

## CHEMISTRY SYLLABUS

(For Post Graduates)

Unit – 1 : Physical Chemistry (1)

Physical States of Matter, Physical Properties & Molecular Structure

### SECTION A

The gaseous State : The mean free path, binary collision frequency (single gas), their dependence on temperature and pressure. Real gases-detailed study of Van der Waals equation. Critical constants of gases, the rule of Cailletet and Mathias. The reduced equation of state and the principle corresponding states. Maxwell's law of distribution of molecular velocities (derivation not required), effect of temperature on the distribution. Expressions for various types of velocities from Maxwell's equation. Kinetic energy distribution. Boltzmann factor and the Boltzmann equation. The barometric formula.

### SECTION B

The liquid state : Surface tension : measurement, applications and temperature dependence.

### SECTION C

(i) Elementary ideas of crystallography – Laws of crystallography, crystal lattices, simple crystal system, ionic covalent crystals, Bragg's method of crystal analysis with illustration of NaCl and KCl crystal faces, Born-Haber cycle.

(ii) Heat capacity of solids, Einstein's specific heat equation, Debye's  $T^3$ -Law (detailed deduction not required).

### SECTION D

Colloidal systems :

(i) Properties of colloids : optical, kinetic and electrical.

(ii) Electrokinetic phenomena; charge and stability of colloids, mechanism of coagulation.

(iii) Determination of Avogadro's number from Perrin distribution equation and Einstein's diffusion equation.

(iv) Ultracentrifuge, Determination of size of colloid particles and molecular weights of macromolecules.

(v) Colloidal electrolytes and their properties (soaps, detergents. Critical micellization concentration), proteins.

SECTION E : Physical Properties and molecular structure :

(i) Polar molecules and dipole moment (derivation equations not required)

(ii) Elementary ideas on molecular spectra, potential energy curves and Raman Spectra, with simple application.

Unit – 2 : Physical Chemistry (2)

Thermodynamics & Its Applications to Equilibrium processes.

### SECTION A

Thermodynamics :

(i) Heats of solution and dilution, heats of neutralisation from bond enthalpies, Kirchoff's equation.

(ii) Carnot's theorem, thermodynamic scale of temperature, refrigeration cycle.

(iii) Detailed treatment of entropy, free energy. Gibbs-Helmholtz equation. Partial molal quantities. Gibb's potential. Gibbs-Duhem equation. Maxwell's relations. Thermodynamic equation of state. Elementary idea of entropy and probability.

(iv) Applications of thermodynamics : Clausius-Clapeyron equation. Nernst distribution law. Joule-Thomson effect, expression for  $(C_p - C_v)$  for Van der Waals gases.

(v) Elements of statistical thermodynamics, Boltzmann distribution, partition functions and their relations with thermodynamic state functions.

#### SECTION B

(i) Chemical equilibria : Homogeneous equilibria. Experimental determination of equilibrium constants. Thermodynamic derivation of the law of mass action. The reaction isotherm & temperature dependence of equilibrium constants (Van't Hoff equation)

(ii) Ionic equilibria : Determination of hydrolysis constant and degree of hydrolysis, Buffer capacity. Neutralisation indicators – theory and application, (pH titration curves). Relative strengths of acids and bases.

#### SECTION C

Electromotive force – Different types of electrodes, glass and quinhydrone electrodes, important reference electrodes. Thermodynamics of a reversible chemical cell, standard electrode potentials and standard emf of Chemical cell (Nernst equation) : Concentration cells, liquid junction potential, salt bridge. Redox potential, Redox series, Redox indicators (Theory and applications). Decomposition potentials, polarisation, overvoltage, Dry cells (Leclanche cell), accumulators (acid and alkali). Applications of e.m.f. measurements-Thermodynamic parameters of electrochemical reactions (enthalpy, entropy and free energy), determination of solubility products, transport numbers, pH,  $K_w$ , valencies of ions and dissociation constants of weak electrolytes. Polarimetric titrations.

