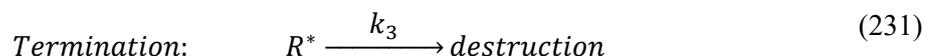
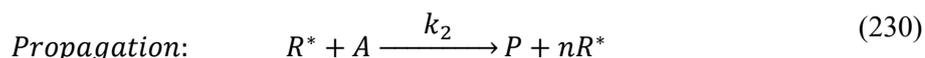
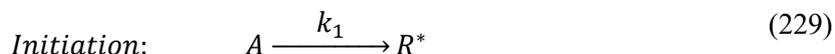


❖ Branching Chain Reactions and Explosions (H₂-O₂ Reaction)

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.

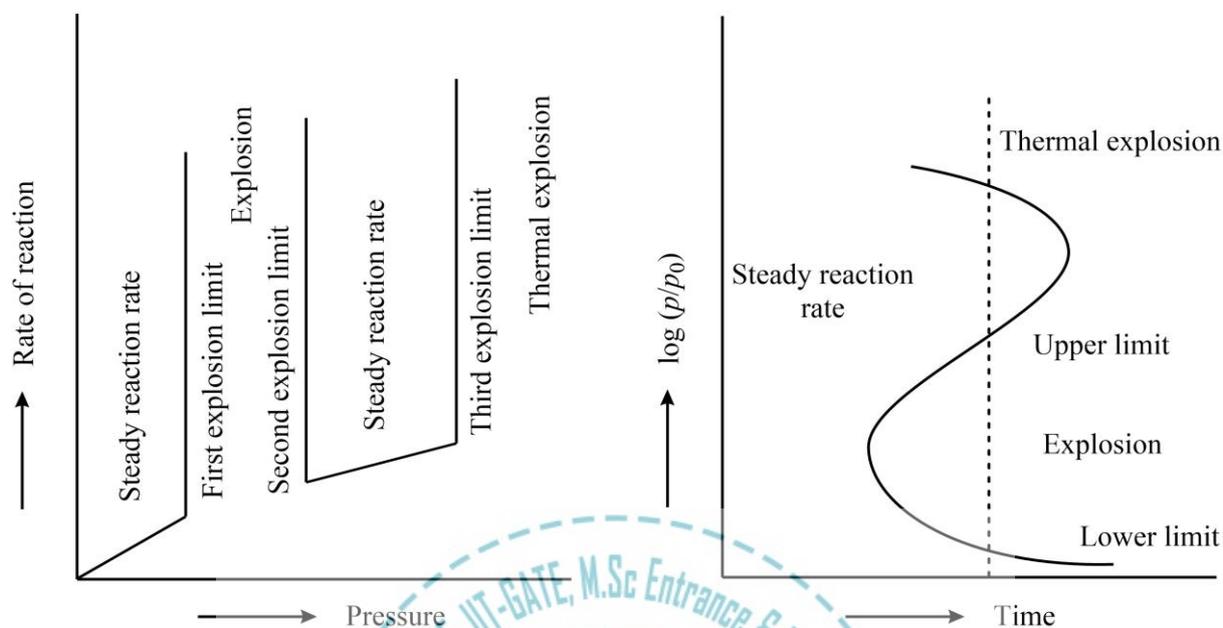


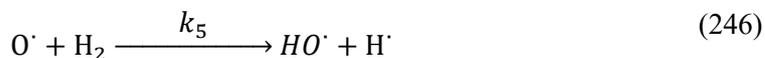
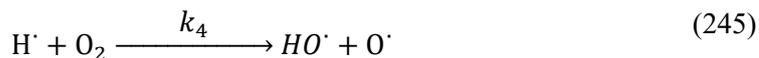
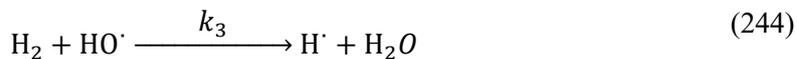
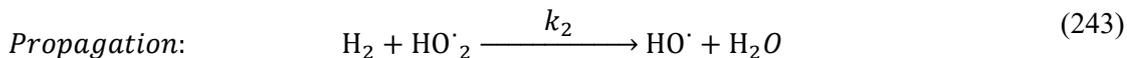
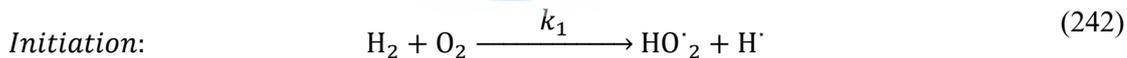
Figure 1. The variation of reaction with pressure in branching chain reactions (left) and variation of relative pressure with time on a logarithmic scale (right).

