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CHAIN REACTIONS OF GAS COMBUSTION, EXPLOSION, AND DETONATION: NEW THEORETICAL ASPECTS

Chapter X. Chain–Thermal Explosion

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Abstract—The existence of two regimes of chain combustion is predicted, the phenomenon of explosion with a chain mechanism is explained, and the condition for the transition of combustion to this regime is formulated. The abrupt changes in the kinetic curves during the transition of combustion to this regime are illustrated and explained. The results of an experimental study of the transition from combustion to explosion are presented; it is found out that the ignition peninsulas, which are presented in courses and monographs on chemical kinetics as kinetically homogeneous regions, actually consist of two regions that are different in all reaction characteristics: the combustion region and the explosion region. Experimental evidence is given of the chain nature of combustion in an explosion under conditions of cumulation and control of such an explosion by means of inhibitors.

Keywords: explosion, heat removal, characteristic reaction time, competition between heat removal and heat release, adiabatic processes

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Explosion is one of the most common combustion regimes. The term "explosion" is often used instead of the words "ignition" and "combustion." However, ignition differs from explosion very much both in reaction rates and in macrokinetics and gas dynamics. Explosive combustion of gases is accompanied by an increase in temperature and pressure in fractions of a thousandth of a second. The blast wave propagates at supersonic speed. Previously generally accepted ideas about explosive combustion, as well as about ignition and flame propagation, were based on a hypothetical model of a one-step reaction between molecular reagents (e.g., [1–5]). To describe the process, the reaction was hypothetically assigned the first kinetic order and the calculated parameters were selected using a hypothetically accepted equation. In Chapter I, it is noted that the extremely low rates of intermolecular reactions, which, unlike free atoms and radicals, are not capable of supporting combustion, was mentioned by N.N. Semenov, e.g., in [6]. However, in some of his subsequent works, including [7], it is argued that the cause of combustion at atmospheric pressure and the cause of the explosion is only heat release. In previous sections of this book, results were presented indicating that reactions between valence-saturated compounds are extremely slow due to their activation energies, exceeding 220 kJ/mol. It was also shown that, in all gas combustion regimes, at any pressure and at any temperature, combustion reactions proceed according to chain mechanisms (e.g., [8–12]). The law of temperature dependence of the rate of combustion reactions of gases was also clarified, according to which the reaction can self-accelerate so strongly that the released heat mainly remains in the combustion chamber. In this case, the gas heated in the combustion zone does not have time to expand to sizes exceeding the size of this zone. The condition for a thermal explosion is expressed by the following relation [13, 14]:

$$vt_{\mathrm{b}} < l, \qquad (1.X)$$

where v is the speed of sound in the reactor volume, t_{b} is the characteristic reaction time, and l is the characteristic size of the combustion source.

Since gas combustion reactions proceed only according to a chain mechanism, the relation (1.X) is the condition for a chain–thermal explosion (CTE). The conditions for the transition of combustion to explosion are created by very high rates and accelerations of the chain reaction, corresponding to the exponential law with the Boltzmann factor in a positive exponent (Chapter IX).

1. EXISTENCE OF TWO KINETIC REGIMES OF DEVELOPED CHAIN COMBUSTION, INDEPENDENT OF THE ROLE OF HEAT AND MASS TRANSFER AND SHOCK COMPRESSION

In [15], by numerically solving the equations of chain combustion using a generalized kinetic scheme upon self-heating, it was established that the branch-

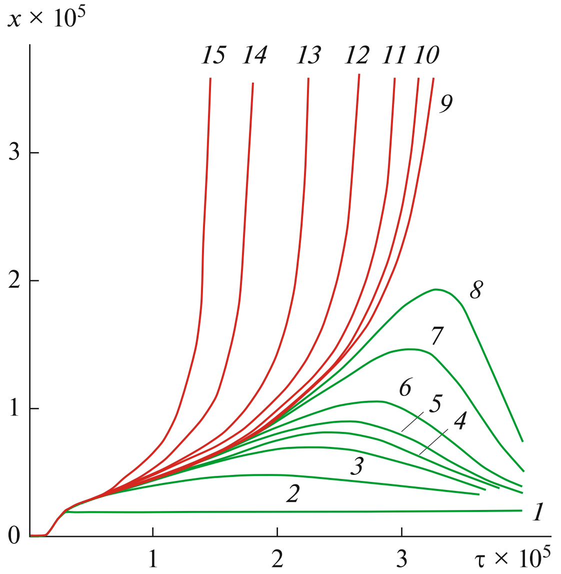

Fig. 1.X. Kinetic curves of CC for various ratios between parameters of heat release and heat removal rates (quantity $\chi \times 10^3$) calculated on the basis of a generalized kinetic scheme of a branching chain reaction. The values of $\chi \times 10^3$ are (*1*) 0, (*2*) 1.00, (*3*) 1.20, (*4*) 1.30, (*5*) 1.35, (*6*) 1.37, (*7*) 1.38, (*8*) 1.381, (*9*) 1.382, (*10*) 1, (*11*) 1.39, (*12*) 1.41, (*13*) 1.45, (*14*) 2.0, and (*15*) 2.50.

ing chain process accompanied by self-heating has two combustion regimes, which differ sharply in reaction rates and self-acceleration values, even at constant pressure. The boundaries between these kinetic regimes are critical. In order to highlight the role of kinetic factors, the transport and convection phenomena—conditions without which the temperature and concentrations distributions in the reactor are uniform—were not taken into account. The dependence of the kinetics of the process on the ratio of the heat release and heat removal rates (χ) was studied.

Figures 1.X and 2.X show the kinetic curves of the concentrations of the active intermediate product (x) and the consumption of the initial reagents (η) related to the gas density at various values of the above-introduced ratio χ. The abscissa axis is dimensionless time. Curves *1* refer to isothermal chain combustion. The increasing numbers of kinetic curves corresponds to the increasing role of self-heating and chain avalanche relative to the heat removal rate. From Fig. 1.X, it can be seen that, in the immediate vicinity of a certain value of the variable χ as it changes by less than 0.01%, a sharp change in the kinetic regime of the reaction occurs upon the transition from curve *8* to curve *9*. Almost at the same χ value, the growth rates of the consumption of the initial reagents (Fig. 2.X) and temperature are abruptly accelerated. Thus, since in the system of equations, concentration and temperature gradients, as well as convection, are not taken into account, the presence of two sharply different kinetic regimes is a feature of branching chain combustion, regardless of the limiting role of heat and mass transfer and regardless of the presence of a shock wave. Obviously, these regimes also differ in all other characteristics.

