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Abstract

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ON THE DIFFUSION OF ACTIVE CENTERS WITH QUADRATIC CHAIN TERMINATION IN THE VOLUME

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In the present work a solution is given to the problem of the spatial stationary distribution of nascent heterogeneous-active centers, under the assumption that they perish at the surface and also in the volume upon collisions with one another, i.e., for the case of quadratic chain termination. (Such a formulation of the problem applies, for example, to a pure mixture of hydrogen with chlorine, in which there are no oxygen impurities that capture active centers (^{1}).) We shall assume that the rate of heterogeneous initiation is much greater than the rate of homogeneous initiation, as is the case for the reaction in a mixture of hydrogen with chlorine*, and that the reaction proceeds in a plane-parallel vessel with distance $2l$ between the walls (one-dimensional problem). Then the distribution of active centers over the volume is described by the differential equation:

$$D\frac{d^2n}{dx^2} - k_p(M)n^2 = 0, \tag{1}$$

where n (1/cm^3) is the concentration of active centers; k_p (cm^6/sec) is the recombination coefficient; (M) (1/cm^3) is the total concentration of the mixture and products; x (cm) is the coordinate measured from the middle of the vessel ($-l \leq x \leq +l$, $2l$ is the length of the vessel); D (cm^2/sec) is the diffusion coefficient of the active centers.

The boundary conditions have the form:

$$D\frac{dn}{dx} = -\frac{1}{4}\varepsilon vn + w_r \quad \text{for } x = l, \tag{2}$$

$$\frac{dn}{dx} = 0 \quad \text{for } x = 0, \tag{3}$$

where ε is the probability of the death of active centers at the wall of the vessel; v (cm/sec) is the mean thermal velocity of motion of the active centers; w_r ($1/\mathrm{cm}^2 \cdot \mathrm{sec}$) is the rate of heterogeneous initiation.

Equality (3) is equivalent to the assumption that the conditions for both walls of the vessel ($x = +l$ and $x = -l$) are identical, i.e., that the distribution $n(x)$ is symmetric with respect to the middle of the vessel $x = 0$.

Let us introduce dimensionless variables:

$$y = \frac{k_p(M)l^2}{D} n, \qquad \xi = \frac{x}{l}.$$

Then equation (1) is written in the form

$$\frac{d^2y}{dx^2} - y^2 = 0, \tag{1a}$$

and the boundary conditions (2) and (3) in the form

$$\frac{dy}{d\xi} = -\alpha y + \beta \quad \text{for } \xi = 1; \qquad \alpha = \frac{\varepsilon v l}{4D}, \qquad \beta = \frac{w_r r^2 k_p(M)}{D^2}; \tag{2a}$$

$$\frac{dy}{d\xi} = 0 \quad \text{for } \xi = 0. \tag{3a}$$

Equation (1a) reduces to a first-order equation, which, after use of condition (3a), assumes the form

$$\left(\frac{dy}{d\xi}\right)^2 = \frac{2}{3}\left(y^3 - y_0^3\right), \tag{4}$$

where $y_0 = y_0(0)$ corresponds to $\xi = 0$.

The solution of this equation can be expressed in terms of the Weierstrass elliptic function $s = \wp(u)$, defined by

$$u = \int_s^\infty \frac{ds}{\sqrt{4s^3 - 1}}$$

(the equianharmonic case (2)), namely

* As can be shown, the rate of homogeneous initiation w_0 may be neglected in comparison with the rate of he

$$y = e_2^{-1} y_0 \wp(u), \qquad u = \omega_2 - e_2 \left(\frac{2}{3}\right)^{1/2} y_0^{1/2} \xi, \tag{5}$$

where $e_2 = \wp(\omega_2) = 4^{-1/3}$, $\omega_2 = 1.52995$.

