

CHAPTER 3

Chemical Dynamics – I

❖ Effect of Temperature on Reaction Rates

The temperature of the system shows a very marked effect on the overall rate of the reaction. In fact, it has been observed that the rate of a chemical reaction typically gets doubled with every 10°C rise in the temperature. However, this ratio may differ considerably and may reach up to 3 for different reactions. Besides, this ratio also varies as the temperature of the reaction increases gradually. The ratio of rate constant at two different temperatures is called as “temperature coefficient” of the reaction. Although we can determine the temperature coefficient between any two temperatures for any chemical reaction, generally it is calculated for 10°C difference.

$$\text{Temperature Coefficient} = \frac{k_{T+10}}{k_T} = 2 - 3 \quad (1)$$

Where k_T and k_{T+10} are rate constants at temperature T and $T+10$, respectively. Now, if once the temperature coefficient is known, you can determine the relative increase or decrease in the overall reaction-rate by using the following relation.

$$\frac{R_2}{R_1} = \frac{k_2}{k_1} = (\text{Temperature Coefficient})^{\frac{T_2-T_1}{\Delta T_{tc}}} \quad (2)$$

Where R_2 and R_1 are the reaction-rates at temperatures T_2 and T_1 , respectively. The ΔT_{tc} is the temperature range for the temperature coefficient.

In order to illustrate the dominance of the effect of temperature change on the reaction rate, consider a reaction in which the temperature of the system is raised from 310°C to 400°C. Now, if the temperature coefficient for 10°C temperature-rise is 2, the relative increase in the rate constant or rate will be

$$\frac{R_2}{R_1} = \frac{k_2}{k_1} = (2)^{\frac{400-310}{10}} \quad (3)$$

$$\frac{R_2}{R_1} = \frac{k_2}{k_1} = (2)^9 = 512 \quad (4)$$

$$\frac{R_2}{R_1} = 512 \quad (5)$$

Hence, a 90°C rise in temperature increases the rate of reaction 512 times, which is definitely huge. Now the question arises, why is it so? What did the temperature do that made this happen? In this section, we will answer these questions.

➤ **Fundamentals of Temperature-Rate Correlation**

Before we discuss the effect of temperature on the reaction rate, we must understand the cause of a reaction itself first. The primary requirement for a reaction to occur is the collision between the reacting molecules. In other words, the reactant molecules must collide with each other to form the product. Therefore, if we assume that every collision results in the formation of the product, the rate of reaction should simply be equal to the collision frequency of the reacting system.

For a reaction between A and B , the collision frequency (Z) is the number of collisions between A and B occurring in the container per unit volume per unit time.

$$Z = n_A n_B \theta_{AB} \sqrt{\frac{8k_B T}{\pi \mu_{AB}}} \quad (6)$$

Where n_A and n_B are the number densities (in the units of m^{-3}) of particles A and B , respectively. The term θ_{AB} is the reaction cross-section (in m^2) when particle A with radius r_A and B with radius r_B collide with each other i.e. $\theta_{AB} = \pi (\sigma_{AB})^2 = \pi (r_A + r_B)^2 = \pi (\sigma_A/2 + \sigma_B/2)^2$. k_B is the Boltzmann's constant ($m^2 kg s^{-2} K^{-1}$). T represents the temperature of the system. The term μ_{AB} represents the reduced mass of the reactants A and B i.e. $\mu_{AB} = m_A m_B / m_A + m_B$. From equation (6), it follows that when we heat the substance, the particles collide more frequently and hence increase the collision frequency. Now one may think that this collision frequency would result in a larger rate of reaction, and therefore, the mystery is solved. However, this isn't sufficient to rationalize the experimental observations. For instance, if we increase the temperature from 300 K to 310 K, the relative increase in the collision frequency (n_Z), and hence in reaction rate, from equation (6) can be determined as given below.

$$n_Z = \sqrt{\frac{310}{300}} = 1.0165 \quad (7)$$

This is only 1.65% increase for a 10° rise in temperature. This is pretty far from the reality i.e. reaction-rate almost gets double (100% increase). So, the actual mechanism is still behind the scene and must be understood.

At this point we must introduce the concept of activation energy, otherwise, the concept cannot be discussed further. The collision of reacting molecules would result in the chemical reaction only if they possess a certain amount of minimum energy i.e. threshold energy. Since every molecule does have some energy, the energy it needs to reach the threshold is less than the actual threshold energy. The energy required by reactant molecules to cross the barrier is called the activation energy or the enthalpy of activation for the reaction. A simple equation can be used to deduce their relationships as given below.

$$\text{Activation energy} = \text{Threshold energy} - \text{Energy actually possessed by the molecules}$$

The rate of a chemical reaction is inversely proportional to the magnitude of the activation energy i.e. larger the activation energy, slower will be the reaction and vice-versa.

