

# 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 10<sup>6</sup> 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.

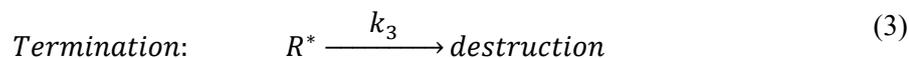
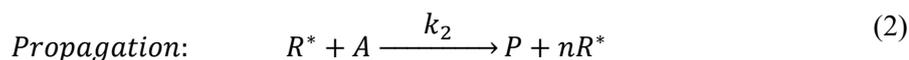
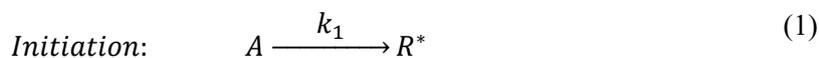
*ii) Propagation:* This step may include many elementary reactions in a cycle in which chain carriers react to forms another chain carrier that continues the chain by entering the next elementary reaction. In other words, we can label these chain carriers as a catalyst for the overall propagation.

*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

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

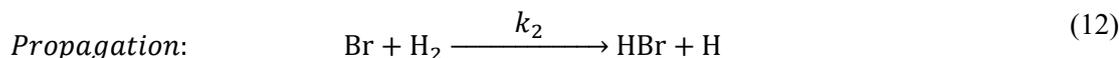
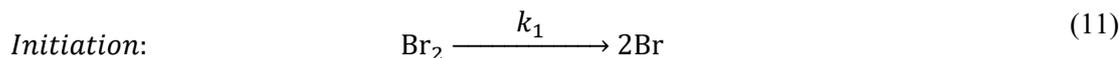
Now we are ready to apply the concept on different types of chain reactions.

➤ **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

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

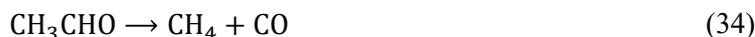
The initial reaction rate expression can be obtained by neglecting  $[HBr]$  i.e.  $1 + k''[HBr]/[Br_2] \approx 1$  as

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

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  $\text{CH}_4$  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

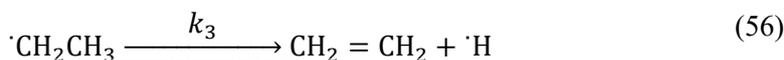
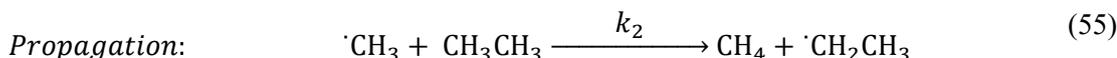
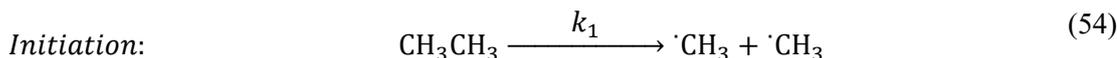
$$\text{Kinetic chain length} = \frac{k}{k_1} [\text{CH}_3\text{CHO}]^{1/2} \quad (52)$$

➤ **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

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

### ❖ Photochemical Reactions (Hydrogen-Bromine & Hydrogen-Chlorine Reactions)

There are many chemical reactions which occur also when the reactants are exposed to light. These reactions are called as photochemical reactions. Now before we discuss the nature and types of photochemical reactions, we need to discuss two laws first; the first is Grotthuss-Draper law while the second one is Stark-Einstein law.

The first law of photochemistry was given by Theodor Grotthuss and John W. Draper, and therefore, got its unique name.

*The first law of photochemistry states that when the light is allowed to strike the reactions mixture, it can be partially transmitted, reflected and absorbed; and it is the absorbed portion of the incident light which is responsible to carry out any chemical change.*

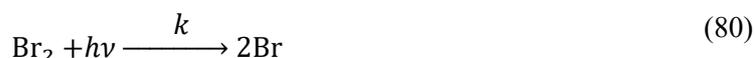
The second law of photochemistry was given by Johannes Stark and Albert Einstein, and therefore, is popularly known as Stark-Einstein law.

*The second law of photochemistry states that one photon of light must be absorbed for one molecule to get activated in a photochemical reaction by a chemical system.*

The quantum yield of a reaction is simply the ratio of number of molecules reacting in a given time to the number of photons absorbed in the same time i.e.

$$\text{Quantum yield}(\phi) = \frac{\text{Number of moles of reactant reacting per second}}{\text{Number of einsteins absorbed per second}} \quad (79)$$

Where one einstein represents one mole of photons ( $6.022 \times 10^{23}$ ). The quantum yield is of two types in photochemical reactions; one for the primary process and the second one for the secondary process. During the course of the primary process, light is absorbed by the reactant and the quantum yield of this part is always unity. Therefore, we can say that the number of radiation-absorbing molecules consumed per unit time in the primary process is equal to intensity of absorbed radiation i.e.  $I_{ab}$  (number of photons striking the sample per unit time). For instance, consider the photo-decomposition



Then, the quantum yield will be

$$\phi = \frac{\text{Number of moles of Br}_2 \text{ decomposed per unit time}}{\text{Number of einsteins absorbed per unit time}} \quad (81)$$

or

$$\phi = \frac{-d[\text{Br}_2]/dt}{I_{ab}} \quad (82)$$

Since  $\phi = 1$  for primary process, we have

$$1 = \frac{-d[\text{Br}_2]/dt}{I_{ab}} \quad (83)$$

or

$$-\frac{d[\text{Br}_2]}{dt} = I_{ab} \quad (84)$$

$$-\frac{d[\text{Br}_2]}{dt} = k[\text{Br}_2] = I_{ab} \quad (85)$$

If rate of formation of Br is asked, then

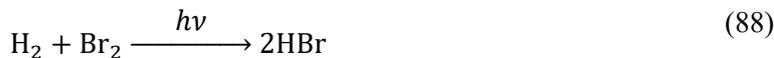
$$-\frac{d[\text{Br}_2]}{dt} = +\frac{1}{2} \frac{d[\text{Br}]}{dt} = k[\text{Br}_2] = I_{ab} \quad (86)$$

$$\frac{d[\text{Br}]}{dt} = 2k[\text{Br}_2] = 2I_{ab} \quad (87)$$

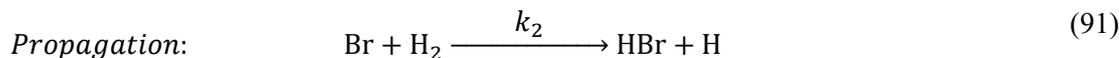
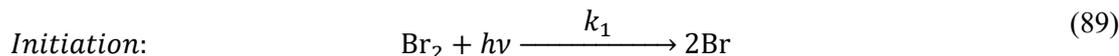
Two of the most common examples of photochemical reactions are hydrogen-bromine and hydrogen-chlorine reactions whose kinetics and nature will be discussed in this section.

➤ **Kinetics of Photochemical Reaction Between Hydrogen and Bromine**

The hydrogen-bromine or the  $H_2$ - $Br_2$  reaction is a typical case of photochemical reactions for which the overall reaction can be written as given below.



Since it is a chain reaction, 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.

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \quad (95)$$

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.

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] = 0 \quad (96)$$

Similarly,

$$\frac{d[Br]}{dt} = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 = 0 \quad (97)$$

Taking negative both side of equation (96), we have

$$-k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] = 0 \quad (98)$$

Using the above result in equation (97), we get

$$2k_1[Br_2] + 0 - 2k_5[Br]^2 = 0 \quad (99)$$

$$2k_5[Br]^2 = 2k_1[Br_2] \quad (100)$$

$$[Br] = \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} \quad (101)$$

Similarly, rearranging equation (96) again

$$k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2] \quad (102)$$

$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} \quad (103)$$

Now using the value of  $[Br]$  from equation (101), the above equation takes the form

$$[H] = \frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad (104)$$

Now rearranging equation (96) again in different mode i.e.

$$k_2[Br][H_2] - k_4[H][HBr] = k_3[H][Br_2] \quad (105)$$

Using the above result in equation (95), we have

$$\frac{d[HBr]}{dt} = k_3[H][Br_2] + k_3[H][Br_2] \quad (106)$$

$$\frac{d[HBr]}{dt} = 2k_3[H][Br_2] \quad (107)$$

After putting the value of  $[H]$  from equation (104), the equation (107) takes the form

$$\frac{d[HBr]}{dt} = \frac{2k_3k_2(k_1/k_5)^{1/2}[Br_2]^{3/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad (108)$$

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

$$\frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_4/k_3)[HBr]/[Br_2]} \quad (109)$$

Now since  $2k_1[Br_2] = 2I_{ab}$ , then

$$k_1^{1/2}[Br_2]^{1/2} = (I_{ab})^{1/2} \quad (110)$$

Using the above result in equation (109), we get

$$\frac{d[HBr]}{dt} = \frac{2k_2(I_{ab}/k_5)^{1/2}[H_2]}{1 + (k_4/k_3)[HBr]/[Br_2]} \quad (111)$$

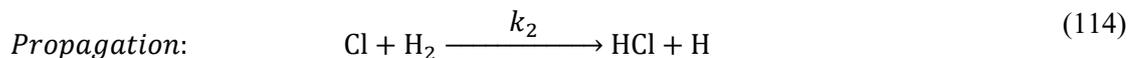
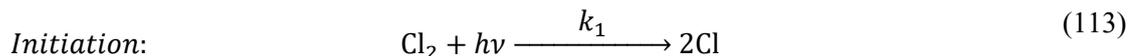
Hence, the rate of hydrogen-bromine reaction is directly proportional to the square root of the intensity of absorbed radiation.

➤ **Kinetics of Photochemical Reaction Between Hydrogen and Chlorine**

The hydrogen-bromine or the  $H_2-Cl_2$  reaction is a typical case of photochemical reactions for which the overall reaction can be written as given below.