Using the boundary condition (2a) and formula (5), we find the equation for determining the integration constant y_0:

$$\left(\frac{2}{3}\right)^{1/2} \left(4\wp^3 - 1\right)^{1/2} y_0^{3/2} = -\alpha e_2^{-1} y_0 \wp + \beta, \tag{6}$$

where the function $\wp$ is taken at $\xi = 1$, i.e., at the argument

$$u = \omega_2 - e_2 \left(\frac{2}{3}\right)^{1/2} y_0^{1/2}.$$

The distribution of active centers is given by the function (5). The mean value of the concentration of active centers over the volume is, obviously, determined by the expression

$$\overline{y} = \int_0^1 y\, d\xi = e_2^{-2} \left(\frac{3}{2}\right)^{1/2} y_0^{1/2} \int_{\omega_2}^{\omega_2 - e_2 (2/3)^{1/2} y_0^{1/2}} \wp(u)\, du =$$

$$= e_2^{-2} \left(\frac{3}{2}\right)^{1/2} y_0^{1/2} \left\{ \zeta \left(\omega_2 - e_2 \left(\frac{2}{3}\right)^{1/2} y_0^{1/2} \right) - \zeta(\omega_2) \right\}, \tag{7}$$

where $\zeta(u)$ is the Weierstrass zeta-function (the functions $\zeta(u)$ and $\wp(u)$ are tabulated in (2)).

In dimensional units the mean concentration $\overline{n}$ of active centers is written in the form:

$$\overline{n}\,(1/\mathrm{cm}^3) = \frac{D}{k_p(M) l^2}\, \overline{y}(\alpha, \beta). \tag{8}$$

Let us examine the function $\overline{y}(\alpha, \beta)$ for some limiting cases. Suppose that the concentration of active centers varies only weakly over the volume of the vessel, i.e., that $y_0^{1/2} \ll 1$. Then the function (5) may be expanded in a series in powers of the argument $y_0^{1/2}\xi$. Taking into account that $d\wp/du = 0$ at $u = \omega_2$ and retaining terms of order $y_0 \xi^2$, we have in this case*

$$\wp = e_2 \left(1 + \frac{1}{2} y_0 \xi^2 + \cdots\right), \qquad \text{i.e.} \quad y = y_0 \left(1 + \frac{1}{2} y_0 \xi^2 + \cdots\right), \tag{9}$$

$$\overline{y} = y_0 \left(1 + \frac{1}{6} y_0 + \cdots \right). \tag{10}$$

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* The expansion (9) can be found directly from equation (1), by substituting into it the series

$$y = \sum_{m=0}^{\infty} a_m \xi^{2m}$$

and determining the coefficients a_m from recurrence relations.

The quantity y_0 is found from equations (6) after substituting into it the expansion (9):

$$y_0^2 + \cdots = -\alpha y_0 (1 + \tfrac{1}{2} y_0 + \cdots) + \beta. \tag{11}$$

Suppose that $\alpha \ll 1$ and $\beta \ll 1$. Then from (11) it follows that

$$y_0 = -\frac{\alpha}{2} \sqrt{\frac{\alpha^2}{2} + \beta}. \tag{12}$$

For $\beta \ll \alpha^2/4$, $y_0 \simeq \beta/\alpha$, and for $\beta \gg \alpha^2/4$, $y_0 \simeq \sqrt{\beta}$. Thus we find the final expressions for the mean concentration:

$$\bar{n} = \frac{w_r}{\frac{1}{4}\varepsilon v} \quad \text{for} \quad w_r \ll \frac{\varepsilon^2 v^2}{16\, l k_p(M)}; \tag{13}$$

$$\bar{n} = \sqrt{\frac{w_r}{k_p(M) l}} \quad \text{for} \quad w_r \gg \frac{\varepsilon^2 v^2}{16\, l k_p(M)}. \tag{14}$$

Expressions (13) and (14) have a simple physical meaning. At low rates of heterogeneous initiation (condition (13)), a small number of chains is initiated at the walls, and therefore the probability of their interaction in the volume (proportional to n^2) is small. This means that the mean concentration $\bar{n}$ is determined by the dynamic equilibrium of the processes of initiation and death of active centers at the wall, $w_r = \frac{1}{4}\varepsilon v \bar{n}$, whence formula (13) follows.

