

S. CHAND'S SUCCESS GUIDES

(Questions and Answers)

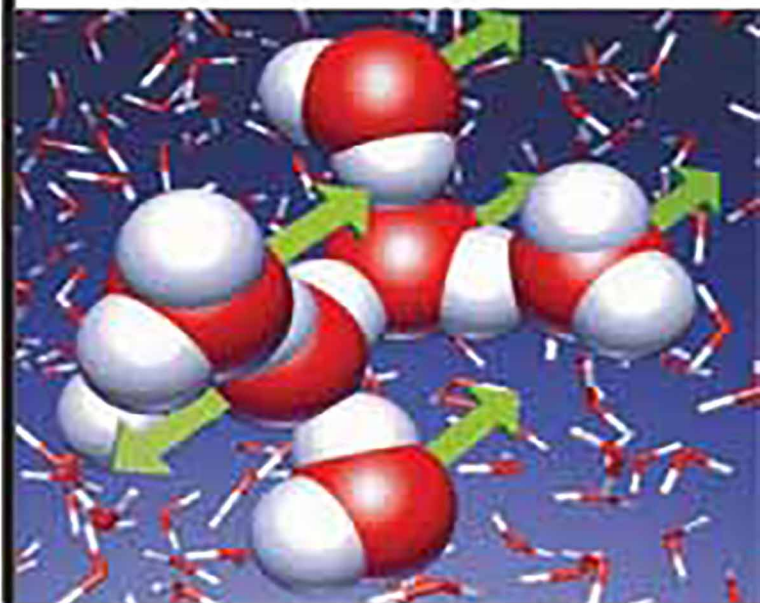
PHYSICAL CHEMISTRY

For B.Sc. I, II and III Year

As per UGC
Model Curriculum

REVISED
EDITION

- Authentic, simple, to the point and modern account of each and every topic
- Relevant, clear, well labelled diagrams
- Easy to understand treatment of most difficult and intricate topics
- Questions from university papers of various Indian Universities have been included in the text



S. CHAND

Dr. R.L. MADAN
G.D. TULI

S. CHAND'S SUCCESS GUIDES
(Questions and Answers)

PHYSICAL CHEMISTRY

For the Students of B.Sc. I, II and III
of All Indian Universities

Also Covering UGC Model Curriculum

[Including Solved Long Answer Type, Short Answer Type
Questions and Numerical Problems]

REVISED AND UPDATED EDITION

Dr. R.L. MADAN

M.Sc., Ph.D.

Former Principal, Govt. College Panchkula
and Former Head of Chemistry Department
Govt. Post-Graduate College
Faridabad

G.D. TULI

Former Principal
Shyam Lal College
Delhi University, Delhi



S. CHAND
PUBLISHING
empowering minds

S. CHAND & COMPANY PVT. LTD.

(AN ISO 9001 : 2008 COMPANY)

RAM NAGAR, NEW DELHI-110 055



S. CHAND & COMPANY PVT. LTD.

(An ISO 9001 : 2008 Company)

Head Office: 7361, RAM NAGAR, NEW DELHI - 110 055

Phone: 23672080-81-82, 9899107446, 9911310888

Fax: 91-11-23677446

Shop at: schandgroup.com; e-mail: info@schandgroup.com

Branches:

