KINETIC THEORY OF TRANSFER IN HETEROGENEOUS CHEMICAL REACTORS IN HIGHLY DISPERSED POROUS BODIES

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The study makes an analytic investigation of the process of transfer of a gas in chemical reactions in porous bodies on the basis of a "dusty gas" model. In the case of a free molecular condition, an expression is derived for the number of molecules which have reacted in the porous body.

Heterogeneous chemical reactions in porous bodies play an important role in chemical technology. The conditions under which such reactions take place are highly diverse. Thus, for example, in the synthesis of artificial diamonds from the gaseous phase, the porous layer has very small thickness and high porosity [1]. Under such conditions, the mean free path of the molecules may be commensurable with the characteristic dimension of the porous body itself (its thickness), so that the diffusion theory will, in general, be incorrect.

For the sake of simplicity, we shall consider a monomolecular heterogeneous reaction of first order. By a heterogeneous reaction of first order, following [2], we mean any process involving the participation of a hard wall and leading to a change in the essential properties of a particle with a probability that is independent of the incident flow (for example, a change in the chemical state of a particle, the absorption of a particle by the wall, etc.).

We shall investigate a "dusty gas" model, i.e., we shall consider the system consisting of the porous body and the gas to be a gaseous mixture such that the molecules of one of its components, which simulate the particles of a porous body, are motionless and have dimensions and mass considerably exceeding the dimensions and mass of real gas molecules [3]. The probability that the molecule will travel a distance x without a collision is equal to

$$W = \exp\left\{-\frac{x}{\lambda}\right\}, \tag{1}$$

where $1/\lambda = 1/\lambda_1 + 1/\lambda_2$; λ_1 and λ_2 are, respectively, the free path lengths of an unreacted molecule with respect to the gas molecules (including molecules which are reaction products) and with respect to the "motionless molecules."

In its motion, the molecule may collide either with a gas molecule, which leads to elastic scattering, or with a "motionless molecule." In the latter case it will either go into chemical reaction (with probability η) or be elastically scattered (with probability $1-\eta$). As in the case of the derivation of the Peierls equation, we shall assume that the elastic scattering is isotropic [4]. The molecules which are reaction products will also be assumed to leave an elementary volume of the porous body isotropically; in their further motion they may collide either with gas molecules or with the four walls only elastically.

We introduce the following notation: $\Phi_1(x)$ and $\Phi_2(x)$ are, respectively, the numbers of unreacted molecules appearing per unit volume of the porous body per unit of time as a result of molecule–molecule collisions and as a result of elastic collisions of molecules with "motionless molecules"; $\Phi_3(x)$ is the number of molecules which are reaction products that appear per unit volume of the solid body per unit of time.

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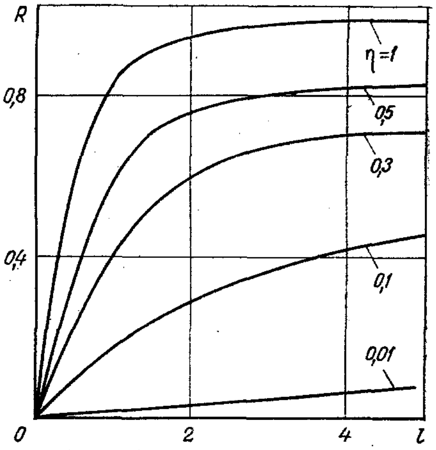

Fig. 1. Relative number of molecules which have reacted in the porous layer, shown as a function of l.

In deriving the equations for the functions $\Phi_1(x)$, $\Phi_2(x)$, $\Phi_3(x)$ in the case of a plane layer of thickness L, taking account of (1), we shall use an approach analogous to the one used in deriving the Peierls equation [4, 5]:

$$\Phi_1(x) = 2\tilde{\Phi}(0) E_2\left(\frac{x}{\lambda}\right)\frac{1}{\lambda_1} + \frac{1}{2}\int_0^L \Phi_1(\xi)\, E_1\left(\frac{|x-\xi|}{\lambda}\right)\frac{d\xi}{\lambda_1} + \frac{1}{2}\int_0^L \Phi_2(\xi)\, E_1\left(\frac{|x-\xi|}{\lambda}\right)\frac{d\xi}{\lambda_1} + 2\tilde{\Phi}(L) E_2\left(\frac{L-x}{\lambda}\right)\frac{1}{\lambda_1}, \quad (2)$$

