

### ❖ Entropy Changes in Reversible and Irreversible Processes

In order to understand the entropy change in reversible and irreversible processes, we need to understand the concept of entropy first. For a Carnot heat engine working at  $T_1$  and  $T_2$ , it has been observed that the heat absorbed ( $q_2$ ) and heat returned ( $q_1$ ) are related as given below.

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \quad (10)$$

or

$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2} \quad (11)$$

or

$$\frac{q_1}{q_2} = \frac{T_1}{T_2} \quad (12)$$

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} \quad (13)$$

$$\frac{q}{T} = \text{constant} \quad (14)$$

Therefore, we can say that for any particular system, the ratio of heat absorbed or lost isothermally and reversibly to the absolute temperature at which this takes place is a constant parameter. If we consider  $q_1$  as the heat absorbed at  $T_1$ , equation (13) becomes

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1} \quad (15)$$

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0 \quad (16)$$

or

$$\sum \frac{q}{T} = 0 \quad (17)$$

#### 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.

Consider a reversible cyclic process, consists of many Carnot cycles. In going from point  $A$  to  $B$  and then back  $A$ , all the closed paths cancel each other that results in parent path  $ABA$ .



Figure 3. A cyclic process made of many Carnot cycles.

For each cycle, we have equation (17), for an infinite number of cycles

$$\sum \frac{\delta q}{T} = 0 \quad (18)$$

Where  $\delta q$  is the extremely small amount of heat absorbed at temperature  $T$  during the course of an isothermal and reversible process. Moreover, the total entropy change of the cyclic process  $ABA$  can be fragmented into two components as:

$$\sum \frac{\delta q}{T} = \sum_{A \rightarrow B} \frac{\delta q}{T} + \sum_{B \rightarrow A} \frac{\delta q}{T} = 0 \quad (19)$$

$$\sum_{A \rightarrow B} \frac{\delta q}{T} = - \sum_{B \rightarrow A} \frac{\delta q}{T} \quad (20)$$

or

$$\left(\frac{q}{T}\right)_{A \rightarrow B} = - \left(\frac{q}{T}\right)_{B \rightarrow A} \quad (21)$$

The physical significance of the equation (21) is that the value of  $q/T$  for the path  $A \rightarrow B$  is the same as the path  $B \rightarrow A$ ; which eventually means that the quantity  $q/T$  is actually a state function. This quantity i.e.  $q/T$  is called as entropy, and is generally labeled as  $S$ . If  $S_A$  and  $S_B$  are the entropies at point A and B, respectively; then we can say that

$$S_A - S_B = \frac{q}{T} \quad (22)$$

$$\Delta S = \frac{q}{T} \quad (23)$$

Hence, the entropy change may be defined as the amount of the heat absorbed isothermally and reversibly divided by the temperature at which the heat is absorbed. Being a state function, the change in entropy always depends upon the initial and final state and not upon the path followed. Moreover, since the heat is absorbed reversibly, it is better to use  $q_{\text{rev}}$  in equation (23) instead of simply  $q$ , therefore

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad (24)$$

For an extremely minute change, the above equation becomes

$$dS = \frac{q_{\text{rev}}}{T} \quad (25)$$

The entropy is an extensive property measured in joule per Kelvin per mole ( $\text{JK}^{-1}\text{mol}^{-1}$ ). The most important significance of entropy is that it can be used to measure the randomness in the system.

### ➤ Entropy Changes in Reversible Processes

Suppose that the heat absorbed by the system and heat lost by the surrounding are under completely reversible conditions. In other words,  $q_{\text{rev}}$  is the heat absorbed and lost by the surrounding at temperature  $T$ , then we can say that the entropy change in the system will be given by the following relation.

$$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T} \quad (26)$$

Similarly, the entropy change in the surrounding will be

$$\Delta S_{\text{surrounding}} = -\frac{q_{\text{rev}}}{T} \quad (27)$$

Therefore, the total entropy change will be

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{rev}}}{T} = 0 \quad (28)$$

Hence, we can conclude that the entropy change in an isolated system is always zero i.e. the sum of entropy change in system and entropy change in the surrounding is zero under reversible conditions.