- AHMEDABAD** : 1st Floor, Heritage, Near Gujarat Vidhyapeeth, Ashram Road, **Ahmedabad** - 380 014, Ph: 27541965, 27542369, ahmedabad@schandgroup.com
- BENGALURU** : No. 6, Ahuja Chambers, 1st Cross, Kumara Krupa Road, **Bengaluru** - 560 001, Ph: 22268048, 22354008, bangalore@schandgroup.com
- BHOPAL** : Bajaj Tower, Plot No. 2&3, Lala Lajpat Rai Colony, Raisen Road, **Bhopal** - 462 011, Ph: 4274723, 4209587, bhopal@schandgroup.com
- CHANDIGARH** : S.C.O. 2419-20, First Floor, Sector - 22-C (Near Aroma Hotel), **Chandigarh** - 160 022, Ph: 2725443, 2725446, chandigarh@schandgroup.com
- CHENNAI** : No. 1, Whites Road, Opposite Express Avenue, Royapettah, **Chennai** - 600014 Ph: 28410027, 28410058, chennai@schandgroup.com
- COIMBATORE** : 1790, Trichy Road, LGB Colony, Ramanathapuram, **Coimbatore** - 6410045, Ph: 2323620, 4217136 coimbatore@schandgroup.com (**Marketing Office**)
- CUTTACK** : 1st Floor, Bhartia Tower, Badambadi, **Cuttack** - 753 009, Ph: 2332580; 2332581, cuttack@schandgroup.com
- DEHRADUN** : 1st Floor, 20, New Road, Near Dwarka Store, **Dehradun** - 248 001, Ph: 2711101, 2710861, dehradun@schandgroup.com
- GUWAHATI** : Dilip Commercial (1st floor), M.N. Road, Pan Bazar, **Guwahati** - 781 001, Ph: 2738811, 2735640 guwahati@schandgroup.com
- HALDWANI** : Bhatt Colony, Talli Bamori, Mukhani, **Haldwani** - 263139 (**Marketing Office**) Mob. 09452294584
- HYDERABAD** : Padma Plaza, H.No. 3-4-630, Opp. Ratna College, Narayanaguda, **Hyderabad** - 500 029, Ph: 27550194, 27550195, hyderabad@schandgroup.com
- JAIPUR** : 1st Floor, Nand Plaza, Hawa Sadak, Ajmer Road, **Jaipur** - 302 006, Ph: 2219175, 2219176, jaipur@schandgroup.com
- JALANDHAR** : Mai Hiran Gate, **Jalandhar** - 144 008, Ph: 2401630, 5000630, jalandhar@schandgroup.com
- KOCHI** : Kachapilly Square, Mullassery Canal Road, Ernakulam, **Kochi** - 682 011, Ph: 2378740, 2378207-08, cochin@schandgroup.com
- KOLKATA** : 285/J, Bipin Bihari Ganguli Street, **Kolkata** - 700 012, Ph: 22367459, 22373914, kolkata@schandgroup.com
- LUCKNOW** : Mahabeer Market, 25 Gwynne Road, Aminabad, **Lucknow** - 226 018, Ph: 4076971, 4026791, 4065646, 4027188, lucknow@schandgroup.com
- MUMBAI** : Blackie House, 11nd Floor, 103/5, Walchand Hirachand Marg, Opp. G.P.O., **Mumbai** - 400 001, Ph: 22690881, 22610885, mumbai@schandgroup.com
- NAGPUR** : Karnal Bagh, Near Model Mill Chowk, **Nagpur** - 440 032, Ph: 2720523, 2777666 nagpur@schandgroup.com
- PATNA** : 104, Citicentre Ashok, Mahima Palace, Govind Mitra Road, **Patna** - 800 004, Ph: 2300489, 2302100, patna@schandgroup.com
- PUNE** : Sadguru Enclave, Ground floor, Survey No. 114/3, Plot no. 8 Alandi Road, Vishrantwadi **Pune** - 411 015 Ph: 64017298 pune@schandgroup.com
- RAIPUR** : Kailash Residency, Plot No. 4B, Bottle House Road, Shankar Nagar, **Raipur** - 492 007, Ph: 2443142, Mb.: 09981200834, raipur@schandgroup.com (**Marketing Office**)
- RANCHI** : Shanti Deep Tower, Opp. Hotel Maharaja, Radium Road, **Ranchi** - 834001 Mob. 09430246440 ranchi@schandgroup.com
- SILIGURI** : 122, Raja Ram Mohan Roy Road, East Vivekanandapally, P.O., Siliguri, **Siliguri** - 734001, Dist., Jalpaiguri, (W.B.) Ph. 0353-2520750 (**Marketing Office**) siliguri@schandgroup.com
- VISAKHAPATNAM** : No. 49-54-15/53/8, Plot No. 7, 1st Floor, Opp. Radhakrishna Towers, Seethammadhara North Extn., **Visakhapatnam** - 530 013, Ph-2782609 (M) 09440100555, visakhapatnam@schandgroup.com (**Marketing Office**)

© 1999, R.L. Madan & G.D. Tuli

All rights reserved. No part of this publication may be reproduced or copied in any material form (including photo copying or storing it in any medium in form of graphics, electronic or mechanical means and whether or not transient or incidental to some other use of this publication) without written permission of the copyright owner. Any breach of this will entail legal action and prosecution without further notice.

Jurisdiction : All disputes with respect to this publication shall be subject to the jurisdiction of the Courts, tribunals and forums of New Delhi, India only.

First Edition 1999

Subsequent Editions and Reprints 2001, 2003, 2005, 2007

Fifth Revised and Enlarged Edition 2009

Sixth Revised Edition 2012

Reprint with corrections 2014 (Twice)

ISBN : 978-81-219-1881-7

Code : 1004D 248

PRINTED IN INDIA

By Rajendra Ravindra Printers Pvt. Ltd., 7361, Ram Nagar, New Delhi -110 055

and published by S. Chand & Company Pvt. Ltd., 7361, Ram Nagar, New Delhi -110 055.

By the Same Author

Success Guide Inorganic Chemistry

Success Guide Organic Chemistry

PREFACE TO THE SIXTH EDITION

The author is pleased to place the fifth enlarged and updated edition of the book at the hands of the students and teachers. Overwhelming response to the earlier editions has encouraged me to undertake thorough revision of the text. Some of the salient features of this edition are :

