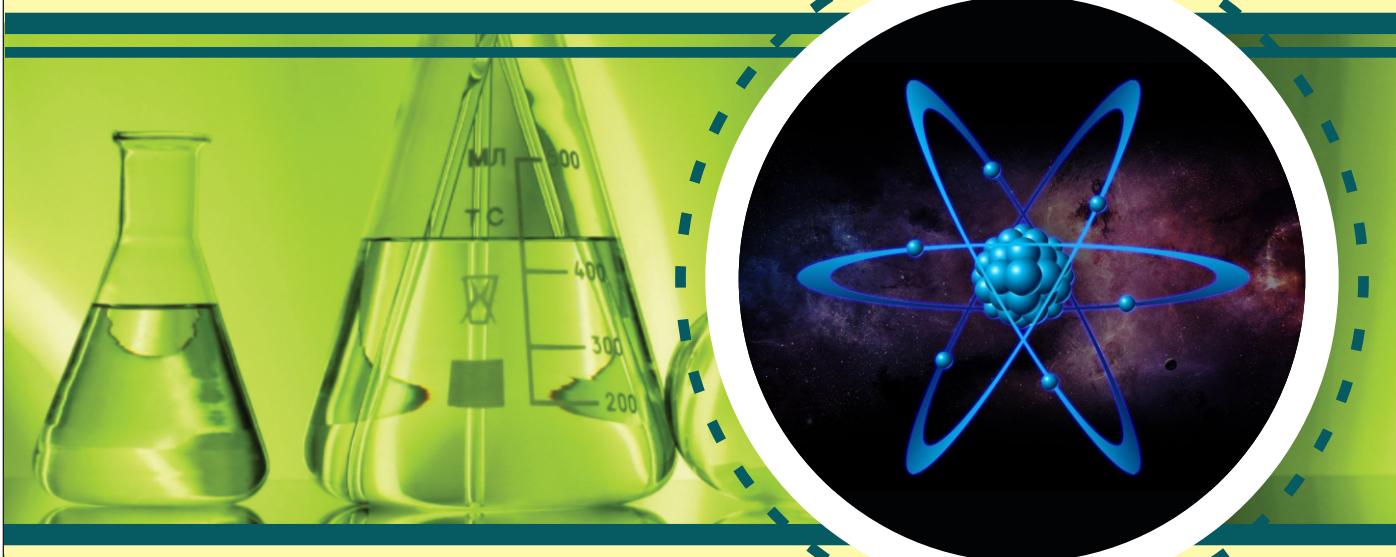


TEXTBOOK OF

# PHYSICAL CHEMISTRY



P.L. Soni  
O.P. Dharmarha  
U.N. Dash

24<sup>th</sup>  
Revised  
Edition

Sultan Chand & Sons

# Textbook of PHYSICAL CHEMISTRY

“Chemistry is concerned with substances, with kinds of matter the materials of which things are made. It is concerned with wood but not the log, with glass but not the bottle, with copper but not the coin, with clay but not the brick. Chemistry is concerned with identifying or characterising properties of substances....[and] with the processes in which substances are transformed into other substances.”

—*I.H. Hildebrand & R.E. Powell*

## ***How to get the best out of this book?***

**You can get the best out of this book** if you start reading a chapter with pen and paper in your hand. Go on reading a para and jotting down the \*\*\* points side by side. Sentences printed in italics or bold type require for particular attention. Your reading should not be passive, but active and \*\*\*. Reading is raising questions and removing doubts. So keep looking for important details and answers to questions that arise in your mind as you and on.

The second step in your plan of reading should be restatement of what you read. Put the book down at intervals, say, after a paragraph or a page, and \*\*\* yourself what you have read, what appears important to you and what does do. This is necessary to ensure that you have grasped correctly. An eminent English writer describes this is ‘double take’. You must have formed some impression in your first reading. Read again. Since your aim is effective learning, you \*\*\* ignore recalling or restating and verifying. Reading, restating and verifying should constitute a simultaneous process. Reading in the specialised way has been found to be thrice as beneficial as ordinary reading.

The third step in your strategy of reading should be writing down briefly what you have studied. Go through the whole chapter reading one paragraph after the other and jotting down the main points that emerge from your reading. Now go through the questions at the end and find out how many of these you can answer without any difficulty. If you are unable to answer any question, don’t get disheartened. Look for its answer in the book.

One of the common complaints of Chemistry students is that they go through a chapter, grasp it at the time of reading but forget it completely after a few days. This leads them to think that their effort has been a sheer wastage of time. Therefore, they try to postpone reading it till a few days before the examination.

But if you postpone the first reading to the examination day, you can learn only two chapters in one days and not even two since you get nervous and the grasp is faulty and you give up the attempt altogether.

Hence your motto should be **reading regularly** and then **revising at regular intervals**. In this way most of the important points will get permanently added to your vocabulary and you will never forget them.

This is extremely essential in the study of Physical Chemistry since, here, various chapters are interrelated. Concepts in the first few chapters are to be constantly applied in the study of subsequent chapters. So each chapter should be properly grasped before proceeding to study the next chapter. **Your effort must be regular and persistent with a lot of self-confidence and determination.**

**AUTHORS**

**Textbook of**

**PHYSICAL CHEMISTRY**

*incorporating SI Units*

**P. L. SONI**

*Formerly Head of Department of Chemistry  
Hand Raj College, Delhi University, Delhi*

**O.P. DHARMARHA**

*Head of the Department of Chemistry  
Rajdhani College, Delhi University, Delhi*

**U.N. DASH**

*Retired Professor of Chemistry  
Utkal University, Bhubaneswar, Odisha*



**Sultan Chand & Sons<sup>®</sup>**

*Educational Publishers  
New Delhi*

**SULTAN CHAND & SONS®**

*Educational Publishers*

23, Daryaganj, New Delhi-110 002

Phones : 011-23281876, 23266105, 23277843 (*Showroom & Shop*)

011-40234454, 23247051 (*Office*)

E-mail : sultanchand74@yahoo.com; info@sultanchandsons.com

Fax : 011-23266357; Website : www.sultanchandsons.com

**ISBN : 978-81-651043-2-4-(TC-634)**

**Price : ₹ 895.00**

First Edition: 1996

Twenty-third Edition: 2007

Twenty-fourth Revised & Updated Edition: 2022

**EVERY GENUINE COPY OF THIS BOOK HAS A HOLOGRAM**



In our endeavour to protect you against counterfeit/fake books, we have pasted a copper hologram over the cover of this book. The hologram displays the full visual image, unique 3D multi-level, multi-colour effects of our logo from different angles when tilted or properly illuminated under a single light source, such as 3D depth effect, kinetic effect, pearl effect, gradient effect, trailing effect, emboss effect, glitter effect, randomly sparkling tiny dots, micro text, laser numbering, etc.

*"A fake hologram does not display all these effects."*

Always ask the bookseller to put his stamp on the first page of this book.

**All Rights Reserved:** No part of this book, including its style and presentation, may be reproduced, stored in a retrieval system, or transmitted in any form or by any means – electronic, mechanical, photocopying, recording or otherwise without the prior written consent of the Publishers. Exclusive publication, promotion and distribution rights reserved with the Publishers.

**Warning:** The doing of an unauthorised act in relation to a copyright work may result in both civil claim for damages and criminal prosecution.

**Special Note:** Photocopy or Xeroxing of educational books without the written permission of Publishers is illegal and against Copyright Act. Buying and selling of pirated books is a criminal offence. Publication of key to this is strictly prohibited.

**General:** While every effort has been made to present authentic information and avoid errors, the author and the publishers are not responsible for the consequences of any action taken on the basis of this book.

**Limits of Liability/Disclaimer of Warranty:** The publisher and the author make no representation or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation warranties of fitness for a particular purpose. No warranty may be created or extended by sales or promotional materials. The advice and strategies contained herein may not be suitable for every situation. This work is sold with the understanding that the publisher is not engaged in rendering legal, accounting, or other professional services. If professional assistance is required, the services of a competent professional person should be sought. Neither the publisher nor the author shall be liable for damage arising herefrom.

**Disclaimer:** The publisher have taken all care to ensure highest standard of quality as regards typesetting, proofreading, accuracy of textual material, printing and binding. However, they accept no responsibility for any loss occasioned as a result of any misprint or mistake found in this publication.

**Author's Acknowledgement:** The writing of a Textbook always involves creation of a huge debt towards innumerable authors and publications. We owe our gratitude to all of them. We acknowledge our indebtedness in extensive footnotes throughout the book. If, for any reason, any acknowledgement has been left out we beg to be excused. We assure to carry out correction in the subsequent edition, as and when it is known.

## **Preface to the Twenty-fourth Edition**

---

In the twenty-fourth Revised and Enlarged edition we have, retained all that in previous edition, incorporated new subject materials and all chapters have been updated catering to the needs of the students of the B.Sc (Hons) and M.Sc courses of all the Indian Universities. All chapters received a major revision, especially to include more solved problems and numerous questions. Latest University questions are given at the end of each chapter. A new type of Question Banks has been included. Step-by-step answers are provided for the in-chapter problems. This is the book which the examiners use.

The present edition incorporates the New Education Policy/CBCS guidelines. It is our proud privilege to acknowledge to a number of authors whose works have been freely consulted while revising this book. Thanks are due to M/s Sultan Chand & Sons for their active co-operation in bringing out this edition in New look at the earliest.

We shall be highly grateful to the readers, if the errors and omissions are detected in this present edition are brought to our notice. It is our belief that this edition will continue to maintain the very high standards, and be of substantial value in the teaching and reading the Text Book of Physical Chemistry.

**Authors**

## **Preface to the Twenty-third Edition**

The major improvements in the latest edition are:

- Thorough revision of first ten chapters of Part I of the book, that is, up to page 1.360.
- Addition of two new chapters namely, Irreversible Thermodynamics and Statistical Thermodynamics at the end of the Part II of the book.

The chapters have been improved by making suitable additions, and modifications to facilitate understanding of the subject-matter. The solved numerical problems in the relevant chapters have been dealt with in SI units.

### **Other Salient features of the book are as under :**

- Emphasis on correlation of various properties of elements and their compounds with their electronic structure and other modern concepts.
- Lucid and elegant style.
- Simple language.
- Dependable information about all concepts of Physical Chemistry.
- Clarity of concepts through problems, solved examples, and objective type questions with answers. Difficult concepts illustrated by a large number of examples, solved problems and diagrams.
- Revised in the light of latest syllabi of various Indian Universities.

