



JYOTI NIVAS COLLEGE AUTONOMOUS, BANGALORE – 560 095

Programme: B.Sc.

VI Semester

CHEMISTRY - VIII NEP

Advanced Physical Chemistry and Spectroscopy II

CREDITS: 4

NO. OF HOURS: 60

COURSE CODE: 21VICH8T

**Course Objectives:**

This course aims to impart to the student, knowledge of:

**I. Understanding Core Concepts:**

1. The fundamental principles and terminologies related to phase equilibria, ionic equilibria, thermodynamics, and molecular structures.
2. The theoretical foundations of electroanalytical techniques, group theory, and mass spectrometry.

**II. Analytical Skills:**

3. Applying the Gibbs Phase Rule, Henderson's equation, and Clausius-Clapeyron equation to solve phase equilibria and thermodynamic problems.
4. Interpreting phase diagrams, calculating degrees of freedom, and understanding the behaviour of one- and two-component systems.

**III. Practical Applications:**

5. Buffers, solubility products, and ionic equilibria in real-world scenarios such as qualitative analysis and buffer preparation.
6. Applying electroanalytical techniques like potentiometry, conductometry, and voltammetry in practical laboratory settings for precise measurements and analysis.

**IV. Critical Thinking:**

7. Analyzing and critique the mechanisms of flame atomic and absorption spectrometry, understanding the principles behind instrumentation and atomization processes.
8. The applications of group theory and symmetry operations in the analysis of molecular structures and chemical reactions.

**Course Outcomes:**

After the completion of this course, the student would be able to:

**I. Understand Core Concepts:**

- CO1. Grasp the fundamental principles and terminologies related to phase equilibria, ionic equilibria, thermodynamics, and molecular structures.
- CO2. Comprehend the theoretical foundations of electroanalytical techniques, group theory, and mass spectrometry.

**II. Showcase Analytical Skills:**

- CO3. Develop the ability to apply the Gibbs Phase Rule, Henderson's equation, and Clausius-Clapeyron equation to solve phase equilibria and thermodynamic problems.
- CO4. Enhance skills in interpreting phase diagrams, calculating degrees of freedom, and understanding the behaviour of one- and two-component systems.

**III. Possess Practical Applications:**

- CO5. Utilize knowledge of buffers, solubility products, and ionic equilibria in real-world scenarios such as qualitative analysis and buffer preparation.

- CO6. Apply electroanalytical techniques like potentiometry, conductometry, and voltammetry in practical laboratory settings for precise measurements and analysis.

#### IV. Develop Critical Thinking:

- CO7. Analyze and critique the mechanisms of flame atomic and absorption spectrometry, understanding the principles behind instrumentation and atomization processes.
- CO8. Evaluate the application of group theory and symmetry operations in the analysis of molecular structures and chemical reactions.

CO No.	Course outcomes statement	Knowledge level
1.	Grasp the fundamental principles and terminologies related to phase equilibria, ionic equilibria, thermodynamics, and molecular structures.	K1, K2, K3
2.	Comprehend the theoretical foundations of electroanalytical techniques, group theory, and mass spectrometry.	K1, K2, K3
3.	Develop the ability to apply the Gibbs Phase Rule, Henderson's equation, and Clausius-Clapeyron equation to solve phase equilibria and thermodynamic problems.	K1, K2, K3
4.	Enhance skills in interpreting phase diagrams, calculating degrees of freedom, and understanding the behaviour of one- and two-component systems.	K1, K2, K3
5.	Utilize knowledge of buffers, solubility products, and ionic equilibria in real-world scenarios such as qualitative analysis and buffer preparation.	K2, K3
6.	Apply electroanalytical techniques like potentiometry, conductometry, and voltammetry in practical laboratory settings for precise measurements and analysis.	K3, K4 & K5
7.	Analyze and critique the mechanisms of flame atomic and absorption spectrometry, understanding the principles behind instrumentation and atomization processes.	K2, K3, K4
8.	Evaluate the application of group theory and symmetry operations in the analysis of molecular structures and chemical reactions.	K3, K4 & K5

