JOURNAL OF CATALYSIS 18, 260–264 (1970)

A Variation of Adsorption Apparatus for the Rapid Determination of Solid Surfaces

GEORGI M. BLIZNAKOV, IVAN V. BAKARDJIEV, AND
EVA M. GOCHEVA

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

Received August 29, 1969

A variation of apparatus for the rapid determination of specific surface areas on the basis of an approximate estimation of point B in the BET theory has been proposed. The system of differential manometers used enables one to measure minimum surface areas of the order of 0.1 m^2/g.

INTRODUCTION

Many adsorption and other methods for the determination of the surface of solids are known. In the present paper, an apparatus for the rapid determination of surfaces using adsorption of air at the boiling point of nitrogen, a differential scheme for measuring the change in pressure due to adsorption, and an approximate method for finding point B of the BET theory, is proposed. The apparatus has two scopes for measuring surfaces, one of them possessing a sensitivity of the order of 0.05 m^2. This enables us to measure specific surface areas larger than 0.1 m^2/g, the minimum surface area measured being 0.4–0.5 m^2. With the known apparatuses (*1–4*) for the rapid determination of surfaces, the samples introduced into the apparatus must have surfaces of at least 5–10 m^2. This means that with adsorbents having small specific surface areas, very large amounts of them should be used. The same lower limit (5–10 m^2) is usually characteristic of apparatuses using nitrogen adsorption (*5–7*).

THEORETICAL

Let two volumes, V_1 and V_2, containing a definite amount of an ideal gas at pressure P_0 and temperature T, be connected with each other forming a closed space. When decreasing the temperature of the gas in one of the volumes, e.g., V_2, down to T', the pressure P_0 will decrease, too, due to the decrease in volume of the gas and the partial adsorption on the walls of the vessel. Then, for the change in pressure of volumes V_1 and V_2, one can write:

$$\Delta P_0 = \left(1 - \frac{V_1 + V_2}{V_1 + V_2(T/T')}\right) P_0 + \frac{RT}{V_1 + V_2(T/T')} n_0. \tag{1}$$

Here, n_0 denotes the gas quantity (moles) adsorbed on the surface of the vessel containing volume V_2. If a definite amount of adsorbent is placed in volume V_2, part of the gas (n mole) will be adsorbed on the adsorbent when decreasing the temperature T down to T'. In this case, the decrease in the initial pressure P_0 will be greater and will be given by the following expression:

$$\Delta P_0 = \left(1 - \frac{V_1 + V_2}{V_1 + V_2(T/T')}\right) P_0 + \frac{RT}{V_1 + V_2(T/T')} n_0 + \frac{RT}{V_1 + V_2(T/T')} n_2. \tag{2}$$

The last term in Eq. (2) expresses the correlation between the adsorbed amount, or the adsorbent surface, respectively, and the change of pressure. The first two terms characterize the background of the apparatus which can easily be eliminated by Eq. (1).

Taking into account that the monomolecular coverage of the adsorbent surface corresponds to the beginning of the linear part of the adsorption isotherm (point B), one can write:

$$\Delta P - \Delta P_0 = \frac{RT}{V_1 + V_2(T/T')} [a_m S_0 + k(P - P_m)] \quad (3)$$

Therein, a_m denotes the amount of adsorbate (moles) taking part in the formation of an unit surface of the monolayer; S_0 is the surface of the adsorbent; P_m, the equilibrium pressure during adsorption corresponding to the monolayer; K, the slope of the linear part of the adsorption isotherm. It is evident that when $P = P_m$, the value of $\Delta P - P_0$ will correspond to the monolayer. This expression can be written as follows:

$$S_0 = m(\Delta P - \Delta P_0) + b. \quad (4)$$

Here, b is a specific value for each sample (adsorbent) and depends on the pressure and temperature at which the measurement is carried out. b was found to have negligible values in comparison with those of the term $m(\Delta P - \Delta P_0)$.

A number of methods for the determination of specific surface areas based on similar approximations are known (*8–11*). The above relationships show that the determination of the surface may be reduced to measurement of the decrease of pressure due to adsorption in a system with a definite volume. In this case, it is only necessary that the equilibrium pressures be in the region of the linear part of the adsorption isotherm.

