SEMESTER –II

PHYSICAL CHEMISTRY-II

THEORY SYLLABUS

Max.Hours: 60 **Max Marks:100**
Course Code: P20/CHE/DSC/203 **Hours per week: 4**
Course Type: DSC –7
No. of credits: 4

<u>COURSE OBJECTIVES:</u>

- The study of Thermodynamics makes the students to deal with non-equilibrium systems, ideal and non-ideal systems.
- Applications of Schrodinger wave equation studied in Quantum chemistry
- Photochemistry helps the students to deal with various processes which are initiated by electronically excited molecules.
- Solid-state chemistry allows the students to understandthe synthesis, structure, and properties of solid phase materials. To study the synthesis, properties and applications of nanoparticles.

<u>COURSE OUTCOMES:</u>

CO1:Write down the thermodynamic properties of ideal, non ideal and ideally dilutesolution. give the concept of fugacity and fugacity coefficient.

CO2: Define lowering of vapour pressure, elevation of B.P. and depression of F.P. derive the relation between molality and elevation of B.P. or depression of F.P.

CO3:Give the concept of distribution and probability and derive Boltzmann distribution law.

CO4: Describe quantum yield and the method of its determination. Derive quantum yield of fluorescence and phosphorescence.

CO5: Describe types of photochemical reactions and photo sensitization reaction.

CO6: Explain E- type delayed fluorescence and principle of flash photolysis
.

CO7: Describe Schrodinger's wave equation for hydrogen atom and separate it in to three component equations.

CO8: Describe variation principle and variation method. Write down the application of variation principle to H atom He, H2+ and H2 molecule
.

CO9: Explain the band theory of metal, insulator and semiconductor. Define p-n junction.

CO10: Classify super conductors and write down the BCS theory of superconductivity

MODULE1:THERMODYNAMICS-II&STATISTICALTHERMODYNAMIC 15 HRS

Ideal solutions.Thermodynamic properties of ideal solutions. Mixing quantities. Vapour pressure -Raoult's law. Thermodynamic properties of ideally dilute solutions. Vapour pressure- Henry's law.
Non ideal systems. Concept of fugacity, fugacity coefficeient. Determination of fugacity.Non ideal solutions. Activities and activity coefficients. Standard-state conventions for non ideal solutions. Determination of activity coefficients from vapour pressure measurements.Activity coefficients of nonvolatile solutes using Gibbs-Duhem equation.
Multi component phase equilibrium: Vapour pressure lowering, freezing point depression and boiling point elevation.

Statistical Thermodynamics: Partition Functions: Concepts of distribution and probability, Boltzmann distribution law. Interpretation of partition functions- translational, rotational, vibrational and electronic partition functions. Relationship between partition functions and thermodynamic functions (only S & G).

MODULE 2: PHOTOCHEMISTRY –I 15HRS

Electronic transitions in molecules. The Franck Condon principle.Electronically excited molecules- singlet and triplet states. Radiative life times of excited states-theoretical treatment. Measured life times.Quantum yield and its determination. Experimental set up of a photochemical reaction. Actinometry-ferrioxalate and uranyl oxalate actinometers – problems.

Derivation of fluorescence and phosphorescence quantum yields. E-type delayed fluorescence- evaluation of triplet energy splitting(ΔEST). Photophysical processes- photophysical kinetics of unimolecular reactions. Calculation of rate constants of various photophysical processes-problems, State diagrams
Photochemical primary processes. Types of photochemical reactions- electron transfer, photodissociation, addition, abstraction, oxidation and isomerization reactions with examples. Effect of light intensity on the rates of photochemical reactions.Photosensitization.Quenching-Stern-Volmer equation.Introduction to fast reactions-Principle of flash photolysis.

MODULE 3: QUANTUM CHEMISTRY-II 15 Hrs

Cartesian, Polar and spherical polar coordinates and their interrelations.
Schrodinger equation for the hydrogen atom- separation into three equations. Hydrogen like wave functions.Radial and angular functions.Quantum numbers n, l and m and their importance. The radial distribution functions. Hydrogen like orbitals and their representation.Polar plots, contour pots and boundary diagrams.
Many electron systems.Approximatemethods.The variation method-variation theorems and its proof.Trial variation function and variation integral.Examples of variational calculations.Pariclein a box.Construction of trial function by the method of linear combinations. Variation parameters.Secular equations and secular determinant.

Bonding in molecules.Molecular orbital theory-basic ideas.Construction of MOs by LCAO, H2+ ion.Thevariationan integral for H2+ ion.Detailed calculation of Wave functions and energies for the bonding and antibonding MOs. Physical picture of bonding and antibonding wave functions.Energy diagram. The MO wave function and the energy of H2 molecule MO by LCAO method and Valence bond method (detailed calculations not required)-comparison of MO and VB models.

MODULE4:SOLIDSTATECHEMISTRY 15 HRS

Electronic properties of metals, insulators and semi-conductors: Electronic structure of solids, Band theory, band structure of metals, insulators and semi-conductors. Electrons, holes and Excitons.The temperature dependence of conductivity of extrinsic semi-conductors.Photo conductivity and photovoltaic effect – p-n junctions.

Superconductivity: Occurrence of superconductivity. Destruction of superconductivity by magnetic fields – Meissner effect.Types of superconductors.Theories of super conductivity – BCS theory.

High temperature superconductors: Structure of defect perovskites. High Tc superconductivity in cuprates. Phase diagram of Y-Ba-Cu-O system. Crystal structure of YBa2Cu3O7-x.Prepartion of 1-2-3 materials.Origin of high Tc superconductivity.

