THE VELOCITY OF PROPAGATION OF THE FRONT OF AN EXOTHERMIC REACTION IN A CONDENSED PHASE

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Abstract

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THE VELOCITY OF PROPAGATION OF THE FRONT OF AN EXOTHERMIC REACTION IN A CONDENSED PHASE

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Ya. B. Zel' dovich and D. A. Frank-Kamenetskii (^1) constructed a theory of the thermal propagation of flame in gases. In deriving approximate analytical formulas for the velocity of propagation of the flame front, they used the analogy between diffusion and heat transfer, i.e., the equality of the diffusion and thermal diffusivity coefficients. This condition made it possible to relate the concentration to the temperature and to reduce the system of two equations (diffusion and heat conduction) to a single equation containing only the temperature.

An analogous problem may also arise when considering exothermic reactions in the condensed phase (for example, polymerization reactions). Namely, one may pose the question of the stationary velocity of the front of propagation of an exothermic reaction in a condensed medium. In this case one can no longer use the equality of the diffusion and thermal diffusivity coefficients, since they may differ from one another by several orders of magnitude. In the present work we shall take the diffusion coefficient to be zero. We emphasize that the case under consideration is not a special case of the Zel' dovich-Frank-Kamenetskii theory, since the equality of the diffusion and thermal diffusivity coefficients is an essential point of their theory.

Let us consider the one-dimensional case. Let, at $x = -\infty$, a substance whose density $\rho = \text{const}$ have temperature T_0, and at $x = \infty$ temperature $T_1 = L/c + T_0$, where L is the heat effect of the reaction and c is the heat capacity. We shall solve the problem in a coordinate system in which the reaction front is at rest. In this system the substance moves with velocity u, which we must determine. In addition, we introduce the notation: $\chi = \lambda/\rho c$ is the thermal diffusivity coefficient (λ is the thermal conductivity coefficient); ρ_1 and ρ_2 are the densities of the initial substance and of the product ($\rho = \rho_1 + \rho_2$); $\eta = \rho_2/\rho$ is the relative concentration of the final product; $f(T, \eta) = \partial\eta/\partial t$ is the rate of the chemical reaction.

The equations of conservation of energy and matter have the form

$$\chi \frac{d^2T}{dx^2} - u\frac{dT}{dx} + \frac{L}{c}f = 0; \tag{1}$$

$$-u\frac{\partial \eta}{\partial x} + f = 0 \tag{2}$$

with boundary conditions $T(-\infty) = T_0,\ \eta(-\infty) = 0,\ T(\infty) = T_1$ and $\eta(\infty) = 1$.

Eliminating the reaction rate from these equations and taking into account the boundary conditions at $x = -\infty$, we find

$$\chi \frac{dT}{dx} - u(T - T_0) + \frac{uL}{c}\eta = 0. \tag{3}$$

Because of the strong dependence of the reaction rate on temperature, the entire reaction will occur at temperatures close to T_1. Therefore we set in

in the reaction zone $T = T_1$; then in this zone

$$\varkappa \frac{dT}{dx} = u\frac{L}{c}(1 - \eta). \tag{4}$$

This relation replaces, in our case, the relation between T and η in the work of Zel' dovich and Frank-Kamenetskii. At one boundary of the reaction zone $dT/dx = 0$, and at the other

$$\left(\frac{dT}{dx}\right)^* = \frac{uL}{c\varkappa}. \tag{5}$$

Using relation (4), one can express the concentration entering into the reaction rate f through the temperature gradient and reduce the problem to a single heat-conduction equation. As in work (1), the second term in this equation may be neglected, since the temperature changes only weakly in the reaction zone. Introducing the new variable $p(T) = dT/dx$, we reduce it to the first-order equation

$$pp' + \frac{L}{c\varkappa}f(T, p) = 0. \tag{6}$$

Let us consider several special cases.

1. **Zero-order reaction:** $f_0 = Z_0 \exp(-E/RT)$. Equation (6) has the solution

$$p^{*2} = -\frac{2LZ_0}{c\varkappa}\int_T^{T^*} \exp\left(-\frac{E}{RT}\right) dT,$$

where the quantities with an asterisk refer to the boundary of the zone. Usually $E \gg RT_1$; therefore the integral is equal to $-e^{-E/RT_1}RT_1^2/E$ (T^* may be set equal to zero). Substituting p^* from (5), we find the reaction-front velocity in the case of a chemical reaction of zero order,

$$u_0 = \sqrt{\frac{2Z_0\varkappa\exp(-E/RT_1)RT_1^2}{LE}}, \tag{7}$$

which coincides with the flame-propagation velocity found in work (1). This is also understandable, since the presence or absence of diffusion should in no way affect the rate of a zero-order reaction.

2. **First-order reaction:** $f_1 = Z_1 e^{-E/RT}(1-\eta)$. Equation (6) is easily integrated and, taking (5) into account, gives the front velocity

$$u_1 = \sqrt{\frac{Z_1\varkappa e^{-E/RT_1}RT_1^2}{LE}}, \tag{8}$$

which differs from u_0 only by the factor $1/\sqrt{2}$.

