Modeling of Combustion of Energetic Materials with Chemically Induced Mechanical Processes

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This article suggests heat and mass transfer equations for a reacting solid, with due regard for its deformation and destruction. The equations are derived with account taken for the relationships of nonequilibrium thermodynamics. Deformations and stresses in a system result from a chemical reaction, which is taken into account through a change in the specific volume of the substance. The applicability of the suggested approach is illustrated by particular simple ignition models for high energetic materials. The models reveal new qualitative mechanisms: the dependence of ignition characteristics on the mechanical properties of materials, the influence of the manner of sample fixing on reaction initiation, and the mechanisms of damage accumulation in the reaction zone. It is shown that the solid-phase reaction zone structure is determined by the reciprocal influence of thermal and deformation processes as well as by chemical transformation.

Nomenclature

A, B = differential operators
A_i = generalized forces
a_i = generalized coordinates
c_ε = specific heat under constant deformation
D_k = diffusion coefficient of component k
E = Young's modulus
E_0 = energy of activation
e = generalized deformation different from zero beyond elasticity limit
e_{ij} = strain tensor deviator
$e_{\xi\xi}$ = deformations
F = free energy
G = shear modulus
g = $\Delta\alpha_{BA}c_\varepsilon\rho_0/\alpha_T Q_0$
h = scalar damage potential
I_1, I_2, I_3 = strain tensor invariants
J = heat flux
J_k = mass flow of component k
K = bulk modulus
k = Boltzmann constant
k_d = rate constant of crack growth
N_k = concentration of component k
p = average (hydrostatic) pressure
Q_c = dimensionless external heat flux
Q_0 = heat of chemical reaction
q_e = external heat flux
R = universal gas constant
r = damage extent
S = entropy
$S_h, S_{\xi\xi}$ = stresses, $S_{11}, S_h = S_{kk}/3$
S_{ha} = $S_h(\tau_a)$
T = temperature
t = time
t_r = relaxation time of heat flux
U = specific internal energy
u_i = displacement of the points of medium, $i = 1, 2, 3; u_1 \equiv u$
V = volume of system
v = specific volume of reacting mixture
v_d = specific volume of damage
W = power density of internal heat sources and sinks
X_i = vector component of external force
x_i = spatial coordinates, $x_1 \equiv x$
y = substance conversion extent
Z_0 = pre-exponential factor
$\alpha_T, \alpha_{ck}, \alpha_S$ = coefficients of thermal, concentration, and structural expansion, respectively
β = RT_*/E_0
γ = $c_\varepsilon\rho_0 RT_*^2/E_0 Q_0$
δ = coherence coefficient for deformation and temperature
δ_{ij} = Kronecker symbol
ε_{ij} = strain tensor component
η = shear coefficient of viscosity
θ = dimensionless temperature
λ, μ = Lame coefficients
λ_T = thermal conductivity
μ_k = chemical potential of component k
ν = Poisson factor
ξ = dimensionless spatial coordinate
ρ_0 = density of medium
σ_{ij} = stress tensor component $\sigma_{11} = \sigma_{xx}$, $\sigma_{22} = \sigma_{yy}, \sigma_{33} = \sigma_{zz}$
τ = dimensionless time
τ_{ij} = stress tensor deviator
χ = $\alpha_d v_d c_\varepsilon\rho_0/(\alpha_T v_0 Q_0)$
χ_{lm} = damage potential
ψ_k = sum of source and sink channels for component k
ω_{lm} = damage tensor

Subscripts
A = reactant
a = adiabatic
B = product
c = concentration
d = damage

e = external
i, j, k, l, m = indexes
s = structural
T = thermal
0   = initial
*   = reference

Superscripts
ch   = chemical
0   = nondeformed

Introduction

A GREAT deal of the data contained in the literature points to the important role of mechanical processes during the combustion of propellants. In particular, instabilities of motor operation are attributed to the possibility of convective combustion in propellant cracks as well as to local failure of charge caused by both external and internal loadings.[1-3] Propellant failure during combustion and the ensuing change in burning rate are associated with structural macrocharacteristics of propellant[1,4] (porosity, grain size, etc.), and changes in mechanical properties or with the effect of thermal stresses resulting from both external heating and high-temperature gradients in the combustion zone.[5-7] Some theoretical approaches relate the propellant burning rate to such external loadings as given tension and external static loading.[4,5,8] At the same time, it is known that stresses and deformations can be caused by the solid-phase reaction, per se, independently of external factors and, in turn, can affect the kinetic behavior of this reaction.[9-15] An attempt has been made[16] to relate the characteristics of the stationary wave front in a solid-phase reaction to the conditions of material failure in the front. A theoretical model has been developed[17] suggesting a thermomechanical type of stationary front instability, which is associated with the reaction rate sensitivity to stresses and deformations. In this work, we propose a generalized approach to the macrokinetic modeling of solid-phase transformations, which takes into account different types of stresses and deformations resulting from changes in temperature and concentration of components as well as from propellant destruction in the reaction zone. Since the reaction zone in highly energetic materials is formed during ignition, and the reaction zone structure predetermines to a large extent the character of the process, investigation of the ignition stage is of interest from the viewpoint of the potentialities of the proposed approach.

Derivation of Basic Equations

Thermodynamic Relationships

The general equations describing coherent processes (temperature stresses,[18] diffusion in stress field,[19,20] material failure including energy dissipation,[21,22] electromechanical phenomena,[23] etc.), are as a rule derived using the methods of nonequilibrium thermodynamics. The best known thermodynamic theories have been reviewed by Petrov and Brankov.[24] Similar techniques are employed in deriving the laws of conservation in the models of reaction media. Chemicomechanical effects are described by Eringen and Ingram,[25] who modeled the chemical reaction zone by the disruption surface wherein substance properties change. Models of reacting solid mixtures have been described,[26,27] and by Dunwoody and Muller.[28] Many works have been concerned with modeling martensite transformations accompanied by structural changes and deformations.[29-31] Reaction diffusion in solid media has also received a considerable amount of study.[19,20,32]

In this work, we restrict our consideration to the case of the isotropic medium without introducing of special internal variables[33-35] for the continua, i.e., we deal with so-called elementary media. It is assumed that all types of deformations and stresses (temperature, concentration, and structural) that accompany chemical reactions in the solid in the first approximation additively change the relative specific volume of the solid

$$\frac{v - v_0}{v_0} = 3 \left[\alpha_T(T - T_0) + \sum_{(k)} \alpha_{ck}(N_k - N_{k0}) \right.$$
$$\left. + \alpha_s(v_d - v_{d0}) \right] \tag{1}$$

The coefficients of linear thermal α_T, concentration α_c, and structural expansion α_s are determined as follows:

$$\alpha_T = \frac{1}{3} \left(\frac{\partial v}{\partial T} \right) v_0^{-1}, \qquad \alpha_{ck} = \frac{1}{3} \left(\frac{\partial v}{\partial N_k} \right) v_0^{-1}$$
$$\alpha_s = \frac{1}{3} \left(\frac{\partial v}{v_d} \right) v_0^{-1} \tag{2}$$

where partial derivatives are taken, with the other parameters constant. Now, to determine the effect of changes in specific volume, incorporated in Eq. (1), on the temperature field and the diffusion of components, we write the law of conservation of energy for a system with a variable number of particles[36] as

$$dU = T \, ds - \sum_{(i)} A_i a_i + \sum_{(k)} \mu_k \, dN_k \tag{3}$$

In a deformed system, the elementary stresses σ_{ij} (determining pressure changes in every elementary volume) act as generalized forces, with the elementary deformations acting as generalized coordinates. Thus,

$$p \, dV = -\sigma_{ij} \, d\varepsilon_{ij} \tag{4}$$

Here, $dV = (1/v_0) \, dv$ refers to the relative change in specific volume due to all processes. By analogy, we introduce one more type of generalized coordinates, the tensor of medium damage ω_{lm} and the corresponding potential χ_{lm}. Examples of the tensor description of damage can be found in Refs. 21, 22, 37, and 38. According to Eq. (1), the damage of a medium can be described through the parameter $r = v_d/v_{d0}$, which yields the tensor ω_{lm} with the components $\omega_{lm} = r$ for $l = m$, $\omega_{lm} = 0$ for $l \neq m$, and $\omega_{lm} = 0$ for $l \neq m$. The corresponding potential is denoted by the letter h.

