

Macrokinetics of Fast Reactions

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Various forms of chemical reaction macrokinetics are considered taking into account the possible acceleration of processes in regions with high parameter gradients, in particular, in the vicinity of shock waves. The possibility of determining the kinetics from data of a dynamic experiment is evaluated.

Key words: kinetics, detonation, explosives, chemical reaction.

INTRODUCTION

Despite extensive studies of chemical reaction kinetics, in most practically important cases one has to use simplifications. The so-called detailed kinetics, which sometimes include many hundreds of reactions, are applicable only to gases, and still give a rather crude description of real processes. Naturally, the accuracy of the models deteriorates in the case of complex gas-dynamic problems, where kinetics is combined with fast flows of the medium (especially in the case of detonation waves). For condensed materials, such kinetics are not used at all because there are no well-established data on elementary reactions behind the shock front (see [1]). Therefore, almost without exception, gas-dynamic processes in dense materials are described using a macrokinetic approach. Having specified the form of kinetic equation, one selects its parameters by comparing calculations and experimental results [2–8]. The most successful models can describe a wide range of phenomena, such as initiation, two- and three-dimensional unsteady motions, interaction of waves with inert materials, critical propagation conditions, etc.

Use is made of both scalar and more complex kinetics with several kinetic equations (for example, [5]). In most cases, the reaction rate is a function of the current parameters of the medium (degree of conversion, pressure, density, temperature, etc.). In such models, the degree of conversion is zero after the passage of a shock front.

Strong nonequilibrium of the medium behind a shock front is unquestionable [1]. The acceleration of the reaction in the vicinity of a shock front due to nonequilibrium in energy distribution has been shown by calculations [9, 10]. The result can be interpreted as a jump in the degree of conversion at the shock front. This possibility has been discussed previously [11, 12]. The experimental situation is ambiguous. In dense explosives, the chemical reaction time (chemical spike duration) is usually a few tens of nanoseconds, and in materials with a large excess of carbon, it is hundreds of nanoseconds (see, e.g., [1]). However, in a number of studies with the highest-density explosives (porosity of about 1%), a chemical spike was not recorded [13–15], which may indicate a sharp narrowing of the reaction zone beyond the resolution of the techniques (about 5 nsec), or a qualitative change in the kinetics. In contrast, in [16], a chemical spike was observed under the same conditions. Later, profiles without a distinct chemical spike were obtained at lower densities [17, 18]. Some discrepancies between the results of [13, 14] and [16, 17] may indicate an important role of the charge structure. We note that empirical kinetics can include the initial energy release in a narrow zone adjacent to the front [2] or a jump at the front [19, 20].

The possibility of accelerating reactions due to nonequilibrium has stimulated the search for kinetics able to describe such effects, in particular, jumps in chemical composition. One of the generalizations that has been considered for a long time is the abandonment of the algebraic form of the reaction equation. It has been suggested [21, 22] that the kinetic equation should include the flow velocity divergence as a material variable. Obviously, in regions with high gradients,

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this variable will be significant. Special experiments have been performed to identify this dependence [23, 24], which, however, have not been successful. In our opinion, this might be caused by an inappropriate choice of the form of the desired relationship.

This paper discusses various types of kinetics with an explicit dependence on derivatives and the possibility of detecting such nonclassical kinetics. Initially, as a starting point, we consider classical kinetics. The next section analyzes two variants of kinetics that explicitly includes derivatives. Next, we discuss the physical mechanisms that could produce such effects, give an example of their influence on the wave structure, and formulate the main conclusions.

CLASSICAL KINETICS AND DYNAMIC EXPERIMENT

As a first step in determining kinetics, it is common to consider the one-dimensional unsteady flow of the reactive medium. We will also follow the usual assumptions of insignificant viscosity, diffusion, and thermal conductivity. Under these assumptions, the dynamics of the reactive medium in Lagrangian variables is described by the equations

$$\frac{\partial V}{\partial t} - V_0 \frac{\partial u}{\partial x} = 0, \quad \frac{\partial u}{\partial t} + V_0 \frac{\partial P}{\partial x} = 0. \quad (1)$$

Here t is time, x is the Lagrangian coordinate, u is the flow velocity, V is the specific volume of the material, V_0 is the initial specific volume (constant for a homogeneous sample), and P is the pressure. The energy equation has the form

$$\frac{\partial E}{\partial t} + P \frac{\partial V}{\partial t} = 0. \quad (2)$$

Next, the equation of state is needed:

$$E = E(P, V, \lambda). \quad (3)$$

Here the parameter λ describes chemical reactions. We restrict ourselves to the simplest version in which λ is a scalar variable which varies from zero in the initial state to 1 in the final equilibrium state (the degree of conversion). Finally, we need the kinetic equation

$$\frac{\partial \lambda}{\partial t} = f(P, V, \lambda). \quad (4)$$

System(1)–(4) is self-contained. Given the form of the thermodynamics (3) and kinetics (4), we obtain solutions that describe the evolution of the system (usually after the shock wave has entered the reactive sample). The adequacy of the adopted model of the medium can be judged by comparing the solutions with experiment. If necessary, models (3) and (4) are adjusted by varying

the parameters. The experimental data are records of the sensors placed in the material or information on the velocity at the sample boundary.

