SYLLABUS FOR PH D CHEMISTRY ENTRANCE TEST-2012

Stereochemistry and Reaction Mechanism

1. **Stereochemistry:** Configuration and chirality, optical isomerism, R,S-convention, enantiotopic and diastereotopic groups, methods of resolution, asymmetric synthesis. Geometrical isomerism E,Z-convention. Conformational analysis; effect of conformation on reactivity.

2. **Reactive Intermediatates:** Generation, structure and reactions of carbocations, carbanions, nitrenes and free radicals.

3. **Nucleophilic substitution:** Mechanisms, Classical and nonclassical carbocations. Reactivity effects of substrate structure, attacking nucleophile, leaving group and reaction medium. Aromatic Nucleophilic substitution: Mechanisms, reactivity, effect of substrate structure, leaving group and attacking nucleophile.

4. **Electrophilic Substitution:** Mechanisms, effect of substrates, leaving group and the solvent polarity on the reactivity. Aromatic- the Arenium ion mechanism, orientation and reactivity, energy profile diagrams, quantitative treatment of reactivity in substrates and electrophiles.

5. **Addition to Carbon-Carbon Multiple Bonds:** Mechanism, direction and stereochemistry, addition to alkenes and alkynes, Transition metal organometallics.

6. **Addition to Carbon-hetero Multiple Bonds;** Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acids, esters and nitriles, Addition of Grignard reagents.

6. **Elimination Reactions:** Reaction mechanism, Direction, stereochemistry, formation of alkenes , alkynes and other multiple bonds.

7. **Ring Expansion and Contraction:** Demjanov ring expansion, Favorskii rearrangement.

REFERENCES:

1. *Stereochemistry of Carbon Compounds* by E. J. Eliel, Tata Mc Graw Hill, **2002.**
2. *Stereochemistry of Organic Compounds* by D. Nasipuri, Wiley, **1994.**
3. *Organic Chemistry* by J. M. Hornback, Books Coley, **1998.**
4. *Organic Chemistry* by P. Y. Bruice, Prentice Hall , **1998.**
5. *Organic Reaction and their Mechanisms* by P. S. Kalsi, New Age International Publishers , 2nd edition, **2007.**
6. *Modern Synthetic Reaction* by H. O. House, W. A. Benjamin, Inc, **1972.**

Thermodynamics and Chemical Kinetics

1. **Law of Thermodynamics:** Exact and Inexact Differentials, Cyclic Rule, Reciprocity Characteristics, Homogenous Function, Euler's Theorm, third Law of thermodynamics, Nernst Heat theorm, Thermodynamic Properties at Absolute Zero, Entropy & Third Law of Thermodynamics.

2. **System of Variable Compositions:** Partial Molar Quantities, Chemical Potential and its Variation with Temperature and Pressure, Chemical Potential of Real Gases & Fugacity, Chemical Potential in ideal Gas Mixture, Concept of Escaping Tendency.

3. **Physical Transformation of Pure Substances and Simple Mixtures:** Phase Diagrams, Phase Stability and Phase Transitions, The Physical Liquid Surface, Thermodynamics function of Mixing.

4. **Chemical Equilibrium:** Spontaneous Chemical Reactions, Response of Equilibria to the Conditions, Thermodynamic Properties of Ions in Solution.

5. **Chemical Kinetics:** Collision theory of Reaction Rates, Arrhenius Equation and Activated Complex Theory, Comparison of Collision and Activated Complex Theory.

6. **Advanced Chemical Kinetics:** Applications of Activated Complex Theory, RRK and RRKM Theory, Theories of Unimolecular Reactions.

7. **Dynamics of Complex Reactions:** Ion-Ion Reactions, Ion-Dipole reactions, Enzyme Kinetics, polymerization Kinetics, Kinetic Salt, Salt Effect.

8. **Dynamics of Fast Reactions:** General Treatment of Chain Reactions, Theories of Branching Chain and Explosion, Flow Methods, Relaxation Techniques, Flash Photolysis.

REFERENCES:

1. *Thermodynamics A core Course* by R. C. Srivastva, S. K. Saha, A. K. Jain, PH I, New Delhi, **2007.**
2. *Physical Chemistry*, P. Atkins, J. D. Paula, Oxford University Press, 7th Indian Edition, **2007.**
3. *An Introduction to Chemical Thermodynamics* by R. P. Rastogi & R. R. Mishra, Vikas Publishing House, 6th Edition **, 2007.**
4. *Chemical Kinetics* by Keith J. Laidler, Pearson Education, 3rd Edition.
5. *Chemical Kinetics* by K. A. Corrnors, VCH, **1998.**
6. *Physical Chemistry* by R. S. Berry, S. A. Rice & J. Ross, Oxford University Press 2nd Edition, **2000.**
7. *Fast Reactions* J. N. Bradley, Oxford University press, **1975.**

Main Group Chemistry

1. **Chemistry of hydrogen:** Ionized forms of Hydrogen, Protonic acids and bases, The Hydrogen Bond, its influence on Properties and influence on structure, Strength of hydrogen bonds and theoretical description.

