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Macroscopic kinetics of thermochemical processes on laser heating: current state and prospects

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Abstract. The characteristic features of the kinetics and dynamics of processes occurring on laser heating of chemically reactive media are analysed. Attention is concentrated on effects due to the macroscopic disequilibrium and the feedbacks between various degrees of freedom of thermochemical systems. Processes stimulated by laser radiation in homogeneous media, the phenomena occurring on laser heating of metals, and the physicochemical processes occurring on laser heating of liquids are considered. Examples of certain technological applications of laser thermochemistry are presented: laser-induced precipitation of a substance from the gas phase, etching and modification of surfaces, synthesis of compounds, etc. The bibliography includes 123 references.

I. Introduction

Among the effects associated with the chemical reactions of substances in the field of a powerful light wave, the photochemical and thermochemical effects differ significantly. Until the end of the 1970s, mainly photochemical processes were investigated. However, during the last decade, there has been a sharp growth of interest in thermochemical processes. This is associated with their wide occurrence and the prospects for their employment to create new progressive technologies in many branches of industry, and effective research methods in the field of nonlinear dynamics.

The characteristic features of the kinetics of thermochemical processes occurring on laser heating of chemically reactive media are associated principally with two factors: with the disequilibrium due to the nonstationary and/or inhomogeneous occurrence of reactions and with the mutual influence (feedback) between the chemical state of the medium and energy and mass transfer processes in the field of the laser radiation. Therefore the main problems in modern laser thermochemistry are as follows: analysis of the mechanisms of the generation of feedbacks between the chemical, thermal, and other degrees of freedom† of the system in various problems; the discovery of the most typical nonlinear features and analysis of the influence of various feedback channels on the kinetics and dynamics of thermochemical processes; the study of self-organisation phenomena induced by the laser radiation during the heating of the test substances; the search for the possible ways of achieving an effective control of thermochemical processes with the aid of lasers.

The complexity of such studies is due to the great variety of specific conditions under which nonlinear thermochemical processes take place, the wide range of variation in the rates of chemical reactions, the different phase states of the reactants (solids, liquids, and gases), and the multiplicity of procedures for the laser heating of chemically reactive media.

In the present review, we have tried to describe the ideas and theoretical and experimental results constituting the basis of modern research into the nonlinear dynamics of laser-induced thermochemical processes. If one compares them with studies carried out within the framework of the macroscopic kinetics and physics of combustion, where the role of disequilibrium and of the feedbacks between different degrees of freedom of the system is also significant, then two factors should be noted. First, the thermochemical processes occurring under the influence of laser radiation are frequently characterised by a high level of disequilibrium. For example, in the laser-induced chemical precipitation of a substance from the gas phase, the temperature may vary at rates up to 10^{10} K s^{-1} and there is a possibility of temperature gradients up to 10^7 K cm^{-1}. The latter factor leads, in particular, to an intense interaction of the thermal, concentration, charge, and other fluxes and can ultimately alter radically the kinetics of the respective processes. Second, laser radiation is itself capable of generating new feedback channels in

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† The degree of freedom is a concept which arose from classical mechanics. In nonlinear dynamics, this concept is used to designate some kind of dynamic characteristic describing the state of the system, for example temperature, concentration of the reactants, etc. The term 'degree of freedom' is frequently used in relation to each differential first-order equation describing the variation of physically different characteristics (thermal degree of freedom, chemical degree of freedom, etc.). The reader may become acquainted with the principal concepts of nonlinear dynamics in the book by M I Rabinovich and D I Trubetskov, *Vvedenie v Teoriyu Kolebanii i Voln* (Introduction to the Theory of Vibrations and Waves) (Moscow: Nauka, 1984).

the system and of altering the dynamic properties of the medium. These factors do in fact indicate the specific features of the laser heating of chemically reactive media compared with heating by nonlaser sources.

II. History of the problem

Quantitative methods for the description of the dynamics of chemical systems arose long after the formulation of the fundamental theoretical ideas in mechanics, optics, theory of electricity, hydrodynamics, and classical electrodynamics. The first fundamental equations of the law of mass action were proposed by Guldberg and Waage, while the mathematical laws of chemical reactions were first formulated and elucidated by van't Hoff.‡ Arrhenius explained the mechanism of the temperature variation of the reaction rate constants and formulated the second fundamental law of chemical kinetics (the Arrhenius equation).

The fundamentally nonlinear nature of these laws makes it possible to understand the theoretical difficulties and problems in the analysis of the dynamics of chemical systems which arose in the initial stage of the development of chemical kinetics. These difficulties were overcome only as a result of the development and application to chemical systems of the ideas and methods of the theory of nonlinear oscillations. (The role which chemical systems have played in the formulation of nonlinear concepts and images such as autowave, reverberator, dissipative structure, etc. is in its turn also well known.)

During the period from 1928 to 1940, Semenov, Zel'dovich, Frank-Kamenetskii, Kharitonov, Todes, and others carried out fundamental studies in the field of the chemical kinetics and physics of combustion, where the dynamics of chemical systems with feedbacks between chemical, thermal, and other degrees of freedom came to the fore. These investigations served as the basis of a new scientific discipline — macroscopic kinetics, within the framework of which the most important basic models, specifying the mechanisms and dynamic manifestations of the action of feedbacks in thermochemical systems, were created and developed.[1,2] Studies on oscillatory chemical reactions have played an important role in the development of macrokinetics.[3-6]

Studies on chemical thermodynamics, devoted to the investigation of the states of equilibrium in chemical systems, served as an ideologically important addition to the research into chemical kinetics. This branch of research, associated with the names of Gibbs, Helmholtz, van't Hoff, van der Waals, Nernst, and others, underwent a qualitatively new development when the ideas of chemical thermodynamics began to be applied to the analysis of nonequilibrium systems. As a result of studies by Onsager, the linear nonequilibrium thermodynamics was created, while studies by Prigogine led to the formulation of nonlinear nonequilibrium thermodynamics and completed the process of merging chemical kinetics and chemical thermodynamics into a single integral science.

Laser thermochemistry constitutes in essence a development and a generalisation of the ideas of macroscopic kinetics and nonequilibrium thermodynamics in relation to a substance placed in the field of laser radiation.

Immediately after the creation of lasers, it was by no means a simple matter to decide whether this introduced anything new into chemistry. Lasers were used initially in photochemistry as sources with a high spectral brightness. The most important discoveries were made when quantum electronics 'assimilated' the IR range. These discoveries are well known (see, for example, Refs 7-12). They include the multiphoton IR photodissociation of molecules, selective as regards substances, which permits laser separation of isotopes, the elimination of small amounts of impurities from gases, etc., as well as effects associated with the generation of a disequilibrium at the level corresponding to the separation between the vibrational and translational temperatures, which permit the laser control of radical synthesis (in particular permit the synthesis of thermally less stable compounds on IR photolysis of more stable compounds — for example the synthesis of CF_3I by the photolysis of CF_3Br in an iodine atmosphere[13]).

Studies in the field of reactions initiated by laser heating developed more slowly. According to Tal'roze's estimates,[14] 170 studies devoted to the thermochemical effect of laser radiation were published in 1977. Among them, it is possible to distinguish three groups of investigations the results of which were of value for subsequent research into the nonlinear dynamics of thermochemical processes.

1. Experimental and theoretical studies devoted to the development of thermochemical instability in reactions involving the heterogeneous oxidation of metals in air under the influence of laser radiation.[15-17]

2. Studies on the thermal bistability and dissipative structures on heating gaseous media by optical radiation.[11,18,19] In a number of investigations,[15-19] attention was first drawn to the fact that a new feedback channel between the chemical and thermal degrees of freedom of the system is created in the field of laser radiation. This feedback is achieved via a change in the absorption characteristics of the system during chemical reaction. In particular, when radiation is absorbed preferentially by the chemical reaction product, a positive feedback is generated in the system, leading to thermochemical instability, bistability, etc.

3. Studies undertaken to determine the conditions governing the separation between the vibrational and translational temperature on laser stimulation of homogeneous reactions (see, for example, Refs 7, 9-14, 20-22). These investigations showed that, at pressures of the gas mixture above 1 torr under typical experimental conditions with continuous-wave CO_2 lasers, the thermal mechanism of chemical reactions predominates in the majority of substances. For this reason, all the remarkable properties of IR-photochemical processes, attention to the possible manifestation of which was drawn already in the studies by Askar'yan (1964) and other workers (for the history of this problem, see Dunskaya[23]), therefore occur as a rule only at fairly low gas pressures. On the other hand, in experiments (see, for example, Oraevskii[9] and Molin et al.[11]) at high pressures of the gas mixture, a marked difference is observed between the products of laser and nonlaser pyrolysis. A marked dependence of the yield of the reaction on the wavelength of the laser radiation, threshold phenomena, etc. were observed. The experimental results clearly indicated a specific disequilibrium of the chemical process during the IR-laser heating of the gases, but the fundamental details of the generation of such disequilibrium remained obscure. The observed discrepancy between the seemingly photochemical behaviour of a number of reactions and the explicit thermal regime governing the injection of the energy of the laser radiation aroused a lively controversy between supporters of particular mechanisms for these reactions. It was of interest to note that at approximately this time a controversy of a similar nature arose concerning the thermal and nonthermal nature of the laser-induced annealing of semiconductors.[24,25]

Thus towards the end of the 1970s, the situation was objectively prepared for the vigorous development of research into the dynamics of the laser heating of chemically reactive media, analysis of the dynamics of heating in the IR spectral range being particularly timely.

‡ Van't Hoff's book *An Outline of Chemical Dynamics* was published in 1884. It laid the foundations for the development of chemical kinetics and, in Semenov's words, outlined the path for its development during the next half century.

III. Thermochemical processes stimulated by laser radiation in homogeneous media

1. The macroscopic disequilibrium and feedbacks

The interaction of light with matter is a complex nonlinear process, which can be arbitrarily divided into several stages: the absorption of light by matter; energy and matter transfer (processes involving heat and mass exchange with the surrounding medium, redistribution of energy among the internal degrees of freedom); the chemical reaction proper. Definite degrees of freedom, the evolution of which actually determines the behaviour of the system, correspond to these stages. The nature of such evolution can change significantly as a result of the interaction (feedbacks) between various degrees of freedom.

Certain types of feedbacks generated in the presence or absence of radiation may be indicated.

1. Purely thermal feedbacks, arising as a consequence of changes in temperature caused by the evolution or absorption of heat in the course of various physicochemical processes. This alters the rates of chemical reactions and transfer processes. Such feedbacks play a key role in problems of the physics of combustion,[1,2] the stability of ideal mixing flow reactors,[5] etc.

2. Selective feedbacks due to local changes in the absorptance of the medium during the process (owing to changes in its chemical composition, density, etc.). As a result of these feedbacks, the local amounts of radiant energy introduced into the test substance are altered.

3. The feedbacks due to various nonlinear optical effects leading to a change in the spatial distribution of the radiation density.

4. Kinetic feedbacks. For example, in the case of multi-pathway chemical reactions, the rate of reaction via one pathway depends on the rates of reaction via the other pathways as a consequence of the change in the chemical composition of the medium. Such feedbacks are responsible for the development of auto-oscillations in Belousov–Zhabotinskii reactions.

In connection with the foregoing, the question arises of the construction and study of the basic mathematical models taking into account the most significant mechanisms affecting the process dynamics. Such study constitutes the basis for the subsequent construction of a theory permitting a quantitative comparison with the experiment. The mathematical procedures necessary for this are provided by the theory of nonlinear oscillations and the theory of stability, bifurcations, and catastrophes.

In the analysis of the chemical action of laser radiation towards the end of the 1970s, use was frequently made of the idea that, if an amount of energy E is introduced into the medium with the aid of laser radiation in the absence of heat and mass transfer, then the chemical result of such thermal action of the radiation should not depend on the particular substance (starting material, reaction product, or buffer component) which absorbs this energy. On the other hand, the dependence of the chemical result not only on the amount of absorbed energy but also on the wavelength of the laser radiation was regarded as indirect proof of a nonequilibrium distribution of the molecules among the vibrational–rotational energy levels. However, it was shown later that, generally speaking, this hypothesis is incorrect. This can be understood from the following considerations.

Evidently the radiant energy absorbed by the reactant determines the change in the temperature of the medium. On the other hand, the chemical result depends on the ratio of the rate of change of temperature $(dT/dt)/T$ and the rate of relaxation of the chemical composition $(dN/dt)/N$. If $(dN/dt)/N \gg (dT/dt)/T$, then the chemical composition is close to equilibrium for the given temperature. In this case, the concentration of the reacted substance (N) depends on the temperature and is determined by the constant for the chemical equilibrium in the reactor, i.e. for a slow change in temperature, the corresponding process is close to equilibrium. For the reverse ratio of the chemical and thermal rates, the process is of a nonequilibrium type. A well-known example, illustrating this fact, is provided by the quenching of the chemical composition on rapid cooling of the reactor. In the general case, the chemical result is a functional of temperature and depends on the way in which this temperature has been reached.

We shall now take into account the change in the absorptance capacity of the medium. Since the different components absorb radiation in different ways at different wavelengths, a feedback is established in the system between the chemical and thermal degrees of freedom. For example, this feedback is positive if radiation is absorbed by the reaction product.[18,19] Thus the dynamics of the change in temperature and hence the chemical result of the laser radiation depend in general not only on the amount of energy absorbed but also on the wavelength of the laser radiation.

We shall now consider the very simple reaction

$$A \rightarrow B + \text{heat}\,. \tag{1}$$

The dependence of the dynamics of this reaction on the wavelength can be conveniently characterised by the selectivity parameter

$$\mu = \frac{\sigma_A - \sigma_B}{\sigma_A + \sigma_B}\,,$$

where σ_A and σ_B are the cross-sections for the absorption of radiation by substances A and B. When μ changes, there is a possibility of a change in the nature of the feedback, in the reactor dynamics, and, naturally, in the chemical result of the exposure to laser radiation. Depending on the chosen values of the parameters, the system can reach a stable stationary state or an auto-oscillatory regime[18,26] and the effect of the limit at the red end of the spectrum as well as threshold and other phenomena normally characteristic of photochemical reactions may be observed.

2. Bifurcations in the chemical state of the medium

In order to demonstrate the characteristic features of reactions in the field of laser radiation, we shall examine the simplest situation where only the reversible reaction

$$A \rightleftarrows B + \text{heat} \tag{2}$$

takes place in a chemical reactor with ideal mixing. The equation for the kinetics of this reaction is

$$\frac{dc}{dt} = k_1(1-c) - k_2 c\,, \tag{3}$$

where c is the concentration of the product B and k_1 and k_2 are the rate constants for the forward and reverse reactions, which depend on temperature in accordance with the Arrhenius law:

$$k_1(T) = k_1^{(0)} e^{-T_1/T}\,, \quad k_2(T) = k_2^{(0)} e^{-T_2/T}\,. \tag{4}$$

The change in the temperature of the medium T is determined from the heat balance equation

$$C\frac{dT}{dt} = AP + W\frac{dc}{dt} - P_1(T)\,, \tag{5}$$

where A is the absorptance of the medium, P the power of the radiation, W the heat of reaction, P_1 the power associated with heat losses, and C the total heat capacity of the medium.

The characteristics of the laser-induced heating are determined by the explicit dependence of the absorptance of the medium A on its chemical composition and temperature and also on the wavelength of the radiation. To make the treatment concrete, we shall assume that the reactor is optically thin in the direction of propagation of the radiation. Then

$$A = [(1-c)\sigma_A + c\sigma_B]Nh\,, \tag{6}$$

where N is the total number of species of substances A and B per unit volume and h is the optical thickness of the reactor.

We shall consider separately the visible and infrared wavelength ranges. In the visible range, the energy of a quantum of the laser radiation $\hbar\omega$ is high, i.e. $\hbar\omega \gg kT$, the temperature dependence of the absorption cross-sections σ_A and σ_B is as a rule extremely weak, and one can assume that σ_A, σ_B = const. Analysis of Eqns (3)–(6) shows that the chemical system considered passes from any kind of initial conditions to a stable stationary state. Allowance for photochemical pathways with participation of electronically excited molecules does not alter this conclusion. There may be several final stationary states (this entails hysteresis phenomena when parameters such as the power and wavelength of the radiation are changed).

The number of stationary states changes when the parameters pass through certain critical (bifurcation) values, in the vicinity of which even slight changes in the latter lead to a sharp alteration of the chemical result. The point is that, starting from the same initial state, the system is able to enter the region of attraction by other final states after passing through the bifurcation point. In this connection, one should note that laser control in the vicinity of bifurcation values does not require much energy expenditure. In other words, even small influences can yield a major effect.

In contrast to the visible region, in the IR region $\hbar\omega \approx kT$ and the absorption cross-sections depends strongly on temperature. As a result, new dynamic regimes arise in the system — the number of stationary states increases and stable auto-oscillations in temperature and concentration and more complex types of hysteresis phenomena become possible.[27]

The foregoing explains the complexity of the behaviour of even simple chemical systems under the influence of laser radiation.