The procedure described above is logically simple but the empirical elements present in it may cause doubt. In particular, there is no confidence in the uniqueness of the set of kinetic and thermodynamic constants obtained in this manner. Of interest therefore are approaches to extracting kinetics from experimental data in a more regular manner.

One of such approaches was proposed in [23–27]. Analysis [25] presupposes that the fields of dynamic variables are determined by the sensor system and calculation [e.g., the field of u is measured by Lagrangian particle velocity sensors, and the fields of V and P are calculated from (1)]. It is also possible to measure pressure by Manganin gauges and calculate V and u or to measure deformations and calculate P and u . The field of E is found from (2) taking into account the Hugoniot condition at the shock wave. Below, we assume that all these fields are known.

Thermodynamics and kinetics are determined as follows. In view of (3), Eq. (2) can be written as [23, 28]

$$\frac{\partial P}{\partial t} + \frac{c^2}{V^2} \frac{\partial V}{\partial t} + \beta \frac{\partial \lambda}{\partial t} = 0, \quad (5)$$

where

$$\beta = \frac{\partial E / \partial \lambda}{\partial E / \partial P}, \quad c^2 = V^2 \frac{\partial E / \partial V + P}{\partial E / \partial P}. \quad (6)$$

In (6), the derivatives of each of the variables P , V , and λ are taken under the assumption of constancy of the remaining two variables. It is easy to show that c is the common frozen sound velocity:

$$c^2 = -V^2 \left(\frac{\partial P}{\partial V} \right)_{S, \lambda}.$$

For example, in the simplest case where the medium is described by the ideal gas equation

$$E = \frac{PV}{\gamma - 1} - \lambda Q \quad (7)$$

with constant adiabatic exponent γ and the reaction heat Q , the following relations hold:

$$c^2 = \gamma PV, \quad \beta = -\frac{(\gamma - 1)Q}{V}.$$

Next, $\dot{P} = -\beta \partial \lambda / \partial t$ is introduced instead of the formal reaction rate $\partial \lambda / \partial t$. From Eq. (5), we obtain

$$\dot{P} = \frac{\partial P}{\partial t} + \frac{c^2}{V^2} \frac{\partial V}{\partial t}. \quad (8)$$

In [23], the quantity \dot{P} introduced in [29] as a measure of the reaction rate is called the general kinetic characteristic (GKC). An example of its determination from experimental data is presented in [23, 24]. (In [22, 25, 26],

the kinetic component \dot{V} of the rate of volume change $\partial V/\partial t$ was used, which does not introduce fundamental changes.) To extract \dot{P} from Eq. (8), one needs to know the speed of sound c . In [23, 24], it was determined from observations of rarefaction waves (i.e., from the same records of sensors).

The use of the GKC as the sought quantity partly eliminates the problem of the formal nature of kinetics of the type (4), for which the notion of chemical variable is not unique. For example, with the same result, instead of the degree of conversion λ , one can use any of its monotonic functions. The quantity \dot{P} does not depend on such transformations. The kinetic characteristics and the speed of sound in the simplest variant are chosen from the known fields of P, V , and E in the form of functions

$$\dot{P} = \dot{P}(P, V, E), \quad c = c(P, V, E). \quad (9)$$

Once expressions (9) are obtained, it is possible to calculate any problems using Eqs. (1), (2), and (8). In this case, Eq. (2) plays the role of a kinetic equation, i.e., the composition variable is replaced by internal energy.

This procedure presupposes that the GKC determined under particular experimental conditions is also appropriate under different conditions. This is true for scalar kinetics of the type (4), (9) but not necessary for kinetics of a more general form. However, this problem is common to most approaches; it is obvious that scalar kinetics is an approximation whose validity should be verified by experiment. To date, scalar kinetics prevail, and their effectiveness can therefore be taken as an empirical fact. Note that vector kinetics reaches a more accurate description by introducing several kinetic variables, whereas scalar kinetics can be adjusted by increasing the number of selected parameters.

KINETICS DEPENDENT ON DERIVATIVES

The approach proposed by Trofimov is to expand the list of arguments of \dot{P} in (9) by adding derivatives: $\text{div} \mathbf{u}$ (in the one-dimensional case, $\partial u/\partial x$) [22] or $\partial V/\partial t$ [23–26]. By virtue of (1), these derivatives are proportional and any of them can be used. Below, we consider the consequences of allowing for the possible dependence of the kinetics on the rate of volume change $\partial V/\partial t$.

