Maharashtra State Eligibility Test for Lectureship

महाराष्ट्र राज्य व्याख्यातापदासाठी राज्यस्तरीय पात्रता चाचणी (सेट) परीक्षा

Conducted by University of Pune

(AS THE STATE AGENCY)

SYLLABUS AND SAMPLE QUESTIONS

Subject Code No.	*Subject*
33	**Chemical Sciences**

UNIVERSITY OF PUNE
Ganeshkhind, Pune-411007

[33] : CHEMICAL SCIENCES

The syllabus consists of two papers, as follows :

Paper II and Paper III will be of 75 minutes and 2½ hours duration respectiveoy. Paper II will be of 100 marks and Paper III will be of 200 marks.

PAPER II

1. Structure and Bonding : Atomic orbitals, electronic configuration of atoms (L-S coupling) and the periodic properties of elements, ionic radii, ionization potential, electron affinity, electronegativity, concept of hybridization. Molecular orbitals and electronic configuration of homonuclear and heteronuclear diatomic molecules. Shapes of polyatomic molecules. VSEPR theory. Symmetry elements and point groups for simple molecules. Bond lengths, bond angles, bond order and bond energies. Resonance. Types of chemical bond (weak and strong). Intermolecular forces. Types of solids, lattice energy.

2. Acids and Bases : Bronsted and Lewis acids and bases. pH and pKa, acid-base concept in non-aqueous media, SHAB concept, Buffer solutions.

3. Redox Reactions : Oxidation numbers, Redox potentials, Electrochemical series, Redox indicators.

4. Introductory Energetics and Dynamics of Chemical Reactions : Law of conservation of energy. Energy and enthalpy of reactions. Entropy, free energy, relationship between free energy change and equilibrium. Rates of chemical reactions (first-and second-order reactions). Arrhenius equation and Concept of transition state. Mechanisms, including S_N1 and S_N2 reactions, electron transfer reactions, catalysis Colligative properties of solutions.

5. Aspects of s, p, d, f Block Elements : General characteristics of each block. Chemical principles involved in extraction and purification of common metals. Coordination chemistry, Structural aspects, isomerism, octahedral and tetrahedral crystal-field spliting of d-orbitals. CFSE, magnetism and colour of transition metal ions. Sandwich compounds metal carbonyls and metal clusters. Rare gas compounds, non-stoichiometric oxides. Radioactivity and transmutation of elements.

6. IUPAC Nomenclature of Simple Organic and Inorganic Compounds.

7. Concept of Chirality : Recognition of symmetry elements and chiral structures, R-S nomenclature, diastereoisomerism in acyclic and cyclic-systems, E-Z isomerism. Conformational analysis of simple cyclic (chair and boat cyclohexanes) and acyclic systems, Interconverison of Fischer, Newman and Sawhorse projections.

8. Common Organic Reactions and Mechanisms : Reactive intermediates. Formation and stability of carbonium ions, carbenes, nitrenes, radicals and arynes. Nucleophilic, electrophilic, radical substitution, addition and elimination reactions. Familiar name reactions : Aldol, Perkin, Stobbe,

Dieckmann condensations ; Hofmann, Schmidt, Lossen, Curtius, Beckmann and Fries rearrangements, Reimer-Tiemann, Reformatsky and Grignard reactions. Diels-Alder reaction, Claisen rearrangement, Friedel-Crafts reaction, Witting reaction. Routine functional group transformations and inter-convertions of simple functionalities. Hydroboration, Oppenauer oxidation, Clemmensen, Wolf-Kishner, Meerwein-Ponndorf Verley and Birch reductions.

9. Elementary principles and applications of electronic, vibrational, NMR, EPR, Mossbauer and mass spectral techniques to simple structural problems.

10. Data Analysis : Types of erros, propogation of errors, accuracy and precision, least-square analysis, average standard diviation.

PAPER III

1. Quantum Chemistry, Planck's quantum theory, wave-particle duality, Uncertainty Principle, operators and commutation relations, postulates of quantum mechanics and Schrodinger equation, free particle, pastick in a box, degeneracy, harmonic oscillator, rigid rotator and the hydrogen atom. Angular momentum including spin coupling of angular momenta including spin-orbit coupling.

2. **The variation method and pertubation theory :** Application to the helium, atom, antisymmetry and Exclusion Principle, Slater determinantal wave functions. Term symobols and spectroscopic states.

3. **Born-Oppenheimer approximation, Hydrogen molecule ion :** LCAO-MO and VB treatments of the hydrogen molecule, electron density, forces and their role in chemical binding. Hybridisation and valence MO, of H_2O, NH_3 and CH_4. Huckel pi-electron theory and its applications to ethylene, butadiene and benzene, idea of self-consistent fields.

4. **Group theoretical representations and quantum mechanics :** Vanishing of intergrals, spectroscopic selection rules for vibrational, electronic, vibronic and Raman spectroscopy. MO treatment of large molecules with symmetry.

