JOURNAL OF CATALYSIS 9, 15–27 (1967)

Studies on Pore Systems in Catalysts

X. Calculations of Pore Distributions from the Adsorption Branch of Nitrogen Sorption Isotherms in the Case of Open Cylindrical Pores

B. Applications

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Received May 10, 1937

An empirical relation is given for the universal t curve of multimolecular nitrogen adsorption, relating the thermodynamic potential of the adsorbed layer at 78°K to its thickness. With the aid of this relation, the equations for the thickness of the adsorbed layer in a cylindrical pore and the pressure at which spontaneous capillary condensation takes place, dependent on pore radius, as given in the preceding part, A, of this series, have been solved numerically. A general equation is derived for the calculation of pore distributions in the case of cylindrical pores, making use of the given concepts. Examples of application to the pore distribution analysis of nitrogen sorption isotherms already published are given. For comparison, the results of a pore distribution calculation along the adsorption branch of the same isotherms, but making use of the Cohan equation for capillary condensation, are given. The results of the former method compare favorably with those of the latter.

1. INTRODUCTION

In the preceding part, A, of this series (Article IX, preceding paper in this issue), it was shown, on grounds of simple thermodynamic reasoning, that the thickness of the adsorbed layer in a cylindrical pore is expected to be different from that on a flat surface at the same pressure. With increasing pressure the adsorbed film, in an open cylindrical pore, becomes unstable at a certain pressure, leading to a spontaneous filling of the pore by capillary condensation. After filling hysteresis is found during desorption by the presence of a different form of meniscus, capillary evaporation during desorption taking place at a lower relative pressure. Such a pore model may be adequate in describing isotherms showing an A-type hysteresis loop. Evidently, the formulas derived in the preceding part of this article may be applied to pore distributions along the adsorption branch of the isotherm (and also to the desorption part with the aid of the modified Kelvin equation) if a mathematical expression is known for the t curve of multimolecular nitrogen adsorption [Article VI of this series (*1*)] in terms of $RT \ln (p_0/p)$ as a function of t. Such a mathematical expression will be given in the following sections. Numerical values will be given for the radii of pores spontaneously filling with capillary condensate at a given relative pressure. With the aid of these values, the pore distribution may be calculated.

2. THE t CURVE

Experimentally found values for the universal t curve of multimolecular adsorption on different inorganic oxides, on carbon blacks, and on barium sulfate have been given in Part VI of this series (*1*). For all these different preparations, the adsorption expressed as 3.54 V_a/V_m, could be represented by a single line, at least up to relative pressures of 0.75 to 0.8. At higher relative pressures, some divergence between the curves is found, probably on account of interparticle capillary condensation. The t curves for titanium dioxide, barium sulfate, and flame-hydrolyzed alumina form a common line, the position of which is somewhat lower than that of the other curves. We may expect for this group the influence of interparticle capillary condensation to be least. The common adsorption isotherm for these preparations has been chosen as the reference curve for relative pressures exceeding 0.8.

Up to a relative pressure of 0.75 to 0.8, the t curve may be expressed by an empirical relation of the Harkins-Jura type, as was shown in a previous publication (*2*)

$$\log (p/p_0) = 0.034 - 13.99/t^2 \qquad (1)$$

An isotherm of this type corresponds to a finite number of adsorbed layers at saturation pressure. In the case of nitrogen, Eq. (1), on extrapolation, would predict a thickness of 20.3 Å for the adsorbed layer at saturation. The t values published in Part VI of this series (*1*) rather suggest an asymptotic approach of the isotherm toward saturation, leading to an infinite thickness and a continuous transition from adsorbed phase to bulk liquid phase. For nitrogen, there is no reason to assume that the isotherm cuts the axis $p/p_0 = 1$ at finite thickness of the adsorbed layer. In fact, it may easily be shown from the equations derived in Part IX of this series for the capillary condensation during adsorption, that in the case of a finite number of adsorbed layers at saturation, it would be impossible to fill pores larger than a certain critical radius with capillary condensate during adsorption, even very near to the saturation pressure.

Experimentally, this would lead to a cutting of the adsorption isotherm at saturation, even in the case of wide-pore adsorbents. For such adsorbents, no indications of this behavior on reaching saturation are found in practice. In accordance with the preceding discussion, it is found that at relative pressures exceeding 0.8, the t values corresponding to Eq. (1) are lower than found in practice. A better empirical representation is given by the following equation:

$$\log (p/p_0) = -16.11/t^2 + 0.1682 \exp(-0.1137\, t) \qquad (2)$$

This equation represents the experimentally found t values at least up to 0.96 relative pressures. At higher pressures, no accurate data are available for the thickness of the adsorbed layer at the present. Extrapolation of (2) leads to an infinite number of layers adsorbed at saturation. Equation (2) has been used as a representation between 0.8 to 1.0 relative pressure. At the lower range of relative pressures, (2) represents the t curve as accurately as (1), down to 0.40 relative pressure. However, below 0.8 relative pressure, that is, for thicknesses of the adsorbed layer less than 10 Å, Eq. (1), being the more simple of the two, is favored for practical uses. It may be stressed that no particular physical significance has been attributed to the different terms and constants in Eqs. (1) and (2). These equations are mere products of convenient curve-fitting procedures. As such, they have proved to be useful for our purposes. Other representations of a different mathematical form may be found, starting from well-known adsorption equations, as for example the BET equation (*2*).