1. A number of questions that appeared in the papers of different universities during the last couple of years have been solved in different chapters.
 2. Physical chemistry in a Nutshell, which is a special feature of the book, has been provided in the beginning. It will prove to be very useful to the students in last minute revision for the examination.
 3. Collision frequency, mean free path, viscosity of a gas and barometric formula have been added to the chapter on gaseous state.
 4. Structural differences between solids, liquids and gases, various intermolecular forces in liquids, hydrogen bonding and Poiseuille's equation have been discussed in the chapter on liquid state.
 5. Powder method and Laue's method for the determination of crystal structure have been added to chapter on solid state.
 6. Various kinds of heats of reaction, Hess's law of constant heat summation and bond energy have been discussed in detail in the chapter on thermodynamics I.
 7. Different techniques for the determination of transition point have been provided. Carbon dioxide, zinc-cadmium and Magnesium-zinc systems have been discussed in the chapter on phase rule.
 8. Dipping calomel electrode, glass electrode, quinhydrone electrodes and $\text{Fe}^{2+} - \text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Fe}^{2+} - \text{KMnO}_4$ titrations have been discussed in the chapter on electrochemical cells. Also various kinds of corrosion, theory and methods of prevention have been treated in this chapter.
 9. In the chapter on physical properties and molecular structure, electronic spectra, width and intensity of spectral lines, Born-Oppenheimer approximation, Frank-condon principle and electronic transitions in σ , π and n -molecular orbitals have been included.
 10. Chapters on solutions and dilute solutions, quantum mechanics and statistical thermodynamics have been expanded to include several new concepts.
 11. Appendix 1 on laws of logarithms and Appendix 2 on mathematical relations, which are quite useful, have been provided at the end but before some useful tables.
- It is hoped that the book in the present form will be found to be even more useful to the reader.

Any suggestions for further improvement of the book are welcome.

DR. R.L. MADAN

Mobile 09971775666

PREFACE TO THE FIRST EDITION

I feel immense pleasure in presenting the Simplified Course in Physical chemistry for B.Sc. I, II and III (Pass and Honours) students of Indian universities. I have written this book keeping in view the difficulties faced by the students, as observed by me during the last three decades. I have presented the matter in a manner that will inspire the students to read physical chemistry with interest.

This book has been written in question-answer style. This will apprise the students of the style and nature of questions that are asked in the examination and the manner of answering them appropriately. Every effort has been made to present the subject matter lucidly by using a simple and clear language. If the student makes an earnest effort, he can follow the subject-matter readily.

A large number of solved numericals have been included for a clear understanding of the subject. Numerous well-labelled structures and diagrams have been given to explain the points. Important principles, laws, concepts and results have been printed in italics or bold to help the students grasp the subject easily. Questions from university papers of various Indian Universities have been included in the text.

I thank Shri Ravindra Kumar Gupta, Director, S. Chand & Co. Ltd., for the inspiration that I received from him. I also thank the staff of this Company for their co-operation and efforts in bringing out the book in a nice form.

I sincerely hope that the book will go a long way to satisfy the long-felt need of students for a friendly book on Physical Chemistry. Any suggestions for improvement of the book are welcome and will be gratefully acknowledged.

DR. R.L. MADAN

Disclaimer : While the authors of this book have made every effort to avoid any mistake or omission and have used their skill, expertise and knowledge to the best of have capacity to provide accurate and updated information. The authors and S. Chand do not give any representation or warranty with respect to the accuracy or completeness of the contents of this publication and are selling this publication on the condition and understanding that they shall not be made liable in any manner whatsoever. S.Chand and the authors expressly disclaim all and any liability/responsibility to any person, whether a purchaser or reader of this publication or not, in respect of anything and everything forming part of the contents of this publication. S. Chand shall not be responsible for any errors, omissions or damages arising out of the use of the information contained in this publication.

Further, the appearance of the personal name, location, place and incidence, if any; in the illustrations used herein is purely coincidental and work of imagination. Thus the same should in no manner be termed as defamatory to any individual.

CONTENTS

<i>Chapters</i>	<i>Pages</i>
<i>Introductory Chapter for Rapid Revision [Physical Chemistry in a Nutshell: Equations, Relations & Formulae]</i>	<i>(xi)—(xxxvi)</i>
1. Gaseous State	1—43
Gas Laws, Ideal and Real Gases, Kinetic Theory of Gases, Derivation of Kinetic Gas Equation, Deduction of Various Gas laws from Kinetic Gas Equation, Some other Deductions from Kinetic Theory of Gases, Maxwell's Distribution of Velocities, Maxwell's Energy Distribution Curves, Different Types of Molecular Velocities, Expression for Most Probable Velocity, (α) Average Velocity (\bar{u}) and Root Mean Square Velocity (u), Relationship between Most Probable Velocity, (α) Average Velocity (\bar{u}) and Root Mean Square Velocity (u), Degrees of Freedom of Motion, Principle of Equipartition of Energy. Collision Frequency and Mean Free Path Deviations from the Laws and Explanation of the Terms-Compressibility Factor and Boyle Temperature, Causes of Deviation from Ideal Behaviour, van der Waals Equation, Units of van der Waals Constants, Significance of van der Waals Constants, Explanation of Behaviour of Real Gases by van der Waals Equation, Limitations of van der Waals Equation, Other Equations of State including Virial Equation, Applications of van der Waals Equation, Critical State (Critical Phenomena and Critical Constants), Measurement of Critical Constants, Andrew's Experiments on Critical Phenomena—Isotherm of Carbon Dioxide, Continuity of State, Van der Waals Equation and the Critical Phenomena, Reduced Equation of State and the Law of Corresponding States, Liquefaction of Gases, Viscosity of a Gas, Barometric Formula.	
2. Liquid State	44—66
Physical Properties of Liquids, Vapour Pressure, Surface Tension, Viscosity, Refractive Index and their Measurement.	
3. Solutions and Dilute Solutions	67—124
Raoult's Law, Henry's Law, Duhem-Margules Equation, Solutions of Solids in Liquids, Solutions of Gases in Liquids, Solutions of Liquids in Liquids, Study of Completely Miscible Liquids, Study of Immiscible Liquids, Study of Partially Miscible Liquids, Lowering of Vapour pressure, Osmotic pressure Elevation in boiling point, Depression in freezing point, Abnormal behaviour of electrolytes.	
4. Chemical Kinetics	125—170
Rate of Reaction, Expressing the Rate of a Reaction, Measurement of the Rate of Reaction, Factors Influencing the Rates of Reactions, Order of a Reaction and Specific Reaction Rate, Reactions of the Zero Order, Reactions of the First Order, Some Important Characteristics of First Order Reactions, Examples of the Reactions of First Order, Some Important Characteristics of First Order Reactions, Examples of the Reactions of First Order, Reactions of the Second Order, Some Important Characteristics of Second Order Reactions, Examples of the Reactions of Second Order, Reactions of the Third Order, Some Important Characteristics of Third Order Reactions, Examples of the Reactions of Third Order, Reactions of Higher Order—Cause of their Rarity, Half-Life Period, Molecularity of a Reaction, Mechanism of a Reaction, Distinction between Order and Molecularity of a Reaction, Methods for the Determination of the Order of a Reaction, Complications in the Determination of the Order of a Reaction, Opposing, Parallel and Consecutive Reactions, Surface	

