

### ❖ Einstein Relation Between the Absolute Mobility and Diffusion Coefficient

Since it is a well-known fact that the diffusion of ions is simply the zig-zag walking of ions from a high-numbered region to a low-numbered region. In other words, we can say the ionic diffusion is the result of a concentration gradient in which a particular type of ions travel from a high concentration region towards a low concentration region until a homogeneity in concentration is reached. On the other hand, the conduction or the ionic migration is a result of the drift velocity component imparted to the ions by the electric force. However, it is important here to recall the fact that this velocity component does not stop the zig-zag walk of diffusion but actually gets superimposed on it. Albert Einstein understood this and formulated a relation between ionic mobility ( $\bar{u}_{abs}$ ) and diffusion coefficient ( $D$ ).

Now, since the conduction, as well as the diffusion, are irreversible processes, they cannot be treated by equilibrium statistical mechanics or by the equilibrium thermodynamics. However, the situation can be considered as a pseudo-equilibrium if the conduction and diffusion take place in the opposite direction but with same rates. To do so, consider an electrolytic solution of salt MX in which some of the cations are radioactive in nature. Now assume that  $M^+$  ions are present in higher concentrations in one region and in lower concentration in some other region. In other words, the tracer ions are present with a concentration gradient. According to Fick's law of diffusion, the overall diffusion flux ( $J_D$ ) must be

$$j_D = -D \frac{dc}{dx} \quad (39)$$

After applying the electric field, the tracer ions will feel the field and will start to move towards the opposite electrode. The drift velocity can be given as

$$v_d = \bar{u}_{abs} \vec{F} \quad (40)$$

The current density produced by this drift velocity is

$$J = z_+ c F v_d \quad (41)$$

The conduction flux can be obtained by dividing the current density by charge carried by one mole of ions i.e.

$$j_c = \frac{z_+ c F v_d}{z_+ F} \quad (42)$$

or

$$j_c = c v_d \quad (43)$$

After using the expression of drift velocity from equation (40) in the above expression, we get

$$j_c = c \bar{u}_{abs} \vec{F} \quad (44)$$

The strength of the applied electric field is varied in such a way that the conduction flux and diffusion flux are equal and opposite. Mathematically, it should be like

$$j_c = -j_D \quad (45)$$

$$j_c + j_D = 0 \quad (46)$$

After using values of  $j_D$  and  $j_c$  from equations (39, 44) in the above expression, we get

$$c \bar{u}_{abs} \vec{F} - D \frac{dc}{dx} = 0 \quad (47)$$

or

$$\frac{dc}{dx} = \frac{c \bar{u}_{abs} \vec{F}}{D} \quad (48)$$

Since there is no net flow of ions, and therefore, this pseudo-equilibrium can be studied by Boltzmann law.

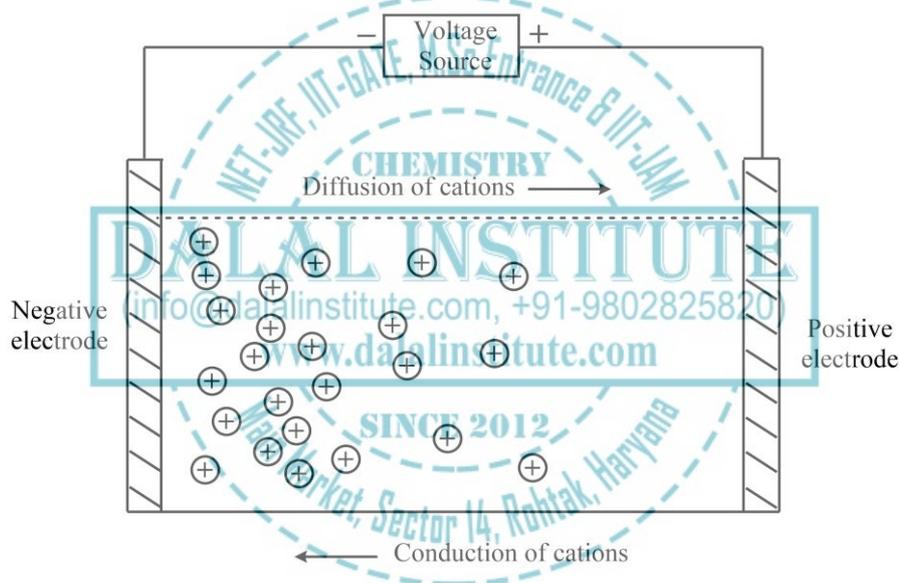


Figure 4. The pseudo-equilibrium when diffusion flux and conduction flux are equal and opposite.