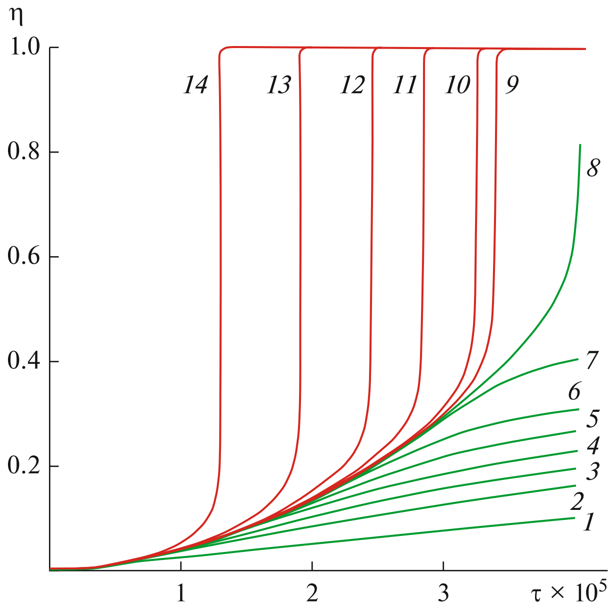

Fig. 2.X. Kinetic curves of relative consumption of starting reagents (η). The curve numbers correspond to the values of $\chi \times 10^3$ in Fig. 1.X.

2. TRANSITION OF COMBUSTION INTO CHAIN–THERMAL EXPLOSION AT LOW PRESSURES

Experimental Technique

The transition of combustion to CTE was also studied experimentally. To provide conditions for better time resolution while preserving the features of the chain nature of the process, in [16], the reaction in a stoichiometric mixture of H_2 and O_2 was conducted at initial pressures of up to 4 kPa in a thermostat in quartz reactors with a diameter of 5.5 and 3.2 cm and a length of 15 and 9 cm. The block diagram of the setup is shown in Fig. 3.X.

The length of the zone of uniform temperature distribution in the tubular furnace was 13 cm, and thus a uniform initial temperature throughout the volume of the reactor was ensured. The specified initial temperature was maintained by a thermostat within 2°. In order to ensure a uniform distribution of the chain carrier concentrations in the reactor and possibly low initial explosion pressures, the walls were treated with hydrofluoric acid.

A measured portion of prepared mixture from the bypass volume was quickly released into the evacuated

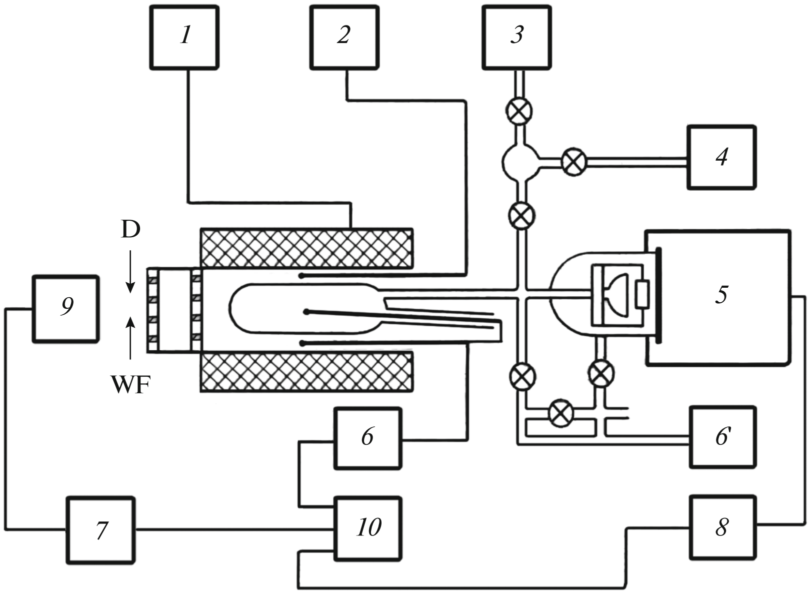

Fig. 3.X. Block diagram of the setup for kinetic studies at low pressures: (*1*) thermocontroller of thermostat and potentiometric temperature recorder, (*2*) thermocouple, (*3*) vacuum unit, (*4*) membrane manometer, (*5*) pressure transducer, (*6*) vacuum post, (*6′–8′*) amplifiers DC, (*9*) photomultiplier, (*10*) multichannel oscilloscope, (D) diaphragm, and (WF) water filter.

reactor. From the moment of inlet, high-speed synchronous recording of chemiluminescence was carried out using a FEU-39 photomultiplier tube and pressure using a piezoquartz sensor or a membrane manometer. In an explosion, combustion is much more intense, and the amplitude of pressure changes is much greater. Therefore, the explosion was detected with a piezoceramic sensor (TsTS). Both sensors were installed in the communication channel connecting the reactor with the bypass volume. The readings of photomultipliers and pressure sensors were recorded on an oscilloscope. After completion of each experiment, the reactor was evacuated to a pressure of 1.5×10^{-2} Pa. The method allows, by freezing out the resulting water vapor, to determine the final degree of burnout of the starting substances.

To reveal the features of thermal ignition determined by the chain mechanism, convection and the limiting role of diffusion in the initial stages of chain self-ignition were excluded. For this purpose, a specially developed method [16] was used, which ensures self-ignition only after the completion of gas injection into the reactor and the establishment of a stationary pressure, uniform throughout the reactor volume. This is achieved by introducing into the initial mixture a fraction of a percent of a slowly oxidizing inhibitor, which prevents self-ignition for the time necessary to establish a uniform volume distribution of temperature and concentrations after gas injection. As a result of the consumption of the inhibitor with time, its concentration falls below the critical value corresponding to the condition for self- ignition, the mixture enters the ignition region and spontaneously ignites. Already at the very initial stages of the onset of hydrogen combustion, the remaining inhibitor burns out and, subsequently, the chain reaction develops in its absence. Thus, the method makes it possible to regulate ignition delays and ensure the onset of combustion in a quiescent gas in the absence of temperature and concentration gradients. The inhibitor was ethane, which terminates the chains according to the reaction

$$H + C_2H_6 = H_2 + C_2H_5.$$

Since the ignition induction period decreases with increasing temperature, the inhibitor content was increased as the initial temperature increased to ensure a delay in self-ignition after the mixture was injected. Differently designated points at the interface between CTE and chain combustion correspond to these different inhibitor contents.