#### SECTION D

Colligative properties : Thermodynamic derivation of Raoult's law for lowering of vapour pressure, elevation of boiling point and depression of freezing point, van't Hoff's osmotic pressure equation, interrelationships between the different colligative properties, abnormal colligative properties.

#### SECTION E

Equilibrium in heterogeneous systems & phase equilibria.

(i) Derivation of phase rule; its significance. Duhem-Margules equation,

(ii) One component system-carbon dioxide, water, sulfur.

### Unit – 3 : Physical Chemistry (3)

Transport Phenomenon : Kinetics & Catalysis : Photochemistry Adsorption & Surface Phenomenon.

#### SECTION A

Viscosity of gases and liquids, viscosity coefficients, and their dependence on temperature. Stoke's Law and terminal velocity, diffusion of gases and solutes in solution (Pick's law).

#### SECTION B

Electrochemistry :

(i) Electrolytic conductance, Transport numbers and their interpretations; Hydration of ions. Determination of ionic speeds. Qualitative treatment of Onsager equation and Debye Huckel Theory.

#### SECTION C

Chemical Kinetics :

(i) Order and molecularity of a reaction, first and second order kinetics. Determination of the order of a reaction. Zero and fractional order reactions.

- (ii) Influence of temperature on the speed of a reaction. Arrhenius equation : Mechanism of uni- and bimolecular reactions from collision theory (detailed) and transition state theory (elementary),
- (iii) Simultaneous reactions : Parallel, consecutive and opposing reactions (simple-treatment), chain reaction (Hydrogen-Bromine reaction).

#### SECTION D

Adsorption and surface chemistry :

- (i) The phenomenon of adsorption on liquid and solid surfaces, Freundlich and Langmuir adsorption isotherms, B.E.T. equation (without derivation), surface area of adsorbents.
- (ii) Gibb's adsorption isotherm. Application of adsorption.

#### SECTION E

Catalysis :

- (i) Catalytic process : Theories of homogeneous and hetero-geneous catalysis (single reactant case).
- (ii) Acid-base catalysis. Kinetic salt effects,
- (iii) Enzyme catalysis and its characteristics,
- (iv) Application of catalysis in different fields.

#### SECTION F

Photochemistry :

- (i) Elementary principles of spectrophotometry-Lambert-Beer's law and its applications :
- (ii) Laws of photochemical reactions; H-Br reaction. H-Cl reaction, HI decomposition, photosensitized reactions, photochemical equilibrium.
- (iii) Elementary ideas of fluorescences and phosphorescence.

### Unit – 4 : Inorganic Chemistry (I)

Atomic Structure; Radioactivity & Nuclear Chemistry; Chemical Bonding.

#### SECTION A

- (i) Qualitative idea on Black-body radiation, photo-electric effect and Compton effect. Plank's quantum equation,
- (ii) Atomic spectra of hydrogen. Bohr's Theory of hydrogen atom (simple mathematical treatment). Sommerfeld extension. Limitation of Bohr-Sommerfeld theory. Quantum numbers, their significance : s,p,d,f-atomic orbitals. Sequence of energy levels. Aufbau principle, Hund's rule, Pauli exclusion principle. Electronic configuration of elements, ground state terms of many electron atoms and ions.
- (iii) Wave-particle duality. Heisenberg Uncertainty principle. de-Broglie relationship, Schrodinger wave equation, wave mechanical inter-pretation of orbital, probability distribution curves, shapes of s, p, d and f orbitals (qualitative).

#### SECTION B

Radioactive decay,  $\alpha$ ,  $\beta$  and  $\gamma$  rays; half life and average life of radioelements. Characteristics of radioactive decay series (different types) and Uranium decay series, Group displacement Law, radioactive equilibrium. Nuclear binding energy (including determining factors), stability of nuclei. Nuclear reactions, (different common types); projectiles, target nuclei, compound nuclei, spallation reaction. Nuclear energy. Elementary ideas on Nuclear fission and fusion reactions. Radio carbon dating. Age of mineral (elementary principle only), Isotopic exchange. Separation and uses of isotopes.