Reactions, Chain Reactions, Effect of Temperature on the Rate of a Reaction (Arrhenius Equation), Theories of Reaction Rates, Kinetics of Reactions involving Ions in Solutions, Primary Salt Effect in Ionic Reactions.

- 5. Surface Chemistry (Adsorption and Catalysis)** **171—197**
Adsorption, Factors affecting the adsorption of gases by solids, Types of Adsorption, Determination of the Amount of Sorption, Adsorption Isotherms, Freundlich Adsorption Isotherm, Langmuir Adsorption Isotherm, BET Equation, Application of BET Equation in the Determination of the Surface Area of the Adsorbents, Adsorption by Solids from Solutions, Effect of Dissolved Substances on the Surface Tension of the Solvent (Adsorption at the Surfaces of Solutions), Gibbs Adsorption Equation, Applications of Gibbs Adsorption Equation, Adsorption isobars, Applications of Adsorption, Catalysis, Homogeneous and Heterogeneous Catalysis, Action of Catalytic Promoters and Inhibitors, Enzyme Catalysis, Mechanism of Enzyme Reactions - Michaelis-Menten Equation.
- 6. Thermodynamics–I (Including Thermochemistry)** **198–252**
Objectives of Thermodynamics, Limitations of Thermodynamics, Definitions of some common thermodynamics terms, Equivalence between Heat and Mechanical work, Zeroth Law of Thermodynamics, First Law of Thermodynamics, Mathematical formulation of the first law of Thermodynamics, Nature of Internal Energy, Work and Heat, Enthalpy or Heat Content, Heat Capacity, Joule-Thomson Effect, Calculation of w , q , ΔE in Isothermal Expansion of an Ideal Gas, Calculation of w , q , ΔE and ΔE in Adiabatic Expansion of an Ideal Gas, comparison of Isothermal and Adiabatic Expansion of an Ideal Gas, Calculation of w , q , ΔE and ΔE in Expansion of a Real Gas (Reversible expansion only), Variation of Heat of Reaction with Temperatures : Kirchoff's Equation. Thermochemistry, Exothermic and Endothermic Reactions Heat of Reaction, Heat of Combustion, Calorific Value, Heat of Formation, Heat of Neutralization, Heat of Solution, Heat of Hydration, Heat of Fusion, Vaporization and Sublimation, Hess's Law of Constant Heat, Summation, Bond Energy.
- 7. Thermodynamics–II** **253—290**
Second Law of Thermodynamics, Carnot Cycle, Carnot Theorem, Entropy, Entropy change in a Reversible Process, Entropy change in an Irreversible Process, Entropy change of the Universe, Entropy change for an Ideal gas under different conditions, Entropy change during phase change, Physical significance of Entropy: Measure of Disorder, Work Function (Helmholtz Free Energy) and Gibbs Free Energy, Variation of Work Function with Temperature and Volume, Variation of Free Energy with Temperature and Pressure, Maxwell Relations, Some other Thermodynamic Relations, Thermodynamic Equation of State, Criteria for Feasibility/Spontaneity of a process, Gibbs-Helmholtz Equation, Clausius-Clapeyron Equation, Elevation in Boiling Point, Depression in Freezing Point, Nernst Heat Theorem, Third Law of Thermodynamics, Importance of the Third Law.
- 8. Thermodynamics–III** **291—303**
Partial Molar Quantities, Chemical Potential (Partial Molar Free Energy), Gibbs-Duhem Equation, Variation of Chemical Potential with Temperature and Pressure, Criterion for Phase Equilibria for Multi-Component System, Criteria for Two-phase Equilibrium for One-Component System, Gibbs Adsorption Equation, Applications of Gibbs Adsorption Equation, Applications of Gibbs Adsorption Equation.

