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CONNECTED EQUATIONS OF HEAT AND MASS TRANSFER IN A CHEMICALLY REACTING SOLID MIXTURE WITH ALLOWANCE FOR DEFORMATION AND DAMAGE

A. G. Knyazeva

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Changes in the properties of a substance due to a chemical reaction (change in the concentration of components), thermal expansion upon heating, and inhomogeneities in the structure of the substance (both in the initial state and during heating and reaction) determine the volume changes $dV/V_0 = (V - V_0)/V_0$ of the substance. For many solids, these changes are small and have no effect on heat and mass transfer processes. For high heating rates or significant differences in the properties of the reactants and products, a volume change dV can lead to the occurrence of stresses in the reaction zone and even to damage (accumulation of defects and inhomogeneities in the structure compared with the initial state). We write these changes in the form

$$dV = \left(\frac{\partial V}{\partial T}\right)_{N_k,v_p} dT + \sum_k \left(\frac{\partial V}{\partial N_k}\right)_{T,v_p,N_{j,j\neq k}} dN_k + \left(\frac{\partial V}{\partial v_p}\right)_{T,N_k} dv_p + \ldots$$

or

$$\frac{V - V_0}{V_0} = 3\Big[\alpha_T(T - T_0) + \sum_k \alpha_k(N_k - N_{k0}) + \alpha_c(v_p - v_{p0})\Big], \qquad (1)$$

where $\alpha_T = (1/3)\,(\partial V/\partial T)V_0^{-1}$ is the coefficient of linear thermal expansion; $\alpha_k = (1/3)\,(\partial V/\partial N_k)V_0^{-1}$ is the coefficient of concentration expansion for each component; $\alpha_c = (1/3)(\partial V/\partial v_p)V_0^{-1}$ is the coefficient of structural expansion; N_k is the concentration of the kth component; v_p is the volume of damage (discontinuities, pores, cracks, etc.). We can speak in general about a change in structure inhomogeneity of one or another type. For simplicity of analysis, we restrict the consideration to overall volume changes. In expansion (1), only first-order terms are taken into account, by virtue of the smallness of the coefficients α_T, α_k, and α_c in accordance with their meaning for a solid medium. Let us determine how small changes (1) manifest themselves in heat and diffusion equations. For this recall that with temperature and volume changes in the system, the free energy F is the main thermodynamic potential [1]. Its total differential is written as

$$dF = dF^0 + dF'. \qquad (2)$$

Here dF^0 is the change in the free energy due to heating and chemical reaction:

$$dF^0 = -SdT + \sum_k \mu_k dN_k, \qquad (3)$$

where μ_k is the chemical potential of the kth component; S is the entropy of a unit volume; and dF' is the change in the free energy during deformation and damage:

$$dF' = \sum_{ij} \sigma_{ij} d\varepsilon_{ij} + \sum_{lm} \chi_{lm} d\omega_{lm}, \qquad (4)$$

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where ε_{ij} are the components of the strain tensor, σ_{ij} are the components of the stress tensor, ω_{lm} are the components of the damage tensor, and χ_{lm} is the corresponding potential. Similar approaches are used in fracture mechanics [2, 3]. According to (1), the damage tensor ω_{ij} can be described by one parameter $r = v_p/v_{p0}$. Hence, $\omega_{lm} = r$ for $l = m$ and $\omega_{lm} = 0$ for $l \neq m$. It follows from (2)-(4) that

$$\begin{aligned} S &= -(\partial F/\partial T)_{N_k,\varepsilon_{ij},\omega_{lm}}, \qquad \sigma_{ij} = (\partial F/\partial \varepsilon_{ij})_{N_k,T,\omega_{lm}}, \\ \mu_k &= (\partial F/\partial N_k)_{\omega_{lm},\varepsilon_{ij},N_{n,n\neq k},T}, \qquad \chi_{lm} = (\partial F/\partial \omega_{lm})_{N_k,T,\varepsilon_{ij}}. \end{aligned} \tag{5}$$

For an isotropic medium, to which we restrict our consideration, and for relatively small strains, the free energy can be expanded into a series in the vicinity of an undeformed state [4, 5], $F(T, N_k, r^0)$, where $r^0 = (v_p/v_{p0})^0$ is the degree of damage of the undeformed medium. In the general case, r^0 depends on the mixture ratio and temperature. Hence, the components of the tensor χ_{ij} in the undeformed state are determined as follows: $\chi_{ij} = (\partial F^0/\partial r^0)_{N_k,T}$. In a particular case, we can assume that $r^0 = \text{const} = 1$ for $\varepsilon_{ij} = 0$. With allowance for terms of second-order smallness with respect to ε_{ij} we have

$$F = F^0(T, N_k, r^0) + \left(\frac{\partial F}{\partial I_1}\right)^0 I_1 + \left(\frac{\partial F}{\partial I_2}\right)^0 I_2 + \left(\frac{\partial^2 F}{\partial I_1^2}\right)^0 \frac{I_1^2}{2} + \ldots, \tag{6}$$

where $I_1 = \varepsilon_{ij} = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}$; $I_2 = \varepsilon_{ij}\varepsilon_{ij}$.

