

## ❖ Debye-Huckel-Onsager Treatment for Aqueous Solutions and Its Limitations

It is a well-known fact that the conductance of weak electrolytic solutions increases with the increase in dilution. This can be easily explained on the basis of Arrhenius's theory of electrolytic dissociation which says that the magnitude of dissociated electrolyte, and hence the number of charge carriers, increases with the increase in dilution. However, the problem arises when the strong or true electrolytes show the same trend but at a much lower scale. We used the word “problem” because even at the higher concentration, the electrolyte dissociates completely inferring that there is no possibility of further dissociation with dilution. This means that there should be no increase in the conductance of strong electrolytes with the addition of water.

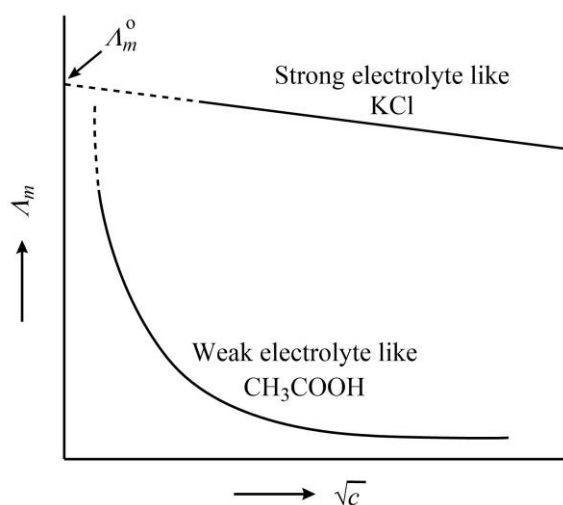


Figure 14. The typical variation of molar conductance ( $\Lambda_m$ ) with the square root of the concentration ( $\sqrt{c}$ ) for strong and weak electrolytes.

The primary reason behind this weird behavior of strong electrolyte is that the conductance of any electrolytic solution depends not only upon the number of charge carriers but also upon the speed of these charge carriers. Therefore, if the dilution does not affect the number of charge carriers in strong electrolytes, it must be affecting the speed of ions to change its conductance. The main factor that is responsible for governing the ionic mobility is ion-ion interactions. Now since these ion-ion interactions are dependent upon the interionic distances, they eventually vary with the population density of charge carriers. Higher population density means smaller interionic distances and therefore stronger ion-ion interactions. On the other hand, the lesser population density of ions would result in larger interionic separations and hence weaker ion-ion interactions.

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 extra water has been added for these extra ions. Thus, we can conclude that there are no ion-ion interactions in weak electrolytes neither at high nor at the low concentration; and hence the rise in conductance with dilution almost a function dissociation only.

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, hindering the speed of various charge carriers. 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 ion-ion interaction with increasing dilution, and therefore, the charge carriers would be freer to move in the solution. Thus, we can conclude that though there is no rise in the number of charge carriers with dilution, the declining magnitude of ion-ion interaction creates faster ions and larger conductance.

➤ **Factor Affecting the Conductance of Strong Electrolytic Solutions**

In 1923, Peter Debye and Erich Huckel proposed an extremely important idea to quantify the conductance of strong electrolytes in terms of these interionic interactions. In this model, a reference ion is thought to be suspended in solvent-continuum of dielectric constant  $\epsilon$  and is surrounded by oppositely charged ions. Besides the ion-ion interaction, the viscosity of the solvent also affects the overall speed of the moving ion. The primary effects which are responsible for controlling the ionic mobility are discussed below.

**1. Asymmetry effect or the relaxation effect:** In the absence of applied electric field, the ionic atmosphere of the reference ion remains spherically symmetrical. This means that the electrostatic force of attraction on the reference ion from all the directions would be the same. However, when the electric field is applied, the ion starts to move towards the oppositely charged electrode. This, in turn, would destroy the spherical symmetry of the cloud, and more ions would be left behind creating a net backward pull to the reference ion. This effect, therefore, would slow down the moving ions and the conductance would be decreased.

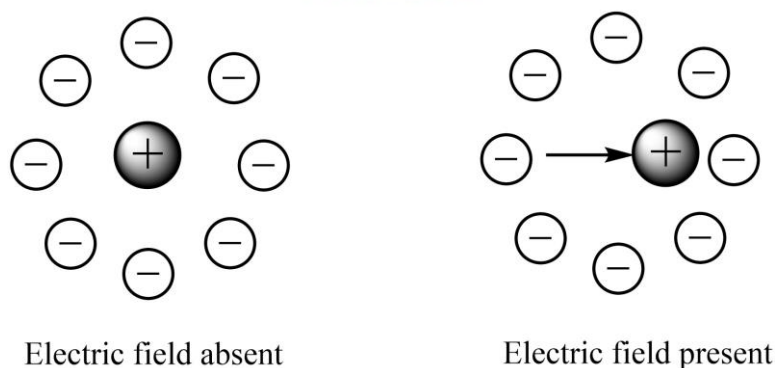


Figure 15. The asymmetric or relaxation effect in the conductance of strong electrolytes.