5. **Spectroscopy :** Theoretical treatment of rotational, vibrational and electronic spectroscopy. Principles of magnetic resonance, Mossbauer and Photoelectron spectroscopy.

6. **Thermodynamics :** First law of thermodynamics, relation between C_p and C_v; enthalpies of physical and chemical changes, temperature depednence of enthaplies. Second law of thermodynamics, entropy, Gibs-Helmholtz equation. Third law of thermodynamics and calculation of entropy.

7. **Chemical Equilibrium :** Free energy and entropy of mixing, partial molar quantities, Gibbs-Duhem equation. Equilibrium constant, temperature dependence of equilibrium constant, phase diagram of one and two-component systems, phase rule.

8. **Ideal and Non-ideal Solutions :** Excess functions, activities, concept of hydration number, activities in electrolytic solutions, mean ionic activity coefficient. Debye-Huckel treatment of dilute electrolyte solutions.

9. **Equilibria in Electrochemical Cells :** Cell reactions, Nernst equation, application of cell EMF measurements.

10. **Surface Phenomena :** Surface tension, adsorption on solids, electrical phenomena at interfaces including electrokinetic micelles and reverse micelles; solutions. Applications of photoelectron spectroscopy, ESCA and Auger spectroscopy to the study of surfaces.

11. **Statistical Thermodynamic probability and entropy :** Maxwell-Boltzmann distribution of velocities, average, most probable and root-mean-square velocities. Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. Partition function, rotational, translational, vibrational and electronic partition functions for diatomic molecules, calculations of thermodynamic functions and equilibrium constants. Theories of specific heat for solids.

12. **Non-equilibrium Thermodynamics :** Postulates and methodologies, linear laws, Gibbs equation, Onsager reciprocal theory.

13. **Reaction Kinetics :** Methods of determining rate laws, Mechanisms of photo-chemical, chain and oscillatory reactions. Collision theory of reaction rates, steric factor, treatment of unimolecular reactions. Theory of absolute reaction rates, comparison of result with Eyring and Arrhenius equations, ionic reactions, salt effect. Homogeneous catalysis and Michaelis-Menten Kinetics; heterogeneous catalysis.

14. **Fast Reactions :** Study of kinetics by stop-flow technique, relaxation method, flash photolysis and magnetic resonance method.

15. **Macromolecules :** Number-average and weight-average molecular weights. Determination of molecular weights. Kinetics of polymerisation. Stereochemistry and mechanism of polymerisation.

16 **Solids :** Dislocations in solids, Schottky and Frenkel defects. Electrical properties. Insulators and semiconductors, band theory of solids, solid-state reactions.

17. **Nuclear Chemistry :** Radioactive decay and equilibrium. Nuclear reactions, Q value, cross-sections, types of reactions. Chemical effects of nuclear transformations, fission and fusion, fission products and fission yields. Radioactive techniques, tracer techniques, neutron activation analysis, counting techniques such as G.M., ionization and proportional counters.

18. **Chemistry of Non-transition Elements :** General discussion on the properties of the non-transition elements, special features of individual elements, synthesis, properties and structure of their halides and oxides, polymorphism of carbon, phosphorus and sulphur. Synthesis, properties and structure of boranes, carboranes, borazines, silicates, carbides, silicones, phosphazenes, sulphur, oxyacids of nitrogen, phophorus, sulphur and halogens. Interhalogens, pseudohalides and noble gas compounds.

19. **Chemistry of Transition Elements :** Coordination chemistry of transition metalions. Stability constants of complexes and their determination, stabilization of unusual oxidation states. Stereochemistry of coordination compounds. Ligand field theory, spliting of d-orbitals in low symmetry environments. Jahn-Teller effect, interpretation of electronic spectra including charge transfer spectra, spectrochemical series, nephelauxetic series. Dia-para-ferro and antiferromagentism, quenching of orbital angular moments, spin orbit coupling. Inorganic reaction mechanisms, substitution reactions, trans-effect and electron transfer reactions, photochemical reactions of chromium and ruthenium complexes. Fluxional molecules. Iso and heteropolyacids, metal clusters. Spin crossover in coordination compounds.

20. **Chemistry of Lanthanides and Acitindes :** Spectral and magnetic properties, use of lanthanide compounds as shift reagents.

21. **Organometallic Chemistry of Transition Elements :** Synthesis, structure and bonding, organometallic reagents in organic synthesis and in homogeneous catalytic reactions (hydrogenation, hydroformylationn, isomerisation and polymerisation), pi-metal complexes, activation of small molecules by coordination.

22. **Topics in Analytical Chemistry :** Adsorption, partition, exclusion, electrochromatography. Solvent extraction and ion exchange methods. Application of atomic and molecular absorption and emmision spectroscopy in quantitative analysis. Light scattering techniques including nephelometry and Raman spectroscopy. Electroanalytical techniques, voltametry, cyclic voltametry, polarography, amperometry, coulometry and conductometry. Ion-selective electrodes. Anodic stripping voltametry, TGA, DTA, DSC and on-line analysers.

