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Chain Processes and the Non-stationary Nature of the State of the Surface

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The reversible non-stationary nature of the solid surface in branched-chain processes (BCP), which is one of the most important factors determining the regular features of chemical reactions of this class, has been demonstrated. The general regular features of non-thermal BCP which have been observed in the last 10-12 years and which are determined by the change in the condition of the surface and in the contribution of heterogeneous processes to the course of chain combustion have been described and systematised. Kinetic models taking account of the non-stationary nature of the surface and the non-unique nature of the stationary states of the system have been discussed.
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INTRODUCTION

One of the most important and general factors in gas-phase chain processes is the reaction of components of the reaction mixture with solid surfaces. These include the surfaces of the reaction vessel, condensed reaction products, and various solid objects or particles introduced into the reaction medium for different purposes (for example, detectors, powdered quenching agents, etc.). The destruction of active intermediates on a solid surface (heterogeneous destruction). leading to termination of the reaction chains, determines to a large extent the regular features of the chain process, including its kinetics and thermal conditions. Heterogeneous termination also determines the magnitude of the concentration gradients of the chain carriers and the rate of the process as a whole. Heterogeneous termination provides a direct channel for the removal of energy from the reacting gas, and hence to a large extent it also determines the temperature gradients in the reaction medium.

A large number of papers have been devoted to the theoretical and experimental study of chain processes under different conditions of heterogeneous chain termination. By taking account of the destruction of the chain carriers on the surface of the reaction vessel, the theory successfully explains such important characteristic features of branched-chain processes (BCP) as the first self-ignition limit, the dependence of the limit on the dimensions of the reaction vessel and the composition of the mixture, and the dependence of the kinetics of the chain process and the first limit on the material of the walls of the reaction vessel.[1-6] The measurement of the first self-ignition limit provides a basis for methods for determining the rate constants of the homogeneous reactions of chain carriers[7-9] and their heterogeneous destruction (see for example Refs.3, 4, 10, and 11).

In a number of cases, chain initiation, that is the formation of active intermediate products involving only the original valence-saturated molecules, also takes place on the surface.[1,3,12-14] The heterogeneous–homogeneous reactions observed over various catalysts have been attributed to heterogeneous initiation.[12,14]

At the same time, up to the present, there has been very little investigation of the role of the surface in chain reactions. Until recently it was considered that chain termination on the surface was the only heterogeneous stage of the process involving the active intermediates. In the examination of the kinetics of chain processes (both in theory and in the treatment of experimental results), the following original propositions relating to the heterogeneous stages were generally accepted.

1. The adsorption of the chain carriers is identical to the reaction involved in their termination. In the quantitative examination of the kinetics of the process, in the solution of the kinetic equations, including their solution by means of a computer, and also in the treatment of experimental data, it was assumed that the sorbed chain carriers rapidly react with identical species to form the original molecules. The properties of the surface were assumed to remain unchanged during the entire process.

2. The heterogeneous destruction of the chain carriers shows first-order kinetics with respect to the concentration of these particles. Thus in the kinetic equations of the chain processes, heterogeneous termination was described by terms which were linearly dependent on the concentrations of the chain carriers.

3. It was generally assumed that if the first self-ignition limit is stable and the kinetic curves giving the concentrations of the components of the reaction mixture are reproducible, then the coefficient of the heterogeneous destruction of the chain carriers (the probability of their destruction on collision with the surface) is constant throughout the entire process. In the study of gas-phase reactions, the surface of the reaction vessel is "conditioned" beforehand by the reaction being studied, to obtain reproducible results. It was assumed that when reproducibility had been achieved, the state of the surface, the efficiency of the heterogeneous termination, and the coefficient of the destruction of the chain carriers on the surface remained unchanged from the beginning to the end of the chain process. The efficiency of the heterogeneous deactivation of the excited species and the accommodation coefficient for the heterogeneous destruction of the atoms and radicals were also assumed to be constant.

The study of BCP and the heterogeneous reactions of free atoms and radicals, however, led the present author to the conclusion that these original propositions are generally inapplicable.[15,16] In constrast to generally accepted ideas, it was found that during and under the influence of a chain reaction, the properties and functions of the surface may undergo extensive reversible changes, and this may not influence the reproducibility of the results. The changes in the state and role of the surface may be brought about by the following factors, not previously taken into account in the theory of chain processes: the chemical reaction of molecules, atoms, and radicals from the gas phase with the surface; the adsorption non-uniformity of the surface; and the reactions of the adsorbate with components of the gas phase.

The possible development of reaction chains involving sorbed atoms and radicals was also noted.[15,16] For example, the works cited gave the following heterogeneous reactions for the oxidation of hydrogen-containing compounds:

$$H_{sorbed} + O_2 \rightarrow HO_2$$
$$H + HO_2 \rightarrow 2OH$$
$$H + HO_2 \rightarrow H_2O + O$$
$$H + HO_2 \rightarrow H_2 + O_2$$

Some of these reactions lead to the transfer of the chain carriers into the volume. Thus the reaction of O_2 with sorbed H atoms and the subsequent stages can lead to the development of chains, which is equivalent to a decrease in the efficiency of the heterogeneous termination.[15,16]

Since the principal regular features of BCP are determined chiefly by the competition between the processes of chain branching and termination, the above heterogeneous processes and the reversible changes in the properties of the surface should play an important role in the process as a whole. Even when the reaction of a sorbed chain carrier with a gas phase species does not lead to the development of chains, but gives the final product, this increases the rate of the chain process, since it provides an additional channel for the consumption of the starting material. The heterogeneous reactions of atoms and radicals, leading to the development of chains, can obviously take place much more rapidly than the decomposition of the molecules on the surface, accompanied by the removal of radicals into the volume. Because of their high rates, the reactions of the type given in Refs.15 and 16 may play an important role even in the fast processes of developing combustion.

It should be noted that until recently, in the study of BCP, most quantitative measurements under static conditions were related to self-ignition limits and to the kinetics of the reaction above the second limit. At the same time, significant changes in the properties of the surface and a contribution from these changes to the process as a whole are to be expected primarily under combustion conditions, in the course of which high concentrations of active intermediate species are produced. It was in the examination of the experimental data under chain combustion conditions that the present author detected significant deviations from the linear theory (see below).

In Ref.15, in the treatment of experimental data from Ref.17, it was found that the observed rates of combustion of H_2 were several times greater than the values calculated by traditional methods which do not allow for the reversible change in the efficiency of the heterogeneous destruction of the chains during combustion. In Refs.15 and 16 it was also shown that the equations used in Ref.17 and in various other studies for the treatment of the experimental data for the most part do not correspond to the actual process: for most experimental conditions (see for example Ref.17), they lead unambiguously to negative values of the concentrations of the starting materials. This is due to the fact that these equations were obtained by the method of quasi-stationary concentrations, without allowance for the homogeneous nonlinear termination of the chains.

Subsequent experiments showed that the change in the properties and the role of the surface during chain combustion, and the significant influence of these changes on the chain process, are important and general properties of a whole class of branched-chain reactions. The principal results of work in which previously unknown general regular features of branched-chain reactions were detected and studied, and the important role of the reversible nonstationary nature of the properties and functions of the surface in these processes was revealed, are described below.

II. GENERAL CHARACTERISTICS OF EXPERIMENTAL PROCEDURE

In most cases the experiments have been carried out under static conditions using vacuum apparatuses, for the most part the standard assemblies for kinetic experiments. A combined procedure was used, involving the simultaneous recording of various kinetic characteristics of the reaction mixture and the process: the pressure of the mixture, the concentrations of the individual components from absorption spectroscopy, the intensity of the chemiluminescence, and, where necessary, temperature.[18-23] The previously prepared reaction mixture was transferred rapidly from an intermediate volume into an evacuated reaction vessel at the required temperature†. An oscillograph was used to record the above characteristics of the reaction system from the start to the end of the experiment. After the experiment with a given portion of gas, the reaction vessel was evacuated. The extent of the evacuation (to ~10^{-4} mmHg) and the evacuation time (3 min after attaining a pressure of ~10^{-4} mmHg) were kept constant in a given series of measurements.

In addition to the vacuum assemblies with lubricated taps, usually employed for kinetic experiments, a high-vacuum assembly in which the taps with lubricant were replaced by metallic vacuum valve taps (without lubricant) was also used. The evacuation system was separated from the rest of the assembly by these valves and by two traps arranged in series and cooled with liquid nitrogen. In the assembly with metal lubricant-free taps, the gas in both traps came into contact only with the cold walls (so-called traps without a hot wall).[23] In the standard assemblies for kinetic experiments, with lubricated taps, high-vacuum Apiezon N (saturated vapour pressure 10^{-9} mmHg) and sometimes Merck (silicone, 10^{-6} mmHg) lubricants were used. In some series of experiments, the vacuum lubricant produced in the Soviet Union (GOST 380183-75) was also used. The experimental procedure has been described in detail.[18-26] When a process was carried out in the same reaction vessel for identical initial conditions, the results of the measurements were the same, irrespective of the grade of lubricant used. Published data[23] show that the results of the study of BCP in this reaction vessel, even in the kinetic range of chain termination and close to the first ignition limit, are independent of whether the reaction vessel is in an ordinary vacuum assembly with lubricated taps or in an assembly in which metal high-vacuum taps without lubricant are used.

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†In the study of the oxidation of phosphorus vapour, the working mixture was prepared in the reaction vessel.[21]

In most of the studies of this series, the primary aim was to determine whether it is possible to describe chain combustion on the basis of the above generally accepted ideas about the role of the surface, the nature of the heterogeneous reactions of the chain carriers, and the constant efficiency of heterogeneous termination during combustion. In addition to various other kinetic characteristics of BCP, use was also made of one of the most fundamental properties of reactions of this class, namely that chain combustion develops (undergoes self-acceleration) only when the rate of chain branching is greater than the rate of chain termination. For heterogeneous termination, this condition for self-acceleration of the process is determined by the inequality:[1-6]

$$2k_b[B] > k_{het} \quad (1)$$

where k_b is the chain branching rate constant; [B] the concentration of the starting material involved in the branching process; and k_{het} the heterogeneous termination rate "constant".

It can be seen that if the initial concentration of the original molecular substance B is greater than its concentration at the lower limit of self-ignition, for example by 2%, then in the absence of appreciable self-heating of the reaction mixture and positive interaction of the chains, immediately after the combustion of this 2% excess of substance above the limit, the rate of branching will become lower than the rate of termination. As a result, the self-acceleration of the combustion, and then the combustion itself, soon stop. This is the case, however, only if k_{het} is constant during the combustion, as previously assumed. If however in addition to the concentration of the substance B there is also a decrease in the "constant" k_{het}, it is obvious that after the combustion of the excess quantity of the starting material relative to the self-ignition limit, the branching process, for a certain time interval, will remain more rapid than the termination, so that the self-acceleration of the combustion will continue. In this case the self-acceleration of the combustion process will stop only at higher degrees of combustion. Thus if the efficiency of the heterogeneous termination decreases during combustion, the observed degree of combustion at the end of the reaction should be greater than that which would be observed if there were no change in the efficiency of the termination on the surface or in the absence of heterogeneous chain branching.