From(5) and (6), we find expressions for the stress components:

$$\sigma_{ij} = \delta_{ij}\frac{\partial F}{\partial I_1} + \delta_{ij} I_1 \frac{\partial^2 F}{\partial I_1^2} + 2\varepsilon_{ij}\frac{\partial F}{\partial I_2}. \tag{7}$$

We determine the coefficients in (6) [or (7)] as in [4, 6] from empirical considerations. For $i \neq j$ from (7) we obtain $\sigma_{ij} = 2\varepsilon_{ij}(\partial F/\partial I_2)_{T,N_k,\omega_{lm}}$, $i \neq j$. From Hooke's second law for pure shear it follows that $\sigma_{ij} = 2G\varepsilon_{ij}$. Hence, we have $(\partial F/\partial I_2) = G$ (G is the shear modulus). For small purely elastic strains $G = \mu$ is valid (μ is the Lamé coefficient or the shear modulus within the limit of elasticity). For systems subjected to nonlinearly elastic or plastic deformations, we have $G = [E/2(1+\nu)](1-e) = \mu(1-e)$ [E is the elasticity modulus (Young's modulus); ν is the Poisson coefficient; and e is the generalized strain function [6, 7], which is different from zero beyond the limit of elasticity)].

For $i = j$ from (7) we find expressions for the components σ_{11}, σ_{22}, and σ_{33}, and, summing these, we obtain

$$\sigma_{ii} = 3\frac{\partial F}{\partial I_1} + \varepsilon_{ii}\left[3\frac{\partial^2 F}{\partial I_1^2} + 2\mu(1-e)\right] \tag{8}$$

where $\varepsilon_{ii} = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33} = I_1$ is the volume change. If there are no volume and mass forces, and the volume change ε_{ii} is due only to thermal, concentration, and structural expansion in the free state, we have $\varepsilon_{ii} = (V - V_0)/V_0$. Hence, the relationship between the expansion coefficients $\partial F/\partial I_1$ and $\partial^2 F/\partial I_1^2$ is written in the form

$$\frac{\partial F}{\partial I_1} = -\frac{dV}{V_0}\left[3\frac{\partial^2 F}{\partial I_1^2} + 2\mu(1-e)\right].$$

If the temperature, the concentrations of the mixture components, and the degree of damage do not change, i.e., the volume of the system is unchanged, from (8), we obtain

$$\sigma_{ii} = \varepsilon_{ii}\left[3\frac{\partial^2 F}{\partial I_1^2} + 2\mu(1-e)\right]. \tag{9}$$

For the uniaxial stressed state of such systems Hooke's first law holds, according to which $\sigma_{11} = E\varepsilon_{11}$, and transverse strains, according to the Poisson law, are related to ε_{11} by the formulas $\varepsilon_{22} = \varepsilon_{33} = -\nu\varepsilon_{11}$. In this case we have $\sigma_{ii} = \sigma_{11} = (E/(1-2\nu))\varepsilon_{ii}$. From a comparison of the latter equality and (9), we obtain $\partial^2 F/\partial I_1^2 = \lambda + 2\mu e/3$, where $\lambda = E\nu/[(1-2\nu)(1+\nu)]$ is the second Lamé coefficient. As a result, the free energy of the undeformed system is written as

$$F = F^0 - \frac{dV}{V_0}\left[\frac{2}{3}\mu + \lambda\right]\varepsilon_{kk} + \varepsilon_{ij}\varepsilon_{ij}\mu(1-e) + \varepsilon_{kk}^2\left[\frac{\lambda}{2} + \frac{\mu}{3}e\right], \tag{10}$$

where the repeated subscripts, as before, denote summation. The generalized Hooke's law for elastoplastic deformations of an isotropic reacting medium with allowance for its degree of damage is written as

$$\sigma_{ij} = -\delta_{ij}\left[\frac{dV}{V_0}\left(\frac{2}{3}\mu + \lambda\right) - \varepsilon_{kk}\left(\lambda + \frac{2}{3}\mu e\right)\right] + 2\mu(1-e)\varepsilon_{ij}. \tag{11}$$

Here the additional terms are due to temperature T and concentration changes and to structural distortions (1). The latter distinguishes these relations from those in [6]. The quantity $K = \lambda + 2\mu/3$ is the modulus of uniform compression. For $e = 0$, from (11), we obtain a relation for the first invariants of the stress and strain tensors in the form

$$\sigma_{kk} = 3K\left(\varepsilon_{kk} - \frac{V - V_0}{V_0}\right),$$

which coincides, in the corresponding limiting cases, with the well-known relationship for purely elastic deformations and constant volume [4] and with the relation obtained in [8] for systems with internal concentration stresses and strains. The analogy among temperature, concentration, and structural stresses also holds true in the presence of viscous deformation. To extend the resulting formula to the case of elastoplastic deformations, we write (10) in a somewhat different form (we set $e = 0$):

$$F = F^0 - K\frac{V - V_0}{V_0}\varepsilon_{kk} + \mu\left[\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{kk}\right]^2 + \frac{K}{2}\varepsilon_{kk}^2.$$

Bezukhov [7], when considering only concentration stresses, separates the part of the free energy that is determined in experiments in the absence of loads ($\sigma_{ij} = 0$). Proceeding similarly, from the latter expression we find that

$$F = F_{\text{chem}} - K\frac{dV}{V_0}\varepsilon_{kk} + \mu\left[\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{kk}\right]^2 + \frac{K}{2}\left(\varepsilon_{kk}^2 + \left[\frac{dV}{V_0}\right]\right)^2,$$

where $F_{\text{chem}} = F^0 - (K/2)\,[dV/V_0]^2$; dV/V_0 takes into account all types of strains that accompany the chemical reaction.

