JOURNAL OF CATALYSIS 3, 32–37 (1964)

Studies on Pore Systems in Catalysts I. The Adsorption of Nitrogen; Apparatus and Calculation

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Received October 22, 1963

A new apparatus for measuring complete nitrogen adsorption–desorption isotherms is described, after the guiding considerations have been laid down. The calculation technique is then briefly explained, whereupon the experimental curve, giving the thickness of the adsorbed layer of nitrogen on alumina preparations as a function of relative pressure, has been newly determined (the *t* curve). It is pointed out which corrections are necessary for older *t* curves.

1. INTRODUCTION

Information about the width of pores in catalysts, used in heterogeneous catalysis, is often obtained from the study of capillary condensation phenomena. These phenomena are always accompanied by the simultaneously occurring phenomena of multimolecular adsorption and a correction for this adsorption is always made in the calculation of pore distribution curves.

In order to make these corrections, figures giving the correct amount of adsorbate as a function of the relative pressure are needed. Nitrogen is mostly used as the adsorbate and the phenomena are studied at liquid nitrogen temperature.

During a systematic investigation program of the pore systems of various aluminum hydroxides, oxyhydroxides, and their dehydration products, obtained at different temperatures, we derived the conclusion that neither the apparatus described in the literature, nor the methods of the above-mentioned corrections were completely suitable for our purposes. The present publication describes the experimental method we used and the methods of calculation and correction. The results obtained with various aluminum hydroxides and oxides are described in the following articles.

2. APPARATUS FOR MEASURING NITROGEN ADSORPTION ISOTHERMS

A great number of apparatuses for measuring nitrogen adsorption have been described in the literature, a comprehensive survey being given by Joy (*1*). For the choice of our apparatus for the measurements of complete adsorption–desorption isotherms we were guided by the following considerations.

(a) An important factor influencing the rate at which equilibrium is reached is the removal of the heat of adsorption or the supply of the heat of desorption.

(b) The establishment of the equilibrium must be clearly indicated.

(c) In order to be able to check for leakages, the total amount of nitrogen adsorbed must be recovered quantitatively on desorption.

(d) The changes in the temperature of the liquid nitrogen bath must be measured continuously.

(e) To avoid supervision overnight it must be possible to interrupt the measurements at certain points.

As none of the apparatus given in the litera-

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ture fulfills all of our requirements, we designed a new one, which is schematized in Fig. 1.

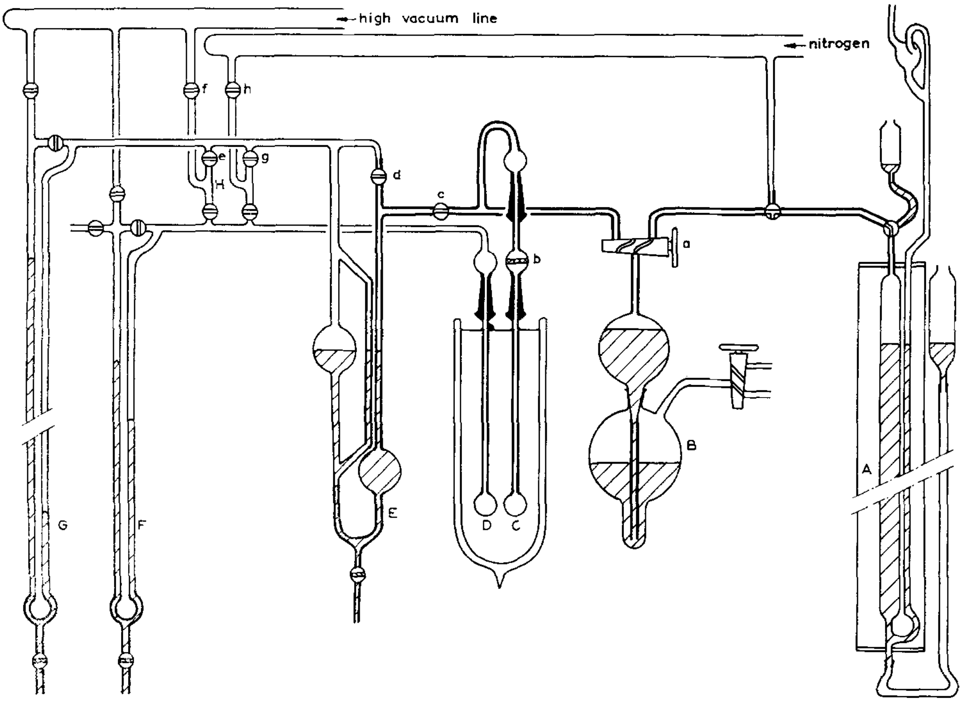

FIG. 1. Schematic drawing of apparatus for measuring nitrogen adsorption isotherms.

