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A. I. ROZLOVSKII

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Abstract

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A. I. ROZLOVSKII

ON THE CRITICAL CONDITIONS FOR IGNITION OF COMBUSTIBLE GAS MIXTURES BY HEATED SOLID BODIES

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The question of the possibility of igniting combustible gas mixtures by heated bodies is of great applied interest both for problems of engine operation and for safety engineering. Ya. B. Zel' dovich (^{1}) obtained an approximate expression for the critical condition for the existence of a stationary thermal regime when ignition is produced by an infinite plane wall having a constant temperature T_s,

$$q_{\mathrm{cr}}^2 = 2\lambda h \int_{T_0}^{T_s} \Phi(a_1, T)\, dT. \tag{1}$$

Here q_{cr} is the critical value of the heat flux from the reaction zone per unit of igniting surface; λ is the thermal conductivity; h is the heat effect of the reaction; Φ is the reaction rate; a is the dimensionless concentration in grams per 1 g of mixture; the subscript 1 refers to the deficient component, whose concentration determines the reactive part of the mixture; changes in the concentrations of the remaining components may be neglected in an approximate calculation.

Neglecting the dependence of Φ on the concentration of the mixture, which becomes depleted near the surface, Ya. B. Zel' dovich obtains

$$q_{\mathrm{cr}}^2 = 2\lambda\theta h \Phi(T_s), \tag{2}$$

where $\theta = RT_s^2/A$ is the characteristic temperature interval, and A is the activation energy. In (^{2}) this solution was refined with allowance for variable concentration and for the similarity of the fields T and a (^{3}). For constant heat capacity c,

$$a_1/a_{01} = (T_b - T)/(T_b - T_0), \tag{3}$$

where the subscript 0 refers to the initial state of the mixture, and b to the products of its combustion.*

Let us note a special circumstance that has not been mentioned previously. Zel' dovich' s solution describes only the case in which the combustion temperature T_b exceeds the ignition temperature T_s. It follows from (3) that when $T_b = T_s$ the reaction at the surface is completely completed, i.e., propagation of a normal flame becomes possible. This means that any heated, catalytically inactive body for which $T_s \geq T_b$ must ignite the combustible mixture. Experiment shows that this is not always so; ignition in this case obeys other laws. As will be shown—

* We shall prove the validity of the similarity condition for the present problem. The equations of thermal conduction and diffusion along the x-axis, neglecting thermal diffusion, have the form:

$$\frac{d}{dx}\lambda\frac{dT}{dx} + h\Phi(a_1, T) = 0, \qquad \frac{d}{dx}D\rho\frac{da_1}{dx} - \Phi(a_1, T) = 0,$$

where D is the diffusion coefficient and ρ is the density. Introducing the variable $H = \int_0^T c\, dT$, we find

$$\frac{dH}{dx} + \frac{Dc\rho}{\lambda}\frac{d(a_1 h)}{dx} = \text{const}.$$

For gas mixtures of nearly equal molecular weight, for which the diffusion and thermal-diffusivity coefficients $(\lambda/c\rho)$ are equal,

$$d(H + a_1 h)/dx = \text{const}.$$

Since at the surface $dT/dx = 0$ and, in the absence of catalysis, $da_1/dx = 0$, const $= 0$, $H + a_1 h = \text{const}' = H_0 + a_{01} h$, whence (3) follows.

specified in (1), equation (1) is applicable for nonplane conditions in the case when the radius of curvature of the igniting surface is large in comparison with the parameter $\sqrt{\lambda\theta/h\Phi(T_s)}$, which is of the order of the width of the reaction zone in the flame and which, even for slow flames, does not exceed tenths of a millimeter.