For further generalization, we separate the deviator part from the stress and strain tensors using the formulas $\tau_{ij} = \sigma_{ij} - \delta_{ij}\sigma_{kk}/3$, $e_{ij} = \varepsilon_{ij} - \delta_{ij}\varepsilon_{kk}/3$.

The fairly general rheological model of a viscoelastic body in [7, 8] uses the operator relationship

$$\mathbf{A}\tau_{ij} = \mathbf{B}e_{ij} \tag{12}$$

where $\mathbf{A}$ and $\mathbf{B}$ are differential operators that are linear in time. For example,

$$\mathbf{A} = a_m\frac{\partial^m}{\partial t^m} + a_{m-1}\frac{\partial^{m-1}}{\partial t^{m-1}} + \ldots + a_1\frac{\partial}{\partial t} + a_0.$$

The above analogy makes it possible to extend the theory of thermoviscoelasticity and concentration viscoelasticity to a more-general case. From (12) and the relationship between the first invariants of the stress and strain tensors, we obtain

$$\mathbf{A}\sigma_{ij} = \mathbf{B}\left[\varepsilon_{ij} - \delta_{ij}\varepsilon_{kk}/3\right] + \delta_{ij}\mathbf{A}K\left[\varepsilon_{kk} - \frac{dV}{V_0}\right],$$

from which for specific types of operators $\mathbf{A}$ and $\mathbf{B}$ we obtain relationships between stresses and strains for the particular cases of viscoelastic media. Thus, for the Maxwell viscoelastic model [9],

$$\mathbf{A} = \frac{1}{2\mu}\frac{\partial}{\partial t} + \frac{1}{2æ}, \quad \mathbf{B} = \frac{\partial}{\partial t}$$

where æ is the shear coefficient of viscosity, we have

$$\dot{\sigma}_{ij} + \frac{\mu}{æ}\sigma_{ij} = 2\mu\dot{\varepsilon}_{ij} + \delta_{ij}\left[\frac{\partial}{\partial t}\left(K\varepsilon_{ij} - K\frac{dV}{V_0}\right) - \frac{2}{3}\mu\dot{\varepsilon}_{ij} + \frac{\mu K}{æ}\left(\varepsilon_{kk} - \frac{dV}{V_0}\right)\right]. \tag{13}$$

In addition to the generalized relations (11) and (13), using (5) we obtain the chemical potentials of the components of the reacting mixture:

$$\mu_k = \mu_k^0 - \varepsilon_{mm}\frac{\partial}{\partial N_k}\left[\frac{dV}{V_0}\left(\frac{2}{3}\mu + \lambda\right)\right] + \varepsilon_{ij}\varepsilon_{ij}\frac{\partial}{\partial N_k}\mu(1-e) + \varepsilon_{mm}^2\frac{\partial}{\partial N_k}\left[\frac{\lambda}{2} + \frac{\mu}{3}e\right]$$

where μ_k^0 is the chemical potential of the kth component in the absence of stresses and strains.

In the same way, we obtain formulas for entropy

$$S = -S_0 + \varepsilon_{mm}\frac{\partial}{\partial T}\left[\frac{dV}{V_0}\left(\frac{2}{3}\mu + \lambda\right)\right] - \varepsilon_{ij}\varepsilon_{ij}\frac{\partial}{\partial T}\mu(1-e) - \varepsilon_{mm}^2\frac{\partial}{\partial T}\left[\frac{\lambda}{2} + \frac{\mu}{3}e\right] \tag{14}$$

and for the damage potential

$$\chi_{lm} = \chi_{lm}^0 - \varepsilon_{kk}\frac{\partial}{\partial \omega_{lm}}\left[\frac{dV}{V_0}\left(\frac{2}{3}\mu + \lambda\right)\right] + \varepsilon_{ij}\varepsilon_{ij}\frac{\partial}{\partial \omega_{lm}}\mu(1-e) + \varepsilon_{kk}^2\frac{\partial}{\partial \omega_{lm}}\left[\frac{\lambda}{2} + \frac{\mu}{3}e\right].$$

In the particular case of constant λ and μ, we have

$$\mu_k = \mu_k^0 - (3\lambda + 2\mu)\,\alpha_k\varepsilon_{mm}, \qquad S = -S^0 + (3\lambda + 2\mu)\,\alpha_T\varepsilon_{mm},$$
$$\chi_{lm} = \chi_{lm}^0 - \delta_{lm}\,(3\lambda + 2\mu)\,\alpha_c v_{p0}\varepsilon_{kk}.$$

According to the definition of the damage tensor, the components of the tensor χ_{lm}^0 are written in a form similar to ω_{lm}:

$$\chi_{lm}^0 = \left(\partial F^0/\partial r^0\right)_{N_k,T} = h^0, \quad l = m; \quad \chi_{lm}^0 = 0, \quad l \neq m.$$

Here h^0 is determined by the internal properties of the medium and its structure. In particular, if r^0 is the relative volume of dislocations in a crystal (accumulations of dislocations), which are potential centers of fracture (formations of microcracks) [10] and potential nucleation sites during initiation of a solid state reaction [11], h^0 is their structural chemical potential. By analogy, one can introduce the potential for damage of various types. Variants of the tensor description of damage in a medium are given, e.g., in [2, 12, 13].

