METHOD FOR THE DISTRIBUTION OF SPECIFIC SURFACE AREA FROM GAS ADSORPTION IN THE MONOMOLECULAR REGION

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Abstract

Full Text

PHYSICAL CHEMISTRY

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METHOD FOR THE DISTRIBUTION OF SPECIFIC SURFACE AREA FROM GAS ADSORPTION IN THE MONOMOLECULAR REGION

(Presented by Academician M. M. Dubinin on 4 VI 1957)

There exist several methods for determining the specific surface area of adsorbents. The most widely used are methods based on gas adsorption. These include the methods of Brunauer, Emmett, and Teller (B.E.T.), Harkins and Jura (H.J.), and Gregg. The latter method is used rarely; recently it was shown ([1]) that it is not independent, but is connected with the B.E.T. equation. The B.E.T. and H.J. methods are based on the measurement of polymolecular adsorption. Therefore they give unreliable surface-area values for finely porous adsorbents, in particular for many activated carbons.

A new method, independent of existing ones, can be based on measurements in the region of monomolecular adsorption. We measured the adsorption of nitrogen at 77.4° K and p/p_s from $1 \cdot 10^{-8}$ to 0.5 on samples of silica gel and aluminum oxide. The measurements were carried out by the volumetric method. At pressures below $1 \cdot 10^{-3}$ mm Hg, equilibrium was reached after 15-25 hr. In determining the pressure, a correction was introduced for the thermomolecular effect ([2]). The adsorption isotherms are shown in Fig. 1.

Fig. 1. Nitrogen adsorption isotherms at 77.4° K and pressures from $1 \cdot 10^{-5}$ to $4 \cdot 10^{2}$ mm Hg. 1 —silica gel, 2 —aluminum oxide.

At small values of the degree of surface coverage Θ, the inhomogeneity of the surface has a great influence on the form of the isotherm. The most active sites are usually covered at low values of p/p_s. At Θ of the order of several tenths, the uncovered portions of the surface that remain are relatively homogeneous, which is characterized by an approximately constant heat of adsorption [see, for example, ([3])]. It may be assumed that measurements in this part of the monomolecular adsorption region ($\Theta > 0.2$–0.3) are suitable for determining

the surface area.

In the indicated region of Θ, the data we obtained are best described by the equation of M. M. Dubinin and L. V. Radushkevich ([4]):

$$a = \frac{w_0}{v} \exp\left[-B\frac{T^2}{\beta^2}\left(\lg\frac{p^0}{p}\right)^2\right], \tag{1}$$

where w_0 and B are constants characteristic of the adsorbent, v is the specific volume of the liquid whose vapors are adsorbed, and β is the affinity coefficient of the characteristic curves.

The equation may also be written in the following form:

$$\lg a = C - D\left(\lg\frac{p_0}{p}\right)^2 = C - D\left(\lg\frac{p}{p_s}\right)^2, \tag{2}$$

where $C = \lg(w_0/v)$ and $D = 0.43BT^2/\beta^2$. M. M. Dubinin, E. D. Zaverina, and L. V. Radushkevich established ([5,6]) that, in the case of benzene adsorption on active carbons, the linear dependence of $\lg a$ on $\left(\lg\frac{p}{p_s}\right)^2$ is observed for p/p_s from 10^{-5}–10^{-4} to 0.01–0.5.

Study of the data shown in Fig. 1, as well as of other published experimental data on adsorption at small Θ, led us to the conclusion that in a certain region all adsorbents obey equation (2), and that the deviation of points from the straight line at high values of p/p_s is the greater, the more macroporous the adsorbent is, i.e., the larger n is (the average number

Table 1

Specific surface area of adsorbents, determined by various methods

No.	Sample	S, m^2/g by B.E.T.	S, m^2/g by G.O.	S, m^2/g by monomolecular adsorption	D	Source
1	Coconut charcoal	1550	–	1410	0.0172	(7)
2	Silica gel	674	–	644	0.0247	author
3	Silica gel K	440	430	422	0.0401	(8)

No.	Sample	S, m^2/g by B.E.T.	S, m^2/g by G.O.	S, m^2/g by monomolecular adsorption	D	Source
4	Aluminosilicate	240	240	249	0.0463	(9)
5	Aluminum oxide	155	158	146	0.0281	author
6	Graphon carbon black	80.4	88.7	83.1	0.0160	(10)
7	Bone charcoal	28.9	26.4	28.3	0.0297	(7)
8	Cerous barium	9.7	9.65	9.6	0.0169	(11)

of layers that can be adsorbed on the pore walls). In the case of finely porous active carbons with $n \simeq 1$, the value w_0/v is equal to the volume of gas adsorbed in the monomolecular layer, a_m. In this case the experimental points, in the coordinates of equation (2), fall on a straight line intersecting the ordinate axis at the point K with ordinate $C = \lg a_m$.

