KINETIC RELATIONSHIPS IN IGNITION BY A HEATED SURFACE UNDER ENGINE CONDITIONS

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KINETIC RELATIONSHIPS IN IGNITION BY A HEATED SURFACE UNDER ENGINE CONDITIONS

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In paper (1) the results were presented of an experimental investigation of ignition by a heated surface in a single-working-cycle apparatus that closely reproduces conditions in an engine; for a number of typical motor fuels, dependences were obtained of the ignition temperatures (T_{ign}) on the compression temperatures and pressures (T_{c} and P_{c}).

Proceeding from the thermal theory of gas ignition by a heated surface, it appears possible, on the basis of the experimental dependences $T_{\mathrm{ign}} = f(T_{\mathrm{c}})$ at $P_{\mathrm{c}} = \mathrm{const}$, to calculate the corresponding values of the apparent activation energies, and, on the basis of the dependences $T_{\mathrm{ign}} = F(P_{\mathrm{c}})$ at $T_{\mathrm{c}} = \mathrm{const}$, the values of the order of the reactions developing near the heated surface at temperatures of 700–900°. Considering that data on the mechanism of chemical reactions at such temperatures are extremely scarce, such data may be of interest all the more because our experiments covered a comparatively wide range of different motor fuels.

As Ya. B. Zel' dovich (2) showed theoretically, the critical conditions for ignition of a gas by a heated surface are determined by the existence of a zero temperature gradient in the reacting gas near this surface. This means that ignition will occur at such a temperature of the heated wall at which the heat removal from the reaction zone into the adjacent, colder gas layers will be completely compensated by the heat of the reactions taking place in the gas layer near the heated surface. Taking into account that, at high values of the activation energy, the thickness of the layer ξ in which the main part of the reaction is concentrated is small in comparison with the distance l between the heated and cold walls, and therefore neglecting differences in the temperature gradients in the absence and in the presence of reaction, one obtains relations connecting the ignition temperature T_{ign} with the dimensions of the vessel and the temperature of its cold walls T_0, for a known dependence of the reaction rate on temperature and pressure, $W = F(T_{\mathrm{ign}}, P)$. In the case of a plane-parallel vessel of infinite extent, under the assumption of purely conductive heat transfer, the relation has the form

$$l = \sqrt{\frac{\lambda E(T_{\mathrm{ign}} - T_0)^2}{2F(T_{\mathrm{ign}}, P) R T_{\mathrm{ign}}^2}}, \tag{1}$$

It is evident that the essence of the matter should not change under any other mode of heat transfer, in particular through transport by turbulent pulsations; the critical ignition conditions will still correspond to a zero temperature gradient near the heated surface. In the case where the surface is washed by a turbulent flow, the main difference reduces to the fact that the entire temperature drop is practically concentrated in a certain, relatively narrow boundary layer, whereas the temperature of the remaining gas may be regarded as unchanged, especially for small dimensions of the heated surface.

Without touching on the question of the true structure of the boundary layer, we shall use, for the purposes of interest to us, the conventional concept of a "reduced film," i.e., such a conventional distance δ between a wall having temperature T_{p} and a gas with temperature T_0 at which the heat removal due to molecular transfer, determined by the quantity λ, in the presence of a linear temperature distribution inside the reduced film, would be equal to the actual heat transfer from the heated surface, characterized by the value of the heat-transfer coefficient α, i.e.,

$$\lambda (T_{\mathrm{p}} - T_0)\, \delta = \alpha (T_{\mathrm{p}} - T_0),$$

whence

$$\delta = \frac{\lambda}{\alpha}. \tag{2}$$

Substituting the latter relation into formula (1), we have:

$$\alpha = \sqrt{\frac{\lambda 2F(T_{\mathrm{p}} P) R T_{\mathrm{p}}^2}{E(T_{\mathrm{p}} - T_0)^2}}. \tag{3}$$

The expression obtained is a considerably more general condition for ignition of a gas by a heated surface. It is equally applicable to any heat-transfer conditions that are accounted for by the value α^*. It must be borne in mind, however, that the possibility of ignition is determined by no means by the mean value of the heat-transfer coefficient referred to the entire surface of the body being flowed over, but by its smallest local values; this circumstance greatly complicates the theoretical consideration of the question of ignition of a gas by bodies heated and moving relative to it, if one operates with dependences of ignition temperatures on such parameters, strongly affecting the heat-transfer conditions, as the size of an incandescent particle or its flight velocity, as was done in works ($^{3-5}$). Still more complicated is the question of ignition of the working mixture in an engine as a result of its contact with one or another overheated part, or with incandescent portions of carbon deposit, in the presence in the combustion chamber of intense and, moreover, highly peculiar turbulent motion of the charge.

