

❖ The Rate-Process Equation for Equivalent Conductivity

The rate-process equation for equivalent conductivity can be derived by recalling the fundamental relation between the ionic drift velocity (v_d) and current density (J) for cation first i.e.

$$J = z_+ c F v_d \quad (110)$$

Where z is the charge number and c is the concentration of the ions. The symbol F represents the Faraday constant. Also, the drift velocity can be assumed as the resultant velocity of the velocity of ions in the direction of the force field ($\vec{v}$) and the velocity of ions in the opposite direction ($\tilde{v}$). Mathematically, we can say as given below.

$$v_d = \vec{v} - \tilde{v} \quad (111)$$

Now, since the velocity is also the ratio of average jump distance (l) to the average time between two successive jumps (τ), we can also write as

$$\vec{v} = \frac{l}{\tau} \quad (112)$$

Furthermore, the jump frequency i.e. number of jumps per unit of time ($k = 1/\tau$) is simply the reciprocal of the mean time between successive jumps. Therefore, the velocities can also be written as

$$\vec{v} = l \vec{k} \quad (113)$$

$$\tilde{v} = l \tilde{k} \quad (114)$$

From the rate-process approach to ionic migration, the values of $\vec{k}$ and $\tilde{k}$ were found to be

$$\tilde{k} = k_D e^{-pX} \quad (115)$$

and

$$\vec{k} = k_D e^{pX} \quad (116)$$

Where k_D is the jumping frequency for diffusion and X is simply the electric field. The expression for symbol $p = z_+ Fl/2RT$. Using values of $\vec{k}$ and $\tilde{k}$ in equation (113, 114), we get

$$\vec{v} = l k_D e^{pX} \quad (117)$$

$$\tilde{v} = l k_D e^{-pX} \quad (118)$$

Now substituting the value of $\vec{v}$ and $\tilde{v}$ in equation (111), we have

$$v_d = l k_D e^{pX} - l k_D e^{-pX} \quad (119)$$

$$v_d = l k_D (e^{pX} - e^{-pX}) \quad (120)$$

Since $e^{pX} - e^{-pX} = 2 \sinh pX$, the equation (120) can also be written as

$$v_d = 2l k_D 2 \sinh pX \quad (121)$$

Now using the value of drift velocity from equation (121) in equation (110), we get the current density as

$$J = z_+ c F (2l k_D 2 \sinh pX) \quad (122)$$

Therefore, it is obvious from the above expression that the current density varies hyperbolically with the applied electric field.



Figure 7. The variation of current density with the applied electric field.

Now since the J/X is equal to specific conductivity (σ), the above equation takes the form

$$\sigma = \frac{J}{X} = z_+ c F \frac{(2l k_D 2 \sinh pX)}{X} \quad (123)$$

Since molar conductivity is $\Lambda_m = \sigma/c$ and equivalent conductivity is $\Lambda_{eq} = \Lambda_m/z_+$; the equation (123) gives

$$\Lambda_{eq} = \frac{\Lambda_m}{z_+} = \frac{\sigma}{z_+ c} = z_+ c F \frac{(2l k_D 2 \sinh pX)}{z_+ c X} \quad (124)$$

$$\Lambda_{eq} = F \frac{(2l k_D 2 \sinh pX)}{X} \quad (125)$$

Which is the equation for equivalent conductivity.

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

[Classes](https://www.dalalinstitute.com/classes/): <https://www.dalalinstitute.com/classes/>

[Books](https://www.dalalinstitute.com/books/): <https://www.dalalinstitute.com/books/>

[Videos](https://www.dalalinstitute.com/videos/): <https://www.dalalinstitute.com/videos/>

[Location](https://www.dalalinstitute.com/location/): <https://www.dalalinstitute.com/location/>

[Contact Us](https://www.dalalinstitute.com/contact-us/): <https://www.dalalinstitute.com/contact-us/>

[About Us](https://www.dalalinstitute.com/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](#)

