EFFECT OF AN ELECTRIC FIELD ON THE IGNITION OF A BINARY MIXTURE OF GASEOUS REACTANTS

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It is shown that under certain conditions in an electric field a reactant can be ignited or can ignite spontaneously before electrical breakdown occurs in the gas.

A lot of research has been done recently in the field of plasma chemistry [1]. Within this framework it would be of interest to study the laws governing the course of chemical reactions in a strong electric field. Such a study would also be of definite importance where problems of explosion-proofing and the theory of spark ignition are concerned, inasmuch as processes occurring prior to electrical spark ignition have usually not been taken into account [2, 3].

We will consider here a system consisting of two infinitely large plane-parallel electrodes with a reactant gas in between. The anode temperature T_0 is held constant. At time $t = 0$ a trapezoidal voltage pulse of a definite shape, width, and amplitude is applied to the electrodes, causing processes to develop in the gas which result in the appearance and subsequent buildup of free charge carriers with an eventual breakdown of the gas. The directional flow of charged particles causes the gas to heat up and induces in it a first-order irreversible exothermal chemical reaction which then proceeds according to the Arrhenius law. The problem is to determine the interelectrode distance at which a reactant will still ignite and then to determine the ignition time.

The mathematical formulation of the problem reduces to the solution of the following partial differential equations in Lagrange variables:

$$\frac{\partial \rho'}{\partial t} = -\rho'^2 \frac{\partial U}{\partial x},$$

$$\frac{\partial U}{\partial t} + \frac{\partial P}{\partial x} = \frac{4}{3}\frac{\partial}{\partial x}\left(M\rho' \frac{\partial U}{\partial x}\right),$$

$$\rho' C_p \frac{\partial T}{\partial t} = \frac{\partial P}{\partial t} + \rho' \frac{\partial}{\partial x}\left(\Lambda \rho' \frac{\partial T}{\partial x}\right)$$

$$+ q k_0 \rho' C \exp\left(-\frac{E_a}{RT}\right) + (C_{p_1} - C_{p_2}) \rho'^3 D \frac{\partial T}{\partial x}\frac{\partial C}{\partial x} + J\cdot E, \tag{1}$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(\rho'^2 D \frac{\partial C}{\partial x}\right) - k_0 C \exp\left(-\frac{E_a}{RT}\right),$$

$$\frac{\partial Y}{\partial t} = U,$$

$$P = \rho' RT\left(\frac{C}{M_1} + \frac{1 - C}{M_2}\right).$$

This sytem of equations (1) must be solved for the following initial and boundary conditions

$$U|_{x=0} = U|_{x=x_*} = 0, \quad U|_{t=0} = 0,$$

$$T|_{x=0} = T|_{x=x_*} = T_0, \quad T|_{t=0} = T_0,$$

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TABLE 1. Comparison between the Ignition Times with and without Hydrodynamic Effects Taken into Account

δ	20	23	24	25	26	27	28
τ_*	1,3696 1,3657	1,2645 1,2372	1,1949 1,1339	1,1873 1,1185	0,9761 0,9439	0,8587 0,8364	0,6935 0,6639

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = \left.\frac{\partial C}{\partial x}\right|_{x=x_*} = 0, \quad C|_{t=0} = C_0,$$

$$\rho'|_{t=0} = \rho_0', \quad x_* = \int_0^L \rho' dY = \rho_0' L. \tag{2}$$

In the derivation of system (1) and the boundary conditions (2) we have made certain assumptions, namely: a) the problem is a plane one-dimensional one; b) the electric field is uniform in space; c) the gas is ionized by collisions with electrons; d) secondary processes at the cathode are negligible; e) electron avalanches are started and built up by the Townsend mechanism [4], with the primary current being an emission current; f) the electrodes are noncatalytic; g) the reacting mixture is a binary one; h) the specific heat of each component is constant; i) thermobaric diffusion and ambipolar diffusion are not taken into account; and j) body forces are negligible.