3. Transient regimes and metastable ordering

Sometimes not only the final states but also transient processes are of practical interest. This is associated with the fact that in chemistry transient processes may be extremely long. Furthermore, particular products of interest may be formed in the intermediate stages, vanishing as the final state is approached.

As an example, we shall consider the imidisation reaction in the field of the continuous radiation from a CO_2 laser.[28] The essential feature of the reaction is as follows. The starting material — the polyamidoacid (PAA) — is heated and water molecules are split off and removed. This results in the formation of a thermostable polymeric aromatic polyimide (PI) (polypyromellitimide), which has useful mechanical and electrical insulating properties. Studies have shown that the quality of the polyimide is higher the more complete the removal of water. In the usual technology for the manufacture of the polyimide (under isothermal conditions), the complete removal of water requires that the process be carried out at higher temperature ($T \gtrsim 670-770$ K, where the rate of evaporation increases); however, under these conditions polyimide thermal degradation processes begin and, in addition, the water formed may cause the hydrolysis of the polyimide. As a result, the degree of imidisation is usually 75%–80%.

If the polyamidoacid is heated with the aid of the radiation from a CO_2 laser, water is in fact fully removed and a degree of imidisation >95% is attained. This can be explained by the fact that water absorbs strongly the CO_2 laser radiation and the laser-induced heating of the polyamidoacid therefore develops as follows. The absorptance of the medium is initially low and at moderate temperatures water is evolved. Then, when a fairly large amount of water has formed, the degree of absorption of the radiation increases and this results in the heating of the substance, leading to the rapid evaporation of water. Subsequently the absorptance again falls and the temperature of the medium diminishes to a level at which there is virtually no degradation of the polyimide. The time during which the system is heated and water is fully removed is short and is insufficient for the development of hydrolysis and thermal degradation of polyimide. Thus a self-organising disequilibrium regime arises where the medium 'knows itself' at which instant it has to heat up more intensely, i.e. the optimum course of the reaction is ensured by the internal dynamic resources of the system and not by the time variation of external controlling parameters.

Compared with monotonic heating in a thermostat, the positive effect during laser-induced heating is attained as a result of the 'timely' rise and decrease in temperature. Such character of the thermal process is confirmed by the results of experiments and numerical modelling.

From a formal mathematical point of view, the polyimidisation reactions during heating in a thermostat and during laser-induced heating differ in the number of occasions when the rate of reaction reaches an extremum (bifurcations in the transient regimes).[30] Such nonmonotonic changes in the rate during laser-induced heating are characteristic of many reactions. For example similar transient oscillations in temperature and rate of reaction occur over a certain range of parameters even during the laser-induced heating of a binary gas mixture involving a reversible reaction.[18]

In the example of the laser-induced polyimide formation reaction examined above, a feedback is established as a result of the change in the absorptance of the system when the chemical composition of the medium is altered. Another mechanism of the appearance of a feedback is determined by the concentration- and temperature-induced changes in the parameters of the heat exchange leading to effects of the type of thermal explosion.[1] It is not difficult to understand that this mechanism can also lead to a different kind of bifurcations in transient regimes.

Thus, even in spatially uniform systems (for example in an ideal mixing reactor), nontrivial changes in both the stationary states and in the transient processes may occur. Table 1 presents the principal mechanisms of the feedbacks and the corresponding nonlinear thermochemical phenomena observed in the laser-induced heating of chemically reactive media. The table also indicates the feedbacks investigated in the usual (nonlaser) macrokinetics.

We have spoken hitherto about point systems. On passing to distributed systems, where heat and mass transfer processes play a significant role, the range of possible regimes expands sharply. The occurrence of diffusion and thermal conductivity can lead to phenomena involving the spontaneous loss of symmetry and spatiotemporal self-organisation and also to the formation of various nonequilibrium structures.[4,6,34] The theoretical dynamics of the corresponding processes is described by coupled diffusion equations:

$$\frac{\partial u}{\partial t} = \nabla(D\nabla u) + Q(u)\,, \tag{7}$$

where u is the vector of state, D the matrix of the diffusion coefficients (in the general case it is nondiagonal and depends on u), and Q the vector of nonlinear sources. A multiplicity of different problems, including the problems of the chemical dynamics of the reactor, reduce to an equation of type (7). In essence the spatiotemporal self-organisation is determined by the presence in Eqn (7) of new feedback channels between spatial gradients (fluxes) of the corresponding quantities. If the feedback generated is positive, then in distributed system instabilities may develop, leading to the formation of either dissipative structures or autowaves.

As an example we shall consider the appearance of thermal diffusion instability during the laser-induced heating of binary gas mixtures.[19,35] In the field of the laser radiation, the temperature gradients may be high and the thermal diffusion mechanism of the transport of matter may be significant. The thermal diffusion flux of the light component (B_l) is usually directed towards the hotter region of the medium, while that of the heavy component (B_h) is directed towards the colder region. This factor leads to separation in space of the components of the nonuniformly heated $B_l + B_h$ gas mixtures.

We shall consider the heating of an optically and thermally thin gas-containing cell (oriented along the x axis) by radiation incident on the cell at right angles to the x axis and having an intensity distribution $I(x) = I$ = const. ($0 < x < L$), where L is the length of the cell. It is assumed that the radiation is absorbed selectively by the light component of the gas. The appearance of instability in the homogeneous state of the gas is due to the fact

Table 1. Typical feedbacks and nonlinear phenomena in macroscopic kinetics.

Feedback mechanisms	Type of nonlinearity	Nonlinear phenomena	Ref.
Heat of zero-order reaction	$P_{exo} = Wk_0 e^{-T_0/T}$	Thermal explosion, thermochemical bistability	29, 1, 3
Heat of reaction of order α	$P_{exo}(N,T) = Wk_0 N^{\alpha} e^{-T_0/T}$	Thermokinetic oscillations	1, 5
Concentration-induced changes in absorption	$\sigma_A = \sigma_A(T)$, $\sigma_B = \sigma_B(T)$	Thermochemical bistability, auto-oscillations, bifurcation of transient regimes, self-stabilisation, Belousov–Zhabotinskii reactions	3, 18, 28
Temperature- and concentration-induced changes in absorption	$\sigma_A = \text{const}$, $\sigma_B = 0$, nonequilibrium chemical kinetic equation	Thermochemical bistability, auto-oscillations	26
Concentration-induced change in heat capacity	$C = C_1 c + C_2(1-c)$	Bifurcations in transient regimes	30
Change in the parameters of heat and mass exchange	$\eta = \eta(v,T)$, $\sigma_0 = \sigma_0(N,T)$	Crisis in heat exchange, thermal explosion, auto-oscillations	2, 31
	$v \neq 0$ (exposure to gas stream)	Auto-oscillations, dissipative structures	32, 33

Note. To make the illustration concrete, the results are presented for the reaction A $\rightleftharpoons$ B. Notation employed: P_{exo} is the power evolved in the reaction, k_0 and T_0 are the parameters of the rate of an Arrhenius-type reaction, N is the amount of the initial reaction component, c is its concentration, σ_A and σ_B are the cross-sections for the absorption of radiation by substances A and B, η is the Newtonian heat exchange coefficient, σ_0 is the blackbody coefficient for the radiative heat exchange, v is the velocity of the gas stream, and C is the heat capacity.

that, in the presence of local temperature fluctuations, a thermal diffusion flux directed to the hot region arises. A local increase in the concentration of the absorbing component and a further growth of temperature gradients then occur. However, by virtue of the thermal conductivity and the usual diffusion, the instability can develop only when the intensity of the radiation I exceeds a critical value. Such a mechanism has been proposed by Nitzan et al.[19] Stabilisation is achieved by virtue of some kind of nonlinear factors. Thus if there is a feedback $B_l \rightleftharpoons B_h$ between the components of the medium, the principal stabilisation mechanism consists in the fact that, in conformity with the reaction kinetics, an effective 'sink' of the light component B_l arises at the points with an excess of the latter, while a 'source' of this component arises at the points where its amount is deficient.

As a result of the development of the instability, the system passes to a stable stationary inhomogeneous state with distributions of temperature and concentrations of the gas components which are periodic with respect to the length of the cell.[19,35] As a consequence of this transition, the average (with respect to space) absorptance of the medium changes. It is found that, over a wide range of values of the parameters, the absorptance diminishes, i.e. the fraction of absorbed energy of the radiation decreases.[36] In other words, the behaviour of the system corresponds qualitatively to the Le Chatelier principle familiar in classical thermodynamics. Nevertheless, this claim is invalid in the general case, i.e. one may indicate a range of parameters in which the average absorptance increases when the medium passes to the inhomogeneous state.

The breakdown of the Le Chatelier principle reflects the fact that the system is far from thermodynamic equilibrium. We may recall that the latter is manifested by the existence of bistability, which is impossible in the case of weak energy and mass exchange between the system and the surrounding medium.

Structure formation phenomena, similar to those examined above, have been widely discussed in various branches of physics and similar equations have been used for their description. Thus the dynamics of a homogeneous two-component system near the instability threshold depends only slightly on the specific form of nonlinearity and can be frequently described by one of the following equations:¶[36]

$$\frac{\partial u}{\partial \tau} = -\frac{\partial^2}{\partial x^2}\left(\frac{\partial^2 u}{\partial x^2} + \beta u + \varepsilon u^2 - u^3\right), \qquad 0 < x < L, \tag{8}$$

or

$$\frac{\partial u}{\partial \tau} = \left[\beta - \left(\frac{\partial^2}{\partial x^2} + k_0^2\right)^2\right] u + \varepsilon u^2 - u^3, \qquad 0 < x < L, \tag{9}$$

where τ, x, and L are respectively the dimensionless time, the coordinate, and the linear dimension of the system, u the deviation of any characteristic of the system (for example, temperature) from its value in the equilibrium homogeneous state, $\beta \simeq I - I_c$ characterises the extent by which the radiation intensity I exceeds the threshold intensity I_c, and the parameter ε is determined by the properties of the medium and describes the quadratic nonlinearity of the system. Eqns (8) and (9) can be obtained as special cases of Eqn (7). They have been proposed for the description of convective and thermoconvective instabilities in liquids, phase transitions in nuclear matter, and the separation of alloys and suspensions into layers.

Eqns (8) and (9) can be investigated by the known methods of the qualitative theory of nonlinear boundary problems. In the first place, it is evident that they have the homogeneous stationary solution $u = 0$. By linearising Eqns (8) and (9) in the vicinity of this solution and assuming that

$$\delta u = (\delta u)_0 \exp(\gamma \tau + iqx), \tag{10}$$

it is easy to find the dependence of the increment γ on the wave number q, which assumes the form

$$\gamma = q^2(\beta - q^2) \tag{11}$$

in the case of Eqn (8), and

$$\gamma = \beta - (q^2 - k_0^2)^2 \tag{12}$$

in the case of Eqn (9). If $\beta > 0$, there is always a range of wave numbers q in which $\gamma > 0$, i.e. the perturbations increase exponentially with time.

We shall now consider Eqn (8) in greater detail. It follows from Eqn (11) that perturbations with the wave numbers $q_m = (\frac{1}{2}\beta)^{1/2}$ grow at the fastest rate (γ is a maximum). The formation in the system of a spatially periodic structure with a period $\lambda_m \simeq 2\pi/q_m$ is therefore to be expected. Numerical integration of Eqn (8) confirms this conclusion. However, it can be demonstrated rigorously that only those solutions of Eqn (8) the period of which is $\lambda_a = 2L$ are asymptotically (at $\tau \to \infty$) stable.

¶ See, for example, also the book *Nelineinye Volny. Dinamika i Evolyutsiya* (Nonlinear Waves. Dynamics and Evolution) (Moscow: Nauka, 1989) p. 113.

Hence it follows that, for sufficiently large values of L, solutions with a period $\lambda \simeq \lambda_m$ are unstable and arise only as intermediate (transition) states.[37] Since states with $\lambda \simeq \lambda_m$ arise almost inevitably in the course of the evolution of the test system, they can be naturally referred to as metastable structures and the appearance of such states can be called metastable self-organisation. The term 'metastable structure' will also be applied because the lifetime of such structures is long: they decompose only under the influence of longer-wavelength perturbations, the time of the increase of which is long (since this process requires the synchronisation of the motion of more extensive sections of the medium). We may note that metastable ordering phenomena are characteristic of many nonlinear dynamic systems. They can arise, for example, in the thermal diffusion separation of gas mixtures, and in the laser-induced annealing and quenching of nonequilibrium vacancies in the surface layers of metals.[38]

4. Thermal diffusion oscillations during nonuniform heating of gas mixtures

We shall consider the heating of a chemically inert gas mixture by a beam of continuous laser radiation. We shall assume that the radiation is absorbed by the heavy component of the mixture via a resonance mechanism. The gas layer is assumed to be optically thin along the axis of the beam. The mathematical model of the process[39] includes diffusion (taking into account concentration and thermal diffusion) and thermal conductivity equations. In the latter, account must be taken of the fact that in the IR region of the spectrum the absorptances of many molecular gases depend strongly on temperature and are often described by the formula

$$A(N,T) = \beta N \exp\left(-\frac{T_a}{T}\right),$$

where N is the molecular density of the absorbing component of the medium.

If the radiation has a uniform intensity distribution with respect to the cross-section of the cell, then only stationary states are stable. In the same case, when the radiation beam has a finite radius stable nonstationary regimes become possible. The mechanism of the generation of oscillations in temperature and the concentrations of the components is as follows. Under the influence of radiation, the mixture is heated and temperature gradients directed towards the axis of the laser beam arise. As a result of thermal diffusion, the heavy component of the mixture is expelled from the beam, so that the absorptance of the medium diminishes, the gas cools, the temperature gradients diminish, and concentration diffusion returns the absorbing component to the region within the limits of the laser beam. The process is then repeated.

We shall now present the results of the numerical analysis of this process.[39] It was found that oscillatory regimes are possible in a restricted range of powers (P) and radii (r_0) of the radiation beam. This region is illustrated in Fig. 1*a*. It is divided into two subregions with different dynamic regimes. For the parameters in the subregion I, the system executes simple auto-oscillations, which are represented on the phase plane by a closed curve without self-intersections (the so called limiting cycle S^1).

On passing to the subregion II, the oscillations are become more complex as a result of the cascade of bifurcations involving the doubling of the period. Typical phase portraits of the complex limiting cycles are presented in Figs 1*b*–1*e*.

In the subregion II in Fig. 1*a*, the system is extremely sensitive to the choice of the radiation parameters. Therefore, under the conditions of a real experiment, when the radiation parameters have been determined with insufficient accuracy or fluctuate, it is difficult to obtain the required complex dynamic regime in a pure form. As regards the characteristic values of the periods of the oscillations, we may point out that, in the vicinity of the stability threshold of the stationary state, they are $\sim(5-10)r_0^2/D$. For typical experimental conditions with diffusion coefficient $D = 0.1$ cm^2 s^{-1} and the laser beam radius $r_0 = 1$ cm, this estimate yields a characteristic time of the order of 1 min.

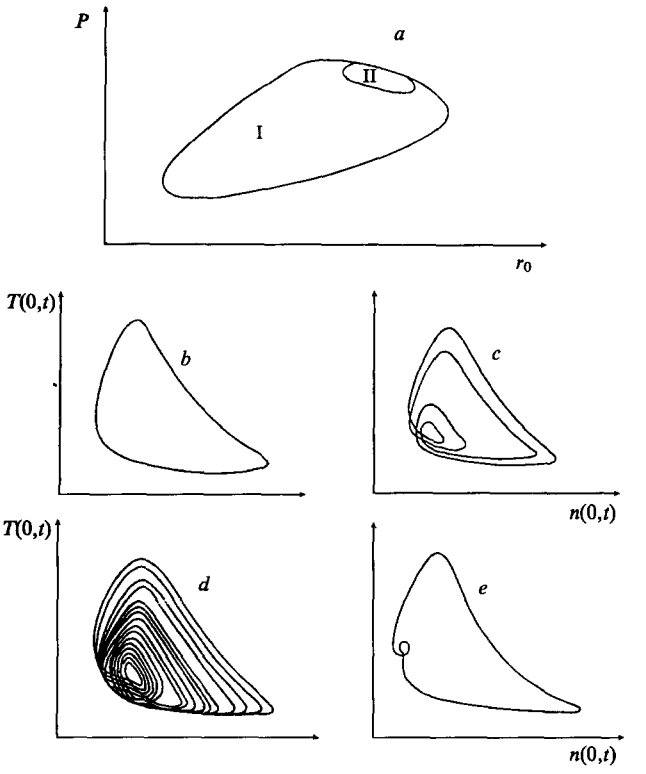


Figure 1. The region of existence of thermodiffusional oscillations (*a*) and typical phase portraits (*b*–*e*).

The diffusional oscillations examined above have been observed in experiments on the laser-induced heating of gas mixtures.[40] Fig. 2 presents the time variations of the power of the laser radiation which has passed through a cell containing a mixture of air and SF_6 as well as a mixture of NH_3 and SF_6. The radiation was absorbed selectively by the heavy component (SF_6). The oscillograms show that the heavy component is periodically ejected outside the limits of the laser beam. The characteristic process times show that there are no gas-dynamic motions of the medium (turbulence, convection) and that mass transfer is diffusional.

