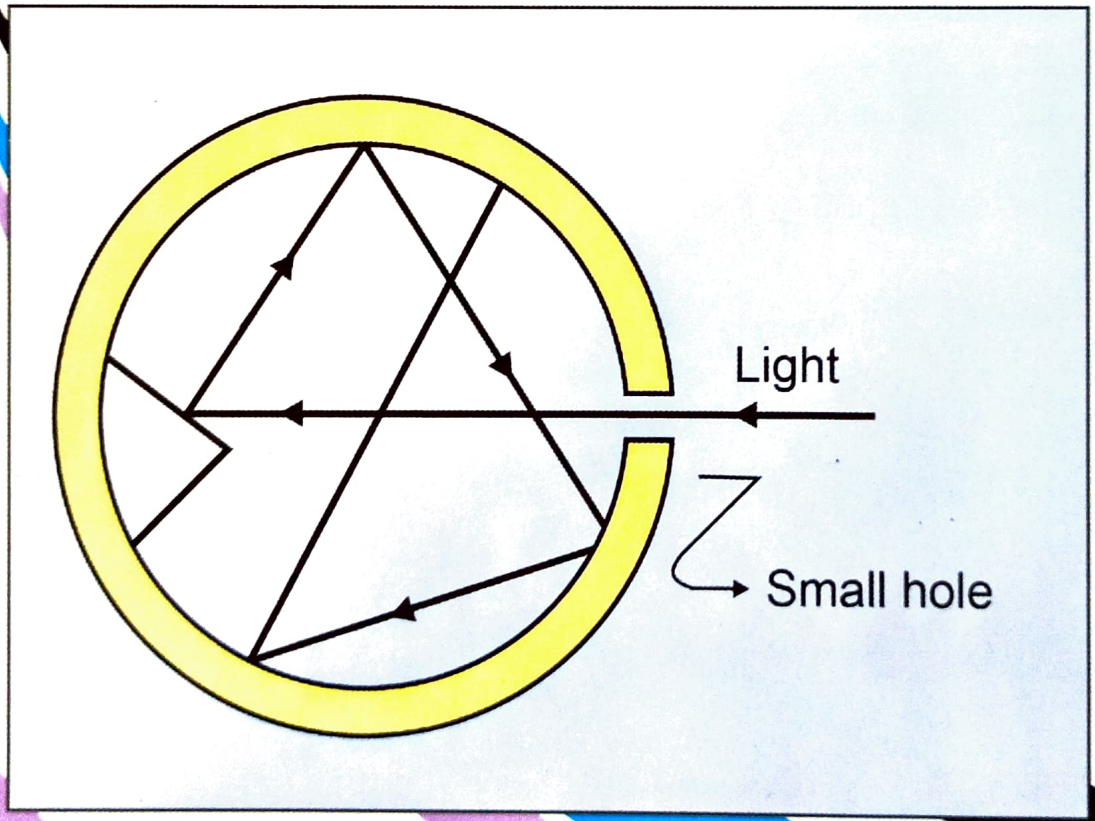
As per New Syllabus
CBCS Pattern
of Shivaji University, Kolhapur
B.Sc. Part-III : Semester-V

PHYSICAL CHEMISTRY

(CHEMISTRY : DSE-E7 : PAPER-XI)

Dr. AVINASH M. NALAWADE
Dr. DNYANDEV N. ZAMBARE
Dr. CHANDRAKANT P. MANE
Dr. ARJUN S. KUMBHAR
Dr. PRAVINA B. PISTE



NIRALI PRAKASHAN
ADVANCEMENT OF KNOWLEDGE

A TEXT BOOK OF

PHYSICAL CHEMISTRY

DSE - E7 : Paper - XI

FOR

B.Sc. Part - III : Semester - V

As Per New Revised CBCS Pattern Syllabus of Shivaji University, Kolhapur w.e.f. June 2020

Dr. AVINASH M. NALAWADE
M.Sc., M.Phil, Ph.D.
Assistant Professor
P.G. Recognized Teacher, Research Guide,
Lal Bahadur Shastri College, Satara

Dr. DNYANDEV N. ZAMBARE
M.Sc., Ph.D.
Professor,
P.G. Recognized Teacher, Research Guide,
Department of Chemistry,
Kisanveer Mahavidyalaya, Wai.

