

## ENTHALPY APPROACH TO THE INVESTIGATION OF THE COMBUSTION PROCESS. I. ENERGY EQUATION FOR SYSTEMS WITH CHEMICAL REACTIONS AND ITS COROLLARIES FOR THE COMBUSTION PROCESS

L. Ya. Kashporov, V. A. Rabinovich, and  
Yu. E. Sheludyak

UDC 536.46

*The differential energy equation is considered for a system with exothermal chemical reactions. The equation is the initial one for phenomenological investigation of the combustion process. It is noted that correct analysis of the combustion process requires reliable temperature dependences of the thermal properties of combustion systems.*

**Introduction.** There are two approaches to investigating the combustion process, namely, the energy and chemico-kinetic ones. The primary energy approach [1, 2] is based on the assumption that in the steady-state combustion wave there exists a critical temperature  $T_m$  similar to the ignition temperature. The steady-state combustion rate is determined from the heat balance equation in the critical cross section of the combustion wave and is inversely proportional to the difference between  $T_m$  and the initial temperature  $T_{in}$ .

The primary energy approach neglects the kinetics of the chemical reaction. Jouguet, Nusselt [3], and Daniell [4] tried to refine the approach developed in [1, 2], using the "chemical" variable  $\eta$ , ranging from  $\eta = 0$  at  $T \leq T_m$  to  $\eta = 1$  at the maximum combustion temperature  $T_c$ . However, this refinement turned out to be insufficient because of the temperature dependence of the chemical reaction rate  $W$  and, accordingly, the fraction  $\eta$  of the combustible system involved in the reaction.

The present-day thermal theory of combustion is based on the chemico-kinetic approach [5–8], according to which the combustion rate is proportional to the square root of the chemical reaction rate at the maximum combustion temperature  $T_c$ , in the case of complete transformation of the combustible system in the leading zone ( $\eta = 1$ ), or at the combustion surface temperature  $T_s$ , in the case of incomplete transformation of the combustible system ( $0 < \eta < 1$ ). Within the chemico-kinetic approach all processes at  $T < T_c$  or  $T < T_s$  are insignificant. Therefore, development of the chemico-kinetic approach is associated with the rejection of the basic postulate of the energy approach, the concept of the existence of a critical temperature  $T_m$  similar to the ignition temperature in the steady-state combustion wave.

The enthalpy approach to investigating the combustion process presented here is an extension of the energy approach to include the continuous relation  $\eta(T)$  in the entire temperature range from  $T_{in}$  to  $T_c$ . However, the critical temperature  $T_m$  is not introduced artificially, as was done in the primary energy approach [1, 2] and in the attempts to refine it [3, 4], but is determined from the critical condition relating thermodynamic properties of the combustible system to kinetic parameters of the chemical reaction in the heated-up layer. The value of  $T_m$  depends on the course of chemical reactions in the heated-up layer of the combustible system at low temperatures. Rejection of the notion of  $T_m$  in the chemico-kinetic approach is due to neglect of the chemical and physical processes that take place at temperatures below  $T_c$  or  $T_s$ .

The existence of a critical temperature  $T_m$  is inherent in every combustible system, and the critical condition determining  $T_m$  is contained in the well-posed differential equation of steady-state combustion.

---

Russian National Research Center for Materials and Substances, State Committee on Standards of the Russian Federation, Moscow, Russia. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 66, No. 3, pp. 291-300, March, 1994. Original article submitted September 14, 1993.

**Distinctive Features of the Thermodynamics of Reactive Systems.** Combustible systems are reactive and in them exothermic chemical reactions can occur under certain conditions. The heating of a reactive substance at a constant rate  $b$ , K/sec, can be expressed as stepwise instantaneous heating by 1 K with a time lag  $t^* = b^{-1}$  at each temperature. In the time  $t^*$  the chemical reaction produces the amount of heat  $h^{\text{chem}} = Q\eta(T, t^*)$ , where  $Q$  is the thermal effect of the reaction. Therefore, by analogy with complex thermodynamic systems performing, apart from the work of expansion, other kinds of work [9], for reactive systems it is possible to introduce the effective enthalpy

