PHYSICAL CHEMISTRY

V. N. VILYUNOV

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. N. VILYUNOV

ON THE MATHEMATICAL THEORY OF THE STEADY BURNING RATE OF A CONDENSED SUBSTANCE

(Presented by Academician V. N. Kondrat' ev, 2 VII 1960)

The mathematical theory of powder combustion was proposed by Ya. B. Zel' dovich ([1]). This theory is applicable to the region of very high pressures, when the heat release in the condensed phase (k-phase) may be neglected in comparison with the heat coming from the gas phase (g-phase), and when the combustion process is controlled by reactions of the g-phase. In the present note a generalization of the theory is given for the case of combustion of a condensed substance at low pressures.

A three-stage model of the combustion process is adopted ([2,3]) (α-, β-, γ-stages). A coordinate system is considered in which the flame is stationary. The steady process of diffusion-thermal propagation of the flame of the i-th stage is described by the system of equations

$$\lambda_i T'' - c_i m T' + Q_i f_i(n, T) = 0, \tag{1}$$

$$\rho_i D_i n'' - m n' - f_i(n, T) = 0, \tag{2}$$

where $T(y)$ is the temperature; $n(y)$ is the ratio of the dimensionless concentrations of the reacting substance; λ_i, D_i are the coefficients of thermal conductivity and diffusion; c_i is the heat capacity; Q_i is the thermal effect of the reaction; $f_i(n, T)$ is the total rate of the chemical reaction; m is the mass burning rate of the powder; ρ_i is the density.

α-Stage (k-phase). It is assumed that $D_\alpha = 0$ and that the rate of the total reaction does not depend on pressure. Equations (1)–(2) admit a first integral

$$\lambda_\alpha T_s' = c_\alpha m(T_s - T_0) - mQ_\alpha \quad \text{or} \quad \lambda_\alpha T_s' = c_\alpha m(T_s - T_{s1}), \tag{3}$$

where T_s is the surface temperature of the k-phase, depending parametrically on the pressure p and the initial temperature T_0; $Q_\alpha = c_\alpha(T_{s1} - T_0)$, where T_{s1}

is the surface temperature in flameless combustion ([2]), when the heat inflow from the g-phase is negligibly small.

The mass burning rate is found by integrating the heat-conduction equation (1), $i = \alpha$, under the boundary conditions

$$y = -\infty, \quad T = T_0 \quad (T'(-\infty) = 0);$$

$$y = 0, \quad T = T_s, \quad \lambda_\alpha T_s' = c_\alpha m (T_s - T_{s1}). \tag{4}$$

In particular, using the approximate method of Ya. B. Zel' dovich and D. A. Frank-Kamenetskii ([4]), we find the dependence of the mass burning rate on the physicochemical characteristics of the k-phase:

$$m^2 = 2\delta k_\alpha \varkappa_\alpha \frac{RT_s^2}{E_\alpha (2T_s - T_{s1} - T_0)} e^{-E_\alpha / RT_s}, \tag{5}$$

where δ is the powder density, k_α is the pre-exponential factor, χ_α is the thermal diffusivity of the κ-phase.

Equation (5) coincides with the formula of A. G. Merzhanov and F. I. Dubovitskii ([5]). The width of the preheating zone of the κ-phase is approximately determined by the expression

$$y_\alpha = \frac{\lambda_\alpha}{c_\alpha m} \ln \frac{0.05 T_0}{T_s - T_0}, \tag{6}$$

Equation (5) still does not make it possible to determine the dependence of the linear burning rate on pressure, since it contains the surface temperature T_s—as yet an unknown function of pressure; in order to determine $m = m(p)$ and $T_s = T_s(p)$, we shall relate the mass burning rate to the physicochemical characteristics of the β-stage.

β-Stage. It is assumed that in the β-stage a net exothermic reaction takes place, leading to products of incomplete combustion (NO, CO). At low pressures this stage is the final stage of the combustion process. The maximum temperature reached in this stage is T_{11}. At high pressures the processes occurring in the β-stage begin to be affected by the flame stage (γ-stage); in this case, at the boundary between the β- and γ-stages a temperature $T_1 > T_{11}$ is reached. It is assumed that T_1, like T_s, depends parametrically on p and T_0. Using the usually adopted assumption $D_\beta = \lambda_\beta / c_\beta \rho_\beta$, we find the first integral of the system (1), (2), $i = \beta$:

$$n = \frac{a}{a_{s1}} = \frac{T_1 - T}{T_1 - T_s} \tag{7}$$

(the integral of Ya. B. Zeldovich).

