

Thermochemical action of laser radiation

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Usp. Fiz. Nauk 138, 45-94 (September 1982)*

The processes induced by laser radiation in chemically active media are examined. Special attention is given to the analysis of different mechanisms of formation of feedback between chemical and thermal degrees of freedom of the system and the resulting complex dynamics of thermochemical processes (such as instabilities, self-oscillation, stochastic regimes, etc.).

PACS numbers: 82.50. — m, 82.20.Hf

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1. INTRODUCTION

Phenomena related to chemical transformations of matter in the field of a powerful light wave occupy a special place among phenomena that result from the interaction of laser radiation with matter.

As is well known, laser radiation can induce chemical reactions in various ways: due to purely thermal action, with the help of resonance excitation of electronic levels of atoms and molecules, as well as due to excitation or breaking of molecular bonds weakened by resonance pumping.¹⁾ In addition, photochemical processes induced by UV and VUV radiation as well as reactions in chemically active laser plasma are being studied intensively. Laser isotope separation should also be mentioned as a special area of laser chemistry. Each of the disciplines indicated solves its own special problems and has its own unique research methods and way of utilizing the unique combination of properties of laser radiation.

¹⁾ Chemical reactions in whose kinetics the excitation of internal degrees of freedom of atoms and molecules by light plays an important role, are called photochemical reactions. They are further subdivided, depending on the magnitude of the excitation energy (compared to the energy of thermal motion of the particles) and the type of excited states, into photochemical processes in the visible range (the term visible range is often omitted), IR photochemical processes, in which excitation of the vibrational levels of molecules is important, etc.

If we follow the history of the appearance of separate areas of laser chemistry, then strange as it may seem the last to appear is laser-induced, thermal initiation of chemical reactions (so-called laser thermochemistry). The reason for this was the conviction of the researchers: "...any application of a quantum generator as a heat source is the most trivial of those possible in chemistry..."¹⁾ To some extent, the absence of interest among physicists in the use of lasers for thermal initiation of chemical reactions also led to the attitude that such research does not require any record-setting parameters of laser radiation. In addition, it was believed that such specific properties of laser radiation as its monochromaticity and coherence do not play a significant role in laser thermochemistry.

A certain amount of time was required to overcome the inertia stemming from these attitudes and to understand the organic connection between laser thermochemistry and such intensively developing disciplines as the theory of nonlinear oscillations and self-oscillatory processes, nonequilibrium thermodynamics and macroscopic kinetics of nonadiabatic reactions, etc. As a result of specific research in recent years in laser thermochemistry, new, nontrivial possibilities for laser control of chemical reactions have been discovered, the number of research papers published has noticeably increased and, most importantly, a definite ideology for research in this area has appeared.

Since laser chemistry is in our opinion a complete science in which the most diverse areas should be de-

veloped equally, we want to draw attention of specialists to resent results obtained in laser thermochemistry, indicate the most interesting work, and describe new phenomena that have been discovered and the level of understanding of the physics of these phenomena that has been achieved.

History of the problem

The history of laser chemistry, beginning soon after the discovery of quantum generators, extends over a period of more than 20 years.¹ The last 15 years have been dominated by research concerning selective photochemical processes. The fundamental results obtained in this area are reflected in the large number of review papers and monographs (as an example, we refer the reader to Refs. 2 and 3, which contain an extensive list of references).

As far as papers on thermal stimulation of chemical reactions using laser radiation are concerned, there were relatively few such papers,²⁾ and not being drawn together by a unified philosophy, they appeared as separate communications which did not add up to a coherent whole. Apparently, for this reason the thermal action of laser radiation was only mentioned in passing in most early reviews. In this respect, several papers in which the idea that such nonphotochemical processes are interesting in themselves was clearly stated are an exception.^{2,4-6} Great interest in thermochemical processes was also shown by researchers working on problems of laser technology.^{7,8}

Since the most interesting papers on laser thermochemistry published up to 1976 were to some extent examined in Refs. 2, 4-8, here we shall restrict ourselves only to some general remarks. During this period, research on laser stimulation of a number of homogeneous combination and exchange reactions, laser pyrolysis of a series of organic compounds, and stimulation of polymerization processes were investigated. A large number of heterogeneous decomposition reactions of organic compounds in the condensed phase, thermal dissociation reactions of a number of semiconducting compounds of the type $A^{III}B^V$, oxidation-reduction reactions on surfaces of solids were also investigated. A number of papers concerned laser-induced synthesis of surface compounds. The corresponding references are contained in Refs. 2 and 4-8.

As a result of this research, the characteristics of the thermochemical action of laser radiation were identified: in many cases, the process did not occur as expected under isothermal conditions at an appropriate temperature. This was manifested both in the complex dependence of the total yield of different reaction products on the laser radiation intensity and in the observed deviation from the isothermal relation between them. In a number of homogeneous reactions, in spite of the high pressure ($P \sim 100-500$ torr) of the gas mixture, when the high VT relaxation rate excludes the

²⁾ According to Ref. 4, approximately 170 papers concerning the thermal action of laser radiation on chemically active media were published up to 1977.

possibility of separating the vibrational temperature from the translational temperature, phenomena that are usually characteristic of IR photochemical processes were nevertheless observed (see Refs. 2, 9, and 10 and references cited therein). The experimental results clearly indicated that the chemical process occurs in a nonequilibrium manner, but the fundamental details of the formation of such a nonequilibrium state remained unclear.

All this presented researchers with the problem of analyzing in greater detail the dynamics of laser heating of chemically active media, stimulated new experiments and the search for adequate theoretical models. This review is concerned with the results of these investigations. We primarily examine work that was completed in the period from 1976 to 1980. In Sec. 2 we discuss the thermal laser control of reactions. In Sec. 3 we examine the basic forms of the dynamics of laser-induced thermochemical processes in systems with a finite number of degrees of freedom, which are described by ordinary differential equations (so-called point systems). Section 4 concerns the dynamics of thermochemical processes in distributed systems described by partial differential equations. Finally, we examine some properties of the propagation of light in homogeneous, chemically active media in Sec. 5.

2. MACROSCOPIC NONEQUILIBRIUM STATE OF THE SYSTEM AND THERMAL FEEDBACK

As is well known,¹¹ a closed system in which chemical reactions occur under conditions of thermodynamic equilibrium is described by a small number of thermodynamic parameters: volume, pressure, temperature and chemical equilibrium constant. However in problems of interest to us here, mass and energy exchange between the systems being examined and the surrounding medium play an important role. Due to this exchange, a given system is not in a state of thermodynamic equilibrium and in order to describe it in detail, it is necessary to know the kinetic equations that determine the reaction rate in each of the reaction channels.³⁾

Establishing the form of such kinetic laws in chemical processes induced by laser radiation represents an independent problem. Let us recall its basic points. If we are talking about homogeneous reactions occurring under the action of IR laser radiation, which is absorbed by the vibrational levels of molecules, then the reaction kinetics depend strongly on the ratio of the rates of energy redistribution relaxation processes between different degrees of freedom of the reacting molecules and the characteristic times of the chemical transformations themselves. If the vibrational excitation of molecules relaxes rapidly into translational energy (this process is described by the VT relaxation time τ_{VT}), then the action of the laser radiation re-

³⁾ The rate of homogeneous reactions is usually defined as the change in the concentration of the substance per unit time, while the rate of heterogeneous reactions is defined as the amount of substance formed (or expended) as a result of a reaction per unit surface per unit time.^{12,13}

duces to equilibrium heating and the reaction occurs by a thermal mechanism. The reaction rate under these conditions depends on a single overall temperature T for the entire system. Of course, this does not exclude the situation when the temperature T can be distributed in the reactor volume in a complicated manner.¹⁴ The thermal and radiative population of states were analyzed in a number of papers¹⁵⁻¹⁹ and the conditions under which the vibrational temperature separates from the translational temperature were determined. The results of this analysis and the experimental data indicate that for mixture pressures ~ 10 torr and higher the reactions occur in a thermal manner.^{2,10,14} Here we should note that there exists in principle a number of possibilities^{9,20,21} for maintaining a nonequilibrium state in the molecule over a time longer than the VT relaxation time of the excited vibrational modes, but, as demonstrated in Refs. 2 and 10 at the present time there is not one experimental situation (for mixture pressures $p \geq 10$ torr) that could not be described by the thermal excitation mechanism.

A somewhat different situation occurs in heterogeneous reactions. In this case, there is a basis for believing that the form of the kinetic law in the presence of IR laser radiation can differ from the case of purely thermal (nonlaser) action. This phenomenon occurs, for example, in some reactions involving heterogeneous oxidation of metals induced by radiation with quantum energy exceeding the width of the forbidden band of the oxide.²² The physical reason for this phenomenon is quite clear. As is well known,¹³ heterogeneous oxidation of metals is a complex process consisting of a series of sequential stages. These include transport of oxygen molecules from the gas volume to the interface between the phases, adsorption of oxygen on the surface, transport of reagents through the oxide layer that separates the reaction products spatially and, finally, the chemical reaction itself. Here, the total reaction rate is limited by the slowest stage. In particular, there exist stages of oxidation when the rate of the process is limited by the electron current arising when chemisorption of oxygen atoms on the oxide surface occurs. By giving rise to electrons in the conduction band of the oxide with the aid of laser radiation it is possible to remove the limitation due to the electronic current. In this case, the total reaction rate will be limited by some other stage of the oxidation process, which changes the form of the kinetic law itself. This area of IR photochemistry of heterogeneous reactions has been intensively developing in recent years.²²

In what follows, we shall examine the thermal processes for which there is a single temperature for all reaction components and we shall assume that the form of the kinetic law and the temperature and pressure dependences of the reaction constants are known. Under these conditions, the nontrivial parts of the problem can be related, in the final analysis, only to the laser induced nonisothermality of the processes and to the details of the formation of the spatial-temporal distribution of the temperature field in the chemically active medium. However such features are not as few in number as may appear at first glance. The nonisothermal-

ity of the process and, more precisely, the complex, programmed form of the temperature field make it possible to realize effective control of chemical processes, while the laser radiation, as will be evident from what follows, is a unique instrument for creating such a temperature field.

a) Macroscopic nonequilibrium state of chemically active media

A chemically active medium left to itself strives to transform in time into some quasiequilibrium state. For closed systems, this will be a thermodynamically stable equilibrium state, characterized by minimum isobaric potential of the system and equal forward and backward reaction rates. For open systems such as flow-through reactors with a constant mass transfer rate, there can be several such stationary states and, in addition, in open systems more complex states can be established, for example, states in which the concentrations of the substances participating in the reaction change in a periodic manner.⁴⁾ The state into which the system will transform among those indicated depends on the values of the reaction rate constants and reactor parameters, as well as on the initial conditions of the problem.

The dynamics of the behavior of a chemically active medium can be represented graphically by constructing the phase picture of the reaction, i.e., by finding the special points, trajectories, etc., in the space defined by the concentrations of the reacting substances.⁵⁾ As an example, Fig. 1 presents the phase picture of one of the models of the catalytic oxidation reaction of carbon monoxide on platinum taken from Ref. 28. The concentrations of the intermediate reaction products $PtO(x)$ and $PtCO(y)$ are shown along the axes of the graph. The system indicated has three stationary states (of which the middle state is unstable) and exhibits relatively simple behavior: dependent on the initial conditions, the system goes into one of two stable, stationary states (catalytic trigger).

In the case of a nonisothermal process, a $(n+1)$ -st degree of freedom, namely, the temperature, is added to the n chemical degrees of freedom of the system. This increase in the number of degrees of freedom increases not only quantitatively but also qualitatively the dynamic possibilities of the system and makes it possible to realize phase trajectories that cannot in principle be attained under isothermal conditions. By varying the

⁴⁾ As an example of chemical systems that exhibit self-oscillations, we mention the autocatalytic oxidation of higher hydrocarbons,¹² the Belousov-Zhabotinskii reactions,^{23,25} kinetic oscillations in the cycle of dark photosynthesis reactions,¹² oxidation of CO on Pt,^{26,27} etc.

⁵⁾ The number and type of singular points and trajectories of the system depend both on the specific form of the kinetic laws and on the number of degrees of freedom of the system. For point systems under isothermal conditions the number of degrees of freedom is determined by the number of reaction channels. In a system with a single degree of freedom, only stationary states can be established, while in systems with two and more degrees of freedom self-oscillations, etc. can arise.

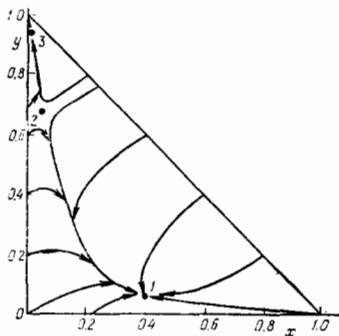


FIG. 1. Phase diagram of oxidation reaction of CO on Pt. $T = 500$ K; $p_{\text{CO}} = 0.23 \cdot 10^{-6}$ Torr; 1, 3) stable stationary states: $x_1 = 0.4$, $y_1 = 0.067$, $x_3 = 0.2 \cdot 10^{-4}$, $y_3 = 0.987$; 2) unstable stationary state: $x_2 = 0.15 \cdot 10^{-1}$, $y_2 = 0.675$ ²⁸.

temperature in a special manner, it is possible to control the chemical process, for example, to switch catalytic trigger-type systems.

Here we have arrived at an important aspect of the problem of controlling reactions, namely, the problem of the limits to the response of the chemically active medium to thermal action. Let us explain what we have in mind. Assume that the temperature changes so slowly that chemical relaxation has time to occur in the system. In this case, the system, located, for example, in a stable stationary state, will remain in this state, i.e., its phase trajectory will coincide with the trajectory of the stationary state. If with such motion several stationary points coalesce, then the system can exhibit hysteresis in the process of adiabatic heating and cooling, i.e., it can return to the state from which it started along a different phase trajectory.

Much greater possibilities for controlling the behavior of the system appear in the case of rapid, nonadiabatic heating. If the temperature in the system changes more rapidly than chemical relaxation occurs in it, then the phase trajectory of the system will move farther away from the trajectory of the given stationary state and macroscopic chemical nonequilibrium will arise in the system.⁶⁾ The nonequilibrium phase trajectory can enter a region of attraction of another stationary state or a limit cycle and so on. As a result, it is possible to switch the regime in which the reaction occurs, to freeze the macroscopic nonequilibrium state with rapid cooling of the system, etc. In all these cases new possibilities for displacing the reaction into the desired direction appear.

As far as the chemical relaxation times are concerned, it is usually not difficult to determine them

⁶⁾ IR photochemistry is based essentially on the same idea only on the microsystem level: the energy is pumped into the chosen mode more rapidly than VT relaxation occurs, as a result of which the vibrational temperature differs from the translational temperature. However, the characteristic relaxation times of micro- and macrosystems differ strongly (the macrosystem can relax quite slowly). Due to this difference, it is much simpler to create a macroscopic nonequilibrium state in the system than a microscopic nonequilibrium state.

when the system is not far from a quasiequilibrium state. We shall demonstrate this for a system with two degrees of freedom. Let the kinetics of the reaction be determined by equations of the form

$$\frac{dx}{dt} = \Phi(x, y), \quad \frac{dy}{dt} = \Psi(x, y), \quad x|_{t=0} = x_0, \quad y|_{t=0} = y_0, \quad (2.1)$$

where x and y are the concentrations of the reacting substances.

If system (2.1) has the stationary solutions $x = x'$, $y = y'$ (there can be several of them), then there arises the problem of investigating the singular points of the system (2.1), which is a well-known problem in the theory of nonlinear oscillations.^{29,30} For small deviations from the equilibrium position, the nature of the relaxation of the perturbation is determined by the roots of the characteristic equation

$$\mu^2 - (a + d)\mu + (ad - bc) = 0, \quad (2.2)$$

where

$$a = \Phi'_x(x^*, y^*), \quad b = \Phi'_y(x^*, y^*), \quad c = \Psi'_x(x^*, y^*), \quad d = \Psi'_y(x^*, y^*). \quad (2.3)$$

As is well known,^{29,30} depending on the signs and magnitudes of the real and imaginary parts $\mu_{1,2}$, four types of singular points are distinguished: saddle, node, focus, and center. There are two relaxation times $\tau_{1,2} = (\text{Re } \mu_{1,2})^{-1}$ near the stable singular points.

Aside from the singular points, singular trajectories of the system can also exist on the phase surface: limit cycles (closed curves which the phase trajectories approach asymptotically). If the system contains a limit cycle, then an additional characteristic time appears; the period of self-oscillations.