$$h^* = h - Q\eta \quad (1)$$

and the effective isobaric heat capacity

$$c_p^* = \left( \frac{dh^*}{dT} \right)_P = c_p - Q \left( \frac{\partial \eta}{\partial T} \right)_{P,t}, \quad (2)$$

where  $h$  and  $c_p$  are the enthalpy and specific heat of the equilibrium mixture of the initial reagent (IR) and reaction products (RP) at the extent of the reaction  $\eta$ :

$$h = h^{\text{IR}} (1 - \eta) + h^{\text{RP}} \eta, \quad (3)$$

$$c_p = c_p^{\text{IR}} (1 - \eta) + c_p^{\text{RP}} \eta + (h^{\text{RP}} - h^{\text{IR}}) \left( \frac{\partial \eta}{\partial T} \right)_{P,t}. \quad (4)$$

The rate of an  $n$ -th-order chemical reaction is determined by the temporal change of the fraction  $\eta$  of the system involved in the reaction under isobaro-isothermal conditions:

$$W = \left( \frac{\partial \eta}{\partial t} \right)_{P,T} = k_n (1 - \eta)^n. \quad (5)$$

The zeroth-order reaction approximation  $W = k_0$  can be used at small  $\eta$ . The reaction rate constant  $k_n$  increases substantially with temperature. The function  $k_n(T)$  is usually presented in the form of the Arrhenius law

$$k_n = k_{0n} \exp(-E/RT), \quad (6)$$

where  $k_{0n}$  is the pre-exponent factor.

Integration of Eq. (5) with the conditions  $\eta = 0$  at  $t = 0$  and  $\eta = 1$  at  $t = \infty$  gives the time dependence of the fraction of the system involved in the reaction for reactions of the zeroth to the  $n$ -th order [3]:

$$\eta = k_0 t; \quad (7)$$

$$\eta = 1 - \exp(-k_1 t); \quad (8)$$

$$\eta = 1 - \frac{1}{1 + k_2 t}; \quad (9)$$

$$\eta = 1 - [1 + (n - 1) k_n t]^{-\frac{1}{n-1}}. \quad (10)$$

Differentiation of Eqs. (7)–(10) with respect to temperature with  $k_n(T)$  in the form of (6) gives the following expressions for the derivative  $(\partial \eta / \partial T)_{P,t}$ :

$$\left(\frac{\partial\eta}{\partial T}\right)_{P,t} = \frac{E}{RT^2}\eta, \quad n = 0; \quad (11)$$

$$\left(\frac{\partial\eta}{\partial T}\right)_{P,t} = -\frac{E}{RT^2}(1-\eta)\ln(1-\eta), \quad n = 1; \quad (12)$$

$$\left(\frac{\partial\eta}{\partial T}\right)_{P,t} = \frac{E}{RT^2}\eta(1-\eta), \quad n = 2; \quad (13)$$

$$\left(\frac{\partial\eta}{\partial T}\right)_{P,t} = \frac{E}{RT^2}(1-\eta)\frac{1-(1-\eta)^{n-1}}{n-1}, \quad n \geq 2. \quad (14)$$

For fixed small values of the time  $t^*$  of the chemical reaction at low temperatures,  $\eta \rightarrow 0$ ,  $(\partial\eta/\partial T)_{P,t} \rightarrow 0$ ,  $h^* = h^{\text{IR}}$ ,  $c_p^* = c_p^{\text{IR}}$ . At high temperatures the reaction will be completed in the time  $t^*$  and  $\eta = 1$ ,  $(\partial\eta/\partial T)_{P,t} = 0$ ,  $h^* = h^{\text{RP}} - Q$ ,  $c_p^* = c_p^{\text{RP}}$ . At intermediate temperatures the derivative  $(\partial\eta/\partial T)_{P,t}$  changes much more sharply than  $c_p$ , and therefore the dependence  $c_p^*(T, t^*)$  should pass through a minimum near the inflection point of  $\eta(T, t^*)$ . The position of the inflection point is determined from the conditions