$$\Phi_2(x) = (1-\eta)\left[2\tilde{\Phi}(0) E_2\left(\frac{x}{\lambda}\right)\frac{1}{\lambda_2} + \frac{1}{2}\int_0^L \Phi_2(\xi) E_1\left(\frac{|x-\xi|}{\lambda}\right)\frac{d\xi}{\lambda_2} + \frac{1}{2}\int_0^L \Phi_1(\xi) E_1\left(\frac{|x-\xi|}{\lambda}\right)\frac{d\xi}{\lambda_2} + 2\tilde{\Phi}(L) E_2\left(\frac{L-x}{\lambda}\right)\frac{1}{\lambda_2}\right], \quad (3)$$

$$\Phi_3(x) = \frac{\eta}{1-\eta}\,\Phi_2(x) + \frac{1}{2}\int_0^L \Phi_3(\xi)\, E_1\left(\frac{|x-\xi|}{\lambda}\right)\frac{d\xi}{\lambda}, \quad (4)$$

where $\Phi = \Phi_1 + \Phi_2$ is the total number of unreacted molecules appearing in a unit volume per unit of time; $\tilde{\Phi}(0)$ and $\tilde{\Phi}(L)$ are the densities of the molecular streams entering the porous body at $x = 0$ and $x = L$, respectively (it is assumed that these molecules are distributed according to a cosine law). Hereafter, for the sake of simplicity, we shall assume that $\tilde{\Phi}(L) = 0$.

In a Knudsen regime of flow $\lambda_1 \gg \lambda_2$, $\Phi_2 \gg \Phi_1$. This justifies setting $\Phi_1 = 0$, $\lambda = \lambda_2$, which simplifies Eqs. (3) and (4). In the equation for $\Phi_2(\Phi_2 = \Phi)$ we introduce the dimensionless coordinate $x_1 = x/L$ and approximate the functions E_1 and E_2 by exponentials [6]. Differentiating the resulting equation twice and combining the result with the original equation, we arrive at an ordinary differential equation whose solution has the form

$$\Phi(x_1) = C\left[\frac{\sqrt{\eta}+1}{\sqrt{\eta}-1}\exp\{2l\sqrt{\eta}\,(2-x_1)\} + \exp\{2l\sqrt{\eta}\,x_1\}\right], \quad (5)$$

where

$$C = \frac{4\tilde{\Phi}(0)(1-\sqrt{\eta})^2(1+\sqrt{\eta})}{\lambda[(1-\sqrt{\eta})^2-(1+\sqrt{\eta})^2\exp\{4l\sqrt{\eta}\}]}.$$

We find the quantity R, defined as the ratio of the number of molecules which have reacted with the porous body to the number of molecules which have entered it:

$$R = \frac{\int_0^L \frac{\eta}{1-\eta}\Phi(x)\,dx}{\tilde{\Phi}(0)}.$$

In the free molecular regime, making use of (5), we obtain

$$R = 2\sqrt{\eta}\,\frac{\exp\{4l\sqrt{\eta}\}(1+\sqrt{\eta}) - 2\exp\{2l\sqrt{\eta}\} + 1 - \sqrt{\eta}}{(1+\sqrt{\eta})^2\exp\{4l\sqrt{\eta}\} - (1-\sqrt{\eta})^2}. \quad (6)$$

As l approaches infinity in (6), we find for R the equation

$$R = \frac{2\sqrt{\eta}}{1+\sqrt{\eta}}.$$

It should be noted that λ is expressed in terms of the porosity as follows [3, 5]:

$$\lambda = \frac{2}{3}\,\frac{\Pi}{1-\Pi}\,d.$$

The values of the function (6) are shown in Fig. 1 as a function of l for different values of η. These results were compared with those of [7], in which a numerical method was used for solving the equation describing the molecular flow of a gas with chemical reactions in an individual cylindrical capillary; the comparison showed good agreement (in making the comparison, we assumed that the mean free path for molecular flow in the capillary is equal to the diameter of the capillary).

The advantage of this method lies in the fact that the resulting formula contains the porosity in a natural manner, whereas when a porous medium is simulated by cylindrical capillaries, the porosity is included in a rather artificial manner.

In conclusion, it should be noted that in order to determine the quantity K, which characterizes the ratio of the number of molecules leaving the porous layer to the number of original molecules which enter it, we find $\Phi_3(x)$ from Eq. (4) and then make use of the formula

$$K = \frac{L}{2\widetilde{\Phi}(0)} \int_0^1 \Phi_3(x) E_2[l(1-x)]\,dx.$$

NOTATION

Π is the porosity;
d is the diameter of sample particle;
L is the thickness of porous body;
$l = L/\lambda$; $E_k(x) = \int_0^1 y^{k-2} \exp\{-x/y\}dy$ is the exponential integral function.

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