As in (^{2}), when thermal expansion is taken into account one assumes $T_0/T \approx T_0/T_s$, since Φ is small outside a comparatively narrow temperature interval near T_s. This gives $\Phi = B a_1^{s_1}(T_0/T_s)^s e^{-A/RT}$, where B is the pre-exponential factor of the rate constant, s is the total order of the reaction, and s_1 is the same for the deficient component. Expanding the exponent in a series (^{4}), we obtain

$$q_{\text{cr}}^2 = 2\lambda h B e^{-A/RT_s}(T_0/T_s)^s \left[a_{01}/(T_b - T_0)\right]^{s_1} \int_{T_0}^{T_s} (T_b - T)^{s_1} e^{-(T_s - T)/\theta}\, dT. \quad (4)$$

The authors of (2) take $s = s_1 = 2$; however, the integrand in (4) contains not $s = s_1 + s_2$ (s_2 being for the excess component), but s_1, which can hardly be greater than unity. Setting $s_1 = 1$, we find

$$\begin{aligned} q_{\text{cr}}^2 &= 2\lambda h B e^{-A/RT_s} \theta (T_0/T_s)^s \left[a_{01}/(T_b - T_0) \right] \left[T_b - T_s + \theta - e^{-(T_s - T_0)/\theta} \right. \\ &\qquad \left. \times (T_b - T_0 + \theta) \right] \approx 2\lambda h B e^{-A/RT_s} a_{01} (T_0/T_s)^s \theta (T_b - T_s + \theta)/(T_b - T_0) \\ &= 2\lambda\theta h \Phi(a_{01}, T_s)(T_b - T_s + \theta)/(T_b - T_0). \end{aligned} \tag{5}$$

Thus, for $s_1 = 1$ the refined solution differs from the approximate expression (2) by the factor $(T_b - T_s + \theta)/(T_b - T_0)$; in solution (2) this correction should be $(T_b - T_s)(T_b - T_s + 2\theta)/(T_b - T_0)^2$; we note that $T_b - T_s$ is not always $\gg 2\theta$.

When igniting gas mixtures that differ strongly in molecular weight, $\vartheta = Dc_p/\lambda \neq 1$. Taking ϑ to be constant, we find

$$d(H + \vartheta a_1 h)/dx = \text{const} = 0; \qquad H + \vartheta a_1 h = \text{const}' = H_b. \tag{6}$$

It follows from this that, when mixtures with $\vartheta \neq 1$ are ignited, the condition $(T_b - T)/(T_b - T_0) = \vartheta a_1/a_{01}$ holds, which in the combustion of these mixtures is also approximately valid for the reaction zone (5). In this case the expression for q_{cr}^2 changes only by the constant factor $1/\vartheta^{s_1}$.

We shall express the quantity q_{cr} in terms of dimensionless similarity criteria, $q_{\text{cr}}(T_s) = \lambda(T_s - T_0)\text{Nu}/d$, where d is the characteristic size of the igniting body. In the high-temperature region $\lambda \sim \sqrt{T_s}$; for the external problem, at $\text{Re} > 200$, $\text{Nu} = 0.54\sqrt{\text{Re}}$ (6). Hence

$$e^{A/RT_s} \sim \frac{(T_b - T_s + RT_s^2/A)\, T_s^{0.5 - s_2}}{(T_s - T_0)^2} \frac{d}{v} = \varphi_1 \quad \text{for } s_1 = 1; \tag{7}$$

$$e^{A/RT_s} \sim \frac{(T_b - T_s + 2RT_s^2/A)(T_b - T_s)}{(T_s - T_0)^2 T_s^{s_2 - 0.5}} \frac{d}{v} = \varphi_2 \quad \text{for } s_1 = 2, \tag{8}$$

where v is the velocity of the gas flow.

To judge the order of the reaction we shall use data on the influence of pressure p on the normal flame speed u_n. For a number of hydrocarbon–air mixtures $u_n \sim p^{-g}$ (7–9), where g has values from 0.25 to 0.40. It is known that $s = 2(1 - g)$, if the combustion products are not dissociated (10). Therefore one may assume that in the mixtures under consideration the overall order of the reaction is somewhat greater than unity. Since it is probable that $s_1 > s_2$, our assumption $s_1 \approx 1$ cannot be regarded as unfounded.