Remember now that the main thermodynamic potential of a chemically reacting system is the free energy[36] $F = U - TS$. Its total differential following from Eq. (3) and the definition of F is

$$dF = -S \, dT + \sum_{(k)} \mu_k \, dN_k + \sum_{(i,j)} \sigma_{ij} \, d\varepsilon_{ij} + \sum_{(l,m)} \chi_{lm} \, d\omega_{lm} \tag{5}$$

Hence,

$$S = -\left(\frac{\partial F}{\partial T} \right)_{N_k, \varepsilon_{ij}, \omega_{lm}}$$

$$\sigma_{ij} = \left(\frac{\partial F}{\partial \varepsilon_{ij}} \right)_{N_k, T, \omega_{lm}}$$

$$\mu_k = \left(\frac{\partial F}{\partial N_k} \right)_{T, \varepsilon_{ij}, N_{n,n \neq k}, \omega_{ij}} \tag{6}$$

$$\chi_{lm} = \left(\frac{\partial F}{\partial \omega_{lm}} \right)_{N_k, T, \varepsilon_{ij}} \quad \text{or} \quad h = \left(\frac{\partial F}{\partial r} \right)_{N_k, T, \varepsilon_{ij}}$$

For the isotropic system it is correct to expand the free energy F into a series in the vicinity of the nondeformed region[24,38]: $F(T, N_k, r_0) = F^0$, where $r^0 = (v_d/v_{d0})^0$ is the damage of the nondeformed medium. This allows us to establish the relation of S, σ_{ij}, μ_k, and χ_{lm} with deformations. Taking into account the terms second-order infinitesimal with respect to ε_{ij} (since all the desired values are determined by differentiation, which leads to a loss in order with respect to ε_{ij}), we have

$$F = F^0(T, N_k, r^0) + \left(\frac{\partial F}{\partial I_1}\right)^0 I_1$$
$$+ \left(\frac{\partial F}{\partial I_2}\right)^0 I_2 + \left(\frac{\partial^2 F}{\partial I_1^2}\right)^0 \frac{I_1^2}{2} + \cdots \quad (7)$$

where $I_1 = \varepsilon_{ij}$ and $I_2 = \varepsilon_{ij}\varepsilon_{ij}$.

Generalized Hooke's Law

The expressions for the stress tensor components are derived from Eqs. (6) and (7):

$$\sigma_{ij} = \delta_{ij}\frac{\partial F^0}{\partial I_1} + \delta_{ij}I_1\frac{\partial F^{0^2}}{\partial I_1^2} + 2\varepsilon_{ij}\frac{\partial F^0}{\partial I_2} \quad (8)$$

where δ_{ij} is the Kronecker symbol, $\delta_{ij} = 1$ if $i = j$, and $\delta_{ij} = 0$ if $i \neq j$. The coefficients in expansions (7) and (8), determined empirically[18-20,38,39] using Hooke's laws for pure shear and one-axis stress as well as the Poisson effect, have the form

$$\left(\frac{\partial F}{\partial I_2}\right) = G, \qquad \left(\frac{\partial^2 F}{\partial I_1^2}\right)^0 = \lambda + \frac{2}{3}\mu e$$
$$\left(\frac{\partial F}{\partial I_1}\right)^0 = -\frac{v - v_0}{v_0}\left(\lambda + \frac{2}{3}\mu\right) \quad (9)$$

The equality $G = \mu$, where μ is the Lamé coefficient or the shear modulus in the limits of elasticity, is valid for purely elastic small deformations. For the systems that experience nonlinear elastic or plastic deformations, $G = [E/2(1 + \nu)] \cdot (1 - e) = \mu(1 - e)$. The generalized deformation function $e^{39,40}$ is different from zero only beyond the elasticity limits. Thus, the free energy of a deformed system can be represented as

$$F = F^0 - \frac{v - v_0}{v_0}K\varepsilon_{kk} + \varepsilon_{ij}\varepsilon_{ij}\mu(1 - e) + \varepsilon_{kk}^2\left(\frac{\lambda}{2} + \frac{\mu}{3}e\right) \quad (10)$$

where the repeated subscript indicates summation. The relation of the tensor components σ_{ij} and ε_{ij} for the elastoplastic deformations of an isotropically reacting medium, taking into account its damage, follows from Eqs. (8) and (9):

$$\sigma_{ij} = -\delta_{ij}\left[\frac{v - v_0}{v_0}\left(\frac{2}{3}\mu + \lambda\right) - \varepsilon_{kk}\left(\lambda + \frac{2}{3}\mu e\right)\right]$$
$$+ 2\mu(1 - e)\varepsilon_{ij} \quad (11)$$

where the change in specific volume is caused by changed temperature T, component concentrations N_k, and structural distortions. The latter differentiates the relationships obtained from those published by Nikitenko,[39] where only the concentration and thermal expansions were taken into account. Equation (11) is the state equation for the solid. The analogy between temperature, concentration, and structural stresses is also valid in the presence of a viscous deformation. For $e = 0$, from Eq. (11) we derive the relation between the first invariants of stress and strain tensors

$$\sigma_{kk} = 3K\left(\varepsilon_{kk} - \frac{v - v_0}{v_0}\right) \quad (12)$$

which clearly coincides with the available relationships for particular cases. Thus, for example, setting $v = v_0$, from Eq. (12) we find the relationship for purely elastic deformations[38] $\sigma_{kk} = 3K\varepsilon_{kk}$. Provided that the specific volume changes only because of thermal expansion, we have the familiar relationships for thermoelastic deformations.[18,38] Similarly, if the specific volume changes only because of changed concentration of components, Eq. (12) coincides with the relationships suggested by Eremeev[19] for a system with internal concentration stresses and deformations.

Viscoelastic Stresses

For further generalization, we define the deviators from the stress and strain tensors, using the formulas

$$\tau_{ij} = \sigma_{ij} - \delta_{ij}\sigma_{kk}/3, \qquad e_{ij} = \varepsilon_{ij} - \delta_{ij}\varepsilon_{kk}/3 \quad (13)$$

The rheological model for a viscoelastic material[18,19] involves the operator relationship

$$A\tau_{ij} = Be_{ij} \quad (14)$$

where A and B are the differential operators linear in time. The previously mentioned analogy allows the theory of thermoviscoelasticity and concentration viscoelasticity to be extended to a more general case. It follows from Eq. (14) and the relationship between the first invariants of stress and strain tensors that

$$A\sigma_{ij} = B(\varepsilon_{ij} - \delta_{ij}\varepsilon_{kk}/3) + \delta_{ij}AK\left(\varepsilon_{kk} - \frac{v - v_0}{v_0}\right)$$

From this equation we obtain relationships between stresses and deformations for particular viscoelastic media for certain types of A and B. For example, for the viscoelastic model of Maxwell,[18]

$$A = \frac{1}{2\mu}\frac{\partial}{\partial t} + \frac{1}{2\eta}, \qquad B = \frac{\partial}{\partial t} \quad (15)$$

we have

$$\dot{\sigma}_{ij} + \frac{\mu}{\eta}\sigma_{ij} = 2\mu\dot{\varepsilon}_{ij} + \delta_{ij}\left[\frac{\partial}{\partial t}\left(K\varepsilon_{ij} - K\frac{v - v}{v_0}\right)\right.$$
$$\left. - \frac{2}{3}\mu\dot{\varepsilon}_{ij} + \frac{\mu K}{\eta}\left(\varepsilon_{kk} - \frac{v - v_0}{v_0}\right)\right] \quad (16)$$

where dots above variables denote differentiation with respect to time. Setting $A = \frac{1}{2}\mu$ and $B = 1$, we obtain the model of a purely elastic body (14) for $e = 0$.

Free Chemical Energy and Chemical Potential of Components

Equation (10) for the free energy of a system can be presented in another way, e.g., for $e = 0$ it is

$$F = F^0 - K\frac{v - v_0}{v_0}\varepsilon_{kk} + \mu\left(\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{kk}\right)^2 + \frac{K}{2}\varepsilon_{kk}^2 \quad (17)$$

Considering the concentration stresses only, Eremeev[19] analyzes individually the part of free energy that is determined in experiments with no loading. Proceeding similarly, the latter equation can be written as

$$F = F^{ch} - K\frac{v - v_0}{v_0}\varepsilon_{kk} + \mu\left(\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{kk}\right)^2$$
$$+ \frac{K}{2}\left[\varepsilon_{kk}^2 + \left(\frac{v - v_0}{v_0}\right)^2\right] \quad (18)$$

where $F^{ch} = F^0 - (K/2)[(v - v_0)/v_0]^2$.