3. DEVELOPED CHAIN COMBUSTION AS A NECESSARY CONDITION FOR CHAIN–THERMAL EXPLOSION

Figure 4.X shows oscillograms of one of the series of experiments, obtained at different initial pressures. The inset shows the dependence of the maximum pressure increase on the initial pressure. The numbers of points in the inset correspond to the numbers of the oscillograms. It is obvious that the increase in pressure accompanying ignition is due to self-heating of the mixture, since, during this reaction, the number of moles decreases monotonically. Point ***a*** corresponds

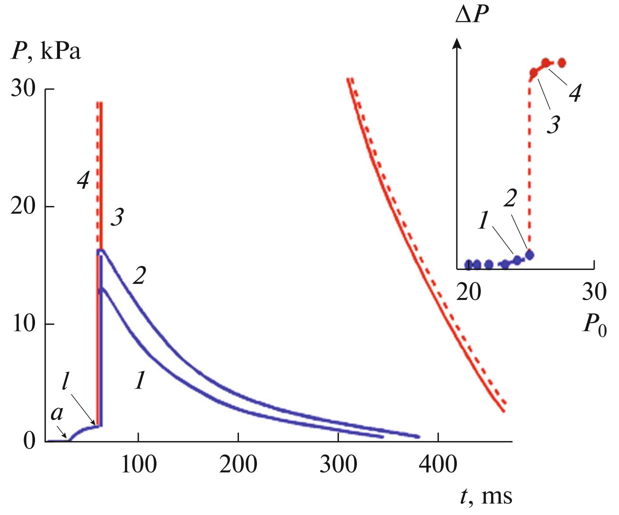

Fig. 4.X. Oscillograms of pressure of a stoichiometric mixture of H_2 and O_2 at an initial temperature of 728 K and initial pressures of (*1*) 26.1, (*2*) 26.7, (*3*) 26.8, and (*4*) 27.2 Torr. (Inset) Maximum increase in pressure vs. its initial value: (dots) beginning of the injection of the flammable mixture into the reactor and (*l*) onset of self-ignition.

to the beginning of the injection of the flammable mixture into the reactor, and point ***l*** corresponds to the onset of self-ignition. It can be seen that, at the moment of self-ignition, the gas pressure is stable.

It follows from the figure that, upon the transition from shot *2* to shot *3*, the combustion intensity increases incomparably more than upon the transition from shot *1* to shot *2*. In this case, the initial pressures in the experiments differ from each other by less than 0.5%. The oscillograms and the values of $\Delta P_{\max}$ show that, in this very narrow range of initial pressures, an abrupt transition to an incomparably more intense combustion takes place. The duration of the pressure increase in shots *3* and *4*, in contrast to shots *1* and *2*, is much shorter than the characteristic time of heat removal from the reactor; combustion is accompanied by a clicking sound effect; i.e., in shots *3* and *4*, an explosion occurs.

Thus, the experiment confirms the prediction of the theory about two combustion regimes. In one of them, self-heating, which also accompanies a chain avalanche, does not lead to a thermal avalanche (oscillograms *1* and *2* in Fig. 4.X). In the other regime, an increase in temperature, acceleration of reaction, and self-heating lead to an explosion (oscillograms *3* and *4*). The transition occurs when the initial concentration increases by less than 0.5%. The abruptness of the transition corresponds to the law of temperature dependence of the reaction rate, (20.IX).

Let us now consider the kinetics of the reaction in the explosion regime. As noted above, in shots *1* and *2* in Fig. 4.X, the self-heating is ~250° and, therefore, at the beginning of the transition to explosion, the temperature is above 970 K. From the values of the rate constants of reactions (I) and (VI) it follows that, even at this temperature, the chain branching reaction (I) is much faster than the trimolecular reaction (VI). In addition, from the values of the rate constant of the reaction

$$HO_2 + H_2 = H_2O_2 + H \qquad \text{(VII)}$$

and the diffusion coefficient for HO_2 radicals, it follows that, at such temperatures and pressures, HO_2 radicals formed in reaction (VI) do not have time to diffuse to the surface and mainly enter into reaction (VII), regenerating atomic hydrogen. This reaction additionally promotes the excess of the rate of chain branching over the rate of chain termination.

In the resulting explosion, intense decomposition of H_2O_2 begins. Despite the fact that reaction (VII) and the decomposition of peroxide are endothermic, they contribute to the self-acceleration of the process as a whole, since, in them, the chain carrier multiplication takes place and, as a result, the exothermic chain process is accelerated. The explosion occurs due to the fact that the concentration of active particles becomes comparable with the concentration of the initial reagents. This ensures extremely high consumption rates of the initial reagents.

From Fig 4.X it is clear that, with a slight increase in the initial pressure above the pressure in shot *3*, the increase in the value of $\Delta P_{\max}$ practically stops. This pattern is determined by the fact that, above the initial pressure in shot *3*, the process is adiabatic and the maximum self-heating is determined by the relation

$$\Delta T_{\max} = \frac{\bar{Q}}{c_V} f_{O_2}, \qquad (2.X)$$

where $\bar{Q}$ is the thermal effect, c_V is the average heat capacity of the gas mixture, and f_{O_2} is the mole fraction of oxygen in the initial mixture. Expression (2.X) implies that, at such initial pressures, the maximum increase in temperature remains the same to the same extent in which the ratio $\frac{\bar{Q}}{c_V}$ remains unchanged. Given that, with complete burnout, the number of moles of the stoichiometric mixture decreases by approximately 1/3, $\Delta P_{\max}$ is obviously related to $\Delta T_{\max}$ as

$$\Delta P_{\max} = 0.67 \frac{\Delta T_{\max}}{T_0}, \qquad (3.X)$$

and, since $\Delta T_{\max}$ is practically unchanged, $\Delta P_{\max}$ remains almost unchanged too. Thus, on the basis of the theory of nonisothermal chain combustion, the entire dependence of the maximum increase in explosion pressure on the initial pressure of the mixture has been explained. The transition of combustion to a chain–thermal explosion at atmospheric pressure is considered in Section 6.

