Soviet-era science, translated into English

A. S. KOMPANEETS, R. I. MOSHKINA

1965

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Abstract

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PHYSICAL CHEMISTRY

A. S. KOMPANEETS, R. I. MOSHKINA

CHAIN TERMINATION ON A SURFACE TAKING INTO ACCOUNT DIFFUSION OF TWO ACTIVE CENTERS

(Presented by Academician V. N. Kondratʹ ev, 10 VIII 1964)

In the general theory of chain reactions, developed by N. N. Semenov (^{1,2,6}), an expression is given for the effective constant of death of active centers on the walls of the reaction vessel. This expression was found for conditions in which chain ignition is possible, in other words, when the multiplication of active centers in the volume is opposed by their death on the surface. We shall show that under conditions where the overall balance of active centers in the volume also leads to a decrease in the number of the more reactive radicals, the effective death constant may have an expression substantially different from that proposed by Semenov. This result may have application in the theory of oxidation of hydrocarbons.

1. Let us write the diffusion equations for two active centers in a cylindrical vessel, taking chemical transformations into account:

$$\frac{\partial n_1}{\partial t} = \frac{D_1}{r}\frac{\partial}{\partial r} r \frac{\partial n_1}{\partial r} - \alpha n_1 + \beta n_2, \tag{1a}$$

$$\frac{\partial n_2}{\partial t} = \frac{D_2}{r}\frac{\partial}{\partial r} r \frac{\partial n_2}{\partial r} + \gamma n_1 - \delta n_2 + q. \tag{1 }$$

For definiteness we shall assume that only the second center is generated in the volume, while only the first dies on the surface.

Let us find the inequality that must be satisfied by the kinetic constants $\alpha, \beta, \gamma, \delta$ so that in the volume there occurs not multiplication, but only a decrease in the number of active centers; this excludes the possibility of the onset of critical conditions.

In the absence of diffusion one may seek n_1 and n_2 in the form $n_1 = C_1' e^{\nu t}$, $n_2 = C_2' e^{\nu t}$; substituting this into (1a,), we find the equation for ν:

$$\nu^2 + \nu(\alpha + \delta) + \alpha\delta - \gamma\beta = 0. \tag{2}$$

This equation must have only negative roots so that there is no multiplication of active centers in the volume, which corresponds to the condition

$$\alpha\delta - \gamma\beta > 0, \tag{3}$$

which will be used below. In the theory of chain ignition the inequality must be the reverse.

To find the death constant k, one must, as usual, solve equations (1a,) in their stationary form, setting $\partial n_1/\partial t = 0$, $\partial n_2/\partial t = 0$. We shall seek n_1 and n_2 in the form

$$n_1 = n_{10} + C_1 I_0(\lambda r), \qquad n_2 = n_{20} + C_2 I_0(\lambda r). \tag{4}$$

Here I_0 is the Bessel function of zero order of purely imaginary argument; n_{10} and n_{20} are a particular solution satisfying the condition

$$-\alpha n_{10} + \beta n_{20} = 0, \qquad \gamma n_{10} - \delta n_{20} + q = 0.$$

Then for λ^2 we obtain the equation

$$(\lambda^2)^2 D_1 D_2 - \lambda^2 (D_1\delta + D_2\alpha) + \alpha\delta - \beta\gamma = 0. \tag{5}$$

This equation has positive roots only when inequality (3) is satisfied. Let us denote the positive roots by $\lambda^{(1)}$ and $\lambda^{(2)}$, respectively, and the corresponding integration constants by $C_1^{(1)}$, $C_1^{(2)}$, $C_2^{(1)}$, $C_2^{(2)}$, with

$$C_2^{(i)} = -C_1^{(i)} \frac{\lambda^{(i)2} D_1 - \alpha}{\beta}. \tag{6}$$

We have assumed that at the vessel surface, at $r = a$, only the radicals n_1 perish, while the radicals n_2 are elastically reflected. The conditions for the applicability of this assumption are specified below. This gives the boundary conditions:

$$-D_1 \left(\frac{dn_1}{dr}\right)_{r=a} = \frac{\varepsilon_1 u_1}{4} n_1(a), \qquad \left(\frac{dn_2}{dr}\right)_{r=a} = 0. \tag{7}$$

