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Abstract

Full Text

Physical Chemistry

M. G. Kaganer

The Isotherm of Nitrogen Adsorption at Low Pressures

(Presented by Academician M. M. Dubinin, May 13, 1958)

Adsorption of gases at low pressures had, until recently, attracted almost no attention from researchers. In connection with the development of the thermodynamics of adsorption, experimental data in this region have acquired important significance, in particular for calculating the surface pressure and entropy of gas molecules adsorbed on a solid surface. Such data are also needed for studying heterogeneous surfaces. Measurements of gas adsorption at low pressures also have practical significance, in particular in vacuum technology. Thus, for example, in metal Dewar vessels for liquefied gases, adsorbents are used to absorb residual gases at pressures of 10^{-5}–10^{-6} mm Hg.

Fig. 1. Nitrogen adsorption isotherms at temperatures of 77.6 and 90.1° K and pressures from $1 \cdot 10^{-5}$ to $5 \cdot 10^{2}$ mm Hg. The numbers on the curves correspond to the sample numbers in Table 1.

Recently a number of works have appeared on adsorption at low pressures, limited mainly to the range of relative pressures $p/p_s > 10^{-6}$. The aim of the present work is to establish regularities in adsorption in the region of low pressures down to the range of applicability of Henry’ s law. For this purpose, nitrogen adsorption isotherms were measured at 77.6 and 90.1° K and at pressures down to $p/p_s = 1 \cdot 10^{-8}$ on several adsorbents. The measurements were carried out by the volumetric method*. At pressures below $1 \cdot 10^{-3}$ mm Hg, equilibrium was reached after 15-25 hours. In determining the pressure, a correction was introduced for the thermomolecular effect (^{1}). The results of the experiments are presented in Fig. 1.

The characteristics of the adsorbents studied are given in Table 1. Measurements for granular silica gel KSM and alumina A-2 had been carried out earlier (2). Table 1 also gives data for a nonporous adsorbent—barium sulfate (3). The specific surface area of the adsorbents was determined by the method proposed by the author (2).

The main difficulty in establishing general dependences at small degrees of surface coverage lies in the strong influence of surface heterogeneity on the adsorption properties in this region. Adsorption here occurs mainly on the most active areas of the surface, in particular in ultrafine pores. As is known, as $p \to 0$ adsorp-

* A. I. Danilina took part in carrying out the experiments.

Table 1

Characteristics of the adsorbents

No.	Sample name	T, °K	S, m^2/g	α	β	D
1	Coconut charcoal	77.6	1561	6.38	7.96	0.0215
1*	» »	90.1	1604	6.22	10.6	0.0335
2	Silica gel KSM, pieces	77.6	629	5.42	4.84	0.0247
3*	Silica gel KSM, gran.	90.1	426	5.84	20.7	0.0448
4*	Silica gel S-U	90.1	393	5.39	5.95	0.0290
5	Silica aerogel	77.6	338	4.96	13.2	0.0414
6*	Silica gel, coarse-porous	90.1	333	5.32	39.5	0.0564
7	Alumogel A-2	77.6	143	5.67	6.69	0.0281
8	Activated alumina	77.6	114	5.70	7.15	0.0275
8*	» »	90.1	113	5.1	11.5	0.0357

Fig. 2. Nitrogen adsorption isotherms in the coordinates of the Williams-Henry equation. The numbers on the curves correspond to the sample numbers in Table 1

Figure 2: Fig. 2. Nitrogen adsorption isotherms in the coordinates of the Williams-Henry equation. The numbers on the curves correspond to the sample numbers in Table 1

No.	Sample name	T, °K	S, m^2/g	α	β	D
9	Barium sulfate	77.4	9.4	5.98	3.20	0.0169

tion should obey Henry' s law. In most experimental studies this region was not reached. In some works a proportionality between adsorption and pressure was found at comparatively high pressures (^{4},^{5}), which is apparently connected with the short duration of the experiments, insufficient for attaining the equilibrium state. For representing experimental data in the region of low pressures several equations have been recommended. Most investigators (^{6}–^{9}) consider the Freundlich equation the most suitable. In a number of cases the equations of M. M. Dubinin and L. V. Radushkevich (^{10}–^{12}) and of Langmuir (^{13}) give a good approximation.

Fig. 2. Nitrogen adsorption isotherms in the coordinates of the Williams-Henry equation. The numbers on the curves correspond to the sample numbers in Table 1.

As follows from the form of the isotherms in Fig. 1, our experimental data in the region of low pressures do not obey the Freundlich equation. The equation of M. M. Dubinin and L. V. Radushkevich (^{14}) in the refined form (^{2}) has the following form:

$$\lg \theta = -D \left(\lg \frac{p}{p_s} \right)^2 , \tag{1}$$

where θ is the degree of surface coverage. The experimental data follow equation (1) at relative pressures from 0.005–0.03 down to 10^{-5}–10^{-4}. In the region of lower pressures the points fall on straight lines in the coordinates $\lg \theta$–$\left(\lg \frac{p}{p_s}\right)^2$ for adsorbents Nos. 1, 5, and 6.

