

## ENTHALPY APPROACH TO THE INVESTIGATION OF THE COMBUSTION PROCESS. II RESULTS OF THERMAL ANALYSIS OF SOME COMBUSTIBLE SYSTEMS

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*Thermal parameters of the critical cross section of the steady-state combustion wave in gaseous mixtures, explosives, nitrocellulose powders, and pyrotechnic and SHS systems are determined from analysis of experimental combustion rates.*

In the preceding paper of the present series [1] it was shown that it follows from the differential energy equation for a chemically reactive system that there exists in the steady-state combustion wave a critical cross section similar to the ignition surface. The critical cross section is unique in that its parameters, namely, the enthalpy  $h_m$ , heat flux  $q_{m0}$ , and temperature  $T_m$ , are independent of the initial temperature  $T_{in}$  and the conditions of heat exchange with the environment. This relationship of the combustion process is demonstrated in the present work on the basis of analysis of experimental data on the combustion rate of the main classes of combustible systems.

According to [1], the steady-state combustion rate  $u$  is determined by the equation

$$u\rho = \frac{q_{m0}(P) + \xi q_{ex}}{h_m(P) - h(T_{in}, P)}, \quad (1)$$

where  $q_{m0}$  is the heat flux in the critical cross section of the combustion wave in the absence of any additional external heat flux  $q_{ex}$ ;  $\xi$  is the fraction of the external heat flux that reaches the critical section of the combustion wave;  $\rho(T_{in}, P)$  and  $h(T_{in}, P)$  are the density and enthalpy of the combustible system under the initial conditions.

Without any external thermal effects (irradiation of the burning specimen, blowing of the combustion surface by a jet of cold inert gas or high-temperature combustion products, etc.), at a fixed pressure  $P$  Eq. (1) has the form

$$(u\rho)^{-1} = \frac{h_m}{q_m} - \frac{1}{q_m} h(T_{in}), \quad (2)$$

and in combustion with an external heat flux, at a fixed pressure and the initial temperature  $T_0$  taken as a reference point for enthalpy, Eq. (1) becomes

$$u\rho = \frac{q_{m0}}{h_m} + \frac{\xi}{h_m} q_{ex}. \quad (3)$$

The parameters  $h_m$ ,  $q_m$ ,  $q_{m0}$  were determined by the least-squares method from the results of approximation of experimental combustion rates by Eqs. (2) and (3). Data on the temperature dependence of density and enthalpy necessary for the analysis were taken from the literature and partly obtained from our studies

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TABLE 1. Thermal Parameters of the Combustion Wave of Gaseous Mixtures

Volume contents of components	Ref.	$T_{in}$ , K	$P$ , MPa	$h_m$ , kJ/kg	$q_m$ , kW/m <sup>2</sup>	$\overline{\delta u}$ , %	$T^*$ , K	$T_m$ , K
0.3H <sub>2</sub> + 0.7 air	[2]	293–583	0.098	883.5	410	1.1	899	943
		583–703	0.098	1277	582	–	1148	1222
0..1CH <sub>4</sub> + 0.9 air	[2]	293–623	0.098	730	250	1.4	907	952
		623–953	0.098	1623	865	3.0	1535	1674
0.095CH <sub>4</sub> <sup>1)</sup> + 0.905 air	[3]	323–473	0.098	547	179	1.7	781	814
		323–473	0.785	554	821	1.7	781	814
		323–473	2.256	550	1369	1.4	774	806
		323–473	6.867	501.5	2185	2.8	740	769

<sup>1)</sup>Methane mixed with 1.33% N<sub>2</sub>, 0.32% CO<sub>2</sub>, and 0.033% O<sub>2</sub> (natural gas without preliminary purification).

on the heat capacity and thermal expansion coefficient. Values of  $\rho$  and  $h$  for mixtures were calculated from additive relations. The initial temperature  $T_0 = 293.15$  K was taken as a reference point for enthalpy.

