PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

B. V. Pavlov

ON THE UPPER LIMIT OF SELF-IGNITION IN A CHAIN UNBRANCHED REACTION

(Presented by Academician V. N. Kondrat' ev, November 28, 1964)

The condition of thermal self-ignition for a homogeneous gas reaction is determined by the relation ([1], [2])

$$wq\frac{E}{RT_0^2} \sim \frac{a}{r_0^2},$$

where T_0 is the temperature of the reactor wall; w is the reaction rate at $T = T_0$; q and E are the heat and activation energy of the reaction; r_0 is the linear dimension of the reactor, and a is a constant. It follows from this that, with increasing pressure, the conditions for ignition can only improve. Therefore it is considered that the upper limit of self-ignition can arise only in a chain branched reaction. However, one can simply indicate a concrete scheme of a chain unbranched reaction in which the existence of an upper limit is possible.

1. Let us consider the following hypothetical one-center scheme.

$\mathrm{A + wall \to R}$,	initiation on the surface of the reactor.
$\mathrm{R + A \to product + R}$,	k, E, chain propagation.
$\mathrm{R + B + M \to RB + M}$,	k_p, termination on impurity B with participation of a third particle M.

The distribution of radicals over the radius in a spherical reactor is determined by the diffusion equation

$$D\nabla_r^2[\mathrm{R}] - k_p[\mathrm{R}][\mathrm{B}][\mathrm{M}] = 0, \qquad [\mathrm{R}] = [\mathrm{R}]_{r_0}\frac{r_0}{r}\frac{\operatorname{sh} r/\rho}{\operatorname{sh} r_0/\rho}, \tag{1}$$

where D is the diffusion coefficient of the radicals; $\rho = 1/\sqrt{k_p[\mathrm{B}][\mathrm{M}]/D}$, and r_0 is the reactor radius.

In the case when $r_0/\rho \gg 1$, [R] at the wall is well approximated by the exponential

$$[\mathrm{R}] \simeq [\mathrm{R}]_{r_0} e^{(r-r_0)/\rho}, \tag{2}$$

and the reaction rate near the reactor surface will be

$$w = k[\mathrm{R}]_{r_0}[\mathrm{A}] e^{(r-r_0)/\rho}. \tag{3}$$

Near the center (3) is certainly incorrect, but for solving the heat-conduction equation this is immaterial, provided only that the approximating function at $r \sim 0$ is sufficiently small; (3) satisfies this requirement, and it may be used in solving the heat-conduction equation.

2. The temperature distribution over the reactor is given by the heat-conduction equation, in which, to simplify the calculation, we approximate the dependence of k on T by the first two terms of the expansion of k in powers of $(T - T_0)$:

$$\lambda \nabla_r^2 T + q k_{T_0} \left(1 + \frac{E(T - T_0)}{RT_0^2}\right) [\mathrm{R}]_{r_0} [\mathrm{A}] e^{(r-r_0)/\rho} = 0; \tag{4}$$

λ is the coefficient of thermal conductivity; q is the thermal effect of the reaction; T_0 is the temperature of the reactor wall; k_{T_0} is the value of k at $T - T_0$.

The solution of (4) must be made subject to the boundary conditions

$$\text{a) } T = T_0 \quad \text{at } r = r_0; \qquad \text{b) } T \text{ is bounded at } r = 0. \tag{5}$$

By the change of variables $T = T_0 + u/r - RT_0^2/E$, $\quad x^2 = 4a\rho^2 e^{r/\rho}$, where

$$a = q\frac{k_{T_0}}{\lambda} \frac{E}{RT_0^2} [A][R]_{r_0} e^{-r_0/\rho}, \tag{4}$$

it is reduced to Bessel' s equation

$$x^2 u'' + x u' + x^2 u = 0.$$

The solution of (4) with conditions (5) is the function

$$T = T_0 + \frac{RT_0^2}{E} \left\{ \frac{r_0}{r} \frac{J_0(2\rho\sqrt{a}\, e^{r/2\rho}) - Y_0(2\rho\sqrt{a}\, e^{r/2\rho}) J_0(2\rho\sqrt{a})/Y_0(2\rho\sqrt{a})}{J_0(2\rho\sqrt{a}\, e^{r/2\rho}) - Y_0(2\rho\sqrt{a}\, e^{r/2\rho}) J_0(2\rho\sqrt{a})/Y_0(2\rho\sqrt{a})} - 1 \right\},$$

where J_0 and Y_0 are Bessel functions of the first and second kinds of zero order. For

$$J_0(2\rho\sqrt{a}\,e^{r_0/2\rho}) - Y_0(2\rho\sqrt{a}\,e^{r_0/2\rho})J_0(2\rho\sqrt{a})/Y_0(2\rho\sqrt{a}) = 0 \qquad (6)$$

the temperature tends to ∞, and the relation between the parameters for which (6) is satisfied gives the self-ignition condition.

Owing to the smallness of $2\rho\sqrt{a}$, $Y_0(2\rho\sqrt{a})$ is a large negative quantity, so that the second term in (6) is small. Therefore one may use the approximate equation

$$J_0(2\rho\sqrt{a}\,e^{r_0/2\rho}) = 0, \qquad (7)$$

whence we obtain the self-ignition condition in the form

$$\frac{D}{k_p[B][M]}\,q\,\frac{k_{T_0}}{\lambda}\,\frac{E}{RT_0^2}[A][R]_{r_0} \geq \frac{\mu_1^2}{4} \qquad (8)$$

(μ_1 is the first zero of J_0).

3. The value of the concentration $[R]_{r_0}$ near the wall is determined by the boundary condition

$$-D\,d[R]/dr\big|_{r=r_0} = \chi_2[R] - \chi_1[A], \qquad (9)$$

where $\chi_1[A]$ is the number of impacts of molecules A on 1 cm^2 of the reactor surface leading to the formation of radicals R; $\chi_2[R]$ is the number of impacts on 1 cm^2 of the surface in which radicals R are destroyed.

Using (2), from (9) we obtain $[R]_{r_0} = \chi_1[A]/(\chi_2 + \sqrt{k_p[B][M]D})$. Since $[A] \sim p,\ [B] \sim p,\ [M] \sim p,\ D \sim 1/p$, then

$$[R]_{r_0} \sim p/(a + p^{1/2}) \quad (a \text{ is a constant}). \qquad (10)$$

Substituting (10) into (8), it is easy to see that the left-hand side decreases with increasing pressure, so that the point of equality in (8) determines the upper limiting value of the pressure at which self-ignition of the reacting mixture still occurs.

4. Condition (8) is easily transformed to the form

$$w_{r_0} q \frac{E}{RT_0^2} \geq \frac{\mu_1^2}{4}\frac{\lambda}{\rho^2},$$

where w_{r_0} is the reaction rate near the wall.

In this form the self-ignition condition has the usual form, but instead of the reactor radius r_0 there appears the thickness of the reaction zone ρ, which depends strongly, as $p^{-3/2}$, on the pressure. It is precisely this latter circumstance that is the physical cause of the appearance of the upper limit.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
23 XI 1964

REFERENCES

[1] N. N. Semenov, *Chain Reactions*, Leningrad, 1934.
[2] D. A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics*, Moscow-Leningrad, 1947.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.