CHAPTER 7

Chemical Dynamics – II

❖ Chain Reactions: Hydrogen-Bromine Reaction, Pyrolysis of Acetaldehyde, Decomposition of Ethane

A German chemist, Max Bodenstein, proposed the idea of chemical chain reactions in 1913. He suggested that if two molecules react with each other, some unstable molecules may also be formed along-products that can further react with the reactant molecules with a much higher probability than the initial reactants. Another German chemist, Walther Nernst, explained the quantum yield phenomena in 1918 by suggesting that the photochemical reaction between hydrogen and chlorine is actually a chain reaction. He proposed that only one photon of light is actually accountable for the formation of 106 molecules of the final product. W. Nernst proposed that the incident photon breaks a chlorine molecule into two individual Cl atoms, each of which initiates a long series of stepwise reactions giving a large amount of hydrochloric acid.

A Danish scientist, Christian Christiansen; alongside a Dutch chemist, Hendrik Anthony Kramers; observed the polymer-synthesis in 1923 and conclude that a chain reaction doesn’t need a photon always but can also be started by the violent collision of two molecules. They also concluded that if two or more unstable molecules are produced during this reaction, the reaction chain could branch itself to grow enormously resulting in an explosion as well. These ideas were the very initial explanations for the mechanism responsible for the chemical explosions. A more sophisticated theory was proposed by Soviet physicist Nikolay Semyonov in 1934 to explain the quantitative aspects. N. Semyonov received the Nobel Prize in 1956 for his work (along with Sir Cyril Norman Hinshelwood for his independent developments).

Steps Involved in a Typical Chain Reaction: The primary steps involved in a typical chain reaction are discussed below.

i) Initiation: This step includes the formation of chain carriers or simply the active particles usually free radicals in a photochemically or thermally induced chemical change.

ii) Propagation: This step may include many elementary reactions in a cycle in which chain carriers react to forms another chain carrier that continues the chain by entering the next elementary reaction. In other words, we can label these chain carriers as a catalyst for the overall propagation.

iii) Termination: This step includes the elementary chemical change in which the chain carriers lose their activity by combining with each other.

It is also worthy to note that the average number of times the propagation cycle is repeated is equal to the ratio of the overall reaction rate to the rate of initiation, and is called as “chain length”. Furthermore, some chain reactions follow very complex rate laws with mixed or fractional order kinetics. In this section, we will discuss nature and kinetics some of the most popular chain reactions such as ethane’s decomposition.
**General Kinetics of Chain Reactions**

On the basis of the chain carriers produced in each propagation step, the chain reactions can primarily be classified into two categories: non-branched or the stationary reactions and branched or the non-stationary reactions. A typical chain reaction can be written as given below.

\[
\begin{align*}
\text{Initiation:} & \quad A \xrightarrow{k_1} R^* \\
\text{Propagation:} & \quad R^* + A \xrightarrow{k_2} P + nR^* \\
\text{Termination:} & \quad R^* \xrightarrow{k_3} \text{destruction}
\end{align*}
\]

Where \(P, R^*\) and \(A\) represent the product, radical (or chain carrier) and reactant molecules, respectively. The symbol represents a number that equals unity for stationary chain reactions and greater than one for non-stationary or the branched-chain reactions. Furthermore, the destruction of the radical in the termination step can occur either via its collision with another radical (in gas phase) or by striking the walls of the container.

The steady-state approximation can be employed to determine the concentration of intermediate or the radical involved in the propagation step. The general procedure for which is to put the overall rate of formation equals to zero. In other words, the rate of formation of \(R^*\) must be equal to the rate of decomposition of the same i.e.

\[
\text{Rate of formation of } R^* = \text{Rate of disappearance of } R^*
\]

\[
k_1[A] - k_2[R^*] - k_2(n-1)[R^*][A] = 0
\]

\[
k_1[A] - k_3[R^*] + k_2(n-1)[R^*][A] = 0 = \frac{d[R^*]}{dt}
\]

or

\[
-k_3[R^*] + k_2(n-1)[R^*][A] = -k_1[A]
\]

\[
[R^*] = \frac{k_1[A]}{k_2(1-n)[A] + k_3}
\]

