SEMESTER –I

PHYSICAL CHEMISTRY-I

THEORY

Programme: M.Sc. **Max.Hours : 60**
Course Code: P20/CHE/DSC/103 **Hours per week: 4**
Type of course: DSC -3 **Max.Marks: 100**
No. of credits : 4

Course Objectives:

- Thermodynamics is the branch of physics that is built upon the fundamental laws that heat and work obey. Statistical thermodynamics provides a means of averaging an assembly tends towards thermal equilibrium.
- Electrochemistry rely heavily on understanding of redox reactions to describe electrochemical cells.
- Quantum chemistry deals with wave mechanics in three dimensions to describe the structure of hydrogen atom and gives an understanding of quantization of angular momentum.
- Chemical kinetics is concerned with determining the speed or rate at which a reaction occurs.

Course Outcome:

CO1: Write down the concept of entropy. Describe 3rd law of thermodynamics and Evaluation Of absolute entropy from heat capacity data.

CO2: Write down Gibb's equations for non equilibrium system and conditions for material and phase equilibrium . Derive Clausius- Clapeyron equation and equation for equilibrium constant of ideal gas reactions.

CO3: Give the concept of partial molar properties and chemical potential. Derive Gibb'sDuhem equation.

CO4: Explain chemical cell and concentration cell(with and without transfer). Derive the Expression of liquid junction potential.

CO5: Write down the applications of EMF measurement. Define electrode polarization, Decomposition potential and concentration over potential.

CO6: Write down Debye – Huckel theory of electrolytic solution and Bjerrume theory of ion Association. Derive Debye – Huckel – Onsagar equation.

CO7: Write down the concept of black body radiation. Describe operators, commutation of Operators eigen function, eigen value and well behaved function.

CO8: Write down the postulates of quantum mechanics. Derive the expression of wave function and energy of particles moving in one and three dimensional box.

CO9: Write down collision theory and transition state theory of reaction rate. Describe Lindemann's theory of unimolecular reaction.

CO10: Write down linear free energy relationship – Hammett and Taft equation. DescribePrimary and secondary sat effect, reactivity – selectivity principle and Hammond postulate

MODULE I -THERMODYNAMICS-I **(15 Hrs)**

Concept of Entropy, Entropy as a function of V and T, Entropy as a function of P and T. Entropy change in isolated systems- Clausius inequality. Entropy change as criterion for spontaneity and equilibrium.

Third law of thermodynamics.Evaluation of absolute entropies from heat capacity data for solids, liquids and gases.Standard entropies and entropy changes of chemical reactions.

Thermodynamic relations.Gibbsequations.Maxwell relations.

Gibbs equations for non-equilibrium systems.Material equilibrium. Phase equilibium. Clausius-Clapeyron equation .Conditions for equilibrium in a closed system.

Chemical potential of ideal gases.Ideal-gas reaction equlibrium-derivation of equilibrium constant.Temperature dependence of equilibrium constant-the van’t Hoff equation.

Solutions: Specifiying the Solution composition. Partial molar poperties-significance.Relation between solution volume and partial molar volume. Measurement of partial molar volumes-slope and intercept methods. The chemical potential.Variation of chemical potential with T and P. Gibbs-Duhem equation-derivation and significance.

MODULE II - ELECTROCHEMISTRY- I **(15 Hrs)**

Electrochemical Cells: Derivation of Nernst equation – problems. Chemical and concentration cells (with and without transference).Liquid junction potential (LJP) – derivation of the expression for LJP – its determination and elimination**.**Types of electrodes. Applications of EMF measurements: Solubility product, potentiometric titrations, determination of pH using glass electrode, equilibrium constant measurements.

Decomposition potential and its significance.Electrode polarization – its causes and elimination.Concentration over-potential.

Concept of activity and activity coefficients in electrolytic solutions.The mean ionic activity coefficient.Debye-Huckel theory of electrolytic solutions. Debye-Huckel limiting law (derivation not required). Calculation of mean ionic activity coefficient.Limitations of Debye-Huckeltheory.Extended Debye-Huckel law.

Theory of electrolytic conductance.Derivation of Debye-Huckel-Onsager equation – its validity and limitations.

Concept of ion association – Bjerrum theory of ion association (elementary treatment)-ion association constant – Debye-Huckel-Bjerrum equation.

MODULE III - QUANTUM CHEMISTRY- I (15 hrs)

A brief review of Black body radiation-Planck's concept of quantization-Planck's equation, average energy of an oscillator (derivation not required), Wave particle duality and uncertain principle-significance of these for microscopic entities. Emergence of quantum mechanics. Wave mechanics and Schrödinger wave equation.

Operator**s**- Operator algebra.Commutation of operators, linear operators. Complex functions. Hermitianoperators.Operators ∇ and ∇^2 .Eigenfunctions and eigenvalues.Degeneracy.Linear combination of eigenfunctions of an operator. Well behaved functions. Normalized and orthogonal functions.

Postulates of quantum mechanics: Physical interpretation of wave function. Observables and Operators.Measurability of operators. Average values of observables. The time dependent Schrodinger equation.Separation of variables and the time-independent Schrodinger equation.

