GAS ABSORPTION AND LIBERATION KINETICS IN POROUS SOLIDS

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A dispersed system model is proposed in which the dispersed phase consists of closed macroscopic pores, distributed over the volume of the solid material (dispersion phase).

Various solids with a loose structure are used in scientific and practical applications [1, 2]. The ratio between the densities of the most closely packed state possible and the loose packed state can serve as a quantitative characteristic of structural "looseness." Thus, for example, a comparison of the densities of carbonaceous materials ($2.25 \cdot 10^3$ kg/m^3 – monocrystalline graphite; $1.9 \cdot 10^3$ kg/m^3 – structural graphite; $(1.2\text{-}1.5) \cdot 10^3$ kg/m^3 – coal [3]) permits estimation of the coal porosity $\mu \sim 0.1$. Traditional gas and pycnometric methods based on penetration of gases or liquids into open pores give lower values of $\mu \sim 10^{-2}$ [4]. This difference indicates the presence in the carbonaceous material of a large quantity of closed pores. Results of electron microscope studies make it possible to estimate their size $r_p \sim 10^{-8}\text{-}10^{-7}$ m [5], so that their concentration in the coals is $N_p \sim 10^{19}\text{-}10^{22}$ m^{-3}. Absorption of gas by coals or other solids containing a large number of pores apparently occurs by rapid penetration of gas molecules through a system of filter channels within the volume of the solid with subsequent diffusion displacement of molecules through the entire material.* Of the processes enumerated, solid-state diffusion is obviously the slowest and, without introducing a noticeable contribution to gas filtration through porous solids, it determines the principles of sorption phenomena. These considerations move us to propose for analysis of such phenomena a model of a porous solid in which the dispersed phase consists of macroscopic pores distributed through the volume of the body, which is the dispersion phase. Within such a model the role of filtration channels is considered by introducing an effective diffusion coefficient through the surface of the solid (see, for example, [6]). Below we will consider the kinetics of gas absorption and liberation by solids of finite dimensions containing a large fixed number of macroscopic pores (coalescence of such pores was studied in [7-9]).

Formulation of Problem and Basic Equations. For simplicity we assume that the porous solid has the form of a sphere, the volume V of which, comparably to the density N_p, has spherically shaped pores of radius r_p, separated from each other by a distance l, significantly greater than r_p, $r_p \ll l \ll R$ ($l \sim N^{-1/3}_p$). The solid is located within a chamber of volume V_c, filled with a gas at a constant temperature T. The gas distribution in the system will be characterized by its density in the solid solution $c(r, t)$, in pores $\rho(r, t)$, and in the free volume of the chamber $n(t)$. Diffusion displacement of the gas within the system may take place by shifts of molecules or complexes of molecules with a vacancy or interstitial atom, or by other methods, considered by the corresponding value of the diffusion coefficient D. We will assume that the solid solution is quite dilute and that interaction of the dissolved molecules with each other may be neglected. Such molecules may in general dissociate and participate in formation of certain chemical compounds [9]. These phenomena will not be considered in the present study. The solid body will be assumed isotropic, and the gas ideal.

We write the equation of molecular diffusion through the solid volume in the presence of pores acting as drains (sources) in the form

$$\frac{\partial c(r, t)}{\partial t} = Dr^{-2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c(r, t)}{\partial r} \right) - 4\pi r_p^2 N_p I(r, t). \tag{1}$$

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*Penetration of gas molecules into the solid can be hindered by the presence of certain materials on the surface.

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The gas density within a pore then changes at a rate

$$\frac{\partial \rho(r,\ t)}{\partial t} = \frac{3}{r_p} I(r,\ t). \tag{2}$$

The boundary condition for Eq. (1) at r = R is the condition of continuity of particle flow through the external surface of the solid

$$D\, \frac{\partial c(R,\ t)}{\partial R} = -I_R(t), \tag{3}$$

which is directly related to the rate of change of gas density in the free chamber volume $V_1 = V_c - V$:

$$\frac{dn(t)}{dt} = \frac{4\pi R^2}{V_1} I_R(t). \tag{4}$$

The initial conditions for Eqs. (1), (2), and (4) are:

$$n(0) = n_0,\ c(r,\ 0) = c_0,\ \rho(r,\ 0) = \rho_0. \tag{5}$$

In general form this diffusion problem is complex. However, when two significantly different characteristic lengths exist, the pore size r_p and the size of the region R over which they are distributed ($R \gg r_p$), the diffusion process can be divided into a local process with characteristic length r_p, which determines the filling (emptying) of pores by gas, and an averaged macroscopic diffusion in the volume V, which has spherical symmetry in the geometry considered [10].

