

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.

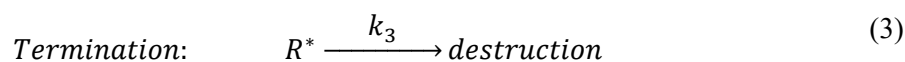
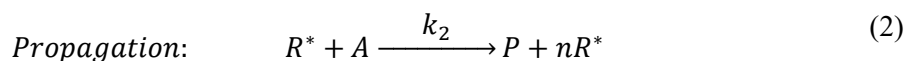
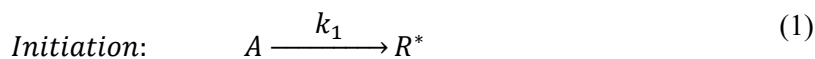
ii) Propagation: This step may include many elementary reactions in a cycle in which chain carriers react to forms another chain carrier that continues the chain by entering the next elementary reaction. In other words, we can label these chain carriers as a catalyst for the overall propagation.

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.



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.

$$\text{Rate of formation of } R^* = \text{Rate of disappearance of } R^* \quad (4)$$

$$k_1[A] = k_3[R^*] + k_2(n-1)[R^*][A] \quad (5)$$

$$k_1[A] - k_3[R^*] + k_2(n-1)[R^*][A] = 0 = \frac{d[R^*]}{dt} \quad (6)$$

or

$$-k_3[R^*] + k_2(n-1)[R^*][A] = -k_1[A] \quad (7)$$

$$[R^*] = \frac{k_1[A]}{k_2(1-n)[A] + k_3} \quad (8)$$

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

$$[R^*] = \frac{k_1[A]}{k_2(1-n)[A] + k_w + k_g} \quad (9)$$

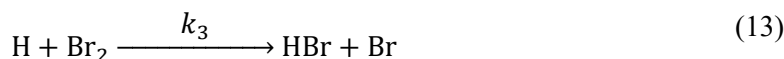
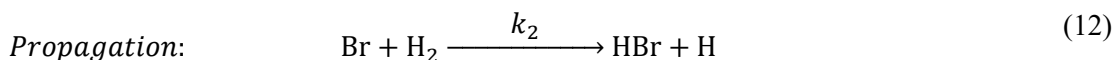
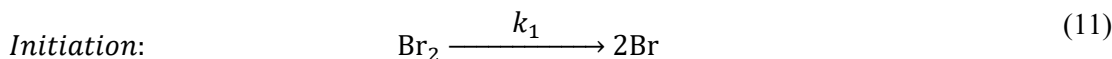
Now we are ready to apply the concept on different types of chain reactions.

➤ **Hydrogen-Bromine Reaction**

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.



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



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.

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \quad (16)$$

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

$$\frac{d[\text{H}]}{dt} = 0 = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \quad (17)$$

Similarly,

$$\frac{d[\text{Br}]}{dt} = 0 = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 \quad (18)$$

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

$$-k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] = 0 \quad (19)$$

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

$$2k_1[\text{Br}_2] + 0 - 2k_5[\text{Br}]^2 = 0 \quad (20)$$

$$2k_5[\text{Br}]^2 = 2k_1[\text{Br}_2] \quad (21)$$

$$[Br] = \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} \quad (22)$$

Similarly, rearranging equation (17) again

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

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

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

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

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

$$k_2[Br][H_2] - k_4[H][HBr] = k_3[H][Br_2] \quad (26)$$

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

$$\frac{d[HBr]}{dt} = k_3[H][Br_2] + k_3[H][Br_2] \quad (27)$$

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

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

$$\frac{d[HBr]}{dt} = \frac{2k_3k_2(k_1/k_5)^{1/2}[Br_2]^{3/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad (29)$$

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

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

Now consider two new constants as

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

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

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

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

$$\left[\frac{d[\text{HBr}]}{dt} \right]_0 = k' [\text{Br}_2]^{1/2} [\text{H}_2]_0 \quad (33)$$

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.



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



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.

$$\frac{d[\text{CH}_4]}{dt} = k_2 [\cdot\text{CH}_3] [\text{CH}_3\text{CHO}] \quad (39)$$

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

$$\frac{d[\cdot\text{CH}_3]}{dt} = 0 = k_1 [\text{CH}_3\text{CHO}] - k_2 [\cdot\text{CH}_3] [\text{CH}_3\text{CHO}] + k_3 [\cdot\text{CH}_2\text{CHO}] - 2k_4 [\cdot\text{CH}_3]^2 \quad (40)$$

Similarly,

$$\frac{d[\cdot\text{CH}_2\text{CHO}]}{dt} = 0 = k_2 [\cdot\text{CH}_3] [\text{CH}_3\text{CHO}] - k_3 [\cdot\text{CH}_2\text{CHO}] \quad (41)$$

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

$$-k_2 [\cdot\text{CH}_3] [\text{CH}_3\text{CHO}] + k_3 [\cdot\text{CH}_2\text{CHO}] = 0 \quad (42)$$