Now because the destruction of the radical in the termination step can occur either via its collision with another radical (in the gas phase) or via striking the walls of the container, the rate constant \(k_3\) can be replaced by the sum of the rate constants of two i.e. \(k_3 = k_w + k_g\). After using the value of \(k_3\) in equation (7), we have

\[
[R^*] = \frac{k_1[A]}{k_2(1-n)[A] + k_w + k_g}
\]

Now we are ready to apply the concept on different types of chain reactions.
The hydrogen-bromine or the \( \text{H}_2\text{Br}_2 \) reaction is a typical case of stationary type chain reactions \((n = 1)\) for which the overall reaction can be written as given below.

\[
\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}
\]

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

\begin{align*}
\textbf{Initiation:} & \quad \text{Br}_2 \xrightarrow{k_1} 2\text{Br} \\
\textbf{Propagation:} & \quad \text{Br} + \text{H}_2 \xrightarrow{k_2} \text{HBr} + \text{H} \\
& \quad \text{H} + \text{Br}_2 \xrightarrow{k_3} \text{HBr} + \text{Br} \\
\textbf{Inhibition:} & \quad \text{H} + \text{HBr} \xrightarrow{k_4} \text{H}_2 + \text{Br} \\
\textbf{Termination:} & \quad \text{Br} + \text{Br} \xrightarrow{k_5} \text{Br}_2
\end{align*}

The net rate of formation of HBr must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

\[
\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[H][\text{Br}_2] - k_4[H][\text{HBr}]
\]

Now, in order to obtain the overall rate expression, we need to apply the steady-state approximation on the \( \text{H} \) and \( \text{Br} \) first i.e.

\[
\frac{d[H]}{dt} = 0 = k_2[\text{Br}][H][H_2] + k_3[H][\text{Br}_2] - k_4[H][\text{HBr}]
\]

Similarly,

\[
\frac{d[\text{Br}]}{dt} = 0 = 2k_1[\text{Br}_2] - k_2[\text{Br}][H_2] + k_3[H][\text{Br}_2] + k_4[H][\text{HBr}] - 2k_5[\text{Br}]^2
\]

Taking negative both side of equation (17), we have

\[
-k_2[\text{Br}][H_2] + k_3[H][\text{Br}_2] + k_4[H][\text{HBr}] = 0
\]

Using the above result in equation (18), we get

\[
2k_1[\text{Br}_2] + 0 - 2k_5[\text{Br}]^2 = 0
\]

\[
2k_5[\text{Br}]^2 = 2k_1[\text{Br}_2]
\]
Similarly, rearranging equation (17) again

\[ k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2] \] (23)

\[ [H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} \] (24)

Now using the value of \([Br]\) from equation (22), the above equation takes the form

\[ [H] = \frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \] (25)

Now rearranging equation (17) again in different mode i.e.

\[ k_2[Br][H_2] + k_4[H][HBr] = k_3[H][Br_2] \] (26)

Using the above result in equation (16), we have

\[ \frac{d[Br]}{dt} = k_2[H][Br_2] + k_3[H][Br_2] \] (27)

\[ \frac{d[HBr]}{dt} = 2k_3[H][Br_2] \] (28)

After putting the value of \([H]\) from equation (24), the equation (28) takes the form

\[ \frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \] (29)

Taking \(k_3[Br_2]\) as common in the denominator and then canceling out the same form numerator, we get

\[ \frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_4/k_3)[HBr]/[Br_2]} \] (30)

Now consider two new constants as

\[ k' = 2k_2(k_1/k_5)^{1/2} \quad \text{and} \quad k'' = k_4/k_3 \] (31)

Using the above results in equation (30), we get

\[ \frac{d[HBr]}{dt} = \frac{k'[Br_2]^{1/2}[H_2]}{1 + k''[HBr]/[Br_2]} \] (32)

The initial reaction rate expression can be obtained by neglecting \([HBr]\) i.e. \(1 + k''[HBr]/[Br_2] \approx 1\) as
\[
\frac{d[HBr]}{dt} = k'[Br_2]^{1/2}[H_2]_0
\]  
(33)

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.

