Considering the error normally involved in the process of fitting the observed intensities to the scale of calculated independent scattering at large s, this result can be interpreted as a coördination number of either 4 or 5. In the light of all evidence, the latter possibility is remote.

The second peak at 3.60 Å. in the distribution curve may be treated in the same way. The area will be given by $\Sigma K_m N_m$, where N_m now represents the number of electrons lying at about 3.6 Å. from atom m. From Table I, the Al–Al distance, 1–2, and the three Cl–Cl distances, 5–8, 3–4 and 5–6, all lie within this peak. There are one such Al–Al distance and eleven such Cl–Cl distances. Then

$$\text{Area} = K_{Al}^2 + 11K_{Cl}^2 = 3470 \text{ electron}^2$$

The measured area (dotted) is 5350 electron². The discrepancy is due mostly to *inter*molecular scattering; that is, there appears to be a large contribution to the liquid scattering due to interference between contiguous Cl atoms in neighboring molecules.

Intermolecular Scattering

The first five peaks in the experimental radial distribution curve have been shown to be due largely to intramolecular scattering. This fact suggests that the rather well-defined sixth and seventh peaks are also due to interference between molecules. In an attempt to determine the extent of intermolecular scattering, the data of Table I were entered into the Zernike and Prins formula

$$I_{eu} = \sum_i \sum_j f_i f_j \frac{\sin r_{ij}s}{r_{ij}s} \qquad (3)$$

This expansion would give the pattern to be expected from Al_2Cl_6 molecules diffracting independently. The upper curve in Fig. 2 shows this computed scattering pattern. The general agreement between the patterns is clear, but the influence of intermolecular scattering considerably distorts the experimental curve. An attempt was made to apply the Warren analysis by defining a new $i(s)$

$$i(s) = \frac{I}{I_{mol}} - 1$$

where I_{mol} is a kind of "molecular structure factor," defined by equation (3). Σf_{coh}^2 may be looked upon as given by equation (3) when all the interatomic r_{ij}'s are omitted, and leads through the Warren analysis to the geometric disposition of *atoms* in the mass. Using the whole of I_{mol} expands Σf_{coh}^2 to include the intramolecular geometry, and it was hoped that the Warren analysis might then lead to a geometric disposition of *molecules*. The results were disappointing and yielded no interpretable information.

Integration of the upper curve in Fig. 2 (scattering from independent molecules) in accordance with equation (1) yields a radial distribution curve similar to Fig. 4. In this "synthetic" curve, the positions of the first five peaks are unchanged from Fig. 4, although the shapes of the peaks are different. The sixth and seventh peaks, however, are shifted from their positions in the observed pattern and moreover are almost completely suppressed in the synthetic distribution. These peaks presumably represent distances between atoms in adjacent molecules but they furnish no information about the molecular orientation.

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[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF BAUGH AND SONS COMPANY, MELLON INSTITUTE]

The Determination of Pore Volume and Area Distributions in Porous Substances. II. Comparison between Nitrogen Isotherm and Mercury Porosimeter Methods

BY LESLIE G. JOYNER, ELLIOTT P. BARRETT AND RONALD SKOLD

Two of the authors have recently proposed a theory and developed a technique for obtaining pore volume and area distrition data on porous substances from low temperature nitrogen desorption isotherms. To obtain additional evidence as to the validity of this method, pore volume distribution curves were determined for some of the same adsorbents by means of a high pressure mercury porosimeter. Satisfactory agreement between the two methods was obtained. Since the two methods are based on independent principles and techniques this agreement constitutes an excellent confirmation of the proposed theory.

A previous publication[1] has described a method for obtaining the pore volume and area distribution of porous substances with respect to pore radius from the desorption branch of the low temperature nitrogen isotherm. The method took into consideration desorption from multilayers as well as Kelvin evaporation from capillaries. In that paper it was shown that for all systems examined the total area obtained from the distribution data was in substantial agreement with the total area as determined by the BET method.[2] (This method of obtaining the distribution curve will be termed the isotherm method.)