- 9. Polymers or Macromolecules** **304—316**
 General Concepts and Definitions, Classification of Polymers, Properties of Polymers, Molecular Weights of Polymers, Methods for the determination of molecular weights of polymers.
- 10. Electrochemistry** **317—380**
 Arrhenius theory of Ionization of Electrolytic Dissociation, Factors on which the Degree of Dissociation Depends, Evidence in favour of Arrhenius Theory, Electrolytic Conductance, Resistance, Specific, Equivalent and Molar Conductance, Cell Constant, Ostwald's Dilution Law, Limitations of Arrhenius Theory, Explanation of the Anomalous Behaviour of Strong Electrolytes-Interionic Effects-Debye-Huckel Theory. Migration of Ions, Migration Velocity of Ions and Change in concentration, Hittorf's Theoretical Device, Transport Number Determination of Transport Number, Factors on which Transport Number depends Applications of Kohlrausch's Law. Applications of Conductance Measurements, Conductometric Titrations, Buffer Solutions and Buffer Mixture, Neutralisation, Salt Hydrolysis, Hydrolysis Constant and Degree of Hydrolysis and pH for solutions of different types of salts in terms of dissociation constant of the weak acid or weak base involved, Electrolysis, Faraday's Laws.
- 11. Electrochemical Cells** **382—436**
 What is an Electrochemical Cell or Galvanic Cell? What is an Electrochemical Cell?, Representation of an Electrochemical Cell, Electrode Potential, EMF of Cell and its Measurement, Standard Cell, Reversible and Irreversible Cell, Reversible Electrodes, Relationship between Electrical Energy and Chemical Energy, Thermodynamics and EMF (i.e Calculations of, and from EMF Data), Measurement of Electrode Potential, Electrochemical Series, Applications of Electrochemical Series, Activity and Activity Coefficient, Standard State, Thermodynamics of a Reversible Cell-Relationship of the E.M.F. with the Activities/Concentrations of the Reactants and Products-Nernst equation for EMF of a Cell, Thermodynamics of Single Electrode Potential - Effect of Concentration of Electrode Potential- Nernst Equation for Electrode Potential, Concentration Cell, Types of Concentration Cells, EMF of Concentration Cell, Liquid Junction Potential, Determination of Activities and Activity Coefficients from EMF Measurements, Application of EMF measurements, Fe^{2+} - $\text{K}_2\text{Cr}_2\text{O}_7$, and Fe^{2+} - KMnO_4 titrations, Concentration Polarization, Polarography, Corrosion-types, Theories and Methods of Prevention.
- 12. Photochemistry** **437—457**
 Laws Governing Absorption of Light, Laws Governing Photochemical Reaction i.e. Laws of Photochemistry, Interpretation of Einsteins Law - Introduction of the term 'Quantum Efficiency', Experimental Determination of Quantum yield of a Photochemical Reaction. Some examples of Photochemical Reactions, Luminescence, Fluorescence and Phosphorescence in terms of excitation of Electrons, Photosensitization, Photo-Inhibitors, Photochemical Equilibrium or Photostationary State.
- 13. Quantum Mechanics** **458—490**
 Black Body and Black Body Radiation, Kirchoff's Law, Spectral Distribution of Black Body Radiation, Explanation of Spectral Distribution on the Basis of Classical Mechanics, Planck's Radiation Law, Schrodinger Wave Equation, Eigen Values and Eigen Functions (or Wave Functions) Born interpretation of the Wave Function-

Significance of the Wave Function, Normalized and Orthogonal Wave Function, Operators, Postulates of Quantum Mechanics, Derivation of Schrodinger Wave Equation on the Basis of Postulates of Quantum Mechanics, Particle in a Box.

