beginning, it requires ...
is called *induction period.*

Steady-State HYPOTESIS

(*ii*) **Steady-State Hypothesis.** The assumptions involved in the steady-state hypothesis is that concentration of reactive intermediates can be assumed to be constant. If '$C_i$' is the reactive intermediate, then

$$[C_i] = \text{Constant}$$

$$\therefore \qquad \frac{d\,[C_i]}{dt} = 0$$

*Note that steady state approximation can only be applied to short-lived (or very species).* The following steps are used to calculate the rate law in terms of stable species

(*a*) The differential rate laws are written down for each species.

(*b*) The differential rate laws of reactive intermediates are put equal to concentration of reactive intermediates are calculated in terms of stable species

(*c*) Steady-state concentrations of intermediates calculated in step (*b*) are substituted expression so that the rate laws can be written only in terms of stable species and products).

(*iii*) **Kinetics of Chain Reactions (Steady State Treatment).** According to steady treatment, the concentration of active intermediate species is constant at any instant i.e.

$$\frac{d\,[R]}{dt} = 0$$

where $R$ is active chain carrier.

Consider the following general chain reaction, in which $A$ is reactant, $R$ is active carrier, $P$ is the product and $\alpha$ is the number of chain carriers produced by the carrier propagation step :

1. *Chain initiation* : $\qquad A \xrightarrow{k_1} R$

2. *Chain propagation* : $\qquad R + A \xrightarrow{k_2} P + R$

3. *Chain termination* : $\qquad R \xrightarrow{k_3} \text{destruction}$

The rate of formation of chain carrier

$$\frac{d\,[R]}{dt} = k_1\,[A] = k_2\,(\alpha - 1)\,[R]\,[A] - k_3\,[R]$$

According to steady-state treatment to $R$,

$$\frac{d\,[R]}{dt} = 0$$

or

$$k_1\,[A] = k_2\,(\alpha - 1)\,[R]\,[A] - k_3\,[R] = 0$$

$$\therefore \qquad R = \frac{k_1\,[A]}{k_2\,(1 - \alpha)\,[A] + k_3}$$

The termination (destruction) of chain carriers may be due to collision with the walls of vessels, or with other molecules in gas phase.

If $\quad k_w$ = Velocity constant for wall reaction

$\quad k_g$ = Velocity constant for gas phase reaction.

Then,

$$k_3 = k_w + k_g$$

$$\therefore \qquad R = \frac{k_1\,[A]}{k_2\,(1 - \alpha)\,[A] + k_w + k_g}$$

The rate of overall reaction is given by step 2

$$\frac{dx}{dt} = k_2\,[R]\;[A]$$

Putting value of [R], we get

$$\frac{dx}{dt} = \frac{k_1 k_2 [A]^2}{k_2(1-\alpha)[A] + k_w + k_g} \quad \text{... (2)}$$

*Chain length.* The chain length of a reaction is defined as the number of cycles (or links) that an active intermediate species can participate in between its formation step and termination step. Mathematically,

$$\text{Chain length} = \frac{\text{Rate of overall reaction}}{\text{Rate of initiation reaction}}$$

$$= \frac{k_1 k_2 [A]^2}{k_1 [A] \ (k_2(1-\alpha)[A] + k_w + k_g)}$$

$$= \frac{k_2 [A]}{k_2 [1-\alpha] [A] + k_w + k_g} \quad \text{... (3)}$$

*Analysis of equation* (1)

$$[R] = \frac{k_1 [A]}{k_2 (1-\alpha) [A] + k_w + k_g}$$

Case 1. When $\alpha = 1$, then

$$[R] = \frac{k_1 [A]}{k_w + k_g}$$

or

$$[R] = \frac{\text{Rate of formation of } R}{\text{Rate of destruction of } R}$$

Such reactions are called *nonbranched or stationary chain reactions.*

Case 2. *Explosion Limits*. When $\alpha > 1$ *i.e.*, more than one chain carriers are produced in chain propagation step, such chain reactions are called *branched* or *non-stationary chain reactions*. A critical situation arise, when

$$k_2 (1-\alpha) [A] + k_w + k_g = 0$$

or

$$k_2 (1-\alpha) [A] = -(k_w + k_g)$$

Then, $[R] = \infty$

Since, overall reaction rate $= k [R] [A]$

Hence, overall rate $= \infty$

That is, reaction proceeds so rapidly that explosion results. In other words, the reaction completes within fraction of a second. Such explosions are called *isothermal explosions.*

The chain carrier destruction rate, $k_w$ depends on the diffusion of $R$ (chain carriers) to the walls and is rapid at low pressure. When at a particular pressure,

(Rate of destruction of $R$ on walls) = (Rate of formation of $R$)

Then, no explosion occurs. This gives lower *explosion limit,* which depends on the size and material of reaction vessel.

As the pressure increases, the diffusion of $R$ to wall decreases, hence $k_w$ decreases, while $k_g$ (*i.e.*, destruction of $R$ due to collisions in gas phase) increases. If pressure increase is continued to such a stage that $(k_w + k_g)$ counter balances $k_2 (1-\alpha) [A]$, *i.e.*,

$$k_w + k_g + k_2 (1-\alpha) [A] = 0$$

then

$$[R] = \infty$$

Hence explosion will occur. This is called *first explosion limit*. With continuous incr... pressure, $k_g$ predominates ($k_w$ is negligible) and the term $(k_w + k_g + k_2 (1 - \alpha) [A])$ ... increases, giving a *second explosion limit*. Above this pressure, reaction proceeds with finite... The third pressure limit is due to thermal effects.

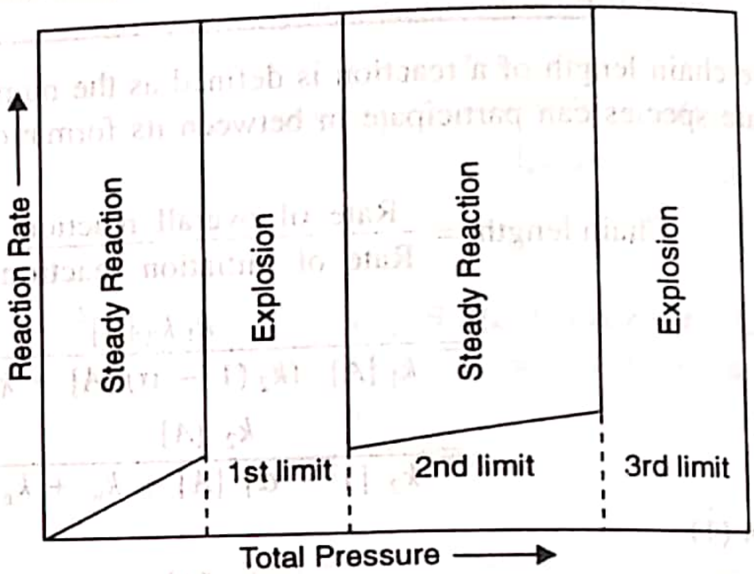


**Fig. 4.8.** Variation of reaction rate with pressure for branching chain reactions.

(*iv*) **Examples of Chain Reactions.** 1. *Thermal Reaction between Hydro...*