It can also be seen from Eqn.(1) that if during combustion the value of k_{het}, on the other hand, increases, that is if the efficiency of the termination increases, then the self-acceleration of the chain process will stop before the decreasing concentration of the starting material reaches the value corresponding to the first ignition limit. There is also a decrease in the final degree of combustion.

The final degree of combustion is defined as the fraction of the starting material used up at the end of the combustion:

$$\eta_\infty = \frac{[B]_0 - [B]_\infty}{[B_0]}$$

where $[B]_0$ and $[B]_\infty$ are the concentrations of the starting material at the initial moment and at the end of the combustion respectively.

The first self-ignition limit (P_1) is the average value between two neighbouring initial pressures (P_0), at the lower of which there is no ignition, while at the higher the gas undergoes self-ignition. The ignition was recorded from the chemiluminescence and from the self-accelerating change in the pressure of the mixture, brought about by the change in the number of moles of the gas in the closed volume as a result of the reaction. For the oxidation of silane and phosphorus vapour and the decomposition of NCl_3, the ignition was also recorded from the self-accelerating decrease in the absorption of light of the appropriate wavelength by the starting material. Additional control of the accuracy of the measured ignition limit is made possible by the fact that as the initial pressure approaches the upper limit, the ignition induction period increases sharply, approaching infinity.[19,25]

The degree of combustion can be readily determined from the initial and final pressures and the stoichiometry of the overall process. For example, the equations for the overall processes $2H_2 + O_2 \rightarrow 2H_2O$ and $2CO + O_2 \rightarrow 2CO_2$ show that the decrease in the number of moles of O_2 at the end of the combustion is equal to the decrease in the number of moles of the entire mixture:

$$\Delta[O_2]_\infty = \Delta[M]_\infty \quad (2)$$

where M represents any component of the mixture, and the subscript ∞ refers to the end of the combustion. Thus the degree of transformation of O_2 (degree of combustion) can be determined from the total pressure of the mixture. For a stoichiometric mixture

$$\eta_\infty^{expt} = \frac{(O_2)_0 - (O_2)_\infty}{(O_2)_0} = 3\frac{P_0 - P_\infty}{P_0} \quad (3)$$

The water vapour formed during combustion is absorbed to a large extent by various surfaces.[19,27,28] To determine correctly the final degree of transformation (degree of combustion) in these processes, a procedure has been proposed,[19,25] in which, when combustion has stopped, the water vapour is frozen out, and the residual pressure in the system is then recorded. The experimental value of the degree of combustion is then given by the expression

$$\eta_\infty^{expt} = (P_0 - P_\infty^w)/P_0 \quad (4)$$

where P_∞^w is the pressure after the water vapour has been frozen out.

In the oxidation of silane and phosphorus vapour the decomposition of nitrogen trichloride, the value of η_∞^{expt} was also determined by absorption spectroscopy.[19,20-22,26]

In the region of the first ignition limit and at temperatures appreciably greater than the temperature of the point of the ignition peninsula, heterogeneous termination in fact becomes the only route for the termination of the reaction chains. Moreover, low concentrations of the reagents close to the first ignition limit and relatively long combustion times decrease the self-heating and the role of termolecular reactions in most experiments. In the kinetic range of the chain termination process, however, there is practically no self-heating or termolecular reactions.[19] All this simplifies the interpretation of the results and makes it possible to reach unambiguous conclusions from the experimental data.

III. HETEROGENEOUS SELF-ACCELERATION OF BRANCHED-CHAIN PROCESSES

Fig.1 gives the oscillograms for a series of experiments with detonating gas at different initial pressures in a quartz vessel with a diameter of 5.5 cm, the surface of which was washed with hydrofluoric acid and treated with pulses of the mixture being studied to stabilise the value of the ignition limit and achieve reproducibility of the kinetics of combustion.[19,25] The chemiluminescence oscillograms are not given in Fig.1. The numbering of the curves corresponds to the sequence of the experiments. The quantitative reproducibility is illustrated by the kinetic curves *2* and *6*.

Because of the low pressures and the relatively high temperatures in these experiments, the rate of the heterogeneous disappearance of the H atoms is more than 150 times the rate of the termolecular reaction (VI)#:

$$H+O_2+M\rightarrow HO_2+M \qquad (VI)$$

Thus it is possible, without loss of accuracy, to neglect reaction (VI) and the reactions of those HO_2 radicals which are formed in this termolecular stage. Since the reaction time is much longer than the heat-removal time (by a factor of more than 10^5), there is no self-heating.[19]

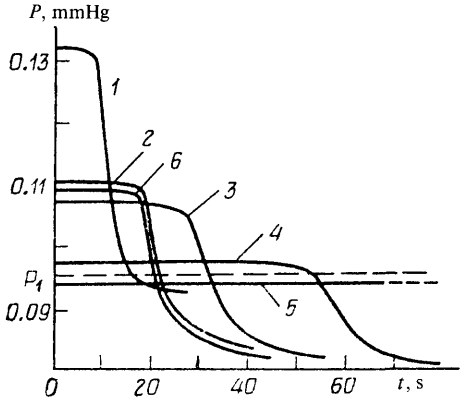


Figure 1. Oscillograms for the change in pressure during the combustion of a $2H_2 + O_2$ mixture at 743 K and different initial pressures (P_1 = 0.095 mmHg).[19,25]

Fig.1 shows that the self-ignition limit P_1 lies between the initial pressures of experiments *4* and *5*, and that, for example, in experiment *4* the magnitude of P_0 and hence the magnitude of $[O_2]_0$ are ~2% greater than the limiting values. If the efficiency of the heterogeneous termination (k_{het}) did not decrease during the combustion, the decrease in pressure accompanying the reaction in experiment *4* would have stopped before the broken line had been reached, that is before P_1. It can be seen from the oscillogram for experiment *4*, however, that the decrease in pressure close to the ignition limit not only does not stop but on the contrary continues to accelerate, even under the limit, reflecting directly the fact that the rate of branching continues to predominate over the rate of chain termination. Since there is no self-heating or purely homogeneous positive interaction of the chains, the predominance of the branching over termination can take place only as a result of a decrease in k_{het} during the combustion. The decrease in the efficiency of the heterogeneous chain termination during the combustion is also indicated by the fact that the combustion stops only after a degree of combustion corresponding to several tens percent O_2, which is greater by an order of magnitude than that expected without allowance for the decrease in the efficiency of the heterogeneous destruction of the chain carriers.

The results of another series of experiments are given in the Table. It can be seen that either ignition does not take place (experiments *3* and *9*), so that there is no combustion, or, if ignition takes place (experiments *1*, *2*, and *4–8*), the reproducible degree of combustion corresponds to tens percent of the mixture, even if the initial concentration is 2% greater than the ignition limit. Thus in this series of experiments at P_0 close to P_1, the degree of combustion is 10 times that expected for a constant efficiency of chain termination.

Final degrees of transformation of a $2H_2 + O_2$ mixture for different initial concentrations (P_1 = 0.097 mmHg, quartz reaction vessel washed with HF, T = 743 K).[19,25]

Expt. No.	P_0, mmHg	η_∞^{expt}, %	P_0/P_1	Expt. No.	P_0, mmHg	η_∞^{expt}, %	P_0/P_1
1	0.103	39	1.06	6	0.133	50	1.33
2	0.099	37	1.02	7	0.103	38	1.06
3	0.095	0	0.98	8	0.099	37	1.02
4	0.099	37	1.02	9	0.095	0	0.98
5	0.160	55	1.65				

The theory of BCP[3] gives the following equation relating the concentration of hydrogen atoms in the isothermal flame of a mixture of H_2 and O_2 to the degree of transformation:

$$\frac{[H]}{[O_2]} = \xi = 2\eta + 2\frac{P_1}{P_0}\ln(1-\eta) \qquad (5)$$

This expression was obtained from the generally accepted scheme for the combustion of hydrogen:

$$OH + H_2 \rightarrow H_2O + H \qquad (I)$$

$$H + O_2 \rightarrow OH + O \qquad (II)$$

$$O + H_2 \rightarrow OH + H \qquad (III)$$

$$H + \text{wall} \rightarrow \text{chain termination} \qquad (IV)$$

and does not take account of changes in the reaction mechanism, the properties of the surface, and the efficiency of heterogeneous chain termination during combustion. In Eqn.(5), the ratio P_1/P_0 replaces the ratio $k_4/2k_2[O_2]_0$, where k_2 and k_4 are the rate constants of reactions (II) and (IV). It is assumed that the value of k_4 remains unchanged during combustion, like the value of k_2.

It can be seen from Eqn.(5) that after combustion, that is when $\xi = 0$, the final degree of transformation is given by the expression

$$\eta_\infty = -\frac{P_1}{P_0}\ln(1-\eta_\infty) \qquad (6)$$

This expression relates η_∞ only to the pressures P_0 and P_1, measured in the same series of experiments and relating to the initial moment of the process. It can be seen from Fig.2 that Eqn.(6) does not describe the large degrees of combustion, nor their abrupt increase immediately above the limit,

The following numbering of the elementary stages of the oxidation of hydrogen is used:

$H_2+O_2\rightarrow 2OH$ (0)
$OH+H_2\rightarrow H_2O+H$ (I)
$H+O_2\rightarrow OH+O$ (II)
$O+H_2\rightarrow OH+H$ (III)
H + wall → chain termination (IV)
$H_{sorbed} + O_2 \rightarrow HO_2$ (V)
$H+O_2+M\rightarrow HO_2+M$ (VI)
$H+HO_2\rightarrow 2OH$ (VII)
$H+HO_2\rightarrow H_2+O_2$ (VIII)
$H+HO_2\rightarrow H_2O+O$ (IX)
HO_2 → chain termination (X)

nor the subsequent marked decrease in the dependence of η_∞^{expt} on P_0/P_1 which takes place in spite of the presence of ten percent of the unreacted substance.