From Eqs. (1) and (2), it is immediately clear that for the adsorption of nitrogen at its normal boiling point, Eq. (12) of Part IX of this series may be written as

$$\frac{\mu_c - \mu_L}{2.303RT} = \frac{-13.99}{t^2} + 0.034, \text{ for } (t \leq 10 \text{ Å}), \qquad (3a)$$

viz.,

$$\frac{\mu_c - \mu_L}{2.303RT} = \frac{-16.11}{t^2} + 0.1682 \exp(-0.1137\, t), \text{ for } t > 10 \text{ Å} \qquad (3b)$$

These relations enable the numerical evaluation of Eqs. (13) and (14) of Part IX of this series, governing the thickness of the adsorbed layer and the relative pressure of capillary condensation in cylindrical pores during adsorption, as well as the corresponding Eq. (15), the modified Kelvin equation for capillary evaporation during desorption.

3. THE EQUILIBRIUM THICKNESS OF THE ADSORBED LAYER AS A FUNCTION OF PORE RADIUS AND PRESSURE

On substitution of the relations (3a) and (3b) in Eq. (13) of the preceding part of this series, and on making use of the following data for liquid nitrogen at 78°K,

$$\gamma = 8.72 \text{ erg/cm}^2,$$
$$V_m = 34.68 \text{ cm}^3\text{/mole},$$

the following relations are obtained for the equilibrium thickness, t_e, of the adsorbed layer, as a function of pore radius

$$\log\left(\frac{p_0}{p}\right) - \frac{13.99}{t_e^2} + 0.034 = \frac{2.02^5}{(r - t_e)} \qquad (4a)$$

for t_e values less than 10 Å. For higher values of t_e the equation takes the numerical form

$$\log\left(\frac{p_0}{p}\right) - \frac{16.11}{t_e^2} + 0.1682 \exp(-0.1137\, t_e) = \frac{2.02^5}{(r - t_e)} \qquad (4b)$$

The numerical values for t_e may be evaluated as a function of r and p/p_0. Equation (4a) is a cubic equation in t_e and may be evaluated by means of standard methods of solving cubic equations (*3*), and picking out the physically possible root. Equation (4b) has to be solved by means of trial and error. Newton's iteration method (*4*) proved to be very useful, although convergence may be slow in the neighborhood of saturation. In this way a complete table may be set up. A shortened version of the table set up by us is presented in Table 1.

4. A FORMAL THICKNESS OF THE ADSORBED LAYER IN CYLINDRICAL PORES

From Table 1, and on comparing with the values for the thickness of the adsorbed layer at a flat surface, as given in Part VI of this series (*1*), it is clear that in cylindrical pores the equilibrium thickness, t_e, of the adsorbed layer is larger than the corresponding t values on a flat surface at the same pressure, even before capillary condensation takes place. The question arises whether deviation from the linear t plot, already frequently observed in the low-pressure region (below $p/p_0 = 0.4$) for sorption isotherms exhibiting an A-type hysteresis loop, has to be attributed to capillary condensation solely, or, in the first instance, to the increase in layer thickness with respect to that on a flat surface, the reference scale of the t plot.

If we define the formal layer thickness as

$$t_f = V_a/S,$$

where V_a is the volume of the adsorbed phase in the pore and S is the total surface area of the pore wall of a cylindrical pore of radius r, the formal thickness is related to the equilibrium thickness, t_e, by

$$t_f = t_e(1 - t_e/2r) \qquad (5)$$

TABLE 1
THE EQUILIBRIUM THICKNESS (Å) OF THE ADSORBED LAYER IN CYLINDRICAL PORES AS A FUNCTION OF r AND p/p_0

p/p_0	r_p (Å)									
	∞	92.8	49.5	33.8	25.8	20.7	17.2	14.2	11.7	9.30
0.9	14.3	25.1								
0.8	10.5	11.8	15.7							
0.7	8.57	9.21	10.4	12.9						
0.6	7.36	7.76	8.21	8.95	11.0					
0.5	6.50	6.70	6.98	7.36	7.94	9.50				
0.4	5.71	5.85	6.03	6.25	6.54	7.01	8.35			
0.3	5.01	5.11	5.23	5.37	5.53	5.76	6.13	7.21		
0.2	4.36	4.44	4.51	4.59	4.69	4.81	4.97	5.25	6.13	
0.1	3.68	3.72	3.76	3.81	3.85	3.91	3.99	4.09	4.28	4.97

TABLE 2
THE FORMAL THICKNESS (Å) OF THE ADSORBED LAYER IN CYLINDRICAL PORES AS A FUNCTION OF r AND p/p_0

	r (Å)									
p/p_0	∞	92.8	49.5	33.8	25.8	20.7	17.1	14.2	11.9	9.30
0.9	14.3	21.7								
0.8	10.5	11.0	13.2							
0.7	8.57	8.76	9.10	10.4						
0.6	7.36	7.43	7.53	7.76	8.65					
0.5	6.50	6.46	6.49	6.56	6.72	7.32				
0.4	5.71	5.67	5.66	5.67	5.71	5.83	6.31			
0.3	5.01	4.98	4.96	4.94	4.94	4.95	5.03	5.38		
0.2	4.36	4.33	4.29	4.28	4.26	4.25	4.25	4.28	4.53	
0.1	3.68	3.65	3.62	3.59	3.57	3.55	3.52	3.51	3.50	3.64

