

Paper : Physical Chemistry

Topic : Chemical Kinetics

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Kinetics of Chain Reactions :-

There are two approaches to the problems of the mathematical representation of chain reactions :

- (i) Non-Steady State Treatment :- This method is followed by Russians. It involves highly complicated mathematical equations.
- (ii) Steady State Treatment :- This method is followed by British and Americans.

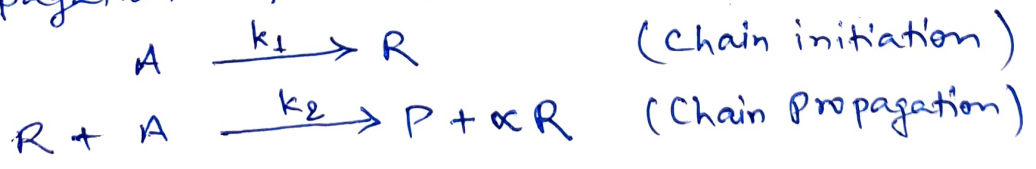
Let us apply here steady state treatment to the general chain reaction.

According to steady state treatment, the concentration of active intermediate species is constant - at any time or instant, i.e.

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

where R is active chain carrier.

Consider a general gaseous chain reaction in which A is the reactant, R is a reactive chain carrier, P is the product and α is the number of chain carriers produced by one carrier in the propagation step. Then, we can write





The chain carrier may be destroyed by either collision against the walls of the vessel or with other molecules.

The rate of formation of chain carrier is given by

$$\frac{d[R]}{dt} = k_1[A] - k_2[R][A] + \alpha k_2[R][A] - k_3[R]$$

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

Assuming steady state approximation for the chain carrier, R, i.e. $\frac{d[R]}{dt} = 0$, we have

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

or,
$$[R] = \frac{k_1[A]}{k_2(1-\alpha)[A] + k_3} \quad \text{--- (2)}$$

The constant k_3 may be considered as equal to the sum of two terms, k_w , the velocity constant for wall reaction and k_g , the velocity constant for the gas phase reaction, so that equation (2) becomes

$$[R] = \frac{k_1[A]}{k_2(1-\alpha)[A] + k_w + k_g} \quad \text{--- (3)}$$

Since the rate of overall reaction is given by step 2 (i.e. chain propagation reaction), then

$$\frac{dx}{dt} = k_2[R][A] \quad \text{--- (4)}$$

By putting the value of $[R]$ from equation (3) in equation (4) we get—

$$\frac{dx}{dt} = \frac{k_1 k_2 [A]^2}{k_2(1-\alpha)[A] + k_w + k_g} \quad \text{--- (5)}$$

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,

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

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

$$\text{or, Chain length} = \frac{k_2 [A]}{k_2(1-\alpha)[A] + k_w + k_g} \quad \text{--- (6)}$$

Analysis of equation (3) :-

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

Case I : When $\alpha = 1$, then

$$[R] = \frac{k_1[A]}{k_w + k_g} \quad \text{--- (7)}$$

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

Such reactions are called non-branched or stationary chain reactions.

Case II : 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.

When $\alpha \gg 1$, then

a critical situation arises. In this case a very large number of chain carriers are produced in the propagation step and the concentration of carrier, $[R]$ becomes almost-infinite. As a result, the rate of reaction becomes almost infinite resulting in explosion.

When $[R]$ tends to infinity, the denominator

of equation (3) tends to zero. i.e.

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

or, $k_2(1-x)[A] = -(k_w + k_g)$

Mathematically, $[R] = \infty$

But since, overall reaction rate = $k[A][R]$

hence overall reaction rate = ∞

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

Explosion Limits :

The chain carrier destruction rate, k_w depends on the diffusion of R (i.e. 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 collision in gas phase) increases. If increase of pressure is continued to such stage that - $(k_w + k_g)$ counter balances

$k_2(1-x)[A]$, i.e.

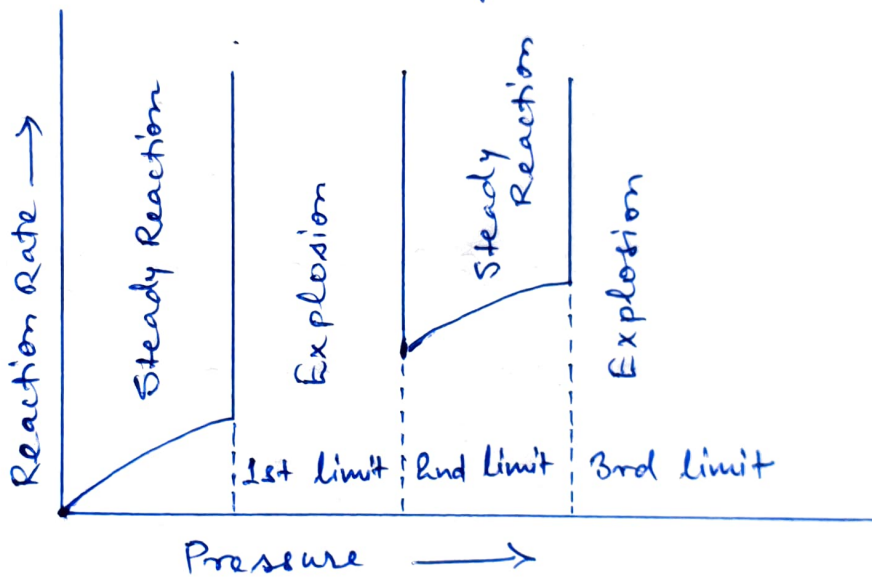
$$k_2(1-x)[A] + k_w + k_g = 0 \quad , \quad \text{then}$$

$$[R] = \infty$$

Hence here explosion will occur. This is called first explosion limit.

With continuous increase of pressure, k_g

predominates (k_w becomes negligible) and the term $(k_2(1-\alpha)[A] + k_w + k_g)$ steadily increases, giving a second explosion limit. Above this pressure, there is a third explosion limit. Here explosions are due to the rise in the temperature of reaction system. Such explosions are known as thermal explosions because they occur due to thermal effects. It has been observed that explosion will take place at all pressures above 600°C (i.e. thermal effect) but no explosion will occur under any pressure conditions below 460°C . The figure shown below gives the variation of explosion limits with pressure.



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