On the basis of the foregoing, the assumption may be made that, for any adsorbent, extrapolation of the rectilinear portion of the isotherm in the indicated coordinates to the ordinate axis ($p/p_s = 1$) leads to the value a_m. This corresponds to the assumption that equation (2) describes adsorption of the first layer of molecules, while deviations at high p/p_s are caused by adsorption in the second and subsequent layers.

The assumption made was fully confirmed by our experimental data and by the data of other researchers on nitrogen adsorption at low pressures. Figure 2 shows nitrogen adsorption isotherms at 77-78°K on eight different adsorbents having surface areas from 10 to 1500 m^2/g. All the isotherms have a rectilinear portion in the coordinates of equation (2) at values of p/p_s from 10^{-4}–10^{-3} to 0.01–0.02, i.e., at Θ from 0.3–0.5 to 0.75–0.9. Consequently, it may be considered that appreciable filling of the seco-

of the second and subsequent layers begins when the first layer is filled to 75-90%.

A comparison of the values of the specific surface obtained by different methods is given in Table 1. The investigators who made measurements for coconut charcoal (⁀7) determined its surface from the Langmuir equation, since the B.E.T. method proved inapplicable. The value they obtained is 1744 m^2/g.

Fig. 2. Nitrogen adsorption isotherms at 77-78° K in the coordinates of the equation of M. M. Dubinin and L. V. Radushkevich. The numbers on the curves correspond to the numbers of the samples in Table 1: a—samples 1-4, b —samples 5-8

Figure 2: Fig. 2. Nitrogen adsorption isotherms at 77-78° K in the coordinates of the equation of M. M. Dubinin and L. V. Radushkevich. The numbers on the curves correspond to the numbers of the samples in Table 1: a—samples 1-4, b—samples 5-8

More correct results are given by the method (^12), based on the use of the complete B.E.T. equation and associated with rather complicated calculations. Determination by this method gave the values $n = 1.20$, $C = 187$, and $a_m = 356$ ncm^3/g, i.e. $S = 1550$ m^2/g. In the remaining cases the values of S were determined in the usual way and taken from the corresponding works without change.

Fig. 2. Nitrogen adsorption isotherms at 77-78° K in the coordinates of the equation of M. M. Dubinin and L. V. Radushkevich. The numbers on the curves correspond to the numbers of the samples in Table 1: *a*—samples 1-4, *b*—samples 5-8.

As is seen from Table 1, the discrepancies between the values obtained by the B.E.T. method and by the proposed method amount on the average to ±4%, reaching 9% for coconut charcoal, which has very fine pores. An advantage of the proposed method is the possibility of reliably determining the surface of any adsorbents, including finely porous active carbons. In addition, the method, based on measuring adsorption at low pressures, is convenient for determining small surface areas of nonporous substances. To determine the surface it is sufficient to measure adsorption at 2-3 points at $p/p_s = 10^{-4}$—10^{-2} ($p = 0.1$—10 mm Hg for nitrogen at 77.4° K).

Equation (2) assumes the following form:

$$\lg \frac{a}{a_m} = -D \left(\lg \frac{p}{p_s} \right)^2 . \tag{3}$$

The representation of isotherms for various adsorbents in absolute coordinates reduces to an equidistant displacement of the isotherms until the points K coincide with the point corresponding to the volume of a monomolecular layer adsorbed by a unit surface area (10.2 μmol/m^2 for nitrogen at 77.4° K).

As follows from Table 1 (the values of D) and from Fig. 2, the absolute isotherms of nitrogen adsorption on different adsorbents in the monomolecular region differ appreciably from one another, which indicates[13] the disturbing influence of pore narrowing. The coefficient D, determined approximately from the isotherms of nitrogen adsorption on powdered quartz and coarse-porous silica gel[13], is equal

to 0.04. This agrees well with the value for coarse-porous adsorbents 3 and 4 in Table 1. Consequently, the absolute isotherm of nitrogen adsorption at 77.4°K on coarse-porous adsorbents is characterized in the region under consideration by a value of D equal to 0.040-0.045.

Thus, the use of the equation of M. M. Dubinin and L. V. Radushkevich, which describes well the monomolecular adsorption of nitrogen on different adsorbents at $\theta = 0.4$-0.8, leads to a new method for determining the specific surface area of adsorbents.

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Note: Figure translations are in progress. See original paper for figures.