For the further analysis, the GKC is a transformation which is convenient in some respects but does not fundamentally affect the result. We shall therefore use a more standard approach which is outlined at the beginning of the previous section. Let us consider the

simplest version of nonclassical kinetics to clearly understand its properties. Instead of Eq. (4), let the following equation hold:

$$\frac{\partial \lambda}{\partial t} = f(V, P, \lambda) - A \frac{\partial V}{\partial t}. \quad (10)$$

Here A is a coefficient that can depend on P, V , and E or on P, V , and λ ; its positive sign corresponds to the acceleration of the reaction under compression (in particular, the final degree of conversion during passage of the shock front). Because the sound velocity in (5) is also determined from experiment, we need to find the propagation velocity of perturbations for system (1), (5), (10). Introducing small perturbations of the unknowns P', V', u' , and λ' which are proportional to $\exp(ikx - i\omega t)$, and linearizing the equation for the short-wavelength case, we obtain

$$\begin{aligned} -i\omega V' - ikV_0 u' &= 0, & -i\omega u' + ikV_0 P' &= 0, \\ \frac{c^2}{V^2} V' + P' + \beta \lambda' &= 0, & \lambda' &= -AV'. \end{aligned} \quad (11)$$

Introducing $c_L = \omega/k$ and following the standard procedure, we have

$$c_L^2 = \frac{V_0^2}{V^2} (c^2 - \beta AV^2). \quad (12)$$

The quantity c_L is the Lagrangian velocity of propagation of small perturbations, which differs from the observed Euler wave velocity c_E in the deformation factor:

$$c_L^2 = c_E^2 \frac{V_0^2}{V^2}, \quad c_E^2 = c^2 - \beta AV^2. \quad (13)$$

Because $\beta < 0$, it follows that $c_E > c$ and small-amplitude waves propagate relative to the material with the thermodynamic frozen speed of sound c only if the kinetics does not include a term which is linear in the derivative $\partial V/\partial t$ (i.e., for $A = 0$).

The possibility of differences in velocities was discussed in the literature, but initially [21, 22, 25, 26], it was assumed that the measured quantity is c . In [27], it is pointed out that there is a difference between the measured and thermodynamic velocities (given a marked role of the derivative $\partial V/\partial t$). It is noted that many of the conclusions should therefore be revised and new methods of processing experimental data are advertised, which were announced to be published soon. However, subsequent publications on this subject have not been found.

An attempt to reveal the dependence of kinetics on derivatives [24] was unsuccessful. For postshock flow, this dependence was not found, and in the shock region, the resolution of the experiments was insufficient. We show that this might be due to the inappropriate form

of the sought dependence. That is, the kinetics was supposed to have the form

$$\dot{P} = F\left(P, V, E, \frac{\partial V}{\partial t}\right), \quad (14)$$

where the expansion of the right side in the additional variable $\partial V/\partial t$ was assumed to begin with the second order. In support of this assumption, two arguments were given:

1) a quadratic dependence works the same way for both compression and expansion of material;

2) the linear part of the kinetics can be eliminated by a suitable transformation of variables and is therefore unimportant.

The first argument does not seem convincing. There are sharp physical differences between shock waves and rarefaction waves. It is in the shock wave that instability of material, nonequilibrium states, excitation of some degrees of freedom, etc. are possible. In addition, quadratic kinetics is poorly compatible with the shock wave since it requires the ill-defined mathematical operation of integration of the squared delta function. Note that in the traditional kinetics, reaction centers in heterogeneous explosives (hotspots) are activated under compression.

Let us consider the second argument in greater detail. Suppose the kinetic equation for λ has the simplest form (10). Replacing the composition variable λ by some function $\alpha = \alpha(V, P, \lambda)$, we write the kinetic equation for the new variable:

$$\frac{\partial \alpha}{\partial t} = \alpha_V \frac{\partial V}{\partial t} + \alpha_P \frac{\partial P}{\partial t} + \alpha_\lambda \frac{\partial \lambda}{\partial t}.$$

Replacing $\partial P/\partial t$ and $\partial \lambda/\partial t$, from (5) and (10) we have

$$\begin{aligned} \frac{\partial \alpha}{\partial t} &= (\alpha_\lambda - \beta \alpha_P) f \\ &+ \left[\alpha_V - \left(\frac{c^2}{V^2} - A\beta \right) \alpha_P - A\alpha_\lambda \right] \frac{\partial V}{\partial t}. \end{aligned}$$

Choosing a transformation such that the coefficient at $\partial V/\partial t$ vanishes, we obtain kinetics without a term linear in the derivative (in this example, algebraic kinetics).