The expression for the mass velocity is found by integrating equations (1), $i = \beta$, under the boundary conditions

$$\begin{aligned} y = 0, \quad T = T_s, \quad \lambda_\alpha T_s' = c_\alpha m\,(T_s - T_{s1}); \\ y = y_1, \quad T = T_1, \lambda_\beta T_1' = c_\beta m\,(T_1 - T_{11}). \end{aligned} \tag{8}$$

Following the method ([4]), we obtain:

$$m^2 = \frac{2\lambda_\beta Z_\beta (\nu_\beta)! \left(\dfrac{RT_1^2}{E_\beta}\right)^{\nu_\beta + 1}}{c_\beta (2T_1 - T_{11} - T_{s1})(T_1 - T_s)^{\nu_\beta}} e^{-E_\beta/RT_1}, \qquad Z_\beta = k_\beta \mu_\beta a_{s1}^{\nu_\beta - 1} \left(\frac{p}{RT_1}\right)^{\nu_\beta}. \tag{9}$$

Formula (9) gives the relation between the mass burning rate and the physico-chemical characteristics of the β-stage. In the integration, the usual expression for the net rate of the chemical reaction was adopted,

$$f_\beta(T) = k_\beta \frac{\mu_\beta}{a_{s1}} \left(\frac{a_{sp}}{RT}\right)^{\nu_\beta} \left(\frac{T_1 - T}{T_1 - T_s}\right)^{\nu_\beta} e^{-E_\beta/RT}, \tag{10}$$

where μ_β is the mean molecular weight; ν_β is the overall reaction order; E_β is the effective value of the activation energy; a_{s1} is the relative concentration of the reacting substance at the interface between the α- and β-stages in flameless combustion; a_s is the relative concentration when the processes of the κ-phase are affected by the ε-phase.

Formula (9) was obtained under the assumption $a_s \equiv a_{s1}$.

The width of the preheating zone of the β-stage is determined by the formula

$$y_1 \simeq \frac{\lambda_\beta}{c_\beta m} \ln \frac{T_1 - T_{s1}}{T_s - T_{s1}}. \tag{11}$$

γ-Stage (flame stage). In this stage an exothermic reaction of interaction takes place between the products of the reaction of the β-stage, chiefly···

way between NO and CO. Taking $D_\gamma = \lambda_\gamma / c_\gamma \rho_\gamma$, we find $n = \dfrac{T_{21} - T}{T_{21} - T_1}$. Integrating equations (1), $i = \gamma$, under the boundary conditions:

$$y = y_1, \quad T = T_1, \quad \lambda_\beta T_1' = c_\beta m\,(T_1 - T_{11});$$

$$y = +\infty, \quad T = T_{21}\,(T'(+\infty) = 0), \tag{12}$$

we obtain

$$m^2 = \frac{2\lambda_\gamma Z_\gamma(\nu_\gamma)!\,(RT_{21}/E_\gamma)^{\nu_\gamma+1}}{c_\gamma(T_{21}-T_{11})(T_{21}-T_1)\nu_\gamma} e^{-E_\gamma/RT_{21}}, \quad Z_\gamma = k_\gamma \mu_\gamma a_1^{\nu_\gamma - 1}\left(\frac{p}{RT_{21}}\right)^{\nu_\gamma}. \tag{13}$$

The width of the preheating zone of the flame stage is found from the formula

$$y_2 - y_1 = \frac{\lambda_\gamma}{c_\gamma m}\ln\frac{T_{21}-T_{11}}{T_1 - T_{11}}. \tag{14}$$

As the pressure increases, T_1 and m increase, and consequently the preheating width decreases. In the limiting case, when $T_1 \to T_{21}$, combustion will take place in two stages. This limiting case will probably be observed in the combustion of powder at very high pressures, when the flame is very close to the surface of the k-phase.