Here ε is approximately equal to the probability that a radical perishes upon a single collision with the wall (7), and u_1 is the mean thermal velocity of the radical. Substituting the solution found into (7), we find the equation for $C_{1,2}^{(i)}$:

$$-D_1(\lambda^{(1)} C_1^{(1)} I_1(\lambda^{(1)} a) + \lambda^{(2)} C_1^{(2)} I_1(\lambda^{(2)} a)) =$$

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$$= \frac{\varepsilon_1 u_1}{4}\left(n_{10} + C_1^{(1)} I_0(\lambda^{(1)} a) + C_1^{(2)} I_0(\lambda^{(2)} a)\right), \tag{8a}$$

$$\lambda^{(1)} C_2^{(1)} I_1(\lambda^{(1)} a) + \lambda^{(2)} C_2^{(2)} I_1(\lambda^{(2)} a) = 0. \tag{8b}$$

The mean value of n_1 over the volume is equal to:

$$\bar{n}_1 = \frac{2}{a^2}\int_0^a n_1 r\,dr = n_{10} + 2\left(\frac{C_1^{(1)}}{a\lambda^{(1)}} I_1(\lambda^{(1)} a) + \frac{C_1^{(2)}}{a\lambda^{(2)}} I_1(\lambda^{(2)} a)\right). \tag{9}$$

The constant of destruction k, by definition (2), is equal to

$$k = \frac{\varepsilon_1 u_1}{2a}\frac{n_1(a)}{\bar{n}_1}. \tag{10}$$

In this formula one must substitute the values of the constants from (6), (8a), (8b). The result has a very cumbersome form. But since a substantial difference from the previous expression for k is obtained when $\lambda^{(1)} a \gg 1$ and $\lambda^{(2)} a \gg 1$, we shall consider only this limiting case. In this case the Bessel functions $I_0(\lambda a)$ and $I_1(\lambda a)$ are replaced by their asymptotic expression $e^{\lambda a}$, and (10) is reduced to the form

$$\begin{aligned} k = \Bigg[\frac{2a}{\varepsilon_1 u_1} + \frac{a}{2\lambda^{(1)}\lambda^{(2)}}\,\frac{(\lambda^{(1)2} + \lambda^{(2)2} + \lambda^{(1)}\lambda^{(2)})D_1 - \alpha}{(\lambda^{(1)} + \lambda^{(2)})D_1^2} - \\ - \frac{D_1(\lambda^{(1)2} + \lambda^{(2)2}) - \alpha}{\lambda^{(1)}\lambda^{(2)} D_1^2}\Bigg]^{-1}. \end{aligned} \tag{11}$$

The second term in the brackets is greater than the third by a factor λa, and the latter must be neglected. The usual formula for k has the form

$$k = \left[\frac{2a}{\varepsilon_1 u_1} + \frac{a^2}{8D}\right]^{-1}.$$

Thus, the diffusion term in the brackets is reduced by a factor $1/\lambda a$. Let us now estimate this quantity for some conditions of experiment (3). At a temperature of the order of 1000°K, the rate constant of the reaction of OH with methane, according to data (4, 5), is $1.5 \cdot 10^{-12}$ cm^3/sec. Assuming that the volume concentration of methane is $2.5 \cdot 10^{18}$, we have the characteristic value

$a = 4 \cdot 10^6$. In order of magnitude, $\lambda = \sqrt{\alpha/D} = 2 \cdot 10^3$, if one assumes that $D \sim 1$ cm^2/s. Thus, if the diameter of the reaction vessel is 1 cm, then $\lambda a = 10^3$.

It is evident that this shifts the experimental conditions very strongly into the kinetic region.

The result obtained can be explained visually in the following way. If one plots the dependence of n_1 on r, it turns out that in the main part of the volume $n_1(r) = n_{10} = \text{const}$. Only near the wall, in a layer of thickness $1/\lambda$, does the radical density decrease by a relative amount of order ε. But since diffusion exists only where there is a density gradient, it effectively supplies radicals to the wall not from the whole volume, but from the fraction $1/\lambda a$ of it. This leads to the corresponding modification of Semenov' s usual formula. It is clear that if multiplication of radicals occurs in the volume, their distribution cannot in any way be constant. In the case under consideration, the destruction of radicals at the surface is not decisive.

