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T. A. Ponizko, A. I. Rozlovskii

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T. A. Ponizko, A. I. Rozlovskii

LOW-TEMPERATURE IGNITION OF COMBUSTIBLE GAS MIXTURES

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The thermal regime of a nonstationary self-accelerating gas reaction that arises when a cold combustible mixture comes into contact with a heated solid wall differs substantially from the regime of self-ignition in a heated vessel because of the more intense heat transfer. This problem was first considered by Ya. B. Zel' dovich (⌢1). He obtained an expression relating the magnitude of the heat flux from the reaction zone at the surface to the rate of chemical transformation. This expression forms the basis for calculating ignition limits.

In the further development of the theory (⌢2, ⌢3), use was made of the fact that the concentration and temperature fields during ignition are similar to those during combustion (⌢4). The solution obtained directly related the critical value of the ignition temperature T_s to the dimensions d and the velocity w of the igniting body; always $w > 0$ because of free convection. Comparison with experimental data ($^{5-}$7) showed that this dependence is usually not obeyed. Deviations from the requirements of the theory are associated with a catalytic reaction on the surface and with the nonstationarity of the thermal regime during ignition (⌢8). The experimental value of T_s is greater than the calculated one, which determines the lower bound for T_s.

The question nevertheless remains open as to the possibility of lower-temperature ignition caused by autocatalytic acceleration of a reaction with pronounced branching. It is known (⌢9) that such a mechanism of reaction occurring in a heated vessel can lead to the appearance of cold flames, often outside the ranges (of concentration and temperature) in which ordinary hot flames arise.

The spontaneous appearance of cold flames in explosive mixtures at low temperatures may lead to a subsequent transition from a cold flame to a hot one, which constitutes the well-known phenomenon of two-stage self-ignition. Rich ether-air mixtures form two consecutively arranged flames in a flat-flame burner: the

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

lower one is cold and the upper one hot (⁀10). Spence and Townend (⁀11) observed a cold and two-stage flame in explosive ether–air mixtures when ignited by moderately heated bodies; however, they did not determine the temperature required for this.

There are no other indications of the possibility of lower-temperature ignition than in works (5-7) and similar studies, which testifies to conditions unfavorable for the development of a cool-flame reaction during ignition. This is evidently due to the insufficient duration of the high-temperature process of generating active products in the gas stream, which prevents their accumulation. It may be expected that cool-flame ignition will be more easily achieved under free convection.

To test the possibility of low-temperature ignition, we determined the values of T_s for air mixtures of a number of combustible gases and vapors under free-convection conditions: methane, hydrogen, B-70 gasoline, acetylene, carbon disulfide, diethyl ether, and ethylene glycol diethyl ether. The mixtures under study were prepared in steel explosion chambers of volume $V = 17$ and 73 liters, in the middle of which heated igniters were placed. The chambers were thermostated at a temperature of 50-70° in order to attain the desired vapor pressure of the fuel. Incandescent lamps (glass) $d = 61$ mm (a), spiral (b) and U-shaped (c) steel tubes $d = 10.5$ mm, and a quartz tube $d = 24$ mm (d) served as igniters. The tubes contained heating elements protected from contact with the explosive mixture. A thermocouple was fastened to the surface of the igniter.

The components were dosed according to their partial pressures and weighed amounts of liquid fuel, and were checked by analysis. After preparation of the mixture and its stirring by the fan present in the chamber, the igniter was heated at a rate of ~ 60 deg/min. Analysis showed that, up to the moment of flame occurrence, the average composition of the mixture in the chamber did not change appreciably. The experimental results are presented in Figs. 1 and 2 as dependences of the found values of T_s on a unified composition variable. The latter, as for flame-propagation limits, is conveniently characterized by the logarithm of the oxidizer-excess coefficient α (12).

Fig. 1. Ignition temperatures of air mixtures of CS_2 and $(C_2H_5)_2O$. 1 –CS_2, igniter (c), $V = 73$ l; 2 –same, igniter (a); 3 –$(C_2H_5)_2O$, igniters (b, c), $V = 73$ l; 4 –same, $V = 17$ l; 5 –same, igniter (a), $V = 73$ l

Fig. 2. Ignition temperatures of air mixtures of C_2H_2, H_2, $(C_2H_5O)_2C_2H_4$,

B-70 gasoline. $V = 73$ l, igniter (d): 1 –H_2; 2 –C_2H_2; 3 –$(C_2H_5O)_2C_2H_4$; 4 – same with stirring; 5 –B-70 gasoline

The absolute values of T_s for mixtures of methane ($> 900°$), hydrogen, gasoline, and ethylene glycol ether are comparable with analogous values obtained in other studies of ignition by a heated body. Methane mixtures did not ignite at the maximum temperature reached by us; the minimum recorded T_s values for the other fuels listed are 640, 855, and 640°, respectively.