In addition to relaxation into the stationary state, another case is also of interest. Assume that the functions $\Phi(x, y)$ and $\Psi(x, y)$ in (2.1) do not vanish simultaneously and the system (2.1) does not have a stationary state.⁷⁾ However, a definite relation is established in time between the components x and y

$$x = f(y), \quad (2.4)$$

which "does not remember" the initial values x_0 and y_0 . In such a system, relaxation to the quasiequilibrium state (2.4) occurs. We shall find the corresponding relaxation time. Assume that at some time relation (2.4) breaks down:

$$x = f(y) + \delta(t), \quad |\delta(t)| \ll f(y). \quad (2.5)$$

Substituting (2.5) into (2.1) yields an equation for $\delta(t)$:

$$\dot{\delta} = -\delta \cdot \tau_x^{-1}, \quad \tau_x^{-1} = f' \Psi'_x(f(y), y) - \Phi'_x(f(y), y). \quad (2.6)$$

The time τ_x describes the corresponding relaxation. We note the following circumstance. The time τ_x depends on the quantity y [or, according to (2.5), on x] and therefore on the time t as well. It is for this reason

⁷⁾ As an example, we mention the heterogeneous oxidation reaction of copper.³¹ This reaction occurs along two channels with the formation of oxides of different stoichiometric composition, which form a two-layer oxide film $\text{CuO}/\text{Cu}_2\text{O}/\text{Cu}$ on the copper surface. The kinetics of such oxidation (Eq. (2.1)) is in this case given by the Wagner-Valensi equations,³¹ which are examined below (see Sec. 3b).

that the given nonstationary situation differs considerably from the case of relaxation to a stationary state.

The second relaxation time can be obtained by destroying the relation (2.4) as a result of a deviation of the concentration of component y from the equilibrium value $y = \varphi(x)$:

$$y = \varphi(x) + \xi(t), \quad |\xi(t)| \ll \varphi(x). \quad (2.7)$$

In this case, instead of the time τ_x , we obtain another time τ_y that does not coincide in general with τ_x :

$$\tau_y^{-1} = \varphi' \Phi'_y(x, \varphi(x)) - \Psi'_y(x, \varphi(x)). \quad (2.8)$$

Sometimes, for example, in the case of two-layer oxidation, where $x = u_0 y$, $u_0 = \text{const}$ (see Sec. 3b), these times can be reduced to a single time with a simple transformation of variables.

Thus, if the characteristic times over which the temperature changes with heating satisfy the condition $\Delta t \ll (\text{Re } \mu_{1,2})^{-1}$ or $\Delta t \ll (\tau_x, \tau_y)$, then the process occurs under conditions of strong macroscopic nonequilibrium of the system. It is easy to see that a laser is a convenient means for creating a measured nonequilibrium state in the system in order to realize a specific action on the course of the chemical reaction.

b) Selective and nonselective thermal feedback

It is well known that the high heating rates necessary for the appearance of macroscopic nonequilibrium state may be created by means other than with the help of a laser. They can be created with the aid of electron beams, electric current, furnace walls, etc. In this connection, it is interesting to elucidate the characteristics of laser action in particular.

As shown in Ref. 32, the most important characteristic is as follows. The change in the temperature of the reagents during the course of a chemical reaction under the action of laser radiation does not only indicate an increase in the number of degrees of freedom of the system. A very significant fact is that the thermal and "chemical" degrees of freedom of the system are coupled to one another. This coupling, on the one hand, stems from the Arrhenius temperature dependence of the reaction rate constants and on the other hand on the change in the absorbing characteristics of the system during the course of the chemical reaction. We note that in addition to heat liberated in the system as the result of the absorption of laser radiation energy, during the course of the reaction purely chemical energy related to the heat of the reaction is also liberated (or absorbed). We shall denote the intensity of energy liberation by such chemical sources by $P_{\text{ex}}^{(i)}$, where i is the number of the reaction channel.

We shall now examine as an example the simplest case when the laser radiation acts on a thermally small volume. In this case, it may be assumed that the temperature is the same at all points of the volume and heat conduction effects can be neglected. The variation of the temperature of such a system will be described by the heat balance equation

$$mc \frac{dT}{dt} = \sum_i P_{\text{ex}}^{(i)} + P(t) A(x_1, \dots, x_n) - P_{\text{loss}}(T), \quad (2.9)$$

where $x_j = x_j(t)$ are the concentrations of the reacting substances, m and c are the mass and heat capacity of the system, $P(t)$ is the power of the laser radiation incident on the system, $P_{\text{loss}}(T)$ is the power of the thermal losses, and A is the absorptivity of the system.

In the general case, the absorption of radiation is described by a function that depends on the concentrations of all the reacting substances. However, the monochromaticity of the laser radiation permits with an appropriate choice of wavelength (especially, in the IR region of the spectrum) introducing thermal energy into the system only through one of the components of the reaction, for example, the j -th component. We shall call thermal coupling of this kind, when the laser radiation is introduced through a preselected reaction channel, selective coupling.

The selectivity of thermal feedback leads to completely different forms of dynamic behavior of the system as a result of laser action when the wavelength of the radiation is tuned from one reaction component to another. If the radiation is absorbed by the final reaction product and the forward reaction is accelerated under the action of heat, then positive feedback is realized in the system: as the concentration of the product increases, absorption increases, the temperature of the system increases, and self-acceleration of the reaction occurs (thermochemical instability). If, on the other hand, radiation is absorbed by the starting substance, then negative feedback is established in the system and the chemical process is self-stabilized. In this case, when laser radiation is absorbed reasonably by some intermediate reaction product, the nature of the feedback can change during the course of the chemical process.

In this case, it is significant that the radiation power $P(T)$ plays the role of a transmission factor along the feedback channel, which makes it possible to control the behavior of the system by varying the power.

As an example of a system with selective thermal feedback, we shall examine the model of a flow-through, homogeneous, chemical reactor with ideal mixing, in which an exothermal reaction occurs: $X \rightarrow Z + Q$ (X is the starting substance, Z is the reaction product, and Q is the heat liberated). Such a model was examined in Refs. 33 and 30 in the absence of laser radiation. We shall now examine the effect of the heat liberated as a result of laser action on the dynamics of the process occurring in the reactor.

The change in temperature γ and concentration x as a function of time τ (all quantities are written in dimensionless form) in the model being examined are described by a system of two equations^{32,34}

$$\begin{aligned} \frac{dx}{d\tau} &= -x \exp\left(-\frac{1}{y}\right) + \lambda(x_0 - x), & x|_{\tau=0} &= x_{\text{in}}, \\ \frac{d\gamma}{d\tau} &= x \exp\left(-\frac{1}{y}\right) + \beta(y_0 - \gamma) - \gamma f(x), & \gamma|_{\tau=0} &= \gamma_{\text{in}}, \end{aligned} \quad (2.10)$$

where the parameter λ characterizes the flow-through efflux velocity of the mixture of products and reagent out of the system, β is the heat transfer coefficient, x_0 is the concentration at the reactor inlet, y_0 is the effective temperature of the reactor walls, γ is a con-

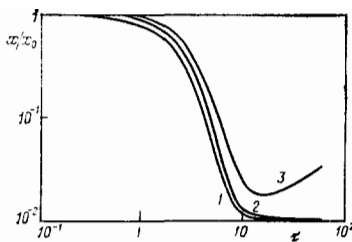


FIG. 2. The change in concentration of the reacting component as a function of the time τ , obtained by numerical integration of the system (2.10). Parameter values: $\lambda = 0.01$, $\beta = 0.03$, $x_0 = 0.5$, $y_0 = 0.125$, $\gamma = 1$, $x|_{\tau=0} = x_0$, $y|_{\tau=0} = y_0$. Curves 1, 2, and 3 show the radiation absorbed by the buffer gas, the reaction product, and the starting substance.²⁴

stant proportional to the laser radiation power, and $f(x)$ is the normalized absorptivity of the substance.

The last term in (2.10) describes different cases of action of laser radiation on the system: $f(x) = 1$ corresponds to resonant absorption of radiation by an added buffer gas that does not participate directly in the reaction; $f(x) = x$ corresponds to absorption of radiation by the starting substance (negative feedback); $f(x) = 1 - x$ corresponds to absorption of radiation by the reaction products (positive feedback). In all cases (even with identical initial states of the system), the results of laser action on the medium will differ when the radiation wavelength is tuned from one reaction component to another. Figure 2 shows an example of the numerical integration of the system (2.10) when all three cases examined are described by the constant γ and have the same initial concentration of starting substance x_{1n} .

The phase picture of the system examined (2.10) can be analyzed in a standard manner (see Ref. 30) with the help of bifurcation curves, i.e., curves along which the critical values of some parameters are conserved; in regions separated by the bifurcation curve, the type (or number) of singular points and trajectories of the system differ. In this case, it is convenient to represent the equations for these curves in parametric form in the coordinates x_0, y_0 for fixed β and λ .

One such bifurcation curve is the curve of saddle boundaries which, as is easily verified (see Ref. 30), coincides with the curve separating regions with one and three stationary solutions. This curve is described by the equation

$$\Delta \equiv ad - bc = 0, \quad (2.11)$$

where the quantities a , b , c , and d are determined from (2.10) by Eqs. (2.3). In parametric form (y_* is a parameter), these equations appear as follows:

a) if radiation is absorbed by the starting substance, then

$$\begin{aligned} x_0 &= \frac{\beta y_*^2 \exp(-1/y_*)}{\lambda(\lambda - \gamma)} \left[1 + \lambda \exp\left(\frac{1}{y_*}\right) \right]^2, \\ y_0 &= y_* - \frac{y_*^2 \exp(-1/y_*)}{\lambda - \gamma} \left[1 + \lambda \exp\left(\frac{1}{y_*}\right) \right] \left[1 + \gamma \exp\left(\frac{1}{y_*}\right) \right]; \end{aligned} \quad (2.12a)$$

b) if radiation is absorbed by the reaction products, then

$$\begin{aligned} x_0 &= \frac{\beta y_*^2 \exp(-1/y_*)}{\lambda(\lambda + \gamma)} \left[1 + \lambda \exp\left(\frac{1}{y_*}\right) \right]^2, \\ y_0 &= y_* - \frac{y_*^2 \exp(-1/y_*)}{\lambda + \gamma} \left[1 + \lambda \exp\left(\frac{1}{y_*}\right) \right] \left[1 - \gamma \exp\left(\frac{1}{y_*}\right) \right] - \frac{\gamma}{\beta}. \end{aligned} \quad (2.12b)$$

The case when laser radiation acts on the buffer gas is obtained from the case $\gamma = 0$ (absence of laser action) with the help of simple equations: $x_0 = x_0(\gamma = 0)$, $y_0 = y_0(\gamma = 0) - \gamma/\beta$. This is easy to see directly from (2.10).

The second bifurcation curve, the boundary of stability of nonsaddle type singular points, is given by the equation

$$\sigma \equiv -(a + d) = 0. \quad (2.13)$$

In parametric form, the equations for x_0 have an identical form for all three cases examined:

$$x_0 = \frac{y_*^2}{\lambda} \left[\beta + 2\lambda + \lambda(\beta + \lambda) \exp\left(\frac{1}{y_*}\right) - \exp\left(-\frac{1}{y_*}\right) \right], \quad (2.14)$$

while the equations for y_0 have the form:

a) if radiation is absorbed by the starting substance, then

$$y_0 = y_* - \frac{y_*^2}{\beta} \left[\beta + \lambda + \exp\left(-\frac{1}{y_*}\right) \right] \left[1 + \gamma \exp\left(\frac{1}{y_*}\right) \right]; \quad (2.14a)$$

b) if radiation is absorbed by the reaction product, then

$$y_0 = y_* - \frac{y_*^2}{\beta} \left[\beta + \lambda + \exp\left(-\frac{1}{y_*}\right) \right] \left[1 - \gamma \exp\left(\frac{1}{y_*}\right) \right] - \frac{\gamma}{\beta}. \quad (2.14b)$$

The case of laser action on the buffer gas is described by the equation

$$y_0 = y_0(\gamma = 0) - \gamma/\beta.$$

These pairs of bifurcation curves are illustrated in Fig. 3 for the case $\beta \gg \lambda^2$ and $\gamma \ll \lambda$. The wedge-shaped curves correspond to the boundary of existence of saddle points, while the loop-shaped curves correspond to the boundary of stability of nonsaddle point singularities. In each of the regions 1–6 (for each pair of bifurcation curves), the phase pictures of the system differ topologically (see Ref. 30 for more detail). For example, in region 2, there exists a stable limit cycle around a single unstable singular point, etc.

Different pairs of bifurcation curves can "creep" onto one another depending on the relations between the parameters λ , β , and γ (for example, with decreasing γ), as a result of which the same point in the space of the parameters x_0 , y_0 , λ , β , and γ can correspond to different dynamics of the stationary motion for systems with different forms of feedback. Thus, even under identical conditions, the reaction can occur completely differently depending on what is absorbing the radiation:

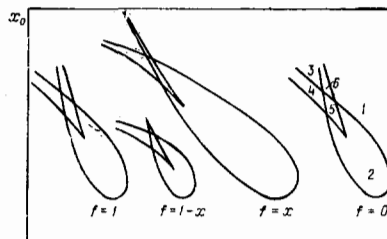


FIG. 3. Typical form of the bifurcation curves (2.11), (2.13) in the case $\beta \gg \lambda^2$, $\gamma \ll \lambda$.³⁴

initial substance, reaction product, or buffer gas.⁸⁾ For this reason, the widely held opinion that only in the case of photochemical processes can the reaction yield change depending on which of the substances absorbs the IR laser radiation energy (tests for the laser-chemical potential of the reaction⁹⁾ is, strictly speaking, incorrect. A difference in the reaction yield will also be observed in the case of thermochemical action of laser radiation in nonequilibrium systems with selective thermal feedback.

It should be noted that selective feedback is characteristic of processes other than thermochemical processes as well. It can also be observed in photochemical reactions. An example is photoaging of polyvinyl chloride under the action of UV radiation.³⁵ The products of the photodecomposition of the polymer forming as a result of the reaction strongly absorb UV radiation and screen the lower-lying layers of polymer from penetration of UV quanta into them. As a result of this, the photochemical reaction is localized on the surface ("aging waves").

Further, it is evident from (2.10) that laser radiation power plays the role of a transfer coefficient along the feedback channel. For this reason, by changing the power of the laser radiation, it is possible to control the thermochemical process. It is easy to see that the possibilities of laser control are not restricted, for example, to control with the aid of characteristic parameters of the chemical reactor (x_0 , y_0 , λ , and β), not to mention the fact that it is much more complicated to control heat transfer or concentration parameters at the reactor inlet than the laser radiation power.

The possibilities of laser control can be broadened in the case of complex reactions with a large number of channels. Under such conditions, it is possible to use the combined action of radiation at different frequencies, thereby realizing different forms of selective feedback along different reaction channels. Here we are talking about creating conditions such that relatively simple forms of laser action (for example, slowly varying continuous radiation power plus pulsed actions, switched on at given times) permit thermal control of processes for which a very complex time dependence of the temperature field is required. We emphasize that this is achieved due to the high self-adaptability of a chemically active medium encompassed by feedback.⁹⁾

⁸⁾We note that the different nature of thermal feedback in thermochemical processes could be a result of not only phenomena related to the change in the concentration of reacting substances but also to the temperature dependence of the absorption coefficient. For homogeneous reactions, such a dependence could result, for example, from the appearance of "hot absorption bands" in the IR region of the spectrum for a number of molecules, such as SF₆, freon C₃F₄C₁₂ and others (see Refs. 2, 10, 14), as a result of which, the maximum in the absorption coefficient shifts into the long wavelength region of the spectrum.

⁹⁾We note at the same time that the use of the combined interaction regimes is of interest in itself for studying nonlinear optical phenomena in semiconductors.³⁶ Here ideas that are in many ways related to the ideas of laser thermochemistry are used.

c) Characteristics of thermochemical processes in distributed systems

So far we have discussed laser control of point systems, i.e., systems with a finite number of degrees of freedom. A number of new characteristics arises with the action of laser radiation on distributed systems, which already have an infinite number of degrees of freedom and are described by partial differential equations. These new characteristics are related to the details of the spatial distribution of the temperature field, established in the chemically active medium under the action of laser radiation. We shall consider some of them.

For definiteness, we shall primarily discuss homogeneous reactions. As noted in Refs. 2, 10, 14, and 37, IR laser heating of reacting substances is distinguished by a "high degree of homogeneity." Here we have in mind the fact that as a result of the volume absorption of radiation energy in the laser interaction region, the temperature at the center of the reactor can greatly exceed the temperature of its input and output windows. For this reason, the effect of heterogeneous processes on the course of the reaction is practically excluded, which is difficult to achieve with the usual heating methods, when heat is transferred to the gas by the reactor walls. In this respect, the experiments in Ref. 14 are most convincing in our opinion. In these experiments it was shown that with the usual heating of a mixture of C₆F₅H and Br₂ in a quartz reactor up to 900 K a large number of products appeared with the participation of heterogeneous reactions (in particular, such products as resin, soot, SiF₄ and others), while when the same mixture was heated with a CO₂ laser up to 900 K and higher the only reaction products were C₆F₅Br and HBr.

Further, the dielectric permittivity of the mixture of starting substances and reaction products at the laser wavelength usually changes during a chemical reaction. This leads not only to a change in the absorbing characteristics of the system, but also to special features in the propagation of radiation through a medium with such chemical inertial nonlinearity, for example, to self-focusing or self-defocusing of radiation.³⁸ These phenomena, in their turn, affect the course of the chemical reaction. Thus, in the case of self-focusing of radiation, appreciably higher temperatures than in the rest of the reactor volume can be attained in the caustic of the "chemical lens." At the same time additional reaction channels can open up and so on.