A direct method of obtaining pore volume distributions by the use of a high pressure mercury porosimeter has been described by Ritter and Drake.[3] (This method will be termed the porosimeter method.) This method is entirely independent of the adsorption isotherm. Therefore

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(1) E. P. Barrett, L. G. Joyner and P. P. Halenda, THIS JOURNAL, **73**, 373 (1951).

(2) S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

(3) H. L. Ritter and L. C. Drake, *Ind. Eng. ,Chem. Anal. Ed.*, **17**, 782 (1945).

it was felt that a comparison between the distribution curves obtained from such porosimeter data with the curves obtained by the isotherm method would be most informative. Agreement between the two curves would constitute an excellent confirmation of the isotherm method.

This paper presents such a comparison for seven adsorbents. Since the porosimeter which was available was not capable of penetrating pores of less than about 30 Å. radius it was necessary to limit the investigation to porous substances which had a considerable proportion of their internal volume in pores of radius larger than 30 Å. Of the twenty-three adsorbents mentioned in the previous paper only the sugar refining adsorbents met this requirement. The distribution curves of more than seven adsorbents were investigated and in each case substantial agreement was obtained between the two methods. The seven examples presented in this paper were selected so as to show typical comparisons for a variety of types of distribution curves.

Experimental

A detailed description of the adsorbents used is beyond the scope of this paper. They were all either bone char or a new synthetic granular adsorbent for sugar refining known as Synthad. Synthad is chemically similar to bone char. Pre-treatments account for the differences in their pore volume distributions. The principle and operation of the porosimeter have been described in detail by Ritter and Drake.[3] Briefly, the adsorbent is placed in a calibrated dilatometer, evacuated, and the dilatometer filled with mercury. The dilatometer is then placed in a high pressure bomb. Since the mercury does not wet the adsorbent, it enters only the very largest pores at atmospheric pressure. As the pressure is increased, however, mercury is forced into smaller pores and the level of the mercury in the dilatometer tube decreases. This level is measured electrically. The diameter of the smallest pore into which mercury can be forced is determined by the pressure, and the volume of the pores filled is calculated from the decrease in the height of the mercury in the dilatometer tube.

The porosimeter used for this work was kindly lent to us by the multiple fellowship of Gulf Research & Development Company at Mellon Institute. It was capable of reaching a maximum pressure of 30,000 p.s.i. In principle the apparatus was the same as that used by Drake.[4] A more detailed description will be published elsewhere.

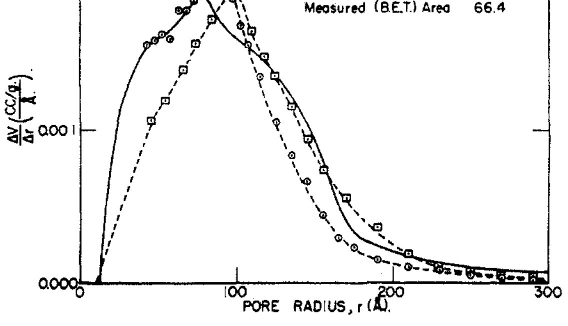

Fig. 1.—Comparison of the pore volume distribution curves obtained from porosimeter data assuming contact angles of 140° and 130° with the distribution curve obtained by the isotherm method; adsorbent I.

A conventional gas adsorption apparatus was used for the determination of the nitrogen adsorption–desorption isotherms. P_0, the vapor pressure of free liquid nitrogen at the adsorption temperature, was measured directly. Since it took several days to determine a single isotherm in sufficient detail, a special narrow necked dewar flask of two-liter capacity was used as the liquid nitrogen bath. This flask held sufficient liquid nitrogen to permit the apparatus to stand overnight without appreciable change in adsorbent temperature. Thus the isotherm could be determined in a single run rather than in several runs at slightly varying temperatures. Considerable care was taken to ensure that saturation had been reached before desorption was started.[5] Since the desorption branch of the isotherm is irreversible, equilibrium in this region was approached from the high pressure side and at no time was the pressure of the system allowed to increase.