The balance equations for any additive quantity a are common for any type of continuous media (with damage and without it) [1, 5]:

$$\frac{\partial a}{\partial t} = -\mathrm{div}\mathbf{J}_a + \dot{\varphi}_a, \tag{15}$$

where $\mathbf{J}_a$ is the flux of the quantity a; $\dot{\varphi}_a$ is the sum of sources and sinks for a (components of the reacting mixture and damage of different types). The Onsager relations between the fluxes and the forces acting on the latter are also identical for continuous media of various types. In addition, we write the equilibrium equation

$$\sigma_{ij,i} + \mathbf{X}_i = 0 \tag{16}$$

where $\mathbf{X}_i$ are the components of the external force vector). For high-velocity processes, (16) should take into account inertial terms.

Let us next consider specific types of reactions and media. We assume that a solid-state reaction described by the scheme $A_s \rightarrow B_s$ proceeds in the system. The initial chemical potential μ^0, entropy S^0, and the initial properties of the medium are determined with allowance for its initial damage. The energy equation in the form of a generalized heat equation for a simple isotropic medium is written as [5]

$$T\frac{\partial S}{\partial t} = -\mathrm{div}\mathbf{J}_q + W,$$

where $T\partial S/\partial t$ is the amount of heat absorbed by a unit volume per unit time; $\mathbf{J}_q$ is the heat flux density; W is the density of the internal heat sources and sinks (for example, of a chemical nature). Ignoring the overlapping effects, i.e., assuming that the heat flux density is proportional only to the temperature gradient $\mathbf{J}_q = -\lambda_T \mathrm{grad\,T}$, taking into account that $\partial S^0/\partial t = -(c_\varepsilon \rho_0 \partial T/\partial t)T^{-1}$ [1, 5], and using (14), we obtain

$$\rho_0 c_\varepsilon \frac{\partial T}{\partial t} = \mathrm{div}(\lambda_T \mathrm{grad}\, T) + W - T\frac{\partial}{\partial t}\varepsilon_{kk}\frac{\partial}{\partial T}\left[K\frac{dV}{V_0}\right]. \tag{17}$$

In the particular case of elastic uniaxial deformation (i.e., when only one component of the tensor $\varepsilon_{ij} - \varepsilon_{11}$ is different from zero), we have

$$\varepsilon_{kk} = \varepsilon_{11} \quad \text{and} \quad \sigma_{11} = (\lambda + 2\mu)\varepsilon_{11} - KdV/V_0, \quad \sigma_{22} = \sigma_{33} = \lambda\varepsilon_{11} - KdV/V_0.$$

For the reaction considered, from (1) we obtain

$$\frac{dV}{V_0} = 3\left[\alpha_T (T - T_0) + \Delta\alpha_\eta \eta + \alpha_c v_{p0} (r - 1)\right]. \tag{18}$$

Here η is the degree of conversion of the substance; the quantity $\Delta\alpha_\eta$ is proportional to the difference in the coefficients of concentration expansion between the product and the reactant. In the general case, the parameter $\Delta\alpha_\eta$ can have any sign. If $\Delta\alpha_\eta > 0$, the concentration stresses are tensile; otherwise, they are compressive. Structural inhomogeneities such as dislocations and microcracks should facilitate tensile-stress relaxation; therefore, it is reasonable to assume that $\alpha_c < 0$. We note that inhomogeneities are themselves sources of stresses, and hence positive values of α_c are possible in principle. In the absence of external forces, from (16), (18), and Hooke's law it follows that

$$\varepsilon_{11} = \frac{3\lambda + 2\mu}{\lambda + 2\mu}\frac{dV}{3V_0}, \tag{19}$$

i.e., the magnitude and sign of strains that accompany a solid-state chemical reaction depend on the temperature (hence on the thermal effect of the reaction), the degree of conversion (or change in the properties of the substance during the reaction), and the damage to the medium. In turn, internal strains directly affect the temperature field. For example, for unchanged λ and μ, we have

$$\rho_0 c_\varepsilon \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\lambda_T\frac{\partial T}{\partial x} + W - T\frac{(3\lambda + 2\mu)^2}{\lambda + 2\mu}\alpha_T^2\left[\frac{\partial T}{\partial t} + \frac{\Delta\alpha_\eta}{\alpha_T}\frac{\partial\eta}{\partial t} + \frac{\alpha_c v_{p0}}{\alpha_T}\frac{\partial r}{\partial t}\right],$$

where the terms in the braces are additional heat sources and sinks, which owe their origin to the connectedness of the deformation, heat transfer, and damage processes in the substance. The extent to which damage processes influence temperature is determined by the specific kinetics of the damage. In many models [13], the damage accumulation rate $\partial r/\partial t$ is a function of pressure $p < 0$, which can be determined as

$$p = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3. \tag{20}$$

Hence, during a chemical reaction the degree of damage is an inherent property of the reaction. In the simplest case, where the accumulation of the reaction product is governed only by the act of chemical transformation, for η we write

$$\frac{\partial\eta}{\partial t} = z_0\varphi_1(\eta)\varphi_2(T, \sigma_{ij}, \varepsilon_{ij}). \tag{21}$$