2. **Chemistry of S-block metals:** Hydrides, Halides, Oxides, Peroxides, Superoxides, Suboxides, Hydroxides, Oxoacid salts Complexes Crowns and Crypts of Alkali Metals and coordination complexes of Alkaline Earth Metals.

3. **Chemistry of Boron and Aluminum:** Boranes, Bonding in boranes, topology of boranes, synthesis and reactivity. Carboranes and mettallocarboranes,Borazine and boron nitride. Chemistry of Aluminum Halides. Aluminum Alkyls. Low oxidation state Al compounds.

4. **Chemistry of Silicon**: Organosilicon Compounds. Sillicates and Aluminosilicates. Low-valent Silicon compounds, silylenes and R_3Si^+.

5. **Inorganic rings, Cages, Clusters and Polymers:** Phosophazenes, Cyclophosphazenes , Polyphosphozenes and the polymers derived from them. Polysilanes.

6. **Chemistry of halogens and nobel gases:** Inter Halogens, Poly Halide Anions, CFC's , Ozone layer and Clathrates.

7. **Chemistry of group 12 elements:** Halides & Oxygen compounds, chalcogenides & Related compounds, low-valent compounds & Formation of coordination complexes.

References:

1. *Main Group Chemistry*, W. Henderson, Royal Society of Chemistry, **2000.**
2. *Advanced Inorganic Chemistry*, F. A. Cotton and G. Wilkinson et. al, Sixth edition John Wiley & Sons, **2003.**
3. *Inorganic Chemistry*, J. E. Huheey et. al, Fourth edition, Pearson, **2005.**
4. *Concepts & Model of Inorganic Chemistry*, B. Douglas et. al, 3rd John Wiley & Sons, **2001.**
5. *Chemistry of Elements*, N. N. Greenwood, Pergamon Press, **2000.**
6. *Inorganic Chemistry 4th edition D. F. Shriver and P. W. Atkins, Oxford University, Oxford, **2006**.*

Basic Biological Chemistry

1. **Cell** :Types of cells and structure and functions

2. **Introduction to Biomolecules:** Carbohydrates, Proteins, Amino acids, Lipids and phospholipids, Biological membranes, transport across membranes.

3. **Nucleic Acids:** Base pairing, double helices, DNA replication, transcription and translation.

4. **Enzymes**: enzyme kinetics and mechanism, nature and application of enzymes.

5. **Biotechnology and its Applications:** Genetic engineering, Potential laboratory biohazards of genetic engineering, Polymerase chain reaction, Pharmaceutical and biopharmaceuticals, Vaccines and monoclonal bodies ,Waster water and sewage treatment, landfill technologies.

6. **Transmission of Nervous impulse & mechanism:** Neurons and its Structure, Nerve Transmission**,** Nerve poisons.

REFERENCES:

1. *Biotechnology*, by J. E. smith, 4th edition, Cambridge, **2004.**
2. *Principle of Biochemistry* by Lehinger, Nelson and Cox, CBS publisher **1993.**
3. *Principles of Biochemistry* ,by T.N. Pattabiraman , Gajanana book publishers and Distributors, **1993.**

Quantum Chemistry

1. **Foundations of Quantum Mechanics:** Operators, Postulates, Matrices and Schrodinger Equation.

2. **Linear Motion and harmonic Oscillators:** Translational, harmonic, particle in a box a penetration through barriers.

3. **Rotational motion and hydrogen atom:** Particle in a ring & on a sphere, motion in a columbic field.

4. **Angular momentum:** Angular momentum operators, definition of states, Composite systems.

5. **Techniques of Approximation:** Perturbation theory, variation theory, HF theoretic, time dependent perturbation.

6. **Atomic Structure:** Hydrogen, Helium & multi electron system.

7. **Molecular Structure:** Born- openheimer approximation MO theory of mono, dia & polyatomic molecules, band theory of solids.

8. **Electronic Structure:** SCF method electron correlation Density functional theory, gradient method, semi-empirical methods & software packages for calculations**.**

9. **Molecular Rotation & Vibration:** Rotation & Vibration in diatomic, polyatomic molecules.

