❖ 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 ration of the rate of the overall reaction to the rate of the initiation step in which the active particles are generated. Mathematically,

$$Kinetic\ chain\ length = \frac{R_p}{R_i} \tag{190}$$

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

$$\mathrm{CH_3CHO \longrightarrow CH_4 + CO} \tag{191}$$

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

$$Initiation: \quad \mathrm{CH_3CHO} \xrightarrow{\quad k_1 \quad} \mathrm{{}^{\cdot}CH_3 + {}^{\cdot}CHO} \tag{192}$$

$$Propagation: \quad \mathrm{{}^{\cdot}CH_3 + CH_3CHO} \xrightarrow{\quad k_2 \quad} \mathrm{CH_4 + {}^{\cdot}CH_2CHO} \tag{193}$$

$$\mathrm{{}^{\cdot}CH_2CHO} \xrightarrow{\quad k_3 \quad} \mathrm{{}^{\cdot}CH_3 + CO} \tag{194}$$

$$Termination: \quad \mathrm{{}^{\cdot}CH_3 + {}^{\cdot}CH_3} \xrightarrow{\quad k_4 \quad} \mathrm{CH_3CH_3} \tag{195}$$

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.

$$\frac{d[\mathrm{CH_4}]}{\mathrm{dt}} = k[\mathrm{CH_3CHO}]^{3/2} \tag{196}$$

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

$$R_i = k_1[\mathrm{CH_3CHO}] \tag{197}$$

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

$$Kinetic\ chain\ length = \frac{k[\mathrm{CH_3CHO}]^{3/2}}{k_1[\mathrm{CH_3CHO}]} = \frac{k}{k_1}[\mathrm{CH_3CHO}]^{1/2} \tag{198}$$

- ***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.

$$CH_3CH_3 \longrightarrow CH_2 = CH_2 + H_2 \tag{199}$$

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

$$Initiation: \quad CH_3CH_3 \xrightarrow{k_1} {}^{\cdot}CH_3 + {}^{\cdot}CH_3 \tag{200}$$

$$Propagation: \quad {}^{\cdot}CH_3 + CH_3CH_3 \xrightarrow{k_2} CH_4 + {}^{\cdot}CH_2CH_3 \tag{201}$$

$${}^{\cdot}CH_2CH_3 \xrightarrow{k_3} CH_2 = CH_2 + {}^{\cdot}H \tag{202}$$

$$CH_3CH_3 + {}^{\cdot}H \xrightarrow{k_4} {}^{\cdot}CH_2CH_3 + H_2 \tag{203}$$

$$Termination: \quad {}^{\cdot}CH_2CH_3 + {}^{\cdot}H \xrightarrow{k_5} CH_3CH_3 \tag{204}$$

The net rate of decomposition of ethane will be

$$-\frac{d[C_2H_6]}{dt} = \left(\frac{k_1k_3k_4}{k_5}\right)^{1/2}[CH_3CH_3] \tag{205}$$

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

$$R_i = k_1[CH_3CH_3] \tag{206}$$

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

$$Kinetic\ chain\ length = \frac{\left(\frac{k_1k_3k_4}{k_5}\right)^{\frac{1}{2}}[CH_3CH_3]}{k_1[CH_3CH_3]} \tag{207}$$

or

$$Kinetic\ chain\ length = \frac{1}{k_1}\left(\frac{k_1k_3k_4}{k_5}\right)^{1/2}\frac{[CH_3CH_3]}{[CH_3CH_3]} \tag{208}$$

