

The application of thermal waves in thermophysical investigation practice is well known [1]. Periodic heating methods permit the complex determination of the thermal properties [1] of a solid that is heated in a medium with harmonically measured parameters by measured space-time and amplitude-phase fluctuations of its temperature. Periodic fluctuations of the heat- and mass-transfer parameters are observed also in many technological processes with disperse media, for instance, in a fluidized bed [2].

Thermal waves and their analogs have recently been utilized in the analysis of catalytic processes and the finishing off of chemical reactors under artificially producible nonstationary conditions [3]. A periodic change in the input parameters permits raising the activity and selectivity of physicochemical processes in such reactors, resulting in growth of the productivity and improvement in the quality of the end product [3]. Questions of catalyst regeneration [4, 5] can here be solved technologically simply when the periodic excitation (ignition) of the main and regeneration combustion waves results in a substantial rise in the lifetime of the continuous operation of reactors.

In this connection, the regularities of solid-phase and heterogeneous ignition [6] of reacting substances under periodic heating in a gaseous oxidizer stream are investigated numerically in this paper. In the approximation of constant transfer coefficients a one-dimensional ignition model is examined when a radiation heat flux is additionally incident on the substance surface and evaporation of the volatile components occurs.

### 1. Formulation of the Problem

Let us consider the nonstationary heat and mass transfer and ignition of a condensed substance subjected to a radiation-convective heat flux when a  $\nu$ -th-order heterogeneous oxidation reaction [6] proceeds on the surface and evaporation (sublimation) of volatile (liquid or solid) components occurs according to the Hertz-Knudsen-Langmuir law [7, 8]. Thermal waves are produced in the solid body by harmonic measurement of the gas stream parameters (the temperature  $\Theta_e$  and the heat elimination coefficient  $Nu$ ):

$$\Pi_i(\tau) = \langle \Pi_i \rangle - \Pi_{mi} \cos(\Omega_i \tau - \varphi_{i0}), \Pi_1 = \Theta_e, \Pi_2 = Nu. \quad (1.1)$$

Here  $\langle \Pi \rangle$ ,  $\Pi_m$ ,  $\Omega$ ,  $\varphi_{i0}$  are the dimensionless mean value of the parameter, the amplitude, the cyclic frequency, and the initial phase of the vibrations;  $i = 1, 2$ .

Taking account of the factors listed, the one-dimensional boundary-value problem on ignition reduces to solving a system of energy and substance conservation equations that are written in dimensionless form as

$$\frac{\partial \Theta_s}{\partial \tau} = \frac{\partial^2 \Theta_s}{\partial \xi^2} + \Delta_s (1 - \eta_s)^n \exp \frac{\Theta_s}{1 + \beta \Theta_s}; \quad (1.2)$$

$$\frac{\partial \eta_s}{\partial \tau} = \gamma_s (1 - \eta_s)^n \exp \frac{\Theta_s}{1 + \beta \Theta_s} \quad (1.3)$$

with the initial and boundary conditions

$$\Theta_s|_{\tau=0} = \Theta_s|_{\xi=\infty} = \Theta_{s0}, \eta_s|_{\tau=0} = 0, \partial \Theta_s / \partial \xi|_{\xi=\infty} = 0; \quad (1.4)$$

$$-\frac{\partial \Theta_s}{\partial \xi} \Big|_{\xi=0} = q_{lw} \left[ 1 - \left( \frac{1 + \beta \Theta_w}{1 + \beta \Theta_{st}} \right)^4 \right] + [\Theta_e(\tau) \Theta_w] [Nu(\tau) - \Delta Nu] -$$

$$-\frac{1}{\gamma_{ev}} \frac{\partial \eta_{evw}}{\partial \tau} + \frac{\Delta_w}{(1 + \beta \Theta_w)^\nu} \exp \frac{b_w \Theta_w}{1 + \beta \Theta_w} = Q_w(\Theta_w, \tau); \quad (1.5)$$

$$\frac{\partial \eta_{evw}}{\partial \tau} = \gamma_{ev} (1 - \bar{p}_e) \frac{\Delta_{ev} (1 - \eta_{evw})}{(1 + \beta \Theta_w)^{0.5}} \exp \frac{b_{ev} \Theta_w}{1 + \beta \Theta_w}, \quad (1.6)$$