$$1 + \ln(1-\eta) = \frac{2RT}{E}, \quad n = 1; \quad (15)$$

$$\frac{n(1-\eta)^{n-1} - 1}{n-1} = \frac{2RT}{E}, \quad n \geq 2. \quad (16)$$

For a first-order reaction  $\eta \approx 0.5-0.6$  at the inflection point. At a sufficiently high thermal effect  $Q$  of the reaction,  $c_p^*(T, t^*)$  can be negative at the minimum point, i.e., the total heat capacity of the reagent-inert envelope system will be less than the heat capacity of the inert envelope. Such phenomena are frequently observed in measurements of the specific heat of combustible systems at high temperatures [10]. In these cases  $c_p^*(T, t^*)$  passes through two critical points where  $c_p^* = 0$ . The positions of these points on the curve  $\eta(T, t^*)$  is determined from the equations

$$\eta = \frac{c_p}{Q} \frac{RT^2}{E}, \quad n = 0; \quad (17)$$

$$-(1-\eta)\ln(1-\eta) = \frac{c_p}{Q} \frac{RT^2}{E}, \quad n = 1; \quad (18)$$

$$\eta(1-\eta) = \frac{c_p}{Q} \frac{RT^2}{E}, \quad n = 2; \quad (19)$$

$$\eta(1-\eta)(1-\eta/2) = \frac{c_p}{Q} \frac{RT^2}{E}, \quad n = 3. \quad (20)$$

At the first critical temperature  $T_m$  the condition  $c_p^* = 0$  is satisfied at  $\eta \sim 10^{-2}$ . At the higher critical temperature  $T_h$  the condition  $c_p^* = 0$  is satisfied at  $(1-\eta) \sim 10^{-2}$ .

Thus, the relation  $h^*(T, t^*)$  of the reactive system should be an S-shaped curve, shown schematically in Fig. 1. On the curve  $h^*(T)$ , the following characteristic points can be distinguished: the maximum point  $h^* = h_m$  at  $T_m$ , the point of transition through the zero value  $h^* = 0$  at  $T = T_s$ , and the minimum point  $h^* = h_{\text{min}}$  at  $T = T_h$ . Figure

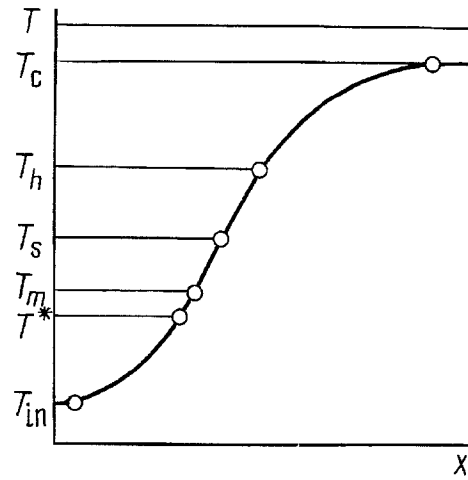
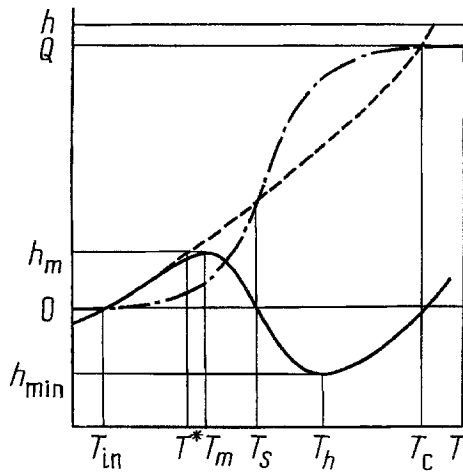


Fig. 1. Schematic dependence of the enthalpy  $h^* = h - h^{\text{chem}}$  of the reactive system on the temperature (solid line). The dashed line is the enthalpy  $h$  of the inert system, the dot-dash line is the heat release  $h^{\text{chem}}$  in chemical reactions.

Fig. 2. Schematic temperature distribution in a steady-state combustion wave.

