

# CHAPTER 4

## Electrochemistry – I: Ion-Ion Interactions

### ❖ The Debye-Huckel Theory of Ion-Ion Interactions

When an ion goes into the solution, it interacts not only with the solvent molecules but also with other ions that are produced as a result of electrolytic dissociation. The interaction of this ion with its solvent-surrounding is quite important as it helps the ion to get stabilized in that medium. Nevertheless, the other types of interactions, i.e., the ion-ion interactions, are also of very much significant value to the overall understanding of the system because these interactions affect a number of properties of these solutions such as partial molar free energy change or the electrolytic conductance. Now, since the phenomenon of ion-ion interactions is a function of interionic separations, which in turn depends upon the population density of these ions; the first step to know this phenomenon must be the rationalization of ionic population density.

In the case of weak electrolytes, the degree of dissociation is very small at high concentrations yielding a very low population density of charge carriers. This would result in almost zero ion-ion interactions at high concentrations. Now, although the degree of dissociation increases with dilution, which in turn also increases the total number of charge carriers, the population density remains almost unchanged since the extra water has also been added for these extra ions. Thus, we can conclude that there are no ion-ion interactions in weak electrolytes, neither at higher nor at the lower concentrations. On the other hand, in the case of strong electrolytes, the degree of dissociation is a hundred percent even at high concentrations yielding a very high population density of charge carriers. This would result in very strong ion-ion interactions at high concentrations. Now, when more and more solvent is added, the total number of charge carriers remains the same but the population density decreases continuously, creating large interionic separations. This would result in a decrease in the magnitude of ion-ion interaction with increasing dilution.

In 1913, a British physicist Samuel Milner proposed the first quantitative explanation of ion-ion interactions in a statistical framework. After that, in 1918, an Indian Chemist, Sir Jnan Chandra Ghosh proposed a model to compute the energy of Coulombic interaction of the ions with an assumption that the ions in the solution are fixed just like in the crystals. The Milner's model was quite complicated mathematically, while Ghosh's model did not consider the distorting effect of thermal motion on the ionic distribution in the solution phase of electrolyte under consideration.

In 1923, Peter Debye and Erich Huckel proposed an extremely important idea to quantify the ion-ion interactions in the solutions of strong electrolytes. In this model, the solute, i.e., the strong electrolyte, is assumed to dissociate completely. They considered the ions as perfect spheres that cannot be polarized by the surrounding electric field while the solvation of ions was ignored. The solvent plays no role other than providing a medium of the constant relative permittivity (dielectric constant). A reference ion was thought to be suspended in solvent-continuum of dielectric constant  $\epsilon$  with zero electrostriction, and this ion is surrounded by oppositely charged ionic cloud.

➤ **Fundamental Concept**

It is quite interesting to recall the fact that like many other coupling effects, the phenomena of ion-ion interaction can also be quantified in terms of free energy change. In this case, it can be achieved by assuming an initial state with no ion-ion interaction and a final state in which the ion-ion interactions do exist; and then calculating the free energy change in going from initial to the final state.

The initial state, i.e., the state with no ion-ion interaction, can be created hypothetically by taking ions in the vacuum. However, since the final state possesses ions in solution, the initial state should also have ions in solution and not in the vacuum, otherwise, two states would differ not only by ion-ion interaction but also in respect of ion-solvent interaction. Conversely, if we imagine some discharged ions in the solution (discharged ions mean no ion-ion interaction) and then charge them up fully, free energy change of ion-ion interaction would be the amount of work done in doing so.



Figure 1. The pictorial representation of the fundamental idea for calculating the free energy of ion-ion in the Debye-Huckel model of ionic interactions.

