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Pore Distributions from Desorption Isotherms

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An improved method has been developed for computing a pore distribution curve from the nitrogen desorption isotherm at −195°C based on the basic assumptions of Barrett, Joyner, and Halenda and Wheeler. Satisfactory agreement was obtained between surface areas computed by the present method and the BET equation. This work is part of a cooperative project between the Bureau of Mines and the Public Health Service, Department of Health, Education and Welfare, on the catalytic oxidation of automotive exhaust.

Barrett, Joyner, and Halenda (*2*) (BJH) developed a method for estimating the distribution of pores in porous solids from the physical desorption isotherms for nitrogen at −195°C, assuming that the pores approximate cylindrical shape. Their procedure was based on the model proposed by Wheeler (*5*, *7*) which is also the basis of the present work.

In the BJH (*2*) and Wheeler (*6*) methods the calculations are laborious and probably only approximate. The present paper describes a straightforward method of calculating a cumulative pore distribution curve using standard mathematical methods. A differential pore distribution can be obtained by numerical differentiation.

In desorption, when the pressure is decreased from the saturation pressure to a relative pressure, x, pores with radii larger than R desorb to leave an adsorbed layer of thickness t on the pore walls. The quantity $R - t$, the Kelvin radius, is related to x by the Kelvin equation, and thickness t as a function of x has usually been established empirically for adsorption on nonporous materials. When the pressure is further decreased, smaller pores desorb and the thickness of the adsorbed layer decreases. The problem in computing a pore distribution curve involves relating a differential amount desorbed dV_a to the differential volume of pores emptied dV.

A New Procedure for Calculating Pore Distributions

The volume of pores emptied, V, is a function of amount adsorbed, V_a, and thickness of monolayer, t, i.e. $V = f(V_a, t)$. Then,

$$dV = (\partial V/\partial V_a)_t dV_a + (\partial V/\partial t)_{V_a} dt \tag{1}$$

$$= (\partial V/\partial V_a)_t \left[dV_a + \frac{(\partial V/dt)_{V_a}}{(\partial V/\partial V_a)_t} dt \right] \tag{2}$$

$$= (\partial V/\partial V_a)_t [dV_a - (\partial V_a/dt)_V dt] \tag{3}$$

$$= (\partial V/\partial V_a)_t [1 - (\partial V_a/dt)_V (dt/dV_a)] dV_a \tag{4}$$

For cylindrical pores the terms in (4) may be evaluated as

$$(\partial V/\partial V_a)_t = R^2/(R - t)^2,$$

and

$$(\partial V_a/\partial t)_V = 2 \int_{V_R}^{V_g} [(R - t')/R^2] dV,$$

where t' is the value of t at the lower limit of integration, and V_g is the volume adsorbed at $x = 1$, to give

$$dV = \frac{R^2}{(R - t)^2} \left[1 - 2 \frac{dt}{dV_a} \int_{V_R}^{V_g} \frac{(R - t')}{R^2} dV \right] dV_a \tag{5}$$

which cannot be evaluated directly because V in the integral is not known. For most of the isotherm the second term within brackets in (5) is substantially smaller than 1, and we may substitute the expression for dV of Eq. (5) into the integral of the same equation. Performing this operation twice leads to

$$dV = \frac{R^2}{(R-t)^2}\left[1 - 2\frac{dt}{dV_a}\int_{V_R}^{V_g}\frac{dV_a}{R-t'} + 4\frac{dt}{dV_a}\int_{V_R}^{V_g}\frac{R-t'}{R^2}\frac{dt}{dV_a}\int_{V_R}^{V_g}\frac{dV_a}{r-t'}dV_a\cdots\right]dV_a \tag{6}$$

In evaluating Eq. (6) we have used the value of t corresponding to R rather than the lower limit of the integral. This approximation usually changes the values of the integrals by less than 1%. Usually the third term within the brackets is less than 15% of the second, and the fourth term presumably falls off in the same manner.

To integrate Eq. (6) numerically, the portion of the desorption isotherm from V_g to V_m is divided into 15 to 20 equidistant intervals of width h, the values of x are determined from the isotherm, and the corresponding values of R and t are read from graphs or tables.