1 also shows the temperature  $T^*$  to which the inert mixture of the initial reagent and reaction products can be heated by the amount of heat

$$h_m = h^*(T_m) = h(T^*).$$

Equation (2) for the specific heat of the reactive system can be written as

$$c_p^* = c_p - Q \frac{\eta}{T^2} \left( \frac{\partial \ln \eta}{\partial 1/T} \right)_{p,t} = c_p - \frac{E}{RT^2} (h - h^*) \frac{1}{f_n(\eta)}, \quad (21)$$

where  $f_n(\eta)$  [11] at small  $\eta$  has the form

$$f_n(\eta) = 1 + \frac{n}{2} \eta.$$

Equation (21) in the form

$$\frac{E}{R} = T^2 \frac{c_p - c_p^*}{h - h^*} f_n(\eta), \quad (22)$$

relates the activation energy of the chemical reaction to thermodynamic properties of the reactive system.

At the critical temperature  $T_m$ ,  $c_p^* = 0$ ,  $h^*(T_m) = h_m = h(T^*)$ , and Eq. (22) assumes the form

$$\frac{E}{R} = \frac{T_m^2 c_p(T_m)}{h(T_m) - h(T^*)} f_n(\eta) = \frac{T_m^2}{T_m - T^*} \frac{c_p(T_m)}{\bar{c}_p(T^*, T_m)} f_n(\eta), \quad (23)$$

where  $\bar{c}_p(T^*, T_m)$  is the average heat capacity of the inert mixture of the initial reagent and reaction products in the region of  $T^*$ ,  $T_m$ . For a zeroth-order reaction and a constant heat capacity Eq. (23) becomes the Semenov equation [12] for the critical ignition temperature

$$\frac{E}{R} = \frac{T_m^2}{T_m - T^*}. \quad (24)$$

Thus, the existence of a critical temperature  $T_m$  similar to the ignition temperature is characteristic of reactive systems with a fixed time  $t^*$  of the chemical reaction. At the critical temperature the effective heat capacity of the reactive system becomes zero and the system is transformed from heat-absorbing to heat-releasing.

In steady-state combustion the temperature distribution in space is time-independent after the combustion wave front coincides with the coordinate origin. The dependence of  $T$  on the coordinate  $x$  in a steady-state combustion wave is shown schematically in Fig. 2. Since  $T(x)$  is a unique function, thermodynamic quantities of a combustible system can be assumed to be functions of temperature alone in each cross section of a steady-state combustion wave. Therefore, the behavior of thermodynamic quantities in a steady-state combustion wave is identical to that of thermodynamic quantities of a reagent heated at a constant rate. In steady-state combustion  $t^*$  is of the order of the time of the complete chemical reaction at the maximum combustion temperature  $T_c$  and amounts to  $10^{-2} - 10^{-5}$  sec.

**Basic Equation of the Thermal Theory of Combustion.** Analysis of any thermal process, combustion included, is based on the energy conservation law, according to which the change in the heat flux  $q$  passing through an elementary volume is equal to the total change in the energy of this volume. For the one-dimensional problem of a reactive system under isobaric conditions, the law is written in the form

$$\frac{\partial q}{\partial x} = \rho \frac{dh^*}{dt}, \quad (25)$$

where  $\rho$  is the density of the combustible system.

Expressing the total derivative  $dh^*/dt$  in terms of partial derivatives with respect to  $x$  (distance) and  $t$  (time), we obtain

$$\frac{\partial q}{\partial x} = \rho \left( \frac{\partial h^*}{\partial t} \right)_x + u\rho \left( \frac{\partial h^*}{\partial x} \right)_t, \quad (26)$$

where  $u = dx/dt$  is the velocity of the layer. Substituting expression (1) for the enthalpy of the reactive system in (26), we obtain for the two limiting cases of ignition of an immovable surface and steady-state combustion the following equation:

$$\frac{\partial q}{\partial x} = \rho \left( \frac{\partial h^*}{\partial t} \right)_x = \rho \left[ \left( \frac{\partial h}{\partial t} \right)_x - Q \left( \frac{\partial \eta}{\partial t} \right)_x \right] = \rho \left( c_p \frac{\partial T}{\partial t} - QW \right); \quad (27)$$

$$\frac{\partial q}{\partial x} = u\rho \left( \frac{\partial h^*}{\partial x} \right)_t = u\rho \left[ \left( \frac{\partial h}{\partial x} \right)_t - Q \left( \frac{\partial \eta}{\partial x} \right)_t \right] = u\rho \frac{\partial T}{\partial x} \left[ c_p - Q \left( \frac{\partial \eta}{\partial T} \right)_t \right] = u\rho \frac{\partial T}{\partial x} c_p^*. \quad (28)$$

