# TEXTBOOK OF PHYSICAL CHEMISTRY



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

## 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 main points side by side. Sentences printed in italics or bold type require for particular attention. Your reading should not be passive, but active and critical. 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 ask 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 cannot 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 day 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

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**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 (NEP-2020)/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 cooperation 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 *Textbook of Physical Chemistry*.

#### 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 20.32.
- 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 dealth 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 oder 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 state 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 1,000 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.

## **Contents**

#### PART-I UNIT-I: CHEMICAL PRINCIPLES

1.	Intr	oduction	1.3
	1.1.	Physical Chemistry	1.3
		1.1.1. Importance of Physical Chemist	
	1.2.	Symbols and Units	
		1.2.1. Derived Physical Quantities and	
		Units	
		1.2.2. Prefixes for SI Units	1.5
		Questions	1.8
2.	Stru	ucture of Atom	2.1
	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	
		2.3.2. Effective Radius of the Nucleus.	
	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	
	2.6.	Nature of Electromagnetic Radiations	
	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	2.10.	The Bohr-Sommerfeld Theory	
		Questions	
		Objective Type	
		Problems	
		Examination Questions	2.20
3.	Stru	ucture of Atom	
	(Mo	odern Picture)	3.1
	3.1.	Wave Particle Dualism of Radiation	
		3.1.1. Photoelectric Effect	
	32	Compton Effect or Compton Scattering	

3.2.	Compton Effect or Compton Scattering3.3
3.3.	Wave-Particle Dualism of Matter-De Broglie
	Wave equation

	3.3.1.	Experimental Proof of de Broglie's
		Equation
	3.3.2.	De Broglie (Matter) Waves and
		Electromagnetic Waves
3.4.	The Ur	certainty Principle
3.5.		Im Mechanical Model of Atom
	3.5.1.	Quantum Mechanical Operators3.9
	3.5.2.	Schrodinger Wave Equation3.24
	3.5.3.	Solution of Schrodinger Wave
		Equation
3.6.		hrodinger Equation for
		gen Atom3.38
3.7.		ility and Electron Density —
		zing the Orbitals
3.8.		Im Numbers
	3.8.1.	Significance of Quantum
		Numbers
	3.8.2.	Principal Quantum Number (n)3.43
	3.8.3.	Subsidiary Quantum Numbers or
		Azimuthal Quantum Number3.44
	3.8.4.	Magnetic Quantum Number
		$(m \text{ or } m_l)$
	3.8.5.	The Spin Quantum Numbers $(m_s)$ 3.44
3.9.		Distribution Functions and
		Probability Distribution Curves3.46
3.10.		umber of Electrons in a Given
		- Pauli's Exclusion Principle
3.11.		Electron Atoms
3.12.		ation of Orbitals by Electrons —
		Principle
	3.12.1.	
	2 1 2 2	Configuration of Atoms
		Exception to the Rule
2 1 2		Violation of Aufbau Principle3.52
3.13.		Rule of Maximum Multiplicity
3.14.	3.13.1.	1
3.14.		of Stability of Half-filled and etely-filled Energy Levels
3.15.		tation
5.15.	3.15.1.	
	5.15.1.	Distribution
	Quarti	Distribution
		<i>ive Type</i> 3.57
		<i>we type</i>
		<i>ms</i>
	Examii	<i>iation Questions</i>

4.1. Historical Background	.4.1
T.1. IIISIOIICAI DACKEIOUIIU	4.1
4.1.1. Mendeleev's Periodic Table	4.1
4.2. Modern Periodic Law	4.2
4.2.1. Periodic Law and Electronic	
Configuration of Elements	4.2
4.3. Modern Periodic Table	4.3
4.3.1. Superiority of the Modern Periodi	c
Table	4.4
4.4. Periodic Variation of Properties of	
Elements	
4.5. Size of Atoms and Ions	4.6
4.5.1. The Crystal Radius	
(atomic or metallic radius)	4.6
4.5.2. The Van der Waal's Radius	
(collision radius)	4.7
4.5.3. Covalent Radius	
4.5.4. The Ionic Radius	
4.5.5. The Bragg-Slater Atomic Radius.	
4.5.6. Atomic Volumes	4.9
4.6. Ionization Energy	4.9
4.6.1. Factors on which Ionization	
Energy Depends	.4.10
4.6.2. The Variation of Ionization	
Energies with Increase in	
Atomic Number	412
4.7. Electron Affinity	.4.12
<ul><li>4.7. Electron Affinity</li><li>4.8. Electronegativity (X)</li></ul>	.4.12
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (<i>X</i>)</li> <li>4.8.1. Pauling Scale of</li> </ul>	.4.12 .4.13
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (X)</li> <li>4.8.1. Pauling Scale of Electronegativity</li> </ul>	.4.12 .4.13
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (<i>X</i>)</li> <li>4.8.1. Pauling Scale of Electronegativity</li> <li>4.8.2. Mulliken Scale of</li> </ul>	.4.12 .4.13 .4.14
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (<i>X</i>)</li> <li>4.8.1. Pauling Scale of Electronegativity</li> <li>4.8.2. Mulliken Scale of Electronegativity</li> </ul>	.4.12 .4.13 .4.14
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (X)</li> <li>4.8.1. Pauling Scale of Electronegativity</li> <li>4.8.2. Mulliken Scale of Electronegativity</li> <li>4.8.3. Allred and Rochow Scale of</li> </ul>	.4.12 .4.13 .4.14 .4.14
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (X)</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (X)</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (χ)</li> <li>4.8.1. Pauling Scale of Electronegativity</li> <li>4.8.2. Mulliken Scale of Electronegativity</li> <li>4.8.3. Allred and Rochow Scale of Electronegativity</li> <li>4.9. Metallic Character</li> <li>4.10. Density, Melting Point and Boiling</li> </ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (χ)</li> <li>4.8.1. Pauling Scale of Electronegativity</li> <li>4.8.2. Mulliken Scale of Electronegativity</li> <li>4.8.3. Allred and Rochow Scale of Electronegativity</li> <li>4.9. Metallic Character</li> <li>4.10. Density, Melting Point and Boiling Point</li> </ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15 .4.15
<ul> <li>4.7. Electron Affinity</li> <li>4.8. Electronegativity (X)</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15 .4.15 .4.17
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.17 .4.20
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.17 .4.20 .4.21
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.17 .4.20 .4.21
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.15 .4.17 .4.20 .4.21 .4.22
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.17 .4.20 .4.21 .4.22 .5.1
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.17 .4.20 .4.21 .4.22 .5.1 5.1
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.15 .4.20 .4.21 .4.22 <b>.5.1</b> 5.1
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.17 .4.20 .4.21 .4.22 <b>.5.1</b> 5.1 5.2
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.17 .4.20 .4.21 .4.22 <b>.5.1</b> 5.1 5.2 5.2
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.15 .4.17 .4.20 .4.21 .4.22 <b>.5.1</b> 5.1 5.2 5.2 5.3 5.3
<ul> <li>4.7. Electron Affinity</li></ul>	.4.12 .4.13 .4.14 .4.14 .4.14 .4.14 .4.15 .4.15 .4.15 .4.15 .4.17 .4.20 .4.21 .4.22 .5.1 5.1 5.2 5.3 5.3 5.6

	5.6.1.	Nuclear Binding Energy Theory5.7
	5.6.2.	Meson Theory of Nuclear Forces5.7
	5.6.3.	Nuclear Fluid Theory5.8
5.7.	Isotope	5
	5.7.1.	The Detection and Study of
		Isotopes
5.8.	Isotopic	Constitution of Elements5.10
5.9.	Separat	ion of Isotopes5.12
	5.9.1.	Gaseous Diffusion Method5.12
	5.9.2.	Electromagnetic Method5.13
	5.9.3.	Thermal-Diffusion Method or
		Soret's Method5.13
	5.9.4.	Distillation Method5.14
	5.9.5.	The Centrifugal Method5.14
	5.9.6.	Electrolytic Method5.14
	5.9.7.	Chemical-exchange Method5.14
5.10.	The Wh	ole-Number Rule and
		Fraction5.15
5.11.		Weights
	5.11.1.	Deviation of Atomic Weights
		from Whole Numbers
	5.11.2.	Some Conclusions from the
		Study of Isotopes5.16
5.12.Isob	ars, Isoto	ones and Isomers
		<i>ns</i> 5.18
		<i>ve Type</i> 5.18
		<i>e Choice Type</i> 5.18
	Problem	<i>ns</i>
	Examin	ation Questions5.20
6. Rad	lioactiv	/ity and Nuclear
Trar	nsform	ation6.1
6.1.	Discove	ery of Radioactivity6.1
6.2.	Nature	of Radiations from Radioactive
	Substan	
	6.2.1.	Alpha Particles6.1
	6.2.2.	Beta Particles6.2
	6.2.3.	Gamma Rays6.2
	6.2.4.	Detection of Radioactivity6.3
6.3.		Reactions and Nuclear Equations6.3
6.4.	Classifi	cation of Nuclear Reactions6.5

6.4.1. Those Induced by Protons......6.6

Emit Radiation? ......6.7

Measurement......6.7

6.4.2.