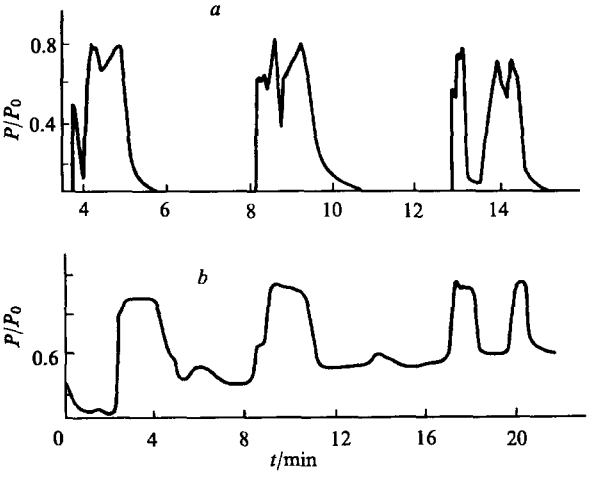


Figure 2. Time variation of the power of the laser radiation which has passed through a cell with SF_6+air (*a*) and SF_6+NH_3 (*b*) mixtures.[39] Power of the radiation incident on the cell $P_0 = 5$ W; length of the cell 20 cm; pressure (torr): (*a*) $P_{SF_6} = 2$, $P_{air} = 20$; (*b*) $P_{SF_6} = 2.5$, $P_{NH_3} = 19$.

5. Travelling fronts and 'chemical solitons'

Hitherto we have spoken of the heating of a gas mixture placed in an optically thin cell. On the other hand, if the optical thinness condition is infringed, there is a possibility of the appearance of qualitatively new dynamic regimes. In particular, combined waves may appear in which the concentration of the reactants and temperature differ markedly from the background values (travelling pulse or 'chemical soliton'). We shall consider this phenomenon in relation to the laser-induced heating of a gaseous medium involving a reversible chemical reaction.

Suppose that the gas mixture has been placed in a long thin cell illuminated from the end-face by radiation with a power P. As mentioned above, in a gaseous medium with a reversible chemical reaction there is a possibility of the phenomenon of thermochemical bistability on heating by laser radiation at a suitable wavelength. This means that, in a certain range of radiant powers ($P_1 < P < P_2$), there exist two stable stationary states differing in temperature and the concentrations of the components. The attenuation of radiation in accordance with the Bouguer (Beer–Lambert) law and transfer processes are not taken into account in this treatment, but they can in fact lead to new interesting effects.

Suppose that in the initial instant the system is in its lowest state as regards concentrations and temperature. If the medium in a certain part of the cell is transferred to a state with an increased concentration of the absorbing component, then the absorption of radiation in this region increases and heating of the gas begins. As a result of heat conduction and the absorption of the energy of the laser radiation, the neighbouring regions also begin to heat up. The size of the absorbing zone then increases until the radiant power behind it becomes less than W_1 — the minimum value necessary for the existence of bistability. The zone formed begins to move towards the laser beam, because, as a result of heat conduction, the region ahead of the zone heats up and the absorption in the latter increases, while the region behind the zone cools as a result of heat losses and the decrease in the heating power. This leads to the formation of a travelling pulse — a localised region in which the medium is in a high-temperature and strongly absorbing state. We may note that a similar phenomenon is observed not only in laser-induced thermochemical processes but also in many others, for example, in the generation of plasma in optical breakdown.[41]

The phenomenon considered above is formally described in terms of the following boundary-value problem.[42] The change in the concentration n of substance B is defined by the equation for reaction kinetics taking into account diffusion:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} + k_A(1-c)\exp\left(-\frac{T_A}{T}\right) - k_B n \exp\left(-\frac{T_B}{T}\right). \qquad (13)$$

We shall assume that $T_A > T_B$, i.e. the equilibrium concentration of substance B,

$$c = \left[1 + \frac{k_B}{k_A}\exp\left(\frac{T_A - T_B}{T}\right)\right]^{-1} \equiv c(T), \qquad (14)$$

increases with temperature.

We shall assume that radiation is absorbed only by substance B

$$\frac{\partial I}{\partial z} = -\beta c I, \quad \beta = \text{const}, \quad I|_{z=0} = I_0, \qquad (15)$$

while the change in the gas temperature is described by the thermal conductivity equation

$$\frac{1}{a}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial z^2} - \frac{1}{k}\frac{\partial I}{\partial z} - \frac{\eta}{k}(T - T_i), \qquad (16)$$

where η is the heat loss per unit length of the cell and T_i the initial temperature of the medium.

We shall assume that the length of the cell exceeds significantly the spatial size of the travelling pulse. Fig. 3 illustrates the dynamics of the formation of a chemical soliton.

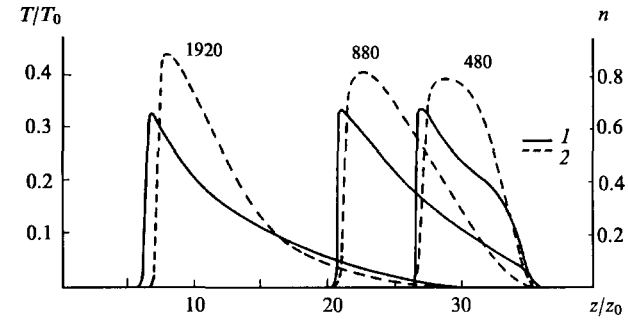


Figure 3. Dynamics of the formation of a chemical soliton. The dimensionless temperature (T/T_0), distance (z/z_0), and concentration c are plotted along the coordinate axes; the numerals opposite the curves denote the dimensionless time (t/t_0): (*1*) temperature profile; (*2*) concentration profile.

The switching caused by longitudinal bistability leads to additional characteristic modulation (kinks) of the intensity of the radiation at the outlet from the medium. For example, if the time variation of the radiation intensity at the inlet to the medium has the form of a triangle (Fig. 4*a*) with an amplitude higher than a certain critical value, the transmitted pulse has the form of a trident (Fig. 4*b*). Phenomena of this kind have been observed in the interaction of laser radiation with semiconductors.[43] The time constant corresponding to the mechanism of the chemical nonlinearity makes it possible to observe kinks in the range of intensities and for durations of laser action differing by several orders of magnitude from those where kinks are observed in semiconductors.

In a medium with a nonuniform energy exchange [the quantity T_i in Eqn (16) is, for example, a monotonically increasing linear function of the coordinate], a cyclic process may occur, consisting of stages involving the 'self-initiation' of the travelling pulse at the remote end of the cell, its subsequent propagation towards the beam, and its 'self-quenching' at the inlet to the reactor (Fig. 5). In terms of external features, such a system may be called a chemical analogue of the Gunn diode. The amplitude, width, velocity, and other parameters of a chemical soliton during its propagation in the medium may vary periodically (or even stochastically). Together with bifurcations, leading to identical changes in the system dynamics throughout the length of the reactor, there is a possibility of bifurcations leading to the appearance of dynamic regimes qualitatively different in different parts of the reactor. This can be manifested, for example, by the fact that part of the reactor is traversed by the 'chemical soliton' as a 'two-hump' species whilst another part is traversed by the soliton as a 'one-hump' species. From the formal point of view, such transformations correspond to bifurcations involving the doubling of the period along the spatial coordinate.

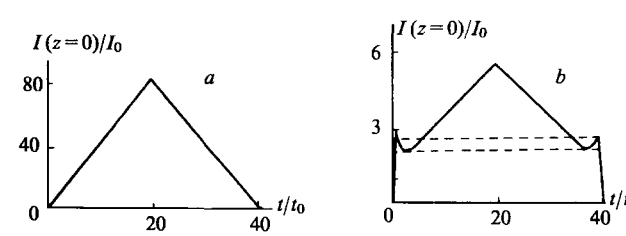


Figure 4. Time modulation of the triangular pulse arising during passage through a bistable medium.[44] Time profile of the incident (*a*) and transmitted (*b*) radiation.

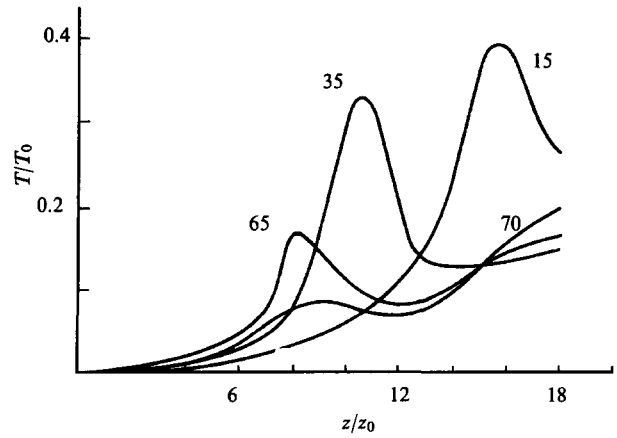


Figure 5. Chemical analogue of the Gunn diode: temperature profile of the field for different times in a medium with a nonuniform energy exchange. The legend is the same as in Fig. 3.

6. Nonlinear optical phenomena in a chemical reactor

The phenomena examined above belong to the class of nonlinear amplitude effects. Even these alone lead to complex dynamics of chemical processes in an optically thick reactor. In reality, together with amplitude effects there are also phase distortions of the wave front associated with the change in the refractive index of the medium during the reaction.

We shall consider this in greater detail. We shall suppose that a chemical reaction A → B takes place in the medium and that the initial substance A and the reaction product B have different optical properties. If the refractive index of substance B (n_B) is greater than that of substance A (n_A), a positive feedback is established, leading to instability. The mechanism of the instability is as follows. In the presence of perturbations, the medium is more strongly heated in the regions with increased intensity compared with the neighbouring regions and the reaction is activated sooner. As a result, the refractive index in these regions increases more rapidly, since $n_B > n_A$, which leads to the deviation of the light rays in this region and to a further increase in the local radiation intensity. The propagation of the radiation in a medium with a chemical inertial nonlinearity is described by the system of thermal conductivity and reaction kinetic equations (taking into account diffusion) together with the Maxwell equations specifying the distributed feedback.

Two cases are distinguished: those of narrow[44] and wide[45] radiation beams. A narrow beam is understood as one for which the radiation intensity distribution across a transverse section is nonuniform. A wide beam corresponds to the situation where the incident radiation is spatially uniform (planar wave).

We shall consider the characteristics of the formation of thermal structures in a nonuniform field of laser radiation. In the course of the development of instability, the optical nonuniformity of the medium increases and the self-focusing of the radiation take place. The self-focusing begins if

$$EN > (EN)_c , \tag{17}$$

where $E = \pi r_0^2 I_0 t$ is the energy of the radiation, N the concentration of the reaction products formed during time t, and $(EN)_c$ is determined by the parameters of the medium, the radiation wavelength, and the constants characterising the rate of reaction.[44] The effective width of the beam $r(z, t)$ may vary nonmonotonically along the beam z axis by virtue of the competition between the diffraction divergence and the focusing action of the 'chemical' lens: constrictions appear in the beam, their number varying in the course of the reaction. As can be seen from Fig. 6, when the self-focusing condition (17) is fulfilled, a beam constriction is generated, which moves from the point in which the radiation enters into the bulk of the medium ($z = 0$) and then, as the initial substance is 'burnt off' and the optical uniformity is restored, it moves in the opposite direction. The law governing the motion of the constriction can be explained qualitatively by considering the medium as an effective lens the focal distance R of which varies with time. The beam profile is now described by the expression

$$f(z) = \sqrt{\left(1 - \frac{z}{R}\right)^2 + \mu\left(\frac{z}{r_0}\right)^2} , \tag{18}$$

where the diffraction parameter $\mu = (kr_0)^{-2}$ and k is the radiation wavenumber.

The position of the constriction z_m corresponds to the minimum in the function $f(z)$:

$$f_{min} = f(z_m) = \sqrt{\frac{\mu(R/r_0)^2}{1 + \mu(R/r_0)^2}} , \quad z_m = \frac{R}{1 + \mu(R/r_0)^2} . \tag{19}$$

Hence it follows that, when $R = \infty$, i.e. when the medium is optically uniform, we have $z_m = 0$. Then, as R diminishes (the optical power of the lens increases), z_m reaches a maximum for a certain value of R and then begins to decrease as R diminishes further ($z_m \simeq R$ when $R \to 0$).

If the variation of the refractive index as a function of the radius is sufficiently great, then, when the beam passes from an optically denser medium to a less dense one, conditions for internal reflection may be fulfilled, as a consequence of which new constrictions appear on the beam — the beam acquires a corrugated profile. The appearance of constrictions implies the appearance of hot spots in which the reaction proceeds more vigorously. Evidently, this phenomenon may lead to the inclusion of high-temperature reaction pathways and hence to a qualitative change in the chemical composition of the reaction products. Under such conditions, it is difficult to predict the chemical result of the action of the laser radiation on the medium.

If the incident radiation has a spatially uniform intensity distribution, different aberrations of the radiation may be observed in the cross-section depending on the initial form of small perturbations — subdivision into 'filaments', the appearance of a nonstationary ring structure, etc. The instability can be convective (displacement) in nature: an intensity maximum arises at the inlet to the medium ($z = 0$) in an elementary tube, and then migrates into the bulk of the medium. The appearance of the maximum and its migration are caused, on the one hand, by the intensification of the optical strength of the chemical lens

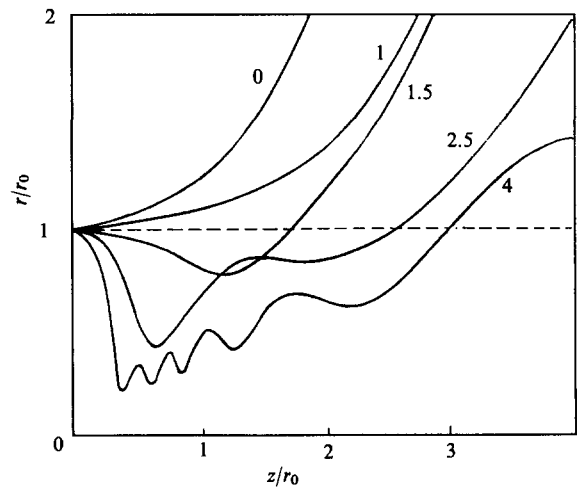


Figure 6. The profile of a radiation beam at different times during the reaction; r = beam radius, z = coordinate along the reactor axis, r_0 = radius of incident beam; the numbers opposite the curves denote dimensionless times.

during the reaction and, on the other, by two stabilising factors: the Bouguer attenuation of the radiation in the medium and the wave relaxation, which moves behind the instability front and is caused by the joint action of heat conduction and diffusion. The relaxation wave leads to the equalisation of the optical density of the medium, as a result of which the beams deviate only slightly from the initial direction before the attainment of the perturbation front.[45]

IV. Thermochemical processes in the laser heating of metals

1. Kinetics and dynamics of heterogeneous reactions and the morphology of the surface

Three major problems are associated with the laser stimulation of heterogeneous reactions.

The first refers to the reaction kinetics. During the last 10–15 years, many investigators observed that the kinetics of heterogeneous reactions in the field of the laser radiation are frequently characterised by different kinetic constants and even by different forms of the kinetic laws from those of the kinetics of isothermal processes (numerous reference data are available for the latter). This means that, for the development of the laser technology, it is essential to carry out an extensive set of studies in order to discover the form of the kinetic laws and the values of the corresponding kinetic constants, their dependence on the intensity and wavelength of the laser radiation, etc. As for homogeneous reactions, it is possible to differentiate photochemical and thermochemical effects. The photochemical effects are characteristic of laser-induced processes involving the oxidation of semiconductors and metals, the oxides of which have semiconducting properties. The 'red limit' of such photoactivity is usually in the visible or UV regions of the spectrum. On the other hand, the effects associated with the thermochemical influence of laser radiation on the reaction kinetics are associated with either high heating rates or high spatial temperature gradients in the oxidised layer.

The second problem concerns the kinetics of oxidation reactions. The observation of thermochemical instability and the first theoretical models of the development of instability on formation of strongly absorbing oxides have played an important role in this connection.[16] Such instability characterises the nonlinear dynamics of a system with a positive feedback in the initial stage. In later stages, where different stabilisation mechanisms begin to operate, the process dynamics become more complex. The experimental observation of the nonmonotonic dependence of the change in the absorption by metallic targets during their laser-induced heating in air has played an important role in the development of these studies.[17] It was found that the sign of the feedback, arising as a consequence of the change in absorption, can change during the process. More complex manifestations of the nonlinear dynamics of thermochemical processes were observed subsequently.

Finally, the third problem is that of the morphology of the surface in the laser initiation of heterogeneous reactions. As early as the beginning of the 1970s, studies on the heat-induced strengthening of metals and alloys led to the observation (see, for example, Rykalin et al.[46]) that in laser-induced heating the morphology of the surface is different from that found on heating in a furnace. The causes of this phenomenon were inadequately investigated at the time. Nowadays, numerous new results have been obtained. It is noteworthy that investigations of the structural changes in the surface under the influence of laser radiation are important for many technological applications, for example, in microelectronics, in integrated optics, in the laser-induced stabilisation of surfaces, etc.