Question papers of recent years examinations of various Universities/Institutes have been incorporated at the end of each chapter. Objective Type and Multiple Choice Questions, and numerical problems with answers incorporated at the end of each chapter are of great help to the candidates preparing for the competitive examinations like JEE/IIT, Medical Entrance Test and Civil Services examinations.

The authors hope that this revised, improved, modified and updated edition would be helpful to the students and the teachers alike.

The authors will greatly appreciate helpful specific suggestions from teachers of the subject to enhance the usefulness of the book for the students.

**Authors**

## **Extracts from Preface to Earlier Edition**

The first edition of this book was received with welcome for its novel approach. Instead of dealing the subject in a routine descriptive manner, the fundamental concepts of chemistry laying emphasis on the underlying physics, were enunciated by which the reader could understand the conceptual basis of the subject. These were extended and further developed mathematically in order that they could apply them to chemical problems. It has been our faith that any introductory course in physical chemistry must have as one of its objectives the effective presentation of a wide variety of topics. It must introduce to its readers the current theories and unifying concepts of the subject. The theory of atomic structure which has been developed by the application of quantum theory and wave mechanics to explain the behaviour of electrons is now generally accepted and it is impossible for a student of chemistry at any level to remain unaware of the influence of the new outlook.

It is our firm conviction that for a clear understanding of the fundamental principles the treatment must be lucid and detailed. We have tried in our writing to avoid gross over-simplification which often leads to misunderstanding about chemical principles.

Some of the special features of the book are as follows:

- The atomic structure has been developed from Rutherford model to wave mechanical treatment in a lucid manner in Chapters 2 and 3. The Schrodinger wave equation and its significance has been amply illustrated through diagrams and analogies making the abstract concept more comprehensive.
- The latest form of Periodic Table with newly adopted group numbers has been exhaustively dealt with correlating the variation of periodic properties with the electronic configuration in chapter 4.
- In the light of the wave mechanical picture of orbitals, the covalent bond theory and molecular orbital theory of bonding have been treated in a simple illustrative manner so that the students can easily follow this rather difficult idea in Chapters 7 and 8.
- With the introduction of new problems and simplified mathematical treatment and illustrations, the chapters on gaseous state, liquid state and solid states have been revised fairly exhaustively. The basic concepts involved have been elucidated most adequately in Chapters 9, 10, 11, 12.
- Chemical Thermodynamics is the foundation of chemistry, Chapters 13, 14, 15, 16 and 17 have been revised with particular stress on the basic principles and their application through solved examples and mathematical build-up. New topic incorporated in revised syllabi of restructured Honours courses in chemistry have been introduced at appropriate places. This would help the readers to recapitulate the fundamental principles discussed in these chapters and apply them accordingly.
- Chapters on chemical equilibrium, Nernst distribution law and phase rule have been revised with emphasis on the basis of thermodynamic principles to make them more comprehensive.

*Question papers of Universities and Institutes provide an index of the quantum and quality of the chemical knowledge imparted to the students in our country and also of the areas being recognised as important. After scanning these papers, the text is revised and made up-to-date accordingly. Important questions, such as essay type and short answer type, have been given at the end of every chapter for the student's guidance. Keeping this in view, the numerical problems and questions from latest University/Institute papers have been put in place of the old ones.*

We are thankful to a large number of students and colleagues from Institutes, Colleges and Universities all over the country, who in response to our Publishers Feedback Programme, have very kindly made valuable suggestions for improvement of the text by incorporating new topics recently introduced in their syllabi. Many of them have liked our simple way of developing basic concepts, illustrated by large number of solved examples. They have especially made a mention of our collection and framing of Objective Type Questions with key at the end of each chapter. They found them very useful for competitive examinations like Civil Services, JEE/IIT and Medical Entrance Tests and have suggested a lot more of such questions to be framed. We thankfully acknowledge their participation in the programme. To meet their demand, Question Banks at the end of each unit and in all about 1000 multiple choice questions have been inserted at the end of each chapter.

It is our earnest hope that we shall continue to receive such criticism and encouragement from all concerned in future also.

*We sincerely hope that the method of presentation in this book will enable the readers to read the subject with pleasure and through understanding. If it does that, we shall feel amply rewarded for the pains taken.*

**Authors**

# **Contents**

---

---

## **UNIT-I: CHEMICAL PRINCIPLES**

<b>1. Introduction.....</b>	<b>1.3</b>
1.1. Physical Chemistry .....	1.3
1.1.1. Importance of Physical Chemistry..	1.3
1.2. Symbols and Units.....	1.4
1.2.1. Derived Physical Quantities and Units .....	1.4
1.2.2. Prefixes for SI Units .....	1.5
<i>Questions</i> .....	1.8
<b>2. Structure of Atom .....</b>	<b>2.1</b>
2.1. Discovery of Electron .....	2.1
2.1.1. Mass of Electron .....	2.2
2.1.2. Charge on Electron.....	2.2
2.2. Discovery of Proton.....	2.4
2.3. Atomic Models .....	2.4
2.3.1. Nuclear Structure .....	2.5
2.3.2. Effective Radius of the Nucleus.....	2.5
2.4. Discovery of Neutrons .....	2.6
2.4.1. Moseley's Experiment and Atomic Number.....	2.6
2.4.2. Mass Number .....	2.7
2.5. Drawbacks in Rutherford Model .....	2.7
2.6. Nature of Electromagnetic Radiations.....	2.7
2.7. Bohr's Model of Atom.....	2.8
2.8. Atomic Spectra – A Clue to Atomic Structure.....	2.10
2.9. Bohr's Quantum Theory of Hydrogen Like Atom .....	2.12
2.9.1. Bohr's Theory and the Line Spectra .....	2.14
2.9.2. Deviation of Energy of an Electron .....	2.15
2.10. The Bohr-Sommerfeld Theory .....	2.17
<i>Questions</i> .....	2.18
<i>Objective Type</i> .....	2.19
<i>Problems</i> .....	2.19
<i>Examination Questions</i> .....	2.20
<b>3. Structure of Atom (Modern Picture) .....</b>	<b>3.1</b>
3.1. Wave Particle Dualism of Radiation.....	3.1
3.1.1. Photoelectric Effect.....	3.1
3.2. Compton Effect or Compton Scattering .....	3.3
3.3. Wave-particle Dualism of Matter–de Broglie Wave equation .....	3.3
3.3.1. Experimental Proof of de Broglie's Equation .....	3.5
3.3.2. De Broglie (Matter) Waves and Electromagnetic Waves .....	3.5
3.4. The Uncertainty Principle.....	3.5
3.5. Quantum Mechanical Model of Atom .....	3.9
3.5.1. Quantum Mechanical Operators .....	3.9
3.5.2. Schrodinger Wave Equation .....	3.24
3.5.3. Solution of Schrodinger Wave Equation .....	3.26
3.6. The Schrodinger Equation for Hydrogen Atom .....	3.38
3.7. Probability and Electron Density — Visualizing the Orbitals .....	3.40
3.8. Quantum Numbers.....	3.41
3.8.1. Significance of Quantum Numbers .....	3.43
3.8.2. Principal Quantum Number ( $n$ ) .....	3.43
3.8.3. Subsidiary Quantum Numbers or Azimuthal Quantum Numbers.....	3.44
3.8.4. Magnetic Quantum Number ( $m$ or $m_l$ ) .....	3.44
3.8.5. The Spin Quantum Numbers ( $m_s$ ) .....	3.44
3.9. Radial Distribution Functions and Radial Probability Distribution Curves .....	3.46
3.10. The Number of Electrons in a Given Orbit—Pauli's Exclusion Principle .....	3.49
3.11. Many Electron Atoms .....	3.50
3.12. Occupation of Orbitals by Electrons— Aufbau Principle .....	3.51
3.12.1. A Handy Method to Write Electronic Configuration of Atoms .....	3.52
3.12.2. Exception to the Rule .....	3.52
3.12.3. Violation of Aufbau Principle .....	3.52
3.13. Hund's Rule of Maximum Multiplicity .....	3.52
3.13.1. Explanation of Hund's Rule .....	3.53
3.14. Cause of Stability of Half-filled and Completely-filled Energy Levels.....	3.53
3.15. $nl^x$ Notation .....	3.55
3.15.1. Box Representation for Electron Distribution .....	3.57
<i>Questions</i> .....	3.57
<i>Objective Type</i> .....	3.59
<i>Problems</i> .....	3.62
<i>Examination Questions</i> .....	3.63

---

<b>4. Classification of Elements.....</b>	<b>4.1</b>		
4.1. Historical Background.....	4.1	5.6.1. Nuclear Binding Energy Theory .....	5.7
4.1.1. Mendeleev's Periodic Table .....	4.1	5.6.2. Meson Theory of Nuclear Forces.....	5.7
4.2. Modern periodic law.....	4.2	5.6.3. Nuclear Fluid Theory .....	5.8
4.2.1. Periodic Law and Electronic Configuration of Elements .....	4.2	5.7. Isotopes.....	5.8
4.3. Modern periodic table.....	4.3	5.7.1. The Detection and Study of Isotopes .....	5.8
4.3.1. Superiority of the Modern Periodic Table .....	4.4	5.8. Isotopic Constitution of Elements.....	5.10
4.4. Periodic Variation of Properties of Elements .....	4.6	5.9. Separation of Isotopes .....	5.12
4.5. Size of Atoms and Ions.....	4.6	5.9.1. Gaseous Diffusion Method.....	5.12
4.5.1. The Crystal Radius ( <i>atomic or metallic radius</i> ).....	4.6	5.9.2. Electromagnetic Method .....	5.13
4.5.2. The Van der Waal's Radius ( <i>collision radius</i> ) .....	4.7	5.9.3. Thermal-Diffusion Method or Soret's Method .....	5.13
4.5.3. Covalent Radius .....	4.7	5.9.4. Distillation Method .....	5.14
4.5.4. The Ionic Radius .....	4.8	5.9.5. The Centrifugal Method.....	5.14
4.5.5. The Bragg-Slater Atomic Radius ...	4.8	5.9.6. Electrolytic Method.....	5.14
4.5.6. Atomic Volumes.....	4.9	5.9.7. Chemical-exchange Method .....	5.14
4.6. Ionization Energy.....	4.9	5.10. The Whole-Number Rule and Packing Fraction .....	5.15
4.6.1. Factors on which Ionization Energy Depends .....	4.10	5.11. Atomic weights.....	5.16
4.6.2. The Variation of Ionization Energies with Increase in Atomic Number.....	4.12	5.11.1. Deviation of Atomic Weights from Whole Numbers.....	5.16
4.7. Electron Affinity .....	4.12	5.11.2. Some Conclusions from the Study of Isotopes .....	5.16
4.8. Electronegativity ( $\chi$ ).....	4.13	5.12. Isobars, Isotones and Isomers.....	5.17
4.8.1. Pauling Scale of Electronegativity .....	4.14	Questions .....	5.18
4.8.2. Mulliken Scale of Electronegativity .....	4.14	Objective Type .....	5.18
4.8.3. Allred and Rochow Scale of Electronegativity .....	4.14	Multiple Choice Type .....	5.18
4.9. Metallic Character .....	4.15	Problems .....	5.19
4.10. Density, Melting Point and Boiling Point.....	4.15	Examination Questions.....	5.20
Questions .....	4.17		
Objective Type .....	4.20		
Multiple Choice .....	4.21		
Examination Questions.....	4.22		
<b>5. Nuclear Chemistry .....</b>	<b>5.1</b>		
5.1. Introduction .....	5.1	<b>6. Radioactivity and Nuclear         Transformation.....</b>	<b>6.1</b>
5.2. Composition of Nucleus .....	5.1	6.1. Discovery of Radioactivity .....	6.1
5.3. Nuclear Properties—Nuclear Mass .....	5.2	6.2. Nature of Radiations from Radioactive Substances .....	6.1
5.3.1. Nuclear Size and Nuclear Density ..	5.2	6.2.1. Alpha Particles .....	6.1
5.3.2. Nuclear Forces .....	5.3	6.2.2. Beta Particles.....	6.2
5.4. Binding Energy or Separation Energy .....	5.3	6.2.3. Gamma Rays .....	6.2
5.5. Structure of Nucleus .....	5.6	6.2.4. Detection of Radioactivity .....	6.3
5.6. Theories Regarding Nuclear Stability .....	5.7	6.3. Nuclear Reactions and Nuclear Equations ..	6.3