The gas burette A has a volume of 100 ml and is divided in tenths of a milliliter. It was calibrated by weighing with mercury; an accuracy of 0.01 ml was obtained. The mercury pump B, which is operated by means of the pressure in the lower bulb, quantitatively transports the gas at the desired rate from burette A to the adsorption tube C (and vice versa); a very accurate construction of the cock a is essential to prevent leakage. The adsorption tube C (volume of the sample bulb ca. 1 ml) is provided with a sintered glass plate b which prevents finely divided samples from being blown through the whole apparatus by a wrong manipulation. To keep the dead space as small as possible the part of C not immersed in the liquid-nitrogen bath is made from capillary tubes with a diameter of 3 mm. The capillary differential manometer E serves to keep the volume of the dead space as constant as possible; both legs should be made from the same precision capillary tube. With the aid of the pressure and vacuum locks H the pressure in the left-hand part of the manometer E is made equal to that in the adsorption tube C; the manometer G shows the pressure left of E.

Any temperature changes of the liquid-nitrogen bath are observed with the manometer F, connected with the tube D in which some purified nitrogen is condensed. High vacuum is obtained with an oil pump and a mercury-diffusion pump; the pressure is measured with a McLeod gauge. Nitrogen gas, which is used as the adsorbate, should be of high purity; traces of oxygen are removed by passing it over a deoxidizing catalyst (B. T. S.-catalyst of B. A. S. F.). Noncondensable gases such as hydrogen are removed by condensation and boiling. The very pure nitrogen obtained after distillation is used for filling the gas burette and the tube D. Using this purified nitrogen in the pressure lock between E and G is not essential; it is done for manipulative reasons.

3. MEASURING PROCEDURE

To calibrate the dead space of C, cocks

c, d, e, and f are opened, which establishes a connection between C and the high-vacuum line. When the pressure is below 10^{-4} mm mercury and the apparatus is checked for leakages, cocks d, e, and f are closed. The dewar flask is filled with liquid nitrogen and placed under C.

Gas burette A is filled in the mean time with purified nitrogen. With the aid of mercury pump B a certain volume of nitrogen is transported from A to C. As the pressure in C increases, the mercury level in the right-hand part of E is lowered. Via cocks g and h the pressure at the other side of E is increased till the levels in the two legs of E are about equal (there would be little sense in making the pressure over both legs exactly equal; the time required for manipulation would not balance the few additional calculations to be made).

If the pressure read on G is equal to p_G mm mercury and the difference between the mercury levels of E is equal to p_E mm (positive if the level is higher on the right-hand side than on the left-hand side), the pressure in C is equal to:

$$p = p_G - p_E \qquad (1)$$

We define the dead space V_d as the volume of nitrogen (in ml STP), which, under measuring conditions (room temperature 20°C, temperature of the liquid nitrogen 78°K, level of the nitrogen in the dewar flask at a fixed mark on tube D) and at an indicated reference level of the mercury in the right-hand leg of E, would give a pressure of 100 mm mercury in the empty sample tube C (as a reference level we chose the reading at which the mercury in both legs has the same level).

If the volume of nitrogen added to C from the gas burette is equal to V (ml STP), we get:

$$V = 0.001p(V_d - Kp_E) \qquad (2)$$

in which K is a constant given by the diameter of the capillary. From a sufficient number of measuring points at various values of p and p_E, the constants V_d and K can be calculated.* In the case of the isotherm measurements the dead space V_d of the empty tube C must be lowered by the sample volume. The volume V_s (in ml STP) of the gas that is displaced by the sample at a pressure of 1000 mm mercury under measuring conditions, is equal to:

$$\begin{aligned} V_s &= (1000/760) \times (273/78) \times V_{sp} \times G \\ &= 4.72 \times V_{sp} \times G \qquad (3) \end{aligned}$$

where V_{sp} represents the specific volume of the sample and G its weight.

