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Abstract

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REFINEMENT OF THE SOLUTION OF THE HEAT-CONDUCTION EQUATION IN A FLAME

(Presented by Academician Ya. B. Zeľ dovich, 19 VIII 1960)

The theory of normal combustion of gases of Ya. B. Zel' dovich—D. A. Frank-Kamenetskii (^{1,2}) describes a one-dimensional process of flame propagation along the coordinate x, characterized by diffusion of one deficient initial component and by similarity of the concentration and temperature fields, by the equation

$$y\,dy/dz + my - \varphi(z) = 0 \tag{1}$$

under the boundary conditions $y(0,1) = 0$, $\varphi(0,1) = 0$. Here m is a dimensionless parameter proportional to the burning velocity; $z = (T_b - T)/(T_b - T_0)$; T is the temperature in the plane x; the dimensionless variable $y \sim dT/dx$; the index b refers to quantities characterizing the combustion products, 0 to the initial state; $\varphi = \Phi(a,T)/\Phi(a_0,T_b)$; Φ is the reaction rate; a is the dimensionless concentration of the deficient component of the mixture in grams per 1 g of mixture; the heat capacity and thermal conductivity of the mixture are assumed constant.

In solving (1), two approximations are admitted that have sometimes raised doubts as to the applicability of the theory at small values of the activation energy. They can be avoided in a numerical solution of (1), but this method is not only cumbersome; it also makes it difficult to analyze the kinetic regularities of the reaction in the flame, which requires a simple analytical dependence of the burning velocity on the kinetic parameters.

The exponential character of the dependence of the reaction rate on temperature leads to the formation of a sharp maximum of φ at T close to T_b. For some value $z = \beta < 1$, one may, with the necessary accuracy, assume $\varphi \approx 0$. This makes it possible to calculate the limiting values

$$m_{\max} = \left[2\int_0^\beta \varphi\, dv(1+\beta)\right]^{1/2} \quad \text{and} \quad m_{\min} = \left[2\int_0^\beta \varphi\, dv\right]^{1/2},$$

between which lies the value of the parameter m; v is the variable of integration. The smaller the value of β, the narrower the interval $m_{\max} - m_{\min}$. In the limit, both values coincide, and the integration may be extended to the entire range of variation of z, taking

$$m = \left[2\int_0^1 \varphi\, dz\right]^{1/2}. \tag{2}$$

This approximate expression, with the use of which the first error admitted by the theory is associated, will be the more accurate the higher the value of the activation energy A. To carry out the integration (2), the exponential entering into the expression for Φ is subsequently expanded in a series by the method of D. A. Frank-Kamenetskii (^{3}); this constitutes the second approximation.

It is assumed that the function Φ has the form

$$\Phi = \text{const} \cdot a^s e^{-A/RT}, \tag{3}$$

where s is the order of the reaction with respect to the deficient component (^{2}). However, the kinetic equation should contain not the dimensionless concentration (partial pressure), but the absolute concentration ρa (ρ is the density), in order to take thermal expansion into account. This refinement gives

$$\varphi(z) = \left(z\frac{T_b}{T}\right)^s e^x e^{-\frac{x}{1-\omega z}} = \frac{e^x}{\omega^s}\left(\frac{1}{1-\omega z} - 1\right)^s e^{-\frac{x}{1-\omega z}}, \tag{4}$$

where $x = A/RT_b,\ \omega = (T_b - T_0)/T_b$.

Let us denote $1/(1 - z\omega) - 1 = p$; then

$$\varphi(p) = \frac{1}{\omega^s} p^s e^{-xp}, \tag{5}$$

$$\int_0^1 \varphi(z)\, dz = \frac{1}{\omega^{s+1}} \int_0^{\omega/(1-\omega)} \frac{p^s e^{-xp}\, dp}{(1+p)^2} \simeq \frac{1}{\omega^{s+1}} \int_0^\infty \frac{p^s e^{-xp}\, dp}{(1+p)^2}, \tag{6}$$

since $\omega/(1-\omega) = (T_b - T_0)/T_0 \gg 1;\ x \gg 1$.