6.7.	Modes of Decay .....	6.8	7.9.	Polarity of Bonds .....	7.9
6.7.1.	Alpha Particle Emission.....	6.8	7.10.	Characteristics of Covalent Compounds ...	7.11
6.7.2.	Beta Particle Emission .....	6.9	7.11.	Fajan's rules.....	7.13
6.8.	Group Displacement Law .....	6.9	7.12.	Deviations from the Octet Rule .....	7.14
6.9.	Rate of Disintegration (Law of Radioactive Decay).....	6.11	7.13.	Molecular Geometry (the Vsepr Theory) .....	7.14
	6.9.1. Half-life Period.....	6.12	7.14.	Electron Pair Donation or Coordinate Valence .....	7.16
	6.9.2. Average Life Period .....	6.13	7.15.	The Hydrogen Bond .....	7.18
	6.9.3. Radioactive Equilibrium .....	6.14	7.16.	The Van der Waals Attraction <i>Questions</i> .....	7.19
6.10.	Radioactive Disintegration Series .....	6.14	<i>Objective Type</i> .....	7.22	
6.10.1.	The Geiger-Nuttal Rule.....	6.16	<i>Problems</i> .....	7.26	
6.11.	Nuclear Transformation .....	6.16			
6.12.	Artificial Transmutation of Elements .....	6.17			
6.13.	Nuclear Fission .....	6.18			
	6.13.1. Atom Bomb.....	6.18			
	6.13.2. Nuclear Reactors .....	6.19			
6.14.	Nuclear Fusion.....	6.20			
	6.14.1. Hydrogen Bomb .....	6.21			
6.15.	Hazards of Radiations.....	6.22			
6.16.	Applications of Radioisotopes.....	6.23			
6.17.	The Synthetic Elements .....	6.25			
6.18.	Nuclear Coulombic Barrier .....	6.26			
6.19.	Radiation Chemistry .....	6.27			
	6.19.1. Radiolysis of Water .....	6.27			
	<i>Questions</i> .....	6.28			
	<i>Objective Type</i> .....	6.31			
	<i>Problems</i> .....	6.33			
	<i>Examination Questions</i> .....	6.36			
<b>7.</b>	<b>Chemical Bonding (I)—</b>				
	<b>Classical Approach.....</b>	<b>7.1</b>			
7.1.	Introduction .....	7.1	8.1.	Introduction .....	8.1
7.2.	Why are Chemical Bonds Formed? .....	7.1	8.2.	The Valence Bond Approach .....	8.1
	7.2.1. The Lewis and Langmuir Concept of Stable Configuration .....	7.1	8.3.	Energy Changes During Bond Formation .....	8.2
	7.2.2. Lewis Symbols .....	7.2		8.3.1. The Wave Mechanical Explanation of Energy Changes .....	8.2
7.3.	Ionic Bond or Electrovalent Bond .....	7.2	8.4.	Sigma and Pi Bonds .....	8.5
7.4.	Lattice Energy.....	7.2	8.5.	Hybridization of Orbitals .....	8.5
	7.4.1. Energetics of Formation of Ionic Substances .....	7.4		8.5.1. <i>sp</i> -Hybridization.....	8.6
	7.4.2. Formation of Ions with Higher Charges.....	7.4		8.5.2. <i>sp</i> <sup>2</sup> -Hybridization .....	8.6
7.5.	Characteristics of Electrovalent Compounds.....	7.5		8.5.3. <i>sp</i> <sup>3</sup> -Hybridization .....	8.7
7.6.	Variable Electrivalence .....	7.6		8.5.4. <i>sp</i> <sup>3</sup> <i>d</i> -Hybridization .....	8.10
7.7.	Inert Pair Effect.....	7.7		8.5.5. <i>sp</i> <sup>3</sup> <i>d</i> <sup>2</sup> -Hybridisation .....	8.11
7.8.	Covalent Bond (by Mutual Sharing of Electrons) .....	7.8		8.5.6. Hybridization and Shapes of Some Simple Molecules.....	8.12
	7.8.1. Lewis Bonding of H <sub>2</sub> .....	7.8	8.6.	Bond lengths .....	8.15
	7.8.2. Lewis Diagrams of some other Molecules and Ions .....	7.8		8.6.1. Correlation of Bond Distances and Hybridization .....	8.15

---

8.11.1. M.O. Diagram of N <sub>2</sub> .....	8.26
8.11.2. M.O. Diagrams of some simple Diatomeric Molecules .....	8.26
8.11.3. M.O. Diagram of Helium .....	8.27
8.11.4. Electronic Configuration of Diatomeric Molecules .....	8.27
8.12. Relationship between Electronic Configuration and Molecular Behaviour ..	8.28
8.12.1. Bond Order.....	8.28
8.13. M.O. Diagrams of Heteronuclear Diatomic Molecules .....	8.30
8.13.1. Molecular Orbital Diagram of Carbon Monoxide, CO .....	8.31
8.13.2. M.O. Diagram of Nitrosyl Ion, NO <sup>+</sup> .....	8.31
8.13.3. M.O. Diagram of Nitric Oxide, NO.....	8.32
8.13.4. M.O. Diagram of Hydrogen Fluoride, HF .....	8.32
8.14. Comparative Study of VB and MO Theories.....	8.32
8.15. Metallic Bond .....	8.33
8.15.1. Electron Sea Model .....	8.33
8.15.2. Resonance Theory .....	8.33
8.15.3. The Molecular Orbital Theory .....	8.34
8.16. Summary of the Three Main Types of Bonds .....	8.35
Questions .....	8.35
Objective Type .....	8.37
Examination Questions.....	8.40
<b>Appendix:</b>	
<i>New Type Question Bank (I)</i> .....	8.43

---

## UNIT-II: STATES OF MATTER

---

<b>9. The Gaseous State.....</b>	<b>9.3</b>
9.1. The Gaseous State .....	9.3
9.2. Gas Laws .....	9.3
9.2.1. Boyle's Law .....	9.3
9.2.2. Charles' Law .....	9.3
9.2.3. Avogadro's Law .....	9.4
9.3. Ideal Gas Law or the Gas Equation .....	9.5
9.3.1. Nature of Gas Constant .....	9.6
9.3.2. Numerical Value of R .....	9.6
9.3.3. Effusion and Diffusion .....	9.7
9.3.4. Dalton's Law of Partial Pressure.....	9.9
9.4. Kinetic Theory of Gases .....	9.10
9.4.1. Postulates of Kinetic Theory of Gases.....	9.11
9.4.2. Validity of the Postulates of the Kinetic Theory of Gases.....	9.11
9.5. Distribution of Molecular Speeds.....	9.12
9.5.1. Maxwell-Boltzmann Law of Distribution of Molecular Velocities .....	9.13
9.5.2. Calculation of Molecular Velocities of Gaseous Molecules .....	9.14
9.5.3. Average Velocity .....	9.14
9.5.4. Most Probable Velocity .....	9.15
9.5.5. Root Mean Square Velocity (RMS Velocity) .....	9.16
9.6. Kinetic Equation for Gases .....	9.18
9.7. Derivation of the Gas Laws from Kinetic Equation .....	9.20
9.7.1. Boyle's Law .....	9.20
9.7.2. Charles's Law.....	9.20
9.7.3. Graham's Law of Gaseous Diffusion .....	9.21
9.7.4. Avogadro's Law .....	9.21
9.7.5. Dalton's Law of Partial Pressures.....	9.22
9.7.6. Kinetic Energy of an Ideal Gas .....	9.22
9.7.7. Calculation of Molecular Velocities .....	9.23
9.8. Collision Diameter, Mean Free Path and Collision Number .....	9.26
9.8.2. Mean Free Path .....	9.28
9.9. Collision Frequency.....	9.29
9.10. Collisions in a Mixture of Gases .....	9.29
9.11. The Barometric Formula .....	9.32
9.12. Viscosity of Gases .....	9.33
9.12.1. The Coefficient of Viscosity .....	9.34
9.12.2. Effect of Temperature and Pressure on Viscosity of Gases.....	9.36
9.13. Degrees of freedom .....	9.36
9.13.1. Translational Degrees of Freedom .....	9.36
9.13.2. Rotational Degrees of Freedom .....	9.37
9.13.3. Vibrational Degrees of Freedom .....	9.37
9.14. Principle of Equipartition of Energies .....	9.39
9.15. Specific Heats and Molar Heats of Gases .....	9.40
9.15.1. Molar Heats of Gases and Kinetic Theory .....	9.41
9.15.2. Ratio of heat Capacities $\bar{C}_p / \bar{C}_v$ and its Variance with Molar Complexity .....	9.42

