Lecture 6. Chain reactions. Chain Concepts. Chain origin. Chain continuation

The purpose of the lecture: to familiarize students with chain reactions and their stages, active centers formed in chain reactions.

Expected results: students gaining knowledge about chain reactions and their stages, about the formation of active centers of chain reactions.

In some cases, in chemical reactions, such active particles as free atoms and radicals, which have free valencies and therefore have high reactivity, act as intermediate products. These particles enter into reactions, as a result of which free atoms and radicals reappear. Such a sequence of periodically repeating reactions involving active particles (free atoms and radicals) is called a chain reaction.

Although the formation of free atoms or radicals requires a high activation energy, their high reactivity and the appearance of new active particles in reactions with saturated molecules lead to the fact that the rate of chain reactions is usually much higher than the rate of non-chain reactions. The nucleation at the beginning of the reaction of a small amount of reactive particles leads to the conversion of a large number of starting materials. Since chain reactions proceed cyclically, the active particle arising at the end of the cycle gives rise to a new cycle, at the end of which the active particle regenerates again.

The chain reactions include various classes. By a chain mechanism, for example, combustion or slow oxidation reactions in the gas phase proceed:

$$2H_2 + O_2 \rightarrow 2H_2O$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
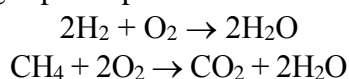
Many reactions involving hydrocarbons (polymerization, decomposition), photochemical reactions (the formation of HCl, HBr, $COCl_2$, etc.), and nuclear chain reactions, such as the decay of uranium-235 or plutonium in a nuclear reactor or bomb, are chain reactions.

The discovery of chain reactions was the result of intensive research on photochemical reactions. In 1912, Einstein formulated the law of interaction of a quantum of light with a molecule, according to which the quantum yield of a photochemical reaction cannot exceed unity. M. Bodenstein, having studied a number of reactions proceeding under the influence of light, discovered that the reaction of chlorine with hydrogen proceeds with a huge quantum yield: up to a million molecules per absorbed quantum. He suggested that the reaction proceeds as a chain of successive transformations: a quantum of light knocks an electron out of a chlorine molecule, which causes a chain of successive transformations of H_2 and Cl_2 to HCl. However, measurements of electrical conductivity showed that electrons do not form in such a system, and Bodenstein in 1916 suggested that the chlorine molecule excited by light is the active center. But this mechanism was not confirmed by subsequent experiments.

In 1918, Christiansen proposed a mechanism for the chain conversion of Cl_2 and H_2 to HCl with the participation of chlorine and hydrogen atoms and the continuation of the chain according to the reactions:

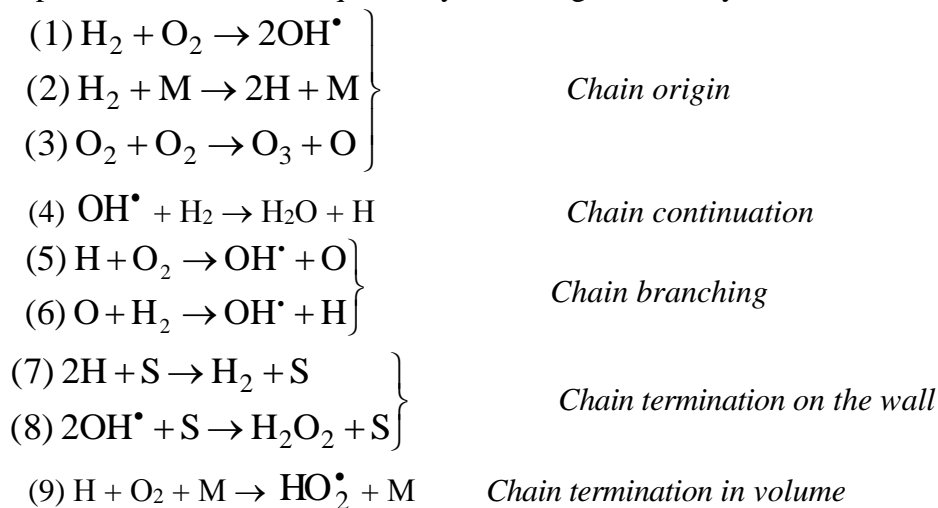$$Cl^{\bullet} + H_2 \rightarrow HCl + H^{\bullet}, H^{\bullet} + Cl_2 \rightarrow HCl + Cl^{\bullet}$$

The generation of atomic chlorine occurs under the influence of light. This scheme has been experimentally confirmed; its individual stages have been thoroughly studied. So in the years 1913-18 a new science was born - the kinetics of chain reactions.