Table 1

T_0, °C	V, cm/sec	p, kg/cm^2	k_p	k_T, 1/°K	$y_1 \cdot 10^4$, cm	$y_n \cdot 10^4$, cm	T_s, °K
+25	0.2	3.0	0.56	0.0049	6.88	122	756
+25	0.4	10.0	0.58	0.0048	22.7	63.1	808
+25	1.0	44.0	0.67	0.0044	5.0	26.2	890
+25	1.4	71.2	0.74	0.0041	2.8	19.0	924
−55	0.2	6.2	0.58	0.0055	37.2	139	756
−55	0.4	19.5	0.63	0.0053	12.8	71.2	808
−55	1.0	71.0	0.87	0.0042	2.5	29.4	890

Formulas (5), (9), (13) solve the problem in principle, i.e., they make it possible to calculate the dependences $m = m(p, T_0)$, $T_s = T_s(p, T_0)$, $T_1 = T_1(p, T_0)$. The calculations are considerably simplified if one considers powder combustion at low pressures, when the influence of the flame stage may be neglected ($T_1 \equiv T_{11}$). For this particular case the pressure coefficient k_p and the temperature coefficient k_T are expressed in the form:

$$k_p = \left(\frac{\partial \ln m}{\partial \ln p}\right)_{T_0} \simeq \frac{\nu_\beta}{2}\left[1 - \frac{\nu_\beta}{T_{11} - T_s}\frac{RT_s^2}{E_\alpha}\right]^{-1}, \tag{15}$$

$$k_T = \left(\frac{\partial \ln m}{\partial T_0}\right)_p \simeq \frac{k_p}{\nu_\beta}\left[\frac{E_\beta}{RT_{11}^2} - \frac{\nu_\beta}{T_{11} - T_s} + \frac{\nu_\beta + 2}{T_{11}}\right]. \quad (16)$$

Analysis of formulas (15) and (16) shows that with increasing T_s (or pressure) k_p increases; the temperature coefficient k_T, for $A > 1$, increases with increasing T_s, while for $A < 1$ it decreases with increasing T_s. The parameter A is equal to

$$A = \frac{E_\alpha}{E_\beta}\left(\frac{T_{11}}{T_s}\right)^2 \left(1 + \frac{\nu_\beta + 2}{E_\beta} RT_{11}\right)^{-1}. \quad (17)$$

Using the formulas obtained, a sample calculation was carried out for nitroglycerin powder. The composition and experimental data for this powder are given in work (6). The data used for the calculation are: $T_{s1} = 700°$K,

$$E_\alpha^* = 32000 \text{ cal/mole}, \quad \delta = 1.6 \text{ g/cm}^3, \quad c_\alpha = c_\beta = 0.35 \text{ cal/g} \cdot \text{deg}, \quad T_{11} = 1085°\text{K},$$

$$E_\beta = 21000 \text{ cal/mole}, \quad \lambda_\alpha = \lambda_\beta = 4 \cdot 10^{-4} \text{ cal/cm} \cdot \text{sec} \cdot \text{deg}, \quad \mu_\beta = 27 \text{ g/mole},$$

$$k_\beta = 0.93 \cdot 10^{10} \text{ sec}^{-1}, \quad \nu_\beta = 1.$$

To simplify the calculations, the exact formula (5) was replaced by the approximate one

$$V = B_\alpha e^{-E_\alpha{}^*/2RT_s}, \quad \text{where } B_\alpha = 0.875 \cdot 10^4 \frac{\text{cm}}{\text{sec}}.$$

The results of the calculation are summarized in Table 1.

Siberian Physicotechnical Institute
at Tomsk State University
named after V. V. Kuibyshev

Received
23 VI 1960

REFERENCES

1. Ya. B. Zel' dovich, ZhETF, **12**, 498 (1942).

2. P. F. Pokhil, *Collected Papers: Physics of Explosion*, **2**, 1953.

3. K. K. Andreev, *Thermal Decomposition and Combustion of Explosives*, Moscow, 1957.

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

5. A. G. Merzhanov, F. I. Dubovitskii, DAN, **129**, No. 1 (1959).

6. R. D. Geckler, *Selected Combustion Problems*, London, 1954, p. 289.

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