K1 – Remember, K2 – Understand, K3 – Apply, K4 – Analyze, K5 – Evaluate, K6 – Create

#### Mapping of COs with POs

	PO 1	PO 2	PO 3	PO 4	PO 5	PO 6	PO 7	PO 8	PO 9	PO 10
CO 1	✓	✓		✓						✓
CO 2	✓	✓		✓						✓
CO 3	✓	✓		✓						✓
CO 4	✓	✓		✓						✓

CO 5	✓	✓		✓			✓		✓	✓
CO 6	✓	✓		✓			✓		✓	✓
CO 7	✓	✓		✓					✓	✓
CO 8	✓	✓		✓						✓

### Programme Objectives aligned with Graduate attributes

- PO1- Knowledge
- PO2- Scientific thinking
- PO3- Entrepreneurial skills
- PO4- Analytical skills
- PO5- Communication skills
- PO6- Social commitment
- PO7- Research and Inquiry
- PO8- Conservation of Environment
- PO9- Employability
- PO10- Academic orientation

### Syllabus

#### Unit I

15 Hours

#### Chapter 1: Phase Equilibria

8 Hours

Phases, components and degrees of freedom of a system (explanation of the terms taking suitable examples), criteria of phase equilibrium (thermal, mechanical and chemical). Gibb's Phase Rule and its thermodynamic derivation. Phase diagrams of one-component systems (water and sulphur systems - phase diagram, explanation of the various equilibria, triple point, application of phase rule to various phases, effect of external pressure on transition temperatures, calculation of the degrees of freedom). Two-component systems (condensed phase rule) involving eutectics, congruent and incongruent melting points (lead-silver system- phase diagram, the effect of impurity elements on the melting point, calculation of the degrees of freedom, eutectic mixture - definition, composition and applications, cooling of molten mixtures and Pattinson's process. Phase diagram of  $\text{FeCl}_3$  -  $\text{H}_2\text{O}$  system. Freezing mixture - definition and applications. Phase diagram of Na - K system.

#### Chapter 2: Ionic Equilibria

7 Hours

*Self-study: Common ion effect: statement and example (ammonium hydroxide - ammonium chloride and acetic acid - sodium acetate). Buffers: types and examples. Buffer action and buffer capacity. pH of buffers- Henderson's equation and its derivation for acidic and basic buffers.*

Problems in calculating the pH of buffers. Solubility product and ionic product - definitions and their applications in the precipitation of II and IV group basic radicals in the qualitative analysis of simple salt mixtures. Analytical and biological applications of buffers.

#### Unit II

15 Hours

#### Chapter 3: Thermodynamics II

7 Hours

Gibb's-Helmholtz equation - derivation from  $dG = VdP - SdT$ . Concepts of partial molar properties - partial molar free energy, chemical potential, partial molar volume and its significance. Derivation of Gibbs-Duhem equation. Concept of fugacity: Determination of fugacity by graphical method. Activity and activity coefficient and its significance. Derivation of van't Hoff reaction isotherm, van't Hoff reaction isochore and Clausius-Clapeyron equation. The application of Clausius-Clapeyron equation to the determination of  $\Delta T_b$  and  $\Delta T_f$  (in detail with derivations). Numerical problems. Nernst heat theorem (qualitative treatment only).

**Chapter 4: Physical Properties and Molecular Structures** **4 Hours**

Dipole moment. Polarisation and orientation of dipoles in an electric field. Clausius-Mossotti equation (derivation). Electrical properties of solids: types of solids-metals, insulators and semiconductors. Pyroelectricity, piezoelectricity, ferroelectricity, inverse piezoelectricity. Definition and examples. Thomson effect, Seebeck effect and Peltier effect - definitions with examples.