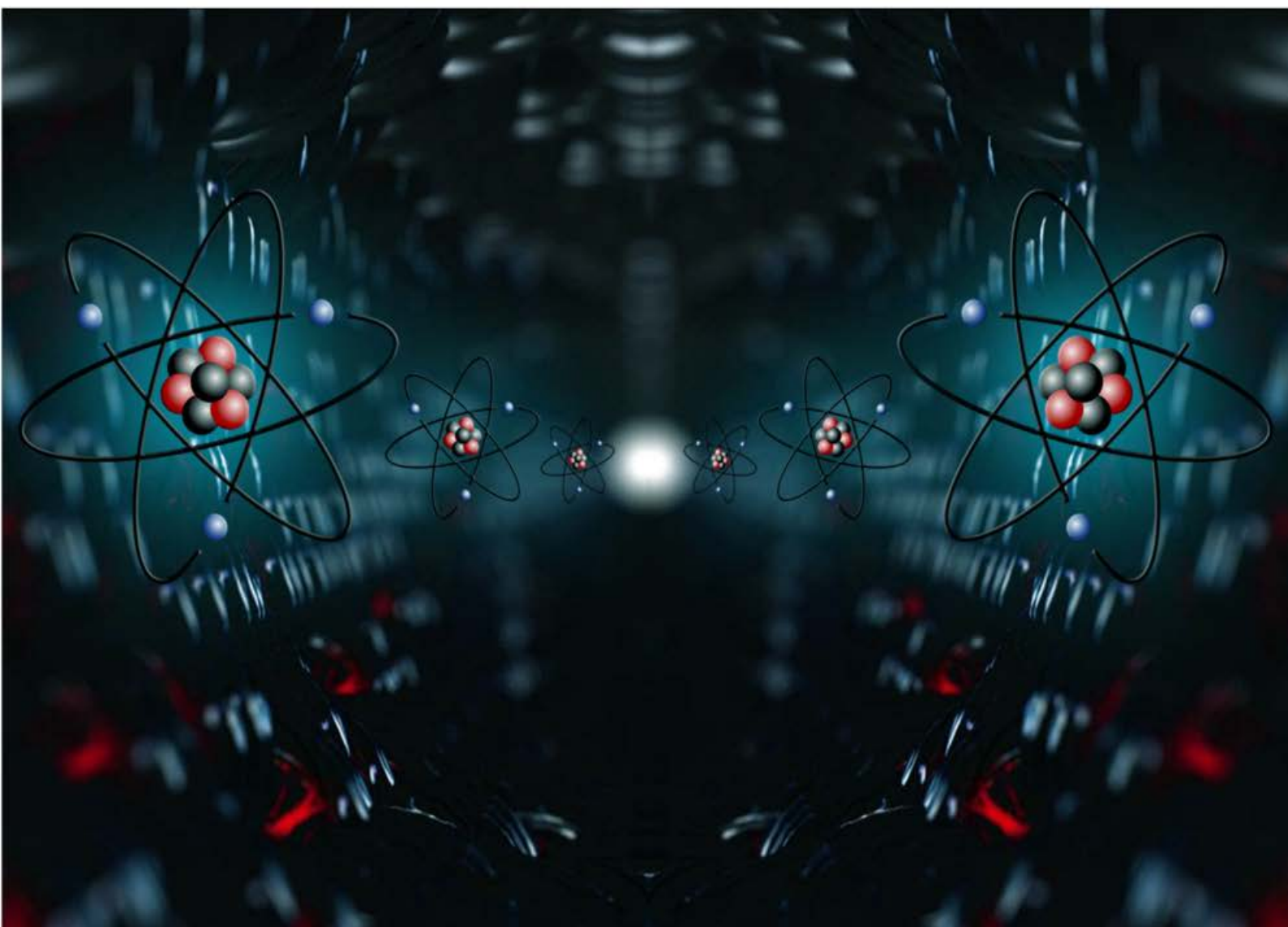
International
Edition



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 Ist Order and IInd Order.....	119
❖ Rate Law for Consecutive & Parallel Reactions of Ist 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



**D DALAL
INSTITUTE**

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

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

www.dalalinstitute.com

MRP: Rs 800.00