Using Eqs. (6) and (18), we determine the chemical potentials of the components of a reacting mixture

$$\mu_k = \mu_k^{ch} - \left(\frac{v - v_0}{v_0} - \varepsilon_{mm}\right) K \frac{\partial}{\partial N_k}\left(\frac{v - v_0}{v_0}\right)$$
$$+ \left(\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{mm}\right)\frac{\partial\mu}{\partial N_k} + 2\left(\varepsilon_{mm} + \frac{v - v_0}{v_0}\right)^2 \frac{\partial K}{\partial N_k}$$

(19)

where μ_k^{ch} is the purely chemical part of the potential μ_k

$$\mu_k^{ch} = \mu_k^0 - \frac{1}{2}\frac{\partial}{\partial N_k}\left[K\left(\frac{v - v_0}{v_0}\right)^2\right]$$

(20)

and μ_k^0 is the chemical potential of the components in the absence of deformation, $\mu_k^0 = \partial F^0/\partial N_k$. When the system is subject to plastic or nonlinear elastic stresses ($e \neq 0$), the expression for μ_k is derived in the same way. In the particular case of constant λ and μ (not explicitly dependent on concentrations), we have

$$\mu_k = \mu_k^0 - K\varepsilon_{mm}\frac{\partial}{\partial N_k}\left(\frac{v - v_0}{v_0}\right)$$

(21)

In the construction of macrokinetic models of various solid-phase reactions, the question arises concerning the mechanism of solid-phase diffusion,[19,20,32] which in fact determines the reaction rate in the solid. In other works, diffusion is an intrinsic stage of such a reaction. Assuming that the mass flow of every component J_k in a reacting mixture depends only on the chemical potential gradient (i.e., is independent of other thermodynamic forces), we determine that

$$J_k = -D_k\nabla N_k + \frac{D_k N_k}{kT} K\nabla\varepsilon_{mm}\frac{\partial}{\partial N_k}\left(\frac{v - v_0}{v_0}\right)$$

(22)

Using the balance equation valid for every additive value,[36] we obtain the equation of transfer

$$\frac{\partial N_k}{\partial t} = \text{div}(D_{k,\text{eff}}\nabla N_k) + \psi_k$$

(23)

with the effective diffusion coefficient

$$D_{k,\text{eff}} = D_k\left\{1 - \frac{N_k}{kT\nabla N_k} K\nabla\left[\varepsilon_{mm}\frac{\partial}{\partial N_k}\left(\frac{v - v_0}{v_0}\right)\right]\right\}$$

(24)

Here, ψ_k is the sum of source and loss channels for component k. Equations (23) and (24) imply two transfer mechanisms: 1) the diffusion transfer of components due to their own mobility and 2) the deformation transfer in which the deformation is a consequence of the chemical reaction. A more rigorous consideration requires that the nature of the diffusion mobility and the dependence of the component k flow J_k on the temperature gradient and on the chemical potential gradients of other components must be taken into account.

Energy Equation

The energy equation in the form of the generalized equation of thermal conductivity for an isotropic medium is written as[24]

$$T\frac{\partial S}{\partial t} = -\text{div}(J) + W$$

(25)

where $T\partial S/\partial t$ is the heat absorbed in unit volume per unit time, J is the heat flux density, and W is the power density

of internal heat sources and sinks (e.g., of chemical origination). From Eqs. (6) and (10), we obtain

$$S = -S^0 + \varepsilon_{mm}\frac{\partial}{\partial T}\left(\frac{v - v_0}{v_0}K\right)$$
$$- \varepsilon_{ij}\varepsilon_{ij}\frac{\partial}{\partial T}\mu(1 - e) - \varepsilon_{mm}^2\frac{\partial}{\partial T}\left(\frac{\lambda}{2} + \frac{\mu}{3}e\right)$$

(26)

or, in the particular case of constant λ and μ (not explicitly dependent on temperature)

$$S = -S^0 + K\varepsilon_{mm}\frac{\partial}{\partial T}\left(\frac{v - v_0}{v_0}\right)$$

(27)

Ignoring cross effects, i.e., assuming the heat flux density to be proportional only to the temperature gradient $J = -\lambda_T\nabla T$, and taking into account that $\partial S^0/\partial t = \partial(\partial F^0/\partial T)/\partial t = -T^{-1}c_\varepsilon\rho_0(\partial T/\partial t)$,[35,36] from the previous equations, we have

$$\rho_0 c_\varepsilon\frac{\partial T}{\partial t} = \text{div}(\lambda_T\nabla T) + W - T\frac{\partial}{\partial t}\varepsilon_{mm}\frac{\partial}{\partial T}\left(K\frac{v - v_0}{v_0}\right)$$

(28)

In the particular case $\alpha_s = \alpha_c = 0$

$$\sigma_{ij,j} + X_i = \rho_0\frac{\partial^2 u_i}{\partial t^2}$$

(29)

we obtain the familiar equations of thermoelasticity complemented by chemical sources. Here, X_i are the vector components of the external force. Now add the definition

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

(30)

to Eqs. (11) and (29).

In deriving the energy equation for reactions proceeding in times comparable with the time of sound-wave propagation through the preheated layer, one should take into account the finiteness of heat flux relaxation time and use the generalized Fourier law

$$J = -\lambda_T\nabla T - t_r\frac{\partial}{\partial t}J$$

(31)

This leads to the more complex equation for energy

$$\left(1 + t_r\frac{\partial}{\partial t}\right)\left\{c_\varepsilon\rho_0\frac{\partial T}{\partial t} + T\frac{\partial}{\partial t}\left[K\varepsilon_{mm}\frac{\partial}{\partial T}\left(\frac{v - v_0}{v_0}\right)\right] - W\right\}$$
$$= \text{div}(\lambda_T\nabla T)$$

(32)

If $\alpha_s = \alpha_c = 0$, from Eqs. (11), (29), and (32) one may derive the equations of coherent general thermoelasticity.[41] Equations (29) and (32) in combination with Eq. (16) yield a generalized equation of thermoviscoelasticity for fast reactions. For slow solid-phase reactions, including combustion processes, the inertial forces (resulting from the considerable difference of characteristic times for chemical reactions and for sound propagation) can be disregarded. Then, instead of Eq. (29), we have the equilibrium equation

$$\sigma_{ij,j} + X_i = 0$$

(33)

Kinetics of the Specific Volume of Damage

The expression for the tensor damage potential follows from Eqs. (6) and (10):

$$\chi_{lm} = \chi_{lm}^0 - \varepsilon_{kk} \frac{\partial}{\partial \omega_{lm}} \left(K \frac{v - v_0}{v_0} \right)$$
$$+ \varepsilon_{ij}\varepsilon_{ij} \frac{\partial}{\partial \omega_{lm}} \mu(1 - e) + \varepsilon_{kk}^2 \frac{\partial}{\partial \omega_{lm}} \left(\frac{\lambda}{2} + \frac{\mu}{3} e \right) \quad (34)$$

where $\chi_{lm}^0 = (\partial F^0/\partial r)_{N_k, T}$ represents the damage potential in the absence of stresses and deformations. In terms of the scalar description of damage

$$h = h^0 - \varepsilon_{kk} \frac{\partial}{\partial r} \left(K \frac{v - v_0}{v_0} \right)$$
$$+ \varepsilon_{ij}\varepsilon_{ij} \frac{\partial}{\partial r} \mu(1 - e) + \varepsilon_{kk}^2 \frac{\partial}{\partial r} \left(\frac{\lambda}{2} + \frac{\mu}{3} e \right) \quad (35)$$

The value of h is determined by the intrinsic properties or the structure of the medium. In particular, if V_s is considered to mean the specific volume of the dislocations for an individual crystal that are the potential centers of damage (formation of microcracks)[42] and the potential site of prevailing formation of the product nucleus on initiating the solid-phase reaction,[10,11] then h is the structural chemical potential of the dislocations. In this case, by analogy with the reacting components, we consider a dislocation flow proportional to ∇h and describe the dislocation concentration kinetics using a balance equation similar to Eq. (23). The corresponding function ϕ includes the rates of formation and the disappearance of dislocations by different mechanisms.[37,43,44] The diffusion equations for micropores and microcracks can be written in the same way. A number of models for the dislocation kinetics have been proposed by different authors.[21,22,43,45–49] The mechanism of thermal activation of microcrack formation[42,48] employs the common nature of damage excitation and reaction in the solid on the microlevel. Application of the kinetic laws of damage growth depends on the particular problem. In many cases, the simplest models[49] are applicable. Most problems are solved using the law

$$\frac{\partial r}{\partial t} = \begin{bmatrix} -\dfrac{p}{\eta_d} (r + r_p), & p < 0 \\[2mm] 0, & p \geq 0 \end{bmatrix} \quad (36)$$

where the damage is assumed to form by the activation mechanism described by the equation $r_p = r_{p0} \exp(p/p_0)$, or by its modifications. The values η_d, r_{p0}, and p_0 in the failure mechanics are taken to be constants inherent in the material ($p_0 < 0$). The coefficient $r_{p0} = v_{p0}/v_{d0}$, in principle, can be equated to unity (i.e., the potential centers of crack formation can be set equal to the initial damage volume), $r_{p0} \equiv 1$; η_d has the meaning and dimensions of dynamic viscosity; p_0 determines the critical level of average pressure p ($p = \sigma_{kk}/3$) from which the formation of microcracks accelerates. Clearly, unconditional extension of the concepts of failure mechanics to the theories under consideration is not valid. Expressions such as Eq. (36) are employed only for some qualitative estimations.