Taking into account that $\varphi \neq 0$ only for $z \ll 1$, and hence $p \ll 1$, we set $1/(1+p)^2 \simeq 1 - 2p$, whence

$$\int_0^1 \varphi\, dz \simeq \frac{1}{\omega^{s+1}} \int_0^\infty p^s(1-2p)e^{-xp}\, dp = \frac{1}{\omega^{s+1}}\left[\Gamma(s+1) - \frac{2}{x}\Gamma(s+2)\right]. \quad (7)$$

For integer s,

$$\int_0^1 \varphi\, dz = \frac{s!}{(x\omega)^{s+1}}\left[1 - \frac{2(s+1)}{x}\right], \quad (8)$$

which, in all essentially important cases, will not differ in principle from the unrefined solution

$$\int_0^1 \varphi\, dz = \frac{s!}{(x\omega)^{s+1}}.$$

Refinement of equation (3) makes it possible to perform the integration without expanding the exponent, which basically eliminates one of the approximations.

Let us estimate the error allowed by expression (2). Introduce the function $y_0(z) > y(z)$, determined by the condition

$$y_0\frac{dy_0}{dz} = \varphi(z), \qquad y_0(z) = \left[2\int_0^z \varphi\, dz\right]^{1/2}. \quad (9)$$

Substituting in (1), instead of y (but not dy/dz), the larger quantity y_0, we find

$$dy/dz > \varphi/y_0 - m = dy_0/dz - m = dy_1/dz, \quad (10)$$

$$y_1 = y_0 - mz + C_1, \quad (10')$$

where C_1 is a constant of integration. At $z = 0$, $y_0 = 0$, i.e., $C_1 = 0$. The function $y_1(z)$ determines the lower sought boundary for the quantity y. To determine its upper boundary y_2, we replace y in (1) in an analogous manner by y_1:

$$dy/dz < \varphi/y_1 - m = dy_2/dz = \varphi/(y_0 - mz) - m. \quad (11)$$

Since in the zone of significant reaction rates $mz \ll y_0$, and when this condition is not fulfilled the term $\varphi/(y_0 - mz) \simeq 0$, the condition

$$1/(y_0 - mz) \simeq 1/y_0 + mz/y_0^2$$

is valid. This makes it possible to calculate the upper value

m—the value $m_{\max}$:

$$\frac{dy_2}{dz} = \frac{dy_0}{dz} + \frac{m}{y_0}\frac{dy_0}{dz}z - m; \tag{12}$$

integration of (12), taking into account the condition $y_2(1) = 0$*, gives

$$\begin{aligned} m_{\max} &= \frac{y_0}{1 - \displaystyle\int_0^1 \frac{1}{y_0}\frac{dy_0}{dz}z\,dz} = \frac{y_0}{1 - \displaystyle\int_0^1 \frac{1}{y_0^2}\varphi(z)z\,dz} \\ &= \left[2\int_0^1 \varphi(v)\,dv\right]^{-1/2} \Bigg/ \left[1 - \int_0^1 \frac{\varphi(z)z\,dz}{2\displaystyle\int_0^z \varphi(v)\,dv}\right]. \end{aligned} \tag{13}$$

We find the lower value $m_{\min}$ from (10′):

$$m_{\min} = y_0(1) = \left[2\int_0^1 \varphi(z)\,dz\right]^{1/2}. \tag{14}$$

To estimate the error of formula (14), let us determine numerically the value of the integral

$$I = \int_0^1 \frac{\varphi(z)z\,dz}{2\displaystyle\int_0^z \varphi(v)\,dv}$$

for reasonable values of the kinetic parameters of the reaction in the flame**. Using equations (4) and (5), we write

$$\int_0^z \varphi(v)\,dv = \frac{1}{\omega^{s+1}}\int_0^{z\omega/(1-z\omega)} \frac{p^s e^{-xp}\,dp}{(1+p)^2} \simeq \frac{1}{\omega^{s+1}}\int_0^{z\omega} p^s e^{-xp}\,dp. \tag{15}$$

Let us note that here the error is not admitted in the exponent of the exponential.

For $s = 1$

$$I = \frac{x\omega^2 e^x}{2}\int_0^1 \frac{z^2 e^{-x/(1-z\omega)}\,dz}{[1-(1+z\omega)e^{-x\omega z}]\,(1-z\omega)} \simeq \frac{x\omega^2}{2}\int_0^1 \frac{z^2\,dz}{e^{x\omega z} - 1 - \omega z}; \tag{16}$$

for $s = 2$

$$I = \frac{x\omega^3 e^x}{2}\int_0^1 \frac{z^3 e^{-x/(1-\omega z)}\,dz}{(1-z\omega)^2\,[2/x^2 - e^{-x\omega z}(2/x^2 + 2\omega z/x + \omega^2 z^2)]} \simeq$$

$$\simeq \frac{x\omega^3}{2}\int_0^1 \frac{z^3\,dz}{\frac{2}{x^2}(e^{x\omega z}-1) - \frac{2\omega z}{x} - \omega^2 z^2}. \tag{17}$$