In developing macrokinetic models of various solid-state reactions [11], the question arises (see, for example, [8, 14, 15]) as to the mechanism of solid-state diffusion, which in essence determines the solid-state reaction rate or is one of the main stages of the reaction. Assuming that the flux of each component $\mathbf{J}_k$

depends only on the gradient of its chemical potential and taking into account the well-known relation for diagonal kinetic coefficients in the Onsager formulas $L_{kk} = D_{kk}N_k/(kT)$ (k is the Boltzmann constant), for unchanged λ, μ we have

$$\mathbf{J}_1 = -L_{11}\left\{\nabla\mu_1^0 + (\alpha_2 - \alpha_1)(3\lambda + 2\mu)\nabla\varepsilon_{kk}\right\}, \quad \mathbf{J}_2 = -L_{22}\left\{\nabla\mu_2^0 - (\alpha_2 - \alpha_1)(3\lambda + 2\mu)\nabla\varepsilon_{kk}\right\}$$

where $\nabla\mu_1^0$, $\nabla\mu_2^0$ are the chemical potentials of the combined reactants and products without taking into account strains, $\nabla\mu_k^0 = kT\nabla N_k/N_k$. Using the concept of the degree of conversion, from (15) and the latter formulas, we obtain

$$\frac{\partial\eta}{\partial t} = \operatorname{div}\left[D'\operatorname{grad}\eta\right] + z_0\varphi_1(\eta)\varphi_2(T, \sigma_{ij}, \varepsilon_{ij}),$$

where

$$D' = D_{22}\left(1 - \Delta\alpha_\eta\frac{3\lambda + 2\mu}{kT}\eta\frac{\nabla\varepsilon_{kk}}{\nabla\eta}\right)$$

is the effective diffusion coefficient. In the particular case of uniaxial strain and constant λ and μ we have

$$\frac{\partial\eta}{\partial t} = \frac{\partial}{\partial x}D_{22}\frac{\partial\eta}{\partial x} + z_0\varphi_1\varphi_2 - \Delta\alpha_\eta(3\lambda + 2\mu)D_{22}\left[\frac{\eta}{kT}\frac{\partial^2\varepsilon_{11}}{\partial x^2} - \frac{\eta}{kT^2}\frac{\partial\varepsilon_{11}}{\partial x}\frac{\partial T}{\partial x} + \frac{1}{kT}\frac{\partial\varepsilon_{11}}{\partial x}\frac{\partial\eta}{\partial x}\right] \tag{22}$$

where ε_{11} is the result of the chemical reaction itself.

The diffusion equation (22) is essentially nonlinear even with such a primitive approach to mass transfer in a solid. When considering specific diffusion mechanisms in crystalline bodies or glass-like polymers, these equations become even more complicated. In this case it is important to take into account possible feedback between the diffusion in a solid body, the chemical reaction rate, and the stresses and strains which inevitably accompany a solid-state reaction. Depending on the value and sign of the resulting total strains, the effective diffusivity can either decrease or increase, and this is determined by the specific type of reaction.

A similar equation of the diffusion type can be derived for the degree of damage r in the medium, in particular for dislocations.

We consider two different examples of use of the suggested approach. The simplest model for the initiation of a solid state reaction $A_s \to B_s$ (unsteady solid- state combustion) includes an energy equation in the form of a generalized heat equation that follows from (19):

$$c'_\varepsilon\rho_0\frac{\partial T}{\partial t} = \lambda_T\frac{\partial^2 T}{\partial x^2} + Q'_0 z_0\varphi_1(\eta)\varphi_2(T) - \varphi_3(T, r),$$

where

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

$$\varphi_2(T) = \exp\left(-\frac{E}{RT}\right); \qquad \varphi_1(\eta) = 1 - \eta; \qquad \varphi_3(T, r) = \frac{\text{æ}}{\gamma}\delta\frac{T}{T_*}\frac{\partial r}{\partial t}$$

is the additional heat release due to damage; $\gamma = c_\varepsilon\rho_0 RT_*^2/(EQ_0)$ is a small parameter in combustion theory; $g = \Delta\alpha_{BA}c_\varepsilon\rho_0/(\alpha_T Q_0)$; $\text{æ} = \alpha_c v_{c0}c_\varepsilon\rho_0/(\alpha_T V_0 Q_0) < 0$; $\delta = (3K\alpha_T)^2 T_*/[(\lambda + 2\mu)c_\varepsilon\rho_0]$ is the coefficient of connectedness of the strain and temperature fields, and also the equation for the stationary product (20), where the heat release function depends only on temperature and on the fraction of the reactant $1 - \eta$ and the initial and boundary conditions are as follows:

$$x = 0: \quad -\lambda_T\frac{\partial T}{\partial x} = q_0, \qquad x \to \infty: \quad \frac{\partial T}{\partial x} = 0, \qquad t = 0: \quad T = T_0, \quad \eta = 0.$$

Strains are related to other quantities by formula (17).