Under quasisteady-state conditions realized when $l \gg r_p$, when the time for establishment of a steady-state gas molecule flow in the pore is significantly less than the characteristic time for change in the molecular distribution far from a pore, the gas flux density into a pore [7-10] is

$$I(r,\ t) = Dr_p^{-1}[c(r,\ t) - v\rho(r,\ t)], \tag{6}$$

where $v = M\Omega\delta$ [11]; $M \lesssim 10^{28}$-10^{29} m^{-3}.

In analogy to Eq. (6), we write the gas molecule flux density through the external surface of the porous solid in the form

$$I_R(t) = \sigma R^{-1}[c(R,\ t) - vn(t)], \tag{7}$$

characterizing the former by the diffusion coefficient σ through the boundary of the solid. Regarding the value of the coefficient σ, we may note the following. If extended macroscopic defects such as cracks, open pore networks, etc., begin on the surface, then diffusion through the surface is easier than volume diffusion and we will have $\sigma \gg D$. When the porous solid surface is coated by a film which hinders penetration of gas molecules into the volume, the opposite inequality $\sigma \ll D$ will be true. In the opposite case, σ does not differ from D (see, for example, [12]).

Solution of Equations and Determination of Gas Molecule Distribution Asymptote. Equations (1), (2), and (4), with conditions (3) and (5), can be solved by performing a Laplace transform with respect to time t. Omitting the simple but lengthy calculations, we will present the expressions for molecule density in the chamber

$$n(t) = n_0\{1 - \alpha\beta J_1(t^*)\} + c_0 v^{-1}\alpha\beta\left\{J_1(t^*) - \frac{\varepsilon_2}{\varepsilon_1}\gamma J_2(t^*)\right\} \tag{8}$$

and the number of gas molecules θ(t) contained in a unit volume of the porous solid:

$$\theta(t) \equiv \frac{4\pi}{V}\int_0^R drr^2\{c(r,\ t) + \mu\rho(r,\ t)\} = 3\alpha v n_0 J_1(t^*) + c_0\left\{1 + \frac{\varepsilon_2}{\varepsilon_1}(1-\gamma) - 3\alpha\left[J_1(t^*) - \frac{\varepsilon_2}{\varepsilon_1}\gamma J_2(t^*)\right]\right\}. \tag{9}$$

Here

$$t^* = \frac{t}{\tau_D};\ \tau_D = \frac{R^2}{D};\ \alpha = \frac{\sigma}{D};\ \mu = \frac{4}{3}\pi r_p^3 N_p;$$

$$\beta = \frac{4\pi R^3 v}{V_1};\ \varepsilon_1 = \frac{3vR^2}{r_p^2};\ \varepsilon_2 = \frac{3\mu R^2}{r_p^2};\ \gamma = 1 - v\frac{\rho_0}{c_0}.$$

The functions J_1 and J_2 appearing in Eqs. (8) and (9) are defined by the integral expression

$$J_n(z) = \frac{1}{2\pi i}\int_{-i\infty+0}^{i\infty+0} ds \exp(sz)\left(\frac{\varepsilon_1}{s+\varepsilon_1+\varepsilon_2}\right)^{n-1} F(s),\ n = 1,\ 2,$$

$$F(s) = \frac{\varkappa(s)\operatorname{cth}\varkappa(s) - 1}{s[s(\varkappa(s)\operatorname{cth}\varkappa(s) - 1 + \alpha) + \alpha\beta(\varkappa(s)\operatorname{cth}\varkappa(s) - 1)]}, \tag{10}$$

$$\varkappa(s) = \left[s\left(1 + \frac{\varepsilon_2}{\varepsilon_1 + s}\right)\right]^{1/2}.$$

As can easily be proved, the total number of gas molecules in the system does not vary over time: $V_1 n + V\theta = \text{const}$.