If the formal thicknesses for a number of pore radii are plotted against the thickness of the adsorbed layer, t, at a flat surface at the same pressure, it turns out that although the equilibrium thickness of the adsorbed layer is increased appreciably, for the lower pressure region the formal thickness often is very close to the t value at a flat surface. In Table 2, the formal thickness is given for the equilibrium thicknesses of Table 1. For not too large radii, the formal thickness only deviates appreciably from the t values at a flat surface in the neighborhood of the pressure where spontaneous capillary condensation is to be expected (see next section). Thus, upward deviations from the linear t plot at pressures below, say, 0.4 relative pressure, are an indication of capillary condensation, and of the presence of narrow pores filling at a low relative pressure. Of course, for pores of radius of the same order as the thickness of the adsorbed layer, the upward deviation upon capillary condensation is negligible and the filling of these pores only results in a downward deviation at increasing pressure on account of blocking. These pores clearly escape analysis along the lines given in this section.

5. THE PRESSURE AT WHICH CAPILLARY CONDENSATION TAKES PLACE

At a certain pressure, the whole cylindrical pore is filled instantaneously with capillary condensate, on account of the lack of stability of the cylindrical adsorbed layer at the walls of the pore. With this pressure of filling corresponds a critical layer thickness, which may be calculated from Eq. (14) of Part IX of this series, with the aid of the expressions (3a) and (3b) for the thermodynamic potential of the adsorbed layer. This critical thickness, t_{cr}, is given by

$$27.98/t_{cr}^3 = 2.02^5/(r - t_{cr})^2, \text{ for } t_{cr} \leq 10 \text{ Å} \quad (6a)$$

viz.,

$$32.22/t_{cr}^3 - 0.1682 \times 0.1137 \exp(-01137\, t_{cr}) = 2.02^5/(r - t_{cr})^2 \text{ for } t_{cr} > 10 \text{ Å} \quad (6b)$$

Equation (6a), again, is a cubic in t_{cr}, and may be solved directly (*3*). Equation (6b) has to be solved by means of trial and error methods, e.g., the well-known iteration method of Newton (*4*). From the critical value for the equilibrium thickness of the adsorbed layer corresponding to a given pore radius, the corresponding pressure may be calculated with the aid of Eqs. (4a) or (4b).

It is well to realize that in all cases the critical thickness is finite, and that capillary condensation during adsorption is to be pictured as a discontinuous process, leading to a sudden stepwise increase in the amount adsorbed by the pore, for the critical thickness, $dt/d(p/p_0)$, becomes infinite, which is an indication of the instability of the adsorbed layer at the critical pressure. An example of the behavior of t as function of

