TRANSIENT DIFFUSION OF GAS IN A HIGHLY DISPERSED SORBING POROUS SOLID

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The transient diffusion of gas in a porous sorbent is considered on the basis of the "dusty" (or "dust-laden") gas model. An equation is derived for the diffusion coefficient.

It is well known that, when a gas molecule interacts with a solid, physical adsorption usually occurs, i.e., the molecule remains for a certain period attached to the surface of the solid, after which desorption takes place. The sorbents used in actual practice are often highly dispersed porous solids, the pore structure being extremely complicated. It is frequently indicated in the literature [1] that transfer phenomena in such materials have to be described statistically.

In this paper we shall use the "dusty gas" model [2, 9] to describe transient diffusion in a highly dispersed solid sorbent. We shall treat the porous solid–gas system as a binary gas mixture in which some molecules, simulating the particles of the porous solid, are immobile and have a size and mass far greater than those of the real gas molecules.

We write the resultant molecular flux directed along the x axis in the solid as follows:

$$q(x,\ t)=\frac{1}{2}\int\limits_{0}^{1}\int\limits_{-a}^{x} n\left(\xi,\ t-\frac{x-\xi}{c\mu}\right)\nu\exp\left\{-\frac{x-\xi}{\lambda\mu}\right\}d\xi d\mu-$$

$$-\frac{1}{2}\int\limits_{0}^{1}\int\limits_{x}^{b} n\left(\xi,\ t-\frac{\xi-x}{c\mu}\right)\nu\exp\left\{-\frac{\xi-x}{\lambda\mu}\right\}d\xi d\mu. \tag{1}$$

Here μ is the cosine of the angle between the x axis and the direction of motion of the molecule, $1/\lambda = (1/\lambda_1) + (1/\lambda_2)$ where λ_1 is the gasdynamic free path, and λ_2 is the free path of the gas molecules relative to the stationary molecules, which is defined in terms of the diameter of the latter and the porosity of the solid in the following way [3, 9]:

$$\lambda_2=\frac{2}{3}\cdot\frac{\Pi}{1-\Pi}; \tag{2}$$

where c is the average molecular velocity, regarded as constant.

The total collision frequency of the gas molecules (both with other gas molecules and with the stationary molecules of the solid) ν is treated as constant in the average-range approximation used in the present analysis.

In deriving Eq. (1) we made the assumptions usually employed in the derivation of the Peierls equation [4].

The integrand in Eq. (1) represents the number of particles which have appeared at the point ξ at the instant of time $t - |x - \xi|/c\mu$ as a result of collisions, have been isotropically scattered, and then have traveled a distance $|x - \xi|/\mu$ without any collisions.

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The quantity ν may be written as $1/T$, where T is the time between two escapes of the molecule from the solid surface:

$$T = \frac{1}{\nu} = \frac{\lambda}{c} + f(\lambda_1, \lambda_2)\tau, \tag{3}$$

where f is the ratio of the number of collisions of the molecule with particles of the porous solid to the total number of collisions $f = \lambda/\lambda_2$.

Let us apply a Laplace transformation to Eq. (1), approximating the exponential integral function E_2 so arising by an exponential [5], and remembering that $n(x, t) = 0$ for $t < |x - \xi|/c\mu$:

$$\bar{q}(x, p) = \frac{3}{8}\nu \int_{-a}^{x} \bar{n}(\xi, p) \exp\left\{-\frac{3}{2}\left(\frac{p}{c} + \frac{1}{\lambda}\right)(x-\xi)\right\} d\xi -$$

$$-\frac{3}{8}\nu \int_{x}^{b} \bar{n}(\xi, p) \exp\left\{-\frac{3}{2}\left(\frac{p}{c} + \frac{1}{\lambda}\right)(\xi - x)\right\} d\xi. \tag{4}$$

Differentiating Eq. (4) twice with respect to x and then combining the result with Eq. (4) itself, we obtain

$$\frac{4}{9} \cdot \frac{\partial^2 \bar{q}}{\partial x^2} = \left(\frac{p^2}{c^2} + \frac{2p}{c\lambda} + \frac{1}{\lambda^2}\right)\bar{q} + \frac{\nu}{3} \cdot \frac{\partial \bar{n}}{\partial x}. \tag{5}$$

In Eq. (5) we now return to the original variables, discarding terms of higher orders of smallness and expressing ν in terms of Eq. (3):

$$q = -\frac{1}{3} \cdot \frac{\lambda^2}{\dfrac{\lambda}{c} + \tau\dfrac{\lambda_1}{\lambda_1 + \lambda_2}} \cdot \frac{\partial n}{\partial x}. \tag{6}$$

It follows that the diffusion coefficient may be written as follows:

$$D = \frac{1}{3} \cdot \frac{\lambda_2^2}{\dfrac{\lambda_2}{c} + \tau} \cdot \frac{\lambda_1}{\lambda_1 + \lambda_2}. \tag{7}$$

We see from Eq. (7) that as $\lambda_2 \to \infty$ the diffusion coefficient assumes the ordinary form

$$D = \frac{1}{3} c\lambda_1,$$

and as $\lambda_1 \to \infty$

$$D = \frac{1}{3} \cdot \frac{\lambda_2^2}{\dfrac{\lambda_2}{c} + \tau}. \tag{8}$$

It is well known [6] that for the free molecular flow of gas along a tube the free path equivalent to λ_2 is equal to the diameter of the capillary. Thus, Eq. (8) yields the well-known result of Clausing for the diffusion coefficient associated with the transient molecular flow of gas along a tube [7].

The special feature of Eq. (8) lies in the fact that it is derived for the porous solid as a whole, i.e., it includes its basic characteristic of porosity in accordance with Eq. (2), and also allows for the influence of intermolecular collisions.

It should be noted that an analogous method may be employed in order to obtain the surface diffusion coefficient in the transient case. The analog of the adsorption time is here the time spent by an adsorbed atom on an active center; the remaining quantities have the same significance as in Eq. (1). If the adsorbed atoms do not collide with each other but only jump between active adsorption centers, we have an analogy of Knudsen diffusion. This analogy was indicated in [8]. Taking this analogy further, we may relate the free path of the adsorbed atom on the surface with the "two-dimensional porosity," i.e., the ratio of the area on the surface free from active centers to the total surface area.

NOTATION

n is the number of particles in unit volume;
π is the porosity;

d	is the diameter of the model particle;
$-a$ and b	are the coordinates of points fairly well removed from the surface under examination;
τ	is the adsorption time;
E_k	exponential integral function:

$$E_k(x) = \int_0^1 y^{k-2} \exp\left\{-\frac{x}{y}\right\} dy.$$

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