

Computation of Pore-Size Distribution in Terms of Surface Area

B. VISWANATHAN AND M. V. C. SASTRI

From the Department of Chemistry, Indian Institute of Technology, Madras, India

Received January 11, 1967; Revised April 4, 1967

A simple method is suggested for computing pore-size distributions in terms of surface areas, instead of pore volumes, directly from low-temperature desorption isotherms of nitrogen. The method yields areas and distribution patterns which are very similar to those obtained with the BJH method, but the computational procedure is much simpler and can be handled conveniently with a conventional desk calculator.

Pore-size distribution data are becoming increasingly important in studies of heterogeneous catalysis, especially in the context of diffusion-controlled processes. In the more important pore-width range of 20 to 200 Å, the distribution is almost invariably obtained by mathematically tracking down the isothermal desorption of a capillary condensate, making use mainly of Kelvin's relation between equilibrium vapor pressure and capillary radius. Some of the more important methods of analysis, applicable to cylindrical pores,* have been reviewed by Wheeler (1). Of these, the most widely used method of computation is that originally developed by Barrett, Joyner, and Halenda (2) (BJH) and more recent modifications of it suggested by Pierce (3), Cranston and Inkley (4), and Dollimore and Heal (5). These involve cumulative compilation procedures which are tedious and time-consuming, unless they are either approximated at the expense of accuracy or handled with a digital computer.

A more direct approach for relating the differential amount of vapor desorbed (dV_a) with the differential volume of the pores emptied at any stage of the desorption has been suggested recently by Anderson (6). His method for deducing $V_{>R}$, though undoubtedly less tedious than the BJH method, uses another kind of "building

block" technique, involving three or four integrations. All these methods lead to pore-size distributions in terms of the pore volumes only.

In this paper, a method is developed for computing the distribution of pore sizes in terms of surface area, which is more appropriate in the case of catalysts. Like the other methods, it is based on the model of the desorption process proposed originally by Wheeler (1), but the equation evolved is simpler for working with desk calculators.

SOLUTION FOR AREA DISTRIBUTION

The volume V_a of the adsorbate (reckoned as liquid volume) held by the solid at any point on the desorption isotherm is expressed by the equation (1)

$$V_a = V_c(<R_c) + tS(>R_c) - \pi l^2 L(>R_c) \quad (1)$$

where $V_c(<R_c)$ denotes the volume of all pores of radii smaller than R_c and hence filled with capillary condensate. The last two terms together give the geometric volume of the annulus of adsorbed vapor in wider pores. Differentiating this equation as such with respect to R_c we get

$$\begin{aligned} \frac{dV_a}{dR_c} &= \frac{dV_c(<R_c)}{dR_c} + t \frac{dS(>R_c)}{dR_c} \\ &+ S(>R_c) \frac{dt}{dR_c} - \pi l^2 \frac{dL(>R_c)}{dR_c} \\ &- \pi L(>R_c) \frac{d(l^2)}{dR_c} \quad (2) \end{aligned}$$

* For slit-shaped pores, a modified treatment is given by B. C. Lippens *et al.*, *J. Catalysis*, **3**, 32 (1964).

Recognizing that, by definition,

$$V_c(<R_c) = \int_0^{R_c} \pi R_c^2 L(R_c) dR_c,$$

$$S(>R_c) = \int_{R_c}^{\infty} 2\pi R_c L(R_c) dR_c$$

and

$$L(>R_c) = \int_{R_c}^{\infty} L(R_c) dR_c$$

and omitting the last term, containing $d(R^2)/dR_c$, Eq. (2) reduces to*

$$\frac{dV_a}{dR_c} = \frac{dS}{dR_c} \left[\frac{t(R_c - t)}{2R_c} - \frac{(R_c - t)}{2} \right] + \frac{dt}{dR_c} S(>R_c) \quad (3)$$

This being a linear differential equation it can be solved for S in terms of dV_a/dR_c and dt/dR_c . The solution may be expressed simply as

$$S(>R_c) = h/g \quad (4)$$

where

$$h = \int_{R_c}^{\infty} \left(\frac{g}{x} \right) \left(\frac{dV_a}{dR_c} \right) dR_c \quad (4a)$$

$$g = \exp \int_0^{R_c} \frac{1}{x} \left(\frac{dt}{dR_c} \right) dR_c \quad (4b)$$

and

$$x = \left[\frac{t(R_c - t)}{2R_c} - \frac{(R_c - t)}{2} \right] \quad (4c)$$

METHOD OF COMPUTATION

Values of the inner capillary radius (r_k) were computed from various relative pressures using the Kelvin equation

* The corresponding equation given by Wheeler (1) is

$$dV_a/dR_c = \pi R_c(R_c - 2t)L(R_c) - (dt/dR_c)S(>R_c).$$

The negative sign of the last term, which is obviously wrong, has vitiated his solution for $S(>R_c)$. Even when this error was corrected, it was found that dropping the last term in Eq. (1) before differentiation greatly impaired the accuracy of computation and raised the range of pore sizes accessible to it to 85 to 300 Å, thus leaving out the more important micropore region.

