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Abstract

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ON THE TIME REQUIRED FOR THE ESTABLISHMENT OF SORPTION EQUILIBRIUM

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In measurements of sorption isotherms, equilibrium in a number of cases is established extremely slowly. Thus, for example, in the experiments of Kuadzhe (1), in the region close to saturation, readings of the sorption values of benzene vapors on natural sorbents (clays) were taken after 1-2 days. Kaganer (2) observed a low rate of sorption at low pressures. According to the author' s data, equilibrium sorption values of nitrogen on carbons, silica gels, and other sorbents investigated in the pressure region below 10^{-3} mm Hg were reached after 15-25 h. The fact of slow sorption of water vapor on activated carbons in the region of the steep rise of the sorption isotherm is well known. The literature contains many other examples of slow sorption of gases and vapors when the process of physical sorption is not complicated by chemical interaction or absorption (3–5).

On the other hand, measurement of the sorption of gases and vapors in the middle region of the isotherm in many cases presents no difficulties with respect to time, since equilibrium is reached rapidly (within several minutes). The reasons for such wide variations in the time required to measure different points of a sorption isotherm have not received sufficient elucidation in the literature, and we considered it expedient to examine briefly the principal causes on which the time required for the establishment of sorption equilibrium depends. By the term sorption in the present work we mean adsorption and capillary condensation.

If the sorption process is not complicated by chemical interaction, then the rate of sorption is determined by the rate of transport of molecules from the gas phase to the adsorption centers of the sorbent. Transfer of substance in a porous sorbent takes place by different mechanisms, but since all known types of transfer have the same dependence on the pressure gradient, the rate of the overall process can formally be described by a diffusion equation with a certain "effective" (or "fictitious") diffusion coefficient, which for brevity we shall call simply the diffusion coefficient.

The diffusion equation for an adsorbing gas in an isotropic porous medium can be written in the form

$$\frac{\partial c}{\partial t} = \frac{D}{1 + f'(c)} \nabla^2 c, \tag{1}$$

where D is the diffusion coefficient, $f'(c)$ is the derivative of the concentration function determined from the equation of the sorption isotherm, a is the sorption value, ∇^2 is the Laplace operator, and t is time.

Integration of equation (1) presents serious mathematical difficulties if the function $f(c)$ is nonlinear. But since in practice this is the most common case, then, sacrificing some accuracy

calculations, one may, in a more or less narrow concentration interval,* take $f'(c) = \Gamma_c =$ const and also take $D = D_c =$ const, since in the general case D varies with loading ($^{6-8}$).

The final conclusions will not change if we carry out the further consideration for the simplest example, taking the sorbent grains to be spherical. The solution of equation (1) for a sphere of radius R, under the additional conditions

$$c(x,0) = c\,, \qquad c(0,t) = c_0, \qquad \frac{\partial c(R,t)}{\partial x} = 0$$

with subsequent integration over the volume and replacement of c by a, has the form

$$\frac{a - a}{a_0 - a} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-n^2 \pi^2 \frac{D_c t}{\Gamma_c R^2}\right]. \tag{2}$$

Here a is the amount of adsorption at time t, a is the initial amount of adsorption at $t = 0$, a_0 is the equilibrium amount of adsorption ($t \to \infty$), $n = 1, 2, 3 \ldots.$ The unity in the expression $1 + f'(c)$ has been omitted, since usually $1 \ll f'(c)$.

According to equation (2), at $a = a_0$, $t = \infty$, i.e., the time for establishment of sorption equilibrium is equal to infinity. In actual practice, however, an experiment, as is known, ends after a finite interval of time. This apparent discrepancy between theory and experiment arises because, after some time from the start of the experiment, the difference between the true equilibrium value of sorption and the observed one becomes smaller than the experimental error, and the experiment is stopped, since the continuing increase in sorption is not detected. If the absolute error of measurement is equal to ξ, then the onset of equilibrium will be recorded when the amount of sorption reaches the value $a_\xi = a_0 - \xi$ (the variant $a_\xi = a_0 + \xi$ is excluded, since it does not satisfy equation (2)).