According to the Townsend collision ionization mechanism [4], we have the following expression for the electric current:

$$J = J_0 \exp(AY), \quad A = \frac{1}{h}\exp\left(-\frac{W}{hEg}\right). \tag{3}$$

Unlike the equations known in ignition theory [6, 7], Eq. (1) of energy conservation accounts for the energy of electrons moving in an electric field and converted into Joulean heat J · E term) which raises the temperature of the medium. With the introduction of dimensionless variables, we obtain a system of equations in dimensionless form:

$$\frac{\partial \rho}{\partial \tau} = -\rho^2 \frac{\partial u}{\partial \xi}, \tag{4}$$

$$\frac{\partial u}{\partial \tau} + \omega \frac{\partial p}{\partial \xi} = \frac{4}{3}\,\frac{\Pr}{\delta}\,\frac{\partial}{\partial \xi}\left(\mu\rho \frac{\partial u}{\partial \xi}\right), \tag{5}$$

$$\rho c_p \frac{\partial \theta}{\partial \tau} = \sigma \frac{\partial p}{\partial \tau} + \frac{\rho}{\delta}\,\frac{\partial}{\partial \xi}\left(\lambda\rho \frac{\partial \theta}{\partial \xi}\right) + \rho c \exp\frac{\theta}{1+\beta\theta}$$

$$+ \frac{L_1}{\delta}(1-\pi_1)\rho^3 d \frac{\partial \theta}{\partial \xi}\,\frac{\partial c}{\partial \xi} + aje, \tag{6}$$

$$\frac{\partial c}{\partial \tau} = \frac{L_1}{\delta}\,\frac{\partial}{\partial \xi}\left(\rho^2 d \frac{\partial c}{\partial \xi}\right) - \gamma c \exp\frac{\theta}{1+\beta\theta}, \tag{7}$$

$$\frac{\partial y}{\partial \tau} = u, \tag{8}$$

$$p = \rho(1+\beta\theta)[c + (1-c)\pi_2], \tag{9}$$

$$j = \exp(m\sqrt{\delta}\,\alpha y), \tag{10}$$

which must be solved for the following initial and boundary conditions:

$$u|_{\xi=0} = u|_{\xi=1} = 0, \quad u|_{\tau=0} = 0,$$

$$\theta|_{\xi=0} = \theta|_{\xi=1} = 0, \quad \theta|_{\tau=0} = 0, \tag{11}$$

$$\left.\frac{\partial c}{\partial \xi}\right|_{\xi=0} = \left.\frac{\partial c}{\partial \xi}\right|_{\xi=1} = 0, \quad c|_{\tau=0} = 1, \quad \rho|_{\tau=0} = 1.$$

This system (4)-(10) was solved numerically on a model BÉSM-4 digital computer by the iteration-interpolation scheme [5]. For these numerical calculations, all components were assumed to have the same molecular weight and the same specific heat, and the transfer coefficients Λ, M, and ρ'D to be all