$$r_k(\text{Å}) = \frac{-4.14}{\log_{10}(p/p_0)} \quad (5)$$

The corresponding values of t , the thickness of the adsorbed multilayers on the pore walls, were determined by using Halsey equation (8) in the form given by Wheeler (1) for nitrogen and used by Dollimore and Heal (5), namely,

$$t(\text{Å}) = -4.3 \left[\frac{5}{\ln(p/p_0)} \right]^{1/3} \quad (6)$$

Hence $R_c = (r_k + t)$ and x [Eq. (4c)] could be obtained for each value of p/p_0 and therefore of t (see Table 1, columns 1 to 5)

Next, to find g , the integral in Eq. (4b), which is the same as

$$\int_0^t \left(\frac{1}{x} \right) dt$$

was evaluated graphically from the plot of $1/x$ vs. t . In this manner a master correlation chart or graph could be prepared giving $g/|x|$ values as a function of p/p_0 (Table 1, cols. 1 and 7) which could apply universally to any adsorption data obtained with nitrogen at its normal boiling point.

The experimental data of V_a vs. p/p_0 could thus be transformed rapidly into one of V_a vs. $g/|x|$ as required by Eq. (4a).

In any actual case, all that one has to do, is to evaluate the integral in Eq. (4a). This can be done either graphically or numerically. The latter method with the aid of the trapezoidal rule was found to be more convenient. Even one division of the interval between successive experimental values of V_a was found to be adequate to yield results comparable with those obtained by more elaborate methods. This is exemplified by the results presented in Table 2, which illustrates the method of computation outlined above. The experimental data used therein were obtained in this laboratory.

RESULTS AND CONCLUSION

The method outlined above was also applied to data obtained on a variety porous solids by other workers. A comparative statement of the cumulative areas derived by different methods is given in Table 3. The area values obtained with the help of

TABLE 1
MASTER CHART FOR g AND $g/|x|$ VALUES

p/p_0	r_k (Å)	t (Å)	$R_c (= r_k + t)$ (Å)	$ x $	$g \times 10^{-85}$	$(g/ x) \times 10^{-85}$ (Å ⁻¹)
0.20	5.92	6.275	12.20	1.426	1.000	0.701
0.30	7.94	6.92	14.86	2.116	1.35	0.638
0.40	10.40	7.57	17.97	3.009	1.71	0.588
0.50	13.75	8.308	22.06	4.292	2.24	0.522
0.60	18.60	9.20	27.80	6.223	2.82	0.453
0.70	26.6	10.40	37.00	9.572	3.09	0.323
0.80	42.7	12.10	54.80	16.63	3.89	0.234
0.85	58.64	13.46	72.10	23.83	4.07	0.171
0.90	91.0	15.56	106.56	38.94	4.27	0.110
0.950	188.0	19.80	207.80	83.95	4.68	0.056
0.970	312.0	23.40	335.40	145.12	5.00	0.033
0.975	376.0	25.03	401.03	176.83	5.25	0.030
1.000					6.00 ^a	

^a Extrapolated value.

Eq. (4) of this paper are seen to be generally in good agreement with those found by the BET and the BJH methods. The distribution plots, $\Delta S/\Delta R_c$ vs. R_c , are also very similar in form to those derived by the BJH method, as may be seen from a typical example shown in Fig. 1.

To summarize, the advantages claimed for the method suggested in this paper are mainly the following:

1. The computational procedure is much simpler, speedier, and more suited to handling with small desk calculators than the BJH and other methods reported hitherto. At any stage of the computation, the total surface area up to that point can be obtained directly without going through the tedious summing up sequences of the BJH method and its modifications (2-5).

(2) The pore-size distribution is obtained

TABLE 2
CALCULATION OF PORE-SIZE DISTRIBUTION FOR A SAMPLE OF ALUMINA (BET AREA, 71.0 m²/g)^a

1 Rel. pressure p/p_0	2 Vol. adsd. (V_a gas) (cc NTP/g)	3 $g \times 10^{-85}$	4 $(g/ x) \times$ $10^{-85}/\text{cm}$	5 $\bar{g} \times 10^{-85}$	6 $h \times 10^{-85}\text{cm}^2$	7 $S(>R_c)$ (m ² /g)	8 $R_c =$ $(r_k + t)$ (Å)	9 Av. R_c (Å)	10 $\Delta S/\Delta R_c$ (m ² /Å)
1.000		6.000							
0.950	140.50	4.600	0.05571	5.300			200.00		
0.943	139.40	4.575	0.0600	5.287	0.06537	0.1923	175.16	187.60	0.00774
0.905	132.00	4.300	0.1075	5.150	0.68350	2.0640	109.95	142.95	0.02871
0.887	125.70	4.175	0.1275	5.087	1.42500	4.3550	94.15	102.10	0.14500
0.865	114.80	4.100	0.1575	5.050	2.97900	9.1730	78.80	86.47	0.31920
0.801	87.80	3.700	0.2250	4.850	8.14300	26.1100	55.10	66.95	0.71500
0.757	59.40	3.500	0.2815	4.750	15.34000	50.2100	45.47	50.29	2.48200
0.735	50.50	3.300	0.3125	4.650	17.99000	60.1600	41.67	43.57	2.60400
0.696	41.10	3.100	0.3575	4.550	21.11000	72.1400	36.68	39.18	2.40800

^a Col. 3: Read off from plot of g vs. p/p_0 (Table 1).