## SECTION C

Nature of chemical bond, Ionic bond. Lattice energy, Solvation energy; Born-Haber cycle (including mathematical calculation). Concepts of polarisation, Fajan's rule. Ionic potential and its applications. Inert pair effect, Covalent bond and coordinate bond,  $\sigma$ - and  $\pi$ - bonds, valence bond theory (simple mathematical treatment)- assumptions, defects. Resonance. Molecular orbital theory (non-Mathematical treatment), application to homo-nuclear diatomic molecules :  $H_2$  to  $F_2$  and hetero-nuclear diatomic molecules. NO, CO and HF and  $H_2O$ ,  $BeF_2$ ,  $CO_2$ , Bond orders; Hybridisation. Bent's rule, shapes of molecules. VSEPR theory. Hydrogen bond and its effects on physical properties, Intermolecular forces (elementary idea). Metallic bond, (qualitative band theory), conductors, semiconductors, superconductors, insulators

## Unit – 5 : Inorganic Chemistry (5)

Chemical Periodicity; Acid-Base, Solvents & Redox Systems; s-&p-Block Elements & their Compounds.

### SECTION A :

Periodic classification of elements on the basis of electronic configuration and periodic variation of properties; atomic radii, ionic radii, ionisation energy; Slater's rule; electron affinity, electro-negativity concept (Pauling & Allred-Rochow scales);

### SECTION B :

Modern concept of acids and bases including SHAB principle, strengths of acids and bases (qualitative idea). Non-aqueous solvents; Liquid ammonia & liquid  $SO_2$  as solvents. Redox Potentials. Formal potentials, applications of redox potentials, variation of redox potentials, under the influence of pH. precipitation and complex formation: dismutation. Choice of indicators in redox titrations. Redox potential diagrams and their applications.

### SECTION C :

Noble gases; isolation, properties and structure of compounds of noble gases.

### SECTION D :

B, Al, Ga, In, Tl- General group comparison. Boric acid, Borax, Boron nitrides, Borazine, Diborane. Borohydrides

### SECTION E :

C, Si, Ge, Sn, Pb-General group comparison. Carbides, silanes, silicon halides, silicic acids, silicones, silicates.

### SECTION F :

N, P, As, Sb, Bi-General group Comparison. Elemental state of P, As, Sb, Bi : Oxides and Oxyacids of Nitrogen and Phosphorus. Hydrazine, Hydroxylamine, Hydrazoic acid, Halides of nitrogen and phosphorus. Nitrides, condensed phosphates. Phosphonitrile compounds.

### SECTION G :

O, S, Se, Te-General group comparison. Hydrides, Halides, Elemental states of S, Se, Te : Oxides and Oxyacids of Sulphur. Selenium, and Tellurium. Thionic acids, sodium thiosulfate, polysulphides, hydrogen peroxide. Ozone, peroxyacids of sulfur.

### SECTION H :

F, Cl, Br, I- General group comparison. Elemental fluorine, Oxygen fluoride, Oxides and Oxyacids of Cl, Br, and I, Interhalogens and Polyhalides, Basic properties of halogens, Pseudohalogens, Fluorocarbons.

## Unit – 6 : Inorganic Chemistry (6)

d-Block Elements & their Compounds : Coordination Chemistry & Organometallics.