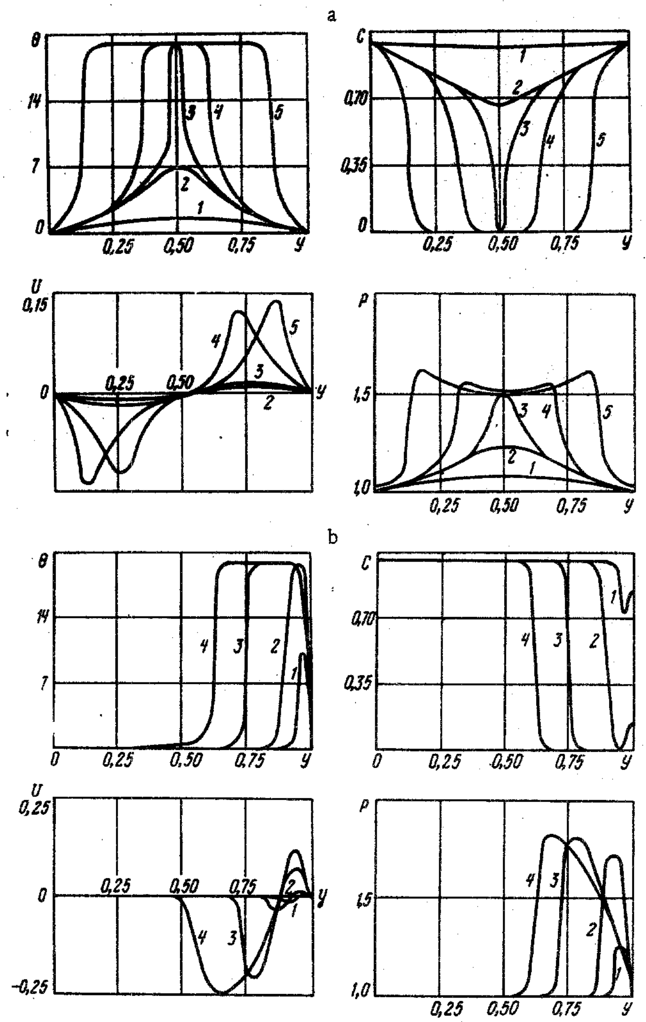

Fig. 1. Profiles of temperature, concentration, velocity, and pressure: a) during spontaneous ignition of the reactant with $\delta = 32$, $\gamma = 0.05$, $\beta = 0.03$, $\alpha = 10^{-12}$, $b = 2.8$, and $\tau_i = 10^{-2}$, at 1) $\tau = 0.6653$, 2) $\tau = 1.0705$, 3) $\tau = 1.0799$, 4) $\tau = 1.1257$, 5) $\tau = 1.1958$; b) during induced ignition of the reactant, with $\delta = 34$, $\gamma = 0.05$, $\beta = 0.03$, $\alpha = 10^{-12}$, $b = 2.8$, and $\tau_i = 10^{-2}$, at 1) $\tau = 0.02607$, 2) $\tau = 0.03707$, 3) $\tau = 0.0904$, 4) $\tau = 0.12718$.

proportional to $\sqrt{T}$. The calculations have revealed two modes of ignition[†]: spontaneous ignition and induced ignition. The former occurs at small values of $m\sqrt{\delta\alpha}$ and is characterized by the maximum temperature and the ignition both occurring at the center of symmetry in the reacting system. The profiles of temperature, concentration, velocity, and pressure shown in Fig. 1a at various instants of time correspond to the spontaneous mode of ignition.

Induced ignition occurs at large values of $m\sqrt{\delta\alpha}$ and the temperature profile which corresponds to this mode of ignition goes through a sharp peak near the anode. Temperature, concentration, velocity, and pressure profiles during induced ignition are shown in Fig. 1b. The peak-temperature nucleus appears first near the anode and then shifts toward the center of symmetry of the reacting system, whereupon ignition occurs at some distance y_* from that center of symmetry.

Thus, the effect of electrically generated heat sources in the volume is a normal ignition occurring prior to electrical breakdown[‡] and characterized by slow burning during a fast temperature rise. This

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[†] A reactant is assumed to ignite at time $t = t_*$, when the maximum dimensionless temperature becomes $\theta_m = 5$. Following this, a transient combustion front is forming fast with $\theta_m = \theta_f = 1/\gamma$ (θ_f denoting the dimensionless flame temperature).

[‡] It is assumed that a gas breaks down when its maximum temperature exceeds 5000°K.

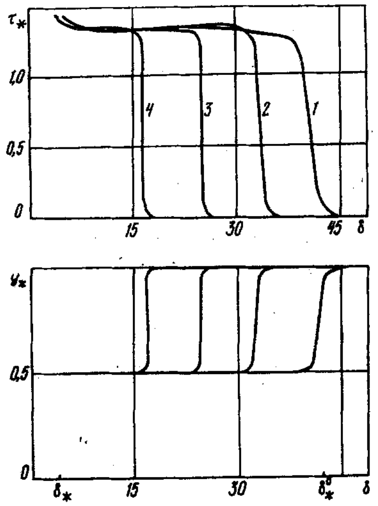

Fig. 2

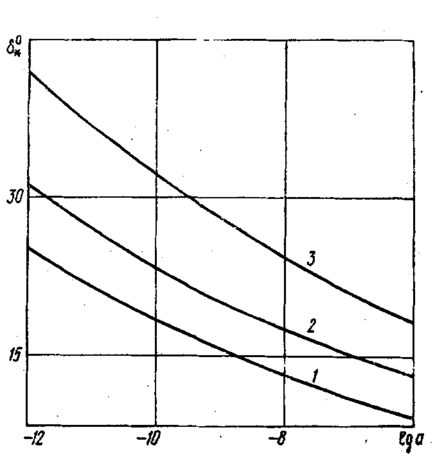

Fig. 3

Fig. 2. Curves of τ_* and y_* vs δ for various values of parameter a: 1) $a = 10^{-12}$; 2) 10^{-10}; 3) 10^{-8}; 4) 10^{-6}, with b = 2.8 and m = 100.