where the dimensionless quantities  $\xi = y/y_*$ ,  $\tau = t/t_*$ ,  $\Theta = (T - T_*)E/RT_*^2$  are the coordinate, time and temperature,  $y_* = (\lambda_s RT_*^2)^{0.5} (\rho_s Q k_0 E)^{-0.5} \exp(E/2RT_*)$ ,  $t_* = (c_{ps} \rho_s RT_*^2) (\rho_s Q k_0 E)^{-1} \exp(E/RT_*)$ ,  $q_* = \lambda_s RT_*^2 / y_* E$  are the length, time and heat flux scales,  $\Delta_s = 1$  is a parameter characterizing the intensity of the solid-phase reaction,  $\Delta_w = y_* E q k_{0w} (\rho_* C_e)^\nu (\lambda_s RT_*^2)^{-1} \exp(-E_w/RT_*)$ ,  $\Delta_{ev} = (A p_0 r m)_{ev} (y_* \rho_s Q k_0)^{-1} (2\pi RT_*/M_{ev})^{-0.5} \exp(E - L_{ev})/RT_*$  are parameters characterizing the intensity of the heterogeneous reaction and the evaporation process,  $Nu = \alpha y_*/\lambda_s$ ,  $q_{lw} = \sigma A_{ef} T_{st}^4 / q_*$  is the coefficient of heat elimination and the radiation heat flux,  $b_{ev} = L_{ev}/E$ ,  $b_w = E_w/E$  are activation energy ratios,  $\gamma = c_{ps} \rho_s RT_*^2 / (\rho Q k_0 E)$ ,  $\beta = RT_*/E$  are parameters,  $Q_w(\Theta_w, \tau)$  is the total heat flux,  $\Omega = 2\pi f t_*$  is the frequency,  $\bar{p}_e = p_e C_{evw} / p_{ev}^i M_{ev} \sum_l C_l / M_l$  is the reduced partial vapor pressure,  $l = e, ev$ ; the dimensional quantities are  $y, t, T$  the transverse coordinate, time and temperature,  $\lambda, c_p, \rho$  the heat conduction coefficient, isobaric specific heat and density,  $E, Q, k_0, n$  the activation energy, thermal effect, preexponential, and order of the solid-phase reaction,  $E_w, q, k_{0w}, \nu$  activation energy, thermal effect, preexponential and order of the heterogeneous reaction,  $L_{ev}, r_{ev}, A_{ev} p_{ev}, M_{ev}$  are the activation energy, heat, preexponential, and molecular weight of the evaporating component,  $\eta = (m_i - m)/(m_i - m_c)$  is the degree of transformation of the solid-phase component,  $m$  is the mass,  $A_{ef}$  is the effective function of the radiation parameters,  $R$  is the universal gas constant,  $\sigma$  is the Stefan-Boltzmann constant,  $\alpha$  is the heat elimination coefficient,  $f$  is the frequency of vibration,  $p$  is the pressure, and  $C$  is the mass concentration.

To close the system of equations (1.2) and (1.3) with the boundary and initial conditions (1.4)-(1.6) the equation of state must be written for the gas and vaporous components

$$\rho = \frac{pM}{RT}, \quad \frac{1}{M_l} = \sum_l \frac{C_l}{M_l}. \quad (1.7)$$

The influence of injection of the evaporating component on the heat elimination coefficient is taken into account by means of the formula

$$\Delta Nu = W_{ev} \left[ (1 - \eta_{evw}) \exp \frac{b_{ev} \Theta_w}{1 + \beta \Theta_w} \right] \frac{1 - \bar{p}_e}{(1 + \beta \Theta_w)^{0.5}}, \quad (1.8)$$

where  $W_{ev}$  is a parameter characterizing the properties of the main and injected flows, the configuration, and the geometric dimensions of the streamlined surface.

The saturated vapor pressure is described by the equation

$$p_{ev}^i = p_{oev} \exp(-L_{ev}/RT_*). \quad (1.9)$$

Utilization of a constant heat elimination coefficient in the boundary condition (1.5) for a harmonically varying temperature assumes quasistationarity of the processes in the gas phase.† Consequently, only the range of low-frequency fluctuations of the gas flow parameters is considered in this paper, when the half-period of one fluctuation considerably exceeds the times of thermal and dynamic relaxation of processes in the boundary layer. Thus if the heat and mass transfer is investigated in the neighborhood of the frontal stagnation point of a hemispherical solid body [9, 10], then the quasistationarity condition for the gas phase will be

$$\frac{1}{2f} \gg \frac{1}{\beta_x} = \frac{2r_w}{3u_e}, \quad (1.10)$$

where  $\beta_x$  is a gasdynamic parameter [9],  $r_w$  is the body radius, and  $u_e$  is the gas velocity on the outer boundary-layer boundary.

