



DEPARTMENT OF PHYSICAL AND NUCLEAR CHEMISTRY AND CHEMICAL OCEANOGRAPHY  
SCHOOL OF CHEMISTRY  
ANDHRA UNIVERSITY

**Paper – IV: PHYSICAL CHEMISTRY- I**

**M.Sc I SEMESTER**

<b>Unit 1</b>	<b>States of Matter</b>	Transport properties of Gases – Thermal Conductivity Diffusion. Theories of liquid structure; Calculation of collision numbers.
	<b>Solids</b>	X – Ray diffraction studies: Bragg's equation – Crystal structure determination, lattice type and lattice dimensions – crystal defects – Band theory of solids – Semiconductors - Theories of specific heats of solids.
<b>Unit 2</b>	<b>Thermodynamics</b>	Free energy, entropy and enthalpy – chemical equilibrium – Thermodynamic criteria of the chemical equilibrium – effect of temperature on equilibrium constant – Vant Hoff isochore – Maxwell relations – Gibbs-Duhem equation; Duhem – margules equations; Classius-Clapeyron equations – Nernst heat theorem. Third law of thermodynamics and determination of absolute entropy – limitation of third law of thermodynamics.
<b>Unit 3</b>	<b>Kinetics I</b>	Theories of Reaction rates – Collision theory – limitation; transition state theory – effect of ionic strength – Debye-Huckel theory – primary and secondary salt effects – effect of dielectric constants of solvent-ion-ion interaction; solvent models – Born-Abraham. Langevin dipole model.
<b>Unit 4</b>	<b>Kinetics II</b>	Effect of substituent – Hamett equation – limitations – Taft equation – prediction of rate constant of a reaction; consecutive reactions, parallel reactions, opposing reactions (unimolecular steps only – no derivation) – specific and general acid-base catalysis – Skrabal diagram – fast reactions – flow systems – temperature and pressure jump methods – relaxation.

**Books suggested:**

For Units 1 and 2

1. Physical Chemistry by Glasstone
2. Physical Chemistry by Moore
3. Physical Chemistry by Castellan

For Units 3 and 4

1. Physical Chemistry (7<sup>th</sup> edition, 2002) by Atkins and Paule.



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**Paper – IV: PHYSICAL CHEMISTRY- II**

**M.Sc II SEMESTER**

<b>Unit 1</b>	<b>Physical methods of molecular structure elucidation</b>	<b>Magnetic properties of molecules theories of magnetic susceptibility – measurement of magnetic susceptibility. Principle and theory of NMR spectroscopy – Nature of spinning particle and its interaction with magnetic field – chemical shift and its origin – spin-spin interaction experimental methods – applications of NMR studies in structural elucidation – structure of ethanol, dimethyl formamide, styrene and acetophenone.</b>
<b>Unit 2</b>	<b>Electron spin resonance</b>	<b>Principle and experimental technique – g-factor, line shapes and line widths – hyperfine interaction – application of ESR studies to the structure of free radicals, metal complexes and biological systems.</b>
<b>Unit 3</b>	<b>Photochemistry</b>	<b>Fluorescence – delayed fluorescence, E(osime) and P(yrin) type – phosphorescence – Jabanowski diagram - photophysical process – intersystem crossing or internal conversion, derivation of Stem-Volmer equation – Quantum yield – Quenching effect – Photochemical equilibrium.</b>
<b>Unit 4</b>	<b>Electrochemistry</b>	<b>Electrochemical cell – Galvanic and electrolytic cell concentration cell with and without transference – effect of complexation on redox potential – ferricyanide/ ferrocyanide couple, Iron(III) phenanthroline couple Determination of standard potential, activity coefficients from EMF data.</b>

**Books Suggested:**

**For Units 1 and 2**

- 1. Fundamentals of Molecular Spectroscopy by Banwell.**
- 2. Spectroscopy by Straw & Walker**

**For Units 3 and 4**

- 1. Physical Chemistry (7<sup>th</sup> edition, 2002) by Atkins and Paule.**
- 2. Physical Chemistry by Glasstone.**

**Paper – IV: PHYSICAL CHEMISTRY- I**

**M.Sc I SEMESTER**

**PRACTICAL IIIIP: PHYSICAL CHEMISTRY PRACTICAL –I**

1. Critical Solution Temperature of partially miscible liquids phenol-water System.
2. Effect of electrolyte (NaCl) on miscibility temperature.
3. Determination of cell constant.
4. Determination of  $P_k$ , value of acetic acid by conductometric method.
5. Conductometric titration of strong acid with strong base (HCL vs NaOH)
6. Conductometric titration of a weak acid strong base (HOAc vs NaOH)

- Books suggested:
9. Practical Experiments in Physical Chemistry by Alexander Finallay.
  10. Experiments in Chemistry by D.V. Jahagirdan. Himalaya Pub. House, 2003.
  11. Physical chemistry experiments by P. Ghosh.