2. The case in which the number of radicals is conserved exactly in the volume requires separate consideration and leads to a different expression for k. The corresponding kinetic equations with diffusion have the form

$$\frac{\partial n_1}{\partial t} = \frac{D_1}{r}\frac{\partial}{\partial r} r \frac{\partial n_1}{\partial r} - \alpha n_1 + \beta n_2, \tag{12a}$$

$$\frac{\partial n_2}{\partial t} = \frac{D_2}{r}\frac{\partial}{\partial r} r \frac{\partial n_2}{\partial r} + \alpha n_1 - \beta n_2 + q. \tag{12b}$$

The kinetic coefficients are chosen so that in a homogeneous system $\partial(n_1 + n_2)/\partial t = q$, i.e., the number of radicals generated in the volume, while mutual chemical transformations do not change the number of free valences. Further setting $\partial n_1/\partial t = \partial n_2/\partial t = 0$, we seek the solution this time in the form

$$n_1 = n_{10} + Ar^2 + C_1 I_0(\lambda r), \qquad n_2 = n_{20} + Br^2 + C_2 I_0(\lambda r). \tag{13}$$

Substituting (13) into (12a, b), we find

$$A = -\frac{q}{4\left(D_1 + \frac{\alpha}{\beta} D_2\right)}; \qquad B = \frac{\beta}{\alpha} A; \qquad \lambda^2 = \frac{\beta}{D_2} + \frac{\alpha}{D_1}; \qquad C_2 = -\frac{D_1}{D_2} C_1.$$

From the second boundary condition (7) we find

$$C_1 = Aa \frac{\alpha D_2}{\beta D_1} \frac{2}{\lambda I_1(\lambda a)}. \tag{14}$$

We now compute $\bar{n}_1$

$$\bar{n}_1 = n_{10} + \frac{Aa^2}{2} + \frac{4\alpha}{\beta} A \frac{D_2}{\lambda^2 D_1}. \tag{15}$$

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For k we obtain the exact formula*

$$k = \left[\frac{2a}{\varepsilon_1 u_1} + \frac{a^2}{8\left(D_1 + \frac{\alpha}{\beta} D_2\right)} (1+\omega) \right]^{-1}, \tag{16}$$

where

$$\omega = \frac{D_2}{\beta} \frac{1}{D_1} \frac{1}{\lambda a} \left(\frac{I_0(\lambda a)}{I_1(\lambda a)} - \frac{2}{\lambda a} \right). \tag{17}$$

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* If the second center can also perish at the wall with probability ε_2, then instead of $1+\omega$ one must write (for $a\lambda \gg 1$) $1 + \omega + (\varepsilon_2 u_2 a / 4\beta D_1 \lambda)(1 + 4\lambda D_1/\varepsilon_1 u_1)$. This imposes an additional restriction on ε_2, in addition to $\varepsilon_2 \ll \varepsilon_1$. We owe the indication of the possible importance of taking ε_2 into account to A. B. Nalbandyan.

For $\lambda a \ll 1$, (16) reduces to the usual formula. As before, we shall be interested in the opposite limiting case, $\lambda a \gg 1$. Then $I_0/I_1 \sim 1$, and the expression for ω is simplified:

$$\omega = \frac{4\alpha}{\beta} \frac{D_2}{D_1} \frac{1}{\lambda a}. \tag{18}$$

A substantial difference from Semenov' s formula occurs if the first radical is much more active than the second, $\alpha \gg \beta$. The quantity $4\alpha/\beta\lambda a$, of course, may be arbitrary. For the experimental condition (3) it is of order unity. We see that in the usual formula the diffusion term is decreased by a factor $2\beta/\alpha$. This may be of the order of 10^{-2}. In contrast to the first case, here the radicals are distributed parabolically throughout the vessel, but the height of the maximum of the distribution is reduced by a factor α/β in comparison with the problem of diffusion of a single active center. But the stationary distribution of radicals here can be established only if their destruction at the wall is taken into account. Thus, here too the kinetic region of the course of the reaction is greatly expanded.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
7 VIII 1964

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

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