OC H 463: ADVANCED PHYSICAL CHEMISTRY

Course Outcome

- It is an advanced level course which helps to understand the concepts of physics and their subsequent applications in the field of chemistry. The concepts of chemical thermodynamics help in the design of processes in chemical industries.
- The concepts of statistical thermodynamics find relevance in understanding the nature of solids and metals in specific.
- Quantum chemistry forms the basis of chemical bonding, photochemistry and spectroscopy.
- Reaction dynamics deals with advanced aspects of chemical kinetics.

UNIT-I Chemical Thermodynamics **[12 Hours]**

Entropy: Physical significance, entropy change in an ideal gas. Entropy change in reversible and irreversible processes. Thermodynamic equations of state.

Free energy, Maxwell's relations and significance. Gibbs – Helmholtz equation and its applications.

Nernst heat theorem: Its consequences and applications. Third law of thermodynamics – statements, applications and Comparison with Nernst Heat theorem.

Chemical affinity and thermodynamic functions. Effect of temperature and pressure on chemical equilibrium- van't Hoff reaction isochore and isotherms.

Chemical potential: variation of chemical potential with temperature. Gibbs – Duhem equation. Thermodynamic functions of mixing, Gibbs – Duhem – Margules equation.

Fugacity: Relationship between fugacity and pressure. Determination of fugacity- graphical method and Lewis Randall rule.

Activity and activity coefficient: Determination of activity by vapour pressure method.

UNIT-II Statistical thermodynamics **[12 Hours]**

Thermodynamic Probability, phase space, micro and macrostates, statistical weight factor, assembly, ensemble-significance, classification and comparison. Derivation of Distribution laws, Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac Laws, Limit of applicability of various laws. Partition function, Significance, Relationship between partition function and thermodynamic functions -Average energy, heat capacity, free energy, chemical potential for molecular particles.

Thermodynamic quantities in terms of partition function of particles: Evaluation of Translational, vibrational, rotational, electronic partition functions. Law of equi-partition principle. Partition function and equilibrium constant. Applications of partition function to mono atomic gases, diatomic molecules.

Statistical thermodynamic properties of solids (Heat capacity): Introduction, thermal characteristics of crystalline solid, Einstein model, Debye modification equilibrium constant.

UNIT-III Quantum Chemistry **[12 Hours]**

Particle waves, its character and significance. De-Broglie concept, uncertainty principle, Formulation of Shrodinger equation- significance and characteristics of wave function, Statistical significance of ψ. Normalization and orthogonality, Acceptable wave functions.

Postulates of quantum Mechanics, Operators, Operator algebra, types and applications, operators for the dynamic variables of a system (position, linear momentum, angular momentum, kinetic energy, potential energy and total energy). Eighen values and Eighen functions. Solution of SE for particle in a box (1D & 3D), particle in a ring, H atom. Applications of quantum mechanics to chemical bonding. Covalent bond-Valence bond and molecular orbital approaches with comparison.

Unit-IV Reaction Dynamics **[12 Hours]**

Kinetics of Composite Reactions: Inorganic reaction mechanism (decomposition of N_2O_5 and phosgene). Organic reaction mechanism-decomposition of acetaldehyde, Gold-Finger, Letort-Niclause rules, combustion of hydrocarbon.

Transition state theory: Derivation of rate constant, equilibrium hypothesis, Concept of tunnelling. Applications of TST to reactions in solution & reaction between atoms, Thermodynamic formulation of transition–state theory, limitations of TST. Extension of TST.

Potential energy surfaces: Features & construction. Theoretical calculation of E_a. Features of potential energy surfaces (attractive and repulsive surfaces for exothermic reaction). A brief account of stripping and rebound mechanisms. Spectroscopy of transient species.

References

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6. Principles of Physical Chemistry, B. R. Puri, L. R. Sharma and M. S. Pathania, Vishal Publishers, (2014).
7. Atomic Structure and Chemical Bond, Manasa Chanda, Tata McGraw Hill, (1991).
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