Let us estimate the frequency band for the conditions of the experiment described in [10]. For  $\beta_x \gg 300 \text{ sec}^{-1}$  the frequency of fluctuation of the temperature, say, should be  $f_1 \ll 150 \text{ Hz}$ . For values  $t_* \sim 1, 10^{-1}, 10^{-2} \text{ sec}$  of the characteristic times of the problem,

†Analogous assumptions and estimates are valid for a constant temperature  $\Theta_e$  for a harmonically varying heat elimination coefficient  $Nu$ .

the band of variation of the cyclic frequency  $\Omega_1$  should not exceed 942, 94.2, and 9.42, respectively.

It was also assumed in the formulation of the problem (1.2)-(1.9) that there are no homogeneous chemical reactions in the boundary layer. To satisfy this condition it is necessary that the Damkeller number  $Da_v = (\beta_x t_{vx})^{-1} \ll 1$  [8] ( $t_{vx}$  is the characteristic time of the gas-phase reaction). Satisfaction of this condition for performance of a physicochemical experiment [10] is achieved because of magnification of the parameter  $\beta_x$ . If condition (1.10) is not satisfied while  $Da_v \geq 1$ , then the system (1.2) and (1.3) must be solved jointly with the boundary layer equations [7] and boundary conditions of the fourth kind, i.e., in an adjoint formulation [7].

## 2. Reduction of the Problem to a System of Integral Equations

Since normal ignition modes with radiation-convective heat and mass transfer are characterized by maximum heat liberation on the surface, we carry out an approximate analysis of the processes being observed in the time dependences of the temperature  $\Theta_w$  and concentrations of the components ( $\eta_{evw}, \eta_{sw}$ ) on the reacting body surface. In particular, the specific feature of the ignition process is a jumplike change in the mentioned variables in time, which indeed the very fact of ignition characterizes [4, 6, 10].

Let us reduce the system (1.2) and (1.3) with the uniqueness conditions (1.4)-(1.6) and Eqs. (1.7)-(1.9) to a system of nonlinear integral equations by using the Laplace transformation [11]. The improper integral in the dimensionless coordinate  $\xi$  can be evaluated by an asymptotic method [12] with the imposition of strongly damped temperature and concentration fluctuations in the space [7]. If envelopes of the spatial distributions  $\Theta_s$  and  $\eta_s$  of  $\xi$  are considered as upper and lower approximations for evaluation of the improper integral, then by limiting ourselves to the first terms of the expansions  $\Theta_s$  and  $\eta_s$  of  $\xi$ , we arrive at a system of Volterra-type nonlinear integral equations

$$\Theta_w(\tau) = \Theta_{si} + \int_0^\tau \frac{Q_w(\Theta_w, \tau')}{\sqrt{\pi(\tau-\tau')}} d\tau' + \int_0^\tau \Delta_s (1 - \eta_{sw})^n \exp \frac{\Theta_w}{1 + \beta \Theta_w} d\tau'; \quad (2.1)$$

$$\eta_{evw}(\tau) = \int_0^\tau \frac{\Delta_{ev} \gamma_{ev} (1 - \eta_{evw}) (1 - \bar{p}_e)}{\sqrt{\pi(\tau-\tau') (1 + \beta \Theta_w)}} \exp \frac{\Theta_w}{1 + \beta \Theta_w} d\tau' \quad (2.2)$$

and the equation for the solid-phase component concentration

$$\eta_{sw}(\tau) = \int_0^\tau \gamma_s (1 - \eta_{sw})^n \exp \frac{\Theta_w}{1 + \beta \Theta_w} d\tau'. \quad (2.3)$$

An algorithm for calculations in the form of quadrature formulas with a mean-weighted source  $\Theta_w^*$  and with the best estimate in the class of R-functions of remainder terms [13]

$$\Theta_m^{(k)} = \Theta_{si} + \frac{2}{\sqrt{\pi}} \sum_{j=1}^m \{ Q_{w(j-1,j)}^{*(k-1)} [ \sqrt{\tau_m - \tau_{j-1}} - \sqrt{\tau_m - \tau_j} ] \} \quad (2.4)$$

is used to solve (2.1)-(2.3) ( $k$  is the number of iterations at the  $m$ -th time point).

Such an algorithm permits finding  $\Theta_m^{(k)}$  as the arithmetic mean of the corresponding upper  $\bar{\Theta}_m$  and lower  $\underline{\Theta}_m$  approximations [13] at each point whereupon  $\Theta_m^{(k)}$  is known to be closer to the exact value  $\Theta_m^*$ , than either  $\bar{\Theta}_m$  or  $\underline{\Theta}_m$  [14]. Because of the more rational selection of the initial approximation in each iteration cycle, a narrower interval  $\underline{\Theta}_m < \underline{\Theta}_m \leq \Theta_m^{av} \leq \bar{\Theta}_m < \bar{\Theta}_m$  of the two-sided approximations is used, which reduces the number of iterations for the same accuracy  $\epsilon_m$ . Trial computations showed good convergence of the iterations (2.4); the accuracy is here magnified two times as compared with [14]. The divergence from the analytic solution [7] does not exceed 1% in the inert heating stage.