### SECTION A :

Terrestrial abundance of the metals; elementary idea of mineral formation, General methods of isolation of metals from their natural sources of occurrence (technical details omitted) Availability in India and the chemistry of isolation of the following metals : Li, Rb, Cs, Ag, Au, Ti, V, Cr, Mn, Co, Ni, Pt, Ra, U

### SECTION B :

Study of the elements of Group IA, IB, IIA and IIB with reference to their chemical reactions and properties (specially redox and coordination)

### SECTION C :

General characteristics of first row transition metals with reference to electronic configuration, oxidation states, redox properties, colour of the ions. Magnetic properties of first transition-metal ions and their complexes. Determination of magnetic susceptibility and its application to complex compounds, Polyvanadates.

### SECTION D :

Introduction to coordination compounds. Werner's theory, Nomenclature of coordination compounds upto two metal atoms. Types of ligands. Chelates and inner-metallic complexes and their applications in chemical analyses. Isomerism of coordination compounds: different types; geometrical and optical isomerisms for coordination numbers 4 and 6. Trans effect. Study of complexes in solution : detection, composition (Job's slope-ratio and mole-ratio methods), stability-potentiometric method. Metal-ligand interactions: Valence Bond and Crystal Field Theories. Application of VB and CFT approaches in explaining stereochemistry, magnetic and spectral features ( $d^1$ - $d^9$  systems) of coordination compounds (coord. No. upto six). Introduction of ligand field theory (qualitative treatment only). Metal ligand bonding, MO concept,  $\sigma$ -and  $\pi$ -bondings in complexes.

### SECTION E :

Metal complexes of  $\pi$ -acid ligands: carbonyls, nitrosyls and cyanides. Introduction of  $\sigma$ -bonded and non-classically bonded organometallics, metal (mono) olefins-Zeise's salt, Metallocenes: Ferrocene, Metal-metal bonded complexes inorganic rings, cages and clusters: boron cage compounds, carboranes and metallocene carboranes. Catalysis by organometallic complexes: substitution, oxidative addition, reductive elimination, insertion reactions, hydrogenation, hydroformylation and polymerization of alkenes; fluxional molecules.

## Unit – 7 : Organic Chemistry (1)

### SECTION A :

Nature of bonds in organic compounds : Atomic orbitals, Molecular orbitals: bonding, non-bonding and antibonding Hybridisation of atomic orbitals with reference of C, N, Cl, Br, I, O; Sigma and Pi-bonds; Electronegativity; Dipole moment (bond moment, group moment, polarisation and polarisability of covalent bond). Inductive and electromeric effects. Energetics of bond cleavage and bond formation: Bond energies and bond distances; Carbocations, Carbanions. Free radicals, ambident ions (definitions, examples). Conjugation, Resonance, Hyperconjugation; Tautomerism with reference to the following system only; Keto-Enol, Nitro-Acinitro, Nitroso-oiximino. Strength of organic acids and bases.

### SECTION B :

Optical activity, optical rotations : Racemization; Elements of symmetry, asymmetric and dissymmetric molecules, configuration and conformation acyclic systems. D-L, and R-S nomenclatures of acyclic systems. Erythro and Threo configurations. Fischer, Sawhorse and Newman projection formula; Geometrical isomerism involving C=C and C=N bonds.

## SECTION C :

Investigation of reaction mechanism : Rate law of a reaction; Activation energy, Transition state, Reaction intermediates, energy profile diagrams involving two transition states. Idea of a reversibility of a reaction. Kinetically and Thermodynamically controlled products: Primary kinetic isotope effects; classification of reagents and reactions; steric inhibition and steric strain in organic molecules. Pericyclic reactions, electrocyclic opening and closure.

## SECTION D :

Mechanism of organic reactions-What and Why? Addition reactions : Electrophilic, Nucleophilic and Radical Classical and non-classical carbonium ion. Comparative study of (i) electrophilic addition at C=C; (ii) Nucleophilic addition at C=O group of aldehydes and ketones; (iii) Nucleophilic substitution at C=O group of acids and their derivatives: Substitution reaction at the saturated carbon atom ( $S_N^1$ ,  $S_N^2$ ,  $S_N^i$ ) and the aromatic system ( $SE_2$ ). Elimination reactions; beta elimination ( $E_1$ ,  $E_2$  and  $E_1cB$ ) and alpha elimination carbenes; polymerisation reactions: Ionic and Free radical mechanisms.