➤ **Entropy Changes in Irreversible Processes**

Every reversible process becomes irreversible even if only one part of it becomes irreversible. To understand this, let us suppose that  $q_{irrev}$  heat lost by the surrounding. Although this heat would be absorbed by the system, the entropy of the system depends upon the heat absorbed reversibly. Therefore, entropy change of the system at an absolute temperature  $T$  will be

$$\Delta S_{system} = \frac{q_{rev}}{T} \quad (29)$$

Similarly, the entropy change of the surrounding will be

$$\Delta S_{surrounding} = -\frac{q_{irrev}}{T} \quad (30)$$

The total entropy of the isolated system (system + surrounding) will be

$$\Delta S_{system} + \Delta S_{surrounding} = \frac{q_{rev}}{T} - \frac{q_{irrev}}{T} \quad (31)$$

Furthermore, as we know that the  $w_{rev} > w_{irrev}$ , and internal energy is a state function that is independent of whether the process is reversible or irreversible. Mathematically, it is

$$\Delta E = q_{rev} - w_{rev} = q_{irrev} - w_{irrev} \quad (32)$$

we can conclude that,

$$\frac{q_{rev}}{T} > \frac{q_{irrev}}{T} \quad (33)$$

$$\frac{q_{rev}}{T} > \frac{q_{irrev}}{T} \quad (34)$$

or

$$\frac{q_{rev}}{T} + \frac{q_{irrev}}{T} > 0 \quad (35)$$

After comparing equation (35) with equation (31), we get

$$\Delta S_{system} + \Delta S_{surrounding} > 0 \quad (36)$$

The physical interpretation of the above equation lies in the fact that all irreversible processes occur via a net increase in entropy. In other words, the total entropy change of an isolated system in any irreversible process is always greater than zero. The results of equation (28) and equation (36) can be combined to give a more generalized form as:

$$\Delta S_{system} + \Delta S_{surrounding} \geq 0 \quad (37)$$

Where the sign of ‘=’ stands from reversible and ‘>’ stands for irreversible phenomena, respectively.

The entropy change in the irreversible process like the flow of heat from the hot end ( $T_2$ ) to cold end ( $T_1$ ) can be calculated using the following relation.

$$\Delta S_{total} = -\frac{q_{rev}}{T_2} + \frac{q_{rev}}{T_1} = q_{rev} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (38)$$

Where  $q_{rev}$  is the amount of heat transferred from  $T_2$  to  $T_1$ .

Furthermore, the Clausius inequality can also be proved from equation (36) which governs that all the irreversible processes are accompanied by a net increase in the entropy.

$$\Delta S_{system} > \Delta S_{surrounding} \quad (39)$$

This can be illustrated with the help of the following examples.

i) *Irreversible isothermal expansion of an ideal gas:* Suppose an ideal gas expanding isothermally and irreversibly against vacuum. The condition isothermal means  $\Delta T = 0$ , which in turn implies that  $\Delta U = 0$ . Hence from the first law of thermodynamics, we have  $dq = 0$  i.e. no heat is transferred from, or to the surrounding giving  $dS_{surrounding} = 0$ .

However, since the  $dS_{system} = R \ln (V_2/V_1)$ . Since  $V_2$  is definitely greater than  $V_1$ , therefore

$$dS_{total} = dS_{system} + dS_{surrounding} = dS_{system} + 0 \geq 0 \quad (40)$$

ii) *Heat flow from hot to the cold end:* Suppose  $dq$  is the amount of heat transferred from temperature  $T_2$  to  $T_1$ . The entropy change at the source will be

$$dS_{source} = -\frac{dq}{T_2} \quad (41)$$

Similarly, the entropy change at the sink will be

$$dS_{sink} = \frac{dq}{T_1} \quad (42)$$

The total entropy change of the system can be calculated as

$$dS_{total} = dS_{source} + dS_{sink} = \frac{dq}{T_1} - \frac{dq}{T_2} \quad (43)$$

or

$$dS_{total} = dq \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (44)$$

Now because the source is always at a higher temperature than sink ( $T_2 > T_1$ ),  $dS_{total}$  will be positive for sure, proving that transfer of heat from a hot body to the cold body occurs via a net entropy increment.