The right-hand side of Eq. (28) for steady-state combustion is proportional to the specific heat of the reactive system. Therefore, at the critical temperature, when  $c_p^* = 0$ , two conditions are satisfied simultaneously:

$$\left( \frac{\partial q}{\partial x} \right)^{cr} = 0; \quad \left( \frac{\partial h^*}{\partial x} \right)_t^{cr} = 0, \quad (29)$$

and the effective enthalpy of the combustible system and the heat flux absorbed by the heated-up layer have maximum values  $h_m$  and  $q_m$ , respectively.

Having integrated Eq. (28) between the initial state  $h^* = h^*(T_{in})$ ,  $q = 0$  and the arbitrary cross section of the combustion wave  $T(x)$ , we obtain

$$u\rho = \frac{q [x(T)]}{h^* [T(x)] - h^* (T_{in})}, \quad (30)$$

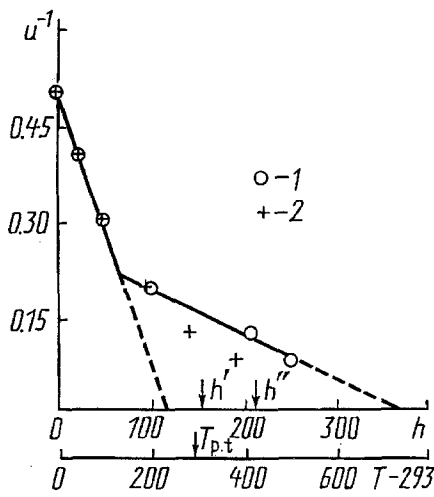


Fig. 3. Plot of the inverse combustion rate of a 0.5  $\text{KClO}_4$  + 0.5 W mixture (weight contents of the components) versus the enthalpy (1) and the temperature (2) from data of [16].  $T_{p.t.} = 574$  K is the temperature of the phase transition of potassium perchlorate;  $h'$  and  $h''$  are the enthalpies of the mixture at  $T_{p.t.}$ .  $u^{-1}$ , sec/mm;  $h$ , kJ/kg;  $T$ , K.

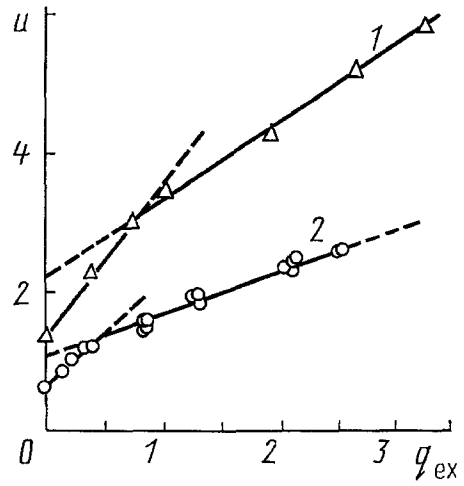


Fig. 4. Plot of the combustion rate of nitroglycerin powders versus the external heat flux at  $P = 0.1$  MPa and  $T_{in} = 293$  K: 1) pyroxylin + 1% C from data of [18]; 2) powder H + 1% PbO from data of [19].  $u$ , mm/sec;  $q_{ex}$ ,  $\text{MW/m}^2$ .

and the mass rate of steady-state combustion is completely determined, if the thermal parameters of the combustion wave  $q[x(T)]$  and  $h^*[T(x)]$  are known, at least for one cross section of the combustion wave  $T(x)$  located between the initial temperature  $T_{in}$  and the maximum combustion temperature  $T_c$ .