Dr. CHANDRAKANT P. MANE
M.Sc., Ph.D.
Head, P.G. Recognized Teacher,
Research Guide,
Department of Chemistry,
Lal Bahadur Shastri College, Satara

Dr. ARJUN S. KUMBHAR
M.Sc., Ph.D.
Assistant Professor
P.G. Recognized Teacher, Research Guide,
P.D.V.P. College, Tasgaon,,
Dist. Sangli

Dr. PRAVINA B. PISTE
M.Sc., M.Phil., Ph.D.
Professor at A.S.C. College,
Ramanandnagar (Burli),
Tal. Palas, Dist. Sangli.
PG Recognized Teacher and Research Guide.

Price ₹ 100.00

NIRALI PRAKASHAN
ADVANCEMENT OF KNOWLEDGE

N4847

B.Sc. Part - III : Physical Chemistry (P-XI) (Sem. V) **ISBN 978-93-90225-74-3**

First Edition : **August 2020**

Published By :
NIRALI PRAKASHAN
Abhyudaya Pragati, 1312 Shivaji Nagar,
Off J.M. Road, PUNE - 411005
Tel - (020) 25512336/37/39. Fax - 25511379
Email : niralipune@pragationline.com

(Polyplate) **Printed By**
YOGIRAJ PRINTERS AND BINDERS
Works: Sr. No. 10\1,Ghule Industrial Estate,
Nanded Village Road,
TAL-HAVELI, DIT-PUNE 411041.
Mobile - 9850046517, 9404225254

DISTRIBUTION CENTRES

PUNE

Nirali Prakashan : 119, Budhwar Peth, Jogeshwari Mandir Lane, Pune 411002, Maharashtra. Tel : (020) 2445 2044, 66022708, Fax : (020) 2445 1538, Email: bookorder@pragationline.com, niralilocal@pragationline.com

Nirali Prakashan : S. No. 28/27, Dhyari, Near Pari Company, Pune 411041 Tel : (020) 24690204 Fax : (020) 24690316 Email : dhyari@pragationline.com, bookorder@pragationline.com

MUMBAI

Nirali Prakashan : 385, S.V.P. Road, Rasdhara Co-op. Hsg. Society Ltd., Girgaum, Mumbai 400004, Maharashtra Tel : (022) 2385 6339 / 2386 9976, Fax : (022) 2386 9976 Email : niralimumbai@pragationline.com

DISTRIBUTION BRANCHES

JALGAON

Nirali Prakashan : 34, V. V. Golani Market, Navi Peth, Jalgaon 425001, Maharashtra, Tel : (0257) 222 0395, Mob : 94234 91860

KOLHAPUR

Nirali Prakashan : New Mahadvar Road, Kedar Plaza, 1st Floor Opp. IDBI Bank Kolhapur 416 012, Maharashtra. Mob : 9850046155

NAGPUR

Pratibha Book Distributors : Above Maratha Mandir, Shop No. 3, First Floor, Rani Jhanshi Square, Sitabuldi, Nagpur 440012, Maharashtra Tel : (0712) 254 7129

DELHI

Nirali Prakashan : Room No. 2, Ground Floor, 4575/15 Onkar Tower, Aggarwal Road, Darya Ganj, New Delhi 110002 Mobile : + 91 9555778814 / +91 9818561840 Email : niralidelhi@pragationline.com

BANGALURU

Nirali Prakashan : Maitri Ground Floor, Jaya Apartments, No. 99, 6th Cross, 6th Main, Malleswaram, Bangaluru 560 003, Karnataka Mob : +91 9449043034 Email: niralibangalore@pragationline.com

www.pragationline.com **info@pragationline.com**

PREFACE

This book is basically intended for B.Sc.-III students for Semester - V Course of Shivaji University, Kolhapur. This book is written according to new syllabus being implemented from June 2020 prescribed by Shivaji University, Kolhapur.

It is our great pleasure to present this book to the students and respected teachers in proper time. The subject matter is presented in simple and lucid language. This book covers all the chapters mentioned in the syllabus. The material is presented in a comprehensive way and the sequence of articles in each chapter helps the students to understand the subject with ease.

Different diagrams and illustrative description is provided to enhance the learning and understanding of the matter by students as well as to enable the teachers to explain the difficult concepts properly. The solved numerical examples, long answer type questions, short answer type questions including multiple type questions are given at the end of each chapter.