As noted in Ref. 4, nonuniform heating of the reactor volume also leads to the fact that the mass yield of reaction products increases for products with higher activation energy compared to the case of uniform heating (with identical average temperature in both cases).

The kinetic phenomena examined above have so far concerned only the temperature dependence of the reaction rate constants. However, in connection with the fact that the reaction rate depends not only on temperature but also on the concentrations of the reacting substances, distributed systems have additional peculiari-

ties related to the details of the diffusion processes under the action of laser radiation. Indeed, the concentrations of substances participating in the reaction vary as a result of the chemical reaction itself and as a result of the diffusion of components. Which of these processes dominates depends on the relation between the characteristic rates of these processes. We recall that the diffusion coefficient itself often depends on the temperature in an activation manner: $D = D_0 \exp(-T_0/T)$, $D_0 = \text{const}$, $T_0 = \text{const}$. Moreover, in laser thermochemistry, in many cases thermal diffusion flow resulting from a temperature gradient can play a role in addition to the diffusion flow resulting from a concentration gradient. As a result, the general expression for the total diffusion flux j has the form³⁹

$$j = -D\nabla c - \frac{D_T}{T} \nabla T,$$

where c is the concentration and D_T is the thermal diffusion coefficient. For example, in the case of diffusion of a light gas in a heavy gas, this leads to the fact that in the process of establishing diffusion equilibrium in a nonuniformly heated gas the light gas concentrates in locations with the higher temperature.³⁹ We note that under nonequilibrium conditions the concentration and temperature gradients can be oriented arbitrarily relative to one another. Since large temperature gradients can be formed in the process of laser heating of matter, thermodiffusion can have an appreciable effect on the course of chemical reactions.⁴⁰ However, previously no attention was paid to the fact that positive feedback can arise for thermodiffusion processes with resonant absorption of energy by one of the components of the mixture. Under these conditions, the thermodiffusion instability will develop and stratification of the mixture will occur.¹⁰⁾ This is an example of a process when the entropy of the system decreases under the action of laser radiation.

For sufficiently fast reactions, special features can also appear in the scattering of laser radiation. Indeed, let us consider a medium in which exothermal reactions occur. Then, with a local increase in the radiation intensity in some region, the temperature in this region will increase and the reaction will be accelerated. This in turn will lead to a further increase in temperature (due to liberation of energy by the reaction itself) and a local increase in pressure. The nonuniform increase in temperature and pressure modulates the index of refraction of the gas. This mechanism for nonlinear self-action of light in the thermodynamically nonequilibrium medium was first examined in Ref. 43, where a chemically active medium was produced in process of photodissociation of compounds of the type CF_3I under the action of UV radiation. However, it is easy to see that the manner in which the active medium is prepared does not play a fundamental role.

The main difference between such chemical scatter-

¹⁰⁾ This process differs from the process of light-induced diffusion, examined in Refs. 41 and 42. For light-induced diffusion, the Doppler broadening of the absorption line must greatly exceed its collisional broadening, i.e., we are talking about quite low pressures of the mixture.

ing and other well studied forms of scattering, for example, stimulated Mandel'shtam-Brillouin scattering (SMBS), as shown in Ref. 43, lies in the fact that the energy causing the perturbation of the medium is taken primarily from the chemical source (exothermal reaction) and not from the light field itself. The light itself is only a controlling element initiating the exothermal reaction. In this case, the gain of such chemical scattering exceeds by a factor of 10^2 – 10^3 the typical values of the gain with SMBS in liquids and gases.⁴³ A number of new phenomena appears in the case of thermal initiation of heterogeneous reactions by laser radiation. In particular, new properties of the mechanism of formation of thermal feedback appear. For example, the polarization and angle of incidence of the radiation begin to play an important role in a number of processes.⁴⁴ New aspects also appear in the dynamics of diffusion processes^{45,46} and so on.

The set of phenomena indicated leads to the fact that the dynamics of laser-driven thermochemical processes in distributed systems can be very complex. It is enough to recall the possibility of a stochastic regime for the course of a reaction (see Sec. 3f for more detail).

Since the purpose of this section was to give only an introductory view of laser thermochemistry, here we did not describe in detail such thermochemical processes. This will be done in what follows. However, even the general considerations presented above, in our opinion, are sufficient to appreciate the uniqueness of laser thermochemistry and to understand the types of problems that we shall discuss.

3. DYNAMICS OF LASER-INDUCED THERMOCHEMICAL PROCESSES IN POINT SYSTEMS

In this section, we shall show with the aid of several examples how the general ideas discussed above are manifested in real situations, i.e., for a specific form of the reaction kinetics, specific mechanisms for changing the absorption characteristics, etc.

It was already mentioned above that the rate of a chemical reaction can be limited by a number of factors. Let us examine, for example, the oxidation of metal in air. One of the most important limiting factors for this process is diffusion of the starting substances through the layer of reaction products (oxide). Since oxygen and metal ions diffuse predominantly and not the neutral atoms, for thin oxide layers electric fields, arising with the separation of charges in the surface layer, strongly affect the diffusion process. For thick oxide layers, the nature of the process changes and the reaction rate is primarily determined by diffusion related to the concentration gradient. This important case is described by a parabolic law¹³:

$$\frac{dx}{dt} = \frac{d(T)}{x}, \quad d(T) = d_0 \exp\left(-\frac{T_d}{T}\right) \quad (3.1)$$

with a characteristic Arrhenius temperature dependence of the constant $d(T)$ ($d_0 = \text{const}$, $T_d = \text{const}$), x is the thickness of the oxide film.

The rate of oxidation can also be limited by diffusion of oxygen in the air toward the surface of the target. In this case, instead of (3.1), more complex expressions arise. For example, in the quasistationary approximation³⁴ we have

$$\frac{dx}{dt} = \frac{d(T)/x}{1 + [\mu \cdot d(T)/x]}, \quad \mu = \frac{R}{D} \frac{\rho'_0}{\rho_0}, \quad (3.2)$$

where R is the effective size of the target, D is the coefficient of diffusion of oxygen in air, ρ'_0 and ρ_0 are the densities of oxygen in the oxide and in air, respectively. It is evident that for $\mu d/x \ll 1$, (3.1) is valid, while in the opposite case, $dx/dt = 1/\mu \approx \text{const}$, i.e., the rate of the reaction is entirely determined by diffusion of oxygen in air.

We shall not discuss further the different kinetic laws and shall proceed to examine specific thermochemical phenomena, introducing the kinetic equations as necessary.

a) Thermochemical instability

In nonisothermal processes, which are of concern in laser thermochemistry, as a result of the Arrhenius temperature dependence of the reaction rate constants, the so-called thermochemical instability, namely, avalanche-like acceleration of the reaction after some characteristic time t_a after the beginning of the process (t_a is the induction period or the reaction activation time) is often observed. This phenomenon occurs both for homogeneous⁶ and heterogeneous reactions.⁴⁷ It is analogous to the inflammation process¹² in combustion physics.

We shall find this time for a simple homogeneous reaction, during which the absorptivity increases linearly with temperature. For a closed system this problem is described by the following equations (in dimensionless variables):

$$\begin{aligned} \frac{dx}{d\tau} &= -x \exp\left(-\frac{1}{y}\right), & x|_{\tau=0} &= 1, \\ \frac{dy}{d\tau} &= \beta(y - y_0), & y|_{\tau=0} &= y_1 \quad (y_1 > y_0); \end{aligned} \quad (3.3)$$

where x is the concentration, y is the temperature, and the quantity β is proportional to the incident laser radiation power.

We shall define the activation time τ_a as the time at which the reaction rate is maximum: $(d^2x/d\tau^2)|_{\tau=\tau_a} = 0$. From (3.3) it is easy to find that the time $\tau_a \geq 0$ exists only when

$$\beta \geq z \exp\left(-\frac{2}{z-1}\right), \quad z = 2\left(y_0 + \sqrt{y_0^2 + \frac{1}{2}}\right) \geq 1. \quad (3.4)$$

If the typical small parameters of the problem are used ($(x_1 - y_0)/y_0 \ll 1$, $\exp(-1/y_0) \ll 1$, $1 - x(\tau_a) \ll 1$, then integrating (3.3) and substituting the corresponding dependences $x(\tau)$ and $y(\tau)$ into the equation $d^2x/d\tau^2 = 0$, we find that

$$\tau_a \approx \frac{1}{\beta} \ln \left[\frac{1}{\beta} \frac{y_0^2}{y_1 - y_0} \exp\left(-\frac{1}{y_0}\right) \right]. \quad (3.5)$$

In the problem examined, the reaction was activated on a background of continuous, rapid increase in temperature. We shall call this type of activation rapid ac-

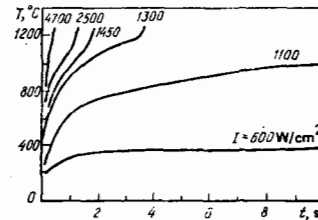


FIG. 4. Time dependence of the target temperature, obtained by heating a steel target with thickness 0.25 mm with different radiation flux densities.⁴⁷

tivation, the time τ_a is insensitive to the parameters of the problem.

In contrast to this, in many problems activation occurs under conditions of a slow change in temperature (quasistationary process). This situation is often encountered, for example, in the case of exothermal reactions. In this case, the reaction can be activated also in the absence of laser radiation (a typical case is spontaneous inflammation¹²).

As will be seen in what follows [Eqs. (3.11) and (3.14)], an exponential dependence of the activation time on the inverse quasistationary temperature is characteristic of quasistationary processes.

In laser thermochemistry, situations when the positive feedback is formed in a system as a result of a variation in the concentration of the reaction products are of special interest. An example is the heterogeneous oxidation reaction of metals in air under the action of CO₂ laser radiation. This type of thermochemical instability was first observed experimentally in Ref. 47 (Fig. 4) and was examined theoretically and experimentally for different cases in Refs. 48–55.

We shall examine the initial stage of heating of a metallic target oxidizing in air. This problem is described by the following system of equations^{52,53}

$$\begin{aligned} \frac{dx}{dt} &= \frac{d}{x} \exp\left(-\frac{T_d}{T}\right), & x|_{t=0} &= 0, \\ m c \frac{dT}{dt} &= P A(x) - P_{\text{loss}}(T), & T|_{t=0} &= T_{\text{in}}, \\ A(x) &= A_0 + b x^2, \\ P_{\text{loss}}(T) &= \eta s (T - T_{\text{in}}), \end{aligned} \quad (3.6)$$

where T is the temperature, x is the thickness of the oxide film on the metal surface, $A(x)$ is the absorptivity of the layered metal+oxide system, A_0 is the absorptivity of the metal, P_{loss} is the power of convective heat losses, η is the convective heat transfer constant, s is the surface area of the target, m is the mass, c is the specific heat capacity of the target, P is the incident laser radiation power, and d and T_d are constants in the parabolic oxidation law.

We introduce the following dimensionless variables:

$$\begin{aligned} y &= \frac{T}{T_d}, & \tau &= \frac{\eta s}{m c} t, & y_{\text{in}} &= \frac{T_{\text{in}}}{T_d}, \\ \mu &= \frac{2 b d P m c}{T_d (\eta s)^2}, & y_0 &= \frac{1}{T_d} \left(T_{\text{in}} + \frac{P A_0}{\eta s} \right). \end{aligned} \quad (3.7)$$

Typical small parameters of the problem are $y_{\text{in}} \ll 1$, $y_0 \ll 1$, and $\mu \ll 1$.

Using (3.7), it is easy to reduce problem (3.6) to a

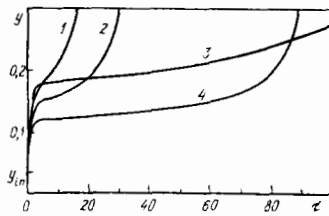


FIG. 5. Examples of numerical solution of Eq. (3.8). $\gamma_{in} = 0.03$. Values of parameters on curves: 1) $\mu = 1$, $y_0 = 0.18$, 2) $\mu = 1$, $y_0 = 0.15$, 3) $\mu = 0.1$, $y_0 = 0.18$, 4) $\mu = 1$, $y_0 = 0.12$.

single differential equation

$$\frac{d^2y}{d\tau^2} + \frac{dy}{d\tau} - \mu \exp\left(-\frac{1}{y}\right), \quad (3.8)$$

$$y|_{\tau=0} = y_{in}, \quad \frac{dy}{d\tau}|_{\tau=0} = y_0 - y_{in}.$$

Examples of the numerical solution of Eq. (3.8) are shown in Fig. 5. We shall define the activation time as the time at which $(d^2y/d\tau^2)|_{\tau=\tau_a} = 0$.

Equation (3.8) can be solved approximately by iteration:

$$y^{(0)} = y_0 + (y_{in} - y_0) \exp(-\tau), \quad (3.9)$$

$$y^{(1)} = y^{(0)} - \mu \int_0^\tau [1 - \exp(\tau_1 - \tau)] \exp\left(-\frac{1}{y^{(0)}(\tau_1)}\right) d\tau_1,$$

and so on.

Considering only the first iteration, we obtain an equation for determining the activation time

$$y_0 \exp(-\Phi) - \text{Ei}(-\Phi) = \tau_0, \quad \Phi = \frac{1}{y} - \frac{1}{y_0}, \quad \tau_0 = \frac{y_0^2}{\mu} \exp\left(\frac{1}{y_0}\right), \quad (3.10)$$

where $\text{Ei}(-\Phi)$ is the integral exponential function.

Substituting (3.9) into (3.10) it is easy to obtain equations for rapid ($\Phi \gg 1$) activation and in the quasistationary case ($\Phi \ll 1$):

$$\tau_a \approx \frac{1}{y_0 - y_{in}} \left[\ln^{-1} \left(\frac{\mu}{y_0 - y_{in}} \right) - y_{in} \right] \quad \text{for } \Phi(\tau_a) \gg 1,$$

$$\tau_a \approx \frac{y_0^2}{\mu} \exp\left(\frac{1}{y_0}\right) \quad \text{for } \Phi(\tau_a) \ll 1. \quad (3.11)$$

Equations (3.11) describe well a number of experimental data (Fig. 6).

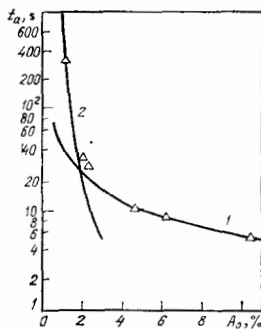


FIG. 6. Theoretical and experimental dependences of the activation time t_a of the oxidation reaction on the value of the initial absorptivity of the target A_0 for oxidation of copper in air by continuous CO_2 laser radiation. Curve 1 was calculated using Eq. (3.11) for $\Phi \gg 1$ (fast activation) and curve 2 was calculated using Eq. (3.11) for $\Phi \ll 1$ (quasistationary heating). The triangles show the experimental points.^{52,53}

Concluding this subsection we shall present a general equation obtained in Ref. 54 for the activation time of the reaction with quasistationary laser heating of oxidizing metals. It is assumed that the stationary temperature T_0 is determined from the conditions

$$PA_0 = P_{\text{loss}}(T_0), \quad P_{\text{loss}}(T) = \nu T^m.$$

The oxidation kinetics are described by an arbitrary exponential law

$$\frac{dx}{dt} = \frac{b_m}{x^m} \exp\left(-\frac{T_m}{T}\right), \quad (3.12)$$

and the following expression is used for the absorptivity

$$A(x) = A_0 + \alpha x^l. \quad (3.13)$$

In this case, we obtain the following equation for the activation time t_a :

$$t_a = \frac{1}{2} \sqrt{\frac{2\tau}{s}} \left(1 + \frac{1}{\sqrt{2s}} \Phi\left(\sqrt{\frac{s}{2}}\right) \right) \frac{1}{l b_m} \left(\frac{A_0 T_0}{\alpha T_m} \right)^l \left(\frac{ns}{l} \right)^s \exp\left(\frac{T_m}{T_0}\right), \quad (3.14)$$

$$s = \frac{m+1}{l},$$

where $\Phi(x)$ is the probability integral. This equation is obtained in calculating the integral using the saddle point method and differs by a numerical factor of the order of unity from equations of the type (3.11).

b) Interference phenomena

In 1977 it was discovered experimentally^{56,57} that the absorptivity of many metals changes nonmonotonically with laser heating in air (Fig. 7).