**Chapter 5: Flame Atomic and Absorption Spectrometry** **4 Hours**

Simple atomisation techniques: flame atomisation and electrochemical atomisation. Processes occurring during atomisation. Basic principles of instrumentation (choice of source, monochromator, detector, choice of flame and burner designs). Single beam and double beam instruments. Sample introduction. Correction methods: two-line and continuum source correction methods. Sources of chemical interferences and their method of elimination.

**Unit III** **15 Hours**

**Chapter 6: Electroanalytical Techniques** **15 Hours**

Self-study: Classification of electroanalytical methods: Potentiometry, Coulometry and Voltammetry (explanation of the principle of each technique). Principle of pH meter, conductometer and potentiometer).

**6.1: Potentiometry and Conductometry**

Potentiometric (acid base and redox, calibration, choice of electrodes) and conductometric titrations. (acid base - 4 types, conductivity cell, cell constant and its determination). Techniques used for the determination of equivalence points (comparison of use of indicator and graphical method). Techniques used for the determination of pKa values (conductometry and potentiometry). Advantages of conductometric and potentiometric methods.

**6.2: Voltammetry**

Polarography – Type of mercury electrodes (dropping mercury electrodes, hanging drop mercury electrode, static mercury drop electrode, mercury thin film electrode). Linear scan polarography. Types of mass transport – Faradaic and non-Faradaic currents. Polarogram – sign conventions. Ilkovic equation and its applications. Half wave potential and its significance. Principles of different voltammetric techniques: linear scan voltammetry, normal pulse voltammetry and differential pulse voltammetry. Cyclic voltammetry: Principle – explanation of electro-oxidation and electro-reduction based on frontier and molecular orbitals. Current – potential relation. Excitation response signal in CV and their significance. Electrochemical reversible and irreversible and quasi-reversible electrochemical processes and diagnostic criteria. Explanation of a typical electrochemical reversible process using the potassium ferricyanide system as an example.

**Unit IV** **15 Hours**

**Chapter 7: Group Theory** **8 Hours**

Definition of groups, subgroups, cyclic groups, conjugate relationships, classes, simple theorems in group theory. Symmetry elements and symmetry operations, point groups, Schoenflies notations, representations of groups by matrices, reducible and irreducible representations, characters of representations, Great Orthogonality Theorem (without proof) and its applications, character tables and their uses (representations for the  $C_n$ ,  $C_{nv}$ ,  $D_{nh}$  groups to be worked out explicitly) Mulliken symbols for irreducible representations Direct products.

**Chapter 8: Mass Spectrometry** **7 Hours**

Basic Principles, instrumentation – inlet systems, ionisation chamber, analyser and detector. The molecular ion – structure and recognition. Fragmentation processes – Representation, basic types and

rules, factors influencing fragmentation. Fragmentation of functional groups – alkanes, cycloalkanes, carbonyl compounds, Mc Lafferty rearrangement.