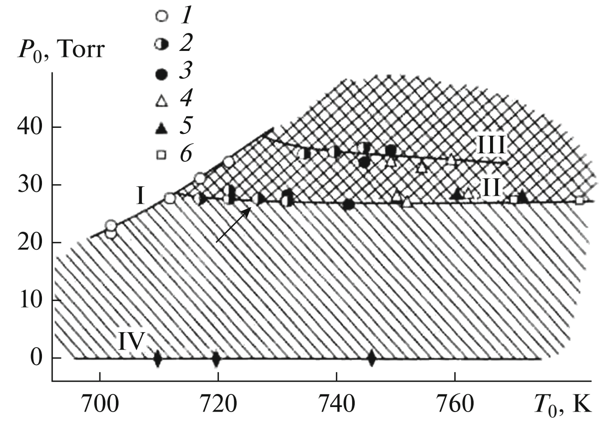

Fig. 5.X. Two kinetic regions in the peninsula of self-ignition of hydrogen with oxygen: the (I) second and (IV) first self-ignition limits in the absence of an inhibitor in a reactor with a diameter of 5 cm; CTE limits in a reactor with a diameter of (II) 5 and (III) 3.2 cm. Inhibitor content in the initial mixture is (*1, 2*) 0, (*3*) 0.2, (*4, 5*) 0.4, and (6) 0.7 mol %.

4. KINETIC NONUNIFORMITY OF THE COMBUSTION CONCENTRATION REGION AND ABRUPTNESS OF TRANSITION TO EXPLOSION

Figure 5.X shows a section of the self-ignition peninsula for a stoichiometric mixture of hydrogen and oxygen, known from monographs [3, 17] and from courses of chemical kinetics. In contrast to all these works, in which this peninsula was considered a homogeneous kinetic combustion region, the results of [16] presented in Fig. 5.X show that the peninsula consists of two regions belonging to qualitatively different kinetic and macrokinetic combustion regimes: the region of chain ignition without explosion and the CTE region. Curves I and IV are the second and first limits of self-ignition of the studied hydrogen-oxygen mixture in a reactor with a diameter of 5.5 cm. The region between curves I, II, and IV corresponds to chain combustion that does not turn into an explosion. Above curve II and to the right of curve I lies the CTE region. The point indicated by the arrow in Fig. 5.X refers to the CTE limit, detected from the data in Fig. 6.X.

According to the sequence described above, ignition and the transition of combustion to explosion also occur at atmospheric pressure, in a propagating explosive and detonation wave, but, of course, much faster.

The presence of a lower CTE pressure limit (Figs. 5.X and 6.X), as well as the kinetic curves in Fig. 3.X, indicates that the CTE regime is realized only when a certain critical reaction rate and, accordingly, a critical heat release rate are reached. Such rates are achieved at pressures above a certain critical value, at which, along with the condition for chain ignition,

$$f = g,$$

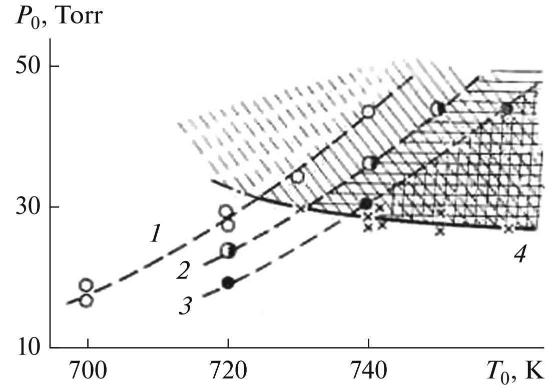

Fig. 6.X. (*1*, *2*, *3*) The second self-ignition and CTE limits; (*4*) the first CTE limit for an explosive mixture. The initial inhibitor content is (*1*) 0, (*2*) 0.2, and (*3*) 0.4 mol %.

condition (1.X) for explosion is also satisfied. The need for a high rate of chain combustion is also due to the fact that, as can be seen from Fig. 5.X, the CTE region is located above curve *3*, since, due to the smaller diameter of the reactor, heat removal is faster and it is necessary to increase the initial pressure of the mixture to accelerate the reaction.

The position of the lower CTE limit at a given temperature does not depend on the inhibitor concentration, since, as mentioned above, self-ignition and subsequent transition to the explosion regime occur when the decreasing inhibitor concentration reaches a critical value related to self-ignition. The subsequent transition to CTE occurs in the absence of an inhibitor. The weak dependence of the lower CTE limit on the initial temperature is explained by the fact that the critical condition for the transition of chain combustion to CTE is determined primarily by the temperature at which the combustion intensity required for this transition to CTE is achieved. This required intensity does not change much in a given initial temperature range.

Figures 5.X and 6.X also show that an explosion occurs only in the presence of chain combustion. An indicator of the chain nature of the reaction is the presence of a second flammability limit, which coincides with the limit for a chain–thermal explosion. In addition, the second limit is inhibited. It can be seen from Fig. 6.XI that the shift of the second auto-ignition limit to the region of high temperatures as the inhibitor concentration increases is accompanied by the same shift of the second explosion limit. Self-ignition arises in a mixture in the absence of temperature gradients and concentrations of chain carriers. In addition, the distances from the center of the reactors to their edges are only 6.5 and 4.5 cm. Therefore, the explosion occurs almost simultaneously throughout the entire volume. Of course, when ignition passes to an explosion regime, temperature and concentration gradients arise and gas motion takes place.

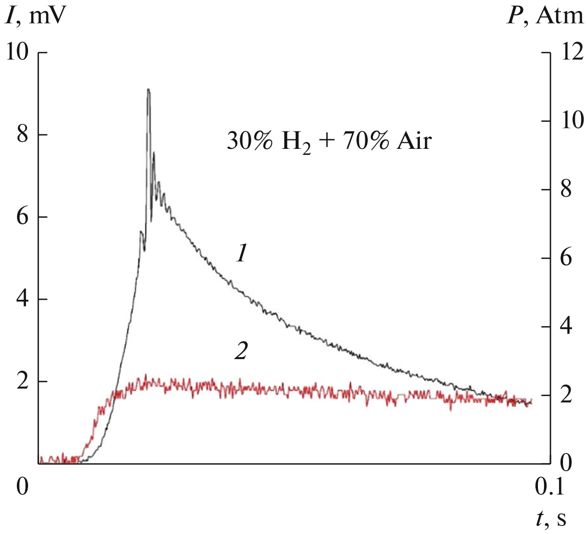

Fig. 7.X. Oscillograms of (*1*) pressure and (*2*) chemiluminescence of ignition and explosion of a mixture of 30% hydrogen in air at 1 atm.