The reason for this phenomenon was first explained in Refs. 58 and 59 and consists of the fact that during the growth process interference variations in the absorptivity of the metal + oxide system (periodic transmission of the coating) can be observed on the surface of a target of a weakly absorbing oxide layer ($\alpha\lambda \ll 1$). This is evident from an analysis of the electrodynamic equation for the absorptivity of a layered system^{60,61}:

$$A(x) = 1 - |r|^2, \quad r = \frac{r_{12} \exp(-2i\psi) + r_{23}}{\exp(-2i\psi) + r_{12} r_{23}}, \quad r_{23} = \frac{r_{12} - r_{13}}{r_{12} r_{13} - 1},$$

$$r_{12} = \frac{1 - \sqrt{\epsilon}}{1 + \sqrt{\epsilon}}, \quad \sqrt{\epsilon} = n - i\kappa, \quad \psi = \frac{2\pi x}{\lambda} \sqrt{\epsilon}, \quad A_0 = 1 - |r_{13}|^2, \quad (3.15)$$

$$r_{13} = \frac{1 - \sqrt{\epsilon_0}}{1 + \sqrt{\epsilon_0}} = -1 + \frac{A_0}{2} \left(1 - i \frac{\kappa_0}{n_0} \right) + \frac{A_0}{2n_0}, \quad \sqrt{\epsilon_0} = n_0 + i\kappa_0,$$

where r_{12} and r_{13} are the amplitude coefficients of reflection of radiation from the oxide and metal, respectively; ϵ and ϵ_0 are the dielectric permittivities of the oxide and metal, respectively; A_0 is the absorptivity of the metal ($A_0 \ll 1$); x is the thickness of the oxide layer; and λ is the wavelength of the laser radiation.

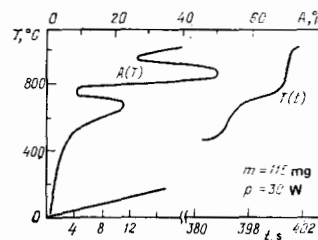


FIG. 7. Experimental dependence of the change in temperature with time $T(t)$ and absorptivity $A(T)$ in heating a copper target in air by continuous CO_2 laser radiation.^{56,57}

For thin oxide layers ($x \ll \lambda/2n$), only the first few terms in the expansion of $A(x)$ in a series in powers of (x/λ) need be considered in the expression for the absorptivity:

$$A(x) = A_0 + a \left(\frac{x}{\lambda}\right) + b \left(\frac{x}{\lambda}\right)^2 + \dots \quad (3.16)$$

The coefficients a, b , etc., are determined from (3.15). Thus, for example,

$$a = -8\pi(1 - A_0) \operatorname{Im} \left(\frac{\epsilon - 1}{\epsilon_0 - 1} \right), \quad (3.17)$$

in the particular case when $\sqrt{\epsilon_0} = n_0(1 + i)$, $n_0 \gg 1$, $A_0 \approx 2/n_0$ (these conditions are obviously satisfied for metals in the far IR region) and $\kappa \ll 1$, we obtain from (3.17)

$$a \approx \pi A_0^2 (n^2 - 1). \quad (3.18)$$

In a case analogous to (3.18), the following expression follows from (3.15) for the constant b in (3.16)⁵²

$$b \approx 4\pi^2 A_0 (n^2 - 1). \quad (3.19)$$

Since the quantity a is of the second order of smallness with respect to A_0 , the change in the absorptivity is in many cases determined by the quadratic term in the expansion of $A(x)$. For very small A_0 the cubic term in the expansion (3.16) is most important. Thus, Eq. (3.13) for $l = 1, 2$, and 3 includes all the basic cases of changes in absorption for a thin oxide layer.

For weakly absorbing oxides ($\alpha\lambda \ll 1$, $\alpha = 4\pi\kappa/\lambda$), in the linear approximation with respect to $A_0 \ll 1$ with $\kappa \ll 1$, there is a simple expression^{52,53} describing several of the first interference oscillations:

$$A(x) = \frac{n^2 A_0 + 2\kappa(\beta x - \sin \beta x)}{n^2 + (1 - n^2) \sin^2(\beta x/2)}, \quad \beta = \frac{4\pi n}{\lambda}. \quad (3.20)$$

For the total number N of interference oscillations, which can be observed in experiments on laser oxidation of metals, the following simple estimate can be obtained from the condition $\alpha x \sim 1$:

$$N \approx \frac{n}{2\pi\kappa}. \quad (3.21)$$

For example, for cuprous oxide Cu_2O at the wavelength $\lambda = 10.6 \mu\text{m}$, $n = 2.45$, $\kappa = 0.027$, we have $N \approx 14$.

In a number of papers^{52,53,62,63} the system of equations describing laser-induced oxidation of metals in air was solved numerically on a computer. Thus, in Refs. 52 and 53, the oxidation of copper under the action of continuous CO_2 laser radiation was examined and dependences $T(t), A(T)$ and others agreeing well with experiment were obtained. A more complex problem was solved in Ref. 62, where heating of a copper target in air under the action of continuous YAG laser radiation ($\lambda = 1.06 \mu\text{m}$) was examined. As it happened, in this case the heating dynamics are affected not only by the cuprous oxide layer Cu_2O but also by the cupric oxide layer CuO . In Ref. 62, an exact equation was used for the absorptivity of the two-layer system $\text{CuO}/\text{Cu}_2\text{O}/\text{Cu}$:

$$A(x, y) = 1 - |R(x, y)|^2, \quad R(x, y) = \frac{r_{12} \exp(-2i\psi_1) + r}{\exp(-2i\psi_1) + r_{12}r}, \quad (3.22)$$

$$r = \frac{r_{23} \exp(-2i\psi_2) + r_{34}}{\exp(-2i\psi_2) + r_{23}r_{34}}, \quad r_{23} = \frac{r_{13} - r_{14}}{r_{12}r_{13} - 1}, \quad r_{34} = \frac{r_{13} - r_{14}}{r_{13}r_{14} - 1},$$

$$\psi_{1,2} = \frac{2\pi}{\lambda} x_{1,2} \sqrt{\epsilon_{k,2}}, \quad \sqrt{\epsilon_k} = n_k + i\kappa_k \quad (k = 0, 1, 2),$$

$$x_1 = x, \quad x_2 = y, \quad r_{12} = \frac{1 - \sqrt{\epsilon_1}}{1 + \sqrt{\epsilon_1}}, \quad r_{13} = \frac{1 - \sqrt{\epsilon_2}}{1 + \sqrt{\epsilon_2}},$$

$$r_{14} = -1 + \frac{A_0}{2} \left(1 - i \frac{\kappa_0}{n_0} \right) + \frac{A_0}{2n_0}, \quad A_0 = \frac{4n_0}{(1+n_0)^2 + \kappa_0^2}.$$

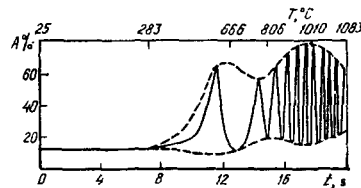


FIG. 8. Theoretical dependence of the change in absorptivity of a copper target with time when the target is heated in air with continuous YAG laser radiation ($\lambda = 1.06 \mu\text{m}$).⁶²

where x is the thickness of the CuO layer and y is the thickness of the Cu_2O layer.

The Wagner-Valensi³¹ equations were used to describe the kinetics of the two-layer oxidation:

$$\frac{dx}{dt} = 2 \frac{d_1(T)}{x} - \mu \frac{d_2(T)}{y}, \quad x|_{t=0} = x_{\text{in}},$$

$$\frac{dy}{dt} = \frac{d_2(T)}{y} - \frac{1}{\mu} \frac{d_1(T)}{x}, \quad y|_{t=0} = y_{\text{in}},$$

$$d_1(T) = d_{10} \exp\left(-\frac{T_1}{T}\right), \quad d_2(T) = d_{20} \exp\left(-\frac{T_2}{T}\right), \quad (3.23)$$

$$\mu = V_x/V_y,$$

where V_x and V_y are the specific volumes of the oxides CuO and Cu_2O , respectively.¹¹⁾

It was found that a two-fold interference pattern in the variation of the absorptivity is manifested in the heating dynamics of such systems: high-frequency interference oscillations, due to the oxide Cu_2O , modulated by low-frequency oscillations, due to the increase in the CuO oxide layer (Fig. 8). We also observed this phenomenon experimentally.⁶²

The dynamics of heating of a copper target by pulsed, periodic CO_2 laser radiation was studied in Ref. 63. Here, the one-dimensional heat conduction equation was solved instead of the heat balance equation [of the type (3.6)]. The results of the calculations^{52,53,62,63} showed that the theoretical models examined describe quite accurately the real experiments over the entire range of temperatures from room to melting temperature.

Interference phenomena are characteristic not only of heterogeneous but also homogeneous reactions. We shall examine the simplest system: laser radiation incident normally on the surface of a homogeneous chemically active medium bounded by parallel planes (for example, a cell with thin transparent windows). The concentrations of the starting substance and of the reaction products change continuously during the chemical reaction and as a result, the dielectric permittivity of the mixture of reagents changes continuously as well. In a number of cases, the dielectric permittivity of such

¹¹⁾ Under isothermal conditions, the Valensi equation follows from (3.23) (Ref. 31):

$$\frac{x}{y} = u_0 = \frac{1}{2} \left[\left(\frac{v}{\mu} - \mu \right) + \sqrt{\left(\frac{v}{\mu} - \mu \right)^2 + 8v} \right], \quad v = d_1(T)/d_2(T).$$

The time for relaxation to the ratio $x/y = u_0$ is determined by the equation⁶² (compare (2.6), (2.8))

$$\frac{x}{y} = u_0 + \delta(t), \quad |\delta| \ll u_0, \quad \delta|_{t=0} = \delta_0, \quad \delta = \delta_0 \exp\left(-\frac{d_2 R}{\mu u_0} \int_0^t \frac{dt}{y^2}\right),$$

$$R = \sqrt{(v - \mu)^2 + 8\mu^2 v}.$$

a mixture is determined by the Lorenz-Lorentz equation⁶⁴:

$$\frac{\varepsilon-1}{\varepsilon+2} = (1-c) \frac{\varepsilon_1-1}{\varepsilon_1+2} + c \frac{\varepsilon_2-1}{\varepsilon_2+2}, \quad (3.24)$$

where ε , ε_1 , and ε_2 are the dielectric permittivities of the mixture, the starting substance, and the reaction products, respectively; c is the concentration of the reaction product. If $|\varepsilon_1 - \varepsilon_2| \ll 1$, then a linear relation follows from (3.24)

$$\varepsilon = \varepsilon_1 + c(\varepsilon_2 - \varepsilon_1). \quad (3.25)$$

Substituting (3.24) or (3.25) into the equation for the absorptivity of a plane parallel layer of the substance it is easy to find the conditions under which interference oscillations of the absorptivity will be observed during the chemical reaction. Indeed, we can write the following expression for A ⁶⁰

$$\left. \begin{aligned} A &= 1 - |r|^2 - |d|^2, \quad r = \frac{r_{12}(e^{-2i\psi} - 1)}{e^{-2i\psi} - r_{21}^2}, \\ d &= \frac{(1 - r_{12}^2)e^{-i\psi}}{e^{-2i\psi} - r_{12}^2}, \quad r_{12} = \frac{1 - \sqrt{\varepsilon}}{1 + \sqrt{\varepsilon}}, \\ \psi &= \frac{2\pi x}{\lambda} \sqrt{\varepsilon}, \quad \sqrt{\varepsilon} = n + i\kappa, \end{aligned} \right\} \quad (3.26)$$

where r and d are the amplitude coefficients of reflection and transmission of radiation and x is the thickness of the medium.

For weakly absorbing systems ($\alpha x \ll 1$, $\alpha \lambda \ll 1$, $\alpha = 4\pi\kappa/\lambda$) we obtain the following approximate equation from (3.26)⁶⁵

$$A \approx 2\kappa \frac{(1+n^2)\beta x - (n^2-1)\sin\beta x}{4n^2 - (1-n^2)^2 \sin^2(\beta x/2)}, \quad \beta = \frac{4\pi n}{\lambda}. \quad (3.27)$$

It is evident from (3.27) and (3.25) that interference oscillations of the absorptivity occur when

$$\Delta c |n_2 - n_1| \geq \frac{\lambda}{2x}, \quad (3.28)$$

where Δc is the change in the concentration during the chemical reaction, n_1 and n_2 are the indices of refraction of the starting substance and of the reaction product, respectively.

Interference oscillations can also appear as a result of thermo-optical expansion of matter^{65, 66} and so on. In particular, interference-induced changes in the characteristics of laser light scattering accompanying thermo-optical expansion of a weakly absorbing spherical region were observed in Ref. 67.

c) Self-stabilizing processes

In this subsection we shall examine a system with negative feedback. This type of feedback is observed in a number of reactions involving reduction of metal from oxides,^{68, 69} nitrides, and other compounds in decomposition reactions of copper formate⁷ and formates of other metals and also in a number of reactions occurring under the action of IR laser radiation. In all these cases, there is an appreciable decrease in the absorptivity of the system during the chemical reaction. A distinguishing characteristic of systems with negative feedback is their ability to self-stabilize the chemical process.

We shall examine as an example the process of re-

duction of a metal from an oxide under the action of CO₂ laser radiation. If we are dealing with thin layers of reduced metal, then the kinetic dependence can be assumed to be linear to a good approximation,¹³ i.e., the kinetics of growth of such layers is described by the equation

$$\frac{dx}{dt} = v \exp\left(-\frac{T_0}{T}\right). \quad (3.29)$$

The absorptivity of the layered oxide + metallic film system is given by Eq. (3.15), in which r_{12} and r_{13} should be interchanged. An expansion of the type (3.16) for small thicknesses of the metallic film (in the case $\kappa \ll 1$, $A_0 \ll 1$) yields

$$A(x) = A_* - bx, \quad A_* = \frac{4n}{(1+n)^2}, \quad b = \frac{64\pi}{\lambda A_0} \frac{n}{(n+1)^3}, \quad (3.30)$$

where A_* is the absorptivity of the pure oxide.

The dynamics of laser heating of such a target in a hydrogen atmosphere are described by equations of the type (3.6) with the corresponding expressions replaced by (3.29) and (3.30). If in these equations we go over to dimensionless variables of the type (3.7), where

$$\mu = \frac{Plmcv}{T_0(\eta\delta)^2}, \quad (3.31)$$

then for the dimensionless temperature y we obtain the following differential equation

$$\begin{aligned} \frac{d^2y}{d\tau^2} + \frac{dy}{d\tau} &= -\mu \exp\left(-\frac{1}{y}\right), \\ y|_{\tau=0} &= y_{in}, \quad \frac{dy}{d\tau}|_{\tau=0} = y_0 - y_{in}. \end{aligned} \quad (3.32)$$

This equation differs from (3.8) only by the sign in front of μ . Examples of a numerical solution of Eq. (3.32) are shown in Fig. 9.

As can be seen from Fig. 9, after the reaction is activated and a highly reflecting metallic layer appears on the surface, the temperature of the target begins to decrease rapidly. It is convenient to choose the time at which $(dy/d\tau)|_{\tau=\tau_a} = 0$ as the activation time of the reaction in this case.

Retaining, as in (3.9), only the first iteration

$$\begin{aligned} y^{(0)} &= y_0 + (y_{in} - y_0) \exp(-\tau), \\ y &= y^{(0)} - \mu \int_0^\tau [1 - \exp(\tau_1 - \tau)] \exp\left(-\frac{1}{y^{(0)}(\tau_1)}\right) d\tau_1, \end{aligned} \quad (3.33)$$

we obtain an equation for determining τ [compare

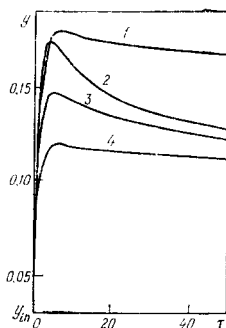


FIG. 9. Examples of numerical solution of Eq. (3.32). $y_{in} = 0.03$. Curve 1) $\mu = 0.1$, $y_0 = 0.18$; 2) $\mu = 1$, $y_0 = 0.18$; 3) $\mu = 1$, $y_0 = 0.15$; 4) $\mu = 1$, $y_0 = 0.12$.

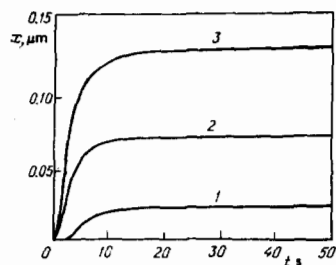


FIG. 10. Theoretical time dependence of the thickness of the reduced copper layer on Cu_2O in a hydrogen H_2 atmosphere by continuous CO_2 laser radiation. The linear equations describing the kinetics of reduction and the equation of heat conduction were solved numerically using an exact equation for the absorptivity $A(x)$ and the following values of the parameters: target mass $m=50$ mg, $v=10^4$ $\mu\text{m/s}$, $T_0=10^4$ K. Laser radiation power $P(W)$: 1(1), 3(2), and 5(3).

(3.10)]

$$\frac{e^{-\Phi}}{\Phi} + \text{Ei}(-\Phi) = \frac{y_0^2}{\mu} \exp\left(\frac{1}{y_0}\right), \quad \Phi = \frac{1}{y} - \frac{1}{y_0}. \quad (3.34)$$

We obtain equations for the cases of rapid activation ($\Phi \gg 1$) and for the quasistationary process ($\Phi \ll 1$) as in (3.11):

$$\tau_a = \frac{1}{y_0 - y_{st}} \left[\ln^{-1}\left(\frac{\mu}{y_0}\right) - y_{in} \right], \quad \Phi \gg 1, \quad (3.35)$$

$$\tau_a = \ln \left[\frac{y_0 - y_{in}}{\mu} \exp\left(\frac{1}{y_0}\right) \right], \quad \Phi \ll 1.$$

We note that in going from the linear to the parabolic law for reduction of the metal, i.e., for large thicknesses of the metallic film, the quadratic term in the expansion of $A(x)$ in powers of x/λ is more important than the linear term. In this case, the form of Eq. (3.32) and, correspondingly, Eqs. (3.35) is retained and only the expression for μ [(3.31) of (3.7)] changes.