**Pyrolysis of Acetaldehyde**

The pyrolysis of acetaldehyde is another typical case of stationary type chain reactions \((n = 1)\) for which the overall reaction can be written as given below.

\[
CH_3CHO \rightarrow CH_4 + CO
\]  
(34)

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

*Initiation:*
\[
CH_3CHO \quad \rightarrow \quad \dot{CH}_3 + \dot{CHO}
\]  
(35)

*Propagation:*
\[
\dot{CH}_3 + CH_3CHO \quad \rightarrow \quad CH_4 + \dot{CH}_2CHO
\]  
(36)

\[
\dot{CH}_2CHO \quad \rightarrow \quad \dot{CH}_3 + CO
\]  
(37)

*Termination:*
\[
CH_3 + CH_3 \quad \rightarrow \quad CH_3CH_3
\]  
(38)

The net rate of formation of \(CH_4\) must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

\[
\frac{d[CH_4]}{dt} = k_2 [\dot{CH}_3][CH_3CHO]
\]  
(39)

Now, in order to obtain the overall rate expression, we need to apply the steady-state approximation on the \([\dot{CH}_3]\) and \([\dot{CH}_2CHO]\) first i.e.

\[
\frac{d[CH_3]}{dt} = 0 = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_2CHO] - 2k_4[CH_3]^2
\]  
(40)

Similarly,

\[
\frac{d[\dot{CH}_2CHO]}{dt} = 0 = k_2[CH_3][CH_3CHO] - k_3[\dot{CH}_2CHO]
\]  
(41)

Taking negative both side of equation (41), we have

\[
-k_2[CH_3][CH_3CHO] + k_3[\dot{CH}_2CHO] = 0
\]  
(42)

Using the above result in equation (40), we get
\[ k_1[\text{CH}_3\text{CHO}] + 0 - 2k_4[\text{CH}_3]^2 = 0 \]  
(43)

\[ [\cdot \text{CH}_3] = \left( \frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2} \]  
(44)

After putting the value of $[\text{CH}_3]$ from equation (44) in equation (39), we have

\[ \frac{d[\text{CH}_4]}{dt} = k_2 \left( \frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2} [\text{CH}_3\text{CHO}] \]  
(45)

\[ \frac{d[\text{CH}_4]}{dt} = k_2 \left( \frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2} \]  
(46)

Now consider a new constant as

\[ k = k_2 \left( \frac{k_1}{2k_4} \right)^{1/2} \]  
(47)

Using in equation (46), we get

\[ \frac{d[\text{CH}_4]}{dt} = k [\text{CH}_3\text{CHO}]^{3/2} \]  
(48)

The kinetic chain length for the same can be obtained by dividing the rate of formation of the product by rate of initiation step i.e.

\[ \text{Kinetic chain length} = \frac{R_p}{R_i} \]  
(49)

Where $R_p$ and $R_i$ are the rate of propagation and rate of initiation respectively. Now since the rate of propagation is simply equal to the overall rate law i.e. equation (48), the rate of initiation can be given as

\[ R_i = k_1[\text{CH}_3\text{CHO}] \]  
(50)

After using the values of $R_p$ and $R_i$ from equation (48, 50) in equation (49), we get the expression for kinetic chain length as

\[ \text{Kinetic chain length} = \frac{k[\text{CH}_3\text{CHO}]^{3/2}}{k_1[\text{CH}_3\text{CHO}]} \]  
(51)

or

\[ \text{Kinetic chain length} = \frac{k}{k_1} [\text{CH}_3\text{CHO}]^{1/2} \]  
(52)
Decomposition of Ethane

The decomposition of ethane is another typical case of stationary type chain reactions \((n = 1)\) for which the overall reaction can be written as given below.