Since it is a chain reaction, the elementary steps for the same can be proposed as



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

$$\frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_3[H][Cl_2] \quad (117)$$

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

$$\frac{d[H]}{dt} = k_2[Cl][H_2] - k_3[H][Cl_2] = 0 \quad (118)$$

Similarly,

$$\frac{d[Cl]}{dt} = 2k_1[Cl_2] - k_2[Cl][H_2] + k_3[H][Cl_2] - 2k_4[Cl] = 0 \quad (119)$$

Taking negative both side of equation (118), we have

$$-k_2[Cl][H_2] + k_3[H][Cl_2] = 0 \quad (120)$$

Using the above result in equation (119), we get

$$2k_1[Cl_2] + 0 - 2k_4[Cl] = 0 \quad (121)$$

or

$$2k_1[Cl_2] = 2k_4[Cl] \quad (122)$$

or

$$[Cl] = \frac{k_1}{k_4} [Cl_2] \quad (123)$$

Similarly, rearranging equation (118) again

$$k_2 [Cl][H_2] - k_3 [H][Cl_2] = 0 \quad (124)$$

or

$$[H] = \frac{k_2 [Cl][H_2]}{k_3 [Cl_2]} \quad (125)$$

Now using the value of  $[Cl]$  from equation (123), the above equation takes the form

$$[H] = \frac{k_2 [H_2] k_1}{k_3 [Cl_2] k_4} [Cl_2] = \frac{k_1 k_2 [H_2]}{k_3 k_4} \quad (126)$$

Using values of  $[Cl]$  and  $[H]$  from equation (123, 126) in equation (117), we have

$$\frac{d[HCl]}{dt} = k_2 \frac{k_1}{k_4} [Cl_2][H_2] + k_3 \frac{k_1 k_2 [H_2]}{k_3 k_4} [Cl_2] \quad (127)$$

or

$$\frac{d[HCl]}{dt} = \frac{k_1 k_2 [Cl_2][H_2]}{k_4} + \frac{k_1 k_2 [H_2][Cl_2]}{k_4} \quad (128)$$

Now since  $2k_1 [Cl_2] = 2I_{ab}$ , then

$$k_1 [Cl_2] = I_{ab} \quad (129)$$

Using the above result in equation (129), we get

$$\frac{d[HCl]}{dt} = \frac{k_2 I_{ab} [H_2]}{k_4} + \frac{k_2 I_{ab} [H_2]}{k_4} \quad (130)$$

or

$$\frac{d[HCl]}{dt} = \frac{2k_2 I_{ab} [H_2]}{k_4} \quad (131)$$

Hence, we can conclude that the rate of hydrogen-bromine reaction is directly proportional to the intensity of absorbed radiation. It is also worthy to note that the quantum yield of the hydrogen-chlorine reaction is much higher than that of hydrogen-bromine reaction which may simply be attributed to the exothermic nature of the second step in  $H_2-Cl_2$  reaction which makes it spontaneous in nature.

## ❖ General Treatment of Chain Reactions (Ortho-Para Hydrogen Conversion and Hydrogen-Bromine Reactions)

In this section, we will discuss the general treatment of some common chain reactions like ortho-para hydrogen conversion and hydrogen-bromine reactions. To do so, we may also recall some concepts discussed earlier in this chapter.

### ➤ Ortho-Para Hydrogen Conversion

The ortho-hydrogen can convert into para-hydrogen and can easily be measured in the temperature range of 700–800°C. The conversion is completely homogeneous in nature and the order of the conversion is 1.5 as total. The widely accepted mechanism is given below.



The equilibrium constant for the above-mentioned molecular-atomic equilibria given by equation (132) can be written as

$$K = \frac{[\text{H}]^2}{[p\text{-H}_2]} \quad (134)$$

$$[\text{H}]^2 = K[p\text{-H}_2] \quad (135)$$

$$[\text{H}] = K^{1/2} [p\text{-H}_2]^{1/2} \quad (136)$$

The net rate of conversion of  $p\text{-H}_2$  must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[p\text{-H}_2]}{dt} = k_2 [p\text{-H}_2] [\text{H}] \quad (137)$$

After using the value of  $[\text{H}]$  from equation (136) in equation (137), we get

$$\frac{d[p\text{-H}_2]}{dt} = k_2 [p\text{-H}_2] K^{1/2} [p\text{-H}_2]^{1/2} \quad (137)$$

or

$$\frac{d[p\text{-H}_2]}{dt} = k_2 K^{1/2} [p\text{-H}_2]^{3/2} \quad (137)$$

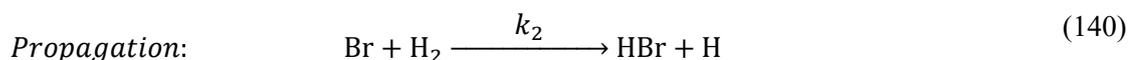
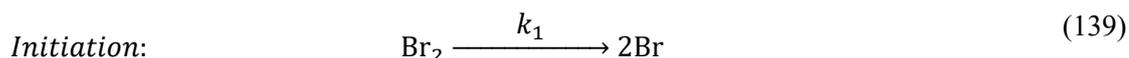
The overall activation energy of the conversion is  $E = E_2 + D/2$  where  $E_2$  is the activation energy of the second step while  $D$  is the dissociation energy of dihydrogen molecule.

➤ **Hydrogen-Bromine Reactions**

The hydrogen-bromine or the  $H_2$ - $Br_2$  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.

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \quad (144)$$

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.

$$\frac{d[H]}{dt} = 0 = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] \quad (145)$$

Similarly,

$$\frac{d[Br]}{dt} = 0 = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 \quad (146)$$

Taking negative both side of equation (145), we have

$$-k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] = 0 \quad (147)$$

Using the above result in equation (146), we get

$$2k_1[Br_2] + 0 - 2k_5[Br]^2 = 0 \quad (148)$$

$$2k_5[Br]^2 = 2k_1[Br_2] \quad (149)$$

$$[Br] = \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} \quad (150)$$

Similarly, rearranging equation (145) again

$$k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2] \quad (151)$$

$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} \quad (152)$$

Now using the value of  $[Br]$  from equation (150), the above equation takes the form

$$[H] = \frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad (153)$$

Now rearranging equation (145) again in different mode i.e.

$$k_2[Br][H_2] - k_4[H][HBr] = k_3[H][Br_2] \quad (154)$$

Using the above result in equation (144), we have

$$\frac{d[HBr]}{dt} = k_3[H][Br_2] + k_3[H][Br_2] \quad (155)$$

$$\frac{d[HBr]}{dt} = 2k_3[H][Br_2] \quad (156)$$

After putting the value of  $[H]$  from equation (152), the equation (156) takes the form

$$\frac{d[HBr]}{dt} = \frac{2k_3k_2(k_1/k_5)^{1/2}[Br_2]^{3/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad (157)$$

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

$$\frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_4/k_3)[HBr]/[Br_2]} \quad (158)$$

Now consider two new constants as

$$k' = 2k_2(k_1/k_5)^{1/2} \quad \text{and} \quad k'' = k_4/k_3 \quad (159)$$

Using in equation (158), we get

$$\frac{d[HBr]}{dt} = \frac{k'[Br_2]^{1/2}[H_2]}{1 + k''[HBr]/[Br_2]} \quad (160)$$

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

$$\left[ \frac{d[\text{HBr}]}{dt} \right]_0 = k' [\text{Br}_2]^{1/2} [\text{H}_2]_0 \quad (161)$$

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.

However, if the initiation occurs by the photon of the incident light, the expression for the overall rate can slightly be modified. Recall the initiation step again via photochemical decomposition i.e.



Then, the quantum yield for this primary change will be

$$\phi = \frac{-d[\text{Br}_2]/dt}{I_{ab}} \quad (163)$$

Where  $I_{ab}$  is the intensity of absorbed radiation. Since  $\phi = 1$  for primary process, we have

$$1 = \frac{-d[\text{Br}_2]/dt}{I_{ab}} \quad (164)$$

$$-\frac{d[\text{Br}_2]}{dt} = I_{ab} \quad (165)$$

$$\frac{d[\text{Br}_2]}{dt} = k[\text{Br}_2] = I_{ab} \quad (166)$$

For the rate of formation of Br, we have

$$-\frac{d[\text{Br}_2]}{dt} = +\frac{1}{2} \frac{d[\text{Br}]}{dt} = k[\text{Br}_2] = I_{ab} \quad (167)$$

$$\frac{d[\text{Br}]}{dt} = 2k[\text{Br}_2] = 2I_{ab} \quad (168)$$

Now since  $2k_1[\text{Br}_2] = 2I_{ab}$ , then

$$k_1^{1/2} [\text{Br}_2]^{1/2} = (I_{ab})^{1/2} \quad (169)$$

Using the above result in equation (158), we get

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2(I_{ab}/k_5)^{1/2}[\text{H}_2]}{1 + (k_4/k_3)[\text{HBr}]/[\text{Br}_2]} \quad (170)$$

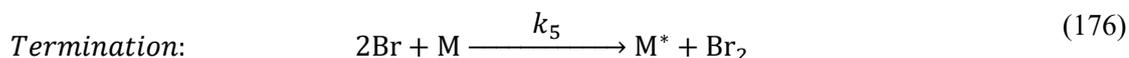
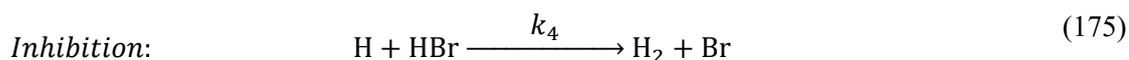
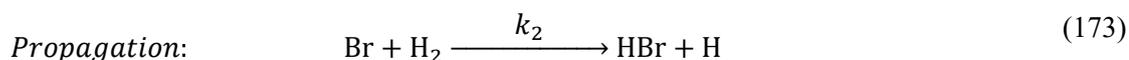
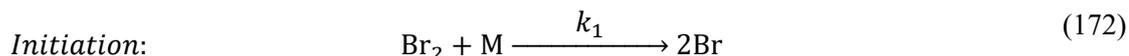
Hence, the rate of hydrogen-bromine reaction is directly proportional to the square root of the intensity of absorbed radiation.

### ❖ 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  $\text{Br}_2$  molecule collides with some other molecule  $\text{M}$  (most another  $\text{Br}_2$ ). All this just requires a sufficiently high temperature of the gas. Another mode of formation of  $\text{Br}$  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 5<sup>th</sup> step, two  $\text{Br}$  combine together, and thus terminating the chain. The molecule  $\text{M}^*$  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  $\text{HBr}$  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

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

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

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.

### ❖ Chain Length

The chain length for any chemical chain reaction may simply be defined as the average number of times that the closed cycle of chain propagation steps is repeated.