Having chosen thermal parameters of the critical cross section  $q_m$  and  $h_m$  to be those determining the combustion rate and assuming that the heat release in the chemical reaction in the thermostating time  $t_T$  at the temperature  $T_{in}$  can be neglected, we obtain

$$u\rho = \frac{q_m}{h_m - h(T_{in})} \quad (31)$$

or

$$(u\rho)^{-1} = \frac{h_m}{q_m} - \frac{1}{q_m} h(T_{in}). \quad (32)$$

At high  $T_{in}$ , when the heat release of the chemical reaction in the thermostating time becomes noticeable, the enthalpy  $h^*(T_{in})$  of the reactive system should be substituted for the enthalpy  $h(T_{in})$  of the inert system in Eq. (31), and the equation for the combustion rate becomes

$$u\rho = \frac{q_m}{[h(T^*) - h(T_{in})] + Q\eta(T_{in}, t_T)}. \quad (33)$$

At high temperatures the combustion rate is not a unique function of  $T_{in}$  but depends on the preliminary thermostating time  $t_T$  at the temperature  $T_{in}$ . In the limit as  $T_{in} \rightarrow T^*$ , the combustion rate does not tend to infinity but is finite:

$$\lim_{T_{in} \rightarrow T^*} u\rho = \frac{q_m}{Q\eta(T^*, t_T)}. \quad (34)$$

In principle, the parameters  $h_m$  and  $q_m$  can be dependent on all factors affecting the combustion rate: the initial temperature  $T_{in}$ , the pressure  $P$ , the contents of the mixture component  $y_i$ , the porosity  $\Pi$ , and the particle sizes  $d_i$  of condensed systems. Analysis of experimental combustion rates in various combustible systems in the coordinates  $(u\rho)^{-1} - h(T_{in})$  carried out in [11, 13-15] and discussed in our next paper shows that  $(u\rho)^{-1} = f[h(T_{in})]$  is a linear function. This is possible only under the condition that the parameters  $h_m$  and  $q_m$  are independent of the initial temperature. Therefore, in the general case the combustion rate as a function of several variables can be expressed in the form

$$u\rho = \frac{q_m(P, y_i, \Pi, d_i)}{h_m(P, y_i, \Pi, d_i) - h(T_{in}, P, y_i)}. \quad (35)$$

Thus, phenomenological analysis of steady-state combustion is reduced to determination of the thermal parameters  $h_m$ ,  $q_m$ , and  $T_m$  for the critical cross section of the combustion wave. Estimates of these parameters can be obtained only with reliable temperature dependences of the enthalpy and specific heat of the combustible system in the temperature range from  $T_{in}$  to  $T_m$ .

The thermal nature of the combustion process is most pronounced when the combustible system experiences phase transformations in the initial temperature range. Figure 3 shows  $u^{-1} = f[h(T_{in})]$  and  $u^{-1} = f(T_{in})$  plotted using data of [16] for a mixture of 50 wt.% tungsten and 50 wt.% potassium perchlorate. At  $T = 574$  K the mixture undergoes a phase transformation, accompanied by the endogeneous effect  $\Delta h_{p,t} \approx 50$  kJ/kg. Inclusion of the temperature dependence of the specific heat and the phase transformation heat leads to linearization of  $u^{-1} = f[h(T_{in})]$ , while  $u^{-1} = f(T_{in})$  is curvilinear.

In determining the thermal parameters  $h_m$  and  $q_m$  of the combustion wave in condensed systems, the dependence of density on temperature should not be neglected. Table 1 contains values of the maximum enthalpy  $h_m$  obtained from data of [17] on the combustion rates of powdered nitroglycerin at  $P = 23.8$  MPa and initial temperatures of  $T_{in} = 273$  and  $323$  K with different ways of including the dependence of the density and enthalpy on the pressure and temperature. For this system neglect of the dependence of density on temperature results in a 20% underestimation of  $h_m$ , while the error in determining  $h_m$  caused by neglect of the dependence of density and enthalpy on pressure does not exceed 3%.