6.4.3.

6.5. Measurement of Activity of

6.5.1. Unit of Radioactivity

6.6. Why do Radioactive Substances

6.7.	Modes of Decay	6.8
	6.7.1. Alpha Particle Emission	
	6.7.2. Beta Particle Emission	
6.8.	Group Displacement Law	6.9
6.9.	Rate of Disintegration	
	(Law of Radioactive Decay)	6.11
	6.9.1. Half-life Period	
	6.9.2. Average Life Period	6.13
	6.9.3. Radioactive Equilibrium	6.14
6.10.	Radioactive Disintegration Series	6.14
	6.10.1. The Geiger-Nuttal Rule	6.16
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	
6.14.	Nuclear Fusion	
	6.14.1. Hydrogen Bomb	
6.15.	Hazards of Radiations	
6.16.	Applications of Radioisotopes	
6.17.	The Synthetic Elements	
6.18.	Nuclear Coulombic Barrier	
6.19.	Radiation Chemistry	
	6.19.1. Radiolysis of Water	
	Questions	
	Objective Type	
	Problems	
	Examination Questions	6.36
7. Che	emical Bonding (i)—	
	ssical Approach	7.1
7.1.	Introduction	
7.2.	Why are Chemical Bonds Formed?	
,	7.2.1. The Lewis and Langmuir Con	

/.1
7.1
7.2
7.2
7.2
7.4
7.4
7.5
7.6
7.7
7.8
7.8
7.8

7.9.	Polarity of Bonds7.9
7.10.	Characteristics of Covalent Compounds7.11
7.11.	Fajan's Rules
7.11.	Deviations from the Octet Rule
7.12.	Molecular Geometry
7.15.	•
<b>-</b> 14	(The VSEPR Theory)7.14
7.14.	Electron Pair Donation or
	Coordinate Valence7.16
7.15.	The Hydrogen Bond7.18
7.16.	The Van der Waals Attraction7.19
	<i>Questions</i> 7.20
	Objective Type7.22
	<i>Problems</i> 7.26
	ory of Chemical Bonding (ii)—
Мо	dern Aproach8.1
8.1.	Introduction
8.2.	The Valence Bond Approach
8.3.	Energy Changes During Bond Formation8.2
0.5.	8.3.1. The Wave Mechanical Explanation
0.4	of Energy Changes
8.4.	Sigma and Pi Bonds
8.5.	Hybridization of Orbitals
	8.5.1. <i>sp</i> -Hybridization8.6
	8.5.2. $sp^2$ -Hybridization
	8.5.3. <i>sp</i> <sup>3</sup> -Hybridization8.7
	8.5.4. $sp^3d$ -Hybridization8.10
	8.5.5. $sp^3d^2$ -Hybridisation8.11
	8.5.6. Hybridization and Shapes of
	Some Simple Molecules8.12
8.6.	Bond Lengths
	8.6.1. Correlation of Bond Distances
	and Hybridization8.15
8.7.	Bond Dissociation Energy (D)8.16
8.8.	Resonance – A Modification of the
	Valence Bond Concept8.16
	8.8.1. Electron Delocalization8.18
8.9.	Molecular Orbital Theory8.19
	8.9.1. Bonding and Antibonding
	Orbitals8.19
	8.9.2. Linear Combination of
	Atomic Orbitals (LCAO)8.19
	8.9.3. Combination of <i>s</i> Orbitals8.22
	8.9.4. Combination of <i>p</i> Orbitals8.22
8.10.	Energy Diagrams for Molecular Orbitals
	(in cases when $2s$ and $2p_z$ Orbitals have
	Energies that are not closer)8.23
	8.10.1. M.O. Diagram of Fluorine
	8.10.2. M.O. Diagram of Oxygen
8.11.	Energy Diagrams for M.O.'s
	(in case of Molecules Consisting of
	Elements in which $2s$ and $2p$ Orbitals lie
	Close to each other)
	51555 to each other)

	8.11.1.	M.O. Diagram of N <sub>2</sub>	8.26
		M.O. Diagrams of some simple	
		Diatomic Molecules	8.26
	8.11.3.	M.O. Diagram of Helium	8.27
	8.11.4.	Electronic Configuration of	
		Diatomic Molecules	8.27
8.12.	Relation	nship between Electronic	
	Configu	ration and Molecular Behaviour	8.28
	8.12.1.	Bond Order	8.28
8.13.	M.O. D	iagrams of	
	Heteror	nuclear 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, HF8.32
8.14.	Comparative Study of VB and
	MO Theories
8.15.	Metallic Bond8.33
	8.15.1. Electron Sea Model8.33
	8.15.2. Resonance Theory8.33
	8.15.3. The Molecular Orbital Theory8.34
8.16.	Summary of the Three Main
	Types of Bonds8.35
	Questions
	Objective Type8.37
	Examination Questions8.40
	Appendix to Unit I8.43

#### **UNIT-II: STATES OF MATTER**

9.	The	Gased	ous State9.3
	9.1.	The Gas	seous State9.3
	9.2.	Gas Lav	ws9.3
		9.2.1.	Boyle's Law9.3
		9.2.2.	Charles' Law9.3
		9.2.3.	Avogadro's Law9.4
	9.3.	Ideal Ga	as Law or the Gas Equation
		9.3.1.	Nature of Gas Constant9.6
		9.3.2.	Numerical Value of R9.6
		9.3.3.	Effusion and Diffusion9.7
		9.3.4.	Dalton's Law of Partial Pressure9.9
	9.4.	Kinetic	Theory of Gases9.10
		9.4.1.	Postulates of Kinetic Theory
			of Gases9.11
		9.4.2.	Validity of the Postulates of the
			Kinetic Theory of Gases9.11
	9.5.	Distribu	tion of Molecular Speeds
		9.5.1.	Maxwell-Boltzmann Law of
			Distribution of Molecular
			Velocities
		9.5.2.	Calculation of Molecular Velocities
			of Gaseous Molecules9.14
		9.5.3.	Average Velocity9.14
		9.5.4.	Most Probable Velocity9.15
		9.5.5.	Root Mean Square Velocity
			(RMS Velocity)9.16
	9.6.	Kinetic	Equation for Gases9.18
	9.7.	Derivat	ion of the Gas Laws from
		Kinetic	Equation9.20
		9.7.1.	Boyle's Law9.20
		9.7.2.	Charles's Law9.20

	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.	Collisic	on Diameter, Mean Free Path and	
	Collisic	on Number	9.26
	9.8.1.	Collision Number (Z <sub>1</sub> )	9.26
	9.8.2.		
9.9.	Collisic	on Frequency	9.29
9.10.	Collisic	ons in a Mixture of Gases	9.29
9.11.	The Ba	rometric Formula	9.32
9.12.	Viscosi	ty 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	s 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.	Princip	le of Equipartition of Energies	9.39
9.15.	Specific	e Heats and Molar Heats of	
	Gases		9.40
	9.15.1.	Molar Heats of Gases and	
		Kinetic Theory	9.41
	9.15.2.		
		and its Variance with Molar	
		Complexity	9.42
		1	

	9.	.15.3.	Comparison of Theoretical
			and Experimental Heat
			Capacity Values9.43
	Q	uestio	<i>ns</i> 9.45
			ve Type9.46
	P	roblen	<i>ıs</i> 9.48
	E	xamin	ation Questions9.49
10	Poal	Gas	es10.1
10.	10.1.		luction—Ideal and Real Gases10.1
	10.1.		tion from Ideal Behaviour10.1
	10.2.	10.2.	
		10.2.	Behaviour10.1
		10.2.2	
		10.2.2	Law10.1
		10.2.3	
			Gay-Lussac's Law10.2
		10.2.4	-
			Law10.2
	10.3.	The C	Cause of Deviations of Real Gases
		from	Ideal Behaviour10.2
	10.4.	Van d	er Waals' Equation10.4
		10.4.	I. Nature of Van der Waals'
			Constant10.5
	10.5.		nation of Real Gas Behaviour
			n der Waals' Equation10.7
	10.6.		lation of Boyle Temperature10.9
	10.7.		ation of the Van der Waals'
		<u>^</u>	ion
		10.7.1	1
		10.7.2	e
		10.7.3	Virial Equations10.12 Berthelot Equations10.12
		10.7.	
		10.7.	
		10.7.	of State10.12
	10.8.	Relat	ive Molecular Mass Values in
		10.8.1	
			Determination of Molecular
			Mass of Gases10.14
	10.9.	Critic	al Phenomena10.15
		10.9.	1. Experimental Measurement
			of the Critical Constants
			of a Gas10.16
		10.9.2	
		10.0	Andrews' Experiments10.17
		10.9.3	1
	10.10	0.1	and Critical State10.18
			lation of Critical Constants
	10.11.		of Corresponding States and
		Reau	ced Equation of State10.21