Nanoparticles and their applications:

Introduction to nanoparticles.Reduced dimensionality in solids – zero dimensional systems, fullerenes, quantum dots. One dimensional systems, carbon nano tubes, preparation of nano particles –top down and bottom up methods. Preparation of nanomaterials- – sol gel methods, and chemical vapour deposition method; thermolysis. Characterization of nanoparticles – experimental methods – powder X-ray diffraction, transmission electron microscopy (TEM), and atomic force microscopy (AFM) (detailed theory and instrumentation are not required). Optical properties of nanoparticles, Applications of nanoparticles.

References Books:

1. Atkin's Physical Chemistry, Peter Atkins And Julio De Paula, Oxford University Press
2. Physical Chemistry, Ira N. Levine, Mcgraw Hill
3. Physical Chemistry-A Molecular Approach, D.A. Mcquarrie And J.D. Simon, Viva Books Pvt Ltd
4. Molecular Thermodynamics, D.A. Mcquarrie And J.D. Simon, University Science Books
5. Quantum Chemistry, Ira N. Levine, Prentice Hall
6. Introduction To Quantum Chemistry, A.K. Chandra, Tata Mcgraw Hill
7. Introduction To Solids, Leonid V. Azaroff, Tata Mcgraw Hill
8. Solid State Chemistry, D.K. Chakrabarthy, New Age International
9. Solid State Chemistry And Its Aplications, A.R. West, Plenum.
10. Fundamentals Of Photochemistry, K.K.Rohtagi-Mukherji, Wiley-Eastern
11. Molecular Photochemistry, N.J. Turro, Benjamin
12. Photochemistry, R.P.Kundall And A. Gilbert, Thomson Nelson
13. Essentials Of Molecular Photochemistry By A. Gilbert And J. Baggott, Blackwell Scientific Publications.
14. Organic Photochemistry By J.M.Coxon And B.Halton, Cambridge University Press.
15. Introductory Photochemistry By A.Cox And T.J.Kemp. Mcgraw-Hill, London.
16. Principles Of The Solid State, H. V. Keer, New Age International
17. Elements Of Physical Chemistry By Peter Atkins And Julio De Paula, Oxford University Press
18. Elements Of Statistical Thermodynamics, L. K. Nash, Addison – Wesley
19. Introduction To Statistical Thermodynamics, T. L. Hill, Addison Wiley
20. Statistical Thermodynamics, M. C. Gupta, New Age International
21. Quantum Chemistry, D.A. Mcquarrie, Prentice Hall
22. Elementary Quantum Chemistry, F. L. Pilar, Mcgraw Hill.
23. Nanostructured Materials And Nanotechnology, Edited By Hari Singh Nalwa, Academic Press
24. Self-Assembled Nanostructures, Jin Zhang, Zhong-Lin Wang, Jun Liu, Shaowei Chen &Gan-Yliu, Kluwer Academic/Plenum
25. Introduction To Nanotechnology, Charles P. Poole Jr, F. J. Owens, Wiley India Pvt. Ltd.
26. The Physics And Chemistry Of Solids By Stephen Elliott, Wiley Publishers. 27. Introductory Photochemistry By A.Cox And T.J.Kemp. Mcgraw-Hill, London.

SEMESTER -II

PHYSICAL CHEMISTRY- II

THEORY MODEL PAPER

COURSE CODE:P20/CHE/DSC/203 **Time: 21/2Hours**
Credits: 4 **Max Marks: 60**

SECTION-A

I Answer the following Questions:- **4 x 10 = 40 M**

1. (a) Explain activity and activity coefficient of nonvolatile solutes using Gibbs-Duhem equation**. [CO1]**
   (b) Derive an equation for the freezing point depression of a solution and Boiling point elevation [CO2]

OR

2. (a) Derive Henry's law expression for ideally dilute solutions**.** [CO1]
   (b) Explain the concepts of distribution and probability and Boltzmann distribution law. [CO3]

3. (a) Derive Stern-Volmer equation**.** [CO5]
   (b) Explain Uranyl oxalate actinometer. [CO4]

OR

4 (a) Give an account of E-type delayed fluorescence. [CO6]
   (b) Explain photophysical Kinetics of unimolecular reactions. **[**CO4]

5 (a) Write the Schrodinger wave equation for the hydrogen atom and separate it into three equations. [CO7]
   (b) State and explain variation theorem. [CO8]

OR

6. (a) Explain given below: i) Polar plots ii) Counter plots iii) Boundary diagram. [CO7]
   (b) Explain the M.O treatment of H_2^+ ion.[CO8]

7. (a) Discuss about BCS theory of superconductivity. [CO10]
   (b) Explain preparation of nanoparticles-Top down and bottom-up method. [CO10]

OR

8. (a) Describe the Phase diagram of the Y-Ba-Cu-O system.[CO10]
   (b) What are Schottky defects? Derive an expression for the number of Schottky defects ina crystal. [CO9**]**

SECTION-B

II Answer any <u>FIVE</u> **5 x 4 = 20 M**

9. Explain Vapour pressure- Roult's Law**.** [CO2]
10. 100 gr of Benzene mixed with 50gr of toluene at 25^{o}C. Find ΔVmix, ΔGmix, ΔHmix ΔSmix (assume an ideal solution**)** [CO1**]**
11. Explain the principle of flash photolysis [CO6]
12. Derive the quantum yield for phosphorescence. [CO4]
13. Explain the basic ideas of MOT? [CO8]
14. Draw radial distribution function of 2S, 3P orbitals. [CO7]
15. What is the Meisner effect? Explain its significance? [CO10]
16. Discuss briefly the difference between SEM and TEM. [CO10]