It should also be noted that the procedure depicted in 'Figure 1' gives the work of charging (i.e., the free energy of ion-ion interaction) for all the ions present in the solution whether they are positive or negative. However, the scientific analysis of electrolytic solutions typically needs the free energy of ionic interactions for individual species. This partial free energy change is called as chemical potential change and is typically denoted as  $\Delta\mu_{i-1}$ . The value of  $\Delta\mu_{i-1}$  for  $i$ th species of radius  $r_i$  can be obtained by computing the work of charging this sphere from a neutral state to its full charge of  $Z_ie_0$ . The work of charging ( $w$ ) a spherical conductor can be given by the following relation (from electrostatics):

$$w = \frac{1}{2} [\text{Charge on the conductor} \times \text{Electrostatic Potential of conductor}] \quad (1)$$

Since the Debye-Huckel model also considers the ions as spherical conductors, the work of charging an ion of radius  $r$  will be

$$w = \frac{1}{2} [Z_i e_0 \times \psi] \quad (2)$$

Where  $\psi$  represents the electrostatic potential of the reference ion due to the influence on it by the Coulombic forces of the neighboring ions. Multiplying equation (2) by Avogadro number, we can obtain the amount of work done required to charge one mole of such ions i.e. the partial molar free energy change.

$$\Delta\mu_{i-I} = N_A w = \frac{N_A}{2} [Z_i e_0 \times \psi] \quad (3)$$

The only thing that is unknown in the above expression is  $\psi$ . Therefore, the partial molar free energy change due to the interaction of  $i$ th species with the rest of the solution requires the determination of electrostatic potential exerted at the reference ion by its ionic-surrounding. Now, from the law of superposition of potentials, we know that the potential at any point due to an assembly of charges is just the sum of the individual potentials exerted at that point by the individual charges. Since the electrostatic potentials depend upon the distances between the charges under consideration, the time-averaged distribution of all ions around must be known (distances from the reference ion are the function of the population distribution of other ions).

Although we know that the total electrostatic potential at the reference ion can be obtained by knowing the distance of each surrounding ion from the reference ion, the number of ions is extremely large making it almost impossible to follow the conventional route to do so. So, instead of dealing with individual ions, Debye and Huckel proposed the revolutionary idea of considering all the surrounding ions as a continuous ionic cloud that surrounds the reference ions. They assigned the discrete charge only to the reference ion which is situated in the solvent's continuum of dielectric constant  $\epsilon$ , i.e., water in this case.

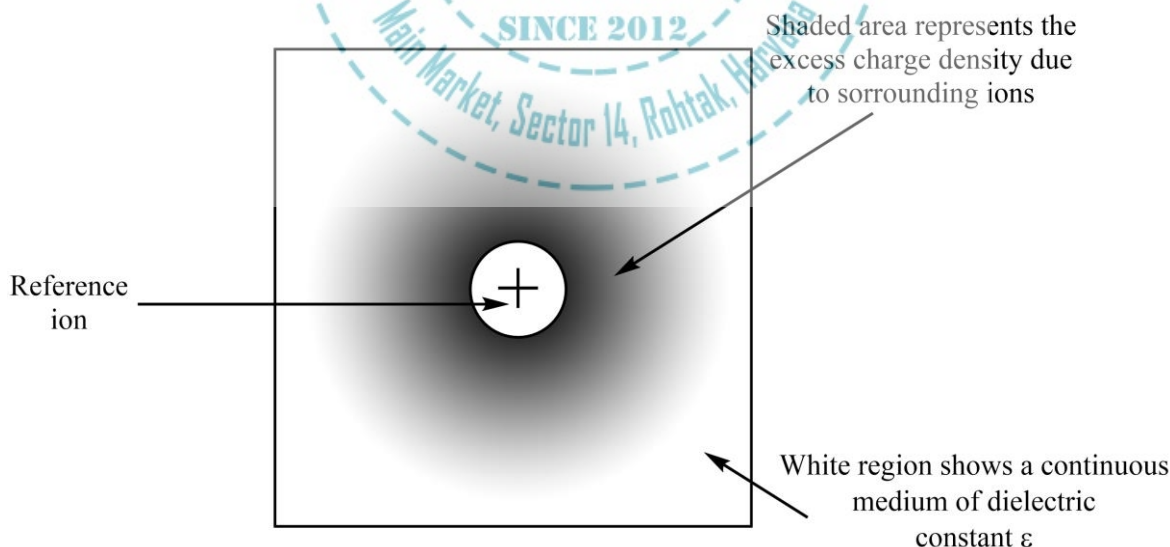


Figure 2. The pictorial representation of reference ion in its ionic cloud.