This can be done at the cost of some complications in other places. For example, in the particular case of the constant A , we can select the transformation

$$\alpha = \lambda + AV.$$

Then, the kinetic equation is simplified to

$$\frac{\partial \alpha}{\partial t} = f.$$

The variable α , in contrast to λ , has no jump at the shock wave. However, instead of (7), the expression for the energy has the form

$$E = \frac{PV}{\gamma - 1} + AVQ - \alpha Q. \quad (15)$$

We note that (7) may represent a physical dependence which does not contradict any fundamental prohibitions (although, in practice, it may be a rather rough approximation). In contrast, the transformations lead to an obviously unphysical additional dependence of the energy on volume (which is compensated for by the occurrence of the nonphysical composition parameter α). Of course, all calculations using (15) will give the same results as those obtained using the original form (7). In particular, the trace of the linear term — the coefficient A of the original kinetics (10) is retained in expression (15).

Using Eq. (10), Eq. (5) is transformed to

$$\frac{\partial P}{\partial t} + \left(\frac{c^2}{V^2} - \beta A \right) \frac{\partial V}{\partial t} + \beta f = 0$$

or

$$\frac{\partial P}{\partial t} + \frac{c_E^2}{V^2} \frac{\partial V}{\partial t} + \beta f = 0. \quad (16)$$

Equation (16) is similar in form to (5) for the case of algebraic kinetics (4) but contains c_E instead of c . We note that (16) can be obtained from (5) by referring the expression $-\beta A \partial V/\partial t$ to the second term rather than the last term. Similarly, instead of Eq. (8), we obtain

$$\dot{P}_{(\alpha)} \equiv -\beta f = \frac{\partial P}{\partial t} + \frac{c_E^2}{V^2} \frac{\partial V}{\partial t}, \quad (17)$$

where $\dot{P}_{(\alpha)}$ is a new GKC; it can be understood as the rate of pressure growth due to variation in the new composition parameter α chosen so as to eliminate the deformation rate from the kinetic equation. It is seen that, as a result of the transformation, the situation formally reduces to the case of algebraic kinetics that does not depend on derivatives. In this case, instead of the thermodynamic (frozen in the parameter λ) speed of sound c , the equations contain the speed c_E which is frozen in the parameter α (c_E is measured in a dynamic experiment). If the difference between c and c_E is ignored, the kinetics component linear in the derivative becomes unobservable.

For comparison, let us consider the kinetics which is quadratic in the derivative $\partial V/\partial t$:

$$\frac{\partial \lambda}{\partial t} = f(V, P, \lambda) + B \left(\frac{\partial V}{\partial t} \right)^2. \quad (18)$$

The linearized system for small perturbations differs from (11) only in the last (kinetic) equation:

$$\lambda' = 2B \frac{\partial V}{\partial t} V'.$$

Instead of (12), we obtain

$$c_L^2 = \frac{V_0^2}{V^2} \left(c^2 + 2\beta B V^2 \frac{\partial V}{\partial t} \right).$$

Accordingly, the observed short-wave sound velocity changes:

$$c_E^2 = c^2 + 2\beta BV^2 \frac{\partial V}{\partial t}. \quad (19)$$

Instead of (16), we obtain

$$\frac{\partial P}{\partial t} + \frac{c_E^2}{V^2} \frac{\partial V}{\partial t} + \beta \left(f - B \left(\frac{\partial V}{\partial t} \right)^2 \right) = 0. \quad (20)$$

It can be seen that the replacement of c by c_E does not mask the differential contribution to the kinetics (although its sign is changed). Thus, for the quadratic kinetics presumed in [23, 24], the dependence on $\partial V/\partial t$ would be seen if it was significant. If, however, the equation is written with the formal isolation of algebraic kinetics

$$\frac{\partial P}{\partial t} + \frac{c_*^2}{V^2} \frac{\partial V}{\partial t} + \beta f = 0,$$

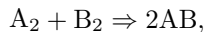
then, in the second term, instead of the thermodynamic or short-wavelength frozen speed of sound, one has to use some intermediate speed of sound

$$c_*^2 = c^2 + \beta BV^2 \frac{\partial V}{\partial t}.$$

This velocity does not have a direct physical meaning and is not a quantity measured in experiment.