		10.11.1. Importance of the Law of
		Corresponding States10.23
	10.12.	Liquefaction of Gases—
		Introductory and Historical10.23
		10.12.1. Methods of
		Liquefaction of Gases10.24
		10.12.2. Uses of Liquefied and
		Compressed Gases10.26
		Questions10.26
		$\tilde{O}$ <i>bjective Type</i> 10.28
		Problems
		Examination Questions10.31
		2
11.	Prop	erties of Liquids11.1
	11.1.	The Liquid State
	11.2.	The Intermolecular Forces
	11.2.	The Structures of Liquid11.3
	11.4.	General Properties of Liquids11.3
	11.5.	Evaporation
	11.5.	Vapour Pressure
	11.0.	Measurement of Vapour Pressure
	11.7.	Boiling Point
	11.8.	Freezing Point
	11.9.	6
		Measurement of Surface Tension
		Parachor
		Viscosity and Fluidity
		Measurement of Viscosity
		Factors Affecting Viscosity
		Viscosity in Everyday Life
		Viscosity and Constitution
	11.18.	Optical Activity
		Questions
		Objective Type
		<i>Problems</i>
		Examination Questions11.31
12	The	Solid State12.1
12.	12.1.	
		Introduction
	12.2.	
	12.3.	Structure of Crystals
	12.4.	Crystal Systems
	12.5.	Lattice Planes and their Designation12.7
	12.6.	Symmetry in Crystals
	12.7.	Crystallography
	12.8.	X-ray Diffraction and Crystal
	10.0	Structure
	12.9.	Determination of Crystal Structure12.16
	12.10.	Indexing of Planes and Structure of

NaCl and KCl.....12.18

Formula and Density of Solids.....12.20

12.11. Number of Atoms per Unit Cell,

xi

12.12.	Packing of	of Constituent Particles in
	Crystals	
12.13.	Types of	Three-dimensional Packing 12.25
12.14.	Packing of	of Crystals and
	Coordina	tion Number12.26
12.15.	Structure	of Simple Ionic Compounds–
	Close Pac	cked Arrangements12.27
	12.15.1.	Ionic Compounds of the
		Types AX <sub>1</sub> 12.28
	12.15.2.	Ionic Compounds of the
		Type AX <sub>2</sub>
	12.15.3.	Limiting Radius Ratio and the
		Geometry of the Crystal12.30
12.16.	Lattice Er	nergy12.30

12.17. Void Space in Closed Packing of
Spheres12.32
12.18. Types of Crystals12.34
12.19. Imperfections or Defects in Solids12.37
12.20. Properties of Solids12.40
12.21. Superconductivity12.42
12.22. Amorphous Solids
12.23. Liquid Crystals
12.24. Polymorphism
12.24.1. Types of Allotropy
(Transition Temperature)12.46
Questions12.47
Objective Type12.48
Problems
Examination Questions12.51
-

#### **UNIT-III: THERMODYNAMICS-I**

13.	Intro	oduction to Chemical		
	Thermodynamics13.3			
	13.1.	Introduction		
	13.2.	Thermodynamic Variables or		
		State Variables		
	13.3.	State Functions and Path Functions13.5		
	13.4.	Thermal Equilibrium13.6		
		13.4.1. Quasiequilibrium Process13.6		
	13.5.	Zeroth Law of Thermodynamics13.6		
		13.5.1. Derivation of the Zeroth Law		
		of Thermodynamics13.7		
	13.6.	Thermodynamic Process13.8		
	13.7.	Exact and Inexact Differentials13.10		
	13.8.	More Properties of Exact		
		Differentials13.12		
		<i>Exercise</i> 13.16		
		Questions13.16		
		Objective Type13.17		
		Problems13.18		
		Examination Questions13.18		
14.	The	First Law of Thermodyamics14.1		
	14.1.	Work and Heat14.1		
	14.2.	First Law of Thermodynamics14.2		
	14.3.	Work done in Isothermal and Adiabatic		
		Changes14.4		
	14.4.	Heat Content or Enthalpy14.4		
	14.5.	Molar Heat at Constant Volume C <sub>y</sub> 14.5		
	14.6.	Thermodynamic Changes in Compression		
		and Expansion of an Ideal Gas14.8		
	14.7.	Work done on the System in Reversible		
		Adiabatic Compression of Ideal		
		Gases14.10		

14.8.	Comparison of Work done in
	Adiabatic Reversible and Isothermal
	Reversible Expansion of an Ideal
	Gas14.13
14.9.	The Joule-Thomson Effect14.21
	<i>Questions</i> 14.24
	Objective Type14.25
	<i>Problems</i> 14.26
	Examination Questions14.27
The	rmochemistry15.1
	Introduction15.1
	Conventions used in Thermochemistry15.1
10.0.	15.3.1. Measurement of
	Enthalpy of Reaction
	15.3.2. Relation of Enthalpy of
	Reaction to Physical
	Conditions
15.4.	Variation of $\Delta H$ with Temperature —
10111	Kirchhoffs Equation
15.5	Relation between Heat of Reaction at
	Constant Pressure ( $\Delta H$ ) and at
	Constant Volume ( $\Delta U$ )
15.6.	Enthalpy of Combustion15.8
	15.6.1. Experimental Determination
	of Enthalpy of Combustion
	(Δ <i>H</i> )15.8
15.7.	Enthalpy of Formation15.10
15.8.	Enthalpy of Solution15.12
	15.8.1. Integral Enthalpy of
	Solution15.12
	15.8.2. Differential Enthalpy of
	Dilution and Solution15.13
	<ul> <li>14.9.</li> <li><b>Thei</b></li> <li>15.1.</li> <li>15.2.</li> <li>15.3.</li> <li>15.4.</li> <li>15.5.</li> <li>15.6.</li> <li>15.7.</li> </ul>

		15.8.3. Enthalpy of Formation of
		Ions15.13
		15.8.4. Experimental Determination
		of Enthalpy of Solution15.14
	15.9.	Enthalpy of Neutralization
	15.7.	15.9.1. Experimental Determination of
	15 10	Enthalpy of Neutralization15.15
		Enthalpy of Hydration15.17
		Enthalpy of Transition15.17
		Thermochemical Laws15.17
	15.13.	Bond Dissociation Enthalpies15.21
		<i>Questions</i> 15.24
		<i>Objective Type</i> 15.25
		<i>Problems</i> 15.26
		Examination Questions15.28
16.		Second Law of
	Ther	modynamics16.1
	16.1.	Spontaneous or Natural Processes
	16.2.	Limitations of First Law of
		Thermodynamics16.1
	16.3.	Second Law of Thermodynamics16.2
	16.4.	Conversion of Heat into Work
	10.1.	(the Carnot Cycle)
	16.5.	Refrigerators
	16.6.	Carnot Theorems
	16.7.	
		Kelvin Scale of Temperature
	16.8.	Entropy and Carnot Cycle
	16.9.	Entropy Change of the Universe in
		Reversible Processes
		Entropy – A Measure of Disorder16.14
		Entropy Calculations16.17
	16.12.	Free Energy16.19
	16.13.	Condition of Equilibrium and
		Spontaneous Change16.20
	16.14.	Variation in $\Delta H$ and $\Delta S$ and the
		Spontaneity or Equilibrium of a
		Reaction or Process16.21
	16.15.	Change in Standard Free Energy
		$(\Delta G^{\circ})$ of the Reactions
	16 16	The Helmholtz Function
	10.10.	(Work Function)
	16 17	The Maxwell Equations
		Thermodynamic Equation of State16.29
	16.10	The Joule – Thomson Inversion Temperature
	10.19.	
	16.00	Cibbs Halashaltz Exactions
		Gibbs-Helmholtz Equations
	16.21.	Free Energy Changes in Chemical Reaction
		- Van't Hoff Isotherm16.35
	16.22.	Thermodynamic Equation for Open Systems
		– Partial Molar Quantities16.36
	16.23.	Partial Molal Free Energy or Chemical
		Potential

16.24. Clapeyron – Clausius Equation
16.25. Variation of Chemical Potential with
Temperature
16.26. Chemical Potential of an Ideal Gas16.42
16.27. Free Energy of Mixture16.43
16.28. Gibbs-Duhem Equation16.43
16.29. Chemical Potential of Solvent in
Binary Ideal Liquid Solution16.44
16.30. The Application of Chemical
Potential16.45
<i>Questions</i> 16.45
$\widetilde{O}$ bjective Type16.46
<i>Problems</i>
Examination Questions16.50
17. The Third Law of
Thermodynamics17.1