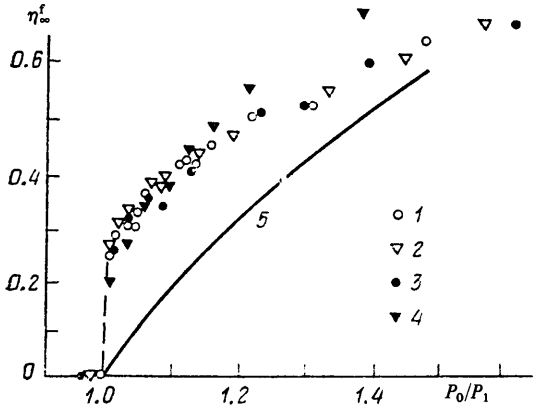


Figure 2. Final degree of transformation at 743 K for a $2H_2 + O_2$ mixture in a quartz vessel with diameter 5 cm, washed with hydrofluoric acid: *1*, *2*) reaction vessel in an assembly with lubricant-free valves, diffusion pump: *1*) oil, *2*) mercury; *3*, *4*) reaction vessel in an ordinary vacuum assembly with lubricated taps, oil diffusion pump; *5*) calculated from Eqn.(6).[23]

The previously accepted ideas about the constancy of the properties and the role of the surface in BCP also do not make it possible to describe the observed development of the chain process with time for all detectable degrees of combustion (Fig.3). It is also possible to compare the observed maximum rate of chain isothermal combustion with the calculated value obtained with the traditional assumption that only chain termination with an unchanged rate "constant" takes place on the surface. It is known that in a system in which combustion has begun, the starting materials are used up practically only in reactions with the chain carrier. Thus in the induction period, that is when the concentration of chain carriers is low, the rate of the process is practically equal to zero (see Fig.1). Thus under combustion conditions, the reaction of H_2 and O_2 molecules with one another can be neglected. The maximum rate of chain combustion is

$$w_{max} = -\left|\frac{d[O_2]}{dt}\right|_{max} = k_2[H]_m[O_2]_m \qquad (7)$$

where t is the time, and $[O_2]_m$ and $[H]_m$ the concentrations of O_2 and atomic hydrogen at the moment corresponding to the maximum rate of the BCP. It is obvious that

$$w_{max} < k_2[H]_{max}[O_2]_0 \qquad (8)$$

where $[H]_{max}$ is the maximum concentration of H atoms, and $[O_2]_0$ the initial O_2 concentration. Eqn.(5) readily gives the following expression for $[H]_{max}$:[19]

$$\frac{[H]_{max}}{[O_2]_0} = \xi_{max} = 2\left(1 - P_1/P_0 + \frac{P_1}{P_0}\ln\frac{P_1}{P_0}\right) \qquad (9)$$

Substituting the value of $[H]_{max}$ from this equation in Eqn.(7) for the conditions of, for example, experiment *3* (Fig.1) ($P_0/P_1 = 1.12$), and using the recommended[30]§ value $k_2 = 2.2 \times 10^{14}_{exp}(-70640/RT)$ $cm^3 mole^{-1} s^{-1}$ gives the calculated value $k_2[H]_{max}[O_2]_0 \cong 10^{13}$ molecule $cm^{-3} s^{-1}$ (that is 7.7×10^{-4} mmHg s^{-1}). From the inequality (8), the discrepancy between experiment and the calculation carried out without allowance for the change in k_{het} during combustion is even greater. There is also a qualitative difference between the dependence of w_{max} on P_0/P_1 observed experimentally and obtained by the traditional calculation.

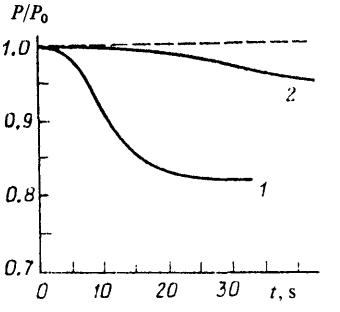


Figure 3. Kinetics of the consumption of O_2 in detonating gas, recorded experimentally (*1*) and calculated using a computer (*2*) according to the reaction scheme (0)–(IV) for a constant k_4 ($P_1 = 0.105$ mmHg). The sections of the curves after the induction periods are given.[29]

An indication that the principal reason for the "anomalies" is to be found in the heterogeneous stages is provided not only by the absence of self-heating and termolecular reactions, but also by the marked dependence of the effect of the anomalies on the material and state of the surface. For example, in reaction vessels from different quartz specimens, differences are observed not only in the ignition limits but also in the final degrees of transformation for a given pressure P_0/P_1.[19,25,31] In a number of other cases, the degrees of combustion are found to be practically identical for appreciably different P_1,[25,31] that is for different initial values of k_{het}. On some surfaces, anomalously high rates and degrees of combustion are not observed, and this does not depend on the value of P_1.

In contrast to the "anomalous" character of the kinetics of the developing combustion and the final degrees of combustion, the behaviour of the system in the induction period is described quantitatively by the familiar[3] expression which does not take account of any change in the value of k_{het} during the process. This also indicates that the factors responsible for the deviation of the kinetics from the linear theory arise during the combustion. Here, as in Refs.19 and 28, the induction period is defined as the time interval from the end of the introduction of the mixture into the reaction vessel to the moment when the greatest curvature is reached on the kinetic pressure curve.

§ Activation energy in J $mole^{-1}$.

Heterogeneous self-acceleration is also observed in the oxidation of CO in the presence of small quantities of H_2.[19,32,33] For example, for a value of $[O_2]_0$ which is 2% greater than $[O_2]_1$, a $2CO + O_2 + 2\%H_2$ mixture under isothermal conditions shows a degree of combustion of 12% (Fig.4), which is several times the value which would be obtained if there were no change in the efficiency of the heterogeneous termination. The anomaly in this case is particularly marked, if account is taken of the fact that in this process there are long chains with infrequent branching,[6,34] and the condition for chain combustion is defined by the inequality

$$2k_2[O_2]\frac{k_3[H_2]}{k_3[H_2]+k_5} \geqslant k_4$$

where k_5 is the rate constant for the heterogeneous disappearance of oxygen atoms. Since the consumption of O_2 and CO is accompanied by the consumption of H_2, which is responsible for the induction, it can be seen from the last expression that if the efficiency of the heterogeneous chain termination remained unchanged, the self-acceleration of the process would not stop until $[O_2]$ became equal to the measured limiting value. As in the case of the examples of the oxidation of H_2 examined above, this process took place isothermally, because of the low pressures and the long combustion times (0.21 mmHg and ~10 s respectively).

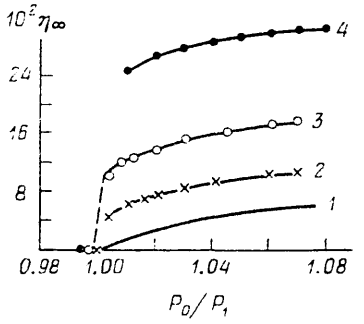


Figure 4. Final degree of combustion of O_2 in a $2CO + O_2 + nH_2$ mixture;[32] *1*) result of the solution of the system of equations for $n = 2\%$; *2*, *3*, *4*) results of the experiment for $n = 1$, 2, and 3% respectively; 723 K.

Heterogeneous self-acceleration is also observed in the branched-chain processes involved in the oxidation of phosphorus vapour[19,21] and silane[22] and the decomposition of nitrogen trichloride.[20,35]

IV. SORPTION OF THE COMPONENTS OF THE REACTION MIXTURE AND ITS ROLE IN COMBUSTION

The adsorption non-uniformity of a solid surface is due to the presence of both defects in the structure of adsorbent and surface compounds of different types. In particular, the surface of quartz under the conditions being considered is hydroxylated to a considerable extent (see for example Refs.36–40), and these hydroxyl groups (isolated or in groups) to a large extent determine the sorption properties of the surface.[36,37] At the temperatures of the experiments on the study of the combustion of H_2, CO, and hydrocarbons, evacuation leads to the partial dehydroxylation of the surface, as shown by the infrared spectra of the surface groups.[36,37] The introduction of water over the surface, however, leads to its rehydroxylation, for example as a result of the opening of siloxane groups.[36,37] The sorption of H_2O does not lead only to the formation of strong hydroxyl bonds "isolated" from one another.[36,37] Under the conditions being considered, water vapour is also extensively chemisorbed on a number of other surfaces used as coatings in kinetic experiments, including B_2O_3;[37] evacuation of the system leads to dehydroxylation of the surface.

Experimental data obtained in recent years show that during chain combustion even at 800–900 K, appreciable adsorption of stable and labile components of the reaction mixture takes place. This obviously influences the properties of the surface. For example, from the stoichiometry of the process

$$2H_2 + O_2 \rightarrow 2H_2O$$

it can be seen that the decrease in the number of moles of the mixture is equal to the number of moles of oxygen reacting.

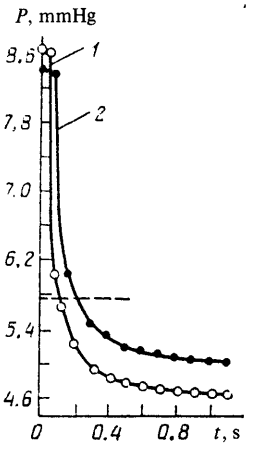


Figure 5. Kinetic curves giving the decrease in pressure during the combustion of a $2H_2 + O_2$ mixture at 923 K over MgO: *1*, *2*) experiments at different initial pressures.[19]

Thus if all the components of the mixture remained in the gas phase, it follows that in a closed volume at the end of the combustion of a stoichiometric mixture, the decrease in pressure should not exceed $^1/_3$ of the initial pressure. It can be seen from Fig.5, however, that, for example, for combustion over MgO the pressure decreases to a much greater extent; the broken line shows the final pressure which would be established for the complete combustion of the mixtures in experiment *1* (Fig.5) if there were no adsorption. Since the pressure of the mixture is lower than the saturated vapour pressure of H_2O, condensation does not take place, and all the additional decrease in pressure is due to adsorption. Special measurements show that during the combustion of H_2 close to the first ignition limit over MgO and over quartz, ~20–30% of the water formed is sorbed.[19,28] This influences the ability of the surface to terminate the reaction chains. The change in the adsorbing power of the surface is obviously accompanied by a change in the conditions of migration of the particles on the surface, that is there is a

change in the specific rate of recombination of the sorbed chain carriers with one another. When a role is played by Hinshelwood's mechanism, this leads to a change in the specific rate of heterogeneous chain termination. Moreover, the decrease in pressure brought about by adsorption leads to an additional change (and in the case being considered, an extensive change) in the coefficients of mass and heat transfer. All this influences the kinetics of BCP.

The adsorption of H_2O vapour on the surface of stainless steel is much weaker. Thus for identical initial conditions and identical values of P_1, the kinetics of combustion are different over MgO and over stainless steel. The extensive adsorption of hydrogen halides formed in the reactions of halogen-containing compounds also influences the efficiency of heterogeneous chain termination.[41]

Special measurements[25] in one of the quartz vessels in which "anomalously" high degrees of combustion were observed showed that the sorption of water vapour beforehand leads not to an increase but to a slight decrease in the extent of combustion.