Alternatively, this can also be visualized in terms of cloud-destruction and cloud-building around the reference ion. In other words, during the movement of ion, the ionic cloud around the reference ion must rebuild itself to keep things natural. Since this rebuilding is not instantaneous and takes some time called as relaxation time, the old cloud exerts a backward pull on the reference ion opposing opposing its speed. All this results in a diminished magnitude of the conductance.

**2. Electrophoretic effect:** After the application of the external electric field, the reference ion and ionic cloud move in opposite directions. During the course of this movement, the solvent associated with the surrounding ions also moves in a direction opposite to the central ion. In other words, we can say that the reference ion has to move against a solvent stream, which makes it somewhat slower than usual. This phenomenon is called as the electrophoretic effect.

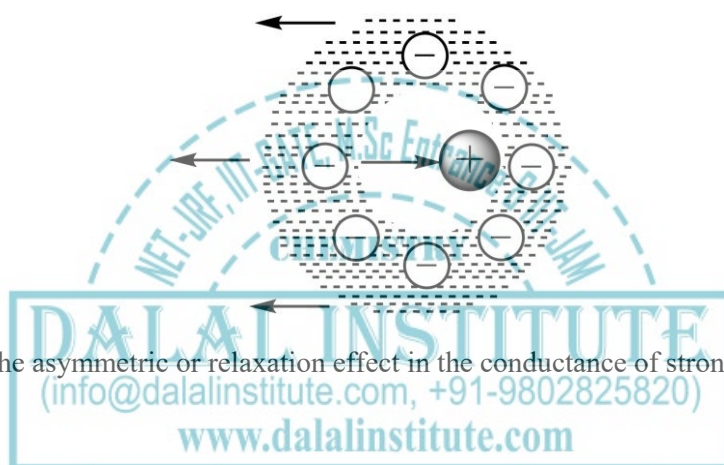


Figure 16. The asymmetric or relaxation effect in the conductance of strong electrolytes.

Since the electrophoretic effect reduces the speed of the ion, the conductance of the electrolytic solution is also affected considerably.

**3. Viscous Effect:** In addition to the asymmetric and electrophoretic effects, another type of resistance also exists which affects the conductance of electrolytic solutions, the “viscous effect”. This is simply the frictional resistance created by the viscosity of the solvent used. For an ion of given charge and size, the ionic mobility as well the conductance decrease with the increase in the magnitude of the viscosity of the solvent used. In other words, less viscous solvents yield higher conductance and vice-versa.

➤ **Mathematical Development of Debye-Huckel-Onsager theory of Strong Electrolytes**

It is a well-known fact that the equivalent conductivity ( $\Lambda$ ) of an electrolytic solution is correlated to the ionic mobilities ( $u$ ) ions involved as

$$\Lambda = F(u_+ + u_-) \quad (176)$$

Where  $F$  is the Faraday constant. Now, recall the ionic mobilities of the cation and anion i.e.

$$u_+ = u_+^0 - \kappa \left( \frac{Z_+ e_0}{6\pi\eta} + \frac{e_0^2 \omega}{6\epsilon kT} u_+^0 \right) \quad (177)$$

$$u_- = u_-^0 - \kappa \left( \frac{Z_- e_0}{6\pi\eta} + \frac{e_0^2 \omega}{6\epsilon kT} u_-^0 \right) \quad (178)$$

Where  $u_+^0$  and  $u_-^0$  are the ionic mobilities of the cation and anions at infinite dilution, respectively. The symbol  $\epsilon$  represents the dielectric constant of the medium whereas  $\eta$  is the coefficient of viscosity.  $Z_+$  and  $Z_-$  are charge numbers of the cation and anion, respectively. The symbol  $e_0$  simply shows the electronic charge. The symbol  $\kappa$  represents ( $n_i^0$  is the bulk concentration)

$$\kappa = \left( \frac{4\pi}{\epsilon kT} \sum_i n_i^0 Z_i^2 e_0^2 \right)^{1/2} = \left( \frac{4\pi Z^2 e_0^2 c}{\epsilon kT} \right)^{1/2} \left( \frac{N_A}{1000} \right)^{1/2} \quad (179)$$