Col. 4: Read off from plot of $g/|x|$ vs. p/p_0 (Table 1).

Col. 5: Mean of the values of g at $p/p_0 = 1$ and at the p/p_0 value under examination, e.g., at $p/p_0 = 0.80$, $g = 1/2 (6.00 + 3.70) = 4.85$.

Col. 6: Integrals evaluated by trapezoidal rule.

Col. 7: $(h/\bar{g}) \times (15.55 \times 10^{-4})m^2g^{-1}$, where 15.55×10^{-4} is conversion factor for V_{gas} to V_{liquid} .

TABLE 3
CUMULATIVE SURFACE AREA (m^2g^{-1}) CALCULATED BY DIFFERENT METHODS

No.	Sample	By BET method (m^2g^{-1})	By this paper Eq. (4)	By BJH method (Approximate method)	By other methods
1	Silica-magnesia ^a	533.0	529.5	538.0	...
2	Alumina gel ^a	319.0	345.5	357.0	...
3	13% Silica-alumina ^a	575.0	566.5	576.0	...
4	Aged silica-alumina ^a	88.0	102.0	96.0	...
5	Silica gel	703.0	725.0	717.0 ^b	706 ^c , 569 ^d
6	Alumina (Houdry)	71.0	72.0
7	Bone char after 32 cycles	62.0	69.5	64.6	54.8 ^e
8	F ₁₂ catalyst (alumina)	120.0	122.0	...	145.0 ^e
9	Shift catalyst II ^f	46.6	46.0
10	Activated alumina ^f	145.8	158.0
11	Silica-alumina (heat-deactivated)	197.5	204.0	...	194.5 ^g

^a Data from W. R. Grace & Co., Clarksville, Maryland.

^b From ref. (7).

^c Anderson's method, ref. (6).

^d Dollimore and Heal method, ref. (5).

^e Conway method, ref. (3).

^f Data from Haldor Topsøe, Hellerup, Denmark.

^g Cranston and Inkley, ref. (4).

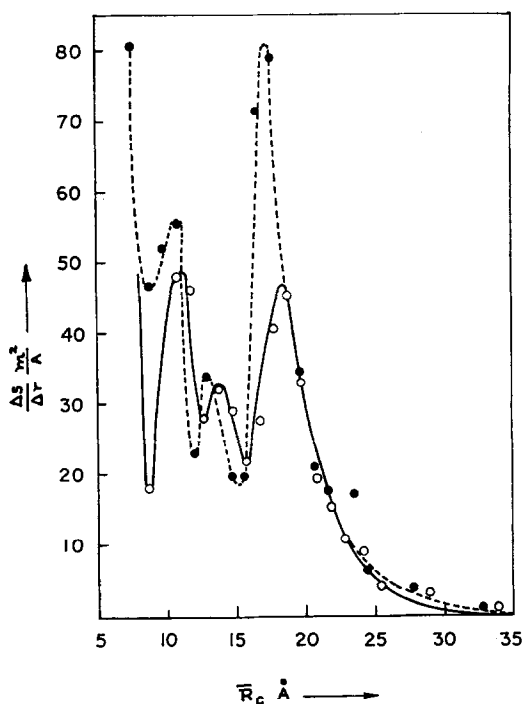


FIG. 1. Pore-size distribution curves for silica gel: —○—, by Eq. (4); - - - ● - - -, by BJH method.

directly in terms of surface area, which is more relevant to catalytic activity than the volume distribution functions yielded by the other methods.

ACKNOWLEDGMENTS

The authors are grateful to Dr. F. G. Ciapetta of W. R. Grace & Co., Clarksville, Maryland, and to the Haldor Topsøe Research Laboratory, Hellerup, Denmark, for sending us the physical adsorption data cited in Table 3.

REFERENCES

1. WHEELER, A., in "Catalysis" (P. H. Emmett, ed.), Vol. 2, p. 111. Reinhold, New York, 1955.
2. BARRETT, E. P., JOYNER, L. G., AND HALENDA, P. P., *J. Am. Chem. Soc.* **73**, 373 (1951).
3. CONWAY, P., *J. Phys. Chem.* **57**, 64 (1953).
4. CRANSTON, R. W., AND INKLEY, F. A., *Advan. Catalysis* **9**, 143. Academic Press, New York, 1957.
5. DOLLIMORE, D., AND HEAL, G. R., *J. Appl. Chem.* **14**, 109 (1964).
6. ANDERSON, R. B., *J. Catalysis* **3**, 50, 301 (1964).
7. IRVING, J. P., AND BUTT, J. B., *J. Appl. Chem.* **15**, 139 (1965).
8. HALSEY, G. D., *J. Chem. Phys.* **16**, 931 (1948).