In a number of processes, rapid sorption of chain carriers, not accompanied by their recombination during the process, also takes place. Thus for example at 400–600 °C, that is at the temperatures of the combustion of H_2, CO, and hydrocarbons, H atoms are rapidly chemisorbed on various surfaces which are often used in kinetic experiments (MgO and various types of technical quartz).[19,25,42] In these experiments, atomic hydrogen was obtained by the dissociation of H_2 on an incandescent tungsten wire and (in some experiments) using a high-frequency discharge. At the heater power used, the rate of chemisorption is limited by the rate of formation of H atoms and is close to the rate of combustion of H_2 with O_2 close to the first ignition limit. In the absence of O_2, some of the atoms remain on the surface for a period of time which is much greater than the time of the combustion of H_2 with O_2. These results are in good agreement with published data on the adsorption of H atoms on the surface of different types of quartz, not accompanied by rapid recombination (see for example Refs.43–47). The adsorption capacity and the rate of adsorption for the MgO surface is tens of times greater than that for the quartz surface.[19,25,42]

It has also been found that molecular oxygen reacts with adsorbed hydrogen atoms.[19,25,42] The characteristic time of this heterogeneous reaction is comparable with the time of combustion of H_2 with O_2 at analogous oxygen concentrations. Since in the experiment with synthetically prepared H atoms the reaction vessel was evacuated before the introduction of O_2, the most strongly chemisorbed H atoms remained on the surface at the start of the reaction. It is obvious that in the experiments on the study of the oxidation of, for example, H_2, some of the atoms adsorbed during the combustion are more weakly attached to the surface and therefore react with O_2 at an even greater rate. Thus some of the chemisorbed hydrogen atoms take part in the chain process, as suggested in Ref.15. The formation of HO_2 radicals in this heterogeneous reaction was observed, for example, in Ref.47. Since, as noted above, under combustion conditions the HO_2 radicals for the most part are involved in reactions in which there is positive interaction of the chains

$$HO_2 + H \rightarrow 2OH$$

it follows that some of the sorbed chain carriers are in fact finally returned to the gas phase, decreasing the efficiency of heterogeneous termination. Thus the mechanism proposed in Refs.15 and 16 has been confirmed experimentally in a number of studies.

The reaction of O_2 with adsorbed H atoms is of course not the only process altering the properties and role of the surface during combustion. At the same time, in addition to heterogeneous self-acceleration, it is the reactions of sorbed atomic hydrogen that led to the after-effect of combustion of H_2 in the oxidation of CO, in spite of the fact that the reaction vessel was evacuated before the introduction of the mixture of CO and O_2.[19,48] Direct experiments proved that the observed strong after-effect is not due to a trace of the molecular component; the introduction of H_2 and even H_2O into the reaction vessel with subsequent evacuation for the same time interval does not influence the combustion of carbon monoxide. On the other hand, treatment of the surface with the flame of a "dry" mixture of CO and O_2, in the course of which mainly oxygen atoms "disappear" on the surface, raises the first ignition limit of hydrogen.[11] Thus the inverse relationship between the state of the surface and the gas-phase process in this case is revealed in the fact that different BCP influence one another as a result of a change in the properties of the surface, which shows a "memory effect".

In a number of BCP taking place at temperatures which are not too high, an important role is also played by the adsorption of the starting materials. One such process is the oxidation of phosphorus vapour (P_4). Studies of this reaction have played an important part in the development of the theory of branched-chain processes. At the same time, the regular features and mechanism of this reaction have not been fully investigated. As in the study of other BCP, until recently no account was taken of possible changes in the state of the surface and change in the efficiency of heterogeneous chain termination. It has been shown experimentally[19,21,49] that under the conditions of the usual experiment with P_4 vapour, extensive adsorption of the vapour on the walls of the reaction vessel and connecting tubes takes place (the saturated vapour pressure is $\sim 2.5 \times 10^{-2}$ mmHg at room temperature). It has also been shown that the destruction of the chain carriers takes place 10^2–10^4 times more intensely on adsorbed phosphorus than on glass and quartz.[11,50] It may be noted that it was because of this previously unrecognised change in the efficiency of heterogeneous chain termination, characteristic of the usual experiment with phosphorus vapour, that the first ignition limit was sufficiently high to be detected and studied in classical experiments.[1,51,52]

EPR has shown[21,53] that during the combustion of P_4 vapour, appreciable quantities of P atoms and phosphorus–oxygen radicals are adsorbed on the walls of the reaction vessel and do not recombine. This to a large extent determines the stoichiometry of the overall gas-phase process. The quantities of these atoms and radicals "condensed" in the matrix of sorbed phosphorus vapour and other components of the mixture change during the combustion. When the combustion process is carried out in a stream, the composition of the sorbed intermediate products changes along the stream.

The influence of sorbed phosphorus on the kinetics of the combustion is shown particularly strongly under conditions when the surface is not completely covered by the adsorbate. Since the adsorbed phosphorus is used up in the reaction with the chain carriers, the efficiency of chain termination decreases during the combustion. Thus under these conditions, anomalously high rates of the process and degrees of combustion are observed.[19,21] The results of one of the experiments are illustrated in Fig.6. P_4 was introduced into an evacuated reaction vessel to give a stationary pressure of 2×10^{-3} mmHg (which is 12 times lower than the saturated vapour pressure over solid white phosphorus). It is obvious that at this low pressure, the surface concentration of adsorbed phosphorus present in equilibrium with the gas phase is also low. When the given P_4 vapour pressure had been established, O_2 was introduced slowly into the

reaction vessel. When the pressure of the mixture reached 4.87×10^{-2} mmHg, the subsequent addition of O_2 was carried out in portions (δ). The pressure of each portion was 2×10^{-4} mmHg. Fig.6 shows that the time intervals between the O_2 supply pulses was 1 min, which is much greater than the ignition induction period. It can be seen from Fig.6 that, for example, in the given series of experiments at 4.98×10^{-2} mmHg, the mixture is under the limit, so that there is no ignition. When the next portion of O_2 is added, the mixture is above the limit, and self-ignition takes place. During combustion under the conditions being considered, there is no homogeneous positive interaction of the chains or self-heating.[19,26] At the same time, Fig.6 shows that the quantity of the mixture which has undergone combustion is ~15 times the quantity of O_2 introduced into the reaction vessel in the last portion, that is the degree of combustion is greater by an order of magnitude than the amount by which O_2 initially exceeds the ignition limit in the given experiment. The maximum rate of the chain combustion is also "anomalously high".

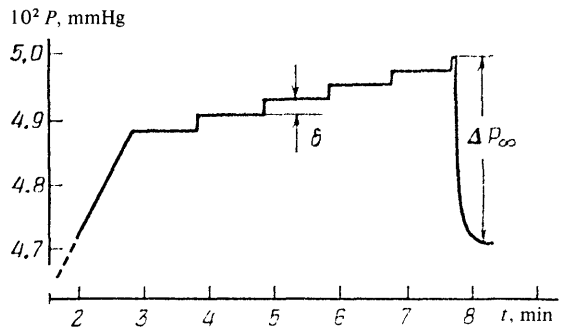


Figure 6. Kinetics of the change in the pressure of P_4 vapour and O_2 for the pulsed introduction of small portions of O_2 into a reaction vessel whose surface was impoverished in phosphorus.[21]

In recent papers,[54-57] the same authors tried to deny that a change in the state of the surface takes place during combustion; these authors state that the "anomalously high" degrees of combustion during the oxidation of H_2 result from the action of some inhibitor liberated from the vacuum lubricant of the taps. The data given in the works cited show, however, that the authors did not evacuate the assembly sufficiently after washing and lubricating the taps, so that the solvent sorbed in the lubricant was desorbed into the reaction vessel; the oscillograms given in Ref.56 show that in the closed reaction vessel in contact with the taps, the pressure increases at a constant temperature, in spite of the fact that in the reaction of H_2 with O_2 the number of moles decreases. This represents a fundamental difference between the experiment in Refs.54–57 and the experiments of all other authors, carried out at the same manometer sensitivity (for example Refs.17, 19, and 25). The introduction of a foreign substance into the reaction vessel in the experiments[54-57] and its inhibiting action are due mainly to the fact that in Ref.56, when the side-arm of the reaction vessel was cooled with liquid nitrogen, the mixture, which was initially under the first self-ignition limit, ignited. These results obviously have no relation to studies by other workers, carried out observing the generally accepted precautions for preventing the introduction of foreign substances into the reaction mixture.

Special experiments[23] showed that with the usual sufficiently thorough evacuation of the assembly, carried out after lubricating the taps, cooling the side-arm of the reaction vessel does not lead to the ignition of a mixture which is directly under the first limit. Moreover, Fig.2 shows that when the familiar requirements of the procedure are fulfilled, the degree of the observed "anomaly" in a given reaction vessel is independent of whether the reaction vessel is in an assembly with metallic lubricant-free valves (open circles and triangles) or in the ordinary apparatus for kinetic experiments with lubricated vacuum taps (black circles and triangles). The same is true of P_1 and the induction period. The results of the measurements coincide, irrespective of whether the connections in front of the intermediate volume are cooled with liquid nitrogen (open circles) or not cooled (open triangles), and also of whether the evacuation is carried out with an oil or a mercury diffusion pump.[23]

In Ref.56, a series of experiments was carried out with continuous cooling of the side-arms of the reaction vessel with liquid nitrogen to prevent the introduction of foreign substances from the insufficiently evacuated lubricant of the taps into the reaction vessel. The oscillograms given show that in all these experiments, the observed maximum rates of the process were appreciably greater (from two to twelve times greater) than the calculated values obtained without allowance for the change in the properties of the surface, that is the reaction rates were "anomalously high" even in those experiments of Ref.56 which the authors called clean. This fact was not noted in Refs.54–56.

It should be specially emphasised that in all the studies, the procedure used in the experiments to detect the "anomalous" kinetics of chain processes, and the vacuum assemblies used, are standard; this procedure and these assemblies have always been used and are still being used to study gas-phase chain processes. In particular, using this procedure and under the same conditions (including the same pressures) as in Refs.19, 23, 25, 29, and 54–57, different authors have determined the principal characteristic features of the first self-ignition limit of mixtures of H_2 with O_2, as a model BCP (see for example Refs.3–5, 10, and 58–60). Thus the assertion in Refs.54–57 that the vacuum lubricant has a distorting influence applies not only to the "anomalies" but also (and particularly) to the generally accepted procedure for studying BCP and to all their familiar regular features, previously established by different workers. As shown above, this assertion by the authors cited,[54-57] which categorises the generally accepted procedure and all the results obtained using it as erroneous, results from the fact that they attribute to the work of other authors the lack of thorough preparation of the assembly for the experiments which was shown in the works cited.