In other words, the chain length of any chain reaction is equal to the ratio of the rate of the overall reaction to the rate of the initiation step in which the active particles are generated. Mathematically,

$$\text{Kinetic chain length} = \frac{R_p}{R_i} \quad (190)$$

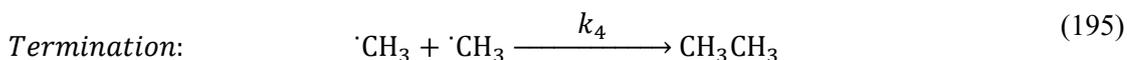
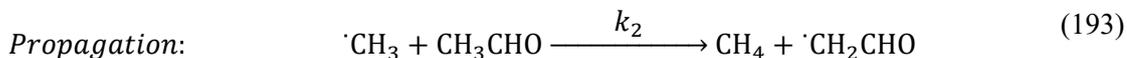
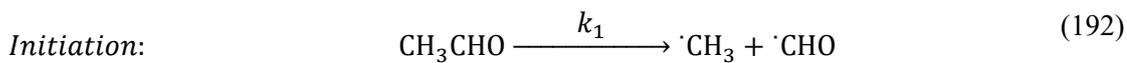
Where  $R_p$  and  $R_i$  are the rate of propagation and rate of initiation respectively. The concept can be well understood by taking the example of thermal decomposition of acetaldehyde and ethane.

#### ➤ Chain length in Case of Thermal Decomposition of Acetaldehyde

The thermal decomposition of acetaldehyde is a typical case of stationary type chain reactions for which the overall reaction can be written as



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



The net rate of formation of  $\text{CH}_4$  must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[\text{CH}_4]}{dt} = k[\text{CH}_3\text{CHO}]^{3/2} \quad (196)$$

Using equation (192), the rate of initiation can be given as

$$R_i = k_1[\text{CH}_3\text{CHO}] \quad (197)$$

Using the values of  $R_p$  and  $R_i$  from equation (196, 197) in equation (190), we get the kinetic chain length as

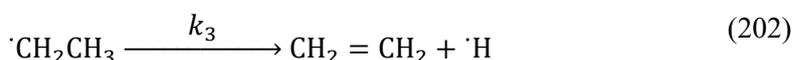
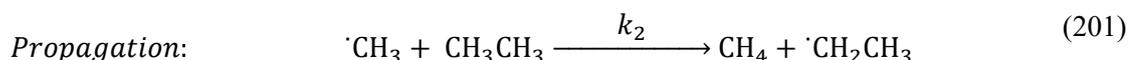
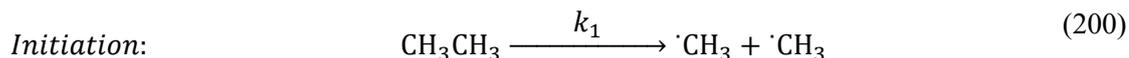
$$\text{Kinetic chain length} = \frac{k[\text{CH}_3\text{CHO}]^{3/2}}{k_1[\text{CH}_3\text{CHO}]} = \frac{k}{k_1} [\text{CH}_3\text{CHO}]^{1/2} \quad (198)$$

➤ **Chain Length in Case of Dehydrogenation of Ethane**

The dehydrogenation of ethane is another typical case of stationary type chain reactions 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 will be

$$\frac{d[\text{C}_2\text{H}_6]}{dt} = \left( \frac{k_1 k_3 k_4}{k_5} \right)^{1/2} [\text{CH}_3\text{CH}_3] \quad (205)$$

Since the rate of propagation is simply equal to the overall rate law i.e. equation (205), the rate of initiation is

$$R_i = k_1 [\text{CH}_3\text{CH}_3] \quad (206)$$

After using the values of  $R_p$  and  $R_i$  from equation (205, 206) in equation (190), we get the expression for kinetic chain length as

$$\text{Kinetic chain length} = \frac{\left( \frac{k_1 k_3 k_4}{k_5} \right)^{1/2} [\text{CH}_3\text{CH}_3]}{k_1 [\text{CH}_3\text{CH}_3]} \quad (207)$$

or

$$\text{Kinetic chain length} = \frac{1}{k_1} \left( \frac{k_1 k_3 k_4}{k_5} \right)^{1/2} \frac{[\text{CH}_3\text{CH}_3]}{[\text{CH}_3\text{CH}_3]} \quad (208)$$

$$\text{Kinetic chain length} = \left( \frac{k_3 k_4}{k_1 k_5} \right)^{1/2} \quad (209)$$

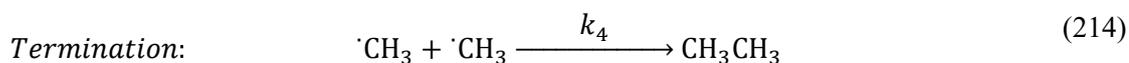
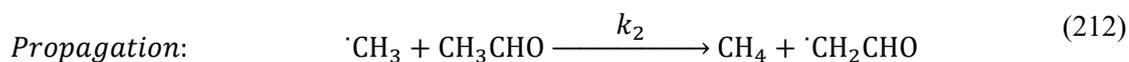
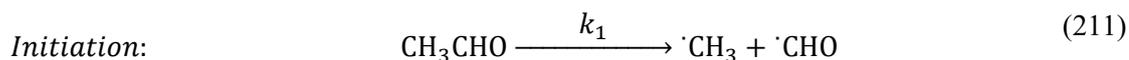
### ❖ Rice-Herzfeld Mechanism of Organic Molecules Decomposition (Acetaldehyde)

In 1934, Frank O. Rice and Karl F. Herzfeld performed an extensive study on the chain reactions and developed special mechanics to account the observed rate laws. In the honor of researchers, this mechanism is popularly known as Rice-Herzfeld mechanism. The conceptual foundation of this mechanism can easily be understood by taking the example of an organic compound, acetaldehyde.

The pyrolysis of acetaldehyde 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  $\text{CH}_4$  must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[\text{CH}_4]}{dt} = k_2[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] \quad (215)$$

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.

$$\frac{d[\cdot\text{CH}_3]}{dt} = 0 = k_1[\text{CH}_3\text{CHO}] - k_2[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\cdot\text{CH}_2\text{CHO}] - 2k_4[\cdot\text{CH}_3]^2 \quad (216)$$

Similarly,

$$\frac{d[\cdot\text{CH}_2\text{CHO}]}{dt} = 0 = k_2[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\cdot\text{CH}_2\text{CHO}] \quad (217)$$

Taking negative both side of equation (217), we have

$$-k_2[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\cdot\text{CH}_2\text{CHO}] = 0 \quad (218)$$

Using the above result in equation (216), we get

$$k_1[\text{CH}_3\text{CHO}] + 0 - 2k_4[\cdot\text{CH}_3]^2 = 0 \quad (219)$$

$$[\cdot\text{CH}_3] = \left(\frac{k_1}{2k_4}\right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2} \quad (220)$$

After putting the value of  $[\cdot\text{CH}_3]$  from equation (220) in equation (215), we have

$$\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{2k_4}\right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2} [\text{CH}_3\text{CHO}] \quad (221)$$

$$\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{2k_4}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2} \quad (222)$$

Now consider a new constant as

$$k = k_2 \left(\frac{k_1}{2k_4}\right)^{1/2} \quad (223)$$

Using in equation (222), we get

$$\frac{d[\text{CH}_4]}{dt} = k[\text{CH}_3\text{CHO}]^{3/2} \quad (224)$$

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.

$$\text{Kinetic chain length} = \frac{R_p}{R_i} \quad (225)$$

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 (224), the rate of initiation can be given as

$$R_i = k_1[\text{CH}_3\text{CHO}] \quad (226)$$

After using the values of  $R_p$  and  $R_i$  from equation (224, 226) in equation (225), we get the expression for kinetic chain length as

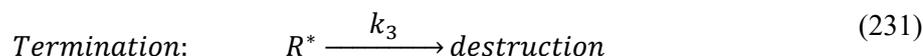
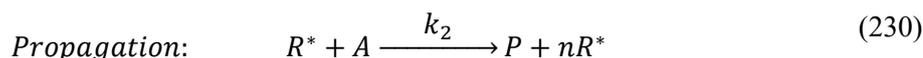
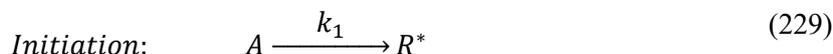
$$\text{Kinetic chain length} = \frac{k[\text{CH}_3\text{CHO}]^{3/2}}{k_1[\text{CH}_3\text{CHO}]} \quad (227)$$

or

$$\text{Kinetic chain length} = \frac{k}{k_1} [\text{CH}_3\text{CHO}]^{1/2} \quad (228)$$

### ❖ Branching Chain Reactions and Explosions (H<sub>2</sub>-O<sub>2</sub> Reaction)

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  $n$  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.

$$\text{Rate of formation of } R^* = \text{Rate of disappearance of } R^* \quad (232)$$

$$k_1[A] = k_3[R^*] - k_2(n-1)[R^*][A] \quad (233)$$

$$k_1[A] - k_3[R^*] + k_2(n-1)[R^*][A] = 0 = \frac{d[R^*]}{dt} \quad (234)$$

or

$$-k_3[R^*] + k_2(n-1)[R^*][A] = -k_1[A] \quad (235)$$

$$[R^*] = \frac{k_1[A]}{k_2(1-n)[A] + k_3} \quad (236)$$

Now because the destruction of the radical in the termination step can occur either via its collision with another radical (in 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 (236), we have

$$[R^*] = \frac{k_1[A]}{k_2(1-n)[A] + k_w + k_g} \quad (237)$$

or

$$[R^*] = \frac{k_1[A]}{-k_2(n-1)[A] + k_w + k_g} \quad (238)$$

For non-stationary or branched chain reactions, more and more radicals are generated in each successive step ( $n > 1$ ). In other words, for every radical consumed in a chain propagation step, more than one chain carriers or radicals are generated. Therefore, the possibility of explosion arises when

$$k_2(n-1)[A] = k_w + k_g \quad (239)$$

The situation can be explained in terms of equation (238) because the abovementioned condition will make the denominator zero, and therefore, making radical concentration to approach infinite. Now because the rate is usually proportional to radical's concentration, a very high rate may lead to an explosion.

### ► *Conditions for Different Types of Explosion limits*

However, it is also worthy to mention that the occurrence of explosion depends upon the experimental temperature and pressure. Typically, three explosion limits are observed as the pressure of the reacting system is raised. To understand the different explosion limits, the behavior of the denominator in equation (238) must be analysed with pressure.