Thus, the time for establishment of sorption equilibrium is determined by the equation

$$\frac{a_\xi - a}{a_0 - a} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-n^2\pi^2 \frac{D_c t_\xi}{\Gamma_c R^2}\right] = N, \tag{3}$$

where N is a constant for the given concentration interval, but may vary in other regions of the isotherm, since it depends not only on the measurement error but also on the difference $a_0 - a$.

It follows from equation (3) that

$$\frac{D_c t_\xi}{\Gamma_c R^2} = k_\xi, \tag{4}$$

where k_ξ is a constant uniquely dependent on N.

Solving equation (4) with respect to t_ξ, we find

$$t_\xi = k_\xi \frac{\Gamma_c R^2}{D_c}. \tag{5}$$

Equation (5) was obtained for sorbent grains having the form of a sphere. For another shape of sorbent grains, a correction factor (shape factor) k_ϕ should be introduced. The quantity R in this case denotes the radius of a sphere of equal volume. Thus

$$t_\xi = k_\phi k_\xi \frac{\Gamma_c R^2}{D_c}. \tag{6}$$

Equation (6) gives the dependence of the time for establishment of sorption equilibrium on the principal factors—the accuracy of measurements, the sorbability of the substance, the grain size, the diffusion coefficient, and the grain shape.

* The condition "in a more or less narrow concentration interval" is automatically fulfilled if, in measuring the sorption isotherm, the number of experimental points is not very small.

For the given sorbent, the ratio of the times t''_ξ and t'_ξ in different regions of the sorption isotherm is expressed by the equation

$$\frac{t''_\xi}{t'_\xi} = \frac{\Gamma''_c}{\Gamma'_c} \frac{D'_c}{D''_c}. \tag{7}$$

In those cases where $D''_c \approx D'_c$, the time required for the establishment of sorption equilibrium is approximately proportional to the sorption coefficient

Γ_c. In this connection it is of interest to note Herbst' s observation (^{9}) that equilibrium is established more slowly in the case of more active carbons. It should be borne in mind, however, that according to equation (6), t_ξ depends on a number of other factors.

Equation (1), as well as all subsequent consequences derived from it, is valid only in the case where the amount of gas being adsorbed is small in comparison with its content in the volume of the apparatus, i.e., when the boundary condition $c(0,t) = c_0$ is fulfilled. If, however, during sorption the pressure in the apparatus changes and $c(0,t) \neq \text{const}$, as, for example, in the volumetric method for measuring sorption isotherms, then the solution of differential equation (1) differs from (2). We shall not give the solution of the equation and the subsequent transformations for this case, which are entirely analogous to those set out above, and shall confine ourselves to the final equation, which has the form

$$t_\xi = k_p k_\phi k_\xi \frac{\Gamma_c R^2}{D_c}, \tag{8}$$

where k_p is a coefficient depending on the ratio of the magnitude of sorption to the gas content in the apparatus.

Equation (8) differs from (6) only by the presence of the coefficient k_p. For an infinitely large system volume, $k_p = 1$, and equation (8) reduces to (6). As the volume of the system decreases or the sorbent charge increases, k_p decreases and sorption equilibrium is established more rapidly. But the use of small volumes and large charges is fraught with the danger of distortion of the measurement results in the hysteresis region, since in the surface layers of the grains, after sorption at high pressure, desorption begins when the pressure is reduced. As a result, the measured value of sorption will be composed of the sorption values in the surface layers of the grains, belonging to the desorption branch, and of the sorption values in the central parts of the grains, belonging to the sorption branch. This undesirable effect increases with increasing hysteresis loop, sorbent grain size, and the difference between the equilibrium and initial concentration when gas is admitted into the system.

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