If we now consider how the thickness of the layer of reduced metal changes with time (Fig. 10), then we can see that beginning at some time after the reaction is activated, this thickness varies very insignificantly, i.e., the total yield of the reaction is determined primarily by the power and not by the energy of the incident laser radiation. This is the circumstance that we had in mind when we mentioned the self-stabilizing capability of the system.

In concluding this subsection, we note that the processes indicated above can occur either in the activation manner examined above (the temperature has a local maximum) or in a nonactivation manner (the temperature increases monotonically to a stationary value $y = y_{st}$). The type of process realized depends in each specific case on the ratio of the characteristic time for establishing a steady state temperature in the target ($\tau \sim 1$) and the activation time of the chemical reaction $\tau = \tau_a$. Expressions (3.35) are valid only in cases when $\tau_a > 1$ (moderate and low laser power) and the process proceeds in an activation manner.

d) Diffusion processes in heterogeneous reactions

As already mentioned above, heterogeneous reactions are affected by a number of successive physicochemical processes, the slowest of which determines the to-

tal rate of the reaction. For example, in heterogeneous oxidation reactions of metals, the reaction rate is often limited by diffusion of reagents through the oxide layer that separates the reaction components spatially.^{13,31}

These processes have a nonchemical origin. They can, on the one hand, strongly affect the dynamics of the chemical reaction and, on the other hand, they can have features similar to thermochemical processes. The latter circumstance is related to the establishment of feedback between the degrees of freedom characterizing the kinetic process and the temperature.

In this section we shall examine two diffusion processes,^{45,47,70,71} in which such feedback is established due to the influence of the spatial concentration distribution of some component on the absorbing characteristics of the system and due to the temperature dependence of the diffusion constant of this component

$$D(T) = D_0 \exp\left(-\frac{T_0}{T}\right). \quad (3.36)$$

We shall examine a system in which the change in temperature is described by the ordinary differential equation of heat balance [an equation of type (3.6)].

The theoretical description of such systems will be based on the simultaneous solution of the following system of equations: heat balance equations, diffusion equations for finding the spatial distribution of the concentration of the diffusing substance, and Maxwell's equations for determining the impedance of the surface with an inhomogeneous distribution of the diffusing component as a function of depth in the substance.

Among problems of this kind that have been examined in the literature we point out the problem of diffusion laser polishing,^{52,45,46} dissolution of oxygen in a surface metal layer,^{45,46,70} diffusion saturation of the surface layer of a metal by doping impurities,⁴⁶ as well as the diffusion model of thermochemical decomposition of semiconducting materials with a complex composition.⁷¹ Due to the similarity of these problems, we shall examine only two of them.

The first problem is related to the dissolution of oxygen in the surface layer of titanium when the layer is heated in air by continuous CO_2 laser radiation. It was shown in Ref. 70, starting from an analysis of the experimental results and based on theoretical estimates, that this process precedes the formation of the oxide film. As a result of diffusion of oxygen in air into the skin layer of the metal, impurity scattering of electrons increases and the electron mobility decreases. As a result, there may be an appreciable increase in the absorptivity.

The distribution of the concentration of microimpurities is found by solving the diffusion equation

$$\frac{\partial N}{\partial t} = D(T) \frac{\partial^2 N}{\partial z^2} \quad (z > 0), \quad N(z, t)|_{z=0} = 0, \quad N|_{z=0} = N_0, \quad N|_{z \rightarrow \infty} = 0. \quad (3.37)$$

The solution is

$$N(z, t) = N_0 \left[1 - \Phi\left(\frac{z}{2\sqrt{\theta}}\right) \right], \quad \theta = D_0 \int_0^t \exp\left(-\frac{T_0}{T(\tau)}\right) d\tau, \quad (3.38)$$

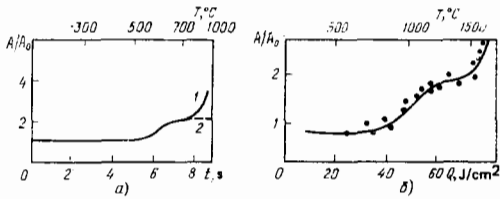


FIG. 11. a) Theoretical dependence of the change in the absorptivity of a thermally thin titanium plate heated in air by continuous CO₂ laser radiation (target mass $m = 50$ mg, incident radiation power $P = 20$ W; curve 1 describes the change in A including the diffusive and oxidative mechanisms, the dashed curve 2 shows only the diffusive mechanism⁴⁵); b) experimental dependence of the change in the absorptivity A/A_0 at $10.6 \mu\text{m}$ for a titanium foil with thickness $50 \mu\text{m}$ heated in air by neodymium laser radiation ($\lambda = 1.06 \mu\text{m}$).⁷⁰

where $\Phi(x)$ is the error integral.

Calculating the surface impedance of the metal using the distribution (3.38) (this is done with the aid of the technique presented in Ref. 72; see also Ref. 46). It is then possible to determine the absorptivity of the metal A_0 . The following approximate expression was obtained in Refs. 45 and 46 for a weakly anomalous skin effect:

$$A_0(t) \approx \begin{cases} A_{01} + (A_{02} - A_{01}) y, & 0 \leq y \leq \frac{\sqrt{\pi} - 1}{\sqrt{\pi}}, \\ A_{02} + \frac{A_{01} - A_{02}}{\pi (y + (2 - \sqrt{\pi})/\sqrt{\pi})}, & y > \frac{\sqrt{\pi} - 1}{\sqrt{\pi}}, \end{cases} \quad (3.39)$$

where δ_0 is the thickness of the skin layer of the pure metal, A_{01} and A_{02} are the absorptivities of pure titanium and titanium saturated to the limit by dissolved oxygen, respectively.

A numerical solution⁴⁵ of the problem (3.6) using Eqs. (3.39) leads to the dependence $A(t)$ shown in Fig. 11. This behavior agrees well with the experimental curves obtained in Refs. 70 and 73. The first rise in the absorption $A(t)$ in Fig. 11 is related to the process of diffusion saturation of the metal surface by oxygen, while the second is related to formation of a chemical compound (oxidation of titanium).

The second problem which we shall consider is related to thermal decomposition of GaAs. In one model of this process,⁷¹ it is assumed that when the decomposition temperature T_D is attained, arsenic is evaporated and the rate of evaporation is limited by the diffusion of arsenic from the bulk of the medium along vacancies and interstices. It is also assumed that additional absorption proportional to the depletion of the volatile component appears in the medium

$$\alpha(z, t) = \alpha_0 \left[1 - \frac{N(z, t)}{N_0} \right], \quad (3.40)$$

$N(z, t)$ is the concentration of arsenic at depth z at time t , and N_0 is the starting value of the arsenic concentration.

It is assumed in the problem that the thickness of the diffusion layer is much smaller than the thickness of the heated layer. For this reason, the diffusion equation is solved with boundary conditions (3.40) and the

diffusion coefficient (3.36) $D = D(T_s)$, $T_s = T(z = 0, t)$. We have [compare (3.38)]

$$N(z, t) = N_0 \Phi \left(\frac{z}{2\sqrt{t\theta}} \right), \quad \theta = D_0 \int_0^t \exp \left(-\frac{T_0}{T_s(\tau)} \right) d\tau. \quad (3.41)$$

Next, the additional absorption is viewed as surface absorption with absorptivity

$$A_1(t) = \int_0^\infty \alpha(z, t) dz = \frac{2}{\sqrt{\pi}} \alpha_0 \sqrt{\theta(T_s)}. \quad (3.42)$$

It is assumed that a layer of a seed inhomogeneity is present on the material surface, giving rise to the starting surface absorption of radiation with absorptivity $A_0 \ll 1$. Taking into account the initial and additional absorption, an integral equation can be obtained for the surface temperature T_s of the semiconductor:

$$T_s(t) = T_{in} + \frac{2I_0 A_0 \sqrt{at}}{\gamma k} + \frac{1}{\sqrt{\pi} k} I_0 \int_0^t \frac{A_1(\tau)}{\sqrt{t-\tau}} d\tau, \quad (3.43)$$

where k and a are the coefficients of thermal conductivity and diffusivity of the substance, respectively; I_0 is the incident light flux density. Solving (3.43) and using the condition $(d^2 T_s / dt^2)|_{t=t_a} = 0$, it is possible to determine, making certain approximations,⁷¹ the activation time of the reaction t_a and temperature T_* at which the thermochemical instability develops $T_* = T_s(t = t_a)$:

$$T_* \approx T_0 \left\{ 2 \ln \left[\frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{t_a}} \sqrt{\frac{D_0 k a T_0}{I_0 A_0^2}} \right] \right\}^{-1}, \quad t_a \approx \frac{\pi k T_*}{4 a I_0^2 A_0^2}. \quad (3.44)$$

e) Reactions with continuous variation of the stoichiometric composition

Two situations can arise during the course of thermochemical reactions: 1) different reaction products form layers with quite distinct boundaries and 2) the boundaries between the layers are very diffuse (or are absent altogether as in homogeneous reactions). The first situation is characteristic in heterogeneous reactions, for example, oxidation of copper with the formation of a layered CuO/Cu₂O/Cu structure,³¹ while the second is characteristic of the oxidation of titanium, when the dimensions of the transition regions between different oxides and the metal (TiO₂/Ti₂O₃/TiO/Ti) are of the order of the thickness of the oxide layers themselves.⁷⁴ The structure of such transition layers can affect the absorption characteristics of the system and, correspondingly, the dynamics of the thermochemical process stimulated by the laser radiation.

In this section we shall examine the characteristics of thermochemical reactions with a continuous variation of the stoichiometric composition of the medium.

One such process is laser stimulated oxidation of alloys in air.⁷⁵ The distinguishing feature of the change in the optical properties of this system stems from the fact that the absorptivity of the alloy varies nonmonotonically with a change in the ratio of its components. As a result of the different rates of oxidation of components and corresponding depletion of the surface layer of one of the elements, the absorptivity can increase or decrease depending on the starting ratio between the components.⁷⁵ The oxidation of X18H10T steel in air stimulated by the free lasing pulse of a neodymium la-

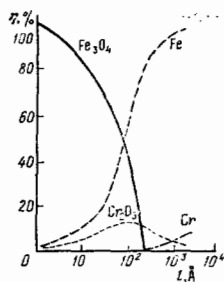


FIG. 12. Experimental dependence of the distribution of different compounds over the depth of the oxide film near the surface of the alloy (X18H10T steel) with thickness $100\ \mu\text{m}$ irradiated by air by a pulse of free generation of a neodymium laser. Pulse duration = $1.3\ \mu\text{s}$. Maximum target temperature $T \approx 450^\circ\text{C}$.⁷⁵

ser was investigated experimentally in Ref. 75. Then the absorptivity of the alloy at $10.6\ \mu\text{m}$ was measured and the composition of oxides and near-surface alloy layers was analyzed using x-ray diffraction spectroscopy together with layer-by-layer etching. Figure 12 shows the distribution of the different compounds in the surface layer obtained in this manner. Using these results and data on the specific electrical resistance of the ternary Fe-Ni-Cr alloy, it is possible to estimate the change in the absorptivity of the substance due to chromium depletion of the surface layer (with simultaneous enrichment by nickel). It was shown in Ref. 75 that in this situation the absorptivity of steel decreases. The mechanism examined in Ref. 75 can explain the decrease in the absorptivity of a number of metals at the initial stage of their heating together with the diffusion processes eliminating trace impurities from the surface layer (laser cleaning effect^{45,46}).

Another important example of reactions with continuous variation of the stoichiometric composition are homogeneous processes such as polymerization, photoaging of polymers, polyimidization, and others. Various forms of thermal feedback can be established in such processes. The sign of the feedback determines whether a thermochemical instability develops in the system or the process is self-stabilized or more complicated dynamics are realized (self-oscillation, stochastic reaction regime, etc.). Several forms of such dynamics will be examined in what follows.

f) Dynamics of laser combustion processes

Positive thermal feedback of purely chemical origin is necessarily present in systems in which exothermal reactions occur. Such feedback can in itself lead to thermal instability of the process, i.e., inflammation of the substance. An example of such processes is the problem of inflammation of metallic powders in a flow of heated oxidizer.⁷⁶ On the other hand, a feature of laser inflammation of substances as indicated in Refs. 77-78 is the interaction of two types of thermal feedback in the system: chemical and laser.¹²⁾ In addition,

¹²⁾ The strong change in the absorptivity of metals during their laser-induced inflammation was also noted in Refs. 51, 79 and 80.

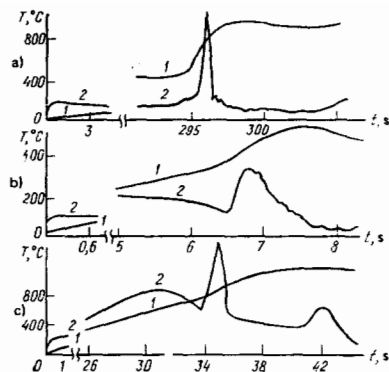


FIG. 13. Experimental oscillograms of the temperature $T(t)$ (1) and its derivative dT/dt (2), obtained during inflammation of metals in air induced by continuous CO_2 laser radiation with power $P \approx 20\ \text{W}$. a) Magnesium, target mass $m = 64.7\ \text{mg}$; b) zinc, $m = 133.8\ \text{mg}$; c) tungsten, $m = 118\ \text{mg}$.⁷⁸

laser inflammation is distinguished by the large variety of accompanying phenomena. We note that the interest in laser inflammation processes is related not only to scientific, but also to the applied significance of such research; we need only to mention the problems of gas-laser working of materials.^{7,81}

The development of a thermochemical instability in the systems examined proceeds more vigorously than in thermally neutral reactions, it is accompanied by a sharp increase in the brightness of the irradiation spot (appearance of a flame), and it is distinctly observed on oscillograms showing the heating rate (spike in the derivative, Fig. 13).

An interesting manifestation of feedback due to a change in the absorbed laser power is the dependence of the inflammation time of the metal on the angle of incidence and polarization of the radiation⁴⁴ (Fig. 14). This effect is related to the strong absorption near the Brewster angle of radiation polarized in the plane of incidence. During the growth process of the oxide layer, the position of the Brewster angle of the layers metal + oxide system varies continuously from the Brewster

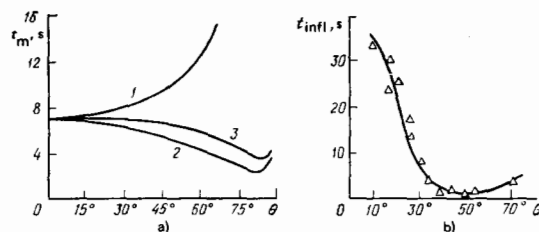


FIG. 14. Theoretical (a) and experimental (b) dependence of the characteristic heating time for metallic targets in air on the angle of incidence of CO_2 laser radiation.⁴⁴ a) Heating of copper target ($m = 0.7\ \text{g}$) to melting temperature (radiation power $P = 1\ \text{kW}$), radiation is polarized perpendicular (1) and parallel (2) to the plane of incidence, 3) unpolarized radiation; b) heating of tungsten plate with thickness $h = 0.2\ \text{mm}$ up to the time of inflammation, unpolarized radiation $P \approx 700\ \text{W}$ (diameter of the radiation beam under normal incidence constituted $\approx 5\ \text{mm}$ and was much less than the characteristic transverse dimensions of the plate $L \approx 5\ \text{cm}$).

angle for the metal

$$\theta_m \approx \frac{1}{2} \left(\pi - \frac{A_0}{\sqrt{2}} \right)$$

to the Brewster angle for the oxide

$$\theta_0 \approx \arccos (n^2 + 1)^{-1/2}$$

(the expression for θ_0 is presented for the case $\kappa=0$), where n is the index of refraction of the oxide and A_0 is the absorptivity of the metal ($A_0 \ll 1$). As a result, there exists an optimum angle at which laser inflammation of the metal occurs with the lowest expenditure of energy.