Owing to the  $x$ -dependent variation, recall the ionic concentration at distance  $x$ , i.e.,

$$c = c_0 e^{-U/kT} \quad (49)$$

Where  $c_0$  is the ionic concentration in the zero potential region while  $U$  is the potential energy of the ion under consideration in the externally applied electric field. Differentiating the above equation w.r.t.  $x$ , we have

$$\frac{dc}{dx} = -c_0 e^{-U/kT} \frac{1}{kT} \frac{dU}{dx} \quad (50)$$

Replacing  $c_0 e^{-U/kT}$  by  $c$  i.e. using equation (49), we get

$$\frac{dc}{dx} = -\frac{c}{kT} \frac{dU}{dx} \quad (51)$$

Since the force is  $F = -dU/dx$ , the above equation takes the form

$$\frac{dc}{dx} = \frac{c}{kT} F \quad (52)$$

From equation (48) and equation (52), we get

$$\frac{c\bar{u}_{abs}\vec{F}}{D} = \frac{c}{kT}\vec{F} \quad (53)$$

$$\frac{\bar{u}_{abs}}{D} = \frac{1}{kT} \quad (54)$$

or

$$D = \bar{u}_{abs}kT \quad (54)$$

Which is the famous Einstein relation between the absolute mobility and diffusion coefficient.

Furthermore, from the phenomenological treatment of the diffusion coefficient, it is also a quite well-known correlation that

$$D = BRT \quad (55)$$

Where  $B$  represents the undetermined phenomenological coefficient and  $R$  is the gas constant. Now, comparing equation (54) and equation (55), we have

$$\bar{u}_{abs}kT = BRT \quad (56)$$

or

$$B = \frac{\bar{u}_{abs}kT}{RT} = \frac{\bar{u}_{abs}k}{R} \quad (57)$$

Since  $N = R/k$ , the above equation can also be written as

$$B = \frac{\bar{u}_{abs}}{N} \quad (58)$$

It is obvious from the above equation that the phenomenological coefficient  $B$  can simply be defined as the ratio of absolute mobility to the Avogadro number. Furthermore, The Einstein relation also connects the phenomena of diffusion with force arising from viscous drag and force of electric field on the ion during its drifting movement. Therefore, the formulation also forms the basis of Stokes-Einstein (viscosity and diffusion) and Nernst–Einstein relation (equivalent conductivity and diffusion).

## 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](http://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](#)

