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Studies on Pore Systems in Catalysts

VI. The Universal *t* Curve

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The thickness t of the layer of nitrogen adsorbed on several well-defined samples (Al_2O_3, TiO_2, $BaSO_4$, ZrO_2, MgO, Ni antigorite, SiO_2, and three graphitized carbon blacks) has been measured as a function of the relative pressure and compared with the t curve given in article I of this series. It may be that this proposed curve needs some slight correction at relative pressure higher than 0.75. Up to this relative pressure it may be used, in the same way as is described in article V of this series, also for other substances than Al_2O_3.

INTRODUCTION

In Part I of this series (*1*) the adsorption of nitrogen at −196°C on various well-selected samples of aluminum hydroxides and aluminum oxides was discussed. In these samples the multimolecular layer of adsorbed nitrogen could be formed freely on all parts of the surface. Owing to this the statistical thickness t could be calculated according to the equation

$$t = 3.54(V_a/V_m)\text{Å} \qquad (1)$$

where V_a is the adsorbed volume of the adsorbate in ml gas STP/g adsorbent and V_m is the volume of gas required to cover the whole surface area of the solid substance unimolecularly, also expressed in ml STP/g adsorbent, calculated by the BET method (*2*). An appreciable influence of the nature of the surface on this thickness of the adsorbed layer was not observable.

In Part V of this series (*3*) it is shown that with the aid of this t curve the total area (S_t) and the surface area and volume of the narrow pores (8–11 Å) could be determined by plotting V_a as a function of t. Also valuable information could be obtained about the shape of the pores, the onset of capillary condensation, the filling of pores, etc.

Since this method may also yield important data for other materials than aluminum hydroxides and oxides investigations have been made in order to find out whether the t curve measured is a universal curve.

EXPERIMENTAL AND RESULTS

All adsorption measurements were carried out with the micro-BET-apparatus as described in Part I of this series (*1*).

To avoid the influence of capillary condensation during the nitrogen adsorption measurements poreless preparations have been used. The preparations and their most important data are given in Table 1.

By means of Eq. (1), the thickness of the adsorbed layer of nitrogen has been calculated as a function of the relative pressure from the adsorption branches of the nitrogen isotherms of the samples given in Table 1, except the graphitized carbon blacks. The results of this calculation are shown in Figs. 1, 2, and 3. For comparative purposes the t curve as measured on the alumina samples given in Part I of this series is given in these figures (drawn line).

DISCUSSION

From Table 1 it is clear that the value of the surface area obtained by means of a V_a/t plot (S_t) is in good agreement with that value obtained by means of the equation

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TABLE 1

SOME CHARACTERISTICS OF THE PREPARATIONS USED

Sample	S_{BET} (m^2/g solid)	S_t[a] (m^2/g solid)	S_t/S_{BET}	Description
SiO_2 (aerosil)	382	382	1.00	Prepared by flame hydrolysis of $SiCl_4$, $AlCl_3$, and $TiCl_4$; commercial products of Degussa (Germany).
Al_2O_3	96.6	94.5	0.98	
TiO_2	56.7	57.2	1.01	
ZrO_2	11.4	11.3	0.99	Commercial product heated at 800°C for 24 hr.
MgO	18.1	18.2	1.00	Prepared by decomposition of $MgCO_3 \cdot$ 3 aq. (nesquehonite) at 800°C for 24 hr. The sample was obtained from Mr. W. F. N. M. de Vleesschauwer and will be published later.
$BaSO_4$	3.40	3.47	1.02	Prepared by mixing solutions of $BaCl_2$ and H_2SO_4 (1:1) at 0°C. After drying heated at 600°C for 8 hr.
Nickel-antigorite	116	115	1.01	Prepared by mixing solutions of $NiSO_4$, Na_2CO_3, and kieselguhr at boiling temperature.
Sterling FT	12.1	13.3	1.10	Commercial carbon blacks graphitized at 2700°C.
Graphon 1	82.3	91.3	1.11	
Graphon 2	90.0	99.3	1.10	

[a] All the values of S_t given are calculated with the aid of the t curve given in Part I of this series (*1*).

