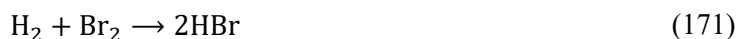
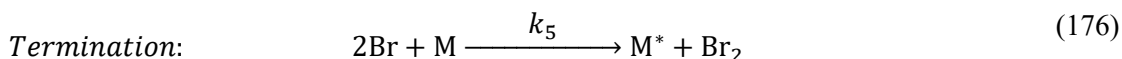
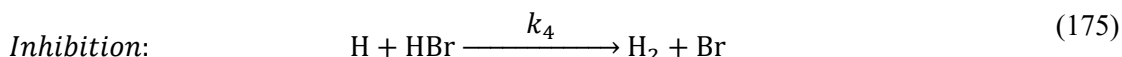
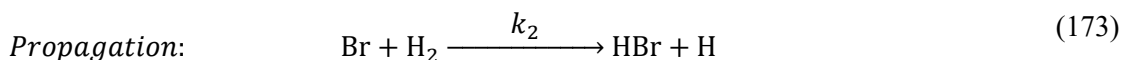
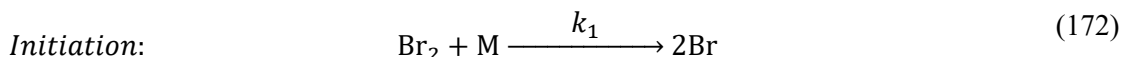


❖ Apparent Activation Energy of Chain Reactions

In order to understand the activation energy profile of chain reactions, consider a typical chain reaction such as the synthesis of hydrogen bromide from its elements.



Furthermore, the elementary steps for the same can be proposed as



It is obvious from the stepwise mechanism that the reaction is actually initiated by the formation of a free radical when one Br_2 molecule collides with some other molecule M (most another Br_2). All this just requires a sufficiently high temperature of the gas. Another mode of formation of Br free radicals is the photochemical activation in which the sample is exposed to light. In second and third reactions, the consumption of a free radical generates another, and therefore, propagates the chain. The same happens in the fourth step, but the molecule of the product is destroyed, and thus inhibited the whole process. Now if these first four steps occur, then the chain would continue for infinite. However, during the course of the 5th step, two Br combine together, and thus terminating the chain. The molecule M^* in the last step represents a thermally-excited which dissipates its energy to other molecules quickly.

The overall rate laws for such chain reactions are quite complex and usually have non-integral orders. The net rate of formation of HBr can be given as

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2]}{1 + (k_4/k_3)[\text{HBr}]/[\text{Br}_2]} \quad (177)$$

Now consider two new constants as

$$k' = 2k_2(k_1/k_5)^{1/2} \quad \text{and} \quad k'' = k_4/k_3 \quad (178)$$

Using in equation (177), we get

$$\frac{d[\text{HBr}]}{dt} = \frac{k'[\text{Br}_2]^{1/2}[\text{H}_2]}{1 + k''[\text{HBr}]/[\text{Br}_2]} \quad (179)$$

The initial reaction rate expression can be obtained by neglecting $[HBr]$ i.e. $1 + k''[HBr]/[Br_2] \approx 1$ as

$$\left[\frac{d[HBr]}{dt} \right]_0 = k' [Br_2]^{1/2} [H_2]_0 \quad (180)$$

Hence, the order of the hydrogen-bromine reaction in the initial stage will be 1.5 only i.e. first-order w.r.t. hydrogen and half w.r.t. bromine. Expanding equation (180), we get

$$\left[\frac{d[HBr]}{dt} \right]_0 = 2k_2 \left(\frac{k_1}{k_5} \right)^{1/2} [Br_2]^{1/2} [H_2]_0 \quad (181)$$

Hence the overall rate constant can be written as

$$k_{overall} = 2k_2 \left(\frac{k_1}{k_5} \right)^{1/2} \quad (182)$$

Now assuming E_1 , E_2 and E_5 are the activation energies for first (initiation), second (propagation) and fifth (termination) steps; we can write general expressions for individual rate constants as

$$k_1 = Ae^{-E_1/RT} \quad (183)$$

$$k_2 = Ae^{-E_2/RT} \quad (184)$$

$$k_5 = Ae^{-E_5/RT} \quad (185)$$

After putting values of k_1 , k_2 and k_5 from equation (183-185) in equation (182), we get

$$k_{overall} = 2Ae^{-E_2/RT} \left(\frac{Ae^{-E_1/RT}}{Ae^{-E_5/RT}} \right)^{1/2} = 2Ae^{-E_2/RT} (e^{-E_1+E_5/RT})^{1/2} \quad (186)$$

$$k_{overall} = 2Ae^{\frac{-E_2}{RT}} e^{\frac{-E_1+E_5}{2RT}} = 2Ae^{\frac{-2E_2-E_1+E_5}{2RT}} = 2Ae^{-\frac{1}{2} \frac{(2E_2+E_1-E_5)}{RT}} \quad (187)$$