2. The effect of laser radiation on the kinetics of heterogeneous reactions

The heterogeneous reactions at the solid–gas interface (oxidation, reduction, nitride formation, etc.) are known[47] to consist of many stages, the transfer of reactants in the gas or solid phase frequently playing the role of the rate-limiting stage. Accordingly, the kinetics of such reactions have a number of features in common with the kinetics of homogeneous reactions whose rate is limited by the diffusional transport of the components. Under these conditions, heterogeneous reactions should be more sensitive to changes in the parameters of the laser radiation than homogeneous reactions, because the diffusion coefficients of atoms in a solid vary more markedly with temperature than in gases (the variation is exponential and not of the power type).

However, as early as 10–15 years ago it was claimed that, for example, in metal oxidation reactions laser radiation exerts no specific influence on the reaction kinetics: the kinetics are exactly the same as during the heating of the target in a furnace. On the other hand, early experiments[48] already showed that the oxidation of copper in air under the influence of laser radiation is faster than in the furnace at the same temperature of the metal.

We shall consider the phenomena associated with the high rates of laser heating. For continuous emission, such rates are attained at the stage involving the development of thermodynamic instability, while for pulsed or repetitively pulsed emission they are attained in each individual pulse. Here it is significant that during rapid heating the distributions of the reactants deviate markedly from those which are established during slow heating. Evidently this is associated with the finite rate of diffusional transport of the components (oxidant and the metal) and with the migration of the metal–reaction product interface, the effective constants of which are functionals of the concentrations. Strictly speaking, the kinetic constants are not of this kind. For example, in relation to the oxidation of metals, the corresponding constants must be found by solving a system of equations for the diffusion of metal and oxidant ions in the layer of reaction products. The changes in the kinetics caused by the high rates of laser heating in heterogeneous reactions have been discussed.[48–52] Under stationary conditions, the kinetics of the heterogeneous oxidation are influenced by the nonuniformity caused by the spatial localisation of the reaction owing to the finite nature of the diameter of the laser beam and the temperature gradients in the oxidised layer. We shall consider the influence of these nonuniformities. The limited size of the laser beam leads, in particular, to the phenomenon of the diffusional limitation of the reaction as regards the supply of the oxidant from the gas phase (see, for example, Bunkin et al.[26] and Prokhorov et al.[49]).

The temperature gradients along the surface of the oxide layer are as a rule significantly lower than across it. The influence of these gradients on the reaction kinetics is various. The temperature gradients along the surface influence the transport of atoms via surface diffusion and thermal diffusion. This entails a change in the spatial distribution of the rate of reaction along the radial coordinate, which alters qualitatively the dependence of the increment in the instability of the planar oxidation front on the parameters of the laser radiation and the perturbation wave number.[53]

The temperature gradients across the oxide layer are more significant. They influence the transport of reactants in the solid phases. There are several mechanisms of the influence of such gradients on the reaction kinetics. The mechanisms determined by the temperature dependence of the diffusion coefficients and the thermal diffusion flux of atoms are fairly evident. Their effect in different models of the laser-induced oxidation has been investigated, for example, by Buzykin and coworkers.[54,55] The phenomena caused by the influence of the temperature gradient on the electrical transport are of special interest. Owing to the high field of the thermo-e.m.f. in an oxide with semiconducting properties, the temperature gradients can lead to both

acceleration and retardation of the reaction. This has been demonstrated experimentally for the oxidation of copper (acceleration) and cobalt (retardation).[56]

Another important factor is accelerated diffusion via the grain boundaries and microcracks formed in the oxide film under the influence of thermal stresses. To a first approximation, the corrections to Wagner's parabolic law, caused by the increased permeability of the oxide, lead to a paralinear oxidation law. It has been observed experimentally[57] that, in the laser-induced heating of cobalt to 1300 K, a linear oxidation law holds up to an oxide thickness $h \simeq 10^5$ A, after which it is replaced by a parabolic law. On the other hand, under isothermal conditions (during oxidation in a furnace) the parabolic law is observed already for thicknesses $h > 10^2$ Å. Such 'extension' of the linear law into the region of high thicknesses may be associated with increased permeability of the oxide layer together with other causes (for example thermal diffusion).

The mechanisms of the influence of the generation of non-equilibrium point defects on the changes in the oxidation kinetics have been investigated vigorously in recent years.[38] The simplest mechanism of such influence may involve a change in the diffusion coefficients of atoms in the oxide, which, according to the Dienes–Damask theory[58] is described by an equation of the following form:

$$D(T) = D_0(T)\frac{N}{N_0(T)},$$

where $D_0(T)$ is the 'equilibrium' value of the diffusion coefficient at the given temperature and N is the concentration of non-equilibrium vacancies which exceeds significantly the equilibrium concentration $N_0(T)$ for the pulsed-periodic application of laser radiation. Such mechanisms make it possible to explain the accelerated growth of the oxide film in the 'low temperature' region which has been observed experimentally.[59]

Thus the studies of the last 10 years have yielded a result of practical and theoretical importance, namely that the kinetics of the laser-induced and isothermal oxidation are different. These differences depend greatly on the nature of the metal and the gas composition of the atmosphere and on the parameters of the target and the laser radiation. The specific mechanisms responsible for such differences proved to be varied. A number of them were discussed above.

3. Laser-induced oxidation

We shall now turn to the dynamics of oxidation reactions under the influence of laser radiation. In the simplest case, the rate of reaction can be characterised by the change in the thickness of the oxide layer dx/dt. This quantity depends on the temperature of the substance and can be expressed in the form

$$\frac{dx}{dt} = f(x, T). \tag{20}$$

In order to determine the reaction dynamics, it is essential to solve Eqn (20) simultaneously with the thermal conductivity equation. We shall consider such dynamics in relation to the problem of the growth of thick ($x > 10^3$ Å) compact oxide layers. In such layers, the reactants are transported by diffusion, which leads to the so called parabolic law

$$\frac{dx}{dt} = \frac{d(T)}{x}, \tag{21}$$

where the quantity $d(T)$ has come to be referred to as the parabolic law constant. At a constant temperature, the thickness of the oxide varies, according to Eqn (21), in conformity with the characteristic diffusion law $x^2 = 2dt$. The temperature variation $d(T)$ is frequently determined by the Arrhenius factor:

$$d(T) = d_0 \exp\left(-\frac{T_d}{T}\right), \tag{22}$$

which is valid within fairly wide temperature ranges.

The dynamics of such a system may be complex. The reason for this is that feedbacks arise in the system between the rates of heating and the rates of chemical reactions. The optical channel for the feedback, arising as a consequence of the dependence of the absorptance A of the irradiated specimen on the thickness of the oxide layer, plays a significant role in the laser-induced oxidation. The optical feedback may be both positive (along the section where the absorptance increases, $dA/dx > 0$) and negative ($dA/dx < 0$).

The positive feedback leads to thermochemical instability. We shall consider this phenomenon in greater detail.

The laser-induced heating of a thermally thin metallic film in an oxidising gas medium is described by the kinetic equations (21) and (22) and the heat balance equation (the heat of reaction is neglected):

$$mc_1\frac{dT}{dt} = PA(x) - P_1(T), \tag{23}$$

where m is the mass of the plate, c_1 is its specific heat, and P_1 is the power associated with the heat loss. Taking into account only the convective heat exchange, we assume that $P_1(T) = \eta S(T - T_1)$, where S is the total area of the heated specimen and η is the heat exchange coefficient.

An explosive increase in temperature (thermochemical instability) is observed after the thickness of the oxide film has increased so much that the change in absorption begins to alter significantly the heat balance, i.e. thermochemical instability develops after the elapse of a certain characteristic time, referred to as the activation time t_a, and not immediately after the start of irradiation. Under typical conditions, this time is proportional to $\exp(T_d/T_0)$, where T_0 is the quasi-stationary temperature to which the specimen is heated when its initial absorptance is equal to the absorptance of the unoxidised metal.

For nonuniform laser irradiation, the temperature maximum is located on the beam axis. Since the activation time increases exponentially with decrease in temperature and the temperature diminishes on moving away from the centre of the beam, an effective self-compression of the temperature field takes place in the course of development of thermochemical instability.

We may note that, by virtue of the temperature dependence defined by Eqn (22), the reaction takes place effectively in the vicinity of the centre of the laser beam. The size of the region may be small, compared not only with the characteristic width of the thermal field but also with the radius of the reaction-initiating beam itself. The above factor is important for laser technology, since it makes it possible to localise the chemical reaction. The effect involving the sharpening and localisation of the temperature field has been observed in experiments on the laser-induced heating of metals in air.[60] This is illustrated in Fig. 7, which shows the time variation of the spatial distribution of the temperature field for the heating of a titanium target by the radiation from a CO_2 laser. Evidently the self-acceleration of the temperature rise is accompanied by the self-compression of the temperature field.

We emphasise that the non-uniformity of the distribution of the radiation intensity is essential for the appearance of localisation effects only at the beginning. It serves as a 'seed' of the instability, which can then develop also in a uniform field. Therefore even small fluctuations in the distribution of the radiation intensity or in the optical characteristics of the test substances play an important role in laser-induced thermochemical processes.

For many metal oxides, the absorptance varies nonmonotonically with increase in thickness. This can be associated with interference due to the penetration of the light beam through a dielectric film the optical thickness of which is a multiple of an integral number of half-waves. Owing to interference oscillations in absorption, the sign of the feedback changes periodically, which results in the pulsation of the heating rate. Such pulsations are of a transient character and are not observed for asymptotic states (at $t \to \infty$).

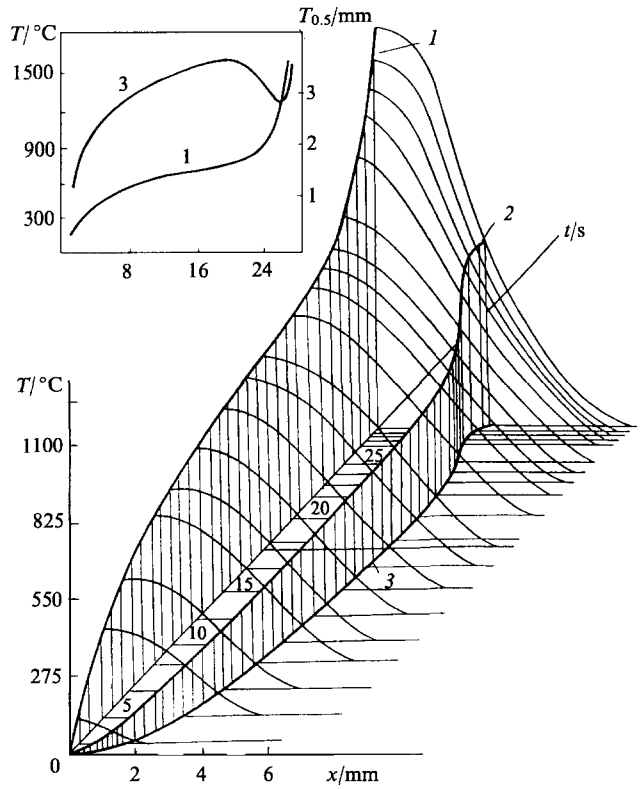


Figure 7. Time evolution of the spatial temperature profile of a titanium plate during its heating by the continuous radiation from a CO_2 laser:[60] power of the laser 40 W: (*1*) temperature $T(0, t)$; (*2*) temperature $0.5T(0, t)$; (*3*) effective radius of the localisation of the temperature field $r_{0.5}$, i.e. the value of the coordinate r for which $T(r_{0.5}, t) = 0.5T(0, t)$.

Another positive feedback channel is provided by the heat of a chemical reaction, which is responsible for the self-inflammation phenomenon[1] and for the appearance of auto-oscillations in a flow reactor with an exothermic reaction.[5] The heat of reaction plays a significant role in laser-induced inflammation processes. The following model, describing the qualitative features of the inflammation of tungsten, has been proposed:[61]

$$\frac{dx}{dt} = \frac{d}{x}\left(\exp\left(-\frac{T_d}{T}\right) - v_0 \exp\left(-\frac{T_s}{T}\right)\right),$$

$$mc_1 \frac{\partial T}{\partial t} = PA(x) - P_1(T) + \rho SW \frac{d}{x} \exp\left(-\frac{T_d}{T}\right) - \qquad (24)$$

$$-\rho SLv_0 \exp\left(-\frac{T_s}{T}\right),$$

where W is the specific heat of the chemical reaction, L the specific heat loss on sublimation, ρ the density of the test substance, v_0 the pre-exponential factor, and the subscripts s and d refer respectively to sublimation and diffusion processes.

In the kinetic equation, account was taken of the change in the thickness of the oxide layer x due to oxidation in accordance with the parabolic law (the first term) and the sublimation of the oxide WO_3 (the second term). The first term on the right-hand side of the heat balance equation describes the absorption of the laser radiation, the second term describes the heat losses caused by heat exchange with the surrounding medium, the third describes the evolution of energy in the reaction, and the fourth describes the loss of energy in sublimation. Analysis shows that there may be a limiting cycle on the phase plane of such a system, corresponding to the auto-oscillatory laser-induced combustion regime. The transitions between different regimes, for example, the trigger and auto-oscillatory regimes, can be achieved by altering the target parameters (mass, thickness) and the power of the incident laser radiation. All the regimes predicted by the theory — passive, latent, trigger, and auto-oscillatory — have been observed experimentally.

A model analogous to that defined by Eqn (24) can be used for the description of the laser-induced oxidation of molybdenum. In this case, the oxide MoO_3 at $T > 800$ °C is in the liquid phase and intense evaporation takes place from the surface of the liquid. The kinetic equation has the same form as Eqn (24), but for molybdenum $T_d < T_s$. The heat balance equation also retains its form, but the quantity W in it has the significance of the difference between the heat of the oxidation reaction and the heat of fusion. For MoO_3, this difference is negative ($W < 0$). Accordingly, the auto-oscillations are significantly associated with the presence of the MoO_3 melt. Experiments[57] confirmed the presence of the auto-oscillatory regime in the oxidation of molybdenum. The oscillations proved to be extremely stable and were observed for a long time — sometimes more than an hour. Part of the experimental oscillogram is presented in Fig. 8.

The oscillatory reactions examined are fairly simple from the standpoint of kinetics, being described by a single differential equation. As the kinetics become more complex, whereupon parallel or consecutive reactions arise, the oscillatory oxidation regimes can change similarly. An example is provided by the catalytic heterogeneous oxidation of ammonia in air on the surface of copper oxide and under the influence of the radiation of a CO_2 laser. The increase in the complexity of the oscillations, occurring apparently via a cascade of bifurcations associated with the doubling of the period, has been observed experimentally.[62]

An increase in the complexity of oscillations also takes place when the problem is transformed into one of the distributed type, i.e. under conditions where radial heat conduction phenomena play a significant role. Thus the transition from the stationary regime in the combustion of titanium to a stochastic regime on changing the conditions in the focusing of the laser radiation onto the surface of the specimen has been demonstrated.[63]

The nature of the complex oscillatory combustion regimes is determined to a large extent by the nature of the metal. We shall consider the case of tungsten. Suppose that the surface of a thin tungsten plate with a radius R is heated by a beam of laser radiation in which the intensity is distributed over the cross-section in accordance with the expression

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

In contrast to Eqn (24), it is now necessary to take into account also the effects of radial heat conduction in the heated specimen. In the limit where $r_0 \gg R$ and the characteristic spatial scale of the changes in the variables is large compared with R, the effects of heat conduction are evidently insignificant. In conformity with the theory of nonlinear oscillations, there is then a possibility either of the attainment of stationary states or of simple auto-oscillations, depending on the radiation intensity. Such phenomena were discussed above.

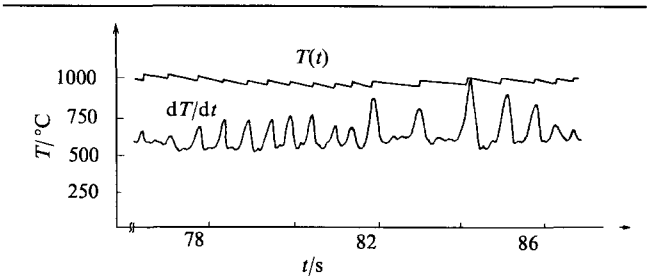


Figure 8. Experimental oscillogram of the $T(t)$ and dT/dt signals in the auto-oscillatory oxidation of molybdenum.[57]

Heat conduction and the nonuniformity of the radiation field lead not only to a quantitative but also to a qualitative change in the process dynamics. We shall fix the power of the radiation $P = \pi r_0^2 I_0$ and shall vary the focusing (i.e. the beam radius r_0) on the surface of the specimen. Numerical analysis leads to the following findings.[64]

In the first place, the presence of the simplest types of attractors—stable stationary states—was established. By virtue of the nonuniformity of the radiation field, the temperature $T(r)$ and the thickness of the oxide $x(r)$ are also found to be nonuniform and $x(r)$ may prove to be a nonmonotonic function of the coordinate r. With increase in the radiation beam radius r_0, the simplest nonstationary ordering arises. This is the limiting cycle S^1, corresponding to the situation where during the period of the oscillations the temperature $T(r, t)$ and the thickness of the oxide $x(r, t)$ reach a maximum once. The process is localised in a region of the order of magnitude of the size of the beam. On further increase in r_0, the dynamics become more complex—cycles S^n are generated corresponding to the situation where in the course of one period the number of local maxima reaches n, with $n > 1$. The increase in complexity takes place as a consequence of consecutive bifurcations associated with the doubling of the period as r_0 increases. This is followed by a range of values of r_0 to which stochastic regimes of different complexity correspond. Fig. 9 presents a diagram illustrating the change in the dynamic regimes as the parameters of the radiation are altered.