Let us consider how well the theory agrees with experimental data ([11,12]), and compare the results of the calculation with the calculations of ([2]). It is necessary to give

a preliminary, even if only approximate, estimate of the magnitude of the activation energy determining θ. In work ([13]) the values of A were calculated for a number of fuel-air mixtures: $A = 26$ kcal/mole for pentane and 16 kcal/mole for hydrogen.

For a mixture of 3% pentane ($T_b = 2222$°K, $v = 4$ m/sec), taking $s_1 = 1$, $s_2 = 0.5$, we find from the dependence $T_s(d)$, according to the data of ([11]), that in the coordinates $\lg \varphi - 1/T_s$ the points lie satisfactorily on a straight line with an angular coefficient corresponding to $A = 27$ kcal/mole, in good agreement with independent data ([13]). In work ([2]), for pentane with $s_1 = 2$ and the simplifications indicated above, $A =$ 35-36 was obtained; assuming $s_1 = 2$, $s_2 = 0$, we find from (8) $A = 33$. An analogous calculation for a mixture with 20% H_2 ($T_b = 1853$°K) ([11]) gives, for $s_1 = 1$, $s_2 = 0.5$, $A = 38.5$ in the region of low temperatures and $A = 20$ in the region of high temperatures; for other variants of the calculation, values larger by 4-7 kcal/mole. If the composition of town gas in ([11]) is the same as in ([12]), then only in the richest of the mixtures studied in ([12]) is $T_b > T_s$. Processing the dependence $T_s(d)$ for a mixture with 20% town gas (50% H_2) at $v = 1.2$ m/sec, $T_b = 2330$°K, $s_1 = 1$, $s_2 = 0.5$ gives $A = 32.5$.

When processing the dependence $T_s(v)$ for mixtures of town gas ([12]) with 16 and 20% fuel, at $s_1 = 1$, the effective $A = 23$ kcal/mole at large v (large T_s), increasing at the minimum among the investigated T_s by a factor of 2-4. Under these conditions the critical T_s depends strongly on the material of the igniting body, and the effect increases with increasing flow velocity. These features were observed still more clearly in the experiments ([14]), in which a turbulent stream was ignited by heated rods. Thus, for pentane, the effective A increases severalfold from a value of the order of 11-12 kcal/mole. The influence of the rod material here is especially great; thus, when stainless steel is replaced by platinum, for $d = 6.3$ mm, $v = 72$ m/sec, the critical T_s of a stoichiometric pentane-air mixture rises by 430°.

It seems probable that all these features, which until now had gone unnoticed and are connected with the manifest catalytic activity of the surface, are due to the transition of the reaction from the kinetic to the diffusion region ([6]). At low flow velocities ignition occurs at low T_s; it is purely homogeneous, and its critical conditions do not depend on the properties of the surface, which plays only the role of a heat source. The beginning of the transition to the diffusion region can already be seen in ([11]) in connection with a certain change in T_s during ignition of hydrogen mixtures by quartz and platinum spheres. The transition to diffusion (catalytic) combustion is manifested in a decrease in the effective activation energy; depletion of the mixture near the surface during a heterogeneous reaction causes an increase in the critical T_s. Let us note that the reaction proceeds in the kinetic region at low flow velocities, and not conversely, as under isothermal conditions.

Let us explain why an increase in temperature has a stronger effect on the catalytic reaction, although its activation energy A_k is usually smaller than the corresponding value for the homogeneous process A_g. The amount of substance reacting homogeneously during ignition is

$$m_g = q_{kp}/h \sim \sqrt{\Phi(T_s)} \sim e^{-A_g/2RT_s}.$$

The analogous quantity for the catalytic reaction is

$$m_k \sim e^{-A_k/RT_s}.$$

Consequently, an increase in temperature has a stronger effect on the heterogeneous reaction if $A_k > A_g/2$ (cf. with ([15])). On the other hand, an increase in v, accompanied by an increase in temperature, accelerates the transport of substance to the surface, and hence also the heterogeneous reaction.

