

Lecture 7. Chain termination. Kinetic laws of chain reaction. Chain length

The purpose of the lecture: to give information about the stage of chain termination, kinetic laws of chain reactions, chain length.

Expected results: students getting information about the kinetic laws of chain reactions, about determining the length of the chain.

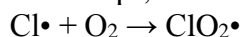
The principle of conservation of free valency is satisfied only in first-order reactions of the free radical. In reactions involving two free radicals or atoms, as a rule, the saturation of the free valence occurs; molecules are formed as products. Such reactions are exothermic, as new bonds form in them, and they proceed with high rate constants. For example, the recombination and disproportionation of alkyl radicals in a solution proceeds with the rate constant of diffusion encounters [10^8 - 10^9 l/(mol·s)]. In the gas phase, atoms recombine with a frequency of triple collisions [$\sim 10^{10}$ l²/(mol²·s)]:



transferring to the third particle M a part of the released energy. If an atom or radical is involved in a chain process, then this type of reaction is the reaction of chain termination (death). This break can occur according to the reactions of active centers of the same type or of different types.

The molecular product formed in the act of death of the chain must be stable under the conditions of the chain process. Otherwise, it breaks up, and chain termination by this reaction does not work.

The cyclic principle necessary for the realization of a chain reaction is violated if a substance is introduced into the system that reacts with one of the leading chains of active centers with the formation of a radical that is not involved in the continuation of the chain. For example, the presence of O₂ in a mixture of H₂+Cl₂, where a chain reaction develops, leads to chain termination by the reaction



The resulting ClO₂• radical does not react with hydrogen and chlorine, so this reaction breaks the chain. The reagent breaking the chain is an inhibitor of the chain reaction. The wall of the reaction vessel may act as a kind of chain reaction inhibitor if adsorption of active centers occurs on it with their subsequent death.

The processes of continuation and death of active centers compete with each other. Therefore, a chain reaction is realized only when the system creates opportunities for the pre-dominant (priority) course of chain continuation reactions. Only under this condition the cycle of chain extension reactions is repeated many times. The average number of chain extension cycles per one active cycle generated in the system is the chain length. For a unbranched chain reaction in a quasistationary mode, the chain length ν is equal to the ratio of the chain extension reaction rate to the termination reaction of chain termination or chain initiation.

So, a chain reaction arises by virtue of the principle of the indestructibility of free valency in reactions of the first order in the radical. For its implementation, three conditions must be met.

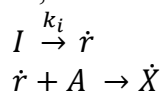
1. The set and structure of the reagents must be such that a cycle of radical transformations with the regeneration of the initial radical (atom) can be realized in the system.

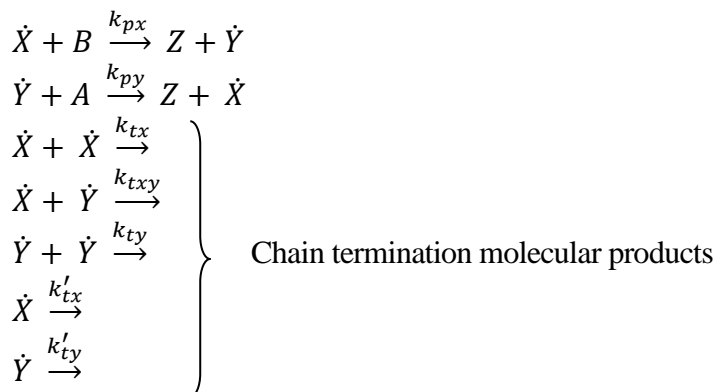
2. In a system of reagents or through a special initiating effect (initiator, light, radiation), it is necessary to generate free radicals.

3. Conditions are chosen such that the continuation proceeds much faster than open circuits.

Kinetic laws of chain reaction

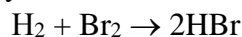
Each particular chain reaction has its own characteristics. However, they all also have common features and kinetic laws arising from the chain mechanism. In this section, the main ones will be examined using the following hypothetical scheme as an example (I is the initiator, A and B are the reagents, X• and Y• are the active centers, Z is the product):



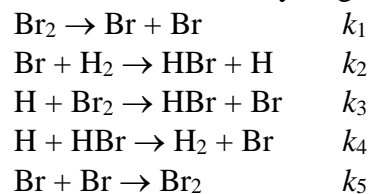


The circuit will be analyzed in a quasistationary mode of $X\cdot$ and $Y\cdot$, when the rates of initiation and breaking of the circuits are almost the same.