The quantity  $\omega$  is defined as

$$\omega = \frac{Z_+ Z_- 2q}{1 + \sqrt{q}} \quad \text{where} \quad q = \frac{Z_+ Z_-}{Z_+ + Z_-} \frac{\lambda_+ + \lambda_-}{Z_+ \lambda_+ + Z_- \lambda_-} \quad (180)$$

After putting the values of  $u_+$  and  $u_-$  from equation (177) and (178) in equation (176), we get

$$\Lambda = F \left[ u_+^0 - \kappa \left( \frac{Z_+ e_0}{6\pi\eta} + \frac{e_0^2 \omega}{6\epsilon kT} u_+^0 \right) \right] + F \left[ u_-^0 - \kappa \left( \frac{Z_- e_0}{6\pi\eta} + \frac{e_0^2 \omega}{6\epsilon kT} u_-^0 \right) \right] \quad (181)$$

In the case of symmetrical electrolytes, we can put  $Z_+ = Z_- = Z$ , and therefore  $Z_+ + Z_- = 2Z$ . Thus, the above equation for such cases takes the form

$$\Lambda = F(u_+^0 + u_-^0) - \left[ \frac{FZ\kappa e_0}{3\pi\eta} + \frac{e_0^2 \omega k}{6\epsilon kT} F(u_+^0 + u_-^0) \right] \quad (182)$$

Since  $F(u_+^0 + u_-^0) = \Lambda^0$ , the equation (182) becomes

$$\Lambda = \Lambda^0 - \left[ \frac{FZ\kappa e_0}{3\pi\eta} + \frac{e_0^2 \omega k}{6\epsilon kT} \Lambda^0 \right] \quad (183)$$

Now expanding above equation further by putting the value of  $\kappa$  from equation (179), we get

$$\Lambda = \Lambda^0 - \left[ \frac{FZ e_0}{3\pi\eta} \left( \frac{8\pi Z^2 e_0^2 N_A}{1000\epsilon kT} \right)^{1/2} + \frac{e_0^2 \omega}{6\epsilon kT} \left( \frac{8\pi Z^2 e_0^2 N_A}{1000\epsilon kT} \right)^{1/2} \Lambda^0 \right] \sqrt{c} \quad (184)$$

Define two constant  $A$  and  $B$  as

$$A = \frac{FZ e_0}{3\pi\eta} \left( \frac{8\pi Z^2 e_0^2 N_A}{1000\epsilon kT} \right)^{1/2} \quad \text{and} \quad B = \frac{e_0^2 \omega}{6\epsilon kT} \left( \frac{8\pi Z^2 e_0^2 N_A}{1000\epsilon kT} \right)^{1/2} \quad (185)$$

Therefore, the equation (184) can be simplified as

$$\Lambda = \Lambda^0 - (A + B\Lambda^0)\sqrt{c} \quad (186)$$

or

$$\Lambda = \Lambda^0 - \text{constant}\sqrt{c} \quad (187)$$

The equation (184) and equation (186) are the popular forms famous Debye-Huckel-Onsager equation for electrolyte solutions. The constants  $A$  and  $B$  can easily be determined from the knowledge of temperature  $T$ , valence type of the electrolyte  $z$ , the viscosity of the medium, the dielectric constant and other universal constants like Avogadro number. From Equation (187), it is obviously a straight line equation which means the for symmetrical electrolytic solutions, we can plot the conductance vs square root of the concentration for which the slope will be negative. The intercept after extrapolation gives the value of conductance of such solutions at infinite dilution.

➤ **Limitations of Debye-Huckel-Onsager Equation**

Since the plot of conductance vs square root of the concentration is linear with negative slope and positive intercept, it seems quite straightforward to study the strong electrolytes. However, it has been observed that the equation (187) is followed only up low and moderate concentrations.

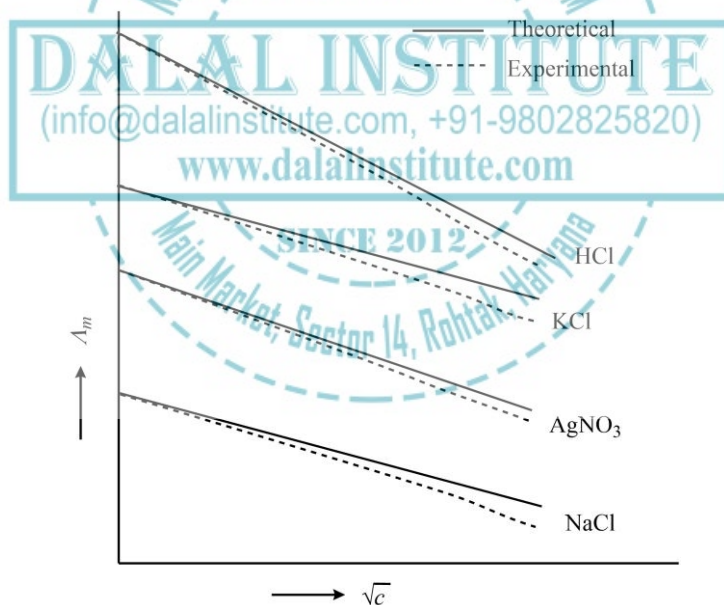


Figure 17. The comparison of theoretical and experimental conductance as a function of concentration for some symmetric electrolytes.