Hence, the Debye-Huckel's idea transformed the complex problem of computing the population density around the reference to the determination of excess charge density ( $\rho$ ). At this point, one might think why the excess charge density is not zero everywhere because the solution as a whole is actually electroneutral. The reason for this behavior lies in the fact that positive centers attract negative density while a negative center tries to accumulate a positive cloud around it. Therefore, in a volume element near positive ion, there should be a more negative charge, i.e., excess negative charge density and vice-versa. This excess negative charge density near a positive center is counterbalanced by excess positive charge density near a negative center, keeping the overall electroneutrality maintained. It should also be mentioned here that since the thermal forces in the solution are always trying to randomize the ionic distribution, the excess charge density diminishes in moving away from the center.

➤ **Mathematical Development**

So far we have discussed the fundamentals aspects of how we can determine the partial molar free energy change generated by the ionic interactions of  $i$ th species. All we need is the electrostatic potential ( $\psi$ ) of the reference ion due to the influence on it by the Coulombic forces of the surrounding. Since  $\psi$ , at a distance  $r$  from the reference ion, depends upon the excess charge density at  $r$ , the first thing we need to develop it mathematically is the correlation between these two parameters, i.e.,  $\psi_r$  and  $\rho_r$ . One such relation for spherically symmetric charge distribution is the Poisson's equation in electrostatics that can be given as:

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi_r}{dr} \right) = -\frac{4\pi}{\epsilon} \rho_r \quad (4)$$

Where  $\psi_r$  and  $\rho_r$  are electrostatic potential and excess charge density in a very small volume element  $dV$  situated at distance  $r$  from the reference ion.

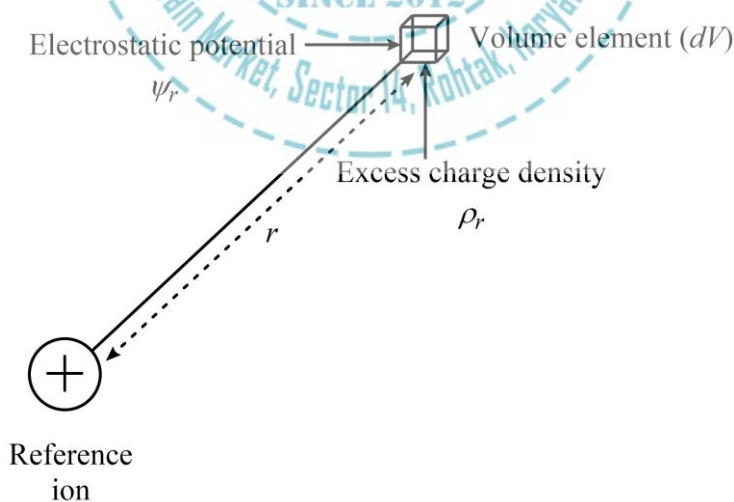


Figure 3. The depiction of electrostatic potential and excess charge density in  $dV$  volume element at a distance  $r$  from the reference ion.