The thermal parameters of the combustion wave  $h_m$  and  $q_m$  obtained are presented in tabulated form for every type of combustible system. The tables also contain the pressures and ranges of initial temperatures at which the combustion rate was measured, the mean-square error  $\overline{\delta u}$  of approximation of the experimental combustion rates, the temperature  $T^*$  to which a nonreacting system can be heated by the heat  $h_m$ , and the temperature  $T_m$  of the critical cross section of the combustion wave determined by the relation

$$T_m = \frac{E}{2R} - \sqrt{\left(\left(\frac{E}{2R}\right)^2 - \frac{E}{R} T^*\right)}. \quad (4)$$

**Gaseous Mixtures.** Table 1 shows estimates of the thermal parameters  $h_m$  and  $q_m$  for hydrogen-air and methane-air mixtures, obtained using data of [2] on the combustion rate at atmospheric pressure, and for natural gas-air mixtures, using the data of [3] on the combustion rate at different pressures. The temperatures  $T_m$  were estimated for  $E = 167.5$  kJ/mole.

The relations  $(\rho\mu)^{-1} = f[h(T_{in})]$  obtained from data of [2] can be represented by two segments of straight lines intersecting at  $T_{in} = 573$ – $623$  K. This suggests the existence of two combustion regimes in gaseous mixtures. For low-temperature combustion the obtained values of  $T_m$  are in reasonable agreement with reported data on self-ignition temperatures of gaseous mixtures, while for high-temperature combustion these values are substantially higher.

The combustion rates for natural gas-air mixtures [3] were measured in a relatively narrow range of initial temperatures, corresponding to low-temperature combustion. As shown by analysis of data of [3], a pressure rise leads to a small decrease in  $h_m$  and a substantial increase in  $q_m$ . The values of  $h_m$  and  $q_m$  for a natural gas-air mixture with a content of the combustible of 9.5 % v/v, given in Table 1, can be described by the equations

$$h_m(P) = 557.41 - 7.633P, \quad \text{kJ/kg}; \quad (5)$$

$$q_m(P) = \frac{2039.9P}{1 + 1.2295P - 0.06527P^2}, \quad \text{kW/m}^2. \quad (6)$$

Equation (1) with  $h_m(P)$  from (5) and  $q_m(P)$  from (6) reproduces the experimental combustion rates [3] for a methane-air mixture in the initial temperature range  $T_{in} = 323$ – $473$  K and in the pressure range 0.1–6.9 MPa with a mean-square error of  $\overline{\delta u} = 2.5\%$ .

Linear relation (2) is also observed in combustion of heterogeneous systems. In [4] the combustion rate of an air suspension of aluminum powder with an average particle size of  $d = 5.7 \mu\text{m}$  was investigated. The aluminum content in the air was  $0.45 \text{ kg/m}^3$ . Experimental data [4] with  $T_{\text{in}}$  in the range 348–594 K were reproduced by Eq. (2) with the parameters  $h_m = 648 \text{ kJ/kg}$  and  $q_m = 139.4 \text{ kW/m}^3$ . The value of  $h_m$  corresponds to heating of the mixture to the melting point of aluminum of 933.6 K and the partial melting of the aluminum in the mixture.

In [5] combustion rates of oxygenated mixtures of fluorine derivatives of propylene in the range  $T_{\text{in}} = 273\text{--}500 \text{ K}$  were studied. Unlike all the other combustible systems, the mass combustion rate of these mixtures decreases as the initial temperature rises. This anomalous behavior of the relation  $u\rho = f(T_{\text{in}})$  can be explained by the thermal and chain mechanism of combustion in these mixtures.