The problem is, however, greatly simplified if, as was done in our experiments, the gas-dynamic conditions of flow of the combustible mixture around the heated surface are kept unchanged and only the temperature or the pressure of the latter is varied. The generalized dependence relating the heat-transfer conditions to the character of the turbulent motion of the gas has the form $\mathrm{Nu} = C\mathrm{Re}^n$. In external flow around bodies placed in a stream, the values of C and n depend both on the Reynolds number, referred to the dimensions of the body being flowed over, and on the turbulence of the stream. In a stream with normal (wall) turbulence, for $80 < \mathrm{Re} < 5 \cdot 10^3$ (where the Reynolds number is referred to the dimensions of the body being flowed over), the value of the exponent $n = 0.46$, and for $5 \cdot 10^3 < \mathrm{Re} < 5 \cdot 10^4$, $n = 0.6$; the same value $n = 0.6$ is also retained in the case of strong turbulence behind grids. Accordingly, for conditions of turbulence of medium intensity in an engine it is evidently possible, without special errors, to take $n = 0.5$.

At one and the same engine speed, the velocity of flow over the heated surface may be considered unchanged—independent of temperature and pressure, in connection with which $\alpha = C\lambda\nu^{-0.5}$. Accordingly, in the case of reactions obeying the Arrhenius law, expression (3) may be written in the following form:

$$\frac{T_{\mathrm{p}}}{T_{\mathrm{p}} - T_{\mathrm{mix}}} \sqrt{\frac{\nu P_{\mathrm{mix}}^n e^{-E/RT_{\mathrm{p}}}}{\lambda E}} = \mathrm{const.} \tag{4}$$

This relation makes it possible to calculate average values of the activation energy and reaction order exponents from the experimental dependences $T_{\mathrm{p}} = f(T\ )$ at $P\ $ = const, taking the quantities E as unchanged within the interval of variation of $T\ $ under consideration. Since in the calculation it is not the absolute values of λ and ν that matter, but only their relative changes with temperature, instead of the values of λ and ν for the mixture under consideration one may, without any substantial error, use their values for air, referring them to the temperature of the gas washing the heated surface, i.e., to $T\ $.

Table 1 gives the experimental values of T_{p} corresponding to a series of compression temperatures $T\ $, for various fuels tested at their stoichiometric ratio with air and at a constant compression pressure $P\ = 8.25$ ata, and the corresponding calculated values of the apparent activation energies in the intervals of $T\ $ considered. Here the values of $T\ $ and $P\ $ are to a considerable extent conditional, since they do not take into account heating of the mixture due to preflame reactions.

* An analogous problem was solved in a more general form in work ([3]).

Table 1

Apparent values of the activation energy (kcal/mole) of various fuels upon ignition by a heated surface in different ranges of compression temperatures; $\alpha = 1$; $P \;= 8.25$ ata. In parentheses are indicated the ignition temperatures T_p at the boundaries of the temperature interval considered

Fuel	Interval T , °K: 550–650	Interval T , °K: 650–725
Benzene	77 (1198)(1180)	77 (1180)(1164)
Isooctane	60 (1187)(1163)	42 (1163)(1130)
Coke-oven gas	73 (1159)(1140)	73 (1140)(1122)
Aviation gasoline B-70	70 (1165)(1140)	68 (1140)(1117)
Triptane	56 (1162)(1137)	56 (1137)(1113)
Diisobutylene	37 (1162)(1121)	37 (1121)(1083)
Cumene	36 (1179)(1134)	36 (1134)(1098)
50% isooctane ++ 50% n-heptane	21 (1183)(1098)	10 (1098)*(1053)

* In the range 650–680° K.