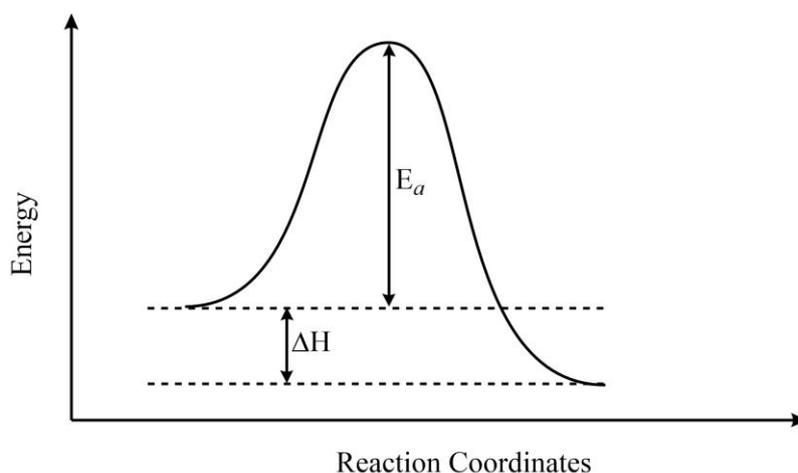


Figure 1. The reaction coordinate diagram for a typical chemical reaction.

Hence, we can say that only effective collisions would result in the chemical reactions, but how can we find the number of molecules having energy high enough to react with each other. For this, we need to go into the basics of energy distribution among a large number of particles i.e. Maxwell's distribution of energies.

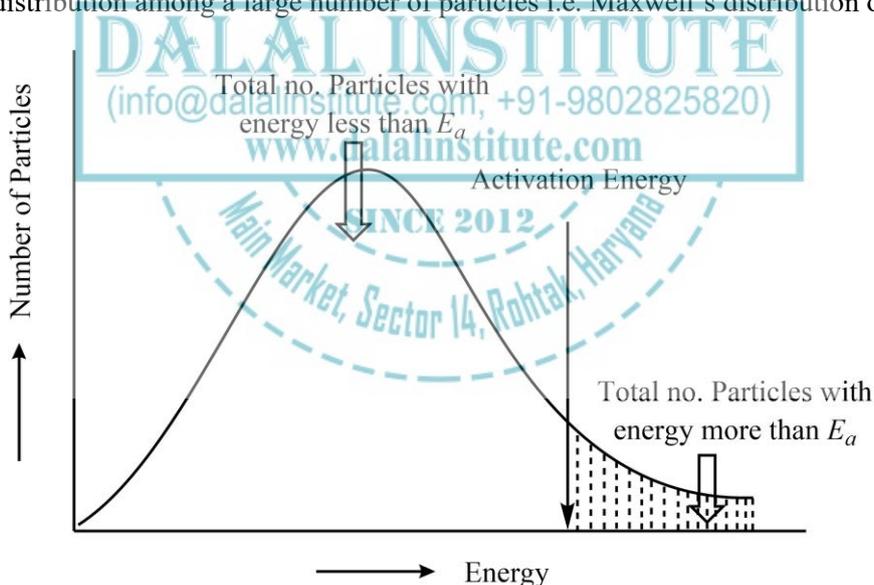


Figure 2. The Maxwell-Boltzmann distribution of energies at temperature T.

After marking the activation energy on the Maxwell-Boltzmann distribution curve, the particle with sufficient energy to react can easily be found from the area under the corresponding curve i.e. dashed area. The undashed area at a particular temperature is quite large, and therefore, represents the number particle whose collision would not result in any reaction chemical change. It can be clearly seen that most of the particles don't have

enough energy, and hence, are unable to yield the product. The reaction-rate will be very small if there are very few particles with enough energy at any time.

However, if the temperature is raised, the maxima of the Maxwell-Boltzmann distribution curve shifts towards higher energy. This makes the number of “efficient particles” to increase and thereby increases the number of effective collisions too. Consider the Maxwell-Boltzmann energy distributions at temperature T and $T+10$.