We may note that, apart from the complex oscillatory regimes examined above, the model under discussion describes the appearance of rotating spiral waves (reverberates) similar to those observed in the Belousov–Zhabotinskii reactions. Fig. 10 presents examples of the profiles of the temperature field in the form of single- and two-arm spirals rotating around the radiation beam axis. In the laser-induced heating of metals, such rotating structures are observed fairly frequently.

Another mechanism for the increase in the complexity of the dynamics operates when metals of the type of titanium are heated.

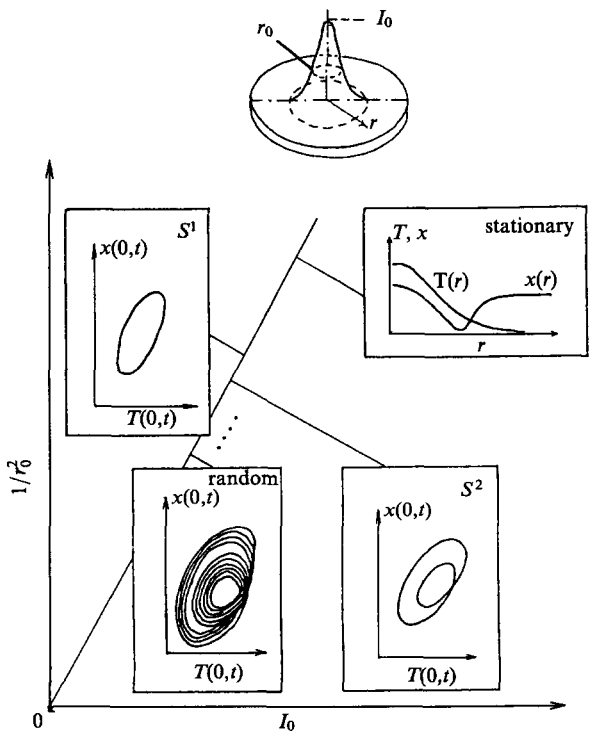


Figure 9. Dependence of the metallic target (tungsten) combustion regime on the beam radius r_0 for a fixed total power of the radiation $P = \pi r_0^2 I_0$.

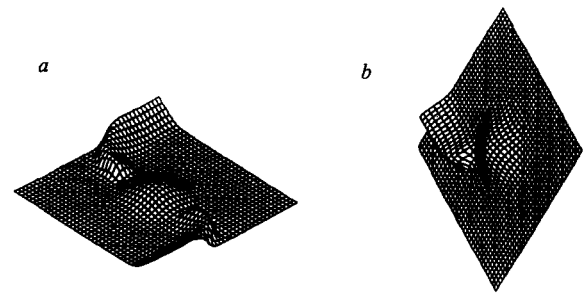


Figure 10. Rotating two-arm (*a*) and single-arm (*b*) spiral temperature field waves for nonuniform laser-induced heating of tungsten.[65]

It is determined by the transport of reactants or reaction products in the gaseous medium surrounding the heated specimen.[66] During the oxidation of the metal, oxygen is removed selectively from the surrounding medium, so that in the vicinity of the target surface the rate of reaction diminishes owing to the deficiency of the oxidant. There is a corresponding decrease also in the rate of consumption of oxygen. As a result of diffusion, its concentration increases again, the reaction is accelerated, and the process is repeated. The foregoing illustrates the possibility of the appearance of auto-oscillatory combustion regimes owing to the diffusion transport of the reactant (oxidant) in the gaseous medium.

Finally, yet another mechanism of the increase in complexity, qualitatively similar to the previous one, is induced by the diffusional transport of reactants through the layer of the oxide.[67] Other heterogeneous reactions with auto-oscillations have also been observed and other mechanisms of auto-oscillations, associated, for example, with the formation of oxide nitrides, the dissolution of scale, etc., have also been observed.

4. Laser-induced reduction

We have examined the dynamics of heterogeneous thermochemical processes due to the presence of a positive feedback between the chemical and thermal degrees of freedom of the system. Such a feedback was generated by the increase in the absorptance of the test substance or in the evolution of energy in the reaction. The opposite situation is one where a negative feedback is established on decrease in the absorptance of the substance or for a negative heat change (endothermic reaction). We shall consider the dynamics of systems with a negative feedback in relation to the reduction of metal oxides to the metals under the influence of laser radiation. In such a system, the negative feedback is established by virtue of the decrease in the absorptance of the test substance from A_{ox} (absorptance of the oxide) to A_m (absorptance of the metal). We have $A_{ox} > A_m$, which leads to a decrease in the energy introduced into the test substance and to a lowering of the heating rate.

We shall illustrate the characteristic features of the dynamics of the reduction reaction in relation to the laser-induced heating of a thermally thin specimen of oxidised metal. This problem is described by the heat balance equation

$$mc_1 \frac{dT}{dt} = PA(x) - P_l(T), \tag{25}$$

and the kinetic equation

$$\frac{dx}{dt} = d\exp\left(-\frac{T_d}{T}\right), \tag{26}$$

where x is the thickness of the layer of metal produced by the reduction process. For an absorptance $A(x)$, one can assume that

$$A(x) \simeq A_{ox}(1 - \beta x), \qquad \beta x \ll 1. \tag{27}$$

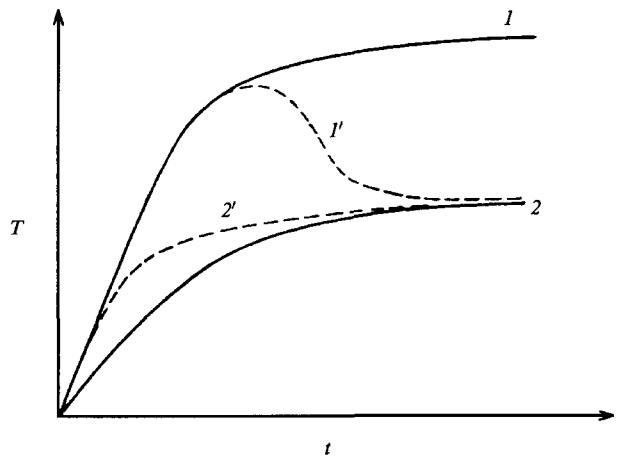


Figure 11. Time variation of the temperature of the specimen for $A(x) = A_{ox}$ (curve *1*) and $A(x) = A_m$ (curve *2*). (*1'*) activated reduction regime; (*2'*) nonactivated reduction regime.

For larger values of x, we have $\beta x \simeq 1$ and we can use the relation

$$A(x) \simeq \frac{x_0}{x}, \tag{28}$$

where x_0 is a characteristic scaling factor. In the reduction of Cu_2O to metallic copper, $x_0 \simeq 15$ Å and Eqn (28) fits satisfactorily the exact relation in the range of copper film thicknesses 50 Å $< x <$ 1000 Å. Fig. 11 presents curves illustrating the variation of the temperature of the specimen for two constant absorptances — corresponding to the pure oxide and the pure metal. In the reduction of the specimen, its heating begins in the state of the pure oxide, i.e. the specimen temperature follows initially curve *1* corresponding to the greater absorptance of the oxide. In the concluding state of the process, laser radiation acts on metallic film (complete reduction) and the temperature $T(t)$ should therefore tend asymptotically to curve *2* (heating of the pure metal). If the heating rate is high (large power of the radiation), the reaction begins in the early stages of the process. The transition from curve *1* to curve *2* takes place for a monotonic increase in temperature (curve *2'*). For slow heating, the reaction is unable to develop appreciably during the characteristic time of the establishment of the quasi-stationary temperature, so that heating takes place for a long time along curve *1*, the departure from it (curve *1'*) occurring at fairly late stages of the process. This in fact explains the nonmonotonic temperature variation for low powers.

The results of the direct numerical integration of Eqns (25) and (26) for the reduction of the lower oxide of copper to the metal under a hydrogen atmosphere are presented in Fig. 12.

We may note that in the laser-induced reduction the effects of heat conduction and of the nonuniformity of the heating process lead, as in the combustion processes discussed above, to changes in the dynamics.

There are numerous experimental situations where feedback channels of different signs exist simultaneously. For example, we have the negative feedback due to the change in absorptance and the positive feedback due to the exothermicity of the reaction. Such a situation is typical for the surface synthesis of titanium nitride on heating a titanium target in a nitrogen atmosphere with exposure to continuous IR radiation. In this case the chemical reaction may be a self-stabilising process for one set of parameters or a process with inflammation or thermochemical instability for another set. Such a combination of processes makes it possible to explain different complex transient pulsations in the heating rate which are not linked directly to the change in the power of the laser radiation, or, for example, to the interference oscillations in the absorption.

V. Physicochemical processes in the laser heating of liquids

We have considered hitherto processes in gaseous media or at solid–gas interfaces. Thermochemical processes initiated by laser radiation in a liquid are also of considerable interest.

1. Thermoelectrochemical instability in the laser-induced heating of absorbing electrolytes

Technologies based on the laser stimulation of electrochemical processes at conducting support–electrolyte solution interfaces have developed vigorously in recent years.[69,70] In the absence of laser radiation, such processes are the concern of classical electrochemistry.[71] The fundamental characteristic of electrochemical processes under equilibrium conditions is the electrochemical potential φ defined by the Nernst formula

$$\varphi = \varphi_0 + \frac{RT}{z_i F} \ln\left(\frac{a_i}{a_m}\right), \tag{29}$$

where z_i is the charge of the potential-generating ion and a_i and a_m are respectively the activities of the ion and the metal.

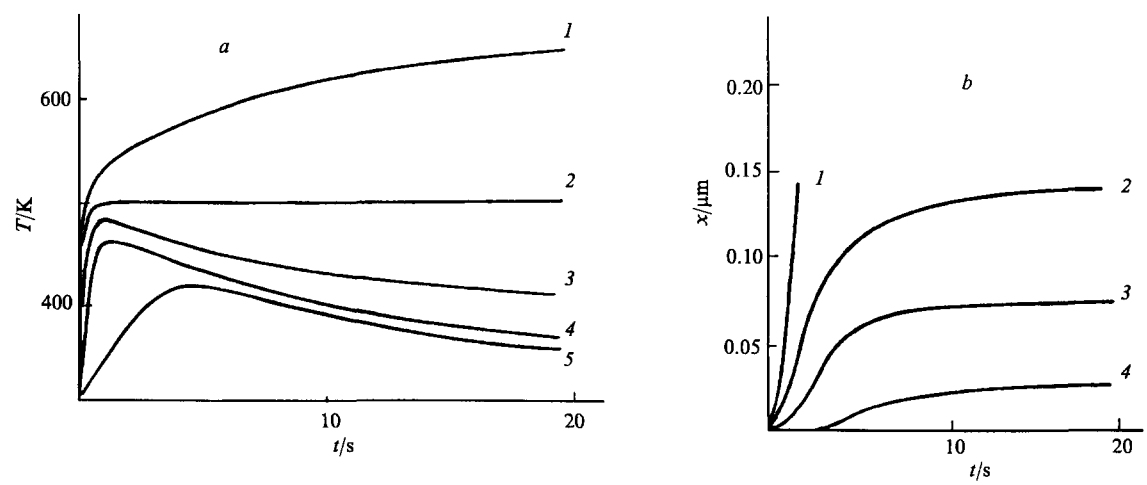


Figure 12. Variation of the temperature (*a*) and thickness of the copper layer (*b*) during its formation by the reduction of Cu_2O under a hydrogen atmosphere:[68] target mass 50 mg; target area 0.4 cm^2; continuous-wave CO_2 laser; power of the radiation (W): (*1*) 42; (*2*) 21; (*3*) 10; (*4*) 5; (*5*) 1.

The hierarchy of the electrode processes depends on the positions of the substances in the series of standard electrode potentials φ_0. For example, in order to precipitate from solutions metals which lie to the left of the material of the support in the above series, it is necessary to apply an external potential U exceeding the corresponding difference between the electrode potentials. However, the laser-induced precipitation of metals can take place in the absence of an external potential (see, for example, von Gutfeld[70] and Bunkin et al.[72]). Von Gutfeld[70] put forward the idea that the precipitation takes place under the influence of the e.m.f. of a microvoltaic cell associated with the temperature variation of the electrode potential $\varphi = \varphi_0(T)$. It was found[73] that the e.m.f. of the voltaic concentration cell associated with the local changes in the activity a_i of the potential-generating ions in solution also makes a comparable contribution. The change in activity is in its turn correlated with the change in the concentration of ions in solution as a result of thermal diffusion during nonuniform laser-induced heating.

We shall now discuss the characteristic features of the laser-induced heating of absorbing electrolytes. The absorption bands of the ionic complexes in solutions are fairly broad, but they are nevertheless well separated in many cases. At the radiation wavelengths in the vicinity of the absorption maximum of the corresponding complexes, the heating rate of the solution is determined mainly by their concentration. For example, in aqueous $CoCl_2$ solutions, the Co^{2+} absorption maximum corresponds to a wavelength of 510 nm,[74] whilst in aqueous $CuSO_4$ solutions the Cu^{2+} absorption maximum is at 800 nm. The sign of the thermal diffusion constant in solutions is such that positively charged metal ions migrate as a rule from the less heated to the more heated region. In nonpolar solvents with such a value of the thermal diffusion constant for the absorbing component of the solution, a positive feedback arises between the thermal and concentration degrees of freedom, which leads to thermal diffusion instability[75] analogous to the thermal diffusion instability in gases.[19] In electrolyte solutions, the development of thermal diffusion instability is complicated by the electrical interaction between the ionic complexes. Furthermore, the change in the distributions of the thermal and concentration fields entails a change in the distribution of the electrochemical potential. Therefore a thermal electrochemical instability may develop in electrolyte solutions.[76] It consists in an avalanche-like increase in the electrochemical potential.

Experimental studies have shown[74,76] that there is a range of parameters in which nonstationary changes in the electrochemical potential are observed: from simple and quasi-harmonic to complex stochastic oscillations. The oscillations are complicated by the cascade of bifurcations associated with the doubling of the period and by the increase in the complexity of the form of the limiting cycle (Fig. 13). A similar qualitative result was obtained in a theoretical study of the purely thermal diffusion instability in a mixture of gases.[39]

The spatially nonuniform distribution of the electrochemical potential on the surface of a metallic support coated by a layer of electrolyte solution leads to the formation of a microvoltaic cell, which permits electrochemical etching and precipitation.[70,74] Thus a microvoltaic cell with an e.m.f. of $\sim$0.6 V can be induced with the aid of a CW YAG-laser having a power up to 50 W. The size of the cell amounts to tens of micrometers and the precipitation current density reaches $\sim$1 A cm^{-2}, which is higher by several orders of magnitude than the values used in traditional electrochemistry. The laser-induced microvoltaic cell therefore permits the establishment of high-speed and at the same time low-temperature (T < 373 K) regimes in the laser treatment of conducting surfaces. This is of significant technological interest.

High-speed laser processes in the liquid-phase treatment of semiconductor surfaces can be achieved similarly. For this type of laser treatment, the use of the pulsed-periodic radiation of a copper vapour-based laser proved the most effective. Under these conditions, high rates of the photogeneration of electron–hole pairs in the semiconductor and fairly high temperature gradients in the electrolyte solutions are also ensured simultaneously. The formation of a microvoltaic cell is due in this case to the semiconducting nature of the support. Calculations have shown[77] that, in the deposition of metals on the surface of gallium arsenide, a microvoltaic cell with an e.m.f. of $\sim$0.5 V is formed mainly due to the Dember effect (i.e. due to the appearance of an e.m.f. as a consequence of the separation in space of the charges of electrons and holes) and the thermo-e.m.f. in the semiconductor, the Dember effect making the main contribution ($\sim$75%).