Rearranging the Poisson's equation for excess charge density, we get

$$\rho_r = -\frac{\varepsilon}{4\pi} \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi_r}{dr} \right) \right] \quad (5)$$

Also, the “linearized Boltzmann distribution” can be used to prove that

$$\rho_r = -\sum_i \frac{n_i^0 Z_i^2 e_0^2 \psi_r}{kT} \quad (6)$$

Where  $n_i^0$  is the bulk concentration of the  $i$ th species and  $k$  is simply the Boltzmann constant. Equating the Poisson's expression with the Boltzmann Formula, i.e., from equation (5) and (6), we get the linearized Poisson Boltzmann equation as:

$$-\frac{\varepsilon}{4\pi} \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi_r}{dr} \right) \right] = -\sum_i \frac{n_i^0 Z_i^2 e_0^2 \psi_r}{kT} \quad (7)$$

or

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi_r}{dr} \right) = \left( \frac{4\pi}{\varepsilon kT} \sum_i n_i^0 Z_i^2 e_0^2 \right) \psi_r \quad (8)$$

Now assume a constant  $\kappa^2$  with value

$$\kappa^2 = \frac{4\pi}{\varepsilon kT} \sum_i n_i^0 Z_i^2 e_0^2 \quad (9)$$

Using the value of equation (9) in equation (8), we get

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi_r}{dr} \right) = \kappa^2 \psi_r \quad (10)$$

The above differential equation is the popular form of linearized Poisson-Boltzmann expression and its solution gives

$$\psi_r = \frac{Z_i e_0}{\varepsilon} \frac{e^{-\kappa r}}{r} \quad (11)$$

Now comparing equation (4) and equation (10), we get

$$\kappa^2 \psi_r = -\frac{4\pi}{\varepsilon} \rho_r \quad (12)$$

or



$$\rho_r = -\frac{\epsilon\kappa^2\psi_r}{4\pi} \quad (13)$$

Now putting the value of electrostatic potential from equation (11) in equation (13), we get the expression for excess charge density as a function of  $r$ .

$$\rho_r = -\frac{\epsilon\kappa^2}{4\pi} \times \frac{Z_i e_0}{\epsilon} \frac{e^{-\kappa r}}{r} \quad (14)$$

$$\rho_r = -\frac{Z_i e_0 \kappa^2}{4\pi r} e^{-\kappa r} \quad (15)$$

Now because the magnitude of  $\rho_r$  is a consequence of the unequal distribution of anions and cations, the above expression also defines the ionic-population-distribution around the reference ion.



Figure 4. The variation of electrostatic potential and excess charge density as a function of the distance  $r$  from the reference ion.

After knowing that the excess charge density decreases exponentially with  $r$ , we can determine the total excess charge ( $dq$ ) at the same distance just by the following relation.

$$dq = \rho_r 4\pi r^2 dr \quad (16)$$

Where  $4\pi r^2 dr$  is the volume element of a hollow spherical shell of thickness  $dr$  with the inner and outer radius as  $r$  and  $r+dr$ , respectively. After putting the value of  $\rho_r$  from equation (15) in equation (16), we have

$$dq = \left( -\frac{Z_i e_0 \kappa^2}{4\pi r} e^{-\kappa r} \right) 4\pi r^2 dr \quad (17)$$

or

$$dq = -Z_i e_0 e^{-\kappa r} \kappa^2 r dr \quad (18)$$

Thus, the exponential part decreases with increasing  $r$  while the non-exponential part shows a continuous increase as we move away from the reference ion.

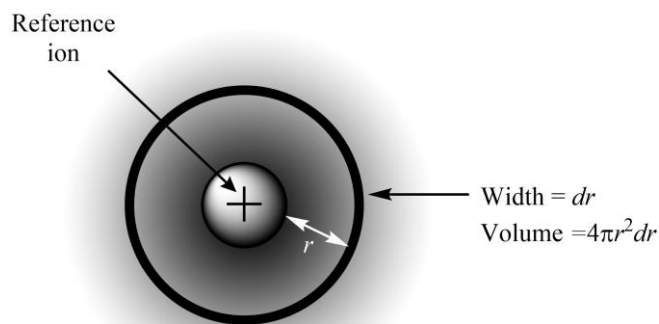


Figure 5. The depiction of excess charge density in a volume element of thickness ' $dr$ ' as a function of the distance  $r$  from the reference ion.