## 3. Results of Parametric Computations

To analyze the influence of the parameters  $\langle \Pi_i \rangle, \Pi_{mi}, \Omega_i, \varphi_{ii}$  on the heat and mass transfer and ignition characteristics of reacting substances, a series of computations was performed for the following initial data:  $\Theta_{si} = -11$ ,  $\langle \Theta_e \rangle = 15.7$ ,  $\beta = 0.049$ ,  $q_{lw} = 3.3$ ,  $(Nu) = 0.1 - 0.3$ ,  $\gamma_s = 0.01$ ,  $n = 1$ ,  $\Delta_w = 0.7$ ,  $b_w = 0.518$ ,  $\nu = 0.33$ ,  $\Delta_{ev} = 10$ ,  $b_{ev} = 0.4$ ,  $\gamma_{ev} = 20$ ,  $W_{ev} = 30.0$ ,  $\bar{p}_e \simeq 0$ .

Presented in Fig. 1 are time dependences  $\Theta_w(\tau)$  and  $\eta_{iW}(\tau)$  for gas temperature fluctuations in a flow for  $\Omega_1 = 5.5$ ,  $\Pi_{m1} = -10$ , and  $\varphi_{ii} = 0$ . A solid body fluctuating heating mode is observed (curve 2) and upon achievement of the critical ignition conditions [6, 10] the temperature  $\Theta_w$  grows by a jump with the lapse of time  $\tau$  because of heat liberation from the solid-phase exothermal reaction. As the ignition time  $\tau_i$  we take the time to reach the temperature  $\Theta_w \geq \langle \Theta_e \rangle$  on the section of the abrupt rise  $\Theta_w(\tau)$ . Connection of the heat liberation from the heterogeneous oxidation reaction on the body surface does not change the nature of the behavior of  $\Theta_w(\tau)$  and  $\eta_{iW}(\tau)$  (lines 1 and 1a); however,  $\tau_i$  diminishes. The qualitative change in  $\Theta_w(\tau)$  in the initial heating period occurs in the presence of evaporation on the surface (curves 3, 3a, and 3b). Heat expenditure in evaporation whose duration is  $\tau \sim 1.6$  (line 3b) results in disappearance of the first heating wave on curve 3 as compared with 1. This slows down the heating as a whole and magnifies  $\tau_i$ .

Heat liberation from the solid-phase reaction resulting in ignition starts on the "crest" of the surface temperature wave in the domain of maximal values of the velocity  $\partial\Theta_w/\partial\tau$ . Here the maximum in the heat flux is also realized on the surface  $\xi = 0$ , as follows from an examination of the spatial distributions  $\Theta_s(\xi, \tau_{ev})$  during inert heating (line 2b). Taken as the inert heating time  $\tau_{ev}$  was the time to reach  $\Theta_w = 0$ . The presence of two maxima on the inert heating curve at the time  $\tau = \tau_{ev}$  [6] permits utilization of the method of splitting into physical processes [15] for the construction of the approximate analytic solutions.

Represented in Fig. 2 are dependences of the ignition time  $\tau_i$  on the fluctuation frequency  $\Omega_i$  for  $\varphi_{ii} = 0$ . Let us examine several cases of practical importance.

If the reacting body is a condensed substance with one effective solid-phase reaction ( $\Delta_S = 1$ ) while the heterogeneous reaction and the evaporation process are missing ( $\Delta_W = 0$ ,  $\Delta_{ev} = 0$ ), then the dependence  $\tau_i(\Omega_i)$  has a strongly damped vibrational nature (curve 2) for  $\Pi_{m1} = -10$  and  $\Pi_{m2} = 0$ . The limit value of the frequency, when the temperature fluctuations in the outer flow do not influence the ignition process, is  $\Omega_1^* \approx 5.5-6$ .

An analogous dependence is also observed for the heterogeneous ignition of pure polymer materials ( $\Delta_S = 0$ ,  $\gamma_S = 0$ ,  $\Delta_{ev} = 0$ ,  $\Delta_W = 0.7$ ) [10] and the value of  $\Omega_1^*$  (line 1) remains the same. The nature of the dependence  $\tau_i(\Omega_i)$  and the variation of the parameters  $\Delta_W$  and  $\Pi_{m1}$  do not change. Thus an increase in  $\Delta_W$  to 2.2 and in  $\Pi_{m1}$  to  $-5$  results only in diminution of  $\tau_i$  (curves 3 and 4).