We are thankful to Nirali Prakashan, Pune for making us a part of their team of Authors. We thank **Mr. Dineshbhai Furia** and **Mr. Jignesh Furia** for publishing this book.

We also thank Mr. Girish Redkar (Head Marketing Dept.) for his co-operation in publishing this book.

Last but not the least we are very much indebted to Mr. Virdhaval Shinde, (Marketing Executives, Kolhapur District) and Mr. Ashok Nanavare (Marketing Executive, Sangli District) for their nice co-operation. We are very much thankful to Mr. Kiran Velankar (Proof Reading), Mrs. Anjali Muley (Graphic Design) and Mr. Malik Shaikh for a neat and error free D.T.P. of this book.

We hope that this book will be found useful by students and teachers. We will appreciate any suggestions for the improvement of the book.

– **Authors**

***

SYLLABUS

(Theory Credits: 02, 30 Hours, 38 Lectures)

Unit 1 : Elementary Quantum Mechanics [08]

1.1 Introduction

1.2 Drawbacks of classical mechanics, Black body radiation, Photoelectric effect, Compton effect, Dual nature of matter and energy : De-Broglie hypothesis.

1.3 The Heisenberg's uncertainty principle

1.4 Concept of energy operators (Hamiltonian)

1.5 Derivation of Schrodinger wave equation. Well behaved function

1.6 Physical interpretation of ψ and ψ^2

1.7 Particle in a one-dimensional box

1.8 Numerical Problems

Unit 2 : Spectroscopy [08]

2.1 Introduction

2.2 Electromagnetic radiation

2.3 Interaction of radiation with matter Electromagnetic spectrum, Energy level diagram

2.4 Rotational spectra of diatomic molecules: Rigid rotator model; moment of inertia; Energy levels of rigid rotator, Selection rules; Intensity of spectral lines, Determination of bond length; Isotope effect, Microwave oven

2.5 Vibrational spectra of diatomic molecules : Simple harmonic oscillator model, Vibrational energies of diatomic molecules, Determination of force constant, Overtones.

2.6 Raman spectra : Concept of polarizability, Pure rotational and Pure vibrational Raman spectra of diatomic molecules, Selection rules.

2.7 Comparative study of IR and Raman spectra, Rule of mutual exclusion - CO_2 molecule

2.8 Numerical Problems

Unit 3 : Photochemistry [06]

3.1 Introduction, Differences between thermal and photochemical processes

3.2 Laws of photochemistry: (i) Grotthus - Draper law, (ii) Lambert's law, (iii) Lambert–Beer's law (with derivation), (iv) Stark-Einstein law.

3.3 Quantum yield, Reasons for high and low quantum yield.

3.4 Factors affecting Quantum yield.

3.5 Photosensitized reactions–Dissociation of H_2, Photosynthesis.

3.6 Photodimerisation of anthracene, decomposition of HI and HBr.

3.7 Jablonski diagram depicting various processes occurring in the excited state : Qualitative description of fluorescence and phosphorescence.

3.8 Chemiluminescence, Electroluminescence and Bioluminescence.

3.9 Numerical Problems

Unit 4 : Solutions **[06]**

4.1 Introduction

4.2 Ideal solutions, Raoult's law, Vapour pressure of ideal and non-ideal solutions of miscible liquids.

4.3 Composition of liquid and vapour, Vapour pressure and boiling point diagrams of miscible liquids. Distillation of miscible liquid pairs.

Type I : Systems with intermediate total vapour pressure. (i.e. System in which b.p. increases regularly – Zeotropic)

Type II : Systems with a maximum in the total vapour pressure. (i.e. System with a b.p. minimum – Azeotropic)

Type III : Systems with a minimum in the total vapour pressure. (i.e. System with a b.p. maximum – Azeotropic).

4.4 Solubility of partially miscible liquids.

(i) Maximum solution temperature type: Phenol–water system.

(ii) Minimum solution temperature type: Triethyl amine–water system.

(iii) Maximum and minimum solution temperature type: Nicotine–water system.

Distillation of partially miscible liquid pairs.