Using the above result in equation (40), we get

$$k_1[\text{CH}_3\text{CHO}] + 0 - 2k_4[\cdot\text{CH}_3]^2 = 0 \quad (43)$$

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

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

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

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

Now consider a new constant as

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

Using in equation (46), we get

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

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.

$$\text{Kinetic chain length} = \frac{R_p}{R_i} \quad (49)$$

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

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

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

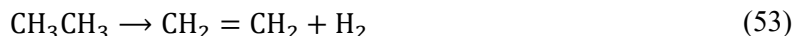
$$\text{Kinetic chain length} = \frac{k[\text{CH}_3\text{CHO}]^{3/2}}{k_1[\text{CH}_3\text{CHO}]} \quad (51)$$

or

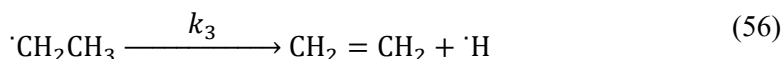
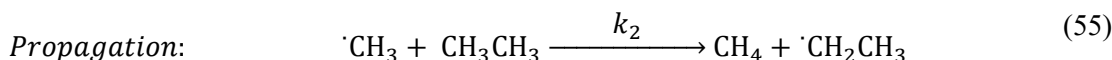
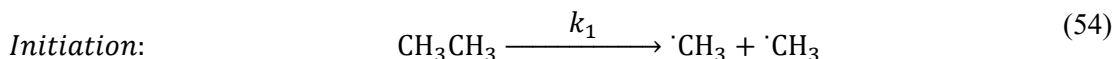
$$\text{Kinetic chain length} = \frac{k}{k_1} [\text{CH}_3\text{CHO}]^{1/2} \quad (52)$$

➤ **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.



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



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

$$-\frac{d[\text{C}_2\text{H}_6]}{dt} = \frac{d[\text{C}_2\text{H}_4]}{dt} = k_3[\cdot\text{CH}_2\text{CH}_3] \quad (59)$$

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.

$$\frac{d[\cdot\text{CH}_3]}{dt} = 0 = 2k_1[\text{CH}_3\text{CH}_3] - k_2[\cdot\text{CH}_3][\text{CH}_3\text{CH}_3] \quad (60)$$

Similarly,

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

Similarly,

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

Rearranging equation (60), we get

$$2k_1 - k_2[\cdot\text{CH}_3] = 0 \quad (63)$$

$$[\cdot\text{CH}_3] = \frac{2k_1}{k_2} \quad (64)$$

Rearranging equation (62), we get

$$k_4[\cdot\text{H}][\text{CH}_3\text{CH}_3] + k_5[\cdot\text{H}][\cdot\text{CH}_2\text{CH}_3] = k_3[\cdot\text{CH}_2\text{CH}_3] \quad (65)$$

$$[\cdot\text{H}] = \frac{k_3[\cdot\text{CH}_2\text{CH}_3]}{k_4[\text{CH}_3\text{CH}_3] + k_5[\cdot\text{CH}_2\text{CH}_3]} \quad (66)$$

After putting the value of $[\cdot\text{CH}_3]$ and $[\cdot\text{H}]$ from equation (64, 66) in equation (61), we have

$$k_2\left(\frac{2k_1}{k_2}\right)[\text{CH}_3\text{CH}_3] - k_3[\cdot\text{CH}_2\text{CH}_3] + k_4\left(\frac{k_3[\cdot\text{CH}_2\text{CH}_3]}{k_4[\text{CH}_3\text{CH}_3] + k_5[\cdot\text{CH}_2\text{CH}_3]}\right)[\text{CH}_3\text{CH}_3] - k_5\left(\frac{k_3[\cdot\text{CH}_2\text{CH}_3]}{k_4[\text{CH}_3\text{CH}_3] + k_5[\cdot\text{CH}_2\text{CH}_3]}\right)[\cdot\text{CH}_2\text{CH}_3] = 0 \quad (67)$$

or

$$k_3k_5[\cdot\text{CH}_2\text{CH}_3]^2 - k_1k_5[\cdot\text{CH}_2\text{CH}_3][\text{CH}_3\text{CH}_3] - k_1k_4[\text{CH}_3\text{CH}_3]^2 = 0 \quad (68)$$

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

$$[\cdot\text{CH}_2\text{CH}_3] = \frac{k_1k_5 + (k_1^2k_5^2 + 4k_1k_5k_3k_4)^{1/2}}{2k_5k_3}[\text{CH}_3\text{CH}_3] \quad (69)$$

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

$$-\frac{d[\text{C}_2\text{H}_6]}{dt} = \frac{d[\text{C}_2\text{H}_4]}{dt} = k_3 \frac{k_1k_5 + (k_1^2k_5^2 + 4k_1k_5k_3k_4)^{1/2}}{2k_5k_3}[\text{CH}_3\text{CH}_3] \quad (70)$$

$$-\frac{d[\text{C}_2\text{H}_6]}{dt} = \frac{k_1k_5 + (k_1^2k_5^2 + 4k_1k_5k_3k_4)^{1/2}}{2k_5}[\text{CH}_3\text{CH}_3] \quad (71)$$

At this stage, defining a new constant as

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

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.