#### 17.

	Ther	modynamics17.1
	17.1.	Entropy at the Absolute Zero17.1
	17.2.	Development of Third Law17.4
	17.3.	Unattainability of Absolute Zero17.5
	17.4.	Thermodynamic Properties at
		Absolute Zero17.5
	17.5.	Tables of Entropies at 298 K17.6
	17.6.	Exceptions to the Third Law :
		The Concept of Residual Entropy17.9
	17.7.	Molecular Basis of Residual Entropy17.9
		Questions
		Objective Type17.11
		Problems
		Examination Questions17.12
10	Char	nical Equilibrium18.1
10.		
	18.1.	Rate of Reaction
	18.2.	Factors which Affect the Rate of a
	10.2	Reaction
	18.3.	Reversible Reactions
	18.4.	The Equilibrium
	18.5.	Stable and Metastable Equilibrium
	18.6.	Criteria of Equilibrium
	18.7.	Law of Mass Action
	18.8.	The Equilibrium Constant
	18.9.	Activity
	18.10.	0,
	18.11.	Free Energy and Chemical
	10 10	Equilibrium
	18.12.	Standard Free Energy and
	10 12	Equilibrium Constant
		Relationship between $K_c$ , $K_p$ and $K_x$ ,18.13
	18.14.	Variation of Equilibrium Constant with
	10.15	Temperature, the Reaction Isochore18.15
		Usefulness of the Equilibrium Constant18.16
	18.16.	Experimental Determination of
		Equilibrium Constants18.17

		Gaseous Reactions of Type I18.17
	18.18.	Gaseous Reactions of Type II18.19
	18.19.	Calculation of the Degree of
		Dissociation from the Vapour
		Density Measurements
	18.20.	Homogeneous Equilibria in
		Liquid State
		Heterogeneous Equilibria18.23
	18.22.	Le Chatelier Principle18.24
	18.23.	Effect of Addition of Inert Gas18.25
		<i>Questions</i>
		Objective Type18.28
		Problems
		Examination Questions
19.	Nern	st Distribution Law19.1
	19.1.	Nernst Distribution Law19.1
	19.2.	Thermodynamics of Solutions19.1
	19.3.	Thermodynamical Derivation of
		Distribution Law19.4
	19.4.	Calculation of the Partition
		Coefficient
	19.5.	Deviation from Distribution Law due
		to Molecular Complexity19.6
	19.6.	Other Limitations of Distribution
		Law19.10
	19.7.	Applications of Distribution Law19.11
	19.8.	Extraction of Substances from
		Solutions19.12
	19.9.	Distribution Law and Henry's Law19.15
		Questions19.15
		$\tilde{O}$ <i>bjective Type</i>
		Problems
		Examination Questions19.19

20.	The	Phase Rule	.20.1
	20.1.	Equilibrium between Phases	20.1
	20.2.	Definitions of Terms Used	
	20.3.	Phase Rule	
	20.4.	Phase Diagrams	
	20.5.	The Water System:	
		A One-component System	20.4
	20.6.	The Carbon Dioxide System	
	20.7.	The Sulphur System (One-Component	
		System Showing Solid-solid	
		Transformations)	20.8
	20.8.	Two-Component System	.20.12
	20.9.	Types of Two-Component Systems inv	olving
		Solid-Liquid Equilibrium	.20.12
	20.10.		
	20.11.	Potassium Iodide-Water System	.20.14
		Freezing Point Diagram with	
		Compound Formation	.20.15
	20.13.	Ferric Chloride-Water System	.20.16
	20.14.	Applications of Eutectics	.20.18
	20.15.	Systems Involving Formation of	
		Compounds with Incongruent	
		Melting Points ( <i>i.e.</i> , showing Peritectic	
		Change)	.20.18
	20.16.	Sodium Chloride-Water System	
		Sodium Sulphate-Water System	
		Gas-Solid Equilibria—	
		Salt Hydrate System	.20.24
		Solved Problems	
		Questions	.20.28
		<i>C</i> <i>Objective Type</i>	
		Examination Question	
		~	

#### PART-II UNIT-IV: SOLUTIONS

#### 21. Solutions.....21.3

21.1.	Solution	-A Homogeneous Mixture21.3
	21.1.1.	Solvent and Solute
	21.1.2.	Solution
21.2.	Why do	Substances Dissolve?21.4
	21.2.1.	Temperature and Solubility21.4
	21.2.2.	Why does a Substance have
		Different Solubilities in
		Different Solvents?21.4
	21.2.3.	Solubility of
		Gases in Liquids21.5
21.3.	Compos	ition of Solutions21.5
		Solutions
	(Solution	n of Gas in Gas)21.8

	21.4.1.	Solutions of Gases in Liquids21.9
	21.4.2.	How the Solubility of a
		Gas is Measured21.11
21.5.	The Ideal	Solutions21.12
	21.5.1.	Raoult's Law of
		Ideal Solutions21.12
	21.5.2.	Solutions of
		Liquids in Liquids21.13
	21.5.3.	Miscible Liquids21.13
	21.5.4.	Boiling Point-Composition
		Curves
	21.5.5.	Relation between the Mole-
		fractions of the Components in
		the Liquid and Vapour Phases.21.14

#### Contents

	21.5.6.	Ideal Solution in
		Terms of Activity21.15
21.6.		l Solutions:
		Coefficients21.16
21.7.		ynamics of Ideal Solutions21.17
	21.7.1.	Gibbs Free Energy Change
		of Mixing ( $\Delta G_{\text{mix}}$ )21.17
	21.7.2.	Enthalpy Change of Mixing
		$(\Delta H_{\rm mix})$
	21.7.3.	Volume Change of Mixing
		$(\Delta V_{\rm mix})$
	21.7.4.	Entropy Change of Mixing
		$(\Delta S_{\rm mix})$
	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
	21.7.7.	Application of Gibbs-Duhem-
		Margules Equation to
<b>01</b> 0	<b>T</b>	Non-ideal Solutions
21.8.	•	f Fractional Distillation21.22
	21.8.1.	Fractional Distillation of
	21.0.2	Liquid Pairs of Type I21.23
	21.8.2.	Fractional Distillation in
	21.0.2	Industry
	21.8.3.	Fractional Distillation of
	21.0.4	Non-ideal Solutions
	21.8.4.	Fractional Distillation of
		Liquid Pairs of Type II
	21.05	( <i>Minimum B.P. Mixtures</i> )21.24
	21.8.5.	Fractional Distillation of Liquid pairs of Type III
		(Maximum B.P. Mixtures)21.25
	21.8.6.	Azeotropic Distillation21.25
	21.8.0.	The Nature of Azeotropic
	21.0.7.	Mixtures
21.9.	Partially	Miscible Liquids21.26
21.).	21.9.1.	Critical Solution Temperature
	21.9.1.	(C.S.T.)
	21.9.2.	Mixtures with Lower
		C.S.T
	21.9.3.	Mixtures with both Lower
		and Upper C.S.T.s
21.10.	Complete	ly Immiscible Liquids
	-	of Solids in Liquids21.30

21.12.	Solid Sol	utions21.30
		<i>ns</i> 21.31
		ve Type21.32
		<i>is</i> 21.33
		ation Questions21.34
Theo	orv of D	ilute Solutions22.1
22.1.	-	ve Properties of
22.1.	-	lutions22.1
	22.1.1.	What Happens when the
	22.1.1.	Solute Undergoes
		Dissociation
	22.1.2.	What Happens when the
		Solute Undergoes
		Association
22.2.	Relative	Lowering of
		ressure
	22.2.1.	Raoult's Law of Relative
		Lowering of Vapour Pressure22.3
	22.2.2.	Relative Lowering of Vapour
		Pressure and Molality of the
		Solution22.4
	22.2.3.	Molecular Mass of Solute from
		Relative Lowering of Vapour
		Pressure
	22.2.4.	Thermodynamic Derivation of
		Relative Lowering of Vapour
		Pressure
22.3.		
	22.3.1.	Preparation of Semi-permeable
	22.2.2	Membrane
	22.3.2.	Semi-permeability22.9
	22.3.3.	Function of the Semi-
	22.3.3.	permeable Membrane22.10
	22.3.4.	Osmotic Pressure
	22.3.5.	Kinetic Molecular Theory
	22.3.3.	of Osmotic Pressure
	22.3.6.	Reverse Osmosis
	22.3.7.	Measurement of Osmotic
		Pressure
	22.3.8.	Theory of Dilute Solutions22.14
	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
	22 2 11	Pressures22.17 Osmotic Pressure of
	22.3.11.	
		Electrolytes22.19

22.