Comparing the above result with Arrhenius rate constant $k = Ae^{-E_a/RT}$, we get

$$E_a = \frac{1}{2}(2E_2 + E_1 - E_5) = E_2 - \frac{1}{2}(E_1 - E_5) \quad (188)$$

Recalling that E_1 , E_2 and E_5 are the activation energies for initiation, propagation and termination steps; the equation (188) can be written in more general form i.e.

$$E_a = E_p - \frac{1}{n}(E_i - E_t) \quad (189)$$

Where n is the order of termination step w.r.t. chain carrier.

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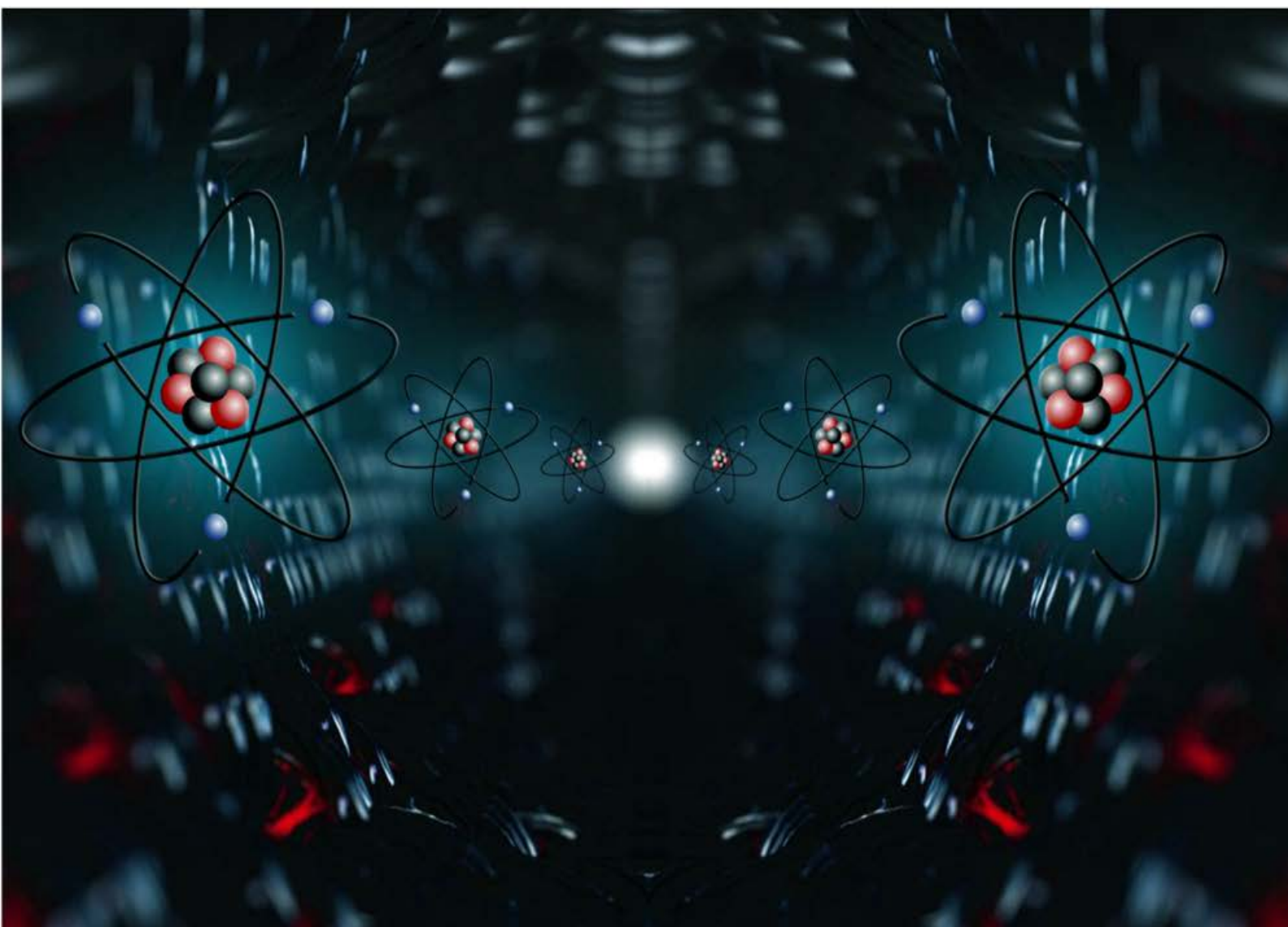
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Table of Contents

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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