A 1.5 times increase in  $\Omega_1^*$  occurs only under conditions of the combined progress of the solid-phase and heterogeneous reactions for  $\Pi_{m1} = -10$  (line 5). If the heating of the reacting body is realized here in a gas flow, when not only the temperature but also the heat elimination coefficient change according to the law (1.1), then during fluctuations in one phase with positive amplitudes ( $\Pi_{m1} = +10$ ,  $\Pi_{m2} = +0.07$ ) we have a diminution in  $\tau_i$  with a simultaneous increase in  $\Omega_1^*$  to 12 (curve 6). If they fluctuate out-of-phase ( $\Pi_{m1} = -10$ ,  $\Pi_{m2} = +0.07$ ), then this results in a reduction of  $\Omega_1^*$  to  $\sim 9$ . However, the dependence  $\tau_i(\Omega_i)$  is aperiodic in nature (curve 7).

It is interesting to trace the nature of the change in  $\tau_i(\Pi_{mi})$  for  $\varphi_{ii} = 0$ ,  $\Omega_i = 1.1, 1.4, 5.5, 9.0$  and  $\langle Nu \rangle = 0.1-0.3$ . The values of  $\Omega_i$  are taken from the appropriate dependences  $\tau_i(\Omega_i)$  at minimax points:  $\Omega_2 = 1.4$  for  $\Pi_{m1} = 0$ ,  $\Pi_{m2} = 0.07$ ;  $\Omega_1 = 1.1$  for  $\Pi_{m1} = -10$ ,  $\Pi_{m2} = 0$  (Fig. 2), and the frequencies  $\Omega_i = 5.5$  and  $9$  are taken as limits from curves 1-4 and 5.

If the dependence  $\tau_i(\Pi_{m1})$  represented in Fig. 3 is determined as a wave fragment as the temperature amplitude changes  $\Pi_{m1} \in [-20 \dots +10]$ , then as the heat elimination coefficient  $\langle Nu \rangle$  increases from 0.1 to 0.3, it changes its orientation to the opposite (lines 1-4). For  $\Omega_i \geq \Omega_i^* \approx 9$  the influence of  $\Pi_{m1}$  on  $\tau_i$  is insignificant (curve 5).

The dependences of  $\tau_i$  on the amplitude  $\Pi_{m2}$  of the heat elimination coefficient fluctuation presented in Fig. 4 are analogous in nature. Here the range of variation is  $\Pi_{m2} \in [-0.2; 0.4]$  and  $\langle Nu \rangle \in [0.1; 0.3]$ . For  $\Omega_2 = 1.4$  as  $\langle Nu \rangle$  increases the wave "crest" shifts downward to the right and for  $\langle Nu \rangle = 0.3$  the dependence  $\tau_i(\Pi_{m2})$  changes its position to the opposite (curves 1-5). For  $\Omega_i \geq 9$   $\tau_i$  diminishes only for positive  $\Pi_{m2}$  (curve 6); however as  $\langle Nu \rangle$  grows, the dependence  $\tau_i(\Pi_{m2})$  becomes nonlinear in the whole range of  $\Pi_{m2}$  (curve 7).

Let us examine the influence of the initial vibration phase  $\varphi_{ii}$  on  $\tau_i$ ; we take the values of  $\Omega_i$  at the minimx points  $\Omega_1 = 1.1$ ,  $\Omega_2 = 1.4$  and  $\Omega_i^* = 5.5$  and  $9$ . The results of computations are presented in Fig. 5 for  $\langle Nu \rangle = 0.1$  and  $0.3$  (upper and lower series of curves, respectively).