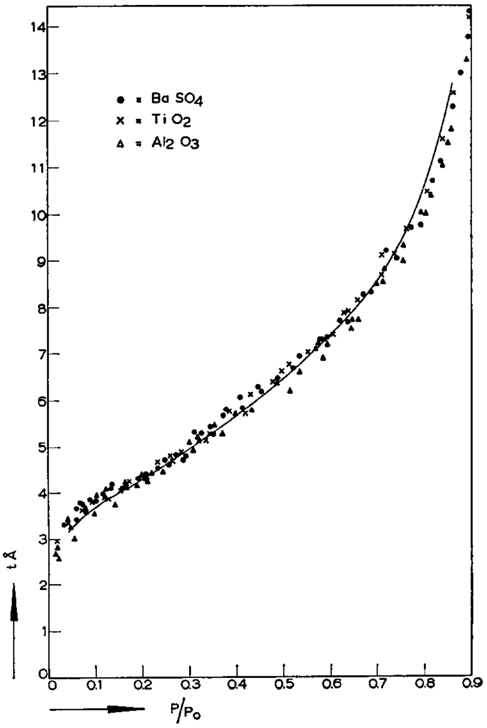

FIG. 1. Calculated t values as a function of the relative pressure for $BaSO_4$, TiO_2, and Al_2O_3.

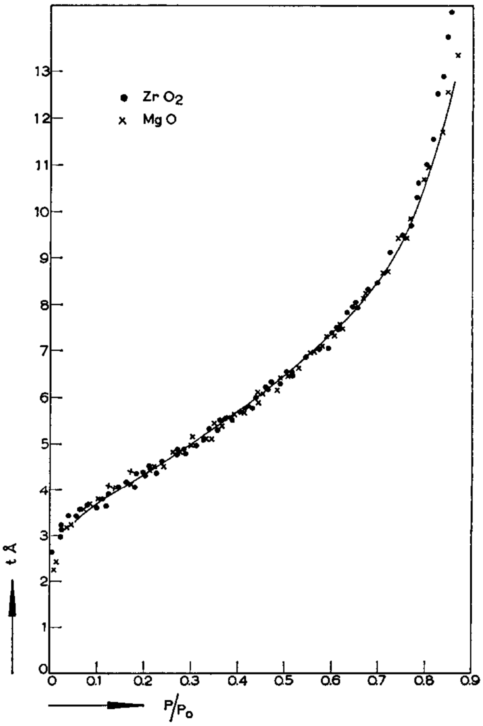

FIG. 2. Calculated t values as a function of the relative pressure for ZrO_2 and MgO.

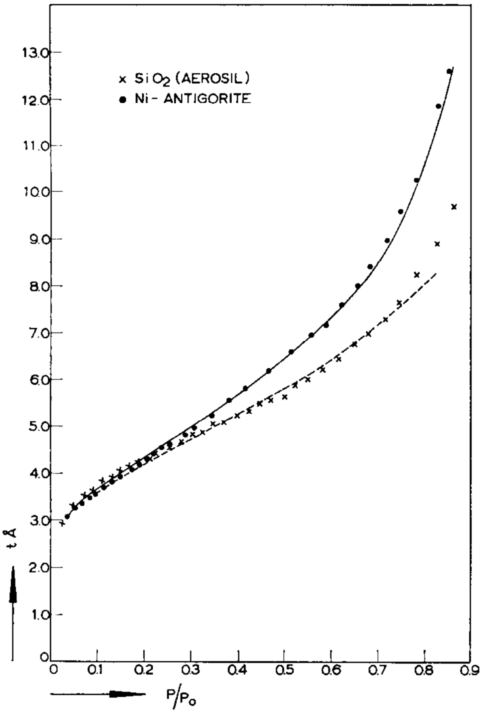

FIG. 3. Calculated t values as a function of the relative pressure for SiO_2 and nickel antigorite.

according to Brunauer, Emmett, and Teller (S_{BET}), except for the graphitized carbon blacks. This is already an indication that the t curve given in Part I of this series may be of a universal character.

