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1965

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Abstract

Full Text

PHYSICAL CHEMISTRY

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SELF-IGNITION IN SYSTEMS WITH UNBRANCHED CHAIN REACTIONS

(Presented by Academician N. N. Semenov on 11 XI 1964)

In the theory of self-ignition, two areas have been worked out in detail: adiabatic ignition, in which the rate of the chemical reaction obeys the Arrhenius equation (thermal explosion), and isothermal chain ignition (chain explosion) ([1]). However, explosions in most cases are chain-thermal, since the chain reactions in this case develop under nonisothermal conditions and their rate, especially immediately before the explosion, will be determined to a considerable extent by the rise of temperature in the system. Knowledge of the specific mechanism and of the rate constants of the reactions is sufficient for solving the problem of the development of an explosion in time in each individual case. However, the rate constants of most reactions have been determined only in a small temperature range, and extrapolating them may lead to considerable errors. Therefore, solving the inverse problem of determining the rate constants of reactions, or their ratios, from ignition delays is of undoubted interest, since the latter can be measured rather accurately over a broad temperature range. In the general case, the complexity of the kinetic equations and the indefiniteness of the very concept of a delay greatly hinder obtaining an analytical dependence between the values of the constants and the ignition delays. However, for systems with a large initial reserve of chemical energy and a strong dependence of the reaction rate on temperature (relatively low ignition temperatures and large activation energies), the moment of ignition under adiabatic conditions is determined rather accurately. In such systems the reaction rate and the temperature, after some time has elapsed, increase sharply, and it may be assumed without large error that at the moment of ignition these values tend to infinity. In this case, according to ([2]), the reaction rate is taken as

$$W(T) = k_0(a)^n \exp\left(-\frac{E}{RT}\right) \simeq k_0(a)^n \exp\left[-\frac{E}{RT_0} + \frac{E}{RT_0^2}(T - T_0)\right],$$

where E is the activation energy; k_0 is the pre-exponential factor; (a) is the concentration of the reactant; n is the reaction order; T_0 and T are the initial and current temperatures.

The thermal theory ([3]) gives the following expression for the ignition delay:

$$\tau = pcT_0/qEW(T_0),$$

where c is the heat capacity; p is the pressure of the mixture; q is the heat effect of the reaction.

In Fig. 1 the dependence of the dimensionless temperature $\theta = [(T-T_0)/RT_0^2]E$ on the dimensionless time t/τ is presented. Curves 2 and 3 were obtained using the exact expression $W(T)$ for RT_0/E, respectively, 0.1 and 0.05. Curve 1 corresponds to the solution using the approximate expression for $W(T)$. As is seen from Fig. 1, the use of the approximate expression $W(T)$ for determining the value of τ does not give a significant error for most combustible systems.

It may be assumed that ignition caused under adiabatic conditions by a simple unbranched reaction is thermal in nature, and that the rate of heat liberation will be determined by the rate of the chain reaction. As a model scheme, the reaction of chlorination or bromination of hydrogen was chosen:

0.	$X_2 + M \to 2X + M,$	$u_0 = k_0(X_2)(M)^2 = W_0(M),$	q_0
I.	$X + H_2 \to HX + H,$	$u_1 = k_1(X)(H_2)(M)^2 = W_1(X)(M),$	q_1
II.	$X_2 + H \to HX + X,$	$u_2 = k_2(X_2)(H)(M)^2 = W_2(H)(M),$	q_2
III.	$HX + H \to X + H_2,$	$u_3 = k_3(HX)(H)(M)^2 = W_3(HX)(H)(M),$	q_3
IV.	$X + X + M \to X_2 + M,$	$u_4 = k_4(X)^2(M)^3 = W_4(X)^2(M),$	q_4
V.	$H + H + M \to H_2 + M,$	$u_5 = k_5(H)^2(M)^3 = W_5(H)^2(M),$	q_5
VI.	$H + X + M \to HX + M,$	$u_6 = k_6(X)(H)(M)^3 = W_6(X)(H)(M),$	q_6

where H and X are, respectively, atoms of hydrogen and halogen; M is any particle; u_i and k_i are the rates and rate constants of the elementary reactions; q_i are the heat effects of the reactions. The concentrations of the reacting components are taken in dimensionless form, relative to the total number of moles in 1 cm^3 (M).