Equation 6 may be simplified by substituting $nh = V_a$ to give

$$dV = \frac{R^2}{(R-t)^2}\left[1 - 2\frac{dt}{dn}\int_0^{n'}\frac{dn}{R-t} + 4\frac{dt}{dn}\int_0^{n'}\frac{R-t}{R^2}\frac{dt}{dn}\int_0^{n'}\frac{dn}{R-t}\cdot dn\right]hdn \tag{7}$$

The term dt/dn is approximated by taking $\frac{1}{2}$ of the difference of the values of t one interval above and below the value of interest. The integral $2\int_0^{n'} dn/(R-t)$ is evaluated numerically using the trapezoida- integration rule, and this quantity is multil plied by dt/dn. The values of the third term are evaluated similarly using the values of the first integral determined previously.

Equation 7 may now be integrated from V_R to V_g to give the volume of pores greater than R, $V_{>R}$,

$$V_{>R} = h\int_0^{n'}\frac{R^2}{(R-t)^2}(G)dn, \tag{8}$$

where G is the quantity within brackets in Eq. 7. Integration of Eq. 8 by the trapezoidal method is continued until $V_{>R}$ exceeds V_g. The surface area is evaluated from the equation $A = 2\int_0^{V_g} dV/R$ in the form

$$A = 2h\int_0^{n''}\frac{R}{(R-t)^2}(G)dn \tag{9}$$

where n'' corresponds to the value of V_a or R at which $V_{>R} = V_g$. Usually n'' is not an integer and the value of A is obtained by trapezoidal integration to the intervals above and below $V_{>R} = V_g$, and A is estimated by linear interpolation.

For evaluating integral (8) it is usually convenient to use the adsorption data in terms of cc (STP), but for integral (9) the actual volume of adsorbate must be used. Therefore, a constant multiplier of $1.546 \times 10^{-3}\,h$ is used in the numerical integration.

The accuracy of the value of (G) used in Eq. (8) may be tested by substituting the differential form of Eq. (8) into Eq. (5) to give

$$(G') = \left\{1 - 2\frac{dt}{dn}\int_0^{n}\frac{R-t'}{R^2}\left[\frac{R^2}{(R-t)^2}(G)\right]dn\right\} \tag{10}$$

where (G') is a better approximation of the quantity (G). Equation (10) is integrated by trapezoidal method. The term $[R^2/(R-t)^2](G)$ in Eq. (10) has been evaluated for integration of Eq. (8). The value of t corresponding to the lower limit of integration t' should be used in Eq. (10). This check is usually unnecessary.

EXAMPLES OF PORE DISTRIBUTION CURVES

The new method was applied to the six nitrogen isotherms at −195° shown in Fig. 1, where amount adsorbed is plotted as V_a/V_g to keep all of the isotherms on the same scale. Data for silica gel of BJH were read from the isotherm in ref. (*2*), and the desorption isotherm is shown as a broken curve in Fig. 1. For some of the other isotherms not enough desorption points are available to define the desorption curve accurately. Values of R and t of BJH (*2*) were used to