Analysis of Particular Problems

Simplest Model of Heat-Flux Ignition of a Solid with Thermoelastic Stresses

Let us consider the excitation of an exothermic reaction at the surface of a semi-infinite solid by an external source. In this case, the deformation may be considered to be uniaxial. Let the reaction be described by the simplest scheme:

$$A_s \rightarrow B_g \quad (37)$$

Since we are interested only in the ignition stage, gas-phase processes and condensed-phase diffusion of the reaction product are not considered. We assume that in the case of highly exothermic reaction and sufficiently intense external heating, the change in the specific volume of the system is totally determined by thermal expansion. Temperature-induced changes in substance properties are neglected. The system of equations of coherent thermoelasticity, corresponding to the simplest problem, follows from Eqs. (11), (28), and (33) and has the form

$$c_\varepsilon \rho_0 \frac{\partial T}{\partial t} = \lambda_T \frac{\partial^2 T}{\partial x^2} + Q_0 Z_0 \phi_1(y)\phi_2(T) - \alpha_T(3\lambda + 2\mu)T \frac{\partial \varepsilon_{xx}}{\partial t} \quad (38)$$

$$\frac{\partial y}{\partial t} = z_0 \phi_1(y)\phi_2(T) \quad (39)$$

$$\frac{\partial \sigma_{xx}}{\partial x} = 0 \quad (40)$$

$$\sigma_{xx} = \varepsilon_{xx}(\lambda + 2\mu) - \alpha_T(3\lambda + 2\mu)(T - T_0)$$
$$\sigma_{yy} = \sigma_{zz} = \lambda\varepsilon_{xx} - \alpha_T(3\lambda + 2\mu)(T - T_0) \quad (41)$$

The relationships (41) in this particular model coincide with the law[38–40] for one-axis deformation (so-called generalized Hooke law[39]).

The boundary and initial conditions are

$$x = 0: \quad \sigma_{xx} = 0, \quad -\lambda_T \frac{\partial T}{\partial x} = q_e \text{ (free end)}$$

$$x \rightarrow \infty: \quad \frac{\partial T}{\partial x} = 0 \quad (42)$$

$$t = 0: \quad T = T_0, \quad y = 0$$

It is taken that the heat release in the chemical reaction obeys the Arrhenius law $\phi_2 = \exp(-E_0/RT)$, and that the kinetic function is of the simplest form $\phi_1 = (1 - y)^n$, where n is the formal reaction order.

The ignition characteristics and the reaction zone structure are to be determined. Using Eq. (40) and relationships (41), we determine that in the system under consideration the deformations follow the changes in temperature profile. For stresses we have $\sigma_{xx} = 0$, $\sigma_{yy} = \sigma_{zz} = -2\mu\sigma_T/(\lambda + 2\mu)$, where $\sigma_T = \alpha_T(3\lambda + 2\mu)(T - T_0)$ are the maximum stresses in an inert body at an instantaneous temperature rise from T_0 to T at its boundary. Hence, from Eq. (38) we have

$$c_\varepsilon \rho_0 \left[1 + \delta \frac{T}{T_*} \right] \frac{\partial T}{\partial t} = \lambda_T \frac{\partial^2 T}{\partial x^2} + Q_0 Z_0 \phi_1(y)\phi_2(T) \quad (43)$$

where $\delta = (3\lambda + 2\mu)^2 \alpha_T^2 T_*/(\lambda + 2\mu)c_\varepsilon \rho_0$ is the coherence coefficient of deformation and temperature fields, and T_* is the characteristic temperature (e.g., the ignition temperature defined later). Equation (43) differs from the energy equation conventionally employed in the ignition theory of condensed substances[50] only by the temperature dependence of effective specific heat of the solid

$$c_\varepsilon' = c_\varepsilon(1 + \delta T/T_*) \quad (44)$$

where c_ε is the specific heat at a constant deformation, which is equal (in terms of the linear theory of thermoelasticity) to the specific heat at a constant volume. Thus, the change in

c_r has a clear physical meaning. In terms of dimensionless variables

$$\theta = \frac{T - T_*}{RT_*^2} E_0, \qquad \xi = \frac{x}{\sqrt{\chi_T t_*}}, \qquad \tau = \frac{t}{t_*}$$

where

$$\chi_T = \frac{\lambda_T}{c_\varepsilon \rho_0}, \qquad t_* = \frac{c_\varepsilon \rho_0 RT_*^2}{E_0 Q_0 Z_0} \exp\left(\frac{E_0}{RT_*}\right) \qquad (45)$$

the problem of ignition of a deformable solid takes the form of

$$[1 + \delta(1 + \beta\theta)]\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\xi^2} + \phi_1(y)\phi_2(\theta) \qquad (46)$$

$$\frac{\partial y}{\partial\tau} = \gamma\phi_1(y)\phi_2(\theta) \qquad (47)$$

$$e_{\xi\xi} = \theta + \theta_0 \qquad (48)$$

$$\tau = 0: \quad \theta = -\theta_0, \quad y = 0 \qquad (49\text{a})$$

$$\xi = 0: \quad -\frac{\partial\theta}{\partial\xi} = Q_e, \qquad \xi \to \infty: \quad \frac{\partial\theta}{\partial\xi} = 0 \qquad (49\text{b})$$

where

$$\phi_2(\theta) = \exp\left(\frac{\theta}{1 + \beta\theta}\right), \qquad \theta_0 = \frac{T_* - T_0}{RT_*^2} E_0$$

$$\beta = \frac{RT_*}{E_0}, \qquad Q_e = \frac{q_e E_0}{RT_*^2}\sqrt{\frac{t_*}{c_\varepsilon \rho_0 \lambda_T}}, \qquad \gamma = \frac{c_\varepsilon \rho_0 RT_*^2}{E_0 Q_0}$$

are the traditional parameters of the ignition theory ($\theta_0 \gg 1, \beta \ll 1, \gamma \ll 1$).[50] The deformation is defined here in the following way:

$$e_{\xi\xi} = \frac{\varepsilon_{xx}}{\varepsilon_*}, \qquad \varepsilon_* = \frac{\alpha_T(3\lambda + 2\mu)}{\lambda + 2\mu}\frac{RT_*^2}{E_0} \qquad (50)$$

Disregarding the dependencies on the small parameter β, let us estimate the ignition characteristics, assuming a zero-order reaction [$n = 0$, $\phi_1(y) = 1$] and using Vilyunov's adiabatic criterion.[50,51] According to this criterion, at the moment of ignition the rates of temperature rise at the boundary $x = 0$ due to an external source (determined from the solution of the inert problem of thermal conductivity) and chemical heat release become comparable. The result for the ignition time is

$$\tau_a(1 + \delta)^{-1} = \theta_0/2 = Q_e^2/\pi \qquad (51)$$

The time τ_a is referred to as the adiabatic induction period or adiabatic ignition time. The ignition temperature, determined by Eq. (51) and coinciding with the result reported by Vilyunov[50] [$T_* = T_*^{(0)}$], is the temperature of the initiation of chemical reactions. However, when compared to the classical thermal theory, where $\tau_a = \tau_a^{(0)} = \theta_0/2$, the ignition time in the first approximation increases by a factor of $(1 + \delta)$. As noted for many materials,[52] (including polymers), the coherence coefficient d calculated at a temperature of T_* is of the order of unity, which makes this coefficient different from that in the thermoelasticity theory, where the initial temperature is chosen as characteristic.

Dynamics of Damage Accumulation in the Surface Layer

For high-energetic materials, thermal stresses appear to be the main reason for surface layer destruction on ignition. For qualitative estimations we use the kinetic law of destruction in the form of Eq. (36) and neglect the effect of damage on heating the propellant. Let us rewrite Eq. (36) in terms of the dimensionless variables $S_h = p/\sigma_*$ ($\sigma_* = \sigma_{T*}/\theta_0$) and τ

$$\frac{\partial r}{\partial\tau} = -S_h k_d\left[r + \exp\left(\frac{S_h}{S_0}\right)\right], \qquad r(0) = 1 \qquad (52)$$

where k_d is the rate constant of crack growth [$k_d = \sigma_{T*}t_*/(\theta_0\eta_d)$], S_0 is the critical average pressure ($S_0 = p_0\theta_0/\sigma_{T*}$), and

$$S_h = -(2/3)\gamma_1(\theta_0 + \theta), \qquad \gamma_1 = 2\mu/(\lambda + 2\mu) \qquad (53)$$

At the stage of inert heating, the temperature at $\xi = 0$ increases by the law $\theta(0, \tau) = -\theta + 2Q_e[\tau/\pi\cdot(1 + \delta)]^{1/2}$. Consequently, from Eq. (51) we have

$$S_h = -\tfrac{2}{3}\gamma_1\sqrt{2\theta_0\tau/(1 + \delta)} \qquad (54)$$

which is valid up to the time τ_a when $S_h(\tau_a) = S_{ha} = -2\gamma_1\theta_0/3$. Assuming the critical stresses (or average pressure) to be comparable to or less than the theoretical strength (e.g., $|p_0| \leq \mu/10$), S_0 is represented as

$$|S_0| = \frac{\gamma_1}{20(3 - 2\gamma_1)}\cdot\frac{\theta_0}{\alpha_T(T_* - T_0)} \gg 1 \qquad (55)$$

The condition $S_h/S_0 \ll 1$ allows the exponent of Eq. (52) to expand by small parameter powers, giving the following estimation to r:

$$r \leq -1 + \tfrac{2}{3}(\gamma_1\theta_0/S_0) + [2 - \tfrac{2}{3}(\gamma_1\theta_0/S_0)]\exp[\gamma_1(2\theta_0)^{1/2}k_d\tau^{3/2}] \qquad (56)$$

Note that the greater the θ_0, i.e., the less the initial temperature of propellant, the larger the damage in the subsurface layer. This is in agreement with the real situation, when the unstable combustion of high-energetic propellants, associated with propellant destruction, is observed on burning at low initial temperatures. The value of k_d, which depends on the dynamic viscosity coefficient, is determined by the propellant type. If $k_d \to 0$, the destruction is insignificant (this is also the case with very large S_0).