We will denote the combustion rate component that is independent of the initial temperature and dependent on the course of chain reactions by  $u_c$ . Then, the total rate of combustion is determined by the equation

$$u = u_c + \frac{q_m}{\rho [h_m - h(T_{\text{in}})]}. \quad (7)$$

Assuming that the mixture is an ideal gas with a constant heat capacity, we can write

$$u = u_c + u_0 \frac{T_{\text{in}}}{T^* - T_{\text{in}}} = u_c \left( 1 + a \frac{T_{\text{in}}}{T^* - T_{\text{in}}} \right), \quad (8)$$

where  $u_0 = q_m R / (c_p P)$ ,  $a = u_0 / u_c$ .

In the limit as  $a \rightarrow 1$  (when the contributions of the chain and thermal mechanisms to the combustion process are roughly the same), Eq. (8) takes the form

$$u^{-1} = u_c^{-1} (1 - T_{\text{in}}/T^*). \quad (9)$$

Using Eq. (9), one can estimate  $u_c$  and  $T^*$  to a first approximation from the experimental relation  $u(T_{\text{in}})$  and then carry out ordinary thermal analysis for the difference in the combustion rates  $u - u_c$ . Analysis of experimental data [5] for a mixture with 40 vol. % hexafluorpropylene  $\text{C}_3\text{F}_6$  and 60 vol. % oxygen gives  $u_c = 0.123 \text{ m/sec}$ , which constitutes 79% of the total combustion rate at  $T_{\text{in}} = 273 \text{ K}$  and 60% at  $T_{\text{in}} = 500 \text{ K}$ . Analysis of the relation  $[(u - u_c)\rho]^{-1} = f[h(T_{\text{in}})]$  gives  $h_m = 938 \text{ kJ/kg}$ ,  $q_m = 110.5 \text{ kW/m}^2$ ,  $T^* = 1067 \text{ K}$ , and  $T_m = 1147 \text{ K}$  for  $E = 138 \text{ kJ/mole}$ .

The authors of [6], where self-ignition of oxygen of hexafluorpropylene mixtures was studied, found a transition from chain ignition at  $T = 555 \text{ K}$ , when the mixture was heated to  $T \sim 1000 \text{ K}$ , to chain and thermal ignition at  $T = 558 \text{ K}$ , when the mixture was heated to  $T \sim 2500$ . It is likely that  $T_m$  of the critical cross section of the combustion wave for these mixtures corresponds to the maximum temperature for a purely chain mechanism of combustion.

**Explosives.** Table 2 shows the thermal parameters  $h_m$  and  $q_m$  obtained with the results of [7, 8] on the combustion rate of nitroglycol at atmospheric pressure and of [9] on the combustion rate of hexogen at various pressures. In estimating  $T_m$  use was made of the values  $E = 146.5 \text{ kJ/mole}$  for nitroglycol and  $E = 175.8 \text{ kJ/mole}$  for hexogen. The table also contains the boiling points  $T_b$  of the explosives at the corresponding pressures.

Depending on the range of initial temperatures, several conditions of combustion of nitroglycol are observed. At  $T_{\text{in}} \leq 293 \text{ K}$   $h_m$  is less than the enthalpy of boiling liquid  $h' = 286.6 \text{ kJ/kg}$ , whereas the critical cross section of the combustion wave is in the condensed phase and  $T_m$  is very close to the boiling point  $T_b$ . At  $293 \text{ K} < T_m < 395 \text{ K}$   $h_m$  is more than  $h'$  and less than the enthalpy of saturated vapor  $h'' = 686 \text{ kJ/kg}$ . For this combustion regime  $T_m = T_b$  too, but the material in the critical cross section of the combustion wave is in a two-phase state. At  $T_{\text{in}} > 395 \text{ K}$   $h_m > h''$  the critical cross section of the combustion wave should be in the gaseous phase with  $T_m$  being 50–100 K above the boiling point. It is possible, however, that this third combustion regime does not really exist and its appearance is attributable to inadequate analysis of experimental data due to neglect of partial decomposition of nitroglycol in the thermostating process at higher temperatures.

