On the Kinetics of Chemical Reactions under Detonation Conditions

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Received June 23, 2008

Abstract—Physical mechanisms leading to the acceleration of chemical reactions in the regions of large gradients of parameters are considered, in particular, in detonation waves. It is shown that a kinetics is possible according to which the reaction rate depends on the temporal derivative of the specific volume.

PACS numbers: 47.70.Rs, 47.70.Pq, 82.33.Vx

DOI: 10.1134/S1063785009020096

According to the classical Zel'dovich–von Neumann–Doering model, a detonation wave represents a complex involving a shock wave, an adjacent chemical reaction zone, and a region of expansion of the explosion products [1]. In the shock wave, the pressure and mass velocity are higher than those at the Jouguet point, where the reaction terminates. This configuration is called the chemical peak. The duration of chemical reactions in high-density explosives (HEs) is usually on the order of 100 ns. However, the chemical peak was not observed in some experiments [2–5] with HEs that had a porosity of about 1%, which may have been related to either a narrow reaction zone (beyond the resolution of the employed methods, which is typically on the order of several nanoseconds) or qualitative changes in the reaction kinetics. More recently, this unusual structure was also observed at low densities [6].

Since the detailed kinetics of reactions accompanying the detonation of high-density condensed explosives is not accessible, the calculations are performed according to a simplified macrokinetic approach, in which the reaction rate is usually considered to be a function of the current parameters of the medium, including the degree of conversion λ (varying from 0 to 1 in the course of reaction), pressure, density, etc. In these models, $\lambda = 0$ after the propagation of the shock wave front. Dremin and other researchers (see [7] and references therein) considered the possibility that a significant fraction of the HE material reacts at the shock front. Trofimov [8] suggested introducing the rate of bulk deformation as a material variable into the kinetic equation. Evidently, this variable can be significant in the regions with high gradients; in particular, it may account for a jump in the energy evolution at the shock wave. However, experiments aimed at the observation of the expected dependence yielded rather ambiguous results [9].
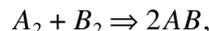
In this Letter, we discuss various physical mechanisms that can lead to an explicit dependence of the reaction kinetics on the derivatives of flow parameters.

A simple variant of the differential kinetics may have the following form:

$$\frac{d\lambda}{dt} = f(P, V, \lambda) - A\frac{dV}{dt}. \tag{1}$$

where t is the time, d/dt is the Lagrange derivative, V is the specific volume, P is the pressure, $A > 0$ is a coefficient (which can depend on P, V, and λ), the sign of which corresponds to acceleration of the reaction under compression (in particular, to a finite conversion during the shock wave front propagation). It should be noted that the linear form of (1) was rejected (in our opinion, without sufficient grounds) by Trofimov in [8] and subsequent investigations.

Now, we will present models in which the presence of a differential term is explicitly manifested. Let us consider the gas-phase reaction
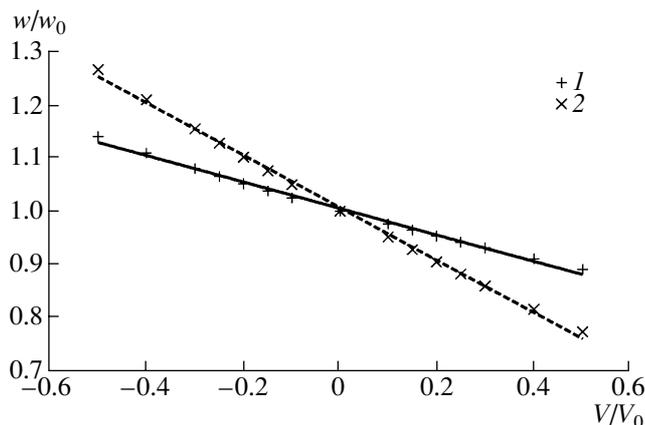
$$A_2 + B_2 \Rightarrow 2AB,$$