The numerical solution of problems (46–49) and (52) is achieved through an implicit differential scheme using iterations for each time layer (the other problems are solved similarly). Examples of the time dependencies of surface temperature $\theta(0, \tau)$, damage $r(0, \tau)$, stresses $S_h(0, \tau)$, and deformations $e_{\xi\xi}(0, \tau)$ are shown in Fig. 1. The calculation was performed for the following set of parameters: $\lambda_T = 2.35 \times 10^{-3}$ W/(cm·K), $c_\varepsilon = 1.46$ J/(g·K), $\rho_0 = 1.6$ g/cm³, $E_0 = 1.456 \times 10^5$ J/mole, $Q_0 = 1200$ J/cm³, $Z_0 = 8.6 \times 10^{-3}$ s⁻¹, and $T_0 = 273$ K, which for $q_e = 45$ W/cm² lead to the dimensionless parameters

$$\beta = 0.032, \qquad \gamma = 0.034, \qquad Q_e = 5.42, \qquad \theta_0 = 16.2$$

We put $S_0 = 4.18$ and $\gamma_1 = 0.292$. The values of δ and k_d were varied. The time of reaction initiation by Eq. (51) is in satisfactory agreement with the numerical calculation of the problem [τ_a and $\tau_a^{(0)}$ for different d are shown as ordinates in Fig. 1a]. Note that the solution [$\theta(0, \tau)$ and τ_a] for $\gamma = 0$ and $\gamma = 0.034$ practically coincide (curve 1). The temperature curve at times corresponding to inert heating deviates slightly from the analytical solution of the problem for $\delta = 0$ and δ
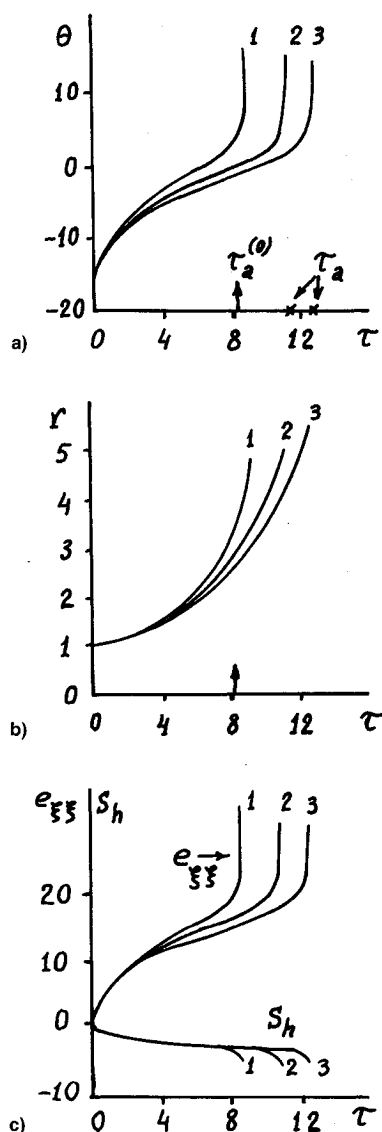
Fig. 1 Time dependencies of a) temperature θ, b) damage r, and c) deformations $e_{\xi\xi}$ and stresses S_h at $\xi = 0$ in a problem on igniting a material with thermoelastic stresses by a constant heat flux ($k_d = 0.03$, $\gamma = 0.034$): 1) $\delta = 0$, $\beta = 0.032$; 2) $\delta = 0.392$, $\beta = 0.054$; 3) $\delta = 0.55$, $\beta = 0.032$.

$\neq 0$, $\beta < 1$. Increasing β leads to a remarkable deviation of the curves from analytical dependence (curve 2).

Ignition with a Hot Body

The effect of stresses and deformations is similar to that described for the case of ignition by an external heat flux if the propellant is ignited under a high temperature $T_s > T_0$ sustained[52] at the boundary $x = 0$. The mathematical equations are as before [Eqs. (38–41)]. The boundary conditions for temperature are conventional for the thermal ignition theory

$$x = 0: \quad T = T_s, \quad x \to \infty: \quad \frac{\partial T}{\partial x} = 0 \quad \text{or} \quad T = T_0$$

The conditions for the mechanical values can vary.

1) In the simplest case, the ignited material can be considered semi-infinite for temperature as well as for stresses and deformations. It is assumed that the end $x = 0$ is not fixed and that $\sigma_{xx}(t, 0) = 0$. Then, in terms of dimensionless var-

iables, the problem has the form of Eqs. (46–49) with the boundary conditions

$$\xi = 0: \quad \theta = 0, \quad \xi \to \infty: \quad \theta = \theta_0 \quad \left(\frac{\partial \theta}{\partial \xi} = 0\right)$$

For an approximate estimation, we employ the quasistationary criterion[53] by which the ignition occurs when the heat flux from the zone of chemical reaction is equal to the heat flux at the boundary $x = 0$ due to external heating. The ignition temperature in this case is the temperature of the hot body $T_* = T_s$. As in the previous problem, stresses and deformations completely follow the change in the temperature field, with the ignition time τ_q being $(1 + \delta)$ times longer than that in the thermal theory:

$$\tau_q = (\theta_0^2/2\pi)(1 + \delta) = \tau_q^{(0)} \cdot (1 + \delta) \tag{57}$$

The time τ_q, $\tau_q^{(0)}$ is referred to as the time of the breakdown of the quasistationary thermal equilibrium.

2) Let the sample be finite for stresses and the following conditions be met:

$$x = 0: \quad u = 0, \quad x = l: \quad \sigma_{xx} = -p_e$$

In this case, the ignition time is determined as before by Eq. (57). The deformations ε_{xx} are defined using the equation derived from the equilibrium equation differentiated with respect to the coordinate and from Eqs. (41). The solution has the form

$$\varepsilon_{xx} = a(T - T_s) + (1/l)\{a(T_s - T_0) - [p_e/(\lambda + 2\mu)]\}x \tag{58}$$

Note that $T(t, 0) = T_s$ and $x = l$ represent the infinity for temperature, $T(t, l) = T_0$, $T = T_0$. Here, $a = \alpha_T(3\lambda + 2\mu)/(\lambda + 2\mu)$. It follows from Eq. (58) that the sign of deformations at different points of the reactant can vary depending on the values of exothermic reaction temperature and layer thickness l. The energy equation remains the same [Eq. (43)].

Sample Fixing, Reaction Rate, and Damage Accumulation

In terms of the simplest model (38–41), the effect of stresses and deformations on the rate of chemical reaction is reflected above all by changes in the temperature field, thus decelerating the heating. Deformations can also change the global chemical parameters of reaction. In particular, as mentioned earlier,[10,12,13] many solid-phase reactions are initiated by both deformation and thermal mechanisms. In complex and multicomponent systems such as propellants, it is difficult to isolate particular stages with certain initiation mechanisms. Qualitative estimations, as in thermal theories, are possible in terms of global macrokinetics. Let us assume that the stress- and deformation-induced changes in the mechanisms of individual stages result in apparent changes in the formal activation energy of the reaction[52,54]

$$E = E_0 - \Delta E$$

where $\Delta E = \beta_{st} \cdot p \cdot dV = \beta_{st} \cdot p \cdot \varepsilon_{xx}$ and β_{st} is the structure-sensitive coefficient. Then, in terms of dimensionless variables, the function of the heat release in the chemical reaction takes the form

$$\phi_2 = \exp\left(\frac{\theta - \psi S_h e_{\xi\xi}}{1 + \beta\theta}\right), \quad \psi = \beta_{st} \frac{\varepsilon_* \sigma_*}{RT_*}$$

Taking into account the relation of stress S_h and deformations that are characteristic of free-end problems, we obtain $S_h \cdot \varepsilon_{xx}$

$= -2\gamma_1(\theta + \theta_0)^{2/3}$. The adiabatic ignition time in the problem of the ignition by heat flux is

$$\tau_a = \tau_a^{(0)}(1 + \delta)f^{-1} \qquad (59)$$

and the corresponding ignition temperature T_* can be determined from the formula

$$Q_e^2/\pi = \theta_0(f/2) \qquad (60)$$

where $f = \exp[-(2\gamma_1\psi\theta_0^2)/3]$.