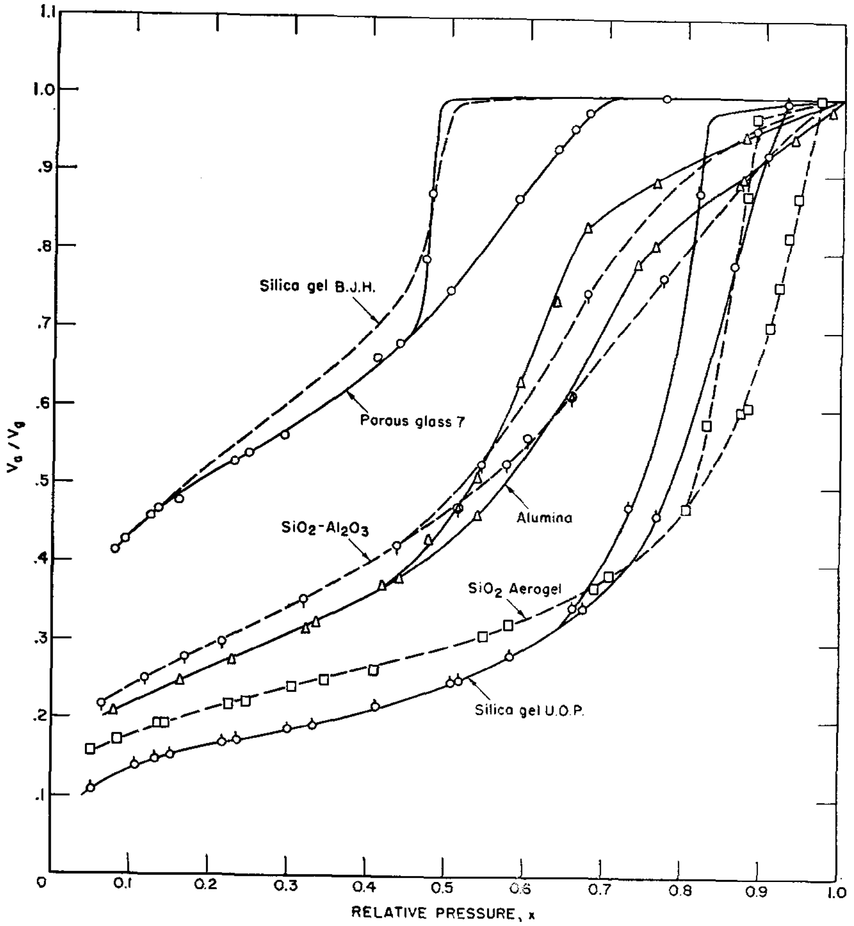

FIG. 1. Nitrogen isotherms at —195°C. The volume adsorbed V_a has been divided by the volume adsorbed at $x = 1$, V_g.

construct graphs of R, $R^2/(R - t)^2$, and $1/(R - t)$ as a function of x.

Figure 2 shows the cumulative pore volume curve for silica gel of BJH. The pore distribution curve was terminated at 425 cc, corresponding to a pore radius of 8.2 Å. The surface area was 806 m²/g, which is less than the BET area, 858 m²/g.

Differential pore distribution curves were obtained by numerical differentiation of values of $V_{>R}$ read at equal intervals of pore radius by an adaptation of the Douglass-Avakian (*1*) method involving central differences. For some intervals the polynomial approximation was inadequate as indicated by the higher differences becoming very large. In these cases the derivative was approximated by the first differences. The differential pore volume curves for the silica gel of BJH is presented in Fig. 2. The differential curve is essentially the same as that published by BJH.

Cumulative and differential pore volume curves for the other isotherms in Fig. 1, each normalized by dividing by V_g, are presented in Fig. 3. Table 1 provides the values of V_g, and surface areas by the BET equation and the present method. Surface areas from Eq. 9 were approximately the same as areas from the BET equation. The average of the absolute values of the percentage difference from BET areas was 6%.

To test the internal consistency of the present method, calculations were made on a composite isotherm obtained by adding the isotherms for silica gel UOP and alumina