Theorems of quantum mechanics. Real nature of the eigen values of a Hermitian operator-significance. Orthogonal nature of the eigen values of a Hermitian operator-significance of orthogonality. Expansion of a function in terms of eigenvalues. Eigen functions of commuting operators-significance. Simultaneous measurement of properties and the uncertainty principle.

Particle in a box- one dimensional and three dimensional.Plots of Ψ and Ψ^2-discussion.Degeneracy of energy levels.Calculations using wave functions of the particle in a box-orthoganality, measurability of energy, position and momentum, average values and probabilities.Application to the spectra of conjugated molecules.

MODULE IV: CHEMICAL KINETICS- I (15 Hrs)

Theories of reaction rates: Collision theory, steric factor. Transition state theory.Thermodynamic formulation of transition state theory. Potential energy surface diagram, Reaction coordinate, Activated complex.Activation parameters and their significance.TheEyringequation.Unimolecularreactions and Lindamann's theory.
Complex reactions- Opposing reactions, parallel reactions and consecutive reactions (all first order type). Chain reactions-general characteristics, steady state treatment.Example- H2-Br2 reaction.Derivation of rate law.

Effect of structure on reactivity- Linear free energy relationships.Hammett and Taft equations-substituent (σ and σ^*) and reaction constant (ρ and ρ^*) with examples. Deviations from Hammett correlations, reasons- Change of mechanism, resonance interaction. Taft fourparameter equation.Correlations for nucleophillicreactions.The Swain – Scott equation and the Edward equation. Reactions in solutions: Primary and secondary salt effects.
The reactivity-selectivity principle – Isokinetic temperature -Isoselectivty rule, Intrinsic barrier and Hammond's postulate.

Reference Books:-

1. Atkins, P., andJulio de Paula.Atkin’s Physical Chemistry. Oxford University press.
2. Levine,I.N.,and McGraw Hill. *Physical Chemistry.*
3. Mcuarrie, D., and Simon,J.D.PhysicalChemistry *A* Molecular approach.Viva BooksPvt.Ltd.
4. McQuarrie,D.A.,and Simon,J.D. Molecular Thermodynamics UniversityScienceBooks.
5. Levine, I.N.Quantum Chemistry.PrenticeHall.
6. Chandra,A.K.Introduction to Quantum Chemistry.TataMcGrawHill.
7. Laidler, K.J. Chemical Kinetics.McGraw Hill.
8. Rajaraman, J., and Kuriacose.Kinetics and Mechanism of Chemical Transformations.
9. Glasstone,S.Introduction to Electrochemistry.
10. Bockris,J. O. M. & Reddy, A. K. N.Plenum.Modern Electrochemistry.
11. MaronS.H.,and Prutton, C.F. Principles of physical chemistry.Oxford&IBH.
12. HowardMaskill.ThePhysicalBasis ofOrganicChemistry. New York:Oxford UniversityPress.
13. Espenson,J. H.Chemical Kinetics and Reaction Mechanisms.McGrawHill.
14. Isaacs, N. S.Physical Organic Chemistry.ELBS.
15. Pilar,F.L. ElementaryQuantum Chemistry.McGrawHill.

SEMESTER -I

PHYSICAL CHEMISTRY- 1

THEORY MODEL PAPER

Course Code: P20/CHE/DSC/103 **Max Marks:60**
Credits: 4 **Max Hours:2½hrs**

SECTION-A

I Answer the following questions **4x10=40 Marks**

1. (a) Derive Van't Hoff's equation. **[CO2]**

   (b) Derive any two Maxwell Relations. **[CO3]**

OR

2. (a) What is chemical potential? Write Gibbs equations for non-equilibrium systems. **[CO2]**

   (b) Derive entropy as a function of temperature and volume. **[CO1]**

3. (a) Explain Bjerrum theory of ionic association. **[CO6]**

   (b) What is liquid junction potential? How is it determined experimentally? **[CO4]**

OR

4. (a) What is a Quinhydrone electrode? How pH of a solution is determined using this Electrode?**[CO5]**

   (b) Derive Debye-Huckel-Onsagar equation. **[CO6]**

5. (a) State and explain the postulates of quantum mechanics. **[CO8]**

   (b) Derive Schrodinger wave equation for particles in 1D box. **[CO8]**

OR

6. (a) Explain the terms: i) Hermitian Operator ii) Linear operator.**[CO7]**

   (b) Show that the function Sin 3x is an Eigenfunction of the d^2/dx^2. What is the Eigenvalue?**[CO7]**

7. (a) Explain the collision theory of reaction rates. **[CO9]**

   (b) Write the mechanism of H_2-Br_2 reaction and derive the rate law. **[CO9]**

OR

8.(a) DeriveEyring equation. **[CO10]**

   (b) Explain Swain Scott & Edward equations. **[CO10]**

SECTION-B

II Answer any FIVE **5 x 4 = 20 M**

9. Explain the determination of absolute entropy of liquids. **[CO1]**
10. Explain partial molar properties by slope method. **[CO3]**
11. Write a short note on electrode potential and decomposition potential. **[CO5]**
12. Derive the Nernst equation for Half-cell potential. **[CO5]**
13. Explain the following:

    i) Well behaved function ii) Normalized wave function **[CO7]**
14. Explain the term degeneracy **[CO8]**
15. Discuss transition state theory of reaction rates. **[CO9]**
16. Derive Taft four parameter equation. **[CO10]**