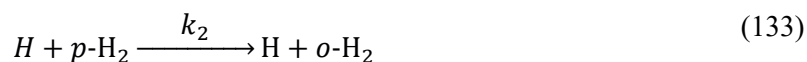


❖ General Treatment of Chain Reactions (Ortho-Para Hydrogen Conversion and Hydrogen-Bromine Reactions)

In this section, we will discuss the general treatment of some common chain reactions like ortho-para hydrogen conversion and hydrogen-bromine reactions. To do so, we may also recall some concepts discussed earlier in this chapter.

➤ Ortho-Para Hydrogen Conversion

The ortho-hydrogen can convert into para-hydrogen and can easily be measured in the temperature range of 700–800°C. The conversion is completely homogeneous in nature and the order of the conversion is 1.5 as total. The widely accepted mechanism is given below.



The equilibrium constant for the above-mentioned molecular-atomic equilibria given by equation (132) can be written as

$$K = \frac{[\text{H}]^2}{[p\text{-H}_2]} \quad (134)$$

$$[\text{H}]^2 = K[p\text{-H}_2] \quad (135)$$

$$[\text{H}] = K^{1/2} [p\text{-H}_2]^{1/2} \quad (136)$$

The net rate of conversion of $p\text{-H}_2$ must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[p\text{-H}_2]}{dt} = k_2 [p\text{-H}_2] [\text{H}] \quad (137)$$

After using the value of $[\text{H}]$ from equation (136) in equation (137), we get

$$\frac{d[p\text{-H}_2]}{dt} = k_2 [p\text{-H}_2] K^{1/2} [p\text{-H}_2]^{1/2} \quad (137)$$

or

$$\frac{d[p\text{-H}_2]}{dt} = k_2 K^{1/2} [p\text{-H}_2]^{3/2} \quad (137)$$

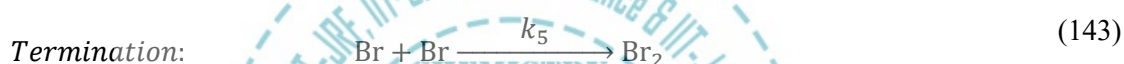
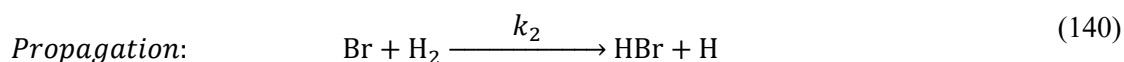
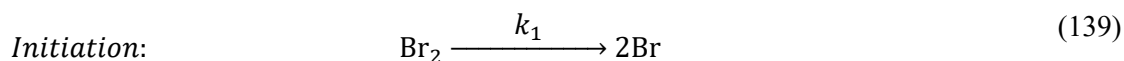
The overall activation energy of the conversion is $E = E_2 + D/2$ where E_2 is the activation energy of the second step while D is the dissociation energy of dihydrogen molecule.

➤ **Hydrogen-Bromine Reactions**

The hydrogen-bromine or the $\text{H}_2\text{-Br}_2$ reaction is a typical case of stationary type chain reactions ($n = 1$) for which the overall reaction can be written as given below.



Furthermore, the elementary steps for the same can be proposed as



The net rate of formation of HBr must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \quad (144)$$

Now, in order to obtain the overall rate expression, we need to apply the steady-state approximation on the H and Br first i.e.

$$\frac{d[\text{H}]}{dt} = 0 = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \quad (145)$$

Similarly,

$$\frac{d[\text{Br}]}{dt} = 0 = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 \quad (146)$$

Taking negative both side of equation (145), we have

$$-k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] = 0 \quad (147)$$

Using the above result in equation (146), we get

$$2k_1[\text{Br}_2] + 0 - 2k_5[\text{Br}]^2 = 0 \quad (148)$$

$$2k_5[\text{Br}]^2 = 2k_1[\text{Br}_2] \quad (149)$$

$$[Br] = \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} \quad (150)$$

Similarly, rearranging equation (145) again

$$k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2] \quad (151)$$

$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} \quad (152)$$

Now using the value of $[Br]$ from equation (150), the above equation takes the form

$$[H] = \frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad (153)$$

Now rearranging equation (145) again in different mode i.e.