Al_2O_3, TiO_2, MgO, ZrO_2, $BaSO_4$, and Nickel Antigorite

Figures 1, 2, and 3 show that the t curves measured to Al_2O_3, TiO_2, MgO, ZrO_2, $BaSO_4$, and nickel antigorite are practically identical with the curve given in Part I of this series. An appreciable influence of the nature of the surface on the thickness of the adsorbed layer is not observable, although such an influence might have been expected considering the difference in structure. The fact, however, that no difference is observed is not surprising, because many authors have, in the past, found indications of the same phenomenon (*4*); in the present work, however, we have laid stress on greater accuracy.

Al_2O_3. It seems obvious that the points of the Al_2O_3 produced by flame hydrolysis (Fig. 1) are in agreement with the t curve given in Part I of this series, also measured on alumina, but nevertheless it is very interesting, because the latter t curve was measured on alumina with slit-shaped wide pores, whereas the alumina used in the present case consists of smooth elementary spherical particles without pores. However, at relative pressures higher than 0.75 the experimental values of the alumina produced by flame hydrolysis fall under the t curve which we published in article I (*1*).

TiO_2, $BaSO_4$. It is remarkable that also the experimental values of TiO_2 and of $BaSO_4$ (Fig. 1) fall under the t curve, used hitherto; they seem, however, to coincide with those of the alumina produced by flame hydrolysis. It may be possible, therefore, that our t curve needs a correction at relative pressures higher than 0.75. We hope to come back to this question in a later article.

ZrO_2. For ZrO_2 the calculated t values are only identical with the values of alumina up till a relative pressure of about 0.75 (Fig. 2). At higher relative pressures more nitrogen is taken up than corresponding with the t curve. The latter phenomenon may easily be ascribed to capillary condensation between the elementary particles, as microscopic observations showed that the preparation used consisted of needles.

From the specific volume V_{sp} and the surface area S_{BET} the mean particle size can be calculated—assuming that the length L of the particles is large compared with the radius r of these particles—according to the equation

$$\frac{V_{sp}}{S_{BET}} = \frac{\pi r^2 L n}{2\pi r L n} = \frac{r}{2} \qquad (2)$$

in which n is the number of particles present in 1 g of material.

For the sample used a value for the radius r of 330 Å was found.

Assuming that the needles are parallelly packed and that each particle is in contact with six other particles, the radius of the cylinder inscribed between three elementary particles was calculated and a value of 50 Å was found. With the aid of the Kelvin equation the Kelvin radius r_k can be calculated at a relative pressure of 0.75. A value of 32.3 Å is found.

During adsorption the radius of cylindrical pores r_p is given by

$$r_p = \tfrac{1}{2}r_k + t. \qquad (3)$$

As was said before, with ZrO_2 capillary condensation starts at a relative pressure of 0.75. At this pressure the thickness t is 9.5 Å. With Eq. (3) a pore radius of 26 Å is found. This value can be compared with the value calculated for the cylinder inscribed between three elementary particles (50 Å). In view of the fact, that the calculated value for this radius is a mean one, it is quite understandable, that in the narrowest pores capillary condensation can start at a relative pressure of 0.75.

MgO. The experimental points of MgO (Fig. 2) at higher relative pressure seem to coincide with the t curve in its present form.

Ni antigorite. The experimental points of this substance (Fig. 3) fall slightly above the published t curve at relative pressures higher than 0.7. An onset of capillary condensation is certainly not excluded in this case (*5*).

SiO_2

In the case of SiO_2, the t values calculated for relative pressures <0.2 are identical with those of alumina. Also in this case, no appreciable influence of the nature of the surface on the thickness of the adsorbed layer is found. Other silica gels show the same pattern (*5*). For relative pressures >0.2, the thickness t calculated for SiO_2 greatly deviates from the values measured with alumina (Fig. 3). This can be explained by an influence of the geometry of the silica (*5*). The t curves for Al_2O_3, TiO_2, MgO, ZrO_2, $BaSO_4$, and nickel antigorite are derived from adsorption isotherms measured with preparations with slit-shaped pores (Al_2O_3 and nickel antigorite) or with preparations with large elementary particles (Al_2O_3, TiO_2, MgO, ZrO_2, and $BaSO_4$) for which the surface can be assumed to be flat and in or between which no capillary condensation takes place at relative pressures lower than 0.7. Two possible geometric explanations for the deviations of SiO_2 are as follows:

(a) The particles of silica gel are built up of very small elementary spherical particles (diameter 64 Å), as a result of which an apparent thickness t_s of the adsorbed layer will be found and not the actual one as given by Eq. (1).