It is obvious that if some impurity had been introduced into the reaction vessel from the vacuum lubricant and had influenced the chain reaction when the usual precautions for ensuring the purity of the reaction mixture had been taken, then a large number of facts would not have been observed—the reliably established characteristic regular features of BCP, familiar from courses of chemical kinetics and from monographs. Examples of these regular features are: the marked dependence of P_1 on the material and the state of the surface of the reaction vessel;[2-6,59] the inverse relationship between the value of P_1 and the diameter of the reaction vessel, including that in the kinetic range of chain termination;[10,58,60] the quantitative agreement between

theory and experiment in the method for controlling ignition by means of metal rods;[4,10] etc.

V. KINETIC MODELS OF THE HETEROGENEOUS SELF-ACCELERATION OF BRANCHED-CHAIN PROCESSES AND A NEW TYPE OF FLAME PROPAGATION

On the basis of data obtained in the study of BCP, including the investigation of the nature of the heterogeneous reactions of the chain carriers and the mechanism of the decrease in the efficiency of termination on the surface, two principal types of kinetic scheme corresponding to the heterogeneous self-acceleration of various processes of chain combustion have been proposed.[19,29] These schemes explain both the ignition limits and the induction periods, and also the kinetics of combustion, including the dependence of the "anomalous" values of w_{max}^{expt} and η_{∞}^{expt} on the initial conditions. Analysis of these schemes shows, in particular, that on a number of surfaces under certain conditions, there is non-uniformity of the stationary states, and this is responsible for the critical phenomena within the ignition range, detected, for example, in Refs.19, 23, 25, 32, and 61.

The first of these reaction schemes takes account of the reactions of the gas-phase components with sorbed atoms and radicals and the subsequent positive interaction of the chains. In the case, for example, of the model BCP of H_2 oxidation, and also the combustion of a number of hydrogen-containing compounds, allowance for the reaction of O_2 with the sorbed H atoms and the reactions of the HO_2 radicals formed, suggested in Refs.15 and 19, leads to the following expression for the effective rate constant of heterogeneous chain termination:

$$k_{het} = k_{het}^0 \left[1 - \beta \frac{k_7 [H]}{(k_7 + k_8 + k_9)[H] + k_{10}} \right] \qquad (10)$$

where k_{het}^0 is the rate of the capture of atomic hydrogen by the surface at unit concentration of these particles in the gas phase (specific rate); β the fraction of sorbed H atoms forming HO_2 radicals with O_2; and k_7, k_8, k_9, and k_{10} the rate constants of the above reactions (VII)–(X) respectively.

Outside the ignition range, and also before the start of the combustion (in the induction period), when the quantity of H atoms is very small, the expression in square brackets in Eqn.(10) is practically equal to unity, so that

$$k_{het} = k_{het}^0$$

Thus in this case the adsorbed H atoms do not influence the efficiency of the heterogeneous termination. During the developed combustion, however, as a consequence of the marked increase in the concentration of atomic hydrogen, the value of k_{het} decreases, as can be seen from Eqn.(10), and tends to its limiting value:

$$k_{het}^c = k_{het}^0 \left(1 - \beta \frac{k_7}{k_7 + k_8 + k_9} \right) \qquad (11)$$

The superscript "c" indicates that the value relates to combustion conditions.

This decrease in the effective rate constant of the heterogeneous chain termination during combustion obviously leads to an additional sharp increase in the rate of the chain process, the concentrations of the chain carriers, and the final degree of transformation, as observed experimentally by the present author in the form of the "anomalies" (for example in Fig.2). Under given conditions, including given concentrations of O_2 and H in the gas phase, the fraction of sorbed hydrogen atoms capable of leading to the formation of HO_2 and to the development of chains depends on the material of the surface. This explains the fact that the extent to which the quantitatively reproducible regular features deviate from those expected on the basis of earlier ideas, that is the magnitude of the "anomalies", depends on the material of the surface¶.

Allowance for the heterogeneous development of the chains also makes it possible to explain the observed sharp decrease in the dependence of the maximum rate and degree of transformation on P_0 when the initial pressure increases above a certain value (see for example Figs.2 and 4). In fact, since the maximum concentrations of the chain carriers usually increase sharply with increase in P_0 and on passing through the first ignition limit, it follows that when the initial pressure is even only slightly greater than P_1, H atoms are formed during combustion in such large quantities that there is an appreciable decrease in k_{het} by the mechanism described above. There is a correspondingly anomalous sharp increase in the values of w_{max}^{expt}, η_{∞}^{expt}, and $[H]_{max}$. At the same time, because of the appreciable concentrations of H atoms even at values of P_0 which are only 1–2% greater than P_1, the constant k_{het} may reach its limiting value defined by Eqn.(11). It is obvious that in this case, with further increase in P_0 in each given experiment, the value of k_{het} will decrease to the above same limiting value, that is by the same amount. As a consequence of the sharp increase in the concentration of chain carriers on ignition, the decrease in k_{het} is complete in the earliest stages of the combustion, and the subsequent chain process proceeds to completion with a new decreased heterogeneous termination rate "constant", equal to k_{het}^c.

There are thus two stable values of k_{het}: one under stationary conditions, equal to k_{het}^0, and another under combustion conditions, given by Eqn.(11). Above a certain initial pressure P_0^* lying in the ignition range, for all values of P_0 the chain combustion takes place with the same stationary value of the heterogeneous termination rate "constant", k_{het}^c, which is much smaller than the initial value k_{het}^0. Since no further decrease in k_{het} takes place with increase in P_0 above P_0^*, the "anomalously" marked increase in η_{∞}^{expt}, w_{max}^{expt}, and $[H]_{max}$ also stops. This means that the dependence of these quantities on P_0 above the initial pressure P_0^* indicated in the absence of other heterogeneous reactions and self-heating should be described, with an accuracy corresponding to the correction for the contribution of the reaction

$$O + OH \rightarrow O_2 + H \qquad (II')$$

by Eqns.(6), (8), and (9), in which, however, the measured value of P_1 is replaced by the value corresponding to the new established value of k_{het}^c.

In fact, it is known that[2-6,59]

$$P_1 = k_{het}/2k_2\gamma_{O_2} \qquad (12)$$

where γ_{O_2} is the mole fraction of O_2. It is therefore obvious that the decrease in k_{het} to k_{het}^c leads to a corresponding lowering of the ignition limit to P_1^c, and the actual abscissae of the measured η_{∞}^{expt} are not P_0/P_1, but P_0/P_1^c. For example, in Fig.7 the experimental dependence of the degree of transformation on P_0/P_1 shows a break at $\eta_{\infty}^{expt} = 0.38$.

¶The reactions of the chains of the type (VII) and (VIII) may involve both desorbed HO_2 radicals and HO_2 radicals situated on the surface. In the general case, therefore, Eqn.(10) contains another negative fraction, analogous to that given, which also increases to its limiting value with increase in the concentration of H atoms during the combustion.

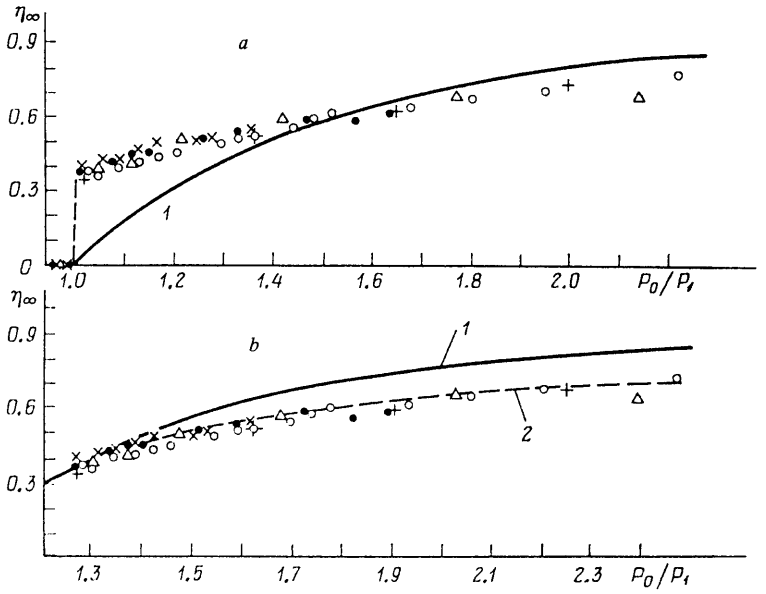


Figure 7. *a*) Change in the degree of transformation of O_2 with change in P_0/P_1 in different series of experiments at 723 K (different point symbols) and the results calculated from Eqn.(6) (curve *1*); *b*) the same data with the values of P_0/P_1 replaced; curve *2*—result of the computer solution of the system of kinetic equations corresponding to reactions (0)–(IV), (II').[19]

According to Eqn.(6), this degree of combustion corresponds to the ratio $P_0/P_1^c = 1.27$ (see curve *1* in Fig.7), which is 25% greater than P_0/P_1 obtained by dividing the initial pressure by the measured value of P_1, that is during the combustion, the values of k^c and P_1 decrease by 25%. Thus by increasing the abscissae of the measured η_∞^{expt} by 25%, it can be shown that all the experimental data lie on the calculated curve obtained by using a computer to solve the system of equations corresponding to the set of stages (0)–(IV) and (II') (broken line and all the experimental points in Fig.7*b*). This calculation was carried out using the published[30] rate constants of the homogeneous stages; the values of k_4 and k_4^c were determined from P_1 and P_1^c using Eqn.(12).

The mechanism of the heterogeneous reactions, examined above, and Eqn.(10), show that k_{het} may decrease even when the specific rate of the capture of these particles by the surface, that is k_{het}^0, does not decrease. The explanation for this may be that the "anomalously" high values of η_∞^{expt} and w_{max}^{expt} are also observed for various surfaces on which the adsorption of the chain carriers takes place in the diffusion range (MgO, stainless steel[19,28,61,62]). Fig.8, in addition to the experimental data of Ref.61, also gives the results of a computer calculation carried out in Ref.63 for the initial conditions of the experiment with allowance for self-heating, termolecular reactions, and homogeneous interaction of the chains, but without allowance for the change in the efficiency of the heterogeneous chain termination. The different calculated curves in Fig.8 correspond to change in the values of the parameters used. The broken calculated curve was obtained using an increased (relative to the recommended value[30]) value of the rate constant of stage (VI). For this value of k_6, the calculated second ignition limit was found to be less than half the measured values. It can be seen that for P_0 only slightly greater than P_1, the observed degrees of combustion are much greater than the calculated values. Moreover, in contrast to the results of the calculation,[63] the experimental curve shows a sharp abrupt increase in η_∞^{expt}, which also stops suddenly with increase in P_0, in spite of the fact that tens percent of the original mixture remain unreacted. Allowance for the reaction of O_2 with adsorbed H atoms makes it possible to explain the observed sharp changes in η_∞ with change in P_0/P_1 (as in the case where the process takes place over a quartz surface). For identical initial conditions and equal values of P_1, the kinetics of the combustion and the degrees of transformation are different over MgO and over stainless steel.[19] The characteristic features of combustion over MgO and over stainless steel, and the role of the non-stationary nature of the surface under these conditions, have been examined in detail.[19,64] In addition to the extensive chemisorption, noted above, of water vapour on the MgO surface during the combustion of hydrogen-containing compounds, which has a marked influence on the properties of the surface, rapid chemisorption of atomic hydrogen also takes place under these conditions. It has been noted[65] that the H atoms obtained by a discharge in H_2 reduce MgO, and in the presence of O_2 the following reactions take place:

$$Mg^{++}O^{2-}Mg^{++} \rightarrow Mg^{++}OH^-Mg^+$$
$$Mg^+ + O_2 \rightarrow Mg^{++}O_2^-$$
$$Mg^{++}O_2^- + H_2 \rightarrow Mg^{++}OH^- + OH$$
$$2Mg^{++}OH^- \rightarrow Mg^{++}O_2^{--}Mg^{++} + H_2O$$

in which the hydroxyl radical is formed.