In terms of the variables

$$\theta = \frac{T - T_*}{RT_*^2/E}, \; \xi = \frac{x}{\sqrt{\text{æ}_T t_*}}, \; \tau = \frac{t}{t_*}, \; r = \frac{v_c}{v_{c0}}, \; e_{11} = \varepsilon_{11}/\varepsilon_*, \; \varepsilon_* = 3\alpha_T K(T_* - T_0)/(\lambda + 2\mu)$$

we write this problem in the form

$$f_1(\theta)\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\xi^2} + \varphi_1(\eta)\varphi_2(\theta)f_2(\theta) - \frac{\partial r}{\partial\tau}f_3(\theta),$$

$$e_{11} = \theta + \theta_0 + \frac{g}{\gamma}\eta + \frac{æ}{\gamma}(r-1), \qquad \frac{\partial\eta}{\partial\tau} = \gamma\varphi_1(\eta)\varphi_2(\theta),$$

$$\xi \to 0: \quad -\partial\theta/\partial\xi = Q_0, \qquad \xi \to 0: \quad \partial\theta/\partial\tau = 0; \qquad \tau = 0: \quad \theta = -\theta_0, \quad \eta = 0, \quad r = 1,$$

where

$$\theta_0 = \frac{T_* - T_0}{RT_*^2/E} \gg 1; \quad Q_0 = \frac{q_0 E\sqrt{æ_T t_*}}{RT_*^2}; \quad \varphi_2(\theta) = \exp\left(\frac{\theta}{1+\beta\theta}\right);$$

$$\varphi_1(\eta) = 1 - \eta; \quad \beta = RT_*^2/E \ll 1;$$

T_* is the characteristic temperature of the process (for example, the ignition temperature [16]); t_* is the characteristic time of chemical reaction (for example, the period of adiabatic induction at temperature T_* [16]). For the accumulation of damage we assume the law which is rather popular in failure mechanics [13]:

$$\frac{\partial v_c}{\partial t} = -\frac{p}{æ_c}\left[v_c + v_c^*\exp\left(-\frac{p}{p_0}\right)\right], \qquad p < 0, \qquad \frac{\partial v_c}{\partial t} = 0, \quad p \geqslant 0.$$

Here p_0 characterizes the critical level of the average pressure (20) that is necessary for the occurrence of damage; $æ_c$ has the meaning and dimensionality of dynamic viscosity; v_c^* is the specific volume of potential centers of formation of cracks or of pores, which essentially can be identified with v_{c0}. In dimensionless variables we have

$$\frac{\partial r}{\partial\tau} = -sk_c\left[r + \exp\left(-\frac{s}{s_0}\right)\right], \qquad s < 0,$$

where $s = p/\sigma_*$; $s_0 = p_0/\sigma_*$; $k_c = \sigma_* t_*/æ_c$; $\sigma_* = \varepsilon_*(\lambda + 2\mu)$. In this case, in contrast to existing theories for similar processes, the physical reason for the temperature dependence of heat capacity is clear. In addition, the dependence of heat release in a chemical reaction on the type of reaction is explicitly obtained, i.e., if the reaction proceeds with volume expansion ($g > 0$), the concentration stresses and strains decrease the total exoeffect; if the reaction proceeds with a decrease in volume ($g < 0$), the effect of an apparent parallel exothermic reaction is observed. According to the meaning of the physical parameters involved in the dimensionless complex, the value of this complex $æ_c$ is most likely small, since $\alpha_c \approx \alpha_T Q_0/(c_\varepsilon \rho_0)$ and $v_c/v_{c0} \ll 1$. The connectedness coefficient δ calculated at temperature T_* is on the order of 1, which distinguishes it from the analogous coefficient in thermoelasticity theory. An example of numerical solution of the problem for $\beta = 0.032$, $\delta = 0.392$, $g = 2$, $\theta_0 = 16.2$, $k_c = 0.03$, $s_0 = 4.18$, $æ = -10^{-2}$, $\gamma = 0.034$ is given in Fig. 1. It is seen from this figure that strains follow the chemical reaction zone deep into the substance and tensile stresses in the front plane lead to damage in the reaction zone. The values of the parameters p_0 and $æ_c$ used in estimating s_0 and k_c are characteristic of failure mechanics.

The calculations show that all possible energetic terms entering into the heat equation (heat release in reaction, endoeffect or exoeffect of the apparent parallel reaction, heat release due to damage, etc.) are comparable in magnitude and, depending on the values of the parameters lead to different modes of propagation of the reaction. As a result, the characteristics of the reaction zone determined in an experiment may not have the physical meaning that was assigned to them according to classical ignition and combustion theories. An analysis of a steady-state model of a solid-state combustion front based on such ideas has been carried out in [17].