	22.3.12.	Osmotic Coefficient	
	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 Pressure22.21	
22.4.	Elevation	of Boiling Point22.22	
	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.	Depressio	on in Freezing Point22.29	
	22.5.1.	Thermodynamic Derivation of	
		Depression of Freezing Point 22.29	

	22.5.2.	I	1 of
		the Depression of Freezing	
		Point	22.32
22.6.	Abnorma	al 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
	Questio	ns	22.36
		ve Type	
		ns	
		ation Questions	
		~	

#### **UNIT-V: SURFACE CHEMISTRY**

#### 23. ADSORPTION ......23.3

23.1.	Introduct	ion23.3
	23.1.1.	How does Adsorption Differ
		from Absorption23.3
	23.1.2.	Adsorption and Absorption
		Occur One after the Other23.4
	23.1.3.	Examples of Adsorbents and
		Adsorbates
23.2.	Adsorptio	on of Gases23.4
	23.2.1.	Physical Adsorption23.5
	23.2.2.	Chemisorption
	23.2.3.	Distinction between
	23.2.3.	Physical Adsorption and
		Chemisorption
23.3.	What Ch	anges the Adsorbed Molecules
25.5.		the Process of Adsorption ?23.6
23.4.		on Isotherms
23.4.	23.4.1.	Freundlich Adsorption
	23.4.1.	Isotherm
	23.4.2.	
	23.4.2.	
	22.4.2	Isotherm
	23.4.3.	Types of Adsorption
	00.4.4	Isotherms
<u> </u>	23.4.4.	BET Theory23.13
23.5.		ental Determination of
		orption
	23.5.1.	Volumetric Method23.20
	23.5.2.	Gravimetric Method23.21
23.6.		Temperature on Adsorption23.22
23.7.		on from Solution23.24
	23.7.1.	Adsorption of Solutes from
		Solutions Depends on the
		Nature of the Adsorbent23.25
	23.7.2.	A Competition between the
		Solute and Solvent Molecules
		takes place in Adsorption
		from Solutions23.25

The	Colloida	al State24.	.1
	Examina	ation Questions23.4	46
	Objectiv	ve Type23.4	45
23.11.	Application	ons of Adsorption23.4	41
23.10.	Emulsifie	rs23.4	40
23.9.	The Gibb	s Adsorption Theorem23.3	37
	23.8.10.	Formation of Surface Films 23.3	37
	23.8.9.	Electrokinetic Phenomena23.3	32
		Ionized Surfactants	31
	23.8.8.	Surface Equation of State for	
		and Applications23.3	31
	23.8.7.		-
	20.0.0.		30
	23.8.6.		,0
			30
	25.0.5.		
	23.8.5		27
	23.8.4.		20
	22.0.4		28
			•
	23.8.3.		
			27
	23.8.1.		
23.8.	Liquid Su		27
		Adsorption from Solutions?23.2	26
		Experimental Data due to	
	23.7.4.	How to Calculate x/m from	
			26
	23.7.3.	Three Types of Mechanical	
	23.9. 23.10. 23.11.	<ul> <li>23.8. Liquid Su 23.8.1.</li> <li>23.8.2. 23.8.3.</li> <li>23.8.4.</li> <li>23.8.5.</li> <li>23.8.6.</li> <li>23.8.6.</li> <li>23.8.7.</li> <li>23.8.8.</li> <li>23.8.9.</li> <li>23.8.10.</li> <li>23.9. The Gibb</li> <li>23.10. Emulsifie</li> <li>23.11. Application Objective Examine</li> </ul>	Adsorption from Solutions23.223.7.4.How to Calculate x/m from Experimental Data due to Adsorption from Solutions?23.223.8.Liquid Surfaces

- - Colloidal Solutions and Suspensions ......24.2

24.3.	Colloidal	State	24.2
24.4.	Preparation	on of Colloidal Solution	24.4
	24.4.1.	Condensation Method	24.5
	24.4.2.	Dispersion Methods	24.5
24.5.	Purificati	on of Colloidal Solution	24.7
24.6.	Propertie	s 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 Stabi	ility of Colloids	24.16
24.8.	The Preci	pitation (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.	Emulsion	IS	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 C	olloidal Particles	24.23
24.12.	Molecula	r Mass of Macromolecules.	24.24
24.13.	Applicati	ons of Colloid Chemistry	24.26
		Electrolytes	
24.15.	Surface A	Active Agents (Surfactants)	24.28

	24.15.1.	Characteristics of Surfactants.	
	24.15.2.	Classification of Surface	
		Active Agents	24.29
24.16.	Micelles.	<u> </u>	
	24.16.1.	Kraft Temperature	
	24.16.2.	Structure of Micelles	
	24.16.3.	Ionic Micelles and their	
		Different Types	
	24.16.4.	Micellization in Non-aqueou	
		Media	
	24.16.5.	Counter Ion Binding to	
		Micelles	
	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 Critica	1
		Concentration of Micelles of	f
		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	
24.17.	Donnan N	Aembrane Equilibrium	.24.40
		ns	
		ре Туре	
	Examina	ation Questions	24.49

#### **UNIT-VI: RATES AND MECHANISMS**

25. 0	Cher	mical Ki	netics25.3
2	5.1.	The Rates	s of Chemical Reactions25.3
		25.1.1.	The Concept of Reaction Rate 25.3
		25.1.2.	Units Employed25.4
		25.1.3.	Variation of Reactant
			Concentration with Time25.4
		25.1.4.	Rate Laws and Rate
			Constants25.5
		25.1.5.	Factors Influencing Reaction
			Rates25.6
2	5.2.	Molecula	rity and Order of Reaction25.7
		25.2.1.	Realation between Molecularity
			and Order of Reaction25.7
		25.2.2.	Order and Molecularity of
			Complex Reactions25.8
2	5.3.	Zero-Ord	er Reactions25.9
2	5.4.	First Orde	er Rate Equations25.10
		25.4.1.	Half-change Time25.12
		25.4.2.	Some Typical First Order
			Reactions25.13
2	5.5.	Second O	rder Rate Equation25.16

	25.5.1.	Hydrolysis of an Ester by	
		an Alkali	25.17
	25.5.2.	Some other Examples of	
		Second Order Reactions	25.19
25.6.	Third Ord	ler Rate Equation	25.19
25.7.	Rate Law	for <i>n</i> th Order Reaction	25.19
25.8.	Fractiona	l Order Reactions	25.20
25.9.	Reactions	with Negative Order	25.21
25.10.	Determin	ation of the Order of a	
	Reaction.		25.21
25.11.	The Effec	t 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 Theory25.43
		25.14.2.	The Transition State Theory
			or Theory of Absolute
			Reaction Rate25.49
	25.15.	Chemical	Kinetics in Solutions25.65
			Reactions in Ideal Solutions25.65
		25.15.2.	Reaction between Ions in
			Solution25.67
		25.15.3.	Diffusion-Controlled Reactions
			in Solution25.71
		25.15.4.	Kinetics of Fast Reactions25.73
		25.15.5.	Kinetics of Slow Reactions25.82
	25.16		r Reaction Dynamics
		25.16.1.	Reactions in Molecular Beams25.89
			Potential Energy Surfaces25.93
		25.16.3.	Transition State Theory in
		20110101	Terms of Statistical Mechanics25.96
	C	Duestions	
			<i>vpe</i> 25.103
			<i>n Questions</i>
00	0-1-	L	00.4
26.			
26.	<b>Cata</b> 26.1.	Substance	es Alter the Speed of a Chemical
26.		Substance Reaction.	es Alter the Speed of a Chemical
26.		Substance Reaction. 26.1.1.	es Alter the Speed of a Chemical 
26.		Substance Reaction. 26.1.1. 26.1.2.	es Alter the Speed of a Chemical 
26.		Substance Reaction. 26.1.1.	es Alter the Speed of a Chemical 
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3.	es Alter the Speed of a Chemical 
26.		Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories of	es Alter the Speed of a Chemical Types of Catalysis
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3.	es Alter the Speed of a Chemical Types of Catalysis
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories 0 26.2.1.	es Alter the Speed of a Chemical Types of Catalysis
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories of	es Alter the Speed of a Chemical Types of Catalysis
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories 0 26.2.1.	es Alter the Speed of a Chemical Types of Catalysis
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories 0 26.2.1. 26.2.2.	es Alter the Speed of a Chemical 
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories 0 26.2.1.	es Alter the Speed of a Chemical Types of Catalysis
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories 0 26.2.1. 26.2.2.	es Alter the Speed of a Chemical 
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories 0 26.2.1. 26.2.2.	es Alter the Speed of a Chemical 26.1 Types of Catalysis
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories 0 26.2.1. 26.2.2.	es Alter the Speed of a Chemical 26.1 Types of Catalysis
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories 0 26.2.1. 26.2.2. 26.2.3.	es Alter the Speed of a Chemical 
26.	26.1.	Substance Reaction. 26.1.1. 26.1.2. 26.1.3. Theories 0 26.2.1. 26.2.2.	es Alter the Speed of a Chemical 26.1 Types of Catalysis