TABLE 2. Thermal Parameters of the Combustion Wave of Explosives

Compound	Ref.	$T_{in}$ , K	$P$ , MPa	$h_m$ , kJ/kg	$q_m$ , kW/m <sup>2</sup>	$\bar{\delta}u$ , %	$T^*$ , K	$T_m$ , K	$T_b$ , K
Nitroglycol	[7]	273–293	0.098	252	110	–	453	465	473
		293–373	0.098	474	207	0.5			
	[8]	293–395	0.098	486	211	3.2			
		373–457	0.098	784	388	3.8			
Hexogen	[9]	293–453	0.098	561.9	304.6	1.8	578	595	613
		293–453	0.49	709.2	1532	1.7	643	664	666
		293–433	0.98	783.9	2550	1.3	673	696	692
		293–413	2.45	783.9	7395	1.0	673	696	729
		293–413	4.9	912.9	13886	0.7	723	750	760

In combustion of hexogen at all the pressures studied the critical cross section of the combustion wave is in the condensed phase and  $T_m$  is close to the boiling point  $T_b$ . Therefore,  $T_m = T_b$  can be assumed and it is possible to calculate  $T^*$  and  $h_m$  corresponding to this condition and to determine the heat flux  $q_m$  consistent with the new value of  $h_m$  from experimental combustion rates. Corrected values of  $h_m$  in the entire range of pressures  $P = 0.098 - 4.9$  MPa studied are reproduced by the equation

$$h_m(P) = 775.95 + 91.73 \ln P - 6.8317 (\ln P)^2, \quad \text{kJ/kg}.$$

The relation  $q_m(P)$  has a bend at  $P = 0.98$  MPa and was approximated by the equations: in the range  $P = 0.098 - 0.98$  MPa

$$q_m(P) = -40.5 + 3854.9P - 1271.9P^2, \quad \text{kW/m}^2;$$

in the range  $P = 0.98 - 4.9$  MPa

$$q_m(P) = -2035.1 + 4968.2P - 334.13P^2, \quad \text{kW/m}^2.$$

Equation (1) with the relations  $h_m(P)$  and  $q_m(P)$  obtained describes initial experimental data on the combustion rate of hexogen with the same error as in the case of description of experimental data for each pressure separately.

The fraction of hexogen reacting in the critical cross section of the combustion wave is determined by the equation

$$\eta(T_m) = \frac{h' - h_m}{Q},$$

where  $h'$  is the enthalpy of boiling liquid;  $Q$  is the reaction heat. For  $E = 175/8$  kJ/mole  $\eta(T_m)$  is 1.7% at  $P = 0.098$  MPa and 3.4% at  $P = 4.9$  MPa. Substituting  $\eta(T_m)$  and  $E$  into the equations of chemical kinetics, it is possible to determine the product of the pre-exponential factor  $k_0$  by the characteristic time  $t^*$  of the chemical reaction in steady-state combustion. Comparison of the combination  $k_0 t^*$  with experimental estimates of kinetic parameters for the hexogen decomposition reaction [10] gives  $t^* = 0.74 \cdot 10^{-2}$  sec for combustion at  $P = 0.098$  MPa and  $t^* = 0.11 \cdot 10^{-4}$  sec for combustion at  $P = 4.9$  MPa.

**Nitrocellulose Powders.** Table 3 shows the thermal parameters  $h_m$  and  $q_m$  found from experimental data of different authors on the combustion rate of H powder. H powder contains 59 wt.% colloxylin, 28 wt.% nitroglycerin, 12 wt.% dinitrotoluene, 1 wt.% centralite, and 1 wt.% vaseline.