The isotherm itself is measured in the same manner as the calibration of the dead space. As all our samples were very sensitive to heating we had to choose as a standard pretreatment degassing at room temperature until the pressure in the whole system was lower than 10^{-4} mm mercury; the time necessary to obtain this pressure varied from 1 to 6 hr. As a criterion that equilibrium was reached we took the point where the pressure in C did not alter more than 0.1 mm in 1 min. In the reversible part of the isotherm equilibrium was reached within some minutes; in the region of capillary condensation this took much more time, especially on desorption.

From the volume of nitrogen V present in C, the pressure p_G, the pressure difference p_E and the weight of the sample G the adsorbed volume V_a in ml STP per gram of material is found:

$$V_a = \frac{1}{G}\left[V - \frac{p_G - p_E}{1000} \times (V_d - V_s - Kp_E)\right] \qquad (4)$$

To obtain the isotherms, the values of V_a are plotted against the relative pressure $x = p/p_0$, in which p represents the equilibrium pressure $p_G - p_E$, and p_0 the saturation pressure. The saturation pressure is found during the measurements of the isotherm as the maximum equilibrium pressure in C. The variations in p_0 during the measurements as a result of the variations in

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* We presume that the ideal gas laws obtain under the given conditions. Though this is not admissible theoretically, it appears in practice that there exists a linear relation between V and $V_d - Kp_E$; even in the neighborhood of the saturation pressure the deviations are still negligibly small compared with the accuracies that can be obtained in this region.

temperature of the liquid nitrogen bath are given by the pressure changes in tube D, in which purified nitrogen is condensed, and which are observed with the manometer F.

4. THE CALCULATION OF THE PORE-SIZE DISTRIBUTION FROM THE DESORPTION BRANCH OF THE ISOTHERMS

The calculation method for the pore-size distribution is based on the Kelvin equation

$$\ln x = \ln p/p_0 = -2\sigma V \cos \psi / RTr_k$$

where σ is the surface tension of the liquid, 8.72 dynes/cm. The contact angle ψ between the surface of the adsorbed liquid nitrogen and the wall of the capillary may be taken to be zero, V is the molecular volume of the adsorbed and/or capillary condensed nitrogen, 34.68 cm^3/mole, T is the temperature of boiling liquid nitrogen, 78°K, and r_k is the so-called Kelvin radius, which can be calculated from the above equation, which reduces to

$$r_k = -4.05/\log x$$

Starting from the highest point of the desorption branch r_k is calculated for various relative pressures separated by small steps of x. The calculation method of the successive steps depends to some extent on the shape of the pores. Barrett, Joyner, and Halenda (*2*) and Cranston and Inkley (*3*) gave a method for cylindrically shaped pores, Steggerda (*4*) and Innes (*5*) for slit-shaped pores.

As the pores of alumina are often slit-shaped (*6*) we shall use the method given by Steggerda (*4*) with some minor modifications. Assuming slit-shaped pores the relation between the Kelvin radius and the wall separation d is given by

$$d = r_k + 2t$$

t being the thickness of the adsorbed layer.

Let us assume that at a relative pressure $x = 1$ all pores (including a part of the intergranular space) are filled with liquid nitrogen. If we divide the desorption branch into pieces corresponding to equal steps in relative pressure of $2\Delta x$, at the beginning of the ith step the relative pressure is $x_i + \Delta x$, the volume adsorbed (expressed in ml liquid nitrogen) $X_{(x_i+\Delta x)}$, the surface area of the pores (or parts of pores) not filled with liquid nitrogen $S_{(x_i+\Delta x)}$, and the thickness of the layer of nitrogen adsorbed on this surface $t_{(x_i+\Delta x)}$. If we lower the relative pressure to $x_i - \Delta x$ the pores having a Kelvin radius between $(r_k)_{(x_i+\Delta x)}$ and $(r_k)_{(x_i-\Delta x)}$ are emptied. If Δx is sufficiently small we may assign to this group of pores a mean Kelvin radius $(r_k)_{x_i}$ corresponding with the relative pressure x_i.