## SECTION E :

Stereochemistry: Atropisomerism-Biphenyls (excluding R-S configuration). Substituted allenes. Resolution of racemic modifications. Walden inversion. Mutarotation. Asymmetric synthesis. Epimerisation; Elementary idea of stereospecific and stereoselective reactions.

## SECTION F :

Molecular Rearrangements : Allylic. Glaisen. Pinacol pinacolone. Acyclic systems : Hofmann, Lossen, Curtius, Schmidt, Fries and Beckmann. Cyclic systems : Demjanov and Favorskii.

## SECTION G :

Elementary idea of the applications of U.V, I.R. and H-NMR spectroscopy for simple organic-molecules.

## Unit – 8 : Organic Chemistry (2)

### SECTION A :

Aliphatic Compounds : Nomenclature and general methods of preparation, properties and reactions with mechanism in respect of the following:

- (i) Hydrocarbons-Alkanes, Alkenes, Alkadienes, Alkynes and their halogen derivatives.
- (ii) Monohydric alcohols;
- (iii) Ethers and thioethers;
- (iv) Carbonyl compounds;
- (v) Saturated monocarboxylic acids and their derivatives;
- (vi) Alkyl nitrites, Nitroalkanes, Nitriles, Isonitriles, Amines, Urea, Diazomethane, Diazoacetic ester.
- (vii) Amino acids and proteins : Definition and Classification; Synthesis (by Gabriel phthalimide method. Strecker's method and Azlactone method), properties and reactions of Glycine and Alanine, Tests, Peptide linkage and its geometry.
- (viii) Carbanion Chemistry with reference to acetoacetic ester, malonic ester and cyanoacetic ester.

### SECTION B :

Alicyclic Compounds : General methods of preparation, properties and reactions with mechanism of alicyclic compounds (one ring only) with upto six carbon atoms : Bayer Strain theory : Conformational aspects boat, half chair and chair forms: axial and equatorial bonds. Conformation, reactions of mono- and di-substituted derivatives only.

## SECTION C :

General methods of preparation, properties, reactions, structure and synthetic uses of Grignard reagents : preparation and uses of Li and Zn alkyls.

## SECTION D :

Carbohydrates: Nomenclature : Classification; Reactions and structure elucidation of Glucose and Fructose: Ascending and descending in sugar series. Aldopentoses, Aldohexoses; Ketopentoses and Ketohexoses; Inter-conversion of aldohexose to ketohexose and vice versa; Configuration of Arabinose, Glucose, Fructose; Conformation of Glucose : Inversion of Sucrose : Ring-chain tautomerism.

## Unit – 9 : Organic Chemistry (3)

### SECTION A :

Aromatic Compounds :

- (i) Idea of aromatic compounds upto 10- $\pi$ -electron system; Aromaticity and Aromatic characters;
- (ii) Benzene; Modern idea of structure, Electrophilic substitution; preparation properties and important reactions with mechanism of homologues of benzene, halogen derivatives: Nucleophilic and cine substitution; Benzyne intermediates; Orientation and reactivity-mechanistic approach
- (iii) Aromatic nitro compounds : General methods of preparation, properties, reactions with mechanism.
- (iv) General methods, of preparation, properties, reactions with mechanism of aromatic Nitriles, Nitroso compounds. Amines, Diamines and Nitro anilines,
- (v) Aromatic diazo compounds, preparation, properties and reactions with mechanism.
- (vi) General methods of preparation, properties and reactions with mechanism of the following classes of compounds : Phenols, Aromatic alcohols, Aromatic aldehydes, Aromatic Ketones, Aromatic carboxylic acids and their derivatives. Phenolic aldehydes and ketones, Phenolic acids. Nitro phenols. Benzoquinones and aromatic sulphonic acids.
- (vii) General methods of preparation, properties, reactions with mechanism of the following bi-functional compounds : Diols, Hydroxy ketones, Hydroxy aldehydes, Dicarbonyl compounds ( $\alpha$ ,  $\beta$  and  $\gamma$ ) keto acids, unsaturated aldehydes. Unsaturated ketones, Unsaturated acids. Lactones.