TABLE 3. Thermal Parameters of the Combustion Wave of Nitroglycerin Powders

Powder	$T_{in}$ , K	$P$ , MPa	$h_m$ , kJ/kg	$q_m$ , kW/m <sup>2</sup>	$\overline{\delta u}$ , %
H [11]	273–291	0.098	63.8	55.4	–
H [11]	291–373	0.098	197.3	164	2.5
H [12, 13]	77–273	0.098	62.7	82.1	1.4
H [12, 13]	323–373	0.098	199.5	258	–
H [12, 13]	123–323	1.96	246.4	1152	1.1
H [12, 13]	323–413	1.96	325.2	1590	0.7
H [14]	213–375	3.04	336.2	2237	2.8
H [14]	248–376	4.02	398.9	3254	3.2
H [14]	251–376	5.00	387.1	3656	2.7
H [14]	195–343	0.098	172.5	190	2.7
in air	358–388	0.098	254.4	363	0.4
H [14]	195–358	0.098	171.8	162	3.3
in a nitrogen jet					
H + 1% C [15]	293–393	0.098	281	368	2.2
H + PbO [15]	293–393	0.098	332	395	1.2

TABLE 4. Correlation of Thermal Parameters of the Combustion Wave of Nitrocellulose Powders Obtained from Analysis of the Relations  $u\rho = f(q_{ex})$  and  $(u\rho)^{-1} = f[h(T_{in})]$

Powder	$u\rho = f(q_{ex})$				$(u\rho)^{-1} = f[h(T_{in})]$				$\overline{\xi}$
	$q_{ex}$ , kW/m <sup>2</sup>	$h_m/\xi$ , kJ/kg	$q_{m0}/\xi$ , kW/m <sup>2</sup>	$\overline{\delta u}$ , %	$T_{in}$ , K	$h_m$ , kJ/kg	$q_m$ , kW/m <sup>2</sup>	$\overline{\delta u}$ , %	
H [14]	0–105	239.5	260.2	0.9	195–343	172.5	189.8	2.7	0.725
	170–390	351.1	501.8	1.8	358–388	254.4	363.4	0.4	
H + 1% C [14]	0–140	212.2	280.5	2.5	195–296	132.2	179.4	2.0	0.63
	140–320	392.1	649.6	1.0	323–373	257.1	391.6	3.4	
H + 1% PbO [15]	0–420	474.1	533.8	3.6	273–374	318.2	373.3	1.0	0.685
	830–2550	1090.1	1945	2.1	–	–	–	–	
Pyroxylin [14]	0–320	192.3	316.2	1.5	294–333	123.2	205	3.6	0.65
	–	–	–	–	333–393	393.2	993	1.2	
Pyroxlin + 1% C [19]	0–754	314	675	2.3	–	(204)	(439)	–	(0.65)
	754–3308	593.5	1966	1.2	–	(386)	(1278)	–	

At low pressures two combustion regimes are observed for H powder. As the pressure increases, the difference between the thermal parameters of low- and high-temperature combustion decreases, and starting from  $P \sim 3$  MPa experimental data on the combustion rate lie on the common straight line  $(u\rho)^{-1} = f[h(T_{in})]$ . The parameters  $h_m$  and  $q_m$  increase with pressure.

At atmospheric pressure combustion rates of H powder obtained in [11] are 1.5-1.6 times lower than the results obtained in [12, 13]. However, the values of  $h_m$  for both sets of experimental data are the same, and the difference in the combustion rates can be ascribed to the difference in the heat fluxes  $q_m$  caused by different conditions of heat exchange in the experiment. The effect of heat exchange with the environment on the combustion rate is shown even more clearly in [14]. Identical samples of H powder were burned in air and in a weak nitrogen jet. In the second case, heat release to the surroundings results in a 15% decrease in  $q_m$  and  $u$  with  $h_m$  remaining unchanged.

Addition of a small amount of admixture to H powder changes sharply the thermal parameters  $h_m$  and  $q_m$ . Addition of as little as 1% of carbon black or lead oxide [15] results in a 1.4-1.6-fold increase in the parameters  $h_m$  and  $q_m$  in comparison with the data of [12, 13] for H powder.