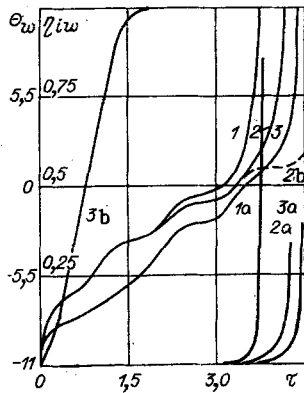


Fig. 1

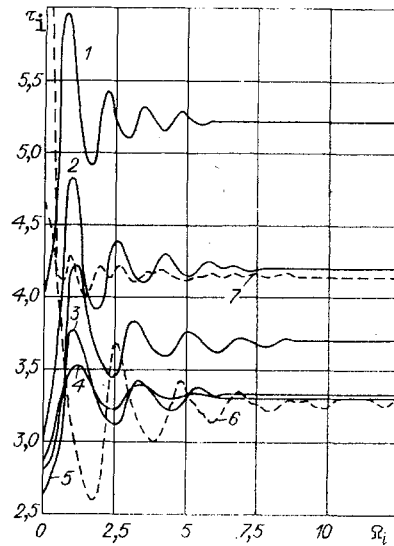


Fig. 2

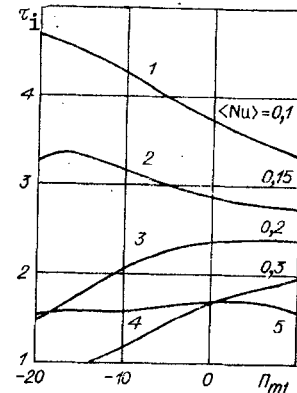


Fig. 3

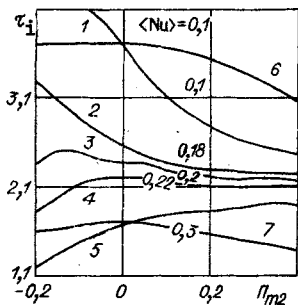


Fig. 4

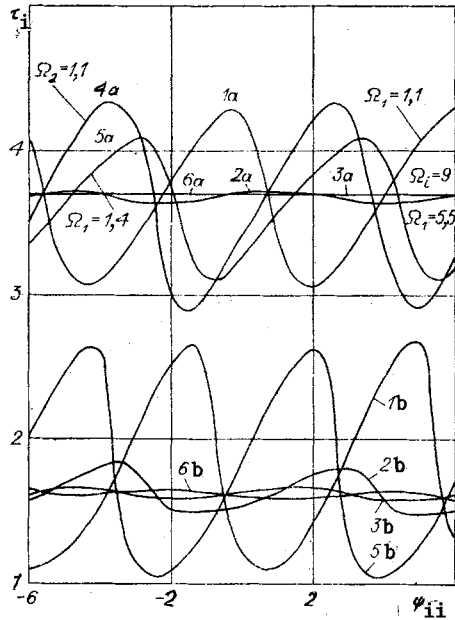


Fig. 5

As should have been expected, the dependences  $\tau_i(\varphi_{ii})$  are quite definitely periodic in nature, where as  $\Omega_i$  increases the vibration amplitude  $\tau_i$  diminishes and is practically zero for  $\Omega_i \geq 9$ . This is observed for both a periodic change in the gas temperature with  $\Pi_{m1} = -10$  (curves 1a-3a) and as the heat elimination coefficient changes with  $\Pi_{m2} = 0.07$  (curves 4a-6a). As  $\langle Nu \rangle$  increases the nature of the dependence  $\tau_i(\Pi_{m1}, \Pi_{m2})$  does not change for temperature fluctuations (lines 1b-3b) and for the heat elimination coefficient (lines 5b-6b).

In conclusion, let us examine the dependence of the degree of transformation of the solid-phase reaction  $\eta_{si}$  determined at the time of ignition  $\tau_i$  on the amplitude of the temperature fluctuations  $\Pi_{m1}$  for different values of  $\langle Nu \rangle$  and  $\Omega_i$  at  $\varphi_{ii} = 0$ . Figure 6 illustrates the nature of the behavior of  $\eta_{si}(\Pi_{m1})$  for  $\langle Nu \rangle = 0.1$  and  $\Omega_i^* = 5.5$ . In the range  $\Pi_{m1} \in [-15; +10]$  the dependence  $\eta_{si}(\Pi_{m1})$  has the form of a parabola (lines 1 and 2), whose branches lie in the domain of high values of  $\eta_{si}$ , i.e., we have degenerate ignition modes [14, 16]. As  $|\Pi_{m1}|$  increases further, the burn-up of the solid-phase component  $\eta_{si}$  diminishes by a jump to the minimal (curves 1a and 2a) and the ignition modes become normal [14].

For limit values  $\Omega_i^* = 9$  (see Fig. 2, line 5), the nature of the dependence  $\eta_{si}(\Pi_{m1})$  does not change; however, for  $\langle Nu \rangle = 0.3$  the domain of the minimum of curve 3 shifts upward by a jump (line 3b). The right branch seems to degenerate and for  $\Pi_{m1} > 10$  the values of  $\eta_{si}$  are