4.5 Vapour pressure and distillation of immiscible liquids, Steam distillation.

Unit 5 : Electromotive Force **[10]**

(Convention: Reduction potentials to be used)

5.1 Introduction

5.2 Thermodynamics of electrode potentials, Nernst equation for electrode and cell potentials in terms of activities.

5.3 E.M.F. series.

5.4 Types of electrodes : Description in terms of construction, representation, half cell reaction and emf equation for

(i) Metal–metal ion electrode.

(ii) Amalgam electrode.

(iii) Metal-insoluble salt electrode.

(iv) Gas electrode.

(v) Oxidation–Reduction electrode.

5.5 Reversible and Irreversible cells.

(i) Chemical cells without transference.

(ii) Concentration cells with and without transference.

(iii) Liquid–Liquid junction potential: Origin, elimination and determination.

5.6 Equilibrium constant from cell emf, Determination of thermodynamic parameters such as ΔG, ΔH and ΔS.

5.7 Applications of emf measurements :

(i) Determination of pH of solution using Hydrogen electrode.

(ii) Solubility and solubility product of sparingly soluble salts (based on concentration cell).

5.8 Numerical Problems.

***

CONTENTS

1. Elementary Quantum Mechanics 1.1 - 1.34

1.1 Introduction 1.1
1.2.1 Drawbacks of Classical Mechanics 1.2
1.2.2 Black Body Radiation 1.3
1.2.3 Photoelectric Effect 1.5
1.2.4 Compton Effect 1.7
1.2.5 Dual Nature of Matter and Energy De-Broglie's Equation (Hypothesis) 1.8
1.3 Heisenberg's Uncertainty Principle 1.12
1.4 Concept of Energy Operators (Hamiltonian) 1.13
1.5 Derivation of Schrodinger's Wave Equation 1.14
1.6 Physical Interpretation of ψ and ψ^2 1.16
1.7 Particle in a One Dimensional Box 1.17
1.8 Numerical Problems 1.23
• Exercises 1.27

2. Molecular Spectroscopy 2.1 - 2.52

2.1 Introduction 2.1
2.2 Electromagnetic Radiations 2.2
2.3 Electromagnetic Spectrum, Energy Level Diagram 2.4
2.4 Rotational Spectra of Diatomic Molecules 2.10
2.4.1 Rigid Rotator Model 2.0
2.4.2 Moment of Inertia 2.11
2.4.3 Energy Levels of Rigid Rotator (Rotational Energies of Diatomic Molecules) 2.12
2.4.4 Selection Rule 2.13
2.4.5 Intensity of Spectral lines 2.15
2.4.6 Determination of Bond length 2.17
2.4.7 Isotope Effect 2.18
2.4.8 Microwave Oven 2.20
2.5 Vibrational Spectra of Diatomic Molecules 2.21
2.5.1 Harmonic Oscillator Model 2.21
2.5.2 Vibrational Energies of a Diatomic Molecule 2.23
2.5.3 Determination of Force Constant 2.26
2.5.4 Overtones 2.27
2.5.5 Interactions of Radiations with Vibrating Molecules 2.29
2.5.6 Applications of Vibrational Spectra 2.29
2.6 Raman Spectra 2.30
2.6.1 Quantum Theory of Raman Effect 2.32
2.6.2 Concept of Polarizability 2.34
2.6.3 Pure Rotational Raman Spectra of Diatomic Molecules 2.36
2.6.4 Vibrational Raman Spectra 2.36
2.6.5 Applications of Raman Spectra 2.37
2.7 Comparative Study of IR and Raman Spectra, Rule of Mutual Exclusion - CO_2 Molecule 2.37
2.7.1 Comparative Study of IR and Raman Spectra 2.37
2.7.2 Rule of Mutual Exclusion 2.39
2.8 Numerical Problems 2.41
• Exercises 2.46

3. Photochemistry 3.1 - 3.32

3.1 Introduction 3.1
3.2 Laws of Photochemistry 3.3
3.3 The Quantum Yield or Quantum Efficiency (ϕ) 3.9
3.4 Factors Affecting Quantum Yield 3.10
3.5 Photosensitized Reactions 3.11
3.6 Photochemical Equilibrium (Dimerization of Anthracene) 3.12
3.7 Decomposition of Hydrogen Iodide 3.14
3.8 Luminescence Phenomenon 3.15
3.9 Fluorescence 3.16
3.10 Jablonski Diagram Depicting various Processes Occurring in the Excited State 3.18
3.11 Chemiluminescence or Electroluminescence 3.20
3.10 Numerical Problems 3.22
• Exercises 3.25