The self-ignition temperature  $T_{in}$  of H powder is 450-480 K, depending on the method used [10]. The enthalpy values for the inert powder  $h^{inert} = 248-309$  kJ/kg correspond to these temperatures. Therefore, for H powder it can be expected that  $h_m > 300$  kJ/kg. However, this condition is realized only at high pressures  $P > 2$  MPa. At atmospheric pressure the  $h_m$  values extracted from the data of [12, 13] correspond to temperatures of  $T^* = 341$  K for low-temperature combustion and  $T^* = 449$  K for high-temperature combustion. This unnatural result, where the temperature of the critical cross section of the combustion wave extracted from analysis of experimental data on the combustion rate is *a priori* lower than the self-ignition temperature can be explained by the pulsating focal combustion of the powder at low pressures [16, 17]. The parameters  $h_m$  and  $q_m$  extracted from analysis of experimental data refer to the whole powder surface but in pulsating focal combustion only part of this surface ignites at each moment. Therefore, the ratio  $h_m/h^{inert}(T_{in})$  gives an idea about the averaged fraction of the ignited surface area in pulsating focal combustion.

The authors of [18] report data on the combustion rate of nitrocellulose powders at superhigh pressures up to 400 MPa for three initial temperatures of 223, 293, and 323 K. For H280 powder, whose formula is close to that of H powder, data of [18] in the ranges  $T_{in} = 323-323$  K and  $P = 30-400$  MPa have a mean-square error of  $\overline{\delta u} = 2.6\%$  and are reproduced by Eq. (1), where

$$h_m(P) = 237.26 + 2.8547 P, \quad \text{kJ/kg};$$

$$q_m(P) = -183 + 325.946 P + 3.68403 \cdot P^2, \quad \text{kW/m}^2.$$

Table 4 shows the correlation of thermal parameters of the combustion wave of nitrocellulose powders at atmospheric pressure obtained from analysis of the relations  $u\rho = f(q_{ex})$  and  $(u\rho)^{-1} = f[h(T_{in})]$ . In Table 4 we also give the heat flux fraction  $\xi$  reaching the critical cross section of the combustion waves, estimated from this correlation. For H powder  $\xi$  is in very good agreement with an estimate made independently in [14]. The relation  $u\rho = f(q_{ex})$ , just as  $(u\rho)^{-1} = f[h(T_{in})]$ , has two linear sections, and the parameters  $h_m$  and  $q_m$  at small heat fluxes  $q_{ex}$  coincide with  $h_m$  and  $q_m$  for low-temperature combustion, while at large  $q_{ex}$  they coincide with  $h_m$  and  $q_m$  for high-temperature combustion. In [19] the combustion rate of pyroxylin with 1% carbon black under irradiation was studied, but the dependence of the combustion rate on the initial temperature was not investigated. Therefore, Table 4 contains bracketed  $h_m$  and  $q_m$  recalculated from the parameters obtained from the relation  $u\rho = f(q_{ex})$  with  $\xi = 0.65$ , which is characteristic of pyroxylin.

At atmospheric pressure the boiling point of the volatile components of H powder and possible products of decomposition of nitrocellulose is 523-553 K. These temperatures correspond to an enthalpy of the inert powder of  $h^{inert} = 405-478$  kJ/kg, while the values of  $h_m$  presented in Tables 3 and 4 are lower. Therefore, for all the nitrocellulose powders studied the critical cross section of the combustion wave occurs in the condensed phase. The only exception is combustion of H+1% PbO powder under high-intensity irradiation. For this combustion regime  $h_m/\xi = 1090$  kJ/kg and  $h_m = 747$  kJ/kg at  $\xi = 0.685$ . This amount of heat is sufficient for heating the powder to the boiling point of the volatile components and their evaporation. Therefore, in this case the critical cross section of the combustion wave should be in the gaseous phase.