The thickness of the adsorbed layer at this relative pressure is t_{x_i}, so that the mean pore width d_{x_i} of this group of pores is:

$$d_{x_i} = (r_k)_{x_i} + 2t_{x_i}$$

Representing the surface area of this group of pores by ΔS_{x_i} the volume ΔV_{x_i} is:

$$\Delta V_{x_i} = \tfrac{1}{2} d_{x_i} \Delta S_{x_i} \qquad (5)$$

At the end of the ith step the pressure is $x_i - \Delta x$, the adsorbed volume of nitrogen $X_{(x_i-\Delta x)}$, the surface area of the pores which are not completely filled with liquid nitrogen $S_{(x_i-\Delta x)}$, and the thickness of the adsorbed layer $t_{(x_i-\Delta x)}$.

During the ith step the desorbed volume is given by:

$$\Delta X_i = X_{(x_i+\Delta x)} - X_{(x_i-\Delta x)} \qquad (6)$$

This desorbed volume is formed by:

a. The volume originating from the capillary evaporation from the ith group of pores at the relative pressure x_i and the decrease of the thickness of the adsorbed layer of this group of pores by lowering the relative pressure from x_i to $x_i - \Delta x$. This volume is equal to

$$\tfrac{1}{2}(d_{x_i} - 2t_{(x_i-\Delta x)}) \cdot \Delta S_{x_i}$$

b. The decrease of the thickness of the adsorbed layer in the pores, which were already emptied at the relative pressure $x_i + \Delta x$, during the lowering of the pressure to $x_i - \Delta x$, equal to

$$(t_{(x_i+\Delta x)} - t_{(x_i-\Delta x)}) \cdot S_{(x+\Delta x)}$$

Now $S_{(x_i+\Delta x)}$, obtained by summing up all contributions ΔS_x of the groups of pores having a width greater than $d_{(x_i+\Delta x)} \equiv d_{(x_{i+1}-\Delta x)}$, consequently is $S_{(x_i+\Delta x)} = \Sigma \Delta S_{x_{i-1}}$.

Equation (6) is then transformed into:

$$\Delta X_i = \tfrac{1}{2}(d_{x_i} - 2t_{(x_i-\Delta x)}) \cdot \Delta S_{x_i} + (t_{(x_i+\Delta x)} - t_{(x_i-\Delta x)}) \cdot \Sigma \Delta S_{x_{i-1}} \quad (7)$$

Combination of (7) and (5) gives after reduction:

$$\Delta V_{x_i} = \tfrac{1}{2} d_{x_i} \cdot \Delta S_{x_i} = (R_{x_i} \cdot \Delta X_i) - (R'_{x_i} \cdot \Sigma \Delta S_{x_{i-1}}) \quad (8)$$

where

$$R_{x_i} = d_{x_i}/(d_{x_i} - 2t_{(x_i-\Delta x)})$$

$$R'_{x_i} = R_{x_i} \cdot (t_{(x_i+\Delta x)} - t_{(x_i-\Delta x)})$$

Summing up all contributions ΔV_x and ΔS_x, respectively, we obtain the cumulative quantities V_{cum_x} and S_{cum_x} representing the total volume and the total surface area of the pores having a width greater than d_x.

5. THE EXPERIMENTAL t VALUES

Schüll *et al.* (7) showed that for a number of nonporous solids, the nitrogen adsorption isotherms of which gave no indications of capillary condensation, the ratio between the adsorbed volume V_a and the volume of the unimolecular layer V_m, if plotted as a function of x could be represented approximately by a single curve. With the aid of this function the thickness of the adsorbed layer as a function of x could be calculated, if for one point of the curve this thickness is known. Schüll supposed that the thickness of a unimolecular layer is equal to the diameter of the nitrogen molecule. Assuming a closest packing of spheres he calculated from the specific volume that this diameter has a value of 4.3 Å. Barrett, Joyner, and Halenda (*2*) adopted Schüll's t curve to establish the values of t for their method of calculating the pore-size distribution. In Schüll's conception, however, the successive layers of the multimolecular adsorption assembly are packed in such a way that each nitrogen molecule of a following layer is situated just on top of a nitrogen molecule of the previous layer. This does not correspond to the idea of the closest packing, which he assumed for the calculation of the diameter of the nitrogen molecule. For the calculation of the t values we have to assign the same density to the adsorbed layer as to the capillary condensed liquid, which is taken to have the density of normal liquid nitrogen. Therefore it is necessary to use in this case a statistical thickness, which we shall define as:

$$t = (X/S) \cdot 10^4\ \text{Å} = (M \cdot V_{sp}/22\,414) \cdot (V_a/S) \cdot 10^4\ \text{Å}$$

where:

t is the statistical thickness of the adsorbed layer;

X, the adsorbed volume in ml of liquid adsorbate;

S, the specific surface area in m²/g of adsorbent;

M, the molecular weight of the adsorbate;

V_{sp}, the specific volume of the adsorbate in ml/g; and

V_a, the adsorbed volume of the adsorbate in ml gas STP/g of adsorbent.

For nitrogen we obtain

$$t = 15.47(V_a/S)\ \text{Å}$$

For S in this equation we shall take the surface area S_{BET} estimated by the well-known BET method from the (V_a vs. x) curves measured by the method described above in Sec. 3. The BET method gives us the value of V_m, the volume of gas in ml STP per gram of adsorbent that should be able to cover the whole surface with a unimolecular layer ("monolayer capacity"). In order to calculate S_{BET} from V_m we need to know the surface area occupied by one nitrogen molecule in the adsorbed layer. We, again, assume the adsorbate to have a close-packed structure, like liquid nitrogen, so that 16.27 Å² may be taken for the surface area occupied by one molecule. In a previous article we have shown that this value leads to the same figures for the surface area of alumina as the completely different and independent lauric acid method (*8*). This figure leads us to

$$S_{\mathrm{BET}} = 4.37 V_m \mathrm{m}^2/\mathrm{g}$$

Introducing this into the equation for t, we obtain:

$$t = 3.54(V_a/V_m)\ \text{Å}$$

6. THE EXPERIMENTAL t CURVE FOR ALUMINAS

We calculated the quantities 15.47

TABLE 1

EXPERIMENTAL THICKNESS t OF THE MULTIMOLECULAR LAYER, ADSORBED ON ALUMINUM HYDROXIDES AND OXIDES

p/p_0	t (Å)	p/p_0	t (Å)	p/p_0	t (Å)	p/p_0	t (Å)
0.08	3.51	0.32	5.14	0.56	6.99	0.80	10.57
0.10	3.68	0.34	5.27	0.58	7.17	0.82	11.17
0.12	3.83	0.36	5.41	0.60	7.36	0.84	11.89
0.14	3.97	0.38	5.56	0.62	7.56	0.86	12.75
0.16	4.10	0.40	5.71	0.64	7.77	0.88	13.82
0.18	4.23	0.42	5.86	0.66	8.02	0.90	14.94
0.20	4.36	0.44	6.02	0.68	8.26	0.92	16.0[a]
0.22	4.49	0.46	6.18	0.70	8.57	0.94	17.5[a]
0.24	4.62	0.48	6.34	0.72	8.91	0.96	19.8[a]
0.26	4.75	0.50	6.50	0.74	9.27	0.98	22.9[a]
0.28	4.88	0.52	6.66	0.76	9.65		
0.30	5.01	0.54	6.82	0.78	10.07		

[a] Extrapolated values.

$V_a/S_{BET} = 3.54\ V_a/V_m$ of the adsorption branches of several well selected samples of aluminum hydroxides and oxides and plotted them as a function of the relative pressure x. At low x values they fall on one curve; at values higher than 0.6 we still observed a rather large divergence, showing that capillary condensation plays a role in some of them.

Comparing our curve with a t curve drawn by Barrett *et al.* (*9*) derived from data of various other substances, but corrected by us by multiplying the figures with a factor (3.54/4.3), because of the considerations of Sec. 5 above, we find that our curve lies slightly above theirs. Also Cranston and Inkley (*3*) published a t vs x curve for substances of very divergent nature; this curve is, especially at low x values, higher than the other two. Provisionally we shall use, for the work on aluminas, our own curve, the values of which are given in Table 1.

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