Results

The volume, V, measured by the dilatometer of the porosimeter is the volume of all pores having radii greater than r. The radius, r, is related to the pressure, p, exerted by the porosimeter by the equation developed by Washburn.[6]

$$r = -2\sigma \cos \theta / kp \qquad (1)$$

where σ is the surface tension of mercury, θ is the angle of contact between the mercury and the pore wall and k is a conversion factor for the units used.

Equation 1 assumes, as does the theory of the isotherm method, that the pores are cylindrical. Aside from this assumption, the principal objection to equation 1 is that, while σ and θ are measurable at atmospheric pressures, there is little known about their values at higher pressures. For the present the assumption has to be made that they do not change with pressure.

Ritter and Drake[3] measured the contact angle of mercury on a wide variety of substances and found that it varied between 135 and 142°. They selected 140° as a reasonable average. However, they admit that this value may be too high due to the presence of adsorbed moisture. Reported values for the contact angle of mercury on glass have varied from 112^5 to 140°.[7]

In comparing the distribution curves from the isotherm method with those from the porosimeter method it was found that much more consistent agreement was obtained with a 130° contact angle than a 140° one. This is demonstrated in Fig. 1 where the distribution curve of a sugar refining adsorbent obtained by the isotherm method is compared with that from the porosimeter method using both 130 and 140° for the contact angle. Inasmuch as the mercury in the porosimeter is in contact with a moisture free surface of adsorbent, the use of 130° for the contact angle is not in serious disagreement with the assumption of Ritter and Drake.[3]

In this work we have followed Ritter and Drake[3] and used 480 dynes per cm. as the surface tension of mercury at 40°, which was the temperature at which the runs were made. It is by no means certain that either σ or θ is independent of pressure. However, thus far it appears that it is possible to obtain good agreement between the isotherm method and the porosimeter method of determining

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[4] L. C. Drake, *Ind. Eng. Chem.*, **41**, 780 (1949).

[5] E. P. Barrett and L. G. Joyner, *J. Anal. Chem.*, in print.

[6] E. W. Washburn, *Proc. Nat. Acad. Sci.*, **7**, 115 (1921).

[7] P. H. Emmett, *Chem. Revs.*, **43**, 103 (1948).

the distribution curve without resorting to such a pressure dependence for either property. The surface tension of the mercury may also be a function of the radius of curvature of the pore. This effect, however, would only be appreciable in the case of very fine pores with radii considerably below 33 Å.

In both the porosimeter and the isotherm method the pore volume distribution curves are obtained by differentiation of the cumulative pore volume curves. Consequently the shape of the distribution curve depends only upon the changes in slope of the cumulative curve within the range of pore radius values over which the differentiation is carried out. Thus the absolute values of cumulative pore volume at particular pore radii are unimportant provided the shape of the curve in the region being differentiated is correct. This is a fortunate circumstance because it is difficult to determine the total pore volume accurately from the adsorption isotherm particularly when the volume of gas adsorbed approaches a relative pressure of unity asymptotically. Such is generally the case for all adsorbents containing a considerable volume in pores of radius greater than 300 Å.

On the other hand, the porosimeter cannot be used to determine the total pore volume because, due to pressure limitations, it cannot measure the volume of very small pores (in our case pores smaller than 33 Å. radius). In short, it is not possible to compare directly the cumulative pore volume curve obtained from the isotherm with that obtained from the porosimeter because the *absolute* value of the cumulative pore volume cannot be estimated with assurance from the isotherm.