		26.2.5.	Use of Catalysts in Industry26.29
		Questions	
			<i>ype</i> 26.31
			<i>n Questions</i>
27	Ph	otochem	istry27.1
21.	27.1		tion27.1
	27.1	27.1.1.	What Does Photochemistry
		2/.1.1.	Tell Us?27.1
		27.1.2.	Chemical Effects Produced by
		27.1.2.	Light Radiations27.1
		27.1.3.	Aquaintance with
		27.1.3.	Photochemical Reactions27.2
		27.1.4.	Differences between Thermal
		27.1.4.	and Photochemical Reactions27.2
	27.2	The Who	le of Incident Radiation is not
	21.2		1: The Laws of Absorption27.3
		27.2.1.	Why does the Intensity of
		27.2.1.	Incident Light Change?27.3
		27.2.2.	The Laws of Absorption27.3
	27.3		Radiation on Chemical
	21.5		s27.7
		27.3.1.	Laws of Photochemistry27.7
		27.3.2.	Deviations in the Law of
		21.3.2.	Photochemical Equivalence27.10
		27.3.3.	Factors Affecting the
		21.5.5.	Quantum Efficiency
		27.3.4.	Experimental Procedure27.12
		27.3.5.	Photochemical Reactions27.14
	27.4		of Radiations27.19
	27.1	27.4.1.	Luminescence
		27.4.2.	Fluorescence
		27.4.3.	Phosphorescence
		27.4.4.	Flash Photolysis27.21
	27.5	. Applicati	on of Photochemistry27.21
		27.5.1.	Photography27.21
		21.5.2.	Photoelectric Effect in
			Wireless27.22
		Questions	
			n Questions27.25
			-

#### **UNIT-VII: ELECTROCHEMISTRY**

#### 28. Electrolysis and Electrical Conductivity......28.3

Electroly	vte Solutions	
Conduct	Electricity	28.3
28.1.1.	Ions in Solution	28.3
28.1.2.	Formation of Ions in Solutio	n.28.4
Substanc	es that Conduct Electricity	28.5
28.2.1.	Metallic Conductance	28.5
28.2.2.	Electrolytic Conductance	28.6
	Conduct 28.1.1. 28.1.2. Substanc 28.2.1.	Electrolyte Solutions Conduct Electricity

28.3.	Electroly	sis28.6
	28.3.1.	Products of Electrolysis28.7
	28.3.2.	Faraday's Laws of Electrolysis28.8
	28.3.3.	Theoretical Importance of the
		Second Law
28.4.	Conducta	nce of Solution28.10
	28.4.1.	Electrolytic Conductivity or
		Specific Conductance
	28.4.2.	Molar Conductivity $(\Lambda_m)$ 28.12

		28.4.3.	Equivalent Conductivity28.13
		28.4.4.	Relation between Equivalent
			Conductivity and Molar
			Conductivity
		28.4.5.	Measurement of Electrolytic
		20.4.5.	
		00.4.6	Conductivity
		28.4.6.	Effect of Dilution on Equivalent
			Conductivity28.18
	28.5.		of Weak and Strong
			tes28.20
		28.5.1.	Arrhenius Theory
		28.5.2.	Degree of Dissociation28.21
		28.5.3.	Drawbacks of the Arrhenius
			Theory
		28.5.4.	Theory of Strong Electrolytes .28.23
		28.5.5.	Derivation of Debye-Hückel-
		20.5.5.	Onsager Conductance
	20 (	Caralizata	Equation
	28.6.		nce at High Frequencies and
			ages
		28.6.1.	Wien Effect
		28.6.2.	Debye-Falkenhagen Effect28.29
	28.7.		Attraction Theory:
		Debye-H	ückel Theory of Strong
		Electroly	tes28.29
		28.7.1.	Activity Co-efficients of
			Electrolytes
		28.7.2.	Debye-Hückel Theory
			Debye-Hückel Theory28.34 ns28.44
		Question	<i>ns</i>
		Question Objectiv	ns
		Question Objectiv Problem	ns
		Question Objectiv Problem Examina	ns
29.	Migr	Question Objectiv Problem Examina	ns
29.	<b>Mig</b> 29.1.	Question Objectiv Problem Examina	ns
29.		Question Objectiv Problem Examina ration of Migration	ns.       28.44         ve Type       28.45         ns.       28.45         ns.       28.46         ation Questions       28.47         Ions       29.1
29.		Question Objectiv Problem Examina ration of Migratior 29.1.1.	ns.       28.44         ve Type       28.45         ns.       28.46         ation Questions       28.47         Ions       29.1         a of Ions       29.1         Experiment       29.2
29.		Question Objectiv Problem Examina ration of Migration	ns.       28.44         ve Type       28.45         ns.       28.46         ation Questions       28.47         Ions       29.1         n of Ions       29.1         Experiment       29.2         The Drift Speed and Mobility
29.		Question Objectiv Problem Examina ration of Migration 29.1.1. 29.1.2.	ns.       28.44         ve Type       28.45         ns.       28.46         ation Questions       28.47         Ions       29.1         n of Ions       29.1         Experiment       29.2         The Drift Speed and Mobility       of Ions         of Ions       29.2
29.		Question Objectiv Problem Examina ration of Migratior 29.1.1.	ns.       28.44         ve Type       28.45         ns.       28.45         ns.       28.46         ation Questions       28.47         Ions       29.1         Experiment       29.2         The Drift Speed and Mobility       of Ions         of Ions       29.2         Current carried by Ions and
29.	29.1.	Question Objectiv Problem Examina ration of Migration 29.1.1. 29.1.2.	ns.       28.44         ve Type       28.45         ns.       28.45         ns.       28.46         ation Questions       28.47         Ions       29.1         ato of Ions       29.1         Experiment       29.2         The Drift Speed and Mobility       of Ions         of Ions       29.2         Current carried by Ions and       Ionic Speeds         Ionic Speeds       29.5
29.		Question Objectiv Problem Examina ration of Migration 29.1.1. 29.1.2. 29.1.3. Speeds of	ns
29.	29.1.	Question Objectiv Problem Examina ration of Migration 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele	ns.       28.44         be Type       28.45         as.       28.45         ation Questions       28.47 <b>Ions</b> 29.1         a of Ions       29.1         Experiment       29.2         The Drift Speed and Mobility       of Ions         of Ions       29.2         Current carried by Ions and       Ionic Speeds         Ionic Speeds       29.5         Flons and Amounts Liberated       29.6
29.	29.1.	Question Objectiv Problem Examina ration of Migration 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1.	ns
29.	29.1.	Question Objectiv Problem Examina ration of Migration 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele	ns
29.	29.1.	Question Objectiv Problem Examina <b>ration of</b> Migration 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1. 29.2.2.	ns
29.	29.1.	Question Objectiv Problem Examina ration of Migratior 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1.	ns.28.44ve Type28.45ts.28.45ts.28.46ation Questions28.47Ions29.1Experiment29.2The Drift Speed and Mobilityof Ions29.2Current carried by Ions andIonic Speeds29.5F Ions and Amounts Liberatedctrodes29.6Hittorf's Theoretical Device29.6Transference Number or29.7Transference Number of Some
29.	29.1.	Question Objectiv Problem Examination of Migration of 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1. 29.2.2. 29.2.3.	ns.28.44ve Type28.45ts.28.45ts.28.46ation Questions28.47Ions29.1Experiment29.2The Drift Speed and Mobilityof Ions29.2Current carried by Ions andIonic Speeds29.5F Ions and Amounts Liberatedctrodes29.6Hittorf's Theoretical Device29.7Transference Number or29.7Transference Number of SomeIons in Aqueous Medium10029.14
29.	29.1.	Question Objectiv Problem Examina <b>ration of</b> Migration 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1. 29.2.2.	ns.28.44ve Type28.45ts.28.45ts.28.46ation Questions28.47Ions29.1Experiment29.2The Drift Speed and Mobilityof Ions29.2Current carried by Ions andIonic Speeds29.5F Ions and Amounts Liberatedctrodes29.6Hittorf's Theoretical Device29.6Transference Number or29.7Transference Number of Some
29.	29.1.	Question Objectiv Problem Examination of Migration of 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1. 29.2.2. 29.2.3.	ns.28.44ve Type28.45ts.28.45ts.28.46ation Questions28.47Ions29.1Experiment29.2The Drift Speed and Mobilityof Ions29.2Current carried by Ions andIonic Speeds29.5F Ions and Amounts Liberatedctrodes29.6Hittorf's Theoretical Device29.7Transference Number or29.7Transference Number of SomeIons in Aqueous Medium10029.14
29.	29.1.	Question Objectiv Problem Examination of Migration of 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1. 29.2.2. 29.2.3.	ns.28.44ve Type28.45ts.28.45ts.28.45ts.28.47 <b>lons</b> 28.47 <b>lons</b> 29.1Experiment29.2The Drift Speed and Mobilityof Ions29.2Current carried by Ions andIonic Speeds29.5F Ions and Amounts Liberatedctrodes29.6Hittorf's Theoretical Device29.6Transference Number orTransference Number of SomeIons in Aqueous Medium29.14Zero and NegativeTransference Numbers29.14
29.	29.1.	Question Objectiv Problem Examina <b>ration of</b> Migration 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1. 29.2.2. 29.2.3. 29.2.4.	ns.28.44ve Type28.45is.28.45is.28.45ation Questions28.47Ions29.1Experiment29.2The Drift Speed and Mobilityof Ions29.2Current carried by Ions andIonic Speeds29.5Flons and Amounts Liberatedctrodes29.6Hittorf's Theoretical Device29.6Transference Number or29.7Transference Number of Some10nis in Aqueous MediumIons in Aqueous Medium29.14Zero and Negative29.14Transference Numbers29.14Factors on which Transport
29.	29.1. 29.2.	Question Objectiv Problem Examina <b>ration of</b> Migration 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1. 29.2.2. 29.2.3. 29.2.4. 29.2.5.	ns.       28.44         be Type       28.45         is.       28.45         is.       28.45         ation Questions       28.47         Ions       29.1         a of Ions       29.1         Experiment       29.2         The Drift Speed and Mobility       of Ions         of Ions       29.2         Current carried by Ions and       29.2         Ionic Speeds       29.5         Flons and Amounts Liberated       29.6         Hittorf's Theoretical Device       29.6         Transference Number or       29.7         Transference Number of Some       10ns in Aqueous Medium         Ions in Aqueous Medium       29.14         Zero and Negative       29.14         Transference Numbers       29.14         Factors on which Transport       Number Depends         Number Depends       29.15
29.	29.1.	Question Objective Problem Examination of Migration 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1. 29.2.2. 29.2.3. 29.2.4. 29.2.5. Ionic Cor	ns.       28.44         be Type       28.45         is.       28.45         ation Questions       28.47 <b>Ions</b> 29.1         a of Ions       29.1         Experiment       29.2         The Drift Speed and Mobility         of Ions       29.2         Current carried by Ions and         Ionic Speeds       29.5         Flons and Amounts Liberated         ctrodes       29.6         Hittorf's Theoretical Device       29.6         Transference Number or       29.7         Transference Number of Some       29.7         Ions in Aqueous Medium       29.14         Zero and Negative       29.14         Factors on which Transport       Number Depends         Number Depends       29.15         ductance       29.16
29.	29.1. 29.2.	Question Objectiv Problem Examina <b>ration of</b> Migration 29.1.1. 29.1.2. 29.1.3. Speeds of at the Ele 29.2.1. 29.2.2. 29.2.3. 29.2.4. 29.2.5.	ns.       28.44         be Type       28.45         is.       28.45         is.       28.45         ation Questions       28.47         Ions       29.1         a of Ions       29.1         Experiment       29.2         The Drift Speed and Mobility       of Ions         of Ions       29.2         Current carried by Ions and       29.2         Ionic Speeds       29.5         Flons and Amounts Liberated       29.6         Hittorf's Theoretical Device       29.6         Transference Number or       29.7         Transference Number of Some       10ns in Aqueous Medium         Ions in Aqueous Medium       29.14         Zero and Negative       29.14         Transference Numbers       29.14         Factors on which Transport       Number Depends         Number Depends       29.15