The activation time of the oxidation reaction with oblique incidence of radiation was determined in Ref. 44. For radiation polarized in the plane of incidence and a parabolic oxidation law, we have⁴⁴

$$t_a(0) = t_0 \frac{A_0^2 \exp(A_1 \cos \theta / A_0)}{\cos^2 \theta \sin^4 \theta}, \quad t_0 = \frac{4}{d} \frac{\pi}{16\pi\kappa A_1} \left(\frac{n^2 \lambda}{16\pi\kappa A_1} \right)^2, \quad A_1 = \frac{\eta s T_d}{P}. \quad (3.45)$$

Equation (3.45) is written for the case when convective heat losses are primarily important in the problem, while the angles of incidence of radiation θ are not too close to the values 0 and $\pi/2$. It is easy to see that the quantity t_a has a minimum at an angle of incidence θ_m , which is determined from the equation

$$\frac{\cos \theta_m \sin^2 \theta_m}{1 - 3 \cos^2 \theta_m} = \frac{2P A_0}{\eta s T_d}. \quad (3.46)$$

The position of the minimum depends on the power P of the incident radiation and varies from angles close to $\pi/2$ for low powers to $\theta_1 = \cos^{-1}(1/\sqrt{3}) \approx 55^\circ$ for $P \rightarrow \infty$. The decrease in energy expended on heating the metal at the optimum angle of incidence can be very appreciable (see Fig. 14). We note that in the experiments described in Ref. 44, unpolarized radiation was used, while energy decreased due to the fact that the increase in the absorptivity for radiation polarized in the plane of incidence exceeded the decrease in absorptivity for radiation polarized perpendicular to the plane of incidence. Following Ref. 73, experiments with polarized CO_2 laser radiation were performed. These experiments confirmed the physical reason for the decrease in energy with oblique incidence of radiation.

In most problems of laser inflammation of metals examined in the literature, development of the thermochemical instability was complete either when the system reached the stationary combustion regime or when self-oscillations were established in it (Fig. 15). If we take into account the fact that such systems usually have two degrees of freedom (temperature and thickness of the oxide layer), then according to the general ideas of the theory of nonlinear oscillations, no other forms of steady-state processes should exist.

As the number of degrees of freedom in nonlinear systems increases, new types of system motion along the phase surface can appear. In particular, if the phase trajectory of a system falls in a region with simultaneous attraction of two unstable limit cycles, then a stochastic dynamics of the system behavior, the so-called strange attractor, is observed.^{25, 82}

For this reason, the regimes of laser combustion of

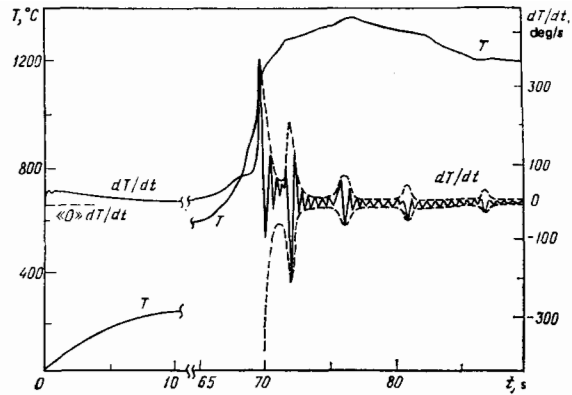


FIG. 15. Experimental dependence of the change in the temperature $T(t)$ and rate of heating dT/dt of a tungsten target ($m=188.3$ mg) in air under the action of continuous CO_2 laser radiation ($P=30$ W). Damped self-oscillations can be seen in the curve of dT/dt after inflammation of the target ($t=70$ s). The damping of the self-oscillations is related to the increase in mass of the target during its oxidation.³⁴

metals with uniform illumination of the target surface and with sharp focusing of radiation, when the spot radius is much less than the dimensions of the target, can differ considerably. Indeed, in the last case, radial heat conduction begins to play an important role. Then the problem transforms into a distributed problem, which indicates the appearance of more than two degrees of freedom in the starting system. These degrees of freedom can be clearly separated by approximately reducing the problem to a finite system of ordinary differential equations and in the simplest case to a system of equations for the temperature and thicknesses of oxide layers at the center and at the periphery of the target.

This change in the dynamics of laser combustion was investigated experimentally in Ref. 83. The stationary combustion regime was observed with uniform illumination of the surface of a titanium target by continuous CO_2 laser radiation, while the transition to the stochastic combustion regime was observed with sharp focusing: the rate of heating of the target varied randomly (Fig. 16). The problem examined in Ref. 83 is an important example of a relatively simple physical system in which stochastic oscillations appear. Analogous ef-

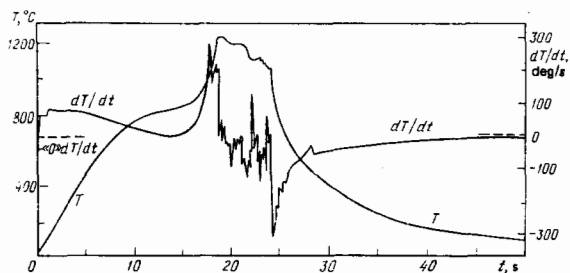


FIG. 16. Experimental oscillogram of $T(t)$ and dT/dt , obtained with sharp focusing of continuous CO_2 laser radiation ($P=18$ W) on a titanium target ($m=50.5$ mg) in air. After target inflammation ($t=17$ s), the heating rate changed in a random manner (the derivative dT/dt underwent chaotic oscillations). The laser was switched-off at $t=24$ s.³⁴

fects can also arise with laser stimulation of homogeneous reactions.

g) Optimal laser control of chemical reactions

The problem of control of chemical reactions belongs to a set of physical problems that have a practical orientation from the very beginning, since we are talking about either reducing the cost of chemical production of some substances or creating new substances with some special properties (superpure metals, etc.) by solving such problems. For this reason, in laser chemistry, besides finding new physical mechanisms for the directed action of laser radiation on the course of chemical reactions, it is also necessary to determine the limiting possible boundaries of the response of a chemically active medium to such forms of interaction and to study the problem of optimal control of reactions. Here we have in mind the possibility of choosing the radiation parameters in such a way that the process proceeds along a trajectory lying as close as possible to the required trajectory. Another approach consists of determining the conditions under which a predetermined quantity characterizing a given process reaches an extremum value, for example, maximum mass yield of some component of the reaction products or minimum energy expenditure per unit mass of the chemical compound formed, etc.⁸⁴

In our opinion, the main advantages of laser thermochemistry must appear precisely in those cases when the relatively expensive laser radiation is used not for simply heating the substance, but for controlling the reaction. In this connection, we recall that self-regulating stable processes in chemical technology very often turn out to be unfavorable for one reason or another. In particular, we recall the example of soft oxidation of organic substances given in Ref. 12: in the lowest stable regime, the reaction rate is inadmissibly small, while in the upper stable regime, the yield of undesirable products of deep oxidation (carbon dioxide and water) is too high. In order to obtain maximum yield of valuable products from incomplete oxidation, it is necessary to learn how to make these processes proceed along the middle, unstable temperature regime. This problem can be completely solved with the help of laser control of the process.

Another example of a problem of optimum control of thermochemical reactions is the problem of minimizing the expenditure of energy on heating metals in an oxidizing medium by laser radiation, which is important for practical applications. Minimizing energy expenditures is one of the most widely used formulations of optimal problems in studying laser working of metals.^{8,81,85} The optimal regime corresponds to the best, with respect to energy expenditures, relation between competing factors: increase in absorptivity of the target during growth of the oxide film and increase in heat losses with an increase in the duration of heating.

Some aspects of this problem were examined in Refs. 44, 63, and 84–87, where in the optimal wavelength,⁸⁶ optimal angle of incidence of the radiation [see (3.46)], optimal power⁸⁷ of the continuous laser radiation were

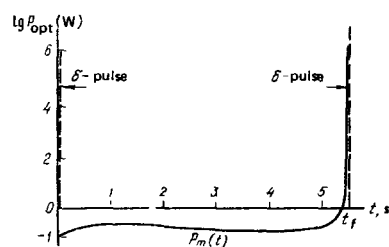


FIG. 17. Main part of the optimal regime for action of CO₂ laser radiation on a copper target in air, obtained as a result of a numerical solution of the problem in optimal control theory⁸⁴ ($t_f = 5.5$ s, $T_0 = 1300$ K).

found. The possibilities of optimization for the basic interaction regimes of existing lasers (continuous,⁸⁷ pulsed,⁸⁴ pulsed-periodic⁶³) were investigated for given temporal shape of the pulse. However, the true minimum in energy expenditures is realized for some complex temporal shape of the laser pulse, which can be found by solving a problem in optimal control theory. Specifically, it is necessary to find the pulse shape (optimal control) that minimizes the energy functional in the presence of coupling⁸⁴:

$$E = \int_0^{t_f} P(\tau) d\tau \rightarrow \min, \quad T(t_f) = T_0 \quad (3.47)$$

(T_0 is the final temperature attained at time t_f). Here it turns out that the optimal power $P = P^*(t)$ [minimizing the functional (3.47)] represents a combination of the overall and special controls (Fig. 17), which is well approximated by the combined laser action regime (combination of continuous and pulsed interactions).

Regimes involving combined action of radiation are of special interest for exothermal reactions, where large energy gains can be attained with their help. This was first demonstrated in Ref. 88, wherein laser inflammation of metals with combined action of radiation was investigated. It was shown in Ref. 88 that the additional action of a Nd-laser pulse sharply decreases energy expenditures on heating a titanium foil in air by continuous CO₂ laser radiation. Combined action for other irradiation regimes and another combination of wavelengths was studied in Refs. 89 and 90. The "laser match" effect in laser-stimulated combustion of metals was also discussed in Ref. 78.

4. DYNAMICS OF LASER-STIMULATED THERMOCHEMICAL PROCESSES IN DISTRIBUTED SYSTEMS

Up to now we have been discussing the characteristics of thermochemical processes in point systems, i.e., in systems with a finite number of degrees of freedom, described by ordinary differential equations. However, in many cases, laser thermochemistry involves distributed, active, kinetic systems with an infinite number of degrees of freedom.

Two types of systems of this kind can be distinguished. The first type involves transport processes such as diffusion, heat conduction, and so on and is described by a system of parabolic equations with nonlinear sources.

$$\frac{\partial x_i}{\partial t} = F_i(x_1, \dots, x_n) + \frac{\partial}{\partial \xi^2} \left(\sum_{j=1}^n D_{ij} \frac{\partial x_j}{\partial \xi} \right), \quad i = 1, \dots, n. \quad (4.1)$$

where x_i are the concentration of substances or the temperature of the medium, ξ are the spatial variables, D_{ij} are the coefficients of diffusion or heat conduction, and F_i are nonlinear sources.

Another type of distributed system is described by nonlinear hyperbolic equations and is encountered in studying propagation of laser radiation in nonlinear media.

It is also possible to have situations when both parabolic and hyperbolic type equations must be used simultaneously in order to describe the process adequately.

The qualitative theory of such distributed systems is much more complicated (and less well developed) than for the corresponding point systems. Although distributed problems in laser thermochemistry were first investigated only very recently, here, as in the case of point systems, the analogy to distributed problems in nonlinear optics, plasma physics, hydrodynamics, biology, etc., to a certain extent helps to understand the reason for a number of observed phenomena.⁹¹⁻⁹⁶

In this section, we shall examine processes that occur in systems of the type (4.1). Section 5 is concerned with problems involving propagation of laser radiation in media with an optical inhomogeneity arising as a result of the occurrence of chemical reactions.

a) Development of instabilities in distributed systems

Since the theory of self-oscillatory processes in distributed kinetic systems was examined in Ref. 96, we shall restrict our attention here to certain ideas of an introductory character, and we shall also refer to some papers that were not included in Ref. 96, which could be interesting for specialists working in laser thermochemistry.

As is well known,⁹⁶ the systems (4.1) exhibit a much larger variety of different types of instabilities than the corresponding point systems of the form

$$\frac{dx_i}{dt} = F_i(x_1, \dots, x_n), \quad i = 1, \dots, n. \quad (4.2)$$

Stationary solutions of the system (4.2) $x_i = x_i^*$ are simultaneously homogeneous, stationary solutions of the system (4.1) with zero boundary conditions of the second kind at $\xi = 0$ and $\xi = L$. The problem of the stability of stationary solutions for point systems was already examined above [see (2.1)–(2.4) and following]. In the case of distributed systems, homogeneous stationary states could be unstable relative to the spatial perturbations of the form

$$x_i - x_i^* = \alpha_i \exp \left(\gamma_i t + \frac{i\pi k}{L} \xi \right). \quad (4.3)$$

For a given wave number k/L and depending on the number of unstable roots (i.e., roots for which $\gamma_i > 0$), the instabilities can be either self-oscillatory with an even number of roots or so-called Turing instabilities, which lead to the formation of stationary dissipative structures with an odd number of roots (for more details see Ref. 96). Such dissipative structures in "non-

laser" chemistry were investigated for a number of autocatalytic reactions, in which hysteresis and quasi-harmonic and contrast dissipative structures were observed.^{23-25, 96-98} Metastable dissipative structures were observed in the course of studying nonlinear heat conduction equations.⁹⁹⁻¹⁰¹

The instability of homogeneous states is only one of the diverse forms of reaction of distributed systems to external actions (perturbation of initial conditions). Even in the simplest case when the distributed system is described by only a single equation of the type (4.1), depending on the form of the function $F(x)$ both threshold and threshold-free self-excitation regimes of the system and appearance of a stationary or a pulsating reaction front can be realized. Systems of this type have been studied in connection with numerous problems in combustion physics,^{96, 102} investigation of the dynamics of activity zones of heterogeneous catalyzers,^{103, 104} etc.

A number of self-oscillatory processes (synchronous oscillations and standing waves, generation of quasi-stochastic waves and so on) was observed in the Belousov-Zhabotinskiĭ reactions.^{23, 96}

Certain types of distributed processes in problems involving the physics of interaction of laser radiation with matter were investigated in papers on the thermal mechanism for breakdown of dielectrics,¹⁰⁵⁻¹⁰⁹ on the investigation of the instability of a planar vaporization front,¹¹⁰ on instabilities of the interface in the growth of a crystal from a supercooled fluid,¹¹¹ and others. A number of such problems were recently examined in Ref. 112.

In this section we shall examine the characteristics of some thermochemical processes in distributed systems: appearance of dissipative spatial structures in problems of laser heating of decomposing substances, the problem of a surface combustion wave (appearance of surface thermochemical instability), and the problem of the volume thermochemical decomposition of some organic dielectrics.

b) Screening of the surface by the products of thermal decomposition of materials

As is well known, the products of combustion of organic materials (soot particles, CO₂ molecules, etc.) strongly absorb radiation with wavelength $\lambda = 10.6 \mu\text{m}$. This increases the expenditure of energy on working such materials, as wood, textolite, etc., with CO₂ laser radiation. It is possible to lessen the screening action of the combustion products by blowing gas over the radiation interaction zone. This problem was examined theoretically in Ref. 113. In the simplest case, it is described by a system of coupled equations, namely, the equation of heat conduction and the diffusion equation for the decomposition products in the gas flow:

$$\begin{cases} \Delta T = 0, & z \leq 0, \\ k \frac{\partial T}{\partial z} \Big|_{z=0} = \begin{cases} I(r, \varphi) - \eta(T_s - T_\infty), & r \leq a, \\ -\eta(T_s - T_\infty), & r > a, \end{cases} \\ I(r, \varphi) = I_0 \theta (a - r) \exp \left\{ -\sigma \int_0^\infty n(r, \varphi, z) dz \right\}, \end{cases} \quad (4.4)$$

$$\begin{cases} D\Delta n - v \frac{\partial n}{\partial r} = 0, & z > 0, \quad z = r \cos \varphi, \\ -D \frac{\partial n}{\partial z} \Big|_{z=0} = Q(r, \varphi), \\ Q(r, \varphi) = Q_0 \sqrt{\frac{T_s}{T_\infty}} \exp\left(-\frac{T_s}{T_\infty}\right), \end{cases} \quad (4.5)$$

where $T_s = T(r, \varphi, z=0)$ is the surface temperature, D is the coefficient of diffusion of a soot particle, T_∞ is the temperature of the gas flow, n is the concentration of soot particles in the gas, v is the gas velocity, k is the coefficient of thermal conductivity of the material, I_0 is the initial radiation flux density (for $z \rightarrow +\infty$), σ is the cross section for absorption of radiation by a soot particle, and $Q(r, \varphi)$ is the flux density of soot particles from the surface. In contrast to the coupling of differential equations via nonlinear sources [see (4.1)] that is usually dealt with in the theory of self-oscillatory processes, in the present system Eqs. (4.4) and (4.5) are coupled via the nonlinear boundary conditions.