Table 1

x	$\omega = 1$	$\omega = 1$	$\omega = 0.85$	$\omega = 0.85$
	$s = 1$	$s = 2$	$s = 1$	$s = 2$
5	0.425	0.763	0.478	0.845
10	0.226	0.423	0.264	0.494
20	0.111	0.214	–	–

The results of calculating the value I, presented in Table 1, show that in the case when the order of the reaction with respect to the deficient component does not exceed one, the use of the approximate theory is not associated with significant errors up to $x = 10 \div 7$. The difference between m_{min} and m_{max} in this case does not exceed 25%. Thus, not only the description of the dependence of the flame velocity on changes in combustion temperature, pressure, and composition, but also the calculation of the absolute values of u_n, as a rule, can be carried out using the formulas of the approximate theory. Only for $s = 2$ does it already give a noticeable error at $\varkappa = 10$, and for calculating the absolute values of u_n numerical integration should be used here. However, $s = 2$ is apparently realized extremely rarely, for example in a hydrazine decomposition flame (^{4}).

Since the refinement (8) decreases the value m_{min}, while the true value $m > m_{\text{min}}$, by taking $m = s!/(\varkappa\omega)^{s+1}$ we admit two errors of different signs, partly compensating each other. To illustrate the role of this circumstance, Table 2 compares the values of m for a number of real combustible systems ($T_0 = 293°$K, $s = 1$), found from the exact solution of equation (1) by numerical integration, with the approximate values $m_0 = s!/(\varkappa\omega)^{s+1}$.

For hydrogen chloride mixtures $a/a_0 = z/\vartheta$ (see (^{2})), where ϑ is the ratio of the diffusion coefficient to the thermal diffusivity, which was calculated by the methods of the theory (^{5}). It follows from Table 2 that the actual error

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* The approximate solutions y_1 and y_2 must satisfy the boundary conditions of the function y, which is achieved by the appropriate choice of the values of m.

** The value I characterizes the value z at which "cutting off" the function φ can be performed without substantial error for determining the parameter m.

Table 2

Combustible system	T_b, °K	A, kcal/mol	$\varkappa$	ω	m_0	m
16% CO + 84% air	1670	40	12.1	0.825	0.1415	0.1396
33.8% CO + 20.9% O_2 + 45.3% N_2	2535	40	7.94	0.884	0.2013	0.1715
70% Cl_2 + 30% H_2	1596	34.6	11.2	0.816	0.05663	0.05561
N_2O (decomposition)	1860	52.5	14.2	0.842	0.1179	0.1150

of the approximate theory in the cases considered does not exceed 17%. Taking into account the dependence of the thermal conductivity of the mixture on temperature also somewhat reduces the error of the approximate formula. When similarity of the temperature and concentration fields is realized,

$$\frac{d}{dx}\frac{\lambda}{c}\frac{dH}{dx} - u\rho\frac{dH}{dx} + h\Phi = 0, \tag{18}$$

where λ is the thermal conductivity, c is the heat capacity of the mixture, h is the heat of reaction,

$$H = \int_0^T c\,dT.$$

Substitution of

$$\frac{\lambda}{c}\frac{dH}{dx} = n$$

gives

$$n\frac{dn}{dz} + u\rho(H_b - H_0)n - h(H_b - H_0)\frac{\lambda}{c}\Phi = 0. \tag{19}$$

This equation differs from (1) (in which φ is determined by expression (4)) by a stronger temperature dependence of the free term, which is equivalent to an increase in the effective value of the parameter $\varkappa$.

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References Cited

1. Ya. B. Zel' dovich, D. A. Frank-Kamenetskii, ZhFKh, **12**, 100 (1938); DAN, **19**, 693 (1938).
2. Ya. B. Zel' dovich, ZhFKh, **22**, 27 (1948).
3. D. A. Frank-Kamenetskii, DAN, **18**, 511 (1938).
4. R. C. Murray, A. R. Hall, Trans. Farad. Soc., **47**, 743 (1951); G. K. Adams, G. W. Stocks, IV Symp. on Combustion, 1953, p. 239; P. Gray, J. C. Lee, H. A. Leach, D. C. Taylor, VI Symp. on Combustion, 1958, p. 255.
5. J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquides*, N. Y., 1954; C. F. Curtiss, J. O. Hirschfelder, J. Chem. Phys., **17**, 550 (1949).

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