10. **Electronic Transition in molecules:** Rotational, Vibronic and electronic states & fates of excited species.

REFERENCES:

1. *Quantum Chemistry*, I. N. Levine, Prentice Hall, **2000.**
2. *Molecular Quantum Mechanics*, P. W. Atkins and R. S. Friendman, OUP, **1997.**
3. *Physical Chemistry*-by P. W. Atkins, Oxford University Press, **1990.**
4. *Introduction to Quantum Mechanics with Applications to Chemistry*, L. Pauling and E. B. Wilson, Dover NY, **1985.**

Pharmaceutical Chemistry

1. **Drug Discovery and Drug Development**: Introduction, Present and Past, Drugs and the medicinal chemist, Classification of drugs, Drug targets specification, Choice of Bioassay, In Vivo and in Vitro tests, Pit falls.

2. **Drug Action at Receptors**: Receptor role, Neuro-transmitters and Hormones, Change of shape by the receptors, Design of Agonists and Antagonists, Drug action on DNA and RNA.

3. **Drug Design, Drug-Target Interactions**: Introduction, Variation of Substituent, Expansion of the Structure, Chain expansion/Contractions, Ring expansion/Contractions, Ring Variation, Ring Fusions, Isosteres.

4. **Pharmacokinetics:** Drug distribution and survival, Pharmacokinetic issues in drug design like Chemical and Metabolic stability, Hydrophilic / hydrophobic balance, Ionization, size and number of hydrogen bonding interactions, Drug dose levels, solubility and membrane permeability, variation of different groups to alter polarity.

5. **Prodrugs:** Introduction, Effect of prodrugs on: improved membrane permeability, prolonged drug activity, masking drug toxicity and side effects, increased chemical stability, targeting of drugs, prodrugs activation by external influence.

6. **Drug administration:** Introduction, oral administration, sublingual administration, rectal administration, epithelial administration, inhalation, injection and implants.

REFERENCES:

1. *Textbook of Pharmacology,* W. C. Bowman, and M. J. Rand, Blackwell Scientific **1980.**
2. *Medicinal Chemistry-the role of organic chemistry in drug,* C. R. Ganellin, and S. M. Roberts, , *research*, Academic Press **1993.**
3. *Medicinal Chemistry-principles and practice*, F. D. King, , The Royal Society of Chemistry **1994**.
4. *Burger's Medicinal Chemistry and drug discovery,* M. E. Wolff, *5th edition* Volume 1-5. Wiley **1995.**

Surface Chemistry Adsorption and Catalysis

1. **Introduction:-**Basics of surface chemistry, surface tension and adsorption

2. **Surface & Colloids:** Coagulation and kinetics of coagulation, spontaneous aging of colloids.

3. **Aggregation Processes**: Coalescence and particle growth, Stability of colloids, Electric properties, theories of structure of electrical double layer, determination of change on colloids particle, size and shape of colloids particles.

4. **Association of colloids**: Self - assembly system, Reversal of phase, emulsion, Macro and Micro emulsion and Aerosols, emulsifying agents, theories of emulsification, gels, sol gel transformation thixotropy.

5. **Electrokinetic Effect**: Electrosmosis, electrophoresis, streaming potential, Dorn effect, stabilization of surfactant solutions.

6. **Adsorption:** Adsorption of gases by solids, solids from solution ,measurement of adsorption factors affecting adsorption, Adsorption Isotherms, , Gibbs adsorption equation, surface films.

7. **Catalysis:** Homogenous and Heterogeneous Catalysts, Acid base catalysis, Biocatalysts, Micellar catalysis, Mechanism of few catalytic reactions.

8. **Nanoscience :**Creation ,Evaluation and Application

REFERENCES:

1. *Basic Principles of Colloids Science*, D. H. Everthi, Royal Society of Chemistry, **1988.**
2. *Basic Physical Chemistry*, W. J. Moore, Printice Hall of India, **1986.**
3. *Surface*, G. Attard and C. Barners, Oxford Science Publications, **1998.**
4. *Physical Chemistry*, 3rd edition , G. W Castellan, Narosa, **2002.**
5. *Basic and Application of Heterogeneous Catalysis*, by M. Booker, Oxford Science Publication, **1998.**
6. *Physical Chemistry of Surfaces*, A. W. Adamoson.

Principle of Organic Synthesis

1. **Introduction:** Target molecule, strategy, methodology and insight, review of synthon approach and antithetic analysis, concepts, functionalization and interconversion of functional groups.

2. **Energetic, Kinetics, and the Investigation of Mechanism:** Energetic, rate and activation energy of reaction, kinetics and the rate limiting step, kinetic and thermodynamic control, investigation methods.