---

9.15.3. Comparison of Theoretical and Experimental Heat Capacity Values .....	9.43	10.11.1. Importance of the Law of Corresponding States .....	10.23
<i>Questions</i> .....	9.45	10.12. Liquefaction of Gases—Introductory and Historical.....	10.23
<i>Objective Type</i> .....	9.46	10.12.1. Methods of Liquefaction of Gases .....	10.24
<i>Problems</i> .....	9.48	10.12.2. Uses of Liquefied and Compressed Gases .....	10.26
<i>Examination Questions</i> .....	9.49	<i>Questions</i> .....	10.26
<b>10. Real Gases.....</b>	<b>10.1</b>	<i>Objective Type</i> .....	10.28
10.1. Introduction—Ideal and Real Gases.....	10.1	<i>Problems</i> .....	10.29
10.2. Deviation from Ideal Behaviour .....	10.1	<i>Examination Questions</i> .....	10.31
10.2.1. Deviation from Ideal Behaviour .....	10.1		
10.2.2. Deviations from Boyle's Law .....	10.1		
10.2.3. Deviations from Charles' or Gay-Lussac's Law.....	10.2		
10.2.4. Deviations from Avogadro's Law .....	10.2		
10.3. The Cause of Deviations of Real Gases from Ideal Behaviour.....	10.2		
10.4. Van der Waals' Equation .....	10.4		
10.4.1. Nature of Van der Waals' Constant .....	10.5		
10.5. Explanation of Real Gas Behaviour by Van der Waals' Equation.....	10.7		
10.6. Calculation of Boyle Temperature.....	10.9		
10.7. Limitation of the Van der Waals' Equation.....	10.11		
10.7.1. Clausius Equation .....	10.11		
10.7.2. Kammerlingh-Onnes Virial Equations .....	10.12		
10.7.3. Berthelot Equations.....	10.12		
10.7.4. Dieterici Equation .....	10.12		
10.7.5. Applications of Equations of State .....	10.12		
10.8. Relative Molecular Mass Values in Gases.....	10.14		
10.8.1. Limiting Density Method for Determination of Molecular Mass of Gases .....	10.14		
10.9. Critical phenomena.....	10.15		
10.9.1. Experimental Measurement of the Critical Constants of a Gas .....	10.16		
10.9.2. The Critical Phenomena and Andrews' Experiments.....	10.17		
10.9.3. The Van der Waals' Equation and Critical State.....	10.18		
10.10. Calculation of Critical Constants.....	10.19		
10.11. Law of Corresponding States and Reduced Equation of State .....	10.21		
10.11.1. Importance of the Law of Corresponding States .....	10.23		
10.12. Liquefaction of Gases—Introductory and Historical.....	10.23		
10.12.1. Methods of Liquefaction of Gases .....	10.24		
10.12.2. Uses of Liquefied and Compressed Gases .....	10.26		
<i>Questions</i> .....	10.26		
<i>Objective Type</i> .....	10.28		
<i>Problems</i> .....	10.29		
<i>Examination Questions</i> .....	10.31		
<b>11. Properties of Liquids .....</b>	<b>11.1</b>		
11.1. The Liquid State .....	11.1		
11.2. The Intermolecular Forces.....	11.1		
11.3. The Structures of Liquid.....	11.3		
11.4. General Properties of Liquids.....	11.3		
11.5. Evaporation.....	11.4		
11.6. Vapour Pressure .....	11.5		
11.7. Measurement of Vapour Pressure .....	11.7		
11.8. Boiling Point.....	11.8		
11.9. Freezing Point.....	11.8		
11.10. Surface Tension .....	11.9		
11.11. Measurement of Surface Tension .....	11.11		
11.12. Parachor .....	11.14		
11.13. Viscosity and Fluidity .....	11.16		
11.14. Measurement of Viscosity .....	11.17		
11.15. Factors Affecting Viscosity.....	11.18		
11.16. Viscosity in Everyday Life .....	11.20		
11.17. Viscosity and Constitution.....	11.21		
11.18. Optical Activity.....	11.23		
<i>Questions</i> .....	11.27		
<i>Objective Type</i> .....	11.28		
<i>Problems</i> .....	11.30		
<i>Examination Questions</i> .....	11.31		
<b>12. The Solid State .....</b>	<b>12.1</b>		
12.1. Introduction .....	12.1		
12.2. Characteristics of Solids .....	12.1		
12.3. Structure of Crystals .....	12.3		
12.4. Crystal Systems .....	12.4		
12.5. Lattice Planes and their Designation .....	12.7		
12.6. Symmetry in Crystals .....	12.10		
12.7. Crystallography .....	12.13		
12.8. X-ray Diffraction and Crystal Structure.....	12.14		
12.9. Determination of Crystal Structure.....	12.16		
12.10. Indexing of Planes and Structure of NaCl and KCl .....	12.18		
12.11. Number of Atoms Per Unit Cell, Formula and Density of Solids .....	12.20		

---

12.12.	Packing of Constituent Particles in Crystals .....	12.22
12.13.	Types of Three-dimensional Packing ..	12.25
12.14.	Packing of Crystals and Coordination Number .....	12.26
12.15.	Structure of Simple Ionic Compounds—Close Packed Arrangements .....	12.27
12.15.1.	Ionic Compounds of the Types $AX_1$ .....	12.28
12.15.2.	Ionic Compounds of the Type $AX_2$ .....	12.29
12.15.3.	Limiting Radius Ratio and the Geometry of the Crystal.....	12.30
12.16.	Lattice Energy.....	12.30
12.17.	Void Space in Closed Packing of Spheres.....	12.32
12.18.	Types of Crystals .....	12.34
12.19.	Imperfections for Defects in Solids .....	12.37
12.20.	Properties of Solids.....	12.40
12.21.	Superconductivity.....	12.42
12.22.	Amorphous Solids .....	12.43
12.23.	Liquid Crystals .....	12.44
12.24.	Polymorphism.....	12.46
12.24.1.	Types of Allotropy (Transition Temperature) .....	12.46
	<i>Questions</i> .....	12.47
	<i>Objective Type</i> .....	12.48
	<i>Problems</i> .....	12.50
	<i>Examination Questions</i> .....	12.51

---

## UNIT-III: THERMODYNAMICS-I

---

<b>13. Introduction to Chemical Thermodynamics.....</b>	<b>13.3</b>	
13.1.	Introduction .....	13.3
13.2.	Thermodynamic Variables or State Variables .....	13.4
13.3.	State Functions and Path Functions.....	13.5
13.4.	Thermal Equilibrium .....	13.6
13.4.1.	Quasiequilibrium Process .....	13.6
13.5.	Zeroth Law of Thermodynamics .....	13.6
13.5.1.	Derivation of the Zeroth Law of Thermodynamics .....	13.7
13.6.	Thermodynamic Process.....	13.8
13.7.	Exact and Inexact Differentials .....	13.10
13.8.	More Properties of Exact Differentials .....	13.12
	<i>Exercise</i> .....	13.16
	<i>Questions</i> .....	13.16
	<i>Objective Type</i> .....	13.17
	<i>Problems</i> .....	13.18
	<i>Examination Questions</i> .....	13.18
<b>14. The First Law of Thermodynamics..</b>	<b>14.1</b>	
14.1.	Work and Heat .....	14.1
14.2.	First Law of Thermodynamics.....	14.2
14.3.	Work done in Isothermal and Adiabatic Changes .....	14.4
14.4.	Heat Content or Enthalpy .....	14.4
14.5.	Molar Heat at Constant Volume $C_v$ .....	14.5
14.6.	Thermodynamic Changes in Compression and expansion of an Ideal Gas.....	14.8
14.7.	Work done on the System in Reversible Adiabatic Compression of Ideal Gases.....	14.10
14.8.	Comparison of Work done in Adiabatic Reversible and Isothermal Reversible Expansion of an Ideal Gas .....	14.13
14.9.	The Joule-Thomson Effect .....	14.21
	<i>Questions</i> .....	14.24
	<i>Objective Type</i> .....	14.25
	<i>Problems</i> .....	14.26
	<i>Examination Questions</i> .....	14.27
<b>15. Thermochemistry .....</b>	<b>15.1</b>	
15.1.	Introduction .....	15.1
15.2.	Conventions used in Thermochemistry	15.1
15.3.	Enthalpy of Reaction .....	15.2
15.3.1.	Measurement of Enthalpy of Reaction.....	15.3
15.3.2.	Relation of Enthalpy of Reaction to Physical Conditions .....	15.3
15.4.	Variation of $\Delta H$ with Temperature — Kirchhoffs Equation.....	15.4
15.5.	Relation between Heat of Reaction at Constant Pressure ( $\Delta H$ ) and at Constant Volume ( $\Delta U$ ).....	15.7
15.6.	Enthalpy of Combustion .....	15.8
15.6.1.	Experimental Determination of Enthalpy of Combustion ( $\Delta H$ ).....	15.8
15.7.	Enthalpy of Formation.....	15.10
15.8.	Enthalpy of Solution .....	15.12
15.8.1.	Integral Enthalpy of Solution .....	15.12
15.8.2.	Differential Enthalpy of Dilution and Solution.....	15.13

