

❖ Ionic Reactions: Single and Double Sphere Models

It is a quite well-known fact that the rate of ionic reactions is generally small, which is obviously due to the larger magnitude of activation energies arising from the very strong nature of electrostatic interactions. The magnitude of the frequency factor in ionic reactions is a function of ionic charges. The frequency factors have larger values if the charges on the participating ions are opposite, while smaller values are obtained in the case of like-charged ions. This behavior can be explained in terms of the kinetic theory of gases; which suggests that oppositely charged ions are more prone to collision due to attraction than the ions colliding with same charges (repulsive forces). Besides the collision theory, the activated complex theory also provides an alternate explanation for the ionic reactions. In this section, we will discuss the rationalization of ionic reactions on the basis of the single-sphere model and the double-sphere model in detail.

➤ Double Sphere Model

Before we discuss the double sphere model of the ionic reactions, a simplified surrounding must be assumed. Although it would be an oversimplification of the actual situation, it is highly beneficial as far as conceptual and quantitative understanding is concerned. To do so, the solvent is considered as continuous surrounding with a ϵ as the dielectric constant.

According to this model, two ions, which can same or opposite charges, combine together to form an activated complex. In the initial state, the ions are considered as discrete; while in the final state, they assumed to form a dumbbell like coordination with ' r ' as the distance of separation between their centers.

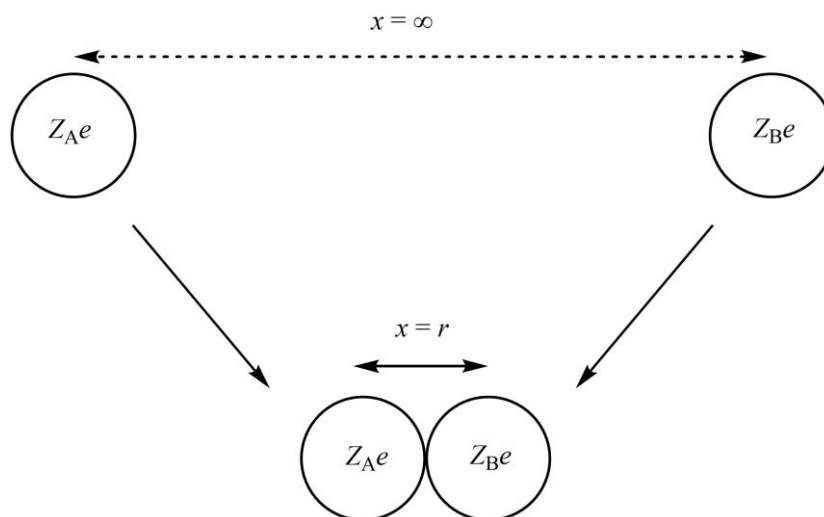


Figure 12. The pictorial depiction of the double-sphere model of ionic reactions.

Now, if Z_A and Z_B are the charge numbers of the participating ions and x as the distance of separation, the force of electrostatic interaction (F_{AB}) between them can be given from the Coulomb's law as:

$$F_{AB} = \frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon x^2} \quad (206)$$

Where ϵ_0 and ϵ are permittivities of the vacuum ($8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$) and the dielectric constant of the solvent used, respectively. The symbol e represents the elementary charge and has a value equal to $1.6 \times 10^{-19} \text{ C}$. The value of parameter varies from ∞ to r with the mutual approach of two ions. The amount of work done in moving the two ions closer by an extant dx will be

$$\text{work} = \text{force} \times \text{displacement} \quad (207)$$

$$dw = F_{AB} \times dx \quad (208)$$

$$dw = -\frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon x^2} dx \quad (209)$$

The negative sign is an indicator of decreasing separation i.e. distance is reduced by dx . The total amount of work done in moving the two ions from $x = \infty$ to $x = r$ will be

$$w = -\int_{\infty}^r \frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon x^2} dx \quad (210)$$

$$w = -\frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon r} \quad (211)$$