3. **Phase Transfer Catalysts:** Introduction, mechanism, types and advantages, preparation of catalysts & application.

4. **Crown Ethers:** Introduction, nomenclature, special Features, nature of donor site and synthetic applications.

5. **Reagents in Organic Synthesis:** Anhydrous aluminium chloride, aluminium isopropoxide, boron trifluride, N-Bromosuccinimide Diazomethane, Fenton's Reagent, Hydrogen peroxide, Lead tetra acetate, Lithium Aluminium Hydride, Osmium Tetroxide, Perbenzoic acid (Peroxybenzoic acid), periodic acid, Raney nickel, selenium dioxide, sodium amide (sodamide), sodium borohydride, $NaBH_4$, Wilkinson's catalyst.

6. **Name Reactions:** Aldol condensation, Allyllic Rearrangement, Baeyer- Villiger Rearrangement, Beckmann Rearrangement , Brich Reduction, Cannizzaro Reaction, Claisen condensation and rearrangement, Curtius reaction, Diels Elders Reactions, Fries Rearrangement, Hofmann Rearrangement, Mannich Reaction, Oppenauer Oxidation, Pinacol-Pinacolone Rearrangement, Reformatsky Reaction, Reamer Tieman Reaction.

7. **Pericyclic Reaction:** Introduction, electrocyclic reactions, theoretical explanation, conservation of orbital symmetry, cycloadditon reactions, frontier molecular orbital approach, sigmatropic rearrangements.

8. **Ring closure and opening reactions:** Formation and opening of rings, Diekmann reaction, Baldwin Rules, Robinson-Annelation, Michael-Robinson addition Thorpe Ziegler reaction, Acylation Cycloaddition, Diels-Alder reaction, Simmons-Smith reaction

REFERENCES:

1. *Organic Synthesis - The Disconnection Approach* by S.Warren, Willey Interscience, **1982.**
2. *Reactions Rearrangements and Reagents*, S. N. Sanyal, Bharti Bhawan , 4th edition.
3. *Organic Synthesis-special Techniques*, V. K. Ahluwalia and R. Aggarwal, Narosa Publishing House, **2005.**
4. *A Guidebook to Mechanism in Organic Chemistry*, P. Sykes, 6th edition, **1981.**
5. *Practical Organic Chemistry*, B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, 5th edition, Pearson Education, **2002.**
6. *Phase Transfer Catalysis: Principles and Techniques*, C. M. Starkes & C. liotta, Acedemic press, Inc, New York, **1998.**
7. *Crown compounds Their characteristics & applications* ,M. Iraoka,Amesterdam,**1982**

Symmetry and Group Theory

1. **Symmetry elements and operations :** Symmetry planes and Reflections, Inversion centre, Proper axes and Proper rotations, Improper axes and Improper rotations.

2. **Relations among Symmetry elements :** Products of symmetry operations, Equivalent symmetry elements and Equivalent atoms, General relations among symmetry elements and operations, symmetry point groups, symmetry classification of molecules.

3. **Representations of groups :** Important rules about irreducible representations and their characters, Relationship between reducible and irreducible representations with examples, construction of character tables.

4. **Molecular orbital theory and its applications :** Symmetry based selection rules for cyclisation reactions, Dimerization of ethylene, Diels-Alder reactions.

5. **Molecular orbital theory for inorganic compounds :** Transformation properties of atomic orbitals, Molecular orbitals for sigma bonding in tetrahedral and octahedral molecules.

6. **Ligand Field theory :** Introduction, Electronic structure of free atoms and ions, splitting of levels and terms in a chemical environment, construction of energy level diagram.

REFERENCES:

1. *Chemical Applications of Group Theory*, F. A. Cotton, Wiley, 3rd edition, **2004.**
2. *Valence Theory*, J.N. Murell et. al, John Wiley **1970.**
3. *Conservation of Orbital Symmetry*, R. B. Woodward and R. Hoffmann Academic Press **1970.**
4. *Introduction to Ligand Fields*, B .N. Figgis, John Wiley **1996.**

Chemistry of Transition and Inner - Transition Elements

1. **Survey of Transition Metal Chemistry –** Electronic configuration, general characteristics, oxidation states, pi-acid ligands, metal complexes, metal- *metal* bond, Quadruple bonds.

2. **Chemistry of First Transition Series –** The elements, compounds, complexes, organometallics and bioinorganic chemistry of first transition series in different oxidation states .

3. **Chemistry of Second & Third Transition Series –** The elements, compounds, complexes, organometallics and bioinorganic chemistry of second and third transition series in different oxidation states .