As a second example we consider a steady-state model of a decomposition reaction $A_s \to B_g$. Macrokinetic models of diffusion reactions are little used. The features of such reactions can be outlined rather briefly. They include localization of the reaction at the interface between the reactant and the product, the important role of transfer processes of one or another type, and the presence of feedback between various physical phenomena accompanying the reaction. The decomposition of solids under isothermal conditions can

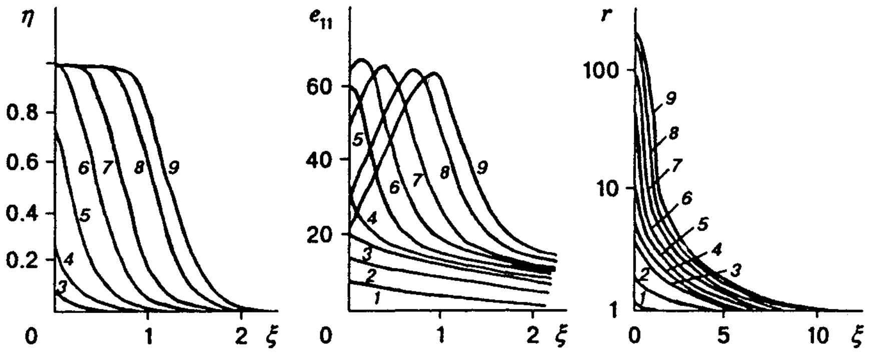

Fig. 1. Spatial distribution of the degree of conversion η, deformations e_{11}, and specific volume of damage r at different moments in time: curves 1–9 correspond to $\tau = 2$, 6, 10, 11.5, 13.3, 15, 16.7, 18.7, and 20

begin on the surface for two main reasons. First, the best conditions for removal of the reaction products (liquid or gaseous) exist there. Second, a solid surface is the most active place for a reactant; inhomogeneities, i.e., potential centers of nucleation of the product are concentrated there. In this case, the initial concentration of the product in the surface layer is a characteristic of the chemical reactivity of the substance. The further reaction has a frontal character due to the presence of feedback between different physical phenomena and the chemical reaction. The simplest steady-state model of reaction-front propagation for the reaction $A_s \to B_g$ (under isothermal conditions) with allowance for deformation and damage follows from (17), (21), and (22) and includes the equation of consumption of the solid reactant A, which is considered immovable,

$$-v_n\frac{d\eta_1}{dx} = -z_1\eta_1^n\eta_2^m, \qquad x > 0,$$

the diffusion equation for the gaseous product B in the solid phase

$$-v_n\frac{d\eta_2}{dx} = D_s\frac{d}{dx}\left\{\frac{d\eta_2}{dx} - \frac{\eta_2}{kT}3K\alpha_T\frac{d\varepsilon_{11}}{dx}\right\} + z_2\eta_1^n\eta_2^m, \qquad x > 0,$$

where $e_{11} = 3K\{\alpha_A(\eta_1 - \eta_{10}) + \alpha_B(\eta_2 - \eta_{20}) + \alpha_c(v_c - v_{c0})\}$, the diffusion equation for the product in the gaseous phase ($\eta_2 \to \eta_g$)

$$-v_n\frac{d\eta_g}{dx} = D_g\frac{d^2\eta_g}{dx^2}, \qquad x < 0,$$

the balance relationships at the interface $x = 0$

$$\eta_g = \eta_2 = \eta_*, \qquad -D_g\frac{d\eta_g}{dx} = -D_s\frac{d\eta_2}{dx} + D_s\frac{\eta_2}{kT}3K\alpha_T\frac{d\varepsilon_{11}}{dx}$$

and the conditions at infinity from $x = 0$

$$x \to \infty: \quad \eta_1 = 1, \quad \eta_2 = 0; \qquad x \to -\infty: \quad \eta_g = \eta_g^\infty.$$

The steady-state problem is written in the system of coordinates connected with the reaction front; the quantity $z_2/z_1 = k_0$ shows how many moles of substance B are formed from substance A; the source terms in the equations for the components reflect the autocatalytic character of most solid-state decomposition reactions [11]; n and m are the formal orders of the reaction with respect to the reactant and the product (as a rule, fractional quantities). The solid–gas interface is determined by the condition $x = 0$: $\eta_1 \to 0$, $v_c/V_0 \to 1$, which in fact corresponds to complete damage. In the stationary problem, the diffusion equation for a gas has only the trivial solution $\eta_g = \eta_g^\infty = \eta_2(0) = \eta_*$. The equations for the solid phase admit the first integral. As a result, the problem is reduced to integration of a system of first-order differential equations, which is