in which a limiting stage is the decay of stable A_2 and B_2 molecules and the reaction rate is proportional to $\exp(-E/kT)$, where E is the activation energy, which for simplicity, is the same for both reactants. Compression of the medium (i.e., negative dV/dt values), implies that colliding molecules approach one another with a velocity increased relative to the chaotic thermal velocity v_T by $\delta u \cong -l\partial u/\partial x = -(l/V)dV/dt$, where l is the mean free path, u is the flow velocity, and x is the coordinate in the wave propagation direction. The corresponding energy increase in the center-of-mass frame can be evaluated as $mv_T\delta u$, where m is the reduced mass of the colliding pair. This energy increment is equivalent to a decrease in the activation energy, so that $\exp(-E/kT)$ must be replaced by $\exp(-E/kT)\exp(mv_T\delta u/kT)$. For $\delta u \ll v_T$, the second exponent is small and the reaction rate increment can be evaluated as

$$\frac{m\text{v}_T\delta u}{kT} \cong \frac{\delta u}{\text{v}_T} \cong \frac{l}{\text{v}_T}\frac{1}{V}\frac{dV}{dt}. \qquad (2)$$

As can be seen, this actually corresponds to a linear differential contribution to the reaction kinetics such that the reaction rate increases upon compression and drops upon expansion.

[1] Although the gaskinetic estimate (2) has a clear physical meaning, the smallness of $l\,m$ makes this correction significant only in the immediate vicinity of the propagating shock wave front, where the deviations from the equilibrium energy distribution are also (at least) no less significant [10]. These effects, which can lead to a jump in the energy evolution at the front, are also possible in condensed substances, where the corresponding contribution is more difficult to evaluate. All of these factors are taken into consideration in molecular dynamics calculations, but this still has only a rather illustrative character. For the existing level of understanding of the course of reactions in dense media, the use of type-(1) kinetics with an empirically selected coefficient A seems to yield an acceptable compromise, which makes it possible to allow for the reaction acceleration at the shock wave front in the first approximation. This approach also takes into account mesoscopic phenomena, such as the compaction leading to the fragmentation of crystals and cumulative processes, the effect of which is much like the molecular-kinetic acceleration of the reaction considered above. Note that a finite energy evolution at the front or in a narrow adjacent zone is also encountered in the empirical kinetics [3, 10].

Let us consider another factor, the characteristic scale of which is the size of inhomogeneity in the substance. According to most models, reactions behind the shock wave front begin at the so-called hot spots (e.g., collapsed pores), which are the sites of energy concentration. The effect of deformation on such focal combustion can be readily understood. Let a combustion

Plots of the relative combustion rate w/w_0 versus relative deformation for (1) $\chi = \chi_0$ and (2) $\chi = \chi_0 V/V_0$.

wave propagate at a velocity w along a material. If the substance is subjected to compression, the temperature gradient in the wave grows with the time, thus increasing the rate of combustion. On the contrary, an extension leads to a decrease in the combustion rate.

In order to obtain a more accurate estimation of the effect of deformation on the combustion rate, let us consider a simple one-dimensional model of a single combustion focus. The combustion wave propagation is described by the equation of heat conduction accompanied by the reaction

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

where T is the absolute temperature, ρ is the density, C is the heat capacity, χ is the thermal diffusivity, x is the microscopic coordinate in the focus, u is the flow velocity, P is the pressure, and $W = d\lambda/dt$ is the reaction rate. Passing to a macroscopic Lagrange coordinate z such that $\rho dx = \rho_0 dz$ and neglecting the work performed by pressure forces, we obtain the following equation:

$$\frac{dT}{dt} = \frac{1}{C}\frac{\partial}{\partial z}\left(C\chi\frac{V_0^2\partial T}{V^2\partial z}\right) + \frac{Q}{C}W. \qquad (3)$$

where $V_0 = 1/\rho_0$ is the initial specific volume. The deformation factor $V/V_0 0$ depends on the time, which is equivalent to the effective thermal diffusivity defined as $\chi_{\text{eff}} = \chi_0(V_0/V)^2$.