It is convenient to go over to dimensionless variables in the system (4.4), (4.5) and to transform it into a system of integral equations for the quantities $I(r, \varphi)$ and $T_s(r, \varphi)$:

$$\begin{aligned} \bar{I}(\bar{r}, \varphi) &= \exp\left\{-\frac{\sigma Q_0 a^2}{D} \int_0^1 \bar{r}_1 d\bar{r}_1 \int_0^{2\pi} \frac{d\varphi_1}{2\pi} \exp\right. \\ &\quad \times \left. \left[\frac{v a}{2D} (r \cos \varphi - \bar{r}_1 \cos \varphi_1) \right] K_0\left(\frac{v a}{2D} \bar{u}\right) \bar{Q}(\bar{r}, \varphi_1)\right\} \theta(1-\bar{r}), \quad (4.6) \\ \bar{T}_s(\bar{r}, \varphi) &= \bar{T}_\infty + \int_0^1 \bar{r}_1 d\bar{r}_1 \int_0^{2\pi} \frac{d\varphi_1}{2\pi} \left\{ \frac{1}{\bar{u}} - \frac{\pi \eta a}{2k} \left[H_0\left(\frac{\eta a}{k} \bar{u}\right) \right. \right. \\ &\quad \left. \left. - N_0\left(\frac{\eta a}{k} \bar{u}\right) \right] \right\} \bar{I}(\bar{r}_1, \varphi_1); \end{aligned}$$

where we have introduced the notation:

$$\left. \begin{aligned} \bar{r} &= \frac{r}{a}, \quad \bar{T}_s = \frac{T_s}{T_0}, \quad T_0 = \frac{a I_0}{k}, \quad \bar{Q} = \frac{Q}{Q_0}, \quad Q_0 = Q|_{r=r_0}, \\ \bar{I} &= \frac{I}{I_0}, \quad \bar{T}_\infty = \frac{T_\infty}{T_0}, \quad \bar{u} = \frac{u}{a}, \\ u &= \sqrt{r^2 + r_1^2 - 2rr_1 \cos(\varphi - \varphi_1)}, \end{aligned} \right\} \quad (4.7)$$

H_0 is the Struve function, N_0 is the Neumann function, and K_0 is a zero order cylindrical function of imaginary argument.

The system (4.6) was solved numerically on a computer using the method of successive iterations. For the total power of the radiation reaching the target surface, the calculations gave the natural result (Fig. 18): as the velocity of the gas flow past the surface in-

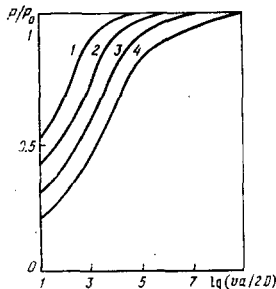


FIG. 18. Theoretical dependence of the radiation power reaching the surface through an absorbing layer of products formed by thermal decomposition of the material. Parameter values: $T_s/T_0=10$, $\bar{T}_\infty=0.1$, $\eta a/k=0$, $\sigma Q_0 a^2/D=10^4$ (1), 10^6 (2), 10^8 (3), and 10^{10} (4).¹¹³

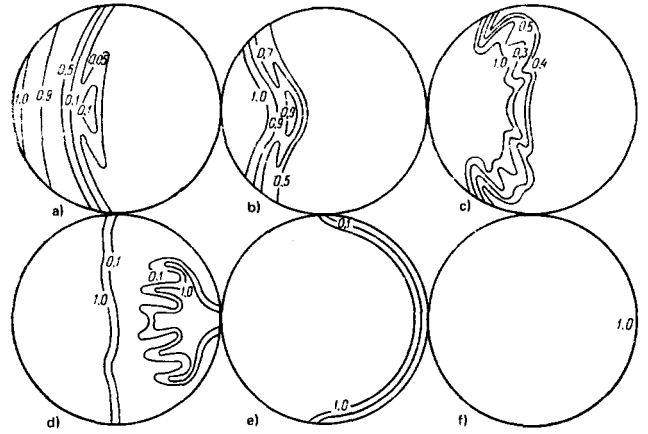


FIG. 19. Distribution of the radiation flux density I/I_0 over the surface area of the irradiated zone as a function of the blow rate. $va/2D=10^1$ (a), 10^2 (b), 10^3 (c), 10^4 (d), 10^5 (e) 10^6 (f); $\eta a/k=0$, $\sigma Q_0 a^2/D=10$.¹¹³

creased, the power increased. However, analysis of the radiation flux density distribution over the target surface showed that beginning with some gas flow velocity, the topography of the function $I(r, \varphi)$ changes considerably (Fig. 19) until the interaction region is no longer screened.

The stability of such dissipative structures was analyzed on a computer using different variations of the form of the zero-order iteration, while the convergence of the iteration procedure was checked by increasing the number of elements in the spatial grid $\{\Delta \bar{r}, \Delta \varphi\}$, the accuracy with which the integrals (4.6) are calculated, and the number of iterations. In the range of variation of the parameters studied, the dissipative structures turned out to be stable, and the iteration procedure converged well.

c) Surface instabilities (surface combustion wave)

When laser radiation interacts with a target whose dimensions are greater than the diameter of the beam, heat conduction effects begin to play an important role. In this section, we shall examine a spatial instability in the form of a traveling surface reaction front. This situation is characteristic of heterogeneous exothermal reactions in which a "seed" region of the reaction of the order of the dimensions of the beam begins to spontaneously expand under the action of the laser radiation, i.e., the reaction of a point located outside the zone of direct action of laser radiation is activated by the liberation of energy by the reaction at other points and by the spatial redistribution of heat by heat conduction. Since this problem has not been examined previously in the literature, we shall consider it in greater detail.

Let a laser beam with radius r_0 be incident on a metallic specimen occupying the half space $r \geq 0$. We shall assume that an exothermal oxidizing reaction with linear kinetics (this is valid for metals whose oxides do not form a compact coating) occurs on the surface of this specimen. For simplicity we shall also assume

that the absorptivity of the target during the growth of the oxide layer rapidly reaches a stationary state $A = \text{const}$. The change in the target temperature in this case is described by the following nonlinear boundary value problem:

$$\left. \begin{aligned} \frac{1}{a} \frac{\partial T}{\partial t} &= \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2}, \quad z > 0, \quad r \geq 0, \\ -k \frac{\partial T}{\partial z} \Big|_{z=0} &= AI(r) + \rho W v \exp \left(-\frac{T_d}{T} \right) \Big|_{z=0}, \\ T \Big|_{t=0} &= 0, \quad T \rightarrow 0 \quad \text{for} \quad \sqrt{r^2 - z^2} \rightarrow \infty \end{aligned} \right\} \quad (4.8)$$

with the natural condition for smoothness at $\delta=0$: $(\partial T / \partial r) \Big|_{r=0} = 0$. Here k and a are coefficients of heat conduction and thermal diffusivity, ρ is the density of the oxide, W is the specific reaction heat liberated by the oxidizing reaction, and v and T_d are constants in the linear oxidation law. We shall assume that the intensity distribution $I(r)$ is Gaussian

$$I(r) = I_0 \exp \left(-\frac{r^2}{r_0^2} \right). \quad (4.9)$$

As the analysis shows, the appearance of an instability in (4.8) and (4.9) in the form of a surface combustion wave has a threshold character. The stability boundary of the localized combustion regime relative to the quantities (I_0, r_0) can be found from the stationary solution of the problem (4.8). Outside the region of stability, the problem (4.8) does not have stationary solutions.

Taking into account the smoothness of $T(r, z)$ at $r=0$, we assume that at $z=0$

$$T(r, 0) \approx T_1 \left(1 - \frac{r^2}{d^2} \right), \quad r^2 \ll d^2, \quad (4.10)$$

and we shall find a relation between the parameters of the problem and the constants T_1 and d that have been introduced. We first note that near the axis of the beam the intensity of energy liberation can also be represented in Gaussian form:

$$I_{\text{ex}} = \rho v W \exp \left(-\frac{T_d}{T} \right) \approx \rho v W \exp \left(-\frac{T_d}{T_1} \right) \exp \left(-\frac{r^2}{b^2} \right), \quad b^2 = d^2 \frac{T_1}{T_d}. \quad (4.11)$$

Taking (4.9) and (4.11) into account, the stationary solution of (4.8) can be written in the form

$$T(r, z=0) = T_0(r) + T_{\text{ex}}(r), \quad (4.12)$$

where $T_0(r)$ is the temperature field arising from absorption of laser radiation energy (4.9), while $T_{\text{ex}}(r)$ is the temperature field arising from the exothermal reaction (4.11):

$$\begin{aligned} T_0(r) &= \frac{\sqrt{\pi}}{2} q T_d \exp \left(-\frac{r^2}{2r_0^2} \right) I_0 \left(\frac{r^2}{2r_0^2} \right), \quad q = \frac{AI_0 r_0}{kT_d}, \quad (4.13) \\ T_{\text{ex}}(r) &= \frac{\sqrt{\pi}}{2} \mu T_d b \exp \left(-\frac{T_d}{T_1} - \frac{r^2}{2b^2} \right) I_0 \left(\frac{r^2}{2b^2} \right), \quad \mu = \frac{\rho W v r_0}{kT_d}. \end{aligned}$$

Expanding (4.13) near the beam axis in powers of r and equating the coefficients with identical powers of r in (4.10) and (4.11), we obtain a system of equations for T_1 and d , which permits finding the functions $T_1(q, \mu)$ and $d(q, \mu)$. This system does not have real solutions for all values of q and μ . Eliminating d from this system of equations, taking into account the appearance of a solution of the equation for T_1 , we obtain an equation in parametric form for the boundary of the region of (q, μ) where the combustion front does not propagate:

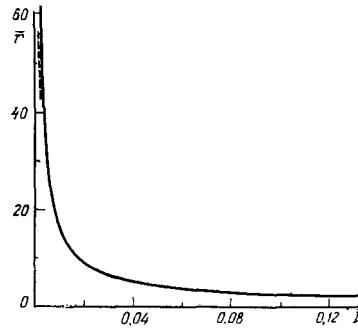


FIG. 20. Graph of the boundary of stability ($\bar{r} = (\rho v W / k T_d) r_0$, $\bar{I} = (A / \rho v W) I_0$). The curve $\bar{r}(\bar{I})$ has a self-intersection point; the position of the "loop" arising in this case is shown by the dashed line (it is not distinguishable on the scale of the figure).

$$\left. \begin{aligned} q - q_1(x) &= \frac{5}{4\sqrt{\pi}} \frac{25}{32} (1-x) \left(\frac{7}{25} + x^2 \right), \\ \mu - \mu_1(x) &= \frac{2}{\pi} \left(\frac{25}{32} \right)^3 (1-x) \left(\frac{7}{25} + x^2 \right)^3 \left(\frac{3}{5} - x \right) \\ &\quad \times \exp \left(\frac{16}{5} \frac{1+x}{(7/25) + x^2} \right), \\ T_1 &= \frac{\sqrt{\pi}}{2} q T_d \frac{32}{25} \frac{1}{1-x^2}. \end{aligned} \right\} \quad (4.14)$$

If r_0 and I_0 fall in the instability region $q > q_1(x)$, $\mu > \mu_1(x)$, then stationary solutions of Eq. (4.8) do not exist and a combustion front propagates along the surface of the specimen. In other words, Eq. (4.14) permits determining the critical values of the beam radius r_0 and intensity I_0

$$r_{0 \text{ cr}} = \frac{kT_d}{\rho v W} \mu_1(x), \quad I_{0 \text{ cr}} = \frac{\rho v W}{A} \frac{q_1(x)}{\mu_1(x)}, \quad (4.15)$$

i.e., the relation $r_{0 \text{ cr}}(I_{0 \text{ cr}})$ given in parametric form.

Figure 20 shows the stability boundary (in dimensionless form) $r_0 = f(I_0)$. As an analysis of Eq. (4.8) shows, a stationary temperature field is established below the stability boundary or inflammation occurs in a region of the order of the beam dimensions (localized combustion). Above the boundary, the region where the reaction occurs loses stability after a certain activation time. At the same time, peaks can be observed in the spatial temperature profile (analogous to those examined in Refs. 100 and 101).

We note that the appearance of a surface combustion wave was observed experimentally in Ref. 80, where laser combustion of tungsten in air stimulated by continuous CO_2 laser radiation was observed. Radiation with power $P \approx 1$ kW was focused onto a spot with dimensions < 1 mm on the face of a long tungsten rod with diameter ~ 1 cm inclined at an angle of 45° .

At first, over a time $t_1 < 1_s$, the tungsten was ignited in a region of the order of the dimensions of the beam, and then after $t_2 \gg t_1$, the combustion front propagated almost in a jump-like manner over the entire end-face of the rod and even onto its lateral surface.

d) Volume instabilities in distributed systems

Phenomena analogous to those examined in the preceding subsection can occur not only on the surface, but also within the volume of a system. As an example, we

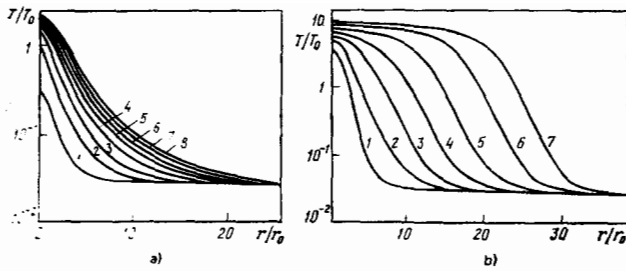


FIG. 21. Profiles of the effective temperature T/T_0 calculated for ZhS-12 glass in Ref. 106 at different times $t = n\Delta t$ (the number n is shown on the graphs) for the cases $I < I^*$ (a) and $I > I^*$ (b).

refer to Ref. 106, wherein a thermal model of optical breakdown of a dielectric with absorbing microinhomogeneities is examined. Such a problem was described in Ref. 106 by a nonlinear heat conduction equation (coefficient of thermal conductivity and coefficient of absorption of the laser radiation varied with temperature as $\sim \exp(-T_0/T)$). In this form, the problem is very similar to well-known problems of a thermal explosion. At the same time, these problems also differ considerably due to the fact that the problem examined is formulated in an infinite space. Due to this formulation, the traditional situation when the stationary equation for the temperature has three solutions $T_1 < T_2 < T_3$, one of which is unstable, does not arise here. The analysis performed in Ref. 106 shows that only two stationary solutions arise in the problem for the characteristic heat localization radius $R_1 < R_2$.¹³⁾ As the laser radiation intensity I increases, these radii converge and become equal at some value of the intensity $I = I^*$. For $I > I^*$, the problem does not have stationary solutions, while for $I < I^*$, the problem has solutions in the form of a localized temperature field. Figure 21 shows an example of the results of a calculation of the temperature profile for the problem indicated in the case $I < I^*$ and $I > I^*$.

The case when nonlinear absorption of linear radiation arises due to chemical reactions occurring in the volume of a substance was investigated in Refs. 114–117. A rigorous analysis of the development of a volume thermochemical instability for such processes was first performed in Ref. 115. In this paper, the problem of the thermal decomposition of a transparent polymer (polymethylmetacrylate) stimulated by laser radiation was examined. The decomposition products (soot) gave rise to increased absorption of radiation.

The change in the soot concentration was described by the equation of chemical kinetics

$$\frac{\partial c}{\partial t} = \nu(1-c) \exp\left(-\frac{T_a}{T}\right), \quad c|_{t=0} = 0, \quad \nu = \text{const}, \quad T_a = \text{const}. \quad (4.16)$$

The coefficient of absorption of the radiation α was as-

¹³⁾ For the case examined in the preceding subsection, these two radii have a clear physical meaning: one of them (R_2) is the characteristic scale of localization of heat due to the action of the laser source ($R_2 \sim r_0$) while the other (R_1) is the characteristic scale of localization of heat due to the "chemical" source (exothermal reaction).

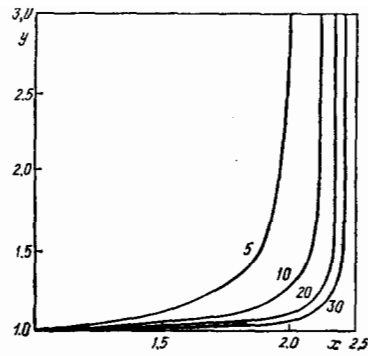


FIG. 22. The growth of the effective inclusion size $y = R/R_0$ with time $x = t/t_0$ for different values of the parameter $\gamma = T_a/T_0$. The quantity γ is indicated by the number labeling each curve.¹¹⁵

sumed to depend on the soot concentration according to the equation

$$\alpha = \alpha_0 c, \quad \alpha_0 = \text{const}. \quad (4.17)$$

The equations of heat conduction and light flux absorption were solved simultaneously with (4.16) and (4.17) in the quasistationary approximation (soot formation process is slow compared to heat conduction). As the analysis of this problem showed, the volume thermochemical instability developed in the presence of a "seed" inclusion, whose initial form was approximated by a sphere with radius R_0 . The instability indicated did not have a threshold and developed over a time

$$t_a \approx \frac{T_a}{T_0 \alpha_0 R_0 \nu} \exp\left(\frac{T_a}{T_0}\right), \quad T_0 = \frac{I_0 R_0}{4k}, \quad (4.18)$$

k is the coefficient of thermal conductivity and I_0 is the laser radiation intensity.

The soot formation process in this problem effectively increases the size of the inclusion $R = R(t)$. The graphs of the function $R(t)$, obtained in Ref. 115 are presented in Fig. 22. We note that Eq. (4.18) for the activation time of the reaction, just as for other quasistationary problems [see (3.14)] contains the characteristic factor $\exp(T_a/T_0)$.

5. NONLINEAR OPTICAL PHENOMENA IN CHEMICALLY ACTIVE MEDIA

As already noted above, one of the basic characteristics of thermochemical processes stimulated by laser radiation is the presence of feedback due, on the one hand, to the temperature dependence of the reaction rate and on the other hand to the variation of the optical properties of the system during the course of the reaction. This circumstance can lead to a number of interesting characteristics in propagation of laser radiation in the medium. We have in mind a new inertial nonlinearity of the medium, leading to self-action of light beams and differing from the traditionally examined mechanisms (see Refs. 91, 118, 119) and nonlinear effects accompanying resonance absorption of radiation (for example, Ref. 120, etc.). The mechanism of the nonlinearity related to laser-stimulated photochemical reactions was discussed in Ref. 121. Here, we shall examine the effect of the thermochemical nonlinearity on the propagation of a laser beam in the medium.³⁸

Depending on the nature of the reactions occurring, such a nonlinearity can lead both to self-focusing and self-defocusing of the beam.