According to Eqs. (8) and (9), the kinetics of gas absorption and liberation in the porous solid are described by the functions J_1 and J_2 with a very complex time dependence. To study the process of system approach to equilibrium and determine the relaxation time, it is sufficient to limit ourselves to consideration of the asymptote of $J_n(z)$ at $z \gg 1$. The latter is determined by the pole of the integrand in Eq. (10) which has the largest real component. Analysis of the features of the function $F(s)$ in the complex plane reveals that the corresponding pole has the form $s = -\xi$, where ξ is the smallest positive root of the transcendental equation

$$y \operatorname{ctg} y = 1 + \frac{\alpha\xi}{\alpha\beta - \xi};\quad y \equiv \left[\xi\left(1 + \frac{\varepsilon_2}{\varepsilon_1 - \xi}\right)\right]^{1/2}, \tag{11}$$

equal to

$$\xi = \frac{1}{2}\left(\varepsilon_1 + \varepsilon_2 + y^2 - \sqrt{(\varepsilon_1 + \varepsilon_2 + y^2)^2 - 4\varepsilon_1 y^2}\right). \tag{12}$$

Finding the residue of the integrand of Eq. (10) at the point $s = -\xi$, we determine the asymptote of J_n and thus $n(t)$ and $\theta(t)$ for large times $t \gg \tau$:

$$n(t) \sim n_\infty + \frac{V}{V_1} 3Kv \exp\left(-\frac{t}{\tau}\right), \tag{13}$$

$$\theta(t) \sim (\mu + v) n_\infty - 3Kv \exp\left(-\frac{t}{\tau}\right). \tag{14}$$

Here n_∞ is the equilibrium gas density in the chamber:

$$n_\infty = \left[1 + (\mu + v)\frac{V}{V_1}\right]^{-1}\left\{n_0 + c_0\frac{V}{V_1}\left[1 + (1 - \gamma)\frac{\mu}{v}\right]\right\}, \tag{15}$$

τ is the relaxation time in the system:

$$\tau = \tau_D \xi^{-1} = R^2/(D\xi),$$

$$K = f^{-1}\left\{n_0 - c_0 v^{-1}\left(1 - \gamma\frac{\varepsilon_2}{\varepsilon_1 + \varepsilon_2 - \xi}\right)\right\}, \tag{16}$$

$$f = \beta + \frac{(\alpha\beta - \xi)^2}{2\alpha^2}\left(1 + \operatorname{ctg}^2 y - \frac{\operatorname{ctg} y}{y}\right)\frac{\xi^2 - 2\varepsilon_1\xi + \varepsilon_1(\varepsilon_1 + \varepsilon_2)}{(\varepsilon_1 - \xi)^2}.$$

Considering Eq. (12), we will analyze Eq. (16) for the relaxation time τ.

If the porosity of the solid μ is small ($\mu \ll v$), then, according to Eq. (12), $\xi = y^2$ and $\tau = R^2/(Dy^2)$. Then for the case $\alpha \ll 1$ it follows from Eq. (11) that $y = \sqrt{3\alpha}$ and the system relaxation time is limited by diffusion through the surface of the porous solid:

$$\tau \sim R^2/\sigma. \tag{17}$$

If the parameter α is not small, then $y \sim 1$ and τ is determined mainly by volume diffusion processes:

$$\tau \sim R^2/D. \tag{18}$$

In the case of high porosity ($\mu >> v$), $\xi = vy^2/\mu$ and the relaxation time $\tau = \mu R^2/(vDy^2)$ as compared to the previous case increases by a factor of μ/v. It can be easily seen that the fraction of "cells" in the solid which will be filled by gas molecules increases by the same amount. Then if $\alpha << 1$, $y = \sqrt{3\alpha}$, and the relaxation time in the gas–porous solid system will be defined by the diffusion process through the solid's surface:

$$\tau \sim \mu R^2/(v\sigma). \tag{19}$$

If $\alpha \gtrsim 1$ ($y \sim 1$) and volume diffusion processes play the dominant role, then

$$\tau \sim \mu R^2/(vD). \tag{20}$$

The results obtained indicate the dominant role of pores in determining the transition to equilibrium of the gas–porous solid system.