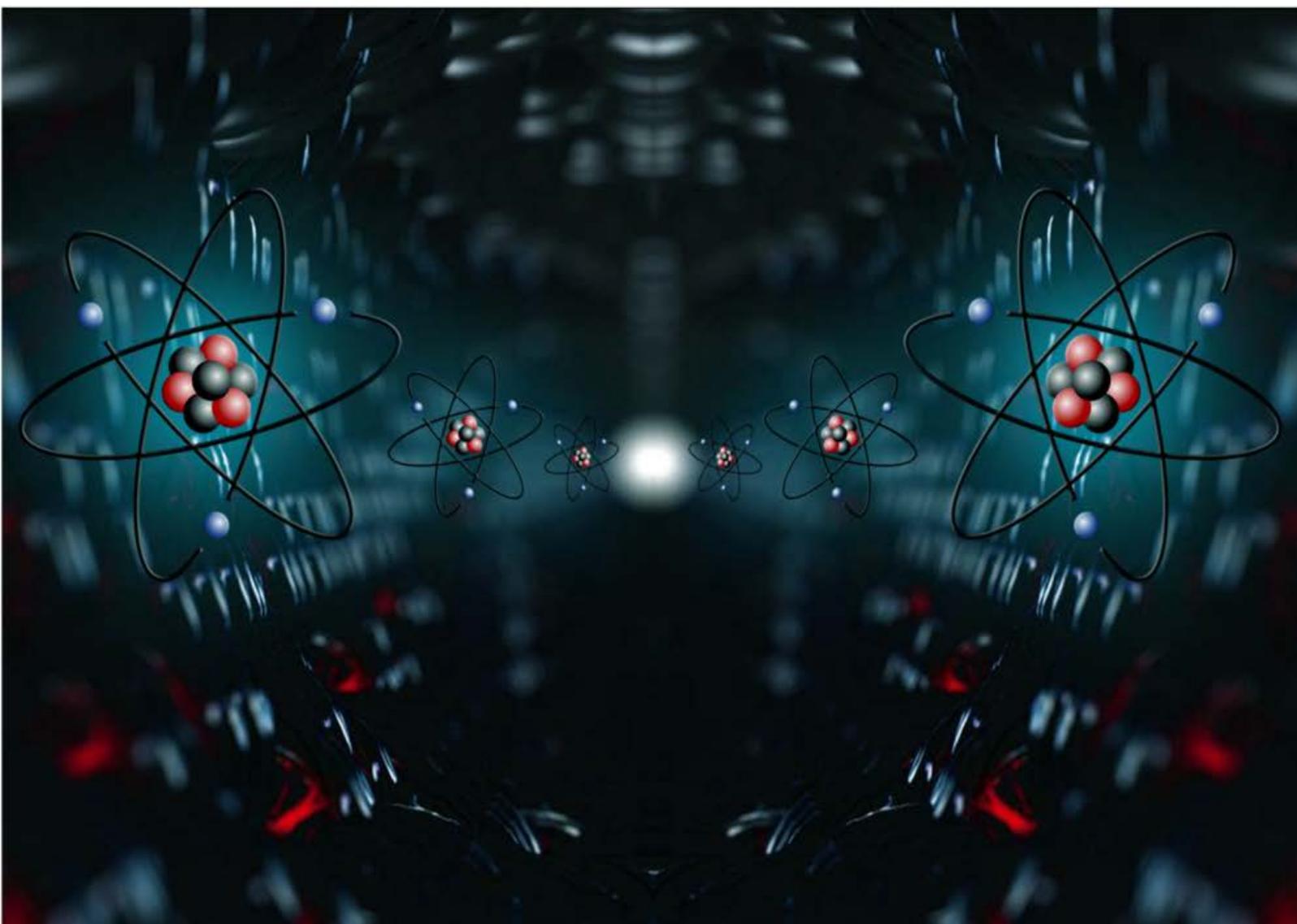
International  
Edition



# A TEXTBOOK OF PHYSICAL CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

**DALAL INSTITUTE**

# Table of Contents

<b>CHAPTER 1</b> .....	<b>11</b>
<b>Quantum Mechanics – I</b> .....	<b>11</b>
❖ 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
<b>CHAPTER 2</b> .....	<b>84</b>
<b>Thermodynamics – I</b> .....	<b>84</b>
❖ 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

<b>CHAPTER 3 .....</b>	<b>113</b>
<b>Chemical Dynamics – I.....</b>	<b>113</b>
❖ 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
<b>CHAPTER 4 .....</b>	<b>160</b>
<b>Electrochemistry – I: Ion-Ion Interactions .....</b>	<b>160</b>
❖ 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 ( $\Lambda$ ) 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
<b>CHAPTER 5 .....</b>	<b>211</b>
<b>Quantum Mechanics – II .....</b>	<b>211</b>
❖ 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
<b>CHAPTER 6 .....</b>	<b>289</b>
<b>Thermodynamics – II.....</b>	<b>289</b>
❖ 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
<b>CHAPTER 7 .....</b>	<b>344</b>
<b>Chemical Dynamics – II .....</b>	<b>344</b>
❖ 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
<b>CHAPTER 8 .....</b>	<b>390</b>
<b>Electrochemistry – II: Ion Transport in Solutions .....</b>	<b>390</b>
❖ 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
<b>INDEX .....</b>	<b>427</b>



*Mandeep Dalal*

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

*Founder & Director, Dalal Institute*

*Contact No: +91-9802825820*

*Homepage: [www.mandeepdalal.com](http://www.mandeepdalal.com)*

*E-Mail: [dr.mandeep.dalal@gmail.com](mailto: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](mailto:info@dalalinstitute.com))

[www.dalalinstitute.com](http://www.dalalinstitute.com)