5. SELF-EXTINCTION OF COMBUSTION AND EXPLOSION AS AN INDICATOR OF THE EFFECT OF PRODUCED WATER

Another indicator of the chain nature of explosion is self-extinguishing [18]. It means that, at moderately high temperatures and pressures, combustion and explosion stop, despite the fact that tens of percent of the mixture remains unreacted. It was found that HO_2 radicals formed in the trimolecular reaction (VI) under these conditions react not only along the chain termination path:

$$HO_2 + \text{wall} \rightarrow \text{termination},$$

but, before their deactivation, they partially disintegrate, regenerating H atoms:

$$HO_2 = H + O_2.$$

The water molecules formed during combustion, due to the proximity of the frequencies of intermolecular vibrations, stabilize HO_2 radicals, reducing the fraction of decomposition and, accordingly, increasing the termination rate. In Chapter II it was shown that, as a result of inhibition by water vapor, the developing explosion stops.

At atmospheric pressure, the temperatures are much higher. Therefore, HO_2 react mainly with H_2 (VII). Self-extinguishing is not observed, but the inhibitory effect of water on combustion at the initial times of combustion and explosion remains. This makes a significant contribution to the ignition induction period.

The transition from combustion to explosion in the atmospheric pressure region is much faster. Figure 7.X shows oscillograms of chemiluminescence and combustion pressure of a mixture of 30% $2H_2$ with air, recorded in [19] at 1 atm in a steel reactor on an experimental setup, the diagram of which is shown in Fig. 1.II in Chapter II. From Fig. 7.X it is clear that, in the ignition that began after the induction period, the increase in pressure, i.e., self-heating, lags behind chemiluminescence by 1–2 ms, then increases with the development of combustion, and, upon reaching ~5.7 atm, i.e., in the region of 1600 K, passes into explosion regime, as evidenced by kinks in the oscillogram (curve *1*). The transition is accompanied by a sound—a click.

6. CTE CONCENTRATION LIMITS

The thermal–chain explosion has concentration limits even in the pressure range below atmospheric pressure. For example, in mixtures of H_2 with O_2 containing less than 15% hydrogen, the role of bimolecular nonlinear chain termination reactions increases:

$$O + HO_2 = OH + O_2 \text{ and } OH + HO_2 = H_2O + O_2,$$
$$O + OH = O_2 + H.$$

This leads to a decrease in the difference between the effective values of the specific rates f_{eff} and g_{eff}. Accordingly, the rate of the chain reaction and the temperature dependence of the rate decrease exponentially, as shown by expressions (19.IX) and (20.IX). As a result, condition (1.X) for the transition of chain combustion to chain–thermal explosion is violated.

Thus, we have revealed the determining role of reaction chains in the explosion regime and shown that the CTE regime, which occurs even at pressures tens of times lower than atmospheric, is realized due to intense chain branching and a very strong temperature dependence of the chain reaction rate, qualitatively different from the Arrhenius law. Favorable conditions for detonation at pressures much lower than atmospheric are created by the extremely strong temperature dependence of the reaction rate, the law (20.IX) of an exponential containing the Boltzmann factor in a positive exponent.

Upon the oxidation of a number of inorganic hydrides and nitrogen trichloride, CTE occurs at very low pressures. Below we consider the transition of monosilane combustion to this regime.

7. CHAIN–THERMAL EXPLOSION OF MONOSILANE WITH OXYGEN

The combustion of silane, due to very intense chain branching, passes into the CTE regime even in the region of the first self-ignition limit: under conditions of particularly strong heat removal due to heterogeneous recombination of chain carriers and accelerated conductive heat transfer. Under these conditions, the participation of adsorbed atoms and radicals in CTE, as well as the phenomenon of heterogeneous chain

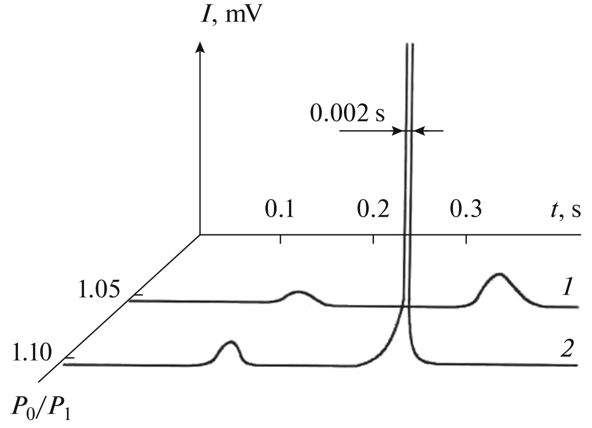

Fig. 8.X. Chain–thermal explosion of the mixture (mole fraction) $0.05SiH_4 + 0.95O_2$ at 2.5 Torr and 470 K and P_0/P_1 equal to (*1*) 1.05 and (*2*) 1.10.

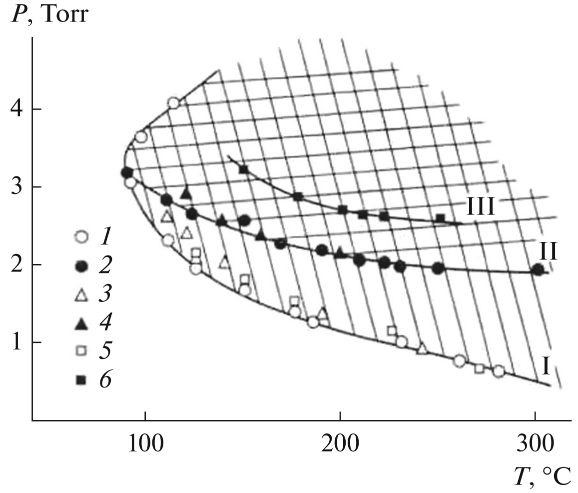

Fig. 9.X. Limits of (I) self-ignition (I) and (II, III) CTE of mixtures (mole fraction): (*1, 2*) $0.05SiH_4 + 0.95O_2$, (*3, 4*) $0.05SiH_4 + 0.45O_2 + 0.5Ar$, and (*5, 6*) $0.05SiH_4 + 0.45O_2 + 0.50He$.

propagation, is also manifested. The experimental technique is similar to that described in Section 2. The oscillograms in Fig. 8.X refer to the double ignition of a portion of a mixture of 5% SiH_4 with 95% O_2 in a reactor with a diameter of 3 cm, discussed in Chapter V. In [20], by the method of simultaneous recording of ignition by two photometers with sensors detecting the glow at different distances from the axis of the cylindrical reactor, it was shown that the first flash occurs at the reactor walls, while the second flash occurs in the bulk. From Fig. 8.X it is clear that an increase in the initial pressure of the mixture by 5% has little effect on the intensity of the first flash. The intensity of the second flash occurring in the volume increases by two orders of magnitude. The glow intensity growth duration is also greatly reduced: to ~0.2 ms. According to the Einstein–Smoluchowski expression, during this time, the released heat moves away from the reaction zone to less than 0.15 fractions of the reactor radius, which means the transition of combustion to explosion regime. Thus, due to the very high intensity of the chain avalanche, the explosion also occurs at pressures hundreds of times lower than atmospheric.