In theoretical analysis and practical application of combustion processes, important characteristics are the temperature coefficient of the combustion rate

$$\beta = \left[ \frac{\partial \ln(u\rho)}{\partial T_{in}} \right]_P$$

and the index

$$\nu = \left[ \frac{\partial \ln(u\rho)}{\partial \ln P} \right]_{T_{in}}.$$

From Eq. (35) we obtain the following expressions for  $\beta$  and  $\nu$ :

$$\beta = \frac{c_p(T_{in}, P)}{h_m(P) - h(T_{in}, P)}; \quad (36)$$

$$\nu = \frac{d \ln q_m(P)}{d \ln P} - P \frac{\frac{dh_m(P)}{dP} - \left[ \frac{dh(T_{in}, P)}{\partial P} \right]_{T_{in}}}{h_m(P) - h(T_{in}, P)}. \quad (37)$$

According to Eq. (36),  $\beta$  depends on thermal properties of the combustible system under the initial conditions and at maximum enthalpy. Therefore,  $\beta$  depends on the nature of the combustible system and the course

TABLE 1. Effect of Using Different Relations  $\rho(T, P)$  and  $h(T, P)$  on the Estimated Maximum Enthalpy  $h_m$  of Nitroglycerin Powder at  $P = 23.8$  MPa

Form of the relations $\rho(T, P)$ and $h(T, P)$	$\rho = \text{const}, h = f(T)$	$\rho = f(T), h = f(T)$	$\rho = f(T), h = f(T, P)$	$\rho = f(T, P),$ $h = f(T, P)$
$h_m, \text{kJ/kg}$	348	419	426	414

of the chemical reaction in the heated-up layer and is independent of high-temperature chemical reactions and the conditions of heat transfer with the environment, the contribution of which to the combustion process is determined by the parameter  $q_m$ .

The index  $\nu$  depends not only on the course of the chemical reaction in the heated-up layer but also on the course of the chemical reaction in the high-temperature zone and the conditions of heat transfer from the high-temperature zone to the critical cross section of the combustion wave. Therefore, depending on the conditions of heat transfer of the burning specimen with the environment, determined by its size and shape, details of the design of the combustion device, blowing and irradiation of the specimen, etc., quite different values of the index  $\nu$  and the combustion rate  $u$  are possible but the index  $\beta$  should be unchanged in this case.

By analogy with  $\beta$  and  $\nu$ , other coefficients can be introduced that characterize the sensitivity of the combustion rate to a change in composition, porosity, particle dispersivity, and other factors affecting the combustion rate.

At constant pressure the combustion rate can change not only due to changes in the initial temperature but also because of irradiation of the burning specimen by the heat flux  $q_{\text{ex}}$  from an external source. In this case, the heat flux in the critical cross section of the combustion wave is determined by the relation

$$q_m = q_{m0} + \xi q_{\text{ex}}, \quad (38)$$

where  $q_{m0}$  is the heat flux in the critical cross section of the combustion wave without irradiation;  $\xi$  is the fraction of the external heat flux arriving at the critical cross section of the combustion wave. Therefore, in the case of external irradiation the combustion rate is determined by the relation

$$u\rho = \frac{q_{m0} + \xi q_{\text{ex}}}{h_m - h(T_{\text{in}})}. \quad (39)$$

Figure 4 shows the relations  $u(q_{\text{ex}})$  for pyroxylin powder doped by 1% carbon black [18] and nitroglycerin powder H doped by 1% lead oxide [19]. These relations are linear, which suggests that the parameters  $h_m$  and  $q_{m0}$  are independent of the conditions of heat exchange with the environment.

Figures 3 and 4 show one more characteristic of steady-state combustion, a stepwise increase in the controlling combustion parameters  $h_m$  and  $q_{m0}$  after certain limiting values of  $T_m$  and  $q_{\text{ex}}$ , corresponding to changes in the combustion regime, are achieved.

Constancy of the parameter  $h_m$  suggests that the characteristic time  $t^*$  of the chemical reaction in steady-state combustion is independent of the initial temperature and the conditions of heat transfer with the environment, i.e., it indicates that  $t^*$  is independent of the internal and external energy state of the combustion system.

**Conclusion.** Thus, a combustion process is a complex physico-chemical phenomenon and in its analysis it is impossible to neglect, even temporarily, either the physical or chemical component.

