SYLLABUS

BLB-03 (Level-10) Experience Nil/ Ph. D. Chemistry/ BE/ B Tech in Mat. Sc. Eng.

INORGANIC CHEMISTRY

Periodicity of elements: Periodicity of Elements: s, p, d, f block elements, the long form of periodic table. Detailed discussion of the following properties of the elements, with reference to s & p-blocks. (a) Effective nuclear charge, shielding or screening effect, variation of effective nuclear charge in periodic table. (b) Atomic radii (van der Waals) (c) Ionic and crystal radii. (d) Covalent radii (octahedral and tetrahedral) (e) Ionization energy, Successive ionization enthalpies and factors affecting ionization energy. (f) Electron gain enthalpy; trends of electron gain enthalpy. (g) Electronegativity, Variation of electronegativity with bond order, partial charge, hybridization.

Chemical bonding

Ionic bond: General characteristics, types of ions, size effects, radius ratio rule and its limitations. Packing of ions in crystals. Born-Landé equation, Born-Haber cycle and its application, Lattice energy and solvation energy and their importance in the context of stability and solubility of ionic compounds, polarizing power and polarizability. Fajan's rules and its applications.

Covalent bond: Valence Bond theory. Hybridization with suitable examples of linear, trigonal planar, square planar, tetrahedral, trigonal bipyramidal and octahedral arrangements, equivalent and non-equivalent hybrid orbitals, Concept of resonance and resonating structures in various inorganic and organic compounds.

MO Approach: Rules for the LCAO method, bonding and antibonding MOs and their characteristics for s-s, s-p and p-p combinations of atomic orbitals, nonbonding combination of orbitals, MO treatment of homonuclear diatomic molecules (N2, O2) and heteronuclear diatomic molecules (CO, NO). Comparison of VB and MO approaches

VSEPR theory, shapes of simple molecules and ions containing lone and bond pairs of electrons, multiple bonding (σ and π bond approach) and bond lengths. Covalent character in ionic compounds, polarizing power and polarizability. Fajan's rules and consequences of polarization. Ionic character in covalent compounds: Bond moment and dipole moment. Percentage ionic character from dipole moment and electronegativity difference.

Metallic Bond: Qualitative idea of valence bond and band theories. Semiconductors and insulators. (ii) Weak Chemical Forces: van der Waals forces, ion-dipole forces, dipole-dipole interactions, induced dipole interactions, Instantaneous dipole-induced dipole interactions. Repulsive forces, Hydrogen bonding (theories of hydrogen bonding, valence bond treatment) Effects of chemical force, melting and boiling points, solubility energetics of dissolution process.

Oxidation-reduction: Redox equations, standard electrode potential and its applications to inorganic reactions. Principles involved in some volumetric analyses (iron and copper).

Acids and Bases: Brönsted-Lowry concept of acid-base reactions, solvated proton, relative strength of acids, types of acid-base reactions, Lewis acid-base concept, Classification of Lewis acids, Hard and Soft Acids and Bases (HSAB) Application of HSAB principle.

Chemistry of s and p Block Elements – I: Periodicity in s- and p-block elements with respect to electronic configuration, atomic and ionic size, ionization enthalpy, electronegativity (Pauling & Mulliken scales). Allotropy in C, S, and P.

Oxidation states with reference to elements in unusual and rare oxidation states like carbides and nitrides), inert pair effect, diagonal relationship and anomalous behaviour of first member of each group.

Chemistry of s and p Block Elements – II: Hydrides and their classification (ionic, covalent and interstitial), structure and properties with respect to stability of hydrides of p- block elements.
Concept of multicentre bonding (diborane).
Structure, bonding and their important properties like oxidation/reduction, acidic/basic nature of the following compounds and their applications in industrial, organic and environmental chemistry.
Hydrides of nitrogen (NH_3, N_2H_4, N_3H, NH_2OH); Oxoacids of P, S and Cl; Halides and oxohalides: PCl_3, PCl_5, $SOCl_2$.

Chemistry of 3d metals
Oxidation states displayed by Cr, Fe, Co, Ni and Co.
A study of the following compounds (including preparation and important properties);
Peroxo compounds of Cr, $K_2Cr_2O_7$, $KMnO_4$, $K_4[Fe(CN)_6]$, sodium nitroprusside, $[Co(NH_3)_6]Cl_3$, $Na_3[Co(NO_2)_6]$.

Transition Elements
Chemistry of Ti, V, Cr Mn, Fe and Co in various oxidation states.

Inorganic Materials of Industrial Importance
Glass: Glassy state and its properties, classification (silicate and nonsilicate glasses). Manufacture and processing of glass. Composition and properties of the following types of glasses: Soda lime glass, lead glass, armoured glass, safety glass, borosilicate glass, fluorosilicate, coloured glass, photosensitive glass.
Ceramics: Important clays and feldspar, ceramic, their types and manufacture. High technology ceramics and their applications, superconducting and semiconducting oxides, fullerenes carbon nanotubes and carbon fibre.
Cements: Classification of cement, ingredients and their role, Manufacture of cement and the setting process, quick setting cements.