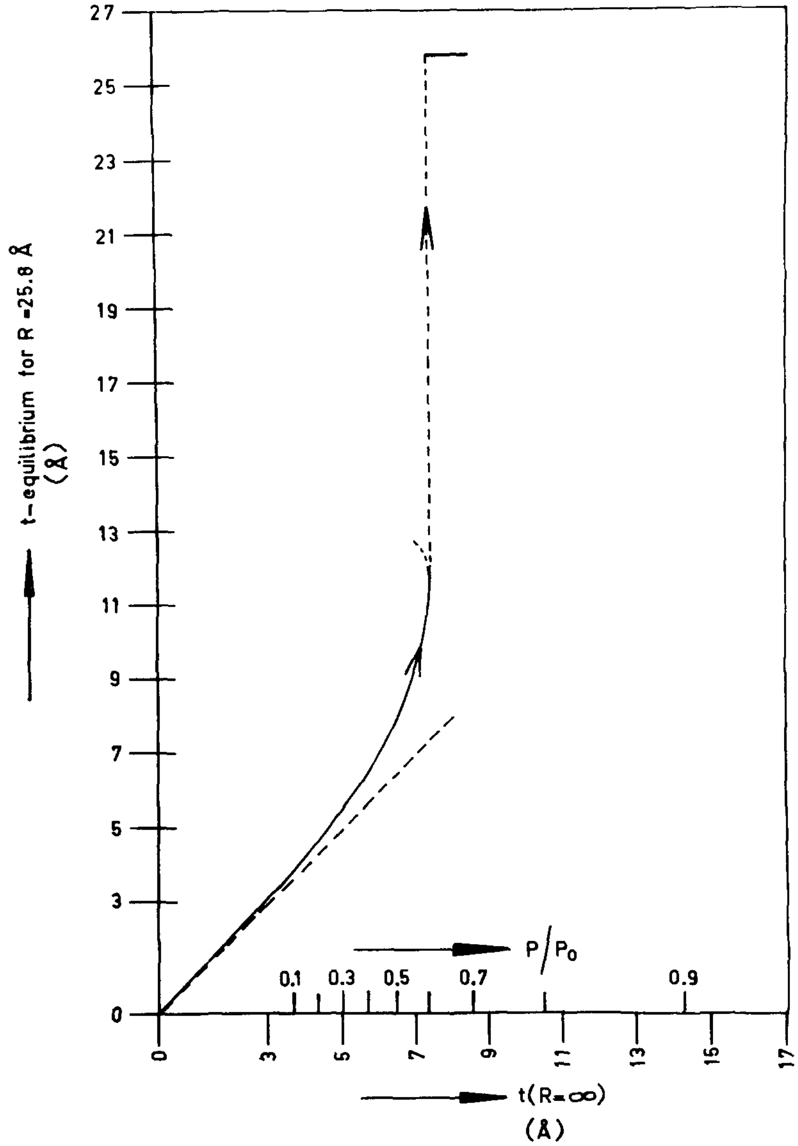

FIG. 1. The equilibrium thickness of the adsorbed nitrogen layer in a cylindrical pore of 25.8-Å radius (*R*), as a function of pressure, in comparison with the corresponding thickness of the adsorbed layer at a flat surface.

p/p_0 in the neighborhood of the critical pressure is given in Fig. 1.

In Table 3, the solutions of Eqs. (6) are given for certain relative pressures. For comparison, the radii as calculated by means of Cohan's equation at the same relative pressures, have been added to the table. It is seen that for each relative pressure the radii as calculated by means of Cohan's equation are smaller.

6. GENERAL FORMULA FOR THE CALCULATION OF PORE DISTRIBUTIONS ALONG THE ADSORPTION BRANCH OF AN ISOTHERM, MAKING USE OF THE MODEL OF CYLINDRICAL PORES

In principle, the calculation of pore distributions from the adsorption branch of an isotherm may be performed along the

TABLE 3

RADII IN (Å) OF OPEN CYLINDRICAL PORES AND THE CORRESPONDING PRESSURES AT WHICH SPONTANEOUS CAPILLARY CONDENSATION TAKES PLACE

p/p_0	Radius, according to Eq. (6)	Radius, according to Cohan's equation
0.9975	2450	1990
0.9925	905	691
0.9875	576	423
0.9825	428	306
0.9775	344	240
0.9725	289	198
0.9675	251	168
0.9625	221	146
0.9575	198	130
0.9525	180	117
0.9475	164	106
0.9425	152	97.5
0.9375	141	90.2
0.9325	131	84.0
0.9275	123	78.6
0.9225	115	73.9
0.9175	109	69.8
0.9125	103	66.1
0.9075	97.6	62.8
0.9025	92.8	59.7
0.89	82.6	53.7
0.87	70.4	46.1
0.85	61.6	40.6
0.83	54.8	36.2
0.81	49.5	32.8
0.79	45.2	30.0
0.77	41.6	27.7
0.75	38.6	25.6
0.73	36.0	23.9
0.71	33.8	22.4
0.69	31.8	21.0
0.67	30.0	19.8

lines developed by Barret, Joyner, and Halenda (*5*) for cylindrical pores. A complication, however, is formed by the fact that, according to Eqs. (4), the thickness of the adsorbed layer in cylindrical pores is not only dependent on the relative pressure, but also on the pore radius.

It is possible to divide the whole range of pore diameters into certain groups of specified mean pore diameter, and to assign to each group a corrected t curve, the proper thickness of the adsorbed layer as a function of pressure to be calculated by means of Eq. (4). As the number of data is increasing

TABLE 3 (*Continued*)

p/p_0	Radius, according to Eq. (6)	Radius, according to Cohan's equation
0.65	28.5	18.8
0.63	27.1	17.8
0.61	25.8	16.9
0.59	24.6	16.1
0.57	23.5	15.3
0.55	22.4	14.7
0.53	21.6	14.0
0.51	20.7	13.5
0.49	19.8	13.0
0.47	19.1	12.4
0.45	18.4	11.9
0.43	17.7	11.5
0.41	17.1	11.1
0.39	16.5	10.6
0.37	15.9	10.1
0.35	15.3	9.80
0.33	14.8	9.41
0.31	14.2	9.05
0.29	13.7	8.71
0.27	13.2	8.38
0.25	12.7	8.05
0.23	12.2	7.73
0.21	11.7	7.43
0.19	11.3	7.12
0.17	10.8	6.80
0.15	10.3	6.50
0.13	9.80	6.18
0.11	9.30	5.85

quickly with the number of groups of pores with specified mean diameter, the method of calculation, although in principle very simple and straightforward, is too lengthy to be performed on a desk calculator or slide rule for routine work. If, however, a high-speed electronic computing device is available, no difficulties are encountered, as the calculation method is easy to program and the data of Eq. (4) only need to be calculated once and stored for later use. If such a device is lacking, or for routine calculations, a simple approximation method is possible, neither more complicated nor more lengthy than an ordinary pore distribution calculation. The method will be given in Section 9.