Fig. 3. Curves of δ_*^0 as a function of a and τ_i, with b = 2.8 and m = 100: 1) $\tau_i = 2$; 2) 10^{-2}; 3) 10^{-4}.

mode was discovered in [6, 7] during ignition of a reactant by a thermal dipole. At the ignition spot the mixture burns out completely and combustion fronts originating here begin to travel in two opposite directions (Fig. 1a, b). As a result of heat transfer in the peak-temperature zone, gas also begins to flow out from here in the same two directions. For this reason, the velocity peak and the pressure peak move in different directions away from the heat source. The gas density in the high-temperature zone decreases slightly only.

It is to be noted that the ignition of a reactant may occur instantaneously during an electric pulse or with some delay after the pulse.

Numerical calculations have shown that, as expected, the hydrodynamic parameters have little effect on the ignition characteristics in the normal mode. Values of the ignition time τ_* are given in Table 1, with (top row) and without hydrodynamic effects taken into account (m = 100, b = 2.8, $\tau_i = 2$, $a = 10^{-12}$, $\gamma = 0.03$, $\beta = 0.02$).

We will also note that the diffusive transfer of energy may be disregarded in the normal ignition mode, since only a small amount of reactant has been burned before the time of ignition. The calculated data indicate that the work of compression forces contributes little in this ignition mode.

The transition between ignition modes is conveniently depicted by a $y_* = y_*(\delta)$ curve, as in [8], with m, a, and b fixed and with y_* denoting the coordinate of the temperature peak at the time of ignition. Such $y_* = y_*(\delta)$ curves and also $\tau_* = \tau_*(\delta)$ curves of the ignition time are shown in Fig. 2 for various values of the parameter a. The value δ_* here represents the explosion limit, i.e., the reacting system does not ignite at $\delta < \delta_*$, because then the amount of heat dissipated through the electrodes exceeds the amount of heat generated by chemical reactions and electrical sources, while δ_*^0 denotes the upper limit of spontaneous ignition. At $\delta_* < \delta < \delta_*^0$ we have y = 0.5 and spontaneous ignition can occur. At $\delta > \delta_*^0$ the coordinate y_* increases fast with δ and ignition is induced. Unlike in the case of ignition by a thermal dipole, the value δ_*^0 here is just as sharply defined as δ_* and the transition zone is very narrow, i.e., a change of ignition modes occurs rapidly. Noteworthy is the appreciable effect of an electric field on the value of δ_*^0 (Fig. 3). These trends can, it seems, be explained by the exponential relation between the intensity of electrical heat sources and δ. An analogous conclusion was reached in [9], after an analysis of instantaneous or finite-time temperature perturbations at the container wall or at various distances y from it.

Calculations have shown that the ignition time τ_* in the spontaneous mode is a weak function of the initial current (characterized by parameter a), and that τ_* decreases fast upon transition to the induced mode of ignition (Fig. 2). It has been established that, as a increases, δ_*^0 decreases and the transition zone narrows down.

In Fig. 3 is shown δ_*^0 as a function of a and of the pulse width τ_i. As τ_i becomes wider, δ_*^0 increases and the transition zone narrows down.

As the pulse amplitude (parameter b) decreases, δ_*^0 increases fast while the profiles $y_* = y_*(\delta)$ and $\tau_* = \tau_*(\delta)$ becomes smoother.

As the slope of the leading pulse edge increases, δ_*^0 increases somewhat (with $b = 2.8$ and $a = 10^{-12}$, $\delta_*^0 = 24$ when $de/d\tau = 10^6$ and $\delta_*^0 = 25$ when $de/d\tau = 10$). As $de/d\tau$ increases, the ignition time τ_* becomes longer in the spontaneous mode but shorter in the induced mode, which can evidently be explained by a higher inertia of the spontaneous ignition process.