## 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](#)

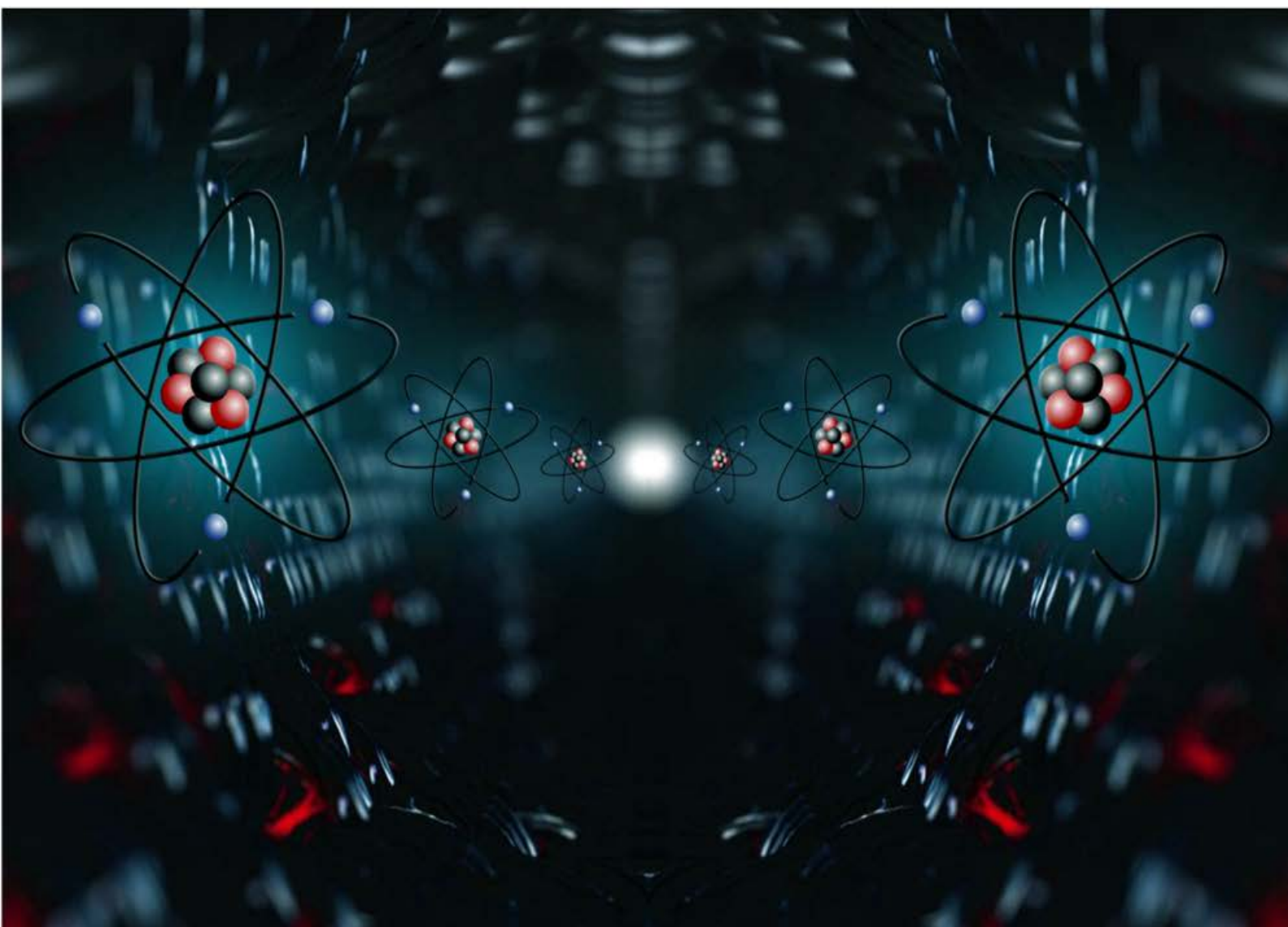
International  
Edition



# 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)