During the course of a chemical reaction, the index of refraction of the medium can vary due to the formation of substances with dielectric permittivity ϵ_2 , differing from the dielectric permittivity ϵ_1 of the starting substance. Thus, if the concentration of the reaction product is c and $|\epsilon_1 - \epsilon_2| \ll |\epsilon_1|$, then the dielectric permittivity of the medium is given by relations following from the Lorenz-Lorentz equation⁶⁴ [see (3.24)]:

$$\begin{aligned} \epsilon &= \epsilon_1 + c(\epsilon_2 - \epsilon_1), & 0 \leq c \leq 1, \\ n &= n_1 + c(n_2 - n_1), & n = n_1 + c(n_2 - n_1), \end{aligned} \quad (5.1)$$

where $\sqrt{\epsilon_k} = n_k + i\kappa_k$ ($k=1, 2$). In what follows, we shall assume for simplicity that $\kappa_1 = \kappa_2 = \kappa = \text{const}$. If $n_2 > n_1$, then a factor leading to self-focusing of the radiation appears in the medium. On the other hand, the condition $n_2 < n_1$ indicates the appearance of a factor leading to defocusing.

However, such a chemical nonlinearity can rarely exist in pure form. More often it is accompanied by a thermal nonlinearity, a number of properties of which were examined previously (see, for example, Ref. 118). Since the index of refraction depends on temperature, together with the chemical nonlinearity there also appears a competing, thermal mechanism for the nonlinearity. The direction of action of this mechanism is determined by the sign of the derivative $\partial n / \partial T$. For $\partial n / \partial T > 0$, the thermal mechanism leads to self-focusing, while in the opposite case, it leads to self-defocusing. In gaseous media, with which we shall be concerned, usually $\partial n / \partial T < 0$, where the derivative is calculated at constant pressure.

The equations that describe the spatial distribution of radiation have the following form in the geometric optics approximation¹¹⁸

$$\begin{aligned} \frac{\partial I}{\partial z} + u \frac{\partial I}{\partial r} + \left(\frac{\partial u}{\partial r} + \frac{u}{r} \right) I + \delta I &= 0, \\ \frac{\partial u}{\partial z} + u \frac{\partial u}{\partial r} = \frac{\partial N}{\partial r}, & \quad N = \frac{\text{Re}(\epsilon - n^2)}{2n^2} = \frac{n^2 - n_0^2 - \kappa^2}{2n^2}, \end{aligned} \quad (5.2)$$

where I is the radiation intensity, u is the inclination of the elementary ray to the beam axis, z is the longitudinal coordinate and r is the transverse (radial) coordinate, δ is the coefficient of absorption of the radiation in the medium [in what follows, we neglect the term δI in (5.2), assuming that the energy losses at the distances of interest are small], and n_0 is the value of n_i at the initial temperature of the medium.

Assuming that $\partial n_1 / \partial T = \partial n_2 / \partial T \equiv \partial n / \partial T$, the quantity $\partial N / \partial r$ can be rewritten approximately in the form ($|n_2 - n_1| \ll n_1$):

$$\frac{\partial N}{\partial r} \approx \frac{1}{n_0} \frac{\partial n}{\partial T} \frac{\partial T}{\partial r} + \frac{n_2 - n_1}{n_0} \frac{\partial c}{\partial r}. \quad (5.3)$$

The change in the temperature of the medium is related to absorption of radiation and the heat liberated by the reaction:

$$\frac{\partial T}{\partial t} = \frac{W}{c_p} \frac{\partial c}{\partial t} + \frac{\delta}{c_p \rho} I, \quad (5.4)$$

where W is the specific reaction heat, c_p is the specific

heat capacity, and ρ is the density of the medium (we assume that $\rho = \text{const}$, $c_p = \text{const}$). In (5.4), we neglected heat conduction effects, assuming that the characteristic times of the processes τ are short compared to the characteristic heat conduction time ($\tau \ll r_0^2/a$, r_0 is the beam radius, and a is the thermal diffusivity of the medium).

Finally, we shall include the kinetic equation of the reaction itself:

$$\frac{\partial c}{\partial t} = k_0(1-c) \exp\left(-\frac{T_0}{T+T_{1n}}\right), \quad (5.5)$$

where k_0 and T_0 are constants for a given reaction and T_{1n} is the initial temperature of the medium.

We shall give the initial and boundary conditions for Eqs. (5.2)–(5.5) in the form

$$\begin{aligned} I|_{z=0} = I_0(r), & \quad u|_{z=0} = 0, \\ c|_{t=0} = 0, & \quad T|_{t=0} = 0. \end{aligned} \quad (5.6)$$

First of all, it is evident from the system of equations (5.2)–(5.5) that if

$$A \equiv \frac{1}{n_0} \frac{\partial n}{\partial T} \frac{W}{c_p} + \frac{n_2 - n_1}{n_0} = 0, \quad (5.7)$$

then the dynamics of the radiation beam are exactly the same as in the absence of a chemical reaction, when only the thermal nonlinearity is present. Indeed, introducing the quantity $\theta = T - (W/c_p)c$, we obtain from (5.2)–(5.5) a system of equations for u , I , and θ , coinciding exactly with the well-known equations describing thermal defocusing.^{118,119}

In the general case, the solution of the problem formulated above presents great difficulties. For this reason, we shall make some simplifying assumptions. First, we shall assume that the changes in the temperature of the medium during the process are small

$$T \ll T_1 = \frac{T_{1n}}{T_0}. \quad (5.8)$$

Further, we shall assume that $c \ll 1$ (i.e., we shall restrict our attention to stages of the process that are far from saturation). Finally, we shall examine only one important case, namely, the near-axial approximation¹¹⁸ (i.e., we shall examine the dynamics of the beam only near the beam axis).

We shall give the radiation intensity distribution at the entrance of the beam to the medium in the form

$$I_0(r) = I_0 \left(1 - \frac{r^2}{r_0^2} \right), \quad r^2 \ll r_0^2. \quad (5.9)$$

For what follows, it is convenient to introduce the following notation:

$$\left. \begin{aligned} \Phi &= \frac{T}{T_1}, & j &= \frac{I}{I_0}, & \tau &= \frac{\delta I_0}{\rho c_p T_1} t, & \xi &= \frac{r}{r_0}, \\ \eta &= \frac{z}{r_0}, & Q &= \frac{1}{\alpha} c, & \alpha &= \frac{\rho c_p T_1}{\delta I_0} d_0, & v &= -\frac{T_1}{n_0} \frac{\partial n}{\partial T} > 0, \\ \gamma &= \alpha \frac{n_2 - n_1}{n_0}, & \beta &= \frac{\partial W}{\delta I_0} d_0, & d_0 &= k_0 \exp\left(-\frac{T_0}{T_{1n}}\right). \end{aligned} \right\} \quad (5.10)$$

Then, using the assumptions adopted with $\alpha \ll 1$, the starting boundary value problem can be rewritten as follows:

$$\left\{ \begin{aligned} j_\eta + \frac{1}{\xi} (\xi u j)_\xi &= 0, & j|_{\eta=0} &= 1 - \xi^2, \\ u_\eta + u u_\xi &= -v \Phi_\xi + \gamma Q_\xi, & u|_{\eta=0} &= 0, \\ Q_\tau &= 1 + \Phi, & \Phi|_{\tau=0} &= 0, \\ \Phi_\tau &= \beta(1 + \Phi) + j, & Q|_{\tau=0} &= 0. \end{aligned} \right. \quad (5.11)$$

In the near-axial approximation, the solution of this system must be sought in the form

$$\begin{aligned} j(\xi, \eta, \tau) &= \frac{1}{f^3(\eta, \tau)} \left(1 - \frac{\xi^2}{f^2(\eta, \tau)} \right), \quad u(\xi, \eta, \tau) = \xi \varphi(\eta, \tau), \\ Q(\xi, \eta, \tau) &= D(\eta, \tau) - \xi^2 F(\eta, \tau), \quad \Phi(\xi, \eta, \tau) = H(\eta, \tau) - \xi^2 B(\eta, \tau). \end{aligned} \quad (5.12)$$

Substituting (5.12) into (5.11) and eliminating some functions leads to a system of equations that is the basic system for further analysis of beam dynamics in a chemically active medium:

$$\begin{cases} f_{\eta\eta} = (2\nu F_\tau - 2\gamma F) f, & f|_{\eta=0} = 1, & F|_{\tau=0} = 0, \\ F_{\tau\tau} = \beta F_\tau + \frac{1}{f^4}, & f_\eta|_{\eta=0} = 0, & F_\tau|_{\tau=0} = 0. \end{cases} \quad (5.13)$$

It should be noted that the number of parameters can be reduced from three to one, with the parameter being $\varepsilon_c = \gamma/\nu\beta$, by a scale transformation of the quantities F, η , and τ in (5.13). Depending on the signs and ratios between the coefficients, the system of equations (5.13) describes different cases of nonlinear beam dynamics in the medium in which the chemical reactions occur.

First of all, for small η the solution of (5.13) is given by the expression

$$f = 1 + \nu \left[\frac{e^{\beta\tau} - 1}{\beta} (1 - \varepsilon_c) + \varepsilon_c \tau \right] \eta^2 + \dots \quad (5.14)$$

It follows from here that for $\tau \ll 1/\beta$ the beam defocuses due to direct heating of the medium by the radiation and formation of a thermal defocusing lens ($f_{\eta\eta}|_{\eta=0} = 2\nu\tau > 0$). Further, if the reaction is exothermal ($\beta > 0$) and, in addition, $\varepsilon_c = \gamma/\nu\beta < 1$, then the thermal defocusing lens is stronger than the focusing lens, which could arise due to the formation of substances with a different value of n . [We note that the quantity $1 - \varepsilon_c$ coincides to within the factor $\sim -\nu\beta$ with the quantity A introduced in (5.7).] In the case of an endothermal reaction $\beta < 0$, $\varepsilon_c < 0$ (as well as in the general case $1/\varepsilon_c < 1$, including $\beta > 0$, $\varepsilon_c < 0$, etc.), thermal defocusing is replaced by focusing due to the increase in the index of refraction. This change in the nature of the process occurs over a time τ , determined from the equation

$$\frac{e^{\beta\tau} - 1}{\beta\tau} = \frac{\varepsilon_c}{\varepsilon_c - 1}. \quad (5.15)$$

Over this time, the chemical lens reaches the point $\eta = 0$ and the beam begins to converge immediately after it enters into the medium.

We note that for an endothermal reaction ($\beta < 0$), when $\gamma = 0$, i.e., the index of refraction does not change due to the chemical reaction, a self-stabilizing process occurs with a transition into the steady-state regime [$f = \sqrt{1 + 2\nu|\beta|^{-1}\eta^2} F_\tau = |\beta|^{-1}$; compare (5.14)]. This nature of the process is a result of the competition of two thermal mechanisms: heating of the medium due to absorption of radiation energy and cooling of the medium due to the endothermal nature of the reaction.

The case $\varepsilon_c = 1$ [compare (5.7)] occupies an intermediate position: for $\gamma > \nu\beta$, the chemical lens becomes stronger than the thermal lens with time and, vice versa, for $\gamma < \nu\beta$, the defocusing factors are dominant over the entire time of the process.

Without stopping to consider the particular solutions and analyzing the system of equations (5.13) in greater

detail, we shall briefly examine the influence of diffraction effects on the beam propagation dynamics in a medium with a chemical inertial nonlinearity. These effects can be included using a technique analogous to that used, for example, in Ref. 122 and reduces to adding to the right side of the first equation in (5.13) the term μ/f^3 , where $\mu = (\gamma_0/R_d)^2$, $R_d = k r_0^2$ is the diffraction length of the beam ($k = 2\pi n_0/\lambda$). We shall examine the particular case $\beta = \nu = 0$, when thermal effects can be neglected. Then we have

$$\begin{cases} f_{\eta\eta} = \frac{\mu}{f^3} - 2\gamma F f, \\ F_{\tau\tau} = \frac{1}{f^4}. \end{cases} \quad (5.16)$$

At the point the beam enters the medium $f|_{\eta=0} = 1$. For this reason, the self-focusing condition (when the focusing action of the chemical lens turns out to be stronger than diffraction divergence) $f_{\eta\eta}|_{\eta=0} < 0$ assumes the form

$$\begin{cases} f_{\eta\eta} = \mu - 2\gamma F < 0 & \text{or} & \frac{\gamma\tau^2}{\mu} > 1, \\ F_{\tau\tau} = 1. \end{cases}$$

In dimensionless form, this condition appears as follows:

$$(Ec) > (Ec)_{cr} = \frac{\pi \rho c_p T_{1n}^2}{k^2 \delta T_0} \frac{n_0}{n_2 - n_1}. \quad (5.17)$$

In other words, in contrast to Ref. 118, the product of the total energy of the laser beam $E = \pi r_0^2 I_0 t$ by the concentration of the reaction product $c = d_0 t$ is critical.

When condition (5.17) is satisfied, a constriction appears in the beam, which at first moves into the bulk of the medium from the point $\eta = 0$ and then, as the reaction continues, begins to move in the opposite direction. The spatial structure of the beam in this case assumes a quite complex form, which changes strongly with time.

Figure 23 shows the behavior of the beam profile $f(\eta)$ at different times τ , found on the basis of the numerical solution of the system of equations (5.16). For sufficiently large τ (when $c \sim 1$), the medium becomes optically homogeneous and the initial beam profile is restored.

Experiments were performed on the pyrolysis of NH_3 and CF_2I (in a mixture with the buffer gas SF_6) by CO_2 laser radiation. The pressure of the gas mixture in the

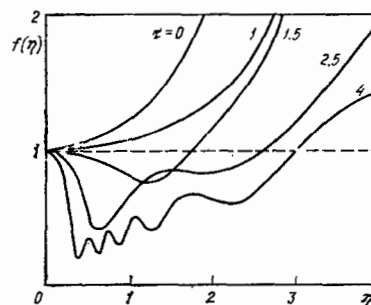


FIG. 23. Behavior of the laser beam profile at different times (for $\gamma = \mu = 1$; the cases $\gamma \neq 1$ and $\mu \neq 1$ reduce to the preceding case by scale transformations of ξ and τ).

cell varied from 10 to 100 torr and the radiation power was 20 W. In passing through the cell, the beam experienced self-focussing several times. In addition, more complicated processes were observed: random change in the transmitted radiation power, division of the beam into several components, etc.

We examined here the simplest example of a chemical nonlinearity. The beam dynamics become much more complicated if more than one final product (with different optical properties) can form in the reaction or if the reaction can proceed via several channels with the formation of different intermediate substances. Additional special features in the propagation of radiation in such media can also arise from the fact that in a thermodynamically nonequilibrium system the relation between the different reaction components depending on the conditions can strongly differ from the thermodynamically equilibrium relation.

6. CONCLUSION

The intense development of laser thermochemistry presented us with a traditional problem: a number of interesting works appeared while this review was being written, in particular, the experimental papers Refs. 123-126 on stimulation of a number of homogeneous reactions. These papers were not included in this review, since in order to interpret them, a special theoretical analysis is required. Nevertheless, on the whole, we feel that the present review correctly reflects the frontiers of research in laser thermochemistry at the middle of 1981.

We do not want the reader to form the opinion that everything is now fundamentally clear in laser thermochemistry and future research can only be concerned with refining some details of specific processes. In our opinion, this is a broad field for research for all specialists interested in the problems discussed here. Problems that have not been researched include thermochemical phenomena in external electric and magnetic fields, problems of kinetics of chemical processes in systems located near a critical point, and many others.

We would like to make a few remarks concerning a class of problems that fell outside the scope of the present review. These include inverse problems of laser thermochemistry, i.e., the possibility of determining the kinetic and optical characteristics of the reaction with the help of relatively simple measurements of the thermodynamics of the processes (temperature, heating rate). Some methods for solving such problems were proposed in Refs. 127 and 128. In our opinion, for heterogeneous processes, there is a possibility in a number of cases to perform diagnostics of atomic characteristics of a surface without using the fine methods of microscopic investigations.

In conclusion, we emphasize once again that although laser thermochemistry is based on thermal control of chemical processes and in this sense we can conceive, purely theoretically, a "nonlaser" method for creating a programmed, optimal, dynamic temperature field,

but there is hardly a way other than a laser for creating such a field. Only the presence of thermal feedback and the high capability for self-organization of the systems involved permit creating in laser thermochemistry complex space-time distributions of such a temperature field. In this sense, we can say that the unique characteristics of laser radiation permit realizing qualitatively new types of thermal control of chemical processes.

We thank A. M. Prokhorov for his interest in the development of research on laser thermochemistry and his constant support.

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Translated by M. E. Alferteff