PHYSICAL CHEMISTRY
Gaseous State
Kinetic molecular model of a gas: postulates and derivation of the kinetic gas equation; collision frequency; collision diameter; mean free path and viscosity of gases, including their temperature and pressure dependence, relation between mean free path and coefficient of viscosity, calculation of σ from η; variation of viscosity with temperature and pressure.
Maxwell distribution and its use in evaluating molecular velocities (average, root mean square and most probable) and average kinetic energy, law of equipartition of energy, degrees of freedom and molecular basis of heat capacities.
Behaviour of real gases: Deviations from ideal gas behaviour, compressibility factor, Z, and its variation with pressure for different gases. Causes of deviation from ideal behaviour. van der Waal's equation of state, its derivation and application in explaining real gas behaviour. Isotherms of real gases and their comparison with van der Waals isotherms, continuity of states, critical state, relation between critical constants and van der Waals constants, law of corresponding states.

Solid state
Nature of the solid state, law of constancy of interfacial angles, law of rational indices, Miller indices, elementary ideas of symmetry, symmetry elements and symmetry operations, seven crystal systems and fourteen Bravais lattices; X-ray diffraction, Bragg's law, a simple account of rotating crystal method and powder pattern method. Analyses of powder diffraction patterns of NaCl, CsCl and KCl. Defects in crystals (stoichiometric and non- stoichiometric). Glasses and liquid crystals.

Chemical thermodynamics

Intensive and extensive variables; state and path functions; isolated, closed and open systems; zeroth law of thermodynamics.

First law: Concept of heat, q, work, w, internal energy, U, and statement of first law; enthalpy, H, relation between heat capacities, calculations of q, w, U and H for reversible, irreversible and free expansion of gases (ideal and van der Waals) under isothermal and adiabatic conditions.

Thermochemistry: Heats of reactions: standard states; enthalpy of formation of molecules and ions and enthalpy of combustion and its applications; calculation of bond energy, bond dissociation energy and resonance energy from thermochemical data, effect of temperature (Kirchhoff's equations) and pressure on enthalpy of reactions.

Carnot cycle, efficiency of heat engine, Carnot theorem

Second Law: Concept of entropy; thermodynamic scale of temperature, statement of the second law of thermodynamics; molecular and statistical interpretation of entropy. Calculation of entropy change for reversible and irreversible processes.

Third Law: Statement of third law, concept of residual entropy, calculation of absolute entropy of molecules.

Free Energy Functions: Gibbs and Helmholtz energy; variation of S, G, A with T, V, P; Free energy change and spontaneity. Relation between Joule-Thomson coefficient and other thermodynamic parameters, inversion temperature, Gibbs-Helmholtz equation, Maxwell relations, thermodynamic equation of state.

Chemical equilibrium

Criteria of thermodynamic equilibrium, degree of advancement of reaction, chemical equilibria in ideal gases, concept of fugacity. Thermodynamic derivation of relation between Gibbs free energy of reaction and reaction quotient (vant Hoff's reaction). Equilibrium constants and their quantitative dependence on temperature, pressure and concentration. Free energy of mixing and spontaneity; thermodynamic derivation of relations between the various equilibrium constants Kp, Kc and Kx. Le Chatelier principle (quantitative treatment) and its applications.

Phase Equilibria

Concept of phases, components and degrees of freedom, Gibbs Phase Rule for nonreactive and reactive systems; Clausius-Clapeyron equation and its applications to solid- liquid, liquid-vapour and solid-vapour equilibria, phase diagram for one component systems, with applications (H2O and sulphur system).

Phase diagrams for systems of solid-liquid equilibria involving eutectic (Pb-Ag system, desilverisation of lead), congruent (ferric chloride-water) and incongruent (sodium sulphate- water) melting points, completely miscible solid solutions (intermediate, medium, maximum freezing points).

Three component systems, water-chloroform-acetic acid system, triangular plots.

Chemical Kinetics

Order and molecularity of a reaction, rate laws in terms of the advancement of a reaction, differential and integrated form of rate expressions up to second order reactions, experimental methods of the determination of orders.

Temperature dependence of reaction rates; Arrhenius equation; activation energy. Collision theory of reaction rates, qualitative treatment of the theory of absolute reaction rates.

ANALYTICAL METHODS IN CHEMISTRY

UV-Visible Spectrometry: Origin of spectra, interaction of radiation with matter, fundamental laws of spectroscopy and selection rules, validity of Beer-Lambert's law. Instrumentation (choice of source, monochromator and detector) for single and double beam instrument;

Infrared Spectrometry: Basic principles of instrumentation (choice of source, monochromator & detector) for single and double beam instrument; sampling techniques.

Qualitative and quantitative aspects of analysis

Flame Atomic Absorption Spectrometry

Basic principles of instrumentation (choice of source, monochromator, detector, choice of flame and Burner designs. Techniques of atomization and sample introduction; Method of background correction, sources of chemical interferences and their method of removal.

Thermal and electro-analytical methods of analysis

Theory of thermo-gravimetry (TG), basic principle of instrumentation. Classification of electro-analytical methods, basic principle of pH metric, potentiometric and conductometric titrations. Techniques used for the determination of equivalence points.

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