On the other hand, when a large number of chains is initiated at the walls per unit time and, consequently, the probability of their interaction and death in the volume is large compared with the probability of death at the walls, the mean concentration of active centers $\bar{n}$ is determined by the equality between the rate of initiation of active centers per unit volume of the vessel, w_r/l, and the rate of their death per unit volume of the vessel, $k_p(M)\bar{n}^2$, whence formula (14) follows.

Let us now consider the case when the concentration of active centers n varies strongly over the volume of the vessel. Since the function $\mathfrak{S}(u)$ is large as $u \to 0$, namely $\mathfrak{S}(u) = \frac{1}{u^2} + \frac{u^4}{28} + \cdots$ as $u \to 0$, it should be assumed that a strong variation of n corresponds to $u = \omega_2 - e_2(2/3)^{1/2} y_0^{1/2} \ll 1$. The boundary condition (6) in this case gives

$$(2/3)^{1/2} \frac{2}{u^3} y_0^{1/2} = -\alpha e_2^{-1} y_0 \frac{1}{u^2} + \beta. \tag{15}$$

We make the assumption $\beta \gg 1$ and $\alpha \ll \beta^{1/3}$. Then from (15) it follows that

$$y_0 \simeq \frac{3\omega_2^2}{2l_2^2}, \qquad \frac{1}{u} \simeq 2^{-1/2} 3^{1/6} y_0^{-1/2} \beta^{1/3}.$$

Since for $u \to 0$, $\zeta(u) = \frac{1}{u} + \cdots$, in this case it follows from (7) that

$$\bar{y} \simeq 18^{1/3} \beta^{1/3}$$

or

$$\bar{n} = \left(\frac{18\, w_r D}{l^3 k_p^2 (M^2)} \right)^{1/3} \quad \text{for} \quad w_r \gg \frac{\varepsilon^3 v^3}{64\, D k_p (M)}. \tag{16}$$

The quantities $\bar{y}(\alpha, \beta)$ that do not satisfy the assumptions made above in deriving (13), (14), and (15) can be found numerically with the aid of tables of $\mathfrak{S}(u)$, $\zeta(u)$ (2). In this way, graphs of the func-

functions $\bar{y}(\alpha, \beta)$ for $\alpha = 0;\ 2;\ 4;\ 6;\ 8;\ 10$, shown in Fig. 1, with the aid of which it is easy to find the mean value of the concentration $\bar{n}$ under any assumptions about the parameters determining the reaction.

Using the theoretical results set forth and the experimental data on the reaction rates in a pure mixture of hydrogen with chlorine, one can draw certain conclusions about the possible elementary processes that took part in this reaction.

Under the conditions of A. M. Markevich[3], at a temperature of 310°, a pressure of the hydrogen-chlorine mixture of 62 mm Hg, $l = 2$ cm, $v_{\mathrm{Cl}} \simeq 6 \cdot 10^4$ cm/sec, $k_p = 10^{-32}$, and $\varepsilon = 5 \cdot 10^{-4}$, we obtain

$$\frac{\varepsilon^2 v^2}{16\, l k_p (M)_j} \simeq 1.5 \cdot 10^{17}.$$

N. N. Semenov and V. V. Voevodskii obtained the value $w_r \sim 10^{11}$ cm^{-2}sec^{-1}. Thus, as can be seen, condition (13) is satisfied*.

Fig. 1

With an increase in the pressure of the mixture and in the diameter, and a decrease in ε, one can achieve fulfillment of condition (14) and calculate k_p. For $\varepsilon \sim 10^{-5}$ and $l \sim 1$ cm, assuming that w_r is proportional to the pressure, we find that condition (14) for the reaction $H_2 + Cl_2$ can be fulfilled at a pressure $> 5 \cdot 10^5$ mm Hg.

In conclusion it should be noted that, by means of the method set forth here, i.e., the introduction of the Weierstrass function, one can also investigate the diffusion of active centers under other conditions in which quadratic chain termination plays an essential role (simultaneous initiation of chains at the walls and in the volume, destruction of active centers both on impurities and by quadratic recombination, etc.).

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[*] Thus, the mean concentration $\bar{n}$ in this case does not depend on the recombination constant k_p, and, consequently, k_p cannot be determined from data (9).