

### ❖ Ionic Drift and Diffusion Potential

In order to understand the link between ionic drift and diffusion potential, consider a solution of monovalent electrolyte with concentration  $c$ . Now assume that this solution is brought in contact with pure water and the boundary of contact is assumed to be  $x = 0$ . Owing to the concentration gradient, both cation as well anions will start moving into pure water immediately.

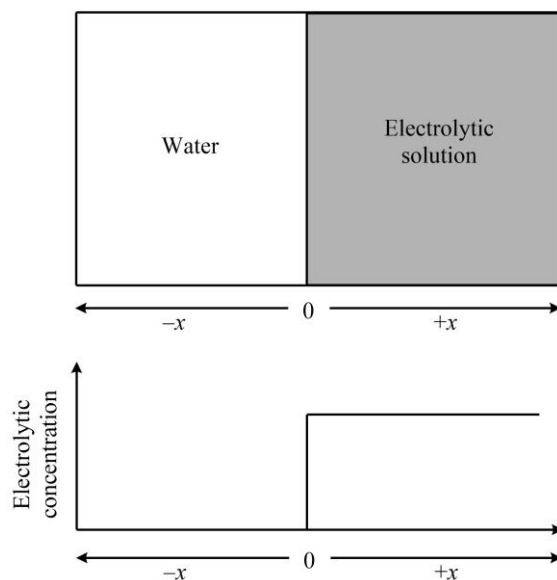


Figure 9. The general depiction electrolytic solution and concentration in contact with water in start.

#### 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.

Now owing to different absolute ionic mobilities of cations and anions (say  $\bar{u}_+ > \bar{u}_-$ ), the Einstein relation can be written for cations and anions as given below.

$$D_+ = \bar{u}_+ kT \quad (162)$$

and

$$D_- = \bar{u}_- kT \quad (163)$$

Where  $D_+$  and  $D_-$  are the diffusion coefficients for cations and anions, respectively. The symbol  $k$  is simply the Boltzmann constant and  $T$  is the temperature. The symbol  $\bar{u}_+$  and  $\bar{u}_-$  represent the absolute ionic mobilities for cation and anion, respectively. Since we have assumed that  $\bar{u}_+ > \bar{u}_-$ , the following must be true

$$D_+ > D_- \quad (164)$$

This implies that the cations will move faster in comparison to anions, will lead the anions in their diffusion race. Now consider two unit-volume-elements at distance  $-x_1$  and  $-x_2$  in the water phase with  $-x_2$  on more left than  $-x_1$ . Since the cations are moving faster than anions, the concentration ratio of the two ( $c_+/c_-$ ) will be higher in volume element at  $-x_2$  than in the volume element at  $-x_1$  distance. In other words, the ratio  $c_+/c_-$  will increase as we move from the boundary to the waterside of the system.

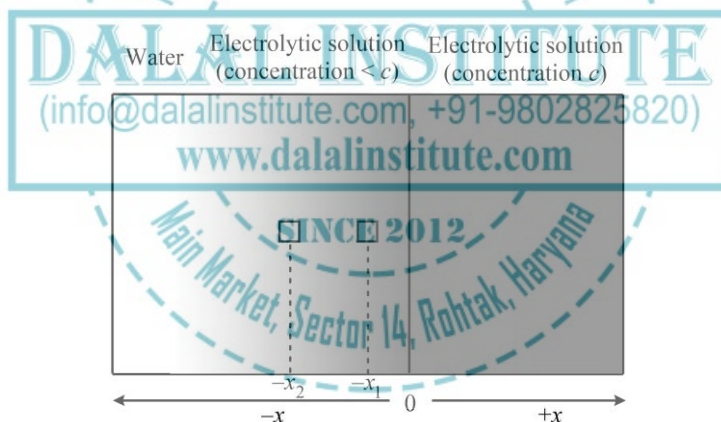


Figure 10. The development of diffusion potential due to different ionic mobilities.

Consequently, a situation will arise in which the positive and negative charges are separated with a negative layer on the left and positive layer on the right. All this will lead to the development of a potential difference that will oppose the faster movement of cations and will reinforce the slower movement of anions. This potential is generally called as the “diffusion potential” and tries to level the ionic mobilities of cations and anions; and hence, tries to maintain the electroneutrality in different parts of the solution. It should also be noted that diffusion potential is also called as the “liquid junction potential” in the case of concentration cells and “membrane potential” if the two solutions are separated by an uncharged membrane.