3. Finally, let us consider the **case of an autocatalytic reaction**:

$$f = Z_1 e^{-E_1/RT_1}(1-\eta) + Z_2 e^{-E_2/RT}\eta(1-\eta). \tag{9}$$

The first term in this expression corresponds to the "priming" reaction; therefore the most interesting case is $Z_1 e^{-E_1/RT} \ll Z_2 e^{-E_2/RT}$. Equation (6) reduces to the linear equation

$$p' - \frac{\varkappa c}{Lu^2} Z_2 \exp(-E_2/RT)\, p = -\frac{1}{u}\left[Z_1\exp(-E_1/RT) + Z_2\exp(-E_2/RT)\right],$$

whose solution is

$$p^* = \frac{Z_2}{u}\exp\left[-\frac{\varkappa c Z_2}{Lu^2}\int_{T^*}^{T}\exp\left(-\frac{E_2}{RT}\right)dT\right]\times$$

$$\times\int_{T^*}^{T}\left[1+\frac{Z_1}{Z_2}\exp\left(-\frac{E_1-E_2}{RT}\right)\right]\exp\left(-\frac{E_2}{RT}\right)\exp\left[\frac{\varkappa c Z_2}{Lu^2}\int_{T}^{T_1}\exp\left(-\frac{E_2}{RT'}\right)dT'\right]dT'. \tag{10}$$

Because of the presence of two exponentials (the increasing $\exp(-E_2/RT)$ and the decreasing

$$\exp\left[\frac{\varkappa c Z_2}{Lu^2}\int_T^{T_1}\exp\left(-\frac{E_2}{RT'}\right)dT'\right]$$

as T increases), the integrand will have a sharp maximum at some temperature T_m (it may coincide with T_1). Therefore we take the factor

$$1+\frac{Z_1}{Z_2}\exp\left(-\frac{E_1-E_2}{RT}\right)$$

at the point of maximum out from under the integral sign. Then the remaining integral is readily evaluated, and after substituting p^* we obtain the value of the front velocity:

$$u=\sqrt{\frac{Z_2\varkappa c\exp(-E_2/RT_1)RT_1^2}{LE\ln\left[1+\frac{Z_2}{Z_1}\exp\left(-\frac{E_2-E_1}{RT_m}\right)\right]}}. \tag{11}$$

Let us now find T_m. The maximum of the integrand is attained at the point where the quantity

$$-\frac{E_2}{RT}+\frac{Z_2\varkappa c}{Lu^2}\int_T^{T_1}\exp\left(-\frac{E_2}{RT'}\right)dT'$$

is maximal.

Equating its derivative to zero and substituting u from (11), we obtain the equation for T_m:

$$\frac{1}{T_m^2}=\frac{1}{T_1^2}\frac{\exp(-E_2/RT_m)}{\exp(-E_2/RT_1)}\ln\left[1+\frac{Z_2}{Z_1}\exp\left(-\frac{E_2-E_1}{RT_m}\right)\right].$$

Putting everywhere, except in the exponential, $T_m=T_1$, we find

$$\frac{1}{T_m}=\frac{1}{T_1}+\frac{R}{E_2}\ln\ln\left[1+\frac{Z_2}{Z_1}\exp\left(-\frac{E_2-E_1}{RT_1}\right)\right]. \tag{12}$$

This is valid, of course, when $T_m<T_1$, i.e. for

$$1+\frac{Z_2}{Z_1}\exp\left(-\frac{E_2-E_1}{RT}\right)\gg e.$$

After substituting T_m into (11), we finally have

$$u=\left\{\frac{Z_2\varkappa c\exp(-E_2/RT_1)RT_1^2}{LE\ln\left\{1+\frac{Z_2}{Z_1}\exp\left(-\frac{E_2-E_1}{RT_1}\right)\left[\ln\left(1+\frac{Z_2}{Z_1}\exp\left(-\frac{E_2-E_1}{RT_1}\right)\right)\right]^{E_1/E_2-1}\right\}}\right\}^{1/2} \tag{13}$$

for

$$1+\frac{Z_2}{Z_1}\exp\left(-\frac{E_2-E_1}{RT_1}\right)\gg e$$

and

$$u=\left\{\frac{Z_2\varkappa c e^{-E_2/RT_1}RT_1^2}{LE\ln\left[1+\frac{Z_2}{Z_1}\exp\left(-\frac{E_2-E_1}{RT_1}\right)\right]}\right\}^{1/2} \qquad (14)$$

for

$$1+\frac{Z_2}{Z_1}\exp\left(-\frac{E_2-E_1}{RT_1}\right)\ll e.$$

Expression (13) tends to zero as $Z_1\to 0$, as it should, since without the "initiating" reaction the velocity of the autocatalytic reaction is zero. Formula (14) as $Z_2\to 0$ goes over into the expression for the front velocity for the case of a first-order reaction u_1.

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CITED LITERATURE

1. Ya. B. Zel' dovich, D. A. Frank-Kamenetskii, *ZhFKh*, **12**, 100 (1938).

Note: Figure translations are in progress. See original paper for figures.