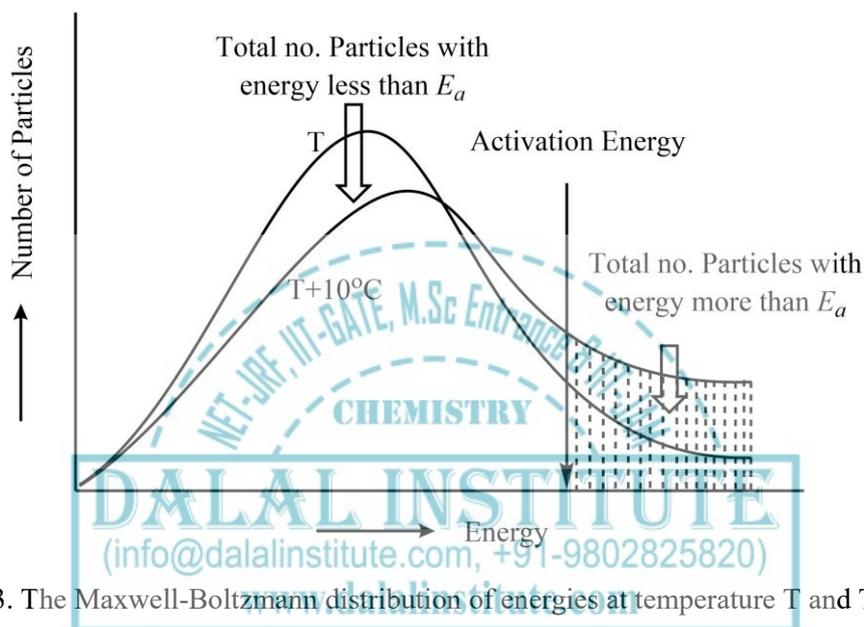


Figure 3. The Maxwell-Boltzmann distribution of energies at temperature T and $T+10^\circ\text{C}$.

Now although the area under the whole curve remains the same, the dashed area is doubled. Thus, the primary reason for almost 100% rise in the overall rate of reaction for every 10°C is the 100% increase in the number of effective collisions.

➤ The Arrhenius Equation

In 1884, the famous Dutch chemist Jacobus Henricus Van't Hoff realized that his equation (Van't Hoff equation) could also be used to suggest a formula for the rates of both forward and backward reactions. In 1889, Svante Arrhenius immediately noticed the importance of this invention and proposed an empirical equation based on Van't Hoff's work. This equation is extremely useful in the modeling of the temperature variation of many chemical reactions. The equation proposed by Arrhenius is

$$k = A e^{-E_a/RT} \quad (8)$$

Where the symbol k , R and T represent rate constant, gas constant and temperature, respectively. A is popularly known as the pre-exponential factor or Arrhenius constant with the units identical to those of the rate constant used, and therefore, will vary depending on the order of the reaction. The term E_a represents the activation energy measured in joule mole^{-1} .

Another popular form of the Arrhenius equation is

$$k = A e^{-E_a/k_B T} \quad (9)$$

The only difference in the equation (8) and equation (9) is the energy units of E_a ; the former one uses energy per mole, which is more common in chemistry, while the latter form uses energy per molecule directly, which is common in physics. The different units are accounted for in using either the gas constant, R , or the Boltzmann constant, k_B , as the multiplier of temperature T . If the reaction is first order, A will have the units of s^{-1} and can be called as collision frequency or frequency factor.

The physical significance of k is that it represents the number of collisions that result in a reaction per second; A is the number of collisions (leading to a reaction or not) per second occurring with the proper orientation to react. The exponential factor is the probability that any given collision will result in a reaction. It can also be seen that either increasing the temperature or decreasing the activation energy (for example through the use of catalysts) will result in an increase in the rate of reaction. Taking the natural logarithm of both side of equation (8), we get

$$\ln k = \ln A + \ln e^{-E_a/RT} \quad (10)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (11)$$

Rearrange the above equation, we get

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (12)$$

The equation (12) has the same form as the equation of straight line i.e. $y = mx + c$; which means that if we plot " $\ln k$ " vs $1/T$, the slope and intercept will yield " $-E_a/R$ " and " $\ln A$ ", respectively.

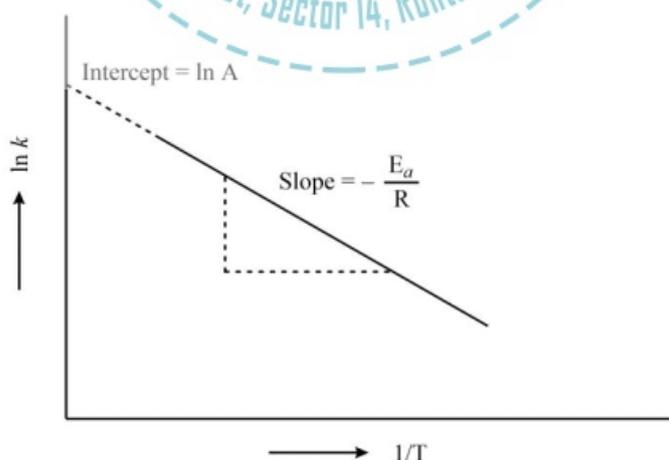


Figure 4. The Arrhenius plot of $\ln k$ vs $1/T$.