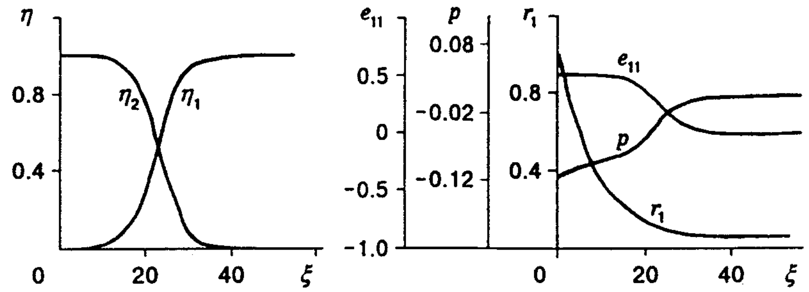

Fig. 2. Profiles of concentrations, stresses, strains, and the degree of damage in a stationary wave of chemical reaction $A_s \to B_g$: $p = 3.5$, $r_{10} = 0.05$, $\omega = 0.3$, $w_n = 3.0$, $æ = 0.1$, $\alpha = 2.0$, $k_0 = 1$, and $\gamma_{c*} = 1.71$

written in terms of the variables $\xi = x/\sqrt{D_s/z_1}$ and $r_1 = v_c/V_0$ (different from r) in the form

$$\frac{d\eta_1}{d\xi} = \eta_1^n \eta_2^m w_n^{-1},$$

$$\frac{d\eta_2}{d\xi}[1 - \omega\eta_2] = -\Big\{w_n\eta_2 + k_0 w_n(\eta_1 - 1) - \omega\alpha^{-1}\eta_1^n\eta_2^{m+1}w_n^{-1} - \frac{\omega æ}{\alpha r_{10}}\eta_2\frac{dr_1}{d\xi}\Big\},$$

$$\frac{dr_1}{d\xi} = \begin{cases} s\gamma_c[r_1 + r_{10}\exp(-s/s_0)]/w_n, & s < 0, \\ 0, & s \geqslant 0, \end{cases}$$

$$e_{11} = \eta_1 - 1 + \alpha\eta_2 + æ(r_1 - r_{10})/r_{10},$$

$$\xi \to \infty: \quad \eta_1 = 1, \quad \eta_2 = 0, \quad r_1 = r_{10} = v_{c0}/V_0 \ll 1;$$

$$\xi \to 0: \quad \eta_1 = \eta_{1*} \ll 1, \quad \eta_2 = \eta_{2*} \leqslant k_0, \quad r_1 \to 1,$$

where $\alpha = \alpha_B/\alpha_A$; $\omega = 3K\alpha_B^2\varepsilon_*/kT\alpha_A$; $\varepsilon_* = 3\alpha_A K N_{A0}/(\lambda + 2\mu)$; $e_{11} = \varepsilon_{11}/\varepsilon_*$; $w_n = v_n/\sqrt{D_s z_1}$; and $æ = \alpha_c v_{c0}/(\alpha_A N_{A0})$.

An analysis shows that to each value of the front velocity $w_n > w_{n*}$ satisfying the conditions of the problem and the monotonicity of the concentration profile $\eta_1 \in]0.1[$ corresponds a unique value of the rate constant of crack growth γ_{c*} that ensures joint steady-state propagation of the chemical reaction zone and the failure zone. Concentration, stress, and strain profiles and the profile of the degree of damage in the reaction zone of a steady-state wave of chemical reaction are shown in Fig. 2.

Note that similar modes of propagation of chemical transformation are observed under real conditions. Thus, degradation in the reaction zone is characteristic of the decomposition of azides, ammonium perchlorate, and potassium permanganate [11, 18], where diffusion is an elementary reaction stage.

In conclusion we note that the coefficients α_k, α_T, and α_c used above are well-known quantities in heat- and mass-transfer theory [6], in the theory of elasticity, in thermomechanics [9], and in the connected theories of matter transfer and of strain [8, 9, 14, 15], but for the consideration of specific physical processes or reactions of different types, these quantities need a more precise definition. Thus, for purely solid-state diffusion in a system of two substances (A and B), the ratio of the concentration expansion coefficients α_A and α_B is assumed to be equal to the ratio of the atomic volumes of the diffusing substances [8, 14]. By the atomic volume is meant the volume occupied by a given atom in its crystalline lattice. If the substances A and B are in different phases, the ratio of the coefficients apparently must be proportional to the ratio of the typical atomic or molecular volumes of these substances. Naturally, as the gaseous product moves in the solid phase toward the gaseous phase, this ratio is changed.

Consequently, the coefficients α_T, α_k, and α_c are in the general case functions of the temperature, of the concentration of components, and of the degree of damage of the medium, as was assumed in [6].

The quantity v_c (volume of damage) has been borrowed from the kinetic theory of failure [2, 3, 13]. Also, numerous models of media with chemical reactions have been described in the literature [5]. For historical reasons, however, these models have not been used widely in macrokinetics.

The above method of deriving transfer equations for a solid, in addition to [19], can be applied not only to the analysis and macrokinetic modeling of slow solid-state reactions, examples of which are given in [11], but also to modeling SHS processes, reactions under specific conditions (for example, under conditions of high pressure and strain), and solid-state detonation. The high chemical reaction rates and anomalous velocities of mass transfer appear to be associated with the above mechanisms of interaction of different physical and chemical processes.

Similar methods, a survey of which is given in [5], can be used to develop models of anisotropic and nonlinear media.

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