### References and Recommended Books

1. Atkins P and Ronald Friedman, Molecular Quantum Mechanics, 5th Edition, Oxford University Press, New York, 2011.
2. Barrow, G.M. Physical Chemistry Tata McGraw-Hill (2007).
3. Castellan, G.W. Physical Chemistry 4th Ed. Narosa (2004).
4. Chandra, A. K. Introductory Quantum Chemistry Tata McGraw-Hill (2001). House, J. E.
5. Towe, J. P. & Peterson, K. Quantum Chemistry, Academic Press (2005).
6. Callen, Herbert Thermodynamics and an Introduction to Themostatistics, 2nd edition, John Wiley & Sons, 1985.
7. V. S. Bagotsky, Fundamentals of Electrochemistry, John Wiley & Sons, Inc. 2006.
8. Samuel Glasstone, An Introduction to Electrochemistry, Read Book Publishers, 2008.
9. K. L. Kapoor, A Text Book of Physical Chemistry: Quantum Chemistry and Molecular Spectroscopy, 5th edition, McGraw Hill Education (India) Private Limited, 2014.
10. Puri, Sharma, Pathania, Principles of Physical Chemistry, 48th edition, Vishal Publishing company.
11. Colin.N. Banwell and Elaine M, Fundamentals of Molecular Spectroscopy, 4th edition, McGraw Hill Education, 2017.
12. Kakkar, R. Atomic & Molecular Spectroscopy: Concepts & Applications, Cambridge University Press (2015).
13. John R. Dyer: Applications of Absorption Spectroscopy of Organic Compounds, Prentice Hall.
14. R.M. Silverstein, G.C. Bassler & T.C. Morill: Spectrometric Identification of Organic Compounds, John Wiley & Sons
15. Kemp W, Organic Spectroscopy, 3rd Edition, Palmgrave Macmillan, 2019.
16. Pavia D L, Lampman G M, Kriz G S and Vyvyan J R, Introduction to Spectroscopy, 5th Edition, Cengage Learning, Delhi, 2015.
17. Cotton F. A. Chemical Applications of Group Theory, 3rd Edition, Wiley 2008.
18. Willard, H.H., Merritt, L.L., Dean, J. & Settle, F.A. Instrumental Methods of Analysis, 7th Ed. Wadsworth Publishing Company Ltd., Belmont, California, USA, 1988.
19. Christian, G.D; Analytical Chemistry, 6th Ed. John Wiley & Sons, New York, 2004.
20. Harris, D. C. Quantitative Chemical Analysis, Ed. New York, W.H. Freeman, 2001.
21. Khopkar, S.M. Basic Concepts of Analytical Chemistry. New Age, International publisher, 2009.
22. Skoog, D.A. Holler F.J. & Nieman, T.A. Principles of Instrumental Analysis, Cengage Learning India Ed., 2023.

## **Chemistry Practical Paper VIII: Advanced Physical Chemistry and Spectroscopy II**

**CREDITS: 2**

**NO. OF HOURS PER WEEK: 4**

**COURSE CODE: 21VICH8P**

### **Course Objectives:**

This course aims to impart to the student skills and knowledge required for

- Preparation and standardization of solutions required for an experiment.
- Use of a colorimeter in the study of the kinetics of a reaction.
- Use of a colorimeter for titrations.
- Use of a colorimeter in the estimation of mixtures.
- Determination of partial molal volume of solutions
- The use of a conductivity meter for determination of specific conductance and solubility of electrolytes
- The use of conductivity meter for titrations (acid base, redox, precipitation).
- Plotting of data in two dimensions and identifying the end point of the titration.
- The working, calibration and use of a potentiometer.
- The use of different reference and working electrodes.
- Methodology of a potentiometric titration for different classes of reactions: acid base, redox, precipitation.

### **Course Specific Outcomes:**

On completion of the course, students should be able to:

- Identify wavelength of maximum absorbance
- Collect data using a colorimeter/spectrophotometer.
- Use colorimeter/spectrophotometer for colorimetric estimations, titrations and kinetic studies.
- Calculate the molal volume of a system at STP using experimental data.
- Learn to work in teams and present experimental results in both oral and written form.
- Use the conductivity meter as a tool for quantitative analysis
- Use conductivity measurements to distinguish between electrolytes (strong and weak)
- Identify problems where conductivity measurements can be used and devise protocols for the experiment.
- Carry out an experiment based on the protocol and find solutions to problems encountered during the experiment
- Use the potentiometer as a tool for quantitative analysis.
- Identify problems where potentiometry measurements can be used and devise protocols for the experiment.
- Carry out the experiment based on the protocol and solve problems encountered during the experiment.

### **Part A:**

1. Potentiometric titration of  $K_2Cr_2O_7$  vs FAS.
2. Potentiometric determination of dissociation constant of Phosphoric acid.
3. Determination of  $pK_a$  of phosphoric acid by pH metric method.
4. Potentiometric titration of acid mixture vs NaOH.
5. Conductometric titration of acid mixture vs NaOH.
6. Conductometric titration of strong acid with salt vs NaOH.