4. **Lanthanides:** Electronic configuration, oxidation states, coordination numbers and stereochemistry, Magnetism and spectra, complexes and organometallic chemistry of lanthanides**.**

5. **Actinides**: Electronic configuration, oxidation states, coordination numbers and stereochemistry, Magnetism and spectra, complexes and organometallic chemistry of Actinides.

6. **Transition Metal Catalyzed Reactions:** Oxidative addition, Elimination reactions, Migration reactions.

7. **Mechanism of Inorganic Reactions:** Inner sphere, Outer sphere, Trans effect.

REFERENCES:

1. *Inorganic Chemistry. 4rt edition D. F. Shriver and P. W. Atkins, Oxford University, Oxford, **2006**.*
2. *Advanced Inorganic Chemistry* by F. A .Cotton and G .Wilkinson et al – Sixth edition, John Wiley & Sons, **2003.**
3. *Inorganic Chemistry* J. E. Huheey et al Fourth edition, Pearson, **2005.**
4. *Concepts & Model of Inorganic Chemistry* B. Douglas et. al, John Wiley & Sons, **2001.**
5. *Chemistry of elements*, N. N. Greenwood Pergamon Press, **2000.**
6. *Ligand Field Theory*, B. N. Figges, Wiley Eastern, **1976.**

Physical Methods of Structure Elucidation

1. **Ultraviolet (UV) Spectroscopy:** Principles, origin, effect of structure, solvents, conjugation and Chromophore and Auxochromes, the Woodword-fieser rules, PES and related spectroscopy.

2. **Microwave Spectroscopy:** Rotation of molecules and rotational spectra-Diatomic molecules, polyatomic molecules-Linear, symmetric top and asymmetric top molecules.

3. **Infrared Spectroscopy:** Principle and instrumentation, Diatomic molecules-Energy of a diatomic molecule-simple harmonic oscillator-Anharmonic Oscillator- diatomic vibrating rotator, vibration-rotation spectrum of dialogue and polyatomic molecules-fundamental.

4. **Raman Spectroscopy:** Raman scattering-Classical and Quantum theories of Raman Effect.

5. **Mossbauer Spectroscopy:** Principles and applications of Mossbauer spectroscopy.

6. **Magnetic Resonance Spectroscopy:** Magnetic resonance- spin angular momentum, Larmor frequency, Relaxation time, NMR spectroscopy of proton and C^{13}Introduction to ESR. Hyperfine structure and double resonance in ESR. Applications of ESR spectroscopy.

7. **Mass Spectroscopy:** Principles instrumentation and applications.

REFERENCES:

1. *Fundamental of Molecular Spectroscopy*, C. N. Banewell, 4th Edition, Tata Mc Graw-Hill Publication, **1995.**
2. *Introduction to Molecular Spectroscopy*, G. N. Barrow, Mc Graw Hill Publications, **1980.**
3. *Spectroscopic Methods in Organic Chemistry*, D. H. Williams and I. Flemings, Tata Mc Graw-Hill Publication, **1994.**
4. *Physical Method in Chemistry*, R. S. Drago, Sunders, **1985.**

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Analytical Principles and Instrumental Methods of Analysis

1. **Data Analysis:** Uncertainties, Errors, calibrations, Mean, Standard Deviation , Least square fit,

2. **Atomic Absorption Spectroscopy:** General principles, instrumental set up and analytical procedures and applications,

3. **Thermo-Analytical Method:** Theory, instrumental requirements and methodology for thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), applications

4. **Chromatographic Methods:** Classification of chromatographic methods according to separation and development procedure, Instrumentation and applications (GC and HPLC)

5. **Electrochemical Techniques:** Conductometry, pH metry, Karl Fischer titration, cyclic voltametry ,Polarography

6. **Modern Methods of Surfaces and Crystal Analysis:** SEM, TEM, AFM, XRD

REFERENCES:

1. *Instrumental Methods of Analysis*, Willard, Merritt, Dean and Settle, CBS Publisher and Distributors.,**1986.**
2. *Thermal Analysis*, W. W. Wendlandt and L. W. Collins, Dowden Hutechin and Ross
3. *Basic Concepts of Analytical Chemistry*, S. M. Khopkar , Wiley Eastern
4. *Thermal Methods of Analysis*, Principles, Application and Problems, J. Haines, Blackie Academic and Professional, **1994.**
5. *Chromatographic Methods*, A. Braithwaite and F. J. Smith, 5^{th} edn. Blackie Academic and Professional, London, **1996.**
6. *Principles of Instrumental Analysis*, Skoog, Holder, Nieman, Fifth edition Thomson Books ,**1998.**