PROCESSES GENERATING DIFFERENTIAL KINETICS

It is easy to give examples of processes in which the differential contribution is obvious. A preliminary consideration of the possible mechanisms was carried out in [30]. We consider the reaction in a gas



in which the limiting step is the decomposition of the stable molecules A_2 and B_2 . Then, the reaction rate contains the factor $\exp(-\varepsilon/k_B T)$, where ε is the activation energy (for simplicity, it is the same for both initial reagents) and k_B is Boltzmann's constant. Compression of this reactive medium, i.e., a negative value of $\partial V/\partial t$ implies the collision of two molecules with the additional velocity δu of the order $-l\partial u/\partial x = -(l/V_0)\partial V/\partial t$, where l is the mean free path. The velocity δu is superimposed on the chaotic velocities of the molecules. The increase in the kinetic energy in the system of the center of mass can be estimated as $mv_T\delta u$, where m is the reduced mass of the colliding pair, v_T is the characteristic chaotic (thermal) velocity. This is equivalent to a reduction in the activation energy, which modifies the activation factor: $\exp(-\varepsilon/kT) \exp(mv_T\delta u/k_B T)$ is

obtained instead of $\exp(-\varepsilon/k_B T)$. For reasonable values of the parameters, the second exponent is small, so that the relative increment in the reaction rate is of the order of

$$\frac{mv_T\delta u}{k_B T} \simeq \frac{\delta u}{v_T} \simeq -\frac{l}{v_T} \frac{1}{V_0} \frac{\partial V}{\partial t}. \quad (21)$$

It is evident that there is indeed a linear differential contribution to the kinetics. During compression, the reaction rate increases, and during expansion, it decreases. Some corrections can arise from accounting for the detailed mechanism of the reaction, which is usually fairly complex. However, one can imagine an even simpler model in which the collision between two reactant molecules leads directly to the formation of two product molecules provided that the collision energy exceeds the predetermined threshold. The products scatter in accordance to the energy and momentum conservation laws. Other collision variants occur without reactions. Although this model is impractical, it is self-consistent and represents a hybrid of molecular dynamics and the cellular automata model. For this system, both the linear differential kinetics and the simplest thermodynamics in the form of (7) hold almost exactly.

Correction of the type (21) is mainly illustrative. Although it has a clear physical meaning, its role in gases is significant only in the nearest vicinity of the shock front, where deviations from the equilibrium energy distribution are at least not less important (see [10]). A similar effect is also possible in condensed materials.

Similar phenomena on a larger scale should accompany the detonation of heterogeneous (e.g., pressed) condensed explosives. Behind the shock front there are pore closure, formation of cumulative microjets, and similar processes that can be regarded as the collision of material microvolumes and which give rise to reaction centers. If these collisions occur against the background of the overall compression or expansion of the medium, one should expect effects similar to the molecular effects considered above, with the difference that the mean free path is replaced by the characteristic size of inhomogeneity of the material a and the thermal velocity of molecules is replaced by the characteristic velocity v_P of flow pulsations on this scale:

$$\frac{\partial \lambda}{\partial t} = \left(\frac{\partial \lambda}{\partial t} \right)_0 \left(1 - \frac{a}{v_P V_0} \frac{\partial V}{\partial t} \right). \quad (22)$$

A similar dependence arises during propagation of the reaction from hot spot [30]. Let a combustion wave propagate in a material at a velocity w . If the material is compressed, the temperature gradient in the wave increases with time, which increases the burning rate. During expansion, conversely, the burning rate decreases.

Let us consider a simple one-dimensional model of a single combustion hot spot. The propagation of the wave is described by the heat conduction equation with the reaction

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} = \frac{1}{\rho C} \frac{\partial}{\partial x} \left(\rho C \chi \frac{\partial T}{\partial x} \right) + \frac{Q}{C} W(T).$$

Here T is the temperature, ρ is the material density, C is the specific heat capacity, χ is the thermal diffusivity, x is the microscopic Eulerian coordinate within the hot spot, u is the flow velocity, and W is the reaction rate. Transforming to the microscopic Lagrangian coordinate z : $\rho dx = \rho_0 dz$, we obtain

$$\frac{\partial T}{\partial t} = \frac{1}{C} \frac{\partial}{\partial z} \left(C \chi \frac{V_0^2}{V^2} \frac{\partial T}{\partial z} \right) + \frac{Q}{C} W(T). \quad (23)$$

Here $V_0 = 1/\rho_0$ is the initial specific volume, and the partial derivative with respect to time is a Lagrangian one (calculated at a constant coordinate z). The deformation factor V_0/V depends on time, which is equivalent to the effective thermal diffusivity defined as $\chi_{\text{eff}} = \chi(V_0/V)^2$.