**Pyrotechnic and SHS Systems.** Pyrotechnic systems and systems of self-propagating high-temperature synthesis are compacted mixtures of powders of different materials. Their combustion rate depends not only on the temperature, pressure, and composition of the mixture, as is the case with the homogeneous systems discussed above, but also on the porosity of the specimen, the dispersity of the components, and other factors.

Thermal parameters of pyrotechnic mixtures [20] and SHS systems [21-25] are presented in Table 5. The combustion rate of pyrotechnic mixtures was studied at atmospheric pressure in air, and that of SHS systems, in an inert gas (helium or argon). The combustion rate of the SHS systems studied is independent of the pressure up

TABLE 5. Thermal Parameters of the Combustion Wave of Pyrotechnic and SHS Systems

System	$T_{in}$ , K	$\Pi$	$h_m$ , kJ/kg	$q_m$ , kW/m <sup>2</sup>	$\overline{\delta u}$ , %	$T^*$ , K
0.5W + 0.5KClO <sub>4</sub> [20]	293–393	0.08	126.9	1013	1.0	533
	493–668	0.08	388.9	5708	0.8	855
0.12B + 0.88Fe <sub>2</sub> O <sub>3</sub> [20]	289–383	0.49	257.5	6217	–	588
	508–668	0.49	570.4	20690	1.6	877
0.31Mg + 0.75Fe <sub>2</sub> O <sub>3</sub> [20]	293–673	0.32	1275	19080	2.1	1368
0.25Al + 0.75Fe <sub>2</sub> O <sub>3</sub> [20]	293–573	0.42	536.7	26530	2.4	885
	573–723	0.42	735.4	43770	0.1	964
0.825Cu + 0.175Al [21]	623–773	0.4	308.2	1134	2.1	883
0.53Zr + 0.47Al [22]	293–673	0.4	422.3	8972	3.7	931.4
0.63Zr + 0.37Al [22]	293–573	0.4	490.7	16190	1.4	933.6
0.46Ti + 0.54Fe [23]	1023–1173	0.4	669.2	40080	2.2	1285
0.8Ti + 0.2C <sup>1)</sup> [24]	293–773	0.45	515	21370	3.4	972
	973–1123	0.45	941	84750	0.6	1355
0.5Ti + 0.2C <sup>2)</sup> [25]	1023–1173	0.3	1579	3935	1.4	1630

<sup>1)</sup>Lamp black.

<sup>2)</sup> Graphite for reactors.

to  $P = 10$  MPa. Table 5 shows the weight contents of the components, the porosity  $\Pi$  of the mixtures, and the values of  $h_m$ ,  $q_m$ ,  $\overline{\delta u}$  and  $T^*$  for various ranges of initial temperatures.

For particular mixtures two combustion regimes are observed and for low temperature combustion of 0.5W + 0.5KClO<sub>4</sub>, 0.12B + 0.88Fe<sub>2</sub>O<sub>3</sub>, and 0.8Ti + 0.2C mixtures, the values of  $T^*$  are known to be lower than the self-ignition temperature. This corresponds to pulsating focal combustion of these mixtures at low initial temperatures.

The values of  $T^*$  for stable high-temperature regimes of combustion are in reasonable agreement with experimental estimates of the ignition temperatures of the mixtures.

For the 0.5W + 0.5KClO<sub>4</sub> mixture,  $h_m$  corresponds to initial melting of potassium perchlorate. For the 0.31Mg + 0.69Fe<sub>2</sub>O<sub>3</sub> mixture,  $h_m$  corresponds to initial boiling of magnesium. For all mixtures containing aluminum, including aluminum in air [4], the values of  $h_m$  correspond to heating the mixtures to the melting point of aluminum. For the 0.25Al + 0.75Fe<sub>2</sub>O<sub>3</sub> mixture, two regimes of combustion are observed and the temperature of the critical cross section of the combustion wave is close to the melting point of aluminum in both cases. However, for low-temperature combustion, aluminum only starts to melt, while for high-temperature combustion all the aluminum in the mixture is melted completely.