For the variation with time of the temperature and of the concentrations of the individual components, the following equations may be written:

$$\begin{aligned} d(X)/dt = {} & 2W_0 - W_1(X) + W_2(H) - 2W_4(X)^2 \\ & - W_6(X)(H) + W_3(H)(HX), \\ d(H)/dt = {} & - W_2(H) + W_1(X) - 2W_5(H)^2 - W_6(X)(H) \\ & - W_3(H)(HX), \end{aligned} \tag{1}$$

$$\begin{aligned} d(HX)/dt &= W_1(X) + W_2(H) + W_6(X)(H) - W_3(H)(HX); \\ c\,d\Delta T/dt &= q_0W_0 + q_1W_1(X) + q_2W_2(H) + q_3W_3(HX)(H) \\ &\quad + q_4W_4(X)^2 + q_5W_5(H)^2 + q_6W_6(H)(X); \end{aligned} \tag{2}$$

Fig. 1

Figure 1: Fig. 1

$$d(H+X)/dt = 2W_0 - 2[W_4(X)^2 + W_6(H)(X) + W_5(H)^2]. \tag{3}$$

Fig. 1

Without restricting the generality of the result, as will be shown below, the second term on the right-hand side of equation (3) may be represented in the form $\overline{W}(X+H)^2$, where $\overline{W}$ is of the order of the recombination rates W_4, W_5, W_6.

The solution of system (1) under the condition of constant temperature, if reaction III is neglected, as well as the change in the concentrations of the initial reactants, has the form

$$(X) \simeq \frac{W_2}{W_1+W_2}\sqrt{\frac{W_0}{\overline{W}}}\ \mathrm{th}\, 2\sqrt{W_0\overline{W}}\, t + 2\frac{W_0W_1}{(W_1+W_2)^2}\left(1 - \frac{\exp[-(W_1+W_2)t]}{\mathrm{ch}\, 2\sqrt{W_0\overline{W}}\, t}\right); \tag{4}$$

$$(H) \simeq \frac{W_1}{W_1+W_2}\sqrt{\frac{W_0}{\overline{W}}}\ \mathrm{th}\, 2\sqrt{W_0\overline{W}}\, t - 2\frac{W_0W_1}{(W_1+W_2)^2}\left(1 - \frac{\exp[-(W_1+W_2)t]}{\mathrm{ch}\, 2\sqrt{W_0\overline{W}}\, t}\right). \tag{5}$$

It was assumed here that $\overline{W} - W_0 \ll W_1 - W_2$. From equations (4) and

From (5) it follows that

$$W_1(\mathrm{X}) - W_2(\mathrm{H}) \simeq \frac{2W_0W_1}{W_1+W_2}\left(1 - \frac{\exp[-(W_1+W_2)t]}{\mathrm{ch}\, 2\sqrt{W_0\bar{W}t}}\right), \tag{6}$$

i.e., the change in the concentration of H atoms follows the change in the concentration of X atoms with the relaxation time $(W_1+W_2)^{-1}$. Since this time is small, the approximate equality (6) may be written in the form

$$W_1(\mathrm{X}) - W_2(\mathrm{H}) \simeq \frac{2W_0W_1}{W_1+W_2}. \tag{7}$$

Substituting the results obtained into equation (2), one can derive the dependence of small temperature changes on time during the reaction.

Fig. 2

The temperature at the initial moment, owing to the endothermic character of the initiation reaction, decreases and after a time $t = |q_0|/2q_2W_1$ reaches a minimum $|\Delta T| = q_0^2W_0/2q_2cW_1$. These expressions, obtained for the case $W_2 \gg W_1$, show that in practice the temperature decrease at the initial stage of the reaction is always small and lasts for a very short time.

The time during which the temperature, due to the reaction, increases enough to raise W_0 by 10% is determined by solving equation (2) with the aid of (4) and (5), and has the form:

$$t_0 = \sqrt{0.1RT_0^2c(W_1 + W_2)/E_0(q_1 + q_2)W_0W_1W_2}.$$

It is evident that t_0 is much smaller than the quantity $(\sqrt{W_0\bar{W}})^{-1}$—the time required for the rate of generation of active centers to become comparable with the rate of their disappearance, if the recombination reactions occur through triple collisions (see equations (4) and (5)). Therefore, in equation (3) one may neglect the term quadratic in concentration: the inequality $2\bar{W}(\mathrm{X}_2 + \mathrm{H})^2 \ll 2W_0$ will be maintained throughout the ignition delay. Thus, the equations for determining the chain-thermal delay in a system with a large initial content of chemical energy and trimolecular termination are written as follows:

$$\frac{d(\mathrm{H} + \mathrm{X})}{dt} = 2W_0, \tag{8}$$

$$\frac{d\Delta T}{dt} = \frac{q_1 + q_2}{c(W_1 + W_2)} W_1W_2(\mathrm{H} + \mathrm{X}). \tag{9}$$