A number of authors have reported the reduction of quartz by atomic hydrogen (see for example Refs.66 and 40), in agreement with the data of Refs.19 and 42.

The development of the chains and a change in the properties of the surface can obviously be brought about by heterogeneous reactions involving species other than atomic hydrogen. There are examples of oxidation involving oxygen present in a chemical compound in the solid phase (see for example Refs.66–69), including O^- radical-anions. Heterogeneous chain termination in other BCP can also be described by equations analogous to Eqns.(10) and (11).

In many cases, the sorption of a gaseous component leads to structural changes in the layer next to the surface, and to phase transformations;[64,70-72] this in turn influences the kinetics of the heterogeneous stages.

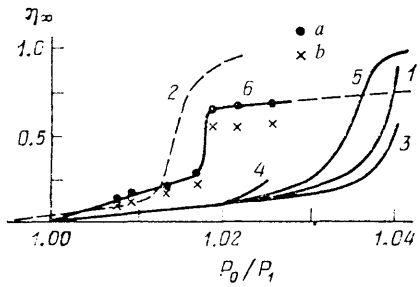


Figure 8. Comparison of the results of the calculation in Ref.63 (curves *1–5*) and the experiment in Ref.61 (points and curve *6*); T = 853 K, stainless steel vessel; curves *1–5*—calculation for different varying combinations of the rate constants; curve *2* (broken line) was displaced to the left along the abscissa by the authors of Ref.63; the points give the experimental data (*a*—with a correction for the volume of the connecting tubes,[31] *b*—results of the measurements without this correction).

In the theory of chain processes it has been assumed that in the absence of reactions involving interaction of the chains, the change in the concentration of active centres (n) with time (t) is described by the equation

$$\frac{dn}{dt} = w_0 + (f - g)n \qquad (13)$$

where w_0 is the rate of the chain initiation, and f and g the rates of chain branching and termination for unit concentration of the chain carriers (that is the coefficients of linear branching and termination of the chains respectively); f and g have been regarded as being independent of n.

With allowance for Eqn.(11), the equation describing the changes in the concentrations of the carriers with time is obtained in the form

$$\frac{dn}{dt} = w_0 + (f - g_0)n + \frac{an^2}{1+bn} \qquad (14)$$

where a and b are the combinations of the quantities k_1, k_2, k_3, and β, and $g_0 \equiv k^0_{het}$. Unlike Eqn.(13), Eqn.(14) is non-linear with respect to n; at the same time the presence in eqn.(14) of a positive term in which the power of the quantity n is greater than unity indicates that a sufficiently high concentrations of the chain carriers in the volume or on the surface, the first ignition limit depends not only on the relationship between f and g_0 but also on the concentrations of the chain carriers and on the ratio of the parameters characterising the heterogeneous development of the chains and the reversible changes in the properties of the surface.

From Eqn.(14) it follows, in particular, that it is possible to lower the first ignition limit by artificially increasing the rate of initiation or by the preliminary adsorption of chain carriers. This conclusion has been confirmed experimentally: the preliminary adsorption of H atoms on magnesium oxide and on quartz leads to the quantitatively reproducible lowering of the first ignition limit in the reactions of H_2 with O_2 and of CO with O_2.[11,19,32,73] The quantitative reproducibility of the results shows that in this case also, the change in the properties of the surface under the influence of active intermediate species is reversible. As noted in Refs.19 and 32, in the combustion of CO the heterogeneous development of the chains may involve O atoms in addition to H atoms. The development of chains involving heterogeneous reactions of free atoms and radicals has also been detected in the branched-chain processes involved in the oxidation of silane[22] and phosphorus vapour[19,29] and the decomposition of NCl_3.[19,20]

Heterogeneous reactions of intermediate species, leading finally to chain development, may also play an important role in flame propagation. For example, it can be seen from Eqn.(14) that dn/dt increases with increase in n more rapidly than according to a linear law; this makes possible the non-thermal propagation of the combustion zone.

A number of studies of the decomposition and degenerate-branched oxidation of organic compounds (for example Refs.47 and 74–76) have shown that the adsorbed fragments of the molecules, reacting with O_2, form peroxy radicals which are transferred to the gas phase. In particular, atomic hydrogen, sorbed on the surface of the reaction tube during the decomposition of peroxyformic acid, reacts with O_2 from the gas phase to give HO_2 radicals. These radicals are removed from the reaction zone by the gas stream; they can be condensed by cooling and detected by EPR.[74] The mechanism proposed[76] for the decomposition of peroxyacetic acid includes the reaction of O_2 with adsorbed CH_3 radicals, leading to the partial removal of the methyl peroxy radical into the gas phase. This reaction, which is the analogue of the proposed[15,16] reaction of O_2 with adsorbed hydrogen atoms, also leads to heterogeneous chain initiation. The formation of OH radicals as a result of the reaction of O_2 with sorbed H atoms has been reported.[72,77,78] In these studies, the atomic hydrogen was obtained by an electric discharge in H_2.

The authors of Refs.38 and 79, who detected the reactions of sorbed methyl radicals with gas-phase components during the thermal decomposition of organic compounds over quartz and over MgO, explain the observed regular kinetic features of the chain process on the basis of a reaction scheme which also includes heterogeneous chain development. In a number of studies, the reaction of sorbed hydrogen atoms with deuterium from the gas phase has been observed (see for example Refs.44 and 79). The need to take account of the change in the efficiency of heterogeneous chain termination has also been pointed out in Refs.80 and 81.

The reactions of sorbed chain carriers must apparently be responsible for the observed[22] unique character of the kinetics of the combustion of silane with oxygen in a closed volume close to P_1, shown in Fig.9. It can be seen that the duration of the chemiluminescence after the attainment of the intensity maximum is ten times that before the maximum. It is difficult to attribute this almost constant (and low) rate of combustion to some negative interaction, since it is known[82,83] that in this process, on the contrary, an important role is played by the positive interaction of the chains. An unambiguous indication of this is provided by the observed[82] non-thermal propagation of the flame in a gas mixture outside the self-ignition range. Thus in the kinetics of combustion shown in Fig.9, heterogeneous chain development is probably of considerable importance. This is also indicated by the conditions of double ignition of a mixture of silane with O_2 in a closed volume, which depends on the previous treatment of the surface by the flame.[22,82]

In another type of heterogeneous process leading to "anomalous" self-acceleration of BCP and to non-uniformity of the stationary states, the principal factors are the non-uniformity of the surface and the disappearance of its active

sites during chain combustion. A specific example of a process of this kind is provided by the oxidation of phosphorus vapour.[29] For simplicity it is assumed that the heterogeneous chain termination is determined by only two types of surface: regions occupied by phosphorus, on which termination is very effective,[19,21] and regions free from phosphorus. In this case, the effective rate constant of the termination is given by the expression:

$$k_{het} = k_f + (k_o - k_f)(1 - b_0)\exp\left(-k\int_0^t n\,dt\right) \qquad (15)$$

where k_0 and k_f are the rate "constants" for termination on the active (occupied by phosphorus) and inactive (free) regions of the surface, b_0 the fraction of the inactive part of the surface at the start of ignition, and k the rate constant for the disappearance of the active sites of the surface (in this case the consumption of sorbed phosphorus).[29] It can be seen from Eqn.(15) that there are two stationary values of k_{het}: in the absence of combustion (before the start of the combustion or outside the ignition range), that is for $t = 0$ and $n = 0$, the value is

$$(k_{het})_{t=0} = k_o(1 - b_0) + k_f b_0 \qquad (16)$$

Under conditions where combustion has begun, however, as a result of the rapid increase in n, the value of k_{het} decreases sharply, tending in the limit to $(k_{het})_\infty = kf$. This decrease in the efficiency of heterogeneous chain termination obviously leads to additional self-acceleration of the chain process and to the "anomalously" high degrees of combustion observed experimentally.

If the rate constant k_f in Eqn.(15) is denoted g_0, and the product of the differences in front of the exponent by α, and if account is taken of the fact that k_{het} is represented by g in Eqn.(13), the latter can be written in the form

$$\frac{dn}{dt} = w_0 + \left[f - g_0 - \alpha\exp\left(-k\int_0^t n\,dt\right)\right]n \qquad (17)$$

Unlike Eqn.(13), Eqn.(17) is non-linear with respect to n, and, like Eqn.(14), it shows that the critical conditions for self-ignition depend on the concentration of chain carriers. Correspondingly, BCP may show kinetic features characteristic of processes with homogeneous positive interaction of the chains. Eqn.(17), like Eqn.(14), shows, in particular, that it is possible to have non-thermal propagation of the flame, brought about by a decrease in the efficiency of heterogeneous chain breaking ahead of the combustion front under the influence of the reaction chain carriers. This phenomenon was in fact detected by the present author; in a mixture of P_4 vapour and O_2 present in a long tube at a pressure under the first self-ignition limit, an isothermal flame passes along the tube if a small spark is produced at one end.[84] Special experiments showed that under these conditions there is no homogeneous interaction of the chains, and the regular features of the propagation of the flame depend on the material and state of the surface.[21,26] In these experiments, the quantity of adsorbed phosphorus was small, because of the low partial pressure, lower than the saturated vapour pressure.

The phenomenon of non-thermal "heterogeneous" propagation of a flame may also obviously take place in other BCP. In the more general case, a change in the efficiency of heterogeneous chain termination under the influence of chain combustion may lead to a change in the rate of propagation or to a change in the length of the combustion zone in the stream. In view of what has been said above, the rate "constant" for heterogeneous chain termination, appearing in the equation describing the propagation of the flame, depends not only on temperature but also on the concentration of chain carriers.