$$k_2[Br][H_2] - k_4[H][HBr] = k_3[H][Br_2] \quad (154)$$

Using the above result in equation (144), we have

$$\frac{d[HBr]}{dt} = k_3[H][Br_2] + k_3[H][Br_2] \quad (155)$$

$$\frac{d[HBr]}{dt} = 2k_3[H][Br_2] \quad (156)$$

After putting the value of $[H]$ from equation (152), the equation (156) takes the form

$$\frac{d[HBr]}{dt} = \frac{2k_3k_2(k_1/k_5)^{1/2}[Br_2]^{3/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad (157)$$

Taking $k_3[Br_2]$ as common in the denominator and then canceling out the same form numerator, we get

$$\frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_4/k_3)[HBr]/[Br_2]} \quad (158)$$

Now consider two new constants as

$$k' = 2k_2(k_1/k_5)^{1/2} \quad \text{and} \quad k'' = k_4/k_3 \quad (159)$$

Using in equation (158), we get

$$\frac{d[HBr]}{dt} = \frac{k'[Br_2]^{1/2}[H_2]}{1 + k''[HBr]/[Br_2]} \quad (160)$$

The initial reaction rate expression can be obtained by neglecting $[HBr]$ i.e. $1 + k''[HBr]/[Br_2] \approx 1$ as

$$\left[\frac{d[\text{HBr}]}{dt} \right]_0 = k' [\text{Br}_2]^{1/2} [\text{H}_2]_0 \quad (161)$$

Hence, the order of the hydrogen-bromine reaction in the initial stage will be 1.5 only i.e. first-order w.r.t. hydrogen and half w.r.t. bromine.

However, if the initiation occurs by the photon of the incident light, the expression for the overall rate can slightly be modified. Recall the initiation step again via photochemical decomposition i.e.



Then, the quantum yield for this primary change will be

$$\phi = \frac{-d[\text{Br}_2]/dt}{I_{ab}} \quad (163)$$

Where I_{ab} is the intensity of absorbed radiation. Since $\phi = 1$ for primary process, we have

$$1 = \frac{-d[\text{Br}_2]/dt}{I_{ab}} \quad (164)$$

$$-\frac{d[\text{Br}_2]}{dt} = I_{ab} \quad (165)$$

$$\frac{d[\text{Br}_2]}{dt} = k[\text{Br}_2] = I_{ab} \quad (166)$$

For the rate of formation of Br, we have

$$-\frac{d[\text{Br}_2]}{dt} = +\frac{1}{2} \frac{d[\text{Br}]}{dt} = k[\text{Br}_2] = I_{ab} \quad (167)$$

$$\frac{d[\text{Br}]}{dt} = 2k[\text{Br}_2] = 2I_{ab} \quad (168)$$

Now since $2k_1[\text{Br}_2] = 2I_{ab}$, then

$$k_1^{1/2} [\text{Br}_2]^{1/2} = (I_{ab})^{1/2} \quad (169)$$

Using the above result in equation (158), we get

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2(I_{ab}/k_5)^{1/2}[\text{H}_2]}{1 + (k_4/k_3)[\text{HBr}]/[\text{Br}_2]} \quad (170)$$

Hence, the rate of hydrogen-bromine reaction is directly proportional to the square root of the intensity of absorbed radiation.

LEGAL NOTICE

This document is an excerpt from the book entitled “A Textbook of Physical Chemistry – Volume 1 by Mandeep Dalal”, and is the intellectual property of the Author/Publisher. The content of this document is protected by international copyright law and is valid only for the personal preview of the user who has originally downloaded it from the publisher’s website (www.dalalinstitute.com). Any act of copying (including plagiarizing its language) or sharing this document will result in severe civil and criminal prosecution to the maximum extent possible under law.



This is a low resolution version only for preview purpose. If you want to read the full book, please consider buying.

Buy the complete book with TOC navigation, high resolution images and no watermark.

Home

CLASSES

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM

Want to study chemistry for CSIR UGC - NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

[READ MORE](#)

BOOKS

Publications

Are you interested in books (Print and Ebook) published by Dalal Institute ?