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

the equation (71) takes the form

$$-\frac{d[\text{C}_2\text{H}_6]}{dt} = k[\text{CH}_3\text{CH}_3] \quad (74)$$

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

$$R_i = k_1[\text{CH}_3\text{CH}_3] \quad (76)$$

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

$$\text{Kinetic chain length} = \frac{k[\text{CH}_3\text{CH}_3]}{k_1[\text{CH}_3\text{CH}_3]} \quad (77)$$

or

$$\text{Kinetic chain length} = \frac{k}{k_1} = \frac{1}{k_1} \left(\frac{k_1 k_3 k_4}{k_5} \right)^{1/2} = \left(\frac{k_3 k_4}{k_1 k_5} \right)^{1/2} \quad (78)$$

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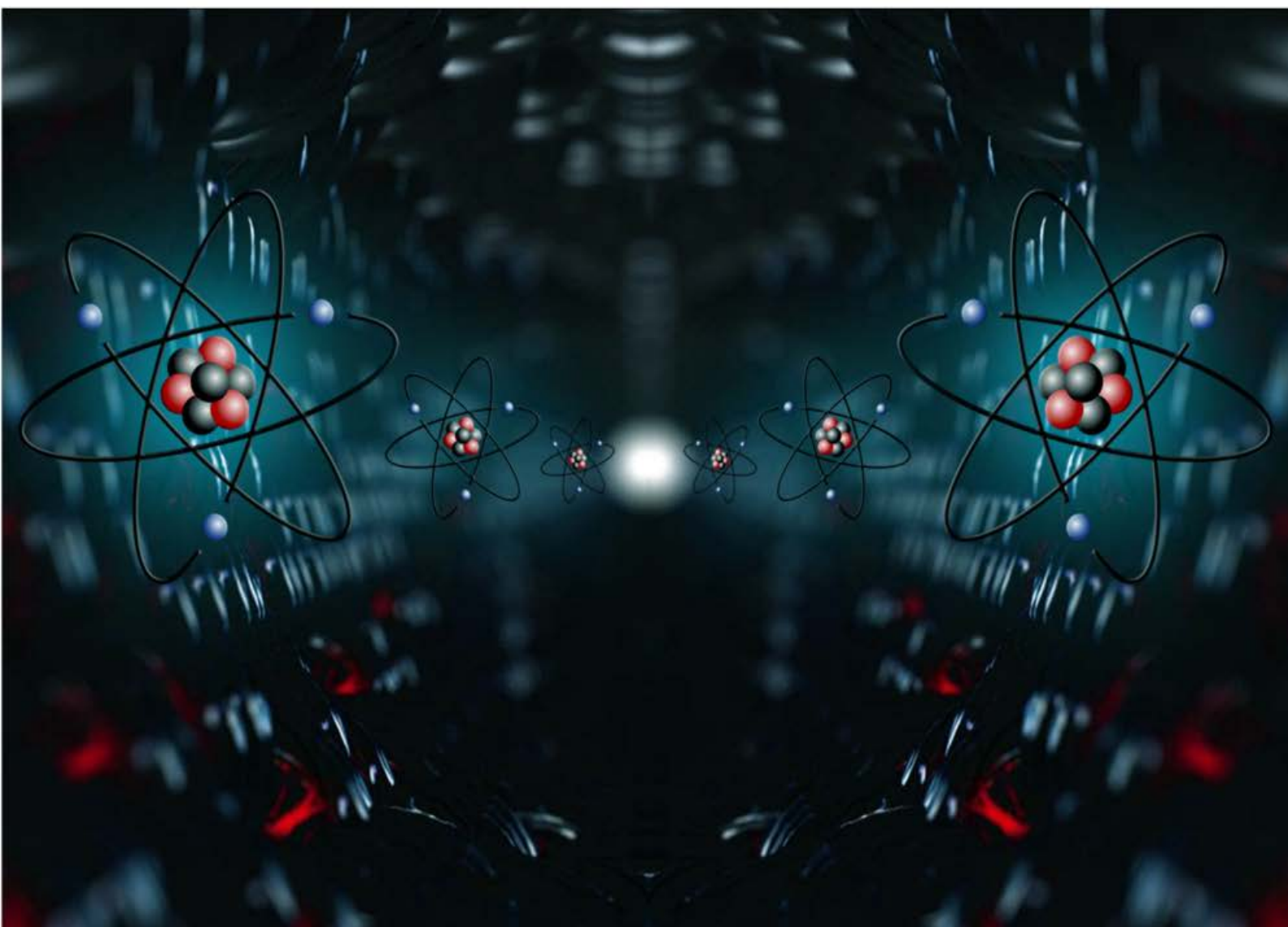
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A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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