- 14. Statistical Mechanics** **491—527**
The Statistical Method, The State of System, Stirling Formula for N, Ensembles Postulates of Statistical Mechanics Maxwell-Boltzmann Distribution Law/ Boltzmann Distribution Law, Statistical Thermodynamics, Relationship between Entropy and Probability, Entropy and Disorder, The Partition Function, Expressions for Thermodynamic Functions in Terms of Partition Function, Separation of Partition Function into Translational Rotational, Vibrational and Electronic Partition Functions, Statistical Calculation of Thermodynamic Functions, Thermodynamic Properties of an Ideal Monoatomic Gas from Partition Function.
- 15. Distribution Law** **528—550**
Definition of Distribution Law, Conditions under which distribution Law is valid, Thermodynamic Derivation of The Distribution Law, Change in the Molecular State and Distribution Law, Applications of Distribution Law.
- 16. Phase Rule** **551—577**
Definition of Phase Rule, Explanation of the terms involved, Deduction of the Phase Rule, Phase Diagrams, The Water System, Carbon Dioxide System, Sulphur system, Application of Phase Rule to Two-Component Systems, Types of Two-Components Systems involving Solid, Liquid Equilibria, General Discussion of the Phase Diagram of Two-Component Systems (Solids) That are miscible in the Liquid Phase, Experimental Determination of the Phase Diagrams of Two-Component Systems, Pattinson's Process for the Desilverisation of Lead, Zinc-Cadmium System Lead-silver system, Potassium Iodide - Water System, Magnesium-Zinc System, Effect of Cooling Potassium Iodide Solution, Freezing Mixtures, Ferric Chloride - Water System, Isothermal evaporation of an unsaturated ferric chloride solution, Sodium Sulphate - Water System.
- 17. Solid State** **578—608**
Solids and their Classification, Points of Difference between Crystalline and Amorphous Solids, Classification of Crystalline Solids, Crystal Structures of Sodium Chloride, Cesium Chloride, Zinc Blende, CaF₂, Na₂O, Packing of Particles, Body-centred Cubic Structure, Tetrahedral and Octahedral voids, Coordination Number, Radium Ratio, Some Terms used in Crystallography, Law of Constancy of Interfacial Angles, Elements of Symmetry, Crystallographic Axes and Axial Ratios, Law of Rational Indices, Identification/Designation of Crystal Planes and Faces, Crystal Systems, Isomorphism and Polymorphism, Space Lattice and Unit Cell, Bravais Lattices, Space Groups, X-Ray Diffraction by Crystals: Study of the Internal Structure Bragg's method, Laue's Method and Powder Method, Structure of Sodium Chloride, Liquid Crystals.
- 18. Physical Properties and Molecular Structure (Including Spectroscopy)** **609—666**
Optical Rotation, Dipole Moment, Magnetic Susceptibility, Molecular Spectroscopy, Absorption and Emission Spectroscopy, Types of Molecular Spectra, Selection Rules, Widths and Intensities of the Spectral Lines, Pure Rotational Spectra of Diatomic Molecules (Infrared Spectra) Raman Spectra, Electronic Spectra, Width and Inten-

sity of Spectral Lines, Born-Oppenheimer Approximation, Frank-Condon Principle, Electronic transitions in σ , π and n M.O. Nuclear Magnetic Resonance (NMR) Spectroscopy, Spin-spin Interaction, Numerical Problems on Rotational, Vibrational, Raman and NMR Spectroscopy.

- 19. Chemical Equilibrium** **667—686**
Reversible reactions, Characteristics of chemical equilibrium, Law of mass action, Law of chemical equilibrium, Vant Hoff's reaction isotherm, Thermodynamic derivation of law of mass action (chemical equilibrium), standard free energy change and equilibrium constant, relation between K_c and K_p , Temperature dependence of equilibrium constant, Vant Hoff's equation, hydrogen-iodine equilibrium, dissociation of PCl_5 , homogeneous and heterogeneous equilibria, dissociation of calcium carbonate, reaction of steam on heated iron, dissociation of ammonium hydrogen sulphide, Le Chatelier principle.
- 20. Colloidal State** **687—703**
Difference between true solution, Colloidal solution and suspension, Phases of colloidal solution, Classification of Colloids, Difference between lyophilic and lyophobic colloids, miscelles, preparation of colloids, dialysis, properties of colloidal solution, Tyndall effect, sedimentation, electrophoresis, Origin of charge, double layer theory, protective colloids, gold number, emulsions, gels, determination of molecular mass of colloids of colloidal particles, applications of colloids.
- 21. Molecular Symmetry and Group Theory** **704—714**
Symmetry Elements, Symmetry Operations, Group Postulates, Abelian and non-Abelian Groups, Point Groups, Characters of Symmetry Operations, Reps, Irreps, Grand Orthogonality Theorem, Construction of Character Table, Problems based on above.
- 22. Mathematical Concepts and Computers** **715—758**
Mathematical Concepts, Two systems of logarithm, Linear graphs and calculations of slopes, Differentiation, Maxima and Minima, Partial Differentiation, Partial Derivatives of Higher Order, Mutually Exclusive Events, Introduction to computers, Hardware and software, Binary system, Operating system.
- Appendix 1 : Laws of Logarithms** **759—759**
- Appendix 2 : Mathematical Relations** **760—761**
- Some Useful Tables** **762—764**
- Note : For topics on structure of atom (Classical and wave-mechanical approach), nuclear chemistry, chemical bonding and acids and bases, consult author's success guide Inorganic Chemistry.

1

GASEOUS STATE

Q. 1. Describe important characteristics of gases.

Ans. Some important characteristics of gases are given below:

- (i) They fill up the whole vessel in which they are placed.
- (ii) They exert pressure on the walls of the vessel in which they are taken.
- (iii) They can be compressed by applying the pressure.
- (iv) Cooling and compression of the gas brings about its liquefaction.
- (v) They exhibit the property of intermixing with one another—a property known as *diffusion*.
- (vi) At ordinary conditions of temperature and pressure, their densities are low.

Q.2. Discuss Boyle's law and Charles' law of gases. (Kumaon 2000; Himachal 2000)

Ans. Boyle's law: It states as follows:

Temperature remaining constant, the volume of a given mass of a gas is inversely proportional to its pressure.