The equilibrium thickness of the adsorbed layer in a pore of radius r_k, at a relative pressure x_k, will be denoted by t_{r_k,x_k}. To perform in practice the distribution calculation, the isotherm is divided into a suitable number of intervals, each interval corresponding to a certain small relative pressure range. For simplicity the calculation is performed in reverse sequence with respect to the actual measurement of the adsorption branch: the calculation is started at saturation, when all the pores are filled with capillary condensate. Thus the first interval corresponds, for example, to a pressure range of 1.000 to 0.995 relative pressure. In general, the kth interval is bounded by $x_{(k-1)}$, the upper pressure bound, and x_k, the lower pressure bound. The change in volume of the adsorbed and condensed phase present in the pores of the adsorbent, over a certain pressure interval, is made up of two contributions:

(1) Upon increasing the relative pressure from x_k to $x_{(k-1)}$, all those pores are filled with capillary condensate, whose mean radius r_k, corresponds to the mean pressure over the pressure interval. Before capillary condensation took place, the pores only carried an adsorbed layer at their walls, with mean thickness $t_{rk,xk}$.

(2) Over the same pressure interval, for all the pores belonging to groups not yet filled with capillary condensate, viz., pores belonging to groups with wider mean pore radius than the radius r_k, an increase in the thickness of the adsorbed layer takes place. This increase is dependent not only on the pressure but also on pore radius, and has to be calculated separately for each group of pores not yet filled with capillary condensate, thus for $(k - 1)$ groups.

When the total pore length of the pores belonging to the kth group of pores, filling at a relative pressure between x_k and $x_{(k-1)}$, with a corresponding mean pore radius r_k, is denoted by L_k, the total surface area by S_k, and the total pore volume of pores in this group by V_k, then it is immediately clear that the change in volume condensed in the porous system over the kth interval, $\Delta V_k{}^c$, is given by

$$\Delta V_k{}^c = \pi(r_k - t_{rk,xk})^2 L_k + \pi \sum_{i=1}^{k-1} L_i[(r_i - t_{ri,xk})^2 - (r_i - t_{ri,x(k-1)})^2] \quad (7)$$

the first part of the right side of (7) corresponding to the increase in adsorbed volume on account of pore filling, the second part corresponding to increase in thickness of the adsorbed layer in the pores not yet filled with capillary condensate.

With the aid of the obvious relations

$$S_k = 2\pi r_k L_k \quad (8)$$

and

$$V_k = \pi r_k{}^2 L_k \quad (9),$$

and after rearranging, Eq. (7) may be written as

$$S_k = \frac{2r_k}{(r_k - t_{rk,xk})^2} \left\{ \Delta V_k{}^c - \sum_{i=1}^{k-1} \frac{S_i}{2r_i} \times [(r_i - t_{ri,xk})^2 - (r_i - t_{ri,x(k-1)})^2] \right\}$$
$$= \frac{2r_k}{(r_k - t_{rk,xk})^2} \times \left[\Delta V_k{}^c - \sum_{i=1}^{k-1} S_i(t_{ri,x(k-1)} - t_{ri,xk}) + \sum_{i=1}^{k-1} \frac{S_i}{2r_i} (t^2_{ri,x(k-1)} - t^2_{ri,xk}) \right] \quad (10)$$

By means of Eq. (10), the whole pore distribution may be performed, starting with the first interval, and in each step making use of the values of S_i obtained from the preceding intervals. The volume of the pores in the kth group, V_k, may directly be computed for each pore group by means of Eq. (9). The calculation is seen to be straightforward but tedious for desk calculations, on account of the summation series at the right side of (10), and the necessity of making use of a table of $t_{ri,xk}$ values. In the usual calculation methods (*5*), t is assumed to be only a function of the pressure, but not of the pore radius. In this case, formula (10) reduces to a far more simple formula, already derived before by several authors (*6*, *7*);

$$S_k = \frac{2r_k}{(r_k - t_{xk})^2} \left[\Delta V_k{}^c - (t_{x(k-1)} - t_{xk}) \times \sum_{i=1}^{k-1} S_i + (t^2_{x(k-1)} - t^2_{xk}) \sum_{i=1}^{k-1} \frac{S_i}{2r_i} \right] \quad (11)$$

Equation (11) in fact is a refinement of the original formula of Barret, Joyner, and Halenda. It has recently been discussed in detail by de Vleesschauwer (*7*).

For a rigorous application of the concepts exposed in Part IX of this series, it is necessary to apply (10) instead of (11). The pressure intervals were chosen as 0.005 relative pressure between $x = 1.000$ and $x = 0.900$, and as 0.02 relative pressure between 0.90 and the lower limit of application of (10) (see next section). The mean radii of the pores, filling over the kth interval of the isotherm, were taken to be equal to the radii of the pores, filling at the mean relative pressure over the interval. These radii are presented in Table 3. The corresponding values for t have to be taken from an extension of Table 1, which may be calculated by means of Eq. (4). Upon summation of V_k and S_k over all the intervals of calculations, the cumulative surface area S_{cum} and the cumulative pore volume V_{cum} are obtained. Under certain restrictions (reliability of the chosen pore model, absence of micropores), S_{cum} and V_{cum} may be expected to be of the same order as S_{BET} and V_p as directly determined from the isotherm.

7. THE LOWER LIMIT OF APPLICATION OF THE PORE DISTRIBUTION CALCULATION

In principle, the pore distribution calculation has to be extended from saturation down to the pressure where a t plot of the adsorption isotherm shows a straight part going through the origin of the t plot. This is impossible in the case of micropores (radii lower than 10 to 15 Å), where the linear part of the t plot is often situated at too low a pressure. In special cases, such a plot exhibits a second straight part at higher relative pressures, corresponding to pores having an appreciably larger radius. In such a case, S_{cum} may be compared to the slope of the part of the t plot representing the surface area present in the group of wider pores. In general, care must be taken in extending the calculations to very low relative pressures, as the formulas for pore radii and equilibrium thickness are bound to be less reliable in the monolayer region, where the method of Part IX is expected to break down.