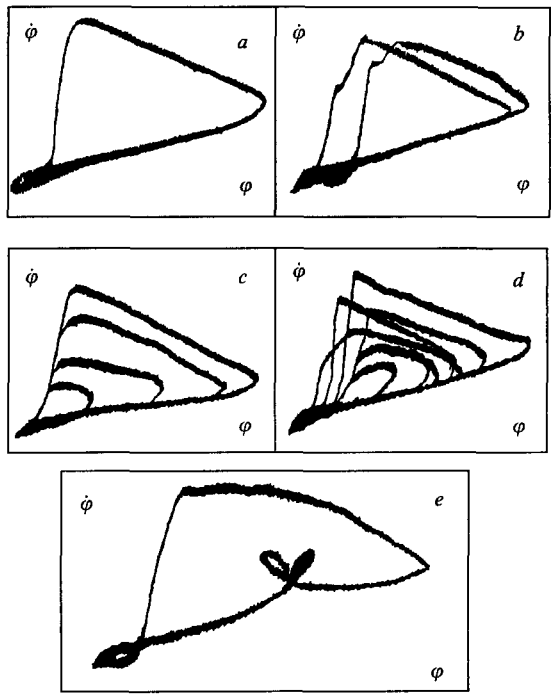


Figure 13. Phase portraits in terms of the variables φ, $\dot\varphi$ on the screen of an oscilloscope with a memory, obtained during the heating of an aqueous $CuSO_4$ solution by the radiation from a continuous-wave YAG-laser: (*a*)–(*d*) changes in the phase portrait as a result of the bifurcations involving the doubling of the period as the power of the laser radiation is varied; (*e*) increase in the complexity of the form of the simple limiting cycle (appearance of an additional 'small loop') as the beam width and the solution concentration are varied.

2. Dissipative structures in the laser-induced heating of thin layers of liquid

When the intensity of the laser radiation is insufficient for the bulk-phase ebullition or surface evaporation of the liquid it does nevertheless excite in the latter surface and bulk-phase hydrodynamic flows. These flows are caused by the convective instability of the nonuniformly heated stationary liquid.

Such convective flows play an important role in laser-induced thermochemical processes associated with the initiation of thermochemical and thermoelectrochemical reactions in solutions and also in processes associated with the formation of a melt on the surface of the test substance in the synthesis of surface compounds.

There exist several mechanisms for the influence of 'laser convection' on reaction kinetics. The rates of many processes in solutions are limited by the rate of supply of the reactant to the reaction zone. Initiation of convective flows promotes the removal of diffusional limitations and the acceleration of both pyrolytic and electrochemical reactions. In absorbing solutions, the situation is more complex because hydrodynamic flows are involved directly in the establishment of different feedbacks between the thermal and other degrees of freedom of the system. In particular, the eddies in the convective flows under the

conditions of nonuniform laser heating of the liquid can greatly intensify the effects of the thermal diffusion separation of the solution similarly to the situation arising in gas thermal diffusion columns with a heated filament in the centre. The hydrodynamic intensification of the separating effect can be characterised by the 'rate of rotation' of the convective eddy in the region of the separation of the test substance during the activation of the thermal diffusion instability. For example, according to Bunkin et al.,[78] the velocity of the convective streams initiated during the laser-induced heating of an aqueous $CuSO_4$ solution by the radiation of a continuous-wave YAG-laser with a power of 5–30 W is 1–30 cm s^{-1} and the rate of rotation of the eddy reaches $\sim 10^3$.

The 'hydrodynamic' feedback between the distributions of the temperature and concentration in the presence of laser-induced convection is established as follows. The increase in temperature gradient in the liquid increases the Rayleigh number. As the latter increases, the effectiveness of the thermal diffusion separation rises, as a result of which the region acted upon by the laser radiation is enriched in the absorbing ions. This increases the temperature gradient in the liquid, and so on. Experiments[73] showed that the effective thermal diffusion coefficient in the system acted upon by the laser radiation can reach values of $\sim 10^{-2}$ cm^2 s^{-1}. This exceeds by three orders of magnitude the molecular thermal diffusion coefficient of the ions in an electrolyte solution.

However, for large Rayleigh numbers (Ra > 5000), turbulence develops, leading to a sharp increase (by five orders of magnitude) in the effective normal diffusion coefficient, as a consequence of which the enriched region rapidly 'dissipates' and the homogeneity of the solution is restored. According to this scenario, auto-oscillations of the electrochemical potential, accompanied by the formation of bubbles and by the ebullition of the solution, may arise.

The development of hydrodynamic and thermal diffusion instabilities is accompanied in many instances by the formation of structures on the surface of the liquid differing from the familiar structures of the type of Benard or Marangoni cells. Among them, structures with a disturbed axial symmetry are of special interest. The appearance of such structures in a layer of a V_2O_5 melt during the laser-induced oxidation of vanadium in air has been noted.[79] It has been shown[80] that, on exposure to the continuous radiation of a YAG-laser with a power up to 150 W, there are three qualitatively different types of structures with a disturbed axial symmetry and three different scenarios for the increase in their complexity as the parameters of the laser radiation are altered (Fig. 14).

In wide beams (Fig. 14*a*), the formation of rotating spiral waves, the number of arms of which varied in the course of the oxidation process (with increase in the thickness of the fused layer of the oxide V_2O_5), has been observed. In the later stages of the oxidation process, the arms of the spiral closed, forming a stationary cellular structure. The rate of rotation of the spiral wave was 0.25–0.3 rev. s^{-1}. In beams having diameters of moderate size (Fig. 14*b*), stationary radial arms appeared, their number increasing as oxidation proceeded. Finally, following sharper focusing (Fig. 14*c*), a reverberator arose—a circular diffuse spot from which hot protuberances broke away periodically, rotating in one direction or another.

The effects observed in experiments[79,80] can be qualitatively explained as follows. During nonuniform laser-induced heating, surface flows arise in the liquid owing to the Marangoni effect together with bulk-phase flows associated with the instability of the radially and nonuniformly heated liquid. As a result, a flow with toroidal symmetry is initiated in the liquid layer, the flow rate becoming zero on the surface of the solid metal. This flow is analogous to the Couette flow between two rotating cylinders closed to form a torus. At certain rates of rotation of the cylinders, Taylor instabilities may develop in the Couette flow, as a result of which toroidal Taylor eddies arise along the entire length of the cylinder at regular intervals. The wave vector k of the resulting structure is then directed at a nonzero angle relative to the vector

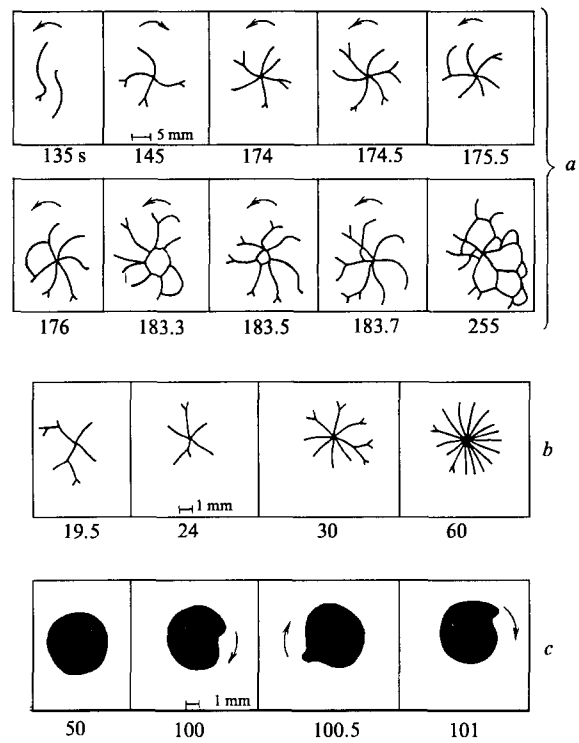


Figure 14. Dynamics of the variation of the thermal field during the heating of vanadium in air by the continuous radiation of an YAG-laser:[80] power of the laser 150 W; lines are streams of V_2O_5 melt at an elevated temperature; (*a*) wide beam 24 mm in diameter; (*b*) medium beam 18 mm in diameter; (*c*) focused beam 12 mm in diameter. The arrows in figures *a* and *c* indicate the direction of rotation of the structures and the numerals represent the times elapsed since the instant when the laser was switched on (seconds).

of the linear rate of rotation of the cylinders. For the geometry of the experiments considered, such instabilities lead to the loss of axial symmetry and to the appearance of isolated radial arms of the flow. In order that the structure obtained should rotate, the imaginary part of the increment at the instant of the loss of stability by the primary flow should be nonzero.

It has not so far been possible to create computer models of three-dimensional nonstationary structures in hydrodynamic streams, based on a direct numerical solution of hydrodynamic equations. For this reason, phenomenological or simplified models, obtained from hydrodynamic equations subject to certain assumptions, are frequently considered. Such are, for example, the Swift–Hohenberg, Kuramoto–Sivashinskii, etc. equations. The spiral waves of the type considered above are described satisfactorily by the phenomenological Arnol'd–Kirichenko equation:[81]

$$\frac{\partial w}{\partial t} = \left[\beta - A\left(k_r^2 + \frac{\partial^2}{\partial r^2}\right)^2 - 2C\left(k_r^2 + \frac{\partial^2}{\partial r^2}\right)\left(k_\varphi^2 + \frac{\partial^2}{\partial \varphi^2}\right) - \right.$$

$$\left. - B\left(k_\varphi^2 + \frac{\partial^2}{\partial \varphi^2}\right)^2\right] w + aw^2 - w^3 , \qquad (30)$$

where w is the order parameter having the significance of the deviation of the temperature from its value in the equilibrium homogeneous state, β the parameter of the supercritical state, r and φ are polar coordinates, and A, B, C, k_r, and k_φ are constants.

Numerical analysis of Eqn (30) makes it possible to describe various spatially nonuniform structures arising on development of thermocapillary instability in a thin layer of liquid. Some examples of such structures are presented in Fig. 15. The results of the calculations (Figs 15*a* and 15*b*) describe qualitatively

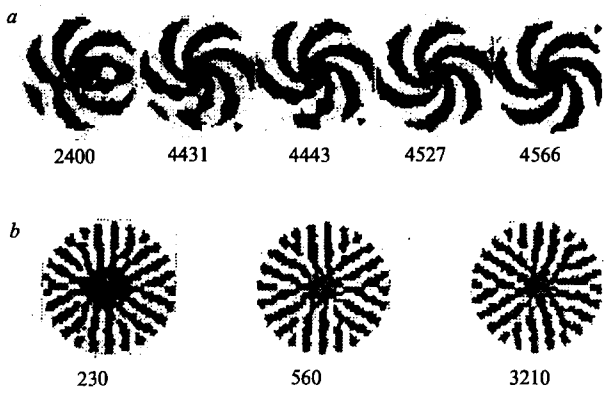


Figure 15. Two-dimensional structures found in the numerical solution of Eqn. (30) for different values of the parameters and different initial conditions (the numerals represent dimensionless times).[81]

correctly the experimentally observed structures (Figs 14*a* and 14*b*). We emphasise that the nonuniformity of the heat source is important for the appearance of these structures. This distinguishes them, for example, from the spiral waves in the Belousov–Zhabotinskii reactions arising in an initially homogeneous system.

VI. Some technological applications

1. Processes with participation of the gas phase: laser-induced precipitation and etching of a substance, separation of gases, and the synthesis of powders

The self-organisation phenomena considered above frequently lead to undesirable technological consequences. Processes with feedbacks due to the heat of a chemical reaction and the change in absorption are most dangerous in this respect. The few examples of a useful effect of the self-organisation phenomena (of the type of self-organising disequilibrium in the polyimide formation and the sharpening and localisation effects discussed above) merely emphasise the validity of the foregoing.

In addition, the dynamics of processes in the field of IR radiation are significantly more complex than in the field of radiation in the visible and UV regions. Therefore the application of the IR lasers such as the CO_2 or CO lasers is in many cases ineffective despite their great technological sophistication and excellent energy parameters. As a result of this, lasers working in the visible and UV ranges, primarily argon and excimer lasers, are mainly used in modern technologies.

Thus in order to achieve stable thermochemical processes, it is necessary to eliminate effects due to the concentration-induced change in absorption, laser radiation in the visible and UV ranges and thermally neutral or even endothermic reactions should be used, and the chemical reaction should be carried out in a region the size of which should not exceed the characteristic scale of unstable perturbations, i.e. a focused laser beam with a diameter not exceeding tens and sometimes even a few micrometers should be employed.

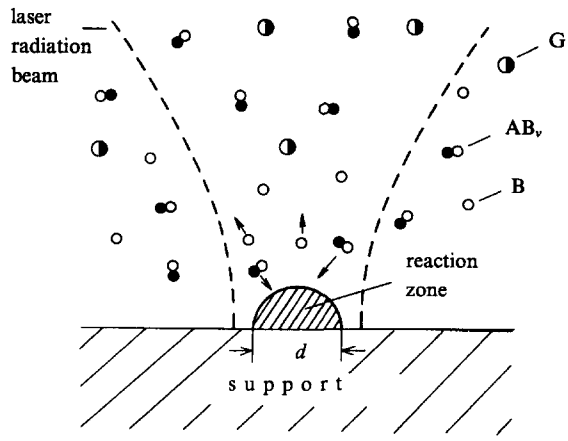


Figure 16. Typical geometry of the irradiation zone in experiments on the laser-induced deposition of a substance from the gas phase ($d = 2r_0$).

Virtually all these requirements are met in the modern technology for the laser-induced precipitation of a substance from the gas phase.[82,83] In the literature this process is frequently designated by LCVD (from the English language term Laser-induced Chemical Vapour Deposition). This technology is already used by a number of companies for the solution of certain problems in microelectronics, integrated optics, etc. and the processes achieved are indeed distinguished by their stability and by the high quality of their technological characteristics.

However, feedbacks cannot be fully excluded from laser-stimulated chemical processes. In the case of LCVD, the main cause of the disequilibrium is high temperature gradients (up to 10^6-10^7 K cm^{-1}), which lead to the interaction of different flows.

In many experiments on LCVD, the gas mixture is transparent to the laser radiation, while the deposit is thermally thin. A simplified scheme of the irradiation zone is illustrated in Fig. 16. The gas pressure usually selected is, on the one hand, not too great to avoid the appearance of an intense eddy convection in the gravitational field, and, on the other, is not too small to make sure that the thermal jump at the solid–gas interface is negligible. Typical ranges of pressures, temperatures, and activation energies for certain LCVD reactions are presented in Table 2.

In many instances, the LCVD process can be represented by the unimolecular decomposition reaction

$$AB_\nu + G \rightarrow A\downarrow + \nu B\uparrow + G, \qquad (31)$$

where AB_ν is a molecule of the gas being decomposed, G a molecule of the diluent gas, A a molecule (atom) of the substance forming the solid deposit, B a molecule of the gaseous fraction of the reaction product, and ν a stoichiometric coefficient. The processes involving the formation of solid carbon in the pyrolysis of methane and other hydrocarbons and the deposition of silicon on pyrolysis of monosilane may serve as examples of

Table 2. Activation energies for certain reactions involving the deposition of material from the gas phase at high temperatures.[83]

Reaction	T/K	Pressure range in mixture/mbar	ΔE/kJ mol^{-1}
$C_2H_2 + H_2 \rightarrow 2C\downarrow + H_2\uparrow + H_2$	1900–2450	50–1000	197.7±0.6
$C_2H_4 + H_2 \rightarrow 2C\downarrow + 2H_2\uparrow + H_2$	2000–2250	300–1000	242.7±1.3
$C_2H_2 + H_2 \rightarrow 2C\downarrow + 3H_2\uparrow + H_2$	2200–2250	300–1000	495.4±2
$CH_4 + H_2 \rightarrow C\downarrow + 2H_2\uparrow + H_2$	2850–3100	500–1000	180.8±1.4
$SiH_4 + H_2 \rightarrow Si\downarrow + 2H_2\uparrow + H_2$	1000–1800	10–1000	183.9±4

type (31) reactions. The elementary rate J of such reactions is described by the unimolecular decomposition law

$$J = k_0 N c_s \exp\left(-\frac{\Delta E}{k_B T_s}\right), \quad (32)$$

where N is the total density of the molecules in the gas, c_s the concentration of the substance AB_ν on the surface of the deposit, ΔE the activation energy for the chemical reaction, k_0 the pre-exponential factor, k_B the Boltzmann constant, and T_s the temperature of the surface. At low temperatures, the concentration of the substance AB_ν is virtually identical throughout the volume (kinetic region). At high temperatures, the rate of formation of the deposit is determined by the rate of supply of the reactant to the reaction zone (diffusional region) rather than by the rate of the elementary step involving the chemical decomposition of the molecules.

The diffusional rate limitation effect can be clearly observed in LCVD processes.[83] However, its manifestations are qualitatively different for equimolecular ($\nu = 1$) and nonequimolecular ($\nu \neq 1$) reactions. Among the reactions listed in Table 2, only that involving the deposition of carbon in the decomposition of acetylene is equimolecular.