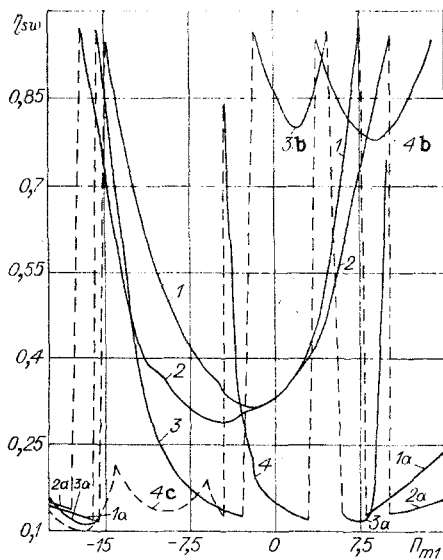


Fig. 6

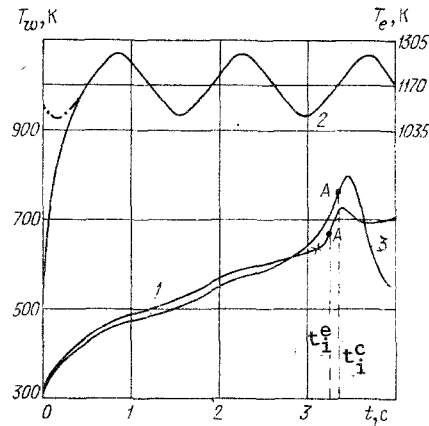


Fig. 7

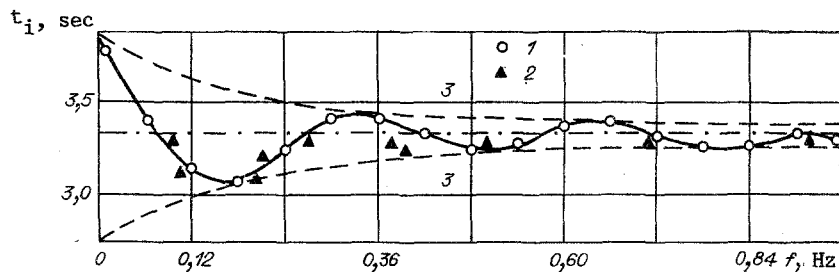


Fig. 8

irregular in nature in the form of a strongly blurred "noise" spectrum. The dependence  $\eta_{si}(\Pi_{m1})$  is analogous in nature for  $\Omega_1 = 1.1$  and  $\langle Nu \rangle = 0.2$ , corresponding to curve 3 in Fig. 3. In this case the dependence  $\eta_{si}(\Pi_{m1})$  shifts to the right (curve 4 in Fig. 6), and the "noise" spectrum of the values  $\eta_{si}$  is observed for  $\Pi_{m1} < -5$ . The lower envelope of the "noise" spectrum in Fig. 6 is denoted by line 4c. The domain of degenerate ignition modes in the form of the truncated parabola 4b lies in the range  $4 < \Pi_{m1} < 19$ .

The results obtained can be utilized for a qualitative analysis of the ignition conditions during excitation of the main and regeneration combustion waves in chemical reactors of periodic action as well as during estimation of the applicability of the thermal theory of ignition [6, 10, 16].

#### 4. Comparison with Experiment

As an example illustrating the possibilities of the proposed computation methodology, we consider the heterogeneous ignition of polymethyl methacrylate (PMMA) in a heated air flow [10, 17]. This polymer has been studied well and there is complete information on its thermo-physical [18] and kinetic parameters for heterogeneous [10, 17] and solid-phase reactions [18]. From the results of a numerical computation and comparison with experiment [18] the  $k_0$  is corrected and equals  $2.34 \cdot 10^7 \text{ sec}^{-1}$ . Values of the remaining parameters are  $E_w = 57 \text{ kJ/mole}$ ,  $q = 3.6 \cdot 10^6 \text{ J/kg}$ ,  $\nu = 0.33$ ,  $k_{ow} = 2 \cdot 10^3 \text{ kg/(m}^2 \cdot \text{sec)} \cdot \text{kg/m}^3$ ,  $E = 110 \text{ kJ/mole}$ ,  $Q = -1.592 \cdot 10^6 \text{ J/kg}$ ,  $n = 1$ ,  $\lambda_s = 0.176 \text{ W/(m} \cdot \text{K)}$ ,  $c_{ps} = 1.605 \text{ kJ/(kg} \cdot \text{K)}$ ,  $\rho_s = 1200 \text{ kg/m}^3$ .

Experiments were performed on the installation in [10, 17]; the harmonic variation of the gas flow parameters according to the law (1.1) was produced by the reciprocating motion of the specimen under investigation along the axis of a quartz tube with electrical heating. Since the gas temperature and the heat elimination coefficient fluctuated in one phase, it could also be considered that the corresponding specimen heating mode is realized because of the resultant action of just one parameter, the gas temperature  $T_e$ , say.