Another problem is that the point where deviation from the linear t plot first occurs, does not coincide in general with the closing point of the hysteresis loop. Thus, in the total distribution calculation, a certain number of pores is included, which show no hysteresis and for which the corresponding pore radii are chosen too small, when Table 3 is used. Correspondingly, the calculated cumulative surface area will be too high, in comparison with the BET surface area. It would in principle be better to apply the radii that may be derived from Eq. (16) of Part IX of this series to these pores, where capillary condensation turns out to be reversible with respect to evaporation. There is no sense in stopping the distribution calculation at the closing point of the hysteresis loop, when deviations from the t plot clearly indicate the presence of pores beyond the closing point of the hysteresis loop; the cumulative surface area must be expected to be low for the closing point in such a case.

In the present article, the point where the first deviation from the linear t plot occurs, has been taken as the lower limit of the pore distribution calculation. If this point is situated at a lower pressure than the closing point of the hysteresis loop, the cumulative areas may be expected to be too high and the results less accurate for those pores that are smaller than corresponding to the closing point of the hysteresis loop.

8. APPLICATIONS

The proposed method of calculation has been applied to a number of isotherms, already published before, of different samples of aluminas (*8*) and zirconias (*9*). For comparison, the pore distribution has been repeated by means of the Cohan equation (*10*) and making use of the simple formula (11), viz., a classical pore distribution making use of the Cohan equation and applied to the adsorption branch.

In Table 4, the results of the computations for different isotherms have been gathered, together with the pressure where the first deviation from the t plot takes place (the lower limit of pore distribution calculation), the closing point of the hysteresis loop, the measured BET surface area, and the pore volume, as determined from the isotherms when extrapolated to $p/p_0 = 1$.

As might be expected, the cumulative areas calculated are somewhat high in

TABLE 4

Cumulative Surface Areas and Pore Volumes, as Calculated by Means of Eq. (11), as Compared to the Application of Cohan's Equation

Sample code	Author	p/p_0 of first deviation from linear t plot	p/p_0 of closing point of hysteresis loop	S_{BET} (m²/g)	S_{cum} (m²/g)	S_{cum} Cohan (m²/g)	V_p (ml/g)	V_{cum} (ml/g)	V_{cum} Cohan (ml/g)
By 580	[a]	0.24	0.42	243	240	382	0.434	0.430	0.427
By 750	[a]	0.24	0.46	134	147	232	0.464	0.472	0.468
BoW 450	[a]	0.70	0.40	68[c]	64	110	0.479	0.479	0.479
MiBo 5	[a]	0.26	0.38	255	273	475	0.496	0.507	0.570
A120	[a]	0.26	0.40	609	673	1040	2.03	2.05	2.15
A270	[a]	0.30	0.51	556	591	890	1.74	1.77	1.86
A450	[a]	0.34	0.51	414	496	708	1.78	1.82	1.88
A750	[a]	0.63	0.63	280	295	485	2.05	2.04	2.06
ZrO_2-280	[b]	0.14	0.42	240	249	504	0.252	0.254	0.323
ZrO_2-320	[b]	0.19	0.45	180	194	390	0.201	0.190	0.262
ZrO_2-390	[b]	0.36	0.53	100	107	182	0.183	0.205	0.215
ZrO_2-450	[b]	0.64	0.64	64	67	119	0.190	0.197	0.218

[a] Isotherms as measured by Lippens (*8*, *11*).

[b] Isotherms as measured by Rijnten (*9*).

[c] Surface present in wide pores, as determined from the *t* plot.

comparison with the BET surface area in nearly all cases. The deviation is approximately 10%, except for the preparation A450 of Lippens, where the deviation amounts to even 20%. Nevertheless, a comparison with the values calculated by means of Cohan's predicted pore radii indicates that the use of the corrected pore values, with the aid of Eq. (10), leads to considerably better results, probably of the right order of magnitude. The cause of the deviations is probably the fact that the calculation is extended over groups of pores where reversible capillary condensation takes place. For this behavior, there may be two different reasons:

(a) If the pore diameters are nonuniform, the pores may become blocked for a certain thickness of the adsorbed layer. If the blocking takes place in the pore rather than at the mouth of the pore, the pore behaves as a pore closed at one end, and no hysteresis takes place. In such a case the filling of the pore is governed by the same equation as the capillary evaporation and is given by Eq. (16) of Part IX of this series, leading to a larger pore radius than used for the calculations.

(b) For very narrow pores, hysteresis inception may occur (see Section 4 of Part IX), so the behavior again is represented rather by the equations for desorption than by adsorption.

All the same, a comparison with the original equation of Cohan leads to a preference for the concepts presented here, especially when the distribution curves are plotted. Some examples are given in Figs. 2 and 3. It is seen that the quantitative application of Cohan's equation leads to absurd curves in most cases, exhibiting a sharp maximum far higher than the total BET surface area present. It thus is shown that pore distributions may be calculated from the adsorption branch of an isotherm in the case of hysteresis, despite the metastability of this branch, provided the proper corrections for adsorption are made.