EXPERIMENTAL METHODS

Figure 1 shows the scheme of the apparatus described above. It is fitted with: an adsorption vacuum pump, P, consisting of an ampoule charged with active carbon; adsorber A with a glass piston and Dewar isolation, in which the samples are placed; a special manometer including the three-knee mercury manometer M_1 and manometer M_2 charged with silicon oil (SO). (When the apparatus is working, the space above the left knee of M_1 is evacuated, while the initial pressure of adsorption, P_0, is maintained above the middle knee, and the space above the right knee is connected with adsorber A.) The difference between the levels in the middle and the right knees of manometer M_1 gives the decrease in pressure, ΔP, due to adsorption and cooling of part of the dead volume of adsorber A. This difference may be measured 16 times as precisely by manometer M_2 which can be turned on by cocks C_4 and C_5. Cocks C_1, C_2, C_3, and C_6 ensure the evacuation of adsorber A (in the presence or absence of a sample) as well as the establishment of the initial pressure of adsorption, P_0, and its maintaining in the space above the middle knee of M_1, and finally, the connection of all the parts of the apparatus with the outer pressure.

Only the case when the more sensitive scope of the apparatus is used, i.e., when manometer M_2 is switched on, is discussed in detail. The other scope of the apparatus works in an analogous manner.

First of all, the dependence expressed by Eq. (1) was studied. With coordinates $\Delta P_0 - P_0$, this dependence is a curve passing through the beginning of the system of coordinates. Its slope decreases with increasing P_0. This course of the curve is due to the fact that n_0 is a function of P_0. Dependence (*1*) was studied with four values of volume V_2 by placing solid bodies (glass pearls) with definite volumes and negligible surfaces into adsorber A. Simultaneously, the temperature in the part of the adsorber containing volume V_2 was decreased down to that of boiling nitrogen; whereas, in the remaining part of the apparatus, room temperature was maintained. Figure 2 (curves 1, 2, 3, 4) shows that the curves representing dependence (*1*) with various values of volume V_2 may be approximated to straight lines within a range of initial pressures of 50–160 Torr. The isobar sections of these straight lines are linear functions of volume V_2 in all cases when $V_2 \ll V_1$. Hence, using the least squares method, the following expression could be written for ΔP_0:

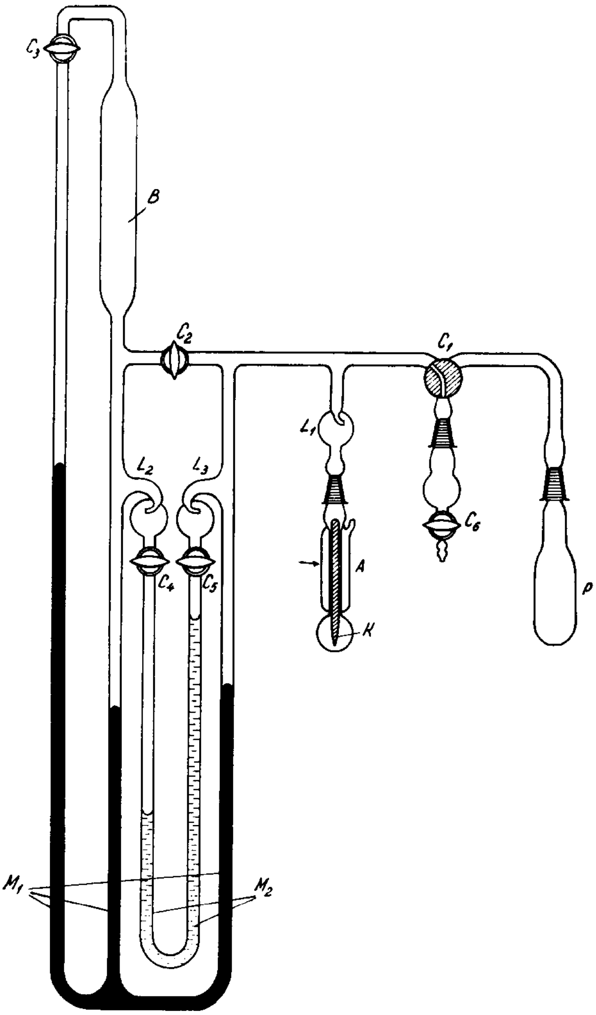

FIG 1. Scheme of the apparatus: A, adsorber with Dewar isolation; K, glass piston for decreasing the dead volume of the adsorber; P, adsorption vacuum pump; M_1, three-knee mercury manometer; M_2, manometer charged with silicon oil; L_1, L_2, L_3, traps for drops or powder; B, ballon for fixing the initial pressure; C_1, three-way cock; and C_2, C_3, C_4, C_5, and C_6, two-way cocks.