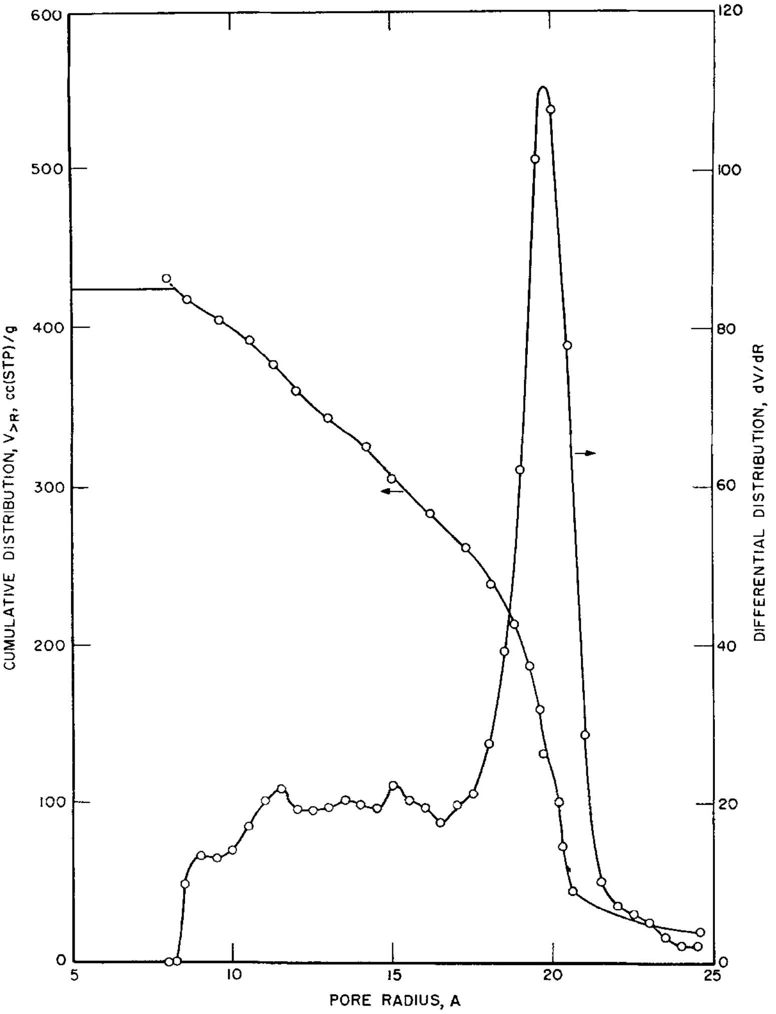

Fig. 2. Cumulative and differential pore distributions for silica gel B.J.H. (ref. 2).

TABLE 1

Surface Areas from Eq. (9) and the BET Equation

Sample		V_g [cc (S.T.P.) N_2 per g]	Surface area (m²/g)	
			BET	This paper, Eq. (9)
Silica gel	BJH	425	858	806
	UOP	590	353	371
	Aerogel	1300	914	820
Porous glass 7		136	255	247
Alumina H-151		240	236	254
Houdry SiO_2-Al_2O_3		285	288	300

as given in Fig. 1. For the composite isotherm, if terms in Eq. 9 calculated by the iterative procedure (i.e., those terms related to the decrease in thickness of multilayers) are not essentially correct, the presence of a system of large pores may greatly change the distribution of smaller pores. The cumulative pore distribution curve of the composite isotherm in Fig. 4 does not differ significantly from the sum of the individual distribution curves (from Fig. 3). The differences at pore radii larger than 60 Å result from using intervals that are too wide to account properly for small changes in amount adsorbed at high relative pressures. Surface areas calculated from the individual and composite isotherms agreed satisfactorily. In the following tabular data, areas of in-