In deriving equation (9), terms much smaller than those entering it were not taken into account, and equation (7) was used. An approximate solution of the system (8)—(9) can be obtained by using the expansion (2) and taking into account that always E_2 and $E_1 < E_0$. This solution, under the initial conditions $t = t_0$, $\Delta T_0 = 0.1RT_0^2/E_0$, and $(\mathrm{X} + \mathrm{H}) = (\mathrm{X} + \mathrm{H})_{t=t_0}$, takes the form

$$t = \sqrt{RT_0^2c(W_1 + W_2)/E_0W_0W_1W_2(q_1 + q_2)}\ \operatorname{arc\,tg}\sqrt{e^\theta - 1}.$$

Since at the moment of ignition $\theta \to \infty$, the ignition delay is

$$\tau = \frac{1}{2}\pi\sqrt{RT_0^2c(W_1 + W_2)/E_0(q_1 + q_2)W_0W_1W_2}. \tag{10}$$

The formula obtained differs from the exact solution of the system of equations (8) and (9) by no more than 6% for E_1 and $E_2 \leq 0.1E_0$, and by no more

than 20% for E_1 and $E_2 \leq 0.4E_0$. Expression (10) can be used to determine the combination k_0, k_1, k_2 as a function of temperature from measured ignition delays. Figure 2 presents the change during the ignition delay of the dimensionless temperature θ as a function of the dimensionless time t/τ. Curves 2 and 3 were obtained by numerical integration of the system of kinetic equations at $T_0 = 1400^\circ$K and $T_0 = 600^\circ$K; curve 1 was obtained with the aid of the approximate analytical formula (10). (The values of k_i and q_i were taken from the data for the system $H_2 + Cl_2$ [4].) It follows from Fig. 2 that the error in determining τ by formula (10) does not exceed 20%.

Let us note that formula (10) gives satisfactory results in calculating τ in the case when the explosive temperature rise $T_{\text{expl}} - T_0$, where T_{expl} is the explosion temperature, exceeds the value $6RT_0^2/E_0$. In this case one can indeed neglect the change in the concentrations of the reactants during the time τ.

The approximate method given for solving the system of kinetic equations can basically be applied to the chain-interaction scheme $H_2 + Cl_2$, where reaction III may be neglected. In the case of $H_2 + Br_2$, reaction III cannot be neglected. However, system of equations (1) can be solved under the assumption that $W_1 \gg W_0$ and $(X_2^0) - (X_2) \simeq (H_2^0) - (H_2) \simeq \frac{1}{2}(HX)$, where the index 0 refers to the initial concentrations of the reactants. Then, omitting terms quadratic in concentration, system (1) can be written in the form:

$$d(HX)/dt \simeq 2W_2(H); \qquad d(H+X)/dt \simeq 2W_0;$$

$$(HX)(q_1 + q_2)/2c = \Delta T;$$

$$\frac{W_1}{W_2 + W_3[2(HX)/2(X_2^0) - (HX)]} \simeq \frac{(H)}{(X)}. \tag{11}$$

The solution of this system under the condition $(HX) \ll 2(H_2^0)$ or $(HX) \ll 2(X_2^0)$ is the following:

$$\frac{t}{\tau} = \int_0^{\alpha(HX)} \frac{\left(1 + \frac{k}{\alpha}v\right)\, dv}{\sqrt{\left(1 - \frac{k}{\alpha}\right)\left[\left(1 + \frac{k/\alpha}{1 - k/\alpha}\, v\right) e^v - 1\right]}}, \tag{12}$$

where τ is determined by equation (10) and

$$k = \frac{W_3}{W_1 + W_2}; \qquad \alpha = \frac{E_0}{RT_0^2}\frac{(q_1 + q_2)}{2c}.$$

For the ignition delay, the following approximate analytical solution was obtained:

$$\tau' = \tau \left[1 + \frac{2W_3 RT_0^2 c}{(W_1 + W_2)E_0(q_1 + q_2)}\right]^{0.56},$$

which agrees to within 2% with the result of numerical integration of equation (12) over the range $0 \leq \alpha(HX) \leq \infty$.

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Received
11 XI 1964

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Note: Figure translations are in progress. See original paper for figures.