**1. The first explosion limit:** When the pressure is very low, the movement of chain carriers towards the wall of the container is very fast resulting in a very large rate of radicals' destruction at walls i.e. high  $k_w$ . Conversely, the probability of radicals colliding with each other at very low pressure resulting in a very low value of  $k_g$ . Therefore, we can conclude that the denominator in equation (238) has a sufficiently large positive value at low pressure giving smooth progression of the reaction without any explosion. However, with the rise in pressure,  $k_w$  declines very rapidly than the increase in  $k_g$ . When a certain pressure value is achieved, the explosion condition is satisfied i.e.

$$k_2(n-1)[A] = k_w + k_g \quad (240)$$

Which is the first explosion limit.

**2. The second explosion limit:** The first explosion limit exists over a wide range of pressure. However, if the pressure is raised continuously, the movement of chain carriers towards the wall of the container is more and more hindered resulting in a very small rate of radicals' destruction at walls i.e. low  $k_w$ . Conversely, the probability of radicals colliding with each other further increases with pressure resulting in the very large value of  $k_g$ . Eventually, we can conclude that the denominator in equation (238) again becomes sufficiently positive giving a steady progression of the reaction. Which is the second explosion limit.

**3. The third explosion limit:** After the second explosion limit, the steady reaction-rate continues over a range of pressure. However, if the pressure is raised continuously, the heat produced in various propagating steps would not be able to leave the system at a rate equal to the rate at which it is produced. Therefore, this thermal effect will keep supporting the rate, eventually leading to a thermally-induced explosion. Which is the third explosion limit.

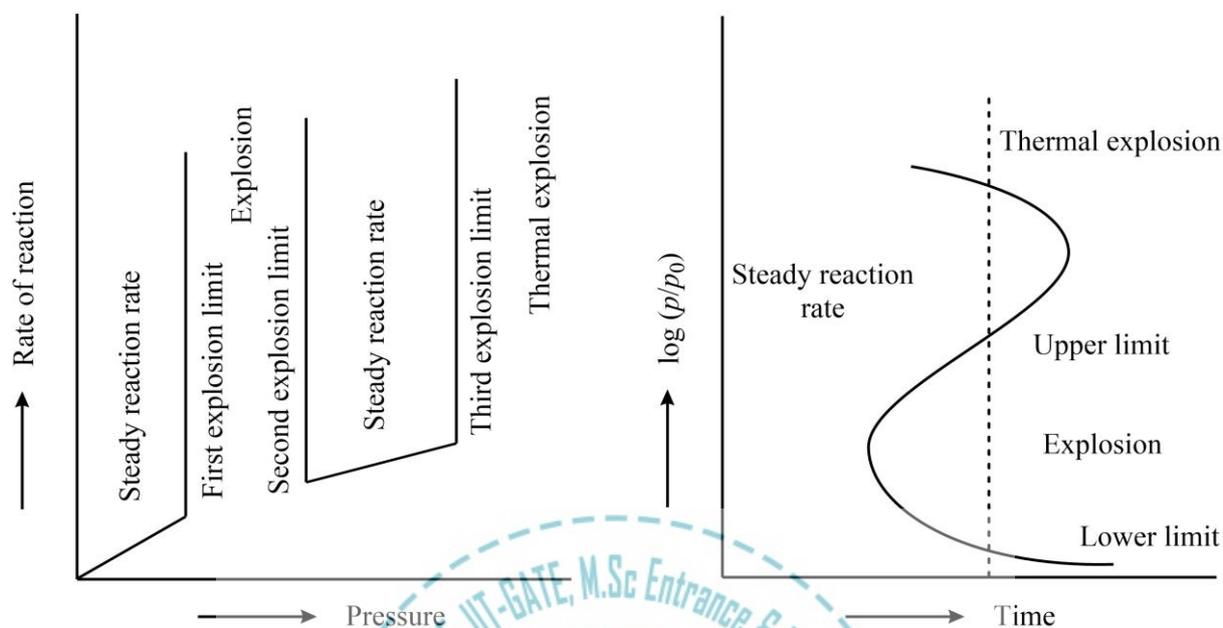


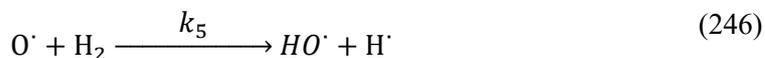
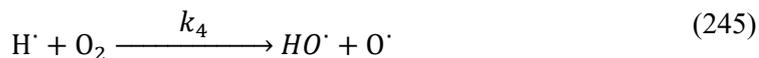
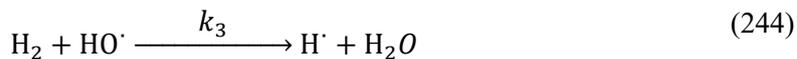
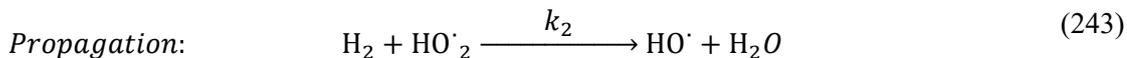
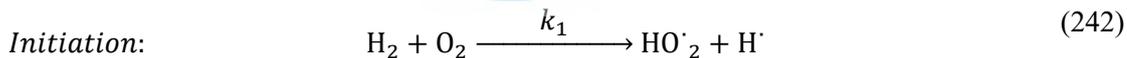
Figure 1. The variation of reaction with pressure in branching chain reactions (left) and variation of relative pressure with time on a logarithmic scale (right).

### ➤ Reaction Profile of $H_2-O_2$ Explosion

The reaction between  $H_2$  and  $O_2$  is a typical example in which all three explosion limits are observed. The net reaction is



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



The step 3<sup>rd</sup> and 4<sup>th</sup> produce more radicals than they consume, producing an explosion.

### ❖ Kinetics of (One Intermediate) Enzymatic Reaction: Michaelis-Menten Treatment

In 1901, a French Chemist, Victor Henri, proposed that enzyme reactions are actually initiated by a bond formed between the substrate and the enzyme. The concept was further developed by German researcher Leonor Michaelis and Canadian scientist Maud Menten, who examined the kinetics of an enzymatic reaction mechanism of invertase. The final model of Michaelis and Menten's treatment was published in 1913 and gained immediate popularity among the scientific community.



Where  $E$  is the enzyme that binds to a substrate  $S$ , and forms a complex  $ES$ . This enzyme-substrate complex then turns into product  $P$ . The overall rate of product formation should be

$$+ \frac{d[P]}{dt} = r = k_2[ES] \quad (248)$$

Since  $[ES]$  is intermediate, the steady-state approximation can be applied i.e.

$$\text{Rate of formation of } [ES] = \text{Rate of decomposition of } [ES] \quad (249)$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] \quad (250)$$

$$k_1[E][S] = (k_{-1} + k_2)[ES] \quad (251)$$

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \quad (252)$$

Now, defining a new parameter named as Michaelis-Menten constant ( $K_m$ ) with the following expression,

$$K_m = \frac{k_{-1} + k_2}{k_1} \quad (253)$$

equation (252) takes the form

$$[ES] = \frac{[E][S]}{K_m} \quad (254)$$

Now, if we put the  $[ES]$  concentration given above into equation (248), we will get the rate of enzyme-catalyzed reaction in terms of substrate concentration and enzyme left unused i.e.  $[E]$ . This is again a problem that can be solved if we obtain the rate expression in terms of total enzyme concentration i.e.  $[E_0]$ ; which would make the calculation of catalytic efficiency much easier. In order to do so, recall the total enzyme concentration mathematically i.e.

$$[E_0] = [E] + [ES] \quad (255)$$

Where  $[E]$  is the enzyme concentration left unused whereas  $[ES]$  represents the enzyme concentration that is bound with the substrate. Rearranging equation (253), we get

$$[E] = [E_0] - [ES] \quad (256)$$

After using the value of  $[E]$  from equation (256) in equation (254), we have

$$[ES] = \frac{\{[E_0] - [ES]\}[S]}{K_m} \quad (257)$$

$$[ES] = \frac{[E_0][S] - [ES][S]}{K_m} \quad (258)$$

Rearranging for  $[ES]$  again

$$K_m[ES] = [E_0][S] - [ES][S] \quad (259)$$

$$K_m[ES] + [ES][S] = [E_0][S] \quad (260)$$

$$[ES] = \frac{[E_0][S]}{K_m + [S]} \quad (261)$$

After putting the value of  $[ES]$  from above equation into equation (248), we get

$$r = \frac{k_2[E_0][S]}{K_m + [S]} \quad (262)$$

If the rate of the enzyme-catalyzed reaction is recorded in the very initial stage, the substrate concentration can also be replaced by the initial substrate concentration i.e.  $[S_0]$ . Therefore, the initial enzyme-catalyzed rate ( $r_0$ ) should be

$$r_0 = \frac{k_2[E_0][S_0]}{K_m + [S_0]} \quad (263)$$

Which is the well-known Michaelis-Menten equation.

Although the equation (263) is the complete form of the Michaelis-Menten equation that has measurable quantities like  $[E_0]$  and  $[S_0]$ , the more popular form of the same includes the maximum initial rate. At very large initial substrate concentration, the  $K_m$  can simply be neglected in comparison to  $[S_0]$  in the denominator, which makes the equation (263) to take the form

$$r_{max} = \frac{k_2[E_0][S_0]}{[S_0]} = k_2[E_0] \quad (264)$$

After using the  $k_2[E_0] = r_{max}$  in equation (263), we have

$$r_0 = \frac{r_{max}[S_0]}{K_m + [S_0]} \quad (265)$$

Which is the most popular form of the Michaelis-Menten equation. The plot of the initial reaction rate for the enzyme-catalyzed reaction is given below.

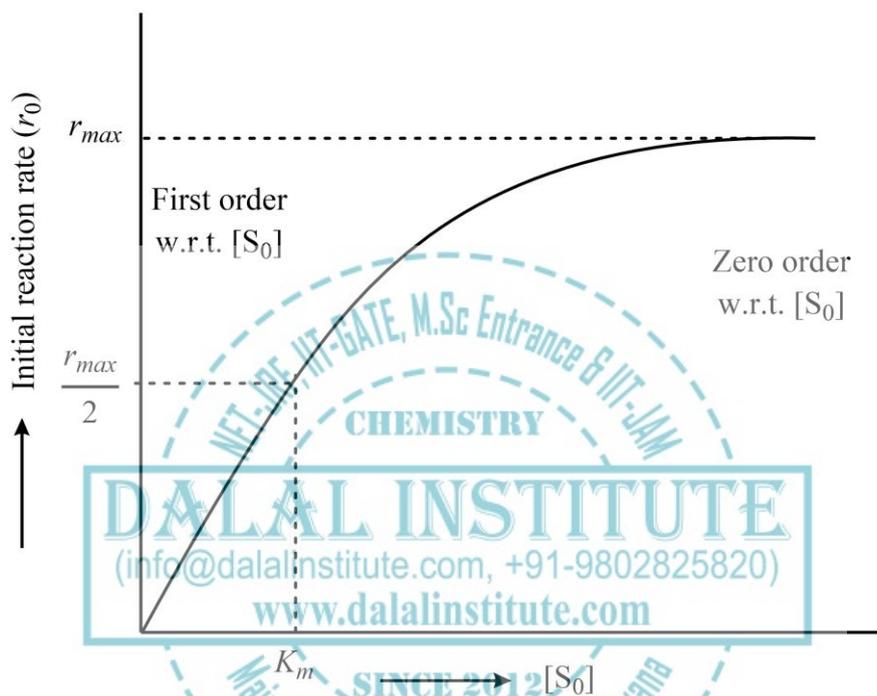


Figure 2. The variation of initial reaction rate as a function of substrate concentration for an enzyme-catalyzed reaction.