\[
\text{CH}_3\text{CH}_3 \rightarrow \text{CH}_2 = \text{CH}_2 + \text{H}_2 \tag{53}
\]

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

**Initiation:**

\[
\text{CH}_3\text{CH}_3 \xrightarrow{k_1} \cdot\text{CH}_3 + \cdot\text{CH}_3 \tag{54}
\]

**Propagation:**

\[
\cdot\text{CH}_3 + \text{CH}_3\text{CH}_3 \xrightarrow{k_2} \text{CH}_4 + \cdot\text{CH}_2\text{CH}_3 \tag{55}
\]

\[
\cdot\text{CH}_2\text{CH}_3 \xrightarrow{k_3} \text{CH}_2 = \text{CH}_2 + \cdot\text{H} \tag{56}
\]

\[
\text{CH}_3\text{CH}_3 + \cdot\text{H} \xrightarrow{k_4} \cdot\text{CH}_2\text{CH}_3 + \text{H}_2 \tag{57}
\]

**Termination:**

\[
\cdot\text{CH}_2\text{CH}_3 + \cdot\text{H} \xrightarrow{k_5} \text{CH}_3\text{CH}_3 \tag{58}
\]

The net rate of decomposition of ethane must be equal to the rate of formation ethylene i.e.

\[
\frac{d[\text{C}_2\text{H}_6]}{dt} = \frac{d[\text{C}_2\text{H}_4]}{dt} = k_3[\cdot\text{CH}_3] \tag{59}
\]

Now, in order to obtain the overall rate expression, we need to apply the steady-state approximation on the \([\cdot\text{H}], [\cdot\text{CH}_3]\) and \([\cdot\text{CH}_2\text{CH}_3]\) first i.e.

\[
\frac{d[\cdot\text{CH}_3]}{dt} = 0 = 2k_1[\text{CH}_3\text{CH}_3] - k_2[\cdot\text{CH}_3][\text{CH}_3\text{CH}_3] \tag{60}
\]

Similarly,

\[
\frac{d[\cdot\text{CH}_2\text{CH}_3]}{dt} = 0 = k_2[\cdot\text{CH}_3][\text{CH}_3\text{CH}_3] - k_3[\cdot\text{CH}_2\text{CH}_3] + k_4[\cdot\text{H}][\text{CH}_3\text{CH}_3] - k_5[\cdot\text{H}][\cdot\text{CH}_2\text{CH}_3] \tag{61}
\]

Similarly,

\[
\frac{d[\cdot\text{H}]}{dt} = 0 = k_3[\cdot\text{CH}_2\text{CH}_3] - k_4[\cdot\text{H}][\text{CH}_3\text{CH}_3] - k_5[\cdot\text{H}][\cdot\text{CH}_2\text{CH}_3] \tag{62}
\]

Rearranging equation (60), we get

\[
2k_1 - k_2[\cdot\text{CH}_3] = 0 \quad \text{or} \quad [\cdot\text{CH}_3] = \frac{2k_1}{k_2} \tag{64}
\]
CHAPTER 7 Chemical Dynamics – II

Rearranging equation (62), we get

\[ k_4[^1H][CH_3CH_3] + k_5[^1H][CH_2CH_3] = k_3[CH_2CH_3] \] (65)

\[ [^1H] = \frac{k_3[CH_2CH_3]}{k_4[CH_3CH_3] + k_5[CH_2CH_3]} \] (66)

After putting the value of [CH_3] and [^1H] from equation (64, 66) in equation (61), we have

\[ k_2 \left( \frac{2k_1}{k_2} \right) [CH_3CH_3] - k_3[CH_2CH_3] + k_4 \left( \frac{k_3[CH_2CH_3]}{k_4[CH_3CH_3] + k_5[CH_2CH_3]} \right) [CH_3CH_3] \]

\[ - k_5 \left( \frac{k_3[CH_2CH_3]}{k_4[CH_3CH_3] + k_5[CH_2CH_3]} \right) [CH_2CH_3] = 0 \] (67)

or

\[ k_3k_5[CH_2CH_3]^2 - k_1k_5[CH_2CH_3][CH_3CH_3] - k_4k_3[CH_3CH_3]^2 = 0 \] (68)