If it is assumed that the elementary particles of the aerosil are perfect spheres with a diameter 64 Å and have a completely smooth surface, and when it is assumed that each particle is in contact with n other particles, the apparent thickness t_s can be calculated from the actual one (t) (*5*). The results of this calculation for $n = 6.6$ are given in Fig. 3 (dotted line). The agreement between this calculated t_s values and measured ones is good.

(b) Owing to the open structure of the arrangement of the surface atoms of the silica-gel elementary particles (*6*), too high a value may be calculated for the surface area. This might mean that the calculated value for t is too small, as a result of which deviations in the t curve may occur.

The Graphitized Carbon Blacks

Using the V_m value calculated with the BET equation in Eq. (1) the t values of the graphitized carbon blacks do not correspond with the universal t curve. However, plotting V_a as a function of the thickness t measured on alumina and other preparations, gives a straight line through the origin and shows that only the points corresponding to lower pressures deviate from this straight line (Fig. 4).

The value of the surface area (S_t) calculated from this V_a/t plot (*3*) is larger than the value obtained by means of the BET equation (Table 1). The ratio S_t/S_{BET} is constant for the three graphitized carbon blacks.

This difference is already indicated in the literature (*7*). The following explanation may be forwarded:

(a) The adsorption of the first layer is more or less localized, so that for this layer the molecular surface of nitrogen (16.27 Å^2) cannot be used. In this case the surface occupied by one nitrogen molecule will be determined by the cell of the graphite.

This possibility is given by Pierce and Ewing (*7*) and they assume that one nitro-

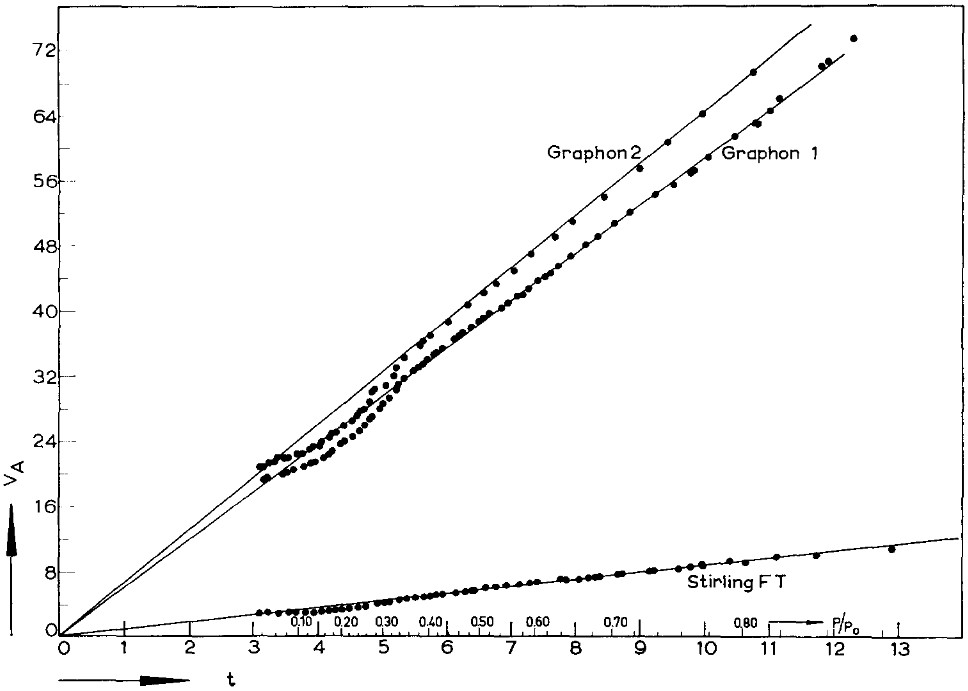

FIG. 4. V_a-t plot of Graphon 1, Graphon 2, and Sterling FT.

gen molecule covers three to four graphite cells. When following layers are adsorbed the first layer is assumed to return to the normal packing.