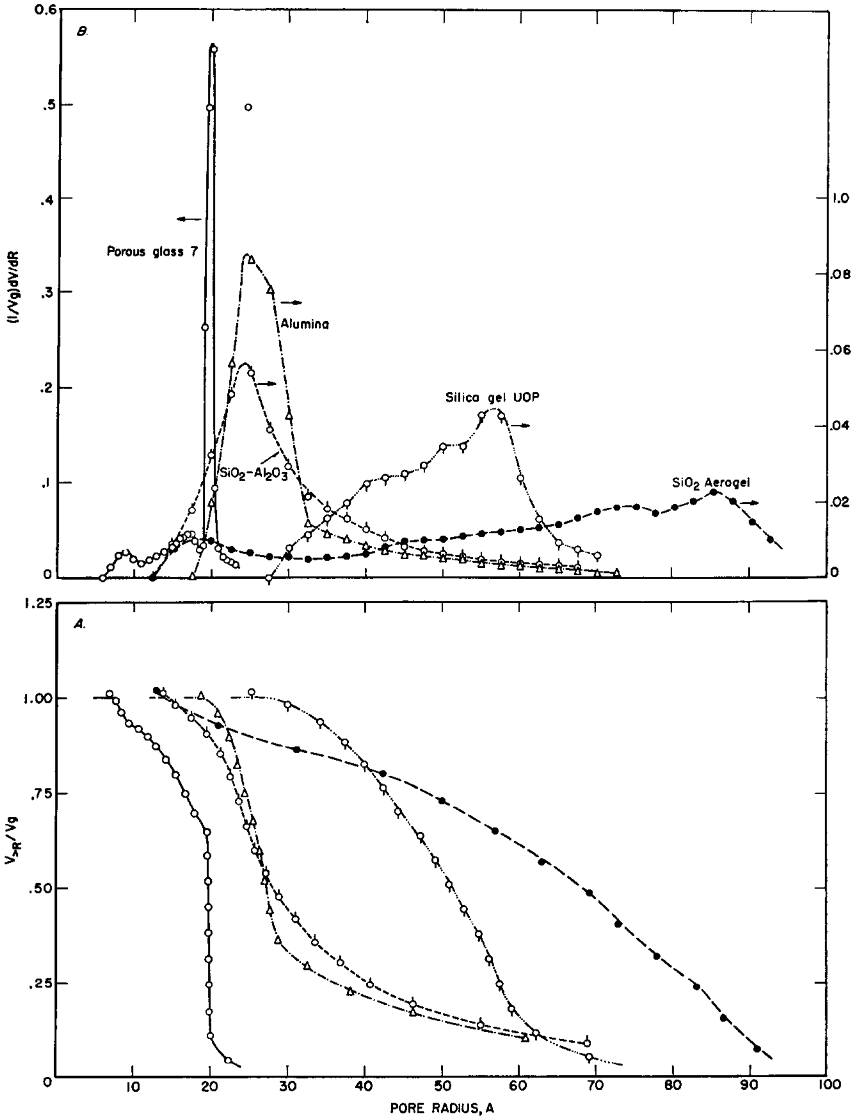

FIG. 3. Cumulative (A) and differential (B) pore distribution curves.

dividual isotherms are computed for a value of $V_g = 1$ cc (STP) and $V_g = 2$ cc (STP) for the composite isotherm:

	Surface areas (m²)	
	BET	Present method
Alumina	0.982	1.056
Silica gel (UOP)	.598	.629
Total	1.580	1.685
Composite isotherm	1.625	1.685

The exact agreement of areas by the present method is fortuitous.

For the composite isotherm the values of (G) were determined from Eq. (10) and compared with values used in Eq. (8). The values of (G) agreed within a few parts per thousand, as shown in Table 2, where values of (G) are tabulated for intervals from $V_{>R} = 0$ to $V_{>R} > V_g$. In evaluating (G) from Eq. (10) the value of t corresponding to the lower limit of integration was used.

DISCUSSION

The present paper describes an improved

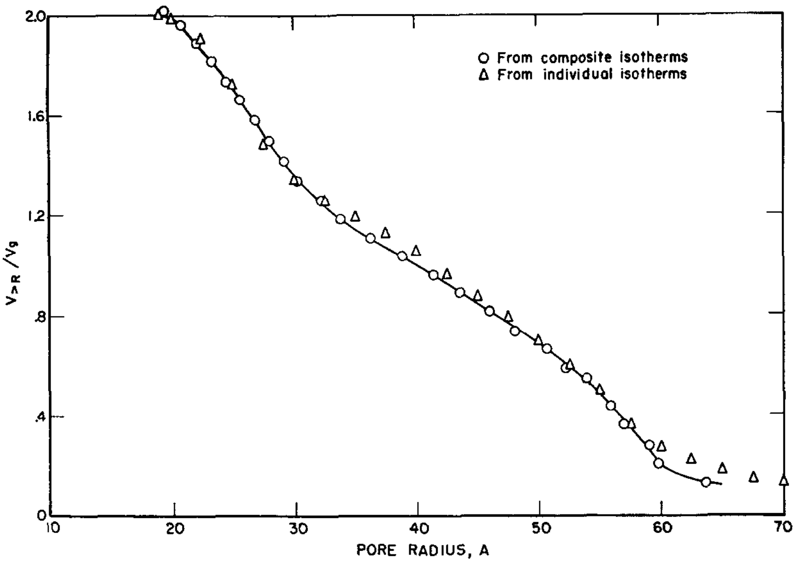

FIG. 4. Cumulative pore distribution for composite isotherm for silica gel (UOP) and alumina compared with data from individual isotherms.