A characteristic feature of chain reactions is the high sensitivity of the speed of these reactions to the presence of certain impurities. For example, carefully dried hydrogen and oxygen react with each other very slowly, but the reaction proceeds at normal speed in the presence of a small amount of water vapor. A mixture of hydrogen with chlorine does not react in the dark at room temperature, but quickly reacts when small amounts of sodium vapor are introduced into the system. In other cases, the presence of impurities leads to a sharp decrease in the reaction rate. For example, during the photochemical initiation of the reaction of hydrogen with chlorine, the rate of formation of hydrogen chloride decreases by about a thousand times in the presence of one percent oxygen.
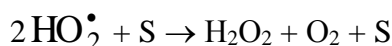
The shape and material of the vessel in which the reaction proceeds affects the speed of many gas reactions. Typically, reactions slow down with an increase in the S/V ratio (S is the vessel surface area, V is its volume). This ratio can practically be changed by introducing fragments of the material of the vessel — glass, quartz, etc., into the vessel.

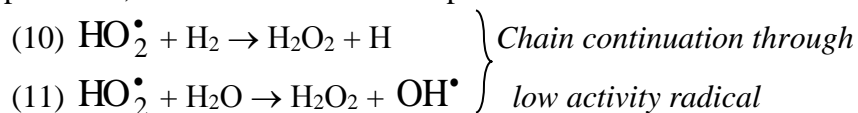There are two types of chain reactions: with unbranched and branched chains.

In a number of reactions, as a result of one elementary act, not one, but two or more chemically active particles, i.e. chain branching occurs. Such reactions are called branched chain reactions. In such reactions, in the initial period of time, the number of active particles and, consequently, the reaction rate increase like an avalanche until the moment when, due to the consumption of the starting material, the reaction rate begins to decrease. An example of such processes is the reaction of hydrogen oxidation, the mechanism of which, according to modern concepts, can be represented as a set of sequentially occurring elementary chemical acts:

$$(1)\ H_2 + O_2 \rightarrow 2OH^\bullet$$
$$(2)\ H_2 + M \rightarrow 2H + M \qquad \text{\textit{Chain origin}}$$
$$(3)\ O_2 + O_2 \rightarrow O_3 + O$$

$$(4)\ OH^\bullet + H_2 \rightarrow H_2O + H \qquad \text{\textit{Chain continuation}}$$

$$(5)\ H + O_2 \rightarrow OH^\bullet + O$$
$$(6)\ O + H_2 \rightarrow OH^\bullet + H \qquad \text{\textit{Chain branching}}$$

$$(7)\ 2H + S \rightarrow H_2 + S$$
$$(8)\ 2OH^\bullet + S \rightarrow H_2O_2 + S \qquad \text{\textit{Chain termination on the wall}}$$

$$(9)\ H + O_2 + M \rightarrow HO_2^\bullet + M \qquad \text{\textit{Chain termination in volume}}$$

Inactive radicals $HO_2^\bullet$ can decompose on the wall:

$$2\,HO_2^\bullet + S \rightarrow H_2O_2 + O_2 + S$$

At high pressures, reactions in volume are possible.:

$$(10)\ HO_2^\bullet + H_2 \rightarrow H_2O_2 + H \qquad \text{\textit{Chain continuation through}}$$
$$(11)\ HO_2^\bullet + H_2O \rightarrow H_2O_2 + OH^\bullet \qquad \text{\textit{low activity radical}}$$

If the branching of the chain is carried out frequently, then even one chain that has initially arisen can lead to the development of many chains. In the extreme case, one can imagine that branching occurs in each link, and then they speak of a completely branched chain reaction. In other cases, branching may occur more rarely.