The analysis of the combustion process is based on the energy conservation law in a reacting medium, and determination of the combustion rate requires information not only on the kinetics of the chemical reaction but also on thermal properties of the reagent and exchange transfer processes of the ignition surface with the high-temperature chemical reaction zone and the environment. The most important consequence of the law of energy conservation in the reactive medium ignored by the present-time theory of combustion is the existence of a critical



cross section in the steady-state combustion wave, the characteristics of which, namely, the heat flux  $q_m$ , enthalpy  $h_m$ , and temperature  $T_m$ , are controlling parameters of the combustion process. Therefore, determination and prediction of these parameters as well as parameters of other characteristic cross sections of the steady-state combustion wave should be an object of the phenomenological theory of combustion.

## NOTATION

$T$ , temperature;  $P$ , pressure;  $x$ , coordinate;  $t$ , time;  $\lambda$ , thermal conductivity;  $c_p$ , isobaric heat capacity;  $h$ , enthalpy;  $\rho$ , density;  $q$ , heat flux;  $u$ , linear rate of combustion;  $\beta$ , temperature coefficient of the combustion rate;  $\nu$ , 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;  $W$ , chemical reaction rate;  $k_0$ , pre-exponential factor;  $E$ , activation energy;  $R$ , universal gas constant;  $n$ , reaction order;  $y_i$ , content of the  $i$ -th component in the mixture;  $\Pi$ , porosity of the mixture;  $d_i$ , average particle size of the  $i$ -th component;  $\xi$ , fraction of the external heat flux arriving at the critical cross section of the combustion wave.

## REFERENCES

1. E. Mallard and M. Le Chatelier, *Ann. Mines*, **4**, Ser. 8, 274-559 (1889).
2. V. A. Mikhel'son, *Uch. Zap. Imperator. Mosk. Univ.*, No. 10, 1-92 (1893).
3. L. N. Khitrin, *Physics of Combustion and Explosion* [in Russian ], Moscow (1957).
4. P. J. Daniell, *Proc. Roy. Soc.*, **126A**, 393-405 (1930).
5. B. Lewis and G. von Elbe, *J. Chem. Phys.*, **2**, No. 8, 537-546 (1934).
6. Ya. B. Zel'dovich and D. A. Frank-Kamenetskii, *Zh. Fiz. Khim.*, **12**, No. 1, 100-105 (1938).
7. A. G. Merzhanov, *Combust. Flame*, **13**, No. 2, 143-156 (1969).
8. V. V. Sychev, *Complex Thermodynamic Systems* [in Russian ], Moscow (1980).
9. Yu. E. Sheludyak, L. Ya. Kashporov, A. Malinin, and V. N. Tsalkov, *Thermal Properties of Components of Combustible Systems* [in Russian ], Moscow (1982).
10. L. Ya. Kashporov, V. A. Rabinovich, and Yu. E. Sheludyak, in: *Thermal Properties of Substances and Materials* [in Russian ], Issue 30, Moscow (1991), pp. 139-147.
11. N. N. Semenov, *Chain Reactions* [in Russian ], Moscow (1986).
12. L. Ya. Kashporov, Yu. E. Sheludyak, V. M. Mal'tsev, et al., in: *Mater. IX All-Union Symp. on Combustion and Explosion, Chernogolovka*, (1989), pp.18-21.
13. L. Ya. Kashporov, Yu. E. Sheludyak, V. M. Mal'tsev, et al., *Fiz. Goreniya. Vzryva*, **28**, No. 3, 8-13 (1992).
14. N. A. Silin, L. Ya. Kashporov, Yu. E. Sheludyak, et al., *Fiz. Goreniya Vzryva*, **28**, No. 5, 27-34 (1992).
15. G. V. Lukashenya and A. L. Podgrebenkov, *Zh. Fiz. Khim.*, **36**, No. 12, 2784-2786 (1962).
16. B. L. Crawford, B. Huggett, F. Daniels, and R. E. Wilfong, *Ind. Eng. Chem., Anal. Chem.*, **19**, No. 9, 630-633 (1947).
17. I. G. Dik, A. B. Zurer, and V. T. Kuznetsov, *Fiz. Goreniya Vzryva*, **15**, No. 3, 77-82 (1979).
18. V. N. Simonenko, *A Study of Unsteady-State Combustion of Powders*, Candidate's Thesis, Novosibirsk (1981).