In [30], Eq. (23) was solved numerically subject to conditions corresponding to a combustion wave with a thin reaction zone. In the absence of deformation, the wave rapidly reached a steady-state regime characterized by the wave velocity w_0 . During forced compression or expansion of a Lagrangian volume of the form $V = V_0(1 - \nu t)$ with the constant coefficient ν , the wave velocity changed gradually with time. The degree of deformation was the same for the starting material and the combustion products. For comparison, the average speed of displacement by a specified Lagrangian distance which corresponds to the burnup of a single hot spot was chosen. The calculations gave an almost linear dependence on the deformation rate:

$$\langle w \rangle = w_0(1 - \theta \nu \tau), \quad (24)$$

where τ is the time of complete burning (macroscopic reaction time), and the coefficient θ is of the order of 1. According to Zel'dovich–Frank–Kamenetskii theory [31], the wave velocity is proportional to the square root of the thermal diffusivity, other things being equal. Calculations [30] agree well with the dependence $w \propto \sqrt{\chi_{\text{eff}}}$ if by χ_{eff} is meant the average value during the burning time τ . The orientation of the burning cell can be arbitrary, and its one-dimensionality is of no significance if the dimensions of the source are small. Macroscopically, in the presence of an external strain field, effects of the same order of magnitude are observed as average ones. The obtained result (24) can be written as

$$\frac{\partial \lambda}{\partial t} = \left(\frac{\partial \lambda}{\partial t} \right)_0 \left(1 - \frac{\theta \tau}{V_0} \frac{\partial V}{\partial t} \right). \quad (25)$$

It is noteworthy that the burning rate dependent on external conditions macroscopically generates an explicit linear dependence on the derivative $\partial V/\partial t$ in the kinetics.

In the problem considered, the strain was assumed to be identical over the entire cell. This approximation is reasonable for detonation of dense explosives whose combustion products are not much different in compressibility from the starting material. In the less extreme case of combustion at lower pressures where the density of gaseous products is tens or hundreds of times lower than the density of the condensed phase, deformation of the burning volume is almost entirely provided by the gas phase and a marked acceleration of the thermal wave in the solid does not occur. It is probably for this reason that such obvious effect has been ignored previously.

The other processes that may contribute to the differential kinetics are the turbulence caused by inhomogeneity of the material and/or instability of the plane front; generation of growing small-scale waves in the active medium, which are considered to be responsible for the transfer of chemical energy to the front (see [1]). Accordingly, one can expect corrections of the type (22) (25) in which the length a or the time τ will be determined by the scale of such processes. It should be noted that in this case, it is not necessary to take into account the turbulent transport of macroscopic energy and momentum; turbulence should be taken into account only in the most sensitive place — the reaction rate law, in which it leads to excitation transfer.

EXAMPLE: DEFORMATION RATE EFFECT ON THE KINETICS

To illustrate the effect of differential kinetics, we consider the simplest case where the thermodynamics of the medium is described by Eq. (7). Then, the steady-state detonation velocity and the final Chapman–Jouguet state are easily found analytically. This allows us to highlight interesting features without going into a detailed description of energetic materials.

We choose kinetics in the form

$$\frac{\partial \lambda}{\partial t} = \frac{1 - \lambda}{\tau} - b \frac{1 - \lambda}{V_0} \frac{\partial V}{\partial t}, \quad (26)$$

where τ is the characteristic reaction time. In (26), the previously used quantity A is set equal to $A = b(1 - \lambda)/V_0$. The contribution of the differential kinetics is governed by the dimensionless coefficient b . With this relationship, not only the algebraic term but also the contribution of the derivative vanishes after the completion of the reaction ($\lambda = 1$). At the phenomenologi-

cal level, this implies that the discussed mechanisms of influence of the differential term can be valid only in a substantially nonequilibrium medium. In the equilibrium zone, the difference between c and c_E also vanishes upon reaching $\lambda = 1$, which allows the Chapman–Jouguet condition to be used in the standard form.

Let us consider steady-state one-dimensional detonation. We use a coordinate system in which the wave front is motionless and assume that the coordinate origin $x = 0$ coincides with the shock front. The material flows into the wave from the left with detonation velocity D , and the reaction zone is at $x > 0$. The structure of the wave is described by the equations

$$\begin{aligned} \frac{dV}{dx} &= \frac{(\gamma - 1)QV_0}{\gamma PV + (\gamma - 1)QbV(1 - \lambda)/V_0 - D^2V^2/V_0^2} \frac{1 - \lambda}{D\tau}, \\ \frac{d\lambda}{dx} &= \frac{V_0}{V} \frac{1 - \lambda}{D\tau} - b \frac{1 - \lambda}{V_0} \frac{dV}{dx}, \quad \frac{dP}{dx} = -\frac{D^2}{V_0^2} \frac{dV}{dx}. \end{aligned} \quad (27)$$

The coordinate x is linked to the reaction time in a Lagrangian particle by the relation $dt = V_0 dx / VD$.