9. Simple Approximation for the Calculation of Pore Distributions along the Adsorption Branch

In the preceding section it was shown that Eq. (10) is applicable for the calculation of pore distributions from the adsorption branch of a nitrogen sorption isotherm if an electronic computing device is at hand. If

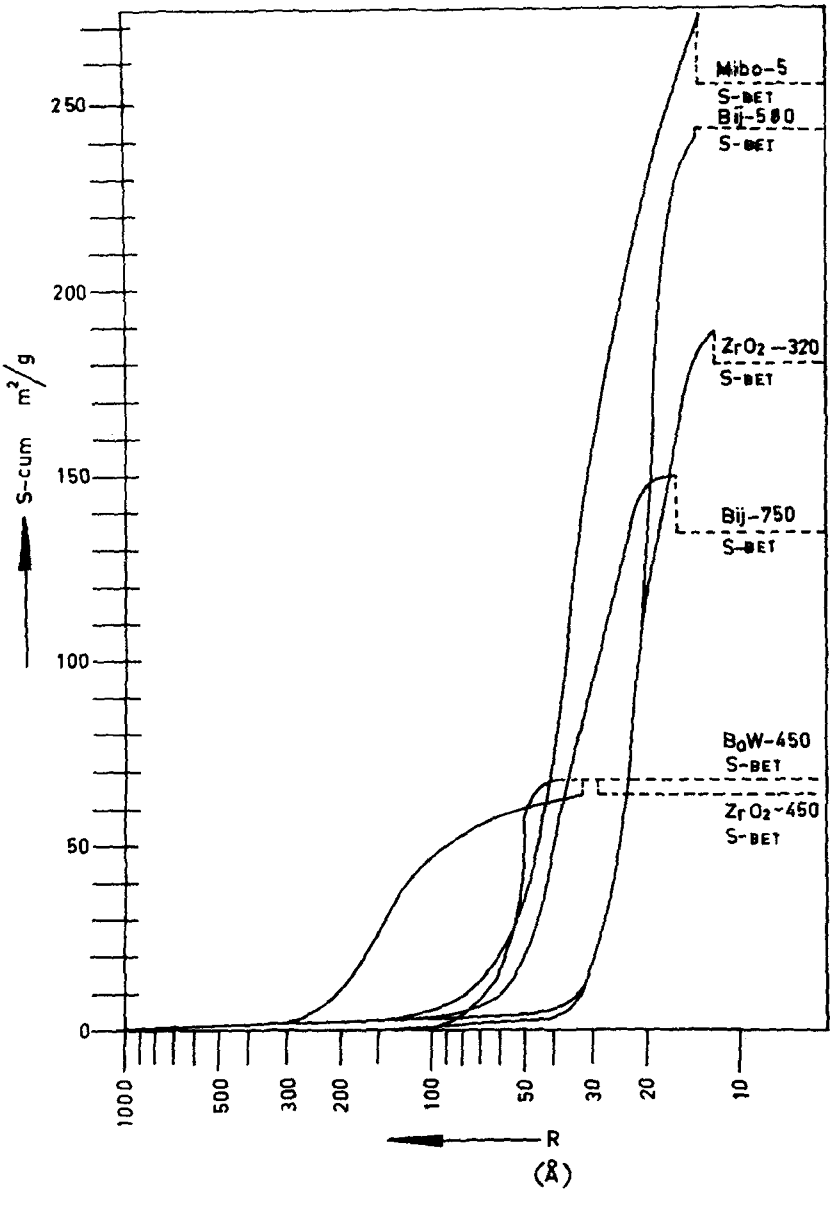

Fig. 2. Examples of pore distribution curves, as calculated with the aid of Eq. (10) and making use of the radii presented in Table 3. The examples are taken from the preparations presented in Table 4.

no such a device is available for routine work, then an approximative calculation method is possible, which, although it is not exact, gives reasonable semiquantitative results in most cases.

It was shown in Section 4 that for not too wide pores the formal thickness of the adsorbed layer is approximately equal to the thickness of the adsorbed layer on a flat surface, as given by the t curve of multimolecular adsorption. This fact may be used for the computation of pore distributions in the following way:

Returning to the analysis given in Section 6, it turned out that the difficulty in calculating the connection between the amount desorbed $\Delta V_k{}^c$ over a certain pressure interval and the area present in pores