$$\Delta P_0 = \left[\left(A + B\frac{g}{\rho}\right)P_0 + C + D\frac{g}{\rho}\right]\frac{\rho_{\mathrm{Hg}}}{\rho_{\mathrm{SO}}}. \qquad (5)$$

Here, g/ρ is the change in volume (cm^3) of adsorber V_2 due to the introduction into it of a sample with weight g(g) and density ρ ($\mathrm{g/cm}^3$) at temperature $T = 20°\mathrm{C}$; at the same temperature, $\rho_{\mathrm{Hg}} = 13.55(\mathrm{g/cm}^3)$ and $\rho_{\mathrm{silicon\ oil}} = 0.81[\mathrm{g/cm}^3]$. The experimental results gave the following values for the constants of the apparatus used: $A = 9.80$ (a dimensionless quantity); $B = -5.94$ (cm^{-3}); $C = 411$(mm Hg); $D = -123$(mm Hg cm^{-3}). Expression (5) enables us to calculate function $\Delta P - P_0$ with different values of volume V_2 which is constantly changing due to the different volumes of adsorbent being placed into adsorber A.

In order to use the apparatus described for the determination of surfaces by applying dependence (4), calibration was carried out. For this purpose, adsorber A was charged with samples of quartz sand and Cr_2O_3 with known specific surface areas determined by the BET method. The values

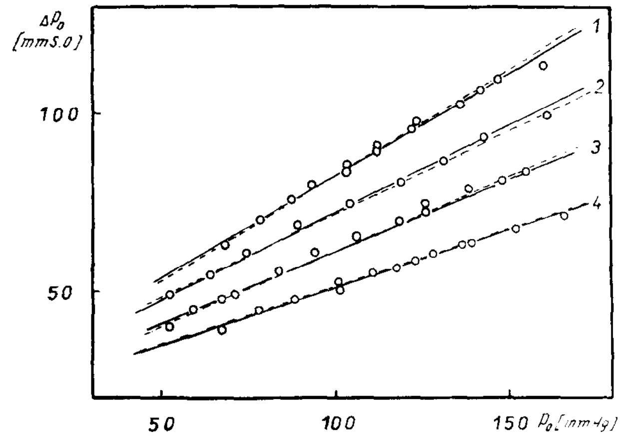

FIG. 2. Dependence of the decrease of pressure, ΔP_0, on the initial pressure, P_0, upon cooling the adsorber with liquid nitrogen: 1, when the adsorber volume is V_2 cm^3; 2, when the adsorber volume is $V_2 - 0.264$ cm^3; 3, when the adsorber volume is $V_2 - 0.504$ cm^3; and 4, when the adsorber volume is $V_2 - 0.740$ cm^3. (– – –), the most probable straight lines calculated from the data for each volume; (——), the most probable straight lines found by using isobar sections in intervals of 50–160 Torr, these sections being given by a linear correlation between ΔP_0 and the adsorber volume.

of ΔP were measured, and the corresponding values of ΔP_0 were calculated according to Eq. (5). A large number of measurements were made with each sample at various initial pressures, P_0, and hence, at various equilibrium pressures, P, too. Figures 3 and 4 show that for each sample introduced into the adsorber, $\Delta P - \Delta P_0$ is independent of the equilibrium pressure of adsorption, P, within the interval of 50–150 Torr. The straight lines 1–9 in Fig. 4 and 3 in Fig. 3 are, indeed, parallel to the axis of abscissae; the dispersion of points shows a standard deviation of 1.20 which corresponds to a surface area of 0.043 m^2. Therefore, to ensure about 10% accuracy, the measured surface should be at least 0.5 m^2. Figure 5 shows the calibration curve, i.e., the dependence of the surface, S_0, on $\Delta P - \Delta P_0$, in which m and b are quantities characteristic of this apparatus and can be calculated from the slope and the section of the ex-