The equation (68) is quadric in nature and can be solved to give

\[ [CH_2CH_3] = \frac{k_1k_5 + (k_1^2k_5^2 + 4k_1k_5k_3k_4)^{1/2}}{2k_5k_3} \] (69)

Now putting the result in equation (59), we get

\[ - \frac{d[C_2H_6]}{dt} \frac{d[C_2H_4]}{dt} = \frac{k_3k_5}{2k_5k_3} \frac{k_1k_5 + (k_1^2k_5^2 + 4k_1k_5k_3k_4)^{1/2}}{[CH_3CH_3]} \] (70)

\[ - \frac{d[C_2H_6]}{dt} \frac{d[C_2H_4]}{dt} = \frac{k_3k_5}{2k_5} \frac{k_1k_5 + (k_1^2k_5^2 + 4k_1k_5k_3k_4)^{1/2}}{[CH_3CH_3]} \] (71)

At this stage, defining a new constant as

\[ k = \frac{k_1k_5 + (k_1^2k_5^2 + 4k_1k_5k_3k_4)^{1/2}}{2k_5} \] (72)

Now owing to the very small rate of initiation step, all the terms \( k_1k_5 \) and \( k_1^2k_5^2 \) can be neglected i.e.

\[ k = \frac{(4k_1k_5k_3k_4)^{1/2}}{2k_5} = \left( \frac{k_1k_3k_4}{k_5} \right)^{1/2} \] (73)

the equation (71) takes the form

\[ - \frac{d[C_2H_6]}{dt} = k[CH_3CH_3] \] (74)
The kinetic chain length for the same can be obtained by dividing the rate of formation of the product by rate of initiation step i.e.

\[ \text{Kinetic chain length} = \frac{R_p}{R_i} \quad (75) \]

Where \( R_p \) and \( R_i \) are the rate of propagation and rate of initiation respectively. Now since the rate of propagation is simply equal to the overall rate law i.e. equation (74), the rate of initiation can be given as

\[ R_i = k_1[C_3H_5] \quad (76) \]

After using the values of \( R_p \) and \( R_i \) from equation (74, 76) in equation (75), we get the expression for kinetic chain length as

\[ \text{Kinetic chain length} = \frac{k[C_3H_5]}{k_1[C_3H_5]} \quad (77) \]

or

\[ \text{Kinetic chain length} = \frac{k}{k_1} = \left( \frac{k_1 k_3 k_4}{k_5} \right)^{1/2} = \left( \frac{k_3 k_4}{k_1 k_5} \right)^{1/2} \quad (78) \]
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# Table of Contents

## CHAPTER 1

**Quantum Mechanics – I**

- 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

**Thermodynamics – I**

- 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 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

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 ............................................................... 173
  ❖ 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

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
- Schrödinger 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
- Schrödinger Wave Equation for Three Dimensional Rigid Rotator …………………………… 231
- Energy of Rigid Rotator ………………………………………………………………………………… 241
- Space Quantization ……………………………………………………………………………………… 243
- Schrödinger 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 (s, p & d) …………………………………………………………………… 281
- Problems …………………………………………………………………………………………………… 287
- Bibliography ……………………………………………………………………………………………… 288

CHAPTER 6 ……………………………………………………………………………………………………… 289

Thermodynamics – II ……………………………………………………………………………………….. 289
- Clausius-Clapeyron Equation …………………………………………………………………………… 289
- Law of Mass Action and Its Thermodynamic Derivation …………………………………………… 293
- Phase Diagram for Two Completely Miscible Components Systems ……………………………… 304
- Eutectic Systems (Calculation of Eutectic Point) …………………………………………………… 311
- Systems Forming Solid Compounds A\textsubscript{x}B\textsubscript{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
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