➤ 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 3rd and 4th produce more radicals than they consume, producing an explosion.

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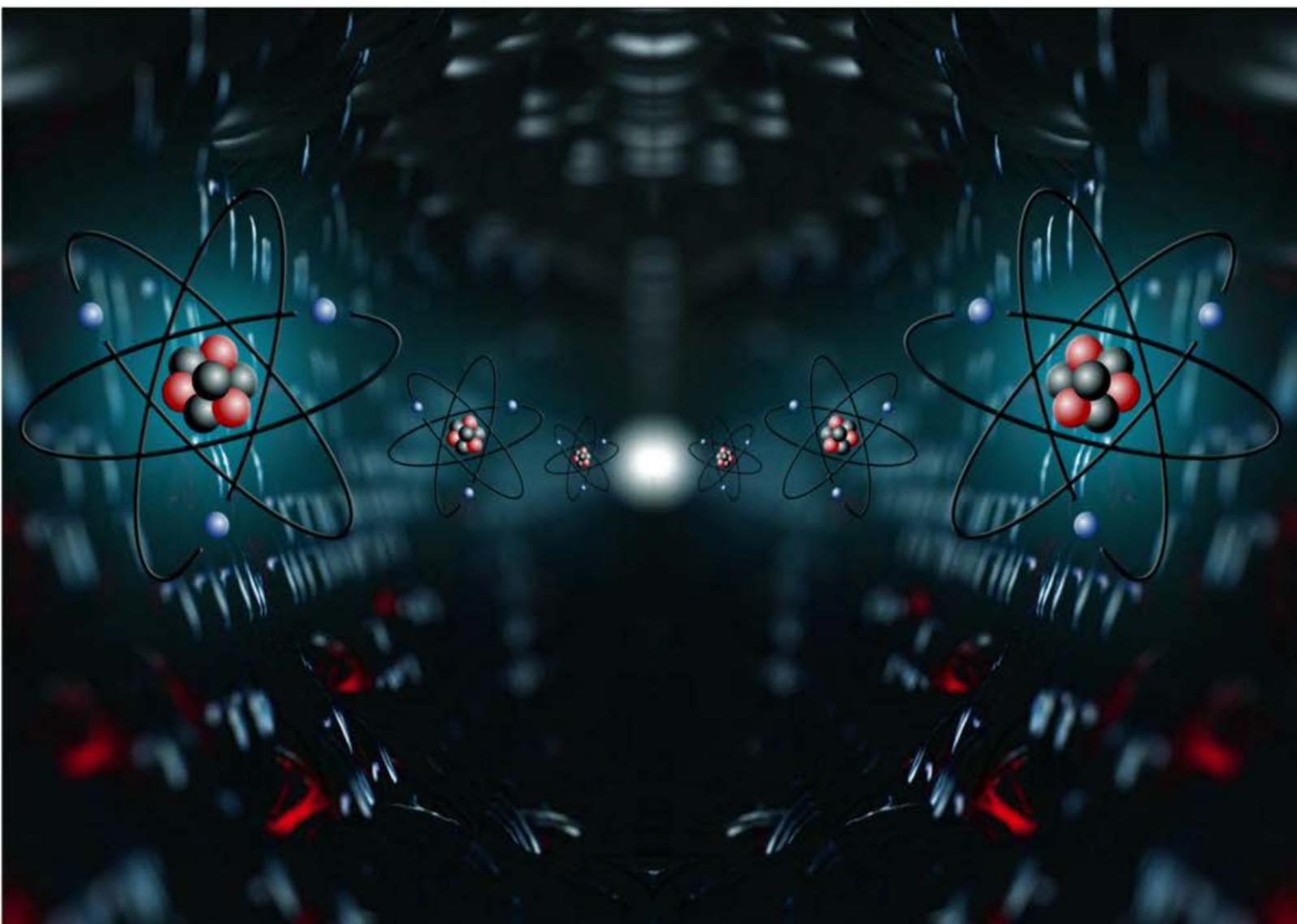
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Volume I

MANDEEP DALAL



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