The significant increase (by a factor of μ/v) of relaxation time in highly porous material can explain the disagreement of gas sorption and desorption isotherms* constructed from experimental data for one and the same porous material (hysteresis) [2], which is apparently caused by the impossibility of establishing complete equilibrium over a finite time in the gas–porous solid system. In fact, since at any finite time t, as follows from Eq. (10), it is true that

$$J_1(t^*) < \frac{1 + \mu/v}{3\alpha\,[1 + (\mu + v)\,V/V_1]},$$

the quantity of gas θ_s absorbed by a unit volume of the porous solid up to time $t = t_s$, when the gas pressure in the chamber becomes equal to p, is always less than the gas density θ_{ds} in the porous solid after attainment of a pressure p in the chamber at the time $t = t_{ds}$ during desorption: $\theta_s < \theta_{ds}$ (coincidence of the values θ_c and θ_{ds} is achieved only at $t = \infty$).

The nonlinear character of the dependence of θ on p observed in the experiments of [2] (sorption isotherm) can be explained in the model considered, according to Eqs. (8) and (9), by the need to record in each experiment not only the pressure in the chamber $p = nkT$ and the amount of gas absorbed by the porous solid θ, but also five more process parameters: n_0, c_0, γ, J_1, and J_2. The first three of these quantities n_0, c_0, and γ describe the system state at the beginning of each stage of the sorption (desorption) process, while J_1 and J_2, being functions of time, characterize the final state of the system. Since, according to Eqs. (13) and (14), at large times t ($t >> \tau$) the dependence of θ on these five parameters can be reduced to the dependence of θ on a single parameter p_∞:

$$\theta = \frac{V_1}{kTV}\,(p - p_\infty) + \frac{\mu + v}{kT}\,p_\infty, \tag{21}$$

$$p_\infty = n_\infty kT$$

[n_∞ being defined by Eq. (15)], then it is sensible to introduce the concept of sorption isotherms in the form of surfaces in the coordinates (p, p_∞, θ).

From the type of relaxation process (sorption, desorption) in the gas–porous solid system for known v and μ, it becomes possible to determine the original quantity of gas $\theta = \theta_0$ in the porous solid. In fact, according to Eq. (21), when the condition

$$\theta_0 < (\mu + v)\,\frac{p_0}{kT}$$

is satisfied, sorption of gas into the porous solid located in the chamber takes place, with a decrease in pressure. When the opposite condition is satisfied, desorption takes place, accompanied by an increase in gas pressure in the chamber.

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*The dependence of the quantity of gas θ absorbed by the solid material (sorbent) on equilibrium gas pressure p within the chamber.

Comparison of experimental results with the theoretical conclusions presented in the present study will permit determination of the parameters of the porous structure of solid bodies and classification of the latter by quantities such as gas capacity as well as gas absorption or desorption rate.

NOTATION

μ, pore volume per unit volume of solid (porosity); $V = (4/3)\pi R^3$, volume of solid (spherically shaped) containing pores; r_p, pore radius; l, distance between pores; $c(r, t)$, gas molecule density in solid solution; $\rho(r, t)$, gas density in pores; $n(t)$, gas density in chamber; V_c, chamber volume; D, gas molecule diffusion coefficient in solid; σ, diffusion coefficient through external surface of porous solid; t, time; r, coordinate; $V_1 = V_c - V$, free volume of chamber; $I_R(t)$, $I(r, t)$, gas molecule flow densities through exterior surface of solid and into pore, respectively; n_0, c_0, and ρ_0, initial values of gas molecule densities in chamber, solid solution, and pores, respectively; v, specific solution volume; δ, solubility of gas molecules; Ω, volume per molecule of solid solution; $\theta(t)$, number of gas molecules absorbed per unit volume of porous solid; τ_D, τ, diffusion times; α, β, ε_1, ε_2, γ, dimensionless combinations of quantities σ, D, R, v, V_1, r_p, μ, ρ_0, c_0, n_∞, equilibrium gas density in chamber; s, complex variable; i, imaginary unit; $J_n(z)$, reverse Laplace transform; p, p_∞, gas pressure in chamber; k, Boltzmann's constant; T, absolute temperature.

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