The explosion limit δ_* and the induction time τ_0 in a constant electric field one can calculate according to approximate formulas based on the iteration formulas in [10]:

$$\delta_* = \delta_{*0}\left(1 + 2.4\gamma^{\frac{2}{3}}\right)(1+\beta)(1-5860\,a), \tag{12}$$

$$\tau_0 = \tau_a\left[1+0.62\,\frac{1-4\Delta^{-2}\sqrt{\gamma}}{(\Delta-0.95)^{0.9}}\right]\left[1-\frac{1+1.5(1-0.1\Delta)}{16}\right](1-30\sqrt{a}). \tag{13}$$

These formulas are valid for $0 < \beta < 0.05$; $0 < \gamma < 0.01$, $1.1 < \Delta < 2.5$, $10^{-15} \le a \le 5\cdot 10^{-5}$, $0 < m \le 100$, $b \ge 2.8$, and they approximate within 7% the results obtained by numerical methods. The effect of parameters m and b, within their earlier specified ranges of variation, is weaker than the accuracy of these formulas. According to (12) and (13), both the explosion limit and the induction time decrease when a increases.

In all calculations the ratios Pr, L_1, ω, and σ have been assigned the value one.

We note, in conclusion, that during an increase in the electric field intensity there occurs a change of the ingition mechanism, namely, the gas breaks down electrically before the self-accelerating chemical reaction has had time to develop. This mode is characterized by an appreciable burnout of the reactant and may be regarded as a degenerate mode of induced ignition.

It must also be noted that our conclusions apply qualitatively to any exothermal induced reaction, insofar as the amount of an original component burned out prior to ignition is small.

NOTATION

t	is the time;
$x = \int_0^Y \rho' dY$	is a Lagrange coordinate;
Y	is an Euler coordinate;
ρ'	is the density;
U	is the velocity;
P	is the pressure;
M	is the dynamic viscosity;
C_p	is the specific heat at constant pressure;
T	is the absolute temperature;
Λ	is the thermal conductivity;
q	is the thermal effect of a chemical reaction;
k_0	is a coefficient in the exponential term;
C	is the mass concentration of nonreactant molecules;
E_a	is the activation energy;
R	is the universal gas constant;
D	is the diffusivity;
J	is the electric current density;
E	is the electric field intensity;
M_1 and M_2	are the molecular weights of the components;
L	is the interelectrode distance;
A	is the first coefficient of Townsend collision ionization;
h	is the length of the mean-free electron path;
g	is the electron charge;

W	is the ionization energy;
E_{st}	is the static breakdown electric field intensity;
$t_* = C_{p_1}RT_0^2/qk_0E_aC_0 \exp E_a/RT_0$	is the characteristic "chemical reaction" time;
$\tau = t/t_*$, $\xi = x/x_*$, and $y = Y/L$	are the dimensionless time, Lagrange coordinate, and Euler coordinate, respectively;
$\rho = \rho'/\rho_0$, $u = U/U_*$, $p = P/P_0$, $c = C/C_0$, $\theta = E_a(T-T_0)/RT_0^2$, $j = J/J_0$, $e = E/E_{st}$, $\alpha = \rho \exp(-b\rho/e)$, and $c_p = c + (1-c)\pi_1$	are dimensionless functions;
$Pr = M_0C_{p_1}/\Lambda_0$	is the Prandtl number;
$L_1 = \rho_0'D_0C_{p_1}/\Lambda_0$	is the Lewis–Semenov number;
$\sigma = E_a/C_{p_1}T_0$, $\gamma = C_{p_1}RT_0^2/qE_aC_0$, $\beta = RT_0/E_a$, $\omega = P_0/\rho_0'U_*^2$, $U_* = L/t_*$, $a = I_0E_{st}/qk_0\rho_0'C_0C_{p_1} \cdot \exp E_a/RT_0$, $m = T_0/h_0(\Lambda_0R/qk_0E_aC_0)^{1/2} \cdot \exp E_a/2RT_0$, $b = W/h_0E_{st}g$, $\pi_2 = M_1/M_2$, $\pi_1 = C_{p_2}/C_{p_1}$, $\delta_{*0} = 3.52$, $\tau_a = 1$, and $\Delta = \delta/\delta_*$	are dimensionless parameters;
$\delta = qk_0E_aC_0L^2\rho_0'/\Lambda_0RT_0^2 \exp(-E_a/RT_0)$	is the Frank–Kamenetskii number;
Upper case letters	denote dimensional quantities;
Lower case letters	denote respective dimensionless quantities.

Subscripts

1 and 2 denote the original reactant and the reaction product, respectively.

Superscript

0 denotes the initial value of a parameter.

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