The kinetic equation of an unbranched chain reaction can be obtained based on the reaction mechanism. For example, a detailed study of the reaction between hydrogen and bromine



showed that the reaction proceeds in several elementary stages with different rate constants k :



Based on this scheme, the rate of formation of hydrogen bromide can be represented by the equation:

$$\frac{dc_{HBr}}{dt} = k_2 c_{Br} c_{H_2} + k_3 c_H c_{Br_2} - k_4 c_H c_{HBr}.$$

Considering the bromine and hydrogen atoms as intermediate products, we can apply to them the principle of stationary concentrations of Bodenstein:

$$\begin{aligned}
 2k_1 c_{Br_2} - k_2 c_{Br} c_{H_2} + k_3 c_H c_{Br_2} + k_4 c_H c_{HBr} - k_5 c_{Br}^2 &= 0. \\
 k_2 c_{Br} c_{H_2} - k_3 c_H c_{Br_2} - k_4 c_H c_{HBr} &= 0.
 \end{aligned}$$

From the sum of these equilibria we find the concentration of bromine atoms:

$$c_{Br} = \sqrt{\frac{2k_1}{k_5}} c_{Br_2}.$$

After substituting this concentration, we obtain the concentration of hydrogen atoms:

$$c_H = \frac{k_2 c_{H_2} \sqrt{\frac{2k_1}{k_5}} c_{Br_2}}{k_3 c_{Br_2} + k_4 c_{HBr}}.$$

Substituting the concentrations of bromine and hydrogen atoms in the equation gives the final equation for the reaction rate:

$$\frac{dc_{HBr}}{dt} = \frac{\frac{2k_2 k_3}{k_4} c_{H_2} \sqrt{\frac{2k_1}{k_5}} c_{Br_2}}{\frac{k_3}{k_4} + \frac{c_{HBr}}{c_{Br_2}}}.$$

Chain length

An important characteristic of the chain process is the chain length — the average number of cycles of radical transformations of reagents into products that are caused by one active center that appears in the system. Chain length $\nu = \nu_B/\nu_i = \nu_A/\nu_i$. It depends or does not depend on ν_i , which is due to how the circuit breaks. When the chains are broken at the centers $X\bullet$ in the first order, the chain length

$$\nu = 2k_{px}(k'_{tx})^{-1}$$

i.e., independent of ν_i . When the chains are broken at the centers $X\bullet$ in a bi-molecular reaction, the chain length

$$\nu = 2k_{px}(2k_{tx})^{-1/2}[B]\nu_i^{-1/2}$$

that is, decreases with increasing ν_i . In the general case, when the circuit termination is carried out in parallel along two channels, ν and ν_i , are connected by the relation:

$$\frac{[B]}{\nu} = \frac{k_{ix}}{2k_{px}} + \frac{k_{tx}}{4k_{px}^2} \frac{\nu_i}{[B]} \nu$$

With short chains, the contribution of initiation to the overall process becomes noticeable, and the reaction rate should be recorded in a more complete form, namely:

$$\nu_A = \nu_i + k_{px}(2k_{tx})^{-1/2}[B]\nu_i^{1/2}.$$

With an increase in the initiation rate, $[X\bullet]$ becomes so high that their recombination proceeds faster than the continuation of the chain. Under such conditions, the chain process becomes a non-chain radical reaction. This transition takes place when the condition

$$\nu_i \geq k_{px}^2 (2k_{tx})^{-1}[B]^2.$$

On the other hand, one can experimentally observe a chain reaction when $\nu_A = \nu_B = 1/2\nu_Z = \nu$ greater than some minimum recorded speed $\nu_{i,min}$. There is a range of ν_i in which the chain reaction can be studied, and this range is determined by the inequality

$$\nu_{i,min} < \nu_i < k_{px}^2 (2k_{tx})^{-1}[B]^2.$$

Literature

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