**Discussion.** Based on the present analysis, it is possible to regard the existence of a critical cross section similar to the ignition surface in a steady-state combustion wave as a theoretically substantiated fact and the independence of its thermal parameters  $h_m$  and  $q_m$  of the initial thermal state and the external thermal effect as an experimentally proved fact. The combustion rate is determined by two independent variables, namely, the enthalpy  $h$ , characterizing the internal physical state of the combustible system, and the heat flux  $q_{ex}$ , characterizing the external physical effect on the combustible system, and two parameters, namely,  $h_m$ , characterizing the chemical reaction proceeding in the heated layer, and  $q_{m0}$ , characterizing the chemical reaction proceeding in the high-temperature zone. The effect of the other factors on the combustion rate depends on their effect on these variables and parameters. Therefore, experimental studies of the combustion relations should be carried out with measured and changed initial temperatures and conditions of heat exchange with the environment.

In designing and operating various kinds of devices, it is necessary to know the dependence of the combustion rate on temperature and pressure. However, extension of the combustion relations found for model specimen, to real devices, neglecting differences in the heat-exchange conditions, can bring about large errors. For

example, the rates of hexogene combustion at  $T_{in} = 293$  K,  $P = 0.49$  MPa and  $P = 4.9$  MPa obtained in [26] exceed the data of [9] by 43.2 and 19.4%, respectively, while the values of  $h_m$  are equal for both sets of data. Therefore, the relation  $u(T, P)$  can be determined only up to a pressure function  $q_{ex}(P)$  that is characteristic for the specific device. The only characteristic of a combustible system independent of the conditions of heat exchange with the environment is the temperature coefficient of the combustion rate:

$$\beta(T_{in}, P) = \left[ \frac{\partial \ln(u\rho)}{\partial T_{in}} \right]_P = \frac{c_p(T_{in}, P)}{h_m(P) - h(T_{in}, P)}$$

Determination of the parameters  $h_m$  and  $q_{m0}$  and construction of the relations  $u(T_{in}, P)$ ,  $\beta(T_{in}, P)$ , and  $\nu(T_{in}, P)$  are impossible without reliable data on the thermal and caloric equation of state of the combustible system.

Therefore, studies of combustion processes must be accompanied by investigation of the temperature dependences of thermal properties of the combustible systems.

For many condensed combustible systems the critical cross section of the combustion wave corresponds to the melting or boiling point of the system or one of its components. This relationship allows characteristics of the combustion process to be predicted in uninvestigated systems, using known thermal properties. On the other hand, this relationship allows thermal properties of compounds at high temperatures and pressures to be determined, using experimental data on the combustion rate. Measurements of combustion rates can also be used to study heat exchange processes because of the direct dependence of the combustion rate on the external heat flux.

Thus, adequate theoretical analysis and purposeful practical application of combustion processes are impossible without reliable data on thermal properties of the combustible systems, and experimental determination of the combustion rate, which is essentially a precision thermal experiment, can form a basis for new methods of investigating thermal properties of compounds and heat exchange processes.

## NOTATION

$T$ , temperature;  $P$ , pressure;  $c_p$ , isobaric heat capacity;  $q$ , heat flux;  $\beta$ , temperature coefficient of the combustion rate;  $u$ , linear rate of combustion;  $\nu$ , index of the pressure dependence of the combustion rate;  $Q$ , thermal effect of the reaction;  $\eta$ , fraction of the combustible system involved in the reaction;  $k_0$ , pre-exponential factor;  $E$ , activation energy;  $R$ , universal gas constant;  $t$ , characteristic time of the chemical reaction in steady-state combustion,  $\Pi$ , porosity;  $\overline{\delta u}$ , mean-square error of the approximation of experimental combustion rates.

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