The work given the above equation is actually the potential energy of the system which would have a negative sign for oppositely charged ions and positive sign if the ions have same charges. Furthermore, we can also say that this work is the free energy change due to electrostatic interactions, therefore, multiplying it by Avogadro number (N) would give the value of the corresponding molar free energy change (ΔG_{EI}^*) i.e.

$$\Delta G_{EI}^* = \frac{NZ_A Z_B e^2}{4\pi\epsilon_0\epsilon r} \quad (212)$$

Correcting the above equation for non-electrostatic contribution ΔG_{NEI}^* , the total molar free energy change for the whole process can be given by the following relation.

$$\Delta G^* = \Delta G_{NEI}^* + \Delta G_{EI}^* = \Delta G_{NEI}^* + \frac{NZ_A Z_B e^2}{4\pi\epsilon_0\epsilon r} \quad (213)$$

Also, from the activated complex theory, we know that

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^*}{RT}} \quad (214)$$

After putting the value of ΔG^* from equation (213) into equation (214), we get

$$k = \frac{RT}{Nh} e^{-\left(\frac{\Delta G_{NEI}^*}{RT} + \frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r}\right)} \quad (215)$$

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G_{NEI}^*}{RT}} \cdot e^{-\frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r}} \quad (216)$$

Taking natural logarithm both side of equation (216), we get

$$\ln k = \ln \frac{RT}{Nh} + \ln e^{-\frac{\Delta G_{NEI}^*}{RT}} + \ln e^{-\frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r}} \quad (217)$$

or

$$\ln k = \ln \frac{RT}{Nh} - \frac{\Delta G_{NEI}^*}{RT} - \frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r} \quad (218)$$

Which can also be expressed as

$$\ln k = \ln k_0 - \frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r} \quad (219)$$

Where k_0 represents the magnitude of the rate constant for the ionic reaction carried out in a solvent of infinite dielectric constant so that the electrostatic interactions become zero.

➤ *Single Sphere Model*

Besides the double-sphere model, another theoretical model that is quite rationalizing is a single-sphere model. Just like the double-sphere model, the solvent is also considered as a continuum with a ϵ as the dielectric constant. However, the primary differentiating aspect of this model is that it considers the two ions, which can same or opposite charges, to form a single-sphere activated complex.

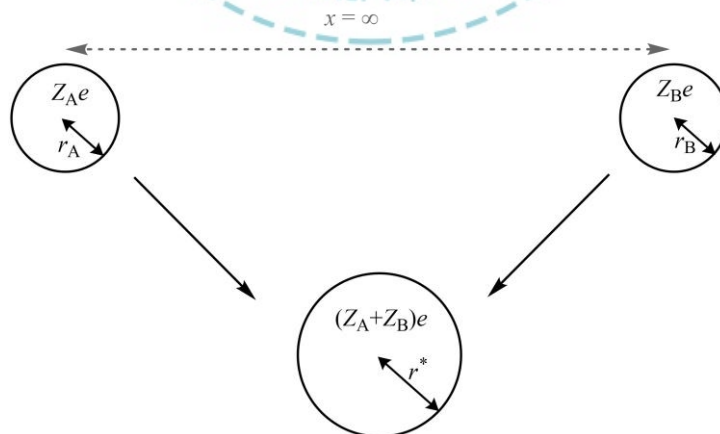


Figure 12. The pictorial depiction of the single-sphere model of ionic reactions.

In the initial state, the ions are considered as discrete; while in the final state, they assumed to form a single-sphere activated complex with ' r^* ' as the overall radius. The rate law for this case was derived by Born by considering the energy required to charge an ion in solution. Now suppose that we need to charge a conducting sphere of radius r from an initial value of zero to the final value Ze . This can be visualized as a process in which a very small charge is $e.d\lambda$ ($\lambda = 0 - Z$) is carried from infinite to this sphere.