In addition to the equation (12), one of the more popular forms of the Arrhenius equation can be derived by converting it to the common logarithm as given below.

$$2.303 \log k = -\frac{E_a}{RT} + 2.303 \log A \quad (13)$$

or

$$\log k = -\frac{E_a}{2.303 RT} + \log A \quad (14)$$

The equation (14) also has the same form as the equation of straight line i.e. $y = mx + c$; which means that if we plot “ $\log k$ ” vs $1/T$, the slope and intercept will yield “ $-E_a/2.303R$ ” and “ $\log A$ ”, respectively.



Figure 5. The Arrhenius plot of $\log k$ vs $1/T$.

To obtain the integrated form of the Arrhenius equation, differentiate the equation (12) as given below.

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad (15)$$

Now integrating the above equation between temperature T_1 and T_2 , we get

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (16)$$

The above equation can be used to find the activation energy if rate constants are known at two different temperatures.

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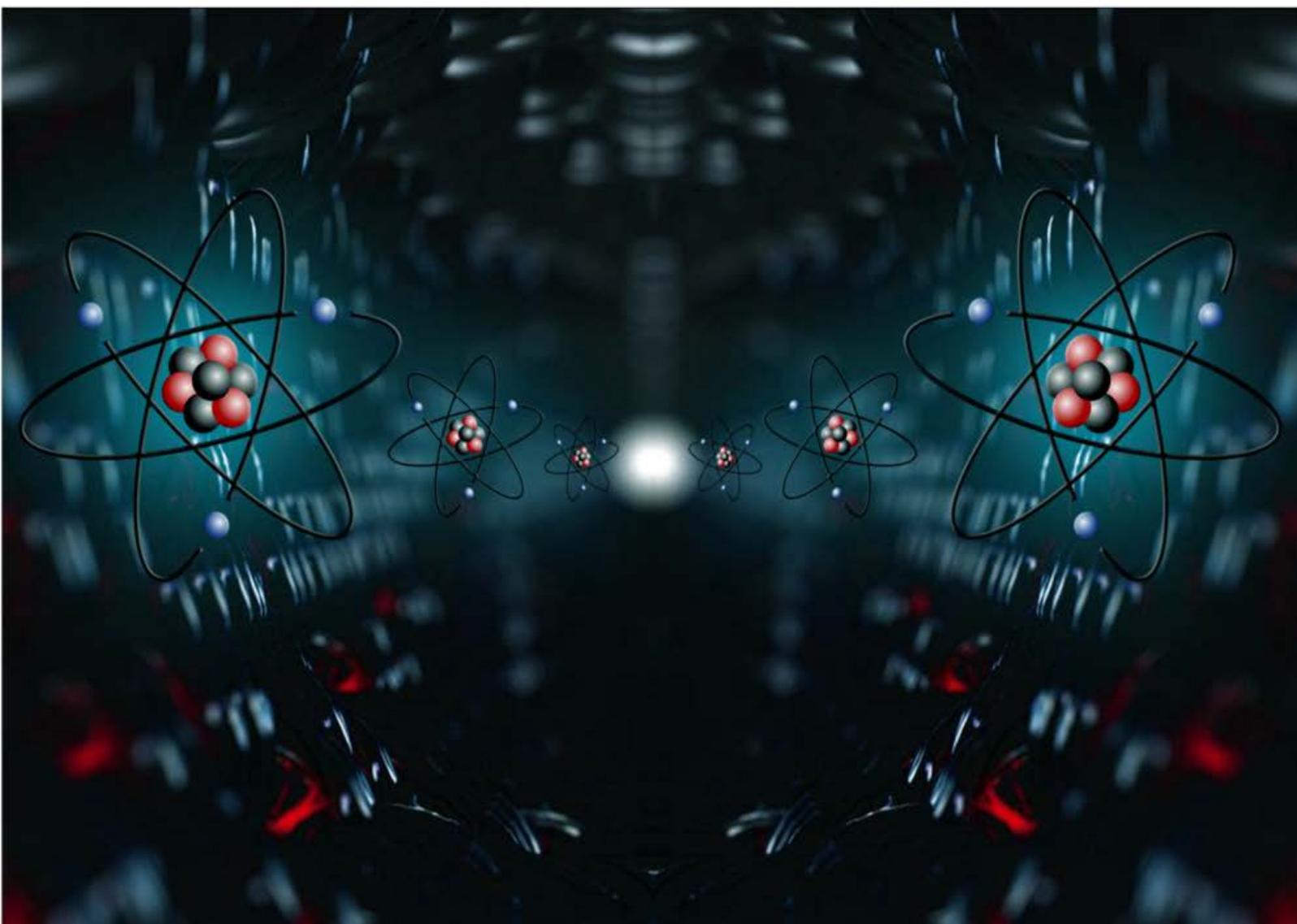
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A TEXTBOOK OF PHYSICAL CHEMISTRY

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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