### ➤ Order of Enzyme Catalysed Reactions

The reaction kinetics of the enzyme-catalyzed reactions can be well understood by looking at the general form of Michaelis-Menten equation.

i) *At high*  $[S_0]$ : When initial substrate concentration is very high,  $K_m$  can be neglected, and the equation (263) takes the form

$$r_0 = \frac{k_2[E_0][S_0]}{[S_0]} = k_2[E_0] \quad (266)$$

Hence, the reaction will be zero-order w.r.t. substrate concentration and first order w.r.t the total enzyme concentration.

ii) *At low*  $[S_0]$ : When initial substrate concentration is low,  $[S_0]$  can be neglected, and the equation (263) takes the form

$$r_0 = \frac{k_2}{K_m} [E_0][S_0] \quad (267)$$

Hence, the reaction will be the first-order w.r.t. substrate concentration and first order w.r.t the total enzyme concentration as well.

➤ **Calculation of Catalytic Efficiency**

The catalytic efficiency of enzyme-catalyzed reactions is simply the maximum overall reaction rate per unit of enzyme concentration. When initial substrate concentration is very high,  $K_m$  can be neglected, and the equation (263) takes the form

$$r_{max} = \frac{k_2 [E_0][S_0]}{[S_0]} = k_2 [E_0] \quad (268)$$

$$k_2 = \frac{r_{max}}{[E_0]} \quad (269)$$

Hence,  $k_2$  is simply equal to the catalytic efficiency of enzyme-catalyzed reactions.

➤ **Calculation of Michaelis-Menten Constant**

The Michaelis-Menten constant of enzyme-catalyzed reactions can simply be calculated once the maximum initial reaction rate is known. When initial substrate concentration is very high,  $K_m$  can be neglected, and the equation (263) takes the form

$$r_{max} = \frac{k_2 [E_0][S_0]}{[S_0]} = k_2 [E_0] \quad (270)$$

After using the  $k_2 [E_0] = r_{max}$  in equation (263), we have

$$r_0 = \frac{r_{max} [S_0]}{K_m + [S_0]} \quad (271)$$

When the initial reaction rate is half of the maximum initial rate i.e.  $r_0 = r_{max}/2$ , we have

$$\frac{r_{max}}{2} = \frac{r_{max} [S_0]}{K_m + [S_0]} \quad (272)$$

$$K_m + [S_0] = 2[S_0] \quad (273)$$

$$K_m = [S_0] \quad (274)$$

Hence, the concentration at which the initial rate is half of the maximum initial rate, will be equal to  $K_m$ .

### ❖ Evaluation of Michaelis's Constant for Enzyme-Substrate Binding by Lineweaver-Burk Plot and Eadie-Hofstee Methods

The conventional approach to determine the Michaelis's constant ( $K_m$ ) involve the plot of initial reaction rate vs initial substrate concentration. Then the Michaelis-Menten constant of enzyme-catalyzed reactions can simply be calculated once the maximum initial reaction rate is known. The typical Michaelis-Menten is used to fit the data is given below.

$$r_0 = \frac{r_{max}[S_0]}{K_m + [S_0]} \quad (275)$$

Where  $r_{max} = k_2[E_0]$  is the maximum initial rate at  $[E_0]$  enzyme concentration whereas  $[S_0]$  is the initial substrate concentration. Finally, the concentration at which the initial rate is half of the maximum initial rate, will be equal to  $K_m$ .

This conventional method, however, suffers from serious limitations like the need for lots of data points until the initial rate becomes constant. Therefore, two other methods are quite popular to find Michaelis's constant without getting the actual plateau in the initial reaction rate. In this section, we will discuss two such methods for the evaluation of Michaelis's constant for enzyme-substrate binding.

#### ➤ *The Lineweaver-Burk Plot to Evaluate Michaelis's Constant*

In order to understand the Lineweaver-Burk method for the determination of the maximum initial rate ( $r_{max}$ ) and Michaelis's constant, we need to rearrange the general Michaelis-Menten equation first i.e. the reciprocal of equation (275) as given below.

$$\frac{1}{r_0} = \frac{K_m + [S_0]}{r_{max}[S_0]} \quad (276)$$

or

$$\frac{1}{r_0} = \frac{K_m}{r_{max}[S_0]} + \frac{[S_0]}{r_{max}[S_0]} \quad (277)$$

or

$$\frac{1}{r_0} = \frac{K_m}{r_{max}} \frac{1}{[S_0]} + \frac{1}{r_{max}} \quad (278)$$

Which is the equation of the straight line ( $y = mx + c$ ). Therefore, if we plot the reciprocal of initial reaction rate vs the reciprocal of initial substrate concentration; the slope and intercepts will give  $K_m/r_{max}$  and  $1/r_{max}$ , respectively.

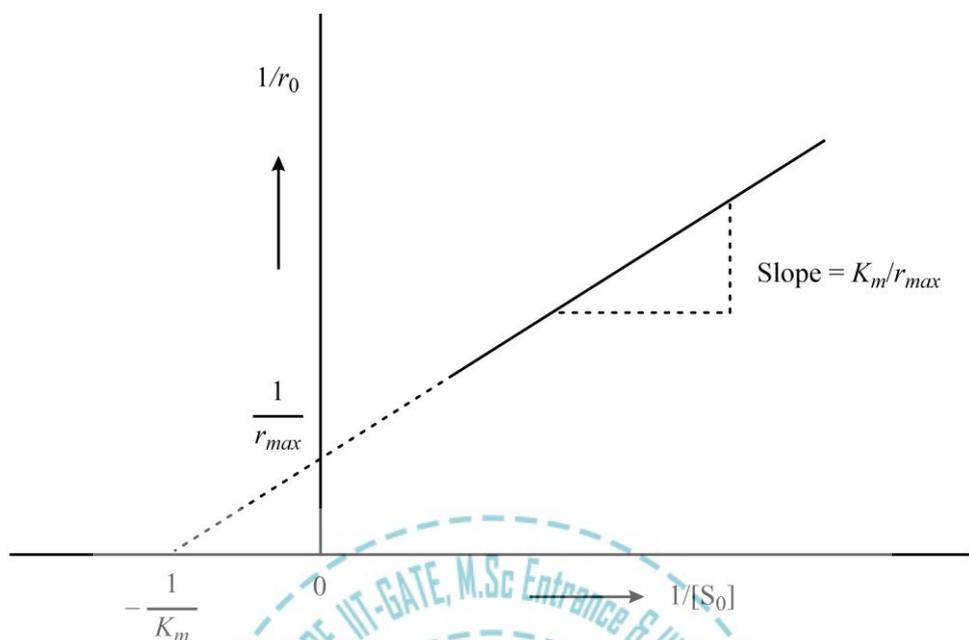


Figure 3. The Lineweaver-burk plot for enzyme-catalyzed reactions to evaluate the maximum initial rate ( $r_{max}$ ) and Michaelis's constant.

It is also worthy to mention that if the intercept is further extrapolated, it will lead to the intercept on the x-axis that equals to  $-1/K_m$ .

➤ **The Eadie-Hofstee Plot to Evaluate Michaelis's Constant**

In order to understand the Eadie-Hofstee method for the determination of the maximum initial rate ( $r_{max}$ ) and Michaelis's constant, we need to rearrange the general Michaelis-Menten equation first i.e. the reciprocal of equation (275) as given below.

$$\frac{1}{r_0} = \frac{K_m + [S_0]}{r_{max}[S_0]} \quad (279)$$

or

$$\frac{1}{r_0} = \frac{K_m}{r_{max}[S_0]} + \frac{[S_0]}{r_{max}[S_0]} \quad (280)$$

or

$$\frac{1}{r_0} = \frac{K_m}{r_{max}} \frac{1}{[S_0]} + \frac{1}{r_{max}} \quad (281)$$

Multiplying both sides by  $r_0$ , we get

$$\frac{r_0}{r_0} = \frac{K_m}{r_{max}} \frac{r_0}{[S_0]} + \frac{r_0}{r_{max}} \quad (282)$$

Rearranging for  $r_0/[S_0]$ , we get

$$\frac{r_0}{r_0} - \frac{r_0}{r_{max}} = \frac{K_m}{r_{max}} \frac{r_0}{[S_0]} \quad (283)$$

$$\frac{r_0}{[S_0]} = \frac{r_0}{r_0} \frac{r_{max}}{K_m} - \frac{r_0}{r_{max}} \frac{r_{max}}{K_m} \quad (284)$$

$$\frac{r_0}{[S_0]} = \frac{r_{max}}{K_m} - \frac{r_0}{K_m} \quad (285)$$

$$\frac{r_0}{[S_0]} = -\frac{1}{K_m} r_0 + \frac{r_{max}}{K_m} \quad (286)$$

Which is the equation of the straight line ( $y = mx + c$ ). Therefore, if we plot the ratio of initial reaction rate to initial substrate concentration vs the initial reaction rate; the slope and intercepts will give  $-1/K_m$  and  $r_{max}/K_m$ , respectively.