**M.Sc II SEMESTER**

**PRACTICAL IIIIP: PHYSICAL CHEMISTRY PRACTICAL – II**

1. Determination of composition of cuprammonium cation.
2. Determination of equilibrium constant of the reaction:  $KI + I_2 = KI_3$
3. Conductometric titration of mixture of a strong acid and weak acid weak acid with a strong base (HCl + HOAc) vs NaOH.
4. Potentiometric titration of iron (II) with  $K_2Cr_2O_7$
5. Determination of relative strength of acids (HCl) by ester hydrolysis
6. Polarimetric determination of relative strength of acids by hydrolysis of sucrose.

- Books suggested:
1. Practical Experiments in Physical Chemistry by Alexander Finallay
  2. Experiments in Chemistry by D.V. Jahagirdan. Himalaya pub. House, 2003.
  3. Physical chemistry experiments by P. Ghosh.

**M.Sc. DEGREE EXAMINATION**  
**SCHOOL OF CHEMISTRY**  
**MODEL QUESTION PAPER**  
**SECOND SEMESTER**  
**PAPER – IV: PHYSICAL CHEMISTRY**  
*(Effective from the admitted batch of 2011 – 2012)*

Time: 3 hours

Max. Marks: 80

**PART – A**

Answer All questions (4x5 = 20)

1. a. Derive VantHoff equation.  
(or)  
b. Derive Clasius – Clapeyron equation.
2. a. What is meant by critical micellar concentration (CMC)? Explain the factors affecting CMC.  
(or)  
b. Describe the experimental technique for ESR spectroscopy.
3. a. Give a brief account of Skrabal diagrams of acid-base catalysis.  
(or)  
b. Describe collision theory of reaction rates.
4. a. What causes fluorescence? Explain.  
(or)  
b. What is delayed fluorescence? Explain.

**PART – B**

Answer All questions (4x15 = 60)

5. a. (i) What is meant by partial molar quantity? Explain different methods for the determination of partial molar quantity.  
(ii) Derive Gibbs-Duhem equation and Duhem-Margules equation.  
(or)  
b. (i) Explain Nernst Heat Theorem.  
(ii) Define third law of thermodynamics and explain the determination of absolute entropy.
6. a. Discuss the thermodynamics of micellization.  
(or)  
b. Write an account of electrically conducting fire resistant and liquid crystal polymers.
7. a. Give an account of primary salt effect, deriving an equation for specific rate dependence on ionic strength of the medium.  
(or)  
b. Derive Hamett and Traf equations and explain substituent effect on specific rates.
8. a. Deduce Stern-Volmer equation emphasizing the determination of fluorescence life times.  
b. Describe the photochemical processes with different quantum yields

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Time: 3 hours

Max. Marks: 80

**PART – A**

Answer All questions (4x5 = 20)

1. a. Explain chemical shift.  
(or)  
b. Discuss spin-spin interaction.
2. a. Explain the significance of 'g-factor'.  
(or)  
b. Describe the experimental technique for ESR spectroscopy.
3. a. What are standard redox potentials? What is the effect of complexation?  
(or)  
b. Give a brief account of fuel cells.
4. a. Describe concentration polarization and its relation to current density.  
(or)  
b. Describe different models of electrode-solution inter phase.

**PART – B**

Answer All questions (4x15 = 60)

5. a. (i) Explain the principle of NMR spectroscopy and explain the nature of spinning particle and its interaction with magnetic field.  
(ii) Explain the NMR spectrum of ethanol and acetophenone.  
(or)  
b. (i) Explain the molecular theory of magnetic susceptibility.  
(ii) Write the method of measurement of magnetic susceptibility.
6. a. Discuss the shapes and widths of spectral lines in esr spectroscopy.  
(or)  
b. Describe the application of esr on the study of free radicals.
7. a. Explain emf calculations in concentration cells with and without transference.  
(or)  
b. Explain the determination of activities from emf measurements.
8. a. Derive Butler-Volmer equation and explain the determination of exchange current density from Tafel plots.  
(or)  
b. Describe voltametry emphasizing its applications yields.