It can be clearly seen that the theory and experiment move apart as the concentration increases. This is simply because some approximation used to derive the Debye-Huckel-Onsager equation are not valid.

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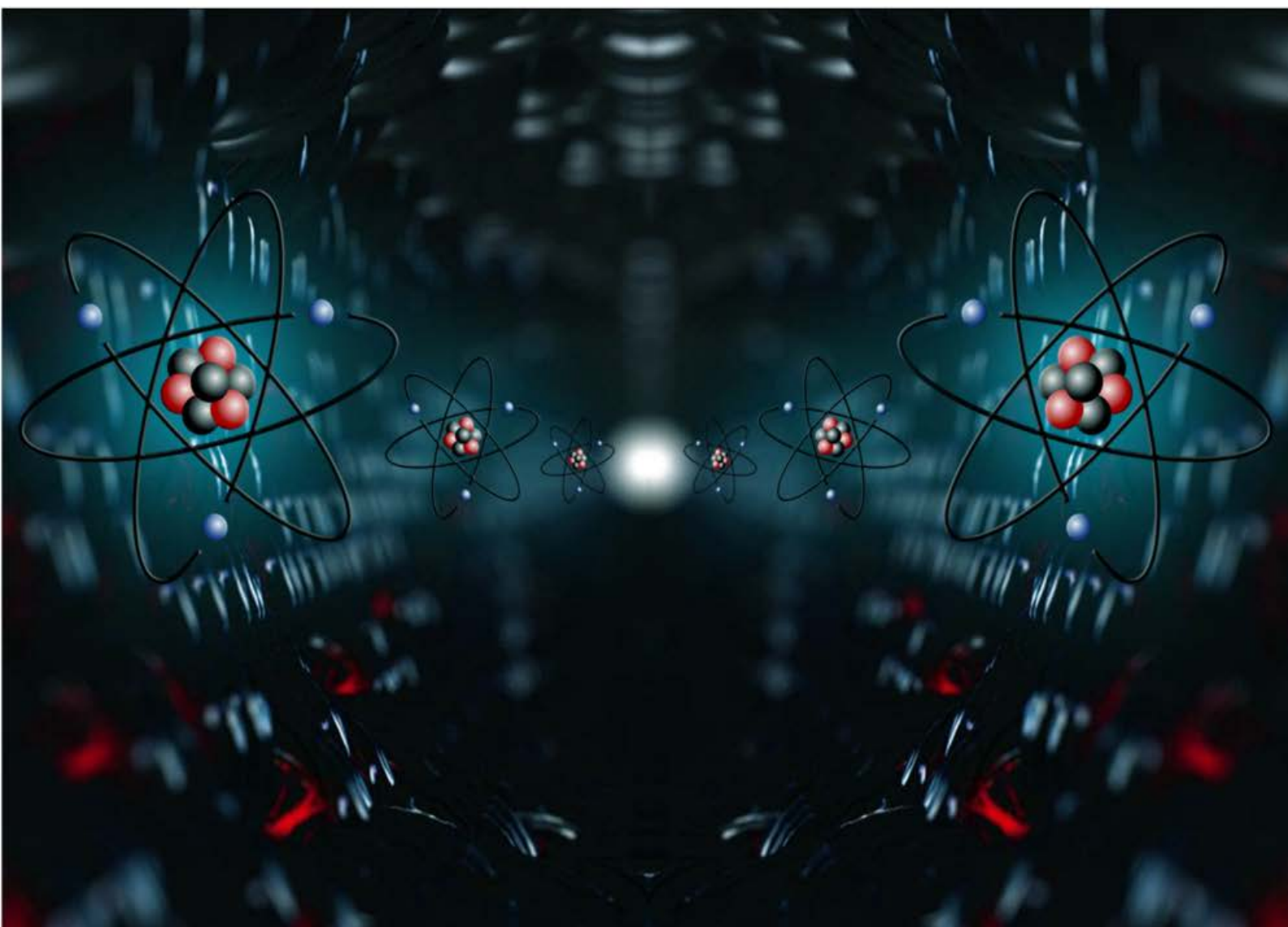
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# Table of Contents

<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>



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