Displayed in Fig. 7 is the periodically varying  $T_e(t)$  (curve 2) measured by a Chromel-Alumel thermocouple. Extrapolation of the curve  $T_e(t)$  to initial time is denoted by the

dash-dots. Presented here is a synchronized recording of the surface temperature  $T_w(t)$  at the frontal stagnation point of a hemispherical PMMA specimen [10, 17] of  $10^{-3}$  m diameter (curve 1). Values of the remaining parameters of the experiment represented are:  $\langle \beta_x \rangle = 345 \text{ sec}^{-1}$ ,  $C_e = 0.23$ ,  $f = 0.714 \text{ Hz}$ ,  $\phi_{ij} = -0.67$ ,  $p_e = 10^5 \text{ N/m}^2$ ,  $A_{ef} = 0.21$ ,  $T_{st} = 1300 \text{ K}$ ,  $M_e = 29 \text{ kg/(k mole)}$ ,  $\rho_e = 0.3 \text{ kg/m}^3$ ,  $c_{pe} = 1.17 \text{ kJ/kg}$ ,  $\beta_{xm} = 21.4 \text{ sec}^{-1}$ ,  $\mu_e \rho_e = 13.83 \cdot 10^{-6} \text{ kg}^2/(\text{m}^4 \cdot \text{sec})$ .

Since the behavior of the curves  $T_w(t)$  in Fig. 7 at the time of ignition differs from the corresponding curves in Fig. 1, then the inflection point A is taken as the ignition criterion. Numerical computations show that the divergence of  $t_i$  determined by this criterion and the criterion  $\Theta_w \geq \langle \Theta_e \rangle$  does not exceed 1-3%. The characteristic temperature  $T_*$  is selected at the point of termination of the inert heating [17] and equals 640 K (denoted by a cross on curve 1).

Computations showed (curve 3) that the discrepancy from experiment does not exceed 1% in the inert heating stage and increases to 25% during progress of the chemical reactions.

The discrepancy between the experimental  $t_i^e$  and computed  $t_i^c$  ignition times is here no worse than 2-3%.

Presented in Fig. 8 are computed and experimental (points 1 and 2) dependences of the ignition time  $t_i$  on the vibration frequency  $f$ . The qualitative agreement between theory and experiment as well as with the results of parametric computations in Fig. 2 raises no doubts. The quantitative agreement is satisfactory, where the experimental points are in the domain between the envelopes 3 and many of them fall on the curve.

Vibrational modes of heat and mass transfer in the catalyst grain [19, 20] can be analyzed numerically by using the methodology proposed; however, the lack of reliable experimental data and sets of kinetic parameters of progressing reactions does not permit this to be done yet.

Therefore, it is established numerically and experimentally that the amplitude-phase characteristics of low-frequency vibrations have substantial influence on the regularities of the ignition of reacting substances during periodic heating.

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#### ON POSSIBLE CAUSES OF BRITTLE FRACTURE

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The process of constructing high-pressure vessels, protective shells of chemical and nuclear reactors, ship hulls, tankers, as well as other large-scale objects includes the stage of material selection as one of the stages.

Until now the problem of brittle fracture has been solved "... by taking traditional empirical measures..." [1], "by trial and error..." [2]. Material selection includes testing of specimens of full-scale thickness by using brittle fracture mechanics methods (FM) and a transitional temperature [3, 4]. It is assumed that if the specimens (including even welds) do not fracture brittlely, brittle fracture of the full-scale object should also not be expected. Such a method of eliminating brittle fracture is most reliable because of the lack of a single brittle fracture criterion in FM [1], and as a rule, the impossibility of direct testing of full-scale objects up to fracture. Because of the indisputable successes of FM the number of brittle fractures of objects computed in conformity with existing strength norms, although sharply reduced, have not been eliminated completely. Data have appeared at this time that raise doubts about the reliability of the method of handling brittle fractures by testing materials specimens of full-scale thickness. The crux of the doubts reduce to two questions. 1. How much is the transfer of test results of standard specimens of full-scale thickness of a carrying metal to real structures representative and full-founded? 2. To what degree are the critical values of the stress intensity factors found in experiments on specimens by FM methods under plane strain  $K_{Ic}$  and the specific energy of material separation per unit surface  $2\gamma$  in correspondence with their values for the self-similar stationary mode of brittle separation of a material?\*

The answer to the first question is closely connected to the possibility of the appearance of geometric scale effects (SE) of an energetic nature during fracture [7, 8] independently of whether the object defects in addition to their dimensions are similar as the FM requires [9, 10] and consists of seeking the necessary conditions for which brittle fracture is possible (or impossible).

Necessary conditions for the nonfracture of pipelines are found in [11] by FM methods using I-integrals under certain simplifying assumptions and the solution of an additional problem. Analysis of this solution in [12] showed that the fundamental meaning of the solution found in [11] is the existence of SE of energetic nature, that follow directly from the

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\*Precisely in such a fracture mode are plane strain conditions satisfied strictly and the value  $2\gamma$  reaches its minimum and is independent of the specimen thickness [5, 6].