Equation (3) was solved using numerical methods. The reaction rate was expressed as $W = (1 - \lambda)\exp(-E/T)/\tau$ and the parameters were set as $Q = C = 1$, $E = 4$, and $\tau = 10$. Initially, a temperature sufficiently high to initiate the combustion wave was set on a small interval of the z axis. In the base variant (i.e., in the absence of deformation, $V_0/V = 1$, $\chi = \chi_0 = 0.4$), a wave was rapidly formed, which propagated at a constant velocity w_0. In the variant with deformation set as $V = V_0(1 + \beta t)$, the wave velocity slowly varied with time. In order to compare this velocity to w_0, the average value was determined for a time t_b necessary for traveling over a fixed Lagrange distance (corresponding to the complete combustion of a unit focus). Plots of the ratio w/w_0 versus relative deformation $\Delta V_0/V = \beta t_b$ are constructed in the figure for two variants, which correspond to a constant thermal diffusivity $\chi = \chi_0$ and that varying with the time as $\chi = \chi_0 V/V_0$. As can be seen, the combustion wave is actually accelerated by compression ($\beta < 0$) and retarded by expansion ($\beta > 0$). The magnitude of the deformation effect well agrees with the relation $w \propto \sqrt{\chi_{\text{eff}}}$, which follows from the Zel'dovich–Frank–Kamenetskii formula [11]. The absence of this effect is also possible (for example at $\chi = \chi_0(V/V_0)^2$ and constant values of Q and C), but only as a low-probable particular case.

The hot cell orientation can be arbitrary and its one-dimensional nature insignificant, provided that the focus size is sufficiently small; in a deformation field, the same (by the order of magnitude) effects will be observed on average. For example, at $\chi = \chi_0$ (curve *1* in the figure), we have

$$\frac{d\lambda}{dt} \approx W_0\left(1 - 0.5\frac{t_b}{V_0}\frac{dV}{dt}\right). \qquad (4)$$

It is remarkable that the variable (due to the variation of conditions) combustion rate macroscopically generates an explicit dependence of the reaction kinetics on the derivatives of flow parameters.

In the proposed model, the deformation is set constant over the entire cell. This approximation is quite reasonable for the detonation of dense HEs, where the compressibility of combustion products does not differ significantly from that of the initial substance. In a less exotic case of combustion, where the density of gaseous products is one or two orders of magnitude smaller than that of the initial condensed phase, the deformation of a burning volume will be almost completely accommodated in the gaseous phase and no significant acceleration of the combustion wave in the solid substance will take place. Apparently, this circumstance explains why this obvious effect was not taken into consideration previously.

The influence of deformation via the thermal mechanism, in contrast to the molecular mechanism considered above, is effective mostly within the chemical peak, i.e., outside of the shock wave front, since the compression time in this front is small. Therefore, each of the two models considered above operates in a particular region, but only their combination can lead to a type-(1) kinetics.

Other processes capable of contributing to the differential kinetics include (i) the turbulence caused by the inhomogeneity of a substance and/or the instability of a plane front and (ii) the excitation of increasing small-scale waves capable of transferring chemical energy to the front in an active medium (see [12]). One can also expect these processes to lead to type-(4) corrections. It is not necessary to make allowances for the additional transfer of macroscopic energy and momentum. The turbulence should only be taken into account in a highly sensitive relation, that is, in the equation describing the law of reaction rate, where it leads to the excitation transfer.

Trofimov [8] demonstrated that a term that is linear with respect to the derivative can be excluded from the kinetic equation by transformation of the composition (conversion) variable λ. Using this result and proceeding from the condition of deformation-induced reaction acceleration, Vorob' et al. [9] expected that the reconstructed kinetics will be quadratic. However, the transformation proposed in [8], which also involves thermodynamic aspects and, hence, influences the processing of data, was not taken into account in [9]. We are intended to show in a special paper that a differential term in the kinetics [9], if at all significant, could only be linear.

In the case of a significant contribution of the differential term, the profiles of parameters change to smoother shapes with a decrease in the shock-wave pressure jump and in the gradient in the chemical reaction zone (in the limiting case, up to a rectangular profile with a final state reached immediately behind the shock wave front). These profiles were obtained, for example, in [2–6].

The linear-differential form of kinetics well agrees with a shock wave, where it ensures a finite jump in the energy evolution. If the contribution due to the processes under consideration is significant, then one may expect that explicit allowance for the differential term would simplify the existing combustion laws by reducing the number of fitting parameters (15 parameters are used to describe the kinetics considered in [3]) and provide a deeper insight into physics of the combustion process.

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Translated by P. Pozdeev

SPELL: 1. gaskinetic, 2. Vorob' - ?