---

15.8.3.	Enthalpy of Formation of Ions.....	15.13
15.8.4.	Experimental Determination of Enthalpy of Solution.....	15.14
15.9.	Enthalpy of Neutralization.....	15.15
15.9.1.	Experimental Determination of Enthalpy of Neutralization....	15.15
15.10.	Enthalpy of Hydration .....	15.17
15.11.	Enthalpy of Transition .....	15.17
15.12.	Thermochemical Laws .....	15.17
15.13.	Bond Dissociation Enthalpies.....	15.21
	<i>Questions</i> .....	15.24
	<i>Objective Type</i> .....	15.25
	<i>Problems</i> .....	15.26
	<i>Examination Questions</i> .....	15.28
<b>16.</b>	<b>The Second Law of Thermodynamics.....</b>	<b>16.1</b>
16.1.	Spontaneous and Natural Processes .....	16.1
16.2.	Limitations of First Law of Thermodynamics .....	16.1
16.3.	Second Law of Thermodynamics .....	16.2
16.4.	Conversion of Heat into Work (the Carnot Cycle) .....	16.3
16.5.	Refrigerators .....	16.8
16.6.	Carnot Theorems from Eqn. (16.15) .....	16.8
16.7.	Kelvin Scale of Temperature .....	16.9
16.8.	Entropy and Carnot Cycle .....	16.11
16.9.	Entropy Change of the Universe in Reversible Processes.....	16.13
16.10.	Entropy—A Measure of Disorder.....	16.14
16.11.	Entropy Calculations .....	16.17
16.12.	Free Energy.....	16.19
16.13.	Condition of Equilibrium and Spontaneous Change.....	16.20
16.14.	Variation in $\Delta H$ and $\Delta S$ and the Spontaneity or Equilibrium of a Reaction or Process .....	16.21
16.15.	Change in Standard Free Energy ( $\Delta G^\circ$ ) of the Reactions.....	16.22
16.16.	The Helmholtz Function (Work Function).....	16.24
16.17.	The Maxwell Equations.....	16.27
16.18.	Thermodynamic Equation of State.....	16.29
16.19.	The Joule—Thomson Inversion Temperature .....	16.32
16.20.	Gibbs-Helmholtz Equations .....	16.32
16.21.	Free Energy Changes in Chemical Reaction—Van't Hoff Isotherm.....	16.35
16.22.	Thermodynamic Equation for Open Systems—Partial Molar Quantities ....	16.36
16.23.	Partial Molal Free Energy or Chemical Potential .....	16.37
16.24.	Clapeyron—Clausius Equation .....	16.39
16.25.	Variation of Chemical Potential with Temperature .....	16.41
16.26.	Chemical Potential of an Ideal Gas ....	16.42
16.27.	Free Energy of Mixture .....	16.43
16.28.	Gibbs-Duhem Equation .....	16.43
16.29.	Chemical Potential of Solvent in Binary Ideal Liquid Solution .....	16.44
16.30.	The Application of Chemical Potential.....	16.45
	<i>Questions</i> .....	16.45
	<i>Objective Type</i> .....	16.46
	<i>Problems</i> .....	16.48
	<i>Examination Questions</i> .....	16.50
<b>17.</b>	<b>The Third Law of Thermodynamics.....</b>	<b>17.1</b>
17.1.	Entropy at the Absolute Zero.....	17.1
17.2.	Development of Third Law .....	17.4
17.3.	Unattainability of Absolute Zero .....	17.5
17.4.	Thermodynamic Properties at Absolute Zero .....	17.5
17.5.	Tables of Entropies at 298 K .....	17.6
17.6.	Exceptions to the Third Law : The Concept of Residual Entropy .....	17.9
17.7.	Molecular Basis of Residual Entropy ...	17.9
	<i>Questions</i> .....	17.10
	<i>Objective Type</i> .....	17.11
	<i>Problems</i> .....	17.12
	<i>Examination Questions</i> .....	17.12
<b>18.</b>	<b>Chemical Equilibrium.....</b>	<b>18.1</b>
18.1.	Rate of Reaction .....	18.1
18.2.	Factors which Affect the Rate of a Reaction .....	18.1
18.3.	Reversible Reactions .....	18.2
18.4.	The Equilibrium.....	18.3
18.5.	Stable and Metastable Equilibrium.....	18.3
18.6.	Criteria of Equilibrium .....	18.3
18.7.	Law of Mass Action .....	18.4
18.8.	The Equilibrium Constant .....	18.4
18.9.	Activity .....	18.8
18.10.	Fugacity .....	18.10
18.11.	Free Energy and Chemical Equilibrium .....	18.11
18.12.	Standard Free Energy and Equilibrium Constant.....	18.12
18.13.	Relationship between $K_c$ , $K_p$ and $K_x$ ... $18.13$	
18.14.	Variation of Equilibrium Constant with Temperature, the Reaction Isochore ....	18.15
18.15.	Usefulness of the Equilibrium Constant.	18.16
18.16.	Experimental Determination of Equilibrium Constants .....	18.17

18.17. Gaseous Reactions of Type I .....	18.17	20. The Phase Rule .....	<b>20.1</b>
18.18. Gaseous Reactions of Type II.....	18.19	20.1. Equilibrium Between Phases .....	20.1
18.19. Calculation of the Degree of Dissociation from the Vapour Density Measurements .....	18.19	20.2. Definitions of terms used.....	20.1
18.20. Homogeneous Equilibria in Liquid State.....	18.22	20.3. Phase Rule .....	20.3
18.21. Heterogeneous Equilibria .....	18.23	20.4. Phase Diagrams .....	20.4
18.22. Le Chatelier Principle.....	18.24	20.5. The Water System: A One-component System .....	20.4
18.23. Effect of Addition of Inert Gas .....	18.25	20.6. The Carbon Dioxide System.....	20.7
<i>Questions</i> .....	18.25	20.7. The Sulphur System ( <i>one-component</i> <i>system showing solid-solid</i> <i>transformations</i> ) .....	20.8
<i>Essay Type</i> .....	18.25	20.8. Two-Component System .....	20.12
<i>Short Answer Type</i> .....	18.26	20.9. Types of Two-Component Systems involving Solid-Liquid Equilibrium ...	20.12
<i>Objective Type</i> .....	18.28	20.10. The Lead-Silver System .....	20.12
<i>Problems</i> .....	18.29	20.11. Potassium Iodide-Water System.....	20.14
<i>Examination Questions</i> .....	18.30	20.12. Freezing Point Diagram with Compound Formation.....	20.15
<b>19. Nernst Distribution Law .....</b>	<b>19.1</b>	20.13. Ferric Chloride-Water System .....	20.16
19.1. Nernst Distribution Law .....	19.1	20.14. Applications of Eutectics.....	20.18
19.2. Thermodynamics of Solutions.....	19.1	20.15. Systems Involving Formation of Compounds with Incongruent Melting Points ( <i>i.e.</i> , showing peritectic change).....	20.18
19.3. Thermodynamical Derivation of Distribution Law .....	19.4	20.16. Sodium Chloride-Water System .....	20.19
19.4. Calculation of the Partition Coefficient .....	19.5	20.17. Sodium Sulphate-Water System .....	20.20
19.5. Deviation from Distribution Law due to Molecular Complexity.....	19.6	20.18. Gas-Solid Equilibria— Salt Hydrate System .....	20.24
19.6. Other Limitations of Distribution Law .....	19.10	<i>Solved Problems</i> .....	20.25
19.7. Applications of Distribution Law .....	19.11	<i>Questions</i> .....	20.28
19.8. Extraction of Substances from Solutions .....	19.12	<i>Objective Type</i> .....	20.28
19.9. Distribution Law and Henry's Law .....	19.15	<i>Examination Question</i> .....	20.30
<i>Questions</i> .....	19.15		
<i>Objective Type</i> .....	19.16		
<i>Problems</i> .....	19.18		
<i>Examination Questions</i> .....	19.19		

## UNIT-IV: SOLUTIONS

<b>21. Solutions.....</b>	<b>21.3</b>	21.4.1. Solutions of Gases in Liquids....	21.9
21.1. Solution—A Homogeneous Mixture .....	21.3	21.4.2. How the Solubility of a Gas is Measured .....	21.11
21.1.1. Solvent and Solute .....	21.3	21.5. The Ideal Solutions.....	21.12
21.1.2. Solution .....	21.3	21.5.1. Raoult's Law of Ideal Solutions .....	21.12
21.2. Why do Substances Dissolve? .....	21.4	21.5.2. Solutions of Liquids in Liquids .....	21.13
21.2.1. Temperature and Solubility.....	21.4	21.5.3. Miscible Liquids .....	21.13
21.2.2. Why does a Substance have Different Solubilities in Different Solvents? .....	21.4	21.5.4. Boiling Point-Composition Curves.....	21.13
21.2.3. Solubility of Gases in Liquids.....	21.5	21.5.5. Relation Between the Mole- fractions of the Components in the Liquid and Vapour Phases.	21.14
21.3. Composition of Solutions .....	21.5		
21.4. Gaseous Solutions (Solution of Gas in Gas) .....	21.8		

---

21.5.6.	Ideal Solution in Terms of Activity .....	21.15
21.6.	Non-ideal Solutions: Activity Coefficients.....	21.16
21.7.	Thermodynamics of Ideal Solutions....	21.17
21.7.1.	Gibbs Free Energy Change of Mixing ( $\Delta G_{\text{mix}}$ ).....	21.17
21.7.2.	Enthalpy Change of Mixing ( $\Delta H_{\text{mix}}$ ).....	21.18
21.7.3.	Volume Change of Mixing ( $\Delta V_{\text{mix}}$ ) .....	21.19
21.7.4.	Entropy Change of Mixing ( $\Delta S_{\text{mix}}$ ).....	21.19
21.7.5.	Relationship between the Composition of the Solution in the Liquid Phase and Partial Vapour Pressures in Gas Phase (Gibbs-Duhem-Margules Equation).....	21.21
21.7.6.	Application of Gibbs-Duhem-Margules Equation to Ideal Solutions .....	21.21
21.7.7.	Application of Gibbs-Duhem-Margules Equation to Non-ideal Solutions .....	21.22
21.8.	Theory of Fractional Distillation .....	21.22
21.8.1.	Fractional Distillation of Liquid Pairs of Type I .....	21.23
21.8.2.	Fractional Distillation in Industry .....	24
21.8.3.	Fractional Distillation of Non-ideal Solutions .....	21.24
21.8.4.	Fractional Distillation of Liquid Pairs of Type II ( <i>Minimum B.P. Mixtures</i> ) .....	21.24
21.8.5.	Fractional Distillation of Liquid pairs of Type III ( <i>Maximum B.P. Mixtures</i> ) .....	21.25
21.8.6.	Azeotropic Distillation.....	21.25
21.8.7.	The Nature of Azeotropic Mixtures .....	21.25
21.9.	Partially Miscible Liquids .....	21.26
21.9.1.	Critical Solution Temperature (C.S.T.).....	21.26
21.9.2.	Mixtures with Lower C.S.T.....	21.28
21.9.3.	Mixtures with both Lower and Upper C.S.Ts .....	21.28
21.10.	Completely Immiscible Liquids .....	21.28
21.11.	Solutions of Solids in Liquids .....	21.30
21.12.	Solid Solutions.....	21.30
	<i>Questions</i> .....	21.31
	<i>Objective Type</i> .....	21.32
	<i>Problems</i> .....	21.33
	<i>Examination Questions</i> .....	21.34
<b>22. Theory of Dilute Solutions.....</b>		<b>22.1</b>
22.1.	Colligative Properties of Dilute Solutions .....	22.1
22.1.1.	What Happens when the Solute Undergoes Dissociation.....	22.1
22.1.2.	What Happens when the Solute Undergoes Association.....	22.1
22.2.	Relative Lowering of Vapour Pressure .....	22.2
22.2.1.	Raoult's Law of Relative Lowering of Vapour Pressure .....	22.3
22.2.2.	Relative Lowering of Vapour Pressure and Molality of the Solution .....	22.4
22.2.3.	Molecular Mass of Solute from Relative Lowering of Vapour Pressure .....	22.4
22.2.4.	Thermodynamic Derivation of Relative Lowering of Vapour Pressure .....	22.6
22.3.	Osmosis .....	22.8
22.3.1.	Preparation of Semi-permeable Membrane .....	22.9
22.3.2.	Theories of Semi-permeability .....	22.9
22.3.3.	Function of the Semi-permeable Membrane .....	22.10
22.3.4.	Osmotic Pressure .....	22.10
22.3.5.	Kinetic Molecular Theory of Osmotic Pressure .....	22.11
22.3.6.	Reverse Osmosis .....	22.11
22.3.7.	Measurement of Osmotic Pressure .....	22.12
22.3.8.	Theory of Dilute Solutions....	22.14
22.3.9.	Thermodynamic Derivation of the Relation between Osmotic Pressure and Concentration of Solute (van't Hoff Equation).....	22.15
22.3.10.	Comparison of Osmotic Pressures .....	22.17
22.3.11.	Osmotic Pressure of Electrolytes .....	22.19