[READ MORE](#)

VIDEOS

Video Lectures

Want video lectures in chemistry for CSIR UGC - NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

[READ MORE](#)

Home: <https://www.dalalinstitute.com/>

Classes: <https://www.dalalinstitute.com/classes/>

Books: <https://www.dalalinstitute.com/books/>

Videos: <https://www.dalalinstitute.com/videos/>

Location: <https://www.dalalinstitute.com/location/>

Contact Us: <https://www.dalalinstitute.com/contact-us/>

About Us: <https://www.dalalinstitute.com/about-us/>

Postgraduate Level Classes (NET-JRF & IIT-GATE)

Admission

[Regular Program](#)
[Test Series](#)

[Distance Learning](#)
[Result](#)

Undergraduate Level Classes (M.Sc Entrance & IIT-JAM)

Admission

[Regular Program](#)
[Test Series](#)

[Distance Learning](#)
[Result](#)

A Textbook of Physical Chemistry – Volume 1

“A Textbook of Physical Chemistry – Volume 1 by Mandeep Dalal” is now available globally; including India, America and most of the European continent. Please ask at your local bookshop or get it online here.

[READ MORE](#)

Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.

[Sign Up](#)

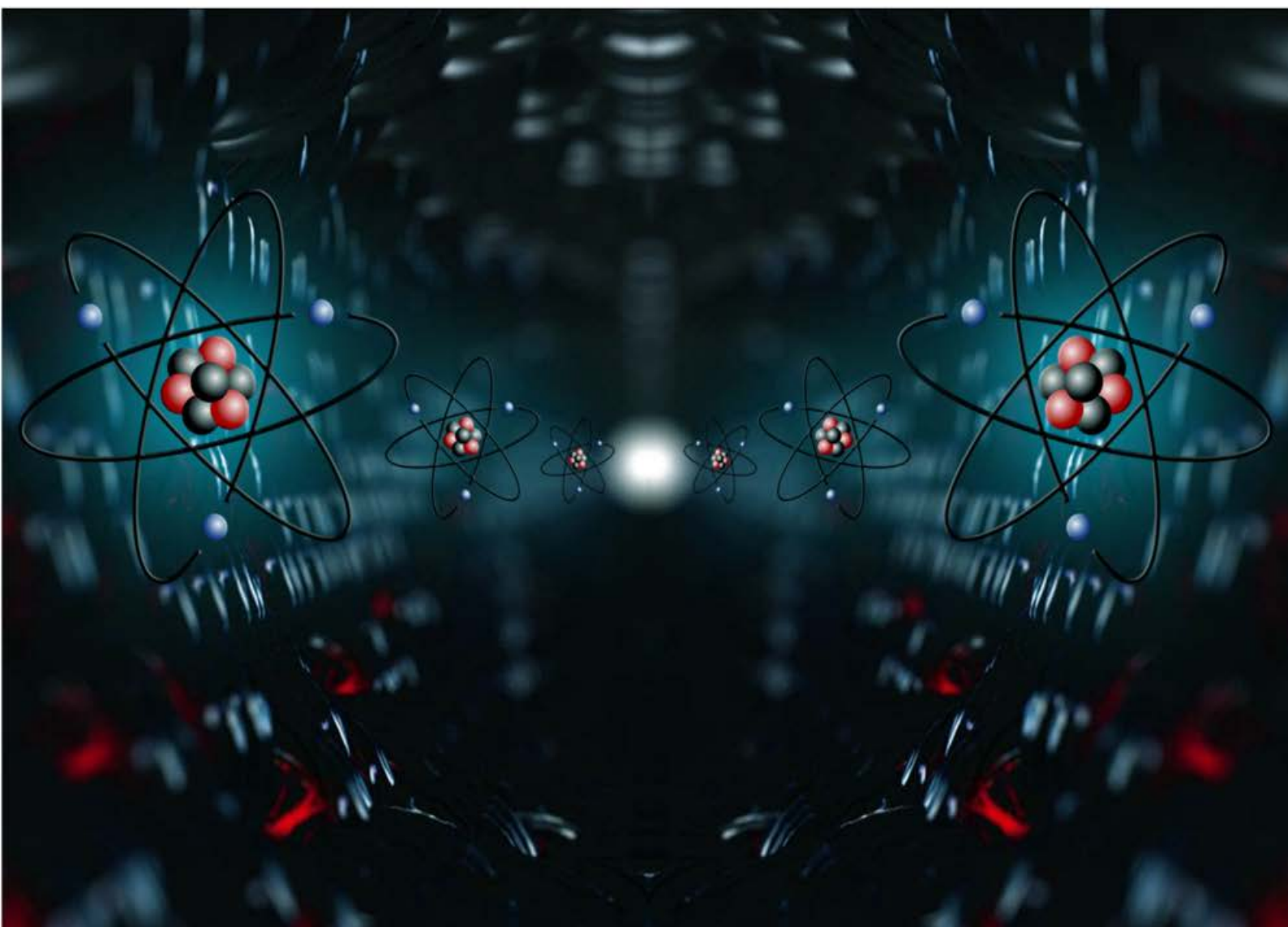
International
Edition



A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

Table of Contents

CHAPTER 1	11
Quantum Mechanics – I	11
❖ Postulates of Quantum Mechanics	11
❖ Derivation of Schrodinger Wave Equation.....	16
❖ Max-Born Interpretation of Wave Functions	21
❖ The Heisenberg's Uncertainty Principle.....	24
❖ Quantum Mechanical Operators and Their Commutation Relations.....	29
❖ Hermitian Operators – Elementary Ideas, Quantum Mechanical Operator for Linear Momentum, Angular Momentum and Energy as Hermitian Operator	52
❖ The Average Value of the Square of Hermitian Operators	62
❖ Commuting Operators and Uncertainty Principle (x & p ; E & t).....	63
❖ Schrodinger Wave Equation for a Particle in One Dimensional Box.....	65
❖ Evaluation of Average Position, Average Momentum and Determination of Uncertainty in Position and Momentum and Hence Heisenberg's Uncertainty Principle.....	70
❖ Pictorial Representation of the Wave Equation of a Particle in One Dimensional Box and Its Influence on the Kinetic Energy of the Particle in Each Successive Quantum Level	75
❖ Lowest Energy of the Particle	80