23. **Bioiorganic Chemistry :** Molecular mechanism of ion transport across membranes, ionophores. Photosynthesis-PS-I, PS-II, nitrogen fixation, oxygen uptake proteins, cytochromes and ferrodoxions.

24. **Aromaticity :** Huckel's rule and concept of aromaticity : annulenes and heteroannulenes, fullerenes. (C_{60})

25. **Stereochemistry and Conformational Analysis :** Newer methods of assymetric synthesis (including enzymatic and catalytic nexus), enantio-and diastereo selective synthesis. Effects of conformation on reactivity in acylic compounds and cyclohexanes.

26. **Selective Organic Name Reactions :** Favorskii reaction, Strok enamine reaction, Michael addition, Mannich reaction, Sharpless asymmetric expoxidation, ene reaction, Barton reaction, Hofmann Loffler-Freytag reaction, Shapiro reaction, Baeyer-Villiger reaction, Chichibabin reaction.

27. **Mechanisms of Organic Reactions :** Labelling and kinetic isotope effects, Hamett equation, σ–δ (sigma-rho) relationship, non-classical carbonium ions, neighbouring group participation.

28. **Pericyclic Reactions :** Selection rules and stereochemistry of electrocyclic reactions, cycloaddition and sigmatrophic shifts, Sommelet-Hauser, Cope and Claisen rearrangements.

29. **Heterocycles :** Synthesis and reactivity of furan, thiophene, pyrrole, pyridine, quinoline, isoquinoline and indole. Skraup synthesis, Fischer indole synthesis.

30. **Reagents in Organic Synthesis :** Use of following reagents in organic synthesis and fuctinal group transformations-Complex metal hydride. Gilman's reagent, lithium, dimethylcuprate, lithim, disopropylamide (LDA) dicyclohexylcarbodimide, 1, 3-dithiane (reactivity umpolung). Trimethy, silyl iodide, tri-n-butyltin hydride, Woodward and Prevost hydroxylation, osmium tetraoxide, DDQ, selenium dioxide, phase transfer catalysts, crown ethers and Merrifield resin. Peterson's synthesis, Wilkinson's catalyst, Baker's yeast.

31. **Chemistry of Natural Products :** Familiarity with methods of structure elucidation and biosynthesis of alkaloids, terpenoids, steroids, carbohydrates and proteins, Conformations of proteins and nucleic acids.

32. **Bioorganic Chemistry :** Elementary structure and function of biopolymers such as proteins and nucleic acids, Genetic code, Mechanism of enzyme action.

33. **Photochemistry :** Principles of energy transfer, cis-trans isomerization, Paterno-Buchi reaction, Norrish Type I and II reactions, photoreduction of ketones, di-pi-methane rearrangement, photochemistry of arenes.

34. **Spectroscopy :** Combined applications of mass, UV-VIS, IR and NMR spectroscopy for structural elucidation of compounds.

SAMPLE QUESTIONS

PAPER II

1. The total number of permitted electrons in a 4f orbital is

   (A) 10, (B) 6,

   (C) 14, (D) 2. Ans. C

2. Which one of the following is a molecular solid ?

   (A) NaCl, (B) Phosphorus,

   (C) Diamond, (D) Iron. Ans. B

3. Thr chiral molecules among the following are

   (i) 1, 1-Dimethylcyclopropane.

   (ii) cis-1, 2-dimethylcyclopropane.

   (iii) trans-1, 2-dimethylcyclopropane.

   (A) All three, (B) (ii) and (iii), (C) only (ii), (D) only (iii). Ans. D

PAPER III

1. The standard heat of hydrogenation of propane in the reaction
   $CH_2 = CHCH_3$ (g) + H_2(g) = C_3 H_8(g) is - 124 kJ/mol.

   The standard heat of combustion of propane in the reaction
   C_3H_8(g) + $5O_2$(g) = $3CO_2$(g) + $4H_2O$ (1) is - 2220 kJ/mol.

   Calculate the standard heat of combustion of propane.
   Given : {H_2(g) + $0.5O_2$(g) = H_2O(l), AH^o = -285.8kJ/mol}

2. Match the following Hammet σ values :

(a)	m - Me	(i) + 0.78
(b)	p - Me	(ii) – 0.27
(c)	p - NO_2	(iii) + 0.12
(d)	p - $COCH_3$	(iv) – 0.07
(e)	m - OMe	(v) + 0.50
(f)	p - OMe	(vi) – 0.17

3. (a) Predict whether the following reactions will proceed via inner, sphere or outer sphere mechanism. Give the products also.

   (i) $[Fe (CN)_6]4 + [Ir Cl_6]^{2-} \rightarrow$

   (ii) $[Co (NH_3)_5 NCS]^{2+} + [Cr (H_2O)_6]^{2+} \rightarrow$

   (b) Name the factors that determine the magnitude of crystal field splitting.

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