22.3.12.	Osmotic Coefficient .....	22.19
22.3.13.	Number-Average Molar Mass and Mass-Average Molar Mass .....	22.20
22.3.14.	Relation Between Osmotic Pressure and Relative Lowering of Vapour Pressure .....	22.21
22.4.	Elevation of Boiling Point .....	22.22
22.4.1.	Thermodynamic Derivation of Elevation of Boiling Point .....	22.23
22.4.2.	Experimental Determination of Elevation of Boiling Point .....	22.26
22.5.	Depression in Freezing Point.....	22.29
22.5.1.	Thermodynamic Derivation of Depression of Freezing Point .....	22.29
22.5.2.	Experimental Determination of the Depression of Freezing Point.....	22.32
22.6.	Abnormal Behaviour of Solutions.....	22.33
22.6.1.	Abnormal Behaviour of Solutions of Electrolytes .....	22.34
22.6.2.	Abnormal Behaviour of Solutions of Solutes undergoing Association in Solution .....	22.35
	<i>Questions</i> .....	22.36
	<i>Objective Type</i> .....	22.39
	<i>Problems</i> .....	22.41
	<i>Examination Questions</i> .....	22.43

## UNIT-V: SURFACE CHEMISTRY

<b>23. ADSORPTION .....</b>	<b>23.3</b>	
23.1.	Introduction .....	23.3
23.1.1.	How does Adsorption Differ from Absorption .....	23.3
23.1.2.	Adsorption and Absorption Occur One after the other .....	23.4
23.1.3.	Examples of Adsorbents and Adsorbates .....	23.4
23.2.	Adsorption of Gases .....	23.4
23.2.1.	Physical Adsorption .....	23.5
23.2.2.	Chemisorption.....	23.5
23.2.3.	Distinction between Physical Adsorption and Chemisorption.....	23.6
23.3.	What changes the Adsorbed Molecules Suffer in the Process of Adsorption ? ....	23.6
23.4.	Adsorption Isotherms .....	23.7
23.4.1.	Freundlich Adsorption Isotherm .....	23.7
23.4.2.	Langmuir Adsorption Isotherm .....	23.9
23.4.3.	Types of Adsorption Isotherms.....	23.11
23.4.4.	BET Theory.....	23.13
23.5.	Experimental Determination of Gas Adsorption .....	23.20
23.5.1.	Volumetric Method .....	23.20
23.5.2.	Gravimetric Method.....	23.21
23.6.	Effect of temperature on Adsorption .....	23.22
23.7.	Adsorption from Solution.....	23.24
23.7.1.	Adsorption of Solutes from Solutions Depends on the Nature of the Adsorbent .....	23.25
23.7.2.	A Competition between the Solute and Solvent Molecules takes place in Adsorption from Solutions.....	23.25
23.7.3.	Three Types of Mechanical Adsorption from Solutions....	23.26
23.7.4.	How to Calculate x/m from Experimental Data due to Adsorption from Solutions? .....	23.26
23.8.	Liquid Surfaces.....	23.27
23.8.1.	Surface Tension and Surface Energy .....	23.27
23.8.2.	Capillary Action .....	23.27
23.8.3.	Pressure Difference Across Curved Surface (Laplace Equation).....	23.28
23.8.4.	Vapour-Pressure of Droplets (Kelvin Equation).....	23.29
23.8.5.	Extent of Adsorption Depends on the Surface Tension of the Solvent .....	23.30
23.8.6.	Surface Catalyzed Oxidation of CO to CO <sub>2</sub> .....	23.30
23.8.7.	Surface Equation of State and Applications.....	23.31
23.8.8.	Surface Equation of State for Ionized Surfactants.....	23.31
23.8.9.	Electrokinetic Phenomena .....	23.32
23.8.10.	Formation of Surface Films .....	23.37
23.9.	The Gibbs adsorption theorem .....	23.37
23.10.	Emulsifiers .....	23.40
23.11.	Applications of Adsorption .....	23.41
	<i>Questions</i> .....	23.43
	<i>Objective Type</i> .....	23.45
	<i>Examination Questions</i> .....	23.46
<b>24. The Colloidal State .....</b>	<b>24.1</b>	
24.1.	Introduction .....	24.1
24.2.	Characteristics of True Solutions, Colloidal Solutions and Suspensions....	24.2

---

24.3.	Colloidal State .....	24.2
24.4.	Preparation of Colloidal Solution .....	24.4
24.4.1.	Condensation Method. ....	24.5
24.4.2.	Dispersion Methods .....	24.5
24.5.	Purification of Colloidal Solution.....	24.7
24.6.	Properties of Colloidal Solution .....	24.7
24.6.1.	Physical Properties.....	24.7
24.6.2.	Optical Properties.....	24.8
24.6.3.	Electrical Properties .....	24.12
24.7.	The Stability of Colloids.....	24.16
24.8.	The Precipitation (Coagulation) of Colloids.....	24.17
24.8.1.	Protection .....	24.19
24.8.2.	Imbibition.....	24.19
24.8.3.	Adsorption.....	24.20
24.9.	Emulsions .....	24.20
24.9.1.	Emulsifying Agents and Preparation of Emulsion .....	24.21
24.9.2.	Properties and Uses of Emulsions.....	24.21
24.9.3.	Microemulsion .....	24.22
24.10.	Gels .....	24.23
24.11.	Size of Colloidal Particles .....	24.23
24.12.	Molecular Mass of Macromolecules .....	24.24
24.13.	Applications of Colloid Chemistry.....	24.26
24.14.	Colloidal Electrolytes .....	24.27
24.15.	Surface Active Agents (Surfactants)....	24.28
24.15.1.	Characteristics of Surfactants..	24.28
24.15.2.	Classification of Surface Active Agents.....	24.29
24.16.	Micelles .....	24.30
24.16.1.	Kraft Temperature .....	24.32
24.16.2.	Structure of Micelles.....	24.32
24.16.3.	Ionic Micelles and their Different Types.....	24.34
24.16.4.	Micellization in Non-aqueous Media .....	24.34
24.16.5.	Counter Ion Binding to Micelles.....	24.34
24.16.6.	Mechanism of Micellization .	24.35
24.16.7.	Determination of Critical Concentration of Micellization .....	24.36
24.16.8.	Factors Affecting the Critical Concentration of Micelles of Surfactant .....	24.36
24.16.9.	Thermodynamics of Micellization .....	24.37
24.16.10.	Solubilization in Surfactant Solutions .....	24.39
24.16.11	Reverse Micelles .....	24.40
24.17.	Donnan Membrane Equilibrium.....	24.40
	Questions.....	24.46
	Objective Type .....	24.48
	Examination Questions .....	24.49

---

## UNIT-VI: RATES AND MECHANISMS

---

25.	<b>Chemical Kinetics .....</b>	<b>25.3</b>
25.1.	The Rates of Chemical Reactions.....	25.3
25.1.1.	The Concept of Reaction Rate ..	25.3
25.1.2.	Units Employed .....	25.4
25.1.3.	Variation of Reactant Concentration with Time.....	25.4
25.1.4.	Rate Laws and Rate Constants.....	25.5
25.1.5.	Factors Influencing Reaction Rates.....	25.6
25.2.	Molecularity and Order of Reaction .....	25.7
25.2.1.	Relation Between Molecularity and Order of Reaction.....	25.7
25.2.2.	Order and Molecularity of Complex Reactions .....	25.8
25.3.	Zero-Order Reactions .....	25.9
25.4.	First Order Rate Equations .....	25.10
25.4.1.	Half-change Time.....	25.12
25.4.2.	Some Typical First Order Reactions.....	25.13
25.5.	Second Order Rate Equation .....	25.16
25.5.1.	Hydrolysis of an Ester by an Alkali .....	25.17
25.5.2.	Some other Examples of Second Order Reactions are ..	25.19
25.6.	Third Order Rate Equation .....	25.19
25.7.	Rate Law for <i>n</i> th Order Reaction .....	25.19
25.8.	Fractional Order Reactions.....	25.20
25.9.	Reactions with Negative Order.....	25.21
25.10.	Determination of the Order of a Reaction .....	25.21
25.11.	The Effect of Temperature on Reaction Rate.....	25.25
25.11.1.	Significance of Activation Energy .....	25.26
25.11.2.	Temperature Coefficient of Reaction Rates .....	25.27
25.12.	Complex Reactions.....	25.27
25.13.	Reaction Mechanism .....	25.38
25.13.1.	Mechanisms of Chemical Reactions .....	25.40
25.14.	Theories of Reaction Rates: Collision Theory .....	25.42