It also seems possible to calculate the absolute values of the critical ignition conditions from the known properties of the combustible mixture. For this purpose it is expedient to replace the reaction-rate quantity Φ, which is difficult to determine, by a macroscopic characteristic of the combustible mixture—its normal flame speed. For all practically important cases

cases the theory of normal combustion gives [(3,5)]

$$u\rho \Big/ \sqrt{\frac{1}{a_{01}}\Phi(a_{01}, T_b)\frac{\lambda}{c}} = \sqrt{\frac{2s_1!}{\vartheta^{s_1}}\left(\frac{\theta}{T_b - T_0}\right)^{s_1+1}} \tag{9}$$

Let us compare the parameters of normal combustion of a mixture of the components under consideration, having a combustion temperature T_s, the corresponding initial concentration a_s, density ρ_s, and normal flame velocity u_s, with the critical conditions for ignition by a heated body of a mixture with concentration a_{cr}. Equations (9) and (4) give, for $s_1 = 1$,

$$u_s = \frac{\lambda}{c\rho_s}\frac{\text{Nu}}{d}\sqrt{\frac{\pi_s}{\pi_{\text{cr}}}\frac{T_b - T_0}{T_s - T_0}\frac{\theta}{T_b - T_s + \theta}} =$$

$$= 0.54\,\frac{\lambda}{Q}\sqrt{\frac{\overline{M}RT_0 v(T_b - T_s)(T_s - T_0)}{p\eta d\pi_s\pi_{\text{cr}}\left(\dfrac{T_b - T_s}{\theta} + 1\right)}}. \tag{10}$$

Here π is the mole fraction of the deficient component, Q is the molar heat of reaction, $\overline{M}$ is the mean molecular weight of the combustible mixture, and η is the viscosity. Equation (10) is valid independently of the value of ϑ, since the additional factor $1/\vartheta^{s_1}$ enters into the expressions both for q_{cr} and for u_s.

For the above-mentioned pentane-air mixture $^{(11)}$, at $d = 3.6$ mm, $T_s = 1373$°K, $\pi_s = 1.122\%$, $v = 4 \cdot 10^2$ cm/sec. Taking $A = 25$ kcal/mole, we find $u_s = 2.7$ cm/sec. According to the data of $^{(16)}$, for lean air mixtures of a series of hydrocarbons (CH_4, C_2H_6, C_2H_4, C_3H_8, C_4H_{10})

$$u_n = 0.794 \bigg/ \left(1 - 2.206 \times \pi \frac{Qp}{RT_0}\right),$$

whence for a mixture with 1.122% pentane we find $u_n = 4.2$ cm/sec, in satisfactory agreement with the calculated value.

For methane, at $d = 6.5$ mm, $\pi_{\text{cr}} = 8.0\%$, $T_b = 2052$°K, $T_s \simeq 1473$°K, $\pi_s = 5.0\%$. Taking $A = 26$ kcal/mole $^{(13)}$, we find $u_s = 2.9$ cm/sec. According to $^{(16)}$ and $^{(17)}$, a 5% methane-air mixture is close to the concentration limit of flame propagation, for which $u_n \simeq 3$ cm/sec is recorded in $^{(16)}$. It follows from the foregoing that the critical conditions for ignition by a heated surface can be calculated with good accuracy from measurements of flame velocities of lean mixtures close to the propagation limits. When a catalytic effect exists, the calculation gives the lower boundary of the critical values of T_s and v.

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All-Union Scientific-Research
Institute of Sanitary-Engineering Equipment

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

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