## 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](#)

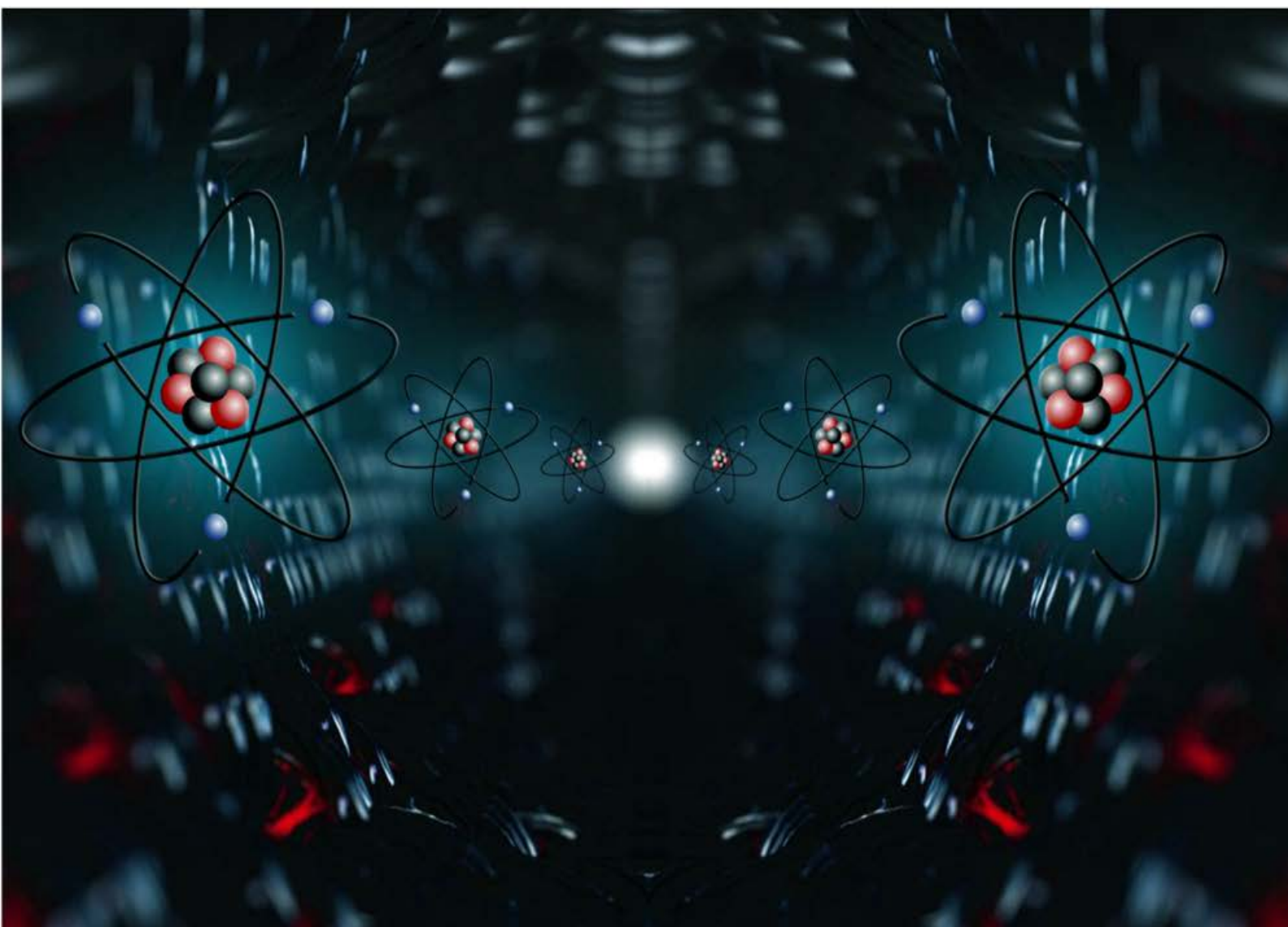
International  
Edition



# 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> .....	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
<b>CHAPTER 4</b> .....	<b>160</b>
<b>Electrochemistry – I: Ion-Ion Interactions</b> .....	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 ( $\Lambda$ ) 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> .....	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
<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)