---

---

25.14.1. Collision Theory .....	25.43	26.2.5. Use of Catalysts in Industry .....	26.29
25.14.2. The Transition State Theory or Theory of Absolute Reaction Rate .....	25.49	<i>Questions</i> .....	26.30
25.15. Chemical Kinetics in Solutions .....	25.61	<i>Objective Type</i> .....	26.31
25.15.1. Reactions in Ideal Solutions.....	25.61	<i>Examination Questions</i> .....	26.32
25.15.2. Reaction Between Ions in Solution .....	25.62		
25.15.3. Diffusion-Controlled Reactions in Solution .....	25.67		
25.15.4. Kinetics of Fast Reactions .....	25.69		
25.15.5. Kinetics of Slow Reactions .....	25.77		
25.16. Molecular Reaction Dynamics .....	25.84		
25.16.1. Reactions in Molecular Beams.....	25.85		
25.16.2. Potential Energy Surfaces .....	25.89		
25.16.3. Transition State Theory in Terms of Statistical Mechanics .....	25.91		
<i>Questions</i> .....	25.94		
<i>Objective Type</i> .....	25.98		
<i>Problems</i> .....	25.100		
<i>Examination Questions</i> .....	25.101		
<b>26. Catalysis .....</b>	<b>26.1</b>		
26.1. Substances Alter the Speed of a Chemical Reaction .....	26.1	27.1. Indroduction.....	27.1
26.1.1. Types of Catalysis .....	26.1	27.1.1. What Does Photochemistry Tell Us? .....	27.1
26.1.2. Function of a Catalyst .....	26.5	27.1.2. Chemical Effects Produced by Light Radiations.....	27.1
26.1.3. Characteristics of Catylytic Action.....	26.6	27.1.3. Aquaintance with Photochemical Reactions .....	27.2
26.2. Theories of Catalysis .....	26.8	27.1.4. Differences between Thermal and Photochemical Reactions .....	27.2
26.2.1. Theory of Homogeneous Catalysis .....	26.8	27.2. The Whole of Incident Radiation is not Absorbed: The Laws of Absorption.....	27.3
26.2.2. Theory of Heterogeneous Catalysis Modern Adsorption Theory (Surface Reactions) .....	26.10	27.2.1. Why does the Intensity of Incident Light Change? .....	27.3
26.2.3. Quantitative treatment of Adsorption Theory of Heterogeneous Catalysis on Reactants (Kinetics of Surface Reactions) .....	26.15	27.2.2. The Laws of Absorption.....	27.3
26.2.4. Kinetics of Homogeneous Catalysis .....	26.21	27.3. Effect of Radiation on Chemical Reactions .....	27.7
		27.3.1. Laws of Photochemistry .....	27.7
		27.3.2. Deviations in the Law of Photochemical Equivalence .....	27.10
		27.3.3. Factors Affecting the Quantum Efficiency .....	27.11
		27.3.4. Experimental Procedure .....	27.12
		27.3.5. Photochemical Reactions .....	27.14
		27.4. Emission of Radiations .....	27.19
		27.4.1. Luminescence .....	27.19
		27.4.2. Fluorescence .....	27.20
		27.4.3. Phosphorescence .....	27.21
		27.4.4. Flash Photolysis .....	27.21
		27.5. Application of Photochemistry .....	27.21
		27.5.1. Photography .....	27.21
		27.5.2. Photoelectric Effect in Wireless .....	27.22
		<i>Questions</i> .....	27.22
		<i>Problems</i> .....	27.25
		<i>Examination Questions</i> .....	27.25

---

## UNIT-VII: ELECTROCHEMISTRY

---

<b>28. Electrolysis and Electrical Conductivity.....</b>	<b>28.3</b>	28.3. Electrolysis .....	28.6
28.1. Electrolyte Solutions Conduct Electricity .....	28.3	28.3.1. Products of Electrolysis .....	28.7
28.1.1. Ions in Solution.....	28.3	28.3.2. Faraday's Laws of Electrolysis .....	28.8
28.1.2. Formation of Ions in Solution .....	28.4	28.3.3. Theoretical Importance of the Second Law .....	28.9
28.2. Substances that Conduct Electricity .....	28.5	28.4. Conductance of Solution .....	28.10
28.2.1. Metallic Conductance .....	28.5	28.4.1. Electrolytic Conductivity or Specific Conductance .....	28.11
28.2.2. Electrolytic Conductance.....	28.6	28.4.2. Molar Conductivity ( $\Lambda_m$ ) .....	28.12

---

28.4.3.	Equivalent Conductivity .....	28.13
28.4.4.	Relation between Equivalent Conductivity and Molar Conductivity.....	28.14
28.4.5.	Measurement of Electrolytic Conductivity.....	28.15
28.4.6.	Effect of Dilution on Equivalent Conductivity.....	28.18
28.5.	Theories of Weak and Strong Electrolytes .....	28.20
28.5.1.	Arrhenius Theory .....	28.20
28.5.2.	Degree of Dissociation.....	28.21
28.5.3.	Drawbacks of the Arrhenius Theory .....	28.22
28.5.4.	Theory of Strong Electrolytes	28.23
28.5.5.	Derivation of Debye-Hückel- Onsager Conductance Equation .....	28.25
28.6.	Conductance at High Frequencies and High Voltages.....	28.29
28.6.1.	Wien Effect .....	28.29
28.6.2.	Debye-Falkenhagen Effect....	28.29
28.7.	Interionic Attraction Theory: Debye-Hückel theory of Strong Electrolytes .....	28.29
28.7.1.	Activity Co-efficients of Electrolytes .....	28.30
28.7.2.	Debye-Hückel Theory.....	28.34
	<i>Questions</i> .....	28.44
	<i>Objective Type</i> .....	28.45
	<i>Problems</i> .....	28.46
	<i>Examination Questions</i> .....	28.47
<b>29.</b>	<b>Migration of Ions .....</b>	<b>29.1</b>
29.1.	Migration of Ions .....	29.1
29.1.1.	Experiment.....	29.2
29.1.2.	The Drift Speed and Mobility of Ions .....	29.2
29.1.3.	Current carried by Ions and Ionic Speeds.....	29.5
29.2.	Speeds of Ions and Amounts Liberated at the Electrodes.....	29.6
29.2.1.	Hittorf's Theoretical Device ...	29.6
29.2.2.	Transference Number or Transport Numbers .....	29.7
29.2.3.	Transference Number of Some Ions in Aqueous Medium .....	29.14
29.2.4.	Zero and Negative Transference Numbers .....	29.14
29.2.5.	Factors on Which Transport Number Depends .....	29.15
29.3.	Ionic conductance .....	29.16
29.3.1.	Kohlrausch Law of Independent Migration of Ions .....	29.16
29.3.2.	Application of Kohlrausch's Law .....	29.25
29.3.3.	Conductometric Titrations ....	29.30
	<i>Questions</i> .....	29.32
	<i>Objective Type</i> .....	29.34
	<i>Problems</i> .....	29.35
	<i>Examination Questions</i> .....	29.37
<b>30.</b>	<b>Ionic Equilibria .....</b>	<b>30.1</b>
30.1.	Introduction .....	30.1
30.1.1.	Dynamic Equilibrium between Ions and the Unionised Molecules.....	30.1
30.1.2.	Dissociation Constant and Ostwald's Dilution Law .....	30.2
30.1.3.	Dissociation of Pure Water.....	30.5
30.1.4.	Logarithmic or p-scale : pH, pOH and pK .....	30.6
30.2.	Solution of Acids and Bases .....	30.12
30.2.1.	Ionic Equilibria in Solutions of a Monobasic Acid (HA)....	30.13
30.2.2.	Ionic Equilibria in Solutions of Monoacid Bases.....	30.19
30.3.	Multiple-stage Equilibria.....	30.22
30.3.1.	Equilibria in Dibasic (or Diprotic) Acid H <sub>2</sub> A.....	30.22
30.3.2.	Ionic Equilibria in Diacid Bases.....	30.25
30.3.3.	Dissociation in Polybasic Acids and Polyacid Bases .....	30.27
30.4.	Common Ion Effect .....	30.30
	<i>Questions</i> .....	30.32
	<i>Objective Type</i> .....	30.33
	<i>Problems</i> .....	30.35
	<i>Examination Questions</i> .....	30.36
<b>31.</b>	<b>Acids and Bases.....</b>	<b>31.1</b>
31.1.	Classical Definition of Acids and Bases .....	31.1
31.1.1.	Proton Concept or Bronsted- Lowry Theory of Acids and Bases .....	31.1
31.1.2.	The Lewis Concept of Acids and Bases .....	31.4
31.1.3.	Relatives Strengths of Acids ...	31.4
31.1.4.	Relatives Strengths of Bases ...	31.7
31.1.5.	Isohydric Solution.....	31.7
31.2.	The Control of the Concentration of H <sup>+</sup> ions—Buffer Solutions.....	31.8
31.2.1.	Composition of Buffer Solutions .....	31.9

---

31.2.2.	Mathematical Expression for the pH of Acidic Buffers and Basic Buffers—Henderson-Hasselbalch Equation .....	31.9	The Nernst Equation of Electrode Potential.....	33.2
31.2.3.	Buffer Capacity.....	31.13	Cell Diagrams and Terminology .....	33.3
31.2.4.	Methods for the Determination of pH .....	31.15	Factors on which Electrode Potential Depends .....	33.4
31.3.	Theories of Indicators.....	31.19	Thermodynamic Explanation of the Electrochemical Potential .	33.4
31.3.1.	The Acid-Base Concept of Indicators—Ostwald's Theory ..	31.19	Thermodynamic Explanation of the Potential Difference at the Interfacial Boundaries.....	33.5
31.3.2.	Quinonoid Theory .....	31.19	Thermodynamic Explanation of Electrode Potential .....	33.5
31.3.3.	pH Changes During Acid-base Titrations .....	31.20	Single Electrode Potentials .....	33.6
31.3.4.	Choice of Indicators and Acid-Base Titrations .....	31.25	Sign of Electrode Potential .....	33.7
31.3.5.	Indicators and Acid-Base Titrations .....	31.25	Reversible and Irreversible Cells .....	33.8
<i>Questions</i>	.....	31.27	Types of Electrodes .....	33.10
<i>Objective Type</i>	.....	31.29	<b>32.</b> Standard Electrode Potential and <i>E.M.F.</i> of Cell .....	33.13
<i>Problems</i>	.....	31.30	32.1. Determination of Standard Electrode Potential .....	33.13
<i>Examination Questions</i>	.....	31.31	32.2. Thermodynamic Concept of Electrode Potential .....	33.14
<b>32. Solubility Product and Hydrolysis...32.1</b>			32.3. Standard Half-Cell Reduction Potentials at 25°C in Aqueous Solution .....	33.15
32.1.	Solubility Product .....	32.1	32.4. Some Uses of Electrode Potentials.....	33.19
32.1.1.	Equilibrium between a Solid Salt and its Ions in Solution, Solubility Product .....	32.1	32.5. Standard emf of the Cell .....	33.19
32.1.2.	Relation between Solubility and Solubility Product of a Sparingly Soluble Salt.....	32.2	32.6. Measurement of <i>EMF</i> : Poggendorff's Compensation Method .....	33.22
32.1.3.	Application of Solubility Product .....	32.3	32.7. The Standard Cell .....	33.22
32.1.4.	Application of Solubility Product in Qualitative Analysis of Cations .....	32.4	32.8. Calculation of EMF of Cell.....	33.23
32.2.	Hydrolysis.....	32.6	<b>33.</b> Types of Electrochemical Cells .....	33.25
32.2.1.	Degree of Hydrolysis and Hydrolysis Constants .....	32.7	33.3.1. Chemical Cells .....	33.27
32.2.2.	Relation between the Hydrolysis Constant and Dissociation Constant .....	32.8	33.3.2. Concentration Cells .....	33.30
32.2.3.	Methods for Determination of Degree of Hydrolysis .....	32.14	33.3.3. Applications of Concentration Cells.....	33.39
<i>Questions</i>	.....	32.17	<b>33.4.</b> Applications of <i>EMF</i> Measurements.....	33.40
<i>Objective Type</i>	.....	32.19	<b>33.5.</b> Electrochemical Cells—The Source of Energy .....	33.63
<i>Problems</i>	.....	32.20	33.5.1. Some Commonly Used Batteries .....	33.63
<i>Examination Questions</i>	.....	32.22	33.5.2. Fuel Cells .....	33.64
<b>33. Electromotive Force.....33.1</b>			<b>33.6.</b> Irreversible Electrode Processes.....	33.65
33.1.	Concept of Electrochemical Cells .....	33.1	33.6.1. Polarization .....	33.66
33.1.1.	Half Cells .....	33.1	33.6.2. Decomposition Potential.....	33.67
33.1.2.	Electrode Potential and Electrolytic Concentration:		33.6.3. Overvoltage.....	33.67
			33.6.4. Corrosion.....	33.75
			33.6.5. Passivity of Metals.....	33.79