4. Solutions 4.1 - 4.30

4.1 Introduction 4.2

4.2 Ideal Solutions, Raoult's Law, Vapour Pressure of Ideal and Non-ideal Solutions of Miscible Liquids 4.4

4.3 Composition of Liquid and Vapour, Vapour Pressure and Boiling Point Diagrams of Miscible Liquids 4.9

4.4 Solubility of Partially Miscible Liquids 4.19

4.5 Vapour Pressure and Distillation of Immiscible Liquids 4.23

• Exercises 4.24

5. Electromotive Force 5.1 - 5.48

5.1 Intoduction 5.1

5.2 Thermodynamics of Electrode Potentials 5.5

5.3 Electrochemical Series 5.8

5.4 Types of Electrodes 5.11

5.4.1 Metal-Metal Ion Electrode 5.11

5.4.2 Amalgam Electrode 5.11

5.4.3 Metal Insoluble Salt Electrode 5.12

5.4.4 Gas Electrode 5.13

5.4.5 Oxidation-Reduction Electrode 5.15

5.5 Reversible and Irreversible Cells 5.16

5.5.1 Reversible Cells 5.16

5.5.2 Irreversible Cells 5.16

5.6 Equilibrium Constant from Cell emf 5.28

5.6.1 Determination of Thermodynamic Parameters ΔG, ΔH, ΔS 5.29

5.7 Applications of emf Measurements 5.30

5.8 Numerical Problems 5.34

• Exercises 5.40

• **References** R.1 - R.1

***

About the Authors

Dr. AVINASH MARUTI NALAWADE
M.Sc., M.Phil, Ph.D.
Assistant Professor, P.G. Recognized Teacher, Research Guide,
Lal Bahadur Shastri College, Satara

Dr. DNYANDEV N. ZAMBARE
M.Sc., Ph.D.
Professor, P.G. Recognized Teacher, Research Guide, Department of Chemistry,
Kisanveer Mahavidyalaya, Wai.

Dr. CHANDRAKANT P. MANE
M.Sc., Ph.D.
Head, P.G. Recognized Teacher, Research Guide,
Department of Chemistry, Lal Bahadur Shastri College, Satara.

Dr. ARJUN S. KUMBHAR
M.Sc., Ph.D.
Assistant Professor, P.G. Recognized Teacher, Research Guide, P.D.V.P. College,
Tasgaon, Dist. Sangli

Dr. PRAVINA B. PISTE
MSc., M.Phil., Ph.D.,
Professor at A.S.C. College, Ramanandnagar (Burli), Tal. Palas, Dist. Sangli. P.G.
Recognized Teacher and Research Guide.

BOOKS AVAILABLE AT

PUNE

Nirali Prakashan	: Sur. No. 28/27, Dhayari-Katraj Road, Near Pari Company, Dhayari, Pune - 411 041. Ph. (020) 24690204 Fax: (020) 24690316 • Email: bookorder@pragationline.com

KOLHAPUR

Nirali Prakashan	: New Mahadwar Road, Kedarling Plaza, 1 st floor, Opp. I.D.B.I. Bank, Kolhapur. Mob. 98500 46155
Mehta Book Sellers	: Bhausingji Road, Kolhapur. Tel. (0231) 2541 881
Granth The Book World	: Rajarampuri 5 th lane, Kolhapur. Tel. (0231) 2544 353
Titus Book Depot	: Rajarampuri 1st lane, Kolhapur. Tel. (0231) 2522 546

SANGLI

Nirali Prakashan	: Haripur Road, Nandrekar Plot, Sangli. Mob. 99215 16852
G. R. Tamhankar Book Sellers	: Saraf Naka, Sangli. Tel. (0233) 2329966
Sankapal Book Stall	: Kapad Peth, Near Church, Sangli. Tel. (0233) 2326447

MIRAJ

Ratnakar Book Stall	: Deval Talkies, Miraj, Tel : (0233) 2222564

SATARA

Alankar Book Stall	: Opp. Science College, Satara. Tel. (02162) 220456

Email: niralipune@pragationline.com • Website: www.pragationline.com

Also find us on www.facebook.com/niralibooks

@nirali.prakashan

N4847

ISBN 93902257-4-4

9789390225743