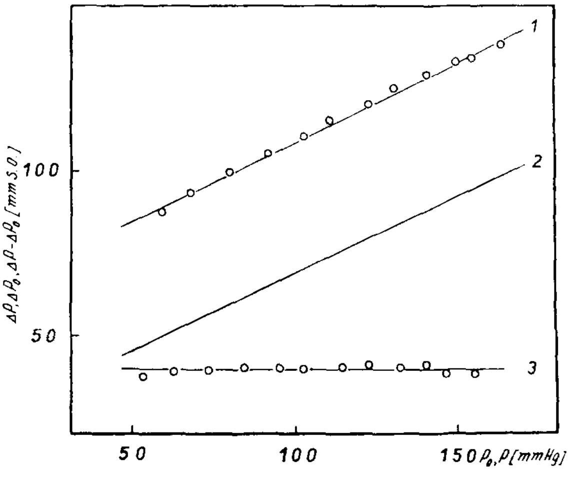

FIG. 3. 1, Dependence of ΔP on P_0 for a surface $S_0 = 1.62$ m^2 introduced into the adsorber; 2, dependence of the change in pressure, ΔP_0, on P_0, calculated on the basis of the volume of the sample introduced into the adsorber; 3, dependence of $\Delta P - \Delta P_0$ on the equilibrium pressure during adsorption $P = P_0 - \Delta P$.

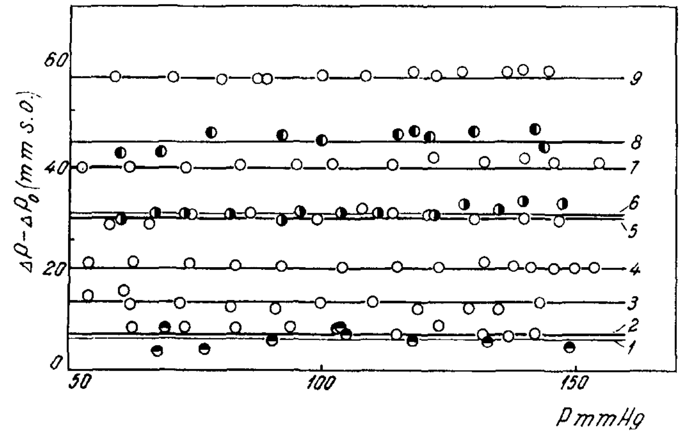

FIG. 4. Dependence of $\Delta P - \Delta P_0$ on the equilibrium pressure of adsorption for the following surfaces introduced into the adsorber: quartz sand—2, $S_0 = 0.23$ m²; 3, $S_0 = 0.47$ m²; 4, $S_0 = 0.69$ m²; 5, $S_0 = 1.17$ m²; 7, $S_0 = 1.62$ m²; 9, $S_0 = 2.39$ m²; Cr_2O_3—8, $S_0 = 1.83$ m²; 6, $S_0 = 1.16$ m²; 1, $S_0 = 0.24$ m².

perimentally obtained straight line. Calculation of the most probable straight line according to dependence (4) gave the following values for m and b: $m = 0.043$ (m² mm silicon oil⁻¹), $b = -0.086$(m²). The calibration curve in Fig. 5 shows that dependence (4) may be reliably used when measuring small surfaces with the lower limit of their dimensions being about 0.5 m².

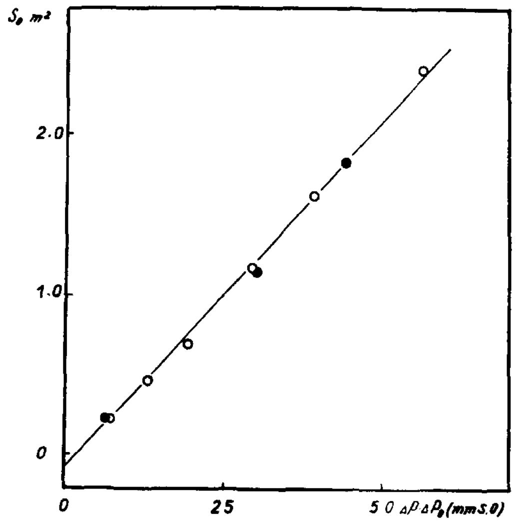

FIG. 5. Calibration curve: dependence of the surface S_0 introduced into the adsorber on $\Delta P - \Delta P_0$: ○, samples of quartz sand; ●, samples of Cr_2O_3.

CONCLUSION

On the basis of the BET theory, a simplified method for the determination of solid surfaces has been developed. An apparatus applying a differential manometer has been constructed, the latter ensuring the maximum sensitivity of 0.05 m² in determining the influence of the volume of the sample being investigated.

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