In contrast to experiments in a flow, mixtures of carbon disulfide and diethyl ether exhibit a clear capacity for low-temperature ignition. For both these fuels the minimum $T_s = 180°$, whereas in a flow $T_s \geq 770°$. The minimum $T_s = 420°$ is somewhat higher for acetylene mixtures.

(in the flow, $T_s \geq$ 700-800°). The observed regularities, incompatible with a thermal ignition mechanism, can be explained only by the development of degenerate branching, made possible by "chemical preparation." The cold flames that appear initiate a thermal explosion.

The known features of mixtures of ethyl ether and carbon disulfide explain their capacity for low-temperature ignition. Thus, cold flames can propagate in air mixtures containing hundredths and even thousandths of a percent of CS_2 ([13]). Under certain conditions, spontaneous ignition of CS_2 mixtures is possible at 80° ([14]). Ethyl ether mixtures readily form cold flames over a wide range of compositions ([15–17,11]).

The comparatively high T_s of gasoline and ethylene glycol ether mixtures indicates a smaller tendency of these combustible systems toward the development of a self-accelerating nonthermal reaction, although mixtures of higher hydrocarbons also give cold flames ([9]). Differences in the size and shape of the igniters, and mixing of the reacting mixture by a fan (2000 rpm with a blade diameter of 18 cm), have little effect on T_s for all the mixtures studied, increasing it in some cases and decreasing it in others.

Low-temperature ignition had not been observed previously, although the free-convection regime was also used ([18–21]). This is due to the chemical specificity of the fuels studied, which have little tendency to form cold flames (H_2, CH_4, C_6H_6, gasoline, C_3H_8).

The mixtures studied ignite at approximately the same fuel-concentration ranges in which flame propagation is possible. The corresponding concentration limits, according to ([22]), are shown in Figs. 1 and 2. For gasoline and hydrogen mixtures, the dependence of T_s on composition displays a characteristic minimum in the region of fuel-lean mixtures. The shift of the ignition limits relative to the flame-propagation limits for gasoline is apparently due to discrepancies in the data on the composition of gasoline. The position of the minimum in the lean-mixture region for hydrogen is associated with the known influence of the large difference between the diffusion coefficient and thermal diffusivity ([23]). The observed character of the dependence $T_s(\alpha)$ indicates a purely thermal ignition mechanism for these mixtures.

For the other fuels, the minimum T_s values correspond to compositions close to the limiting ones. These mixtures have the minimum flame velocities for the given fuel, i.e., they are the most phlegmatic. Such a dependence of T_s on composition is due to the nonthermal nature of the reaction acceleration associated with the development of degenerate branching. It is characteristic that, in carbon disulfide mixtures, T_s decreases without limit as the mixture is depleted in fuel, while for both ethers and acetylene it decreases in the opposite direction. It is known that cold flames form more readily in lean carbon disulfide mixtures; the presence of CS_2 in rich mixtures of various fuels does not affect the flame-propagation limits (see ([11])). Conversely, in ethyl ether mixtures, an excess of fuel favors the development of cold flames.

The observed dependence $T_s(\alpha)$ indicates that the ignition mechanism of acetylene and ethylene glycol ether mixtures is also not purely thermal, and that degenerate branching participates in the development of the reaction. The character of the dependence $T_s(\alpha)$ for ignition in a flow ([7,24]) indicates weak development of degenerate branching for any fuel. The minimum $T_s = 655°$ was observed for hydrogen, which in general does not produce cold flames.

We obtained a series of high-speed photographic recordings of the glow during ignition of ether–air mixtures. They confirm the two-stage ignition mechanism: the first flame, with indistinct contours, after a noticeable delay passes into a much brighter hot flame with a sharply defined front boundary. It must be assumed that the first recorded weak glow, which gives rise to the thermal explosion, already represents the second stage of the process—the so-called blue flame, having a high tem-

temperature than the cold one. As can be seen from the photographic records, a hot-flame kernel can arise at a certain distance from the igniter.

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