The investigation showed that the initial portion of the isotherm for all the adsorbents studied can, with sufficient approximation, be repres-

is determined by a straight line in the coordinates $\lg \dfrac{a}{p}$–a of the Williams–Henry equation:

Fig. 3. Nitrogen adsorption isotherms on silica gel C-U at 90.1° K. 1 –equation (1), 2 –equation (3)

Figure 3: Fig. 3. Nitrogen adsorption isotherms on silica gel C-U at 90.1° K. 1 –equation (1), 2 –equation (3)

$$\lg \frac{a}{p} = A - Ba, \tag{2}$$

where a is the adsorbed amount of gas, p is the corresponding pressure, and A and B are constants. In Fig. 2 the initial portions of the isotherms we obtained are plotted in these coordinates. The points fall on straight lines at pressures below 1-$2 \cdot 10^{-3}$ mm Hg. Equation (2) can also be represented in the following form:

$$\lg \frac{\theta}{p/p_s} = \alpha - \beta\theta, \tag{3}$$

where α and β are dimensionless constants.

Fig. 3. Nitrogen adsorption isotherms on silica gel C-U at 90.1° K. 1 –equation (1), 2 –equation (3)

Equation (3) can serve to represent the adsorption isotherm for θ from 0 to 0.1-0.3, whereas equation (1) covers the region of θ from 0.1-0.5 to 0.75-0.9. Thus, the two equations cover almost the entire monomolecular adsorption region. Fig. 3 gives, as an example, the adsorption isotherm for silica gel C-U. As can be seen from the figure, the transition from equation (1) to (3) occurs here at a value of θ of about 0.2. An analogous picture is observed for the other adsorbents studied as well. The exceptions are silica gels Nos. 3 and 6, in which the transition covers a fairly broad region, $\theta = 0.03$-0.3, and coconut charcoal at 90.1° K, with a transition region $\theta = 0.1$-0.6. It should be noted here that in the last three cases the experimental points in the transition region lie on straight lines in the coordinates $\lg\theta$–$\left(\lg \frac{p}{p_s}\right)^2$ with new values of D.

In some cases, for example in calculating the entropy of adsorbed molecules, it is important to extrapolate the experimental data to $p = 0$. The results of this work show that a reliable method of extrapolation is the construction of the adsorption isotherm in the coordinates $\lg \frac{a}{p}$–a. As $p \to 0$, the quantity a/p tends to a definite limit, which can easily be found from the graph.

The linear Henry region appears on the isotherms at very low pressures. Practically (with an accuracy of about 1%) a linear dependence exists at $p/p_s \leq 10^{-7}$-10^{-8}, which corresponds to a degree of coverage $\theta < 0.01$.

Fig. 4. Dependence between the constants of equations (1) and (3)

Figure 4: Fig. 4. Dependence between the constants of equations (1) and (3)

As can be seen from Table 1, the coefficients α and β of equation (3), as well as D in equation (1), differ from one another for different adsorbents. Consequently, the absolute (per 1 m^2 of surface) isotherms of nitrogen adsorption by different adsorbents, including coarsely porous ones, do not coincide with one another in the monomolecular region. According to the results of measurements, as the average pore sizes decrease the coefficient α, as a rule, increases, whereas β and D decrease. An increase in temperature leads to a decrease in a and an increase in β; the coefficient D increases in this case (according to theory it is proportional to the square of the absolute temperature). The investigation made it possible to establish that the coefficients α, β, and D are related to one another by a definite functional dependence. Fig. 4 gives the values of $\lg\beta/\alpha$ as a function of D. It may be considered that the straight line obtained expresses a general law for the adsorption of nitrogen by various adsorbents at temperatures below the critical temperature. The dependence found can be represented by the equation

$$\frac{\lg\beta}{\alpha} = 26.2\,D \tag{4}$$

The data of Table 1 lead to a conclusion that is paradoxical at first glance: the more macroporous the adsorbent, the larger the coefficient β, which characterizes the deviation of the adsorption isotherm at low pressures from Henry’ s law. The reason for this phenomenon is as follows. Adsorbents prepared by ordinary methods, including such macroporous ones as silica aerogel (average pore size about 200 Å), contain a certain number of ultrafine pores, in which adsorption at the very lowest pressures mainly takes place. Therefore the values of α, which characterize adsorption in the indicated region, are close to one another for different adsorbents. In macroporous adsorbents the number of fine pores is comparatively small; therefore in them the value of the ratio $\dfrac{\theta}{p/p_s}$ rapidly falls, as a small fraction of the surface is filled, to values corresponding to adsorption in wide pores. As an example one may point to adsorbents Nos. 5 and 6 (Fig. 2b). A specially prepared homogeneous macroporous adsorbent, completely lacking fine pores, should have comparatively small values of α and β, while retaining a rather high value of D. In this case relation (4) apparently remains valid.

Fig. 4. Dependence between the constants of equations (1) and (3).

On the basis of the foregoing, a method may be proposed for constructing the adsorption isotherm in the monomolecular region down to $\theta = 0$ from three experimental points. Two points should be obtained in the region $\theta = 0.5$–0.75

and one at $\theta = 0.1$. In the case of nitrogen adsorption at its boiling temperature, two measurements should be made at a pressure of 0.5-5.0 mm Hg and one measurement at $p = 1\text{-}2 \cdot 10^{-3}$ mm Hg. Plotting the first two points on a graph in the coordinates $\lg a - \left(\lg \frac{p}{p_s}\right)^2$ and drawing a straight line through them, one can find a_m—the amount of gas adsorbed in the monomolecular layer—and D. With the aid of relation (4) we find the constants α and β of equation (3), substituting into it the values a/a_m and p/p_s for the third point.

The use of the established regularities eliminates the need to carry out lengthy and laborious measurements at low pressures.

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