		29.3.2.	Application of Kohlrausch's	
			Law	
		29.3.3.	Conductometric Titrations	
			<i>ns</i>	
			ve Type	
			!\$	
		Examina	ation Questions	.29.37
).	lonio	: Equilit	oria	30.1
	30.1.	Introducti	on	
		30.1.1.	Dynamic Equilibrium betwee	en
			Ions and the Unionised	
			Molecules	30.1
		30.1.2.	Dissociation Constant and	
			Ostwald's Dilution Law	
		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	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	
	30.3.	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 Ac	ids
			and Polyacid Bases	
	30.4.		Ion Effect	
		Question	ns	.30.32
		Objectiv	ve Type	.30.33
		Problem	l\$	.30.35
		Examina	ation Questions	.30.36
۱.	Acid	s and B	ases	31.1
	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.	Relative Strengths of Acids	31.4
		31.1.4.	Relative Strengths of Bases .	
		31.1.5.	Isohydric Solution	
	31.2.		rol of the Concentration of	
			Buffer Solutions	31.8
		31.2.1.	Composition of Buffer	

30.

31.

	31.2.2.	Mathematical Expression for the
		pH of Acidic Buffers and Basic
		Buffers – Henderson-Hasselbalch
		Equation
	31.2.3.	Buffer Capacity
	31.2.4.	Methods for the Determination
		of pH31.15
31.3.	Theories	of Indicators
	31.3.1.	The Acid-Base Concept of
		Indicators – Ostwald's Theory 31.19
	31.3.2.	Quinonoid Theory
	31.3.3.	pH Changes During
		Acid-base Titrations
	31.3.4.	Choice of Indicators and
		Acid-Base Titrations
	31.3.5.	Indicators and
		Acid-Base Titrations31.25
Q	Juestions.	
(	Dbjective T	<i>Type</i>
I	Problems	
E	Examinatio	on Questions

#### 32. Solubility Product and Hydrolysis...32.1

32.1.	Solubility	y Product	32.1
	32.1.1.	Equilibrium between a Solid	
		Salt and its Ions in Solution,	the
		Solubility Product	32.1
	32.1.2.	Relation between Solubility	and
		Solubility Product of a Spari	
		Soluble Salt	
	32.1.3.	Application of	
	0211101	Solubility Product	32.3
	32.1.4.	Application of Solubiity Pro	
		in Qualitative Analysis of	
		Cations	32.4
32.2.	Hydrolys	sis	
	32.2.1.	Degree of Hydrolysis and	
		Hydrolysis Constants	32.7
	32.2.2.	Relation between the Hydrol	
		Constant and Dissociation	- <u>j</u>
		Constant	32.8
	32.2.3.	Methods for Determination of	
	0212101	Degree of Hydrolysis	
	Ouestio	ms	
		ve Type	
		ns	
		ation Questions	
		z	
		_	

#### 33. Electromotive Force......33.1

- 33.1.2. Electrode Potential and Electrolytic Concentration:

			The Nernst Equation	
			of Electrode Potential	33.2
	33.1.3	3.	Cell Diagrams and	
			Terminology	33.3
	33.1.4	1.	Factors on which Electrode	
			Potential Depends	
	33.1.5	5.	Thermodynamic Explanatio	
			the Electrochemical Potenti	
	33.1.6	5.	Thermodynamic Explanatio	
			the Potential Difference at t	
			Interfacial Boundaries	
	33.1.7	7	Thermodynamic Explanatio	
	00111		Electrode Potential	
	33.1.8	2	Single Electrode Potentials	
	33.1.9		Sign of Electrode Potential	
	33.1.1		Reversible and Irreversible	
	55.1.1	10.	Cells	33.8
	33.1.1	11	Types of Electrodes	
33.2			Electrode Potential and E.M	
33.2				
	33.2.1.		ermination of Standard	
	55.2.1.		ctrode Potential	33 13
	33.2.2.	The	ermodynamic Concept of	
	55.2.2.	Fla	ctrode Potential	33 14
	33.2.3.		ndard Half-Cell Reduction	
	55.2.5.		entials at 25°C in Aqueous	
			ution	33 15
	33.2.4.		ne Uses of Electrode	
	33.2.4.		entials	22 10
	33.2.5.		ndard E.M.F. of the Cell	
	33.2.6.		asurement of E.M.F. :	
	55.2.0.		gendorff's Compensation	
			thod	33.77
	33.2.7.		e Standard Cell	
	33.2.8.		culation of E.M.F. of Cell	
33.3.			ectrochemical Cells	
55.5.	33.3.1.		emical Cells	
	33.3.2.		contration Cells	
			plications of Concentration	
	55.5.5.		ls	33 30
33.4.	Applica		s of E.M.F. Measurements	
33.5.			nical Cells –	
55.5.			of Energy	33 63
	33.5.1		Some Commonly	
	55.5.1	1.	Used Batteries	33 63
	33.5.2	,	Fuel Cells	
22.6			le Electrode Processes	
33.6	. irreve 33.6.1		Polarization	
	33.6.2		Decomposition Potential	
	33.6.2			
			Overvoltage	
	33.6.4		Corrosion	
	33.6.5	).	Passivity of Metals	33.79