For computational purposes the isotherm method arbitrarily ignores the volume in pores larger than 300 Å. radius. In order to compare the cumulative pore volume curve thus obtained with the curve obtained from the porosimeter data it is necessary to correct the isotherm curve for the volume in pores larger than 300 Å. radius. To make this correction the apparent densities of the adsorbents were measured both by displacement of helium and by displacement of mercury and the total pore volume was computed from the difference between the results. The difference between this measured total pore volume and that assumed for the isotherm method constitutes the volume in pores larger than 300 Å. radius. This volume was added to all points on the isotherm cumulative curve to give an "absolute" curve. These values are shown in Table I.

Table I

Computation of Volume Added to Isotherm Cumulative Curve to Obtain Cumulative Pore Volume between r_p = 300 Å. and $r_p = \infty$

	Pore volume, cc./g.		
Adsorbent	In pores less than 300 Å.	Total volume by density difference	In pores greater than 300 Å.
I	0.219	0.299	0.080
II	.240	.346	.106
III	.325	.431	.106
IV	.274	.373	.099
V	.296	.380	.084
VI	.172	.257	.085
VII	.272	.326	.054

Even though the absolute position of neither cumulative curve is necessary in order to obtain its corresponding distribution curve between any reasonable limits, such as 10 to 300 Å. radius, it is of interest, for comparison purposes, to superimpose the "absolute" curves as correctly as possible. Rather than utilize the ordinate corresponding to the maximum pressure limit, *i.e.*, 35 Å. radius, regarding the reliability of which some doubt was felt, the cumulative pore volume shown by the porosimeter at 40 Å. radius was used as a reference point. The entire porosimeter curve was then adjusted so as to bring the volume at 40 Å. radius into coincidence with the volume on the "absolute" isotherm curve at that radius. An example of the results yielded by this procedure is shown in Fig. 2.

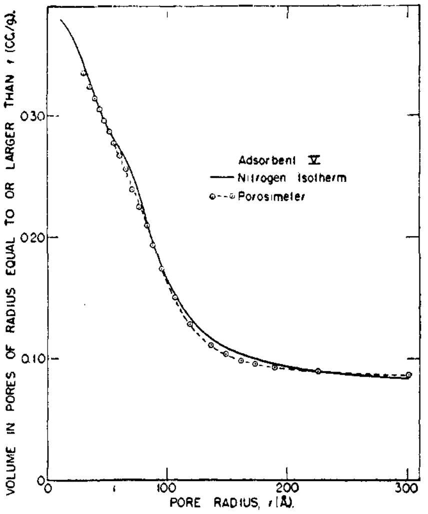

Fig. 2.—Comparison of the "absolute" cumulative pore volume curve obtained from porosimeter data with that obtained by the isotherm method; adsorbent V.

Figure 1, 3, 4 and 5 compare the pore volume distribution curves as determined by the two methods for several adsorbents which exhibit a variety of types of distribution curves. The porosimeter data do not extend below 33 Å. radii since this is the size pore corresponding to the maximum pressure, 30,000 p.s.i., available in the porosimeter. However, in order to estimate the area from the porosimeter data, it was necessary to extrapolate the porosimeter curve down to the smallest radius indicated by the isotherm method. The cumulative pore volume curve obtained from the isotherm was used as a guide in this extrapolation.

Since the primary purpose of this paper is to demonstrate that the two methods give substantially the same distribution curves, interpretation of the distribution curves is beyond its scope.

The distribution curves for adsorbents I, II and III which are shown in Figs. 1 and 3 all exhibit a single, more or less symmetrical, peak. The agreement between the distribution curves determined by the two methods is remarkably good for adsorbent II. Even though the agreement as to the height and location of the peak is not as perfect

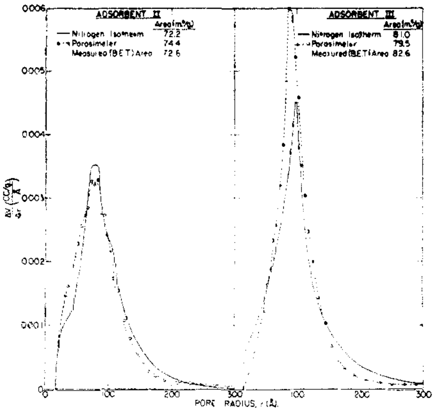

Fig. 3.—Comparison of the distribution curves obtained by the porosimeter method with those obtained by the isotherm method for adsorbents II and III.