Now, if Z_A and Z_B are the charge numbers of the participating ions and x as the distance of separation between the sphere and the "increment" at any time, the force of electrostatic interaction (dF) between them can be given from the Coulomb's law as:

$$dF = \frac{\lambda e^2 d\lambda}{4\pi\epsilon_0\epsilon x^2} \quad (220)$$

Where ϵ_0 and ϵ are permittivities of the vacuum ($8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$) and the dielectric constant of the solvent used, respectively. The symbol e represents the elementary charge and has a value equal to $1.6 \times 10^{-19} \text{ C}$. The amount of work done in moving the "increment" closer by an extant dx will be

$$dw = dF \times dx \quad (221)$$

$$dw = \frac{\lambda e^2 d\lambda}{4\pi\epsilon_0\epsilon x^2} dx \quad (222)$$

The total amount of work done can be obtained by carrying out the double integration with respect to $x = \infty - r$ and $\lambda = 0 - Z$ i.e.

$$w = \frac{e^2}{4\pi\epsilon_0\epsilon} \int_0^Z \int_{\infty}^r \frac{\lambda}{x^2} d\lambda dx \quad (223)$$

$$w = \frac{Z^2 e^2}{8\pi\epsilon_0\epsilon r} \quad (224)$$

The work given the above equation is actually the contribution of the electrostatic interactions to the Gibbs energy of the ion i.e.

$$G_{EI} = \frac{Z^2 e^2}{8\pi\epsilon_0\epsilon r} \quad (225)$$

In the light of the above correlation, the electrostatic contribution to the Gibbs free energy of discrete ions and activated complex can be written as

$$G_{EI}(A) = \frac{Z_A^2 e^2}{8\pi\epsilon_0\epsilon r_A} \quad (225)$$

$$G_{EI}(B) = \frac{Z_B^2 e^2}{8\pi\epsilon_0\epsilon r_B} \quad (226)$$

$$G_{EI}^* = \frac{(Z_B + Z_A)^2 e^2}{8\pi\epsilon_0\epsilon r^*} \quad (227)$$

Hence, the change in electrostatic contribution can be obtained simply by subtracting the sum of individual contributions from the overall contribution i.e.

$$\Delta G_{EI}^* = \frac{(Z_B + Z_A)^2 e^2}{8\pi\epsilon_0\epsilon r^*} - \frac{Z_A^2 e^2}{8\pi\epsilon_0\epsilon r_A} - \frac{Z_B^2 e^2}{8\pi\epsilon_0\epsilon r_B} \quad (228)$$

or

$$\Delta G_{EI}^* = \frac{e^2}{8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (229)$$

Correcting the above equation for non-electrostatic contribution ΔG_{NEI}^* , the total molar free energy change for the whole process can be given by the following relation.

$$\Delta G^* = \Delta G_{NEI}^* + \Delta G_{EI}^* = \Delta G_{NEI}^* + \frac{Ne^2}{8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (230)$$

Also, from the activated complex theory, we know that

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^*}{RT}} \quad (231)$$

After putting the value of ΔG^* from equation (230) into equation (231), we get

$$k = \frac{RT}{Nh} e^{-\left(\frac{\Delta G_{NEI}^*}{RT} + \frac{Ne^2}{RT8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \right)} \quad (232)$$

Taking natural logarithm both side of equation (232) and rearranging, we get

$$\ln k = \ln \frac{RT}{Nh} - \frac{\Delta G_{NEI}^*}{RT} - \frac{Ne^2}{RT8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (233)$$

Which can also be expressed as

$$\ln k = \ln k_0 - \frac{Ne^2}{RT8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (234)$$

Where k_0 represents the magnitude of the rate constant for the ionic reaction carried out in a solvent of infinite dielectric constant so that the electrostatic interactions become zero.