In order to find the distance of maximum "excess charge", we need to differentiate the equation (18) with respect to  $r$ , and then derivative needs to be put equal to zero i.e.

$$\frac{dq}{dr} = -Z_i e_0 \kappa^2 (e^{-\kappa r} - \kappa r e^{-\kappa r}) = 0 \quad (19)$$

Since  $-Z_i e_0 \kappa^2$  is non zero for sure, the above equation holds true only if

$$e^{-\kappa r} - \kappa r e^{-\kappa r} = 0 \quad (20)$$

Which implies

$$r = \kappa^{-1} \quad (21)$$

Also from equation (9), we have

$$\kappa = \left( \frac{4\pi}{\epsilon k T} \sum_i n_i^0 Z_i^2 e_0^2 \right)^{1/2} \quad (22)$$

Hence, the radius of maximum excess charge from the center of the reference ion can be obtained by putting the value of  $\kappa$  from equation (22) in equation (21), we get  $r_{max}$  or the "Debye-Huckel length" as

$$r_{max} = \left( \frac{\epsilon k T}{4\pi \sum_i n_i^0 Z_i^2 e_0^2} \right)^{1/2} \quad (23)$$

At this point, we have understood most of the ideas of Debye-Huckel's theory of ion-ion interaction, and the question we raised initially is near to its end, i.e., to calculate the molar chemical potential change of ion-ion interaction. Now, although we have calculated the electrostatic potential, we cannot use the same in equation (3) because what we have obtained contains the contributions from the ionic cloud as well as from the reference ion itself. Therefore, before we calculate the partial molar free energy of ion-ion interaction, we need to separate potential from the ionic cloud and from the central ion first. The total electrostatic potential at a distance  $r$  can be fragmented as given below.

$$\psi_r = \psi_{ion} + \psi_{cloud} \quad (24)$$

$$\psi_{cloud} = \psi_r - \psi_{ion} \quad (25)$$

From the formulation of potential due to a single charge at a distance  $r$ , we know that

$$\psi_{ion} = \frac{Z_i e_0}{\epsilon r} \quad (26)$$

Now using the value of  $\psi_r$  from equation (11) and of  $\psi_{ion}$  from equation (26) into equation (25), we get

$$\psi_{cloud} = \frac{Z_i e_0}{\epsilon} \frac{e^{-\kappa r}}{r} - \frac{Z_i e_0}{\epsilon r} \quad (27)$$

$$\psi_{cloud} = \frac{Z_i e_0}{\epsilon r} (e^{-\kappa r} - 1) \quad (28)$$

Now because the value of  $\kappa$  is proportional to  $\sum_i n_i^0 Z_i^2 e_0^2$ , at very large dilution  $\kappa$  becomes very small and  $e^{-\kappa r}$  and can be expanded as  $1 - \kappa r$  ( $e^x = 1 + x$ ). Therefore, equation (28) takes the form

$$\psi_{cloud} = \frac{Z_i e_0}{\epsilon r} (1 - \kappa r - 1) \quad (29)$$

$$\psi_{cloud} = -\frac{Z_i e_0 \kappa}{\epsilon} \quad (30)$$

Hence, potential due to ionic cloud is independent of the distance  $r$  in this case. Now putting the value of  $\psi_{cloud}$  from equation (30) into equation (3), we get

$$\Delta\mu_{i-I} = N_A w = \frac{N_A}{2} \left[ Z_i e_0 \times \left( -\frac{Z_i e_0 \kappa}{\epsilon} \right) \right] \quad (31)$$

$$\Delta\mu_{i-I} = -\frac{N_A Z_i^2 e_0^2 \kappa}{2\epsilon} \quad (32)$$

Hence, the Debye-Huckel's model gives the theoretical value of  $\Delta\mu_{i-I}$  arising from ion-ion interactions. Now before we check the validity of the Debye-Huckel model, we will discuss the many aspects of mathematical treatment Debye-Huckel model in more detail in forthcoming sections.