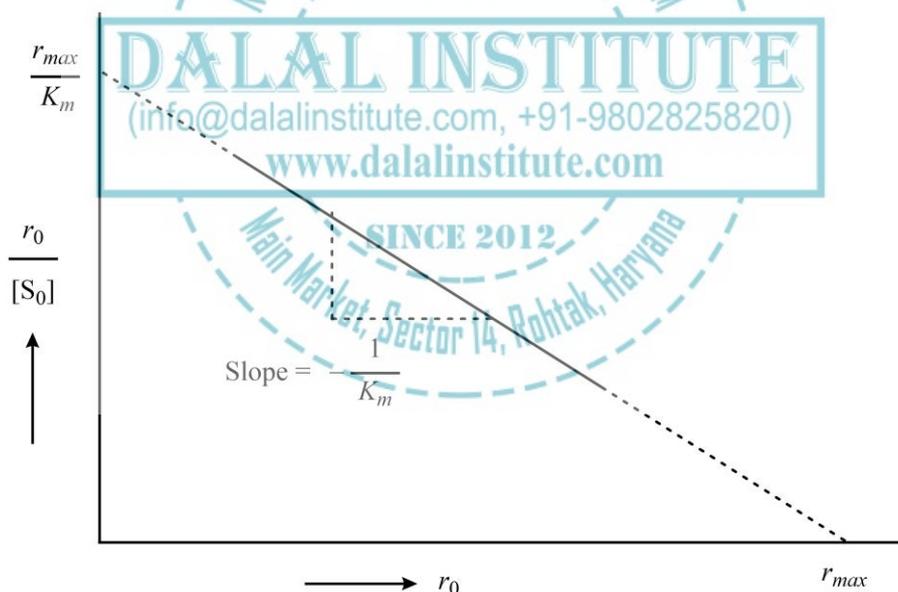


Figure 4. The Eadie-Hofstee plot for enzyme-catalyzed reactions to evaluate the maximum initial rate ( $r_{max}$ ) and Michaelis's constant.

It is also worthy to mention that if the intercept is further extrapolated, it will lead to the intercept on the  $x$ -axis that equals to  $r_{max}$ .

## ❖ Competitive and Non-Competitive Inhibition

An enzyme inhibitor is a compound that binds to an enzyme and decreases its overall activity, and the phenomenon is typically known as “enzyme inhibition”. Two of the most common enzyme inhibition processes will be discussed in this section.

### ➤ Competitive Inhibition

In the case of competitive enzyme inhibition, the binding of an inhibitor prevents the binding of the substrate and the enzyme. This type of behavior is actually achieved by blocking the binding site of the target molecule (the active site) by some means. The competitive enzyme inhibition can be classified into two types as discussed below.

**1. Fully competitive inhibition:** The fully competitive inhibition occurs when an enzyme ( $E$ ) binds with the substrate ( $S$ ) and inhibitor ( $I$ ) separately, and it is only the enzyme-substrate complex ( $ES$ ) that will convert into the product. This whole process can be described mathematically as



After applying the steady-state approximation on  $ES$ , we have

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0 \quad (289)$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] \quad (290)$$

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \quad (291)$$

When  $[S_0] \gg [E_0]$ , we can assume  $[S_0] \approx [S]$ , and also

$$[E_0] = [E] + [ES] + [EI] \quad (292)$$

$$[E] = [E_0] - [ES] - [EI] \quad (293)$$

Now recalling the equilibrium constant for inhibition equilibria i.e.

$$K_3 = \frac{k_3}{k_{-3}} = \frac{[EI]}{[E][I]} \quad (294)$$

$$K_1 = \frac{1}{K_3} = \frac{[E][I]}{[EI]} \quad (295)$$

Hence, we can say

$$[EI] = \frac{[E][I]}{K_1} \quad (296)$$

After using the value of  $[EI]$  from equation (296) into equation (293), we have

$$[E] = [E_0] - [ES] - \frac{[E][I]}{K_1} \quad (297)$$

$$[E] = \frac{K_1[E_0] - K_1[ES] - [E][I]}{K_1} \quad (298)$$

$$K_1[E] = K_1[E_0] - K_1[ES] - [E][I] \quad (299)$$

$$K_1[E] + [E][I] = K_1[E_0] - K_1[ES] \quad (300)$$

$$[E] = \frac{K_1[E_0] - K_1[ES]}{K_1 + [I]} \quad (301)$$

Using the above-derived result in equation (291), we have

$$[ES] = \frac{k_1[S]}{k_{-1} + k_2} \frac{K_1[E_0] - K_1[ES]}{K_1 + [I]} = \frac{[S]}{K_m} \frac{K_1[E_0] - K_1[ES]}{K_1 + [I]} \quad (302)$$

$$[ES] = \frac{K_1[E_0][S] - K_1[ES][S]}{K_m K_1 + K_m [I]} \quad (303)$$

Now rearranging further for  $[ES]$ , we get

$$K_m K_1 [ES] + K_m [I] [ES] = K_1 [E_0] [S] - K_1 [ES] [S] \quad (304)$$

$$K_m K_1 [ES] + K_m [I] [ES] + K_1 [ES] [S] = K_1 [E_0] [S] \quad (305)$$

$$[ES] = \frac{K_1 [E_0] [S]}{K_m K_1 + K_m [I] + K_1 [S]} \quad (306)$$

Since the rate of formation of product is

$$r_0 = k_2 [ES] \quad (307)$$

Using the value of  $[ES]$  from equation (306) in equation (307), we get

$$r_0 = \frac{k_2 K_1 [E_0] [S]}{K_m K_1 + K_m [I] + K_1 [S]} \quad (308)$$

Since  $k_2 [E_0]$  is  $r_{max}$ , the equation (308) takes the form

$$r_0 = \frac{r_{max} K_I [S]}{K_m K_I + K_m [I] + K_I [S]} \quad (309)$$

Taking the reciprocal to get Lineweaver-Burk plot

$$\frac{1}{r_0} = \frac{K_m K_I + K_m [I] + K_I [S]}{r_{max} K_I [S]} \quad (310)$$

$$\frac{1}{r_0} = \frac{K_m K_I}{r_{max} K_I [S]} + \frac{K_m [I]}{r_{max} K_I [S]} + \frac{K_I [S]}{r_{max} K_I [S]} \quad (311)$$

$$\frac{1}{r_0} = \left( \frac{K_m}{r_{max}} + \frac{K_m [I]}{r_{max} K_I} \right) \frac{1}{[S]} + \frac{1}{r_{max}} \quad (312)$$

Rearranging further and using initial substrate concentration, we get

$$\frac{1}{r_0} = \frac{K_m}{r_{max}} \left( 1 + \frac{[I]}{K_I} \right) \frac{1}{[S_0]} + \frac{1}{r_{max}} \quad (313)$$

After comparing with equation without enzyme inhibition i.e.

$$\frac{1}{r_0} = \frac{K_m}{r_{max}} \frac{1}{[S_0]} + \frac{1}{r_{max}} \quad (314)$$

it is clear that the intercepts in both the equations are the same whereas the slope has been increased from  $K_m/r_{max}$  to  $(K_m/r_{max})(1 + [I]/K_I)$ . This implies that enzyme inhibition changed the  $K_m$  to  $K_m(1 + [I]/K_I)$ .

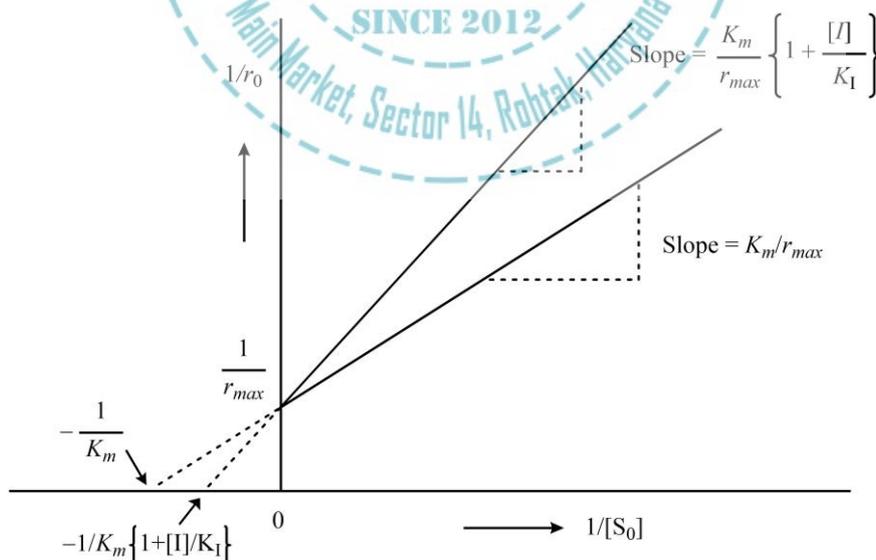
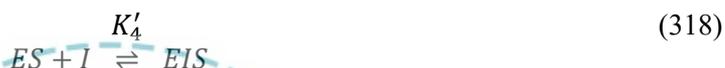


Figure 5. Lineweaver-Burk plot for enzyme-catalyzed reaction with fully competitive enzyme inhibition.

**2. Partially competitive inhibition:** The partially competitive inhibition occurs when the enzyme ( $E$ ) binds with the substrate ( $S$ ) and inhibitor ( $I$ ) simultaneously, and complex  $ES$  and  $EI$  also combine with  $I$  and  $S$  to give  $EIS$ . Also, besides the enzyme-substrate complex ( $ES$ ), the complex  $EIS$  will also convert into the product with the same rate of reaction. This whole process can be described mathematically as



According to classical Michaelis-Menten equation  $K_m = (k_2 + k_{-1})/k_1$ ; however, if  $k_2 \ll k_{-1}$ , we have  $K_m = k_{-1}/k_1$  or  $K_m = 1/K'_1$ . Now, set the following results

$$K_m = \frac{1}{K'_1} = \frac{[E][S]}{[ES]} \quad (320)$$

$$K_2 = \frac{1}{K'_2} = \frac{[E][I]}{[EI]} \quad (321)$$

$$K_3 = \frac{1}{K'_3} = \frac{[EI][S]}{[EIS]} \quad (322)$$

$$K_4 = \frac{1}{K'_4} = \frac{[ES][I]}{[EIS]} \quad (323)$$

Following enzyme conservation, we have

$$[E_0] = [E] + [ES] + [EI] + [EIS] \quad (324)$$

Using values of  $[ES]$ ,  $[EI]$  and  $[EIS]$  from equation (320-322) into equation (324), we get

$$[E_0] = [E] + \frac{[E][S]}{K_m} + \frac{[E][I]}{K_2} + \frac{[E][I][S]}{K_2K_3} \quad (325)$$

$$[E] = \frac{K_m[E_0]}{K_m(1 + [I]/K_2) + [S](1 + K_m[I]/K_2K_3)} \quad (326)$$

The overall reaction rate of product formations should be

$$r_0 = k_2[ES] + k_2[EIS] \quad (327)$$

After using values of  $[ES]$  and  $[EIS]$  from equation (320, 322) into equation (327), we get

$$r_0 = k_2 \frac{[E][S]}{K_m} + k_2 \frac{[E][I][S]}{K_2 K_3} \quad (328)$$

Substituting the value of  $[E]$  from equation (326) in (328), and rearranging at initial substrate concentration

$$r_0 = \frac{k_2[E_0][S_0]}{\{K_m(1 + [I]/K_2)/(1 + K_m[I]/K_2K_3)\} + [S_0]} \quad (329)$$

Since  $k_2[E_0]$  is  $r_{max}$ , equation (329) takes the following form after the reciprocal to get Lineweaver-Burk plot

$$\frac{1}{r_0} = \frac{\{K_m(1 + [I]/K_2)/(1 + K_m[I]/K_2K_3)\}}{r_{max}} \frac{1}{[S_0]} + \frac{1}{r_{max}} \quad (330)$$

After comparing with equation without enzyme inhibition i.e.

$$\frac{1}{r_0} = \frac{K_m}{r_{max}} \frac{1}{[S_0]} + \frac{1}{r_{max}} \quad (331)$$

it is clear that intercepts in both the equations are the same whereas the slope has been varied from  $K_m/r_{max}$  to  $\{K_m(1 + [I]/K_2)/(1 + K_m[I]/K_2K_3)\}/r_{max}$ . This implies that enzyme inhibition changed the  $K_m$  to  $\{K_m(1 + [I]/K_2)/(1 + K_m[I]/K_2K_3)\}$ .