The existence of the lower and upper limits of ignition can be qualitatively explained as follows. At pressures below the lower limit, active particles easily diffuse to the walls of the vessel where they die. The breaking of chains on the walls prevails over the branching, and a quick reaction does not develop. With increasing pressure, diffusion to the walls becomes more difficult, and the number of double collisions of types (5) and (6) increases, which lead to branching of the chains; the nucleation and branching of chains begin to prevail over the cliff. As a result, the reaction self-accelerates and can result in self-ignition or explosion, which occurs inside the ignition peninsula.

With a further increase in pressure, triple collisions in the volume become more and more likely, leading to chain termination. If the pressure exceeds the value of the upper limit II, the break begins to prevail over the development of chains and the possibility of a quick reaction disappears.

Chain origin

The formation of radicals that initiate a chain process occurs through a variety of reactions. First, radicals can arise from starting materials. For example, the chain decomposition of acetaldehyde begins with its monomolecular decomposition via the C-C bond (D_{C-C} = 338.6 kJ/mol):

$$CH_3CHO \rightarrow CH_3\bullet + \bullet CHO$$
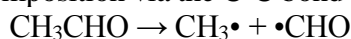
Thermolysis often occurs on the wall S of the reaction vessel, for example:

$$Cl_2 + S \rightarrow Cl — S + Cl\bullet$$
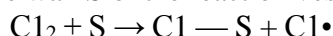
The formation of a chemisorbed chlorine atom facilitates such a process, reducing the activation energy. Radicals can be generated by the bimolecular reaction of reagents, as, for example, in the oxidation of hydrocarbons by the reaction

$$RH + O_2 \rightarrow R\bullet + HO_2\bullet$$
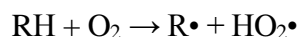
Secondly, a chain reaction is initiated by introducing an initiator or initiating system. Peroxides and azo compounds are used as initiators of liquid-phase chain reactions. Thus, azoisobutyronitrile decomposes into radicals by the reaction

$$(CH_3)_2(CN)CN=NC(CN)(CH_3)_2 \rightarrow N_2 + 2(CH_3)_2(CN)C\bullet$$

Radicals can occur in redox systems. For example, to initiate emulsion polymerization, the H_2O_2 + Fe^{2+} system is used, which initiates radicals by reaction

$$H_2O_2 + Fe^{2+} \rightarrow HO\bullet + Fe^{3+} + HO^-$$

Dibenzoylperoxide and dimethylaniline generate radicals by reaction

$$PhCOOOCOPh + PhN(CH_3)_2 \rightarrow PhCOO\bullet + PhN^+(CH_3)_2 + PhCO_2^-$$
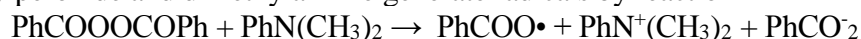
Thirdly, a chain reaction can be initiated by generating photochemical radicals, for example:

$$Cl_2 + hv \rightarrow 2Cl\bullet$$
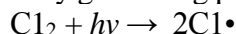
or by penetrating radiation (γ-rays, electrons, α-particles).
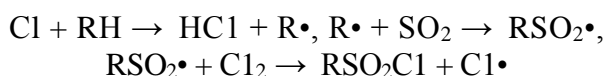
Chain continuation

Free atoms and radicals formed in the system react with molecules. If a sequence of radical reactions arises in the system, which constitutes a cycle of transformations with the regeneration of the initial radical form, then in this case a chain reaction is possible. A cycle of radical transformations with conservation of free valency and regeneration of the initial particle is called <u>a chain link</u>. A chain link may consist of one or more elementary stages. In the radical polymerization of the vinyl monomer $CH_2=CHX$, the unit consists of one elementary stage (R$\bullet$ is the macroradical):

$$R\bullet + CH_2=CHX \rightarrow RCH_2\bullet CHX$$
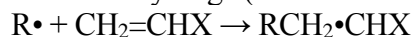
In the chain reaction of chlorine with hydrogen, the chain link includes two successive stages:

$$Cl + H_2 \rightarrow HCl + H\bullet, H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$$
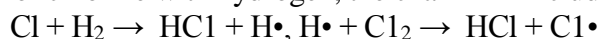
The chain sulfochlorination of hydrocarbon RH proceeds as an alternation of three elementary acts:

$$Cl + RH \rightarrow HCl + R\bullet, R\bullet + SO_2 \rightarrow RSO_2\bullet,$$
$$RSO_2\bullet + Cl_2 \rightarrow RSO_2Cl + Cl\bullet$$