The characteristic features of the kinetics of equimolecular reactions are determined mainly by factors such as the temperature dependence of the density and the diffusion coefficient, the existence of a thermal diffusion flux of the substance, and the presence of a diluent gas. On the other hand, the nonlinearity caused by the diffusional thermal effect as well as the concentration- and temperature-induced changes in the thermal conductivity are insignificant. In particular, thermal diffusion can lead to large (of 1–2 orders of magnitude) quantitative differences in the rate of reaction, depending on the choice of the diluent gas G.[84]

In nonequimolecular reactions, for example

$$Mo(CO)_6 \rightarrow Mo\downarrow + 6\,CO\uparrow ,$$

a directed gas flow (chemical convection) arises owing to the inconstancy of the number of molecules in the gas phase.[85,86] This effect exerts a strong influence on the reaction kinetics. In a theoretical analysis of the LCVD process, the viscosity and the nonisobaric effects are usually neglected and it is also assumed that the specific heats of the medium c_p and c_v as well as the thermal diffusion constant α are invariant. The kinetics of the LCVD process can then be described by a system of three equations: two continuity equations (for AB_ν molecules and for the gas as a whole) and the heat transfer equation (the equation for the thermal conductivity in a moving gas). This model presupposes a series of nontrivial phenomena due to the interaction of the diffusion and convective streams of the test substance. For example, for $\nu > 1$ the convective gas flow is directed away from the surface of the deposit into the bulk of the medium and therefore should seemingly inhibit the reaction. Indeed, at relatively low temperatures of the deposit this is what happens. However, at high temperature, over a certain range of values of the parameter $b = \nu - 1$, the convective flow directed from the reaction zone ($b > 0$) promotes not the retardation but actually the acceleration of the deposition of the substance. For simplicity, we shall assume that there is no thermal diffusion flow. The cause of this result is then the interaction of the flows, which takes place in accordance with the following scheme. Convection itself at $\nu > 1$ prevents diffusion (the displacement flow is directed in opposition to the diffusion flow) and at the same time it promotes the transfer of the more heated gas into the bulk of the medium and hence additional heating of the medium around the deposit. Such heating increases the diffusion coefficient, which entails an increase in the diffusion flux. The overall result is determined by the competition between two effects — the increase in the convective displacement and the increase in the opposed diffusion flux. If this leads to an increase in the concentration of the gas being decomposed in the vicinity of the surface of the support, then, by virtue of the concentration dependence of the rate of diffusion, a positive feedback arises between the concentration and diffusion fluxes.

Analysis shows that, when account is taken of the thermal diffusion flux, a complex system of feedbacks is generated between the convective, diffusion, thermal diffusion, and thermal fluxes. As a result, the overall effect cannot be determined merely on the basis of the principle of the superposition of independent material fluxes.

One of the consequences of the interaction of the fluxes is the possibility of the formation of a diffusion barrier in the vicinity of the zone where the nonstoichiometric reaction takes place.[86] This barrier is overcome by means of thermal diffusion, while ordinary diffusion and convection behind the diffusion barrier transfer the substance in the direction away from the deposit.

Thus the transfer of the test substance, which determines the reaction kinetics under the nonequilibrium conditions typical for LCVD, is complex even in the absence of a change in the absorptance of the substance or additional energy evolution by the chemical reaction itself. High temperature gradients entail effects, which cannot be eliminated, associated with the parametric interaction of different fluxes arising by virtue of the temperature and concentration dependences of the kinetic coefficients.

We have considered hitherto the LCVD process without paying attention to the form of the deposit obtained, actually assuming that it is spherically symmetrical. On the other hand, in many practical applications the spatial distribution of the deposit plays an important role. It is determined by the type of reaction and its conditions. Consider, for example, the laser-induced tungsten deposition reaction

$$WF_6 + 3H_2 + G \underset{k_{se}}{\overset{k_{sd},\,k_v}{\rightleftarrows}} W\downarrow + 6HF + G . \quad (33)$$

In contrast to the reaction (31), the above reaction is not unimolecular. The forward pathway involves the decomposition of tungsten hexafluoride, which may occur both on the surface (rate constant k_{sd}) and in the bulk phase (k_v). The reverse reaction (etching) takes place on the surface and is characterised by the rate constants k_{se}. Different activation energies correspond to all three pathways, so that different reactions can predominate in different temperature ranges. Furthermore, the reaction rates depend greatly on the partial pressures of the components of the gas mixture. The combination of all these factors actually determines

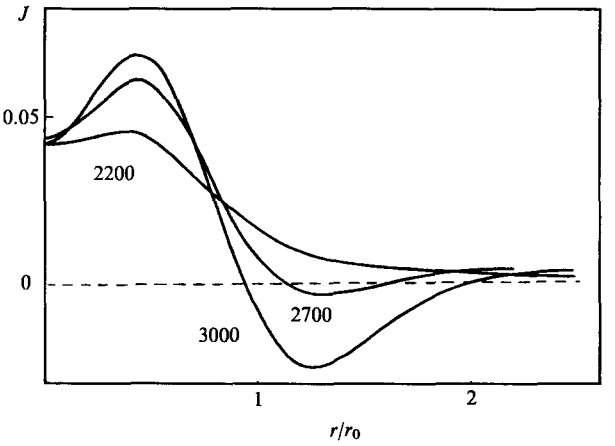


Figure 17. Typical spatial profiles of the deposit formed under the influence of laser radiation under the conditions of the diffusional limitation of the reaction for open surface and bulk-phase deposition reaction pathways and in the presence of the reverse reaction (etching).[83] The numerals opposite the curves denote the surface temperatures along the beam axis (in kelvins).

the form of the deposit produced. If the forward reaction (k_{sd}) predominates, the deposit is well localised within the limits of the radiation zone. On the other hand, if the bulk-phase reaction (k_v) predominates, then tungsten atoms are transported over large distances by diffusion in the gas and the characteristic dimensions of the deposit can appreciably exceed the size of the irradiation spot. As a result of etching, the thickness of the deposit diminishes and this can lead to the formation of a deposited substance profile which is nonmonotonic with respect to the radius. We may also note that the complex form of the deposit may be caused by the diffusional rotation of the transport of reactants in the gas phase as well.[87] Figs 17 presents the results of calculations[88] illustrating the foregoing. The minima on the curve are associated with the etching and/or diffusional limitation. The parts of the curve below the 'zero' level correspond to the etching of the support. The experimental results indicate the validity of the foregoing.[89] Fig. 18 presents photomicrographs of tungsten deposits obtained on decomposition of WF_6 and WCl_6.

Laser deposition from the gas phase is used in microelectronics not only in order to obtain localised deposits but also for the deposition of stripes with the aid of a moving laser source. The so called direct drawing regime is used for this purpose. As an example, Fig. 19 presents photographs of stripes of tungsten deposited by this method on silicon plates. The significant technological characteristics of the deposit are its height and width, conductivity, adhesion to the support, etc. It is fairly difficult to select a laser deposition regime in which the stripes possess the required technological characteristics.

The attempts to use lasers for the deposition of local structures by LCVD methods (for example from the vapours of organometallic compounds) were undertaken as early as the end of the 1960s.[91] However, the results of these studies were in most cases negative — it was not possible to ensure the required technological parameters. During this period, many specialists shared the view that the poor quality of the stripes is mainly caused by the inadequate characteristics of the lasers themselves. Almost fifteen years were needed in order to understand that the 'technological' difficulties have deep physical roots. They are associated with the capacity of nonequilibrium systems to undergo self-organisation.

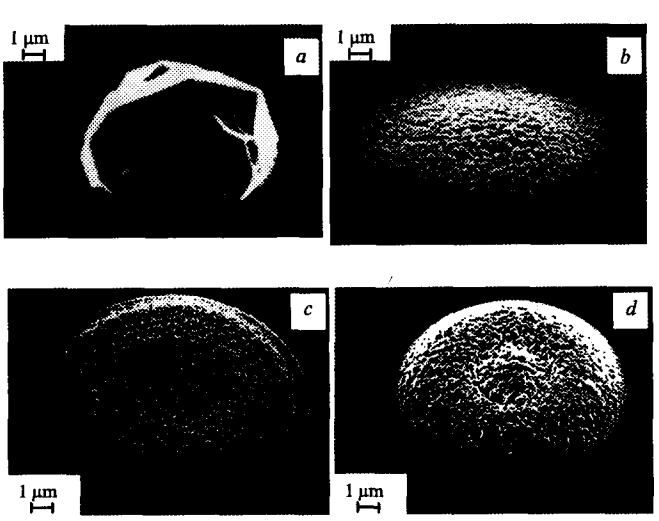


Figure 18. Photomicrographs of tungsten deposits in the decomposition of WF_6 (*a* and *b*) by the radiation of an argon laser (λ = 514.5 nm) and in the decomposition of WCl_6 by the radiation of a dye laser (λ = 680 nm) (*c* and *d*) at different partial pressures and for different irradiation conditions.

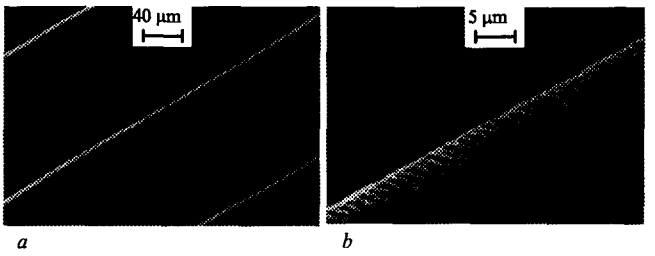


Figure 19. Photomicrographs of tungsten stripes deposited from a $WF_6 + H_2$ mixture on silicon plates under the influence of the radiation from a Kr^+ laser (λ = 647.1 nm).[90]

For a theoretical determination of the form of the deposited stripe it is necessary to solve chemical kinetic equations simultaneously with the equations for the thermal field generated by the moving laser source. In contrast to the problems discussed above, in problems of this kind the negative feedback between the deposition kinetics and temperature, determined by the influence of the form of the stripe itself on the distribution of the thermal field, proved to be significant. Since the thermal conductivity of the metallic stripe is many times greater than the thermal conductivity of the support (particularly a dielectric support), an additional heat flux arises from the irradiation zone towards the side away from the direction of movement of the source. Such outflow of heat is higher the greater the cross-section of the stripe. The presence of such 'geometrical' feedback together with other factors (for example, the change in absorption) leads to numerous instabilities and self-organisation phenomena: the deposits are formed in many cases with an internal structure, with various pulsations in the thickness and width of the stripe, etc.[83] In order to discover the optimum treatment conditions, it is in many cases necessary to employ the methods of the self-organisation theory.

The related problem of the high-temperature laser synthesis of powders from the gas phase is closely associated with LCVD processes. Many refractory compounds (boron nitride and carbide, silicon nitride, the oxides of certain metals, etc.) can be synthesised in the form of finely dispersed powders with particle sizes ranging from tens to hundreds of ångströms if the laser radiation is focused directly in the gas mixture.[92] Such powders have practical applications as abrasive materials and they can also be pressed and sintered in the form of shaped specimens. Examples are provided[92] by the synthesis of silicon carbide powders, i.e.

$$SiH_4 + CH_4 \rightarrow SiC\downarrow + 4H_2\,, \tag{34}$$

or

$$2SiH_4 + C_2H_4 \rightarrow 2SiC\downarrow + 6H_2\,, \tag{35}$$

and also the synthesis of silicon nitride, i.e.

$$4NH_3 + 3SiH_4 \rightarrow Si_3N_4\downarrow + 12H_2\,. \tag{36}$$

The reactions frequently have high activation energies and a high temperature is therefore required to carry them out. There is no special difficulty in attaining a local temperature of several thousand degrees with the aid of lasers. The particles formed in the course of the elementary reactions subsequently coalesce and form clusters. Similar processes have been observed at high temperatures also in the reactions occurring in the laser-induced deposition of a substance.[83] In this case the growth of the deposit is no longer a result of the elementary process (31) considered above, but is due to the transport of clusters in the gaseous medium and their subsequent deposition on the support.

Different mechanisms of the laser-induced nucleation are possible. For example, if the gaseous medium absorbs weakly the laser radiation, the reaction can be initiated first in the vicinity of impurity absorbing centres (impurity species, dust particles, etc.) and can then attain a self-supporting regime due to absorption in the cluster itself. A similar mechanism can operate in the nucleation in LCVD processes.[83]

The kinetics proper of the growth of the cluster constitute a separate problem. The cluster can grow both as a result of 'sticking' to other clusters and as a result of the increase in its intrinsic volume. In particular, if the synthesis on the surface of the nucleus takes place more effectively than in the bulk of the gas, then the cluster may grow via the same mechanism as the deposit in LCVD.

Effects associated with the change in activation energy due to strong surface tension forces play a significant role for microclusters. The physicochemical properties of microclusters differ markedly from those of the corresponding macroformations.[93]

In discussing LCVD processes above, we spoke of molecular mass transfer due to conventional diffusion, thermal diffusion, and chemical convection. By virtue of nucleation, other mass transfer mechanisms are also possible. For example, in the usual (nonlaser) problems of the chemical deposition of a substance, clusters migrate via thermophoresis,[94] as a result of which the particles are expelled from the more heated to the less heated region. It would therefore seem that microclusters should not settle at all on the heated surface. However, experiments have demonstrated an effective flux of clusters onto the heated surface. Direct experimental measurements of the distribution of temperature in the boundary layer over the heated deposition surface[95] showed that, owing to the considerable evolution of energy on coalescence of the microclusters, caused by the decrease in their surface energy, an additional intense heating of the gas takes place in the cluster growth zone. For example, on formation of carbon clusters from hydrocarbons, cluster formation leads to additional heating of the gas regardless of whether the decomposition reaction itself is exothermic or endothermic. This results in the establishment of a nonmonotonic distribution of temperature with a maximum which is separated from the heated wall by 200–500 μm. The temperature at the maximum exceeds by 300–500 K that of the wall itself.[95] As a consequence, a thermophoretic force directed towards the wall is generated. On the other hand, in the case of the laser-induced synthesis of powders, apart from thermophoresis, other forces acting on the particles arise, for example forces associated with the radiometric effect (at low gas pressures), etc.

In nonequimolecular reactions, the force due to the difference between the flux recoil momenta (associated with the chemical convection in the gas) on the 'hot' and 'cold' sides of the particle, also acts on the microparticle. In contrast to thermophoresis and the radiometric force, which expel the particle with the 'cold' side in front, the directional forces associated with the chemical convection depend on the stoichiometry of the reaction. This phenomenon can be properly referred to as 'chemophoresis'. The chemophoretic effect can be readily understood with the aid of the following considerations.

Suppose that a spherically symmetrical particle with a radius R is in a temperature field $T(z)$ with a constant gradient $\gamma = \mathrm{d}T/\mathrm{d}z$. Then the boundary condition for the rate of migration of a gas v on the surface of the particle is

$$v = bc_{AB}k_0 \exp\left(-\frac{T_a}{T}\right), \tag{37}$$

where c_{AB} is the concentration of the substance AB_ν on the surface of the particle, $b = \nu - 1$, and $T_a = \Delta E/k_B$. We shall assume that the reaction proceeds in the kinetic region (c_{AB} = const.). The temperature of the surface of the particle is

$$T = T(\theta) = T_0 + \gamma R\cos\theta, \tag{38}$$

so that the temperature drop across the particle is $2\gamma R$. The component of the gas momentum, summed over the surface, is

$$P_z \simeq Mbc_{AB}k_0 \int_0^\pi \left[2\pi R^2 \sin\theta\cos^2\theta \times \right.$$
$$\left. \times \exp\left(-\frac{T_a}{T_0 + \gamma R\cos\theta}\right)\right]\mathrm{d}\theta =$$
$$= Mbc_{AB}k_0 \exp\left(-\frac{T_a}{T_0}\right) 2\pi R^2\varphi, \tag{39}$$

where in the limit $\gamma R \ll T_0$ we have

$$\varphi \simeq \int_{-1}^{1} y^2 \exp(-\xi y)\,\mathrm{d}y = \left(\frac{2}{\xi} + \frac{4}{\xi^3}\right)\sinh\xi - \frac{4}{\xi^2}\cosh\xi,$$

$$\xi = \frac{T_a}{T_0^2}\gamma R.$$

By virtue of the symmetry of the problem, all the remaining components of the momentum (P_x and P_y) become zero. Hence, as a result of the recoil, the particle acquires a nonzero momentum equal to $-P_z$. It is seen from Eqn (39) that the chemophoretic force depends not only on the gradient γ but also on the temperature T_0. Its pressure dependence is therefore different from that of the force due to the radiometric effect and is determined by the reaction kinetics. It is also noteworthy that the chemophoretic force may be considerable.

The laser-induced etching process is closely related to deposition. The etching effects arise when the chemical interaction of the surface atoms of the support (for example, a silicon plate) with the reactive molecules or radicals of the gas phase results in the formation of a more volatile substance (for example, a $SiCl_4$ molecule), which leads to the removal of the solid phase. Chemically reactive molecules can arise in the gas phase on laser-induced thermal dissociation of, for example, halogen-containing gases (for the specific features of such processes, see Karlov et al.[96]). Whilst referring the readers to the original communications as regards the details of this technology (see, for example, Bäuerle,[83] Takai et al.[97] as well as the references quoted therein), we may note that channels with a width and depth ranging from several to several tens of micrometers can be formed in semiconductors, ferrites, and other materials by means of laser-induced chemical etching. The rate of the laser-induced etching can greatly exceed[97] the rate of the plasma-chemical etching[98] usually employed in microelectronics. Apart from the evident applications of the laser-induced etching technology in microelectronics, to which many of the investigations have been directed, this technology can also be employed in micromechanics[99] (preparation of miniature mechanical components, for example, in accelerometers, with dimensions corresponding to several tens of micrometres, etc.).