Figure 9.X shows the first and second self-ignition limits and the CTE limit of a mixture of 5% SiH_4 in mixtures containing various amounts of O_2, Ar, and He. It can be seen from the figure that, despite the significant difference in the gas kinetic characteristics of these gases, the first limit does not depend on the mixture composition. This means that heterogeneous chain termination is limited not by the diffusion of active particles to the surface, but by the kinetics of their capture by the surface. But the CTE limits are located above the limit for chain self-ignition. Moreover, in a mixture with He, this limit is significantly higher than in mixtures with the same amount of O_2 and Ar, which is in good agreement with the higher thermal conductivity of helium. Partial replacement of the oxygen with argon does not affect the transition limit, since the thermal conductivities of these two gases differ little.

It can be seen from the figure that the self-ignition peninsula for a mixture of SiH_4 with O_2, like the self-ignition peninsula for H_2 with O_2, consists of two regions, one of which refers to self-ignition without transition to the explosion regime, and the second, shaded more strongly, to a regime with the simultaneous realization of a chain avalanche and thermal avalanche.

An indicator of the fact that the explosion regime of combustion follows the chain reaction mechanism is that CTE occurs only in the case of chain combustion. Indeed, as follows from Fig. 9.X, at pressures above curve *2*, to the right of the cape of the peninsula, where there is no chain self-ignition, a chain–thermal explosion also does not occur.

The chain mechanism of the process in this regime is also evidenced by the presence of hysteresis of the critical condition—an unambiguous indicator of the dependence of the kinetics of reaction chain termination on changing properties of the surface. In this case, hysteresis manifests itself in the fact that the critical pressure for the transition from one combustion regime to another depends on whether the limit is measured by reducing the pressure of the mixture from experiment to experiment on the side of the combustion region or, on the contrary, by increasing the pressure on the side below the self-ignition limit. Hysteresis is also an indicator of the participation of adsorbed chain carriers in the occurrence of a chain–thermal explosion.

The transition to CTE and the achievement of high intensity of this regime are facilitated by the reactions of nonlinear chain branching, the role of which is very

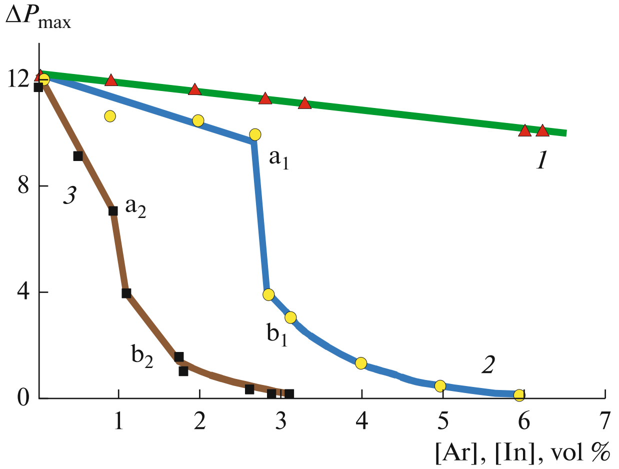

Fig. 10.X. Effect of (*1*) argon, (*2*) freon, and (*3*) propylene additives on the maximum increase in ignition temperature of 40% H_2 in air.

large, as was shown in Chapters V and VII for silane oxidation and the decomposition of nitrogen trichloride.

8. DIFFERENCE IN THE EFFECT OF ADDITIVES ON COMBUSTION AND EXPLOSION

The realization of the explosion regime requires not only a chain avalanche, but also a very high reaction rate corresponding to the explosion condition (1.X). Additives of inert gases affect only gas concentrations and partially the heat capacity of the mixture. Therefore, their effect cannot be strong. Inhibitors break the reaction chains and, therefore, have a stronger effect. It takes less inhibitor to reduce the rate of a reaction than to suppress the reaction completely. This determines the greater effect of the inhibitor on the explosion compared to the effect on a nonexplosive combustion regime. This is confirmed by the experimental results given below.

Figure 10.X illustrates the effect of various additives on the critical conditions for the occurrence of a chain–thermal explosion and on its intensity upon the combustion of a mixture of 40% hydrogen in air in a cylindrical reactor [10, 21]. An indicator of the maximum combustion intensity is the maximum value of the increase in pressure (ΔP_{max}) with time, caused by self-heating of the mixture. In the absence of an inhibitor, the reaction proceeds in the mode of a chain–thermal explosion with a characteristic sound effect and a short-term pressure surge. From Fig. 10.X it is clear that argon additives reduce ΔP_{max} only slightly, since their effect is caused only by dilution. The effect of freon and hydrocarbon additives is not only much stronger, but also qualitatively different. Curves *2* and *3*, related to freon and hydrocarbon, have kinks at points a_1, b_1 and a_2, b_2, respectively. At additive concentrations corresponding to the indicated points, the maximum chemiluminescence intensity also changes abruptly (not shown in the figure). It can be seen from the figure that, with an increase in the initial contents of freon and hydrocarbon, the explosion intensity drops much more sharply than is observed with an increase in the argon content. This difference is due to the fact that the effect of freon and hydrocarbon on the explosion is determined not by dilution, but by terminating reaction chains, i.e., inhibition. The different slopes of curves *2* and *3* to the left of points a_1 and a_2 indicate the dependence of the explosion suppression efficiency on the chemical properties of additives and on their ability to terminate reaction chains.

With an increase in the inhibitor content in the initial mixtures to the right of the abscissa of the points a_1 and a_2, the maximum combustion intensity, which is characterized, among other things, by the values of ΔP_{max} and the pressure growth rate, drops abruptly as a result of violation of the condition for a thermal avalanche. Combustion of mixtures, the inhibitor content in which is greater than the abscissa of points b_1 and b_2 proceeds in a relatively slow regime and is not accompanied by an explosion. Thus, each inhibitor is characterized by two critical concentrations, one of which relates to the flammability limit and the other to the limit for a thermal chain explosion. It can be seen from Fig. 10.X that, to prevent CTE, less inhibitor is required than to prevent ignition.