Chain extension may include not only the reaction of radicals with molecules, but also the decomposition reaction. For example, chain ethane decomposition involves reactions

$$H\bullet + CH_3CH_3 \rightarrow H_2 + C_2H_5\bullet, C_2H_5\bullet \rightarrow CH_2=CH_2 + H\bullet$$
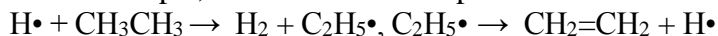
Rarely, chain reactions are found where chain continuation occurs by the reaction of two radicals. For example, isobutane oxidation involves the following steps:

$$(CH_3)_3C\bullet + O_2 \rightarrow (CH_3)_3COO\bullet,$$
$$2(CH_3)_3COO\bullet \rightarrow 2(CH_3)_3CO\bullet + O_2,$$
$$(CH_3)_3CO\bullet + (CH_3)_3CH \rightarrow (CH_3)_3COH + (CH_3)_3C\bullet$$
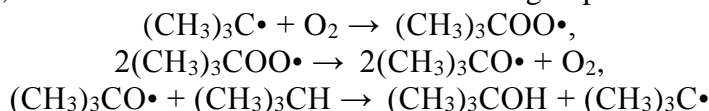
A chain extension may include not one, but two or more parallel cyclic reactions of chain continuation.
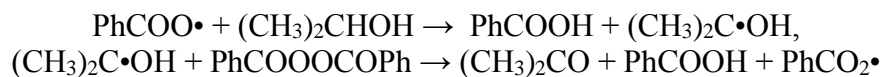
As shown by the analysis of the stages of chain continuation in various chain reactions, two principles are at the heart of their implementation in nature. First, the principle of the indestructibility of free valency in reactions involving one free ¬ atom or radical. If the radical isomerizes or decomposes, then an atom or radical is always present in the reaction products. If a radical reacts with

a molecule - detaches an atom, a group or joins via a multiple bond, then in these cases the free valency is preserved, since the odd number of electrons characteristic of the reagents on the outer electronic shells of the products is preserved. Thus, in reactions of an atom or radical with a valence-saturated molecule and in monomolecular reactions of free radicals, due to the conservation of an odd number of electrons in the orbitals of reagents and products, there is necessarily a particle with an odd number of radicals (atom or radical)

Far from all systems, the appearance of free radicals causes a chain reaction. For example, the decomposition of dibenzoyl peroxide in the hydrocarbon RH causes the following reactions:

$$PhCOOOCOPh \rightarrow 2PhCOO\bullet, PhCOO\bullet + RH \rightarrow PhCOOH + R\bullet,$$
$$R\bullet + R\bullet \rightarrow RR \text{ (или } RH + \text{Олефин)}$$

Although radicals are generated in such a system and free valency is retained in the reaction of the interaction between RhCOO and RH, a chain reaction does not occur, since a cyclic sequence of stages with the conservation of free valency is not realized. Therefore, secondly, it is very important to fulfill one more condition: the principle of cyclicality of the radical stages while maintaining free valency. To realize a chain reaction, such a combination of reagents is necessary that a cycle of transformations takes place with the preservation of free valency and the reproduction of the initial radical (atom). In the above example, it is enough to replace the hydrocarbon with secondary alcohol so that a chain reaction of the decomposition of dibenzoyl peroxide occurs with the following stages of chain continuation:

$$PhCOO\bullet + (CH_3)_2CHOH \rightarrow PhCOOH + (CH_3)_2C\bullet OH,$$
$$(CH_3)_2C\bullet OH + PhCOOOCOPh \rightarrow (CH_3)_2CO + PhCOOH + PhCO_2\bullet$$

Literature

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