Among the problems of the kinetics of the laser-induced etching, we may note the diffusional limitation of the reaction (as regards the supply of the etching agent and the removal of the volatile reaction products) similar to that examined above for the LCVD process. In the range of high temperatures, diffusional limitation should restrict the rate of reaction. On the other hand, experiments[97] have shown that the rates of etching are high compared with those which could occur under the conditions of diffusional limitation. One of the explanations of this technologically favourable effect is that, at the high pressures of the gas mixtures used for etching, an intense gravitational convection develops which removes the diffusional limitation.

There exist also purely chemical problems of etching associated with the multistage nature of many reactions and the participation in the latter of intermediate surface products.[100] As in the case of LCVD, further development of the technology of the laser-induced chemical etching requires special research which would make it possible to understand more fully the nature of the process and the possibility of its optimisation.

Laser-induced separation of gases is based on the thermal diffusion effect. In the usual thermal diffusion columns, a heated filament is used as the source generating a nonuniform thermal field.[101] Such a column operates also in the case where the function of the heated filament is assumed by a beam of laser radiation absorbed in the gas mixture. However, as we have seen above, laser radiation can intensify the effect associated with the thermal diffusion separation of the mixture as a result of the positive feedback established between the concentration and thermal degrees of freedom of the system. In the usual thermal diffusion column, convection in the gravitational field plays an

important role in intensifying the separation effect.[101] Laser radiation can enhance also this convective effect as a result of the positive feedback between convection, thermal diffusion, and the heat evolved. The existence of different kinds of positive feedbacks renders the separation of the gas mixture in a laser thermal diffusion column more effective than in the usual column. This has been confirmed by direct experiments.[102]

2. Processes at the interface between two solid phases: direct drawing, etching, and synthesis

The action of laser radiation on the surface of a solid on which films of other solids have been deposited leads to the modification of the properties of the film and/or the surface of the solid (support). With the aid of such solid-phase sandwich structures, it is possible to achieve virtually all types of microchemical treatment of the surface: deposition of metals, etching of the surface, syntheses of various compounds on the surface of the support. One is dealing with a solid-phase microtreatment technology which is an alternative to the traditional technologies (plasma, gas-phase, and liquid-phase technologies).

Certain metal salts, for example those of formic and oxalic acids, readily decompose on heating to the pure metal and volatile components. The decomposition of copper formate may serve as an example:

$$Cu(HCOO)_2 \rightarrow Cu\downarrow + H_2O\uparrow + CO\uparrow + CO_2\uparrow. \quad (40)$$

The process temperature under the usual conditions is 598 K. Copper formate is deposited on the surface in the form of a powder or a suspension. The thin surface layer is then acted upon by a laser, which results in the formation of copper stripes on various supports.[91] It is possible to obtain solid films of organic substances by using various solvents, which then volatilise during drying. Metallic stripes, formed from the resinates of various metals,[83] triphenylphosphine complexes of univalent gold,[103] etc. are deposited by this procedure.

The laser-induced decomposition of certain substances, for example poly(vinyl chloride) films, results in the formation of free radicals, chlorine molecules, etc., which can etch the support. Multilayer structures of the support–decomposable film–glass type are used in the experiment. Laser radiation acts from the side of the transparent glass. Under these conditions, one can obtain etched channels in the glass several ångströms deep and several tens of micrometres wide.

The most detailed studies have been carried out on the laser-induced synthesis of substances from thin films.[104,105] Extremely pure compounds of various elements, including compounds of the type $A^{III}B^{V}$ (AlSb, AlAs), $A^{II}V_x^{VI}$ (CdTe, CdSe, ZnSe), $A^{IV}B^{VI}$ ($GeSe_2$, GeSe), ternary compounds ($CuInSe_2$), etc. have been synthesised. This technology can be used to record information on high-capacity optical discs and also in microelectronics and integrated optics.

Many scientific problems are associated with the preparation of compounds from thin-film structures. We shall elucidate some of them in relation to the synthesis of the binary compounds A+B → AB (in particular of AlSb from aluminium and antimony films). Experiments have shown[104] that, when such a structure is heated in an ordinary furnace up to the melting point of aluminium (933 K), about 100 s is required for the formation of the AlSb film. The reason for this is fairly simple: the initial AlSb layer is formed at the site of contact between aluminium and antimony. The melting point of AlSb (1353 K) exceeds the melting points of its constituent elements. The solid film formed therefore separates the components in space. In this case, the rate of reaction is limited by the diffusion of atoms through the layer of AB, as happens in reactions involving the heterogeneous oxidation of metals. On the other hand, under the conditions of pulsed laser action, which heats the film to the same temperature, the synthesis takes place effectively during the laser pulse of 10 ns. If the validity of the estimated temperature is accepted and it is postulated that the formation of the film is limited by diffusion, then this means that the coefficients of the diffusion of atoms through the AlSb layer acted upon by laser radiation should be anomalously high (of the order of 10^{-2} cm^2 s^{-1}). We recall that the phenomenon of the anomalously rapid diffusion first attracted attention in the analysis of the laser-induced annealing of semiconductors.[24,25] Experiments have shown[104] that in the laser-induced synthesis of films there is a threshold energy equal to the energy necessary to fuse aluminium. On the other hand, if the multilayer structure prepared is subjected to preliminary annealing at 623 K for 30 min and longer, then the threshold energy required for the synthesis increases by 60% and corresponds to the melting point of AlSb. The possible explanations of the results of these experiments are as follows: in contrast to experiments in a furnace, exposure to laser radiation does not result in the formation of a planar AlSb layer but instead the liquids are rapidly mixed with subsequent chemical reaction; owing to the heat of the chemical reaction in the film, under certain irradiation conditions, 'inflammation' takes place over a brief period, as a result of which the film of the compound synthesised melts.

The presence of a melt is indicated, for example, by structures of the type of Benard bridges (Fig. 20), which were observed in the synthesis of CdSe and a number of other films. However, there is also evidence that the laser-induced synthesis is accelerated also in the solid phase of the film. It may be that such increased 'permeability' of the solid films is associated with the presence in the latter of non-equilibrium vacancies. This mechanism of the acceleration has been discussed.[38] The experimental results can also be interpreted as the effect of the decrease in the melting point[104] of the solid film presaturated by nonequilibrium vacancies.[104]

Finally, yet another interesting problem, observed in the course of a study of the laser-induced synthesis of thin-film compounds, is that of the presence of large (up to 1 μm, i.e. many times greater than the thickness of the film) single crystals of many compounds (AlSb, $GeSe_2$, $CuInSe_2$, etc.) on irradiation of the initial structure with 10^{-6} s laser pulses. In order to account for these effects, the idea of the 'polymerisation' of liquids, in particular $GeSe_2$, has been put forward.[104] We may note that the rapid crystallisation of films from the melt in the synthesis of compounds differs significantly from the analogous process in the laser-induced annealing of semiconductors, where there is epitaxial growth of the film, for example of silicon, from the melt on an orienting support. In the synthesis of thin-film compounds, there is no orienting support and the crystal nuclei formed are oriented at random. Therefore, in the rapid laser-induced synthesis, polycrystalline or amorphous films should be



Figure 20. Photomicrograph of the convective ridges formed in the synthesis of the CdSe sandwich structure on glass in air;[104] power of the laser 1 W; typical cell size ~10 μm; ratio of the ridge width to thickness ~50.

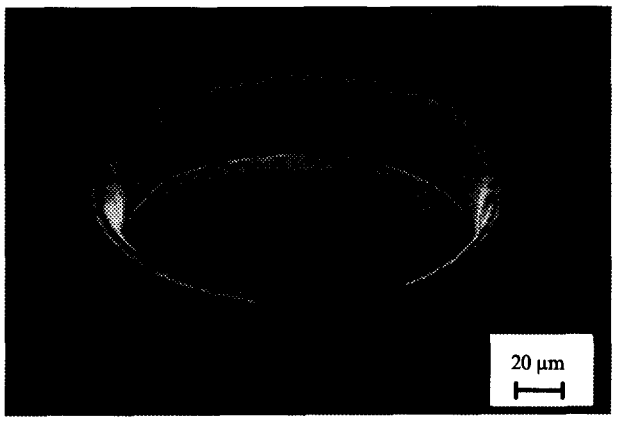


Figure 21. Crater formed in a $LiNbO_3$ single crystal on exposure to a XeCl excimer laser (500 pulses with an overall energy density of 2.7 J cm^{-2}). The half-height diameter of the beam was 175 μm.

observed depending on the rate of cooling, which does in fact frequently occur. On the other hand, the formation of large single crystals during rapid crystallisation on a nonorienting support is possible because of the orienting forces of the external mechanical stresses.[106] One should therefore analyse carefully the experimental conditions in order to eliminate fully the possibility of the generation of such stresses.

Other features of the laser-induced synthesis have also been noted—such as the retention of the high stoichiometry of the compounds obtained, the dependence of the orientation of the synthesised film on the wavelength of the laser radiation observed in certain cases, etc.[104, 105]

3. Laser-induced ablation of polymers

An important aspect of laser chemistry is associated with the phenomenon of laser-induced ablation, i.e. the effect of the removal of material under the influence of radiation, in which the resulting crater contains no traces of the melt or any kinds of mechanical failures (Fig. 21). The properties of the laser-induced ablation make it an attractive procedure for various applications in microelectronics, medicine, and other fields.[107-109]

The laser-induced ablation of polymers is usually carried out with the aid of excimer lasers. The characteristic features of this process are as follows: the existence of an irradiation energy density threshold, the change in the optical properties of the substance in the course of exposure to radiation, a nonequilibrium distribution with respect to the velocities of the products removed.

The existence of the threshold may be due to different causes. One of them is thermal sublimation with a pronounced Arrhenius temperature dependence of propagation of the velocity of the sublimation front.[109] Another cause is the development in the substance of elastic stresses,[107] which must reach critical values necessary for removing a significant amount of mass. Yet another cause may be multiphoton (or stepwise) absorption,[107, 108] which requires fairly high light intensities.

The change in the optical properties of the test substance may be associated both with irreversible processes, for example, with thermochemical or photochemical reactions,[107] as well as reversible processes, for example with the passage of light due to the saturation of the populations of the levels between which the transition responsible for the absorption of light takes place.[110]

The distribution with respect to composition and velocities of the products removed is of great interest.[107] Indeed, the products of the ablation of polymers include both low-molecular-mass fragments (pure carbon, simple organic molecules, and small clusters) as well as fragments with a moderate molecular mass close to that of the monomers (or part of the monomers) of the initial substance. In addition, the removal of large clusters (lumps of the initial polymer) and large carbon particles is observed. The latter is of particular interest in connection with the synthesis[111] of macromolecular carbon C_{60}. In the velocity distribution of products, the equilibrium (Maxwellian) fraction and the fraction comprising nonequilibrium fast particles are clearly differentiated.[107] So far this complex pattern cannot be convincingly explained within the framework of the concept of secondary photolysis or multiphoton absorption.

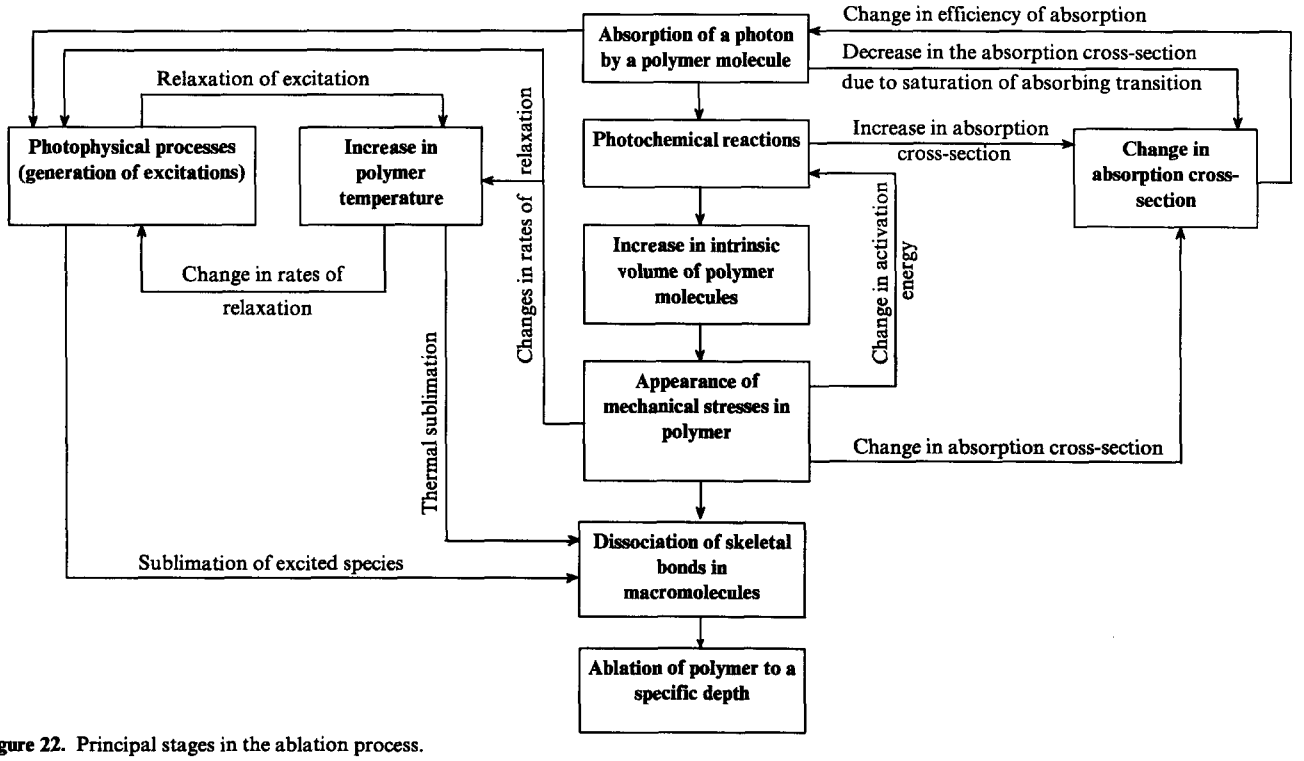


Figure 22. Principal stages in the ablation process.

The data on the dynamics of the development of mechanical stresses in the system and the dynamics of the removal of material during ablation[107] agree better with the thermal sublimation model than with the model involving the photothermomechanical removal, according to which the main bulk of the substance is carried away in the relaxation wave after the operation of the laser radiation pulse has ceased.

The behaviour of species in an electronically excited state plays an important role in the ablation process. The presence of such species in strongly absorbing polymers is not open to doubt.[110] Together with the change in the optical properties,[110] there exist many other pathways by means of which the excited species can affect the kinetics and dynamics of the laser-induced ablation. The sublimation of these species takes place with a reduced activation energy, which permits the assumption of the existence of a cold sublimation regime at a surface temperature below the melting point. Furthermore, such sublimation alters the velocity distributions of the species eliminated.

The characteristic features of the ablation can also be associated with the relaxation process during fusion. In view of the relative slowness of these processes even at temperatures appreciably greater than the melting point,[112] sublimation may be faster than fusion. This probably explains the absence of traces of fusion even at high surface temperatures.

Finally, mention may be made of an important factor associated with the influence of mechanical stresses in the substance on the activation energies of various processes.[113] Such stresses may arise both owing to the usual thermoelasticity and owing to the different volume of the products of the chemical reactions compared with the starting material.[114] Many other factors can also play an important role in the ablation processes. A scheme of the principal stages in the ablation process, similar to that quoted by Kitai et al.,[112] is presented in Fig. 22. Evidently the process is fairly complex and its complete description is almost impossible. Therefore simplified models have to be often used. The most pronounced simplification consists in the fact that the process is assumed to be purely photophysical and of the threshold type, i.e. the entire substance in which the density of the absorbed energy φ exceeds a certain threshold density φ_0 is removed. In this case the thickness of the layer of the substance removed is

$$h = \frac{1}{\alpha}\ln\left(\frac{\varphi}{\varphi_0}\right), \tag{41}$$

where α is the absorption coefficient for the radiation. This empirical formula reproduces qualitatively the behaviour $h = h(\varphi)$ in the vicinity of the ablation threshold and is therefore frequently used in the analysis of the experimental data (as a rule without justification).



Figure 23. Specimen prepared from a multilayer photoresist with the aid of a KrF laser.[120]

Owing to the large number of positive feedbacks, the laser-induced ablation is characterised by many instabilities and spontaneously generated structures (some of them have been observed experimentally in a number of investigations[115–119]). However, it is possible to select empirically conditions under which polymers can be treated effectively and phototemplates for submicron lithography may be obtained. An example of one such structure is presented in Fig. 23.

* * *

Within the framework of a short review, it is difficult to provide an exhaustive list of the technological applications of laser thermochemistry. The foregoing text merely illustrates certain aspects of the applied research. The list may be significantly expanded, for example by including studies in the field of laser thermolithography,[121] microtreatment of a surface in a liquid,[70,74] selective laser-induced extraction from liquids,[122] etc. However, we believe that even the present review is sufficient to demonstrate that laser thermochemistry[123] is a rapidly developing field, which is of great scientific interest and has numerous practical applications.

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