The damage growth in the problem of ignition by a hot body obeys the law

$$r = [1 + \exp(S_h/S_0)]\exp(-S_h k_c\tau) - \exp(S_h/S_0) \qquad (61)$$

under practically constant stresses S_h, the value of S_h being dependent on fixing conditions. For an infinite sample with a free end $S_h = S_{ha} = -2\gamma_1\theta_0/3$, these stresses accelerate the reaction. Therefore, the formula for the time τ_q of quasistationary equilibrium breakdown (57) must be complemented with the factor f^{-1}, as in Eq. (59). For samples finite for mechanical disturbances, we have

$$e_{\xi\xi} = \theta + \xi(\theta_0 - S_e)/L$$

$$S_{\xi\xi} = -\theta_0 + \xi(\theta_0 - S_e)/L \qquad (62)$$

$$S_h = [2(1 - \gamma_1)(\theta_0 - S_e)\xi/L - 2\gamma_1\theta - 3\theta_0]/3$$

where $L = 1/x_*$ and $S_e = p_e/\sigma_*$. Consequently, as $\xi \to 0$ when $\theta = 0$, and $e_{\xi\xi} \to 0$ when $\theta = 0$, and $e_{\xi\xi} \to 0$, there is no additional activation of the reaction; however, the sample can be destroyed under practically constant stresses $S_h = -\theta_0$, which are greater than those in the previous case. The reaction acceleration by the deformation mechanism is possible at $\xi > 0$ when $e_{\xi\xi} \neq 0$.

Thus, the mechanical conditions at the end of the sample manifest themselves not only in deformation and stress fields, but also in the extent of destruction and stress fields, and in the extent of destruction of the surface layer and the rate of chemical reaction. In terms of the thermal theory, to estimate the ignition time on igniting by a hot body or by a convective flow at a large heat exchange coefficient, it was sufficient to use Eq. (57). However, an account of the mechanical effects shows that the deformation forces have essentially different effects on the reaction kinetics and destruction. It seems plausible that the different effects of stresses and deformations on the rate of chemical reaction (at the surface or in the bulk) are responsible for the different global kinetic parameters determined from experiments on ignition under different conditions with data treated in terms of the thermal model.

Ignition Model Taking into Account Concentration Stresses

In all previous ignition models, the question of whether the reaction product is gas or solid was not important and the properties of the product were disregarded. Our model allows taking into account one more parameter, concentration expansion, which gives rise to concentration stresses. For the simplest reaction scheme (37) or

$$A_s \to B_s \qquad (63)$$

the second summand in brackets in Eq. (1) may be presented in the form

$$\sum_{(k)} \alpha_{ck}(N_k - N_{k0}) = y\Delta\alpha_{BA}$$

where y is the extent of substance conversion (or the fraction of the reaction product) $y = N_B/N_{A0}$, $\Delta\alpha_{BA} = (\alpha_B - \alpha_A)N_{A0}$. Here, N_{A0} is the reference value, and α_B and α_A are the

concentration expansion coefficients of the product and reactant, respectively. If the reaction proceeds to extend the volume, $\Delta\alpha_{BA} > 0$ and vice versa in the opposite situation. The large positive values of $\Delta\alpha_{BA}$ may be considered characteristic of the reactions yielding gaseous products. The system of equations in this problem is presented by Eqs. (38–42) with the term $\Delta\alpha_{BA}(3\lambda + 2\mu)y$ added to Eq. (41).

Similar transformations yield the new heat release function in Eq. (43) for the thermal conductivity

$$\phi_2'(T) = \phi_2(T)\cdot(1 - \delta gT/T_*)$$

where $g = \Delta\alpha_{BA}c_\varepsilon\rho_0/\alpha_TQ_0$.

Thus, if the reaction proceeds to expand the volume, $g > 0$, then the effect of concentration stresses is equivalent to initiation of an endothermic reaction concurrent with the basic reaction in the vicinity of $T = T_*$ or to a decrease in total chemical heat release. The regime of induction ignition involving two distinct stages 1) the inert heating and 2) the reaction under practically adiabatic conditions,[50] does not necessarily realize. If $g < 0$, explosion-type ignition regimes are possible, when at $t \to t_a$ the rate of temperature rise $\partial T/\partial t$ dramatically increases in a short time.

Let us consider a problem on ignition by a constant heat flux [condition (42)]. In dimensionless variables, the energy equation is

$$[1 + \delta(1 + \beta\theta)]\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\xi^2} + \phi_1(y)\phi_2(\theta)[1 - \delta g(1 + \beta\theta)] \qquad (64)$$

Deformations $e_{\xi\xi}$ and stresses S_h depend on both temperature and conversion extent

$$e_{\xi\xi} = \theta + \theta_0 + (g/\gamma)y, \qquad S_h = -\tfrac{2}{3}\gamma_1 e_{\xi\xi} \qquad (65)$$

The other equations are not changed. Estimations of the ignition time in problem (59), (64), and (65) under conditions (49) (if this regime is realized), using the adiabatic criterion, yield:

$$\theta_a = -\frac{\theta_0}{\theta_0 + 1}\,l''\left(\frac{\tau_a}{\tau_a^{(0)}}\frac{1 - \delta g}{1 + \delta}\right)$$

$$\frac{\tau_a}{\tau_a^{(0)}}\frac{(1 - \delta g)^2}{1 + \delta} = \left(\frac{\tau_a}{\tau_a^{(0)}}\frac{1 - \delta g}{1 + \delta}\right)^{2\theta_0/(\theta_0 + 1)} \qquad (66)$$

where $\tau_a^{(0)} = \theta_0/2$. The reference temperature in this case is the temperature of initiation of chemical reactions $T_*^{(0)}$ for $\delta = g = 0$. For the ignition time at $\theta_0 \gg 1$, Eq. (66) yields the familiar result $\tau_a = \tau_a^{(0)}(1 + \delta)$. The temperature is estimated by the equation

$$\theta_a = -l''(1 - \delta g) \qquad (67)$$

When such estimations are valid and classic ignition regimes are realized, the only limiting condition for the parameters is $g < 1/\delta$.

The numerical solution of the problem shows the presence of different reaction regimes in such a system (Fig. 2). The classic ignition is realized at $g \leq 0$ and in a very narrow region of positive g values (curves 1, 2, and 3). Such regimes are characterized by high temperatures, a dramatically increasing reaction rate at $\tau \to \tau_a$, small negative and high positive values of average pressure S_h after initiation of chemical reaction, and by slight damage of the surface layer. As g increases, the ignition regime degenerates and the reaction proceeds under the action of an external source ("exothermic pyrolysis," curves 4 and 5). The rate of damage growth significantly exceeds the rate of temperature rise. In this case the surface layer de-
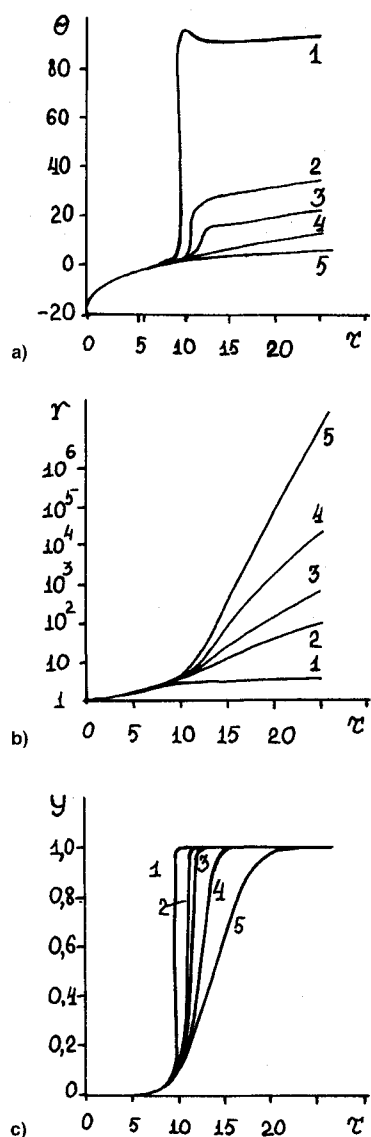
Fig. 2 Effect of concentration expansion on the time dependencies of a) temperature, b) damage, and c) conversion extent at $\xi = 0$ ($\beta = 0.032$, $k_d = 0.03$, $\delta = 0.392$): 1) $g = -5$; 2) $g = -0.5$; 3) $g = 0.5$; 4) $g = 2$; d) $g = 5$.

struction is very significant: the specific volume of damages, calculated in accord with kinetic law (52), increases by several orders of magnitude. Hence, the energetic effects resulting from concentration stresses during the reaction can play the role of sources or sinks in the parallel exo- or endothermic reaction (for details, see Ref. 55).

The possibility of nonthermal initiation of the chemical reaction due to changing the free energy of the system can be taken into account in the model with concentration and structural stresses and deformations and by changing the temperature field as described above and in the thermoelastic model.[54] From Eq. (10), in the first approximation we have $dF = -[(v - v_0)/v_0]K\varepsilon_{kk}$. Then, if the reaction proceeds to reduce the volume ($g < 0$), the concentration stresses decelerate the reaction; at $g > 0$ the reaction accelerates due to the concentration stresses. The complex interrelations of the phenomena do not permit us to make an unambiguous conclusion about the combined effect of the concentration and structural expansions on the reaction kinetics.