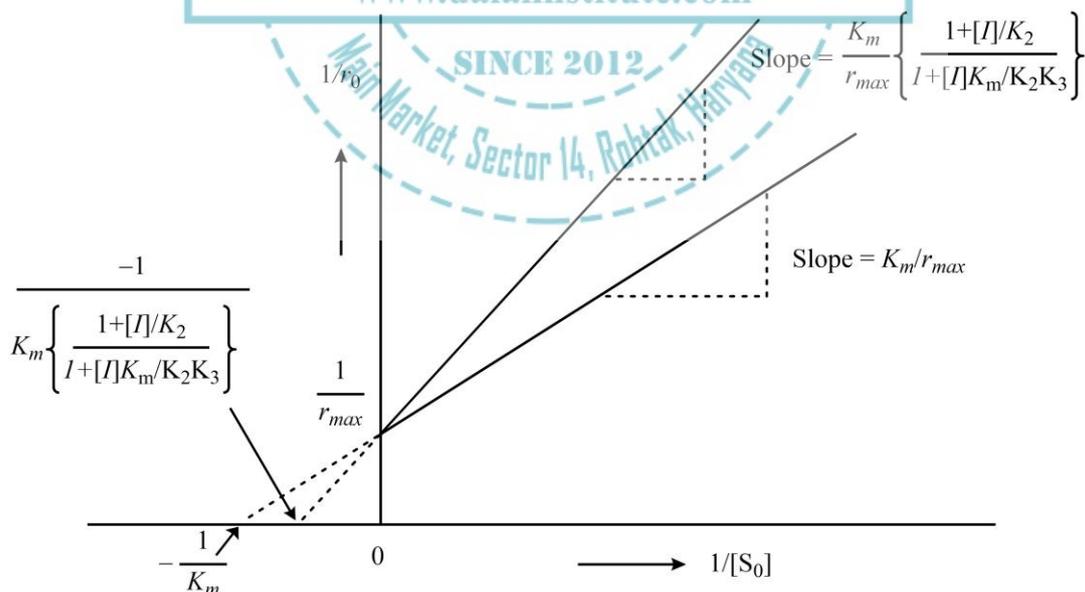


Figure 6. The Lineweaver-Burk plot for partially competitive enzyme inhibition.

➤ **Non-Competitive Inhibition**

Non-competitive inhibition may simply be defined as the enzyme inhibition where the inhibitor decreases the activity of the enzyme catalysis and binds equally well to the enzyme whether or not it has already bound the substrate. The non-competitive enzyme inhibition can be classified into two types as discussed below.

**1. Fully non-competitive inhibition:** The fully non-competitive inhibition occurs when an enzyme ( $E$ ) binds with inhibitor ( $I$ ), and complex  $ES$  and  $EI$  also combine with  $I$  and  $S$  to give  $EIS$ . However, it is only the enzyme-substrate complex ( $ES$ ) that converts into the product. This whole process can be described mathematically as



According to classical Michaelis-Menten equation  $K_m = (k_2 + k_{-1})/k_1$ , however, if  $k_2 \ll k_{-1}$ , we have  $K_m = k_{-1}/k_1$  or  $K_m = 1/K'_1$ . Now, set the following results

$$K_m = \frac{1}{K'_1} = \frac{[E][S]}{[ES]} = \frac{[E][S]}{[EIS]} \quad (336)$$

$$K_I = \frac{1}{K'_2} = \frac{[E][I]}{[EI]} = \frac{[ES][I]}{[EIS]} \quad (337)$$

Following enzyme conservation, we have

$$[E_0] = [E] + [ES] + [EI] + [EIS] \quad (338)$$

$$[E] = [E_0] - [ES] - [EI] - [EIS] \quad (339)$$

Using values of  $[ES]$ ,  $[EI]$  and  $[EIS]$  from equation (336-337) into equation (338), we get

$$[E_0] = [E] + \frac{[E][S]}{K_m} + \frac{[E][I]}{K_I} + \frac{[E][I][S]}{K_m K_I} \quad (340)$$

$$[E] = \frac{[E_0]}{(1 + [S]/K_m)(1 + [I]/K_I)} \quad (341)$$

The overall reaction rate of product formations should be

$$r_0 = k_2[ES] \quad (342)$$

After using values of  $[ES]$  from equation (336) into equation (342), we get

$$r_0 = k_2 \frac{[E][S]}{K_m} \quad (343)$$

Substituting the value of  $[E]$  from equation (341) in (343), and rearranging at initial substrate concentration

$$r_0 = \frac{k_2[E_0][S_0]}{(K_m + [S_0])(1 + [I]/K_I)} \quad (344)$$

Since  $k_2[E_0]$  is  $r_{max}$ , the equation (344) takes the form

$$r_0 = \frac{r_{max}[S_0]}{(K_m + [S_0])(1 + [I]/K_I)} \quad (345)$$

Taking the reciprocal to get Lineweaver-Burk plot

$$\frac{1}{r_0} = \frac{K_m}{r_{max}} \left(1 + \frac{[I]}{K_I}\right) \frac{1}{[S_0]} + \frac{1}{r_{max}} \left(1 + \frac{[I]}{K_I}\right) \quad (346)$$

After comparing with equation without enzyme inhibition i.e.

$$\frac{1}{r_0} = \frac{K_m}{r_{max}} \frac{1}{[S_0]} + \frac{1}{r_{max}} \quad (347)$$

it can be clearly seen that intercept is increased from  $1/r_{max}$  to  $(1/r_{max})(1 + [I]/K_I)$  whereas the  $K_m$  has remained the same.

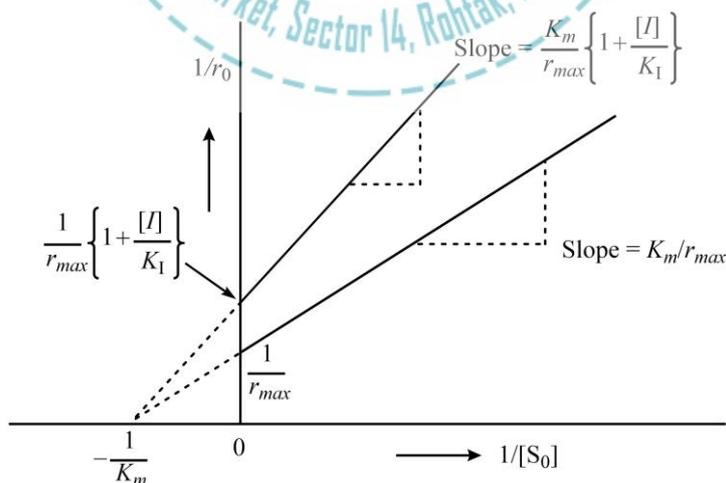


Figure 7. The Lineweaver-Burk plot for fully non-competitive enzyme inhibition.

**2. Partially non-competitive inhibition:** The partially non-competitive inhibition occurs when an enzyme ( $E$ ) binds with inhibitor ( $I$ ), and complex  $ES$  and  $EI$  also combine with  $I$  and  $S$  to give  $EIS$ . However, unlike fully non-competitive inhibition, besides the enzyme-substrate complex ( $ES$ ), the complex will also convert into the product. This whole process can be described mathematically as



and



and



and



and



According to classical Michaelis-Menten equation  $K_m = (k_2 + k_{-1})/k_1$ ; however, if  $k_2 \ll k_{-1}$ , we have  $K_m = k_{-1}/k_1$  or  $K_m = 1/K'_1$ . Now, set the following results

$$K_m = \frac{1}{K'_1} = \frac{[E][S]}{[ES]} \quad (353)$$

and

$$K_I = \frac{1}{K'_2} = \frac{[E][I]}{[EI]} \quad (354)$$

and

$$K_m = \frac{1}{K'_1} = \frac{[EI][S]}{[EIS]} \quad (355)$$

and

$$K_I = \frac{1}{K'_2} = \frac{[ES][I]}{[EIS]} \quad (356)$$

Following enzyme conservation, we have

$$[E_0] = [E] + [ES] + [EI] + [EIS] \quad (357)$$

Using values of  $[ES]$ ,  $[EI]$  and  $[EIS]$  from equation (353-356) into equation (357), we get the following expression.

$$[E_0] = [E] + \frac{[E][S]}{K_m} + \frac{[E][I]}{K_I} + \frac{[E][I][S]}{K_m K_I} \quad (358)$$

or

$$[E] = \frac{[E_0]}{(1 + ([S]/K_m)(1 + [I]/K_I))} \quad (359)$$

The overall reaction rate of product formations should be

$$r_0 = k_2[ES] + k'[EIS] \quad (360)$$

After using the values of  $[ES]$  and  $[EIS]$  from equation (353-356) into equation (360), we get the following result.

$$r_0 = k_2 \frac{[E][S]}{K_m} + k' \frac{[E][I][S]}{K_m K_I} \quad (361)$$

Now, substituting the value of  $[E]$  from equation (359) in (361), and rearranging at the initial substrate concentration

$$r_0 = \frac{(k_2[E_0][S_0] + k'[E_0][S_0][I]/K_I)/(1 + [I]/K_I)}{K_m + [S_0]} \quad (362)$$

Using  $k_2[E_0]$  is  $r_{max}$  and then taking the reciprocal to get the Lineweaver-Burk plot, we get the following relation.

$$\frac{1}{r_0} = \frac{K_m(1 + [I]/K_I)}{(r_{max} + k'[E_0][I]/K_I)} \frac{1}{[S_0]} + \frac{(1 + [I]/K_I)}{(r_{max} + k'[E_0][I]/K_I)} \quad (363)$$

After comparing the result given above with the general equation without enzyme inhibition, i.e., we can conclude some important points.

$$\frac{1}{r_0} = \frac{K_m}{r_{max}} \frac{1}{[S_0]} + \frac{1}{r_{max}} \quad (364)$$

it can be clearly seen that intercept is increased from  $1/r_{max}$  to  $(1 + [I]/K_I)/(r_{max} + k'[E_0][I]/K_I)$  whereas the  $K_m$  has remained the same.