9. CHAIN NATURE OF A DEVELOPED EXPLOSION IN CUMULATION

An indicator showing that the chain reaction mechanism and the laws of chain processes are also of determining importance in the developed explosion regime are the results of controlling the characteristics of this combustion regime by influencing the competition between chain branching and termination. This is illustrated by data from [22], in which the explosion of a stoichiometric hydrogen-air mixture was initiated by an explosion of 3 g of hexogen in a volume of 160 l. The reactor, located in a concrete chamber for studying explosions, comprises steel cone **a** (Fig. 11.X) covered at the bottom with a rubber shell **d**. Along the element of the cone **a** and at its vertex, pressure sensors $\mathbf{c_1}$–$\mathbf{c_6}$ are located. Hexogen was placed in carrier **b**. After each experiment, the explosion chamber was evacuated. The inhibitor content in the mixture, which varied in different experiments, was determined using a flow meter. The readings of the pressure sensors were recorded on an oscilloscope and on a computer.

Figure 12.X shows the dependence of the drop in the maximum explosion pressure and the time the blast wave reaches the vertex of the cone on the initial

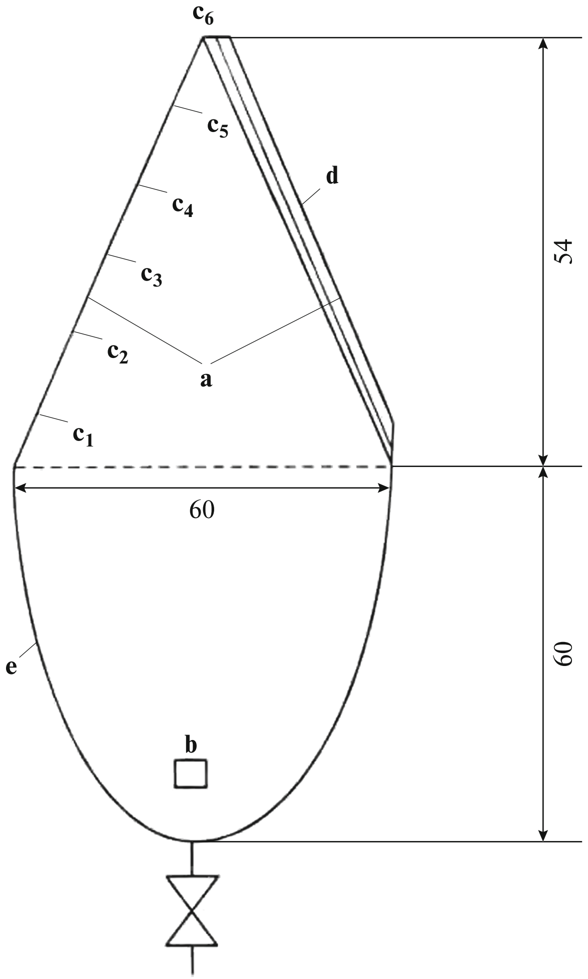

Fig. 11.X. Schematic of a conical reactor: (**a**) steel cone, (**b**) detonator, ($\mathbf{c_1}$–$\mathbf{c_6}$) pressure sensors, (**d**) slot window, and (**e**) rubber shell. Dimensions are given in cm.

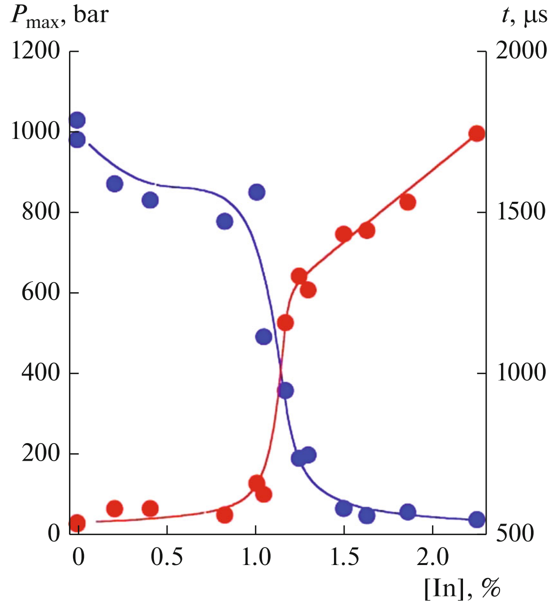

Fig. 12.X. (Blue circles) Maximum pressure and (red circles) the time the blast wave reaches the vertex of the cone vs. the initial content of the inhibitor—propylene.

content of the inhibitor: propylene. It can be seen that, when an explosion is initiated in the absence of an inhibitor, the pressure at the vertex reaches 1000 bar. In the presence of an inhibitor and with an increase in its content in the initial mixture to 0.95%, the maximum pressure jump gradually decreases, indicating a decrease in the explosion intensity. In the region of 0.95–1% inhibitor, the pressure drop sharply increases, reflecting the suppression of the explosion regime by the inhibitor, and, in the presence of more than 1.5% propylene, no gas explosion is detected. It follows from Fig. 12.X that the decrease in explosion pressure caused by inhibition is accompanied by an increase in the time the blast wave reaches the vertex of the cone. These results are direct evidence of the chain nature of a developed explosion at pressures from hundreds to thousands of atmospheres. At the same time, these results are a clear refutation of the statements made in [3–7, 17] about the thermal nature of the explosion of a hydrogen-air mixture at atmospheric pressure. The statements of the authors of these works were based on calculations carried out by the author of [4, 7], who a priori considered the explosion to be non-chain and proceeding as a one-stage intermolecular reaction. In Chapter II of this monograph, as well as in [11], the causes of the calculation error are also explained.

A sharp decrease in the maximum pressure surge, i.e., explosion intensity, with an increase in the inhibitor content in the range of 1–1.5% is the result of a significant termination of the reaction chains, leading to violation of condition (1.X). An increased dependence of the explosion intensity on the inhibition rate appears in accordance with the exponential function (20.IX), where the quantity g includes the product of the inhibition rate constant and the inhibitor concentration.

In a number of processes, it is necessary to prevent an explosion without suppressing combustion. An example is the problem of eliminating the "knock" mode in internal combustion engines. The action of antiknock agents, as already mentioned, is presumably explained by the prevention of the accumulation of peroxides, the decomposition of which proceeds as a thermal explosion. The above data on controlling the intensity of combustion and explosion, as well as on preventing an explosion while maintaining the combustion regime, show the promise of using inhibitors to optimize the operating regime of power plants using flammable gases and to ensure explosion safety.