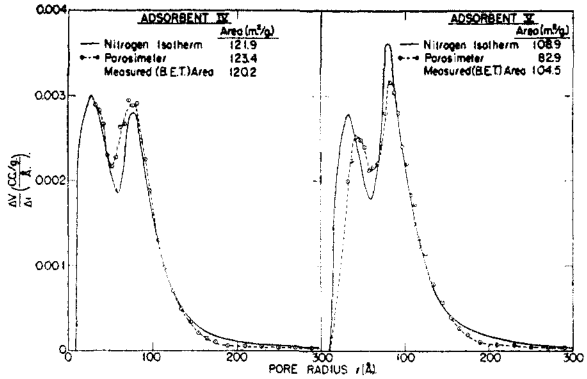

Fig. 4.—Comparison of the distribution curves obtained by the porosimeter method with those obtained by the isotherm method for adsorbents IV and V.

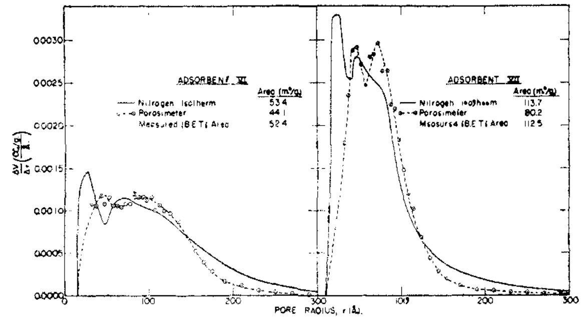

Fig. 5.—Comparison of the distribution curves obtained by the porosimeter method with those obtained by the isotherm method for adsorbents VI and VII.

for adsorbents I and III as it is for II it is still very satisfactory and both methods produce curves of very similar shape.

Four bimodal distribution curves are shown in Figs. 4 and 5. For adsorbent IV the comparison is excellent. Unfortunately the porosimeter data do not extend to low enough radii to cover the peak at the smaller radius for sample IV but they do for sample V. In sample V, however, the porosimeter does not show quite the extreme of maxima and minima that the isotherm method indicates. This is also the case in the very broad curve for adsorbent VI. For adsorbents VI and VII the two methods do not locate the peaks at the same radii but the over-all shape of the two curves agree very well. Also, in the case of adsorbent VI, a sample identical with that used in the adsorption measurements was not available. Therefore, it was necessary to make the porosimeter run on a similar, but not identical, material.

The conclusion which can be drawn from these results is that the distribution curve as derived by the indirect isotherm method is in good agreement, indeed much better agreement than was at first hoped for, with the same curve as determined directly by the porosimeter. If the distribution curve is simple, with well defined maxima and minima, the methods produce essentially the same curve. On the other hand, if the distribution curve is complicated or has broad maxima and minima the two methods still give the same general shape but the porosimeter method appears to give less distinct detail.

It is probably safe to conclude in view of the close agreement obtained by two such diverse methods that they both yield essentially correct pore volume distributions. The porosimeter has the advantage of rapidity but is a bulky and very expensive piece of apparatus particularly if small pores are to be investigated. The isotherm method requires less expensive equipment but the time required to obtain an accurate desorption isotherm is much greater than is required to obtain the porosimeter data. It is the authors' belief that a porosimeter capable of exerting 500 to 1000 p.s.i. and the adsorption apparatus would be the most efficient of equipment. The porosimeter could be used for investigation of the pore volume distribution in pores greater than 300 Å. radius while the isotherm would cover the smaller pore range.

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