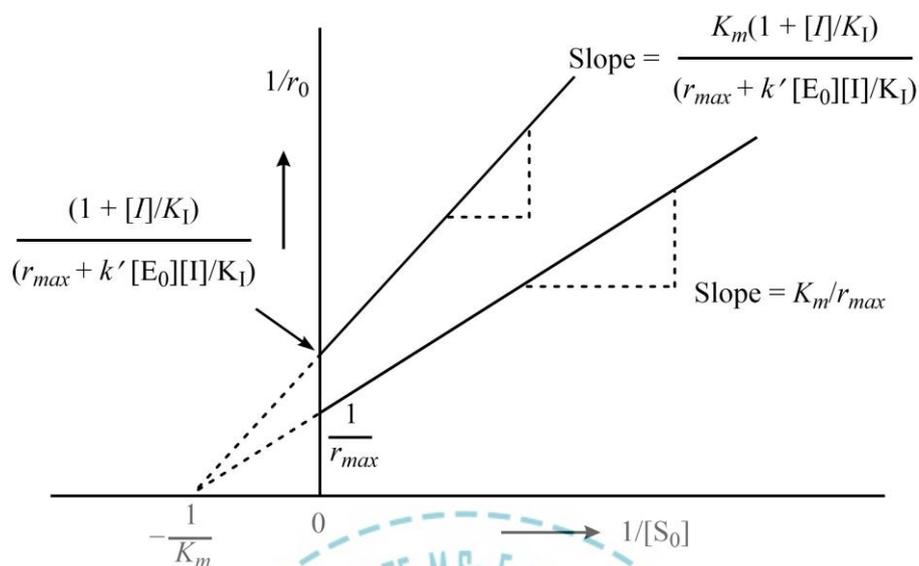


Figure 8. The Lineweaver-Burk plot for partially non-competitive enzyme inhibition.



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**❖ Problems**

- Q 1. What are chemical chain reactions? Discuss their general kinetics.
- Q 2. Derive and discuss the rate law for the decomposition of ethane.
- Q 3. Define photochemical reactions. How they are different from thermochemical reactions?
- Q 4. What is the photochemical quantum yield of a reaction? Derive and discuss the same for photochemical combination  $\text{H}_2\text{-Br}_2$  case.
- Q 5. Derive and discuss the Rice-Herzfeld mechanism of decomposition of Acetaldehyde.
- Q 6. Define the chain length.
- Q 7. Calculate the expression for the chain length for the dehydrogenation of ethane.
- Q 8. What are the branching chain reactions? How they lead to the situation of the explosion?
- Q 9. Derive and discuss the conventional Michaelis-Menten equation for enzyme-catalyzed reactions.
- Q 10. How would you treat Michaelis-Menten equations to get Lineweaver-Burk plot?
- Q 11. Discuss the Eadie-Hofstee method for the evaluation of Michaelis-Menten constant in enzyme-catalyzed reactions.
- Q 12. What is enzyme inhibition? Discuss the fully competitive enzyme inhibition in detail.

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### ❖ Bibliography

- [1] B. R. Puri, L. R. Sharma, M. S. Pathania, *Principles of Physical Chemistry*, Vishal Publications, Jalandhar, India, 2008.
- [2] P. Atkins, J. Paula, *Physical Chemistry*, Oxford University Press, Oxford, UK, 2010.
- [3] E. Steiner, *The Chemistry Maths Book*, Oxford University Press, Oxford, UK, 2008.
- [4] S. A. Arrhenius, *Über die Dissociationswärme und den Einfluß der Temperatur auf den Dissociationsgrad der Elektrolyte*. Z. Phys. Chem. 4 (1889) 96–116.
- [5] S. A. Arrhenius, *Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren*. Z. Phys. Chem. 4 (1889) 226–248.
- [6] K. J. Laidler, *Chemical Kinetics*, Harper & Row, New York, USA, 1987.
- [7] K. J. Laidler, *The World of Physical Chemistry*, Oxford University Press, Oxford, UK, 1993.
- [8] H. Eyring, *The Activated Complex in Chemical Reactions*, J. Chem. Phys. 3 (1935) 107-115.
- [9] K. L. Kapoor, *A Textbook of Physical Chemistry Volume 5*, Macmillan Publishers, New Delhi, India, 2011.

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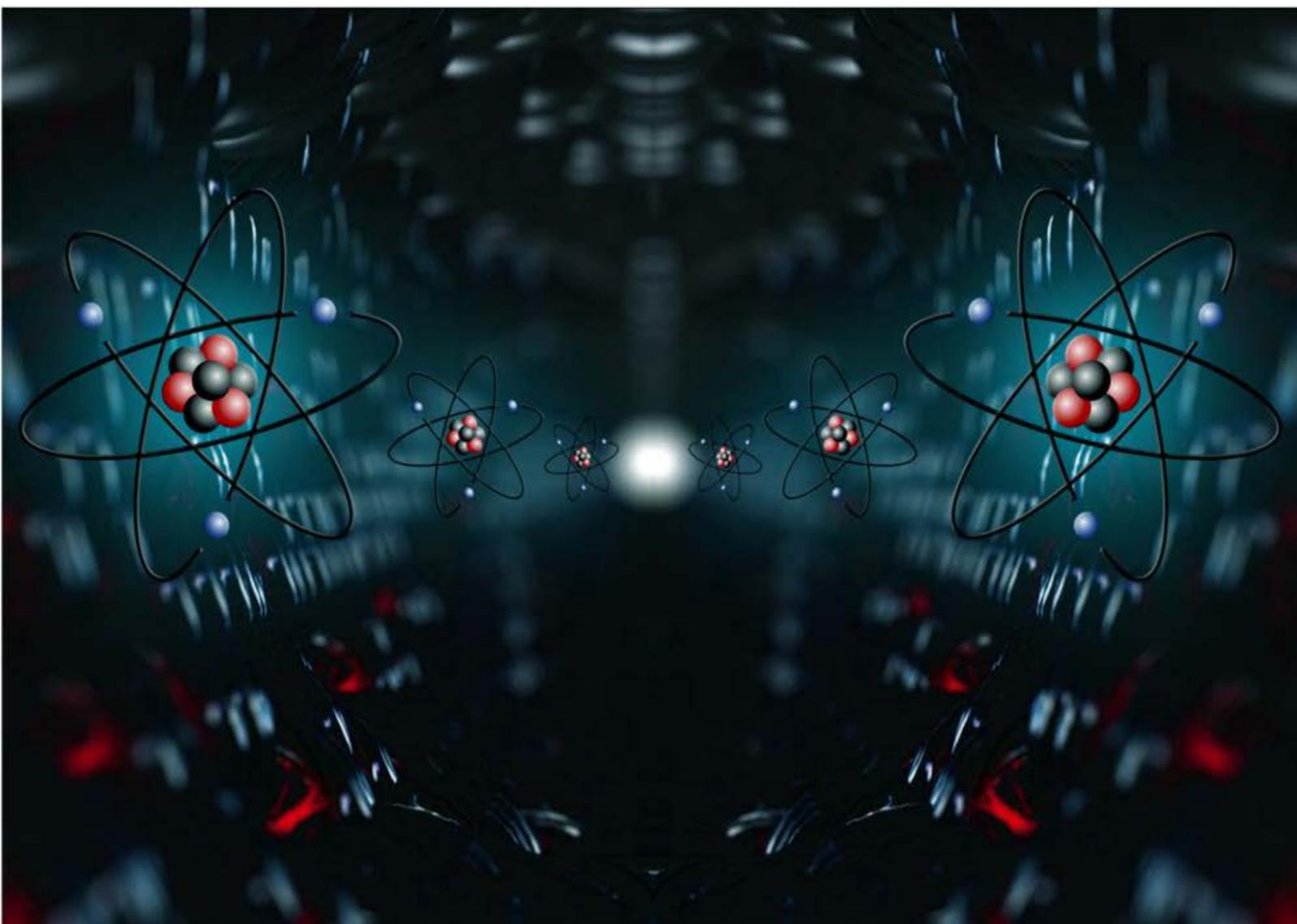
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**MANDEEP DALAL**



*First Edition*

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# Table of Contents

<b>CHAPTER 1</b> .....	<b>11</b>
<b>Quantum Mechanics – I</b> .....	<b>11</b>
❖ 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
<b>CHAPTER 2</b> .....	<b>84</b>
<b>Thermodynamics – I</b> .....	<b>84</b>
❖ 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

<b>CHAPTER 3 .....</b>	<b>113</b>
<b>Chemical Dynamics – I.....</b>	<b>113</b>
❖ 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
<b>CHAPTER 4 .....</b>	<b>160</b>
<b>Electrochemistry – I: Ion-Ion Interactions .....</b>	<b>160</b>
❖ 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 ( $\Lambda$ ) 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
<b>CHAPTER 5 .....</b>	<b>211</b>
<b>Quantum Mechanics – II .....</b>	<b>211</b>
❖ 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
<b>CHAPTER 6 .....</b>	<b>289</b>
<b>Thermodynamics – II.....</b>	<b>289</b>
❖ 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
<b>CHAPTER 7 .....</b>	<b>344</b>
<b>Chemical Dynamics – II .....</b>	<b>344</b>
❖ 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
<b>CHAPTER 8 .....</b>	<b>390</b>
<b>Electrochemistry – II: Ion Transport in Solutions .....</b>	<b>390</b>
❖ 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
<b>INDEX .....</b>	<b>427</b>



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