### SECTION B :

Polynuclearhydrocarbons : Synthesis, reaction and structures of Naphthalene and Anthracene; Synthesis (only) of Phenanthrene.

### SECTION C :

Heterocyclic Compounds; General methods of synthesis, properties and important reactions of the following compounds. Pyrrole, Furan, Thiophene, Pyridine, Quinoline and Indole and derivatives of Pyrrole and Pyridine.

### SECTION D :

Dyes : Classification. Elementary idea of colour and constitution; Preparation and uses of Phenolphthalein, Methyl orange, Congo red, Malachite green, Alizarin and Indigo.

### SECTION E :

Problems incorporating reactions including in the syllabus.

## Unit – 10 : Advanced Level Chemistry & Application Oriented Chemistry.

### SECTION A :

Bioinorganic Chemistry : Essential and trace elements of life, role of metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+/2+}$ ,  $\text{Cu}^{2+/1+}$ ,  $\text{Zn}^{2+}$ ) in biology. Basic reactions in the biological systems. Transport of ion across biological membrane,  $\text{Na}^+$  ion pump. Transport and storage of metabolic energy. ATP-ADP interconversion.  $\text{O}_2$ -uptake proteins: hemoglobin and myoglobin; electron transport proteins: cytochromes and ferredoxins; redox metalloenzymes: catalase, peroxidase, super oxide dismutase, ascorbate oxidase. Bioinorganic chemistry of nitrogen fixation, respiratory electron transport chain, photosynthesis. Toxic effects of metal ions, Chelation therapy, metal dependent diseases, metal complexes as drugs.

### SECTION B :

Chemical Analysis : Principles & Applications : Gravimetric and titrimetric (acid-base, redox, complexometric EDTA) estimations of common cations and anions (single & in mixtures). Chemical separation techniques: chromatography, ion exchange, solvent extraction: Instrumental methods of analysis: conductometry, potentiometry, polarography, amperometry, UV-VIS spectrophotometry, flame photometry, AAS and AES spectrometry. neutron activation analysis. IR, NMR and ESR spectroscopy applications to simple inorganic and organic systems. Analysis of complex materials: ores, alloys, drugs, pharmaceutical, air and water samples. Error analysis.

### SECTION C :

Chemistry on Materials : Production and uses of stainless steels and alloy steels, glass and ceramic materials, Portland cement (composition and setting). Chemical and biofertilizers. natural and synthetic rubbers, synthetic fibres, biopolymers and biodegradable polymers; common drugs and pharmaceuticals, common pesticides (applications and residual toxicity). Solid, liquid and gaseous fuels, coal based chemicals and petrochemicals ( $\text{C}_1$  to  $\text{C}_3$  compounds); oils, soaps and detergents, hydrogenation of oils, production of vanaspati and margarine. Constituents and formulations of paints and vernishes, common cosmetics and perfumes, food additives and preservatives.

### SECTION D :

Environmental Chemistry : Environmental segments: atmosphere, hydrosphere, lithosphere and biosphere. Environmental cycles : hydrologic cycle, oxygen-, nitrogen-, carbon-, phosphorus- and sulfur cycles, composition and structure of the atmosphere. Chemical and photochemical reactions in the atmosphere, ozone layer and its importance. Major air pollutants and their sources, green house effect, acid rain, photochemical smog; air pollution-control measures, Environmental role of water; major water pollutants, water quality parameters, water treatment: (domestic, industrial and waste water.)