❖ Problems	82
❖ Bibliography	83
CHAPTER 2	84
Thermodynamics – I	84
❖ Brief Resume of First and Second Law of Thermodynamics.....	84
❖ Entropy Changes in Reversible and Irreversible Processes.....	87
❖ Variation of Entropy with Temperature, Pressure and Volume	92
❖ Entropy Concept as a Measure of Unavailable Energy and Criteria for the Spontaneity of Reaction	94
❖ Free Energy, Enthalpy Functions and Their Significance, Criteria for Spontaneity of a Process ...	98
❖ Partial Molar Quantities (Free Energy, Volume, Heat Concept).....	104
❖ Gibb's-Duhem Equation.....	108
❖ Problems	111
❖ Bibliography	112

CHAPTER 3	113
Chemical Dynamics – I.....	113
❖ Effect of Temperature on Reaction Rates.....	113
❖ Rate Law for Opposing Reactions of 1st Order and 2nd Order.....	119
❖ Rate Law for Consecutive & Parallel Reactions of 1st Order Reactions	127
❖ Collision Theory of Reaction Rates and Its Limitations	135
❖ Steric Factor.....	141
❖ Activated Complex Theory	143
❖ Ionic Reactions: Single and Double Sphere Models	147
❖ Influence of Solvent and Ionic Strength.....	152
❖ The Comparison of Collision and Activated Complex Theory	157
❖ Problems.....	158
❖ Bibliography.....	159
CHAPTER 4	160
Electrochemistry – I: Ion-Ion Interactions	160
❖ The Debye-Huckel Theory of Ion-Ion Interactions	160
❖ Potential and Excess Charge Density as a Function of Distance from the Central Ion.....	168
❖ Debye-Huckel Reciprocal Length	173
❖ Ionic Cloud and Its Contribution to the Total Potential	176
❖ Debye-Huckel Limiting Law of Activity Coefficients and Its Limitations.....	178
❖ Ion-Size Effect on Potential.....	185
❖ Ion-Size Parameter and the Theoretical Mean - Activity Coefficient in the Case of Ionic Clouds with Finite-Sized Ions.....	187
❖ Debye-Huckel-Onsager Treatment for Aqueous Solutions and Its Limitations.....	190
❖ Debye-Huckel-Onsager Theory for Non-Aqueous Solutions.....	195
❖ The Solvent Effect on the Mobility at Infinite Dilution	196
❖ Equivalent Conductivity (Λ) vs Concentration $C^{1/2}$ as a Function of the Solvent	198
❖ Effect of Ion Association Upon Conductivity (Debye-Huckel-Bjerrum Equation)	200
❖ Problems.....	209
❖ Bibliography.....	210
CHAPTER 5	211
Quantum Mechanics – II	211
❖ Schrodinger Wave Equation for a Particle in a Three Dimensional Box	211