The dependence of the rates of branching (*1*) and termination (*2*) on the concentration of active intermediate products in the heterogeneous development of the chains and the passivation of the surface (the cases to which Eqns.(14) and (17) respectively relate) is given in Fig.10. At values of n greater than the abscissa of the second intersection of the curves or the point of tangency of the curves, chain branching predominates over termination, to an extent which is greater, the larger n becomes. This leads to self-ignition of the mixture, non-thermal propagation of the flame, etc. If the termination graph lies below the straight line *2'*, the mixture undergoes self-ignition for all values of n.

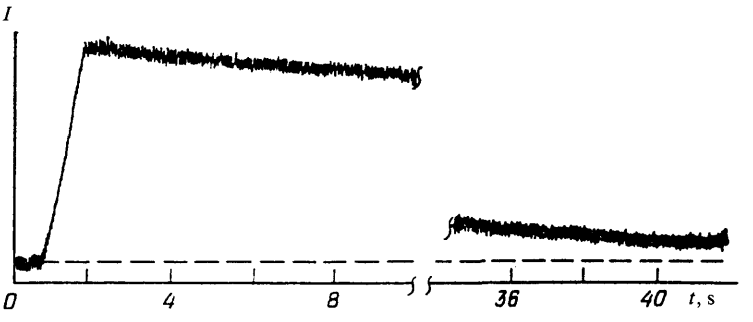


Figure 9. Oscillograms showing the change in the chemiluminescence during the combustion of silane in the mixture: 8% SiH_4 + 76.5% O_2 + 15.5% He; T = 473 K, P_0 = 0.96 mmHg.[22]

A mathematical description has been given[85] for the non-thermal propagation of a flame, brought about by the decrease in the efficiency of heterogeneous chain rupture ahead of the reaction front.

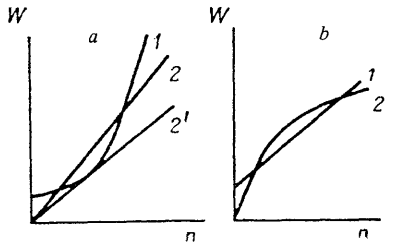


Figure 10. Rates of branching (*1*) and termination (*2*) in the cases corresponding to Eqns.(14) (*a*) and (17) (*b*).[29]

VI. PULSED CHAIN COMBUSTION AND THE NON-STATIONARY NATURE OF THE STATE OF THE SURFACE

A characteristic manifestation of the inverse relationship between the kinetics and mechanism of the heterogeneous reactions of chain carriers and gas-phase BCP is the condition of repeated self-ignition in a closed volume close to the first limit, which has been detected and studied for the decomposition of NCl_3 [19,20] and the oxidation of carbon monoxide,[18,19,48] silane,[22,82] and phosphorus vapour.[19,21,26,49] In most experiments, the concentrations of the reagents were very low, and ignition was not accompanied by self-heating.

The pulsed combustion of, for example, hydrocarbons and CO was also observed earlier.[86] The pressure of the mixture was several hundred mmHg, however, and the process was accompanied by considerable self-heating of the mixture. On this basis, the periodic ignition in the closed volume was related to the self-heating.[86-88] It is not excluded that under certain conditions, self-heating is in fact one of the necessary conditions for repeated ignition.[89,90] It cannot be assumed, however, that self-heating is necessary for pulsed conditions in all cases. Close to the first ignition limit, the regular features of the pulsations are determined to a large extent by the dependence of the reactions of the sorbed chain carriers, the desorption of the molecular reagents, and the change in the efficiency of the heterogeneous termination on the nature of the surface and on the type of BCP. In the oxidation of CO and P_4 vapour and the decomposition of NCl_3, the number of ignitions for a single introduction of gas into the reaction vessel may be greater than 50, depending on the initial conditions, including the quantity of sorbed chain carriers.

The decisive role of chemisorbed chain carriers in, for example, the pulsed combustion of CO over an MgO surface was shown by the following experiment.[48] It was established that when the ignition of a "dry" mixture of CO and O_2 was carried out repeatedly, the number of pulsations decreased from one experiment to another. Since the concentration of the original reagents and the other conditions remained unchanged in all the experiments, the marked decrease in the number of pulsations was due to the change in the properties of the surface. The introduction into this reaction vessel of H_2, water vapour (the original promoters), CO_2 (the combustion product), or a mixture of H_2 and O_2 at a pressure below its first ignition limit, with subsequent evacuation, led to practically no increase in the number of ignitions of the $2CO + O_2$ mixture introduced into the reaction vessel after the evacuation. If however two or three ignitions of H_2 with O_2 were carried out in this "exhausted" reaction vessel, then after evacuation the picture of repeated ignition of CO was restored. This shows that intermediate combustion products, that is hydrogen atoms, are chemisorbed on the surface, remain partly on the surface after evacuation, and subsequently lead to the repeated ignition of the mixture of CO and O_2 when it is introduced into the reaction vessel.

The pulsed combustion of CO over, for example, MgO is explained as follows.[19] As shown by EPR spectroscopy,[11,91] in the combustion of CO in the presence of hydrogen or water vapour under the given conditions, tens percent of H_2 (H_2O) are present as atoms and radicals. An appreciable proportion of the latter disappear on the surface. As noted above, there is considerable chemisorption of H atoms during combustion. As a result, there is a decrease in the concentration in the reaction mixture of hydrogen (or water), which acts as the initiator of the given chain reaction; as a result, the combustion stops. After some time, the initiator is returned from the wall into the volume (as H_2 or H_2O molecules), and when its concentration exceeds the critical value, the mixture ignites again. Since some of the O_2 and CO are used up in each ignition, the pulsations are gradually quenched.

Under certain oscillation conditions, the intensity of the ignitions passes through a maximum with increase in their sequence number.[19,20,21,92] The explanation given in Ref.19 for this regular feature was based on allowance for the changes in the ignition period, the quantity of desorbed reagent (starting material, inductor, etc.), and the properties of the surface. The conclusions reached[18,19] about the important role of the reversible non-stationary nature of the properties of the surface under pulsating CO combustion conditions agrees with the fundamental ideas in later papers.[80,81,93,94]

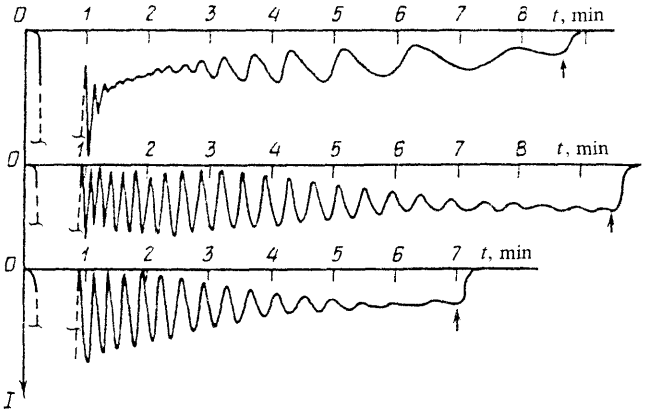


Figure 11. Repeated ignition of NCl_3 in a mixture with helium over different surfaces; the arrow indicates the moment of evacuation.

The active role of the non-stationary state of the surface (primarily as a result of the change in the concentration of chain carriers sorbed on it) under pulsating conditions is also indicated directly by data on the oxidation of silane.[22,83]

This chain reaction shows reversible changes in the properties of the surface, which have a marked influence on the course of the BCP, the "memory effect" of the surface, and hysteresis.

Fig.11 gives oscillograms showing the change in the intensity of the absorption of light (at a wavelength of 248 nm) by nitrogen trichloride under conditions of repeated ignition in a closed volume over NaCl. The increase in the concentration of NCl_3 between ignitions was due to its desorption. The difference in the pulsation conditions in different experiments was due to the fact that the preliminary treatment of the surface, including its treatment by the reactions of the chain carriers, was carried out in different ways.[20] The observed change in the period of the fluctuations and the extent of the combustion on the first oscillogram shows that the efficiency of the heterogeneous chain termination decreases during ignition.

In the study of BCP pulsed conditions, an extremely fruitful approach is to analyse mathematical models of the reactions using, in particular, the methods of stability theory, if account is taken of the reactions of the sorbed chain carriers in the analysis of the phase trajectories;[19] for this purpose, at least one of the axes of the phase space must be assigned to these sorbed species.

VII. HETEROGENEOUS SELF-RETARDATION OF BRANCHED-CHAIN PROCESSES

On a number of surfaces, as a result of heterogeneous reactions of the components of the reacting mixture, the efficiency of chain termination may increase (in contrast to the decrease described above).[29,96] In this case, the values of the rates and the final degrees of combustion reproduced quantitatively in the experiment are lower than the values calculated from the linear theory, that is they are "anomalously" low. This heterogeneous self-retardation has been detected[25,95] for the combustion of detonating gas over NaCl and over alkaline $K_2B_4O_7$.

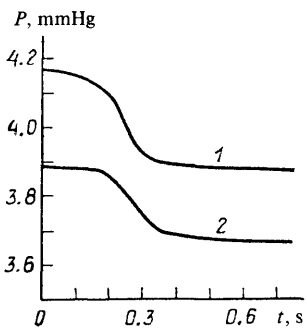


Figure 12. Oscillograms showing the change in the pressure of a $2H_2 + O_2$ mixture over NaCl in two experiments with different initial partial pressures of oxygen $P_0(O_2)$ equal to 1.39 mmHg (curve *1*) and 1.29 mmHg (curve *2*); P_1 = 3.19 mmHg.

Fig.12 gives as examples oscillograms showing the change in the pressure of the mixture with time in two experiments of one of the series at 787 K (quartz vessel with diameter 5.2 cm, covered with sodium chloride). The O_2 pressure at the limit ($P_1(O_2)$) was 1.06 mmHg. Thus for example in the first experiment the initial oxygen pressure $P_0(O_2)$ was greater than $P_1(O_2)$ by 0.3 mmHg. This means that if the efficiency of the heterogeneous chain termination did not increase during the combustion, the self-acceleration of the process would stop after the combustion of this quantity of O_2 in excess over the limit. Since according to the stoichiometry of the process the decrease in the O_2 pressure, within an accuracy corresponding to the concentrations of the active intermediate chain-carrier species, is equal to the decrease in the pressure of the mixture as a whole ($\Delta P(O_2) = \Delta P$), then for a constant value of k_{het}^c the self-acceleration would stop (that is the kinetic curve would show an inflection) only at $\Delta P \cong 0.33$ mmHg. Fig.12 shows, however, that the self-acceleration stops well before this quantity of O_2 has undergone combustion. The inflection (see for example curve *1*) is observed at a value of ΔP equal to only 0.14 mmHg, that is at an O_2 pressure which is 18% greater than $P_1(O_2)$, measured in the same series of experiments. Fig.12 also shows that the combustion stops at $\Delta P = 0.29$ mmHg, that is at an O_2 pressure which is even slightly greater than $P_1(O_2)$. At the same time, if the efficiency of the heterogeneous chain termination were constant, then when this value of $P(O_2)$ had been reached, the reaction should have taken place at maximum rate. The same "premature" stoppage of the chain combustion also takes place in the second experiment.