7. Study of hydrolysis of methyl acetate in two different concentrations of HCl and reporting the relative strength.
8. Study of hydrolysis of methyl acetate at two different temperatures of HCl and reporting the relative strength.

**Part B:**

1. Colorimetric determination of dissociation constant of indicator (phenolphthalein/methyl orange)
2. Determination of degree of hydrolysis for aniline hydrochloride at room temperature and calculation of dissociation constant of the base by pH metry.
3. Determination of acidic, basic dissociation constants and isoelectric point of amino acids by pH metry.
4. Determination of pH of acetic acid/sodium acetate buffer by pH metry
5. Evaluation of Arrhenius for  $K_2S_2O_8$  vs KI by colorimetry
6. Determination of DO by Winkler's method.
7. Combined spectral problems (UV, IR,  $^1H$  NMR) – 2 sessions

**References and Recommended Books**

1. Findlay's practical physical chemistry revised by P. B. Levitt, Longman's London (1966).
2. Experiments in Physical Chemistry by Shoemaker and Garland, McGraw Hill International Edn. (1966)
3. Advanced Practical Physical Chemistry by J. B. Yadav, Goel Publications Meerut (1988)
4. Senior Practical Physical Chemistry by B. C. Kosla, Simla Printers New Delhi (1987)
5. Experimental Physical Chemistry by Daniel et al., McGraw Hill, New York (1962).
6. Practical Physical Chemistry by A.M James and P. E. Pritchard, Longman's Group Ltd (1968).
7. Experimental Physical Chemistry by Wilson, Newcombe & others, Pergamon Press, New York (1962)
8. Experimental Physical Chemistry by R. C. Behra and B Behra, Tata McGraw, New Delhi (1983)
9. Experimental Physical Chemistry by V. D. Atavale and Parul Mathur, New Age International, New York (2001)
10. Physical Chemistry Laboratory Principles and Experiments by H. W. Salberg J. I. Morrow, S. R. Cohen and M. E. Green Macmillan publishing Co. New York. Delhi (2006).

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**JYOTI NIVAS COLLEGE AUTONOMOUS, BANGALORE- 560095**  
**III B.Sc., VI Semester, 21VICH8T**  
**Chemistry VIII**  
**Advanced Physical Chemistry and Spectroscopy II**  
**End Semester Question Paper Format for Theory**

Maximum Marks: **60**

Time: **2 Hrs 30 mins**

The question paper shall have **Sections A, B and C**. **Section A** shall consist of **9** questions of **2** marks each of which the student answers **5** questions. **Section B** shall consist of **8** questions of **4** marks each of which the student answers **5** questions. **Section C** shall consist of **4** questions of **10 (can be split as 5+5 and 6+4)** marks of which the student answers **3** questions to give due weightage to all chapters. The question paper shall consist of questions drawn from the respective chapters such that the marks allotted to these chapters are in proportion to the number of teaching hours prescribed. **Paper setters are requested to avoid 2 marks questions in Section B.**

**Blue print of Question Paper**

Unit	Chapter Title	Hours of Teaching	Marks Allotted
I	Chapter 1: Phase Equilibria	15	23
	Chapter 2: Ionic Equilibria	(8+7)	(13+10)
II	Chapter 3: Thermodynamics II	15	22
	Chapter 4: Physical Properties and Molecular Structures	(7+4+4)	(10+6+6)
	Chapter 5: Flame Atomic and Absorption Spectrometry		
III	Chapter 6: Electroanalytical Techniques	15	22
IV	Chapter 7: Group Theory	15	23
	Chapter 8: Mass Spectrometry	(8+7)	(13+10)
<b>Total</b>		<b>60</b>	<b>Sec A: 9 x 2 = 18</b> <b>Sec B: 8 x 4 = 32</b> <b>Sec C: 4 x 10 = 40</b> <b>Total = 90</b>
<b>Max. Marks for students: 60 (A: 5 x 2=10 + B: 5 x 4 = 20 + C: 3 x 10 = 30)</b>			



JYOTI NIVAS COLLEGE AUTONOMOUS, BANGALORE- 560095

III B.Sc., VI Semester, 21VICH8T

Chemistry VIII

Advanced Physical Chemistry and Spectroscopy II

Model Question Paper

Time: 2:30 Hrs.