## 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](#)

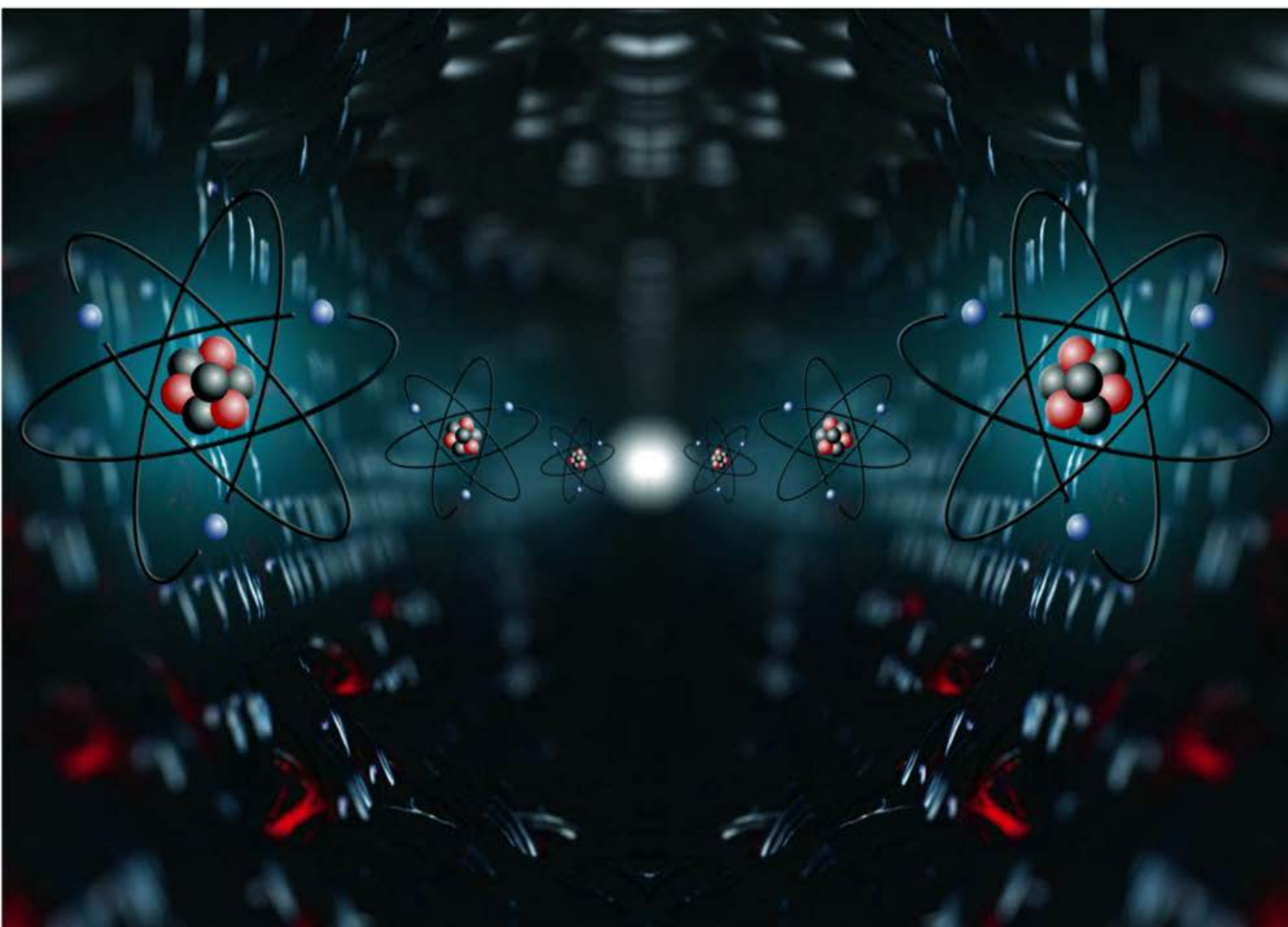
International  
Edition



# 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)