33.6.6.	Polarography	33.79
33.6.7.	Amperometric Titrations	33.94
Questio	ns	33.97

Objective Type	.33.102
Problems	.33.104
Examination Questions	.33.105

#### **UNIT-VIII: STRUCTURE OF MOLECULES**

34.		sical Properties and mical Constitution34.3		
			the Physical Properties	
	34.1.			
		34.1.1.	Four Classes of Physical	
		2412	Properties	
		34.1.2.	Physical Properties and	
		24.1.2	Chemical Constitution	
		34.1.3.	Influence of Pressure and	
			Temperature on Physical	
		~ -	Properties	
	34.2.		oortant Physical Properties	
			ng Molecular Structure	
		34.2.1.	Molar Volumes	
		34.2.2.	Parachor	
		34.2.3.	Refractive Index	
		34.2.4.	Viscosity and Constitution34.17	
		34.2.5.	Optical Activity and	
			Chemical Constitution	
	34.3.	Electric P	roperties Elucidating the Molecular	
		Structure		
		34.3.1.	Dipole Moments34.20	
		34.3.2.	Electrical Polarization of	
			Molecules	
		34.3.3.	Dipole Moments and	
			Dielectric Constant	
		34.3.4.	Dielectric Polarization and	
			Dielectric Constant	
		34.3.5.	Determination of Dielectric	
			Constant, $\in_{\mathbf{r}}$	
		34.3.6.	Determination of Dipole	
			Moments	
		34.3.7.	Molar Refraction and Molar	
			Polarization : Dependence of	
			Polarizability on Frequency 34.31	
		34.3.8.	Bond Moments and the Molecular	
			Dipole Moment34.33	
		34.3.9.	Dipole Moments and	
			Molecular Structure	
		34.3.10.	Group Moments	
	34.4.	Magnetic	Properties of Molecules34.37	
		34.4.1.	Magnetic Permeability	
		34.4.2.	Theories of Diamagnetism and	
			Paramagnetism	
		34.4.3.	Measurement of Magnetic	
			Susceptibility34.44	

		34.4.4.	Applications of Magnetic
			Susceptibilities
		Questie	ons
		Objecti	ive Type34.48
		Problem	ns34.49
		Examir	nation Questions34.51
35.	Spe	ctrosco	ру35.1
	35.1.	The Elec	etromagnetic Spectrum35.1
		35.1.1.	Electromagnetic Radiations35.1
		35.1.2.	Different Regions in
			Electromagnetic Spectrum35.3
		35.1.3.	Absorption Spectroscopy35.3
		35.1.4.	Molecular Energies
		35.1.5.	Measurement of the Amount
			of Light Absorbed35.6
		35.1.6.	Mechanism of Interaction of
			Radiation with Materials35.6
	35.2.	Molecul	ar Spectra35.8
		35.2.1.	Molecular Rotation
		35.2.2.	Types of Molecular Spectra35.9
		35.2.3.	Rotational Spectra of Diatomic
			Molecules (Microwave Spectra) -
			Rigid Rotator35.11
		35.2.4.	Vibrational Spectra
			(Near Infrared Spectra)35.24
		35.2.5.	Simultaneous Rotation and
			Vibration in Molecules –
			Diatomic Vibrating Rotator 35.37
		35.2.6.	Electronic Spectra35.48
		35.2.7.	Light Scattering and Raman
			Spectroscopy35.53
		35.2.8.	Magnetic Resonance
			Spectroscopy35.60
	(	Objective [	Туре35.98
	1	Examinatio	on Questions35.100
36.	Мас		cules36.1
	36.1.	Macrom	olecules – A Class of Molecular
		Colloids	
		36.1.1	Polymers $-A$ Class of

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

Macromolecules in Solutions		
36.2.1.	Molar Masses of	
	Macromolecules	
36.2.2.	Determination of Molar	
	Masses of	
	Macromolecules	
	36.2.1.	

36.2.3.	Stereochemistry of	
	Macromolecules in Solu	tion .36.39
36.2.4.	Functional Polymers	36.47
Questions		36.52
Objective T	ype	36.53
Problems		36.54
Examinatio	n Questions	36.55

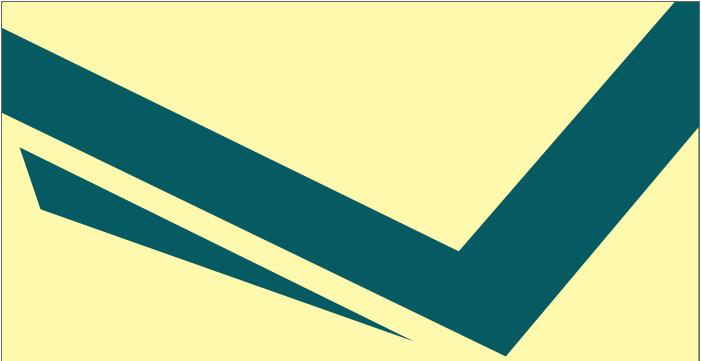
#### **UNIT-IX: THERMODYNAMICS-II**

## **37. Irreversible Thermodynamics......37.3** 37.1. From the Equilibrium to the

37.1.	From the Equilibrium to the		
	Non-Equ	ilibrium Thermodynamics37.3	
	37.1.1.	Thermodynamic-	
		Phenomenological Theory	
		of Irreversible Processes	
	37.1.2.	Looking Back to Look Forward :	
		Fundamentals of	
		Thermodynamics	
37.2.	Laws of	Thermodynamics	
	37.2.1.	Energy and Heat (First Law of	
	0712111	Thermodynamics)	
	37.2.2.	Entropy and Absolute	
	57.2.2.	Temperature (Second Law of	
		Thermodynamics)	
37.3.	Equilibri	um and Stationary States37.21	
57.5.	37.3.1.	Equilibrium in Homogeneous	
	57.5.1.	Systems	
	37.3.2.	Equilibrium in Heterogeneous	
	57.5.2.	Systems	
	37.3.3.	Equilibrium in Continuous	
	57.5.5.		
37.4.	Enome the	Systems	
37.4.		Equilibrium to the	
	37.4.1.	ilibrium States	
	37.4.1.	Conservation of Energy in	
	27.4.2	Open System	
	37.4.2.	Entropy Flow and Entropy	
	27.4.2	Production in Open Systems37.31	
	37.4.3.	Phenomenological	
	27.4.4	Equations	
	37.4.4.	Entropy Production due to	
		Diffusion in Systems at	
	27 4 5	Uniform Temperature	
	37.4.5.	Entropy Production due to	
		Diffusion in Systems at	
	2716	Non-uniform Temperature37.45	
	37.4.6.	Entropy Production due to	
	37.4.7.	Viscosity	
		Electrokinetic Effects	
_			
I	элаттанс	on Questions	

38.	Stat	istical T	hermodynamics38.1		
	38.1.	8.1. From Microscopic Properties to			
			ppic Properties		
		38.1.1.	Statistical Mechanics:		
			Postulates		
		38.1.2.	Statistical Probability		
		38.1.3.	Phase Space		
		38.1.4.	What do the Microstate and		
			Macrostate tell us?		
		38.1.5.	System, Assembly and		
			Ensemble		
		38.1.6.	Liouville's Theorem		
		38.1.7.	Statistical Equilibrium		
		38.1.8.	Entropy and Probability		
		38.1.9.	Entropy is a Function of the		
			Probability of the		
	20.2	D'stall at	Thermodynamic State		
	38.2.	Distribution of Particles Among			
		Energy S 38.2.1.	tates		
		38.2.1.	Maxwell-Boltzmann		
			Statistics		
		38.2.2.	Partition Functions and		
		30.2.2.	Thermodynamic Functions38.31		
		38.2.3.	Solved Problems		
	38.3.		Back to Look Forward :		
	56.5.	Quantum Statistics			
		38.3.1.	Bose-Einstein Statistics		
		38.3.2.	Fermi-Dirac Statistics		
		38.3.3.	Comparison Amongst Maxwell-		
		50.5.5.	Boltzmann, Bose-Einstein and		
			Fermi-Dirac Statistics		
		38.3.4.	Solved Problems		
		Questio	<i>ns</i>		
			<i>ve Type</i>		
			38.70		
		Examina	ation Questions		
Ар	Appendix A.1-A.6				

Index	I.1-	-I.1	12
-------	------	------	----



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

- □ The book has been designed to incorporate the guidelines of the New Education Policy (NEP) 2020 and the Choice-Based Credit System (CBCS) to ensure that the content aligns with the latest educational standards.
- □ The subject matter has been organized to enhance the understanding and enable the readers to navigate through the concepts easily.
- To ensure uniformity and accuracy, International System of Units has been used throughout the book.
- □ Emphasis is placed on explaining the fundamental concepts, principles and applications to develop strong foundation in the topic.
- □ The book includes a number of solved examples integrated into the text to provide students multiple opportunities to apply the topics.
- □ Furthermore, a variety of questions and numerical exercises are given at the end of each chapter in line with the examinations conducted for B.Sc., M.Sc. and Professional courses.
- □ In order to cater to the advanced requirements of Master's level education, certain chapters contain additional subject material in line with the M.Sc. Syllabi.
- D New typography and appealing format make the book strain free and reader friendly.



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