From the data of Table 1 it is seen that the values of E_{app} are constant at those compression temperatures at which, under the conditions of these experiments, the corresponding combustible mixture is still far from autoignition. When, however, preflame processes begin to develop in the mixture, caused by its heating from compression above a certain limit, the value of E_{app}, calculated by formula (4), decreases sharply. Such a decrease in E_{app} may be caused by two reasons: acceleration of reactions near the heated surface by active products of preflame oxidation in the volume, and a decrease in heat removal due to an increase in the temperature of the mixture in the course of this same preflame oxidation.

Calculations show that the influence of the latter factor on the calculated values of E_{app} is very substantial. Thus, for example, in order in the case of isooctane to retain, in the region of high T , the same value $E_{\text{app}} = 60$ kcal/mole, which was obtained in the interval T from 550 to 650° K, it is sufficient to assume that the actual temperature of the compressed mixture is only 38° higher than that adopted in the calculation under the assumption of absence of any self-heating (i.e., to put T equal to 763° K instead of 725° K). In exactly the same way, if one proceeds from the fact that in reality the activation energy of the 50-octane mixture is constant and close to the activation energy of isooctane, for example, taking for it $E_{\text{app}} = 50$ kcal/mole, then an ignition temperature $T_p = 1100°$ K must correspond to a compression temperature not of 650° K (as indicated in Table 1), but $T \simeq 780°$ K, i.e., 130° higher; and such self-heating of the mixture at the end of the low-temperature stage of oxidation is quite real for paraffin fuels.

Thus, it may evidently be considered that the entire observed decrease in ignition temperatures as the mixture approaches the conditions of its autoignition from compression is due only to the rise in temperature

in the cool-flame stages; the decreases in E_{app} obtained at high T_{c} should be regarded as purely fictitious.

As for the calculated values of E_{app} in the region of T_{c} where they are not distorted by the influence of preflame processes, for such fuels as benzene, isooctane, coke-oven gas, and B-70 gasoline ($E_{\text{app}} = 70$–77 kcal/mol), these values substantially exceed those known from experiments with ignition by compression (^{6}), as well as by incandescent bodies ($^{3-5}$), but agree closely with those obtained in heated vessels at temperatures > 680°C (^{7,8}), approaching the energies of rupture of the principal intramolecular bonds. In contrast, for diisobutylene and cumene considerably lower E_{app} values are obtained (36–37 kcal/mol), likewise strictly constant at all T_{c}, and in this connection there is no basis for assuming here any influence of preflame processes. In the literature there are no data on the activation energies of these hydrocarbons in the temperature range under consideration.

Using relation (4), it appears possible to calculate the values of the reaction order in ignition by a heated surface from the experimental dependences $T_{\text{p}} = f(P_{\text{c}})$ at $T_{\text{c}} \simeq \text{const}$ (see (^{1}), Fig. 2), taking the value of E_{app} in accordance with the data of Table 1. In doing so, in both cases only those ranges of variation of P_{c} and T_{c} are considered in which no distorting influence of preflame self-heating is detected.

Table 2

Values of the reaction-order indices for various fuels upon ignition by a heated surface; $\alpha = 1$; $P_{\text{c}} = 4$–12 ata, $T_{\text{c}} = 637$–652°K

Fuel	T_{p}, °K	$E_{\text{app}}, \frac{\text{kcal}}{\text{mol}}$	n
Benzene	1185—1180	77	0.1
Isooctane	1172—1140	60	0.6
Diisobutylene	1150—1060	37	0.8

Table 2 gives the values of n, calculated in the manner indicated, for three fuels, averaged over the considered intervals of variation of P_{c} and T_{c} and, correspondingly, of T_{p}. It is seen from the table that, in the case of isooctane and diisobutylene, the values of n prove to be close to those known from the literature for ignition, for example, of liquid fuels injected into heated air (^{7}). In contrast, for benzene a reaction order close to zero was obtained, evidently indicating the leading role, in the present case, of heterogeneous processes accompanied by high saturation of the surface.

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