❖ The Concept of Degeneracy Among Energy Levels for a Particle in Three Dimensional Box	215
❖ Schrodinger Wave Equation for a Linear Harmonic Oscillator & Its Solution by Polynomial Method	217
❖ Zero Point Energy of a Particle Possessing Harmonic Motion and Its Consequence	229
❖ Schrodinger Wave Equation for Three Dimensional Rigid Rotator.....	231
❖ Energy of Rigid Rotator	241
❖ Space Quantization.....	243
❖ Schrodinger Wave Equation for Hydrogen Atom: Separation of Variable in Polar Spherical Coordinates and Its Solution	247
❖ Principal, Azimuthal and Magnetic Quantum Numbers and the Magnitude of Their Values.....	268
❖ Probability Distribution Function.....	276
❖ Radial Distribution Function	278
❖ Shape of Atomic Orbitals (<i>s</i> , <i>p</i> & <i>d</i>).....	281
❖ Problems.....	287
❖ Bibliography	288
CHAPTER 6	289
Thermodynamics – II.....	289
❖ Clausius-Clapeyron Equation.....	289
❖ Law of Mass Action and Its Thermodynamic Derivation	293
❖ Third Law of Thermodynamics (Nernst Heat Theorem, Determination of Absolute Entropy, Unattainability of Absolute Zero) And Its Limitation.....	296
❖ Phase Diagram for Two Completely Miscible Components Systems	304
❖ Eutectic Systems (Calculation of Eutectic Point).....	311
❖ Systems Forming Solid Compounds A_xB_y with Congruent and Incongruent Melting Points	321
❖ Phase Diagram and Thermodynamic Treatment of Solid Solutions.....	332
❖ Problems.....	342
❖ Bibliography	343
CHAPTER 7	344
Chemical Dynamics – II	344
❖ Chain Reactions: Hydrogen-Bromine Reaction, Pyrolysis of Acetaldehyde, Decomposition of Ethane.....	344
❖ Photochemical Reactions (Hydrogen-Bromine & Hydrogen-Chlorine Reactions).....	352
❖ General Treatment of Chain Reactions (Ortho-Para Hydrogen Conversion and Hydrogen-Bromine Reactions).....	358

❖ Apparent Activation Energy of Chain Reactions	362
❖ Chain Length	364
❖ Rice-Herzfeld Mechanism of Organic Molecules Decomposition (Acetaldehyde)	366
❖ Branching Chain Reactions and Explosions (H_2-O_2 Reaction)	368
❖ Kinetics of (One Intermediate) Enzymatic Reaction: Michaelis-Menten Treatment	371
❖ Evaluation of Michaelis's Constant for Enzyme-Substrate Binding by Lineweaver-Burk Plot and Eadie-Hofstee Methods	375
❖ Competitive and Non-Competitive Inhibition	378
❖ Problems	388
❖ Bibliography	389
CHAPTER 8	390
Electrochemistry – II: Ion Transport in Solutions	390
❖ Ionic Movement Under the Influence of an Electric Field	390
❖ Mobility of Ions	393
❖ Ionic Drift Velocity and Its Relation with Current Density	394
❖ Einstein Relation Between the Absolute Mobility and Diffusion Coefficient	398
❖ The Stokes-Einstein Relation	401
❖ The Nernst-Einstein Equation	403
❖ Walden's Rule	404
❖ The Rate-Process Approach to Ionic Migration	406
❖ The Rate-Process Equation for Equivalent Conductivity	410
❖ Total Driving Force for Ionic Transport: Nernst-Planck Flux Equation	412
❖ Ionic Drift and Diffusion Potential	416
❖ The Onsager Phenomenological Equations	418
❖ The Basic Equation for the Diffusion	419
❖ Planck-Henderson Equation for the Diffusion Potential	422
❖ Problems	425
❖ Bibliography	426
INDEX	427



Mandeep Dalal

(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)

Founder & Director, Dalal Institute

Contact No: +91-9802825820

Homepage: www.mandeepdalal.com

E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands).

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV

ISBN: 978-81-938720-1-7



9 788193 872017 >

MRP: Rs 800.00

D DALAL
INSTITUTE

Main Market, Sector-14, Rohtak, Haryana-124001

(+91-9802825820, info@dalalinstitute.com)

www.dalalinstitute.com