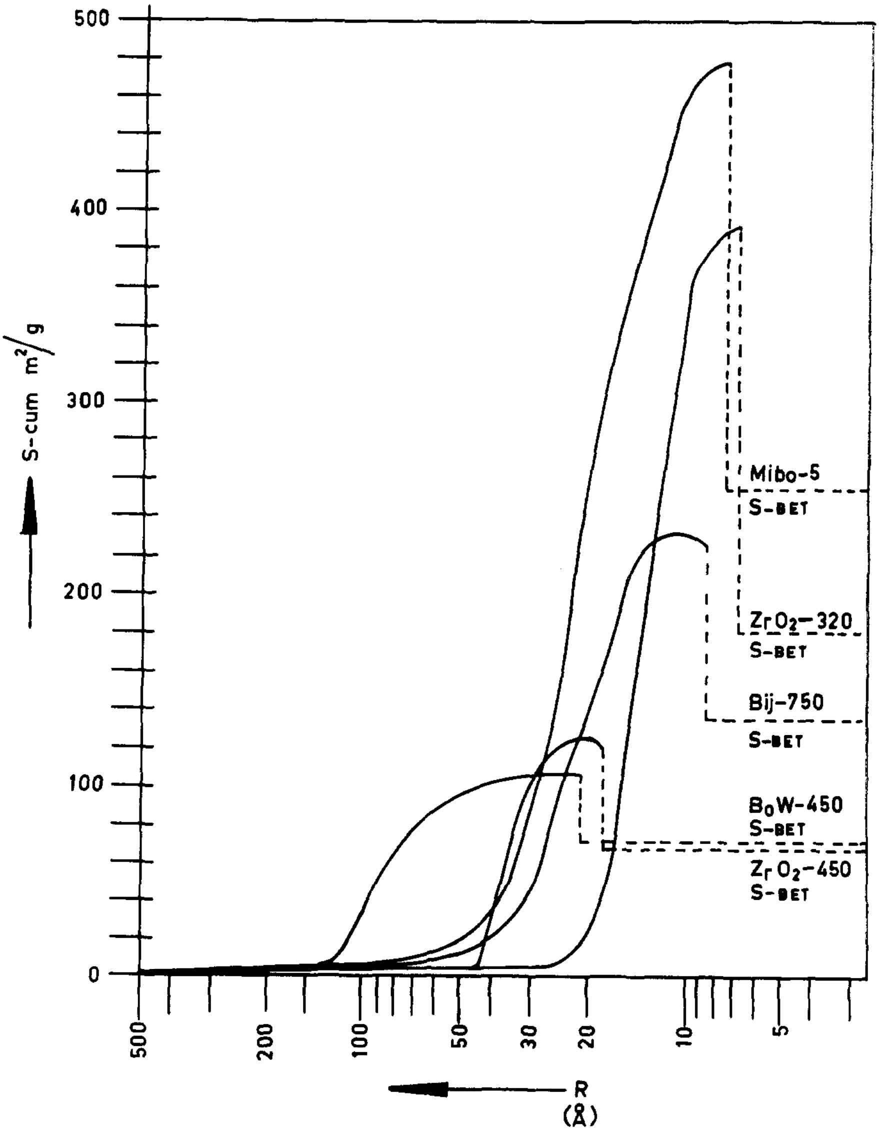

FIG. 3. Examples of pore distributions curves, as calculated with the aid of Eq. (11) and making use of the radii calculated from Cohan's equation. The examples are taken from the preparations presented in Table 4.

with radius r_k, was seated in the application of the correction term for the change in thickness in the adsorbed layer in all the pores not filled with capillary condensate. According to the analysis of Section 6, this correction is given by a complicated summation series [see Eq. (7)]. If the result of Section 4, viz., the equality of the formal thickness to the thickness of the adsorbed layer at a flat surface at the same pressure, would apply strictly, then the correction term would simply reduce to the following equation:

$$(t_{x(k-1)} - t_{xk}) \sum_{i=1}^{k-1} S_i,$$

and the fundamental equation for calculating the pore distribution could be written as

$$S_k = \frac{2r_k}{(r_k - t_{rk,xk})^2} \left[\Delta V_k{}^{c} - (t_{x(k-1)} - t_{xk}) \sum_{i=1}^{k-1} S_i\right] \quad (12)$$

Equation (12) is much simpler to handle than Eq. (10). However, a certain loss of accuracy occurs, leading to results frequently being high in comparison with the results from Eq. (10). Its application should be restricted to semiquantitative routine work and only when an electronic computer is lacking. Especially the representation of wider pores is erroneous, the thickness of the adsorbed layer here being appreciably higher than is predicted from the accidental equality of the formal thickness of the adsorbed layer and the thickness on a flat surface at the same pressure. On account of the fact that the calculation of the kth step of the pore distribution computation makes use of the results of all preceding $k - 1$ steps, erroneous results in the preceding steps will influence the results of the kth step. It is important to realize that for every method of pore distribution calculation, this internal dependence exists, even leading to a tendency to "correct" the errors of the preceding steps when a pore distribution calculation is extended down to very small pressures. A pore distribution calculation, therefore, should always be performed in conjunction with an analysis of the t plot, showing the lower limit of application of the pore distribution, viz., the pressure where no pores are to be expected any more, or the presence of micropores, where the concepts underlying pore distribution calculations are no longer viable.

10. Conclusions

It has been shown that the adsorption branch of a nitrogen sorption isotherm may be used for the calculation of pore distribution in the case of the existence of an A-type hysteresis loop, making use of the model of open cylindrical pores and of the equations derived in Part IX of this series. The results of this calculation have been shown to be a major improvement over the results obtained by making use of the Cohan equation, viz., the Kelvin equation as applied to the cylindrical meniscus formed by the adsorbed layer present in open cylindrical pores. The treatment given here is an example of the rigorous application of the t curve of multimolecular nitrogen adsorption to the analysis of porous systems.

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