(b) Another possibility is that the adsorbed nitrogen molecules lose one freedom of rotation. In that case the surface area occupied by one nitrogen molecule is not determined by the mean diameter, but by the diameter along the axis of the molecule. According to de Boer (*8*) this means that the surface area occupied by a nitrogen molecule, rotating in a flat lying position, is a factor $(3.3/3.15)^2 = 1.10$ greater. The ratio S_t/S_{BET} given in Table 1 is in good agreement with this factor. Also in this case it is assumed that when the second layer is formed the molecules in the first layer regain their freedom of rotation.

(c) As already mentioned by de Boer (*8*) a stepwise isotherm should be expected on a very smooth homogeneous surface (like graphite). In this case it cannot be expected that the BET equation will give the real surface area. Due to the step(s) a too low value of V_a is just found in the regions used for the BET method.

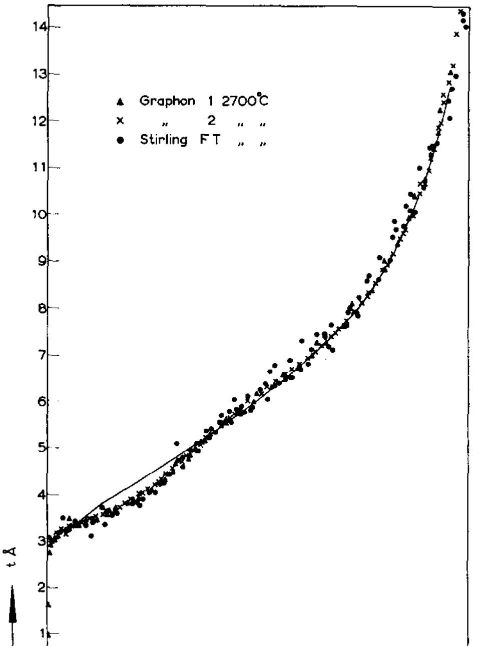

FIG. 5. Calculated t values as a function of the relative pressure for graphitized carbon blacks.

In all three cases one may conclude that the surface area S_t obtained from the V_a/t plot using the t values of alumina is a better one than the surface area obtained with the BET equation.

When using the value S_t for the calculation of the t values the obtained t curve is exactly the same as the universal t curve above relative pressures of about 0.35 (Fig. 5).

GENERAL CONCLUSION

It may be that the t curve published in article *I* of this series (*1*) needs some slight correction at relative pressures higher than 0.75. Up to this relative pressure it may be used, in the same way as is described in Article V of this series (*3*), also for other substances than Al_2O_3.

REFERENCES

1. LIPPENS, B. C., LINSEN, B. G., AND DE BOER, J. H., *J. Catalysis* **3**, 32 (1964).

2. BRUNAUER, S., EMMETT, P. H., AND TELLER, E., *J. Am. Chem. Soc.* **60**, 309 (1938).

3. LIPPENS, B. C., AND DE BOER, J. H., *J. Catalysis,* **4**, 319 (1965).

4. BRUNAUER, S., "The Adsorption of Gases and Vapors," Chap. X. Oxford Univ. Press, London, 1945.

5. LINSEN, B. G., thesis, Technological Univ. of Delft, 1964.

6. OKKERSE, C., thesis, Technological Univ. of Delft, 1961.

7. PIERCE, C., AND EWING, B., *J. Am. Chem. Soc.* **84**, 4070 (1962); PIERCE, C., AND EWING, B., *J. Phys. Chem.* **68**, 2562 (1964).

8. DE BOER, J. H., "The Dynamical Character of Adsorption." Oxford Univ. Press, London, 1953.