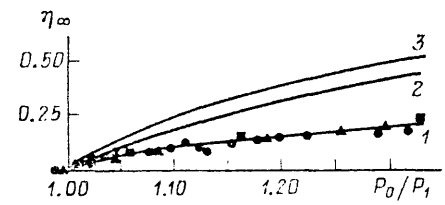


Figure 13. Dependence of the final degree of transformation of H_2 with O_2 on P_0/P_1: *1*) experiment over NaCl (the different point symbols correspond to the data from different series of experiments at 787 K); *2*, *3*) calculated from Eqn.(6) and from the analogous equation for the diffusion range.[95]

Fig.13 gives the dependence of the degree of transformation on P_0/P_1, obtained experimentally and calculated from Eqn.(6), and also using the analogous equation for the diffusion range of termination.[95] The results of the measurements are reproduced quantitatively in different series of experiments. The values of P_1 measured in different series also coincide. At the same time, the data show that the observed values of η_∞^{expt} are ~2.5 times lower than the results of the calculation which does not take account of the change in k_{het}^c during the combustion. The experimental values of the maximum rates are also several times smaller than the calculated values. Thus the results obtained show that self-retardation of the combustion of a $2H_2 + O_2$ mixture takes place over NaCl. This self-retardation is revealed primarily by the fact that the concentrations of the starting materials remaining after combustion are higher than the quantitatively reproducible limiting concentrations measured in the same experiments.

A noteworthy feature is that the first ignition limit of detonating gas in a quartz vessel with a non-continuous coating of MgO, for example, at 869 K is 3.88 mmHg, that is it is close to the value of P_1 over NaCl at 787 K. At the same time, in contrast to the combustion over NaCl, in the

case of MgO the values of w_{max}^{expt} and η_{∞}^{expt}, observed in the absence of self-heating, are appreciably greater than the calculated values obtained without allowance for the change in the properties of the surface during combustion.[19,62] The dependence on P_0/P_1 over MgO differs qualitatively from that observed over NaCl. The sorption of H_2O on NaCl is slight,[95] and, which is more important, does not lead to any significant increase in the specific rate of chain termination. Resonance fluorescence and emission spectroscopy have shown directly[97] that atomic hydrogen, formed in a flame of H_2 and O_2, with NaCl and KCl surfaces leads to the appearance of sodium and potassium atoms respectively in the gas phase. A change takes place in the chemical composition of the surface, which becomes darker. The reaction of the H atoms with the Cl^- ions of the crystal lattice apparently leads to the reduction of metal cations, some of which volatilise (metal atoms were detected in the gas phase), and some are oxidised. The heterogeneous destruction of atoms on the surfaces of metals and their oxides is extremely efficient.[6,50]

Reaction in the volume according to the scheme:

$$Na_2 + H \rightarrow Na + NaH$$

is also not excluded. In this case, the reproducibility of the kinetic data is ensured by the fact that the layer of NaCl above the quartz surface is sufficiently thick.

Analysis has shown[29] that self-retardation of the combustion of detonating gas also takes place in the experiments corresponding to the kinetic curves given in Ref.98; after combustion has stopped, the O_2 concentration remains higher than the concentration corresponding to the first ignition limit and measured in the same experiments. At the same time, if the rates of branching and termination are linearly dependent on the concentration of chain carriers, then it is known that the chain combustion undergoes self-acceleration until the concentration of the starting material is higher than the first ignition limit.[1-5] Thus if in Ref.98 the results of the measurements were reproduced, this means that in these experiments there was self-retardation of the combustion of H_2, which was not noted in the work cited. On the contrary, the authors cited,[98] pointing out the slight discrepancy between the experimental data and one of the approximate equations, and attributing this influence merely to the ballast volume, consequently point out the quantitative agreement between the experimental data on the dependence of the maximum rate on the decrease in pressure and the results of the calculation carried out using an equation which does not take account of the change in the state of the surface. This agreement was illustrated[98] using diagrams. The quantitative agreement between the calculation and the experimental data of Ref.98 was also mentioned in Refs.1 and 4. Since at the same time the kinetic curves giving the change in pressure in Ref.98, as already noted, show marked self-retardation of the combustion, good reproducibility apparently was not obtained. In Ref.99, in the section giving the data on the detection, above $K_2B_4O_7$, of "anomalously" high degrees of combustion of H_2, that is degrees of combustion greater than the calculated values, it is pointed out that in a vessel insufficiently pretreated by ignitions, the observed degrees of combustion are lower than the calculated values in the initial series of experiments.

Analysis of the regular features of the pulsed combustion of NCl_3 in various series of experiments in Ref.35 also reveal heterogeneous self-retardation of BCP over various surfaces.

In view of the non-uniformity of surfaces and the variety of heterogeneous processes, it is possible that in addition to reactions leading to the self-retardation of BCP, other process take place simultaneously on other centres, leading to a decrease in the efficiency of heterogeneous termination.

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In most experiments to reveal the heterogeneous factors and carry out the most complete investigation of their role in the mechanism of chain reactions (for example in Refs.2-4, 19-23, 25-29, and 32), the processes were carried out under isothermal conditions. At the same time it is obvious that the characteristic features of the chemical mechanism of BCP, including the change in the efficiency of heterogeneous chain termination, and also the reversible non-stationary nature of the properties of the surface, play an important part in the non-isothermal process (see Figs.5 and 8 and also Refs.19, 31, 61, and 64). Since heterogeneous termination is one of the principal routes for the removal of energy from the reaction system, the change in the rate "constant" of this termination influences the thermal conditions of BCP not only through the change in the kinetics of the combustion, but also directly.

It should be noted that the nature, rate, and role in the chain process of the reactions of sorbed chain carriers with molecular components differ fundamentally from the familiar heterogeneous decomposition of valence-saturated molecules, which is also sometimes accompanied by the removal of atoms and radicals into the reaction volume (see for example Refs. 12-14 and 100-107). The decomposition of the original molecules with the transfer of active fragments from the surface to the volume in the chain process is only heterogeneous chain initiation. A variation of this initiation is the decomposition of intermediate molecular products on the surface in many processes involved in the slow oxidation of organic compounds in the liquid and gas phases†.[47,75,101-103] Chain initiation by the reactions of molecular intermediate products (degenerate branching) increases the rate of the process. In the absence of appreciable self-heating, however, it cannot lead to the high rates characteristic of chain combustion or to "anomalous" features analogous to those described above.

The branching of the chains was not degenerate in any of the processes studied in a series of investigations to detect and study the non-stationary nature of the surface in chain combustion processes (see for example Refs.15, 19, 21, 22, and 32); in these processes, branching is brought about by active centres, that is free atoms and radicals, which undergo reactions differing qualitatively from decomposition. The lifetimes of these particles in the reaction mixture are much shorter than the time of the development of one chain. Thus the reaction chain during its development becomes branched, in contrast to the case of degenerate branching. The heterogeneous processes responsible for the observed regular features (for example in Refs.16, 19-23, 25-29, 32, 48, and 84) are also not due to the decomposition of intermediate species formed in the homogeneous stages. Moreover, the rates of the heterogeneous stages involving the chain carriers in the processes studied in the works cited are 10 times the rates of the reactions which play a role in degenerate-branched processes.

As noted in Ref.29, the reversible changes in the properties of the surface and the reactions of sorbed species should also have a significant influence in the combustion of hydrocarbons, including "cold flame" conditions and the

†In some liquid-phase oxidation processes, isomerisation of a peroxide radical takes place on the surface, with subsequent decomposition to a valence-saturated molecule and another radical.[102]

negative temperature dependence of the rate. Regular features indicating this type of heterogeneous process were observed in Refs.108–110, where it was shown that in the oxidation of hydrocarbons taking place only in the presence of a heterogeneous catalyst, the self-heating of the mixture in the centre of the reaction vessel is greater than that directly over the catalyst. The authors cited[108–110] also detected "hysteresis" phenomena, fluctuating hydrocarbon combustion conditions above the catalyst.

The emission of excited molecules from the surface into the gas phase, observed in some studies (see for example Ref.111) may also influence the kinetics of the chain reaction, if these molecules are involved in the stage limiting the rate of the process.

It was also pointed out in Ref.29 that the non-stationary nature of the properties of the surface should lead to a change with time in the rate "constant" of heterogeneous deactivation; in this process also, an inverse relationship to the state of the surface should be expected. This must be taken into account in processes taking place with the participation of excited species, including those in fluorination processes. Appreciable non-stationary character may also be shown by the value of the energy accommodation coefficient in heterogeneous recombination, both in chain processes and in plasma-chemical processes.

Thus a large number of new regular kinetic features have been detected for different types of BCP over different surfaces. The principal factors determining these regular features have been revealed. It has been shown that the development of chain combustion with time, and also the dependence of the main characteristics of the process on the initial conditions, differ qualitatively and quantitatively from those expected on the basis of earlier ideas which did not take account of the heterogeneous development of the chains and the reversible change in the efficiency of heterogeneous termination during combustion.

The above examples of the theoretical interpretation of the observed phenomena show that for the description of the regular kinetic features of BCP, the theory should take account of both those reactions whose rates are directly proportional to the concentrations of the chain carriers and those reactions whose rates show a non-linear dependence on these concentrations, while appreciable non-linearity appears in the course of the heterogeneous chain termination. Thus even in the initial stages of chain combustion, when the consumption of the starting materials can still be neglected, the process corresponds to non-linear differential equations.

The reversible changes detected and studied in the last twelve or thirteen years in the state, role, and composition of the solid surface during gas-phase branched-chain reactions, and also the marked influence of these changes on the process as a whole, are opening up new perspectives for the solution of various applied problems. Since heterogeneous recombination is accompanied by fairly strong chemisorption of chain carriers and their reaction with the solid surface, it is possible to bring about a directed change in the composition and properties of surfaces using appropriate chain processes (see for example Refs.22, 83, and 97). By selecting the solid material, it is possible to achieve the removal, from the surface into the gas reaction medium, of active intermediate species with the required chemical character, including species containing atoms from the solid phase.[97] By carrying out appropriate preliminary chemical modification of the surface using a gas-phase process, it is possible to bring about the chain reaction between the given starting materials for given initial conditions and ignition limits at different rates to give different final compositions (see for example Refs.19, 22, and 48).

The subsequent development of the theory of branched-chain processes and the solution of applied problems related to combustion or the existence of heterogeneous chain termination require allowance for the above regular features and factors.

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