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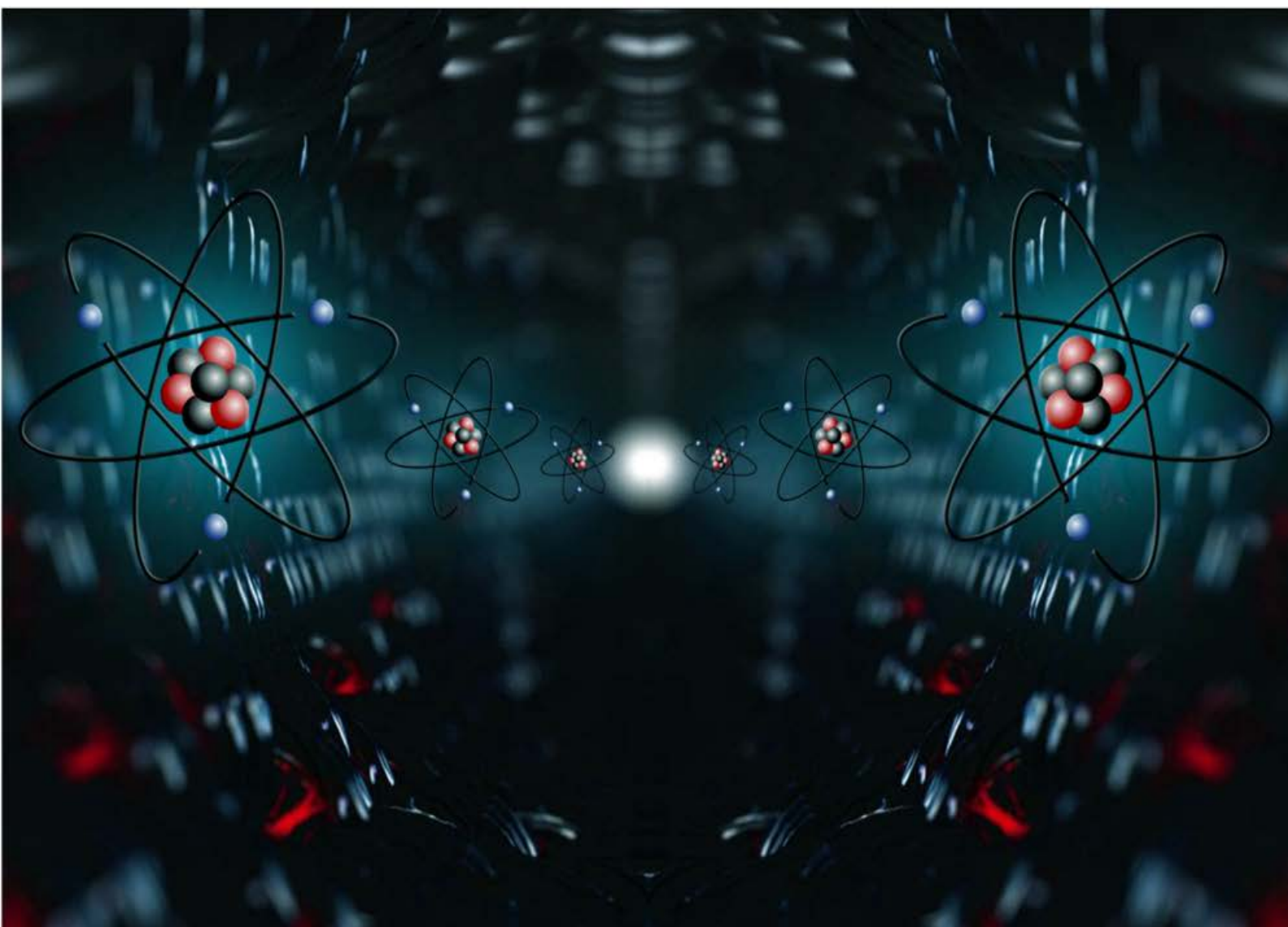
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Volume I

MANDEEP DALAL



First Edition

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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 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 |
| 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 |



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