33.6.6. Polarography .....	33.79	<i>Objective Type</i> .....	33.102
33.6.7. Amperometric Titrations.....	33.94	<i>Problems</i> .....	33.104
<i>Questions</i> .....	33.97	<i>Examination Questions</i> .....	33.105

## UNIT-VIII: STRUCTURE OF MOLECULES

<b>34. Physical Properties and Chemical Constitution .....</b>	<b>34.3</b>	34.4.4. Applications of Magnetic Susceptibilities .....	34.45
34.1. What are the Physical Properties .....	34.3	<i>Questions</i> .....	34.46
34.1.1. Four Classes of Physical Properties .....	34.3	<i>Objective Type</i> .....	34.48
34.1.2. Physical Properties and Chemical Constitution .....	34.4	<i>Problems</i> .....	34.49
34.1.3. Influence of Pressure and Temperature on Physical Properties .....	34.5	<i>Examination Questions</i> .....	34.51
34.2. Some Important Physical Properties Elucidating Molecular Structure.....	34.5	<b>35. Spectroscopy .....</b>	<b>35.1</b>
34.2.1. Molar Volumes.....	34.5	35.1. The Electromagnetic Spectrum .....	35.1
34.2.2. Parachor .....	34.6	35.1.1. Electromagnetic Radiations ...	35.1
34.2.3. Refractive Index.....	34.11	35.1.2. Different Regions in Electromagnetic Spectrum .....	35.3
34.2.4. Viscosity and Constitution ...	34.17	35.1.3. Absorption Spectroscopy .....	35.3
34.2.5. Optical Activity and Chemical Constitution .....	34.18	35.1.4. Molecular Energies .....	35.5
34.3. Electric Properties Elucidating the Molecular Structure .....	34.20	35.1.5. Measurement of the Amount of Light Absorbed .....	35.6
34.3.1. Dipole Moments.....	34.20	35.1.6. Mechanism of Interaction of Radiation with Materials.....	35.6
34.3.2. Electrical Polarization of Molecules.....	34.22	35.2. Molecular Spectra.....	35.8
34.3.3. Dipole Moments and Dielectric Constant.....	34.23	35.2.1. Molecular Rotation .....	35.9
34.3.4. Dielectric Polarization and Dielectric Constant.....	34.24	35.2.2. Types of Molecular Spectra ...	35.9
34.3.5. Determination of Dielectric Constant, $\epsilon_r$ .....	34.30	35.2.3. Rotational Spectra of Diatomic Molecules (Microwave Spectra)-Rigid Rotator.....	35.11
34.3.6. Determination of Dipole Moments .....	34.31	35.2.4. Vibrational Spectra (Near Infra-red Spectra).....	35.24
34.3.7. Molar Refraction and Molar Polarization : Dependence of Polarizability on Frequency ..	34.31	35.2.5. Simultaneous Rotation and Vibration in Molecules – Diatomic Vibrating Rotator .....	35.37
34.3.8. Bond Moments and the Molecular Dipole Moment.....	34.33	35.2.6. Electronic Spectra .....	35.48
34.3.9. Dipole Moments and Molecular Structure .....	34.35	35.2.7. Light Scattering and Raman Spectroscopy .....	35.53
34.3.10. Group Moments .....	34.36	35.2.8. Magnetic Resonance Spectroscopy .....	35.60
34.4. Magnetic Properties of Molecules.....	34.37	<i>Questions</i> .....	35.93
34.4.1. Magnetic Permeability .....	34.37	<i>Objective Type</i> .....	35.98
34.4.2. Theories of Diamagnetism and Paramagnetism .....	34.39	<i>Problems</i> .....	35.99
34.4.3. Measurement of Magnetic Susceptibility.....	34.44	<i>Examination Questions</i> .....	35.100
<b>36. Macromolecules .....</b>	<b>36.1</b>	<b>36.1. Macromolecules—A Class of Molecular Colloids.....</b>	<b>36.1</b>
36.1.1. Polymers—A Class of Macromolecules.....	36.1	36.1.2. Bio-polymers or Bio-colloids.....	36.10
36.1.3. Association Colloids .....	36.12		

---

36.2.	Macromolecules in Solutions .....	36.13	
36.2.1.	Molar Masses of Macromolecules.....	36.13	36.2.3. Stereochemistry of Macromolecules in Solution .36.39
36.2.2.	Determination of Molar Masses of Macromolecules.....	36.16	36.2.4. Functional Polymers .....36.47
	<i>Questions</i> .....		<i>Questions</i> .....36.52
	<i>Objective Type</i> .....		<i>Objective Type</i> .....36.53
	<i>Problems</i> .....		<i>Problems</i> .....36.54
	<i>Examination Questions</i> .....		<i>Examination Questions</i> .....36.55

---

## UNIT-IX: THERMODYNAMICS-II

---

<b>37.</b>	<b>Irreversible Thermodynamics.....</b>	<b>37.3</b>	<b>38.</b>	<b>Statistical Thermodynamics .....</b>	<b>38.1</b>
37.1.	From the Equilibrium to the Non-Equilibrium Thermodynamics.....	37.3	38.1.	From Microscopic Properties to Macroscopic Properties .....	38.1
37.1.1.	Thermodynamic-Phenomenological Theory of Irreversible Processes .....	37.4	38.1.1.	Statistical Mechanics: Postulates .....	38.2
37.1.2.	Looking Back to Look Forward : Fundamentals of Thermodynamics.....	37.4	38.1.2.	Statistical Probability .....	38.2
37.2.	Laws of Thermodynamics .....	37.5	38.1.3.	Phase Space.....	38.3
37.2.1.	Energy and Heat (First Law of Thermodynamics) .....	37.5	38.1.4.	What do the Microstate and Macrostate Tell us? .....	38.4
37.2.2.	Entropy and Absolute Temperature (Second Law of Thermodynamics) .....	37.10	38.1.5.	System, Assembly and Ensemble.....	38.4
37.3.	Equilibrium and Stationary States .....	37.21	38.1.6.	Liouville's Theorem.....	38.6
37.3.1.	Equilibrium in Homogeneous Systems .....	37.23	38.1.7.	Statistical Equilibrium .....	38.9
37.3.2.	Equilibrium in Heterogeneous Systems .....	37.24	38.1.8.	Entropy and Probability .....	38.9
37.3.3.	Equilibrium in Continuous Systems .....	37.25	38.1.9.	Entropy is a Function of the Probability of the Thermodynamic State .....	38.10
37.4.	From the Equilibrium to the Non-Equilibrium States .....	37.27	38.2.	Distribution of Particles Among Energy States .....	38.12
37.4.1.	Conservation of Energy in Open System .....	37.29	38.2.1.	Classical Distribution Law : Maxwell-Boltzmann Statistics .....	38.12
37.4.2.	Entropy Flow and Entropy Production in Open Systems...37.31		38.2.2.	Partition Functions and Thermodynamic Functions ...38.31	
37.4.3.	Phenomenological Equations.....	37.35	38.2.3.	Solved Problems .....	38.41
37.4.4.	Entropy Production due to Diffusion in Systems at Uniform Temperature.....	37.43	38.3.	Looking Back to Look Forward : Quantum Statistics.....	38.43
37.4.5.	Entropy Production due to Diffusion in Systems at Non-uniform Temperature ....	37.45	38.3.1.	Bose-Einstein Statistics.....	38.44
37.4.6.	Entropy Production due to Viscosity.....	37.47	38.3.2.	Fermi-Dirac Statistics .....	38.51
37.4.7.	Electrokinetic Effects.....	37.48	38.3.3.	Comparison Amongst Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac Statistics .....	38.62
	<i>Questions</i> .....	37.51	38.3.4.	Solved Problems .....	38.63
	<i>Examination Questions</i> .....	37.53		<i>Questions</i> .....	38.64
				<i>Objective Type</i> .....	38.68
				<i>Problems</i> .....	38.70
				<i>Examination Questions</i> .....	38.71
			<b>APPENDIX</b>	<b>..... A.1-A.6</b>	
			<b>INDEX</b>	<b>.....</b>	

## **Salient Features of the Revised Edition of the Book**

- The Book incorporates the New Education Policy/CBCS guidelines.
- The entire subject matter has been presented with proper sub-headings to facilitate readers to understand the subject matter in a more systematic manner.
- SI units are used throughout.
- In few chapters, some subject materials have been added catering to the need of M. Sc. Syllabi.
- Simple, systematic and logical development of the subject with emphasis on the underlying fundamental concepts, principles and applications are the attractive aspects of the Book.
- A number of solved examples well integrated into the body of the text has been included which will give the students manifold opportunities to understand the topics being presented.
- Various questions and numerical (include by objective type and multiple question type) that are set in the Examination of B.Sc., M.Sc. or competitive courses have been given at the end of each chapter.
- Inclusion of a new type of Question Banks has been made.
- The book has been thoroughly revised and imparted a new look.



**Sultan Chand & Sons**  
*Publishers of Standard Educational Textbooks*  
23 Daryaganj, New Delhi-110002  
Phones : 011-23281876, 23277843, 23266105  
Email : sultanchand74@yahoo.com  
info@sultanchandsons.com  
Website : sultanchandsons.com



TC-634



9 788180 545870