Thus, if V is the volume of the gas at pressure P , then

$$V \propto \frac{1}{P} \quad (\text{At constant temperature})$$

or

$$P V = \text{constant}$$

If V_1 is the volume of the gas at pressure P_1 and V_2 is the volume at pressure P_2 , then

$$P_1 \times V_1 = P_2 \times V_2$$

Charles law:

Pressure remaining constant, the volume of a given mass of a gas increases or decreases by $1/273$ of its volume at 0°C for every degree rise or fall of temperature.

Thus if V_0 is the volume of a gas at 0°C and V_t is the volume at $t^\circ\text{C}$, then mathematically, the law may be written as

$$\begin{aligned} V_t &= V_0 + \frac{V_0}{273} \times t \\ &= V_0 \left(1 + \frac{t}{273} \right) \\ &= V_0 \left(\frac{273+t}{273} \right) \end{aligned} \quad \dots(1.1)$$

Thus at $t = -273^{\circ}\text{C}$

$$V_t = V_0 \left(\frac{273 - 273}{273} \right) \\ = 0$$

This means that at -273°C , the volume of the gas is reduced to zero *i.e.*, the gas ceases to exist; in fact, the gas gets liquefied. *This temperature (-273°C) at which the gas ceases to exist is called **Absolute Zero**.* It is represented by 0 K. Thus

$$-273^{\circ}\text{C} = 0 \text{ K}$$

or $0^{\circ}\text{C} = 273 \text{ K}$

This means that to convert $t^{\circ}\text{C}$ into K, we should add 273

$$\therefore t^{\circ}\text{C} = (t + 273) \text{ K} = T \text{ K}$$

Putting $273 + t^{\circ}\text{C} = T \text{ K}$ in equation (1.1), we get

$$V_t = V_0 \frac{T}{273}$$

This implies that

$$V_t \propto T \text{ if pressure remains constant}$$

or simply, $V \propto T$ if pressure remains constant.

Thus the Charles law may also be defined as follows:

Pressure remaining constant, the volume of a given mass of a gas is directly proportional to its absolute temperature.

Mathematically, the law may also be written as

$$\frac{V}{T} = \text{constant, if pressure is kept constant}$$

or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ under constant pressure

where V_1 is the volume of the gas at pressure P_1 and V_2 is the volume at pressure P_2 .

Q.3. State and explain Avogadro's law.

(Meerut 2000)

Ans. Avogadro's law may be defined as under:

Under similar conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.

In other words, if temperature and pressure are kept constant, the volume (V) of a gas is directly proportional to the number of molecules (N) present in the gas. Mathematically,

$$V \propto N \text{ (At constant } P \text{ and } T)$$

It has been found that one mole of every gas (*i.e.*, 22.4 litres at *N.T.P.*) contains 6.023×10^{23} molecules. This number is known as **Avogadro's Number** and is usually represented by N_0 .

Obviously, the number of moles (n) of a gas may be calculated as follows:

$$n = \frac{N}{N_0}$$

As N_0 is a constant quantity, we can say that

$$n \propto N$$

Hence the equation, $V \propto N$, may also be written as:

$$V \propto n, \text{ where } n \text{ is the number of moles of the gas.}$$

Q. 4. How is combined gas equation obtained?

Ans. It is obtained by the combination of Boyle's law, Charles' law and Avogadro's law.

According to *Boyle's law*,

$$V \propto \frac{1}{P} \quad \text{if } T \text{ is kept constant} \quad \dots(1.2)$$

According to *Charles law*,

$$V \propto T \text{ if } P \text{ is kept constant} \quad \dots (1.3)$$

According to *Avogadro's law*,

$$V \propto n \text{ if } T \text{ and } P \text{ are kept constant} \quad \dots (1.4)$$

Combining equations (1.2), (1.3) and (1.4), we get

$$V \propto \frac{1}{P} \times T \times n$$

or
$$V = R \times \frac{1}{P} \times T \times n$$

where R is a constant of proportionality and is called *Gas Constant*.

or
$$PV = nRT \text{ for } n \text{ moles of the gas.}$$

This equation is known as *Gas Equation*.

Q. 5. Give the postulates of kinetic theory of gases.

(*G. Nanakdev 2000; Nagpur 2002; Lucknow 2002; Guwahati 2006; Vidyasagar 2007; Purvanchal 2007*)

- Ans.** (i) Every gas is made up of a large number of extremely small particles called molecules. All the molecules of a particular gas are identical in mass and size and differ from gas to gas.
- (ii) The molecules of a gas are separated from each other by large distances so that the actual volume of the molecules is negligible as compared to the total volume of the gas.
- (iii) The distances of separation between the molecules are so large that the forces of attraction or repulsion between them are negligible.
- (iv) The molecules are supposed to be moving continuously in different directions with different velocities. Hence, they keep on colliding with one another (called molecular collisions) as well as on the walls of the containing vessel.
- (v) The pressure exerted on the walls of the containing vessel is due to the bombardment of the molecules on the walls of the containing vessel.
- (vi) Since the molecules are moving with different velocities, they possess different kinetic energies. However, the average kinetic energy of the molecules of a gas is directly proportional to the absolute temperature of the gas.
- (vii) Molecules are supposed to be perfectly elastic hard spheres so that no energy is lost when the molecules collide with one another or with the walls of the vessel.
- (viii) The force of gravitation on the molecules is also supposed to be negligible.