$$Kinetic\ chain\ length = \left(\frac{k_3k_4}{k_1k_5}\right)^{1/2} \tag{209}$$

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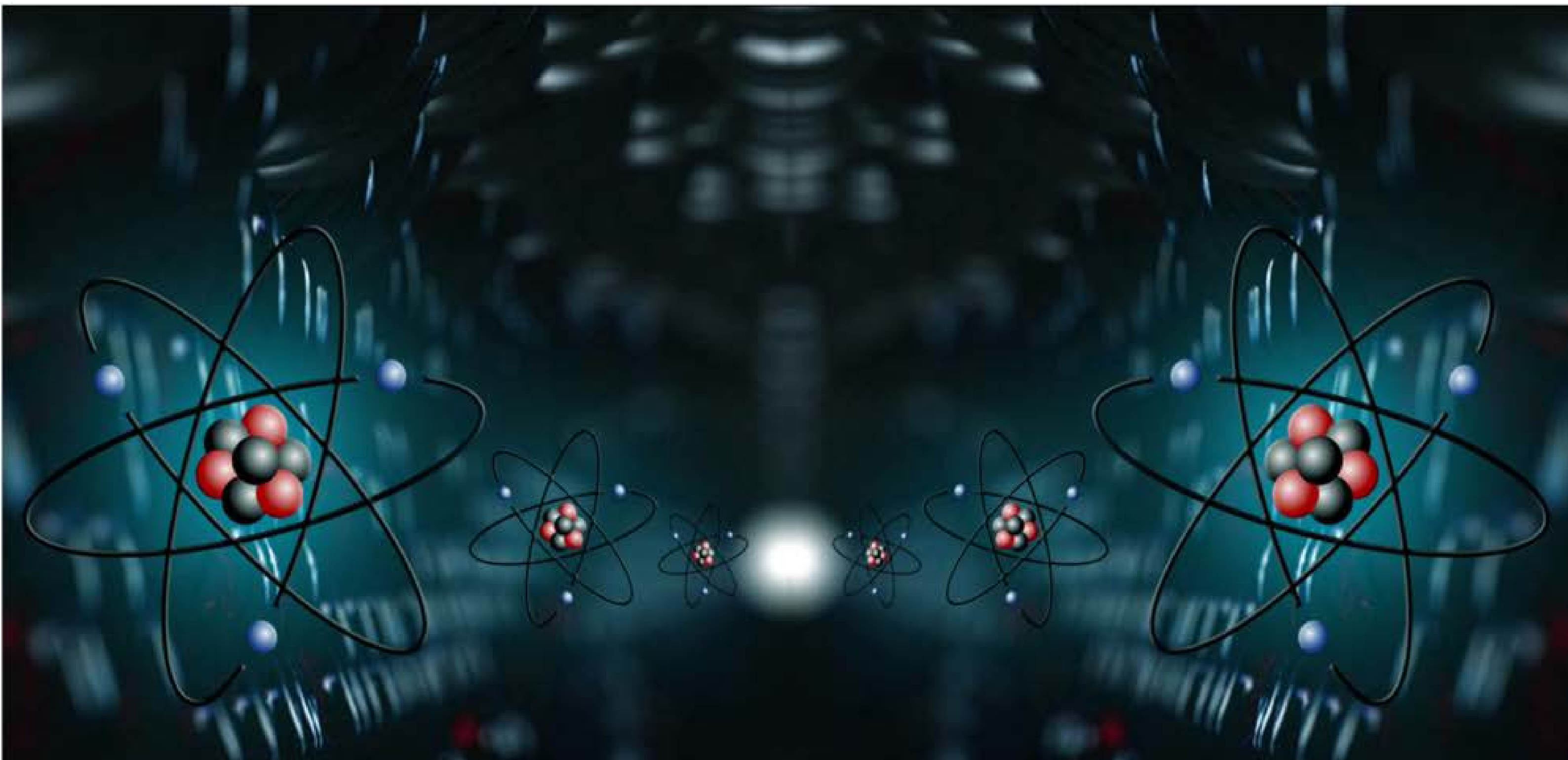
Volume I

MANDEEP DALAL



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ISBN: 978-81-938720-1-7
MRP: Rs 800.00

DALAL INSTITUTE
Main Market, Sector-14, Rohtak, Haryana-124001
(+91-9802825820, info@dalalinstitute.com)
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