The initial values at $x = 0$ are found from the conditions at the shock front. In the plane P – V , the initial pressure and volume correspond to the point of intersection of the Rayleigh–Michelson and adiabat (generally speaking, with partial conversion):

$$\begin{aligned} P &= P_0 + \frac{D^2}{V_0^2}(V_0 - V), \\ \frac{PV}{\gamma - 1} - \lambda Q - \frac{P_0 V_0}{\gamma - 1} &= \frac{P + P_0}{2}(V_0 - V). \end{aligned} \quad (28)$$

Closure of this system requires an additional constraint on the initial degree of conversion λ . We adopt the simplest assumption that kinetics (26) is valid not only in the zone of smooth flow behind the shock front but also within the front (which is in essence a segment of the largest volumetric strain). We represent the front as a very narrow but finite region of compression and integrate the kinetic equation (26) over this region, separating the variables λ and V ; the contribution of the algebraic term can be ignored:

$$\ln \left(\frac{1}{1 - \lambda} \right) = b \frac{V_0 - V}{V_0}.$$

Then, the initial values of P_S and V_S are determined by the intersection of the Rayleigh–Michelson line [the first of Eqs. (28)] and the modified shock adiabat on which the degree of conversion is $\lambda = 1 - \exp(-b(1 - V/V_0))$:

$$\begin{aligned} P &= [2(\gamma - 1)Q(1 - \exp(-b(1 - V/V_0))) \\ &+ P_0((\gamma + 1)V_0 - (\gamma - 1)V)] / [(\gamma + 1)V - (\gamma - 1)V_0]. \end{aligned} \quad (29)$$

The detonation velocity corresponding to the tangency of the Rayleigh–Michelson line and the equilibrium detonation adiabat is equal to

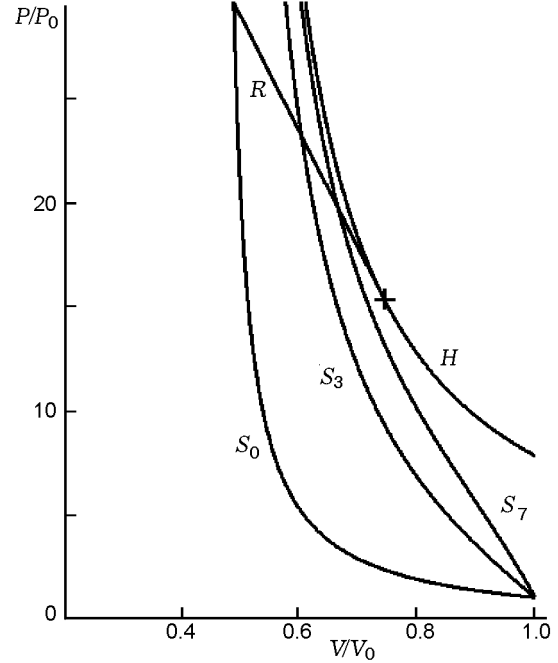


Fig. 1. P – V diagram of the detonation wave: the plus sign denotes the Chapman–Jouguet state.

$$D = \sqrt{\frac{(\gamma^2 - 1)Q}{2} + \gamma P_0 V_0} + \sqrt{\frac{(\gamma^2 - 1)Q}{2}}.$$

For the calculation, we chose values $P_0 = 1$ GPa, $V_0 = 1$ cm³/g, $\gamma = 2.7$, and $Q = 4$ kJ/g. With this choice, the main parameters of the shock waves are similar in order of magnitude to the real parameters for condensed explosives: detonation velocity $D = 7.456$ km/sec, Chapman–Jouguet pressure $P_J = 15.294$ GPa, and specific volume in the Jouguet state $V_J = 0.7429$ cm³/g.

Figure 1 shows the frozen adiabat S_0 , the equilibrium detonation adiabat H , the Rayleigh line R tangential to the detonation adiabat, and the two shock adiabats with the final degree of conversion defined by Eq. (29): S_3 for $b = 3$ and S_7 for $b = 7$. The intersection of S_b and R corresponds to the state after the shock front; next, the image point descends along the straight line R to the point of tangency with H . The adiabats S_b begin at the point (P_0, V_0) ; for small b , they are close to the frozen adiabat S_0 (at the front, the degree of conversion is low), and for large values of b , they rapidly approach H . Since for any value of b , the curve S is below H and above S_0 , the intersection of S with the line R tangential to H certainly exists for $V < V_J$. Because of the reactions at the front, the maximum pressure at the point of intersection is always lower than that in the frozen case. At the starting point, the slope of the adiabats S_3 and S_7 exceeds the slope of S_0 . This reflects