The model allows analysis of transient ignition regimes for systems with solid-phase reaction products. The detailed numerical solution of the problem shows that in the first case ($g > 0$) a self-sustaining solid-phase chemical reaction wave

is possible after switching off the external source. In the other case ($g < 0$) the velocity of the front of the reaction with the solid-phase products slows down. When the reaction front is far from the surface and the effect of the external source, even if its action is insignificant, the reaction stops. The self-sustaining reaction is possible in the presence of additional heat supply, e.g., due to destruction in the front.

Determination of Global Kinetic Parameters

There is one more approach to estimation of the ignition characteristics. Let the ignition temperature T_a at the given set of the parameters $\delta \neq 0$, $g \neq 0$ be the reference temperature T_* [i.e., it is assumed that $\tau = \tau_a$, $\theta(0, \tau_a) = 0$] at the ignition instant. This leads to the relationships

$$(1 - \delta g)\theta_0 = \frac{2}{\pi} Q_e^2$$

$$\tau_a = \frac{\theta_0(1 + \delta)}{2(1 - \delta g)} = \frac{Q_e^2(1 + \delta)}{\pi(1 - \delta g)^2}$$ (68)

which are meaningful only at $\delta < 1/g$. These expressions make is possible to take into account the mechanical properties of the propellant in estimating the global kinetic parameters E_0 and $Q_0 Z_0$, provided that the coefficients of the linear thermal expansion α_T and the coefficients of the concentration expansion of the product and reactant are determined independently. Indeed (as in the thermal ignition theory[50]) in terms of dimensional variables, the above equations can be written as follows:

$$\ln\left(\frac{t_a}{1 - T_0/T_a}\right) = \ln\left\{\frac{1 + \delta(T_a)}{2[1 - \delta(T_a)g]} T_a \frac{c_\varepsilon \rho_0}{Q_0 Z_0}\right\} + \frac{E_a}{R} \frac{1}{T_a}$$

$$T_a - T_0 = \left\{\frac{4}{\pi} \frac{q_e^2 t_a}{c_\varepsilon \rho_0 \lambda_T[1 + \delta(T_a)]}\right\}^{1/2}$$ (69)

Let us make simple estimations of E_0 and $Q_0 Z_0$ for a double-base propellant $N + 1\%$ carbon black. Typical values of ignition time as a function of heat flux are listed in Table 1. It is assumed that $\lambda_T = 2.35 \times 10^{-3}$ J/(cm·s·K), $c_\varepsilon = 1.47$ J/(g·K), and $\rho_0 = 1.6$ g/cm³. Treatment of the data in Table 1 in terms of the parameters $1/T_a$ and $\ln(t_a/(1 - T_0/T_a)]$ yields $E_a \approx 191$ kJ/mole and $Q_0 Z_0 = 2.66 \times 10^{21}$ J/(g·s) for $\gamma = g = 0$. For the real values of λ, μ, α_T, and $\Delta\alpha_{BA}$, we may accept $\delta(T_0) = 0.206$ and $g = 0.25[\delta(T_a) = \delta(T_0)T_a/T_0]$. In this case, a similar treatment yields $E_a \approx 233$ kJ/mole and $Q_0 Z_0 \approx 3.46 \times 10^{26}$ J/(g·s). Note that the activation energy changes by 20% and the total heat release rate, which is equal to $Q_0 Z_0 \exp(-E/RT)$, increases to $T_a = 200-300°C$ by a factor of 3–18.

The ignition time can be estimated in a similar way via the quasistationary criterion.[53]

Effect of Damage on Reaction Zone Structure

In a more general formulation of the problem, with all physicochemical processes characteristic of solid ignition mutually related, analytical estimations appear to be impossible, particularly with a model in which the damage to the subsurface layer due to chemical reaction and high-temperature

Table 1 Ignition time vs heat flux

q_e, W/cm²	t_i, s
46.09	0.13
26.40	0.39
10.48	2.00
7.12	4.00

gradients affects heating through a change in the specific volume of the substance. In this case, for the simplest reaction scheme (37) or (63), we have

$$\varepsilon_{xx} = \frac{\alpha_T(3\lambda + 2\mu)}{\lambda + 2\mu}\left[(T - T_0) + \frac{\Delta\alpha_{BA}}{\alpha_T}y + \frac{\alpha_s v_{d0}}{\alpha_T}(r - 1)\right] \tag{70}$$

Hence, the thermal conductivity equation (43) is replaced by

$$c'_\varepsilon\rho_0\frac{\partial T}{\partial t} = \lambda_T\frac{\partial^2 T}{\partial x^2} + Q'_0 Z_0\phi_1(y)\phi_2(T) - \phi_3(T, r)$$

where

$$c'_\varepsilon = c_\varepsilon\left(1 + \delta\frac{T}{T_*}\right), \qquad Q'_0 = Q_0\left(1 - \delta g\frac{T}{T_*}\right)$$

$$\phi_3(T, r) = \frac{\chi}{\gamma}\delta\frac{T}{T_*}\frac{\partial r}{\partial t} \tag{71}$$

is the additional heat supply due to destruction and $\chi = \alpha_s v_d c_\varepsilon\rho_0/(\alpha_T v_0 Q_0) < 0$. For reasonable values of the physical parameters involved in the new dimensionless complex, the value of χ will probably be small since $\alpha_s \sim \alpha_T Q_0/c_\varepsilon\rho_0$ and $v_{d0}/v_0 < 1$. Thus, the effect of this parameter on temperature is weak.

In terms of dimensionless variables, the thermal conductivity equation and the relations of the deformation to the other parameters take the form

$$f_1(\theta)\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\xi^2} + \phi_1(y)\phi_2(\theta)f_2(\theta) - \frac{\partial r}{\partial\tau}f_3(\theta) \tag{72}$$

$$e_{\xi\xi} = \theta + \theta_0 + \frac{g}{\gamma}y + \frac{\chi}{\gamma}(r - 1) \tag{73}$$

where $f_1(\theta) = 1 + \delta(1 + \beta\theta), f_2(\theta) = 1 - \delta g(1 + \beta\theta)$, and $f_3(\theta) = \delta(1 + \beta\theta)\chi/\gamma$.

A numerical solution of problems (72), (73), (47), and (52) under conditions (49), and with the previous reference parameters, is exemplified in Fig. 3. Even at small structural expansion coefficients, the self-sustaining combustion is possible with an additional energy supply due to reaction zone damage within a sufficiently wide range of positive g. Since all the processes are coherent, by the time "forced" (Fig. 3) or self-sustaining combustion is established, the system has been destroyed to a certain extent, but not disintegrated. The boundary stresses and deformations decrease almost to zero (or to those stresses caused only by the external heat source) when the reactant is completely converted to the product. A similar pattern is observed in the bulk as the reaction propagates inward: the region of maximum stresses and deformations moves together with the reaction zone, but does not coincide with the zone of complete conversion.

It is natural that the chemical reaction changes the substance properties. For example, a new level of damage different from the initial one $r_0 = 1$ is formed (see preceding). In real situation, the value of r affects the thermophysical and mechanical characteristics of the energetic material. This effect can also be taken into account in the model. In the case when the crack formation can be described by one parameter[56] (in our problem, it is damage r), the shear and bulk compression modules can be approximated by the functions

$$G = G_0\exp(-\zeta_G r), \qquad K = K_0\exp(-\zeta_K r) \tag{74}$$

where ζ_G, ζ_K, G_0, and K_0 are the constants inherent in the material. Assuming these equations to be valid in our case
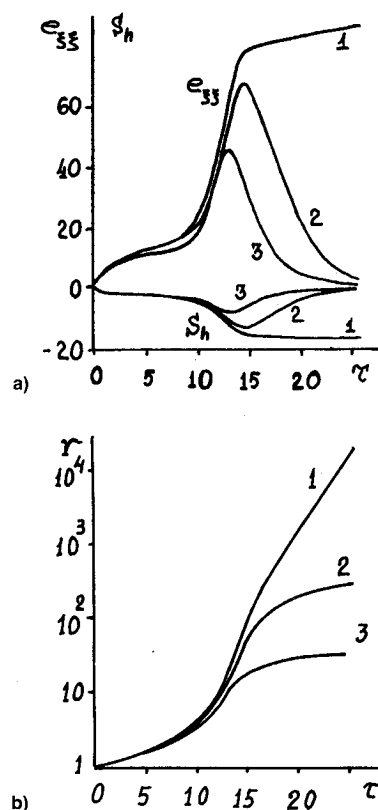

Fig. 3 Effect of damage on the time dependencies of a) $e_{\xi\xi}$ and S_h and b) r at $\xi = 0$ ($\beta = 0.032$, $k_d = 0.03$, $\delta = 0.392$, $g = 2$): 1) $\chi = 0$, 2) $\chi = -0.01$, and 3) $\chi = -0.1$.

and accepting that $\zeta_G = \zeta_K = \zeta$, we obtain a model similar to the previous one, but with the other pattern of functions f_1, f_2, and f_3 incorporated in the thermal conductivity equation:

$$f_1(\theta) = 1 + \delta(1 + \beta\theta)\exp(-\zeta r)$$

$$f_2(\theta) = 1 - \delta g(1 + \beta\theta)\exp(-\zeta r) \tag{75}$$

$$f_3(\theta) = \delta(1 + \beta\theta)\exp(-\zeta r)[\chi/\gamma - \zeta e_{\xi\xi}]$$

Now the stresses and deformations are related as

$$S_h = -\tfrac{2}{3}\gamma_1\exp(-\zeta r)e_{\xi\xi} \tag{76}$$

The calculations show the variable elastic properties of the material are the reason for increasing the reaction zone width and the velocity of the reaction front propagation into the bulk.

