonuclear energy, Hydrogen bomb, Nuclear Cross Sections. Nuclear Fission and Fusion, Q-Values. Uses of radioactive isotopes.

Electrochemistry: Debye-Hackle Theory (Mathematical Derivation), Thermodynamics of electrified interfaces Lipmann's Equation, Determination of dissociation constant of mono basic acids by conductometry and potentiometry, Gouy-ChapmanTheory, Polarization and Overvoltage, Bulter-Volmer equation, Principle of polarography, Equation of polarographic wave, Ilkovic equation.

Solid State Chemistry: Bonding in solids and electronic structure in solids, bond theory-metals, semiconductors and insulators, defects in crystals, calculation of schotky and Frenkel defects using statistical method, non-stoichiometry, solid electrolytes, diffusion in solids, electrical conductivity in solids, super conductivity, perovskites

Macromolecules: Kinetics and Mechanism of Polymerization, Molecular weight of macromolecules (Number average and weight average Molecular weight), Methods of determining molecular weight of polymers, Properties of polymers and applications, Examples

Polymer chemistry: Functionality of monomers, degree of polymerization. Types of polymerization: addition, condensation and copolymerization. Glass transition temperature (Tg), Number average, weight average and viscosity average molecular weight of polymers. Molecular weight determination by light scattering, osmotic, centrifuge and viscosity methods. Gel permeation chromatography.

References

1. Peter Atkins, **Physical Chemistry**, 8th ed., Oxford University Press, New Delhi, 2007. 2. K.J. Laidler, **Chemical Kinetics,** 3rd ed., Pearson Education Inc, New Delhi, 2008.
3. S. Glasstone, **Text Book of Physical Chemistry**, D. Von Nostrand Inc., 2006.
4. Willard, Merit Dean and Settle, **Instrumental Methods of Analysis**, CBS Publishers, IV Edn., 1986.
5. Gowariker and Viswanathan, **Polymer Science**, Wiley Eastern, 1986.

Unit IV: Analytical Chemistry

Volumetric Method of Analysis: Primary and Secondary standards, Principles of volumetric analysis, Acid–base titration. Titration in non-aqueous solvents, Complex metric titrations, Precipitation titrations (Mohr's titration, Volhard's titration, adsorption indicators, Fajan's titration), Redox titrations, Theoretical aspects of titration curves and end point evaluation, Choice and suitability of indicator in each case.

Instrumental analysis: pH metry (Principle of instrumentation and mechanism of pH by glass electrode), Potentiometry, Conductometry and types of electrodes and explanation of the nature of titration curves

Fundamentals of Spectrophotometry and UV-Visible Spectroscopy: Properties of light, absorption of light, interaction of light with matter and origin of spectra. The spectrophotometer-calibration, sources of light, monochromators and detectors. Beer's law in chemical analysis, photometric accuracy, Ring bom Plot, Derivative Spectro photometry

Fundamental of NMR & CMR Spectroscopy: Principal, basic of NMR (Peak height, Peak signal, Chemical shift,) instrumentation and applications of NMR, Criteria for a compound to be NMR active. Basic components of instrumentation of PMR and CMR. Shielding- deshielding, splitting, TMS. Resolution and multiplicity.

MASS Spectroscopy: Theory, instrumentation and modifications; Unit mass and molecular ions; Important terms-singly and doubly charged ions, meta stable peak, base peak, is otropic mass peaks, relative intensity, etc.; Recognition of M+ ion peak;

General fragmentation rules: Fragmentation of various classes Of organic molecules, including compounds containing oxygen, sulphur, nitrogen and halogens; α-, β-, allylic and benzylic cleavage.

Fourier Transform Infrared Spectrscopy: Principle, Types of vibrations in IR, Different important group frequency criteria for compound to be IR active, Instrumentation of FT-IR. Importance of H-bonding, Examples of Organic compounds.

Thermal Methods of Analysis: Principle, theory, instrumentation and applications of TGA, DTA, DSC.

Chromatography: Classification of stationary and mobile phase Column Chromatography, Normal and Reverse Phase Chromatography Paper Chromatography, Preparative TLC, Principle and examples of detection methods Thin Layer Chromatography (TLC), Ion Exchange Chromatography

References

1. Skoog, West, Holler & Crouch, **Fundamentals of Analytical Chemistry**, 9th ed., Holt-Saunders International Edition, USA, 2014.
2. Gary D Christian, **Analytical Chemistry**, 7th ed., John Wiley and Sons Inc. New Jersey, USA, 2014.
3. Skoog, West, Holler & Crouch, **Principles of Instrumental Analysis**, 6th ed., Holt-Saunders International Edition, USA, 2007.
4. Daniel C. Harris, **Quantitative Chemical Analysis**, 8th ed., W.H. Freeman and Company, USA, 2010.
5. Galen W. Ewing, **Instrumental Methods of Chemical Analysis,** 2nd ed., McGraw-Hill Inc., USA, 1985.
6. M E Brown, **Introduction to Thermal Analysis Techniques and Applications,** 2nd ed., Springer Science & Business Media, USA, 2001.
7. P. S. Kalsi, **Spectroscopy of Organic Compounds,** 6th ed.,New Age International Ltd. India, 2007.
8. Y. R. Sharma, **Elementary Organic Spectroscopy: Principles and Chemical Applications,** Revised ed., S Chand Publications Ltd., India, 2010.

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