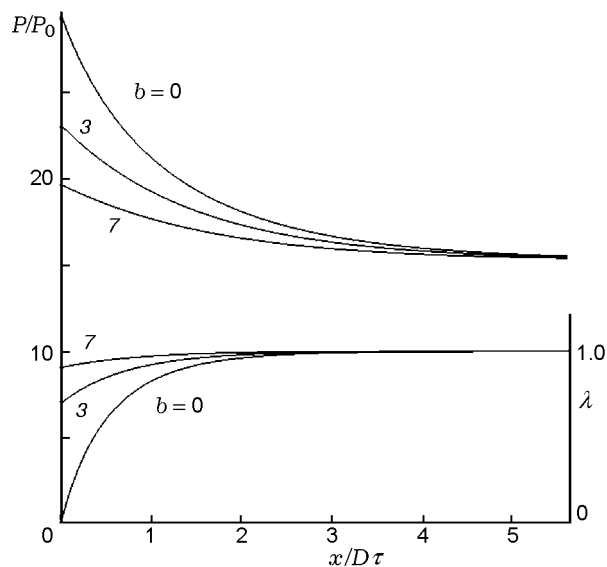


Fig. 2. Structure of the detonation wave for various contributions of the differential term: the upper curves are pressure profiles for $b = 0, 3$ and 7 , the lower curves are profiles of the degree of conversion for the same values of b .

the fact that the physical speed of sound in the initial state is higher than the thermodynamic speed (which determines the initial slope of S_0).

Figure 2 compares the shock structures for classical kinetics ($b = 0$) and for kinetics with an appreciable contribution of the differential term ($b = 3$ and 7). The profiles were obtained by integrating system (27) with the initial conditions at the shock front following from the numerical solution of Eqs. (28) and (29). It is seen that the fast reaction at the front reduces the maximum pressure in the chemical spike. The excess of the pressure in the front over the P_j for $b = 3$ is approximately half that in the classical version $b = 0$, and for $b = 7$, it is 3.3 times smaller. In this case, the degrees of conversion immediately behind the front are 70 and 90%, respectively. A further increase in b will lead to a further reduction in the pressure contrast at the chemical spike, up to the complete disappearance of the latter (the reaction will proceed to completion within the shock front). Note that for the chosen kinetics (for a constant value of τ) the afterburning zone behind the front does not narrow but only the initial deviation from the equilibrium state decreases.

DISCUSSION

With an appreciable contribution of the differential term, the profiles of the parameters become smoother

(the jump in the shock wave weakens, and the gradient in the zone of the chemical spike decreases, up to a rectangular profile in the limit, where the final state is reached immediately behind the shock wave). Thus, the model qualitatively describes the experimental data of [13–15, 17, 18]. The absence of a pronounced chemical spike in these studies can be explained by the reaction at the shock front. In the model considered, the transformation at the front occurs instantaneously due to the presence of the derivative $\partial V/\partial t$ in the kinetic equation. The shock front can be defined as a region with significant pulsations in the compressed material, and its actual thickness is determined by the characteristic size of the initial inhomogeneities (see, for example, [17, 18]), and a significant transformation within the front is possible at a finite but sufficiently high reaction rate. In the above, we considered a number of mechanisms that can greatly enhance the reaction within the compression region. The term containing $\partial V/\partial t$ describes this acceleration of the reaction at the front phenomenologically.

With the kinetics linear in the derivative (10), the transformation from (2) to (16) is general in nature, i.e., does not depend on the dimension of the problem and the specific form of the coefficient A and the function f . Therefore, technically, systems with this kinetics are identical to systems with algebraic kinetics with somewhat modified thermodynamics (the speed of sound is renormalized from c to c_E and the internal energy form is changed).

This unobservability of linear differential kinetics does not mean, however, that the contribution of the derivative does not make sense. Internal energy is a definite function of state, though poorly known at the moment, and the nonuniqueness is apparent and is due to the limited information obtained in dynamic experiments (only mechanical parameters are measured). In practice, the usefulness of dynamic data is related to the limited region of their application excluding external heat flow. This can be illustrated by the simplest example of a nonreactive medium. As is known, the dependence $E(P, V)$ is determined dynamically, i.e., the internal energy is expressed not in terms of natural variables. This description is thermodynamically incomplete [32]; an analog of the situation for classical household thermodynamics would be the condition that only data of measurements of adiabatic compressibility can be used while specific heat cannot be measured. Naturally, in a nonequilibrium reacting medium, the situation is only complicated.

Thus, the elimination of the kinetic term linear in the derivative is not a transformation of little significance for data processing. Moreover, this transforma-

tion cannot be considered a natural one that gives some important advantages in writing equations. Rather, the elimination of the linear term leads to difficulties. It is because of this restriction that the dependence on the derivative in [23, 24] in the postshock region could be lost. It can be concluded that the differential term of the kinetics in these papers (if it was important at all) could only be linear.

CONCLUSIONS

Linear expressions of the type (22), (25) naturally follow from the conventional assumptions of microscopic reaction mechanisms. It is therefore promising to search for differential kinetics in the simple linear approximation (4). In this case, additional information is needed to distinguish between the quantities c and c_E . Linear differential kinetics agrees well with the shock wave, in which it provides a finite jump in energy release. If the contribution of such processes is significant, one should expect that an explicit account of the differential term will simplify the currently used kinetic laws, reducing the number of adjustable parameters.

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