Figure 4 shows spatial distributions for dimensionless heat release due to the chemical reaction (Fig. 4a):

$$q_{ch} = \phi_1(y)\phi_2(\theta) \tag{77}$$

and the destruction (Fig. 4b):

$$q_r = -f_3(\theta, r)\frac{\partial r}{\partial\tau} \tag{78}$$

which is characteristic of the forced reaction regime by scheme $A_s \to B_s$. The heat release q_{ch} is practically compensated by the endoeffect of the apparent parallel reaction. The reaction front propagation is supported by the external source and the damages in the reaction zone.

The oscillating combustion regimes are characterized by extremely nonuniform spatial distributions; however, here q_{ch} is an order of magnitude higher than q_r. There are also mild
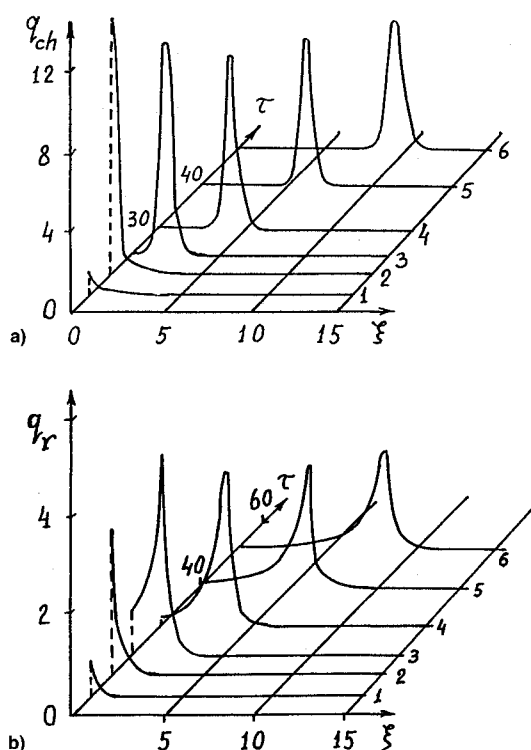
Fig. 4 Spatial distributions of dimensionless heat release due to a) chemical reaction and b) destruction characteristic of the forced reaction regime. $g = 2$, $\chi = -0.01$, $\zeta = 0.1$, $\beta = 0.032$, $S_0 = 4.18$, $\theta_0 = 16.2$, $\gamma = 0.034$, $\delta = 0.392$, $k_d = 0.03$. Dimensionless time τ: 1) 6.0, 2) 11.6, 3) 18.7, 4) 28, 5) 40, and 6) 52.

regimes of reaction wave propagation, with all energy effects comparable in magnitude. Thus, the global characteristics of the reaction zone determined experimentally do not necessarily have the physical meaning assigned to them by classic ignition and combustion theories.

Comments on the Effects of Diffusion and Siscoelastic Stresses in Solid

We shall briefly describe two simple models for reaction schemes (37) and (63). If a solid-phase reaction yields gaseous products, they can escape through the cracks and pores formed during the reaction. The only physical mechanism of gas transport is the diffusion. Normally, the diffusion in the solid phase is very slow; its characteristic rate is much lower than the rate of heat transfer. Thus, the classic thermal theory of ignition and combustion disregarded the diffusion in the solid, restricting its consideration of reactions to equations like Eq. (39). In studying transient regimes in solid propellant ignition, various conventional criteria were used in determining the solid surface and the velocity of its motion. Some of the criteria are associated with achievement of a given extent of material depletion at the surface; in this case, if the surface does not move, no substance is supplied to the gas phase.[58,59] Another method is approximate simulation of solid propellant decomposition in the condensed phase by pyrolysis,[57,59] which yields incorrect values for the transient burning rate. As follows from the general relationships for the free chemical energy, the chemical potential of the reactants, and the phenomenological equation for the diffusion (23), the motive force accelerating the diffusion transport of the ration products to the gas phase are the stresses and deformations resulting from the chemical reaction. For the simplest reaction scheme, the equation for the product concentration is

$$\frac{\partial y}{\partial t} = D_k \frac{\partial^2 y}{\partial x^2} - D_k(3\lambda + 2\mu)(\alpha_B - \alpha_A)\frac{\partial}{\partial x}\left(\frac{y\Delta\varepsilon_{xx}}{kT}\right) + Z_0\phi_1\phi_2$$

(79)

This approach to modeling solid-phase processes in the ignition and combustion of solid propellants allows one to determine the ignition characteristics by reaching a certain value of damage or a certain value of the condensed-phase reaction products supplied to the gas phase. These values can be easily compared with experimental data. Adding the Hooke law relationships written for the one-axis deformation, the free-end conditions, and the system of gas-phase equations to the system of Eqs. (38), (70), and (79), we obtain a more realistic ignition model than that based on the classic thermal ignition theory. Analyzing the ignition stage, we may restrict ourselves to a simplified formulation of the problem (disregarding the gas phase) with the boundary conditions of the third kind at the boundary $x = 0$ (i.e., the problem is simplified by introduction of the effective mass transfer coefficient). Preliminary calculations have shown that for sufficiently small y values, which are characteristic of the heating stage up to the moment of initiation of the chemical reaction t_a, the results are almost the same as those for $D_k = 0$. Additional consideration should be given to the analysis of ignition transients and combustion at $D_k \neq 0$, which leads to qualitatively new effects. The ignition and combustion model for two-component propellants[60] can be complemented in a similar manner.

The other model that needs further development is the ignition model involving viscoelastic stresses. In a problem concerning the ignition of a semi-infinite layer, the transformed deformation equation has the form

$$\left(\frac{4}{3}G + K\right)\frac{\partial\varepsilon_{xx}}{\partial t} + \frac{GK}{\eta}(\varepsilon_{xx} - \varepsilon_\nu) - K\frac{\partial\varepsilon_\nu}{\partial t} = 0 \quad (80)$$

where $\varepsilon_\nu = (v - v_0)/v_0$ is the deformation resulting from the chemical reaction. For the stresses we have $\sigma_{xx} = 0$; the two components different from zero ($\sigma_{yy} = \sigma_{zz} = \sigma$) can be determined from the differential equation

$$\frac{\partial\sigma}{\partial t} + \frac{G}{\eta}\sigma = \left(K - \frac{2}{3}G\right)\frac{\partial\varepsilon_{xx}}{\partial t} + \frac{GK}{\eta}(\varepsilon_{xx} - \varepsilon_V)$$

$$- K\frac{\partial\varepsilon_V}{\partial t} = 2G\frac{\partial\varepsilon_{xx}}{\partial t} \quad (81)$$

The equations for thermal conductivity and chemical kinetics remain unchanged [Eqs. (38) and (39)]. An analysis of the problem concerning ignition by constant heat flux [condition (42)] reveals a strong dependence of process behavior and reaction zone structure on viscoelastic deformations. This dependence is similar to those considered above, excluding one point. The stresses (and the average pressure) are small, which gives $r \approx 1$ in the reaction with the previous destruction kinetics [Eq. (36)] and the above reference parameters. Further studies on designing the kinetic law of destruction in the reaction zone should explicitly take into account the thermofluctuation mechanism of microcrack formation,[48] the common nature of the damage, and the excitation of the chemical reaction in the vicinity of nonuniformities in the solid.

Conclusions

This article suggests basic equations for the description of mass and heat transfer, taking account of deformations and destructions in chemically reacting media. The applicability of the proposed approach to the macrokinetic modeling of physicochemical transformations in solids is illustrated in the ignition problems. Results of calculation show that the apparent change in the energy of activation and in the different physicochemical characteristics of the reaction zone can occur due to the effects of mechanical stresses and deformations on chemical transformations in the condensed phase. The mechanical effects are an intrinsic feature of the physicochemical behavior of energetic materials upon heating.

It follows from this study that accounting for the mechanical effects can lead to a 20% change in the energy of activation for global exothermic reactions and to the variation of total heat release in the condensed phase within an order of magnitude. The energetics of the reaction zone incorporate the heat release due to chemical reactions and dissipation of mechanical energy in the solid.

The approach considered in constructing transfer equations for the solid, in addition to those available, is applicable to the analysis and macrokinetic modeling of not only slow solid-phase reaction,[10] but also self-sustaining high-temperature synthesis, reactions proceeding under special conditions (e.g., under high pressures and deformations), and solid-phase detonation.

The high rates of chemical reactions, anomalous rates of mass transfer under mechanical effects, and the possibility of controlling the burning rate under static loading all appear to be related to the interaction mechanisms of the different physical and chemical processes described above.

Acknowledgment

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