Q. 6. Derive kinetic gas equation $PV = \frac{1}{3} mnu^2$.

(*G. Nanakdev, 2000; Lucknow 2002; Garhwal 2010*)

Ans. Consider a cubical vessel containing the gas (Fig. 1.1). Suppose,

Total number of molecules present in the gas = n ,

Mass of each molecule of the gas = m ,

Length of each side of the cube = l cm.

According to the kinetic theory of gases, the molecules of the gas are moving in different

directions with different velocities. Consider any one molecule, moving with a velocity ϑ_1 cm/sec in any direction. The velocity can be resolved into three mutually perpendicular components ϑ_x , ϑ_y and ϑ_z parallel to X-axis, Y-axis, and Z-axis respectively as shown in Fig. 1.1. Then mathematically,

$$\vartheta_1^2 = \vartheta_x^2 + \vartheta_y^2 + \vartheta_z^2 \quad \dots(i)$$

Now, consider the motion of the molecule due to component ϑ_x only. Due to this component, the molecule will strike the opposite faces A and B which are at right angles to the X-axis.

Momentum of molecule due to component ϑ_x just before it strikes the face A

$$= m\vartheta_x$$

As the molecules are supposed to be perfectly elastic, after colliding the face A , the molecule will return with the same velocity. As the direction has changed, the velocity will now be taken as $-\vartheta_x$. Hence

Momentum of the molecule due to component ϑ_x just after it strikes the face A

$$= m \times (-\vartheta_x) = -m\vartheta_x$$

\therefore Change of the momentum of the molecule in *one collision* on the face A due to component ϑ_x

$$= m\vartheta_x - (-m\vartheta_x) = 2m\vartheta_x$$

Now let us calculate the number of collisions which take place on the face A in one second due to component ϑ_x .

For next collision on the face A , the molecule has to travel from face A to B and then back from B to A i.e., a total distance of

$$l + l = 2l \text{ cm}$$

As the component being considered is ϑ_x cm/sec, this means that the distance travelled by the molecule in one second is ϑ_x cm.

\therefore Number of collisions which take place on the face A in one second due to component ϑ_x

$$= \frac{\vartheta_x}{2l}$$

As the change of momentum in one collision is $2m\vartheta_x$

\therefore Change of momentum of the molecule in one second due to component ϑ_x for collisions on the face A

$$= 2m\vartheta_x \times \frac{\vartheta_x}{2l} = \frac{m\vartheta_x^2}{l}$$

Similarly, change of momentum of the molecule in one second due to component ϑ_x for collisions on the face B

$$= \frac{m\vartheta_x^2}{l}$$

\therefore Change of momentum of the molecule in one second due to component ϑ_x for collisions on the opposite faces perpendicular to X-axis.

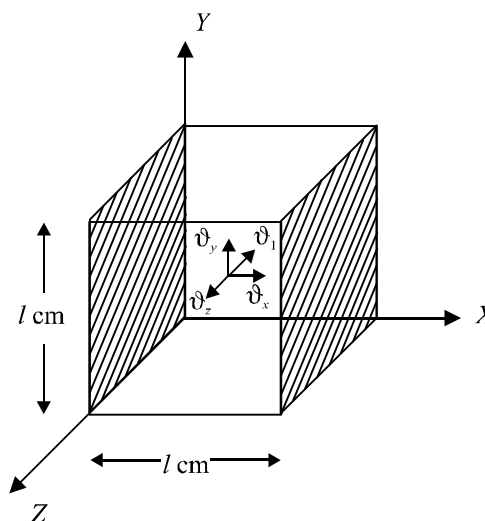
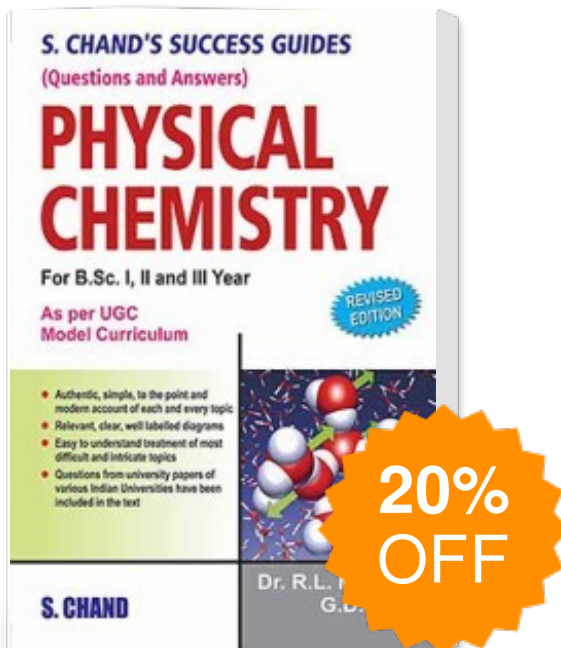


Fig. 1.1. A cubical vessel containing n molecules of the gas.

SChand Success Guide In Physical Chemistry



Publisher : SChand Publications ISBN : 9788121918817

Author : Gaurav Madan

Type the URL : <http://www.kopykitab.com/product/10734>



Get this eBook