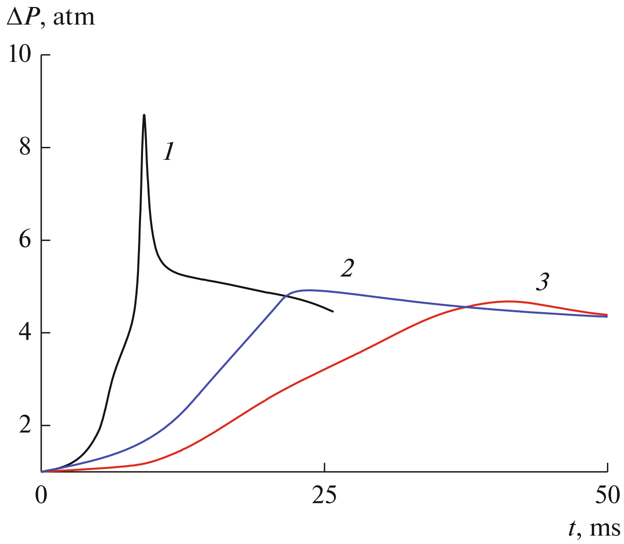

Fig. 13.X. Kinetic curves of pressure changes upon combustion of mixtures with air: (*1*) 33% H_2, (*2*) 33% H_2 + 2% C_3H_6, and (*3*) 22% H_2 + 11% CO + 2% C_3H_6.

10. DEPENDENCE OF CTE INTENSITY ON THE CHARACTER OF BRANCHING CHAINS

In Chapter III it was shown that, at given rates of elementary acts of reproduction and loss of the branching active center, the rate of the branching chain process is determined by the average proportion α of links in each branch of the chain in which the actual branching occurs.

In [22], to clarify the role of chain branching in an explosion with a given thermal effect, the dependence of the combustion kinetics of hydrogen mixtures and the synthesis of gas with air was studied. As a measure of branching, the actual rate of chain branching is considered:

$$v_b = 2k_2[O_2]\alpha, \tag{4.X}$$

where α is the probability for O atoms to enter a chain branching reaction, equal to

$$\alpha = \frac{k_3[H_2]}{k_3[H_2] + k_{-2}[OH]}. \tag{5.X}$$

Since there is less chain branching in the CO oxidation reaction, for a given total mole fraction of fuel, the combustion reaction rate for synthetic gas is lower. This is observed in experiment.

The conditions for the realization of chain ignition are much wider than the conditions for CTE, so an explosion can be prevented without violating them. To this end, it is necessary to reduce the rate of the combustion reaction, e.g., by partially replacing hydrogen with CO (Fig. 13.X). From the above it follows that, when using synthetic gas as a fuel, the intensity of its combustion can be varied both with the help of inhibitors and by changing the ratio of the H_2 and CO concentrations.

The suppression of an explosion by inhibitors and its self-inhibition once again show the fallacy of the interpretation of an explosion, denying its chain nature.

11. CHANGES IN COMBUSTION AND EXPLOSION CHARACTERISTICS OF MIXTURES UPON THEIR DILUTION

The usually considered characteristics of flammable gas mixtures refer to a composition that is constant over time. However, in many cases, the composition of an inhibitor-containing mixture changes for one or another reason, e.g., as a result of leakage of the mixture from the volume where it was stored. Obviously, along with this, its flammability characteristics also change. Data on the concentration limits for ignition and chain–thermal explosion make it possible to predict the nature of changes in the ability of gas mixtures to ignite and explode in such situations. Figure 14.XI shows the concentration regions of ignition and combustion (red area), as well as chain–thermal explosion (yellow area), in the inhibitor content–fuel content coordinates. On the PR line, the abscissa and ordinate of each point S are the percentages of inhibitor and fuel, respectively.

If a mixture, whose initial composition corresponds, e.g., to the coordinates of point L, is diluted, then, along with a decrease in the fuel concentration, the inhibitor concentration decreases proportionally. Therefore, the figurative point of the mixture in Fig. 14.X moves to the origin of the coordinates along the straight line LO. If dilution continues, the point enters the ignition region and, continuing its movement, leaves this region. Obviously, ignition can only occur if, during the time the mixture is in the ignition area, an initiating pulse occurs and if, at the same time, the ignition induction period is shorter than the time the mixture is in this region. The inhibitor, by reducing the branching factor φ, thereby increases the induction period. In this case, this means that, due to the presence of an inhibitor, the probability of the mixture igniting is reduced, since its composition has time to leave the ignition concentration region. When the inhibitor percentages are equal to the abscissa of points K on the section of straight line FK, the figurative point only touches the boundary of the ignition region at the point F. This corresponds to the critical slope angle α of the straight line OK.

It can be seen from Fig. 14.X that, when diluted with air, a combustible mixture initially located outside the ignition region can be found in the region of a chain–thermal explosion only at inhibitor concentrations significantly lower than the concentrations corresponding to the ignition region. This is the region of initial compositions rich in fuel. In addition, upon dilution, the mixture remains in the thermal chain

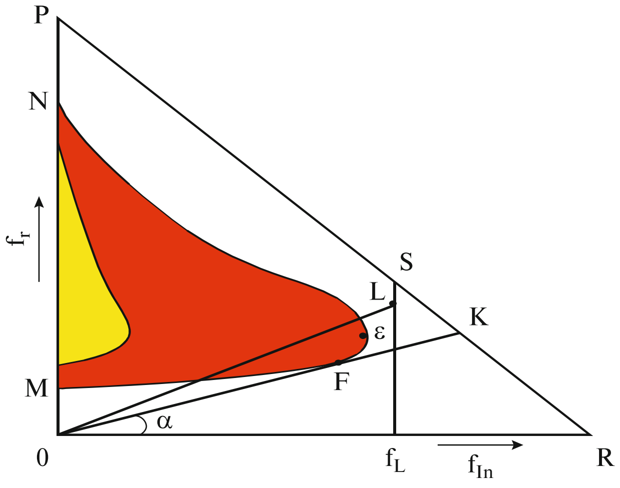

Fig. 14.X. Movement of the figurative point of the mixture composition in the area of fuel and inhibitor concentrations upon dilution with air: (red shading) the area of ignition and combustion and (yellow shading) the area of chain–thermal explosion.

explosion region for a much shorter time than in the ignition region without explosion. Figure 14.XI also shows that, if the inhibitor concentration is sufficient to prevent the ignition of any composition of the combustible mixture in a closed volume (abscissa of the point ε), then the ignition of the gas leaking into the air cannot go into the CTE regime.

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CONFLICT OF INTEREST

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ADDITIONAL INFORMATION

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