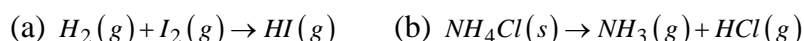
Max. Marks: 60

### Section A

Answer any five of the following questions.

(5 x 2 = 10)

1. How many phases, component and degrees of freedom are in each of the following systems:



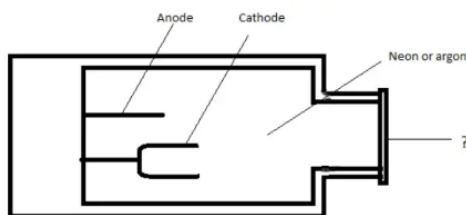
2. Differentiate between eutectic point and triple point.

3. Vapour pressure of water at 95°C and 100°C are 634 and 760 mm respectively. Calculate the molar heat of vaporization,  $\Delta H_{vap}$ , of water between 95°C and 100°C.

4. Define chemical potential. Is it an intensive or an extensive property?

5. Define piezoelectricity and ferroelectricity.

6. The following diagram shows a picture of hollow cathode lamp. Identify the unmarked component. What is it made of?



7. Write the matrix representation of identity (E) and  $\sigma_v(xz)$ .

8. What do the Mulliken symbols  $A_{1g}$  and  $B_{2u}$  signify?

9. What is meant by half wave potential? Write its significance.

### Section B

Answer any five of the following questions.

(5 x 4 = 20)

10. Define reduced phase rule. Describe phase diagram for TWO component Pb-Ag system.

11. Mention the application of solubility product in the precipitation of group II and IV basic radicals in qualitative analysis of salt mixtures.

12. Derive Clausius-Mossotti equation.

13. Discuss the basic principles of instrumentation of atomic absorption spectrometry.
14. Show that  $C_{2v}$  point group obeys all the rules of group theory.
15. Give the structure of compound  $C_{10}H_{12}O$ , whose mass spectrum shows  $m/z$  values of 15, 43, 57, 91, 105 and 148.
16. Write the principle for conductometric titrations. What are the advantages of conductometric titration over conventional volumetric methods?
17. Write the basic principle of linear scan voltammetry and differential scanning voltammetry.

### Section C

Answer any three of the following questions.

(3 x 10 = 30)

18. a) Draw and discuss the phase diagram of sulphur which exhibits the phenomenon of enantiotropy.  
b) How is buffer capacity of  $CH_3COOH-CH_3COONa$  system maintained if we add small amount of strong acid (HCl) or strong base (NaOH) in the buffer? (5+5)
19. a) Derive Gibbs-Duhem equation.  
b) Define fugacity. How is it determined by graphical method? (5+5)
20. a) Construct the group multiplication table for a cyclic group of order = 4, explaining the rules involved.  
b) What do you understand by metastable ions or peaks? How these are recognized in the mass spectrum and what is their importance? (5+5)
21. a)  $25\text{ cm}^3$  of a solution of HCl (0.1M) is being titrated potentiometrically against a std. (0.1 M) sol. of NaOH using a hydrogen electrode as the indicator electrode and saturated calomel electrode (S.C.E.) as the reference electrode. What would be the emf of the cell initially and after the addition of 20, 25.10, 30.00  $\text{cm}^3$  of NaOH solution?  
b) Why CV has been recognized as the most versatile electrochemical technique? How can you determine whether a reaction is reversible or not with the help of "Equation of the polarographic wave"? (5+5)

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