TABLE 2
VALUES OF (G) COMPARED FOR COMPOSITE ISOTHERM

G		G		G	
From Eq. (10)	Used in Eq. (8)	From Eq. (10)	Used in Eq. (8)	From Eq. (10)	Used in Eq. (8)
1.000	1.000	.913	.915	.766	.767
.967	.968	.900	.898	.833	.834
.932	.935	.888	.890	.861	.861
.979	.981	.849	.852	.791	.792
.985	.985	.865	.868	.749	.750
.983	.984	.845	.847	.730	.730
.968	.970	.788	.790	.711	.709
.949	.950	.805	.806	.660	.655
.940	.941	.803	.803	.588	.579
				.494	.480

method of computing pore distribution curves based on the original assumptions of BJH (*2*) and Wheeler (*5*, *6*). These assumptions include:

(a) Pores are cylindrical in shape and the adsorbed phase may be regarded as a continuum rather than composed of discrete molecules.

(b) For porous solids, the average thickness of adsorbed layer, t, at any given relative pressure is the same as observed on nonporous solids.

(c) The Kelvin equation applied to the desorption isotherm is valid even for pores with radii as small as 2 to 3 molecular diameters.

(d) The density of the adsorbate is that of normal liquid.

In addition two factors that may lead to incorrect surface areas and pore distributions may be added to the uncertainties listed above:

(e) Roughness of the surface of molecular size.

(f) Bottleneck pores that desorb at a lower value of R than the average radius of the pore.

In the present procedure the cummulative pore distribution curve is stopped at a value of R where $V_{>R} = V_g$, and the extension of this curve to smaller values of R is attributed to multilayer adsorption. If the basic assumptions are incorrect, the cummulative curve may be terminated at an incorrect point and the portion of the distribution for small values of R may be eliminated or included incorrectly.

The present numerical method is more accurate than the approximate procedures of BJH (*2*) and Wheeler (*6*), and the calculating time is no greater. The present calculations can be made as exact as required by decreasing the size of the intervals of V_a. The present calculations were made with a desk calculator; however, the procedure could be readily adapted to modern computers, using polynomial approximations for R and t as a function of x. The quantity $(R - t')$ in the integrals of Eq. (6) could be evaluated exactly, and higher terms in the series of Eq. (8) could be computed.

Possibly improved values of Kelvin radii could be obtained, especially as applied to pores approaching molecular dimensions. These investigations could, however, be supported only by the internal consistency of the data, as there is no unequivocal method of determining surface area of porous solids. Part of the pore volume curve can be checked by mercury porosimeter data, and good agreement was obtained by Joyner, Barrett, and Skold (*4*) for the common portions of pore distribution curves, if a contact angle of 130° was used for mercury in the Washburn equation.

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REFERENCES

1. AVAKIAN, A. S., AND DOUGLASS, R. D., described in MICKLEY, H. S., SHERWOOD, T. K., AND REED, C. E., "Applied Mathematics in Engineering," pp. 25–28. McGraw-Hill, New York, 1957.

2. BARRETT, E. P., JOYNER, L. G., AND HALENDA, P. P., *J. Am. Chem. Soc.* **73,** 373 (1951).

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

4. JOYNER, L. G., BARRETT, E. P., AND SKOLD, R., *J. Am. Chem. Soc.* **73,** 3155 (1951).

5. WHEELER, A., Presentations at *Catalysis Symposia, Gibson Island, AAAS Conferences,* June 1945 and June 1946.

6. WHEELER, A., *in* "Catalysis" (P. H. Emmett, ed.), Vol. 2, pp. 118–120. Reinhold, New York, 1955.

7. WHEELER, A., *in* "Catalysis" (P. H. Emmett, ed.), Vol. 2, p. 113. Reinhold, New York, 1955.